Synthesis and Characterization of Polyamine Bicycles for Anion Binding

by

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the degree of Doctor of Philosophy

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Abstract

This thesis details the interaction between anions, such as Br^-, Cl^-, and F^- and a group of familiar Schiff base derived azacryptands. Often these systems are synthesized by tosylating *i.e.*, protecting, the bridging amine sites to prevent them from undesirable interactions. Only after detosylation to retrieve the secondary amines are the anion binding properties investigated. Through our research, we have discovered that when protected (tosylated), the *m*-xylyl azacryptand [1,4,12,15,18,26,31,39–octaazapentacyclo [13.13.13.1.^{6,10}1.^{20,24}1.^{33,37}] tetratetraconta-6, 7,9,20(43), 21,23,33(42),34,36–nonaene], $N(CH_2CH_2NHCH_2$-m-xylyl-$CH_2NHCH_2CH_2)_3N$), **12**, is readily capable of being protonated at the bridgehead amines. As a result it is also capable of binding anions. Results from these studies are presented, including the binding of the Br^- ion, and the crystallographic findings for both the bromide and neutral tosylated azacryptand receptor. Two species were isolated: the neutral cryptand and the dibromide salt. Binding studies and crystal structures are discussed within.

Structural aspects of the binding of halides in the *p*-xylyl octaaza cryptand [1,4,11,14,17,24,29,36-octa-azapentacyclo [12.12.12.2^{6,9}.2^{19,22}.2^{31,34}]-tetratetraconta-6 (43), 7,9(44), 19(41), 20,22(42), 31(39), 32,34(40)-nonaene], $N(CH_2CH_2NHCH_2$-*p*-xylyl-$CH_2NHCH_2CH_2)_3N$), **13**, were examined. Crystallographic results for two different F^- ion complexes indicated cascade-like coordination, with two F^- ions inside the tren-based cavity, bridged by a H_2O molecule. In two different Cl^- structures, a single Cl^- ion and a H_2O molecule occupied the cavity. Association

constants for the anions, determined by NMR titrations in aqueous solution at pH 5, revealed *Log K* = 3.15(5) and 3.37(3) for F^- and Cl^-, respectively.

Aspects of the binding of halides, the HSO_4^- ion, and the SO_4^{2-} ion in the pyridine-based octaaza cryptand [1,4,12,15,18,26,31,39,42,23,44-undecaaza-pentacyclo-[13.13.13.$1^{6,10}$.$1^{20,24}$.$2^{33,37}$]-tetratetraconta-6,7,9,20(43),21,23,33(42),3436-nonaene], $N(CH_2CH_2NHCH_2$-*pyridine*-$CH_2NHCH_2CH_2)_3N$), **14**, were examined. Crystallographic results for the Br^- ion complex indicated cleft binding, with three internal bromides and three external Br^- ions. Association constants for the anions determined by NMR titrations in aqueous solution at pH 3.0 (pH 4.0 for F^-), revealed *Log K* = 3.6 (F^-), 1.7 (Cl^-), 1.0 (Br^-), and less than 1.0 (I^-). A 1:2 ligand-to-anion binding mode was observed for the SO_4^{2-} ion, with respective binding constants of log 4.6 and 2.6. Titrations performed in DMSO-d_6 determined the binding constant with HSO_4^- to be log 3.2.

Various methods were used to analyze the ligands and to measure ligand-anion interactions, including mass spectroscopy, ^{1}H NMR, ^{13}C NMR, X-ray crystallography, and elemental analysis.

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Also, I thank my husband, David, for his support and patience. He dealt with the house not being as clean as it should have been and with many take out meals when I was too tired to cook. His confidence in me gave me the strength to continue, and his humor made the journey that much more enjoyable.

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Chapter 1 Background and Introduction

1.1 Introduction

Supramolecular chemistry defined by Jean-Marie Lehn as "the chemistry beyond the molecule, the chemistry of non–covalent interactions,"[1] illustrates a unique way of thinking of molecular interfaces. Atoms interact through bonds to form molecules, and molecules can interact through non-covalent interactions (electrostatic, hydrogen bonds, van der Waals forces) to form supramolecular complexes. Lehn continued to state that these complexes serve many possible functions, such as recognition, catalysis, and transport. While this thesis will focus on anion chemistry and in particular, anions with macrocyclic receptors, it is necessary to introduce and provide a brief history of metal and supramolecular chemistry.

Supramolecular systems include, but are not limited to, crown ethers,[2] *katapinands*,[3,4] and amine-based macrocycles.[5] Early supramolecular chemistry studies, which often involved alkali metal cations, later progressed to anion recognition. Generally, complex stability increases as the order of the system increases from acyclic to cyclic to multi-cyclic, leading to more advanced ligand design.[6,7,8] Depending on the charge, shape, and size of the guest, ligands and receptors, can be tailored to suit specific guests. In addition, receptors initially used to form complexes with metal ions were found to be suitable anion receptors under modified conditions. Metal and anion coordination also overlap when relating the coordinate covalent bonds in transition metal complexes to the hydrogen bonds formed in anion complexes.[9] As such, anion binding plays significant roles in areas such as biological chemistry, environmental chemistry, and nuclear waste remediation. While the supramolecular chemistry of ions is a vast field, an overview of significant moments will introduce further research in this thesis. After these topics are discussed, factors affecting anion binding and the significance of anion binding will be addressed.

1.2 Historical Perspective

1.2.1 The Chelate Effect

The *chelate effect* demonstrates that metal complexes with multidentate ligands have a higher stability than complexes with related monodentate ligands. Replacing NH_3 with 1,2-diaminoethane as shown in **Reaction 1,**[10] increases the overall stability by more than 10^8.

$$\mathbf{[Ni(NH_3)_6]^{2+} + 3NH_2CH_2CH_2NH_2 \rightarrow [Ni(NH_2CH_2CH_2NH_2)_3]^{2+} + 6NH_3}$$

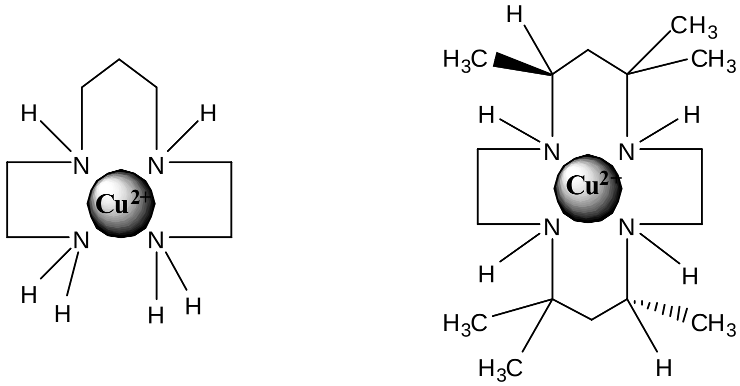
Reaction 1: Demonstration of the chelate effect; $\Delta G^\circ = -11.77$ kcal/mol

Thermodynamically, the ethylene diamine complex is more stable as the replacement of six NH_3 ligands with three ethylene diamine groups will generate seven species in solution as opposed to four species in the reactants. In addition, for the bidentate ligand to dissociate, both amine-metal bonds must break at the same time. Also, the kinetic stability of the bidentate complex will be increased, because as the first amine forms a bond with the metal ion, the second amine would bind much more quickly because of its closer proximity to the metal center.

1.2.2 The Macrocyclic Effect

Macrocyclic ligands are multidentate ligands that have donor groups integrated within or attached to a cyclic framework. The identity and number of donor atoms influence the size of the ligand cavity. As such, macrocycles often form complexes with cations and, as discovered more recently, anions. These complexes display enhanced kinetic and thermodynamic stability resulting from the *macrocyclic effect*,[11] which is an even stronger effect than the chelate effect.

In the first transition metal macrocyclic complex, Cabbiness and Margerum determined that a Cu(II) complex of a macrocycle, **2,** was about 10^4 times more stable than the corresponding acyclic amine, **1**, with Log K values of 28 and 23.9, respectively (**Figure 1**).[12,13] As the order of the system increased from acyclic to macrocyclic, the K increased. The chelate effect predicted that the complex with the macrocycle would be more stable, as one additional chelate ring would be formed. However, when the stability of the complex turned out to be a factor of ten higher than the authors expected, they deemed the additional stability a result of what they named the "macrocyclic effect."

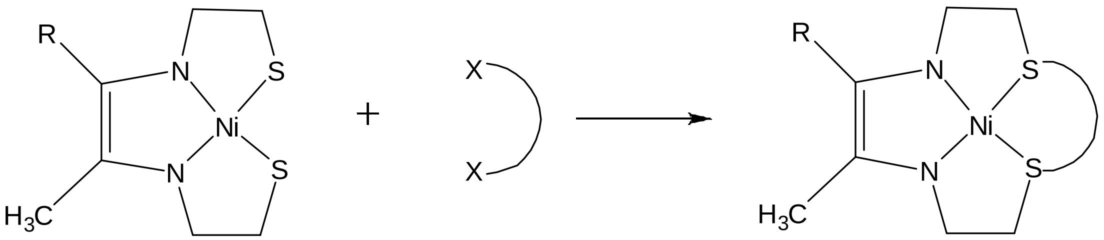


1 **2**

Figure 1: Cabbiness and Margerum’s Cu(II) complexes.[12,13]

Macrocycles can be synthesized independently or have their synthesis directed by the presence of a metal ion. This procedure is called template synthesis.[14] As a major discovery, Daryle Busch was the first to make mixed amine-thioether macrocycles from a planned synthesis (**Scheme 1**). These macrocyclic chelate compounds represent the first deliberate use of a metal ion to secure the chelate rings.[15] The metal ion, in this case, nickel(II), chelates the functional groups, such as those found in α-α’-dibromo-*o*-xylene, in turn directing the stereochemistry of the reaction. This process is termed the *kinetic template* effect, for which, Busch states, “the succession of reaction steps is determined by the metal ion.”[15]

Scheme 1: Example of Busch's template synthesis of a mixed Schiff-base amine-thioether macrocycle.

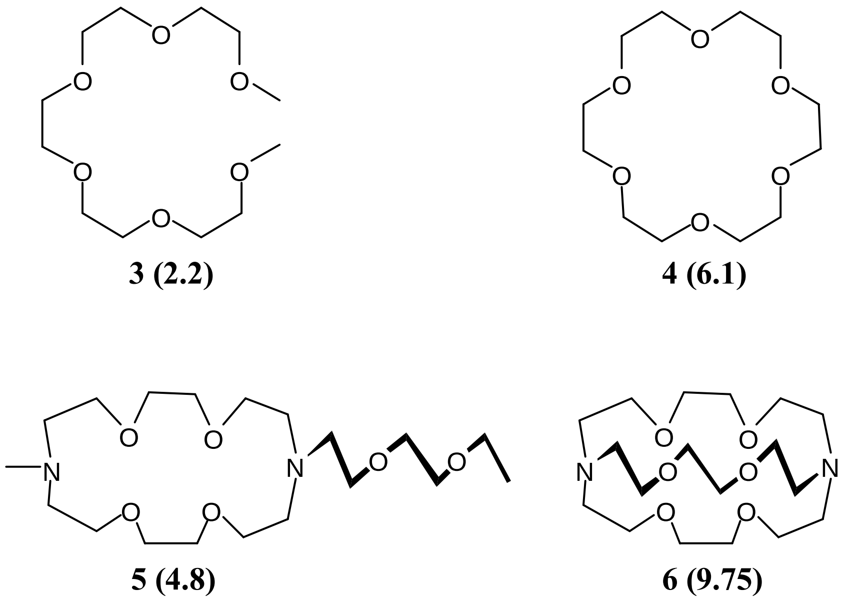


1.2.3 The Cryptate Effect

Macropolycyclic complexes, as opposed to monocyclic complexes (**Figure 2**), display enhanced stability, in addition to that contributed by the macrocyclic effect. High stability, high complexation selectivity, and metal cation shielding characterize the cryptate effect, as termed by Lehn.[16] These qualities result from the rigidity and shape of the ligand that afford inclusion of the guest inside the host's cavity. Terminology denotes the free versus the complexed ligand. Adding the ending *–and* refers to the uncomplexed ligand, while the ending *–ate* refers to the metal/ligand complex,[17] *i.e.*, cryptand versus cryptate.

As shown in **Figure 2,** the K^+ complex of the macrocycle first reported by Pederson,[2] **4**, is 10^4 times more stable than the related acyclic complex, **3**, (macrocyclic effect), and the K^+ cryptate, **6**, is 10^5 times more stable than the monocyclic analogue, **5** (cryptate effect). This demonstrates that the cryptate effect is larger than the corresponding macrocyclic effect.

The metal ion, K^+, interacts with the receptors through non-covalent ion-dipole interactions, rather than forming coordinate covalent bonds as shown by Cabbiness and Margerum's Cu(II) complex **2**.[12,13] The crown ether, as opposed to the acyclic ether, is pre-organized and does not have to expend energy to 'wrap' itself around the metal center–the energy has already been expended upon synthesis of the crown. While **5** has the same number of binding sites as **4**, the complex formed with K^+ is weaker, resulting from the necessity of the arm rearranging itself. However, the corresponding bicycle **6** forms the most stable complex with K^+ because of its cavity. The degree of pre-organization increases from the monocycle to the bicycle.



3 (2.2)

4 (6.1)

5 (4.8)

6 (9.75)

Figure 2: Demonstration of the macrocyclic and cryptate effects. Log K_s of the K^+ complexes of **3**, **4**, **5**, and **6** in methanol (top) and water/methanol (5:95) (bottom) are provided in parentheses.[16]

Macropolycyclic compounds are ideal agents for molecular recognition. These molecules have hollow cavities that allow guest inclusion. Indeed, the pre-organized structure facilitates substrate binding by non–covalent interactions, namely electrostatic forces (if charged), hydrogen bonds, and coordinate covalent bonds. Neutral molecules can interact via hydrogen bonds or dipole-dipole forces, while lone-pair electrons facilitate metal-ion coordination. Depending upon their charge, functionality, shape, or size, these receptors can form inclusion complexes with various types of guests, such as biological species, metal cations, and simple organic ions. These hosts, as well, may also demonstrate molecular recognition of species based on shape, like linear, spherical, or tetrahedral, as will be discussed below.

1.2.4 Crown Ethers

Macrocyclic chemistry made significant strides in 1968 in the areas of metal and anion binding. Pederson's paper describing the complexation of alkali metals by crown ethers (**Figure 3**) started the field of alkali metal cation coordination.[2] The interaction between the positively-charged metal ion and the ether oxygens is considered primarily electrostatic. The diameter of the crown influences the strength of the binding with the metal ion, the better the size match between the crown and the cation, the stronger the binding. **Table 1** illustrates the compatibility in size between the simple crowns and cations.[18] These crown-ethers are easily synthesized and highly selective for alkali metals, and accordingly, these advances spawned much research in binding of metal cations. However, Gökel later published, however, that the size-match theory does not always hold true. The stability constants for a series of crown ethers, from 12-crown-4 to 24-crown-8 with Ca^{2+}, K^+, Na^+, and NH_3^+ in anhydrous MeOH, demonstrated that K^+ was most strongly bound with all of the crowns, and 18-crown-6 bound all the cations the strongest. Therefore, while cavity size often plays an important factor in binding interactions, other factors should be considered, for example solvation effects and ligand flexibility.[19]

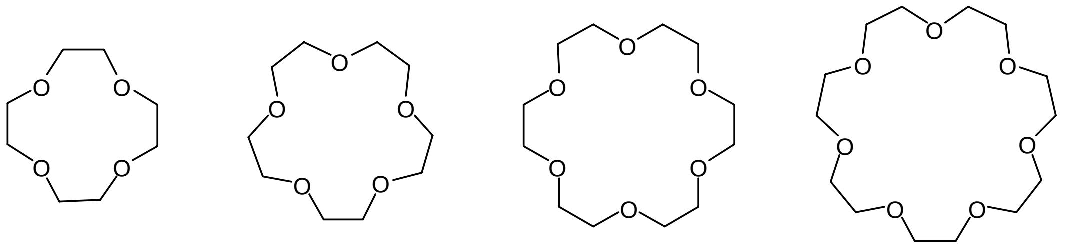

7 **8** **4** **9**

Figure 3: Pederson's crown ethers (**4**) 12-crown-4; (**7**) 15-crown-5; (**8**) 18-crown-6; (**9**) 21-crown-7.[2]

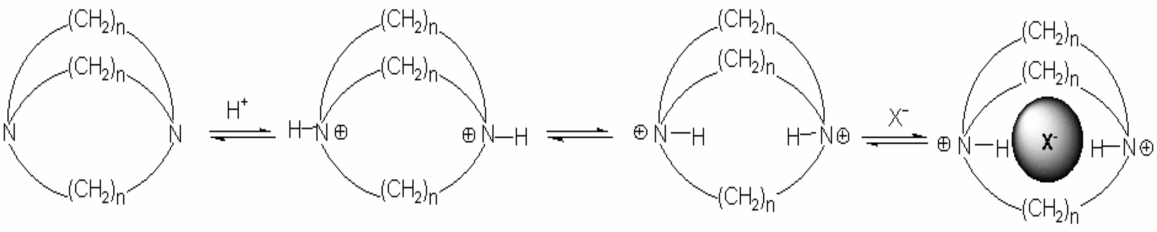
The impact of a paper published in the same year at the other end of the spectrum, anion binding, was not immediately significant. Park and Simmons introduced bicyclic ammonium ligands, *katapinands* that encapsulated halides.[3,4] While Pederson's paper spawned much research, the Park and Simmons paper received less attention. Their research focused on the previously unstudied, but equally important, area of anion complexation.

Table 1: A comparison between the diameter of alkali metals and corresponding crown ethers.[18]

Crown	Diameter (pm)	Cation	Diameter (pm)
12-crown-4	120-150	Li^+	136
15-crown-5	170-220	Na^+	190
18-crown-6	260-320	K^+	266
21-crown-7	340-430	Cs^+	338

1.3 Emergence of Anion Coordination Chemistry

In 1968, Park and Simmons reported that *katapinands*, from the Greek to 'swallow-up', had an affinity for halides. They found that the nitrogen bridgeheads on these diazabicyclic molecules exist in conformations where the nitrogen lone pair electrons are directed either inside (in/endo) or outside (out/exo) of the ligand's cavity (**Figure 4**).[3] These ligands isomerize by nitrogen inversions and prototropic reactions.[4] When protonated, the nitrogen units adopt an *endo-endo* conformation with both hydrogens directed towards the center of the cavity. Furthermore, because of the more rigid structure imparted by the arms joining the two tertiary amines, the protons in the *in-in* conformation are shielded, and hence, rates of deprotonation are diminished. The effect has been termed "proton cage."[20] These halide inclusion complexes, structurally characterized in 1975,[21] are what many consider the first demonstrations of supramolecular anion complexes.



n = 7-10
10

n = 7-10
$H_2\mathbf{10}^{2+}$
exo-exo

n = 7-10
$H_2\mathbf{10}^{2+}$
endo-endo

n = 7-10
$H_2\mathbf{10}^{2+}\cdot X^-$

Figure 4: From left to right, Parks and Simmons' katapinand **10**, diammonium katapinand **$H_2\mathbf{10}^{2+}$**, and halide katapinate **$H_2\mathbf{10}^{2+}\cdot X^-$**.[3,4]

As an example Park and Simmons' *katapinand*, **10**, with n=10, forms an inclusion complex with halides, **$H_2\mathbf{10}^{2+}\cdot X^-$**, and is specific for the Cl^- ion, with a stability of approximately $K = 4$ in 50% CF_3COOD, for n = 9 (**Figure 4**). The authors reported that the *katapinate* complex displays an affinity for the Cl^- ion resulting from the concentration of positive charge and hydrogen bonding within the ligand cavity. While the receptor displayed minimal selectivity of Cl^- over Br^-, this ligand was the first example of a synthetic receptor encapsulating an inorganic anion.[4] While much of the early work, including the above example, involved the complexation of spherical halides, studies later expanded to include anions that are more complex. However, before delving further into the history of the supramolecular chemistry of anions, it is necessary to discuss the factors that affect anion binding.

1.4 Factors Affecting Anion Binding

Anions pose difficulties unique from cation binding. First, anions are larger than their corresponding isoelectronic cations, and hence, have a lower charge density, making them more diffuse. This yields weaker electrostatic interactions resulting from higher polarizability and softer ions. While metal ions are spherical, anions exhibit a variety of geometries, **Figure 5**, which may bring about more complex design of complementary hosts.[22] Additionally, anions may be sensitive to pH if they can be protonated at lower pHs, causing a loss of negative charge. Refer to **Table 2** for radii and free energies of hydration (ΔG°_{hyd}). The pK_a for F^- is 3.3 and that for HSO_4^- is 2.0. Other halides listed in the table are conjugate bases of strong acids.[17]

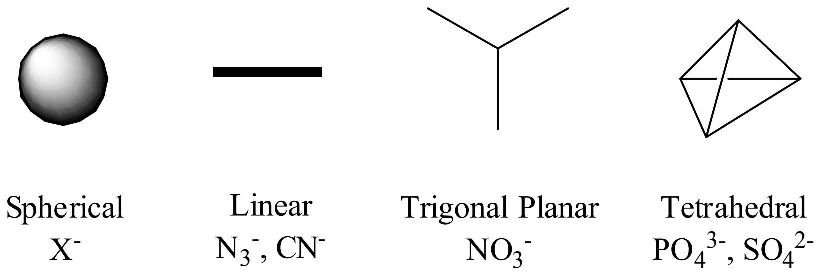


Figure 5: Cartoon depicting four anion topologies.

Electrostatic interactions are an overwhelming force in anion solvation. When comparing isoelectronic cations and anions, anions have larger free energies of solvation. As such, the host and solvent compete for the anion. Therefore an anion in aqueous solution must be ‘dehydrated’, requiring energy, before it can bind with the ligand.

Table 2: Physical properties of selected ions.[17]

Ion	**Radius (Å)**	**$\Delta G^\circ_{hydration}$ (kJ/mol)**
F^-	1.33	−465
Cl^-	1.81	−340
Br^-	1.95	−315
I^-	2.16	−275
SO_4^{2-}	2.30	−1080
Li^+	0.69	−475
Na^+	1.02	−365
K^+	1.38	−295
Cs^+	1.70	−250

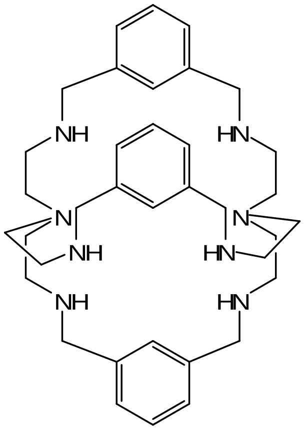
The Hofmeister series,[23] which lists anions in the order of decreasing hydrophobicities (increasing hydrophilicities), draws a parallel with anion hydration energies.[17] The series is based on anions on the right being the most likely to precipitate proteins out of an aqueous solution. One would expect that the more hydrophilic the anion, the more it would interact with the polar solvent molecules, especially water. This makes the effective concentration of the protein higher in the remaining solvent, and the protein precipitates out of the water. Anion selectivity would follow this sequence, unless some host-guest interaction, be it cavity size, shape, number of bonds, etc., overcomes this preference.[24] In the order of decreasing hydrophobicities, the Hofmeister series is shown below:

$$\mathbf{SCN^- > ClO_4^- > I^- > ClO_3^- > Br^- > NO_3^- > Cl^- > CH_3CO_2^- > H_2PO_4^- > SO_4^{2-} \sim F^-}$$

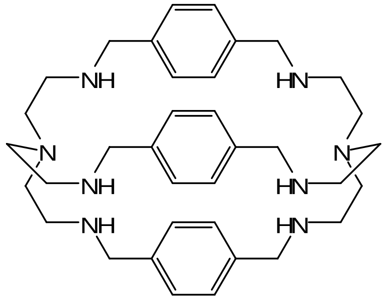
Another aspect mentioned above, the pK_as of the amine receptor, plays an important role in anion binding. The basicity of the amine groups will affect the ligand's ability to interact with anions. Bowman-James and coworkers have reported the protonation constants (**Table 3**) of **12**, **13**, and **14** (**Figure 6**).[25,26] In aqueous solution, it can be assumed that the ligands would be hexa-protonated below pH 6. Bowman-James determined the affinity of **12** for F^- by potentiometric titration.[7] Weak binding with the F^- ion was observed above pH 7. However, not until below this pH, when the ligand is penta- and hexaprotonated, did considerable binding occur. While the strongest binding occurred when the ligand is hexaprotonated, this is near the pK_a of F^-. Therefore, the hexaprotonated ligand would be a suitable choice for anion complexation.

1.5 Additional Significance of Anions

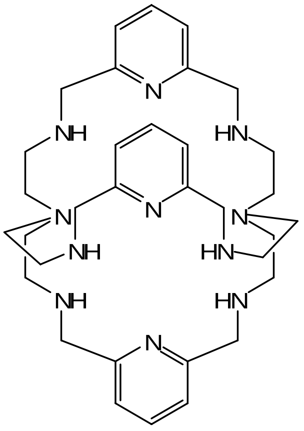
Anions play important roles biologically and environmentally, with up to 75% of enzyme cofactors and substrates estimated to be anions.[17, 22] The environmental significance of anions is demonstrated by the introduction of the F^- ion into drinking water and the presence of NO_3^- in ground water from fertilizer run-off resulting in eutrophication.[27] Additionally, PO_4^{3-} run-off from fertilizers and hog farms[28] has been connected with the eutrophication of ponds and rivers from over-abundance of algae bloom[29]. While not directly addressed in this research, it is important to remember that anions are highly significant in environmental and biological chemistry.



12



13



14

Figure 6: Selected polyamine bicycles. Clockwise from top left corner: MEACryp **(12)**, PEACryp **(13)**, PyEACryp **(14).**

Table 3: Stepwise protonation constants of ligands **12**, **13**, and **14** at 25 ^{O}C and I = 0.1 M (KTs). Values in parentheses represent the standard deviation of the last digit.

Reaction	**Log K$_a$ 12**	**Log K$_a$ 13**	**Log K$_a$ 14**
$L + H^+ \rightleftarrows HL^+$	10.98(4)	9.6(1)	9.61(1)
$HL^+ + H^+ \rightleftarrows H_2L^{2+}$	9.30(4)	9.00(4)	8.83(1)
$H_2L^{2+} + H^+ \rightleftarrows H_3L^{3+}$	9.08(4)	8.62(8)	7.90(1)
$H_3L^{3+} + H^+ \rightleftarrows H_4L^{4+}$	7.38(5)	7.3(1)	7.17(1)
$H_4L^{4+} + H^+ \rightleftarrows H_5L^{5+}$	6.89(5)	5.80(4)	6.58(2)
$H_5L^{5+} + H^+ \rightleftarrows H_6L^{6+}$	6.58(5)	5.68(2)	5.79(2)
$H_6L^{6+} + H^+ \rightleftarrows H_7L^{7+}$	2.81(9)	*Not given*	1.98(2)

Anions also are present in nuclear waste. Located on the Columbia River in Washington State, the Hanford Site was established during World War II in 1943 as part of the Manhattan Project to produce plutonium for the use in atomic weapons. While most of the reactors were no longer used after the 1960s, nuclear waste remains onsite.[30,31] As such, the nuclear waste tanks at the Hanford site, where SO_4^{2-} ion sequestering is a top priority, have a basic pH due to previous treatment with NaOH. Sulfate inhibits the vitrification of tank waste at sites such as Hanford, because of its low solubility (<1%) in borosilicate glass and, hence, has been identified as a pressing concern.[31,32] Sequestering of the SO_4^{2-} ion would reduce tank waste volume and increase the efficiency of nuclear waste remediation.

1.6 Nomenclature

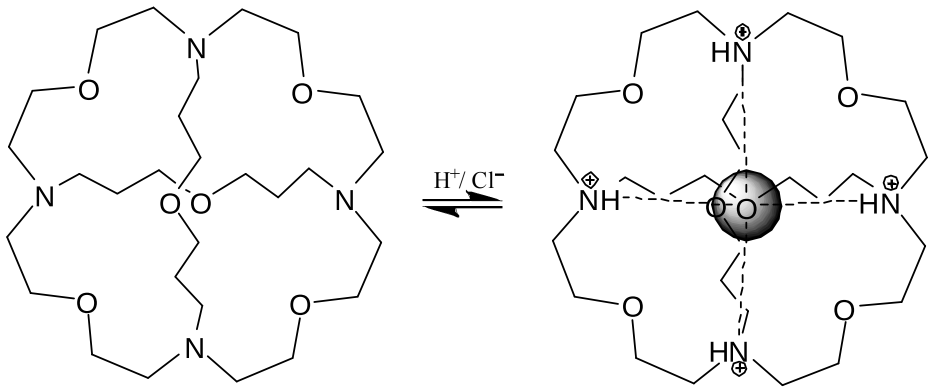
Before returning to further developments in anion coordination, it is important to address the nomenclature of the ligand systems used in this thesis. The nomenclature system used in this thesis follows the conventions developed by the late Robert Hay, professor of chemistry at St. Andrews University in Scotland.[33] For example, one of the ligands used in this study is abbreviated MEACryp, **12**. Its full name is [1,4,12,15,18,26,31,39–octaazapentacycle–[13.13.13.1.1.1.]tetratetraconta–6,7,9,20(43),21,23,33(42),34,36–nonaene]. One can immediately understand the convenience of a condensed nomenclature.

The first letter in the name designates the spacer group, with M representing the *meta*-xylyl group, P representing the *para*-xylyl group, and Py representing the pyridine group. The second letter represents the number of carbon atoms between the nitrogen atoms, with E representing the ethylene group and P representing the propylene group. The third letter indicates the functionality of the nitrogen next to the spacer, with A indicating an amine group. The naming is complete if the ligand is a monocycle. However, if the ligand is a bicycle, cryp is added to denote this. Therefore, **12** would be named MEACryp, **13** would be named PEACryp, and **14** would be named PyEACryp.

As the concerns and significance of anion binding have been attended to, it is now possible to return to a further presentation of a historical perspective of macrocyclic and supramolecular chemistry of anions.

1.7 Further Developments in Anion Coordination

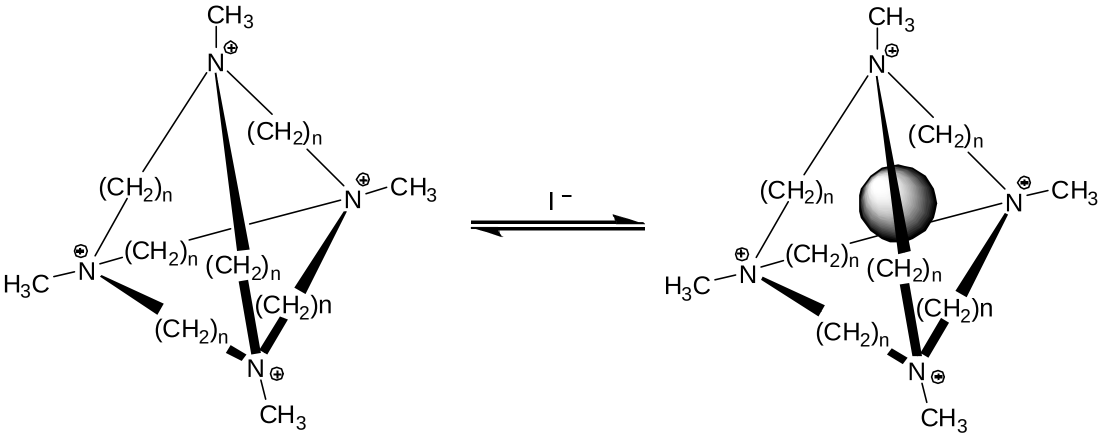
In the late 1970’s and early 1980’s, metal and anion coordination chemistry overlapped with a macrotricyclic “soccer ball” ligand, **15,** targeted at binding K^+, Rb^+, Cs^+, and NH_4^+.[34,35] In addition to its metal affinity, this ligand also bounds anions. The tetraprotonated ligand, $\mathbf{H_415^{4+}}$, also displays selectivity between Cl^- and Br^- by a factor of 1000, whereas the *katapinand*, **11**, shows a selectivity between the two halides by only a factor of approximately 8. The Cl^- coordinates in the center of the ligand cavity **15,** and exhibits a tetrahedral coordination to the protonated amines through hydrogen bonds (**Figure 7**).[34,35,36,37]



15 $\mathbf{H_415^{4+}\cdot Cl^-}$

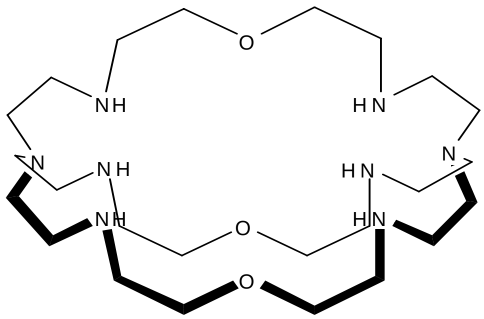
Figure 7: Lehn’s polyamine "soccer ball" **15** and $\mathbf{H_415^{4+}\cdot Cl^-}$ complex. Charges omitted for clarity.[34-37]

While hydrogen bonding plays an important role in anion binding, electrostatic interactions are also significant in anion coordination. Schmidtchen synthesized quaternized polyammonium cations, such as, **16** (**Figure 8**), that utilized electrostatic interactions for the binding of anions, in turn minimizing the pH dependence.[38] He later reported a crystal structure of I⁻ encapsulated by the cation with the six-carbon chain spacer. The I⁻ ion is symmetrically located in the cavity of the macrotricycle and is held in place by electrostatic interactions with the ammonium groups, featuring almost perfect tetrahedral coordination. The average $N^+\cdots I^-$ distance is 4.54(2) Å.[39]

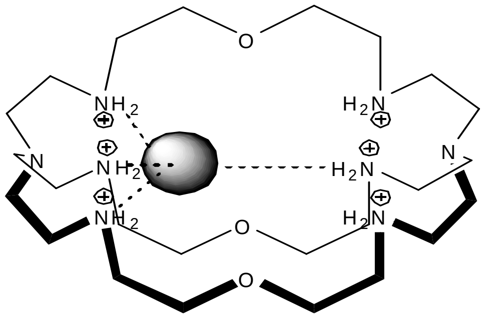


16 **16·I⁻**

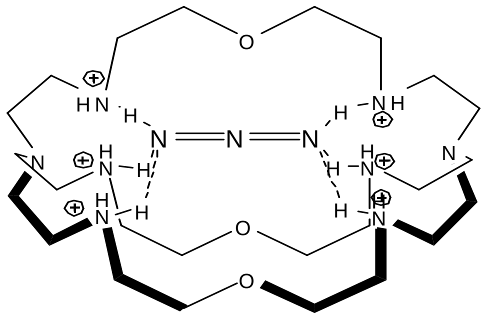
Figure 8: Schmidtchen's polyammonium N-methylated ligand **16** and I⁻ complex. Counter-ions (BF_4^- or TsO^-) omitted for clarity.[39]



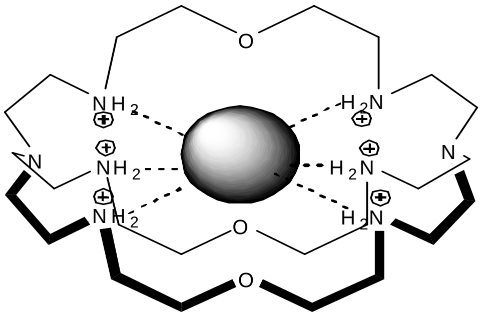
17



$H_6 17^{6+} \cdot F^-$



$H_6 17^{6+} \cdot N_3^-$



$H_6 17^{6+} \cdot X^-$

X=Br$^-$ or Cl$^-$

Figure 9: O-Bistren, **17**, and various anion complexes. SCN$^-$ counter-ions omitted for clarity.

Another key ligand in supramolecular chemistry was **17**, coined bistren by Martell and Lehn because of its two tren units.[40,41] Bistren cryptands are composed of two tris(2–aminoethyl)amine subunits, which are linked by a given spacer group. Those linked by a diethylether moiety are labeled as O-Bistren. Lehn isolated the crystals of four anion cryptates of **17** with the following anions: F$^-$, Cl$^-$, Br$^-$, and N_3^- (**Figure 9**).[40,41] With the N_3^- complex, five external ClO_4^- or NO_3^- ions counter-balance the remaining positive charges. In the F$^-$ complex, the F$^-$ ion binds in a tetrahedron of hydrogen bonds and is shifted toward one side of the cavity.

However, Br^- and Cl^- are both coordinated in an octahedral array of hydrogen bonds near the center of the cavity, along the N–N bridgehead axis.[41] With N_3^-, which also lies on the N–N bridgehead axis, the two terminal nitrogens have three hydrogen bonds from the secondary amines arranged in a pyramidal array.[40] Protonation of the secondary amines formed a stable anion receptor, which formed stable complexes with N_3^-, F^-, Cl^-, Br^-, and I^-, with respective Log *K*s of 4.3, 4.1, 3.0, 2.6, and 2.15 in water.[41] From this and other data, Lehn deduced that $\mathbf{H_6 17^{6+}}$ displays linear recognition of molecules comparable in size to its ellipsoidal cavity.

While Lehn was able to crystallize the hexaprotonated bistren cryptate of the F^- ion, his intent was to isolate the cryptate of bifluoride, FHF^-, because he showed earlier that $\mathbf{H_6 17^{6+}}$ binds linear anions, like N_3^-.[1] In 1998, Bowman-James and Mason isolated a crystal with the cryptand **12**, a tren–based bicycle with *m*–xylyl spacers, encapsulating two NO_3^- ions, $\mathbf{[H_6 12(NO_3)_2][NO_3]_4 \cdot 2H_2O}$. The structure had four additional NO_3^- counter-ions, and the two internally bound NO_3^- ions, each forming hydrogen bonds with the adjacent amine protons.[24] As this cavity was able to incorporate two discrete anions, an attempt to crystallize FHF^- or $2F^-$ ions was made with this macrocycle. The crystal structure obtained, however, was not that of the FHF^- complex, but the results indicated formation of a ditopic inclusion complex. Incorporated inside the cavity, and shifted from the central axis, were F^- and H_2O, with $2FHF^-$, 1.5 SiF_6^{2-}, and $6H_2O$ located outside the cavity.[42] Four hydrogen bonds, one from the internal H_2O molecule and three from the ammonium hydrogen atoms, give the F^- ion a pseudo–tetrahedral coordination. Consequently, this was the first reported example of a Schiff base-derived receptor forming an inclusion complex with two discrete guests. An additional aspect of the research presented in this thesis further explores the attempt to capture FHF^- in an azamacrocyclic cavity.

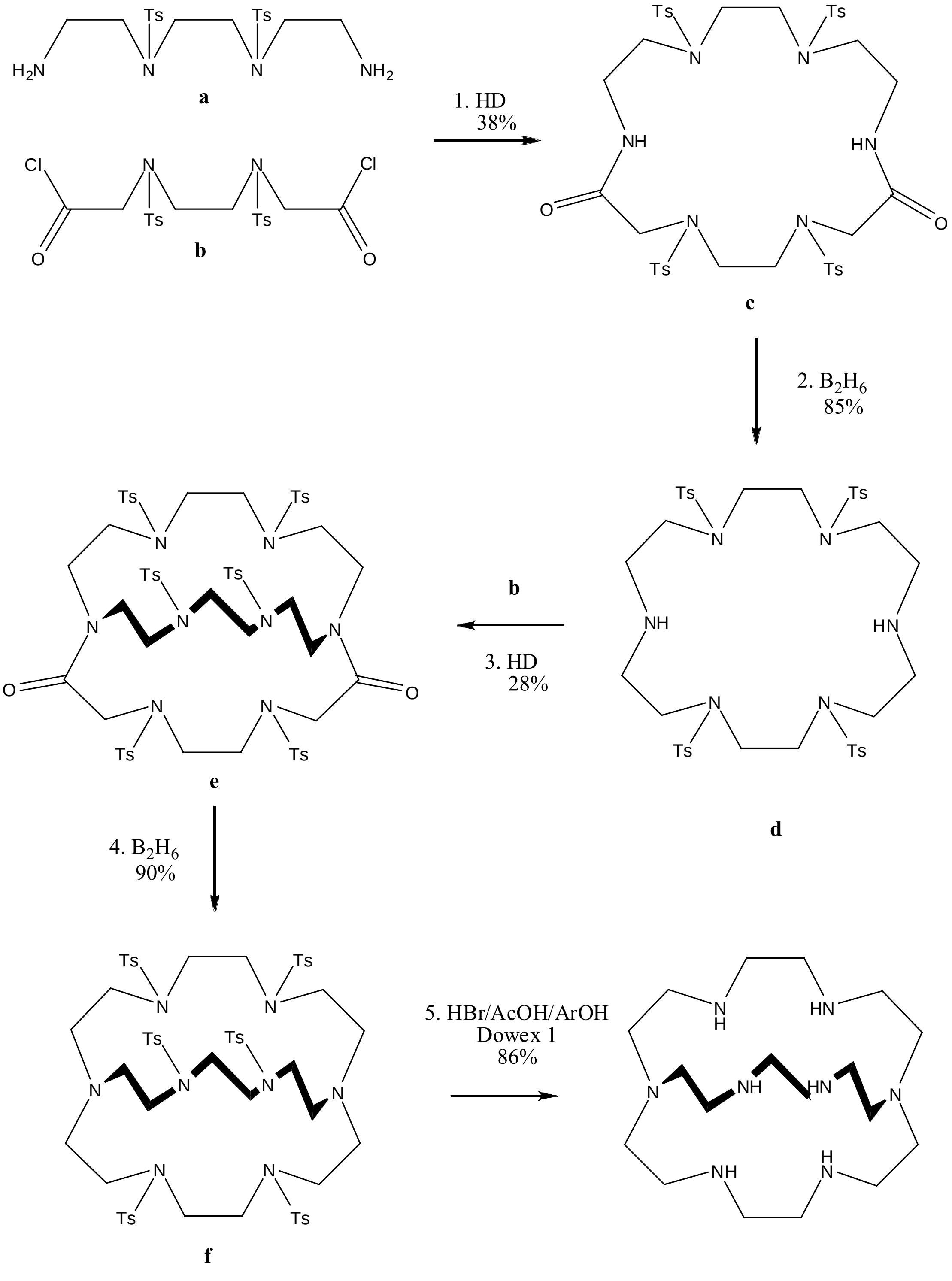
1.8 Synthesis of Cryptand Receptors

It is possible to synthesize polyaza cryptand through multiple methods, such as metal-ion templating (Schiff base and non-Schiff base), protection and deprotection, and Schiff base synthesis without a metal ion template. While the ligands in this thesis were synthesized using non-template Schiff base methods, it is necessary to show the progression of previous techniques.

As shown earlier in **Scheme 1**, Busch developed a method to synthesize mixed amine-thioether macrocycles using a metal ion template.[15] Further progression of synthetic methods occurred about 20 years later when Lehn, *et al.* employed a method to synthesize polyaza macrocycles without metal-ion templates, using a series of protections and deprotections (**Scheme 2**).[6,43] While this is a viable method for the synthesis of these macrocycles, it requires multiple, tedious steps. As such, different approaches were pursued.

Whether used independently or with a template, a common synthetic route is the use of the Schiff base condensation, which initially utilized metal-ion templates. M. Nelson worked in this area by examining the condensation reactions between 2,6-diacetyl pyridines and diamines in the company of a range of metal ions. He found that the type of macrocycles formed depends on the ratio of starting materials, the length of the amine chain, and the type of metal ion used.[44]

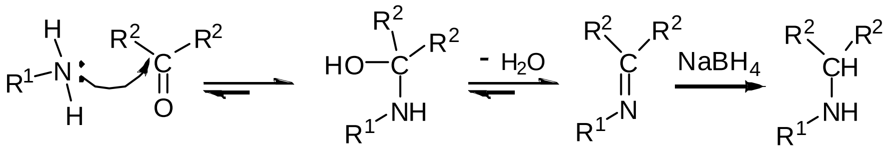
Scheme 2: Cryptand Synthesis by protection/deprotection[6,43]



The synthetic methods of polyamine macrocyles advanced further by using non-template Schiff base condensation, followed by reduction to produce the desired product. This one-pot synthesis is beneficial for many reasons: low-cost reagents, ease of synthesis, short reactions time, and decent yields.

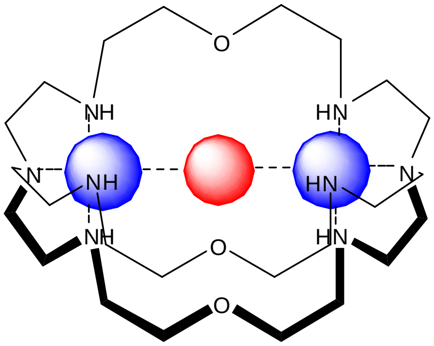
The mechanism for a Schiff base condensation, followed by reduction to yield a saturated system, is shown in **Scheme 3**. Researchers altered their synthetic strategies by using non-template Schiff base condensations, between amines and aromatic or heterocyclic aldehydes, followed by BH_4 reduction of the imine to the amine, to make easily synthesized and readily available receptors.[45,46,47] With a modification, this method will be used to synthesize the aforementioned amine receptors, **12**, **13**, and **14**. This method is used because it is a more straightforward route than previously used methods. Previous methods involved protecting the secondary nitrogens with tosylate, condensing with an acyl halide, ending with deprotection to yield the free ligand.[6,43]

Scheme 3: Mechanism of Schiff base condensation, followed by reduction.



1.9 From Metal to Anion Cascade Complexes

Lehn noticed that azacryptands display the tendency to form cascade complexes in which the ligand encapsulates two metal ions coordinated to a central anion (**Figure 10**).[41,43,48,49,50,51] Multiple ligands have been shown to form cascade complexes, with a range of metal ions and bridging anions.[41,43,48,49,50,51,52,53,54,55,56] The Bowman-James group has observed simultaneous binding of both neutral and anionic species with $\mathbf{H_6 12^{6+}}$.[7,22,24,57] As such, it has been speculated that similar ligands could form *anion* cascade complexes.



18

Figure 10: Drawing of a generic 2M^{n+} metal cascade complex **18**.

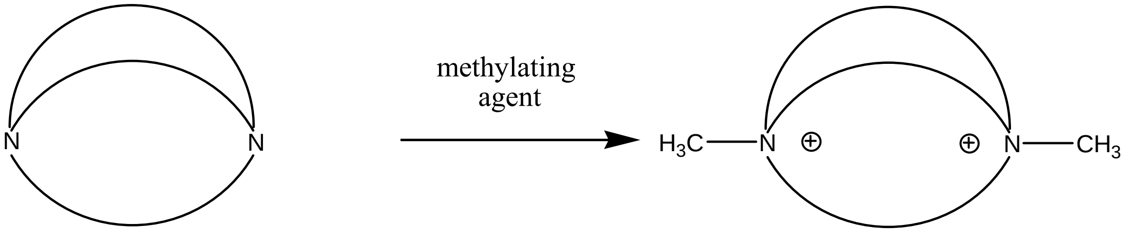
Unprotonated, each tren subunit in cryptands can interact with a transition metal cation and form a binuclear cryptate, as demonstrated by bistren and its analogues.[48] The metal ions usually exhibit trigonal pyramidal coordination with four of the ligand amine coordination sites. However, since the fifth (axial) coordination site on the metal ion is vacant, these complexes are ideal for additional coordination at the vacant site. An additional species can be incorporated between the two metal ions, simultaneously occupying the axial coordination site for both metal ions, thus forming a cascade complex. The cryptand coordinates each of the metal ions, and the anion bridges or “cascades” between the two metal ions. In addition to the oxygen spacer groups, using a *m*–xylyl spacer, for example, has yielded other cascade complexes, in which two metal ions are linked by a third neutral or anion species. Harding and Menif were able to isolate crystalline **12** dicopper(II) cascade complexes of NCO^-, N_3^-, and CO_3^-, respectively.[52,53]

The last several years have been successful in expanding anion coordination chemistry. [5,22, 58] As alluded to above, it is not surprising that several results demonstrate structural corollaries with transition metal and anion coordination chemistry.[9] The Bowman-James group has isolated a ditopic NO_3^- complex (**Figure 30**) [7,24] and a two-to-one ligand “sandwich” of SO_4^{2-}.[59] Additionally, the group has illustrated the chelate and macrocyclic effects in the stabilization of anion complexes. [7,22,59, 60] As such, the parallels between the binding modes in transition metal complexes (coordinate covalent bonds) and anion complexes (hydrogen bonds) continue to be demonstrated.

1.10 Synthesis of a quaternary nitrogen anion receptor

An additional goal of this research project was to synthesize a nitrogen-based macrocycle receptor selective for the SO_4^{2-} ion. Receptors, such as MEACryp, **12**, and PEACryp, **13**, become protonated as the pH of their solution decreases. Stronger binding occurs as the ligand increases its degree of protonation.[7,22] If a charged species could be synthesized without protonation (**Scheme 4**), it would be possible to have a receptor whose binding ability would be virtually pH independent. One method to achieve this would be selective quaternization.[59]

Scheme 4: Formation of generic dimethylated azabicycle



1.11 Conclusion

Jean-Marie Lehn described supramolecular chemistry as "the chemistry of non-covalent interactions."[1] The development of transition metal macrocyclic compounds by those such as Busch,[15] Cabbiness and Margerum,[12,13] and Pederson,[2] while not supramolecular species, layed a foundation for much progress in supramolecular chemistry. Park and Simmons[3,4] found that diazabicyclic compounds called *katapinands*, exhibited an affinity for halides. Additionally, ligands, previously designed for metal coordination have been shown to be good hosts for anions. For example, Lehn's cryptands, when protonated, made suitable anion receptors.[40] The systems described in this chapter encompass various areas, from metal to anion to cascade complexes, to inclusion complexes with monotopic, ditopic, and tritopic guests. The work in the Bowman-James group has further extended this research by studying the interaction between anions and such ligands as amine macrocycles. This thesis expands on these findings by probing the affinity of three Schiff base-derived cryptands for various anions.

Chapter 2 Experimental Section

2.1 Reagents and Starting Materials

Chemicals were reagent grade and purchased from Aldrich. Solvents were reagent grade and purchased from Fisher Scientific and used with no other purification, other than drying over the specified molecular sieves when required. Deuterated solvents were were purchased from Cambridge Isotope Laboratories, Inc.

2.2 Physical Methods

Fast atom bombardment (FAB) spectra were obtained with a VG Analytical Ltd., ZAB HS mass spectrometer equipped with an argon gun, operated at 6 keV and 0.8 mA emission in the Mass Spectrometry Laboratory at the University of Kansas. 3-Nitrobenzyl alcohol (FAB/NBA) was the matrix used with all samples. Elemental analyses were performed at Desert Analytics, Tucson, Arizona.

Crystal structures were obtained by X-ray crystallography at the X-Ray Crystallographic Center at the University of Kansas by Drs. Douglas Powell and Victor Day. Intensity data for compounds were collected using a Bruker APEX ccd area detector[61] mounted on a Bruker D8 goniometer using graphite-monochromated Mo Kα radiation. Crystal structure data were corrected for absorption by the semi-empirical method.[62] Space groups were determined by systematic absences and statistical tests and verified by subsequent refinement. Structure were solved by direct methods and refined by full-matrix least-squares methods on F^2.[63] Hydrogen atom positions were initially determined by geometry and refined by a riding model.

NMR data were collected on a Brüker Avance 500 spectrometer at 500 MHz.

Data were collected in either $CDCl_3$, D_2O, or DMSO-d_6 at 25 ^OC unless stated otherwise. Solvent references were either tetramethylsilane (TMS) or 3-(trimethylsilyl)-propionic acid-D4, sodium salt (TSP) in a capillary tube. For ^{19}F NMR, sodium fluoride was used as an internal reference.

Titrations were performed by 15-20 measurements in $CDCl_3$ or other appropriate solvent. Aliquots from stock solution of anion were gradually added to the stock solution of the ligand. In D_2O, the pD of the solution was calculated by adding 0.6 to the pH reading. The titrations were performed until the ratio of A:L was 10:1. Binding constants were calculated by following proton chemical shifts. Association constants, K, were calculated using Sigma plot and EQNMR,[84] both non-linear regression curve fitting programs.

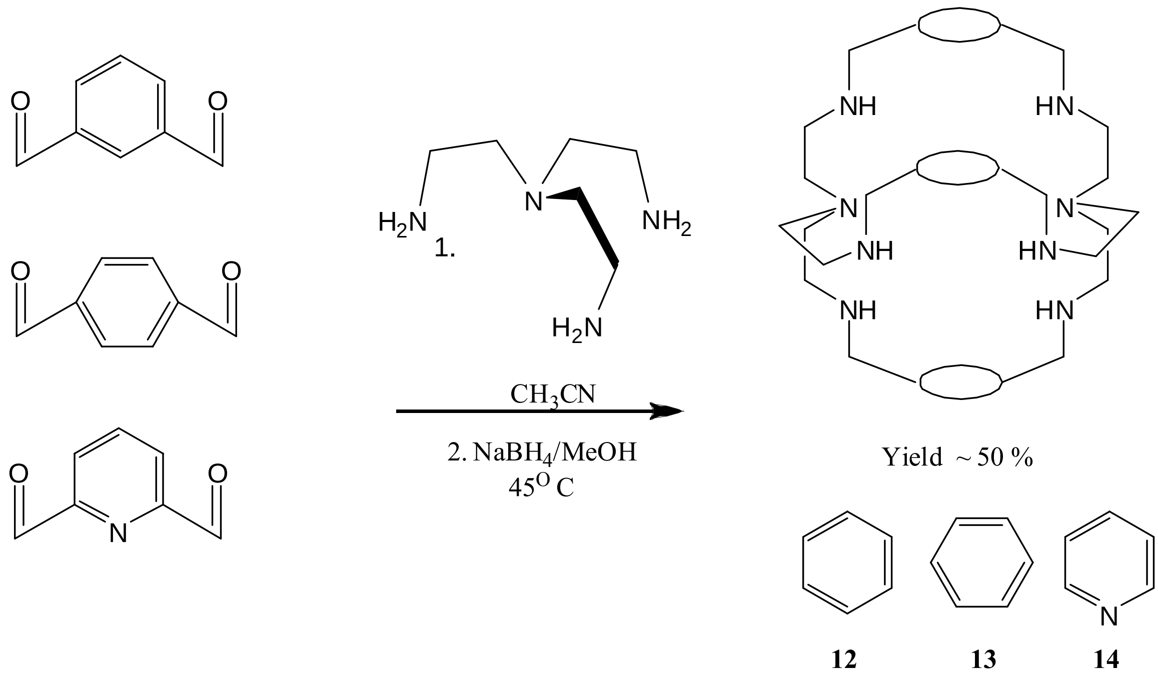
For Job plots solutions of anions and ligands were prepared in D_2O, and the pD was adjusted to 5.0 +/– 0.1 by solutions of KOH and TsOH in D_2O. The total concentration of the ligand plus the anion were kept at 10 mM. The total volumes were kept at 500 μL and varied in 50 μL increments.

For previously synthesized systems, mass spectroscopy and ^1H NMR were used to characterize the compound. When necessary, elemental analyses were obtained to determine purity.

2.3 Schiff Base Condensation

The synthesis of the reduced Schiff base-derived cryptands follows previously published procedures.[25,46,47] A general reaction is shown below (**Scheme 5**).

Scheme 5: Schiff base condensation followed by reduction



2.4 Modification of Schiff Base Synthesis

In a typical reaction, a CH_3CN solution containing three equivalents of dialdehyde and a CH_3CN solution containing two equivalents of tren was added to a round-bottom flask containing CH_3CN and stirred at room temperature (25 ^{O}C) for approximately 48 h. The solvent was removed under vacuum, and the remaining solid was dissolved in CH_2Cl_2 and washed with H_2O then filtered to remove polymer. The solvent was removed under vacuum, and the product was redissolved in MeOH. To this solution, $NaBH_4$ (20 eq.) was added over 30 minutes. The solution was heated to 45 ^{O}C and stirred for 3 h. The solvent was removed under vacuum, and the remaining solid was dissolved in CH_2Cl_2, washed, and filtered, as described above. The solvent was evaporated, and a solid powder was collected.

After several syntheses, the procedure was modified to combine condensation and reduction into one vessel, in order to enhance yield and purity; methanol was used instead of CH_3CN for both steps, and the condensation was performed in an ice bath at 0 ^{O}C instead of 25 ^{O}C. This modified method produced a larger overall yield for **12,** for example, as compared to Mason (an increase of ~ 30%),[25] and this method also yielded a powder instead of an oil for **13** and **14**, thus indicating that this method may produce a product of greater initial purity without additional steps.

2.5 Amine Macrocycles

2.5.1 MEACryp Schiff Base
[1,4,12,15,18,26,31,39–octaaza–pentacyclo–[13.13.13.1.1.1.]tetratetraconta–4,6,7,9,11,18,20(43),21,23,26,31,33(42),34,36,38–pentadecaene]

Yield 3.40 g (64.1%). Product was obtained during earlier syntheses.

2.5.2 MEACryp Amine (12)
[1,4,12,15,18,26,31,39–octaazapentacycle–[13.13.13.1.1.1.]tetratetraconta–6,7,9,20(43),21,23,33(42),34,36–nonaene]

Yield 2.88 g (83.2%). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 ^{O}C): δ 2.59 (br t, 12H, N*CH₂*), 2.63 (br t, 12H, NCH_2*CH₂*), 3.62 (s, 12H, C*H₂*Ar), 7.07 (s, 3H, Ar*H*), 7.19 (m, 6H, Ar*H*), 7.29 (s, 3H, Ar*H*): ^{13}C NMR ($CDCl_3$, 500 MHz, 25 ^{O}C): 47.65, 53.51, 55.10 (aliphatic); 126.90, 127.18, 128.27, 140.52 (Ar).

2.5.3 PEACryp Amine (13)
[1,4,11,14,17,24,29,36–octaaza–pentacyclo–[12.12.12.2.2.2.]tetratetraconta–6,7,9,19,20,22,31,32,34–nonaene]

A light yellow powder was obtained rather than the oil obtained by Mason.[24] Yield 4.60 g (85.5%). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 ^{O}C): δ 2.66 (br t, 12H, N*CH₂*), 2.82 (br t, 12H, NCH_2*CH₂*), 3.68 (s, 12H, ArC*H₂*), 6.88 (s, 12H, Ar*H*). ^{13}C NMR ($CDCl_3$, 500 MHz, 25 ^{O}C): 47.67, 53.57, 54.25 (aliphatic); 127.54, 138.5 (Ar). Anal. Calcd. for ($C_{36}H_{54}N_8$): C, 72.20; H, 9.09; N, 18.71. Fd.: C, 71.53; H, 8.97; N, 18.61.

2.5.4 PyEACryp Amine (14) [1,4,12,15,18,26,31,39,42,43,44]undecaazapentacyclo-[13.13.13.1.^{6,10}1.^{20,24}1.^{33,37}]tetraconta-6,7,9,20(43)21,23,33(42),34,36-nonaene].

A light yellow powder was isolated rather than the oil obtained by Mason.[25] Yield 1.48 g (30.0%). ^{1}H NMR (400 MHz, 25 ^{O}C, $CDCl_3$, TMS): δ 2.70 (m, 24H, NCH_2 CH_2,), 3.88 (s, 12H, ArCH_2), 7.08 (d, 6H, Ar*H*), 7.46 (t, 3H, Ar*H*). ES$^+$-MS: *m/z* 602.4 [**H14**]$^+$.

2.6 Synthesis of Tosylated Species

2.6.1 Ts$_6$MEACryp (Ts$_6$12)

MEACryp **12** (3.0 g, 5.02 mmol) was dissolved in 175 mL of CH_3CN and heated to 80 °C. Solid K_2CO_3 (10.4 g, 75.3 mmol) was added to the ligand solution, and the solution was allowed to stir and reflux for 20 min., after which solid TsCl (11.4 g, 60.2 mmol) was added. After several hours, a precipitate began to form. After refluxing for 48 h, a light brown precipitate was filtered and washed in warm EtOH for 4 h. The product was recovered as a white precipitate and dried in vacuo. Yield: 7.4 g (97.0%). **Ts$_6$12** (0.304 g, 2.00 x 10^{-4} mol) was dissolved in 10 mL $CHCl_3$ to prepare a 20mM solution. After 12 h. of slow diffusion by diethyl ether, yellow crystals suitable for X–ray analysis formed. Yield 0.243 g (80%). ^{1}H NMR (400 MHz, 25 ^{O}C, $CDCl_3$,): δ 1.81 (t, 12H, NCH_2), 2.49 (s, 18H, CH_3), 2.81 (t, 12H, NCH_2CH_2), 4.08 (s, 12H, CH_2Ar), 7.07 (s, 3H, Ar*H*), 7.24 (d, 6H, Ar*H*), 7.35 (t, 3H, Ar*H*), 7.42 (d, 12H, Ts), 7.80 (d, 12H, Ts). ^{13}C NMR (100.61 Hz MHz, 25 ^{O}C,

$CDCl_3$): δ 21.8, 47.7, 53.4, 54.7 (aliphatic); 127.5, 128.6, 129.1, 129.5, 130.2, 136.2, 137.0, 143.9 (Ar). FAB-MS m/z 1523.6 [**$HTs_6$12**]$^+$; Anal. Calcd. for $C_{78}H_{90}N_8O_{12}S_6$: C, 61.47; H, 5.95; N, 7.35. Found: C, 61.59; H, 6.05; N, 7.33.

2.6.2 $Ts_6H_2 12^{2+}\cdot 2TsO^-$

A 5mM solution of **$Ts_6$12** in DMSO was prepared. To this solution was added two equivalents of TsOH. FAB–MS ($CHCl_3^+$-TG/G) m/z 762 corresponding to M/Z = 2 (the diprotonated species without anion coordination). ^{1}H NMR (DMSO, 500 MHz, 25 ^{O}C): δ 1.73 (t, 12H, N*CH_2*), 2.35 (m, 18H, *CH_3*), 2.73 (t, 12H, NCH_2*CH_2*), 4.16 (s, 12H, C*H_2*Ar), 7.11 (s, 3H, Ar*H*), 7.23 (d, 6H, Ar*H*), 7.25 (t, 3H, Ar*H*), 7.53 (d, 16H, Ts), 7.81 (d, 16H, Ts).

2.6.3 Bromide Salt
$Ts_6H_2 12(Br)_2 \cdot 1.87CHCl_3$

$Ts_6$12 (0.15 g, 1.0 x 10^{-4} mol) was dissolved in 10 mL $CHCl_3$/MeOH (1:1, v:v) mixture to prepare a 10 mM solution. HBr (48%) was added until the solution reached a pH reading of approximately 2. A fine, white precipitate formed immediately and was filtered from the solution. The precipitate was dissolved in CH_3OH. Crystals suitable for X–ray analysis formed after three weeks of slow diffusion by diethyl ether. Yield 0.135 g (80%). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 ^{O}C): δ 2.53 (s, 18H, C*H_3*), 3.17 (t, 12H, NC*H_2*), 3.40 (t, 12H, NCH_2*CH_2*), 4.40 (s, 12H, C*H_2*Ar), 7.21 (m, 9H, Ar*H*), 7.34 (s, 3H, Ar*H*), 7.43 (d, 12H, Ts), 7.81 (d, 12H, Ts), 9.34 (s, 2H, N*H*). Anal. Calcd. for $C_{78}H_{92}N_8O_{12}Br_2S_6$: C, 55.64; H 5.51; N 6.66. Found: C 55.28; H 5.60; N 6.69.

2.6.4 $\mathbf{CH_3Ts_612^{+}\cdot BF_4^{-}/\ (CH_3)_2Ts_612^{2+}\cdot\ 2BF_4^{-}}$ (mixed salt)

Methylation was performed using the method described in Tabushi, *et al.*[64] In an argon atmosphere, $\mathbf{Ts_612}$ (1.00 g, 0.000657 mol) was dissolved in dry CH_2Cl_2 (100 mL). Trimethyloxonium tetrafluoroborate (0.263 g, 0.00178 mol) was added to this solution. The reagents were stirred overnight. The solvent was removed under reduced pressure, yielding an orange precipitate. A solid–liquid extraction was performed using a Soxhlet apparatus and MeOH. The solution was refluxed at 90 ^{O}C for 14 h. The MeOH was removed under reduced pressure, and the precipitate was dried *in vacuo*. Mixed yield 0.145 g. ESI^{+}–MS (MeOH/Formic Acid– TG/G) m/z 1537.6 corresponds to $\mathbf{CH_3Ts_612^{+}}$ without a BF_4^{-} counter-ion $[M]^{+}$, and 769.4 corresponds to $\mathbf{(CH_3)_2Ts_612^{2+}}$ without BF_4^{-} counter-ions $[M]^{2+}$. TLC showed two spots. Further attempts to isolate the mono- from the dimethylated product were unsuccessful.

2.6.5 $\mathbf{CH_3Ts_612^{+}\ I/(CH_3)_2Ts_612^{2+}\cdot 2I^{-}}$ (mixed salt)

$\mathbf{Ts_612}$ (0.300 g, 0.00197 mol) and K_2CO_3 (0.36 g, 0.0018 mol) were dissolved in dioxane (30 mL). After heating the reaction mixture at 80 ^{O}C for 30 minutes, CH_3I (0.80 mL, 1.8 g) was added, and the mixture was allowed to react for 5 days. An orange precipitate formed and was separated from the organic layer through a coarse fritted funnel. The organic layer was collected, and the dioxane was removed under reduced pressure. The resulting orange oil was washed with $CHCl_3$, leaving a yellow powder undissolved. The organic layer was collected and the solvent was removed under reduced pressure. The resultant orange powder was dried *in vacuo*. Mixed yield 0.155 g. FAB-MS (MeOH/Formic Acid TG/G) m/z 1537.6 corresponds to $\mathbf{CH_3Ts_6 12^+}$ without an I^- counter-ion $[M]^+$, and 769.4 corresponds to $\mathbf{(CH_3)_2Ts_6 12^{2+}}$ without two I^- counter-ions $[\mathbf{12}]^{2+}$. TLC showed two spots. Further attempts to isolate the mono- from the dimethylated product were unsuccessful.

2.7 Synthesis of PEACryp (13) Salts

2.7.1 Fluoride Salt

$[H_6 13(F)_2(H_2O)][SiF_6]_2 \cdot 12H_2O$

The F^- ion complex was obtained by titrating a neutral solution of **13** (30 mg, 50 mmol) with a 48% solution of HF to pH 2. A white crystalline powder formed immediately and was recrystallized from *i*-PrOH and H_2O to yield X-ray quality colorless crystals. Yield: 45 mg (78%). ^1H NMR (500 MHz, 25 ^OC, D_2O, TSP): δ 2.87 (t, 12H, NCH_2,), 3.31 (t, 12H, NCH_2CH_2), 4.25 (s, 12H, $ArCH_2$), 7.43 (d, 12H, Ar*H*). ^{13}C NMR (125 MHz, D_2O, TSP): d 45.0, 48.8, 51.0 (aliphatic), 129.8, 131.9 (aromatic); FAB-MS: m/z 599 $[\mathbf{H13}]^+$, 619 $[\mathbf{H_2 13^{2+}} + F^-]$, 639 $[\mathbf{H_3 13^{3+}} + 2F^-]$. Anal. Calcd. for ($C_{36}H_{80}N_8F_{14}O_9Si_2$): C, 39.70; H. 7.21; N, 10.28. Fd.: C, 39.77; H, 7.04; N, 10.23.

2.7.2 Chloride Salt

$[H_6 13(Cl)(H_2O)][Cl]_5 \cdot 4H_2O \cdot CH_3OH$.

The Cl^- complex was obtained by dissolving **13** (30 mg, 50 μmol) in MeOH (2 mL) and adding 6N HCl (about 200 μL). The white precipitate that formed was redissolved in *i*-PrOH with a few drops of H_2O. Crystals suitable for X-ray analysis were obtained from slow diffusion of MeOH. Yield: 35 mg (75%). ^1H NMR (500 MHz, 25 ^OC, D_2O, TSP): δ 2.84 (t, 12H, NCH_2,), 3.35 (t, 12H, NCH_2CH_2), 4.29 (s, 12H, $ArCH_2$), 7.47 (d, 12H, Ar*H*). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 44.6, 49.5, 51.2 (aliphatic), 129.9, 131.6 (aromatic). FAB-MS: *m/z* 599 $[H\mathbf{13}]^+$, 635 $[H_2\mathbf{13}^{2+} + Cl^-]$, 671 $[\mathbf{H_3 13}^{3+} + 2Cl^-]$, 704 $[\mathbf{H_4 13}^{3+} + 3Cl^-]$. Anal. Calcd. for ($C_{36}H_{72}N_8Cl_6O_6$): C, 46.70; H. 7.83; N, 12.10. Fd.: C, 46.41;H, 7.66; N, 12.16.

2.7.3 Mixed Fluoride/Chloride Salt

$[H_6 13(F)_2(H_2O)][Cl]_2[SiF_6] \cdot 10H_2O$

The mixed F^- /Cl^- complex was obtained by dissolving equimolar amounts (10 μmol) of the F^- and Cl^- salts of **13** in *i*-PrOH (2 mL) with 5 drops of H_2O. Crystals suitable for X-ray analysis were grown in seven days in a dessicator under the vapor of *i*-PrOH. ^1H NMR (500 MHz, 25 ^OC, $CDCl_3$, TMS) δ 2.84 (t, 12H, NCH_2,), 3.33 (t, 12H, NCH_2CH_2), 4.27 (s, 12H, $ArCH_2$), 7.46 (d, 12H, Ar*H*). ^{13}C NMR (125 MHz, $CDCl_3$, TMS) d 44.6, 49.2, 51.2 (aliphatic), 130.0, 131.7 (aromatic); M.S.: m/z (FAB) 599 $[\mathbf{H13}]^+$, 619 $[\mathbf{H_2 13^{2+}} + F^-]$, 635 $[H_2\mathbf{13}^{2+} + Cl^-]$, 639 $[\mathbf{H_3 13}^{3+} + 2F^-]$, 671 $[\mathbf{H_3 13}^{3+} + 2Cl^-]$; Anal. Calcd.

for ($C_{36}H_{80}N_8F_8Cl_2O_{10}Si$): C, 41.73; H. 7.78; N, 10.82. Fd.: C, 41.69;H, 7.82; N, 10.78.

2.7.4 Bromide Salt

$[H_613(Br)(H_2O)][Br]_5\cdot6.25H_2O$

The Br^- complex was obtained by dissolving **13** (30 mg, 50 μmol) in MeOH (2 mL) and adding 48% HBr (300 μL) dropwise. The white precipitate that formed was collected and washed with Et_2O. Crystals suitable for X-ray diffraction were obtained by recrystallization from MeOH and H_2O. Yield: 40 mg (65%). ^1H NMR (500 MHz, 25 ^OC, D_2O, TSP): δ 2.83 (t, 12H, NC*H*$_2$,), 3.33 (t, 12H, NCH_2C*H*$_2$), 4.28 (s, 12H, ArC*H*$_2$), 7.48 (s, 12H, Ar*H*). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 44.5, 49.4, 51.3 (aliphatic), 129.8, 131.6 (aromatic). FAB-MS: *m/z* 599 [**H13**]$^+$, 685 [**$H_2$13**$^{2+}$ + Br^-], 765 [**$H_3$13**$^{3+}$ + $2Br^-$]. Anal. Calcd. for ($C_{36}H_{78}N_8Br_6O_6$): C, 36.24; H. 6.54; N, 9.400. Fd.: C, 36.15; H, 6.48; N, 9.48.

2.8 PyEACryp (14) Salts

2.8.1 Tosylate Salt

$H_714^{7+}\cdot7TsO^-$

^1H NMR (400 MHz, 25 ^OC, D_2O, TSP): δ 2.31 (s, 21H, C*H*$_3$), 3.13 (d, 12H, NC*H*$_2$), 3.35 (d, 12H, NCH_2C*H*$_2$), 4.32 (s, 12H, ArC*H*$_2$), 7.23 (d, 14H, Ts), 7.27 (s, 3H, Ar*H*), 7.53 (d, 14H, Ts), 7.79 (d, 6H, Ar*H*). Analyzed for

$C_{33}H_{51}N_{11}\cdot 7(TsOH)\cdot(CH_3OH)\cdot 5(H_2O)$ Calculated: C, 51.67; H. 6.32; N, 7.99. Fd.: C, 51.54; H, 5.87; N, 7.98.

2.8.2 Bromide Salt

$[H_6 14(Br)_3(H_2O)][Br]_3\cdot H_2O_{2.25/4}$

In a glass vial, HBr (5 drops) was added to a MeOH solution of **14** (5.5 mM, 6.00 mL) until the solution was acidic (pH < 2). This resulted in the formation of a fine, yellow powder. Addition of ether to the solution resulted in additional precipitation of a light yellow solid. The solid was filtered and rinsed with ether. Yield 36.0 mg (90%). Orange crystals suitable for X-ray diffraction were obtained by dissolving the salt (9.9 mg) in methanol (2 mL) and allowing slow diffusion by ether. Analyzed for $C_{33}H_{57}N_{11}\cdot(Br)_6\cdot(H_2O)_{2.5}$ Calculated: C, 36.45; H, 5.28; N, 14.17; Br, 44.09. Fd.: C, 35.14; H, 5.50; N, 13.66; O, 3.19; Br, 42.51.

Chapter 3 Tosylated MEACryp

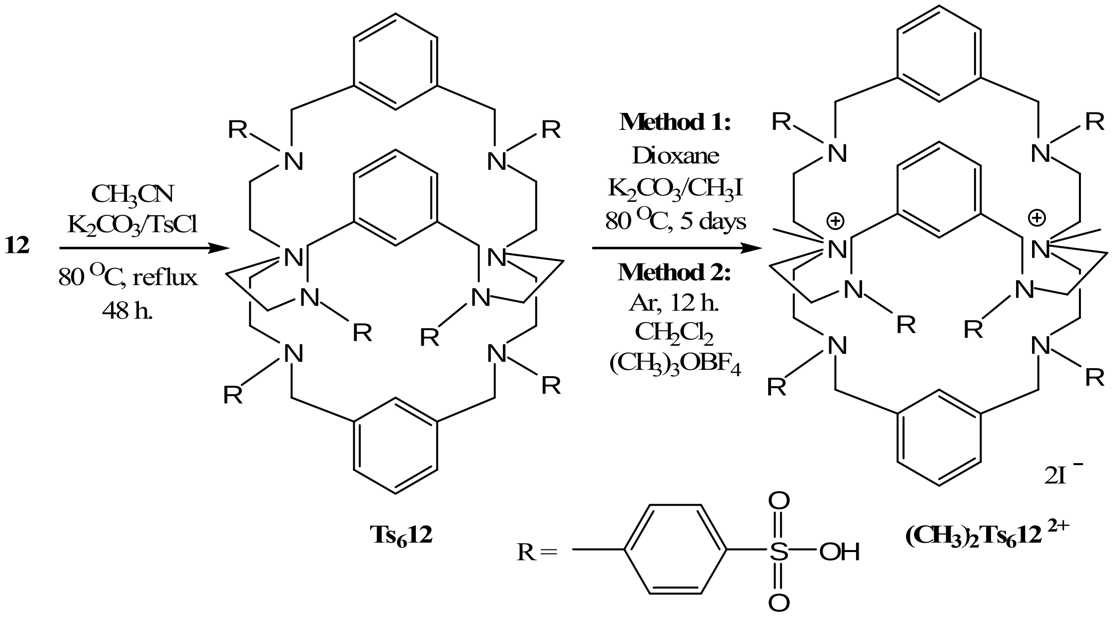
3.1 Synthesis of a Divalent Receptor

3.1.1 Background

As mentioned in **Chapter 1**, the abundance of the SO_4^{2-} ion in nuclear waste is a growing concern, as the SO_4^{2-} ion's low solubility in borosilicate glass inhibits the vitrification process.[31,32] As such, designing a ligand to sequester SO_4^{2-} would be beneficial in remediation of nuclear waste. As the binding ability of amine-based receptors is often pH dependent, the basicity of the waste tanks at the Hanford and Savannah River sites limits the use of these ligands for extracting SO_4^{2-}. However, as these ligands are relatively simple to synthesize in high yield, modification of these systems for use in the waste tanks would be a possible approach.

It was decided to synthesize a divalent receptor with the intent of sequstering SO_4^{2-}. MEACryp, **12**, was selected as the target ligand because it is a pre-organized cryptand and soluble in organic solvents, such as $CHCl_3$. As shown in **Table 3**, **12** is not hexa-protonated until pH reaches approximately 6, although initial protonation (and binding) usually happens near pH 10.[65] Since the tanks are at a basic pH,[31,32] hydrogen-bonding interactions would not be as plentiful as they would be under acidic conditions. Additionally, as fewer nitrogens become doubly protonated, there are fewer opportunities for electrostatic interaction. However, **12** has two tertiary bridgehead amine nitrogens, which upon quaternization, would yield a pH independent divalent receptor. **Scheme 6** depicts the proposed synthesis of a divalent receptor.

Scheme 6: Proposed synthesis of a divalent receptor.



3.1.2 Amine Protection

One of the simplest methods of quaternization would be to methylate the tertiary anime nitrogen with CH_3I. First, it would be necessary to protect the secondary nitrogens from methylation, as this would result in six additional counter-anions, which may compete for binding with the target anion SO_4^{2-}. Therefore, it was necessary to select an appropriate protecting group.

Scheme 6 shows the proposed synthesis of a divalent receptor. Tosyl chloride, TsCl, was used as the protecting agent for several reasons. First, it can be used as a protecting group for secondary amines, such as those found in **12**. Additionally, the tosyl group is an electron-withdrawing group,[66] thereby inhibiting methylation at the secondary nitrogens. **$Ts_6$12** was synthesized with TsCl in 97%

yield.[67] Signals expected from the twelve unique carbon atoms present in **$Ts_6$12** were confirmed by ^{13}C NMR. Comparison of the ^{1}H NMR peak integrations supported the presence of six tosyl groups. Elemental analysis confirmed these results.

3.1.3 Methylation Techniques

<u>Method 1:</u>

Following protection of the ligand, methylation of **$Ts_6$12** was attempted using CH_3I (**Scheme 6, Method 1**).[39,59] Upon isolation of a product, a mass spectrum showed three peaks of interest: **$CH_3Ts_612^+$** ($[m/z]^+ = 1538.6$); **$(CH_3)_2Ts_612^{2+}$** ($[m/z]^{2+} = 776.3$); and the free ligand, **$Ts_6$12** ($[m/z]^+ = 1523.5$). These results, along with TLC plate spotting, indicated that more than one species were present in the recovered product, whose identities were most likely **$Ts_6$12**, **$CH_3Ts_612^+$**, and **$(CH_3)_2Ts_612^{2+}$**. Recrystallization with CH_3Cl/ether was employed in an attempt to separate components in the reaction mixture. However, it was inefficient in separating the mixed species, as at least two distinct types of crystals were formed, and only the free base, **$Ts_6$12,** was successfully isolated to obtain a crystal structure. Structural data will be discussed later in the chapter. Refer to **Chapter 8** for a detailed crystal structure report.

<u>Method 2:</u>

Difficulties with the **Method 1** methylation procedure prompted the pursuit of a different reaction for several reasons. First, the possible products, **$Ts_6$12**, **$CH_3Ts_6$12$^+$**, and **$(CH_3)_2Ts_6$12^{2+}**, were difficult to separate from one another, as described above. Second, the use of CH_3I as a methylating agent required harsh conditions over several days. Third, it was presumed that I^- would interfere with binding, and ion exchange would be necessary if CH_3I were used as the methylating agent. We sought to find an alternate methylation technique to minimize these constraints. A methylation technique published by Tabushi and co-workers,[64] involving $(CH_3)_3OBF_4$ as the methylating agent in dry CH_2Cl_2 was implemented **(Scheme 6, Method 2)**. This method has several advantages over the use of CH_3I. First, the reaction occurs under milder conditions, ambient temperature versus refluxing at 80 ^{O}C. Generally, the reaction is complete in approximately one day, as opposed to approximately five days for CH_3I. Additionally, because of its larger size and weaker basicity, BF_4^- as a counter-ion was considered less likely to interfere with binding.[59]

A preliminary ^1H NMR of the precipitate indicated a mixture of products, similar to the results found for the synthesis using CH_3I. Solubility tests confirmed that the reaction product was marginally soluble in MeOH, while **$Ts_6$12** was insoluble in MeOH. After washing the product in MeOH, and collecting and removing the solvent under reduced pressure, a mass spectrum was obtained. ESI^+–MS displayed two peaks corresponding to **$CH_3Ts_6$12$^+$** ($[m/z]^+ = 1537.6$) and **$(CH_3)_2Ts_6$12^{2+}** ($[m/z]^{2+} = 769.4$) in approximately equal proportions, as well as a peak of approximately half the intensity corresponding to the **$Ts_6$12** ($m/z=1523.4$).

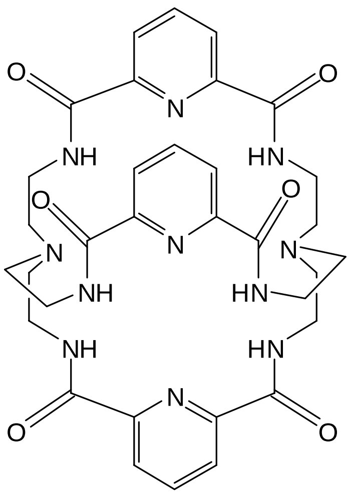
After washing with CH_3OH, a subsequent mass spectrum showed a reduction, but not a complete elimination, in the relative proportion of **$Ts_6$12** to the methylated species. It was decided to pursue a more extreme separation technique. Therefore, a solid–liquid extraction using a Soxhlet apparatus and a refluxing CH_3OH mobile phase was used in an attempt to isolate **$(CH_3)_2Ts_612^{2+}$**. It was assumed that the divalent species would be more soluble in methanol than **$Ts_6$12** or **$(CH_3)_2Ts_612^{2+}$**. After methylation and extraction, a combined yield of approximately 10% was obtained, compared to Tabushi's 40% yield.[64] This was a qualitative yield and not pure **$(CH_3)_2Ts_612^{2+}$**.

After the extraction, the isolated product was checked by ESI^+–MS spectrum. While both **$CH_3Ts_612^+$** and **$(CH_3)_2Ts_612^{2+}$** were observed, the intensity of the **$(CH_3)_2Ts_612^{2+}$** signal was twice the intensity of the **$CH_3Ts_612^+$** signal, with **$Ts_6$12** again about half the intensity of **$CH_3Ts_612^+$**. While signal intensity relates to structural stability in the instrument, these results indicate that the use of the solid–liquid extraction described previously does increase the proportion of **$(CH_3)_2Ts_612^{2+}$** in the recovered product. However, the overall yield is still lower than the CH_3I technique. The lower yield might be due to the presence of electron-withdrawing protecting groups on the secondary amines, which decrease the reactivity of neighboring tertiary amines toward the electrophiles. Despite this, methylation using $(CH_3)_3OBF_4$ has the potential to produce a higher yield if the technique is modified and the extraction is improved. However, due to the difficulties in isolating a dimethylated analogue of **$Ts_6$12**, research involving the properties of **$Ts_6$12** was pursued.

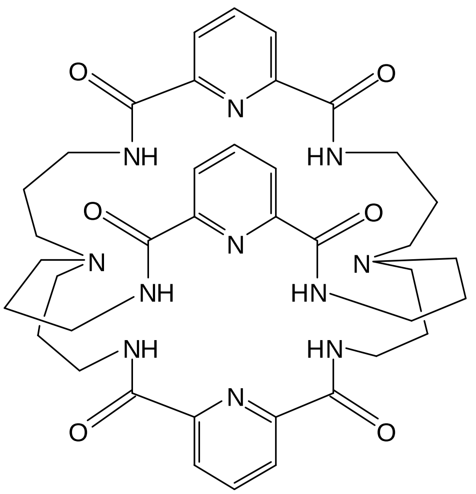
3.1.4 Comparison to Amide Analogues

Bowman-James, *et al.,* attempted methylation of a different tren-based amido cryptand, PyEAmCryp, **19**, with little success. However, expansion of the cavity from a tren-based to a trpn-based linker, tris(2-aminopropyl)amine, facilitated quarternization and yielded a dimethylated species in 80% yield.[68] It is thought that the trpn-based cryptand, PyPAmCryp **20** allows better quaternization yields because of its larger cavity compared to the tren-based cryptand **19**. Refer to **Figure 11** for drawings of **19** and **20**.

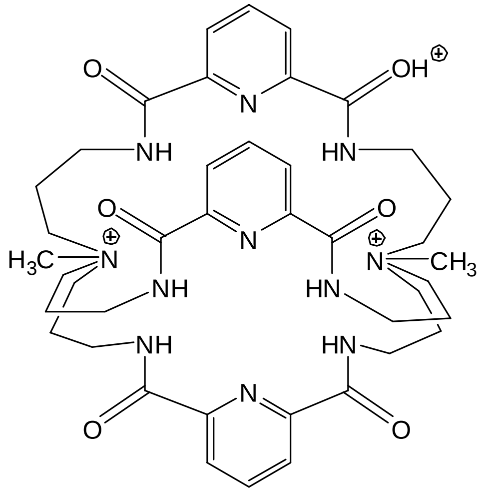
Overall, binding studies overall show that dimethylated PyPAmCryp **$(CH_3)_2 20^{2+}$** binds anions with affinities comparable to those of PyEAmCryp **19** and of PyPAmCryp **20**. However, upon quaternization, the dimethylated cryptand adopts a bowl-like structure, which favors binding with $H_2PO_4^-$. These results indicate that methylation of known ligands is a viable method for synthesizing anion receptors. As such, future modification of **$Ts_6 12$** by replacing the tren group with trpn may result in increased yield of the dimethylated product.



19



20



$(CH_3)_2 20^{2+}$

Figure 11: Clockwise from top left PyEAmCryp (**19**), PyPAmCryp (**20**), and quaternized PyPAmCryp **$(CH_3)_2 20^{2+}$**.

3.2 Studies Involving the Tosylated Receptor: $\mathbf{Ts_6 12}$ and $\mathbf{Ts_6 12 \cdot 2Br^-}$

3.2.1 Background

While the above section discussed the research goal of methylation of the test amine, other quaternized species, such as protonated ligands, are a viable and active area in anion receptor chemistry.[6,38,39] For this reason, it was decided to explore the properties of **$Ts_6$12** in acidic conditions.

Tosylation is often a necessary step in synthesizing organic compounds. The tosylate group functions as a protecting group for secondary amine nitrogens. The electronegative sulfonyl group withdraws electron density from the corresponding nitrogen, which prevents further condensation. Once the desired syntheses are performed, the protecting group is removed, and the properties of the resulting species are studied. Tosylation is viewed as a necessary evil, and hence, the properties of tosylated species often are ignored. However, tosylate derivates are relatively easy to crystallize due to the bulkiness of the group.[56]

3.2.2 Crystal Structures

In an effort to examine the effect of protonation, crystals of **$Ts_6$12** and its Br^- complex were grown and analyzed as previously described. The structures **$Ts_6$12** and **$Ts_6$12·2HBr** (**Figure 12**) are compared below. **$Ts_6$12** crystallizes with 1.5 moles of CH_3CN and 0.183 moles of $CHCl_3$, **$[Ts_6 12]\cdot CH_3CN \cdot 0.183CHCl_3$**. **$Ts_6$12** and $CHCl_3$ both sit on the crystallographic 3-fold axis. Relevant distances are listed in

Table 4 and a detailed numbering scheme is provided in **Chapter 8**. The packing diagram for **$Ts_6$12** (**Figure 13)** shows overlap between tosylates on adjacent bicycles. The Br^- salt crystallized with 1.87 moles of $CHCl_3$, **$[Ts_6H_2 12(Br)_2]\cdot 1.87CHCl_3$**. Rather than sitting on the 3-fold axis, both Br^- ions lie off-center between two of the cryptand arms and each are hydrogen bonded with one of the endo-oriented amine protons.

The similarities between the two crystal structures are remarkable, as demonstrated in **Figure 12**. For example, both of the cryptands are approximately the same size, even though one is diprotonated. The distance between the bridgehead amines, N(1)–N(16), is 5.006 Å in **$Ts_6$12**, while in **$[Ts_6H_2 12(Br)_2]$** this distance is 5.200 Å. The slight elongation most likely results from two factors: the electrostatic repulsion of the two *in-in* protons, and the two relatively large halides occupying the arms of the cryptand. The cavity size of the free ligand is smaller than the free base, **12**, found by Mason at 5.57 Å.[25]

The hydrogen bond distances in the Br^- complex are 3.058(4) Å for N(16)–Br(1) and 3.128(4) Å for N(1)–Br(2). The structure is unique among many of the protonated azacryptand structures, as there are only the two hydrogen bonding sites. Additionally, while many of the protonated azacryptand crystal structures contain multiple molecules of water and extensive hydrogen bonding networks within the protonated amines, no water is found within **$[Ts_6H_2 12(Br)_2]$**.

One may hypothesize that, because there is so little change in the size of the cavity upon encapsulation, the cavity of **$Ts_6$12**, in terms of size, is complementary for binding two Br^- ions. Since there is a small change in cavity size, the ligand may be pre-organized to encapsulate the bromide ions, making the binding more favorable than if the host were to alter its size to accommodate the guests.

Martell isolated a crystal with the free ligand **12** and Br^-, **$[H_8 12 (Br)_3][Br]_5 \cdot 6H_2O$**.[53] In this structure, eight nitrogens are protonated, including the bridgehead amines. However, unlike the crystal structure of **$Ts_6 12$**, the protons on the bridgehead amines have an *exo* rather than *endo* orientation. Furthermore, the distance between the bridgehead amines is significantly larger at 7.60 Å. Three Br^- ions are directly coordinated to the ligand but none are located inside the cavity. The ions lie between the cryptand arms, as in **$Ts_6 12$**. Additional discussion of Martell's Br^- complex is addressed in **Chapter 5**.

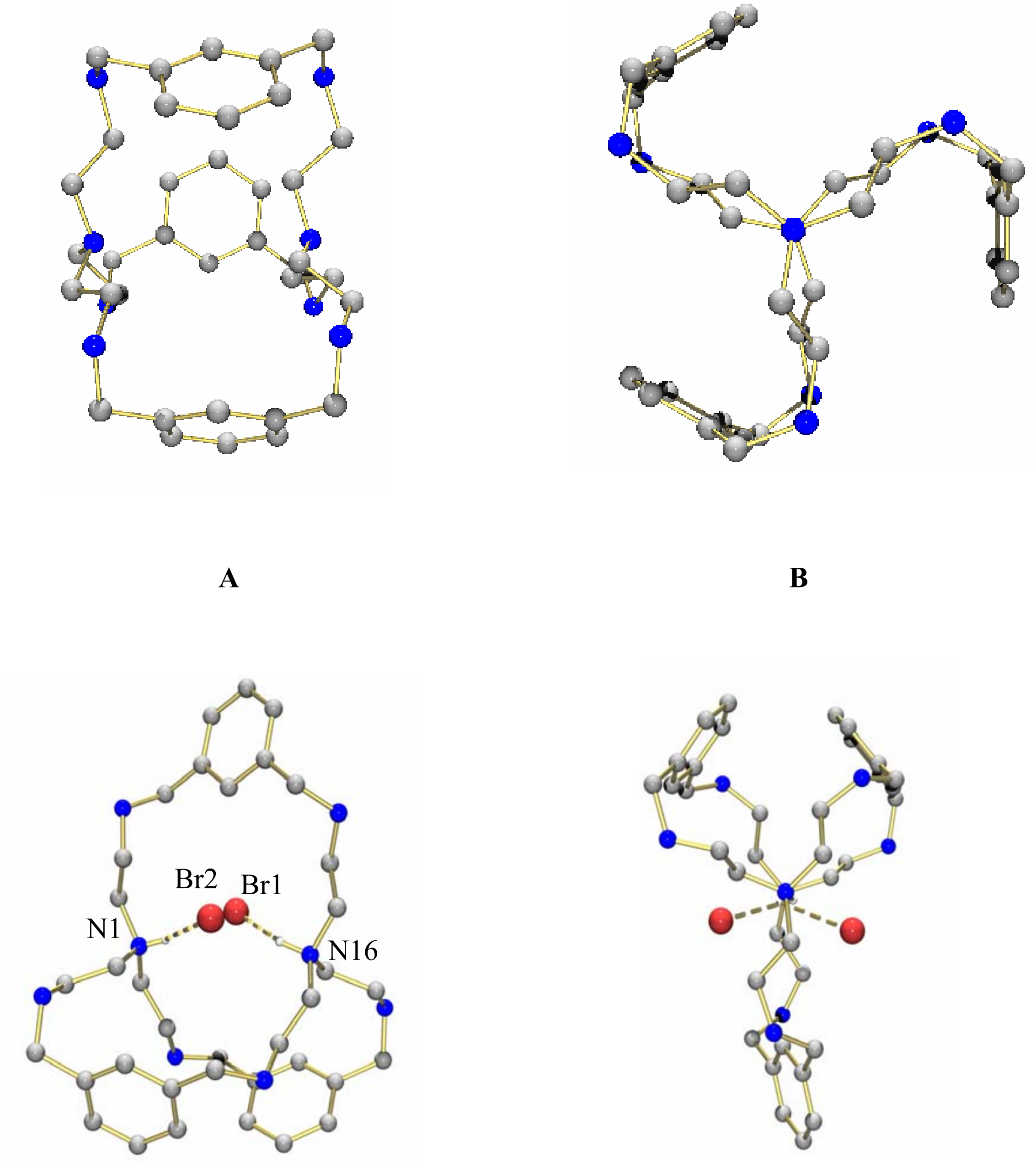


Figure 12: Two views each of **$Ts_6$12** (A and B) and **[$Ts_6H_2$12(Br)$_2$]** (C and D). Carbon-bound hydrogen atoms, tosyl groups, and solvent are omitted for clarity. Diagrams (A) and (C) show views of the cavity. Diagrams (B) and (D) are views down the bridgehead ammonium groups.

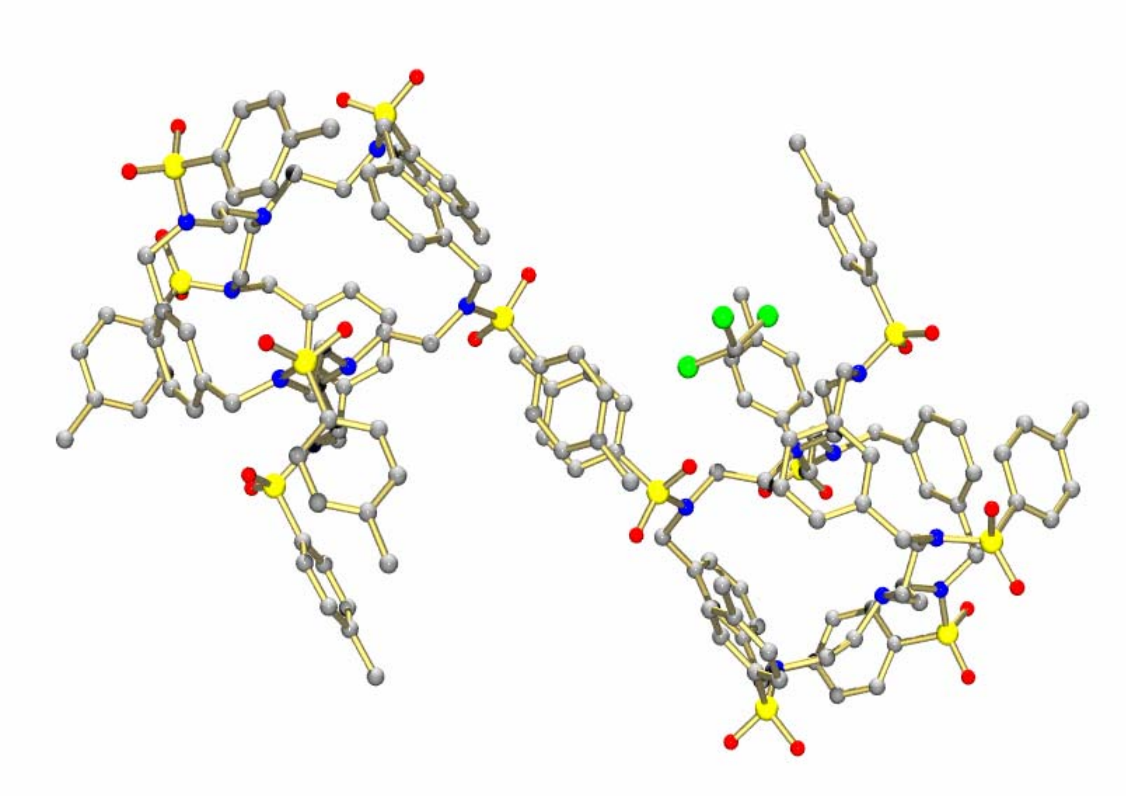


Figure 13: Packing diagram of **Ts$_6$12** shows the overlap tosylate groups between two bicycles. An extended packing diagram is located in **Chapter 7**.

3.2.3. Comparison to Amide Crystal Structures

It is interesting to compare crystal structures of several of Bowman-James' mono- and diprotonated amide complexes, **[H19(Cl)]**, [69] **[$H_2$19 (SO_4)]**, [70] **[$H_2$20($Cl)_2$],**[68] and **[$H_2$20 (SO_4)]** [70] with that of **[$Ts_6H_2$12($Br)_2$]**. Focus will lay with the hydrogen bond distances between the protonated bridgehead amine nitrogen and the corresponding anion. Refer to **Table 4** for selected hydrogen bond distances.

PyEAmCryp **19** forms a Cl^- complex, **[H19(Cl)]**.[68] This is a result of the large affinity of **19** for HCl, which it abstracts from $CDCl_3$. There is an expansion of the cavity from **19** (5.868 Å) to the Cl^- complex with **19** (7.070 Å). One of the bridgehead amine nitrogens becomes protonated and forms a hydrogen bond with the halide (3.200 Å). As with both the halide complexes mentioned above, the Cl^- ion lies off-center from the N-N axis.

PyEAmCryp **19** also forms a SO_4^{2-} complex, **[$H_2$19(SO_4)]**.[70] There is an expansion of the cavity from **19** (5.868 Å) to the SO_4^{2-} complex (7.492 Å). Both bridgehead amine nitrogens become protonated and form hydrogen bonds with the SO_4^{2-} ion (2.662 and 2.657 Å). The SO_4^{2-} ion lies slightly off the N-N axis. The larger expansion for **[$H_2$19(SO_4)]** as compared to **[H19(Cl)]** may result from the SO_4^{2-} electrostatic repulsion of the two *in-in* protons.

The propyl amide cryptand, **[$H_2$20(SO_4)]**,[70] crystallized diprotonated with a single SO_4^{2-} anion cascading between two H_2O molecules encapsulated in the cavity. The diprotonated Cl^- complex **[$H_2$20($Cl)_2$]** crystallized with two encapsulated Cl^- ions joined by a H_2O molecule. Only the bridgehead nitrogens were protonated, as a result of the amide groups. Cascading aspects will be discussed in **Chapter 4**.

Previously in the chapter, it was suggested that cavity size may play a role in quaternization yields. Crystal data support this hypothesis in that the N-N distance in **$Ts_6$12** (5.006 Å) is significantly smaller than that of **20** (6.850 Å). While there may be other factors involved, these data reinforce this hypothesis.

Additionally, just as there is cavity elongation from **$Ts_6$12** (5.006 Å) to **[$Ts_6H_2$12$(Br)_2$]** (5.200 Å), there is also cavity expansion from **20** (6.850 Å) to **[$H_2$20(SO_4)]** (7.623 Å) and to **[$H_2$20$(Cl)_2$]** (7.971 Å). The cavity expansion for the amine cryptate is minimal due to the placement of the of the Br^- ions in the cavity. Rather than lying on a line connecting the bridgehead amines, the Br^- ions lie off-center between the cryptand arms. However, with the amide cryptate of SO_4^{2-}, the anion lies directly between the bridgehead nitrogens. This maximizes electrostatic repulsion, forcing the cavity to enlarge to accommodate the anionic (and water) guests. Additionally, this allows the presumption that there may be a better fit between Br^- and **12** than between **20** and its corresponding anions.

Table 4: Selected atom and hydrogen bond distances for complexes of **Ts$_6$12**, **19**, and **20**.

Ligand	Atoms	Distances (Å)
Ts$_6$12	N(1)···N(16)	5.006
[Ts$_6$H$_2$12(Br)$_2$]	N(1)-H(1)···Br(2)	3.128(4)
	N(16)-H(16)···Br(1)	3.058(4)
	N(1)- N(16)	5.200
19	N(1)-N(16)	5.868
[H19(Cl)]	N(1)-H(1)···Cl(1)	3.19999(12)
	N(1)-N(16)	7.070
[H$_2$19(SO$_4$)]	N(1)-H(1)···O(4)	2.662(2)
	N(16)-H(16)···O(3)	2.657(2)
	N(1)-N(16)	7.492
20	N(1)-N(16)	6.850
[H$_2$20(Cl)$_2$]	N(1)-H(1)···Cl(1)	3.165(4)
	N(18)-H(18)···Cl(2)	3.192(4)
	N(1)-N(18)	7.971
[H$_2$20(SO$_4$)]	N(1A)-H(1A)···O(1C)	2.789(2)
	N(18A)-H(18A)···O(2C)	2.685(2)
	N(1A)- N(18A)	7.623

The hydrogen bond distances between the three halide complexes **[Ts$_6$H$_2$12(Br)$_2$], [H19(Cl)]**, and **[H$_2$20(Cl)$_2$]** can be compared. For the ligand systems **12**, **19**, and **20**, the focus is on hydrogen bonds formed from the bridgehead protons. In the above complexes, the hydrogen bonds range from approximately 3.0 to 3.2 Å. From the data, it appears that for these types of systems, hydrogen bonds formed between the protonated bridgehead amine and the halide can be expected to be found in this range.

3.3 Proton Cages

The phenomenon of the *endo* hydrogens described in the previous section is another example of the proton cages[20] described in **Chapter 1**, (**Figure 4**). This class of cryptands was first identified by Park and Simmons in 1968 [3,4] and later expanded on by Lehn, with the synthesis of proton cryptates**.**[71,72,73] The research of **$Ts_6$12** described herein and the amide analyses conducted by Bowman-James *et al.* [68,69] further extends studies in this area.

3.4 NMR Studies

3.4.1 Binding Constants

The affinity of **$Ts_6$12** for anions was investigated using ^{1}H NMR spectroscopy. Binding constants were calculated using Sigma Plot software by fitting the proton signals to a 1:1 association model. A ^{1}H NMR titration performed with **$Ts_6$12** (5mM) and tetra-*n*–butylammonium (*n*Bu_4NX) halides (50 mM) in $CDCl_3$ indicated that Br^- does not bind with **$Ts_6$12** when the apical nitrogens are not protonated with a positive charge. From this data, one can surmise that the hydrogen bonds and electrostatic interactions in **$Ts_6H_2$12$\cdot$2Br^-** add to the stability of the host–guest complex, and that the cryptand alone does not effectively bind the Br^- anion.

The above premise is supported further by ^{1}H NMR data. The affinity of **$Ts_6$12** for Br^- in the presence of two equivalents of TsOH **($Ts_6H_2$12^{2+})** was investigated using ^{1}H NMR. The tosyl salt did not display a NH proton signal, which was not observed until after the addition of Br^{-}. Nevertheless, when $n$$Bu_4NBr$ is added to the tosyl salt, an NH signal appears at 9.34 ppm in $CDCl_3$. The fact that the NH proton is seen only in the presence of Br^{-} indicates that the anion also serves to stabilize the protonated amine, as noted by others.[74] One of Lehn's monoprotonated proton cryptates displayed a R_3NH^+ peak at 9.67 in D_2O in the presence of the Br^{-} ion.[72] While the solvents differ, Lehn's data support the above conclusions.

Table 5: Binding constants (Log *K*) of various anions (50 mM) with $\mathbf{Ts_6H_2 12^{2+}\cdot 2TsO^-}$ (5 mM) in $CDCl_3$

Anion	**Log *K* (M^{-1})**
Br^{-}	2.40
Cl^{-}	2.67
F^{-}	Slow Exchange
I^{-}	No binding

A subsequent ^1H NMR titration of $\mathbf{Ts_6H_2 12^{2+}\cdot 2TsO^-}$ in $CDCl_3$, using Ar-CH_2 as the reference peak, indicated that the Br^{-} ion binds weakly with the ligand (*Log K* = 2.40) (**Figure 14**). As expected, no binding with the Br^{-} ion was observed without the presence of TsOH resulting from a lack of hydrogen bonding and electrostatic interactions. However, a slightly larger affinity was observed for Cl^{-} (*Log K* = 2.67), and no interaction was observed with I^{-} (**Table 5**). These findings can be expected because of the heightened hydrogen-bonding tendencies of Cl^- and lessened tendencies of I^- compared to Br^-.

While we did observe some interaction between the ligand and the F^- ion, no NH resonance signals were observed by ^1H NMR. A binding constant could not be calculated due to slow exchange and spectral complexity. ^{19}F NMR were performed at low temperatures, and while interactions were observed, no conclusions could be substantiated because of the broadness of the peaks.

3.5 Conclusions, Further Remarks, and Further Research

In conclusion, protective tosylation has generally been considered a necessary evil in the synthesis of a variety of amine-based receptors. However, by virtue of the same chemistry that allows the tosyl group to protect amines from further condensation, its protecting influence can be used to shift protonation to less accessible sites. The protonation of the two remaining amines provides the ditopic anion receptor with charge complementarity for monovalent halides or potentially the monotopic receptor for divalent anions. The isolation and characterization of the ditopic, *in-in* dibromide complex also demonstrates the important role that the anions play in stabilizing the protons on the apical nitrogen in these large azacryptands. Furthermore, because of the bulky tosyl groups, which make these receptors less water soluble than simple amines, they may be of utility in applications such as liquid-liquid extraction. Thus, this finding provides structural and NMR corroboration of the capability of these systems for binding anions, and that anion binding does further shield the NH protons so that they are readily visible in the NMR spectra. While these ligand have yet to show superiority over other anion receptors, they serve as an example of an overlooked class of potential anion receptors.

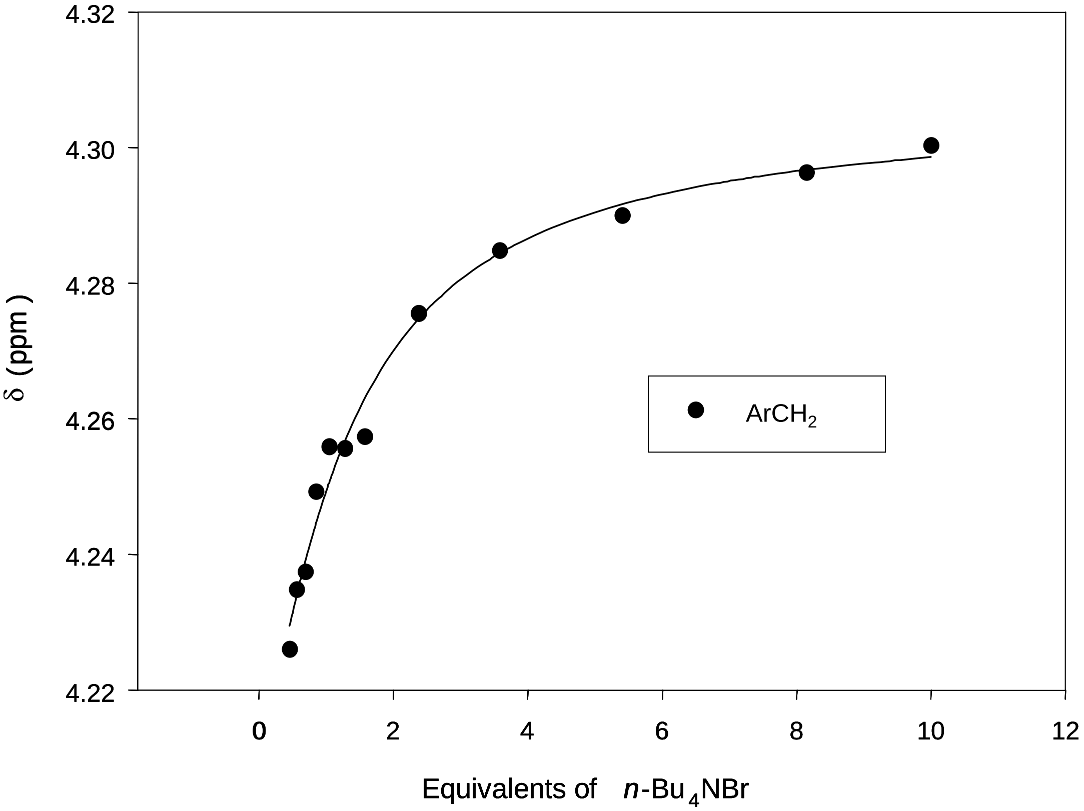


Figure 14: ^{1}H NMR titration of $\mathbf{Ts_6H_2 12^{2+} \bullet 2TsO^-}$ (5 mM) with nBu$_4$NBr (50 mM) in CDCl$_3$.

Chapter 4 PEACryp

4.1 Introduction

Azacryptands are capable of binding two species simultaneously, as demonstrated by Bowman-James' ditopic NO_3^- and F^-/H_2O structures with **12.**[24,42] Based on the results of these experiments, an analogue of this cryptand was examined. The use of *para*–xylyl spacers, to yield PEACryp, **13**, results in an enlarged cavity. Refer to **Figure 6** for drawings of **12** and **13**. A crystal structure of this species was indicated encapsulation of two F^- ions and a H_2O molecule, the first example of an azamacrocycle hosting two F^- ions cascading with a H_2O molecule (**Figure 15)**.[26]

4.2 Crystal Structures of 13

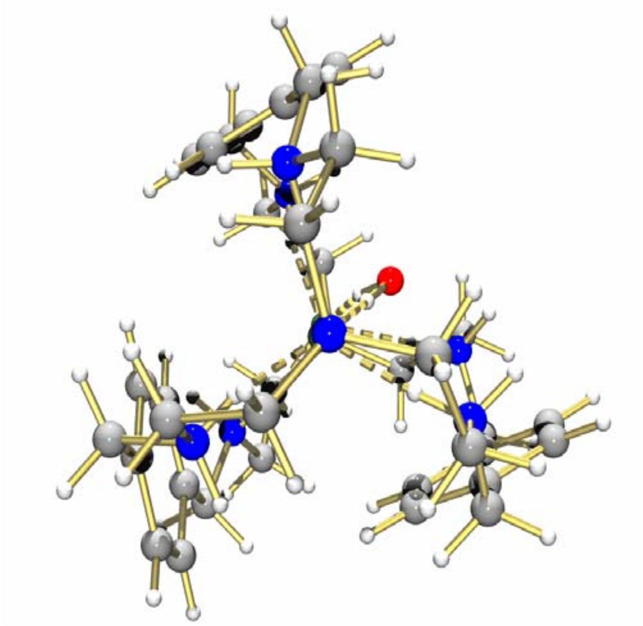
4.2.1 Fluoride Cascade

The hexa–protonated complex, $\mathbf{[H_6 13(F)_2(H_2O)][SiF_6]_2 \cdot 12H_2O}$, encapsulates two F^- ions and is bordered by two externally bound SiF_6^{2-} ions and twelve H_2O molecules. Looking through the N–N axis of the molecule shows that the F^- ions are placed in the cavity along the axis, while the central H_2O molecule serves to link the two encapsulated F^- ions. The F^- ions are slightly removed from a line connecting the bridgehead nitrogens (0.124 and 0.229 Å). Each F^- ion occupies the center of a distorted tetrahedron coordinated with the H_2O molecule and the three hydrogens on secondary amino groups of the tren unit. Hydrogen bonds between **12** and F^- range from 2.6 to 2.7 Å, and hydrogen bonds formed between H_2O and F^- are approximately 2.7 Å. The H_2O molecule lies off the center axis, resulting in the distorted tetrahedral geometry. Selected atom-atom and hydrogen bond distances are given in **Table 6**.

Several variables were modified to discern the binding of F^- with **13**, including, competitive anions, concentration, pH, ratio of host to guest (L:A), and temperature. These topics will be discussed in later sections.

4.2.2 Chloride Complex

The Cl^- complex of **13** crystallizes with six Cl^- ions, five H_2O molecules, and one molecule of solvent (**Figure 16**).[75] One Cl^- and one H_2O are located inside the cavity. As in the F^- anion cascade complex, there are many hydrogen bonds between **13** and the external water molecules, which range from 2.8 to 2.9 Å. The molecule of CH_3OH is outside of the cavity and sits between the two cryptand arms. The internal Cl^- ion has a coordination similar to that of the F^- ion structure. The internal Cl^- is tetrahedrally hydrogen bonded to three hydrogens of secondary amino groups on one tren unit and one hydrogen of the internal H_2O molecule. Hydrogen bonds between the host and Cl^- range from 3.0-3.3 Å, which are longer than in the F^- complex. When compared to the F^- complex, the Cl^- and H_2O are not as close to the bridgehead nitrogens (3.580 and 3.320 Å, respectively). The distance across the cavity, N(1)-N(16), for the Cl^- complex (10.093 Å) is shorter than the F^- complex (10.717 Å). This is to be expected for only two, rather than three, species in the cavity. Refer to (**Table 6**) for selected bond distances.



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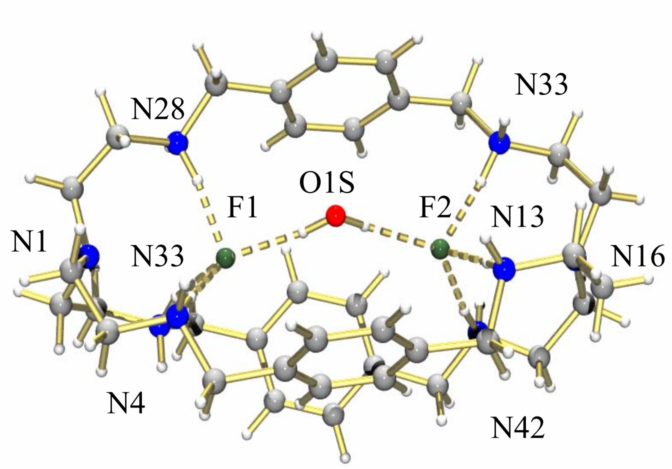


B

Figure 15: Drawings of **[H$_6$13(F)$_2$(H$_2$O)][SiF$_6$]$_2$·12H$_2$O** (external H$_2$O and SiF$_6^{2-}$ omitted for clarity); (A) view down the N-N bridgehead axis; (B) F$^-$ cascade with H$_2$O molecule inside the cavity.

Table 6: Selected hydrogen bonding interactions and atom distances for **$[H_6 13(F)_2(H_2O)][SiF_6]_2 \cdot 13H_2O$**.

Atoms	**Distance (Å)**
F(1)···H(4B)-N(4)	2.6703(14)
F(1)···H(28B)-N(28)	2.6042(14)
F(1)···H(33B)-N(33)	2.7237(12)
F(1)···H(1SA)-O(1S)	2.7090(13)
F(2)···H(13A)-N(13)	2.6538(14)
F(2)···H(19B)-F(19)	2.6820(14)
F(2)•••H(42A)-N(42)	2.6100(14)
F(2)···H(1SB)-O(1S)	2.7168(13)
O(1S)···H(2SA)-O(2S)	2.8886(15)
O(1S)···H(3SA)-O(3S)	2.8614(15)
F(1)···F(2)	4.736
F(1)···N(1)	2.994
F(2)•••N(16)	3.002
N(1)•••N(16)	10.717

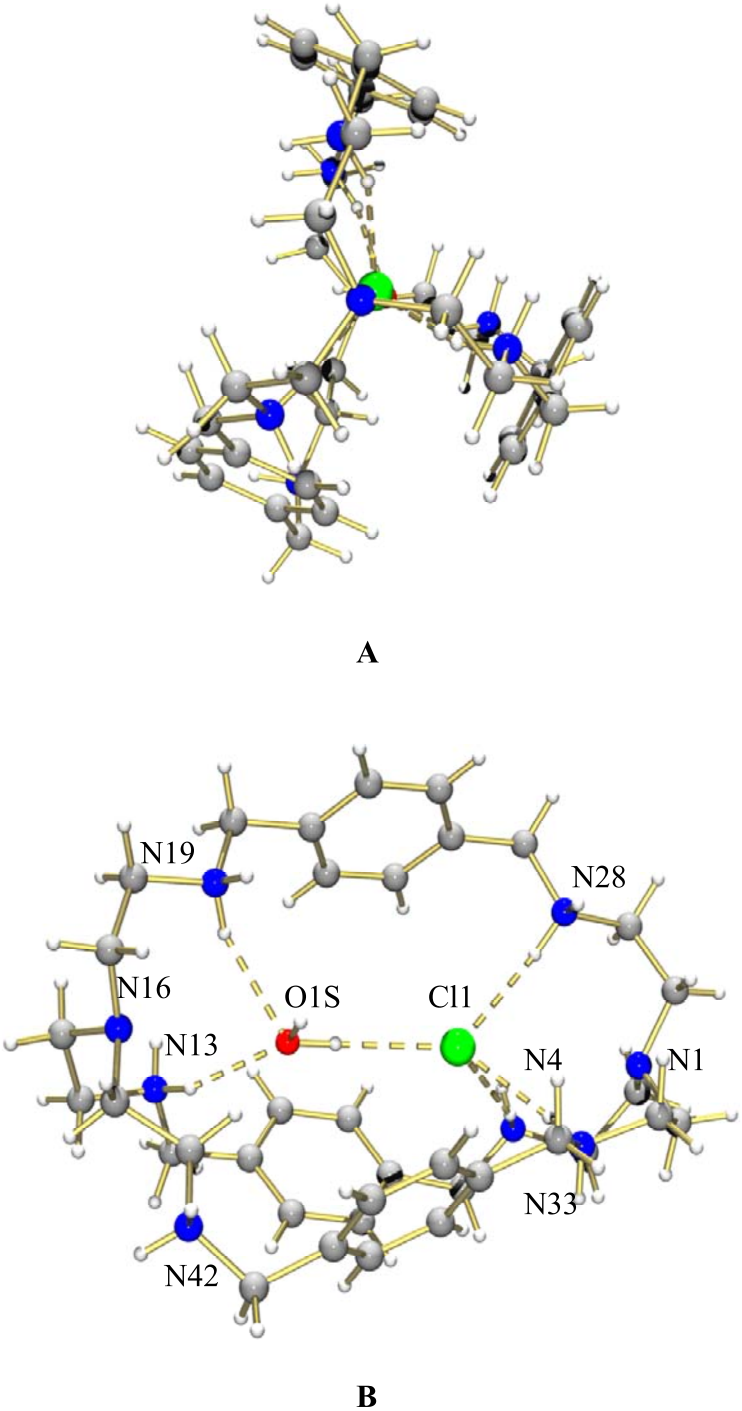


Figure 16: Drawings of **[$H_6$13(Cl)(H_2O)][Cl]$_5$·4H_2O·CH_3OH**: (A) side view showing Cl^- and H_2O inside the cavity; (B) view down the three-fold axis.

Table 7: Selected hydrogen bonding interactions and atom distances for **$[H_613(Cl)(H_2O)][Cl]_5{\cdot}4H_2O{\cdot}CH_3OH$**.

Atoms	**Distance (Å)**
Cl(1)···H(4B)-N(4B)	3.129(3)
Cl(1)···H(28B)-N(28B)	3.167(3)
Cl(1)···H(33B)-N(33B)	3.089(3)
Cl(1)···H(1SA)-O(1S)	3.245(2)
O(1S)···H(13A)-N(13)	2.831(3)
O(1S)···H(19A)-N(19)	2.935(3)
Cl(1)···N(1)	3.580
O(1S)···N(16)	3.320
N(1)···N(16)	10.093

4.2.3 Mixed Fluoride/Chloride Complex

The selectivity of **13** was probed with regard to F^- and Cl^-. A complex containing both anions of F^- and Cl^- was obtained from an equimolar mixture of anion salts of the cryptand, **$[H_613(F)_2(H_2O)][Cl]_2[SiF_6]{\cdot}10H_2O$**, as described in **Chapter 2**. Upon isolation of this crystal, it was discovered that two F^- ions remained in the cavity, while two Cl^-ions and one SiF_6^{2-} were externally bound as counter-ions. The structure was identical to that of **Figure 15** with the Cl^- ions in place of the SiF_6^{2-} counter-ion and two fewer H_2O molecules. This study indicated that **13** was selective for F^- over Cl^- in the solid state. In sections below, the selectivity in solution was tested by ^{1}H- and ^{19}F NMR measurements.

4.2.4 Bromide Complex

The Br^- complex of **13** crystallizes with six Br^- and 6.25 H_2O molecules, $\mathbf{[H_613(Br)(H_2O)][Br]_5{\cdot}6.25H_2O}$.[75] Two crystallographically independent hexa-protonated host bicycles were found in a unit, with disorder found in one of the bicycles. The first host molecule (**Figure 17**) contained Br^- on one side of the cavity and three disordered H_2O molecules on the other side. This cryptand had a Br^- ion located on one side of the cavity with respective occupancies of 0.972 and 0.022. One of the external Br^- ions had respective occupancies of 0.850, 0.170(2), and 0.44(2). The internal Br^- ion forms hydrogen bonds with three hydrogens of secondary amino groups on one tren unit and four hydrogen atoms of four internal H_2O molecules. Hydrogen bonds with the Br^- ion range from 3.2 to 3.8 Å. The hydrogen bonds between the bicycle and the Br^- ion are approximately 3.4 to 3.5 Å, while the bonds to the two closer H_2O molecules are about 3.2 Å. The bonds to the other two H_2O molecules range from 3.6 to 3.8 Å, which makes their status as hydrogen bonds debatable. The N-N distance is 10.147 Å, which is longer than in the Cl^- complex (10.093 Å) and shorter than the F^- complex (10.717 Å). Refer to **Chapter 8** for additional data.

The second host molecule, which did not show disorder, also had Br^- ion on one side of the cavity but only one H_2O molecule on the other side. Since the second host bears a structural resemblance to the Cl^- complex and shows no disorder, the second cation host is the main species addressed in the discussion (**Figure 18**).

Hydrogen bonds with the internal Br^- ion range from 3.1 to 3.4 Å. The internal Br^- ion has a similar coordination to that of the other structures forming a tetrahedral coordination with three hydrogens of secondary amino groups on one tren unit and one hydrogen atom of the internal H_2O molecule. The hydrogen bonds between the bicycle and the Br^- ion are approximately 3.3 Å, while the bond to the H_2O molecule is about 3.1 Å. The N-N distance is 10.377 Å, which is longer than in the Cl^- complex (10.093 Å) and shorter than the F^- complex (10.717 Å). This is consistent with the presence of two rather than three guests in the cavity. Refer to **Table 8** for selected bond distances. The Br^- ion and H_2O molecule (3.798 Å and 3.539 Å) are further from the bridgehead amines than in the Cl^- complex, which is consistent with Br^- being larger than Cl^-.

Table 8: Selected hydrogen bond and atom distances for **$H_6$13(Br)(H_2O)** (second host).

Atoms	**Distances (Å)**
Br(5)···H(13D)-N(13B)	3.350(4)
Br(5)···H(19D)-N(19B)	3.318(4)
Br(5)···H(42D)-N(42B)	3.285(4)
Br(5)···H(6SA)-O(6S)	3.067(5)
N(1B)-N(16B)	10.377
Br(5)···N(16B)	3.798
O(6S)···N(1B)	3.539

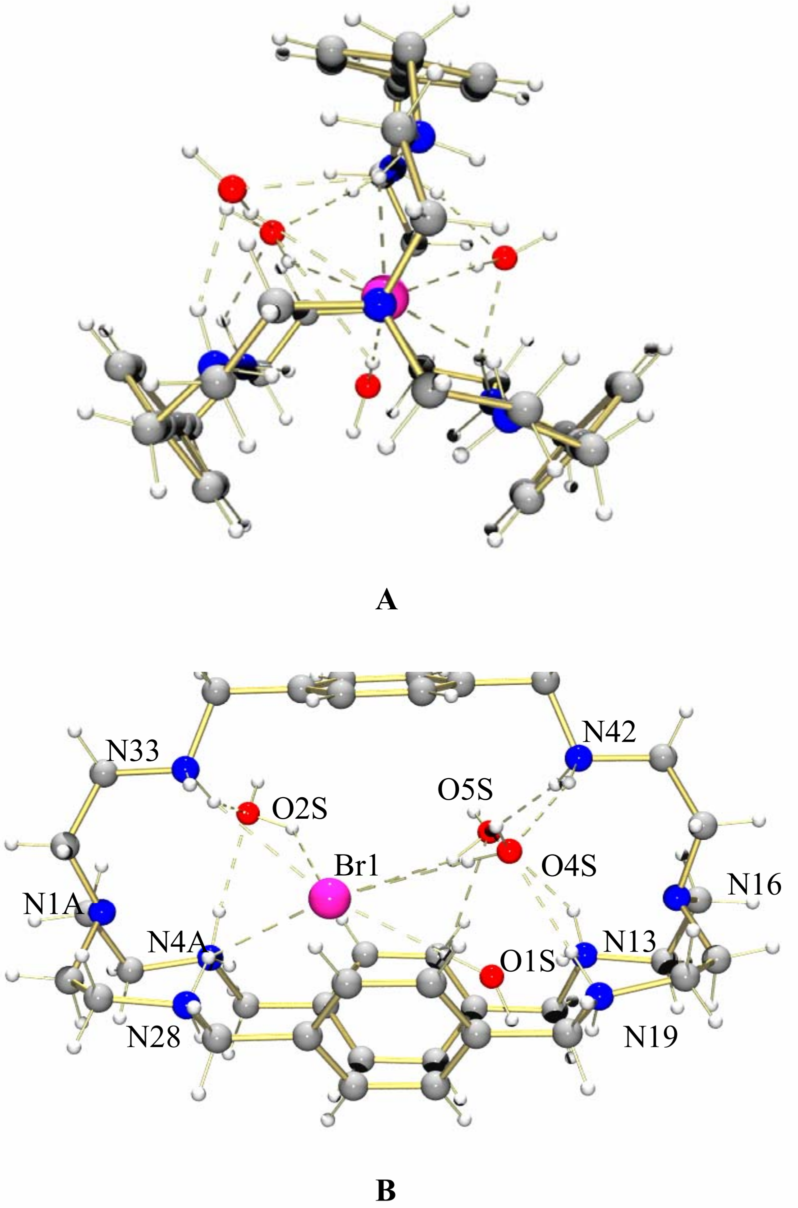


Figure 17: Drawing of the first cation of **$[H_6\mathbf{13}(Br)(H_2O)][Br]_5{\cdot}6.25H_2O$**. (A) side view showing Br^- and H_2O inside the cavity; (B) view down the three-fold axis.

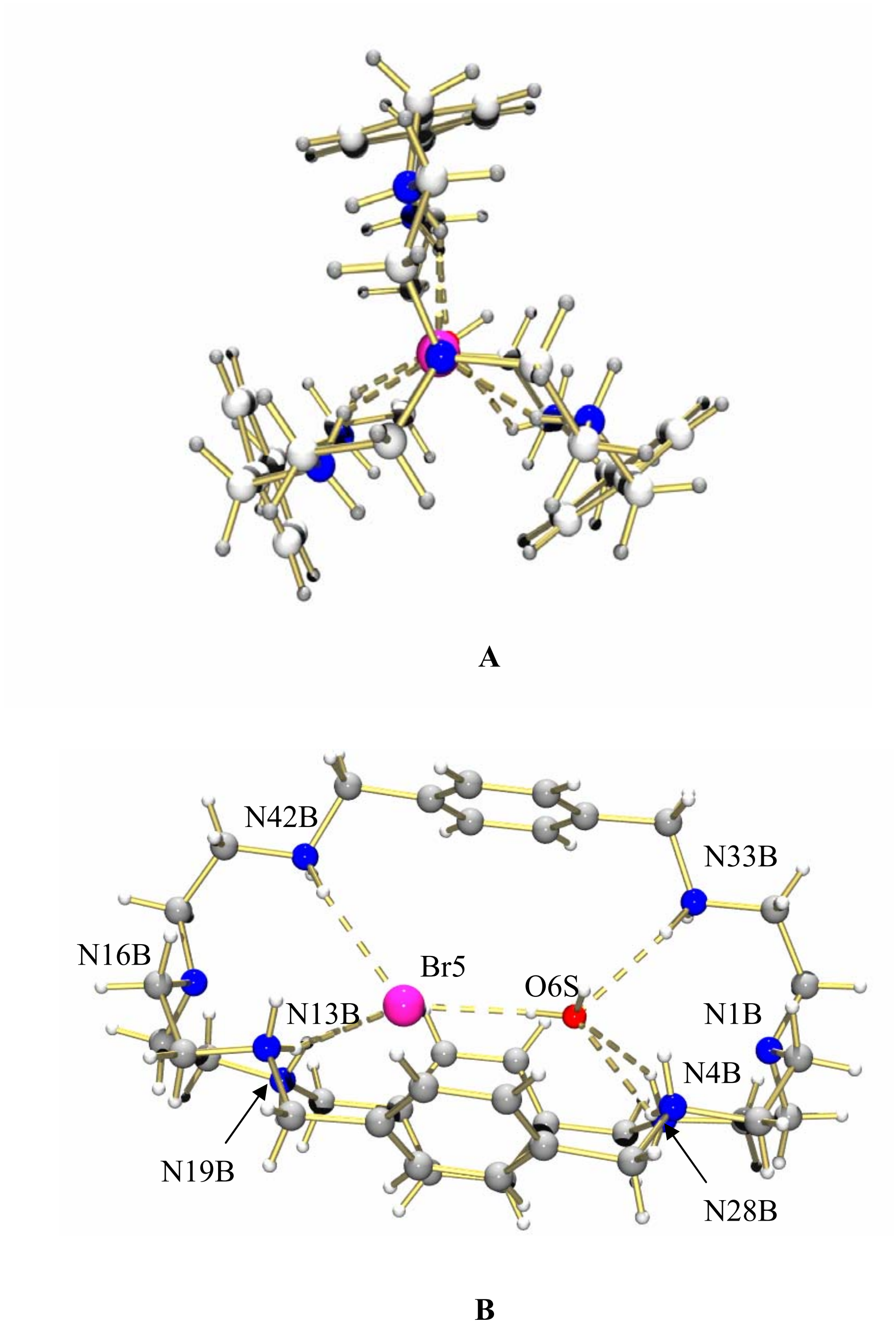


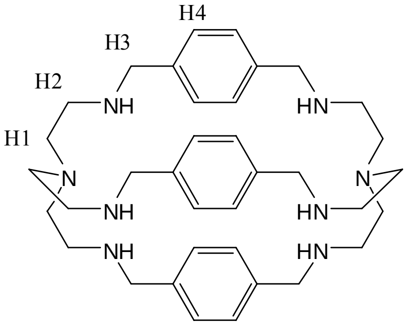
Figure 18: Drawing of the second cation of **[$H_6$13(Br)(H_2O)][Br]$_5$·6.25H_2O**. (A) side view showing Br^- and H_2O inside the cavity; (B) view down the three-fold axis.

4.3 NMR Studies

4.3.1 ^{1}H NMR Affinity Studies

Affinity studies were conducted between **13** and the Br$^-$, Cl$^-$, and F$^-$ ions. ^{1}H NMR titrations of **13** with the halide salts were performed in D_2O at pD 5.0.[25,26] Binding constants (**Table 9**) were calculated using Sigma Plot software by fitting the aliphatic proton signals to a 1:1 association model.

The crystal structure showed the presence of two F$^-$ ions in the host's cavity. This prompted an investigation to determine if the binding interactions of these species were the same in solution as in the solid state. An ^{1}H NMR titration of **13** with F$^-$ showed moderate shifting of the aromatic protons and one of the ethylene protons (**Figure 19**), and the titration curve (**Figure 20**) gave the best fit for a 1:1 host-to-guest (**13**: F$^-$) ratio. Although the most significant shifts occur up to a 1:1 ratio of L:A, there is still some shifting up to a ratio of 1:2. While the magnitude of the shift does not necessarily correlate with the strength of binding, one can infer from these data that there may be an equilibrium in solution between the 1:1 and 1:2. Potentiometric studies were unable to conclude decisively which species were present at low pH values.[26] Binding constants are listed in **Table 9**.



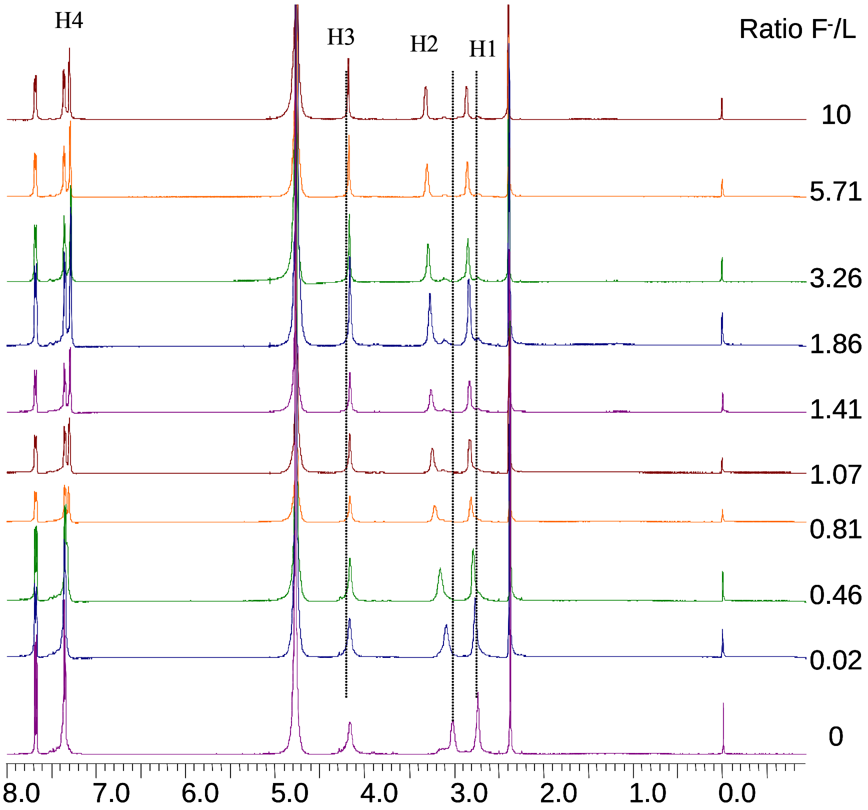


Figure 19: ^{1}H NMR titration in D_2O at pD = 5.0+/-0.1 at 25 ^{O}C where [F^-] = 20mM and [**13**] = 2mM.

Table 9: Association constants (*Log K*) of **13** with anions in D_2O at pD = 5.0 +/- 0.1 at 25 ^{O}C.

X^-	**Log K/dm^{3}mol^{-1}**
Br^-	3.34(4)
Cl^-	3.37(3)
F^-	3.15(5)

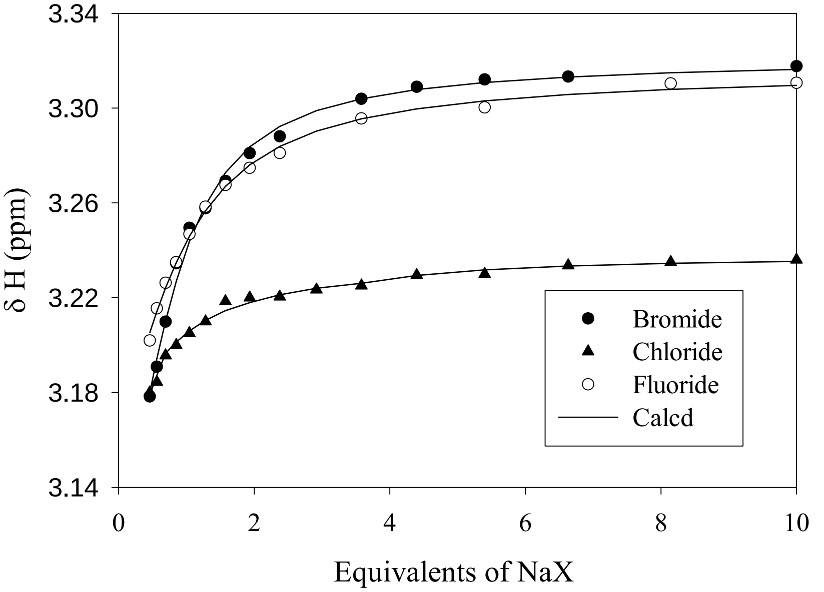


Figure 20: ^{1}H NMR titration curve in D_2O at pD = 5.0 ± 0.1 at 25 ^{O}C where [A^-] = 20mM and [**13**] = 2mM.

An ^{1}H NMR titration of **13** with NaCl and NaBr at pD 5.0 also indicated a 1:1 host-to-guest ratio (**Figure 20)**. As with the F^- complex, there was a small downfield shift observed for the aliphatic proton signals. This is the same 1:1 binding ratio as shown in the F^- complex. The crystal structures of the Cl^- and Br^- complexes were consistent with these results.

The NMR titration data of **13** gave the best fit for a 1:1 binding model of L:A for all three anions and yielded Log K = 3.15(5), 3.37(3) and 3.34(4) for F^-, Cl^-, and Br^-, respectively (**Figure 20**). The binding constant obtained for Br^- is comparable to that obtained for Cl^- but larger than that of F^-. The slightly weaker affinity of the F^- ion as compared to the Cl^- or Br^- ions may be due to the poorer fit of a single F^- ion in the cavity.

4.3.2 Job Plots

A Job Plot[76] was constructed using the same conditions as the ^{1}H NMR titration (**Figure 21**). The total concentration of **13** and NaF was equal to 10 mM. A maximum value for $\Delta\delta$ at 0.6 was obtained, which provided a close indication of a 1:1 complex. This was in accord with the results from the ^{1}H NMR titration and, when examined together, these results lead to several conclusions. First, the preferred species in solution may not be the preferred solid-state species. It was clear that the binuclear F^- anion cascade complex was favored in the solid-state, as mentioned in a previous section. Additionally, the titrations and Job plot data indicate that the mononuclear complex was probably the major species in solution. However, the binuclear species may only be significantly present at a lower pH.[26]

A second Job plot (**Figure 22**), under the same conditions as above, was constructed for **13** and Cl^-. It gave a maximum value for $\Delta\delta$ at 0.55 to 0.60, which was approximately the same ratio of L:A calculated for the F^- complex . This value was a close approximation to a 1:1 host-to-guest complex, which is comparable to the value obtained through ^{1}H NMR titration (**Figure 20**). The crystal structure described earlier, which showed one Cl^- internally bound with one H_2O, was consistent with these results.

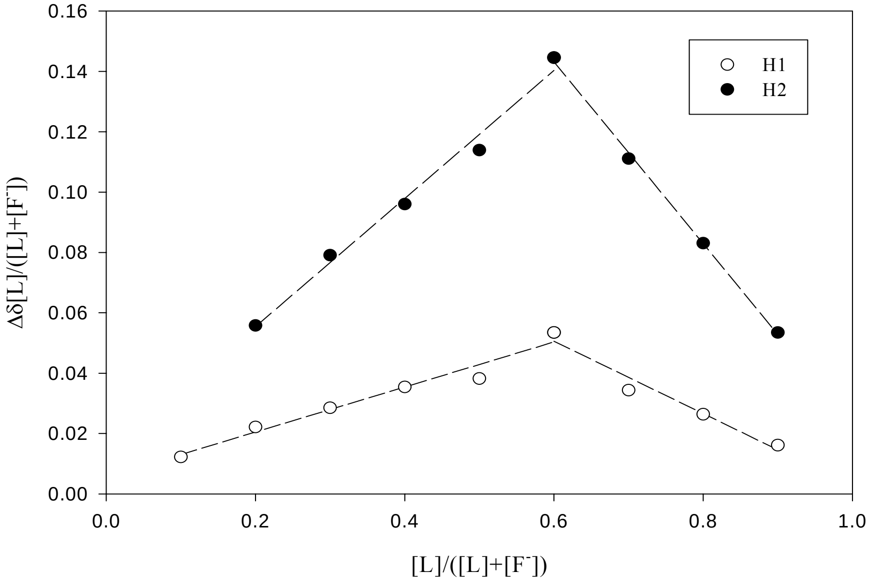


Figure 21: Job plot of **13** with NaF in D_2O at pD = 5.0 ± 0.1 at 25 ^OC. Total concentration of [**13** + NaF] = 10 mM.

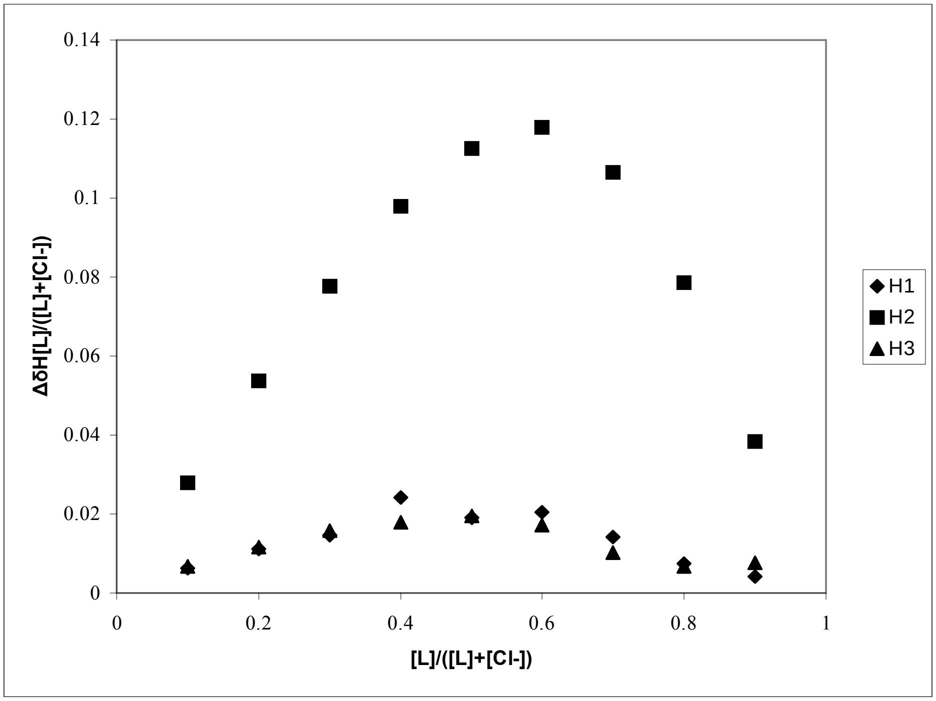


Figure 22: Job plot of **13** with NaCl in D_2O at pD = 5.0 +/- 0.1 at 25 ^{O}C. Total concentration of [**13** + NaCl] = 10 mM.

4.3.3 ^{19}F NMR Studies

The solution structure of the F^{-} complex was monitored with ^{19}F NMR spectroscopy (**Figure 24**). The signal at δ = -78 ppm was designated as an internal F^{-} ion, while the signal at δ = -113 ppm was characteristic of a free, solvated F^{-} ion.[42] Both of these signals were present at pH = 5.0. As the pH increased, the signal at δ = -78 ppm remained sharp until pH 5.5, broadened at pH 6.5 and 7.0, and had disappeared at pH 7.5. The internal F^{-} signal remained stable until pH = 7.0, as opposed to the behavior observed by Bowman-James *et al.* in the complex between

12 and F$^-$ where the signal disappeared by pH = 6.5.[42] This indicated that **13** stabilized F$^-$ inside the cryptand at a higher pH.

In a DMSO/H_2O mixture (40/60 DMSO/H_2O with a 10% DMSO–*d6* standard) at 263 K, a ^{19}F NMR study was performed in which the concentration of **13** and the F$^-$ ion were both 25 mM, and the concentration of the Cl$^-$ ion was varied from 0–500 mM. As shown in **Figure 25** not until the concentration of the Cl$^-$ ion was 10–20 times that of the F$^-$ ion did Cl$^-$ expel F$^-$ from inside the cavity. This was observed as a disappearance of the internal F$^-$ signal at approximately -80ppm. As such, ^{19}F NMR competition studies and equilibrium studies in crystal formation show that **13** shows selectivity in binding the F$^-$ ion over the Cl$^-$ ion in both the solid state and solution.

4.4 Other Cascade Complexes

4.4.1 Metal Cascade Complexes

Another viable method of anion coordination involves using dinuclear cationic systems. Rather than relying on hydrogen bonds, these systems rely on coordinate-covalent bonds between the metals and bidentate anion. As previously mentioned,[53] Menif and co-workers were able to isolate a dinuclear complex of copper with **12**, **$[Cu_2(\mu\text{-}CO_3)(12)(H_3O)]Br_3{\cdot}3H_2O$** (**Figure 23**). Each copper atom displays trigonal bipyramidal coordination, with the three axial sites and one equatorial site coordinated to each tren unit. The remaining axial site on each copper is coordinated to different oxygen atoms on the CO_3^{2-} anion. The anion lies off the N-N bridgehead axis between two of the cryptand arms, with the remaining oxygen coordinated to a H_3O^+ ion. The Cu-Cu distance is 5.850 Å. Harding also isolated dinuclear complexes of copper with **12**, with a μ-coordinated N_3^- or OCN^- ions, **$[Cu_2(N_3)(12)][ClO_4]_3\cdot CH_3CN\cdot 1.5EtOH$** and **$[Cu_2(NCO)(12)][ClO_4]_3\cdot CH_3CN \cdot 1.5\ EtOH$**, respectively.[52] Only recently have metal cascades been observed with **13**.[77,78,79] The last example by Suresh and Ghosh,[79] the only example of perfect linear M-NNN-M recognition of N_3^-, has a cavity size of 10.263 Å. This is significantly smaller than the cavity size of the F^- cascade complex (10.717 Å)[26] The intention of providing only a few examples is not to minimize the number of metal-cascade complexes but to illustrate the behavior of these systems. These structures are analogous to the F^- cascade complex described earlier in the chapter. The F^- ions replace the metal ions, with tetrahedral rather than trigonal bipyramidal coordination, and the H_2O molecule replaces the cascading anion.

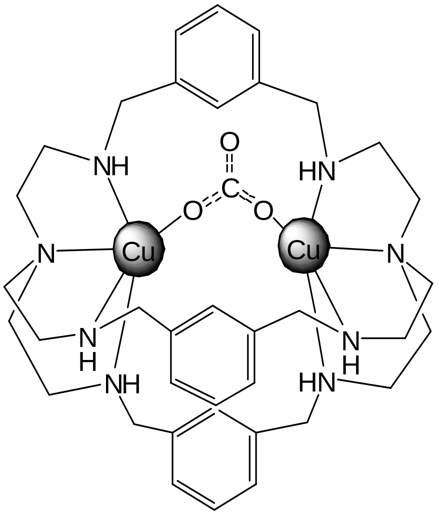


Figure 23: Martell's copper cascade with **12**, **$[Cu_2(\mu CO_3)(12)(H_3O)]$-$Br_3\cdot 3H_2O$**. Internal H_2O molecule omitted for clarity.[53]

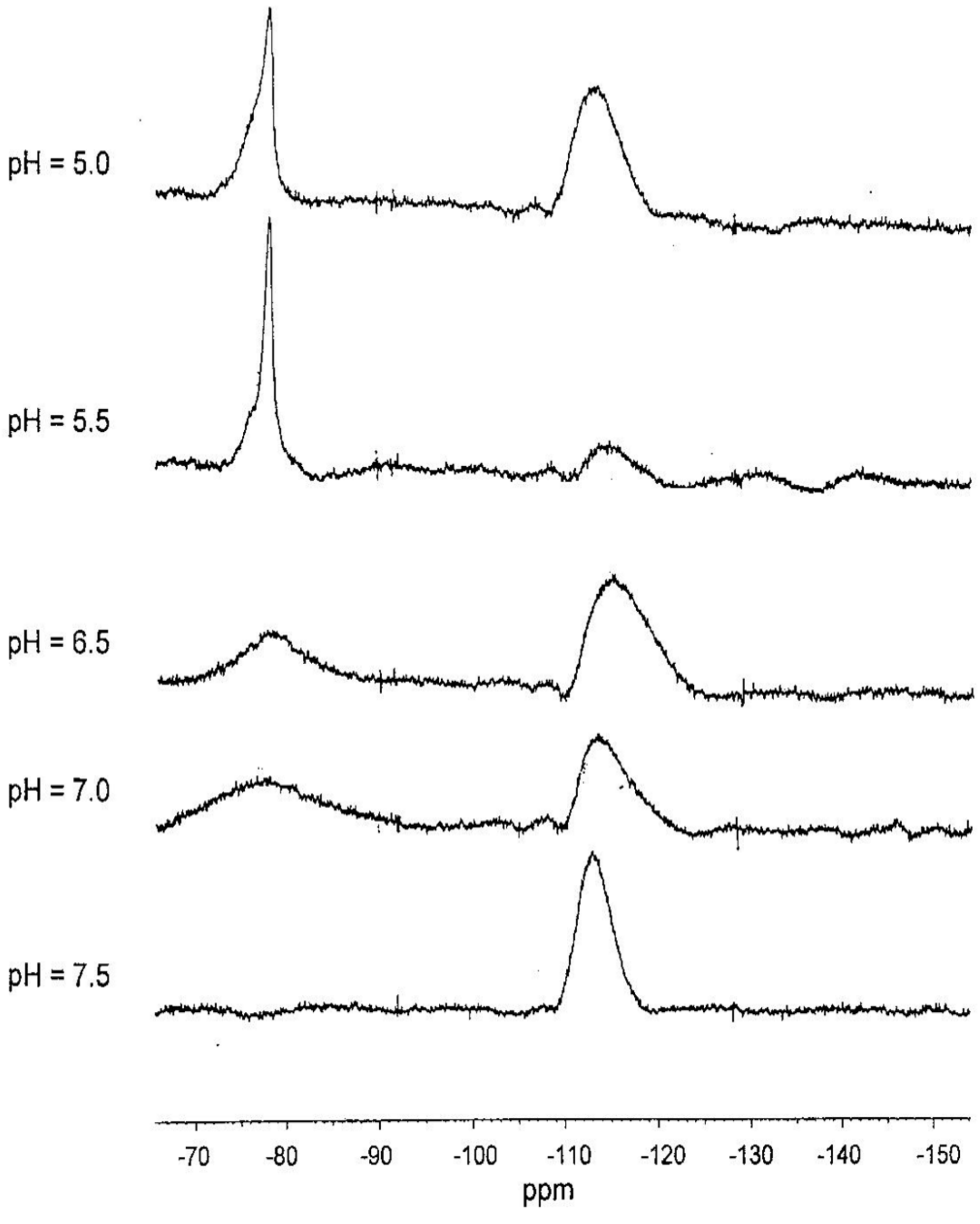


Figure 24: ^{19}F NMR spectra of NaF:$\mathbf{H_6 13^{6+} \cdot 6TsO^-}$ in 0.1M KTs at 263 K in DMSO:H_2O (40:60). [**13**] = [F^-] = 10mM.

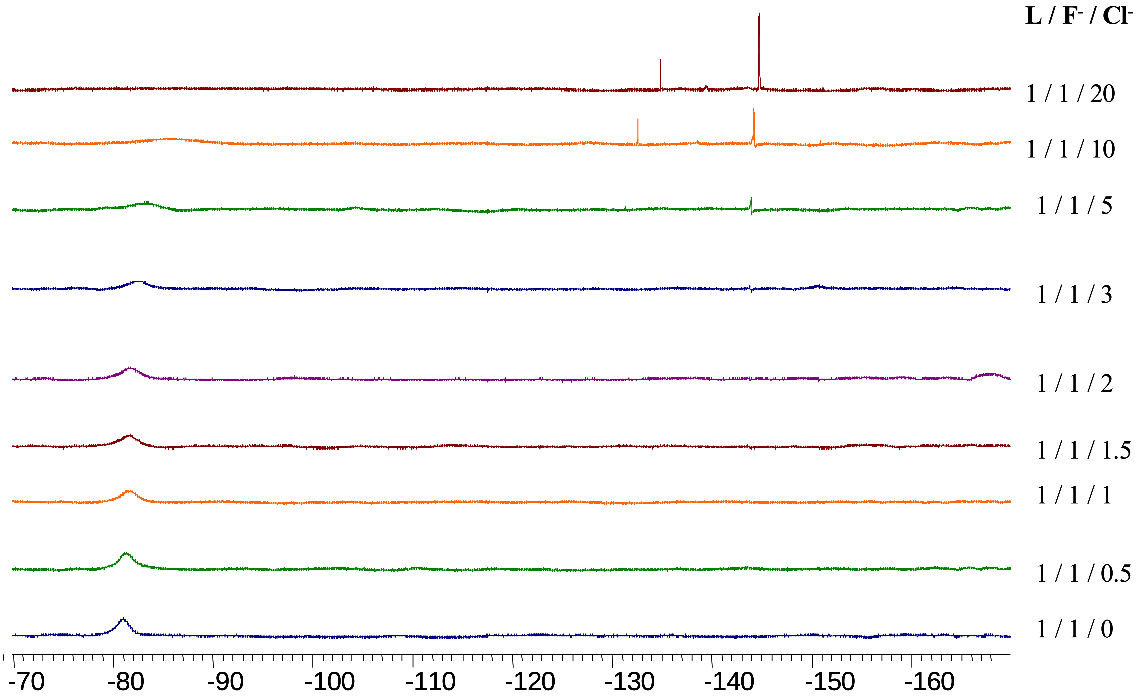


Figure 25: ^{19}F NMR of **13**: F^-:Cl^- in DMSO/H_2O (40/60, with 10% DMSO-d_6) at pH 5.0 ± 0.1 at 263 K; [**13**] = [NaF] = 25mM.

4.4.2 Anion Cascade Complexes

As discussed in Chapter 3, since the isolation of the F^- cascade complex with **13**, Bowman-James *et al.* have shown additional examples of anion cascade complexes, which will now be discussed in further detail for comparison purposes.[68]

Bowman-James *et al.* were able to crystallize a complex between SO_4^{2-} and the propyl amide cryptand, **20**, forming the neutral complex **[H$_2$20(SO$_4$)(H$_2$O)$_2$]·3H$_2$O·CH$_3$CN** (**Figure 26**). [68] The resulting crystal structure showed a SO_4^{2-} anion cascading between two H_2O molecules inside the cavity.

Hydrogen bonds are between approximately 2.6 and 3.0 Å. Each of the cascading H_2O molecules in the cascade forms two hydrogen bonds with the amide hydrogens on the same arms, while the SO_4^{2-} ion forms a total of seven hydrogen bonds: two to amide hydrogens, three to H_2O molecules, and two to the protonated bridgehead amines. The ligand adopts a Y-shape typical of amido cryptands[59] and amine[81] with pyridine spacers. The SO_4^{2-} ion lies slightly off the N-N axis, with the H_2O molecules each located between the two arms.

An additional complex was observed with Cl^-, **[$H_2$20(Cl)$_2$(H_2O)]·CH_3OH**, in which the two internal Cl^- ions are linked by a cascading H_2O molecule (**Figure 27**). This complex has the same Y-shape as the SO_4^{2-} complex and has three guests within the cavity. Each Cl^- ion forms hydrogen bonds with a protonated bridgehead amine and adjacent amide protons. The fourth hydrogen bond is formed with the H_2O molecule, which also forms hydrogen bonds with adjacent amide protons. Hydrogen bonds fall between 3.0 and 3.6 Å. This structure is analogous to the F^- cascade complex discussed earlier in the chapter, **[$H_6$13(F)$_2$(H_2O)]**, where hydrogen bonds fall between 2.6 and 2.9 Å. However, in the case of the Cl^- cascade with **20**, the anions lie between the cryptand arms, while in the F^- cascade, all three species lie on the 3-fold axis of the cryptand. Moreover, the propyl cascade lacks additional counter-ions necessary to complete the charge neutrality in the amine cascade. These three examples of anion complexes with amide and amine macrocycle further extend anion coordination chemistry by forming cascade complexes which were once only found for metal cations.

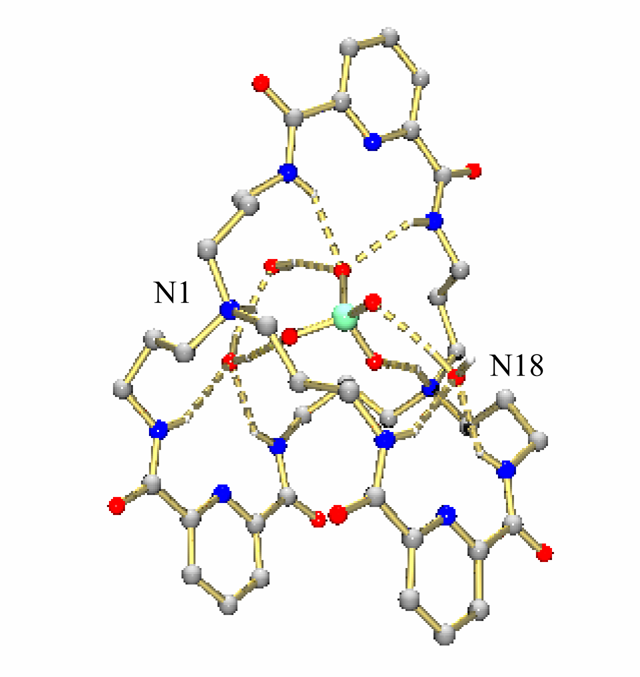


Figure 26: Sulfate cascade with **20**. Carbon-bound hydrogen atoms omitted for clarity.[68]

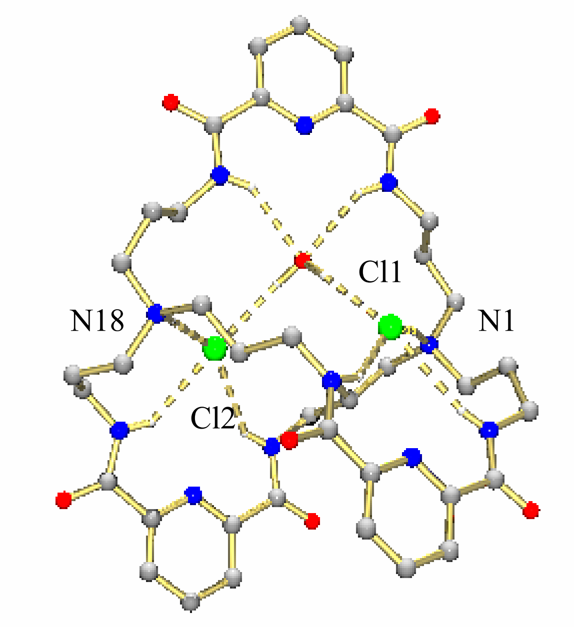


Figure 27: Chloride cascade with **20**. Carbon-bound hydrogen atoms omitted for clarity. [68]

4.4.3 Successful Isolation of Bifluoride Complex

In 2006, Lehn's mission for encapsulation of the FHF$^-$ ion was achieved by Bowman-James.[80] The receptor **21** (**Figure 28**) was synthesized by linking two amide-based monocycles with ethylene groups to form a tricycle. It was intended to isolate the F$^-$ complex with this ligand. However, the FHF$^-$ complex, **[*n*Bu$_4$N][21(FHF)]·3H$_2$O**, was isolated instead (**Figure 29**). The crystal structure showed that each monocycle bound FHF$^-$ through two hydrogen bonds with a terminal fluorine atom, with the N-H distances being 2.754 and 2.724 Å. The remaining amide protons form intramolecular hydrogen bonds. The F···F distance was 2.475 Å with an almost linear FHF bond angle of 168(4)°.

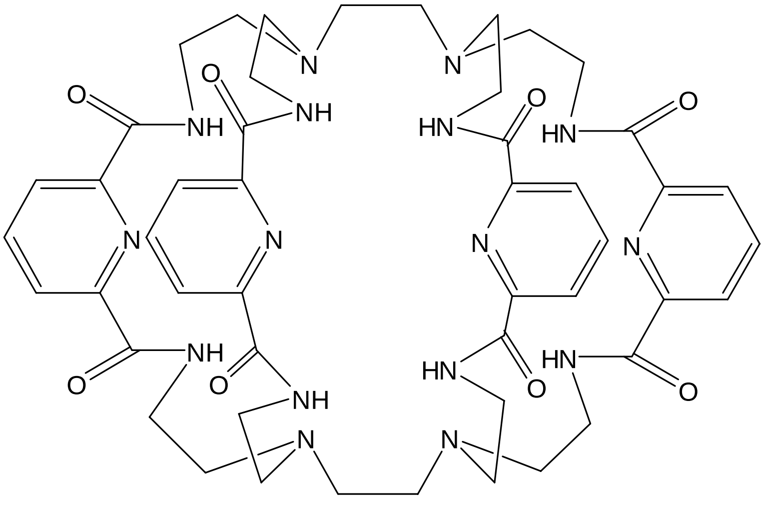


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Figure 28: Drawing of amide tricycle **21**.

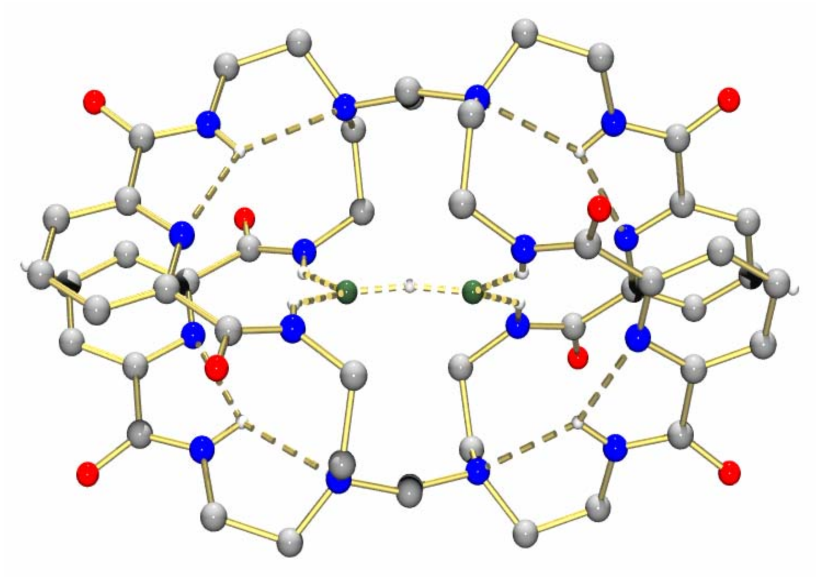


Figure 29: Drawing of FHF¯ complex with **21**. Carbon-bound hydrogen atoms omitted for clarity.

As discussed previously, the Bowman-James group had made multiple attempts to capture FHF¯ by increasing the bicycle cavity sizes from **12** to **13**. However, as this first structural example of FHF¯ encapsulation shows, it was necessary to increase the dimensionality of the cavity from bi- to tricyclic. The F···F distance in the F¯ cascade of **13** (4.736 Å) is twice as long as the F···F separation in the FHF¯ complex (2.475 Å), and the binding of FHF¯ (Log *K* = 3.74) is significantly larger than that of F¯ with **13** (Log *K* = 3.15). Titration data of the tricycle with F¯ were complicated, suspected in part due to the synthesis of FHF¯. The mode of binding between the tricycle and FHF¯ is counter to the binding mode between Lehn's O-Bistren complex with N_3^-, in which the N_3^- ion is collinear with the bridgehead nitrogen groups (**Figure 9**).[40] It may be supposed that the reason structural evidence of FHF^- encapsulation was not observed sooner was that the dimensionality of the bicyclic cryptand hosts was not appropriate for this anion.

4.5 Conclusions, Further Remarks, and Further Research

The structure of the F^- complex with the azacryptand **13** represents the first example of two F^- within a single azacryptand cavity.[26,75] Additionally, a new class of cascade complexes with H_2O as the cascade has been identified. In this new class, anions replace metal ions and hydrogen bonds replace dative (coordinate covalent) bonds in transition metal cascade complexes. This research has been furthered by the discovery of other anion cascade complexes by the Bowman-James research group.[68] These finding continue to extend the similarities between traditional transition metal coordination chemistry and anion coordination chemistry.

Chapter 5 PyEACryp

5.1 Introduction

Another modification of Schiff base-derived ligands is the substitution of the spacer group. An extension of the studies on **12** in **Chapter 3** would be the replacement of the *m*-xylyl spacer with a corresponding pyridine moiety. As demonstrated by Mason[25] and Nelson,[81] PyEACryp **14** prefers anion complexation by cleft binding rather than inclusion in the cavity.

One can discern the difference in binding modes in the solid state between the two systems (**12** versus **14**) by looking at crystallographic studies of NO_3^- complexes.[25,58] In the **$[H_6 12(NO_3)_2][NO_3]_4$** structure, Bowman-James found two discrete NO_3^- ions were bound inside the cavity in an eclipsed orientation along the N-N bridgehead axis (**Figure 30**).[24] However, in **$[H_6 14(NO_3)_5][NO_3]_4$** Nelson found that one NO_3^- is bound in the cleft of the ligand, parallel to two of the pyridine rings, with two pairs of π-stacked NO_3^-.[58] A similar structure **$[H_6 14(NO_3)_4][NO_3]_4$** was reported by Mason,[25] where in addition to the NO_3^- ion held in the 'Y', three other NO_3^- ions are bound between the other arms. Nelson has obtained other oxo-anion structures with **14**, namely ClO_4^-, ReO_4^-, $C_2O_4^{2-}$ (oxalate),[81,82] and SiF_6^{2-}.[83] An example of the cleft binding typical of this ligand is shown in **Figure 31** with the ClO_4^- complex.[82]

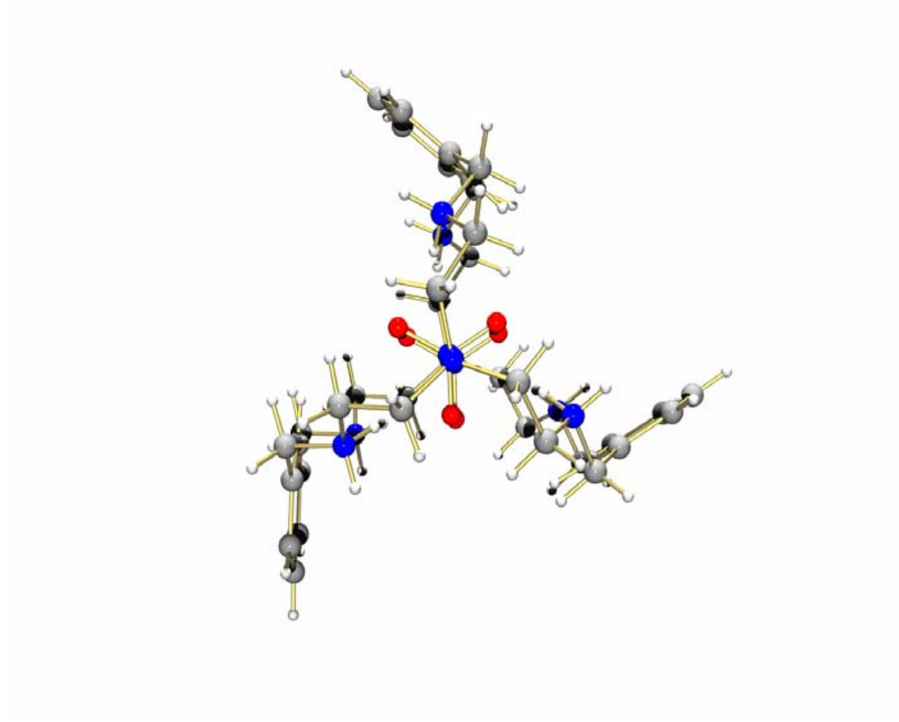


Figure 30: Drawing of **[$H_6$12(NO_3)$_2$][NO_3]$_4$·2H_2O** with H_2O and external NO_3^- molecules omitted for clarity.[7]

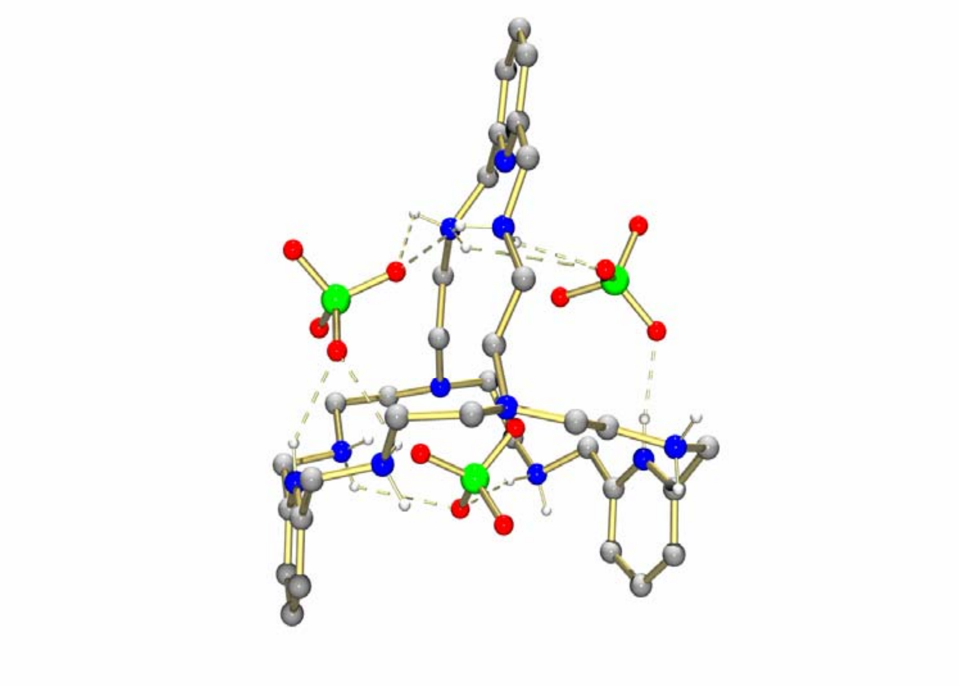


Figure 31: Drawing of **[$H_8$14(ClO_4)$_3$][ClO_4]$_5$·5H_2O**. Carbon-bound hydrogen atoms, external ClO_4^- ions, and H_2O molecules omitted for clarity.[82]

5.2 Crystal structures

5.2.1 Bromide Structure-Original

The data obtained for **$[H_614(Br)_3(H_2O)][Br]_3{\cdot}2.25H_2O$** were calculated on a possibly twinned crystal. However, reviewing the refined structure has merit (**Figure 32**). Of the six Br^- ions identified, five Br^- ions were defined, one was highly disordered, Br(6), and found in six positions. The Br^- ion (6A) with the highest occupancy (0.52) will be the one referenced in the discussion below.

The cavity size of **$[H_614(Br)_3(H_2O)][Br]_3{\cdot}2.25H_2O$** (5.628 Å) is smaller than cavity size McKee found for **$[H_814(ClO_4)_3][(ClO_4)_5]{\cdot}5H_2O$** (6.997 Å).[82] In the ClO_4^- complex, it is also interesting to note that rather than the bridgehead nitrogens becoming protonated, two of the three pyridine nitrogens are protonated.[82] The authors believe this occurs because of hydrogen bond stabilization within the crystal lattice. This cavity expansion most likely results from the protonation of the pyridine nitrogen, resulting in an increased positive-charge density inside the cavity. Hydrogen bonds between **14** and the ClO_4^- ions range from approximately 2.8 to 3.1 Å.

Hydrogen bonds between the Br^- ions and the amine groups in **$[H_614(Br)_3(H_2O)][Br]_3{\cdot}2.25H_2O$** range from 3.18 to 3.57 Å (**Table 10**). These values are comparable to hydrogen bond distances found between **13** and Br^- (approximately 3.1 to 3.4 Å) (**Table 8**) but longer than those found between **14** and ClO_4^-**.**[82] Three Br^- ions are found in the clefts: Br(1), Br(2), and Br(5). Br(1) forms hydrogen bonds with amine groups on two adjacent arms, on the ‘Y’ end of the bicycle. Br(2) is located at the other end of the cavity and forms hydrogen bonds with H_2O and an arm of the bicycle. Br(5) is bound to three amine hydrogens, two of which are on the same arm. An additional H_2O molecule is located outside of the cavity and forms a hydrogen bond with Br(4). From the packing diagram shown in **Chapter 7**, it is observed that two of the external Br^- ions (3 and 6A) form bridges between different bicycles.

The structure of **14** with Br^- is reminiscent of one obtained by Martell.[53] In Martell's structure, the ligand forms a 'Y'-shaped figure, with three of the Br^- ions between the cryptand arms and remaining five anions located outside the internal cavity, **$[H_8 12(Br)_3][Br]_5 \cdot 6H_2O$**. As with **$[H_6 14(Br)_3][Br]_3$**, none of the Br^- ions are located directly inside the ligand cavity but rather between two of the arms.

The cavity size of Martell's complex (7.60 Ǻ) is almost 2 Ǻ larger than that found in **$[H_6 14(Br)_3][Br]_3$**. While this difference may not be explained by simply two factor (different crystallization methods, different spacer groups), one factor may have made a larger contribution to the cavity expansion, namely the protonation of the bridgehead amines. The octaprotonated species has a larger positive charge density within the cavity that forces expansion of the said cavity to minimize intermolecular repulsion.

Table 10: Selected hydrogen bonding interactions and atom distances for **$[H_614(Br)_3(H_2O)][Br]_3{\cdot}2.25H_2O$**. (Initial Refinement)

Atoms	**Distance (Å)**	**Atoms**	**Distance (Å)**
N(4)-H(4A)···Br(1)	3.282(6)	O(1S)-H(1SA)···Br(2)	3.214(5)
N(4)-H(4B)···Br(2)	3.185(7)	N(13)-H(13B)···Br(3)	3.215(6)
N(13)-H(13A)···Br(1)	3.428(6)	N(19)-H(19A)···O(1S)	2.907(8)
N(4)-H(28B)···Br(5)	3.309(6)	N(19)-H(19B)···Br(4)	3.216(6)
N(33)-H(33A)···Br(5)	3.275(8)	N(28)-H(28A)···O(1S)	2.907(8)
N(42)-H(42A)···Br(1)	3.279(5)	N(33)-H(33B)···Br(6A)	3.551(11)
N(42)-H(42B)···Br(5)	3.571(6)	N(1)···N(16)	5.628

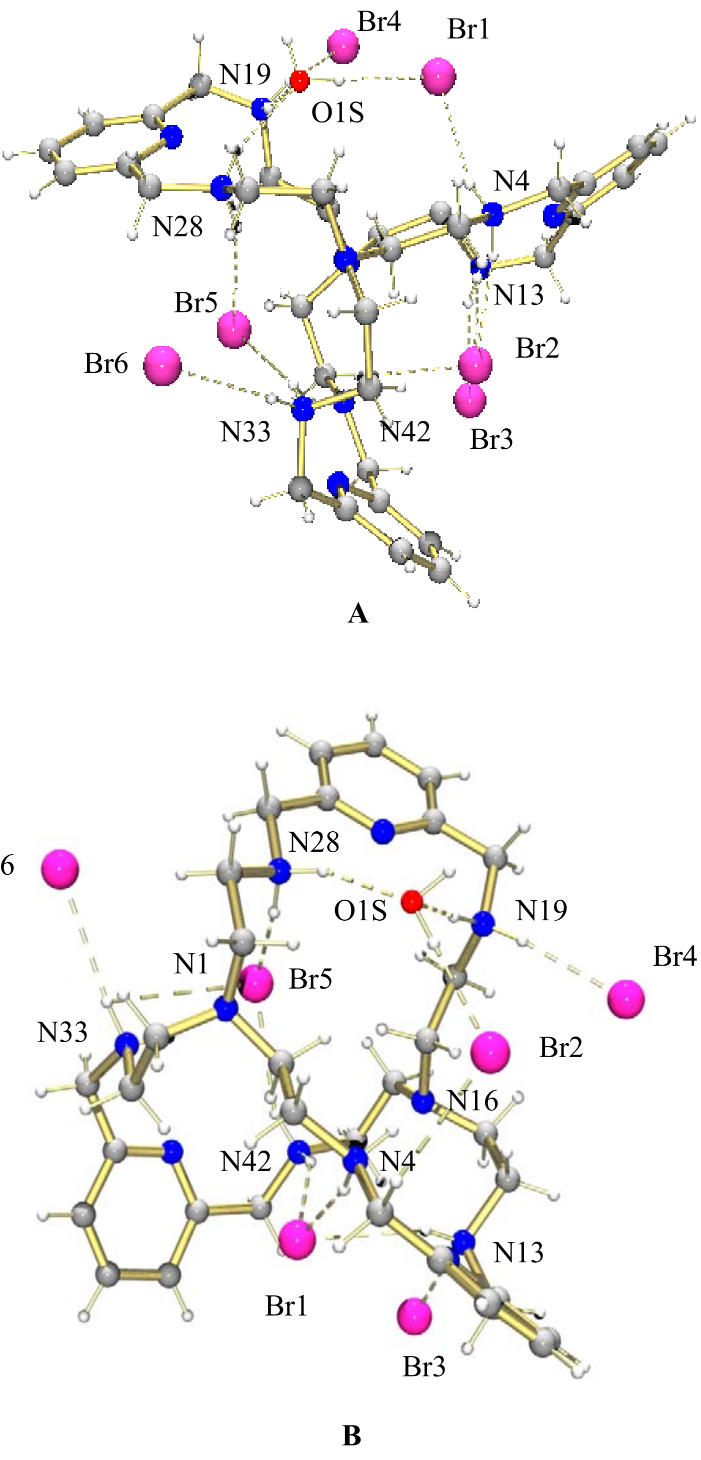


Figure 32: Initial refinement of the Br$^-$ complex with **15**. (A) Ball-and-stick drawing of $\mathbf{[H_6 14(Br)_3(H_2O)][Br]_3 \cdot 2.25H_2O}$ with a view down the N-N axis**.** (B) Drawing with a view of the cavity.

5.2.2 Bromide Structure-Refined

Further refinement the complex formed between **15** and Br^- yielded a modified structure, **$[H_614(Br)_3(H_2O)][Br]_3\cdot4H_2O$ (Figure 33)**. The total number of data used for this refinement is considerably higher than with the initial structure (13856 versus 8061) and the R1 value for "observed" reflections is lower (0.055 vs. 0.063) than for the earlier structure. The major difference between the two refinements is the disorder for the Br^- anions and H_2O molecules of crystallization. In the second refinement, all but one of the six Br^- anions (Br4) are disordered over at least two sites, and there are five H_2O molecules of which three also are disordered. The final occupancy factors for the Br^- anions are: Br(1A), 0.83; Br(1B), 0.17; Br(2A), 0.97; Br(2B), 0.03; Br(3A), 0.79; Br(3B), 0.21; Br(4), 1.00; Br(5A), 0.77; Br(5B), 0.23; Br(6A), 0.44; Br(6B), 0.38; and Br(6C), 0.18. The final occupancy factors for the water molecule oxygen atoms are: O(1W), 1.00; O(2W), 1.00; O(3W), 0.87; O(3W’), 0.13; O(4W), 0.83; O(4W’), 0.17; O(5W), 0.55; O(5W’), 0.24; and O(5W”), 0.21. The Br^- ions and H_2O molecules with the highest occupancies are used to calculate hydrogen bond distances.

Hydrogen bonds between the Br^- ions and the amine groups in **$[H_614(Br)_3(H_2O)][Br]_3\cdot4H_2O$** range from 3.18 to 3.65 Å (**Table 11**), similar to the distances observed for [**$H_614(Br)_3(H_2O)][Br]_3\cdot2.25H_2O$**. The primary difference between the two structures is the additional H_2O molecules in the latter structure, which accounts for the residual electron density from the previous structure.

Table 11: Selected hydrogen bonding interactions and atom distances for **$[H_6 14(Br)_3(H_2O)][Br]_3 \cdot 4H_2O$**. (Second refinement)

Atoms	**Distance (Å)**	**Atoms**	**Distance (Å)**
N(4)-H(4A)···Br(1A)	3.273(4)	O(1S)-H(1SA)···Br(2)	3.216
N(4)-H(4B)···Br(2A)	3.187(4)	N(13)-H(13A)···Br(3A)	3.233(5)
N(13)-H(13B)···Br(1A)	3.420(4)	N(19)-H(19A)···O(1S)	2.912(4)
N(28)-H(28B)···Br(5A)	3.243(8)	N(19)-H(19B)···Br(4A)	3.218(4)
N(33)-H(33B)···Br(5A)	3.342(8)	N(28)-H(28A)···O(1S)	2.926(5)
N(42)-H(42A)···Br(1A)	3.279(3)	N(33)-H(33A)···Br(6A)	3.581(8)
N(42)-H(42B)···Br(5A)	3.651(9)	N(1)···N(16)	5.631

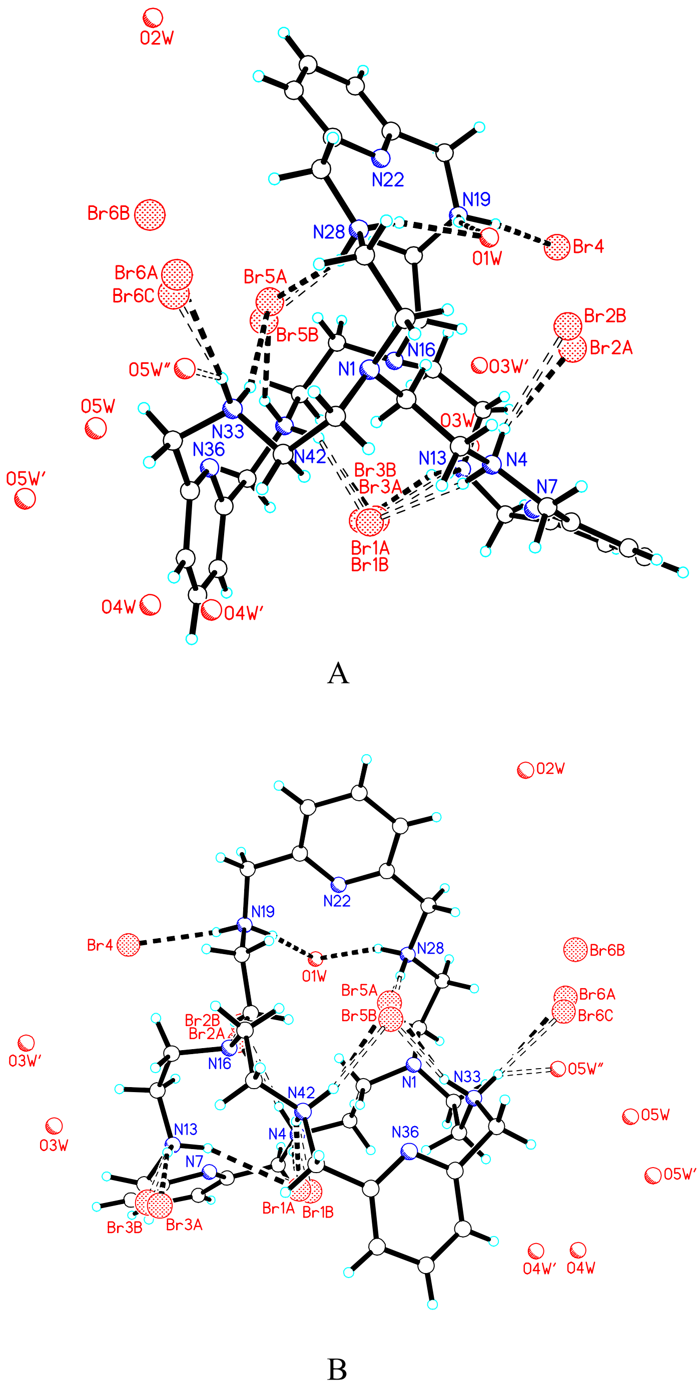


Figure 33 Second refinement of the Br$^-$ complex with **15**. (A) Ball-and-stick drawing of **$[H_614(Br)_3(H_2O)][Br]_3{\cdot}4H_2O$** with a view down the N-N axis**.** (B) Drawing with a view of the cavity. Filled-in dashes represent hydrogen bonds with the primary interactions and open-dashed bonds represent hydrogen bonds with the secondary interactions.

5.3 ^{1}H NMR Affinity Studies

The binding affinity of **14** for the halides (X^-) and SO_4^{2-} were measured at pD = 3.0, except for F^-, which was measured at pD = 4.0 because of its pK_a (3.15)[42] (**Figure 34** and **Figure 35**). Binding constants were calculated using Sigma Plot software by fitting the proton signals to a 1:1 association model and using EQNMR to a 1:2 association model. Depending on the anion, different protons were used to calculate the binding constants. The proton signals followed yielded the largest binding constants.

Titration curves for Cl^-, Br^-, and I^- showed small downfield shifts of the benzyl protons, while the titration curve for F^- showed a small upfield shift of the ethylene protons. All halides displayed a best fit to a 1:1 binding with **14** (**Figure 34** and **Figure 35**), and binding increased from I^- to F^-**,** as predicted by the Hofmeister series.[23] The binding constant for F^- (Log K = 3.6) is one hundred times greater than that for Cl^- (Log K = 1.7) (**Table 11**). It may be presumed that F^- ion has the largest binding constant of the halides because it is more basic and fits better in the cavity. This is contrary to the binding of the halides with **13,** where the *para*-xylyl bicycle shows a larger affinity for Cl^- and Br^- over F^-. This may be explained by a better size fit between the Cl^- and Br^- anions and **13** because of the *para*-xylyl ligand's larger cavity size compared to **14** (**Table 13**).

Of the halides fluoride showed the strongest binding with **14**. While a 1:2 binding mode was observed in the crystal structure of F^- and **13** (obtained at pH < 2.0), a 1:2 complex was not observed at the pD in which the titration was performed (pD = 5.0). One may expect binding for F$^-$ to be enhanced at lower pHs, which would result from enhanced binding due to the formation of the cascade complex. As the cavity of **14** is smaller than that of **13**, the lack of evidence of a ditopic F$^-$ complex with **14** is not surprising.

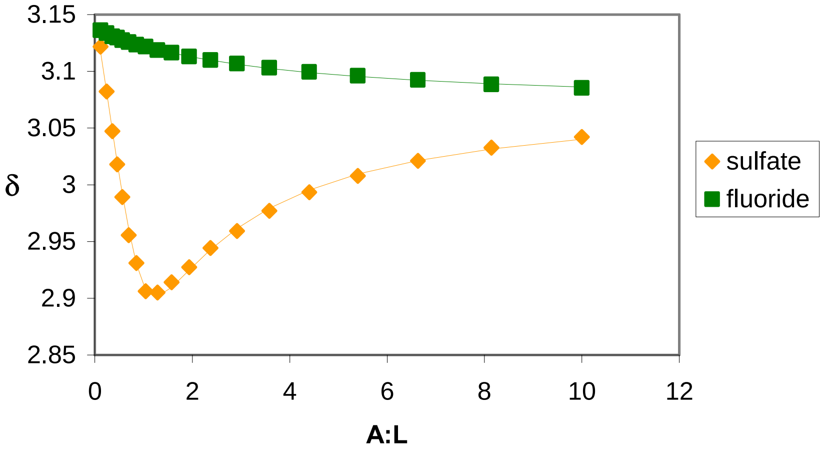


Figure 34: Titration curve of PyEACryp **14** ($[L]_o$=2mM) and NaX ($[A]_o$=20mM) in D_2O at pD=3.0 (SO_4^{2-}) and at pD=4.0 (F$^-$) at 25 ^{O}C following proton *a* (**Figure 35**).

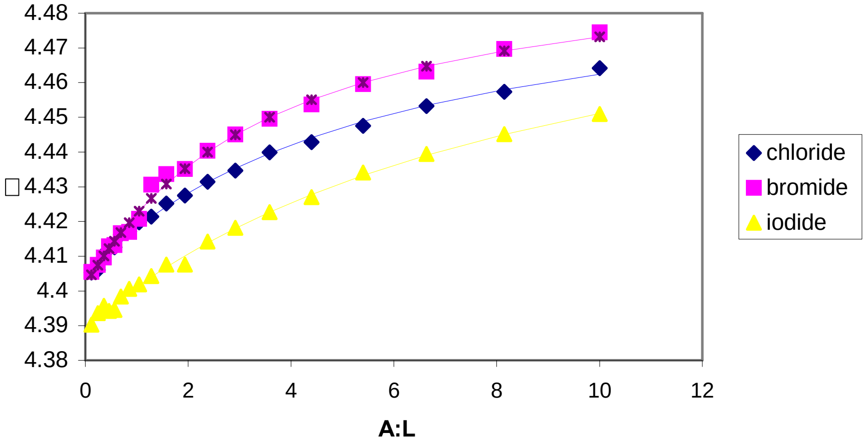
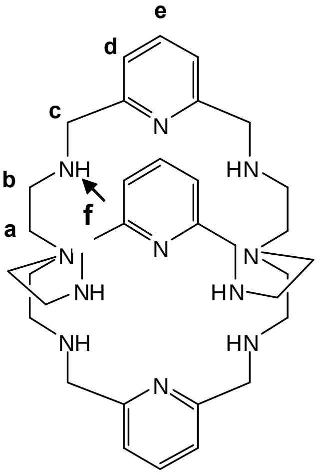


Figure 35: Titration curve of PyEACryp **14** ($[L]_o$=2mM) and NaX ($[A]_o$=20mM) in D_2O at pD=3.0 at 25 ^{O}C following proton *c*.

Table 12: Binding constants for **14** with various anions. 1:1 binding constants calculated using Sigma Plot, and 1:2 binding constant calculated using EQNMR.[84] [a] indicates proton used to calculate binding constant.



14

Anion	**Log K_a (M^{-1})**	**Proton[a]**	**pD**	**Solvent**
F^-	3.6	a	4.0	D_2O
Cl^-	1.7	c	3.0	D_2O
Br^-	1.0	c	3.0	D_2O
I^-	< 1.0	c	3.0	D_2O
SO_4^{2-}	4.6(K_1);2.6(K_2)	a	3.0	D_2O
HSO_4^-	3.2	f	---	DMSO-d_6

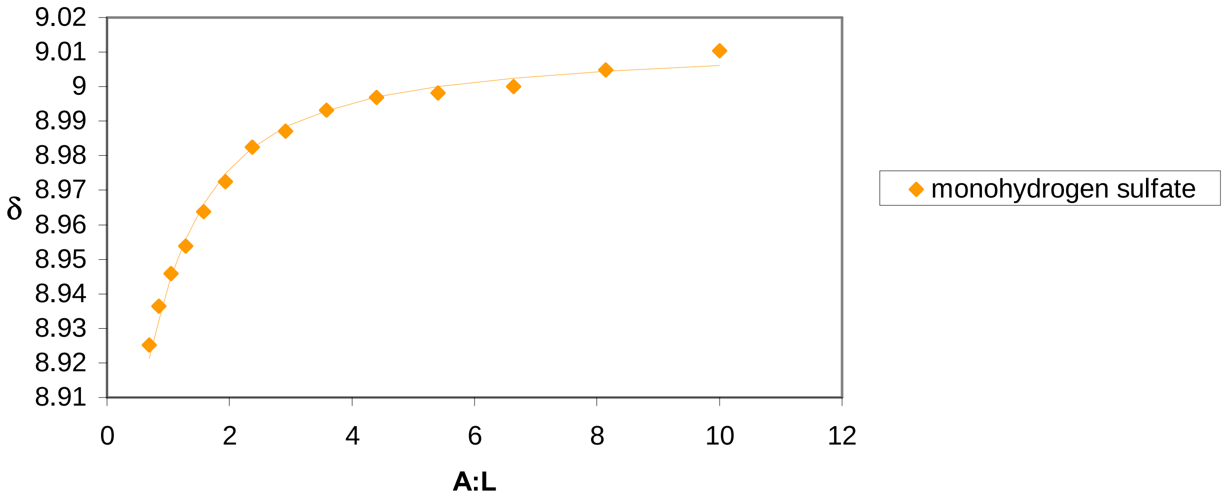


Figure 36: Titration curve for PyEACryp **14** ($[L]_o$=2mM) and $n\mathrm{Bu_4NHSO_4}$ ($[A]_o$=20mM) in DMSO-d_6 at 25 ^{O}C following proton *f*.

Table 13: Summary of binding constants for **Ts$_6$12**, **13**, and **14.** Conditions cited in corresponding references.[a]Ref. 67; [b]Ref. 25; [c]t = 298 K ± 0.1; μ = 0.100 M (KTs;) [d]Ref. 26, 67; [e]Chapter 5; [f] unable to determine using potentiometric technique. All ligands are hexaprotonated.

Anion /Ligand	**Ts$_6$12[a]**	**12**	**13 [d]**	**14[e]**
F⁻	slow exchange	4.70 [b, c]	3.15	3.60
Cl⁻	2.67	---[f]	3.37	1.70
Br⁻	2.40	--- [f]	3.34	1.00
I⁻	no binding	--- [f]	---	< 1.0

The affinity for SO_4^{2-} was observed under the same conditions as above (**Figure 34**). Since the pD is >2, interference by HSO_4^- is highly unlikely. In addition to having a larger binding constant than the F^- ion (Log *K* 4.6 versus 3.6), it appears that the SO_4^{2-} ion forms a 1:2 complex with **14** in solution.

$$H_614^{6+} + SO_4^{2-} \rightarrow H_614^{6+} \cdot SO_4^{2-} \qquad K_1 = 4.6\ M^{-1}$$

$$H_614^{6+} \cdot SO_4^{2-} + SO_4^{2-} \rightarrow H_614^{6+} \cdot 2SO_4^{2-} \qquad K_2 = 2.6\ M^{-1}$$

The titration curve shows a small upfield shift until approximately a ratio of 1:1 anion to ligand, at which time the direction of the ethylene proton shift switches downfield. The error in fitting the data to a 1:1 association model was very large. However, when using a 1:2 association model with EQNMR, the error of the binding constant was less than 15%. While solid-state structure does not necessarily equate to solution structure, a crystal structure would provide support to this hypothesis. Attempts to isolate a crystal of the SO_4^{2-} salt with **14** proved unsuccessful.

These results are interesting in comparison to the previous studies. In 2001, Bowman-James and co-workers used potentiometry to determine the binding of **12** with SO_4^{2-} at pD = 3.0.[7] They found a binding constant of Log *K* = 4.43 when the ligand is hexaprotonated. This is slightly less than the binding constant stated above with **14** (Log K_1 = 4.6). Nelson, however, using potentiometry determined the binding constant between **14** and SO_4^{2-} to be Log *K* = 6.08 when the ligand is hexaprotonated.[58] Neither group reported association constants for 1:2 complexation.

While Nelson has not reported a solid-state structure with **14** and SO_4^{2-}, Bowman-James and co-workers were able to isolate a complex between **12** and SO_4^{2-}, **[H$_8$12(SO$_4$)][SO$_4$]$_2$[HSO$_4$]$_2$·5.25H$_2$O·2CH$_3$OH**.[70] In this structure SO_4^{-} is encapsulated in the cavity and forms a five-coordinate, pseudo-trigonal pyramidal coordination (**Figure 37**). Hydrogen bonds between the ligand and SO_4^{2-} range from approximately 2.6 to 2.8 Å. While two additional SO_4^{2-} ions and two HSO_4^{-} ions are coordinated with the ligand, they are located outside the cavity.

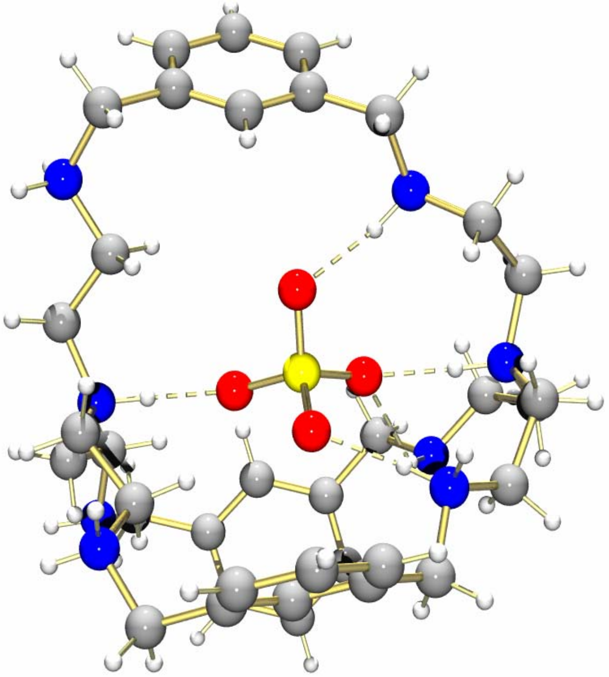


Figure 37: Drawing of Bowman-James' SO_4^{2-} complex with **12**.[70]

In a separate study, the binding of the HSO_4^- ion with **14** was observed in DMSO-d_6 (**Figure 36**). The titration curve showed a small downfield shift of the amine proton, and the binding constant was calculated to be Log K = 3.2. Bowman-James studied the affinity between HSO_4^- and **19**, the amide analogue of **14** (**Figure 11**). Under the same conditions (DMSO-d_6, [L] = 2 mM, [A^-] = 20 mM), the binding of HSO_4^- with **19** was calculated to be Log K = 1.83,[70] over an order of magnitude less than that found for **14**. This can be explained by the charge on the bicycles. In the case of **14**, the ligand is hexaprotonated, $\mathbf{H_6 14^{6+}}$, while **19** remains neutral in DMSO**.** In other solvents, for example CD_3CN, **19** abstracts a proton from HSO_4^- forming the salt, as shown by the appearance of minor peaks in the NMR spectrum. However, these peaks were not observed in DMSO.

5.4 Conclusions

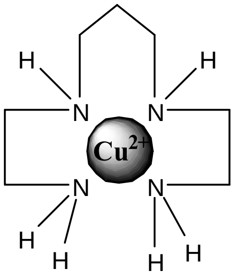
The binding properties of PyEACryp **14** with the halides, SO_4^{2-}, and HSO_4^- were probed. The binding for the halides in D_2O followed the Hofmeister series,[23] with a marked increase from the Cl^- to the F^- ion. This may be explained by the F^- ion's higher charge density and basicity. The binding constant observed for the F^- ion with the pyridine-based ligand **14** is supported by that found by Mason using potentiometric methods.[25] Further studies, including the isolation of a crystal, would help clarify these details.

Sulfate demonstrated a 1:2 binding mode with **14** in D_2O. The binding constant was larger than that of the F^- ion, which is to be expected because of the

SO_4^{2-} ion's divalent charge and greater basicity. Hydrogen sulfate had a binding constant of Log $K = 3.2$ in DMSO-d_6.

The crystal structure of the Br^- ion complex shows three halides bound in the clefts of the ligand and three coordinated externally. All Br^- ions have at least two hydrogen bonds, both to amines and H_2O molecules. The external Br^- ions are sandwiched between two different bicycles. The cleft binding is similar to that found for oxoanions and **14,** as demonstrated by Mason[25] and Nelson.[81]

Chapter 6 Structural Index



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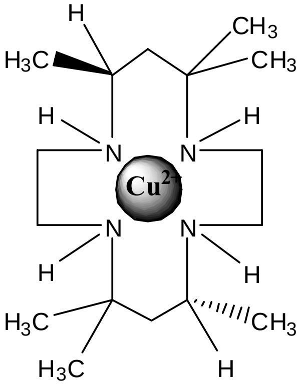

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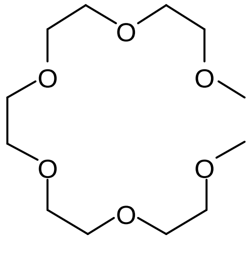

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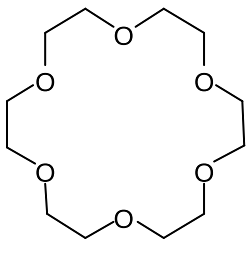

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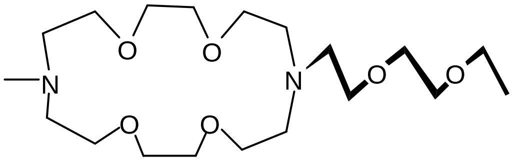

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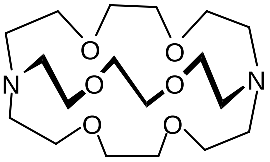

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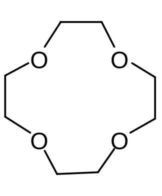

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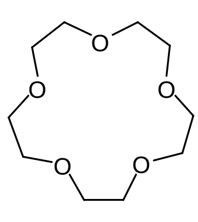

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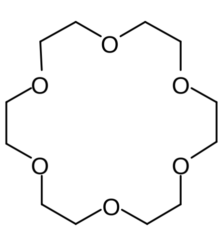
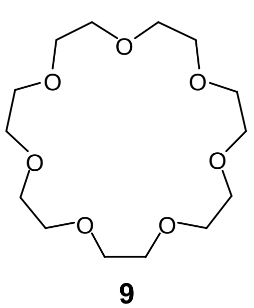


4



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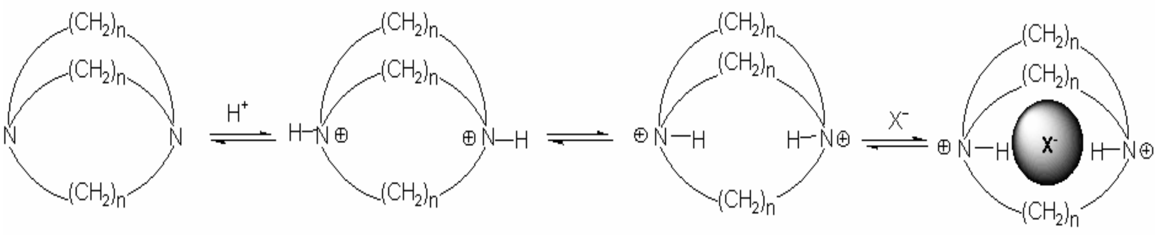
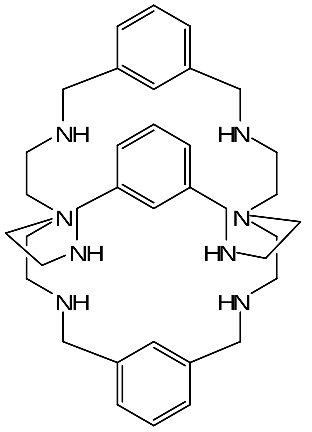


n = 7-10
10

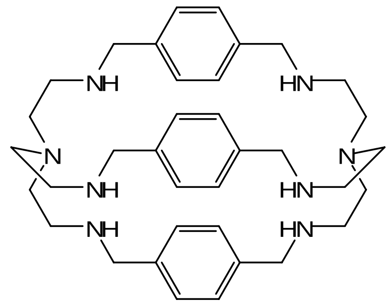
n = 7-10
H_210^{2+}
exo-exo

n = 7-10
H_210^{2+}
endo-endo

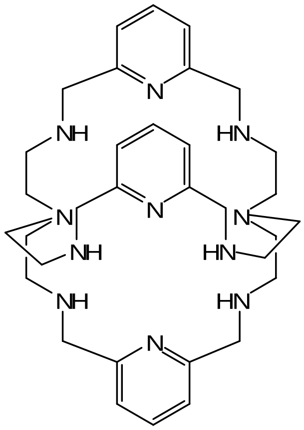
n = 7-10
$H_210^{2+}\cdot X^-$



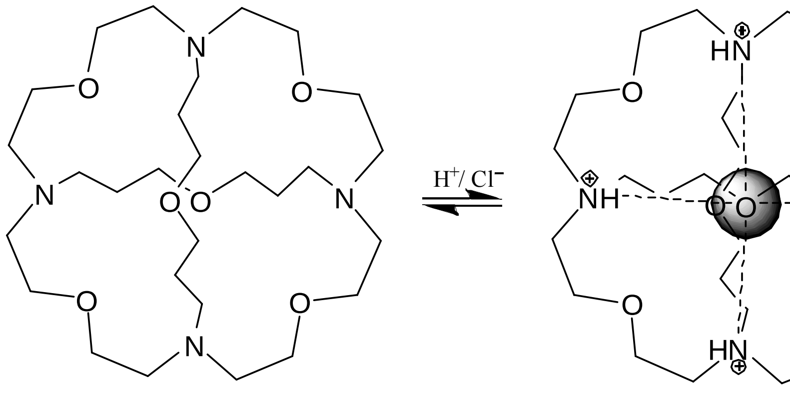
12



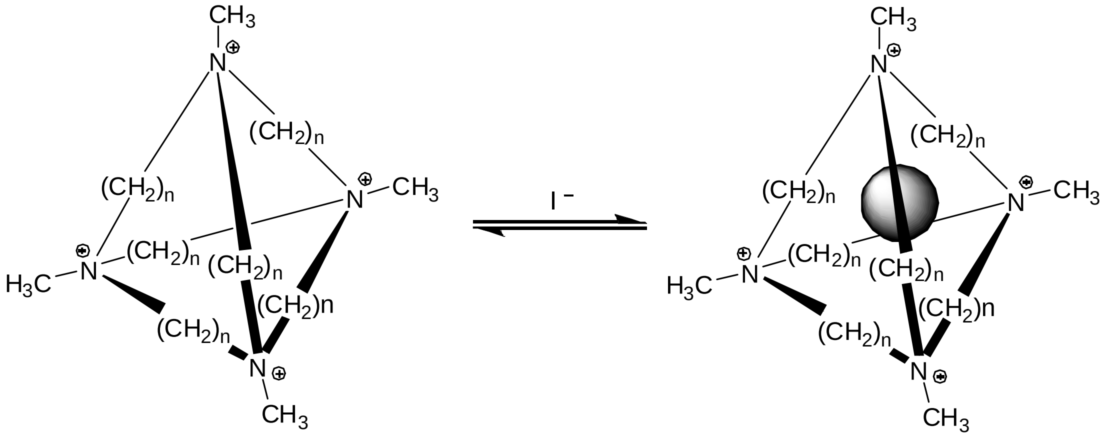
13



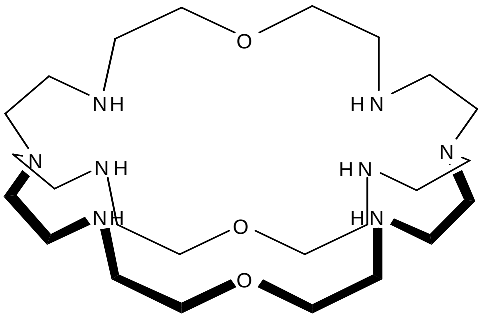
14



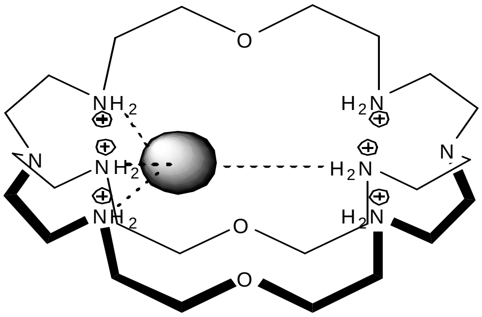
15 **$H_4$15^{4+}·Cl$^-$**



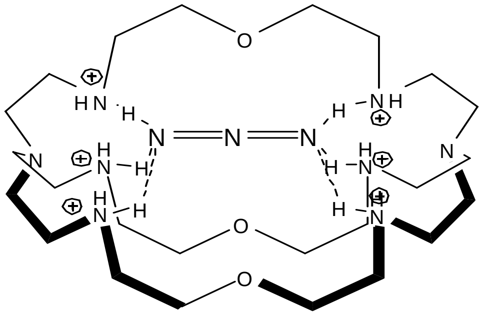
16 **16·I$^-$**



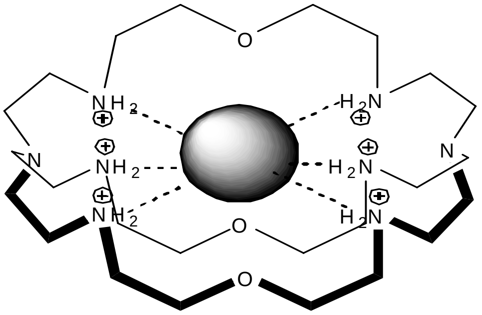
17



$H_6 17^{6+} \cdot F^-$

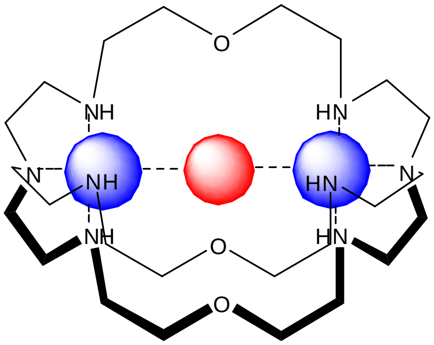


$H_6 17^{6+} \cdot N_3^-$



$H_6 17^{6+} \cdot X^-$

$X = Br^-$ or Cl^-



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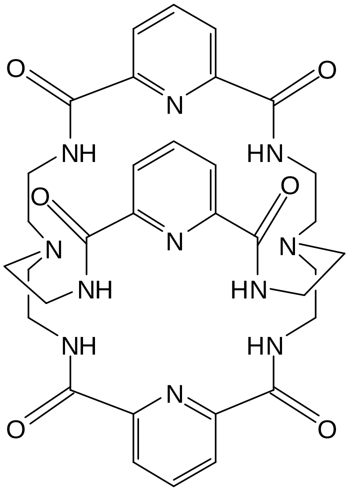

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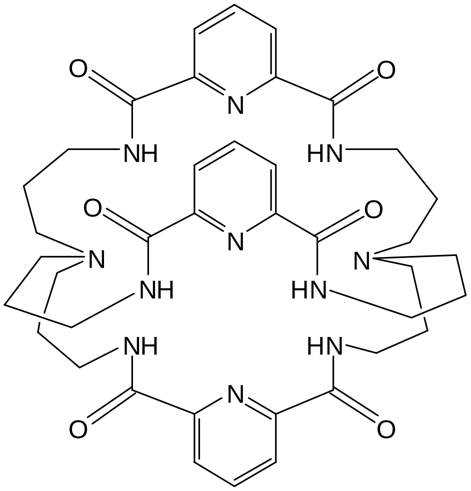
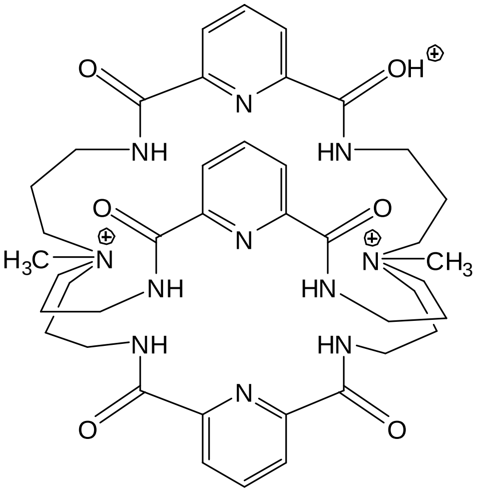
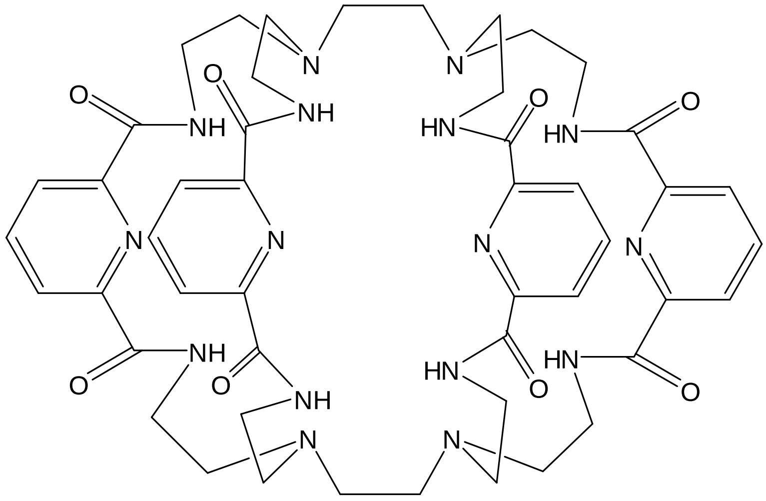


20



$(CH_3)_2 20^{2+}$



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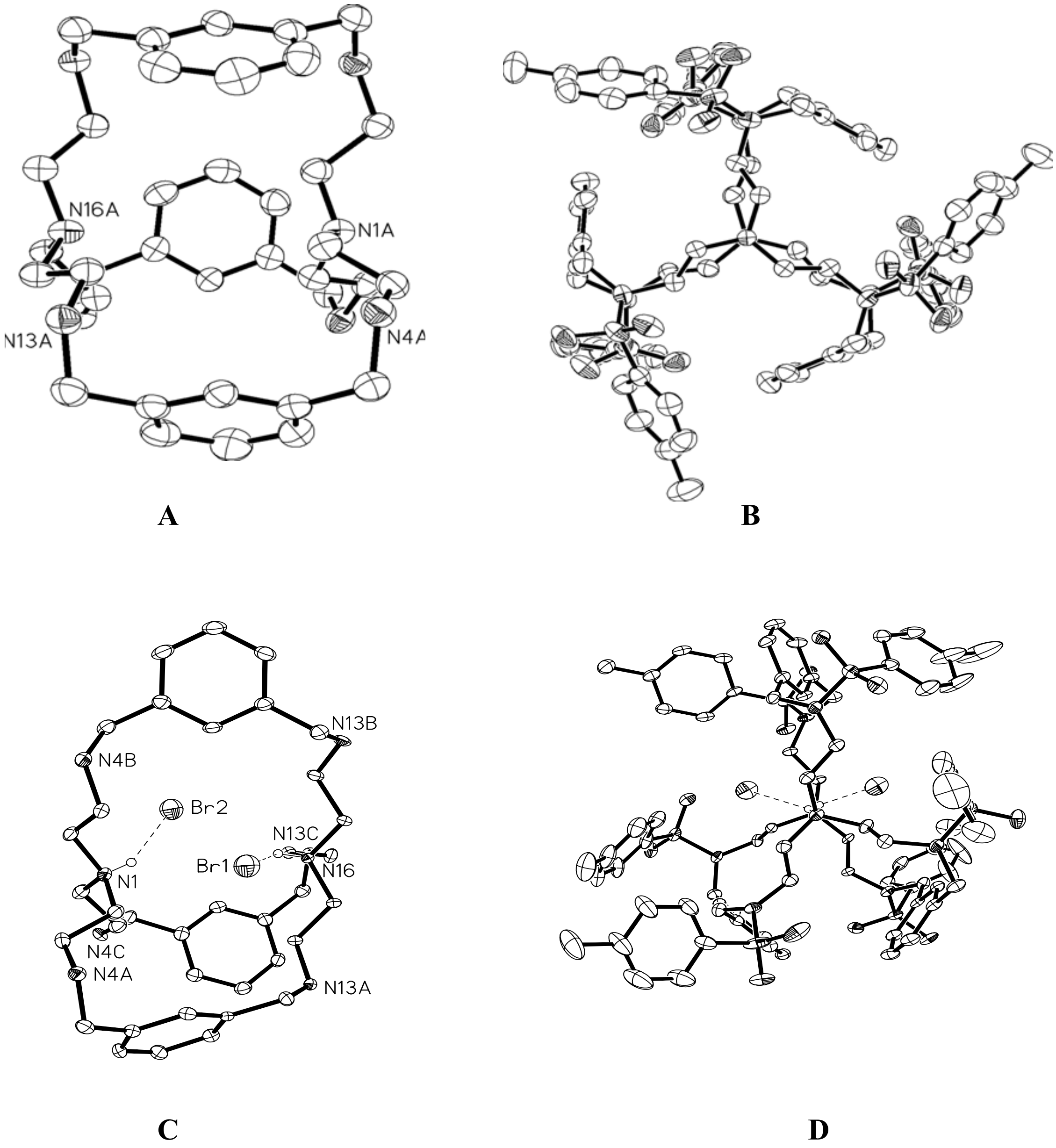

Figure A-1: Two views each of **Ts$_6$12** (A and B) and **[Ts$_6$H$_2$12(Br)$_2$]** (C and D). In (A) and (C) the tosyl groups omitted for clarity. Diagrams (C) and (D) are views down the bridgehead ammonium groups. Thermal ellipsoids are at 50% probability.

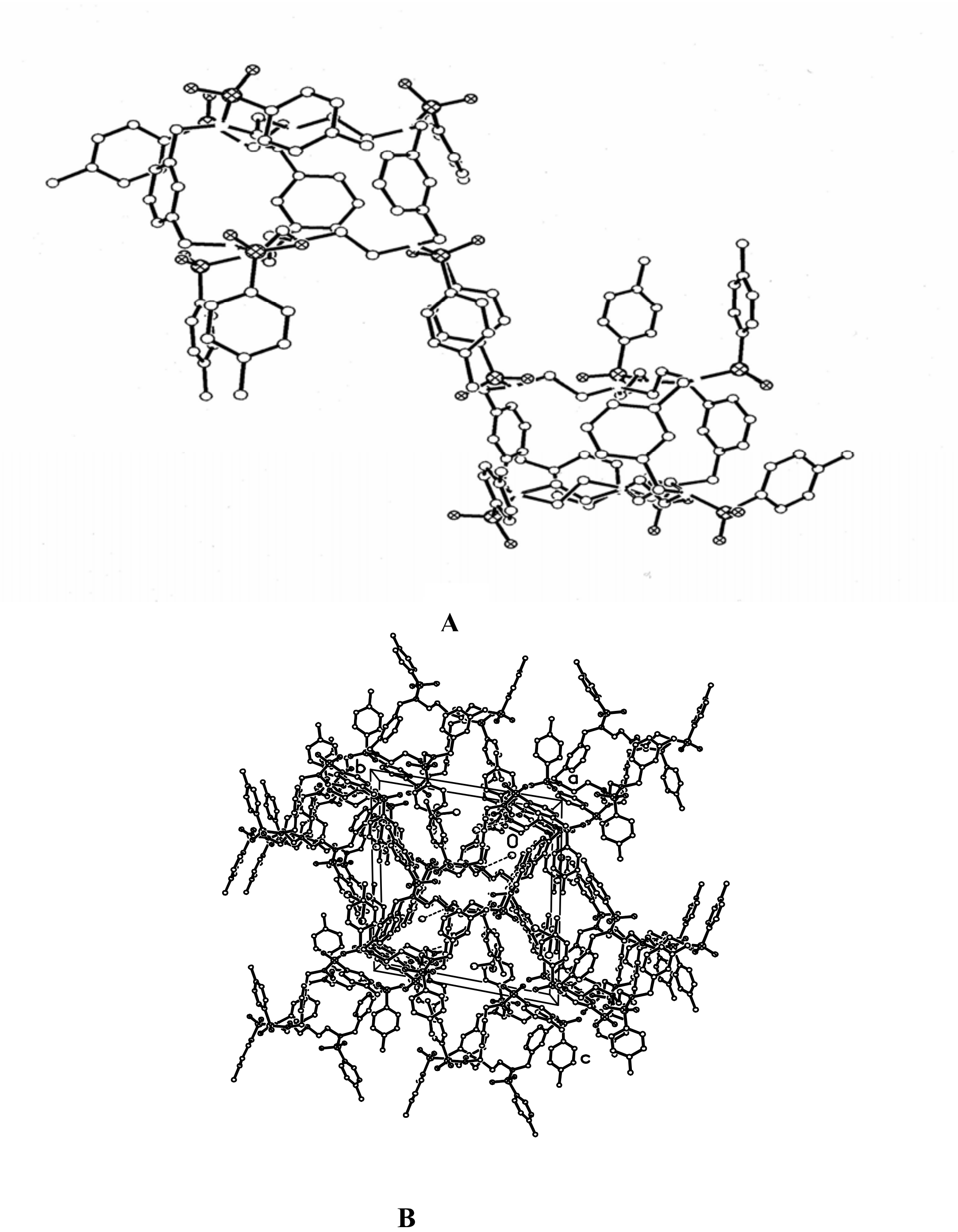

Figure A-2: Two views of **Ts$_6$12** (A and B). (A) shows overlap of two molecules, and (B) is a packing diagram viewed down the *c* axis.

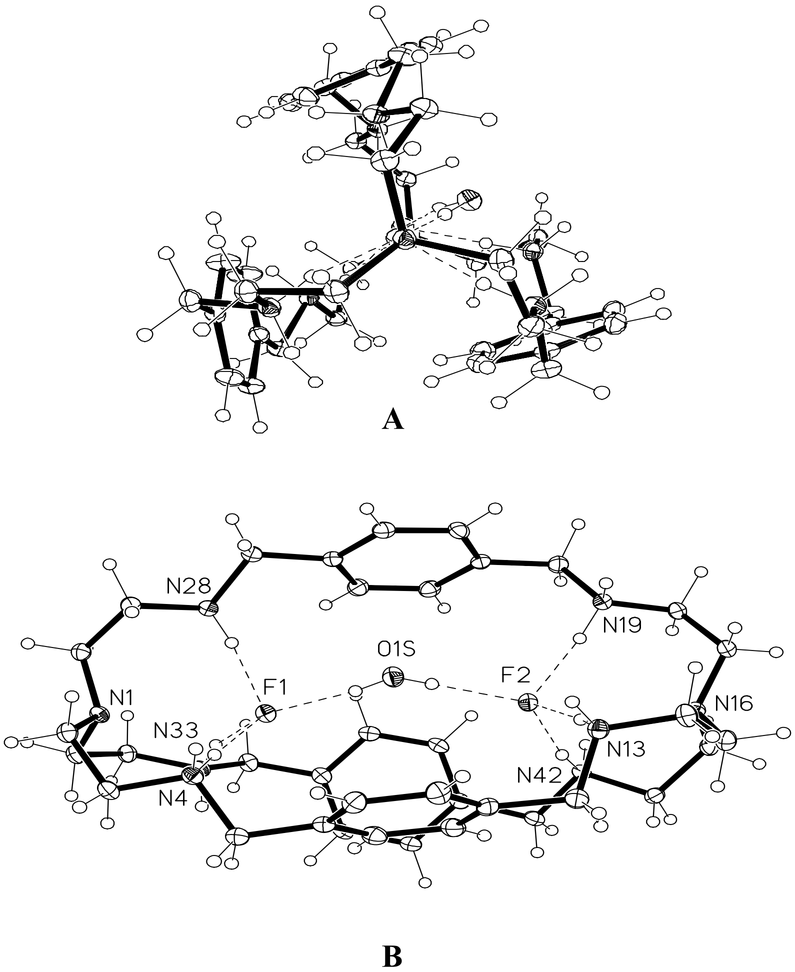

Figure A-3: Two ORTEP drawings of **$[H_613(F)_2(H_2O)][SiF_6]\cdot 12H_2O$** (external H_2O and SiF_6^{2-} omitted for clarity) (A and B); (A) shows view down the N-N bridgehead axis; (B) shows F^- cascade with H_2O inside the cavity.

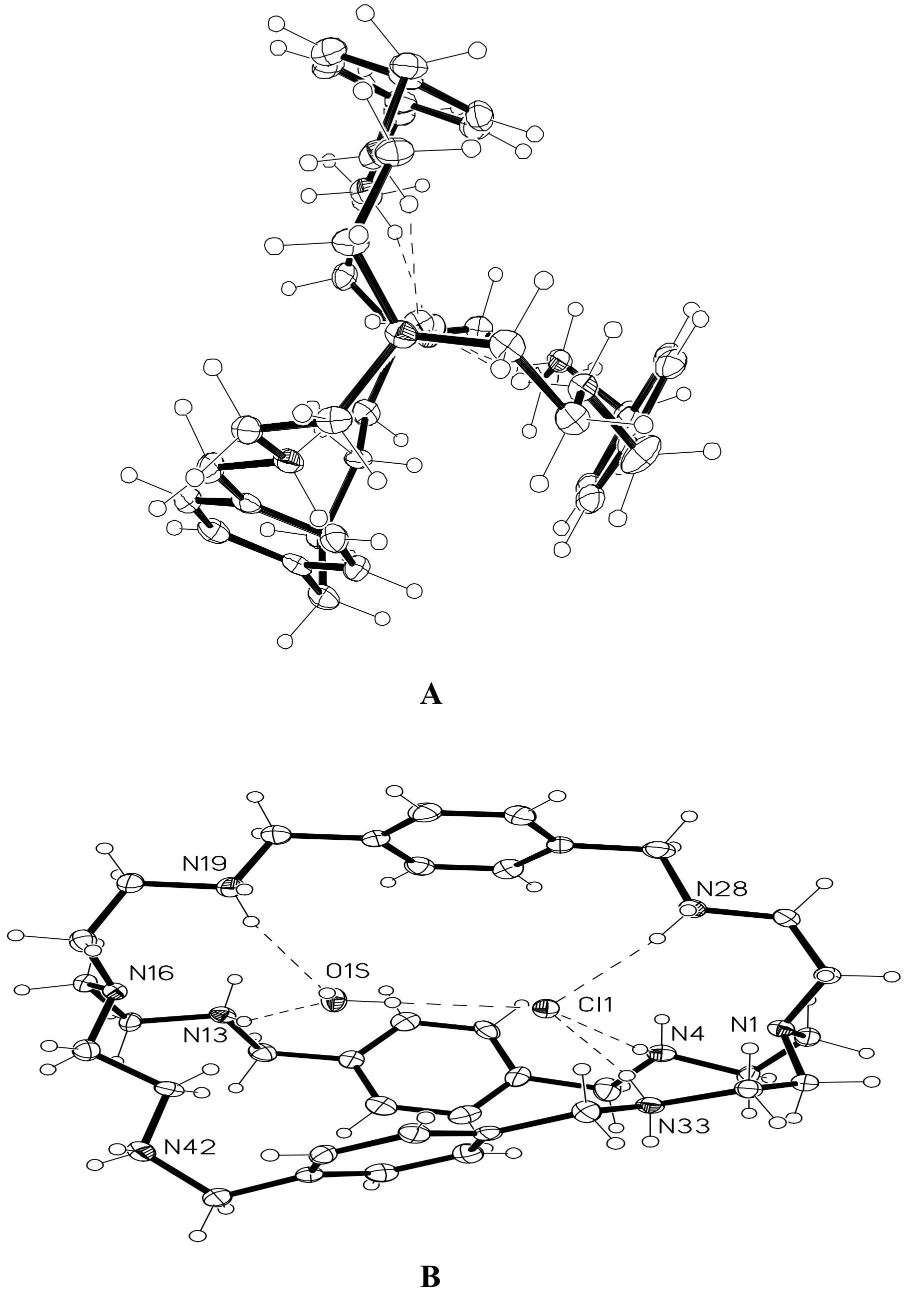

Figure A-4: ORTEP drawing of **$[H_6 13(Cl)(H_2O)][Cl]_5\cdot 4H_2O\cdot CH_3OH$**: (A) shows a side view showing Cl^- and H_2O inside the cavity; (B) shows a view down the three-fold axis.

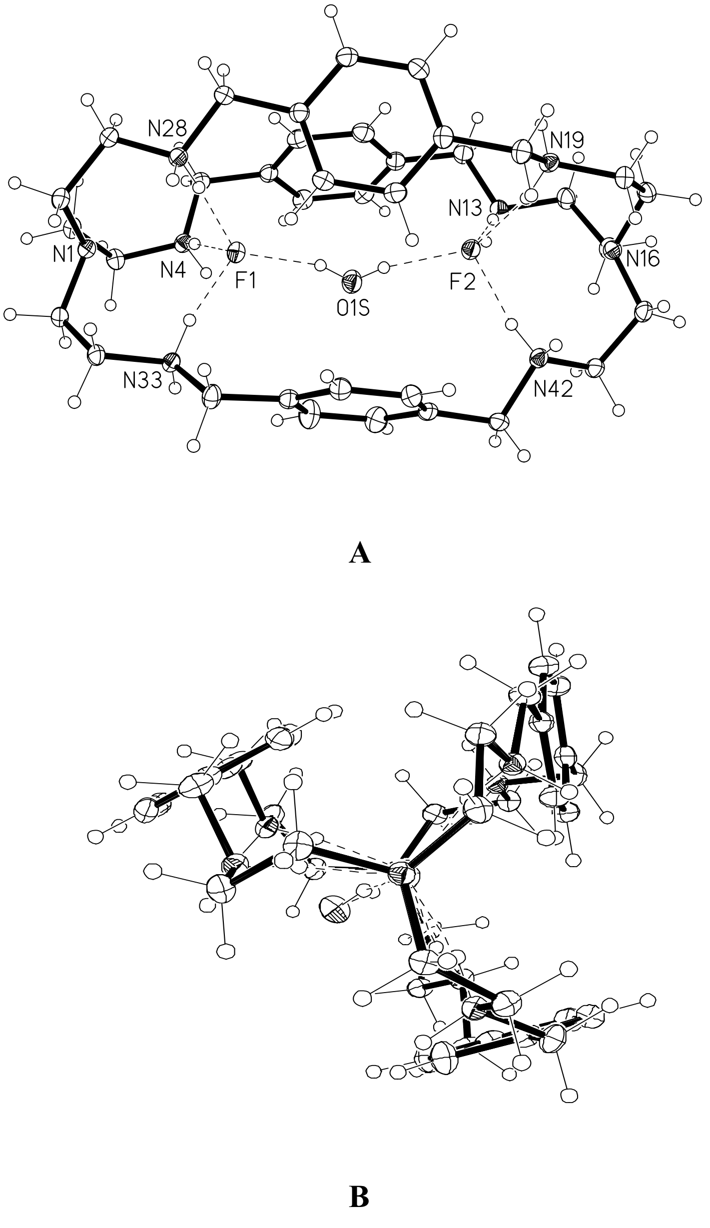

Figure A-5: ORTEP drawing of **[$H_6$13(F)$_2$(H_2O)][Cl]$_2$[SiF_6]•10H_2O**: (A) side view; (B) view down the pseudo-threefold axis.

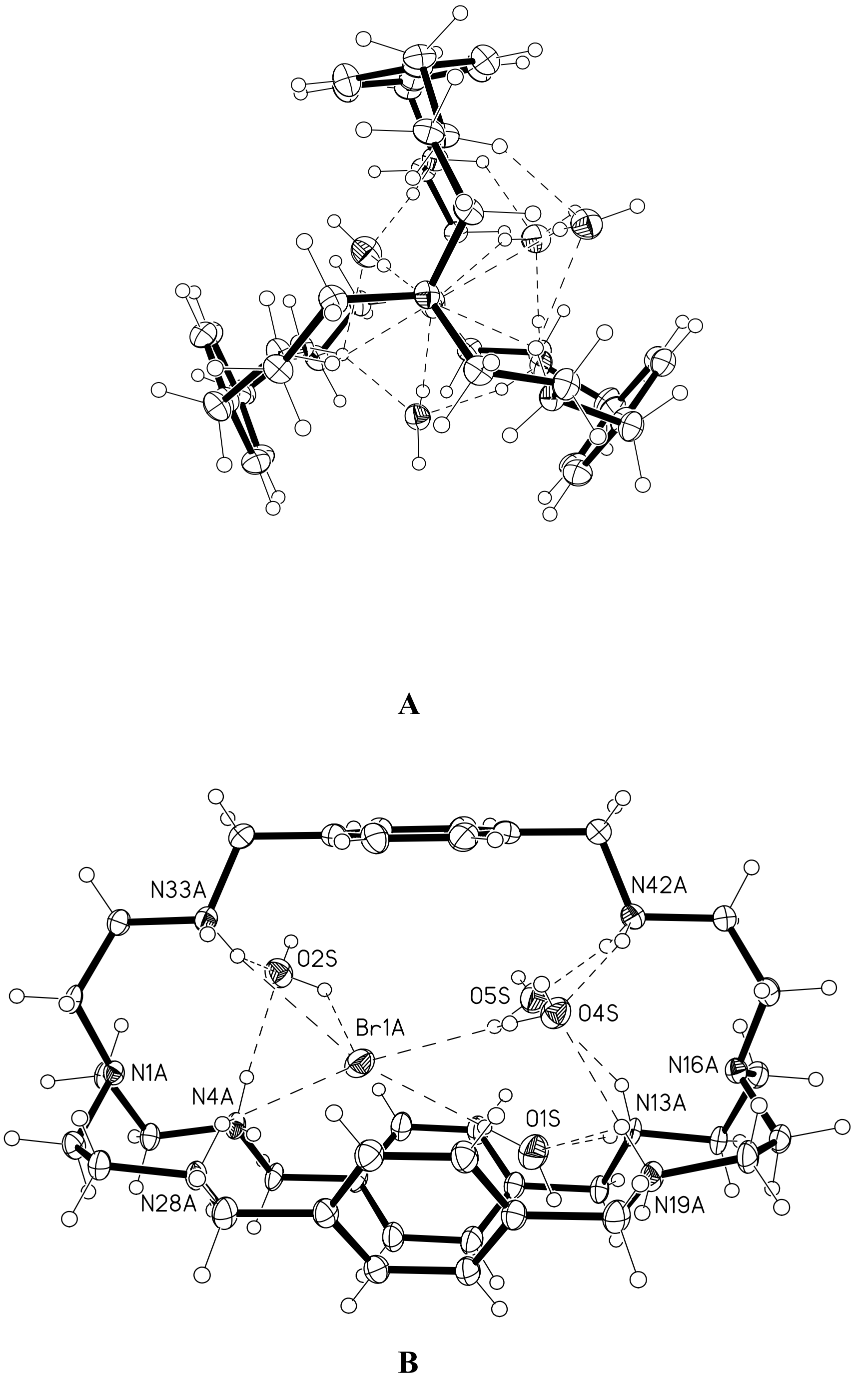

Figure A-6: ORTEP drawing of the first cation of **$[H_613(Br)(H_2O)][Br]_5 \cdot 6.25H_2O$** (A and B). (A) shows a view down the N-N axis; (B) shows the side view with Br^- and H_2O inside the cavity.

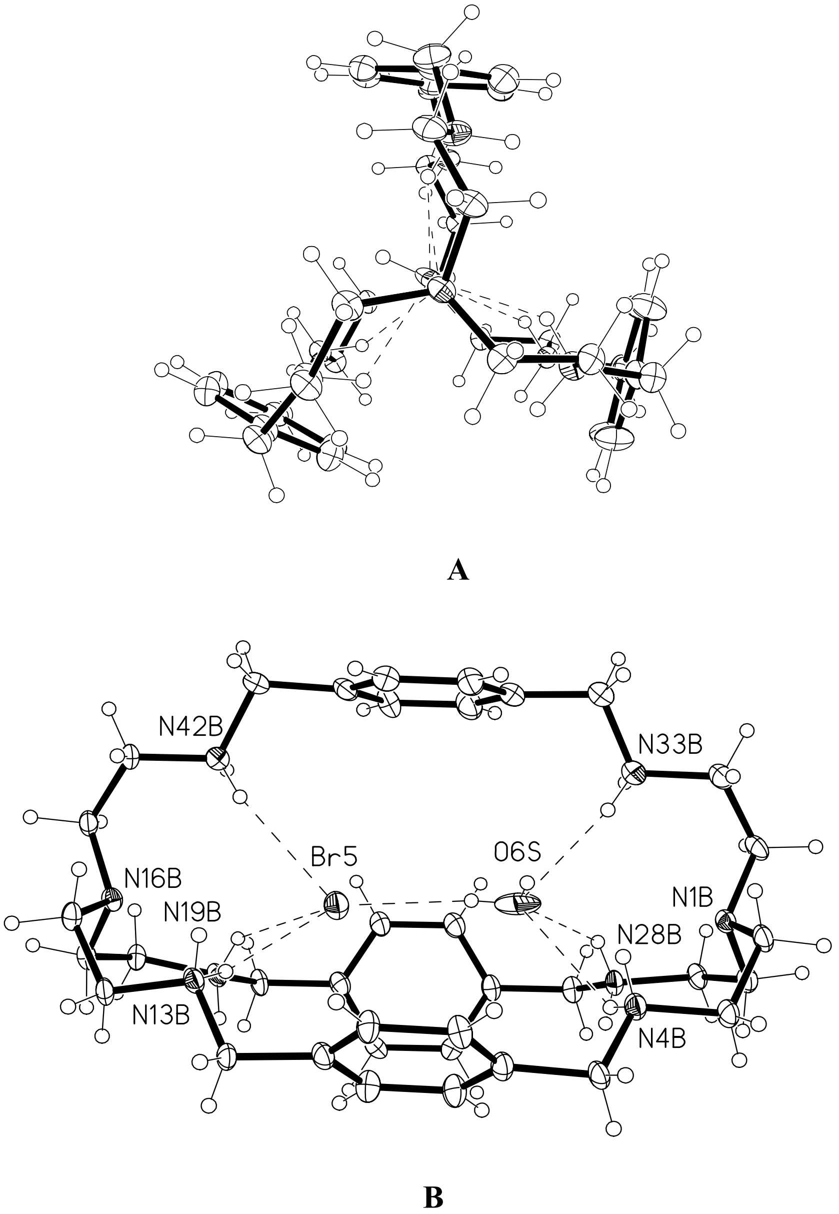

Figure A-7: ORTEP drawing of the second cation of **[$H_6$13(Br)(H_2O)][Br]$_5$ ·6.25H_2O** (A and B). (A) shows a view down the N-N axis; (B) shows the side view with Br$^-$ and H_2O inside the cavity.

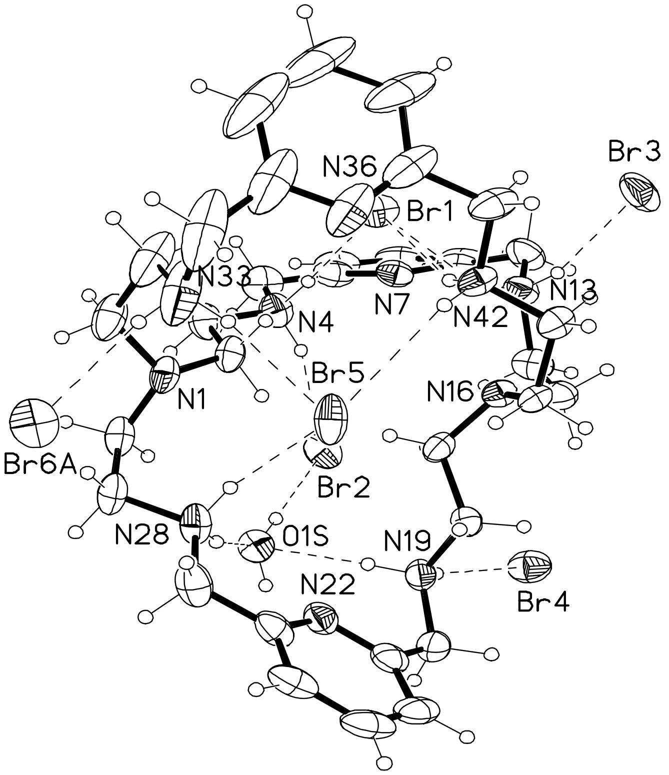

Figure A-8: ORTEP drawing of **[H$_6$14(Br)$_3$(H$_2$O)][Br]$_3$•2.25H$_2$O** with numbering scheme shown.

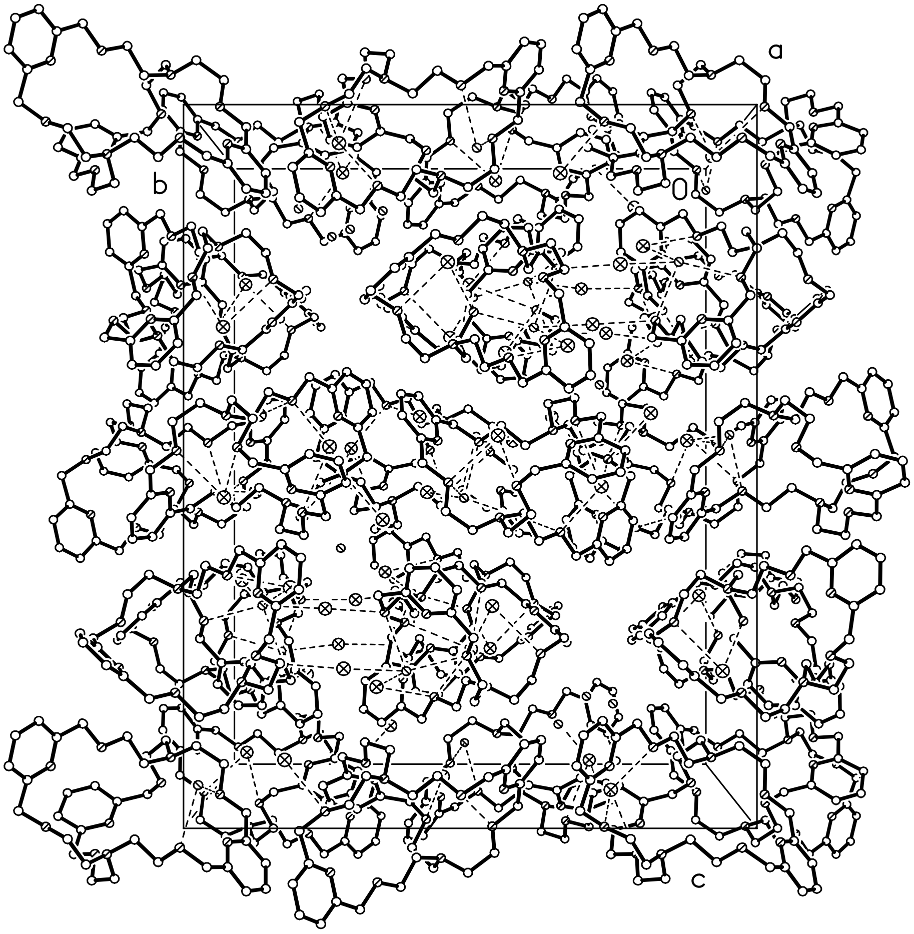

Figure A-9: Packing diagram of **[$H_6$14(Br)$_3$(H_2O)][Br]$_3$•2.25H_2O** as viewed down the *c* axis.

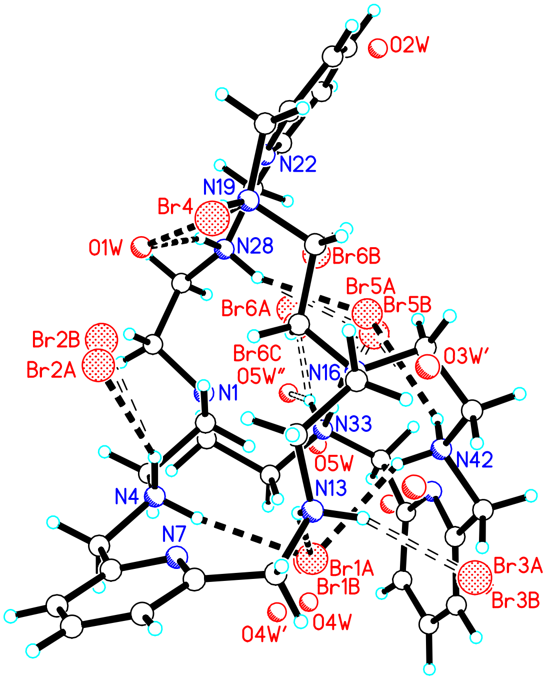

Figure A-10: Ball and stick drawing of **[$H_6$14$(Br)_3(H_2O)$][$Br]_3$•4H_2O** providing an alternate view.(Second refinement)

Chapter 8 Appendix of Crystallographic Data

Structural Data for Ts$_6$12

Table A-1. Crystal data and structure refinement for **Ts$_6$12**.

Identification code	01001a	
Empirical formula	$(C_{78}\ H_{90}\ N_8\ O_{12}\ S_6)1.5(C_2\ H_3\ N)0.183(CHCl_3)$ $C_{81.18}\ H_{94.68}\ Cl_{0.55}\ N_{9.50}\ O_{12}\ S_6$	
Formula weight	1607.50	
Crystal system	Trigonal	
Space group	R-3	
Unit cell dimensions	a = 21.9335(6) Å	α = 90°
	b = 21.9335(6) Å	β = 90°
	c = 65.463(3) Å	γ = 120°
Volume	27273.6(16) Å^3	
Z	12	
Density (calculated)	1.174 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	298(2) K	
F(000)	10196	
Absorption coefficient	0.226 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9605 and 0.9478	
Theta range for data collection	2.08 to 26.00°	
Reflections collected	58095	
Independent reflections	11906 [R(int) = 0.0674]	
Data / restraints / parameters	11906 / 240 / 790	
$wR(F^2$all data)	$wR2$ = 0.2124	
$R(F$ obsd data)	$R1$ = 0.0624	
Goodness-of-fit on F^2	0.910	
Observed data [I > 2σ(I)]	4885	
Largest and mean shift / s.u.	0.024and 0.000	
Largest diff. peak and hole	0.718 and -0.296 e/Å^3	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o{}^2)^2] \}^{1/2}$ $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

Table A-2. Atomic coordinates and equivalent isotropic displacement parameters (Å) for **Ts$_6$12**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1A)	0.72148(6)	0.14983(6)	0.478713(17)	0.0722(3)
S(2A)	0.69188(6)	0.13759(6)	0.581176(15)	0.0681(3)
N(1A)	0.6667	0.3333	0.49038(8)	0.0569(14)
C(2A)	0.67808(19)	0.27525(18)	0.49600(6)	0.0599(10)
C(3A)	0.65205(19)	0.22001(18)	0.47912(5)	0.0593(10)
N(4A)	0.65321(16)	0.15586(15)	0.48520(4)	0.0608(8)
C(5A)	0.5845(2)	0.0912(2)	0.48721(6)	0.0694(11)
C(6A)	0.5460(2)	0.09607(18)	0.50578(6)	0.0592(10)
C(7A)	0.57035(19)	0.09358(17)	0.52492(6)	0.0560(10)
C(8A)	0.4904(2)	0.1076(2)	0.50402(7)	0.0755(12)
C(9A)	0.4594(2)	0.1158(2)	0.52093(8)	0.0861(14)
C(10A)	0.4840(2)	0.1138(2)	0.54030(7)	0.0741(12)
C(11A)	0.54050(19)	0.10243(17)	0.54228(6)	0.0576(10)
C(12A)	0.5688(2)	0.1004(2)	0.56330(6)	0.0693(11)
N(13A)	0.64533(16)	0.15145(14)	0.56460(4)	0.0583(8)
C(14A)	0.66938(19)	0.22541(17)	0.55954(5)	0.0576(10)
C(15A)	0.64199(18)	0.26074(18)	0.57366(6)	0.0582(10)
N(16A)	0.6667	0.3333	0.56685(8)	0.0548(14)
O(17A)	0.78139(14)	0.21732(16)	0.48259(5)	0.0863(9)
O(18A)	0.71500(17)	0.08890(16)	0.48866(5)	0.0986(10)
C(19A)	0.7165(2)	0.1357(2)	0.45216(6)	0.0649(11)
C(20A)	0.7582(2)	0.1905(2)	0.43905(7)	0.0817(13)
C(21A)	0.7527(2)	0.1803(2)	0.41817(7)	0.0910(15)
C(22A)	0.7069(2)	0.1159(3)	0.41002(7)	0.0827(13)
C(23A)	0.6658(3)	0.0618(2)	0.42281(7)	0.0924(15)
C(24A)	0.6700(2)	0.0706(2)	0.44401(7)	0.0825(13)
C(25A)	0.7012(3)	0.1046(3)	0.38722(8)	0.123(2)
O(26A)	0.65616(16)	0.06311(14)	0.58468(4)	0.0865(9)
O(27A)	0.70893(17)	0.18220(17)	0.59845(4)	0.0929(9)
C(28A)	0.7713(2)	0.1630(2)	0.56828(6)	0.0644(11)
C(29A)	0.7709(2)	0.1414(2)	0.54832(7)	0.0780(12)
C(30A)	0.8324(2)	0.1561(2)	0.53882(7)	0.0885(14)
C(31A)	0.8966(3)	0.1935(3)	0.54926(9)	0.0928(15)
C(32A)	0.8957(3)	0.2147(3)	0.56915(8)	0.0957(16)
C(33A)	0.8341(3)	0.2006(2)	0.57839(7)	0.0843(13)
C(34A)	0.9654(3)	0.2106(3)	0.53883(10)	0.135(2)
S(1B)	0.90871(6)	0.15714(6)	0.392662(17)	0.0745(3)

S(2B)	0.97405(6)	0.20142(6)	0.291261(16)	0.0765(3)
N(1B)	1.0000	0.0000	0.38340(8)	0.0659(15)
C(2B)	0.9764(2)	0.0492(2)	0.37700(6)	0.0699(11)
C(3B)	0.9959(2)	0.1063(2)	0.39298(6)	0.0687(11)
N(4B)	0.98284(17)	0.16250(16)	0.38608(5)	0.0680(9)
C(5B)	1.0458(2)	0.2332(2)	0.38469(6)	0.0724(12)
C(6B)	1.0940(2)	0.23536(19)	0.36774(6)	0.0612(10)
C(7B)	1.07483(19)	0.23481(18)	0.34755(6)	0.0602(10)
C(8B)	1.1552(2)	0.2347(2)	0.37186(7)	0.0713(12)
C(9B)	1.1957(2)	0.2323(2)	0.35627(7)	0.0749(12)
C(10B)	1.1755(2)	0.2308(2)	0.33642(7)	0.0693(11)
C(11B)	1.11467(19)	0.23258(18)	0.33181(5)	0.0547(9)
C(12B)	1.09325(19)	0.2328(2)	0.30973(6)	0.0650(11)
N(13B)	1.01901(16)	0.17989(15)	0.30615(5)	0.0616(8)
C(14B)	0.9935(3)	0.1052(3)	0.31314(11)	0.068(2)
C(15B)	1.0227(4)	0.0703(3)	0.29969(11)	0.081(3)
C(14')	1.0074(5)	0.1101(3)	0.29817(11)	0.058(3)
C(15')	1.0191(5)	0.0706(4)	0.31509(13)	0.068(3)
N(16B)	1.0000	0.0000	0.30791(10)	0.0714(17)
O(17B)	0.85637(15)	0.08482(16)	0.39122(5)	0.0942(10)
O(18B)	0.90265(17)	0.20882(17)	0.38104(5)	0.0986(10)
C(19B)	0.9167(2)	0.1815(2)	0.41844(6)	0.0681(11)
C(20B)	0.8943(3)	0.1316(2)	0.43333(8)	0.0955(15)
C(21B)	0.9040(3)	0.1521(3)	0.45365(8)	0.1066(17)
C(22B)	0.9359(2)	0.2212(3)	0.45919(7)	0.0901(15)
C(23B)	0.9555(2)	0.2698(3)	0.44400(8)	0.0956(16)
C(24B)	0.9470(2)	0.2515(2)	0.42378(7)	0.0832(13)
C(25B)	0.9476(3)	0.2428(3)	0.48152(8)	0.137(2)
O(26B)	1.0015(5)	0.2735(2)	0.29851(12)	0.090(3)
O(27B)	0.9696(5)	0.1911(5)	0.26924(6)	0.094(3)
O(26')	1.0061(5)	0.27698(19)	0.28883(12)	0.104(2)
O(27')	0.9646(4)	0.1587(4)	0.27322(8)	0.098(2)
C(28B)	0.8891(2)	0.15854(19)	0.30214(6)	0.0618(10)
C(29B)	0.8796(2)	0.1707(2)	0.32263(7)	0.0789(13)
C(30B)	0.8122(3)	0.1402(3)	0.33051(7)	0.0903(14)
C(31B)	0.7539(2)	0.0960(2)	0.31875(7)	0.0831(13)
C(32B)	0.7652(2)	0.0850(3)	0.29899(7)	0.0961(16)
C(33B)	0.8319(2)	0.1158(2)	0.29075(7)	0.0856(14)
C(34B)	0.6822(3)	0.0628(3)	0.32788(8)	0.129(2)
Cl(1S)	1.0495(3)	0.08592(16)	0.44505(7)	0.153(2)
C(1S)	1.0000	0.0000	0.43726(19)	0.053(4)
N(1T)	0.8916(11)	0.4175(13)	0.4039(3)	0.124(3)
C(2T)	0.8985(14)	0.3973(15)	0.4186(3)	0.117(3)
C(3T)	0.8895(18)	0.3754(19)	0.4401(3)	0.117(4)

N(1U)	0.8951(4)	0.4078(18)	0.4285(4)	0.118(3)
C(2U)	0.8402(4)	0.3948(13)	0.4259(5)	0.115(3)
C(3U)	0.7634(3)	0.3602(5)	0.42417(19)	0.096(4)
N(1V)	0.8343(3)	0.3619(5)	0.40071(19)	0.124(3)
C(2V)	0.8184(3)	0.3548(5)	0.38442(19)	0.136(4)
C(3V)	0.7807(3)	0.3214(5)	0.36547(19)	0.155(6)
N(1W)	0.8845(9)	0.4024(17)	0.4322(2)	0.114(3)
C(2W)	0.8730(9)	0.4047(15)	0.4158(2)	0.120(2)
C(3W)	0.8368(13)	0.3919(15)	0.3961(3)	0.126(4)
N(1X)	0.6667	0.3333	0.4251(5)	0.091(5)
C(2X)	0.7227(4)	0.3549(16)	0.4214(5)	0.097(4)
C(3X)	0.7974(6)	0.376(2)	0.4206(7)	0.109(3)

Table A-3. Bond lengths [Å] and angles [°] for **Ts$_6$12**.

S(1A)-O(17A)	1.427(3)	N(16A)-C(15A)#2	1.471(4)
S(1A)-O(18A)	1.428(3)	C(19A)-C(24A)	1.382(5)
S(1A)-N(4A)	1.624(3)	C(19A)-C(20A)	1.385(5)
S(1A)-C(19A)	1.759(4)	C(20A)-C(21A)	1.381(6)
S(2A)-O(27A)	1.418(3)	C(21A)-C(22A)	1.367(6)
S(2A)-O(26A)	1.434(3)	C(22A)-C(23A)	1.361(6)
S(2A)-N(13A)	1.619(3)	C(22A)-C(25A)	1.508(6)
S(2A)-C(28A)	1.757(4)	C(23A)-C(24A)	1.398(6)
N(1A)-C(2A)	1.463(4)	C(28A)-C(33A)	1.372(6)
N(1A)-C(2A)#1	1.463(4)	C(28A)-C(29A)	1.389(5)
N(1A)-C(2A)#2	1.463(4)	C(29A)-C(30A)	1.369(6)
C(2A)-C(3A)	1.524(5)	C(30A)-C(31A)	1.403(6)
C(3A)-N(4A)	1.475(4)	C(31A)-C(32A)	1.386(7)
N(4A)-C(5A)	1.470(4)	C(31A)-C(34A)	1.522(7)
C(5A)-C(6A)	1.514(5)	C(32A)-C(33A)	1.366(6)
C(6A)-C(8A)	1.368(6)	S(1B)-O(17B)	1.422(3)
C(6A)-C(7A)	1.374(5)	S(1B)-O(18B)	1.425(3)
C(7A)-C(11A)	1.373(5)	S(1B)-N(4B)	1.629(3)
C(8A)-C(9A)	1.359(6)	S(1B)-C(19B)	1.752(4)
C(9A)-C(10A)	1.388(6)	S(2B)-O(26')	1.449(3)
C(10A)-C(11A)	1.386(5)	S(2B)-O(27B)	1.455(3)
C(11A)-C(12A)	1.519(5)	S(2B)-O(27')	1.457(3)
C(12A)-N(13A)	1.482(4)	S(2B)-O(26B)	1.460(3)
N(13A)-C(14A)	1.471(4)	S(2B)-N(13B)	1.616(3)
C(14A)-C(15A)	1.510(5)	S(2B)-C(28B)	1.764(4)
C(15A)-N(16A)	1.471(4)	N(1B)-C(2B)#3	1.471(4)
N(16A)-C(15A)#1	1.471(4)	N(1B)-C(2B)	1.471(4)

N(1B)-C(2B)#4	1.471(4)
C(2B)-C(3B)	1.519(5)
C(3B)-N(4B)	1.470(5)
N(4B)-C(5B)	1.477(5)
C(5B)-C(6B)	1.516(5)
C(6B)-C(8B)	1.377(5)
C(6B)-C(7B)	1.385(5)
C(7B)-C(11B)	1.368(5)
C(8B)-C(9B)	1.370(5)
C(9B)-C(10B)	1.369(5)
C(10B)-C(11B)	1.387(5)
C(11B)-C(12B)	1.521(5)
C(12B)-N(13B)	1.471(4)
N(13B)-C(14B)	1.514(6)
N(13B)-C(14')	1.514(6)
C(14B)-C(15B)	1.504(7)
C(15B)-N(16B)	1.465(5)
C(14')-C(15')	1.505(7)
C(15')-N(16B)	1.465(6)
N(16B)-C(15')#3	1.465(6)
N(16B)-C(15')#4	1.465(6)
N(16B)-C(15B)#3	1.465(6)
N(16B)-C(15B)#4	1.465(5)
C(19B)-C(20B)	1.361(6)
C(19B)-C(24B)	1.378(5)
C(20B)-C(21B)	1.386(6)
C(21B)-C(22B)	1.362(7)
C(22B)-C(23B)	1.360(7)
C(22B)-C(25B)	1.519(6)
C(23B)-C(24B)	1.369(6)
C(28B)-C(33B)	1.354(5)
C(28B)-C(29B)	1.404(5)
C(29B)-C(30B)	1.383(6)
C(30B)-C(31B)	1.389(6)
C(31B)-C(32B)	1.362(6)
C(31B)-C(34B)	1.488(6)
C(32B)-C(33B)	1.378(6)
Cl(1S)-C(1S)	1.716(3)
C(1S)-Cl(1S)#3	1.716(3)
C(1S)-Cl(1S)#4	1.716(3)
N(1T)-C(2T)	1.106(4)
C(2T)-C(3T)	1.467(4)
N(1U)-C(2U)	1.104(4)
C(2U)-C(3U)	1.466(4)
N(1V)-C(2V)	1.1086
C(2V)-C(3V)	1.4670
N(1W)-C(2W)	1.107(4)
C(2W)-C(3W)	1.466(4)
N(1X)-C(2X)	1.102(4)
C(2X)-C(3X)	1.464(4)
O(17A)-S(1A)-O(18A)	119.9(2)
O(17A)-S(1A)-N(4A)	106.10(16)
O(18A)-S(1A)-N(4A)	107.01(18)
O(17A)-S(1A)-C(19A)	107.58(19)
O(18A)-S(1A)-C(19A)	108.48(19)
N(4A)-S(1A)-C(19A)	107.13(18)
O(27A)-S(2A)-O(26A)	117.65(19)
O(27A)-S(2A)-N(13A)	112.25(17)
O(26A)-S(2A)-N(13A)	106.52(17)
O(27A)-S(2A)-C(28A)	106.7(2)
O(26A)-S(2A)-C(28A)	109.19(17)
N(13A)-S(2A)-C(28A)	103.67(17)
C(2A)-N(1A)-C(2A)#1	113.91(19)
C(2A)-N(1A)-C(2A)#2	113.91(19)
C(2A)#1-N(1A)-C(2A)#2	113.91(19)
N(1A)-C(2A)-C(3A)	110.5(3)
N(4A)-C(3A)-C(2A)	112.6(3)
C(5A)-N(4A)-C(3A)	116.5(3)
C(5A)-N(4A)-S(1A)	119.1(3)
C(3A)-N(4A)-S(1A)	117.6(2)
N(4A)-C(5A)-C(6A)	110.0(3)
C(8A)-C(6A)-C(7A)	119.0(4)
C(8A)-C(6A)-C(5A)	121.7(4)
C(7A)-C(6A)-C(5A)	119.2(4)
C(11A)-C(7A)-C(6A)	121.8(4)
C(9A)-C(8A)-C(6A)	120.6(4)
C(8A)-C(9A)-C(10A)	120.7(4)
C(11A)-C(10A)-C(9A)	119.3(4)
C(7A)-C(11A)-C(10A)	118.7(4)
C(7A)-C(11A)-C(12A)	121.0(4)
C(10A)-C(11A)-C(12A)	120.3(4)
N(13A)-C(12A)-C(11A)	110.8(3)
C(14A)-N(13A)-C(12A)	117.8(3)
C(14A)-N(13A)-S(2A)	116.5(2)
C(12A)-N(13A)-S(2A)	118.6(2)
N(13A)-C(14A)-C(15A)	114.4(3)
N(16A)-C(15A)-C(14A)	110.1(3)
C(15A)-N(16A)-C(15A)#1	111.2(2)

C(15A)-N(16A)-C(15A)#2	111.2(2)
C(15A)#1-N(16A)-C(15A)#2	111.2(2)
C(24A)-C(19A)-C(20A)	118.9(4)
C(24A)-C(19A)-S(1A)	120.8(3)
C(20A)-C(19A)-S(1A)	120.2(3)
C(21A)-C(20A)-C(19A)	120.5(4)
C(22A)-C(21A)-C(20A)	120.9(4)
C(23A)-C(22A)-C(21A)	119.0(4)
C(23A)-C(22A)-C(25A)	120.1(4)
C(21A)-C(22A)-C(25A)	120.9(5)
C(22A)-C(23A)-C(24A)	121.4(4)
C(19A)-C(24A)-C(23A)	119.3(4)
C(33A)-C(28A)-C(29A)	119.4(4)
C(33A)-C(28A)-S(2A)	119.9(3)
C(29A)-C(28A)-S(2A)	120.6(3)
C(30A)-C(29A)-C(28A)	120.7(4)
C(29A)-C(30A)-C(31A)	120.0(5)
C(32A)-C(31A)-C(30A)	118.4(5)
C(32A)-C(31A)-C(34A)	121.2(5)
C(30A)-C(31A)-C(34A)	120.5(5)
C(33A)-C(32A)-C(31A)	121.2(5)
C(32A)-C(33A)-C(28A)	120.3(5)
O(17B)-S(1B)-O(18B)	120.5(2)
O(17B)-S(1B)-N(4B)	106.44(18)
O(18B)-S(1B)-N(4B)	106.75(19)
O(17B)-S(1B)-C(19B)	107.8(2)
O(18B)-S(1B)-C(19B)	107.9(2)
N(4B)-S(1B)-C(19B)	106.76(18)
O(26')-S(2B)-O(27B)	91.5(4)
O(26')-S(2B)-O(27')	118.6(4)
O(27B)-S(2B)-O(27')	28.3(4)
O(26')-S(2B)-O(26B)	25.4(3)
O(27B)-S(2B)-O(26B)	116.7(4)
O(27')-S(2B)-O(26B)	144.0(4)
O(26')-S(2B)-N(13B)	112.5(4)
O(27B)-S(2B)-N(13B)	123.7(5)
O(27')-S(2B)-N(13B)	102.2(3)
O(26B)-S(2B)-N(13B)	98.0(4)
O(26')-S(2B)-C(28B)	115.7(4)
O(27B)-S(2B)-C(28B)	110.3(4)
O(27')-S(2B)-C(28B)	102.2(3)
O(26B)-S(2B)-C(28B)	101.5(4)
N(13B)-S(2B)-C(28B)	103.70(18)
C(2B)#3-N(1B)-C(2B)	112.2(2)
C(2B)#3-N(1B)-C(2B)#4	112.2(2)
C(2B)-N(1B)-C(2B)#4	112.2(2)
N(1B)-C(2B)-C(3B)	110.5(3)
N(4B)-C(3B)-C(2B)	112.8(3)
C(3B)-N(4B)-C(5B)	115.3(3)
C(3B)-N(4B)-S(1B)	117.7(3)
C(5B)-N(4B)-S(1B)	117.9(3)
N(4B)-C(5B)-C(6B)	110.4(3)
C(8B)-C(6B)-C(7B)	118.7(4)
C(8B)-C(6B)-C(5B)	121.6(4)
C(7B)-C(6B)-C(5B)	119.6(4)
C(11B)-C(7B)-C(6B)	121.5(4)
C(9B)-C(8B)-C(6B)	120.6(4)
C(10B)-C(9B)-C(8B)	120.0(4)
C(9B)-C(10B)-C(11B)	120.7(4)
C(7B)-C(11B)-C(10B)	118.5(4)
C(7B)-C(11B)-C(12B)	120.8(3)
C(10B)-C(11B)-C(12B)	120.7(3)
N(13B)-C(12B)-C(11B)	111.8(3)
C(12B)-N(13B)-C(14B)	118.1(4)
C(12B)-N(13B)-C(14')	114.4(4)
C(14B)-N(13B)-C(14')	39.2(4)
C(12B)-N(13B)-S(2B)	117.5(2)
C(14B)-N(13B)-S(2B)	123.3(3)
C(14')-N(13B)-S(2B)	105.6(4)
C(15B)-C(14B)-N(13B)	110.7(4)
N(16B)-C(15B)-C(14B)	108.3(4)
C(15')-C(14')-N(13B)	109.7(5)
N(16B)-C(15')-C(14')	109.3(5)
C(15')-N(16B)-C(15')#3	110.2(4)
C(15')-N(16B)-C(15')#4	110.2(4)
C(15')#3-N(16B)-C(15')#4	110.2(4)
C(15B)#3-N(16B)-C(15B)	107.3(4)
C(15B)#3-N(16B)-C(15B)#4	107.3(4)
C(15B)-N(16B)-C(15B)#4	107.3(4)
C(20B)-C(19B)-C(24B)	119.6(4)
C(20B)-C(19B)-S(1B)	120.3(3)
C(24B)-C(19B)-S(1B)	120.2(3)
C(19B)-C(20B)-C(21B)	119.4(5)
C(22B)-C(21B)-C(20B)	121.8(5)
C(23B)-C(22B)-C(21B)	117.5(5)
C(23B)-C(22B)-C(25B)	121.4(5)

C(21B)-C(22B)-C(25B)	121.1(5)
C(22B)-C(23B)-C(24B)	122.3(5)
C(23B)-C(24B)-C(19B)	119.4(4)
C(33B)-C(28B)-C(29B)	118.9(4)
C(33B)-C(28B)-S(2B)	120.9(3)
C(29B)-C(28B)-S(2B)	120.1(3)
C(30B)-C(29B)-C(28B)	119.3(4)
C(29B)-C(30B)-C(31B)	121.4(4)
C(32B)-C(31B)-C(30B)	117.6(4)
C(32B)-C(31B)-C(34B)	122.5(5)
C(30B)-C(31B)-C(34B)	119.9(5)
C(31B)-C(32B)-C(33B)	121.9(4)
C(28B)-C(33B)-C(32B)	120.9(4)
Cl(1S)-C(1S)-Cl(1S)#3	111.6(4)
Cl(1S)-C(1S)-Cl(1S)#4	111.6(4)
Cl(1S)#3-C(1S)-Cl(1S)#4	111.6(4)
N(1T)-C(2T)-C(3T)	161(2)
N(1U)-C(2U)-C(3U)	166(2)
N(1V)-C(2V)-C(3V)	160.5
N(1W)-C(2W)-C(3W)	163.0(18)
N(1X)-C(2X)-C(3X)	167(3)

Symmetry transformations used to generate equivalent atoms:
#1 -y+1, x-y, z #2 -x+y+1, -x+1, z #3 -y+1, x-y-1, z
#4 -x+y+2, -x+1, z

Table A-4. Anisotropic displacement parameters ($Å^2$x 10^3) for **Ts₆12**. The anisotropic displacement factor exponent takes the form: $-2 \pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1A)	80(1)	76(1)	71(1)	-9(1)	-3(1)	47(1)
S(2A)	96(1)	73(1)	54(1)	1(1)	3(1)	56(1)
N(1A)	53(2)	53(2)	64(3)	0	0	27(1)
C(2A)	60(2)	60(2)	64(2)	1(2)	-5(2)	33(2)
C(3A)	63(2)	56(2)	57(2)	4(2)	7(2)	28(2)
N(4A)	68(2)	53(2)	61(2)	-1(2)	9(2)	31(2)
C(5A)	75(3)	56(2)	64(3)	-5(2)	0(2)	23(2)
C(6A)	56(2)	45(2)	63(3)	-4(2)	0(2)	15(2)
C(7A)	56(2)	49(2)	58(2)	-4(2)	2(2)	23(2)
C(8A)	66(3)	81(3)	69(3)	-1(2)	-5(2)	29(2)
C(9A)	68(3)	97(3)	100(4)	1(3)	-3(3)	47(3)
C(10A)	56(2)	69(3)	89(3)	-3(2)	14(2)	26(2)
C(11A)	56(2)	42(2)	62(3)	-1(2)	6(2)	16(2)
C(12A)	77(3)	52(2)	66(3)	0(2)	12(2)	23(2)
N(13A)	69(2)	45(2)	59(2)	3(1)	2(2)	28(2)
C(14A)	60(2)	51(2)	59(2)	-1(2)	-1(2)	25(2)
C(15A)	51(2)	54(2)	70(3)	0(2)	1(2)	26(2)
N(16A)	45(2)	45(2)	75(4)	0	0	22(1)
O(17A)	67(2)	98(2)	92(2)	-30(2)	-10(2)	41(2)
O(18A)	141(3)	99(2)	92(2)	6(2)	-2(2)	87(2)
C(19A)	67(2)	62(2)	68(3)	-13(2)	3(2)	34(2)
C(20A)	80(3)	65(3)	81(3)	-12(2)	12(2)	22(2)
C(21A)	94(3)	75(3)	83(3)	-8(3)	22(3)	26(3)
C(22A)	91(3)	87(3)	70(3)	-14(3)	9(3)	44(3)
C(23A)	110(4)	74(3)	83(3)	-25(3)	-3(3)	39(3)
C(24A)	90(3)	56(3)	93(3)	-1(2)	15(3)	30(2)
C(25A)	130(5)	136(5)	87(4)	-28(3)	3(3)	54(4)
O(26A)	117(2)	75(2)	90(2)	30(2)	36(2)	64(2)
O(27A)	133(2)	118(2)	63(2)	-23(2)	-19(2)	89(2)
C(28A)	79(3)	59(2)	62(3)	1(2)	-6(2)	39(2)
C(29A)	72(3)	84(3)	78(3)	-13(2)	-2(2)	39(2)
C(30A)	78(3)	102(4)	85(3)	2(3)	14(3)	44(3)
C(31A)	81(3)	96(3)	109(4)	35(3)	17(3)	49(3)

C(32A)	77(3)	98(4)	98(4)	17(3)	-10(3)	33(3)
C(33A)	99(3)	84(3)	70(3)	2(2)	-10(3)	46(3)
C(34A)	79(4)	169(6)	148(5)	38(4)	21(4)	55(4)
S(1B)	76(1)	77(1)	71(1)	-11(1)	1(1)	38(1)
S(2B)	75(1)	98(1)	61(1)	13(1)	-2(1)	46(1)
N(1B)	61(2)	61(2)	75(4)	0	0	31(1)
C(2B)	70(3)	68(3)	75(3)	-3(2)	-5(2)	37(2)
C(3B)	72(3)	70(3)	62(3)	2(2)	3(2)	33(2)
N(4B)	77(2)	60(2)	63(2)	-1(2)	11(2)	32(2)
C(5B)	83(3)	65(3)	63(3)	-9(2)	1(2)	31(2)
C(6B)	64(2)	55(2)	57(2)	-3(2)	-1(2)	24(2)
C(7B)	56(2)	62(2)	66(3)	-1(2)	-1(2)	32(2)
C(8B)	64(3)	72(3)	64(3)	1(2)	-10(2)	23(2)
C(9B)	60(2)	90(3)	74(3)	2(2)	-10(2)	37(2)
C(10B)	59(2)	73(3)	73(3)	-1(2)	4(2)	31(2)
C(11B)	54(2)	48(2)	56(2)	3(2)	2(2)	21(2)
C(12B)	62(2)	64(2)	60(2)	5(2)	2(2)	25(2)
N(13B)	65(2)	49(2)	70(2)	-4(2)	-13(2)	28(2)
C(14B)	62(5)	64(5)	65(5)	0(4)	1(4)	23(4)
C(15B)	79(5)	80(6)	99(7)	1(5)	-1(5)	50(5)
C(14')	67(6)	50(6)	52(6)	-1(5)	8(5)	26(5)
C(15')	79(7)	55(6)	83(8)	-11(5)	-26(6)	42(5)
N(16B)	47(2)	47(2)	120(5)	0	0	24(1)
O(17B)	72(2)	85(2)	111(2)	-36(2)	-2(2)	27(2)
O(18B)	121(2)	117(2)	85(2)	5(2)	-8(2)	80(2)
C(19B)	65(2)	63(3)	72(3)	0(2)	11(2)	29(2)
C(20B)	117(4)	69(3)	88(4)	-1(3)	20(3)	37(3)
C(21B)	134(4)	102(4)	71(3)	8(3)	29(3)	50(4)
C(22B)	71(3)	111(4)	73(3)	-20(3)	5(2)	34(3)
C(23B)	84(3)	80(3)	94(4)	-29(3)	8(3)	20(3)
C(24B)	87(3)	61(3)	85(3)	-7(2)	14(3)	25(2)
C(25B)	114(4)	201(6)	81(4)	-38(4)	-3(3)	68(4)
O(26B)	85(4)	61(4)	123(7)	76(4)	24(5)	36(3)
O(27B)	87(4)	140(5)	45(3)	40(3)	0(3)	48(4)
O(26')	95(4)	85(3)	121(6)	89(3)	18(4)	37(3)
O(27')	96(4)	171(6)	34(3)	15(3)	-4(3)	72(4)
C(28B)	68(2)	61(2)	61(3)	-5(2)	-7(2)	35(2)
C(29B)	68(3)	83(3)	75(3)	-23(2)	-10(2)	30(2)
C(30B)	84(3)	116(4)	69(3)	-14(3)	4(3)	48(3)
C(31B)	67(3)	93(3)	82(3)	4(3)	-2(3)	34(3)
C(32B)	73(3)	114(4)	73(3)	-18(3)	-17(3)	26(3)
C(33B)	78(3)	108(4)	57(3)	-18(2)	-9(2)	36(3)
C(34B)	78(4)	167(6)	113(4)	25(4)	9(3)	40(4)
Cl(1S)	166(5)	163(4)	125(4)	-36(3)	-42(3)	79(4)
C(1S)	53(6)	53(6)	55(11)	0	0	26(3)

N(1T)	113(4)	118(4)	118(4)	4(4)	9(4)	41(4)
C(2T)	108(3)	114(3)	116(3)	3(3)	5(3)	45(3)
C(3T)	107(5)	114(5)	115(5)	2(5)	4(5)	44(5)
N(1U)	108(4)	114(4)	116(4)	3(4)	1(4)	45(4)
C(2U)	108(3)	112(3)	115(3)	1(3)	6(3)	47(3)
C(3U)	97(5)	99(5)	101(5)	-4(4)	10(4)	55(4)
N(1V)	114(4)	120(4)	119(4)	11(4)	7(4)	44(3)
C(2V)	114(5)	134(6)	137(6)	2(5)	13(5)	44(5)
C(3V)	120(8)	162(8)	149(9)	8(8)	23(8)	47(7)
N(1W)	106(4)	112(4)	113(4)	3(4)	2(4)	46(4)
C(2W)	111(3)	115(3)	116(3)	3(3)	6(3)	44(3)
C(3W)	112(5)	122(5)	127(5)	8(5)	10(5)	46(4)

Table A-5. Hydrogen coordinates and isotropic displacement parameters for **Ts$_6$12**.

	x	y	z	U(eq)
H(2AA)	0.6532	0.2538	0.5086	0.072
H(2AB)	0.7279	0.2932	0.4983	0.072
H(3AA)	0.6043	0.2075	0.4755	0.071
H(3AB)	0.6814	0.2400	0.4671	0.071
H(5AA)	0.5913	0.0510	0.4885	0.083
H(5AB)	0.5566	0.0847	0.4750	0.083
H(7A)	0.6081	0.0857	0.5261	0.067
H(8A)	0.4738	0.1097	0.4911	0.091
H(9A)	0.4212	0.1229	0.5195	0.103
H(10A)	0.4629	0.1199	0.5518	0.089
H(12A)	0.5441	0.1117	0.5736	0.083
H(12B)	0.5604	0.0534	0.5660	0.083
H(14A)	0.6548	0.2276	0.5457	0.069
H(14B)	0.7204	0.2516	0.5599	0.069
H(15A)	0.5909	0.2344	0.5737	0.070
H(15B)	0.6584	0.2612	0.5875	0.070
H(20A)	0.7900	0.2345	0.4443	0.098
H(21A)	0.7806	0.2177	0.4095	0.109
H(23A)	0.6344	0.0180	0.4173	0.111
H(24A)	0.6417	0.0330	0.4525	0.099
H(25A)	0.7050	0.0640	0.3840	0.185
H(25B)	0.7385	0.1452	0.3806	0.185
H(25C)	0.6566	0.0975	0.3826	0.185
H(29A)	0.7285	0.1166	0.5413	0.094
H(30A)	0.8316	0.1413	0.5255	0.106
H(32A)	0.9378	0.2390	0.5763	0.115

H(33A)	0.8348	0.2164	0.5916	0.101
H(34A)	1.0040	0.2382	0.5479	0.202
H(34B)	0.9708	0.2368	0.5266	0.202
H(34C)	0.9648	0.1677	0.5355	0.202
H(2BA)	0.9258	0.0237	0.3751	0.084
H(2BB)	0.9982	0.0706	0.3641	0.084
H(3BA)	0.9688	0.0852	0.4053	0.082
H(3BB)	1.0453	0.1266	0.3964	0.082
H(5BA)	1.0710	0.2450	0.3976	0.087
H(5BB)	1.0316	0.2678	0.3820	0.087
H(7B)	1.0339	0.2360	0.3446	0.072
H(8B)	1.1692	0.2358	0.3853	0.086
H(9B)	1.2369	0.2317	0.3592	0.090
H(10B)	1.2028	0.2287	0.3259	0.083
H(12C)	1.1007	0.2791	0.3063	0.078
H(12D)	1.1228	0.2232	0.3008	0.078
H(14C)	1.0081	0.1056	0.3271	0.081
H(14D)	0.9424	0.0785	0.3127	0.081
H(15C)	1.0055	0.0666	0.2858	0.098
H(15D)	1.0737	0.0979	0.2994	0.098
H(14E)	0.9598	0.0824	0.2930	0.069
H(14F)	1.0398	0.1181	0.2870	0.069
H(15E)	1.0681	0.0957	0.3192	0.082
H(15F)	0.9905	0.0671	0.3268	0.082
H(20B)	0.8726	0.0841	0.4299	0.115
H(21B)	0.8883	0.1178	0.4638	0.128
H(23B)	0.9754	0.3170	0.4475	0.115
H(24B)	0.9615	0.2860	0.4137	0.100
H(25D)	0.9084	0.2090	0.4895	0.205
H(25E)	0.9519	0.2883	0.4830	0.205
H(25F)	0.9900	0.2448	0.4863	0.205
H(29B)	0.9183	0.1990	0.3308	0.095
H(30B)	0.8057	0.1495	0.3440	0.108
H(32B)	0.7269	0.0559	0.2908	0.115
H(33B)	0.8377	0.1070	0.2772	0.103
H(34D)	0.6481	0.0335	0.3179	0.193
H(34E)	0.6724	0.0988	0.3323	0.193
H(34F)	0.6800	0.0347	0.3394	0.193
H(1S)	1.0000	0.0000	0.4223	0.064
H(3TA)	0.8902	0.3321	0.4413	0.175
H(3TB)	0.8454	0.3687	0.4451	0.175
H(3TC)	0.9273	0.4112	0.4480	0.175
H(3UA)	0.7484	0.3931	0.4278	0.144
H(3UB)	0.7440	0.3217	0.4336	0.144
H(3UC)	0.7474	0.3429	0.4106	0.144

H(3VA)	0.7935	0.3575	0.3553	0.232
H(3VB)	0.7309	0.2982	0.3678	0.232
H(3VC)	0.7934	0.2878	0.3608	0.232
H(3WA)	0.8570	0.4345	0.3882	0.189
H(3WB)	0.7873	0.3741	0.3978	0.189
H(3WC)	0.8441	0.3574	0.3892	0.189
H(3XA)	0.8053	0.3502	0.4101	0.163
H(3XB)	0.8113	0.3666	0.4335	0.163
H(3XC)	0.8247	0.4256	0.4177	0.163

Table A-6. Torsion angles [°] for **Ts$_6$12**.

C(2A)#1-N(1A)-C(2A)-C(3A)	-139.7(4)
C(2A)#2-N(1A)-C(2A)-C(3A)	87.3(5)
N(1A)-C(2A)-C(3A)-N(4A)	-172.0(3)
C(2A)-C(3A)-N(4A)-C(5A)	113.3(3)
C(2A)-C(3A)-N(4A)-S(1A)	-95.8(3)
O(17A)-S(1A)-N(4A)-C(5A)	-166.9(3)
O(18A)-S(1A)-N(4A)-C(5A)	-37.8(3)
C(19A)-S(1A)-N(4A)-C(5A)	78.4(3)
O(17A)-S(1A)-N(4A)-C(3A)	42.9(3)
O(18A)-S(1A)-N(4A)-C(3A)	172.0(3)
C(19A)-S(1A)-N(4A)-C(3A)	-71.8(3)
C(3A)-N(4A)-C(5A)-C(6A)	-70.6(4)
S(1A)-N(4A)-C(5A)-C(6A)	138.9(3)
N(4A)-C(5A)-C(6A)-C(8A)	105.5(4)
N(4A)-C(5A)-C(6A)-C(7A)	-70.1(4)
C(8A)-C(6A)-C(7A)-C(11A)	-0.1(5)
C(5A)-C(6A)-C(7A)-C(11A)	175.6(3)
C(7A)-C(6A)-C(8A)-C(9A)	-0.5(6)
C(5A)-C(6A)-C(8A)-C(9A)	-176.1(4)
C(6A)-C(8A)-C(9A)-C(10A)	0.9(7)
C(8A)-C(9A)-C(10A)-C(11A)	-0.7(6)
C(6A)-C(7A)-C(11A)-C(10A)	0.4(5)
C(6A)-C(7A)-C(11A)-C(12A)	-179.2(3)
C(9A)-C(10A)-C(11A)-C(7A)	0.0(6)
C(9A)-C(10A)-C(11A)-C(12A)	179.6(4)
C(7A)-C(11A)-C(12A)-N(13A)	54.2(4)
C(10A)-C(11A)-C(12A)-N(13A)	-125.3(4)
C(11A)-C(12A)-N(13A)-C(14A)	55.0(4)
C(11A)-C(12A)-N(13A)-S(2A)	-155.6(3)
O(27A)-S(2A)-N(13A)-C(14A)	46.0(3)

O(26A)-S(2A)-N(13A)-C(14A)	176.1(2)
C(28A)-S(2A)-N(13A)-C(14A)	-68.7(3)
O(27A)-S(2A)-N(13A)-C(12A)	-103.8(3)
O(26A)-S(2A)-N(13A)-C(12A)	26.3(3)
C(28A)-S(2A)-N(13A)-C(12A)	141.5(3)
C(12A)-N(13A)-C(14A)-C(15A)	63.4(4)
S(2A)-N(13A)-C(14A)-C(15A)	-86.6(3)
N(13A)-C(14A)-C(15A)-N(16A)	-177.8(3)
C(14A)-C(15A)-N(16A)-C(15A)#1	-80.9(5)
C(14A)-C(15A)-N(16A)-C(15A)#2	154.5(3)
O(17A)-S(1A)-C(19A)-C(24A)	170.4(3)
O(18A)-S(1A)-C(19A)-C(24A)	39.3(4)
N(4A)-S(1A)-C(19A)-C(24A)	-75.9(4)
O(17A)-S(1A)-C(19A)-C(20A)	-11.3(4)
O(18A)-S(1A)-C(19A)-C(20A)	-142.4(4)
N(4A)-S(1A)-C(19A)-C(20A)	102.4(4)
C(24A)-C(19A)-C(20A)-C(21A)	0.6(7)
S(1A)-C(19A)-C(20A)-C(21A)	-177.8(4)
C(19A)-C(20A)-C(21A)-C(22A)	-0.7(7)
C(20A)-C(21A)-C(22A)-C(23A)	0.6(8)
C(20A)-C(21A)-C(22A)-C(25A)	-179.6(5)
C(21A)-C(22A)-C(23A)-C(24A)	-0.3(8)
C(25A)-C(22A)-C(23A)-C(24A)	179.9(5)
C(20A)-C(19A)-C(24A)-C(23A)	-0.3(7)
S(1A)-C(19A)-C(24A)-C(23A)	178.0(4)
C(22A)-C(23A)-C(24A)-C(19A)	0.2(7)
O(27A)-S(2A)-C(28A)-C(33A)	19.9(4)
O(26A)-S(2A)-C(28A)-C(33A)	-108.2(4)
N(13A)-S(2A)-C(28A)-C(33A)	138.6(3)
O(27A)-S(2A)-C(28A)-C(29A)	-164.5(3)
O(26A)-S(2A)-C(28A)-C(29A)	67.4(4)
N(13A)-S(2A)-C(28A)-C(29A)	-45.8(4)
C(33A)-C(28A)-C(29A)-C(30A)	1.1(6)
S(2A)-C(28A)-C(29A)-C(30A)	-174.5(3)
C(28A)-C(29A)-C(30A)-C(31A)	-0.1(7)
C(29A)-C(30A)-C(31A)-C(32A)	0.0(7)
C(29A)-C(30A)-C(31A)-C(34A)	-179.7(5)
C(30A)-C(31A)-C(32A)-C(33A)	-0.9(7)
C(34A)-C(31A)-C(32A)-C(33A)	178.8(5)
C(31A)-C(32A)-C(33A)-C(28A)	1.9(7)
C(29A)-C(28A)-C(33A)-C(32A)	-2.0(6)
S(2A)-C(28A)-C(33A)-C(32A)	173.6(4)
C(2B)#3-N(1B)-C(2B)-C(3B)	144.8(4)
C(2B)#4-N(1B)-C(2B)-C(3B)	-87.7(6)
N(1B)-C(2B)-C(3B)-N(4B)	171.7(3)

C(2B)-C(3B)-N(4B)-C(5B)	-117.7(4)
C(2B)-C(3B)-N(4B)-S(1B)	95.9(4)
O(17B)-S(1B)-N(4B)-C(3B)	-39.0(3)
O(18B)-S(1B)-N(4B)-C(3B)	-168.9(3)
C(19B)-S(1B)-N(4B)-C(3B)	75.9(3)
O(17B)-S(1B)-N(4B)-C(5B)	175.4(3)
O(18B)-S(1B)-N(4B)-C(5B)	45.5(3)
C(19B)-S(1B)-N(4B)-C(5B)	-69.6(3)
C(3B)-N(4B)-C(5B)-C(6B)	67.5(4)
S(1B)-N(4B)-C(5B)-C(6B)	-146.1(3)
N(4B)-C(5B)-C(6B)-C(8B)	-104.4(4)
N(4B)-C(5B)-C(6B)-C(7B)	72.6(5)
C(8B)-C(6B)-C(7B)-C(11B)	1.0(6)
C(5B)-C(6B)-C(7B)-C(11B)	-176.2(3)
C(7B)-C(6B)-C(8B)-C(9B)	-1.1(6)
C(5B)-C(6B)-C(8B)-C(9B)	176.0(4)
C(6B)-C(8B)-C(9B)-C(10B)	0.2(6)
C(8B)-C(9B)-C(10B)-C(11B)	0.8(6)
C(6B)-C(7B)-C(11B)-C(10B)	0.0(5)
C(6B)-C(7B)-C(11B)-C(12B)	-179.4(3)
C(9B)-C(10B)-C(11B)-C(7B)	-0.9(6)
C(9B)-C(10B)-C(11B)-C(12B)	178.5(4)
C(7B)-C(11B)-C(12B)-N(13B)	-49.6(5)
C(10B)-C(11B)-C(12B)-N(13B)	131.1(4)
C(11B)-C(12B)-N(13B)-C(14B)	-50.9(5)
C(11B)-C(12B)-N(13B)-C(14')	-94.6(5)
C(11B)-C(12B)-N(13B)-S(2B)	140.7(3)
O(26')-S(2B)-N(13B)-C(12B)	-19.2(5)
O(27B)-S(2B)-N(13B)-C(12B)	88.8(5)
O(27')-S(2B)-N(13B)-C(12B)	109.1(4)
O(26B)-S(2B)-N(13B)-C(12B)	-40.9(5)
C(28B)-S(2B)-N(13B)-C(12B)	-144.9(3)
O(26')-S(2B)-N(13B)-C(14B)	173.0(5)
O(27B)-S(2B)-N(13B)-C(14B)	-78.9(6)
O(27')-S(2B)-N(13B)-C(14B)	-58.7(5)
O(26B)-S(2B)-N(13B)-C(14B)	151.3(5)
C(28B)-S(2B)-N(13B)-C(14B)	47.4(4)
O(26')-S(2B)-N(13B)-C(14')	-148.1(5)
O(27B)-S(2B)-N(13B)-C(14')	-40.1(6)
O(27')-S(2B)-N(13B)-C(14')	-19.9(5)
O(26B)-S(2B)-N(13B)-C(14')	-169.8(5)
C(28B)-S(2B)-N(13B)-C(14')	86.2(4)
C(12B)-N(13B)-C(14B)-C(15B)	-71.9(6)
C(14')-N(13B)-C(14B)-C(15B)	23.1(6)
S(2B)-N(13B)-C(14B)-C(15B)	95.8(6)

N(13B)-C(14B)-C(15B)-N(16B)	176.4(5)
C(12B)-N(13B)-C(14')-C(15')	73.6(8)
C(14B)-N(13B)-C(14')-C(15')	-31.6(6)
S(2B)-N(13B)-C(14')-C(15')	-155.6(6)
N(13B)-C(14')-C(15')-N(16B)	173.6(6)
C(14')-C(15')-N(16B)-C(15')#3	-99.6(11)
C(14')-C(15')-N(16B)-C(15')#4	138.6(8)
C(14')-C(15')-N(16B)-C(15B)#3	-56.0(10)
C(14')-C(15')-N(16B)-C(15B)	24.2(6)
C(14')-C(15')-N(16B)-C(15B)#4	96.2(9)
C(14B)-C(15B)-N(16B)-C(15')	-32.7(7)
C(14B)-C(15B)-N(16B)-C(15')#3	44.8(10)
C(14B)-C(15B)-N(16B)-C(15')#4	-118.0(7)
C(14B)-C(15B)-N(16B)-C(15B)#3	85.0(9)
C(14B)-C(15B)-N(16B)-C(15B)#4	-160.0(6)
O(17B)-S(1B)-C(19B)-C(20B)	20.6(4)
O(18B)-S(1B)-C(19B)-C(20B)	152.2(4)
N(4B)-S(1B)-C(19B)-C(20B)	-93.4(4)
O(17B)-S(1B)-C(19B)-C(24B)	-160.5(4)
O(18B)-S(1B)-C(19B)-C(24B)	-29.0(4)
N(4B)-S(1B)-C(19B)-C(24B)	85.4(4)
C(24B)-C(19B)-C(20B)-C(21B)	-1.8(7)
S(1B)-C(19B)-C(20B)-C(21B)	177.1(4)
C(19B)-C(20B)-C(21B)-C(22B)	-0.4(8)
C(20B)-C(21B)-C(22B)-C(23B)	2.7(8)
C(20B)-C(21B)-C(22B)-C(25B)	-178.6(5)
C(21B)-C(22B)-C(23B)-C(24B)	-2.9(8)
C(25B)-C(22B)-C(23B)-C(24B)	178.4(5)
C(22B)-C(23B)-C(24B)-C(19B)	0.8(8)
C(20B)-C(19B)-C(24B)-C(23B)	1.6(7)
S(1B)-C(19B)-C(24B)-C(23B)	-177.3(4)
O(26')-S(2B)-C(28B)-C(33B)	109.7(5)
O(27B)-S(2B)-C(28B)-C(33B)	7.8(6)
O(27')-S(2B)-C(28B)-C(33B)	-20.6(5)
O(26B)-S(2B)-C(28B)-C(33B)	132.1(5)
N(13B)-S(2B)-C(28B)-C(33B)	-126.6(4)
O(26')-S(2B)-C(28B)-C(29B)	-67.6(5)
O(27B)-S(2B)-C(28B)-C(29B)	-169.6(5)
O(27')-S(2B)-C(28B)-C(29B)	162.0(4)
O(26B)-S(2B)-C(28B)-C(29B)	-45.3(5)
N(13B)-S(2B)-C(28B)-C(29B)	56.0(4)
C(33B)-C(28B)-C(29B)-C(30B)	-1.6(6)
S(2B)-C(28B)-C(29B)-C(30B)	175.8(4)
C(28B)-C(29B)-C(30B)-C(31B)	2.1(7)
C(29B)-C(30B)-C(31B)-C(32B)	-1.5(8)

C(29B)-C(30B)-C(31B)-C(34B)	178.6(5)
C(30B)-C(31B)-C(32B)-C(33B)	0.5(8)
C(34B)-C(31B)-C(32B)-C(33B)	-179.6(5)
C(29B)-C(28B)-C(33B)-C(32B)	0.6(7)
S(2B)-C(28B)-C(33B)-C(32B)	-176.8(4)
C(31B)-C(32B)-C(33B)-C(28B)	0.0(8)
C(2X)#2-N(1X)-C(2X)-C(3X)	-80(17)
C(2X)#1-N(1X)-C(2X)-C(3X)	142(15)
C(2X)#1-N(1X)-C(2X)-C(2X)#2	-137(5)
C(2X)#2-N(1X)-C(2X)-C(2X)#1	137(5)

Symmetry transformations used to generate equivalent atoms:
#1 -y+1, x-y, z #2 -x+y+1, -x+1, z #3 -y+1, x-y-1, z #4 -x+y+2, -x+1, z

Structural Data for $\mathbf{Ts_6H_212(Br)_2}$

Table B-1. Crystal data and structure refinement for $\mathbf{Ts_6H_212(Br)_2}$.

Identification code	01047	
Empirical formula	$(C_{78}\ H_{92}\ N_8\ O_{12}\ S_6)^{2+}\quad 2Br^-\quad 1.87(C\ H\ Cl_3)$	
	$C_{79.87}\ H_{93.87}\ Br_2\ Cl_{5.62}\ N_8\ O_{12}\ S_6$	
Formula weight	1909.59	
Crystal system	Triclinic	
Space group	$P\ \bar{1}$	
Unit cell dimensions	a = 15.2308(10) Å	α = 96.720(2)°
	b = 16.0947(11) Å	β = 107.374(2)°
	c = 19.8831(14) Å	γ = 102.707(2)°
Volume	4449.5(5) $Å^3$	
Z	2	
Density (calculated)	1.425 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
$F(000)$	1974	
Absorption coefficient	1.282 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8933 and 0.6553	
Theta range for data collection	1.09 to 25.00°	
Reflections collected	25946	
Independent reflections	15615 [R(int) = 0.0203]	
Data / restraints / parameters	15615 / 399 / 1177	
$wR(F^2$all data)	$wR2$ = 0.2507	
$R(F$ obsd data)	$R1$ = 0.0780	
Goodness-of-fit on F^2	1.053	
Observed data [I > 2σ(I)]	12404	
Largest and mean shift / s.u.	0.012and 0.000	
Largest diff. peak and hole	1.619 and -2.120 $e/Å^3$	

$$wR2 = \{ \Sigma\ [w(F_o^2 - F_c^2)^2] / \Sigma\ [w(F_o^{\ 2})^2]\ \}^{1/2}$$

$$R1 = \Sigma\ ||F_o| - |F_c|| / \Sigma\ |F_o|$$

Table B-2. Atomic coordinates and equivalent isotropic displacement parameters for **Ts$_6$H$_2$12(Br)$_2$**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1A)	0.24743(9)	0.30172(8)	0.57621(6)	0.0196(3)
S(2A)	0.71139(8)	0.71312(8)	0.92840(6)	0.0174(3)
N(1)	0.2415(3)	0.5918(3)	0.6145(2)	0.0168(8)
C(2A)	0.2911(4)	0.5221(3)	0.6291(3)	0.0198(10)
C(3A)	0.2896(4)	0.4652(3)	0.5615(3)	0.0194(10)
N(4A)	0.3260(3)	0.3916(3)	0.5825(2)	0.0187(9)
C(5A)	0.4243(4)	0.3925(4)	0.5838(3)	0.0235(11)
C(6A)	0.4963(3)	0.4727(3)	0.6352(3)	0.0198(10)
C(7A)	0.5032(3)	0.4892(3)	0.7075(3)	0.0182(10)
C(8A)	0.5553(4)	0.5313(4)	0.6107(3)	0.0229(11)
C(9A)	0.6186(4)	0.6061(4)	0.6568(3)	0.0241(11)
C(10A)	0.6244(4)	0.6232(3)	0.7285(3)	0.0203(10)
C(11A)	0.5669(3)	0.5641(3)	0.7544(2)	0.0156(10)
C(12A)	0.5742(4)	0.5782(3)	0.8332(3)	0.0179(10)
N(13A)	0.6068(3)	0.6714(3)	0.8670(2)	0.0158(8)
C(14A)	0.5371(3)	0.7224(3)	0.8540(2)	0.0145(9)
C(15A)	0.4873(3)	0.7226(3)	0.9104(2)	0.0150(9)
N(16)	0.3950(3)	0.7474(3)	0.8828(2)	0.0124(8)
O(17A)	0.1822(3)	0.3251(2)	0.60973(19)	0.0261(8)
O(18A)	0.2999(3)	0.2421(3)	0.6032(2)	0.0307(9)
C(19A)	0.1808(4)	0.2612(3)	0.4843(3)	0.0208(10)
C(20A)	0.0837(4)	0.2534(3)	0.4601(3)	0.0283(12)
C(21A)	0.0310(5)	0.2203(4)	0.3876(3)	0.0380(15)
C(22A)	0.0749(5)	0.1979(4)	0.3394(3)	0.0440(17)
C(23A)	0.1708(6)	0.2050(5)	0.3648(4)	0.052(2)
C(24A)	0.2262(4)	0.2357(4)	0.4377(3)	0.0341(14)
C(25A)	0.0178(8)	0.1661(6)	0.2609(4)	0.076(3)
O(26A)	0.7723(3)	0.6619(3)	0.91417(19)	0.0260(8)
O(27A)	0.7351(2)	0.8048(2)	0.92928(19)	0.0241(8)
C(28A)	0.6998(4)	0.7000(3)	1.0125(3)	0.0198(10)
C(29A)	0.6780(7)	0.6192(4)	1.0276(3)	0.053(2)
C(30A)	0.6699(8)	0.6108(5)	1.0952(4)	0.071(3)
C(31A)	0.6857(5)	0.6797(5)	1.1461(3)	0.0356(14)
C(32A)	0.7079(4)	0.7620(4)	1.1300(3)	0.0298(13)
C(33A)	0.7141(4)	0.7723(4)	1.0634(3)	0.0260(12)
C(34A)	0.6804(6)	0.6714(6)	1.2200(3)	0.053(2)
S(1B)	-0.07938(9)	0.40703(8)	0.60856(7)	0.0214(3)
S(2B)	0.16537(9)	0.76658(8)	1.00667(6)	0.0199(3)

C(2B)	0.1340(3)	0.5570(3)	0.5803(3)	0.0187(10)
C(3B)	0.0945(3)	0.5040(3)	0.6284(3)	0.0193(10)
N(4B)	-0.0069(3)	0.5014(3)	0.6140(2)	0.0180(9)
C(5B)	-0.0286(4)	0.5820(3)	0.6421(3)	0.0207(10)
C(6B)	-0.0368(4)	0.5899(3)	0.7163(3)	0.0212(11)
C(7B)	0.0430(3)	0.5994(3)	0.7771(3)	0.0196(10)
C(8B)	-0.1240(4)	0.5903(4)	0.7255(3)	0.0267(12)
C(9B)	-0.1317(4)	0.5987(4)	0.7935(3)	0.0296(13)
C(10B)	-0.0530(4)	0.6060(4)	0.8533(3)	0.0268(12)
C(11B)	0.0352(3)	0.6073(3)	0.8454(3)	0.0202(10)
C(12B)	0.1223(4)	0.6159(3)	0.9106(3)	0.0215(11)
N(13B)	0.1801(3)	0.7067(3)	0.9417(2)	0.0189(9)
C(14B)	0.2421(3)	0.7495(3)	0.9043(3)	0.0175(10)
C(15B)	0.3423(3)	0.7379(3)	0.9360(3)	0.0159(10)
O(17B)	-0.0659(3)	0.3463(2)	0.5559(2)	0.0300(9)
O(18B)	-0.1720(3)	0.4226(2)	0.59604(19)	0.0247(8)
C(19B)	-0.0436(4)	0.3728(4)	0.6910(3)	0.0258(12)
C(20B)	0.0286(5)	0.3327(6)	0.7036(4)	0.059(2)
C(21B)	0.0590(7)	0.3077(9)	0.7688(6)	0.105(5)
C(22B)	0.0176(6)	0.3227(9)	0.8219(5)	0.088(4)
C(23B)	-0.0561(4)	0.3624(5)	0.8072(3)	0.0437(17)
C(24B)	-0.0890(4)	0.3867(4)	0.7412(3)	0.0274(12)
C(25B)	0.0527(8)	0.2936(13)	0.8921(7)	0.151(8)
O(26B)	0.1083(3)	0.7092(3)	1.03696(19)	0.0256(8)
O(27B)	0.2591(3)	0.8190(3)	1.05137(19)	0.0269(8)
C(28B)	0.1020(3)	0.8399(3)	0.9700(3)	0.0196(10)
C(29B)	0.0028(4)	0.8185(4)	0.9508(3)	0.0236(11)
C(30B)	-0.0452(4)	0.8767(4)	0.9225(3)	0.0258(12)
C(31B)	0.0026(4)	0.9558(4)	0.9129(3)	0.0256(11)
C(32B)	0.1025(4)	0.9760(4)	0.9327(3)	0.0277(12)
C(33B)	0.1523(4)	0.9191(4)	0.9619(3)	0.0261(12)
C(34B)	-0.0505(4)	1.0184(4)	0.8822(3)	0.0345(13)
S(1C)	0.46067(10)	0.74870(12)	0.51523(7)	0.0350(4)
S(2C)	0.40923(9)	1.05084(8)	0.88709(6)	0.0199(3)
C(2C)	0.2827(3)	0.6542(3)	0.5742(3)	0.0207(10)
C(3C)	0.3881(4)	0.6973(3)	0.6148(3)	0.0223(11)
N(4C)	0.4237(3)	0.7693(3)	0.5824(2)	0.0197(9)
C(5C)	0.4440(4)	0.8580(3)	0.6203(3)	0.0201(10)
C(6C)	0.5223(3)	0.8823(3)	0.6929(3)	0.0189(10)
C(7C)	0.5132(3)	0.9370(3)	0.7485(3)	0.0185(10)
C(8C)	0.6040(4)	0.8526(3)	0.7061(3)	0.0214(11)
C(9C)	0.6749(4)	0.8787(3)	0.7735(3)	0.0221(11)
C(10C)	0.6640(4)	0.9336(3)	0.8282(3)	0.0198(10)
C(11C)	0.5831(4)	0.9632(3)	0.8158(3)	0.0191(10)
C(12C)	0.5718(3)	1.0231(3)	0.8763(3)	0.0205(10)

N(13C)	0.4829(3)	0.9901(3)	0.8909(2)	0.0179(9)
C(14C)	0.4700(3)	0.9099(3)	0.9193(3)	0.0172(10)
C(15C)	0.4060(3)	0.8330(3)	0.8593(2)	0.0148(9)
O(17C)	0.5603(4)	0.7851(5)	0.5345(3)	0.0327(15)
O(17D)	0.5609(15)	0.8278(16)	0.5343(12)	0.020(5)
O(18C)	0.4292(3)	0.6552(3)	0.4923(2)	0.0433(12)
C(19C)	0.4015(5)	0.7956(6)	0.4487(4)	0.0267(17)
C(20C)	0.4536(6)	0.8456(6)	0.4153(5)	0.048(2)
C(21C)	0.4050(7)	0.8800(7)	0.3580(5)	0.061(3)
C(22C)	0.3064(7)	0.8636(6)	0.3352(5)	0.049(2)
C(23C)	0.2559(8)	0.8148(7)	0.3730(6)	0.049(3)
C(24C)	0.3028(6)	0.7807(5)	0.4288(5)	0.036(2)
C(25C)	0.2533(9)	0.8983(7)	0.2709(6)	0.069(3)
C(19D)	0.389(2)	0.8252(16)	0.4527(19)	0.037(5)
C(20D)	0.4216(15)	0.9120(15)	0.4542(14)	0.040(5)
C(21D)	0.3601(16)	0.9532(12)	0.4112(15)	0.042(6)
C(22D)	0.2712(16)	0.9056(14)	0.3635(15)	0.046(5)
C(23D)	0.246(2)	0.8146(16)	0.357(2)	0.043(5)
C(24D)	0.300(2)	0.7760(13)	0.4060(19)	0.035(5)
C(25D)	0.200(2)	0.951(2)	0.322(2)	0.071(11)
O(26C)	0.4631(3)	1.1390(2)	0.92129(19)	0.0236(8)
O(27C)	0.3369(3)	1.0068(3)	0.9130(2)	0.0286(9)
C(28C)	0.3603(4)	1.0506(4)	0.7946(3)	0.0265(12)
C(29C)	0.4030(5)	1.1142(4)	0.7648(3)	0.0323(13)
C(30C)	0.3724(5)	1.1078(4)	0.6905(3)	0.0385(15)
C(31C)	0.2996(5)	1.0364(5)	0.6456(3)	0.0424(17)
C(32C)	0.2562(5)	0.9745(5)	0.6766(3)	0.0408(15)
C(33C)	0.2859(4)	0.9797(4)	0.7509(3)	0.0333(13)
C(34C)	0.2695(7)	1.0274(6)	0.5648(3)	0.059(2)
Br(1)	0.29925(5)	0.56005(5)	0.80137(4)	0.0448(2)
Br(2)	0.21521(5)	0.75100(4)	0.70537(4)	0.0407(2)
C(1S)	0.3218(11)	0.6525(8)	0.1376(8)	0.050(4)
Cl(1S)	0.2408(8)	0.5493(10)	0.1087(9)	0.088(5)
Cl(2S)	0.4183(14)	0.6561(11)	0.1064(7)	0.072(4)
Cl(3S)	0.3608(11)	0.6832(12)	0.2313(8)	0.115(5)
C(1T)	0.3367(8)	0.6596(8)	0.1247(7)	0.053(5)
Cl(1T)	0.2479(8)	0.5609(9)	0.0964(8)	0.061(3)
Cl(2T)	0.4395(10)	0.6481(8)	0.1066(8)	0.060(3)
Cl(3T)	0.3635(9)	0.7020(9)	0.2159(8)	0.085(4)
C(1U)	0.0381(4)	0.0444(6)	0.6614(4)	0.094(5)
Cl(1U)	0.1006(4)	0.1316(3)	0.6343(3)	0.088(2)
Cl(2U)	-0.0856(4)	0.0295(5)	0.6276(4)	0.120(3)
Cl(3U)	0.0775(5)	0.0571(4)	0.7551(3)	0.117(3)
C(1V)	0.0468(7)	0.0924(4)	0.6126(4)	0.094(7)

Cl(1V)	-0.0360(5)	0.1505(3)	0.5801(3)	0.078(2)
Cl(2V)	-0.0017(6)	-0.0193(3)	0.5790(5)	0.125(4)
Cl(3V)	0.0911(7)	0.1152(6)	0.7066(4)	0.126(4)

Table B-3. Bond lengths [Å] and angles [°] for **Ts$_6$H$_2$12(Br)$_2$**.

S(1A)-O(18A)	1.431(4)	C(28A)-C(33A)	1.381(7)
S(1A)-O(17A)	1.440(4)	C(29A)-C(30A)	1.406(9)
S(1A)-N(4A)	1.626(4)	C(30A)-C(31A)	1.337(10)
S(1A)-C(19A)	1.766(5)	C(31A)-C(32A)	1.392(9)
S(2A)-O(26A)	1.435(4)	C(31A)-C(34A)	1.516(8)
S(2A)-O(27A)	1.436(4)	C(32A)-C(33A)	1.383(8)
S(2A)-N(13A)	1.629(4)	S(1B)-O(17B)	1.439(4)
S(2A)-C(28A)	1.764(5)	S(1B)-O(18B)	1.441(4)
N(1)-C(2A)	1.495(6)	S(1B)-N(4B)	1.641(4)
N(1)-C(2C)	1.501(6)	S(1B)-C(19B)	1.761(5)
N(1)-C(2B)	1.516(6)	S(2B)-O(26B)	1.435(4)
C(2A)-C(3A)	1.526(7)	S(2B)-O(27B)	1.442(4)
C(3A)-N(4A)	1.467(6)	S(2B)-N(13B)	1.619(4)
N(4A)-C(5A)	1.487(6)	S(2B)-C(28B)	1.771(5)
C(5A)-C(6A)	1.520(7)	C(2B)-C(3B)	1.520(7)
C(6A)-C(8A)	1.389(8)	C(3B)-N(4B)	1.474(6)
C(6A)-C(7A)	1.399(7)	N(4B)-C(5B)	1.494(6)
C(7A)-C(11A)	1.395(7)	C(5B)-C(6B)	1.509(7)
C(8A)-C(9A)	1.386(8)	C(6B)-C(8B)	1.396(7)
C(9A)-C(10A)	1.392(7)	C(6B)-C(7B)	1.401(7)
C(10A)-C(11A)	1.397(7)	C(7B)-C(11B)	1.391(7)
C(11A)-C(12A)	1.523(6)	C(8B)-C(9B)	1.386(8)
C(12A)-N(13A)	1.479(6)	C(9B)-C(10B)	1.385(8)
N(13A)-C(14A)	1.462(6)	C(10B)-C(11B)	1.394(7)
C(14A)-C(15A)	1.531(6)	C(11B)-C(12B)	1.520(7)
C(15A)-N(16)	1.508(6)	C(12B)-N(13B)	1.480(7)
N(16)-C(15C)	1.497(6)	N(13B)-C(14B)	1.474(6)
N(16)-C(15B)	1.509(6)	C(14B)-C(15B)	1.529(6)
C(19A)-C(20A)	1.384(8)	C(19B)-C(20B)	1.369(9)
C(19A)-C(24A)	1.386(8)	C(19B)-C(24B)	1.397(8)
C(20A)-C(21A)	1.396(8)	C(20B)-C(21B)	1.378(10)
C(21A)-C(22A)	1.380(10)	C(21B)-C(22B)	1.406(12)
C(22A)-C(23A)	1.368(11)	C(22B)-C(23B)	1.384(11)
C(22A)-C(25A)	1.505(9)	C(22B)-C(25B)	1.507(10)
C(23A)-C(24A)	1.405(9)	C(23B)-C(24B)	1.394(8)
C(28A)-C(29A)	1.361(8)	C(28B)-C(33B)	1.390(8)

C(28B)-C(29B)	1.394(7)	C(28C)-C(29C)	1.378(9)
C(29B)-C(30B)	1.382(8)	C(28C)-C(33C)	1.397(8)
C(30B)-C(31B)	1.386(8)	C(29C)-C(30C)	1.394(8)
C(31B)-C(32B)	1.403(8)	C(30C)-C(31C)	1.397(10)
C(31B)-C(34B)	1.501(8)	C(31C)-C(32C)	1.381(11)
C(32B)-C(33B)	1.384(8)	C(31C)-C(34C)	1.513(9)
S(1C)-O(17C)	1.415(6)	C(32C)-C(33C)	1.397(9)
S(1C)-O(18C)	1.447(5)	C(1S)-Cl(1S)	1.750(4)
S(1C)-N(4C)	1.623(4)	C(1S)-Cl(3S)	1.750(4)
S(1C)-O(17D)	1.67(2)	C(1S)-Cl(2S)	1.750(4)
S(1C)-C(19C)	1.719(9)	C(1T)-Cl(1T)	1.750(4)
S(1C)-C(19D)	2.096(19)	C(1T)-Cl(3T)	1.750(4)
S(2C)-O(27C)	1.437(4)	C(1T)-Cl(2T)	1.750(4)
S(2C)-O(26C)	1.442(4)	C(1U)-Cl(1U)	1.749(4)
S(2C)-N(13C)	1.635(4)	C(1U)-Cl(3U)	1.750(4)
S(2C)-C(28C)	1.764(5)	C(1U)-Cl(2U)	1.751(4)
C(2C)-C(3C)	1.522(7)	C(1V)-Cl(1V)	1.749(4)
C(3C)-N(4C)	1.470(7)	C(1V)-Cl(2V)	1.749(4)
N(4C)-C(5C)	1.455(6)	C(1V)-Cl(3V)	1.750(4)
C(5C)-C(6C)	1.514(7)	O(18A)-S(1A)-O(17A)	119.7(2)
C(6C)-C(7C)	1.391(7)	O(18A)-S(1A)-N(4A)	106.6(2)
C(6C)-C(8C)	1.394(7)	O(17A)-S(1A)-N(4A)	106.4(2)
C(7C)-C(11C)	1.387(7)	O(18A)-S(1A)-C(19A)	109.2(2)
C(8C)-C(9C)	1.394(7)	O(17A)-S(1A)-C(19A)	106.5(2)
C(9C)-C(10C)	1.394(7)	N(4A)-S(1A)-C(19A)	107.9(2)
C(10C)-C(11C)	1.383(7)	O(26A)-S(2A)-O(27A)	120.5(2)
C(11C)-C(12C)	1.527(7)	O(26A)-S(2A)-N(13A)	106.6(2)
C(12C)-N(13C)	1.467(6)	O(27A)-S(2A)-N(13A)	106.5(2)
N(13C)-C(14C)	1.467(6)	O(26A)-S(2A)-C(28A)	107.8(2)
C(14C)-C(15C)	1.528(7)	O(27A)-S(2A)-C(28A)	107.0(2)
C(19C)-C(20C)	1.369(12)	N(13A)-S(2A)-C(28A)	108.0(2)
C(19C)-C(24C)	1.393(11)	C(2A)-N(1)-C(2C)	113.9(4)
C(20C)-C(21C)	1.406(13)	C(2A)-N(1)-C(2B)	113.1(4)
C(21C)-C(22C)	1.386(14)	C(2C)-N(1)-C(2B)	111.8(4)
C(22C)-C(23C)	1.411(14)	N(1)-C(2A)-C(3A)	114.0(4)
C(22C)-C(25C)	1.531(12)	N(4A)-C(3A)-C(2A)	108.2(4)
C(23C)-C(24C)	1.372(11)	C(3A)-N(4A)-C(5A)	117.9(4)
C(19D)-C(20D)	1.370(12)	C(3A)-N(4A)-S(1A)	117.1(3)
C(19D)-C(24D)	1.393(11)	C(5A)-N(4A)-S(1A)	121.6(3)
C(20D)-C(21D)	1.407(14)	N(4A)-C(5A)-C(6A)	110.4(4)
C(21D)-C(22D)	1.387(14)	C(8A)-C(6A)-C(7A)	119.1(5)
C(22D)-C(23D)	1.412(15)	C(8A)-C(6A)-C(5A)	120.4(4)
C(22D)-C(25D)	1.531(13)	C(7A)-C(6A)-C(5A)	120.5(5)
C(23D)-C(24D)	1.373(12)	C(11A)-C(7A)-C(6A)	120.8(5)

C(9A)-C(8A)-C(6A)	120.6(5)
C(8A)-C(9A)-C(10A)	120.4(5)
C(9A)-C(10A)-C(11A)	119.8(5)
C(7A)-C(11A)-C(10A)	119.4(4)
C(7A)-C(11A)-C(12A)	119.1(4)
C(10A)-C(11A)-C(12A)	121.5(4)
N(13A)-C(12A)-C(11A)	111.9(4)
C(14A)-N(13A)-C(12A)	118.3(4)
C(14A)-N(13A)-S(2A)	119.6(3)
C(12A)-N(13A)-S(2A)	121.3(3)
N(13A)-C(14A)-C(15A)	112.1(4)
N(16)-C(15A)-C(14A)	110.6(4)
C(15C)-N(16)-C(15A)	114.1(4)
C(15C)-N(16)-C(15B)	114.4(4)
C(15A)-N(16)-C(15B)	109.6(3)
C(20A)-C(19A)-C(24A)	120.9(5)
C(20A)-C(19A)-S(1A)	119.5(4)
C(24A)-C(19A)-S(1A)	119.5(4)
C(19A)-C(20A)-C(21A)	119.4(6)
C(22A)-C(21A)-C(20A)	120.9(6)
C(23A)-C(22A)-C(21A)	118.5(6)
C(23A)-C(22A)-C(25A)	121.2(8)
C(21A)-C(22A)-C(25A)	120.2(7)
C(22A)-C(23A)-C(24A)	122.5(6)
C(19A)-C(24A)-C(23A)	117.7(6)
C(29A)-C(28A)-C(33A)	120.1(5)
C(29A)-C(28A)-S(2A)	120.3(4)
C(33A)-C(28A)-S(2A)	119.6(4)
C(28A)-C(29A)-C(30A)	119.0(6)
C(31A)-C(30A)-C(29A)	122.2(6)
C(30A)-C(31A)-C(32A)	118.2(5)
C(30A)-C(31A)-C(34A)	122.5(7)
C(32A)-C(31A)-C(34A)	119.2(6)
C(33A)-C(32A)-C(31A)	120.9(5)
C(28A)-C(33A)-C(32A)	119.5(5)
O(17B)-S(1B)-O(18B)	119.2(2)
O(17B)-S(1B)-N(4B)	106.4(2)
O(18B)-S(1B)-N(4B)	105.3(2)
O(17B)-S(1B)-C(19B)	106.8(3)
O(18B)-S(1B)-C(19B)	109.6(2)
N(4B)-S(1B)-C(19B)	109.2(2)
O(26B)-S(2B)-O(27B)	119.6(2)
O(26B)-S(2B)-N(13B)	106.7(2)
O(27B)-S(2B)-N(13B)	106.5(2)
O(26B)-S(2B)-C(28B)	109.2(2)
O(27B)-S(2B)-C(28B)	106.0(2)
N(13B)-S(2B)-C(28B)	108.3(2)
N(1)-C(2B)-C(3B)	109.5(4)
N(4B)-C(3B)-C(2B)	109.9(4)
C(3B)-N(4B)-C(5B)	117.3(4)
C(3B)-N(4B)-S(1B)	116.5(3)
C(5B)-N(4B)-S(1B)	118.5(3)
N(4B)-C(5B)-C(6B)	116.5(4)
C(8B)-C(6B)-C(7B)	118.7(5)
C(8B)-C(6B)-C(5B)	120.2(5)
C(7B)-C(6B)-C(5B)	121.0(4)
C(11B)-C(7B)-C(6B)	120.7(5)
C(9B)-C(8B)-C(6B)	120.5(5)
C(10B)-C(9B)-C(8B)	120.4(5)
C(9B)-C(10B)-C(11B)	120.0(5)
C(7B)-C(11B)-C(10B)	119.6(5)
C(7B)-C(11B)-C(12B)	119.9(4)
C(10B)-C(11B)-C(12B)	120.5(5)
N(13B)-C(12B)-C(11B)	113.6(4)
C(14B)-N(13B)-C(12B)	118.4(4)
C(14B)-N(13B)-S(2B)	117.7(3)
C(12B)-N(13B)-S(2B)	123.1(3)
N(13B)-C(14B)-C(15B)	109.4(4)
N(16)-C(15B)-C(14B)	110.5(4)
C(20B)-C(19B)-C(24B)	122.0(5)
C(20B)-C(19B)-S(1B)	118.2(5)
C(24B)-C(19B)-S(1B)	119.8(4)
C(19B)-C(20B)-C(21B)	118.7(7)
C(20B)-C(21B)-C(22B)	121.4(7)
C(23B)-C(22B)-C(21B)	118.5(6)
C(23B)-C(22B)-C(25B)	121.9(8)
C(21B)-C(22B)-C(25B)	119.5(8)
C(22B)-C(23B)-C(24B)	120.9(6)
C(23B)-C(24B)-C(19B)	118.3(5)
C(33B)-C(28B)-C(29B)	120.7(5)
C(33B)-C(28B)-S(2B)	119.3(4)
C(29B)-C(28B)-S(2B)	120.0(4)
C(30B)-C(29B)-C(28B)	119.0(5)
C(29B)-C(30B)-C(31B)	121.8(5)
C(30B)-C(31B)-C(32B)	118.2(5)
C(30B)-C(31B)-C(34B)	121.1(5)
C(32B)-C(31B)-C(34B)	120.7(5)
C(33B)-C(32B)-C(31B)	121.1(5)

C(32B)-C(33B)-C(28B)	119.2(5)
O(17C)-S(1C)-O(18C)	114.8(4)
O(17C)-S(1C)-N(4C)	111.3(3)
O(18C)-S(1C)-N(4C)	105.4(3)
O(17C)-S(1C)-O(17D)	24.0(8)
O(18C)-S(1C)-O(17D)	137.7(9)
N(4C)-S(1C)-O(17D)	103.7(9)
O(17C)-S(1C)-C(19C)	109.4(4)
O(18C)-S(1C)-C(19C)	109.3(3)
N(4C)-S(1C)-C(19C)	106.2(3)
O(17D)-S(1C)-C(19C)	91.0(8)
O(17C)-S(1C)-C(19D)	108.9(9)
O(18C)-S(1C)-C(19D)	119.1(8)
N(4C)-S(1C)-C(19D)	95.5(13)
O(17D)-S(1C)-C(19D)	87.7(11)
C(19C)-S(1C)-C(19D)	12.4(12)
O(27C)-S(2C)-O(26C)	119.5(2)
O(27C)-S(2C)-N(13C)	106.0(2)
O(26C)-S(2C)-N(13C)	109.1(2)
O(27C)-S(2C)-C(28C)	110.4(3)
O(26C)-S(2C)-C(28C)	106.6(2)
N(13C)-S(2C)-C(28C)	104.2(2)
N(1)-C(2C)-C(3C)	110.8(4)
N(4C)-C(3C)-C(2C)	110.5(4)
C(5C)-N(4C)-C(3C)	118.7(4)
C(5C)-N(4C)-S(1C)	120.9(4)
C(3C)-N(4C)-S(1C)	119.0(3)
N(4C)-C(5C)-C(6C)	115.2(4)
C(7C)-C(6C)-C(8C)	118.5(5)
C(7C)-C(6C)-C(5C)	119.0(4)
C(8C)-C(6C)-C(5C)	122.5(5)
C(11C)-C(7C)-C(6C)	122.0(5)
C(6C)-C(8C)-C(9C)	120.1(5)
C(8C)-C(9C)-C(10C)	120.2(5)
C(11C)-C(10C)-C(9C)	120.2(5)
C(10C)-C(11C)-C(7C)	119.0(5)
C(10C)-C(11C)-C(12C)	119.7(4)
C(7C)-C(11C)-C(12C)	121.3(4)
N(13C)-C(12C)-C(11C)	113.1(4)
C(14C)-N(13C)-C(12C)	118.7(4)
C(14C)-N(13C)-S(2C)	121.5(3)
C(12C)-N(13C)-S(2C)	119.1(3)
N(13C)-C(14C)-C(15C)	110.4(4)
N(16)-C(15C)-C(14C)	113.8(4)
C(20C)-C(19C)-C(24C)	121.7(8)
C(20C)-C(19C)-S(1C)	118.3(6)
C(24C)-C(19C)-S(1C)	119.9(6)
C(19C)-C(20C)-C(21C)	118.6(8)
C(22C)-C(21C)-C(20C)	121.1(8)
C(21C)-C(22C)-C(23C)	118.4(8)
C(21C)-C(22C)-C(25C)	120.9(8)
C(23C)-C(22C)-C(25C)	120.7(9)
C(24C)-C(23C)-C(22C)	120.8(10)
C(23C)-C(24C)-C(19C)	119.3(8)
C(20D)-C(19D)-C(24D)	121.6(9)
C(20D)-C(19D)-S(1C)	127.2(13)
C(24D)-C(19D)-S(1C)	111.2(13)
C(19D)-C(20D)-C(21D)	118.6(10)
C(22D)-C(21D)-C(20D)	120.8(9)
C(21D)-C(22D)-C(23D)	118.3(9)
C(21D)-C(22D)-C(25D)	121.0(10)
C(23D)-C(22D)-C(25D)	120.6(10)
C(24D)-C(23D)-C(22D)	120.5(13)
C(23D)-C(24D)-C(19D)	118.9(9)
C(29C)-C(28C)-C(33C)	120.5(5)
C(29C)-C(28C)-S(2C)	120.0(4)
C(33C)-C(28C)-S(2C)	119.1(5)
C(28C)-C(29C)-C(30C)	120.0(6)
C(29C)-C(30C)-C(31C)	120.5(7)
C(32C)-C(31C)-C(30C)	118.6(6)
C(32C)-C(31C)-C(34C)	120.9(7)
C(30C)-C(31C)-C(34C)	120.5(7)
C(31C)-C(32C)-C(33C)	121.7(6)
C(32C)-C(33C)-C(28C)	118.7(6)
Cl(1S)-C(1S)-Cl(3S)	110.9(4)
Cl(1S)-C(1S)-Cl(2S)	110.9(4)
Cl(3S)-C(1S)-Cl(2S)	111.2(4)
Cl(1T)-C(1T)-Cl(3T)	111.6(4)
Cl(1T)-C(1T)-Cl(2T)	110.8(4)
Cl(3T)-C(1T)-Cl(2T)	111.0(4)
Cl(1U)-C(1U)-Cl(3U)	111.1(4)
Cl(1U)-C(1U)-Cl(2U)	112.1(4)
Cl(3U)-C(1U)-Cl(2U)	110.6(4)
Cl(1V)-C(1V)-Cl(2V)	111.5(4)
Cl(1V)-C(1V)-Cl(3V)	110.9(4)
Cl(2V)-C(1V)-Cl(3V)	111.3(5)

Table B-4. Anisotropic displacement parameters ($Å^2$x 10^3) for **$Ts_6H_2$12(Br)$_2$**. The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1A)	23(1)	22(1)	15(1)	4(1)	6(1)	8(1)
S(2A)	12(1)	28(1)	13(1)	3(1)	5(1)	7(1)
N(1)	14(2)	19(2)	14(2)	-1(2)	1(2)	4(2)
C(2A)	18(2)	21(2)	18(2)	-1(2)	1(2)	9(2)
C(3A)	22(3)	23(3)	13(2)	2(2)	5(2)	8(2)
N(4A)	17(2)	19(2)	19(2)	-1(2)	4(2)	7(2)
C(5A)	19(3)	29(3)	21(3)	-5(2)	7(2)	9(2)
C(6A)	17(2)	27(3)	16(2)	0(2)	5(2)	11(2)
C(7A)	17(2)	22(2)	19(2)	4(2)	8(2)	8(2)
C(8A)	20(3)	39(3)	12(2)	4(2)	7(2)	12(2)
C(9A)	20(3)	37(3)	19(3)	6(2)	10(2)	9(2)
C(10A)	16(2)	27(3)	18(2)	2(2)	5(2)	7(2)
C(11A)	12(2)	24(2)	12(2)	0(2)	3(2)	11(2)
C(12A)	21(2)	20(2)	14(2)	2(2)	5(2)	9(2)
N(13A)	13(2)	22(2)	11(2)	-2(2)	2(2)	7(2)
C(14A)	10(2)	19(2)	15(2)	3(2)	5(2)	6(2)
C(15A)	13(2)	21(2)	14(2)	3(2)	5(2)	10(2)
N(16)	9(2)	17(2)	11(2)	0(2)	2(2)	4(2)
O(17A)	32(2)	30(2)	20(2)	3(2)	15(2)	10(2)
O(18A)	36(2)	29(2)	27(2)	10(2)	4(2)	16(2)
C(19A)	27(3)	14(2)	17(2)	-1(2)	5(2)	3(2)
C(20A)	27(3)	22(3)	30(3)	1(2)	4(2)	6(2)
C(21A)	35(3)	25(3)	37(3)	-4(3)	-7(3)	7(3)
C(22A)	50(4)	34(3)	26(3)	-5(3)	-6(3)	-2(3)
C(23A)	68(5)	47(4)	32(4)	-14(3)	29(4)	-6(4)
C(24A)	32(3)	36(3)	30(3)	-7(3)	16(3)	0(3)
C(25A)	100(7)	66(6)	28(4)	-16(4)	-5(4)	6(5)
O(26A)	19(2)	44(2)	20(2)	4(2)	7(2)	19(2)
O(27A)	19(2)	30(2)	23(2)	8(2)	7(2)	4(2)
C(28A)	19(2)	29(3)	10(2)	0(2)	3(2)	7(2)
C(29A)	111(7)	26(3)	15(3)	2(2)	22(4)	2(4)
C(30A)	138(9)	34(4)	23(3)	9(3)	26(4)	-14(4)
C(31A)	41(3)	56(4)	14(3)	9(3)	13(3)	14(3)
C(32A)	32(3)	39(3)	21(3)	0(2)	7(2)	21(3)
C(33A)	29(3)	31(3)	19(3)	2(2)	8(2)	14(2)
C(34A)	63(5)	81(6)	16(3)	14(3)	16(3)	13(4)
S(1B)	22(1)	23(1)	16(1)	4(1)	3(1)	3(1)
S(2B)	15(1)	29(1)	15(1)	-1(1)	7(1)	5(1)

C(2B)	13(2)	22(2)	17(2)	0(2)	0(2)	5(2)
C(3B)	17(2)	25(3)	14(2)	3(2)	3(2)	8(2)
N(4B)	17(2)	20(2)	16(2)	2(2)	3(2)	6(2)
C(5B)	17(2)	21(3)	22(3)	3(2)	3(2)	7(2)
C(6B)	19(3)	23(3)	22(3)	0(2)	7(2)	7(2)
C(7B)	10(2)	24(3)	23(3)	-1(2)	5(2)	5(2)
C(8B)	14(2)	31(3)	31(3)	1(2)	3(2)	8(2)
C(9B)	14(3)	36(3)	35(3)	-5(3)	9(2)	3(2)
C(10B)	19(3)	32(3)	26(3)	-5(2)	12(2)	0(2)
C(11B)	13(2)	22(3)	22(3)	-1(2)	5(2)	2(2)
C(12B)	17(2)	25(3)	20(3)	1(2)	6(2)	4(2)
N(13B)	14(2)	25(2)	18(2)	-4(2)	9(2)	4(2)
C(14B)	13(2)	22(2)	18(2)	1(2)	8(2)	5(2)
C(15B)	12(2)	23(2)	14(2)	2(2)	7(2)	7(2)
O(17B)	37(2)	25(2)	24(2)	-2(2)	11(2)	4(2)
O(18B)	18(2)	30(2)	20(2)	6(2)	1(2)	4(2)
C(19B)	20(3)	36(3)	26(3)	17(2)	10(2)	8(2)
C(20B)	50(4)	107(7)	68(5)	71(5)	47(4)	53(5)
C(21B)	75(6)	228(14)	113(8)	144(10)	80(6)	117(8)
C(22B)	44(4)	204(12)	72(6)	107(8)	42(4)	70(6)
C(23B)	24(3)	85(5)	32(3)	30(3)	15(3)	16(3)
C(24B)	20(3)	36(3)	27(3)	14(2)	8(2)	7(2)
C(25B)	84(7)	370(20)	114(9)	185(14)	82(7)	142(12)
O(26B)	24(2)	35(2)	22(2)	5(2)	14(2)	9(2)
O(27B)	17(2)	39(2)	19(2)	-6(2)	3(2)	5(2)
C(28B)	14(2)	27(3)	17(2)	-3(2)	6(2)	7(2)
C(29B)	18(3)	28(3)	22(3)	-3(2)	10(2)	0(2)
C(30B)	14(2)	34(3)	27(3)	-4(2)	9(2)	4(2)
C(31B)	20(3)	30(3)	25(3)	-3(2)	7(2)	7(2)
C(32B)	22(3)	24(3)	36(3)	1(2)	14(2)	2(2)
C(33B)	14(2)	29(3)	32(3)	-4(2)	10(2)	0(2)
C(34B)	30(3)	34(3)	40(3)	4(3)	11(3)	11(3)
S(1C)	18(1)	65(1)	19(1)	-6(1)	8(1)	8(1)
S(2C)	22(1)	21(1)	16(1)	1(1)	2(1)	11(1)
C(2C)	16(2)	22(3)	21(3)	3(2)	2(2)	5(2)
C(3C)	17(2)	22(3)	24(3)	1(2)	3(2)	4(2)
N(4C)	20(2)	26(2)	15(2)	0(2)	9(2)	7(2)
C(5C)	18(2)	21(3)	18(2)	2(2)	1(2)	6(2)
C(6C)	17(2)	19(2)	18(2)	5(2)	5(2)	1(2)
C(7C)	15(2)	19(2)	23(3)	6(2)	7(2)	5(2)
C(8C)	20(3)	23(3)	21(3)	3(2)	7(2)	6(2)
C(9C)	17(2)	28(3)	24(3)	8(2)	7(2)	7(2)
C(10C)	16(2)	25(3)	16(2)	6(2)	4(2)	3(2)
C(11C)	18(2)	19(2)	18(2)	2(2)	7(2)	3(2)
C(12C)	16(2)	22(3)	21(3)	2(2)	4(2)	3(2)

N(13C)	17(2)	21(2)	17(2)	4(2)	4(2)	10(2)
C(14C)	19(2)	15(2)	14(2)	1(2)	1(2)	6(2)
C(15C)	15(2)	17(2)	14(2)	4(2)	5(2)	6(2)
O(17C)	19(3)	49(4)	27(3)	-3(3)	11(2)	3(3)
O(17D)	10(7)	32(9)	21(7)	10(7)	11(6)	-1(7)
O(18C)	37(2)	56(3)	33(2)	-18(2)	8(2)	22(2)
C(19C)	26(3)	34(4)	15(3)	3(3)	7(3)	0(3)
C(20C)	41(4)	65(5)	36(4)	18(4)	15(3)	2(4)
C(21C)	60(5)	73(6)	48(5)	31(5)	22(4)	-1(5)
C(22C)	55(5)	40(4)	37(4)	20(3)	5(4)	-5(4)
C(23C)	43(4)	42(4)	44(6)	24(4)	-1(4)	-6(3)
C(24C)	31(4)	36(4)	38(5)	20(3)	5(3)	0(3)
C(25C)	82(8)	60(6)	50(6)	36(5)	1(5)	6(6)
C(19D)	33(7)	45(7)	29(7)	16(7)	7(6)	-1(7)
C(20D)	35(9)	47(9)	34(8)	19(8)	11(7)	-2(8)
C(21D)	40(10)	37(10)	40(10)	24(9)	8(9)	-9(9)
C(22D)	45(8)	40(8)	41(8)	26(7)	3(7)	-4(7)
C(23D)	41(7)	40(7)	36(8)	27(7)	-2(7)	-1(7)
C(24D)	32(7)	39(7)	28(8)	19(7)	6(7)	-2(6)
C(25D)	70(20)	56(19)	70(20)	38(17)	-1(18)	-1(17)
O(26C)	31(2)	19(2)	17(2)	-2(1)	2(2)	10(2)
O(27C)	26(2)	32(2)	32(2)	5(2)	13(2)	13(2)
C(28C)	31(3)	29(3)	16(3)	1(2)	-2(2)	17(2)
C(29C)	51(4)	24(3)	20(3)	1(2)	3(3)	20(3)
C(30C)	59(4)	34(3)	26(3)	8(3)	9(3)	28(3)
C(31C)	58(4)	45(4)	23(3)	1(3)	0(3)	33(3)
C(32C)	37(3)	44(4)	32(3)	1(3)	-4(3)	17(3)
C(33C)	27(3)	35(3)	30(3)	-1(3)	-3(2)	12(3)
C(34C)	91(6)	64(5)	20(3)	7(3)	1(4)	44(5)
Br(1)	40(1)	49(1)	39(1)	-3(1)	9(1)	11(1)
Br(2)	39(1)	39(1)	37(1)	-3(1)	9(1)	9(1)
C(1S)	53(8)	37(7)	59(8)	16(6)	12(7)	15(6)
Cl(1S)	47(4)	41(4)	195(12)	41(5)	55(6)	21(3)
Cl(2S)	43(5)	101(7)	68(4)	47(4)	11(3)	5(4)
Cl(3S)	131(8)	180(11)	64(5)	34(6)	29(5)	103(9)
C(1T)	54(9)	38(7)	54(8)	19(7)	0(7)	8(7)
Cl(1T)	34(4)	31(3)	104(6)	19(4)	3(4)	5(2)
Cl(2T)	39(5)	45(4)	90(5)	25(3)	10(3)	14(3)
Cl(3T)	93(5)	95(6)	52(5)	5(4)	16(4)	12(6)
C(1U)	92(11)	57(9)	145(13)	28(9)	69(10)	2(8)
Cl(1U)	106(4)	63(3)	129(5)	24(3)	90(4)	17(3)
Cl(2U)	77(4)	140(6)	136(6)	66(5)	20(4)	15(4)
Cl(3U)	136(6)	97(5)	123(5)	28(4)	61(5)	10(4)
C(1V)	91(13)	44(11)	149(15)	24(11)	60(12)	-8(10)
Cl(1V)	98(5)	58(3)	83(4)	22(3)	28(4)	30(3)

Cl(2V)	84(5)	44(3)	220(11)	10(5)	14(6)	23(3)
Cl(3V)	117(7)	137(7)	100(6)	18(5)	-11(5)	51(6)

Table B-5. Hydrogen coordinates and isotropic displacement parameters for **Ts$_6$H$_2$12(Br)$_2$**.

	x	y	z	U(eq)
H(1)	0.2466	0.6221	0.6499	0.020
H(2AA)	0.2604	0.4847	0.6564	0.024
H(2AB)	0.3583	0.5494	0.6597	0.024
H(3AA)	0.2236	0.4439	0.5270	0.023
H(3AB)	0.3302	0.4992	0.5381	0.023
H(5AA)	0.4278	0.3923	0.5349	0.028
H(5AB)	0.4399	0.3397	0.5992	0.028
H(7A)	0.4640	0.4488	0.7249	0.022
H(8A)	0.5522	0.5201	0.5620	0.028
H(9A)	0.6583	0.6459	0.6394	0.029
H(10A)	0.6673	0.6749	0.7597	0.024
H(12A)	0.5109	0.5526	0.8369	0.021
H(12B)	0.6195	0.5479	0.8594	0.021
H(14A)	0.4885	0.6982	0.8058	0.017
H(14B)	0.5698	0.7830	0.8543	0.017
H(15A)	0.4740	0.6642	0.9224	0.018
H(15B)	0.5299	0.7644	0.9548	0.018
H(16)	0.3524	0.7077	0.8434	0.015
H(20A)	0.0532	0.2704	0.4926	0.034
H(21A)	-0.0361	0.2130	0.3712	0.046
H(23A)	0.2010	0.1884	0.3319	0.062
H(24A)	0.2924	0.2390	0.4544	0.041
H(25A)	-0.0394	0.1874	0.2495	0.114
H(25B)	-0.0012	0.1024	0.2497	0.114
H(25C)	0.0569	0.1880	0.2322	0.114
H(29A)	0.6684	0.5692	0.9929	0.064
H(30A)	0.6526	0.5543	1.1051	0.085
H(32A)	0.7190	0.8118	1.1654	0.036
H(33A)	0.7281	0.8287	1.0526	0.031
H(34A)	0.6948	0.6172	1.2314	0.080
H(34B)	0.6160	0.6704	1.2205	0.080
H(34C)	0.7269	0.7207	1.2559	0.080
H(2BA)	0.1181	0.5201	0.5326	0.022
H(2BB)	0.1047	0.6059	0.5735	0.022
H(3BA)	0.1008	0.4442	0.6191	0.023
H(3BB)	0.1314	0.5304	0.6794	0.023

H(5BA)	-0.0895	0.5857	0.6080	0.025
H(5BB)	0.0220	0.6327	0.6423	0.025
H(7B)	0.1032	0.6006	0.7718	0.024
H(8B)	-0.1785	0.5849	0.6848	0.032
H(9B)	-0.1913	0.5994	0.7992	0.036
H(10B)	-0.0590	0.6101	0.8997	0.032
H(12C)	0.1010	0.5905	0.9479	0.026
H(12D)	0.1631	0.5819	0.8966	0.026
H(14C)	0.2453	0.8121	0.9100	0.021
H(14D)	0.2155	0.7235	0.8524	0.021
H(15C)	0.3783	0.7819	0.9805	0.019
H(15D)	0.3375	0.6797	0.9485	0.019
H(20B)	0.0572	0.3222	0.6682	0.070
H(21B)	0.1090	0.2797	0.7780	0.126
H(23B)	-0.0846	0.3732	0.8427	0.052
H(24B)	-0.1410	0.4121	0.7305	0.033
H(25D)	0.1071	0.2701	0.8931	0.227
H(25E)	0.0012	0.2485	0.8969	0.227
H(25F)	0.0726	0.3432	0.9320	0.227
H(29B)	-0.0313	0.7646	0.9572	0.028
H(30B)	-0.1129	0.8620	0.9091	0.031
H(32B)	0.1365	1.0295	0.9259	0.033
H(33B)	0.2200	0.9341	0.9762	0.031
H(34D)	-0.0051	1.0719	0.8819	0.052
H(34E)	-0.0889	1.0322	0.9116	0.052
H(34F)	-0.0927	0.9918	0.8330	0.052
H(2CA)	0.2476	0.6992	0.5675	0.025
H(2CB)	0.2751	0.6227	0.5261	0.025
H(3CA)	0.3971	0.7196	0.6657	0.027
H(3CB)	0.4251	0.6540	0.6137	0.027
H(5CA)	0.3847	0.8668	0.6272	0.024
H(5CB)	0.4620	0.8982	0.5897	0.024
H(7C)	0.4575	0.9571	0.7401	0.022
H(8C)	0.6114	0.8146	0.6691	0.026
H(9C)	0.7309	0.8589	0.7821	0.027
H(10C)	0.7122	0.9506	0.8742	0.024
H(12E)	0.6267	1.0307	0.9207	0.025
H(12F)	0.5733	1.0809	0.8635	0.025
H(14E)	0.4408	0.9163	0.9573	0.021
H(14F)	0.5330	0.8990	0.9411	0.021
H(15E)	0.3420	0.8429	0.8401	0.018
H(15F)	0.4329	0.8305	0.8198	0.018
H(20C)	0.5211	0.8567	0.4305	0.058
H(21C)	0.4403	0.9152	0.3346	0.073
H(23C)	0.1887	0.8054	0.3597	0.058

H(24C)	0.2683	0.7473	0.4536	0.044
H(25G)	0.2997	0.9385	0.2566	0.104
H(25H)	0.2099	0.9286	0.2841	0.104
H(25I)	0.2165	0.8495	0.2308	0.104
H(20D)	0.4846	0.9438	0.4838	0.048
H(21D)	0.3795	1.0143	0.4148	0.050
H(23D)	0.1908	0.7797	0.3193	0.051
H(24D)	0.2763	0.7168	0.4079	0.042
H(25J)	0.1585	0.9618	0.3501	0.106
H(25K)	0.1606	0.9139	0.2756	0.106
H(25L)	0.2344	1.0064	0.3153	0.106
H(29C)	0.4533	1.1623	0.7949	0.039
H(30C)	0.4012	1.1523	0.6702	0.046
H(32C)	0.2047	0.9272	0.6465	0.049
H(33C)	0.2562	0.9359	0.7713	0.040
H(34G)	0.2092	0.9820	0.5426	0.088
H(34H)	0.3188	1.0117	0.5476	0.088
H(34I)	0.2608	1.0827	0.5519	0.088
H(1SA)	0.2879	0.6950	0.1168	0.060
H(1TA)	0.3117	0.7020	0.0966	0.063
H(1UA)	0.0520	-0.0094	0.6415	0.113
H(1VA)	0.1017	0.1119	0.5952	0.113

Table B-6. Torsion angles [°] for **Ts$_6$H$_2$12(Br)$_2$**.

C(2C)-N(1)-C(2A)-C(3A)	-59.5(5)
C(2B)-N(1)-C(2A)-C(3A)	69.6(5)
N(1)-C(2A)-C(3A)-N(4A)	-170.7(4)
C(2A)-C(3A)-N(4A)-C(5A)	-105.1(5)
C(2A)-C(3A)-N(4A)-S(1A)	95.4(4)
O(18A)-S(1A)-N(4A)-C(3A)	-176.9(3)
O(17A)-S(1A)-N(4A)-C(3A)	-48.1(4)
C(19A)-S(1A)-N(4A)-C(3A)	66.0(4)
O(18A)-S(1A)-N(4A)-C(5A)	24.4(4)
O(17A)-S(1A)-N(4A)-C(5A)	153.2(4)
C(19A)-S(1A)-N(4A)-C(5A)	-92.8(4)
C(3A)-N(4A)-C(5A)-C(6A)	58.8(6)
S(1A)-N(4A)-C(5A)-C(6A)	-142.6(4)
N(4A)-C(5A)-C(6A)-C(8A)	-121.7(5)
N(4A)-C(5A)-C(6A)-C(7A)	57.4(6)
C(8A)-C(6A)-C(7A)-C(11A)	1.2(7)
C(5A)-C(6A)-C(7A)-C(11A)	-177.9(4)
C(7A)-C(6A)-C(8A)-C(9A)	-1.4(8)

C(5A)-C(6A)-C(8A)-C(9A)	177.7(5)
C(6A)-C(8A)-C(9A)-C(10A)	0.4(8)
C(8A)-C(9A)-C(10A)-C(11A)	0.8(8)
C(6A)-C(7A)-C(11A)-C(10A)	0.0(7)
C(6A)-C(7A)-C(11A)-C(12A)	-178.3(4)
C(9A)-C(10A)-C(11A)-C(7A)	-1.0(7)
C(9A)-C(10A)-C(11A)-C(12A)	177.2(5)
C(7A)-C(11A)-C(12A)-N(13A)	-153.7(4)
C(10A)-C(11A)-C(12A)-N(13A)	28.1(6)
C(11A)-C(12A)-N(13A)-C(14A)	79.3(5)
C(11A)-C(12A)-N(13A)-S(2A)	-111.6(4)
O(26A)-S(2A)-N(13A)-C(14A)	-162.6(3)
O(27A)-S(2A)-N(13A)-C(14A)	-32.8(4)
C(28A)-S(2A)-N(13A)-C(14A)	81.8(4)
O(26A)-S(2A)-N(13A)-C(12A)	28.4(4)
O(27A)-S(2A)-N(13A)-C(12A)	158.3(4)
C(28A)-S(2A)-N(13A)-C(12A)	-87.1(4)
C(12A)-N(13A)-C(14A)-C(15A)	90.6(5)
S(2A)-N(13A)-C(14A)-C(15A)	-78.7(5)
N(13A)-C(14A)-C(15A)-N(16)	-160.2(4)
C(14A)-C(15A)-N(16)-C(15C)	-56.2(5)
C(14A)-C(15A)-N(16)-C(15B)	174.0(4)
O(18A)-S(1A)-C(19A)-C(20A)	127.1(4)
O(17A)-S(1A)-C(19A)-C(20A)	-3.4(5)
N(4A)-S(1A)-C(19A)-C(20A)	-117.4(4)
O(18A)-S(1A)-C(19A)-C(24A)	-51.4(5)
O(17A)-S(1A)-C(19A)-C(24A)	178.1(4)
N(4A)-S(1A)-C(19A)-C(24A)	64.1(5)
C(24A)-C(19A)-C(20A)-C(21A)	-0.7(8)
S(1A)-C(19A)-C(20A)-C(21A)	-179.2(4)
C(19A)-C(20A)-C(21A)-C(22A)	-2.1(9)
C(20A)-C(21A)-C(22A)-C(23A)	3.1(10)
C(20A)-C(21A)-C(22A)-C(25A)	-177.3(7)
C(21A)-C(22A)-C(23A)-C(24A)	-1.3(11)
C(25A)-C(22A)-C(23A)-C(24A)	179.0(7)
C(20A)-C(19A)-C(24A)-C(23A)	2.4(9)
S(1A)-C(19A)-C(24A)-C(23A)	-179.2(5)
C(22A)-C(23A)-C(24A)-C(19A)	-1.3(11)
O(26A)-S(2A)-C(28A)-C(29A)	-48.6(6)
O(27A)-S(2A)-C(28A)-C(29A)	-179.6(6)
N(13A)-S(2A)-C(28A)-C(29A)	66.2(6)
O(26A)-S(2A)-C(28A)-C(33A)	130.7(4)
O(27A)-S(2A)-C(28A)-C(33A)	-0.3(5)
N(13A)-S(2A)-C(28A)-C(33A)	-114.5(4)
C(33A)-C(28A)-C(29A)-C(30A)	0.3(12)

S(2A)-C(28A)-C(29A)-C(30A)	179.6(7)
C(28A)-C(29A)-C(30A)-C(31A)	-2.0(15)
C(29A)-C(30A)-C(31A)-C(32A)	2.0(14)
C(29A)-C(30A)-C(31A)-C(34A)	-177.9(9)
C(30A)-C(31A)-C(32A)-C(33A)	-0.4(10)
C(34A)-C(31A)-C(32A)-C(33A)	179.5(6)
C(29A)-C(28A)-C(33A)-C(32A)	1.3(9)
S(2A)-C(28A)-C(33A)-C(32A)	-178.0(4)
C(31A)-C(32A)-C(33A)-C(28A)	-1.2(9)
C(2A)-N(1)-C(2B)-C(3B)	57.3(5)
C(2C)-N(1)-C(2B)-C(3B)	-172.5(4)
N(1)-C(2B)-C(3B)-N(4B)	156.1(4)
C(2B)-C(3B)-N(4B)-C(5B)	-74.4(5)
C(2B)-C(3B)-N(4B)-S(1B)	136.6(4)
O(17B)-S(1B)-N(4B)-C(3B)	-53.8(4)
O(18B)-S(1B)-N(4B)-C(3B)	178.8(3)
C(19B)-S(1B)-N(4B)-C(3B)	61.2(4)
O(17B)-S(1B)-N(4B)-C(5B)	157.6(4)
O(18B)-S(1B)-N(4B)-C(5B)	30.1(4)
C(19B)-S(1B)-N(4B)-C(5B)	-87.5(4)
C(3B)-N(4B)-C(5B)-C(6B)	-91.0(5)
S(1B)-N(4B)-C(5B)-C(6B)	57.4(5)
N(4B)-C(5B)-C(6B)-C(8B)	-114.7(5)
N(4B)-C(5B)-C(6B)-C(7B)	67.2(6)
C(8B)-C(6B)-C(7B)-C(11B)	1.4(8)
C(5B)-C(6B)-C(7B)-C(11B)	179.5(5)
C(7B)-C(6B)-C(8B)-C(9B)	-1.1(8)
C(5B)-C(6B)-C(8B)-C(9B)	-179.1(5)
C(6B)-C(8B)-C(9B)-C(10B)	-0.5(9)
C(8B)-C(9B)-C(10B)-C(11B)	1.7(9)
C(6B)-C(7B)-C(11B)-C(10B)	-0.3(8)
C(6B)-C(7B)-C(11B)-C(12B)	178.9(5)
C(9B)-C(10B)-C(11B)-C(7B)	-1.3(8)
C(9B)-C(10B)-C(11B)-C(12B)	179.6(5)
C(7B)-C(11B)-C(12B)-N(13B)	88.1(6)
C(10B)-C(11B)-C(12B)-N(13B)	-92.7(6)
C(11B)-C(12B)-N(13B)-C(14B)	-76.0(5)
C(11B)-C(12B)-N(13B)-S(2B)	93.2(5)
O(26B)-S(2B)-N(13B)-C(14B)	-176.0(3)
O(27B)-S(2B)-N(13B)-C(14B)	-47.2(4)
C(28B)-S(2B)-N(13B)-C(14B)	66.5(4)
O(26B)-S(2B)-N(13B)-C(12B)	14.6(5)
O(27B)-S(2B)-N(13B)-C(12B)	143.5(4)
C(28B)-S(2B)-N(13B)-C(12B)	-102.9(4)
C(12B)-N(13B)-C(14B)-C(15B)	-93.3(5)

S(2B)-N(13B)-C(14B)-C(15B)	96.9(4)
C(15C)-N(16)-C(15B)-C(14B)	58.8(5)
C(15A)-N(16)-C(15B)-C(14B)	-171.6(4)
N(13B)-C(14B)-C(15B)-N(16)	157.4(4)
O(17B)-S(1B)-C(19B)-C(20B)	32.2(7)
O(18B)-S(1B)-C(19B)-C(20B)	162.6(6)
N(4B)-S(1B)-C(19B)-C(20B)	-82.5(6)
O(17B)-S(1B)-C(19B)-C(24B)	-147.7(5)
O(18B)-S(1B)-C(19B)-C(24B)	-17.2(6)
N(4B)-S(1B)-C(19B)-C(24B)	97.7(5)
C(24B)-C(19B)-C(20B)-C(21B)	-1.9(14)
S(1B)-C(19B)-C(20B)-C(21B)	178.2(9)
C(19B)-C(20B)-C(21B)-C(22B)	-0.1(19)
C(20B)-C(21B)-C(22B)-C(23B)	1(2)
C(20B)-C(21B)-C(22B)-C(25B)	179.5(14)
C(21B)-C(22B)-C(23B)-C(24B)	0.3(16)
C(25B)-C(22B)-C(23B)-C(24B)	-178.3(11)
C(22B)-C(23B)-C(24B)-C(19B)	-2.2(11)
C(20B)-C(19B)-C(24B)-C(23B)	3.0(10)
S(1B)-C(19B)-C(24B)-C(23B)	-177.1(5)
O(26B)-S(2B)-C(28B)-C(33B)	156.6(4)
O(27B)-S(2B)-C(28B)-C(33B)	26.4(5)
N(13B)-S(2B)-C(28B)-C(33B)	-87.6(4)
O(26B)-S(2B)-C(28B)-C(29B)	-22.3(5)
O(27B)-S(2B)-C(28B)-C(29B)	-152.5(4)
N(13B)-S(2B)-C(28B)-C(29B)	93.5(4)
C(33B)-C(28B)-C(29B)-C(30B)	1.0(8)
S(2B)-C(28B)-C(29B)-C(30B)	179.9(4)
C(28B)-C(29B)-C(30B)-C(31B)	-0.3(8)
C(29B)-C(30B)-C(31B)-C(32B)	0.3(8)
C(29B)-C(30B)-C(31B)-C(34B)	-179.8(5)
C(30B)-C(31B)-C(32B)-C(33B)	-0.9(8)
C(34B)-C(31B)-C(32B)-C(33B)	179.2(5)
C(31B)-C(32B)-C(33B)-C(28B)	1.6(8)
C(29B)-C(28B)-C(33B)-C(32B)	-1.6(8)
S(2B)-C(28B)-C(33B)-C(32B)	179.5(4)
C(2A)-N(1)-C(2C)-C(3C)	-57.8(5)
C(2B)-N(1)-C(2C)-C(3C)	172.4(4)
N(1)-C(2C)-C(3C)-N(4C)	-169.7(4)
C(2C)-C(3C)-N(4C)-C(5C)	107.3(5)
C(2C)-C(3C)-N(4C)-S(1C)	-85.8(5)
O(17C)-S(1C)-N(4C)-C(5C)	54.0(6)
O(18C)-S(1C)-N(4C)-C(5C)	179.0(4)
O(17D)-S(1C)-N(4C)-C(5C)	30.1(9)
C(19C)-S(1C)-N(4C)-C(5C)	-65.0(5)

C(19D)-S(1C)-N(4C)-C(5C)	-58.8(7)
O(17C)-S(1C)-N(4C)-C(3C)	-112.7(5)
O(18C)-S(1C)-N(4C)-C(3C)	12.3(4)
O(17D)-S(1C)-N(4C)-C(3C)	-136.6(9)
C(19C)-S(1C)-N(4C)-C(3C)	128.3(4)
C(19D)-S(1C)-N(4C)-C(3C)	134.5(7)
C(3C)-N(4C)-C(5C)-C(6C)	62.9(6)
S(1C)-N(4C)-C(5C)-C(6C)	-103.9(5)
N(4C)-C(5C)-C(6C)-C(7C)	-143.2(5)
N(4C)-C(5C)-C(6C)-C(8C)	37.5(7)
C(8C)-C(6C)-C(7C)-C(11C)	0.6(7)
C(5C)-C(6C)-C(7C)-C(11C)	-178.7(5)
C(7C)-C(6C)-C(8C)-C(9C)	-0.8(7)
C(5C)-C(6C)-C(8C)-C(9C)	178.5(5)
C(6C)-C(8C)-C(9C)-C(10C)	0.8(8)
C(8C)-C(9C)-C(10C)-C(11C)	-0.6(8)
C(9C)-C(10C)-C(11C)-C(7C)	0.5(7)
C(9C)-C(10C)-C(11C)-C(12C)	179.8(5)
C(6C)-C(7C)-C(11C)-C(10C)	-0.5(7)
C(6C)-C(7C)-C(11C)-C(12C)	-179.8(5)
C(10C)-C(11C)-C(12C)-N(13C)	-124.7(5)
C(7C)-C(11C)-C(12C)-N(13C)	54.6(6)
C(11C)-C(12C)-N(13C)-C(14C)	65.8(6)
C(11C)-C(12C)-N(13C)-S(2C)	-123.7(4)
O(27C)-S(2C)-N(13C)-C(14C)	-2.2(4)
O(26C)-S(2C)-N(13C)-C(14C)	127.7(4)
C(28C)-S(2C)-N(13C)-C(14C)	-118.7(4)
O(27C)-S(2C)-N(13C)-C(12C)	-172.4(4)
O(26C)-S(2C)-N(13C)-C(12C)	-42.4(4)
C(28C)-S(2C)-N(13C)-C(12C)	71.1(4)
C(12C)-N(13C)-C(14C)-C(15C)	-100.8(5)
S(2C)-N(13C)-C(14C)-C(15C)	88.9(4)
C(15A)-N(16)-C(15C)-C(14C)	-61.0(5)
C(15B)-N(16)-C(15C)-C(14C)	66.4(5)
N(13C)-C(14C)-C(15C)-N(16)	175.7(4)
O(17C)-S(1C)-C(19C)-C(20C)	11.8(8)
O(18C)-S(1C)-C(19C)-C(20C)	-114.8(7)
N(4C)-S(1C)-C(19C)-C(20C)	132.0(7)
O(17D)-S(1C)-C(19C)-C(20C)	27.4(11)
C(19D)-S(1C)-C(19C)-C(20C)	102(5)
O(17C)-S(1C)-C(19C)-C(24C)	-169.7(7)
O(18C)-S(1C)-C(19C)-C(24C)	63.8(8)
N(4C)-S(1C)-C(19C)-C(24C)	-49.5(8)
O(17D)-S(1C)-C(19C)-C(24C)	-154.1(11)
C(19D)-S(1C)-C(19C)-C(24C)	-80(5)

C(24C)-C(19C)-C(20C)-C(21C)	-2.1(15)
S(1C)-C(19C)-C(20C)-C(21C)	176.4(8)
C(19C)-C(20C)-C(21C)-C(22C)	-0.5(16)
C(20C)-C(21C)-C(22C)-C(23C)	3.0(18)
C(20C)-C(21C)-C(22C)-C(25C)	-177.6(10)
C(21C)-C(22C)-C(23C)-C(24C)	-3.2(18)
C(25C)-C(22C)-C(23C)-C(24C)	177.4(11)
C(22C)-C(23C)-C(24C)-C(19C)	0.8(17)
C(20C)-C(19C)-C(24C)-C(23C)	1.9(15)
S(1C)-C(19C)-C(24C)-C(23C)	-176.6(8)
O(17C)-S(1C)-C(19D)-C(20D)	-27(4)
O(18C)-S(1C)-C(19D)-C(20D)	-162(3)
N(4C)-S(1C)-C(19D)-C(20D)	87(4)
O(17D)-S(1C)-C(19D)-C(20D)	-16(4)
C(19C)-S(1C)-C(19D)-C(20D)	-122(8)
O(17C)-S(1C)-C(19D)-C(24D)	152(3)
O(18C)-S(1C)-C(19D)-C(24D)	18(4)
N(4C)-S(1C)-C(19D)-C(24D)	-93(3)
O(17D)-S(1C)-C(19D)-C(24D)	163(3)
C(19C)-S(1C)-C(19D)-C(24D)	58(4)
C(24D)-C(19D)-C(20D)-C(21D)	5(6)
S(1C)-C(19D)-C(20D)-C(21D)	-176(3)
C(19D)-C(20D)-C(21D)-C(22D)	-6(5)
C(20D)-C(21D)-C(22D)-C(23D)	-2(5)
C(20D)-C(21D)-C(22D)-C(25D)	173(4)
C(21D)-C(22D)-C(23D)-C(24D)	11(6)
C(25D)-C(22D)-C(23D)-C(24D)	-164(4)
C(22D)-C(23D)-C(24D)-C(19D)	-12(6)
C(20D)-C(19D)-C(24D)-C(23D)	4(7)
S(1C)-C(19D)-C(24D)-C(23D)	-175(4)
O(27C)-S(2C)-C(28C)-C(29C)	155.2(4)
O(26C)-S(2C)-C(28C)-C(29C)	24.0(5)
N(13C)-S(2C)-C(28C)-C(29C)	-91.4(5)
O(27C)-S(2C)-C(28C)-C(33C)	-32.9(5)
O(26C)-S(2C)-C(28C)-C(33C)	-164.1(4)
N(13C)-S(2C)-C(28C)-C(33C)	80.6(5)
C(33C)-C(28C)-C(29C)-C(30C)	-0.3(9)
S(2C)-C(28C)-C(29C)-C(30C)	171.5(5)
C(28C)-C(29C)-C(30C)-C(31C)	-1.2(9)
C(29C)-C(30C)-C(31C)-C(32C)	2.7(9)
C(29C)-C(30C)-C(31C)-C(34C)	-177.2(6)
C(30C)-C(31C)-C(32C)-C(33C)	-2.8(10)
C(34C)-C(31C)-C(32C)-C(33C)	177.1(6)
C(31C)-C(32C)-C(33C)-C(28C)	1.4(9)
C(29C)-C(28C)-C(33C)-C(32C)	0.3(9)

S(2C)-C(28C)-C(33C)-C(32C)	-171.7(5)

Table B-7. Hydrogen bonds for **Ts$_6$H$_2$12(Br)$_2$** [Å and °].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(1)-H(1)···Br(2)	0.78	2.44	3.128(4)	147.4
N(16)-H(16)···Br(1)	0.92	2.30	3.058(4)	140.0

Structural Data for $H_6$13$(F)_2(H_2O)$

Table C-1. Crystal data and structure refinement for **$H_6$13$(F)_2(H_2O)$**.

Identification code	01024	
Empirical formula	$(C_{36}H_{60}N_8)^{6+}$ $2(SiF_6)^{2-}$ $2F^-$ $13(H_2O)$ $C_{36}H_{86}F_{14}N_8O_{13}Si_2$	
Formula weight	1161.31	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.8304(11) Å	α = 84.404(3)°
	b = 15.9973(19) Å	β = 89.959(3)°
	c = 17.417(2) Å	γ = 77.098(2)°
Volume	2656.5(5) Å^3	
Z	2	
Density (calculated)	1.452 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	1232	
Absorption coefficient	0.180 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9632 and 0.8936	
Theta range for data collection	1.67 to 30.64°	
Reflections collected	22911	
Independent reflections	15608 [R(int) = 0.0248]	
Data / restraints / parameters	15608 / 0 / 655	
$wR(F^2$all data)	$wR2$ = 0.1189	
$R(F$ obsd data)	$R1$ = 0.0443	
Goodness-of-fit on F^2	0.974	
Observed data [$I > 2\sigma(I)$]	12226	
Largest and mean shift / s.u.	0.001and 0.000	
Largest diff. peak and hole	0.491 and -0.298 e/Å^3	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$ $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

Table C-2. Atomic coordinates and equivalent isotropic displacement parameters for **$H_613(F)_2(H_2O)$**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	0.26869(11)	0.85793(7)	0.22081(6)	0.0128(2)
C(2)	0.23074(14)	0.88237(9)	0.29845(8)	0.0154(3)
C(3)	0.11197(14)	0.84506(9)	0.32970(8)	0.0153(3)
N(4)	0.15289(11)	0.74927(7)	0.34450(7)	0.0139(2)
C(5)	0.02803(14)	0.71276(9)	0.36225(9)	0.0181(3)
C(6)	0.06383(13)	0.61656(9)	0.37536(8)	0.0155(3)
C(7)	0.12475(14)	0.57472(9)	0.44463(8)	0.0175(3)
C(8)	0.15314(15)	0.48588(9)	0.45709(8)	0.0183(3)
C(9)	0.03334(14)	0.56818(10)	0.31821(8)	0.0184(3)
C(10)	0.06044(14)	0.47955(10)	0.33126(9)	0.0185(3)
C(11)	0.11991(14)	0.43753(9)	0.40048(8)	0.0168(3)
C(12)	0.14741(15)	0.34132(9)	0.41520(9)	0.0201(3)
N(13)	0.29611(12)	0.30157(7)	0.39950(7)	0.0150(2)
C(14)	0.33465(15)	0.20594(9)	0.41775(8)	0.0174(3)
C(15)	0.28097(15)	0.15975(9)	0.35653(8)	0.0165(3)
N(16)	0.34177(11)	0.17613(7)	0.28117(6)	0.0128(2)
C(17)	0.48555(14)	0.12514(9)	0.27802(8)	0.0147(2)
C(18)	0.57093(14)	0.16501(9)	0.21902(8)	0.0147(3)
N(19)	0.58248(11)	0.25254(7)	0.23615(7)	0.0137(2)
C(20)	0.67063(14)	0.29086(9)	0.17872(8)	0.0163(3)
C(21)	0.66652(13)	0.38282(9)	0.19093(8)	0.0144(2)
C(22)	0.72760(14)	0.40274(9)	0.25695(8)	0.0159(3)
C(23)	0.71805(14)	0.48795(9)	0.26961(8)	0.0157(3)
C(24)	0.60081(14)	0.44943(9)	0.13745(8)	0.0170(3)
C(25)	0.59503(14)	0.53473(9)	0.14899(8)	0.0174(3)
C(26)	0.65260(13)	0.55473(9)	0.21579(8)	0.0145(3)
C(27)	0.65329(14)	0.64508(9)	0.23148(9)	0.0174(3)
N(28)	0.52521(11)	0.71101(7)	0.20445(7)	0.0146(2)
C(29)	0.52139(14)	0.79329(9)	0.23898(8)	0.0159(3)
C(30)	0.40988(14)	0.86720(9)	0.20216(8)	0.0151(3)
C(31)	0.16701(14)	0.90676(9)	0.16243(8)	0.0146(2)
C(32)	0.16639(14)	0.85930(9)	0.09112(8)	0.0151(3)
N(33)	0.13966(9)	0.77188(6)	0.11193(5)	0.0136(2)
C(34)	0.15130(9)	0.72081(6)	0.04329(5)	0.0157(3)
C(35)	0.12850(14)	0.63174(9)	0.06557(8)	0.0145(2)
C(36)	0.23964(15)	0.56110(10)	0.07293(10)	0.0221(3)
C(37)	0.21897(15)	0.47885(10)	0.09443(10)	0.0230(3)
C(38)	-0.00464(14)	0.61922(9)	0.07921(9)	0.0186(3)
C(39)	-0.02546(14)	0.53782(9)	0.10113(8)	0.0175(3)
C(40)	0.08620(14)	0.46709(9)	0.10961(8)	0.0144(2)

C(41)	0.05472(14)	0.38056(9)	0.13166(8)	0.0160(3)
N(42)	0.17583(11)	0.31332(7)	0.16451(6)	0.0130(2)
C(43)	0.13108(14)	0.23463(9)	0.19780(8)	0.0150(3)
C(44)	0.25485(14)	0.16026(9)	0.21840(8)	0.0148(3)
Si(1A)	0.16338(4)	0.79687(2)	0.57326(2)	0.01414(8)
F(1A)	0.23962(9)	0.80612(6)	0.48702(5)	0.02259(19)
F(2A)	0.31879(9)	0.79271(6)	0.61655(5)	0.02401(19)
F(3A)	0.20359(9)	0.68970(5)	0.57399(5)	0.02035(18)
F(4A)	0.09130(9)	0.78849(6)	0.66020(5)	0.02211(18)
F(5A)	0.01012(9)	0.80208(6)	0.52872(5)	0.02318(19)
F(6A)	0.12234(10)	0.90483(6)	0.57303(6)	0.0270(2)
Si(1B)	0.61346(4)	0.77027(3)	0.00389(2)	0.01601(8)
F(1B)	0.77275(8)	0.77583(5)	-0.03112(5)	0.01751(17)
F(2B)	0.58663(8)	0.71815(6)	-0.07216(5)	0.01896(17)
F(3B)	0.54433(9)	0.86460(6)	-0.04713(6)	0.0268(2)
F(4B)	0.45665(9)	0.76384(7)	0.03896(5)	0.0290(2)
F(5B)	0.64398(9)	0.82402(7)	0.07846(5)	0.0288(2)
F(6B)	0.68311(9)	0.67815(7)	0.05509(6)	0.0303(2)
F(1)	0.28799(8)	0.66775(5)	0.23056(5)	0.01578(16)
F(2)	0.34157(8)	0.36458(5)	0.25754(5)	0.01501(16)
O(1S)	0.38680(10)	0.51116(6)	0.30915(6)	0.0171(2)
O(2S)	0.44037(13)	0.63942(8)	0.40374(7)	0.0296(3)
O(3S)	0.51428(11)	0.39110(7)	0.43522(6)	0.0225(2)
O(4S)	0.68410(14)	0.70551(9)	0.42212(8)	0.0378(3)
O(5S)	0.63871(12)	0.89208(8)	0.37777(6)	0.0256(2)
O(6S)	0.81579(11)	0.94422(7)	0.47452(7)	0.0237(2)
O(7S)	0.40082(12)	0.92748(8)	0.46175(7)	0.0297(3)
O(8S)	0.75245(11)	0.94700(7)	0.24061(6)	0.0220(2)
O(9S)	0.93685(11)	1.04368(7)	0.27176(6)	0.0238(2)
O(10S)	0.87211(10)	0.80229(7)	0.17148(6)	0.0205(2)
O(11S)	0.71104(10)	1.03279(7)	0.08325(6)	0.0217(2)
O(12S)	0.07657(11)	0.88521(7)	0.87997(6)	0.0232(2)
O(13S)	0.85979(11)	0.92390(7)	-0.02037(7)	0.0250(2)

Table C-3. Bond lengths [Å] and angles [°] for **$H_6$13(F)$_2$(H$_2$O)**.

N(1)-C(30)	1.4614(17)	C(26)-C(27)	1.4983(19)
N(1)-C(31)	1.4632(17)	C(27)-N(28)	1.4935(17)
N(1)-C(2)	1.4689(17)	N(28)-C(29)	1.4926(17)
C(2)-C(3)	1.5042(19)	C(29)-C(30)	1.5117(19)
C(3)-N(4)	1.4914(17)	C(31)-C(32)	1.5182(18)
N(4)-C(5)	1.4926(17)	C(32)-N(33)	1.4904(16)
C(5)-C(6)	1.495(2)	N(33)-C(34)	1.5028
C(6)-C(7)	1.388(2)	C(34)-C(35)	1.5052(16)
C(6)-C(9)	1.3907(19)	C(35)-C(36)	1.3812(19)
C(7)-C(8)	1.381(2)	C(35)-C(38)	1.3845(19)
C(8)-C(11)	1.3926(19)	C(36)-C(37)	1.391(2)
C(9)-C(10)	1.379(2)	C(37)-C(40)	1.3813(19)
C(10)-C(11)	1.384(2)	C(38)-C(39)	1.380(2)
C(11)-C(12)	1.498(2)	C(39)-C(40)	1.3856(19)
C(12)-N(13)	1.4948(18)	C(40)-C(41)	1.4989(19)
N(13)-C(14)	1.4938(18)	C(41)-N(42)	1.4869(17)
C(14)-C(15)	1.5133(19)	N(42)-C(43)	1.4896(17)
C(15)-N(16)	1.4665(17)	C(43)-C(44)	1.5151(19)
N(16)-C(44)	1.4636(17)	Si(1A)-F(3A)	1.6699(9)
N(16)-C(17)	1.4696(17)	Si(1A)-F(5A)	1.6768(9)
C(17)-C(18)	1.5090(19)	Si(1A)-F(4A)	1.6776(9)
C(18)-N(19)	1.4884(17)	Si(1A)-F(6A)	1.6833(10)
N(19)-C(20)	1.4979(17)	Si(1A)-F(1A)	1.6866(10)
C(20)-C(21)	1.4985(19)	Si(1A)-F(2A)	1.6893(9)
C(21)-C(24)	1.3857(19)	Si(1B)-F(6B)	1.6522(10)
C(21)-C(22)	1.3935(19)	Si(1B)-F(3B)	1.6763(10)
C(22)-C(23)	1.3845(19)	Si(1B)-F(4B)	1.6784(9)
C(23)-C(26)	1.3902(19)	Si(1B)-F(2B)	1.6832(9)
C(24)-C(25)	1.387(2)	Si(1B)-F(5B)	1.6883(10)
C(25)-C(26)	1.3895(19)	Si(1B)-F(1B)	1.6977(9)
C(30)-N(1)-C(31)	111.18(11)	C(7)-C(8)-C(11)	120.28(14)
C(30)-N(1)-C(2)	111.36(10)	C(10)-C(9)-C(6)	120.04(14)
C(31)-N(1)-C(2)	111.43(10)	C(9)-C(10)-C(11)	120.79(13)
N(1)-C(2)-C(3)	111.98(11)	C(10)-C(11)-C(8)	119.15(13)
N(4)-C(3)-C(2)	111.84(11)	C(10)-C(11)-C(12)	120.84(13)
C(3)-N(4)-C(5)	110.72(10)	C(8)-C(11)-C(12)	120.01(13)
N(4)-C(5)-C(6)	112.51(11)	N(13)-C(12)-C(11)	110.61(11)
C(7)-C(6)-C(9)	119.42(13)	C(14)-N(13)-C(12)	113.99(11)
C(7)-C(6)-C(5)	120.79(13)	N(13)-C(14)-C(15)	111.95(11)
C(9)-C(6)-C(5)	119.78(13)	N(16)-C(15)-C(14)	111.92(11)
C(8)-C(7)-C(6)	120.30(13)	C(44)-N(16)-C(15)	111.28(10)

C(44)-N(16)-C(17)	111.21(10)
C(15)-N(16)-C(17)	111.18(11)
N(16)-C(17)-C(18)	112.49(11)
N(19)-C(18)-C(17)	111.93(11)
C(18)-N(19)-C(20)	111.76(10)
N(19)-C(20)-C(21)	110.95(11)
C(24)-C(21)-C(22)	118.89(13)
C(24)-C(21)-C(20)	120.76(12)
C(22)-C(21)-C(20)	120.35(12)
C(23)-C(22)-C(21)	120.09(13)
C(22)-C(23)-C(26)	120.96(13)
C(21)-C(24)-C(25)	120.99(13)
C(24)-C(25)-C(26)	120.14(13)
C(25)-C(26)-C(23)	118.87(13)
C(25)-C(26)-C(27)	123.20(13)
C(23)-C(26)-C(27)	117.87(12)
N(28)-C(27)-C(26)	114.95(11)
C(29)-N(28)-C(27)	110.33(10)
N(28)-C(29)-C(30)	112.57(11)
N(1)-C(30)-C(29)	112.77(11)
N(1)-C(31)-C(32)	111.82(11)
N(33)-C(32)-C(31)	110.77(11)
C(32)-N(33)-C(34)	111.64(6)
N(33)-C(34)-C(35)	111.10(6)
C(36)-C(35)-C(38)	118.77(13)
C(36)-C(35)-C(34)	120.78(12)
C(38)-C(35)-C(34)	120.46(11)
C(35)-C(36)-C(37)	120.86(13)
C(40)-C(37)-C(36)	120.05(13)
C(39)-C(38)-C(35)	120.54(13)
C(38)-C(39)-C(40)	120.72(13)
C(37)-C(40)-C(39)	119.03(13)
C(37)-C(40)-C(41)	123.37(12)
C(39)-C(40)-C(41)	117.54(12)
N(42)-C(41)-C(40)	114.65(11)
C(41)-N(42)-C(43)	111.24(10)
N(42)-C(43)-C(44)	111.69(11)
N(16)-C(44)-C(43)	112.68(11)
F(3A)-Si(1A)-F(5A)	90.71(5)
F(3A)-Si(1A)-F(4A)	90.50(5)
F(5A)-Si(1A)-F(4A)	91.33(5)
F(3A)-Si(1A)-F(6A)	179.65(5)
F(5A)-Si(1A)-F(6A)	89.27(5)
F(4A)-Si(1A)-F(6A)	89.15(5)
F(3A)-Si(1A)-F(1A)	89.99(5)
F(5A)-Si(1A)-F(1A)	90.20(5)
F(4A)-Si(1A)-F(1A)	178.39(5)
F(6A)-Si(1A)-F(1A)	90.36(5)
F(3A)-Si(1A)-F(2A)	89.78(5)
F(5A)-Si(1A)-F(2A)	178.85(5)
F(4A)-Si(1A)-F(2A)	89.70(5)
F(6A)-Si(1A)-F(2A)	90.25(5)
F(1A)-Si(1A)-F(2A)	88.77(5)
F(6B)-Si(1B)-F(3B)	179.02(6)
F(6B)-Si(1B)-F(4B)	89.28(5)
F(3B)-Si(1B)-F(4B)	91.11(5)
F(6B)-Si(1B)-F(2B)	91.17(5)
F(3B)-Si(1B)-F(2B)	89.72(5)
F(4B)-Si(1B)-F(2B)	91.19(5)
F(6B)-Si(1B)-F(5B)	89.62(6)
F(3B)-Si(1B)-F(5B)	89.47(5)
F(4B)-Si(1B)-F(5B)	90.47(5)
F(2B)-Si(1B)-F(5B)	178.16(5)
F(6B)-Si(1B)-F(1B)	90.17(5)
F(3B)-Si(1B)-F(1B)	89.44(5)
F(4B)-Si(1B)-F(1B)	179.45(6)
F(2B)-Si(1B)-F(1B)	88.79(4)
F(5B)-Si(1B)-F(1B)	89.55(4)

Table C-4. Anisotropic displacement parameters ($Å^2 x 10^3$) for **$H_6 13(F)_2(H_2O)$**. The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	13(1)	12(1)	12(1)	-1(1)	0(1)	-1(1)
C(2)	18(1)	14(1)	14(1)	-2(1)	-1(1)	-3(1)
C(3)	16(1)	13(1)	15(1)	0(1)	2(1)	0(1)
N(4)	14(1)	14(1)	13(1)	-1(1)	0(1)	-2(1)
C(5)	14(1)	16(1)	24(1)	-1(1)	3(1)	-3(1)
C(6)	12(1)	16(1)	19(1)	-2(1)	3(1)	-3(1)
C(7)	20(1)	19(1)	16(1)	-4(1)	3(1)	-6(1)
C(8)	21(1)	18(1)	15(1)	0(1)	2(1)	-4(1)
C(9)	15(1)	21(1)	18(1)	-3(1)	-2(1)	-2(1)
C(10)	16(1)	20(1)	22(1)	-8(1)	1(1)	-4(1)
C(11)	15(1)	16(1)	21(1)	-3(1)	6(1)	-5(1)
C(12)	17(1)	17(1)	26(1)	-3(1)	6(1)	-3(1)
N(13)	17(1)	14(1)	14(1)	-2(1)	1(1)	-4(1)
C(14)	23(1)	14(1)	15(1)	-1(1)	0(1)	-2(1)
C(15)	20(1)	14(1)	16(1)	-1(1)	2(1)	-5(1)
N(16)	13(1)	13(1)	12(1)	-1(1)	0(1)	-3(1)
C(17)	15(1)	12(1)	17(1)	0(1)	-1(1)	-2(1)
C(18)	15(1)	12(1)	17(1)	-3(1)	1(1)	-2(1)
N(19)	13(1)	13(1)	15(1)	-1(1)	0(1)	-3(1)
C(20)	15(1)	15(1)	19(1)	-2(1)	4(1)	-4(1)
C(21)	11(1)	15(1)	17(1)	-1(1)	3(1)	-4(1)
C(22)	14(1)	15(1)	17(1)	2(1)	-1(1)	-1(1)
C(23)	13(1)	18(1)	16(1)	-1(1)	-1(1)	-4(1)
C(24)	16(1)	19(1)	17(1)	-1(1)	-2(1)	-5(1)
C(25)	16(1)	17(1)	18(1)	4(1)	-3(1)	-4(1)
C(26)	11(1)	14(1)	18(1)	-1(1)	1(1)	-3(1)
C(27)	13(1)	15(1)	24(1)	0(1)	-5(1)	-2(1)
N(28)	13(1)	13(1)	18(1)	-1(1)	-1(1)	-2(1)
C(29)	14(1)	14(1)	19(1)	-3(1)	-2(1)	-2(1)
C(30)	16(1)	13(1)	17(1)	-1(1)	1(1)	-4(1)
C(31)	17(1)	12(1)	14(1)	0(1)	-2(1)	-1(1)
C(32)	17(1)	14(1)	14(1)	0(1)	-1(1)	-3(1)
N(33)	14(1)	13(1)	13(1)	-1(1)	-1(1)	-1(1)
C(34)	19(1)	15(1)	13(1)	-3(1)	-1(1)	-2(1)
C(35)	16(1)	15(1)	12(1)	-2(1)	-1(1)	-2(1)
C(36)	13(1)	18(1)	35(1)	-1(1)	3(1)	-2(1)
C(37)	13(1)	15(1)	38(1)	0(1)	2(1)	1(1)
C(38)	14(1)	15(1)	24(1)	-2(1)	-2(1)	2(1)

C(39)	11(1)	18(1)	22(1)	-1(1)	0(1)	-1(1)
C(40)	14(1)	15(1)	14(1)	-3(1)	-1(1)	-2(1)
C(41)	12(1)	15(1)	20(1)	-1(1)	-2(1)	0(1)
N(42)	12(1)	13(1)	13(1)	-2(1)	0(1)	-1(1)
C(43)	13(1)	16(1)	17(1)	0(1)	0(1)	-5(1)
C(44)	17(1)	13(1)	15(1)	-2(1)	-1(1)	-4(1)
Si(1A)	16(1)	13(1)	13(1)	0(1)	-1(1)	-4(1)
F(1A)	25(1)	32(1)	13(1)	-1(1)	1(1)	-12(1)
F(2A)	22(1)	34(1)	19(1)	-2(1)	-5(1)	-11(1)
F(3A)	25(1)	14(1)	21(1)	-3(1)	-3(1)	-1(1)
F(4A)	28(1)	20(1)	18(1)	-1(1)	7(1)	-4(1)
F(5A)	17(1)	23(1)	28(1)	4(1)	-7(1)	-5(1)
F(6A)	39(1)	13(1)	29(1)	0(1)	2(1)	-7(1)
Si(1B)	11(1)	22(1)	14(1)	-2(1)	0(1)	-1(1)
F(1B)	15(1)	19(1)	19(1)	-2(1)	4(1)	-4(1)
F(2B)	17(1)	20(1)	20(1)	-6(1)	1(1)	-3(1)
F(3B)	27(1)	19(1)	30(1)	-5(1)	-9(1)	6(1)
F(4B)	13(1)	51(1)	26(1)	-14(1)	5(1)	-8(1)
F(5B)	18(1)	51(1)	19(1)	-15(1)	1(1)	-8(1)
F(6B)	21(1)	33(1)	33(1)	18(1)	-5(1)	-7(1)
F(1)	16(1)	14(1)	17(1)	-1(1)	0(1)	-2(1)
F(2)	16(1)	13(1)	16(1)	-2(1)	1(1)	-3(1)
O(1S)	19(1)	14(1)	18(1)	-1(1)	-1(1)	-3(1)
O(2S)	43(1)	25(1)	23(1)	-3(1)	-7(1)	-11(1)
O(3S)	22(1)	22(1)	22(1)	0(1)	-2(1)	-2(1)
O(4S)	44(1)	32(1)	37(1)	-2(1)	-11(1)	-8(1)
O(5S)	26(1)	30(1)	24(1)	-6(1)	3(1)	-9(1)
O(6S)	20(1)	18(1)	31(1)	6(1)	-4(1)	-5(1)
O(7S)	29(1)	25(1)	37(1)	-4(1)	11(1)	-9(1)
O(8S)	24(1)	23(1)	20(1)	-3(1)	2(1)	-5(1)
O(9S)	27(1)	23(1)	21(1)	-6(1)	0(1)	-3(1)
O(10S)	15(1)	24(1)	22(1)	-7(1)	0(1)	-2(1)
O(11S)	18(1)	21(1)	24(1)	-2(1)	1(1)	0(1)
O(12S)	21(1)	25(1)	24(1)	-5(1)	3(1)	-6(1)
O(13S)	24(1)	22(1)	31(1)	-9(1)	10(1)	-9(1)

Table C-5. Hydrogen coordinates and isotropic displacement parameters for **$H_6$13(F)$_2$(H_2O)**.

	x	y	z	U(eq)
H(2A)	0.2038	0.9460	0.2966	0.019
H(2B)	0.3130	0.8619	0.3337	0.019
H(3A)	0.0809	0.8698	0.3784	0.018
H(3B)	0.0325	0.8613	0.2923	0.018
H(4A)	0.2157	0.7341	0.3854	0.017
H(4B)	0.1957	0.7266	0.3018	0.017
H(5A)	-0.0405	0.7310	0.3189	0.022
H(5B)	-0.0164	0.7364	0.4089	0.022
H(7A)	0.1470	0.6073	0.4837	0.021
H(8A)	0.1955	0.4576	0.5045	0.022
H(9A)	-0.0062	0.5962	0.2701	0.022
H(10A)	0.0380	0.4469	0.2923	0.022
H(12A)	0.1269	0.3250	0.4696	0.024
H(12B)	0.0851	0.3193	0.3816	0.024
H(13A)	0.3126	0.3147	0.3482	0.018
H(13B)	0.3531	0.3258	0.4281	0.018
H(14A)	0.2956	0.1903	0.4682	0.021
H(14B)	0.4375	0.1867	0.4222	0.021
H(15A)	0.3038	0.0970	0.3724	0.020
H(15B)	0.1781	0.1791	0.3520	0.020
H(17A)	0.4833	0.0665	0.2653	0.018
H(17B)	0.5311	0.1197	0.3295	0.018
H(18A)	0.6656	0.1274	0.2181	0.018
H(18B)	0.5271	0.1689	0.1673	0.018
H(19A)	0.6210	0.2492	0.2848	0.016
H(19B)	0.4947	0.2880	0.2356	0.016
H(20A)	0.6362	0.2880	0.1258	0.020
H(20B)	0.7682	0.2570	0.1839	0.020
H(22A)	0.7758	0.3578	0.2933	0.019
H(23A)	0.7568	0.5010	0.3157	0.019
H(24A)	0.5591	0.4365	0.0922	0.020
H(25A)	0.5516	0.5796	0.1112	0.021
H(27A)	0.6653	0.6462	0.2878	0.021
H(27B)	0.7351	0.6615	0.2063	0.021
H(28A)	0.5246	0.7208	0.1515	0.018
H(28B)	0.4472	0.6908	0.2184	0.018
H(29A)	0.6135	0.8083	0.2330	0.019
H(29B)	0.5041	0.7849	0.2949	0.019

H(30A)	0.4238	0.9218	0.2198	0.018
H(30B)	0.4200	0.8708	0.1454	0.018
H(31A)	0.1895	0.9634	0.1475	0.018
H(31B)	0.0727	0.9173	0.1847	0.018
H(32A)	0.0931	0.8928	0.0542	0.018
H(32B)	0.2576	0.8539	0.0657	0.018
H(33A)	0.0516	0.7772	0.1317	0.016
H(33B)	0.2029	0.7428	0.1496	0.016
H(34A)	0.2450	0.7164	0.0210	0.019
H(34B)	0.0811	0.7511	0.0034	0.019
H(36A)	0.3314	0.5688	0.0632	0.027
H(37A)	0.2962	0.4307	0.0987	0.028
H(38A)	-0.0823	0.6670	0.0734	0.022
H(39A)	-0.1173	0.5302	0.1105	0.021
H(41A)	-0.0204	0.3872	0.1700	0.019
H(41B)	0.0189	0.3604	0.0854	0.019
H(42A)	0.2192	0.3349	0.2024	0.016
H(42B)	0.2392	0.2990	0.1264	0.016
H(43A)	0.0697	0.2177	0.1600	0.018
H(43B)	0.0766	0.2477	0.2447	0.018
H(44A)	0.2206	0.1075	0.2338	0.018
H(44B)	0.3126	0.1500	0.1722	0.018
H(1SA)	0.3505	0.5576	0.2818	0.020
H(1SB)	0.3744	0.4702	0.2844	0.020
H(2SA)	0.4334	0.5931	0.3808	0.036
H(2SB)	0.4547	0.6195	0.4544	0.036
H(3SA)	0.4894	0.4346	0.4017	0.027
H(3SB)	0.6026	0.3660	0.4236	0.027
H(4SA)	0.6761	0.7616	0.4019	0.045
H(4SB)	0.6025	0.6888	0.4102	0.045
H(5SA)	0.6986	0.9067	0.4062	0.031
H(5SB)	0.5645	0.9098	0.4004	0.031
H(6SA)	0.8536	0.9849	0.4594	0.028
H(6SB)	0.8850	0.9078	0.4981	0.028
H(7SA)	0.3658	0.8844	0.4750	0.036
H(7SB)	0.3525	0.9729	0.4787	0.036
H(8SA)	0.7181	0.9292	0.2802	0.026
H(8SB)	0.8032	0.9811	0.2530	0.026
H(9SA)	0.9238	1.0782	0.3089	0.029
H(9SB)	0.9427	1.0734	0.2258	0.029
H(10S)	0.8415	0.8450	0.1953	0.025
H(10T)	0.8127	0.8039	0.1398	0.025
H(11S)	0.6331	1.0597	0.0692	0.026
H(11T)	0.7002	0.9989	0.1278	0.026
H(12S)	0.1387	0.9055	0.8933	0.028

H(12T)	0.0072	0.9049	0.9059	0.028
H(13S)	0.8160	0.9578	0.0090	0.030
H(13T)	0.8178	0.8813	-0.0197	0.030

Table C-6. Torsion angles [°] for **$H_6$13(F)$_2$(H_2O)**.

C(30)-N(1)-C(2)-C(3)	-159.84(11)
C(31)-N(1)-C(2)-C(3)	75.40(14)
N(1)-C(2)-C(3)-N(4)	67.06(14)
C(2)-C(3)-N(4)-C(5)	-170.17(11)
C(3)-N(4)-C(5)-C(6)	178.43(11)
N(4)-C(5)-C(6)-C(7)	77.29(16)
N(4)-C(5)-C(6)-C(9)	-104.01(14)
C(9)-C(6)-C(7)-C(8)	-0.9(2)
C(5)-C(6)-C(7)-C(8)	177.84(12)
C(6)-C(7)-C(8)-C(11)	-0.5(2)
C(7)-C(6)-C(9)-C(10)	1.6(2)
C(5)-C(6)-C(9)-C(10)	-177.13(12)
C(6)-C(9)-C(10)-C(11)	-1.0(2)
C(9)-C(10)-C(11)-C(8)	-0.4(2)
C(9)-C(10)-C(11)-C(12)	179.06(12)
C(7)-C(8)-C(11)-C(10)	1.1(2)
C(7)-C(8)-C(11)-C(12)	-178.34(12)
C(10)-C(11)-C(12)-N(13)	97.63(15)
C(8)-C(11)-C(12)-N(13)	-82.93(16)
C(11)-C(12)-N(13)-C(14)	176.20(11)
C(12)-N(13)-C(14)-C(15)	76.88(15)
N(13)-C(14)-C(15)-N(16)	62.32(15)
C(14)-C(15)-N(16)-C(44)	-158.49(11)
C(14)-C(15)-N(16)-C(17)	76.95(14)
C(44)-N(16)-C(17)-C(18)	79.76(14)
C(15)-N(16)-C(17)-C(18)	-155.64(11)
N(16)-C(17)-C(18)-N(19)	60.61(14)
C(17)-C(18)-N(19)-C(20)	178.40(11)
C(18)-N(19)-C(20)-C(21)	172.93(11)
N(19)-C(20)-C(21)-C(24)	-111.25(14)
N(19)-C(20)-C(21)-C(22)	68.01(15)
C(24)-C(21)-C(22)-C(23)	2.18(19)
C(20)-C(21)-C(22)-C(23)	-177.10(12)
C(21)-C(22)-C(23)-C(26)	-2.5(2)
C(22)-C(21)-C(24)-C(25)	-0.2(2)

C(20)-C(21)-C(24)-C(25)	179.10(12)
C(21)-C(24)-C(25)-C(26)	-1.6(2)
C(24)-C(25)-C(26)-C(23)	1.3(2)
C(24)-C(25)-C(26)-C(27)	178.55(12)
C(22)-C(23)-C(26)-C(25)	0.7(2)
C(22)-C(23)-C(26)-C(27)	-176.69(12)
C(25)-C(26)-C(27)-N(28)	37.13(19)
C(23)-C(26)-C(27)-N(28)	-145.57(12)
C(26)-C(27)-N(28)-C(29)	166.44(12)
C(27)-N(28)-C(29)-C(30)	168.91(11)
C(31)-N(1)-C(30)-C(29)	-156.36(11)
C(2)-N(1)-C(30)-C(29)	78.73(14)
N(28)-C(29)-C(30)-N(1)	69.65(15)
C(30)-N(1)-C(31)-C(32)	79.50(13)
C(2)-N(1)-C(31)-C(32)	-155.63(11)
N(1)-C(31)-C(32)-N(33)	56.19(14)
C(31)-C(32)-N(33)-C(34)	-174.91(8)
C(32)-N(33)-C(34)-C(35)	178.23(10)
N(33)-C(34)-C(35)-C(36)	-104.10(12)
N(33)-C(34)-C(35)-C(38)	75.80(12)
C(38)-C(35)-C(36)-C(37)	-0.7(2)
C(34)-C(35)-C(36)-C(37)	179.22(13)
C(35)-C(36)-C(37)-C(40)	-0.7(2)
C(36)-C(35)-C(38)-C(39)	1.2(2)
C(34)-C(35)-C(38)-C(39)	-178.72(12)
C(35)-C(38)-C(39)-C(40)	-0.3(2)
C(36)-C(37)-C(40)-C(39)	1.7(2)
C(36)-C(37)-C(40)-C(41)	178.84(14)
C(38)-C(39)-C(40)-C(37)	-1.2(2)
C(38)-C(39)-C(40)-C(41)	-178.52(13)
C(37)-C(40)-C(41)-N(42)	21.91(19)
C(39)-C(40)-C(41)-N(42)	-160.87(12)
C(40)-C(41)-N(42)-C(43)	169.73(11)
C(41)-N(42)-C(43)-C(44)	169.79(11)
C(15)-N(16)-C(44)-C(43)	80.09(14)
C(17)-N(16)-C(44)-C(43)	-155.37(11)
N(42)-C(43)-C(44)-N(16)	66.10(14)

Table C-7. Hydrogen bonds for **$H_6$13(F)$_2$(H_2O)** [Å and °].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(4)-H(4A)···F(1A)	0.92	2.24	2.9163(14)	129.4
N(4)-H(4A)···O(2S)	0.92	2.39	3.0939(17)	133.8
N(4)-H(4B)···F(1)	0.92	1.76	2.6703(14)	170.4
N(13)-H(13A)···F(2)	0.92	1.75	2.6538(14)	166.1
N(13)-H(13B)···O(3S)	0.92	2.09	2.9302(16)	150.5
N(13)-H(13B)···O(4S)#1	0.92	2.65	3.1026(18)	111.2
N(19)-H(19A)···F(2A)#1	0.92	1.83	2.7158(15)	160.6
N(19)-H(19B)···F(2)	0.92	1.78	2.6820(14)	164.7
N(28)-H(28B)···F(1)	0.92	1.69	2.6042(14)	169.1
N(28)-H(28A)···F(4B)	0.92	2.07	2.9580(16)	161.1
N(28)-H(28A)···F(5B)	0.92	2.49	3.1003(16)	124.5
N(28)-H(28A)···F(6B)	0.92	2.34	3.0577(16)	135.1
N(33)-H(33A)···O(10S)#2	0.92	1.87	2.7844(13)	173.1
N(33)-H(33B)···F(1)	0.92	1.83	2.7237(12)	163.1
N(42)-H(42A)···F(2)	0.92	1.72	2.6100(14)	163.4
N(42)-H(42B)···F(1B)#3	0.92	2.16	2.8302(14)	129.2
N(42)-H(42B)···F(2B)#3	0.92	1.93	2.8144(14)	159.7
O(1S)-H(1SA)···F(1)	0.85	1.87	2.7090(13)	171.1
O(1S)-H(1SB)···F(2)	0.85	1.89	2.7168(13)	163.9
O(2S)-H(2SA)···O(1S)	0.89	2.02	2.8886(15)	165.2
O(2S)-H(2SB)···O(3S)#1	0.91	1.93	2.8181(16)	164.7
O(3S)-H(3SA)···O(1S)	0.85	2.05	2.8614(15)	159.6
O(3S)-H(3SB)···F(3A)#1	0.90	1.91	2.7978(14)	165.9
O(4S)-H(4SA)···O(5S)	0.92	2.04	2.9428(18)	168.2
O(4S)-H(4SB)···O(2S)	0.93	1.94	2.8564(18)	169.0
O(5S)-H(5SA)···O(6S)	0.85	1.89	2.7372(16)	174.3
O(5S)-H(5SB)···O(7S)	0.83	1.91	2.7375(16)	168.7
O(6S)-H(6SA)···F(6A)#4	0.84	1.86	2.6743(14)	161.4
O(6S)-H(6SB)···F(5A)#5	0.86	1.89	2.7120(14)	159.5
O(7S)-H(7SA)···F(1A)	0.85	1.95	2.7712(15)	163.0

O(7S)-H(7SB)...O(6S)#4	0.85	2.09	2.9100(16)	159.7
O(8S)-H(8SA)...O(5S)	0.82	1.96	2.7848(16)	176.7
O(8S)-H(8SB)...O(9S)	0.86	1.87	2.7183(15)	170.6
O(9S)-H(9SA)...F(4A)#4	0.88	2.22	2.9963(14)	146.2
O(9S)-H(9SA)...F(6A)#4	0.88	2.13	2.9227(15)	148.3
O(9S)-H(9SB)...O(12S)#4	0.90	1.89	2.7646(16)	163.6
O(10S)-H(10S)...O(8S)	0.83	1.91	2.7419(15)	172.8
O(10S)-H(10T)...F(5B)	0.80	1.92	2.7059(14)	167.2
O(11S)-H(11S)...F(3B)#6	0.81	1.90	2.7116(13)	170.9
O(11S)-H(11T)...O(8S)	0.92	2.07	2.9290(16)	153.3
O(12S)-H(12S)...O(11S)#4	0.80	2.01	2.8070(15)	173.4
O(12S)-H(12T)...O(13S)#7	0.84	1.93	2.7481(15)	166.3
O(13S)-H(13S)...O(11S)	0.83	1.98	2.8110(15)	176.7
O(13S)-H(13T)...F(1B)	0.87	1.87	2.7147(14)	164.2

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1, -z+1 #2 x-1, y, z #3 -x+1, -y+1, -z
#4 -x+1, -y+2, -z+1 #5 x+1, y, z #6 -x+1, -y+2, -z
#7 x-1, y, z+1

Structural Data for $H_6$13(Cl)(H_2O)

Table D-1. Crystal data and structure refinement for **$H_6$13(Cl)(H_2O)**.

Identification code	01023	
Empirical formula	$(C_{36} H_{60} N_8)^{6+}$ 6Cl^- 5(H_2 O) (C H_3 O H)	
	$C_{37} H_{74} Cl_6 N_8 O_6$	
Formula weight	939.74	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.4706(6) Å	α = 90°
	b = 15.7895(9) Å	β = 101.164(2)°
	c = 27.0054(15) Å	γ = 90°
Volume	4798.5(5) $Å^3$	
Z	4	
Density (calculated)	1.301 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	2008	
Absorption coefficient	0.408 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9799 and 0.9229	
Theta range for data collection	1.50 to 26.00°	
Reflections collected	30048	
Independent reflections	9438 [R(int) = 0.0901]	
Data / restraints / parameters	9438 / 0 / 514	
$wR(F^2$all data)	$wR2 = 0.0873$	
$R(F$ obsd data)	$R1 = 0.0449$	
Goodness-of-fit on F^2	0.762	
Observed data [$I > 2\sigma(I)$]	4575	
Largest and mean shift / s.u.	0.000and 0.000	
Largest diff. peak and hole	0.643 and -0.553 e/$Å^3$	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o{}^2)^2] \}^{1/2}$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

Table D-2. Atomic coordinates and equivalent isotropic displacement parameters for **$H_6$13(Cl)(H_2O)**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	0.3215(2)	0.44521(16)	0.05108(9)	0.0169(7)
C(2)	0.3437(3)	0.3750(2)	0.01805(12)	0.0192(8)
C(3)	0.4569(3)	0.3279(2)	0.03851(11)	0.0183(8)
N(4)	0.4555(2)	0.29133(16)	0.08918(9)	0.0185(7)
C(5)	0.5677(3)	0.2456(2)	0.11014(13)	0.0287(9)
C(6)	0.5823(3)	0.2237(2)	0.16530(12)	0.0206(8)
C(7)	0.5106(3)	0.1642(2)	0.18265(13)	0.0215(8)
C(8)	0.5318(3)	0.1415(2)	0.23306(13)	0.0213(8)
C(9)	0.6729(3)	0.2608(2)	0.19932(13)	0.0226(9)
C(10)	0.6938(3)	0.2378(2)	0.24948(13)	0.0222(8)
C(11)	0.6257(3)	0.17752(19)	0.26691(12)	0.0170(8)
C(12)	0.6541(3)	0.1507(2)	0.32113(12)	0.0217(9)
N(13)	0.5756(2)	0.19251(16)	0.35276(9)	0.0170(7)
C(14)	0.6277(3)	0.1887(2)	0.40757(11)	0.0184(8)
C(15)	0.5500(3)	0.23285(19)	0.43905(12)	0.0184(8)
N(16)	0.5285(2)	0.32205(16)	0.42454(9)	0.0171(7)
C(17)	0.4320(3)	0.3573(2)	0.44730(12)	0.0203(8)
C(18)	0.3119(3)	0.3216(2)	0.42448(12)	0.0213(8)
N(19)	0.2784(2)	0.34112(16)	0.36960(9)	0.0192(7)
C(20)	0.1680(3)	0.2955(2)	0.34546(12)	0.0222(8)
C(21)	0.1338(3)	0.3122(2)	0.28965(12)	0.0193(8)
C(22)	0.1763(3)	0.2608(2)	0.25582(13)	0.0212(8)
C(23)	0.1441(3)	0.2748(2)	0.20442(13)	0.0209(8)
C(24)	0.0579(3)	0.3783(2)	0.27144(12)	0.0234(8)
C(25)	0.0255(3)	0.3919(2)	0.21972(13)	0.0236(9)
C(26)	0.0689(3)	0.3408(2)	0.18604(12)	0.0185(8)
C(27)	0.0377(3)	0.3566(2)	0.13019(12)	0.0228(9)
N(28)	0.1306(2)	0.40954(16)	0.11252(9)	0.0185(7)
C(29)	0.1110(3)	0.4128(2)	0.05667(12)	0.0201(8)
C(30)	0.1961(3)	0.4723(2)	0.03771(12)	0.0176(8)
C(31)	0.3996(3)	0.51782(19)	0.04585(11)	0.0180(8)
C(32)	0.4152(3)	0.57769(19)	0.09048(11)	0.0179(8)
N(33)	0.4918(2)	0.53939(15)	0.13587(9)	0.0164(6)
C(34)	0.5064(3)	0.5968(2)	0.18050(11)	0.0177(8)
C(35)	0.5915(3)	0.56354(19)	0.22645(12)	0.0163(8)
C(36)	0.6635(3)	0.4933(2)	0.22513(12)	0.0198(8)
C(37)	0.7416(3)	0.4682(2)	0.26866(12)	0.0199(8)

C(38)	0.5991(3)	0.6066(2)	0.27164(12)	0.0181(8)
C(39)	0.6775(3)	0.5819(2)	0.31464(12)	0.0192(8)
C(40)	0.7499(3)	0.5120(2)	0.31325(12)	0.0173(8)
C(41)	0.8381(3)	0.4828(2)	0.35905(12)	0.0210(8)
N(42)	0.7831(2)	0.45911(16)	0.40300(10)	0.0204(7)
C(43)	0.6734(3)	0.4063(2)	0.39019(12)	0.0176(8)
C(44)	0.6382(3)	0.3729(2)	0.43762(12)	0.0211(8)
Cl(1)	0.38515(7)	0.38477(5)	0.18129(3)	0.0188(2)
Cl(2)	0.72224(7)	0.46380(5)	0.09780(3)	0.0234(2)
Cl(3)	0.34343(7)	0.09550(5)	0.34601(3)	0.0247(2)
Cl(4)	0.22450(8)	0.18485(6)	0.07308(4)	0.0330(3)
Cl(5)	0.75071(8)	0.62976(6)	0.45505(3)	0.0291(2)
Cl(6)	0.91253(8)	0.27085(5)	0.40106(4)	0.0329(2)
O(1S)	0.46135(18)	0.33354(13)	0.29951(8)	0.0231(6)
O(2S)	0.3845(2)	0.48665(13)	0.32718(8)	0.0269(6)
C(2S)	0.3088(3)	0.5319(2)	0.28741(12)	0.0290(9)
O(3S)	0.8099(2)	0.32919(15)	0.01863(9)	0.0381(7)
O(4S)	0.1701(2)	0.49665(14)	0.39077(9)	0.0353(7)
O(5S)	1.0305(3)	0.42491(19)	0.45683(11)	0.0686(10)
O(6S)	0.4877(2)	0.5813(2)	0.40575(11)	0.0787(12)

Table D-3. Bond lengths [Å] and angles [°] for **$H_6$13(Cl)(H_2O)**.

N(1)-C(2)	1.476(4)	C(15)-N(16)	1.470(4)
N(1)-C(30)	1.477(4)	N(16)-C(17)	1.476(4)
N(1)-C(31)	1.479(4)	N(16)-C(44)	1.476(4)
C(2)-C(3)	1.505(4)	C(17)-C(18)	1.505(4)
C(3)-N(4)	1.488(4)	C(18)-N(19)	1.489(4)
N(4)-C(5)	1.489(4)	N(19)-C(20)	1.493(4)
C(5)-C(6)	1.506(4)	C(20)-C(21)	1.505(4)
C(6)-C(9)	1.377(4)	C(21)-C(22)	1.380(4)
C(6)-C(7)	1.389(4)	C(21)-C(24)	1.388(4)
C(7)-C(8)	1.383(4)	C(22)-C(23)	1.383(4)
C(8)-C(11)	1.392(4)	C(23)-C(26)	1.383(4)
C(9)-C(10)	1.378(4)	C(24)-C(25)	1.391(4)
C(10)-C(11)	1.372(4)	C(25)-C(26)	1.379(4)
C(11)-C(12)	1.498(4)	C(26)-C(27)	1.502(4)
C(12)-N(13)	1.508(4)	C(27)-N(28)	1.503(4)
N(13)-C(14)	1.486(4)	N(28)-C(29)	1.482(4)
C(14)-C(15)	1.516(4)	C(29)-C(30)	1.513(4)

C(31)-C(32)	1.515(4)
C(32)-N(33)	1.491(3)
N(33)-C(34)	1.491(4)
C(34)-C(35)	1.516(4)
C(35)-C(38)	1.385(4)
C(35)-C(36)	1.386(4)
C(36)-C(37)	1.391(4)
C(37)-C(40)	1.376(4)
C(38)-C(39)	1.380(4)
C(39)-C(40)	1.387(4)
C(40)-C(41)	1.511(4)
C(41)-N(42)	1.496(4)
N(42)-C(43)	1.494(4)
C(43)-C(44)	1.510(4)
O(2S)-C(2S)	1.434(3)
C(2)-N(1)-C(30)	110.1(2)
C(2)-N(1)-C(31)	110.2(2)
C(30)-N(1)-C(31)	109.4(2)
N(1)-C(2)-C(3)	112.8(2)
N(4)-C(3)-C(2)	111.6(3)
C(3)-N(4)-C(5)	112.0(2)
N(4)-C(5)-C(6)	114.2(3)
C(9)-C(6)-C(7)	118.8(3)
C(9)-C(6)-C(5)	119.2(3)
C(7)-C(6)-C(5)	121.9(3)
C(8)-C(7)-C(6)	120.3(3)
C(7)-C(8)-C(11)	120.4(3)
C(6)-C(9)-C(10)	120.6(3)
C(11)-C(10)-C(9)	121.2(3)
C(10)-C(11)-C(8)	118.6(3)
C(10)-C(11)-C(12)	120.1(3)
C(8)-C(11)-C(12)	121.4(3)
C(11)-C(12)-N(13)	112.9(3)
C(14)-N(13)-C(12)	112.2(2)
N(13)-C(14)-C(15)	111.9(3)
N(16)-C(15)-C(14)	112.1(3)
C(15)-N(16)-C(17)	110.5(3)
C(15)-N(16)-C(44)	111.5(2)
C(17)-N(16)-C(44)	111.7(2)
N(16)-C(17)-C(18)	112.9(3)
N(19)-C(18)-C(17)	111.7(3)
C(18)-N(19)-C(20)	111.6(2)
N(19)-C(20)-C(21)	112.8(3)
C(22)-C(21)-C(24)	119.1(3)
C(22)-C(21)-C(20)	120.2(3)
C(24)-C(21)-C(20)	120.7(3)
C(21)-C(22)-C(23)	120.7(3)
C(26)-C(23)-C(22)	120.5(3)
C(21)-C(24)-C(25)	120.0(3)
C(26)-C(25)-C(24)	120.8(3)
C(25)-C(26)-C(23)	119.0(3)
C(25)-C(26)-C(27)	121.3(3)
C(23)-C(26)-C(27)	119.7(3)
C(26)-C(27)-N(28)	111.4(3)
C(29)-N(28)-C(27)	111.4(2)
N(28)-C(29)-C(30)	112.7(3)
N(1)-C(30)-C(29)	113.5(3)
N(1)-C(31)-C(32)	112.8(3)
N(33)-C(32)-C(31)	111.2(2)
C(32)-N(33)-C(34)	112.0(2)
N(33)-C(34)-C(35)	113.9(3)
C(38)-C(35)-C(36)	118.6(3)
C(38)-C(35)-C(34)	118.2(3)
C(36)-C(35)-C(34)	123.2(3)
C(35)-C(36)-C(37)	119.8(3)
C(40)-C(37)-C(36)	121.3(3)
C(39)-C(38)-C(35)	121.5(3)
C(38)-C(39)-C(40)	119.9(3)
C(37)-C(40)-C(39)	118.9(3)
C(37)-C(40)-C(41)	119.0(3)
C(39)-C(40)-C(41)	122.1(3)
N(42)-C(41)-C(40)	114.0(3)
C(43)-N(42)-C(41)	115.0(2)
N(42)-C(43)-C(44)	110.5(2)
N(16)-C(44)-C(43)	110.0(2)

Table D-4. Anisotropic displacement parameters (Å^{2}x 10^3) for **$H_6$13(Cl)(H_2O)**. The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	15(2)	18(2)	18(2)	0(1)	2(1)	-2(1)
C(2)	20(2)	20(2)	17(2)	1(2)	3(2)	-2(2)
C(3)	22(2)	20(2)	13(2)	0(2)	5(2)	-2(2)
N(4)	17(2)	17(2)	23(2)	-2(1)	6(1)	2(1)
C(5)	26(2)	36(2)	25(2)	8(2)	6(2)	17(2)
C(6)	23(2)	22(2)	19(2)	3(2)	9(2)	10(2)
C(7)	16(2)	25(2)	21(2)	-2(2)	-2(2)	6(2)
C(8)	22(2)	17(2)	26(2)	1(2)	8(2)	5(2)
C(9)	22(2)	16(2)	32(2)	6(2)	11(2)	4(2)
C(10)	19(2)	19(2)	28(2)	-3(2)	3(2)	4(2)
C(11)	18(2)	14(2)	19(2)	1(2)	5(2)	6(2)
C(12)	17(2)	23(2)	24(2)	-2(2)	2(2)	5(2)
N(13)	15(2)	15(2)	20(2)	1(1)	2(1)	0(1)
C(14)	20(2)	21(2)	14(2)	3(2)	3(2)	1(2)
C(15)	19(2)	22(2)	15(2)	2(2)	3(2)	-2(2)
N(16)	16(2)	21(2)	14(2)	-1(1)	2(1)	-4(1)
C(17)	23(2)	21(2)	17(2)	-3(2)	3(2)	3(2)
C(18)	19(2)	28(2)	17(2)	3(2)	4(2)	3(2)
N(19)	20(2)	19(2)	19(2)	3(1)	4(1)	1(1)
C(20)	20(2)	24(2)	23(2)	1(2)	4(2)	-3(2)
C(21)	16(2)	23(2)	19(2)	2(2)	5(2)	-4(2)
C(22)	18(2)	20(2)	25(2)	3(2)	2(2)	-1(2)
C(23)	24(2)	18(2)	22(2)	-4(2)	7(2)	-2(2)
C(24)	19(2)	29(2)	24(2)	-5(2)	9(2)	2(2)
C(25)	18(2)	28(2)	25(2)	3(2)	4(2)	2(2)
C(26)	16(2)	21(2)	18(2)	2(2)	2(2)	-7(2)
C(27)	16(2)	26(2)	27(2)	-1(2)	4(2)	-4(2)
N(28)	16(2)	20(2)	20(2)	3(1)	3(1)	3(1)
C(29)	15(2)	26(2)	18(2)	0(2)	0(2)	-1(2)
C(30)	14(2)	23(2)	15(2)	0(2)	3(1)	-2(2)
C(31)	14(2)	22(2)	18(2)	2(2)	3(2)	-1(2)
C(32)	15(2)	16(2)	22(2)	6(2)	2(2)	1(1)
N(33)	13(2)	17(2)	19(2)	1(1)	2(1)	-2(1)
C(34)	21(2)	18(2)	15(2)	-6(2)	4(1)	2(2)
C(35)	13(2)	16(2)	19(2)	4(2)	4(2)	-5(1)

C(36)	21(2)	18(2)	20(2)	-3(2)	4(2)	-2(2)
C(37)	17(2)	16(2)	28(2)	2(2)	6(2)	2(2)
C(38)	17(2)	17(2)	20(2)	0(2)	3(2)	0(2)
C(39)	21(2)	22(2)	15(2)	-1(2)	5(2)	-7(2)
C(40)	17(2)	18(2)	17(2)	2(2)	3(2)	-8(2)
C(41)	22(2)	21(2)	19(2)	4(2)	3(2)	-6(2)
N(42)	17(2)	24(2)	19(2)	2(1)	-1(1)	0(1)
C(43)	11(2)	20(2)	21(2)	0(2)	1(2)	-2(2)
C(44)	23(2)	22(2)	18(2)	-1(2)	3(2)	-1(2)
Cl(1)	19(1)	20(1)	17(1)	0(1)	3(1)	1(1)
Cl(2)	21(1)	27(1)	22(1)	-3(1)	4(1)	1(1)
Cl(3)	22(1)	24(1)	28(1)	5(1)	5(1)	-4(1)
Cl(4)	32(1)	31(1)	34(1)	7(1)	1(1)	-11(1)
Cl(5)	34(1)	32(1)	24(1)	-5(1)	12(1)	-6(1)
Cl(6)	22(1)	26(1)	53(1)	5(1)	13(1)	3(1)
O(1S)	27(2)	24(1)	17(1)	3(1)	2(1)	7(1)
O(2S)	30(2)	25(1)	24(2)	-1(1)	1(1)	2(1)
C(2S)	26(2)	27(2)	32(2)	3(2)	3(2)	2(2)
O(3S)	54(2)	26(2)	38(2)	-3(1)	17(1)	0(1)
O(4S)	42(2)	26(2)	39(2)	-1(1)	11(1)	6(1)
O(5S)	62(2)	81(2)	55(2)	-10(2)	-6(2)	11(2)
O(6S)	25(2)	116(3)	91(3)	-74(2)	0(2)	8(2)

Table D-5. Hydrogen coordinates and isotropic displacement parameters for **$H_6$13(Cl)(H_2O)**.

	x	y	z	U(eq)
H(2A)	0.3480	0.3980	-0.0157	0.023
H(2B)	0.2762	0.3349	0.0139	0.023
H(3A)	0.4674	0.2818	0.0149	0.022
H(3B)	0.5251	0.3671	0.0409	0.022
H(4A)	0.3925	0.2545	0.0868	0.022
H(4B)	0.4445	0.3341	0.1109	0.022
H(5A)	0.6357	0.2811	0.1053	0.034
H(5B)	0.5703	0.1926	0.0907	0.034
H(7A)	0.4467	0.1390	0.1598	0.026
H(8A)	0.4819	0.1011	0.2447	0.026
H(9A)	0.7214	0.3026	0.1881	0.027
H(10A)	0.7565	0.2643	0.2724	0.027
H(12A)	0.7381	0.1648	0.3353	0.026

H(12B)	0.6452	0.0885	0.3230	0.026
H(13A)	0.5640	0.2482	0.3431	0.020
H(13B)	0.5027	0.1662	0.3470	0.020
H(14A)	0.7071	0.2158	0.4137	0.022
H(14B)	0.6383	0.1288	0.4182	0.022
H(15A)	0.4729	0.2029	0.4350	0.022
H(15B)	0.5887	0.2298	0.4751	0.022
H(17A)	0.4301	0.4195	0.4429	0.024
H(17B)	0.4490	0.3452	0.4840	0.024
H(18A)	0.3129	0.2595	0.4293	0.026
H(18B)	0.2515	0.3457	0.4421	0.026
H(19A)	0.3396	0.3258	0.3539	0.023
H(19B)	0.2667	0.3985	0.3654	0.023
H(20A)	0.1019	0.3132	0.3619	0.027
H(20B)	0.1800	0.2338	0.3510	0.027
H(22A)	0.2282	0.2153	0.2680	0.025
H(23A)	0.1740	0.2388	0.1816	0.025
H(24A)	0.0280	0.4143	0.2943	0.028
H(25A)	-0.0271	0.4370	0.2075	0.028
H(27A)	-0.0400	0.3859	0.1220	0.027
H(27B)	0.0300	0.3017	0.1121	0.027
H(28A)	0.1286	0.4636	0.1250	0.022
H(28B)	0.2045	0.3872	0.1249	0.022
H(29A)	0.0285	0.4314	0.0433	0.024
H(29B)	0.1205	0.3552	0.0436	0.024
H(30A)	0.1731	0.4765	0.0005	0.021
H(30B)	0.1884	0.5294	0.0519	0.021
H(31A)	0.3656	0.5495	0.0148	0.022
H(31B)	0.4785	0.4963	0.0421	0.022
H(32A)	0.4517	0.6311	0.0817	0.021
H(32B)	0.3364	0.5914	0.0982	0.021
H(33A)	0.5653	0.5275	0.1287	0.020
H(33B)	0.4585	0.4892	0.1435	0.020
H(34A)	0.4277	0.6059	0.1895	0.021
H(34B)	0.5355	0.6524	0.1711	0.021
H(36A)	0.6594	0.4626	0.1946	0.024
H(37A)	0.7902	0.4197	0.2676	0.024
H(38A)	0.5493	0.6542	0.2731	0.022
H(39A)	0.6817	0.6128	0.3451	0.023
H(41A)	0.8818	0.4332	0.3495	0.025
H(41B)	0.8966	0.5286	0.3696	0.025
H(42A)	0.8384	0.4300	0.4260	0.025
H(42B)	0.7648	0.5080	0.4184	0.025
H(43A)	0.6878	0.3582	0.3686	0.021

H(43B)	0.6078	0.4408	0.3710	0.021
H(44A)	0.7031	0.3374	0.4565	0.025
H(44B)	0.6250	0.4208	0.4595	0.025
H(1SA)	0.4405	0.3476	0.2667	0.028
H(1SB)	0.4365	0.3841	0.3088	0.028
H(2S)	0.4191	0.5179	0.3539	0.032
H(2SB)	0.2430	0.5575	0.3005	0.044
H(2SC)	0.2770	0.4926	0.2600	0.044
H(2SD)	0.3546	0.5764	0.2746	0.044
H(3SB)	0.7937	0.2752	0.0256	0.046
H(3SA)	0.7862	0.3660	0.0401	0.046
H(4SA)	0.1408	0.4985	0.4193	0.042
H(4SB)	0.1995	0.5482	0.4004	0.042
H(5SA)	1.0189	0.3729	0.4432	0.082
H(5SB)	1.0784	0.4195	0.4873	0.082
H(6SA)	0.4256	0.6118	0.4116	0.094
H(6SB)	0.5631	0.5954	0.4195	0.094

Table D-6. Torsion angles [°] for **H$_6$13(Cl)(H$_2$O)**.

C(30)-N(1)-C(2)-C(3)	-163.3(3)	N(13)-C(14)-C(15)-N(16)	-57.7(3)
C(31)-N(1)-C(2)-C(3)	75.9(3)	C(14)-C(15)-N(16)-C(17)	167.1(3)
N(1)-C(2)-C(3)-N(4)	59.1(3)	C(14)-C(15)-N(16)-C(44)	-68.1(3)
C(2)-C(3)-N(4)-C(5)	-179.2(3)	C(15)-N(16)-C(17)-C(18)	-70.1(3)
C(3)-N(4)-C(5)-C(6)	167.4(3)	C(44)-N(16)-C(17)-C(18)	165.2(3)
N(4)-C(5)-C(6)-C(9)	-114.7(3)	N(16)-C(17)-C(18)-N(19)	-61.3(3)
N(4)-C(5)-C(6)-C(7)	68.4(4)	C(17)-C(18)-N(19)-C(20)	171.8(3)
C(9)-C(6)-C(7)-C(8)	-1.4(5)	C(18)-N(19)-C(20)-C(21)	-178.5(3)
C(5)-C(6)-C(7)-C(8)	175.6(3)	N(19)-C(20)-C(21)-C(22)	90.0(4)
C(6)-C(7)-C(8)-C(11)	-0.5(5)	N(19)-C(20)-C(21)-C(24)	-91.1(4)
C(7)-C(6)-C(9)-C(10)	1.5(5)	C(24)-C(21)-C(22)-C(23)	0.1(5)
C(5)-C(6)-C(9)-C(10)	-175.5(3)	C(20)-C(21)-C(22)-C(23)	179.1(3)
C(6)-C(9)-C(10)-C(11)	0.2(5)	C(21)-C(22)-C(23)-C(26)	0.1(5)
C(9)-C(10)-C(11)-C(8)	-2.1(5)	C(22)-C(21)-C(24)-C(25)	0.1(5)
C(9)-C(10)-C(11)-C(12)	177.0(3)	C(20)-C(21)-C(24)-C(25)	-178.8(3)
C(7)-C(8)-C(11)-C(10)	2.2(5)	C(21)-C(24)-C(25)-C(26)	-0.6(5)
C(7)-C(8)-C(11)-C(12)	-176.9(3)	C(24)-C(25)-C(26)-C(23)	0.9(5)
C(10)-C(11)-C(12)-N(13)	100.0(4)	C(24)-C(25)-C(26)-C(27)	-178.1(3)
C(8)-C(11)-C(12)-N(13)	-81.0(4)	C(22)-C(23)-C(26)-C(25)	-0.6(5)
C(11)-C(12)-N(13)-C(14)	-161.1(3)	C(22)-C(23)-C(26)-C(27)	178.3(3)
C(12)-N(13)-C(14)-C(15)	178.5(3)	C(25)-C(26)-C(27)-N(28)	94.5(4)

C(23)-C(26)-C(27)-N(28)	-84.4(4)
C(26)-C(27)-N(28)-C(29)	170.2(3)
C(27)-N(28)-C(29)-C(30)	174.6(3)
C(2)-N(1)-C(30)-C(29)	76.6(3)
C(31)-N(1)-C(30)-C(29)	-162.2(3)
N(28)-C(29)-C(30)-N(1)	64.7(3)
C(2)-N(1)-C(31)-C(32)	-159.1(2)
C(30)-N(1)-C(31)-C(32)	79.7(3)
N(1)-C(31)-C(32)-N(33)	72.3(3)
C(31)-C(32)-N(33)-C(34)	-179.0(3)
C(32)-N(33)-C(34)-C(35)	-175.4(3)
N(33)-C(34)-C(35)-C(38)	-171.6(3)
N(33)-C(34)-C(35)-C(36)	9.7(4)
C(38)-C(35)-C(36)-C(37)	-0.5(5)
C(34)-C(35)-C(36)-C(37)	178.3(3)
C(35)-C(36)-C(37)-C(40)	-0.5(5)
C(36)-C(35)-C(38)-C(39)	1.0(5)
C(34)-C(35)-C(38)-C(39)	-177.7(3)
C(35)-C(38)-C(39)-C(40)	-0.7(5)
C(36)-C(37)-C(40)-C(39)	0.9(5)
C(36)-C(37)-C(40)-C(41)	-178.8(3)
C(38)-C(39)-C(40)-C(37)	-0.3(5)
C(38)-C(39)-C(40)-C(41)	179.3(3)
C(37)-C(40)-C(41)-N(42)	-120.3(3)
C(39)-C(40)-C(41)-N(42)	60.1(4)
C(40)-C(41)-N(42)-C(43)	44.4(4)
C(41)-N(42)-C(43)-C(44)	169.7(3)
C(15)-N(16)-C(44)-C(43)	115.6(3)
C(17)-N(16)-C(44)-C(43)	-120.3(3)
N(42)-C(43)-C(44)-N(16)	179.0(2)

Table D-7. Hydrogen bonds for **$H_6$13(Cl)(H_2O)** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4A)...Cl(4)	0.92	2.19	3.096(3)	169.7
N(4)-H(4B)...Cl(1)	0.92	2.28	3.129(3)	152.7
N(13)-H(13A)...O(1S)	0.92	2.01	2.831(3)	147.4
N(13)-H(13B)...Cl(3)	0.92	2.14	3.047(3)	170.1
N(19)-H(19A)...O(1S)	0.92	2.22	3.088(3)	157.6
N(19)-H(19B)...O(4S)	0.92	2.10	2.859(3)	139.5
N(19)-H(19B)...O(2S)	0.92	2.32	2.935(3)	124.3
N(28)-H(28A)...Cl(3)#1	0.92	2.23	3.136(3)	170.2
N(28)-H(28B)...Cl(1)	0.92	2.32	3.167(3)	152.6
N(33)-H(33B)...Cl(1)	0.92	2.19	3.089(3)	165.0
N(33)-H(33A)...Cl(2)	0.92	2.35	3.243(3)	163.2
N(42)-H(42B)...Cl(5)	0.92	2.18	3.095(3)	170.9
N(42)-H(42A)...O(5S)	0.92	2.20	2.977(4)	141.5
N(42)-H(42A)...Cl(6)	0.92	2.78	3.328(3)	119.5
O(1S)-H(1SA)...Cl(1)	0.90	2.35	3.245(2)	179.6
O(1S)-H(1SB)...O(2S)	0.90	1.83	2.727(3)	179.4
O(2S)-H(2S)...O(6S)	0.90	1.78	2.676(3)	178.9
O(3S)-H(3SB)....Cl(5)#2	0.90	2.43	3.331(2)	179.6
O(3S)-H(3SA)...Cl(2)	0.90	2.41	3.306(3)	179.7
O(4S)-H(4SA)...O(5S)#3	0.90	2.11	2.852(4)	138.6
O(4S)-H(4SB)...Cl(4)#1	0.90	2.38	3.285(2)	179.2
O(5S)-H(5SA)...Cl(6)	0.90	2.20	3.038(3)	154.6
O(5S)-H(5SB)...Cl(5)#4	0.90	2.39	3.224(3)	155.0
O(6S)-H(6SA)...Cl(4)#1	0.90	2.18	3.077(3)	179.1
O(6S)-H(6SB)...Cl(5)	0.90	2.25	3.147(3)	179.1

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2, y+1/2, -z+1/2 #2 -x+3/2, y-1/2, -z+1/2

#3 x-1, y, z #4 -x+2, -y+1, -z+1

Structural Data for [$H_6$13(F)$_2$(H_2O)][Cl]$_2$

Table E-1. Crystal data and structure refinement for **[$H_6$13(F)$_2$(H_2O)][Cl]$_2$**.

Identification code	01028	
Empirical formula	$(C_{36}H_{60}N_8)^{6+}$ $6Cl^-$ $(SiF_6)^{2-}$ $2F^-$ $10(H_2O)$	
	C36 H80 Cl2 F8 N8 O10 Si	
Formula weight	1036.07	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	*a* = 10.2614(8) Å	α = 81.842(2)°
	b = 14.6708(11) Å	β = 84.129(2)°
	c = 17.2858(13) Å	γ = 76.707(2)°
Volume	2500.3(3) $Å^3$	
Z	2	
Density (calculated)	1.376 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	1104	
Absorption coefficient	0.242 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9833 and 0.9332	
Theta range for data collection	1.75 to 30.54°	
Reflections collected	21593	
Independent reflections	14660 [R(int) = 0.0217]	
Data / restraints / parameters	14660 / 0 / 586	
$wR(F^2$all data)	$wR2 = 0.1284$	
$R(F$ obsd data)	$R1 = 0.0468$	
Goodness-of-fit on F^2	1.009	
Observed data [$I > 2\sigma(I)$]	10673	
Largest and mean shift / s.u.	0.001and 0.000	
Largest diff. peak and hole	0.545 and -0.326 e/$Å^3$	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$ $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

Table E-2. Atomic coordinates and equivalent isotropic displacement parameters for **$[H_6 13(F)_2(H_2O)][Cl]_2$**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	0.50814(13)	0.17110(9)	0.29903(7)	0.0139(2)
C(2)	0.65411(15)	0.15540(11)	0.27885(9)	0.0170(3)
C(3)	0.71605(16)	0.22724(11)	0.30840(10)	0.0175(3)
N(4)	0.66156(13)	0.32617(9)	0.27290(8)	0.0159(3)
C(5)	0.72208(17)	0.35151(12)	0.19232(10)	0.0206(3)
C(6)	0.66874(16)	0.45443(11)	0.16523(9)	0.0175(3)
C(7)	0.72547(16)	0.52274(12)	0.18850(10)	0.0192(3)
C(8)	0.67494(16)	0.61765(12)	0.16626(10)	0.0194(3)
C(9)	0.56023(17)	0.48320(12)	0.11832(10)	0.0204(3)
C(10)	0.50889(17)	0.57808(12)	0.09607(10)	0.0210(3)
C(11)	0.56554(16)	0.64636(12)	0.11978(9)	0.0186(3)
C(12)	0.51216(18)	0.74940(12)	0.09396(10)	0.0232(3)
N(13)	0.42692(13)	0.80039(9)	0.15745(8)	0.0168(3)
C(14)	0.37913(17)	0.90260(11)	0.12760(10)	0.0197(3)
C(15)	0.26894(16)	0.95397(11)	0.18137(10)	0.0178(3)
N(16)	0.14251(13)	0.92181(9)	0.18559(8)	0.0155(2)
C(17)	0.07475(16)	0.94750(11)	0.11214(9)	0.0175(3)
C(18)	-0.01511(16)	0.88030(11)	0.10552(9)	0.0173(3)
N(19)	0.06335(13)	0.78163(9)	0.10394(8)	0.0150(2)
C(20)	-0.02652(16)	0.71435(11)	0.10333(10)	0.0174(3)
C(21)	0.05269(15)	0.61477(11)	0.10270(9)	0.0159(3)
C(22)	0.07513(16)	0.55631(12)	0.17292(9)	0.0185(3)
C(23)	0.14950(16)	0.46423(12)	0.17368(9)	0.0184(3)
C(24)	0.10456(17)	0.57955(12)	0.03270(9)	0.0195(3)
C(25)	0.17932(17)	0.48788(11)	0.03322(9)	0.0185(3)
C(26)	0.20397(15)	0.42977(11)	0.10391(9)	0.0149(3)
C(27)	0.28877(16)	0.33216(11)	0.09912(9)	0.0171(3)
N(28)	0.32303(13)	0.27768(9)	0.17658(7)	0.0143(2)
C(29)	0.42119(16)	0.18676(11)	0.16797(9)	0.0158(3)
C(30)	0.44332(16)	0.12681(11)	0.24693(9)	0.0160(3)
C(31)	0.47854(15)	0.13813(11)	0.38206(9)	0.0155(3)
C(32)	0.33902(16)	0.18502(11)	0.41290(9)	0.0161(3)
N(33)	0.32178(13)	0.28945(9)	0.40786(8)	0.0142(2)
C(34)	0.18009(15)	0.33549(11)	0.43200(10)	0.0176(3)
C(35)	0.15467(16)	0.44163(11)	0.42130(9)	0.0165(3)
C(36)	0.24729(17)	0.48829(12)	0.44054(11)	0.0241(4)
C(37)	0.21897(18)	0.58581(12)	0.43426(11)	0.0228(3)
C(38)	0.03233(17)	0.49449(12)	0.39532(9)	0.0187(3)
C(39)	0.00310(17)	0.59224(12)	0.39025(10)	0.0202(3)

C(40)	0.09704(17)	0.63898(11)	0.40969(9)	0.0180(3)
C(41)	0.07162(19)	0.74436(11)	0.40837(9)	0.0213(3)
N(42)	0.06815(13)	0.79717(9)	0.32737(8)	0.0157(2)
C(43)	0.08592(17)	0.89526(11)	0.32860(9)	0.0168(3)
C(44)	0.05233(16)	0.95616(11)	0.25177(9)	0.0178(3)
Cl(1)	0.25249(5)	0.80518(3)	-0.04833(3)	0.02879(10)
Cl(2)	0.07088(4)	0.22202(3)	0.27071(2)	0.02314(9)
Si(1A)	0.68869(4)	0.84320(3)	0.31625(3)	0.01545(9)
F(1A)	0.82907(10)	0.77470(7)	0.27645(6)	0.0214(2)
F(2A)	0.59237(11)	0.78328(8)	0.27837(7)	0.0334(3)
F(3A)	0.69503(11)	0.76672(8)	0.39722(6)	0.0307(3)
F(4A)	0.55031(11)	0.91271(7)	0.35373(7)	0.0272(2)
F(5A)	0.78657(12)	0.90139(9)	0.35389(8)	0.0404(3)
F(6A)	0.68393(14)	0.91851(9)	0.23386(7)	0.0481(4)
F(1)	0.39671(9)	0.37943(6)	0.27097(5)	0.01675(18)
F(2)	0.23198(9)	0.71293(6)	0.21657(5)	0.01681(18)
O(1S)	0.40564(12)	0.56270(8)	0.28105(7)	0.0223(2)
O(2S)	0.56478(13)	0.60696(9)	0.37441(7)	0.0240(3)
O(3S)	0.46361(12)	0.68025(8)	0.51035(7)	0.0213(2)
O(4S)	0.70683(14)	0.42247(9)	0.38602(8)	0.0288(3)
O(5S)	0.34795(12)	0.85555(9)	0.44619(7)	0.0246(3)
O(6S)	0.80756(12)	1.00591(9)	0.46851(7)	0.0235(3)
O(7S)	0.03412(14)	0.19957(10)	0.09545(8)	0.0314(3)
O(8S)	0.28353(14)	0.13141(10)	0.02021(8)	0.0319(3)
O(9S)	0.01035(14)	0.11301(10)	0.43866(8)	0.0307(3)
O(10S)	0.66277(15)	1.00038(10)	0.08478(8)	0.0326(3)

Table E-3. Bond lengths [Å] and angles [°] for **[H$_6$13(F)$_2$(H$_2$O)][Cl]$_2$**.

N(1)-C(30)	1.4708(19)	C(10)-C(11)	1.394(2)
N(1)-C(31)	1.472(2)	C(11)-C(12)	1.504(2)
N(1)-C(2)	1.475(2)	C(12)-N(13)	1.505(2)
C(2)-C(3)	1.518(2)	N(13)-C(14)	1.500(2)
C(3)-N(4)	1.497(2)	C(14)-C(15)	1.517(2)
N(4)-C(5)	1.499(2)	C(15)-N(16)	1.471(2)
C(5)-C(6)	1.507(2)	N(16)-C(44)	1.467(2)
C(6)-C(7)	1.391(2)	N(16)-C(17)	1.470(2)
C(6)-C(9)	1.395(2)	C(17)-C(18)	1.519(2)
C(7)-C(8)	1.383(2)	C(18)-N(19)	1.488(2)
C(8)-C(11)	1.398(2)	N(19)-C(20)	1.4995(19)
C(9)-C(10)	1.384(2)	C(20)-C(21)	1.501(2)

C(21)-C(22)	1.390(2)	C(35)-C(38)	1.396(2)
C(21)-C(24)	1.391(2)	C(36)-C(37)	1.384(2)
C(22)-C(23)	1.389(2)	C(37)-C(40)	1.386(2)
C(23)-C(26)	1.388(2)	C(38)-C(39)	1.388(2)
C(24)-C(25)	1.386(2)	C(39)-C(40)	1.396(2)
C(25)-C(26)	1.397(2)	C(40)-C(41)	1.505(2)
C(26)-C(27)	1.504(2)	C(41)-N(42)	1.501(2)
C(27)-N(28)	1.4895(19)	N(42)-C(43)	1.4949(19)
N(28)-C(29)	1.4912(19)	C(43)-C(44)	1.515(2)
C(29)-C(30)	1.523(2)	Si(1A)-F(3A)	1.6618(11)
C(31)-C(32)	1.517(2)	Si(1A)-F(6A)	1.6716(12)
C(32)-N(33)	1.4923(19)	Si(1A)-F(4A)	1.6761(11)
N(33)-C(34)	1.4995(19)	Si(1A)-F(5A)	1.6872(12)
C(34)-C(35)	1.506(2)	Si(1A)-F(2A)	1.6952(12)
C(35)-C(36)	1.382(2)	Si(1A)-F(1A)	1.6988(11)
C(30)-N(1)-C(31)	111.61(12)	C(22)-C(21)-C(20)	119.89(14)
C(30)-N(1)-C(2)	110.89(12)	C(24)-C(21)-C(20)	121.03(14)
C(31)-N(1)-C(2)	111.25(12)	C(23)-C(22)-C(21)	120.80(15)
N(1)-C(2)-C(3)	112.24(13)	C(26)-C(23)-C(22)	120.12(15)
N(4)-C(3)-C(2)	112.84(13)	C(25)-C(24)-C(21)	120.29(15)
C(3)-N(4)-C(5)	114.44(13)	C(24)-C(25)-C(26)	120.58(15)
N(4)-C(5)-C(6)	109.87(13)	C(23)-C(26)-C(25)	119.10(15)
C(7)-C(6)-C(9)	118.86(15)	C(23)-C(26)-C(27)	123.88(14)
C(7)-C(6)-C(5)	120.10(15)	C(25)-C(26)-C(27)	117.02(14)
C(9)-C(6)-C(5)	121.02(15)	N(28)-C(27)-C(26)	114.18(13)
C(8)-C(7)-C(6)	120.84(15)	C(27)-N(28)-C(29)	111.78(12)
C(7)-C(8)-C(11)	120.22(15)	N(28)-C(29)-C(30)	111.25(12)
C(10)-C(9)-C(6)	120.59(16)	N(1)-C(30)-C(29)	111.90(12)
C(9)-C(10)-C(11)	120.42(16)	N(1)-C(31)-C(32)	112.51(12)
C(10)-C(11)-C(8)	119.08(15)	N(33)-C(32)-C(31)	111.75(12)
C(10)-C(11)-C(12)	120.50(16)	C(32)-N(33)-C(34)	111.05(12)
C(8)-C(11)-C(12)	120.41(15)	N(33)-C(34)-C(35)	113.03(12)
C(11)-C(12)-N(13)	113.11(13)	C(36)-C(35)-C(38)	118.93(15)
C(14)-N(13)-C(12)	109.90(12)	C(36)-C(35)-C(34)	121.39(15)
N(13)-C(14)-C(15)	112.91(13)	C(38)-C(35)-C(34)	119.60(14)
N(16)-C(15)-C(14)	113.52(13)	C(35)-C(36)-C(37)	120.49(16)
C(44)-N(16)-C(17)	110.93(13)	C(36)-C(37)-C(40)	121.09(16)
C(44)-N(16)-C(15)	110.80(13)	C(39)-C(38)-C(35)	120.55(15)
C(17)-N(16)-C(15)	113.05(12)	C(38)-C(39)-C(40)	120.26(15)
N(16)-C(17)-C(18)	110.77(12)	C(37)-C(40)-C(39)	118.66(15)
N(19)-C(18)-C(17)	111.62(13)	C(37)-C(40)-C(41)	117.69(15)
C(18)-N(19)-C(20)	111.52(12)	C(39)-C(40)-C(41)	123.62(15)
N(19)-C(20)-C(21)	111.42(12)	N(42)-C(41)-C(40)	113.70(13)
C(22)-C(21)-C(24)	119.08(15)	C(43)-N(42)-C(41)	110.61(12)

N(42)-C(43)-C(44)	111.34(13)	F(6A)-Si(1A)-F(2A)	90.20(8)
N(16)-C(44)-C(43)	112.34(13)	F(4A)-Si(1A)-F(2A)	90.16(6)
F(3A)-Si(1A)-F(6A)	178.93(7)	F(5A)-Si(1A)-F(2A)	179.11(6)
F(3A)-Si(1A)-F(4A)	90.98(6)	F(3A)-Si(1A)-F(1A)	90.34(6)
F(6A)-Si(1A)-F(4A)	89.99(6)	F(6A)-Si(1A)-F(1A)	88.69(6)
F(3A)-Si(1A)-F(5A)	90.28(7)	F(4A)-Si(1A)-F(1A)	178.67(6)
F(6A)-Si(1A)-F(5A)	90.14(8)	F(5A)-Si(1A)-F(1A)	89.18(6)
F(4A)-Si(1A)-F(5A)	90.66(6)	F(2A)-Si(1A)-F(1A)	90.01(5)
F(3A)-Si(1A)-F(2A)	89.37(6)		

Table E-4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **$[H_6 13(F)_2(H_2O)][Cl]_2$**. The anisotropic displacement factor exponent takes the form:

$$-2\pi^2[h^2 a^{*2} U_{11} + ... + 2hk\, a^* b^* U_{12}]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	14(1)	13(1)	14(1)	-3(1)	-1(1)	-3(1)
C(2)	16(1)	14(1)	21(1)	-3(1)	-1(1)	-3(1)
C(3)	16(1)	16(1)	20(1)	-1(1)	-3(1)	-4(1)
N(4)	16(1)	15(1)	17(1)	-3(1)	0(1)	-4(1)
C(5)	24(1)	19(1)	18(1)	-3(1)	5(1)	-4(1)
C(6)	19(1)	16(1)	16(1)	-3(1)	4(1)	-4(1)
C(7)	14(1)	22(1)	21(1)	-4(1)	1(1)	-4(1)
C(8)	19(1)	19(1)	22(1)	-5(1)	4(1)	-8(1)
C(9)	22(1)	23(1)	18(1)	-5(1)	1(1)	-9(1)
C(10)	20(1)	25(1)	18(1)	-2(1)	1(1)	-5(1)
C(11)	19(1)	19(1)	16(1)	-1(1)	6(1)	-4(1)
C(12)	26(1)	20(1)	20(1)	1(1)	8(1)	-3(1)
N(13)	15(1)	16(1)	18(1)	-1(1)	1(1)	-4(1)
C(14)	20(1)	16(1)	22(1)	2(1)	1(1)	-5(1)
C(15)	19(1)	14(1)	22(1)	-2(1)	1(1)	-7(1)
N(16)	17(1)	14(1)	15(1)	-1(1)	0(1)	-4(1)
C(17)	21(1)	14(1)	17(1)	0(1)	-3(1)	-4(1)
C(18)	17(1)	15(1)	20(1)	-2(1)	-2(1)	-2(1)
N(19)	17(1)	14(1)	15(1)	-3(1)	1(1)	-5(1)
C(20)	17(1)	15(1)	22(1)	-3(1)	-2(1)	-5(1)
C(21)	14(1)	14(1)	20(1)	-2(1)	-2(1)	-5(1)
C(22)	20(1)	20(1)	15(1)	-3(1)	0(1)	-4(1)
C(23)	22(1)	19(1)	14(1)	-1(1)	-1(1)	-4(1)
C(24)	25(1)	18(1)	15(1)	1(1)	-2(1)	-4(1)

C(25)	23(1)	18(1)	14(1)	-3(1)	1(1)	-5(1)
C(26)	16(1)	15(1)	15(1)	-2(1)	-1(1)	-5(1)
C(27)	23(1)	15(1)	13(1)	-1(1)	-1(1)	-4(1)
N(28)	15(1)	14(1)	14(1)	-3(1)	0(1)	-3(1)
C(29)	17(1)	14(1)	16(1)	-3(1)	-1(1)	-2(1)
C(30)	17(1)	13(1)	19(1)	-3(1)	-2(1)	-4(1)
C(31)	18(1)	12(1)	16(1)	-1(1)	-2(1)	-2(1)
C(32)	19(1)	12(1)	18(1)	-1(1)	0(1)	-5(1)
N(33)	14(1)	13(1)	16(1)	-3(1)	0(1)	-3(1)
C(34)	14(1)	14(1)	24(1)	-2(1)	2(1)	-2(1)
C(35)	17(1)	16(1)	15(1)	-2(1)	4(1)	-3(1)
C(36)	18(1)	20(1)	35(1)	-4(1)	-6(1)	-3(1)
C(37)	22(1)	20(1)	29(1)	-5(1)	-2(1)	-9(1)
C(38)	20(1)	18(1)	18(1)	-3(1)	-2(1)	-3(1)
C(39)	22(1)	19(1)	18(1)	-2(1)	-3(1)	0(1)
C(40)	24(1)	15(1)	14(1)	-2(1)	5(1)	-4(1)
C(41)	34(1)	15(1)	14(1)	-1(1)	4(1)	-5(1)
N(42)	17(1)	13(1)	16(1)	-2(1)	2(1)	-4(1)
C(43)	22(1)	13(1)	16(1)	-3(1)	1(1)	-5(1)
C(44)	20(1)	13(1)	20(1)	-2(1)	1(1)	-3(1)
Cl(1)	34(1)	38(1)	20(1)	-10(1)	8(1)	-19(1)
Cl(2)	17(1)	32(1)	21(1)	2(1)	-1(1)	-10(1)
Si(1A)	18(1)	12(1)	16(1)	-3(1)	0(1)	-2(1)
F(1A)	20(1)	21(1)	23(1)	-8(1)	0(1)	-1(1)
F(2A)	23(1)	37(1)	44(1)	-22(1)	-12(1)	-1(1)
F(3A)	33(1)	30(1)	22(1)	8(1)	1(1)	-1(1)
F(4A)	25(1)	18(1)	36(1)	-7(1)	9(1)	-1(1)
F(5A)	27(1)	43(1)	62(1)	-36(1)	11(1)	-18(1)
F(6A)	57(1)	33(1)	32(1)	16(1)	16(1)	14(1)
F(1)	18(1)	14(1)	19(1)	-3(1)	-1(1)	-3(1)
F(2)	18(1)	14(1)	18(1)	-2(1)	1(1)	-3(1)
O(1S)	25(1)	17(1)	25(1)	-3(1)	-5(1)	-4(1)
O(2S)	31(1)	20(1)	23(1)	-4(1)	-3(1)	-8(1)
O(3S)	24(1)	20(1)	21(1)	-5(1)	-2(1)	-4(1)
O(4S)	36(1)	25(1)	26(1)	-7(1)	-1(1)	-7(1)
O(5S)	22(1)	23(1)	27(1)	-5(1)	2(1)	-2(1)
O(6S)	25(1)	23(1)	22(1)	-5(1)	-1(1)	-3(1)
O(7S)	33(1)	37(1)	24(1)	-10(1)	1(1)	-7(1)
O(8S)	33(1)	36(1)	31(1)	-10(1)	-2(1)	-13(1)
O(9S)	34(1)	33(1)	26(1)	7(1)	-6(1)	-14(1)
O(10S)	40(1)	29(1)	30(1)	-6(1)	-6(1)	-6(1)

Table E-5. Hydrogen coordinates and isotropic displacement parameters for **$[H_613(F)_2(H_2O)][Cl]_2$**.

	x	**y**	**z**	**U(eq)**
H(2A)	0.6713	0.1589	0.2212	0.020
H(2B)	0.6977	0.0913	0.3018	0.020
H(3A)	0.6991	0.2234	0.3661	0.021
H(3B)	0.8145	0.2113	0.2963	0.021
H(4A)	0.6757	0.3671	0.3052	0.019
H(4B)	0.5703	0.3346	0.2707	0.019
H(5A)	0.6997	0.3124	0.1556	0.025
H(5B)	0.8210	0.3387	0.1929	0.025
H(7A)	0.7999	0.5039	0.2201	0.023
H(8A)	0.7147	0.6635	0.1826	0.023
H(9A)	0.5212	0.4372	0.1015	0.024
H(10A)	0.4346	0.5968	0.0644	0.025
H(12A)	0.4581	0.7556	0.0485	0.028
H(12B)	0.5886	0.7798	0.0766	0.028
H(13A)	0.3543	0.7736	0.1732	0.020
H(13B)	0.4762	0.7950	0.2001	0.020
H(14A)	0.3453	0.9075	0.0752	0.024
H(14B)	0.4560	0.9339	0.1216	0.024
H(15A)	0.3006	0.9449	0.2347	0.021
H(15B)	0.2515	1.0224	0.1627	0.021
H(17A)	0.1428	0.9454	0.0671	0.021
H(17B)	0.0201	1.0127	0.1105	0.021
H(18A)	-0.0831	0.8826	0.1506	0.021
H(18B)	-0.0630	0.9009	0.0570	0.021
H(19A)	0.1128	0.7640	0.1472	0.018
H(19B)	0.1222	0.7787	0.0600	0.018
H(20A)	-0.0789	0.7328	0.0564	0.021
H(20B)	-0.0906	0.7181	0.1503	0.021
H(22A)	0.0392	0.5796	0.2210	0.022
H(23A)	0.1631	0.4248	0.2220	0.022
H(24A)	0.0887	0.6185	-0.0157	0.023
H(25A)	0.2141	0.4644	-0.0149	0.022
H(27A)	0.2404	0.2966	0.0717	0.021
H(27B)	0.3731	0.3372	0.0671	0.021
H(28A)	0.2460	0.2655	0.2040	0.017
H(28B)	0.3588	0.3134	0.2049	0.017
H(29A)	0.5078	0.1999	0.1440	0.019

H(29B)	0.3874	0.1514	0.1326	0.019
H(30A)	0.3558	0.1172	0.2723	0.019
H(30B)	0.5001	0.0641	0.2386	0.019
H(31A)	0.5457	0.1514	0.4137	0.019
H(31B)	0.4868	0.0690	0.3883	0.019
H(32A)	0.2715	0.1706	0.3822	0.019
H(32B)	0.3231	0.1589	0.4682	0.019
H(33A)	0.3435	0.3133	0.3573	0.017
H(33B)	0.3792	0.3031	0.4399	0.017
H(34A)	0.1598	0.3134	0.4878	0.021
H(34B)	0.1183	0.3156	0.4007	0.021
H(36A)	0.3310	0.4531	0.4582	0.029
H(37A)	0.2842	0.6168	0.4470	0.027
H(38A)	-0.0315	0.4633	0.3810	0.022
H(39A)	-0.0812	0.6275	0.3735	0.024
H(41A)	-0.0152	0.7662	0.4380	0.026
H(41B)	0.1428	0.7597	0.4355	0.026
H(42A)	0.1355	0.7660	0.2951	0.019
H(42B)	-0.0126	0.7995	0.3076	0.019
H(43A)	0.1800	0.8930	0.3385	0.020
H(43B)	0.0270	0.9237	0.3719	0.020
H(44A)	-0.0413	0.9573	0.2416	0.021
H(44B)	0.0584	1.0216	0.2561	0.021
H(1SA)	0.3918	0.5086	0.2681	0.027
H(1SB)	0.3351	0.5987	0.2568	0.027
H(2SA)	0.5187	0.6037	0.3418	0.029
H(2SB)	0.5985	0.6577	0.3494	0.029
H(3SA)	0.5003	0.6555	0.4739	0.026
H(3SB)	0.4299	0.7315	0.4967	0.026
H(4SA)	0.6685	0.4905	0.3852	0.035
H(4SB)	0.6646	0.3982	0.4122	0.035
H(5SA)	0.4022	0.8754	0.4104	0.029
H(5SB)	0.3073	0.8980	0.4716	0.029
H(6SA)	0.7773	0.9758	0.4330	0.028
H(6SB)	0.8495	0.9644	0.5057	0.028
H(7SA)	-0.0471	0.1982	0.0913	0.038
H(7SB)	0.0349	0.2095	0.1427	0.038
H(8SA)	0.2942	0.0812	-0.0188	0.038
H(8SB)	0.1951	0.1444	0.0435	0.038
H(9SA)	-0.0543	0.0876	0.4336	0.037
H(9SB)	0.0264	0.1423	0.3939	0.037
H(10S)	0.6836	1.0593	0.0805	0.039
H(10T)	0.6725	0.9846	0.1361	0.039

Table E-6. Torsion angles [°] for **$[H_613(F)_2(H_2O)][Cl]_2$**.

C(30)-N(1)-C(2)-C(3)	158.65(13)
C(31)-N(1)-C(2)-C(3)	-76.51(15)
N(1)-C(2)-C(3)-N(4)	-62.20(17)
C(2)-C(3)-N(4)-C(5)	-80.20(17)
C(3)-N(4)-C(5)-C(6)	-175.23(13)
N(4)-C(5)-C(6)-C(7)	82.45(18)
N(4)-C(5)-C(6)-C(9)	-95.95(18)
C(9)-C(6)-C(7)-C(8)	0.5(2)
C(5)-C(6)-C(7)-C(8)	-177.89(15)
C(6)-C(7)-C(8)-C(11)	0.0(2)
C(7)-C(6)-C(9)-C(10)	-0.7(2)
C(5)-C(6)-C(9)-C(10)	177.66(15)
C(6)-C(9)-C(10)-C(11)	0.5(2)
C(9)-C(10)-C(11)-C(8)	0.1(2)
C(9)-C(10)-C(11)-C(12)	178.43(15)
C(7)-C(8)-C(11)-C(10)	-0.3(2)
C(7)-C(8)-C(11)-C(12)	-178.64(15)
C(10)-C(11)-C(12)-N(13)	103.91(18)
C(8)-C(11)-C(12)-N(13)	-77.75(19)
C(11)-C(12)-N(13)-C(14)	179.28(14)
C(12)-N(13)-C(14)-C(15)	167.41(14)
N(13)-C(14)-C(15)-N(16)	-66.90(18)
C(14)-C(15)-N(16)-C(44)	166.01(13)
C(14)-C(15)-N(16)-C(17)	-68.75(17)
C(44)-N(16)-C(17)-C(18)	-79.78(16)
C(15)-N(16)-C(17)-C(18)	155.05(13)
N(16)-C(17)-C(18)-N(19)	-61.80(17)
C(17)-C(18)-N(19)-C(20)	175.84(13)
C(18)-N(19)-C(20)-C(21)	-179.33(13)
N(19)-C(20)-C(21)-C(22)	93.01(17)
N(19)-C(20)-C(21)-C(24)	-86.97(18)
C(24)-C(21)-C(22)-C(23)	0.7(2)
C(20)-C(21)-C(22)-C(23)	-179.26(15)
C(21)-C(22)-C(23)-C(26)	0.8(2)
C(22)-C(21)-C(24)-C(25)	-1.0(2)
C(20)-C(21)-C(24)-C(25)	178.97(15)
C(21)-C(24)-C(25)-C(26)	-0.2(2)
C(22)-C(23)-C(26)-C(25)	-2.0(2)
C(22)-C(23)-C(26)-C(27)	178.30(15)
C(24)-C(25)-C(26)-C(23)	1.7(2)
C(24)-C(25)-C(26)-C(27)	-178.57(15)
C(23)-C(26)-C(27)-N(28)	-6.4(2)
C(25)-C(26)-C(27)-N(28)	173.90(13)
C(26)-C(27)-N(28)-C(29)	-172.65(13)
C(27)-N(28)-C(29)-C(30)	-173.58(12)
C(31)-N(1)-C(30)-C(29)	155.63(12)
C(2)-N(1)-C(30)-C(29)	-79.72(15)
N(28)-C(29)-C(30)-N(1)	-65.64(16)
C(30)-N(1)-C(31)-C(32)	-77.74(15)
C(2)-N(1)-C(31)-C(32)	157.82(12)
N(1)-C(31)-C(32)-N(33)	-60.92(16)
C(31)-C(32)-N(33)-C(34)	175.09(13)
C(32)-N(33)-C(34)-C(35)	-175.05(13)
N(33)-C(34)-C(35)-C(36)	-41.4(2)
N(33)-C(34)-C(35)-C(38)	141.97(15)
C(38)-C(35)-C(36)-C(37)	0.1(3)
C(34)-C(35)-C(36)-C(37)	-176.50(16)
C(35)-C(36)-C(37)-C(40)	0.9(3)
C(36)-C(35)-C(38)-C(39)	-1.2(2)
C(34)-C(35)-C(38)-C(39)	175.51(15)
C(35)-C(38)-C(39)-C(40)	1.2(2)
C(36)-C(37)-C(40)-C(39)	-0.8(3)
C(36)-C(37)-C(40)-C(41)	176.98(16)
C(38)-C(39)-C(40)-C(37)	-0.2(2)
C(38)-C(39)-C(40)-C(41)	-177.90(15)
C(37)-C(40)-C(41)-N(42)	111.03(17)
C(39)-C(40)-C(41)-N(42)	-71.3(2)
C(40)-C(41)-N(42)-C(43)	-162.23(14)
C(41)-N(42)-C(43)-C(44)	-167.42(13)
C(17)-N(16)-C(44)-C(43)	151.69(13)
C(15)-N(16)-C(44)-C(43)	-81.89(15)
N(42)-C(43)-C(44)-N(16)	-63.14(17)

Table E-7. Hydrogen bonds for **[H$_6$13(F)$_2$(H$_2$O)][Cl]$_2$** [Å and °].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(4)-H(4B)···F(1)	0.92	1.75	2.6518(16)	165.6
N(4)-H(4A)···O(4S)	0.92	1.80	2.7032(18)	166.1
N(13)-H(13A)···F(2)	0.92	1.75	2.6612(16)	170.2
N(13)-H(13B)···F(2A)	0.92	1.86	2.7741(17)	173.7
N(19)-H(19A)···F(2)	0.92	1.77	2.6704(16)	167.0
N(19)-H(19B)···Cl(1)	0.92	2.23	3.1337(14)	167.7
N(28)-H(28A)···Cl(2)	0.92	2.20	3.1212(13)	174.6
N(28)-H(28B)···F(1)	0.92	1.72	2.6316(16)	168.1
N(33)-H(33A)···F(1)	0.92	1.77	2.6722(16)	166.4
N(33)-H(33B)···O(3S)#1	0.92	1.98	2.8829(17)	166.2
N(42)-H(42A)···F(2)	0.92	1.76	2.6607(16)	165.4
N(42)-H(42B)···F(1A)#2	0.92	1.89	2.7925(17)	166.8
N(42)-H(42B)···F(5A)#2	0.92	2.39	2.9653(18)	120.7
O(1S)-H(1SA)···F(1)	0.90	1.88	2.7418(15)	160.4
O(1S)-H(1SB)···F(2)	0.90	1.85	2.6792(15)	153.5
O(2S)-H(2SA)···O(1S)	0.79	1.89	2.6490(17)	163.6
O(2S)-H(2SB)···F(2A)	0.93	2.06	2.9239(18)	155.6
O(2S)-H(2SB)···F(3A)	0.93	2.35	3.0408(17)	131.7
O(3S)-H(3SA)···O(2S)	0.79	1.95	2.7313(17)	170.3
O(3S)-H(3SB)···O(5S)	0.77	1.94	2.7035(17)	171.2
O(4S)-H(4SA)···O(2S)	0.98	1.79	2.7535(18)	165.9
O(4S)-H(4SB)···O(3S)#1	0.71	2.18	2.8885(18)	178.0
O(5S)-H(5SA)···F(4A)	0.85	1.87	2.7039(17)	165.0
O(5S)-H(5SB)···O(6S)#3	0.82	1.96	2.7801(17)	173.6
O(6S)-H(6SA)···F(5A)	0.92	1.85	2.7249(17)	158.0
O(6S)-H(6SB)···O(9S)#1	0.89	1.87	2.7257(18)	159.7
O(7S)-H(7SA)···Cl(1)#4	0.85	2.32	3.1494(15)	166.3
O(7S)-H(7SB)···Cl(2)	0.85	2.32	3.1627(14)	171.0
O(8S)-H(8SA)···O(10S)#5	1.05	1.72	2.763(2)	171.2
O(8S)-H(8SB)···O(7S)	0.94	1.86	2.784(2)	164.3
O(9S)-H(9SA)···O(6S)#6	0.85	2.05	2.8493(19)	156.0

O(9S)-H(9SB)...Cl(2)	0.85	2.33	3.1847(14)	179.8
O(10S)-H(10S)...Cl(1)#7	0.93	2.21	3.1320(15)	169.5
O(10S)-H(10T)...F(6A)	0.89	1.83	2.6919(19)	162.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1, -z+1 #2 x-1, y, z #3 -x+1, -y+2, -z+1
#4 -x, -y+1, -z #5 -x+1, -y+1, -z #6 x-1, y-1, z
#7 -x+1, -y+2, -z

Structural Data for $H_613(Br)(H_2O)$

Table E-1. Crystal data and structure refinement for **$H_613(Br)(H_2O)$**.

Identification Code	01066a	
Empirical formula	$(C_{36}H_{60}N_8)^{6+}$ 6Br$^-$ 7.23(H_2O)	
	$C_{36}H_{74.46}Br_6N_8O_{7.23}$	
Formula weight	1214.63	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 10.7509(5) Å	α = 107.737(2)°
	b = 19.0486(8) Å	β = 101.134(2)°
	c = 26.3302(12) Å	γ = 90.680(2)°
Volume	5024.7(4) Å^3	
Z	4	
Density (calculated)	1.606 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
$F(000)$	2457	
Absorption coefficient	4.844 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7937 and 0.2191	
Theta range for data collection	1.59 to 30.54°	
Reflections collected	42510	
Independent reflections	29320 [R(int) = 0.0333]	
Data / restraints / parameters	29320 / 7 / 1070	
$wR(F^2$all data)	$wR2 = 0.1717$	
$R(F$ obsd data)	$R1 = 0.0619$	
Goodness-of-fit on F^2	1.060	
Observed data [I > 2σ(I)]	22733	
Largest and mean shift / s.u.	0.002and 0.000	
Largest diff. peak and hole	2.254 and -1.648 e/Å^3	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$ $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

Table E-2. Atomic coordinates and equivalent isotropic displacement parameters for **$H_613(Br)(H_2O)$**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1A)	0.5131(3)	0.3317(2)	0.04284(15)	0.0151(7)
C(2A)	0.5289(4)	0.2522(2)	0.03257(18)	0.0172(8)
C(3A)	0.4608(4)	0.2162(2)	0.06478(18)	0.0171(8)
N(4A)	0.5139(4)	0.2449(2)	0.12452(16)	0.0181(7)
C(5A)	0.4606(5)	0.1999(3)	0.15435(19)	0.0192(9)
C(6A)	0.4907(5)	0.2358(2)	0.21491(19)	0.0182(8)
C(7A)	0.6057(5)	0.2271(3)	0.2463(2)	0.0230(9)
C(8A)	0.6303(5)	0.2596(3)	0.3025(2)	0.0234(10)
C(9A)	0.4007(5)	0.2765(3)	0.2408(2)	0.0245(10)
C(10A)	0.4253(5)	0.3080(3)	0.2965(2)	0.0257(10)
C(11A)	0.5418(5)	0.3007(2)	0.32804(19)	0.0180(8)
C(12A)	0.5677(5)	0.3383(2)	0.38876(19)	0.0182(8)
N(13A)	0.6572(4)	0.4064(2)	0.40422(16)	0.0188(8)
C(14A)	0.6724(5)	0.4498(3)	0.46239(18)	0.0187(8)
C(15A)	0.7726(5)	0.5136(3)	0.4792(2)	0.0199(9)
N(16A)	0.7401(4)	0.5717(2)	0.45299(16)	0.0166(7)
C(17A)	0.6385(4)	0.6132(3)	0.47621(19)	0.0200(9)
C(18A)	0.5750(5)	0.6623(3)	0.44395(19)	0.0209(9)
N(19A)	0.5179(4)	0.6182(2)	0.38681(16)	0.0189(8)
C(20A)	0.4298(5)	0.6603(3)	0.3577(2)	0.0208(9)
C(21A)	0.3991(4)	0.6223(2)	0.29698(19)	0.0181(8)
C(22A)	0.4497(5)	0.6516(3)	0.2625(2)	0.0206(9)
C(23A)	0.4215(5)	0.6176(3)	0.2069(2)	0.0208(9)
C(24A)	0.3167(4)	0.5586(3)	0.2742(2)	0.0195(9)
C(25A)	0.2884(4)	0.5247(3)	0.2183(2)	0.0194(9)
C(26A)	0.3402(4)	0.5537(2)	0.18391(19)	0.0175(8)
C(27A)	0.3062(5)	0.5198(3)	0.12310(19)	0.0195(9)
N(28A)	0.3643(4)	0.4479(2)	0.10316(15)	0.0168(7)
C(29A)	0.3438(4)	0.4214(3)	0.04227(19)	0.0179(8)
C(30A)	0.3803(4)	0.3426(2)	0.02106(19)	0.0176(8)
C(31A)	0.5969(4)	0.3625(3)	0.01541(18)	0.0168(8)
C(32A)	0.7362(4)	0.3705(3)	0.04144(19)	0.0187(9)
N(33A)	0.7647(4)	0.4198(2)	0.09931(16)	0.0175(7)
C(34A)	0.9051(4)	0.4389(3)	0.1197(2)	0.0204(9)
C(35A)	0.9394(4)	0.4735(3)	0.1802(2)	0.0188(9)
C(36A)	0.9152(5)	0.5470(3)	0.2048(2)	0.0226(9)

C(37A)	0.9482(5)	0.5779(3)	0.2610(2)	0.0233(10)
C(38A)	0.9978(4)	0.4328(3)	0.2124(2)	0.0206(9)
C(39A)	1.0313(4)	0.4639(3)	0.2685(2)	0.0204(9)
C(40A)	1.0063(4)	0.5365(3)	0.2933(2)	0.0211(9)
C(41A)	1.0406(5)	0.5691(3)	0.3534(2)	0.0244(10)
N(42A)	0.9286(4)	0.5652(2)	0.37913(17)	0.0205(8)
C(43A)	0.9632(4)	0.5912(3)	0.44018(19)	0.0205(9)
C(44A)	0.8532(5)	0.6234(3)	0.4653(2)	0.0212(9)
N(1B)	0.2185(4)	1.0739(2)	0.46205(16)	0.0160(7)
C(2B)	0.2037(5)	1.0146(3)	0.48611(19)	0.0185(8)
C(3B)	0.2808(5)	0.9486(3)	0.46688(19)	0.0195(9)
N(4B)	0.2460(4)	0.9129(2)	0.40697(16)	0.0181(7)
C(5B)	0.3011(5)	0.8401(2)	0.38840(19)	0.0190(9)
C(6B)	0.2660(5)	0.8070(3)	0.32725(19)	0.0187(9)
C(7B)	0.1673(5)	0.7526(3)	0.3028(2)	0.0209(9)
C(8B)	0.1386(5)	0.7206(3)	0.24668(19)	0.0207(9)
C(9B)	0.3322(5)	0.8307(3)	0.2947(2)	0.0226(9)
C(10B)	0.3042(5)	0.7988(3)	0.2385(2)	0.0228(9)
C(11B)	0.2076(4)	0.7426(2)	0.21434(19)	0.0182(8)
C(12B)	0.1846(4)	0.7054(2)	0.15387(18)	0.0176(8)
N(13B)	0.0932(4)	0.7444(2)	0.12275(16)	0.0160(7)
C(14B)	0.0946(4)	0.7169(2)	0.06392(18)	0.0167(8)
C(15B)	-0.0041(4)	0.7513(2)	0.03122(19)	0.0171(8)
N(16B)	0.0228(4)	0.8313(2)	0.04214(16)	0.0146(7)
C(17B)	0.1326(4)	0.8424(2)	0.01851(19)	0.0177(8)
C(18B)	0.1920(4)	0.9208(3)	0.04011(19)	0.0185(8)
N(19B)	0.2386(4)	0.9438(2)	0.10057(16)	0.0166(7)
C(20B)	0.3090(5)	1.0188(2)	0.12165(19)	0.0186(9)
C(21B)	0.3320(4)	1.0504(2)	0.18258(19)	0.0180(8)
C(22B)	0.2511(5)	1.0989(3)	0.2072(2)	0.0265(11)
C(23B)	0.2742(5)	1.1307(3)	0.2630(2)	0.0270(11)
C(24B)	0.4353(5)	1.0310(3)	0.2154(2)	0.0280(11)
C(25B)	0.4588(5)	1.0633(3)	0.2716(2)	0.0280(11)
C(26B)	0.3805(5)	1.1143(3)	0.29556(19)	0.0191(9)
C(27B)	0.4103(5)	1.1543(3)	0.35603(19)	0.0203(9)
N(28B)	0.3618(4)	1.1116(2)	0.38797(16)	0.0180(7)
C(29B)	0.3807(5)	1.1567(2)	0.44727(19)	0.0187(9)
C(30B)	0.3482(4)	1.1100(3)	0.48151(19)	0.0189(9)
C(31B)	0.1278(5)	1.1297(3)	0.4795(2)	0.0205(9)
C(32B)	-0.0100(5)	1.1052(3)	0.4502(2)	0.0226(9)
N(33B)	-0.0274(4)	1.0909(3)	0.39040(17)	0.0221(8)
C(34B)	-0.1664(5)	1.0822(3)	0.3636(2)	0.0260(10)
C(35B)	-0.1887(5)	1.0483(3)	0.3029(2)	0.0229(10)
C(36B)	-0.1550(5)	1.0862(3)	0.2695(2)	0.0274(11)

C(37B)	-0.1805(5)	1.0534(3)	0.2131(2)	0.0244(10)
C(38B)	-0.2478(5)	0.9765(3)	0.2792(2)	0.0230(9)
C(39B)	-0.2738(5)	0.9449(3)	0.2232(2)	0.0226(9)
C(40B)	-0.2407(4)	0.9825(3)	0.1896(2)	0.0199(9)
C(41B)	-0.2746(4)	0.9470(3)	0.1286(2)	0.0201(9)
N(42B)	-0.1609(4)	0.9246(2)	0.10378(17)	0.0181(7)
C(43B)	-0.1964(4)	0.8724(3)	0.04757(19)	0.0184(8)
C(44B)	-0.0894(4)	0.8622(3)	0.01681(18)	0.0174(8)
Br(1A)	0.61489(5)	0.43220(3)	0.20533(2)	0.02505(15)
Br(1B)	0.673(2)	0.4806(12)	0.3067(11)	0.040(7)
Br(2)	0.19380(4)	0.31567(3)	0.119353(19)	0.01985(10)
Br(3)	0.33887(5)	0.48515(3)	0.397381(19)	0.02195(10)
Br(4)	0.61085(4)	0.56597(2)	0.09316(2)	0.02004(10)
Br(5)	0.09256(5)	0.92243(3)	0.19556(2)	0.02245(10)
Br(6)	0.43242(4)	0.81575(3)	0.116761(19)	0.01981(10)
Br(7)	0.54850(5)	0.98527(3)	0.396871(19)	0.02090(10)
Br(8)	0.11161(5)	1.23940(3)	0.38137(2)	0.02616(11)
Br(9)	-0.02488(4)	1.06897(3)	0.089495(19)	0.02003(10)
Br(10)	0.74250(5)	0.24912(3)	0.50003(2)	0.02703(11)
Br(11)	0.5000	0.0000	0.0000	0.02734(15)
Br(12)	0.0000	0.5000	0.0000	0.02385(14)
Br(13)	-0.06068(5)	0.89472(3)	0.37584(3)	0.02335(16)
Br(14)	-0.2301(6)	0.7377(3)	0.3780(2)	0.0357(17)
Br(15)	0.9456(10)	0.3927(6)	0.3798(5)	0.020(3)
O(1S)	0.5492(4)	0.4713(2)	0.32397(17)	0.0309(9)
O(2S)	0.7719(4)	0.2976(2)	0.14955(16)	0.0258(7)
O(3S)	0.8753(4)	0.3344(3)	0.42813(18)	0.0327(9)
O(4S)	0.7133(4)	0.6135(2)	0.32153(17)	0.0235(8)
O(5S)	0.8209(4)	0.4163(2)	0.32761(17)	0.0277(8)
O(6S)	0.1317(4)	0.9874(2)	0.3199(2)	0.0346(10)
O(7S)	-0.1390(4)	0.7948(2)	0.15128(17)	0.0279(8)
O(8S)	-0.1005(4)	0.6288(2)	0.09456(19)	0.0357(10)
O(9S)	0.0032(4)	0.2366(2)	0.17443(17)	0.0290(8)
O(10S)	0.6558(4)	0.7343(2)	0.18124(17)	0.0285(8)
O(11S)	-0.0199(5)	0.7365(3)	0.4087(2)	0.0359(11)
O(12S)	0.6263(4)	0.8085(2)	0.38029(18)	0.0288(9)
O(13S)	-0.0518(5)	1.2937(3)	0.28144(19)	0.0421(11)
O(14S)	-0.3126(4)	1.1297(2)	0.09682(19)	0.0389(11)
O(15S)	0.7597(4)	0.7405(3)	0.29028(19)	0.0309(9)

Table E-3. Bond lengths [Å] and angles [°] for **$H_6$13(Br)(H_2O)**.

N(1A)-C(2A)	1.473(6)	C(36A)-C(37A)	1.387(7)
N(1A)-C(30A)	1.474(6)	C(37A)-C(40A)	1.397(7)
N(1A)-C(31A)	1.475(6)	C(38A)-C(39A)	1.384(7)
C(2A)-C(3A)	1.518(6)	C(39A)-C(40A)	1.391(7)
C(3A)-N(4A)	1.490(6)	C(40A)-C(41A)	1.482(7)
N(4A)-C(5A)	1.501(6)	C(41A)-N(42A)	1.503(6)
C(5A)-C(6A)	1.498(6)	N(42A)-C(43A)	1.499(6)
C(6A)-C(7A)	1.390(7)	C(43A)-C(44A)	1.511(7)
C(6A)-C(9A)	1.397(7)	N(1B)-C(30B)	1.471(6)
C(7A)-C(8A)	1.391(7)	N(1B)-C(2B)	1.474(6)
C(8A)-C(11A)	1.383(7)	N(1B)-C(31B)	1.480(6)
C(9A)-C(10A)	1.376(7)	C(2B)-C(3B)	1.524(6)
C(10A)-C(11A)	1.396(7)	C(3B)-N(4B)	1.484(6)
C(11A)-C(12A)	1.507(6)	N(4B)-C(5B)	1.493(6)
C(12A)-N(13A)	1.506(6)	C(5B)-C(6B)	1.508(6)
N(13A)-C(14A)	1.478(6)	C(6B)-C(9B)	1.382(7)
C(14A)-C(15A)	1.514(7)	C(6B)-C(7B)	1.385(7)
C(15A)-N(16A)	1.484(6)	C(7B)-C(8B)	1.385(7)
N(16A)-C(17A)	1.475(6)	C(8B)-C(11B)	1.381(7)
N(16A)-C(44A)	1.476(6)	C(9B)-C(10B)	1.388(7)
C(17A)-C(18A)	1.530(7)	C(10B)-C(11B)	1.390(7)
C(18A)-N(19A)	1.486(6)	C(11B)-C(12B)	1.502(6)
N(19A)-C(20A)	1.496(6)	C(12B)-N(13B)	1.505(6)
C(20A)-C(21A)	1.509(7)	N(13B)-C(14B)	1.479(6)
C(21A)-C(22A)	1.387(7)	C(14B)-C(15B)	1.518(6)
C(21A)-C(24A)	1.395(6)	C(15B)-N(16B)	1.476(5)
C(22A)-C(23A)	1.379(7)	N(16B)-C(17B)	1.478(6)
C(23A)-C(26A)	1.390(6)	N(16B)-C(44B)	1.481(6)
C(24A)-C(25A)	1.386(7)	C(17B)-C(18B)	1.511(6)
C(25A)-C(26A)	1.388(7)	C(18B)-N(19B)	1.496(6)
C(26A)-C(27A)	1.501(6)	N(19B)-C(20B)	1.501(6)
C(27A)-N(28A)	1.500(6)	C(20B)-C(21B)	1.501(6)
N(28A)-C(29A)	1.497(6)	C(21B)-C(22B)	1.379(7)
C(29A)-C(30A)	1.519(6)	C(21B)-C(24B)	1.397(7)
C(31A)-C(32A)	1.507(6)	C(22B)-C(23B)	1.379(7)
C(32A)-N(33A)	1.496(6)	C(23B)-C(26B)	1.390(7)
N(33A)-C(34A)	1.501(6)	C(24B)-C(25B)	1.388(7)
C(34A)-C(35A)	1.496(7)	C(25B)-C(26B)	1.380(7)
C(35A)-C(38A)	1.386(7)	C(26B)-C(27B)	1.509(7)
C(35A)-C(36A)	1.403(7)	C(27B)-N(28B)	1.489(6)

N(28B)-C(29B)	1.508(6)	C(36B)-C(37B)	1.395(7)
C(29B)-C(30B)	1.527(7)	C(37B)-C(40B)	1.393(7)
C(31B)-C(32B)	1.527(7)	C(38B)-C(39B)	1.380(7)
C(32B)-N(33B)	1.487(6)	C(39B)-C(40B)	1.388(7)
N(33B)-C(34B)	1.508(6)	C(40B)-C(41B)	1.510(7)
C(34B)-C(35B)	1.499(7)	C(41B)-N(42B)	1.501(6)
C(35B)-C(36B)	1.389(8)	N(42B)-C(43B)	1.484(6)
C(35B)-C(38B)	1.403(7)	C(43B)-C(44B)	1.512(7)

C(2A)-N(1A)-C(30A)	109.7(3)	C(25A)-C(26A)-C(23A)	118.5(4)
C(2A)-N(1A)-C(31A)	109.9(3)	C(25A)-C(26A)-C(27A)	121.7(4)
C(30A)-N(1A)-C(31A)	108.6(4)	C(23A)-C(26A)-C(27A)	119.8(4)
N(1A)-C(2A)-C(3A)	114.9(4)	N(28A)-C(27A)-C(26A)	113.0(4)
N(4A)-C(3A)-C(2A)	112.5(4)	C(29A)-N(28A)-C(27A)	111.4(3)
C(3A)-N(4A)-C(5A)	111.4(3)	N(28A)-C(29A)-C(30A)	111.8(4)
C(6A)-C(5A)-N(4A)	112.8(4)	N(1A)-C(30A)-C(29A)	114.2(4)
C(7A)-C(6A)-C(9A)	119.1(4)	N(1A)-C(31A)-C(32A)	114.8(4)
C(7A)-C(6A)-C(5A)	120.9(4)	N(33A)-C(32A)-C(31A)	113.1(4)
C(9A)-C(6A)-C(5A)	119.9(4)	C(32A)-N(33A)-C(34A)	111.1(4)
C(6A)-C(7A)-C(8A)	119.8(5)	C(35A)-C(34A)-N(33A)	112.3(4)
C(11A)-C(8A)-C(7A)	121.1(5)	C(38A)-C(35A)-C(36A)	119.4(5)
C(10A)-C(9A)-C(6A)	120.8(5)	C(38A)-C(35A)-C(34A)	119.6(4)
C(9A)-C(10A)-C(11A)	120.3(5)	C(36A)-C(35A)-C(34A)	121.0(4)
C(8A)-C(11A)-C(10A)	119.0(4)	C(37A)-C(36A)-C(35A)	119.9(5)
C(8A)-C(11A)-C(12A)	122.0(4)	C(36A)-C(37A)-C(40A)	120.4(5)
C(10A)-C(11A)-C(12A)	119.0(4)	C(39A)-C(38A)-C(35A)	120.6(5)
N(13A)-C(12A)-C(11A)	110.5(4)	C(38A)-C(39A)-C(40A)	120.3(5)
C(14A)-N(13A)-C(12A)	112.1(4)	C(39A)-C(40A)-C(37A)	119.3(5)
N(13A)-C(14A)-C(15A)	111.9(4)	C(39A)-C(40A)-C(41A)	120.1(5)
N(16A)-C(15A)-C(14A)	114.6(4)	C(37A)-C(40A)-C(41A)	120.5(5)
C(17A)-N(16A)-C(44A)	108.4(4)	C(40A)-C(41A)-N(42A)	111.6(4)
C(17A)-N(16A)-C(15A)	108.8(4)	C(43A)-N(42A)-C(41A)	112.8(4)
C(44A)-N(16A)-C(15A)	109.0(4)	N(42A)-C(43A)-C(44A)	112.0(4)
N(16A)-C(17A)-C(18A)	113.9(4)	N(16A)-C(44A)-C(43A)	115.3(4)
N(19A)-C(18A)-C(17A)	111.2(4)	C(30B)-N(1B)-C(2B)	110.6(4)
C(18A)-N(19A)-C(20A)	112.8(4)	C(30B)-N(1B)-C(31B)	108.6(4)
N(19A)-C(20A)-C(21A)	111.6(4)	C(2B)-N(1B)-C(31B)	108.2(4)
C(22A)-C(21A)-C(24A)	118.6(4)	N(1B)-C(2B)-C(3B)	114.4(4)
C(22A)-C(21A)-C(20A)	120.4(4)	N(4B)-C(3B)-C(2B)	112.1(4)
C(24A)-C(21A)-C(20A)	121.0(4)	C(3B)-N(4B)-C(5B)	113.1(4)
C(23A)-C(22A)-C(21A)	120.8(4)	N(4B)-C(5B)-C(6B)	111.1(4)
C(22A)-C(23A)-C(26A)	120.8(5)	C(9B)-C(6B)-C(7B)	118.9(4)
C(25A)-C(24A)-C(21A)	120.3(5)	C(9B)-C(6B)-C(5B)	120.3(4)
C(24A)-C(25A)-C(26A)	120.9(4)	C(7B)-C(6B)-C(5B)	120.8(4)

C(6B)-C(7B)-C(8B)	120.5(5)
C(11B)-C(8B)-C(7B)	120.5(4)
C(6B)-C(9B)-C(10B)	120.9(5)
C(9B)-C(10B)-C(11B)	119.7(5)
C(8B)-C(11B)-C(10B)	119.4(4)
C(8B)-C(11B)-C(12B)	121.7(4)
C(10B)-C(11B)-C(12B)	118.9(4)
C(11B)-C(12B)-N(13B)	112.3(4)
C(14B)-N(13B)-C(12B)	110.7(3)
N(13B)-C(14B)-C(15B)	111.5(4)
N(16B)-C(15B)-C(14B)	113.9(4)
C(15B)-N(16B)-C(17B)	108.8(3)
C(15B)-N(16B)-C(44B)	109.8(3)
C(17B)-N(16B)-C(44B)	109.4(3)
N(16B)-C(17B)-C(18B)	113.4(4)
N(19B)-C(18B)-C(17B)	111.2(4)
C(18B)-N(19B)-C(20B)	111.5(4)
C(21B)-C(20B)-N(19B)	112.6(4)
C(22B)-C(21B)-C(24B)	118.8(5)
C(22B)-C(21B)-C(20B)	120.5(4)
C(24B)-C(21B)-C(20B)	120.7(4)
C(21B)-C(22B)-C(23B)	121.0(5)
C(22B)-C(23B)-C(26B)	120.3(5)
C(25B)-C(24B)-C(21B)	120.0(5)
C(26B)-C(25B)-C(24B)	120.6(5)
C(25B)-C(26B)-C(23B)	119.1(5)
C(25B)-C(26B)-C(27B)	121.3(4)
C(23B)-C(26B)-C(27B)	119.6(4)
N(28B)-C(27B)-C(26B)	112.8(4)
C(27B)-N(28B)-C(29B)	111.1(4)
N(28B)-C(29B)-C(30B)	111.2(4)
N(1B)-C(30B)-C(29B)	112.9(4)
N(1B)-C(31B)-C(32B)	113.7(4)
N(33B)-C(32B)-C(31B)	111.9(4)
C(32B)-N(33B)-C(34B)	111.2(4)
C(35B)-C(34B)-N(33B)	112.6(4)
C(36B)-C(35B)-C(38B)	119.1(5)
C(36B)-C(35B)-C(34B)	122.1(5)
C(38B)-C(35B)-C(34B)	118.8(5)
C(35B)-C(36B)-C(37B)	120.3(5)
C(40B)-C(37B)-C(36B)	120.4(5)
C(39B)-C(38B)-C(35B)	120.1(5)
C(38B)-C(39B)-C(40B)	121.1(5)
C(39B)-C(40B)-C(37B)	119.0(5)
C(39B)-C(40B)-C(41B)	119.5(4)
C(37B)-C(40B)-C(41B)	121.5(5)
N(42B)-C(41B)-C(40B)	113.1(4)
C(43B)-N(42B)-C(41B)	112.4(4)
N(42B)-C(43B)-C(44B)	113.7(4)
N(16B)-C(44B)-C(43B)	113.9(4)

Table E-4. Anisotropic displacement parameters (Å^{2}x 10^3) for **$H_6$13(Br)(H_2O)**. The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1A)	16(2)	14(2)	12(2)	0(1)	3(1)	2(1)
C(2A)	25(2)	14(2)	12(2)	1(2)	6(2)	5(2)
C(3A)	24(2)	12(2)	12(2)	-1(2)	3(2)	1(2)
N(4A)	25(2)	14(2)	13(2)	2(1)	4(1)	-1(1)
C(5A)	29(2)	15(2)	11(2)	-1(2)	7(2)	-2(2)
C(6A)	28(2)	12(2)	13(2)	0(2)	8(2)	0(2)
C(7A)	28(2)	24(2)	15(2)	3(2)	5(2)	6(2)
C(8A)	27(2)	24(2)	16(2)	1(2)	3(2)	6(2)
C(9A)	26(2)	27(2)	15(2)	0(2)	2(2)	7(2)
C(10A)	28(2)	29(3)	16(2)	0(2)	6(2)	6(2)
C(11A)	25(2)	13(2)	15(2)	2(2)	5(2)	2(2)
C(12A)	27(2)	14(2)	12(2)	1(2)	4(2)	0(2)
N(13A)	27(2)	20(2)	9(2)	2(2)	6(1)	2(2)
C(14A)	26(2)	18(2)	10(2)	1(2)	4(2)	3(2)
C(15A)	23(2)	21(2)	16(2)	6(2)	5(2)	0(2)
N(16A)	18(2)	14(2)	15(2)	2(1)	3(1)	0(1)
C(17A)	21(2)	21(2)	14(2)	-1(2)	4(2)	4(2)
C(18A)	25(2)	18(2)	14(2)	-2(2)	3(2)	4(2)
N(19A)	23(2)	14(2)	16(2)	-2(1)	5(2)	4(1)
C(20A)	26(2)	16(2)	19(2)	2(2)	6(2)	6(2)
C(21A)	21(2)	15(2)	16(2)	2(2)	4(2)	1(2)
C(22A)	24(2)	18(2)	17(2)	2(2)	3(2)	-3(2)
C(23A)	24(2)	17(2)	19(2)	3(2)	5(2)	-1(2)
C(24A)	21(2)	19(2)	15(2)	2(2)	3(2)	-2(2)
C(25A)	20(2)	17(2)	17(2)	-1(2)	3(2)	-3(2)
C(26A)	20(2)	14(2)	16(2)	1(2)	3(2)	3(2)
C(27A)	24(2)	17(2)	15(2)	1(2)	4(2)	7(2)
N(28A)	20(2)	16(2)	11(2)	0(1)	3(1)	5(1)
C(29A)	23(2)	18(2)	13(2)	3(2)	3(2)	4(2)
C(30A)	20(2)	14(2)	14(2)	-1(2)	1(2)	2(2)
C(31A)	23(2)	18(2)	8(2)	1(2)	6(2)	4(2)
C(32A)	20(2)	19(2)	14(2)	-1(2)	6(2)	2(2)
N(33A)	19(2)	20(2)	14(2)	4(2)	5(1)	2(1)
C(34A)	19(2)	24(2)	18(2)	4(2)	7(2)	2(2)
C(35A)	17(2)	20(2)	18(2)	3(2)	5(2)	-3(2)

C(36A)	24(2)	20(2)	21(2)	5(2)	2(2)	-1(2)
C(37A)	27(2)	18(2)	24(2)	4(2)	9(2)	-3(2)
C(38A)	18(2)	23(2)	19(2)	5(2)	4(2)	0(2)
C(39A)	19(2)	23(2)	21(2)	8(2)	6(2)	1(2)
C(40A)	17(2)	25(2)	20(2)	6(2)	3(2)	-6(2)
C(41A)	20(2)	32(3)	18(2)	3(2)	4(2)	-5(2)
N(42A)	16(2)	28(2)	16(2)	7(2)	0(1)	0(2)
C(43A)	18(2)	26(2)	15(2)	4(2)	3(2)	-1(2)
C(44A)	24(2)	19(2)	17(2)	0(2)	4(2)	-2(2)
N(1B)	20(2)	14(2)	13(2)	2(1)	4(1)	4(1)
C(2B)	25(2)	17(2)	12(2)	1(2)	6(2)	5(2)
C(3B)	26(2)	15(2)	13(2)	-1(2)	3(2)	4(2)
N(4B)	24(2)	16(2)	13(2)	3(2)	4(1)	5(1)
C(5B)	28(2)	15(2)	13(2)	1(2)	6(2)	7(2)
C(6B)	26(2)	15(2)	13(2)	3(2)	3(2)	4(2)
C(7B)	27(2)	19(2)	15(2)	3(2)	7(2)	0(2)
C(8B)	24(2)	19(2)	14(2)	0(2)	2(2)	-4(2)
C(9B)	27(2)	20(2)	16(2)	0(2)	4(2)	-5(2)
C(10B)	27(2)	24(2)	16(2)	5(2)	4(2)	-2(2)
C(11B)	24(2)	15(2)	14(2)	2(2)	4(2)	4(2)
C(12B)	22(2)	15(2)	11(2)	0(2)	1(2)	3(2)
N(13B)	20(2)	13(2)	13(2)	1(1)	4(1)	3(1)
C(14B)	23(2)	16(2)	9(2)	1(2)	3(2)	2(2)
C(15B)	23(2)	13(2)	13(2)	1(2)	2(2)	-1(2)
N(16B)	18(2)	12(2)	14(2)	4(1)	4(1)	1(1)
C(17B)	25(2)	16(2)	12(2)	3(2)	5(2)	1(2)
C(18B)	22(2)	19(2)	12(2)	2(2)	3(2)	-2(2)
N(19B)	19(2)	12(2)	15(2)	-2(1)	5(1)	-1(1)
C(20B)	24(2)	15(2)	14(2)	-1(2)	6(2)	-4(2)
C(21B)	21(2)	13(2)	17(2)	0(2)	6(2)	-1(2)
C(22B)	30(2)	29(3)	16(2)	0(2)	3(2)	11(2)
C(23B)	32(3)	26(2)	18(2)	-1(2)	4(2)	12(2)
C(24B)	24(2)	34(3)	21(2)	-2(2)	7(2)	11(2)
C(25B)	23(2)	38(3)	17(2)	1(2)	0(2)	10(2)
C(26B)	26(2)	15(2)	14(2)	0(2)	5(2)	0(2)
C(27B)	25(2)	19(2)	15(2)	3(2)	5(2)	-1(2)
N(28B)	23(2)	18(2)	11(2)	1(1)	4(1)	1(1)
C(29B)	23(2)	14(2)	14(2)	-2(2)	5(2)	-1(2)
C(30B)	21(2)	19(2)	14(2)	1(2)	4(2)	0(2)
C(31B)	25(2)	17(2)	18(2)	0(2)	9(2)	7(2)
C(32B)	25(2)	26(2)	19(2)	7(2)	9(2)	10(2)
N(33B)	20(2)	29(2)	19(2)	7(2)	7(2)	5(2)
C(34B)	20(2)	37(3)	21(2)	6(2)	7(2)	6(2)
C(35B)	20(2)	25(2)	22(2)	3(2)	6(2)	7(2)
C(36B)	31(3)	25(2)	24(3)	2(2)	9(2)	3(2)

C(37B)	33(3)	23(2)	19(2)	4(2)	12(2)	5(2)
C(38B)	24(2)	25(2)	20(2)	7(2)	6(2)	4(2)
C(39B)	21(2)	24(2)	22(2)	5(2)	5(2)	5(2)
C(40B)	19(2)	23(2)	19(2)	5(2)	9(2)	8(2)
C(41B)	16(2)	23(2)	21(2)	5(2)	8(2)	5(2)
N(42B)	17(2)	19(2)	17(2)	4(2)	4(1)	2(1)
C(43B)	19(2)	18(2)	12(2)	-2(2)	2(2)	0(2)
C(44B)	23(2)	16(2)	11(2)	2(2)	2(2)	3(2)
Br(1A)	24(1)	31(1)	24(1)	11(1)	9(1)	8(1)
Br(1B)	38(11)	28(10)	61(16)	17(10)	27(11)	10(8)
Br(2)	23(1)	19(1)	17(1)	1(1)	7(1)	3(1)
Br(3)	27(1)	22(1)	15(1)	3(1)	7(1)	2(1)
Br(4)	22(1)	16(1)	20(1)	2(1)	6(1)	2(1)
Br(5)	26(1)	21(1)	19(1)	4(1)	5(1)	2(1)
Br(6)	22(1)	20(1)	15(1)	1(1)	5(1)	2(1)
Br(7)	25(1)	18(1)	16(1)	1(1)	3(1)	3(1)
Br(8)	31(1)	26(1)	22(1)	7(1)	9(1)	8(1)
Br(9)	25(1)	17(1)	17(1)	3(1)	5(1)	3(1)
Br(10)	29(1)	26(1)	30(1)	12(1)	10(1)	6(1)
Br(11)	29(1)	23(1)	26(1)	0(1)	8(1)	-2(1)
Br(12)	28(1)	21(1)	22(1)	3(1)	9(1)	4(1)
Br(13)	22(1)	19(1)	25(1)	3(1)	1(1)	3(1)
Br(14)	39(3)	41(3)	18(3)	-3(2)	4(2)	-10(2)
Br(15)	22(3)	19(3)	20(3)	3(2)	8(2)	2(2)
O(1S)	36(2)	28(2)	26(2)	4(2)	10(2)	7(2)
O(2S)	27(2)	23(2)	25(2)	4(2)	3(1)	1(1)
O(3S)	28(2)	43(2)	33(2)	17(2)	11(2)	12(2)
O(4S)	25(2)	28(2)	21(2)	11(2)	6(2)	6(2)
O(5S)	32(2)	26(2)	24(2)	5(2)	9(2)	2(2)
O(6S)	21(2)	19(2)	64(3)	15(2)	5(2)	10(1)
O(7S)	30(2)	23(2)	29(2)	2(2)	14(2)	3(2)
O(8S)	33(2)	25(2)	43(3)	-4(2)	21(2)	-5(2)
O(9S)	39(2)	19(2)	30(2)	3(2)	16(2)	2(2)
O(10S)	29(2)	20(2)	32(2)	5(2)	2(2)	3(1)
O(11S)	43(3)	29(2)	38(3)	13(2)	9(2)	10(2)
O(12S)	37(2)	23(2)	25(2)	2(2)	10(2)	2(2)
O(13S)	53(3)	45(3)	32(2)	16(2)	12(2)	23(2)
O(14S)	28(2)	31(2)	41(3)	-9(2)	0(2)	10(2)
O(15S)	34(2)	32(2)	26(2)	10(2)	2(2)	-2(2)

Table E-5. Hydrogen coordinates and isotropic displacement parameters for **$H_6$13(Br)(H_2O)**.

	x	y	z	U(eq)
H(2AA)	0.6208	0.2452	0.0413	0.021
H(2AB)	0.4974	0.2262	-0.0068	0.021
H(3AA)	0.3695	0.2252	0.0578	0.020
H(3AB)	0.4677	0.1621	0.0519	0.020
H(4AA)	0.4951	0.2933	0.1377	0.022
H(4AB)	0.6009	0.2439	0.1307	0.022
H(5AA)	0.3671	0.1923	0.1415	0.023
H(5AB)	0.4954	0.1508	0.1456	0.023
H(7A)	0.6674	0.1989	0.2293	0.028
H(8A)	0.7090	0.2536	0.3238	0.028
H(9A)	0.3217	0.2824	0.2197	0.029
H(10A)	0.3627	0.3349	0.3136	0.031
H(12A)	0.4868	0.3523	0.4004	0.022
H(12B)	0.6056	0.3037	0.4078	0.022
H(13A)	0.7353	0.3925	0.3971	0.023
H(13B)	0.6266	0.4355	0.3831	0.023
H(14A)	0.6966	0.4170	0.4850	0.022
H(14B)	0.5901	0.4692	0.4692	0.022
H(15A)	0.7873	0.5366	0.5192	0.024
H(15B)	0.8532	0.4939	0.4702	0.024
H(17A)	0.6748	0.6444	0.5140	0.024
H(17B)	0.5728	0.5776	0.4779	0.024
H(18A)	0.5080	0.6881	0.4618	0.025
H(18B)	0.6390	0.7002	0.4440	0.025
H(19A)	0.4738	0.5765	0.3868	0.023
H(19B)	0.5819	0.6032	0.3682	0.023
H(20A)	0.4696	0.7106	0.3654	0.025
H(20B)	0.3501	0.6653	0.3716	0.025
H(22A)	0.5044	0.6957	0.2773	0.025
H(23A)	0.4581	0.6381	0.1839	0.025
H(24A)	0.2799	0.5382	0.2971	0.023
H(25A)	0.2328	0.4810	0.2032	0.023
H(27A)	0.2125	0.5114	0.1114	0.023
H(27B)	0.3348	0.5549	0.1060	0.023
H(28A)	0.4501	0.4539	0.1178	0.020
H(28B)	0.3287	0.4129	0.1148	0.020
H(29A)	0.3952	0.4544	0.0303	0.022
H(29B)	0.2532	0.4239	0.0265	0.022
H(30A)	0.3232	0.3094	0.0304	0.021

H(30B)	0.3665	0.3280	-0.0192	0.021
H(31A)	0.5696	0.4117	0.0147	0.020
H(31B)	0.5854	0.3302	-0.0228	0.020
H(32A)	0.7653	0.3210	0.0402	0.022
H(32B)	0.7846	0.3909	0.0201	0.022
H(33A)	0.7346	0.3963	0.1208	0.021
H(33B)	0.7238	0.4624	0.1018	0.021
H(34A)	0.9504	0.3934	0.1092	0.024
H(34B)	0.9336	0.4735	0.1021	0.024
H(36A)	0.8762	0.5755	0.1830	0.027
H(37A)	0.9312	0.6276	0.2777	0.028
H(38A)	1.0149	0.3832	0.1959	0.025
H(39A)	1.0716	0.4355	0.2901	0.025
H(41A)	1.0729	0.6213	0.3629	0.029
H(41B)	1.1096	0.5422	0.3681	0.029
H(42A)	0.8677	0.5938	0.3678	0.025
H(42B)	0.8939	0.5172	0.3674	0.025
H(43A)	1.0357	0.6291	0.4524	0.025
H(43B)	0.9906	0.5490	0.4531	0.025
H(44A)	0.8831	0.6426	0.5053	0.025
H(44B)	0.8276	0.6659	0.4526	0.025
H(2BA)	0.1127	0.9971	0.4772	0.022
H(2BB)	0.2294	1.0355	0.5263	0.022
H(3BA)	0.3724	0.9652	0.4774	0.023
H(3BB)	0.2665	0.9119	0.4853	0.023
H(4BA)	0.2738	0.9440	0.3900	0.022
H(4BB)	0.1588	0.9060	0.3964	0.022
H(5BA)	0.2693	0.8058	0.4055	0.023
H(5BB)	0.3948	0.8469	0.4002	0.023
H(7B)	0.1190	0.7371	0.3246	0.025
H(8B)	0.0709	0.6832	0.2303	0.025
H(9B)	0.3978	0.8694	0.3110	0.027
H(10B)	0.3509	0.8153	0.2165	0.027
H(12C)	0.1502	0.6538	0.1454	0.021
H(12D)	0.2665	0.7040	0.1418	0.021
H(13C)	0.0124	0.7367	0.1278	0.019
H(13D)	0.1154	0.7944	0.1359	0.019
H(14C)	0.0775	0.6625	0.0506	0.020
H(14D)	0.1800	0.7286	0.0584	0.020
H(15C)	-0.0095	0.7257	-0.0081	0.021
H(15D)	-0.0881	0.7430	0.0395	0.021
H(17C)	0.1045	0.8288	-0.0216	0.021
H(17D)	0.1978	0.8088	0.0263	0.021
H(18C)	0.2640	0.9246	0.0224	0.022
H(18D)	0.1285	0.9546	0.0309	0.022

H(19C)	0.2916	0.9098	0.1093	0.020
H(19D)	0.1705	0.9445	0.1172	0.020
H(20C)	0.3918	1.0153	0.1102	0.022
H(20D)	0.2595	1.0529	0.1052	0.022
H(22B)	0.1783	1.1106	0.1853	0.032
H(23B)	0.2173	1.1638	0.2792	0.032
H(24B)	0.4895	0.9957	0.1993	0.034
H(25B)	0.5295	1.0501	0.2937	0.034
H(27C)	0.5036	1.1641	0.3687	0.024
H(27D)	0.3722	1.2025	0.3630	0.024
H(28C)	0.4039	1.0692	0.3848	0.022
H(28D)	0.2767	1.0980	0.3740	0.022
H(29C)	0.3259	1.1987	0.4511	0.022
H(29D)	0.4702	1.1772	0.4609	0.022
H(30C)	0.4096	1.0716	0.4809	0.023
H(30D)	0.3574	1.1419	0.5197	0.023
H(31C)	0.1530	1.1758	0.4728	0.025
H(31D)	0.1336	1.1411	0.5192	0.025
H(32C)	-0.0363	1.0596	0.4572	0.027
H(32D)	-0.0655	1.1440	0.4650	0.027
H(33C)	0.0104	1.0486	0.3754	0.026
H(33D)	0.0118	1.1296	0.3839	0.026
H(34C)	-0.2127	1.0508	0.3788	0.031
H(34D)	-0.2013	1.1314	0.3723	0.031
H(36B)	-0.1145	1.1347	0.2852	0.033
H(37B)	-0.1566	1.0795	0.1906	0.029
H(38B)	-0.2699	0.9496	0.3016	0.028
H(39B)	-0.3150	0.8966	0.2075	0.027
H(41C)	-0.3337	0.9027	0.1200	0.024
H(41D)	-0.3196	0.9821	0.1119	0.024
H(42C)	-0.1176	0.9662	0.1031	0.022
H(42D)	-0.1073	0.9028	0.1252	0.022
H(43C)	-0.2690	0.8907	0.0270	0.022
H(43D)	-0.2249	0.8238	0.0493	0.022
H(44C)	-0.1217	0.8289	-0.0207	0.021
H(44D)	-0.0623	0.9107	0.0142	0.021
H(1SA)	0.5678	0.4604	0.2907	0.037
H(1SB)	0.4889	0.4598	0.3405	0.037
H(2SA)	0.7578	0.3252	0.1821	0.031
H(2SB)	0.8426	0.2746	0.1573	0.031
H(3SA)	0.9455	0.3167	0.4168	0.039
H(3SB)	0.8488	0.3039	0.4449	0.039
H(4SA)	0.7310	0.6489	0.3080	0.028
H(4SB)	0.6941	0.5709	0.2958	0.028
H(5SA)	0.7538	0.4104	0.2999	0.033

H(5SB)	0.8654	0.3763	0.3195	0.033
H(6SA)	0.1246	0.9841	0.2870	0.042
H(6SB)	0.0765	0.9597	0.3272	0.042
H(7SA)	-0.0912	0.8308	0.1788	0.033
H(7SB)	-0.1827	0.7708	0.1678	0.033
H(8SA)	-0.1827	0.6161	0.0917	0.043
H(8SB)	-0.0686	0.5890	0.0747	0.043
H(9SA)	0.0593	0.2587	0.1626	0.035
H(9SB)	-0.0153	0.1897	0.1536	0.035
H(10C)	0.6459	0.6863	0.1611	0.034
H(10D)	0.5887	0.7549	0.1670	0.034
H(11A)	-0.0259	0.7796	0.4015	0.043
H(11B)	0.0503	0.7433	0.4346	0.043
H(12E)	0.6729	0.7917	0.3546	0.035
H(12F)	0.6330	0.8581	0.3886	0.035
H(13E)	0.0135	1.2726	0.2982	0.050
H(13F)	-0.0456	1.2760	0.2459	0.050
H(14E)	-0.2346	1.1243	0.0891	0.047
H(14F)	-0.3627	1.0968	0.0676	0.047
H(15E)	0.8246	0.7767	0.3000	0.037
H(15F)	0.7291	0.7383	0.2552	0.037

Table E-6. Torsion angles [°] for **H$_6$13(Br)(H$_2$O)**.

C(30A)-N(1A)-C(2A)-C(3A)	-68.5(5)
C(31A)-N(1A)-C(2A)-C(3A)	172.2(4)
N(1A)-C(2A)-C(3A)-N(4A)	-65.9(5)
C(2A)-C(3A)-N(4A)-C(5A)	-170.3(4)
C(3A)-N(4A)-C(5A)-C(6A)	-168.3(4)
N(4A)-C(5A)-C(6A)-C(7A)	-84.4(5)
N(4A)-C(5A)-C(6A)-C(9A)	97.9(5)
C(9A)-C(6A)-C(7A)-C(8A)	-0.9(8)
C(5A)-C(6A)-C(7A)-C(8A)	-178.7(5)
C(6A)-C(7A)-C(8A)-C(11A)	0.1(8)
C(7A)-C(6A)-C(9A)-C(10A)	0.4(8)
C(5A)-C(6A)-C(9A)-C(10A)	178.2(5)
C(6A)-C(9A)-C(10A)-C(11A)	1.0(8)
C(7A)-C(8A)-C(11A)-C(10A)	1.3(8)
C(7A)-C(8A)-C(11A)-C(12A)	-178.3(5)
C(9A)-C(10A)-C(11A)-C(8A)	-1.8(8)
C(9A)-C(10A)-C(11A)-C(12A)	177.8(5)

C(8A)-C(11A)-C(12A)-N(13A)	75.3(6)
C(10A)-C(11A)-C(12A)-N(13A)	-104.3(5)
C(11A)-C(12A)-N(13A)-C(14A)	173.0(4)
C(12A)-N(13A)-C(14A)-C(15A)	174.1(4)
N(13A)-C(14A)-C(15A)-N(16A)	65.9(5)
C(14A)-C(15A)-N(16A)-C(17A)	71.6(5)
C(14A)-C(15A)-N(16A)-C(44A)	-170.4(4)
C(44A)-N(16A)-C(17A)-C(18A)	75.0(5)
C(15A)-N(16A)-C(17A)-C(18A)	-166.6(4)
N(16A)-C(17A)-C(18A)-N(19A)	58.9(5)
C(17A)-C(18A)-N(19A)-C(20A)	166.6(4)
C(18A)-N(19A)-C(20A)-C(21A)	165.7(4)
N(19A)-C(20A)-C(21A)-C(22A)	-107.8(5)
N(19A)-C(20A)-C(21A)-C(24A)	74.1(6)
C(24A)-C(21A)-C(22A)-C(23A)	-1.4(7)
C(20A)-C(21A)-C(22A)-C(23A)	-179.5(4)
C(21A)-C(22A)-C(23A)-C(26A)	1.0(7)
C(22A)-C(21A)-C(24A)-C(25A)	1.2(7)
C(20A)-C(21A)-C(24A)-C(25A)	179.3(4)
C(21A)-C(24A)-C(25A)-C(26A)	-0.6(7)
C(24A)-C(25A)-C(26A)-C(23A)	0.1(7)
C(24A)-C(25A)-C(26A)-C(27A)	-177.3(4)
C(22A)-C(23A)-C(26A)-C(25A)	-0.3(7)
C(22A)-C(23A)-C(26A)-C(27A)	177.1(4)
C(25A)-C(26A)-C(27A)-N(28A)	-72.8(6)
C(23A)-C(26A)-C(27A)-N(28A)	109.8(5)
C(26A)-C(27A)-N(28A)-C(29A)	-171.8(4)
C(27A)-N(28A)-C(29A)-C(30A)	-169.5(4)
C(2A)-N(1A)-C(30A)-C(29A)	164.3(4)
C(31A)-N(1A)-C(30A)-C(29A)	-75.6(5)
N(28A)-C(29A)-C(30A)-N(1A)	-57.6(5)
C(2A)-N(1A)-C(31A)-C(32A)	-72.6(5)
C(30A)-N(1A)-C(31A)-C(32A)	167.4(4)
N(1A)-C(31A)-C(32A)-N(33A)	-59.4(5)
C(31A)-C(32A)-N(33A)-C(34A)	-168.1(4)
C(32A)-N(33A)-C(34A)-C(35A)	-167.2(4)
N(33A)-C(34A)-C(35A)-C(38A)	106.0(5)
N(33A)-C(34A)-C(35A)-C(36A)	-75.0(6)
C(38A)-C(35A)-C(36A)-C(37A)	-0.9(7)
C(34A)-C(35A)-C(36A)-C(37A)	-179.8(4)
C(35A)-C(36A)-C(37A)-C(40A)	0.5(7)
C(36A)-C(35A)-C(38A)-C(39A)	0.5(7)
C(34A)-C(35A)-C(38A)-C(39A)	179.5(4)
C(35A)-C(38A)-C(39A)-C(40A)	0.2(7)
C(38A)-C(39A)-C(40A)-C(37A)	-0.6(7)

C(38A)-C(39A)-C(40A)-C(41A)	179.0(4)
C(36A)-C(37A)-C(40A)-C(39A)	0.3(7)
C(36A)-C(37A)-C(40A)-C(41A)	-179.4(5)
C(39A)-C(40A)-C(41A)-N(42A)	-97.4(5)
C(37A)-C(40A)-C(41A)-N(42A)	82.3(6)
C(40A)-C(41A)-N(42A)-C(43A)	174.5(4)
C(41A)-N(42A)-C(43A)-C(44A)	151.2(4)
C(17A)-N(16A)-C(44A)-C(43A)	-175.0(4)
C(15A)-N(16A)-C(44A)-C(43A)	66.7(5)
N(42A)-C(43A)-C(44A)-N(16A)	62.0(6)
C(30B)-N(1B)-C(2B)-C(3B)	-67.6(5)
C(31B)-N(1B)-C(2B)-C(3B)	173.6(4)
N(1B)-C(2B)-C(3B)-N(4B)	-59.7(5)
C(2B)-C(3B)-N(4B)-C(5B)	-168.9(4)
C(3B)-N(4B)-C(5B)-C(6B)	-178.5(4)
N(4B)-C(5B)-C(6B)-C(9B)	80.3(6)
N(4B)-C(5B)-C(6B)-C(7B)	-99.7(5)
C(9B)-C(6B)-C(7B)-C(8B)	2.4(7)
C(5B)-C(6B)-C(7B)-C(8B)	-177.7(4)
C(6B)-C(7B)-C(8B)-C(11B)	-0.3(8)
C(7B)-C(6B)-C(9B)-C(10B)	-2.6(7)
C(5B)-C(6B)-C(9B)-C(10B)	177.5(5)
C(6B)-C(9B)-C(10B)-C(11B)	0.6(8)
C(7B)-C(8B)-C(11B)-C(10B)	-1.7(7)
C(7B)-C(8B)-C(11B)-C(12B)	175.8(4)
C(9B)-C(10B)-C(11B)-C(8B)	1.6(7)
C(9B)-C(10B)-C(11B)-C(12B)	-176.0(4)
C(8B)-C(11B)-C(12B)-N(13B)	94.2(5)
C(10B)-C(11B)-C(12B)-N(13B)	-88.3(5)
C(11B)-C(12B)-N(13B)-C(14B)	167.4(4)
C(12B)-N(13B)-C(14B)-C(15B)	175.7(4)
N(13B)-C(14B)-C(15B)-N(16B)	67.4(5)
C(14B)-C(15B)-N(16B)-C(17B)	71.1(5)
C(14B)-C(15B)-N(16B)-C(44B)	-169.3(4)
C(15B)-N(16B)-C(17B)-C(18B)	-163.8(4)
C(44B)-N(16B)-C(17B)-C(18B)	76.3(5)
N(16B)-C(17B)-C(18B)-N(19B)	59.7(5)
C(17B)-C(18B)-N(19B)-C(20B)	174.5(4)
C(18B)-N(19B)-C(20B)-C(21B)	167.5(4)
N(19B)-C(20B)-C(21B)-C(22B)	-96.5(5)
N(19B)-C(20B)-C(21B)-C(24B)	83.4(6)
C(24B)-C(21B)-C(22B)-C(23B)	2.9(8)
C(20B)-C(21B)-C(22B)-C(23B)	-177.2(5)
C(21B)-C(22B)-C(23B)-C(26B)	0.3(9)
C(22B)-C(21B)-C(24B)-C(25B)	-3.2(8)

C(20B)-C(21B)-C(24B)-C(25B)	176.9(5)
C(21B)-C(24B)-C(25B)-C(26B)	0.3(9)
C(24B)-C(25B)-C(26B)-C(23B)	2.9(9)
C(24B)-C(25B)-C(26B)-C(27B)	-175.2(5)
C(22B)-C(23B)-C(26B)-C(25B)	-3.2(8)
C(22B)-C(23B)-C(26B)-C(27B)	175.0(5)
C(25B)-C(26B)-C(27B)-N(28B)	-85.5(6)
C(23B)-C(26B)-C(27B)-N(28B)	96.4(5)
C(26B)-C(27B)-N(28B)-C(29B)	-173.7(4)
C(27B)-N(28B)-C(29B)-C(30B)	-172.1(4)
C(2B)-N(1B)-C(30B)-C(29B)	164.5(4)
C(31B)-N(1B)-C(30B)-C(29B)	-76.9(5)
N(28B)-C(29B)-C(30B)-N(1B)	-55.8(5)
C(30B)-N(1B)-C(31B)-C(32B)	165.3(4)
C(2B)-N(1B)-C(31B)-C(32B)	-74.6(5)
N(1B)-C(31B)-C(32B)-N(33B)	-61.6(5)
C(31B)-C(32B)-N(33B)-C(34B)	-168.2(4)
C(32B)-N(33B)-C(34B)-C(35B)	-164.7(4)
N(33B)-C(34B)-C(35B)-C(36B)	-70.5(6)
N(33B)-C(34B)-C(35B)-C(38B)	110.8(5)
C(38B)-C(35B)-C(36B)-C(37B)	0.4(8)
C(34B)-C(35B)-C(36B)-C(37B)	-178.3(5)
C(35B)-C(36B)-C(37B)-C(40B)	0.5(8)
C(36B)-C(35B)-C(38B)-C(39B)	-1.2(7)
C(34B)-C(35B)-C(38B)-C(39B)	177.6(4)
C(35B)-C(38B)-C(39B)-C(40B)	1.0(7)
C(38B)-C(39B)-C(40B)-C(37B)	-0.1(7)
C(38B)-C(39B)-C(40B)-C(41B)	-178.0(4)
C(36B)-C(37B)-C(40B)-C(39B)	-0.6(7)
C(36B)-C(37B)-C(40B)-C(41B)	177.2(5)
C(39B)-C(40B)-C(41B)-N(42B)	-110.3(5)
C(37B)-C(40B)-C(41B)-N(42B)	71.9(6)
C(40B)-C(41B)-N(42B)-C(43B)	164.3(4)
C(41B)-N(42B)-C(43B)-C(44B)	166.9(4)
C(15B)-N(16B)-C(44B)-C(43B)	76.0(5)
C(17B)-N(16B)-C(44B)-C(43B)	-164.7(4)
N(42B)-C(43B)-C(44B)-N(16B)	61.5(5)

Table E-7. Hydrogen bonds for **$H_6$13(Br)(H_2O)** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4A)-H(4AB)...O(2S)	0.92	1.99	2.822(5)	149.2
N(4A)-H(4AB)...O(14S)#1	0.92	2.36	2.911(6)	118.2
N(13A)-H(13A)...O(3S)	0.92	2.07	2.794(6)	134.9
N(13A)-H(13A)...O(5S)	0.92	2.36	2.967(6)	123.8
N(19A)-H(19A)...Br(3)	0.92	2.37	3.275(4)	169.2
N(19A)-H(19B)...O(4S)	0.92	2.09	2.946(6)	155.2
N(28A)-H(28A)...Br(1A)	0.92	2.76	3.507(4)	138.5
N(28A)-H(28A)...Br(4)	0.92	3.03	3.556(4)	118.3
N(28A)-H(28B)...Br(2)	0.92	2.39	3.276(4)	162.9
N(33A)-H(33A)...O(2S)	0.92	2.24	3.002(6)	139.2
N(33A)-H(33A)...Br(1A)	0.92	2.70	3.433(4)	137.6
N(33A)-H(33B)...Br(4)	0.92	2.37	3.287(4)	171.1
N(42A)-H(42A)...O(4S)	0.92	1.97	2.837(5)	155.7
N(42A)-H(42A)...Br(14)#2	0.92	2.90	3.726(8)	149.8
N(42A)-H(42B)...O(5S)	0.92	1.96	2.864(6)	168.4
N(4B)-H(4BA)...O(6S)	0.92	2.51	3.117(6)	123.8
N(4B)-H(4BA)...Br(7)	0.92	3.00	3.606(4)	124.4
N(4B)-H(4BB)...Br(13)	0.92	2.31	3.228(4)	175.9
N(13B)-H(13C)...O(7S)	0.92	2.07	2.839(5)	140.6
N(13B)-H(13C)...O(8S)	0.92	2.21	2.834(5)	124.2
N(13B)-H(13D)...Br(5)	0.92	2.51	3.350(4)	151.7
N(19B)-H(19C)...Br(6)	0.92	2.39	3.299(4)	170.6
N(19B)-H(19D)...Br(5)	0.92	2.52	3.318(4)	145.8
N(28B)-H(28C)...Br(7)	0.92	2.29	3.186(4)	164.0
N(28B)-H(28D)...O(6S)	0.92	2.48	3.240(6)	140.4
N(33B)-H(33C)...O(6S)	0.92	2.22	3.056(6)	150.6
N(33B)-H(33C)...Br(13)	0.92	3.02	3.645(5)	126.3
N(33B)-H(33D)...Br(8)	0.92	2.36	3.277(5)	171.1
N(42B)-H(42C)...Br(9)	0.92	2.34	3.254(4)	172.0
N(42B)-H(42D)...O(7S)	0.92	2.40	3.086(6)	131.4
N(42B)-H(42D)...Br(5)	0.92	2.49	3.285(4)	144.5

O(1S)-H(1SB)...Br(3)	0.91	2.36	3.211(4)	155.5
O(1S)-H(1SA)...O(4S)	0.90	3.09	3.238(6)	91.1
O(1S)-H(1SA)...O(5S)	0.90	2.93	3.110(6)	92.9
O(1S)-H(1SA)...Br(1A)	0.90	2.30	3.203(4)	179.9
O(2S)-H(2SA)...Br(1A)	0.90	2.56	3.217(4)	130.0
O(2S)-H(2SB)...O(9S)#2	0.90	1.91	2.803(6)	173.2
O(3S)-H(3SA)...Br(8)#1	0.90	2.47	3.347(4)	166.4
O(3S)-H(3SB)...Br(10)	0.90	2.46	3.334(5)	164.3
O(4S)-H(4SA)...O(15S)	0.89	1.97	2.850(6)	168.9
O(4S)-H(4SB)...Br(1A)	0.88	2.95	3.825(4)	176.0
O(5S)-H(5SA)...Br(1A)	0.90	2.79	3.636(4)	156.1
O(5S)-H(5SB)...O(13S)#1	0.90	1.92	2.791(6)	163.5
O(6S)-H(6SA)...Br(5)	0.84	2.29	3.067(5)	154.8
O(6S)-H(6SB)...Br(13)	0.87	2.65	3.498(5)	165.1
O(7S)-H(7SA)...Br(5)	0.90	2.50	3.237(4)	139.6
O(7S)-H(7SB)...O(10S)#3	0.90	2.00	2.824(6)	152.2
O(8S)-H(8SA)...Br(4)#3	0.90	2.42	3.303(4)	169.2
O(8S)-H(8SB)...Br(12)	0.89	2.42	3.282(4)	162.3
O(9S)-H(9SA)...Br(2)	0.89	2.43	3.313(4)	172.8
O(9S)-H(9SB)...Br(9)#4	0.89	2.39	3.265(4)	167.0
O(10S)-H(10C)...Br(4)	0.90	2.41	3.301(4)	169.6
O(10S)-H(10D)...Br(6)	0.90	2.46	3.343(4)	168.7
O(11S)-H(11A)...Br(13)	0.90	2.50	3.391(5)	175.0
O(11S)-H(11B)...Br(10)#5	0.89	2.51	3.399(5)	173.6
O(12S)-H(12E)...Br(13)#2	0.90	3.31	3.765(5)	113.9
O(12S)-H(12F)...Br(7)	0.90	2.56	3.398(4)	155.0
O(13S)-H(13E)...Br(8)	0.92	2.50	3.316(4)	147.4
O(13S)-H(13F)...O(9S)#6	0.91	1.98	2.874(6)	168.9
O(14S)-H(14E)...Br(9)	0.90	2.50	3.335(4)	154.5
O(14S)-H(14F)...Br(11)#7	0.90	2.38	3.275(4)	171.1
O(15S)-H(15E)...Br(13)#2	0.92	2.61	3.404(5)	145.3
O(15S)-H(15F)...O(10S)	0.91	1.93	2.838(6)	177.2

Symmetry transformations used to generate equivalent atoms: #1 x+1, y-1, z #2 x+1, y, z #3 x-1, y, z #4 x, y-1, z #5 -x+1, -y+1, -z+1 #6 x, y+1, z #7 x-1, y+1, z

Structural Data for $H_6$14$(Br)_3(H_2O)$–Initial Refinement

Table F-1. Crystal data and structure refinement for **$[H_6$14$(Br)_3(H_2O)]\cdot 1.25H_2O$**

Empirical formula	$(C_{33}H_{57}N_{11})^{6+}(Br)_6^{-}$ $(H_2O)_{2.25}$	
	$C_{33}H_{61.5}Br_6N_{11}O_{2.25}$	
Formula weight	1127.89	
Crystal system	Tetragonal	
Space group	$I4_1/a$	
Unit cell dimensions	a = 24.470(4) Å	α= 90°
	b = 24.470(4) Å	β= 90°
	c = 31.613(8) Å	γ= 90°
Volume	18929(6) Å^3	
Z, Z'	16, 1	
Density (calculated)	1.583 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	9032	
Absorption coefficient	5.131 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.628 and 0.206	
Theta range for data collection	2.10 to 24.71°	
Reflections collected	74111	
Independent reflections	8061 [R(int) = 0.0422]	
Data / restraints / parameters	8061 / 25 / 506	
wR(F^2 all data)	$wR2$ = 0.2062	
R(F obsd data)	$R1$ = 0.0629	
Goodness-of-fit on F^2	1.065	
Observed data [$I > 2\sigma(I)$]	6443	
Largest and mean shift / s.u.	0.003and 0.000	
Largest diff. peak and hole	1.857 and -1.043 e/Å^3	

$wR2 = \{ \Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o{}^2)^2] \}^{1/2}$

$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

Table F-2. Atomic coordinates and equivalent isotropic displacement parameters for **$[H_614(Br)_3(H_2O)]\cdot 1.25H_2O$**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	0.2186(2)	0.5542(3)	0.42618(18)	0.0359(13)
C(2)	0.2580(3)	0.5987(3)	0.4315(2)	0.0369(16)
C(3)	0.2761(3)	0.6272(3)	0.3911(2)	0.0433(17)
N(4)	0.3184(3)	0.6681(3)	0.40302(18)	0.0402(14)
C(5)	0.3429(3)	0.6987(3)	0.3673(2)	0.0488(19)
C(6)	0.3829(3)	0.7393(3)	0.3836(2)	0.0430(18)
N(7)	0.3798(2)	0.7506(2)	0.42476(19)	0.0366(13)
C(8)	0.4217(3)	0.7651(3)	0.3574(3)	0.049(2)
C(9)	0.4579(3)	0.8004(3)	0.3749(3)	0.052(2)
C(10)	0.4551(3)	0.8123(3)	0.4178(3)	0.0458(19)
C(11)	0.4139(3)	0.7868(3)	0.4411(3)	0.0399(17)
C(12)	0.4031(4)	0.8043(3)	0.4858(3)	0.0483(19)
N(13)	0.3772(3)	0.7598(2)	0.51089(19)	0.0384(13)
C(14)	0.4155(3)	0.7150(3)	0.5241(3)	0.0457(18)
C(15)	0.3931(3)	0.6857(3)	0.5625(2)	0.0378(16)
N(16)	0.3433(2)	0.6551(2)	0.55378(17)	0.0321(12)
C(17)	0.3549(3)	0.6036(3)	0.5315(2)	0.0341(15)
C(18)	0.3769(3)	0.5587(3)	0.5610(2)	0.0357(15)
N(19)	0.4079(2)	0.5163(2)	0.53694(18)	0.0356(13)
C(20)	0.4177(3)	0.4676(3)	0.5633(2)	0.0448(18)
C(21)	0.3667(3)	0.4355(3)	0.5693(2)	0.0411(17)
N(22)	0.3296(3)	0.4389(2)	0.53804(18)	0.0377(13)
C(23)	0.3592(4)	0.4025(3)	0.6047(2)	0.049(2)
C(24)	0.3129(4)	0.3712(3)	0.6069(3)	0.056(2)
C(25)	0.2737(4)	0.3742(3)	0.5750(3)	0.0467(19)
C(26)	0.2843(3)	0.4091(3)	0.5413(2)	0.0418(17)
C(27)	0.2442(4)	0.4122(3)	0.5051(2)	0.0486(19)
N(28)	0.2563(3)	0.4594(3)	0.47681(19)	0.0406(14)
C(29)	0.2279(3)	0.4550(3)	0.4350(2)	0.0456(18)
C(30)	0.2421(3)	0.5044(3)	0.4075(2)	0.0421(17)
C(31)	0.1678(3)	0.5690(4)	0.4054(3)	0.054(2)
C(32)	0.1343(4)	0.6095(6)	0.4319(3)	0.078(3)
N(33)	0.1184(3)	0.5832(5)	0.4728(2)	0.084(3)
C(34)	0.0732(4)	0.6149(8)	0.4946(4)	0.118(4)
C(35)	0.0885(4)	0.6705(7)	0.5040(3)	0.101(3)

N(36)	0.1276(3)	0.6798(4)	0.5323(2)	0.0686(19)
C(37)	0.0645(5)	0.7158(10)	0.4825(4)	0.136(5)
C(38)	0.0771(6)	0.7666(10)	0.4922(4)	0.136(5)
C(39)	0.1192(4)	0.7777(6)	0.5228(3)	0.093(3)
C(40)	0.1427(4)	0.7310(5)	0.5406(2)	0.065(2)
C(41)	0.1890(3)	0.7378(4)	0.5717(2)	0.0491(18)
N(42)	0.2289(2)	0.6927(2)	0.56647(17)	0.0339(13)
C(43)	0.2714(3)	0.6927(3)	0.6002(2)	0.0355(15)
C(44)	0.3113(3)	0.6456(3)	0.5926(2)	0.0319(14)
Br(1)	0.24828(3)	0.74139(3)	0.47099(2)	0.0453(2)
Br(2)	0.42578(3)	0.59910(3)	0.42254(3)	0.0450(2)
Br(3)	0.31645(5)	0.83661(3)	0.57867(3)	0.0615(3)
Br(4)	0.52115(3)	0.58299(3)	0.53948(3)	0.0522(3)
Br(5)	0.20913(3)	0.55093(4)	0.54468(2)	0.0487(3)
Br(6A)	0.07720(12)	0.44424(14)	0.46786(8)	0.0554(6)
Br(6B)	0.0640(6)	0.4614(7)	0.4605(5)	0.022(4)
Br(6C)	0.0755(2)	0.4073(3)	0.4852(3)	0.036(3)
Br(6D)	0.0785(3)	0.3988(3)	0.5058(5)	0.029(4)
Br(6E)	0.0820(5)	0.4000(5)	0.5298(6)	0.033(5)
Br(6F)	0.4535(6)	0.8089(6)	0.5878(5)	0.054(5)
Br(6G)	0.1529(8)	0.8079(8)	0.4112(6)	0.049(7)
Br(6H)	0.0296(9)	0.4736(9)	0.5666(7)	0.084(8)
O(1S)	0.36730(19)	0.4882(2)	0.45280(15)	0.0388(11)
O(2S)	-0.0216(5)	0.6696(6)	0.3928(3)	0.172(6)
O(3S)	0.5000	0.7500	0.6250	0.266(19)

Table F-3. Bond lengths [Å] and angles [°] for **$[H_{6}14(Br)_{3}(H_{2}O)]\cdot 1.25H_{2}O$**.

N(1)-C(31)	1.451(10)	C(5)-H(5B)	0.9900
N(1)-C(2)	1.464(9)	C(6)-N(7)	1.334(10)
N(1)-C(30)	1.471(10)	C(6)-C(8)	1.407(11)
C(2)-C(3)	1.522(10)	N(7)-C(11)	1.321(10)
C(2)-H(2A)	0.9900	C(8)-C(9)	1.356(13)
C(2)-H(2B)	0.9900	C(8)-H(8)	0.9500
C(3)-N(4)	1.487(9)	C(9)-C(10)	1.390(13)
C(3)-H(3A)	0.9900	C(9)-H(9)	0.9500
C(3)-H(3B)	0.9900	C(10)-C(11)	1.398(10)
N(4)-C(5)	1.482(9)	C(10)-H(10)	0.9500
N(4)-H(4A)	0.9200	C(11)-C(12)	1.497(11)
N(4)-H(4B)	0.9200	C(12)-N(13)	1.488(9)
C(5)-C(6)	1.487(12)	C(12)-H(12A)	0.9900
C(5)-H(5A)	0.9900	C(12)-H(12B)	0.9900

N(13)-C(14)	1.501(9)	C(29)-H(29B)	0.9900
N(13)-H(13A)	0.9200	C(30)-H(30A)	0.9900
N(13)-H(13B)	0.9200	C(30)-H(30B)	0.9900
C(14)-C(15)	1.514(11)	C(31)-C(32)	1.534(12)
C(14)-H(14A)	0.9900	C(31)-H(31A)	0.9900
C(14)-H(14B)	0.9900	C(31)-H(31B)	0.9900
C(15)-N(16)	1.456(9)	C(32)-N(33)	1.495(14)
C(15)-H(15A)	0.9900	C(32)-H(32A)	0.9900
C(15)-H(15B)	0.9900	C(32)-H(32B)	0.9900
N(16)-C(17)	1.470(9)	N(33)-C(34)	1.517(14)
N(16)-C(44)	1.475(8)	N(33)-H(33A)	0.9200
C(17)-C(18)	1.540(9)	N(33)-H(33B)	0.9200
C(17)-H(17A)	0.9900	C(34)-C(35)	1.44(2)
C(17)-H(17B)	0.9900	C(34)-H(34A)	0.9900
C(18)-N(19)	1.494(9)	C(34)-H(34B)	0.9900
C(18)-H(18A)	0.9900	C(35)-N(36)	1.329(12)
C(18)-H(18B)	0.9900	C(35)-C(37)	1.43(2)
N(19)-C(20)	1.477(10)	N(36)-C(40)	1.331(15)
N(19)-H(19A)	0.9200	C(37)-C(38)	1.32(3)
N(19)-H(19B)	0.9200	C(37)-H(37)	0.9500
C(20)-C(21)	1.487(12)	C(38)-C(39)	1.44(2)
C(20)-H(20A)	0.9900	C(38)-H(38)	0.9500
C(20)-H(20B)	0.9900	C(39)-C(40)	1.399(15)
C(21)-N(22)	1.344(10)	C(39)-H(39)	0.9500
C(21)-C(23)	1.392(11)	C(40)-C(41)	1.510(12)
N(22)-C(26)	1.331(10)	C(41)-N(42)	1.481(9)
C(23)-C(24)	1.370(13)	C(41)-H(41A)	0.9900
C(23)-H(23)	0.9500	C(41)-H(41B)	0.9900
C(24)-C(25)	1.395(13)	N(42)-C(43)	1.490(9)
C(24)-H(24)	0.9500	N(42)-H(42A)	0.9200
C(25)-C(26)	1.389(10)	N(42)-H(42B)	0.9200
C(25)-H(25)	0.9500	C(43)-C(44)	1.528(9)
C(26)-C(27)	1.508(11)	C(43)-H(43A)	0.9900
C(27)-N(28)	1.490(10)	C(43)-H(43B)	0.9900
C(27)-H(27A)	0.9900	C(44)-H(44A)	0.9900
C(27)-H(27B)	0.9900	C(44)-H(44B)	0.9900
N(28)-C(29)	1.496(9)	O(1S)-H(1SA)	0.8991
N(28)-H(28A)	0.9200	O(1S)-H(1SB)	0.8998
N(28)-H(28B)	0.9200	O(2S)-H(2SA)	0.9001
C(29)-C(30)	1.529(11)	O(2S)-H(2SB)	0.9000
C(29)-H(29A)	0.9900	O(3S)-H(3SA)	0.934
C(31)-N(1)-C(2)	115.4(7)	N(1)-C(2)-H(2A)	108.3
C(31)-N(1)-C(30)	111.1(6)	C(3)-C(2)-H(2A)	108.3
C(2)-N(1)-C(30)	113.9(5)	N(1)-C(2)-H(2B)	108.3
N(1)-C(2)-C(3)	115.9(6)	C(3)-C(2)-H(2B)	108.3

H(2A)-C(2)-H(2B)	107.4
N(4)-C(3)-C(2)	107.4(6)
N(4)-C(3)-H(3A)	110.2
C(2)-C(3)-H(3A)	110.2
N(4)-C(3)-H(3B)	110.2
C(2)-C(3)-H(3B)	110.2
H(3A)-C(3)-H(3B)	108.5
C(5)-N(4)-C(3)	115.4(6)
C(5)-N(4)-H(4A)	108.4
C(3)-N(4)-H(4A)	108.4
C(5)-N(4)-H(4B)	108.4
C(3)-N(4)-H(4B)	108.4
H(4A)-N(4)-H(4B)	107.5
N(4)-C(5)-C(6)	109.9(6)
N(4)-C(5)-H(5A)	109.7
C(6)-C(5)-H(5A)	109.7
N(4)-C(5)-H(5B)	109.7
C(6)-C(5)-H(5B)	109.7
H(5A)-C(5)-H(5B)	108.2
N(7)-C(6)-C(8)	121.3(8)
N(7)-C(6)-C(5)	116.0(6)
C(8)-C(6)-C(5)	122.7(7)
C(11)-N(7)-C(6)	119.0(6)
C(9)-C(8)-C(6)	119.1(8)
C(9)-C(8)-H(8)	120.4
C(6)-C(8)-H(8)	120.4
C(8)-C(9)-C(10)	119.9(7)
C(8)-C(9)-H(9)	120.0
C(10)-C(9)-H(9)	120.0
C(9)-C(10)-C(11)	117.2(8)
C(9)-C(10)-H(10)	121.4
C(11)-C(10)-H(10)	121.4
N(7)-C(11)-C(10)	123.2(8)
N(7)-C(11)-C(12)	116.7(6)
C(10)-C(11)-C(12)	119.8(7)
N(13)-C(12)-C(11)	111.6(6)
N(13)-C(12)-H(12A)	109.3
C(11)-C(12)-H(12A)	109.3
N(13)-C(12)-H(12B)	109.3
C(11)-C(12)-H(12B)	109.3
H(12A)-C(12)-H(12B)	108.0
C(12)-N(13)-C(14)	114.6(6)
C(12)-N(13)-H(13A)	108.6
C(14)-N(13)-H(13A)	108.6
C(12)-N(13)-H(13B)	108.6
C(14)-N(13)-H(13B)	108.6
H(13A)-N(13)-H(13B)	107.6
N(13)-C(14)-C(15)	110.1(6)
N(13)-C(14)-H(14A)	109.6
C(15)-C(14)-H(14A)	109.6
N(13)-C(14)-H(14B)	109.6
C(15)-C(14)-H(14B)	109.6
H(14A)-C(14)-H(14B)	108.2
N(16)-C(15)-C(14)	113.2(6)
N(16)-C(15)-H(15A)	108.9
C(14)-C(15)-H(15A)	108.9
N(16)-C(15)-H(15B)	108.9
C(14)-C(15)-H(15B)	108.9
H(15A)-C(15)-H(15B)	107.7
C(15)-N(16)-C(17)	111.8(5)
C(15)-N(16)-C(44)	111.6(5)
C(17)-N(16)-C(44)	111.5(5)
N(16)-C(17)-C(18)	112.8(5)
N(16)-C(17)-H(17A)	109.0
C(18)-C(17)-H(17A)	109.0
N(16)-C(17)-H(17B)	109.0
C(18)-C(17)-H(17B)	109.0
H(17A)-C(17)-H(17B)	107.8
N(19)-C(18)-C(17)	111.3(6)
N(19)-C(18)-H(18A)	109.4
C(17)-C(18)-H(18A)	109.4
N(19)-C(18)-H(18B)	109.4
C(17)-C(18)-H(18B)	109.4
H(18A)-C(18)-H(18B)	108.0
C(20)-N(19)-C(18)	110.8(6)
C(20)-N(19)-H(19A)	109.5
C(18)-N(19)-H(19A)	109.5
C(20)-N(19)-H(19B)	109.5
C(18)-N(19)-H(19B)	109.5
H(19A)-N(19)-H(19B)	108.1
N(19)-C(20)-C(21)	111.2(6)
N(19)-C(20)-H(20A)	109.4
C(21)-C(20)-H(20A)	109.4
N(19)-C(20)-H(20B)	109.4
C(21)-C(20)-H(20B)	109.4
H(20A)-C(20)-H(20B)	108.0
N(22)-C(21)-C(23)	122.6(8)
N(22)-C(21)-C(20)	116.3(6)
C(23)-C(21)-C(20)	121.1(7)
C(26)-N(22)-C(21)	118.2(6)

C(24)-C(23)-C(21)	118.3(8)
C(24)-C(23)-H(23)	120.9
C(21)-C(23)-H(23)	120.9
C(23)-C(24)-C(25)	120.1(8)
C(23)-C(24)-H(24)	119.9
C(25)-C(24)-H(24)	119.9
C(26)-C(25)-C(24)	117.4(8)
C(26)-C(25)-H(25)	121.3
C(24)-C(25)-H(25)	121.3
N(22)-C(26)-C(25)	123.4(8)
N(22)-C(26)-C(27)	117.1(6)
C(25)-C(26)-C(27)	119.5(7)
N(28)-C(27)-C(26)	111.4(6)
N(28)-C(27)-H(27A)	109.3
C(26)-C(27)-H(27A)	109.3
N(28)-C(27)-H(27B)	109.3
C(26)-C(27)-H(27B)	109.3
H(27A)-C(27)-H(27B)	108.0
C(27)-N(28)-C(29)	112.4(6)
C(27)-N(28)-H(28A)	109.1
C(29)-N(28)-H(28A)	109.1
C(27)-N(28)-H(28B)	109.1
C(29)-N(28)-H(28B)	109.1
H(28A)-N(28)-H(28B)	107.9
N(28)-C(29)-C(30)	109.8(6)
N(28)-C(29)-H(29A)	109.7
C(30)-C(29)-H(29A)	109.7
N(28)-C(29)-H(29B)	109.7
C(30)-C(29)-H(29B)	109.7
H(29A)-C(29)-H(29B)	108.2
N(1)-C(30)-C(29)	109.7(6)
N(1)-C(30)-H(30A)	109.7
C(29)-C(30)-H(30A)	109.7
N(1)-C(30)-H(30B)	109.7
C(29)-C(30)-H(30B)	109.7
H(30A)-C(30)-H(30B)	108.2
N(1)-C(31)-C(32)	111.8(6)
N(1)-C(31)-H(31A)	109.3
C(32)-C(31)-H(31A)	109.3
N(1)-C(31)-H(31B)	109.3
C(32)-C(31)-H(31B)	109.3
H(31A)-C(31)-H(31B)	107.9
N(33)-C(32)-C(31)	109.5(10)
N(33)-C(32)-H(32A)	109.8
C(31)-C(32)-H(32A)	109.8
N(33)-C(32)-H(32B)	109.8
C(31)-C(32)-H(32B)	109.8
H(32A)-C(32)-H(32B)	108.2
C(32)-N(33)-C(34)	111.3(11)
C(32)-N(33)-H(33A)	109.4
C(34)-N(33)-H(33A)	109.4
C(32)-N(33)-H(33B)	109.4
C(34)-N(33)-H(33B)	109.4
H(33A)-N(33)-H(33B)	108.0
C(35)-C(34)-N(33)	112.7(9)
C(35)-C(34)-H(34A)	109.0
N(33)-C(34)-H(34A)	109.0
C(35)-C(34)-H(34B)	109.0
N(33)-C(34)-H(34B)	109.0
H(34A)-C(34)-H(34B)	107.8
N(36)-C(35)-C(37)	118.9(16)
N(36)-C(35)-C(34)	119.2(13)
C(37)-C(35)-C(34)	121.9(12)
C(35)-N(36)-C(40)	119.7(11)
C(38)-C(37)-C(35)	121.8(13)
C(38)-C(37)-H(37)	119.1
C(35)-C(37)-H(37)	119.1
C(37)-C(38)-C(39)	120.2(14)
C(37)-C(38)-H(38)	119.9
C(39)-C(38)-H(38)	119.9
C(40)-C(39)-C(38)	114.3(15)
C(40)-C(39)-H(39)	122.8
C(38)-C(39)-H(39)	122.8
N(36)-C(40)-C(39)	125.0(10)
N(36)-C(40)-C(41)	116.2(8)
C(39)-C(40)-C(41)	118.8(12)
N(42)-C(41)-C(40)	109.9(7)
N(42)-C(41)-H(41A)	109.7
C(40)-C(41)-H(41A)	109.7
N(42)-C(41)-H(41B)	109.7
C(40)-C(41)-H(41B)	109.7
H(41A)-C(41)-H(41B)	108.2
C(41)-N(42)-C(43)	112.4(6)
C(41)-N(42)-H(42A)	109.1
C(43)-N(42)-H(42A)	109.1
C(41)-N(42)-H(42B)	109.1
C(43)-N(42)-H(42B)	109.1
H(42A)-N(42)-H(42B)	107.9
N(42)-C(43)-C(44)	109.5(6)
N(42)-C(43)-H(43A)	109.8

C(44)-C(43)-H(43A)	109.8
N(42)-C(43)-H(43B)	109.8
C(44)-C(43)-H(43B)	109.8
H(43A)-C(43)-H(43B)	108.2
N(16)-C(44)-C(43)	110.6(5)
N(16)-C(44)-H(44A)	109.5
C(43)-C(44)-H(44A)	109.5
N(16)-C(44)-H(44B)	109.5
C(43)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	108.1
O(3S)-Br(6F)-H(3SA)	24.9
H(1SA)-O(1S)-H(1SB)	96.4
H(2SA)-O(2S)-H(2SB)	110.7

Table F-4. Anisotropic displacement parameters (Å^{2}x 10^3) for **[H$_6$14(Br)$_3$(H$_2$O)]·1.25H$_2$O**. The anisotropic displacement factor exponent takes the form:

$$-2\pi^2[h^2 a^{*2} U_{11} + ... + 2hk a^* b^* U_{12}]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	25(3)	53(4)	30(3)	-6(3)	-1(2)	-6(3)
C(2)	34(4)	50(4)	26(3)	-5(3)	-1(3)	-5(3)
C(3)	46(4)	50(4)	34(4)	-8(3)	5(3)	-4(3)
N(4)	45(3)	45(3)	31(3)	-4(3)	7(3)	-3(3)
C(5)	52(5)	56(5)	37(4)	7(4)	14(4)	1(4)
C(6)	50(4)	39(4)	40(4)	6(3)	13(3)	14(3)
N(7)	37(3)	33(3)	40(3)	2(3)	10(3)	5(3)
C(8)	50(5)	51(5)	46(4)	18(4)	21(4)	15(4)
C(9)	44(4)	37(4)	75(6)	23(4)	23(4)	11(3)
C(10)	38(4)	26(4)	73(6)	15(3)	7(4)	9(3)
C(11)	38(4)	27(3)	55(5)	11(3)	7(3)	10(3)
C(12)	65(5)	27(4)	53(5)	3(3)	4(4)	-6(3)
N(13)	47(4)	29(3)	39(3)	2(2)	4(3)	1(3)
C(14)	35(4)	41(4)	61(5)	4(4)	5(4)	-1(3)
C(15)	33(4)	34(4)	46(4)	1(3)	-2(3)	1(3)
N(16)	29(3)	34(3)	33(3)	3(2)	0(2)	4(2)
C(17)	34(4)	42(4)	27(3)	3(3)	-5(3)	4(3)
C(18)	44(4)	32(4)	30(3)	-4(3)	-2(3)	3(3)
N(19)	33(3)	38(3)	36(3)	-9(2)	-4(2)	3(2)
C(20)	53(5)	44(4)	38(4)	-7(3)	-9(3)	12(4)
C(21)	58(5)	30(4)	35(4)	-7(3)	5(3)	12(3)
N(22)	49(4)	32(3)	32(3)	-4(2)	2(3)	-1(3)
C(23)	66(5)	42(4)	39(4)	-1(3)	5(4)	31(4)
C(24)	82(6)	35(4)	50(5)	6(4)	22(5)	27(4)
C(25)	63(5)	27(4)	50(5)	0(3)	23(4)	5(3)
C(26)	61(5)	30(4)	34(4)	-7(3)	12(3)	-2(3)
C(27)	57(5)	49(4)	39(4)	-3(3)	7(4)	-23(4)
N(28)	41(3)	49(4)	32(3)	-5(3)	1(3)	-15(3)
C(29)	41(4)	57(5)	39(4)	-5(3)	-11(3)	-15(4)
C(30)	35(4)	55(5)	36(4)	-9(3)	-5(3)	-10(3)
C(31)	30(4)	94(7)	37(4)	-17(4)	-1(3)	1(4)
C(32)	35(4)	163(11)	36(4)	-28(5)	-1(3)	28(5)
N(33)	32(4)	176(8)	43(4)	-34(5)	7(3)	-15(4)
C(34)	27(4)	267(10)	61(6)	-73(7)	9(4)	-3(6)
C(35)	29(4)	230(9)	45(5)	-50(6)	0(3)	41(5)

N(36)	29(3)	147(6)	30(3)	-11(4)	7(2)	21(4)
C(37)	57(7)	299(12)	52(6)	-29(9)	-14(5)	81(10)
C(38)	82(9)	265(10)	62(8)	6(10)	-9(6)	115(10)
C(39)	61(6)	165(7)	53(6)	25(6)	15(4)	73(6)
C(40)	39(4)	128(6)	27(4)	8(4)	12(3)	38(4)
C(41)	41(4)	71(5)	35(4)	11(3)	10(3)	25(3)
N(42)	31(3)	45(3)	26(3)	9(2)	5(2)	8(2)
C(43)	33(3)	46(4)	28(3)	6(3)	4(3)	3(3)
C(44)	32(3)	35(4)	29(3)	7(3)	-4(3)	4(3)
Br(1)	48(1)	53(1)	35(1)	7(1)	12(1)	11(1)
Br(2)	43(1)	43(1)	49(1)	-5(1)	13(1)	-3(1)
Br(3)	106(1)	42(1)	36(1)	-10(1)	12(1)	9(1)
Br(4)	41(1)	51(1)	64(1)	7(1)	1(1)	2(1)
Br(5)	46(1)	73(1)	27(1)	-11(1)	7(1)	-21(1)
Br(6A)	54(1)	65(2)	47(1)	0(1)	15(1)	-12(1)
O(1S)	34(3)	41(3)	41(3)	-1(2)	4(2)	-2(2)
O(2S)	139(9)	332(18)	43(5)	-82(7)	-32(5)	28(10)

Table F-5. Hydrogen coordinates and isotropic displacement parameters for **$[\mathrm{H_6}14(\mathrm{Br})_3(\mathrm{H_2O})]\cdot 1.25\mathrm{H_2O}$**.

	x	y	z	U(eq)
H(2A)	0.2908	0.5839	0.4458	0.044
H(2B)	0.2417	0.6264	0.4506	0.044
H(3A)	0.2914	0.6004	0.3710	0.052
H(3B)	0.2446	0.6456	0.3775	0.052
H(4A)	0.3029	0.6928	0.4214	0.048
H(4B)	0.3459	0.6504	0.4173	0.048
H(5A)	0.3138	0.7177	0.3512	0.059
H(5B)	0.3615	0.6730	0.3479	0.059
H(8)	0.4225	0.7577	0.3279	0.059
H(9)	0.4852	0.8170	0.3578	0.062
H(10)	0.4802	0.8368	0.4308	0.055
H(12A)	0.4380	0.8150	0.4993	0.058
H(12B)	0.3788	0.8366	0.4857	0.058
H(13A)	0.3494	0.7447	0.4951	0.046
H(13B)	0.3619	0.7749	0.5348	0.046
H(14A)	0.4518	0.7307	0.5308	0.055
H(14B)	0.4201	0.6888	0.5006	0.055
H(15A)	0.4212	0.6603	0.5734	0.045

H(15B)	0.3854	0.7129	0.5850	0.045
H(17A)	0.3820	0.6107	0.5089	0.041
H(17B)	0.3209	0.5905	0.5179	0.041
H(18A)	0.4012	0.5754	0.5825	0.043
H(18B)	0.3460	0.5412	0.5760	0.043
H(19A)	0.3884	0.5065	0.5132	0.043
H(19B)	0.4408	0.5306	0.5282	0.043
H(20A)	0.4319	0.4790	0.5913	0.054
H(20B)	0.4457	0.4443	0.5497	0.054
H(23)	0.3856	0.4017	0.6267	0.059
H(24)	0.3074	0.3474	0.6303	0.067
H(25)	0.2411	0.3532	0.5762	0.056
H(27A)	0.2459	0.3779	0.4885	0.058
H(27B)	0.2067	0.4159	0.5165	0.058
H(28A)	0.2934	0.4614	0.4724	0.049
H(28B)	0.2456	0.4912	0.4900	0.049
H(29A)	0.1879	0.4534	0.4395	0.055
H(29B)	0.2393	0.4210	0.4206	0.055
H(30A)	0.2823	0.5081	0.4055	0.050
H(30B)	0.2275	0.4990	0.3787	0.050
H(31A)	0.1459	0.5356	0.4004	0.065
H(31B)	0.1761	0.5856	0.3776	0.065
H(32A)	0.1563	0.6427	0.4375	0.094
H(32B)	0.1012	0.6204	0.4161	0.094
H(33A)	0.1484	0.5815	0.4903	0.100
H(33B)	0.1068	0.5481	0.4677	0.100
H(34A)	0.0404	0.6152	0.4762	0.142
H(34B)	0.0633	0.5961	0.5212	0.142
H(37)	0.0387	0.7092	0.4606	0.163
H(38)	0.0584	0.7960	0.4789	0.164
H(39)	0.1300	0.8137	0.5302	0.112
H(41A)	0.2074	0.7733	0.5668	0.059
H(41B)	0.1745	0.7376	0.6009	0.059
H(42A)	0.2456	0.6960	0.5405	0.041
H(42B)	0.2106	0.6599	0.5669	0.041
H(43A)	0.2539	0.6884	0.6282	0.043
H(43B)	0.2914	0.7278	0.6000	0.043
H(44A)	0.3363	0.6422	0.6171	0.038
H(44B)	0.2907	0.6109	0.5899	0.038
H(1SA)	0.3837	0.5192	0.4444	0.047
H(1SB)	0.3980	0.4681	0.4551	0.047
H(2SA)	0.0112	0.6814	0.3835	0.206
H(2SB)	-0.0206	0.6336	0.3984	0.206
H(3SA)	0.4627	0.7478	0.6189	0.319

Table F-6. Torsion angles [°] for **$[\mathrm{H_6}14(\mathrm{Br})_3(\mathrm{H_2O})]\cdot 1.25\mathrm{H_2O}$**.

C(31)-N(1)-C(2)-C(3)	-57.8(8)
C(30)-N(1)-C(2)-C(3)	72.6(8)
N(1)-C(2)-C(3)-N(4)	-176.3(6)
C(2)-C(3)-N(4)-C(5)	177.5(6)
C(3)-N(4)-C(5)-C(6)	178.1(6)
N(4)-C(5)-C(6)-N(7)	-16.0(9)
N(4)-C(5)-C(6)-C(8)	164.6(7)
C(8)-C(6)-N(7)-C(11)	0.1(10)
C(5)-C(6)-N(7)-C(11)	-179.4(6)
N(7)-C(6)-C(8)-C(9)	2.6(11)
C(5)-C(6)-C(8)-C(9)	-178.0(7)
C(6)-C(8)-C(9)-C(10)	-2.3(11)
C(8)-C(9)-C(10)-C(11)	-0.4(10)
C(6)-N(7)-C(11)-C(10)	-3.0(10)
C(6)-N(7)-C(11)-C(12)	170.9(6)
C(9)-C(10)-C(11)-N(7)	3.2(10)
C(9)-C(10)-C(11)-C(12)	-170.5(7)
N(7)-C(11)-C(12)-N(13)	30.6(9)
C(10)-C(11)-C(12)-N(13)	-155.3(7)
C(11)-C(12)-N(13)-C(14)	75.7(9)
C(12)-N(13)-C(14)-C(15)	157.0(6)
N(13)-C(14)-C(15)-N(16)	67.2(8)
C(14)-C(15)-N(16)-C(17)	76.8(7)
C(14)-C(15)-N(16)-C(44)	-157.6(6)
C(15)-N(16)-C(17)-C(18)	77.5(7)
C(44)-N(16)-C(17)-C(18)	-48.1(7)
N(16)-C(17)-C(18)-N(19)	-157.9(6)
C(17)-C(18)-N(19)-C(20)	-166.8(6)
C(18)-N(19)-C(20)-C(21)	73.2(7)
N(19)-C(20)-C(21)-N(22)	28.4(9)
N(19)-C(20)-C(21)-C(23)	-153.6(6)
C(23)-C(21)-N(22)-C(26)	-0.6(10)
C(20)-C(21)-N(22)-C(26)	177.3(6)
N(22)-C(21)-C(23)-C(24)	2.1(10)
C(20)-C(21)-C(23)-C(24)	-175.8(7)
C(21)-C(23)-C(24)-C(25)	-2.1(11)
C(23)-C(24)-C(25)-C(26)	0.9(11)
C(21)-N(22)-C(26)-C(25)	-0.8(10)
C(21)-N(22)-C(26)-C(27)	-177.9(6)
C(24)-C(25)-C(26)-N(22)	0.6(11)
C(24)-C(25)-C(26)-C(27)	177.7(7)
N(22)-C(26)-C(27)-N(28)	-14.5(10)
C(25)-C(26)-C(27)-N(28)	168.2(7)
C(26)-C(27)-N(28)-C(29)	164.3(6)
C(27)-N(28)-C(29)-C(30)	-179.7(7)
C(31)-N(1)-C(30)-C(29)	-99.0(7)
C(2)-N(1)-C(30)-C(29)	128.5(6)
N(28)-C(29)-C(30)-N(1)	-67.0(8)
C(2)-N(1)-C(31)-C(32)	-65.2(10)
C(30)-N(1)-C(31)-C(32)	163.1(8)
N(1)-C(31)-C(32)-N(33)	-62.8(10)
C(31)-C(32)-N(33)-C(34)	-164.6(8)
C(32)-N(33)-C(34)-C(35)	-59.6(12)
N(33)-C(34)-C(35)-N(36)	-66.6(13)
N(33)-C(34)-C(35)-C(37)	110.7(12)
C(37)-C(35)-N(36)-C(40)	1.5(13)
C(34)-C(35)-N(36)-C(40)	178.8(8)
N(36)-C(35)-C(37)-C(38)	-5(2)
C(34)-C(35)-C(37)-C(38)	177.6(13)
C(35)-C(37)-C(38)-C(39)	5(2)
C(37)-C(38)-C(39)-C(40)	-1.4(19)
C(35)-N(36)-C(40)-C(39)	2.2(13)
C(35)-N(36)-C(40)-C(41)	-177.4(7)
C(38)-C(39)-C(40)-N(36)	-2.3(14)
C(38)-C(39)-C(40)-C(41)	177.3(9)
N(36)-C(40)-C(41)-N(42)	35.2(9)
C(39)-C(40)-C(41)-N(42)	-144.4(7)
C(40)-C(41)-N(42)-C(43)	-171.8(6)
C(41)-N(42)-C(43)-C(44)	-179.5(6)
C(15)-N(16)-C(44)-C(43)	89.1(7)
C(17)-N(16)-C(44)-C(43)	-145.2(6)
N(42)-C(43)-C(44)-N(16)	67.2(7)

Table F-7. Hydrogen bonds for **$[H_6 14(Br)_3(H_2O)]\cdot 1.25H_2O$** [Å and °].

D-H¨A	d(D-H)	d(H¨A)	d(D¨A)	<(DHA)
N(4)-H(4A)¨Br(1)	0.92	2.38	3.282(6)	167.4
N(4)-H(4B) ¨Br(2)	0.92	2.33	3.185(7)	154.6
N(13)-H(13A) ¨Br(1)	0.92	2.59	3.428(6)	151.4
N(13)-H(13B) ¨Br(3)	0.92	2.33	3.215(6)	160.4
N(19)-H(19A) ¨O(1S)	0.92	2.03	2.922(7)	163.0
N(19)-H(19B) ¨Br(4)	0.92	2.37	3.216(6)	152.3
N(28)-H(28A) ¨O(1S)	0.92	2.02	2.907(8)	161.2
N(28)-H(28B) ¨Br(5)	0.92	2.43	3.309(6)	158.9
N(33)-H(33B) ¨Br(6A)	0.92	2.64	3.551(11)	169.6
N(33)-H(33B) ¨Br(6B)	0.92	2.38	3.288(19)	170.9
N(33)-H(33A) ¨Br(5)	0.92	2.39	3.275(8)	160.4
N(42)-H(42A) ¨Br(1)	0.92	2.46	3.279(5)	147.8
N(42)-H(42B) ¨Br(5)	0.92	2.76	3.571(6)	147.8
O(1S)-H(1SA) ¨Br(2)	0.90	2.31	3.214(5)	179.8
O(1S)-H(1SB) ¨Br(4)#4	0.90	2.35	3.247(5)	179.0
O(2S)-H(2SB) ¨Br(6E)#5	0.90	2.84	3.33(2)	115.3
O(2S)-H(2SA) ¨O(2S)#6	0.90	2.21	3.09(2)	166.1

Symmetry transformations used to generate equivalent atoms:

#4 -x+1, -y+1, -z+1   #5 -x, -y+1, -z+1   #6 -y+3/4, x+3/4, -z+3/4

Structural Data for $H_6$14$(Br_3)_3(H_2O)$–Second Refinement

Table G-1. Crystal data and structure refinement for **[$H_6$14$(Br)_3(H_2O)$][$Br]_3\cdot 4H_2O$**.

Empirical formula	$(C_{33}H_{57}N_{11})^{6+}(Br)_6^{-}$ $(H_2O)_5$ $C_{33}H_{67}Br_6N_{11}O_5$	
Formula weight	1177.44	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$I4_1/a - C_{4h}^6$ (No. 88)	
Unit cell dimensions	a = 24.470(4) Å	α = 90.000°
	b = 24.470(4) Å	β = 90.000°
	c = 31.613(8) Å	γ = 90.000°
Volume	18929(6) $Å^3$	
Z	16	
Density (calculated)	1.653 Mg/m^3	
Absorption coefficient	5.139 mm^{-1}	
F(000)	9472	
Crystal size	0.45 x 0.40 x 0.10 mm^3	
Theta range for data collection	1.97 to 30.10°.	
Index ranges	$-34 \leq h \leq 34$, $-32 \leq k \leq 34$, $-44 \leq l \leq 44$	
Reflections collected	109555	
Independent reflections	13856 [$R_{int} = 0.058$]	
Completeness to theta = 30.10°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.548	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13856 / 3 / 582	
Goodness-of-fit on F^2	1.128	
Final R indices [I>2sigma(I)]	$R_1 = 0.055$, $wR_2 = 0.169$	
R indices (all data)	$R_1 = 0.097$, $wR_2 = 0.185$	
Largest diff. peak and hole	1.077 and -1.595 e.$Å^{-3}$	

$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ $wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

Table G-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **$[H_6 14(Br)_3(H_2O)][Br]_3 \cdot 4H_2O$**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	2187(1)	5540(2)	4260(1)	35(1)
C(2)	2576(2)	5987(2)	4317(1)	35(1)
C(3)	2759(2)	6276(2)	3909(1)	41(1)
N(4)	3182(2)	6684(2)	4032(1)	40(1)
C(5)	3432(2)	6987(2)	3675(1)	50(1)
C(6)	3833(2)	7395(2)	3835(1)	41(1)
N(7)	3803(1)	7505(1)	4245(1)	37(1)
C(8)	4217(2)	7650(2)	3577(2)	48(1)
C(9)	4580(2)	8005(2)	3757(2)	54(1)
C(10)	4551(2)	8124(2)	4176(2)	44(1)
C(11)	4139(2)	7871(2)	4409(2)	41(1)
C(12)	4029(2)	8041(2)	4857(2)	47(1)
N(13)	3774(2)	7599(1)	5111(1)	37(1)
C(14)	4150(2)	7159(2)	5240(2)	44(1)
C(15)	3929(2)	6857(2)	5630(1)	36(1)
N(16)	3433(1)	6549(1)	5538(1)	31(1)
C(17)	3550(2)	6038(2)	5317(1)	32(1)
C(18)	3767(2)	5589(2)	5611(1)	35(1)
N(19)	4079(1)	5162(1)	5367(1)	34(1)
C(20)	4179(2)	4674(2)	5631(2)	44(1)
C(21)	3668(2)	4353(2)	5695(1)	40(1)
N(22)	3295(2)	4388(1)	5380(1)	38(1)
C(23)	3589(2)	4027(2)	6047(1)	47(1)
C(24)	3127(2)	3716(2)	6070(2)	55(1)
C(25)	2735(2)	3744(2)	5749(1)	44(1)

C(26)	2844(2)	4086(2)	5413(1)	40(1)
C(27)	2440(2)	4121(2)	5050(1)	47(1)
N(28)	2558(2)	4592(2)	4767(1)	40(1)
C(29)	2279(2)	4551(2)	4348(2)	45(1)
C(30)	2419(2)	5040(2)	4077(1)	41(1)
C(31)	1679(2)	5693(2)	4054(1)	50(1)
C(32)	1346(2)	6090(3)	4321(2)	76(2)
N(33)	1180(2)	5832(3)	4727(1)	77(2)
C(34)	730(2)	6110(5)	4949(2)	118(4)
C(35)	888(2)	6720(4)	5036(2)	101(3)
N(36)	1274(2)	6801(3)	5324(1)	68(2)
C(37)	646(3)	7175(7)	4817(3)	161(7)
C(38)	783(4)	7684(6)	4928(3)	149(6)
C(39)	1188(2)	7771(4)	5226(2)	84(2)
C(40)	1426(2)	7312(3)	5405(2)	61(2)
C(41)	1885(2)	7379(2)	5717(1)	46(1)
N(42)	2293(1)	6928(1)	5666(1)	34(1)
C(43)	2715(2)	6922(2)	6001(1)	34(1)
C(44)	3109(2)	6455(2)	5926(1)	32(1)
Br(1A)	2488(1)	7417(1)	4712(1)	36(1)
Br(1B)	2389(10)	7379(5)	4665(6)	131(6)
Br(2A)	4258(1)	5994(1)	4224(1)	43(1)
Br(2B)	4274(9)	5810(30)	4291(9)	38(7)
Br(3A)	3132(4)	8362(1)	5782(1)	59(1)
Br(3B)	3254(3)	8385(4)	5796(3)	42(1)
Br(4)	5211(1)	5830(1)	5395(1)	51(1)
Br(5A)	2110(2)	5474(4)	5450(1)	38(1)
Br(5B)	2026(5)	5626(6)	5436(2)	25(1)
Br(6A)	771(2)	4428(2)	4671(1)	54(1)
Br(6B)	770(1)	4035(1)	4970(3)	214(4)
Br(6C)	724(6)	4580(5)	4670(4)	73(4)
O(1W)	3676(1)	4883(1)	4528(1)	39(1)
O(2W)	1614(5)	2904(6)	6007(4)	364(12)
O(3W)	4539(4)	8076(4)	5881(2)	171(4)

O(3W')	5000	7500	6250	96(7)
O(4W)	-220(3)	6679(4)	3933(2)	127(4)
O(4W')	229(11)	6823(10)	3805(8)	67(9)
O(5W)	-274(5)	5274(5)	4323(3)	130(4)
O(5W')	-814(5)	5877(5)	4583(5)	41(4)
O(5W")	609(9)	5099(8)	4438(6)	87(10)

Table G-3. Bond lengths [Å] for **$[H_{6}14(Br)_{3}(H_{2}O)][Br]_{3}\cdot 4H_{2}O$**

N(1)-C(31)	1.452(5)	C(20)-C(21)	1.490(7)
N(1)-C(2)	1.462(5)	C(21)-N(22)	1.353(6)
N(1)-C(30)	1.468(6)	C(21)-C(23)	1.382(6)
C(2)-C(3)	1.537(6)	N(22)-C(26)	1.333(6)
C(3)-N(4)	1.490(5)	C(23)-C(24)	1.365(8)
N(4)-C(5)	1.484(5)	C(24)-C(25)	1.398(7)
C(5)-C(6)	1.488(7)	C(25)-C(26)	1.378(6)
C(6)-N(7)	1.324(5)	C(26)-C(27)	1.516(7)
C(6)-C(8)	1.393(6)	C(27)-N(28)	1.486(6)
N(7)-C(11)	1.323(6)	N(28)-C(29)	1.494(5)
C(8)-C(9)	1.365(8)	C(29)-C(30)	1.512(6)
C(9)-C(10)	1.359(7)	C(31)-C(32)	1.523(7)
C(10)-C(11)	1.394(6)	C(32)-N(33)	1.490(8)
C(11)-C(12)	1.499(7)	N(33)-C(34)	1.472(8)
C(12)-N(13)	1.485(5)	C(34)-C(35)	1.567(13)
N(13)-C(14)	1.474(5)	C(35)-N(36)	1.325(7)
C(14)-C(15)	1.537(6)	C(35)-C(37)	1.438(15)
C(15)-N(16)	1.457(5)	N(36)-C(40)	1.331(9)
N(16)-C(17)	1.460(5)	C(37)-C(38)	1.336(18)
N(16)-C(44)	1.480(5)	C(38)-C(39)	1.383(12)
C(17)-C(18)	1.535(5)	C(39)-C(40)	1.387(8)
C(18)-N(19)	1.507(5)	C(40)-C(41)	1.504(7)
N(19)-C(20)	1.475(6)	C(41)-N(42)	1.497(5)

N(42)-C(43)	1.480(5)	C(43)-C(44)	1.515(5)

Table G-4. Bond angles [°] for **$[H_614(Br)_3(H_2O)][Br]_3 \cdot 4H_2O$**.

C(31)-N(1)-C(2)	114.8(4)	C(23)-C(21)-C(20)	122.0(4)
C(31)-N(1)-C(30)	111.7(3)	C(26)-N(22)-C(21)	117.7(4)
C(2)-N(1)-C(30)	114.9(3)	C(24)-C(23)-C(21)	118.6(5)
N(1)-C(2)-C(3)	115.5(3)	C(23)-C(24)-C(25)	120.2(4)
N(4)-C(3)-C(2)	106.9(3)	C(26)-C(25)-C(24)	117.1(5)
C(5)-N(4)-C(3)	115.0(3)	N(22)-C(26)-C(25)	123.9(5)
N(4)-C(5)-C(6)	110.3(4)	N(22)-C(26)-C(27)	116.7(4)
N(7)-C(6)-C(8)	121.3(5)	C(25)-C(26)-C(27)	119.4(4)
N(7)-C(6)-C(5)	115.7(4)	N(28)-C(27)-C(26)	111.8(3)
C(8)-C(6)-C(5)	123.0(4)	C(27)-N(28)-C(29)	113.2(3)
C(11)-N(7)-C(6)	119.2(4)	N(28)-C(29)-C(30)	110.3(3)
C(9)-C(8)-C(6)	118.6(5)	N(1)-C(30)-C(29)	110.3(4)
C(10)-C(9)-C(8)	120.6(4)	N(1)-C(31)-C(32)	112.0(4)
C(9)-C(10)-C(11)	117.3(5)	N(33)-C(32)-C(31)	110.7(6)
N(7)-C(11)-C(10)	122.8(5)	C(34)-N(33)-C(32)	114.8(6)
N(7)-C(11)-C(12)	116.5(4)	N(33)-C(34)-C(35)	109.8(6)
C(10)-C(11)-C(12)	120.5(4)	N(36)-C(35)-C(37)	120.5(10)
N(13)-C(12)-C(11)	112.7(3)	N(36)-C(35)-C(34)	116.0(8)
C(14)-N(13)-C(12)	114.7(4)	C(37)-C(35)-C(34)	123.5(8)
N(13)-C(14)-C(15)	110.6(3)	C(35)-N(36)-C(40)	118.2(7)
N(16)-C(15)-C(14)	112.4(4)	C(38)-C(37)-C(35)	119.5(8)
C(15)-N(16)-C(17)	112.0(3)	C(37)-C(38)-C(39)	120.1(9)
C(15)-N(16)-C(44)	111.1(3)	C(38)-C(39)-C(40)	117.0(9)
C(17)-N(16)-C(44)	111.6(3)	N(36)-C(40)-C(39)	124.4(6)
N(16)-C(17)-C(18)	113.1(3)	N(36)-C(40)-C(41)	116.0(5)
N(19)-C(18)-C(17)	111.3(3)	C(39)-C(40)-C(41)	119.6(7)
C(20)-N(19)-C(18)	110.8(3)	N(42)-C(41)-C(40)	110.3(4)
N(19)-C(20)-C(21)	111.4(3)	C(43)-N(42)-C(41)	113.2(3)
N(22)-C(21)-C(23)	122.4(5)	N(42)-C(43)-C(44)	109.8(3)
N(22)-C(21)-C(20)	115.6(4)	N(16)-C(44)-C(43)	110.7(3)

Symmetry transformations used to generate equivalent atoms: #1: -x, -y+1, -z+1.

Table G-5. Anisotropic displacement parameters ($Å^2$ x 10^3) for **$[H_614(Br)_3(H_2O)][Br]_3 \cdot 4H_2O$**. The anisotropic displacement factor exponent takes the form:

$$-2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	25(2)	53(2)	28(2)	-6(1)	0(1)	-8(1)
C(2)	32(2)	47(2)	26(2)	-6(2)	0(2)	-4(2)
C(3)	44(2)	50(3)	30(2)	-7(2)	4(2)	-7(2)
N(4)	43(2)	44(2)	32(2)	-3(2)	9(2)	-1(2)
C(5)	59(3)	57(3)	34(2)	6(2)	12(2)	1(2)
C(6)	44(2)	40(2)	38(2)	6(2)	15(2)	10(2)
N(7)	37(2)	34(2)	41(2)	2(1)	12(2)	5(1)
C(8)	50(3)	49(3)	46(3)	17(2)	20(2)	14(2)
C(9)	47(3)	37(2)	79(4)	26(2)	28(3)	13(2)
C(10)	37(2)	26(2)	68(3)	14(2)	9(2)	9(2)
C(11)	37(2)	26(2)	60(3)	10(2)	7(2)	8(2)
C(12)	62(3)	27(2)	53(3)	2(2)	8(2)	-7(2)
N(13)	44(2)	28(2)	39(2)	0(1)	3(2)	0(1)
C(14)	33(2)	37(2)	62(3)	6(2)	5(2)	-1(2)
C(15)	31(2)	34(2)	43(2)	1(2)	-1(2)	1(2)
N(16)	26(2)	34(2)	34(2)	4(1)	1(1)	2(1)
C(17)	33(2)	41(2)	24(2)	0(2)	-2(2)	1(2)
C(18)	40(2)	32(2)	31(2)	-4(2)	-2(2)	4(2)
N(19)	32(2)	39(2)	33(2)	-7(1)	-1(1)	1(1)
C(20)	48(3)	44(2)	42(2)	-8(2)	-11(2)	14(2)
C(21)	58(3)	29(2)	32(2)	-5(2)	4(2)	12(2)
N(22)	47(2)	34(2)	32(2)	-4(1)	0(2)	-3(2)
C(23)	62(3)	42(2)	36(2)	-1(2)	4(2)	29(2)
C(24)	84(4)	34(2)	46(3)	6(2)	23(3)	28(2)

C(25)	62(3)	25(2)	44(2)	2(2)	18(2)	7(2)
C(26)	56(3)	29(2)	36(2)	-7(2)	10(2)	-3(2)
C(27)	54(3)	49(3)	38(2)	-3(2)	4(2)	-25(2)
N(28)	38(2)	49(2)	34(2)	-4(2)	-2(2)	-13(2)
C(29)	42(2)	53(3)	42(2)	-6(2)	-10(2)	-15(2)
C(30)	35(2)	53(3)	34(2)	-9(2)	-4(2)	-10(2)
C(31)	31(2)	86(4)	32(2)	-17(2)	-3(2)	-1(2)
C(32)	35(3)	155(6)	36(3)	-27(3)	-2(2)	20(3)
N(33)	33(2)	160(5)	39(2)	-31(3)	3(2)	-10(3)
C(34)	23(3)	271(12)	59(4)	-66(6)	6(2)	7(4)
C(35)	26(3)	227(10)	50(3)	-46(5)	9(2)	35(4)
N(36)	29(2)	144(5)	30(2)	-14(3)	4(2)	24(3)
C(37)	59(5)	370(20)	53(4)	-44(8)	-19(3)	114(9)
C(38)	91(7)	300(17)	54(5)	11(7)	-5(4)	133(10)
C(39)	51(3)	148(7)	53(3)	20(4)	11(3)	53(4)
C(40)	34(2)	116(5)	31(2)	10(3)	13(2)	33(3)
C(41)	40(2)	64(3)	33(2)	11(2)	10(2)	26(2)
N(42)	29(2)	45(2)	27(2)	8(1)	5(1)	7(1)
C(43)	31(2)	43(2)	29(2)	5(2)	3(2)	6(2)
C(44)	35(2)	34(2)	28(2)	3(2)	-2(2)	2(2)
Br(1A)	37(1)	45(1)	26(1)	7(1)	9(1)	11(1)
Br(1B)	138(8)	101(6)	153(11)	-22(6)	73(7)	-25(6)
Br(2A)	42(1)	38(1)	48(1)	-3(1)	13(1)	-3(1)
Br(3A)	104(2)	38(1)	35(1)	-7(1)	15(1)	3(1)
Br(3B)	34(4)	52(3)	40(2)	-25(3)	-11(2)	12(2)
Br(4)	40(1)	50(1)	63(1)	7(1)	1(1)	2(1)
Br(5A)	39(1)	48(2)	28(1)	-8(1)	5(1)	-6(1)
Br(5B)	31(2)	22(3)	24(1)	-4(1)	6(1)	3(2)
Br(6A)	65(1)	43(2)	53(1)	-9(1)	17(1)	-17(1)
Br(6B)	51(1)	90(2)	501(10)	-119(4)	42(3)	-11(1)
Br(6C)	82(4)	64(8)	74(4)	-29(4)	52(3)	-31(4)
O(1W)	36(2)	44(2)	36(2)	0(1)	4(1)	-2(1)
O(2W)	235(11)	468(19)	389(17)	-362(16)	219(12)	-227(13)
O(3W)	272(12)	164(8)	79(5)	-32(5)	28(6)	-111(8)

O(3W')	74(7)	74(7)	140(18)	0	0	0
O(4W)	82(5)	265(10)	33(3)	-67(4)	-16(3)	17(5)
O(5W)	150(10)	147(10)	94(8)	-49(7)	-37(7)	-49(8)
O(5W')	28(6)	30(7)	66(10)	20(6)	-8(6)	-25(5)
O(5W")	117(17)	64(13)	80(13)	-59(11)	74(12)	-70(12)

Table G-6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $\mathbf{[H_{6}14(Br)_{3}(H_{2}O)][Br]_{3}\cdot 4H_{2}O}$.

	x	y	z	U(eq)
H(2A)	2904	5842	4461	42
H(2B)	2409	6262	4507	42
H(3A)	2913	6009	3707	50
H(3B)	2444	6461	3773	50
H(41)	3026	6933	4214	48
H(42)	3454	6506	4178	48
H(5A)	3143	7177	3512	60
H(5B)	3618	6728	3483	60
H(8)	4227	7578	3282	58
H(9)	4854	8170	3587	65
H(10)	4802	8369	4305	52
H(12A)	4377	8151	4992	57
H(12B)	3784	8363	4856	57
H(131)	3624	7751	5351	44
H(132)	3493	7448	4957	44
H(14A)	4513	7317	5306	53
H(14B)	4195	6898	5003	53
H(15A)	4212	6603	5736	43
H(15B)	3851	7126	5856	43
H(17A)	3824	6109	5093	39
H(17B)	3212	5907	5178	39

H(18A)	4009	5754	5827	41
H(18B)	3457	5414	5760	41
H(191)	3884	5063	5131	41
H(192)	4408	5305	5280	41
H(20A)	4324	4789	5909	53
H(20B)	4456	4440	5493	53
H(23)	3851	4021	6269	56
H(24)	3072	3480	6304	66
H(25)	2407	3537	5762	53
H(27A)	2456	3778	4884	57
H(27B)	2066	4158	5165	57
H(281)	2929	4614	4725	48
H(282)	2448	4909	4899	48
H(29A)	1879	4534	4390	55
H(29B)	2396	4212	4203	55
H(30A)	2821	5077	4056	49
H(30B)	2273	4986	3788	49
H(31A)	1460	5361	4000	60
H(31B)	1762	5864	3777	60
H(32A)	1566	6421	4379	91
H(32B)	1016	6204	4162	91
H(331)	1076	5477	4674	93
H(332)	1478	5820	4904	93
H(34A)	655	5922	5221	141
H(34B)	394	6095	4775	141
H(37)	390	7114	4597	193
H(38)	603	7986	4801	178
H(39)	1297	8130	5304	101
H(41A)	2067	7736	5671	55
H(41B)	1738	7374	6008	55
H(421)	2112	6599	5666	41
H(422)	2462	6965	5407	41
H(43A)	2538	6879	6281	41
H(43B)	2916	7273	6001	41

H(44A)	3358	6420	6172	39
H(44B)	2902	6109	5899	39

Table G-7. Torsion angles [°] for **$[H_6 14(Br)_3(H_2O)][Br]_3 \cdot 4H_2O$**.

C(31)-N(1)-C(2)-C(3)	-58.6(5)
C(30)-N(1)-C(2)-C(3)	72.8(5)
N(1)-C(2)-C(3)-N(4)	-175.7(3)
C(2)-C(3)-N(4)-C(5)	176.9(4)
C(3)-N(4)-C(5)-C(6)	178.1(4)
N(4)-C(5)-C(6)-N(7)	-15.2(6)
N(4)-C(5)-C(6)-C(8)	165.1(4)
C(8)-C(6)-N(7)-C(11)	0.9(6)
C(5)-C(6)-N(7)-C(11)	-178.8(4)
N(7)-C(6)-C(8)-C(9)	2.4(6)
C(5)-C(6)-C(8)-C(9)	-177.9(4)
C(6)-C(8)-C(9)-C(10)	-2.6(7)
C(8)-C(9)-C(10)-C(11)	-0.2(6)
C(6)-N(7)-C(11)-C(10)	-4.0(6)
C(6)-N(7)-C(11)-C(12)	170.9(4)
C(9)-C(10)-C(11)-N(7)	3.7(6)
C(9)-C(10)-C(11)-C(12)	-171.1(4)
N(7)-C(11)-C(12)-N(13)	30.3(6)
C(10)-C(11)-C(12)-N(13)	-154.6(4)
C(11)-C(12)-N(13)-C(14)	75.0(5)
C(12)-N(13)-C(14)-C(15)	157.6(4)
N(13)-C(14)-C(15)-N(16)	67.4(5)
C(14)-C(15)-N(16)-C(17)	77.7(4)
C(14)-C(15)-N(16)-C(44)	-156.8(3)
C(15)-N(16)-C(17)-C(18)	77.4(4)
C(44)-N(16)-C(17)-C(18)	-47.9(4)
N(16)-C(17)-C(18)-N(19)	-158.1(3)
C(17)-C(18)-N(19)-C(20)	-167.3(3)

C(18)-N(19)-C(20)-C(21)	72.7(4)
N(19)-C(20)-C(21)-N(22)	28.9(5)
N(19)-C(20)-C(21)-C(23)	-153.2(4)
C(23)-C(21)-N(22)-C(26)	-1.3(6)
C(20)-C(21)-N(22)-C(26)	176.6(4)
N(22)-C(21)-C(23)-C(24)	2.3(6)
C(20)-C(21)-C(23)-C(24)	-175.5(4)
C(21)-C(23)-C(24)-C(25)	-2.3(6)
C(23)-C(24)-C(25)-C(26)	1.3(6)
C(21)-N(22)-C(26)-C(25)	0.3(6)
C(21)-N(22)-C(26)-C(27)	-178.4(4)
C(24)-C(25)-C(26)-N(22)	-0.3(6)
C(24)-C(25)-C(26)-C(27)	178.3(4)
N(22)-C(26)-C(27)-N(28)	-14.0(6)
C(25)-C(26)-C(27)-N(28)	167.3(4)
C(26)-C(27)-N(28)-C(29)	163.6(4)
C(27)-N(28)-C(29)-C(30)	-179.6(4)
C(31)-N(1)-C(30)-C(29)	-99.0(4)
C(2)-N(1)-C(30)-C(29)	128.0(4)
N(28)-C(29)-C(30)-N(1)	-66.6(5)
C(2)-N(1)-C(31)-C(32)	-65.1(6)
C(30)-N(1)-C(31)-C(32)	161.9(5)
N(1)-C(31)-C(32)-N(33)	-62.9(6)
C(31)-C(32)-N(33)-C(34)	-162.8(5)
C(32)-N(33)-C(34)-C(35)	-57.0(7)
N(33)-C(34)-C(35)-N(36)	-70.4(7)
N(33)-C(34)-C(35)-C(37)	108.6(7)
C(37)-C(35)-N(36)-C(40)	0.3(8)
C(34)-C(35)-N(36)-C(40)	179.4(4)
N(36)-C(35)-C(37)-C(38)	-4.7(12)
C(34)-C(35)-C(37)-C(38)	176.3(8)
C(35)-C(37)-C(38)-C(39)	5.1(15)
C(37)-C(38)-C(39)-C(40)	-1.4(13)
C(35)-N(36)-C(40)-C(39)	3.7(7)

C(35)-N(36)-C(40)-C(41)	-176.8(4)
C(38)-C(39)-C(40)-N(36)	-3.2(8)
C(38)-C(39)-C(40)-C(41)	177.2(6)
N(36)-C(40)-C(41)-N(42)	36.2(5)
C(39)-C(40)-C(41)-N(42)	-144.2(4)
C(40)-C(41)-N(42)-C(43)	-171.7(4)
C(41)-N(42)-C(43)-C(44)	179.9(3)
C(15)-N(16)-C(44)-C(43)	88.8(4)
C(17)-N(16)-C(44)-C(43)	-145.5(3)
N(42)-C(43)-C(44)-N(16)	67.1(4)

Symmetry transformations used to generate equivalent atoms: #1: -x, -y+1, -z+1.

Table G-8. Hydrogen bonds for **$[H_614(Br)_3(H_2O)][Br]_3\cdot4H_2O$**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(41)...Br(1A)	0.92	2.37	3.273(4)	167.6
N(4)-H(41)...Br(1B)	0.92	2.38	3.264(11)	161.9
N(4)-H(42)...Br(2A)	0.92	2.34	3.187(4)	153.6
N(4)-H(42)...Br(2B)	0.92	2.65	3.51(4)	156.8
N(13)-H(131)...Br(3B)	0.92	2.28	3.162(10)	160.2
N(13)-H(131)...Br(3A)	0.92	2.35	3.233(5)	159.7
N(13)-H(132)...Br(1A)	0.92	2.58	3.420(4)	151.9
N(13)-H(132)...Br(1B)	0.92	2.86	3.71(3)	154.1
N(19)-H(191)...O(1W)	0.92	2.02	2.912(4)	162.7
N(19)-H(192)...Br(4)	0.92	2.38	3.218(4)	152.1
N(28)-H(281)...O(1W)	0.92	2.04	2.926(5)	161.5
N(28)-H(282)...Br(5A)	0.92	2.37	3.243(8)	157.7
N(28)-H(282)...Br(5B)	0.92	2.65	3.546(13)	164.0
N(33)-H(331)...O(5W")	0.92	1.65	2.449(16)	143.4
N(33)-H(331)...Br(6C)	0.92	2.36	3.264(14)	168.5
N(33)-H(331)...Br(6A)	0.92	2.67	3.581(8)	169.7
N(33)-H(332)...Br(5B)	0.92	2.20	3.093(12)	162.3

N(33)-H(332)...Br(5A)	0.92	2.47	3.342(8)	158.8
N(42)-H(421)...Br(5B)	0.92	2.50	3.332(12)	151.0
N(42)-H(421)...Br(5A)	0.92	2.84	3.651(9)	148.3
N(42)-H(422)...Br(1A)	0.92	2.46	3.279(3)	148.0
N(42)-H(422)...Br(1B)	0.92	2.56	3.357(16)	145.1

Symmetry transformations used to generate equivalent atoms: #1: -x, -y+1, -z+1.

Chapter 9 References

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