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# Accepted Article

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# Tetrameric and Dimeric [N···I<sup>+</sup>···N] Halogen-Bonded Supramolecular Cages

Lotta Turunen,<sup>[a]</sup> Anssi Peuronen,<sup>[a]</sup> Samu Forsblom,<sup>[a]</sup> Elina Kalenius,<sup>[a]</sup> Manu Lahtinen<sup>\*[a]</sup> and Kari Rissanen<sup>\*[a]</sup>

**Abstract:** Tripodal *N*-donor ligands are used to form halogenbonded assemblies *via* structurally analogous Ag<sup>+</sup>-complexes. Selective formation of discrete tetrameric I<sub>6</sub>L<sub>4</sub> and dimeric I<sub>3</sub>L<sub>2</sub> halonium cages, wherein multiple [N···1<sup>+</sup>···N] halogen bonds are used in concert, can be achieved by using sterically rigidified cationic tris(1-methyl-1-azonia-4-azabicyclo[2.2.2]octane)-mesitylene ligand, L1(PF<sub>6</sub>)<sub>3</sub>, and flexible ligand 1,3,5-tris(imidazole-1-ylmethyl)-2,4,6-trimethylbenzene, L2, respectively. The iodonium cages, I<sub>6</sub>L1<sub>4</sub>(PF<sub>6</sub>)<sub>18</sub> and I<sub>3</sub>L2<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub>, were obtained through the [N···Ag<sup>+</sup>···N]  $\rightarrow$  [N···I<sup>+</sup>···N] cation exchange reaction between the corresponding Ag<sub>6</sub>L1<sub>4</sub>(PF<sub>6</sub>)<sub>18</sub> and Ag<sub>3</sub>L2<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub> coordination cages, prepared as intermediates, and I<sub>2</sub>. The synthesized metallo- and halonium cages were studied in solution by NMR, in gas phase by ESI-MS and in the solid-state by single crystal X-ray diffraction.

#### Introduction

Halogen bonding (XB) is a non-covalent interaction between a polarized halogen atom and a Lewis base.<sup>[1]</sup> During the last decade XB has found applications in variety of research fields including crystal engineering, material sciences, medicinal chemistry and organocatalysis.<sup>[2]</sup> Halonium ions are interesting class of XB donors which are able to form three-center-four-electron (3*c*4*e*) bonds with two XB acceptor moieties.<sup>[3,4]</sup> Behavior of halonium ions in bis-pyridine complexes have been carefully studied in solution and in the solid-state.<sup>[3,5–7]</sup> Recently, we reported syntheses and characterizations of dimeric and hexameric capsules solely based on [N···I<sup>+</sup>···N] bonds.<sup>[8]</sup> It has been shown that [N···I<sup>+</sup>···N] bond is a strong interaction that exhibits highly predictable bond parameters.<sup>[4]</sup> Hence, it is particularly well-suited for the self-assembly studies of halogen-bonded supramolecular species/complexes.

Among different supramolecular assemblies coordination cages, as metallosupramolecular complexes, have attracted particular attention during the last two decades. The keen interest toward coordination cages is partly due to their fascinating structural features, but also because of the increase in number of potential applications that exploit their well-defined cavities.<sup>[9–13]</sup> These systems are prepared by coordination-driven

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self-assembly from spatially pre-organized organic ligands (L) and metal cations (M) with known coordination geometry. One of the commonly used group of ligands is bowl-shaped tripodal *N*-donor ligands which enables the construction of various types of coordination cages such as dimeric  $M_3L_2$ , tetrahedral  $M_6L_4$  and octahedral  $M_6L_8$  species.<sup>[14,15]</sup> The exact cage topology is mostly governed by the connectivity and coordination geometry of the metal ion as well as the structural and chemical properties of the ligand. Furthermore, counter anions, reaction conditions (*e.g.* solvent and temperature) as well as possible auxiliary ligands can all have an effect to the outcome in the self-assembly process.

We have been interested in investigating the behavior of the [N···I<sup>+</sup>···N] halogen bond in connection with spatially organized multitopic XB acceptors.8 In this work we extend this approach to two different tripodal XB acceptor ligands, L1(PF<sub>6</sub>)<sub>3</sub> and L2 (Scheme 1), both of which have previously been used in the construction of coordination cages and are easily prepared according to the reported procedures.<sup>[16,17]</sup> The ligand L2 is known to adapt different geometries due to the flexibility of the imidazole arms and hence different topologies including cages and polymeric structures with different metals and counter ions have been reported.<sup>[18-21]</sup> On the other hand, the self-assembly of L1(PF<sub>6</sub>)<sub>3</sub> with metal cations is to a great extent affected by the intra- and intermolecular steric interactions of the bulky DABCO groups which stabilize the bowl-shaped all-cis conformation of the ligand and restrict the spatial orientation of the N-donor moieties. Recently, we reported Pd2+ and Cu2+ based cages of  ${\rm L1}^{\rm 3^+,[22]}$  Their self-assembly was shown to result in tetrahedral M<sub>6</sub>L1<sub>4</sub> species instead of the expected M<sub>6</sub>L<sub>8</sub> due to the steric interactions between the DABCO groups around the metal node leading to linear N-M-N coordination. The corresponding Ag<sub>6</sub>L1<sub>4</sub>(PF<sub>6</sub>)<sub>18</sub> was not known, but due to the linear nature of the  $[N \cdots Ag^{+} \cdots N]$  bond, it was anticipated that once  $Ag_6L1_4(PF_6)_{18}$  is obtained the  $[N \cdots Ag^{+} \cdots N] \rightarrow [N \cdots I^{+} \cdots N]$  cation exchange reaction would result in the analogous halogen-bonded tetrameric halonium cage  $I_6L1_4(PF_6)_{18}$ .



Scheme 1. Structures of ligands L1(PF<sub>6</sub>)<sub>3</sub> and L2.

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In this contribution we report the results of NMR spectroscopic, mass spectrometric and single crystal X-ray structural studies of the  $[N^{\dots}l^+ \cdots N]$  halogen-bonded tetrameric  $I_6L1_4(PF_6)_{18}$  and dimeric  $I_3L2_2(PF_6)_3$  halonium cages. Through the parent  $Ag^+$ -coordination complexes and, subsequently applying the  $[N^{\dots}Ag^+ \cdots N] \rightarrow [N^{\dots}l^+ \cdots N]$  cation exchange reaction,<sup>8</sup> we obtain the isostructural halogen-bonded cages. The single crystals of the halonium ion assemblies have turned out to be very challenging to obtain,<sup>[8]</sup> yet in this work we present the first X-ray structural characterization of the supramolecular cages constructed via multiple  $[N^{\dots}l^+ \cdots N]$  halogen bonds.

#### **Results and Discussion**

Syntheses of the [N···I<sup>+</sup>···N] bonded capsules follow the previously reported procedures.<sup>[8]</sup> The halonium cages are obtained first by reacting  $L1(PF_6)_3$  and L2 with silver hexafluorophosphate (AgPF<sub>6</sub>) followed by the addition of molecular iodine. The self-assembly of Ag<sup>+</sup> and I<sup>+</sup> species was monitored by <sup>1</sup>H NMR in CD<sub>3</sub>CN (Figure S1). Somewhat surprisingly, the addition of AgPF<sub>6</sub> into the L1(PF<sub>6</sub>)<sub>3</sub> in CD<sub>3</sub>CN solution did not result in noticeable shifting of the L1(PF<sub>6</sub>)<sub>3</sub> proton signals. This may be due to solvation of Ag<sup>+</sup> as a [Ag(acetonitrile)<sub>4</sub>]<sup>+</sup> complex which seems to be energetically favored over the [Ag<sub>6</sub>L1<sub>4</sub>]<sup>18+</sup> in acetonitrile. However, after the addition of I2, which was accompanied by an immediate precipitation of AgI and color change of the initially colorless solution to yellow (to mark the presence of slight excess of I2), the <sup>1</sup>H NMR spectrum reveals a new set of downfield shifted L1(PF<sub>6</sub>)<sub>3</sub> signals together with minor peaks of unreacted  $L1(PF_6)_3$  (Figure S1c). Specifically, the merging of the two triplets that arise from the asymmetric DABCO environment into one peak at 3.6 ppm is due to the formation of the six symmetric [N…I<sup>+</sup>…N] halogen bonds.

To provide more evidence for the expected formation of the  $[I_6L1_4]^{18+}$  cage, diffusion-ordered NMR spectroscopy (DOSY) measurements were performed. Two set of signals were observed in the <sup>1</sup>H DOSY spectrum of the expected  $I_6L1_4(PF_6)_{18}$  indicating the presence of two discrete species (Figure S2). These were with diffusion coefficient (*D*) of  $1.06 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and considerable lower value of  $6.09 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  (CD<sub>3</sub>CN, 298 K), which correspond to a mixture of unreacted L1(PF<sub>6</sub>)<sub>3</sub> and a definitely larger species with radius of 1.05 nm (diameter of 2.1 nm) according to the Stokes-Einstein equation. The size correlates very well to our previous observations of Cu<sup>2+</sup> and Pd<sup>2+</sup> complexes with M<sub>6</sub>L1<sub>4</sub> stoichiometry (size derived from the single crystal X-ray structure of Cu<sub>6</sub>L1<sub>4</sub>(PF<sub>6</sub>)<sub>24</sub>).<sup>[22]</sup>

Unfortunately, our efforts to characterize either  $Ag_6L1_4(PF_6)_{18}$  or  $I_6L1_4(PF_6)_{18}$  further with ESI-MS were not successful. This is not surprising considering the high positive charge density (+18) of the assemblies. In gas phase, the stabilizing solvent and anion interactions are absent and close proximity of the silver and iodonium cations with the cationic ligand likely results in repulsion and fragmentation of the cages.

The penultimate way to investigate the nature of the formed species is to crystallize both  $Ag_6L1_4(PF_6)_{18}$  and  $I_6L1_4(PF_6)_{18}$ .

Crystals emerged from a methanol solution of AgPF<sub>6</sub> and L1(PF<sub>6</sub>)<sub>3</sub> upon slow diffusion with ethyl acetate. Although no complexation between Ag<sup>+</sup> and L1(PF<sub>6</sub>)<sub>3</sub> was observed in solution by NMR, the single crystal X-ray analysis revealed the formation of a Ag<sub>6</sub>L1<sub>4</sub>(PF<sub>6</sub>)<sub>18</sub> as a 2 nm cage (measured from the far-cornered H-atoms, Figure 1). The metallocage crystallized in a high-symmetry space group (tetragonal *I*-42m) and is similarly two-fold disordered as the Cu<sub>6</sub>L1<sub>4</sub>(PF<sub>6</sub>)<sub>24</sub> tetrameric cage.<sup>[22]</sup> The six Ag(I) ions and four ligands form a total of six [N···Ag<sup>+</sup>···N] coordination environments with normal Ag-N bond distances and nearly linear to slightly bent N–Ag<sup>+</sup>–N bond angles, thus being structurally analogous to the Cu<sub>6</sub>L1<sub>4</sub>(PF<sub>6</sub>)<sub>24</sub>.<sup>[22]</sup>



**Figure 1.** The ball-and-stick (left) and CPK (right) presentations of the crystal structure of Ag<sub>6</sub>L1<sub>4</sub>(PF<sub>6</sub>)<sub>18</sub>. The N–Ag–N bond lengths and angles are in the range of 2.27 - 2.32 Å and 160 - 177°, respectively. Disordered ligands, solvent molecules and all anions are omitted for clarity.

The reaction between  $Ag_6L1_4(PF_6)_{18}$  and  $I_2$  in acetonitrile and the subsequent slow evaporation of the solvent led to the crystallization of colorless plates. The single crystal X-ray analysis of the crystals provided proof of the formation of the expected  $I_6L1_4(PF_6)_{18}$  halonium cage (Figure 2). The solid state structure of  $I_6L1_4(PF_6)_{18}$  consists of six I<sup>+</sup> cations each of which binds to two distinct ligands resulting in a tetrahedral cage analogous to Ag<sub>6</sub>L1<sub>4</sub>(PF<sub>6</sub>)<sub>18</sub> and Cu<sub>6</sub>L1<sub>4</sub>(PF<sub>6</sub>)<sub>24</sub>.<sup>[22]</sup> Contrary to  $Ag_6L1_4(PF_6)_{18}$ , the  $I_6L1_4(PF_6)_{18}$  crystallizes in a lower symmetry space group (orthorhombic Pmna) and does not show the symmetry-related two-fold disorder of the cage framework, thus facilitating its structural analysis. The six [N…I<sup>+</sup>…N] halogen bonds have N-I distances ranging from 2.26 to 2.35 Å. The [N···I<sup>+</sup>···N] halogen bonds are less symmetric than what is generally observed for [N···I<sup>+</sup>···N] halogen bond from smaller XB acceptor moieties.<sup>[4]</sup> However, these have very seldom more than one undisturbed [N…I+...N] halogen bond, whereas in I<sub>6</sub>L1<sub>4</sub>(PF<sub>6</sub>)<sub>18</sub> the large and highly charged L1 ligand can induce geometric strains and distort each of the six [N···I<sup>+</sup>···N] bonds. Nevertheless, only very minor bending from the ideally linear [N···I<sup>+</sup>···N] halogen bonds occurs as all [N···I<sup>+</sup>···N] angles are larger than 175°. This is characteristic to the [N…I<sup>+</sup>…N] halogen bond, owing to the anisotropic charge distribution of the I<sup>+</sup> cation, and is in stark contrast to the N-Ag-N environments which are prone to higher coordination numbers and significant distortions from the linear coordination geometry. This highlights the predictable nature of the [N…I+...N] halogen bond and its applicability in self-assembly of even larger supramolecular

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assemblies.<sup>[8]</sup> Despite coordinative differences, the  $I_6L1_4(PF_6)_{18}$ binds the  $PF_6^-$  anions similarly as its metallosupramolecular analogues  $Ag_6L1_4(PF_6)_{18}$  and  $Cu_6L1_4(PF_6)_{24}^{[22]}$ . Four out of the 18  $PF_6^-$  anions reside inside the endohedral cavity of the halonium cage, each occupying one of the four cationic ligand pockets. This anion binding arises primarily from the electrostatic interactions between the cationic  $L1^{3+}$  ligand and the anions.



**Figure 2.** The ball-and-stick (left) and CPK (right) presentations of the crystal structure of  $I_6L1_4(PF_6)_{18}$ . The N–I–N bond lengths and angles are in the range of 2.26 - 2.35 Å and 175 - 177°, respectively. Solvent molecules and all anions are omitted for clarity.

As a structurally similar tripodal supramolecular building block **L2** has two significant differences to **L1**. Firstly, **L2** is noncharged and secondly has greater structural flexibility, meaning that by using different metal cations, counteranions, reaction conditions and metal-ligand stoichiometry, cages and polymeric structures are plausible.<sup>[18–21]</sup> Of these the I<sub>3</sub>**L2**<sub>2</sub>X<sub>3</sub> is expected to be prominent as several Ag<sub>3</sub>**L2**<sub>2</sub>X<sub>3</sub> complexes (where X = N<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup> OTF or PF<sub>6</sub><sup>-</sup>) have been observed under similar conditions.<sup>[19,21,23,24]</sup> Contrary to highly-charged **L1**, **L2** does not impose additional electrostatic interactions and can lead to less-disturbed stronger [N···1<sup>+</sup>···N] halogen bonds.

The consecutive reactions of AgPF<sub>6</sub> and I<sub>2</sub> with L2 in CD<sub>3</sub>CN showed a shifted set of signals in <sup>1</sup>H NMR spectrum in both cases. Comparison between the two spectra shows that I<sup>+</sup> induces a larger downfield shift to the ligand signals than Ag<sup>+</sup> (Figure 3). The <sup>1</sup>H DOSY measurements (Figures 3d and S3) revealed single species for both  $Ag^+$  and  $I^+$  complexes with D of 8.46 x  $10^{-10}$  m<sup>2</sup>·s<sup>-1</sup> and 7.86 x  $10^{-10}$  m<sup>2</sup>·s<sup>-1</sup> in acetonitrile at 298K, respectively. The measured D values correspond to spherical objects with diameters of 1.52 nm and 1.63 nm whereas the corresponding estimated  $^{[18,19,21,23,24]}$  values for  $M_3L2_2^{3+}$  and  $M_6L2_4^{6+}$  are roughly 1.3 - 1.4 nm and 1.65 - 1.9 nm, respectively. Hence, no conclusive analysis on the compositions can be drawn from the DOSY data alone. Instead, the composition was verified by ESI-MS analysis, in which only the formation of dimeric complex was detected and ions [I<sub>3</sub>L2<sub>2</sub>]<sup>3+</sup> at *m*/z 367 and  $[I_3L2_2+PF_6]^{2+}$  at m/z 623 appeared in spectra (Figure S4 and Table S1). The possible tetrameric ions  $[I_6L2_4]^{6+}$ and  $[I_6L2_4+2PF_6]^{4+}$  could result in from overlapping *m*/z values of 367 and 623, but isotopic distributions and charge states corresponded only with the stoichiometry of the dimer.



Figure 3. <sup>1</sup>H NMR spectra (CD<sub>3</sub>CN, 400 MHz, 298 K) of (a) L2, (b) Ag<sub>3</sub>L2<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub> and (c) I<sub>3</sub>L2<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub>, and (d) the <sup>1</sup>H DOSY NMR spectrum of I<sub>3</sub>L2<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub>.

The single crystals of Ag<sub>3</sub>L2<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub> could be obtained by diffusing ethyl acetate into the respective acetonitrile solution whereas crystals of I<sub>3</sub>L2<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub> emerged upon slow evaporation of an acetonitrile solution of Ag<sub>3</sub>L2<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub> after reaction with I<sub>2</sub> and filtration. The single crystal X-ray analysis confirmed the formation of the dimeric metallo- and halonium cages. The  $[N \cdots I^{\dagger} \cdots N]$  halogen bonds in the structure of  $I_3 L2_2 (PF_6)_3$  are symmetric and very close to linear with all six N-I distances and three N-I-N angles being 2.233(6) Å and 177.0(4)°, respectively due to the hexagonal crystal symmetry. Comparison of these bond parameters to the data available in the Cambridge Structural Database (CSD) shows that the  $[N\cdots l^{*}\cdots N]$  halogen bonds in the  $I_3L2_2(PF_6)_3$  dimer are very close to the corresponding values of previously reported [N···I<sup>+</sup>···N] structures<sup>[25]</sup>, thus again nicely demonstrating the robustness and predictability of the [N···I<sup>+</sup>···N] halogen bond as a robust supramolecular motif.



**Figure 3.** The ball-and-stick and CPK (right) presentations of the  $D_3$  symmetric helical coordination cage  $Ag_3L2_2^{3^+}$  (top left) and its  $C_{3h}$  symmetric analogue,  $I_3L2_2^{3^+}$ , assembled using  $[N \cdots I^+ \cdots N]$  3c4e halogen bond (below left). The N–Ag–N and N–I–N bond lengths (Å) and angles (°): Ag–N = 2.110(5), I–N = 2.233(6); N–Ag–N = 178.2(4), N–I–N = 177.0(4). Anions and solvent molecules are omitted for clarity.

When comparing the two structurally analogous cages,  $Ag_3L2_2(PF_6)_3$  and  $I_3L2_2(PF_6)_3$ , it becomes apparent that they show structural similarities but also differ significantly. The coordination environment of Ag<sup>+</sup> in Ag<sub>3</sub>L2<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub> has clearly shorter Ag-N bonds [2.110(5) Å] compared to the I-N bonds [2.223(6) Å] in I<sub>3</sub>L2<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub>, while the N-Ag-N angles are very close to linear [178.2(4)°] being remarkably similar with I<sub>3</sub>L2<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub>. The N-Ag-N environment is known to be easily distorted away from linearity by coordinating counteranions as demonstrated, for example, by the nitrate and azide analogues of  $Ag_3L2_2(PF_6)_3$ .<sup>[19,23]</sup> On the contrary, the geometry of the [N···I<sup>+</sup>···N] unit is expected to be mostly undisturbed by counteranions as the contact surface of the I<sup>+</sup> cation, perpendicular to the [N···I<sup>+</sup>···N] halogen bonds, is not electrophilic but rather charge-neutral or even nucleophilic. This is attributable to the  $p_x^2 p_y^2 p_z^0$  valence p-orbital occupancy of the iodonium cation.[26]

The different charge distributions of the Ag<sup>+</sup> and I<sup>+</sup> cations is reflected also in the host-guest chemistry of the respective supramolecular  $M_3L2_2^{3+}$  cages. In the solid state  $Ag_3L2_2^{3+}$  clearly encapsulates one PF<sub>6</sub><sup>-</sup> anion within its endohedral cavity. The PF<sub>6</sub><sup>-</sup> is severely disordered over three major symmetry-related positions which were analyzed to reside at the Ag–Ag–Ag plane and being stabilized by van der Waals contacts between fluorine atoms and Ag<sup>+</sup> ( $d(F\cdots Ag) \approx 3.0 - 3.1$  Å). This analysis is supported by an earlier study of a hydrate structure of Ag<sub>3</sub>L2<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub> in which the equatorial fluorine atoms of an

encapsulated (non-disordered) PF<sub>6</sub><sup>-</sup> anion reside at the Ag-Ag-Ag plane within 2.8 - 3.1 Å away from the Ag<sup>+</sup> cations.<sup>[24]</sup> In the case of  $I_3L2_2(PF_6)_3$  the residual electron density suggests that one PF<sub>6</sub><sup>-</sup> anion occupies the endohedral cavity and is disordered over two major positions along the  $C_3$  axis of the host, perpendicular to the I-I-I plane (see residual electron density maps of non-masked refinements of Ag<sub>3</sub>L2<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub> and  $I_3L2_2(PF_6)_3$  in figure S5). This is reasonable when considering the cationic nature of the halonium cage which gives the impetus for the encapsulation of the anionic guest whereas the repulsive nature of the fluorine...I\* interaction perpendicular to the N-I-N bonds pushes the anion away from the I-I-I plane. Hence, although the anion within the cavity of I<sub>3</sub>L2<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub> could not be well resolved, the results suggest that the anisotropic charge distribution of the I<sup>+</sup> cation has a directing effect in the host-guest chemistry of the respective supramolecular assemblies. This phenomenon could be exploited in tuning of the interior of a supramolecular host and thus gaining target-specificity toward e.g. charge-depleted guest species.

#### Conclusions

This work presents the use of two structurally different N-donor tripodal ligands L1(PF<sub>6</sub>)<sub>3</sub> and L2 in the formation of discrete cationic supramolecular halonium cages  $I_{6}L1_{4}^{18+}$  and  $I_{3}L2_{2}^{3+}$ from their parent metallosupramolecular cages Ag<sub>6</sub>L14<sup>18+</sup> and  $Ag_3L2_2^{3+}$ , respectively, by reaction with molecular iodine. In addition to comprehensive NMR spectroscopic and ESI-MS spectrometric evidence, the [N···I<sup>+</sup>···N] halogen-bonded cages were structurally characterized for the first time at an atomic resolution by single crystal X-ray crystallography. The NMR spectroscopic results illustrated the difficulty of the cationic and sterically challenging ligand  $L1(PF_6)_3$  to form the tetrameric metallosupramolecular cage with Ag<sup>+</sup> cations in acetonitrile, whereas the robust  $[N \cdots Ag^{\dagger} \cdots N] \rightarrow [N \cdots I^{\dagger} \cdots N]$  cation exchange reaction resulted effortlessly in the desired tetrahedral  $I_6L1_4^{18+}$ halonium cage. Despite the different behavior of the Ag<sup>+</sup> and I<sup>+</sup> cations with  $L1(PF_6)_3$  in solution, both tetrameric  $M_6L1_4$  (M = Ag or I) cages could be obtained and characterized in the solid state by single crystal X-ray crystallography. In the case of the ligand L2, selective formation of dimeric  $M_3L2_2X_3$  cages with AgPF<sub>6</sub> and subsequently with I<sup>+</sup> in solution, in the gas phase and in the solid state was observed.

In conclusion, the results presented herein show that the  $[N\cdots l^*\cdots N]$  halogen bonds are very robust and reliable connectors when constructing large supramolecular assemblies with predictable structural features. The robustness of the  $[N\cdots l^*\cdots N]$  unit is highlighted by the fact that, although the native iodonium cation  $(l^*)$  is considered to be a highly reactive species the  $[N\cdots Ag^*\cdots N] \rightarrow [N\cdots l^*\cdots N]$  cation exchange reaction does not need dry solvents during the self-assembly process or during the analyses. The crystal structures of the halonium cages clearly demonstrate the propensity of the  $[N\cdots l^*\cdots N]$  motif to systematically yield linear coordination whereas the analogous  $[N\cdots Ag^*\cdots N]$  unit is more prone to deformation. This difference would be more dramatic in the presence of coordinating anions

#### **Experimental Section**

Ligands  $L1(PF_6)_3$  and L2 were synthesized according to the reported procedures.<sup>[16,17]</sup> NMR spectra were recorded on a Bruker Avance III 500 or Avance 400 spectrometers. All signals are given as  $\delta$  values in ppm using residual solvent signals as the internal standard. ESI-MS experiments were performed on AB Sciex QSTAR Elite ESI-Q-TOF mass spectrometer equipped with an API 200 TurbolonSpray ESI source from AB Sciex (former MDS Sciex) in Concord, Ontario (Canada). Single crystal X-ray data were collected with either Agilent SuperNova, equipped with multilayer optics monochromated dual source (Cu and Mo) and Atlas detector, using Cu Ka (1.54184 Å) radiation or Bruker-Nonius/Kappa CCD diffractometer using Mo Ka (0.71073 Å) radiation. In the latter case, data acquisitions, reductions and absorption corrections were made using programs  $\mathsf{COLLECT}^{[27]},\ \mathsf{DENZO}\text{-}\mathsf{SMN}^{[28]}$  and SADABS<sup>[29]</sup> whereas the data collected with Agilent SuperNova was treated within the CrysAlis<sup>Pro</sup> program package<sup>[30]</sup>. The structures were solved with ShelXS<sup>[31]</sup> program and refined on  $F^2$  by full matrix least squares techniques with ShelXL<sup>[32]</sup> program in Olex<sup>2</sup> (v.1.2)<sup>[33]</sup> program package. Anisotropical displacement parameters were applied for all atoms except hydrogens which were calculated into their ideal positions using isotropic displacement parameters 1.2-1.5 times of the host atom. Olex<sup>2</sup> solvent mask routine was used to treat the residual electron density corresponding to disordered anions and solvent molecules in the crystal lattices. Details of solvent mask procedure together with crystallographic data table can be found in ESI (table S2).

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Applying the robust  $[N \cdots Ag^* \cdots N] \rightarrow [N \cdots I^* \cdots N]$  cation exchange reaction to silver metallocages from tripodal *N*-donor halogen ligands results in the corresponding halonium cages.

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