# Metal Iodides in Polyiodide Networks: Synthesis and Structure of Binary Metal Iodide−Iodine Compounds Stable under Ambient Conditions

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The reaction between $HgI_2(C_6N_4H_{12})$ and HI in ethanol solution results in the binary metal iodide−iodine complexes $[C_6N_4H_{13}]_2(Hg_2I_6)_{1/2}(HgI_3)\cdot{}^1/_2I_2$, which are stable under ambient conditions. The structure consists of $C_6N_4H_{13}^+$ cations, discrete trigonal $HgI_3^-$ ions, and $\cdots Hg_2I_6^{2-}\cdots I_2\cdots Hg_2I_6^{2-}\cdots$ chains in the crystallographic *b* direction, which are formed by $I_2$ molecules connecting the bridging iodines of the $Hg_2I_6^{2-}$ dimers. The intra- and intermolecular I−I distances of iodine in the chain are 2.7402(15) and 3.438(1) Å, respectively. The Raman spectrum of $[C_6N_4H_{13}]_2(Hg_2I_6)_{1/2}(HgI_3)\cdot{}^1/_2I_2$ confirms the interaction between the iodine molecules and $Hg_2I_6^{2-}$ ions. The structure of $[NH_4](HgI_3)\cdot H_2O$, obtained during the synthesis of $[C_6N_4H_{13}]_2(Hg_2I_6)_{1/2}(HgI_3)\cdot{}^1/_2I_2$, is also reported. Crystal data for $[C_6N_4H_{13}]_2(Hg_2I_6)_{1/2}(HgI_3)\cdot{}^1/_2I_2$: $a = 14.275(3)$ Å, $b = 19.721(4)$ Å, $c = 10.416(2)$ Å, orthorhombic space group *Pbam*; $Z = 4$. Crystal data for $[NH_4](HgI_3)\cdot H_2O$: $a = 8.7246(4)$ Å, $b = 9.7860(3)$ Å, $c = 11.1103(4)$ Å, orthorhombic space group *Ama*2; $Z = 4$.

## Introduction

In previous investigations we have shown that $(R_3S)I_x$ (R = Me/Et and $x = 2-11$) polyiodides are appropriate reaction media for the synthesis of modified polyiodides.[1−3] In these reactions the addition of iodide acceptors or metal iodides to the $(R_3S)I_x$ melts exposes iodine to a competition for iodide ions. This enables the insertion of guest atoms into the polyiodide networks, thus modifying the $I^-$-donating properties as compared with the pure polyiodide anions. Consequently, a knowledge of how the polyiodides alter in structure and physical properties with different guest molecules makes it possible to exercise synthetic control and to design polyiodides with specific properties. This is of special interest since polyiodides have found applications in several areas because of their ability to introduce mixed valence in stacked compounds and their properties as conductors through the proposed Grotthus mechanism.[4−8]

The synthesis of modified polyiodides using the $(R_3S)I_x$ system has an unfortunate property: the compounds obtained are unstable under ambient conditions, and consequently the investigation of physical properties is quite difficult. The size of the cation has been found to be an important factor affecting the thermal stability.[4,5,9] Thus, a synthetic route where a larger and more bulky cation is used could eliminate the undesired properties of the former synthetic media.

The compound, hexamethylenetetramine (hmt), $C_6N_4H_{12}$, has previously been used in the synthesis of polyiodides.[10−12] In these syntheses hmt/hmt-RI was reacted with iodine or hmt was reacted with HI in an equimolar ratio followed by the addition of $I_2$ in amounts corresponding to the polyiodide of target. Because of the size and shape of hmt, it seems suited for stabilizing polyiodides having large formal building blocks. Consequently, hmt seemed to be an appropriate candidate in the search for modified polyiodides stable under ambient conditions.

In this work we report a new synthetic route of introducing metal iodides into polyiodide networks by the use of a metal iodide−hmt adduct, $HgI_2\cdot$hmt, as the starting material.[13] The structure of the product $[C_6N_4H_{13}]_2(Hg_2I_6)_{1/2}(HgI_3)\cdot{}^1/_2I_2$, **1**, and the Raman spectrum together with an interpretation of the spectral features are presented. The structure and Raman spectrum of $[NH_4](HgI_3)\cdot H_2O$, **2**, formed during the synthesis of **1**, are also reported.

## Results and Discussion

Compound **1** was made from the reaction between HI and $HgI_2\cdot(C_6N_4H_{12})$ [$HgI_2\cdot$hmt] in an ethanol solution under ambient conditions. The reaction can be regarded as proceeding in two principal steps: (1) protonation and complex formation of $HgI_2\cdot$hmt followed by dissociation which results in the formation of $hmtH^+$ ($C_6N_4H_{13}^+$) and complex iodomercurates(II) such as $HgI_3^-$ and $Hg_2I_6^{2-}$ and (2) oxidation of $I^-$ by air to form $I_2$.

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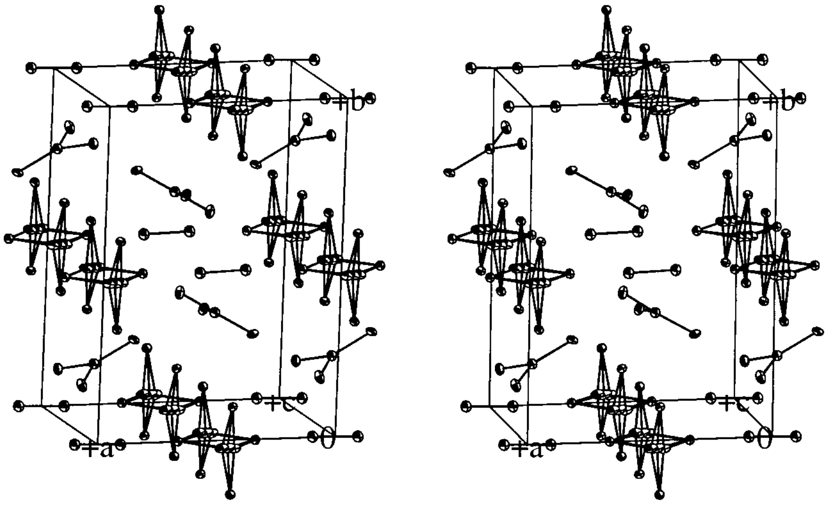

**Figure 1.** Stereographic view of the crystal packing for **1**. The cations are omitted for clarity.

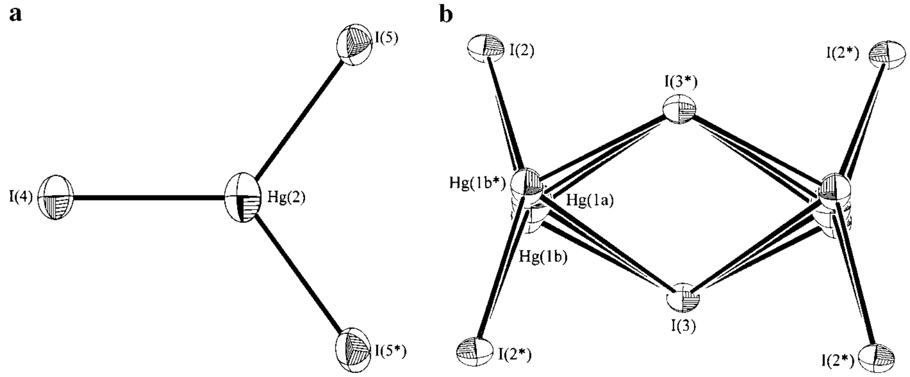

**Figure 2.** (a) $HgI_3^-$ and (b) $Hg_2I_6^{2-}$ ions in the structure of **1** (50% probability ellipsoids are given).

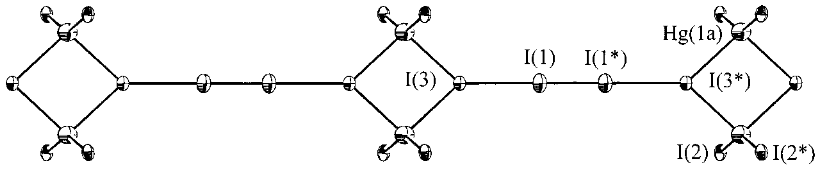

**Figure 3.** Infinite chain structure in **1** (only the mercury Hg(1a) of the $Hg_2I_6^{2-}$ anion is shown) (50% probability ellipsoids are given).

During step 2, a peak at approximately 110 cm$^{-1}$ shows up in the Raman spectrum of the reaction mixture, which confirms the formation of polyiodides. After evaporation of the solvent, a mixture of **1** and **2** precipitates; easily separable because of the differences in crystal shape and color.

The structure of **1** consists of discrete $HgI_3^-$ ions, hmtH$^+$ cations, and $Hg_2I_6^{2-}$ ions bridged by $I_2$ molecules (Figures 1 and 2). The planar (by symmetry) $HgI_3^-$ ions have Hg−I distances of 2.6850(8) and 2.7267(8) Å and I−Hg−I angles of 125.744(13)° [I(4)−Hg(2)−I(5)] and 108.45(3)° [I(5)−Hg(2)−I(5*)] (Table 1). The $Hg_2I_6^{2-}$ ions have the Hg atoms disordered over three positions: Hg(1a), Hg(1b), and Hg(1b*), where the central mercury [Hg(1a)] has the highest occupancy (see Experimental Section). The terminal Hg−I distances are in the range 2.63−2.72 Å, while the bridging Hg−I distances are 3.104(5) [Hg(1a)−I(3)] and 2.858(14) Å [Hg(1b)−I(3)]. The bridging Hg−I distance of 3.104(5) Å is significantly larger compared with the distances in discrete $Hg_2I_6^{2-}$ dimers without disorder.[14] All of the other Hg−I distances seem to be of normal magnitude.[14]

The $I_2$ molecules coordinated to the bridging iodine molecules of the $Hg_2I_6^{2-}$ ions have an intramolecular I−I distance of 2.7402(15) Å, which is longer than the I−I distance of pure iodine [2.715(6) Å in the solid state and 2.667(2) Å in the gas phase].[15,16] This indicates that the iodine molecules interact significantly with the $Hg_2I_6^{2-}$ ions, which can be regarded to substitute the $I^-$ donor in pure polyiodides. The intermolecular I−I distance of 3.438(1) Å is within the range of what has been reported as bonding distances or secondary bonds in polyiodide compounds.[17,18] The iodine molecules coordinated to $Hg_2I_6^{2-}$ can thus be viewed as forming infinite chains in the crystallographic *b* direction (Figure 3).

The cations, hmtH$^+$, have C−N and C−C distances which are of normal magnitude (Table 1).[19−22] The position of the H$^+$ ion can be extracted from the fact that there is one nitrogen

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**Table 1.** Selected Bond Lengths (Å) and Angles (deg) of **1** and **2**

| **1** | | **2** | |
|---|---|---|---|
| I(1)−I(1*) | 2.7402(15) | Hg−I(1) | 2.721(2) |
| Hg(1a)−I(2) | 2.658(2) | Hg−I(2) | 2.7183(15) |
| Hg(1a)−I(2*) | 2.659(2) | Hg−I(3) | 2.8691(9) |
| Hg(1a)−I(3) | 3.104(5) | | |
| Hg(1b)−I(2) | 2.632(12) | I(1)−Hg−I(3) | 109.21(3) |
| Hg(1b)−I(2*) | 2.715(14) | I(1)−Hg−I(2) | 120.30(6) |
| Hg(1b)−I(3) | 2.858(14) | I(2)−Hg−I(3) | 108.52(3) |
| Hg(2)−I(4) | 2.6850(8) | I(3)−Hg−I(3*) | 98.96(4) |
| Hg(2)−I(5) | 2.7267(8) | Hg−I(3)−Hg* | 100.54(4) |
| C(1)−N(1) | 1.530(8) | | |
| C(1)−N(3*) | 1.424(8) | | |
| C(2)−N(2) | 1.426(10) | | |
| C(2)−N(1) | 1.508(10) | | |
| C(3)−N(2) | 1.470(8) | | |
| C(3)−N(3) | 1.457(8) | | |
| C(4)−N(3) | 1.469(7) | | |
| C(5)−N(5) | 1.432(7) | | |
| C(5)−N(4) | 1.522(7) | | |
| C(6)−N(4) | 1.508(9) | | |
| C(6)−N(6) | 1.432(9) | | |
| C(7)−N(5) | 1.485(6) | | |
| C(8)−N(6) | 1.427(7) | | |
| C(8*)−N(5) | 1.453(6) | | |
| Hg(1a)−I(3)−Hg(1a*) | 82.7(2) | | |
| I(2)−Hg(1a)−I(2*) | 149.1(3) | | |
| I(2)−Hg(1a)−I(3*) | 101.09(9) | | |
| I(3)−Hg(1a)−I(3*) | 97.3(2) | | |
| I(3)−Hg(1a)−I(2) | 99.2(9) | | |
| Hg(1b)−I(3)−Hg(1b) | 95.3(7) | | |
| I(3)−Hg(1b)−I(2) | 106.4(5) | | |
| I(3)−Hg(1b)−Hg(1b*) | 132.1(4) | | |
| I(3)−Hg(1b)−I(2*) | 106.2(4) | | |
| I(2)−Hg(1b)−Hg(1b*) | 87.0(17) | | |
| I(2)−Hg(1b)−I(2*) | 146.8(5) | | |
| I(4)−Hg(2)−I(5) | 125.744(13) | | |
| I(4)−Hg(2)−I(5*) | 125.745(13) | | |
| I(5)−Hg(2)−I(5*) | 108.45(3) | | |

**Table 2.** Crystallographic Data for **1** and **2**

| | **1** | **2** |
|---|---|---|
| formula | $C_{12}H_{26}Hg_2I_7N_8$ | $H_6HgI_3NO$ |
| *M* | 1571.89 | 617.35 |
| cryst size/mm | 0.21 × 0.25 × 0.28 | 0.08 × 0.09 × 0.42 |
| cryst syst | orthorhombic | orthorhombic |
| *a*/Å | 14.275(3) | 8.7246(4) |
| *b*/Å | 19.721(4) | 9.7860(3) |
| *c*/Å | 10.416(2) | 11.1103(4) |
| *V*/Å$^3$ | 2932.4(10) | 948.59(6) |
| space group | *Pbam* (No. 55) | *Ama*2 (No. 40) |
| *Z* | 4 | 4 |
| $D_c$/g cm$^{-3}$ | 3.561 | 4.323 |
| $\mu$/cm$^{-1}$ | 178.45 | 259.11 |
| radiation | Mo Kα $\lambda = 0.710\ 69$ | Mo Kα $\lambda = 0.710\ 69$ |
| *T*/°C | 293 | 293 |
| $R_F{}^a$ | 0.046 | 0.043 |
| $R_{wF}{}^a$ | 0.081 | 0.091 |

$^a$ $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

atom in each cation that has significantly longer C−N distances than the other ones. The nitrogen atoms N(1) and N(4) clearly have longer C−N distances in this case (Table 1), thus indicating that they are protonated.

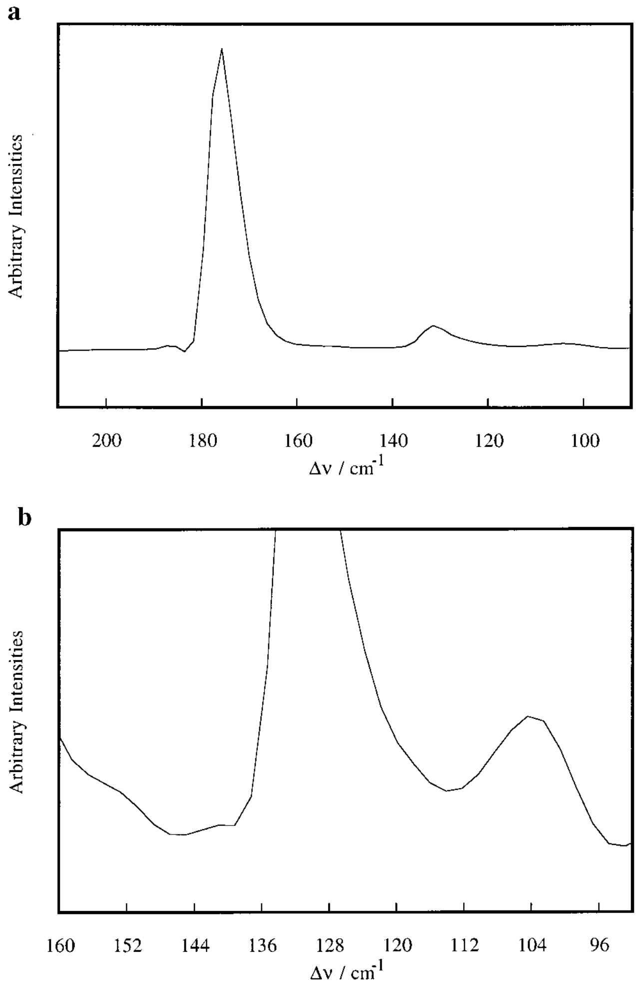

**Figure 4.** (a) Raman spectrum of **1** at room temperature in the range 100−220 cm$^{-1}$. (b) High-gain trace of the Raman spectrum of **1** at room temperature in the range 92−160 cm$^{-1}$.

The Raman spectrum of **1** shows spectral features at 175, 152, 131, and 104 cm$^{-1}$ (Figure 4) (relative Raman intensities 100, 2, 9, and 3, respectively). The peak at 131 cm$^{-1}$ agrees with the symmetric Hg−I stretch of $HgI_3^-$.[23−26] However, the Hg−I stretches of $Hg_2I_6^{2-}$ have also been reported in this region, making it difficult to uniquely assign this band. The peak at 153 cm$^{-1}$ is consistent with the frequency reported for the asymmetric stretch of $HgI_3^-$, while the peak at 105 cm$^{-1}$ belongs to the bridging Hg−I stretch of $Hg_2I_6$.[24−27] The stretching frequency of free iodine in solid state is at about 180 cm$^{-1}$ and shifts to lower wavenumbers when iodine interacts with a species that can donate electron density into its σ* antibonding orbital. Consequently, the peak at 175 cm$^{-1}$ can be assigned to the $\nu_1$ stretch of $I_2$.[28−31] Notable in the Raman spectrum of **1** is

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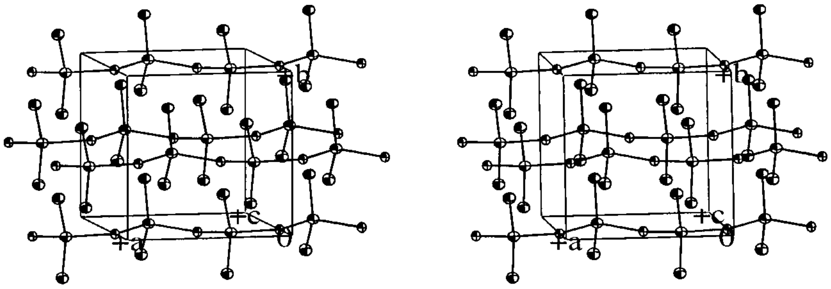

**Figure 5.** Stereographic view of the crystal packing for **2**.

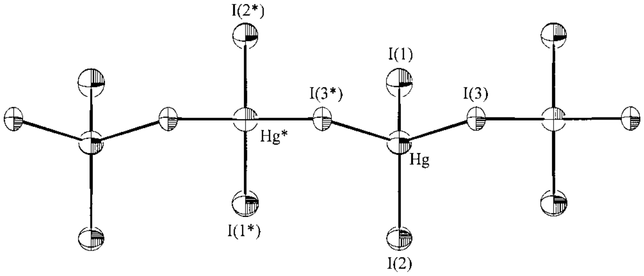

**Figure 6.** Chain structure of **2**. The cations and water molecules are omitted for clarity.

that the peaks from the Hg−I stretch modes are very weak when compared to the $\nu_1$ peak of iodine.

A few other binary metal iodide−iodine complexes exist in the literature; however, none of them are stable under ambient conditions.[1−3,32] There exist two compounds that contain dimeric $M_2I_6^{2-}$ ions: $(Et_3S)[Hg_2I_6]_{1/2}\cdot 3I_2$ and $(Me_3S)[Cd_2I_6]_{1/2}\cdot 3I_2$. In the cadmium compound, the $Cd_2I_6^{2-}$ ions are coordinated by $I_2$ molecules in such a way that a network of infinite zigzag chains of $Cd_2I_6^{2-}$ complexes interspaced by $I_{10}$ units are formed. The mercury compound also displays a network structure, but in this case the $I_2$ molecules coordinate directly to the terminal iodides of $Hg_2I_6^{2-}$. Thus, in neither of these $M_2I_6^{2-}$ compounds do the iodine molecules coordinate to the bridging iodides as in **1**. Two binary metal iodide−iodine compounds containing gold(III) iodide exist, namely, $(NH_4)[AuI_4]\cdot {}^1/_2I_2$ and $(Et_3S)[AuI_4]\cdot 2I_2$. Both contain square-planar $AuI_4^-$ ions that are coordinated with $I_2$ molecules to form chain structures, but they show no similarity to **1**. However, recently Pennington et al. reported a nonbinary metal iodide−iodine complex, (4-cyanopyridine)cadmium(II) iodide·diiodine, where the bridging iodides of $CdI_2$ coordinate to iodine in a way similar to that of **1**.[33] The intramolecular I−I distance in $I_2$ was found to be 2.757(1) Å, while the intermolecular I−I distances were 3.367(1) and 3.436(1) Å. Simple quantum chemical calculations (Hartree−Fock level, LANL2DZ basis set of the Gaussian94 package) indicate similar donating abilities of both terminal and bridging iodides in $Cd_2I_6^{2-}$ and $Hg_2I_6^{2-}$, based on MO's, charge, and electron-density distributions.

The synthetic route applied for obtaining **1** also results in the mercury compound $[NH_4](HgI_3)\cdot H_2O$, **2**, which consists of $NH_4^+$ ions and infinite chains of corner-sharing $HgI_4^{2-}$ tetrahedra and water molecules (Figures 5 and 6). The bridging Hg−I distance is 2.8691(9) Å, and the terminal Hg−I distances are 2.721(2) and 2.7183(15) Å.

The Raman spectrum of **2** shows spectral features at 120, 131, and 150 cm$^{-1}$, which seem to be consistent with the observed distorted, tertrahedral $HgI_4$ units in the structure. The formation of **2** is probably a consequence of the hydrolysis of hmt, which is a result of the low pH, and the complex formation between $HgI_2$ and $I^-$ in excess.[21] The hydrolysis products are $NH_4^+$ and formaldehyde.[21]

The synthetic route presented is of special interest since it opens the possibility to incorporate AgI and CuI in the polyiodides by applying the analogous method used for **1** with the hmt adducts of AgI and CuI instead. This was not possible with the former synthetic approach because of the very high instability of the compounds formed under ambient conditions.

## Experimental Section

**Preparations.** The synthesis of $HgI_2\cdot$hmt has been described elsewhere.[13] Aqueous HI (67% Merck) and 95% ethanol were used. To 200 mL of 95% ethanol were added 0.50 g of $HgI_2\cdot$hmt and 0.48 g of HI. The solution turned yellow directly after the addition of HI, and after stirring, the solution turned red because of the oxidation of $I^-$ to $I_2$. The solution was then decanted to an open beaker and left for evaporation. Black crystals of **1** stable at room temperature were formed after evaporation, and the yield was approximately 30% (with respect to $HgI_2\cdot$hmt). Yellow crystals of **2** formed simultaneously. Different ratios of the reactants were tested, but the optimum yield of **1** was obtained in the range 1:2−1:3 of the molar ratio between $HgI_2\cdot$hmt and HI. The yield of hydrolysis product **2** was found to increase with HI concentration.

**Vibrational spectroscopy.** The backscattering of the compounds was recorded using the 1064 nm radiation from a Nd:YAG laser in a Bio-Rad FT-Raman spectrometer. The radiation was recorded using a nitrogen-cooled, Ge-diode detector and 4 cm$^{-1}$ resolution.

**X-ray Crystallography.** Single crystals of **1** and **2** were obtained from the reaction mixture after evaporation of the solvent at room temperature. The crystal data for the structures are presented in Table 2. The data were collected at room temperature for both compounds on a Siemens SMART CCD diffractometer. The space group was determined to be *Pbam* for **1** and *Ama*2 for **2**. The SADABS method was used to correct for absorption effects.[34] The structures were solved by direct methods using the SHELXTL-PLUS program package and refined on $F^2$.[35] The mercury atoms of **1** are disordered over three distinct orientations Hg(1b), Hg(1a), and Hg(1b*). The occupancy of the central mercury [Hg(1a)] is 0.527 while the occupancies for the other two mercury atoms are 0.236. The hmt hydrogen atoms in **1** were put in calculated positions, while the hydrogen atoms of $NH_4^+$ and $H_2O$ in **2** were not located.

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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