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The Crystal and Molecular Structure of the Tetrameric Methyl-2-mercaptobenzimidazole·AgBr (Acetone Solvate) Complex: Mode of Complex Formation Between Silver Bromide and Thione Type Photographic Stabilizers

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The complex formed from the reaction of an important thione based stabilizer in conventional silver halide photography, methyl-2-mercaptobenzimidazole (MBI), and silver bromide has been isolated for the first time as a single crystal and characterized by X-ray structure techniques. The resulting compound is tetrameric and has the formulation $[AgBr{\cdot}MBI]_4$ and also contains residual solvent from the crystallization process. The crystal and molecular structure of $[AgBr{\cdot}MBI]_4$ consists of intertwined dimers of $[AgBr]_2$ four-membered rings that connect the foundational silver-mercaptobenzimidazole $[AgS]_4$ eight-membered rings into a high molecular weight polymeric network superstructure. The complex demonstrates the powerful silver halide solubilization properties of the thiourea type ligand. The bridging sulfur remains in the thione form and N-H···Br-Ag hydrogen bonds suggest the title complex is an intermediate in the formation of the deprotonated AgMBI complex. Normal Ag-Br and Ag-S bond lengths were found: Ag-S = 2.5026(8), Ag-Br = 2.7423(9) and 2.7956(10) Å, $C_{9.50}H_{11}AgBrN_2O_{0.50}S$, Cell Data: $I4_1/amd$, a = 19.1034(2) Å, b = 19.1034(2) Å, c = 13.5019(2) Å.

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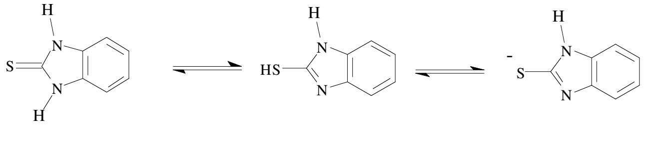
Introduction

Methyl-2-mercaptobenzimidazole, MBI, and its analogs have been of great interest in conventional AgX (X = Cl, Br, I) imaging materials for antifoggant properties,[1–6] for shelf stability,[7] and for stabilization of heat-developed images by post application of the stabilizer.[8,9] Despite this high interest there is very little data reported on the coordination chemistry of MBI. For example, MBI has been found to adsorb to silver halide surfaces, as demonstrated by ESCA and XANES spectroscopies[10,11] in which coordination occurs through the deprotonated thiol sulfur. The AgMBI complex and, apparently, HBr are the result of this complex formation process. Also, during Ostwald ripening/recrystallization processes of silver halide grains the rates of ion transport are dramatically affected by MBI and related ligands.[12,13] In addition, MBI is used for the quantitative determination of silver ions as the resulting AgMBI complex is extremely insoluble in water.[14–16] Other than some thermal and UV absorption data[14] not much is known about the nature of the AgMBI complex, and especially how the MBI is bonded to the silver.

For comparison purposes it is useful to think of MBI as an N,N'-disubstituted thiourea, TU, derivative. In this case, the relevant literature is slightly more extensive and revealing. Similar to MBI, thioureas are well known additives to AgX emulsions for stabilization,[17] surface complexers/Ostwald ripening agents,[18–20] and as sulfur sources for chemical sensitization.[21] While several reports describe the coordination chemistry of thiourea derivatives with AgX[22–25] only three structures have been reported, $AgTU_2Cl$[26] and Ag $(CH_3TU)_3Cl$[27] and $Ag(Et_2TU)_3I$.[28] These latter complexes are interesting in that in all cases the structure determination reveals that the sulfurs are coordinated in the thione form while adsorption of TU from solution on to AgX crystals in photographic emulsions appear to result in sulfur coordination via the deprotonated thiol sulfur.[10,11]

In addition to the coordination chemistry of TU and MBI, these ligands are well known to exhibit a tautomeric equilibrium, as illustrated below, comprising the thione, thiol and deprotonated thiol.



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Each form could produce strikingly different coordination compounds. The thione form is apparently the preferred mode in solution.[10,29]

We have been investigating the coordination chemistry of Ag^+ with nitrogen, phosphorous and oxygen donors in order to better understand the role of various ligands in the metallic image formation reaction in imaging materials containing silver coordination compounds.[30–35] We have now found that reaction between the silver bromide and MBI in organic media readily forms an extremely stable, colorless complex having the stoichiometry $[AgBr{\cdot}MBI]_4$. This is the first complex of AgBr containing the important photographic stabilizer MBI which has now been characterized by its crystal and molecular structure. Previously, we reported the structure of a silver complex with a different stabilizer, a tribromomethyl-benzothiazole ligand.[34] To our knowledge, there is only one other structure determination reported for a silver complex of a photographic stabilizer, that with 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (TAI).[36] The stabilizer apparently functions by complexing silver forming a highly polymeric structure. Similar to the known TU structures with silver chloride, the sulfur in the $[AgBr{\cdot}MBI]_4$ complex is coordinated in the thione form and bridges the silver atoms. However, the bi-functional bridging groups, Br and S, act to create a three dimensional superstructure which determines the solid state properties. The nature of the $[AgBr{\cdot}MBI]_4$ structure, its bonding and physical properties are described below.

Experimental

The 5-methyl derivative of MBI used in the preparation of the title complex was found to be a mixture of isomers in which the methyl group is in either the 4 or 5 position. As a result of this mixture, the structure of the complex shows both isomers in the lattice, although for clarity, only the 5-methyl version is shown in the figures.

Preparation of $[AgBr{\cdot}MBI]_4$. $[AgBr{\cdot}MBI{\cdot}(ac\text{-}etone)_{0.5}]_4$. A 1×1 cm sheet of AgBr, 0.25 mm thick (Wilmad Glass), was placed in 10 mL of acetone containing 0.20 g MBI, capped and allowed to stand in the dark. Within a few hours colorless needles could be observed to grow off the surface. After 4 days the crystals were rinsed with acetone, air dried and removed from the AgBr surface. The complex is very light stable, and poorly soluble in acetone, acetonitrile, THF, and MeOH. Elemental analysis is in excellent agreement with the assignment and structure, and the solvated acetone carbonyl is clearly observed in the IR at 1710 cm^{-1}.

Alternatively, the microcrystalline version of the $[AgBr{\cdot}MBI]_4$ complex can be easily prepared directly from AgBr powder. A dispersion of 0.22 g AgBr and 0.20 g MBI in 10 mL acetone, stirred in the dark five hours, produces a white, light stable powder.

THF may also be used as a solvent for the preparation of $[AgBr{\cdot}MBI]_4$, although crystal growth from the AgBr sheet is slower and the resulting crystals are more cubic. In this latter case, these crystals also contain solvent which is slowly lost from the solid; clear, colorless crystals become opaque after several weeks on standing in air. The solvent content apparently is reversible, placing the latter crystals back into a THF environment regenerates the clear crystals.

AgMBI reference. Mixing Na^+MBI^- and silver nitrate in water produced a thick yellow paste which dried to a fine powder.

TABLE I. Elemental analysis of AgBr·MBI complexes (Galbraith Laboratories).

Complex	C, % found	C, % theory	H, % found	H, % theory	N, % found	N, % theory
$[AgBr{\cdot}MBI]$*	29.73	27.38	2.85	2.01	7.33	7.98
$[AgBr{\cdot}MBI{\cdot}(acetone)_{0.5}]_4$*		29.95		2.91		7.35
$[AgBr{\cdot}MBI]_4$**	27.72	27.38	2.68	2.01	7.20	7.98
AgMBI		35.45		2.60		10.33

* from AgBr sheet; ** from AgBr powder

TABLE II. Crystal Data and Structure Refinement

Color / Shape	colorless / parallelepiped
Empirical formula	$C_{9.50}H_{11}AgBrN_2O_{0.50}S$
Formula weight	381.04
Temperature	173(2) K
Crystal system	Tetragonal
Space group	$I4_1/amd$
Unit cell dimensions	$a = 19.1034(2)$ Å $\alpha = 90^{\circ}$
(4224 reflections in full θ range)	$b = 19.1034(2)$ Å $\beta = 90^{\circ}$
	$c = 13.5019(2)$ Å $\gamma = 90^{\circ}$
Volume	4927.38(10) $Å^3$
Z	16
Density (calculated)	2.055 Mg/m^3
Absorption coefficient	5.021 mm^{-1}
Diffractometer / scan detector	Siemens SMART / CCD area
Radiation / wavelength 0.71073 Å	MoKα (graphite monochrom.) /
F(000)	2944
Crystal size	0.10 x 0.15 x 0.40 mm
θ range for data collection	1.85 to 27.87°
Index ranges	$-24 \le h \le 25$, $-16 \le k \le 24$, $-17 \le l \le 17$
Reflections collected	14876
Independent / observed reflections	1554(R_{int} = 0.0487) / 1063([$I>2\sigma(I)$])
Absorption correction	SADABS
Range of relative transmission factors	0.95 and 0.70
Refinement method	Full-matrix least-squares on F^2
Computing	SHELXTL, Version 5
Data / restraints / parameters	1519 / 0 / 95
Goodness-of-fit on F^2	0.969
SHELX-93 weight parameters	0.0726, 13.1074
Final R indices [$I>2\sigma(I)$]	R1 = 0.0400, wR2 = 0.1031
R indices (all data)	R1 = 0.0737, wR2 = 0.1349
Extinction coefficient	0.00028(10)
Largest difference peak and hole	0.900 and -0.792 $eÅ^{-3}$

Structure Determination. The details for the structure determination are given in Table II. Bond distances and angles of the title complex are shown in Table III. Due to the symmetry constraints of the space group and the mixture of the 4-methyl-2-MBI and 5-methyl-2-MBI isomers, the methyl group is disordered between C4 and C3 and is disordered across the symmetry axis. C5A and C5B were located and refined at 25% occupancy each. In addition, the solvent has high thermal motion and the solvent methyl hydrogen atoms are disordered about the symmetry axis.

Description of the structure of $[AgBr{\cdot}MBI{\cdot}(acetone)_{0.5}]_4$. The structure of the $[AgBr{\cdot}MBI{\cdot}(acetone)_{0.5}]_4$ complex is best described as a 3D polymeric lattice built on 8-membered $[SAg(Br)]_4$ rings and 4-membered $[AgBr]_2$ rings. For visualization purposes, the foundational 8-membered $[SAg(Br)]_4$ ring construction, is shown in Fig. 1.

TABLE III. [AgBr·MBI·(acetone)$_{0.5}$]$_4$ Bond Lengths [Å] and Angles [°].

Ag-S	2.5026(8)	S-C(1)	1.701(9)
Ag-Br#2	2.7423(9)	N-C(2)	1.400(7)
Ag-Br	2.7956(10)	N-C(1)	1.350(6)
C(2)-C(2)#3	1.390(13)	C(1)-N#3	1.349(6)
C(3)-C(5B)	1.27(3)	C(2)-C(3)	1.391(9)
C(4)-C(4)#3	1.37(2)	C(3)-C(4)	1.373(10)
O-C(6)	1.31(3)	C(4)-C(5A)	1.39(3)
C(6)-C(7)#4	1.56(2)	C(6)-C(7)	1.56(2)

S#1-Ag-S	121.16(10)	C(1)-N-C(2)	109.4(5)
S-Ag-Br#2	110.64(5)	N-C(1)-S	125.9(4)
S-Ag-Br	108.02(2)	C(2)#3-C(2)-C(3)	121.7(5)
Ag#2-Br-Ag	84.89(3)	C(3)-C(2)-N	131.8(7)
C(1)-S-Ag	108.47(5)	C(5B)-C(3)-C(2)	129.3(13)
Br#2-Ag-Br	95.11(3)	C(4)#3-C(4)-C(3)	122.7(5)
C(1)-S-Ag#5	108.49(5)	C(3)-C(4)-C(5A)	118(2)
Ag#5-S-Ag	143.04(10)	O-C(6)-C(7)#4	132(2)
N-C(1)-N#3	108.1(7)	C(5B)-C(3)-C(4)	115.1(13)
N#3-C(1)-S	126.0(4)	C(4)-C(3)-C(2)	115.6(8)
C(2)#3-C(2)-N	106.5(3)	C(4)#3-C(4)-C(5A)	118(2)
C(7)-C(6)-C(7)#4	97(4)	O-C(6)-C(7)	132(2)

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

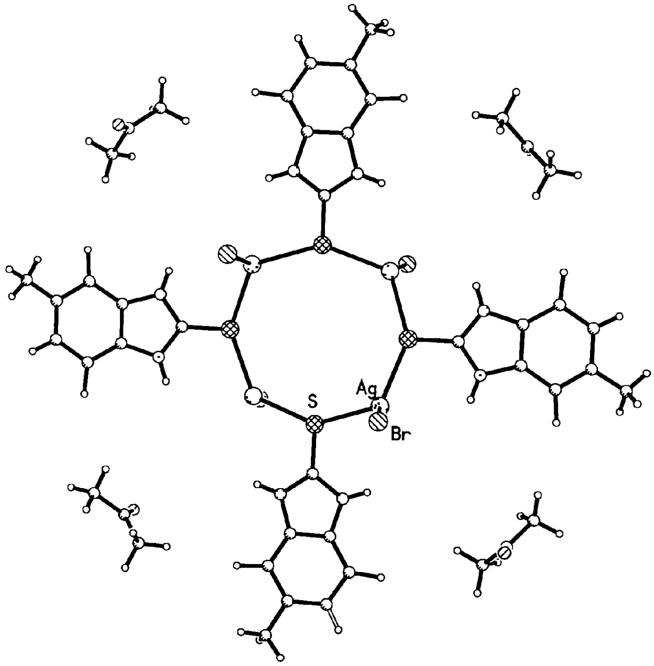

Figure 1. Molecular structure and 8-membered [AgS]$_4$ ring in [AgBr·MBI]$_4$.

The basic 8-membered ring structure of the title complex is comprised of alternating Ag-S linkages resulting from MBI bridging the silver atoms. Bromine remains coordinated to the silver so the sulfur linkage is a thione and both nitrogens of the MBI are protonated, in contrast to the reaction between AgBr and MBI in aqueous media in which the deprotonated AgMBI complex was reported.[10,11,37] Acetone is in the crystal lattice of the title complex, as seen in Fig. 1, but it does not play any role in the silver coordination.

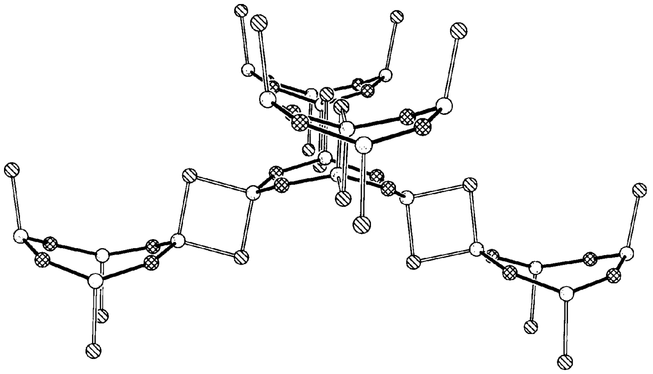

Figure 2. Molecular structure and 8-membered [AgS]$_4$ ring in [AgBr·MBI]$_4$.

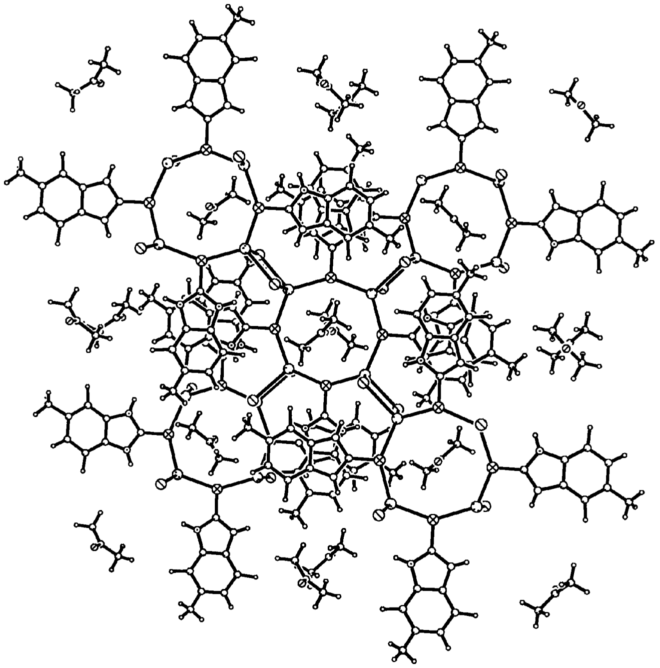

Figure 6. Crystal structure of [AgBr·MBI·(acetone)$_{0.5}$]$_4$ revealing the second channel and aromatic stacking interactions.

The 8-membered [SAg(Br)]$_4$ ring is boat-shaped, not planar, unlike [Ag(O$_2$CR)]$_2$, for example, which is well known to form planar, 8-membered carboxylate ring systems.[30] The [SAg(Br)]$_4$ ring, 90° to the view in Fig. 1, is shown in Fig. 2:

Each boat shaped [SAg]$_4$ ring resides at the junction of two perpendicular sinsuoidal polymers propagated by the [AgBr]$_2$ bridges. In the *a* and *b* directions, this 3D structure produces cavities. Figure 3 (*posted on the IS&T website, www.imaging.org, and included in the J. Imag. Sci. Tech. CD-ROM, only*), indicates all of the Br bridges are directed inward.

Figure 4 (*posted on the IS&T website, www.imaging.org, and included in the J. Imag. Sci. Tech. CD-ROM, only*), shows in the *c* direction that two unique cavities or channels are formed. The 8-membered rings stack such that channels are formed in the *c*-direction. In addition, four columns of 8-membered [SAg]$_4$ rings define a second type of channel in the *c* direction. The solvent molecules reside above and below the 8-membered rings, with the

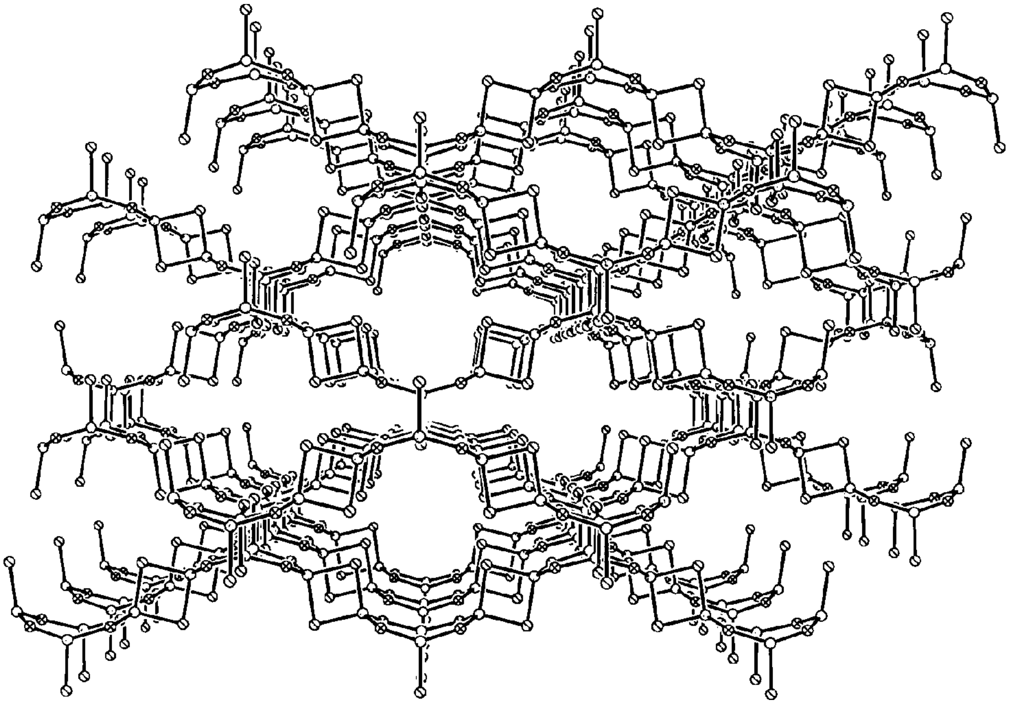

Figure 3. Cavities produced by inward directed bromine linkages in the [AgBr•MBI•(acetone)$_{0.5}$]$_4$ complex.

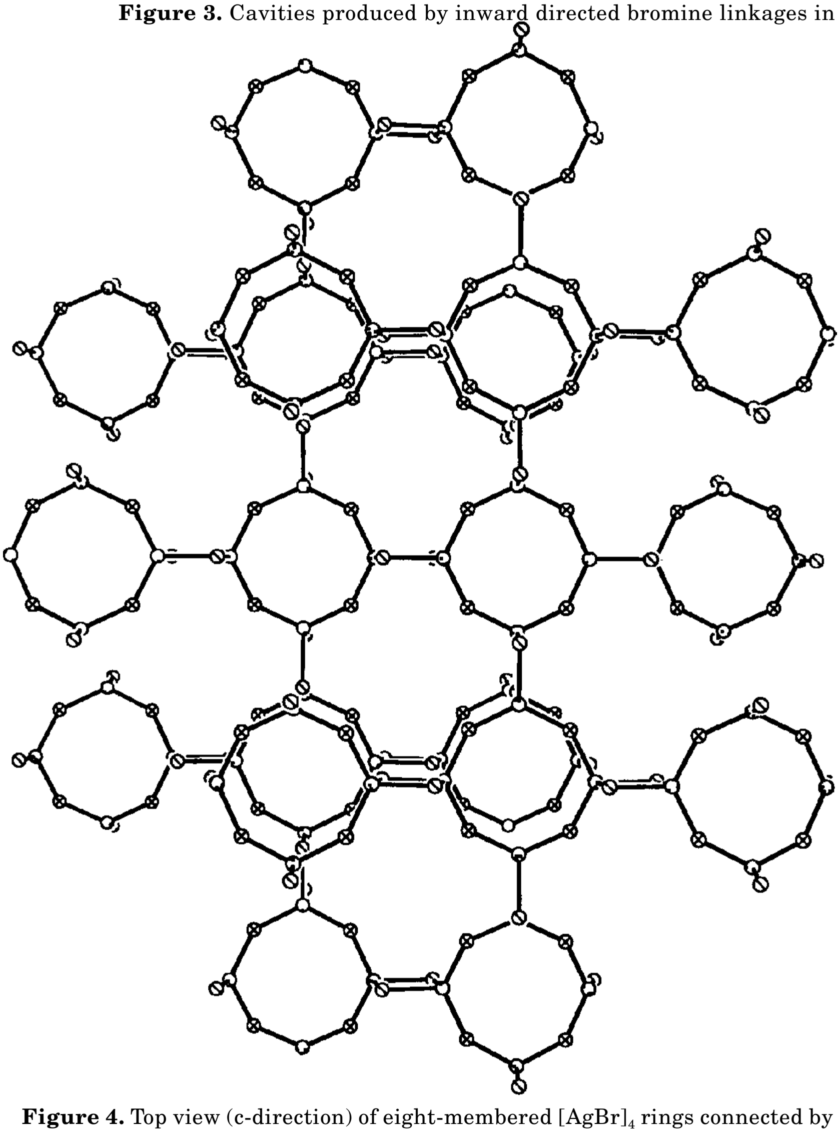

Figure 4. Top view (c-direction) of eight-membered [AgBr]$_4$ rings connected by the four-membered [AgBr]$_2$ rings in the [AgBr•MBI•(acetone)$_{0.5}$]$_4$ complex.

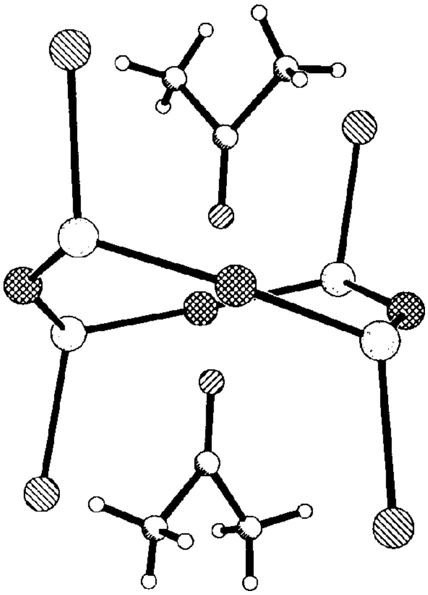

Figure 5. Acetone solvent molecule orientation in the [AgBr•MBI• (acetone)$_{0.5}$]$_4$ complex.

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oxygen atoms directed toward the center of each ring, [*see Fig. 5 (posted on the IS&T website, www.imaging.org, and included in the J. Imag. Sci. Tech. CD-ROM, only)*]. The closest Ag···O contacts are 3.317 Å, while the closest S···O contacts are 3.363 Å.

The second channel is occupied by the MBI ligands which are face-to-face stacked with each molecule perpendicular to those stacked above and below as shown in Fig. 6.

The Ag-Br bond lengths, shown in Table III, in the $[AgBr]_2$ dimer are 2.7423(9) and 2.7956(10) Å which are significantly shorter than in the starting AgBr lattice,[1] 2.887 Å. By comparison to other known Ag-Br complexes, however, these distances are quite normal. Some examples of Ag-Br distances in silver complexes include a dinitrile bridged $[AgBr]_2$ dimer having AgBr distances of[38] 2.736(3), 2.836(3), 2.781(3), and 2.831(3) Å, 2.742(1) and 2.734(1) Å Ag-Br bond distances have been reported for a triphenylphosphine bridged $[AgBr]_2$ dimer,[39] and 2.7431(13) and 2.9453(14) Å for a bis(dimethylphosphino)methane bridged $[AgBr]_2$ dimer.[40] The Ag-Br distance has been reported as short as[41] 2.448 Å. Monomeric [AgBr·ligand] complexes appear to exhibit slightly shorter Ag-Br bond distances, such as 2.636(1) Å in a thiocrown ether complex,[42] 2.629(1) Å in a triphenylphosphine complex,[43] and an average of 2.69(1) Å for a series of complexes having various ratios of triphenylphosphine to AgBr.[44]

The Ag-S bond lengths in the S-Ag-S units from the bridging MBI ligand are all 2.5026(8) Å. As noted above, comparisons to reported structures in the literature are limited to the few thiourea silver complexes. Ag-S bond distances of 2.48-2.59 Å have been reported for the polymeric *bis*-(thiourea)silver(I) chloride,[26] 2.520(2) and 2.665(3) Å for the monomeric[27] $Ag(CH_3TU)_3Cl$, 2.593(1) Å for the $Ag(Et_2TU)_3I$ (also monomeric)[28], and 2.48-2.61 Å for the *bis*-thiourea thiocyanate version.[45] A benzoylthiourea silver complex has been reported in which the Ag-S bonds are 2.47-2.54 Å (the SH counterion in this complex is coordinated to the silver as well: its Ag-S distance[46] is 2.79 Å). As a reference, long Ag-S distances claimed to be weak bonds have been found in a dithiole-2-thione (non-thiourea) silver complex and amount to 2.91 and 3.04 Å.[47]

It is significant to note that the N-H in the title complex is H-bonded to the bromine of the $[AgBr]_2$ ring. The H···Br distance is 2.516 Å and the N-H···Br angle is 170.6º. The hydrogen bond is probably relevant to the mechanism of adsorption to the AgBr in aqueous solutions in which HBr is eliminated, and is discussed below.

It is also significant that the separation between the MBI molecules in the crystal is in the 3.5 to 3.8 Å range and indicative of face-to-face aromatic stacking.

Acetone is in the lattice of the title complex, although it has no role in silver coordination, and can be removed by suitable heating (see DSC/TGA results).

Thermal Analysis

The thermal analysis of the title complex provides some insight into its stability. The DSC of $[AgBr{\cdot}MBI{\cdot}(acetone)_{0.5}]_4$ clearly shows two main transitions. The first transition, centered at 136°C, appears to be a melting point, however, TGA shows that it is actually due to weight loss from the crystals. The weight loss (6.9%) corresponds to 0.5 moles of acetone (7.6%, theory), in excellent agreement with the elemental analysis and solid state structure determination. The second transition, beginning around 225°C, in the DSC is due to decomposition as can be seen from the corresponding weight loss in this temperature range in the TGA. The complex decomposition results in silver bromide (51.1% residue found, 49.6% theory) by 400°C.

Discussion

The facile formation of the $[AgBr{\cdot}MBI{\cdot}(acetone)_{0.5}]_4$ complex, and the fact that it contains the thione bridged $[AgBr]_2$ dimers, clearly demonstrates that the MBI ligand is a strong complexing agent for silver. In addition, the robust stability of the title complex indicates that these types of complexes may be expected to be relatively inert in photographic films. Because there are only a few stable complexes containing the AgX group reported in the literature one may further conclude that the TU based ligands are, along with phosphines, amongst the strongest complexing groups for silver ion with this anion.

The fact that the sulfur of the MBI is in the thione form in the $[AgBr{\cdot}MBI{\cdot}(acetone)_{0.5}]_4$ complex, however, is interesting in its contrast to the reported deprotonated thiol form of the MBI when adsorbed to AgBr.[10,11,37] In our study, the preparation of the title complex was accomplished from organic solvents while conventional AgX investigations were carried out at neutral (presumably) pH. The contrasting results are a little surprising as a simple change in solvents might not be expected to give such different products. That is, the generic reaction sequence may be written as follows:

$$AgBr + H\text{-}MBI \rightarrow [AgBr{\cdot}H\text{-}MBI] \rightarrow AgMBI + HBr$$

In our study, the intermediate, title complex was clearly isolated while the final AgMBI is reported to be the adsorbed product under aqueous conditions.[10,11,37] The intermediate [AgBr·H-MBI] requires no deprotonation reaction while the formation of AgMBI requires elimination of the strong acid, HBr. If the pK_a of the ligand is sufficiently low the formation of AgMBI would not be surprising. The reaction of another mercapto-azo stabilizer, phenylmercaptotetrazole, falls into the latter category as its pK_a is 2.95, however, that of MBI is substantially higher,[37] 10.07. This discrepancy simply confirms that pK_a by itself would not be a good guide to the complex formation and stabilization mechanism in photographic materials.

It would be useful to review the structural properties of the silver complexes reported which have photographic stabilizers as ligands to establish a trend, however, there are too few at this time. It may be relevant to note that all three complexes[34,36] reveal that the silver is four coordinate. In two cases a pair of strong Ag-N bonds are matched with a pair of weaker Ag-O/Ag-N bonds. In the case of $[AgBr{\cdot}MBI(acetone)_{0.5}]_4$, however, both bonding pairs, Ag-S and Ag-Br are in the normal range for strong bonds. It appears that at least one pair of strong Ag-ligand bonds are needed for stabilization properties but further structural requirement conclusions cannot be made at this time. In addition, the contribution of the poor solubility properties of the $[AgBr{\cdot}MBI(acetone)_{0.5}]_4$ and Ag(TAI) complexes to the stabilization mechanism needs to be taken into account.

It should be further noted, however, that hydrogen bonding is clearly occurring between the Br in the $[AgBr]_2$ ring and the N-H of the MBI. In this sense, it appears that the $[AgBr{\cdot}MBI{\cdot}(acetone)_{0.5}]_4$ complex is a unique example of the structure of the intermediate prior to the complete reaction of HBr formation and elimination. It is difficult to conclude, based on the data so far, however, if the face-to-face stacking of the aromatic rings of the MBI in the solid state structure arrange the N-H groups into close proximity with the Br of the $[AgBr]_2$ rings or vice versa.

Conclusions

Thione based stabilizers, such as MBI, are strong complexing agents for silver, including silver ions that are difficult to complex such as when incorporated as part of a silver halide lattice. The $[AgBr{\cdot}MBI{\cdot}(acetone)_{0.5}]_4$ complex resulting from the reaction of MBI with AgBr is very stable and it is shown that it contains four coordinate silver ions having two strong Ag-S and two strong Ag-Br bonds. From a coordination chemistry point of view these types of stabilizers may be considered as derivatives of thioureas. MBI is an extremely powerful solvent for AgBr and has the ability to dissolve it as the thione complex and form a stable, N-H···Br-Ag hydrogen bonded complex. This N-H···Br-Ag hydrogen bonded might be an intermediate prior to the deprotonation reaction of the complex during the formation of the silver halide stabilizer, AgMBI.

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