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The Molecular Structure of [bis-(2-Tribromomethylsulfonyl-benzothiazole)-silver(I)-tetrafluoroborate·(acetone)] [Ag{$(C_7H_4NS)SO_2CBr_3\}_2BF_4\cdot Me_2CO$]: A Possible Model for Bromine Elimination of Silver Halide Fog Centers

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The crystal and molecular structure of [bis-(2-tribromomethylsulfonyl-benzothiazole)-silver(I)-tetrafluoro-borate·(acetone)] solvate, [Ag{$(C_7H_4NS)SO_2CBr_3\}_2BF_4\cdot Me_2CO$], has been determined by single crystal x-ray analysis. The space group is $P2_1/c$, a = 16.985(5) Å, b = 10.426(3) Å, c = 19.693(4) Å, ß = 111.78(2)°, V = 3238 Å^3. Chelation by the 2-tribromomethyl-sulfonyl) benzothiazole ligand occurs through the ring nitrogen and sulfone oxygen, resulting in a distorted tetrahedral configuration around the silver atom. This complex is proposed as part of an alternative model for fog center removal in silver halide photographic constructions, in contrast to the theory of bromine radical formation from tribromomethyl compounds. Compounds containing tribromomethyl groups, which also possess sites capable of coordinating with a silver halide surface, may act as ligands to position the bromine on the silver halide surface. This placement of the bromine near the fog centers is suggested as a route to enhance the efficiency of this class of compounds as antifoggants.

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Introduction

Tribromomethyl-substituted compounds have been discovered to be useful antifoggants and stabilizers for silver halide photographic constructions.[1] Compounds that can also complex with silver ion complicate the mode of reactivity. One example of this class of ligands is 2-tribromomethylsulfonyl-benzothiazole[1a–d] (Fig. 1).

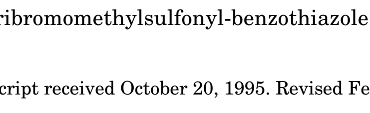

Figure 1. 2-tribromomethylsulfonyl-benzothiazole.

These molecules have the potential for binding with a silver halide surface via either Ag–N or Ag–S ring coordination, as well as to position the available bromine to facilitate its transfer to fog centers within the silver halide crystal. The position of the tribromomethylsulfone substituent on the benzothiazole makes a chelate ring containing an Ag–Br bond also possible. Complicating the situation in ligands containing the sulfone, however, is the possibility of silver-(sulfone)oxygen coordination.

The purpose of this work was to prepare a silver complex of 2-tribromomethylsulfonyl-benzothiazole and identify the mode of coordination between this ligand and silver. Such information might then provide a better understanding of how these tribromomethyl compounds may function as antifoggants in silver halide-based imaging systems. The [bis-(2-tribromomethylsulfonylbenzothiazole)silver(I)-tetrafluoroborate] complex described here comprises two 2-tribromomethylsulfonylbenzothiazole ligands coordinated to the silver through the ring nitrogen and weak Ag–O=S– bonds. There is no indication of Ag···Br bonding. The implications of this coordination on the elimination of fog centers in silver halide-based photographic materials are discussed.

Experimental

Synthesis of [bis-(2-tribromomethylsulfonyl-benzothiazole)-silver(I)-tetrafluoroborate]. Under subdued light, 0.20 g 2-tribromomethylsulfonyl-benzothiazole[1c] (0.45 mmol) is dissolved in 2 mL CH_2Cl_2, followed by addition of 0.10 g $AgBF_4$ (0.50 mmol, Aldrich). A light, fluffy solid appears after shaking in the dark for 1 h. Separation, washing, and drying yields 90 mg (36%) of off-white [bis-(2-tribromomethylsulfonyl-benzothiazole-silver(I)-tetrafluoroborate], which is stable to air and light. Molecular weight ($C_{16}H_8N_2S_4O_4Br_6AgBF_4$) = 1094.59. Elemental analysis, found (calculated): C = 17.3 (17.56), H = 0.6 (0.73), N = 2.5 (2.56), and Ag = 9.6 (9.85). The complex is soluble in acetone, acetonitrile, and THF, from which it rapidly forms an uncharacterized fine white solid, but is insoluble in ethanol. X-ray-quality crystals were prepared by dissolving, under subdued light, 0.45 g

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2-tribromomethylsulfonyl-benzothiazole and 0.22 g $AgBF_4$ (1:1.1 mol ratio) in about 10 mL of acetone. This solution was filtered through glass fiber paper and allowed to stand in the dark to evaporate slowly. The pale yellow crystals that formed at the top of the glass walls were free 2-tribromomethylsulfonyl-benzothiazole. The next lower set of colorless crystals was confirmed, by differential scanning colorimetry (DSC) and IR, to be the same as the crystals prepared in CH_2Cl_2 (except for the presence of acetone). All analytical results reported are for the CH_2Cl_2 preparation, except for the x-ray crystal structure determination.

X-ray Data Collection. The space group of the title compound (transparent single crystal, parallelepiped) was determined to be the centric $P2_1/c$ from the systematic absences. Least-squares refinement with isotropic thermal parameters led to R = 0.114. The geometrically constrained hydrogens were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. High thermal motion was noted for the anion and the solvent molecule, but a disorder model could not be resolved. The methyl hydrogen atoms were not included in the final refinement. Refinement of nonhydrogen atoms with anisotropic temperature factors produced final values of R = 0.050 and R_w = 0.053.

Differential Scanning Calorimetry. DSC was performed using a thermal analyzer (TA Instruments Model 9900) with a dual sample DSC (Model 910) cell. Thermogravimetric analysis (TGA) results were obtained (TA Instruments TGA Model 951). The heating rate was 10°C/min under an N_2 purge of approximately 50 mL/min. IR spectra were recorded on a spectrophotometer (Perkin Elmer 983), using samples in Nujol on KBr plates.

Results and Discussion

Benzothiazole compounds are used as silver halide sensitizing dyes,[2] fog inhibitors,[3] diffusion transfer agents,[4] photothermographic materials,[5] and lithographic materials.[6] Considering this wide range of commercial applications, it is surprising that only a limited number of reports characterize the silver complexes of these compounds.[7] With the exception of the powder diffraction of a 2-methylbenzothiazole complex of silver,[8] there have been no structural characterizations of such complexes. We are interested in the role of 2-tribromomethylsulfonyl-benzothiazole and its silver complex in the elimination of fog centers in an AgX crystal. Both issues, the structure of the complex and a suggested mechanism for fog center removal, are discussed below.

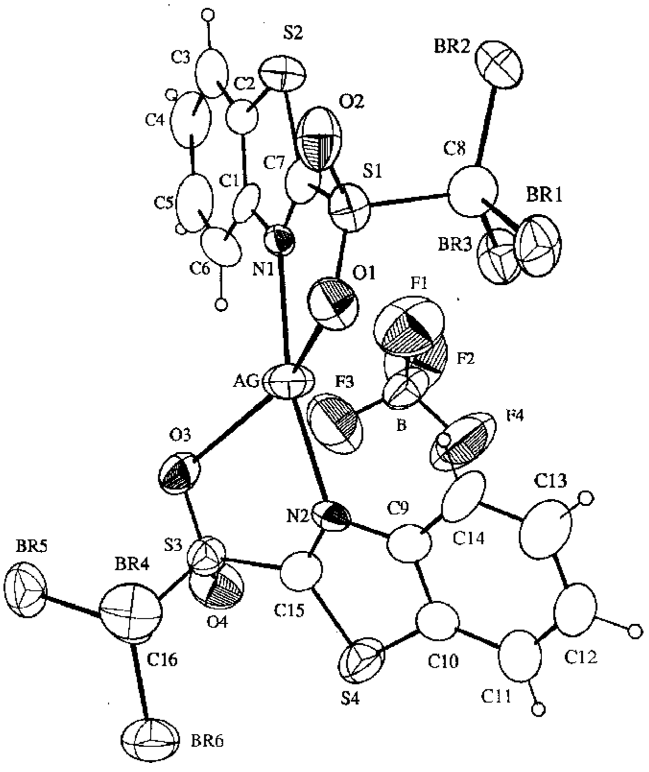

Figure 2. ORTEP drawing of [Ag–(2-tribromomethylsulfonyl-benzothiazole)$_2$(BF_4)] (acetone omitted for clarity).

Structure of [bis-(2-tribromomethylsulfonyl-benzothiazole)-silver(I)-tetrafluoroborate]. The four different potential coordinating groups in the 2-tribromomethylsulfonyl-benzothiazole ligand (ring sulfur, ring nitrogen, sulfone oxygen, and bromine) make six structural conformations possible. The first two conformations involve monodentate bonding with silver through the ring nitrogen (i.e., Ag–N) or the ring sulfur (Ag–S). The third and fourth structures are chelates with either ring donor atom (N or S) and Br (six-membered ring). The fifth and six possibilities involve chelating with either ring donor atom (N or S) and O (from SO_2) (five-membered ring). There is evidence in the literature for either Ag–S[7g] or Ag–N[7a] coordination from the benzothiazole

TABLE I. Selected Bond Distances (Å) and Angles (°) for $[Ag\{(C_7H_4NS)SO_2CBr_3\}_2BF_4]\cdot Me_2CO$

Atoms	Distance	Atoms	Distance
Ag–-O(1)	2.729(9)	Ag–-O(3)	2.720(9)
Ag–-N(1)	2.203(9)	Ag–-N(2)	2.20(1)
Br(1)—C(8)	1.94(1)	Br(2)—C(8)	1.89(1)
Br(3)—C(8)	1.92(1)	Br(4)—C(16)	1.92(1)
Br(5)—C(16)	1.93(1)	Br(6)—C(16)	1.90(1)
S(1)—O(1)	1.42(1)	S(1)—O(2)	1.42(1)
S(1)—C(7)	1.77(1)	S(1)—C(8)	1.85(1)
S(2)—C(2)	1.76(1)	S(2)—C(7)	1.73(1)
S(3)—O(3)	1.427(9)	S(3)—O(4)	1.43(1)
S(3)—C(15)	1.79(1)	S(3)—C(16)	1.84(1)
S(4)—C(10)	1.73(1)	S(4)—C(15)	1.75(1)
B—F(1)	1.35(2)	B—F(2)	1.34(2)
B—F(3)	1.35(2)	B—F(4)	1.34(2)
Atoms	**Angle**	**Atoms**	**Angle**
O(1)—Ag–-O(3)	147.2(3)	O(1)—Ag–-N(1)	69.6(3)
O(3)—Ag–-N(1)	118.7(3)	O(1)—Ag–-N(2)	108.4(3)
O(3)—Ag–-N(2)	70.9(3)	N(1)—Ag–-N(2)	165.9(4)
O(1)—S(1)—O(2)	121.7(6)	O(1)—S(1)—C(7)	105.9(6)
O(2)—S(1)—C(7)	108.4(6)	O(1)—S(1)—C(8)	108.0(6)
O(2)—S(1)—C(8)	107.6(6)	C(7)—S(1)—C(8)	103.6(6)
Ag–-O(1)—S(1)	113.7(5)	Ag–-O(3)—S(3)	113.6(5)
Ag–-N(1)—C(1)	122.6(8)	Ag–-N(1)—C(7)	127.4(8)
Ag–-N(2)—C(15)	125.4(9)	Ag–-N(2)—C(9)	122.4(9)
Br(1)—C(8)—Br(3)	110.4(7)	Br(1)—C(8)—Br(2)	111.2(7)
Br(1)—C(8)—S(1)	104.6(7)	Br(2)—C(8)—Br(3)	112.1(7)
Br(3)—C(8)—S(1)	108.0(7)	Br(2)—C(8)—S(1)	110.1(7)
Br(4)—C(16)—Br(5)	111.0(7)	Br(4)—C(16)—Br(6)	110.8(6)
Br(5)—C(16)—Br(6)	109.8(7)	Br(4)—C(16)—S(3)	108.8(7)
Br(5)—C(16)—S(3)	105.0(6)	Br(6)—C(16)—S(3)	111.2(8)
F(1)—B—F(2)	107(2)	F(1)—B—F(3)	110(2)

TABLE II. Final Fractional Coordinates for $[Ag\{(C_7H_4NS)SO_2CBr_3\}_2BF_4]\cdot Me_2CO$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eqv)*
Ag	0.70185(7)	0.6063(1)	1.00966(7)	3.46
Br(1)	0.6330(1)	1.0364(1)	0.84365(9)	3.69
Br(2)	0.4671(1)	0.8863(2)	0.74858(9)	3.49
Br(3)	0.6412(1)	0.7382(1)	0.81568(9)	3.8
Br(4)	0.8641(1)	0.6530(1)	1.2406(1)	4.21
Br(5)	0.8365(1)	0.3693(2)	1.2859(1)	4.33
Br(6)	1.0140(1)	0.4542(2)	1.2866(1)	4.6
S(1)	0.5543(2)	0.8463(3)	0.9137(2)	2.43
S(2)	0.4120(2)	0.6497(3)	0.8570(2)	2.44
S(3)	0.8575(2)	0.4204(3)	1.1439(2)	2.59
S(4)	0.9965(2)	0.5463(4)	1.1032(3)	3.83
O(1)	0.6347(6)	0.8456(8)	0.9723(5)	3.26
O(2)	0.4879(7)	0.9284(8)	0.9138(5)	3.65
O(3)	0.7673(6)	0.4290(8)	1.1172(5)	3.09
O(4)	0.9006(7)	0.303(1)	1.1437(6)	4.33
N(1)	0.5667(6)	0.5935(9)	0.9389(5)	1.71
N(2)	0.8406(6)	0.623(1)	1.0543(6)	2.23
C(1)	0.5213(8)	0.476(1)	0.9252(7)	2.22
C(2)	0.4365(8)	0.489(1)	0.8824(7)	1.89
C(3)	0.382(1)	0.385(1)	0.8640(7)	2.98
C(4)	0.418(1)	0.269(1)	0.8887(8)	3.41
C(5)	0.504(1)	0.254(1)	0.9321(9)	3.83
C(6)	0.5571(9)	0.358(1)	0.9518(7)	2.42
C(7)	0.5172(8)	0.686(1)	0.9049(7)	2.3
C(8)	0.5720(9)	0.875(1)	0.8279(8)	3.13
C(9)	0.8828(9)	0.702(1)	1.0247(8)	2.82
C(10)	0.9675(9)	0.675(1)	1.0433(8)	2.74
C(11)	1.016(1)	0.744(2)	1.0133(9)	4.04
C(12)	0.979(1)	0.840(2)	0.9648(9)	4.56
C(13)	0.894(1)	0.867(2)	0.948(1)	5.39
C(14)	0.847(1)	0.801(2)	0.9768(9)	4.19
C(15)	0.8911(9)	0.543(1)	1.0967(8)	2.64
C(16)	0.8949(9)	0.476(1)	1.2394(7)	2.68
B	0.757(1)	0.377(2)	0.896(1)	3.57
F(1)	0.6915(7)	0.459(1)	0.8710(7)	7.21
F(2)	0.7350(8)	0.272(1)	0.8547(7)	7.74
F(3)	0.7725(8)	0.347(1)	0.9668(6)	7.48
F(4)	0.8271(7)	0.427(1)	0.8913(8)	8.78
O(5)	1.205(1)	0.405(1)	1.360(1)	8.55
C(17)	1.238(1)	0.504(2)	1.367(2)	7.57
C(18)	1.261(2)	0.533(3)	1.297(2)	12.54
C(19)	1.261(2)	0.586(2)	1.426(2)	11.1

* *B*(eqv) = 4/3[a^2ß$_{11}$ + b^2ß$_{22}$ +c^2ß$_{33}$ + *ab*(cosg)ß$_{12}$ + *ac*(cosß)ß$_{13}$ + *bc*(cosa)ß$_{23}$]

TABLE III. Summary of Data Collection and Structure Refinement for $[Ag\{(C_7H_4NS)SO_2CBr_3\}_2BF_4]\cdot Me_2CO$

Formula weight	1152.7
Temperature, °C	18
Diffractometer/scan	Enraf-Nonius CAD-4/ω-2θ
Range of relative transmission factors, %	28/100
Radiation graphite monochromator	MoKα (l + 0.71073)
Maximum crystal dimensions, mm	0.10 × 0.35 × 0.35
Scan width	0.80 = 0.35 tanθ
Standard reflections	800; 040; 008
Decay of standards	–13% (linear decay correction applied)
Reflections measured	6236
2θ range, deg	$2 \leq 2\theta \leq 50$
Range of h, k, l	+20, +12, ±23
Reflections observed $[F_o \geq 5\sigma(F_o)]$[†]	2525
Computer programs[‡]	SHELX[§]
Structure solution	SHELXS[§]
No. of parameters varied	379
Weights	$[\sigma(F_o)^2 + 0.00005\ F_o^2]^{-1}$
GOF	0.86
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.05
R_w	0.053
Largest feature final difference map	0.8 e$^-$ Å^{-3}
Formula units/unit cell	4
D_{calc}, g/cm^{-3}	2.36
μ_{calc}, cm^{-1}	87.54

[†] Corrections: Lorentz polarization and absorption (empirical, psi scan).

[‡] Neutral scattering factors and anomalous dispersion corrections are from standard reference sources. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, England, Vol. IV, 1974, pp. 72, 99. 149 (present distributor: Kluwer Academic Publishers, Dordrecht).

[§] G. M. Sheldrick, SHELX76, a system of computer programs for X-ray structure determination as locally modified, University of Cambridge, England (1976); G. M. Sheldrick, SHELX, *Acta Cryst.* **A46**, 467 (1990).

group. Easy coordination with either the sulfone oxygen or the tribromomethyl bromine could also occur, owing to the position of the tribromomethylsulfone on the coordinating aromatic ring, producing five- and six-membered rings, respectively. Thus, simple monodentate coordination of the first two options could be considered unlikely. The BF_4^- counterion is expected to be noncoordinating.

The molecular structure of the 2-tribromomethylsulfonyl-benzothiazole complex with $AgBF_4$ has now been determined by single crystal x-ray analysis. The complex (Fig. 2) has the stoichiometry [Ag(2-tribromomethylsulfonyl-benzothiazole)$_2$(BF_4)·(Me_2CO)]. The title complex contains a five-membered ring structure involving silver coordination with the ring nitrogen and a rare Ag–O(sulfone) coordination, in preference to the six-membered ring involving a silver–bromine complex. Any Ag···Br interaction in the solid state is minimal. Selected bond distances and angles are shown in Table I, final fractional coordinates in Table II, and details of the data collection and structure refinement in Table III.

The reaction of this 2-tribromomethylsulfonyl-benzothiazole ligand with silver tetrafluoroborate proceeds easily and results in a stable silver complex. The strong affinity of the sp^2 nitrogen for silver, demonstrated by the 2.203(9) and 2.20(1) Å Ag–N bond lengths, drives the complex formation. The normal Ag–N bond length for silver complexes of aromatic nitrogen is 2.1–2.2 Å.[9]

Simple thioethers are generally poor ligands in comparison with the nitrogen, although in combination, such as in cyclic thio crown ethers, ligands having relatively high affinity for silver are known.[10] Whereas an Ag–S bound benzothiazole complex has been reported on the basis of IR data,[7g] no known silver benzothiazole complexes have been fully characterized by x-ray analysis. Thus, it is not surprising that the thioether group in the title complex is uninvolved in complexation to silver.

The long Ag–O$_{sulfone}$ bond lengths, 2.729(9) and 2.720(9) Å, compared with more typical 2.3 to 2.5-Å[11] values, clearly indicate a weak bond. The long Ag–O$_{sulfone}$ bond is actually

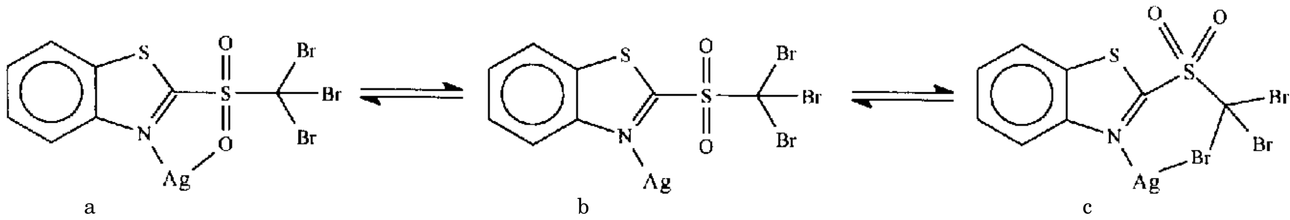

Figure 3. Solution equilibria of [Ag–(2-tribromomethylsulfonyl-benzothiazole)] (other ligands to silver not shown).

normal, however, when compared with the few other known Ag–$O_{sulfone}$ structures in the literature. These reports include Ag–O bond distances in the 2.47- to 2.71-Å range.[12] Nonsilver E–O–S(O)–R_2 complexes for which crystallographic data are known, where E = Sb and As,[13] are also limited. These latter compounds exhibit E–O bond lengths that range from 2.84 to 2.88 Å. Such bond lengths are 0.5 Å shorter than the van der Waals radii, but clearly longer than the Ag–O bond length in the [bis-(2-tribromomethylsulfonyl-benzothiazole-silver(I)-tetrafluoroborate] complex.

All of the S=O bond lengths in the title complex are essentially the same, 1.427(9), 1.42(2), and 1.43(1) Å, and are typical of uncoordinated sulfone S=O bond lengths.[14] The S=O bond lengths are expected to be different, however, depending on the Ag–O bond strength. The normal bond lengths observed are not different, further indicating the weak character of the Ag–$O_{sulfone}$ bond. In two of the known Ag–$O_{sulfone}$ complexes, the S=O bond lengths do increase somewhat and range from 1.42–1.46 Å.[11a,b] Thus, it can be concluded that the Ag–O bond contributes little to the overall stability of the title complex. Bonding to the silver in the solid state occurs because of the oxygen atom's fortuitous position relative to the strongly bonding ring nitrogen.

Recently, the crystal structures of organic halide ligands that complex with silver to form silver–halide bonds have been reported.[15] In the case of bromine, an α-bromoalkylketone chelates silver via the carbonyl and the bromine, to form a stable five-membered ring complex. The formation of the Ag–Br bond appears to lengthen the C–Br bond from 1.915(6) to 1.963(6) Å. This report proposes that the increase in the C–Br distance, caused by silver coordination with the Br, promotes the loss of the bromine to form AgBr in the solid state.

Inspection of the [bis-(2-tribromomethylsulfonyl-benzothiazole)-silver(I)-tetrafluoroborate] complex's molecular structure demonstrates clearly that there is no Ag–Br bond, and the three-dimensional lattice reveals no significant Ag···Br interaction in the solid state. The shortest Ag···Br distance is 3.8 Å, which is far longer than the normal Ag–Br bond length of 2.7–2.9 Å.[15] The bromines' closest intermolecular contacts in the lattice are with other bromines.

In the solid state, the weak Ag–$O_{sulfone}$ bond in the five-membered ring chelate is preferred over the Br–Ag bond in the alternative six-membered ring structure. The long Ag–O distance, however, suggests that, in solution, the silver is no longer chelated to the ligand. This situation is illustrated in Fig. 3. The equilibrium between the N–Ag–O chelate [Fig. 3(a)] and the N–Ag complex [in Fig. 3(b)], through facile –S = O– release, will be shifted to the right. Evidence for this equilibrium shift is found in the decomposition of the title complex in acetonitrile. Simple rotation of the tribromomethyl group could then generate a significant Ag···Br interaction, in competition with the Ag···O = S– interaction [Fig. 3(c)]. This point is significant when discussing the ligand's possible antifoggant properties (see below).

The tetrafluoroborate anion in the title complex appears to be arranged to enable Ag···F interactions. Its position and symmetrical arrangement relative to the silver suggests more than a coincidental orientation. The Ag···F distances of 3.08(1) and 3.19(1) Å are indicative of weak interactions at best. A similarly arranged tetrafluoroborate anion, however, exhibiting an Ag···F separation of 3.011(8) Å, has been reported as a weak Ag–F bond.[16]

Thermal and Spectroscopic Characterization of [bis-(2-tribromomethylsulfonyl-benzothiazole)-silver(I)-tetrafluoroborate]. DSC and TGA results for [bis-(2-tribromomethylsulfonyl-benzothiazole)-silver(I)-tetrafluoroborate] are shown in Fig. 4. The DSC scan shows weak, broad endotherms centered at 80 and 140°C (a pink-gray color is visually detected at this point), followed by an endotherm centered at 225°C. The TGA results indicate that loss of volatiles is just beginning in this temperature range. A complicated weight loss transition, comprising of three overlapping regions, starts at 250°C. The first region covers nearly 100°C, yet amounts to only 3% weight loss (33 amu). The second weight loss (15.4%) corresponds approximately to the loss of two bromine atoms, presumably one from each ligand. Catastrophic decomposition immediately follows, ending with Ag_2S (not AgBr) as the calculated residual product.

The IR spectrum of [bis-(2-tribromomethylsulfonyl-benzothiazole)-silver(I)-tetrafluoroborate] (Fig. 5) in Nujol shows the expected broad BF_4^- absorption near 1050 cm^{-1} and the C–Br stretch at 605 cm^{-1}, which is unchanged from the free ligand. The S=O bands are found at 1165 and 1365 cm^{-1}.[17]

Possible Mechanism for Antifoggant Properties of Tribromomethyl Compounds Containing a Silver Complexing Group. The antifoggant and stabilizing mechanism of tribromomethyl compounds in silver halide photographic materials is usually attributed to the equilibrium loss of bromine radicals, which then oxidize the metallic silver fog centers.[18] Such radical formation is de-

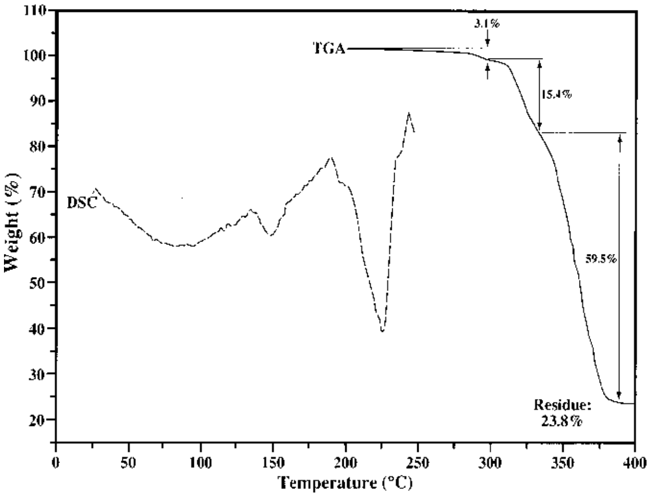

Figure 4. DSC and TGA results for [bis-(2-tribromomethylsulfonyl-benzothiazole)-silver(I)-tetrafluoroborate].

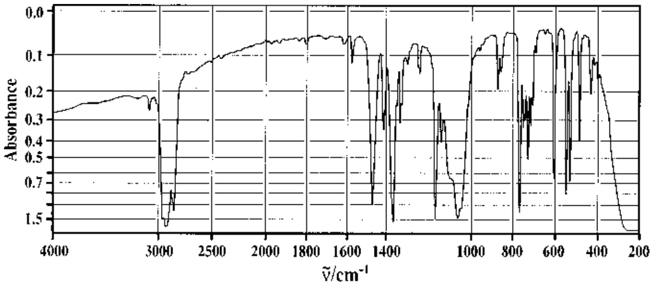

Figure 5. IR spectrum of [bis-(2-tribromomethylsulfonyl-benzothiazole)-silver(I)- tetrafluoroborate].

pendent only on the stability of the starting compound, and independent of its location in the film. This process is inherently inefficient, because many radicals would be distributed at locations unrelated to fog centers. Coordination of the antifoggant to the silver halide crystals could improve the efficiency of this reaction. The chelating ability of the reported α-bromo-alkylketone (which includes the formation of an Ag–Br bond)[15] and its ability to generate AgBr subsequently by activating the C–Br bond suggest that a similar Ag–Br bonded structure could form between 2-tribromomethylsulfonyl-benzothiazole and a silver halide surface. Fog centers within the silver halide crystal might then be eliminated through bromine transfer from the surface complex of 2-tribromomethylsulfonyl-benzothiazole, with AgBr as the byproduct.

Removal of fog centers from a silver halide crystal has been related to the size of the Ag_n° cluster.[19] These reports discuss the relationship of the oxidation potential of silver halide developers to their efficacy in development of specific size silver clusters. Silver atom clusters of 5 to 6 atoms or less are prone to oxidation in the presence of an oxidizing species, whereas clusters containing more atoms are prone to further growth by additional Ag^+ reduction. It is reasonable, therefore, to expect that elimination of fog centers in silver halide materials would be most effective for centers that are still in the small silver atom cluster stage. Bromine transfer from the tribromomethyl group to the silver atom cluster, facilitated via suitable orientation by the coordinated ligand, would produce AgBr and result in the loss of the fog center.

Surface complexation of the benzothiazole ligand is required for this mechanism to be efficient; otherwise significant bromine radical formation in the vicinity of the fog centers would be necessary. In the case of silver bromide, an AgBr-(2-amino-benzothiazole) complex has been reported in which the ring nitrogen is bound to silver bromide.[7a] This particular complex is a good model for the proposed mechanism involving complexation of the 2-tribromomethylsulfonyl-benzothiazole with a silver halide crystal. That is, complexation with the silver halide surface provides the needed proximity of the tribromomethyl group to the fog center. Subsequent bromine radical transfer could result in removal of small metallic silver clusters, thus providing the observed antifoggant properties. Unfortunately, our attempts to prepare and isolate a 2-tribromomethylsulfonyl-benzothiazole complex with silver bromide were not successful.

The mechanism implied by the AgBr-(2-amino-benzothiazole) model complex provides for complexation to an coordinatively unsaturated silver ion that is close to the fog center. Complexation of the tribromomethylsulfonylbenzothiazole directly to the surface of the Ag° fog center might also occur. Nitrogen donors such as mercaptobenzothiazole[20] and imidazole[21] are known to bond to metallic silver surfaces. Ligands containing nitrogen donors have also been found to undergo substantial activation upon bonding to metallic silver surfaces.[22] In the case of the tribromomethylsulfonyl-benzothiazole ligand, it can be most efficient in bromine transfer and fog center elimination because the complex occurs at the fog site, not just near it.

Although the mechanism suggested is reasonable for tribromomethylsulfonyl-benzothiazole and related coordinating ligands containing tribromomethyl groups, it cannot rule out other possible antifoggant mechanisms, such as simple bromine radical loss[18] from the uncoordinated ligand.

Conclusions

The [bis-(2-tribromomethylsulfonyl-benzothiazole)-silver(I)-tetrafluoroborate] complex contains a five-membered Ag–N–C–S–O chelate ring, in preference to the alternative six-membered Ag–N–C–S–C–Br ring containing an Ag–Br bond. In addition, the silver coordination sphere contains only the ring nitrogen and the oxygen from the $\mathrm{SO_2}$ group. The ring sulfur of the benzothiazole is not involved with silver coordination. There is no significant Ag···Br interaction in the lattice of the complex. The Ag–N bond lengths are normal for silver complexes of aromatic nitrogen, but the Ag–O bond lengths are long and illustrate the weak bonding capability of the $\mathrm{SO_2}$ ligand. The complex is one of the few in which an Ag–O–S(O)–R linkage has been determined crystallographically.

Complexation of the 2-tribromomethylsulfonyl-benzothiazole to coordinatively unsaturated silver ions on the surface of silver halide crystals could provide the needed proximity of the tribromomethyl group to the fog centers. Subsequent bromine transfer could easily lead to small silver atom cluster oxidation, thereby accounting for the antifoggant properties of ligands containing tribromomethyl groups. The antifoggant efficiency of these compounds could be attributed at least in part to their ability to coordinate to silver in either the ionic or atomic state.

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