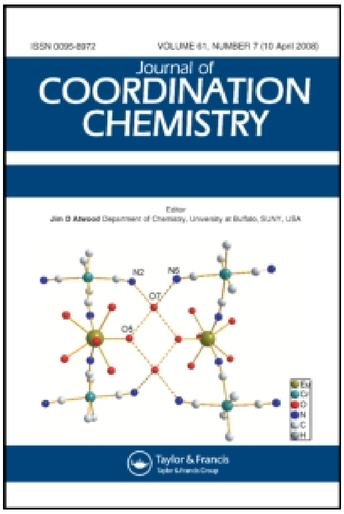

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NEUTRAL COMPLEXES OF SILVER HALIDES AND TETRAMETHYLTHIURAM MONOSULFIDES

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The preparation and characterization of 1 : 1 adducts of silver halides AgX (X = Cl, Br, I) with N,N,N′,N′-tetramethylthiuram monosulfides is reported. The products are characterized by elemental analyses, magnetic measurements and IR-Raman spectroscopy. The data are interpreted in terms of a halogen-dibridged structure of D_{2h} symmetry.

Keywords: Silver; Thiuram; Tetramethylthiuram monosulfides

INTRODUCTION

N,N,N′,N′-Tetraalkylthiuram disulfides are the semi-esters of N,N-dialkyldithiocarbamate anions. Previous publications have offered a general background as to the most important applications of these molecules [1]. These species are related by the two-electron redox process:

$$R_2NC(S)S - SC(S)NR_2 + 2e^- = 2R_2NC(S)S^-$$

The chemistry of the ligands above and various copper(0), (I) and (II) species has proved rich and occasionally unexpected. Thus the disulfides and copper metal afford Cu(II) dithiocarbamates, while copper(I) or (II) halides yield, respectively, Cu(II) or (III) dithiocarbamates. The *mono*sulfides, available through S-abstraction from the disulfides may lead to Cu(I)

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adducts of considerable structural variety in the solid states [2–5]. A logical extension of these studies includes silver(0) and (I) metal species.

Based on the reactivity and stability of its coordination complexes, the silver(I) ion has been classified as a class B or "soft" acid, where P- and S-donors are preferred over N- and P- congeners. However, many systems involving silver(I) and S-donors feature cluster or oligomeric arrays of considerable complexity [6]. With a view to extending the list of possible structural motifs so far known, a study of the coordination chemistry of silver halides with thiuram sulfides has now been undertaken.

The coordinating properties of silver halides have been rarely studied. Complexes with sulfur donors have been reported and unambiguously characterized only for AgL_2Cl systems (L = thiourea [7], dimethylformamide [8]). Our hopes of expanding this meager series by structurally characterizing a number of thiuram monosulfide complexes with silver halides have been frustrated by the solubility properties of the materials isolated.

EXPERIMENTAL

General Preparative Methods, Spectroscopy and Analyses

The ligand was purchased from Fluka and purified as described previously [9]. Silver halides were obtained from aqueous solutions of silver nitrate and sodium halides in the appropriate mole ratios. Solvents were used without purification. Microanalytical services were available at the University of Concepción. IR and Raman spectra were obtained by techniques already described [10].

Preparation of the Complexes

The 1 : 1 adducts of silver halides and the ligand were prepared by a general method which consisted of dissolving 2.0 mmol. (0.416 g) of the ligand in 5.0 mL of acetonitrile and adding 1.0 mmol. of the halide with continuous stirring. After 6 to 18 hours of reaction, depending on the grain size of the halide, the white-gray appearance of the halide had changed to a dull (X = Cl) or lemon-yellow (X = I) and the amorphous solids were filtered off, washed with fresh acetonitrile (3 mL) followed by diethyl ether (5 mL), and dried by suction. Yields were essentially quantitative, indicating that little complex was left in solution. Further purification was impossible, due to the insolubility of the products. Spectroscopic characterization was therefore carried out on these crude materials.

TABLE I Characteristic IR frequencies[a] for Me$_4$tms and its silver halide complexes

Band[b]	*Me$_4$tms*	*AgMe$_4$tmsCl*	*AgMe$_4$tmsBr*	*AgMe$_4$tmsI*
(i)	1507	1510	1510	1514
(ii)	995, 961	986, 938	988, 946	989, 946
(iii)	863, 853	868, 855	867, 857	868, 857

[a] Frequencies are reported in cm^{-1}.
[b] See text for a description of these features.

TABLE II IR and Raman spectra below 500 cm^{-1} for silver halide complexes[a]

Mode	*AgMe$_4$tmsCl*	*AgMe$_4$tmsBr*	*AgMe$_4$tmsI*
Ag-X, Raman	161, 158	155, 124	124, 118
Ag-X, IR	172, 160	145	129, 110
Ag-S, Raman	311, 286	326, 283	324, 280
Ag-S, IR	322, 275	335, 279	330, 287

[a] The ligand is transparent below 500 cm^{-1}.

Chlorobis(N,N-dimethylthiocarbamoyl)sulfidosilver(I)

AgMe$_4$tmsCl: pale yellow solid, m.p: 128°C, *Anal.* Calcd. for $C_6H_{12}N_2S_3AgCl$ (%) C, 20.5; H, 3.4; N, 8.0; 5, 27.4; Cl, 10.1. Found: C, 20.3; H, 3.2; N, 7.8; 5, 27.8; Cl, 10.3. IR data are reported in Tables I and II.

Bromobis(N,N-dimethylthiocarbamoyl)sulfidosilver(I)

AgMe$_4$tmsBr: lemon yellow solid, m.p: 148°C, *Anal.* Calcd. for $C_6H_{12}N_2S_3AgBr$ (%) C, 18.2; H, 3.1; N, 7.1; S, 24.3; Br, 20.2. Found: C, 18.3; H, 3.2; N, 7.1; 5, 24.4; Br, 20.6. For IR data see Tables I and II.

Iodobis(N,N-dimethylthiocarbamoyl)sulfidosilver(I)

AgMe$_4$tmsI: bright yellow solid, m.p: 153°C, *Anal.* Calcd. for $C_6H_{12}N_2S_3AgI$ (%) C, 16.3; H, 2.7; N, 6.3; S, 21.7; I, 28.6. Found: C, 16.0; H, 2.4; N, 6.1; S, 21.5; I, 28.8. See Tables I and II for IR data.

RESULTS AND DISCUSSION

Preparative

Solutions of tetramethylthiuram monosulfide in acetonitrile react with silver halides over a period of several hours at room temperature to yield the insoluble 1:1 yellow adducts. Spectroscopic evidence as discussed below, indicates that these are true complexes and not mixtures of the starting materials. The adducts are insoluble in all common organic solvents with the exception of pyridine and dimethylsulfoxide. Presumably drastic changes which involve the displacement of thiuram disulfide occur in these solvents. All three halide complexes (Cl, Br, I) exhibit a 1:1-electrolyte behavior when they are dissolved in the manner just described. Attempts to determine molecular weights by osmometry in the case of the chloro-derivative are also consistent with a pattern of dissociation and ligand displacement similar to:

$$AgLX + nS = AgS_n^+ + X^- + L$$

No efforts have been made to ascertain further the nature of the materials in these solutions. When the preparative work just described was attempted using thiuram monosulfides bearing the higher homologues in the alkyl series (Et, *n*-Pr, *i*-Pr), no visible reaction was apparent at room temperature over several days. This observation is surprising, considering the prolific coordination chemistry found in the case of copper(I) halides, but may well be related to a higher lattice energy attendant to the silver salts, as reflected by the values of their solubility products in aqueous solution.

Solid State Characterization

Circumstantial evidence in favor of adduct formulations comes from the observation that the materials isolated through the reaction described above do not show the photosensitivity commonly associated with silver halides. All complexes in the series prepared are diamagnetic and thus consistent with a closed shell electron configuration involving silver(I) species. Although the diamagnetic nature of the materials isolated is no proof of complexation, it does rule out formulations involving hypervalent states, not uncommon in systems containing thiuram sulfides [1]. The remainder of the structural characterization is based on IR and Raman spectroscopy.

Table I shows selected IR and Raman bands observed for the free ligand and its silver complexes in the region 4000–6000 cm^{-1}. The features observed correspond to vibrations of the ligand modified by coordination to the metal. The small but distinct shift in many of these bands with a change in the nature of the halogen supports the proposal that the complexes under discussion cannot be ionic in the solid.

The vibrational spectrum of the ligand is normally interpreted on the basis of three distinct modes [11]: (i) the band located near 1500 cm^{-1} (thiureide band) due to the C—N stretching mode which has an important double bond character. This band also has important contributions from S—C═S bending modes (ii) the band near 1000 cm^{-1} attributed to a C═S stretch and (iii) a band in the 880–840 cm^{-1} region, which is related to the C—S stretching mode associated with the thioether-like linkage.

Band (i) is shifted some 10 to 20 cm^{-1} in the complexes with respect to the free ligand. This shift is of the same order of magnitude as the one found in the copper(I) complexes [10] and is absolutely in agreement with complexation of the ligand to the metal centers. As pointed out above, the increase in the magnitude of the shift in progressing through the series $I \geq Br \geq Cl$ follows the electron-withdrawing power of the ancillary ligand and hints at a non-ionic structure, where minor shifts would have been observed.

Free ligand as well as complexes show bands in the region 990–1010 cm^{-1} and these can be assigned to C═S stretching modes. The doublet aspect of this absorption defies explanation so far, as a single band is expected [12]. A doublet is also observed in the region 840–860 cm^{-1}, which can be assigned to a C—S stretch.

Table II summarizes the spectroscopic data below 500 cm^{-1} for the complexes under study. Assignments are based on previous work [10]. The silver—halogen stretching bands appear at frequencies which are somewhat lower than typical terminal values and are believed to arise from bridged structures. A working model is thus considered, based on a halogen-dibridged dimeric formulation of D_{2h} symmetry. Two Raman-active (A_g+B_{1g}) and two IR-active ($B_{2u} \pm B_{3u}$) Ag—S stretching bands, as well as two Raman-active (A_g+B_{2g}) in addition to two IR-active ($B_{1u}+B_{3u}$) Ag—X modes are expected according to this model. The data in Table II are in good agreement with the structure proposed. The differences observed between IR and Raman spectra are significant enough that adherence to the rule of mutual exclusion is still observed. This situation is similar to the one observed in the case of $CuMe_4tmsX$ (X = Cl and I) [3]. However, an alternative structure based on oligomeric chains of halogen-bridged $\cdots Ag(S_2)X—$ units is also consistent with the vibrational spectra and cannot be summarily discarded. It is interesting to contrast the present results with those obtained for the analogous copper(I) complexes. For the latter compounds, a similar halogen-dibridged structure was anticipated on the basis of vibrational spectroscopy for the Me-substituted derivatives, while the evidence for the Et series pointed at monomeric tricoordinate formulations [10]. Single crystal X-ray diffraction studies fully confirmed these expectations [3, 4].

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