The Reaction of Silver(1) lons with Organic Compounds Containing the HN-C=S Grouping. Part II.¹. Some Thiourea Derivatives

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The formation of some sparingly soluble silver(1) complexes with thiourea and some of its derivatives (HL) is investigated. Thiourea, thiosemicarbazide, guanylthiourea, and dithiobiuret all give polymeric [Ag₂(HL)₃](NO₃), species. Dithiobiuret also forms AgL in non-acidified solutions. Infrared studies are used to establish the bonding in the complexes.

THE reaction of thiourea (I; R = H) with silver(I) ions is known to produce a series of water-soluble complexes, $[AgTu_n]^+$ (Tu = thiourea), where *n* is $3,^{2,3}$ 2,4 or 1.5 Thiosemicarbazide (I; $R = NH_2$) (Tsz) behaves similarly.³ We, and others,^{5,6} have noticed that these compounds also each form a sparingly soluble species with silver(I), which dissolves in an excess of either silver(I) ions or ligand. We have characterised these species, and also the similar sparingly soluble complex of dithiobiuret (I; $R = CS \cdot NH_2$) (HDB).



EXPERIMENTAL

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Guanyl thiourea and dithiobiuret were prepared by a known method.⁷ The other derivatives were commerically

RESULTS

Thiourea, thiosemicarbazide, and dithiobiuret all form sparingly soluble $[Ag_2Tu_3](NO_3)_2$ complexes in acidic solutions. The thiourea complex is hydrated; the water content corresponds to more than 2.5 molecules for three thiourea molecules. These conclusions are supported by elemental analyses (Table 1) and potentiometric titrations (Table 2, Figure 1). Guanylthiourea [I; $R = C(:NH)NH_2$] (GTu) does not form a sparingly soluble complex, but a potentiometric titration (Figure 2) shows that a soluble $[Ag_2GTu_3]^{2+}$ complex is formed.

There is little previous evidence for the existence of these species. Kuz'mina and Songina⁵ detected this thiourea complex in 10-14N-sulphuric acid by use of polarography, and Harlay⁸ reported the thiosemicarbazide species.

Wronski⁹ found a 2Ag: 3 thiourea or thiosemicarbazide end-point in a titration of silver and ligand solutions, using 5-4'-dimethylaminobenzylidenerhodanine as indicator.

TABLE 1

		Found (%)					Required (%)				
		М. р.	Ċ	Н	N	s	c	Н	N	s	
g,Tu,][(NO ₃),,2·5H ₂ O *	White powder	152.5-153.5° (decomp.)	5.7	$2 \cdot 9$	18.5	15.8	5.9	$2 \cdot 8$	18.3	15.7	
g,Tsz, (NO ₃),	White powder	166-167 (decomp.)	6.1	$2 \cdot 6$	$25 \cdot 4$	15.4	5.9	$2 \cdot 5$	25.1	15.7	
$g_{2}HDB_{3}(NO_{3})_{2}$ (pH 0)	Pale grey-brown powder	174·5-175 (decomp.)	9.9	1.9	$21 \cdot 2$		9.7	$2 \cdot 0$	20.7		
gDB] (pH 2.5)	Yellow-green powder	Did not melt			18.8				17.4		
gDB] (pH 4)	Dark grey-brown powder	Did not melt			14.4			—	17.4		
					/	201					

* $H_2O = 7.7\%$ (loss in weight in vacuo at 78°). Reqd. for $2.5H_2O$: 7.3%.

available. Infrared spectra were determined for potassium bromide discs on a Perkin-Elmer model 21 spectrometer. That of silver dithiobiuret was also obtained in Nujol, and was essentially the same as by the other method. Potentiometric titrations were carried out as described previously,¹ except that 10^{-2} M-solutions were used for the pH measurements.

Preparation of the Complexes.—Tris(thiourea)disilver nitrate was precipitated from a solution of thiourea (0.23 g., 0.003 mole) in water (20 ml.) containing concentrated nitric acid (0.5 ml.) by adding a solution of silver nitrate (0.35 g.)0.002 mole) in water (10 ml.). The precipitate was washed well with dilute nitric acid, and dried under a vacuum over silica gel. The similar thiosemicarbazide complex was also prepared in this way. The dithiobiuret complexes were prepared by adding silver nitrate solution (0.001 mole) to an aqueous solution of dithiobiuret (0.001 mole) at various acidities (see main text). The analyses and properties of these complexes are given in Table 1.

¹ Part I, W. I. Stephen and A. Townshend, J. Chem. Soc., 1965, 3738.

 ² W. S. Fyfe, J. Chem. Soc., 1955, 1032.
 ³ V. F. Toropova and L. S. Kirillova, Zhur. neorg. Khim., 1960, **5**, 575.

In addition to its typical thiourea behaviour, dithiobiuret also forms a yellow-green, approximately 1:1 precipitate

TABLE 2

Results of potentiometric titrations

	Ligand		
Compound	Ag : Ligand	Conditions	acidity
Thiourea	2:3.1	Dil. HNO ₃	nil
Thiosemicarbazide	2:3.1	Dil. HNO ₃ †	nil
Guanylthiourea	$\left. \begin{array}{c} 2:3{\cdot}0\\ 2:1{\cdot}0* \end{array} \right\}$	No acid †	Weak base
Dithiobiuret	1:1.1	0.2N-HNO3	Weak acid 20
	1:0.8	No acid	$pK_1 = 9$
* Silver sulphid	+ Aqueous eth	and $(1 \cdot 1 v/v)$	

with silver ions in less-acidic solutions (Figure 2). One hydrogen ion is eliminated per silver ion complexed (Figure 3). It was not possible to isolate a pure sample of this

⁴ M. Nardelli, L. Cavalca, and A. Braibanti, Gazzetta, 1957,

87, 903. ⁵ N. N. Kuz'mina and O. A. Songina, Zhur. analit. Khim., 1963, **18**, 323.

M. Levy, U.S.P. 2,739,893/1956.

- ⁹ F. Kurzer, Org. Synth., 1956, **35**, 69.
 ⁸ V. Harlay, Compt. rend., 1935, **200**, 1220.
 ⁹ M. Wronski, Talanta, 1965, **12**, 593.

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complex; the analyses of the species obtained at two different pH values (Table 1) indicate the presence of some 2:3 complex (pH 2.5) or silver sulphide (pH 4).

Decomposition of the Complexes.—All the complexes decompose, more or less readily, to silver sulphide. The decomposition usually begins as the molar ratio of silver(I) to ligand approaches 1:1. The reaction occurs most easily with guanylthiourea; this system has



FIGURE 1 Titration of 10⁻²M-thiourea (20 ml.) with 10⁻²Msilver nitrate; A = region of precipitation



FIGURE 2 Titrations of (A) 10⁻²M-guanylthiourea (20 ml.) and (B) 10-2M-dithiobiuret (10 ml.) with 10-2M-silver nitrate



FIGURE 3 DH Titrations of (A) 10⁻²M-guanylthiourea (10 ml.) and (B) 10-2M-dithiobiuret (10 ml.) with 10-2M-silver nitrate

therefore been studied in more detail. Figure 2 indicates that, after the formation of [Ag₂GTu₃]²⁺, decomposition is occurring until 2 moles of silver per mole of guanyl thiourea have been added. Figure 3 shows that hydrogen ions

¹⁰ Yu. I. Usatenko and A. S. Sukhoruchkina, Zhur. analit. Khim., 1963, 18, 1447.

J. E. Stewart, J. Chem. Phys., 1957, 26, 248.

¹² K. Swaminathan and H. M. N. H. Irving, J. Inorg. Nuclear Chem., 1964, 26, 1291.

 R. W. Olliff, J. Chem. Soc., 1965, 2036.
 A. I. Grigor'ev, T. Wên-Lsia, I. D. Kolli, and V. I. Spitsyn, Russ. J. Inorg. Chem., 1964, 9, 1397.

are generated during the decomposition; 1.0 hydrogen ion has been released per silver ion precipitated by the end of the reaction. These reactions conform to those labelled (1) and (2) below:

$$H_{g}R^{+}-S^{-}+Ag^{+} = HR^{-}S^{-}Ag^{+}+H^{+} \qquad (1)$$

$$\downarrow Ag^{+}$$

$$Ag_{g}S^{+}+H^{+}+R \qquad (2)$$

Dithiobiuret reacts in exactly the same way; the further release of hydrogen ions after the 1:1 end-point (Figure 3) is due to this decomposition. This is undoubtedly the reason for the 2Ag: 1 ligand species detected 10 at pH 5.6. The similar reaction with thiourea is markedly reduced if a little nitric acid is added.

Infrared Studies .--- The relevant infrared absorption bands of thiourea, thiosemicarbazide, and dithiobiuret, and their 2:3 silver complexes, are in Table 3. The assignments of the bands for thiourea are those of previous workers.11,12 The changes that occur on complexing with silver(I) are similar to those observed in other metal-thiourea complexes.¹²⁻¹⁴ The near-constancy of the N-H frequencies implies no metal-nitrogen bonding. The increase in the C-N frequency arises from a greater contribution from the canonical forms (II) of thiourea. A metal-sulphur bond would increase this contribution, whereas a metal-nitrogen bond would have the opposite effect. The decrease in frequency of the strong C=S absorptions at 1433 and 721 cm.⁻¹ confirms the presence of metal-sulphur bonds.

The spectra of thiosemicarbazide and dithiobiuret are very similar to that of thiourea, and the bands have been assigned by comparison with thiourea. The shifts that occur on complexing with silver(I) are likewise similar, and indicate that silver bonds only to sulphur. Small but definite decreases in the N-H frequencies at 3290, 1643, 1621, and 1009 cm.⁻¹ for thiosemicarbazide can be attributed to weak hydrogen-bonding, perhaps with nitrate.

DISCUSSION

The infrared studies show only silver-sulphur bonding between ligand and metal in the 2:3 complexes. This means that thiosemicarbazide functions as a unidentate ligand, completely analogous to thiourea, as it does in [AgTsz]Cl,¹⁵ and not as a bidentate ligand, which occurs in some zinc ¹⁶ and nickel ¹⁷ chelates. This argument also applies to guanylthiourea and dithiobiuret. The $([Ag_2Tu_3]^{2+})_n$ constitution is, of course, that expected for a polymeric species in which the silver is trigonally bound, and each sulphur bonds to two silver ions. It has been shown 18 that silver(I) is indeed trigonally bound in some of its strongest π -bonded complexes, and the most highly complexed silver-thiourea species² is [AgTu₃]⁺. The polymeric structure accounts for the low solubility of these species.

¹⁵ M. Nardelli, G. F. Gasparri, G. G. Battistini, and A. Musatti, Chem. Comm., 1965, 187.

¹⁶ L. Cavalca, M. Nardelli, and G. Branchi, Acta Cryst., 1960, **13**, 688.

¹⁷ L. Cavalca, M. Nardelli, and G. Fava, Acta Cryst., 1962, 15, 1139.

¹⁸ S. Ahrland, J. Chatt, N. R. Davies, and A. A. Williams, J. Chem. Soc., 1958, 264, 276.

J. Chem. Soc. (A), 1966

		S	ome infrared	ba	nds (cm. ⁻¹) of t	he thiourea	deriv	atives and	thei	r silver(1) co	omplexes
	Tu		$[Ag_2Tu_3]^{2+}$ Tsz $[Ag_2Tsz_3]^{2+}$ HDB 3450sh hr. 3420sh hr.			$[Ag_2HDB_3]^2$	+ Assignment					
	3260s, br		3300s, br		329 0s		3260m		3000s, br	{	3230s 3100s	$\gamma ({ m NH}) \ \gamma ({ m NH})$
* {	$1630 { m sh}$ $1588 { m ss}$		1625s 1600s		1643s 1621s		1627s 1606s		1633w 1613s		1636w, sh 1603m	$\left. ight\} \operatorname{NH}_2$ def.
	1468s	{	1513w 1485m		$1537\mathrm{s}$ $1515\mathrm{sh}$		1531m 1515sh		1552s, br 1500sh		1556s 1527w, sh	γ (C–N)
5	1433s	<u>ر</u>	1430w 1410w	Į	1489m	{	1470w	{	1492s	{	1480m	$\int dr $
* {	1396w	l	1388s	l	1390w	L	1387s 1370s, br	۱{	$1405 \mathrm{s}$ $1387 \mathrm{sh}$	l {	1400w, sh 1383m	$\int \gamma(c-3)$
	1091s		10 94 m		1009s		1004m		1113s		1106 m	$ ho-NH_2$
	$735 \mathrm{sh}$,			809s	(817sh		786s		778w]
ł	727sh 721s	ł	729m 703m			ł	811sh 804s		744s 717w	{	721m 706m	$ \left. \right\} Mostly C=S \text{ some } C-N $

TABLE 3

* The splitting of these peaks in KBr was also noted by Stewart.¹¹

Dithiobiuret shows typical thiourea behaviour in fairly acidic solutions, but as the acidity is reduced, reaction (1) becomes predominant. Copper(1) has also been shown to give this latter reaction with dithiobiuret.¹⁹ It is noteworthy that dithiobiuret is a very weak acid,²⁰ whereas, of the other thiourea derivatives studied, two are neutral and the one is a weak base. This accords with the prediction ¹ of the functional group necessary for reaction (1) to take place. All the thiourea derivatives could be forced to enter into reaction (1) either by increasing the silver concentration, or reducing the acidity. Under these conditions, however, the reaction continues to reaction (2), with the formation of the sulphide.

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¹⁹ M. M. Baldwin, U.S.P. 2,959,515/1960.

²⁰ Yu. I. Usatenko and A. S. Sukhoruchkina, *Zhur. analit. Khim.*, 1963, **18**, 1295.