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COMPOSITION AND INFRARED SPECTRA OF SILVER SALTS OF SUBSTITUTED 1,2,4-TRIAZOLE-3-THIONES AND THIAZOLIDINE-2-THIONE

A. PARENTICH,* L. H. LITTLE* and R. H. OTTEWILL†

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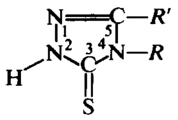
Abstract—I. R. spectral studies of silver salts of certain substituted triazole thiones and thiazolidine-2-thione prepared by different methods, have been carried out. As a result of these studies nitrate and nitrato complexes of the silver organic salts were characterized. Analytical data were used to determine the composition of these salts.

INTRODUCTION

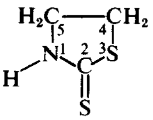
THE ADSORPTION of certain thioamides on silver halides has been studied because of the behaviour of the compounds as photographic stabilizers[1]. Silver salts of these materials can be formed. The spectra of the silver salts have been used by Tamura *et al.*[2] and Little and Ottewill[3] to assign structures of species adsorbed on silver halides. The work in this paper has been carried out to resolve problems arising from the variation found[3] in the i.r. spectra of these salts.

EXPERIMENTAL

The Ag salts of the following materials were prepared and studied.



Substituted-1,2,4-triazole-3-thione



Thiazolidine-2-thione

4-phenyl-1,2,4-triazole-3-thione (PTT) $R = \text{Ph}, R' = \text{H}$ (m.p. = 171°C)
4-ethyl-5-methyl-1,2,4-triazole-3-thione (EMTT) $R = C_2H_5, R' = CH_3$ (m.p. = 133°C)
4-methyl-5-ethyl-1,2,4-triazole-3-thione (METT) $R = CH_3, R' = C_2H_5$ (m.p. = 139°C)
4-methyl-1,2,4-triazole-3-thione (MTT) $R = CH_3, R' = \text{H}$ (m.p. = 167°C)
4-phenyl-5-methyl-1,2,4-triazole-3-thione (PMTT) $R = \text{Ph}, R' = CH_3$ (m.p. = 223°C)
thiazolidine-2-thione (TT) (m.p. = 105°C).

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*Department of Physical Chemistry, The University of Western Australia Nedlands, Western Australia.

†School of Chemistry, The University, Bristol, England.

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2. M. Tamura, H. Hada, J. Noguchi and S. Hayashi, *J. phys. Chem.* **66**, 559 (1962).
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The preparation of the various triazoles is given elsewhere[4]. In the preparation of the silver salts of these compounds, it was found that the concentrations of the reactants determined the nature of the products. The following methods were used to obtain the different products.

Method 1

Approximately equimolar quantities of $AgNO_3$ and thioamide were used. 1 ml of 1 M $AgNO_3$ was added to 100 ml of 10^{-2} M thioamide. A gelatinous precipitate was obtained in this preparation.

Method 2

Excess silver nitrate was used. 10 ml of 1 M $AgNO_3$ were added to 50 ml of 10^{-2} M thioamide. A gelatinous precipitate was obtained. Silver salts of PTT were also prepared by this method using alternatively silver acetate and silver sulphate in place of silver nitrate.

Method 3

An almost saturated solution of thioamide (25 ml of between 2×10^{-2} and 10^{-1} M), which had been warmed to 85°C, was added to an excess of a concentrated solution of silver nitrate (10 ml, 5 M). A white precipitate, which settled quickly, was obtained.

In methods 1, 2 and 3 the precipitates were divided into two parts. One part was washed and centrifuged several times with water to remove excess nitrate. The other was washed and centrifuged several times with water, with sodium chloride solution, and finally with water to remove excess sodium chloride. The samples were then allowed to dry in a vacuum desiccator for 48 hr before the spectra were recorded.

Method 4

5 ml of 1 M $AgNO_3$ in 50% aqueous ethanol were added to 5×10^{-3} moles of thioamide in 50 ml of aqueous ethanol. The gelatinous precipitate was converted to a white powder on boiling (5 min). The suspension was cooled to room temperature and filtered. The residue was washed with 50% aqueous ethanol and ether. The resultant material was dried in a vacuum desiccator for 48 hr before its spectrum was recorded.

Preparation of AgPTT *and* AgMTT *from* D_2O *solutions of the reactants*

Silver salts of PTT and MTT were prepared from D_2O solutions of the reactants in the following manner. AgPTT was prepared by adding 2 ml of a 5 M solution of silver nitrate in D_2O to 2 ml of a 2×10^{-2} M solution of PTT in D_2O, which had been heated at 90°C for approximately 9 days. The precipitated AgPTT was washed and centrifuged twice with 1·5 ml of D_2O and dried *in vacuo* for 2 days before its spectrum was recorded.

AgMTT was prepared by the same method using 4 ml of 2×10^{-2} M MTT and 2 ml of 5 M silver nitrate.

To record the i.r. spectra, the materials were ground with potassium chloride and pressed into microdisks *in vacuo* at a pressure of 6–7 tons/in^2. The samples were mounted in a potassium bromide beam condenser and the spectra recorded on a Perkin–Elmer 521 spectrophotometer.

The potassium chloride used to prepare the pellets was purified by fusing AR material at 800°C for 2 hr to remove any organic matter. On cooling, this material was dissolved in distilled water and filtered. The filtrate was acidified with hydrochloric acid and the precipitated potassium chloride was filtered and dried at 450°C for 2 hr.

The spectra of the silver complexes of all the thioamides studies here were recorded as nujol mulls as well as in KCl pellets. In other cases hexachlorobutadiene mulls were studies.

The contributions to the spectra by the nitrate and nitrato groups (only those which are removable by sodium chloride washing) were obtained by point subtraction of the spectra of the salt washed materials from those of the water washed materials. In this way it was possible to make the nitrato assignments shown in Table 4.

RESULTS AND DISCUSSION

Silver salts of PTT (AgPTT) *prepared by methods* 1, 2 *and* 4

The spectrum of Ag PTT prepared by method 1 shows weaker absorption in the 1370 cm^{-1} region than that of the material prepared by method 2 where an

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[4] A. Parentich and L. H. Little, To be published.

excess of silver nitrate was used. Absorption in this region (see Fig. 1a) arises from nitrate groups included in the silver salt.

Confirmation of this assignment was obtained by the following methods:

1. The silver salts of PTT were prepared using silver sulphate and silver acetate, respectively, in place of silver nitrate. The nitrate band at 1370 cm^{-1} was replaced by a sulphate band at 1100 cm^{-1} (Fig. 1c) and an acetate band at 1550 cm^{-1} when the respective anions were used.
2. Chloride washing removed nitrate as indicated by the disappearance of nitrate bands [compare (a) and (b), Fig. 1] whereas repeated washing with water only succeeded in removing very small quantities of nitrate. Chloride washing of salts containing sulphate and acetate ions also led to their replacement by chloride.

For the materials prepared by methods 2 and 3 where excess silver nitrate was used, analytical data (Tables 1 and 2) show that the percentage of silver present is in excess of the amount required for the formula Ag PTT for which the silver percentage is 38·0%. The molar excess of silver is very nearly equal to the

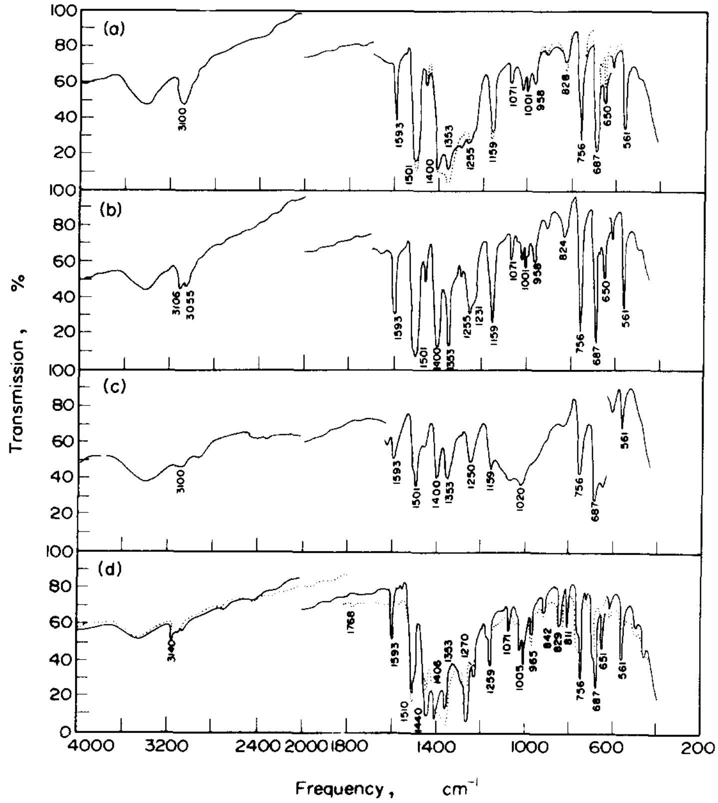

Fig. 1. Spectra of AgPTT. (a) Solid line: Prepared by method 2 (water washed) Dotted line: Re-recording of pellet after standing for six months. (b) Prepared by method 2 (chloride washed). (c) Prepared by method 2 using silver sulphate in place of silver nitrate (water washed). (d) Solid line: Prepared by method 4 using an excess of silver nitrate. Dotted line: Re-recording of pellet after standing for 6 months.

Table 1. Nitrate and chloride complexes of some of the thioamides (prepared by method 2)

Material	x value (a) based on C% (b) based on S%		Analyses (% of various elements) C	H	N	S	Ag	O(Diff.)	Cl
		Actual	25·42	1·8	12·61	8·24	44·65	6·28	
AgPTT. xAgNO$_3$	(a) 0·55	Expected	25·42	1·6	13·14	8·48	44·2	6·40	
	(b) 0·61	Expected	24·8	1·56	13·06	8·24	44·82	7·56	
		Actual	25·24	1·84	10·77	8·62	44·7		6·15
Ag PTT. xAgCl	(a) 0·67	Expected	25·24	1·58	11·05	8·42	47·4		6·25
	(b) 0·61	Expected	25·85	1·63	11·3	8·62	46·8		5·85
AgMTT. xAgNO$_3$		Actual	10·08	1·51	14·35	8·82	54·99	10·25	
	(a) 0·8	Expected	10·06	1·12	14·86	8·94	54·25	10·73	
Ag MTT. xAgCl		Actual	10·54	1·26	11·74	9·27	57·00		9·67
	(a) 0·84	Expected	10·57	1·17	12·27	9·35	58·00		8·71
Ag EMTT. xAgNO$_3$		Actual	13·28	1·92	12·65	7·25	52·77	12·13	
	(a) 1·19	Expected	13·24	1·76	12·96	7·05	52·30	12·69	
Ag EMTT. xAgCl		Actual	13·15	2·02	9·71	7·27	55·3		11·16
	(a) 1·44	Expected	13·13	1·75	9·19	7·00	57·85		11·18
Ag PMTT. xAgNO$_3$		Actual	23·29	2·12	12·05	6·83	45·58	10·13	
	(a) 0·975	Expected	23·29	1·73	12·01	6·9	45·95	10·10	
Ag PMTT. xAgCl		Actual	22·35	2·02	10·51	6·56	42·8		5·83
	(a) 1·29	Expected	22·35	1·66	8·7	6·63	51·2		9·47

Table 2. Nitrato complexes of Ag PTT and Ag PMTT (prepared by method 3)

Material		Analyses (% of various elements)							'x'*
		C	H	N	S	Ag	O(diff.)	Cl	value
Ag PTT. xAgNO$_3$	(a)†	21·44	1·78	12·29	7·16	46·2	11·13	0	0·97
		(21·44)	(1·35)	(12·42)	(7·16)	(47·5)	(10·34)	(0)	
	(b)†	21·38	1·70	11·52	7·04	46·3	10·82	1·22	0·98
		(21·38)	(1·34)	(12·40)	(7·12)	(47·4)	(11·04)	(0)	
Ag PMTT. xAgNO$_3$	(a)	23·16	1·98	11·93	6·95	46·29	9·69		0·99
		(23·16)	(1·71)	(11·98)	(6·86)	(46·04)	(10·18)		
	(b)	23·24	1·90	11·74	6·96	41·7		< 0·5	0·98
		(23·24)	(1·72)	(11·98)	(6·88)	(46·0)	(10·13)	(0)	

Note: Calculated values based on the value of x are shown in parenthesis.

*The x value is calculated on the carbon analysis.

†(a) Material centrifuged and washed with water (3 washes). (b) Material centrifuged and washed with water, sodium chloride solution and finally water (3 washes for each).

molar quantity of nitrate present. Silver salts of all the thioamides can be prepared and have the composition silver organic. *x* silver nitrate, where the term "organic" refers to the heterocyclic thioamide and *x* is the molar proportion of the two, which for the concentration of reagents used in this work, varied between 0 and approximately 1·5.

Actual and expected analysis figures for the silver salt complexes of the various thioamides prepared by using method 2 are given in Table 1. The water washed materials are shown as silver organic. *x* silver nitrate and the salt washed as silver organic. *x* silver chloride. The value of *x* for the materials prepared was determined from the carbon or sulphur analysis figures. From this, the expected analysis figures for the other elements were calculated.

It is evident from the nitrogen and oxygen analyses for the water washed materials and from the nitrogen and chlorine results for the salt washed materials, that there is an approximately 1 : 1 replacement of nitrate by chloride after sodium chloride washing for most of the complexes. However, for the PMTT complexes, spectral and analytical results indicate that the replacement of nitrate by chloride is not complete. In the spectrum of the salt washed PMTT strong adsorption in the 1370 $\mathrm{cm^{-1}}$ region of the spectrum indicates that nitrate is still present. In addition, the high nitrogen and low chlorine percentages confirm this (Table 1).

The spectrum of the silver salt of PTT prepared by method 4 is similar to the spectra of the materials prepared by methods 1 and 2. The bands arising from the organic portion of the molecule are similar, the spectra differing mainly in the intensity of the band at 1370 $\mathrm{cm^{-1}}$ due to nitrate.

There is spectral and analytical evidence to show that the material obtained by method 4 consisted of the silver organic salt with a small quantity of parent material and nitrate ion for which the counter ion could be silver and/or hydronium ion. The presence of very weak bands at 1550 and 940 $\mathrm{cm^{-1}}$ (due respectively to thioamide I and V absorptions [4]) in the spectrum of the material (Fig. 2C) indicates that some parent material is present, whereas the absorption in the 1370 $\mathrm{cm^{-1}}$ region is evidence of the presence of nitrate ion. The percentage of silver in the silver salt is less than would be expected for the pure 1 : 1 silver organic salt. (Found 34·4%; calculated 38·0%.) This could arise in two ways:

1. From the presence of a large proportion of parent organic material.
2. From the presence of hydronium ions in addition to silver ions as counter ions for the nitrate.

The weak intensities of the 1550 and 940 $\mathrm{cm^{-1}}$ bands in the spectrum of this material indicate that the low silver analysis is not due entirely to the presence of parent material. Although characteristic bands due to hydronium ions are not apparent in the spectrum, the high hydrogen and low silver analyses suggest the presence of these ions.

The spectrum of the thioamide component of the silver salt was unchanged after standing for 6 months in a potassium chloride pellet. In addition to the absorption at 1370 $\mathrm{cm^{-1}}$, a weak band appears at approximately 829 $\mathrm{cm^{-1}}$ in the spectrum of the silver salt containing nitrate ions. The assignment of these are discussed below.

On prolonged boiling (up to 30 hr) of an aqueous suspension of the PTT obtained by method 4, the unreacted parent materials combined and a pure 1 : 1

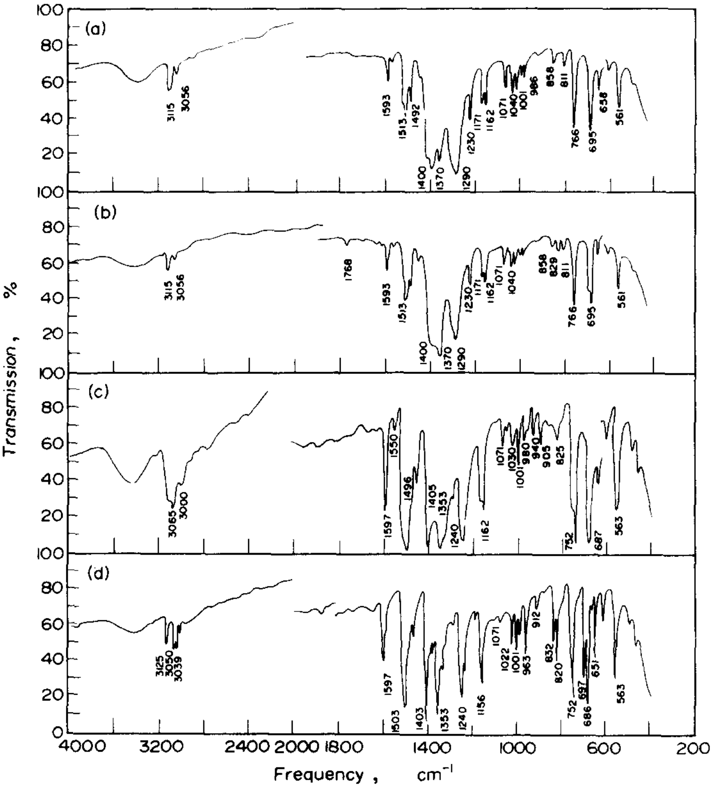

Fig. 2. Spectra of AgPTT. (a) Prepared by method 3 (water washed). (b) Re-recording of the KCl pellet in (a) after standing for six months. (c) Prepared by method 4 (water washed). (d) Sample in (c) boiled in water for 30 hr.

silver organic salt resulted as shown by the disappearance of the 1500 and 940 cm^{-1} bands [compare Fig. 2(c) and (d)]. The following reaction takes place:

$$\text{Ag PTT}.x\ \text{AgNO}_3 + x\text{HPTT} \rightarrow (1+x)\ \text{AgPTT} + x\text{H}^+ + x\text{NO}_3^-.$$

In this equation the parent material has been shown as HPTT to emphasize the ionizable hydrogen.

The experimental analysis results for the digested material, with expected values shown in parenthesis, were as follows:

C 33·9% (33·8%); H 2·5% (2·1%); N 14·6% (14·8%)
S 10·9% (11·3%); and Ag 35·5% (38·0%).

Ag PTT *prepared by method 3*

The spectrum (Fig. 2(a)) indicates that the material obtained by method 3 differs from the materials obtained by methods 1, 2 and 4. The most significant spectral differences occur in the region 1400–1200 cm^{-1}. Bands appear at 1400, 1290 and 811 cm^{-1} replacing the bands at 1370 and 829 cm^{-1} in the spectra discussed previously. It is considered that these differences are due to the presence of nitrato groups in the silver salt prepared by method 3 in place of nitrate groups present when methods 1, 2 and 4 were used.

Nitrate and nitrato groups

Several workers [5–8] have discussed the vibrational assignments of nitrate and nitrato groups in inorganic and organic compounds assuming D_{3h} and C_{2v} symmetry, respectively. Nitrate groups give rise to i.r. absorption at approximately 1390, 830 and 720 cm^{-1} due, respectively, to the NO_2 asymmetric stretching ν_3 (E'); out-of-plane bending ν_2 (A_2''), and in-plane bending ν_4 (E') vibrations. Nitrato groups, however, produce i.r. absorption bands at approximately 1500, 1270, 1000, 790 and 710 cm^{-1} due, respectively, to the NO_2 asymmetric ν_4 (B_1), and symmetric ν_1 (A_1) stretching, NO stretching ν_2 (A_1) and NO_2 out-of-plane ν_6 (B_6) and-in-plane ν_5 (B_1) bending vibrations.

On the basis of these investigations assignments for the nitrate ion (D_{3h}) and nitrato group (C_{2v}) have been made for the silver salt complexes of the various thioamide studied here. For the nitrate complexes, the ν_3 (E') NO_2 asymmetric stretching vibration occurs at 1370–1350 cm^{-1} and the ν_2 (A_2'') out-of-plane bending vibration at 830–824 cm^{-1}. The nitrato band assignments are given in Tables 3 and 4. Methods 1, 2 and 4 produce predominantly nitrate and method 3 produces nitrato complexes.

Analytical data show that the composition of the nitrato complex is Ag organic.x $AgNO_3$ where x, calculated on the carbon analysis, is approximately 1 (see Table 2). For PTT, a small quantity of nitrate (less than 10%) was detected in the nitrato complex prepared by method 3. This was replaced by chloride washing as shown by the disappearance of a weak band due to the ν_2 out-of-plane bending vibration (829 cm^{-1}) and by the chloride analysis of 1·22% for the sodium chloride washed material (Table 2).

It is interesting to note that on washing and centrifugation of the nitrato complex prepared by method 3 with sodium chloride solution, there is no spectral evidence of the replacement of nitrato groups by chloride. There was spectral evidence to show that approximately 30% nitrato was converted to nitrate when the material was allowed to stand in the KCl pellet for 6 months [compare spectra (a) and (b), Fig. 2]. A decrease in the intensity of the nitrato bands (1400, 1290, 811 cm^{-1}) and a corresponding increase in the intensity of the nitrate bands (1370, 829 cm^{-1}) were observed. Although chloride ion does not immediately replace the nitrato group in the complex, there is a slow replacement of this group by the chloride ion of the KCl pellet.

Confirmation of the assignments for nitrate and nitrato is provided by the frequencies of the combination and overtone bands:

$$\text{nitrate} \quad 2295\,\text{cm}^{-1}\ (\nu_1+\nu_2)\ [9],\ 1768\,\text{cm}^{-1}\ (\nu_1+\nu_4)\ [10]$$

$$\text{nitrato} \quad 1735\,\text{cm}^{-1}\ (\nu_2+\nu_5)\ [10\text{–}12]\ \text{or}\ (\nu_2+\nu_3)\ [12].$$

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Table 3. Band assignments for nitrato group (C_{2v} symmetry) for silver complexes* (prepared by method 3)

Material	$\nu_4(B_1)$ NO_2 asymmetric stretching	$\nu_1(A_1)$ NO_2 symmetric stretching	$\nu_2(A_1)$ NO stretching vibration	$\nu_6(B_6)$ Out-of-plane rocking	NaCl washing	Standing† in KCl pellet
Ag PTT. $AgNO_3$	1400 (s)	1300- 1290(s)	1045– 1040 (w)	811 (m)	No effect	slowly converted to nitrate ion
Ag PMTT. $AgNO_3$	1456– 1420 (m)	1300 (s)– 1290	1045(w)– 1040	811 (m)	No effect	slowly converted to nitrate ion

*More than one peak may appear in the region of the spectrum associated with fundamental vibrational modes of nitrato groups.

†The spectra of pellets that had been standing for up to 6 months were re-recorded to study the effect of chloride ion on the nitrato group.

s — strong, m — medium, w — weak.

Table 4. Band assignments for nitrato group (C_{2v} symmetry) for silver complexes (prepared by methods* 1, 2 and 4)

Material	Preparative method used	$\nu_4(B_1)$ NO_2 asymmetric stretching	$\nu_1(A_1)$ NO_2 symmetric stretching	$\nu_2(A_1)$ NO symmetric	$\nu_6(B_6)$ Out-of-plane rocking vibration	Type of† nitrato
Ag PTT.x $AgNO_3$	1, 2 and 4	1420(w)	1330–1290(w)		815(w)	1
Ag PTT.x $AgNO_3$	4 using excess $AgNO_3$	1445(s) 1455(m) 1420–1400(w)	1270(s) 1330–1290(w)	1005(m) 1040 (vw)	842(m) 811	2 1
Ag PMTT.x $AgNO_3$	2	1420(s)	1270(s)	1040(sh)	805(m)	2
Ag EMTT.x $AgNO_3$	2	1420(sh)	1276(s)	1024(ms) 1065(w)	800(m) 815 (w)	2
Ag METT.x $AgNO_3$	2	1458(m) 1430(m)	1226(s) 1279(m) 1320(w)	1021(m) 1030(w)	811 (w) 795 (w)	2
Ag MTT.x $AgNO_3$	2	1420(m)	1247(ms) 1227(w)	1019(w) 1035(w) 1045(w)	802 (w) 822(w)	2
Ag MTT.x $AgNO_3$	2 from concentrated D_2O solutions	1500(m) 1467(m) 1400(m)	1248(ms) 1330(w)	889(m) 1021(w) 1045–1035(w)	800(w) 815(w)	2
Ag TT.x $AgNO_3$	2 and 3	1550(sh) 1372(m)	1285(sh) 1315(sh)		816(m) 809 (w)	

*The nitrate complexes of the thioamides prepared by these methods contain small quantities of nitrato material. Several peaks may appear in the region of the spectrum associated with fundamental vibrational modes of nitrato groups.

†Type 1 Nitrato: not removed on chloride washing but slowly converted to nitrate ion in KCl pellet. Type 2 Nitrato: removed on chloride washing and slowly converted to nitrate in KCl pellet.

s – strong; ms – medium strong; m – medium; w – weak; vw – very weak; sh – shoulder.

The assignments were checked by noting the replacement of the 1735 cm^{-1} band by bands at 2295 and 1768 cm^{-1} on the conversion of nitrato to nitrate when the material was allowed to stand in the KCl pellet.

Small amounts of nitrato with bands at 1420, 1330–1290 and 815 cm^{-1} can be present in the nitrate complex. This nitrato, unlike the nitrato present in the silver salts prepared by method 3, is replaced by chloride on sodium chloride washing. This nitrato was also converted to nitrate on standing in the KCl pellet. The graphs in Fig. 3 were obtained by a point subtraction of the 1500–1200 cm^{-1} region of the spectrum of sodium chloride washed Ag PTT (Fig. 1(b)) from the corresponding portions of the spectra of the water washed materials (Fig. 1(a)). These clearly indicate that nitrato as well as nitrate groups are present in the water washed material. It is also evident that the nitrato bands (1420 and 1330–1290 cm^{-1}) are weaker and the nitrate band (1370 cm^{-1}) is stronger in the spectrum of the KCl pellet after it had been standing for 6 months, than the corresponding bands in the spectrum of the freshly prepared pellet. This indicates that nitrato to nitrate conversion had occurred during standing. Small changes indicating nitrato to nitrate conversion occurred in the 830 cm^{-1} region but these cannot be clearly seen from Fig. 1(a).

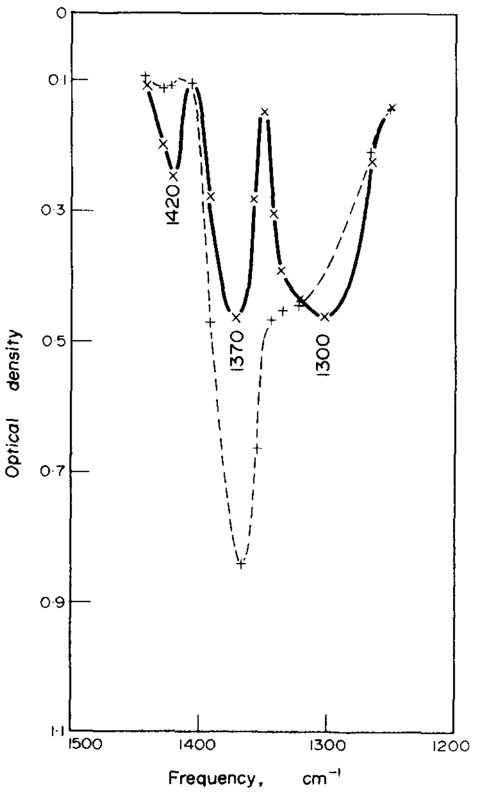

Fig. 3. Difference spectra showing nitrate and nitrato groups in AgPTT. Solid line: Fig. 1(b) subtracted from the solid spectrum in Fig. 1(a). Dotted line: Fig. 1(b) Subtracted from the dotted spectrum in Fig. 1(a).

For the nitrate complex no assignment has been made for the ν_4 NO_3 in-plane bending mode which is normally weak. The intensity of absorption in the 1030 cm^{-1} region decreased on sodium chloride washing due probably to the removal of nitrate. Absorption in this region is due to either the ν_2 vibration of a small amount of nitrato present in the nitrate complex or to the ν_1 (A_1) NO_3 symmetric stretching vibration of the nitrate ion which, although i.r. inactive in the isolated ion, could appear due to the distortion of the ion in the field of the crystal.

There is spectral evidence to show that mixed nitrate and nitrato complexes of PTT have been formed by method 4 by using, instead of equimolar quantities of organic and silver nitrate, an excess of silver nitrate.

In the spectrum of the mixed complex prepared by this method (Fig. 1(d), solid line) bands due to another type of nitrato group are present at 1440, 1270, 1005 and 842 cm^{-1} in addition to weaker bands at 1400, 1290, 1040 and 811 cm^{-1} due to a smaller amount of the type of nitrato discussed previously. The presence of two types of nitrato groups could arise in two ways:

1. The nitrato groups are co-ordinated to the silver atoms by bonds having different degrees of covalent character. Ferraro[13] has used the difference between the frequencies of the ν_4 and ν_1 vibrations of the nitrato groups (C_{2v} symmetry) as a measure of degree of covalent character of the metal oxygen bond. In addition, Gatehouse *et al.* [5], have used the frequency of the ν_2 vibration of the nitrato group as a measure of the covalency of this bond. On the basis of the criteria set by these workers, it is possible that in the Ag PTT prepared by method 4 using an excess of silver nitrate, the metal–oxygen bond of the nitrato group giving rise to bands at 1440, 1270, 1005 and 842 cm^{-1} has a higher degree of covalent character. It is surprising that a group having a greater degree of covalent character should be replaced more easily by chloride ion than the other type of nitrato group.
2. The nitrato group giving rise to bands at 1400, 1290, 1040 and 811 cm^{-1} (type-1) is unidentate, whereas the nitrato group giving rise to bands at 1440, 1270, 1005 and 842 cm^{-1} (type-2) is bidentate. However, Topping[7] has stated that it is not possible to distinguish between unidentate and bidentate ligation on the basis of the difference between the frequencies of the ν_4 and ν_1 vibrations of the nitrato group and Allpress and Hambly[14] have shown that unidentate and bidentate nitrato groups produce similar spectra.

There is spectral evidence to show that the type-2 nitrato group is partially replaced by chloride on washing with sodium chloride solution and is appreciably changed to nitrate ion on standing in a KCl pellet for 6 months. This is indicated by the weakening of the characteristic type-2 nitrato bands discussed above [Fig. 1(d)]. Such behaviour may be compared to that of the material prepared by method 3 (type-1 nitrato) for which the nitrato group was not replaced by chloride washing and was only slowly converted (30%) to nitrate ion on standing in the KCl pellet for the same period [compare Figs. 2(a) and (b)].

The presence of more than one type of nitrato group was also found in the silver salts of the other thioamides studied. It is interesting to note that some of

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13. J. Ferraro, *J. inorg. nucl. Chem.* **10,** 319 (1959).
14. J. G. Allpress and A. N. Hambly, *Aust. J. Chem.* **12,** 573 (1959).

these nitrato groups were readily removed on sodium chloride washing whereas others were not. This contrasting behaviour was used to assign the various bands to the vibrational modes of particular nitrato species (Table 4).

Prolonged heating of aqueous dispersions of nitrate and mixed nitrate/nitrato complexes of Ag PTT in the presence of excess silver nitrate solution resulted in the conversion of these materials into the more stable type-1 nitrato normally prepared by method 3. This was evidenced by the fact that the spectrum of the original material was similar to that shown in Fig. 1(a) (nitrate) or Fig. 1(d) (nitrate/nitrato), whereas that of the digested material was similar to the spectrum in Fig. 2(a). In addition analysis of the digested material indicated that this had the same composition as that obtained by method 3 (i.e. $x = 1$). Digesting the nitrato material prepared by method 3 for 30 hr at 90°C in an aqueous solution containing an excess of PTT resulted in the conversion of the complex to a pure 1 : 1 Ag PTT salt according to the equation

$$\text{Ag PTT. AgNO}_3 + \text{H PTT} \rightarrow 2\,\text{Ag PTT} + H^+ + \text{NO}_3^-.$$

The resulting material has a spectrum similar to that shown in Fig. 2(d). Analytical results further indicated that the material was a 1 : 1 Ag PTT salt.

Infrared spectra of the silver salts of PTT

The spectra of the materials prepared by methods 1, 2 and 4 (nitrate salts) have a broad double band with peaks at 3106 and 3055 cm^{-1} (Fig. 1(a)). This absorption could arise from the νNH vibration of some unreacted PTT in the Ag PTT or from the olefinic and aromatic νCH vibrations of the Ag PTT. As a result of the work described elsewhere [4] it is considered that these peaks are due to the olefinic and aromatic νCH vibrations, respectively.

The assignments were made after comparing the spectra of the silver salts prepared from mildly and drastically deuterated parent materials, the latter treatment resulting in a deuterium exchange of the olefinic CH group. The assignments were confirmed by studying the spectra of the silver salts of several triazoles for which methyl and ethyl groups were substituted at the 4 and 5 positions of the triazole ring. Deuteration studies [4] show that the olefinic hydrogen in-plane deformation band occurs at 1155 cm^{-1}.

In the spectrum of the nitrato complex (Fig. 2(a)) the bands due to the organic part of the complex are similar to those of the 1 : 1 Ag PTT salt (Fig. 2(d)) in that they are sharp and the olefinic CH stretching band is raised in frequency to 3125–3115 cm^{-1}.

Ag *salts of* PMTT

The silver salts of all the thioamides studied are silver organic–silver nitrate complexes. Only PTT and PMTT, the two triazoles having a benzene ring substituted in the 4-position, from relatively stable–nitrato complexes (stable to sodium chloride washing) in addition to nitrate complexes.

Silver salts of PMTT were prepared by methods 4, 3 and 2. The spectra of the resultant materials indicated that the complexes were respectively, nitrate (containing a small quantity of nitrato), nitrato (with 10% nitrate) and approximately equimolar nitrate–nitrato types. More than one type of nitrato group may be present in the silver salts of PMTT. The vibrational assignments for these groups are given in Tables 3 and 4.

The behaviour of the Ag salts of PMTT to sodium chloride washing was similar to that of the Ag salts of PTT, the nitrato groups in salts prepared by method 3 being unaffected. The nitrato group in salts prepared by other methods are slowly replaced by chloride on sodium chloride washing. This was shown by both spectroscopic and analytical data.

Although stable to sodium chloride washing, there was spectral evidence to show that the nitrato complexes of Ag PMTT (prepared by method 3) are slowly converted (70% in 2 months) to nitrate in the KCl pellet. It was found that the nitrato bands at 1456–1420, 1300–1290, 1045 and 811 cm^{-1} in the initial spectrum were replaced by the nitrate bands at 1366 and 829 cm^{-1}.

Other minor spectral changes indicative of the nitrato to nitrate conversion occurred. The band at 1735 cm^{-1} ($\nu_2+\nu_5$) was replaced by a band at 1765 cm^{-1} ($\nu_1+\nu_4$). The change from nitrato does not occur when the bulk material is not incorporated in the KCl pellet.

On sodium chloride solution washing of the complex prepared by methods 2 and 4 both the nitrate and nitrato groups are slowly replaced by chloride.

Ag *salts of* EMTT, METT *and* MTT

Complexes containing predominantly nitrato groups could not be prepared. Approximately equimolar nitrate–nitrato complexes resulted from both methods 2 and 3. More than one type of nitrato group was present in the silver salts and both the nitrate ions and nitrato groups were replaced by chloride ion on sodium chloride washing. After standing in the KCl pellet the nitrato group was replaced by the chloride of the KCl and converted to nitrate ion.

In the spectrum of Ag MTT prepared from D_2O solutions of the reactants, bands arising from the ν_4 and ν_1 vibrational modes of the nitrato group occur at 1500 and 1248 cm^{-1}, respectively, giving a ν_4 minus ν_1 value of 252 cm^{-1} whereas in spectrum of Ag MTT prepared from H_2O solutions it is 173 cm^{-1} (1420–1247 cm^{-1}). As discussed earlier this difference in the splitting of the ν_4 and ν_1 vibrational bands could be due either to the difference in the degree of covalent character of metal–oxygen bond of the nitrato group or to the presence in the first case of bidentate and in the second of unidentate nitrato groups. This type of nitrato possibly resulted because highly concentrated solutions of the reagents were used. It is unlikely that bridging nitrato groups are present, since the separation of the ν_4 and ν_1 vibrational bands is not as large as would be expected [15] for these groups.

Ag *salts of* TT

Preparative methods 1 and 4 resulted in a AgTT.xAgNO$_3$ complex for which the nitrate group was present in the form of nitrate ion (D_{3h} symmetry). Nitrate bands appeared at 1340 (ν_3) and 826 cm^{-1} (ν_2) in the spectrum of the complex. When an aqueous dispersion of this complex was digested on a steam bath for a short time (up to 15 min) before centrifugation and washing, spectral and analytical data indicated that a 1 : 1 AgTT salt had been obtained.

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[15] B. O. Field and C. J. Hardy, *J. chem. Soc.* 4433 (1964).

When using methods 2 and 3 a nitrato complex resulted. However, the nitrato group, unlike those nitrato complexes of AgPTT and AgPMTT, was not stable to chloride washing or to standing even for a short time (up to 1 hr) in the KCl pellet. Because of this it was necessary to record the spectra of these materials as nujol and hexachlorobutadiene mulls. The nitrato group assignments are shown in Table 4. In addition these complexes contain a small quantity of nitrate ion, of the type present in the silver salt prepared by methods 1 and 4. Spectral and analytical data indicate that this nitrate could not be completely be replaced by chloride on sodium chloride washing.

It is interesting to note the effect that the presence of the nitrato group has on a strong band appearing in the 1500 cm^{-1} region of the spectra of the silver salts of TT. In the 1 : 1 AgTT salt the band appears at 1525 cm^{-1} whereas in the spectrum of the silver salt prepared by method 2 or 3, the band broadens considerably and appears in the region 1550–1540 cm^{-1} for the water washed material. The corresponding band appears at 1515 cm^{-1} in the spectrum of the parent material and has been assigned to νCN or δNH absorption [3, 4, 16]. It is likely, therefore, that the $AgNO_3$ of the complex $AgTT.xAgNO_3$ is co-ordinated in the vicinity of the $-N-C{=}S$ group. In addition this is supported by minor differences which occur in the 1000 cm^{-1} region, where it is considered that νCS absorption occurs [3, 4, 16].

The water washed material contains co-ordinated water. Water bands at 3520, 3440, 3380 and 1626 cm^{-1} were present in the nujol spectra of these materials even after the materials had been dried *in vacuo* for 6–7 days, whereas drying *in vacuo* for 1 day was sufficient to remove moisture from the sodium chloride washed material.

SUMMARY

The silver salts of the thioamides studied are complexes of the silver organic salts and the silver nitrate used in their preparation, the molar proportion of silver nitrate to silver organic (x) depending on the type of complex and the preparative method used.

The following types of complexes may be prepared:

1. Complexes containing predominantly nitrate groups in the form of nitrate ions (D_{3h} symmetry). In these complexes x varies between 0 and approximately 1·5.
2. Nitrato complexes in which the nitrate groups are covalently bonded to the silver atom through one of the oxygen atoms. The value of x for these compounds is approximately 1.
3. Mixed nitrate–nitrato complexes containing varying proportions of nitrate ions to nitrato groups.

Whereas it was possible to prepare the first and third types of complexes for all the thioamides, the second type could only be prepared for the materials PTT and PMTT, the two triazoles with benzene substituted at the 4-position of the heterocyclic ring. Both nitrate ions and nitrato groups were replaced by chloride on sodium chloride washing and on standing in the KCl pellet in types (1) and (3) while the nitrato groups in the second type were not replaced by chloride on sodium chloride washing and were only slowly replaced on standing in the KCl pellet.

16. R. Mecke and R. Mecke, *Chemie* **89**, 343 (1956).