684. *The Reaction of Silver*(I) *Ions with Organic Reagents Containing the* HN-C=S *Grouping. Part I. Rhodanine and Related Compounds*

By W. I. Stephen and A. Townshend

The reactions between silver(I) ions and rhodanine and a number of related heterocyclic compounds have been investigated by simple electrometric methods, which have enabled the nature of these reactions to be elucidated. A comparison of the behaviour of suitably substituted compounds towards silver(I) ions has enabled us to ascertain the function of each group in the rhodanine molecule with respect to silver, and to establish an analytico-functional group for silver. A suggested structure that accords with the known composition and properties of silver rhodanide is given.

RHODANINE[1] and some similar heterocyclic compounds precipitate silver(I) ions from aqueous solution. The reaction is generally assumed to involve the replacement of the acidic imino-hydrogen by the silver ion. However, the precise analytico-functional group responsible for the highly selective action of these compounds, and the structures of the resulting complexes are not known, although Feigl has shown that there must be a C=S group adjacent to the imino-group for these sparingly soluble silver complexes to form. The formation of apparently similar silver complexes by 3-substituted rhodanines, which have no imino-hydrogen, seems to contradict previous hypotheses about the mechanism of this reaction. Such theories, however, are based on mainly qualitative investigations.[2-5] The present investigation, therefore, was designed to obtain quantitative information about the reaction of silver(I) ions with rhodanine and similar compounds, so that the reaction mechanism could be elucidated with more certainty. Potentiometric techniques were used to follow the change in silver and hydrogen ion concentrations during the reactions. The only measurements made on the precipitates were those of their infrared spectra, elemental analyses having been found to be unreliable.[2]

The heterocyclic compounds have been selected so that each differs from rhodanine in only one part of the molecule; the function of each part in the reaction with silver(I) ions has thus been deduced, and the analytico-functional grouping determined. It has also been possible to assign a feasible structure to silver rhodanide.

---

[1] F. Feigl and I. Pollak, *Mikrochem.*, 1926, **4**, 185.

[2] J. V. Dubský, V. Šindelář, and V. Černák, *Mikrochem.*, 1938, **25**, 124.

[3] F. Feigl, " Chemistry of Specific, Selective and Sensitive Reactions," Academic Press (New York), 1949, p. 208.

[4] A. Meyer, *Congr. int. Quim. Pura apl.*, 1934, **9**, (IV), 393 in *Chem. Zentr.*, 1937, (I), 3337.

[5] J. V. Dubský, *Mikrochem.*, 1946, **28**, 145.

Behaviour of Rhodanines and Related Compounds with Silver Ions.—Potentiometric titrations of silver(I) with ten compounds of the rhodanine type were carried out in acidified and unacidified solutions. The constitutions of the compounds formed, as deduced from these experiments, are summarised in Table 1.

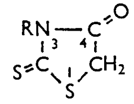
TABLE 1

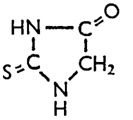
Stoicheiometry of reactions of rhodanine and related compounds with silver(I) ions

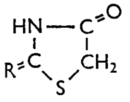
	Colour of precipitate and ratio of reactants in ppt.		
Compound	Ag: compound non-acidified	Ag: compound acidified *	Comments
1. Rhodanine (I; R = H)	Pale green 1 : 0·94	White 1 : 0·95	Weak acid, pK_a ~ 5·2
2. 2-Thiohydantoin (II)	Pink 1 : 0·99	Pale pink 1 : 0·99 †	Weak base
3. Thiazolidine-2:4-dione (III; R = O)	—	—	No apparent silver binding. Faint turbidity after 2 days
4. Pseudothiohydantoin (III; R = NH)	Pink 1 : 1·00	Pale pink 1 : 1·00	Weak base
5. Thiazolidine-2,4-dione 2-oxime (III; R = NOH)	Grey-brown 1 : 1·04	White 1 : 1·00	Weak acid, pK_a ~6·8
6. 3-Phenylrhodanine (I; R = C_6H_5)	Brown —	Brown —	No apparent silver binding. The brown ppt. formed during 24 hr.
7. 3(4-Picolyl)rhodanine (I; R = $CH_2{\cdot}C_5H_4N$)	Dark brown —	Dark brown —	The ppt. formed during 56 hr.; indication of 1 : 1 product
8. Thiazolidine-2-thione (IV)	White 1 : 0·86	White 1 : 0·78	Ppt. dissolved to form a 1 : 2 species with excess of reagent
9. Pyrrolidine-2-thione (V)	White 1 : 0·64	White 1 : 0·91	Ppt. dissolved to form a 1 : 2 species with excess of reagent
10. 5-Isonitrosorhodanine (VI)	Cream 1 : 1·08	Cream 1 : 1·08	Weak acid, pK_a ~ 5·4

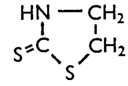
* 0·1N-Nitric acid unless otherwise stated. † Also in 0·2N-nitric acid.

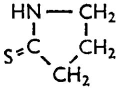
Rhodanine (I; R = H) formed the expected 1 : 1 species (Figure 1) in both acidified and unacidified media. The generation of hydrogen ions in unacidified media (Figure 2) was found to be due to (*a*) the acid dissociation of rhodanine, and (*b*) the reaction of the silver ions with rhodanine to form silver rhodanide. The generation of hydrogen ions ceased abruptly when the silver(I) : rhodanine ratio was 0·99 : 1. At this point, 1·2 hydrogen ions had been released by reactions (*a*) and (*b*) per silver ion added. These observations, and the linear relationship between the generation of hydrogen ions and the addition of silver ions, are in accordance with the reaction sequence

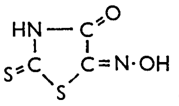

(I)


(II)


(III)


(IV)


(V)


(VI)

$$HR \rightleftharpoons H^+ + R^-$$
$$Ag^+ + R^- \rightleftharpoons AgR\downarrow,$$

where HR = rhodanine.

2-Thiohydantoin (II) reacts with a similar selection of metal ions as does rhodanine,[6] and Dubsky [2] has reported that a violet-red 1 : 1 silver complex is precipitated; this is confirmed in the present study. The reagent differs from rhodanine in that the ring sulphur atom is replaced by a second imino-group, making the compound a weak base. The interaction of the base and of its silver complex with hydrogen ions during the pH titration

---

[6] V. M. Turkevich and V. F. Gevlich, *Zhur. analit. Khim.*, 1956, **11**, 180.

makes the interpretation of the results of this titration more difficult (Figure 2, D). It is possible to calculate the amount of protonation of the free base during the titration, and to correct the results for this (Figure 2, E), but this could not be done for the silver complex.

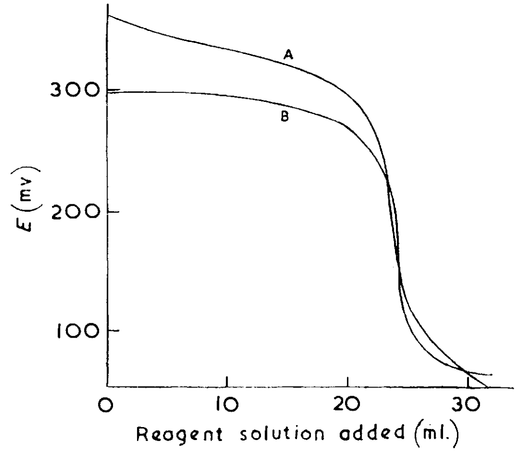
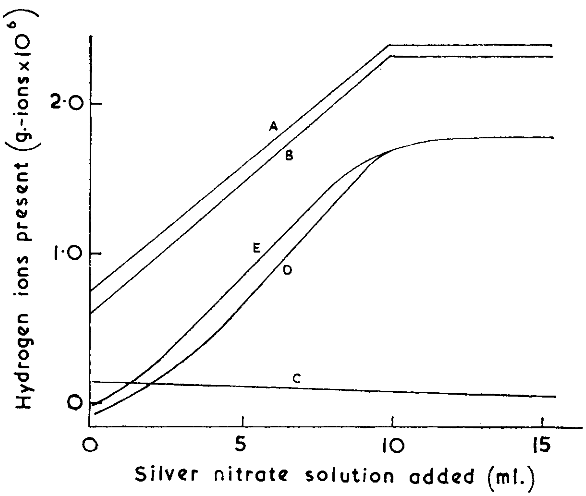


FIGURE 1. Titration of 10^{-2}M-solution of silver nitrate (25 ml.) with a 10^{-2}M-solution of rhodanine in (A) unacidified solution, (B) initially 0·16N-nitric acid

FIGURE 2. Change in hydrogen-ion content of unacidified, 2×10^{-4}M-solutions (10 ml.) on titration with 2×10^{-4}M-solution of silver nitrate. (A) rhodanine + blank, (B) rhodanine only [(A) — (C)], (C) blank, (D) 2-thiohydantoin, after subtracting the blank, (E) correction of (D) for protonation of uncomplexed 2-thiohydantoin.



Thus, the apparent release of 0·9 protons per silver(I) ion complexed is slightly less than the real value by that amount associated as $[AgRH]^+$; this means that the precipitation of the complex is incomplete under the conditions studied. The precipitation reaction, however, is similar to that of rhodanine with silver(I) ions.

Thiazolidine-2:4-dione (III; R = O) is reported to form silver salts,[2] but it has also been stated [3,7] that the presence of a keto-group in position 2 prevents the precipitation of silver(I). A hot aqueous solution of this reagent did, however, give with silver(I) ions a slight turbidity, which soon coagulated to a white precipitate. No indication of silver binding was given by the potentiometric titration (Figure 3). Pseudothiohydantoin (III; R = NH) behaved almost identically to 2-thiohydantoin (Figure 3); 1·3 hydrogen ions were generated per silver ion precipitated, which again accorded with the rhodanine reaction. Thiazolidine-2,4-dione 2-oxime (III; R = NOH) also formed a 1 : 1 complex (Figure 3), but the small drop in potential indicated that it was more dissociated than the hydantoin or rhodanine complexes. This dissociation was also indicated by the way in which the generation of hydrogen ions gradually decreased with the addition of silver

[7] V. M. Turkevich, *Farm. Zhur.*, 1959, **6**, 9.

ions, although it did not cease at the 1 : 1 end-point, and a small quantity was produced by excess of silver ions. Eventually, 1·2 hydrogen ions had been released per silver(I) ion complexed.

The 3-substituted rhodanines should not, according to existing theories of the rhodanine–silver(I) reaction, behave like rhodanine, and it was disturbing to note that such compounds did appear to react with silver and other metal ions. Turkevich [6] concluded that the brown or cherry colour that 3-phenylrhodanine gives with silver(I) ions involved complex formation rather than salt formation. Tests with five 3-substituted rhodanines showed that this reaction was a general one; with silver(I) ions, all five compounds gave coloured or turbid solutions, which eventually deposited brownish precipitates overnight. 3-4′-Picolylrhodanine, which initially gave a heavy, white turbidity with silver(I) ions, reacted quickly, whilst 3-phenylrhodanine required some minutes for colour formation; these two reagents were investigated quantitatively. No end-point was detected potentiometrically or conductometrically with 3-phenylrhodanine, although the solution became brown during the titration; after 24 hours, a brown precipitate was obtained. Analysis for carbon and hydrogen showed that this precipitate contained little organic material. Titration of silver(I) with 3-4′-picolylrhodanine gave no indication of an end-point, although the solution became dark and turbid. In the reverse titration, after each portion of silver(I) had been added, the potential immediately rose, and then gradually fell over a period of hours, with accompanying darkening of the solution and precipitation of a brown solid. Eventually, an indication of a 1 : 1 product was obtained, but the lengthy nature of the titration (56 hours) necessarily throws some doubt upon this result. The extreme slowness of these reactions indicates little similarity with the silver(I)–rhodanine reaction. The reaction cannot be simple complex formation, but involves decomposition of the organic molecule. It is hoped to report a more detailed investigation of these reactions in a future Communication.

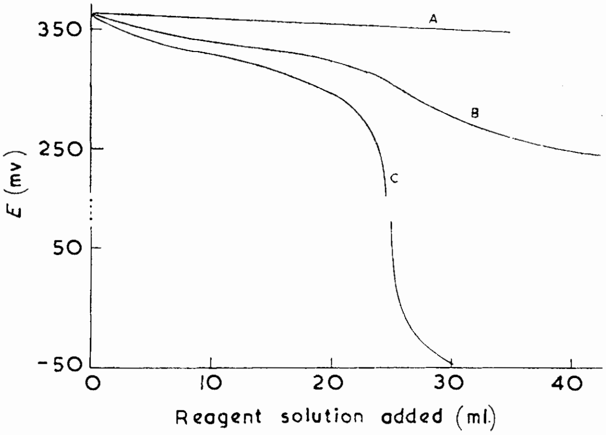


FIGURE 3. Titration of 10^{-2}M-solution of silver nitrate (25 ml.) in unacidified solution with 10^{-2}M-solutions of (A) thiazolidine-2,4-dione, (B) thiazolidine-2,4-dione 2-oxime, and (C) pseudothiohydantoin

In the titration of silver(I) with thiazolidine-2-thione (IV) (Figure 4), the potential drop at the end-point was only slightly less than that with rhodanine. The precipitate dissolved in an excess of reagent solution, the potentiometric titration indicating the formation of an approximately 1 silver(I) : 2 thione species soluble in 0·1N-nitric acid. The process was more pronounced with pyrrolidine-2-thione (V), which indicated the formation of 1 : 1 and 1 : 2 silver : thione species in acidified and unacidified solutions (Figure 5); in the latter, however, some decomposition to silver sulphide occurred near the second end-point. The relative potential drop indicated that the precipitation was far less complete with pyrrolidine-2-thione. The production of hydrogen ions during these reactions with pyrrolidine-2-thione (Figure 6) and thiazolidine-2-thione was similar. The quantity of hydrogen ions generated reached a maximum near the end-point corresponding to the

1 : 1 precipitate (pyrrolidine-2-thione, 1 silver : 0·9 thione, 0·6 H^+ per silver ion present; thiazolidine-2-thione, 1 silver : 1·0 thione, 1·2 H^+ per silver ion present). It then diminished and, with pyrrolidine-2-thione, most of the hydrogen ions were taken up again by the thione as the 1 : 2 end-point was reached. These results also indicate that the extent of the precipitation reaction is again much less with the pyrrolidine-2-thione, and that the extent of formation of a soluble complex is correspondingly increased. The reactions occurring, therefore, were: (*a*) a rhodanine type of precipitation, (*b*) the redissolution of the precipitate in the presence of more thione:

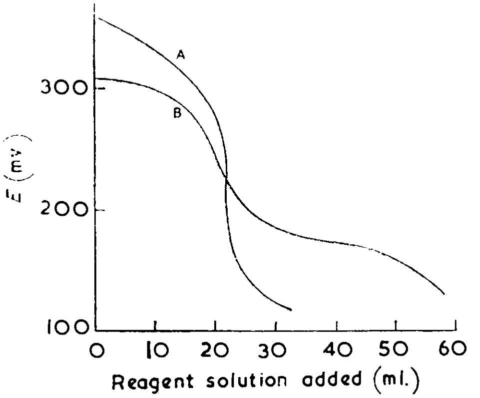


FIGURE 4. Titration of 10^{-2}M-solution of silver nitrate (25 ml.) with a 10^{-2}M-solution of thiazolidine-2-thione in (A) non-acidified solution, (B) initially 0·16N-nitric acid

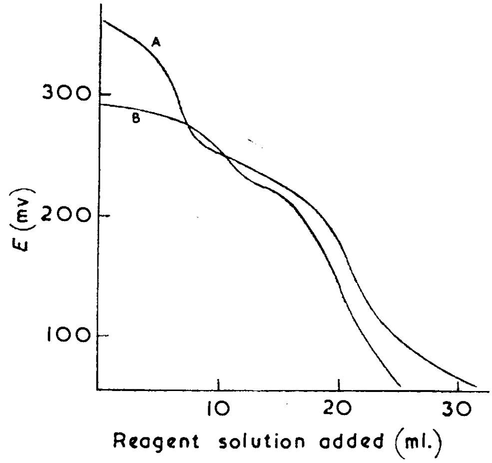


FIGURE 5. Titration of 10^{-2}M-solution of silver nitrate (10 ml.) with a 10^{-2}M-solution of pyrrolidine-2-thione in (A) unacidified solution, (B) initially 0·16N-nitric acid

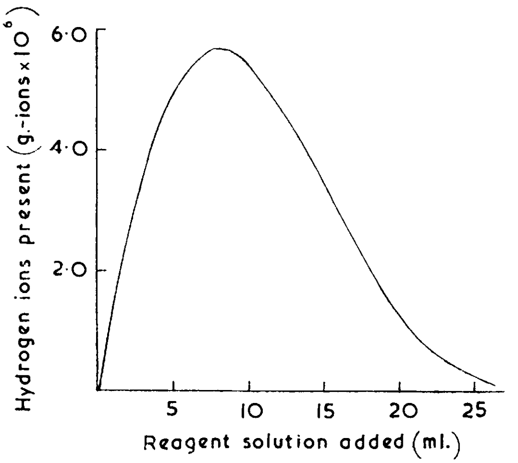


FIGURE 6. Change in hydrogen-ion content of a 10^{-2}M-solution of silver nitrate (10 ml.) on titration with a 10^{-2}M-solution of pyrrolidine-2-thione

$$AgR + RH + H^+ \rightleftharpoons [Ag(RH)_2]^+$$

In the acidic medium, the mass-action effect of the hydrogen ions would tend to oppose the precipitation reaction and aid the solubilising process. The potentiometric titration curves of pyrrolidine-2-thione (Figure 5) and thiazolidine-2-thione (Figure 4) showed that in acidic solutions the potential drop to the precipitation reaction was indeed decreased, whilst that of the complexing reaction was correspondingly increased.

The 5-substituted rhodanines are known to undergo precipitation reactions typical of rhodanine; of these, 5-isonitrosorhodanine was chosen for study because of its appreciable solubility in water. Addition of the reagent to silver(I) ions, in solution in dilute nitric acid or in unacidified solutions, resulted in slow decomposition, which competed with the precipitation reaction. The reverse titration, however, was free of this interference; 0·86 hydrogen ion was generated per silver ion bound.

Infrared Analysis.—The infrared spectrum of rhodanine (solid, in paraffin,[8] and in potassium bromide) has typical absorbances at 3065, 2905, 1709, 1439, 1232, 1183, 1080, and 820 cm.$^{-1}$. Recent work [9] on thiazolidines and oxazolidines has led to the assignment of certain of these absorbances to particular single or mixed vibrations: ν N–H, 3065 cm.$^{-1}$; ν C=O, 1709 cm.$^{-1}$; thioamide band III (involving C=S), 1080 cm.$^{-1}$

TABLE 2

Compound	Medium	Peak frequencies (cm.$^{-1}$)		
		νN–H	νC=O	Thioamide band III
Rhodanine	KBr	3050	1706	1085
Silver rhodanide *	KBr	—	1685	1017
Rhodanine	HCBD	3100	1715	—
Silver rhodanide	HCBD	—	1690	—
Rhodanine	Paraffin [6]	3065	1709	1080

* The spectra of the precipitates obtained from acidified and non-acidified solutions were essentially the same.

Measurement of the spectra of rhodanine and silver rhodanide in potassium bromide and in hexachlorobutadiene (HCBD), gave the relevant peak frequencies shown in Table 2.

It is significant that there is no N–H group present in silver rhodanide, indicating that the imino-hydrogen is replaced by the silver. The C=O vibration is little changed, but the C=S mixed vibration frequency is reduced by 68 cm.$^{-1}$, which may possibly be the effect of a silver–sulphur bond.

A comparison of the spectra of rhodanine and 2-thiohydantoin enabled some of the peaks in the spectrum of the latter to be assigned to certain bond vibrations, as shown in Table 3.

TABLE 3

Compound	Medium	Frequencies (cm.$^{-1}$)	
		νN–H	νC=O
Rhodanine	HCBD	3100	1715
2-Thiohydantoin	HCBD	3200 3280	1715
Silver 2-thiohydantoin	HCBD	3150	1660

The double peak resulting from the two imino-groups in different environments in 2-thiohydantoin becomes a single peak in the silver complex, indicating that one imino-group only is concerned in the reaction with silver, variations in other peaks are difficult to interpret.

Infrared analysis of the product obtained from the reaction of 3-phenylrhodanine with silver was inconclusive because of scattering attributed to metallic silver; there were, however, indications of the presence of the nitrate ion.

The Effect of Variations in the Rhodanine Molecule on its Reaction with Silver(I) *Ions. Position* 1. Replacement of =S by =NH does not affect the rhodanine type of precipitation reaction. This is supported by Feigl's statement [3] that oxygen in this position is also without effect.

Position 2. Replacement of the thioketo-group has a profound effect. C=O gives no reaction, C=NOH allows some reaction, whilst C=NH gives as good a reaction as rhodanine itself.

Position 3. Silver(I) ions do react with rhodanine derivatives having no imino-hydrogen. The reaction, however, is entirely different from that with rhodanine. It is

---

[8] K. F. Jennings, in *Infrared Card Index* (*Code No.* 222), Butterworth (London), 1958.

[9] R. Mecke and R. Mecke, *Chem. Ber.*, 1956, **89**, 343; C. N. R. Rao, R. Venkataraghavan, and T. R. Kasturi, *Canad. J. Chem.*, 1964, **42**, 36.

slow, gives no detectable end-point in the potentiometric titration, and produces a coloured precipitate of no simple composition.

Position 4. A methylene group in place of the carbonyl function still allows a rhodanine type of reaction to occur, although a more dissociated product is formed. However, strong acid, or an excess of the organic reagent, favours the dissolution of the precipitate with the formation of a soluble, $[Ag(RH)_2]^+$ complex. When the ring sulphur atomis also replaced by a methylene group, this behaviour is accentuated.

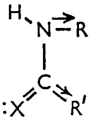
Position 5. Substitution at this position is without effect on the rhodanine type of reaction.

Functional Requirements for the Silver–rhodanine Reaction.—The results indicate that only the removal of the imino-hydrogen, or replacement of the thioketo-function by a keto-group, prevents a rhodanine type of reaction. If the reaction occurring with silver(I) is simple salt-formation resulting from the replacement of the acidic imino-proton, then substitution of the thioketo-function by a keto-group should facilitate this process, because of the greater electronegativity of the keto-group. Because the opposite is true, the thioketo-group must have another function, *i.e.*, actual silver bonding.

If silver bonding occurs at the 2- and 3-positions, the reaction of the compounds described above can be explained. Sulphur forms strong bonds with silver(I) ions, as does =NH. With =NOH, the oxygen draws electrons away from the nitrogen, making them less available for co-ordination, and hence forming a more weakly bound species. An even more electrophilic centre at the 2-position such as a keto-group, which is known to bond only very weakly with silver(I) ions, gives no reaction at all. In general, although a reagent may have a similar acidity to rhodanine, the absence of a strong silver-binding centre at position 2 reduces, or prevents, a rhodanine type of precipitation reaction.

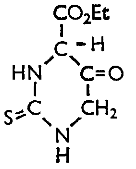
The existence of methylene groups at positions 1 and 4 has the effect of reducing the acidity of the imino-hydrogen, with a corresponding reduction in the extent of the precipitation. As the imino-group becomes less acidic, however, an alternative reaction becomes evident which involves simple complexing and formation of a soluble species without removal of any hydrogen ions. This is similar to the reaction of silver(I) ions with thiourea, and will be dealt with in a later Paper.

The functional group required for a rhodanine type of precipitation reaction is therefore (VII). Many other reagents having this grouping (VIII,[10] IX [11]) have been observed to give reactions similar to those of rhodanines with silver.

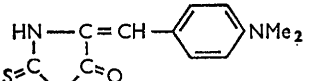


(VII)

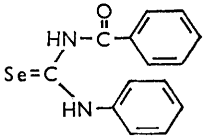
$\ddot{X}$ = S or NR''



(VIII)



(IX)



(X)

1-Benzoyl-3-phenylselenourea [12] (X) also gives similar reactions, showing that in (VII) X = Se is also a good donor.

The Structure of Silver Rhodanide.—Structures that have been previously suggested for silver rhodanide were formulated when the structural requirements of such compounds were little understood. Thus structures such as (XI) [2] and (XII) [13,14] are completely erroneous on the basis of present-day co-ordination theory of the silver(I) ion.

[10] S. E. Sheppard and H. R. Brigham, *J. Amer. Chem. Soc.*, 1936, **58**, 1046.

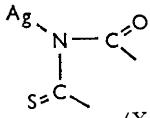
[11] E. Pedley, *Analyt. Chim. Acta*, 1952, **7**, 387.

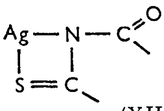
[12] F. Pino-Pérez, F. Burríel-Martí, and J. M. Balcells, *Anales real Soc. españ. Fís. Quím.*, 1959, **55***B*, 579.

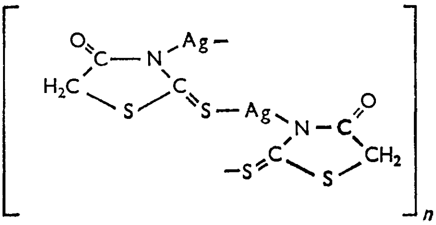
[13] J. H. Yoe and L. A. Sarver, " Organic Analytical Reagents," Chapman and Hall (New York), 1941, p. 158.

[14] H. Lux, T. Niedermaier, and K. Petz, *Z. analyt. Chem.*, 1959—1960, **171**, 173.

Structure (XI) cannot be seriously considered, because it does not take into account the function of the thioketo-group, and structure (XII), apart from any consideration of the strain involved in the four-membered ring, does not conform to any of the known stereochemical properties of the silver(I) ion.


(XI)


(XII)


(XIII)

Generally, the complexes of silver(I) ions with amines are linear $[AgL_2]^+$ compounds, and binding with sulphur-containing ligands gives tetrahedral $[AgL_4]^+$ species, a direct consequence of weak Ag–S π-bonding,[15,16] although in certain thiourea derivatives trigonal $[AgL_3]^+$ complexes are postulated[17] because of stronger Ag–S π-bonding. The only available information on how ligands with both nitrogen and sulphur as donors react with silver(I) ions concerns silver thiocyanate.[18] This compound is a polymer, $[-Ag-S-C-N-]_n$, *i.e.*, the silver bonds almost linearly with a sulphur and a nitrogen atom. There are, however, longer and therefore weaker Ag–S bonds between adjacent polymer chains. It is reasonable, therefore, to conclude that because the thiocyanate and rhodanide ions both have the same $S-C-N^-$ sequence, both form compounds of similar structure with silver(I); silver rhodanide would then have the structure (XIII). In this instance, there may also be weak Ag–S bonding between adjacent polymers.

This structure explains the 1 : 1 constitution of silver rhodanide, the loss of one proton per silver ion bound, and the function of the thioketo-group, whilst it retains the recognised stereochemistry of the silver(I) ion.

EXPERIMENTAL

Sources of Organic Reagents.—These are fully described elsewhere.[19] All commercial materials were purified by repeated crystallisation. Rhodanine was prepared by the procedure described by Campbell and McKail;[20] *2-thiohydantoin* was B.D.H. Ltd. material, *thiazolidine-2:4-dione* was Eastman-Kodak, and *pseudothiohydantoin* was from K and K Laboratories, Inc. Thiazolidine-2,4-dione 2-oxime was prepared by the reaction of hydroxylammonium chloride and rhodanine in ethanolic pyridine.[19] The preparation of 3-phenylrhodanine was based on von Braun's general procedure[21] for the synthesis of 3-substituted rhodanines. 3-4′-Picolylrhodanine was prepared as for 3-phenylrhodanine. The product was twice crystallised from aqueous ethanol, forming pale, yellow-brown plates, m. p. 149—150° (Found: C, 47·9; H, 4·0. $C_9H_8N_2OS_2$ requires C, 48·2; H, 3·6%). Thiazolidine-2-thione was Eastman-Kodak material. Pyrrolidine-2-thione was prepared by the reaction of 2-pyrrolidone with phosphorus pentasulphide in xylene. 5-Isonitrosorhodanine was prepared by the method described by Gränacher.[22]

Other Reagents.—10^{-2}M-Silver nitrate was obtained by appropriate dilution of a stock 0·1M-solution prepared from dry AnalaR silver nitrate. The solution was standardised by potentiometric titration with a solution of sodium chloride (primary standard grade). Nitric acid was *ca.* 2N, and potassium nitrate an *ca.* 1M-aqueous solution.

---

[15] S. Ahrland, J. Chatt, N. R. Davies, and A. A. Williams, *J.*, 1958, 264.
[16] S. Ahrland, J. Chatt, N. R. Davies, and A. A. Williams, *J.*, 1958, 276.
[17] S. Ahrland and J. Chatt, *Chem. and Ind.*, 1955, 96.
[18] I. Lindqvist, *Acta Cryst.*, 1957, **10**, 29.
[19] A. Townshend, Ph.D. Thesis, Birmingham University, 1963.
[20] N. Campbell and J. E. McKail, *J.*, 1948, 1251.
[21] J. von Braun, *Ber.*, 1902, **35**, 3368.
[22] C. Gränacher, H. Reis, and E. Pool, *Helv. Chim. Acta*, 1922, **5**, 382.

Organic reagents were used as 1 × 10^{-2}M-solutions in ethanol or ethanol–water 2 × 10^{-4}M-solutions were prepared by dilution of the 1 × 10^{-2}M-solutions with water.

Water was distilled from all-glass apparatus.

Titrations.—Potential differences and pH values were measured on a PYE (11086) pH-millivoltmeter with silver and glass electrodes, respectively, and a calomel reference electrode immersed in 10^{-3}M-potassium nitrate solution. The titrations were carried out at room temperature (20° ± 1°) in a 100 ml. beaker, and this solution was stirred with a Teflon-coated paddle. The pH titrations merely involved following the change in pH of the reaction solution during the titrations. By assuming that pH = $-\log [H^+]$, *i.e.*, neglecting all changes of medium, the hydrogen-ion concentration of the solution ($[H^+]$) was calculated, and converted into the amount of hydrogen ions present in the volume of solution under investigation. The pH-meter was standardised with buffer solutions of pH 4·01 and 6·99 (Burroughs Wellcome buffer tablets, made up as recommended). Blank titrations (omitting only the organic reagent) were also carried out, and blank values subtracted. Estimations of the acidities of some of the reagents were made on the basis of the pH of their aqueous solutions, according to the equations:

$$K_A = [H^+][H^+_R]/(c - [H^+_R]),$$

where $[H^+_R]$ is the hydrogen ion concentration resulting from the introduction of the organic acid and c the concentration of the organic acid had it not dissociated.

Titration Procedures.—Potentiometric titrations were carried out with the 10^{-2}M-silver nitrate and reagent solutions, in acidified and unacidified media. The nitric acid (2 ml.) was used for acidification. The pH titrations were carried out in non-acidified solutions, with the 2 × 10^{-4}M-solutions, or occasionally, the 10^{-2}M-solutions. In the latter instance, the potassium nitrate solution (2 ml.) was also added.

Preparation of Silver Rhodanide and Silver 2-Thiohydantoide.—The precipitates obtained in the potentiometric titrations were filtered off, and washed with much water followed by much hot ethanol. The solids were dried over silica gel and finally over phosphorus pentoxide.

Infrared Analysis.—The infrared spectra of rhodanine, 2-thiohydantoin, and their respective silver complexes were obtained with a Perkin-Elmer model 21 spectrometer fitted with a sodium chloride prism.

One of us (A. T.) thanks British Industrial Plastics Limited, Oldbury, for the award of a scholarship. We are grateful to Professor R. Belcher for his interest in and support of this work.

CHEMISTRY DEPARTMENT, BIRMINGHAM UNIVERSITY,
BIRMINGHAM 15.

[*Received, July 28th,* 1964.]