

of the neighboring N—H group; for RED they are on the same side of the CuN<sub>4</sub> plane and opposite the H atoms of the N—H groups. The equatorial geminal methyl groups lie away from the metal-ion center and their bond axes are parallel to each other. (5) The Cu atom and four N atoms are coplanar for ORG and coplanar within 0.05 Å for RED (the four N atoms form a slightly distorted rectangle). (6) With respect to the Cu atom, the bite angle of the six-membered ring is 94.8 (2)°, while that of the five-membered ring is 85.2 (2)°. (7) For both isomers, the five-membered rings are *gauche* and the six-membered ring a twist-boat. (8) The double bonds between N(2)—C(6) and between N(4)—C(14) [labeled as N(2')—C(6') here]\* are shorter than all the other single bonds for both crystals. (9) Both isomers of the diene involve a *trans* configuration of the imine groups and exhibit a certain

\* N(2') and C(6') are the center-related atoms of N(2) and C(6) respectively.

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## Structures of Three Polymeric Complexes [Silver(I) Nitrate]<sub>x</sub>–1,4-Oxathiane, (AgNO<sub>3</sub>)<sub>x</sub>·C<sub>4</sub>H<sub>8</sub>OS [x = 1 (I), 2 (II), 6 (III)]

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**Abstract.** (I)  $M_r = 274.04$ , monoclinic,  $P2_1/c$ ,  $a = 6.12$  (1),  $b = 7.39$  (1),  $c = 18.13$  (2) Å,  $\beta = 97.0$  (3)°,  $U = 813.7$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.24$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 21.4$  mm<sup>-1</sup>,  $F(000) = 536$ ,  $T = 293$  K, final  $R = 0.090$  for 886 unique reflexions. (II)  $M_r = 443.91$ , monoclinic,  $P2_1/c$ ,  $a = 12.065$  (2),  $b = 6.259$  (3),  $c = 13.527$  (2) Å,  $\beta = 82.42$  (2)°,  $U = 1012.6$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.91$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 3.8$  mm<sup>-1</sup>,  $F(000) = 1012$ ,  $T = 293$  K, final  $R = 0.060$  for 1821 observed reflexions. (III)  $M_r = 1123.41$ , triclinic,  $P\bar{1}$ ,  $a = 10.7347$  (9),  $b = 13.1367$  (13),  $c = 7.2488$  (3) Å,  $\alpha = 91.556$  (5),  $\beta = 92.668$  (5),  $\gamma = 89.141$  (8)°,  $U = 1020.6$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 3.65$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 5.4$  mm<sup>-1</sup>,  $F(000) = 1036$ ,  $T = 293$  K, final  $R = 0.057$  for 5308 observed reflexions. (I), (II) and (III) are polymeric lattice complexes in which Ag atoms are coordinated by the S atoms of 1,4-oxathiane at about

2.5 Å and by nitrate groups with  $2.4 < \text{Ag—O} < 3.1$  Å. In (II) and (III) the O atom of 1,4-oxathiane is also coordinated. The coordination numbers of the Ag atoms vary from six to ten, with irregular geometries. There are no strongly bonded polymeric fragments common throughout the series.

**Introduction.** The crystal structures of the 1,4-oxathiane (tx) complexes of silver perchlorate, AgClO<sub>4</sub>.tx and AgClO<sub>4</sub>.2tx have been described recently (Barnes, Blyth & Paton, 1982). Walton (1966) reported the preparation and IR spectrum of AgNO<sub>3</sub>.tx (I). In the present work two new complexes, (AgNO<sub>3</sub>)<sub>2</sub>.tx (II) and (AgNO<sub>3</sub>)<sub>6</sub>.tx (III) have been prepared and the crystal structures of (I), (II) and (III) have been determined.

**Experimental.** A sample of Walton's preparation of (I) was available. (II) and (III) were prepared together by

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symmetry: an approximate twofold (C<sub>2</sub>) axis in the red molecule and an inversion center in the orange molecule. The temperature factors of the perchlorate ion are high as is usually observed for perchlorate crystals.

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allowing 1,4-oxathiane vapour to diffuse into aqueous silver nitrate for 48 h at room temperature in a sealed vessel. A high yield of colourless crystals up to 7 mm in each direction was obtained. Structure determination has shown that these are  $(\text{AgNO}_3)_6 \cdot \text{tx}$  (III); analysis: Ag 56.1, C 4.3, H 0.8, N 8.1, S 4.0%; required for  $(\text{AgNO}_3)_6 \cdot \text{C}_4\text{H}_8\text{OS}$ : Ag 57.61, C 4.28, H 0.7, N 7.48, S 2.85%. A search for small perfect crystals yielded one crystal which proved after structure determination to have composition  $(\text{AgNO}_3)_2 \cdot \text{tx}$  (II).

All refinements minimized  $\sum w(|F_o| - |F_c|)^2$ . All calculations performed on the Dundee University DEC 10 computer using *SHELX76* (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978) program packages. Atomic scattering parameters from *International Tables for X-ray Crystallography* (1974).

(I) Data collected from equi-inclination Weissenberg photographs using intensities determined by SERC Microdensitometer Service, Daresbury Laboratory, England. Levels  $(0-2)kl$  recorded for a crystal  $0.39 \times 0.28 \times 0.08$  mm and levels  $h(0-6)l$  for a crystal  $0.25 \times 0.23 \times 0.11$  mm. Absorption corrections applied. Structure solved by centrosymmetric direct-methods routine *EEES*. An *E* map suggested positions for Ag and S atoms. Structure extended in stages by least-squares refinement and Fourier synthesis. All non-H atoms located by  $R = 0.22$ . Refinement continued with anisotropic thermal parameters for all non-H atoms, and H atoms included on calculated positions with a single refineable isotropic thermal parameter. An empirical correction for secondary extinction applied,  $g = 0.03538$ . Final refinement: 102 refined parameters,  $R = 0.090$ ,  $wR = 0.091$ ,  $w = 1/[\sigma(F) + 0.014368F^2]$ ;  $(\Delta/\sigma)_{\text{mean}} = 0.015$ ,  $(\Delta/\sigma)_{\text{max}} = 0.064$ ; max. difference peak =  $2.21 \text{ e } \text{Å}^{-3}$  (close to Ag atom).

(II) Data collected for layers  $h(0-8)l$  on a Stoe STADI II diffractometer (Physics Department, Dundee University) using a crystal  $0.36 \times 0.22 \times 0.13$  mm. No variation in intensity of standard reflexions with time. 2139 independent reflexions collected, of which 1821 had  $F > 4\sigma$ .  $R_{\text{int}} = 0.052$ . *EEES* revealed two independent Ag atoms. Extension of structure by refinement and Fourier synthesis revealed two nitrate groups and an oxathiane molecule. With anisotropic thermal parameters for Ag, and isotropic thermal parameters for all other non-H atoms  $R$  fell to 0.18. Anisotropic thermal parameters for all other non-H atoms, introduction of H atoms on calculated positions with a single refineable isotropic thermal parameter and an empirical correction for secondary extinction ( $g = 0.00167$ ) allowed refinement to continue to convergence. Absorption corrections investigated but an insignificant improvement obtained and final  $F_o$  values not corrected for absorption. Final refinement: 147 refined parameters,  $R = 0.060$ ,  $wR = 0.066$ ,  $w = 1/[\sigma(F) +$

$0.01084F^2]$ ;  $(\Delta/\sigma)_{\text{mean}} = 0.002$ ,  $(\Delta/\sigma)_{\text{max}} = 0.012$ ; max. difference peak =  $1.68 \text{ e } \text{Å}^{-3}$  (close to Ag atoms).

(III) After a photographic data set [as for (I)] gave positions for Ag atoms but would not show light atoms, data collected on an Enraf-Nonius CAD-4F diffractometer (SERC facility at Edinburgh University). No variation in intensity of standard reflexions with time. 6168 reflexions collected up to  $\theta = 30^\circ$  yielding 5308 unique reflexions with  $F > \sigma_F$ .  $R_{\text{int}} = 0.036$ . Absorption corrections applied at time of data collection using a  $\varphi$ -scan technique. Structure solved using direct-methods routine *TANG* (Ashida, 1973). The sixth most likely *E* map gave positions for seven Ag atoms. Two of these were on the centres of symmetry at (0,0,0) and (0,0.5,0.5). A structure-factor calculation phased by these atoms alone gave  $R = 0.40$ . An electron density map revealed positions for the nitrate groups. Further refinement and Fourier synthesis showed that the oxathiane groups lie about the centres of symmetry (0.5,0.5,0) (molecule 30) and (0.5,0,0.5) (molecule 40). This requires end-for-end disorder of these molecules with average site occupancy (0.50 O + 0.50 S). A model with O and S exactly superimposed refined satisfactorily. There was no evidence in the Fourier maps to allow separation of these positions or to divide the C atoms on to the slightly different sites which they must occupy when bonded to O or to S. This suggested that the Ag-S and the Ag-O distances are very similar in this compound (as in others, see below). The nitrate group at N(17) was found to be disordered; the two sets of oxygen positions were assumed to have equal occupancy. In the final model isotropic thermal parameters were used for the disordered nitrate group and oxathiane molecules with anisotropic thermal parameters for all other atoms. An empirical correction for secondary extinction was applied ( $g = 0.00569$ ) but no attempt was made to introduce H atoms. Thermal parameters for the disordered (S,O) site did not converge satisfactorily, continuing to oscillate by  $5\sigma$  after convergence of all other parameters.

The alternative possibility that the ligand was in fact 1,4-dithiane (dt) from contaminated oxathiane was examined. [Dalziel, Hitch & Ross (1969) have reported the formation and IR spectra of  $\text{AgNO}_3 \cdot \text{dt}$ ,  $(\text{AgNO}_3)_2 \cdot \text{dt}$  and  $\text{AgNO}_3 \cdot 2\text{dt}$ .] However, (III) showed the typical IR spectrum of tx and the crystal structure would not refine satisfactorily when the model was modified to replace tx by dt. Another possibility considered was that the space group should be *P1* with ordered oxathiane molecules. Again no satisfactory refinement was obtained.

Final refinement: 301 independent parameters,  $R = 0.057$ ,  $wR = 0.082$ ,  $w = 0.6579$  [ $\sigma(F) + 0.007735F^2$ ];  $(\Delta/\sigma)_{\text{mean}} = 0.169$ ,  $(\Delta/\sigma)_{\text{max}} = 0.66$  [excluding (S,O) thermal parameters]; max. difference peak =  $2.13 \text{ e } \text{Å}^{-3}$  [close to Ag(6)].

Table 1. Silver nitrate-1,4-oxathiane (1:1) atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters for the non-H atoms with e.s.d.'s in parentheses

	x	y	z	$U_{eq}^*/U$ ( $\text{\AA}^2 \times 10^3$ )
Ag(1)	3258 (3)	200 (2)	2709 (1)	46 (1)
S(1)	4673 (7)	-1990 (5)	1819 (2)	32 (1)
O(4)	4590 (22)	-2332 (21)	96 (6)	136 (5)
C(2)	6330 (39)	-794 (22)	1200 (10)	49 (5)
C(3)	6614 (39)	-1970 (30)	525 (11)	57 (6)
C(5)	3157 (34)	-3452 (27)	467 (8)	46 (5)
C(6)	2380 (32)	-2513 (32)	1129 (11)	54 (6)
N	-195 (27)	-2175 (21)	3322 (7)	42 (4)
O(10)	1123 (26)	-1016 (21)	3629 (8)	149 (6)
O(11)	-1571 (38)	-2835 (33)	3671 (12)	213 (11)
O(12)	-25 (22)	-2796 (26)	2671 (9)	174 (8)

$$* U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses for (I)

Ag(1)-S(1)	2.512 (4)	C(3)-O(4)	1.406 (23)
Ag(1)-S(1)'	2.527 (4)	O(4)-C(5)	1.432 (22)
Ag(1)-O(12)'	2.500 (18)	C(5)-C(6)	1.512 (24)
Ag(1)-O(10)	2.414 (18)	C(6)-S(1)	1.805 (18)
Ag(1)-O(12)	2.984 (17)	N(9)-O(10)	1.259 (19)
Ag(1)-O(11)	2.967 (17)	N(9)-O(11)	1.214 (24)
S(1)-C(2)	1.831 (20)	N(9)-O(12)	1.283 (19)
C(2)-C(3)	1.528 (29)		
S(1)-Ag(1)-S(1)'	123.3 (3)	C(2)-S(1)-C(6)	96.9 (10)
S(1)-Ag(1)-O(10)	117.5 (4)	S(1)-C(2)-C(3)	110.0 (13)
S(1)'-Ag(1)-O(10)	111.3 (4)	C(2)-C(3)-O(4)	111.9 (19)
S(1)-Ag(1)-O(12)'	121.9 (4)	C(3)-O(4)-C(5)	113.5 (16)
O(10)-Ag(1)-O(12)'	86.2 (4)	O(4)-C(5)-C(6)	112.2 (16)
S(1)'-Ag(1)-O(12)'	87.3 (4)	C(5)-C(6)-S(1)	110.9 (14)
S(1)-Ag(1)-O(11)	83.5 (4)	O(10)-N(9)-O(11)	119.4 (17)
S(1)-Ag(1)-O(12)	77.9 (4)	O(11)-N(9)-O(12)	118.3 (17)
Ag(1)-S(1)-C(2)	110.0 (6)	O(12)-N(9)-O(10)	122.0 (17)
Ag(1)-S(1)'-C(2)'	108.2 (6)		
Ag(1)-S(1)-C(6)	106.5 (7)		
Ag(1)-S(1)'-C(6)'	112.0 (7)		

Symmetry code: (')  $-x, 0.5 + y, 0.5 - z$ .

Table 3. Silver nitrate-1,4-oxathiane (2:1) atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters for the non-H atoms with e.s.d.'s in parentheses

	x	y	z	$U_{eq}/U$ ( $\text{\AA}^2 \times 10^3$ )
Ag(1)	3107 (1)	4907 (1)	3524 (1)	46 (1)
Ag(2)	1894 (1)	3857 (2)	6478 (1)	50 (1)
S(1)	2376 (2)	-3392 (4)	5159 (2)	34 (1)
C(2)	3390 (7)	-1560 (16)	5561 (6)	41 (2)
C(3)	3598 (7)	252 (15)	4839 (8)	39 (2)
O(4)	2604 (5)	1457 (12)	4770 (5)	45 (2)
C(5)	1760 (7)	300 (18)	4355 (7)	40 (2)
C(6)	1296 (6)	-1509 (14)	5019 (6)	35 (2)
N(10)	4516 (6)	1422 (13)	1995 (5)	35 (2)
O(11)	3521 (5)	1952 (15)	2361 (6)	57 (2)
O(12)	4704 (6)	812 (13)	1124 (5)	49 (2)
O(13)	5274 (5)	1556 (13)	2533 (5)	51 (2)
N(20)	533 (5)	4684 (12)	2842 (5)	37 (2)
O(21)	1533 (5)	4293 (13)	2461 (5)	47 (2)
O(22)	-212 (5)	4682 (15)	2297 (5)	58 (2)
O(23)	321 (6)	4988 (15)	3749 (5)	54 (2)

$U_{eq}$  as defined in Table 1.

Table 4. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses for (II)

	(1)	(2)
Ag(1)⋯Ag(2)	4.123 (1)	
Ag(1)⋯Ag(2)*	4.052 (1)	
Ag-S(1)	2.508 (2)	2.492 (2)
Ag-O(4)	2.757 (6)	2.794 (6)
Ag-O(11)	2.437 (6)	2.481 (5)†
Ag-O(12)	2.802 (6)†	
Ag-O(13)	2.487 (7)†	
Ag-O(21)	2.558 (5)	2.385 (6)‡
Ag-O(22)		2.610 (7)*
Ag-O(23)		2.824 (7)*
N-O(1)	1.280 (7)	1.272 (7)
N-O(2)	1.230 (8)	1.236 (7)
N-O(3)	1.245 (7)	1.235 (8)
S(1)-C(2)	1.811 (7)	
C(2)-C(3)	1.495 (11)	
C(3)-O(4)	1.431 (8)	
O(4)-C(5)	1.424 (9)	
C(5)-C(6)	1.507 (10)	
C(6)-S(1)	1.786 (7)	
S(1)-Ag-O(4)	76.7 (1)	76.2 (1)
S(1)-Ag-O(11)	155.5 (2)	111.1 (2)
S(1)-Ag-O(21)	111.0 (1)	168.0 (1)
S(1)-Ag-O(12)	89.67 (2)	
S(1)-Ag-O(13)	119.3 (2)	
S(1)-Ag-O(22)		107.5 (2)
S(1)-Ag-O(23)		83.1 (1)
O(1)-N-O(2)	119.7 (6)	118.9 (6)
O(2)-N-O(3)	118.7 (6)	119.5 (6)
O(3)-N-O(1)	121.6 (6)	121.5 (6)
C(6)-S(1)-C(2)	98.3 (3)	
S(1)-C(2)-C(3)	110.3 (5)	
C(1)-C(3)-O(4)	111.9 (6)	
C(3)-O(4)-C(5)	114.0 (6)	
Ag-S(1)-C(2)	111.1 (2)	109.3 (2)
Ag-S(1)-C(6)	111.3 (2)	115.3 (2)
Ag-O(4)-C(5)	105.6 (4)	116.3 (4)
Ag(1)-S(1)-Ag(2)	111.1 (1)	
Ag(1)-O(4)-Ag(2)	95.9 (2)	

Column (1) has atoms Ag(1) and N(10) to O(13); column (2) has atoms Ag(2) and N(20) to O(23).

\* Ag at  $-x, -y, -z$ .

† Ag at  $-x, 0.5 + y, 0.5 - z$ .

‡ Ag at  $x, 0.5 - y, 0.5 + z$ .

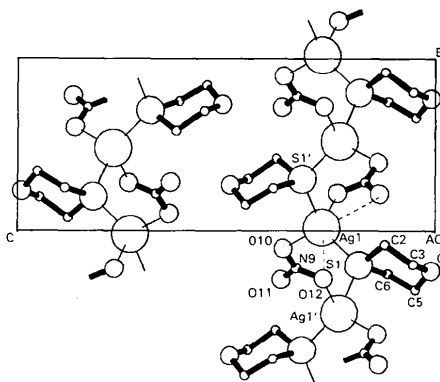


Fig. 1. Silver nitrate-1,4-oxathiane (1:1), seen projected onto the *bc* plane.

**Discussion.** (I) Atomic coordinates are given in Table 1, with interatomic distances and angles in Table 2.\* The structure is shown in Fig. 1. The Ag atoms are linked into chains parallel to **b**.  $\text{Ag}\cdots\text{Ag} = 4.378 \text{ \AA}$ . There are four bonds to Ag under  $2.53 \text{ \AA}$ , from S(1), S(1)', O(10) and O(12)'. These vectors form a very distorted tetrahedron. In addition there are contacts to O(11) at  $2.967(17) \text{ \AA}$  and to O(12) at  $2.984(17) \text{ \AA}$ . The oxathiane O atom does not bond to Ag. S(1) has a rather distorted tetrahedral environment with  $\text{Ag}(1)\text{—S}(1)\text{—Ag}(1)' = 120.7(5)^\circ$ .

(II) Atomic coordinates are given in Table 3, interatomic distances and angles in Table 4. The structure is a three-dimensional polymer as shown in Fig. 2. The two independent Ag atoms have very similar environments. There is an approximate symmetry operation  $0.5 - x, \sim y, z$  connecting the halves of the asymmetric unit. Each Ag is surrounded by six atoms, S(4) at  $2.49 \text{ \AA}$ , three O atoms at  $2.43\text{--}2.61 \text{ \AA}$  and two O atoms at  $2.8 \text{ \AA}$ . The geometry is irregular, and the four short bonds do not form any reasonable distortion of a tetrahedron.

The shortest  $\text{Ag}\cdots\text{Ag}$  distances occur in the **c** direction,  $\text{Ag}(1)\cdots\text{Ag}(2) = 4.123(1)$ ,  $\text{Ag}(1)\cdots\text{Ag}(2)' = 4.052(1) \text{ \AA}$ . Ag(1) and Ag(2) are symmetrically bridged by S(4) of one oxathiane molecule and by O(1) of another oxathiane molecule (Scheme A). Ag(1) and Ag(2) are bridged by O(11) of one nitrate group and by O(21) of another (Scheme B). The Ag—O(11) bonds are almost equal ( $2.43, 2.48 \text{ \AA}$ ); those to O(21) are less so ( $2.38, 2.56 \text{ \AA}$ ). Fragments A and B are both planar. The angle between the normals to these planes is  $80.7(5)^\circ$ .

\* Lists of structure factors, anisotropic thermal parameters (I, II and III) and H-atom coordinates (I and II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38920 (52 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

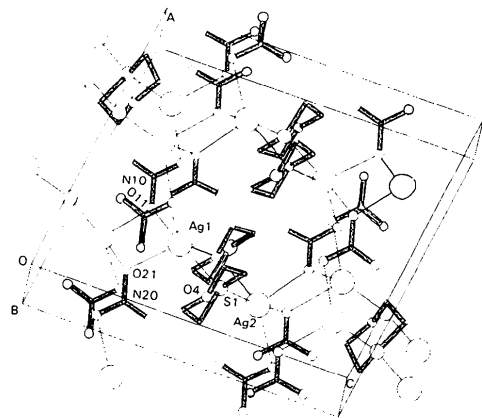
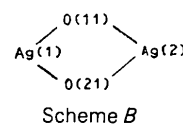
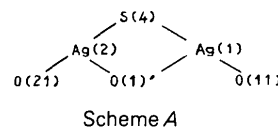
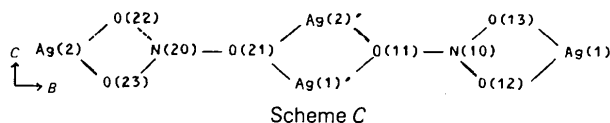


Fig. 2. Silver nitrate-1,4-oxathiane (2:1), viewed perpendicular to the nitrate groups.



The coordination of the nitrate groups is shown in Scheme C. Each nitrate group is connected to three Ag atoms.



In the **a** direction oxathiane molecules connect Ag(1), Ag(2) pairs. The dimensions of the oxathiane molecule are normal. S(4) and O(1) are in tetrahedral environments with Ag(1) axial and Ag(2) equatorial at S(1) and Ag(1) equatorial and Ag(2) axial at O(4).

The S(4)—Ag—O(1) angles in (II) are only  $76.5^\circ$ , leading to an intermolecular S $\cdots$ O contact of  $3.077 \text{ \AA}$ , compared with  $3.30 \text{ \AA}$  for the sum of van der Waals radii and  $3.13 \text{ \AA}$  for the intramolecular S $\cdots$ O distance. It is very difficult to see why this occurs. The only gain would appear to be the tetrahedral geometry at O(1) which cannot represent strong covalent bonding at  $2.77 \text{ \AA}$  and so much show the optimization of directional ion-dipole interactions.

(III) Atomic coordinates are given in Table 5 and interatomic distances and angles in Table 6. The structure is shown in Fig. 3. There are numerous  $\text{Ag}\cdots\text{Ag}$  distances between  $3.59$  [ $\text{Ag}(3)\cdots\text{Ag}(5)$ ] and  $4.10 \text{ \AA}$ . Sheets of Ag atoms in the **bc** plane are made up of Ag(2), Ag(3), Ag(4) and Ag(7). These are crosslinked by  $\text{Ag}(5)\cdots\text{Ag}(6)\cdots\text{Ag}(1)$ , giving a chain joining Ag(2) at the origin to Ag(7) at  $(1.0, 0.5, 0.5)$ . The disordered oxathiane molecule (30) has [S(31), O(131)] bonded to Ag(1) and Ag(6) and [S(31)', O(131)'] bridging to Ag(1)' and Ag(6)' in the adjacent chain. Similarly the oxathiane molecule (40) has [S(41), O(141)] coordinated to Ag(5) and Ag(6) and [S(31)', O(131)'] bridging to Ag(5)' and Ag(6)' in its adjacent chain. The remaining space in the lattice is occupied by the six nitrate groups. Every nitrate O atom has at least one contact to Ag between  $2.4$  and  $2.9 \text{ \AA}$ . The nitrate group at N(17) has two coplanar positions for the O atoms related by a twist of  $34(1)^\circ$ . These positions give different but equally favourable contacts to Ag atoms. Each unique Ag atom has a different, irregular, coordination geometry. Counting contacts below  $2.9 \text{ \AA}$ , Ag(1), Ag(4) and Ag(6) are

seven-coordinate, Ag(2) and Ag(3) are eight coordinate, Ag(5) is nine-coordinate and Ag(7) is ten-coordinate.

These three structures can be compared with the 1,3,5-trithiane (tt) complexes of AgNO<sub>3</sub> and with AgClO<sub>4</sub>.tx and AgClO<sub>4</sub>.2tx (Table 7).

AgNO<sub>3</sub> has a unique structure with an intricate network of Ag<sup>+</sup> and NO<sub>3</sub><sup>-</sup> in three dimensions (Lindley & Woodward, 1966). (III) has a similar network of Ag atoms constrained by the directional Ag—S and Ag—O(tx) bonds. In (II) something of a network survives but the increased concentration of oxathiane gives a more open structure with much longer Ag—O(tx) bonds. (I) is like AgNO<sub>3</sub>.tt and AgNO<sub>3</sub>.2tt in having a ribbon structure with four strong bonds to Ag. The O of oxathiane is not coordinated. It appears that

the unit  $\text{Ag} \begin{array}{c} \diagup X \\ \diagdown X \end{array} \text{Ag}$  (X=O or S), which is found in these

Table 5. Silver nitrate-1,4-oxathiane (6:1) atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters for the non-H atoms with *e.s.d.*'s in parentheses

	<i>U</i> <sub>eq</sub> as defined in Table 1.			<i>U</i> <sub>eq</sub> / <i>U</i> ( $\text{\AA}^2 \times 10^3$ )
	<i>x</i>	<i>y</i>	<i>z</i>	
Ag(1)	-2331 (1)	-3972 (1)	11442 (1)	50 (1)
Ag(2)	0	0	0	51 (1)
Ag(3)	278 (1)	-2113 (1)	13250 (1)	37 (1)
Ag(4)	-191 (1)	-2885 (1)	8232 (1)	37 (1)
Ag(5)	2306 (1)	-968 (1)	6775 (1)	51 (1)
Ag(6)	5385 (1)	-2445 (1)	7727 (1)	62 (1)
Ag(7)	0	5000	5000	45 (1)
N(1)	7520 (5)	-3102 (4)	5329 (8)	33 (1)
O(2)	-1399 (5)	-3373 (4)	14465 (8)	42 (1)
O(3)	6483 (5)	-3267 (5)	4648 (8)	47 (1)
O(4)	7669 (6)	-2687 (5)	6905 (8)	50 (1)
N(5)	2453 (5)	-1877 (4)	10626 (8)	35 (1)
O(6)	1434 (5)	-1653 (4)	9735 (9)	50 (1)
O(7)	3455 (6)	-1698 (6)	9946 (9)	55 (1)
O(8)	2381 (6)	-2254 (5)	12135 (8)	50 (1)
N(9)	996 (5)	-4468 (4)	11135 (7)	30 (1)
O(10)	185 (6)	-3948 (5)	11900 (12)	67 (2)
O(11)	1431 (6)	4787 (6)	1848 (8)	64 (2)
O(12)	1343 (6)	-4233 (5)	9559 (7)	50 (1)
N(13)	-1007 (5)	-550 (4)	15934 (8)	30 (1)
O(14)	-1390 (7)	-827 (6)	14363 (8)	64 (2)
O(15)	-177 (6)	-1082 (6)	16720 (12)	69 (2)
O(16)	8550 (7)	235 (6)	6631 (12)	71 (2)
N(17)	2344 (5)	6502 (4)	5897 (8)	34 (1)
O(18)	2083 (14)	5558 (11)	5750 (19)	55 (3)
O(18A)	2737 (14)	5575 (11)	5981 (19)	54 (3)
O(19)	3467 (14)	-3192 (12)	5861 (20)	60 (3)
O(19A)	3034 (14)	-2721 (12)	6114 (20)	61 (3)
O(20)	1474 (10)	7159 (9)	5952 (15)	42 (2)
O(20A)	1157 (11)	6618 (9)	5689 (15)	43 (2)
N(21)	-2315 (5)	-1465 (4)	10650 (7)	31 (1)
O(22)	6733 (10)	-1940 (9)	10786 (12)	108 (4)
O(23)	7601 (13)	9453 (6)	470 (12)	97 (4)
O(24)	-1338 (8)	-1936 (10)	10728 (9)	102 (4)
S(31)	-4321 (2)	-3978 (2)	9540 (3)	22 (1)
C(32)	-4504 (7)	-4975 (6)	8110 (10)	38 (1)
C(36)	-5533 (7)	-4049 (6)	10862 (10)	40 (1)
S(41)	4607 (2)	-937 (2)	6223 (3)	19 (3)
C(42)	5323 (8)	94 (6)	7016 (11)	44 (2)
C(43)	4917 (7)	1032 (6)	5952 (10)	38 (1)
O(131)	-4321 (2)	-3978 (2)	9540 (3)	69 (8)
O(141)	4607 (2)	-937 (2)	6223 (3)	35 (6)

structures, has no special stability. The shortest Ag...Ag distance increases linearly with 1/*D*<sub>x</sub> along the series AgNO<sub>3</sub> (3.30 Å), (III), (II), (I) (4.39 Å).

Table 6. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses for (III)

(a) Bonds to Ag atoms			
Ag(1)—O(2)	2.442 (6)	S(31)—Ag(1)—O(2)	140-1 (1)
Ag(1)—O(3)	2.829 (6)	S(31)—Ag(1)—O(3)	92-8 (1)
Ag(1)—O(10)	2.707 (6)	S(31)—Ag(1)—O(10)	153-4 (2)
Ag(1)—O(11)'	2.796 (6)	S(31)—Ag(1)—O(22)	68-0 (2)
Ag(1)—O(12)'	2.668 (7)	S(31)—Ag(1)—O(24)	102-2 (2)
Ag(1)—O(18)'	2.953 (6)		
Ag(1)—O(18A)'	2.903 (8)		
Ag(1)—O(22)	2.882 (12)		
Ag(1)—O(24)	2.961 (12)		
Ag(1)—S(31)	2.488 (2)		
Ag(2)—O(6)	2.651 (5)	O(6)—Ag(2)—O(15)	63-4 (2)
Ag(2)—O(15)	2.737 (8)	O(6)—Ag(2)—O(16)	109-5 (2)
Ag(2)—O(16)	2.855 (8)	O(6)—Ag(2)—O(23)	109-7 (2)
Ag(2)—O(23)	2.723 (13)	O(6)—Ag(2)—O(24)	66-6 (2)
Ag(2)—O(24)	3.011 (12)		
Ag(3)—O(3)	2.736 (5)	O(8)—Ag(3)—O(2)	138-1 (2)
Ag(3)—O(6)	2.966 (6)	O(8)—Ag(3)—O(6)	45-3 (2)
Ag(3)—O(8)	2.436 (6)	O(8)—Ag(3)—O(10)	81-1 (3)
Ag(3)—O(10)	2.580 (7)	O(8)—Ag(3)—O(14)	143-4 (3)
Ag(3)—O(14)	2.584 (8)	O(8)—Ag(3)—O(15)	120-6 (2)
Ag(3)—O(15)	2.882 (8)	O(8)—Ag(3)—O(16)'	68-5 (3)
Ag(3)—O(16)'	2.783 (8)	O(8)—Ag(3)—O(20)	77-8 (3)
Ag(3)—O(20)	2.492 (11)		
Ag(3)—O(20A)	2.599 (12)		
Ag(3)—O(24)	2.474 (7)		
Ag(4)—O(2)	3.068 (5)	O(4)—Ag(4)—O(12)	141-7 (3)
Ag(4)—O(4)	2.462 (6)	O(4)—Ag(4)—O(15)	139-9 (3)
Ag(4)—O(6)	2.582 (6)	O(4)—Ag(4)—O(20)	114-9 (2)
Ag(4)—O(10)	3.044 (8)	O(4)—Ag(4)—O(20A)	107-6 (3)
Ag(4)—O(11)'	2.846 (8)	O(4)—Ag(4)—O(24)	75-8 (2)
Ag(4)—O(12)	2.575 (6)		
Ag(4)—O(15)	2.638 (8)		
Ag(4)—O(20)	2.492 (11)		
Ag(4)—O(20A)	2.464 (11)		
Ag(4)—O(24)	2.526 (7)		
Ag(5)—O(6)	2.570 (6)	O(6)—Ag(5)—O(7)	48-0 (2)
Ag(5)—O(7)	2.746 (7)	O(6)—Ag(5)—O(15)	65-5 (2)
Ag(5)—O(14)'	2.678 (7)	O(6)—Ag(5)—O(19A)	86-8 (4)
Ag(5)—O(15)	2.669 (7)	O(6)—Ag(5)—O(20)	81-9 (2)
Ag(5)—O(16)'	2.786 (7)	S(41)—Ag(5)—O(6)	122-9 (1)
Ag(5)—O(19)	3.223 (15)	S(41)—Ag(5)—O(7)	75-0 (1)
Ag(5)—O(19A)	2.462 (15)	S(41)—Ag(5)—O(15)	169-8 (2)
Ag(5)—O(20)	2.673 (11)	S(41)—Ag(5)—O(19A)	71-3 (4)
Ag(5)—O(23)'	2.781 (8)	S(41)—Ag(5)—O(20)	108-5 (2)
Ag(5)—S(41)	2.523 (2)		
Ag(6)—O(3)	2.758 (6)	O(4)—Ag(6)—O(3)	47-6 (2)
Ag(6)—O(4)	2.563 (6)	O(4)—Ag(6)—O(7)	154-0 (2)
Ag(6)—O(7)	2.830 (7)	O(4)—Ag(6)—O(19)	125-7 (4)
Ag(6)—O(19)	2.600 (14)	O(4)—Ag(6)—S(31)	80-4 (2)
Ag(6)—O(19A)	2.757 (15)	S(31)—Ag(6)—O(19)	92-6 (3)
Ag(6)—O(22)	2.664 (9)	S(31)—Ag(6)—O(22)	72-4 (3)
Ag(6)—S(31)	2.443 (2)	S(31)—Ag(6)—S(41)	166-4 (2)
Ag(6)—S(41)	2.407 (2)		
Ag(7)—O(2)	2.682 (5)	O(2)—Ag(7)—O(18)	109-4 (4)
Ag(7)—O(10)	2.686 (8)	O(2)—Ag(7)—O(20A)	69-7 (3)
Ag(7)—O(11)	2.818 (7)	O(2)—Ag(7)—O(10)	61-3 (2)
Ag(7)—O(18)	2.397 (15)	O(10)—Ag(7)—O(18)	85-2 (4)
Ag(7)—O(18A)	3.090 (15)	O(10)—Ag(7)—O(20A)	69-7 (3)
Ag(7)—O(20A)	2.505 (12)		
(b) 1,4-Oxathiane molecules			
S(31)—C(32)	1.656 (8)	Ag(1)—S(31)—Ag(6)	112-5 (1)
S(31)—C(36)	1.657 (8)	C(32)—S(31)—C(36)	102-9 (4)
S(41)—C(42)	1.644 (8)	C(32)—S(31)—Ag(1)	114-9 (3)
S(41)—C(46)	1.680 (8)	C(32)—S(31)—Ag(6)	107-7 (3)
		Ag(5)—S(41)—Ag(6)	102-7 (1)
		C(42)—S(41)—Ag(5)	114-7 (3)
		C(42)—S(41)—Ag(6)	112-2 (3)

Symmetry code: (') *x* + 1, *y* + 1, *z* + 1.

When 1,4-oxathiane complexes to Ag the S atom is always found to be coordinated, with the Ag–S vectors forming part of a tetrahedral environment at the S atom. The O atom of 1,4-oxathiane may interact strongly, weakly or not at all with the Ag. Ignoring (III) where the S,O disorder makes the distance of doubtful validity, the shortest Ag–S distances, 2.44 Å, are found where the ligand forms only one Ag–S bond. The longest occur where it forms several bonds to Ag but only one from each S atom, 2.63 Å. One S atom bridging two Ag atoms gives Ag–S 2.51 Å and one bridging S plus a strong O–Ag interaction gives Ag–S 2.59 Å. The sum of covalent radii is 2.57 Å.

The interaction of Ag<sup>+</sup> ions with oxo-anions or monodentate oxygen ligands is usually regarded as electrostatic. Within a compound there is usually a wide range of Ag···O distances from 2.40 to as much as 3.10 Å. In some cases, *e.g.* AgNO<sub>3</sub>, (II) and (III), the Ag atoms have high coordination numbers and the geometry is not readily reduced to any simple stereochemistry. However, in other cases where the distances fall in the same range the stereochemistry is close to a simple pattern. This is seen for the coordinated 1,4-dioxane in AgClO<sub>4</sub>·3dx (Prosen & Trueblood, 1956) where the anionic O atoms are not coordinated and for the coordinated anion in AgClO<sub>4</sub>·2tx, where the O atoms of tx are not coordinated.

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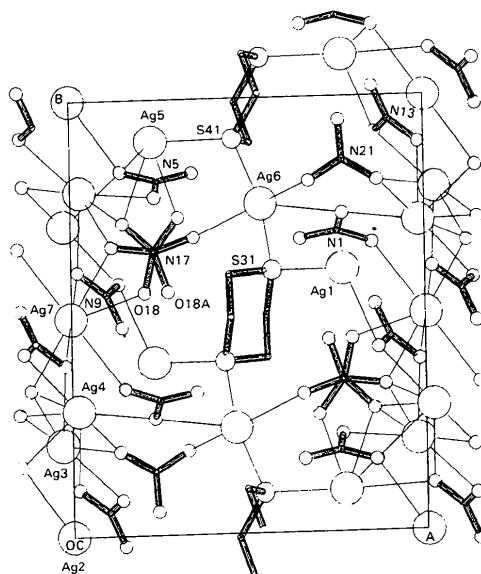


Fig. 3. Silver nitrate–1,4-oxathiane (6:1), seen projected onto the *ab* plane. Both positions of the disordered nitrate group at N(17) are shown. The disordered 1,4-oxathiane molecules are drawn symmetrically.

Table 7. Coordination of Ag atoms in cyclic ether and thioether complexes

Complex	Reference	Ag–S (Å)	Ag–O (Å)	Comments
(I)	(a)	2.512 (4) 2.527 (4)		Ag–S–Ag bridges, O not coordinated
(II)	(a)	2.507 (3) 2.492 (3)	2.763 (5) 2.796 (4)	Ag–S–Ag and Ag–O–Ag bridges
(III)	(a)	2.488 (2) 2.523 (2) 2.443 (2) 2.407 (2)	2.488 (2) 2.523 (2) 2.443 (2) 2.407 (2)	S,O disorder, Ag–S, O–Ag bridges
AgClO <sub>4</sub> ·2tx	(b)	2.411 (7) 2.463 (5)		S coordinated to one Ag only, O not coordinated. Ag–O (ClO <sub>4</sub> ) at 2.62 Å. Trigonal-planar coordination.
AgClO <sub>4</sub> ·tx	(b)	2.574 (4) 2.607 (4)	2.496 (14)	Ag–S–Ag and Ag–O–Ag bridges. Ag–O(ClO <sub>4</sub> ) 2.47, 2.67 Å. O(tx) axial in square-pyramidal coordination.
AgNO <sub>3</sub> ·2tt	(c)	2.59 (2) 2.60 (2) 2.46 (2)		Two S atoms of one ligand each coordinate to a different Ag. One S atom of other ligand coordinates to Ag.
AgNO <sub>3</sub> ·tt	(d)	2.60 (2) 2.65 (2) 2.69 (2)		Each S atom monodentate but ligands shared between Ag atoms.
AgClO <sub>4</sub> ·3dx	(e)		2.46	O monodentate but ligands bridging between Ag atoms. Octahedral coordination.

References: (a) This work. (b) Barnes *et al.* (1982). (c) Domenicano, Scaramuzza, Vaciago, Ashworth & Prout (1968). (d) Ashworth, Prout, Domenicano & Vaciago (1968). (e) Prosen & Trueblood (1956).

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## Dichloro[phenyldi(2-pyridyl)phosphine-*N,N'*]cobalt(II) Hemiethanolate, [Co(C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>P)Cl<sub>2</sub>]<sub>½</sub>C<sub>2</sub>H<sub>6</sub>O

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**Abstract.**  $M_r = 417.1$ , monoclinic,  $P2_1/c$ ,  $a = 16.249$  (3),  $b = 12.078$  (2),  $c = 19.642$  (2) Å,  $\beta = 99.21$  (2)°,  $V = 3805$  (1) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.456$  g cm<sup>-3</sup>,  $T = 294$  K,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu(\text{Mo } K\alpha) = 12.69$  cm<sup>-1</sup>,  $F(000) = 1672$ , final  $R = 0.029$  over 2425 reflections. Crystals of this synthetic organometallic compound contain disordered ethanol solvate molecules and monomeric Co<sup>II</sup> complex molecules. The Co atom is tetrahedrally coordinated to two Cl atoms [average Co–Cl = 2.221 (1) Å] and two pyridines [average Co–N = 2.031 (2) Å]. The dipyridylphosphine forms a six-membered chelate ring in the boat conformation.

**Introduction.** Phenyldi(2-pyridyl)phosphine (Phpy<sub>2</sub>P) is one member of a series of heterocyclic compounds synthesized (Newkome & Hager, 1978*a,b,c*) specifically as sequestering agents for transition-metal ions. The analogous Ph<sub>2</sub>pyP has been shown (Inoguchi, Mahrle, Neugebauer, Jones & Schmidbauer, 1983) to coordinate through the P atom, although N-monodentate and P,N-bidentate coordinations are conceivable. Likewise, Phpy<sub>2</sub>P might be expected to participate in a number of binding modes: N- or P-monodentate, N,N'- or N,P-bidentate, or even tridentate ligation. The crystal structure reported herein illustrates the N,N'-bidentate bonding mode of Phpy<sub>2</sub>P with CoCl<sub>2</sub>.

**Experimental.** Blue crystals grown by slow evaporation from ethanol,  $D_m$  not determined, well formed crystal  $ca$  0.54 × 0.20 × 0.22 mm glued to a glass fiber

mounted on an Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo  $K\alpha$  radiation; preliminary survey of reflections revealed systematic absences ( $0k0$ ,  $k$  odd,  $h0l$ ,  $l$  odd) which uniquely define monoclinic space group  $P2_1/c$ ; lattice parameters derived from least-squares refinement of 25 well centered reflections ( $26^\circ \leq 2\theta \leq 30^\circ$ ); total of 4809 intensity data measured ( $\omega/2\theta$  scans) in one quadrant:  $2^\circ \leq 2\theta \leq 43^\circ$ ,  $0 \leq h \leq 16$ ,  $0 \leq k \leq 12$ ,  $-20 \leq l \leq 20$ ; no systematic variation in three periodically remeasured intensities; empirical absorption correction ( $\psi$  scans) applied to 4361 unique reflections, minimum relative transmission coefficient 0.918. Positions of two Co and two Cl atoms determined by direct methods, and those of all other atoms in the two independent organometallic molecules from successive Fourier difference syntheses. From residual electron density in an otherwise anomalous void, the existence of a highly disordered molecule of ethanol was deduced. Model refined by weighted full-matrix least squares of the 2425 structure amplitudes which met the criterion  $|F| > 6\sigma(|F|)$ ;  $\sum w(\Delta F)^2$  minimized,  $w = [\sigma^2(|F|) + 0.05|F|^2]^{-1}$ . The disordered ethanol model assumed thirteen orientations and eight distinct non-hydrogen sites, with assigned occupancy factors [C(1S) to C(8S)] 8/13, 7/13, 4/13, 4/13, 5/13, 4/13, 4/13, and 3/13. All disordered atoms treated as thermally isotropic C atoms, and disordered H atoms ignored. All non-hydrogen atoms of the organometallic molecules treated anisotropically, and H atoms placed in calculated positions with a common fixed thermal parameter ( $B = 5.0$  Å<sup>2</sup>). A total of 429 variables