Preparation and thermal analysis of 1,4-Oxathian Complexes of Silver(I) perchlorate and Copper(I) perchlorate. Crystal structures of perchlorato-1,4-oxathian silver(I), perchloratiobis-(1,4-oxathian) silver(I) and tetrakis (1,4-oxathian) copper(I) perchlorate.

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Summary: The new compounds $AgClO_4 \cdot tx(III)$, $AgClO_4 \cdot 2tx(IV)$ and $CuClO_4 \cdot 4tx$ (V) are reported. On heating, III and $AgClO_4 \cdot 3tx(I)$ explode without previous decomposition. IV and V also explode after partial loss of oxathian(tx). $CuClO_4 \cdot 3tx(II)$ decomposes in two steps to CuCl without explosion. The crystal structures of III, IV and V have been determined.

III Orthorhombic $Pca2_1$, a = 9.597(5), b= 6.369(6), c= 13.643(4)A. z=4. R=0.080 for 836 reflexions. The structure is polymeric with square pyramidal coordination at the silver atom. Ag-S = 2.59 A, Ag-O = 2.47 - 2.67 A.

IV Monoclinic $P2_1$, a = 6.62(1), b = 16.80(2), c = 6.34(2) A, c = 94.5°, z = 2. R = 0.073 for 1303 reflexions. The structure is trigonal monomeric, with Ag-S = 2.44 A, Ag-O = 2.62 A, S-Ag-S = 160.3°.

V Monoclinic $P2_1/n$, a = 18.47(2), b = 7.75(1), c = 17.64(2) A, c = 92.5°, Z = 4. R = 0.097 for 1433 reflexions. The structure contains tetrahedral Cu (tx) 4^+ cations Cu-S = s.32 A.

The role of 1,4-dioxan (dx) in its solid adducts is now well characterised. The dioxan forms bridges either by direct coordination[1] or by outer-sphere hydrogen-bonding[2]. These complexes often have significant vapour pressures at room temperature,[3] and decompose endothermically at elevated temperature losing 1,4-dioxan unchanged.[4] By comparison the complexes of 1,4-oxathian (tx) are relatively unexplored. Walton[5] has reported the preparation and spectra of a number of complexes with metal halides or metal salts. The crystal structures of $HgCl_2$, 2tx and $PdBr_2$, 2tx have been determined.[6,7] Both contain monomeric complexes with only the S-atom of tx coordinated. There have been no previous reports of tx as a bridging ligand either by S $\frac{M}{M}$ or $M\text{-}S\text{-}C_4H_8\text{-}O\text{-}M$ bridges. Nothing is known of the thermal behaviour of tx complexes, whether the tx is evolved unchanged or whether it decomposes.

Walton[5] reported $AgClO_4$, 3tx(I) and $CuClO_4$, 3tx (II) and suggested that these were analogues of the 1,4-dioxan complex $AgClO_4 \cdot 3dx$.[6] Since this would appear to be the only report of a complex of copper(I) perchlorate with a thioether ligand we have extended the study of these d^{10} systems. In addition to I and II we have prepared the new compounds $AgClO_4$, tx(III), $AgClO_4$, 2tx(IV) and $CuCl)_4$, 4tx(V). The crystal structures of (III), (IV) and (V) have been determined. We have also examined the thermal decomposition of all five compounds.

Experimental

A sample of the original preparation of I was donated by Fowles, Rice and Walton[9]. It was prepared as previously reported[5]. Walton obtained $AgClO_4 \cdot 3tx(I)$ by the addition of liquid tx to ethanolic $AgClO_4$ at room temperature. In our laboratory, possibly slightly warmer, the product of this reaction nolic $AgClO_4$ at room temperature. In our laboratory, possibly slightly warmer, the product of this reaction was $AgClO_4$, tx(III) as large colourless crystals. Satisfactory analysis were obtained for I, II, and III. Since I and II did not contain suitable single crystals for X-ray studies Debye-Scherrer photographs were recorded.

IV and V were prepared by exposing ethanolic solutions of $AgClO_4$ or $Cu (ClO_4)_2$ $6H_2O$ to thioxan vapour in a desiccator for several days. In each case large colourless crystals were obtained. The silver compound (IV) is air stable but light sensitive and was stored dry. $CuClO_4 \cdot 4tx(V)$ is oxidized by air to ill defined copper(II) products. It was stored under the green mother liquor, under which conditions it has remained stable for over a year. IV and V were analysed only by X-ray structure determination.

Thermal analysis by differential scanning calorimetry (d.s.c.) (differential enthalpic analysis) and

by thermogravimetry followed techniques reported previously[4]. all experiments were conducted at atmospheric pressure in nitrogen flowing at ca. 20 ml min⁻¹. D.s.c. experiments were carried out in aluminium pans which were closed but not sealed. T ʳ experiments took place in open aluminium pans. The thermal reactions were also observed on a hot stage microscope to detect changes in crystallinity and melting points.

After preliminary oscillation ans Weissenberg photographs diffraction data for III were collected on a Stoe Stadi II 2-circle diffractometer and for IV and V by Weissenberg photographs, the intensities of which were measured by the Science Research

Council Microdensitometer Service, Daresbury Laboratory, England. All calculations were performed on the Dundee University DEC 10 computer using the SHELX 76 program system[10] and the plotting proram₁ PLUTO. Atomic scattering factors and anaomalous scattering parameters were taken from International Tables[11]. All crystals were mounted in Lindemann glass capillaries.

III polymeric Perchlorato (i,4-oxathian) silver, $C_4H_8AgClO_5S$. Monoclinic, space group $Pca2_1$, a = 9.597(5), b = 6.369(6), c = 13.643(4) Å, z = 4, Dc = 2.49. Mo Kα. radiation, μ 27 cm⁻¹, F_{000} = 604. Data collected for levels hk (0-9), 846 unique reflexions with $F_o > 2\sigma F_o$.

Table 1. Perchlorato-1,4-oxathian silver(I)

a) Atomic coordinates (x10⁴) and equivalent isotropic thermal parameters (x10⁵) with estimated standard deviations in parentheses.

	X/A	Y/B	Z/C	UEQ	
Ag1	− 1603 (1)	5437 (2)	649 (0)	30 (0)	
Cl11	− 2406 (6)	4254 (6)	10100 (10)	26 (2)	
S1	765 (3)	3539 (5)	7655 (9)	24 (1)	
C2	698 (30)	1859 (50)	6576 (32)	41 (7)	
C3	− 802 (17)	503 (27)	6820 (20)	16 (3)	
04	− 584 (13)	9040 (21)	7679 (33)	35 (3)	
05	− 549 (18)	97 (27)	8572 (19)	12 (3)	
C6	555 (17)	1578 (27)	8580 (19)	8 (2)	
012	6577 (16)	5580 (39)	10837 (22)	38 (9)	
013	− 1550 (24)	3117 (40)	10722 (24)	42	(10)*
014	− 3325 (42)	2854 (75)	9548 (47)	116	(21)*
015	− 1742 (27)	5496 (37)	9601 (29)	64	(12)*

$Ueq = 1/3\ \Sigma_i\ \Sigma_j\ U_{ij}\ a^*_i\ a^*_j$

* isotropic U used in refinement

b) Anisotropic thermal parameters (x 10³) with e.s.d.s. in parentheses

	U11	U22	U33	U23	U13	U12
Ag1	26 (0)	25 (0)	40 (2)	− 2 (1)	1 (1)	7 (0)
Cl11	18 (1)	32 (1)	28 (5)	0 (3)	12 (2)	3 (2)
S1	17 (1)	15 (1)	40 (4)	− 18 (3)	− 8 (3)	−3 (1)
012	16 (7)	78 (15)	20 (23)	− 46 (12)	4 (7)	− 14 (7)
013	41 (11)	40 (11)	46 (26)	28 (11)	34 (11)	27 (8)
014	83 (25)	99 (27)	165 (54)	−105 (31)	10 (26)	− 10 (18)
015	68 (15)	50 (13)	74 (31)	−6ᷛ (15)	60 (16)	− 36 (10)

The direct methods routine TANG showed the positions of the silver atom. The structure was expanded by least squares refinement alternated with difference syntheses to show all the non hydrogen atoms. R 0.15 with isotropic thermal parameters for all atoms except Ag. Refinement continued with anisotropic thermal parameters for all atoms except the C and O atoms of the 1,4-oxathian. Convergence occurred at R 0.080. Hydrogen atoms were not included. An attempt to use rigid body refinement (see IV below) gave no improvement in R in this case. The final atomic coordinates and thermal parameters are given in Table 1. Table 2 contains selected interatomic distances and angles. The structure is isslustrated in Fig. 1.

IV Perchloratiobis (1,4-oxathian) silver, C_8H_{16} $AgClO_6S_2$. Monoclinic, space group $P2_1$ from systematic absences, a = 6.62(1), b = 16.80(2), c = 6.34(2)Å, c = 94.5(1)$^\circ$, z = 2, Dc = 1.96. Ni filtered CuKa radiation, μ = 157.2 cm^{-1}, F_{000} = 416. Levels collected (0-5)kl, hk(0-5). 1292 unique reflexions above background.

The structure was solved using the direct methods routine TANG. The best E-map showed the AgS_2 fragment. Refinement of these atoms gave R 0.15. An electron density map revealed all the

other non-hydrogen atoms except for three of the perchlorate oxygen atoms. Refinement with anisotropic Ag and all other atoms isotropic including putative oxygen atoms of the perchlorate group gave R 0.15. After absorption corrections were applied refinement continued to R 0.095 with anisotropic Ag, S and Cl.

Since several bond lengths and angles were unsatisfactory the 1,4-oxathian molecule and the perchlorate group were idealised with S-C = 1.81, C-C = 1.54, C-O = 1.45, Cl-O = 1.45 and O. . .) 2.36 Å. Refinement then continued with anisotropic thermal parameters for all atoms with the 1,4-oxathian and perchlorate moieties refined as rigid groups. Convergence occurred at R 0.073. Hydrogen atoms were no included. The largest peaks on the final difference map were all close to the silver atom.

Atomic coordinates and thermal parameters are given in Table 3. The refined band lengths and bond angles are shown in Fig. 2.

V Tetrakis(1,4-oxathian)copper(I) perchlorate, $C_{16}H_{32}CuClO_8S_4$, monoclinic, space group $P2_1/n$ from systematic absences, a = 18.47(2), b = 7.75(1), c = 17.64(2) Å, ^{b} = 92.5(1)$^\circ$, z = 4 Dc = 1.52 Ni filtered CuKα radiation, μ = 71.5 cm^{-1}, F_{000} = 1652. Levels collected h (0-6)l and levels (0-3) for a crystal

Table 2. Interatomic distances (Å) and angles (deg) for perchlorato-1,4-oxathian silver, with e.s.d.s in parentheses

|			
Ag1 – S1	2.575 (4)	Ag1 – S1'	2.607 (4)
Ag1 – O4''	2.496 (14)	Ag1 – O12	2.473 (25)
Ag1 – O15	2.667 (39)	C3 – O4	1.51 (4)
Ag1 – Ag1'	4.831 (2)	O4 – C5	1.39 (5)
S1 – C2	1.82 (4)	C5 – C6	1.42 (2)
C2 – C3	1.71 (3)	C6 – S1	1.79 (2)
Cl11 – O12	1.64 (2)	Cl11 – C14	1.46 (4)
Cl11 – O13	1.39 (3)	Cl11 – O15	1.22 (3)
S1 – Ag1 – S1'	166.5 (4)	S1' – Ag1 – O4	98.6 (4)
S1 – Ag1 – O4	94.9 (3)	S1' – Ag1 – O12	90.2 (5)
S1 – Ag1 – O12	90.7 (4)	S1' – Ag1 – O15	92.7 (3)
S1 – Ag1 – O15	92.7 (4)	O4 – Ag1 – O12	88.8 (4)
O12 – Ag1 – O15	176.3 (5)	O4 – Ag1 – O15	89.4 (1.2)
C2 – S1 – C6	99 (1)	C3 – C4 – C5	113 (1)
O12 – Cl11 – O13	104 (2)	O12 – Cl11 – O14	111 (2)
Ag1 – S1 – C2	104.0 (6)	Ag1 – O4 – C5	118. (6)
Ag1 – S1 – Ag1'	137.5 (4)		

SILVER PERCHLORATE-1,4-OXATHIAN (1/1)
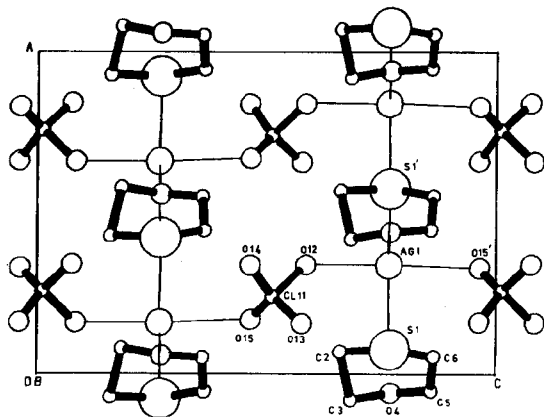
Fig. 1 . Parchlorato-1, 4-oxathian silver (I), projected onto the ac plane. The square pyramidal coordination of the Ag atom is completed by O4 of the oxathian molecule in the next cell above.
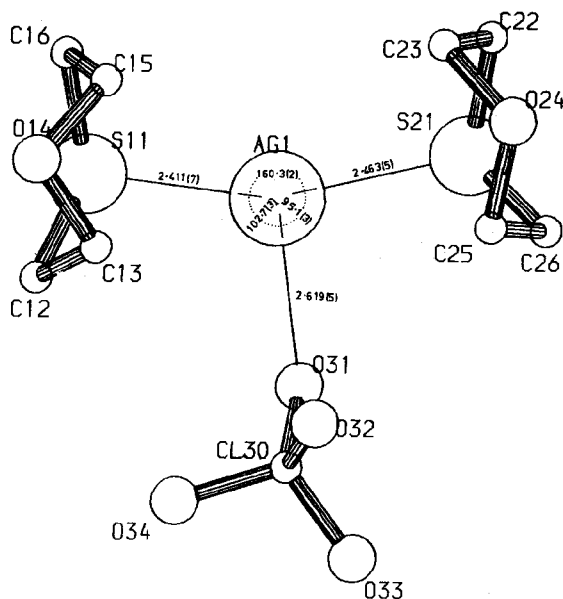
Fg. 2 : Perchlorato bis (1, 4-oxathian) silver (I) viewed normal to the plane S(11), S(21), O(31).

Table 3. Perchlorato-bis(1,4-oxathian) silver(I).

a) Atomic coordinates $(x10^4)$ and equivalent isotropic thermal parameters $(x10^3)$ with estimated standard deviations in parentheses.

	X/A	Y/B	Z/C	UEQ
Ag1	8467 (')	1657 (2)	4754 (1)	43 (0)
S11	9138 (8)	252 (2)	4471 (5)	43 (1)
C12	6743 (8)	− 182 (2)	3486 (5)	43 (3)
C13	6381 (8)	283 (2)	1398 (5)	134 (3)
O14	7615 (8)	− 102 (2)	− 95 (5)	32 (2)
O15	9267 (8)	457 (2)	334 (5)	70 (3)
C16	10671 (8)	'172 (2)	2238 (5)	23 (2)
S21	8948 (7)	3109 (0)	4595 (6)	43 (1)
C22	10353 (7)	3350 (0)	2342 (6)	50 (3)
C23	9403 (7)	2999 (0)	250 (6)	35 (3)
O24	7575 (7)	3463 (0)	− 205 (6)	102 (3)
C25	6070 (7)	3236 (0)	1224 (6)	29 (2)
C26	6794 (7)	3637 (0)	3336 (6)	97 (3)
Cl30	3879 (6)	1561 (5)	6701 (7)	64 (1)
O31	5886 (6)	1709 (5)	7679 (7)	70 (3)
O32	3791 (6)	1807 (5)	4503 (7)	97 (3)
O33	2403 (6)	2002 (5)	7788 (7)	143 (3)
O34	3431 (6)	718 (5)	6797 (7)	88 (3)

$$Ueq = 1/3 \ \Sigma_i \ \Sigma_j \ U_{ij} \ a^*_i \ a^*_j$$

b) Anisotropic thermal parameters $(\times 10^3)$ with e.s.d.s in parentheses

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu (1)	89 (3)	45 (2)	29 (2)	− 2 (1)	− 10 (2)	0 (2)
Cl (1)	55 (4)	106 (5)	55 (3)	− 9 (4)	− 2 (3)	− 25 (4)
O (21)	75 (14)	232 (27)	78 (11)	− 34 (15)	1 (11)	− 112 (17)
O (22)	109 (18)	224 (30)	152 (20)	− 14 (21)	− 29 (16)	59 (21)
O (23)	195 (25)	199 (28)	102 (15)	− 67 (18)	− 24 (16)	− 67 (23)
O (24)	251 (31)	179 (27)	120 (18)	70 (19)	− 81 (19)	− 56 (25)
S (31)	68 (5)	61 (4)	61 (3)	− 8 (3)	− 11 (3)	− 14 (4)
C (32)	63 (18)	109 (23)	59 (14)	36 (15)	− 18 (14)	− 63 (17)
C (33)	81 (23)	119 (28)	92 (20)	63 (21)	3 (21)	− 3 (21)
O (34)	104 (16)	94 (15)	78 (11)	11 (11)	9 (12)	− 16 (13)
C (35)	116 (28)	155 (31)	47 (14)	36 (19)	− 4 (17)	8 (27)
C (36)	35 (16)	103 (23)	75 (16)	23 (16)	11 (14)	− 20 (16)
S (41)	103 (5)	40 (4)	29 (2)	− 5 (2)	− 5 (3)	0 (4)
C (42)	82 (21)	92 (22)	53 (14)	− 23 (15)	9 (15)	− 11 (19)
C (43)	144 (33)	123 (31)	55 (17)	− 19 (18)	6 (20)	70 (28)
O (44)	137 (20)	75 (15)	54 (10)	− 32 (10)	− 14 (12)	47 (15)
C (45)	102 (25)	90 (24)	77 (17)	− 64 (17)	− 36 (17)	49 (20)
C (46)	69 (19)	109 (22)	44 (12)	− 20 (15)	− 19 (13)	48 (18)
S (51)	95 (5)	48 (4)	54 (3)	2 (3)	− 14 (4)	4 (4)
S (52)	88 (20)	74 (19)	38 (11)	18 (12)	13 (13)	71 (18)
C (53)	126 (27)	80 (22)	59 (15)	15 (15)	− 12 (17)	49 (21)
O (54)	161 (20)	44 (12)	87 (12)	6 (10)	− 3 (13)	22 (12)
C (55)	89 (21)	74 (20)	53 (13)	− 5 (15)	5 (15)	29 (18)
C (56)	130 (26)	76 (20)	45 (13)	− 12 (13)	− 16 (15)	22 (20)
S (61)	100 (5)	46 (4)	37 (3)	3 (3)	− 1 (3)	− 10 (4)
C (62)	130 (28)	78 (23)	91 (19)	13 (17)	− 83 (20)	− 12 (20)
C (63)	110 (25)	89 (23)	78 (17)	− 6 (17)	− 22 (18)	50 (20)
O (64)	91 (16)	103 (15)	45 (9)	− 6 (10)	− 13 (10)	− 18 (14)
C (65)	91 (26)	65 (21)	69 (16)	11 (16)	− 45 (18)	− 21 (20)
C (66)	51 (16)	95 (21)	58 (13)	33 (14)	− 20 (13)	− 1 (16)

mounted in the diagonal. 1433 unique reflexions above background.

This structure was solved by the centrosymmetric direct methods routine EEES. The best E-map showed the fragment Cu, S_4,Cl. Refinement of these atoms gave R 0.39. An electron density map at this point showed all the remaining non-hydrogen atoms. Refinement continued to R 0.18 (all atoms isotropic), R 0.15 (Cu, S, Cl anisotropic) and converged at R 0.097 with all non hydrogen atoms anisotropic and isotropic hydrogen atoms at calculated positions. Atomic coordinates and thermal parameters are given in Table 4, with interatomic distances and.

angles in Table 5. The structure is shown in Fig. 3.

Results and Discussion

Walton[5] suggested that I and II might be isostructrual with $AgClO_4$, 3dx. This is not the case. X-ray powder photographs whow that I and II are different from each other and that both are of much lower symmetry than either cubic $AgClO_4$, 3dx[8] or the low-temperature rhombohedral form of the same structure found in $NaClO_4$. 3dx[12]. In the light of the discussion of III, IV and V below, it seems most likely that I and II are polymeric, possibly with MS_4 tetrahedral coordination as found in $Cu(thiourea)_3Cl$.

Table 4. Tetrakis (1,4-oxathian) copper (I) perchlorate

a)   Atomic coordinates (x10^4) and equivalent isotropic thermal parameters (x10^3) with estimated standard deviations in parentheses.

	x/a	y/b	z/c	Ueq
Cu (1)	2526 (2)	5894 (4)	4898 (2)	54 (2)
Cl (1)	4967 (3)	2523 (9)	2519 (3)	72 (4)
O (21)	4414 (10)	1520 (33)	2767 (10)	128 (20)
O (22)	5520 (12)	1498 (39)	2264 (13	161 (22)
O (23)	5281 (14)	3684 (36)	3071 (12)	164 (25)
O (24)	4731 (16)	3595 (36)	1886 (13)	183 (28)
S (31)	1744 (3)	3746 (8)	4531 (3)	63 (4)
C (32)	1155 (13)	3349 (37)	5307 (12)	77 (19)
C (33)	559 (15)	1992 (44)	5077 (16) 97	(23)
O (34)	71 (11)	2834 (25)	4536 (10)	92 (14)
C (35)	481 (17)	3101 (47)	3834 (13)	106 (26)
C (36)	1043 (12)	4514 (38)	3891 (38)	67 (19)
S (41)	2263 (4)	6847 (7)	6132 (3)	57 (4)
C (42)	1612 (14)	8495 (35)	6000 (12)	72 (18)
C (43)	1508 (20)	9591 (47)	6739 (14)	107 (27)
O (44)	2197 (14)	410 (25)	6906 (9)	88 (15)
C (45)	2782 (15)	9404 (39)	7085 (14)	89 (20)
C (46)	3021 (13)	8281 (35)	6417 (11)	74 (17)
S (51)	3688 (4)	4768 (8)	5137 (3)	65 (4)
C (52)	3630 (14)	3453 (32)	5987 (11)	66 (17)
C (53)	4291 (17)	2412 (36)	6070 (13)	88 (∠2)
O (54)	4406 (12)	1224 (21)	5480 (10)	97 (14)
C (55)	4561 (15)	2083 (35)	4760 (12)	72 (19)
C (56)	3884 (15)	3065 (35)	4503 (12)	83 (20)
S (61)	2670 (4)	8478 (8)	4277 (3)	61 (4)
C (62)	3515 (16)	8526 (37)	3808 (14)	99 (22)
C (63)	3564 (16)	7245 (38)	3127 (14)	92 (21)
O (64)	3012 (11)	7758 (24)	2567 (8)	79 (14)
C (65)	2311 (17)	7455 (35)	2789 (14)	75 (20)
C (66)	2057 (12)	8832 (34)	3457 (11)	68 (18)

$$U_{eq} = 1/3 \ \Sigma_i \ \Sigma_j \ U_{ij} \ a^*_i \ a^*_j$$

III is polymeric. Fig. 1. Each tx ligand is bonded to three silver atoms by axial (2.607 Å) and equatorial (2.575 Å) bonds at S1 and by a bond approximately bisecting the acial and equatorial positions at O(4) (2.50 Å). The perchlorate anion bridges two silve⁻ atoms (2.57 Å, arverage). Each silver atom has quare pyramidal five-coordination, the basal plane being distorted by folding about the line O(12),

Ag(1), O(15) to give the S(1)-Ag(1)-S(1') angle of 166.5°.

IV is a molecular complex. The silver atom has trigonal planer coordination with tow sulphur atoms at 2.411, 2.463 Å and O931) of the perchlorate group at 2.62 Å. The S(11)-Ag(1)-S(21) angle is 160.3°. Ag(1) lies 0.156 Å out of the plane of the ligand atoms.

b) Anisotropic thermal parameters $(\times 10^3)$ with e.s.d.s. in parentheses.

	U11	U22	U33	U23	U13	U12
Ag1	52 (0)	34 (0)	44 (0)	0 (1)	12 (0)	− 2 (1)
S11	68 (3)	32 (2)	27 (2)	2 (1)	1 (2)	− 10 (2)
C12	44 (5)	14 (4)	74 (5)	17 (5)	24 (5)	0 (4)
C13	121 (6)	157 (6)	125 (6)	− 49 (6)	11 (6)	28 (6)
O14	20 (4)	46 (4)	28 (4)	− 10 (4)	1 (3)	3 (4)
C15	76 (6)	94 (6)	40 (5)	− 7 (5)	7 (5)	− 28 (6)
C16	26 (5)	23 (4)	20 (4)	− 6 (4)	10 (4)	− 2 (4)
S21	55 (3)	36 (2)	43 (2)	− 7 (1)	27 (2)	− 15 (2)
C22	43 (5)	55 (5)	54 (5)	− 20 (5)	14 (5)	23 (5)
C23	65 (5)	20 (5)	22 (4)	20 (4)	12 (5)	− 12 (5)
O24	109 (6)	107 (6)	87 (5)	57 (5)	− 21 (5)	− 3 (6)
C25	20 (5)	27 (4)	39 (5)	31 (4)	− 2 (5)	12 (4)
C26	98 (6)	87 (6)	112 (6)	0 (6)	40 (6)	28 (6)
Cl30	36 (2)	101 (4)	55 (2)	19 (3)	7 (1)	13 (3)
O31	55 (5)	84 (5)	71 (5)	33 (5)	8 (4)	9 (6)
O32	108 (6)	100 (5)	81 (5)	88 (4)	− 14 (5)	− 27 (5)
O33	73 (5)	190 (6)	176 (6)	77 (6)	74 (5)	43 (5)
O34	64 (5)	87 (5)	118 (5)	8 (5)	32 (5)	- 40 (5)

Both oxathian molecules use axial lone pairs for coordination. The torsion angles are 58.8° [C(13), C(12), S(11), Ag(1)] and 53.3° [C(23), C(22), S(21), Ag(1)]; Both the S. . .O vectors of the oxathian molecules lie on the same side of the S-Ag-S line leaving ample space for the ClO_4 - ion. There are no intermolecular contacts under 3.8 Å. The oxygen atoms O(14), O(24) of the oxathian molecules take no part in complex formation.

V contains tetrahedral cations and anions with no close contacts between them, Fig. 3. The CuS_4 tetrahedra. The Cu-S bonds range between 2.279 and 2.370 Å, spread over 13σ whereas the Cl-O bonds lying between 1.370 and 1.449 Å range over only 4σ. Similarly the S-Cu-S angles range from 99.9° to 125.8° compared with 105.2 to 115.1° for the O-Cl-O angles. The oxathian molecules 30, 40 and 50 have the Cu atom in the equatorial position, whereas oxathian 60 adopts the axial configuration. The torsion angles C-C-S-Cu are 176.1, 167.7, 167.7 66.9°. The distortion of the tetrahedron does not reflect the axial-equatorial division. The closest approximation to a local C_3 axis lies along the copper-S(31) (equatorial) direction.

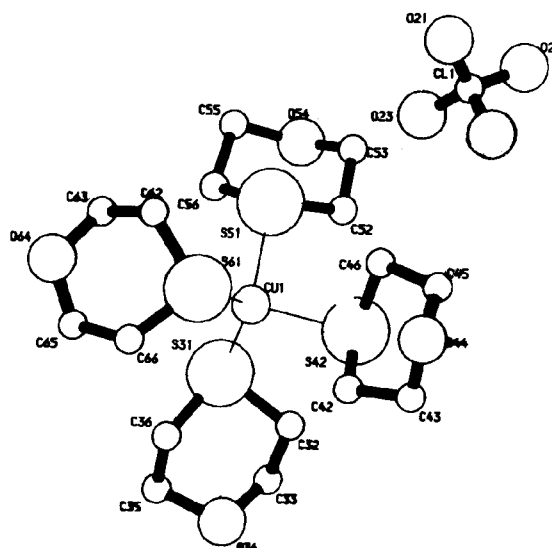As in IV the oxathian oxygen atoms take no part

Fig. 3 :   Tetrakis (1, 4-oxathian) copper (I) perchlorate viewed normal to the ac plane.

in bonding to the metal. The ligand molecules are packed to give no significant interactions; the shortest contacts being O(34). . .C(42). c.38 Å and O(21). . . C(65) 3.28 Å. All other intermolecular contacts exceed 3.65 Å.

Table 5. Interatomic distances (Å) and angles (deg)
for the tetrakis (1,4-oxathian(copper(I) perchlorate,
with e.s.d.s in parentheses.

a) Copper coordination sphere		b) Perchlorate ion	
Cu (1) – S (31)	2.279 (7)	Cl (1) – O (21)	1.370 (20)
Cu (1) – S (41)	2.370 (6)	Cl (1) – O (22)	1.387 (25)
Cu (1) – S (51)	2.333 (8)	Cl (1) – O (23)	1.426 (24)
Cu (1) – S (61)	2.303 (6)	Cl (1) – O (24)	1.449 (23)
S (31) – Cu (1) – S (41)	109.6 (2)	O (21) – Cl (1) – O (22)	110.3 (1.5)
S (31) – Cu (1) – S (51)	110.4 (3)	O (21) – Cl (1) – O (23)	115.1 (1.2)
S (31) – Cu (1) – S (61)	125.8 (2)	O (21) – Cl (1) – O (24)	111.6 (1.3)
S (41) – Cu (1) – S (51)	99.9 (2)	O (22) – Cl (1) – O (23)	107.4 (1.4)
S (41) – Cu (1) – S (61)	101.4 (2)	O (22) – Cl (1) – O (24)	106.7 (1.4)
S (51) – Cu (1) – S (61)	106.4 (3)	O (23) – Cl (1) – O (24)	105.2 (1.4)

c) Oxathian ligands

	Molecule 30	Molecule 40	Molecule 50	Molecul 60
S (1) – C (2)	1.812 (24)	1.762 (27)	1.827 (22)	1.799 (30)
C (2) – C (3)	1.562 (40)	1.575 (37)	1.465 (39)	1.564 (38)
C (3) – O (4)	1.445 (34)	1.440 (43)	1.412 (31)	1.444 (32)
O (4) – C (5)	1.493 (32)	1.359 (37)	1.473 (29)	1.390 (38)
C (5) – C (6)	1.508 (43)	1.544 (36)	1.516 (38)	1.671 (35)
C (6) – S (1)	1.784 (24)	1.840 (26)	1.788 (26)	1.820 (21)
S (1) – C (2) – C (3)	111.0 (1.7)	112.9 (1.8)	108.3 (1.7)	114.9 (2.0)
C (2) – C (3) – O (4)	106.1 (2.3)	105.5 (2.4)	116.0 (2.1)	106.8 (2.2)
C (3) – O (4) – C (5)	06.5 (2.0)	118.8 (2.3)	112.4 (1.8)	113.5 (1.9)
C (4) – C (5) – C (6)	114.5 (2.1)	113.4 (2.0)	107.2 (2.1)	112.6 (2.1)
C (5) – C (6) – S (1)	106.1 (2.0)	108.1 (1.7)	111.9 (1.6)	106.3 (1.6)
C (6) – S (1) – C (2)	95.2 (1.1)	96.0 (1.2)	96.5 (1.1)	98.8 (1.1)

In this table Molecule 30 has atoms numbered S(31) to C(36) etc.

III is the first structure to be reported in which tx acts as a bridging ligand. This structure shows both $\frac{Ag}{Ag}$ S and Ag-SC$_4$H$_8$O-Ag bridges. The geometry is very similar to one found in bisthioureasilver(I) chloride, where the Ag. . .Ag distance is 4.71 Å and the Ag-S-Ag angle 133° compared with 4.83 Å and 138° in the present structure.

The closest analogue to IV is perchloratobis (tricyclohexy-phosphine) copper(I)[13] where the P-Cu-P angle is 144.5° and the Ci-O distance 2.220 Å with the Cu atom 0.08 Å out of the ligand plane.

It is interesting that the S-Ag-S angle is similar in III and IV (160.3, 166.5°). Similar values re also found in AgSCN[4] and in Ag$_3$AsS$_3$.[15] IV appears to be the first structurally characterised monomeric example of 3-coordinate Ag(I). There are a few polymeric examples but these involve short Ag. . .Ag distances as well as three bonds to sulphur or notrogen ligands.[16,17]

Silver-sulphur interactions have been reviewed by Prout et al[18,19]. The sum of the covalent radii is 2.57 Å compared with observed values ranging from 2.43 to 2.98 Å over a variety of S-donor ligands. The

Table 6. Differenial Scanning Calorimetry and Thermogravimetric Analysis on silver(I) perchlorate-1,4-oxathian complexes.

Com·	Endotherm		$\Delta H/kJ$ mol^{-1}	$\Delta W\%$ obs	Notes
	T1	T_2			
Ag·	355	361	2.0 ± 0.2	0	*
	368	371	9.4 ± 0.3	0	melting
		(510)			exothermic
					explosion
AgClO$_4$.tx	403	407	11.1 ± 0.2	0	*
(III)	490	496	10.0 ± 0.2	0	melting
		(523)			exotherm and
					explosion
AgClO$_4$.2tx	377	381	16.4 ± 0.7	0	*
(IV)	399	403	3.0 ± 0.3	0	*
	480		500	12	unreprod. endo
					with melting
					endotherm followed
				(523)	by exothermic
					explosion

Experiments were conducted at atmospheric pressure under nitrogen flowing at 20 cm^3 min^{-1}, heating at 8.33 deg. min^{-1} on samples of 2-10 mg. T$_1$ was the minimum temperature at which reaction was detected. T$_2$ was the peak temperature of the transition. ΔW_{obs} co·· ·nes d.s.c. and t.g. measurements. Temperatures in parentheses refer to exotherms.

* Reversible phase change.

Ag-S distance in III (2.59 Å) is significantly longer than in IV (2.44 Å) where the coordination number is lower and the ligands are non-bridging.

The bond length (2.50 Å) for Ag-O(tx) in III is close to that of 2.46 Å in AgClO$_4$. 3dx^8, in both cases the Ag-O vactor bisects the axial and equatorial positions relative to the 6-membered ring. These distances are at the short end of the range of ionic or ion dipole Ag-O interactions, for example distances of 2.48 - 2.99 Å are found in the structure of AgNO$_3$[20], whereas the Ag-O$_{(ClO_4)}$ distances in II and IV suggest weaker interactions.[4]

AgNO$_3$[20], whereas the Ag-O$_{(ClO_4)}$ distances in II and IV suggest weaker interactions.[4]

Monomeric tetrahedral Cu^{I}S$_4$ occurs in [Cu[thioacetamide]^{4}Cl][21] in which S-Cu = 2.343 Å and the S-Cu-S angles are 112.3 and 103.9°. There

are several examples of polymers containing Cu^{I}S$_4$ tetrahedra including Cu(thiourea)$_3$, Cl[22] in which Cu-S range from 2.28 to 2.43 Å and the S-Cu-S angles from 100 to 116° giving a distortion similar o that of V.

The results of differential scanning calorimetry and thermogravimetric analyses on the oxathian complexes are reported in Tables 6 and 7. AgClO$_4$ does not decompose below its melting point (731 K)[23,24] and does not explode at higher tempratures. CuClO$_4$ is not well characterised as an independent compound.

The AgClO$_4$ complexes I, III and IV do not decompose before melting, Table 6. The melts explode at 510-525 K compared with 418 K for the much less stable AgClO$_4$, C$_6$H$_6$.[25] For I and II there is no weight loss on melting or up to the explosion

Table 7. Differential scanning colorimetry and thermogravimetric analyses on Cu(I)
perchlorate - 1,4-oxathian complexes.

| Compound | Endotherm | | ΔH/kJ mol^{-1} | $\Delta W\%_{obs}$ | $\Delta W\%Th$ | Notes |
	T_1	T_2				
CuClO$_4$	318	323	1.0 ± 0.5	0		Small exotherm
(II)	385	388	a	6b		melting
		(450)	2.0 ± 1.0	53 ± 2		Small exotherm
		(498)	2.0 ± 1.0	55 ± 2 c		Small exotherm
Cu(tx)$_4$ClO$_4$	363	373.5	10.2 ± 0.5	5 b		d
(V)	376	382	19.1 ± 0.5	10 b		d
	423	427	a	25 b		melting
	360	408	140.0 ± 20	37.5 ± 1.0	35.96	e
	453	470	a	68.0 ± 2.0d	71.86	Decomp. to CuClO$_4$
		(480)				Small exotherm exothemic
		(500)				explosion.

Experimental conditions as in Table 6.

a) ΔH not measured because of overlapping reaction.

b) Weight loss due to underlying reaction

c) A further weight loss occurred between 520-570 K to a final weight loss of 76.6%. Formation of CuCl requires 79.2%. No detectable d.s.c. peak accompanied this weight loss.

d) Reversible phase change.

e) Reaction measured on samples initially melted, then cooled to 300 K. ΔH corrected for material decomposed during initial melting.

temperature. IV melts with decomposition giving a reproducible weight loss of 12% which might represent the reaction

$$2(AgCl)_4, 2tx) \rightarrow (AgClo_4)_2 \ 3tx + tx \ vapour$$

for which the predicted weight loss is 12.5%

I, III and IV are far more thermally stable than AgClO$_4$, 3dx which decomposes to AgClO$_4$, dx at 397 K and thence to AgClO$_4$ at 420 K^3.

The CuClO$_4$ complexes II and V are of low ther-

mal stability, Table 7. II shows a weight loss of ~ 53% in the region 370-470 K and a further weight loss step to pale gree impure CuCl by 570°. These weight losses are not accompanied by the well developed endotherms usually observed for desolvation reactions. The d.s.c. record only shows only two small exotherms above the melting point at 388 K. These exotherms must represent the balance of exothermic and endothermic reactions involving the ClO$_4$⁻ and tx moieties.

Compound V melts at 427 K but simulataneous-

ly there is a slow endothermic reaction requiring up to 1 hr for completion on samples of less than 10 mg. This reaction occurs r pidly in samples which have been melted and then cooled to 300 K. The weight loss of 37.5% in consistent with

$$Cu(tx)_4 \, ClO_4 \rightarrow Cu(tx)_2 ClO_4 + 2tx \; vapour$$
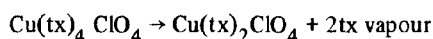
The gaseous effluent may well be degradation products of tx, although the ΔH of $70kJ \, mol^{-1}$ per mole of tx lost is comparable with values found for the loss of 1,4-dioxan[3,4]. The $Cu(tx)_2 ClO_4$ forms as a solid which decomposes in a typical rapid endotherm at 470 K to give a product, tentatively identified as $CuClO_4$, which explodes at 500 K. $Cu(CH_3CN)_4 ClO_4$ desolvates at 448 K and the residue explodes at 483 K.[26]

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