## Addition Compounds of 1,3,5-Trithian with Mercury(11) and Silver(1) Salts

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The preparation from ethanolic solution and analysis of the 1:1 addition compounds C<sub>3</sub>H<sub>6</sub>S<sub>3</sub>,HgX<sub>2</sub> where X = CI, Br, and I are described. The trithian can be recovered by extraction into benzene in the presence of hydrochloric acid. The preparation from aqueous solution and analysis of the 1:1 addition compounds C<sub>3</sub>H<sub>6</sub>S<sub>2</sub>,AgNO<sub>3</sub>,  $C_{3}H_{6}S_{3}$ , AgNO<sub>3</sub>, H<sub>2</sub>O, and  $C_{3}H_{6}S_{3}$ , AgBF<sub>4</sub>, H<sub>2</sub>O are also described. Conductivity measurements show that the  $(C_{3}H_{6}S_{3}Ag)^{+}$  ion exists in aqueous solution. The 1:1 addition compounds  $C_{3}H_{6}S_{3}$ , AgX, prepared by the reaction of the nitrate with the appropriate alkali halide, have been analysed. Their photosensitivity differs from that of the simple silver halides.

The unit-cell dimensions, cell contents, and X-ray diffraction powder data are reported.

1,3,5-TRITHIAN is the stable trimer of thioformaldehyde. Electron diffraction studies in the vapour phase,<sup>1</sup> dipole moments in benzene solution,<sup>2</sup> and X-ray diffraction in the solid state 3 prove that it has the "chair" configuration. The n.m.r. spectrum has been reported.4 The bond lengths and bond angles, found by electron diffraction, are shown in the Figure. These are consistent with the  $sp^3$  hybridisation of the valence electrons



Chair configuration of 1,3,5-trithian C-S, 1·81 Å; S-S, 3·05 Å; ∠CSC, 114·5°; ∠SCS, 106·5°

of the sulphur atoms and, in the chair configuration, there will be "lone pairs" of electrons available for donation in equatorial and axial directions. 1,3,5-Trithian, therefore, could act as either a unidentate, bidentate, or terdentate ligand.

There is no evidence that the hydrogen atoms of the methylene groups are active, although they are in the sym-sulphone.<sup>5</sup> We have observed that trithian dissolves in concentrated sulphuric acid to give an unstable yellow solution and presumably this indicates the presence of sulphonium species.

Adducts of trithian with mercury(II) chloride, silver nitrate, and platinum(II) chloride were described by Hofmann and Girard in 1870,6 but no recent work has

<sup>1</sup> O. Hassal and H. Viervoll, Acta Chem. Scand., 1947, 1, 149. <sup>2</sup> K. E. Calderbank and R. J. W. Le Fèvre, J. Chem. Soc., 1949, 199.

<sup>3</sup> N. F. Moerman and E. H. Wiebenga, Z. Krist., 1937, 323.

been reported with this interesting ligand. We now give the preparation, analysis, and properties of the series of 1:1 addition compounds with mercury(II) halides and silver(I) salts.

## EXPERIMENTAL

1,3,5-Trithiane (Eastman-Kodak) was used without purification. All other materials were of reagent grade.

Mercury(II) Addition Compounds.--The adducts  $C_3H_6S_3$ , HgX<sub>2</sub>, where X = Cl, Br, and I, were prepared by Soxhlet extraction of 1:1 molar mixtures of the reactants with absolute ethanol and recrystallised in the same way. For the chloride and bromide, it was convenient to dissolve the simple halides in ethanol and extract only the trithian from the thimble. The yields were nearly quantitative in all cases and no other product was detected when the molar ratios were varied over a five-fold range. Attempts to prepare the fluoride adduct were unsuccessful; trithian dissolves in a solution of mercury(II) oxide in excess of aqueous hydrofluoric acid but the unstable white crystalline product could not be isolated.

Analysis. Mercury and halogen were analysed gravimetrically after oxidation with concentrated nitric acid in Carius tubes at 190°, to avoid loss of mercury. Carbon and hydrogen were determined at the Organic Microanalysis Laboratory, Imperial College. Results of duplicate analyses (sulphur by difference) were: 1,3,5-trithian-mercury(II) chloride (Found: C, 8.8; H, 1.3; Cl, 17.3; Hg, 48.6; S, 24.0. Calc. for  $C_3H_6S_3$ , HgCl<sub>2</sub>: C, 8.8; H, 1.5; Cl, 17.3; Hg, 48.9; S, 23.5%); 1,3,5-trithian-mercury(II) bromide (Found: C, 7.4; H, 1.2; Br, 32.3; Hg, 40.1; S, 19.1.  $C_{3}H_{6}S_{3}$ , HgBr<sub>2</sub> requires C, 7.2; H, 1.2; Br, 32.1; Hg, 40.2; S, 19.3%); 1,3,5-trithian-mercury(II) iodide (Found: C, 6.0; H, 0.9; Hg, 34.1; I, 43.0; S, 16.1. C<sub>3</sub>H<sub>6</sub>S<sub>3</sub>,HgI<sub>2</sub> requires C, 6·1; H, 1·0; Hg, 33·9; I, 42·8; S, 16·2%).

Properties. The compounds crystallise as needles; the chloride and bromide are colourless and the iodide is pale yellow. They are all insoluble in water and most organic

<sup>4</sup> E. Campaigne, N. F. Chamberlain, and B. E. Edwards, J. Org. Chem., 1962, **27**, 135. <sup>5</sup> R. Camps, Chem. Ber., 1892, **25**, 233.

<sup>6</sup> A. W. Hofmann and A. Girard, Jahr. Ber., 1870, 591.

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TABLE 1

Space group	x	M.W.	a (Å)	b (Å)	c (Å)	U (Å <sup>3</sup> )	$D_{\rm m}$ (g./c.c.)	$D_{c}$
$P2_{1}2_{1}2$ ( $D_{2}^{3}$ , No. 18)	Cl	409.8	$13.65 \pm 0.03$	$14 \cdot 32 \pm 0 \cdot 03$	$\textbf{4.30} \pm \textbf{0.01}$	840.4	3.22	3.24
$P2_{1}2_{1}2$ $(D_{2}^{3}, \text{ No. } 18)$	$\mathbf{Br}$	498.7	13.67	14.98	4.41	$902 \cdot 8$	3.68	3.67
$P2_{1}22$ $(D_{2}^{2}, \text{ No. } 17)$	I	<b>592·7</b>	14.12	15.64	4.55	$1004 \cdot 2$	3.90	3.92

solvents, but slightly soluble in dimethylformamide and dioxan, at room temperature. They are stable in air for prolonged periods. On heating the chloride, bromide, and iodide decompose at  $189-189 \cdot 5^{\circ}$ ,  $200-200 \cdot 5^{\circ}$ , and  $208-208 \cdot 5^{\circ}$ , respectively; the black residue contains mercury(II) sulphide. The trithian can be extracted quantitatively from the compounds into benzene in the presence of concentrated hydrochloric acid. The rate of extraction is in the order chloride > bromide > iodide.

Crystallography. X-Ray diffraction data, obtained from single-crystal and Weissenberg photographs about two axes using  $\text{Cu}-K_{\alpha}$  radiation, are in Table 1:  $\text{C}_{3}\text{H}_{6}\text{S}_{3}\text{HgX}_{2}$ , all orthorhombic, showing straight extinction and pronounced cleavage along needle axis (c), n > 1.74, negative elongation and low birefringence. All densities measured by displacement in benzene, chloroform, and carbon tetra-chloride and cell content Z = 4.

Table 2 summarises X-ray diffraction powder data, obtained with 11.64 cm. cameras with  $Cu-K_{\alpha}$ -radiation, and

TABLE 2	
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## Observed X-ray powder results for 1,3,5-trithianmercury(II) balides

			our y (11)	11011000			
	C <sub>3</sub> H <sub>6</sub> S <sub>3</sub> ,HgCl <sub>2</sub>		C <sub>3</sub> H <sub>6</sub> S	3,HgBr	C <sub>3</sub> H <sub>6</sub> S <sub>8</sub> ,HgI <sub>3</sub>		
		sin* 0		sin²∂		$\sin^2 \theta$	
hkl	R.I.*	(obs.)	R.I.*	(obs.)	R.I.*	(obs.)	
)20	10	0.0115	10	0.0106	10	0.0097	
้ถึง	5	0.0128	ĩõ	0.0126	10	0.0119	
20	ň	0.0147		0 0120	îõ	0.0130	
30	-	00111		-	10	0.0220	
220	10	0.0245	10	0.0232			
10	10				2	0.0294	
01	2	0.0320					
01			6	0.0337	2	0.0318	
011	5	0.0348					
11	i	0.0380					
320	ī	0.0404	5	0.0391			
21	ī	0.0436			6	0.0382	
21	-		4	0.0446			
940	4	0.0461					
11	7	0.0476	9	0.0460	10	0.0428	
40	ì	0.0495					
100	2	0.0508	2	0.0509			
221	1	0.0564					
31	3	0.0580					
240	1	0.0590	2	0.0549	4	0.0510	
20	4	0.0623	4	0.0613			
)50					3	0.0606	
50					4	0.0638	
231	7	0.0709	8	0.0675			
321	2	0.0723	7	0.0700			
)41	3	0.0783	6	0.0733	10	0.0674	
111			8	0.0844		_	
250	7	0.0855					
241			1	0.0860		-	
	3	0.0912					
520			3	0.0902	4	0.0839	
140	5	0.0972	7	0.030			
)60	4	0.1043	1	0.0956	10	0.0873	
60			4	0.0984			
341	1	0.1071					
51			1	0.0998			
530					4	0.0961	
31	4	0.1090	2	0.1055			
260	7	0.1170	7	0.1083	-	0.1007	
					э	0.1005	
16		-		0 1107			
100			7	0.1101		0.1101	
110		-			ð	0.1121	
940		0 1001					
90	4	0.1261			1	0.1171	
100 100	1	0.1989	_		T	0.1111	
004	1	0.1200					
102	1	0.1977	6	0.1243			
				1.14.20			

used for the refinement of unit cell dimensions given above. A structure determination of  $C_3H_6S_3$ ,  $HgCl_2$  is in progress.

Addition Compounds.—The Silver(1) adduct  $C_3H_8S_3$ , AgNO<sub>3</sub>, H<sub>2</sub>O was prepared by heating a 1:1 molar mixture of trithian and silver nitrate in water for 1 hr. under nitrogen. C<sub>3</sub>H<sub>6</sub>S<sub>3</sub>,AgBF<sub>4</sub>,H<sub>2</sub>O was prepared in the same way, with a solution of silver fluoroborate.<sup>7</sup> After filtration the hot solutions were cooled slowly and the products recrystallised from hot water, under nitrogen. Average yields were about 80%. When a more concentrated solution of trithian and silver nitrate was used and the product recrystallised from hot silver nitrate solution (2% w/v), the adduct  $C_3H_6S_3$ , AgNO<sub>3</sub> was obtained (80% yield). The adducts  $C_3H_6S_3$ , AgX, where X = Cl, Br, and I, were prepared by reactions of solutions of the nitrate with the appropriate alkali halide.

Analysis. Silver was analysed gravimetrically after the compounds had been oxidised by digestion with concentrated nitric acid. This reaction, with the nitrates, is vigorous. Carbon and hydrogen were determined at the Organic Microanalysis Laboratory, Imperial College. Water was determined by the Pregl absorption method, and the presence or absence of water was confirmed from the infrared spectra. Nitrate and fluoroborate were determined gravimetrically using Nitron reagent. The results of duplicate analyses (sulphur by difference) were: 1,3,5-trithian-silver(I) nitrate monohydrate (Found: C, 11.4; H, 2.7; Ag, 33.0; H<sub>2</sub>O, 5.5; NO<sub>3</sub>, 18.9; S, 29.6. Calc. for  $C_{3}H_{6}S_{3}$ , AgNO<sub>3</sub>, H<sub>2</sub>O: C, 11·1; H, 2·5; Ag, 33·1; H<sub>2</sub>O, 5·5; NO<sub>3</sub>, 19.0; S, 29.5%); 1,3,5-trithian-silver(1) nitrate (Found: C, 11.9; H, 2.3; Ag, 34.9; NO<sub>3</sub>, 20.0; S, 30.9. C3H6S3,AgNO3 requires C, 11.7; H, 2.0; Ag, 35.0; NO3, 20.1; S, 31.2%; 1,3,5-trithian-silver(1) fluoroborate monohydrate (Found: C, 10.5; H, 2.5; Ag, 30.5; BF<sub>4</sub>, 24.3;  $H_2O$ , 5.0; S, 27.2.  $C_3H_6S_3$ , AgBF<sub>4</sub>,  $H_2O$  requires C, 10.3; H, 2·3; Ag, 30·7; BF<sub>4</sub>, 24·7; H<sub>2</sub>O, 5·1; S, 27·4%); 1,3,5trithian-silver(1) chloride (Found: C, 13.0; H, 2.4; Ag, 38.1; Cl, 12.5; S, 34.0. C<sub>3</sub>H<sub>6</sub>S<sub>3</sub>,AgCl requires C, 12.8; H, 2.2; Ag, 38.3; Cl, 12.6; S, 34.2%); 1,3,5-trithiansilver(1) bromide (Found: C, 11.4; H, 2.0; Ag, 33.0; Br, 24.3; S, 29.3. C<sub>3</sub>H<sub>6</sub>S<sub>3</sub>,AgBr requires C, 11.1; H, 1.9; Ag, 33.1; Br, 24.5 S, 29.4%); 1,3,5-trithian-silver(1) iodide (Found: C, 10.0; H, 1.7; Ag, 28.7; I, 33.9; S, 25.7. C<sub>3</sub>H<sub>6</sub>S<sub>3</sub>,AgI requires C, 9.7; H, 1.6; Ag, 28.9; I, 34.0; S, 25.8%).

Properties. The two nitrate adducts have different crystal habits; the monohydrate crystallises as large plates and the anhydrous compound as fine needles. The fluoroborate monohydrate crystals are small plates. They are all moderately soluble in water, about 0.5% (w/v), but insoluble in ethanol and other solvents. They decompose slowly in air and their aqueous solutions decompose rapidly on heating, to give a black precipitate that contains silver sulphide. Their decomposition temperatures are 155—156, 169—170, 187.5—188.5°, respectively, and some trithian is sublimed off on decomposition. Conductivity experiments on the nitrate adducts in aqueous solution show that they are 1:1 electrolytes (Found:  $\Lambda_{\infty} = 124$  mhos, ionic con-

<sup>7</sup> H. S. Booth and D. R. Martin, "Boron Trifluoride and its Derivatives," J. Wiley, New York, and Chapman and Hall, London, 1949, p. 124.

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		-	sil	ver(I) :	salts			
	C3H6S3,AgNO3,H2O		C3H5S3,AgNO3			C3H6S3,AgBF4,H3O		
hkl	R.I.*	$\sin^2 \theta$	hkl	R.I.*	sin² θ	hkl	R.I.*	$\sin^2 \theta$
$\{ \begin{array}{c} 020\\ 011 \end{array} \}$	3	0.0084	110	1	0.0048	110	3	0.0078
iii'	ł	0.0132	120	ł	0.0079	020	10	0.0098
021	10	0.0146	200	10	0.0149	120	1	0.0120
121	$^{2}$	0.0194	210	2	0.0129	001	1	0.0111
210	8	0.0201	040	_ <del>1</del>	0.0120	011	2	0.0191
130	1	0.0236	001	1	0.0198	200	4	0.0208
201	ŧ	0.0247	140	10	0.0207	101	3	0.0223
$\{220\\211\}$	5	0.0271	121	4	0.0228	210	3	0.0233
102	5	0.0304	230	3	0.0245	111	1	0.0247
040	2	0.0337	$\bar{2}11$	ł	0.0258	021	2	0.0263
022	2	0.0342	$\overline{1}31$	7	0.0280	130	6	0.0273
122	5	0.0387	121	2	0.0330	220	6	0.0307
041	5	0.0401	$\overline{2}31$	3	0.0343	201	3	0.0379
310 \			290.1					
202	. 6	0.0449	121	n	0.0380	040	5	0.0302
032 (		0.0442	080	0	0.0380	040	0	0.0392
141 ]			000 )					
212	1	0.0463	160	2	0.0422	230	5	0.0428
$\left\{ \begin{array}{c} 320\\ 311 \end{array} \right\}$	4	0.0202	$\left\{ \begin{smallmatrix} 201 \\ 151 \end{smallmatrix} \right\}$	1	0.0449	310	1	0.0494
$\{050\\ see \}$	2	0.0524	051	<b>2</b>	0.0466	301	2	0.0638
042	5	0.0592	340	4	0.0208	002	3	0.0678
142	3	0.0638	$\frac{151}{241}$	12	0.0553	012	1	0.0200
023	ł	0.0662	061	1	0.0581	321	4	0.0732
312	2	0.0692	400	3	0.0603	112	1	0.0750
100.5			350 J		0 0000			0 0.00
423   250	7	0.0709	$\overline{4}21$	<b>2</b>	0.0639	250	1	0.0817
400	7	0.0745	080	1	0.0680	<b>4</b> 00 l	1	0.0839
			7-4			151 5	-	0 0002
411	4	0.0834	171	1	0.0202	$\left\{\begin{array}{c} 410\\ 331 \end{array}\right\}$	4	0.0852
332 )	,	0.0964	T12)	1	0.0740	000	4	0.0070
161 🐧	\$	0.0804	<u>202</u>	Ź	0.0140	000		0.0919
421	2	0.0894	T22	8	0.0773	212	1	0.0902
043	1	0.0913	0125	-	0.0000	100		
	-	0 0020	171 }	1	0.0806	420	4	0.0923
			261					
350	1	0.0942	022	a	0.0835	401	1	0.0006
			$\overline{2}32$		0 0000	401	Ž	0.0990
	-		$\frac{312}{312}$	-				
252	2	0.0966	181	2	0.0863	$\frac{411}{341}$	1	0.1022

TABLE 3

Observed X-ray powder results for 1,3,5-trithiane-

ductance of nitrate ion = 71 mhos), and this proves that the species  $C_3H_6S_3$ , Ag<sup>+</sup> exists in solution. The chloride and bromide adducts are white and the iodide pale yellow powders. They are all insoluble in water and decompose at 150° with sublimation of trithian and leave residues of

Crystallography. X-Ray diffraction data, obtained from single crystal and Weissenberg photographs about two axes by use of Cu- $K_{\alpha}$  radiation, are: C<sub>3</sub>H<sub>6</sub>S<sub>3</sub>,AgNO<sub>3</sub>,N<sub>2</sub>O, M =326.2, orthorhombic  $a = 11.30 \pm 0.02$  Å,  $b = 16.87 \pm 0.02$ 0.03 Å,  $c = 9.64 \pm 0.02$  Å, U = 1835.7 Å<sup>3</sup>,  $D_{\rm m} = 2.36$  g./c.c. (displacement in benzene, chloroform, and carbon tetrachloride) Z = 8,  $D_c = 2.36$  g./c.c. Space group  $P_{cam}$  $(D''_{2h})$ , No. 57). Straight extinction, no pronounced cleavage, n > 1.74, positive elongation and high birefringence.

 $C_{3}H_{6}S_{3}$ , AgNO<sub>3</sub>, M = 308.1, monoclinic,  $a = 13.13 \pm$ 0.03 Å,  $b = 23.7 \pm 0.1$  Å,  $c = 5.73 \pm 0.01$  Å,  $\beta = 107^{\circ} \pm$ 10',  $U = 1704 \cdot 2^{\circ} \text{ Å}^3$ ,  $D_{\text{m}} = 2 \cdot 41 \text{ g./c.c.}$  (displacement in benzene, chloroform, carbon tetrachloride) Z = 8,  $D_c =$ 2.40 g./c.c., space group  $P_{2_1}/b$  ( $C_{2h}^5$  No. 14) oblique extinction (15°), cleavage along needle axis (c), n > 1.74, positive elongation, high birefringence.

 $C_3H_6S_3$ , AgBF<sub>4</sub>, H<sub>2</sub>O, M = 351.0, orthorhombic, a = $10.72 \pm 0.02$  Å,  $b = 15.61 \pm 0.03$  Å,  $c = 5.91 \pm 0.01$  Å, U = 989.2 Å<sup>3</sup>,  $D_{\rm m} = 2.32$  g./c.c. (displacement in benzene, chloroform, carbon tetrachloride) Z = 4,  $D_c = 2.35$  g./c.c., space group  $P_{2_12_12}$  ( $D_2^3$ , No. 18), straight extinction, no pronounced cleavage, n 1.68-1.74, positive elongation, high birefringence.

Table 3 summarises X-ray diffraction powder data, obtained with 11.64 cm. cameras with  $Cu-K_{\alpha}$  radiation and used for the refinement of the unit cell dimensions given above. The powder data for the halide adducts have not been indexed.

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