Synthetic, Structural, and Spectroscopic Studies of the Ligating Properties of Organic Disulphides: *X*-Ray Structures of Mercury(II) Chloride–Dimethyl Disulphide (1/1) and Triethylammonium Trichloromercurate†

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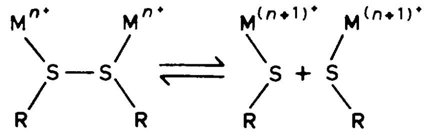
The synthesis of a series of complexes of mercury(II) halides with dimethyl and diethyl disulphide has been attempted, but of the products thereby formed, only $HgCl_2{\cdot}Me_2S_2$ (**1**) was sufficiently stable to be characterised by an *X*-ray crystallographic structure determination. Complex (**1**) crystallizes in the monoclinic space group *C*2/*c*, with cell dimensions (at 20 °C) $a = 14.865(4)$, $b = 9.185(1)$, $c = 12.441(3)$ Å, $\beta = 109.23(1)°$, and $Z = 8$. The structure was solved by the heavy-atom method, and refined to *R* 0.043 (*R*′ 0.044) for 1 118 observed reflections. The structure consists of –Hg–Cl–Hg–Cl– chains, with the disulphide molecule loosely and asymmetrically co-ordinated in a bridging mode between adjacent pairs of mercury atoms. When using commercial Me_2S_2 (without further purification) a crystalline by-product, $[NHEt_3][HgCl_3]$ (**2**), was unexpectedly obtained, and its structure determination was carried out to confirm its identity. Crystals of (**2**) are monoclinic, space group $P2_1/n$, with cell dimensions (at 20 °C) $a = 7.639(2)$, $b = 14.711(1)$, $c = 11.074(3)$ Å, $\beta = 100.28(1)°$, and $Z = 4$. The structure was refined to *R* 0.046 (*R*′ 0.033) for 1 074 observed reflections. The origin of complex (**2**) from the '$HgCl_2$–Me_2S_2' reaction is discussed.

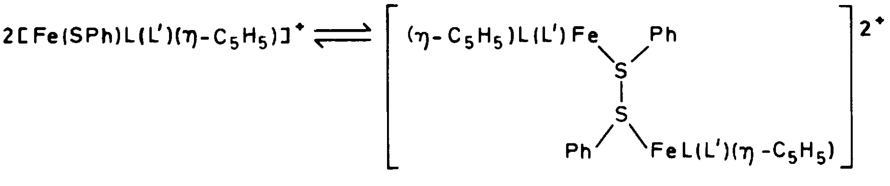
Of the many possible sulphur donor groups available in biological systems, the disulphide moiety, R–S–S–R, has been the least well studied in model compound systems. Of those complexes which have been made and their structures determined, the majority fall into two groups. First, functionalized disulphides such as $(Me_2NCH_2CH_2S)_2$, in which the binding to a metal receptor is assisted by the chelation of the functional group, have been examined, particularly by Seff and co-workers.[1] The second general class of complexes involves structures with simple disulphides symmetrically bridging two metal atoms.[2] In most of these examples, at least one other, different bridging ligand, such as chloride, is also present. More recently Roesky *et al.*[3] reported the unique structure of the $[Ag_2(Ph_2S_2)_4]^{2+}$ cation which possesses both bridging and unidentate Ph_2S_2 ligands. There is no other bridging ligand present in this cation and, significantly, there is a degree of asymmetry in the attachment of the bridging disulphide moieties. In general, disulphides may be considered as poor ligands. For example Sigel *et al.*[4] showed that for a range of 'soft' metal ions they are weaker donors than thioethers.

Recently there has been renewed interest in the redox chemistry of metal–disulphide systems. In particular, we have been interested in redox reactions of the type shown in equation (1). Treichel and Rosenhein[5] have reported such a system with the equilibrium (2). Stiefel and co-workers[6] noted that in a bis(thiolate)molybdenum(VI) complex an unusually short S···S separation existed which might represent a situation intermediate between (A) and (B) above. This they described as 'partial bond formation'. Similar observations in our work on tungsten thiolate complexes[7,8] prompted us to begin a synthetic, Raman spectroscopic, and structural study of selected examples of disulphide complexes which might have some biological relevance.



(A) (B) (1)

In an earlier publication[9] we reported the structure of $2CuI{\cdot}Et_2S_2$ and discussed the S–S stretching vibration in the Raman spectra of a series of Cu^I halide–disulphide complexes. The present paper extends this study to some reactions involving mercury(II) halides with organic disulphides. It was anticipated that Hg^{2+} should be a good candidate for forming complexes with R_2S_2, and there is continuing interest in the toxicology of this metal ion. It transpired that few complexes are sufficiently stable to isolate and characterize completely, but $HgCl_2{\cdot}Me_2S_2$ (1) was subjected to a single-crystal *X*-ray structure determination which we report here. Complex (1) is found to exhibit a number of unique features for disulphide complexes as described below. In addition, an unexpected, and initially puzzling, by-product was obtained from the reaction of reagent-grade Me_2S_2 and $HgCl_2$, namely $[NHEt_3][HgCl_3]$ (2), whose origin and structure we also discuss in this paper.



(2)

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† *Supplementary data available* (No. SUP 56484, 4 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Experimental

Preparations.—$HgCl_2 \cdot Me_2S_2$ (**1**) was prepared by refluxing a mixture of anhydrous $HgCl_2$ (*ca.* 1 g) and an excess of dimethyl disulphide (dried and redistilled) at ~109 °C. After 16 h the resulting cloudy solution was filtered and placed in a freezer at −25 °C for 1—2 d until colourless crystals were formed. The product sometimes appeared pale orange when commercial Me_2S_2 (Aldrich, 99%) was used without further purification. As discussed below, a second product, $[NHEt_3][HgCl_3]$ (**2**), was also obtained from the reaction employing 99% grade Me_2S_2. Crystals of (**1**) are relatively unstable and lose Me_2S_2 upon standing. Hence it proved impossible to obtain good analytical data. However, the *X*-ray crystal structure determination reported below effectively confirms the identity of this compound.

The sample of Me_2S_2 supplied by Aldrich, which had initially been used as received (since a g.c. analysis showed it to be 99% pure), gave rise to the completely unexpected product, $[NHEt_3][HgCl_3]$ (**2**), when reacted with $HgCl_2$. The precipitation of this product preceded that of the desired compound (**1**). We therefore undertook a search for impurities which might account for this observation. It was ascertained that the presence of water was necessary to obtain (**2**) as a product since, when the Me_2S_2 was dried over molecular sieves before use only (**1**) could be obtained from the Me_2S_2–$HgCl_2$ reaction. Subsequent re-addition of H_2O to the system again yielded small quantities of (**2**) upon cooling of the reaction solution. The presence of small amounts of NEt_3 in the commercial reagent was then confirmed by a g.c.–m.s. study of the undistilled Me_2S_2.

Attempts to prepare $HgCl_2 \cdot Et_2S_2$ and $HgI_2 \cdot Me_2S_2$ by direct reaction of the appropriate mercury salt and organic disulphide yielded crystalline products, but upon isolation these crystals decomposed even more rapidly than (**1**), and were not further studied.

Raman spectroscopic measurements were performed by Dr. R. A. Kydd and Mr. J. Bartlett in this Department using a Jarrell Ash model 25-100 double-monochromator spectrometer; argon-ion laser excitation was provided by a Coherent Radiation CR-4 source. The sample was sealed in a capillary during the spectral measurement to prevent decomposition.

X-Ray Crystallography.—The crystal data and experimental conditions are summarized in Table 1. Computing was performed at the University of Calgary with the use of the *X*-RAY 76 package of programs.[10] Both complexes were sealed in capillaries under an atmosphere of nitrogen and the $HgCl_2 \cdot Me_2S_2$ sample also included a drop of mother-liquor. The space groups were determined with use of the indexing routines of the diffractometer and by examination of the intensities measured during data collection. These were confirmed by the distribution of *E* values calculated from a *K*-curve[10] and by the successful solution and refinement of the structures. The intensity data were collected on an Enraf-Nonius CAD-4F automated diffractometer using an ω—2θ scan mode and Mo-K_α radiation (λ = 0.710 69 Å, graphite monochromator). The data were corrected for background, Lorentz and polarization effects, and absorption using DIFABS[11] (empirical method). Absorption coefficients were found to range from 0.56 to 1.77 for (**1**) and from 0.54 to 1.41 for (**2**).

Atomic scattering factors for non-hydrogen atoms were from Cromer and Mann[12] and were corrected for the real and imaginary parts of the anomalous dispersion,[13] hydrogen atom scattering factors were taken from ref. 14. With each structure the positions of the Hg atoms were determined from a Patterson synthesis and the remaining atoms were located by standard difference Fourier syntheses. All structures were refined by full-matrix least-squares techniques as described previously.[15] Hydrogen atoms could not be located and were not included in the models. In the final cycles all the non-hydrogen atoms were refined anisotropically and weighting schemes were included $\{w = [\sigma^2(F_o) + 0.000\,01(F_o^2)]^{-1}\}$ in both cases.

Results and Discussion

The direct reaction of mercury(II) chloride or mercury(II) iodide with either Me_2S_2 or Et_2S_2 yields crystalline products after cooling the solutions to *ca.* 0 °C. However, in most cases the disulphide complexes decompose after the crystals are removed from the mother-liquor. The compound $HgCl_2 \cdot Me_2S_2$ (**1**) also decomposes on standing, but, by rapidly transferring a crystal to a capillary and sealing it in with a drop of the mother-liquor,

Table 1. Crystallographic details for $HgCl_2 \cdot Me_2S_2$ (**1**) and $[NHEt_3][HgCl_3]$ (**2**)

Complex	(1)	(2)
Formula	$C_2H_6Cl_2HgS_2$	$C_6H_{16}Cl_3HgN$
M	365.69	409.15
a/Å	14.865(4)	7.639(2)
b/Å	9.185(1)	14.711(1)
c/Å	12.441(3)	11.074(3)
β/°	109.23(1)	100.28(1)
U/Å^3	1 603.8(7)	1 224.5(4)
Z	8	4
Space group	$C2/c$	$P2_1/n$
μ(Mo-K_α)/cm^{-1}	206.3	134.2
F(000)	1 312	764
D_c/g cm^{-3}	3.03	2.21
Scan range ($\Delta\omega$)/°	1.5(0.66 + 0.347 tan θ)	1.5(0.60 + 0.347 tan θ)
Scan speed/° min^{-1}	0.7—3.4	0.6—3.4
$\theta_{max.}$/°	25	25
No. of unique reflections	1 414	2 153
No. of observed reflections [$I > 3\sigma(I)$]	1 118	1 074
No. of variables	67	101
Max. residual electron density/e Å^{-3}	1.62 [Hg(2)]	1.61 (Hg)
Isotropic extinction parameter	8.1(3) × 10^{-5}	4.2(3) × 10^{-5}
Goodness of fit	1.06	1.12
R, R'	0.043, 0.044	0.046, 0.033

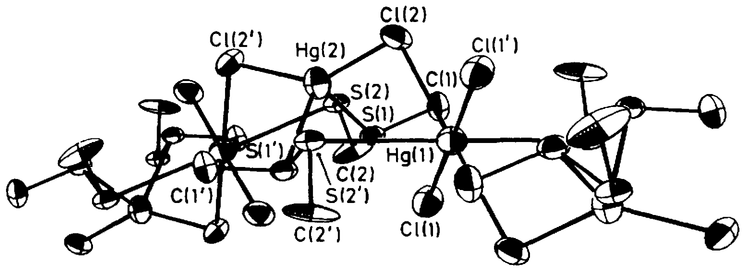

Figure 1. An ORTEP drawing (50% probability limit) of the $HgCl_2{\cdot}Me_2S_2$ polymer showing the atomic-labelling scheme

Table 2. Atomic co-ordinates ($\times 10^4$) for the non-hydrogen atoms of $HgCl_2{\cdot}Me_2S_2$ (**1**)

Atom	*x*	*y*	*z*
Hg(1)*	2 500	7 500	0
Hg(2)*	0	819(1)	2 500
Cl(1)	3 325(3)	9 177(6)	1 332(4)
Cl(2)	1 580(3)	−59(6)	3 363(4)
S(1)	324(3)	2 662(5)	954(3)
S(2)	−570(3)	1 809(5)	−527(3)
C(1)	1 484(10)	2 217(21)	916(15)
C(2)	−660(15)	3 360(23)	−1 440(16)

* Some co-ordinates for these atoms are set by the symmetry of the space group.

Table 3. Unique bond lengths (Å) and angles (°) for $HgCl_2{\cdot}Me_2S_2$ (**1**)

Hg(1)–Cl(1)	2.299(5)	Hg(2)–Cl(2)	2.379(4)
Hg(1)–Cl(2B)	3.115(5)	Hg(2)–S(1)	2.722(5)
Hg(1)–S(2D)	3.209(5)	S(1)–S(2)	2.040(5)
		S(1)–C(1)	1.79(2)
		S(2)–C(2)	1.80(2)
Cl(1)–Hg(1)–Cl(2B)	88.9(1)	Cl(1)–Hg(1)–S(2E)	91.2(1)
Cl(1)–Hg(1)–S(2D)	88.8(1)	Cl(2B)–Hg(1)–S(2D)	104.2(1)
Cl(1)–Hg(1)–Cl(2C)	91.1(1)	Cl(2C)–Hg(1)–S(2D)	75.8(1)
Cl(2)–Hg(2)–S(1)	98.7(1)	Cl(2)–Hg(2)–S(1F)	105.6(1)
Cl(2)–Hg(2)–Cl(2F)	140.4(2)	S(1)–Hg(2)–S(1F)	103.0(1)
Hg(2)–S(1)–S(2)	100.6(2)	Hg(1G)–S(2)–S(1)	95.7(2)
Hg(2)–S(1)–C(1)	105.8(6)	Hg(1G)–S(2)–C(2)	95.0(8)
S(2)–S(1)–C(1)	103.6(6)	S(1)–S(2)–C(2)	99.0(6)
Hg(1A)–Cl(2)–Hg(2)	101.2(2)		

Capital letters in the atom number denote the following equivalent positions: A $x,1-y,\frac{1}{2}+z$; B $x,1-y,z-\frac{1}{2}$; C $\frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}-z$; D $\frac{1}{2}+x,\frac{1}{2}+y,z$; E $-x,1-y,-z$; F $-x,y,\frac{1}{2}-z$; G $x-\frac{1}{2},y-\frac{1}{2},z$.

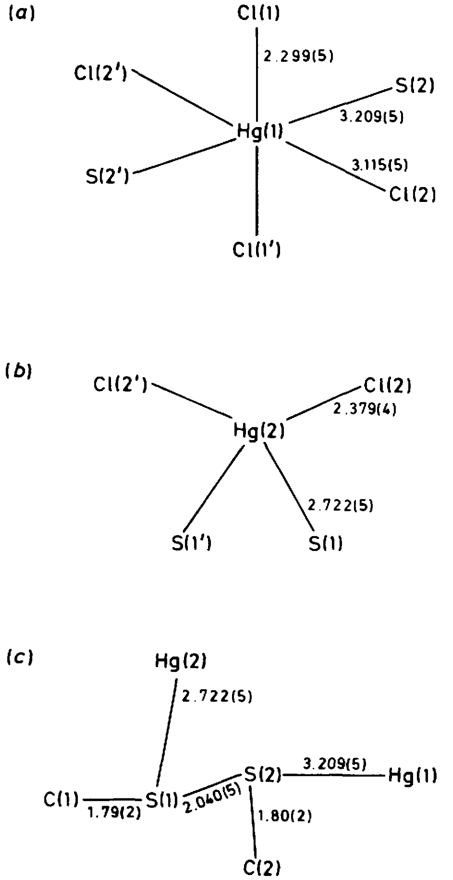

Figure 2. The $HgCl_2{\cdot}Me_2S_2$ chain may be represented by (*a*) the octahedral co-ordination sphere about Hg(1), (*b*) the tetrahedral geometry about Hg(2), and (*c*) the asymmetric linkage of the Me_2S_2 unit to the two Hg atoms

we were able to collect a data set at room temperature. The atomic co-ordinates for (**1**) are presented in Table 2, while in Table 3 the unique bond lengths and angles are given. Figure 1 illustrates the connectivity of this polymeric molecular structure. There are two types of mercury environments connected by bridging chloride and dimethyl disulphide ligands. Hg(1) occupy sites with $\bar{1}$ symmetry, and have a greatly compressed octahedral co-ordination [Figure 2(*a*)]. The axial bonds to the terminal Cl(1) atoms are in the range normally found for digonal Hg^{II}–Cl bonds (2.26—2.32 Å).[16] However, the equatorial bonds are much longer [3.115(5) Å] being only slightly shorter than the van der Waals contact. Such arrangements are found in the crystal structures of the compounds $Na[HgCl_3]$, $Na[HgCl_3]{\cdot}2H_2O$, and $[NH_4][HgCl_3]$ which possess tetragonally compressed $HgCl_6$ octahedra.[17] The Hg(2) ions occupy sites of two-fold symmetry as shown in Figure 2(*b*). The Hg(2)–Cl(2) bond lengths are slightly shorter than those normally found[18] in tetrahedral chloromercury complexes (2.58—2.62 Å). The Cl(2) atoms, which formally bridge between Hg(1) and Hg(2), are therefore much more strongly associated with Hg(2) than Hg(1).

The co-ordination of Hg(2) to S(1) [2.722(5) Å] is much weaker than that found in the distorted $HgCl_2S_2$ tetrahedral unit in the structure of Hg(SPr^i)Cl [Hg–S 2.537(6) Å].[19] Furthermore, as shown in Figure 2(*c*), the co-ordination mode of the Me_2S_2 is very unsymmetrical with the Hg(1)–S(2) interaction being barely within contact distance. This situation appears to be the most unsymmetrical bridging organic disulphide so far reported. Even in the $[Ag_2(Ph_2S_2)_4]^{2+}$ cation the bridging disulphide Ag–S bond lengths only differ by *ca.* 0.135 Å,[3] compared with almost 0.5 Å in the present structure.

Table 4. Raman spectral data for ν(S–S) in dimethyl disulphide complexes

Compound	ν(S–S)/cm^{-1}	Ref.
Me_2S_2	504	9
$HgCl_2{\cdot}Me_2S_2$	493	This work
$CuCl{\cdot}Me_2S_2$	482	9
$n$$CuI{\cdot}Me_2S_2$	475	9

Table 5. Atomic co-ordinates (Hg, Cl × 10^4; N, C × 10^3) for the non-hydrogen atoms of $[NHEt_3][HgCl_3]$ (**2**)

Atom	*x*	*y*	*z*
Hg	−2 287.8(9)	289.5(5)	622.1(6)
Cl(1)	−678(5)	−1 180(2)	381(4)
Cl(2)	−1 474(6)	724(3)	2 706(4)
Cl(3)	−4 388(6)	867(4)	−1 026(5)
N	69(2)	808(1)	332(2)
C(1)	250(3)	835(2)	386(2)
C(2)	267(3)	939(1)	397(2)
C(3)	−64(4)	828(2)	419(2)
C(4)	−238(2)	816(1)	376(2)
C(5)	69(3)	711(2)	303(3)
C(6)	169(3)	678(2)	203(2)

Table 6. Bond distances (Å) and angles (°) for $[NHEt_3][HgCl_3]$ (**2**)

Hg–Cl(1)	2.525(4)	N–C(1)	1.46(3)
Hg–Cl(2)	2.368(5)	N–C(3)	1.55(3)
Hg–Cl(3)	2.362(5)	N–C(5)	1.47(3)
Hg–Cl(1A)	2.997(5)	C(1)–C(2)	1.53(3)
Hg–Cl(3B)	3.154(5)	C(3)–C(4)	1.34(3)
		C(5)–C(6)	1.52(4)
Cl(1)–Hg–Cl(2)	106.6(2)	Hg–Cl(1)–Hg(A)	94.6(1)
Cl(1)–Hg–Cl(3)	120.2(2)	Hg–Cl(3)–Hg(B)	98.6(2)
Cl(1)–Hg–Cl(1A)	85.4(1)		
Cl(1)–Hg–Cl(3B)	88.4(1)	C(1)–N–C(3)	112(2)
Cl(2)–Hg–Cl(3)	132.8(2)	C(1)–N–C(5)	109(2)
Cl(2)–Hg–Cl(1A)	99.2(1)	C(3)–N–C(5)	110(2)
Cl(2)–Hg–Cl(3B)	94.9(1)	N–C(1)–C(2)	112(2)
Cl(3)–Hg–Cl(1A)	90.6(1)	N–C(3)–C(4)	118(2)
Cl(3)–Hg–Cl(3B)	81.4(2)	N–C(5)–C(6)	119(2)

Capital letters in the atom number denote the following equivalent positions: A $\bar{x},\bar{y},\bar{z}$; B $\bar{x} - 1,\bar{y},\bar{z}$.

Consistent with this weak metal–sulphur interaction the sulphur–sulphur bond length [2.040(5) Å] is only slightly longer than that found in free Me_2S_2 [2.022(3) Å].[20] This differs significantly from the S–S bond length of 2.111(13) Å found in $[Re_2Br_2(CO)_6(S_2Me_2)]$.[2] The C–S–S–C torsion angle [90(1)°] is clearly in agreement with the expectation of ~90° for a stable conformation. Not surprisingly, the Raman spectral data (Table 4) are also consistent with the interpretation that the S–S bond in the co-ordinated Me_2S_2 in (**1**) is only slightly weaker than in the free disulphide.

The unexpected isolation of $[NHEt_3][HgCl_3]$ (**2**) from solutions of $HgCl_2$ in reagent-grade Me_2S_2 (as proven by the *X*-ray crystallographic characterization of this compound discussed below) is worthy of some comment. It was found that trace quantities of NEt_3 and water present in the reagent-grade Me_2S_2 gave rise to the following, presumed, reactions (3)—(5).

$$HgCl_2 + H_2O \longrightarrow Hg(OH)Cl + HCl \qquad (3)$$

$$NEt_3 + HCl \longrightarrow [NHEt_3]^+ + Cl^- \qquad (4)$$

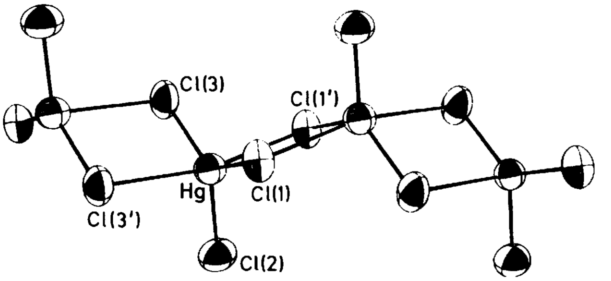

Figure 3. An ORTEP drawing (50% probability limit) of the $[HgCl_3]^-$ chain. Only the unique section of anion is labelled for clarity

$$[NHEt_3]^+ + HgCl_2 + Cl^- \longrightarrow \underset{\textbf{(2)}}{[NHEt_3][HgCl_3]} \qquad (5)$$

In the absence of water the salt (**2**) was not obtained, and an excess of water also precluded this synthesis. Being unaware of the possible presence of NEt_3 in Me_2S_2 (presumably it is utilized in the purification process, after the initial Merox process for the oxidation of thiols), we at first believed that compound (**2**) was an oxonium salt $[OEt_3][HgCl_3]$ on the basis of ^1H and ^{13}C n.m.r. data. Hence we undertook a crystal structure, which did not fully resolve the issue. However, the subsequent identification of NEt_3 by a g.c.–m.s. analysis of the Me_2S_2 indicated the true identity of (**2**). The atomic co-ordinates for (**2**) are shown in Table 5. The bond angle and bond length data in Table 6, and the anion chain presented in Figure 3, indicate that $[NHEt_3][HgCl_3]$ adopts the same pattern of Hg–Cl interactions as several other $[HgCl_3]^-$ salts. The anions possess one terminal Hg–Cl bond [Hg–Cl(2)], and two chlorides which loosely co-ordinate to adjacent mercury atoms to create effective five-fold (approximately trigonal bipyramidal) co-ordination. The chains so created run parallel to the *a* axis. The complexes $[SMe_3][HgCl_3]$ and $[NEt_4][HgCl_3]$ possess very similar structures.[21,22] The axial Hg–Cl bonds in the trigonal bipyramid [average length 3.077(5) Å] are much longer than the bonds in the plane. This compound represents yet another example of the ability of mercury(II) to complete an 'effective co-ordination' as described by Grdenic.[17] We note, in passing, that of the crystal structures of salts of the $[HgCl_3]^-$ anion so far published, the vast majority possess cations which have three-fold symmetry.

The possible reactions of mercury(I) halides with disulphides were investigated briefly. The likely result would be the oxidative addition of RSSR to the Hg–Hg bond. While no crystalline products were obtained, the absence of a ν(S–S) stretching mode in the Raman spectra of products so obtained suggested that this was indeed the result. However to date we have been unable to purify and characterize these products.

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