Crystal Structure of Di-μ-chloro-dichlorobis(methyl pyrrolidine-1-carbodithioate)dimercury(II)

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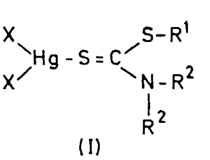
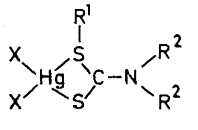
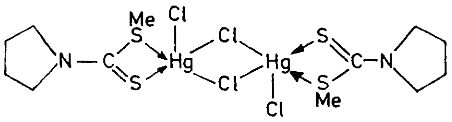
The crystal structure of the title compound has been determined from *X*-ray diffractometer data and refined by full-matrix least-squares to *R* 0·09 (all 1167 data). Crystals are triclinic, space group $P\bar{1}$, a = 8·618(1), b = 8·637(1), c = 8·544(1) Å, α = 90·72(1), β = 101·67(1), γ = 113·73(1)°, Z = 2. The mercury atom is irregularly four-co-ordinated by two crystallographically equivalent bridging chlorine atoms, Hg–Cl, Cl′, 2·57, 2·78(1) Å, Hg–Cl–Hg′, 92·7(3)°, leading to a pseudo dimeric molecule about the centre of symmetry; a second non-bridging chlorine is at 2·37(1) Å, and the non-methylated sulphur of the unidentate dithioester at 2·42(1) Å. The C–S distances in the ester are not equal C=S(Hg) 1·68(4), C–S(Me) 1·77(4) Å, S–C–S, 123(2)°. The remainder of the dithiocarbamate ligand geometry is as expected.

A NUMBER of synthetic and structural reports have recently appeared concerning derivatives or adducts of mercury(I) and mercury(II) chloride, the latter behaving as a Lewis acid with a variety of mono- and di-thio-ligands, both uni- and bi-dentate.[1-17] The dithio-ligand species have been derived from the dithio-carbamic and -phosphoric acids and the xanthates, or their oxidation products such as the thiuram disulphides. A related series of 1 : 1 adducts of the mercury(II) halides with the *S*-alkyl *NN*-dialkyldithiocarbamate esters $R^1S{\cdot}CS{\cdot}NR^2_2$ has been reported;[4] of the two structures (I) and (II) considered feasible, (I) was favoured on the basis of spectroscopic and molecular-weight and conductivity measurements, the mercury atom being supposedly three-co-ordinate. As this is one of the less-common co-ordination numbers of mercury(II), a structure determination was undertaken.


(I)


(II)

A number of complexes of the type $HgCl_2(MeS{\cdot}CS{\cdot}NR_2)$ were prepared by mixing solutions of the reactants in ethanol.[14,18] $HgCl_2[MeS{\cdot}CS{\cdot}N(CH_2)_4]$ yielded crystals suitable for structure determination, and the structure (III) was solved, by use of a crystal 0·06 × 0·04 × 0·15 mm.


(III)

EXPERIMENTAL

Cell dimensions were obtained by a least-squares fit of the angular parameters of 15 reflections centred in the counter aperture of a Syntex $P\bar{1}$ diffractometer. A unique data set in the range $2\theta < 100°$ (Cu-K_α radiation, Ni filtered, $\lambda = 1{\cdot}5418$ Å) was collected by a conventional 2θ—θ scan, yielding 1167 independent reflections, all of which were used in the subsequent structure determination and refinement with unit weights.

Crystal Data.—$C_6H_{11}Cl_2HgS_2$, M = 432·7, Triclinic, a = 8·618(1), b = 8·637(1), c = 8·544(1) Å, α = 90·72(1), β = 101·67(1), γ = 113·73(1)°, U = 567·1 Å³, D_m = 2·50, Z = 2, D_c = 2·53, $F(000)$ = 400. μ(Cu-K_α) = 337 cm⁻¹. Space group $P\bar{1}$ (C_i^1).

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares to a final R of 0·086, R' $\{[\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}\}$ 0·12; anisotropic thermal parameters for the heavy non-carbon atoms were of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Non-methyl hydrogen atoms were included towards the end of the refinement, in calculated positions. No parameter shift in the final cycle was $>0{\cdot}1\sigma$ and a final difference-Fourier map showed no significant features. Scattering factors for the neutral atoms were taken from ref. 19, those for mercury, chlorine, and sulphur being corrected for the effects of anomalous dispersion ($\Delta f'$,$\Delta f''$).[20] All data processing, including absorption correction and computation, was carried out on the CDC 6200 machine at the

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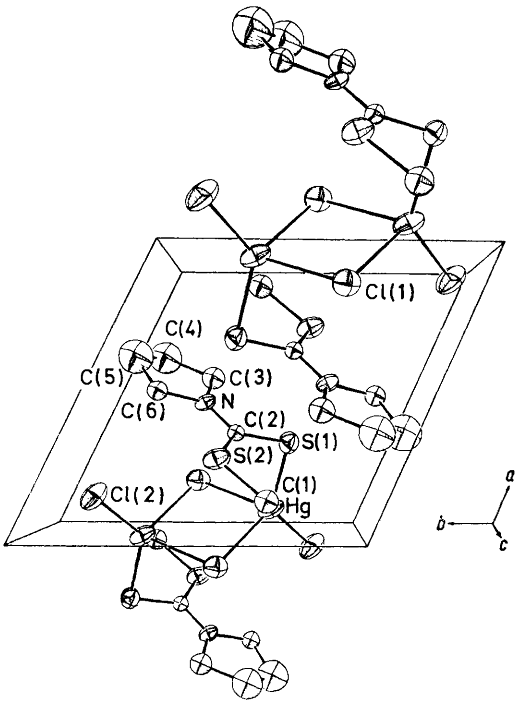
TABLE 1

Final atomic fractional cell (× 10^3, for Hg × 10^4) and thermal (× 10^3) parameters, with least-squares estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	0536(2)	3029(2)	0234(2)	38(1)	45(1)	38(1)	0(1)	2(1)	−8(1)
Cl(1)	842(1)	399(1)	125(1)	45(6)	50(6)	42(5)	17(5)	14(4)	14(4)
Cl(2)	110(1)	905(1)	200(1)	64(7)	42(6)	49(6)	0(5)	−4(5)	−8(5)
S(1)	317(1)	348(1)	220(1)	44(6)	33(5)	44(6)	15(5)	3(5)	−4(4)
S(2)	262(1)	550(1)	480(1)	37(5)	46(6)	35(5)	7(5)	12(4)	0(4)
N	468(3)	682(3)	293(3)	23(16)	28(16)	23(15)	2(13)	−4(12)	−7(12)
C(1)	110(5)	332(5)	487(5)	45(10) *					
C(2)	354(5)	534(4)	316(4)	25(8) *					
C(3)	565(5)	702(5)	159(5)	45(10) *					
C(4)	641(7)	893(7)	159(7)	90(17) *					
C(5)	639(8)	979(8)	297(8)	100(18) *					
C(6)	510(4)	848(4)	380(4)	33(9) *					

* Isotropic.

University of Western Australia, by use of a local adaption of the '*X*-ray '72' program system.[21] Estimated hydrogen atom positions and structure factor tables are listed in Supplementary Publication No. SUP 21124 (8 pp, 1 microfiche).* Results are shown in Tables 1 and 2.



Unit-cell contents and atomic numbering, projected down the *c* axis (perspective view; 50% ellipsoids)

TABLE 2

Interatomic distances (< 3·0 Å) and angles (°) with least-squares estimated standard deviations in parentheses

Hg–S(1)	2·42(1)	S(1)–Hg–Cl(1^{I})	115·1(3)
Hg–Cl(1^{I})	2·57(1)	S(1)–Hg–Cl(1^{II})	101·5(3)
Hg–Cl(1^{II})	2·78(1)	S(1)–Hg–Cl(2^{III})	131·9(4)
Hg–Cl(2^{III})	2·37(1)	Cl(1^{I})–Hg–Cl(1^{II})	87·3(3)
		Cl(1^{I})–Hg–Cl(2^{III})	107·5(4)
		Cl(1^{II})–Hg–Cl(2^{III})	101·8(3)
		Hg(1)–Cl(1^{I})–Hg(1^{IV})	92·7(3)
S(1) ··· S(2)	3·04(2)	C(1)–S(2)–C(2)	103(2)
C(1)–S(2)	1·82(4)	S(1)–C(2)–S(2)	123(2)
C(2)–S(1)	1·68(4)	N–C(2)–S(1)	124(3)
C(2)–S(2)	1·77(4)	N–C(2)–S(2)	112(3)
C(2)–N	1·31(4)	C(2)–S(1)–Hg	99(1)
N–C(3)	1·52(5)	C(2)–N–C(3)	122(3)
N–C(6)	1·48(5)	C(2)–N–C(6)	126(3)
C(3)–C(4)	1·51(7)	C(3)–N–C(6)	112(3)
C(4)–C(5)	1·39(10)	N–C(3)–C(4)	100(4)
C(5)–C(6)	1·53(7)	C(3)–C(4)–C(5)	114(5)
		C(4)–C(5)–C(6)	107(4)
		C(5)–C(6)–N	105(4)

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

I $x - 1, y, z$
II $1 - x, 1 - y, \bar{z}$
III $\bar{x}, 1 - y, \bar{z}$
IV $\bar{x}, \bar{y}, \bar{z}$

DISCUSSION

The mercury atom, positioned close to the origin, is bridged asymmetrically to its inversion image by a pair of inversion-related chlorine atoms [Hg–Cl($1^{I,II}$) 2·57 and 2·78(1), Cl(1^{I})–Hg–Cl(1^{II}) 87·3(3), Hg–Cl(1^{I})–Hg^{IV} 92·7(3)°] to form a centrosymmetric dimer. A third co-ordination site is filled by an independent chlorine atom Cl(2) at 2·37(1) Å, and the fourth by the non-methylated sulphur atom S(1) of the dithioester at 2·42(1) Å. The angular geometry about the mercury atom is highly irregular, the angles X–Hg–Y ranging from 87 to 132°; as might be expected the smallest of the angles is contained by the two longest contacts Cl($1^{I,II}$) while the largest is spanned by the pair of closest contacts, Cl(2) and S(1). The validity of describing the mercury as being 'three-co-ordinate' in the solid state is dubious, whatever it may be in solution, since four close contacts are involved; it would be of interest to compare the Raman spectra of the solid and solution in order to examine this point further. A well-defined example of planar three-co-ordination about a central mercury atom is found in the complex [$Hg(tu)_2Cl$] Cl (tu = thiourea),[1,2] in which the two Hg–S distances are 2·42 Å and Hg–Cl 2·57 Å; the system, however, is HgS_2Cl, rather than $HgSCl_2$. It seems unlikely that examples of three-co-ordinate $HgSCl_2$ will be observed in the solid state; the tendency, exemplified in the present case, seems to be for the co-ordination type to become $HgSCl(Cl_{1/2})_2$, by virtue of a bridging chlorine giving rise to pseudo four-co-

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index Issue.

[21] '*X*-Ray System' of programs, Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A., June, 1972.

ordination. Similar examples occur (Table 3) in the complexes $(Et_2S)2HgCl_2$ (A) [10] and $(HgCl_2)2/3(tu)$ (B).[4]

TABLE 3

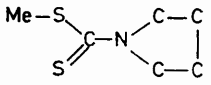
	Present work	(A)	(B)
Hg–S	2·42	2·40	2·40
Hg–Cl	2·37	2·35	2·39
S–Hg–Cl	132°	158°	155°
Hg–Cl(bridge)	2·57, 2·78	2·70, 2·85	2·84, 2·94

An Hg–S distance of *ca.* 2·40 Å is quite usual, and occurs in a variety of co-ordination types, *e.g.*, linear $Hg(S{\cdot}CS{\cdot}NEt_2)_2$,[7,8] and $Hg(S{\cdot}PS{\cdot}OPr^i{}_2)_2$.[15] However, by contrast the Hg–S distances in both forms of $[Hg(tu)_4]Cl_2$ are >2·50 Å.[3,5]

Clearly the ester is unidentate, co-ordinating to the mercury through S(1); the Hg · · · S(2) distance is very much greater and exceeds 3·8 Å. The equation of the ligand plane, described in an orthogonal frame (X,Y,Z), related to the $[x,y,z]$ frame by the transformation

$$[X,Y,Z] = \begin{bmatrix} a & b\,.\cos\gamma & c\,.\cos\beta \\ 0 & b\,.\sin\gamma & c\,.\,(\cos\alpha - \cos\beta\,.\cos\gamma)/\sin\gamma \\ 0 & 0 & U/a\,.\,b\,.\sin\gamma \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

and defined by S(1),S(2),N,C(2),C(3),C(6) is: $0{\cdot}743X - 0{\cdot}092Y + 0{\cdot}663Z = 1{\cdot}601$; deviations (Å) of atoms from this plane are: S(1) 0·03, S(2) 0, C(2) −0·04, N(1) 0·02, C(3) −0·01, C(6) 0·01 (σ 0·025 Å); Hg 2·33, C(1) −0·10, C(4) −0·26, and C(5) −0·02. The methyl group thus conforms to the ligand plane fairly well, but the deviation of the mercury is gross. Within the five-membered pyrrolidine ring, the usual large deviation [22,23] of one of the outer carbon atoms, C(4), is observed, the associated angle C(3)–C(4)–C(5) being considerably larger (114°) than the remainder and accompanied by high thermal motion. The difference between the C(2)–S(1) and C(2)–S(2) distances [1·68 and 1·77(4) Å] is significant at better than the 2σ level; this, together with the observation that C(2)–N is, as is usual in complexes of this type, *ca.* 1·31 Å, suggests that the canonical forms (IV) and (V) which would be expected to contribute to the bonding in the free ester may also be significant here. If the less significant difference between S(2)–C(1) and S(2)–C(2) [1·82 and 1·77(4) Å] is real, then form (VI) may also contribute significantly by the use of suitable *d* orbitals on S(2). The shortness of C(2)–S(1) is somewhat surprising in view of the involvement of S(1) in bond formation to the mercury; this S(1)–Hg bond presumably utilises the *p*- (or *d*-) orbital on the sulphur, since the mercury is grossly distorted from the ligand plane, lying almost at right angles to it [C(2)–S(1)–Hg 99°]. The angle S(1)–C(2)–S(2) [123(2)°] is significantly larger than that observed in the (presumably) highly strained symmetrical bidentate dithiocarbamate–metal complexes (*ca.* 110°),[24] and is more comparable with that observed in the free dithiocarbamate anion [25] and in the thiuram disulphide [26] (*ca.* 120°). Likewise the S(1) · · · S(2) distance [3·04(2) Å] is more compatible with the latter where it is usually *ca.* 3·0 Å, rather than the former where it is usually *ca.* 2·8 Å. There is a significant difference between the angles N–C(2)–S(1) and N–C(2)–S(2) [124 and 112(3)°]; the larger of the two angles is opposed to the C=S double bond.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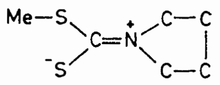
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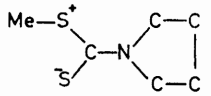
(VI)

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