Crystal Structure of Bis(*NN*-diethyldithiocarbamato)mercury(II)

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The crystal structure of the title compound, has been determined by single crystal *X*-ray diffraction by conventional heavy-atom methods. The structure was refined by block-diagonal least-squares procedures to a final *R* of 0·12 for 810 visually estimated reflections. Crystals are monoclinic, $P2_1/a$, a = 11·861(8) b = 15·02(1), c = 4·751(4) Å, β = 106·30(6)°, Z = 2. The centrosymmetric mercury atoms have three pairs of sulphur contacts in a highly distorted array, one pair close [Hg–S 2·397(6) Å], and the others arising out of a sharing of the second sulphur between adjacent mercury atoms [Hg–S 2·990(7), Hg–S′ 3·307(7) Å] yielding a helical quasi-polymeric array. The asymmetric co-ordination of the ligand is reflected in associated distortion of the CS_2 geometry [C–S, 1·69(2) 1·76(2) Å, S–C–S 120(1)°]. The remainder of the ligand geometry is normal.

DURING structural studies on transition metal dithiochelate complexes, the mercury(II) complex of *NN*-diethyldithiocarbamate was examined and its unit cell found to be non-isomorphous with those of the zinc and cadmium derivatives.[1,2] Moreover, the small size of the cell coupled with a density determination showed that in the observed symmetry of $P2_1/a$, occupancy of a special position of symmetry $\bar{1}$ by the mercury atom was implied; the co-ordination geometries of tetrahedral or octahedral with bidentate ligands are specifically excluded in these circumstances. To assist in delineation of the molecular geometry a structure determination was undertaken. During the course of this work the structure of the related complex $[Hg\{(Pr^iO)_2PS_2\}_2]$ was reported;[3] in this structure the mercury does not have site-symmetry $\bar{1}$, having five near-mercury-neighbours and is implicitly different in its geometry from the present compound.

EXPERIMENTAL

The complex was prepared by the addition of a stoicheiometric quantity of the sodium salt of the ligand in water to an aqueous solution of mercury(II) nitrate, and was recrystallized from chloroform. Crystals suitable for *X*-ray work were grown as large, irregular, interlocked, yellow leaves by the slow evaporation of a chloroform solution. A block-shaped section 0·10 × 0·05 × 0·13 mm was cut and used for the subsequent structure determination; preliminary photography showed it to be a single crystal.

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[1] H. P. Klug, *Acta Cryst.*, 1966, **21**, 536; M. Bonamico, G. Mazzone, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 898.

[2] A. Domenicano, L. Torelli, A. Vaciago, and L. Zambonelli, *J. Chem. Soc.* (*A*), 1968, 1351.

[3] S. L. Lawton, *Inorg. Chem.*, 1971, **10**, 329.

Non-integrated X-ray data were collected at room temperature by use of the multiple-film equi-inclination Weissenberg method with the crystal section mounted about a and c respectively for the layers 0—$4kl$, $hk0$—2. There was no evidence for deterioration in the crystal during data collection, either from reflection quality or later agreement analyses. Nickel-filtered copper radiation was used throughout [$\lambda(K_{\alpha1}) = 1{\cdot}5406$, $\lambda(K_{\alpha2}) = 1{\cdot}5444$, $\lambda(K_{\bar{\alpha}}) = 1{\cdot}5418$ Å).[4]

The unit cell was calibrated by use of a Syntex $P\bar{1}$ automatic diffractometer. Angular orientation parameters were refined for 15 reflections and the unit cell fitted by a least-squares routine, the reflection being allocated a weight $w = \sin\theta$.

Crystal Data.—$C_{10}H_{20}HgN_2S_4$, $M = 496{\cdot}6$, Monoclinic, $a = 11{\cdot}861(8)$, $b = 15{\cdot}02(1)$, $c = 4{\cdot}751(4)$ Å, $\beta = 106{\cdot}30(6)^\circ$, $U = 812$ Å^3, $D_m = 1{\cdot}98$ ($\pm 0{\cdot}03$) (flotation, cyclohexane–bromoform), $Z = 2$, $D_c = 2{\cdot}04$, $F(000) = 456$. Space group $P2_1/a$ (No. 14, C^5_{2h})[5] from systematic absences. μ(Cu-K_α) = 229 cm^{-1}, transmission coefficient range 0·116—0·375.

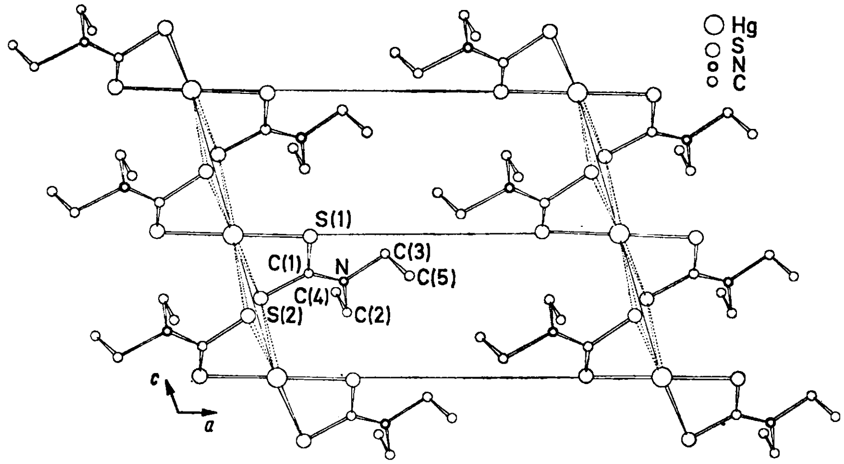

FIGURE 1 View of adjacent unit-cell pair contents projected down b; the lower half of the cell only is shown for clarity. The atom numbering scheme is given

The intensities of 810 independent, observed reflections were visually estimated by use of a graded intensity strip calibrated with a microdensitometer; only these non-zero reflections were included in the structure determination. The raw data were corrected for absorption[6] and Lorentz and polarization factors and then scaled by internal correlation, all reflections being assigned unit weights.[7]

Structure Determination.—The number of formula units in the unit cell ($Z = 2$) implies that the asymmetric unit is one half of the formula unit and occupancy of a special position of symmetry $\bar{1}$ by the mercury atom. This assumption was vindicated by the computation of an unmodified three-dimensional Patterson synthesis computed on all data. A structure-factor calculation on the basis of mercury atoms positioned at (0,0,0), ($\frac{1}{2}$,$\frac{1}{2}$,0) with an arbitrary isotropic thermal parameter B 3·0 Å^2 gave R 0·54. The sulphur atoms were located in a subsequent three-dimensional Fourier synthesis giving an initial R 0·38; anisotropic thermal motion of the mercury was pronounced to the extent that the co-ordinating atoms were indistinct. Accordingly, the mercury atom was refined by use of a block-diagonal (3 × 3, 6 × 6) least-squares routine and with anisotropic thermal motion of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$, the sulphur atom positional and isotropic thermal parameters being included in the refinement (a local program SFLS 1, 2 by A.I.M. Rae was used). The function $w(|F_o| - |F_c|)^2$ was minimized during the refinement, with unit weights on each reflection and after six cycles R was 0·18. A Fourier synthesis at this stage located all remaining non-hydrogen atoms. With anisotropic thermal parameters for the sulphur atoms, the atomic positional and thermal parameters for all atoms were refined to a final R 0·122. During this refinement, a weighting scheme of the form $w = (a + |F_o| + b|F_o|^2 + c|F_o|^3)^{-1}$ was applied to the data, a, b, and c being redetermined as refinement proceeded. Final parameter shifts were $< 0{\cdot}2\sigma$. A final difference Fourier was substantially flat, the largest peak (of the order of 0·5 carbon atom) being at the mercury site. Final weighting scheme constants were $a = 0{\cdot}90$, $b = 0{\cdot}28$, $c = 0{\cdot}003$.

Scattering factors employed for neutral mercury were taken from ref. 8, corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$ according to ref. 9), and for sulphur, nitrogen, and carbon from ref. 8. The final set of observed and calculated structure factors are given in Supplementary Publication No. SUP 20552 (3 pp., 1 microfiche).* Final atomic fractional cell and thermal parameters are given in Table 1, with least-squares estimated standard deviations which should be treated circumspectly in view of the block-diagonal refinement procedure. The unit-cell contents are

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[4] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 59.

[5] Ref. 4, vol. I, p. 99.

[6] N. W. Alcock in 'Crystallographic Computing,' Munksgaard, Copenhagen, 1971, p. 271; Program ABSCOR.

[7] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, 1965, **18**, 129.

[8] Ref. 4, p. 210 ff.

[9] Ref. 4, p. 213 ff.

depicted in Figure 1 which also gives the atomic nomenclature system. Interatomic distances and angles computed [10] are given in Table 2(*a*); a least-squares plane calculated through the ligand is given in Table 2(*b*).

TABLE 1

Final atomic positional co-ordinates and thermal parameters of the asymmetric unit with block-diagonal least-squares estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	$B/Å^2$
Hg	0	0	0	*
S(1)	0·1979(5)	0·0270(4)	0·9911(13)	*
S(2)	0·0200(5)	0·1366(5)	0·5583(15)	*
N	0·247(2)	0·162(1)	0·679(4)	4·3(4)
C(1)	0·162(2)	0·114(1)	0·734(4)	3·2(3)
C(2)	0·237(2)	0·230(2)	0·462(5)	4·4(5)
C(3)	0·379(2)	0·145(2)	0·860(5)	4·9(5)
C(4)	0·222(3)	0·320(2)	0·595(6)	6·9(7)
C(5)	0·435(3)	0·081(3)	0·713(8)	7·5(7)

* Anisotropic thermal parameters ($\times 10^4$)

Atom	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Hg	54(1)	−21(1)	185(7)	52(1)	62(4)	730(9)
S(1)	42(4)	−4(5)	44(20) †	59(2)	60(10) †	480(20) †
S(2)	50(4)	18(5)	200(20) †	52(3)	40(10) †	870(40) †

† Rounded.

TABLE 2

(*a*) Interatomic distances (Å) and angles (°), with block diagonal least-squares estimated standard deviations in parentheses

(i) 'Bonded' parameters within the asymmetric unit, $Hg(S_2CNEt_2)$

Hg–S(1)	2·397(6)	C(1)–N	1·32(3)
Hg–S(2)	2·990(7)	N–C(2)	1·43(5)
S(1)–C(1)	1·76(2)	N–C(3)	1·57(3)
S(2)–C(1)	1·69(2)	C(2)–C(4)	1·53(4)
S(1) · · · S(2)	2·99(1)	C(3)–C(5)	1·46(5)
S(1)–Hg–S(2)	66·4(2)	S(1)–C(1)–S(2)	120(1)
Hg–S(1)–C(1)	95·1(7)	S(1)–C(1)–N	119(1)
Hg–S(2)–C(1)	77·5(7)	S(2)–C(1)–N	121(1)
N–C(2)–C(4)	109(2)	C(1)–N–C(2)	127(2)
N–C(3)–C(5)	111(2)	C(1)–N–C(3)	121(2)
		C(2)–N–C(4)	112(2)

(ii) 'Non-bonded' distances (<3·5 Å) and angles (selected)

$Hg^I \cdots S(2)$	3·307(7)	$S(1) \cdots S(2)$	2·99(1)
$S(2) \cdots Hg \cdots S(2)^I$	97·8(2)		

The Roman numeral I denotes the transformation: (*x*, *y*, 1 + *z*) (see Figure 2).

(*b*) Equation of the least-squares plane through the ligand expressed in orthogonal co-ordinates: $X = ax + cz \cos \beta$, $Y = by$, $Z = cz \sin \beta$. Deviations (Å) of atoms from the plane are given

Plane: S(1), S(2), N(1), C(1)—(3)

Equation: $-0{\cdot}268X + 0{\cdot}659Y + 0{\cdot}703Z = 3{\cdot}230$

Deviations: Hg 0·33, S(1), −0·06, S(2) 0·06, C(1) 0·00, N(1) 0·00, C(2) −0·07, C(3) 0·07, C(4) 1·35, C(5) −1·27

Computation was carried out on a DEC PDP 10 at the University of Western Australia.

DISCUSSION

The basis of the structure is the sequence of linear arrays of mercury atoms, spaced by the distance $c = 4{\cdot}75$ Å, at the positions $(0,0,n)$, $(\frac{1}{2},\frac{1}{2},n)$, n integral. Each mercury atom is surrounded by an array of four sulphur atoms, necessarily coplanar with it, from a pair of centrosymmetrically related dithiocarbamate ligands. A dominant tendency for utilization of linear *sp* hybrid bonding in this complex is evidenced by the fact that one pair of sulphur atoms, S(1), is at a markedly shorter distance [2·397(6) Å] than the other, S(2) [2·990(7) Å]. The ligand is not coplanar with the mercury atom [Table 2(*b*)]. S(2) is bridged to the neighbouring mercury atom at (0,0,1) at a distance close to the van der Waals' distance [3·307(7) Å; van der Waals' Hg · · · S contact, >3·35 Å].[3] Each mercury atom is thus surrounded by a highly distorted array of three pairs of sulphur atoms at 2·397, 2·990, and 3·307 Å. The overall result is displayed in Figures 1 and 2; Figure 2 also shows the overall result over several units cells, the mercury and sulphur atoms comprising a helical chain. Although the 'bonds' in this chain of length 3·307 Å must be very weak, the appearance of a rather similar chain in the structure of the *OO*′-di-isopropyl phosphorodithioate [3] invites comparison and suggests that intermolecular mercury–sulphur van der Waals' interactions dominate the crystal packing in these complexes. In the phosphorodithioate, however, the mercury atom is non-centrosymmetric and has only five near neighbours at 2·39, 2·39, 2·75, 2·89, and 3·41 Å. The functions of the ligands in the latter complex are different. In one ligand, which has a solely chelating function, the mercury–sulphur distances are similar to those found in the present structure, being 2·39 and 2·89 Å; the other ligand has a bridging function between successive mercury sites, one sulphur bonding to a mercury at 2·39 Å, and having a long contact at 3·40 Å, the other bonding to a previous mercury atom at 2·75 Å. As in this structure, the bonding of the mercury is dominated by *sp* hybrids, leading to a pair of approximately opposed bonds, to sulphur atoms each 2·39 Å (S–Hg–S 149·7°).

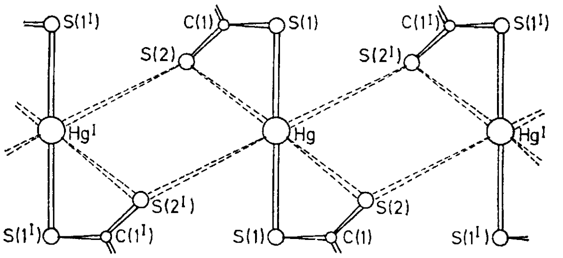

FIGURE 2 View of $[HgS_2]_n$ helical pseudo-polymeric array along the crystallographic *c* axis

The present structure * is in contrast to those of the various bis(dithiocarbamato)-derivatives of zinc and

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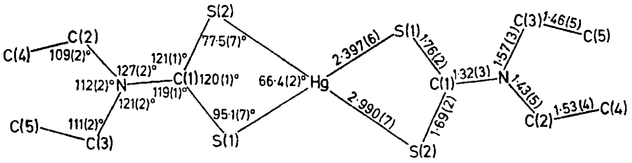
* *Note added in proof:* The isolation of three forms of this complex from acetone has recently been reported (H. Iwasaki, *Abs. 9th Internat. Congr. Cryst.*, Kyoto, 1972, vol. VI-32, p. S85). One form corresponds to that discussed in the present paper and structural details are in good agreement; a second form exhibits a similar structure to that of the zinc and cadmium analogues.[1,2]

[10] M. E. Pippy and F. R. Ahmed, Div. Pure and Appl. Phys., NRC, Ottawa, Canada, Program No. NRC 12 (BONDSCAN).

cadmium,[1,2] which are more akin to the structure of $[\mathrm{Hg}\{(\mathrm{Pr^iO})_2\mathrm{PS}_2\}_2]_\infty$ in which one ligand acts as a chelate and the other as a strong bridge.[3]

The ligand CS_2 geometry is akin to that found in related structures, *e.g.* $[\mathrm{As}(\mathrm{CS_2{\cdot}NEt_2})_3]$,[11] where the metal–sulphur bonds are of disparate length, and the carbon–sulphur distance has an inverse relation to the metal–sulphur. {A similar phenomenon is also found in $[\mathrm{Hg}\{(\mathrm{Pr^iO})_2\mathrm{PS}_2\}_2]_\infty$;[3] Hg–S(1), C(1)–S(1), 2·397, 1·76; Hg–S(2), C(1)–S(2), 2·990, 1·69 Å}. The S–C–S angle [120(1)°] is close to that found in the free ion,[12] and presumably reflects the absence of any constraint due to chelation.

The remainder of the ligand geometry is usual[13] within the limits of the rather large experimental errors on the outer atoms which are a consequence of the dominance of the scattering by the mercury atom. The disposition of the terminal carbon atoms is usual, as is the carbon–nitrogen distance [C(1)–N 1·32(3) Å] which reflects the π conjugation throughout the ligand.



[2/1520 *Received*, 29*th July*, 1972]

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[11] M. Colapiètro, A. Domenicano, L. Scaramuzza, and A. Vaciago, *Chem. Comm.*, 1968, 302.

[12] M. Colapietro, A. Domenicano, and A. Vaciago, *Chem. Comm.*, 1968, 572.

[13] R. Eisenberg, *Progr. Inorg. Chem.*, 1970, **12**, 295, and references therein.