Crystal Structure of a New Mercury(II) Complex Dichloromercury–2/3Thiourea

By **Peter Donald Brotherton** and **Allan Henry White**,* Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, 6009 Western Australia

The title compound has been isolated. Its composition and crystal structure have been determined from single-crystal *X*-ray photographic data by the heavy-atom method, and refined by block-diagonal least-squares to *R* 0·10 for 408 visually estimated reflections. Crystals are monoclinic, space group $P2_1/c$, $a = 8{\cdot}00(1)$, $b = 14{\cdot}99(2)$, $c = 7{\cdot}21(1)$, $\beta = 93{\cdot}5(5)°$, $Z = 6$ (for $HgCl_2$,2/3tu).

The complex is effectively $[\{HgCl(tu)\}Cl]_n,\frac{n}{2}HgCl_2$ (tu = thiourea), and consists of mercury atoms co-ordinated by thiourea (Hg–S, 2·40 Å) and chlorine (Hg–Cl, 2·39 Å, S–Hg–Cl, 155°); a further chlorine bridges these units in an infinite chain (Hg–Cl 2·84 and 2·94 Å) parallel to *c*. Discrete $HgCl_2$ molecules, centred on special positions, occupy interstices between the chains.

PREVIOUS studies have suggested the existence of mercury(II) chloride–thiourea (tu) adducts $HgCl_2,tu_n$, $n = 1$—4,[1] and the structures of several have been determined by *X*-ray crystallography.[2-6] During the preparation of $HgCl_2,tu_2$,[3] slow evaporation over a period of weeks yielded in addition a minute quantity of colourless needles. As the amount produced was too small for analysis or i.r. spectroscopic study and we have been unable to produce it since in greater quantity, a crystal-structure determination was carried out to establish its identity and structure.

EXPERIMENTAL

Photographic multiple-film equi-inclination Weissenberg data were collected from a single prismatic needle section (0·01 × 0·06 × 0·07 mm) about *a* and *c*; cell calibration was effected by superposition of aluminium powder lines ($a = 4{\cdot}0494$ Å) [7] on zero-layer photographs about all axes.

Crystal Data.—$HgCl_2(tu),0{\cdot}5HgCl_2 \equiv Hg_{1{\cdot}5}Cl_3tu \equiv Hg_{1{\cdot}5}Cl_3SCN_2H_4$, $M = 483{\cdot}4$, Monoclinic, $a = 8{\cdot}00(1)$, $b = 14{\cdot}99(2)$, $c = 7{\cdot}21(1)$ Å, $\beta = 93{\cdot}5(5)°$, $U = 863$ Å^3, $Z = 4$ for $Hg_{1{\cdot}5}Cl_3tu$ (or $Z = 6$ for $HgCl_2$,2/3tu), $D_c = 3{\cdot}72$ g cm^{-3}, $F(000) = 844$. Ni-filtered Cu-$K_{\bar{\alpha}}$ radiation, $\lambda = 1{\cdot}5418$ Å,[8] $\mu = 610$ cm^{-1}, transmission coefficient range 0·05—0·52, data layers 0—3*kl*, *hk*0—3. Space group $P2_1/c$ (C_{2h}^5, No. 14).[9]

The available data set was limited by both the size of the crystal available, and absorption; it was measured and processed, and the structure solved and refined by our usual methods,[10] yielding a final residual *R* 0·103 for 408 reflections. Sixteen low-angle reflections appeared to be badly affected by extinction and were deleted from the final data set, although an inadequate absorption correction might equally well be the cause of the deficiency in agreement of these low-angle reflections in view of the high value of μ; the use of anisotropic thermal parameters in the refinement although justified by a ratio test on *R*, seems to confirm this since β_{33} is negative.

---

[1] *Inorg. Synth.*, 1960, **6**, 27.

[2] K. K. Cheung, R. S. McEwen, and G. A. Sim, *Nature*, 1965, **205**, 383.

[3] P. D. Brotherton, P. C. Healy, C. L. Raston, and A. H. White, *J.C.S. Dalton*, 1973, 334.

[4] A. Korczynski, *Roczniki Chem.*, 1968, **42**, 1207.

[5] A. Korczynski, M. Nardelli, and M. Pellinghelli, *Cryst. Struct. Comm.*, 1972, **1**, 327.

[6] P. D. Brotherton and A. H. White, preceeding paper.

[7] B. W. Delf, *J. Appl. Phys.*, 1963, **14**, 345.

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

[9] Ref. 8, vol. I, 2nd edn., 1965, p. 99.

[10] P. W. G. Newman and A. H. White, *J.C.S. Dalton*, 1972, 1460, 2238.

At refinement termination all parameter shifts were $< 0{\cdot}2\sigma$; a final difference map showed ripples approximating in size to a carbon atom in the vicinity of some of the heavy atoms. Final weighting scheme constants were $a = 3{\cdot}8$, $b = 0{\cdot}07$ $[w = (a + |F_o| + b|F_o|^2)^{-1}]$. Scattering factors were for the neutral atoms,[11] that for mercury being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[12] Final $|F_o|$ and $|F_c|$ are given in Supplementary Publication No. SUP 20828 (7 pp., 1 microfiche).* Final atomic co-ordinates and thermal parameters are listed in Table 1, and interatomic distances and angles in Table 2.

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

TABLE 1

Final atomic fractional cell and thermal parameters of the asymmetric unit. Block-diagonal (3 × 3, 6 × 6) least-squares estimated standard deviations are in parentheses

Atom	x	y	z	$B/\text{Å}^2$	
Hg(1)	0·8506(4)	0·1329(2)	0·5300(5)	*	
Cl(11)	1·125(2)	0·083(1)	0·632(3)	*	[3·0(4)] †
Cl(12)	0·936(2)	0·188(1)	0·171(3)	*	[2·0(4)] †
S	0·551(2)	0·121(1)	0·484(3)	*	[3·3(5)] †
C	0·476(11)	0·231(6)	0·444(11)	4·8(20)	
N(11)	0·317(9)	0·237(5)	0·343(11)	6·1(19)	
N(12)	0·569(8)	0·310(5)	0·442(9)	5·1(17)	
Hg(2)	0	0	0	*	
Cl(2)	0·276(2)	0·016(1)	0·110(2)	*	[2·3(4)] †

Atom	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Hg(1)	61(4)	13(6)	−41(11)	43(2)	−6(8)	146(9)
Cl(11)	68(26)	20(31)	79(84)	40(13)	−14(40)	197(60)
Cl(12)	35(21)	13(28)	54(63)	26(10)	−27(36)	153(53)
S	65(26)	−15(30)	−14(86)	36(12)	72(45)	245(74)
Hg(2)	79(7)	−5(8)	−11(18)	47(3)	14(10)	133(13)
Cl(2)	93(29)	78(34)	−61(68)	53(13)	−59(36)	−27(44)

* Anisotropic thermal parameters (× 10^4), in the form $\exp[-(\beta_{11}h^2 + \beta_{12}hk + \beta_{12}hl + \beta_{22}k^2 + \beta_{23}kl + \beta_{33}l^2)]$.

† Isotropic B at R 0·108.

TABLE 2

Interatomic distances (Å) (< 3·5 Å) and angles (deg.)

(*a*) Within the discrete $HgCl_2$ molecule and about Hg(2)

Hg(2)–Cl(2)	2·32(2)	Cl(2)–Hg(2)–Cl(2^{II})	180·0°
Hg(2) ··· Cl(11^{III})	3·15(2)	Cl(2)–Hg(2) ··· Cl(11)	84·3(6)
Hg(2) ··· Cl(12^{IV})	3·13(2)	Cl(2)–Hg(2) ··· Cl(12)	86·8(6)

(*b*) Within the $[\{Hg(tu)Cl\}Cl]_n$ chain

Hg(1)–Cl(11)	2·39(2)	Cl(11)–Hg(1)–Cl(11^{V})	75·0(6)
Hg(1) ··· Cl(11^{V})	3·45(2)	Cl(11)–Hg(1)–Cl(12)	96·0(6)
Hg(1)–Cl(12)	2·84(2)	Cl(11)–Hg(1)–Cl(12^{VI})	89·5(6)
Hg(1)–Cl(12^{VI})	2·94(2)	Cl(11)–Hg(1)–S	155·0(7)
Hg(1)–S	2·40(2)	S–Hg(1)–Cl(12)	101·0(6)
S–C	1·77(9)	S–Hg(1)–Cl(12^{VI})	108·7(6)
C–N(11)	1·43(11)	Cl(12)–Hg(1)–Cl(12^{VI})	89·3(5)
C–N(12)	1·39(11)	Hg(1)–S–C	106(3)
		S–C–N(11)	115(6)
		S–C–N(12)	128(6)
		N(11)–C–N(12)	114(7)
		Hg(1)–Cl(12)–Hg(1)	121·2(6)

(*c*) Other

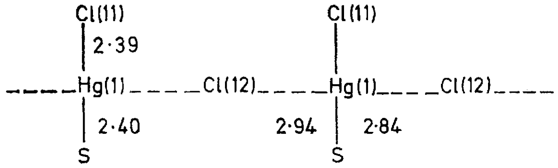
N(11) ··· Cl(11^{VII})	3·42(8)	N(12) ··· Cl(12^{VI})	3·28(7)
N(11) ··· Cl(12^{IV})	3·31(8)	N(12) ··· Cl(2^{VIII})	3·37(7)

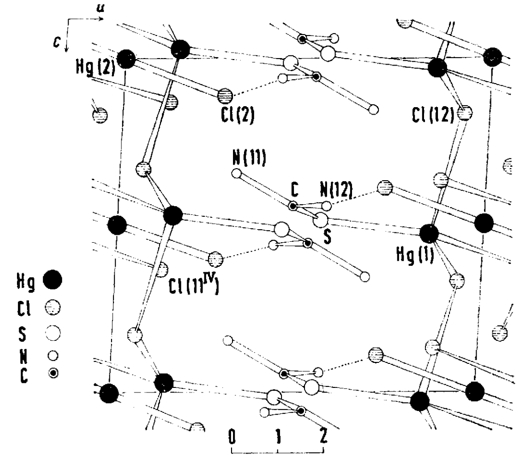
Transformations of the asymmetric unit relative to the reference molecule at x, y, z:

II $\bar{x}, \bar{y}, \bar{z}$
III $x - 1, y, z - 1$
IV $x - 1, y, z$
V $2 - x, \bar{y}, 1 - z$
VI $x, \frac{1}{2} - y, \frac{1}{2} + z$
VII $1 - x, \frac{1}{2} - y, z - \frac{1}{2}$
VIII $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$

DISCUSSION

The cell contents, depicted in the Figure, are comprised of infinite chains of Hg(tu)Cl units bridged by further chlorine atoms:





Unit-cell contents projected down *b*, showing atomic numbering

The chains are interleaved with discrete $HgCl_2$ molecules, centrosymmetric about the mercury atom sited on the special position and similar to the parent $HgCl_2$, being linear with Hg–Cl 2·32(2) Å [*cf.* 2·25 (crystal),[13] 2·34 (vapour)[14]]. Other contacts of this mercury atom, Hg(2), [Hg(2) ··· Cl(11) 3·15 and Hg ··· Cl(12) 3·13 Å] are greater than the usual van der Waals' estimate of 3·0 Å.[15] Constraint of the molecule within the lattice appears to take place by hydrogen bonding of Cl(2) to N(12) [N(12) ··· Cl(2^{VIII}), 3·37(7) Å]. Within the polymeric chain, Hg(1) displays an irregular four-co-ordination dominated by the usual tendency to adopt the linear *sd*

---

* For details see Notice to Authors, No. 7, in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

[11] Ref. 9, p. 210.

[12] Ref. 9, p. 213.

[13] D. Grdenić, *Arkiv Kemi*, 1950, **2**, 14.

[14] A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, *Trans. Faraday Soc.*, 1937, **33**, 852.

[15] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960, p. 260.

hybridized configuration. There are two short contacts to the non-bridging chlorine Cl(11) [2·39(2) Å] and the sulphur atom of the thiourea [2·40(2) Å]. The S–Hg(1)–Cl(11) angle is 155°. The Hg(1)–S distance is comparable to that observed in [Hg(tu)$_2$Cl]Cl (2·42 Å) [2,3] in which the mercury atom is trigonally planar co-ordinated, but is shorter than the range of Hg–S distances (*ca.* 2·49—2·60 Å) observed in both [Hg(tu)$_4$]Cl$_2$ derivatives; [5,6] the Hg(1)–Cl(11) distance, while greater than that found in HgCl$_2$, is appreciably shorter than that observed in [Hg(tu)$_2$Cl]Cl [2·57(1) Å].[2,3] Broadly, these trends reflect the changes in effective co-ordination number in the manner expected; in detail, however, it might be expected that the Hg(1)–S distances should differ also between the present structure and that of [Hg(tu)$_2$Cl]Cl. Cl(12) which bridges Hg(1) atoms at distances of 2·84, 2·94(2) Å approaching the van der Waals' contact is probably to be regarded as bonding to Hg(1) rather than existing as an ionic chlorine, by virtue of the distortion of the Cl(11)–Hg(1)–S geometry from linearity with concomitant increase in bond lengths. The thiourea geometry is normal within the large error limits; participation of the p_π system in Hg–S bonding appears to be slight (Table 3). The mercury environment in this structure closely resembles that in the derivative Et$_2$S,2HgCl$_2$ (*i.e.* [{HgCl(Et$_2$S)}Cl]$_n$,nHgCl$_2$) [16] in which there is a close Hg–Cl distance (2·35 Å) and a sulphur atom at 2·40 Å at an angle of 158°, with two other more remote bonding Hg–Cl contacts (2·70, 2·85 Å); this latter complex, however, has a more complex polymeric disposition.

It seems likely that the as yet undetermined structure of HgCl$_2$(tu) should correspond to the polymeric species observed in the present structure. The infrared spectrum of HgCl$_2$(tu) has been reported [17] and interpreted in terms of tetrahedrally co-ordinated mercury and terminal and bridging chlorines leading to a dimer by analogy with the i.r. spectrum of [(Ph$_3$P)HgX$_2$]$_2$ (ref. 18) and the structure of [(Et$_3$As)HgI$_2$]$_2$ (ref. 19); the spectrum of our polymeric model would not be expected to differ significantly from that observed.

TABLE 3

Least-squares planes, referred to orthogonal frame (Å) in the form $pX + qY + rZ = s$ where $X = ax + cz \cos \beta$, $Y = by$, $Z = cz \sin \beta$. Atomic deviations (Å) are given in square brackets

	p	q	r	s	σ(Å)
Plane (1): S, C, N(11), N(12)	−0·3972	0·1188	0·9100	1·763	0·07
[Hg(1) 0·66, S, −0·04, C 0·12, N(11) −0·04, N(12) −0·05]					
Plane (2): Hg(1), S, C	−0·1431	0·1243	0·9819	3·052	

Angle between planes: (1)–(2) 15·2°

[3/961 *Received*, 14*th May*, 1973]

---

[16] C.-I. Brändén, *Arkiv Kemi*, 1963, **22**, 83.

[17] G. Marcotrigiano and R. Battistuzzi, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 969.

[18] G. B. Deacon, J. H. S. Green, and D. J. Harrison, *Spectrochim. Acta*, 1968, **24**, *A*, 1921.

[19] R. C. Evans, F. G. Mann, H. S. Peiser, and D. Purdie, *J. Chem. Soc.*, 1940, 1209.