Crystal Structure of Chlorobis(thiourea)mercury(II) Chloride

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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, and refined by block-diagonal least-squares to *R* 0·08 for 359 visually estimated reflections. Crystals are orthorhombic, space group *Pmmn*, a = 6·44 ± 0·01, b = 12·76 ± 0·02, c = 5·91 ± 0·01 Å, Z = 2.

The mercury atom is co-ordinated in an unusual approximately trigonal planar conformation by the two equivalent thiourea sulphur atoms and a chlorine atom (Hg–S 2·42 ± 0·01, Hg–Cl 2·57 ± 0·01 Å; S–Hg–Cl 110·8 ± 0·2, S–Hg–S 138·4 ± 0·2°). The other ' ionic ' chlorine atom lies normal to this plane, between and equidistant from a pair of mercury atoms at 3·22 Å. The thiourea molecules and the mercury and co-ordinated chlorine atoms are coplanar (Hg–S–C 110·0 ± 0·9°); their intramolecular geometry is as expected.

THERE are few structural studies for co-ordination complexes of mercury(II) in which the ligating atoms are other than first-row elements or halides.[1] Among the sulphur ligands thiourea [tu,SC$(NH_2)_2$] is remarkable in reputedly forming a series of complexes with mercury(II) chloride of stoicheiometry $HgCl_2(tu)_n$ (n = 1—4).[2] A communication by Cheung, McEwen, and Sim[3] has reported the heavy-atom geometry in $HgCl_2(tu)_2$; Korczynski[4] carried out a structure determination of $HgCl_2(tu)_3$. In these complexes the co-ordination geometries of the mercury atom are unusual, the former being trigonal planar and the latter a highly distorted trigonal bipyramid. As part of a study directed toward the delineation of the nature and stereochemistry of the mercury(II) bonding in this series $HgCl_2(tu)_n$, we report the crystal structure redetermination of the complex $HgCl_2(tu)_2$.

EXPERIMENTAL

The complex was prepared by the slow evaporation at room temperature of a solution containing a stoicheiometric (1 : 2) molar ratio of mercury(II) chloride and thiourea, the solution having been filtered to remove a slight quantity of an initial black precipitate (presumably mercury) which formed during the first day. Crystals were deposited as thin square plates; a section 0·047 × 0·050 × 0·113 mm was used in the subsequent structure determination.

X-Ray data were collected by the multiple-film equi-inclination Weissenberg method; unit-cell calibration was effected by superimposing aluminium powder lines ($a_{298\,K}$ = 4·0494 Å)[5] on zero-layer photographs about a and c. Nickel-filtered copper radiation was used throughout.[6] No evidence was found for crystal deterioration during data collection.

Crystal Data.—$C_2H_8Cl_2HgN_4S_2$, M = 399·6, Orthorhombic, a = 6·44 ± 0·01, b = 12·76 ± 0·02, c = 5·91 ± 0·01 Å, U = 485·6 Å^3, D_m = 2·76 ± 0·01 (by flotation), Z = 2, D_c = 2·76, $F(000)$ = 372. Space group *Pmmn* (No. 59, second setting, D_{2h}^{13}) from systematic extinctions $\{hk0\}$, $h + k = 2n + 1$.[7] $\mu(\text{Cu-}K_\alpha)$ = 389·6 cm^{-1}, transmission coefficient range, 0·047—0·259.

The intensities of 359 independent observed reflections collected from the layers 0—2kl and hk0—2 were visually

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[1] D. Grdenić, *Quart. Rev.*, 1965, **19**, 303 and references therein; H. L. Roberts, *Adv. Inorg. Chem. Radiochem.*, 1968, **11**, 309.

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

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

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

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

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

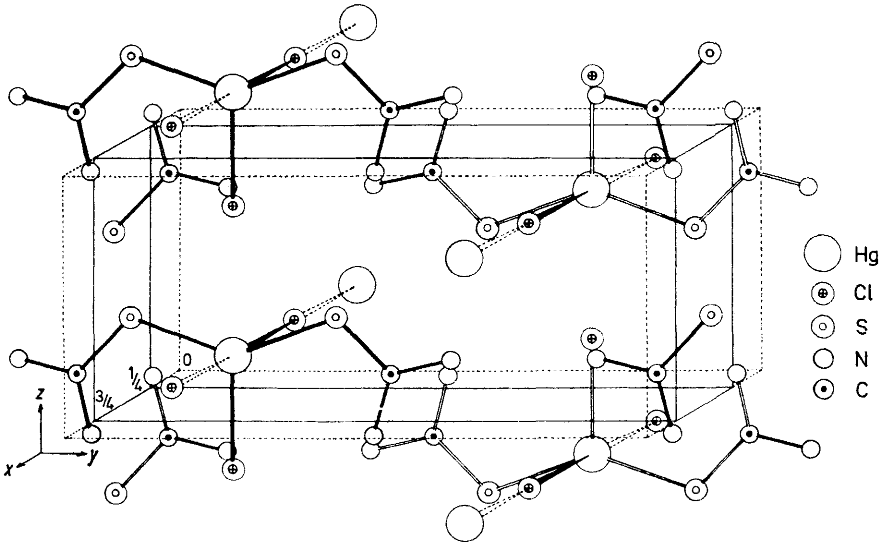
[7] Ref. 6, vol. 1, 2nd edn., 1965, p. 148.

estimated; those used in the final structure determination did not include zeros or those whose intensities were measured as 1 (±0·5). The raw data were corrected for absorption[8] and Lorentz and polarization factors and scaled by internal correlation.[9]

The structure was solved by the heavy-atom method. With the use of isotropic thermal parameters throughout several cycles of block diagonal (3 × 3, 6 × 6) least-squares refinement (local programs, SFLS1, 2 by A. I. M. Rae) the residual converged to 0·18. A weighting scheme of the form $w = (a + |F_o| + b|F_o|^2 + c|F_o|^3)^{-1}$ was introduced and found appropriate, the quantity $\Sigma w(|F_o| - |F_c|)^2$ being minimized and a, b, and c being adjusted as refinement proceeded. Anisotropic thermal parameter refinement of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ with appropriate restraints (see Table 1) was introduced, initially for the mercury atom only, and then the chlorine and sulphur atoms, converging to a final R of 0·081, R' being 0·106 $\{R' = [\Sigma w(|F_o| = |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. (A ratio test carried out on each introduction of thermal anisotropy showed it to be significant at >99%.[10]) Final weighting-scheme constants were a 17·11, b 0·015, and c 2·9 × 10⁻⁵. The final set of data omits six reflections which appeared to be heavily affected by extinction. A difference-Fourier map, calculated on the final set of $|F_o|$ and $|F_c|$, showed no significant features.

Parameter shifts in the final cycle of least-squares refinement were <0·5σ for the carbon atoms and <0·25σ the remainder. Scattering factors used for neutral atoms were taken from ref. 11, interpolated by the local program FCURV, those for the mercury being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[12] Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20570 (4 pp., 1 microfiche).* Final atomic positional and thermal parameters are listed in Table 1. Least-squares estimated standard deviations, derived from block-diagonal refinement, are likely to be underestimates. The unit-cell contents are depicted in the Figure which also gives the crystallographic numbering system used. Hydrogen atom positions were estimated by assuming them to be coplanar with the remainder of the thiourea molecule and taking N–H 1·00 Å, and H–N–H 120°. Interatomic distances and angles[13] are given in Table 2.

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



Unit cell contents and atomic numbering system used; open lines show bonds in the plane $x = \frac{1}{4}$, thick black lines show bonds in the plane $x = \frac{3}{4}$

DISCUSSION

The structure is composed entirely of atoms occupying sites of at least m symmetry in the planes $x = 0{\cdot}25$, 0·75, the symmetry of the mercury and the chlorine sites

TABLE 1

Final atomic fractional cell parameters and thermal parameters (all x co-ordinates are $x = \frac{3}{4}$) with standard deviations in parentheses

Atom	y	z	B/Å²	Site-symmetry
Hg	0·25	0·2508(3)	*	*mm*
Cl(1)	0·75	0·748(2)	*	*mm*
Cl(2)	0·25	0·816(2)	*	*mm*
S	0·4270(5)	0·396(1)	*	*m*
C	0·516(2)	0·173(6)	3·0(5)	*m*
N(1)	0·616(3)	0·231(4)	5·0(7)	*m*
N(2)	0·495(2)	−0·039(4)	3·3(4)	*m*

* Anisotropic thermal parameters (×10⁴).

Atom	β_{11}	β_{22}	β_{33}	β_{23}
Hg	348(6)	35(1)	175(5)	
Cl(1)	264(28)	55(7)	214(32)	
Cl(2)	326(30)	30(4)	126(21)	
S	293(19)	40(3)	163(17)	7(14)

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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 page copies).

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

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

[10] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

[11] Ref. 6, p. 210.

[12] Ref. 6, p. 213.

[13] M. E. Pippy and F. R. Ahmed, Program BONDSCAN, Divn. Pure and Appl. Phys., NRC, Ottawa, Canada.

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Bonding distances and angles within the $[HgCl\{SC(NH_2)_2\}_2]^+$ entity

Hg–S	2·416(6)	C–N(1)	1·31(4)
Hg–Cl(2$^{\mathrm{I}}$)	2·57(1)	C–N(2)	1·28(4)
S–C	1·74(3)		
Cl(2$^{\mathrm{I}}$)–Hg–S	110·8(2)	S–C–N(1)	116(2)
Hg–S–C	110·0(9)	S–C–N(2)	127(2)
S–Hg–S$^{\mathrm{II}}$	138·6(2)	N(1)–C–N(2)	117(2)

(*b*) Interspecies non-bonding distances (<3·5 Å)

Hg · · · Cl(1)	3·22(1)	Cl(1) · · · N(1)	3·50(3)
S · · · Cl(2$^{\mathrm{III}}$)	3·35(1)	Cl(1) · · · N(1$^{\mathrm{IV}}$)	3·33(3)
Cl(2) · · · N(2$^{\mathrm{IV}}$)	3·24(2)	Hg · · · Cl(2)	3·34(1)
Cl(1) · · · N(2$^{\mathrm{IV}}$)	3·49(2)		

Atoms derived by transformation of the asymmetric unit (x, y, z) are defined by superscript Roman numerals:

I	$x, y, z - 1$	III	$1 - x, 1 - y, 1 - z$
II	$x, \frac{1}{2} - y, z$	IV	$x, y, 1 + z$

being higher (Table 1). The mercury atom is co-ordinated in the plane by chlorine Cl(2) at a distance of 2·57 ± 0·01 Å and by the two sulphur atoms from two thiourea molecules related by the mirror $y = 0{\cdot}25$ at 2·416 ± 0·006 Å, the angle Cl(2)–Hg–S being 110·8 ± 0·2°. The array is thus a distorted trigonal plane, the dimensions being in good agreement generally with those reported in ref. 3 [Hg–S 2·37, Hg–Cl 2·56 Å; S–Hg–Cl 110° 37′]. Cl(1) is located perpendicular to the mercury atom in the $[HgCl\{SC(NH_2)_2\}_2]^+$ plane and at 3·22 ± 0·01 Å from it. In spite of the variability in estimates of the van der Waals radius ascribable to mercury(II),[1] it seems legitimate to regard this chlorine as ionic and the complex is best formulated as $[HgCl\{SC(NH_2)_2\}_2]Cl$. The geometry of the one independent thiourea molecule (Table 1) agrees within the wide limits of error obtained with other structures containing the species.[14]

The crystal packing of the cation and anion species appears to be a consequence of hydrogen bonding between the thiourea amino-hydrogen atoms and the two chlorine species. From the results of other structures, it seems reasonable to regard all atoms in the thiourea as coplanar;[*,14–16] with this assumption and the geometry postulated earlier, all nitrogen atoms lie within 3·50 Å of one of the chlorine atoms, implying short hydrogen–chlorine distance of *ca.* 2·2—2·6 Å [*cf.* sum of van der Waals radii 3·0 Å (ref. 16)].[17] The 'ionic' chlorine Cl(1) is surrounded by NH_2 hydrogen atoms in a planar array, the upper and lower positions normal to the plane being occupied by the mercury (Table 2).

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[*] In particular, Truter[14] gives the structure of the free molecule as C–S 1·720 ± 0·009, C–N 1·340 ± 0·006, and N–H 0·96 ± 0·06 Å. Elcombe and Taylor[15] give N–H 1·01 ± 0·01 Å.

[14] M. R. Truter, *Acta Cryst.*, 1967, **22**, 556.

[15] M. M. Elcombe and J. C. Taylor, *Acta Cryst.*, 1968, **A24**, 410.

[16] M. S. Weininger, J. E. O'Connor, and E. L. Amma, *Inorg. Chem.*, 1969, **8**, 424.

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