Crystal Structure of a New Form (β) of Tetrakis(thiourea)mercury(II) Chloride

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The crystal structure of the title compound has been determined by photographic *X*-ray methods by the heavy-atom method, and refined by block-diagonal least-squares to *R* 0·096 for 1203 independent reflections. Crystals are monoclinic, space group $P2_1/a$, *a* = 33·45(5), *b* = 8·47(2), *c* = 6·09(1) Å, β = 92·2(3)°, *Z* = 4. As in the other (α) form the cell contains discrete $[Hg\{CS(NH_2)_2\}_4]^{2+}$ and Cl^- units, the mercury atom being in a highly distorted tetrahedron of sulphur atoms [Hg–S 2·51—2·62 Å, S–Hg–S 112—117°].

THIOUREA (tu) has been reported to form a series of complexes with mercury(II) chloride, with stoicheiometries $HgCl_2(tu)_n$ (n = 1—4).[1] Structural data have been reported for the n = 2,3 derivatives [2-4] and a further structural determination was undertaken on $HgCl_2(tu)_4$. By use of the preparative method given in the literature,[1] but with more concentrated warm solutions, crystallization of the complex occurred simultaneously in two different forms from two different nuclei in the same Petri dish. One of the forms, compact polyhedra, appeared identical with that previously reported (α); the other (thick rods) appeared to be a new phase (β). The analyses of the two samples were identical with that expected for $HgCl_2(tu)$. The structures of both phases have been determined; during the course of our work, however, a structure determination of the α-form was reported,[5] and as our results are in substantial agreement, we do not describe that structure, and report only that of the β-form.

EXPERIMENTAL

Photographic multiple-film equi-inclination Weissenberg data were collected on a single prismatic crystal section (0·07 × 0·10 × 0·15 mm) about *b* and *c*; cell calibration was effected by superposition of aluminium powder lines (*a* = 4·0494 Å) [6] on zero-layer photographs.

Crystal Data.—$C_4H_{16}Cl_2HgN_8S_4$, *M* = 575·9, Monoclinic, *a* = 33·45(5), *b* = 8·47(2), *c* = 6·09(1) Å, β = 92·2(3)°, D_m = 2·20(2), *Z* = 4, D_c = 2·22 g cm^{-3}, *F*(000) = 1096. Space group $P2_1/a$ (C^5_{2h}, No. 14).[7] Cu-K_α radiation (Ni-filtered), λ = 1·5418 Å,[8] μ = 284 cm^{-1}, transmission coefficient range 0·05—0·23.

Data for the layers *h*0—3*l* and *hk*0—3 were measured, processed, and refined by our usual methods,[9] yielding a final residual *R* 0·096 (1203 reflections), $R' \{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma(w|F_o|^2)]^{\frac{1}{2}}\}$ 0·12; the weighting scheme was of the form $w = (a + |F_o| + b|F_o|^2)^{-1}$ (final values: *a* 1·34, *b* 0·19). Final difference-Fourier maps showed no significant features and at refinement termination, all parameter shifts were $< 0{\cdot}2\sigma$. Scattering factors were for the neutral atoms,[10] that for mercury being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[11] 31 Low-angle reflections which appeared to be heavily affected by exinction were not included in the final data set. [Final $|F_o|$ and $|F_c|$ are given in Supplementary Publication No. SUP 20769 (3 pp., 1 microfiche].* Anisotropic thermal parameters quoted are of the form $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)$. Block-diagonal least-squares estimated standard deviations are given in parentheses in Tables 1 and 2, which list atomic co-ordinates and molecular geometry. Least-squares planes are given in Table 3.

TABLE 1

Final atomic fractional co-ordinates and thermal parameters

Atom	*z*	*y*	*z*	*B*/Å²
Hg	0·13540(4)	0·0738(2)	0·4158(2)	*
S(1)	0·1187(2)	0·359(1)	0·475(1)	2·4(1)
C(1)	0·0823(6)	0·351(3)	0·679(3)	0·7(4)
N(11)	0·0958(7)	0·333(2)	0·893(4)	2·4(5)
N(12)	0·0461(7)	0·352(3)	0·638(4)	3·0(5)
S(2)	0·2033(2)	0·011(1)	0·598(1)	2·7(1)
C(2)	0·2369(9)	−0·015(4)	0·398(5)	3·3(7)
N(21)	0·2333(8)	0·026(4)	0·199(5)	4·0(6)
N(22)	0·2734(11)	−0·087(4)	0·453(6)	6·0(9)
S(3)	0·1365(2)	−0·019(1)	0·021(1)	3·1(2)
C(3)	0·1507(10)	−0·222(5)	0·035(1)	4·4(8)
N(31)	0·1456(9)	−0·312(4)	−0·135(6)	4·9(7)
N(32)	0·1657(8)	−0·282(3)	0·222(4)	3·9(6)
S(4)	0·0781(2)	−0·099(1)	0·572(2)	2·9(2)
C(4)	0·0546(10)	−0·172(5)	0·335(6)	4·3(8)
N(41)	0·0606(9)	−0·305(4)	0·256(5)	4·7(7)
N(42)	0·0340(10)	−0·077(4)	0·197(6)	5·3(8)
Cl(1)	0·1891(2)	0·365(1)	0·046(1)	2·9(2)
Cl(2)	0·0106(2)	0·307(1)	0·149(1)	3·1(2)

* Anisotropic thermal parameters (× 10⁶).

	β_{11}	β_{12}	β_{13} †	β_{22} †	β_{23} †	β_{33} †
Hg	684(14)	−23(87)	1080(120)	8960(26)	−4660(52)	21560(450)

† Rounded.

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

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[10] Ref. 8, p. 210.

[11] Ref. 8, p. 213.

DISCUSSION

The cell contents (Figure) consist of discrete $[Hg(tu)_4]^{2+}$ cations and Cl^- anions. The crystal packing is dominated by $Cl^- \cdots NH_2$ interactions, the environment of each chloride ion being the hydrogen atoms of some six or seven amino-groups, nitrogen–chlorine distances being *ca.* 3·2—3·4 Å (Table 2).

TABLE 2

Interatomic distances (Å) and angles (deg.)

(*a*) Cation geometry

i =	(1)	(2)	(3)	(4)
Hg–S(*i*)	2·506(8)	2·544(8)	2·527(8)	2·617(8)
S(*i*)–C(*i*)	1·77(2)	1·70(3)	1·79(4)	1·73(4)
C(*i*)–N(*i*1)	1·38(3)	1·27(4)	1·29(5)	1·25(5)
C(*i*)–N(*i*2)	1·23(3)	1·39(5)	1·32(4)	1·34(5)
Hg–S(*i*)–C(*i*)	103·3(8)	108·6(11)	105·5(12)	102·3(12)
S(*i*)–C(*i*)–N(*i*1)	117(2)	128(3)	120(3)	125(3)
S(*i*)–C(*i*)–N(*i*2)	124(2)	119(3)	120(3)	121(3)
N(*i*1)–C(*i*)–N(*i*2)	119(2)	113(3)	120(3)	113(3)

S(1)–Hg–S(2)	109·9(3)	S(2)–Hg–S(3)	107·7(3)
S(1)–Hg–S(3)	116·6(3)	S(2)–Hg–S(4)	112·2(3)
S(1)–Hg–S(4)	108·3(3)	S(3)–Hg–S(4)	102·1(3)

(*b*) Chloride contacts (<3·5Å)

$Cl(1) \cdots N(11^{II})$	3·23(2)	$Cl(2) \cdots N(11^{II})$	3·31(2)
$Cl(1) \cdots N(21)$	3·35(3)	$Cl(2) \cdots N(12)$	3·18(3)
$Cl(1) \cdots N(21^{III})$	3·33(3)	$Cl(2) \cdots N(12^{II})$	3·39(3)
$Cl(1) \cdots N(22^{IV})$	3·28(4)	$Cl(2) \cdots N(41^{V})$	3·36(3)
$Cl(1) \cdots N(22^{III})$	3·36(4)	$Cl(2) \cdots N(42)$	3·36(3)
$Cl(1) \cdots N(31^{IV})$	3·27(3)	$Cl(2) \cdots N(42^{V})$	3·20(3)
$Cl(1) \cdots N(32^{VI})$	3·28(3)		

(*c*) Sulphur–nitrogen contacts (<3·5Å)

$S(3) \cdots N(11)$	3·35(3)	$S(4) \cdots N(31)$	3·35(3)
$S(3) \cdots N(21)$	3·40(3)		

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

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

TABLE 3

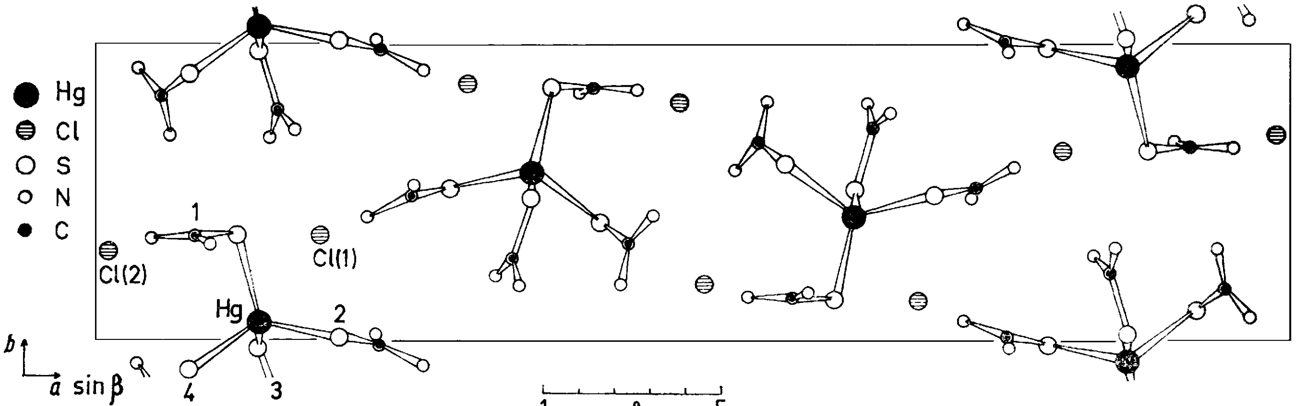
(*a*) Ligand planes in the cation, in the form $pX + qY + rZ = s$,* with atomic deviations (Å) in square brackets. Atoms defining the plane are italicized

Plane	*p*	*q*	*r*	*s*	σ/Å
(*a*): Ligand (1)	0·0131	0·9959	0·0896	3·341	0·01
[*S(1)* −*0·01*, *C(1)* *0·02*, *N(11)* −*0·01*, *N(12)* −*0·01*, Hg −2·43]					
(*b*): Hg S(1), C(1)	0·7108	0·0592	0·7009	5·031	
(*c*): Ligand (2)	0·3916	0·8924	0·2242	3·502	0·00
[*S(2)* *0·00*, *C(2)* *0·00*, *N(21)* *0·00*, *N(22)* *0·00*, Hg −0·64]					
(*d*): Hg, S(2), C(2)	0·2163	0·9759	0·0284	1·661	
(*e*): Ligand (3)	0·9307	0·2356	−0·2798	4·171	0·00
[*S(3)* *0·00*, *C(3)* *0·01*, *N(31)* *0·00*, *N(32)* *0·00*, Hg − 0·61]					
(*f*): Hg, S(3), C(3)	0·9625	0·2618	−0·0713	4·342	
(*g*): Ligand (4)	0·8292	0·2840	−0·4815	0·122	0·04
[*S(4)* *0·02*, *C(4)* −*0·07*, *N(41)* *0·02*, *N(42)* *0·02*, Hg 2·51]					
(*h*): Hg, S(4), C(4)	−0·6089	0·7933	−0·0072	−2·280	

(*b*) Angles (deg.) between plane normals:

(*a*)–(*b*)	83·5	(*e*)–(*f*)	12·2
(*c*)–(*d*)	15·8	(*g*)–(*h*)	74·0

* *X*, *Y*, *Z* are orthogonal co-ordinates in Å where $X = ax + cz \cos \beta$, $Y = by$, and $Z = cz \sin \beta$.



Unit-cell contents, projected down *c*, showing the ligand numbering system

Within the cation, the four ligands are co-ordinated to the metal atom *via* the sulphur atom, as is usual. The ligands are planar, but not coplanar with the mercury atom, which deviates by *ca.* 0·6—2·5 Å (Table 3). The mercury–sulphur distances are irregular, varying between *ca.* 2·51—2·62 Å and the sulphur–mercury–sulphur angles between *ca.* 102—117°. An approximate inverse correlation exists between the distance Hg–S(*i*) and the sum of angles $\sum_j [S(i)\text{–}Hg\text{–}S(j)]$. Similar irregularities are found in the HgS_4 co-ordination tetrahedron in the α-form[5] and in fact, in all other 'tetrahedral' $M(tu)_4^{n+}$ species reported[12,13] (except $[Hgtu_4]^{2+}[Co(NCS)_4]^{2-}$ in which the point-symmetry of

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the mercury atom is abnormally high).[14] In the present structure, the Hg–C–S to thiourea dihedral angle is very variable and indicates a wide variation in the participation of the p_π orbital of the sulphur atom in bonding; such variations have been previously observed,[12,15] and in the present structure, there appear to be no observable consequences of this in the metal or ligand geometries: it is probable that all the irregularities described are a consequence of the strong hydrogen interactions involved in the crystal packing. Although in both α- and β-forms there is no apparent correlation of variation in Hg–S distance with the degree of p_π participation by the sulphur atom, it is clear that in both α- and β-forms the Hg–S distances are significantly longer than that observed in $[Hg(tu)_2Cl]Cl$ (2·42 Å) [2,4] the environment of the mercury atom in the latter being trigonal planar, presumably as a consequence of decrease in co-ordination number.

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