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The Crystal Structures of Dimeric and Monomeric Forms of Mercury(II) *N*,*N*-Diethyldithiocarbamate, $Hg_2(S_2CNEt_2)_4$ and $Hg(S_2CNEt_2)_2$

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The crystal structures of two modifications of mercury(II) *N*,*N*-diethyldithiocarbamate, which crystallize simultaneously from acetone, have been determined by X-ray methods. Both crystals are monoclinic with the space group $P2_1/a$. The cell dimensions are $a=16\cdot662$ (8), $b=10\cdot954$ (6), $c=9\cdot861$ (6) Å, $\beta=111\cdot8$ (2)°, $Z=2$ (dimers) (α-form); and $a=11\cdot807$ (3), $b=14\cdot930$ (5), $c=4\cdot723$ (4) Å, $\beta=106\cdot26$ (4)°, $Z=2$ (monomers) (β-form). The structures were solved by heavy-atom methods, and refined by a block-diagonal least-squares program to R indices of 0·067 and 0·045 for α and β forms respectively. The crystals of the α form consist of isolated dimeric units of tetrakis-(*N*,*N*-diethyldithiocarbamato)dimercury(II). The molecular structure of this binuclear complex is similar to those of *N*,*N*-diethyldithiocarbamates of zinc and cadmium. The metal atom is five-coordinate, with Hg–S distances of 2·418, 2·520, 2·663, 2·698 and 3·137 Å. The crystals of the β form are composed of essentially monomeric bis-(*N*,*N*-diethyldithiocarbamato)mercury(II). Each mercury atom occupies a centre of symmetry with the two ligand molecules coordinated in a plane through the sulphur atoms. The two independent Hg–S bond distances are 2·398 and 2·965 Å, showing a linear bicovalent character. These units are linked together by a weak intermolecular metal–sulphur interaction (Hg–S: 3·292 Å) to form an infinite chain parallel to the c axis.

Introduction

The crystal structure analysis of mercury(II) *N*,*N*-diethyldithiocarbamate was undertaken as a part of a series of investigations on dithioacid complexes of heavy metals. The present study follows the structure determination of lead(II) *N*,*N*-diethyldithiocarbamate, $Pb(S_2CNEt_2)_2$ (Pb dtc_2; Iwasaki & Hagihara, 1972), in which the molecular structure was found to be similar to those of lead salts of various xanthates and of diethyl dithiophosphate; the molecules were essentially monomeric and the coordination of sulphur atoms around the lead atom was based on a distorted tetragonal pyramidal configuration.

It was found that the reaction of $HgCl_2$ with sodium *N*,*N*-diethyldithiocarbamate gave three kinds of crystal. Since each of them at first seemed to belong to a different polymorph of Hg dtc_2, the three modifications were named α, β and γ respectively (Iwasaki, 1972*a*). The crystal structures of the three forms were determined by X-ray methods (Iwasaki, 1972*a*, *b*), and it was established that the α, β and γ forms actually corresponded to crystals of Hg_2dtc_4, $Hgdtc_2$ and $Hg_3Cl_2dtc_4$ ($=HgCl_2.2Hgdtc_2$) respectively. The present paper describes the structures of α and β forms, and reports that the molecule has a linear bicovalent bond in the monomeric form while the mercury atom is five-coordinate in the dimeric form. At a final stage of the preparation of this paper, the author was informed by a private communication that Healy & White (1973) had independently analysed the structure of the β form. However, a brief description of the structural parameters of this form determined in the present study will also be included here for reasons explained later.

Preparation and crystal data

Sodium *N*,*N*-diethyldithiocarbamate, NaS_2CNEt_2 (Na dtc), was added to an aqueous solution of mercury(II) dichloride in a molar ratio 2:1, and a fine yellowish powder was precipitated. The powder was dried and dissolved in acetone. Three types of crystal were obtained by slow evaporation of the solvent. The simultaneous growth of the three types of crystal was often observed in the same beaker. The crystals of the α form were most easily obtained when the evaporation rate of the solvent was slow.

The unit-cell dimensions were measured from zero-level Weissenberg photographs using a Straumanis-type cassette and Cu $K\alpha$ radiation ($\lambda=1\cdot54051$ Å for $K\alpha_1$). The crystal data are summarized in Table 1.

The structure determination of α form

The intensity data for the α form were collected on equi-inclination Weissenberg photographs around the b axis up to the 8th layer and around the c axis to the 6th layer. The specimen was approximately cylindrical with average radii of 0·08 and 0·07 mm for the b and c axes respectively. The multiple-film technique was employed, and the intensities were measured by the use of a microphotodensitometer. They were corrected by the usual Lorentz, polarization and spot-shape factors and also for absorption assuming a cylindrical approximation. The relative structure amplitudes were put on a common scale by a least-squares procedure. A few inaccurate reflexions were omitted, giving a total of 1849 independent reflexions.

A three-dimensional Patterson map indicated the positions of the mercury atoms. The remaining non-hydrogen atoms were located from conventional heavy-atom Fourier maps. The atomic parameters thus obtained were refined by the block-diagonal least-squares program *RBDLS*-32 written by the author, with anisotropic temperature factors for mercury and sulphur atoms and with isotropic temperature factors for nitrogen and carbon atoms. The *R* value was 0·129. Additional cycles of least-squares refinement with anisotropic thermal factors for all 17 atoms gave a final *R* of 0·067 for 1849 observed reflexions. The positions of the hydrogen atoms could not be determined. The quantity $\sum w(kF_o - F_c)^2$ was minimized, where w is the weight of each reflexion, and k is a scale factor. The weighting scheme employed was: $w = 1{\cdot}0$ for $0 < |F_o| \leq 100$, and $w = (100/F_o)^2$ for $|F_o| > 100$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). In the final cycles of the refinement, the dispersion corrections were also taken into account, the correction factors being $\Delta f' = -5{\cdot}0$, $\Delta f'' = 8{\cdot}5$ for Hg and $\Delta f' = 0{\cdot}3$, $\Delta f'' = 0{\cdot}6$ for S respectively. These values were set constant for all ranges of $\sin\theta/\lambda$.

The final atomic parameters and their standard deviations are listed in Table 2. A comparison of observed and calculated structure factors is given in Table 3. In spite of the space group being centrosymmetric, $P2_1/a$, with the conventional choice of the origin of the unit cell, the F_c's are complex owing to the presence of $\Delta f''$ terms. The signs of the F_c's refer to those of the real part of the calculated structure factors.

Table 1. *The crystal data*

Form	α	β	γ
Colour	Deep yellow	Pale yellow	Pale yellow
Habit	Rhomboidal	Column, irregular	Needle
Crystal system	Monoclinic	Monoclinic	Triclinic
a (Å)	16·662 (8)	11·807 (3)	18·562 (2)
b (Å)	10·954 (6)	14·930 (5)	10·157 (8)
c (Å)	9·861 (6)	4·723 (4)	11·012 (4)
α (°)	90	90	113·06 (5)
β (°)	111·8 (2)	106·26 (4)	97·06 (2)
γ (°)	90	90	91·24 (3)
V (Å^3)	1670·6 (24)	799·3 (15)	1890·2 (15)
Space group	$P2_1/a$	$P2_1/a$	$P\bar{1}$
Chemical unit	Hg_2dtc_4*	Hg dtc_2*	$Hg_3Cl_2dtc_4$*
M.W.	994·3	497·1	1265·8
D_m (g cm^{-3})	–	2·06	2·2
D_x	1·976	2·064	2·223
Z	2	2	2
μ for Cu $K\alpha$ (cm^{-1})	227·6	238·1	292·8
Mo $K\alpha$	110·6	115·7	145·9

* dtc = $S_2CN(C_2H_5)_2$.

Table 2. *Final atomic coordinates and anisotropic temperature factors of* α-Hg_2dtc_4 *with their standard deviations*

Atomic coordinates are multiplied by 10^4. Thermal parameters refer to the expression

$$T = \exp\left[-10^{-3}.2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)\right].$$

The B_{eq} values are the equivalent isotropic temperature factors proposed by Hamilton (1959).

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
Hg	4507 (1)	703 (1)	3141 (1)	37 (0)	37 (0)	58 (0)	20 (0)	16 (0)	0 (1)	3·5
S(1)	2932 (3)	864 (4)	2779 (6)	40 (2)	31 (2)	50 (3)	2 (2)	20 (2)	10 (2)	3·1
S(2)	3789 (3)	2588 (5)	1412 (6)	41 (2)	39 (3)	56 (3)	0 (2)	21 (2)	11 (2)	3·5
S(3)	4390 (3)	517 (4)	7254 (7)	52 (3)	28 (2)	91 (4)	12 (2)	51 (3)	10 (3)	4·0
S(4)	5276 (3)	1972 (4)	5637 (6)	28 (2)	41 (2)	50 (3)	−5 (2)	21 (2)	0 (2)	3·0
N(1)	2156 (11)	2788 (15)	1177 (19)	48 (9)	27 (8)	56 (10)	7 (7)	19 (8)	3 (8)	3·4
N(2)	3974 (9)	2780 (13)	6352 (17)	26 (7)	27 (7)	50 (9)	−2 (5)	22 (7)	3 (7)	2·5
C(1)	2872 (10)	2118 (17)	1704 (18)	26 (8)	36 (9)	21 (9)	4 (7)	3 (7)	−1 (8)	2·3
C(2)	4503 (10)	1868 (16)	6368 (19)	16 (7)	39 (10)	34 (10)	0 (6)	11 (7)	−6 (8)	2·3
C(3)	1338 (13)	2467 (20)	1482 (24)	42 (11)	49 (12)	54 (13)	8 (9)	17 (10)	−8 (10)	3·8
C(4)	2106 (18)	3952 (24)	304 (30)	74 (14)	59 (20)	70 (17)	23 (13)	22 (12)	19 (15)	5·4
C(5)	781 (16)	1701 (27)	240 (29)	45 (16)	90 (16)	68 (17)	−3 (12)	5 (14)	4 (13)	5·7
C(6)	2427 (17)	5018 (23)	1332 (29)	69 (15)	49 (14)	84 (17)	16 (12)	33 (14)	18 (13)	5·2
C(7)	3359 (13)	2781 (18)	7045 (22)	45 (10)	39 (10)	54 (13)	9 (8)	26 (9)	−3 (9)	3·5
C(8)	3978 (14)	3915 (19)	5532 (25)	48 (16)	40 (16)	61 (19)	−1 (12)	22 (14)	13 (15)	3·9
C(9)	2440 (17)	2354 (25)	5994 (32)	60 (12)	65 (12)	92 (14)	11 (9)	17 (11)	5 (10)	6·0
C(10)	4571 (18)	4851 (23)	6481 (31)	87 (17)	36 (13)	86 (18)	−15 (12)	38 (15)	−9 (13)	5·4

The crystal structure of the α-form

The crystal structure of α-mercury(II) *N*,*N*-diethyldithiocarbamate projected along the *c* axis is shown in Fig. 1. As can be seen, the crystal consists of isolated dimer units of tetrakis-(*N*,*N*-diethyldithiocarbamato)-dimercury(II), Hg_2dtc_4. The molecular shape, atomic numbering and thermal ellipsoids of atoms are illustrated in Fig. 2. Interatomic distances and bond angles are listed in Table 4. The equations of the planes and the deviation of each atom from these planes are given in Table 5.

The dimer is centrosymmetric and composed of two mercury atoms and four dtc groups. Two of the four ligand molecules act as bidentates while the other two are bridging ligands. Within a molecule, there is an eight-membered ring consisting of two mercury, four sulphur and two carbon atoms; the ring assumes the 'chair' conformation. As far as only strong bonds are concerned, the metal atom is coordinated by four sulphur atoms at distances of 2·418, 2·520, 2·663 and 2·698 Å respectively, to form a strongly distorted tetrahedral configuration. The distortion of the tetrahedron arises partly from the formation of a four-membered ring by mercury and the chelating ligand, the angle S(1)–Hg–S(2) being 70·0°. On the other hand, the two shortest bonds make an angle of 146·0°. The distance between Hg and S(4), 2·698 Å, is the longest of the four short bonds, but it is still definitely shorter than the fifth contact [Hg–S(4'), 3·137 Å] which can be compared with the sum of van der Waals radii between Hg^{2+} and S^{2-} (3·3 Å). Thus, the complex has a typical dimeric nature.

Although S(4') is bonded to Hg' at a distance of 2·698 Å, it is also shared by another mercury atom (Hg). If this fifth Hg–S contact is taken into account, the mercury atom can be better regarded as effectively five-coordinate, with a distorted tetragonal pyramidal environment. In fact, the mean 'basal' plane of the pyramid, composed of four sulphur atoms [S(1), S(2), S(3') and S(4')], is planar within the errors of 0·1 Å, and the vector Hg–S(4) is nearly perpendicular to this basal plane, the angle being 87·3°. The mercury atom (Hg) is deviated by 0·54 Å upwards from this plane. The pentacoordination of the mercury atom has been commonly observed in various mercury–sulphur systems (Lawton, 1971).

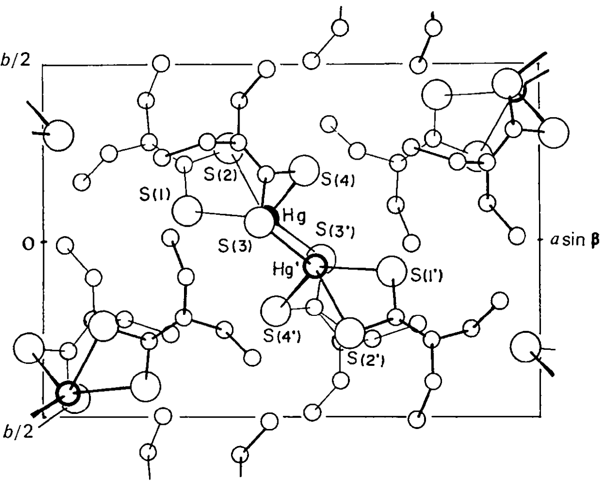
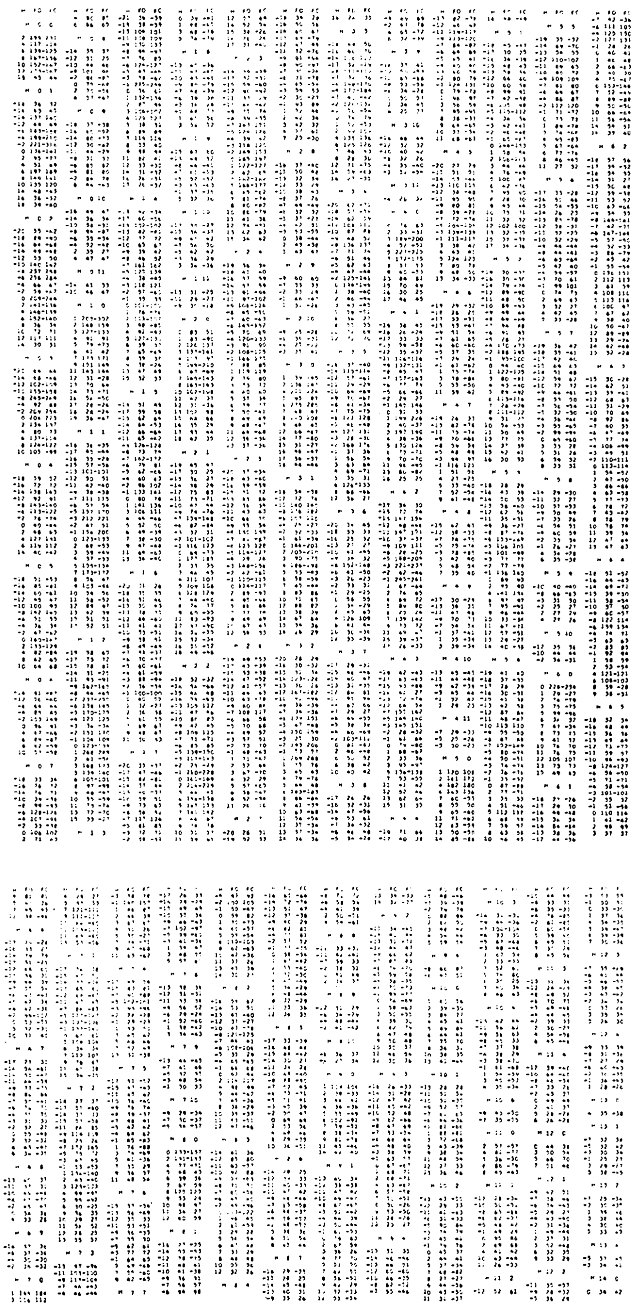


Fig. 1. The crystal structure of α-mercury(II) *N*,*N*-diethyldithiocarbamate projected along the *c* axis.

Table 3. *Observed and calculated structure factors for tetrakis*(*N*,*N-diethyldithiocarbamato*)*dimercury*(II) (*α form*)



The mercury atom lies nearly on both of the planes of two carbamate groups. The deviations of Hg from these planes are quite small: 0·19 Å from ligand I [including S(1) and S(2)] and 0·09 Å from ligand II [including S(3′) and S(4′)]. The dihedral angles between the plane of the carbamate group and the plane passing

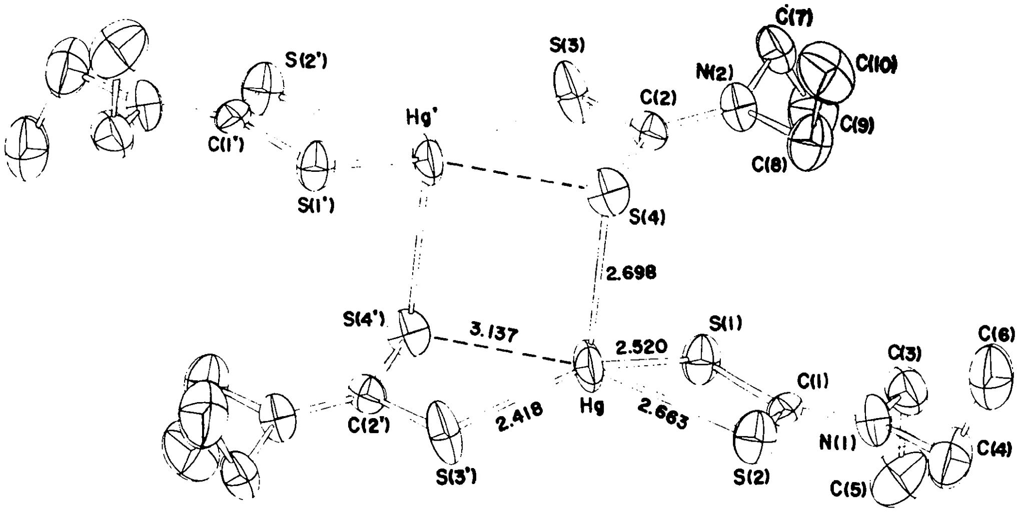


Fig. 2. The molecular structure of Hg_2dtc_4. Thermal ellipsoids are drawn to include 50% of the probability distribution

Table 4. *Interatomic distances* (Å) *and bond angles* (°) (*α form*)

(*a*) Bond distances within a molecule			
Hg–S(1)	2·520 (6)		
Hg–S(2)	2·663 (6)		
Hg–S(4)	2·698 (6)		
Hg–S(3′)	2·418 (7)		
Hg–S(4′)	3·137 (6)		
S(1) –C(1)	1·715 (19)	S(3) –C(2)	1·764 (19)
S(2) –C(1)	1·735 (20)	S(4) –C(2)	1·698 (21)
C(1)–N(1)	1·33 (2)	C(2)–N(2)	1·33 (2)
N(1)–C(3)	1·54 (3)	N(2)–C(7)	1·43 (3)
N(1)–C(4)	1·52 (3)	N(2)–C(8)	1·49 (3)
C(3)–C(5)	1·49 (4)	C(7)–C(9)	1·57 (3)
C(4)–C(6)	1·51 (4)	C(8)–C(10)	1·49 (3)
(*b*) Non-bonding distances within a molecule			
Hg—Hg′	3·744 (1·5)	Hg—S(3)	4·136 (7)
S(1) -S(2)	2·975 (8)	S(3) -S(4)	3·002 (9)
S(1) -S(3)	4·190 (8)	S(2) -S(4)	4·035 (7)
S(1) -S(4)	4·061 (6)	S(3) -S(4′)	4·128 (6)
S(1) -S(4′)	4·187 (6)	S(4) -S(4′)	4·497 (8)
S(2) -S(3′)	4·420 (8)		
(*c*) Bond angles			
S(1)–Hg–S(2)	70·0 (2)	S(2)–Hg–S(3′)	120 ·8(2)
S(1)–Hg–S(4)	102·2 (2)	S(2)–Hg–S(4′)	158·5 (2)
S(1)–Hg–S(3′)	146·0 (2)	S(4)–Hg–S(3′)	107·5 (2)
S(1)–Hg–S(4′)	94·9 (2)	S(4)–Hg–S(4′)	100·6 (2)
S(2)–Hg–S(4)	97·6 (2)	S(3′)–Hg–S(4′)	63·9 (2)
Hg–S(1)–C(1)	87·9 (6)	Hg′–S(3)–C(2)	99·0 (7)
Hg–S(2)–C(1)	83·0 (6)	Hg′–S(4)–C(2)	76·8 (6)
S(1)–C(1)–S(2)	119·2 (9)	S(3)–C(2)–S(4)	120·2 (10)
S(1)–C(1)–N(1)	121·4 (16)	S(3)–C(2)–N(2)	116·5 (15)
S(2)–C(1)–N(1)	119·2 (15)	S(4)–C(2)–N(2)	123·3 (15)
C(1)–N(1)–C(3)	122 (2)	C(2)–N(2)–C(7)	126 (2)
C(1)–N(1)–C(4)	122 (2)	C(2)–N(2)–C(8)	120 (2)
C(3)–N(1)–C(4)	116 (2)	C(7)–N(2)–C(8)	114 (2)
N(1)–C(3)–C(5)	107 (2)	N(2)–C(7)–C(9)	113 (2)
N(1)–C(4)–C(6)	110 (2)	N(2)–C(8)–C(10)	112 (2)
Hg—S(4)–C(2)	100·0 (6)		

Table 4 (*cont.*)

(*d*) Intermolecular contacts less than 4·0 Å

Symmetry codes

	x,	y,	z
None	x,	y,	z
i	$0·5-x$,	$-0·5+y$,	$-z$
ii	$0·5+x$,	$0·5-y$,	z
iii	$1-x$,	$1-y$,	$1-z$
iv	$0·5-x$,	$-0·5+y$,	$1-z$
v	$0·5+x$,	$0·5-y$,	$1+z$
vi	$-0·5+x$,	$0·5-y$,	$-1+z$
vii	$0·5-x$,	$0·5+y$,	$1-z$

Hg ····C(4^{i})	3·96 (2) Å
S(1)····C(4^{i})	3·67 (3)
S(1)····C(6^{i})	3·98 (3)
S(2)····C(5^{ii})	3·98 (3)
S(2)····C(6^{i})	3·91 (3)
S(2)····C(10^{iii})	3·93 (3)
S(3)····C(6^{iv})	3·81 (3)
S(4)····C(9^{ii})	3·57 (3)
N(2) ···C(5^{v})	3·94 (3)
C(1)····C(4^{i})	4·00 (3)
C(1)····C(6^{i})	3·66 (3)
C(2)····C(5^{v})	3·94 (3)
C(5)····C(10^{vi})	3·89 (4)
C(6)····C(7^{vii})	3·87 (4)
C(6)····C(9^{vii})	3·62 (4)
C(8)····C(10^{iii})	3·90 (4)
C(10)···C(10^{iii})	3·71 (5)

through Hg and the two sulphur atoms belonging to each carbamate group are 4·5° and 2·6° for groups I and II respectively.

The carbamate groups are planar except for the terminal methyl groups. The two methyl groups on each ligand are shifted in opposite directions from the ligand plane, as is usually observed. The interatomic distances and angles within the ligands are quite normal. A conjugated nature of the S_2CN– groups is indicated by short C–N bond lengths (mean: 1·33 Å). The dihedral angle between the two ligand planes is 24·9°, while the planes passing through Hg, S(1) and S(2), and Hg, S(3′) and S(4′) make an angle of 30·4°.

The structure determination of the β form

The crystals of the *β* form were generally irregular in external shape, and the specimen used for the X-ray work was ground approximately cylindrically (mean diameter: 0·13 mm) with respect to the rotation axis. The intensities were collected on an equi-inclination type automatic diffractometer RIKEN READ-1 (Sakurai, Ito & Iimura, 1970) around the *c* axis up to the 14th layer and around the *b* axis to the first layer. The latter data were used only for relative scaling of the former data, and were not included in the final set of reflexion data. Mo $K\alpha$ radiation monochromated by graphite was used, and the crystal was rotated in an ω–Y mode at scanning rate of 1°/min. Some unreliable reflexions were omitted, and a total of 1048 reflexions, which have intensities larger than three times their standard deviations, were considered observed.

The structure was deduced from Patterson maps, and refined by a block-diagonal least-squares program with anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were not located. The weighting scheme employed was: $w=0·6$ if $|F_o|<14$, $w=1·0$ if $14\le|F_o|\le80$ and $w=(80/F_o)^2$ if $|F_o|>80$. Dispersion corrections were applied to atomic scattering factors, with $\Delta f'=-2·9$, $\Delta f''=10·1$ for Hg and $\Delta f'=$

Table 5. *Equations of planes* (*α form*)

Equations are expressed in the form $AX+BY+CZ=D$, where X, Y and Z are coordinates along the cell edges in Å. Those for planes 1, 2 and 3 are the least-squares planes, with all weights equal to 1. Planes 1 and 2 are the ligand I and II respectively. Plane 3 corresponds to the basal plane of the tetragonal pyramid surrounding the mercury atom. The values of A, B, C and D are multiplied by 10^3.

Plane	A	B	C	D	Atoms defining the plane
1	−5	556	774	2605	S(1), S(2), C(1), N(1), C(3), C(4)
2	380	362	649	7678	S(3), S(4), C(2), N(2), C(7), C(8)
3	170	481	736	3382	S(1), S(2), S(3′), S(4′)
4	− 65	596	767	2349	Hg, S(1), S(2)
5	375	321	668	5137	Hg, S(3′), S(4′)

Deviations of atoms from the planes (Å)

Plane	Hg	S(1)	S(2)	C(1)	N(1)	C(3)	C(4)	C(5)	C(6)
1	0·185	0·017	0·017	−0·04	−0·03	0·02	0·02	−1·39	1·45
	Hg′	S(3)	S(4)	C(2)	N(2)	C(7)	C(8)	C(9)	C(10)
2	−0·089	−0·050	0·054	−0·01	0·01	0·06	0·06	−1·36	1·29
	Hg	S(1)	S(2)	S(3′)	S(4′)	S(4)	C(1)	C(2′)	
3	0·543	−0·082	0·078	−0·076	0·080	3·238	−0·22	−0·18	
4	–	–	–	−1·216	−0·847	2·632	0·01	−0·06	
5	–	−1·169	−0·927	–	–	2·569		0·04	

Angles between the planes (°)

	2	3	4	5
1	24·9	11·0	4·5	25·9
2		13·9	29·3	2·6
3			15·4	15·0
4				30·4

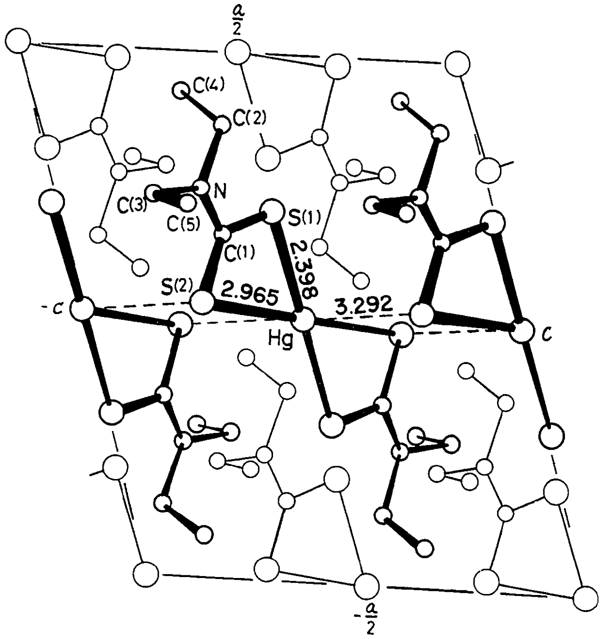


Fig. 3. The crystal structure of β-mercury(II) *N*,*N*-diethyldithiocarbamate projected along the *b* axis.

0·1, $\Delta f''=0{\cdot}2$ for S. Other factors involved in the refinement procedures are the same as those for the α form. The final *R* value is 0·045 for 1048 reflexions. The final atomic parameters with their standard deviations are given in Table 6. A comparison of the observed and calculated structure factors is shown in Table 7.

The crystal structure of the β form

Healy & White (1973; hereafter abbreviated to HW) have recently reported the structure of this form. Their structure is essentially the same as ours. However, since the accuracy of the present results seems a little better (HW's structure is based on 810 visually estimated data with the final *R* of 0·122), it will be convenient to present these results briefly.

The crystal structure viewed along the *b* and *c* axes is shown in Figs. 3 and 4 respectively. Interatomic distances and bond angles are summarized in Table 8. The equations of the planes are given in Table 9.

Table 7. *Observed and calculated structure factors for bis-(N,N-diethyldithiocarbamato)mercury*(II) (*β form*)

In contrast to the α form, crystals of the β form consist essentially of monomeric units of bis-(*N*,*N*-diethyldithiocarbamato)mercury(II). The mercury atom adopts a planar configuration as a result of the requirement of the space group, with two types of independent Hg–S distances of 2·398 and 2·965 Å (*cf.* 2·397 and 2·990 Å according to HW). The nearest intermolecular mercury contact occurs at a distance of 3·292 Å (HW: 3·307 Å) to two sulphur atoms (Fig. 3). Since the direction of this weak bond is approximately perpendicular to the plane composed of Hg, S(1) and S(2) atoms, the metal atom has a distorted octahedral en-

Table 6. *Final atomic coordinates and anisotropic temperature factors of* β-Hg dtc$_2$ *with their standard deviations*

Notations are the same as those given in Table 2.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
Hg	0 (0)	0 (0)	0 (0)	51 (0)	48 (0)	65 (0)	− 9 (1)	35 (0)	11 (1)	4·0
S(1)	1995 (3)	276 (2)	−57 (8)	48 (2)	59 (2)	47 (2)	−11 (1)	23 (1)	8 (1)	3·9
S(2)	208 (3)	1362 (3)	−4395 (9)	51 (3)	51 (2)	66 (3)	0 (1)	31 (2)	5 (2)	4·2
N	2509 (9)	1605 (7)	−3204 (20)	46 (5)	49 (6)	29 (5)	− 3 (5)	26 (4)	− 8 (4)	3·0
C(1)	1648 (10)	1156 (8)	−2709 (27)	47 (6)	31 (6)	47 (7)	− 8 (5)	27 (6)	−21 (5)	3·1
C(2)	3784 (14)	1452 (11)	−1508 (34)	69 (9)	72 (10)	56 (9)	−18 (8)	35 (8)	7 (8)	4·9
C(3)	2324 (13)	2301 (8)	−5466 (34)	67 (10)	38 (9)	65 (10)	4 (7)	38 (8)	10 (7)	4·1
C(4)	4377 (17)	779 (13)	−3030 (42)	72 (11)	84 (13)	80 (13)	16 (9)	30 (10)	19 (10)	6·1
C(5)	2212 (18)	3228 (12)	−3961 (54)	85 (13)	63 (11)	145 (19)	− 9 (10)	69 (13)	−21 (11)	7·1

vironment. The short intermolecular Hg–S bonds extend along the *c* axis to give an infinite linear-chain structure. All intramolecular bond distances and angles are normal.

Discussion

Crystals of both α and β forms contain two dtc groups per mercury atom. In the α form, one dtc group acts as a chelating ligand whereas the other carbamate group acts as a bridging ligand. One of the sulphur atoms in the latter ligand [S(4′)] is partly shared by another metal atom, showing an incomplete chelation of that ligand. In the β form, however, two dtc groups connected by a centre of inversion act mainly as chelating ligands, and the whole structure is essentially monomeric. In this case, the S(1) atom is strongly coordinated to the metal atom at 2·398 Å while the other sulphur atom [S(2)] forms rather a weak bond (2·965 Å), and the chelation is again somewhat incomplete. The latter sulphur atom is partly shared by a neighbouring

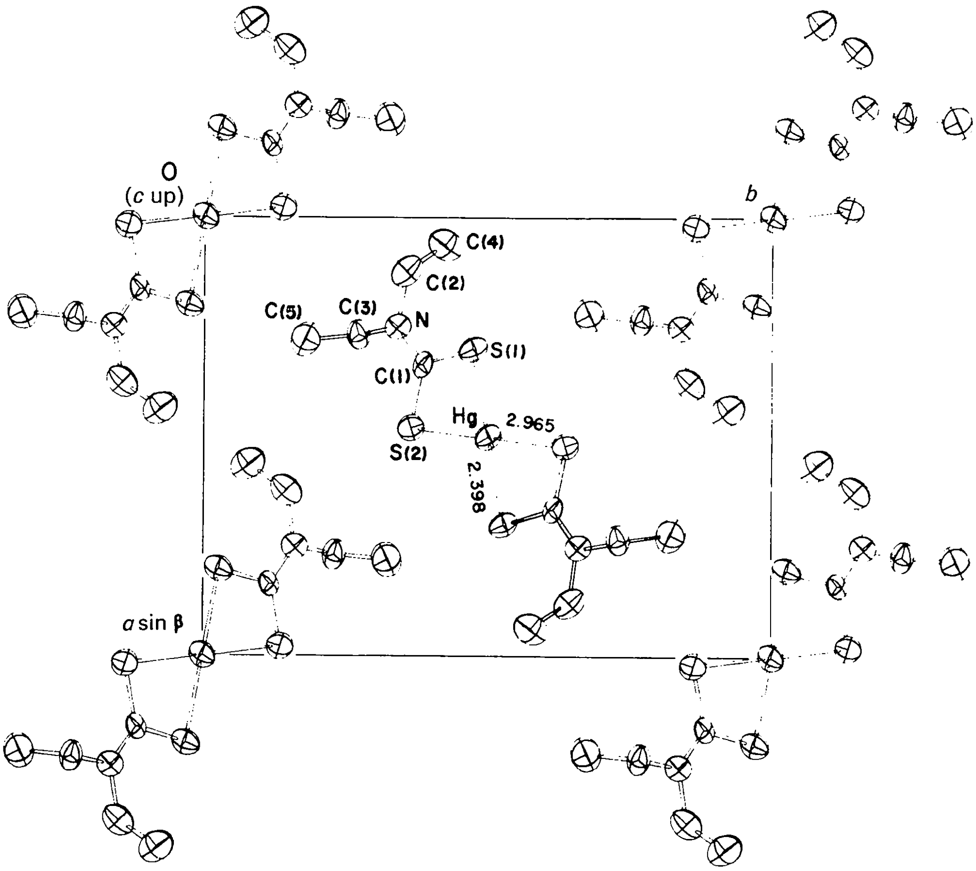


Fig. 4. The crystal structure of β-mercury(II) *N*,*N*-diethyldithiocarbamate projected along the *c*-axis. Thermal ellipsoids are drawn to include 50% of the probability distribution.

Table 8. *Interatomic distances* (Å) *and bond angles* (°) (*β form*)

(*a*) Bond distances within a molecule			
Hg—S(1)	2·398 (4)	N—C(2)	1·51 (2)
Hg—S(2)	2·965 (4)	N—C(3)	1·46 (2)
S(1)–C(1)	1·782 (12)	C(2)–C(4)	1·52 (3)
S(2)–C(1)	1·691 (12)	C(3)–C(5)	1·58 (3)
C(1)–N	1·29 (2)		
(*b*) Bond angles			
S(1)–Hg—S(2)	66·4 (1)	C(1)–N—C(2)	122·9 (11)
Hg—S(1)–C(1)	95·8 (4)	C(1)–N—C(3)	122·4 (10)
Hg—S(2)–C(1)	79·3 (5)	N—C(2)–C(4)	111·9 (12)
S(1)–C(1)–N	118·2 (8)	N—C(3)–C(5)	108·0 (14)
S(2)–C(1)–N	123·9 (9)		

Table 8 (*cont.*)

(*c*) Intermolecular contacts less than 4·0 Å

Symmetry codes:

None	x,	y,	z
i	x,	y,	$1+z$
ii	$0·5-x$,	$-0·5+y$,	$1-z$
iii	$-0·5+x$,	$0·5-y$,	z
iv	$0·5+x$,	$0·5-y$,	z
v	$-x$,	$-1-y$,	$-z$
vi	$-x$,	$-1-y$,	$1-z$
vii	$-\ 1-x$,	$-1-y$,	$-z$
viii	$-\ 1-x$,	$-1-y$,	$1-z$

Hg····S(2^{i})	3·292 (4) Å
Hg····C(1^{i})	3·856 (11)
S(1)····N^{i}	3·699 (10)
S(1)···C(1^{i})	3·839 (14)
S(1)···C(3^{i})	3·677 (14)
S(1)···C(4^{i})	3·777 (17)
S(1)···C(5^{ii})	3·582 (20)
S(2)···C(3^{iii})	3·856 (15)
S(2)···C(5^{iii})	3·652 (22)
N·····C(3^{i})	3·87 (2)
C(1)···C(3^{i})	3·71 (2)
C(2)···C(3^{i})	3·93 (3)
C(2)···C(4^{i})	3·99 (3)
C(4)···C(5^{iv})	3·80 (3)
C(4)···C(4^{v})	3·55 (3)
C(4)···C(4^{vi})	3·66 (3)

Non-bonding sulphur–sulphur contacts

S(1)···S(2)	2·976 (5)
S(1)···S(2^{i})	4·170 (6)
S(1)···S(2^{vii})	3·974 (5)
S(1)···S(2^{viii})	4·497 (6)

mercury atom at a distance of 3·292 Å, resulting in the formation of a linear chain, although the interaction between the monomeric units is considerably weaker than that in the α form.

The relationship between the molecular structure of the α form and that of the β form can be easily seen in Fig. 2. In the monomeric form the complex is almost planar. On the other hand, in the dimeric form, the two dtc groups coordinated to one Hg atom are not coplanar as a result of the pseudo-tetragonal pyramidal configuration around the mercury atom.

The crystal and molecular structure of the α form resembles those of Zn_2dtc_4 (Bonamico, Mazzone, Vaciago & Zambonelli, 1965) and Cd_2dtc_4 (Domenicano, Torelli, Vaciago & Zambonelli, 1968) and is also somewhat similar to that of Cu_2dtc_4 (Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli, 1965). The intramolecular distances and angles related to metal–sulphur bonds in these compounds are compared in Table 10, in which corresponding values in mercury diisopropyldithiophosphate (Lawton, 1971) are also included for comparison. In spite of a close similarity between the general features of Hg_2dtc_4 and those of Zn and Cd complexes, there is a significant discrepancy between the distribution of distances of five short metal–sulphur contacts in the Hg compound and those in Zn and Cd compounds. It is apparent that the mercury complex is more dissymmetric as compared with other dimeric dithiocarbamates of group II*b* elements.

The complex molecule of Hg dtc_2 takes a planar configuration in crystals of the β form. The planar dtc complex is also found in the nickel compound (α form; Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965). However, in the case of the nickel compound, four Ni–S distances are almost the same (two at 2·195 and two at 2·207 Å), and the shortest intermolecular nickel contact is to methylene carbon atoms at 3·54 Å. In view of these lengths the Ni dtc_2 (α form) is more completely monomeric than the mercury complex, and the degree of dissymmetry of two types of metal–sulphur bond is again more remarkable in the mercury compound.

Lawton (1971) discussed the stereochemical configuration of a mercury(II) ion surrounded by several sulphur atoms, and showed that the mercury environment is largely classified into two categories. In one of them the Hg(II) ion exhibits a strong tendency to form linear bicovalent bonds in which two of the Hg–S distances (2·36–2·49 Å) are definitely shorter than others (type *A*), while in another, the Hg atom is attached to four ligand atoms at 2·49–2·66 Å with tetrahedral symmetry (type *B*). According to Lawton's classification, the β-Hg dtc_2 clearly belongs to type *A*, and the bonds have a typical linear-bicovalent character. The dimeric form also has two relatively short Hg–S bonds (2·418 and 2·520 Å), the angle between them being 146·0°. However, since these bond lengths cannot be said to be unequivocally shorter than the other two bonds (2·662 and 2·698 Å), it seems more appropriate to con-

Table 9. *Equations of planes* (*β form*)

Notations are the same as those used in Table 5.
The plane 1 is the least-squares plane, and corresponds to the ligand.

Plane	*A*	*B*	*C*	*D*	Atoms defining the plane
1	−260	662	747	−315	S(1), S(2), C(1), N, C(2), C(3)
2	−118	719	691	0	Hg, S(1), S(2)

Deviations of atoms from the plane (Å).

Plane	Hg	S(1)	S(2)	C(1)	N	C(2)	C(3)	C(4)	C(5)
1	0·315	−0·045	0·047	−0·00	0·00	0·06	−0·05	−1·33	1·43
2	–	–	–	0·13	0·33	0·54	0·36	−0·76	1·87

The angle between planes 1 and 2 is 8·9°.

sider these four lengths as being alike and distributed around 2·57 Å. This is in contrast to the other examples listed by Lawton which have definitely two short and two or more long Hg–S bonds, as in mercury diisopropyldithiophosphate (see Table 10). Thus, the α form may be better described as having an intermediate character between type *A* and type *B*. In the disordered form of mercury diethyldithiophosphate, the mercury atoms seem to be tetrahedrally surrounded by four sulphur atoms at distances of *ca.* 2·56 Å (Watanabe, 1972, 1973). Considering these facts, it is interesting that a gradual change between two extreme configurations adopted by mercury–sulphur systems, linear bicovalent and tetrahedral, is observed in a series of dithioacid complexes of mercury.

The molecules of mercury *N*,*N*-diethyldithiocarbamate exist as dimers in the α form and as monomers in the β form. This type of polymorphism has also been observed, for example, for bis-(*N*-methylsalicylaldiminato)copper(II). This complex (Cu msa_2) is known to crystallize in three modifications. In crystals of the α and β forms the molecules are essentially monomeric (Lingafelter, Simmons, Morosin, Scheringer & Freiburg, 1961) while in the γ form they are dimeric (Hall, Sheat & Waters, 1968). The molecular structure of the dimeric form (Cu_2msa_4) and the structural relationship between the monomeric and dimeric forms are somewhat similar to those found in the Hg–dtc system. In all three modifications the copper atom has two chelating msa ligands and is attached by two oxygen and two nitrogen atoms. In crystals of the γ form, one of the msa groups per Cu atom acts also as a partially bridging ligand, and the two monomer units are held together by two Cu–O bonds to form a dimer. In that case, however, these two Cu–O bonds connecting the monomer units are 2·43 and 2·46 Å in length, and are considerably weaker than the Cu–O coordination bonds within the basic monomer units (1·87–1·90 Å). Therefore, this complex is better described as being in a state intermediate between monomer and dimer. The repulsion of bulky ligand groups is perhaps responsible for such an incomplete dimerization. In this respect it is to be noted that the degree of dimerization is more complete in the α form of Hg–dtc complex.

Although the molecular weight of Hg dtc_2 in a solvent has not yet been measured, it is very likely that monomers and dimers are coexistent (at least in acetone), corresponding to two crystal modifications. When crystals of the β form were dissolved in acetone, crystals of both α and β forms could be precipitated by a slow evaporation of the solvent. The presence of different kinds of molecular clustering seems to be rather common in complexes with dithioacid ligands. According to Domenicano *et al.* (1968), the Cd dtc_2 complex crystallizes as dimers, but the monomers and dimers are coexistent in benzene, the relative amount of the two forms depending on atmospheric pressure. In the case of the Cu dtc_2 complex, the molecules are again dimeric in the solid state whereas they are monomeric in benzene of chloroform under certain conditions (Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli, 1965). Mercury diisopropyldithiophosphate is poly-

Table 10. *A comparison of metal–sulphur interactions in some dithioacid complexes with five coordinations*

Metal–sulphur contacts (Å)	Cu_2dtc_4	Zn_2dtc_4	Cd_2dtc_4	α-Hg_2dtc_4	$Hg_\infty ptp_{2\infty}$*
	2·297	2·331	2·536	2·418	2·388†
	2·301	2·355	2·547	2·520	2·391
	2·317	2·383†	2·594	2·663	2·748
	2·339	2·443	2·644†	2·698†	2·888
	2·851†	2·815	2·800	3·137	3·408
σ (mean)	0·002	0·003	0·003	0·006	0·005
S–metal–S angles (°)					
(*a*) Angles within the chelating ligand					
	76·5	69·6	67·5	63·9	62·0
	77·3	75·8	70·9	70·0	76·3
(*b*) Angles within a 'monomer' unit					
	161·8‡	137·7‡	145·3‡	146·0‡	109·0
	172·3	160·0	158·9	158·5	134·1
	101·5	93·6	99·3	94·9	81·6
	102·3	106·9	109·7	120·8	89·4
(*c*) Angles involving the 'bridging' sulphur atoms					
	4 at	4 at	4 at	4 at	1 at
	93·1	94·4	96·9	97·6	149·7‡
	~100·4	~112·1	~107·6	~107·5	3 at
					95·8
					~118·5
σ (mean)	0·2	0·2	0·1	0·2	0·2

* Hg diisopropyldithiophosphate.

† The metal–sulphur bond connecting two (or more) 'monomeric' units to form dimers or polymers. In $Hg_\infty ptp_{2\infty}$, the approximation of 'monomer unit' is not good.

‡ The angle involving two shortest metal–sulphur bonds.

meric in crystals and dissociates into monomers in benzene (Lawton, 1971).

Since the stereochemistry of a metal complex undoubtedly depends not only on the intramolecular metal–ligand interactions but also on the effect of the molecular environment, the appearance of different molecular shapes in solution and in the solid should be possible in some cases. In the description of the structure of coordination compounds, however, we frequently encounter a statement such as 'monomers and dimers are coexistent in solutions but the complex is monomeric in crystals'. Although it is doubtful whether both types of stable crystals corresponding to the monomeric and dimeric forms could always be obtained, such a conclusion may sometimes be misleading unless a careful examination of the polymorphism of the grown crystals is made. The crystal structure of the 'γ form', $Hg_3Cl_2dtc_4$, will appear shortly in a separate paper.

The calculations in this study were carried out on FACOM 270-30 Computer installed in this Institute. Figs. 2 and 4 were drawn by *ORTEP* (Johnson, 1965). Other computations were made with the programs *ANSFR*-32 (Fourier synthesis) and *RBDLS*-32 (least-squares refinement) written by the author, and with the universal crystallographic computation system UNICS (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967).

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Structure and Conformation of Orthorhombic L-Cysteine

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The crystal structure of an orthorhombic form of L-cysteine has been determined by X-ray diffraction. The molecule crystallizes in the space group $P2_12_12_1$ with four molecules in a unit cell of dimensions $a = 8{\cdot}116 \pm 3$, $b = 12{\cdot}185 \pm 4$, $c = 5{\cdot}426 \pm 2$ Å; density $D_x = 1{\cdot}50$, $D_{\rm meas} = 1{\cdot}47$ g cm^{-3}. After full-matrix refinement, the R value was 3·75% for the 1062 observed reflexions. The molecule exists as a zwitterion with a three-dimensional network of hydrogen bonds. Conformational angles are close to those observed in other cysteinyl residues. The thiol hydrogen was not located.

Introduction

Although the crystal structures of monoclinic cysteine and several closely related compounds have been determined by X-ray diffraction (Lakshminarayanan, Sasisekharan & Ramachandran, 1967; Harding & Long, 1968; Hendrickson & Karle, 1971) hydrogen atoms were not located; hence, details of hydrogen bonding are not available for this class of compounds. Since such interactions are likely to be of importance in the biological activity we have attempted to provide details of the hydrogen-bond geometry as well as accurate bond distances and conformational parameters in our study of the orthorhombic form of L-cysteine.