Irregular Three-Coordination in Mercury: Structures of Phenyl- and Methylmercury(II) Dithizonate*

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Abstract

$[Hg(C_6H_5)(C_{13}H_{11}N_4S)]$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 5.991$ (3), $b = 20.68$ (1), $c = 17.129$ (9) Å, $\beta = 99.40$ (5)°, $Z = 4$. $[Hg(CH_3)(C_{13}H_{11}N_4S)]$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 14.866$ (7), $b = 11.194$ (6), $c = 4.557$ (3) Å, $\alpha = 89.30$ (5), $\beta = 95.85$ (5), $\gamma = 97.62$ (5)°, $Z = 2$. Final $R = 0.058$ and 0.061 respectively. In both structures the Hg atom exhibits planar, irregular three-coordination, the geometry at the Hg atom being approximately T-shaped, with the dithizone residue $(C_{13}H_{11}N_4S^-)$ acting as a bidentate ligand coordinating through S and N. The imino proton participates in a weak intramolecular hydrogen bond which stabilizes the N—N—C—N—N chain in an *anti,s-trans* configuration relative to the formal C=N double and C—N single bonds.

Introduction

Irradiation by visible light of solutions of mercury(II) bis(dithizonate) $[Hg(Hdz)_2, (1)]$ in organic solvents induces a colour change from yellow to blue (Irving, 1977; Meriwether, Breitner & Colthup, 1965; Meriwether, Breitner & Sloan, 1965; Webb, Bhatia, Corwin & Sharp, 1950). This and the thermal reverse reaction proceed sufficiently slowly ($t_{1/2}$ of the order of minutes) for kinetic measurements to be made (Geosling, Adamson & Gutierrez, 1978; Meriwether, Breitner & Colthup, 1965; Meriwether, Breitner & Sloan, 1965), and spectrophotometric data (Carlin, 1966; Hutton & Irving, 1979a; Meriwether, Breitner & Colthup, 1965) point to the equilibrium (1) ⇌ (2) where the conformation of only one of the dithizone residues is shown in detail.

** IUPAC nomenclature: (1,5-Diphenylthiocarbazonato-N,S)-phenylmercury(II) *and* -methylmercury(II).

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(1, yellow)   (2, blue)
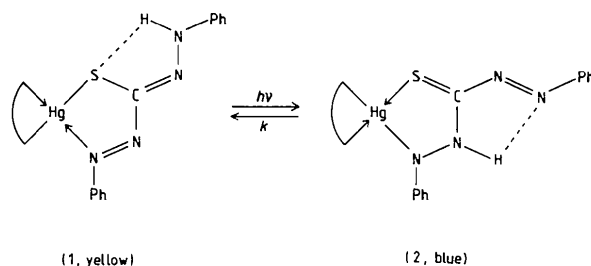
A series of solid complexes from organomercury(II) cations and dithizone have recently been prepared (Hutton & Irving, 1979a,b) which display similar photochromism (yellow ⇌ blue) when suitably irradiated in organic solvents, and which are fully 100 times more soluble than (1), allowing IR and NMR investigations of the two isomers (Hutton & Irving, 1979b). It has not proved possible to isolate a specimen of the blue isomer by irradiating crystals of the stable yellow form: photo-isomerization does not appear to proceed at a measurable rate in the absence of a solvent. Nor has it proved possible to secure crystals of the blue form by carefully and slowly concentrating a solution kept in the blue form by constant and intense illumination: only the stable yellow form crystallizes out. Whereas it has only been possible to assign the structure of the blue isomers [*cf.* (2)] of organomercury(II) dithizonates, $RHg(Hdz)$, from spectroscopic measurements on irradiated solutions, that of the yellow forms of phenylmercury(II) dithizonate [PhHg(Hdz), (I)] and methylmercury(II) dithizonate [MeHg(Hdz), (II)] have now been established unambiguously by X-ray crystallography and are discussed in relation to that of mercury(II) bis(dithizonate) which shows a distorted tetrahedral coordination about Hg with strong Hg—S bonds and weakly coordinated N atoms [as (1); Alsop, 1971; Harding, 1958]. Since dithizone is a bidentate chelating agent the interesting possibility of three-coordination about the Hg atom arises in the 1:1 dithizonates derived from organomercury(II).

Experimental

(I) was prepared by shaking an aqueous solution of phenylmercury(II) acetate with an equivalent amount of dithizone (1,5-diphenylthiocarbazone, H_2dz) dissolved in chloroform. The organic phase was washed consecutively with water, $1M$ ammonia solution, and water, and then dried with sodium sulphate before being filtered and evaporated to dryness at room temperature. The residue was purified by chromatography (alumina/benzene) and then recrystallized from benzene/ethanol. Fragile red-brown needles elongated along a were obtained by slow evaporation at room temperature from benzene/1-butanol.

(II) was prepared similarly, purified chromatographically and recrystallized from benzene/n-hexane. Crystals for X-ray measurements, prepared as above for (I), were elongated along c. Microanalysis and m.p. data are given in Table 1.

Preliminary cell dimensions and space-group symmetry were determined from photographs. For (I) the systematic absences $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$ indicated the space group $P2_1/c$. No systematic absences were found for (II); the space group $P\bar{1}$ was

chosen from analysis of E statistics and confirmed by successful refinement of the structure. Lattice constants were obtained by least squares from the settings of 25 high-order reflections measured on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·7107 Å). Three reference reflections were periodically monitored to check stability. The data were corrected for Lorentz–polarization effects but not for absorption. Crystal data and experimental details are listed in Table 1.

Solution and refinement of the structures

Both structures were solved by locating the Hg atoms in Patterson maps; subsequent weighted difference syntheses yielded the positions of all the remaining non-hydrogen atoms and several peaks were found in chemically reasonable positions for H atoms. The final full-matrix least-squares refinement was carried out with the Hg and S atoms treated anisotropically and the remaining non-hydrogen atoms isotropically. The aromatic H atoms were constrained to ride at 1·08 Å from their respective parent C atoms, their positions being .dictated by the geometry of the molecule. Their isotropic temperature factors were treated as a single parameter. The methyl H atoms in (II) were similarly placed in calculated positions and refined as a rigid group with a single temperature factor. In both structures the imino proton, H(N5), which had been revealed in previous difference maps, was fixed at 1·00 ± 0·01 Å from N(5) and its temperature factor was refined independently. Details of the final refinements are given in Table 1. The weighting schemes were chosen to give the smallest systematic variation of $w\Delta^2$ with the magnitude of F_o, as shown by analyses of variance computed after the final cycles.* In the final cycle for each structure the mean e.s.d. in the parameters of the non-hydrogen atoms was >100 times the average parameter shift, while final difference maps were smooth except close to Hg where the largest residual peaks were 1·0 (I) and 2·2 e Å^{-3} (II). Complex neutral-atom scattering factors were taken from Cromer & Mann (1968) for Hg, C, N and S, and from Stewart, Davidson & Simpson (1965) for H, with dispersion corrections from Cromer & Liberman (1970). Table 2 lists the final fractional coordinates for the non-hydrogen atoms [but including H(N5)] of both (I) and (II).

Table 1. *Crystal data and experimental and refinement parameters for the crystal structures of* (I) *and* (II)

Crystal data	Compound (I)	Compound (II)
Molecular formula	[Hg(C₆H₅)(C₁₃H₁₁N₄S)]	[Hg(CH₃)(C₁₃H₁₁N₄S)]
M_r	533·03	470·96
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	5·991 (3)	14·866 (7)
b (Å)	20·68 (1)	11·194 (6)
c (Å)	17·129 (9)	4·557 (3)
α (°)		89·30 (5)
β (°)	99·40 (5)	95·85 (5)
γ (°)		97·62 (5)
V (Å³)	2094 (2)	748 (1)
D_m (Mg m⁻³)	1·63	2·01
D_c (Mg m⁻³)	1·69 for Z = 4	2·09 for Z = 2
μ(Mo $K\alpha$) (mm⁻¹)	7·17	10·0
$F(000)$	1016	444
Melting point (K)	445–446	425–428
Composition		
%C found (calc.)	42·25 (42·8)	35·9 (35·7)
%H	3·1 (3·0)	3·0 (3·0)
%N	10·45 (10·5)	11·85 (11·9)
Data collection		
Crystal dimensions (mm)	0·50 × 0·04 × 0·02	0·70 × 0·05 × 0·15
Scan mode	ω–2θ	ω–2θ
Scan width (°θ)	1·2	1·2
Scan speed (°θ s⁻¹)	0·04	0·04
Range scanned (2θ) (°)	6–40	6–46
Stability of standard reflections (%)	1·3	1·5
Number of reflections collected	2029	2062
Number of observed reflections	1354 with I(rel) > $2\sigma I$(rel)	1836 with I(rel) > $2\sigma I$(rel)
Refinement		
Number of variables	117	106
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0·058	0·061
$R_w = \Sigma w^{1/2}\|\|F_o\| - \|F_c\|\|/\Sigma w^{1/2}\|F_o\|$	0·060	0·058
Weighting scheme w	$(\sigma^2 F_o + 0·0018F_o^2)^{-1}$	$(\sigma^2 F_o)^{-1}$
U_{iso} of H atoms in calculated positions		
Aromatic (Å²)	0·08 (2)	0·08 (2)
Methyl (Å²)	–	0·10 (4)
U_{iso} of constrained imino H(N5) (Å²)	0·05 (7)	0·03 (4)
Range of U_{iso} values for non-H atoms (Å²)	0·035 (6)–0·087 (11)	0·040 (4)–0·073 (6)

Table 2. *Fractional coordinates* $(\times 10^3$; *for* Hg *and* S $\times 10^4)$ *of the non-hydrogen atoms* [*but including* H(N5)] *for* (I) *and* (II), *with e.s.d.'s in parentheses*

	Compound (I)			Compound (II)		
	x	y	z	x	y	z
Hg	1881 (2)	5825 (1)	124 (1)	1105 (1)	1661 (1)	4102 (2)
S	3293 (12)	4835 (3)	707 (4)	1085 (3)	71 (4)	7650 (11)
N(1)	−19 (3)	564 (1)	136 (1)	275 (1)	114 (1)	487 (3)
N(2)	68 (4)	520 (1)	184 (1)	293 (1)	27 (1)	657 (3)
C(3)	247 (4)	483 (1)	163 (2)	220 (1)	−29 (1)	805 (4)
N(4)	336 (4)	450 (1)	224 (1)	246 (1)	−113 (1)	982 (3)
N(5)	522 (4)	416 (1)	217 (1)	183 (1)	−171 (1)	1137 (3)
H(N5)	522 (36)	404 (9)	160 (4)	117 (2)	−159 (11)	1110 (27)
C(1A)	115 (4)	668 (1)	−55 (1)	82 (1)	308 (1)	141 (4)
C(2A)	−95 (4)	679 (1)	−91 (1)			
C(3A)	−132 (5)	734 (1)	−136 (2)			
C(4A)	25 (5)	775 (1)	−147 (2)			
C(5A)	240 (5)	763 (1)	−110 (2)			
C(6A)	277 (5)	708 (1)	−68 (2)			
C(1B)	−201 (4)	601 (1)	158 (1)	351 (1)	168 (2)	338 (4)
C(2B)	−265 (4)	654 (1)	116 (2)	342 (1)	282 (2)	223 (4)
C(3B)	−439 (5)	692 (2)	136 (2)	412 (1)	338 (2)	70 (4)
C(4B)	−554 (5)	671 (2)	198 (2)	489 (1)	282 (2)	35 (4)
C(5B)	−489 (5)	616 (1)	240 (2)	495 (1)	171 (2)	154 (4)
C(6B)	−302 (5)	581 (2)	221 (2)	426 (1)	112 (2)	302 (4)
C(1C)	643 (4)	383 (1)	280 (2)	204 (1)	−269 (1)	1315 (4)
C(2C)	845 (5)	354 (2)	274 (2)	132 (1)	−328 (2)	1469 (4)
C(3C)	962 (6)	319 (2)	336 (2)	150 (1)	−427 (2)	1647 (4)
C(4C)	902 (6)	316 (2)	406 (2)	234 (1)	−465 (2)	1666 (4)
C(5C)	692 (6)	346 (2)	415 (2)	304 (1)	−407 (2)	1522 (4)
C(6C)	557 (5)	381 (1)	348 (2)	288 (1)	−307 (2)	1341 (4)

All computations were performed at the Computer Centre of the University of Cape Town on a Univac 1100/81 computer with *SHELX* (data reduction, structure solution and refinement), *XANADU* (molecular geometry) and *PLUTOX* (illustrations) (Sheldrick, 1976; Roberts & Sheldrick, 1975; Motherwell, 1975).

Results and discussion

The molecular structure of (I) with atomic nomenclature is shown in Fig. 1; in (II) a methyl group replaces phenyl ring *A*. Bond lengths and angles for (I) and (II) are given in Figs. 2 and 3 respectively for two molecules which relate to each other by a centre of symmetry. Both crystals consist of discrete molecules, each containing a dithizone residue acting as a bidentate ligand coordinating through S and N. One phenyl group (*B*) of the ligand is attached to the chelate ring whereas the other phenyl group (*C*) is extended as far as posible from the central Hg atom with two intervening N atoms that hold it in the *trans* configuration. The coordination geometries of (I) and (II) are illustrated in Fig. 4. In each compound the Hg atom exhibits planar, irregular three-coordination, the geometry at the Hg atom being approximately T-shaped.
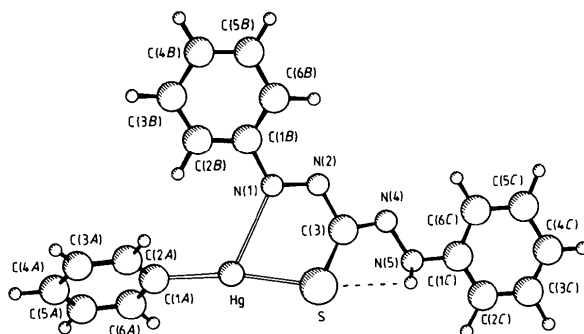

Fig. 1. Perspective view of the molecular structure of (I) with atomic nomenclature; in (II) a methyl group replaces phenyl ring *A*. The dashed line indicates a hydrogen bond.

Mercury coordination

The Hg—C distances of 2·12 (2) (I) and 2·06 (1) Å (II) appear normal [*cf.* 2·10 Å in the adducts of diphenylmercury with methylated phenanthrolines (Canty & Gatehouse, 1972) and 2·06 (2) Å in gaseous CH_3HgCl (Gordy & Sheridan, 1954)], while Grdenić (1965) has remarked on the longer Hg—C bonds in aryl- compared with alkylmercury(II) derivatives. The Hg—S lengths [I, 2·372 (7); II, 2·389 (4) Å] do not depart from accepted values and it appears from recent tabulations (Lawton, 1971; Wong, Carty & Chieh,
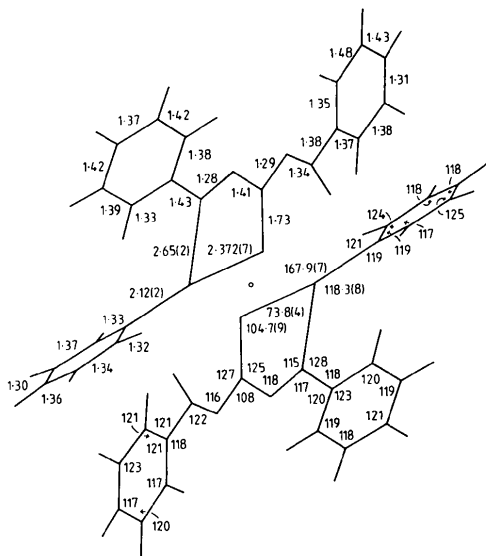
Fig. 2. Two molecules of (I) related by a centre of inversion. The upper molecule shows bond lengths (Å; e.s.d.'s not shown are 0·03–0·04 for C—C and 0·03 Å for C—N, C—S and N—N), while the lower molecule gives the bond angles (°; e.s.d.'s not shown are 2–4°).
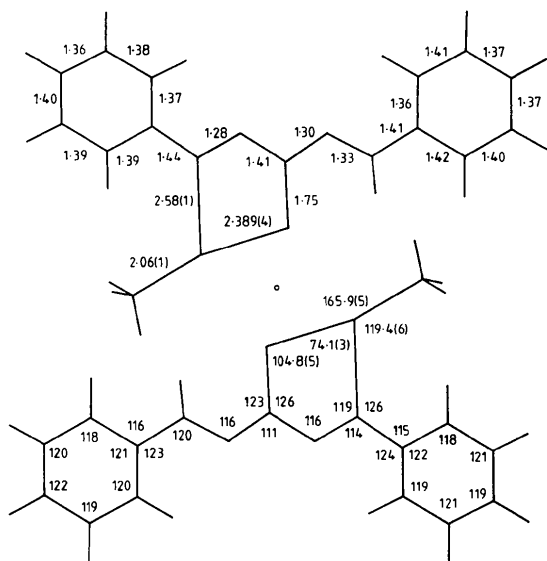

Fig. 3. Two molecules of (II) related by a centre of inversion. The upper molecule shows bond lengths (Å; e.s.d.'s not shown are 0·02–0·03 for C—C and 0·02 Å for C—N, C—S and N—N), while the lower molecule gives the bond angles (°; e.s.d.'s not shown are 1–2°).

1977a) that all reliable Hg—S distances in truly two-coordinate Hg compounds lie within the narrow range 2·32–2·42 Å. Thus a strong covalent Hg—S bond is found in both (I) and (II) which may be compared with the Hg—S distance of 2·33 (1) Å in Hg(Hdz)₂ (1) (Alsop, 1971). These Hg—S distances, which increase in the order (1) < (I) < (II), correspond
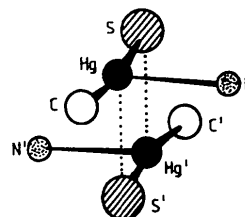

Fig. 4. The coordination spheres of the Hg atoms in molecules of (I) and (II) related by a centre of inversion. The closest interaction (dotted line) is Hg···S' [3·69 (2) (I); 3·58 (2) Å (II)].

with decreasing Lewis acidity of the cations: $Hg^{2+} >$ $C_6H_5Hg^+ > CH_3Hg^+$. The Hg—N distances of 2·65 (2) (I) and 2·58 (1) Å (II) are respectively 0·50 and 0·57 Å shorter than the sum (3·15 Å) of the van der Waals radii according to Bondi (1964) [r(Hg) 1·55, r(S) 1·80, r(N) 1·60, r(C) 1·77, r(H) 1·17 Å] and thus constitute weak bonds (Grdenić, 1965). They may be compared with the Hg—N distances found in mercury(II) complexes of 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen) with higher coordination numbers for Hg, e.g. 2·24 (3) and 2·43 (3) Å in [CH₃Hg(bpy)]NO₃ (irregular three-coordination; Canty & Gatehouse, 1976), 2·373 (9) and 2·399 (8) Å in [HgBr₂(bpy)]₂ (five-coordinate; Craig, Farhangi, Graddon & Stephenson, 1973), 2·42 (2)–2·52 (2) Å in [Hg(SCN)₂-(phen)₂] (six-coordinate; Beauchamp, Saperas & Rivest, 1974) and 2·56 (4) Å in Hg(Hdz)₂ (1) (four-coordinate; Alsop, 1971). Covalent Hg—N distances are usually ~2·1 Å (Grdenić, 1965). It was anticipated that the Hg—N(1) distance of 2·65 (2) Å in (I) would be considerably shortened in (II), where there is no phenyl group (A) attached to Hg to hinder close approach of N(1) to Hg. That the Hg—N(1) distance in (II) [2·58 (1) Å] is not substantially shorter illustrates the characteristically very weak residual Lewis acidity of the near-linear R—Hg—S unit. However, the C—Hg—S angle does decrease from 167·9 (7)° in (I) to 165·9 (5)° in (II), reflecting slightly decreased tendency for Hg 6s-orbital character to be concentrated in the Hg—C and Hg—S bonds. The concomitant increase in the Hg—S length in (II) was pointed out above.

Apart from the primary three-coordination there is a weak secondary interaction between the Hg atom in the reference molecule at x,y,z and the S atom of the molecule at $-x$, $1-y$, $-z$ in (I) or at $-x$, $-y$, $1-z$ in (II) (Fig. 4). This Hg···S' distance is 3·69 (2) (I) or 3·58 (2) Å (II) which is respectively 0·54 or 0·43 Å longer than the van der Waals sum (Bondi, 1964); thus according to Grdenić's (1965) criterion S' is outside the coordination sphere of Hg in both (I) and (II), even if an upper limit of 1·73 (Grdenić, 1965) or 1·75 Å (Barr, Goldstein, Hairs, McPartlin & Markwell, 1974) for the radius of Hg is adopted. There are no other secondary interactions in either compound.

In the nomenclature of Grdenič (1965) the Hg atoms in (I) and (II) have a characteristic coordination of two (C—Hg—S) but within their effective coordination range are the N(1) atoms of the azo groups, making the geometry at Hg approximately T-shaped. While the largest category of organomercury(II) compounds is characterized by digonal coordination and linear or almost linear (170–180°) geometry with sp-hybridized Hg (Chieh, 1978; Chieh & Leung, 1976; Grdenič, 1965; Kitaigorodskii, 1961; Mills,Preston & Kennard, 1968; Müller, 1973; Taylor, Wong, Chieh & Carty, 1975; Wong, Carty & Chieh, 1977a,b), a few examples of three-coordinate mercury(II) complexes have been reported (Barba Behrens, Cartwright, Goodgame & Skapski, 1978; Canty & Gatehouse, 1976; Fatuzzo, Nitsche, Roetschi & Zingg, 1962; Fenn, 1966; Sleight & Prewitt, 1973; White, 1963) and weak supplementary bonds are well known to complete the effective coordination of mercury(II) compounds (Grdenič, 1965; Wells, 1975). Whether these longer distances can be considered to be covalent bonds or simply electrostatic interactions still seems to be under discussion (Hursthouse, 1973); nevertheless, a possible type of bonding in these structures has been suggested by Orgel (1958). Approximately trigonal geometry for Hg^{2+} in compounds like $[S(CH_3)_3][HgI_3]$ (Fenn, 1966) and $HgTiO_3$ (Sleight & Prewitt, 1973) can be satisfactorily accounted for by an sp^2-hybridization bonding model. However, for (I) and (II) the irregular coordination geometry (Fig. 4) is clearly inconsistent with sp^2 hybridization and presumably reflects the strong tendency towards linear geometry in organomercury(II) compounds and the low acceptor properties of linear organomercury compounds towards additional donor atoms (Canty & Gatehouse, 1976, and references therein; Grdenič, 1965). The coordination geometry now found in (I) and (II) implies that it is possible that chloromercury(II) dithizonate, HgCl(Hdz), exists as a monomer with a near-linear Cl—Hg—S system rather than as a Cl-bridged dimer (Alsop, 1971; Briscoe & Cooksey, 1969).

The dithizone residue

The bond lengths in the dithizone residue (Figs. 2 and 3) reveal a marked delocalization of π electrons within the N—N—C—N—N chain and with the phenyl rings. While the formal double bonds C(3)=N(4) (I, 1·29; II, 1·30 Å) and N(1)=N(2) (I, II, 1·28 Å) are clearly extended in comparison with isolated double bonds, the formal single bonds N(2)—C(3) (I, II, 1·41 Å) and N(4)—N(5) (I, 1·34; II, 1·33 Å) are noticeably shortened. The S—C(3) lengths (I, 1·73; II, 1·75 Å) are of the expected magnitude and show that the electron delocalization found in the Ph—N—N—C—N—N—Ph chain does not discernibly extend to the S atom and that the S—C(3) bond order is ∼1·0 in both com-

Table 3. *Chelate-ring torsion angles* (°) *for* (I) *and* (II)

The convention is that of Klyne & Prelog (1960). E.s.d.'s are *ca* 1°.

	(I)	(II)
Hg—N(1)—N(2)—C(3)	−6	−4
S—C(3)—N(2)—N(1)	−11	2
N(2)—C(3)—S—Hg	21	0
C(3)—S—Hg—N(1)	−14	−2
N(2)—N(1)—Hg—S	14	3

pounds (Laing, 1977). The S—C(3) bond order is probably decreased by donation of electron density to the Hg acceptor upon coordination, for the S—C bond order in crystalline dithizone is given as 1·2 (Laing, 1977). Bond distances and angles relating to the phenyl groups are generally satisfactory in spite of one or two dubious C—C distances in (I); the mean C—C distance in the three phenyl rings of (I) is 1·37 (5) Å and in the two phenyl rings of (II) is 1·39 (2) Å.

The parameters for several least-squares planes and a list of torsion angles have been deposited.* Table 3 gives the chelate-ring torsion angles. It can be seen that in (I) the chelate ring is slightly buckled [the largest deviation from the least-squares plane defined by the chelate ring is 0·15 (3) Å] whereas the chelate ring in (II) is more planar [largest deviation 0·03 (3) Å]. In each structure the whole ligand residue is quite closely coplanar, suggesting that the chelate ring and thiocarbazone chain are conjugated with phenyl rings *B* and *C*; the same conclusion was reached above in considering the thiocarbazone bond lengths. The dithizone residue in (II) is actually more planar than in (I), and consideration of the bond lengths in the ligand residues (Figs. 2 and 3) shows a consistent increase in single-bond character and decrease in double-bond character in the bond lengths of (II) compared with (I), although these bond-length differences are within their e.s.d.'s. The largest deviation from the plane of the thiocarbazone chain [N—N—C(S)—N—N] is 0·12 (3) (I) or 0·03 (3) Å (II). In (I) the plane of phenyl ring *A* is twisted 59 (3)° from the plane defined by the remainder of the molecule, thereby avoiding steric interaction with the phenyl ring (*B*) attached to the donor N atom. That the latter ring does not twist out of the plane is ascribed to the extensive electron delocalization throughout the dithizone residue, as evidenced by the bond lengths found in the Ph—N—N—C—N—N—Ph chain and the planarity discussed above.

In both structures the imino H(N5) participates in a weak intramolecular hydrogen bond to S, effectively locking the dithizone residue in an *anti,s-trans* configuration. The H(N5)···S distances of 2·40 (9) (I) and 2·43 (8) Å (II) [for fixed N(5)—H(N5) lengths of 1·00 (1) Å] are significantly less than the sum of the
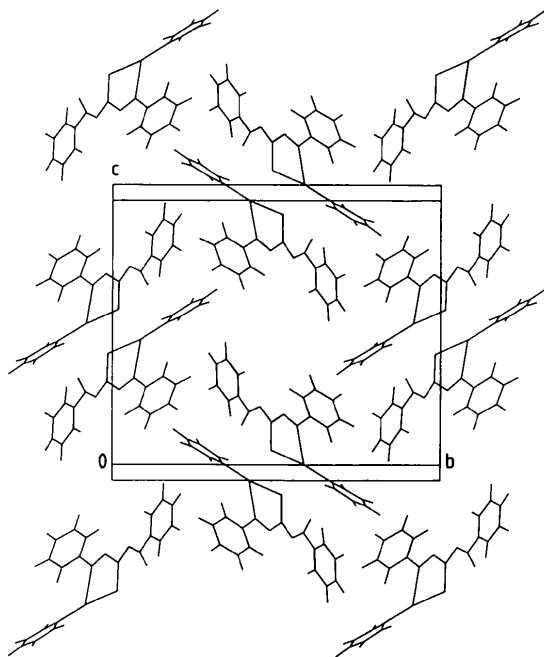
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* See deposition footnote.

Fig. 5. The molecular packing in (I) viewed down a*.

Fig. 6. The molecular packing in (II) viewed down [001].

van der Waals radii, while the N(5)···S separations are 2·92 (3) (I) and 2·86 (2) Å (II). The H(N5)···S distances of ~2·4 Å are the same as that found in xanthane hydride (Stanford, 1963) where the H atoms were located approximately and the presence of an almost linear intermolecular N–H···S hydrogen bond was reported. Although the distances are favourable for a strong intramolecular hydrogen bond, the stereochemistry of the sp^2-hybridized N(5) does not allow linearity of the N(5)—H(N5)···S angle [I, 112 (8); II, 109 (5)°] and thus the hydrogen bond formed is considerably weakened. Hydrogen bonding is nevertheless favoured here by the fact that in the configuration adopted one of the lone pairs of electrons on S is oriented towards H(N5). The *anti,s-trans* configuration of the N—N—C—N—N chain adopted in these structures is the same as that found in Hg(Hdz)₂ (I) (Alsop, 1971; Harding, 1958), Zn(Hdz)₂ (Mawby & Irving, 1972), Ni(Hdz)₂ (Laing & Alsop, 1970), Ni(Hdz)₂(bpy) (Math & Freiser, 1970), Cu(Hdz)₂ (Bryan & Knopf, 1961) and in crystals of the free ligand itself (Laing, 1977).

Molecular packing

Projections of the molecular packing of (I) and (II) are given in Figs. 5 and 6. Crystals of (I) consist of single molecules with a weak Hg···S′ interaction to the S atom in a molecule which is related by a centre of symmetry, as discussed above. These dimeric groups may be considered as packing units. The only other noteworthy intermolecular contact is S···S′ [3·48 (3)
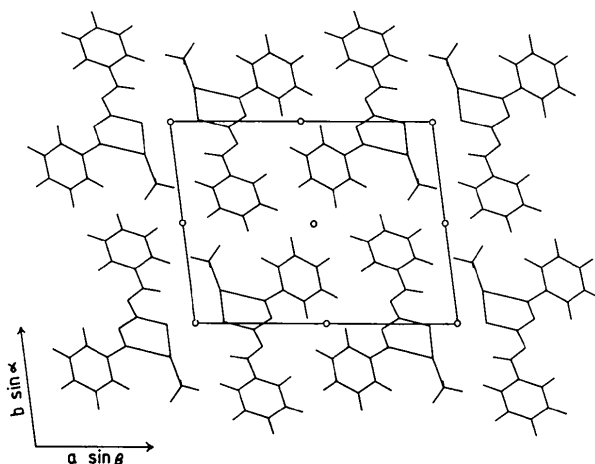
Å], and while there are several other contacts slightly less than the sum of the van der Waals radii, it is not believed that any of these has any important influence on the structure. Molecules of (II) are separated by normal van der Waals contacts; the weak Hg···S′ interaction was discussed above and the dimeric groups may be considered as packing units. The molecules are stacked along c, their mean planes forming an angle of 51 (1)° with the (001) plane.

References

ALSOP, P. A. (1971). *The Structure and Properties of Dithizone and the Metal Dithizonates.* PhD Thesis, Univ. of London.

BARBA BEHRENS, N., CARTWRIGHT, B. A., GOODGAME, D. M. L. & SKAPSKI, A. C. (1978). *Inorg. Chim. Acta*, **31**, L471–L472.

BARR, R. M., GOLDSTEIN, M., HAIRS, T. N. D., McPARTLIN, M. & MARKWELL, A. J. (1974). *J. Chem. Soc. Chem. Commun.* pp. 221–223.

BEAUCHAMP, A. L., SAPERAS, B. & RIVEST, R. (1974). *Can. J. Chem.* **52**, 2923–2927.

BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.

BRISCOE, G. B. & COOKSEY, B. G. (1969). *J. Chem. Soc. A,* pp. 205–211.

BRYAN, R. F. & KNOPF, P. M. (1961). *Proc. Chem. Soc.* p. 203.

CANTY, A. J. & GATEHOUSE, B. M. (1972). *Acta Cryst.* B28, 1872–1888.

CANTY, A. J. & GATEHOUSE, B. M. (1976). *J. Chem. Soc. Dalton Trans.* pp. 2018–2020.

CARLIN, C. H. (1966). *Structural Analyses in the Dithizone Series.* PhD Thesis, The Johns Hopkins Univ., Baltimore.

CHIEH, C. (1978). *Can. J. Chem.* **56**, 560–563.

CHIEH, C. & LEUNG, L. P. C. (1976). *Can. J. Chem.* **54**, 3077–3084.

CRAIG, D. C., FARHANGI, Y., GRADDON, D. P. & STEPHENSON, N. C. (1973). *Cryst. Struct. Commun.* **3**, 155–158.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

FATUZZO, E., NITSCHE, R., ROETSCHI, H. & ZINGG, S. (1962). *Phys. Rev.* **125**, 514–516.

FENN, R. H. (1966). *Acta Cryst.* **20**, 20–23.

GEOSLING, C., ADAMSON, A. W. & GUTIERREZ, A. R. (1978). *Inorg. Chim. Acta*, **29**, 279–287.

GORDY, W. & SHERIDAN, J. (1954). *J. Chem. Phys.* **22**, 92–95.

GRDENIĆ, D. (1965). *Q. Rev. Chem. Soc.* **19**, 303–328.

HARDING, M. M. (1958). *J. Chem. Soc.* pp. 4136–4143.

HURSTHOUSE, M. B. (1973). *Molecular Structure by Diffraction Methods*, Vol. 1, Spec. Period. Rep., p. 726. London: The Chemical Society.

HUTTON, A. T. & IRVING, H. M. N. H. (1979a). Unpublished data.

HUTTON, A. T. & IRVING, H. M. N. H. (1979b). *J. Chem. Soc. Chem. Commun.* pp. 1113–1114.

IRVING, H. M. N. H. (1977). *Dithizone.* Analytical Sciences Monographs No. 5, pp. 36–40. London: The Chemical Society.

KITAIGORODSKII, A. I. (1961). *Organic Chemical Crystallography*, pp. 144–151, 316–321. New York: Consultants Bureau.

KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.

LAING, M. (1977). *J. Chem. Soc. Perkin Trans.* 2, pp. 1248–1252.

LAING, M. & ALSOP, P. A. (1970). *Talanta*, **17**, 242–244.

LAWTON, S. L. (1971). *Inorg. Chem.* **10**, 328–335.

MATH, K. S. & FREISER, H. (1970). *J. Chem. Soc. Chem. Commun.* pp. 110–111.

MAWBY, A. & IRVING, H. M. N. H. (1972). *J. Inorg. Nucl. Chem.* **34**, 109–115.

MERIWETHER, L. S., BREITNER, E. C. & COLTHUP, N. B. (1965). *J. Am. Chem. Soc.* **87**, 4448–4454.

MERIWETHER, L. S., BREITNER, E. C. & SLOAN, C. L. (1965). *J. Am. Chem. Soc.* **87**, 4441–4448.

MILLS, J. C., PRESTON, H. S. & KENNARD, C. H. L. (1968). *J. Organomet. Chem.* **14**, 33–41.

MOTHERWELL, W. D. S. (1975). Private communication.

MÜLLER, U. (1973). *Z. Naturforsch. Teil B*, **28**, 426–428.

ORGEL, L. E. (1958). *J. Chem. Soc.* pp. 4186–4190.

ROBERTS, P. & SHELDRICK, G. M. (1975). Private communication.

SHELDRICK, G. M. (1976). *SHELX.* Univ. Chemical Laboratory, Cambridge.

SLEIGHT, A. W. & PREWITT, C. T. (1973). *J. Solid State Chem.* **6**, 509–512.

STANFORD, R. H. (1963). *Acta Cryst.* **16**, 1157–1162.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TAYLOR, N. J., WONG, Y. S., CHIEH, P. C. & CARTY, A. J. (1975). *J. Chem. Soc. Dalton Trans.* pp. 438–442.

WEBB, J. L. A., BHATIA, I. S., CORWIN, A. H. & SHARP, A. G. (1950). *J. Am. Chem. Soc.* **72**, 91–95.

WELLS, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed., pp. 916–926. Oxford: Clarendon Press.

WHITE, J. G. (1963). *Acta Cryst.* **16**, 397–403.

WONG, Y. S., CARTY, A. J. & CHIEH, C. (1977a). *J. Chem. Soc. Dalton Trans.* pp. 1801–1808.

WONG, Y. S., CARTY, A. J. & CHIEH, P. C. (1977b). *J. Chem. Soc. Dalton Trans.* pp. 1157–1160.