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## The Structure of Diiodo{ *S,S'*-dimethyl-2,6-bis[1-(2-thiophenylimino)ethyl]pyridine}cadmium(II)

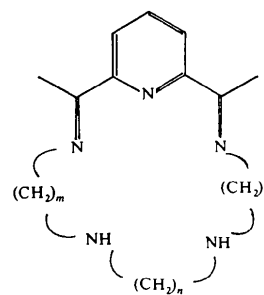
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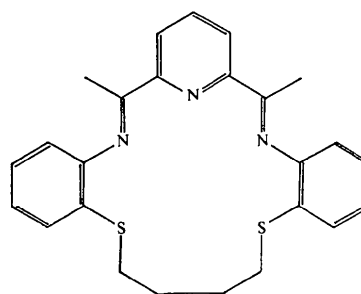
(Received 10 April 1978; accepted 15 May 1978)

**Abstract.** C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>S<sub>2</sub>CdI<sub>2</sub>, *M<sub>r</sub>* = 771.8, orthorhombic, *Pbn*2<sub>1</sub>, *Z* = 4, *a* = 13.366 (9), *b* = 19.266 (8), *c* = 10.230 (11) Å, *d<sub>c</sub>* = 1.95, *d<sub>m</sub>* = 1.89 (5) g cm<sup>-3</sup>, *U* = 2634.3 Å<sup>3</sup>, *F*(000) = 1380, *μ*(Mo *Kα*) = 34.3 cm<sup>-1</sup>. 1148 independent above-background reflections were measured on a diffractometer and refined by a full-matrix least-squares method to *R* = 0.068. In the complex, the potentially quinquedentate ligand is only terdentate bonding to the Cd through three N atoms [2.40 (4), 2.33 (3), 2.41 (3) Å] with the two S atoms twisted out of the ligand plane well away from the metal. The coordination sphere is completed by two I atoms [2.713 (4), 2.726 (4) Å]. The geometry of the coordination sphere is close to a trigonal bipyramid with both I atoms in equatorial sites.

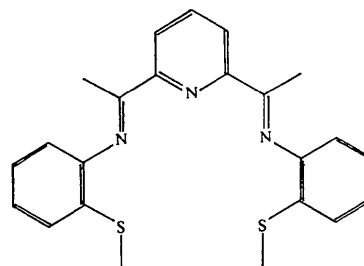
**Introduction.** Seven-coordinate (pentagonal bipyramidal) structures of the type *ML<sub>2</sub>(L-L-L-L-L)*, *L* and *L-L-L-L-L* being monodentate and pentadentate ligands respectively, have become well established (Drew, 1977). In the majority of examples the pentadentate ligand is closely planar. Indeed with ligands 2,2,2-N<sub>3</sub> and 2,3,2-N<sub>3</sub> [shown as (I)] the deviations of contributing atoms from the *ML<sub>5</sub>* girdle are less than 0.25 Å (Drew, Othman, McFall, McIlroy & Nelson, 1977*a*). We have been investigating structures of complexes which contain analogous but more flexible ligands to determine whether they too have seven-coordinate structures. We have previously shown (Drew & Hollis, 1978*a*) that the complex Zn(2,4,2-N<sub>3</sub>S<sub>2</sub>)I<sub>2</sub>, [2,4,2-N<sub>3</sub>S<sub>2</sub> shown as (II)] has a five-coordinate structure with a ZnN<sub>3</sub>I<sub>2</sub> coordination sphere. We have suggested that this is due to the steric requirements of the butane linkage between S atoms. As a further example of this class of compounds we have chosen Cd(2,0,2-N<sub>3</sub>S<sub>2</sub>Me<sub>2</sub>)I<sub>2</sub> [2,0,2-N<sub>3</sub>S<sub>2</sub>Me<sub>2</sub> shown as (III)] and report here its crystal and molecular structure.



- (I) *n* = 2, *m* = (2,2,2-N<sub>3</sub>)  
*n* = 3, *m* = 2 (2,3,2-N<sub>3</sub>)  
*n* = 2, *m* = 3 (3,2,3-N<sub>3</sub>)



(II) (2,4,2-N<sub>3</sub>S<sub>2</sub>)



(III) (2,0,2-N<sub>3</sub>S<sub>2</sub>Me<sub>2</sub>)

Cd(2,0,2-N<sub>3</sub>S<sub>2</sub>Me<sub>2</sub>)I<sub>2</sub> was prepared according to Lindoy & Busch (1974). The yellow powder that was formed was washed with acetone and dissolved in nitromethane. Crystals formed on controlled evaporation of the solvent.

A crystal with dimensions 0.5 × 0.7 × 0.2 mm was mounted with its *c* axis parallel to the instrument axis of a General Electric XRD 5 diffractometer which was equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Zr-filtered Mo radiation was used. The stationary-crystal-stationary-counter method was used with a 4° take-off angle and counting time of 10 s. Individual backgrounds were taken from plots of background against 2θ. 1832 independent reflections were measured with 2θ < 45° of which 1144 with *I* > 2σ(*I*) were used in subsequent calculations. An absorption correction was applied.

The Patterson map indicated that the correct space group was *Pbn*2, and the position of one heavy atom was obtained. Subsequent Fourier maps gave the positions of the rest of the molecule. The structure was refined using a full-matrix least-squares method with a

weighting scheme that gave similar values for *w*Δ<sup>2</sup> with ranges of *F*<sub>o</sub> and sin θ/λ. It was *w*<sup>1/2</sup> = 1 for *F*<sub>o</sub> < 120 and *w*<sup>1/2</sup> = 120/*F*<sub>o</sub> for *F*<sub>o</sub> > 120. Cd, I and S atoms were refined anisotropically and other atoms isotropically. H atoms were given standard calculated positions and included in the structure-factor calculation but not refined. Calculations were made using the *SHELX* 76 set of programs (G. M. Sheldrick, 1976) at the University of London Computer Centre (CDC 7600). Scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The final list of positions is given in Table 1, bond lengths and angles are in Table 2. The final difference Fourier map was featureless. The zero-weighted reflections gave no large discrepancies.\*

**Discussion.** The molecule and atomic numbering system are given in Fig. 1. The metal atom is five-coordinate being bonded to three N atoms and two I atoms in a distorted trigonal bipyramidal environment. The two S atoms are twisted out of the ligand plane well away from the metal (>4.4 Å).

\* Lists of structure factors, anisotropic thermal parameters and additional bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33624 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional coordinates* (× 10<sup>4</sup>) *with estimated standard deviations in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>
Cd	-2271 (2)	-0977 (1)	0000*
I(1)	-1495 (2)	-1921 (1)	-1687 (5)
I(2)	-3781 (2)	-1371 (1)	1630 (5)
C(1)	-3548 (35)	-0640 (25)	-3603 (51)
C(2)	-3880 (35)	-0540 (24)	-2425 (48)
N(3)	-3154 (25)	-0218 (19)	-1457 (40)
C(4)	-2973 (26)	0419 (20)	-1471 (41)
C(5)	-2313 (32)	0676 (22)	-0366 (42)
N(6)	-1773 (22)	0170 (14)	0286 (30)
C(7)	-1140 (26)	0340 (19)	1191 (32)
C(8)	-0666 (23)	-0231 (17)	1918 (32)
N(9)	-0929 (22)	-0847 (15)	1552 (37)
C(10)	-0561 (29)	-1496 (19)	2248 (38)
C(11)	0300 (33)	-1746 (23)	1815 (51)
S(12)	0966 (11)	-1384 (7)	0501 (18)
C(13)	1580 (42)	-2051 (29)	-0242 (67)
C(16)	-2748 (52)	0174 (41)	-5636 (76)
S(17)	-2378 (10)	-0466 (10)	-4213 (15)
C(18)	-4311 (44)	-0979 (30)	-4478 (57)
C(19)	-5214 (40)	-1027 (29)	-3971 (53)
C(20)	-5482 (49)	-0950 (35)	-2830 (73)
C(21)	-4815 (35)	-0588 (25)	-1969 (50)
C(22)	-3398 (33)	1044 (23)	-2341 (44)
C(23)	-2041 (28)	1365 (19)	-0141 (47)
C(24)	-1383 (34)	1540 (23)	0707 (48)
C(25)	-0898 (27)	1052 (20)	1462 (42)
C(26)	0042 (32)	-0117 (24)	2939 (42)
C(27)	-1075 (35)	-1725 (26)	3296 (66)
C(28)	-0671 (51)	-2315 (35)	3938 (65)
C(29)	0217 (41)	-2570 (28)	3487 (67)
C(30)	0666 (36)	-2363 (25)	2461 (53)

\* Parameter fixed.

Table 2. *Dimensions of the cadmium coordination sphere*

Remaining dimensions in the molecule are given in the supplementary publication.

Cd—I(1)	2.713 (4) Å	I(1)—Cd—I(2)	119.1 (1)°
Cd—I(2)	2.726 (4)	I(1)—Cd—N(3)	101.6 (9)
Cd—N(3)	2.398 (37)	I(1)—Cd—N(6)	127.4 (7)
Cd—N(6)	2.326 (28)	I(1)—Cd—N(9)	101.8 (8)
Cd—N(9)	2.408 (33)	I(2)—Cd—N(3)	100.7 (9)
		I(2)—Cd—N(6)	113.4 (7)
		I(2)—Cd—N(9)	100.2 (8)
		N(3)—Cd—N(6)	68.8 (11)
		N(3)—Cd—N(9)	135.5 (11)
		N(6)—Cd—N(9)	66.7 (10)

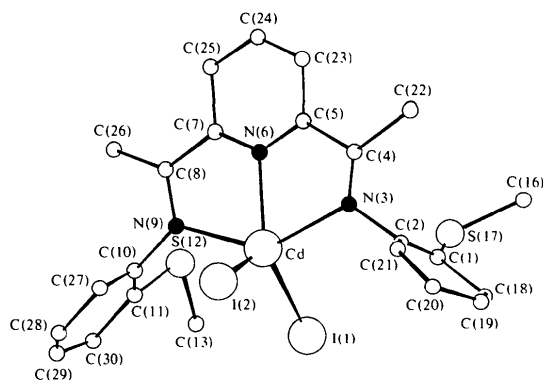
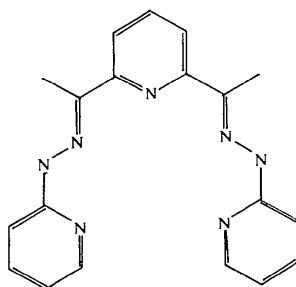


Fig. 1. Cd(2,0,2-N<sub>3</sub>S<sub>2</sub>Me<sub>2</sub>)I<sub>2</sub> showing the numbering scheme.

The most interesting question to ask about this structure is why the S atoms are not bonded to the metal. In the Zn(2,4,2-N<sub>3</sub>S<sub>2</sub>)I<sub>2</sub> complex (Drew & Hollis, 1978*a*), it is clear that the S atoms cannot be bonded to the metal because of steric constraints introduced by the butyl chain. This is not the case for the present molecule, as in our view it is possible for the S atoms to be bonded to the metal as part of an approximately planar girdle without the two methyl groups coming too close to each other. For example in [Zn(H<sub>2</sub>-dapp)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> [H<sub>2</sub>dapp is shown as (IV)] (Wester & Palenik, 1976) the two pyridine rings on adjacent N atoms bonded to the metal are far more rigid than adjacent methyl groups. Yet in that cation close contacts are avoided by the pyridine rings twisting out of the ligand plane in opposite directions so that they intersect at an angle of 38°. In TaCl<sub>3</sub>(prcd)<sub>2</sub> [prcd = *N,N'*-diisopropylacetamide (Drew & Wilkins, 1974)], adjacent N atoms in the pentagonal girdle are bonded to isopropyl groups. These are well removed from each other by the N atoms being respectively above and below the girdle plane.\*

(IV) H<sub>2</sub>dapp

The present structure indicates that many *ML*<sub>2</sub>(*L-L-L-L-L-L*) complexes that have been prepared have a coordination number of seven solely because of the rigidity of the planar macrocycle. With an analogous but more flexible ligand as in the present case, the metal is electronically and sterically satisfied by a lower coordination number.

There are of course several ways in which such a complex can have a lower coordination number. There are precedents for a coordination number of six in the form *ML(L-L-L-L-L)*, e.g. [Cd(3,2,3-N<sub>3</sub>)Br]<sup>+</sup> and [Hg(3,2,3-N<sub>3</sub>)Br]<sup>+</sup> (Nelson, McFall, Drew, Othman & Mason, 1977) and Tl(2,0,2-N<sub>3</sub>S<sub>2</sub>)Me (Henrick, Matthews & Tasker, 1977). There are two ways in which the structure can be five-coordinate, either by dropping two bonds to the monodentate ligands or two

\* It could be argued that such non-planarity in the girdle, necessary to keep the methyl groups apart, would be impossible because it would lead to close contacts between the ligand and the bulky I atoms. However, replacement of I by Br or Cl leads to identical structures. The Br analogue is isomorphous while a crystal structure determination on the Cl analogue (which is not isomorphous) has shown that the molecular geometry is identical (Drew & Hollis, 1978*b*).

of the bonds to the pentadentate ligand (to drop one of each seems unlikely). Examples of the first type include [Ag(3,2,3-N<sub>3</sub>)]<sup>+</sup> (Nelson *et al.*, 1977) and [Ag(3,2,3-N<sub>3</sub>S<sub>2</sub>)]<sup>+</sup> (Drew & Nelson, 1978). (In both examples the anion is not likely to bond to the metal, being ClO<sub>4</sub><sup>-</sup> and BPh<sub>4</sub><sup>-</sup> respectively.)

A third example Zn(2,0,2-N<sub>3</sub>S<sub>2</sub>) (Goedken & Christoph, 1973) is neutral. These three structures all contain an approximate twofold axis through the *M-N*<sub>py</sub> bond with the other donor atoms alternatively above and below the least-squares plane of *ML*<sub>5</sub> by distances of up to 1.7 Å. This large amount of non-planarity does not mean that the ligands could not adopt a more planar configuration in a seven-coordinate complex if required. For example different conformations are found in a six-coordinate complex [Cd(3,2,3-N<sub>3</sub>)Br]<sup>+</sup> (Nelson *et al.*, 1977) and a seven-coordinate complex [Mn(3,2,3-N<sub>3</sub>)(NCS)<sub>2</sub>] (Drew, Othman, McFall, McIlroy & Nelson, 1977*b*) which are far closer to planarity.

The structure of Cd(2,0,2-N<sub>3</sub>S<sub>2</sub>Me)<sub>2</sub>I<sub>2</sub> is best described as a distorted trigonal bipyramid, the major distortion arising from the need for the angle between adjacent N atoms to be approximately 68°. The two I atoms are in equatorial positions [2.713 (4), 2.726 (4) Å] and the N atoms in the remaining sites [2.40 (4), 2.33 (3), 2.41 (3) Å]. The Cd-N(6) bond is considerably shorter than the other two bonds, an effect which is consistently observed in complexes containing this type of ligand. Cd-I bond lengths are comparable to Cd-I(terminal) bond lengths in [CdI<sub>2</sub>L] (*L* = C<sub>3</sub>H<sub>5</sub>NO) (Sawitzki & von Schnering, 1974) and

Table 3. *Least-squares planes in the form Ax + By + Cz = D, where x,y,z are orthogonalized coordinates, with distances (Å) of relevant atoms from the planes given in square brackets*

	A	B	C	D	
Plane 1	N(3), N(6), N(9), C(4), C(5), C(7), C(8), C(22), C(23), C(24), C(25), C(26)	0.74	-0.04	-0.67	1.98
	[N(3) -0.11, N(6) 0.01, N(9) 0.06, Cd -0.18, C(5) -0.11, C(4) 0.02, C(7) 0.00, C(8) 0.02, C(22) 0.15, C(23) -0.05, C(24) -0.00, C(25) -0.00, C(26) 0.01, I(1) 1.82, I(2) -2.77, S(12) 2.70, S(17) 2.57]				
Plane 2	C(1), C(2), C(18), C(19), C(20), C(21)	-0.27	-0.91	-0.30	1.24
	[C(1) 0.02, C(2) -0.05, C(18) -0.03, C(19) 0.06, C(20) -0.07, C(21) 0.06, S(17) 0.10, C(16) 1.81, N(3) -0.04]				
Plane 3	C(10), C(11), C(27), C(28), C(29), C(30)	0.52	0.61	0.60	0.75
	[C(10) -0.01, C(11) 0.03, C(27) 0.00, C(28) -0.01, C(29) 0.03, C(30) -0.04, S(12) 0.11, C(13) -0.69, N(6) -0.11]				

Angles between planes: 1 and 2 88.2, 1 and 3 87.5, 2 and 3 76.5°.

[Cd<sub>2</sub>I<sub>6</sub>]<sup>2-</sup> (Orioli & Ciampolini, 1972) which range from 2.693 (1) to 2.724 (1) Å.

The molecule has approximate C<sub>s</sub> symmetry, the mirror plane passing through the metal, pyridine N and I atoms. The two benzene rings are twisted out of the pyridine ring plane by angles of 88.2 and 87.5°. Details of these three least-squares planes are given in Table 3. Note that the S atoms are on the same side of the macrocycle. I(1), which is on the same side of the pyridine ring plane as the S atoms, is 1.82 Å from the plane and I(2) -2.77 Å. The disparity is no doubt due to possible steric contact between I(1) and the *S*-methyl-2-thiophenyl groups. Thus the five-coordinate structure is somewhat distorted towards a square pyramid but not as much as is observed in Zn(2,4,2-N<sub>3</sub>S<sub>2</sub>)I<sub>2</sub> where, due to the butyl group, the I atoms are respectively -0.3 and 3.3 Å from the plane of the unsaturated part of the macrocycle.

Both methyl groups are twisted out of the plane of the phenyl rings with torsion angles C(10)-C(11)-S(12)-C(13) and C(2)-C(1)-S(17)-C(16) being -148.9 and -121.6° respectively. Both groups have high thermal parameters.

There are no intermolecular contacts significantly less than the sum of the van der Waals radii. The minimum is a C...C contact of 3.29 Å.

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## Structure du *trans*-Dibromo(tétraphénylporphinato)titane(IV)

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(Reçu le 15 mars 1978, accepté le 15 mai 1978)

**Abstract.** C<sub>44</sub>H<sub>28</sub>N<sub>4</sub>TiBr<sub>2</sub> (TPPTiBr<sub>2</sub>), tetragonal, *I4/m*, *a* = 13.757 (2), *c* = 9.880 (1) Å, *D*<sub>c</sub> = 1.457 g cm<sup>-3</sup>, *V* = 1870 Å<sup>3</sup>, *Z* = 2. The structure was refined to a conventional *R* = 0.078. The two axial Br ligands are in a *trans* position with respect to the macrocycle. The bond length Ti<sup>IV</sup>-Br is 2.454 (2) Å. The compound is isotopic with TPPSnCl<sub>2</sub>.

**Introduction.** Des complexes dihalogénures de la tétraphénylporphine de titane(IV) (TPPTiX<sub>2</sub>) (*X* = F, Cl, Br) ont été isolés récemment, et quelques unes de leurs propriétés ont été décrites (Nakajima, Latour & Marchon, 1977). Ils fournissent une voie d'accès aux porphyrines de titane à bas degré d'oxydation. La compréhension des mécanismes de catalyse homogène

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