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Crystal and Molecular Structure of Dichloro-1-diphenylphosphino-2-diethylaminoethanemercury(II) at 138 K

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Reported accounts of the interaction of zinc, cadmium, and mercury halides with Lewis base ligands reveal complexes, $(MX_2)_nL_m$, exhibiting a wide diversity of ligand to metal moiety ratios [1, 6]. While detailed structural investigations of several of the complexes demonstrate a propensity for these metals to achieve coordination numbers ranging from two to perhaps as high as nine, they apparently prefer an environment of two, four, or six neighbors [5, 6]. Quite frequently these metals display two sets of bonds within their coordination sphere as exemplified by the tendency of mercury to form several weaker bonds or contacts in addition to strong approximately diagonal bonds. Examples of this expanded secondary valence phenomenon include a (2 + 4) coordination polyhedron around mercury in $K_2HgCl_4 \cdot H_2O$ [2], $HgCl_2$·azoxyanisole [3], and $HgCl_2$·(2-imidazolidinone)$_2$ [4]; a (3 + 1) one in bis(iodo-N, N-diethyldithiocarbamatomercury(II)) [5]; and a (3 + 2) one in $[(CH_3)_2C_2H_5P]_3(HgCl_2)_2$ [6].

In the past decade there has been widespread interest in the interaction of a variety of metal systems with potentially chelating 'mixed' multidentate ligands, species possessing at least two different Lewis base centers strategically located along a chain or in ortho positions on a phenyl ring [7–12]. Because of this 'mixed' ligand interest and the multiplicity of coordination geometries exhibited by the Group IIB metals, an investigation of the crystal and molecular structures of $(MX_2)_nL_m$ species (where M = Zn, Cd, Hg; X = Cl, Br, I; and L = "mixed" ligand) has been initiated.

TABLE I. Positional (×10^4) Parameters for Atoms. Calculated standard deviations for the last digit are in parentheses.

	x/*a*	y/*b*	z/*c*
Hg	1213.2(3)	1022.3(4)	4673.8(4)
P	1723(2)	2236(3)	6400(3)
Cl(1)	942(3)	–1109(3)	4629(4)
Cl(2)	736(2)	1824(3)	2679(3)
N	2940(7)	1175(9)	4676(9)
C(1)	1242(9)	762(13)	9953(12)
C(2)	871(7)	131(11)	8882(11)
C(3)	1014(8)	591(12)	7806(12)
C(4)	1533(7)	1590(10)	7796(10)
C(5)	1901(8)	2185(12)	8860(11)
C(6)	1712(8)	1726(12)	9925(10)
C(7)	1290(8)	3710(11)	6345(11)
C(8)	586(9)	3994(12)	6921(13)
C(9)	219(9)	5137(14)	6848(14)
C(10)	532(9)	5974(11)	6117(13)
C(11)	1223(11)	5715(13)	5521(13)
C(12)	1584(9)	4587(13)	5599(12)
C(13)	2912(8)	2395(11)	6484(13)
C(14)	3315(7)	1318(11)	5933(11)
C(15)	3267(8)	48(12)	4256(13)
C(16)	3092(9)	2196(12)	3908(12)
C(17)	2882(10)	–300(14)	2941(14)
C(18)	4066(10)	2514(15)	3892(14)

TABLE II. Bond Angles in Degrees. Estimated standard deviations are given in parentheses.

Cl(1)–Hg–P	127.3(1)°	C(13)–P–C(4)	108.0(6)°
Cl(1)–Hg–N	103.3(3)	C(7)–P–C(13)	105.6(6)
Cl(1)–Hg–Cl(2)	109.0(1)	C(4)–P–C(7)	106.7(5)
Cl(2)–Hg–P	123.5(1)	Hg–N–C(14)	102.9(7)
Cl(2)–Hg–N	96.1(3)	Hg–N–C(16)	108.1(8)
P–Hg–N	77.7(3)	Hg–N–C(15)	109.8(8)
Hg–P–C(13)	105.8(4)	C(15)–B–C(16)	112.2(10)
Hg–P–C(7)	115.9(4)	C(14)–N–C(15)	108.6(9)
Hg–P–C(4)	114.2(4)	C(16)–N–C(14)	114.8(10)

Crystals of the 1:1 adduct formed as a result of the interaction of an equal molar ratio of $HgCl_2$ an $(C_6H_5)_2PC_2H_4N(C_2H_5)_2$ in ethanol [1], are well developed prismatic but are unstable in the presence of air, moisture and organic solvents. A crystal of dimensions 0.8 × 0.7 × 0.2 mm was selected for all X-ray measurements. Unit cell dimensions and intensity data were collected at 138 K using a CAD-4 counter diffractometer controlled by a PDP8/E computer and fitted with a low temperature apparatus. The crystals of the compound are monoclinic, a = 15.264(10), b = 11.309(2), c = 11.442(16) Å, β = 100.3(1)° at 138 K, space group $P2_1/n$, Z = 4.

Intensities of 4012 unique reflections with $2\theta \leqslant 53°$ were measured by using graphite-monochromated MoKα radiation. Lorentz, polarization and absorption corrections were applied to the intensity data and each structure amplitude was assigned an experimental weight obtained from counting statis-

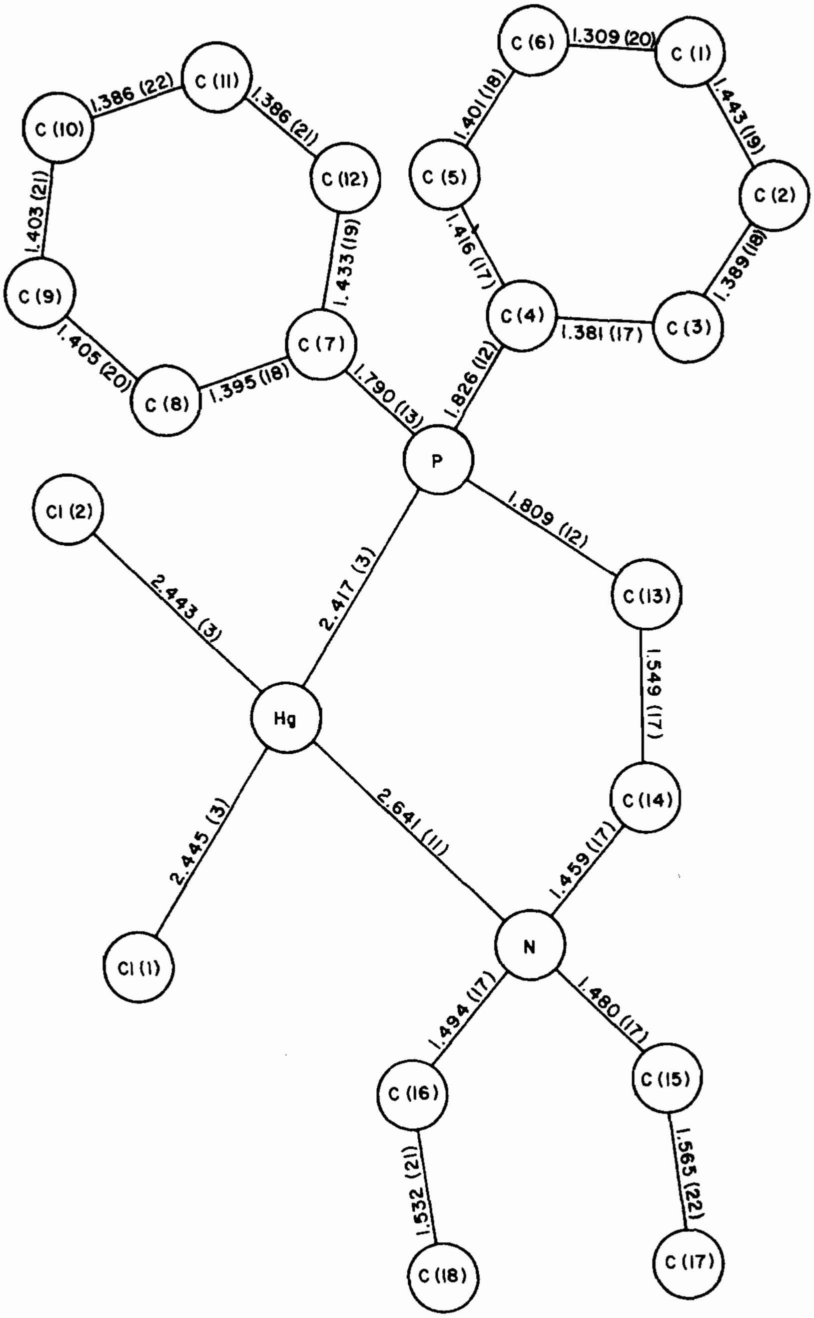

Fig. 1. Skeletal structure of the molecule $HgCl_2[(C_6H_5)_2PC_2H_4N(C_2H_5)_2]$ with the atom numbering scheme and bond distances. Estimated standard deviations are given within parentheses.

tics [13]. The structure was solved by the heavy-atom technique and was refined by block-diagonal least-squares to $R = 0.076$ for 3650 observed reflections and 0.083 for all data. The final positional parameters are given in Table I. Bond distances are shown in a schematic drawing of the molecule in Fig. 1 and the important bond angles are listed in Table II.

The crystal structure of the compound consists of essentially monomeric molecules. Figure 2 shows a stereoview of two monomeric units related by crystallographic center of symmetry. The mercury atom is covalently bound to two chlorine atoms and the nitrogen and phosphorus atoms from the chelated bidentate ligand, and it lies at the geometric center of a highly distorted tetrahedron as evidenced by the

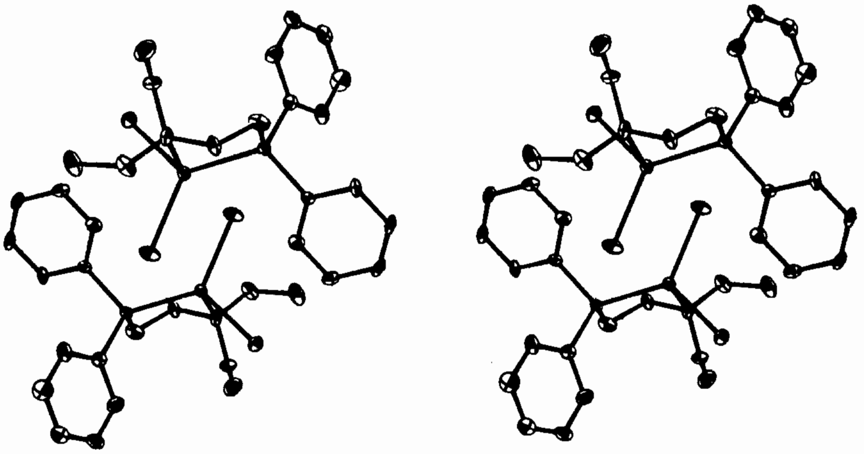

Fig. 2. A stereoview of two monomeric units related by center of symmetry.

wide variation in X–Hg–Y angles, ranging between 77.7(3)° and 127.3(1)°. Although the P–Hg–Cl angles are rather large, they are not all that unusual for pseudotetrahedral mercury(II) complexes with organic ligands [6, 14]. However, the unexpectedly small N–Hg–P angle of 77.7° does indicate some strain within the five-membered chelate ring.

The Hg–Cl bond distances (2.446 and 2.443 Å) are in good agreement with the sum of the approximate tetrahedral covalent radii for Hg and Cl (1.48 + 0.99 = 2.47 Å) [15, 16]. On the other hand the Hg–P bond distance of 2.417 Å is more consistent with the sum of the covalent radii for diagonal Hg and P (1.30 + 1.10 = 2.40 Å) [15, 16] than for tetrahedral Hg and P (1.48 + 1.10 = 2.58 Å). Typical experimental values for tetrahedral mercury(II)–phosphorus bond distances range from 2.487, 2.489 Å in ($Hg(SCN)_2[P(C_6H_5)_3]_2$) [17] to 2.52–2.56 Å in $PbHgP_4$ [18]; 2.498, 2.531 Å in $HgI_2[(C_6H_5)_2PC_2H_4]_2S$ [19]; and 2.557, 2.574 Å in $HgI_2[P(C_6H_5)_3]_2$ [20]. Perhaps Hg–P d_π–d_π bonding becomes important in strengthening the bond and thus reducing the bond length in this complex. Although the mercury–nitrogen bond distance (2.641 Å) exceeds the sum of the Hg and N covalent radii (1.48 + 0.70 = 2.18 Å) [15, 16] and is indicative of weak coordination, it is within the sum of the van der Waals radii (1.50 + 1.5 = 3.0 Å) [16] and is consistent with values quoted for several complexes, *e.g.*, 2.60 Å in dichlorobispyridinemercury(II) [21]; 2.67 and 2.62 Å in chlorotrichloromethyl(1,10-phenanthroline)mercury(II) [14]; and 2.953 Å in dichlorobis(2-imidazolidinone)mercury(II) [7].

Although the strongly bonded coordination environment about the mercury atom is tetrahedral, there is a close approach of two monomers such that an intermolecular Cl···Hg contact of 3.522(4) Å may be construed as an expansion of the secondary valence of mercury from four to five. Even though Grdenic has quoted a van der Waals radius of 1.50 Å for mercury, he also stated that a value less than 1.73 Å was indicative of some form of bonding [15]. Thus the sum of the van der Waals radii for mercury and chlorine (1.73 + 1.80 = 3.53 Å) implies very weak intermolecular, dimeric bonding through bridged chlorine atoms.

Both the nitrogen and phosphorus atoms in the chelated bidentate ligand exhibit near tetrahedral geometry with X–N–Y and X–P–Y angles ranging from 102.9(7) to 114.9(1.0)° and 105.6(6) to 116.0(4)°, respectively. The phenyl ring angles are typical and range from 117(1)° to 122(1)°.

References

1 L. W. Houk and G. R. Dobson, *J. Chem. Soc. A*, 1846 (1968).
2 K. Aurivillius and C. Stalhandske, *Acta Chem. Scand., 27,* 1086 (1973).
3 A. T. McPhail and G. A. Sim, *Chem. Comm.*, 21 (1966).
4 R. J. Majeste and L. M. Trefonas, *Inorg. Chem., 11,* 1834 (1972).
5 C. Chieh, *Can. J. Chem., 55,* 65 (1977).
6 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 28,* L169 (1978).
7 D. Gatteschi, C. A. Ghilardi, A. Orlandini and L. Sacconi, *Inorg. Chem., 17,* 3023 (1978).
8 C. Mealli, S. Midollini and L. Sacconi, *Inorg. Chem., 17,* 632 (1978).
9 P. Stoppioni, P. Dapporto and L. Sacconi, *Inorg. Chem., 17,* 718 (1978).
10 L. Sacconi and M. DiVaira, *Inorg. Chem., 17,* 810 (1978).
11 M. Bacci and C. A. Ghilardi, *Inorg. Chem., 13,* 2398 (1974).
12 M. DiVaira, S. Midollini and L. Sacconi, *Inorg. Chem., 17,* 816 (1978).
13 M. B. Hossain and D. van der Helm, *Inorg. Chem., 17,* 2893 (1978).
14 A. D. Redhouse, *Chem. Comm.*, 1119 (1972).

15 D. Grdenic, *Quart. Rev. Chem. Soc., 19,* 393 (1965).
16 L. Pauling, 'The Chemical Bond', Cornell University Press (1968).
17 R. C. Makhija, A. L. Beuchamp and R. Rivest, *J. Chem. Soc. Dalton,* 2447 (1973).
18 H. Krebs and Th. Lidwig, *Z. Anorg. Chem., 294,* 257 (1958).
19 Karin Aurivillius and L. Fälth, *Chemica Scripta, 4,* 215 (1973).
20 L Fälth, *Chemica Scripta, 9,* 71 (1976).
21 D. Grdenic and I. Krstanovic, *Arkiv F. Kemi, 27,* 143 (1955).