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Structure of Dichloro[N,N,N',N' -tetraethyl-3-diphenylphosphino-1,2-propanediamine-N,N']zinc(II)

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Abstract. $ZnCl_2[(C_6H_5)_2PCH_2CHN(C_2H_5)_2CH_2N(C_2H_5)_2]$, $C_{23}H_{35}Cl_2N_2PZn$, triclinic, $P\bar{1}$ (at 138 K), $a = 11\cdot206$ (6), $b = 12\cdot436$ (5), $c = 10\cdot005$ (4) Å, $\alpha = 106\cdot55$ (3), $\beta = 97\cdot80$ (3), $\gamma = 105\cdot64$ (3)°, $Z = 2$, $V = 1252\cdot46$ Å^3, $D_c = 1\cdot343$ g cm^{-3}, $R = 0\cdot029$ for 5160 reflections (Mo $K\alpha$ radiation). The environment about the zinc atom is a distorted tetrahedron with two chlorine atoms and two amino groups from the potentially tridentate ligand occupying the apices.

Introduction. The interaction of the Group II*b* metal (zinc, cadmium, and mercury) halides with Lewis-base neutral ligands yields complexes $(MX_2)_n L_m$ that span a wide diversity of ligand-to-metal ratios (Evans, Mann, Peiser & Purdie, 1940; Houk & Dobson, 1968; Fawcett, Ou, Potenza & Schugar, 1978; DiVaira & Orioli, 1968). Although detailed X-ray crystallographic studies of several of these complexes reveal metal coordination numbers ranging from two to perhaps nine, an environment of two, four, or six ligands is most often encountered (Fawcett, Ou, Potenza & Schugar, 1978; Orioli & Ciampolini, 1972; Cameron & Forrest, 1971; DiVaira & Orioli, 1968). Very frequently the secondary valence is satisfied by additional weak or moderate bonds to the metal. While the numbers of crystallographic structural investigations of zinc and cadmium complexes are probably comparable, more extensive studies of mercury compounds are prevalent in the literature. Available data on

the structural chemistry of zinc-halide Lewis-base-ligand complexes indicate a preference for achieving four coordination and usually a distorted tetrahedral environment (Baenziger & Schultz, 1971).

In the recent past 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 (Gatteschi, Ghilardi, Orlandini & Sacconi, 1978; Mealli, Midollini & Sacconi, 1978; Sacconi & DiVaira, 1978; DiVaira, Midollini & Sacconi, 1978). Because of this 'mixed' ligand interest and the multiplicity of coordination geometries exhibited by the Group II*b* metals, an investigation of the crystal and molecular structures of $(MX_2)_n L_m$ species (where M = Zn, Cd, Hg; X = Cl, Br, I; and L = 'mixed' ligand) has been initiated (Sen Gupta, Houk, van der Helm & Hossain, 1980; Houk, Sen Gupta, Hossain & van der Helm, 1982).

The interaction of an equal molar ratio of $ZnCl_2$ and the 'mixed' ligand $(C_6H_5)_2PCH_2CHN(C_2H_5)_2CH_2N(C_2H_5)_2$ (PNN) in ethanol yields white crystals of the 1:1 adduct $ZnCl_2(PNN)$ (Houk & Dobson, 1968). The fairly well developed prismatic crystals were found to be unstable in the presence of air, moisture, and organic solvents. All X-ray measurements were carried out with a single crystal of dimensions $0\cdot50 \times 0\cdot50 \times 0\cdot15$ mm on a Nonius CAD-4 automatic diffractometer, fitted with a low-temperature (cold N$_2$ gas stream) device.

The crystals were triclinic, space group $P\bar{1}$, which was confirmed by Patterson analyses and structure refinements. The cell parameters were obtained by a least-squares fit to the 2θ and -2θ values of 48 reflections distributed throughout reciprocal space.

The intensities of all unique reflections with $2\theta \leq 53°$ were measured at 138 (2) K using graphite-monochromatized Mo $K\alpha$ radiation and $\theta-2\theta$ scan techniques. The scan width (x) was calculated by $x = (A + B \tan \theta)°$ for each reflection, where $A = 0.80$ and $B = 0.14$. A horizontal receiving aperture with a variable width $(3.5 + 0.86 \tan \theta)$ mm and constant height of 6 mm was located 173 mm from the crystal. The maximum scan time for each reflection was 50 s, with two-thirds of the time spent on scanning the peak and one-sixth of the time spent on each background. A standard reflection $(5\bar{4}1)$ was monitored after every 3000 s. The change in the standard reflection intensity during data collection was less than 3%. Out of the total 5160 reflections, the intensities of 328 reflections had values $I < 2\sigma (I)$ and were considered unobserved. The data were corrected for Lorentz, polarization and absorption effects $(\mu = 1.29$ mm^{-1}, maximum and minimum transmissions were 0.82 and 0.52, respectively) (Coppens, Leiserowitz & Rabinovich, 1965).

Table 1. *Positional* ($\times 10^5$) *and equivalent isotropic thermal parameters for non-hydrogen atoms*

Calculated standard deviations for the last digit are in parentheses.

	x	y	z	U_{eq}* (Å²)
Zn(1)	−32094 (2)	−6548 (2)	84137 (2)	0.0146 (1)
Cl(1)	−52917 (3)	−10756 (3)	77574 (5)	0.0220 (1)
Cl(2)	−25180 (3)	−17483 (3)	95658 (5)	0.0259 (1)
P(1)	−109 (3)	27904 (2)	67812 (3)	0.0141 (1)
N(1)	−20292 (11)	11681 (10)	92532 (13)	0.0141 (5)
N(2)	−24123 (11)	−8233 (10)	66008 (14)	0.0149 (4)
C(1)	−15471 (15)	12184 (15)	118244 (18)	0.0235 (6)
C(2)	−10236 (15)	13352 (14)	105241 (16)	0.0183 (6)
C(3)	−27252 (15)	20404 (14)	97044 (16)	0.0185 (6)
C(4)	−37128 (15)	20640 (15)	85273 (19)	0.0228 (6)
C(5)	−14341 (14)	13271 (13)	80255 (15)	0.0140 (5)
C(6)	−12014 (14)	1855 (13)	72212 (15)	0.0158 (5)
C(7)	−32480 (15)	−6849 (14)	54037 (16)	0.0200 (6)
C(8)	−26788 (19)	−5905 (18)	41325 (19)	0.0313 (7)
C(9)	−20918 (15)	−19469 (14)	61293 (18)	0.0209 (6)
C(10)	−32548 (16)	−30515 (15)	55113 (19)	0.0261 (7)
C(11)	−2081 (15)	23876 (14)	84147 (15)	0.0165 (5)
C(12)	−11557 (15)	36033 (14)	67988 (16)	0.0176 (6)
C(13)	−22469 (15)	31082 (15)	56878 (16)	0.0215 (6)
C(14)	−32272 (16)	35943 (16)	57213 (19)	0.0271 (7)
C(15)	−31231 (18)	45795 (18)	68530 (20)	0.0300 (7)
C(16)	−20295 (18)	51015 (15)	79620 (20)	0.0290 (7)
C(17)	−10554 (15)	46121 (15)	79288 (18)	0.0226 (6)
C(18)	15497 (14)	39439 (13)	74221 (15)	0.0169 (6)
C(19)	25871 (15)	37076 (14)	80871 (16)	0.0206 (6)
C(20)	38124 (15)	45042 (16)	84280 (18)	0.0265 (6)
C(21)	40297 (16)	55529 (15)	81210 (19)	0.0275 (6)
C(22)	30134 (18)	57897 (15)	74561 (19)	0.0258 (7)
C(23)	17847 (15)	49897 (14)	70913 (18)	0.0216 (6)

* $U_{eq} = (\frac{1}{3}\pi^2) \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 2. *Bond distances* (Å)

Standard deviations for the last digit are in parentheses.

Zn−Cl(1)	2.2090 (5)	N(1)−C(2)	1.505 (2)
Zn−Cl(2)	2.2354 (5)	N(1)−C(3)	1.504 (2)
Zn−N(1)	2.143 (1)	N(1)−C(5)	1.511 (2)
Zn−N(2)	2.111 (1)	N(2)−C(6)	1.487 (2)
C(1)−C(2)	1.525 (3)	N(2)−C(7)	1.497 (2)
C(3)−C(4)	1.515 (3)	N(2)−C(9)	1.498 (2)
C(7)−C(8)	1.518 (3)		
C(9)−C(10)	1.517 (3)	P−C(11)	1.864 (2)
C(5)−C(6)	1.529 (2)	P−C(12)	1.834 (2)
C(5)−C(11)	1.537 (2)	P−C(18)	1.829 (2)

Table 3. *Bond angles* (°)

Standard deviations for the last digit are in parentheses.

Cl(1)−Zn−Cl(2)	117.08 (2)	C(11)−P−C(12)	98.2 (1)
Cl(1)−Zn−N(1)	118.77 (4)	C(11)−P−C(18)	101.5 (1)
Cl(2)−Zn−N(1)	111.98 (4)	C(12)−P−C(18)	104.6 (1)
Cl(2)−Zn−N(2)	106.31 (4)		
N(1)−Zn−N(2)	88.01 (5)	P−C(11)−C(5)	108.6 (1)
Cl(1)−Zn−N(2)	109.99 (4)	P−C(12)−C(13)	117.5 (1)
		P−C(12)−C(17)	123.5 (1)
Zn−N(1)−C(2)	108.8 (1)	P−C(18)−C(19)	119.2 (1)
Zn−N(1)−C(3)	114.8 (1)	P−C(18)−C(23)	121.9 (1)
Zn−N(1)−C(5)	102.7 (1)		
C(2)−N(1)−C(3)	108.5 (1)	N(1)−C(2)−C(1)	113.6 (1)
C(3)−N(1)−C(5)	111.4 (1)	N(1)−C(3)−C(4)	115.9 (1)
C(2)−N(1)−C(5)	110.4 (1)	N(1)−C(5)−C(6)	110.0 (1)
		N(1)−C(5)−C(11)	116.1 (1)
Zn−N(2)−C(6)	100.0 (1)		
Zn−N(2)−C(7)	111.1 (1)	N(2)−C(6)−C(5)	111.4 (1)
Zn−N(2)−C(9)	112.7 (1)	N(2)−C(7)−C(8)	115.9 (2)
C(6)−N(2)−C(7)	112.4 (1)	N(2)−C(9)−C(10)	113.4 (1)
C(7)−N(2)−C(9)	111.9 (1)		
C(6)−N(2)−C(9)	108.2 (1)	C(6)−C(5)−C(11)	109.9 (1)

The positions of Zn and Cl atoms were obtained from a three-dimensional Patterson map, and the complete structure was solved by the heavy-atom technique. All hydrogen atoms were located from a difference Fourier map. The structure was refined by using a block-diagonal least-squares routine (Ahmed, 1966) with anisotropic thermal parameters for non-hydrogen atoms. The observed structure factors were corrected for anomalous dispersion of zinc. Refinements converged to a final R factor of 0.024 for 4646 reflections included in the least-squares calculations, and 0.029 for all 5160 reflections. The scattering factors for Zn, Cl, P, N, and C atoms were taken from *International Tables for X-ray Crystallography* (1974), and those for hydrogen from Stewart, Davidson & Simpson (1965). The final parameters are listed in Table 1.* The atom numbering scheme followed in the

* Lists of structure factors, anisotropic thermal parameters, hydrogen atom parameters, and phenyl bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36703 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
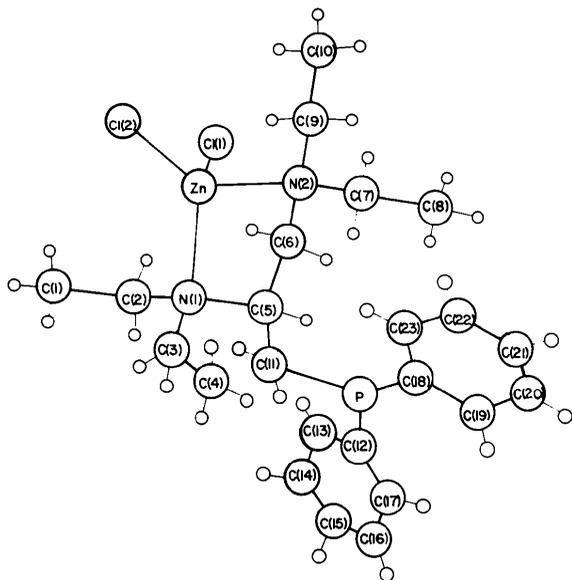
Fig. 1. Atom numbering in dichloro[N,N,N',N'-tetraethyl-3-di-phenylphosphino-1,2-propanediamine-N,N']zinc(II).

text is shown in Fig. 1. Bond distances and angles are given in Tables 2 and 3 respectively.

Discussion. A stereoscopic view of the molecule is shown in Fig. 2.

The two chlorine atoms and the two amino nitrogens from the chelated bidentate ligand coordinate to the zinc center forming a distorted tetrahedron. Apparently the uncoordinated, sterically demanding, diphenylphosphino group cannot be accommodated in the already crowded coordination sphere about the zinc. The increase in conductivity observed when CH$_3$I is added to a solution of ZnCl$_2$(PNN) (Houk & Dobson, 1968) can be easily attributed to the quaternization of the uncoordinated phosphorus atom yielding the ionic ZnCl$_2$[(C$_6$H$_5$)$_2$P$^+$(CH$_3$)CH$_2$CHN(C$_2$H$_5$)$_2$CH$_2$N(C$_2$-H$_5$)$_2$].I$^-$ species.

The ligand–metal–ligand angles deviate significantly from the regular tetrahedral values with the Cl–Zn–N angle of 118·8°, the Cl–Zn–Cl angle of 117·1°, and the N–Zn–N angle of 88·0°. Increased Cl–M–Cl angles as M decreases in size are a common phenomenon in tetrahedral MCl$_2$ complexes (Makhija, Beauchamp & Rivest, 1973).
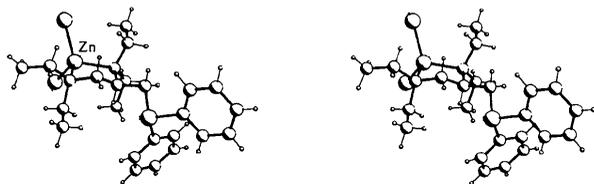
The Zn—Cl bond lengths (2·209 and 2·235 Å) are slightly less than the sum of the covalent radii of the Zn and Cl atoms (1·31 + 0·99 = 2·30 Å) (Pauling, 1967), but are comparable with data for similar ZnCl$_2$(N)$_2$ complexes, e.g. 2·206 and 2·198 Å in ZnCl$_2$(1-methyl-tetrazole)$_2$ (Baenziger & Schultz, 1971) and 2·207 and 2·198 Å in ZnCl$_2$(1,10-phenanthroline) (Reimann, Block & Perloff, 1966). The Zn—N bond lengths (2·143 and 2·111 Å) are slightly greater than the sum of the covalent radii of the Zn and N atoms (1·31 + 0·70 = 2·01 Å) but are close to those observed for similar compounds, e.g. 2·04 and 2·06 Å for ZnCl$_2$-(1-methyltetrazole)$_2$ (Baenziger & Schultz, 1971) and 2·05 and 2·07 Å in ZnCl$_2$(1,10-phenanthroline) (Reimann et al., 1966). The difference in the two Zn—Cl distances [Zn—Cl(1) = 2·209 Å, Zn—Cl(2) = 2·235 Å] and the two Zn—N distances [Zn—N(1) = 2·143 Å and Zn—N(2) = 2·111 Å] is significant. In the case of the nitrogen atoms this is correlated with the observation that all bond distances for N(2) are smaller than those for N(1).

The uncoordinated phosphorus atom displays the three predictable, pyramidal angles of 98·2 to 104·6°. The phosphorus-to-aromatic-carbon bond distances (1·829 and 1·834 Å) are slightly shorter than the phosphorus–aliphatic one (1·864 Å).

The conformation of the five-membered chelate ring comprising Zn—N(1)—C(5)—C(6)—N(2) is an envelope and is similar to that in di-μ-chloro-bis[chloro(1-diethylamino-2-diphenylphosphinoethane)cadmium(II)] (Houk, Sen Gupta, Hossain & van der Helm, 1982). The sum of the endocyclic torsion angles in the present case is 173·9° compared to 175·5° in the Cd complex. The two phenyl rings are planar; the dihedral angle between the two rings is 63·7 (2)°. Phenyl C—C distances range from 1·376 (3) to 1·402 (3) Å and the C—C—C angles from 118·3 (2) to 120·8 (2)°.

Fig. 2. Stereoscopic view of the molecule.

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Structure of a 1:2 Complex of Sodium Perchlorate and 1,4,7,10-Tetraoxacyclododecane (12-Crown-4)

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Abstract. $Na(C_8H_{16}O_4)_2ClO_4$, monoclinic, $P2_1/a$, $a = 15.420$ (8), $b = 15.245$ (10), $c = 9.650$ (5) Å, $\beta = 92.13$ (4)°, $V = 2267$ (4) Å^3. $D_c = 1.391$ g cm^{-3}, $Z = 4$, $\mu(Mo\ K\alpha) = 1.972$ cm^{-1}. Final $R_1 = 0.0712$ for 1401 reflections with $F_o > 3\sigma(F_o)$. The sodium ion forms a sandwich structure with two 12-crown-4 rings. The eightfold coordination about the sodium ion may be described as slightly distorted rectangular antiprismatic with the heteroatoms being planar to within ±0.01 Å. The perchlorate group is not bonded to any other atoms and is disordered.

Introduction. Since the early 1960's there has been an upsurge of interest in the coordination complexes of macrocyclic compounds which may serve as models for certain naturally occurring bioinorganic systems. Macrocycles display an unusual affinity for the alkali- and alkaline-earth-metal ions, and, indeed, the tendency for the oxygen atoms of crown ethers to coordinate to these species significantly exceeds their tendency to coordinate with transition-metal ions (Hughes, Haltiwanger, Pierpont, Hampton & Blackmer, 1980).

It has been found that the configuration of a macrocyclic complex depends on the relative sizes of the complexed ion and the cavity. If the cavity is significantly larger than the ion, the ligand wraps around the ion forming a three-dimensional structure. If the cavity is only slightly larger, the macrocycle will tend to pucker so that all of the heteroatoms are coordinated. When the size of the hole is commensurate with the size of the metal ion, the coordination geometry will be planar. In cases where the cavity is smaller than the ion, the macrocycle retains its planar configuration, but the metal ion remains outside the plane of the ligand, and a sandwich structure is noted.

The formation of 1:2 'sandwich' compounds of Na$^+$ with 12-crown-4
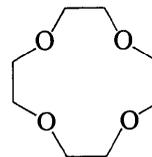
has been confirmed by crystallographic studies which describe structures containing several water molecules within the crystal lattice (van Remoortere & Boer, 1974; Boer, Neuman, van Remoortere & Steiner, 1974). Although not complexed to the metal ion, the water molecules were found to form a hydrogen-bonded network that interacted with the anion. In contrast, this investigation describes an anhydrous species and reveals that the aqueous array is not necessary for the stability of the crystal, and seems to have little effect on the stability of the metal–crown complexation as evidenced by the Na–O bond distances.

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