

son affinité pour le mercure dépasse celle de N(1), site normal de fixation du proton dans l'adénine non dissociée et ses dérivés alkylés.

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Structure of Di- μ -chloro-bis[chloro(1-diethylamino-2-diphenylphosphinoethane)cadmium(II)]

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Abstract

[CdCl₂{(C₆H₅)₂PC₂H₄N(C₂H₅)₂}]₂, monoclinic, *P*2₁/*c*, *a* = 19.944 (10), *b* = 12.247 (4), *c* = 15.956 (9) Å, β = 96.10 (3)°, *V* = 3875.3 Å³ at 138 (2) K, *M_r* = 937.4, *Z* = 4, *D_c* = 1.606 Mg m⁻³. The final *R* value is 0.063 for all 8001 data. The crystal contains two different pairs of centrosymmetric dimeric molecules per unit cell. The overall structure of the two independent dimeric molecules is the same, although there are some minor geometric differences. The N and P atoms from the chelated bidentate ligand along with a terminal Cl atom (Cl₁) and two bridging Cl atoms (Cl₂, Cl₃) form a distorted trigonal-bipyramid environment about each Cd atom. Since both independent molecular dimers are characterized by very asymmetric Cl bridges and a long Cd–N bond distance, the Cd environment may be alternately described as a (3 + 2) five-coordinate species utilizing three strong bonds to the P, terminal Cl and one of the Cl bridge atoms and weaker ones with the N and the second bridging Cl atoms.

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Introduction

A wide diversity of Group IIb metal complexes, (MX₂)_nL_m, result upon the interaction of zinc, cadmium, and mercury halides with Group Va and VIa neutral ligands (Evans, Mann, Peiser & Purdie, 1940; Houk & Dobson, 1968; Fawcett, Ou, Potenza & Schugar, 1978; DiVaira & Orioli, 1968). Crystallographic studies of several of these complexes reveal a range of metal coordination numbers from two to nine, although two, four, and six are predominant (Fawcett, Ou, Potenza & Schugar, 1978; Orioli & Ciampolini, 1972; Cameron & Forrest, 1971; DiVaira & Orioli, 1968). Often the secondary valence is satisfied by a combination of strongly and moderately or weakly bound ligands in the coordination sphere.

Although the structural chemistry of cadmium halide complexes with Lewis-base ligands – the primary subject of this report – is much less complete than that of its family member mercury, data that are available overwhelmingly depict the Cd atom tetrahedrally or

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octahedrally surrounded by ligands and the formula unit linked in an infinite chain network through bridging halide atoms.

Recently 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 IIb metals, an investigation of the crystal and molecular structures of $(MX_2)_nL_m$ species (where $M = \text{Zn}, \text{Cd}, \text{Hg}$; $X = \text{Cl}, \text{Br}, \text{I}$; and $L =$ 'mixed' ligand) has been initiated.

Experimental

The interaction of an equal molar ratio of CdCl_2 and the 'mixed' ligand $(\text{C}_6\text{H}_5)_2\text{PC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2$ (NP) in ethanol yields white crystals of the 1:1 adduct $\text{CdCl}_2 \cdot (\text{NP})$ (Houk & Dobson, 1968). The crystals are fairly well developed and prismatic in form but are moderately unstable in the presence of air, moisture, and organic solvents. However, the crystals are stable at low temperature (138 K). A single crystal was selected, with dimensions $0.52 \times 0.52 \times 0.19$ mm, and after mounting transferred to the diffractometer which was equipped with a low-temperature nitrogen gas stream. On the basis of the Laue symmetry ($2/m$) and observed systematic absences ($0k0, k = 2n + 1; h0l, l = 2n + 1$), the monoclinic space group $P2_1/c$ was uniquely determined. The unit-cell dimensions were determined at 138 K, using $\text{Mo } K\alpha_1$ radiation. The cell parameters were obtained by a least-squares fit to the $+2\theta$ and -2θ data of 32 reflections distributed throughout reciprocal space. No meaningful room-temperature cell constants and density measurements could be obtained due to the instability of the crystals at that temperature.

The intensities of all reflections with $2\theta \leq 53^\circ$ were measured by using monochromatized $\text{Mo } K\alpha$ radiation and applying θ - 2θ scan techniques. The scan width was adjusted to the dispersion and calculated with the formula $\theta = (A + B \tan \theta)^\circ$ for each reflection, where $A = 0.70$ and $B = 0.13$. 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. A reflection was scanned for a maximum time of 40 s, with two thirds of the time spent on scanning the peak (P) and one-sixth of the time spent on each of the left and right backgrounds (LB and RB). The unscaled intensities (I) were calculated as $I = P - 2(\text{RB} + \text{LB})$. A standard reflection (743) was monitored after every 44 reflections. The change in the

standard reflection intensity during data collection was less than 1%. The orientation of three reflections was automatically checked every 200 measurements. When the $2\theta, \omega, \varphi$, or χ angles of these three reflections were changed by more than 0.1° , a new orientation matrix was automatically obtained from a list of 11 reflections. There were 727 reflections which could not be distinguished from the background on the basis that the intensity (I) was less than $2\sigma(I)$. These reflections were assigned intensities equal to $I^{1/2}$ for the purpose of least-squares refinement. Lorentz, polarization, and absorption corrections ($\mu = 1.47 \text{ mm}^{-1}$) (Coppens, Leiserowitz & Rabinovich, 1965) were applied to the data. Each structure factor was assigned a weight given by $w_F = 1/\sigma_F^2$ (Ealick, van der Helm & Weinheimer, 1975).

A three-dimensional sharpened Patterson map was calculated in which the Cd-Cd vectors were easily identified. These vectors led to two independent Cd atom positions on two different crystallographic centers of symmetry and clearly indicated the presence of two independent centrosymmetric dimeric pairs (referred to in the text as 'molecule A' and 'molecule B'). Structure factor calculations with the refined Cd positions gave an R factor of 0.388 for all reflections. Subsequent difference Fourier syntheses revealed the positions of all the non-hydrogen atoms in the two molecules. These atoms were refined first isotropically, and later with anisotropic thermal parameters. The effect of anomalous dispersion of Mo radiation by Cd atoms was included. A final difference Fourier map was calculated, which revealed only the phenyl H atoms. Those atoms were included with isotropic temperature factors in the least-squares calculation. The refinement was discontinued when the maximum parameter shifts for all non-hydrogen atoms were less than $\frac{1}{3}$ of their corresponding standard deviations. Final R values were 0.058 for the 7274 observed reflections and 0.063 for all 8001 reflections.

All least-squares refinements were carried out by using a block-diagonal least-squares program (Ahmed, 1966) in which the quantity $\sum w_F(|KF_o| - |F_c|)^2$ was minimized. The scattering factors for Cd, Cl, P, N, and C atoms were taken from *International Tables for X-ray Crystallography* (1974), and for the H atoms from Stewart, Davidson & Simpson (1965).

Results and discussion

The final positional parameters of all non-hydrogen atoms are listed in Table 1.* The atom numbering

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36262 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters for non-hydrogen atoms*

Standard deviations of the last digit are in parentheses.

$$U_{eq} = (\frac{1}{3}\pi^2) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
Molecule A				
Cd	617.0 (2)	1130.1 (2)	4715.6 (2)	0.0162 (1)
Cl _i	1261.5 (6)	1723.6 (9)	6011.9 (7)	0.0199 (5)
Cl _b	586.7 (6)	-889.0 (9)	4572.2 (7)	0.0200 (5)
P	25.8 (6)	2386.8 (9)	3583.2 (7)	0.0155 (5)
N	1522 (2)	1468 (3)	3774 (2)	0.0178 (17)
C(1)	1406 (2)	2589 (4)	3431 (3)	0.0202 (21)
C(2)	702 (2)	2729 (4)	2942 (3)	0.0198 (21)
C(3)	1501 (3)	614 (4)	3106 (3)	0.0230 (22)
C(4)	2044 (3)	715 (5)	2494 (3)	0.0343 (28)
C(5)	2188 (2)	1478 (4)	4316 (3)	0.0224 (22)
C(6)	2383 (3)	370 (4)	4687 (3)	0.0279 (25)
C(7)	-633 (2)	1808 (4)	2847 (3)	0.0180 (20)
C(8)	-841 (3)	2371 (4)	2091 (3)	0.0227 (22)
C(9)	-1338 (3)	1928 (4)	1529 (3)	0.0259 (23)
C(10)	-1642 (2)	959 (4)	1692 (3)	0.0224 (22)
C(11)	-1444 (3)	406 (4)	2440 (3)	0.0213 (21)
C(12)	-939 (2)	823 (4)	3012 (3)	0.0192 (21)
C(13)	-354 (2)	3642 (4)	3897 (3)	0.0183 (20)
C(14)	-956 (2)	3547 (4)	4271 (3)	0.0202 (21)
C(15)	-1293 (3)	4467 (4)	4519 (3)	0.0236 (23)
C(16)	-1012 (3)	5499 (4)	4402 (3)	0.0252 (24)
C(17)	-418 (3)	5602 (4)	4053 (3)	0.0251 (23)
C(18)	-80 (3)	4686 (4)	3805 (3)	0.0219 (23)
Molecule B				
Cd	5744.2 (2)	4565.3 (3)	4355.1 (2)	0.0184 (1)
Cl _i	6745.1 (7)	5609.5 (11)	4826.0 (9)	0.0318 (6)
Cl _b	5086.8 (6)	3657.8 (9)	5426.4 (7)	0.0212 (5)
P	5321.8 (6)	4173.2 (10)	2774.7 (7)	0.0158 (5)
N	6315 (2)	2809 (3)	4047 (2)	0.0181 (17)
C(1)	5850 (2)	2201 (4)	3424 (3)	0.0207 (21)
C(2)	5675 (2)	2810 (4)	2590 (3)	0.0212 (21)
C(3)	6954 (2)	3132 (4)	3698 (3)	0.0252 (23)
C(4)	7371 (3)	2188 (5)	3388 (4)	0.0387 (30)
C(5)	6430 (3)	2109 (4)	4807 (3)	0.0265 (24)
C(6)	6886 (3)	2614 (6)	5527 (4)	0.0418 (32)
C(7)	4419 (2)	4063 (4)	2441 (3)	0.0185 (20)
C(8)	4168 (2)	3457 (4)	1738 (3)	0.0193 (21)
C(9)	3477 (3)	3402 (4)	1507 (3)	0.0239 (23)
C(10)	3039 (3)	3961 (4)	1972 (3)	0.0256 (23)
C(11)	3286 (3)	4566 (4)	2669 (3)	0.0256 (24)
C(12)	3974 (2)	4617 (4)	2912 (3)	0.0202 (21)
C(13)	5636 (3)	5054 (4)	1997 (3)	0.0193 (22)
C(14)	5943 (3)	6037 (4)	2246 (3)	0.0215 (22)
C(15)	6142 (3)	6759 (4)	1650 (3)	0.0247 (23)
C(16)	6046 (3)	6517 (4)	803 (3)	0.0255 (23)
C(17)	5767 (3)	5517 (5)	545 (3)	0.0285 (25)
C(18)	5561 (3)	4795 (5)	1129 (3)	0.0281 (25)

scheme followed in the text is shown in Fig. 1. Interatomic bond distances calculated on the basis of the final parameters are found in Table 2. Corresponding bond angles are given in Table 3. The crystal structure of the compound consists of two pairs of centrosymmetric dimeric molecules per unit cell. Perspective views of the two molecules are shown in Figs. 1 and 2.

In each of the dimeric molecules the environment about the Cd atom is a highly distorted trigonal bipyramid. One of the bridging Cl atoms (Cl_i) and the N atom from the chelated bidentate ligand are in the apical positions; the ligand P atom, another bridging Cl (Cl_b) and a terminal chlorine (Cl_t) atom occupy the equatorial positions.

The trigonal-planar angles, with ideal values of 120°, vary between 112.46 and 125.66°. The angles formed by apical atoms and those in the trigonal plane, with ideal values of 90°, vary between 76.11 and 97.90°, while the angles formed by the apical atoms are 166.6 and 170.3°. There are therefore significant differences from the ideal trigonal-bipyramidal geometry.

There are some significant differences in metal-ligand bond distances and angles in the two crystallographically distinguishable molecules. The bond length Cd-Cl_b is 2.484 Å in molecule A, whereas it is 2.520 Å in molecule B; the length Cd-P is 2.563 Å in molecule A, but it is 2.617 Å in B. Differences in bond angles are much more significant. For example, the Cl_i-Cd-Cl_b angle in molecule A is 112.46, but 119.57° in B; the P-Cd-Cl_i angle in A is 89.97, and 97.43° in B; and the P-Cd-Cl_b angle in A is 121.87, and 115.80° in B. The bridging Cd-Cl_b-Cd' bond angles of 94.7 and 95.7° for molecules A and B, respectively, are comparable. As observed in the HgCl₂·(NP) analog (Sen Gupta, Houk, van der Helm & Hossain, 1980), the chelate-to-cadmium angles of 77.6 and 76.1°, respectively for A and B, indicate some strain in the five-membered ring.

The two molecules have also some significant conformational differences. The main difference is in the conformation of the five-membered chelate ring comprising the Cd, N, C(1), C(2) and P atoms. In both molecules the torsion angle C(2)-P-Cd-N is close to 0° and the rings assume, therefore, an envelope

Table 2. *Bond distances (Å)*

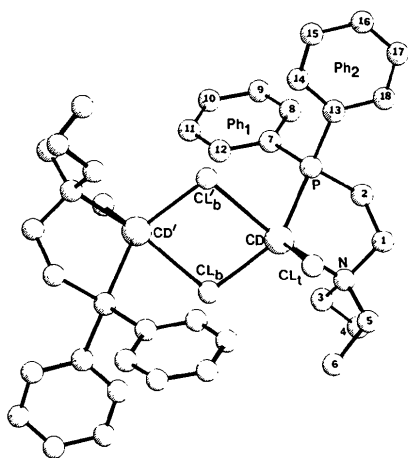
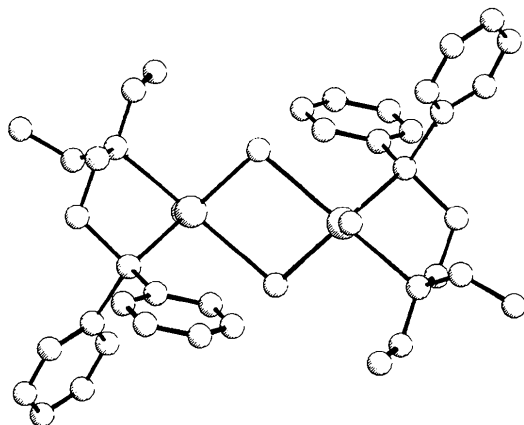
Standard deviations for the last digit are in parentheses.

	Molecule A	Molecule B		Molecule A	Molecule B	Molecule A	Molecule B	
Cd-Cl _i	2.4277 (12)	2.4220 (14)	C(3)-C(4)	1.538 (8)	1.536 (8)	C(11)-C(12)	1.383 (7)	1.387 (7)
Cd-Cl _b	2.4835 (11)	2.5204 (12)	C(5)-C(6)	1.515 (7)	1.519 (8)	C(12)-C(7)	1.390 (7)	1.398 (6)
Cd-Cl _t	2.7788 (12)	2.7797 (12)	P-C(2)	1.826 (4)	1.848 (5)	C(13)-C(14)	1.401 (6)	1.389 (7)
Cd-P	2.5634 (12)	2.6168 (12)	P-C(7)	1.811 (5)	1.828 (4)	C(14)-C(15)	1.391 (7)	1.387 (7)
Cd-N	2.503 (4)	2.507 (4)	P-C(13)	1.808 (6)	1.806 (5)	C(15)-C(16)	1.403 (7)	1.377 (7)
N-C(1)	1.487 (6)	1.486 (6)	C(7)-C(8)	1.413 (7)	1.393 (7)	C(16)-C(17)	1.367 (8)	1.389 (8)
N-C(3)	1.491 (6)	1.497 (6)	C(8)-C(9)	1.376 (8)	1.390 (7)	C(17)-C(18)	1.388 (8)	1.379 (8)
N-C(5)	1.506 (6)	1.483 (6)	C(9)-C(10)	1.370 (7)	1.386 (8)	C(18)-C(13)	1.404 (7)	1.413 (7)
C(1)-C(2)	1.542 (6)	1.533 (7)	C(10)-C(11)	1.392 (7)	1.383 (7)			

Table 3. Bond angles ($^\circ$)

Estimated standard deviations for the last digit are given in parentheses.

	Molecule A	Molecule B		Molecule A	Molecule B		Molecule A	Molecule B
$\text{Cl}_l\text{-Cd-Cl}_h$	112.46 (4)	119.57 (4)	$\text{Cd-P-C}(7)$	118.0 (2)	120.0 (2)	$\text{P-C}(13)\text{-C}(14)$	116.8 (3)	119.7 (4)
$\text{Cl}_h\text{-Cd-P}$	121.87 (4)	115.80 (4)	$\text{Cd-P-C}(13)$	119.4 (2)	116.9 (2)	$\text{P-C}(13)\text{-C}(18)$	124.5 (4)	122.1 (4)
$\text{Cl}_l\text{-Cd-P}$	125.66 (4)	124.48 (4)	$\text{C}(2)\text{-P-C}(7)$	104.7 (2)	105.5 (2)	$\text{C}(7)\text{-C}(8)\text{-C}(9)$	119.3 (5)	120.0 (4)
$\text{Cl}'_l\text{-Cd-Cl}_l$	94.91 (4)	91.75 (4)	$\text{C}(2)\text{-P-C}(13)$	108.4 (2)	105.3 (2)	$\text{C}(8)\text{-C}(9)\text{-C}(10)$	121.4 (5)	119.9 (5)
$\text{Cl}'_l\text{-Cd-Cl}_h$	85.31 (4)	84.27 (4)	$\text{C}(7)\text{-P-C}(13)$	102.5 (2)	104.3 (2)	$\text{C}(9)\text{-C}(10)\text{-C}(11)$	119.5 (4)	120.3 (5)
$\text{Cl}'_l\text{-Cd-P}$	89.97 (4)	97.43 (4)	$\text{C}(1)\text{-N-C}(3)$	113.2 (4)	112.3 (3)	$\text{C}(10)\text{-C}(11)\text{-C}(12)$	120.4 (5)	120.4 (5)
N-Cd-Cl_l	96.41 (9)	97.90 (9)	$\text{C}(1)\text{-N-C}(5)$	107.3 (3)	106.8 (3)	$\text{C}(11)\text{-C}(12)\text{-C}(7)$	119.9 (4)	119.6 (4)
N-Cd-Cl_h	96.97 (9)	91.97 (9)	$\text{C}(3)\text{-N-C}(5)$	111.9 (4)	113.1 (4)	$\text{C}(12)\text{-C}(7)\text{-C}(8)$	119.4 (4)	119.8 (4)
N-Cd-P	77.56 (9)	76.11 (9)	$\text{N-C}(1)\text{-C}(2)$	112.7 (4)	113.9 (4)	$\text{C}(13)\text{-C}(14)\text{-C}(15)$	121.0 (4)	120.4 (4)
$\text{Cl}'_l\text{-Cd-N}$	166.57 (9)	170.28 (9)	$\text{N-C}(3)\text{-C}(4)$	115.4 (4)	115.6 (4)	$\text{C}(14)\text{-C}(15)\text{-C}(16)$	118.7 (5)	121.0 (5)
$\text{Cd-Cl}_h\text{-Cd}'$	94.69 (4)	95.73 (4)	$\text{N-C}(5)\text{-C}(6)$	113.0 (4)	114.3 (4)	$\text{C}(15)\text{-C}(16)\text{-C}(17)$	120.9 (5)	119.3 (5)
$\text{Cd-N-C}(1)$	106.2 (3)	107.3 (3)	$\text{P-C}(2)\text{-C}(1)$	112.2 (3)	110.9 (3)	$\text{C}(16)\text{-C}(17)\text{-C}(18)$	120.6 (5)	120.3 (5)
$\text{Cd-N-C}(3)$	110.2 (3)	105.6 (3)	$\text{P-C}(7)\text{-C}(8)$	119.3 (4)	122.2 (3)	$\text{C}(17)\text{-C}(18)\text{-C}(13)$	120.0 (5)	120.7 (5)
$\text{Cd-N-C}(5)$	107.8 (3)	111.7 (3)	$\text{P-C}(7)\text{-C}(12)$	121.3 (3)	118.0 (3)	$\text{C}(18)\text{-C}(13)\text{-C}(14)$	118.7 (4)	118.2 (4)
$\text{Cd-P-C}(2)$	102.8 (2)	103.3 (2)						

Fig. 1. A perspective view of molecule *A* showing the atom-numbering scheme followed in the text. Carbon atoms are designated by numerals only.Fig. 2. A perspective view of molecule *B*.

conformation with an approximate mirror plane passing through C(1) and the middle of the P—Cd bond (Table 4). Relative to the Cd—Cl_l vector they are different, however. The C(1) atom in molecule *A* is displaced in the same direction, while in molecule *B* this atom is displaced in the opposite direction as Cl_l from the least-squares plane through the five atoms of the chelate ring. This results in different values for the torsion angles Cl_l—Cd—N—C(3) and Cl_l—Cd—N—C(5) in the two molecules (Table 4). The relative orientation of the two phenyl rings is also different in the two molecules. The plane of the phenyl ring Ph₁ (Fig. 1) is approximately perpendicular to the central four-membered ring (Cd, Cl_l, Cl_h, Cd') in both the molecules (the interplanar angle is 87° in molecule *A*, and 85° in molecule *B*). The phenyl ring Ph₂ is nearly parallel to the plane of the four-membered ring (the interplanar angle is 2° in molecule *A*, while it makes an angle of 60° with the four-membered ring in molecule *B*).

The Cd—Cl_l bond distances of 2.428 and 2.422 Å in the two molecules are in good agreement with the sum of the reported covalent radii for Cd and Cl (1.48 + 0.99 = 2.47 Å) (Pauling, 1967) and with values for typical cadmium chloride phosphine and amine com-

Table 4. Torsion angles ($^\circ$) of the chelate rings

E.s.d.'s are 0.2–0.4°.

	Molecule A	Molecule B
$\text{C}(2)\text{PCdN}$	–4	6
$\text{PCdNC}(1)$	32	–33
$\text{CdNC}(1)\text{C}(2)$	–59	60
$\text{NC}(1)\text{C}(2)\text{P}$	57	–56
$\text{C}(1)\text{C}(2)\text{PCd}$	–23	21
$\text{Cl}_l\text{CdNC}(1)$	–93	–154
$\text{Cl}_l\text{CdNC}(3)$	144	87
$\text{Cl}_l\text{CdNC}(5)$	22	–36

plexes, e.g. Cd–Cl = 2.440 and 2.504 Å in the monomeric four-coordinate $\text{CdCl}_2[(\text{C}_6\text{H}_5)_3\text{P}]_2$ (Cameron & Forrest, 1971) and 2.485 and 2.497 Å in the (4 + 2) six-coordinate $\text{CdCl}_2(1\text{-methylcytosine})_2$ (Gagnon, Beauchamp & Tranqui, 1979). The centrosymmetric dimers *A* and *B* exhibit rather unusual asymmetry with both strong (2.484 and 2.520 Å) and moderate (2.779 and 2.780 Å) bridging Cd–Cl bond lengths. The shorter ones are consistent with covalent bonds. The longer Cd–Cl_b bond lengths are consistent with the sum of the ionic radii (2.78 Å) (Bigoli, Braibanti, Lanfredi, Tiripicchio & Camellini, 1971) and thus indicate that the bond should be considered prevalently ionic. These longer Cd–Cl_b bond lengths are also consistent with those found in the literature, e.g. 2.73 Å in $\text{CdCl}_2(\text{thiocarbohydrazide-}N,S)_2$ (Bigoli *et al.*, 1971) and 2.742, 2.754, and 2.802 Å in $\text{CdCl}_2(\text{NH}_2\text{C}_3\text{H}_6\text{NH}_2)$ (Andreotti, Cavalca, Pellinghelli & Sgarabotto, 1971).

The Cd–P bond distances of 2.563 and 2.617 Å are quite consistent with the sum of the covalent radii for Cd and P (1.48 + 1.10 = 2.58 Å) (Pauling, 1967) and with typical experimental values of 2.632 and 2.635 Å in $\text{CdCl}_2[(\text{C}_6\text{H}_5)_3\text{P}]_2$ (Cameron & Forrest, 1971).

Although the Cd–N bond distances in *A* and *B* (2.502 and 2.506 Å) fall within the sum of the van der Waals radii for Cd and N (1.50 + 1.5 = 3.0 Å) (Pauling, 1967), they considerably exceed the sum of the covalent radii (1.48 + 0.70 = 2.18 Å) and typically reported values such as 2.292 and 2.289 Å in $\text{CdCl}_2(\text{NH}_2\text{C}_3\text{H}_6\text{NH}_2)$ (Andreotti *et al.*, 1971), 2.34 Å in $\text{CdCl}_2(\text{thiocarbohydrazide-}N,S)_2$ (Bigoli *et al.*, 1971), and 2.281 and 2.296 Å in $\text{CdCl}_2(1\text{-methylcytosine})$ (Gagnon *et al.*, 1979). Since the axial Cd–N bond is so unusually long and presumably weak and the long Cd–Cl_b is in the other axial position, the best description of the bonding about the Cd atom is probably a (3 + 2) strong-trigonal-weak-axial environment. The deviation from perfect trigonal-bipyramidal geometry may be attributable to a complex combination of steric crowding imposed by the bulky NP ligand, subtle electronic factors involving the hard and soft nature of the Lewis-base centers of the chelated ligand, crystal-packing interactions, and perhaps most importantly the restrictions placed on the P–Cd–N bond angle within the five-membered chelate ring.

The marked increase in electrical conductivity of $\text{CdCl}_2 \cdot (\text{NP})$ in the presence of CH_3I is presumably due to the cleavage of the long and thus weak Cd–N bond and the formation of the quaternized ionic $[\text{CdCl}_2(\text{C}_6\text{H}_5)_2\text{PC}_2\text{H}_4\text{N}^+(\text{CH}_3)(\text{C}_2\text{H}_5)_2]_2 \cdot 2\text{I}^-$ species (Houk & Dobson, 1968). It is noteworthy that in $\text{CdCl}_2 \cdot (\text{NP})$ as compared to the $\text{HgCl}_2 \cdot (\text{NP})$ adduct the *M*–N bond length is decreased 0.14 Å and the *M*–P bond length is increased 0.15 and 0.20 Å, respectively, for *A* and *B*. Although certain specific steric and electronic factors may be operative, these changes in bond lengths

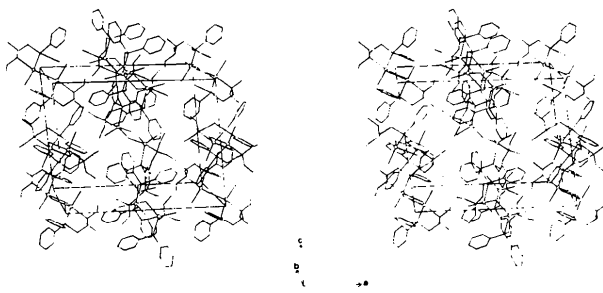


Fig. 3. A stereoview of the packing in the crystal structure of $[\text{CdCl}_2\{(\text{C}_6\text{H}_5)_2\text{PC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2\}]_2$.

are consistent with the harder Lewis acid (Cd) being more tightly bound to the harder base and more weakly bound to the softer base. Since the Cd–Cd distances of 3.875 and 3.934 Å (*A* and *B*, respectively) far exceed the sum of the covalent radii for two Cd atoms ($2 \times 1.48 = 2.96$ Å) (Pauling, 1967), there is apparently no interaction between the metal atoms.

The environment about each of the N and P atoms in the chelated bidentate ligand is approximately tetrahedral with *X*–N–*Y* and *X*–P–*Y* angles ranging from 105.6 to 113.2° and 102.5 to 120.0°, respectively. Apparently, steric interaction between the phenyl rings and the Cl atoms results in opened Cd–P–C(phenyl) angles of 116.9 to 120.0° and closed C(phenyl)–P–C(phenyl) angles of 102.5 and 104.3° (in *A* and *B*, respectively). The internal Cd–P–C(2) angle of 102.8 to 103.3° in the five-membered chelate ring is also closed relative to the tetrahedral angle.

The phenyl rings are planar within experimental error. The r.m.s. deviation of individual atoms from the least-squares plane in Ph_2 is 0.009 Å in molecule *A* and 0.013 Å in molecule *B*. These values are about 3–4 times larger than the corresponding deviations in the ring Ph_1 (0.004 Å in molecule *A*, and 0.003 Å in molecule *B*). The phenyl-ring distances and angles are typical. Fig. 3 shows the packing in the crystal structure.

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Structure of *trans*-Trichlorobis[diethyl(phenyl)phosphine]hydroxorhenium(IV)

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Abstract

The crystal-structure determination of one of the three isomers (the violet form) obtained by reacting ReO_4^- , PEt_2Ph and HCl in boiling ethanol is reported. $\text{C}_{20}\text{H}_{31}\text{Cl}_3\text{OP}_2\text{Re}$, $M_r = 642.0$, is monoclinic, $P2_1/a$; $a = 23.899$ (4), $b = 13.017$ (3), $c = 7.781$ (2) Å, $\gamma = 91.21$ (2)°, $Z = 4$, $D_c = 1.76$ Mg m $^{-3}$, $\mu(\text{Mo } K\alpha) = 5.24$ mm $^{-1}$. The structure has been determined from 3338 observed reflections and refined to an R factor of 0.034. Structural data and IR spectra agree in indicating that the violet complex corresponds to the formula $[\text{Re}(\text{OH})\text{Cl}_3(\text{PEt}_2\text{Ph})_2]$.

Introduction

Reaction of perrhenates, diethyl(phenyl)phosphine and hydrochloric acid in boiling ethanol (Chatt & Rowe, 1962) yields a mixture of three complexes, a blue (I), green (II) and violet one (III), whose analyses indicate the formula $[\text{ReOCl}_3(\text{PEt}_2\text{Ph})_2]$. (I) was identified as a *cis* isomer of $[\text{ReOCl}_3(\text{PEt}_2\text{Ph})_2]$ on the grounds of its dipole moment (36.1×10^{-30} Cm), while (II) (dipole

moment = 5.7×10^{-30} Cm) was confirmed to be the *trans* isomer by a two-dimensional X-ray structure determination (Ehrlich & Owston, 1963). (III) has too low a dipole moment (10.0×10^{-30} Cm) to be the other *cis* isomer and, unlike (I) and (II), is paramagnetic in the solid state ($\mu_{\text{eff}} = 17.80 \times 10^{-24}$ J T $^{-1}$); it was assigned the formula *trans*- $[\text{Re}(\text{OH})\text{Cl}_3(\text{PEt}_2\text{Ph})_2]$, because preliminary X-ray results indicated cell parameters almost identical with those of (II) but there was a strong element of doubt as the IR spectrum showed a possible $\text{Re}=\text{O}$ bond and no OH absorption. In a following paper (Chatt, Garforth, Johnson & Rowe, 1964) the same violet complex (III) was interpreted as a solid solution of 10–22% of a new, intensely violet, complex of Re^{IV} , *i.e.* *trans*- $[\text{ReCl}_4(\text{PEt}_2\text{Ph})_2]$ in green *trans*- $[\text{ReOCl}_3(\text{PEt}_2\text{Ph})_2]$ (II), in spite of the fact that the separation of the two components was not actually achieved and the two compounds were not isomorphous.

This paper reports the crystal-structure determination of (III) and will show that structural data and IR spectra agree in indicating that (III) corresponds to the formula first suggested by Chatt & Rowe (1962), *i.e.* *trans*- $[\text{Re}(\text{OH})\text{Cl}_3(\text{PEt}_2\text{Ph})_2]$.