

**CRYSTAL STRUCTURE OF DICADMIUM(II)
ETHYLENEDIPHOSPHINETETRAACETATE OCTAHYDRATE**

Jaroslav PODLAHA and Jana PODLAHOVÁ

Department of Inorganic Chemistry, Charles University, 128 40 Prague 2

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The crystal structure of the title compound containing a phosphorus analogue of EDTA as the ligand was determined from single-crystal X-ray diffraction data and refined to $R = 0.028$ for 1 920 observed reflections. The crystals are monoclinic, space group $P2_1/c$, $a = 8.6169(8)$, $b = 16.0539(9)$, $c = 8.2504(6)$ Å, $\beta = 103.458(7)^\circ$ and $Z = 2$. The structure is completely different from that of the nitrogen prototype, $[\text{CdEDTA}]^{2-}$. It consists of double-stranded polymeric layers which are composed of metal coordination polyhedra linked by μ_6 -hexadentate ligands; the layers lie parallel to the bc plane and are joined along the a axis through hydrogen bonding donated by water molecules. Because of steric requirements of phosphorus, the coordination polyhedron around Cd is greatly distorted and can best be described as a $5 + 3$ type. One P atom, two oxygen atoms from two monodentate carboxylate groups and two water molecules form an approximate trigonal bipyramid and further three more remote carboxylate oxygens complete the arrangement, resulting in an O_7P distorted bicapped trigonal prism.

Recent interest in the chemistry of functionalized phosphines is a result mainly of their use as ligands in homogeneous catalysis. The well-known Shell Higher Olefin Process¹ is an example of industrial catalysis based on carboxyphosphines. Any understanding of the function of these catalysts requires a knowledge of their structure, namely of the ability of potential hard and soft donors to coordinate the particular metal ion. In our laboratory, we have investigated carboxyphosphines with the general formulae $\text{R}_{3-n}\text{P}(\text{CH}_2\text{CO}_2\text{H})_n$, $n = 1-3$, and $[-\text{CH}_2\text{P}(\text{Ph})_{2-m}(\text{CH}_2 \cdot \text{CO}_2\text{H})_m]$, $m = 1, 2$. The ligand with $m = 2$, ethylenediphosphetetraacetic acid, H_4L , is a formal analogue of the familiar EDTA. The study of its acid-base equilibria², and complex formation in solution³ and in the solid state⁴ have demonstrated that the prevailing factor in its coordination behaviour is a strong tendency to behave as a bidentate P,P'-donor towards soft metal ions ($\log \beta_{12} > 20$) and, in contrast, a negligible tendency ($\log \beta_{11} < 3$) to bind hard metals such as Ca(II). From this point of view it appeared interesting to investigate the coordination mode for an ion lying on the borderline between the hard and soft metals. The Cd(II) ion, for instance, forms the sparingly soluble Cd_2L complex³ characterized by $\log \beta_{21} = 10.38$ in solution. The present paper describes a crystallographic study of the related solid, $\text{Cd}_2\text{L} \cdot 8 \text{H}_2\text{O}$.

EXPERIMENTAL

The compound is formed as a microcrystalline precipitate on mixing neutral or slightly acidic aqueous solutions of the ligand and of a Cd(II) salt in a ratio of Cd/L. >0.7 or 0.9 (for pH 4 or 7 respectively). Single crystals were grown at room temperature from a deaerated solution containing 1 mmol $\text{Na}_4\text{L}\cdot\text{H}_2\text{O}$ (ref.⁵) and 1 mmol $\text{Cd}(\text{ClO}_4)_2$ in 250 ml of 0.02 mol dm^{-3} acetate buffer with pH 4.0. After washing with water and drying in air, the yield of colourless prismatic crystals was 80% based on Cd. For $\text{Cd}_2\text{L}\cdot 8 \text{H}_2\text{O}$ ($\text{C}_{10}\text{H}_{28}\text{Cd}_2\text{O}_{16}\text{P}_2$ (691.1) calculated: 32.53% Cd, 8.96% P, 20.86% H_2O ; found: 32.5% Cd, 8.87% P; weight loss at 170°C under Ar, 20.9%. IR (Nujol and hexachlorobutadiene mulls) 3 500 m, 3 320 sh, 3 210 bs, 1 640 w (H_2O); 1 562 vs, 1 374 s (OCO). A thermogravimetric curve recorded in air documents stepwise dehydration (two water molecules at $50-60^\circ\text{C}$, further four at $70-90^\circ\text{C}$ and the last two at $150-155^\circ\text{C}$), followed by decomposition of the ligand starting at 310°C .

The crystallographic data are summarized in Table I. The density was determined by flotation in bromoform-chloroform mixtures. The structure was solved by the heavy atom method and refined by a full-matrix least-squares procedure based on F -values⁶. All the hydrogen atoms were located in the difference map. The positional and anisotropic displacement parameters of non-H atoms and positional parameters of O-bonded hydrogen atoms were refined simultaneously, while the C-bonded H atoms were fixed in their theoretical positions. Two different group isotropic displacement parameters, one for C-bonded and another for O-bonded ones, were assigned and refined for H-atoms. Absorption and extinction effects were neglected. Scattering factors were taken from International Tables (1974).

RESULTS AND DISCUSSION

Final fractional coordinates are given in Table II and bond distances and angles in Table III*. Figure 1 shows a perspective view of the $\text{Cd}_2\text{L}\cdot 8 \text{H}_2\text{O}$ fragment with atom numbering. Crystal packing can be seen in Figs 2 and 3.

The $\text{Cd}_2\text{L}\cdot 8 \text{H}_2\text{O}$ molecule is centrosymmetric about the centre of the $\text{PCH}_2\text{CH}_2\text{P}$ fragment. The structure is polymeric and consists of layers arranged parallel to the bc plane and composed of Cd(II) coordination polyhedra linked by μ_6 -hexadentate ligand anions and hydrogen bonds.

In contrast to Cd(II) carboxylates containing only light atoms⁷, the environment of the Cd(II) ion in the present structure is less clearly defined: it consists of nine potential donor atoms at the distances of 2.230 to 3.698 Å from Cd. The method recommended by Brunner⁸ was applied to define the coordination number. The largest gaps in the ordered series of reciprocal metal-ligand distances lie after eight and then after five neighbours and the coordination polyhedron is therefore best described as a 5 + 3 type (Fig. 4). Logically, the closest atoms lying at the metal-ligand distances range of 2.230–2.547 Å are those that are directly chemically bonded to Cd(II): two oxygens from the monodentate carboxylate groups (O11^i , O21), one phosphorus (P^{ii}) and two water molecules (O1 , O2); for the symmetry code,

* Supplementary material comprising the anisotropic displacement parameters, hydrogen atom coordinates and structure factor tables is available from the authors upon request.

TABLE I
Crystal data, measurement and refinement details

Formula	$C_{10}H_{12}Cd_2O_8P_2 \cdot 8 H_2O$
M.w.	691.1
Space group	$P2_1/c$ (No. 14)
Cell dimensions (\AA , $^\circ$)	$a = 8.6169(8)$, $b = 16.0539(9)$ $c = 8.2504(6)$, $\beta = 103.458(7)$
V (\AA^3)	1 110.0(1)
Z	2
D_m , D_x (g cm^{-3})	2.044, 2.067
Radiation	$\text{MoK}\alpha$, $\lambda = 0.71073 \text{\AA}$
Absorption correction	None, $\mu = 2.1 \text{ mm}^{-3}$
$F(000)$	684
Temperature (K)	293
Crystal dimensions (mm)	$0.07 \times 0.15 \times 0.20$
No. of reflections for lattice param. determination	19 ($17^\circ < \theta < 24^\circ$)
Diffractometer	CAD4
Scan mode	$\omega - 4/3 \theta$
$\sin(\theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.62
Standard reflections (variation)	3 after every 2 hours (<1%)
Interval h ; k ; l	-10, 10; 0, 19; -10, 10
No. of reflections measured used [$I > 1.96 \sigma(I)$]	4 518 1 920
Residual electron. density (Δ/σ) _{max} for non-H atoms	0.91, -0.70 e \AA^{-3} 0.24, -0.25
Function minimized	$\sum w(F_o - F_c)^2$
Weight	$1/(\sigma^2(F_o) + 0.0009 F^2)$
R , wR , R_{int}	0.028, 0.031, 0.016

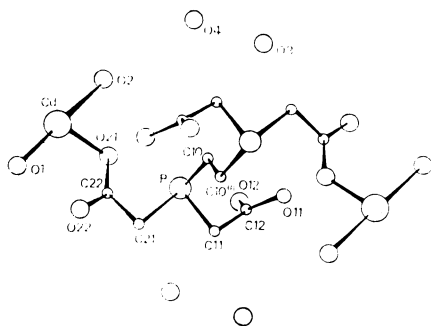


Fig. 1
Perspective view of the $\text{Cd}_2\text{L} \cdot 8 \text{H}_2\text{O}$ fragment with atom numbering

TABLE II

Fractional coordinates ($\cdot 10^4$) of non-H atoms with e.s.d.'s in parentheses. Symmetry code: i, $-x, y - 1/2, -z - 1/2$; ii, $x, 1/2 - y, z + 1/2$; iii, $-x, 1 - y, -z$; iv, $x - 1, 1/2 - y, z - 1/2$; v, $x - 1, y, z - 1$; vi, $x - 1, y, z$; vii, $-x, 1 - y, -z - 1$; viii, $-x, 1/2 + y, -z - 1/2$; ix, $x, 1/2 - y, z - 1/2$. $U_{eq} = 1/3 \sum_i \sum_j a_i^* a_j^* U_{ij}$

Atom	x/a	y/b	z/c	$U_{eq}(\cdot 10^3), \text{\AA}^2$
Cd	814.5(3)	1686.0(4)	1165.5(3)	28.8(4)
P	1580(1)	4405.8(8)	-1548(1)	22.1(4)
O1	-1431(4)	2278(2)	1689(4)	47(1)
O2	3082(3)	1112(2)	108(4)	37(1)
O3	3926(4)	5852(3)	2748(5)	66(1)
O4	3944(5)	7297(4)	811(6)	86(2)
O11	630(3)	6301(2)	-3607(3)	36(1)
O12	1758(3)	5435(2)	-5607(3)	40(1)
O21	1327(3)	2851(2)	-88(4)	50(1)
O22	3058(4)	2955(2)	2298(4)	55(1)
C10	-170(4)	4744(2)	-801(4)	30(1)
C11	2551(4)	5359(2)	-2085(4)	28(1)
C12	1603(4)	5722(2)	-3717(4)	27(1)
C21	3043(3)	4022(2)	266(4)	27(1)
C22	2442(5)	3214(2)	892(5)	33(1)

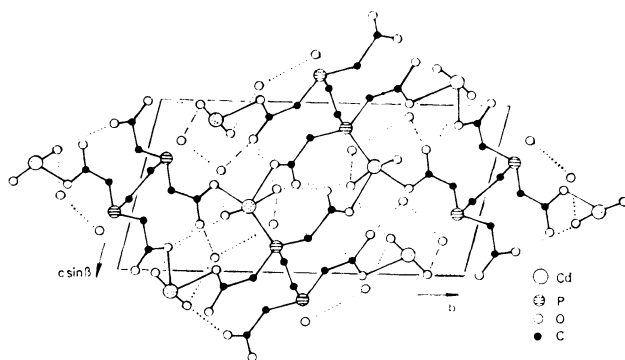


FIG. 2

Projection of the unit cell content onto the $bc \sin \beta$ plane

see Table II. It follows from the values of the shape-determining parameters⁹ that this O₄P polyhedron can be approximated as a distorted trigonal bipyramid with apical water molecules. The distortion originates mainly from the bulkiness of phosphorus, analogously to other Cd(II)-phosphine complexes¹⁰⁻¹³.

Pentacoordination is, however, completely absent amongst simple Cd(II) carboxylates, where higher coordination numbers dominate, evidently as a result of a more favorable ratio of the atomic radii. In the present structure, the compromise between the large and soft phosphorus and the small and hard oxygens leads to another compromise: the five closest neighbours are supplemented by three more remote carboxylate oxygens (O12ⁱ, O22, O12ⁱⁱ) at the distances of 2.814–3.109 Å, to yield

TABLE III
Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

Bonds		Angles	
Cd—O21	2.230(3)	O1—Cd—O21	90.4(1)
Cd—O1	2.285(3)	O2—Cd—O21	83.8(1)
Cd—O2	2.494(3)	P ⁱⁱ —Cd—O21	151.1(1)
Cd—P ⁱⁱ	2.547(1)	O11 ⁱ —Cd—O21	85.5(1)
Cd—O11 ⁱ	2.272(3)	O2—Cd—O1	170.6(1)
P—C10	1.839(4)	P ⁱⁱ —Cd—O1	103.4(1)
P—C11	1.847(3)	O11 ⁱ —Cd—O1	89.1(1)
P—C21	1.825(3)	P ⁱⁱ —Cd—O2	85.2(1)
O11—C12	1.269(4)	O11 ⁱ —Cd—O2	83.0(1)
O12—C12	1.241(4)	O11 ⁱ —Cd—P ⁱⁱ	119.5(1)
O21—C22	1.247(5)	C11—P—C10	106.8(2)
O22—C22	1.230(5)	C21—P—C10	106.8(2)
C10—C10 ⁱⁱⁱ	1.526(5)	Cd ^{ix} —P—C10	111.1(1)
C11—C12	1.519(5)	C21—P—C11	102.2(2)
C21—C22	1.530(5)	Cd ^{ix} —P—C11	116.5(1)
		Cd ^{ix} —P—C21	112.7(1)
		Cd ^{viii} —O11—C12	111.2(2)
		C22—O21—Cd	107.3(2)
		C10 ⁱⁱⁱ —C10—P	116.2(2)
		C12—C11—P	110.5(2)
		O12—C12—O11	123.2(3)
		C11—C12—O11	116.5(3)
		C11—C12—O12	120.3(3)
		C22—C21—P	109.8(2)
		O22—C22—O21	123.5(3)
		C21—C22—O21	116.6(3)
		C21—C22—O22	119.9(3)

the geometrical coordination number $5 + 3$ for Cd. However, none of these three oxygens participates in chemical bonding to Cd. Two of them (O12ⁱ, O22) belong to the carboxylate groups which are already bound to Cd through O11ⁱ and O21 but the differences between the Cd—O11ⁱ, Cd—O12ⁱ and Cd—O21, Cd—O22 distances are 0.700 and 0.584 Å, respectively, thus clearly excluding the possibility of chelate bonding⁷. As expected, the eight-coordination polyhedron around Cd is greatly distorted and its exact classification is therefore difficult if not impossible, since small changes in the distances and/or angles can easily lead to interconversion between the energetically close idealized polyhedra of this order⁹. Inspection of the shape-determining parameters indicate that the O₇P polyhedron resembles a bicapped trigonal prism with Pⁱⁱ and O21 atoms as the caps covering two trapezoidal faces.

The ligand anion, L⁴⁻, makes use of all its six donor atoms for coordination but, in sharp contrast to EDTA (ref.¹⁴), to six different Cd(II) ions. Such a type of

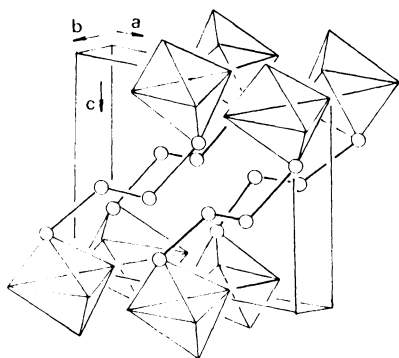


FIG. 3
Linking of the CdO₄P polyhedrons by hydrogen bonds

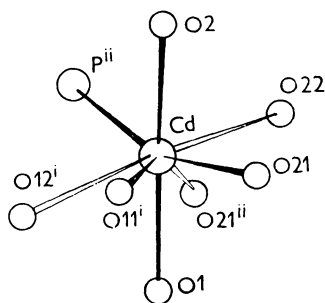


FIG. 4
Coordination polyhedron around Cd

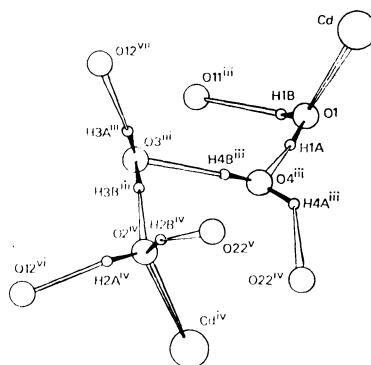


FIG. 5
Hydrogen bonding scheme

bridging is uncommon amongst ligands with high denticity. It has, however, an analogue in a series of phosphinecarboxylates: zinc(II)phosphinidynetripionate¹⁵ does contain μ_4 -tetradentate ligands. The μ_6 -bonding requires, of course, the ligand backbone be highly flexible. Comparison of the conformations which are adopted by the ligand in its hitherto structurally characterized derivatives^{2,16} demonstrates that essentially unhindered rotation can occur around all its bonds. Consequently, individual ligand arrangements in these structures do not provide sufficient information for generalization. On the other hand, the local geometry of the donor groups of the ligand is quite normal, corresponding to a distorted tetrahedron at phosphorus and a nearly perfect *syn*-conformation of both carboxylate groups, characterized by torsional angles of -2.1° and 2.3° for C1—O21—C22—O22 and Cd—O11ⁱ—C12ⁱ—O12ⁱ, respectively.

The asymmetric unit contains four water molecules which are of three various types with respect to the coordination to Cd and/or the number of hydrogen bonds in which they participate: O1, O2 and O3 + O4 (Fig. 5). From the eight hydrogen bonds which are present in the structure, five operate within the layers and three link the layers in the *a*-direction. It is noteworthy that the 1 + 1 + 2 discrimination of the types of water molecules is reflected in the IR spectrum and, in particular, in the stepwise dehydration which could well proceed in the order O1, O3 + O4, O2 with increasing temperature.

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