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A New Structural Type for 1:1 Complexes of Cadmium Dihalides with Unidentate Ligands: $CdCl_2(PhMe_2P)$

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The crystal structure of dimethylphenylphosphinecadmium(II) chloride has been determined from single-crystal X-ray diffraction data collected on a two-circle diffractometer. The analysis was carried out on 2820 reflections and refined by full-matrix least-squares calculations to a final R of 0.037. The crystals are monoclinic, space group $P2_1/n$ with a = 7.057(5), b = 12.471(7), c = 12.905(8) Å, β = 93.08(5)° and Z = 4. The structure is polymeric $CdCl_2(PhMe_2P)$ units are linked together by chlorine-bridges to give single chains running parallel to the a-axis. Each cadmium is pentaco-ordinate with one phosphorus and four chlorine atoms forming an elongated trigonal bipyramidal arrangement about the metal atom.

Introduction

The literature contains reports of a vast number of complexes of metal dihalides with unidentate ligands, but few attempts have been made to systematize, let alone rationalize, the structures adopted. In the case of $CdX_2(L)$ systems (L = unidentate ligand) the only structure which has been authenticated is a double-chain arrangement in which cadmium is octahedrally co-ordinated, as in $CdCl_2(MeNHCONH_2)$ [1], $CdCl_2$(imidazole) [2], and $CdCl_2(MeCSNH_2)$ [3]. A dimeric halogen-bridged structure involving tetraco-ordinated cadmium atoms has often been suggested, but the evidence is unconvincing [4].

In our recent work on mercury(II) halide systems [5, 6] we have shown that the structure adopted by 1:1 complexes of type $HgX_2(R_3P)$ is critically dependent upon the nature of the phosphine donor, and some rationalization of the observed trends is possible. However, none of the structures determined appears to show any relationship to the double-strand chain structures found for the cadmium complexes referred to above [1–3], despite the fairly close relationships found with some (but not all) trihalogeno salts of these two metals, $[MX_3]^-$ [7–9].

We have therefore undertaken a systematic study of the structures of $CdX_2(L)$ complexes. Our first result, the subject of the present paper, is noteworthy in that it establishes a new structural type which has not previously been considered by workers in this field.

Experimental

Dimethylphenylphosphinecadmium(II) chloride was prepared as previously described [10], by the addition of an alcoholic solution of the phosphine to a hot alcoholic solution of hydrated cadmium chloride ($CdCl_2 \cdot 2\frac{1}{2}H_2O$) in a 1:1 molar ratio. Recrystallisation from ethanol gave colourless needles suitable for single-crystal X-ray analysis.

Crystal Data

$CdC_8H_{11}Cl_2P$, M_r = 321.5. Monoclinic, $P2_1/n$, a = 7.057(5), b = 12.471(7), c = 12.905(8) Å, β = 93.08(5)°, U = 1134.0 Å^3, D_m (by flotation) = 1.90, D_c = 1.88 g cm^{-3}. Z = 4, Mo-$K\alpha$, λ = 0.7107 Å, μ(Mo-$K\alpha$) = 23.0 cm^{-1}, $F(000)$ = 624.

Intensity Measurements

A crystal of dimensions 0.10 × 0.10 × 0.48 mm was mounted with the a-axis coincident with the rotation (ω) axis of a Stöe Stadi 2 two-circle diffractometer. Using monochromated Mo-$K\alpha$ radiation and the background–ω scan–background technique, 3314 unique reflections were measured, of which 2820 had $I > 3\sigma(I)$ and were considered to be observed [the net intensity $I = T - B$, where T = scan count, B = mean background count over the scan width; $\sigma(I) = \sqrt{T + Bc/2t}$, where c = scan time, t = time for background measurements at each end of the scan]. Corrections for Lorentz, polarisation and absorption effects were made.

Structure Determination and Refinement

The cadmium atom position was determined from the three-dimensional Patterson function and the

TABLE I. Final Atomic Parameters. Estimated Standard Deviations for Non-Hydrogen Atoms are Given in Parentheses.

Fractional Co-ordinates (Cd × 10^5; remaining atoms × 10^4)

	x	y	z
Cd	25383(5)	2221(2)	5148(2)
Cl(1)	4219(2)	936(1)	−978(1)
Cl(2)	648(2)	−1399(1)	−13(1)
P	2623(2)	850(1)	2405(1)
C11	1522(8)	−173(3)	3186(4)
C12	2384(10)	−601(6)	4081(5)
C13	1447(12)	−1397(6)	4612(5)
C14	−331(12)	−1707(6)	4313(5)
C15	−1202(10)	−1293(6)	3414(5)
C16	−263(8)	−515(5)	2864(4)
C2	1336(12)	2079(5)	2639(5)
C3	4952(11)	1097(6)	3002(6)
H12	3765	−321	4366
H13	2159	−1774	5279
H14	−1072	−2278	4773
H15	−2592	−1569	3143
H16	−948	−176	2171
H21	−96	2010	2306
H22	2038	2744	2286
H23	1299	2213	3465
H31	5838	402	2903
H32	4836	1252	3819
H33	5574	1784	2640

Anisotropic Thermal Parameters (×10^4) of the Form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	290(2)	411(2)	337(2)	−23(1)	53(1)	−29(1)
Cl(1)	298(5)	450(5)	379(5)	24(4)	52(3)	83(4)
Cl(2)	310(5)	374(5)	675(7)	20(4)	−56(5)	−40(4)
P	375(6)	340(4)	337(5)	20(4)	29(4)	−20(4)
C11	383(24)	402(20)	310(18)	21(15)	22(16)	−35(14)
C12	504(33)	704(35)	457(26)	−72(27)	155(24)	88(25)
C13	721(48)	695(37)	480(28)	−96(33)	−93(28)	97(26)
C14	638(42)	640(33)	553(31)	−196(30)	92(27)	41(27)
C15	430(32)	750(37)	570(31)	−175(28)	20(24)	14(27)
C16	374(26)	516(24)	467(24)	−20(20)	−23(19)	−2(20)
C2	807(50)	440(25)	592(32)	191(28)	115(30)	−132(23)
C3	490(36)	654(33)	646(35)	−150(27)	−115(27)	−116(28)

remaining atoms were located from successive difference electron-density maps. Hydrogen atoms were included in positions calculated from the geometry of the molecule (C–H = 1.08 Å). Common isotropic temperature factors were applied to methyl and phenyl hydrogens and refined to final values of $U = 0.170(30)$ and $0.057(10)$ Å^2 respectively. Scattering factors were calculated [11] using an analytical approximation and the weighting scheme adopted was $w = 1.0000/[\sigma^2(F_o) + 0.0086\,(F_o)^2]$. Full matrix refinement with anisotropic temperature factors for all non-hydrogen atoms gave the final $R = 0.037$ and $R' = 0.047$. The final difference map showed no peaks greater than 0.24 e Å^{-3}. Final atomic parameters are listed in Table I, bond distances and angles in Table II. A list of observed and calculated structure factors is available from the Editor.

Calculations

All calculations, apart from preliminary data processing, were carried out on an IBM 370/165 computer at the SRC Computing Centre Daresbury, using the SHELX computing package [12].

TABLE II. Bond Lengths (A) and Angles (°) with Estimated Standard Deviations in Parentheses.

Symmetry Code

none	*x, y, z*
none	*−x, −y, −z*
none	*1 − x, −y, −z*

Bond Lengths (A)

Cd–Cl(1)	2.481(1)	P–C3	1.803(7)
Cd–Cl(2)	2.497(1)	C11–C12	1.384(7)
Cd–Cl(1″)	2.745(1)	C11–C16	1.373(7)
Cd–Cl(2′)	2.734(1)	C12–C13	1.394(10)
Cd–P	2.560(1)	C13–C14	1.350(11)
P–C11	1.825(5)	C14–C15	1.384(10)
P–C2	1.815(6)	C15–C16	1.391(9)

Bond Angles (°)

Cl(1)–Cd–Cl(2)	110.50(2)	Cd–P–C11	108.9(1)
Cl(1)–Cd–Cl(1″)	86.00(2)	Cd–P–C2	115.5(2)
Cl(1)–Cd–Cl(2′)	92.60(2)	Cd–P–C3	115.7(3)
Cl(1)–Cd–P	130.00(4)	C11–P–C2	105.4(3)
Cl(2)–Cd–Cl(1″)	93.40(2)	C11–P–C3	106.8(3)
Cl(2)–Cd–Cl(2′)	87.10(2)	C2–P–C3	103.7(4)
Cl(2)–Cd–P	119.50(3)	P–C11–C12	123.3(5)
Cl(1″)–Cd–Cl(2′)	178.60(4)	P–C11–C16	117.4(4)
Cl(1″)–Cd–P	88.70(4)	C12–C11–C16	119.2(5)
Cl(2′)–Cd–P	92.20(2)	C11–C12–C13	119.1(6)
		C12–C13–C14	121.4(6)
		C13–C14–C15	119.8(6)
		C14–C15–C16	119.1(6)
		C15–C16–C11	121.1(5)

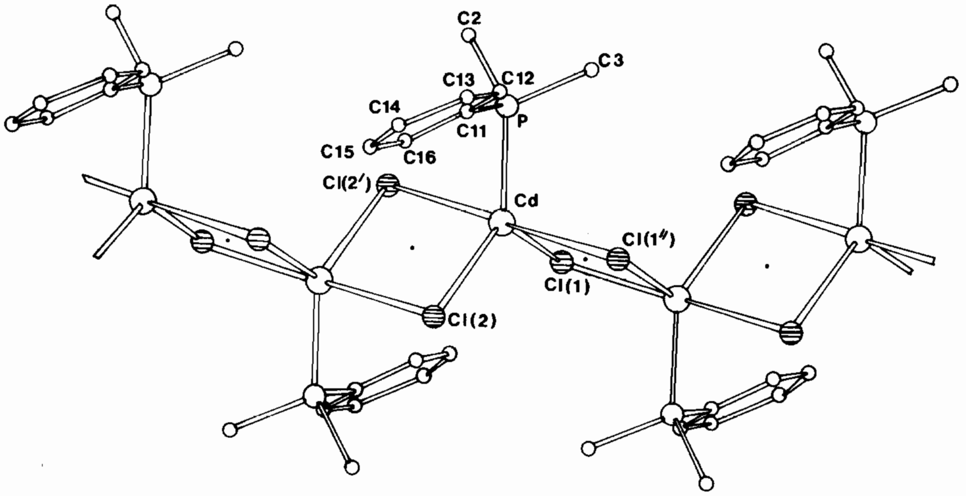

Fig. 1. Single chain running parallel to the *a*-axis.

Results and Discussion

Dimethylphenylphosphinecadmium(II) chloride adopts an unexpected polymeric structure in which cadmium is five co-ordinate (Fig. 1). $CdCl_2(PhMe_2P)$ units are linked together by chlorine-bridges to give single chains running parallel to the *a*-axis. The resulting arrangement is quite different to the double-strand chains found [1–3] in other $CdCl_2(L)$ systems containing unidentate ligands [L = $MeNHCONH_2$, imidazole or $MeCSNH_2$] and in which cadmium is octahedrally co-ordinated. Although the pyridine-N-

TABLE III. Equations of Least-Squares Planes Referred to Orthogonal Axes[a] with Distances (Å) of Relevant Atoms from the Planes in Square Brackets.

Plane A: Cd, Cl(1), Cl(2), P.

$-0.7738X + 0.5899Y - 0.2307Z + 1.3725 = 0.0000$

[Cd, 0.027; Cl(1), −0.009; Cl(2), −0.008; P, −0.010; Cl(1″), −2.707; Cl(2′), 2.753; C11, −0.347; C2, 1.542; C3, −1.242]

Plane B: C11, C12, C13, C14, C15, C16

$0.4311X - 0.7177Y - 0.5468Z + 1.7311 = 0.0000$

[C11, 0.001; C12, −0.014; C13, 0.023; C14, −0.020; C15, 0.007; C16, 0.002; P, −0.004]

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[a] The orthogonalization matrix for the plane-equations is:

$$\begin{matrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{matrix}$$

oxide complex $CdI_2(C_5H_5NO)$ [13] contains single-strand chains, the involvement of both halogen and ligand atoms in the bridging is in contrast to the present chlorine-bridged structure.

The cadmium atom is essentially coplanar with P, Cl(1), Cl(2) (Table III), but the trigonal arrangement about the central atom is distorted with bond angles varying from 110.5 [Cl(2)–Cd–Cl(1)] to 130.0° [P–Cd–Cl(1)]. This angular distortion reflects the greater steric requirement of the phosphine ligand compared to that of the two chlorine atoms. While the Cd–Cl(1) and Cd–Cl(2) distances (mean 2.489 Å) are similar to those found [14] in monomeric $CdCl_2(Ph_3P)_2$ [2.504, 2.440(6) Å], they are significantly shorter than the Cd–Cl distances involving chlorine atoms bonded to two cadmium atoms found [1–3] in the polymeric $CdCl_2(L)$ complexes, L = $MeNHCONH_2$ [2.58, 2.62 Å], imidazole [2.604, 2.601(4) Å], or $MeCSNH_2$ [2.57, 2.66(2) Å]. Further chlorine atoms [Cl(2′), Cl(1″)] increase the co-ordination about cadmium to five, giving an elongated trigonal bipyramidal arrangement in which the Cl(1″)–Cd–Cl(2′) grouping is almost linear (178.6°) and the (axial chlorine)–Cd–(equatorial atom) bond angles lie close to 90° (86.0–93.4°). The chlorine-bridges are very asymmetric; the Cd–Cl(1″) and Cd–Cl(2′) distances (mean 2.740 Å) are substantially greater than the Cd–Cl(1) and Cd–Cl(2) values and are comparable with the distances found [2, 3] for chlorine atoms bonded to three cadmium atoms in the polymeric complexes $CdCl_2$ (imidazole) (mean 2.711 Å) and $CDCl_2(MeCSNH_2)$ (mean 2.760 Å).

The phosphine ligand is strongly co-ordinated to cadmium with the Cd–P distance of 2.560(1) Å being significantly less than that found [14] in $CdCl_2(Ph_3P)_2$ [2.635, 2.632(6) Å]. The bond lengths in the phosphine ligand lie within expected ranges. Angular distortion about phosphorus, with the Cd–P–C11 bond angle (108.9°)for example being much smaller than the Cd–P–CH_3 values (mean 115.6°), can be attributed to the asymmetric nature of the phosphine ligand. The phenyl ring is twisted out of the Cd, P, Cl(1), Cl(2) mean plane by 50.9°, presumably to minimise steric interactions within the chain.

The single-chain structure with pentaco-ordinate metal atoms, which characterises the present complex, is similar to that found in $HgCl_2(Et_3P)$ [5]. In the phosphine complexes $HgCl_2(R_3P)$ (R = Me, Et, Bu or Ph) we have found [5, 6] that the size of the phosphine ligand plays an important role in determining the type of structure adopted. While small ligands (R = Me, Et) give rise to polymers, the more bulky tributyl- and triphenylphosphines form tetrameric and dimeric structures respectively. Such size effects appear to be less critical for the analogous cadmium complexes. Thus examination of the far-infrared spectra of the $CdX_2(L)$ complexes (X = Cl or Br; L = Ph_2MeP, $PhMe_2P$ or Et_3P) suggests that despite the differing steric requirements of the phosphine ligands, the complexes are isostructural. While the structural effect of ligand size may be less important for such cadmium complexes, the nature of the halogen does appear to play a significant structural role. Thus $CdI_2(Et_3P)$ appears from its far-infrared spectrum to have a different type of structure to that found for $CdCl_2(PhMe_2P)$.

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