

Bis(methyltriphenylphosphonium) Tetraiodocadmate

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(Received 8 March 1978; accepted 21 March 1978)

Abstract. $C_{38}H_{36}CdI_4P_2$, $M_r = 1174.6$, trigonal, $a = 10.978$ (2), $c = 63.968$ (13) Å, $U = 6676.4$ Å³; systematic extinctions: hkl , $-h + k + l \neq 3n$; $hh2\bar{h}l$, $l \neq 3n$; $hh0l$, $h + l \neq 3n$, $l \neq 2n$; space group $R\bar{3}c$ or $R3c$ (hexagonal axes); $R\bar{3}c$ (No. 167, D_{3d}^6) from structure analysis; $D_c = 1.75$ for $Z = 6$, $D_m = 1.76$ g cm⁻³; Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 33$ cm⁻¹. The structure consists of tetrahedral $[(CH_3)(C_6H_5)_3P]^+$ cations and disordered CdI_4^{2-} anions stacked parallel to c . The Cd–I distances are 2.730 (6) and 2.794 (2) Å, and the P–C distances 1.83 (3) for P–C(methyl) and 1.77 (2) Å for P–C(phenyl).

Introduction. Small transparent tetragonally distorted cubic crystals of $[(CH_3)(C_6H_5)_3P]_2CdI_4$ were kindly supplied by Dr J. C. Green. The selected crystal was mounted on a Nonius CAD-4F PDP8-controlled κ geometry diffractometer; cell dimensions and the orientation matrix were obtained by a least-squares fit to the setting angles of 16 reflexions.

The intensities of reflexions with $\sin \theta/\lambda < 0.55$ Å⁻¹ were measured by an $\omega/2\theta$ scan, a variable scan rate and an ω scan angle of $(1.00 + 0.35 \tan \theta)^\circ$. Mo $K\alpha$ radiation was used with a graphite monochromator. Reflexions with $I < 3\sigma(I)$ were not included in subsequent calculations. Corrections were made for

Lorentz and polarization effects, but not for absorption. A set of 569 independent structure amplitudes was obtained.

With six molecules present in the unit cell it is not possible to have an ordered structure of symmetry $R\bar{3}c$. Patterson and Fourier techniques revealed the Cd, I and P atoms; this partial structure refined well in space group $R3c$ with Cd, two P and one I on positions 6(a) 3 [(0,0,z)] and the other I in a general position. Difference Fourier syntheses revealed the C atoms of the methyl and phenyl groups which were included in the refinement. Fourier syntheses also showed the presence of further electron density in the region of the CdI_4^{2-} group along z , and this has been interpreted as disordered CdI_4^{2-} .

Refinement was by full-matrix least squares, anisotropic thermal motion being assumed for Cd, I and P, with constraints (Waser, 1963; Rollett, 1969) applied to the phenyl groups and to the disordered CdI_4^{2-} group. This model, in space group $R3c$ with unit weights, led to an R of 0.075.

With disordered CdI_4^{2-} present in the structure it is possible to refine in space group $R\bar{3}c$ with one I on position 18(e) 2 [($x, 0, \frac{1}{4}$)], and Cd, P, methyl C, and the second I on positions 12(c) 3 [(0,0,z)]. Similar refinement to that in the noncentrosymmetric space group led to an R of 0.059. This was taken as confirmation of the centrosymmetric space group $R\bar{3}c$ and no further calculations were made in $R3c$.

Table 1. Fractional atomic coordinates, with estimated standard deviations in parentheses

	x	y	z
I(1)	0.2412 (2)	0	0.2500
I(2)	0	0	0.30661 (7)
Cd(1)	0	0	0.26394 (7)
P(1)	0	0	0.4473 (1)
C(1)	0	0	0.4186 (4)
C(2)	0.175 (2)	0.076 (2)	0.4564 (2)
C(3)	0.222 (2)	0.171 (2)	0.4726 (3)
C(4)	0.354 (2)	0.222 (2)	0.4811 (4)
C(5)	0.436 (2)	0.174 (3)	0.4740 (4)
C(6)	0.397 (2)	0.079 (3)	0.4572 (5)
C(7)	0.262 (2)	0.028 (2)	0.4488 (4)
H(3)	0.1585	0.2040	0.4783
H(4)	0.3879	0.2940	0.4925
H(5)	0.5295	0.2058	0.4809
H(6)	0.4623	0.0497	0.4515
H(7)	0.2279	-0.0427	0.4373

Table 2. Interatomic distances (Å) and bond angles (°)

Cd(1)–I(1)	2.794 (2)	I(1)–Cd(1)–I(1')	110.32 (8)
Cd(1)–I(2)	2.730 (6)	I(1)–Cd(1)–I(2)	108.61 (8)
P(1)–C(1)	1.83 (3)	C(1)–P(1)–C(2)	109.3 (5)
P(1)–C(2)	1.77 (2)	C(2)–P(1)–C(2')	109.6 (5)
C(2)–C(3)	1.37 (2)	P(1)–C(2)–C(3)	121 (1)
C(3)–C(4)	1.38 (3)	P(1)–C(2)–C(7)	120 (1)
C(4)–C(5)	1.33 (3)	C(7)–C(2)–C(3)	119 (2)
C(5)–C(6)	1.40 (3)	C(2)–C(3)–C(4)	121 (2)
C(6)–C(7)	1.40 (3)	C(3)–C(4)–C(5)	119 (2)
C(7)–C(2)	1.38 (2)	C(4)–C(5)–C(6)	122 (2)
		C(5)–C(6)–C(7)	118 (2)
		C(6)–C(7)–C(2)	120 (2)

Symmetry code: (i) \bar{y} , $x - y$, z ; or $y - x$, \bar{x} , z .

Refinement continued with anisotropic thermal motion assumed for all non-hydrogen atoms and the constraints on both the CdI_4^{2-} group and the phenyl group were removed. Difference syntheses permitted the location of the phenyl H atoms. They were positioned geometrically ($\text{C-H} = 1.0 \text{ \AA}$; $U_{\text{iso}} = 0.05 \text{ \AA}^2$) and included in the structure factor calculations, their location being readjusted after each cycle. There was, however, no evidence of the methyl H atoms. In the final refinement each reflexion was assigned a weight ($\sqrt{w} = 1$ if $|F_o| \leq 4$, otherwise $\sqrt{w} = 4/|F_o|$). The final R was 0.049 and R_w 0.089 for 569 reflexions.

All calculations were performed on the Oxford University ICL 1906A computer with the Oxford *CRYSTALS* package (Carruthers, 1975). Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

The final positional parameters are given in Table 1.* Table 2 lists interatomic distances and interbond angles for the non-hydrogen atoms, with e.s.d.'s calculated from the full variance-covariance matrix.

Discussion. The stacking arrangement of the ions parallel to c is shown in Fig. 1, which also illustrates the nature of the disorder in the CdI_4^{2-} ion. The coordination geometry about each Cd is tetrahedral. $\text{Cd}(1)\text{-I}(2)$ along the threefold axis [$2.730(6) \text{ \AA}$] is shorter than $\text{Cd}(1)\text{-I}(1)$ [$2.794(2) \text{ \AA}$]. The large U_{33} value for I(1) [$0.092(1) \text{ \AA}^2$] suggests that this atom does not lie exactly at $z = 0.25$, but that this is an average position for two atoms which the refinement procedure was not able to resolve. The angles about Cd [$\text{I}(1)\text{-Cd}(1)\text{-I}(1')$ $110.32(8)$ and $\text{I}(1)\text{-Cd}(1)\text{-I}(2)$ $108.61(8)^\circ$] indicate that the geometry does not deviate significantly from a regular tetrahedron. This configuration agrees with that found from X-ray diffraction in aqueous solution for Na_2CdI_4 , where the Cd-I distance is $2.79(1) \text{ \AA}$ (Ohtaki, Maeda & Ito, 1974).

The geometry of the cation can be compared with that found for triphenylphosphine (Daly, 1964) and for trimethylphosphine by microwave spectroscopy (Lide & Mann, 1958) and by electron diffraction (Bartell & Brockway, 1960). The angles about P [$109.3(5)$ and $109.6(5)^\circ$] are normal, as is $\text{P}(1)\text{-C}(1)$ [$1.83(3) \text{ \AA}$]

* Lists of structure factors and anisotropic thermal parameters for the non-hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33485 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

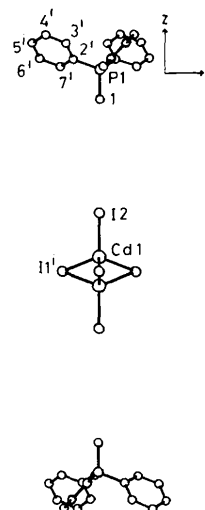


Fig. 1. The $[(\text{CH}_3)(\text{C}_6\text{H}_5)_3\text{P}]_2\text{CdI}_4$ molecule projected down a . For clarity, C atoms are denoted by their serial number only.

along the threefold axis. The $\text{P}(1)\text{-C}(\text{phenyl})$ distance of $1.77(2) \text{ \AA}$ is shorter than that found for $\text{P}(\text{C}_6\text{H}_5)_3$ [$1.828(3) \text{ \AA}$], but is similar to those found in the $(\text{C}_6\text{H}_5)_4\text{P}^+$ cation, e.g. $1.775(7) \text{ \AA}$ in $(\text{C}_6\text{H}_5)_4\text{PCuCl}_3$ (Textor, Dubler & Oswald, 1974). The benzene ring is planar within experimental error, the average C-C bond length is 1.38 \AA and the average C-C-C bond angle is 120° .

We thank the Rhodes Trust for a Rhodes Visiting Fellowship at Somerville College, Oxford (to CC).

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