

Table 2. Intermolecular contacts (Å) involving nitrate 1

O(10)—Hg(3)	2.71 (2)	O(11)—Hg(7) ⁱⁱ	2.90 (2)
O(10)—Hg(9) ⁱ	2.66 (2)	O(11)—Hg(9)	2.99 (2)
O(11)—Hg(3)	3.02 (2)		

Symmetry code

- (i) $x, y, -1 + z$
(ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$

selected assuming the usual value (1.40 Å) for the van der Waals radius of oxygen (Cotton & Wilkinson, 1972) and using one half of the Hg—Hg separation observed here as the van der Waals radius of mercury (1.65 Å). This is intermediate between the two values proposed by Grdenić (1965), that is 1.50 Å, which undoubtedly correspond to an appreciable Hg...O bonding effect, and 1.76 Å, which probably indicates a vanishingly weak interaction. Only nitrate ions 1 and 3 take part in Hg...O contacts. Interatomic distances are given in Table 2 and Fig. 2; a detailed list of angles has been deposited.* All contacts are within $\pm 15^\circ$ from the mercury equatorial plane (perpendicular to the C—Hg—N bonds) and Fig. 3 shows that each mercury is efficiently surrounded by another mercury and/or a nitrate O atom. While the Hg...O interactions in the corresponding perchlorate salt are weak, the shortest Hg...O distance being 2.85 Å (Hubert & Beauchamp, 1980), shorter contacts 2.62–2.71 Å are found in the present nitrate compound, indicating greater basicity of the nitrate ions. Fig. 2 shows how the disordered nitrate ion interacts with neighboring Hg atoms. In either orientation, two relatively short contacts remain.

The present structure reinforces our previous conclusion that once the imidazole ring has been saturated

* See deposition footnote.

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X-ray Structure of Bis(benzyltriphenylphosphonium) Hexachlorodidcadmate

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Abstract

The molecular and crystal structure of the title compound was determined by X-ray diffractometry. The structure was solved by direct and Fourier methods and refined by least-squares techniques to $R =$

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by mercury coordination to N(7) and N(9), the first site attacked by the metal on the pyrimidine ring is N(3) instead of N(1). Since the packing patterns in the nitrate and in the perchlorate salts are totally different, we conclude that the preference for N(3) rather than N(1) cannot result from solid-state effects, but should be ascribed to electronic distribution in the purine ring.

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0.055 for 2655 non-zero independent reflections. Crystals are triclinic, space group $P\bar{1}$ with two $[P(C_6H_5)_3(C_7H_7)]_2[Cl_2Cd_6]$ formula units in a unit cell of dimensions $a = 20.593$ (20), $b = 12.832$ (15), $c = 12.730$ (18) Å, $\alpha = 120.84$ (5), $\beta = 117.84$ (6), $\gamma = 83.97$ (5)°. The structure is built up of well separated ions. The hexachlorodidcadmate anion geometry consists of two distorted tetrahedra joined by a double

Cl atom bridge, with the two Cd atoms and two bridging Cl atoms in a nearly square-planar conformation. The benzyltriphenylphosphonium cations adopt a slightly distorted tetrahedral symmetry around the P atoms with the P–C(phen) bonds in very nearly staggered conformations (*gauche*⁻, *gauche*⁺, and *trans*) with respect to the C(phen)–CH₂ bonds of the benzyl residues. The most significant average bond distances are: Cd–Cl_b, 2.532 (6), Cd–Cl_t, 2.391 (5), P–C(*sp*²) 1.78 (2), and P–C(*sp*³) 1.80 (2) Å. The interatomic distances between the ions correspond to normal van der Waals distances.

Introduction

In the course of structural studies on homogeneous catalysts, a compound with elemental composition C₅₀H₄₄Cd₂Cl₆P₂ (I) was obtained by reacting CdCl₂ with triphenylphosphine and C₆H₅CH₂Cl. Although the stoichiometry of a substance is a rather poor guide to the coordination of the metal, various alternative structures may be suggested for the compound, such as a monomeric planar [CdCl₃]⁻ ion (*D*_{3h} symmetry), a not previously reported dimeric [Cd₂Cl₆]²⁻ anion, an infinite chain composed of Cd atoms bridged by three Cl atoms, +CdCl₃]⁻, as in [N(CH₃)₄][CdCl₃] (Morosin, 1972), or a [Cd₂Cl₆]²ⁿ⁻ polyion, as in NH₄[CdCl₃] (Rolies & De Ranter, 1978*a*) and Rb[CdCl₃] (MacGillivray, Nijveld, Dierdorff & Karsten, 1939). It is therefore possible that the Cd^{II} coordination varies considerably in earlier proposed ion structures. In order to investigate the stereo-geometry of Cd^{II} in bis(benzyltriphenylphosphonium) hexachlorodicadmate we have carried out a structural determination.

Experimental

Preliminary cell parameters and the space group were obtained from Weissenberg photographs. A small colourless crystal of (I), dimensions 0.5 × 0.3 × 0.5 mm, was enclosed in a Lindemann-glass capillary tube filled with dry nitrogen and mounted on a Picker FACS 1 four-circle computer-controlled diffractometer equipped with a scintillation counter and a pulse-height analyser. Accurate cell dimensions and an orientation matrix were obtained from a least-squares fit of ω , χ , ϕ and 2θ values from 12 independent reflections.

Crystal data

C₅₀H₄₄Cd₂Cl₆P₂, *M*_r = 1144.41, triclinic, *a* = 20.593 (20), *b* = 12.832 (15), *c* = 12.730 (18) Å, α = 120.84 (5), β = 117.84 (6), γ = 83.97 (5)°, *U* = 2513.86 Å³, *Z* = 2, *D*_o = 1.48, *D*_c = 1.51 Mg m⁻³,

$\mu(\text{Mo } K\alpha) = 1.25 \text{ mm}^{-1}$; space group *P* $\bar{1}$ from the structure determination.

Intensity data were collected by the use of Zr-filtered Mo *K* α radiation ($\lambda = 0.71069 \text{ \AA}$) with $2\theta \leq 35^\circ$. The moving-crystal–moving-counter technique was used with a 2θ scan rate of 1° min^{-1} and a scan range of $2.0\text{--}2.5^\circ$ in order to allow for the greater separation of the *K* α_1 and *K* α_2 peaks at increasing 2θ values. Background counts of 10 s were measured at each end of every 2θ scan. Three standard reflections, measured after every 50 reflections, showed no fluctuations greater than $\pm 5\%$ during data collection. 3193 independent reflections were measured, of which 2655 were considered observed with $I \geq 2.50\sigma$ ($\sigma = [N_s + (t_s/t_b)^2 N_b]^{1/2}$, where *N*_s is the total peak count during the time of scanning *t*_s, and *t*_b is the time spent in measuring the *N*_b background counts). An arbitrary intensity equal to $0.5 \times$ the observable limit was assigned to the non-significant reflections. All intensities were corrected for Lorentz and polarization effects. No absorption correction was introduced ($\mu R = 0.38$).

The structure was solved by the multi-solution tangent-refinement method (Germain, Main & Woolfson, 1971). The automatically chosen starting set is reported in Table 1. Among the eight solutions obtained on the basis of the values (2π or π) of the phase angles *A*, *B*, and *C*, the correct one (solution 8) stood out as having the highest value for the combined figure of merit; the phase angles *A*, *B* and *C* were all π . An *E* map phased on this information led to a clear picture of the [Cd₂Cl₆]²⁻ anion and also permitted the location of the two P atoms with the four C atoms linked to one of them. Coordinates of the remaining C atoms were obtained from successive Fourier maps and on the basis of stereochemical considerations. The

Table 1. *Tangent-formula results*

(a) Starting set

<i>h</i>	<i>k</i>	<i>l</i>	<i>E</i>	Phase angle
-3	5	1	4.04	360°
-5	-6	5	3.11	360
-3	2	2	2.58	360
-5	1	3	3.08	<i>A</i>
-12	-4	6	3.07	<i>B</i>
-6	-2	6	3.03	<i>C</i>

(b) Tangent-formula output

Number of set	ABSFOM	ψ_0	RESID	COMBINED-FOM
1	1.008	5044	34.58	2.000
2	0.900	2753	41.08	0.888
3	0.900	3062	41.08	0.768
4	1.008	4362	34.58	2.264
5	1.005	3440	34.78	2.563
6	0.902	2465	40.88	1.053
7	0.902	2764	40.88	0.937
8	1.005	2849	34.78	2.792

Table 2. *Final fractional coordinates with estimated standard deviations in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Cd(1)	0.70764 (6)	-0.13252 (9)	0.74833 (10)	C(43)	0.4452 (8)	-0.7011 (12)	0.9292 (13)
Cd(2)	0.81976 (6)	0.07304 (9)	1.11182 (10)	C(44)	0.5075 (8)	-0.5884 (11)	1.3366 (13)
Cl(1)	0.6836 (2)	-0.0829 (4)	0.5802 (4)	C(45)	0.5480 (8)	-0.7003 (13)	1.3254 (14)
Cl(2)	0.8508 (2)	0.0188 (3)	1.2833 (4)	C(46)	0.5081 (10)	-0.8162 (14)	1.2306 (18)
Cl(3)	0.6575 (2)	-0.3376 (3)	0.6650 (4)	C(47)	0.5478 (16)	-0.9179 (19)	1.2181 (27)
Cl(4)	0.6806 (2)	0.0219 (4)	0.9416 (4)	C(48)	0.6235 (16)	-0.8856 (21)	1.3037 (33)
Cl(5)	0.8446 (2)	-0.0955 (3)	0.9206 (4)	C(49)	0.6601 (13)	-0.7681 (18)	1.4038 (30)
Cl(6)	0.8630 (2)	0.2781 (3)	1.1912 (4)	C(50)	0.6246 (9)	-0.6789 (14)	1.4117 (19)
P(1)	1.0320 (2)	0.3052 (3)	0.6931 (3)	H(2)	1.019	0.543	0.903
P(2)	0.4997 (2)	-0.5490 (3)	1.2150 (4)	H(3)	0.914	0.653	0.886
C(1)	0.9599 (7)	0.3938 (10)	0.6804 (13)	H(4)	0.802	0.584	0.665
C(2)	0.9676 (7)	0.5066 (12)	0.8036 (13)	H(5)	0.789	0.396	0.450
C(3)	0.9097 (8)	0.5686 (14)	0.7922 (14)	H(6)	0.894	0.276	0.458
C(4)	0.8472 (8)	0.5312 (12)	0.6682 (16)	H(8)	1.120	0.129	0.592
C(5)	0.8396 (8)	0.4263 (13)	0.5502 (15)	H(9)	1.156	0.079	0.411
C(6)	0.8988 (7)	0.3579 (11)	0.5560 (13)	H(10)	1.121	0.194	0.298
C(7)	1.0592 (7)	0.2691 (11)	0.5658 (13)	H(11)	1.046	0.354	0.343
C(8)	1.1022 (8)	0.1790 (12)	0.5371 (14)	H(12)	1.006	0.406	0.527
C(9)	1.1231 (8)	0.1515 (12)	0.4373 (15)	H(14)	1.120	0.538	0.834
C(10)	1.1030 (9)	0.2171 (14)	0.3746 (15)	H(15)	1.240	0.650	1.061
C(11)	1.0615 (9)	0.3062 (17)	0.3998 (18)	H(16)	1.294	0.566	1.209
C(12)	1.0386 (9)	0.3326 (15)	0.4992 (16)	H(17)	1.235	0.366	1.141
C(13)	1.1129 (7)	0.3836 (10)	0.8564 (12)	H(18)	1.120	0.242	0.900
C(14)	1.1458 (7)	0.4984 (11)	0.8994 (13)	H(191)	0.957	0.104	0.538
C(15)	1.2111 (8)	0.5610 (12)	1.0263 (16)	H(192)	1.042	0.110	0.675
C(16)	1.2418 (8)	0.5128 (14)	1.1079 (15)	H(21)	0.853	0.195	0.586
C(17)	1.2110 (8)	0.4015 (16)	1.0705 (15)	H(22)	0.777	0.183	0.687
C(18)	1.1447 (7)	0.3345 (13)	0.9378 (13)	H(23)	0.841	0.160	0.896
C(19)	0.9950 (7)	0.1591 (10)	0.6504 (12)	H(24)	0.972	0.146	0.993
C(20)	0.9531 (7)	0.1665 (11)	0.7246 (12)	H(25)	1.042	0.131	0.871
C(21)	0.8794 (8)	0.1806 (13)	0.6742 (16)	H(27)	0.519	-0.340	1.482
C(22)	0.8375 (9)	0.1776 (15)	0.7342 (20)	H(28)	0.473	-0.140	1.532
C(23)	0.8718 (10)	0.1621 (12)	0.8454 (17)	H(29)	0.401	-0.093	1.354
C(24)	0.9438 (10)	0.1511 (14)	0.8982 (15)	H(30)	0.367	-0.246	1.108
C(25)	0.9842 (8)	0.1491 (13)	0.8335 (13)	H(31)	0.406	-0.448	1.046
C(26)	0.4658 (7)	-0.4073 (11)	1.2585 (13)	H(33)	0.608	-0.337	1.352
C(27)	0.4854 (10)	-0.3207 (14)	1.3969 (15)	H(34)	0.739	-0.314	1.399
C(28)	0.4607 (11)	-0.2091 (17)	1.4243 (17)	H(35)	0.786	-0.502	1.276
C(29)	0.4182 (10)	-0.1838 (15)	1.3235 (18)	H(36)	0.712	-0.707	1.140
C(30)	0.4001 (9)	-0.2659 (12)	1.1913 (16)	H(37)	0.585	-0.733	1.108
C(31)	0.4223 (8)	-0.3774 (13)	1.1578 (14)	H(39)	0.358	-0.676	1.110
C(32)	0.5900 (7)	-0.5325 (10)	1.2334 (13)	H(40)	0.259	-0.820	0.864
C(33)	0.6318 (7)	-0.4206 (13)	1.3081 (15)	H(41)	0.280	-0.884	0.668
C(34)	0.7040 (8)	-0.4069 (13)	1.3306 (15)	H(42)	0.401	-0.827	0.704
C(35)	0.7312 (7)	-0.5116 (14)	1.2669 (16)	H(43)	0.498	-0.663	0.948
C(36)	0.6891 (8)	-0.6247 (13)	1.1901 (14)	H(441)	0.539	-0.509	1.443
C(37)	0.6187 (7)	-0.6396 (14)	1.1697 (15)	H(442)	0.453	-0.610	1.319
C(38)	0.4341 (7)	-0.6634 (12)	1.0409 (13)	H(46)	0.445	-0.832	1.162
C(39)	0.3676 (8)	-0.7057 (13)	1.0209 (16)	H(47)	0.516	-1.016	1.151
C(40)	0.3137 (9)	-0.7853 (14)	0.8866 (17)	H(48)	0.656	-0.965	1.280
C(41)	0.3254 (8)	-0.8238 (13)	0.7754 (14)	H(49)	0.723	-0.749	1.477
C(42)	0.3908 (9)	-0.7863 (14)	0.7948 (14)	H(50)	0.654	-0.582	1.488

positional and the isotropic thermal parameters of the non-hydrogen atoms of the ions were refined by several cycles of block-diagonal least squares (b.d.l.s.) using the program of Immirzi (1967). Atomic scattering factors were calculated from the expression given by Vand, Eiland & Pepinsky (1957) using the parameter values of Moore (1963). The weighting scheme of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) was adopted: $1/w = A + B|F_o| + C|F_o|^2$, where $A = 2F_o(\text{min.})$, $B = 1$, and $C = 2/F_o(\text{max.})$. The con-

ventional $R (= \sum |k|F_o| - |F_c| / \sum k|F_o|)$ value dropped to 0.097 for the significant reflections. Some more cycles of b.d.l.s. refinement were run, with anisotropic thermal parameters for all the non-hydrogen atoms of the ions. The H atoms were introduced into the calculations with $B = 5.0 \text{ \AA}^2$ but not refined, their coordinates being defined on stereochemical grounds ($C-H = 1.08 \text{ \AA}$, $C-C-H = 120$ or 109.5°). Refinement converged to $R = 0.055$ for the 2655 non-zero reflections with $R' = 0.067$, including the

non-observed reflections. The final shifts of the atomic parameters were negligible, all being well below the corresponding σ . A difference Fourier map did not reveal any unexplained features.

Table 2 reports the final fractional coordinates and the corresponding standard deviations of the atoms of the independent ions.* All calculations were carried out on the Univac 1110/20 computer of these laboratories using a local program set.

Results and discussion

Fig. 1 shows the ionic structure of (I) together with the atom-labelling scheme and 30% probability thermal-vibration ellipsoids. The packing of the ions in the crystal is shown in Fig. 2. Both figures were obtained by means of ORTEP (Johnson, 1965). The geometric parameters of the ions with their estimated standard deviations are reported in Table 3.

The crystal structure of (I) consists of well separated hexachlorodicadmite anions and phosphonium cations at interionic distances. The observed $[\text{Cd}_2\text{Cl}_6]^{2-}$ structural unit thus differs from the infinite $[\text{CdCl}_3]_n^-$ chain in $[\text{N}(\text{CH}_3)_4][\text{CdCl}_3]$ (Morosin, 1972), from the non-isolated $[\text{Cd}_2\text{Cl}_6]^{2-}$ unit in $[\text{CdCl}_2(\text{H}_2\text{NC}_3\text{H}_6\text{NH}_2)]$ (Andreotti, Cavalca, Pellinghelli & Sgarabotto, 1971) and may eventually be identical with the polynuclear species in $[\text{CdCl}_3]^-$ -containing piperidinium and morpholinium complexes (Marcotrigiano, Menabue & Pellacani, 1976).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35319 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

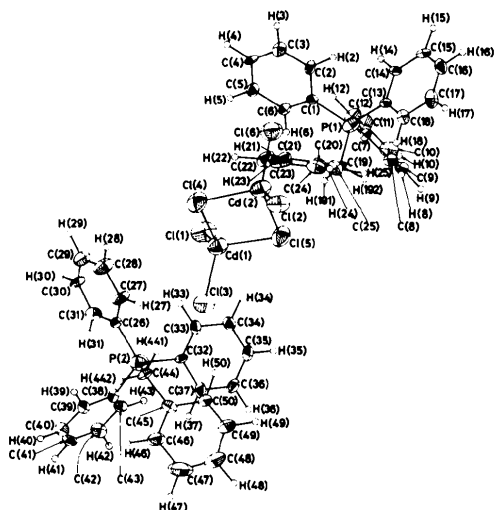


Fig. 1. View of $[\text{P}(\text{C}_6\text{H}_5)_3(\text{C}_7\text{H}_7)]_2[\text{Cd}_2\text{Cl}_6]$ indicating the atom-labelling scheme and the 30% probability thermal-vibration ellipsoids.

The binuclear $[\text{Cd}_2\text{Cl}_6]^{2-}$ anion, also likely to be present in some boronium salts (Coates & Ridley, 1964), can be described as a slightly distorted edge-condensed bitetrahedron, as in the case of $[\text{Cd}_2\text{Br}_6]^{2-}$ (Cras, Willemse, Gal & Hummelink-Peters, 1973) and $[\text{Hg}_2\text{I}_6]^{2-}$ (Beurskens, Bosmann & Cras, 1972) and in dimeric halogen-bridging M_2X_6 compounds (Hargittai & Hargittai, 1977).

The Cd atoms are thus joined by a double Cl atom bridge (Fig. 3) in such a way that two Cd atoms and two bridging Cl atoms (Cl_b) are in a slightly distorted square-planar arrangement with the four terminal Cl atoms (Cl_t) being above and below the bridge plane. Displacements from the best plane through Cd(1), Cd(2), Cl(4) and Cl(5) (equation: $-0.0319x - 0.6894y + 0.7236z - 3.2243 = 0$, referring to the a^* , b' , c orthogonal axis system with b' in the a^*b^* plane) are $\pm 0.052 \text{ \AA}$ for the atoms defining the plane (r.m.s.).

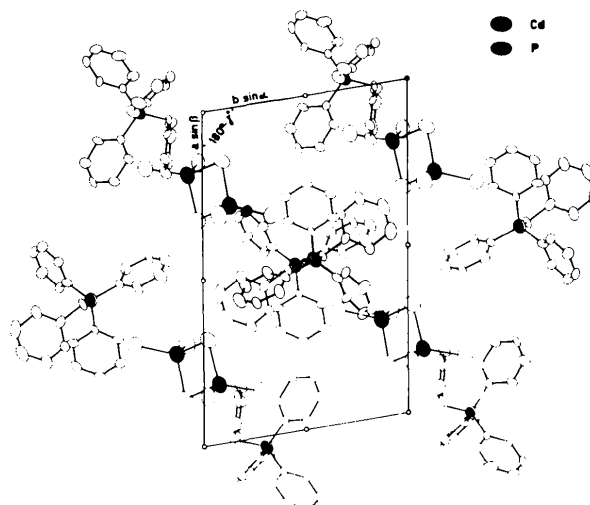


Fig. 2. Packing arrangement of $[\text{P}(\text{C}_6\text{H}_5)_3(\text{C}_7\text{H}_7)]_2[\text{Cd}_2\text{Cl}_6]$ viewed down the c axis.

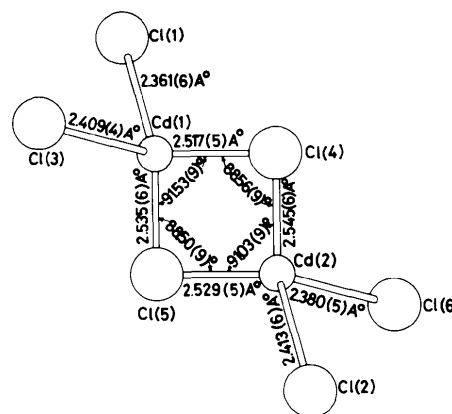


Fig. 3. Geometry of the $[\text{Cd}_2\text{Cl}_6]^{2-}$ anion in bis(benzyltriphenylphosphonium) hexachlorodicadmite.

Table 4 (cont.)

Compound ^(a)	Bond lengths (Å) ^(b)		Cd polyhedron	Structural unit	CN(Cd) ^(c)	Reference
	Cd—Cl ₁	Cd—Cl ₆				
CdCl ₂ (solid)		2.658 (n.d.)	CdCl ₆	Sheets	6	(q)
CdCl ₂ ·2NaCl·3H ₂ O		2.77 (1) ^(d)	MCl ₆ (M = Cd, Na)	Sheets	6	(r)
NH ₃ [CdCl ₃]	2.512 (2)	2.645–2.714 (2)	CdCl ₆	[Cd ₂ Cl ₆] _n ²⁻	6	(s)
Rb[CdCl ₃]	2.49 (n.d.)	2.64–2.67 (n.d.)	CdCl ₆	[Cd ₂ Cl ₆] _n ²⁻	6	(t)
[N(CH ₃) ₄][CdCl ₃]		2.641 (1)	CdCl ₆	†CdCl ₃ † _n	6	(u)
[OC(NH ₂)NH ₂][CdCl ₃]	2.52 (n.d.)	2.59–2.73 (n.d.)	CdCl ₆	Chains	6	(v)
[N(CH ₃)H ₃] ₂ [CdCl ₄] (ORT) ^(e)	2.537 (n.d.)	2.644 (n.d.)	CdCl ₆	2 D layers	6	(w)
(MLT)	2.572 (3)	2.636–2.647 (2)	CdCl ₆	2 D layers	6	(x)
(THT)	2.523 (4)	2.651 (1)	CdCl ₆	2 D layers	6	(x)
[C ₂ H ₆ N ₂ H ₆][CdCl ₄]	2.581 (2)	2.670 (2)	CdCl ₆	2 D layers	6	(y)
[N ₂ H ₃] ₃ [CdCl ₅]	2.56, 2.64 (n.d.)	2.68 (n.d.)	CdCl ₆	[CdCl ₅] _n ³⁻	6	(z)
K ₄ [CdCl ₆]		2.64 (n.d.)	CdCl ₆	[Cl ₃ CdCl ₃ K] _n ³⁻	6	(aa)
[Co(en) ₃] ₂ [CdCl ₆]Cl ₂ ·2H ₂ O	2.588–2.765 (3)		CdCl ₆	[CdCl ₆] ⁴⁻	6	(bb)
[N(C ₃ H ₇)H ₃] ₂ [CdCl ₄] (low temperature)		2.561–2.668 (2)	CdCl ₆	2 D layers	6	(cc)
(room temperature)		2.535–2.667 (2)	CdCl ₆	2 D layers	6	(cc)
[N(CH ₃) ₂ H] ₂ [Cd ₂ Cl ₅]·2H ₂ O		2.548–2.705 (1)	CdCl ₆	Chains	6	(dd)
	2.494 (1)	2.579–2.751 (1)	CdCl ₆ O	Chains	6	(dd)
[CdCl ₂ taa]		2.57–2.89 (2)	CdCl ₂ S	Chains	6	(ee)
[CdCl ₂ ·OC(NH ₂)NHCH ₃]		2.58–2.67 (n.d.)	CdCl ₂ O	†CdCl ₂ † _n	6	(ff)
[CdCl ₂ (p-H ₂ NC ₆ H ₄ NO ₂)]·H ₂ O		2.60–2.62 (n.d.)	CdCl ₂ O	Stacks	6	(gg)
CdCl ₂ ·H ₂ O		2.697 (5), ax.;	CdCl ₂ O	Chains	6	(hh)
		2.569–2.672 (5) eq.				
CdCl ₂ ·2.5H ₂ O		2.539–2.555 (6)	CdCl ₂ O	3 D network	6	(ii)
		2.559–2.682 (6)	CdCl ₄ O ₂			
[CdCl ₂ (HCONH ₂) ₂]		2.833–2.912 (8)	CdCl ₄ O ₂	†CdCl ₂ † _n	6	(jj)
[Cd(biu) ₂ Cl ₂]		2.55–2.62 (1)	CdCl ₄ O ₂	†CdCl ₂ † _n	6	(kk)
[CdCl ₂ ·OC(NH ₂) ₂] ₂		2.64 (n.d.)	CdCl ₄ O ₂	†CdCl ₂ † _n	6	(ll)
[CdCl ₂ ·OC(CH ₃)NH ₂] ₂		2.58, 2.66 (n.d.)	CdCl ₄ O ₂	†CdCl ₂ † _n	6	(mm)
[Cd(NH ₃) ₂ Cl ₂]		2.71 (n.d.)	CdCl ₄ N ₂	†CdCl ₂ † _n	6	(nn)
[CdCl ₂ (py) ₂]		2.65 (5)	CdCl ₄ N ₂	†CdCl ₂ † _n	6	(oo, pp)
[CdCl ₂ (ImH) ₂] _∞		2.706, 2.731 (2)	CdCl ₄ N ₂	†CdCl ₂ † _n	6	(qq)
[CdCl ₂ (H ₂ NC ₃ H ₆ NH ₂)]	2.494 (2)	2.742–2.802 (2)	CdCl ₄ N ₂	[Cd ₂ Cl ₆] _n ²⁻	6	(rr)
[Cd(C ₂ N ₂ H ₄)Cl ₂]		2.572–2.647 (3)	CdCl ₄ N ₂	†CdCl ₂ † _n	6	(ss)
[CdCl ₂ (dpt)] ₂	2.75 (1)	2.63–2.65 (1)	CdCl ₃ N ₃	[Cd ₂ Cl ₆] _n ²	6	(tt)
[CdCl(OH)]		2.69 (n.d.)	CdCl ₃ O ₃	Layers	6	(uu)
[CdCl ₂ (H ₂ O)(SN ₄ C ₂ H ₄) ₂]	2.494 (3)	2.60–2.63 (1)	CdCl ₃ NSO	[CdCl ₂]	6	(vv)
[CdCl ₂ (HGly-Gly) ₂]	2.563 (5)		CdCl ₃ O ₄	[CdCl ₂]	6	(ww)
[CdCl ₂ ·SC(NHNH ₂) ₂] ₂	2.73 (1)		CdCl ₃ S ₂ N ₂	[CdCl ₂]	6	(xx)
[CdCl(Gly-Gly)(OH) ₂]	2.564 (5)		CdClO ₄ N	[CdCl] ⁺	6	(ww)
[CdCl(en) ₂ (NCS)]	2.71 (1)		CdClN ₃	[CdCl] ⁺	6	(yy)

(a) Abbreviations: biu, biuret; Bz, benzyl; chinH, quinolinium; dpt, bis(2-aminopropyl)amine; en, ethylenediamine; HGly-Gly, ⁺NH₃CH₂CONHCH₂CO₂⁻; ImH, imidazole; Ph, phenyl; py, pyridine; taa, thioacetamide; ax., axial; eq., equatorial.

(b) Average values or range (in case of significant spread).

(c) Coordination numbers: 4, tetrahedron; 5, trigonal bipyramid; 6, octahedron.

(d) M = †Cd + †Na; as Na—Cl = 2.820 Å, it follows that Cd—Cl = 2.67 Å.

(e) THT, ORT and MLT crystallize in the space groups *I4/mmm*, *Cmca* and *P2₁/a*, respectively.

References: (f) Lister & Sutton (1941); (g) Paulus & Goetlicher (1969); (h) Richardson, Franklin & Thompson (1975); (i) Bart, Bassi & Calcaterra (1980a); (j) Bart, Bassi & Calcaterra (1980c); (k) Nardelli, Cavalca & Braibanti (1957); (l) Cavalca, Domiano, Musatti & Sgarabotto (1968); (m) Cameron, Forrest & Ferguson (1971); (n) McCusker & Seff (1978); (o) Epstein & Bernal (1971); (p) Long, Herlinger, Epstein & Bernal (1970); (q) Wyckoff (1960); (r) Boistelle, Pépe, Simon & Leclaire (1974); (s) Rolies & De Ranter (1978a); (t) MacGillavry, Nijveld, Dierdorp & Karsten (1939); (u) Morosin (1972); (v) Nardelli & Boldrini (1963); (w) Chapuis, Arend & Kind (1975); (x) Chapuis, Kind & Arend (1976); (y) Willett (1977); (z) Braibanti & Tiripicchio (1966); (aa) Bergerhoff & Schmitz-Dumont (1956); (bb) Veal & Hodgson (1972); (cc) Chapuis (1978); (dd) Bats, Fuess & Daoud (1979); (ee) Rolies & De Ranter (1978b); (ff) Nardelli, Coghi & Azzoni (1958); (gg) Volodina & Ablov (1968); (hh) Leligny & Monier (1974); (ii) Leligny & Monier (1975); (jj) Mitschler, Fischer & Weiss (1967); (kk) Cavalca, Nardelli & Fava (1960); (ll) Nardelli, Cavalca & Fava (1957); (mm) Cavalca, Nardelli & Coghi (1957); (nn) MacGillavry & Bijvoet (1936); (oo) Paulus (1969); (pp) Zannetti (1960); (qq) Flook, Freeman, Huq & Rosalky (1973); (rr) Andreotti, Cavalca, Pellinghelli & Sgarabotto (1971); (ss) Villa, Coghi, Mangia, Nardelli & Pelizzi (1971); (tt) Cannas, Cristini & Marongiu (1978); (uu) Hoard & Grenko (1934); (vv) Griffith & Amma (1979); (ww) Flook, Freeman, Moore & Scudder (1973); (xx) Bigoli, Braibanti, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini (1971); (yy) Shvelashvili, Porai-Koshits, Kvitashvili, Shchedrin & Sarishvili (1974).

displacement 0.103 Å); displacements of atoms out-of-plane are -2.024, 1.955, 2.055 and -2.144 Å for Cl(1), Cl(2), Cl(3) and Cl(6), respectively.

As may be seen from Table 4, the Cd-Cl_l bond lengths in the isolated [Cd₂Cl₆]²⁻ anion of approximate *D*_{2d} (*mmm*) symmetry, average 2.391 (5) Å, are the shortest Cd-Cl distances reported so far in the solid state and are close to those found in tetrachlorocadmite ions (2.43-2.45 Å). It is worth mentioning that Cd-Cl_l distances in other chlorocadmite ions cover a wide range (2.44-2.76 Å), which is partly due to hydrogen bonding. This holds, for example, for the Cd-Cl_l distances reported for tris(ethylenediamine)cobalt(III) hexachlorocadmite(II) dichloride dihydrate (Veal & Hodgson, 1972), in which the cadmate ion shows a considerably distorted octahedral symmetry.

Similarly, the Cd-Cl_b bond lengths in (I), average 2.532 (6) Å, are amongst the shortest Cd-Cl_b distances reported and are close to those found in the octahedrally coordinated CdCl₂·2.5H₂O, 2.539-2.555 (6) Å (Leligny & Monier, 1975). Appreciably longer Cd-Cl_b distances, up to 2.91 Å, are found in a variety of other hexacoordinated Cd^{II} structures (Table 4).

The occurrence of the [Cd₂Cl₆]²⁻ anion in a crystal structure without secondary-bonding effects (hydrogen bonds) makes it possible to assess the effects of electronic forces on the Cd-Cl_b and Cd-Cl_l bond lengths. The ratio Cd-Cl_b/Cd-Cl_l in (I) is 1.059, *i.e.* close to the average value (1.050) in a variety of compounds: NH₄[CdCl₃], [OC(NH₂)NH₃][CdCl₃], [N(CH₃)H₃]₂[CdCl₄], [C₃H₆N₂H₆][CdCl₄], [N₂H₅]₃[CdCl₅] and [CdCl₂(H₂NC₃H₆NH₂)] (see Table 4). In these compounds the individual values cover a wide range (1.01-1.12), but in all cases hydrogen-bonding effects are present. It should also be noted that in the trigonal-bipyramidal [CdCl₅]³⁻ anion (Epstein & Bernal, 1971) the Cd-Cl_{eq}/Cd-Cl_{ax} ratio is only 1.014.

The anion structure was checked by bond-valence analysis. Bond valences (*s*) were calculated from bond lengths (*R*) by the equation $s = (R/R_0)^{-N}$, where the parameters *R*₀ and *N* were obtained according to Brown & Shannon (1973) using the following set of (almost) regular chlorocadmium environments in the solid state of Table 4 [compound, bond strength in valence units (v.u.), bond distance in Å]: [CdCl₄(chinH)₂], [C₁₂H₂₀N₄O₂S][CdCl₄].H₂O, [Ph₃PBz]₂[CdCl₄].2C₂H₄Cl₂, [Ph₃PC₂H₄OH]₂[CdCl₄], 0.5, 2.450 (4); [Co(NH₃)₆][CdCl₅], 0.40, 2.547 (2); CdCl₂ (solid), [N(CH₃)₄][CdCl₃], K₄[CdCl₆], 0.33, 2.646 (-) Å. On the basis of the parameters so derived (*R*₀ = 2.155 Å, *N* = 5.4) the bond-valence values for Cd-Cl_b and Cd-Cl_l bonds in the [Cd₂Cl₆]²⁻ anion are close to 0.40 and 0.55-0.60 v.u., respectively, with valence sums around Cd(1) and Cd(2) of 2.01 and 1.96 v.u.

The bond angles of the [Cd₂Cl₆]²⁻ anion differ

considerably from the tetrahedral values and range from 118.49 (10) to 88.50 (9)°. This is due to the particular conformation adopted by the anion with the following average bond angles: Cl_b-Cd-Cl_b 91.31 (9), Cl_l-Cd-Cl_l 118.10 (10), Cl_l-Cd-Cl_b 111.02 (10), and Cd-Cl_b-Cd 88.53 (9)°. Similar values for Cl_b-Cd-Cl_b angles have been observed in structures consisting of Cd atoms linked to their neighbours by double chloride bridges forming infinite -Cd-Cl₂-Cd-ribbons, namely [CdCl₂(py)₂] (88.1°) (Paulus, 1969), [Cd(urea)₂]Cl₂ (91°) (Nardelli, Cavalca & Fava, 1957), [CdCl₂(HCONH₂)₂] [89.8 (3)°] (Mitschler, Fischer & Weiss, 1967), [Cd(biuret)₂Cl₂] [91.5 (3)°] (Cavalca, Nardelli & Fava, 1960) and [Cd(ImH)₂Cl₂] [88.2 (2)°] (Flook, Freeman, Huq & Rosalky, 1973). In all these cases the octahedral coordination is completed by two Cd-O or Cd-N bonds. It is obvious that the Cd-Cl_b bond lengths in these ribbons depend upon the bond orders of the bonds perpendicular to the plane of the Cd and Cl atoms. In accordance with expectation, in infinite linear -Cd-Cl₃-Cd- chains with an octahedral Cd^{II} environment a different Cl_b-Cd-Cl_b angle is observed, namely 83.91 (3)° in [N(CH₃)₄][CdCl₃] (Morosin, 1972). The Cl_b...Cl_b separation of 3.620 (6) Å in (I) corresponds to the sum of the ionic radii (3.62 Å) of the chloride ions, while the Cl_b...Cl_l and Cl_l...Cl_l separations are at least 3.941 (7) Å.

The two [P(C₆H₅)₃(CH₂C₆H₅)₃]⁺ cations of (I) show a quasi-perfect tetrahedral symmetry with an average P-C(*sp*²) distance of 1.78 (2) Å (range 1.76-1.78 Å), in contrast to the slightly longer average P-C(*sp*³) distance of 1.80 (2) Å (range 1.80-1.81 Å). Distortion of the coordination sphere around the P atom, probably due to close contacts, is expressed by the spread in the C-P-C angles (105.8-113.2°). The mean value of the C-P-C bond angles is 109.5 (4)° with no significant differences between C(*sp*²)-P-C(*sp*³) and C(*sp*²)-P-C(*sp*²). Our observations agree with literature data concerning the organophosphonium cations (Daly, 1970; Corbridge, 1974). The average value of the C...C bond lengths of the phenyl rings is 1.38 (3) Å (range 1.34-1.45 Å) while the average value of the endocyclic bond angles is 120.0 (10)° (range 115.3-123.9°). The mean exocyclic C(*sp*³)-C(*sp*²) bond is 1.53 (2) Å.

The conformation of the phosphonium cations may be described in terms of the torsion angles around the P-CH₂ bonds. In agreement with other findings in such cations (Bart, Bassi & Calcaterra, 1980*a,b*), the P-C(*sp*²) bonds are nearly staggered (*gauche*⁺, *gauche*⁻ and *trans*) with respect to the CH₂-C(*sp*²) bonds of the benzyl residues, as shown in Fig. 4. Mean values for C(*sp*²)-C(*sp*³)-P-C(*sp*²) torsion angles are 64.8, -56.6 and 184.1° in six independent benzyl-triphenylphosphonium cations (Bart, Bassi & Calcaterra, 1980*a,b*; this paper), with P-C(*sp*³)-C(*sp*²)-C(*sp*²)-94.8 and 88.5° on average.

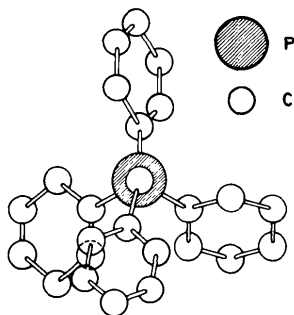


Fig. 4. View along the P—C(sp^3) bond of a benzyltriphenylphosphonium cation in $[P(C_6H_5)_3(C_7H_7)]_2[Cd_2Cl_6]$.

The conformations of the phenyl groups, expressed by the torsion angles around the P—C(sp^2) bonds with respect to the P—CH₂ bonds, are intermediate between staggered and eclipsed for the cation centred on P(2), as is usually found, but nearly staggered and eclipsed for the cation centred on P(1). Rotation around the P—C(sp^2) bonds in benzyltriphenylphosphonium cations is likely to be due to packing requirements. No abnormally short non-bonded interactions were found (Table 3).

The arrangement of the ions in the unit cell is shown in Fig. 2. As already mentioned, the main feature of the packing is that the ions are far apart with very few interactions between the phosphonium and $[Cd_2Cl_6]^{2-}$ ions. The interion van der Waals distances have acceptable values with the lowest Cd···H, Cl···H, Cl···C and C···C interactions being 3.37, 2.73, 3.76 and 3.42 Å, respectively.

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Détermination Structurale du μ -Butadiynylène-bis[triphénylétain(IV)]-Chloroforme, $[\text{Sn}_2\text{C}_4(\text{C}_6\text{H}_5)_6] \cdot \text{CHCl}_3$, et du μ -Butadiynylène-bis[triphénylplomb(IV)]-Dichlorométhane, $[\text{Pb}_2\text{C}_4(\text{C}_6\text{H}_5)_6] \cdot \text{CH}_2\text{Cl}_2$

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Abstract

Crystals of the compounds $(\text{C}_6\text{H}_5)_3\text{MC}_4\text{M}(\text{C}_6\text{H}_5)_3$ ($M = \text{Sn}, \text{Pb}$) present isotypical cubic cells whose lattice constants are $a = 15.55$ (1) Å (Sn) and $a = 15.40$ (1) Å (Pb). The space group is $Pa\bar{3}$ and there are four formula units in the unit cell. The structures have been determined at 238 K by single-crystal X-ray analysis and refined to final R values of 5% (Sn) and 7% (Pb). The Sn–C and Pb–C bond lengths are respectively 2.136 (5) and 2.202 (8) Å, but the metal substitution does not affect the bonding properties of the $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ diacetylene chain. Only a slight modification can be observed in the orientation of the phenyl groups inside the molecules: the angles between the aromatic plane and the C(phenyl)– M –C(diacetylene) plane are respectively $\theta_{\text{Sn}} = 49.6^\circ$ and $\theta_{\text{Pb}} = 53.2^\circ$. In each compound, solvent molecules are included in large cavities, and present orientational disorder phenomena.

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Introduction

Les molécules de diacétylène $R-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-R'$ peuvent présenter, suivant la nature de leurs substituants R et R' , un phénomène de polymérisation à l'état solide: c'est le cas, par exemple, du composé dans lequel $R = R' = \text{CH}_3-\text{C}_6\text{H}_4-\text{SO}_2-\text{O}-\text{CH}_2-$ (PTS) (Baughman, 1977; Wegner, 1977, 1978; Chance & Patel, 1978). Cette polymérisation peut être induite de diverses manières, en particulier par absorption de photons dans le proche UV. Les états électroniques excités du groupement $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ jouant un rôle déterminant dans le processus de photopolymérisation, Bertault, Fave & Schott (1979) se sont attachés à étudier l'état excité de plus basse énergie, soit l'état triplet, très peu connu jusqu'alors. Ces auteurs ont montré, par spectrographie d'excitation et d'émission sur monocristaux, que cet état triplet pouvait être mis en évidence dans les composés pour lesquels $R = R' =$

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