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Crystal and Molecular Structure of Bis(β-hydroxyethyltriphenylphosphonium) Tetrachlorocadmate

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*The molecular and crystal structures of the title compound were determined by X-ray diffraction using direct and Fourier methods (*R = *0.052 for 1875 non-zero independent reflections). Crystals are monoclinic, space-group* $P2_1/n$ *with* $4\{[CdCl_4]\cdot 2[(C_6H_5)_3PCH_2CH_2OH]\}$ *formula units in a unit-cell of dimensions* a = *18.010(8),* b = *18.574(8),* c = *12.178(6) Å, β = 93.03(6)°. The structure consists of a O–H---Cl hydrogen bonded array of β-hydroxyethyltriphenylphosphonium cations and tetrachlorocadmate anions, both of slightly distorted tetrahedral symmetry around the heavy atoms. The P–C(*sp^2*) bonds are in nearly* staggered *conformations (*gauche –, gauche +, *and* trans*) with respect to the C–C bond of the β-hydroxyethyl moiety. The most significant average bond distances are: Cd–Cl, 2.448(4) Å; P–C(*sp^2*) 1.77(1) Å with P–C(*sp^3*) 1.80(1) and O---Cl 3.11(1) Å. Interionic distances conform to normal van der Waals Distances.*

Introduction

During investigations on homogeneous catalysts, obtained by reacting CdX_2 (X = Cl, Br) with triphenylphosphine and RX (R = $-CH_2C_6H_5$, $-CH_2-CH_2OH$), several products were isolated. In previous papers [1–3] we have reported on the molecular and crystal structure of three of these reaction products which are built up of well separated ions. We now describe the structural features of a 1:2 complex obtained by reacting $CdCl_2$, $P(C_6H_5)_3$, and $ClCH_2CH_2OH$, expected to show more pronounced cation–anion interaction.

Experimental

Bis(β-hydroxyethyltriphenylphosphonium) tetrachlorocadmate, (I), was obtained in two different crystalline modifications by crystallization from various solvents. Using a mixture of *sym*-tetrachloroethane and DMF in the ratio 4:1, transparent needle-like crystals (I*a*) were obtained while a mixture of *sym*-tetrachloroethane and 1,2-butanediol in the ratio 4:1 gave transparent platelets (I*b*).

Crystals of (I*a*) were mounted on a Weissenberg camera (Cu-Kα radiation) for the determination of approximate unit-cell dimensions and space-group. A small crystal, essentially a parallelepiped, with dimensions 0.2 X 0.2 X 0.4 mm was then mounted on a Picker FACS 1 four-circle computer-controlled diffractometer equipped with a scintillation counter and a pulse-height analyser. Orientation matrix and refined unit-cell dimensions with their e.s.d. values were obtained from a least-squares fit of χ, ϕ, ω and 2θ values from 12 independent reflections.

Crystal Data

$C_{40}H_{40}O_2CdCl_4P_2$: Mol. wt. 868.95; monoclinic, a = 18.010(8), b = 18.574(8), c = 12.178(6) Å, β = 93.03(6)°; U = 4068.06 Å^3; Z = 4; D_o = 1.41 g cm^{-3}; D_c = 1.418 g cm^{-3}. Space-group $P2_1/n$ from systematic absences ($0k0$) for k odd, ($h0l$) for $h + l$ odd. F(000) = 1768; μ(Mo-Kα) = 9.1 cm^{-1}.

Intensity data were collected using Zr filtered Mo-Kα radiation (λ = 0.71069 Å), with the ω–2θ scanning technique in the angular range $5° \leqslant 2\theta \leqslant 35°$. The 2θ scan rate was 1° min^{-1} and the scan range 2.0° + Δ, where Δ was varied to allow for the separation of the Kα_1 and Kα_2 peaks at increasing 2θ values. Background counts were measured for 10 *s* each at the extremes of each scan. Three standard reflections were measured after every 50 reflections, and the oscillations (±7%) were used for scaling purposes. Out of the 2579 independent reflections measured 1875 were considered observed, having $I > 2\sigma(I)$ ($\sigma = [N_s + (t_s/t_b)^2 N_b]^{1/2}$, 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 0.5X the observable limit was assigned to the non-significant reflections. All intensities were corrected for Lorentz and polarization effects, but not for absorption (μR = 0.2).

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*Deceased.

TABLE I. Tangent Formula Results.

a) Tangent formula input

h	k	l	$\|E\|$	Phase angle	
7	7	1	3.54	2π	Origin fixing reflections
–4	7	0	2.84	π	
–1	4	0	2.73	π	
4	0	6	3.33	A	
–7	3	4	2.75	B	
8	3	1	2.54	C	

b) Tangent formula output

Numset	ABS FOM	ψ_0	Resid	Combined FOM
1	0.5970	1210	58.84	1.020
2	0.5851	1501	57.32	0.832
3	0.7068	1702	53.37	1.043
4	0.6910	1808	55.59	0.838
5	0.9530	2156	46.74	1.377
6	1.1792	2459	35.32	1.999
7	0.9531	2148	46.84	1.379
8	1.1792	2458	35.32	2.001

Determination and Refinement of the Structure

The structure was solved by the MULTAN procedure [4] in a straightforward manner. Normalized structure factor amplitudes $|E| \geqslant 1.213$ (600 reflections) were used to define the phase relationships; another 50 reflections of very low $|E|$ values (0.108–0.057) were input into the calculations for the sake of the ψ_0 figure of merit. Out of the 30331 phase relationships found 4990 were saved. The starting set was automatically chosen (Table I). From the eight possible sign combinations A, B and C (2π or π) the right solution (no. 8) stood out by its figures of merit (Table I); its phase angles A, B and C were π, 2π and π. An E-map phased with this information yielded the positional parameters of the tetrachlorocadmate anion. A subsequent $F(hkl)$ and $\rho\,(xyz)$ calculation based on this moiety permitted location of all non-hydrogen atoms of the molecule. Refinement was performed by means of a general least-squares program [5] minimizing $\Sigma w(|F_o| - |F_c|)^2$. Atomic scattering factors were taken according to refs. 6 and 7. Weights were attributed following Cruickshank *et al.* [8] according to the scheme: $1/w = A + B|F_o| + C|F_o|^2$, where $A = 2F_o$ (min), $B = 1$, and $C = 2/F_o$ max. After block-diagonal least-squares refinement of the positional and isotropic thermal parameters the conventional $R = \Sigma|k|F_o| - |F_c||/\Sigma k|F_o|$ value was 0.092 for the non-zero reflections. Allowance for thermal anisotropy and the introduction of carbon bonded hydrogen atoms in fixed positions into the F (hkl) calculations with B = 5.0 Å^2 led to rapid convergence to R = 0.052 for the non-zero reflections (R = 0.081 including non-observed reflections). At this stage the shifts of the atomic parameters were

TABLE II. Final Fractional Coordinates with Estimated Standard Deviations in Parentheses.

Atom	x/a	y/b	z/c
Cd	0.18871(6)	0.16848(6)	0.46583(8)
Cl(1)	0.2169(2)	0.1796(2)	0.2730(3)
Cl(2)	0.1591(2)	0.0441(2)	0.5145(3)
Cl(3)	0.2914(2)	0.2020(3)	0.5960(4)
Cl(4)	0.0859(2)	0.2511(2)	0.4961(3)
P(1)	–0.0152(2)	0.0523(2)	0.7668(3)
P(2)	0.4420(2)	0.0829(2)	0.2571(3)
C(1)	0.0205(7)	–0.0370(7)	0.7746(9)
C(2)	0.0878(7)	–0.0489(7)	0.8385(9)
C(3)	0.1144(7)	–0.1217(8)	0.8413(11)
C(4)	0.0786(8)	–0.1762(7)	0.7850(12)
C(5)	0.0158(8)	–0.1605(7)	0.7230(12)
C(6)	–0.0141(7)	–0.0930(7)	0.7197(11)
C(7)	–0.1033(7)	0.0569(6)	0.8318(10)
C(8)	–0.1402(7)	–0.0044(7)	0.8592(11)
C(9)	–0.2108(8)	0.0021(9)	0.9068(12)
C(10)	–0.2385(8)	0.0694(8)	0.9175(11)
C(11)	–0.2061(8)	0.1291(8)	0.8867(13)
C(12)	–0.1348(7)	0.1233(7)	0.8418(10)
C(13)	0.0483(7)	0.1117(7)	0.8359(10)
C(14)	0.0382(7)	0.1332(7)	0.9444(10)
C(15)	0.0890(8)	0.1796(9)	0.9971(12)
C(16)	0.1469(9)	0.2060(10)	0.9444(13)
C(17)	0.1589(9)	0.1843(10)	0.8376(14)
C(18)	0.1096(7)	0.1368(7)	0.7827(11)
C(19)	–0.0262(7)	0.0709(7)	0.6211(9)
C(20)	–0.0696(9)	0.1405(8)	0.5928(12)
C(21)	0.5384(7)	0.0767(7)	0.2658(9)
C(22)	0.5778(7)	0.0337(8)	0.3386(11)
C(23)	0.6532(8)	0.0283(8)	0.3482(11)
C(24)	0.6938(8)	0.0769(9)	0.2824(12)
C(25)	0.6584(8)	0.1207(8)	0.2071(12)
C(26)	0.5798(7)	0.1198(8)	0.1991(12)
C(27)	0.4011(7)	0.0024(7)	0.2983(10)
C(28)	0.3335(7)	0.0010(7)	0.3472(10)
C(29)	0.2986(8)	–0.0633(7)	0.3702(11)
C(30)	0.3285(9)	–0.1265(7)	0.3439(11)
C(31)	0.3958(8)	–0.1286(8)	0.2916(13)
C(32)	0.4334(8)	–0.0630(7)	0.2735(12)
C(33)	0.4094(7)	0.0985(7)	0.1206(9)
C(34)	0.3755(8)	0.1618(8)	0.0852(11)
C(35)	0.3513(11)	0.1727(9)	–0.0233(13)
C(36)	0.3615(8)	0.1209(9)	–0.0986(13)
C(37)	0.3927(10)	0.0560(11)	–0.0676(13)
C(38)	0.4173(9)	0.0484(9)	0.0440(12)
C(39)	0.4174(7)	0.1609(7)	0.3365(10)
C(40)	0.4562(7)	0.1659(8)	0.4536(12)
O(1)	–0.0375(5)	0.2016(5)	0.6478(8)
O(2)	0.4275(6)	0.1138(6)	0.5224(8)
H(2)	0.119	–0.005	0.881
H(3)	0.165	–0.134	0.891
H(4)	0.101	–0.230	0.789
H(5)	–0.012	–0.204	0.678
H(6)	–0.066	–0.083	0.671
H(8)	–0.116	–0.058	0.846
H(9)	–0.242	–0.045	0.932

(continued on facing page)

TABLE II. *(continued)*

Atom	x/a	y/b	z/c
H(10)	−0.291	0.073	0.958
H(11)	−0.235	0.181	0.895
H(12)	−0.104	0.172	0.816
H(14)	−0.007	0.111	0.991
H(15)	0.080	0.198	1.083
H(16)	0.183	0.244	0.985
H(17)	0.209	0.204	0.797
H(18)	0.120	0.120	0.698
H(191)	0.028	0.076	0.589
H(192)	−0.056	0.026	0.582
H(201)	−0.069	0.149	0.505
H(202)	−0.126	0.134	0.617
H(22)	0.547	0.001	0.397
H(23)	0.683	−0.011	0.403
H(24)	0.754	0.078	0.290
H(25)	0.691	0.157	0.156
H(26)	0.551	0.155	0.138
H(28)	0.307	0.054	0.367
H(29)	0.244	−0.063	0.409
H(30)	0.300	−0.177	0.363
H(31)	0.416	−0.181	0.265
H(32)	0.490	−0.065	0.241
H(34)	0.368	0.205	0.147
H(35)	0.322	0.224	−0.049
H(36)	0.347	0.132	−0.185
H(37)	0.397	0.010	−0.127
H(38)	0.445	−0.001	0.073
H(391)	0.432	0.208	0.291
H(392)	0.358	0.160	0.345
H(401)	0.515	0.157	0.448
H(402)	0.446	0.219	0.487

negligibly small and well below the corresponding e.s.d. A final ΔF map did not show the hydroxy hydrogen atoms and revealed no unexpected features. A list of F(obs) − F(calc) is available upon application to the Authors. Table II reports the final fractional coordinates of the atoms of the independent unit. Table III lists the anisotropic thermal parameters of the non-hydrogen atoms.

Results and Discussion

Figure 1 shows the structure of the independent unit of (**I***a*) together with the atom labelling scheme and thermal vibration ellipsoids. The crystal packing is shown in Fig. 2. Both figures were obtained by means of the ORTEP computing and drawing program [9]. The geometric parameters of (**I***a*) with the e.s.d. values are reported in Table IV.

The structure of (**I***a*) consists of tetrachlorocadmate anions and phosphonium cations. Each anion is linked through two Cl- - -H–O hydrogen bonds to two different phosphonium cations, thus establishing a well defined 1:2 complex.

Tetracoordinated ions may exhibit tetrahedral (T_d), distorted tetrahedral (D_{2d} or C_s) or square-planar (D_{4h}) symmetries. On the basis of the number of d-electrons and the spin state, T_d symmetry is predicted as the most stable structure for tetracoordinate d^{10} complexes [10]. This is confirmed for a variety of halide complexes of cadmium(II) [1–3, 11]. Distortions from T_d symmetry may occur, depending on many factors [12–14]. In (**I***a*) the

TABLE III. Anisotropic Thermal Parameters (Å^2) in the form exp $-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)$. Standard deviations are appended in brackets as units in the last place.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cd	4.99(6)	6.03(6)	5.50(6)	−0.90(5)	0.44(4)	−0.97(5)
Cl(1)	5.6(2)	7.4(2)	5.5(2)	−0.0(2)	0.5(2)	−0.7(2)
Cl(2)	4.2(2)	5.7(2)	6.7(2)	−0.6(2)	−0.2(2)	−0.7(2)
Cl(3)	6.3(3)	10.3(3)	7.0(2)	−3.0(2)	−0.2(2)	−1.2(2)
Cl(4)	7.1(2)	7.2(2)	7.4(2)	0.8(2)	1.1(2)	−2.2(2)
P(1)	3.6(2)	4.0(2)	4.3(2)	−0.1(2)	−0.2(1)	−0.4(2)
P(2)	4.1(2)	4.2(2)	4.2(2)	−0.1(2)	0.2(2)	0.4(2)
C(1)	4.7(7)	4.9(7)	2.9(6)	−0.8(6)	−0.1(5)	−0.2(5)
C(2)	5.5(8)	5.4(8)	2.7(6)	−0.0(6)	0.4(5)	−0.1(6)
C(3)	4.4(7)	7.1(9)	5.5(8)	0.4(7)	−1.3(6)	0.5(7)
C(4)	5.9(8)	4.7(8)	6.3(8)	1.0(6)	−0.7(6)	0.7(6)
C(5)	6.3(8)	3.9(7)	7.4(9)	1.6(6)	−2.0(7)	−3.3(7)
C(6)	4.6(7)	4.2(7)	6.9(8)	0.3(6)	0.3(6)	0.2(6)
C(7)	5.6(8)	3.5(7)	4.0(6)	−0.6(6)	0.4(6)	−1.3(5)
C(8)	4.5(7)	4.9(7)	5.8(8)	−0.3(6)	−0.5(6)	−0.9(6)
C(9)	5.0(8)	7.9(9)	6.2(8)	−0.3(7)	0.7(6)	−1.5(7)
C(10)	5.1(8)	7.9(9)	5.0(7)	−0.5(7)	−0.2(6)	−0.7(7)

(continued overleaf)

TABLE III. *(continued)*

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(11)	6.0(9)	6.2(9)	8.0(10)	1.3(7)	−0.1(7)	−0.0(8)
C(12)	6.0(8)	5.6(8)	3.9(7)	1.1(6)	0.4(6)	−0.2(6)
C(13)	4.2(7)	5.5(8)	4.1(7)	−0.6(6)	1.6(5)	0.2(6)
C(14)	5.2(8)	5.8(8)	3.9(7)	−0.6(6)	0.8(6)	−0.4(6)
C(15)	5.8(9)	8.3(10)	6.4(9)	−1.2(7)	−0.9(7)	0.2(8)
C(16)	7.8(10)	9.9(12)	7.2(10)	−2.2(9)	0.6(8)	−1.4(9)
C(17)	6.8(10)	10.2(12)	7.7(10)	−2.7(9)	0.9(8)	−0.7(9)
C(18)	4.8(8)	6.0(8)	4.9(7)	−0.9(6)	0.7(6)	−0.7(6)
C(19)	3.8(7)	5.1(7)	4.6(7)	0.9(6)	−0.6(5)	−0.8(6)
C(20)	7.3(9)	5.9(9)	6.4(9)	−0.2(7)	−0.5(7)	−1.0(7)
C(21)	4.1(7)	5.6(7)	3.0(6)	0.5(6)	0.4(5)	0.9(5)
C(22)	3.0(7)	7.6(9)	6.4(8)	1.5(6)	0.0(6)	1.4(7)
C(23)	4.8(8)	8.2(10)	5.8(8)	1.7(7)	−1.9(6)	1.7(7)
C(24)	4.6(8)	10.0(11)	6.7(9)	−0.6(8)	−1.4(7)	2.3(8)
C(25)	6.7(9)	6.8(9)	6.2(8)	−1.0(7)	1.2(7)	2.3(7)
C(26)	3.8(7)	6.7(9)	7.6(9)	0.1(6)	0.8(6)	2.0(7)
C(27)	5.3(8)	4.4(7)	3.9(7)	0.5(6)	0.3(6)	1.2(6)
C(28)	6.6(8)	4.3(7)	3.1(6)	−0.4(6)	0.4(6)	0.1(6)
C(29)	6.5(9)	4.9(8)	5.3(8)	−1.0(6)	1.7(6)	−0.4(6)
C(30)	9.1(10)	4.3(8)	5.5(8)	0.1(7)	−0.2(7)	−0.6(6)
C(31)	6.8(9)	4.5(8)	9.4(11)	0.3(7)	−1.3(8)	−1.2(7)
C(32)	4.8(8)	5.5(8)	7.3(9)	−1.0(6)	0.6(7)	0.4(7)
C(33)	4.2(7)	4.3(7)	3.8(6)	0.5(6)	−0.1(5)	0.4(6)
C(34)	7.4(9)	6.2(9)	4.5(8)	−1.0(7)	−1.2(7)	1.2(6)
C(35)	11.8(13)	7.4(10)	6.1(9)	0.2(9)	−2.3(9)	1.9(8)
C(36)	5.8(9)	9.3(11)	6.8(9)	1.0(8)	1.1(7)	0.4(8)
C(37)	9.1(11)	12.6(14)	5.1(8)	4.4(10)	−0.9(8)	−2.7(9)
C(38)	7.0(9)	8.4(10)	5.3(8)	1.3(8)	0.5(7)	−1.3(7)
C(39)	5.8(8)	3.6(7)	4.5(7)	−0.0(6)	0.7(6)	−1.2(6)
C(40)	4.5(8)	7.9(10)	6.6(9)	−1.2(7)	−0.0(6)	1.9(7)
O(1)	8.0(6)	5.6(5)	7.9(6)	1.5(5)	1.2(5)	0.7(5)
O(2)	10.7(8)	7.4(6)	6.3(6)	0.4(6)	−0.1(5)	−0.4(5)

TABLE IV. Molecular Parameters. Standard deviations are appended as units in the last significant digit.

a) Bond lengths (in Å)

Cd–Cl(1)	2.439(4)
Cd–Cl(2)	2.453(4)
Cd–Cl(3)	2.450(4)
Cd–Cl(4)	2.449(4)
Average	2.448(4)
P(1)–C(1)	1.78(1)
P(1)–C(7)	1.81(1)
P(1)–C(13)	1.77(1)
P(1)–C(19)	1.80(1)
P(2)–C(21)	1.74(1)
P(2)–C(27)	1.75(1)
P(2)–C(33)	1.76(1)
P(2)–C(39)	1.80(1)
C(1)–C(2)	1.43(2)
C(33)–C(34)	1.39(2)
C(34)–C(35)	1.38(2)
C(35)–C(36)	1.35(2)
C(36)–C(37)	1.36(3)
C(37)–C(38)	1.41(2)
C(38)–C(33)	1.34(2)
Average	1.37(2)
C(39)–C(40)	1.52(2)
C(40)–O(2)	1.39(2)

b) Bond angles (in degrees)

Cl(1)–Cd–Cl(2)	111.8(1)
Cl(1)–Cd–Cl(3)	114.4(1)
Cl(1)–Cd–Cl(4)	106.9(1)
Cl(2)–Cd–Cl(3)	104.5(1)
Cl(2)–Cd–Cl(4)	112.2(1)

c) Torsion angles (in degrees)

C(20)–C(19)–P(1)–C(1)	170
C(20)–C(19)–P(1)–C(7)	51
C(20)–C(19)–P(1)–C(13)	−72
C(40)–C(39)–P(2)–C(21)	−48
C(40)–C(39)–P(2)–C(27)	75
C(40)–C(39)–P(2)–C(33)	193
P(1)–C(19)–C(20)–O(1)	55
P(2)–C(39)–C(40)–O(2)	−71
C(19)–P(1)–C(1)–C(2)	125
C(19)–P(1)–C(1)–C(6)	−53
C(19)–P(1)–C(7)–C(8)	103
C(19)–P(1)–C(7)–C(12)	−70
C(19)–P(1)–C(13)–C(14)	147
C(19)–P(1)–C(13)–C(18)	−35

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TABLE IV. *(continued)*

C(2)–C(3)	1.43(2)
C(3)–C(4)	1.36(2)
C(4)–C(5)	1.35(2)
C(5)–C(6)	1.36(2)
C(6)–C(1)	1.37(2)
Average	1.38(2)

C(7)–C(8)	1.38(2)
C(8)–C(9)	1.42(2)
C(9)–C(10)	1.36(2)
C(10)–C(11)	1.32(2)
C(11)–C(12)	1.42(2)
C(12)–C(7)	1.36(2)
Average	1.38(2)

C(13)–C(14)	1.40(2)
C(14)–C(15)	1.39(2)
C(15)–C(16)	1.35(2)
C(16)–C(17)	1.38(2)
C(17)–C(18)	1.40(2)
C(18)–C(13)	1.40(2)
Average	1.39(2)

C(19)–C(20)	1.51(2)
C(20)–O(1)	1.41(2)

C(21)–C(22)	1.37(2)
C(22)–C(23)	1.36(2)
C(23)–C(24)	1.43(2)
C(24)–C(25)	1.35(2)
C(25)–C(26)	1.42(2)
C(26)–C(21)	1.38(2)
Average	1.39(2)

C(27)–C(28)	1.38(2)
C(28)–C(29)	1.38(2)
C(29)–C(30)	1.34(2)
C(30)–C(31)	1.40(2)
C(31)–C(32)	1.42(2)
C(32)–C(27)	1.39(2)
Average	1.38(2)

Cl(3)–Cd–Cl(4)	107.1(1)
Average	109.5(1)

C(1)–P(1)–C(7)	110.1(3)
C(1)–P(1)–C(13)	109.6(3)
C(1)–P(1)–C(19)	105.1(3)
C(7)–P(1)–C(13)	108.8(3)
C(7)–P(1)–C(19)	110.9(3)
C(13)–P(1)–C(19)	112.4(3)
Average	109.5(3)

C(21)–P(2)–C(27)	111.3(4)
C(21)–P(2)–C(33)	110.5(3)
C(21)–P(2)–C(39)	106.5(3)
C(27)–P(2)–C(33)	106.5(3)
C(27)–P(2)–C(39)	114.0(3)
C(33)–P(2)–C(39)	107.9(3)
Average	109.5(3)

P(1)–C(1)–C(2)	118.1(6)
P(1)–C(1)–C(6)	122.5(7)
P(1)–C(7)–C(8)	120.9(7)
P(1)–C(7)–C(12)	117.4(6)
P(1)–C(13)–C(14)	120.9(6)
P(1)–C(13)–C(18)	119.6(6)
P(1)–C(19)–C(20)	114.8(6)
C(19)–C(20)–O(1)	113.4(5)

P(2)–C(21)–C(22)	124.2(7)
P(2)–C(21)–C(26)	119.4(6)
P(2)–C(27)–C(28)	122.6(7)
P(2)–C(27)–C(32)	119.5(7)
P(2)–C(33)–C(34)	123.4(7)
P(2)–C(33)–C(38)	120.7(7)
P(2)–C(39)–C(40)	116.1(6)
C(39)–C(40)–O(2)	111.7(5)

The average value of the endocyclic angles of each phenyl group is 120.0(10)°

C(39)–P(2)–C(21)–C(22)	97
C(39)–P(2)–C(21)–C(26)	–80
C(39)–P(2)–C(27)–C(28)	28
C(39)–P(2)–C(27)–C(32)	203
C(39)–P(2)–C(33)–C(34)	3
C(39)–P(2)–C(33)–C(38)	183

d) Most significant non-bonded distances. (C- -C, C- -Cl and C- -O < 3.6 Å; Cl- -Cl < 4.0 Å; Cl- -O < 3.8 Å)

C(1)- -C(8)	3.18(2)
C(2)- -C(13)	3.07(2)
C(2)- -C(18)	3.54(2)
C(6)- -C(7)	3.53(2)
C(6)- -C(8)	3.34(2)
C(6)- -C(19)	3.29(2)
C(12)- -C(14)	3.30(2)
C(12)- -C(20)	3.31(2)
C(12)- -O(1)	3.35(2)
C(13)- -O(1)	3.16(2)
C(18)- -O(1)	3.27(2)
C(21)- -C(32)	3.22(2)
C(21)- -C(38)	3.43(2)
C(21)- -C(40)	3.23(2)
C(22)- -C(32)	3.24(2)
C(22)- -C(40)	3.60(2)
C(26)- -C(33)	3.19(2)
C(34)- -C(39)	3.13(2)
C(27)- -O(2)	3.43(2)
Cl(1)- -Cl(4)	3.925(5)
Cl(2)- -Cl(3)	3.875(6)
Cl(3)- -Cl(4)	3.940(6)
Cl(3)- -O(2)	3.13(1)
Cl(3)- -C(10)	3.58(1)
Cl(4)- -O(1)	3.10(1)

$[CdCl_4]^{2-}$ ion has a *quasi*-perfect tetrahedral symmetry with an average Cd–Cl bond length of 2.448(4) Å (range 2.439–2.453 Å) and an average value of the Cl–Cd–Cl bond angles of 109.5(1)° (range 104.5–114.4°). The shortest Cl- - -Cl distance (3.87 Å) is somewhat longer than the sum of the ionic radii (3.62 Å) of the chloride ions. The geometry conforms to other $[CdCl_4]^{2-}$ anions (*cf.* Table IV of ref. 3).

Using the equation $S = (R/R_o)^{-N}$, relating bond valence (S) and bond length (R) according to Brown and Shannon [15] with the parameters R_o = 2.155 Å and N = 5.4 [3], the valence sum around Cd(II) deviates only 0.01 valence unit from the atomic valence with similar discrepancies for each of the chlorine atoms. The fairly weak secondary bonding effects Cl- - -H–O, present in the structure, do not greatly influence the Cd–Cl bond lengths. It is noticed that in diquinolinium tetrachlorocadmate [16] stronger hydrogen bonding (N–H- - -Cl, 3.06 Å) affects more severe distortions in the $[CdCl_4]^{2-}$ anion from its inherent equilibrium configuration (Cd–Cl, 2.428–2.486(6) Å; deviations from tetrahedral angles up to 10°).

As in case of bis(triphenylbenzylphosphonium) cadmates [1–3], the $[(C_6H_5)_3PCH_2CH_2OH]^+$ cations of (I*a*) show a *quasi*-perfect tetrahedral symmetry with an average P–C(sp^2) bond length of 1.77

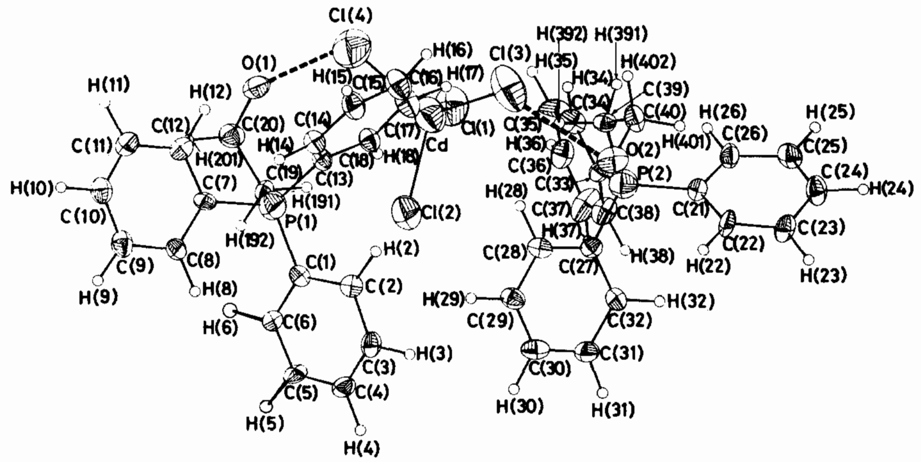

Fig. 1. The molecule of bis(β-hydroxyethyltriphenylphosphonium) tetrachlorocadmate, showing the atom labelling scheme and 30% probability thermal vibration ellipsoids.

TABLE V. Structural Data for O–H- - -Cl Bonded Structures.[a]

Compound[b]	O- - -Cl	<O–H- - -Cl	Method[c]	Ref.
$MnCl_2 \cdot 4H_2O$	3.168–3.291(2)	158.7–174.1(3)	N	18
	3.281–3.417(2)[d]	113.0–148.3(3)[d]	N	18
$MgCl_2 \cdot 6H_2O$	–	142.0–179.1(4)	N	19
$MgCl_6 \cdot 12H_2O$	3.112–3.261(8)	–	X	20
$BaCl_2 \cdot 2H_2O$	3.130–3.303(n.d.)	125.1–171.0(n.d.)	N	21
$CdCl_2 \cdot H_2O$	3.21–3.30(2)	143.3–158.4(n.d.)	X	22
$CuCl_2 \cdot 2H_2O$	3.176(n.d.)	170.7(n.d.)	N	23
$LiClO_4 \cdot 3H_2O$	2.986(n.d.)	158.0(n.d.)	N	24
$K_2CuCl_4 \cdot 2H_2O$	3.116(5)	173.3(5)	N	25
β-$RbMnCl_3 \cdot 2H_2O$	3.18–3.47(2)[d]	127–172(2)[d]	N	26
$CoCl_2 \cdot 2.5C_2H_5OH$	3.171–3.329(4)	–	X	27
$C_6H_{12}O_6 \cdot MgCl_2 \cdot 4H_2O$	2.986–3.268(4)	–	X	28
L-Glutamic acid·HCl	3.043(8)	170.3(10)	N	29
L-Lysine·HCl·$2H_2O$	3.220–3.254(5)	169.7–172.7(6)	N	30
Glycylglycine·HCl·H_2O	3.086(4)	161.1(5)	N	31
L-Tyrosine·HCl	3.045(3)	165.6(3)	N	32
Ephedrine·HCl	3.06(3)	–	X	33
Adenine·HCl·$0.5H_2O$	3.12(5)	–	X	34
Guanine·HCl·H_2O	3.16(4)	–	X	35
Tropolone·HCl	2.86–2.97(2)	–	X	36
D(–)Isoleucine·HCl	3.05–3.24(5)	–	X	37
$[Ni(C_5H_{11}N_2O)_2H^+]Cl^- \cdot H_2O$	3.176–3.199(6)	163.4–173.8(5)	N	38
$[Coen_3]Cl_3 \cdot 3H_2O$	3.34(n.d.)	–	X	39
$(C_6H_5)_3PO \cdot HCl$	2.747(2)	176.6(32)	X	40
$(C_6H_5)_3AsO \cdot HCl$	2.817–2.854(17)	–	X	41
$HCl \cdot H_2O$	2.95(1)	–	X	42
NH_3OHCl	3.042(9)	144.2(7)	N	43

[a] Distances in Å, angles in degrees. [b] en, ethylenediamine. [c] N, neutron diffraction; X, X-ray diffraction. [d] Bifurcated.

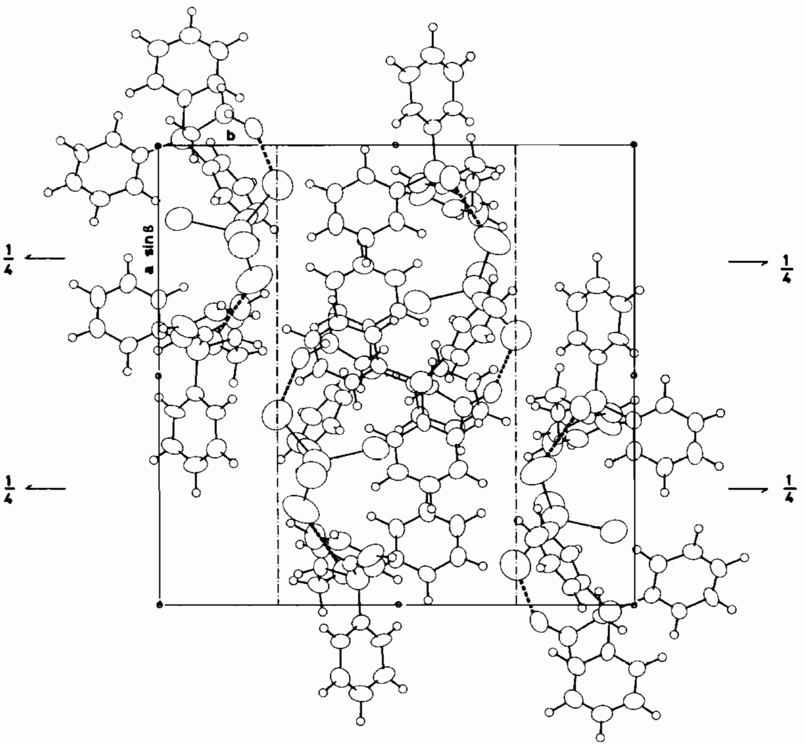

Fig. 2. Structure of bis(β-hydroxyethyltriphenylphosphonium)tetrachlorocadmate viewed down the c-axis.

Å (range 1.74–1.81 Å) and a slightly longer P–C(sp^3) distance of 1.80(1) Å. Distortion of the coordination sphere around the phosphorus atom, probably due to close contacts, is expressed by the spread in the C–P–C angles (105.1–114.0°). The mean value of the C–P–C bond angles is 109.5(3)° with no significant difference between C(sp^2)–P–C(sp^3) and C(sp^2)–P–C(sp^2). These values are in good agreement with other literature data concerning the organo-phosphonium ions [17].

The average value of the C$\overset{\cdots}{-}$C bond lengths of the phenyl rings is 1.38(2) Å (range 1.32–1.43 Å), while the average value of the endocyclic bond angles is 120.0° (range 115.8–125.5°). The dimensions of the β-hydroxyethyl moieties (Table IV) conform to expected values.

The conformation of the phosphonium cations may be described in terms of the torsion angles around the P–C(sp^3) bonds. In agreement with triphenylbenzylphosphonium cations [1–3] the P–C(sp^2) bonds are in nearly *staggered* conformation (*gauche* +, *gauche* – and *trans*) with respect to the C–C bond of the β-hydroxyethyl residues. The orientations of the phenyl groups, expressed by the torsion angles around the P–C(sp^2) bonds with respect to the P–CH$_2$ bond, are intermediate between *staggered* and *eclipsed* conformations. The C–O bonds are *gauche* ± with respect to the corresponding P–C(sp^3) bonds. No abnormally short non-bonded intramolecular distances are noticed (Table IV).

Hydroxy hydrogens (not included in the refinement) were positioned parallel to the C(20)–H(201) and C(40)–H(401) trajectories at d(O–H) = 1.0 Å. This leads to H- -Cl(3) and H- -Cl(4) distances of about 2.24 Å, and Cl(3)–H–O(2) and Cl(4)–H–O(1) bond angles of 136°, apparently conforming with Baur's requirement for hydrogen bonding involving positioning of the hydrogen atom as close as possible to a potential hydrogen bond acceptor [44]. This is also apparent from the fact that hydrogen bonding between hydroxy oxygen atoms and chlorine atoms has been postulated for O–H- -Cl separations in the range of 2.75 to 3.35 Å (Table V). The Cl- -O separations for Cl(3) and Cl(4) to O(2) and O(1) are 3.13(1) and 3.10(1) Å, respectively. The arrangement serves as a stabilizing influence for maintenance of the complex. This is at variance with the results from related crystal structures of $CdX_4\cdot 2[(C_6H_5)_3PCH_2C_6H_5]$ (X = Cl, Br) [1, 2] and $Cd_2Cl_6\cdot 2[(C_6H_5)_3PCH_2C_6H_5]$ [3].

An independent confirmation of the fact that the potential energy of the hydrogen atom has been influenced by an acceptor atom comes from the characteristic frequencies of the vibrations involving the hydroxy hydrogen atom. The O–H stretching vibration in the infrared is found at 3380 cm^{-1}. This may be compared with values of 3600 cm^{-1} for non hydrogen-bonded O–H groups, and the range of 3600 to 1700 cm^{-1} when the O–H group is involved in a hydrogen bond [45, 46]. The arrangement of the ions in the unit-cell is shown in Fig. 2. The main feature of the packing is hydrogen bonding between the two phosphonium cations and the $[CdCl_4]^{2-}$ anion, leading to a well-defined molecular entity (Fig. 1). Interionic van der Waals distances take up acceptable values with the lowest Cd- -H, Cl- -H, Cl- -C, C- -C, C- -H, C- -O, O- -H and H- -H interactions being 3.12, 2.52, 3.45, 3.48, 3.00, 3.06, 2.50 and 2.34 Å, respectively.

Crystal Structure of a Polymorph

As already mentioned above, different polymorphs of bis(β-hydroxyethyltriphenylphosphonium) tetrachlorocadmate were observed. Crystal data for modification (1*b*) are: monoclinic, a = 16.054(9), b = 14.741(10), c = 16.964(9) Å, β = 93.91(5)°; U = 4005.22 Å^3; Z = 4; D_c = 1.440 g cm^{-3}. Probable space-groups: *Cc* or *C*2/*c*, from systematic absences (*hkl*) for $h + k$ odd and (*h*0*l*) for l odd.

Following the experimental procedures described above, 3520 independent reflections were measured of which 1622 were considered as observed according to the criterion $I > 2\sigma(I)$. The MULTAN method failed to reveal the correct structure, whereas the Patterson synthesis indicated the Cd position (at an almost special position, $y \approx ½$) but failed to show a clear picture of the Cd co-ordination sphere. Subsequent $F(hkl)$ and $\rho(xyz)$ calculations led to a satisfactory location of the cations, but the $[CdCl_4]^{2-}$ anion was mirrored at (0 ½ 0). No further attempts were made to refine the structure, which is presumably either twinned or disordered (statistically or dynamically).

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