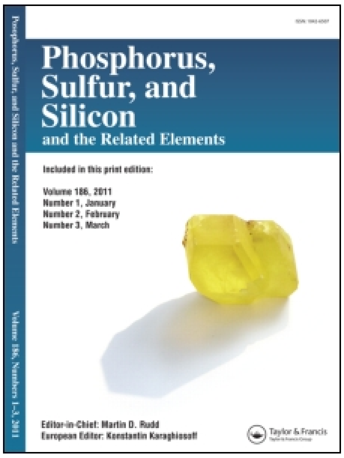

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CRYSTAL AND MOLECULAR STRUCTURE OF BIS(TRIPHENYLBENZYLPHOSPHONIUM) TETRABROMOCADMATE

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The molecular and crystal structure of *bis*(triphenylbenzylphosphonium)tetrabromocadmate has been determined by x-ray diffractometer data. Crystals are triclinic, space-group $P\bar{1}$ with two formula units in a unit-cell of dimensions $a = 12.506(6)$, $b = 10.471(5)$, $c = 18.396(13)$ Å, $\alpha = 93.07(4)°$, $\beta = 105.75(5)°$, $\gamma = 92.58(4)°$. The structure was solved by direct and Fourier methods and refined by least-squares techniques to $R = 0.061$ for 3723 independent observed reflections. The structure consists of tetrabromocadmate (II) anions and triphenylbenzylphosphonium cations, both with a *quasi*-perfect tetrahedral symmetry around the cadmium and phosphorus atoms. The most significant average bond distances are: Cd-Br, 2.588(2) Å, P—C (Phen), 1.794(5) Å and P—CH_2, 1.806(6) Å. The P—C (Phen) bonds are in slightly distorted *staggered* conformation (*gauche-*, *gauche* +, and *trans*) in respect of the C (Phen)-CH_2 bonds of the benzyl residues. The interatomic distances between the ions correspond to the usual Van der Waals distances.

INTRODUCTION

During investigations on homogeneous catalysts obtained by reacting CdX_2 (X = Cl, Br) with triphenylphosphine and $C_6H_5—CH_2X$, several products were isolated. In a previous paper we have reported on the molecular and crystal structure of the clathrate compound *bis*(triphenylbenzylphosphonium)tetrachlorocadmate · $2(C_2H_4Cl_2)$.[1] We have now extended this work to the reaction product obtained when X = Br to determine the nature of the ionic species present.

EXPERIMENTAL

Bis(triphenylbenzylphosphonium)tetrabromocadmate (I) was obtained in a stable crystalline form by crystallization from a mixture of butanediol and DMF in the ratio 4:1. Transparent, needle-like crystals of (I) were initially mounted on a Weissenberg camera (CuKα radiation) for the determination of approximate cell-dimensions and space-group.

A small crystal with dimensions 0.2 × 0.2 × 0.3 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

$C_{50}H_{44}CdBr_4P_2$: Mol. wt. 1138.93; triclinic, $a = 12.506(6)$, $b = 10.471(5)$, $c = 18.396(13)$ Å, $\alpha = 93.07(4)°$, $\beta = 105.75(5)°$, $\gamma = 92.58(4)°$; $U = 2310.7$ Å^3; $D_0 = 1.625$ g, cm^{-3}; $D_c = 1.636$ g.cm^{-3}; $Z = 2$; m.p. 226°C. Space-group $P\bar{1}$ from structure determination. μ(MoKα) = 42.0 cm^{-1}, F(000) = 562. Intensity data were collected with Zr filtered MoKα radiation (λ = 0.71069 Å) in the angular range $5° \leqslant 2\theta \leqslant 45°$, using the moving-crystal moving-counter technique with a 2θ scan rate of 1° min^{-1} and a scan range of (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 2θ scan. Three standard reflections were measured periodically to monitor intensity fluctuations during the data collection (up to ± 5%). Of the 5992 independent reflections measured, 3723 were assumed as significant according to the criterion $I \geqslant 2.5\sigma(I)$ ($\sigma = [N_s + (t_s/t_b)^2 N_b]^{1/2}$, 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 0.5 times the observable limit was assigned to the non significant reflections. All intensities were corrected for Lorentz and polarization effects, but not for absorption (μR = 0.63).

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The structure was solved by the MULTAN procedure[2] in a straightforward manner.

Refinement was performed by means of a general least-squares program[3] which minimizes $\sum w(|F_0| - |F_c|)^2$. Atomic scattering factors were calculated according to Ref. 4 with the values of Ref. 5 for the parameters. Weights were attributed according to Cruickshank *et al.*[6] After block-diagonal least-squares refinement of the positional

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† Deceased.

and isotropic thermal parameters the conventional $R = \sum \,|k|F_0| - |F_c|\,|/k|F_0|$ value was 0.095 for the non-zero reflections. After allowance for thermal anisotropy and the introduction of hydrogen atoms in fixed positions into the structure factor calculations with $B = 5.0$ Å^2, the refinement rapidly converged to $R = 0.061$ at a point when the shifts were negligibly small and well below the corresponding e.s.d. A final ΔF map did not show unexplained features.

Table 1 reports the final fractional coordinates and the corresponding standard deviations (in

TABLE I

Final fractional coordinates with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Cd	0.12859(8)	0.34529(9)	0.29071(5)
Br(1)	0.01707(11)	0.32369(14)	0.14640(8)
Br(2)	−0.00243(13)	0.36835(15)	0.37587(9)
Br(3)	0.24572(13)	0.14784(15)	0.31930(9)
Br(4)	0.25582(14)	0.55070(16)	0.30798(11)
P(1)	0.7157(2)	0.0945(3)	0.3890(2)
P(2)	0.8007(3)	0.6351(3)	0.0365(2)
C(1)	0.6156(9)	−0.0227(11)	0.4032(7)
C(2)	0.6329(12)	−0.0754(12)	0.4749(7)
C(3)	0.5542(12)	−0.1598(12)	0.4879(7)
C(4)	0.4595(13)	−0.1938(14)	0.4308(8)
C(5)	0.4383(12)	−0.1399(15)	0.3594(9)
C(6)	0.5161(11)	−0.0526(14)	0.3468(8)
C(7)	0.6787(10)	0.2529(12)	0.4117(6)
C(8)	0.7515(11)	0.3410(13)	0.4602(7)
C(9)	0.7252(14)	0.4607(15)	0.4743(10)
C(10)	0.6185(16)	0.4946(16)	0.4445(10)
C(11)	0.5382(13)	0.4068(16)	0.3935(11)
C(12)	0.5682(11)	0.2843(13)	0.3792(8)
C(13)	0.7169(9)	0.0783(12)	0.2917(7)
C(14)	0.7466(10)	0.1924(12)	0.2602(8)
C(15)	0.7639(13)	0.1851(16)	0.1889(9)
C(16)	0.7517(13)	0.0645(16)	0.1505(8)
C(17)	0.7258(14)	−0.0424(15)	0.1831(8)
C(18)	0.7118(12)	−0.0362(13)	0.2524(7)
C(19)	0.8556(9)	0.0715(11)	0.4460(7)
C(20)	0.9024(10)	−0.0460(12)	0.4163(6)
C(21)	0.8887(10)	−0.1677(12)	0.4403(7)
C(22)	0.9359(11)	−0.2693(14)	0.4148(8)
C(23)	1.0045(12)	−0.2539(15)	0.3666(8)
C(24)	1.0209(12)	−0.1301(14)	0.3439(8)
C(25)	0.9702(11)	−0.0293(14)	0.3709(8)
C(26)	0.7411(10)	0.5797(12)	0.1093(7)
C(27)	0.7921(12)	0.6158(15)	0.1837(9)
C(28)	0.7403(15)	0.5717(16)	0.2376(9)
C(29)	0.6427(14)	0.4996(13)	0.2174(9)
C(30)	0.5920(14)	0.4682(14)	0.1426(9)
C(31)	0.6433(14)	0.5044(14)	0.0889(8)
C(32)	0.6988(9)	0.7200(12)	−0.0255(7)
C(33)	0.6073(11)	0.7673(17)	−0.0080(7)
C(34)	0.5324(11)	0.8350(14)	−0.0568(9)
C(35)	0.5479(11)	0.8583(12)	−0.1283(8)
C(36)	0.6370(12)	0.8130(15)	−0.1490(9)
C(37)	0.7119(12)	0.7444(13)	−0.0976(9)
C(38)	0.9223(12)	0.7399(13)	0.0773(8)
C(39)	0.9205(13)	0.8680(13)	0.0620(9)
C(40)	1.0127(14)	0.9508(14)	0.1002(10)
C(41)	1.1048(13)	0.9041(16)	0.1496(9)
C(42)	1.1055(10)	0.7791(14)	0.1630(9)
C(43)	1.0157(10)	0.6931(12)	0.1292(8)
C(44)	0.8437(11)	0.5036(13)	−0.0137(7)
C(45)	0.7508(11)	0.3993(12)	−0.0521(7)
C(46)	0.7483(15)	0.2855(15)	−0.0170(9)
C(47)	0.6706(14)	0.1881(15)	−0.0576(9)
C(48)	0.6032(15)	0.2035(20)	−0.1254(11)
C(49)	0.6072(13)	0.3186(16)	−0.1608(8)
C(50)	0.6848(13)	0.4130(16)	−0.1244(9)
H(2)	0.707	−0.048	0.519
H(3)	0.568	−0.200	0.542
H(4)	0.397	−0.264	0.440
H(5)	0.362	−0.167	0.314
H(6)	0.502	−0.010	0.292
H(8)	0.834	0.311	0.490
H(9)	0.784	0.533	0.509
H(10)	0.595	0.588	0.460
H(11)	0.456	0.436	0.367
H(12)	0.508	0.214	0.344
H(14)	0.757	0.283	0.293
H(15)	0.789	0.271	0.162
H(16)	0.732	0.082	0.090
H(17)	0.732	−0.115	0.141
H(18)	0.707	−0.110	0.293
H(191)	0.908	0.156	0.443
H(192)	0.854	0.061	0.503
H(21)	0.837	−0.180	0.478
H(22)	0.921	−0.367	0.433
H(23)	1.043	−0.333	0.346
H(24)	1.072	−0.119	0.305
H(25)	0.989	0.066	0.354
H(27)	0.868	0.676	0.200
H(28)	0.781	0.596	0.296
H(29)	0.605	0.466	0.261
H(30)	0.512	0.416	0.124
H(31)	0.608	0.471	0.030
H(33)	0.596	0.748	0.048
H(34)	0.460	0.871	−0.040
H(35)	0.488	0.911	−0.169
H(36)	0.651	0.829	−0.203
H(37)	0.783	0.709	−0.112
H(39)	0.850	0.904	0.019
H(40)	1.009	1.053	0.091
H(41)	1.175	0.972	0.178
H(42)	1.180	0.746	0.200
H(43)	1.107	0.594	0.144
H(441)	0.876	0.542	−0.057
H(442)	0.908	0.458	0.026
H(46)	0.807	0.275	0.039
H(47)	0.665	0.094	−0.033
H(48)	0.546	0.129	−0.156
H(49)	0.547	0.332	−0.215
H(50)	0.695	0.499	−0.152

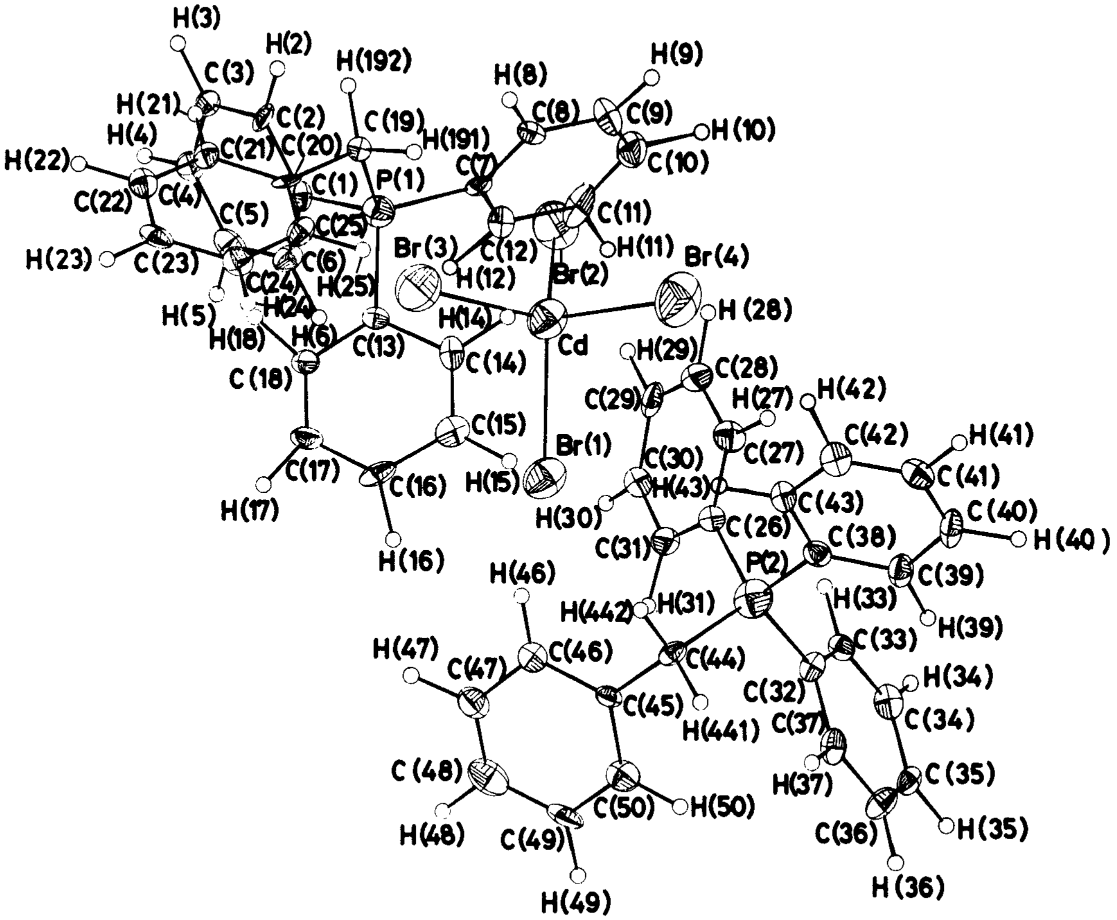

FIGURE 1 View of $[CdBr_4]^{2-}\cdot 2[(C_6H_5)_3PCH_2C_6H_5]^+$ indicating the atom labelling scheme and 30% probability thermal vibration ellipsoids.

parentheses) of the atoms of the independent unit. The anisotropic thermal parameters of the non-hydrogen atoms and the list of calculated and observed structure amplitudes, together with details about the structure solution (tangent formula results) have been deposited.†

RESULTS AND DISCUSSION

A view of the structure of a molecule of (I) is shown in Figure 1 together with the atom labelling scheme and the thermal vibration ellipsoids. The packing of the molecules in the crystals is shown in Figure 2.

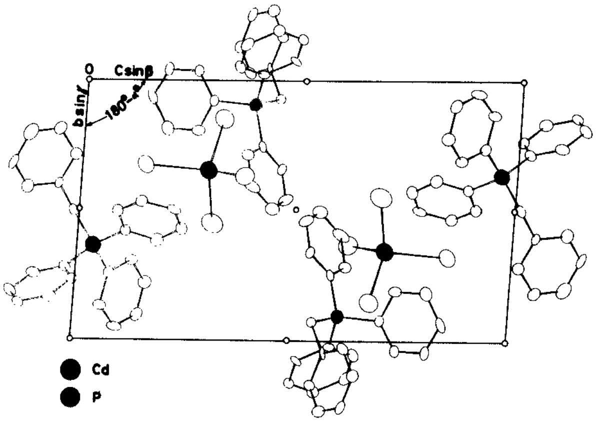

FIGURE 2 Packing arrangement of $[CdBr_4]^{2-}\cdot 2[(C_6H_5)_3PCH_2C_6H_5]^+$ as viewed down the a axis of the unit-cell.

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† Copies are available at the Cambridge Crystallographic Data Centre, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW, England.

TABLE II

Molecular parameters. Standard deviations are appended as units in the last place

a) Bond distances (Å)

Cd—Br(1)	2.635(2)
Cd—Br(2)	2.566(2)
Cd—Br(3)	2.582(2)
Cd—Br(4)	2.570(2)
Average	2.588(2)
P(1)—C(1)	1.794(12)
P(1)—C(7)	1.800(12)
P(1)—C(13)	1.793(12)
P(1)—C(19)	1.812(13)
P(2)—C(26)	1.809(14)
P(2)—C(32)	1.771(15)
P(2)—C(38)	1.795(15)
P(2)—C(44)	1.799(12)
C(1)—C(2)	1.424(21)
C(1)—C(6)	1.397(21)
C(2)—C(3)	1.371(20)
C(3)—C(4)	1.371(24)
C(4)—C(5)	1.420(26)
C(5)—C(6)	1.380(21)
Average	1.394(22)
C(7)—C(8)	1.368(18)
C(7)—C(12)	1.410(19)
C(8)—C(9)	1.341(19)
C(9)—C(10)	1.368(30)
C(10)—C(11)	1.431(20)
C(11)—C(12)	1.384(20)
Average	1.384(21)
C(13)—C(14)	1.433(19)
C(13)—C(18)	1.357(20)
C(14)—C(15)	1.384(22)
C(15)—C(16)	1.395(21)
C(16)—C(17)	1.364(25)
C(17)—C(18)	1.333(20)
Average	1.378(21)
C(19)—C(20)	1.524(15)
C(20)—C(21)	1.388(19)
C(20)—C(25)	1.354(18)
C(21)—C(22)	1.362(18)
C(22)—C(23)	1.401(20)
C(23)—C(24)	1.406(23)
C(24)—C(25)	1.392(18)
Average (phenyl)	1.384(19)
C(26)—C(27)	1.368(22)
C(26)—C(31)	1.375(21)
C(27)—C(28)	1.411(23)
C(28)—C(29)	1.356(25)
C(29)—C(30)	1.366(26)
C(30)—C(31)	1.376(22)
Average	1.375(23)
C(32)—C(33)	1.375(16)
C(32)—C(37)	1.416(22)
C(33)—C(34)	1.363(24)
C(34)—C(35)	1.414(22)
C(35)—C(36)	1.367(19)
C(36)—C(37)	1.393(26)
Average	1.388(21)
C(38)—C(39)	1.386(21)
C(38)—C(43)	1.418(23)
C(39)—C(40)	1.407(24)
C(40)—C(41)	1.386(28)
C(41)—C(42)	1.346(23)
C(42)—C(43)	1.389(19)
Average	1.389(23)
C(44)—C(45)	1.549(19)
C(45)—C(46)	1.388(23)
C(45)—C(50)	1.380(25)
C(46)—C(47)	1.407(24)
C(47)—C(48)	1.324(31)
C(48)—C(49)	1.406(30)
C(49)—C(50)	1.363(23)
Average (phenyl)	1.378(26)

b) Bond angles (degrees)

Br(1)—Cd—Br(2)	111. 38(3)
Br(1)—Cd—Br(3)	108.15(4)
Br(1)—Cd—Br(4)	105.61(4)
Br(2)—Cd—Br(3)	111.85(3)
Br(2)—Cd—Br(4)	109.20(3)
Br(3)—Cd—Br(4)	110.48(4)
Average	109.4(9)
C(1)—P(1)—C(7)	109.9(3)
C(1)—P(1)—C(13)	108.3(3)
C(1)—P(1)—C(19)	112.3(3)
C(7)—P(1)—C(13)	110.0(3)
C(7)—P(1)—C(19)	109.0(3)
C(13)—P(1)—C(19)	107.2(3)
Average	109.5(7)
C(26)—P(2)—C(32)	107.5(4)
C(26)—P(2)—C(38)	110.6(4)
C(26)—P(2)—C(44)	111.3(3)
C(32)—P(2)—C(38)	109.4(4)
C(32)—P(2)—C(44)	111.2(4)
C(38)—P(2)—C(44)	106.9(3)
Average	109.5(7)
P(1)—C(1)—C(2)	119.5(7)
P(1)—C(1)—C(6)	120.1(7)
P(1)—C(7)—C(8)	122.9(7)
P(1)—C(7)—C(12)	117.5(7)
P(1)—C(13)—C(14)	116.2(7)
P(1)—C(13)—C(18)	123.6(7)
P(1)—C(19)—C(20)	111.4(5)
C(19)—C(20)—C(21)	122.8(6)
C(19)—C(20)—C(25)	118.6(6)
P(2)—C(26)—C(27)	119.7(8)
P(2)—C(26)—C(31)	119.4(8)
P(2)—C(32)—C(33)	124.5(7)
P(2)—C(32)—C(37)	118.8(8)
P(2)—C(38)—C(39)	119.4(7)
P(2)—C(38)—C(43)	119.8(7)
P(2)—C(44)—C(45)	115.4(5)
C(44)—C(45)—C(46)	117.9(7)
C(44)—C(45)—C(50)	119.7(8)

The average value of the endocyclic angles of the phenyl groups is 120.0(3)°

c) Torsion angles (in degrees)

C(20)—C(19)—P(1)—C(1)	72
C(20)—C(19)—P(1)—C(7)	194
C(20)—C(19)—P(1)—C(13)	−47
C(45)—C(44)—P(2)—C(26)	58
C(45)—C(44)—P(2)—C(32)	−62
C(45)—C(44)—P(2)—C(38)	179
P(1)—C(19)—C(20)—C(21)	−90
P(1)—C(19)—C(20)—C(25)	98
P(2)—C(44)—C(45)—C(46)	−103
P(2)—C(44)—C(45)—C(50)	87
C(19)—P(1)—C(1)—C(2)	31
C(19)—P(1)—C(1)—C(6)	205
C(19)—P(1)—C(7)—C(8)	5
C(19)—P(1)—C(7)—C(12)	187
C(19)—P(1)—C(13)—C(14)	−87
C(19)—P(1)—C(13)—C(18)	80
C(44)—P(2)—C(26)—C(27)	116
C(44)—P(2)—C(26)—C(31)	−65
C(44)—P(2)—C(32)—C(33)	140
C(44)—P(2)—C(32)—C(37)	−42
C(44)—P(2)—C(38)—C(39)	125
C(44)—P(2)—C(38)—C(43)	−60

Both figures have been obtained by means of the ORTEP computing and drawing program.[7] The geometric parameters of the molecule with their estimated standard deviations are reported in Table II. The structure of (I) is built up of well separated tetrabromocadmate anions and phosphonium cations, not unlike the situation encountered in the clathrate *bis*(triphenylbenzylphosphonium)tetrachlorocadmate. $2(Cl_2C_2H_4)$ (II). This is in accordance with the views held by Cotton *et al.*[8] with regard to analogous Ni(II) compounds and contrasts with the proposals of Yamamoto.[9]

The $[CdBr_4]^{2-}$ ion in (I) has a *quasi*-perfect tetrahedral symmetry with an average Cd—Br bond length of 2.588(2) Å (range 2.566–2.635 Å) and an average value of the Br—Cd—Br angles of 109.4(9)° (range 105.6–111.8°). The $[CdBr_4]^{2-}$ structure may be compared to the edge-condensed $[Cd_2Br_6]^{2-}$ bitetrahedron[10] with $\langle Cd—Br_t \rangle$ = 2.528(5) and $\langle Cd—Br_b \rangle$ = 2.672(5) Å. It is noticed that also in case of $[CdCl_4]^{2-}$ and $[Cd_2Cl_6]^{2-}$ the shorter $Cd—Cl_t$ bonds are found in the bitrahedron.[11] This is rationalized by bond-strength analysis. Using the equation $s = (R/R_o)^{-N}$, relating bond-strength (s) and bond length (R) according to Brown and Shannon[12] with the parameters $R_0 = 2.307$ Å and $N = 6$ of Brown *et al.*,[13] the valence sum around Cd(II) in (I) deviates only 0.01 valence unit (v.u.) from the atomic valence, with discrepancies up to 0.05 v.u. for the bromine atoms. In the absence of secondary bonding effects (hydrogen bonding, etc.) the dimensions of the $[CdBr_4]^{2-}$ anion, as determined here for the first time, are to be considered as characteristic of the species.

The recent crystal structure determinations of dichinoliniumtetrachlorocadmate (III),[14] *bis*-(β-hydroxyethyltriphenylphosphonium) tetrachlorocadmate (IV),[15] thiaminium tetrachlorocadmate monohydrate (V)[16] and the clathrate mentioned above (II)[1] allow comparison of $[CdBr_4]^{2-}$ with the tetrahedral $[CdCl_4]^{2-}$ ion with $Cd—Cl_t$ bond distances of 2.457(6) (III), 2.448(4) (IV), 2.453(1) (V) and 2.441(5) Å (II). The difference in bond distance is close to the value expected on the basis of the ionic radii of the chloride and bromide ions ($\Delta r = 0.17$ Å). It is also noticed that octahedral Cd—Br distances, usually of $Cd—Br_b$ type, are considerably longer than $Cd—Br_t$ bond lengths (cf. also Ref. 11). Examples are $CdBr_2$(solid) (2.76 Å),[17] $CdBr_2 \cdot 4H_2O$ (2.746(4) Å)[18], $CdBr_2(C_5H_5N)_2$ (2.76 Å),[19] $RbCdBr_3$(2.626–2.866(2) Å)[13], $CdBr_2$ (dioxan) (2.73(1) Å)[20] and $\{CdBr[SC(CH_3)_2CH(NH_3)COO]H_2O\} \cdot 2H_2O$ (2.625–3.049(1) Å).[21] Even longer $Cd—Br_t$ distances have been observed for seven co-ordinate cadmium(II) in (*N*,*N*′-3,7-diazanonane-1,9-diyl)-2,6-diacetiminopyridine) bromocadmium(II)tetrabromocadmium(II), 2.775 (3) and 3.037(3) Å.[22] The shortest Br—Br distance in $[CdBr_4]^{2-}$ of (I) (4.146 Å; mean 4.225 Å) is somewhat longer than the sum of the ionic radii of the bromide ions (3.90 Å).

As in the case of the clathrate (II), the two $[(C_6H_5)_3PCH_2C_6H_5]^+$ cations of (I) show a *quasi*-perfect tetrahedral symmetry with an average P—C(Phen) bond length of 1.794(5) Å (range 1.771–1.809 Å) and a $P—CH_2$ average distance of 1.806(6) Å (range 1.799–1.812 Å); the mean value of the C—P—C bond angles is 109.5° (range 106.9°–112.3°). These values are in good agreement with the literature data concerning the organophosphonium ions.[1,23]

The average value of the C $\overset{\dots}{=}$ C bond lengths of the phenyl rings is 1.384(4) Å (range 1.324–1.433 Å), while the average value of the endocyclic bond angles is 120.0(3)° (range 116.2(7)–122.7(7)°). The average exocyclic $C(sp^3)$–$C(sp^2)$ bond measures 1.536(9) Å.

The conformation of the phenyl rings and of the benzyl groups around the phosphorus atoms is best described in terms of the torsional angles around the $P—CH_2$ bonds. The P—C(Phen) bonds are in nearly *staggered* conformation (*gauche* +, *gauche* −, and *trans*) with the CH_2—C (Phen) bond of the benzyl residues. The values of the torsional angles around the P—C(Phen) bonds in respect of the $P—CH_2$ bonds indicate conformations intermediate between *staggered* and *eclipsed*. The situation is analogous to the conformation of the cations in *bis*(triphenylbenzylphosphonium) tetrachlorocadmate $\cdot 2(Cl_2C_2H_4)$.[1] No abnormally short non-bonded intramolecular distances are worth reporting.

The arrangement of the ions in the unit-cell is shown in Figure 2. The remarkable aspect of the packing is that the phosphonium ions are far apart with very few interactions with the $[CdBr_4]^{2-}$ ions. The shortest Van der Waals distances for Cd --- H, Br --- H, Br --- C, P --- H, C --- C, C --- H and H --- H are the normal values of 3.68, 2.76, 3.63, 3.44, 3.64, 2.76 and 2.42 Å, respectively.

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