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Key indicators

Single-crystal X-ray study
T = 120 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.026
wR factor = 0.058
Data-to-parameter ratio = 18.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Triphenyl(benzoylmethyl)phosphonium hexabromodicadmate(II): supramolecular aggregation through extensive C—H···Br and C—H···O interactions

In the title phosphonium metalate, $(\text{C}_{26}\text{H}_{22}\text{OP})_2[\text{Cd}_2\text{Br}_6]$, the two methylene H atoms of the cation are involved in C—H···Br and C—H···O interactions. These interactions link the cations and the centrosymmetric anions to form rings of graph-set $R_2^2(9)$ and $R_2^2(12)$, and form chains along the *c* axis.

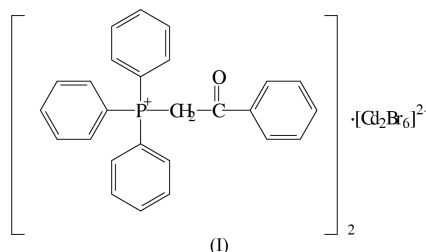
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Comment

Hg^{II} salts exhibit strong reactivity with benzoylmethylenetriphenylphosphorane (BPPY) to form organometallics (Kalyanasundari *et al.*, 1995, 1999). In order to determine the mode of reactivity of the ylide with a cadmium salt, the reaction between BPPY and $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ was carried out. The ^1H NMR data in $\text{DMSO}-d_6$ indicated the formation of a phosphonium derivative and also revealed that it was different from $[(\text{C}_6\text{H}_5)_3\text{PCH}_2\text{COC}_6\text{H}_5]^+\text{Br}^-$. A single-crystal X-ray diffraction experiment was then performed to obtain the structural details of the new phosphonium derivative, (I).



The results show that centrosymmetric dimers are formed from CdBr_3 and $\text{Ph}_3\text{PCH}_2\text{COPh}$ units, yielding $\text{Cd}_2\text{Br}_6^{2-}$ ions in which Cd^{2+} is tetrahedrally coordinated by two terminal and two bridging Br^- ions (Fig. 1). The $\text{Cd}_2\text{Br}_6^{2-}$ ion is interposed between the two phosphonium cations, and the two bridging Br^- ions are unsymmetrically bonded to Cd. The H1—C1—H2 angle [$107.97(1)^\circ$] indicates that the angle around the ylidic carbon of the parent ylide [$115.3(4)^\circ$ and $123.0(4)^\circ$ corresponding to two non-equivalent molecules in the asymmetric unit; Kalyanasundari *et al.*, 1994] has been reduced because of protonation at the ylidic carbon. The torsion angle P1—C1—C2—O1 [$19.1(3)^\circ$] is slightly larger than those found in the parent ylide [$0.9(8)$ and $-2.2(9)^\circ$] and confirms the near *cis* orientation of the P and O centres. The P1···O1 distance [$2.918(2) \text{ \AA}$] is comparable to that observed in the parent ylide and is significantly shorter than the sum of the van der Waals radii of P and O (3.3 \AA ; Dunitz, 1979).

The dimeric structure is stabilized mainly by two types of secondary interactions, *viz.* a C1—H1···O1 interaction and a C1—H2···Br1 interaction (Table 2). The former, which links

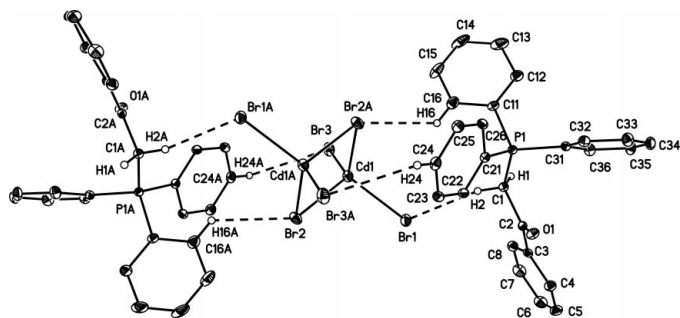


Figure 1
Displacement ellipsoid plot (30% probability) of (I), showing the centrosymmetric dimers formed by the cations through hydrogen bonding with the anion. H atoms not involved in hydrogen bonding have been omitted for clarity.

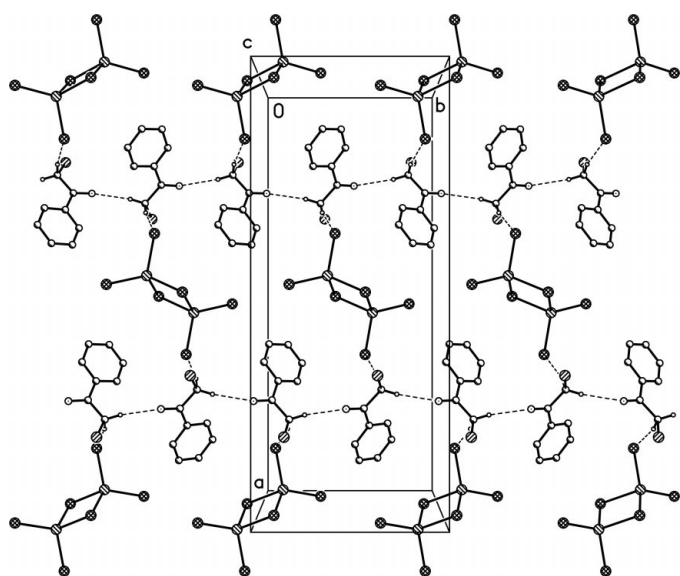


Figure 2
Packing plot showing the two main C—H interactions forming layers of cations and anions perpendicular to the *a* axis. H atoms, except for H1 and H2, and the C atoms of the phenyl rings of the triphenylphosphonium fragment have been omitted for clarity.

the cations along the *b* axis (Fig. 2), can be considered to be strong (Jeffrey, 1997), with the H1...O1 distance being 2.48 (3) Å and the C1—H1...O1 angle 167 (2)°. The latter, an interaction between H2 and Br1 within the asymmetric unit at a distance of 3.584(2) Å, is comparable to the corresponding distance in the adduct of CHCl₃ and Br[−] (3.56 Å in an average of four structures; Steiner, 1998). In conjunction, both interactions link cations and anions along the *c* axis, forming layers perpendicular to the *a* axis, as shown in Fig. 2. These layers are linked along the *a* axis through other weaker C—H...Br interactions, summarized in Table 2. The hydrogen bonding in the ylide Ph₃PCHPh (Yufit *et al.*, 2000) and in the phosphonium salts (Baby Mariyatra *et al.*, 2002) may arise due to the acidity of the CH or CH₂ group, respectively.

The phosphonium metalate formation contrasts with the C-coordination of the BPPY with Hg^{II} (Kalyanasundari *et al.*, 1995) and the O-coordination with U^{VI} (Kalyanasundari, 1998). It is, however, comparable to the formation of a tetra-

chlorocobaltate salt formed by the reaction of the same ylide with CoCl₂·6H₂O (Albanese *et al.*, 1989). The formation of the phosphonium and Cd₂Br₆^{2−} ions can be explained by the initial hydrolysis of CdBr₂, forming HBr, with subsequent interaction of a proton and Br[−] with the ylidic carbon and CdBr₂, respectively.

Experimental

The title compound was prepared by the reaction of CdBr₂ and benzoylmethylenetriphenylphosphorane (BPPY) in methanol in a 1:1 ratio. Slow evaporation of the solvent gave twinned crystals. ¹H NMR (DMSO-*d*₆, p.p.m.): δ 6.12 [*d*, 2H, ²*J*(P—H) = 13.2 Hz], 7.36–8.08 (*m*, 20H). Diffraction quality crystals of (I) were obtained by recrystallizing these crystals in ethanol.

Crystal data

(C₂₆H₂₂OP)₂[Cd₂Br₆]
M_r = 1467.08
Orthorhombic, *Pbcn*
a = 25.7075 (15) Å
b = 10.7351 (9) Å
c = 18.8469 (14) Å
V = 5201.2 (7) Å³
Z = 4
*D*_x = 1.874 Mg m^{−3}

Mo *K*α radiation
Cell parameters from 736 reflections
θ = 10.3–20.5°
μ = 5.53 mm^{−1}
T = 120 (2) K
Irregular prism, colourless
0.42 × 0.28 × 0.15 mm

Data collection

Bruker SMART 6000 CCD diffractometer
ω scans
Absorption correction: by integration (*XPREP* in *SHELXTL*; Bruker, 1998)
*T*_{min} = 0.221, *T*_{max} = 0.531
30677 measured reflections

7011 independent reflections
5580 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.033
*θ*_{max} = 29.2°
h = −30 → 35
k = −14 → 14
l = −25 → 22

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.026
wR (*F*²) = 0.058
S = 1.02
7011 reflections
377 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0241P)^2 + 2.9606P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/*σ*)_{max} = 0.005
Δ*ρ*_{max} = 0.59 e Å^{−3}
Δ*ρ*_{min} = −0.35 e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

P1—C11	1.789 (2)	C2—C3	1.484 (3)
P1—C31	1.790 (2)	Cd1—Br3	2.5243 (4)
P1—C21	1.793 (2)	Cd1—Br1	2.5523 (3)
P1—C1	1.799 (2)	Cd1—Br2 ⁱ	2.6540 (4)
O1—C2	1.214 (3)	Cd1—Br2	2.6791 (3)
C1—C2	1.521 (3)		
C11—P1—C31	111.04 (11)	C3—C2—C1	118.5 (2)
C11—P1—C21	105.46 (10)	Br3—Cd1—Br1	112.680 (11)
C31—P1—C21	112.83 (10)	Br3—Cd1—Br2 ⁱ	114.298 (12)
C11—P1—C1	106.35 (11)	Br1—Cd1—Br2 ⁱ	111.567 (11)
C31—P1—C1	107.74 (11)	Br3—Cd1—Br2	119.626 (12)
C21—P1—C1	113.25 (11)	Br1—Cd1—Br2	104.061 (11)
C2—C1—P1	113.23 (16)	Br2 ⁱ —Cd1—Br2	92.779 (10)
O1—C2—C3	122.3 (2)	Cd1 ⁱ —Br2—Cd1	87.221 (10)
O1—C2—C1	119.2 (2)		
Br3—Cd1—Br2—Cd1 ⁱ	−120.101 (14)	P1—C1—C2—O1	19.1 (3)
Br1—Cd1—Br2—Cd1 ⁱ	113.051 (12)		

Symmetry code: (i) 2 − *x*, 2 − *y*, −*z*.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C1—H1 \cdots O1 ⁱⁱ	0.94 (3)	2.48 (3)	3.405 (3)	167 (2)
C1—H2 \cdots Br1	0.91 (3)	2.70 (3)	3.584 (2)	166 (2)
C16—H16 \cdots Br2 ⁱ	0.93 (3)	3.02 (3)	3.694 (3)	131 (2)
C24—H24 \cdots Br3 ⁱ	0.94 (2)	3.06 (3)	3.710 (2)	128.0 (19)
C25—H25 \cdots Br2 ⁱⁱⁱ	0.90 (3)	3.04 (3)	3.718 (3)	133 (2)

Symmetry codes: (i) $2-x, 2-y, -z$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, z$; (iii) $x, 2-y, \frac{1}{2}+z$.

All H atoms were located from difference Fourier maps and their positions and isotropic displacement parameters were refined. The C—H bond distances range from 0.88 (3) to 0.99 (3) Å.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINTE-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 1998); software used to prepare material for publication: *SHELXTL-NT*.

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