

Dominant cation–cation supramolecular motifs in crystals. Hexagonal arrays of sextuple phenyl embraces in halometalate salts of MePh_3P^+

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The crystal structures of five compounds with phosphonium cations and bromocadmate anions have been determined, and analysed in terms of the supramolecular interactions which determine the lattice types. The salts $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]$ and $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]\cdot\text{CH}_2\text{Cl}_2$ crystallise in a large rhombohedral lattice in which dimers of cations in sextuple phenyl embraces (SPE) form a pseudo-diamondoid array, with the anions (and CH_2Cl_2) contained in cavities surrounded by 12 cations. The same hexagonal array of sextuply embracing cations occurs also in $[\text{MePh}_3\text{P}]_2[\text{CdI}_4]$ and $[\text{MePh}_3\text{P}]_2[\text{Cu}_4\text{I}_6]$, with the dimensions of the array of cations quite variable according to the size and shape of the anion. This newly recognised lattice type (HASPE, hexagonal array of sextuple phenyl embraces) is maintained principally by the strongly attractive SPEs and by attraction between the anion and surrounding cations. The HASPE is a crystal structure type with general occurrence. The cations in the crystal structures of $[\text{Ph}_4\text{P}]_2[\text{CdBr}_4]$ and $[\text{Ph}_4\text{P}]_2[\text{Cd}_2\text{Br}_6]$ occur as zigzag infinite sextuple phenyl embraces (ZZISPEs), chains of cations which are orthogonal and parallel respectively. Determination of the crystal structure of $[\text{HPh}_3\text{P}]_2[\text{CdBr}_4]$ reveals an absence of specific cation–cation interactions.

In the field of inorganic crystal supramolecularity we identify two general uncertainties and one fundamental challenge.¹ The uncertainties are (1) whether a crystallised compound represents the most abundant species of a dynamic equilibrium mixture in solution, and (2) the extent to which the molecular structure and stereochemistry in solution is distorted by the crystal environment. The basic challenge is to be able to understand supramolecular interactions in crystals to the extent that crystal packing can be predicted and engineered. These uncertainties are amplified for anionic metal halide (X) complexes, $[\text{M}_m\text{X}_n]^{z-}$, which normally are involved in multicomponent equilibria in solution. There is now a large accumulation of data on the crystal structures of anionic metal complexes with halide ligands. The structures for Cu and Ag have been reviewed by Jagner and Helgesson,² and Hg structures reviewed by House *et al.*,³ with the general conclusion that the cation with which the anionic complex is crystallised can have a profound influence on the composition and structure of the anion. The previous reviewers were unable to interpret clearly the influence of the cation, and little correlation between anion structure and cation properties was evident. Rohl and Mingos^{4–7} have analysed the packing of neutral molecules and ions in crystals.

In previous papers we have described the multiple phenyl embraces between the Ph_4P^+ cations in a wide variety of crystalline compounds.^{8–10} The most prominent of these embraces is the sextuple phenyl embrace (SPE), in which three phenyl groups on one molecule face three phenyl groups on an adjacent molecule, and interleave them such that the partially positive H atoms of any ring are directed towards the negative π density of a ring on the other cation (see Fig. 1). These local attractions are the established edge-to-face (ef) local supramolecular motifs of phenyl rings, and there is a concerted cycle of six such ef interactions in the SPE. The net attractive energy between two Ph_4P^+ cations embracing in this motif is calculated

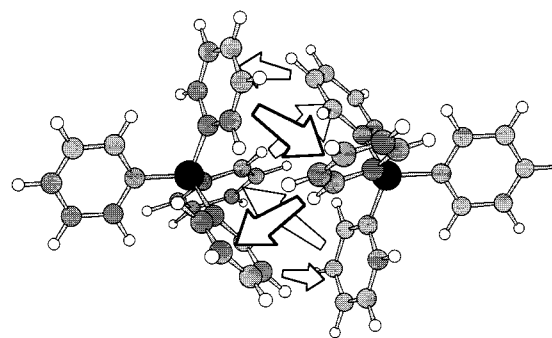


Fig. 1 The sextuple phenyl embrace adopted by pairs of Ph_4P^+ cations in crystals: the arrows identify the six concerted edge-to-face phenyl–phenyl interactions

to be in the range 50–80 kJ mol⁻¹,⁹ which is stronger than most hydrogen bonds. In further investigations we have shown that extended networks of multiple phenyl embraces between Ph_4P^+ cations are also a general feature of crystal supramolecularity.^{10,11} In particular, the zigzag infinite sextuple phenyl embrace (ZZISPE) is a general chain motif of Ph_4P^+ cations, often arranged in crystals as parallel chains between which there are stacks of anions.¹⁰ An SPE requires three phenyl groups per molecule, and therefore triphenylphosphonium cations RPh_3P^+ are also able to participate in SPEs. Accordingly we are investigating the crystal supramolecularity of such cations, and particularly MePh_3P^+ and HPh_3P^+ which are able to retain three-fold symmetry. In this paper we describe the structures of new crystals containing the cations MePh_3P^+ , HPh_3P^+ or Ph_4P^+ , with anions $[\text{CdBr}_4]^{2-}$ or $[\text{Cd}_2\text{Br}_6]^{2-}$.

We have discovered that MePh_3P^+ with $[\text{CdBr}_4]^{2-}$ forms a large rhombohedral lattice in which the SPEs lie along three-fold axes and dominate the lattice packing, causing the anions to be partially disordered in order to maintain the lattice symmetry. This rhombohedral lattice of embracing cations occurs in the crystal structures of $[\text{MePh}_3\text{P}]_2[\text{CdI}_4]$ and $[\text{MePh}_3\text{P}]_2$

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[Cu₄I₆], which also have cation-enforced orientational disorder of the anions. This lattice of cations is able to undergo large dimensional changes to accommodate anions of different sizes.

Experimental

Preparations and crystallisations

[MePh₃P]₂[CdBr₄]. The salt MePh₃PBr (1.79 g, 5.00 mmol) dissolved in boiling absolute ethanol (10 cm³) was added dropwise to a solution of CdBr₂·4H₂O (0.868 g, 2.50 mmol) in boiling absolute ethanol (35 cm³) with constant stirring. The product formed immediately as a white precipitate which was collected and washed with cold absolute ethanol [Found (Calc.): C, 45.54 (46.26); H, 3.99 (3.67%)]. The crystals used in the diffraction analysis were obtained from a solution in hot ethanol layered with cyclohexane.

[MePh₃P]₂[CdBr₄]·CH₂Cl₂. The salt MePh₃PBr (0.38 g, 1.00 mmol) and CdBr₂·4H₂O (0.344 g, 1.00 mmol) were dissolved in a hot solution of methylene chloride (100 cm³) plus absolute ethanol (35 cm³). This solution was warmed to effect slow evaporation, forming well shaped clear crystals during one week [Found (Calc.): C, 44.29 (43.71); H, 3.98 (3.57%)]. These crystals were stable at room temperature and were used for the diffraction analysis. On heating these crystals effervesced at 130 °C, and then melted at 130–132 °C, which is also the m.p. of [MePh₃P]₂[CdBr₄].

[HPh₃P]₂[CdBr₄]. To CdBr₂·4H₂O (0.172 g, 0.50 mmol) suspended in MeCN (*ca.* 2 cm³) was added HBr (48%, aq, *ca.* 0.5 cm³) to cause dissolution. This solution was added to a solution of Ph₃P (0.261 g, 1.0 mmol) in MeCN (*ca.* 15 cm³) containing *ca.* 1 cm³ of 48% aqueous HBr. There was no immediate precipitation, and the mixture was allowed to evaporate very slowly. After 20 d, the flat rectangular plates which formed were removed and washed twice with *ca.* 0.1 cm³ of 10:1 (v:v) 48% HBr–MeCN. This preparation was based on the methods of Taylor and Tuck.¹²

[Ph₄P]₂[CdBr₄]. The salt CdBr₂·4H₂O (0.344 g, 1.00 mmol) and Ph₄PBr (0.838 g, 2.00 mmol) were dissolved together in methylene chloride (100 cm³) and absolute ethanol (35 cm³) with heating. Crystals of the product formed during evaporation of this solution during several days, and were characterised by X-ray diffraction.

[Ph₄P]₂[Cd₂Br₆]. The salt CdBr₂·4H₂O (0.688 g, 2.00 mmol) and Ph₄PBr (0.838 g, 2.00 mmol) were dissolved together in methylene chloride (100 cm³) and absolute ethanol (35 cm³) with heating. Crystals of the product formed during evaporation of this solution during several days, and were characterised by X-ray diffraction.

[Ph₄P]₂[HgBr₄]. The salt Ph₄PBr (2.10 g, 5 mmol) dissolved in boiling absolute ethanol (5 cm³) was added dropwise to a solution of HgBr₂ (0.901 g, 2.5 mmol) in boiling absolute ethanol (5 cm³) with constant stirring. The product formed as a white precipitate immediately and was collected on a glass filter and washed with cold absolute ethanol. These crystals were isomorphous with [Ph₄P]₂[CdBr₄].

X-Ray crystallography

Reflection data were measured at 21(1) °C using an Enraf-Nonius CAD-4 diffractometer in θ – 2θ scan mode with graphite-monochromated molybdenum radiation (λ 0.7107 Å). Data were measured to $2\theta_{\max}$ of 50° (45° for [HPh₃P]₂[CdBr₄]) with an ω scan angle of (0.50 + 0.35 tan θ). Corrections were made for absorption using the analytical method of de Meulenaer and Tompa¹³ and for any decomposition. Reflections with $I > 3\sigma(I)$ were considered observed.

The structures were determined by direct phasing using the program SIR 92.¹⁴ Hydrogen atoms of the cations were included in calculated positions and were assigned thermal parameters equal to those of the atom to which they were bonded. Positional and anisotropic thermal parameters for the non-hydrogen atoms of [HPh₃P]₂[CdBr₄], [Ph₄P]₂[CdBr₄] and [Ph₄P]₂[Cd₂Br₆] were refined on F using full-matrix least squares.

The anion in [MePh₃P]₂[CdBr₄] lies on a 32 site, and therefore must be disordered. Initially, the Cd and one Br (Br^{ax}) were situated on the three-fold axis while the remaining Br atoms (Br^{eq}) which are related by the three-fold axis were positioned on the two-fold axes which are perpendicular to the three-fold axis. There are two possible sites for the Cd atom, corresponding to application of the two-fold axes, and these were assumed to be equally occupied. The structure was refined anisotropically, using RAELS.¹⁵ In the final refinement, the [CdBr₄]²⁻ ion was modelled as a rigid group of C_3 symmetry. The Cd and Br^{ax} atoms were fixed on the three-fold axis (but allowed to move along it) while Br^{eq} was allowed to move off the two-fold axis: the displacement of Br^{eq} from the two-fold axis was 0.17 Å, causing small variation in the Br^{ax}–Cd–Br^{eq} angles. The thermal motion of the anion was described using a 15 parameter TLX rigid body parameterisation,¹⁶ while the cation was refined anisotropically (T is the translation tensor, L the libration tensor and X the origin of libration).

The composition of [MePh₃P]₂[CdBr₄]·CH₂Cl₂ was unknown when attempts were made to solve its structure. The structure appeared to be very similar to that of [MePh₃P]₂[CdBr₄], but there had been an increase in the c cell dimension of the otherwise isomorphous cell. Since CH₂Cl₂ had been used as a solvent, it was thought that the cavity could contain one [CdBr₄]²⁻ ion and one CH₂Cl₂ molecule disordered over two possible sites for [CdBr₄]²⁻ ions in the previous structure. The CH₂Cl₂ molecule was incorporated into the structure at positions indicated from a Fourier-difference map. The Cl atoms were located around the three-fold axis such that each position would be $\frac{2}{3}$ occupied. The C atom was positioned on the three-fold axis. Rigid group refinement of the [CdBr₄]²⁻ anion was as described above for the non-solvated species, with the Br^{eq} atom 0.12 Å from the two-fold axis. The CH₂Cl₂ was also refined as a rigid group. In the final refinement the C atom was held on the three-fold axis and the rigid group was allowed rotational freedom. Thermal motions for the rigid groups were described using 15 parameter TLX rigid body parameterisations.¹⁶ The cation was refined anisotropically.¹⁵

Reflection weights used for all structures were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. The weighted residual is defined as $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were taken from ref. 17. A DEC Alpha-AXP workstation was used for calculations. Crystallographic details for the crystal structures of [MePh₃P]₂[CdBr₄], [MePh₃P]₂[CdBr₄]·CH₂Cl₂, [HPh₃P]₂[CdBr₄], [Ph₄P]₂[CdBr₄] and [Ph₄P]₂[Cd₂Br₆] are provided in Table 1.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/483.

Energy calculations

Through-space interaction energies were calculated with an atom–atom model, as described previously.^{1,9} For the dispersion energy the relevant van der Waals parameters r_s (Å) and e^s (kJ mol⁻¹) respectively were: H 1.50, 0.17; C 2.00, 0.65; P 2.10, 0.87; Cd 2.05, 0.87; Br 2.3, 0.90. For evaluation of the coulombic energy contributions atomic partial charges were obtained

Table 1 Crystallographic details

	[MePh ₃ P] ₂ [CdBr ₄]	[MePh ₃ P] ₂ [CdBr ₄] CH ₂ Cl ₂	[HPh ₃ P] ₂ [CdBr ₄]	[Ph ₄ P] ₂ [CdBr ₄]	[Ph ₄ P] ₂ [Cd ₂ Br ₆]
Formula	C ₃₆ H ₃₆ Br ₄ CdP ₂	C ₃₆ H ₃₆ Br ₄ CdCl ₂ P ₂	C ₃₆ H ₃₂ Br ₄ CdP ₂	C ₄₈ H ₄₀ Br ₄ CdP ₂	C ₄₈ H ₄₀ Br ₆ Cd ₂ P ₂
<i>M</i>	986.7	1258.9	958.6	1110.8	1383.0
Crystal description	{001}(-102) (10-2)(-107) (0-14)(01-4) (-11-2)(1-12)	Irregular fragment	{010}{001}{111} (-110)(-1-10) (311)	{021}{001}{112} (0-10){01-1}	{100}{010} {-111}{11-1}
Crystal symmetry	Rhombohedral	Rhombohedral	Orthorhombic	Monoclinic	Triclinic
Space group	<i>R</i> $\bar{3}c$	<i>R</i> $\bar{3}c$	<i>Pbca</i>	<i>C2/c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	10.865(3)	10.821(2)	17.825(7)	11.325(4)	9.98(1)
<i>b</i> /Å	10.865(3)	10.821(2)	21.84(1)	19.751(6)	10.11(1)
<i>c</i> /Å	59.23(3)	62.39(1)	19.188(7)	20.705(7)	13.13(1)
α /°				92.58(2)	108.53(5)
β /°					94.15(6)
γ /°	120	120			100.34(5)
<i>U</i> /Å ³	6055(3)	6327(2)	7471(6)	4627(3)	1224(2)
<i>Z</i>	6	6	8	4	1
<i>F</i> (000)	2892	3144	3728	2184	664
<i>D</i> _c /g cm ⁻³	1.62	1.69	1.70	1.59	1.88
μ /cm ⁻¹	45.6	45.0	49.3	39.9	58.1
Crystal dimensions	0.13 × 0.13 × 0.09	≈0.14 × 0.14 × 0.13	0.10 × 0.14 × 0.16	≈0.08 × 0.10 × 0.27	0.14 × 0.08 × 0.13
No. of intensity measurements	2588	2715	5410	4326	4560
No. of independent observed reflections	600	682	1884	2665	3263
No. of reflections (<i>m</i>) and variable (<i>n</i>) in final refinement	600, 71	682, 80	1884, 388	2665, 249	3263, 262
<i>R</i> = $\sum w \Delta F /\sum w F_o $	0.043	0.030	0.049	0.032	0.027
<i>R</i> ' = $[\sum w \Delta F ^2/\sum w F_o ^2]$ ^{1/2}	0.056	0.033	0.052	0.041	0.035
<i>s</i> = $[\sum w \Delta F ^2/(m-n)]^{1/2}$	2.37	1.43	1.60	1.34	1.23
Crystal decay	None	None	1→0.94	1→0.96	None
Maximum, minimum transmission coefficients	0.67, 0.49	0.61, 0.45	0.58, 0.53	0.69, 0.51	0.60, 0.50
<i>R</i> for (<i>p</i>) multiple measurements	979, 0.018	1112, 0.016	—	152, 0.021	416, 0.013

by fitting them to the electrostatic potentials of these and related molecules: the electrostatic potentials were evaluated from the total electron density by non-local density functional methods. The atomic charges calculated in this way are intermediate between those calculated using the conventional Mulliken and Hirshfeld methods: the intermolecular coulombic energies are not sensitive to variations of atomic charge in this range. The charges used here were [(C^{-0.06}H^{+0.07})₃-(C^{-0.1}H^{-0.15})₃P^{+0.4}] and [Cd^{+0.4}(Br^{-0.6})₄]; the permittivity ϵ was set as d_{ij}^{-1} .

Results and Discussion

The geometries of the individual cations and anions in these compounds are normal and need no comment. The main significance of these compounds derives from their crystal packing.

Crystal structure of [MePh₃P]₂[CdBr₄]

All MePh₃P⁺ cations occur as SPE dimers, with a P...P separation of 6.38 Å and the two methyl groups linearly opposed, as shown in Fig. 2. The P...P vectors of the SPE interactions are aligned with three-fold axes of the lattice, and there is an inversion centre at the centroid of the SPE, so each SPE has $\bar{3}$ symmetry. The unit cell is hexagonal, 10.86 × 59.23 Å, with space group *R* $\bar{3}c$. The array of the cation P atoms and anion locations in this unit cell is shown in Fig. 3. In addition to the prominent P...P vectors of the SPE (coloured pink in Fig. 3), there are puckered hexagonal nets of P atoms (coloured blue in Fig. 3), within which all P...P distances are 7.18 Å, and all P...P...P angles 98°. The hexagonal net of P atoms is comprised of fused P₆ chairs. The connections between the hexagonal nets are the P...P vectors of the SPEs, which are directed alternately up and down from contiguous P atoms in

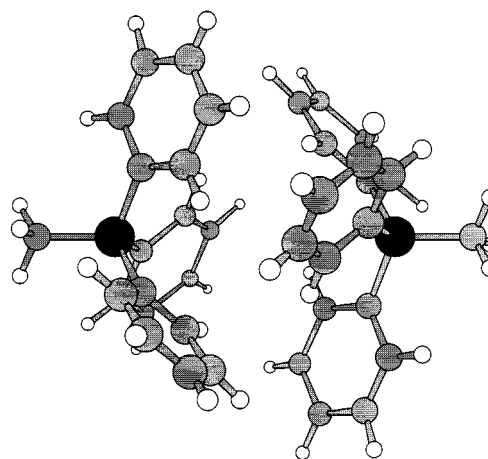


Fig. 2 The tight sextuple phenyl embrace (SPE) adopted by a pair of MePh₃P⁺ cations in crystalline [MePh₃P]₂[CdBr₄]. This SPE has exact $\bar{3}$ symmetry

one hexagonal net, and thus the three-dimensional array of P atoms is prolate diamondoid, elongated along the hexagonal axis. The centroids of the SPEs, which lie on $\bar{3}$ sites (special positions *b* in space group *R* $\bar{3}c$), form layers of triangular grids within which the centroid-centroid distances are 10.9 Å. This lattice of cations in tight SPEs is named the hexagonal array of sextuple phenyl embraces (HASPE).

The [CdBr₄]²⁻ anions are located at the centroids of the P₆ chairs as shown in Fig. 3. These anion sites have 32 (*D*₃) crystallographic symmetry, and therefore the tetrahedral anions are necessarily disordered, as shown in Fig. 4. As three Br atoms of each anion lie on the two-fold axes at these sites, the two orientations of the [CdBr₄]²⁻ anion at each site are effectively mirrored by a plane perpendicular to the three-fold axis. In the

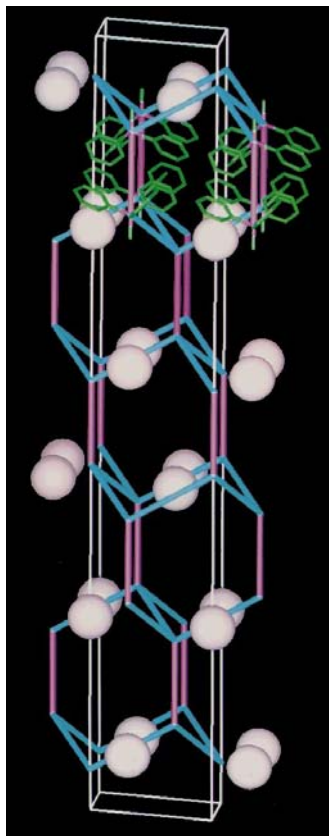


Fig. 3 Contents of the unit cell (white box, hexagonal, 10.9×59.2 Å) of crystalline $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]$. The white spheres show the location of the anions, and the pink and blue rods connect the P atoms of the cations, in a pseudo-diamondoid array. Carbon atoms (green) for eight cations are shown. The pink rods signify the SPE interactions of cation dimers

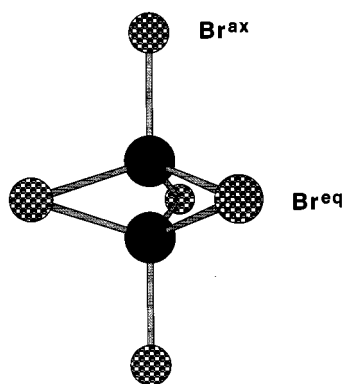


Fig. 4 The disordered positions of the $[\text{CdBr}_4]^{2-}$ anion at a 32 site in crystalline $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]$

following the three Br atoms off the three-fold axis are labelled equatorial, Br^{eq} , and the two on-axis positions for the fourth Br atom are labelled Br^{ax} .[‡]

In addition to the SPEs which link the puckered hexagonal nets of cations, there are cation–cation interactions within these nets. Fig. 5 shows axial and lateral views of a net. As the cations are directed alternately up and down from the hexagonal net, each CH_3 group (shown in yellow) of one cation lies between three Ph groups (of these the two Ph groups included in Fig. 5

[‡] In the final refinement (see Experimental section), the Br^{eq} atoms were allowed to move slightly off the two-fold axis, but rigid group C_3 symmetry for the $[\text{CdBr}_4]^{2-}$ ion was maintained. In this general discussion we assume that the Br^{eq} lies on the two-fold axis, but any dimensions quoted refer to the actual refined positions.

are coloured blue) from the three adjacent cations in the net. Around the hexagonal net there are also *ef* interactions between Ph groups of 1–3 related cations: the two blue Ph rings in Fig. 5 show this. Each anion is surrounded by six cations in the immediate chair-hexagon. In addition to these six cations, there is another triangle of cations either side (along the three-fold axis) of the chair-hexagon, so that there are 12 cations surrounding the anion sites. Although the 32 site illustrated in Fig. 3 is at the centre of the chair-hexagon, the actual location of each anion is displaced along the three-fold axis (see Fig. 4), and so any one anion is within contact of $3 + 6$ cations. These contacts are shown in Fig. 6. Each Br^{eq} atom of an anion is near H(2) (2.84 Å), H(2) (2.90 Å) and H(3) (2.93 Å) atoms of Ph groups of three surrounding cations, and Br^{ax} also makes contact (3.08 Å) with each H(4) atom on three surrounding cations. The slight rotation of the three-fold axis of the $[\text{CdBr}_4]^{2-}$ ion from the three-fold axis of the unit cell[‡] allows the $\text{Br}^{\text{eq}} \cdots \text{H}$ distances to be equalised.

Fig. 7 is a space-filling picture of the cations and anions in one hexagonal net of the lattice.

In summary, the essential features of ion *locations* in this lattice are (1) a prolate diamondoid array of MePh_3P^+ cations, connected by SPEs along the *c*-axis of the hexagonal lattice, and by $\text{CH}_3 \cdots \text{Ph}$ and $\text{Ph} \cdots \text{Ph}$ interactions within the puckered hexagonal net of cations normal to this axis, and (2) $[\text{CdBr}_4]^{2-}$ anions located at the centres of the hexagons in the puckered net of cations, and constrained by $\text{Br} \cdots \text{H}$ interactions. However, there is a more subtle feature which derives from the *rotational* conformations of ions around the three-fold axes. A diamond lattice repeats after three puckered hexagonal nets, whereas the crystal structure of $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]$ has six hexagonal nets along the *c* axis of 59.23 Å. Hexagonal nets separated by *c*/2 (*i.e.* 1.4 sequenced in the stack of nets) in $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]$ differ in their rotational conformation about the three-fold axes. The symmetry element which relates ions separated by *c*/2 is a *c* glide plane. The reason for the doubling of the repeat along *c* derives from the interactions between the anion and cation shown in Fig. 6, specifically the $\text{H} \cdots \text{Br}^{\text{eq}}$ interactions in Fig. 6(a) prevent rotation of the anion about its three-fold axis. Thus the rotational conformation of the anion is locked into the rotational conformations of the cations in its puckered net. The SPEs which link cations in contiguous nets are centrosymmetric, and consequently the cations in one net are rotated by 180° relative to those in adjacent nets. Therefore the anions in successive layers of anions are also rotated by 180° . Then, after the diamondoid repeat of three hexagonal nets there is rotation of anions (and their surrounding cations) by $3 \times 180^\circ$, and thus identity requires 3×2 layers.

What attractive energies maintain this lattice? We have calculated the through-space energies for the relevant components: all of the energies quoted here are *attractive*. The SPE has an attractive energy of 83.8 kJ mol^{-1} for the $\text{Ph}_3\text{-Ph}_3$ set, and a total attractive energy for $\text{MePh}_3\text{P}^+ \cdots \text{MePh}_3\text{P}^+$ of 69.3 kJ mol^{-1} . In the chair-hexagon of cations, the 1–3 related cations have a net attraction of 4.4 kJ mol^{-1} mainly due to two Ph rings, while the 1–2 related cations have Me-Ph attraction of 2.6 kJ mol^{-1} , and total $\text{Ph}_3\text{-Ph}_3$ attraction of 11.7 kJ mol^{-1} (of which one pair of Ph rings contributes 7.2 kJ mol^{-1}). There are substantial attractive energies, mostly coulombic, between $[\text{CdBr}_4]^{2-}$ and its surrounding cations: between $[\text{CdBr}_4]^{2-}$ and cations in the chair-hexagon (taking into account the actual disorder) there are three independent energies for anion–cation pairs, namely 73.7 , 74.8 and 90.4 kJ mol^{-1} ; between $[\text{CdBr}_4]^{2-}$ and one of the three cations nearer to Br^{ax} the anion–cation energy is 45.1 kJ mol^{-1} .

Crystal structure of $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4] \cdot \text{CH}_2\text{Cl}_2$

This compound was crystallised from a mixture with a Br^-

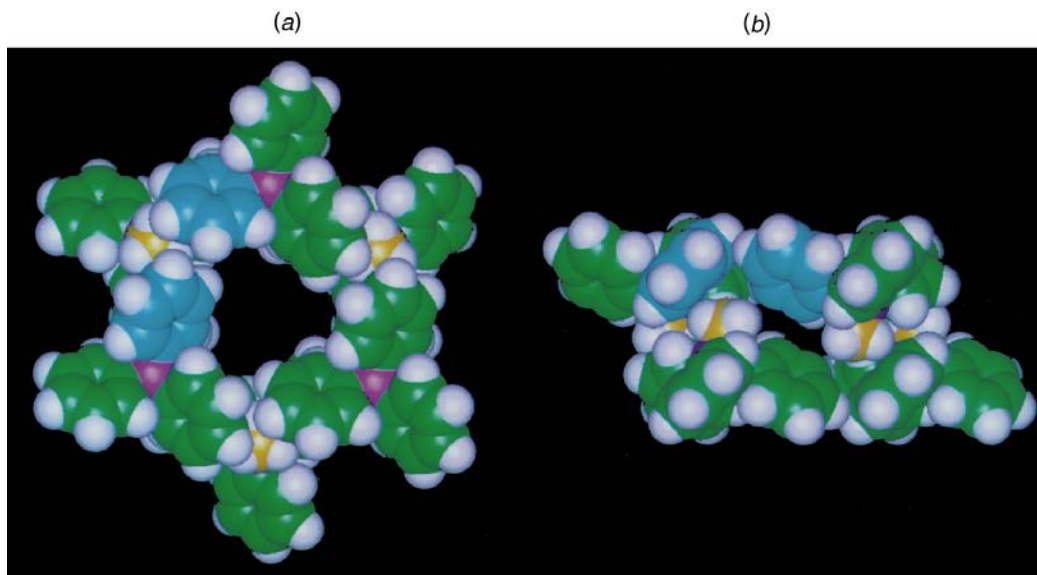


Fig. 5 Three-fold (a) and approx two-fold (b) views of six MePh_3P^+ cations which comprise a hexagon in chair conformation in the hexagonal net of cations in crystalline $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]$. The P atoms are pink, and the carbon atoms of the methyl groups are coloured yellow: the alternation of pink and yellow in (a) shows the up-down alternation of cation methyl vectors around the hexagon. Three SPE (not shown) occur on either side of the hexagon, and the trigonal array of canted phenyl groups Ph₃ which form an SPE is evident around each pink P atom in (a). Two of the phenyl groups in 1–3 cations around the hexagon are coloured blue, to emphasise the π interaction between them, and to show how the CH_3 group of the intervening cation nestles between these two Ph groups (and a third not shown) with $\text{C-H}\cdots\text{Ph}$ interactions

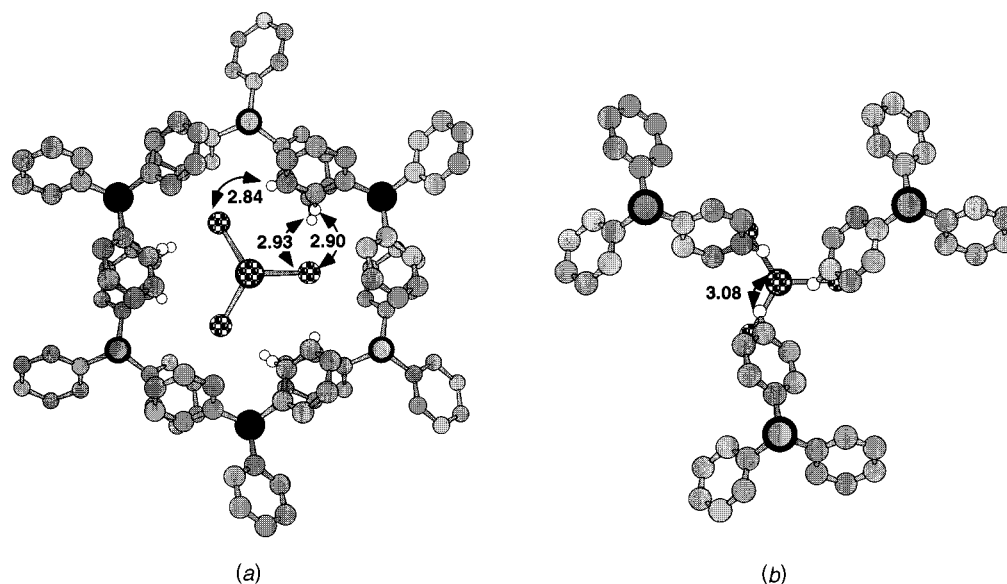


Fig. 6 (a) A $[\text{CdBr}_4]^{2-}$ anion near the centre of a $[\text{MePh}_3\text{P}^+]_6$ chair-hexagon, showing the H atoms which most closely approach Br^{eq} , at the distances marked: the view direction is along the three-fold axis of the unit cell, and the very slight rotation of the three-fold $[\text{CdBr}_4]^{2-}$ anion from this axis can be discerned. (b) The three MePh_3P^+ cations which are near Br^{ax} of an anion, with the shortest $\text{H}\cdots\text{Br}^{\text{ax}}$ distance marked. The Cd atom is black, Br bubbled, C grey, H white and P black

Cd^{2+} ratio of 3:1, and which was intended to crystallise the $[\text{Cd}_2\text{Br}_6]^{2-}$ ion with MePh_3P^+ . Thus, in the presence of MePh_3P^+ the bromocadmate anion which crystallises does not match the stoichiometry of the crystallisation solution (in contrast to crystallisation with Ph_4P^+ : see below).

The crystal structure of $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]\cdot\text{CH}_2\text{Cl}_2$ is similar to that of $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]$, in that the space group is the same, the general array of ions is the same, and the unit cell is slightly larger. The location of the cations was unequivocal and showed that the two structures had dimensional differences. The $\text{P}\cdots\text{P}$ separation of the SPE in $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]\cdot\text{CH}_2\text{Cl}_2$ is 6.74 Å, 0.36 Å longer, while the $\text{P}\cdots\text{P}$ separation within the hexagonal net is virtually unchanged at 7.24 Å. The location of the additional CH_2Cl_2 is inside the cavity which contains the $[\text{CdBr}_4]^{2-}$ anion: this cavity, which has an

ellipsoidal shape elongated along the three-fold axis, accommodates both species simultaneously along the ellipsoid axis, resulting in the expansion of the c dimension of the lattice by 3.2 Å.

The CH_2Cl_2 molecule is centred on the three-fold axis in the cavity, with one C–H bond collinear with the three-fold axis and directed towards the centre of the cavity and between the $(\text{Br}^{\text{eq}})_3$ set of the partner $[\text{CdBr}_4]^{2-}$. This attractive relationship between the CH_2Cl_2 and $[\text{CdBr}_4]^{2-}$ is shown in Fig. 8. There is three-fold rotational disorder of the other C–H and $(\text{C–Cl})_2$ bonds, and adherence to the 32 crystallographic site symmetry of the cavity requires the locations of the $[\text{CdBr}_4]^{2-}$ and CH_2Cl_2 to be disordered. The shortest contacts between the CH_2Cl_2 and surrounding cations are $\text{Cl}\cdots\text{C}$ 3.2 Å (which is comparable to the shortest contacts of this type present in the Cambridge

Table 2 Comparative dimensions of the lattices and anions in four crystals with comparable hexagonal arrays of MePh_3P^+ cations (distances in Å, angles in °)

Compound {refcode}	Space group	Cell dimensions <i>a, c</i>	SPE length $\text{P}\cdots\text{P}$	Dimensions of hexagonal net		Anion $\cdots\text{P}$ radical, axial	Anion length ^a	Anion cross-section ^b
				$\text{P}\cdots\text{P}$	$\text{P}\cdots\text{P}\cdots\text{P}$			
$[\text{MePh}_3\text{P}^+]_2[\text{CdBr}_4]^{2-}$	$R\bar{3}c$	10.9, 59.2	6.38	7.18	98.4	6.5, 11.6	6.6	Triangular, 7.8
$[\text{MePh}_3\text{P}^+]_2[\text{CdBr}_4]^{2-} \cdot \text{CH}_2\text{Cl}_2$	$R\bar{3}c$	10.8, 62.4	6.74	7.24	96.7	6.5, 12.2	7.3	Triangular, 7.8
$[\text{MePh}_3\text{P}^+]_2[\text{CdI}_4]^{2-}$ {MTPHCl}	$R\bar{3}c$	11.0, 64.0	6.74	7.45	94.9	6.6, 12.6	7.5	Triangular, 9.1
$[\text{MePh}_3\text{P}^+]_2[\text{Cu}_4\text{I}_6]^{2-}$ {MPPICU}	$R\bar{3}c$	14.0, 40.1	6.22	8.07	119.7	8.1, 6.9	4.5	Circular, 20.0

^a Atom–atom length of the anion along the three-fold axis, including disorder positions. ^b Cross-sectional shape and area (Å², calculated to atom centres) of the anion, perpendicular to the three-fold axis.

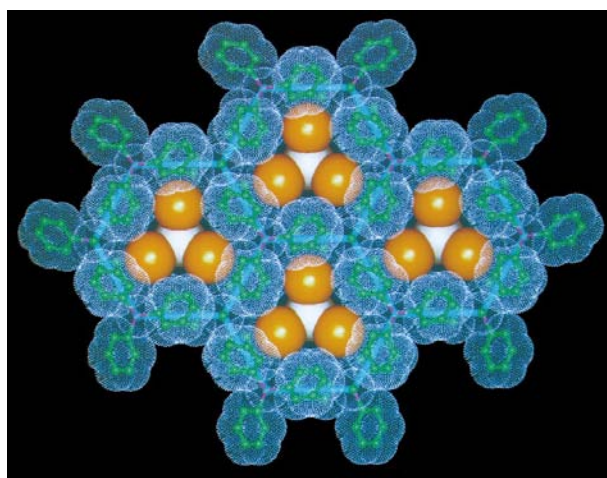


Fig. 7 Space-filling view of cations and anions in one hexagonal net of $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]$. All anions are shown oriented in the same direction along the three-fold axes, but can be disordered by reflection through the plane of the Br^{eq} atoms

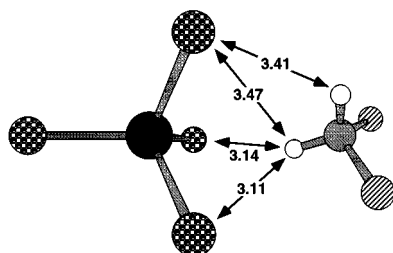


Fig. 8 The $[\text{CdBr}_4]^{2-} \cdot \text{CH}_2\text{Cl}_2$ embrace within the cavity of crystalline $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4] \cdot \text{CH}_2\text{Cl}_2$

Structural Data Base¹⁸) and $\text{Cl}\cdots\text{H}$ 2.7 Å. § The hexagonal lattice in $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]$ could be considered to be an inclusion host, with CH_2Cl_2 as guest. We are exploring this concept further, with evidence that other molecules can occupy the cavity in place of CH_2Cl_2 .

Related crystal structures of $[\text{MePh}_3\text{P}]_2[\text{CdI}_4]$ and $[\text{MePh}_3\text{P}]_2[\text{Cu}_4\text{I}_6]$

Interrogation of the Cambridge Structural Database reveals two other compounds which have similar crystal structures, namely $[\text{MePh}_3\text{P}]_2[\text{CdI}_4]$ ¹⁹ and $[\text{MePh}_3\text{P}]_2[\text{Cu}_4\text{I}_6]$.²⁰ The cell

§ As in the case of $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]$, the Br^{eq} of the anion were allowed to refine away from the two-fold axis. Similarly, in the final refinement, the CH_2Cl_2 molecule was allowed to refine away from the ideal location described here. The C atom was held on the three-fold axis.

dimensions vary, as do the lattice dimensions, defined by the SPE $\text{P}\cdots\text{P}$ distance, the $\text{P}\cdots\text{P}$ distance around the hexagonal net, and the $\text{P}\cdots\text{P}\cdots\text{P}$ angle which defines the extent of ring puckering: these dimensions are provided in Table 2. However all of these compounds have the same general array of cations, SPE motifs, and of anions within this network of cations, and the same symmetry.

Of the four compounds listed, $[\text{MePh}_3\text{P}]_2[\text{Cu}_4\text{I}_6]$ differs from the other three in that its hexagonal net is nearly planar, as shown by the $\text{P}\cdots\text{P}\cdots\text{P}$ angle (119.7°), with the *c* axis consequently *ca.* 20 Å shorter and the *a* axis *ca.* 3 Å longer. The variation in the dimensions and puckering of the net are related to the overall dimensions of the anions as portrayed in their disordered state. Fig. 9 shows the lattice array for $[\text{MePh}_3\text{P}]_2[\text{Cu}_4\text{I}_6]$ in the same style as Fig. 3, and Fig. 10 shows the collection of atoms for the disordered $[\text{Cu}_4\text{I}_6]^{2-}$ ions. Only the Cu atoms need be disordered for $[\text{Cu}_4\text{I}_6]^{2-}$ to adopt the 32 site symmetry.

It is clear from comparison of Figs. 4 and 10 that disordered $[\text{CdBr}_4]^{2-}$ is prolate while disordered $[\text{Cu}_4\text{I}_6]^{2-}$ is oblate, and from comparison of Figs. 3 and 9 that the hexagonal net of cations in the $[\text{CdBr}_4]^{2-}$ crystal can undergo substantial concerted compression in order to accommodate $[\text{Cu}_4\text{I}_6]^{2-}$. It is remarkable that the lattice is able to adjust with the degree of geometrical variation presented in Table 2: the variation is however consistent with the energy calculations because the (blue) interactions within the hexagonal net are less energetic than the (pink) SPE and the attraction between the anion with surrounding cations. We comment that the isostructural relationship between $[\text{MePh}_3\text{P}]_2[\text{Cu}_4\text{I}_6]$ and the other compounds could not have been detected *via* the usual test for isomorphous lattices.

Finally, we note (Table 2) that the lattice of $[\text{MePh}_3\text{P}]_2[\text{CdI}_4]$ accommodates $[\text{CdI}_4]^{2-}$ which is larger than $[\text{CdBr}_4]^{2-}$ by weakening (elongating) the SPE, increasing the dimensions of the hexagonal net, and slightly flattening the hexagonal net, changes which also account for the difference between $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4] \cdot \text{CH}_2\text{Cl}_2$ and $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]$.

Table 2 also contains the dimensions of the disordered objects included in each lattice. These are the atom–atom length along the *c* axis and the approximate cross-sectional areas. There is a direct correlation between the anion length and the *c* cell dimension, and in addition, the cross-sectional area is correlated to the *a* (*b*) cell dimension.

There remains the question as to why $[\text{MePh}_3\text{P}]_2[\text{Cd}_2\text{Br}_6]$ did not crystallise from the solution which has this composition. We have computer modelled the structure of the crystal which has $[\text{Cd}_2\text{Br}_6]^{2-}$ in the cavity. Although this anion does not conform to 32 symmetry, it is possible that it, like $[\text{CdBr}_4]^{2-}$, would be accommodated if it were disordered. However, it was not possible to locate $[\text{Cd}_2\text{Br}_6]^{2-}$ within the ellipsoidal cavity of $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4] \cdot \text{CH}_2\text{Cl}_2$ without introducing unacceptably

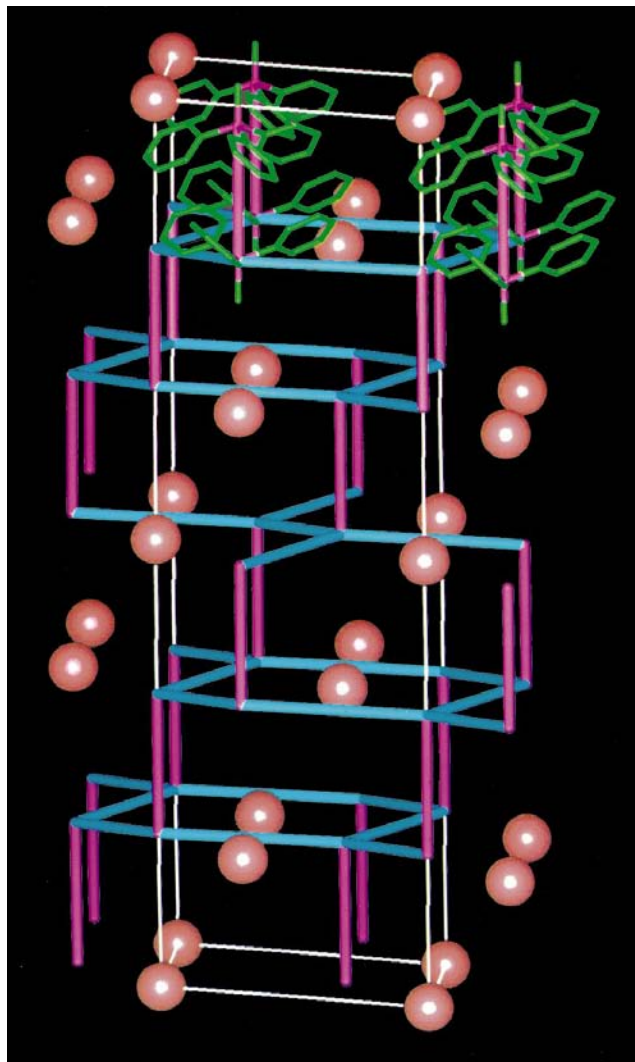


Fig. 9 Contents of the unit cell (white box) of crystalline $[\text{MePh}_3\text{P}]_2[\text{Cu}_4\text{I}_6]$. The components are represented in the same manner as for Fig. 3, except that the centres of the disordered $[\text{Cu}_4\text{I}_6]^{2-}$ ions are shown as buff spheres

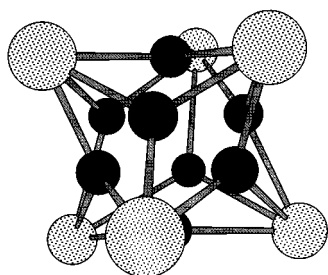


Fig. 10 Atom positions for the disordered $[\text{Cu}_4\text{I}_6]^{2-}$ anion at a 32 site in crystalline $[\text{MePh}_3\text{P}]_2[\text{Cu}_4\text{I}_6]$: three-fold axis vertical. The I positions are not disordered, but there are two sets of Cu positions, shown as dark and light

short anion/cation contacts. It is possible, however, that some rearrangement of the host lattice could allow inclusion of $[\text{Cd}_2\text{Br}_6]^{2-}$. The dimensions of a disordered $[\text{Cd}_2\text{Br}_6]^{2-}$ are approximately 6.3 \AA in length with a roughly circular cross sectional area of 12.9 \AA^2 . By comparison of the corresponding dimensions for the other disordered anions/solvent molecules incorporated into this lattice (Table 2) it seems likely that $[\text{Cd}_2\text{Br}_6]^{2-}$ could be accommodated if a (and b) increased while c decreased. Perhaps it remains to optimise the preparative conditions in order to crystallise $[\text{MePh}_3\text{P}]_2[\text{Cd}_2\text{Br}_6]$.

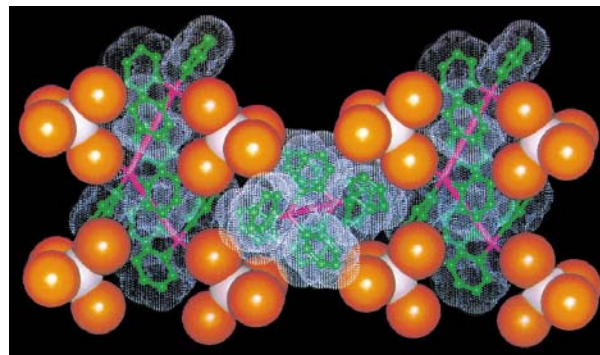


Fig. 11 Crystal structure of $[\text{Ph}_4\text{P}]_2[\text{CdBr}_4]$ showing the two orthogonal ZZISPE chains of cations (pink rods) which separate the $[\text{CdBr}_4]^{2-}$ ions

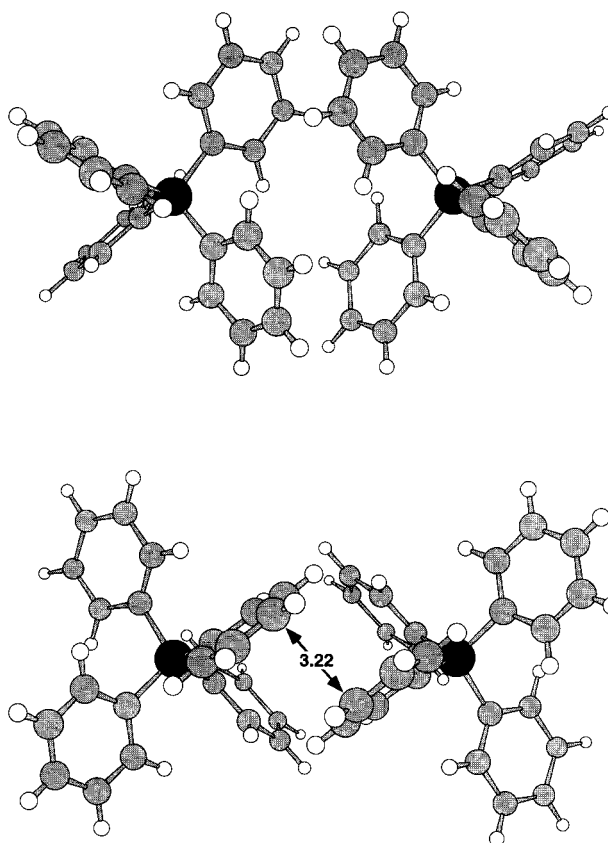


Fig. 12 Orthogonal views of the unusual quadruple phenyl embrace which occurs between ZZISPE chains in crystalline $[\text{Ph}_4\text{P}]_2[\text{CdBr}_4]$

Crystal structures of $[\text{Ph}_4\text{P}]_2[\text{CdBr}_4]$ and $[\text{Ph}_4\text{P}]_2[\text{Cd}_2\text{Br}_6]$

These two compounds were crystallised from mixtures containing $\text{Br}^- - \text{Cd}^{2+}$ ratios of 4 and 3 respectively, and the composition of the crystallised anion matches the stoichiometry of the solution. Unlike MePh_3P^+ , Ph_4P^+ can engage two SPEs and frequently does so with the zigzag infinite sextuple phenyl embrace (ZZISPE) which we have previously described.¹⁰ Crystalline $[\text{Ph}_4\text{P}]_2[\text{CdBr}_4]$ and crystalline $[\text{Ph}_4\text{P}]_2[\text{Cd}_2\text{Br}_6]$ both contain ZZISPEs, but with different inter-ZZISPE motifs. The salt $[\text{Ph}_4\text{P}]_2[\text{CdBr}_4]$ contains orthogonal ZZISPE chains where the $\text{P} \cdots \text{P}$ distances are alternately 6.41 and 6.65 \AA , as shown in Fig. 11. Where the orthogonal chains abut, the $\text{P} \cdots \text{P}$ distance of 7.41 \AA represents an unusual quadruple phenyl embrace which incorporates two face-to-face interactions, shown in Fig. 12. The anions in $[\text{Ph}_4\text{P}]_2[\text{CdBr}_4]$ are positioned in the cavities created between the cation chains (see Fig. 11).

Two other tetrahalometalate structures are isomorphous

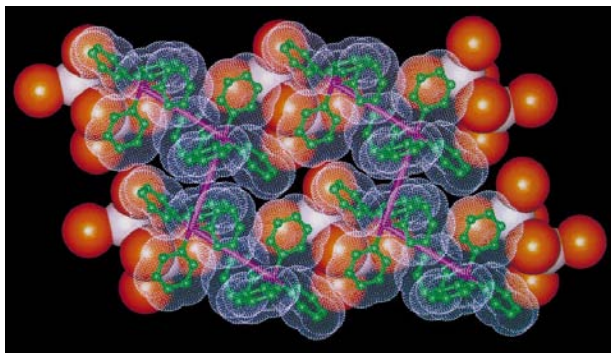


Fig. 13 Crystal structure of $[\text{Ph}_4\text{P}]_2[\text{Cd}_2\text{Br}_6]$ showing two coplanar but opposed ZZISPE chains of cations (pink rods). The centrosymmetric $[\text{Cd}_2\text{Br}_6]^{2-}$ ions form layers between the cation layers

with $[\text{Ph}_4\text{P}]_2[\text{CdBr}_4]$, namely $[\text{Ph}_4\text{P}]_2[\text{HgBr}_4]$ and $[\text{Ph}_4\text{P}]_2[\text{NiCl}_4]$ {TADGAG},[†] but in addition there are other structures with chemically diverse anions which adopt the same cation packing with orthogonal ZZISPEs. These include $[\text{Ph}_4\text{P}]_2[\text{MoSe}_4]$ {GEPFIQ}, $[\text{Ph}_4\text{P}]_2[\text{WSe}_4]$ {GEPFOW}, $[\text{Ph}_4\text{P}]_2[\text{NbS}_2(\text{SH})]$ {YUBDUU}, $[\text{Ph}_4\text{P}]_2[\text{S}_2\text{Mo}(\mu\text{-S})_2\text{Cu}(\text{CN})]$ {BECPII10}, $[\text{Ph}_4\text{P}]_2[\text{Se}_2\text{Mo}(\mu\text{-Se})_2\text{Cu}(\text{CN})]$ {POPCEC}, $[\text{Ph}_4\text{P}]_2[\text{CoCl}(\text{N}_3)_3]$ {FURHEF} and three cubane type Fe–S clusters, $[\text{Ph}_4\text{P}]_2\{[\text{Fe}(\text{Br})_4\text{S}_4]\}$ {DEXXIN}, $[\text{Ph}_4\text{P}]_2\{[\text{Fe}(\text{SH})_4\text{S}_4]\}$ {FAGREK} and $[\text{Ph}_4\text{P}]_2\{[\text{Fe}(\text{Cl})_2\{\text{Fe}(\text{S}_2\text{CNET}_2)_2\text{S}_4]\}$ {DAMNUA}.

In crystalline $[\text{Ph}_4\text{P}]_2[\text{Cd}_2\text{Br}_6]$ the ZZISPEs are parallel and coplanar, with P···P SPE distances alternately 6.63 and 6.59 Å in each chain (see Fig. 13). Where the chains come closest together, the P···P distance is 8.44 Å and the arrangement is that of a parallel quadruple phenyl embrace (PQPE). There is a centre of symmetry at the centroid of each SPE and the centroid of the PQPE. Consequently there is a pseudo-hexagonal planar array of cations, a motif which occurs frequently in compounds containing Ph_4P^+ and will be reported separately.¹¹ The anions, which themselves contain a centre of symmetry, form layers between the cation layers, as shown in Fig. 13.

Other $[\text{Ph}_4\text{X}]_2[\text{M}_2\text{Y}_6]$ crystal structures fall into two crystal classes, triclinic $P\bar{1}$ and monoclinic $P2_1/c$ (or equivalent). In both cases, the structures are layered, but in the monoclinic case, the SPEs can be longer and the layer undulates. These structures are: (a) triclinic $[\text{Ph}_4\text{P}]_2[\text{Hg}_2\text{I}_6]$ {CUGFIT}, $[\text{Ph}_4\text{P}]_2[\text{Mn}_2\text{Br}_6]$ {GAYWIM}, $[\text{Ph}_4\text{P}]_2[\text{Zn}_2\text{Cl}_6]$ {KAVHEU}, $[\text{Ph}_4\text{P}]_2[\text{Cd}_2\text{Cl}_6]$ {KAVHIY}, $[\text{Ph}_4\text{As}]_2[\text{Hg}_2\text{Cl}_6]$ {KASTED}; (b) monoclinic $[\text{Ph}_4\text{P}]_2[\text{Cu}_2\text{Cl}_6]$ {JADNOR, TPHCLC}, $[\text{Ph}_4\text{As}]_2[\text{Cu}_2\text{Cl}_6]$ {TPHASC01}, $[\text{Ph}_4\text{Sb}]_2[\text{Cu}_2\text{Cl}_6]$ {DADZUD}; $[\text{Ph}_4\text{P}]_2[\text{Cd}_2\text{Br}_6]$ is in the triclinic class.

Crystal structure of $[\text{HPh}_3\text{P}]_2[\text{CdBr}_4]$

Salts containing the triphenylphosphonium cation HPh_3P^+ form a large rhombohedral lattice similar to that of $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]$, and dominated by cation interactions.²¹ Therefore we prepared $[\text{HPh}_3\text{P}]_2[\text{CdBr}_4]$ and examined its crystal structure. The structure is a three-dimensional array of cations containing cavities where the anions are located, but unlike the other structures reported in this paper the crystal structure of $[\text{HPh}_3\text{P}]_2[\text{CdBr}_4]$ does not exhibit any SPE interactions.

One of the features of halometalate complexes with the cation HPh_3P^+ is the occurrence of hydrogen bonds between the cation P–H and the halogen atoms of the anions. In $[\text{HPh}_3\text{P}]_2[\text{CdBr}_4]$ each H–P is directed towards an anion giving rise to H···Br interactions of 2.61 and 2.80 Å, well within the

range of 2.5–3.1 Å found for similar contacts in other structures. In addition there are other H···Br contacts for aromatic H atoms of comparable length to those found for $[\text{MePh}_3\text{P}]_2[\text{CdBr}_4]$. This structure seems to have rather inefficient packing, as indicated by the high thermal motion of the ring carbon atoms. It is reasonable to question why this cation does not give HASPE crystalline packing (which indeed does occur for some other halometalates, e.g. $[\text{HPh}_3\text{P}]_2[\text{Ga}_2\text{Cl}_6]$ {FUPSEO}). We surmise that the empty space resulting from the substitution of H for Me is too large to allow this to form and that the required variation in the host lattice would be too great.

Conclusion

We have identified a new structure type for structurally molecular salts involving the three-fold cation MePh_3P^+ , which dimerises to form strong sextuple phenyl embraces as a dominant supramolecular motif. Secondary phenyl embraces generate a diamondoid network of cations, forming cavities which contain a dianion which is orientationally disordered as necessary to adhere to the symmetry dictated by the cation array. The anion cavity can also contain the small molecule CH_2Cl_2 in a host-guest relationship. This structure type is named the hexagonal array of sextuple phenyl embraces (HASPE). This matrix of embracing cations is dimensionally adjustable, and undergoes concertina compression to accommodate the more oblate anion $[\text{Cu}_4\text{I}_6]^{2-}$, or concertina expansion to accommodate CH_2Cl_2 with the anion. The main contributions to the favourable lattice energy are the strongly attractive SPEs (69 kJ per mol of $[\text{MePh}_3\text{P}]_2$), and the attractions between an anion and the 12 cations which surround its cavity. Corresponding compounds with Ph_4P^+ and the anions $[\text{CdBr}_4]^{2-}$ or $[\text{Cd}_2\text{Br}_6]^{2-}$ form the previously described ZZISPEs as the key supramolecular motif for the cations.

Returning to the questions raised at the outset, about the integrity of composition and structure for halometalate anions, we note that a solution with the stoichiometry of $[\text{Cd}_2\text{Br}_6]^{2-}$ crystallised this anion with Ph_4P^+ but crystallised $[\text{CdBr}_4]^{2-}$ with MePh_3P^+ . The stable lattice of embracing MePh_3P^+ cations has changed the identity of the anion crystallising from solution.

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