High symmetry crystal supramolecularity: $-XPh_3$ molecules in cubic lattices†

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The majority of molecular crystals in the Cambridge Structural Database involve relatively low symmetry molecules, engaged by intermolecular interactions with restricted symmetry, resulting in the preponderant occurrence of a small number of relatively low symmetry crystallographic space groups as expounded by Brock and Dunitz. We are examining some contrasting crystal structure types that contain higher symmetry molecules involved in high symmetry intermolecular motifs and generating high symmetry space groups. This paper considers molecules containing XPh_3 groups, engaged in multiple phenyl embraces with local S_6 ($\bar{3}$) symmetry, generating crystal lattices with cubic symmetry. The conceptual framework for these analyses also involves the presence, symmetry, and occupancy of cavities in high symmetry lattices, with extensions to crystal trapping of unusual species such as $[Cu_2Br_5]^{2-}$ and $[Cu_8Br_{15}]^{6-}$. The compounds included in the analyses of crystal packing and symmetry in this paper are $(MePh_3P^+)_2[Cu_2Br_5]^{2-}$, $Ph_3POGaCl_3$, Ph_3AsI_2, $N(Ph\text{-}2\text{-}OMe)_3$, Ph_3SnCl, $Ph_3PAuCCAuPPh_3 \cdot (C_6H_6)_2$, $Ph_3PAu(B_6H_6)AuPPh_3$, $(Ph_3PH^+)_2[SnCl_6]^{2-}$, and $(Ph_3MeP^+)_6\,[Cu_8Br_{15}]^{6-}$. Concerts of edge-to-face (EF) and offset-face-to-face (OFF) local interactions between phenyl groups generate bimolecular $(EF)_6 = 6PE$ with symmetry S_6, hexamolecular $(EF)_6$ with symmetry S_6, trimolecular $(EF)_3$, hexamolecular $(OFF)_6$, and two-dimensional $\{(OFF)_6\}_\infty$. Crystal supramolecular analysis includes description of the asymmetric segments of intermolecular motifs, as well as the conventional asymmetric sector of the molecule.

Crystal supramolecularity—the investigation of intermolecular interactions through analysis of packing in molecular crystals—involves considerations of molecular shape and size and peripheral functionalities. It also necessarily involves considerations of symmetry, repetition, and space-filling.[1–3] A number of authors[3–5] have analysed the frequencies of occurrence of crystal space groups in the Cambridge Structural Database[6] (CSD) and noted that organic (*i.e.*, molecular) compounds frequently crystallise in one of a small number of space groups, and that 77% of the crystals surveyed were in one of four space groups: $P2_1/c$ (itself occurring in 38% of crystals), $P\bar{1}$, $P2_12_12_1$ and $C2/c$.[4,5] The incisive analysis by Brock and Dunitz[3] provided reasons for this, principally through consideration of the symmetry elements compatible or not with the common intermolecular interactions. The essence of the Brock–Dunitz intepretation of the occurrence of certain low symmetry space groups is that (1) organic molecules have low symmetry and (2) intermolecular interactions are generally incompatible with mirror and pure rotation symmetry elements (that bring like functionalities together), and favour glide, screw and inversion elements that permit the juxtaposition of opposites (such as positive/negative, donor/acceptor). The influence of intermolecular interactions is determined by their energies, and Filippini and Gavezotti[7] ranked the energy importance of symmetry operators in a restricted set of organic molecular crystals, with the conclusion that inversion centres, twofold screw axes, and glide planes are dominant. The abundant space groups for molecular organic crystals are thus understood in terms of the relatively low symmetry of most organic molecules and the symmetry elements preferred in the intermolecular motifs.

Therefore, the symmetry aspects of crystal supramolecular analysis involve the concept of molecular symmetry combining with the symmetries of intermolecular interactions, to yield the crystal lattice symmetry. These components are presented schematically in Fig. 1. Molecules normally have more than one recognisable intermolecular motif, as pictured. These

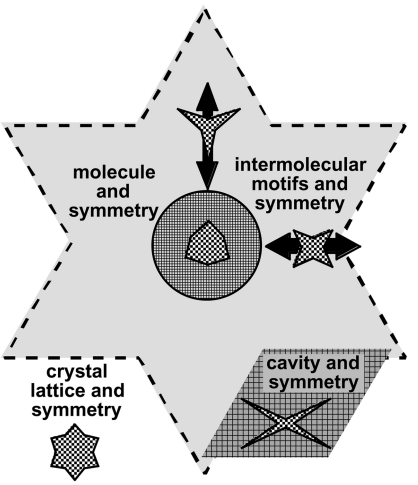

Fig. 1 Schematic representation of the concepts of entities and their local symmetries that comprise a crystal lattice and its symmetry (*i.e.*, space group). The entities are the molecule (centre), intermolecular interaction motifs (arrows), the crystal lattice (large outline), and cavities in the lattice (lower right). The chec stars are merely icons for the symmetry components, and do not imply any particular symmetry.

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concepts of separation of *intra*molecular symmetry and *inter*-molecular symmetry were expressed by Gavezzotti in terms of the "space group for the entire molecule".[5] There is another component that needs to be recognised and included in this conceptual framework, because the packing of the molecules can generate secondary cavities in the lattice, according to molecular size, shape and symmetry, and the extent and symmetry of intermolecular interactions. These cavities or cages have site symmetries (Fig. 1) and may be occupied by additional molecules. These extra molecules (sometimes called guests) may or may not possess the site symmetry of the cavity: they may be ordered or disordered.

The entities in our analyses of crystal supramolecularity and its symmetry properties are the molecule(s), the intermolecular interaction motifs, the complete crystal lattice, and the cavities or sites that may occur in the lattice. Each entity has its own symmetry and its asymmetric unit, or asymmetric segment. For the molecules, the interaction motifs, and the cavities, the symmetry is point symmetry, and the crystal symmetry (space group) combines these, with translation. While the molecular symmetry and the space group are normally explicit in descriptions of crystals, the symmetry of intermolecular interactions is not. Brock and Dunitz made them explicit, but considered that the symmetry of intermolecular interactions had a maximum order of two, and commented that higher symmetry (order 3, 4, 6) in intermolecular interactions would be unlikely "because molecules are seldom wedge-shaped".[3]

We are investigating some exceptions to these norms, specifically systems that possess unusually high symmetry in the molecule and/or in the intermolecular motifs.[8]

Multiple phenyl embrace motifs (and, more generally, multiple aryl embrace motifs) are concerted collections of local edge-to-face (EF) and/or offset-face-to-face (OFF) interactions between phenyl (aryl) groups.[9–26] While the individual EF and OFF motifs have no or low inherent symmetry, their concerts can and often do. For molecules with XPh_3 functions the ideal symmetry for the sixfold phenyl embrace (6PE) comprised of $(EF)_6$, is $\bar{3}$ [see Fig. 2(a)]. The enlarged 6PE E6PE; [Fig. 2(b)] also has ideal $\bar{3}$ symmetry,[16] as does the 6AE [Fig. 2(c)] as it occurs between metal complexes $[M(bipy)_3]^{z}$.[17] The O4PE [Fig. 2(d)] has ideal $\bar{4}$ symmetry, and in compounds of the type XPh_4, which crystallise in space group $P\bar{4}2_1c$, this symmetry is imposed. The terpy embrace,[21,27] involving molecules $[M(terpy)_2]^{z}$ and analogues, has $\bar{4}$ symmetry between four complexes [Fig. 2(e)], but this embrace is commonly extended in two dimensions to utilise fully all faces and edges of the terpy ligands.

In this paper we consider molecules containing XPh_3 groups. Previously we described a class of crystal structures for some XPh_3 containing molecules in the trigonal space groups $R\bar{3}$, $P\bar{3}$, $R\bar{3}c$, $P\bar{3}c1$, forming a lattice type called the hexagonal array of 6PE (HA6PE).[13,15] The first section of this paper presents the HA6PE lattice and its variables in terms of the concepts of Fig. 1, and in terms of the asymmetric unit of each of the entities. Then we describe and interpret some crystal structures of similar compounds that crystallise in the cubic space group $Pa\bar{3}$.

Symmetry analysis of the HA6PE lattice

Molecules (and molecular ions) crystallising with the HA6PE lattice contain at least one XPh_3 moiety, with molecular symmetry normally C_3 (3) or S_6 ($\bar{3}$).[15] They engage in at least one 6PE, with symmetry $\bar{3}$. A characteristic of the HA6PE lattice is that the threefold axes of all molecules and of the 6PE are parallel and aligned with the principal axis of a trigonal crystal lattice. Thus, threefold molecular symmetry and threefold embrace symmetry combine to yield threefold lattice symmetry. However, the details of the lattice symmetry and the space group are controlled by additional intermolecular interactions between these threefold chains of molecules (see below). Additional edges and faces of the phenyl groups of XPh_3 are used in OFF and 4PE motifs, which occur in a hexagonal array. These are multimolecular multiple phenyl embraces, whereas the 6PE are bimolecular. The multimolecular embraces normally involve groups of six molecules in a hexagonal array, often puckered. Fig. 3 shows both the parallel 6PE and the puckered hexagon of six molecules in a multimolecular $(EF)_6$ embrace. The 6PE are directed alternately to opposite sides of the hexagonal array.

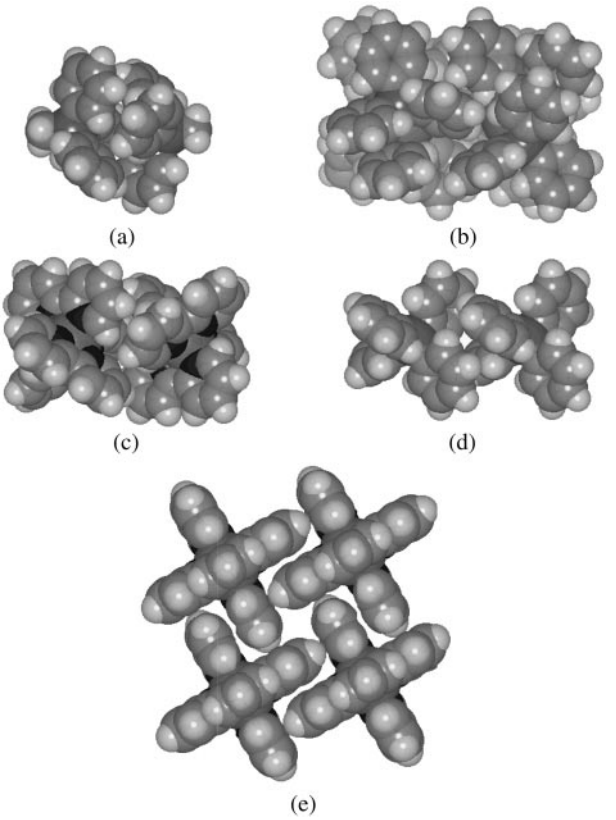

Fig. 2 Multiple phenyl (aryl) embraces and their symmetries. (a) The ideal 6PE [$\bar{3}$] for $XPh_3\cdots Ph_3X$. (b) The expanded 6PE [$\bar{3}$] between two $[Rh(PPh_3)_3]^+$ cations in CIDHUS. (c) The sixfold aryl embrace (6AE) [$\bar{3}$] between two $[M(bipy)_3]$. (d) The orthogonal fourfold phenyl embrace (O4PE) [$\bar{4}$]. (e) The terpy embrace of four molecules [$\bar{4}$], which can be extended in two dimensions.

The HA6PE lattice has two significant characteristics. First, there is transmittal of symmetry information through the 6PEs and the multimolecular embraces, which can have subtle influences on the space group symmetry and therefore on the cell dimensions.[15] For example, in a number of HA6PE structures six hexagonal layers are required for repetition along the trigonal axis (unit cell dimensions c are of the order of 60 Å) and the space group is $R\bar{3}c$ (as distinct from the three-layer repeat more commonly found when the space group is $R\bar{3}$). Second, the puckering of the hexagon of multimolecular embraces is quite variable, by elongation or compression along the trigonal axis. This allows efficient filling of space by molecules of different shapes and volumes and it also allows the incorporation of additional molecular species, especially the counter ions where (as illustrated above) the HA6PE is constructed from Ph_3XY^+ ions. In this way the HA6PE lattice can enclose space with variable volume but fixed symmetry. It is this aspect of the HA6PE lattice that led to the trapping of the unusual anion $[Cu_2Br_5]^{2-}$, which has not been detected in solution.[28] Fig. 3(a) shows the encapsulation of $[Cu_2Br_5]^{2-}$ by six 6PE, each $(MePh_3P^+)_2$, with one additional $MePh_3P^+$

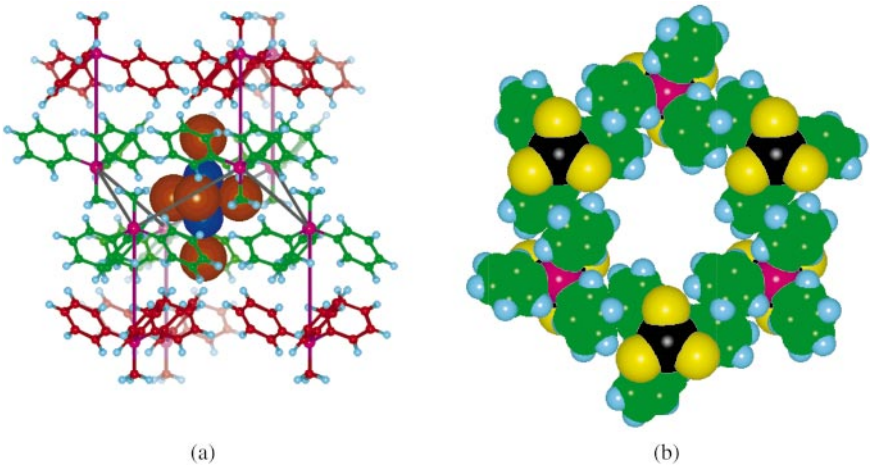

Fig. 3 Essential components of the HA6PE lattice. (a) Side view of part of the HA6PE lattice as it occurs in $(MePh_3P)_2[Cu_2Br_5]$ (CSD refcode SOBXIQ):[28] P magenta, Cu blue, Br brown. H cyan. Six parallel 6PE (marked as magenta rods P···P), each involving two $MePh_3P^+$ ions coloured green and red, are axially directed from a puckered hexagon of hexamolecular embraces (grey P···P rods). The counter ion, here $[Cu_2Br_5]^{2-}$, is located at the centre of the puckered hexagon. Each 6PE has $\bar{3}$ symmetry and the anion site has 32 symmetry. (b) Axial view of the hexamolecular embrace of six $Ph_3POGaCl_3$ molecules (CSD refcode JEJLEP; Ga black, Cl yellow), which is extended to form the two-dimensional hexagonal array, almost planar. Each edge of the hexagon is a well developed OFF interaction and the hexamolecular embrace is $(OFF)_6$. Three of the Ph_3P that form 6PE towards the reader are evident.

capping each end of the cage, around a site of symmetry 32 (D_3). This exemplifies the concept of cavity and cavity symmetry (Fig. 1).

To summarise the symmetry components of the HA6PE lattice, using the two compounds in Fig. 3 as examples: the principal molecule, $MePh_3P^+$ or $Ph_3POGaCl_3$, has C_3 symmetry, with one phenyl group in the asymmetric sector; the bimolecular embrace (6PE) has S_6 ($\bar{3}$) symmetry and one EF interaction in the asymmetric segment; the multimolecular embrace has two-dimensional hexagonal symmetry, variably puckered, again with one $(Ph)_2$ interaction in the asymmetric segment; the generated cavity has D_3 (32) symmetry, imposed on the counterion $[Cu_2Br_5]^{2-}$. All of this information is part of the description of the crystal supramolecularity.

Cubic lattices of XPh_3 molecules engaged in 6PE

Crystal packing of Ph_3AsI_2 [FESKAP02]

The molecule Ph_3AsI_2 (with linear As–I–I bonding) similarly forms 6PEs, and in crystals FESKAP02 does this in a cubic lattice, space group $Pa\bar{3}$.[29] A collinear pair of 6PE repeating along a threefold axis is shown in Fig. 4(a) and their occurrence along all of the threefold axes in the cubic lattice is presented in Fig. 4(b). The 6PE has $\bar{3}$ symmetry. The I···I gap between 6PE pairs occurs at the body-centre and edge-centres of the cell, and is surrounded by phenyl groups, as described below.

The asymmetric unit for intermolecular interactions is simply PhAsII. The phenyl ring is involved in four EF interactions, two in the 6PE, and two with adjacent molecules, as shown in Fig. 5.

The two iodine atoms provide considerable intermolecular stabilisation in this crystal, all as phenyl···I_2 and none as I_2···I_2. Six phenyl rings from six molecules surround the I_2 group, as shown in Fig. 6. Locally there are I_2···phenyl face and I···H–C at phenyl edge interactions, but these are not as ideal as those observed in many polyiodide crystal structures,[30–34] where there is more conformational freedom.

Crystal packing of $N(Ph\text{-}2\text{-}OMe)_3$ [JAPCIM]

A quite different molecule, tri(2-methoxyphenyl)amine, $N(Ph\text{-}2\text{-}OMe)_3$, crystallises with the same space group and effectively identical unit cell size as Ph_3AsI_2 (JAPCIM, $a = 15.32$ Å; FESKAP02, $a = 15.45$ Å).[35] Clearly the I_2 component and its intermolecular stabilising influences are absent, and the obvious question concerns the atoms and interactions that occupy the corresponding $\bar{3}$ domains of the crystal. There is

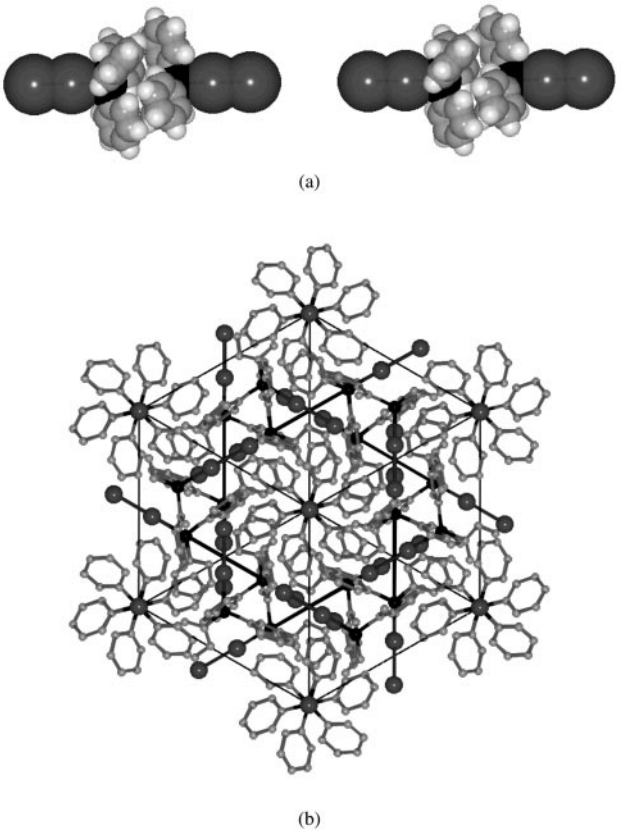

Fig. 4 Supramolecular components and their organisation in the crystal structure of Ph_3AsI_2 [FESKAP02]. (a) Two pairs of 6PE embracing Ph_3AsI_2 molecules as they occur along threefold axes of crystals FESKAP02, with an I···I separation of 9.44 Å. (b) Projection along a threefold axis of the cubic crystal [*i.e.*, along one of the units in (a)], with other oblique 6PE motifs marked as black connections As···As. 3_1 and 3_2 screw axes alternate around the sextants of this projection.

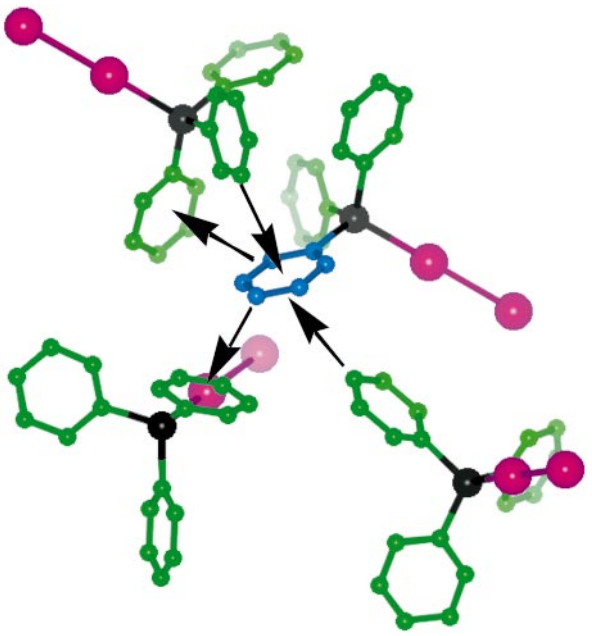

Fig. 5 The four EF interactions formed by the phenyl ring (blue) in the asymmetric unit of FESKAP02. The top two EF are part of the 6PE, the lower two EF interactions involve different molecules. Note that both faces and two edges of the phenyl ring are involved.

a molecular difference: N(Ph-2-OMe)$_3$ is close to planar at N (in fact the 6PE is very slightly inverted[14]) and the methoxy carbon atom is coplanar with the phenyl ring. This allows the formation of sequences of C–H···O motifs in place of the phenyl···I$_2$ motifs in FESKAP02.

Even though there are some large differences in the types of intermolecular motifs for N(Ph-2-OMe)$_3$ and Ph$_3$AsII, the symmetries and the asymmetric sectors of the molecule, the intermolecular interactions, and the crystal lattice are the same.

Crystal packing of Ph$_3$SnCl [TPSNCL03]

We now turn to a molecule with the same symmetry and similar dimensions to Ph$_3$AsII, namely Ph$_3$SnCl, as it crystallises in polymorph TPSNCL03.[36] The crystal packing and the intermolecular motifs are very similar to those of Ph$_3$AsII in FESKAP02, but the crystal lattice is rhombohedral, space group $R\bar{3}$. There are 1.33 molecules in the asymmetric unit. The principal difference is that there are two crystallographically different 6PE, one with $\bar{3}$ symmetry and one with lower $\bar{1}$ symmetry. The threefold 6PE will be labelled "axial", and differentiated with blue carbon atoms in Fig. 6 and 7: the other will be labelled "oblique". Both 6PE are compressed [Sn···Sn distances are 5.29 (axial), 5.57 Å (oblique)] with flattening of the Sn coordination and of the EF comprising the 6PE. Fig. 7 shows the overall crystal packing and the positions of the axial and oblique 6PE. Analogies with the packing in the corresponding cubic lattice [Fig 4(b)] are clear. A principal difference is that the pseudo-threefold axes of the oblique 6PE are not collinear in the rhombohedral structures, as they are in the cubic structure. We first describe some of the features of this crystal packing, and then consider the cause of the reduction in crystal symmetry.

The surroundings of the molecules on the threefold axes are shown in Fig. 8. The Cl···Cl separation between 6PE along this axis is long, 9.08 Å, but the central $\bar{3}$ site is fully surrounded by a set of six oblique 6PE. Within this domain the asymmetric unit of EF intermolecular motifs, in addition to the 6PE, is shown in Fig. 8(c). There is also a considerable

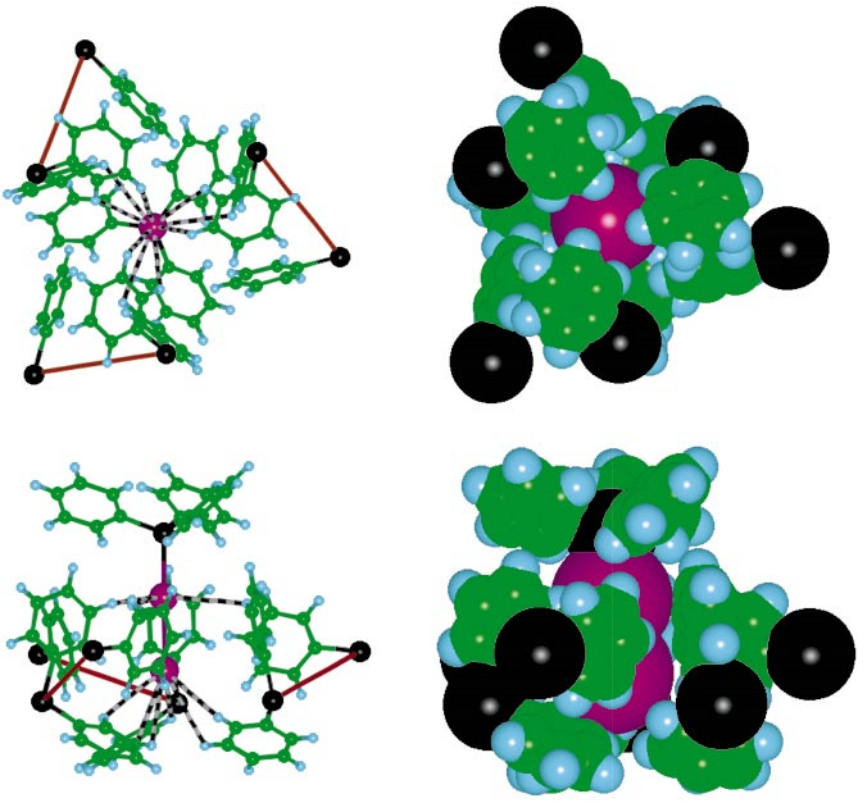

Fig. 6 The intermolecular interactions of the I$_2$ group in Ph$_3$AsI$_2$ [FESKAP02], shown in threefold projection (top) and from the side (bottom). Uninvolved phenyl rings are omitted. Phenyl edge C–H···I and phenyl face C···I interactions are marked as black and white candystripes on the left (the brown As···As connection is the 6PE) and space-filling representations are on the right.

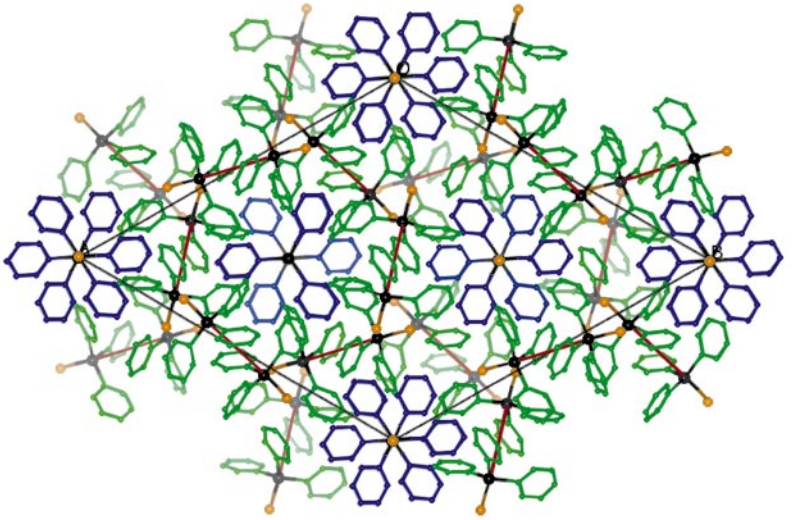

Fig. 7 Projection of the hexagonal setting of the crystal structure of Ph_3SnCl [TPSNCL03]. The oblique 6PE (green molecules) are evident as brown rods: phenyl rings involved in the axial 6PE are coloured blue. 3_1 and 3_2 axes alternate around each chain of axial molecules.

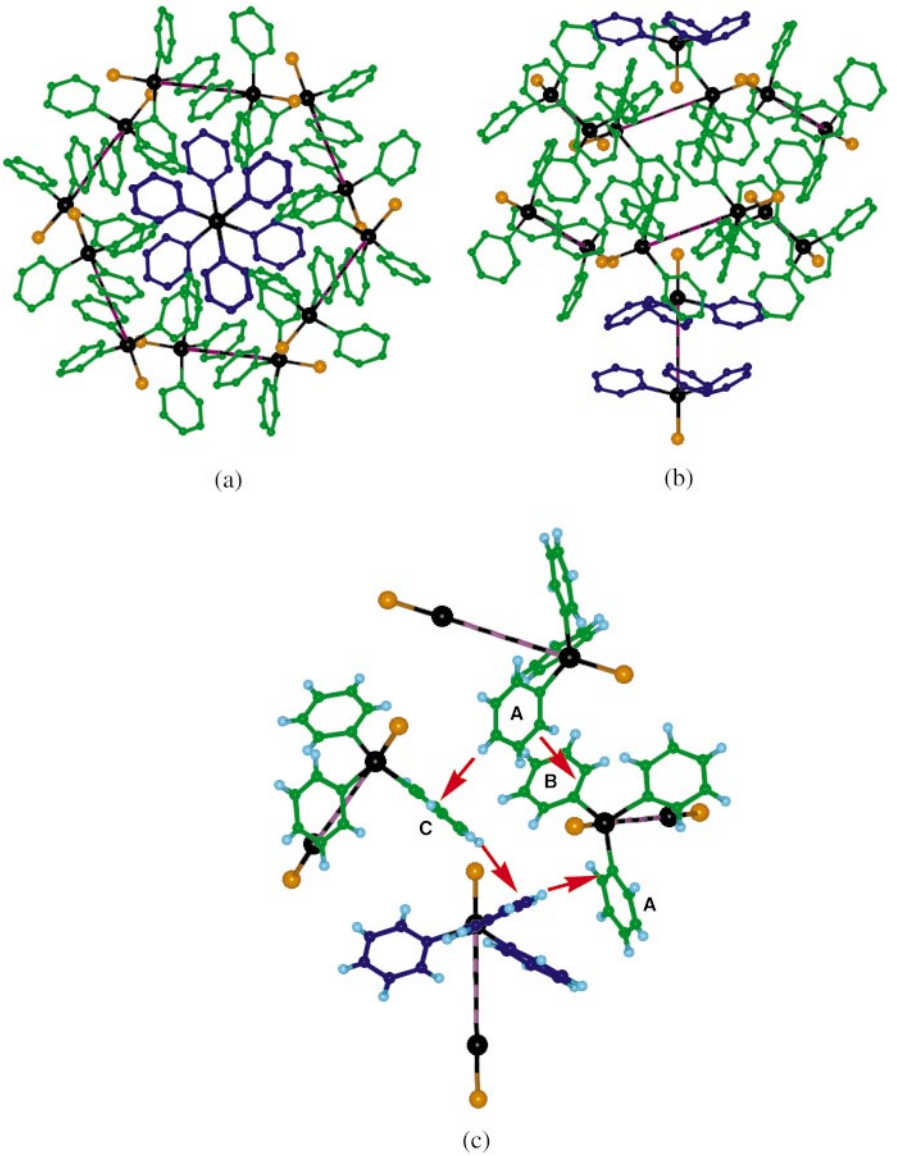

Fig. 8 Detail of intermolecular motifs in the crystal packing of Ph_3SnCl [TPSNCL03]. (a) Axial projection of the array of oblique 6PE around an axial 6PE on the threefold axis. (b) Side view of (a), showing the $\bar{3}$ site between two axial 6PE and set of six oblique 6PE that surround it. (c) The asymmetric segment of the interactions present in (b), with the EF interactions (except those in the 6PE) identified. The four crystallographically unique phenyl rings are A, B, C, and one coloured blue.

number of C–H···Cl interactions involving both molecules, not marked on the figures.

In summary of the crystal lattices described in this section, there is a cubic lattice type that is adopted by two chemically different molecules [Ph_3AsII and $N(Ph\text{-}2\text{-}OMe)_3$], each with symmetry C_3, involving chemically different but symmetrically identical intermolecular motifs. Another molecule, Ph_3SnCl, that is chemically analogous to Ph_3AsII uses similar motifs but with lower symmetry crystal packing. A key question is the reason for the difference, or why either did not crystallise in the lattice of the other. It is probable that the absence in Ph_3SnCl of the more voluminous and intermolecularly attractive I atoms allows the non-6PE EF interactions [Fig. 5 and 8(c)] to be improved. While the C–H···Cl interactions in Ph_3SnCl do not appear to be high quality, they are numerous and probably contribute appreciably to the lattice energy. There are polymorphs of some of these compounds and we will describe the alternative crystal packings in a separate paper before undertaking a fuller analysis.

Cubic lattices of XPh_3 molecules not engaged in 6PE

We now consider a set of molecules that contain one or two XPh_3 groups, as listed in Table 1. These molecules are very similar to many of the molecules that crystallise with the HA6PE lattice, but there are two distinctive differences. One is that these crystals are cubic rather than trigonal and the other is that the crystal packing is devoid of 6PE motifs. However, as will become apparent, the bimolecular $(EF)_6$ motif of the 6PE is replaced by a hexamolecular $(EF)_6$ motif. Some of these high symmetry lattice packings enclose cavities, occupied by guest molecules.

There is considerable chemical diversity amongst the compounds in Table 1. We describe first the crystal packing of $Ph_3PAuCCAuPPh_3$ [KABBEU][37] as a Ph_3XYXPh_3 type crystallising with a guest molecule, then $Ph_3PAu(B_6H_6)$-$AuPPh_3$ [TURKAS][38] as a related molecule not including a guest, then $(Ph_3PH^+)_2[SnCl_6]^{2-}$ [FAFVOX][39] as a two component crystal of type Ph_3X, and finally describe a rather different system, $(Ph_3MeP^+)_6[Cu_8Br_{15}]^{6-}$ [LODJIX].[40]

Crystal packing of $Ph_3PAuCCAuPPh_3 \cdot (C_6H_6)_2$ [KABBEU]

As shown in Fig. 9(a), this linear molecule with symmetry S_6 has a very thin waist, and has the phenyl groups conformed to lie close to parallel to the molecular axis: this conformation of phenyl rings disfavours the 6PE, which is consistent with the absence of the 6PE in this crystal. Fig. 9(b) shows the threefold projection of KABBEU. The $Ph_3PAuCCAuPPh_3$ and C_6H_6 molecules are both located on the threefold axes and there are similarities to the crystal structure of FESKAP02 described above.

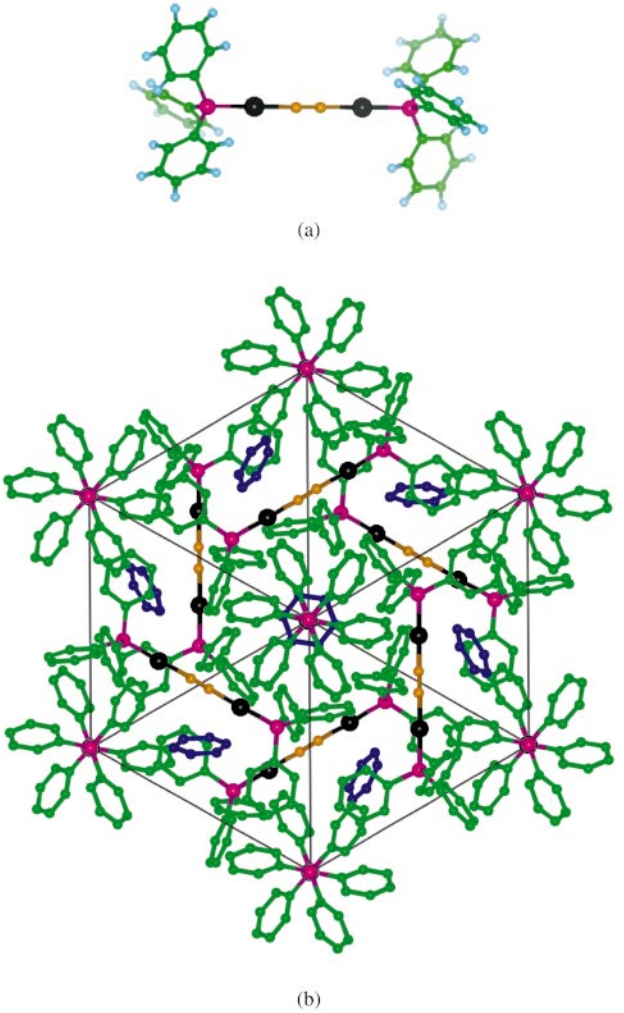

Fig. 9 The molecule $Ph_3PAuCCAuPPh_3$ and its crystal packing in KABBEU, space group $Pa\bar{3}$. Carbon atoms of the guest benzene molecule are coloured blue. (a) The $Ph_3PAuCCAuPPh_3$ molecule with S_6 ($\bar{3}$) symmetry. (b) Threefold projection of the lattice, with acetylide C atoms coloured orange to facilitate their recognition. Molecules are located on the projection axis and on the other oblique threefold axes. There are 3_1 or 3_2 screw axes in each sextant.

The asymmetric segment for intermolecular interactions is PhPAuC and part of the guest benzene. Two representations of this domain are presented in Fig. 10, with the conclusion that the only significant intermolecular motifs are an EF from one phenyl group to another, and a vertex (benzene) to face (phenyl).

Table 1 Compounds containing an XPh_3 group that crystallise in the cubic space group $Pa\bar{3}$.

Compound	REFCODE	Guest	a/Å
$Ph_3SnCCCCSnPh_3$	BUTSNA	$CHCl_3$	15.55
$Ph_3PbCCCCPbPh_3$	BUTSNB	CH_2Cl_2	15.40
$Ph_3SbCCCCSnPh_3$	CAFSAD	Dioxane	15.67
$(4\text{-}MeOPh)_3C–CC–CC–C(4\text{-}MeOPh)_3$	CINGIP	$CHCl_3$	16.38
$(Ph_3PH^+)_2[SnCl_6]^{2-}$	FAFVOX	—	17.08
$(Ph_3ClP^+)_2(Cl^-)_2$	RACJUA	CH_2Cl_2	15.99
$Ph_3PAuCCAuPPh_3$	KABBEU	Benzene	16.13
$(3\text{-}MePh)_3PAuCCAuP(3\text{-}MePh)_3$	KABBOE	Benzene	16.21
$Ph_3PCu(B_6H_6)CuPPh_3$	TURJUL	—	16.87
$Ph_3PAu(B_6H_6)AuPPh_3$	TURKAS	—	17.05
$(Ph_3MeP^+)_6[Cu_8Br_{15}]^{6-}$	LODJIX	—	23.10

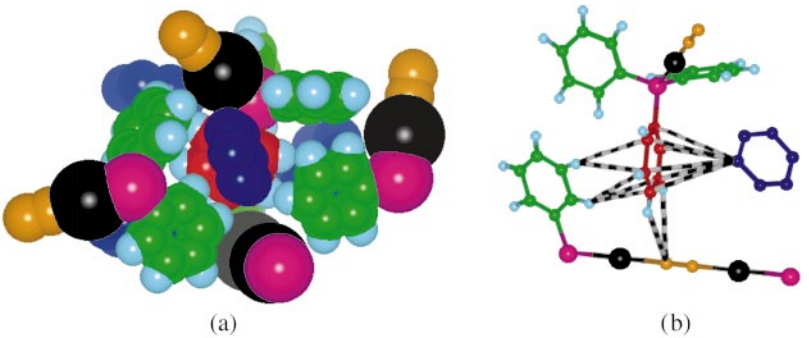

Fig. 10 Two orthogonal representations of the asymmetric segment of intermolecular motifs in $Ph_3PAuCCAuPPh_3$, KABBEU. The one phenyl ring of the asymmetric unit is coloured red and the guest benzene is blue. In (a) the phenyl rings on either side of benzene do not form good EF interactions with it. (b) The two good EF interactions to opposite faces of the phenyl ring are marked with black and white candystripes. There are also C–H···C interactions involving the acetylide bridge, as marked.

The good Ph···Ph EF motif shown in Fig. 10 generates a well-formed $(EF)_6$ hexamolecular cycle, with $\bar{3}$ symmetry, illustrated in Fig. 11(a). Further views of the $(EF)_6$ cycle can be found in the ESI (Fig. S1 and S2). The C–H···C (acetylide) interactions [Fig. 10(b)] provide support. There is some empty space in the centre of the $(EF)_6$, which is a small unoccupied cavity with $\bar{3}$ symmetry: it could accommodate only a very small guest molecule. However, Fig. 9(b) shows that there are guest benzene molecules along the threefold axes: where are they located? There is in fact a larger cavity in this crystal structure, created by a rhombohedron of $Ph_3PAuCCAuPPh_3$ molecules and containing two benzene guest molecules. Fig. 11(b) shows cutaway views of this cavity and the space within it. There are molecules at the poles of the cavity on its threefold axis, and six around the equator: these six form the $(EF)_6$ motif, which provides a girdle for the cavity. The benzene guest molecules lie either side of this $(EF)_6$ motif [Fig. 11(b)] and are separated by it. The three VF motifs [see Fig. 10(b)] between each benzene and surrounding molecules are evident in Fig. 11(c).

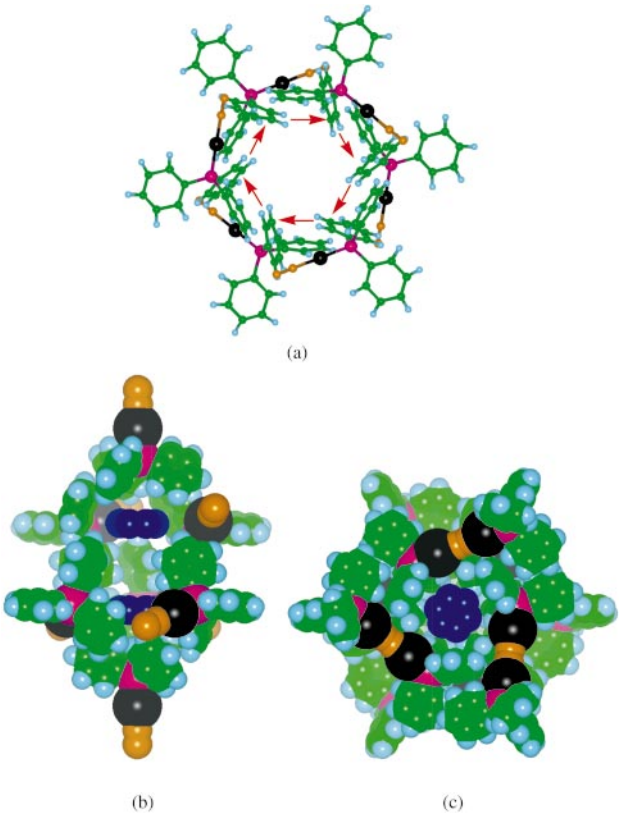

Fig. 11 (a) The hexamolecular $(EF)_6$ motif with $\bar{3}$ symmetry between parts of $Ph_3PAuCCAuPPh_3$ molecules in crystalline KABBEU: uninvolved terminal $AuPPh_3$ groups are omitted. This is the Ph···Ph EF motif of Fig. 10(b). The cycle of six molecules with the EF interactions are marked as red arrows. (b) Cutaway view of the rhombohedral cavity in KABBEU, generated by eight $Ph_3PAuCCAuPPh_3$ molecules and containing two benzene guest molecules that are located above and below the $(EF)_6$ motif, which girdles the cavity. This side view has the front molecule omitted, showing how the guest benzene molecules are located on either side of the central $(EF)_6$ motif. The perpendicular separation of the benzene molecules is >7 Å. (c) Top view of the cavity in (b), with one molecule omitted, showing the three benzene-vertex-to-phenyl-face (VF) interactions.

Crystal packing of $Ph_3PAu(B_6H_6)AuPPh_3$ [TURKAS]

In this molecule with S_6 symmetry, a hexaborane cluster connects two $AuPPh_3$ groups.[38] The molecule is slightly longer (P···P = 10.0 Å) than $Ph_3PAuCCAuPPh_3$ (P···P = 9.75 Å). The crystal packing and the $(EF)_6$ hexamolecular motif are the same as in KABBEU, described above. The difference is the absence of a guest molecule in TURKAS and this leaves empty spaces (see ESI Fig. S3). The quality of the crystal structure determination for TURKAS is good. Examination of the empty cavity indicates that it is very similar to that shown in Fig. 11 and that the slightly enlarged mid-section of the molecule (B_6H_6 *vs.* C_2) has little influence on the cross-section of the cavity.

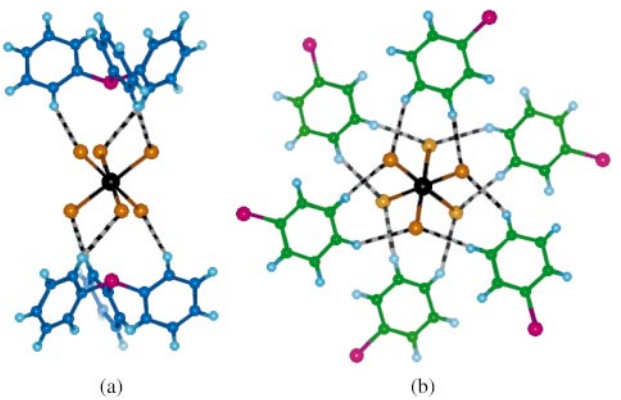

Fig. 12 The immediate surrounds of an $[SnCl_6]^{2-}$ ion in $(Ph_3PH^+)_2[SnCl_6]^{2-}$ [FAFVOX]. The two cations on the common threefold axis are coloured blue and relevant phenyl groups from six equatorial cations are green: well-formed C–H···Cl interactions are marked as black and white candystripes. (a) Side view of the coaxial $Ph_3PH\cdots Cl_3SnCl_3\cdots HPPh_3$ set: phosphonium hydrogen atoms (not included) are directed at Cl_3 faces of the anion. (b) Threefold axial view with the axial Ph_3PH^+ ions omitted.

Crystal packing of $(Ph_3PH^+)_2[SnCl_6]^{2-}$ [FAFVOX]

The crystal packing of this compound can be related to the two preceding compounds by recognising the association of two cations and one anion as $Ph_3PH\cdots Cl_3SnCl_3\cdots HPPh_3$, along a common threefold axis, as illustrated in Fig. 12(a). The phosphonium H atom is directed at the centre of a Cl_3 face, to which three phenyl H atoms form good C–H···Cl interactions. Six Ph_3PH^+ ions surrounding this threefold entity each have one phenyl ring directed towards a pair of Cl atoms of the anion [Fig. 12(b)], chelating it with two C–H···Cl interactions that are analogous to the C–H···acetylide interactions for KABBEU [see Fig. 10(b)].

The remainder of the crystal packing is then similar to that of KABBEU and TURKAS. The asymmetric segment for the intermolecular interactions of Ph_3PH^+ is one Ph ring, which accepts one and donates one EF to other Ph rings. This generates the hexamolecular $(EF)_6$ motif, similar to that shown in Fig. 11(a), around the girdle of the $\bar{3}$ domain along the threefold axis between $[SnCl_6]^{2-}$ ions. The cavity in the $\bar{3}$ domain is shown in Fig. 13.

Crystal packing of $(Ph_3MeP^+)_6[Cu_8Br_{15}]^{6-}$ [LODJIX]

An abbreviated description of parts of the crystal packing in this unusual compound has been reported.[40] The unprecedented mixed-valence ion $[Cu_8Br_{15}]^{6-}$ is comprised of two $(\mu_3\text{-}Br)_4(CuBr)_4$ cubanoid clusters sharing a linear Br atom, and has a dumbell shape with $\bar{3}$ symmetry (Fig. 14). The space group is $Pa\bar{3}$ as in the previous compounds, but the cell volume is *ca.* 2.5 times larger. Description of the crystal packing is now definitely facilitated by recognition of the asymmetric segments of intermolecular interactions. The asymmetric unit of the molecular components is one complete Ph_3MeP^+ ion, together with the two chemically distinct Cu and four chemically distinct Br in the anion. The anions are well separated and there are no interactions between them, so the intermolecular interactions to be assessed are $Ph_3MeP^+\cdots Ph_3MeP^+$ and $Ph_3MeP^+\cdots[Cu_8Br_{15}]^{6-}$. In analysing the crystal packing it is also helpful to examine the arrangement of molecules on and around the threefold axes, recognising that this compound is different from previous structures in that the Ph_3MeP^+ ions do not lie on the threefold axes.

Fig. 14 is a simplified representation of the arrangement of Ph_3MeP^+ around the threefold axis, in relation to the position of $[Cu_8Br_{15}]^{6-}$ on it, at a $\bar{3}$ site. The P atoms and their separations are marked. Details of the types of interactions around one cation, identified by their P···P separations, are provided in Fig. 15. There are no concerted multiple phenyl embraces between pairs of cations. There are, however, concerted multimolecular motifs, occurring as cycles. The locations of these cycles are marked on Fig. 14.

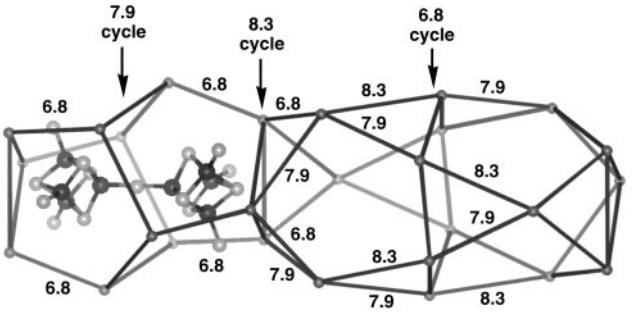

Fig. 14 The net of Ph_3MeP^+ locations around the threefold axis (P atoms only), in relation to the location of $[Cu_8Br_{15}]^{6-}$ in $(Ph_3MeP^+)_6[Cu_8Br_{15}]^{6-}$ [LODJIX]. The distances (in Å) are the P···P separations, identifying the interactions.

Fig. 16 shows details of the three types of concerted cyclic multimolecular embrace involving Ph_3MeP^+, namely the "8.3 cycle" which is $(EF)_3$, the "7.9 cycle", which is $[(EF)_3]_6$ around the centre of $[Cu_8Br_{15}]^{6-}$, and the "6.8 cycle", which is $[EF + CH_3\cdots Ph]_6$. The 6.8 and 8.3 cycles of cations close the threefold axis between anions.

The complete lattice is the array of these threefold assemblies (Fig. 14 and 16) along the four threefold axes that pass through the unit cell in space group $Pa\bar{3}$. In considering the dominant forces in the formation of this lattice, and the question of whether the multimolecular multiple phenyl embraces of the cations dictate the anion's shape, or whether the anion assembles the surrounding cations, the local interactions between $[Cu_8Br_{15}]^{6-}$ and Ph_3MeP^+ need to be evaluated. The asymmetric unit of these C–H···Br is shown in Fig. 17. There are six pairs of cations around one anion, and so the total number of interactions is six times those shown: some but not all of these C–H···Br have good geometry.

We can conclude that the unusual redox state of $[Cu_8Br_{15}]^{6-}$ is determined by the crystal lattice. The packing of the cations determines that the charge associated with the cavity they form, containing the anion, is necessarily $6-$. This requires that the oxidation states be formally $7Cu^{I} + Cu^{II}$,

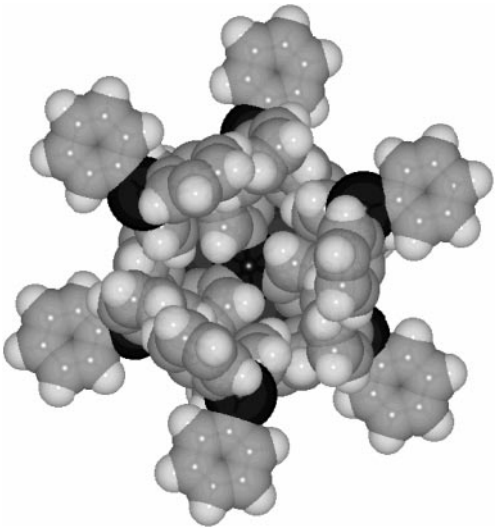

Fig. 13 The rhombohedral cavity along a threefold axis in $(Ph_3PH^+)_2[SnCl_6]^{2-}$ [FAFVOX], revealed by removal of an axial Ph_3PH^+.

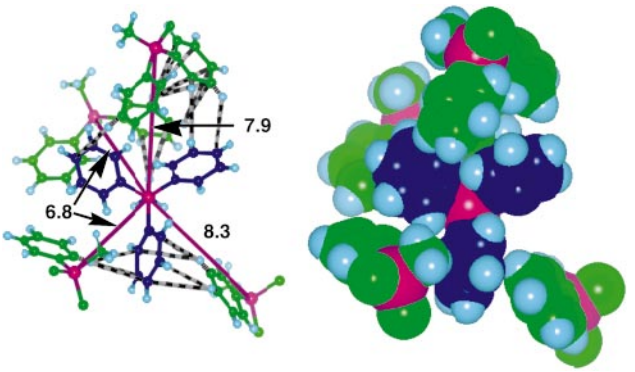

Fig. 15 Details of the interactions between one Ph_3MeP^+ in LODJIX, coloured blue, and its surrounds. Edge-to-face phenyl···phenyl contacts, marked as black and white candystripes, are not well-developed.

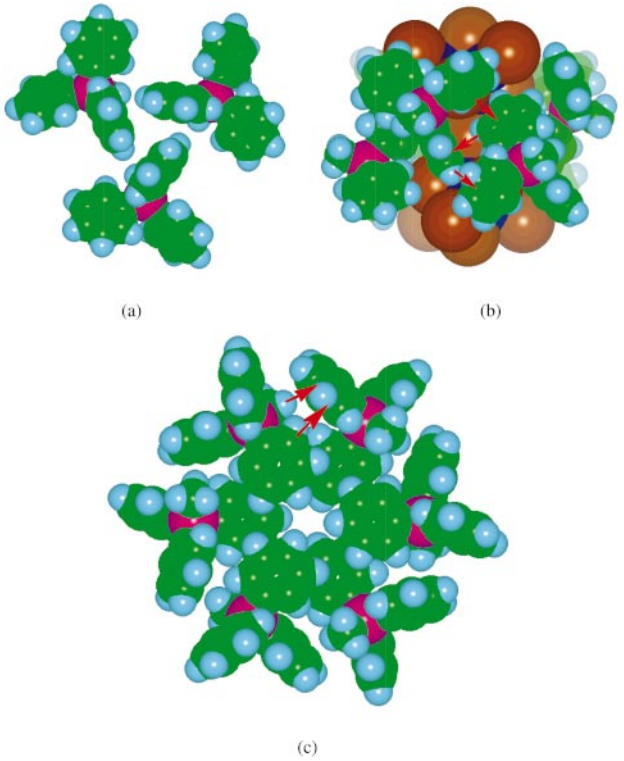

Fig. 16 (a) The triangular $(EF)_3$ motif comprising the "8.3 cycle" of Ph_3MeP^+ in $(Ph_3MeP^+)_6[Cu_8Br_{15}]^{6-}$ [LODJIX]. (b) Side view of the puckered "7.9 cycle" of six Ph_3MeP^+ surrounding $[Cu_8Br_{15}]^{6-}$. The asymmetric set of EF interactions between contiguous cations is arrowed. (c) Axial view of the very slightly puckered "6.8 cycle" of six Ph_3MeP^+. The six phenyl rings in the centre form pseudo-OFF interactions, with plane separations of *ca.* 3.5 Å. Around the periphery there are EF interactions and methyl-H-to-phenyl interactions: an asymmetric set is arrowed.

whereas the geometry of the anion presents a distribution of Cu atoms types as $6+2$. There is no evidence that $[Cu_8Br_{15}]^{6-}$ exists as such in solution, and it is clear that there is electronic, and probably geometric entrapment in this crystal lattice.[40]

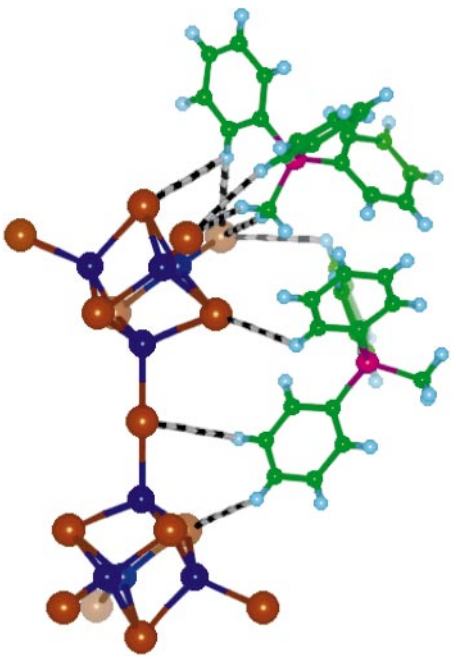

Fig. 17 The asymmetric unit of Ph_3MeP^+ interactions with $[Cu_8Br_{15}]^{6-}$ in $(Ph_3MeP^+)_6[Cu_8Br_{15}]^{6-}$ [LODJIX].

Discussion

In this report for molecules in the class XPh_3, we have described various combinations of symmetry amongst the four components of crystal supramolecular analysis: molecule—intermolecular motif—crystal lattice—cavity (Fig. 1). The molecular symmetry of the XPh_3 entity has been C_3 or S_6 or C_1. The intermolecular motifs have been bimolecular $(EF)_6 = 6PE$ with symmetry S_6, hexamolecular $(EF)_6$ with symmetry S_6, trimolecular $(EF)_3$, hexamolecular $(OFF)_6$, and two-dimensional $[(OFF)_6]_\infty$ in the HA6PE lattice. The combinations of these molecular and intermolecular symmetries have yielded trigonal and cubic space groups, and the lattice cavities containing guest molecules or counter ions are consequently also of high symmetry. The common theme is high symmetry, generally threefold, and these systems are therefore exceptions to the predominant occurrence of asymmetric or twofold intermolecular motifs and the low symmetry space groups.

Different combinations of molecules and intermolecular motifs have been highlighted. The HA6PE lattice is dominated by parallel 6PE, aligned with the principal trigonal axis, whereas Ph_3AsII forms similar 6PE but positioned on the threefold axes of a cubic lattice. In fact, Ph_3AsII, when co-crystallised with toluene, forms an HA6PE lattice.[15] A relatively small modification of molecular properties, from Ph_3AsII to Ph_3SnCl, causes concomitant small variations of the intermolecular motifs: the molecules and motifs are in similar locations in these two crystals [FESKAP02 and TPSNCL03], but the asymmetric segment changes and the crystal lattice type change, from cubic to trigonal. Then there is a different combination of intermolecular motifs, in a set of crystals (Table 1) that maintain the high lattice symmetry (cubic), but use hexamolecular embrace motifs and do not possess the otherwise common bimolecular 6PE. The crystal structure of $(Ph_3MeP)_6[Cu_8Br_{15}]$ shows that a high symmetry (S_6, $\bar{3}$) multimolecular motif can be formed from molecules without symmetry.

In each case it has been helpful to describe the asymmetric segment of the intermolecular motifs, as well as the conventional asymmetric sector of the molecule.

The crystal engineering prospects for compounds of this type are illustrated by the two examples where unusual and unprecedented copper bromide anions, $[Cu_2Br_5]^{2-}$ and $[Cu_8Br_{15}]^{6-}$, have been trapped in cavities in high symmetry crystals (trigonal and cubic) constructed from embracing Ph_3MeP^+ ions. In particular, it appears that the concerted and symmetrical (and stabilising) interactions between Ph_3MeP^+ have engineered the net charge on the cavities in their lattice, and thereby controlled the redox state of the metal compounds that occupy the cavities. The conformational flexibility of the HA6PE lattice, described previously,[15] allows variation of the shape and size (but not charge and symmetry) of its lattice cavities.

In our next paper we describe other combinations of symmetric molecules and motifs[41] and will, in subsequent papers, analyse the polymorphism that occurs for some of these Ph_3X compounds.

Acknowledgements

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