Crystal Supramolecular Motifs: Columns of Embracing Ph$_3$PMe$^+$ or Ph$_3$PCl$^+$ Cations Controlling Formation of [Cu$_3$X$_8^{2-}$]$_n$ (X = Cl, Br)

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The crystal structures of (Ph$_3$P)$_2$[Cu$_3$Cl$_6$] (I) (triclinic, space group $P$1, $a = 9.480(6)$ Å, $b = 10.243(8)$ Å, $c = 11.232(6)$ Å, $\alpha = 86.76(4)^\circ$, $\beta = 66.62(5)^\circ$, $\gamma = 83.92(4)^\circ$, $Z = 1$) and (Ph$_3$PMe)$_2$[Cu$_3$Br$_6$] (2) (triclinic, space group $P$1, $a = 9.795(4)$ Å, $b = 10.472(4)$ Å, $c = 11.392(4)$ Å, $\alpha = 86.67(3)^\circ$, $\beta = 66.67(3)^\circ$, $\gamma = 83.14(3)^\circ$, $Z = 1$), reported here, demonstrate a new supramolecular motif for cations of the type Ph$_4$PY$^+$ where Y is CH$_3$ or Cl. The crystals contain columns of cations propagated by alternating 6-fold phenyl embraces (6PE) and pseudo-6PE: the pseudo-6PE described here contains four phenyl rings and two hetero groups (Cl or CH$_3$), and is symbolized as 4P2Y. The zigzag sequence of cations engaged in ⋯6P⋯4P2Y⋯6P⋯4P2Y⋯ is similar to the zigzag chain of infinite 6-fold phenyl embraces (ZZI6PE) frequently adopted by Ph$_4$PY$^+$ cations in crystals. One-dimensionally nonmolecular anion chains with repeat unit [Cu$_3$X$_8$] run parallel to and between the columns of cations. The coordination geometry in the [Cu$_3$X$_8^{2-}$]$_n$ chain has not been observed in crystals with other cations, and it is postulated that the attractive interactions between cations in the pseudo-ZZI6PE crystal supramolecular motif control the geometry of the anions through the requirement for commensurability of cation columns and anion chains.

Introduction

In previous papers we have shown that there are attractive intermolecular interactions between Ph$_4$P$^+$ cations in crystals. These supramolecular influences, perhaps surprising as attractive interactions between ions of the same charge, are due to particular geometrical associations—supramolecular motifs—in which there are concerted sets of the fundamental edge-to-face (ef), vertex-to-face (vf), and offset-face-to-face (off) interactions between phenyl rings. The 6-fold phenyl embrace, 6PE, has a concerted set of six ef interactions between three phenyl groups on each of two Ph$_4$P$^+$ cations. There are two main classes of 4-fold phenyl embraces involving two phenyl rings on each of two Ph$_4$P$^+$ cations: one (the orthogonal 4-fold phenyl embrace, O4PE) has a concert of four ef interactions, while the other (parallel 4-fold phenyl embrace, P4PE) contains one off and two ef interactions. These pairwise motifs are commonly extended into chains and layers, by the use of all of the phenyl groups on Ph$_4$P$^+$. The zigzag infinite chain of 6-fold phenyl embraces (ZZI6PE; see Figure 1) arises through the use of two sets of three phenyl groups on each Ph$_4$P$^+$ ion, and occurs in a large number of crystals with a variety of anions. In these crystals the ZZI6PE chains of cations are usually parallel, and may be separated from each other or may be linked further by 4PE to yield layers of cations.

More elaborate crystal supramolecular lattices of cations have been identified, and deployed for crystal engineering. Analogous crystal supramolecular motifs involve Ph$_4$P$^+$ cations on the peripheries of metal complexes, and bipy and terpy ligands in metal complexes.

In this paper we report a modification of the ZZI6PE motif which occurs with the methyltriphenyolphosphonium and chlorotriphenyolphosphonium cations, Ph$_3$PMe$^+$ and Ph$_3$PCl$^+$, in the isomorphous compounds (Ph$_3$P)$_2$[Cu$_3$Cl$_6$] (1) and (Ph$_3$PMe)$_2$-[Cu$_3$Br$_6$] (2). These crystals are unique in that the anion is structurally nonmolecular in one dimension: supramolecular

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cation chains are packed with parallel one-dimensionally nonmolecular anion chains, and the two chain types are geometrically commensurate. In this context we raise a key question for the crystal engineering of halometalate anions: is the crystal packing dominated and determined by the cation supramolecular motifs, or by coordination within the halocuprate anion?

Experimental Section

Preparation and Crystallization of (Ph₃PCl)₂[Cu₃Cl₈] 1. The compound [Ph₃PCl(Cl)PPh₃]⁺[ClHCl]⁻ (3) was crystallized from the following reaction. Ph₃P (2 g, 7.6 mmol) and CCl₄ (10 mL, 76 mmol) were stirred at room temperature under nitrogen for 1 h to give a colorless solution. CuCl₂ (0.5 g, 3.8 mmol) and CH₂CN (10 mL) were mixed at room temperature to give a khaki-brown-colored mixture. Although most of the CuCl₂ remained unsolubilized, the supernatant solution was transferred under nitrogen to the Ph₃P/CCl₄ mixture. Upon addition the mixture turned burgundy but changed to yellow after 5 min of stirring and after 10 min darkened to orange. After the reaction mixture was allowed to stand overnight, solvent was removed under vacuum to give large block-shaped, pale yellow crystals which were characterized by crystal structure determination as [Ph₃PCl(Cl)PPh₃]⁺[ClHCl]⁻.

[Ph₃PCl(Cl)PPh₃]⁺[ClHCl]⁻ (0.396 g, 0.62 mmol) and CuCl₂ (0.083 g, 0.62 mmol) were dissolved in 2-propanol (700 mL) and stirred thoroughly. The green solution was allowed to stand at ambient temperature, overnight. Although not all of either solid dissolved immediately, a bright orange solution formed immediately. After the solution was stirred for 30 min, all the solid had dissolved. After 12 h at room temperature and with no stirring, large orange, block-shaped intergrown crystals formed. The crystals were collected, washed with cold chloroform (in which they are partially soluble), and air-dried. These crystals decompose slowly as partially soluble), and air-dried. These crystals decompose slowly and are isomorphous. The chloro homologue [3, (Ph₃PMe)₂[Cu₃Br₈]], also forms isomorphous crystals [NIJZEL, in the Cambridge Structural Database]. In this structure type there are parallel columns of cations and anions, aligned with the crystallographic a axis. The anion chain is shown in Figure 2, and is comprised of regular square planar CuX₄ units which share vertexes and edges, with weaker secondary X---Cu coordination to 2/3 of the Cu atoms. The chain is essentially linear, being propagated by centers of inversion.
Table 1. Bond Distances and Angles in the Anion Chains [Cu₃X₈²⁻]₁ of 1 and 2

<table>
<thead>
<tr>
<th></th>
<th>X = Cl</th>
<th>X = Br</th>
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<tbody>
<tr>
<td></td>
<td>Cu₁–X₁</td>
<td>Cu₂–X₃</td>
</tr>
<tr>
<td></td>
<td>2.318(1) 2.452(1)</td>
<td>2.299(1) 2.446(1)</td>
</tr>
<tr>
<td>Cu₁–X₄</td>
<td>2.252(1) 2.392(1)</td>
<td>Cu₂–X₄</td>
</tr>
<tr>
<td></td>
<td>2.642(1) 2.734(1)</td>
<td></td>
</tr>
<tr>
<td>Cu₂–X₁</td>
<td>2.339(1) 2.466(1)</td>
<td>Cu₂–X₃</td>
</tr>
<tr>
<td></td>
<td>2.300(1) 2.437(1)</td>
<td></td>
</tr>
<tr>
<td>X₁–Cu₂–X₂</td>
<td>88.4(1) 88.9(1)</td>
<td>X₂–Cu₂–X₃</td>
</tr>
<tr>
<td></td>
<td>91.6(1) 91.1(1)</td>
<td>91.8(1) 92.9(1)</td>
</tr>
<tr>
<td>X₁–Cu₂–X₃</td>
<td>90.7(1) 90.2(1)</td>
<td>X₄–Cu₂–X₃</td>
</tr>
<tr>
<td></td>
<td>90.2(1) 90.8(1)</td>
<td>100.2(1) 96.2(1)</td>
</tr>
<tr>
<td>X₁–Cu₂–X₄</td>
<td>79.2(1) 81.3(1)</td>
<td>Cu₁–Cu₁–Cu₂</td>
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<tr>
<td></td>
<td>86.7(1) 83.6(1)</td>
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<tr>
<td>X₁–Cu₂–X₅</td>
<td>174.6(1) 174.2(1)</td>
<td>Cu₁–Cu₂–X₃ ii</td>
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<tr>
<td></td>
<td>174.2(1) 174.6(1)</td>
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<tr>
<td>X₂–Cu₂–X₃</td>
<td>157.3(1) 153.2(1)</td>
<td>Cu₁–Cu₂–X₃ ii</td>
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<tr>
<td></td>
<td>98.2(1) 102.9(1)</td>
<td></td>
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</tbody>
</table>

Figure 3. Parallel alignment of the chains of cations and of anions in crystalline 1. The ellipses enclose one cation chain and one anion chain: the plane formed by the P atoms in the pseudo-ZZI₆PE chain of cations is marked by the line in the enclosed cation chain. The planes of the cation–anion layers and the cation–cation layers discussed in the text are marked. This is a projection along the crystallographic a axis: Cu and P atoms are black; Cl atoms are speckled; H atoms are omitted.

Details of the bond distances and angles in the [Cu₃X₈²⁻]₁ chains of 1 and 2 are listed in Table 1, and intramolecular dimensions of the cations, which are normal, are provided in the Supporting Information.

Crystal Packing. The crystal packing involves supramolecular chains of cations parallel to the one-dimensionally non-molecular anions. This is illustrated in Figure 3, which is a projection along the axis of the chains. The next stage in understanding this crystal structure type involves examination of the details of the column of cations: Figure 4 shows this column as it occurs in 2. The column is a zigzag sequence of alternating 6PE and pseudo-6PE, both centrosymmetric. The 6PE for a (Ph₃PMe⁺)₂ pair is identified by a P⋯P separation of 5.95 Å in Figure 4, and has the P–methyl vectors collinear and exo to the P⋯P vector. This is in fact a very good 6PE motif, according to the orientations of the six phenyl rings in the interaction zone and the quality of the local ef interactions. The pseudo-6PE, identified by the P⋯P separation of 6.05 Å in Figure 4, has methyl groups replacing two phenyl groups in the 6PE. The zigzag alternation of 6PE and pseudo-6PE is called the pseudo-ZZI₆PE, being entirely analogous to the standard ZZI₆PE of Figure 1.
In the pseudo-ZZI6PE, the P separation is 5.96 Å. While the 6PE motifs are standard, the 4P2Y pseudoembraces occur in other crystalline compounds, particularly in crystals containing Ph3 PCl, and we shall provide details and energy calculations in a future publication.

**Cation–Anion Commensurability.** Next we analyze the commensurability of the anion chains and the cation columns.

**Discussion**

The cation Ph3PCI+ which occurs in compound 1 is usually formed by the reaction of Ph3P with Cl2.17–19 Our reaction systems used Ph3P with CCl4 in the presence of copper(II) halides (the objective was to prepare Ph3PCCl3+ cations20–22) and generated Ph3PCl(Cl)PPh3+, which subsequently degraded to Ph3PCI+ in the presence of CuCl2 in acetonitrile. Compounds of Ph3PCI+ with halometalate anions [MCl6]2- (M = Mo, Sn) form tight 6PE motifs (P⋯P = 5.6 Å) in another supramolecular lattice which we have previously described as the hexagonal array of 6-fold phenyl embraces (HA6PE).7

Here the Ph3PCI+ forms a pseudo-ZZI6PE motif, with an alternation of 6P and 4P2Y motifs along the column. Our results show also that Ph3PMe+ can form a similar pseudo-ZZI6PE motif. One of the characteristics of the Ph3PMe+ cation is its

![Figure 6](Image 82x356 to 267x744)

**, Alignment and closest contacts for the anion chains and the cation columns in 1 and 2. The \( \text{cationCl} \cdots \text{Clanion} \) and \( \text{cation methylH} \cdots \text{Br anion} \) distances (Å) are marked. The anions and cations are propagated by two centers of inversion per repeat unit.**
adoption of the HA6PE lattice type, and so both of the 3-fold triphenylphosphonium cations, Ph3PCl+ and Ph3PMe+, can form both the HA6PE lattice and the pseudo-ZZI6PE motif.

The pseudo-ZZI6PE motif formed by Ph3EY (E = group 14 or 15) could have an alternative sequence of local interactions, namely, repeated 5P1Y rather than the alternating 6P and 4P2Y observed in 1 and 2 (see Figure 8). We have identified instances of this alternative, in which the linear supramolecular motif of cations is often propagated by a 21 crystal symmetry element, and will describe them separately.

In crystalline 1 and 2, together with isostructural (Ph3PMe)2[Cu3Cl8]16, the pseudo-ZZI6PE columns are all parallel, and accommodate the anions in cavities between the columns. This is one of several standard lattice types for the ZZI6PE motif.

In these three crystals the cation columns are associated with and commensurate with an unusual copper halide chain, which has not been observed with any other cation. Examination of the copper(II) halide compounds in the Cambridge Structural Database reveals structures containing [Cu2X6]2−, [Cu2X12]4−, [Cu3X11]3−, [Cu5X14]4−, and Cu2X4, but only one anion with the composition [Cu3Br8]2−. In this crystal structure [ZACSAX23] which contains the N-methyl-2-picolinium cation, the [Cu3Br8]2− salt has the chain structure shown in Figure 9, propagated through secondary Br−Cu bonds of 2.76 Å.

We postulate that the different [Cu3X2−]∞ chain formed in the three crystals with Ph3PY+ cations has been influenced by the formation of the cation column with a pseudo-ZZI6PE motif in them. It is likely that the details of the coordination and bridging of copper have been controlled by the requirements of the cation motif. Validation of this hypothesis (and more certain answers to the question raised in the Introduction) will require further geometrical information from crystals of related compounds and phase variants, and calculations of intra- and intermolecular energies.

Acknowledgment. The support of this research by the Australian Research Council is gratefully acknowledged.

Supporting Information Available: ORTEP drawings for 1, 2, and 3 with thermal ellipsoids drawn at the 20% probability level and crystallographic information in CIF format for 1, 2, and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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