Inorg. Chem. **2000,** *39,* 401−405

Crystal Supramolecular Motifs: Columns of Embracing Ph_3PMe^+ or Ph_3PCl^+ Cations Controlling Formation of $[Cu_3X_8{}^{2-}]^1_\infty$ (X = Cl, Br)

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Received July 7, 1999

The crystal structures of $(Ph_3PCl)_2[Cu_3Cl_8]$ (**1**) (triclinic, space group $P\bar{1}$, $a = 9.480(6)$ Å, $b = 10.243(8)$ Å, $c = 11.232(6)$ Å, $\alpha = 86.76(4)°$, $\beta = 66.62(5)°$, $\gamma = 83.92(4)°$, $Z = 1$) and $(Ph_3PMe)_2[Cu_3Br_8]$ (**2**) (triclinic, space group $P\bar{1}$, $a = 9.795(4)$ Å, $b = 10.472(4)$ Å, $c = 11.392(4)$ Å, $\alpha = 86.67(3)°$, $\beta = 66.67(3)°$, $\gamma = 83.14(3)°$, $Z = 1$), reported here, demonstrate a new supramolecular motif for cations of the type Ph_3PY^+ 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_4P^+ cations in crystals. One-dimensionally nonmolecular anion chains with repeat unit $[Cu_3X_8]$ run parallel to and between the columns of cations. The coordination geometry in the $[Cu_3X_8{}^{2-}]^1_\infty$ 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_4P^+ cations in crystals.[1,2] 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**) attractions between phenyl rings.[3] The 6-fold phenyl embrace, 6PE, has a concerted set of six **ef** interactions between three phenyl groups on each of two Ph_4P^+ cations.[1,2] There are two main classes of 4-fold phenyl embraces involving two phenyl rings on each of two Ph_4P^+ 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.[2]

These pairwise motifs are commonly extended into chains and layers, by the use of all of the phenyl groups on Ph_4P^+. 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_4P^+ ion, and occurs in a large number of crystals with a variety of anions.[4] 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.[5]

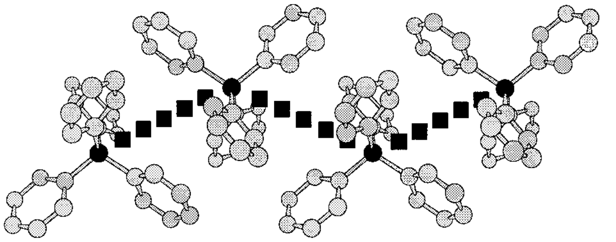

Figure 1. Zigzag infinite chain of 6-fold phenyl embraces (ZZI6PE) formed by Ph_4P^+ cations (H atoms omitted, P black): each line of black squares is a 6PE.

More elaborate crystal supramolecular lattices of cations have been identified,[6,7] and deployed for crystal engineering.[8,9] Analogous crystal supramolecular motifs involve Ph_3P ligands on the peripheries of metal complexes,[10] and bipy and terpy ligands in metal complexes.[11,12]

In this paper we report a modification of the ZZI6PE motif which occurs with the methyltriphenylphosphonium and chlorotriphenylphosphonium cations, Ph_3PMe^+ and Ph_3PCl^+, in the isomorphous compounds $(Ph_3PCl)_2[Cu_3Cl_8]$ (**1**) and $(Ph_3PMe)_2$-$[Cu_3Br_8]$ (**2**). These crystals are unique in that the anion is structurally nonmolecular in one dimension: supramolecular

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10.1021/ic990803r CCC: $19.00

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 $(Ph_3PCl)_2[Cu_3Cl_8]$ 1. The compound $[Ph_3PC(Cl)PPh_3]^+[ClHCl]^-$ (**3**) was crystallized from the following reaction. Ph_3P (2 g, 7.6 mmol) and CCl_4 (10 mL, 76 mmol) were stirred at room temperature under nitrogen for 1 h to give a colorless solution. $CuCl_2$ (0.5 g, 3.8 mmol) and CH_3CN (10 mL) were mixed at room temperature to give a khaki-brown-colored mixture. Although most of the $CuCl_2$ remained undissolved, the supernatant solution was transferred under nitrogen to the Ph_3P/CCl_4 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 $[Ph_3PC(Cl)PPh_3]^+$-$[ClHCl]^-$.

$[Ph_3PC(Cl)PPh_3]^+[ClHCl]^-$ (0.396 g, 0.62 mmol) and $CuCl_2$ (0.083 g, 0.62 mmol) were placed in a Schlenk tube, and CH_3CN (10 mL) added. The reagents were stirred at room temperature, under nitrogen. 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 over time to give a dull, light orange solid.

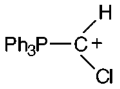
Crystallization of $(Ph_3PMe)_2[Cu_3Br_8]$ 2. A mixture of Ph_3PMeBr (0.893 g, 2.5 mmol), $CuBr_2$ (0.557 g, 2.5 mmol), and 48% aqueous HBr (1 mL, 8.8 mmol) was dissolved in 2-propanol (700 mL) and stirred thoroughly. The green solution was allowed to stand at ambient temperature. Black crystals which grew for 12 h were collected. The same product is formed for variation of the $CuBr_2/HBr:Ph_3PMeBr$ ratio between 1:10 and 10:1. If allowed to stand for longer periods in the mother liquor, the crystals of $(Ph_3PMe)_2[Cu_3Br_8]$ redissolve and dark red crystals of $(Ph_3PMe)_2[Cu_2Br_5]$[8] are formed.

Crystals of $(Ph_3PMe)_2[Cu_3Br_8]$ show no signs of air or moisture instability. They have a black streak, and change to form a green solution when dissolved in acetonitrile.

Crystal Structure Determinations. Reflection data were measured with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using graphite-monochromatized molybdenum radiation (λ 0.7107 Å). Data for **1** and **2** were corrected for absorption using analytical methods, but those for **3** were not as the absorption coefficient was very low. Reflections with $I > 3\sigma(I)$ were considered observed. Data processing procedures have been described.[13] The structures were determined by direct phasing and Fourier methods. For isomorphous **1** and **2**, the asymmetric unit comprises one cation and $Cu_{1.5}X_4$ (X = Cl or Br). In the refinement of all three compounds, each phenyl ring of the cation was described as a single planar rigid group with *mm*2 symmetry, refineable for translation and rotation. Hydrogen atoms were included in calculated positions. A 12-variable **TL** group (where **T** is the translation tensor and **L** is the libration tensor) was used to assign the thermal motion to each phenyl ring. Positional and anisotropic thermal parameters for the Cu, P, and halogen atoms were refined in the normal way. Reflection weights used 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 $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from the *International Tables for X-ray Crystallography*.[14] Refinement used RAELS.[15] Crystallographic details are given below.

1. $C_{36}H_{30}Cl_{10}Cu_3P_2$, $M = 1069.8$, triclinic, space group $P\bar{1}$, $a = 9.480(6)$ Å, $b = 10.243(8)$ Å, $c = 11.232(6)$ Å, $\alpha = 86.76(4)°$, $\beta = 66.62(5)°$, $\gamma = 83.92(4)°$, $V = 995(1)$ Å^3, $D_c = 1.78$ g cm^{-3}, $Z = 1$, $\mu_{Mo} = 23.79$ cm^{-1}, $2\theta_{max} = 50°$, min and max transmission factors 0.61 and 0.83. A total of 3707 intensity data were recorded, leading to 3509 unique reflections ($R_{merge} = 0.010$), of which 3065 were considered observed. Final residuals R and R_w were 0.026 and 0.043 for the observed data.

Initially refinement converged at $R = 0.035$, with a residual density peak about 1.4 Å from the Cl atom of the cation. As the precursor in the preparation of this compound contained $[Ph_3PC(Cl)PPh_3]^+$, the cation $Ph_3PC(H)Cl^+$ was probably present during crystallization, and the additional density was modeled with


$$\mathrm{Ph_3P{-}C^{+}(H)(Cl)}$$

as a minor component. Refinement revealed a 7% presence of this alternative cation, and R dropped to 0.026.

2. $C_{38}H_{36}Br_8Cu_3P_2$, $M = 1384.5$, triclinic, space group $P\bar{1}$, $a = 9.795(4)$ Å, $b = 10.472(4)$ Å, $c = 11.392(4)$ Å, $\alpha = 86.67(3)°$, $\beta = 66.67(3)°$, $\gamma = 83.14(3)°$, $V = 1065.2(8)$ Å^3, $D_c = 2.16$ g cm^{-3}, $Z = 1$, μ_{Mo} 90.22 cm^{-1}, $2\theta_{max}$ 50°, min and max transmission factors 0.20 and 0.45. A total of 3974 intensity data were recorded, giving 3731 unique reflections ($R_{merge} = 0.021$), of which 3058 were considered observed. Final residuals R and R_w were 0.026 and 0.036 for the observed data.

3. $[Ph_3PC(Cl)PPh_3]^+[ClHCl]^-$, $C_{37}H_{31}Cl_3P_2$, $M = 644.0$, monoclinic, space group $P2_1/c$, $a = 13.655(6)$ Å, $b = 17.009(4)$ Å, $c = 16.145(8)$ Å, $\beta = 120.49(1)°$, $V = 3231(2)$ Å^3, $D_c = 1.32$ g cm^{-3}, $Z = 4$, μ_{Mo} 4.10 cm^{-1}, $2\theta_{max} = 50°$. A total of 5890 intensity data were recorded, leading to 5673 unique reflections ($R_{merge} = 0.015$) of which 3326 were considered observed. Final residuals R and R_w were 0.058 and 0.077 for the observed data.

Results

Crystalline **1** and **2** are isomorphous. The chloro homologue of **2**, $(Ph_3PMe)_2[Cu_3Cl_8]$, also forms isomorphous crystals [NIJZEL, in the Cambridge Structural Database].[16] 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 CuX_4 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.

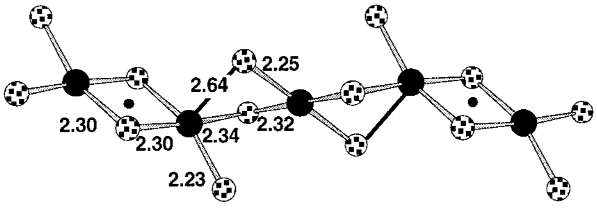


Figure 2. Part of the $[Cu_3X_8^{2-}]^1_\infty$ chain in **1** and **2**: distances marked are for **1**, X = Cl. Inversion centers at the central Cu atom and at the dots propagate the chain. The Cu atoms have primary square planar coordination and are linked by vertexes and edges: a secondary X---Cu bond which occurs at two out of three Cu atoms is drawn.

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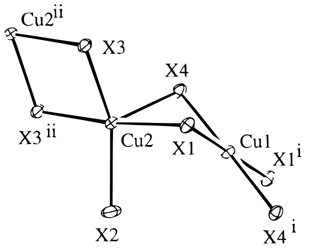
Table 1. Bond Distances and Angles in the Anion Chains $[Cu_3X_8^{2-}]^1_\infty$ of **1** and **2**[a]



dimension	X = Cl (**1**)	X = Br (**2**)	dimension	X = Cl (**1**)	X = Br (**2**)
Cu1−X1	2.318(1)	2.452(1)	Cu2−X3	2.299(1)	2.446(1)
Cu1−X4	2.252(1)	2.392(1)	Cu2−X4	2.642(1)	2.734(1)
Cu2−X1	2.339(1)	2.466(1)	Cu2−X3^{ii}	2.300(1)	2.437(1)
Cu2−X2	2.227(1)	2.384(1)			
X1−Cu1−X4	88.4(1)	88.9(1)	X2−Cu2−X3^{ii}	93.8(1)	92.9(1)
X1−Cu1−X4^{i}	91.6(1)	91.1(1)	X3−Cu2−X4	104.3(1)	103.9(1)
X1−Cu2−X2	91.6(1)	92.8(1)	X3−Cu2−X3^{ii}	84.2(1)	85.3(1)
X1−Cu2−X3	90.7(1)	90.2(1)	X4−Cu2−X3^{ii}	100.2(1)	96.2(1)
X1−Cu2−X4	79.2(1)	81.3(1)	Cu1−X1−Cu2	86.7(1)	83.6(1)
X1−Cu2−X3^{ii}	174.6(1)	174.2(1)	Cu2−X3−Cu2^{ii}	95.8(1)	94.7(1)
X2−Cu2−X3	157.3(1)	153.2(1)	Cu1−X4−Cu2	81.1(1)	79.2(1)
X2−Cu2−X4	98.2(1)	102.9(1)			

[a] i, 1 − *x*, 1 − *y*, 1 − *z*; ii, − *x*, 1 − *y*, 1 − *z*.

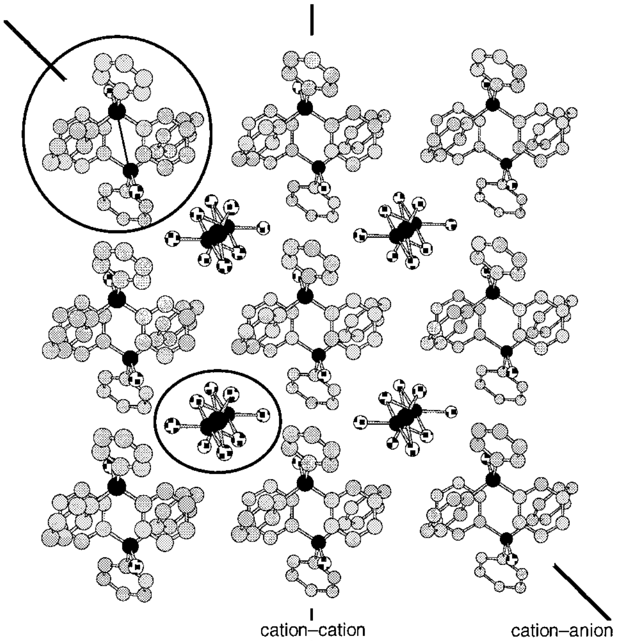


Figure 3. Parallel alignment of the chains of cations and of anions in crystalline **1**. The ellipses enclose one cation chain and one anion chain: the plane formed by the P atoms in the pseudo-ZZI6PE chain of cations is marked by the line in the enclosed cation chain. The planes of the cation−anion 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 $[Cu_3X_8^{2-}]^1_\infty$ 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.

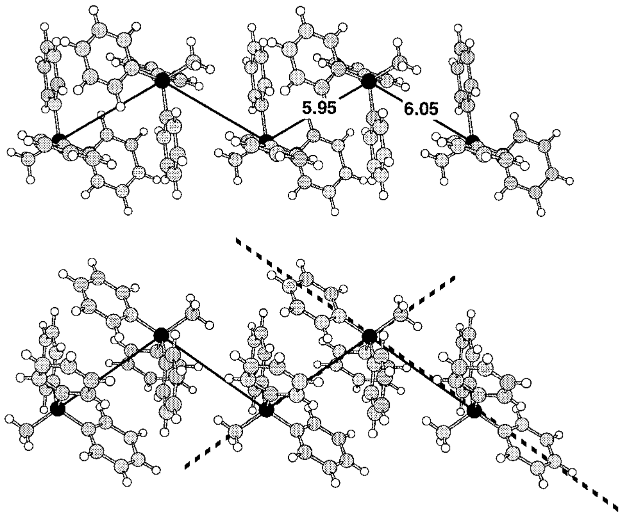
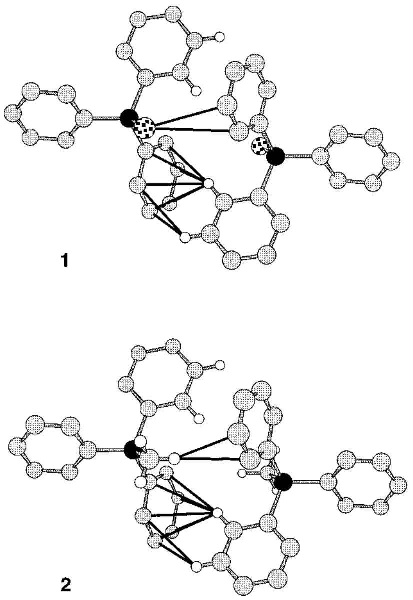


Figure 4. Two views of the column of cations in **2**. The top view defines the P···P vectors, which alternate along the column as 5.95 Å for the 6PE and 6.05 Å for the pseudo-6PE. There are centers of inversion between adjacent cations. The lower view is perpendicular to the plane of the P atoms (see Figure 3), and the striped lines show how the methyl groups exo to the 6PE and the phenyl groups exo to the pseudo-6PE are effectively collinear with the P···P vectors.


1

2

Figure 5. Centrosymmetric 4P2Y motifs in **1** and **2**. Only H atoms with significant intermolecular interactions are included. Half of the prominent H···C and Cl···C interactions are marked as intermolecular lines.

Crystal Packing. The crystal packing involves supramolecular chains of cations parallel to the one-dimensionally nonmolecular 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 $(Ph_3PMe^+)_2$ 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.

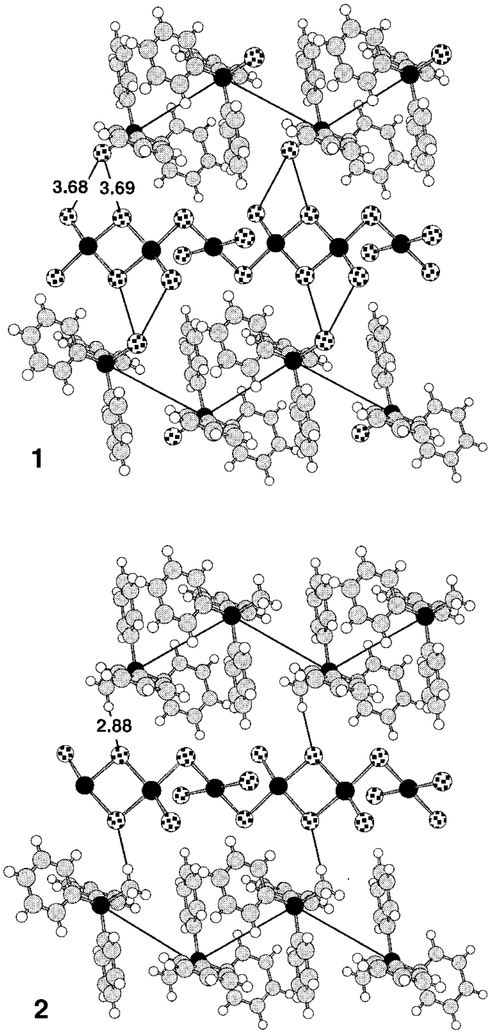


Figure 6. Alignment and closest contacts for the anion chains and the cation columns in **1** and **2**. The $^{\text{cation}}$Cl···Cl$^{\text{anion}}$ and $^{\text{cation methyl}}$H···Br$^{\text{anion}}$ distances (Å) are marked. The anions and cations are propagated by two centers of inversion per repeat unit.

In **1** the pseudo-ZZI6PE column of cations is similar to that of **2**, but with Cl instead of Me. The P···P separation in the 6PE of **1** is substantially shorter, at 5.61 Å, and for the pseudo-6PE the P···P separation is 5.96 Å.

4P2Y Pseudoembraces. While the 6PE motifs are standard,[1,2] the embraces which involve four phenyl groups and two hetero groups Y (Cl in **1**, Me in **2**) need to be examined more closely. These motifs are symbolized as 4P2Y. As shown in Figure 5, one phenyl group of each cation forms good C−H···C interactions to the face of a phenyl ring on the other, and the heterogroup forms favorable Cl···C or C−H···C interactions to the other phenyl ring on the opposite cation. There is a total of four such local interactions, rather than the six concerted interactions of the 6PE, and we regard this 4P2Y motif as a pseudoembrace. The 4P2Y motif is not as linear as the 6PE; that is, the P···P−C$^{\text{exo}}$ angles deviate from 180°, and the conformations around the P−C$^{\text{phenyl}}$ bonds in the interaction zone are different. However, the variation of local geometry in the 4P2Y motif still permits the ideal 6PE either side of it in the cation columns. The 4P2Y motif occurs in other crystalline compounds, particularly in crystals containing Ph_3PO, 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. Figure 6 shows the alignment of the anion chains and the closest cation column, which occur in the layers marked as “cation−anion” in Figure 3. In **1** the Cl of the cation is 3.68 Å from two of the Cl atoms of the anion while in **2** there is a C−H···Br hydrogen bond at 2.88 Å. Atoms of the 4P2Y motif are more closely associated with the anion chain than are those of the compact 6PE motif. The repeat distance common to the anion chain and cation column is 9.48 Å in **1** and 9.80 Å in **2**: this is shorter than most ZZI6PE motifs involving only Ph_4P^+, where the average repeat distance is 11.0 Å.

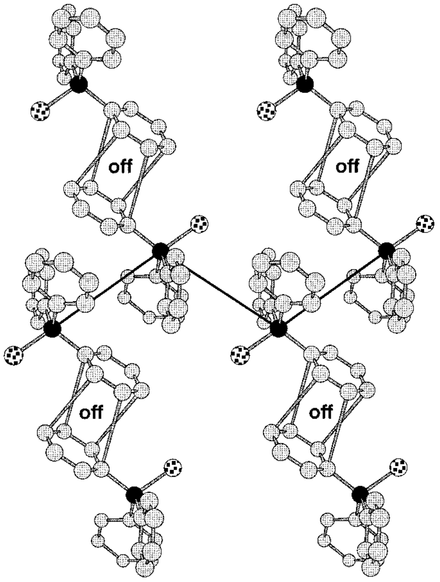


Figure 7. Offset-face-to-face interactions (**off**) between Ph_3PCl^+ cations in the pseudo-ZZI6PE column (center, horizontal) of **1** and those in adjacent pseudo-ZZI6PE. Hydrogen atoms are omitted.

It can be seen from Figure 3 that the P_∞ planes of all of the cation columns are parallel, and occur in layers marked as “cation−cation” in Figure 3. Within these layers there are attractive interactions between the cation columns, in the form of excellent offset-face-to-face interactions between phenyl groups on the edges of the columns. These **off** interactions are shown in Figure 7.

Discussion

The cation Ph_3PCl^+ which occurs in compound **1** is usually formed by the reaction of Ph_3P with Cl_2.[17−19] Our reaction systems used Ph_3P with CCl_4 in the presence of copper(II) halides (the objective was to prepare $Ph_3PCCl_3^+$ cations[20−22]) and generated $Ph_3PC(Cl)PPh_3^+$, which subsequently degraded to Ph_3PCl^+ in the presence of $CuCl_2$ in acetonitrile. Compounds of Ph_3PCl^+ with halometalate anions $[MCl_6]^{2-}$ (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 Ph_3PCl^+ forms a pseudo-ZZI6PE motif, with an alternation of 6P and 4P2Y motifs along the column. Our results show also that Ph_3PMe^+ can form a similar pseudo-ZZI6PE motif. One of the characteristics of the Ph_3PMe^+ cation is its

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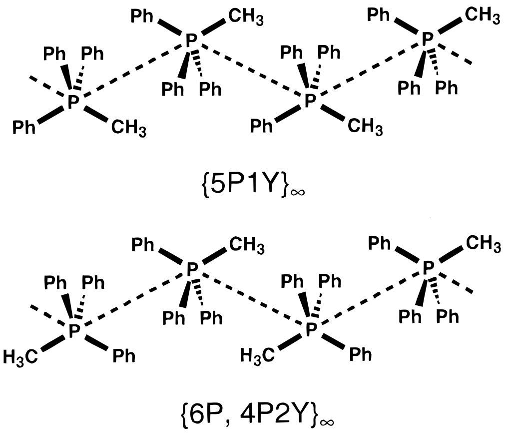

Figure 8. Two alternations of local embraces possible in the pseudo-ZZI6PE motif.

adoption of the HA6PE lattice type,[7] and so both of the 3-fold triphenylphosphonium cations, Ph_3PCl^+ and Ph_3PMe^+, can form both the HA6PE lattice and the pseudo-ZZI6PE motif.

The pseudo-ZZI6PE motif formed by Ph_3EY (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 2_1 crystal symmetry element, and will describe them separately.

In crystalline **1** and **2**, together with isostructural $(Ph_3PMe)_2[Cu_3Cl_8]$,[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.[4]

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 $[Cu_2X_6]^{2-}$, $[Cu_4X_{12}]^{4-}$, $[Cu_4X_{11}]^{3-}$, $[Cu_5X_{14}]^{4-}$, $[Cu_6X_{14}]^{2-}$, and Cu_2X_4, but only one anion with the composition $[Cu_3Br_8]^{2-}$. In this crystal structure [ZACSAX[23]] which contains the *N*-methyl-2-picolinium cation, the $[Cu_3Br_8]^{2-}$ salt has the chain structure shown in Figure 9, propagated through secondary Br−Cu bonds of 2.76 Å.

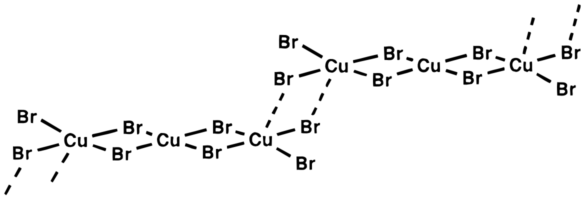

Figure 9. Chain of secondarily linked $Cu_3Br_8^{2-}$ anions in crystals [ZACSAX] with the *N*-methyl-2-picolinium cation.

We postulate that the different $[Cu_3X_8{}^{2-}]^1_\infty$ chain formed in the three crystals with Ph_3PY^+ 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.

IC990803R

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