

Poly[dimethyldiphenylphosphonium  
[di- $\mu_4$ -iodido-tetra- $\mu_3$ -iodido-penta-  
copper(I)]]Ehsan Jalilian<sup>a\*</sup> and Sven Lidin<sup>b</sup><sup>a</sup>Department of Environmental and Material Chemistry, Arrhenius Laboratory, Stockholm University, 106 91 Stockholm, Sweden, and <sup>b</sup>Polymer and Materials Chemistry, Lund University, 221 00 Lund, Sweden

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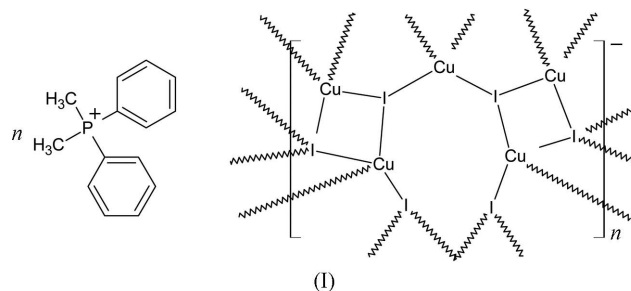
The title compound,  $\{(C_{14}H_{16}P)[Cu_5I_6]\}_n$ , prepared from the reaction between copper powder, iodine and dimethyldiphenylphosphonium iodide in hydroxyacetone, features an anion that consists of a continuous two-dimensional Cu–I sheet [Cu–I = 2.5960 (14)–2.6994 (13) Å and Cu–I–Cu = 63.28 (5)–114.25 (5)°]. The cation, which lies on a mirror plane, is a typical dimethyldiphenylphosphonium ion. The structure shows a strong tendency towards segregation of the inorganic and organic parts of the structure into separate subspaces. The two-dimensional Cu–I sheet displays a pronounced subcell with pseudo-tetragonal symmetry that is broken by ordered vacancies on the Cu position. The symmetry is further reduced by the orientation of the interleaved organic counter-ion that is inclined with respect to the pseudo-mirror planes defined by the Cu–I sheet normal, perpendicular to the *b* axis.

## Comment

Copper(I) halide complexes are well known for their structural variations. They exist in several different oligo- and polymeric forms, from discrete anion complexes to chains and sheets. It is also well known that this wide variation is due to the ability of copper to adopt different local geometries, primarily trigonal planar and tetrahedral coordination. The type of counter-ion is crucial for stabilizing different complexes. Typically, small counter-ions give rise to chains or two- or three-dimensional Cu–I complexes, but discrete Cu–I anions are formed when a large or bulky counter-ion is employed. Other important factors that influence the type of compound formed are the synthesis temperature and the solvent employed.

The title compound, (I) (Fig. 1), crystallizes in the space group *Ama2*, but there is a pronounced pseudosymmetry, indicating further centring (*Fmm2*). This is caused by the peculiar nature of the two rather well separated parts of the

structure. The title compound is layered, consisting of anionic nets of composition  $\{[Cu_5I_6]^{-}\}_{2\infty}$  interleaved with organic layers hosting the dimethyldiphenylphosphonium (DMDPP) counter-ions. Unlike in the pure iodide, the organic moieties form a dense herringbone pattern, as might be expected from their shape. The  $\{[Cu_5I_6]^{-}\}_{2\infty}$  entity appears to be a new addition to the zoo of Cu–I species.



Naked two-dimensional Cu–I polymeric species are relatively rare. The archetype is found in the trigonal and rhombohedral forms of CuI itself (Keen & Hull, 1995; Shan *et al.*, 2009), where electroneutral double layers display iodide surfaces that are separated by van der Waals gaps. There are also several examples of intercalation compounds with this basic motif (Cariati *et al.*, 2001; Shibaeva & Lobkovskaya, 1988; Wu *et al.*, 2008; Hartl & Brudgam, 1989; Mishra *et al.*, 2007). In the title compound, however, the anionic net has an underlying tetragonal rather than trigonal symmetry. Cu atoms form a defect, almost square-planar arrangement, with iodide above and below, in an arrangement reminiscent of that formed by BiO in BiOCl (Keramidas *et al.*, 1993). Defect-free, the layer would be charge neutral, but every sixth Cu position is missing in a regular manner, giving rise to a superstructure in the layer. Along the *a* direction, the unit cell is trebled by the alternation of defect-free rows of Cu<sup>I</sup> cations and rows where every second Cu<sup>I</sup> cation is missing. As a consequence, along the *c* direction the unit cell is doubled due to the

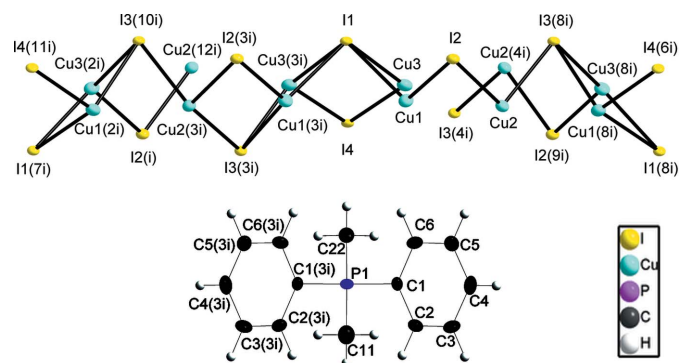
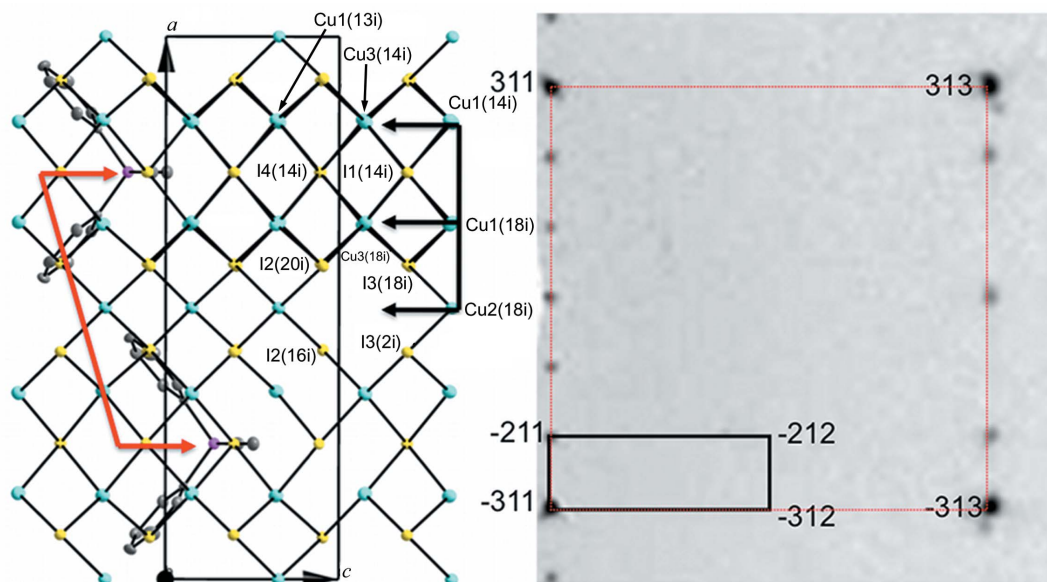


Figure 1

An overview of the title compound, with the *a* axis horizontal and the *b* axis vertical. All non-H atoms are shown as displacement ellipsoids at the 50% probability level. [Symmetry codes: (i)  $-\frac{1}{2} + x, 1 - y, -1 + z$ ; (2i)  $-\frac{1}{2} + x, 1 - y, z$ ; (3i)  $\frac{3}{2} - x, y, z$ ; (4i)  $x, y, -1 + z$ ; (6i)  $2 - x, 1 - y, 1 + z$ ; (7i)  $1 - x, 1 - y, z$ ; (8i)  $2 - x, 1 - y, z$ ; (9i)  $2 - x, 1 - y, -1 + z$ ; (10i)  $-\frac{1}{2} + x, 1 - y, 3 + z$ ; (11i)  $1 - x, 1 - y, 1 + z$ ; (12i)  $-\frac{3}{2} - x, y, -1 + z$ .]

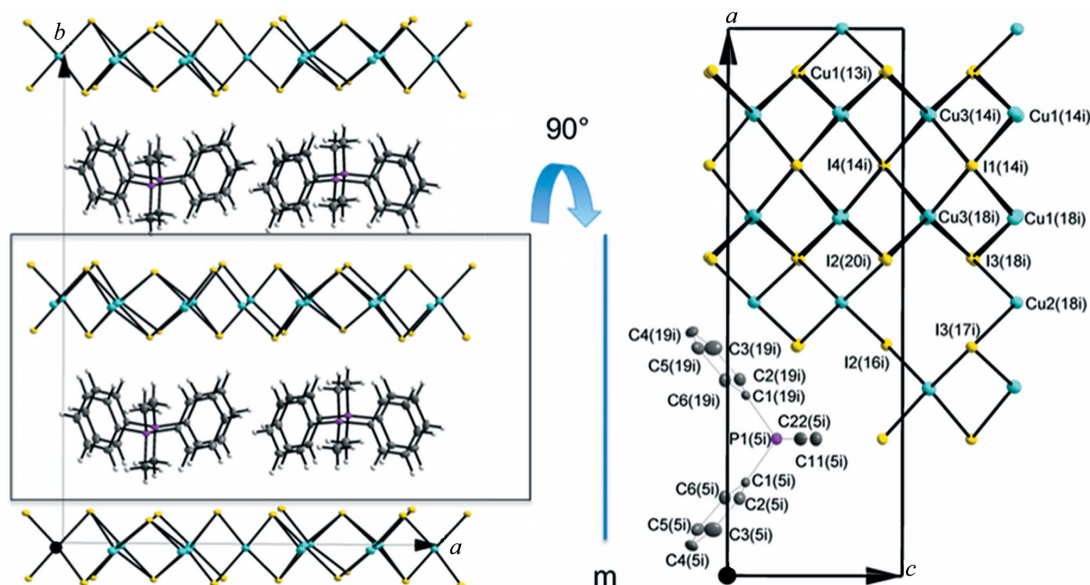

**Figure 2**

The diffraction pattern of the title compound displays a pronounced subset of strong reflections (square) corresponding to the square net of iodides. The smaller black rectangle indicates the true reciprocal cell. The  $a^*$  direction shows a sixfold superstructure caused by two effects: (i) the absence of every third Cu position along the  $a$  direction in every second row along the  $b$  direction, as indicated by the triple arrow in black, and (ii) the out-of-step arrangement of the counter-ion herringbone stacks, as indicated by the double arrows. The doubling of the cell along  $c$  is caused by the Cu defects being localized to every second row of Cu positions, and by the counter-ion stacking. All non-H atoms are shown as displacement ellipsoids at the 50% probability level. [See Fig. 1 for symmetry codes; additionally, (13i)  $x, \frac{1}{2} + y, -\frac{1}{2} + z$ ; (14i)  $x, \frac{1}{2} + y, \frac{1}{2} + z$ ; (16i)  $-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$ ; (18i)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$ ; (20i)  $\frac{3}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$ .]

alternation of defect-free rows and rows with every third Cu position missing. The missing  $\frac{1}{3}$  of the Cu positions thus generate a sixfold,  $3 \times 2$  superstructure in the  $ac$  plane. To complicate matters further, the DMDPP counter-ions are stacked in a herringbone pattern along the  $c$  direction, and the relative positions of these rows are out of step along the  $a$  direction, generating a further doubling of the unit cell along  $a$ . Thus, overall, the result is a  $6 \times 2$  superstructure as seen in both the direct-space image and the reciprocal-space image in Fig. 2.

Since the scattering from the  $\text{Cu}_5\text{I}_6$  layer completely dominates the diffraction pattern of the compound, this superstructuring is evident in the reconstructed reciprocal-lattice layer perpendicular to  $[010]$  in Fig. 2. The symmetry allowed by the defect-free CuI layer is  $4/mmm$ , and the defects lower the local symmetry to  $mmm$ . Further, a slight tilting of the DMDPP molecules with respect to the normal of the plane defined by CuI violates the reflection perpendicular to  $c$ , and the space-group symmetry is reduced to  $Ama2$ . It is notable that the Cu positions are described by larger displacement ellipsoids than the I atoms. This reflects a common phenomenon in Cu–I cluster systems. The size mismatch between Cu and I leads to a large configurational freedom for Cu within the convex hull defined by the I positions. At room temperature, many polymeric species are ionic conductors. The  $\text{Cu}_5\text{I}_6$  layer is subject to relaxation around the vacancies, and this, together with the tendency of the DMDPP counterion to form dense flat layers, is probably responsible for the stabilization of this unique form of a bidimensional Cu–I anion. The unit-cell packing is shown in Fig. 3 (projected along

$c$ ). Cu2 is located at the intersection of a mirror plane perpendicular to  $a$  and a pseudo-mirror plane perpendicular to  $c$ , facing two defects. There is room for the surrounding iodides to relax into and, since they are all related by symmetry (or pseudosymmetry), Cu2 displays the most homogeneous tetragonal coordination of all the three independent Cu-atom positions in the structure, with two bond distances of 2.6516 (14) Å and two of 2.6594 (14) Å. The Cu3 position faces Cu<sup>I</sup> cations in three directions and a defect on one side. The Cu3 position moves towards the defect and, as a consequence, the  $\text{Cu3I}_4$  tetrahedron is highly irregular with two short bonds [2.6042 (13) and 2.5952 (13) Å] and two long bonds [2.6908 (14) and 2.6997 (13) Å]. Cu1 finally displays the most severe distortions of the tetrahedron. Like Cu3, it is displaced from the mirror plane, avoiding short Cu3...Cu3 contacts and it is the Cu<sup>I</sup> cation furthest away from the defects. As for Cu3, there are two groups of distances, two short and two long, but the spread is larger: the values are 2.6022 (13), 2.6167 (13), 2.6981 (13) and 2.7356 (13) Å. The distances from the defect to the surrounding iodides are 2.611 Å, well below the average Cu–I contacts for each of the Cu positions (2.663 Å for Cu1, 2.656 Å for Cu2 and 2.648 Å for Cu3). This indicates that the defects are a necessary condition for the stability of the layer under ambient conditions. It would be interesting to attempt the synthesis of similar compounds with larger layer-forming counter-ions to dilute the cationic charge to create chemical pressure to reduce the number of defects. The limiting factor in determining the stability of the Cu–I layer may well be Cu–Cu contacts rather than Cu–I contacts. In the title compound, there are a number of short (below


**Figure 3**

On the left is shown a packing plot of the structure along *c*. The box signifies the section of the bounded projection along *b* (a single layer of counter-ions and one Cu–I sheet) shown on the right. For clarity in this projection, the Cu–I network has been cut away around the only counter-ion shown. The atoms are shown as displacement ellipsoids at the 50% probability level. [See Fig. 1 for symmetry codes; additionally, (5i)  $1 - x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (17i)  $-\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$ ; (19i)  $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ .]

3 Å) Cu··Cu distances. Cu2 and Cu3 each has two such contacts [2.803 (1) and 2.994 (1) Å, respectively] and, as a consequence, Cu1 has three. It may prove hard to increase these numbers significantly.

## Experimental

For the preparation of (I), dimethyldiphenylphosphonium iodide (3.98 mmol), iodine (5.03 mmol) and copper powder (20.02 mmol) were mixed and heated under reflux in hydroxyacetone (50 ml) under a nitrogen atmosphere. After 4 h, the solution became pale yellow, indicating the transformation of iodine to iodide. The mixture was filtered while hot and the solution kept in a refrigerator. Colourless crystals of (I) formed over the course of several days.

### Crystal data

(C <sub>14</sub> H <sub>16</sub> P)[Cu <sub>5</sub> I <sub>6</sub> ]	<i>V</i> = 2510.70 (9) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 1294.4	<i>Z</i> = 4
Orthorhombic, <i>Ama</i> 2	Mo <i>K</i> α radiation
<i>a</i> = 18.2110 (5) Å	<i>μ</i> = 11.61 mm <sup>-1</sup>
<i>b</i> = 23.6861 (4) Å	<i>T</i> = 100 K
<i>c</i> = 5.8206 (1) Å	0.16 × 0.11 × 0.05 mm

### Data collection

Oxford Diffraction Excalibur3 diffractometer with a Sapphire-3 CCD detector	45244 measured reflections
Absorption correction: gaussian ( <i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	5260 independent reflections
<i>T<sub>min</sub></i> = 0.274, <i>T<sub>max</sub></i> = 0.593	3765 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R<sub>int</sub></i> = 0.070

### Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.041	H-atom parameters constrained
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.065	Δρ <sub>max</sub> = 1.87 e Å <sup>-3</sup>
<i>S</i> = 1.02	Δρ <sub>min</sub> = -2.73 e Å <sup>-3</sup>
5260 reflections	Absolute structure: Flack (1983)
126 parameters	Flack parameter: 0.43 (4)

The structure was solved by charge flipping, giving the I-, Cu-, P- and a major part of the C-atom positions. Subsequently, the remaining C-atom positions were found using difference Fourier analysis. The H atoms were located by geometric methods and were allowed to ride, with methyl C–H = 1.00 Å [*U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C)] and phenyl C–H = 0.95 Å [*U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C)]. The Flack parameter (Flack, 1983) was calculated, yielding a value close to 0.5, *viz.* 0.43 (4). Refining the compound as a single crystal in either of the two possible absolute structures, or as a racemic twin, leads to indistinguishable results. In the final refinement, a racemic twin model was used, leading to the twin fraction 0.43 (4). The main electron residuals are around the iodides.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *Superflip* (Oszlányi & Sütő, 2004); program(s) used to refine structure: *JANA2000* (Petricek *et al.*, 2000); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *JANA2000*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MX3031). Services for accessing these data are described at the back of the journal.

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