

Bis(1,3,4-trimethylpyridinium) tetra- chloridocuprate(II) and bis(1,3,4- trimethylpyridinium) tetrabromido- cuprate(II): an examination of the A_2CuX_4 *Fdd2* structure type

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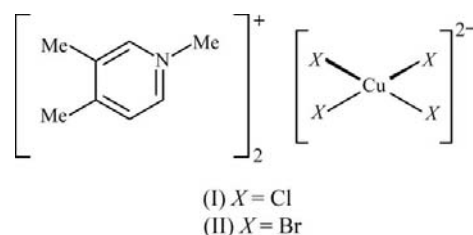
The title bis(1,3,4-trimethylpyridinium) tetrahalidocuprate(II) structures, $(C_8H_{12}N)_2[CuCl_4]$, (I), and $(C_8H_{12}N)_2[CuBr_4]$, (II), respectively, consist of flattened $[CuX_4]^{2-}$ tetrahedral complex anions and planar 1,3,4-trimethylpyridinium cations. Chloride compound (I) is a rare example of an A_2CuCl_4 structure with an elongated unit cell in the polar space group *Fdd2*. The $[CuCl_4]^{2-}$ anions have twofold rotational symmetry and are arranged in distorted hexagonal close-packed (hcp) layers, which are interleaved with layers of cations, each in a four-layer repeat sequence, to generate the elongated axis. The organic cations stack along $[101]$ or $[10\bar{1}]$ in alternating layers. The methyl groups *meta* on the cation ring and the larger of the *trans* Cl—Cu—Cl angles both face the same direction along the polar axis and are the most prominent features determining the polarity of the structure. Bromide compound (II) crystallizes in a centrosymmetric structure with a similar layer structure but with only a two-layer repeat sequence. Here, symmetry-inequivalent cations are segregated into alternating layers with cations, forming hcp layers of inversion-related cation pairs in one layer and parallel stacks of cations in the other. The change in space group when the larger Br^- ion is present suggests that the 1,3,4-trimethylpyridinium ion has a minimal size to allow the *Fdd2* A_2CuX_4 structure type.

Comment

The structural chemistry of halidocuprate compounds with an A_2CuX_4 stoichiometry is rich, ranging from layer perovskite structures, in which the copper(II) ion possesses an elongated octahedral geometry (Long *et al.*, 1997), to thermochromic compounds, with isolated square-planar $[CuCl_4]^{2-}$ anions in the low-temperature phase which transform into flattened tetrahedral anions at higher temperature (Riley *et al.*, 1998).

Isolated $[CuX_4]^{2-}$ anions with a compressed or flattened tetrahedral geometry are well known and by themselves merit little comment. However, A_2CuX_4 compounds with isolated $[CuX_4]^{2-}$ ions are, in many cases, found to crystallize in complicated extended structures. A_2CuCl_4 compounds with high-symmetry cations, such as $(CH_3)_4N^+$ (Gesi, 1982) and $(CH_3)_4P^+$ (Pressprich *et al.*, 1989; Nishijima & Mashiyama, 2000), exhibit commensurately and incommensurately modulated superstructures. Larger high-symmetry cations, such as $(CH_3)_4As^+$ and $(CH_3)_4Sb^+$, yield compounds that crystallize in high-symmetry tetragonal or cubic space groups with, in some cases, commensurate modulations (Pressprich *et al.*, 1991, 2002). The low-symmetry $(C_2H_5)_2NH_2^+$ cation produces an elongated unit cell with three unique $[CuCl_4]^{2-}$ anions in which the degree of flattening varies dramatically at low temperature (Willett & Twamley, 2007), while undergoing a thermochromic phase transition at higher temperature to a smaller unit cell with two unique $[CuCl_4]^{2-}$ anions (Bloomquist *et al.*, 1988).

A rare A_2CuX_4 structure type with an elongated cell in the space group *Fdd2* was first reported by Pauling (1966) for $[(C_6H_5)_3CH_3As]_2[CuX_4]$ ($X = Cl$ or Br). Although no structure was determined, this structure type is unique from the cubic *P2₁3* structures found for other first-row transition metals. Later, the $[(C_6H_5)_3CH_3P]_2[CuCl_4]$ structure was determined (El Essawi, 1997), with unit-cell constants differing only slightly from those of the arsonium analogue. The corresponding tetrachloridomanganate and tetrachloridocobaltate salts were also found to crystallize in cubic unit cells with cell-axis lengths close to those found in their arsonium analogues. More recently, the $\{Cu[H_3C_5N(CH_2N^iPr_2)_2]Cl\}_2[CuCl_4]$ structure has been reported (Vedernikov *et al.*, 2002), with the longest elongated unit-cell axis in this class, *viz.* 56.083 (2) Å, compared with values of 32.27 (2) and 32.791 Å, respectively, for the two previously mentioned chloride structures. Against this background, we now present the crystal structures of the title compounds, (I) and (II).



Compound (I) crystallizes at room temperature in the space group *Fdd2* with an elongated unit-cell axis of 35.3359 (7) Å, and it is the newest addition to this structure type. The structures of the organic cation and complex anion are illustrated in Fig. 1. The bond lengths and angles for the organic cation agree with expected values (Ladd & Palmer, 1994). Bond lengths and angles for the complex anion are presented in Table 1. The $[CuCl_4]^{2-}$ anion in (I) possesses twofold rotation symmetry about *c*. The *trans*-Cl—Cu—Cl angles of 129.41 (5)° for Cl1—Cu1—Cl1ⁱ and 134.79 (4)° for Cl2—Cu1—Cl2ⁱ [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, z$] are typical for isolated $[CuCl_4]^{2-}$ anions in the absence of strong hydrogen

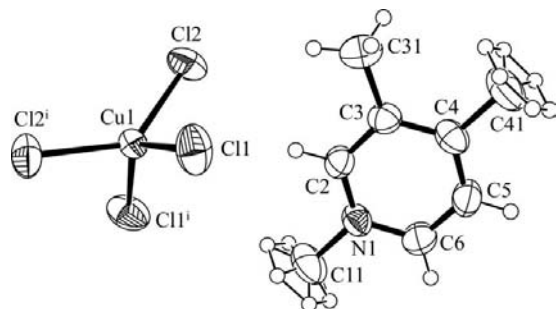


Figure 1

The organic cation and complex anion of chloride structure (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, z$.]

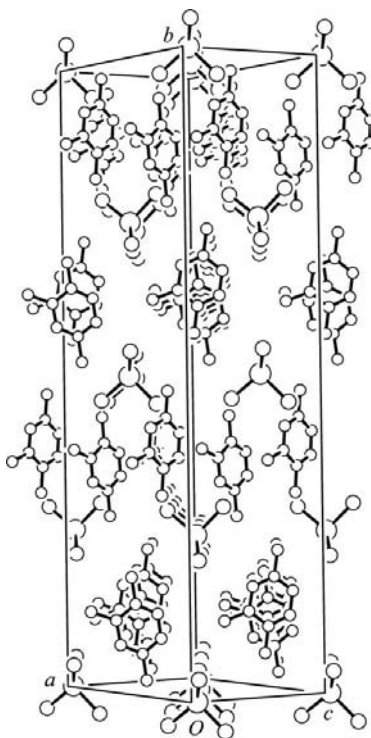


Figure 2

A packing diagram for (I), viewed parallel to the [101] lattice line. The view is down the stacks of organic cations in alternate layers that nest between lines of complex anions.

bonding from the organic cation (Willett, 1991). The shortest $H \cdots Cl$ contacts in this structure are long (ca 2.77–2.78 Å) with unfavourable $C-H \cdots Cl$ angles (ca 145°), thus supporting the notion that strong hydrogen bonding is absent. The twofold rotation axis bisects the two large *trans*-Cl—Cu—Cl angles, with the smaller *trans* angle facing the positive *c*-axis direction and the larger facing the negative *c*-axis direction.

The organic cations and complex anions in (I) are separated into interleaved layers that stack parallel to [010], with a four-layer repeat sequence for each. Within the anionic layer, the complexes pack in a distorted hexagonal close packed (hcp) arrangement, with an *a*- to *c*-axis length ratio of 1.517, less than the ideal value of 1.732. All the anions within the layer are translationally equivalent with the Cl1—Cu1—Cl2 plane

almost parallel to (101) and with the Cl1ⁱ—Cu1—Cl2ⁱ plane almost parallel to (10 $\bar{1}$). Neighbouring layers are related by a diamond glide-plane operation perpendicular to [100], such that successive diamond glide-plane operations generate the four-layer repeat sequence that yields the long *b* axis of the unit cell. The large *trans*-Cl—Cu—Cl angles define planes that are almost at 45° to the *a* and *b* axes [the Cl1—Cu1—Cl1ⁱ plane forms an angle of 50.22 (2)° and the Cl2—Cu1—Cl2ⁱ plane forms an angle of 40.19 (2)° with respect to the *b* axis]. The diamond glide-plane operation switches the orientation of these two planes in neighbouring anion layers.

Within the cation layer the long axis of the cation, from the N atom to the opposite C atom in the ring, is almost parallel [7.42 (7)°] to [010] and hence almost perpendicular to the layer plane. This places the methyl group in the *meta* position in the ring within the layer. The methyl groups in the *meta* positions for all the cations all face in the negative *c*-axis direction, another consequence of the polar space-group symmetry. The C3—C31 bond forms an angle of 26.54 (15)° with respect to *c*, and angles of 73.05 (15) and 70.20 (16)° with respect to axes *a* and *b*. The direction of the C3—C31 bond differs from cation to cation, but the component of the bond relative to *c* is the same for all. The methyl group attached to the N atom on the cation ring penetrates into the anionic layer. Since the N atom is formally the seat of positive charge on the cation, this would place the N atom close to the formally negative Cl[−] ions of the complex. The shortest $N \cdots Cl$ contact distance is 3.777 (2) Å to Cl1.

The cation layer consists of parallel stacks of aromatic rings along [101] or, in alternating layers, along [10 $\bar{1}$], with complex anions nesting in voids between cation stacks. Neighbouring cations in a stack are related by a *d*-glide operation perpendicular to *b*, with a distance of 3.9652 (1) Å between cation planes. The cations are staggered in the stack so that the C atom in the *para* position in the ring sits approximately above the centres of the two neighbouring rings. Neighbouring stacks in the layer can be related by lattice translations. A packing diagram viewed parallel to [101], showing the layered structure and looking down the stacks of organic cations in two of the layers, is presented in Fig. 2.

Cation stacking along [101] and [10 $\bar{1}$] also occurs in the [(C₆H₅)₃CH₃P]₂[CuCl₄] structure, where two different phenyl rings of the cation form facing pairs with phenyl rings on two neighbouring cations. The bulky ⁱPr groups in {Cu[H₃C₅N(CH₂NⁱPr)₂]₂Cl]₂[CuCl₄] prevent phenyl ring stacking, but similar stacks can be discerned in which the ⁱPr groups of neighbouring cations abut. The [(C₆H₅)₃CH₃P]₂[CuCl₄] and {Cu[H₃C₅N(CH₂NⁱPr)₂]₂Cl]₂[CuCl₄] structures both have the four-layer repeat sequence and twofold rotational symmetry of the [CuCl₄]^{2−} ion, as in (I). However, the twofold axis in these cases bisects the smaller Cl—Cu—Cl angles so that the compression axis of the flattened tetrahedron is not perpendicular to the elongated axis of the unit cell. In this manner, the larger aspect of the flattened [CuCl₄]^{2−} ion is placed more within the anion layer so as to accommodate better the spacing enforced by the bulkier cations. The compression axis is most closely aligned with the elongated axis in the [(C₆H₅)₃CH₃P]₂-

[CuCl₄] structure, while the [CuCl₄]²⁻ ion has the largest Cl—Cu—Cl angle in the [Cu{H₃C₅N(CH₂NⁱPr)₂}Cl]₂[CuCl₄] structure. This variation in the orientation and structure of the [CuCl₄]²⁻ ion suggests that cation stacking determines a structure type in which the stereochemical flexibility of the [CuCl₄]²⁻ ion allows it to occupy voids that a regular tetrahedral complex could not.

The structure of corresponding bromide compound (II) offers an interesting contrast, since it does not crystallize in the space group *Fdd2*. Instead, it is found to crystallize in the monoclinic space group *P2₁/c* with the longest unit-cell axis, *a*, about half as long as the elongated axis in the chloride salt. The structures of the organic cation and complex anion in (II) are presented in Fig. 3. Bond lengths and angles of the organic cation agree with expected values (Ladd & Palmer, 1994). Bond lengths and angles for the complex ion are presented in Table 2. The extended structure in (II) has interleaved layers of [CuBr₄]²⁻ anions and of organic cations that stack along *a*, each in a two-layer repeat sequence. Within the anion layer, the complexes pack in an hcp arrangement, although with a *b*/*c*-axis length ratio of 1.775, which is less distorted from the ideal value (1.732) than in (I). Within the layer, two neighbouring complexes are related by *c*-axis translations and the other four by *c*-glide-plane operations. The two large *trans*-Br—Cu—Br angles are very similar [130.66 (3)° for Br2—Cu1—Br3 and 129.58 (3)° for Br1—Cu1—Br4].

The most striking feature of the structure of (II) is the segregated packing of symmetry-inequivalent organic cations into layers with very different arrangements. Cation 1 (containing atom N11) packs in a layer along the *bc* faces of the unit cell, while cation 2 (containing atom N21) packs in a parallel layer midway in the unit cell.

The molecular axis of cation 1 (as defined by the N11—C14 line) is almost perpendicular to the layer plane, forming a small angle of 9.24 (11)° relative to the normal to the layer plane. Cation 1 forms inversion-related pairs in which the parallel cation planes are separated by a distance of 3.56 (2) Å. The cation pairs form an hcp layer where two neighbouring pairs are related by a *c*-axis translation, while the other four neighbours are related by a *c*-glide operation. Since the normal to the cation plane forms an angle of 36.43 (7)° with respect to *b*, the orientation of the planes of the neighbours related by the *c*-glide is switched. The inversion-related cations in each pair are shifted along their molecular axes relative to one another so that the N atom of each extends into opposite anionic layers. Complex anions from neighbouring layers nest in the voids formed by neighbouring cation pairs.

Cation 2 packs to give a corrugated layer made up of uneven stacks of cations parallel to *c*. This stacking bears some resemblance to the cation stacking in (I), but with substantial differences. Within a given stack, the molecular axes of the cations all point in the same direction along *a*, rather than in alternating directions as seen in (I). The molecular axes, however, are not parallel to *a* but tilted at an angle of 13.57 (12)° [and at an angle of 79.89 (11)° with respect to *b*]. Neighbouring cations within the stack are related by a *c*-glide

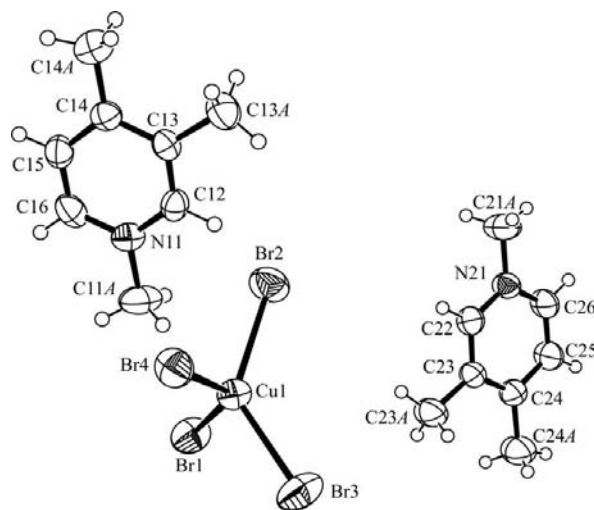


Figure 3

The organic cation and complex anion of bromide structure (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

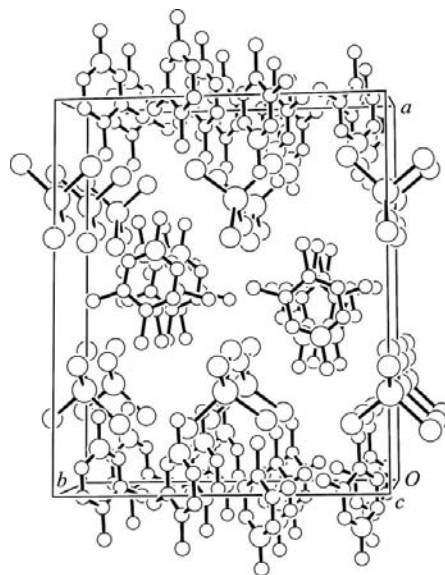


Figure 4

A packing diagram for (II), viewed parallel to the *c* axis. The stacks of cation 2 are visible in the middle layer, while the hcp pairs of cation 1 are found in the top and bottom layers of the illustration.

operation which switches the orientation of the cation plane relative to *b*, so neighbouring cations are not coplanar, and it also switches the orientation of the molecular axis relative to *a*. This results in unevenness in the stacking and in the staggering of the molecular axes within the stack, so as to increase the distance between the formal seats of positive charge on neighbouring cations [4.1886 (1) Å, as measured by half of the *c*-axis length] is larger than that found in (I). Expansion of the unit cell to accommodate the larger bromide complex allows for this looser stacking of the cations. Neighbouring stacks in the layer

are related by inversion and are offset from one another along *a* so that the N atoms of the stack penetrate into the nearest anion layer, thus giving rise to the layer corrugation. Complex anions nest in grooves between stacks. A packing diagram of the structure viewed down *c* (and down the stacks of cation 2) is presented in Fig. 4.

The 1,3,4-trimethylpyridinium cation is the smallest of the four cations for which the *Fdd2* A_2CuX_4 structure type has been found. The fact that bromide structure (II) is not isomorphous with chloride structure (I) – unlike the situation for the methyltriphenylarsonium salts – and has a significantly different packing of the organic cations, indicates that this ion has a minimal size required to form this structure type. However, the other (1-methyltutidininium)₂[CuCl₄] structures studied so far do not exhibit this structure type (Bond, 2009). Thus, while cation size may be an important consideration in forming this structure type, cation structure must also play an important role.

Experimental

Both title compounds were prepared by slow evaporation of approximately 6 *M* HCl or HBr solutions of 1,3,4-trimethylpyridinium halide and copper(II) chloride dihydrate or copper(II) bromide, respectively, in a 2:1 stoichiometry. 1,3,4-Trimethylpyridinium halide was prepared by the reaction of 3,4-lutidine with an excess of iodomethane. The mixture was then stirred with an excess of silver halide to convert the iodide to the chloride or bromide salt. The resulting silver halide solid was removed by filtration. Suitable crystals of (I) and (II) were obtained by slow evaporation of the filtrates, giving yellow prism-like crystals of (I) and dark-purple prism-like crystals of (II).

Compound (I)

Crystal data

(C ₈ H ₁₂ N) ₂ [CuCl ₄]	<i>V</i> = 4084.92 (11) Å ³
<i>M_r</i> = 449.71	<i>Z</i> = 8
Orthorhombic, <i>Fdd2</i>	Mo <i>K</i> α radiation
<i>a</i> = 13.2423 (2) Å	<i>μ</i> = 1.59 mm ^{−1}
<i>b</i> = 35.3359 (7) Å	<i>T</i> = 298 K
<i>c</i> = 8.7298 (1) Å	0.30 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer	24053 measured reflections
Absorption correction: Gaussian (grid of 8 × 8 × 8 sampling points; Farrugia, 1999; Coppens <i>et al.</i> , 1965)	3101 independent reflections
<i>T_{min}</i> = 0.661, <i>T_{max}</i> = 0.874	2457 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R_{int}</i> = 0.080

Table 1

Selected geometric parameters (Å, °) for (I).

Cu1—Cl1	2.2410 (7)	Cu1—Cl2	2.2419 (6)
Cl1 ¹ —Cu1—Cl1	129.41 (5)	Cl1—Cu1—Cl2	99.10 (3)
Cl1—Cu1—Cl2 ¹	99.80 (3)	Cl2 ¹ —Cu1—Cl2	134.79 (4)

Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, z$.

Table 2

Selected geometric parameters (Å, °) for (II).

Cu1—Br1	2.3854 (6)	Cu1—Br3	2.3639 (6)
Cu1—Br2	2.3881 (6)	Cu1—Br4	2.3943 (6)
Br1—Cu1—Br3	99.58 (2)	Br2—Cu1—Br3	130.66 (3)
Br1—Cu1—Br2	101.16 (2)	Br2—Cu1—Br4	100.76 (2)
Br1—Cu1—Br4	129.58 (3)	Br3—Cu1—Br4	99.45 (2)

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	H-atom parameters constrained
$wR(F^2) = 0.087$	$\Delta\rho_{\max} = 0.37 \text{ e Å}^{-3}$
<i>S</i> = 1.03	$\Delta\rho_{\min} = -0.43 \text{ e Å}^{-3}$
3101 reflections	Absolute structure: Flack (1983),
107 parameters	with 1374 Friedel pairs
1 restraint	Flack parameter: -0.015 (12)

Compound (II)

Crystal data

(C ₈ H ₁₂ N) ₂ [CuBr ₄]	<i>V</i> = 2212.93 (7) Å ³
<i>M_r</i> = 627.55	<i>Z</i> = 4
Monoclinic, <i>P2₁/c</i>	Mo <i>K</i> α radiation
<i>a</i> = 17.8882 (4) Å	<i>μ</i> = 8.21 mm ^{−1}
<i>b</i> = 14.8736 (3) Å	<i>T</i> = 298 K
<i>c</i> = 8.3772 (1) Å	0.21 × 0.17 × 0.09 mm
<i>β</i> = 96.854 (1)°	

Data collection

Nonius KappaCCD area-detector diffractometer	37761 measured reflections
Absorption correction: Gaussian (grid of 8 × 8 × 8 sampling points; Farrugia, 1999; Coppens <i>et al.</i> , 1965)	5071 independent reflections
<i>T_{min}</i> = 0.242, <i>T_{max}</i> = 0.534	3469 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R_{int}</i> = 0.083

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	215 parameters
$wR(F^2) = 0.090$	H-atom parameters constrained
<i>S</i> = 1.04	$\Delta\rho_{\max} = 0.46 \text{ e Å}^{-3}$
5071 reflections	$\Delta\rho_{\min} = -0.46 \text{ e Å}^{-3}$

For both compounds, H atoms were included in calculated positions and treated as riding atoms, with C—H = 0.93–0.96 Å and with $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C})$, where *k* = 1.2 for aromatic H atoms and 1.5 for methyl H atoms. In compound (II), the C11 and C41 methyl groups were refined with twofold disorder (occupancies of 0.5 and 0.5).

For both compounds, data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3035). Services for accessing these data are described at the back of the journal.

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