

catena-Poly[bis(trimethylphenylammonium) [hexa- μ -chlorido-dichloridotricuprate(II)]: an alternating zigzag chain of CuCl_4 and Cu_2Cl_6 complexes

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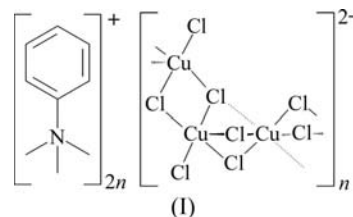
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The title compound, $\{(\text{C}_9\text{H}_{14}\text{N})_2[\text{Cu}_3\text{Cl}_8]\}_n$, consists of parallel chains of alternating quasiplanar Cu_2Cl_6 and planar CuCl_4 complexes separated by trimethylphenylammonium cations. Both inorganic complexes possess inversion symmetry. Pairs of neighboring chloride ions of the CuCl_4 complex each form a symmetric bridge and an asymmetric bridge to Cu_2Cl_6 complexes on either side. The Cu_2Cl_6 complex contains two symmetric chloride bridges between the copper cations with a terminal chloride bound to each five-coordinated Cu^{II} ion. The CuCl_4 complex completes its coordination environment by forming two long semicoordinate contacts to the bridging chloride ions of neighboring Cu_2Cl_6 complexes. The use of the bridging rather than the terminal chloride ions to form semicoordinate contacts generates a new zigzag chain structure that differs from the straight chain structures found for other $\text{A}_2\text{Cu}_3\text{Cl}_8$ compounds. The zigzag chain structure is adopted so as to conform to the shorter repeat distance dictated by stacking of the organic cations.

Comment

Copper(II)-halide chain compounds continue to show an amazing diversity of structure. Compounds such as CsCuCl_3 (Schlueter *et al.*, 1966) or $(\text{CH}_3)_4\text{NCuCl}_3$ [Willett *et al.*, 1988; refcode MATCCU01 in the Cambridge Structural Database (CSD, Version 5.30; Allen, 2002)] adopt the straightforward CsNiCl_3 structure type. In the holostructure, neighboring Ni^{2+} cations are linked by symmetric tri- μ -chloride bridging. For ACuCl_3 compounds, however, two of the three bridges between neighboring Cu^{2+} ions in the chain are asymmetric as a result of Jahn–Teller distortion (Muller & Roy, 1974). For octahedral Cu^{2+} , the Jahn–Teller distortion is primarily axial to produce a (4+2)-coordination geometry in which the $\text{Cu}\cdots\text{Cl}$ distances for the two semicoordinated ligands can range from

2.7 Å to well over 3 Å. It has long been recognized that semicoordinated ligands with $\text{Cu}\cdots\text{Cl}$ distances of 3 Å or more can still interact significantly with the Cu^{2+} ion and affect the geometrical arrangement of the coordinated ligands. In the extreme limit, the distortion leads to complete removal of one or two axial ligands to give square-pyramidal or square-planar Cu^{2+} , respectively (Smith, 1976; Reinen, 1983). Thus, strongly hydrogen-bonding donor cations, such as cyclohexylammonium (Groenendijk *et al.*, 1981; BAPYUM) or 2-amino-6-methylpyridinium (Geiser *et al.*, 1986; CIGNOV10), can interact with the chain to stabilize terminal chloride ligands and yield symmetrically dibridged chains of CuCl_5 square pyramids. Use of bulky cations leads to segmented chains in which tri- μ -halide-bridged segments of face-sharing octahedra are linked by two symmetrically bridging halide ions. These segments are of varying length, as found in $[(\text{CH}_3)_3\text{NC}_2\text{H}_5]_4\text{-Cu}_5\text{Cl}_{14}$ (Bond *et al.*, 1990; TABNOZ), $[(\text{CH}_3)_2\text{N}(\text{C}_2\text{H}_5)_2]_3\text{-Cu}_4\text{Cl}_{11}$ (Fujii *et al.*, 1995; ZACJES), $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]_2\text{Cu}_3\text{Cl}_8$ (El Essawi, 1997; NIJZEL), $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]_2\text{Cu}_3\text{Br}_8$ (Lorenzo *et al.*, 2000; LITHEB), $[(\text{C}_6\text{H}_5)_3\text{PCl}]_2\text{Cu}_3\text{Cl}_8$ (Lorenzo *et al.*, 2000; LITHAX), $[(\text{CH}_3\text{CN})_2(15\text{-crown-5})\text{Cu}]\text{Cu}_3\text{Cl}_8$ (Belsky *et al.*, 1991; JIZBUP) and (1-*n*-butyl-3-methylimidazolium) $_2\text{-Cu}_3\text{Cl}_8$ (Sun *et al.*, 2005; FIYPUZ). In some cases, segmented chains form as stacks of quasiplanar di- or tricopper complexes in which neighboring complexes are linked by two asymmetric bridges involving semicoordinate contacts, *e.g.* $(i\text{-C}_3\text{H}_7\text{NH}_3)_2\text{Cu}_2\text{Cl}_6$ (Roberts *et al.*, 1981; IPAMCU01) and $[1,2\text{-}(\text{CH}_3)_2\text{C}_6\text{H}_5\text{N}]_2\text{Cu}_3\text{Br}_8$ (Bond *et al.*, 1995; ZACSAX). The $(i\text{-C}_3\text{H}_7\text{NH}_3)_2\text{Cu}_2\text{Cl}_6$ structure is especially interesting since it transforms to the CsNiCl_3 -type structure at higher temperature upon weakening of the hydrogen bonding from the organic cation. The charge compensation principle has successfully rationalized this wide array of chain structures by considering hydrogen-bonding interactions from the organic cations that reduce ligand–ligand repulsion, stabilize square-planar or (4+1) coordination geometries, or induce terminal (rather than bridging) halide formation in the chain (Willett, 1991). The structure presented here, namely *catena*-poly[bis(trimethylphenylammonium) [hexa- μ -chlorido-dichloridotricuprate(II)]] (I), contains terminal chain chloride ligands in the absence of strong NH hydrogen bonding, thus posing a challenge to these traditional rationalizations for copper(II)-halide chain structures.



The structure of (I) consists of parallel zigzag inorganic chains separated by trimethylphenylammonium cations (Figs. 1 and 2). Table 1 lists bond lengths and angles within the chloridocuprate(II) chain. At first glance the inorganic chain structure consists of alternating planar CuCl_4 and quasiplanar

Cu_2Cl_6 complexes, with neighboring complexes linked by one symmetric (Cl3) and one asymmetric (Cl2) bridge. The CuCl_4 complex has inversion symmetry (at Cu2) and closely approximates square planarity. The copper ions in the Cu_2Cl_6 complex are five-coordinated with a distorted square-pyramidal arrangement in which atom Cl2 is the axial ligand and lies out of the plane of the complex. The basal ligands all have short bond lengths; the bond length to atom Cl1, the terminal chloride, is the shortest. Atom Cu1 sits above the basal ligands slightly, as indicated by *trans* Cl–Cu–Cl angles of approximately 169° . The axial ligand that bridges to atom Cu2 is bent toward Cu2, as shown by the acute Cl2–Cu1–Cl3 angle of $82.31(3)^\circ$. The Cu_2Cl_6 complex possesses inversion symmetry so that the axial ligands of the neighboring copper(II) ions are oriented in opposite directions. Neighboring CuCl_4 and Cu_2Cl_6 complex planes form an angle of $61.53(2)^\circ$ with respect to each other.

The inorganic chain structures of the other $\text{A}_2\text{Cu}_3\text{Cl}_8$ compounds listed above can be described in the same basic terms as an alternating chain of planar CuCl_4 and quasiplanar Cu_2Cl_6 complexes. However, the chain structures in these cases are straight, rather than zigzag as in (I). This arises from a remarkable difference in the way the CuCl_4 complex in (I) completes its coordination environment. In the straight chain structures, the CuCl_4 complex forms long semicoordinate contacts to terminal chloride ions of neighboring Cu_2Cl_6 units to give itself (4+2)-coordination and to produce the straight chain (e.g. NIJZEL, LITHEB, LITHAX, JIZBUP and FIYPUZ). This behavior is easily explained in terms of the charge compensation principle, since without strong hydrogen bonding from the organic cation the terminal chloride should interact more strongly with a neighboring copper cation to form an asymmetric bridge. In contrast, the CuCl_4 complex in (I) completes its coordination environment by forming semi-

coordinate contacts to the bridging chloride ions (Cl4) of neighboring Cu_2Cl_6 complexes and leaving atom Cl1 as a completely terminal ligand. This occurs in spite of the fact that the quaternary N atom is incapable of the strong NH hydrogen bonding expected to stabilize terminal halide ligands within the chain (Willett, 1991). In both the straight and the zigzag chains, the CuCl_4 complex also acts as the central complex of a tricopper segment linked to neighboring segments by the symmetric dibridging in the Cu_2Cl_6 complexes.

The semicoordinate contact angles about Cu2 are strained, as shown by the Cl···Cu–Cl angles, which deviate by an average of $10.04(4)^\circ$ from 90° . However, they are not as strained as those in the $(\text{C}_6\text{H}_5)_3\text{PR}^+$ salts, where average deviations of $17.59(4)^\circ$ for NIJZEL ($R = \text{CH}_3$) and $15.31(6)^\circ$ for LITHAX ($R = \text{Cl}$) are found. In these cases, the larger strain arises from the straight chain stretching to accommodate the repeat distance enforced by the bulky cations. Indeed, the semicoordinate Cu···Cl contact distance in these latter salts is approximately 0.4 \AA longer [Cu···Cl = $3.467(3) \text{ \AA}$ for $R = \text{CH}_3$ and $3.309(3) \text{ \AA}$ for $R = \text{Cl}$] than here, even though the semicoordinated ligand in (I) is a bridging ligand. Other straight chain $[\text{Cu}_3\text{Cl}_8]^{2-}$ compounds with less bulky counter-ions are less strained, as shown by shorter Cu···Cl bonds [$2.786(5) \text{ \AA}$ for JIZBUP and $2.9582(7) \text{ \AA}$ for FIYPUZ] and smaller distortions in average Cl···Cu–Cl angles [$11.3(2)^\circ$ for JIZBUP and $9.30(4)^\circ$ for FIYPUZ]. Repeat distances for the tricopper chain segment reflect these strains, with values of $9.539(8) \text{ \AA}$ for NIJZEL and $9.480(6) \text{ \AA}$ for LITHAX compared to the shorter values of $9.330(3) \text{ \AA}$ for JIZBUP, $9.278(1) \text{ \AA}$ for FIYPUZ and $7.4496(1) \text{ \AA}$ here.

The segmented chain structures arise as a means of accommodating bulkier organic cations. In $(\text{CH}_3)_4\text{NCuCl}_3$, a uniformly tribridged chain occurs (MATCCU01), but the slightly bulkier $(\text{CH}_3)_3\text{N}(\text{C}_2\text{H}_5)^+$ cation yields a chain of pentacopper segments (TABNOZ). The even bulkier $(\text{CH}_3)_2\text{N}(\text{C}_2\text{H}_5)_2^+$ cation yields a chain of tetracopper segments

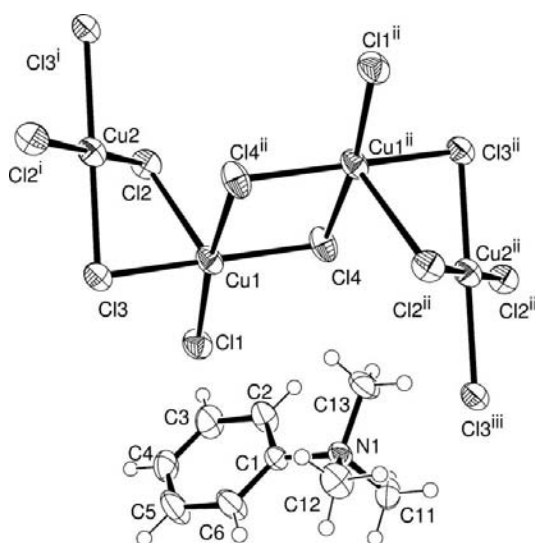


Figure 1
An ORTEP (Burnett & Johnson, 1996) diagram with atom labels of the organic cation and a section of the chloridocuprate(II) chain. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x + 1, y, z$.]

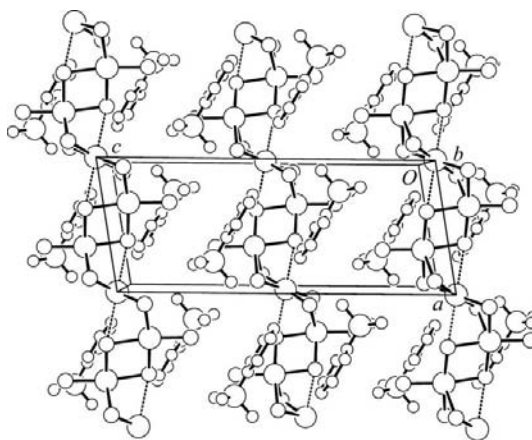


Figure 2
The unit-cell packing, viewed down the *b* axis and showing the cation pair stacking and inorganic chain parallel to the *a* axis. For clarity, H atoms have been omitted, N and Cu atoms are drawn as large circles, and C and Cl atoms are drawn as small circles.

(ZACJES). Shorter chain segments require more frequent dibridging along the chain. Since the dibridging is charge neutral, it requires no counter-ion. Thus the presence of more dibridging provides more room to pack bulkier cations. It is not surprising, then, that a chain of $[\text{Cu}_5\text{Cl}_{14}]^{4-}$ segments is found with the *N,N*-dimethylpiperidinium cation (Talley *et al.*, 1999). While this cation is larger than $(\text{CH}_3)_2\text{N}(\text{C}_2\text{H}_5)_2^+$ by one C atom, the organic ring structure is more constrained than the two ethyl groups of $(\text{CH}_3)_2\text{N}(\text{C}_2\text{H}_5)_2^+$, so the cation is, arguably, less bulky. The trimethylphenylammonium cation of (I) replaces one methyl group of $(\text{CH}_3)_4\text{N}^+$ (MATCCU01) with a phenyl group that should be less bulky than the saturated organic ring structure in *N,N*-dimethylpiperidinium. Therefore, the formation of a $[\text{Cu}_3\text{Cl}_8]^{2-}$ rather than a $[\text{Cu}_5\text{Cl}_{14}]^{4-}$ segmented chain at first seems puzzling.

The longest dimension of the trimethylphenylammonium cation, as measured by the $\text{H4} \cdots \text{H12B}$ distance plus twice the van der Waals radius of hydrogen (1.2 Å), can be generously estimated as 9.27 Å. This value is close to the lower limit of the repeat distance of the $[\text{Cu}_3\text{Cl}_8]^{2-}$ segments found in FIYPUZ. Hence, it is conceivable that a straight chain structure of tricopper segments could arise if trimethylphenylammonium cations were to stack end-to-end along their longest dimension, but it is unlikely that this would be an efficient packing mode for them. In this regard, the folding back of the $[\text{Cu}_3\text{Cl}_8]^{2-}$ segment to form a zigzag chain can be explained as a means of accommodating the packing requirements of a cation of considerably less bulk than those that are normally found with segmented $[\text{Cu}_3\text{Cl}_8]^{2-}$ chains. The use of bridging ligands in (I) to form semicoordinate contacts arises to meet the packing needs of the organic cation, with charge compensation now a secondary factor at best.

Lorenzo *et al.* (2000) have carefully analyzed the LITHEB, LITHAX and JIZBUP structures and concluded that 'it is likely that the details of coordination and bridging of copper have been controlled by the requirements of the $[(\text{C}_6\text{H}_5)_3\text{PR}^+]$ cation motif'. In this regard, it is worthwhile considering the organic cation packing motif here. The trimethylphenylammonium cations form parallel stacks of inversion-related pairs along the *a* axis, as shown in Fig. 2. Each inorganic chain is surrounded by four neighboring cation pair stacks and *vice versa*. The aromatic rings of each pair are coplanar and are separated by an interplanar spacing of 3.934 (6) Å. The normal to the aromatic ring plane forms an angle of 49.92 (6)° with respect to the *a* axis and is almost perpendicular to the *b* axis. This tilt angle efficiently allows the cations to aggregate phenyl rings inside the stack while placing two of the three methyl groups on the periphery. Neighboring cation pairs are also related by inversion, so that the cation stack follows a similar line of inversion centers along the *a* axis as does the inorganic chain. The cation pair inversion center is at the same *x* coordinate as the Cu_2Cl_6 inversion center, and the inversion center between cation pairs is at the same *x* coordinate as the CuCl_4 inversion center. The methyl group of a cation in one pair abuts the phenyl ring of a cation in the neighboring pair, with a contact distance $[\text{C4} \cdots \text{C11}^{\text{iii}} = 3.549 (5) \text{ \AA}$; symmetry code: (iii) $x + 1, y, z$] close to the sum of the van der Waals

radii. The packing modes of the trimethylphenylammonium cation are varied in other structures, but cation stacking with the phenyl ring tilted relative to the stacking axis is a common motif. In particular, trimethylphenylammonium ozonide (Korber & Jansen, 1992; KUDYOX) contains stacking of inversion-related cation pairs with a repeat distance of 7.130 (2) Å, which very closely resembles the cation pair stacking in (I). In KUDYOX, the tilt angle and the interplanar spacing are slightly smaller than those in (I), thus contributing to the marginally lower repeat distance.

Lorenzo *et al.* (2000) ask the question, is the crystal packing in halidocuprate(II) compounds dominated or determined by organic cation supramolecular motifs, or by coordination within the halidocuprate anion? Their answer, with respect to the $[(\text{C}_6\text{H}_5)_3\text{PR}]_2\text{Cu}_3\text{X}_8$ compounds, is that cation supramolecular motifs dominate, but that validation is still required by geometrical information from related compounds. The structural details of (I) support the conclusion of Lorenzo *et al.* that cation supramolecular motifs do indeed determine the overall crystal packing, at least for cations bulkier than $(\text{CH}_3)_4\text{N}^+$. Specifically, the zigzag chain structure in (I) is adopted to match the repeat distance dictated by the stacking of organic cation pairs. In this regard, it is significant that the organic cation packing in (I) is rational and with precedent, while the halidocuprate chain structure defies traditional rationalization (Willett, 1991).

$\text{C}-\text{H} \cdots \text{Cl}$ hydrogen bonding seems to be of little importance in the structure. Two of the three shortest $\text{H} \cdots \text{Cl}$ contact distances are to the terminal chloride (see Table 2). These short interactions might provide some weak CH hydrogen bonding to the terminal chloride that could further stabilize the zigzag chain structure. However, these contacts are significantly longer than those in the dibridged ACuCl_3 chains, such as BAPYUM or CIGNOV10, in which $\text{H} \cdots \text{Cl}$ contact distances to the terminal ligand are less than 2.5 Å.

The bond lengths and angles within the trimethylphenylammonium cation agree with expected values (Ladd & Palmer, 1994). The conformation of the phenyl ring plane is staggered with respect to the methyl groups, and forms a $\text{C2}-\text{C1}-\text{N1}-\text{C1X}$ torsion angle of 85.6 (3)° with atom C11, 154.2 (3)° with atom C12 and 34.4 (3)° with atom C13. A study of similar torsion angles of trimethylphenylammonium cations compiled from the CSD indicates that this staggered arrangement of the phenyl ring is less frequent than the eclipsed conformation. A histogram of these torsion angles (Fig. 3) shows that the more frequent torsion angles are approximately 0, 60, 120 and 180°, corresponding to an eclipsed conformation of the aromatic ring with one of the methyl groups. Less frequent torsion angles occur at approximately 30, 90 and 150°, and correspond to the staggered conformation seen in (I). Elongated ring C atom displacement ellipsoids perpendicular to the ring plane indicate a high degree of librational motion. Librational motion of the methyl groups at higher temperature may render the eclipsed conformation untenable. The large displacement parameters perpendicular to the ring then arise as it is buffeted by nonbonding repulsive interactions with the methyl

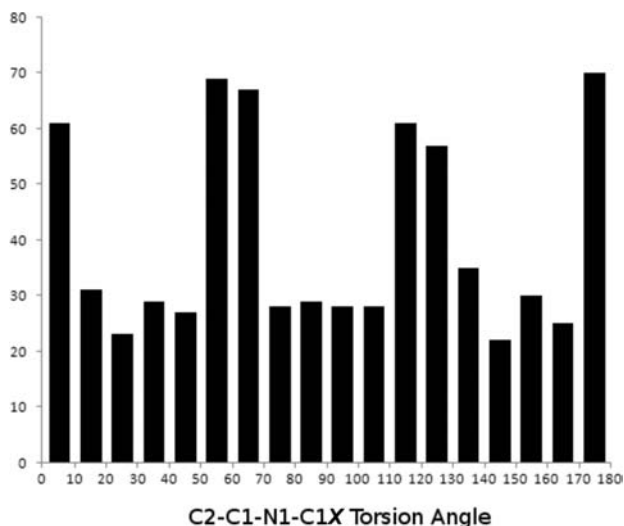


Figure 3
A histogram compiled from data in the CSD of C2,6–C1–N1–ClX torsion angles [the atom-numbering scheme for (I) is used] in the range 0–180° for trimethylphenylammonium cations (Allen, 2002).

groups. Below 200 K a phase transition to a triclinic unit cell is observed, although crystal damage during the transition has so far prevented a completely suitable structure determination of the low-temperature phase. The best structure determination yet, obtained at 100 K [$R = 0.0932$ and $F^2 > 2\sigma(F^2)$], has established connectivity and shows a rearrangement of the organic cation to an eclipsed conformation while maintaining the gross structure of the inorganic chain (Bond, 2009).

Experimental

Trimethylphenylammonium iodide was prepared by reaction of *N,N*-dimethylaniline (5 ml, 0.04 mol) with a molar excess of iodomethane. The chloride salt was prepared by halide ion exchange with a molar excess of silver chloride. Trimethylphenylammonium chloride and copper(II) chloride were dissolved in a 1:1 ratio in 100 ml of approximately 6 M HCl solution. Red crystals of (I) were obtained upon evaporation.

Crystal data

(C₉H₁₄N)₂[Cu₃Cl₈] $V = 1360.35$ (4) Å³
 $M_r = 746.7$ $Z = 2$
 Monoclinic, $P2_1/c$ Mo $K\alpha$ radiation
 $a = 7.4496$ (1) Å $\mu = 3.12$ mm⁻¹
 $b = 10.0211$ (2) Å $T = 200$ K
 $c = 18.4713$ (4) Å $0.30 \times 0.24 \times 0.18$ mm
 $\beta = 99.420$ (1)°

Data collection

Nonius KappaCCD diffractometer 11596 measured reflections
 Absorption correction: multi-scan 5947 independent reflections
 (DENZO/SCALEPACK; 4127 reflections with $I > 2\sigma(I)$
 Otwinowski & Minor, 1997) $R_{int} = 0.033$
 $T_{min} = 0.416$, $T_{max} = 0.548$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$ 145 parameters
 $wR(F^2) = 0.129$ H-atom parameters constrained
 $S = 1.08$ $\Delta\rho_{max} = 1.32$ e Å⁻³
 5947 reflections $\Delta\rho_{min} = -1.70$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1–Cl1	2.2240 (8)	Cu1–Cl4 ⁱⁱ	2.3547 (7)
Cu1–Cl2	2.6045 (8)	Cu2–Cl2	2.2446 (7)
Cu1–Cl3	2.3085 (7)	Cu2–Cl3	2.3411 (7)
Cu1–Cl4	2.2873 (8)	Cu2–Cl4 ⁱⁱ	2.9297 (7)
Cl1–Cu1–Cl2	99.47 (3)	Cl4–Cu1–Cl4 ⁱⁱ	83.62 (3)
Cl1–Cu1–Cl3	94.21 (3)	Cl2–Cu2–Cl3	89.92 (3)
Cl1–Cu1–Cl4	93.10 (3)	Cl2–Cu2–Cl4 ⁱⁱ	85.19 (2)
Cl1–Cu1–Cl4 ⁱⁱ	169.62 (3)	Cl3–Cu2–Cl4 ⁱⁱ	74.73 (2)
Cl2–Cu1–Cl3	82.31 (3)	Cu1–Cl4–Cu1 ⁱⁱ	96.38 (3)
Cl2–Cu1–Cl4	104.47 (3)	Cu1–Cl2–Cu2	78.50 (2)
Cl2–Cu1–Cl4 ⁱⁱ	90.89 (3)	Cu1–Cl3–Cu2	82.99 (2)
Cl3–Cu1–Cl4	169.08 (3)	Cu1–Cl4–Cu2 ⁱⁱ	141.09 (3)
Cl3–Cu1–Cl4 ⁱⁱ	87.77 (3)		

Symmetry code: (ii) $-x + 1, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2–H2 \cdots Cl1 ^{iv}	0.93	2.77	3.639 (3)	156
C11–H11A \cdots Cl1 ⁱⁱⁱ	0.96	2.79	3.739 (3)	170
C11–H11C \cdots Cl2 ^v	0.96	2.78	3.683 (3)	158

Symmetry codes: (iii) $x + 1, y, z$; (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.

All H atoms were visible in electron-density difference maps. Positions for H atoms were calculated to give an idealized geometry in a riding model, with C–H bond lengths of 0.93 Å for aromatic H atoms and 0.96 Å for methyl H atoms. $U_{iso}(H)$ values were fixed at $1.2U_{eq}(C)$ for aromatic H atoms and $1.5U_{eq}(C)$ for methyl H atoms.

Data collection: COLLECT (Bruker, 2004); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993); 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: GA3139). Services for accessing these data are described at the back of the journal.

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