

## Bis[*N,N'*-(2-chlorobenzylidene)-ethylenediamine- $\kappa^2N,N'$ ]copper(I) dichloridocuprate(I) acetonitrile solvate

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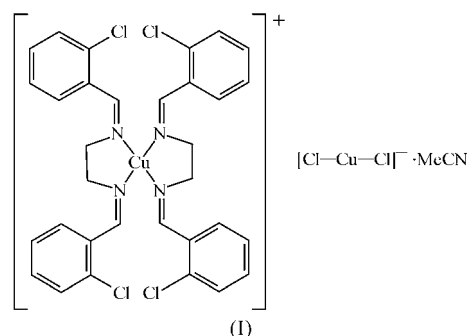
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The 1:1 adduct of *N,N'*-bis(2-chlorobenzylidene)ethylenediamine (cb<sub>2</sub>en) with copper(I) chloride proves to be an ionic compound with Cu<sup>I</sup>-centred cations and anions, [Cu(C<sub>16</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>)<sub>2</sub>][CuCl<sub>2</sub>]·CH<sub>3</sub>CN. In the cation, the Cu<sup>I</sup> atom has a flattened tetrahedral coordination geometry, with a small bite angle for the chelating ligands, which form a double-helical arrangement around the metal centre. The anion is almost linear, as expected. The packing of the cations involves intermolecular  $\pi$ - $\pi$  interactions, which lead to columns of translationally related cations along the shortest unit-cell axis, with anions and solvent molecules in channels between them.

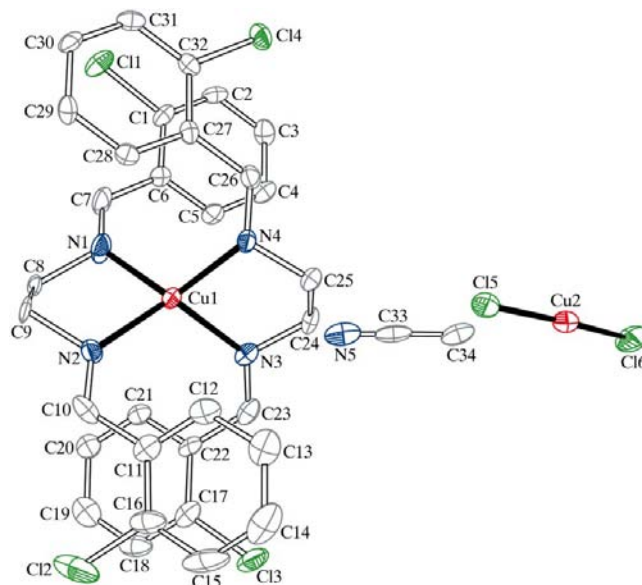
### Comment

The coordination chemistry of copper(I) complexes has received increased attention over the last few decades. This is mainly due to the potential application of these complexes in catalytic processes (Fife *et al.*, 1985; Bowker *et al.*, 1988; Bowmarker *et al.*, 2000), photosensitization reactions (Horváth, 1994; Kutal, 1990), light-harvesting studies (Rosi *et al.*, 1999; Dietrich-Buchecker & Sauvage, 1987) and the design of supramolecular arrays (Meghdadi *et al.*, 2002; Foster *et al.*, 2000). Reaction of copper(I) halides, CuX, with nitrogen-based ligands (*L*) yields CuXL<sub>*n*</sub> adducts. The steric, electronic and conformational effects imparted by the coordinated ligands play an important role in influencing the properties of the resulting metal complexes. A thorough understanding of these effects can serve as the basis for the rational design of complexes with specific and predictable properties. The number of ligands bound to the monovalent Cu<sup>I</sup> ion is greatly influenced by both the chemical nature and the geometry of the ligand *L*, and the particular choice of halogen *X* (Lange *et al.*, 2000). Although structural reports on [Cu<sup>I</sup>L<sub>4</sub>]<sup>+</sup> complex

cations (where *L* is an *N*-donor ligand) are numerous (Alcon *et al.*, 2000; Miller & Karpishin, 1999; Panja *et al.*, 2002), there are a limited number of studies of copper(I) complexes with isolated linear dihalidocuprate(I) anions (Amirnasr *et al.*, 2005; Mirkhani *et al.*, 2004). The structures of halidocuprate(I) compounds are exceptionally varied, and the nature of the cation plays an important role in determining the coordination number of Cu<sup>I</sup> in halidocuprates and the tendency of the anions to form extended structures (Andersson & Jagner, 1989; Hasselgren *et al.*, 1999). Thus, bulky cations with well screened charges tend to favour the formation of discrete anions in which Cu<sup>I</sup> has a low coordination number. It has been recognized that cation properties, such as size, shape and the distribution of positive charge, are of importance for the anion configurations adopted by halidocuprates(I).



In this context, we decided to examine the nature of the complex formed with an unconjugated diimine ligand. The title complex, (I), was prepared by reacting the bidentate ligand *N,N'*-bis(2-chlorobenzylidene)ethylenediamine (cb<sub>2</sub>en) with CuCl. The structure determination of (I) is consistent



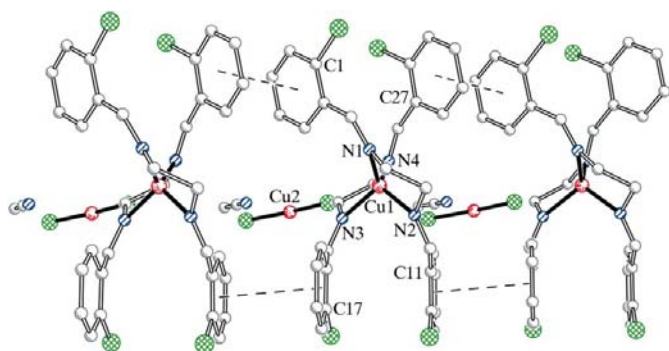
**Figure 1**  
The asymmetric unit of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity, and only one component is shown for each disordered group.

with the stoichiometry of a 1:1 copper(I) chloride–ligand adduct,  $[\text{CuCl}(L)]$ . The structural connectivity, however, is that of an ionic complex, the asymmetric unit of the structure comprising a bis(ligand)copper(I) cation and a dichlorido-cuprate(I) anion, together with a molecule of acetonitrile solvent,  $[\text{L}_2\text{Cu}]^+[\text{CuCl}_2]^- \cdot \text{MeCN}$  (Fig. 1).

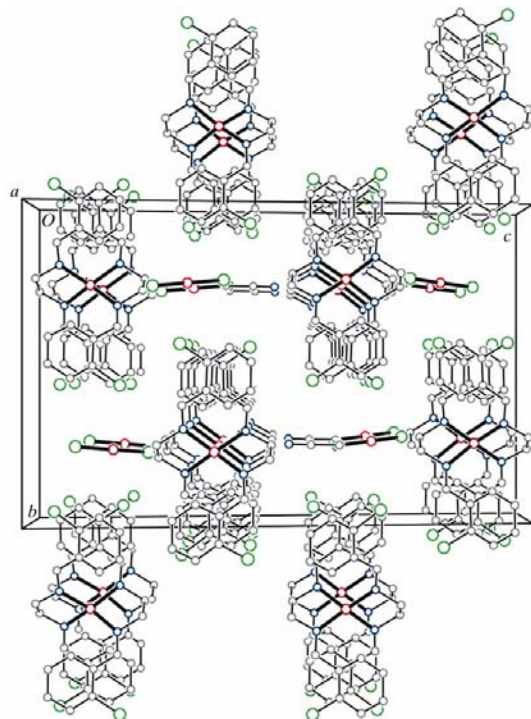
The anion of (I) has no crystallographic symmetry, and one Cl atom is disordered over two sites. Neither of these gives a completely linear coordination (Table 1). The geometry is in good agreement with that of several other previously reported examples (Kaiser *et al.*, 1974; Engelhardt *et al.*, 1984).

The cation of (I) has a markedly flattened tetrahedral geometry and also lies in a general position with no crystallographic symmetry. The angles at the  $\text{Cu}^{\text{I}}$  atom in the cation

are similar to the corresponding angles for ethylenediamine complexes (Engelhardt *et al.*, 1984), with a small bite angle for the chelating ligand. The two ligands form a double-helical arrangement around the  $\text{Cu}^{\text{I}}$  atom. Within the cation, the two benzene rings of each ligand are almost parallel to those of the other, with a dihedral angle of  $2.73$  ( $16^\circ$ ) for rings C1–C6 and C27–C32, and  $0.38$  ( $17^\circ$ ) for rings C11–C16 and C17–C22, and with interplanar spacings of about  $3.6 \text{ \AA}$  in each case. This does not give rise to intramolecular  $\pi$ – $\pi$  stacking, since the pairs of rings are substantially displaced laterally, the centroid-to-centroid distances being  $4.877$  (4) and  $4.846$  (4)  $\text{Å}$ , respectively. However, the same pairs of rings are similarly close to parallel in adjacent molecules along the short  $a$  axis (dihedral angles are the same by symmetry), and here there is intermolecular  $\pi$ – $\pi$  stacking (Fig. 2), the centroid-to-centroid distances being  $3.645$  (3) and  $3.536$  (3)  $\text{Å}$ , respectively, and the interplanar spacings being  $3.532$  and  $3.523$   $\text{Å}$ , respectively. This stacking produces columns of cations along the  $a$  axis, with anions and solvent molecules occupying the channels between them (Fig. 3).



**Figure 2**  
The stacking of cations of (I) via  $\pi$ – $\pi$  interactions.



**Figure 3**  
The crystal packing in (I), viewed along the  $a$  axis, showing the columns of cations, with anions and solvent molecules in channels.

## Experimental

The title compound was prepared by the reaction of  $\text{CuCl}$  and  $\text{cb}_2\text{en}$  (molar ratio 1:1) in an acetonitrile solution at room temperature. The solution was then concentrated under vacuum. Red crystals of (I) were formed by vapour diffusion of diethyl ether into the concentrated solution.

### Crystal data

$[\text{Cu}(\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{N}_2)_2][\text{CuCl}_2] \cdot \text{C}_2\text{H}_3\text{N}$	$V = 3548$ (4) $\text{Å}^3$
$M_r = 849.42$	$Z = 4$
Monoclinic, $P2_1/n$	Synchrotron radiation
$a = 7.845$ (5) $\text{Å}$	$\lambda = 0.8462$ $\text{Å}$
$b = 16.965$ (10) $\text{Å}$	$\mu = 1.68$ $\text{mm}^{-1}$
$c = 26.915$ (15) $\text{Å}$	$T = 120$ (2) K
$\beta = 97.896$ (9) $^\circ$	$0.10 \times 0.10 \times 0.10$ mm

### Data collection

Bruker APEXII CCD diffractometer	30485 measured reflections
Absorption correction: multi-scan (TWINABS; Bruker, 2004)	30485 independent reflections
$T_{\text{min}} = 0.730$ , $T_{\text{max}} = 0.850$	15283 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.000$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$	24 restraints
$wR(F^2) = 0.127$	H-atom parameters constrained
$S = 0.79$	$\Delta\rho_{\text{max}} = 0.71$ $\text{e \AA}^{-3}$
30485 reflections	$\Delta\rho_{\text{min}} = -0.84$ $\text{e \AA}^{-3}$
456 parameters	

**Table 1**  
Selected geometric parameters ( $\text{Å}$ ,  $^\circ$ ).

Cu1–N1	2.024 (3)	Cu2–Cl6	2.171 (5)
Cu1–N2	2.024 (3)	N1–C7	1.277 (4)
Cu1–N3	2.039 (3)	N1–C8	1.535 (8)
Cu1–N4	2.014 (3)	N1–C8A	1.502 (8)
Cu2–Cl5	2.0862 (14)	N2–C9	1.534 (8)
N1–Cu1–N2	85.09 (12)	Cl5–Cu2–Cl6	170.5 (4)
N1–Cu1–N4	115.87 (13)	Cu1–N2–C9	108.7 (4)
N2–Cu1–N3	115.33 (12)	Cu1–N2–C10	133.5 (3)
N3–Cu1–N4	85.18 (12)		

The small size and weak diffraction of the crystals necessitated the use of synchrotron radiation. The crystal was found to be a non-merohedral rotation twin about (100), with symmetry-inequivalent reflections overlapping in the diffraction pattern, making it impossible to merge equivalent reflections before the refinement with *SHELXL* HKLF5 style data (*SHELXTL*; Bruker, 2005). The twin law is (1 0 0/ 0 -1 0/-0.8867 0 -1). A number of reflections were rejected in the data processing because of problems with spot shape or masking by the beam-stop. The deposited structure factors are in the format generated by the undocumented LIST 7 instruction of *SHELXTL* (and *SHELXL97*), in which the contributions of the twin components are identified following refinement of the twin fraction; this was 0.5415 (5):0.4585 (5).

All H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C–H distances in the range 0.95–0.99 Å, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  [ $1.5U_{\text{eq}}(\text{C})$  for methyl H atoms]. One Cl atom of the anion was modelled as disordered over two positions, with occupancy factors 0.55 (2):0.45 (2). Twofold disorder was also found for the CH<sub>2</sub>CH<sub>2</sub> bridge of one of the ligands in the cation, with occupancy factors 0.515 (15):0.485 (15); restraints were applied to the displacement parameters of these disordered atoms.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINTE* (Bruker, 2004); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2005); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3174). Services for accessing these data are described at the back of the journal.

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