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Bis[*N*,*N*′-bis(diphenylmethylene)-ethylenediamine-κ^2N,N']copper(I) dichlorocuprate(I)

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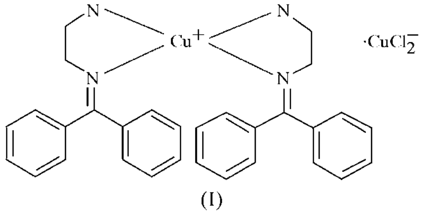
The 1:1 adduct of *N*,*N*′-bis(diphenylmethylene)ethylenediamine (bz$_2$en) with copper(I) chloride, *viz*. $[Cu(C_{28}H_{24}N_2)_2][CuCl_2]$, has been synthesized. The structure contains cationic moieties of Cu^I ions (Cu on a twofold axis) coordinated to four N atoms of two bz$_2$en molecules (in a distorted tetrahedron) and linear dichlorocuprate(I) anions (with Cu on an inversion centre). These cations and anions are packed in columns along *b*. The packing of the cation and anion columns involves a significant C—H···Cl interaction and four short intermolecular C—H···π contacts, two of which are between cation columns.

Comment

The reaction of copper(I) halides, Cu*X*, with nitrogen-based ligands (*L*) yields Cu*XL*$_n$ adducts. The number of ligands bound to the monovalent Cu ion is influenced greatly by both the chemical nature and geometry of the ligand *L* and the type of halogen *X* (Zubieta *et al.*, 1983; Kirchner *et al.*, 1987; Alyea *et al.*, 1990). 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(benzophenone)ethylenediimine (bz$_2$en) with CuCl.



(I)

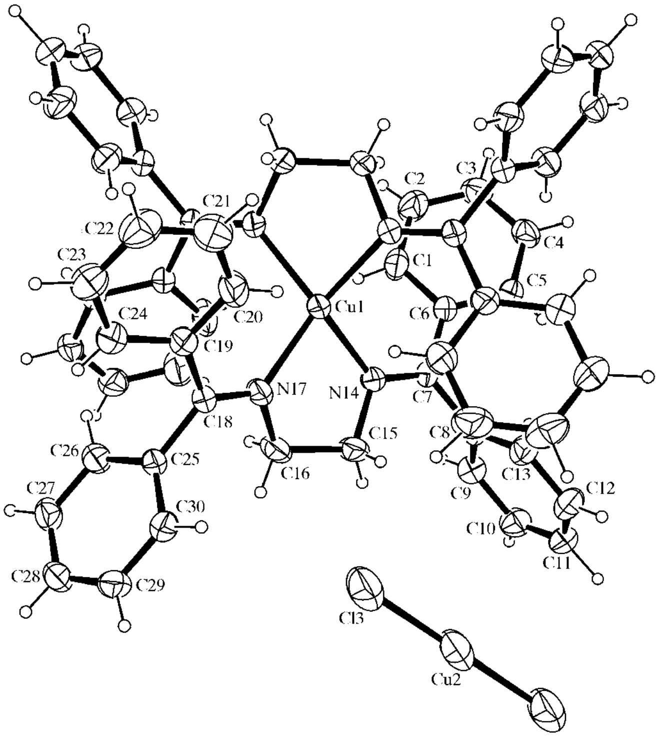


Figure 1
A view of the cation and anion of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 25% probability level and H atoms are shown as small spheres of arbitrary radii.

The structure determination of (I) is consistent with the stoichiometry of a 1:1 copper(I) chloride–ligand adduct. The atom disposition, however, is that of an ionic complex, the asymmetric unit of the structure comprising a bis(ligand)-copper(I) cation and a dichlorocuprate(I) anion (Fig. 1). The Cu^I atom of the dichlorocopper(I) anion lies on a centre of symmetry, the anion thus being linear [Cu—Cl = 2.0832 (8) Å]. The geometry of (I) (Table 1) is in good agreement with that

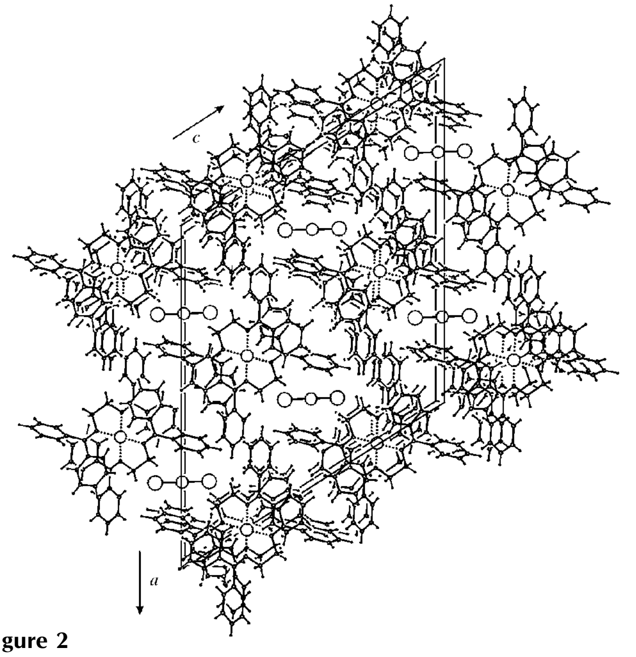


Figure 2
The crystal packing in (I), viewed along the *b* axis, showing the columns of cations and anions.

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of several other established examples (Kaiser *et al.*, 1974; Engelhardt *et al.*, 1984).

The Cu atom of the cation is on a twofold axis, coordinated to four N atoms belonging to two symmetry-related bz$_2$en molecules in a distorted tetrahedral geometry. The N—Cu—N bond angles found in (I) [85.98 (8), 109.50 (8), 134.7 (1) and 140.0 (1)°] are similar to the corresponding data for ethylenediamine chelate rings (Engelhardt *et al.*, 1984). The Cu—N bond lengths [2.030 (2) and 2.099 (3) Å] and angles are similar to those in the related bz$_2$en copper(I) perchlorate (2:1) complex, in which a perchlorate ion acts as counter-ion (Chowdhury *et al.*, 2000). All the benzene rings in (I) are planar, with a maximum out-of-plane deviation for atom C26 of 0.010 (2) Å. The acute angles made by the pairs of rings connected to the same N atom are 85.51 (9) and 80.26 (8)°.

The crystal packing of (I) involves columns of cations and anions packed along the *b* axis (Fig. 2). A significant interaction between the cation and anion columns is provided by a short C—H···Cl contact (Table 2). No short C—H···π interactions are found between rings belonging to the same N atom. There are, however, four short intramolecular C—H···π interactions (Table 2), two of which (involving atoms H4 and H12) are between different cation columns.

A calculation using *PLATON* (Spek, 1990) indicated four equivalent solvent-accessible voids of 26 Å^3. The final difference Fourier synthesis did not show any significant electron density in these areas.

Experimental

The title compound was prepared by the reaction of CuCl and bz$_2$en (molar ratio 1:1) in a mixed acetonitrile–tetrahydrofuran (1:4) solution at room temperature. The solution was then concentrated under vacuum. Red crystals of (I) were formed by vapour diffusion of ether into the concentrated solution.

Crystal data

$[Cu(C_{28}H_{24}N_2)_2][CuCl_2]$
$M_r = 975.02$
Monoclinic, $C2/c$
$a = 26.126$ (9) Å
$b = 9.337$ (5) Å
$c = 23.649$ (9) Å
$\beta = 122.48$ (5)°
$V = 4867$ (5) Å^3
$Z = 4$

$D_x = 1.33$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 16.0$–$22.0°$
$\mu = 2.39$ mm^{-1}
$T = 294$ K
Block, red
0.40 × 0.30 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
10 026 measured reflections
5017 independent reflections
3291 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.038$

$\theta_{\rm max} = 75.0°$
$h = -32 \rightarrow 32$
$k = 0 \rightarrow 11$
$l = -29 \rightarrow 29$
3 standard reflections
frequency: 60 min
intensity decay: <0.5%

Refinement

Refinement on F^2
$R(F) = 0.053$
$wR(F^2) = 0.137$
$S = 1.55$
5017 reflections
292 parameters
H-atom parameters constrained

$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
$(\Delta/\sigma)_{\rm max} = 0.02$
$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 0.14 × 10^{-5}

Table 1
Selected geometric parameters (Å, °).

Cu1—N14	2.030 (2)	Cu2—Cl3	2.0832 (8)
Cu1—N17	2.099 (2)	N14—C7	1.271 (3)
N14—Cu1—N14$^{\rm ii}$	140.0 (1)	N14—Cu1—N17$^{\rm ii}$	109.50 (8)
N14—Cu1—N17	85.98 (8)	N17—Cu1—N17$^{\rm ii}$	134.7 (1)

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

Table 2
Hydrogen-bonding geometry (Å, °).

*Cg*1–*Cg*4 are the centroids of rings C1–C6, C8–C13, C19–C24 and C25–C30, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C21—H21···Cl3$^{\rm i}$	0.95	2.71	3.652 (4)	173
C26—H26···*Cg*1$^{\rm ii}$	0.95	3.08	3.922 (4)	148
C4—H4···*Cg*2$^{\rm iii}$	0.95	2.99	3.812 (4)	146
C13—H13···*Cg*3$^{\rm ii}$	0.95	2.79	3.729 (4)	167
C12—H12···*Cg*4$^{\rm iv}$	0.95	2.89	3.791 (4)	158

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

H atoms were placed in calculated positions, with C—H distances of 0.95 Å, and treated as riding atoms, with $U_{\rm iso}({\rm H}) = 1.3U_{\rm eq}({\rm C})$.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD*-4 *Operations Manual*; data reduction: *PROCESS* in *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR* (Burla *et al.*, 1989); program(s) used to refine structure: *LSFM* in *MolEN*; molecular graphics: *ORTEP*II (Johnson, 1976) and *ORTEP*-3 (Farrugia, 1998); software used to prepare material for publication: *BTABLE, PTABLE* and *CIF* in *MolEN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1057). Services for accessing these data are described at the back of the journal.

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