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A mixed copper(I)/copper(II) complex coordinated by a multidentate amidato ligand

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Key indicators

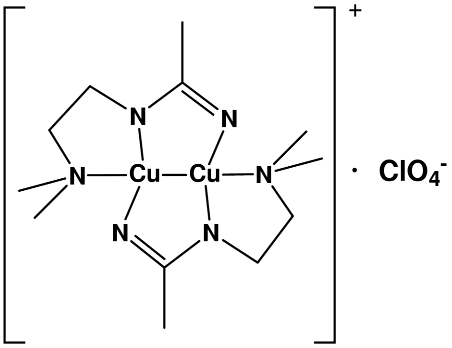
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
R factor = 0.042
wR factor = 0.125
Data-to-parameter ratio = 9.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The compound described in this paper, bis{1-[2-(*N*,*N*-dimethylamino)ethylamino]ethaniminato}dicopper(I,II) perchlorate, $[Cu_2(C_6H_{13}N_3)_2]ClO_4$, is the product of the reaction of $[(H_3CCN)_4Cu]ClO_4$ with a substituted triazine ring system. The complex is a copper(I)/copper(II) compound in which each Cu atom has a square-planar coordination environment; the Cu—Cu distance is 2.4552 (14) Å. The two Cu atoms are bridged by an amidate ligand, which was apparently formed in a ring-cleavage reaction of the triazine ring. Each cation has a twofold axis perpendicular to the Cu–amidate plane, bisecting the Cu—Cu bond.

Comment

Amine ligands with a high number of coordination sites have attracted much interest due to their complexation of specific metals, depending on the nature of the ligand, such as number of coordination sites, ring structure, rigidity, *etc*. Widely known compounds, such as crown ethers or cryptands, are expensive, often toxic, and difficult to synthesize; accordingly, there is a search for new classes of multidentate ligands. Promising systems include derivatives of 1,3,5-triazacyclohexanes (triazines) because of their straightforward preparation, starting from cheap reagents (Kaufman, 1975; Köhn *et al.*, 1996). We are interested in ligands which contain additional coordination sites at substituents attached to the heterocyclic atoms. *N*,*N*′,*N*″-Tris(dimethylaminoethyl)hexahydro-*s*-triazine is one example of such a ligand which has already been used in our group in the complexation of CuBr (Kickelbick *et al.*, 2002).



(I)

For a comparison of different Cu^I sources, $[(CH_3CN)_4Cu]ClO_4$ was also used as a Cu^I source. Surprisingly, a dicopper complex with an amidate ligand as cation and a perchlorate anion was obtained from this reaction (Fig. 1).

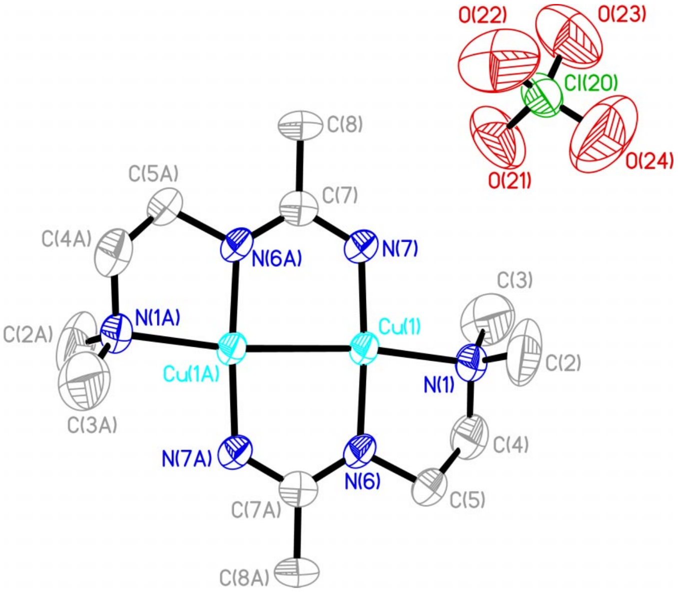


Figure 1
The structure of the anion and one of the two cations, with displacement ellipsoids at the 50% probability level. For clarity, H atoms have been omitted.

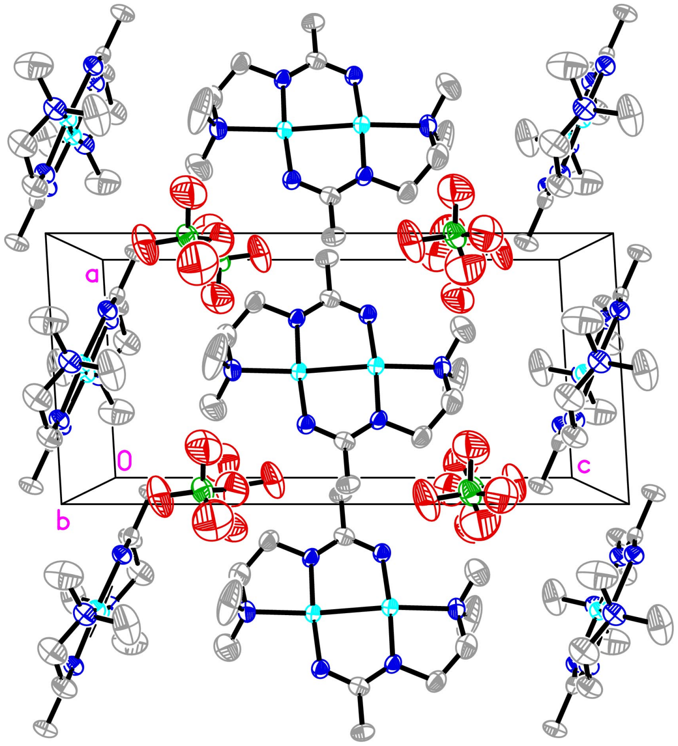


Figure 2
Projection of the structure along [010], showing displacement ellipsoids at the 40% probability level. For clarity, H atoms have been omitted.

The asymmetric unit of the title compound, (I), consists of two half-cations and one anion. In this paper, the structural parameters of only one cation are discussed. The bond lengths and angles of the second cation differ only within experimental error. The complex shows a structure similar to other dicopper–amidate complexes (Hathaway & Murphy, 1980). Each Cu atom has a square-planar coordination sphere. Each metal is coordinated by three N atoms, with bonding distances of 2.116 (5) (Cu1—N1), 1.879 (5) (Cu1—N6) and 1.872 (5) Å (Cu1—N7), and one Cu atom at a distance of 2.4552 (14) Å. The rather short and nearly equal C—N distances of 1.322 (8) (C7—N6^{i}) [symmetry code (i): $1-x$, $1-y$, $2-z$] and 1.346 (8) Å (N7—C7), as well as the N6^{i}—C7—N7 angle of 118.5 (5)°, are typical for the amidate bonding situation with a delocalized negative charge. For reasons of charge balance, *viz*. two negative charges per cation from the amidate ligands and one negative charge from the perchlorate anion, the compound has to be a Cu^{I}/Cu^{II} complex.

Layers of copper complexes are stacked along the *b* axis of the crystal, with amidate–copper planes perpendicular to each other (Fig. 2).

The mechanism of formation of the complex is, as yet, unclear. A possible explanation of the cleavage is a reaction of free or coordinated acetonitrile with the triazine ring N atoms, followed by a cleavage of the ring and coordination of the product to the Cu^{I} atoms. However, we do not have any information supporting this speculation and additional experiments are needed to clarify the issue.

Experimental

N,N′,N″-Tris(dimethylaminoethyl)hexahydro-*s*-triazine was prepared following the procedure of Kaufman (1975). 0.375 g (1 mmol) of [$(CH_3CCN)_4Cu$]ClO_4, 7.5 ml of acetonitrile and 0.300 g (1 mmol) of the triazine were mixed and stirred until a clear solution was obtained. The solution was allowed to stand for several weeks under an argon atmosphere, yielding a green suspension from which green crystals were isolated.

Crystal data

[$Cu_2(C_6H_{13}N_3)_2$]ClO_4
M_r = 474.87
Monoclinic, $P2_1/c$
a = 7.6752 (3) Å
b = 16.2561 (6) Å
c = 16.0299 (6) Å
β = 93.365 (1)°
V = 1996.58 (13) Å^3
Z = 4
D_x = 1.600 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4499 reflections
θ = 2.5–25.1°
μ = 2.29 mm^{-1}
T = 293 (2) K
Irregular, green
0.42 × 0.07 × 0.05 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.446, $T_{\max}$ = 0.894
10319 measured reflections
2087 independent reflections
1737 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.031
$\theta_{\max}$ = 20.8°
$h = -7 \rightarrow 7$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.125
S = 1.08
2087 reflections
227 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0734P)^2 + 3.6797P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.68 e Å^{-3}
$\Delta\rho_{\min}$ = −0.30 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0002 (4)

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Table 1
Selected geometric parameters (Å, °).

Cu1—N7	1.872 (5)	C5—N6	1.466 (8)
Cu1—N6	1.879 (5)	N7—C7	1.346 (8)
Cu1—N1	2.116 (5)	N6—C7^{i}	1.322 (8)
Cu1—Cu1^{i}	2.4552 (14)	C7—C8	1.507 (9)
N7—Cu1—N6	174.3 (2)	C7^{i}—N6—C5	121.6 (5)
N7—Cu1—N1	99.5 (2)	C7^{i}—N6—Cu1	123.8 (4)
N6—Cu1—N1	85.7 (2)	C5—N6—Cu1	114.6 (4)
N7—Cu1—Cu1^{i}	87.95 (15)	N6^{i}—C7—N7	118.5 (5)
N6—Cu1—Cu1^{i}	87.04 (15)	N6^{i}—C7—C8	121.9 (6)
N1—Cu1—Cu1^{i}	171.68 (14)	N7—C7—C8	119.6 (6)
C7—N7—Cu1	122.6 (4)		

Symmetry code: (i) $1 - x, 1 - y, 2 - z$.

H atoms were located from difference Fourier maps and were refined as riding.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL*97.

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