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Tetra-μ-chloro-chloro(*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)(1,1,3-trimethyl-2-imidazolium)dicopper(I)-copper(II)

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The title compound, [$Cu_3Cl_5(C_6H_{16}N_2)(C_6H_{13}N_2)$], was isolated from a reaction between $Cu(OH)_2$, $(CF_3)_3COH$, C_6H_6, [2-(dimethylamino)ethyl]dimethylamine (TMEDA), and tetrahydrofuran (THF), and contains two inequivalent copper(I) centers as well as a square-pyramidal copper(II) center all linked by μ_2-chloro bridges. The 1,1,3-trimethyl-2-imidazolium cation results from the cyclization of a coordinated molecule of TMEDA and contains localized C—N and C═N bonds in contrast to the delocalized C═N bonds observed in other coordinated 1,1,3-trimethyl-2-imidazolium cations.

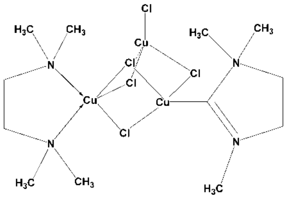
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.034
wR factor = 0.077
Data-to-parameter ratio = 18.3

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

Comment

The title compound, (I), was isolated from a reaction between $Cu(OH)_2$, $(CF_3)_3COH$, C_6H_6, [2-(dimethyl-amino)ethyl]dimethylamine (TMEDA), and tetrahydrofuran (THF) (George & Purdy, 1992). Crystals were obtained from a C_6D_6 solution containing a small amount of $CFCl_3$. As seen from a consideration of coordination geometry, charge balance, and analysis of bond lengths and angles, this compound consists of two copper(I) (Cu2 and Cu3) and one copper(II) (Cu1) metal centers. All three copper centers are in unique coordination environments. One copper(I) center is coordinated by two μ_2-chloro ligands and a terminal chloro ligand in a trigonal planar arrangement. The other copper(I) center is in a distorted tetrahedral environment and coordinated by three μ_2-chloro ligands and the carbon donor from a 1,1,3-trimethyl-2-imidazolium cation (see below). The copper(II) center is in a square pyramidal environment consisting of the two N-donors from [2-(dimethylamino)ethyl]dimethylamine (TMEDA) and three μ_2-chloro ligands, with a τ index of 0.08 (Addison *et al.*, 1984)]. The TMEDA ligand is disordered over two equivalent conformations with relative occupancies of 0.645 (5) and 0.355 (5).



(I)

The stoichiometry of the title compound is intriguing from many points of view. The 1,1,3-trimethyl-2-imidazolium cation must have come from the condensation of one molecule of coordinated TMEDA. There is a precedent for this in the literature. Coordination of the amino groups of TMEDA to a

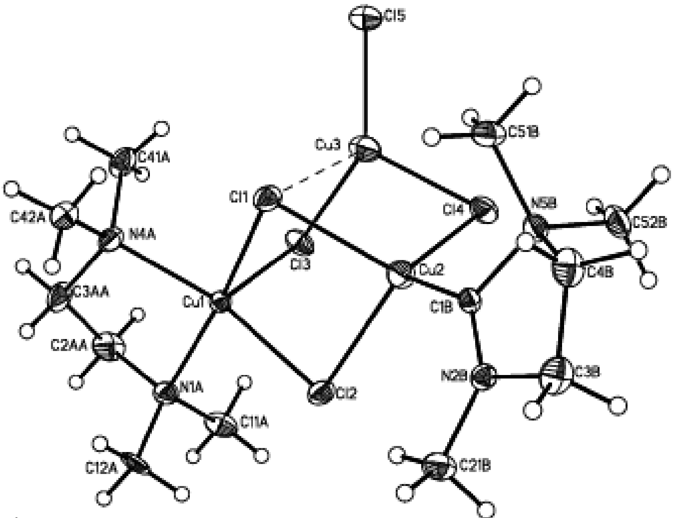


Figure 1
View of the molecule of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level.

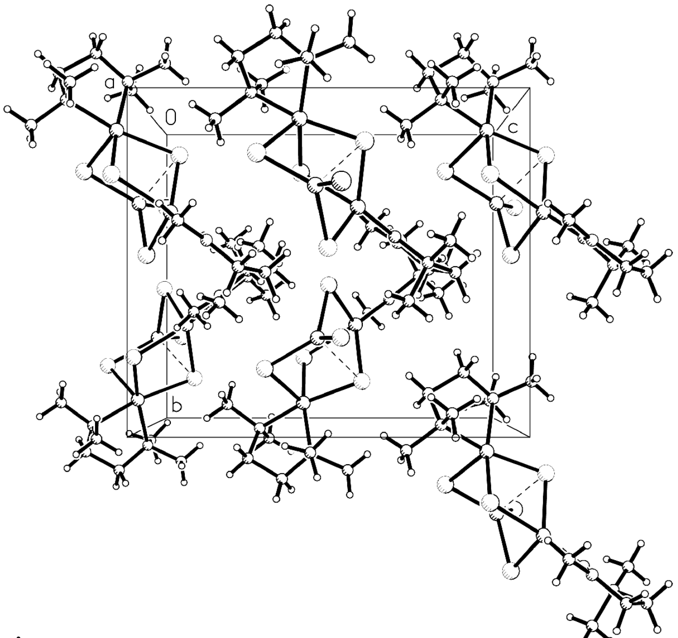


Figure 2
The molecular packing of (I), viewed down the *a* axis

metal results in higher acidity of adjacent methyl and methylene protons and thus can lead to condensation of a coordinated TMEDA moiety (Kokozay & Sienkiewicz, 1995). In the imidazolium ring, C1*B* forms a C═N (C1*B*—N2*B* 1.292 Å) and a C—N bond (C1*B*—N5*B* 1.515 Å), and thus is negatively charged, while N2*B* and N5*B* both form four bonds and thus are positively charged. N2*B* forms an N═C bond (N2*B*—C1*B* 1.292 Å), an N—C bond (N2*B*—C3*B* 1.467 Å), and an N—C bond to a terminal methyl group (N2*B*—C21*B* 1.456 Å), while N5*B* forms two single C—N bonds in the five-membered imidazolium ring and two C—N bonds to the terminal methyl groups. N2*B* is also positively charged as it forms an N═C (N2*B*—C1*B* 1.292 Å), an N—C bond (N2*B*—C3*B* 1.467 Å), and an N—C bond to a terminal methyl group (N2*B*—C21*B* 1.456 Å). Thus this condensation product is positively charged overall.

In the five-membered ring, this localization of the C—N and C═N bonds is unusual. In recent years, there has been a great deal of interest in 'Arduengo-type' carbenes (Arduengo *et al.*, 1993) as ligands to transition metals (Tulloch *et al.*, 2003; Danopoulos *et al.*, 2003) as their electronic characteristics are comparable to those of phosphine ligands (Green *et al.*, 1997). In these complexes, the imidazolium cation invariably has only one substituent at each nitrogen (Arnold *et al.*, 2001; Olbrich *et al.*, 1993; Tulloch *et al.*, 2001, 2003; Danopoulos *et al.*, 2003). However, in the present instance, since the imidazolium cation is a result of the cyclization of one molecule of coordinated TMEDA, there are two substituents on one nitrogen and only one on the other. This asymmetric substitution prevents the delocalization observed in other 'Arduengo-type' carbene complexes. In previous complexes, containing Cu attached *via* a negative C to a five-membered imidazolium ring, the two C—N bonds are almost equivalent, indicating charge delocalization.

Experimental

The reaction between $Cu(OH)_2$, $(CF_3)_3COH$, C_6H_6, TMEDA, and THF was carried out as previously described (George & Purdy, 1992). The mother liquor of the crystallization was evaporated under vacuum to remove solvent, and the residue was sublimed under vacuum, affording a blue sublimate at 338–358 K. The sublimate was dissolved in C_6D_6 containing a small amount of $CFCl_3$ in a sealed NMR tube. After 10 years, the NMR tube was opened, and the blue–green crystals were loaded into thin-wall glass capillaries.

Crystal data

$[Cu_3Cl_5(C_6H_{16}N_2)(C_6H_{13}N_2)]$
$M_r = 597.26$
Orthorhombic, $Pca2_1$
$a = 15.5111\ (14)$ Å
$b = 11.0313\ (9)$ Å
$c = 12.7192\ (12)$ Å
$V = 2176.4\ (3)$ Å^3
$Z = 4$
$D_x = 1.823$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 6021 reflections
$\theta = 2.6–28.3°$
$\mu = 3.52$ mm^{-1}
$T = 293\ (2)$ K
Irregular block, **blue–green**
0.33 × 0.31 × 0.26 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (Sheldrick, 1999)
$T_{min} = 0.232$, $T_{max} = 0.400$
18 409 measured reflections
5275 independent reflections
4598 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 28.4°$
$h = -20 \rightarrow 20$
$k = -14 \rightarrow 13$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.077$
$S = 1.06$
5275 reflections
288 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.3117P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.052$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Absolute structure: Flack (1983), 2430 Friedel pairs
Flack parameter = 0.017 (12)

H atoms were treated as riding, with C—H distances of 0.96 or 0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ and $1.2U_{eq}(C)$, respectively.

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Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Sheldrick, 1999); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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