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Di-μ-hydroxo-bis[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)copper(II)] dichloride from X-ray powder data

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Key indicators

Powder X-ray study
T = 295 K
Mean σ(C–C) = 0.018 Å
R factor = 0.023
wR factor = 0.033
Data-to-parameter ratio = 7.0

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

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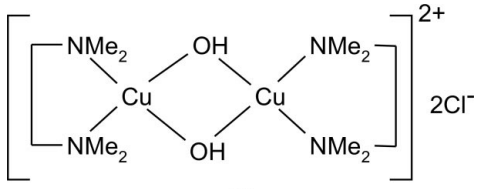
The crystal structure of the title complex, $[Cu_2(OH)_2(TMEDA)_2]Cl_2$ (TMEDA is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, $C_6H_{16}N_2$), has been characterized by X-ray powder diffraction. The cation is a binuclear complex with a Cu···Cu distance of 3.031 (7) Å and occupies a special position of 222 symmetry, while the chloride anions are on a twofold axis. There is a hydrogen bond linking a bridging hydroxy group with the anion [O···Cl = 2.993 (14) Å].

Comment

During the past five years, binuclear complexes of Cu^{II} have been used as catalysts in *N*-arylation processes of imidazoles by arylboronic acids (Collman, Zhong, Zeng & Costanzo, 2001; Collman, Zhong, Zhang & Costanzo 2001). Although the most active and widely used complex from this series, $[Cu_2(TMEDA)_2(OH)_2]Cl_2$ (TMEDA is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, $C_6H_{16}N_2$), (I), has been known for about 50 years, full structural data for this complex are still not available; single crystals of the title compound have not yet been obtained because of its solubility properties, and only cell parameters (*a* = 16.582 Å, *b* = 18.282 Å, *c* = 12.582 Å and space group *Fdd*2) have been reported (Meinders *et al.*, 1979). The development of the powder diffraction technique has enabled us to study the structure of (I) (Fig. 1 and Table 1).



(I)

The cation of the title compound is a binuclear copper complex with a Cu1···Cu1^{i} [symmetry code (i): $x, \frac{1}{4}-y, \frac{5}{4}-z$] distance of 3.031 (7) Å. The complex occupies a special position of 222 symmetry, so that atoms Cu1, Cl1, O1 and H1 are in special positions on twofold axes.

The bridging hydroxyl group (O1/H1) acts as a donor of a hydrogen bond, with the chloride anion (Cl1) serving as an acceptor (Table 2). Thus, the cation is bonded to two chloride anions.

The crystal structure of the title compound is isostructural with its bromide analogue $[Cu_2(TMEDA)_2(OH)_2]Br_2$, described by Mitchell *et al.* (1970). In both structures, apparent shortening of the C1—C1^{ii} bond [1.397 (17) Å; symmetry code (ii): $\frac{1}{4}-x, \frac{1}{4}-y, z$] in the dimethylene fragment of TMEDA is

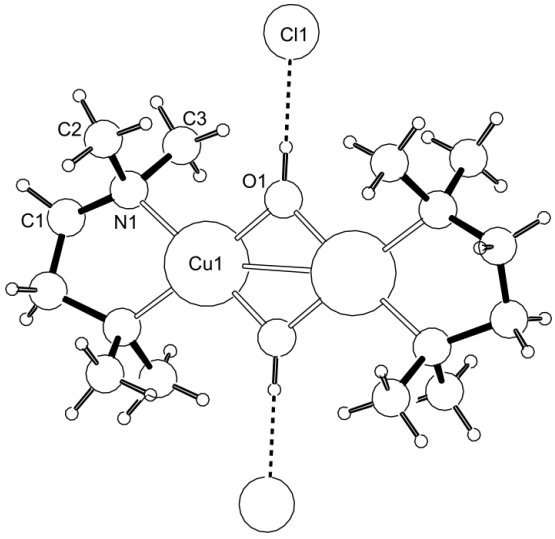


Figure 1
*PLUTON*96 (Spek, 1996) view of the title compound, with the atom-numbering scheme.

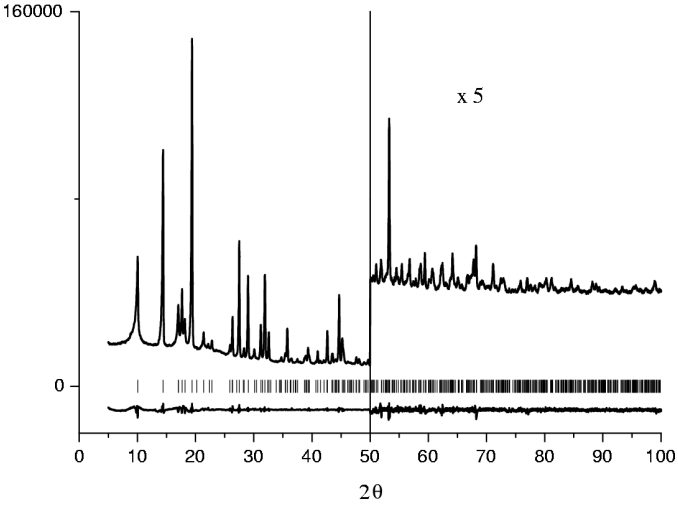


Figure 2
Rietveld plot for the title compound. The upper trace is the observed profile and the lower trace is the difference between observed and calculated; indexed lines are shown between these traces.

the result of highly anisotropic displacement parameters of the corresponding C atoms.

Experimental

The title compound was prepared using the well established procedure described by Collman, Zhong, Zhang & Costanzo (2001).

Crystal data

$[Cu_2(OH)_2(C_6H_{16}N_2)_2]Cl_2$
M_r = 464.43
Orthorhombic, *Fddd*
a = 16.612 (9) Å
b = 18.311 (9) Å
c = 12.598 (7) Å
V = 3832 (4) Å^3
Z = 8
D_x = 1.610 Mg m^{-3}
Cu $K\alpha_1$ radiation
λ = 1.54060 Å
μ = 5.40 mm^{-1}
T = 295 (2) K
Colourless
Specimen shape: flat sheet
15 × 15 × 0.5 mm
Particle morphology: lump-like

Data collection

Huber Guinier camera G670 diffractometer
Specimen mounting: pressed as a thin layer in the specimen holder of the camera
Specimen mounted in transmission mode
503 independent reflections
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 12$
$2\theta_{min}$ = 5.00, $2\theta_{max}$ = 100.00°
Increment in 2θ = 0.01°

Refinement

Refinement on I_{net}
R_p = 0.0226
R_{wp} = 0.0328
R_{exp} = 0.0089
S = 3.70
Profile function: split-type pseudo-Voigt
72 parameters
H-atom parameters not refined
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{max}$ = 0.02
$\Delta\rho_{max}$ = 0.3 e Å^{-3}
$\Delta\rho_{min}$ = −0.3 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.088 (11)	C2—N1	1.505 (19)
Cu1—O1	1.956 (8)	C3—N1	1.47 (2)
C1—C1^{ii}	1.397 (17)	N1—C1	1.549 (16)
N1—Cu1—O1	104.7 (3)	C2—N1—C3	105.9 (12)
N1—C1—C1^{ii}	106.8 (12)	C2—N1—C1	115.4 (11)
Cu1—N1—C2	107.1 (9)	C3—N1—C1	107.9 (11)
Cu1—N1—C3	96.7 (9)	Cu1—O1—H1	129.2
Cu1—N1—C1	121.2 (7)		

Symmetry codes: (ii) $\frac{1}{4} - x, \frac{1}{4} - y, z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···Cl1	0.93	2.06	2.993 (14)	180

Orthorhombic cell dimensions of the title compound were determined with *TREOR* (Werner *et al.*, 1985) using first 38 peak positions. The space group *Fddd* was chosen on the basis of systematic extinction rules. Intensities for the structure determination and refinement were collected from a Guinier camera with an image-plate detector using 0.01° steps. H atoms were placed in calculated positions, with U_{iso}(H) fixed at 0.05 Å^2, and their parameters were not refined. The specimen turned out to be texture free.

Data collection: *HUBER G*670 *Software* (Huber, 1998); cell refinement: *MRIA* (Zlokazov & Chernyshev, 1992); program(s) used to solve structure: *MRIA* and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *MRIA* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLUTON* (Spek, 1996); software used to prepare material for publication: *MRIA*, *SHELXL*97 and *PARST* (Nardelli, 1995).

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