Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

A centrosymmetric hydroxo-bridged pentamethyldiethylenetriamine copper(II) complex, {[(pmdeta)-Cu(OH)]$_2$}$^{2+}$·2Br$^-$·2MeCN

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Received 2 July 2001
Accepted 16 July 2001
Online 20 July 2001

The title compound, di-μ-hydroxo-bis[(1,1,4,7,7-pentamethyldiethylenetriamine)copper(II)] dibromide acetonitrile disolvate, [Cu$_2$(OH)$_2$(C$_9$H$_{23}$N$_3$)$_2$]Br$_2$·2CH$_3$CN, is the reaction product of CuBr with 1,1,4,7,7-pentamethyldiethylenetriamine (pmdeta) in water-containing acetonitrile. The cation is the dimer of an asymmetrically hydroxo-bridged complex of copper(II) coordinated by 1,1,4,7,7-pentamethyldiethylenetriamine. The centrosymmetric structure contains distorted square-pyramidally coordinated Cu atoms.

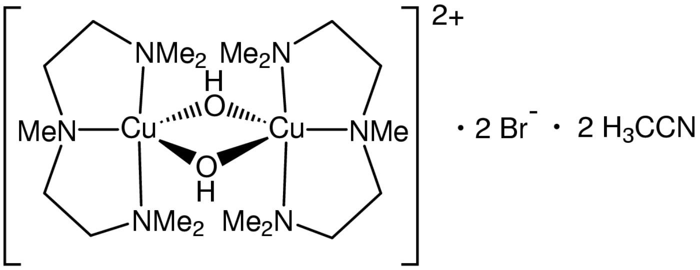
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.031
wR factor = 0.080
Data-to-parameter ratio = 17.3

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

Comment

Di-μ-hydroxo-bridged complexes of transition metals are a widely known structural type. Due to the rather small bridging ligands, there is often the possibility of a metal–metal interaction. If this takes place, a spin–spin interaction is possible when unpaired electrons are present, which makes such molecules interesting model compounds for spin-coupling phenomena.



(I)

The complex described in this study, (I) has two Cu^{II} centers with a separation of 3.0022 (7) Å. The asymmetric unit of the crystal contains only half of the cation. Therefore, a centrosymmetric dimeric structure is obtained (Fig. 1). The bromide counter-ions as well as the acetonitrile molecules included in the crystal do not show any interactions with the copper centers, as illustrated in the packing diagram (Fig. 2). Although the compound was synthesized from a Cu^I halide, the structure contains Cu^{II} ions. A possible explanation for the oxidation process is a disproportionation reaction which is known for Cu^I amine complexes. This structure is related to another (pmdeta)Cu^{II} compound bridged by two hydroxo ligands, which contains perchlorate as the anion (Scott *et al.*, 1995). This related complex also shows a distorted square pyramidal coordination sphere around the Cu atoms and two hydroxo bridges with Cu—O distances [1.964 (4) and 1.893 (5) Å] similar to those in the present structure [1.904 (2)

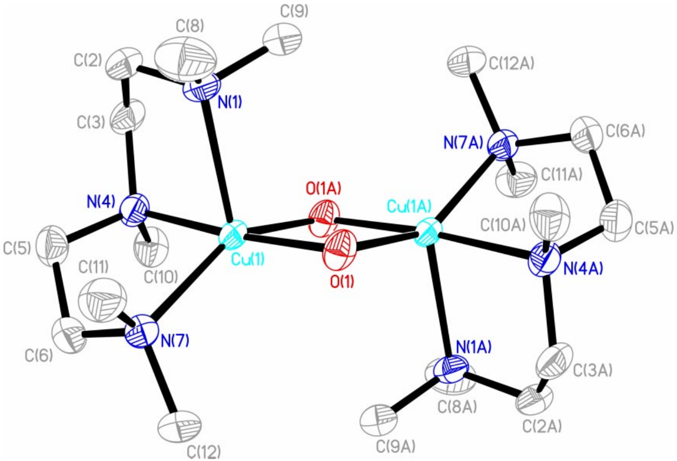


Figure 1
The structure of the dimeric cation with ellipsoids at the 50% probability level. The asymmetric unit contains also one Br^- anion and one molecule of acetonitrile. For clarity, H atoms have been omitted.

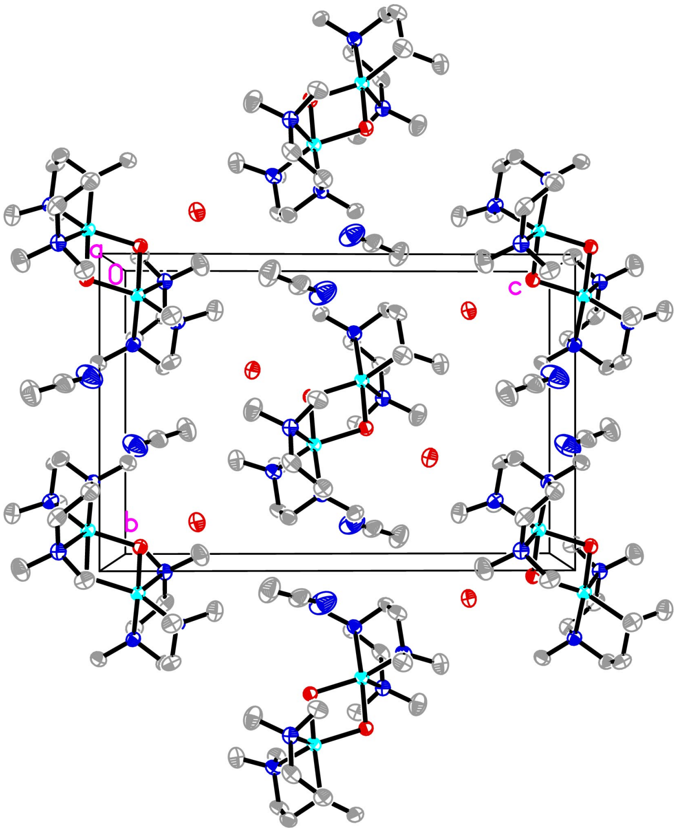


Figure 2
Projection of the structure along [100], showing ellipsoids at the 50% probability level. For clarity, H atoms have been omitted.

and 1.988 (2) Å]. This bonding situation seems to be common in this type of Cu^{II} complex and was also observed in the hydroxo-bridged cyclic triamine Cu^{II} compounds *N*,*N*′,*N*′′-trimethyl-1,4,7-triazacyclononane [Cu—O 1.936 (4) and 1.939 (4) Å; Chaudhuri *et al.*, 1985], *N*-4-but-1-ene-1,4,7-triazacyclononane [Cu—O 1.929 (2) Å; Farrugia *et al.*, 1996] and other triazacyclononane complexes with different substitution patterns (Mahapatra *et al.*, 1996). A special feature of the title compound is its distortion of the square-pyramidal coordination sphere. None of the above related structures displays such large differences in the equatorial Cu—N distances [Cu—$N_{equatorial}$ 2.040 (3) and 2.137 (3) Å; Cu—N_{axial} 2.340 (2) Å]. While usually the equatorial N atoms have the same distances to the Cu atom (within experimental uncertainties), the difference of the Cu—N distances in the title compound is nearly 0.1 Å.

Experimental

CuBr (4.53 g, 0.0316 mol) was suspended under stirring in water-saturated acetonitrile (50 ml) under an argon atmosphere in a Schlenk flask. Pentamethlyethylenediamine (5.48 g, 0.0316 mol) was slowly added and the mixture was heated to 323 K for 15 min. The solution was cooled to room temperature and was allowed to stand for two weeks. The solvent was evaporated and dark-green crystals were isolated.

Crystal data

$[Cu_2(OH)_2(C_9H_{23}N_3)_2]Br_2\cdot 2C_2H_3N$
$M_r = 749.64$
Monoclinic, $P2_1/c$
$a = 9.2580$ (5) Å
$b = 10.9165$ (6) Å
$c = 16.4073$ (8) Å
$\beta = 91.543$ (1)°
$V = 1657.60$ (15) Å^3
$Z = 2$
$D_x = 1.502$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5499 reflections
$\theta = 2.7$–$24.2°$
$\mu = 3.72$ mm^{-1}
$T = 293$ (2) K
Irregular, green
0.28 × 0.24 × 0.18 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.390$, $T_{max} = 0.512$
4696 measured reflections
2820 independent reflections
2389 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 24.7°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.080$
$S = 1.07$
2820 reflections
163 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 0.5272P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.904 (2)	Cu1—N7	2.137 (3)
Cu1—O1^i	1.988 (2)	Cu1—N1	2.340 (2)
Cu1—N4	2.040 (3)	Cu1—Cu1^i	3.0022 (7)
O1—Cu1—O1^i	79.06 (9)	O1—Cu1—N1	95.09 (9)
O1—Cu1—N4	174.48 (9)	O1^i—Cu1—N1	103.15 (9)
O1^i—Cu1—N4	97.15 (9)	N4—Cu1—N1	81.80 (10)
O1—Cu1—N7	100.16 (9)	N7—Cu1—N1	110.67 (9)
O1^i—Cu1—N7	146.06 (9)	Cu1—O1—Cu1^i	100.94 (9)
N4—Cu1—N7	85.23 (10)		

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

H atoms were located by difference Fourier maps and refined with a riding model.

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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