Instrumental Achievements

Crystal Structure of [Bis(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)-*O*,*O*′-μ-*O*,*O*′-oxalato]dihydroxy Dicopper(II)

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The oxidative and non-oxidative alkali-catalyzed reactions of L-ascorbic acid have attracted great interest, since similar degradation products are formed as in its metabolism.[1,2] The effects of the metal ions on the degradation of L-dehydroascorbic acid and oxalate formation with Co(II) and Gd(II) ions as a decomposition product of L-ascorbic acid in aqueous metal solutions have been clarified.[3,4]

The title compound was prepared from mixtures of L-ascorbic acid (0.14 g, 0.8 mmol), *N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminoethane (0.12 mL, 0.8 mmol) and copper(II) methoxide (0.1 g, 0.8 mmol) in absolute methanol (70 mL). After filtration, a blue solution was set aside for crystallization at ambient temperature for a few days. Suitable blue crystals were obtained by recrystallization from ethanol.

The results of an X-ray structure determination are given in Tables 1 – 4.

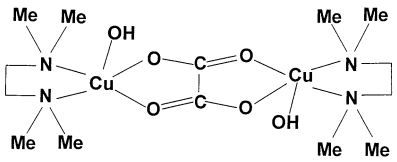

Fig. 1 Chemical diagram.

Table 1 Crystal and experimental data

Formula: $C_{14}H_{34}N_4O_6Cu_2$	
Formula weight = 481.53	
Crystal system: triclinic	
Space group: $P\bar{1}$	$Z = 1$
a = 7.288(1)Å	
b = 7.461(1)Å	
c = 10.701(1)Å	
α = 69.65(1)°	
β = 78.17(1)°	
γ = 81.45(1)°	
V = 532.1(1)Å^3	
D_x = 1.50 g/cm^3	R = 0.024
wR = 0.033	
λ(Mo K$_\alpha$) = 0.71073 Å	
$(\Delta/\sigma)_{max}$ = 0.01	
$(\Delta\rho)_{max}$ = 0.62 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.41 eÅ^{-3}	
No. of reflections used=2044	
Measurements: Enraf-Nonius CAD-4 diffractometer	
Program system: CAD-4 EXPRESS Software	
Structure determination: SHELXS86	
Refinement: full matrix	

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Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	*x*	*y*	*z*	B_{eq}/Å^2
Cu	0.39579(3)	0.02365(3)	0.76351(2)	2.038(5)
O1	0.5859(2)	0.2544(1)	0.6302(1)	1.95(2)
O2	0.2910(2)	0.1171(2)	0.9446(1)	2.77(3)
O3	0.5941(2)	–0.1068(2)	0.8756(1)	2.52(3)
N1	0.1686(2)	0.1406(2)	0.6700(2)	2.42(3)
N2	0.2774(3)	–0.2377(3)	0.8219(2)	2.56(4)
C1	0.4143(4)	–0.3825(3)	0.7809(3)	3.79(6)
C2	0.2160(4)	–0.3094(4)	0.9694(3)	4.14(6)
C3	0.1120(3)	–0.1980(3)	0.7520(3)	3.40(5)
C4	0.0252(3)	0.0015(4)	0.7413(3)	3.28(5)
C5	0.0981(4)	0.3290(3)	0.6859(3)	3.46(5)
C6	0.2065(4)	0.1683(4)	0.5239(2)	3.76(5)
C7	0.4119(3)	0.0646(3)	1.0195(3)	2.13(4)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

Table 3 Bond distances (Å) and angles (°)

Cu-O3	1.989(1)	N1-C5	1.479(3)
Cu-N1	2.036(2)	O2-C7	1.242(3)
Cu-O2	2.236(2)	O3-C7'	1.258(3)
Cu-N2	2.090(2)	N2-C1	1.479(3)
Cu-O1	2.260(1)	N2-C3	1.487(3)
N1-C4	1.482(3)	N2-C2	1.473(3)
N1-C6	1.476(3)	C4-C3	1.504(3)
C7-C7'	1.564(3)		
O3-Cu-N1	172.64(6)	Cu-N1-C5	111.5(2)
O3-Cu-O2	79.34(6)	C4-N1-C6	110.7(2)
O3-Cu-N2	89.26(7)	C4-N1-C5	109.6(2)
O3-Cu-O1	91.21(5)	C6-N1-C5	107.4(2)
N1-Cu-O2	96.21(7)	Cu-O2-C7	108.9(1)
N1-Cu-N2	85.92(7)	Cu-N2-C1	110.7(1)
N1-Cu-O1	95.49(5)	Cu-N2-C3	106.0(1)
O2-Cu-N2	101.85(7)	Cu-N2-C2	110.8(2)
O2-Cu-O1	102.43(5)	C1-N2-C3	110.3(2)
N2-Cu-O1	155.37(6)	C1-N2-C2	109.2(2)
Cu-N1-C4	104.0(1)	C3-N2-C2	109.8(2)
Cu-N1-C6	113.5(1)	N1-C4-C3	109.5(2)
N2-C3-C4	108.8(2)	C7-C7'-O2	117.5(1)
Cu-O3-C7'	116.7(1)	C7-C7'-O3	116.7(1)

Table 4 Torsion angles (°)

O3-Cu-N1-C4	-26.9(6)	O1-Cu-O2-C7	-8.4(1)
O2-Cu-N1-C4	-79.2(1)	O3-Cu-N2-C3	-179.3(1)
O1-Cu-N1-C4	177.7(1)	O2-Cu-N2-C3	101.7(1)
O3-Cu-O2-C7	7.5(1)	O1-Cu-N2-C3	-88.0(2)

The title compound (Fig. 2) consists of symmetry related *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMED) ligands and hydroxy ions bonded to Cu(II) ions, linked by planar bridging oxalate ligands, in *trans* positions. The configuration around the Cu atom is given by the torsion angles (Table 4). The bond lengths and angles of the oxalate ligand are not significantly different from those of the free oxalate ions.[5] In the oxalate ligand, the Cu–O2 [2.236(2)Å] bond is longer than Cu–O3 [1.989(1)Å]. The H-atoms positions were calculated geometrically, 0.95 Å from the correponding atoms, and refined using a riding model.

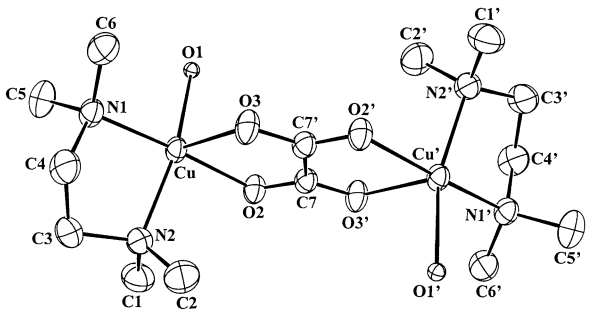

Fig. 2 Molecular structure of the title compound with atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

References

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