

Bis(*N,N'*-dimethylethylenediamine)-
copper(II) oxalate dihydrateHe-Dong Bian, Jing-Yuan Xu,
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Key indicators

Single-crystal X-ray study

 $T = 293\text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$ R factor = 0.028 wR factor = 0.075

Data-to-parameter ratio = 12.8

For details of how these key indicators were
automatically derived from the article, see
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Bis(*N,N*-dimethylethylenediamine)copper(II) oxalate dihydrate, $[\text{Cu}(\text{C}_4\text{H}_{12}\text{N}_2)_2](\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$, has been synthesized. Both the cation and anion are centrosymmetric. The Cu atom is in a distorted square geometry, coordinated by the four N atoms of the bidentate ligands. There are long $[2.583(2)\text{ \AA}]$ axial contacts to water. The crystal structure of the complex has a two-dimensional structure through hydrogen bonding.

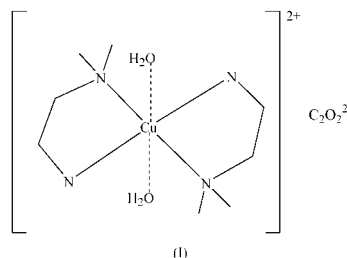
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Comment

Mononuclear complexes containing *N,N'*-dimethylethylenediamine (dmen) have been studied extensively. These complexes have an important role in thermal and magnetic chemistry (Smékal *et al.*, 2002; Senocq *et al.*, 1999). Otherwise, dmen can also form supramolecular complexes with other bridging ligands, such as N_3^- , SCN^- and Cl^- (Mondal *et al.*, 2000; Bian *et al.*, 2003). In this paper, bis(*N,N'*-dimethylethylenediamine)copper(II) oxalate dihydrate, (I), has been synthesized and its structure described.



The structure of (I) is shown in Fig. 1. The geometrical parameters and hydrogen bonding data for (I) are listed in Tables 1 and 2, respectively. The Cu atom in (I) is in a distorted square geometry, coordinated by the four N atoms of two bidentate ligands, distances ranging from 1.988 (2) to 2.103 (2) \AA . The values are similar to those in other copper(II) complexes containing dmen (Narayanan & Bhadbhade, 1995; Senocq *et al.*, 1999). However, the distances of the central atom and two water O atoms show some weak interaction, which may be viewed as a weak coordination mode (Guilera & Steed, 1999; Sun *et al.*, 2001). Thus the environment of the Cu atom can also be described as a tetragonally distorted octahedron. The basal plane contains the four N atoms, N1, N2, N1ⁱⁱ and N2ⁱⁱ (symmetry codes in Table 2), at an average distance of 2.051 (6) \AA , while the axial positions are filled by two water–O atoms at a distance of 2.583 (2) \AA .

The crystal structure has a number of hydrogen bonds (Fig. 2). The H atoms of the water molecules and the N atoms of the ligands are involved in hydrogen bonding with the oxalate dianion. An infinite two-dimensional network of extensive hydrogen bonds stabilizes the crystal structure.

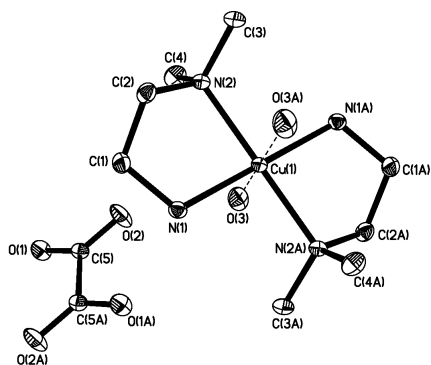


Figure 1
A view of the molecular structure of (I) with the atom-numbering scheme and 30% displacement ellipsoids. H atoms have been omitted.

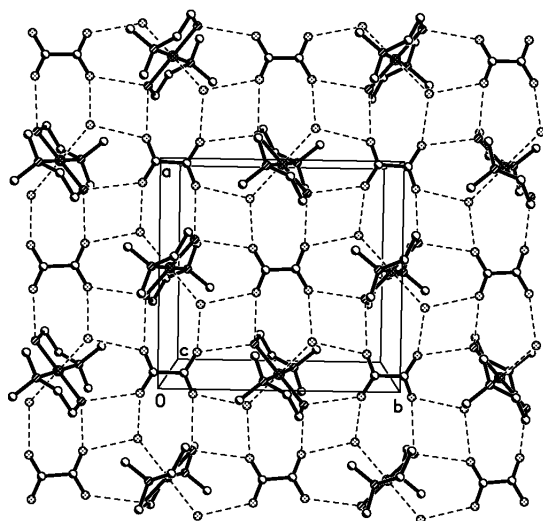


Figure 2
The two-dimensional network structure of hydrogen bonds in complex (I).

Experimental

0.5 mmol $\text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ was dissolved in 10 ml distilled water and 0.5 mmol *N,N*-dimethylethylenediamine in 5 ml H_2O was added dropwise. The mixture was stirred for 0.5 h and then filtered. The filtrate was allowed to stand in air at room temperature for several weeks, yielding blue single crystals suitable for X-ray analysis.

Crystal data

$[\text{Cu}(\text{C}_4\text{H}_{12}\text{N}_2)_2](\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$
 $M_r = 363.90$
 Orthorhombic, *Pbca*
 $a = 10.482$ (3) Å
 $b = 11.026$ (3) Å
 $c = 13.146$ (4) Å
 $V = 1519.3$ (8) Å³
 $Z = 4$
 $D_x = 1.591$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 5693 reflections
 $\theta = 3.1\text{--}25.0^\circ$
 $\mu = 1.47$ mm⁻¹
 $T = 293$ (2) K
 Prism, blue
 $0.30 \times 0.20 \times 0.05$ mm

Data collection

Bruker CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.779$, $T_{\max} = 0.929$
 5693 measured reflections

1341 independent reflections
 1021 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -5 \rightarrow 12$
 $k = -13 \rightarrow 13$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.075$
 $S = 1.09$
 1341 reflections
 105 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 1.2775P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu1—N1	1.988 (2)	Cu1—O3 ⁱ	2.583 (2)
Cu1—N2	2.103 (2)		
N1 ⁱⁱ —Cu1—N1	180	N1—Cu1—O3 ⁱ	88.89 (8)
N1 ⁱⁱ —Cu1—N2	95.20 (8)	N2—Cu1—O3 ⁱ	83.75 (7)
N1—Cu1—N2	84.80 (8)	N2—Cu1—O3 ⁱⁱⁱ	96.25 (7)
N2—Cu1—N2 ⁱⁱ	180	O3 ⁱ —Cu1—O3 ⁱⁱⁱ	180
N1 ⁱⁱ —Cu1—O3 ⁱ	91.11 (8)		

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (ii) $-x, 2 - y, -z$; (iii) $x - \frac{1}{2}, \frac{3}{2} - y, -z$.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1C···O1 ^{iv}	0.90	2.06	2.924 (3)	161
N1—H1D···O2 ⁱ	0.90	2.05	2.927 (3)	165
O3—H3D···O1	0.884 (15)	1.942 (16)	2.824 (3)	176 (3)
O3—H3E···O2 ^v	0.881 (17)	1.910 (19)	2.779 (3)	169 (3)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (iv) $1 - x, 2 - y, -z$; (v) $\frac{1}{2} + x, \frac{3}{2} - y, -z$.

H atoms of the water molecules were located in a difference Fourier map and were refined isotropically with restrained bond lengths. H atoms of *N,N*-dimethylethylenediamine were positioned geometrically and refined using a riding model with C—H = 0.97 Å for CH₂, C—H = 0.96 Å for CH₃ and N—H = 0.90 Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998) and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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