

Ibrahim Uçar,^a Okan Zafer
Yeşilel,^b Ahmet Bulut,^{a*}
Halis Ölmez^b and
Orhan Büyükgüngör^a^aDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, TR-55139 Kurupelit-Samsun, Turkey, and ^bDepartment of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, TR-55139 Kurupelit-Samsun, Turkey

Correspondence e-mail: abulut@omu.edu.tr

Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.031
wR factor = 0.083
Data-to-parameter ratio = 18.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Diaquabis(*N,N*-dimethylethylenediamine- κ^2N,N')-copper(II) squarate

The crystal structure determination of the title compound, $[\text{Cu}(\text{C}_4\text{H}_{12}\text{N}_2)_2(\text{H}_2\text{O})_2](\text{C}_4\text{O}_4)$, is reported. It adopts an elongated octahedral *trans*- $[\text{CuN}_4\text{O}_2]$ coordination geometry with the Cu^{II} atom located at a centre of symmetry. The axial $\text{Cu}-\text{O}$ bond length is 2.6066 (17) Å, while the equatorial $\text{Cu}-\text{N}$ bond lengths are 1.9849 (16) and 2.1102 (16) Å. Intermolecular $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds are responsible for linking the complex cation to the squarate dianion, forming layers. The anion is also centrosymmetric.

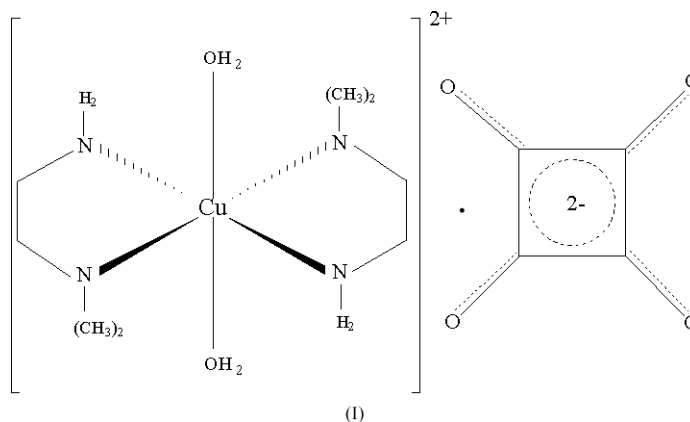
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Comment

Copper(II) complexes having ethylenediamine derivatives have potential applications especially in developing photocontrolling materials such as hybrid materials (Choy *et al.*, 2002), photochromism (Takahashi *et al.*, 2002), and thermochromism (Narayanan & Bhadbhade, 1998). The structure of a number of semi-coordinated Cu^{II} complexes with *N*-substituted ethylenediamine ligands have been systematically investigated: *N*-ethylethylenediamine (*N*-eten; Grenthe *et al.*, 1979), ethylenediamine (en; Maxcy & Turnbull, 1999), *N*-methylethylenediamine (*N*-Meen; Akitsu & Einaga, 2003), *N,N*-dimethylethylenediamine (*N*-Me₂en; Akitsu & Einaga, 2004*a*; İçbudak *et al.*, 2003) and *N,N'*-dimethylethylenediamine (*N'*-Me₂en; Akitsu & Einaga, 2004*b*; İçbudak *et al.*, 2003). As part of our ongoing research on squaric acid (H_2Sq) and its mixed-ligand metal complexes (Uçar *et al.*, 2004; Yeşilel *et al.*, 2004), the title compound, (I), has been synthesized and its crystal structure (Fig. 1) is reported.



The crystal structure consists of a complex cation and a squarate dianion. The title complex adopts an elongated octahedral *trans*- $[\text{CuN}_4\text{O}_2]$ coordination geometry, in which atom Cu1 is located at a centre of symmetry. The axial $\text{Cu}1-\text{O}1$ semi-coordination bond distance is 2.6066 (17) Å (the semi-coordination bond range is 2.22–2.89 Å for H_2O ; Hath-

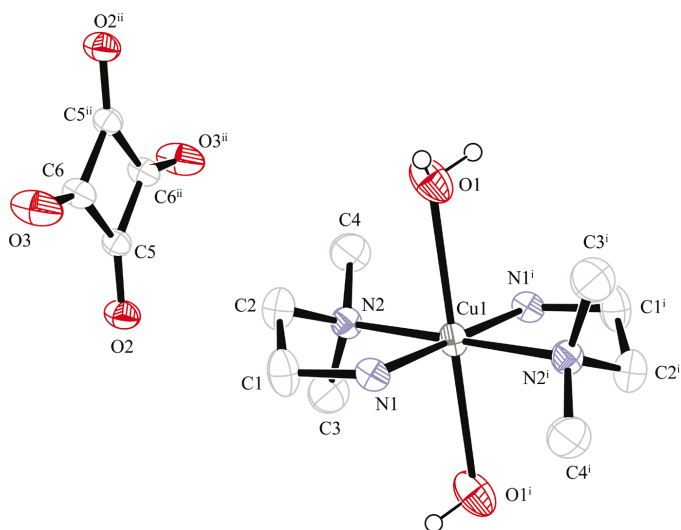


Figure 1
An ORTEP-3 (Burnett & Johnson, 1996) view of the constituent ions of (I), showing the atom-numbering scheme and 40% probability displacement ellipsoids. The H atoms of methylene and methyl groups have been omitted for clarity. [Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $1-x, -y, -z$.]

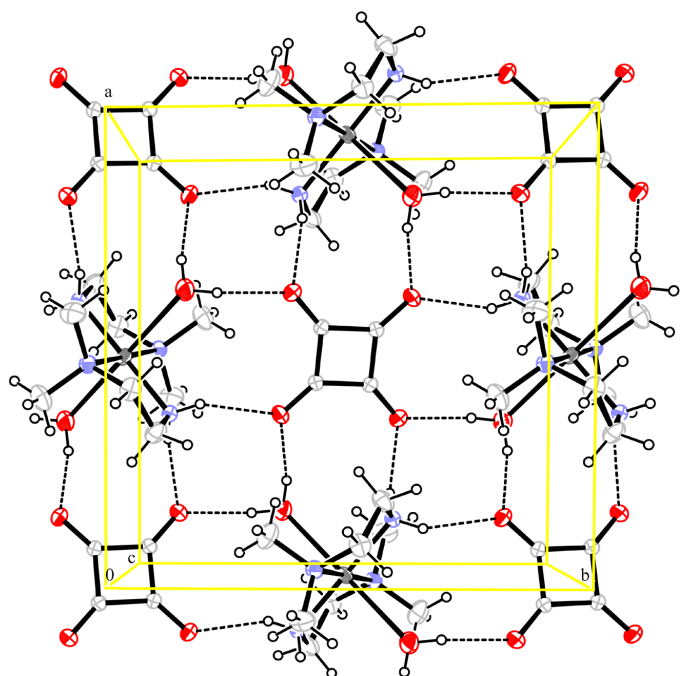


Figure 2
A view of the hydrogen-bonding interactions (dashed lines) in (I).

away, 1973). The corresponding Cu—O bond lengths for the en, *N*-Meen, *N*-Eten and *N*-Me₂en complexes are 2.579 (4), 2.569 (2), 2.594 (3) and 2.605 (4) Å, respectively (Akitsu & Einaga, 2003; Grenthe *et al.*, 1979; Akitsu & Einaga, 2004a; İçbudak *et al.*, 2003; Maxcy & Turnbull, 1999). The Cu—N1(NH₂) and Cu1—N2(NMe₂) bond distances in the title complex are 1.9849 (16) and 2.1102 (16) Å, respectively. These Cu—N bond lengths are found to be almost the same as in Cu^{II} complexes with *N,N*-dimethylethylenediamine and *N,N'*-dimethylethylenediamine ligands (Akitsu & Einaga, 2004b; İçbudak *et al.*, 2003). The corresponding Cu—N(NH₂) bond

distances were found to be 2.012 (2) and 2.019 (2) Å for the en, 2.004(2) Å for the *N*-Meen and 2.013 (3) Å for the *N*-Eten complexes (Maxcy & Turnbull, 1999; Akitsu & Einaga, 2003). The difference in the Cu—N bond lengths observed in the title complex may be attributed to the steric hindrance of the methyl groups. The N1—Cu1—N2 bond angle of the chelate ligand is 85.02 (6)°, slightly larger than that of the *N*-Meen complex [84.58 (7)°]. The N1—C1—C2—N2 torsion angle [49.8 (3)°] is found to be almost the same as in the related study of copper(II) complexes having ethylenediamine derivatives (İçbudak *et al.*, 2003; Akitsu & Komorita, 2002).

The crystal packing of the title complex is illustrated in Fig. 2. O—H...O and N—H...O hydrogen bonds are formed between the complex cation and the squarate dianion (Table 2). Each centrosymmetric squarate dianion links four centrosymmetric [Cu(*N*-Me₂en)(H₂O)₂]²⁺ cations to each other *via* hydrogen bonds. These hydrogen bonds are responsible for linking the ions into layers which lie parallel to the *ab* plane (Fig. 2).

Experimental

Squaric acid (H₂Sq; 0.57 g, 5 mmol) dissolved in 25 ml water was neutralized with NaOH (0.40 g, 10 mmol) and added to a hot solution of copper(II) chloride dihydrate (0.853 g, 5 mmol) dissolved in 50 ml water. The mixture was refluxed at 353 K for 12 h and then cooled to room temperature. The green crystals which formed were filtered off and washed with water and methanol, and dried in a vacuum. A solution of *N,N*-dimethylethylenediamine (0.176 g, 2 mmol) in water (50 ml) was added dropwise with stirring to a suspension of CuSq·2H₂O (0.212 g, 1 mmol) in water (50 ml). The mixture was stirred at 323 K for 12 h and then cooled to room temperature. After a few days, well formed crystals were selected for X-ray studies.

Crystal data

[Cu(C₄H₁₂N₂)₂(H₂O)₂](C₄O₄)
M_r = 387.92
 Orthorhombic, *Pbca*
a = 11.3829 (9) Å
b = 11.5359 (12) Å
c = 13.0358 (10) Å
V = 1711.8 (3) Å³
Z = 4
D_x = 1.505 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 8046 reflections
 θ = 1.6–29.2°
 μ = 1.31 mm⁻¹
T = 293 (2) K
 Block, violet
 0.4 × 0.3 × 0.2 mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: by integration (*X-RED32*;
 Stoe & Cie, 2002)
T_{min} = 0.577, *T_{max}* = 0.875
 15461 measured reflections

2313 independent reflections
 1387 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
 θ_{\max} = 29.3°
h = -14 → 15
k = -15 → 15
l = -16 → 17

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.031
wR(*F*²) = 0.083
S = 0.87
 2313 reflections
 123 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.50 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0099 (9)

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	2.6066 (17)	Cu1—N2	2.1102 (16)
Cu1—N1	1.9849 (16)		
N1—Cu1—N2	85.02 (6)	O1—Cu1—N2	84.61 (6)
O1—Cu1—N1	89.21 (6)		
N1—C1—C2—N2	49.8 (3)		

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>
O1—H2...O3 ⁱⁱⁱ	0.848 (10)	1.946 (12)	2.778 (2)	167 (3)
O1—H1...O2 ^{iv}	0.843 (10)	1.928 (13)	2.756 (2)	167 (3)
N1—H4...O3 ^v	0.855 (10)	2.092 (14)	2.886 (2)	154 (2)
N1—H3...O2 ^{vi}	0.867 (9)	2.105 (13)	2.928 (2)	158 (2)

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

H atoms attached to C atoms were placed at calculated positions ($C-H = 0.96-0.97$ Å) and were allowed to ride on the parent atom [$U_{iso}(H_{methyl}) = 1.5U_{eq}(C)$ and $U_{iso}(H_{methylene}) = 1.2U_{eq}(C)$]. The other H atoms were located in a difference map and were refined with the N—H and O—H distances restrained to be 0.87 (2) and 0.85 (2) Å, respectively.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s)

used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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