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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 = 0.026

$wR$  factor = 0.050

Data-to-parameter ratio = 13.6

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

## Bis(triethanolamine- $\kappa^3N,O,O'$ )copper(II) squarate

In the crystal structure of the title compound,  $[\text{Cu}(\text{C}_6\text{H}_{15}\text{NO}_3)_2](\text{C}_4\text{O}_4)$ , the cations and anions are located on inversion centres and a supramolecular architecture is formed. Two triethanolamine (TEA) ligands coordinate to the  $\text{Cu}^{\text{II}}$  ion through four O atoms and two N atoms acting as  $N,O,O'$ -tridentate ligands, resulting in a distorted octahedral environment, with Cu—O bond distances of 2.0199 (17) and 2.288 (2) Å and a Cu—N distance of 2.0340 (18) Å. The squarate ( $\text{C}_4\text{O}_4^{2-}$ ) anions and  $[\text{Cu}(\text{TEA})_2]^{2+}$  cations are linked to each other by hydrogen bonding between coordinated hydroxyl H atoms of TEA and squarate O atoms, forming layers. Adjacent layers are interlinked by hydrogen bonding between free hydroxyl H atoms of TEA and one of the squarate O atoms.

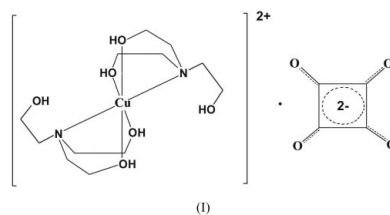
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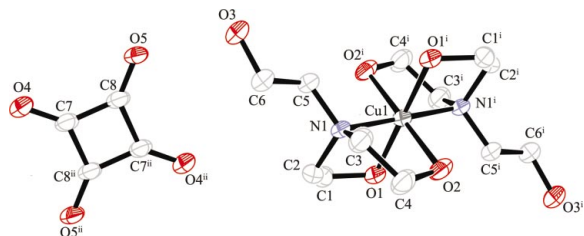
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#### Comment

Many workers from a variety of scientific disciplines are interested in the crystal design and engineering of multi-dimensional arrays and networks containing metal ions as nodes. Metal-ion-containing supramolecular structures can be used as zeolite-like materials (Venkataraman *et al.*, 1995; Kepert & Rosseinsky, 1999), catalysts (Fujita *et al.*, 1994) or magnetic materials (Kahn, 1993). In order to elucidate the properties of these types of crystals, a detailed knowledge of the supramolecular structure is needed. In this context, squaric acid and its metal complexes are of potential interest, since these compounds are frequently used to build cocrystals (Bouma *et al.*, 1999; Bertolasi *et al.*, 2001; Bulut *et al.*, 2003). The triethanolamine (TEA) molecule is also used as a ligand as it readily forms coordination compounds with almost all metal ions and behaves as an  $N$ - and  $O$ -donor ligand. The interaction of transition metal ions with TEA results in the formation of high-coordinate complexes (Topcu *et al.*, 2002; Whitmire *et al.*, 1999; Yesilel *et al.*, 2004). We report here the structure of bis(triethanolamine- $\kappa^3N,O,O'$ )copper(II) squarate, (I).

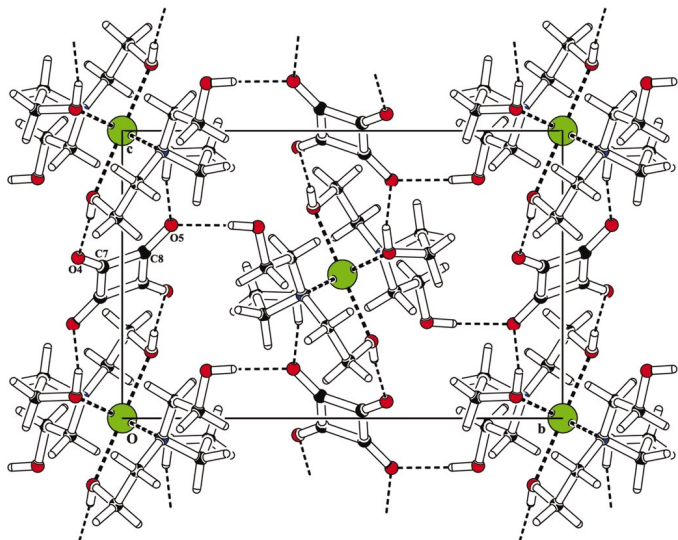


An *ORTEP*III (Burnett & Johnson, 1996) view of (I) and its atom-labelling scheme are shown in Fig. 1. The crystal structure contains a complex  $[\text{Cu}(\text{TEA})_2]^{2+}$  cation and an uncoordinated squarate anion. In the complex cation, the  $\text{Cu}^{\text{II}}$  ion lies on a centre of symmetry. It is coordinated by two TEA ligands and each TEA ligand acts as a tridentate ligand



**Figure 1**

An ORTEP-3 (Burnett & Johnson, 1996) view of (I). Displacement ellipsoids are shown at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i)  $-x, 1-y, 1-z$ ; (ii)  $1-x, -y, 1-z$ .]



**Figure 2**

A PLATON (Spek, 1997) view of the molecular packing down the  $a$  axis.

through two of the three hydroxyl O atoms and the amine N atom, resulting in a six-coordinate  $\text{Cu}^{\text{II}}$  ion. The  $\text{Cu}^{\text{II}}$  ion is in a distorted octahedral geometry with the coordinated hydroxyl O atoms of two TEA ligands forming the equatorial plane (O1/O2/O1<sup>i</sup>/O2<sup>i</sup>), while atoms N1 and N1<sup>i</sup> are located in axial positions (symmetry code as in Fig.1 caption). The coordination geometry around the  $\text{Cu}^{\text{II}}$  ion is irregular, presumably due to the steric constraints arising from the shape of the polydentate ligands. In the complex, the Cu—O distances are 2.0199 (17) and 2.288 (2) Å and the Cu—N distance is 2.0340 (18) Å, while the bond angles at copper range from 80.85 (7) to 94.24 (7)°. These bond distances and angles are comparable with those observed for other Cu complexes of TEA (Tudor *et al.*, 2001; Topcu, 2002; Whitmire *et al.*, 1999).

The squarate anions lie on centres of symmetry and play an important role in the supramolecular architecture. Each squarate anion is surrounded by four centrosymmetric  $[\text{Cu}(\text{TEA})_2]^{2+}$  cations. The squarate O atoms participate in two independent intermolecular hydrogen bonds (see Table 2 for details) with the hydroxyl H atoms (O atoms lie on equatorial plane) of the TEA ligands, forming layers parallel to the  $ac$  plane. Adjacent layers are interconnected by hydrogen bonding between one of the squarate O atoms and the free hydroxyl O atom of TEA [O3 $\cdots$ O5 = 2.736 (3) Å], as shown in Fig. 2.

## Experimental

Squaric acid (Sq; 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 triethanolamine (0.298 g, 2 mmol) in methanol (50 ml) was added dropwise with stirring to a suspension of  $\text{CuSq}\cdot 2\text{H}_2\text{O}$  (0.212 g, 1 mmol) in water (100 ml). The mixture was refluxed 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

$[\text{Cu}(\text{C}_6\text{H}_{15}\text{NO}_3)_2](\text{C}_4\text{O}_4)$   
 $M_r = 473.97$   
 Monoclinic,  $P2_1/c$   
 $a = 8.145 (5) \text{ \AA}$   
 $b = 13.634 (5) \text{ \AA}$   
 $c = 9.082 (5) \text{ \AA}$   
 $\beta = 101.206 (5)^\circ$   
 $V = 989.3 (9) \text{ \AA}^3$   
 $Z = 2$

$D_x = 1.591 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 9392 reflections  
 $\theta = 2.3\text{--}25.8^\circ$   
 $\mu = 1.16 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Prism, green  
 $0.4 \times 0.3 \times 0.2 \text{ mm}$

### Data collection

Stoe IPDS-2 diffractometer  
 $\varphi$  scans  
 Absorption correction: by integration (*X-RED32*; Stoe & Cie, 2002)  
 $T_{\text{min}} = 0.783, T_{\text{max}} = 0.928$   
 3720 measured reflections

1912 independent reflections  
 1256 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.028$   
 $\theta_{\text{max}} = 25.9^\circ$   
 $h = -9 \rightarrow 9$   
 $k = -16 \rightarrow 0$   
 $l = -11 \rightarrow 11$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.050$   
 $S = 0.77$   
 1912 reflections  
 141 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0189P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Cu1—O1	2.0199 (17)	N1—C5	1.484 (3)
Cu1—N1	2.0340 (18)	N1—C3	1.485 (3)
Cu1—O2	2.288 (2)	N1—C2	1.496 (3)
O1—C1	1.434 (3)	O4—C7	1.246 (3)
O2—C4	1.416 (3)	O5—C8	1.255 (3)
O3—C6	1.416 (3)	C7—C8	1.448 (3)
O1—Cu1—N1	84.93 (8)	O4—C7—C8	135.7 (2)
O1—Cu1—O2	94.24 (7)	O5—C8—C7	135.0 (2)
N1—Cu1—O2	80.85 (7)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
O1—H1 $\cdots$ O5 <sup>iii</sup>	0.84 (1)	1.74 (1)	2.559 (2)	166 (3)
O2—H2 $\cdots$ O4 <sup>iii</sup>	0.84 (1)	1.80 (1)	2.632 (2)	171 (3)
O3—H3 $\cdots$ O5	0.82	1.92	2.736 (3)	177

Symmetry code: (iii)  $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$ .

Hydroxyl atoms H1 and H2 were found in a difference map and their parameters were refined with the O—H distance restrained to be 0.85 (1) Å. The other H atoms were placed at calculated positions (O—H = 0.82 Å and C—H = 0.97 Å) and allowed to ride on the parent atom [ $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$  or  $1.2U_{\text{eq}}(\text{C})$ ].

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: *ORTEP3* (Burnett & Johnson, 1996) and *PLATON* (Spek, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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