Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')copper(I) hydrogen squarate hemihydrate

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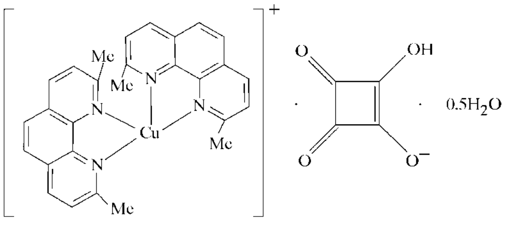
Received 28 February 2005
Accepted 4 April 2005
Online 13 May 2005

In the crystal structure of the synthetically prepared title compound, $[Cu(C_{14}H_{12}N_2)_2](C_4HO_4)\cdot 0.5H_2O$ or $[Cu(dmphen)_2](HSq)\cdot 0.5H_2O$ (dmphen is 2,9-dimethyl-1,10-phenanthroline or neocuproine and HSq is hydrogen squarate), the Cu^{I} centre has distorted tetrahedral coordination geometry comprised of four N atoms from two bidentate dmphen ligands. The squarate monoanions form a ten-membered dimer, graph set $R_2^2(10)$, linked by two strong intermolecular O—H···O hydrogen bonds. These squarate dimers are linked into chains that propagate along the [100] direction. An extensive three-dimensional network of C—H···O hydrogen bonds and π–π interactions is responsible for stabilization of the crystal structure.

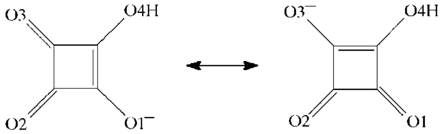
Comment

Copper(I) complexes continue to be a subject of interest, not only due to their being inexpensive, environmentally friendly and flexible in coordination geometry, but also due to their rich photochemical and photophysical properties (Armaroli, 2001; Fu *et al.*, 2004). Numerous early studies on copper(I) complexes with 2,9-disubstituted-1,10-phenanthroline were geared towards their use as metal-selective analytical tools (Diehl *et al.*, 1972). More recently, there has been a renewed interest in the photochemical properties of bis(1,10-phenanthroline)copper(I) compounds as candidates for the development of photonic devices, including sensors, photovoltaic devices and switches (Castellano & Meyer, 1997; Miller & Karpishin, 1999; Baranoff *et al.*, 2000). It is well known that copper complexes with 1,10-phenanthroline and their substituted derivatives generally exhibit low-energy metal-to-ligand charge-transfer (MLCT) states. In addition, the redox chemistry of copper phenanthroline is of particular interest, due to the fact that $[Cu(phen)_2]^+$ or $[Cu(phen)_2]^{2+}$ undergoes a coordination change during redox processes from a four-coordinate tetrahedral geometry in the Cu^{I} state to a five-coordinate (or six-coordinate) environment upon oxidation to Cu^{II}.

Squaric acid, H_2Sq, is a very strong dibasic acid and has been studied for potential application to xerographic photoreceptors, organic solar cells and optical recording (Seitz & Imming, 1992; Liebeskind *et al.*, 1993). It is also a useful tool for constructing crystalline architectures because of its rigid and flat four-membered ring framework (Reetz *et al.*, 1994). In our ongoing research on squaric acid, we have synthesized some mixed-ligand copper(II) complexes of squaric acid and their structures have been reported (Uçar *et al.*, 2004; Bulut *et al.*, 2004). In these compounds, the squaric acid is found as the dianion, Sq^{2-}, while in the present study, the monoanion of squaric acid, HSq^-, is observed. To our knowledge, there are only a few examples of transition metal(I) complexes of hydrogen squarate (Braga *et al.*, 2000), and no Cu^{I} complexes with hydrogen squarate acting as a counter-monoanion. In the present study, the title compound, $[Cu(dmphen)_2](HSq)\cdot 0.5H_2O$ (diphen is 2,9-dimethyl-1,10-phenanthroline), (I), has been synthesized and its crystal structure (Fig. 1) is reported.



(I)



The Cu^{I} ion of (I) is bonded to two bidentate dmphen ligands through their N atoms and the coordination sphere is

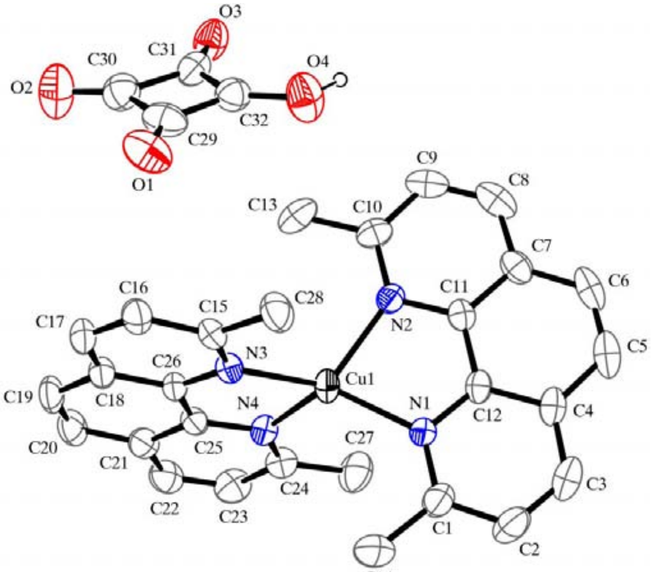


Figure 1
The copper coordination in (I), with displacement ellipsoids drawn at the 30% probability level. The H atoms of the neocuproine ligands have been omitted for clarity.

distorted away from ideal tetrahedral towards a trigonal–pyramidal geometry. The major distortion involves the wider N1—Cu1—N3 angle of 136.87 (12)° and the narrower N3—Cu1—N4 angle of 82.02 (12)°, due mostly to the five-membered chelate rings and the steric bulk of the ligands with methyl groups. The dihedral angle of 79.20 (12)° between the two CuNN planes is in agreement with the typical range of 70–80° for Cu(NN)$_2$ (NN are substituted bipyridines and phenanthrolines; Bardwell *et al.*, 1996; Bulut *et al.*, 2004). The Cu1—N bond distances vary from 2.017 (2) to 2.059 (3) Å, which are within the normal range for [Cu(NN)$_2$]$^+$ complexes, where NN signifies substituted 1,10-phenanthroline (Dobson *et al.*, 1984; Blake *et al.*, 1998; Lemoine & Viossat, 2001). The internal geometric features of the dmphen ligands are in agreement with those established in previous studies (Kon *et al.*, 1987; Kovalevsky *et al.*, 2003).

The C—C distances in the planar squarate ring system of (I) reflect partial double-bond character for C31—C32 [1.411 (5) Å] and C29—C32 [1.434 (5) Å], and single-bond character for C30—C31 [1.498 (5) Å] and C29—C30 [1.490 (6) Å]. These lengths represent average values for the two possible resonance structures (see scheme). The bond distances of the carbonyl bonds [O1—C29 = 1.237 (4) Å and O3—C31 = 1.251 (4) Å] indicate that the negative charge is located partially on atoms O1 and O3, whereas the O2—C30 distance [1.211 (4) Å] reflects double-bond character. The C—C and C—O distances observed for the HSq$^-$ anion could, in principle, be interpreted equally well as the result of crystallographic disorder of a single resonance structure related to a second disorder component by rotation of 180° around the line joining C30 and C32.

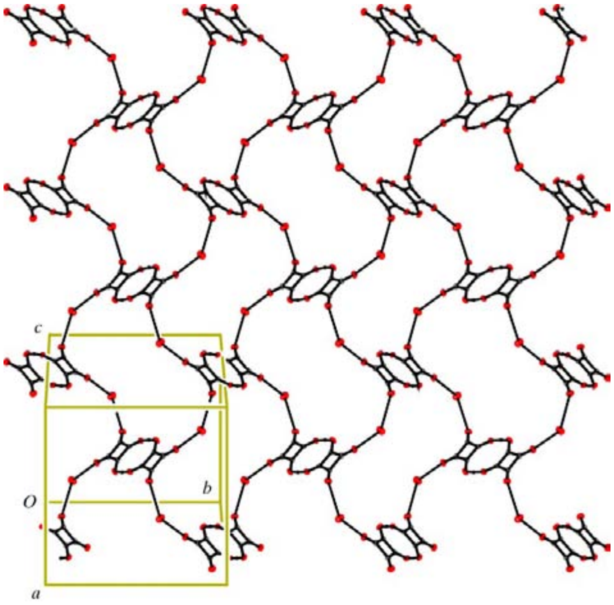


Figure 2
The orientation of the ribbons formed by hydrogen squarate self-recognition. Displacement ellipsoids are drawn at the 5% probability level.

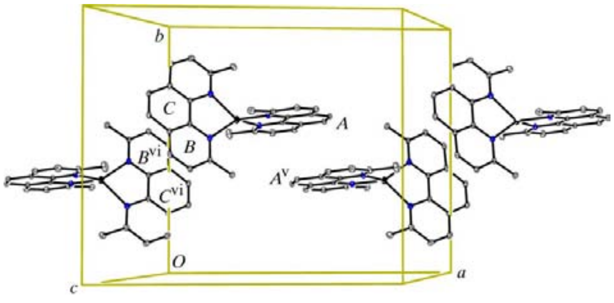


Figure 3
The monomeric entities in the crystal structure of (I), linked by π–π stacking interactions between the aromatic rings of the neocuproine ligands. Displacement ellipsoids are drawn at the 5% probability level. [Symmetry codes: (v) $1-x, 1-y, -z$; (vi) $-x, 1-y, -z$.]

A structural feature of (I) is the extensive network of hydrogen bonds. Two inversion-related squarate monoanions are linked by pairs of strong negative charge-assisted O—H···O$^{\frac{1}{2}-}$ bonds, in which the O···O distance is 2.535 (4) Å, to form a head-to-head centrosymmetric $R_2^2(10)$ dimer (Table 2). Such a dimeric unit has been found in a many other hydrogen squarates. A search of the current CSD system (February 2005 update, Allen, 2002) revealed 18 structures with these dimeric units; the range of O···O separations in the O—H···O hydrogen bonds was 2.471–2.575 Å with a mean value of 2.516 Å. This self-recognition of the hydrogen squarate ions in (I) leads to the formation of stacked ribbons which propagate along the [100] direction (Fig. 2).

In compound (I), the water molecule was refined with a site occupancy of 0.5 and the H atoms attached to atom O5 were not located. Fig. 2 shows all positions of water atom O5, but it should be kept in mind that, according to the model refined, this atom is not present in all asymmetric units. The uncoordinated monoanion and complex cation are linked by intermolecular C—H···O hydrogen bonds (Table 2).

In the extended structure of (I), shown in Fig. 3, there are also π–π interactions. These intermolecular interactions occur between the two symmetry-related dmphen rings (ring *A*, C4–C7/C11/C12) of neighbouring molecules. Ring *A* is oriented in such a way that the perpendicular distance from *A* to *A*$^{\rm v}$ is 3.485 Å, the closest interatomic distance being C6···C12$^{\rm v}$ [3.522 (6) Å; symmetry code (v) $1-x, 1-y, -z$]; the distance between the ring centroids is 3.525 (2) Å. The other π–π contact occurs between dmphen rings *B* (N3/C15–C18/C26) and *C* (C18–C21/C25–C26). The perpendicular distance between rings *B* and *C* (*C* to *B*$^{\rm vi}$) is 3.483 Å, the closest interatomic distance is C15···C19$^{\rm vi}$ [3.494 (5) Å; symmetry code: (vi) $-x, 1-y, -z$] and the dihedral angle between the planes of these rings is 1.74°. The distance between the ring centroids is 3.719 (2) Å. Additionally, there is also a π–π contact between rings *B* of neighbouring molecules. For the π–π stacking interaction, the perpendicular distance from *B* to *B*$^{\rm vi}$ is 3.514 Å, the closest interatomic distance being C17···C26$^{\rm vi}$ [3.524 (5) Å]; the distance between the ring centroids is 3.746 (2) Å.

Experimental

Squaric acid (0.57 g, 5 mmol) dissolved in water (25 ml) was neutralized with NaOH (0.40 g, 10 mmol) and the resulting solution added to a hot solution of CuCl$_2$·H$_2$O (0.77 g, 5 mmol) in water

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(50 ml). The mixture was stirred at 333 K for 12 h and then cooled to room temperature. The yellow crystals which formed were filtered off, washed with water and alcohol, and dried *in vacuo*. A solution of neocuproine (0.435 g, 2 mmol) in methanol (50 ml) was added dropwise with stirring to a suspension of CuSq·2H_2O (0.21 g, 1 mmol) in water (50 ml). In the highly basic media, $\mathrm{Cu}^{\mathrm{II}}$ was reduced to Cu^{I} and the squarate dianion was protonated. The bright-red solution was refluxed for about 2 h and then cooled to room temperature. A few days later, well formed red crystals of (I) were selected for X-ray studies.

Crystal data

$[\mathrm{Cu}(\mathrm{C}_{14}\mathrm{H}_{12}\mathrm{N}_2)_2](\mathrm{C}_4\mathrm{HO}_4)\cdot0.5\mathrm{H}_2\mathrm{O}$
$M_r = 602.11$
Monoclinic, $P2_1/c$
$a = 15.9664$ (10) Å
$b = 13.7530$ (12) Å
$c = 13.5082$ (11) Å
$\beta = 112.343$ (6)°
$V = 2743.5$ (4) Å^3
$Z = 4$
$D_x = 1.455$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5048 reflections
$\theta = 1.6$–28.0°
$\mu = 0.84$ mm^{-1}
$T = 297$ (2) K
Plate, red
0.31 × 0.25 × 0.19 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\min} = 0.728$, $T_{\max} = 0.924$
22 893 measured reflections
4828 independent reflections
2280 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.131$
$\theta_{\max} = 25.0°$
$h = -18 \rightarrow 18$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.075$
$S = 0.81$
4828 reflections
387 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.011P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—Cu1	2.017 (2)	C29—C30	1.490 (6)
N2—Cu1	2.053 (3)	C30—O2	1.211 (4)
N3—Cu1	2.028 (3)	C30—C31	1.498 (5)
N4—Cu1	2.059 (3)	C31—O3	1.251 (4)
C29—O1	1.237 (4)	C31—C32	1.411 (5)
C29—C32	1.434 (5)	C32—O4	1.308 (4)
N1—Cu1—N3	136.87 (12)	N1—Cu1—N4	120.29 (11)
N1—Cu1—N2	82.42 (11)	N3—Cu1—N4	82.02 (12)
N3—Cu1—N2	116.84 (11)	N2—Cu1—N4	124.33 (11)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O3$^{\mathrm{i}}$	0.93 (4)	1.63 (5)	2.535 (4)	164 (4)
C3—H3···O3$^{\mathrm{ii}}$	0.93	2.44	3.227 (5)	142
C6—H6···O1$^{\mathrm{iii}}$	0.93	2.51	3.263 (5)	139
C16—H16···O1	0.93	2.55	3.263 (5)	134

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

H atoms attached to C atoms were placed in calculated positions (C—H = 0.93 and 0.96 Å) and allowed to ride on their parent atom [$U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$]. The remaining H atom (of squarate) was located in a difference map. At this stage, the maximum difference density of 1.48 e Å^{-3} (the ratio of maximum/minimum residual density is 5.62) indicated the presence of a possible atom site. A check of the solvent-accessible volume using *PLATON* (Spek, 2003) showed a total potential volume of 40.6 Å^3. Attempts to refine this peak as a water O atom (O5) resulted in a partial occupancy of 0.5. H atoms attached to O5 were not located.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1124). Services for accessing these data are described at the back of the journal.

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