

**Bis(1,10-phenanthroline- $\kappa^2N,N'$ )-  
 (squarato- $\kappa O$ )copper(II) trihydrate**

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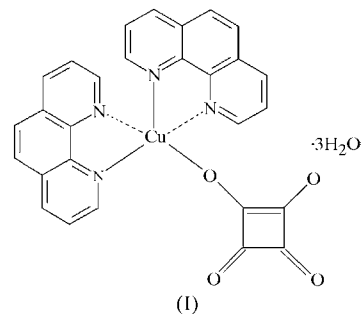
The title mononuclear [Cu(sq)(phen)<sub>2</sub>].3H<sub>2</sub>O complex [sq is squarate (C<sub>4</sub>O<sub>4</sub>) and phen is 1,10-phenanthroline (C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)] has been synthesized and the structure consists of a neutral mononuclear [Cu(sq)(phen)<sub>2</sub>] unit and three solvate water molecules. The Cu<sup>II</sup> ion has distorted square-pyramidal coordination geometry, comprised of one carboxylate O atom from a monodentate squarate ligand and four N atoms from two chelating phen ligands. An extensive three-dimensional network of OW–H···O/OW hydrogen bonds, face-to-face  $\pi$ – $\pi$  interactions between the 1,10-phenanthroline aromatic rings and a weak  $\pi$ –ring interaction are responsible for crystal stabilization.

**Comment**

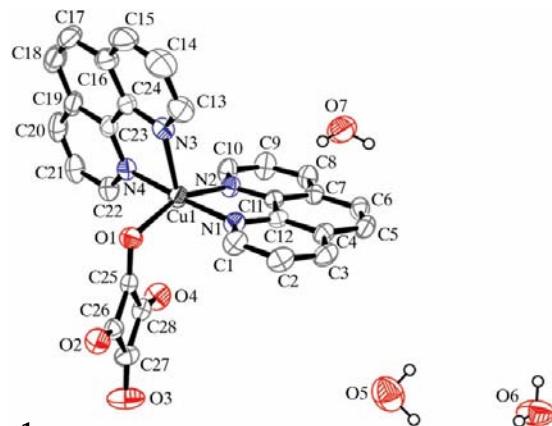
Studies of the coordination chemistry of the squarate ligand have attracted increasing attention because it gives rise to a wide variety of complexes and adopts mono- or polydentate coordination modes when acting as a ligand towards first row transition metal ions. The squarate dianion does not act like a chelating ligand but rather like a bridge between two or more metal atoms as a mono- or polydentate ligand (Bernardinelli *et al.*, 1988; Solans *et al.*, 1990; Castro *et al.*, 1999; Crispini *et al.*, 2000; Shu *et al.*, 2000; Yang *et al.*, 2003), or as a counter-ligand in some compounds (Castan *et al.*, 1992; Uçar *et al.*, 2004; Yeşilel *et al.*, 2004). Therefore, very few structures of mononuclear complexes of the squarate ligand have been reported to date (Solans *et al.*, 1990; Grove *et al.*, 2002; Kirchmaier *et al.*, 2003). Additionally, mixed-ligand metal complexes of 1,10-phenanthroline (phen) and its substituted derivatives continue to attract attention because this moiety plays an important role in biological systems, such as binding of small molecules to DNA (Xu *et al.*, 2002; Macias *et al.*, 2003; Mudasir *et al.*, 2003; Sastri *et al.*, 2003; Maheswari & Palaniandavar, 2004). 1,10-Phenanthroline (phen) has also been extensively used as a ligand in both analytical and preparative coordination chemistry (Idriss *et al.*, 1980; Templeton & Pollak, 1989; Koch

& Ackermann, 1992; Lorenzo *et al.*, 1998; Shabir & Forrow, 2003).

Commonly,  $\pi$ – $\pi$  stacking interactions have been observed in mixed-ligand phen complexes (Castillo *et al.*, 2001; Zhou *et al.*, 2001; Liang *et al.*, 2002; Guo *et al.*, 2004), and  $\pi$ – $\pi$  interactions in aromatic rings play vital roles in highly efficient and specific biological reactions, and control many molecular-recognition and self-assembly processes in solid-state and crystal engineering (Hunter, 1994; Desiraju, 1995; Claessens & Stoddart, 1997; Roesky & Andruh, 2003; Shi *et al.*, 2004). In this context, the title mixed-ligand complex, (I), of copper squarate with phen has been prepared and its crystal structure is reported here.



A view of the molecule of (I) and its atom-numbering scheme are shown in Fig. 1. Compound (I) has distorted square-pyramidal coordination geometry comprised of one carboxylate O atom from a monodentate squarate ligand and four N atoms from two chelating phen ligands. The coordinated squarate O atom [Cu1–O1 = 1.9623 (16) Å] and three phen N atoms [Cu1–N = 1.9913 (19)–2.03731 (18) Å] form the equatorial plane, whereas the fourth phen N atom is in the apical position [Cu1–N3 = 2.188 (2) Å]. The angles subtended at the Cu atom by the phen ligands are 81.68 (7) and 79.99 (8)°, which are in agreement with those previously reported for other phen-containing Cu<sup>II</sup> complexes (Solans *et al.*, 1990; Castro *et al.*, 1999; Castillo *et al.*, 2001). These ‘bite’ angles are far from the ideal value of 90° because of the constrained geometry of the phen ring systems. There is also a significant tetragonal distortion of the equatorial plane



**Figure 1**  
 A view of the Cu coordination in (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. Phenanthroline H atoms have been omitted for clarity and water H atoms are shown as small spheres of arbitrary radii.

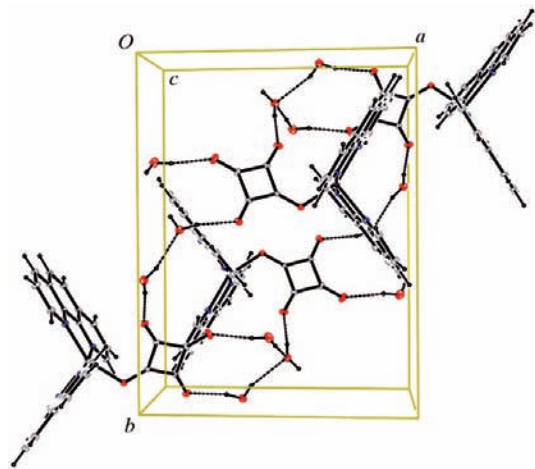
[maximum atomic deviation of 0.2739 (10) Å for atom N2], in which the Cu atom is 0.1639 (8) Å out of this mean plane.

The squarate ligand is essentially planar and the largest deviation from the mean plane is 0.0166 (13) Å for atom O2. The dihedral angle between the Cu basal equatorial plane and the squarate plane is 83.50 (5)°. The phen ligands are approximately planar, with r.m.s. deviations of 0.052 and 0.0127 Å for phen 1 (N1/N2/C1–C12) and phen 2 (N3/N4/C13–C24), respectively. The largest deviations from the mean planes are 0.024 (2) Å for atom C9 and 0.083 (3) Å for atom C14. The average C–C (1.40 Å) and C–N bonds (1.34 Å) and angles (120°) within the rings are in agreement with those previously reported for 1,10-phenanthroline-coordinated Cu<sup>II</sup> complexes (Potočňák *et al.*, 1996; Parker *et al.*, 1996). The dihedral angles between the squarate plane and the phen mean planes are 82.80 (4) and 64.65 (4)°, while that between the phen mean planes is 70.00 (3)°.

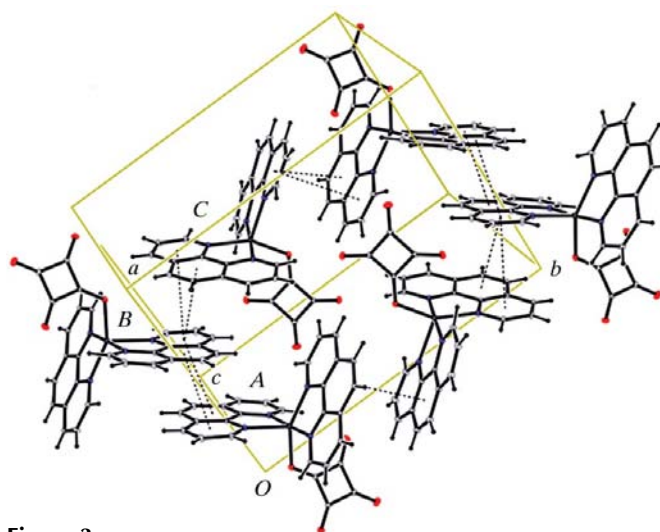
In complex (I), the Cu1–O1 bond distance is nearly identical to that observed in [Cu(C<sub>4</sub>O<sub>4</sub>)(phen)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O (Solans *et al.*, 1990), in which the Cu–O distance is 1.967 (2) Å, whereas this distance is 0.033 Å shorter than that in [Cu<sub>2</sub>(C<sub>4</sub>O<sub>4</sub>)(phen)<sub>4</sub>](ClO<sub>2</sub>)<sub>2</sub> $\cdot$ 2H<sub>2</sub>O (Castro *et al.*, 1999). This is clearly due to the fact that the squarate ligand is coordinated to the Cu atom in a monodentate fashion and therefore most of the negative charge is located on the coordinated O atom. These C–O bond distances of the squarate ligand are found to be similar to those of related monodentate squarate complexes (Bernardinelli *et al.*, 1988; Solans *et al.*, 1990).

The crystal packing in (I) is formed by intermolecular hydrogen bonding (Fig. 2), and  $\pi$ – $\pi$  and  $\pi$ –ring (Fig. 3) interactions. Each neutral complex unit is linked to a second unit *via* hydrogen-bonding interactions through the solvate water molecules and the O atoms of the squarate ligand. The uncoordinated O atoms of the squarate, which are linked to each other by means of two solvate molecules, also make a contribution to the crystal packing (Table 2).

A phen ligand belonging to a unit A at (x, y, z – 1) and that belonging to a crystallographically related unit B at (1 – x,



**Figure 2**  
The three-dimensional structure of the neutral complex (I). Displacement ellipsoids are drawn at the 5% probability level. Dashed lines illustrate the hydrogen bonds.



**Figure 3**  
An illustration of a sheet of neutral monomeric entities in the crystal structure of (I), linked by stacking  $\pi$ – $\pi$  and  $\pi$ –ring interactions (dashed lines) between the aromatic rings and the H atoms of the phenanthroline ligands. Displacement ellipsoids are drawn at the 5% probability level.

–y, 1 – z) are stacked nearly parallel to each other, with a dihedral angle between their aromatic rings [ring 1 (N3/C24/C13–C16) and ring 2 (C16–C19/C23/C24)] of 2.85° (Fig. 3). For the  $\pi$ – $\pi$  stacking interaction, the interplanar separations of these aromatic rings are in the range 3.400–3.435 Å [ $Cg1 \cdots Cg2 = 3.7124$  (15) Å;  $Cgx$  denotes the centroid of phen ring  $x$ ] and the shortest interatomic contact is 3.444 Å. The third neighbouring phen ligand, belonging to a unit C at ( $x + \frac{1}{2}$ ,  $\frac{1}{2} - y$ ,  $z - \frac{1}{2}$ ), is stacked nearly parallel to units A and B. The dihedral angle between aromatic rings 1 and 3 (C4–C7/C11/C12) (located in units B and C, respectively) is 9.59°, while this angle between aromatic rings 1 and 4 (N2/C7–C11) is 9.32°. For the  $\pi$ – $\pi$  stacking interaction, the interplanar separation of these aromatic rings (1 and 3) is in the range 3.525–3.603 Å [ $Cg1 \cdots Cg3 = 3.6891$  (15) Å] and the shortest interatomic contact is 3.429 Å, whereas the interplanar separation of the aromatic rings 1 and 4 is in the range 3.608–3.894 Å [ $Cg1 \cdots Cg4 = 4.1592$  (15) Å] and the shortest interatomic contact is 3.814 Å.

In the structure of (I) there is also a weak C–H $\cdots$  $\pi$  interaction between C5–H4 (of a phen ligand) and a phen ring (Fig. 3). The C–H $\cdots$ Cg contact distance between the centroid of a phen ring and the H atoms nearest that phen ring is 3.20 Å. The perpendicular distance between atom H4 and the centre of the phen ring is 3.12 Å and the C–H $\cdots$ Cg angle is 88°.

These intermolecular interactions, namely an extensive network of hydrogen bonds,  $\pi$ – $\pi$  stacking and  $\pi$ –ring interactions, are responsible for constructing an infinite three-dimensional lattice in the crystal structure of (I).

## Experimental

Squaric acid (H<sub>2</sub>Sq; 0.57 g, 5 mmol) dissolved in water (25 ml) 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 water (50 ml). The mixture was stirred at 353 K for 12 h and then cooled to

room temperature. The dark green crystals which formed were filtered off, washed with water and dried *in vacuo*. A solution of 1,10-phenanthroline (0.72 g, 4 mmol) in ethanol (20 ml) was added dropwise with stirring to a suspension of CuSq·2H<sub>2</sub>O (0.42 g, 2 mmol) in water (50 ml). The mixture was then stirred at 323 K for 12 h and cooled to room temperature. After a few days, well formed crystals of (I) were selected for X-ray studies.

## Crystal data

[Cu(C <sub>4</sub> O <sub>4</sub> )(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> ]·3H <sub>2</sub> O	$D_x = 1.529 \text{ Mg m}^{-3}$
$M_r = 590.05$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 16 767 reflections
$a = 12.5563 (9) \text{ \AA}$	$\theta = 1.6\text{--}28.0^\circ$
$b = 16.2910 (10) \text{ \AA}$	$\mu = 0.91 \text{ mm}^{-1}$
$c = 12.6208 (9) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 96.896 (6)^\circ$	Prism, dark green
$V = 2563.0 (3) \text{ \AA}^3$	$0.42 \times 0.28 \times 0.17 \text{ mm}$
$Z = 4$	

## Data collection

Stoe IPDS-2 diffractometer	5051 independent reflections
$\omega$ scans	3155 reflections with $I > 2\sigma(I)$
Absorption correction: by integration ( <i>X-RED32</i> ; Stoe & Cie, 2002)	$R_{\text{int}} = 0.105$
$T_{\text{min}} = 0.736$ , $T_{\text{max}} = 0.89$	$\theta_{\text{max}} = 26.0^\circ$
36 262 measured reflections	$h = -15 \rightarrow 15$
	$k = -20 \rightarrow 20$
	$l = -15 \rightarrow 15$

## Refinement

Refinement on $F^2$	H atoms: see below
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2]$
$wR(F^2) = 0.068$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.82$	$(\Delta/\sigma)_{\text{max}} = 0.001$
5051 reflections	$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
385 parameters	$\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

C25—O1	1.278 (3)	N2—Cu1	2.0371 (18)
C26—O2	1.248 (3)	N3—Cu1	2.188 (2)
C27—O3	1.232 (3)	N4—Cu1	1.9913 (19)
C28—O4	1.245 (3)	O1—Cu1	1.9623 (16)
N1—Cu1	1.9931 (18)		
O1—Cu1—N4	92.03 (7)	N1—Cu1—N2	81.68 (7)
O1—Cu1—N1	91.03 (7)	O1—Cu1—N3	95.41 (7)
N4—Cu1—N1	176.81 (8)	N4—Cu1—N3	79.99 (8)
O1—Cu1—N2	153.50 (7)	N1—Cu1—N3	98.80 (7)
N4—Cu1—N2	95.96 (7)	N2—Cu1—N3	110.84 (7)

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O7—H17 $\cdots$ O4 <sup>i</sup>	0.80 (4)	2.03 (4)	2.825 (3)	175 (4)
O7—H18 $\cdots$ O6 <sup>ii</sup>	0.78 (4)	2.01 (4)	2.775 (4)	165 (4)
O5—H19 $\cdots$ O7 <sup>iii</sup>	0.92 (5)	1.96 (5)	2.874 (4)	169 (4)
O5—H20 $\cdots$ O3 <sup>iii</sup>	0.81 (4)	2.04 (5)	2.825 (4)	162 (4)
O6—H21 $\cdots$ O7 <sup>iii</sup>	0.74 (4)	2.17 (4)	2.878 (4)	160 (4)
O6—H22 $\cdots$ O2 <sup>i</sup>	0.82 (4)	1.96 (4)	2.764 (3)	167 (3)

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

H atoms on C atoms were placed in calculated positions (C—H = 0.93  $\text{\AA}$ ) and were allowed to ride on their parent atom [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ]. The remaining H atoms were located in a difference map and refined isotropically.  $\Delta\rho_{\text{max}}$  and  $\Delta\rho_{\text{min}}$  were found at distances of 0.73 and 0.86  $\text{\AA}$  from atoms O1 and Cu1, respectively.

Data collection and cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED32* (Stoe & Cie, 2002); structure solution: *SIR97* (Altomare *et al.*, 1999); refinement: *SHELXL97* (Sheldrick, 1997); graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1754). Services for accessing these data are described at the back of the journal.

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