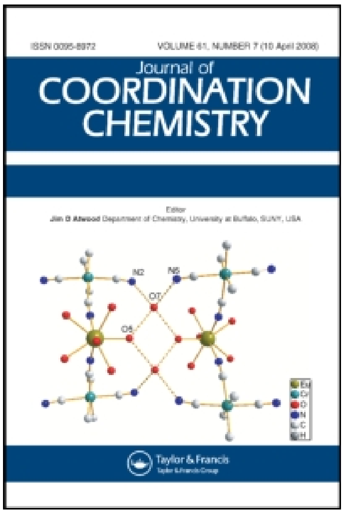

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Spectrothermal properties and crystal structure of a polynuclear μ-squarato(O^1,O^3)bis(monoethanolamine)copper(II) complex, [Cu(μ-sq)(mea)$_2$]<b><i>n</i>

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Spectrothermal properties and crystal structure of a polynuclear μ-squarato(O^1,O^3)bis(monoethanolamine)copper(II) complex, $[Cu(\mu\text{-}sq)(mea)_2]_n$

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Catena-*poly*-*trans*-μ-(squarato-O^1,O^3)bis(monoethanolamine)copper(II), $[Cu(\mu\text{-}C_4O_4)(C_2H_7NO)_2]_n$ has been prepared and characterized by elemental analysis, IR, UV-Vis, EPR, thermal analysis and single crystal X-ray diffraction. The compound crystallizes in the triclinic system, space group *P*-1, with $a = 5.1435(7)$, $b = 7.2931(10)$, $c = 7.5198(11)$ Å, $\alpha = 105.940(11)^\circ$, $\beta = 98.731(11)^\circ$, $\gamma = 101.981(11)^\circ$ and $Z = 1$. The structure contains chains of squarato-O^1,O^3-bridged polynuclear copper(II) units. The configuration around each copper is distorted octahedral with two nitrogen and two oxygen atoms of two bidentate neutral monoethanolamine (N, O) ligands and two oxygen atoms of two squarato (μ-O^1,O^3) ligands. These chains are held together by an extensive three-dimensional network of N-H $\cdots$ O type intermolecular hydrogen bonds and van der Waals forces. The IR, UV-Vis and EPR spectra, magnetic study and thermal analysis of the complex are described.

Keywords: Copper(II) complex; Squaric acid; Monoethanolamine; X-ray analysis; Thermal analysis; EPR studies

1. Introduction

Squaric acid, $H_2C_4O_4$ (3,4-dihydroxycyclobut-3-ene-1,2-dione, H_2sq, scheme 1(a)), synthesized for the first time by Cohen *et al*. in 1959 [1], has been of much interest because of its cyclic structure and possible aromaticity. It belongs to the series of cyclic oxocarbons of formula $H_2C_nO_n$ ($n = 3$–6 for deltic, squaric, croconic and rhodizonic acids, respectively); coordination chemistry of the squarate ligand has been investigated in some detail [2–21]. The squarate anion ($C_4O_4^{2-}$, sq) does not behave like a chelating ligand but rather as a bridge between two or more metal atoms. In all the cases described, squaric acid is coordinated to a different metal atom and either mono-dimensional chain or bi-dimensional or tri-dimensional polymers are obtained. Diaqua and tetraaqua complexes of sq with transition metals were reported [2–9]. Synthesis and structural

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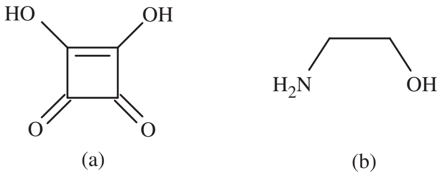

Scheme 1. Squaric acid (a), monoethanolamine (b).

characterization of mixed-ligand transition metal complexes of sq with mono- and bidentate N-donor ligands such as pyridine [10], imidazole [11], 2,2′-bipyridine [11–15] and 1,10-phenanthroline [13–16] appear in recent literature. In some transition metal complexes, the squaric acid acts as a counter ion [17–22]. However, most of them have monomeric or dimeric structures and very little has been reported to date about structures of mixed-ligand polynuclear squarato(O^1,O^3)-copper(II) complexes [3, 11, 23–25]. Solidstate thermal studies of several metal squarate and mixed ligand metal squarate complexes have been reported, indicating high thermal stability of the squarate moiety [26–30]. In the present paper, we describe the synthesis, spectroscopic, thermal studies and crystal structure of a polynuclear mixed-ligand copper(II) complex of sq with monoethanolamine (mea, scheme 1(b)), *trans*-$[Cu(\mu\text{-sq})(mea)_2]_n$.

2. Experimental

2.1. *Materials and measurements*

All chemicals used were analytical reagents. Elemental analysis for C, H and N was carried out at the TÜBİTAK Marmara Research Centre. Magnetic susceptibility measurements at room temperature were performed using a Sherwood Scientific MXI model Gouy magnetic balance. Reflectance spectra were obtained using a GBC Cintra 20 UV-Vis spectrometer in the range 900–200 nm. The IR spectrum was recorded in the 4000–200 cm^{-1} region with a Mattson 1000 FT-IR spectrometer using KBr pellets. TG8110 thermal analyzer was used to record simultaneous TG, DTG and DTA curves in static air at a heating rate of 10 $K\,min^{-1}$ in the temperature range 20–1000°C using platinum crucibles. Highly sintered α-Al_2O_3 was used as a reference and the DTG sensitivity was 0.05 mgs^{-1}.

2.2. *Preparation of the* $[Cu(\mu\text{-}sq)(mea)_2]_n$

A solution of monoethanolamine (0.25 g, 4 mmol) in methanol (10 mL) was added dropwise upon stirring to a solution of $CuSq \cdot 2H_2O$ [9] (0.42 g, 2 mmol) in distilled water (20 mL). The solution was heated to 60°C in a temperature-controlled bath and stirred for 6 h at 60°C. The reaction mixture was then slowly cooled to room temperature. The green crystals formed were filtered and washed with 10 mL of cold distilled water and methanol and dried in air. $[Cu(\mu\text{-sq})(mea)_2]_n$: Yield ca. 78.5%; dp 203°C. Anal. Calcd for $[Cu(C_4O_4)(C_2H_7NO)_2]$ (%): C, 32.3; H, 4.7; N, 9.4. Found: C, 31.7; H, 4.9; N, 9.1.

Table 1. Crystallographic data for $[Cu(\mu\text{-sq})(mea)_2]_n$.

Compounds	$[Cu(\mu\text{-sq})(mea)_2]_n$
Empirical formula	$C_8H_{14}N_2O_6Cu$
M_r	297.75
T (K)	296 (2)
Radiation, λ (Å)	Mo K_α, 0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a (Å)	5.1435(7)
b (Å)	7.2931(10)
c (Å)	7.5198(11)
α (°)	105.94(1)
β (°)	98.73(1)
γ (°)	101.98(1)
V (Å^3)	258.71(6)
Z	1
D_c (g cm^{-3})	1.911
μ (mm^{-1})	2.132
F(000)	153
Crystal size (mm)	0.080 × 0.257 × 0.560
θ range (°)	3.45-26.00
Index range (h, k, l)	−6/6, −8/8, −9/9
Reflections collected	3500
Independent reflections (R_{int})	1010 (0.149)
Completeness to 2θ	998
Reflections with $I > 2\sigma(I)$	984
Absorption correction	Integration (STOE X-RED (stoe&cie, 2002))
T_{min}, T_{max}	0.5269; 0.8950
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1010/1/83
Goodness-of-fit on F^2	1.085
Final R indices [$I > 2\sigma(I)$]	0.0486 $wR_2 = 0.1323$
R indices (all data)	0.0497 $wR_2 = 0.1330$
Max. and min. shift/esd	0.000/0.000
Largest dill, peak and hole (e Å^{-3})	0.792 and −0.584

2.3. *Crystallographic analysis*

Data collection was performed on a STOE IPDS II image plate detector using Mo K_α radiation ($\lambda = 0.71073$ Å). Intensity data were collected in the θ range 3.45–26.00° at 296 K. Details of data collection and crystal structure determinations are given in table 1. Data collection: Stoe X-AREA [31]. Cell refinement: Stoe X-AREA [31]. Data reduction: Stoe X-RED [31]. The structure was solved by direct-methods using SIR97 [32] and anisotropic displacement parameters of the non-hydrogen atoms were determined in a full-matrix least-squares refinement based on F^2 using SHELXL-97 [33]. Molecular drawings were obtained using ORTEP-III [34].

3. Results and discussion

3.1. *IR spectra*

The most important IR absorption bands of $[Cu(\mu\text{-sq})(mea)_2]_n$ are listed in table 2. The infrared spectrum showed a broad and intense band located around 3200 cm^{-1} due to

Table 2. Selected IR spectral data[a].

	$[Cu(\mu\text{-sq})(mea)_2]_n$	Squaric acid[b]
νO–H	3502 m	3462 s
νN–H	3305 w, 3252 m	–
νC–H	2970 vw, 1937 w, 2828 w	–
νC=O	1786 w	1822 w
νC=C	1598 w	1643 m
ν[(C–O) + (C–C)]	1524, 1486 vs	1530, 1516 vs
νCu–O_{mea}	429 w	–
νCu–O_{sq}	477 w	–
νCu–N	615 w	–

[a] w = weak; vw = very weak; s = strong; vs = very strong; m = medium.
[b] Reference [35].

the hydrogen bond (OH and NH_2) stretching vibrations. The band at 3502 cm^{-1} may be assigned to the hydroxyl group of the mea ligand, while the νNH_2 stretching vibration appears as two split bands at 3305 and 3552 cm^{-1}. The weak peaks in the 2970–2828 cm^{-1} range are due to νCH stretching. A very strong absorption centered at 1524 and 1486 cm^{-1} is assigned to a combination of squarato C–O and C–C stretching vibrations, respectively. This absorption is characteristic of salts of $C_nO_n^{2-}$ ions and is at 1500 cm^{-1} in the IR spectrum of $K_2C_4O_4$ [9]. This band is slightly split, suggesting, when compared to $K_2C_4O_4$, that the symmetry is lower than D_{4h}, confirmed by X-ray investigation. Additional weak bands are observed at 1786 and 1598 cm^{-1} which are evidence for the presence of localized squarate C=O and C=C bonds. These stretching vibrations are found at 1822 and 1643 cm^{-1} in the IR spectrum of free squaric acid [35]. The νCu–O_{mea}, νCu–O_{sq} and νCu–N vibrations are observed as weak bands at 429, 477 and 615 cm^{-1}, respectively.

3.2. *Diffuse reflectance, EPR and magnetic susceptibility*

The diffuse reflectance spectrum of the $[Cu(\mu\text{-sq})(mea)_2]_n$ complex exhibits a distinct absorption band at 680 nm. This value was assigned to $^2E_g \rightarrow {}^2T_{2g}$ d–d transitions. The title complex exhibits an experimental magnetic moment value of 1.70 BM corresponding to one unpaired electron.

The powder EPR spectrum of the complex at room temperature is given in figure 1. The three lines in the spectrum show that the environment of the Cu^{2+} is close to orthorhombic geometry. The principal g values are $g_x = 2.11$, $g_y = 2.05$ and $g_z = 2.29$. The Cu^{2+} hyperfine splitting is too small to be measured, indicating that the unpaired electron is distributed over the ligands.

3.3. *Thermal analysis*

Thermal decomposition of $[Cu(\mu\text{-sq})(mea)_2]_n$ proceeds in two stages (figure 2). The first mass loss stage was observed in the range of 203–382°C. Although the decomposition process is initially exothermic, an endothermic contribution is also observed in the DTA curve (DTA: 217 and 220°C). This stage is related to the decomposition of the complex: two moles mea ligands release (exp. 41.85,

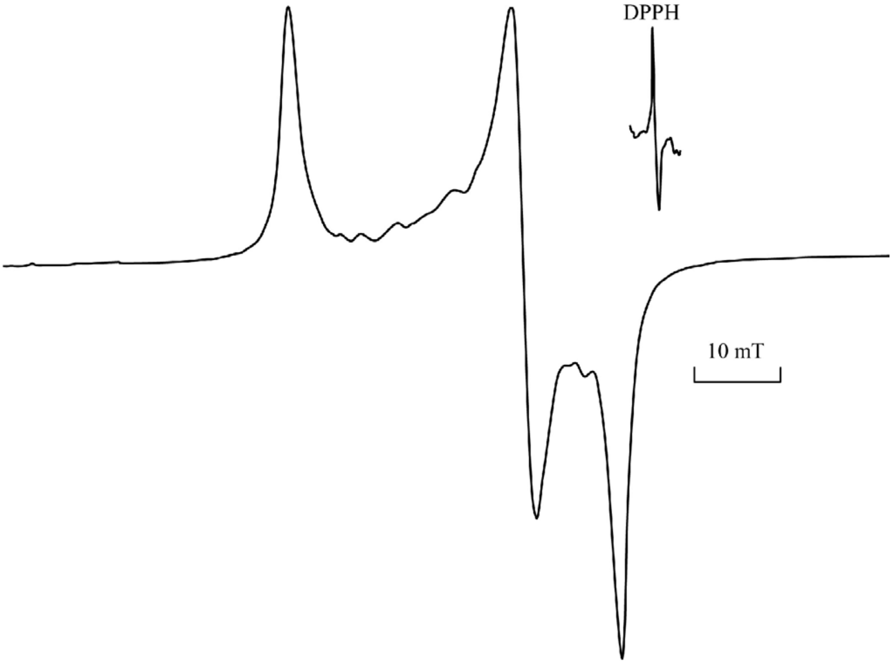

Figure 1. X-band EPR spectra of [Cu(μ-sq)(mea)$_2$]$_n$.

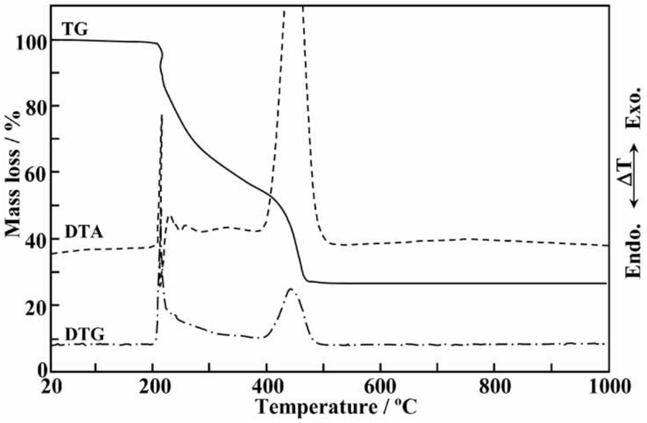

Figure 2. TG, DTG and DTA curves of [Cu(μ-sq)(mea)$_2$]$_n$.

Calcd 41.03%). A similar decomposition behavior has been reported for [Cu(sac)$_2$(mea)$_2$] and [Cu(ox)(mea)$_2$], where sac and ox are the saccharinate and oxalate anions, respectively [36, 37]. The second stage is related to the decomposition of the squarato ligand (exp. 31.30, Calcd 32.26%) and burning of the organic residue, in the temperature range of 383–493°C (DTG$_{max}$: 447°C). The total loss of mass, 73.15% agrees well with the calculated value of 73.29%. The final product of decomposition was identified by IR spectroscopy to be CuO.

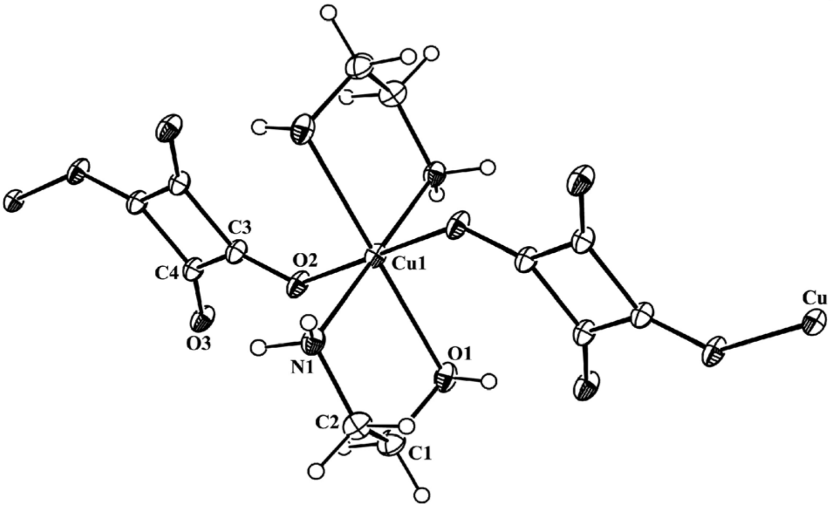

Figure 3. Molecular structure of $[Cu(\mu\text{-sq})(mea)_2]_n$.

Table 3. Selected bond lengths and hydrogen bonding geometry for $[Cu(\mu\text{-sq})(mea)_2]_n{}^{a}$.

Bond lengths (Å) and angles (°)				
Cu(1)–N(l)	1.983 (3)	C(3)–O(2)	1.251(5)	
Cu(1)–O(l)	2.373 (3)	C(4)–O(3)	1.244 (5)	
Cu(1)–O(2)	2.036 (3)	C(3)–C(4)	1.467 (5)	
		C(3)–C(4)^{i}	1.468 (5)	
N(1)–Cu(1)–N(1)^{i}	180.00(0)	O(2)–Cu(1)–O(1)^{i}	97.97(11)	
N(1)–Cu(1)–O(1)	81.15(12)	O(2)–Cu(1)–N(1)^{i}	90.84(13)	
N(1)–Cu(1)–O(1)^{i}	98.85(12)	O(1)^{i}–Cu(1)–O(2)^{i}	82.03(11)	
N(1)–Cu(1)–O(2)	89.16(13)	O(1)^{i}–Cu(1)–N(1)^{i}	81.15(12)	
N(1)–Cu(1)–O(2)^{i}	90.84(13)	O(2)^{i}–Cu(1)–N(1)^{i}	89.16(13)	
O(1)–Cu(1)–O(1)^{i}	180.00(13)	C(3)–C(4)–C(3)^{i}	89.5(3)	
O(1)–Cu(1)–O(2)	82.03(11)	C(4)–C(3)–C(4)^{i}	90.5(3)	
O(1)–Cu(1)–O(2)^{i}	97.97(11)	O(3)–C(4)–C(3)	133.9(4)	
O(1)–Cu(1)–N(1)^{i}	98.85(12)	O(2)–C(3)–C(4)	132.4(3)	
O(2)–Cu(1)–O(2)^{i}	180.00(14)			
Hydrogen bonds				
D–H–A	d(D–H)	d(H–A)	rf(D–A)	∠ (DHA)
O(1)–H(1)···O(3)^{iii}	0.81(2)	1.85(2)	2.659(4)	175(5)
N(1)–H(1c)···O(1)^{ii}	0.90	2.63	3.348(4)	138
N(1)–H(1c)···O(2)^{ii}	0.90	2.19	2.988(4)	147
N(1)–H(1d)···O(3)^{ii}	0.90	2.27	0.051(4)	146

Symmetry operations $^{(i)}$ $1-x$, $1-y$, $1-z$; $^{(ii)}$ $x-1$, y, z; $^{(iii)}$ $x-1$, y–1, z.

3.4. *Crystal structure of* $[Cu(\mu\text{-sq})(mea)_2]_n$

A fragment of the structure of *catena*-*poly*-*trans*-μ-(squarato-O^1,O^3) bis(monoethanolamine)copper(II) is shown in figure 3, with selected bond lengths and bond angles together with the hydrogen bonds listed in table 3. The structure of the complex is described as a distorted octahedron. Each copper atom is trans-connected to two molecules of mea (Cu(1)–O(1) = 2.373(3) Å, Cu(1)–N(1) = 1.982(4) Å) and two molecules of sq (Cu(1)–O(2) = 2.036(3) Å) ligands. The squarate anion acts as a O^1-O^3-bridging ligand so that one-dimensional zig-zag chains of trans-squarato(O^1,O^3) bridged copper(II) ions are built. The zig-zag chain runs parallel to the *b* axis. The mea acts as a bidentate amine N- and hydroxyl O-donor ligand and occupies the *trans* positions of the coordination octahedron forming a five-membered chelate ring. The Cu–O_{sq} bond length is 2.036(3) Å in the Cu(II) complex, comparable with those reported for $[Cu_2(bipy)_4sq](CF_3SO_3)_2 \cdot 6H_2O$ [15]. It is slightly longer than those found in $\{[Cusq(ina)_2(H_2O)_2] \cdot 2H_2O\}_n$ (ina = isonicotinamide) [23], but somewhat shorter than that in $[Cusq(prazine)]_n$ [25] and $\{[Cusq(imidazole)_2] \cdot 2H_2O\}_n$ [11]. The Cu–O_{mea} and Cu–N bond distances of 2.373(3) and 1.983(3) Å, respectively, are typical for copper(II)-mea complexes [37–42]. The five-membered Cu1, O1, C1, C2 and N1 chelate ring is nearly planar. The intra chain Cu–Cu distances of 8.004 Å is significantly longer than in related Cu(II) complexes: 7.425 Å in $\{[Cu(sq\text{-}O^1,O^3)(H_2O)_2(ina)_2] \cdot 2H_2O\}_n$ [23], 7.851 Å in $[Cu(sq\text{-}O^1,O^3)(H_2O)_2(im)_2]_n$ [11] and 7.981 Å in $[Cu_2(sq\text{-}O^1,O^3)(H_2O)_2(apox)]_n \cdot nH_2O$ [43]. The intermolecular Cu(1)–Cu(1)^I = 5.143, (i: *x*, *y*, 1 + *z*) and Cu(1)–Cu(1)^{ii} = 7.293 Å (ii: 1 + *x*, *y*, *z*)] distances are shorter than intramolecular distances.

The squarato ligand is almost planar, and the O2–C3–C4–O3 torsion angle is 0.6(8)°. The C(3)–O(2) bond length [1.251(5) Å] is somewhat longer than the C(4)–O(3) distance [1.244(5) Å] as expected from O(2) ··· Cu coordination. There is no difference between the C–C bond lengths [1.467(5) and 1.468(5) Å for C(3)–C(4) and C(3)–C(4)^i respectively] which are close to the values found in other squarato complexes [3, 4, 11–15, 43–45], although smaller than those reported for $[M(H_2O)_6](HC_4O_4)_2 \cdot 2H_2O$ (M = Co(II) and Ni(II)) [47]. The O–C–C angles vary between 132.36 and 137.12° and the C–C–C angles are equal to 89.5(3) and 90.5(3)°, respectively. Comparison of values of the Cu–O_{sq}, Cu–O_{mea}, Cu–N with average C–O and C–C distances, and of the O_{mea}–Cu–N_{mea} angle for similar squarate and monoethanolamine metal complexes can be found in table 4.

The Cu–O_{mea} bond distance (2.373(3) Å) is significantly longer than the Cu–O_{sq} and Cu–N bonds (2.036(3) and 1.982(3) Å, respectively), and this result in the formation of elongated distorted octahedral geometry along the Cu–O_{mea} bonds as a consequence of the Jahn-Teller effect. Thus, N and O_{sq} atoms form the equatorial plane of the coordination octahedron, while the hydroxyl O atoms occupy the axial positions.

These chains are linked by moderate hydrogen bonds between the non-coordinating oxygen atoms of the squarate anions to both oxygen and nitrogen atoms of the monoethanolamine ligand and between the coordinated oxygen atoms of the squarate anions and nitrogen atoms of the ethanolamine ligand. The packing of the molecules is due to van der Waals forces and to hydrogen bonds between O(1)–H(1) ··· O(3)^{iii}, N(1)–H(1c) ··· O2^{ii}, N(1)–H(1c) ··· O(1)^{ii} and N(1)–H(1d) ··· O(3)^{ii} (see table 3). Figure 4 shows the crystal packing of the compound.

4. Conclusions

Catena-poly-trans-μ-(squarato-O^1,O^3)bis(monoethanolamine)copper(II) crystallizes in the triclinic system with space group *P*-1. The squarate anion acts as a O^1-O^3-bridging ligand so that one-dimensional zig-zag chains of trans-squarato(O^1,O^3) bridged copper(II) ions are built. The mea acts as a bidentate amine *N*- and hydroxyl *O*-donor ligand and occupies *trans* positions of the coordination octahedron forming

Table 4. Comparison of the bond distances and angles of the squarato and monoethanolamine metal complexes[a].

Complex	Squarato mode/ complex type	Cu · · · Cu (Å)	$Cu–O_{sq}$ (Å)	$C–O_{sq}$ and $C–C_{sq}$ (Å)	$Cu–O_{mea}$ and $Cu–N_{mea}$ (Å)	$O_{mea}–Cu–N_{mea}$ (Å)
$[Cu(ox)(mea)_2]$[b]	–	–	–	–	2.433, 2.023	78.17
$[Cu(sac)_2(mea)_2]$[c]	–	–	–	–	2.326, 1.992	80.97
$[Cu(\mu\text{-}sq)(mea)_2]$ (*This work*)	μ-1,3/chain	8.004	2.036	1.248, 1.468	2.373, 1.983	81.15
$[Cu(sq)(H_2O)_2(ina)_2] \cdot 2H_2O$[d]	μ-1,3/chain	7.425	1.992	–	–	–
$[Cu(sq)(H_2O)_2(im)_2]$[e]	μ-1,3/chain	7.851	2.475	1.240, 1.520	–	–
$[Cu_2(sq)(H_2O)_2(apox)]_n \cdot nH_2O$[f]	μ-1,3/chain	7.981	1.952	1.251, 1.466	–	–
$[Cu(sq)(H_2O)(terpy)] \cdot H_2O$[g]	μ-1,2/chain	7.770	1.946	1.257, 1.445	–	–
$[Cu_2(sq)(H_2O)_2(terpy)_2] \cdot (ClO_4)_2$[h]	μ-1,3/binucl	7.770	2.333	1.255, 1.461	–	–
$[Cu_2(sq)(bipy)_4](CF_3SO_3)_2 \cdot 6H_2O$[i]	μ-1,3/binucl	7.424	2.005	1.246, 1.464	–	–
$[Cu_2(sq)(phen)_4](CF_3SO_3)_2 \cdot 3H_2O$[j]	μ-1,2/binucl	4.912	1.995	1.280, 1.468	–	–
$[Cu_2(sq)(SalNEt_2)_2(H_2O)] \cdot H_2O$[k]	μ-1,2/binucl	5.210	1.962	1.253, 1.460	–	–

[a] ox = oxalate, sac = saccharinato, ina = isonicotinamide, im = imidazole, H_2apox = *N*,*N*′-bis(3-aminopropyl)oxamide, terpy = 2,2′:6′,2″-terpyridine, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, $SalEt_2$ = N-(2-(diethylamino)ethyl)-salicylideneaminate.

[b] Yılmaz *et al*., 2003 [37]; [c] Yılmaz *et al*., 2001 [38]; [d] Ucar *et al*., 2005 [23]; [e] Bernardinelli *et al*., 1989 [11]; [f] Castro *et al*., 2001 [43]; [g,h] Solans *et al*., 1990 [14]; [i,j] Castro *et al*., 1999 [15]; [k] Xanthopoulos *et al*., 1993 [44].

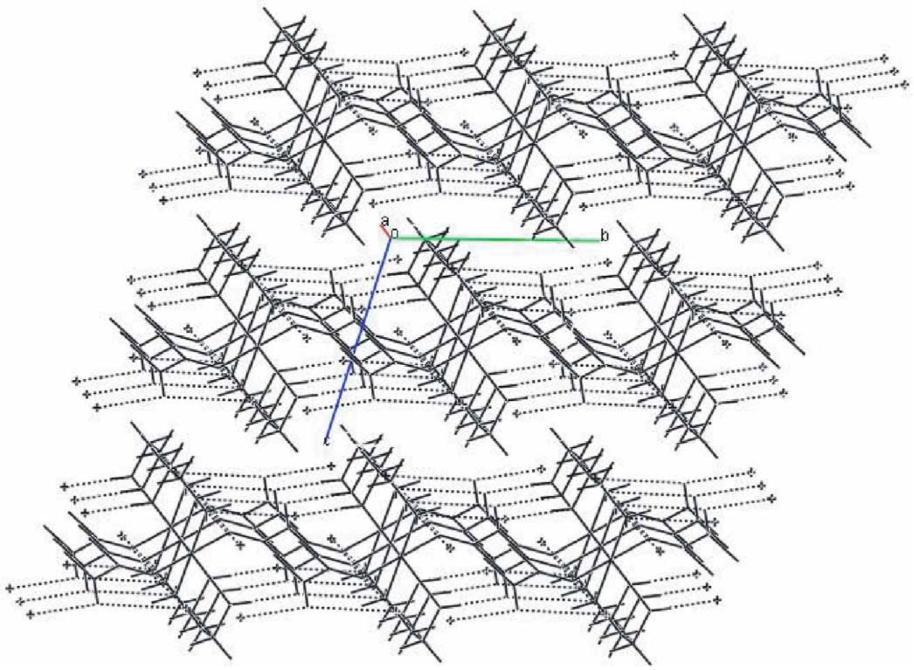

Figure 4. Packing diagram of $[Cu(\mu\text{-sq})(mea)_2]_n$.

a five-membered chelate ring. The d–d transition spectrum and magnetic susceptibility of the title complex are compatible with octahedral configuration. The Cu^{2+} hyperfine splitting is too small to be measured, indicating that the unpaired electron is distributed over the ligands. The complex is stable up to 203°C and decomposes in two stages.

Supplementary material

Crystallographic data for the structure reported here have been deposited at the CCDC as supplementary data, CCDC No. 276484. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (E-mail: deposit@ccdc.cam.ac.uk).

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