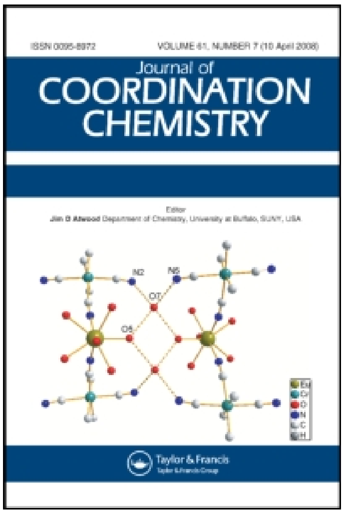

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Synthesis, spectral, thermal, and structural studies of copper(II)-squarate coordination polymer with 2-hydroxyethylpyridine, $\{[Cu(\mu\text{-sq})(etpy)_2] \cdot H_2O\}$*_n*

Okan Zafer Yeşılel[a]; Hakan Erer[a]; Mustafa Serkan Soylu[b]; Orhan Büyükgüngör[c]
[a] Faculty of Arts and Sciences, Department of Chemistry, Eskişehir Osmangazi University, Eskişehir, Turkey [b] Faculty of Arts and Sciences, Department of Physics, Giresun University, Giresun, Turkey [c] Faculty of Arts and Sciences, Department of Physics, Ondokuz Mayıs University, Samsun, Turkey

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Synthesis, spectral, thermal, and structural studies of copper(II)-squarate coordination polymer with 2-hydroxyethylpyridine, $\{[Cu(\mu\text{-sq})(etpy)_2]\cdot H_2O\}_n$

OKAN ZAFER YEŞİLEL*†, HAKAN ERER†,
MUSTAFA SERKAN SOYLU‡ and ORHAN BÜYÜKGÜNGÖR§

†Faculty of Arts and Sciences, Department of Chemistry,
Eskişehir Osmangazi University, 26480, Eskişehir, Turkey
‡Faculty of Arts and Sciences, Department of Physics,
Giresun University, Giresun, Turkey
§Faculty of Arts and Sciences, Department of Physics,
Ondokuz Mayıs University, 55139, Kurupelit, Samsun, Turkey

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Polynuclear Cu(II)-squarate complex with 2-hydroxyethylpyridine, $\{[Cu(\mu\text{-sq})(etpy)_2]\cdot H_2O\}_n$ has been prepared and characterized by elemental analysis, magnetic susceptibility, thermal analysis, IR, and UV-Vis spectroscopic studies (H_2sq = squaric acid and etpy = 2-hydroxyethylpyridine). The structure of the complex was determined by single crystal X-ray diffraction. Density functional theory (DFT) and Hartree–Fock (HF) calculations were performed using the GAUSSIAN 03 program. The complex crystallizes in the monoclinic system, space group $P2_1/c$. The structure contains chains of squarato-O^1,O^3-bridged polynuclear copper(II) units held together by intermolecular hydrogen bonds, weak π–π and van der Waals interactions. The distorted octahedral geometry of Cu(II) is completed by two neutral bidentate etpy ligands through the nitrogen of pyridine and hydroxyl O atom. Thermal decomposition of the complex is studied from 30 to 500°C in a static air atmosphere.

Keywords: Squarato complex; 2-Hydroxyethylpyridine complex; Coordination polymer

1. Introduction

Supramolecular frameworks have potential applications in catalysis, NLO, sensors, and magnetism [1–5]. The coordination properties of squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, $H_2C_4O_4$, H_2sq) were very interesting as a polyfunctional ligand which can be a μ_2–μ_6 bridging ligand between metals. There has been increased interest in the squarate complexes with *N*- or *O*-donor ligands due to possible dinuclear, polynuclear, and supramolecular complexes [6–26]. It is also a useful tool for constructing crystalline architectures due to hydrogen bonding and π–π interactions [27–31]. Recently, supramolecular organoammonium squarate salts of squaric acid have been reported [27–37].

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*Corresponding author. Email: yesilel@ogu.edu.tr

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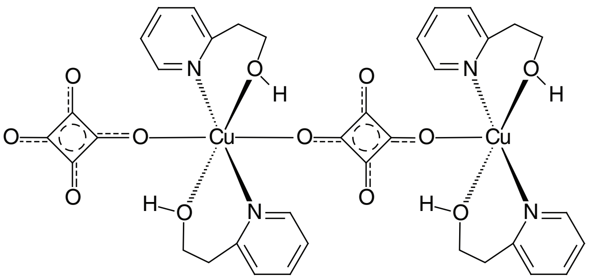

Scheme 1. Chemical diagram of the complex.

In the present article, we describe the synthesis, spectral (FT-IR, UV-Vis), thermal studies, DFT and HF calculations and crystal structure of a polynuclear copper(II)-squarate complex with 2-hydroxyethylpyridine (etpy), $\{[Cu(\mu\text{-sq})(etpy)_2]\cdot H_2O\}_n$ (**1**) (scheme 1).

2. Experimental

2.1. *Materials and measurements*

All chemicals used were analytical reagents purchased commercially. IR spectrum was obtained with a Perkin Elmer 100 FT-IR Spectrometer using KBr pellets from 4000 to 400 cm^{-1}. The UV-Vis spectrum was obtained for DMF solution of the complex (10^{-3} M) with a Shimadzu UV-3150 spectrometer in the range 900–190 nm. Magnetic susceptibility measurement at room temperature was performed using a Sherwood Scientific MXI model Gouy magnetic balance. Elemental analyses for C, H, and N were performed using a Carlo Erba 1106 microanalyser. A Perkin Elmer Diamond TG/DTA Thermal Analyzer was used to record simultaneous TG, DTG, and DTA curves in static air at a heating rate of 10°C min^{-1} from 30 to 500°C using platinum crucibles.

2.2. *Preparation of* $\{[Cu(\mu\text{-}sq)(etpy)_2]\cdot H_2O\}_n$

A solution of 2-hydroxyethylpyridine (0.49 g, 4 mmol) in methanol (10 mL) was added dropwise with stirring to a solution of $CuSq\cdot 2H_2O$ [41] (0.42 g, 2 mmol) in distilled water (20 mL). The solution was heated to 60°C and stirred for 6 h, then slowly cooled to room temperature. The green crystals which formed were filtered and washed with 10 mL of cold distilled water and methanol, and dried in air. Anal. Calcd for **1** $C_{18}H_2ON_2O_7Cu$: C, 49.15; H, 4.58; N, 6.37. Found: C, 49.23; H, 4.52; N, 6.39%.

2.3. *Crystallographic analysis*

Diffraction experiments were carried out at 296 K on a Stoe IPDS diffractometer. The structure was solved by direct methods and refined using SHELXS97 and SHELXL97 [38]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares [38]. Hydrogen atoms were placed in geometrically idealized positions and refined as riding atoms. Data collection: X-Area, cell refinement: X-Area, data reduction: X-RED [39]; program(s) used for molecular graphics: ORTEP-3 for Windows [40]; software used to prepare material for publication: WinGX [41].

2.4. *Computations*

Hartree–Fock and DFT are used to obtain equilibrium geometry and fundamental vibrational frequencies of $\{[Cu(\mu\text{-sq})(etpy)_2]\cdot H_2O\}_n$. All calculations have been performed with standard GAUSSIAN 03W [42] software. DFT is B3LYP-Becke's three parameter hybrid method [43] using the correlation functional of Lee *et al.* [44]. The standard 6-31G(d) basis set was applied in all calculations. The standard analytical procedure, implemented in GAUSSIAN was used. Both HF and B3LYP methods overestimate the frequencies of fundamental vibrations significantly. Thus, for a better correspondence between experimental and calculated values, the HF and B3LYP results were modified using the empirical scaling factor reported by Scott and Radom [49].

3. Results and discussion

3.1. *UV-Vis spectroscopy and magnetism*

The electronic spectrum in DMF exhibits a broad absorption band at 460 nm, assigned to $^2E_g \rightarrow {}^2T_{2g}$. Strong absorption bands below 300 nm are due to intraligand transitions of the ligands. The complex exhibits a magnetic moment of 1.64 B.M., lower than the expected value, indicating antiferromagnetic effect.

3.2. *Thermal analysis*

Thermal decomposition of the complex was performed in static air from 30 to 500°C and shows three decomposition stages (Supplementary material). An endothermic peak in the range of 60–112°C corresponds to the loss of crystal water (found 4.10, Calcd 4.88%, $DTA_{max} = 86°C$). The anhydrous complex is thermally stable to 190°C. The TGA curve shows that complex exhibits a continuous mass loss in the temperature range 190–248°C and therefore, it is difficult to calculate mass loss values. However, endothermic DTA peaks at 205°C and 231°C may correspond to removal of two etpy ligands, while the exothermic peak at 300°C is characteristic for degradation of the squarate. The decomposition ends at 322°C to give metallic Cu. The overall mass loss of 85.57% (Calcd 85.27%) agrees with the proposed structure.

3.3. *Crystal structure*

The relevant crystal data and experimental conditions along with the final parameters are summarized in table 1. A fragment of the structure of *trans*-μ-(squarato-O^1,O^3)bis(2-hydroxyethylpyridine)copper(II) hydrate, $\{[Cu(\mu\text{-sq})(etpy)_2]\cdot H_2O\}_n$ (**1**) is shown figure 1, while experimental and calculated bond lengths and angles together

Table 1. Crystal data and structure refinement parameters for **1**.

Empirical formula	$C_{18}H_{20}CuN_2O_7$
Formula weight	439.90
Temperature (K)	293(2)
Wavelength (Å)	0.71073 Mo-Kα
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimension (Å, °)	
a	8.2204(3)
b	14.1727(4)
c	16.4045(6)
β	104.377(3)
V (Å^3)	1851.36(11)
Z	4
Absorption coefficient (mm^{-1})	1.22
D_{Calcd} (Mg m^{-3})	1.578
Crystal size (mm^3)	0.67 × 0.31 × 0.12
θ range for data collection (°)	1.44–28.03
Measured reflections	14672
Independent reflections	3642
Absorption correction	Integration Stoe X-RED [39]
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	0.068
$R[F^2 > 2\sigma(F^2)]$	0.034
$wR(F^2)$	0.087
Goodness-of-fit on F^2	1.02
Largest difference peak and hole (e Å^{-3})	0.46; −0.52

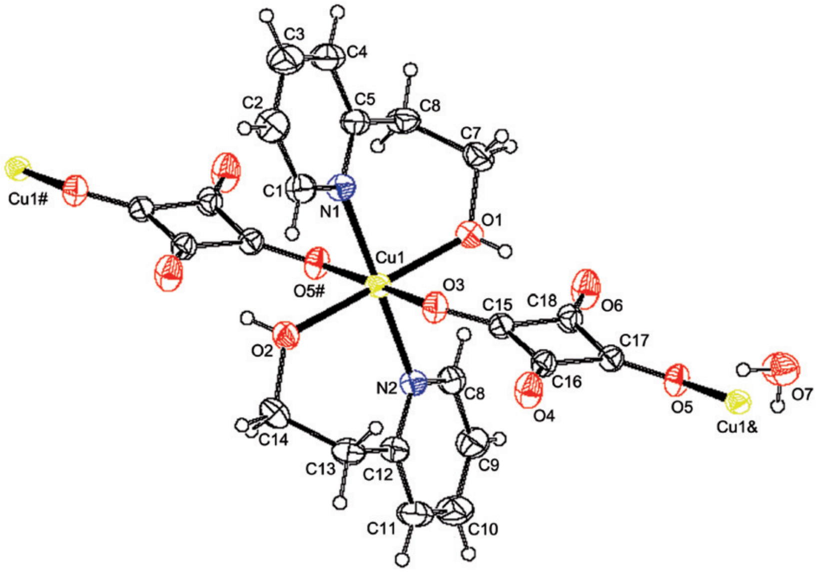

Figure 1. The molecular structure of **1** showing the atom numbering scheme. The thermal ellipsoids are plotted at the 50% probability level.

with the hydrogen bonds are listed in tables 2 and 3, respectively. The structure is a distorted octahedron with copper *trans*-connected to two molecules of etpy (Cu(1)–O(1) = 2.0186(16) Å, Cu(1)–O(2) = 2.024(16) Å, Cu(1)–N(1) = 2.0205(19) Å, Cu(1)–N(2) = 2.0304(19) Å), and two molecules of sq (Cu(1)–O(3) = 2.3459(15) Å,

Table 2. Experimental and calculated bond lengths and angles (Å, °).

Selected Atoms	Experimental	B3LYP	HF
$\{[Cu(\mu\text{-sq})(etpy)_2]\cdot H_2O\}_n$			
N1–Cu1	2.0205(19)	1.9724	2.1115
N2–Cu1	2.0304(19)	1.9672	2.0869
O1–Cu1	2.0186(16)	3.2096	2.2466
O2–Cu1	2.0240(16)	2.1402	3.3243
O3–Cu1	2.3459(15)	1.9578	2.1256
$O5^i$–Cu1	2.3567(15)	–	–
C15–C16	1.454(3)	1.5029	1.4822
C16–C17	1.458(3)	1.5514	1.5094
C17–C18	1.457(3)	1.4851	1.4983
C18–C15	1.468(3)	1.4524	1.4706
O3–C15	1.247(3)	1.2531	1.2250
O4–C16	1.259(3)	1.2092	1.2053
O5–C17	1.250(2)	1.2130	1.1978
O6–C18	1.252(3)	1.2719	1.2176
O1–Cu1–N1	90.13(7)	72.49	88.98
O1–Cu1–O2	179.38(7)	151.318	156.246
N1–Cu1–O2	89.34(7)	99.104	81.369
O1–Cu1–N2	89.91(7)	78.342	103.891
N1–Cu1–N2	178.15(7)	142.919	135.468
O2–Cu1–N2	90.61(7)	94.749	69.799
O1–Cu1–O3	91.87(6)	95.265	105.034
N1–Cu1–O3	88.35(7)	106.581	103.555
O2–Cu1–O3	88.43(6)	113.339	98.335
N2–Cu1–O3	93.50(6)	98.322	113.396
O1–Cu1–O5(i)	89.95(6)	–	–
N1–Cu1–O5(i)	90.67(7)	–	–
O2–Cu1–O5(i)	89.75(6)	–	–
N2–Cu1–O5(i)	87.48(6)	–	–
O3–Cu1–O5(i)	177.94(5)	–	–

Symmetry codes: (i) $x \pm 1$, y, z.

Table 3. Hydrogen bonding interactions in **1**.

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (°)
O7–H7C···O5	0.86(4)	2.01(4)	2.847(3)	164(4)
O1–H1A···O6	0.81(3)	1.73(3)	2.534(2)	172(3)
O7–H7D···O4(iii)	0.87(4)	2.01(5)	2.853(3)	163(4)
O2–H2A···O4(ii)	0.85(3)	1.72(3)	2.557(2)	172(3)

Symmetry codes: (ii) $x-1$, y, z, (iii) $-x \pm 2$, $y-1/2$, $-z \pm 3/2$.

Cu(1)–O(5)^i = 2.3567(15) Å, (i): $x - 1$, y, z). The squarate anion is a O^1-O^3-bridging ligand so that 1-D zigzag chains of *trans*-squarato (O^1,O^3) bridged copper(II) ions are built. The perfectly zigzag chain is parallel to the *a*-axis as shown in figure 2. The etpy ligand is bidentate through pyridine *N*– and hydroxyl *O*– forming a six-member chelate ring.

The Cu–O_{sq} bond length is comparable with those reported for $[Cu_2(bipy)_4(\mu\text{-sq})](CF_3SO_3)_2\cdot 6H_2O$ [3] and slightly longer than those found in $\{[Cu(\mu\text{-sq})(ina)_2(H_2O)_2]\cdot 2H_2O\}_n$ (ina = isonicotinamide) [19] and $[Cu(\mu\text{-sq})(pyrazine)]_n$ [5].

The six-membered chelate rings deviate from planarity significantly. The intrachain Cu–Cu distance of 8.2204(5) Å is significantly longer than in related Cu(II) complexes:

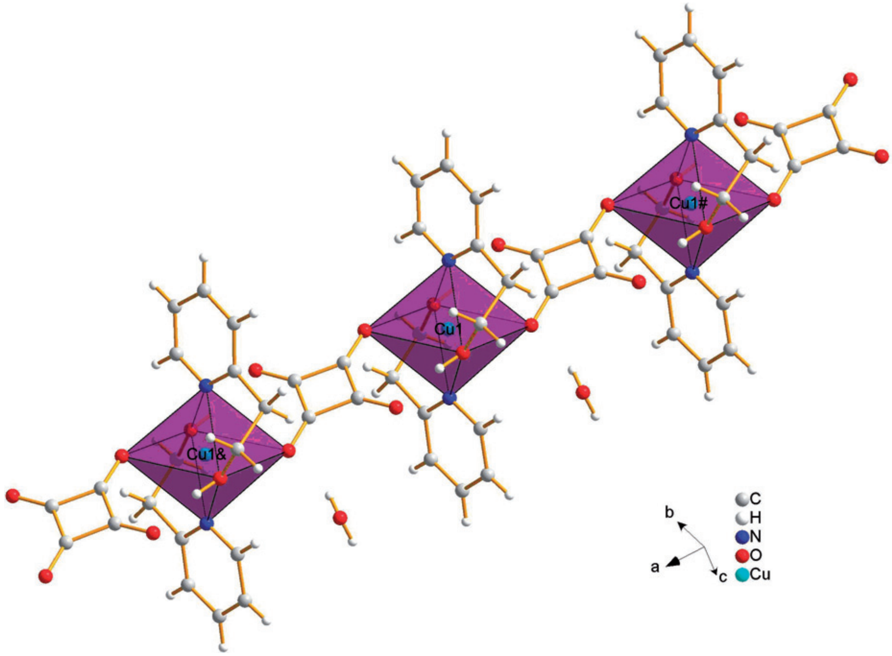

Figure 2. The 1-D chain structure for **1** showing the coordination environment (octahedral are shaded dark, 30% probability ellipsoids).

7.425 Å in $\{[Cu(\mu\text{-sq-}O^1,O^3)(H_2O)_2(ina)_2]\cdot 2H_2O\}_n$ [19], 7.851 Å in $[Cu(\mu\text{-sq-}O^1,O^3)(H_2O)_2(im)_2]_n$ [20] and 7.981 Å in $[Cu_2(\mu\text{-sq-}O^1,O^3)(H_2O)_2(apox)]_n\cdot nH_2O$ [6]. The intermolecular Cu(1)–Cu(1)^i distance of 8.2095(5)Å (i: x, $0.5-y$, $0.5+z$) is shorter than the intramolecular distance.

The squarate is almost planar with maximum deviation from planarity *via* O6 at 0.052(2)Å. There are no differences between C–C bond lengths [between 1.454(3) and 1.468(5) Å] and they are close to the values found in other squarate complexes [18, 19], although smaller than those reported for $[M(H_2O)_6](HC_4O_4)_2\cdot 2H_2O$ (M = Co(II) and Ni(II)) [46]. The squarate anion possesses a pronounced delocalization.

The zigzag chains running along *a*-axis are linked by moderate hydrogen bonds between non-coordinating oxygens of the squarate anions and oxygen of 2-hydroxyethylpyridine and between the coordinated oxygens of squarate and water. There are also weak π–π and van der Waals interactions responsible for the interchain packing and molecular stabilization (figure 3a and 3b).

3.4. *IR spectroscopy*

Experimental and calculated vibrational wavenumbers (cm^{-1}) of the most important IR bands of $\{[Cu(\mu\text{-sq})(etpy)_2]\cdot H_2O\}_n$ are listed in table 4. The spectrum showed a broad and intense band located at 3435 cm^{-1} due to the hydrogen bond $\nu(OH)_{water}$. The band at 3523 cm^{-1} may be assigned to the hydroxyl group of the etpy ligand. Weak absorptions in the 2982–2854 cm^{-1} range are due to ν(CH). Strong absorptions centered at 1636, 1609, and 1512 cm^{-1} are assigned to a combination of squarate C=O and C–C

Table 4. Experimental and calculated vibrational wavenumbers (cm^{-1}).

	$([Cu(\mu\text{-sq})(etpy)_2]\cdot H_2O)_n$	B3LYP	HF
ν(C–H)	3119–3043	3141–3080	3063–3018
$\nu(CH_2)$	2982–2854	2999–2848	2970–2854
ν(C=O)	1636	1647	1758
ν(C–C)	1609	1612	1599
ν(Cu–N)	651	643	627
ν(Cu–O)	457	439	444

stretching vibrations, respectively, characteristic of salts of $C_nO_n^{2-}$ [37]. This large band is split, suggesting lower symmetry than $K_2C_4O_4$, confirmed by the X-ray investigation. The $\nu Cu{-}O_{mea}$, $\nu Cu{-}O_{sq}$, and νCu–N vibrations are observed at 457, 515, and 651 cm^{-1}, respectively, as weak bands.

3.5. *DFT and HF calculations*

The DFT and HF calculations have been performed using the GAUSSIAN 03 program [42]. The B3LYP/6-31G basis set was used for geometry optimization and DFT B3LYP/6-31G basis set was applied to calculate IR frequencies. The ground-state geometries were obtained in the gas phase by full geometry optimization, starting from the structural data. Owing to the overlaps of absorption bands, it is difficult to identify the vibration modes in the IR spectra and in this case, the frequencies derived from the DFT calculations especially B3LYP basis set may be helpful to distinguish the vibration modes.

Optimized geometry parameters, i.e. bond lengths and angles, computed by HF and DFT methods are compared with X-ray data in table 2. The numbering of the atoms in $\{[Cu(\mu\text{-sq})(etpy)_2]\cdot H_2O\}_n$ is shown in figure 1. Calculated bond lengths and angles deviate significantly from the experimental X-ray data for Cu(II) coordination. In contrast, both HF and B3LYP predict that the $(C{-}C)_{sq}$, $(C{=}O)_{sq}$, $(C{-}C)_{etpy}$, and $(C{-}N)_{etpy}$ bond lengths agree with the experimental measurements.

The harmonic vibrational wavenumbers computed by the B3LYP/6-31G(d) and HF approach and the corresponding experimental values are collected in table 4. The DFT and HF harmonic vibrational wavenumbers are usually higher than experimental values, due to the neglect of anharmonicity, incomplete treatment of electron correlation, and the use of finite one-particle basis sets. The overestimation is systematic and can be corrected by scaling the wavenumbers [45].

In the high-frequency region (3000–3500 cm^{-1}), the C–H ring stretching modes are observed between 3119 and 3043 cm^{-1}; the frequencies of this mode is well predicted by B3LYP method (in the region from 3141 to 3080 cm^{-1}) and by HF (in the region from 3063 to 3018 cm^{-1}).

The symmetric and asymmetric $\nu(CH_2)$ modes are in the frequency region of 2982–2854 cm^{-1}; DFT calculation predicted them in the frequency region of 2999–2848 cm^{-1} and HF in the region of 2970–2854 cm^{-1}. These results compare well with the experimental results (the mean deviation between experimental and calculated data is about 17 cm^{-1}).

Strong absorptions centered at 1636 and 1609 cm^{-1} are assigned to a combination of squarato C=O and C–C band stretching vibrations, respectively. The B3LYP/

Table 5. Some selected Mulliken charges for **1**.

Atom	B3LYP	HF
Cu	0.930	0.733
N1	−0.596	−0.726
N2	−0.580	−0.714
O3	−0.575	−0.508
O5	−0.528	−0.505
O4	−0.609	−0.696
O6	−0.609	−0.621
C15	0.347	0.391
C16	0.315	0.351
C17	0.227	0.382
C18	0.302	0.345

6-31G(d) method reproduces very well the frequency of the C–C stretching mode, 1612 cm^{-1} for ν(C–C). The C=O stretching vibration also well predicted by this method (1647 cm^{-1}) but HF method overestimates significantly the frequency of C=O as 1758 cm^{-1}. C–C stretching mode is calculated in the 1599 cm^{-1} frequency value for the HF method.

The $\nu(\mathrm{Cu{-}O_{etpy}})$ and ν(Cu–N) are observed at 457 and 651 cm^{-1}, respectively, and predicted at 439 and 643 cm^{-1} (B3LYP) and 444 and 627 cm^{-1} (HF), respectively.

The electrostatic energy is the Coulomb potential energy, $V = q_i q_j/(4\pi\varepsilon_0 R_{ij})$, where q_i and q_j are a pair of atomic charges separated by R_{ij} distance. The problem is in determining atomic charges. The most popular are Mulliken charges which provide important information about electronegativity despite the fact that Mulliken [47] analysis was not devised for estimating intermolecular interactions. It gives charges that are very dependent on the basis set and are often chemically unrealistic [48]. Nevertheless, as a comparison of various methods of deriving atomic charges, Wiberg and Rabben [49] concluded that no atomic point charge model is capable of exactly reproducing the electrostatic potential in the van der Waals region around a wide range of molecules.

The Mulliken population analysis of **1** show that positive charges are mostly distributed on squarate rings though the phenyl ring bears some positive charge. The negative charges are primarily localized on the four oxygens. The nitrogen of hydroxyethylpyridine is more negatively charged than coordinated squarate oxygens as shown in table 5. As a result of negative charge distribution, $\mathrm{Cu{-}N_{etpy}}$ and $\mathrm{Cu{-}O_{etpy}}$ bond lengths are shorter than $\mathrm{Cu{-}O_{sq}}$, and hydroxyethylpyridine has a stronger interaction with copper than bridged squarate anion.

4. Conclusions

Trans-μ-(squarato-O^1,O^3)bis(2-hydroxyethylpyridine)copper(II) hydrate, $\{[\mathrm{Cu}(\mu\text{-sq})(\mathrm{etpy})_2]\cdot\mathrm{H_2O}\}_n$ has been prepared and characterized by X-ray diffraction and computational methods. The complex crystallizes in the monoclinic system, space group $P2_1/c$. Each Cu(II) center is octahedrally coordinated by two *trans* 2-hydroxyethylpyridines and two *trans* squarates. The structure contains chains of

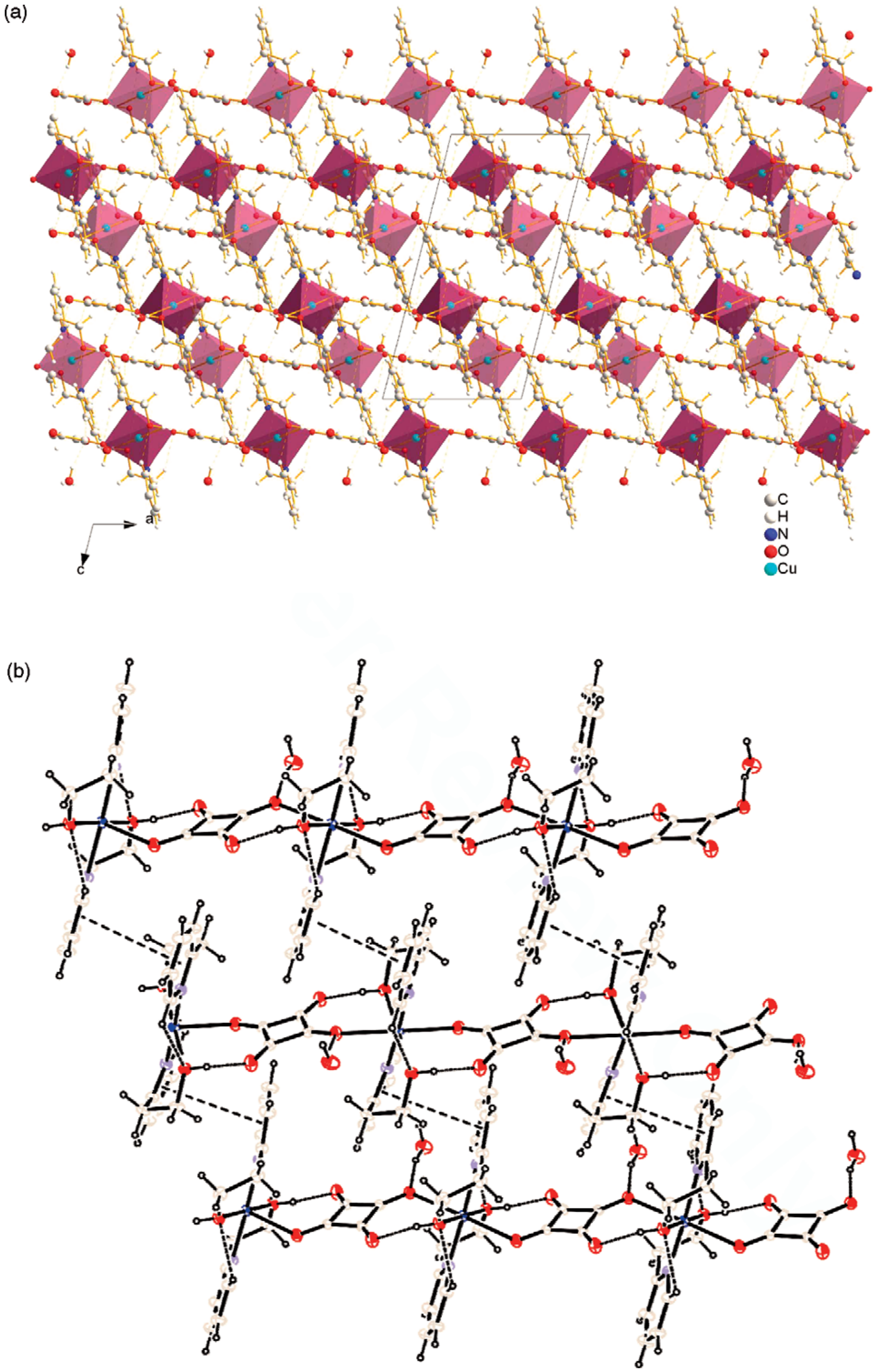

Figure 3. Crystal packing and H bond (a) and π–π (b) interactions. Octahedral representations are drawn as shaded dark.

squarato-O^1,O^3-bridged polynuclear copper(II) units held together by O–H $\cdots$ O intermolecular hydrogen-bond interactions.

Infrared bands were assigned with the help of force field calculations. The majority of the experimental frequencies are well reproduced by the B3LYP/6-31G method and satisfactorily by HF/6-31G. Comparison of the theoretical with the experimental spectra provides important information about the ability of these computational methods to describe the vibrational modes. For a better correspondence between experimental and calculated values, the HF and B3LYP results were modified using the empirical scaling factor, reported by Scott and Radom [45].

Calculated bond lengths and angles significantly deviate from the experimental X-ray data for around the Cu(II) coordination. In contrast to this, both HF and B3LYP predict that the $(C–C)_{sq}$, $(C=O)_{sq}$, $(C–C)_{etpy}$, and $(C–N)_{etpy}$ bond lengths agree with the previously reported values.

Supplementary material

CCDC-676224 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [orfrom the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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References

[1] O.M. Yaghi, H. Li, C. Davis, D. Richardson, T.L. Groy. *Acc. Chem. Res.*, **31**, 474 (1998).

[2] H.P. Jia, W. Li, Z.F. Ju, J. Zhang. *Eur. J. Inorg. Chem.*, 4264 (2006).

[3] A. Demessence, G. Rogez, R. Welter, P. Rabu. *Inorg. Chem.*, **46**, 3426 (2007).

[4] P.J. Hagrman, D. Hagrman, J. Zubieta. *Angew. Chem.*, **111**, 2798 (1999).

[5] Y.C. Liang, M.C. Hong, J.C. Liu, R. Cao. *Inorg. Chim. Acta*, **328**, 152 (2002).

[6] I. Castro, M.L. Calatayud, J. Sletten, M. Julve, F. Lloret. *C.R. Acad. Sci. Paris, Chimie/Chem.*, **4**, 235 (2001).

[7] C.E. Xanthopoulos, M.P. Sigalas, G.A. Katsoulos, C.A. Tsipis, C.C. Hadjikostas, A. Terzis, M. Mentzafos. *Inorg. Chem.*, **32**, 3743 (1993).

[8] B.D. Alleyne, L.A. Hall, H.A. Hosein, H. Jaggernauth, A.J.P. White, D.J. Williams. *J. Chem. Soc., Dalton Trans.*, 3845 (1998).

[9] R. Kirchmaier, E. Altin, A. Lentz. *Z. Kristallogr. New Cryst. Struct.*, **218**, 1 (2003).

[10] I. Castro, M.L. Calatayud, J. Sletten, F. Lloret, M. Julve. *Inorg. Chim. Acta*, **287**, 173 (1999).

[11] L.H. Huo, X.L. Cheng, H. Zhao, W. Ng. *Acta Cryst.*, **E61**, m460 (2005).

[12] C. Näther, I. Jeß. *Acta Cryst.*, **C57**, 260 (2001).

[13] M. Dan, C.N.R. Rao. *Solid State Sci.*, **5**, 615 (2003).

[14] H. Grove, J. Sletten, M. Julve, F. Lloret, J. Cano. *J. Chem. Soc., Dalton Trans.*, 259 (2001).

[15] J. Sletten, H. Daraghmeh, F. Lloret, M. Julve. *Inorg. Chim. Acta*, **279**, 127 (1998).
[16] J.C. Trombe, L. Sabadie, P. Millet. *Solid State Sci.*, **4**, 1209 (2002).
[17] A. Crispini, D. Pucci, I. Aiello, M. Ghedini. *Inorg. Chim. Acta*, **304**, 219 (2000).
[18] O.Z. Yeşilel. *J. Coord. Chem.*, **59**, 1675 (2006).
[19] I. Ucar, A. Bulut, O. Büyükgüngör. *Acta Cryst.*, **C61**, m218 (2005).
[20] G. Bernardinelli, D. Deguenon, R. Soules, P. Castan. *Canadian J. Chem.*, **67**, 1158 (1988).
[21] S.C. Manna, J. Ribas, E. Zangrando, N.R. Chaudhuri. *Inorg. Chim. Acta*, **360**, 2589 (2007).
[22] C.C. Corrêa, R. Diniz, L.H. Chagas, B.L. Rodrigues, M.I. Yoshida, W.M. Teles, F.C. Machado, L.F.C. de Oliveira. *Polyhedron*, **26**, 989 (2007).
[23] S.S. Massoud, F.A. Mautner, R. Vicente, J.S. Dickens. *Inorg. Chim. Acta*, **361**, 299 (2008).
[24] S.C. Manna, E. Zangrando, J. Ribas, N.R. Chaudhuri. *Inorg. Chim. Acta*, **358**, 4497 (2005).
[25] O. Angelova, V. Velichka, T. Kolev, V. Radomirska. *Acta Cryst.*, **C52**, 3252 (1996).
[26] J. Greve, I. Jeß, C. Näther. *J. Solid State Chem.*, **175**, 328 (2003).
[27] T. Kolev, Z. Glavcheva, R. Petrova, O. Angelovs. *Acta Cryst.*, **C56**, 110 (2000).
[28] V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli. *Acta Cryst.*, **B57**, 591 (2001).
[29] S. Mathew, G. Paul, K. Shivasankar, A. Choudhury, C.N.R. Rao. *J. Mol. Struct.*, **641**, 263 (2002).
[30] Md.B. Zaman, M. Tomura, Y. Yamashita. *Acta Cryst.*, **C62**, 621 (2001).
[31] R. Mattes, J. Ebbing, A. Gruss, J. Koppe, K. Majcher. *Z. Naturforsch.*, **58B**, 27 (2003).
[32] T. Kolev, R. Wortmann, M. Spiteller, W.S. Sheldrick, M. Heller. *Acta Cryst.*, **E60**, o956 (2004).
[33] S.L. Georgopoulos, R. Diniz, B.L. Rodrigues, M.I. Yoshida, L.F.C. Oliveira. *J. Mol. Struct.*, **753**, 147 (2005).
[34] O.Z. Yeşilel, M. Odabaşoğlu, O. Büyükgüngör. *J. Mol. Struct.*, **874**, 151 (2008).
[35] C.K. Lam, T.C.W. Mak. *Tetrahedron*, **56**, 6657 (2000).
[36] T. Kolev. *J. Mol. Struct.*, **846**, 139 (2007).
[37] R. West, H.Y. Niu. *J. Chem. Soc.*, 2589 (1963).
[38] G.M. Sheldrick. *SHELXS–97 and SHELXL–97, Program for Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
[39] Stoe & Cie. X-Area (Version 1.18) and X-Red32 (Version 1.04), Stoe&Cie, Darmstadt, Germany (2002).
[40] L.J. Farrugia. *J. Appl. Cryst.*, **30**, 565 (1997).
[41] L.J. Farrugia. *J. Appl. Cryst.*, **32**, 837 (1999).
[42] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople. *Gaussian 03, Revision A.1*, Gaussian, Inc., Pittsburgh, PA (2003).
[43] A.D. Becke. *J. Chem. Phys.*, **98**, 5648 (1993).
[44] C. Lee, W. Yang, R.G. Parr. *Phys. Rev.*, **B37**, 785 (1988).
[45] A.P. Scott, L. Radom. *J. Phys. Chem.*, **100**, 16502 (1996).
[46] I. Brach, J. Rozière, B. Anselment, K. Peters. *Acta Cryst.*, **C43**, 458 (1987).
[47] R.S. Mulliken. *J. Chem. Phys.*, **23**, 1833 (1955).
[48] S.L. Price. In *Molecular Interactions, from Van der Waals to Strongly Bound Complexes*, S. Scheiner (Ed.), p. 305, Wiley, Chichester (1997).
[49] K.B. Wiberg, P.R. Rabben. *J. Comput. Chem.*, **14**, 1504 (1993).