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A comparative study of the structural, electrochemical and magnetic properties of Copper(II)-squarate coordination frameworks

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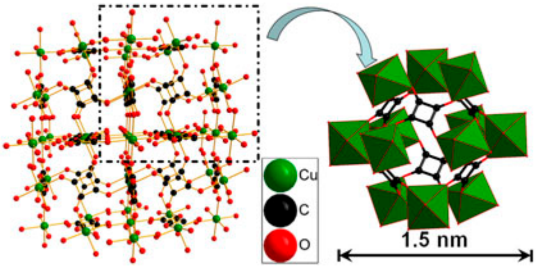

Perspective view of the 3-D cage-like network of $\{[Cu(C_4O_4)(H_2O)_2]\cdot 0.33H_2O\}_n$ (**2**). View of voids in the framework with van der Waals spheres (mean diameters 1.5 nm) inside.

Three new copper(II)–squarate coordination polymers, 1-D double-chain $\{Cu(C_4O_4)(H_2O)_2(DMF)\}_n$ (**1**) ($C_4O_4^{2-}$ = dianion of 3,4-dihydroxy-3-cyclobuten-1,2-dione), 3-D network $\{[Cu(C_4O_4)(H_2O)_2]\cdot 0.33H_2O\}_n$ (**2**), and 3-D network $\{[Cu(C_4O_4)(H_2O)_2]\cdot 0.33CH_3OH\}_n$ (**3**), have been synthesized and characterized structurally. The complexes show altered assembly behavior in different solvent systems, which can further affect the physical properties of the frameworks. Cyclic voltammetry experiments show that **1**, **2**, and **3** have rich redox activities and both Cu(II) ions and squaric acid ligands are involved in redox process. Magnetic characterization on **3** shows the effect of weak antiferromagnetic exchange.

Keywords: Squaric acid; Copper; Crystal structure; Redox properties; Magnetism

1. Introduction

Coordination polymers, also known as metal organic frameworks (MOFs), have flexible structures and functional applications [1]. However, controllable synthesis of MOFs is a

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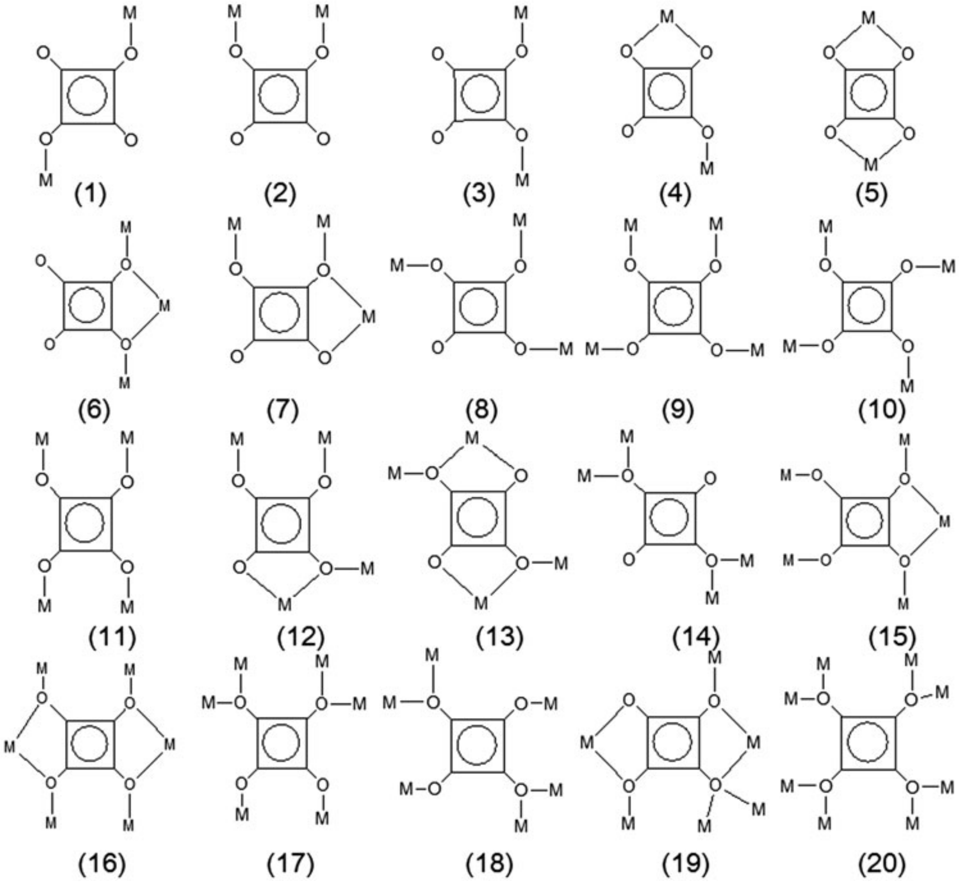
*Corresponding authors. Email: zhoujl@csu.edu.cn (J.-L. Zhou); yanjun@csu.edu.cn (J. Yan) challenge since many factors affect self-assembly, such as the chemical structure of the ligands chosen, the coordination geometry preferred by the metal, reaction temperature, counter ions, solvent system, pH, metal-to-ligand ratio, and methods of crystallization [2]. Solvent is a crucial parameter in influencing the formation of the MOFs, leading to their structural and dimensional variations [3], supra-molecular isomerism [4], and new topologies based on variation of the conformations of ligands [5]. Systematic investigation of the effect of solvent on self-assembly of complexes with the highly symmetrical multi-topic ligands still remains unexplored.

The present study constructs a series of complexes from highly symmetrical polyfunctional units such as squarate dianion. The squarate possesses a four-membered cyclic aromatic structure characterized by extensive π electron delocalization over the carbons and oxygens, which has been widely used as a bridging ligand with various coordination modes (μ^2 to μ^8 bridges shown in scheme 1) to build up coordination polymers with novel extended networks [6]. The planar D_{4h} structures of squarate have been well established. By changing the counter ions in the polyoxothioanion system with squarate template, a series of new clusters such as chiral $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ and $[(Mo_2O_2S_2)_2(OH)_2(C_4O_4)]$



Scheme 1. Coordination modes of squarate on the construction of coordination polymers.

polyoxothiometalate building blocks are isolated [7]. Herein, we focus on assembly of copper(II)–squarate complexes. By varying the reaction solvent, three new copper(II)–squarate coordination polymers, 1-D double-chain $\{Cu(C_4O_4)(H_2O)_2(DMF)\}_n$ (**1**), 3-D cage-like network $\{[Cu(C_4O_4)(H_2O)_2]\cdot 0.33H_2O\}_n$ (**2**), and 3-D network $\{[Cu(C_4O_4)(H_2O)_2]\cdot 0.33CH_3OH\}_n$ (**3**), are isolated, in which the coordinated solvent molecules in the framework decrease from two water molecules and one DMF molecule in **1** to two water molecules in **2** and **3**. Variation of coordination and guest solvent molecules affects the structures of the complexes, as well as the electrochemical, thermodynamic, and magnetic properties. Unexpectedly, the guest solvent molecules in the frameworks can also influence the electrochemical properties.

2. Experimental section

2.1. *Materials and instruments*

All reagents were commercially available and used without purification. IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer with KBr pellets from 4000 to 400 cm^{-1}. Elemental analyses were performed on a Perkin-Elmer 240C Elemental Analyzer. UV spectra were recorded on a UV-2450 ultraviolet spectrophotometer from 200 to 700 nm. Powder X-ray diffraction measurements were performed on a Rigaku D/max 2500 X-ray diffractometer. Crystal structure determination was carried out on a Bruker SMART-APEX 1000 area-detector diffractometer. Thermogravimetric analyses were performed from 20 to 800 K at a heating rate of 10 K min^{-1} under Ar. Electrochemical experiments were carried out at room temperature using a CHI 660/700E Electrochemical workstation. Magnetic susceptibility data were obtained on polycrystalline samples using a Quantum Design MPMS-XL7 SQUID magnetometer. Data were recorded in 1000 Oe field while warming the samples from 1.8 to 300 K. Diamagnetic corrections were made for both the sample holder and the compound estimated from Pascal's constants [8].

2.2. *Synthesis*

2.2.1. Preparation of $\{Cu(C_4O_4)(H_2O)_2(DMF)\}_n$ (1). A mixture of $CuCl_2\cdot 2H_2O$ (17.4 mg, 0.1 mM) and squaric acid (12.2 mg, 0.1 mM) were taken in DMF and stirred for 6 h at ambient temperature. The mixture was filtered immediately and the filtrate was placed at room temperature until dark green crystals with needle-like morphology of **1** suitable for X-ray crystallographic analysis were collected after 1 week and washed with methanol and Et_2O, yield 47.5% (based on Cu). Anal. Calcd for **1** ($C_7H_{11}CuNO_7$) (%): C, 29.5; H, 3.86; N, 4.91. Found (%): C, 30.19; H, 3.89; N, 5.02. FT-IR (KBr, cm^{-1}): 3427(w), 2892(m), 1498(vs), 1100(s), 948(s), 762(s), 469(w), 421(w).

2.2.2. Preparation of $\{Cu(C_4O_4)(H_2O)_2\cdot 0.33H_2O\}_n$ (2). A mixture of $CuCl_2\cdot 2H_2O$ (120 mg, 0.70 mM) and squaric acid (90 mg, 0.80 mM) was added to solution of 60 mL CH_3OH/H_2O (10 : 1, v/v). The solution was stirred thoroughly 6 h at ambient temperature and the solution turned from light green to greenish yellow. The mixture was filtered, and the filtrate evaporated at room temperature until green square plate crystals were obtained after 3 days with an yield of approximate 62.4% (based on Cu). Anal. Calcd for **2** ($C_4H_{4.66}CuO_{6.33}$) (%): C, 22.05; H, 2.12. Found (%): C, 22.02; H, 2.14. FT-IR (KBr, cm^{-1}): 3083(s), 2237(w), 1605(vw), 1799(vs), 1100(s), 857(w), 743(w), 654(w), 471(w).

2.2.3. Preparation of {[Cu(C_4O_4)(H_2O)$_2$]·0.33CH_3OH}$_n$ (3). A mixture of $CuCl_2·2H_2O$ (174 mg, 1 mM) and squaric acid (114 mg, 1 mM) were taken in 50 mL methanol to give a green solution. The mixture was stirred for 12 h at room temperature. Dark green square plate crystals of **3** suited for single crystal X-ray diffraction were obtained after 3 days with an yield of approximate 68% (based on Cu). Anal. Calcd for **3** ($C_{4.33}H_{5.32}CuO_{6.33}$) (%): C, 23.37; H, 2.35. Found (%): C, 23.35; H, 2.39. FT-IR (KBr, cm^{-1}): 3060(s), 2242(w), 1804 (m), 1499(vs), 1097(s), 990(w), 961(m), 785(w), 685(w), 469(m), 430(w), 408(w).

2.3. *X-ray crystallography*

A selected crystal of **1–3** was mounted on a glass fiber capillary which was put on a Bruker SMART-APEX 1000 area-detector diffractometer with a CCD detector using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Absorption corrections were applied using multiscan program SADABS [9]. The structures were solved by

Table 1. Details of the crystallographic data collection, structural determination, and refinements for **1–3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_7H_{11}CuNO_7$	$C_4H_4CuO_6$	C_4CuO_6
Formula weight	284.71	211.61	207.58
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Trigonal	trigonal
Space group	*P21/c*	*R-3*	*R-3*
a (Å)	11.187(2)	11.7555(3)	22.9554(5)
b (Å)	7.7450(13)	11.7555(3)	22.9554(5)
c (Å)	12.060(2)	14.8987(7)	14.0645(4)
α (°)	90.00	90.00	90.00
β (°)	103.960(10)	90.00	90.00
γ (°)	90.00	120.00	120.00
V (Å^3)	1014.0(3)	1783.04(11)	6418.4(3)
Z	4	9	36
Calculated density (Mg m^{-3})	1.865	1.774	1.933
μ (mm^{-1})	2.175	2.738	3.041
θ (°)	3.15–25.99	4.85–25.98	2.8–25.97
F(0 0 0)	580	945	3636
Index ranges	$-12 \le h \le 13$	$-14 \le h \le 14$	$-28 \le h \le 28$
	$-9 \le k \le 8$	$-14 \le k \le 14$	$-28 \le k \le 28$
	$-14 \le l \le 9$	$-18 \le l \le 18$	$-17 \le l \le 17$
Reflections collected	6501	6679	35,176
Independent reflections	1987	753	2796
R_{int}	0.0281	0.0411	0.0974
Data/restraints/parameters	1987/0/167	753/42/58	2796/491/234
Goodness-of-fit on F^2	1.049	1.359	1.064
Final R indices [$I > 2\sigma(I)$]^{a,b}	$R_1 = 0.0296$	$R_1 = 0.0429$	$R_1 = 0.1315$
	$wR_2 = 0.0679$	$wR_2 = 0.1218$	$wR_2 = 0.3226$
R indices (all data)	$R_1 = 0.0460$	$R_1 = 0.0444$	$R_1 = 0.1320$
	$wR_2 = 0.0757$	$wR_2 = 0.1238$	$wR_2 = 0.3231$

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $^bwR_2 = \sum\left[w(F_o^2 - F_c^2)^2/\sum\left[w(F_o^2)^2\right]\right]^{1/2}$.

direct methods and refined with a full-matrix least-squares technique using SHELXTL-97 [10]. All non-hydrogen atoms were refined with anisotropic displacement parameters; Carbon-bonded hydrogens were included in calculated positions and refined in the riding mode. Crystallographic data and details of data collections and structure refinements of **1–3** are listed in table 1.

3. Result and discussion

3.1. *Structural description*

3.1.1. Structure of $\{Cu(C_4O_4)(DMF)(H_2O)_2\}_n$ (1). The X-ray analysis of **1** shows that it crystallized in the monoclinic space group $P2_1/c$ and each Cu(II) coordinated with two squarate ligands, three water molecules, and one DMF. The squarate ligands are μ-1,3-bridging and are *trans* coordinated to form a polymer chain unit. This Cu(II) complex exhibits the expected Jahn–Teller distortion with four equatorial Cu–O distances from 1.970 (2) to 1.994(2) Å, and the axial bond length to DMF of 2.345(2) Å and to the water ligand of 2.569(2) Å. The equivalent bond lengths within the squarate ligand are comparable to those previously reported in the literature [11]. However, the chain unit is further condensed to form a double-chain structure by sharing two coordination waters, forming the $\{Cu_2(H_2O)_4(DMF)_2\}$ linker, as shown in figure 1, which is different from $Cu(C_4O_4)(DMF)_2(H_2O)_2$ isolated in the similar system with the existence of organic cations (tetraethylammonium aminosquarate) [12]. The chain propagation occurs along the crystallographic *c* direction with a Cu…Cu separation of 7.745(1) Å and an associated contraction of the Cu–O–C (squarate) angle of 132.0(1)°, as well as the Cu…Cu separations in $\{Cu_2(H_2O)_4(DMF)_2\}$ is 3.527(1) Å. Further, the polymer chain conformation is stabilized via pairs of inter- /intra-molecular O–H…O hydrogen bonds between one hydrogen of coordinated water and the non-coordinated oxygen on squarate with O…O distance of 2.645(1) Å. The TGA data analysis shows **1** contains no additional guest molecules in the

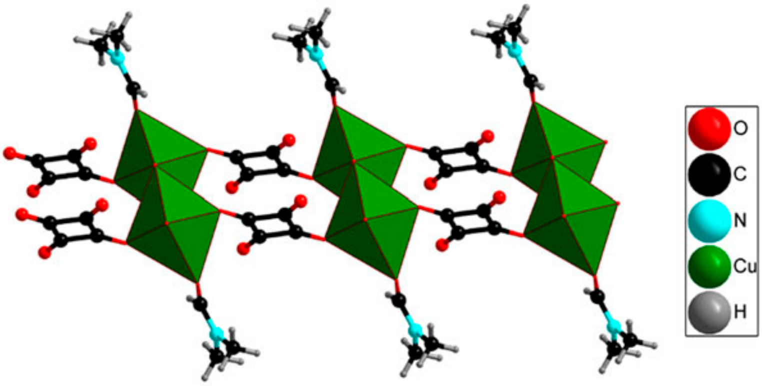


Figure 1. Structural view of the 1-D double-chain of **1**. The DMF and squarate ligands are shown in ball and stick mode, and the $\{CuO_6\}$ units are presented in green polyhedron (Atom color codes: green, Cu; black, C; blue, N; red, O; gray, H) (see http://dx.doi.org/10.1080/00958972.2015.1024113 for color version).

crystal structure. The first weight loss of 17.91% from 171 to 206 °C is attributed to the loss of coordinated H_2O. Dehydration occurs at temperature higher than the boiling point of water due to the coordination of water to metal centers and strong hydrogen bonding interactions. The weight loss of the second stage is 27.53%, due to loss of DMF or decomposition of the framework (see supplemental data).

3.1.2. Structure of $\{Cu(C_4O_4)(H_2O)_2{\cdot}0.33H_2O\}_n$ (2). Attempts to synthesize the analogous complexes under conditions similar to those used in the synthesis of **1** but replacing the DMF with 1 : 10 methanol/water solvent resulted in the formation of **2**, $Cu(C_4O_4)(H_2O)_2{\cdot}0.33H_2O$. The X-ray analysis of **2** shows that it crystallized in the trigonal space group *R-3* and each Cu(II) coordinated with four squarate ligands and two water molecules. The squarate is μ-1,2,3,4-bridging and is *trans* coordinated to form a 3-D network. This pseudo-cubic cage network is similar but differs significantly from those reported by Hall and Robl *et al.* [13]. The differences between the present trigonal structure and the tetragonal structures lie in the relative orientation of the squarate rings on the three pairs of opposite faces of the cubes. Herein, they are all eclipsed in **2**, as shown in figure 2. By contrast in the tetragonal structures of Hall, two of these have eclipsed relationships, while the third is staggered. The coordination mode of $CuC_4O_4{\cdot}2H_2O$ reported by Robl is Cu(II) coordinated with two squarate ligands and four water molecules which is different from **2**. The coordination geometry of **2** at copper is slightly distorted octahedral. There are four long [to the squarate ligands, ranging from 2.142(5) to 2.169(5) Å] and two short Cu–O distances [to the aqua ligands, 1.949(4) and 1.963(4) Å]. The basic building unit of the network is the cage-like $\{(Cu_{12}(C_4O_4)_6\}$ with diameter of 1.5 nm, which is structurally similar to the Keggin-type cluster in polyoxometalate chemistry and contains a water guest. The guest molecules are highly disordered and their positions cannot be precisely located by

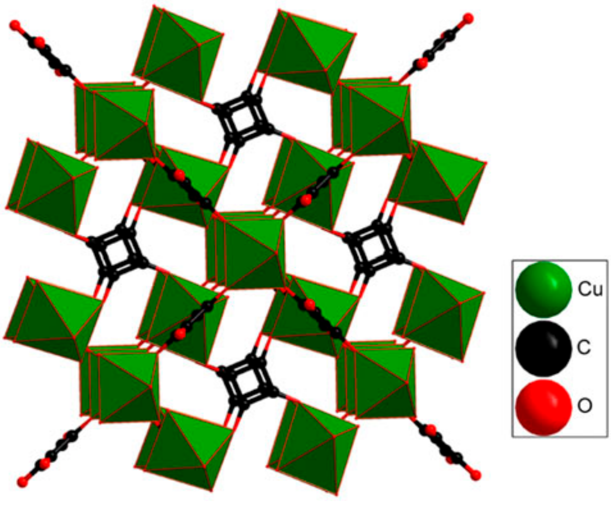


Figure 2. Perspective view of the 3-D cage-like network of **2**. The squarate ligands are shown in ball and stick mode, and the $\{CuO_6\}$ units are presented in green polyhedron. The guest water molecules and hydrogens are omitted for clarity (Atom color codes: green, Cu; black, C; red, O) (see http://dx.doi.org/10.1080/00958972.2015.1024113 for color version).

X-ray diffraction. The TGA data analysis of **2** shows weight loss begins from 195 to 238 °C with 13.14%, which is attributed to the loss of guest water molecules and a portion of coordinated water. The second stage from 276 to 347 °C with 32.56% corresponds to a continuous phase transition. It is reported that dehydration results in a four-coordinate geometry of the metal center which is evidently more stable upon loss of coordinated water molecules and the presence of the coordinated unsaturated metal centers may enable the material to act as a solvent-inclusion compound [14].

3.1.3. Structure of $[Cu(C_4O_4)(H_2O)_2]\cdot 0.33(CH_3OH)$ (3). When Cu(II) reacted with squaric acid in pure methanol, **3** formed as cubic crystals and was isolated. Similar to **2**, single X-ray diffraction analysis shows that **3** forms a 3-D copper–squarate network. However, due to the disordered squarate in the structure, obtaining the detail structural information is not successful yet. As shown in figure 3, the powder X-ray diffraction analyses on this framework confirm its highly crystalline nature, but the pattern data do not well correlate with incorporation of squarate ligands in either pure "staggered" or "eclipsed" orientation. Further, the TGA data analysis shows that **3** contains two coordinated water molecules and methanol guest molecules in the framework with a weight loss of 22.12% between 149 and 202 °C. The second stage of weight loss at 350 °C is missing in the case of **3**, consist with previous reported data on squarate complex with other transition metal ions [15]. Additionally, changing the ratio of squarate and copper ions does not affect the assembly of the complex. When excess squaric acid was added, it crystallized with pure squaric acid without solvent in the structure.

3.2. *IR and UV–vis spectroscopy*

Compounds **1–3** were synthesized by direct mixing of copper(II) salts and squaric acid with different solvents, DMF for **1**, CH_3OH/H_2O for **2**, and pure CH_3OH for **3**, respectively. The

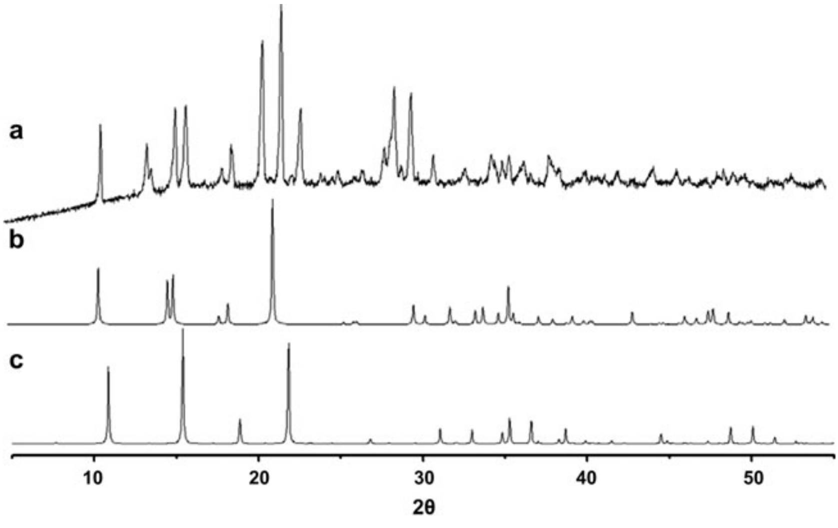


Figure 3. Powder XRD pattern of **3** (a) which is the combination of simulated pure "staggered" (b) and "eclipsed" (c) orientation frameworks.

most relevant IR features are those associated with the different structures of three compounds. The broad absorption peaks at 3000–3400 cm^{-1} are caused by *ν*(N–H) for **1** and *ν*(O–H) for **2** and **3**. A quite strong absorption at 1485, 1527, and 1527 cm^{-1} for **1**, **2**, and **3**, respectively, which are attributed to *ν*(C=O) exhibit blueshift compared with the absorption spectrum of squaric acid, due to coordination with copper. The absorption peaks of *ν*(C–O) which around 1100 cm^{-1} of the three compounds exhibit redshift compared with some other squarate coordination polymers [16]. The IR assignments are consistent with the structural determination. Moreover, the UV–vis spectroscopies of **1** in DMF, **2** in CH_3OH/H_2O (10 : 1, v/v), and **3** in methanol solution show that **1** and **3** have similar absorption peaks, while the λ_{max} of **2** is very weak. This result may be caused by solvation of water and methanol, so that the effect of vibration and rotation in **2** is restricted. The medium intensity absorption around 271 nm of conjugated carbonyl of squaric acid indicates that these compounds have *π*–*π** electron transitions (see supplemental data).

3.3. *Cyclic voltammetry (CV)*

Cyclic voltammetry measurements were performed at room temperature to characterize the redox activities of these three compounds. A three-electrode cell with a magnetic glass carbon electrode, a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode was used for electrochemical measurements. The electrolyte solution was acetonitrile with $TBAPF_6$ as supporting electrolyte. The solution was bubbled with highly pure nitrogen for 15 min before measurements. During the electrochemical processes, charge balance was maintained by migration of PF_6^- into the pores during oxidation and TBA^+ counter-cations into the pores during reduction. The scan rate was at 100 mV s^{-1}. The concentration of the three compounds was kept at 0.01 M in all measurements.

Comparison of the cyclic voltammograms of these three compounds with squaric acid shows that there are oxidation peaks at 0.68 V attributed to squaric acid, while the corresponding reduction peak is −1.09 V (see supplemental data). The squaric acid displays observable irreversible Faradaic redox processes which are sophisticated with three stepwise oxidation processes and one reduction process. In the case of these three compounds, there are all exited Cu(II) → Cu(I) processes with $E_{1/2}$ = 0.7, 0.76, and 0.75 V (figure 4). Both **1**

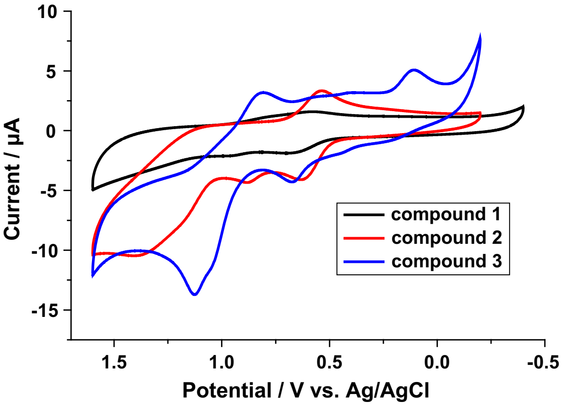


Figure 4. Cyclic voltammogram of **1–3**. The scan rate was at 100 mV s^{-1}.

and **2** are characterized by one reversible redox process with $E_{pa} = 0.86$ V, 0.93 V and $E_{pc} = 0.54$ V, 0.57 V, respectively. The anodic and cathodic regions are similar to corresponding copper complexes, demonstrating that the electronic properties have a significant influence on the electronic communication among redox metal centers [17]. Compound **3** is characterized by two reduction processes at 0.818 and 0.118 V *versus* Ag/Ag^+ and a sharp oxidation at −1.12 V. One plausible reason may be that the guest methanol molecules in this compound also participate in the redox processes.

3.4. *Magnetic properties*

The magnetic susceptibility data of **3** were collected from 1.8 to 300 K (figure 5). The $\chi_M T$ value is 0.435 $cm^3 K M^{-1}$ at 300 K for **3**, which is higher than the spin only value of 0.375 $cm^3 K M^{-1}$ ($g = 2.0$) expected for a total spin $S = 1/2$ [18], owing to mixing of angular momentum from excited states via spin–orbit coupling [19]. As expected, from the Cu (II) d^9 configuration, these data are consistent with the Cu(II) one-spin electron configuration. The $\chi_M T$ decreases continuously with decreasing temperature and when the temperature is below 27.6 K, the $\chi_M T$ decreases rapidly and then reaches a minimum of 0.1268 $cm^3 K M^{-1}$ near 2.7 K. The magnetic susceptibility data fit the Curie–Weiss law with $\theta = -1.559$ K and a Curie constant C of 0.4695 $cm^3 K M^{-1}$ ($s = 1/2$, $g_{ave} = 2.24$), which corresponds to an effective magnetic moment (μ_{eff}) per copper ion of 1.92 BM. These values which are calculated from the slope of $1/\chi_p$ *versus* T have some differences with $\mu_{eff} = 1.76$ BM of $[Cu(OH)_4(C_4O_4)_2]^{6-}$ due to the various coordination modes of squaric acid [20]. Curie constant C of **3** is similar with those expected for a $S = 1/2$ ion of Cu(II)-containing compounds with average g_{ave} ca. ~2.2 [21]. The linear relationship between $1/\chi_p$ and T indicates that the susceptibility is temperature-independent. This result also shows that there is no strong evidence indicating the metal–metal interaction behavior within the frameworks. Consequently, the negative θ value is indicative of antiferromagnetic interactions among copper centers which are logically expected from the geometrical

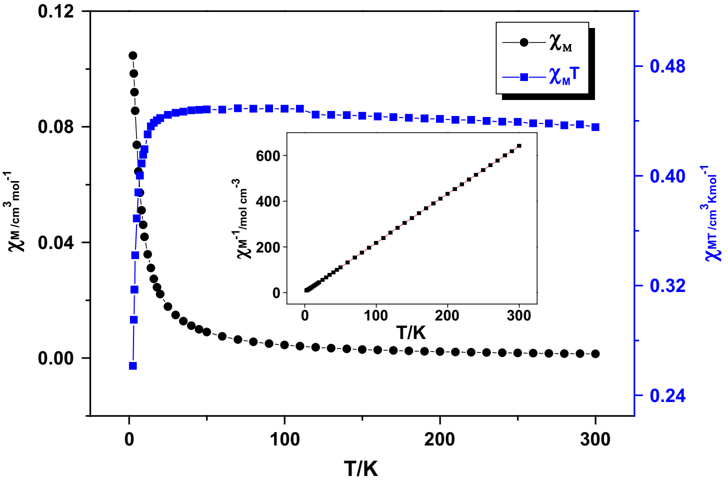


Figure 5. Plots of χ_M, $\chi_M T$ and $\chi_M{}^{-1}$ *vs.* T for **3**.

arrangement of Cu(II) centers, whereas the magnetic exchange interactions of adjacent copper ions mediated through squaric acid ligands are weakly antiferromagnetic.

4. Conclusion

Three new copper(II)-squarate coordination polymers $Cu(C_4O_4)(H_2O)_2(DMF)$ (**1**), $Cu(C_4O_4)(H_2O)_2·0.33H_2O$ (**2**), and $Cu(C_4O_4)(H_2O)_2·0.33CH_3OH$ (**3**) have been synthesized and studied by thermogravimetric analysis, optical spectroscopy, electrochemistry, and magnetism. These compounds coordinating with different solvent molecules have different structures, which are the main reasons affecting their properties. Cyclic voltammetry experiments show that both the Cu(II)ions and squaric acid ligands are involved in redox processes, and **1**, **2**, and **3** have different redox activities. Magnetic study reveals that **3** shows weak antiferromagnetic interactions.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data center, CCDC numbers 1021049, 1021050 and 1021051 for complexes **1–3**. Copies of this information may be obtained free of charge on application from the director, CCDC, 12 Union Road, Cambridge CB@ 1EZ, UK; fax: +44 1223 336033, email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.

Disclosure statement

No potential conflict of interest was reported by the authors.

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Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2015.1024113].

References

[1] (a) D. Lässig, J. Lincke, J. Moellmer, C. Reichenbach, A. Moeller, R. Gläser, G. Kalies, K.A. Cychosz, M. Thommes, R. Staudt. *Angew. Chem. Int. Ed.*, **50**, 10344 (2011); (b) Y. Peng, V. Krungleviciute, I. Eryazici, T.H. Joseph, K.F. Omar, T. Yildirim. *J. Am. Chem. Soc.*, **135**, 11887 (2013); (c) S. Horike, M. Dinca, K. Tamaki, J.R. Long. *J. Am. Chem. Soc.*, **130**, 5854 (2008); (d) Y. Song, C. Massera, O. Roubeau, P. Gamez, A.M. Manotti-Lanfredi, J. Reedijk. *Inorg. Chem.*, **43**, 6842 (2004); (e) J.L. Zhou, Y.Y. Wang, Q. Ling, M.D. Zhang, Q.X. Yang, H.G. Zheng. *CrystEngComm.*, **15**, 616 (2013); (f) D. Liu, C. Poon, K. Lu, C. He, W.B. Lin. *Nat. Commun.*, **5**, 4182 (2014).

[2] (a) Y.T. Wang, H.H. Fan, H.Z. Wang, X.M. Chen. *Inorg. Chem.*, **44**, 4148 (2005); (b) L. Carlucci, G. Ciani, S. Rizzato. *New J. Chem.*, **27**, 483 (2003); (c) G.H. Cui, J.R. Li, J.L. Tian, X.H. Bu, S.R. Batten. *Cryst. Growth Des.*, **5**, 1775 (2005); (d) I.S. Lee, D. MokShin, Y.K. Chung. *Eur. J. Inorg. Chem.*, **10**, 3158 (2004); (e) S.T. Wu, L.S. Long, R.B. Huang, L.S. Zheng. *Cryst. Growth Des.*, **7**, 1746 (2007); (f) X.Q. Lu, J.J. Jiang, C.L. Chen, B.S. Kang, C.Y. Su. *Inorg. Chem.*, **44**, 4515 (2005); (g) D.M. Shin, I.S. Lee, D. Cho, Y.K. Chung. *Inorg. Chem.*, **42**, 7722 (2003).

[3] J. Yang, G.D. Li, J.J. Cao, Q. Yue, G.H. Li. *Eur. J. Inorg. Chem.*, **13**, 3248 (2007).

[4] (a) B. Moulton, M.J. Zaworotko. *Chem. Soc. Rev.*, **101**, 1629 (2001); (b) L. Pérez-García, D.B. Amabilino. *Chem. Soc. Rev.*, **36**, 941 (2007).

[5] (a) P.P. Cui, J.L. Wu, X.L. Zhao, D. Sun, L.L. Zhang, J. Guo. *Cryst. Growth Des.*, **11**, 5182 (2011); (b) X.H. Bu, Y.B. Xie, J.R. Li. *Inorg. Chem.*, **42**, 7422 (2003); (c) L. Carlucci, G. Ciani, D.M. Proserpio. *CrystEng-Comm.*, **4**, 121 (2002).

[6] (a) F. Gándara, B. Gómez-Lor, M. Iglesias, N. Snejko, A. Monge. *Chem. Commun.*, **17**, 2393 (2009); (b) D.S. Yufit, D.J. Price, J.A.K. Howard, S.O.H. Gutschke, A.K. Powell, P.T. Wood. *Chem. Commun.*, **16**, 1561 (1999); (c) R. Vlcente, J. Cano, E. Rulz, S.S. Massoud, F.A. Mautner. *Inorg. Chem.*, **47**, 4648 (2008); (d) C.E. Rowland, C.L. Cahill. *Inorg. Chem.*, **49**, 8668 (2010); (e) B. Zheng, J.F. Bai. *CrystEngComm.*, **11**, 271 (2009); (f) J. Greve, I. Jeß, C. Näther. *J. Solid State Chem.*, **175**, 328 (2003); (g) S. Neeraj, M.L. Noy, C.N.R. Rao, A.K. Cheetham. *Solid State Sci.*, **4**, 1231 (2002).

[7] H.Y. Zang, N.M. Haralampos, L.L. De, R. Benjamin, C. Leroy. *Angew. Chem. Int. Ed.*, **52**, 6903 (2013).

[8] O. Kahn. *Molecular Magnetism*, VCH, New York (1993).

[9] G.M. Sheldrick. *SADABS 2.05*, University of Göttingen, Göttingen (2002).

[10] G.M. Sheldrick. *SHELXL-97: Program for Crystal Structure Solution and Refinement*, University of Göttingen, Göttingen (1997).

[11] (a) I. Castro, M.L. Calatayud, F. Lioret, J. Sletten, M. Julve. *J. Chem. Soc., Dalton Trans.*, 2397 (2002); (b) H. Grove, J. Sletten, M. Julve, F. Lloret, J. Cano. *J. Chem. Soc., Dalton Trans.*, 259 (2001); (c) C.H. Yang, C.M. Chuo, G.H. Lee, C.C. Wang. *Inorg. Chim. Acta.*, **6**, 135 (2003); (d) C.E. Xanthopoulos, M.P. Sigalas, G.A. Katsoulos, C.A. Tsipis, C.C. Hadjikostas, A. Terzis, M. Mentzafos. *Inorg. Chem.*, **32**, 3743 (1993).

[12] 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).

[13] (a) H.A. Hosein, H. Jaggernauth, B.D. Alleyne, L.A. Hall. *Inorg. Chem.*, **38**, 3716 (1999); (b) C. Robl, A. Weiss. *Z. Naturforsch.*, **41b**, 1341 (1986).

[14] T.K. Maji, G. Mostafa, S. Sain, J.S. Prasad, N.R. Chaudhuri. *CrystEngComm.*, **3**, 155 (2001).

[15] P.M. Usov, T.D. Keene, D.M. D'Alessandro. *Aust. J. Chem.*, **66**, 429 (2013).

[16] C.C. Wang, W.C. Chung, H.W. Lin, S.C. Dai, J.S. Shiu, G.H. Lee, H.S. Sheu. *CrystEngComm.*, **13**, 2130–2136 (2011).

[17] (a) M. Tümer, D. Ekinci, F. Tümer, A. Bulut. *Spectrochim Acta A.*, **67**, 916 (2007); (b) D.F. Li, S. Li, D. Yang, J.H. Yu, J. Huang, Y.Z. Li, W. Tang. *Inorg. Chem.*, **42**, 6071 (2003); (c) H.Y. Zang, N.M. Haralampos, Y. Jun, D.L. Long. *J. Am. Chem. Soc.*, **134**, 11376 (2012).

[18] (a) O. Kahn. *Molecular Magnetism*, VCH, New York (1993); (b) R.L. Carlin, K. Kopinga, O. Kahn. *Inorg. Chem.*, **25**, 1786 (1986).

[19] (a) L.H. Xu, H.X. Wang, L.N. Zhu. *J. Coord. Chem.*, **65**, 1051 (2012); (b) T. Garber, S.V. Wallendael, D.P. Rillema, M. Kirk, W.E. Hatfield, J.H. Welch, P. Singh. *Inorg. Chem.*, **29**, 2863 (1990); (c) M. Liang, W.Z. Wang, Z.Q. Liu, D.Z. Liao, Z.H. Jiang, S.P. Yan, P. Cheng. *J. Coord. Chem.*, **56**, 1473 (2003).

[20] G.M. Frankenbach, M.A. Beno, A.M. Kini. *Inorg. Chim. Acta.*, **192**, 195 (1992).

[21] (a) R. Cini, P. Colamarino, P.L. Orioli, L.S. Smith, P.R. Newman, H.D. Gillman. *Inorg. Chem.*, **16**, 3223 (1977); (b) F. Costantino, T. Bataille, N. Audebrand, E.L. Fur. *Cryst. Growth Des.*, **7**, 1881 (2007); (c) Y. Akhriff, J. Server-Carrió, A. Sancho, J. García-Lozano, E. Escrivá. *Inorg. Chem.*, **40**, 6832 (2001); (d) J.L. Zhou, M.M. Wang, Y.Y. Wang, H.W. Yang, K.J. Zhong. *J. Coord. Chem.*, **66**, 772 (2013); (e) I. Castro, M.L. Calatayud, J. Sletten, F. Lioret, M. Julve. *Inorg. Chim. Acta.*, **287**, 173 (1999).