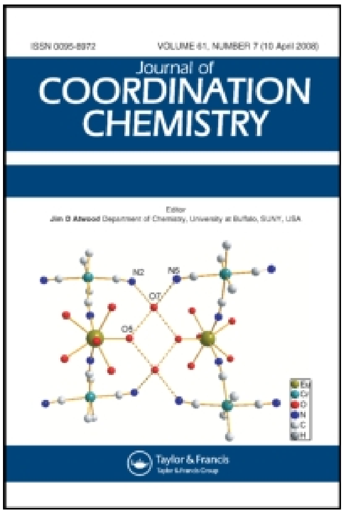

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Speciation and transformation in the synthesis of $Cu_4(im)_4(C_4O_3H_6)_2(NO_2)_4(H_2O)_4$ and $[(phen)Cu(C_2O_4)(H_2O)] \cdot H_2O$

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Speciation and transformation in the synthesis of $Cu_4(im)_4(C_4O_3H_6)_2(NO_2)_4(H_2O)_4$ and $[(phen)Cu(C_2O_4)(H_2O)] \cdot H_2O$

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Two complexes, $Cu_4(im)_4(C_4O_3H_6)_2(NO_2)_4(H_2O)_4$ (**1**), $[(phen)Cu(C_2O_4)(H_2O)] \cdot H_2O$ (**2**) (im = imidazole, phen = 1,10-phenanthroline), were synthesized and structurally characterized by elemental analysis, IR, UV, TG and single crystal X-ray diffraction. During the synthesis of compound **1**, citric acid lost two of its carboxylato groups and was decomposed into 3-hydroxybutanoic acid, the NO_3^- ions were reduced to NO_2^- ions. In compound **1**, a tetranuclear Cu(II) complex was built up of four Cu(II) ions connected by two 3-hydroxybutanoic anions. In the preparation of compound **2**, tartaric acid was decomposed into oxalic acid. Compound **2** is constructed by one phen, one oxalic anion and one water molecule coordinated directly to Cu(II).

Keywords: Copper; Citric acid; Tartaric acid; Crystal structure; Synthesis; Speciation

1. Introduction

Citrate is widespread in nature and has many applications in different fields [1]. With three carboxylato groups and one hydroxyl present, citric acid can exhibit different coordination modes and interesting chemical reactivity. A series of metal-citrate complexes have been reported [2–34]. However, in the previous work, a nitrogen donor, which can block the extension of multi-dimensional architectures, was rarely introduced into such complexes [35–37]. We attempted to synthesize a complex in which citric acid and imidazole act as oxygen donor and nitrogen donor. Citric and tartaric acids, can easily lose their carboxylato groups at higher temperature [38], however, previous work rarely reported the transformations during synthesis. In the presence of NO_3^- under hydrothermal condition, citric acid lost two of its carboxylato groups and decomposed into 3-hydroxybutanoic acid (scheme 1a) and NO_3^- was reduced to NO_2^- during the synthesis of compound **1**. Tartaric acid, a good chiral ligand for metal coordination

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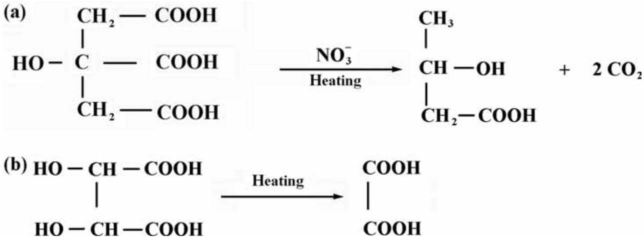

Scheme 1. Speciation and transformations in the synthesis of compounds **1** (a) and **2** (b).

compounds is stable when conventional methods are utilized [39–49], but was decomposed into oxalic acid (scheme 1b) under hydrothermal condition during synthesis of compound **2**.

2. Experimental

2.1. *Materials and methods*

All chemicals purchased were of reagent grade and used without further purification. C, H, and N elemental analyses were performed on a Perkin-Elmer 240c elemental analyzer. Infrared spectra were recorded as KBr pellets on a Nicolet 170SXFT/IR spectrometer. UV spectra were measured on an Analytikjena Specord 2000 UV spectrophotometer. TG analyses were carried out under nitrogen between 50 and 600°C with a heating rate of $10^\circ\mathrm{C\,min^{-1}}$ on a ZRY-2P simultaneous thermal analyzer. X-ray power diffraction (XRD) patterns were obtained on a Japan Rigaku D/max γA X-ray diffractometer equipped with graphite monochromatized Cu-Kα radiation ($\lambda = 0.154060$ nm). The 2θ range used was from 10–80° in steps of $4^\circ\,\mathrm{min^{-1}}$.

2.2. *Synthesis of $Cu_4(im)_4(C_4O_3H_6)_2(NO_2)_4(H_2O)_4$ (1)*

A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.5 mmol, 0.1208 g), citric acid (0.5 mmol, 0.1051 g), imidazole (1 mmol, 0.068 g) and H_2O (12 mL) was adjusted to pH = 6.54 by 2 N NaOH aqueous solution. The synthesis was carried out in a Teflon-lined autoclave. The reaction mixture was heated at 115°C for three days, followed by slow cooling to room temperature. The resulting blue solution was filtered and left to stand undisturbed. Upon slow evaporation at room temperature for three days, blue block single crystals were collected (yield: ca 90% based on Cu). Elemental Anal. Found: C, 24.51; H, 3.83; N, 16.23%. Calcd for $Cu_4C_{20}N_{12}H_{36}O_{18}$: C, 24.29; H, 3.64; N, 17.00%. IR (KBr, $\mathrm{cm^{-1}}$): 3421(s), 3167(m), 3067(w), 2931(m), 2855(m), 1581(s), 1412(m), 1392(m), 1324(w), 1076(m), 955(w), 853(w), 754(m), 652(s).

2.3. *Synthesis of $[(phen)Cu(C_2O_4)(H_2O)] \cdot H_2O$ (2)*

A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.5 mmol, 0.1208 g), tartaric acid (0.5 mmol, 0.075 g), phen (0.5 mmol, 0.099 g) and H_2O (12 mL) was adjusted to pH = 6.17 by 2 N NaOH

Table 1. Crystal data and structure refinements for compounds **1** and **2**.

Compound	**1**	**2**
Formula	$Cu_4C_{20}N_{12}H_{36}O_{18}$	$CuC_{14}N_2H_{12}O_6$
M	923.64	367.80
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$P2_1/n$
a (Å)	11.87(2)	8.430(2)
b (Å)	21.66(4)	9.659(3)
c (Å)	7.71(15)	17.427(3)
α (°)	90	90
β (°)	116.76(3)	103.9970(10)
γ (°)	90	90
V (Å^3)	1770.0(6)	1376.8(6)
Z	2	4
ρ_{calcd} (g cm^{-3})	1.733	1.774
μ (mm^{-1})	2.455	1.622
$F(000)$	926	748
Goodness-of-fit on F^2	0.927	1.048
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0672$, $wR_2 = 0.1623$	$R_1 = 0.0276$, $wR_2 = 0.0724$
R indices (all data)	$R_1 = 0.1294$, $wR_2 = 0.1995$	$R_1 = 0.0336$, $wR_2 = 0.0769$

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

aqueous solution. The reaction mixture was sealed in a Teflon-lined autoclave and heated at 115°C for three days, followed by slow cooling to room temperature. The resulting green block crystals of compound **2** were isolated by mechanical separation from a green amorphous solid, then washed with water (yield: ca 90% based on Cu). Elemental Anal. Found: C, 45.88; H, 3.33; N, 7.75%. Calcd for $CuC_{14}N_2H_{12}O_6$: C, 45.78; H, 3.27; N, 7.63%. IR (KBr, cm^{-1}): 3419(m), 3045(w), 2911(w), 1639(s), 1503(w), 1413(m), 1321(s), 1222(w), 1134(w), 831(s), 775(s), 720(s), 519(s).

2.4. *Crystallographic studies*

Single crystals of dimensions $0.36 \times 0.33 \times 0.31\,mm^3$ for compound **1**, $0.35 \times 0.33 \times 0.28\,mm^3$ for compound **2** were used for structure determination. XRD data of compounds **1** and **2** were collected on a Bruker-AXS CCD area detector-equipped diffractometer with graphite-monochromatized Mo-Kα ($\lambda = 0.71073$ Å) radiation at room temperature. A total of 4114 (1544 unique, $R_{int} = 0.0905$) reflections of compound **1** ($-14 \le h \le 11$, $-25 \le k \le 24$, $-9 \le l \le 8$, $2.14 < \theta < 25.01$), a total of 6894 (2422 unique, $R_{int} = 0.0350$) reflections of compound **2** ($-9 \le h \le 9$, $-10 \le k \le 11$, $-20 \le l \le 20$, $2.43 < \theta < 25.03$) were measured. An empirical absorption correction from ψ scan was applied. Both structures were solved by direct methods and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were added in their calculated positions. All calculations were performed using the SHELXTL-97 program [50, 51]. The CCDC reference numbers are the following: 254,056 for compound **1**, 255,633 for compound **2**. Their crystallographic details are summarized in table 1. Selected bond lengths and angles of compounds **1** and **2** are listed in tables 2 and 3. Distances and angles involving selected hydrogen bonding interactions of compound **2** are shown in table 4.

Table 2. Selected bond lengths (Å) and angles (°) for compound **1**.

Cu(1)–O(4)	1.971(6)	Cu(1)–O(1)	1.940(4)
Cu(1)–O(2)	1.962(6)	Cu(1)–N(1)	1.970(8)
O(1)–Cu(1)#1	1.940(4)	O(4)–C(4)	1.229(7)
C(4)–C(3)	1.539(13)	C(3)–C(1)#2	1.52(2)
O(1)–Cu(1)–O(2)	88.8(3)	O(1)–Cu(1)–N(1)	172.9(3)
O(2)–Cu(1)–N(1)	87.8(3)	O(1)–Cu(1)–O(4)	93.3(3)
O(2)–Cu(1)–O(4)	165.3(3)	N(1)–Cu(1)–O(4)	88.4(3)
Cu(1)–O(1)–Cu(1)#1	128.2(4)	C(1)–O(1)–Cu(1)	115.8(2)
O(1)–C(1)–C(3)#2	116.3(13)	C(1)#2–C(3)–C(4)	110.4(11)
C(4)–O(4)–Cu(1)	135.3(6)	C(2)–C(1)–O(1)	119.4(17)
C(2)–C(1)–C(3)#2	124.3(17)	O(4)–C(4)–O(4)#1	126.3(10)

Symmetry transformations used to generate equivalent atoms, #1: x, $-y+2$, z #2: $-x+2$, $-y+2$, $-z+2$.

Table 3. Selected bond lengths (Å) and angles (°) for compound **2**.

Cu(1)–O(3)	1.9323(15)	Cu(1)–O(1)	1.9347(16)
Cu(1)–N(1)	1.9967(18)	Cu(1)–N(2)	2.0078(18)
Cu(1)–O(5)	2.207(2)	N(2)–C(12)	1.322(3)
O(1)–C(1)	1.266(3)	O(3)–C(2)	1.274(3)
O(2)–C(1)	1.216(3)	O(4)–C(2)	1.212(3)
C(1)–C(2)	1.554(4)	N(1)–C(7)	1.350(3)
C(4)–C(5)	1.361(3)	C(9)–C(14)	1.431(3)
N(1)–Cu(1)–N(2)	82.08(8)	O(3)–Cu(1)–O(1)	84.90(7)
O(3)–Cu(1)–O(5)	94.83(8)	O(1)–Cu(1)–N(2)	167.77(8)
N(2)–Cu(1)–O(5)	95.64(8)	C(7)–N(1)–Cu(1)	112.73(15)
C(2)–O(3)–Cu(1)	112.91(15)	C(2)–O(3)–Cu(1)	112.91(15)

Table 4. Distances (Å) and angles (°) involving selected hydrogen bonding for compound **2**.

19	H	B	A–H distance	H···B distance	A···B distance	∠A–H···B
O(5)	H(15)	O(1)	0.815	2.514	2.945	163.7
O(5)	H(16)	O(6)	0.855	1.886	2.739	174.7
O(6)	H(17)	O(3)	0.827	2.054	2.873	170.6
O(6)	H(18)	O(2)	0.814	2.256	3.004	153.0
C(10)	H(10)	O(4)	0.930	2.361	3.205	150.9

3. Results and discussion

3.1. *Synthesis*

Hydrothermal synthesis proved a useful technique in preparation of solid-state oxides. In a relatively low temperature and autogenous pressure environment, problems of different solubility for ligands are minimized. In our cases, such method was involved in the synthesis of both **1** and **2**. Compound **1** was synthesized by hydrothermal technique combined with conventional method. Such new routine was the first time to be introduced into the preparation of metal-citrate complexes. The temperature and the autogenous pressure in sealed autoclave play important roles in the synthesis of compound **1**. In order to keep the boiling state of solvent water, the temperature cannot be lower than 100°C. As we know, citric acid, as a kind of alcoholic acid can easily lose carboxylato groups at higher temperature [38]. Considering the relatively lower temperature in the prior work [2–34], we chose 115°C as the temperature of the hydrothermal reaction. Other counter anions such as SO_4^{2-}, CH_3COO^-, or Cl^- were introduced instead of NO_3^- in parallel experiments, but the corresponding products cannot be obtained, which indicates that the reaction is closely related with the nature of counter anion. The NO_3^- ions can act as oxidants and be reduced to NO_2^- ions under weak acidic condition [52], assisting in decomposition of citric acid. The preparation of compound **1** was dependent on the molar ratio of reactants and not related to the reaction pH as long as it was weakly acidic. We examined molar ratios of citric acid and imidazole of 1 : 1, 1 : 2 and 1 : 3; compound **1** only can be obtained from the 1 : 2 molar ratio.

In the synthesis of compound **2**, tartaric acid decomposed into oxalic acid. Compound **2** can be obtained when NO_3^- ions were replaced by other anions such as Cl^-, SO_4^{2-}, CH_3COO^-, which indicated that the decomposition of tartaric acid had nothing to do with the counter anions and was only related with the intrinsic characteristics of tartaric acid. The crystallization of compound **2** was susceptible to the reaction pH value, when the pH value was adjusted above 8 or below 4, the crystals of compound **2** were not obtained in good quality.

According to literature [53, 54], compound **2** can also be synthesized when oxalic acid was used as the starting material, which indicated that the first step was decomposition of tartaric acid into oxalic acid. Tartaric acid is stable under routine conditions [39–49] and hydrothermal technique was first used in the synthesis of compound **2** in the present work [53, 54], that the hydrothermal temperature (above 100°C) and autogenous pressure in a sealed autoclave for several days played an important role in the decomposition of tartaric acid.

3.2. *Description of crystal structures*

As shown in scheme 1(a) and figure 1(a), citric acid lost two carboxylato groups and was decomposed into 3-hydroxybutanoic acid. The NO_3^- ions were reduced to NO_2^- ions in the synthesis of compound **1**. One oxygen atom of the NO_2^- ion has two positions owing to the crystallographic disorder of O(3) and O(3A). Their occupancy factors are 60 and 40%, respectively. Compound **1** consists of a tetranuclear Cu(II) structure, which is built from four Cu(II) ions connected by two 3-hydroxybutanoic anions. The four Cu(II) are coplanar and only one of them is crystallographically unique. The Cu1 ··· Cu1A and Cu1 ··· Cu1C distances are 3.491 and 3.914 Å, respectively. Cu(1) exhibits a square-planar geometry and is four coordinate with one nitrogen and three oxygen atoms. N(1) is from imidazole ligand. Two oxygen atoms O(1) and O(4) are from the hydroxyl and carboxylato group of two 3-hydroxybutanoic anions, respectively. O(2) is from NO_2^- (figure 1a). The Cu–O distances range from 1.940(4)–1.971(6) Å. The Cu–N bond length is 1.970(8) Å. Valence sum calculation shows that the copper in compound **1** is +2 [55]. The carboxylato group of

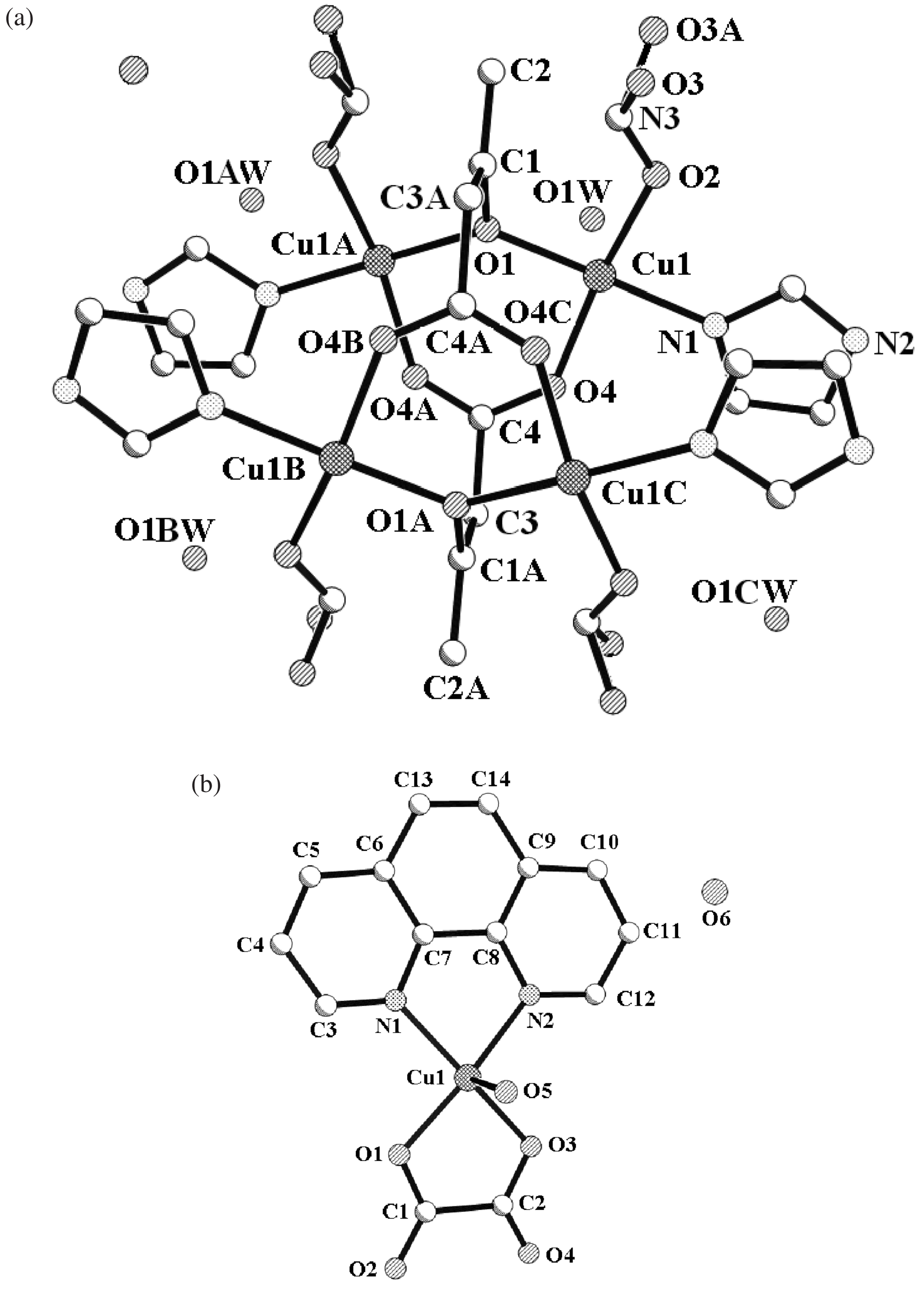

Figure 1. Ball and stick representation of $Cu_4(im)_4(C_4O_3H_6)_2(NO_2)_4(H_2O)_4$ (**1**) (a) and $[(phen)Cu(C_2O_4)(H_2O)]\cdot H_2O$ (**2**) (b) H atoms omitted for clarity.

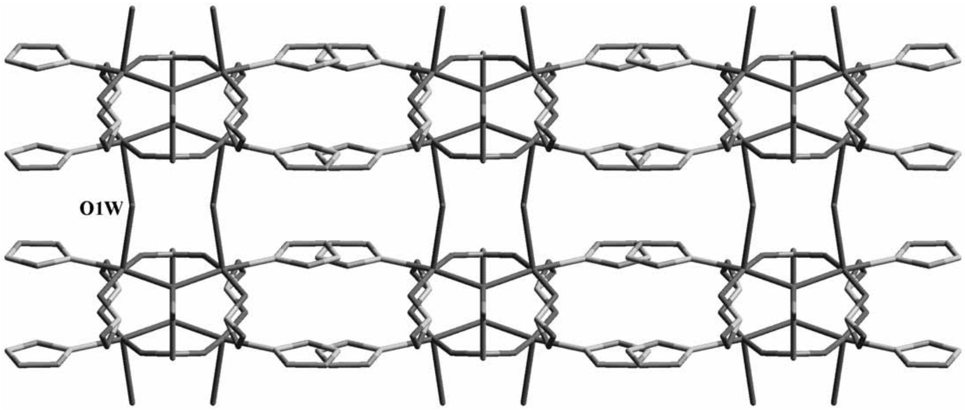

Figure 2. One dimensional chain in compound **1** formed by tetranuclear Cu(II) complexes connected via oxygen-bridge (H atoms omitted for clarity).

3-hydroxybutanoic anion links two Cu(II) via bidentate coordination. The oxygen atom from hydroxyl group is μ_2–O, connecting another two Cu(II). The flexible carbon chain of 3-hydroxybutanoic anion (for example, the bond angles of C(3A)–C(1)–O(1), C(1A)–C(3)–C(4) are 116.3(13)°, 110.4(11)°, respectively) makes it possible to form the tetranuclear Cu(II) complex in which the two symmetrical 3-hydroxybutanoic anions are *cis*, *cis*-conformations. In the tetranuclear Cu(II) complex, two equivalent six membered rings are observed, each of which is built up of two Cu(II) centers linked by one hydroxyl and one carboxylato group from different 3-hydroxybutanoic anions (figure 1a).

Figure 2 shows a view down the *a* axis with the oxygen atoms from water molecules connecting each tetranuclear Cu(II) complex via weak oxygen-bridges (the Cu–O distance is 2.507 Å) to form a one-dimensional chain (figure 2).

In the preparation of compound **2**, tartaric acid was decomposed into oxalic acid. There is one dissociated water molecule in the crystal. Cu(1) is in a square-pyramidal coordination sphere, coordinated by two nitrogen atoms and three oxygen atoms (figure 1b). N(1) and N(2) are from phen molecule, O(5) is from water, O(1) and O(3) are from oxalic dianions and the oxalic dianions are monodentate. The Cu–O distances range from 1.9323(15) to 2.207(2) Å and the distance of Cu(1)–O(5) is longer than those of Cu(1)–O(1) and Cu(1)–O(3) (table 3). The Cu–N distances are in the range of 1.9967(18)–2.0078(18) Å. Hydrogen bonding interactions exist within ligands and water molecules (table 4 and figure 3).

3.3. *IR spectrum*

The IR spectrum of compound **1** shows characteristic bands of carboxylato groups at 1581 and 1412 $\mathrm{cm^{-1}}$. These bands appear at 1639 and 1413 $\mathrm{cm^{-1}}$ in the IR spectrum of compound **2**. The absence of the characteristic bands around 1700 $\mathrm{cm^{-1}}$ attributed to protonated carboxylato groups in compounds **1** and **2** indicates complete deprotonation

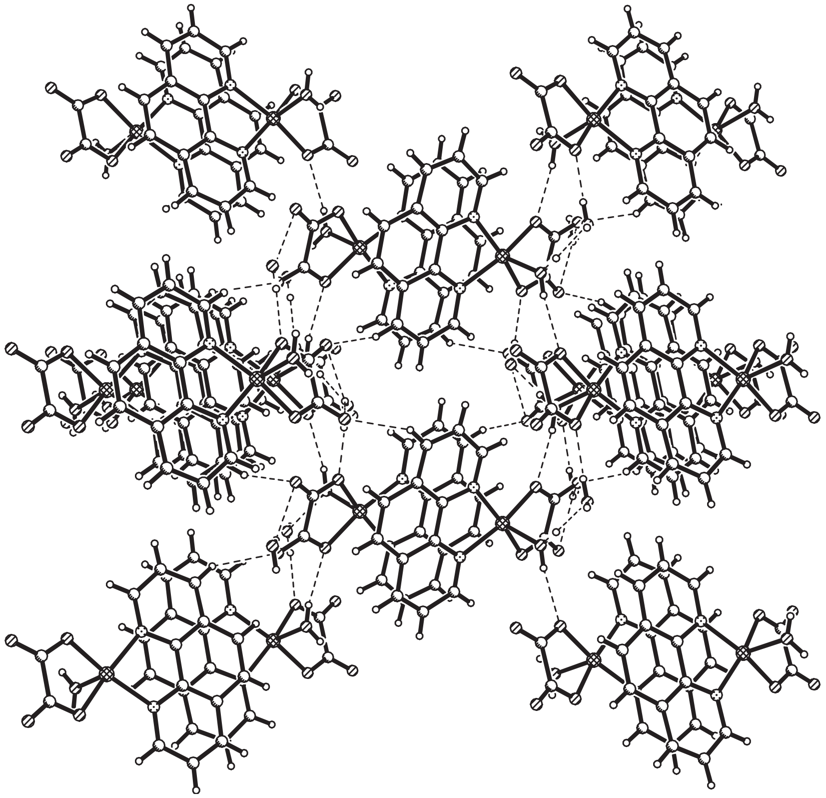

Figure 3. Crystal packing of compound **2** viewed down *a* axis.

upon reaction with Cu^{2+} in the two compounds, in agreement with the single crystal X-ray diffraction analyses [56].

3.4. *UV spectrum*

There is one intense peak at 207 nm attributed to the electron-transfer of carboxylato groups in the UV spectrum of compound **1** with water as solvent. It shifts to 206 nm in the UV spectrum of compound **2**. The intense peak at 271 nm in the UV spectrum of compound **2** is attributed to the delocalized electron-transfer of aromatic phen ring.

3.5. *TG analysis*

Compound **1** is stable at temperatures lower than 270°C (see figure S1 in the supporting information). The TG curve of compound **1** exhibits a steady weight loss under N_2 in the range of 270–580°C, which corresponds to the release of water molecules, NO_2^- and organic ligands (3-hydroxybutanoic anions and imidazole). The weight loss is 60.35%, in accord with the calculated value (59.66%). Compound **2** begins to lose weight at 180°C and does not lose weight above 550°C (figure S2). The total weight loss is

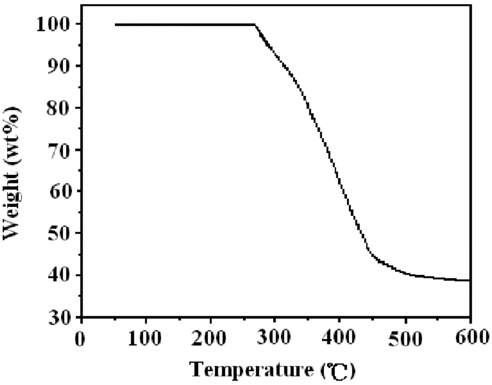

Figure S1.

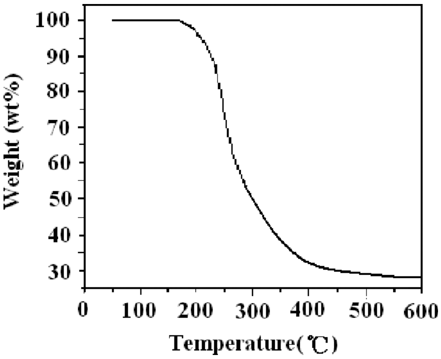

Figure S2.

71.21%, in accord with the calculated value (71.98%), which corresponds to the release of water and organic ligands (oxalic dianions and phen molecule).

Heating compound **1** or **2** at 600°C in air for 2 h yielded black powder. XRD patterns of the black powders (figure S3) can be indexed to pure monoclinic CuO [space group *C*2/*c*] with lattice constants *a*: 4.685 Å, *b*: 3.425 Å, *c*: 5.130 Å and *β*: 99.549° (JCPDS 45-0937), indicating that the final product of both **1** and **2** is CuO after TG analyses.

4. Concluding remarks

In summary, we have synthesized and characterized two complexes $Cu_4(im)_4(C_4O_3H_6)_2(NO_2)_4(H_2O)_4$ (**1**) and $[(phen)Cu(C_2O_4)(H_2O)]\cdot H_2O$ (**2**). Both are involved in speciation and transformation under hydrothermal conditions. The hydrothermal technique is proved again to be a powerful method for the creation of novel inorganic–organic hybrid materials. The speciation and transformation in the synthesis of compound **1** is closely related with nitrate, whereas in the synthesis of compound **2**, it is only related with the hydrothermal condition.

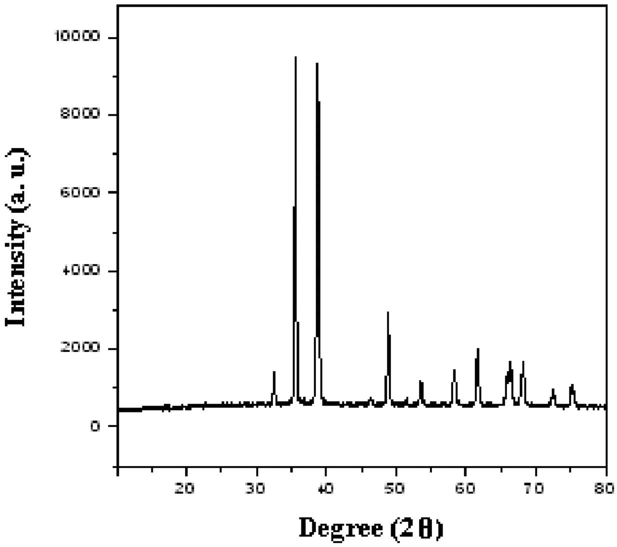

Figure S3.

Supporting material

X-ray crystallographic files in CIF format for the structure determination of compounds **1** and **2** may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: t44-1223-336033; Email: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version.

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