

## Research Article

<http://dx.doi.org/10.21060/cis.2014.211>

# Design, synthesis, structural and spectra characterize of Metal (II) Formate complexes $[M(O_2CH)_2] \cdot n(\text{Solvent})$ (M = Mn, Cu)

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Received: October 26, 2013; accepted: January 18, 2014

**Abstract:** Formate anion is the simplest carboxylate, compared with other carboxylate, it owns more excellent coordination ability. We used  $M(OAc)_2 \cdot n H_2O$  (M=Mn, Cu) as a raw starting material, hydrothermal synthesis methods assisted by DMF hydrolysis which produced the formyl were adopted to prepare metal(II) formates complexes,  $Mn(HCOO)_3 \cdot NH_2(CH_3)_2$  (1) and  $Cu(HCOO)_3 \cdot H_3C_2O_3$  (2). The as-prepared products were characterized by elemental analysis, IR spectroscopy, X-ray single-crystal, powder diffraction and thermogravimetric analysis. Structural analysis shows that complex 1 is three-dimensional grid shapes, and complex 2 is a 1D chain structure.

**Keywords:** Hydrothermal synthesis, Crystal structure, DMF hydrolysis.

## 1. INTRODUCTION

A great deal of attention has been attracted from the designs, synthesis, structure and properties of coordination polymers in recent years, due to their potential applications in the fields of catalysis, molecular electronics, sensor design and optics[1-5]. Carboxylate anion is very versatile ligands in the light of the wide variety of coordination modes, they exhibit in many metal coordination compounds. In the metal-polycarboxylate complexes system, the aliphatic decarboxylate ligands, such as HCOOH,  $H_2C_2O_4$ ,  $HOOC(CH_2)_nCOOH$  and so on, are used with a strong linear bridging ability. Compared to other carboxylates, formate shows minimal steric hindrance, and it was chosen due to its known ability to form 2D or 3D structures. For example,  $[Cu(HCOO)_2(HCOOH)_2]_n$ [6],  $[Fe(O_2CH)_2] \cdot 1/3HCO_2H$ [7],  $[Mn_{12}O_{12}(O_2CCH_3)_{16}(OH_2)_4] \cdot 4H_2O \cdot 2CH_3CO_2H$ [8]. The formate anion is the simplest carboxylate, many compounds have been described in the literatures which are structurally characterized by single-crystal X-ray diffraction, but most reported compounds have been synthesized by the reaction of corresponding metal acetates and formic acid. In order to further study on the various structure and functional property of the

formate complexes, in this work, two complexes were synthesized by the reaction of  $M(OAc)_2 \cdot n H_2O$  (M=Mn, Cu) in the system of  $H_2O/DMF$  at 80 °C. It is worthy to note that in the reaction course, DMF hydrolysis produced the formyl anion, in the mean time, the formyl anion and metal ions assembled *in situ* to form metal formate supermolecular complexes.

## 2. EXPERIMENTAL

### 2.1 General Procedures

All chemicals purchased were of reagent grade or better and used without further purification. IR spectras were recorded on a JASCO FT/IR-480 PLUS Fourier Transform spectrometer with pressed KBr pellets in the range 200–4000  $cm^{-1}$ . The elemental analyses for C, H, and N were carried out on a Perkin Elmer 240C automatic analyzer. Thermogravimetric analyses (TGA) were performed under atmosphere with a heating rate of 10 °C/min on a Perkin Elmer Diamond TG/DTA. X-ray powder diffraction (PXRD) patterns were obtained on a Bruker Advance-D8 equipped with Cu K $\alpha$  radiation ( $\lambda=1.54183\text{\AA}$ ), in the range  $5^\circ < 2\theta < 50^\circ$ , with a step size of  $0.02^\circ$  ( $2\theta$ ) and an count time of  $2\sigma$  per step.

#### 2.1. Preparation of $Mn(HCOO)_3 \cdot NH_2(CH_3)_2$ (1)

A mixture of  $Mn(OAc)_2 \cdot 4H_2O$  (0.1244 g, 0.5 mmol),  $H_2O$  (10 mL, 556 mmol) and DMF (3 mL) were placed in a beaker flask, and stirred for 3 hour at room temperature, then adjusted pH with 1M hydrochloric acid to 4. The mixture was introduced into a reaction kettle and then heated statically at 80 °C for 3 days. Resulting colorless product was then filtered off, washed with water, then dried in air. Anal. Calcd. for  $C_5H_{11}O_6NMn$  (%): C, 25.56 ; H, 4.76 ; N, 5.97 and Found (%): C, 25.44 ; H, 4.70 ; N, 5.93. IR (KBr pellet,  $\nu/cm^{-1}$ ): 3061 (m), 1592 (s), 1469 (w), 1460 (w), 1367 (s) 1349 (s), 1025 (s), 794 (s).

## 2.2. Preparation of $\text{Cu}(\text{HCOO})_3 \cdot \text{H}_3\text{C}_2\text{O}_3$ (**2**)

The preparation is similar to **1** except that  $\text{Cu}(\text{OAc}) \cdot 2\text{H}_2\text{O}$  (0.1088 g, 0.5 mmol) instead of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  was used. Blue crystals of **2** were obtained after washing with water for several times. Anal. Calcd. for  $\text{C}_5\text{H}_6\text{O}_9\text{Cu}$  (%): C, 21.86; H, 2.35. Found(%): C, 21.94; H, 2.21. IR (KBr pellet,  $\text{v}/\text{cm}^{-1}$ ): 3055 (m), 1577 (s), 1472 (w), 1440 (w), 1364 (s), 1341 (s), 1025 (s), 825 (m), 803 (s).

**Table 1** Crystal data of complexes **1** and **2**\*

Complexes	<b>1</b>	<b>2</b>
Formula	$\text{C}_5\text{H}_{11}\text{NO}_6\text{Mn}$	$\text{C}_5\text{H}_6\text{O}_9\text{Cu}$
Molecular weight	236.09	273.64
Crystal system	Trigonal	Monoclinic
Space group	$R\bar{3}c$	$C2/c$
$a$ (Å)	8.3335(6)	13.681(3)
$b$ (Å)	8.3335(6)	8.7192(16)
$c$ (Å)	22.891(3)	8.8542(16)
$\alpha$ (°)	90	90
$\beta$ (°)	90	123.837(2)
$\gamma$ (°)	120	90
$V$ (Å <sup>3</sup> )	1376.7(2)	877.3(3)
$Z$	6	4
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.709	2.072
Crystal size/mm	0.25 × 0.15 × 0.01	0.17 × 0.14 × 0.09
F(000)	726	548
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	1.438	2.523
$\theta$ / (°)	3.34 to 28.76	2.94 to 25.00
Reflections collected	2439	2104
Independent reflections ( $I > 2\sigma(I)$ )	387 (357)	771 (668)
Parameters	25	71
$\Delta(\rho)$ ( $\text{e nm}^{-3}$ )	211 and -238	605 and -543
Goodness of fit	1.134	1.137
$R^a$	0.0201 (0.0227) <sup>b</sup>	0.0301 (0.0356)
$wR_2^a$	0.0511 (0.0525) <sup>b</sup>	0.0820 (0.0855)

\* $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ ;  $[F_o > 4\sigma(F_o)]$ .

<sup>b</sup> Based on all data

## 2.3. Crystallography

Suitable single crystals of the two compounds were mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). All the measured independent reflections ( $I > 2\sigma(I)$ ) were used in the structural analyses, and semi-empirical absorption corrections were applied using SADABS program[9]. Crystal structures were solved by the direct method. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined by using a riding model. All calculations were performed using the SHELX-97 program[10]. Crystal data and details of the data collection and the structure refinement are given in Table 1. Selected bond distances and angles are given in Table 2.

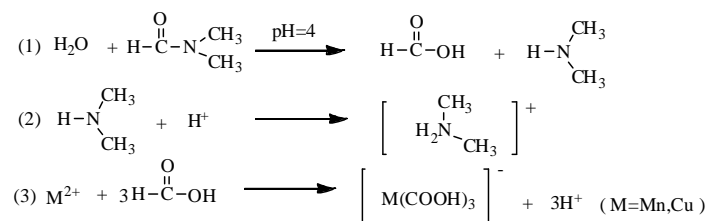
## 3. RESULTS AND DISCUSSION

### 3.1. Synthesis

In our work, complexes **1** and **2** were synthesized by the reaction of  $\text{M}(\text{OAc})_2 \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Mn}, \text{Cu}$ ) and DMF. But the experimental results found that the composition of the final products do not included DMF, they are metal (II) formate complexes. This maybe because in the reaction course, there are two new reactions to occur: one is that DMF hydrolysis produced the formyl anion; the other is the formyl anion and metal ions assembled in situ to form metal formate supermolecular complexes. It is worthy to note about the importance of the hydrolysis of DMF in a weak acid experimental condition ( $\text{pH} = 4$ ) (Scheme1).

### 3.2. IR spectra

The broad absorption bands appearing at 3061, 3055  $\text{cm}^{-1}$  indicate the presence of C-H stretching of formic acid. The bands at 1592 and 1577  $\text{cm}^{-1}$  are attributed to the characteristic asymmetrical stretching vibration of the C=O. The bands at the range of 1472–1440  $\text{cm}^{-1}$  are attributed to the characteristic symmetrical stretching vibration of the C=O. The band at the range of 1341–1367  $\text{cm}^{-1}$  is assigned to the stretching vibration of the C-O. The FTIR spectra of the complexes are very much consistent with the structural analysis result. In addition, the detailed appointments of the IR spectra data for the complexes **1** and **2** are shown in Table 3.



**Scheme 1.** Hypothetical reactions process by hydrolysis of DMF leading to formate complexes.

**Table 2** Selected Bond distances (Å) and Angles (°) for complexes **1** and **2**\*

Complex 1					
Mn-O	2.1880(9)	Mn-O <sup>#1</sup>	2.1880(9)	Mn-O <sup>#2</sup>	2.1880(9)
Mn-O <sup>#3</sup>	2.1880(9)	Mn-O <sup>#4</sup>	2.1880(9)	Mn-O <sup>#5</sup>	2.1880(9)
O-Mn-O <sup>#1</sup>	89.20(4)	O-Mn-O <sup>#2</sup>	180.0	O <sup>#1</sup> -Mn-O <sup>#2</sup>	90.80(4)
O-Mn-O <sup>#3</sup>	89.20(4)	O <sup>#1</sup> -Mn-O <sup>#3</sup>	90.80(4)	O <sup>#2</sup> -Mn-O <sup>#3</sup>	90.80(4)
O-Mn-O <sup>#4</sup>	90.80(4)	O <sup>#1</sup> -Mn-O <sup>#4</sup>	180.0	O <sup>#2</sup> -Mn-O <sup>#4</sup>	89.20(4)
O <sup>#3</sup> -Mn-O <sup>#4</sup>	89.20(4)	O-Mn-O <sup>#5</sup>	90.80(4)	O <sup>#1</sup> -Mn-O <sup>#5</sup>	89.20(4)
O <sup>#2</sup> -Mn-O <sup>#5</sup>	89.20(4)	O <sup>#3</sup> -Mn-O <sup>#5</sup>	180.0	O <sup>#4</sup> -Mn-O <sup>#5</sup>	90.80(4)
Complex 2					
Cu-O2	1.969(2)	Cu-O2 <sup>#1</sup>	1.969(2)	Cu-O1	1.974(2)
Cu-O1 <sup>#1</sup>	1.974(2)				
O2-Cu-O2 <sup>#1</sup>	180.00(8)	O2-Cu-O1	91.46(9)	O2 <sup>#1</sup> -Cu-O1	88.54(9)
O2-Cu-O1 <sup>#1</sup>	88.53(9)	O2 <sup>#1</sup> -Cu-O1 <sup>#1</sup>	91.47(9)	O1-Cu-O1 <sup>#1</sup>	180.0

\*Symmetry codes: #1: -x, -y, -z; #2: -x+y, -x, z; #3: x-y, x, -z; #4: y, -x+y, -z; #5: -y, x-y, z for **1**; #1: -x+3/2, -y+1/2, -z+1 for **2**.

### 3.3. PXRD spectra

The simulation (a) and experimental (b) PXRD spectrum of complexes **1** and **2** are shown in fig.2 and fig .3. From the picture we get that the experimental PXRD spectrum accords with the simulation PXRD spectrum. And it indicated that complexes **1** and **2** are pure phase, without any impurities.

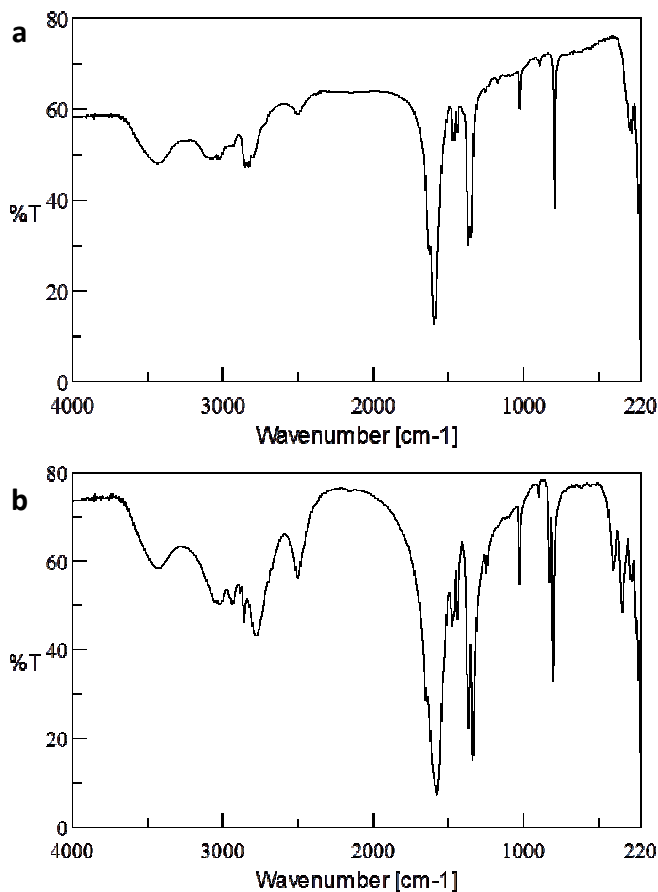
### 3.4 Crystal structure of complexes

#### Crystal structure of complex 1

Complex **1** is crystallized in the trigonal system with R-3c space group. Selected bond distances and angles of complex **1** are given in Table 2. X-ray single crystal analysis indicates that complex **1** is made up of a Mn(HCOO)<sub>3</sub><sup>-</sup> anion, and a free NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub><sup>+</sup> cation. The Mn(II) centre is coordinated by six oxygen atoms (O, O<sup>#1</sup>, O<sup>#2</sup>, O<sup>#3</sup>, O<sup>#4</sup> and O<sup>#5</sup>; #1: y, -x+y, -z; #2: -x, -y, -z; #3: x-y, x, -z; #4: -y, x-y, z; #5: -x+y, -x, z) from six formate

**Table 3** The IR spectra adscription and comparison of the complexes **1** and **2**

Complexes	<b>1</b>	<b>2</b>
$\nu_{(C-H)}$	3061	3055
$\nu_{as(C=O)}$	1592	1577
$\nu_{s(C=O)}$	1469,1460	1472,1440
$\nu_{C-O}$	1367,1349	1364,1341

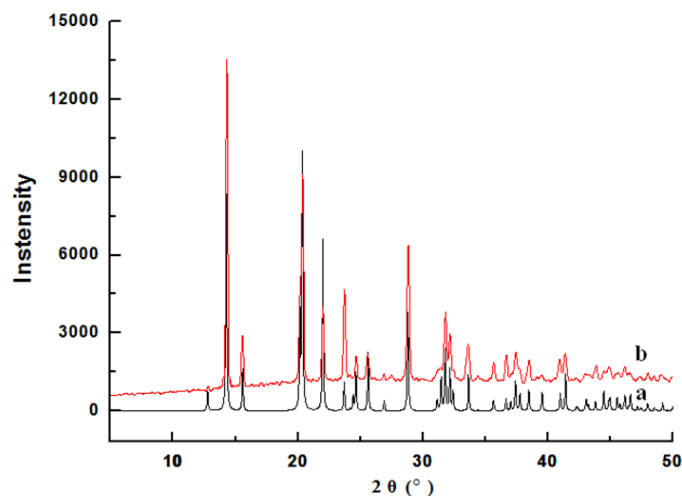


**Figure 1.** The IR spectra of complexes **1**(a) and **2**(b)

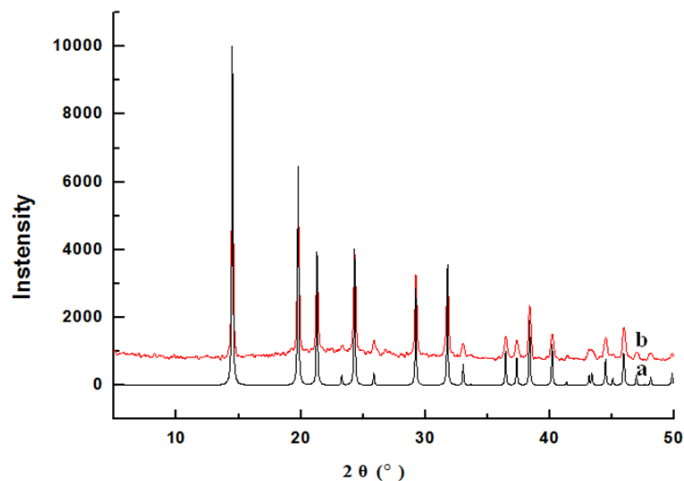
ions to form an octahedron geometry, as shown in Fig.4(a). The adjacent manganese ions are linked by the formate which acted as a bridge adopting a  $\mu_2\text{-}\eta^1\text{:}\eta^1$  mode to form three 1D chains along the a, b, c axes, respectively. In the meantime, the chains are connected by formic acid molecules which act as bridging ligands, then formed lattice structure (shown in Fig.4(b)). In addition, the Mn–O bond lengths are all 2.1880(9) Å, and O–Mn–O angles are divided into two groups, one group is corresponding to cis with angles in the range of 89.20(4) to 90.80(4)° and other to trans O–Mn–O with an angle of 180.00°.

### Crystal structure of complex 2

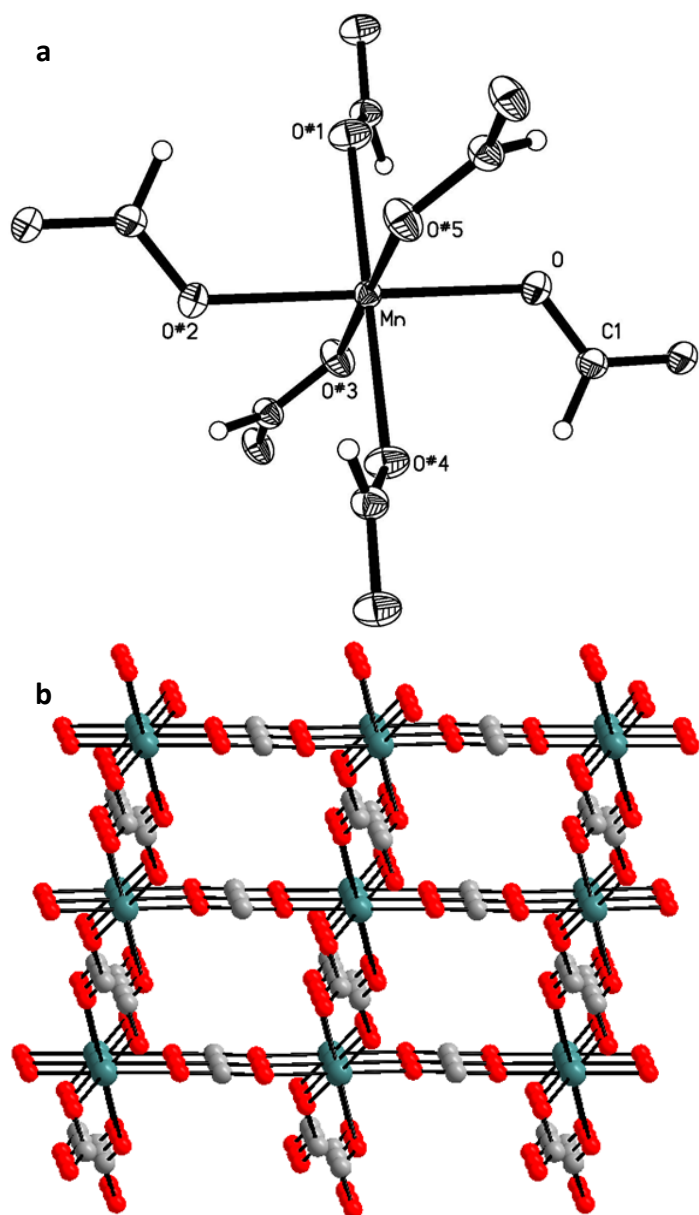
Complexes 2 are crystallized in the Monoclinic system with  $C2/c$  space group. Selected bond distances and angles of complex 2 are given in table 2. X-ray single crystal analysis indicates that complex 2 is made up of a  $\text{Cu}(\text{HCOO})_3^-$  anion, and a free formic anhydride. Free moiety is a protonated formic anhydride, and there is an electrostatic force between  $\text{Cu}(\text{HCOO})_3^-$  anion and the



**Figure 2.** The simulation (a) and experimental (b) PXRD spectrum of complex 1



**Figure 3.** The simulation (a) and experimental (b) PXRD spectrum of complex 2



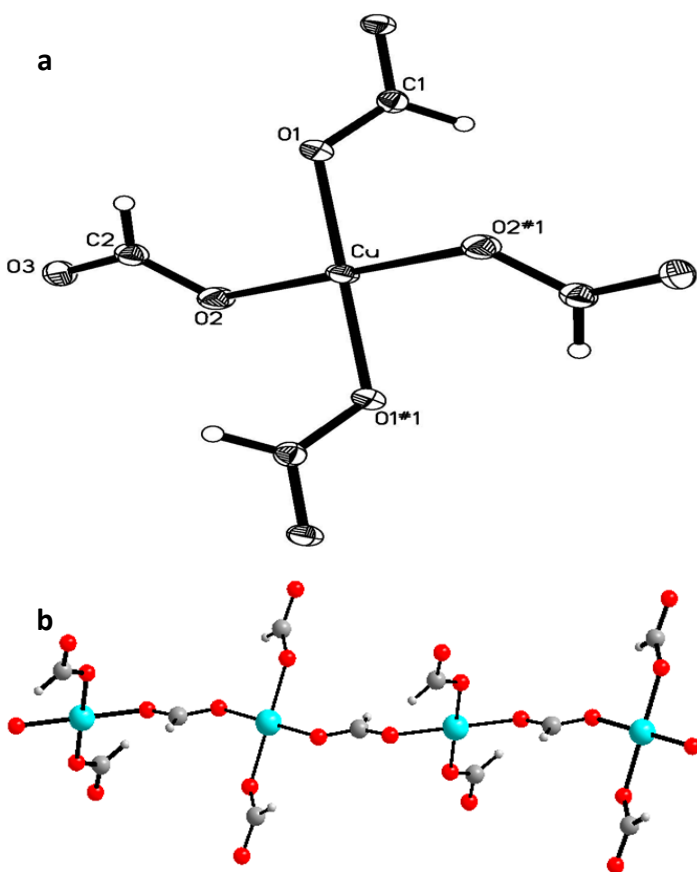
**Figure 4** (a) The coordination environment of Mn Symmetry codes: #1: -x, -y, -z; #2: -x+y, -x, z; #3: x-y, x, -z; #4: y, -x+y, -z; #5: -y, x-y, z (b) A 3D structure of complex 1 (All H atoms were omitted for clarity).

free formic anhydride. From the fig. 5(a), It is found that Cu(II) is coordinated to four oxygen atoms (O1, O1<sup>#1</sup>, O2 and O2<sup>#1</sup>; #1: -x+3/2, -y+1/2, -z+1) from four formate ions to form the square planar geometry. In this case, formic acid is bidentate coordination which adopts unidentate and  $\mu_2\text{-}\eta^1\text{:}\eta^1$  binding modes. And it acts as bridging ligand connecting two adjoining Cu(II) by  $\mu_2\text{-}\eta^1\text{:}\eta^1$  binding mode to form an infinite one-dimensional chain (shown in fig. 5(b)). The Cu–O bond lengths range from 1.969(2) to 1.974(2) Å, and O–Cu–O angles are divided into two groups, one corresponding to cis which angles vary from 88.53(9) to 91.47(9)° and other to trans O–Cu–O which angle is 180.00(8)°.

### Crystal structure of complex 2

Complexes **2** are crystallized in the Monoclinic system with  $C2/c$  space group. Selected bond distances and angles of complex **2** are given in table 2. X-ray single crystal analysis indicates that complex **2** is made up of a  $\text{Cu}(\text{HCOO})_3^-$  anion, and a free formic anhydride. Free moiety is a protonated formic anhydride, and there is an electrostatic force between  $\text{Cu}(\text{HCOO})_3^-$  anion and the free formic anhydride. From the fig. 5(a), It is found that Cu(II) is coordinated to four oxygen atoms (O1, O1<sup>#1</sup>, O2 and O2<sup>#1</sup>; #1:  $-x+3/2, -y+1/2, -z+1$ ) from four formate ions to form the square planar geometry. In this case, formic acid is bidentate coordination which adopts unidentate and  $\mu_2-\eta^1:\eta^1$  binding modes. And it acts as bridging ligand connecting two adjoining Cu(II) by  $\mu_2-\eta^1:\eta^1$  binding mode to form an infinite one-dimensional chain (shown in fig. 5(b)). The Cu–O bond lengths range from 1.969(2) to 1.974(2) Å, and O–Cu–O angles are divided into two groups, one corresponding to *cis* which angles vary from 88.53(9) to 91.47(9)° and other to *trans* O–Cu–O which angle is 180.00(8)°.

Though formic acid shows the same kind of coordination mode ( $\mu_2-\eta^1:\eta^1$ ), X-ray single crystal analysis reveals that complex **1** is three-dimensional grid shapes, and complex **2** is a 1D chain, they have their own different structures. These may be corresponding to

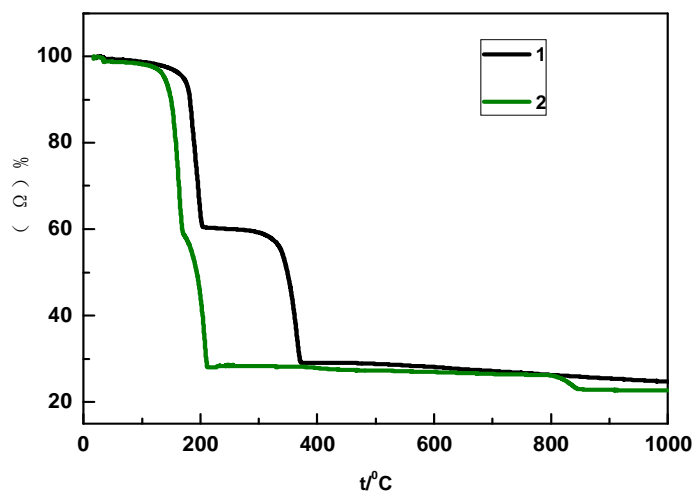


**Figure 5** (a) The coordination environment of Cu Symmetry codes:; #1:  $-x+3/2, -y+1/2, -z+1$  (b) A view of a 1D chain structure of complex **2**

different metals own different coordination numbers, and in this work, Mn is hexa-coordinate, Cu is four-coordination. It is found that one ligand can produce multiple different frameworks under appropriate conditions.

### 3.5. Thermogravimetric properties

The TGA data of the complex **1** indicates two obvious weight losses shown in Fig.6. The first weight loss starts at ca. 47~255 °C to give a total weight loss of 39.36% (Calcd. 39.44%), corresponding to the loss of a free  $(\text{NH}_2(\text{CH}_3)_2^+)$  ion and a coordination of formic acid molecule. And then at ca. 255~984 °C gives a total loss of 30.54% (calcd. 30.5%), corresponding to the loss of a  $-\text{COO}^-$  group and a CO molecule. There are also two stages in the process of thermal decomposition of complex **2**. The first weight loss begins at ca. 47~255 °C to give a weight total loss of



**Figure 6** The TG curves for complexes **1** and **2**

71.41% (calcd. 70.92%), due to the loss of a free  $\text{H}_2\text{C}_2\text{O}_3$  molecule, two coordination of formic acid molecules and a  $-\text{CHO}$  group. And then the two-step was attributed to the removal of an oxygen atom from 252 °C to 975 °C with the loss of 5.82% (calc. 5.84%).

### CONCLUSION

Although the hydrothermal condition has been commonly considered as the reason for this phenomenon in literature, in our work, the DMF can hydrolyze leading to a weak acid. To the best of our knowledge, in spite of having many references to explore the reason of DMF hydrolysis in the reaction process (e.g. strong base, high temperature, etc.), a detailed DMF hydrolysis catalytic mechanism is not clear up to now [11]. Based on investigating the reaction processes in literature and our experiment observed in detail, we speculated that an acidic environment in the reaction system could have played a subtle role during the hydrolysis of DMF.

### Acknowledgements

We thank the Natural Science Foundation of China (No. 21371086)



and Guangxi Key Laboratory of Information Materials (Guilin University of Electronic Technology), P.R. China (Project No. 1210908-06-K) for financial assistance.

### Supporting Information Available

Tables of atomic coordinates, an isotropic thermal parameters, and complete bond distances and angles have been deposited with the Cambridge Crystallographic Data Center. Copies of this information may be obtained free of charge, by quoting the publication citation and deposition numbers CCDC for complexes **1** and **2**: 967369 and 967370, respectively, from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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