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Polyhedron 22 (2003) 3097–3103

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Syntheses and crystal structures of three open-frameworks of metal succinates containing a 4,4′-bipyridine ligand

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Received 2 April 2003; accepted 27 June 2003

Abstract

Three new divalent transitional metal succinates with an additional bipy (bipy = 4,4′-bipyridine) ligand have been synthesized by hydrothermal reactions and structurally determined. The structure of $[Cu(C_4H_4O_4)(bipy)(H_2O)_2]\cdot 2H_2O$ (**1**) features a 3D open framework formed by 1D $[Cu(bipy)]^{2+}$ chains along the diagonal axis of *b* and -*c* that are interconnected by $Cu(C_4H_4O_4)$ helixes along the *c*-axis. The lattice water molecules are located at the cavities of the framework. In $Zn(C_4H_4O_4)(bipy)$ (**2**), each zinc cation is octahedrally coordinated by two chelate carboxylate groups from two succinates and 2 N atoms from two bipy molecules, and the ZnO_4N_2 octahedra are interconnected by bridging succinate ligands into a 1D chain along the ⟨0 1 1⟩ direction. Such chains are further linked into a ⟨0 1 1⟩ layer via π–π stacking interaction between the pyridine rings. In $[Co(bipy)(H_2O)_4]$ $(C_4H_4O_4)\cdot 4H_2O$ (**3**), each pair of octahedral cobalt(II) ions is bridged by a bipy ligand, resulting in a 1D $[Co(bipy)(H_2O)_4]^{2+}$ chain, and the succinate ligands and lattice water molecules are sandwiched between two $[Co(bipy)(H_2O)_4]^{2+}$ chains to form a ⟨0 1 1⟩ layer via hydrogen bonding. The layers are further interconnected into a 3D network via hydrogen bonds among carboxylate oxygen atoms, aqua ligands, and lattice water molecules.

Keywords: Hydrothermal reaction; Crystal structure; Succinate; Bipy; Open-framework

1. Introduction

The generation of three-dimensional open coordination frameworks based on transitional metals is one of the most important research areas due to their potential applications as catalysts, hosts in intercalation compounds and materials with desirable electronic properties [1–5]. Metal dicarboxylates, such as metal oxalates, have been reported recently to form a large variety of open-frameworks [6–8]. Several new types of open-frameworks of cobalt, cadmium and nickel succinates have also been synthesized by hydrothermal reactions, which are usually layered or microporous materials [9–13]. In addition, several metal succinates with a 1D chain structure have also been reported [14–16]. Introduction of a second competing ligand such as 1,10-phenanthroline (phen) has been found to lower the dimensionality of the structure since its chelation to the metal ion leaves fewer sites for succinate coordination. The structure of Zn(phen) $(C_4H_4O_4)$ is a 1D polymeric chain and that of $[Zn_2(phen)_4(C_4H_4O_4)_2]\cdot(C_4H_6O_4)\cdot 11H_2O$ contains a dimeric unit [17]. 4,4′-Bipyridine (bipy), on the other hand, can bridge two metal ions to form a polymeric chain, so its incorporation into metal carboxylates can lead to the formation of many new open frameworks. Recently, several 2D and 3D open-frameworks of transition metal bipy maleates and fumarates have been reported [18,19]. Succinic acid is more flexible than maleic acid and fumaratic acid, and thus it should be able to form metal-bipy-succinate open frameworks, which have not been reported yet. By hydrothermal reactions of metal chloride with bipy and succinic acid, three new inorganic–organic hybrid materials with open framework structures have been isolated, namely $[Cu(C_4H_4O_4)(bipy)(H_2O)_2]\cdot 2H_2O$ (**1**) whose structure features a 3D open framework formed

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doi:10.1016/S0277-5387(03)00467-4

by 1D Cu(bipy) chains interconnected by $Cu(C_4H_4O_4)$ helixes, $Zn(C_4H_4O_4)$(bipy) (**2**) featuring a 2D layer built from 1D chains via π–π interaction between the pyridine rings, and $[Co(bipy)(H_2O)_4](C_4H_4O_4) \cdot 4H_2O$ (**3**) with a hydrogen bonded 3D network structure. Herein we report their preparation and crystal structures.

2. Experimental section

2.1. Materials and methods

All starting materials were purchased from Shanghai Reagent Co. and were used without further purification. All the materials are of reagent grade. Elemental analyses were performed on a Vario EL III elemental analyzer. IR spectra were recorded on a Magna 750 FT-IR spectrophotometer using the KBr pellet technique in the range of 4000–400 cm^{-1}. Thermogravimetric analyses were carried out with a TGA/SBTA851 unit, at a heating rate of 15 °C/min under a nitrogen atmosphere.

2.2. Synthesis of $[Cu(C_4H_4O_4)(bipy)(H_2O)_2] \cdot 2H_2O$ (**1**), $Zn(C_4H_4O_4)(bipy)$ (**2**) and $[Co(bipy)(H_2O)_4](C_4H_4O_4) \cdot 4H_2O$ (**3**)

The three complexes were synthesized by hydrothermal reactions in a similar manner. A mixture of 1.0 mmol of metal chloride, 1.0 mmol of succinic acid and 1.0 mmol of bipy in 20 ml of H_2O was heated at 150 °C for 3 days. Blue crystals of **1**, colorless crystals of **2** and pink crystals of **3** were obtained in a yield of 70.8%, 82.5% and 80.6%, respectively.

$[Cu(C_4H_4O_4)(bipy)(H_2O)_2] \cdot 2H_2O$ *Anal.* Calc. for **1**: C, 41.19; H, 4.90; N, 6.86. Found: C, 39.03; H, 4.27; N, 6.28%. IR (cm^{-1}): 3456(vs), 3359(vs), 3086(s), 2980(m), 2900(m), 1564(vs), 1421(vs), 1306(m), 1027(m), 823(s), 648(s), 494(m).

$Zn(C_4H_4O_4)$(bipy) *Anal.* Calc. for **2**: C, 58.32; H, 4.05; N, 11.34. Found: C, 57.20; H, 3.48; N, 10.88%. IR (cm^{-1}): 3089(m), 3047(s), 2950(m), 2929(m), 1560(vs), 1425(vs), 1217(vs), 816(vs), 623(vs).

$[Co(bipy)(H_2O)_4](C_4H_4O_4) \cdot 4H_2O$ *Anal.* Calc. for **3**: C, 35.34; H, 5.89; N, 5.89. Found: C, 34.70; H, 4.92; N, 5.19%. IR (cm^{-1}): 3095(w), 3041(w), 2943(w), 1950(m), 1705(vs), 1603(vs), 1412(vs), 1184(vs), 1070(vs), 818(vs), 623(vs), 548(m).

2.3. Crystal structure determination

Crystal data of **1**, **2** and **3** were collected on a Siemens Smart CCD system using Mo Kα radiation ($\lambda = 0.71069$ Å) at room temperature. An absorption correction based on SADABS was also applied [20–22].

The structures were solved using direct methods (SHELXTL) and refined by least-squares methods with atomic anisotropic thermal parameters for all non-hydrogen atoms [20–22]. Refinements of **1** in space group $P6_1$ gave slightly larger R values, and a large absolute structure parameter, hence the correct space group is $P6_5$. All hydrogen atoms were generated geometrically, assigned fixed isotropic thermal parameters and included in the structure factor calculations. The data collection and refinement parameters are summarized in Table 1. Important bond lengths and angles for the three complexes are listed in Table 2. Further details on the

Table 1
Crystal data and structure refinement for **1**, **2** and **3**

Compound	**1**	**2**	**3**
Formula	$C_{14}H_{20}CuN_2O_8$	$C_{24}H_{20}N_4O_4Zn$	$C_{14}H_{28}CoN_2O_{12}$
M	407.86	493.81	475.31
Crystal system	hexagonal	monoclinic	triclinic
Space group	$P6_5$	$I2/a$	$P1$
a (Å)	11.095(1)	14.674(2)	7.1670(3)
b (Å)	11.095(1)	9.809(1)	7.7540(5)
c (Å)	24.981(3)	15.593(3)	9.8622(6)
α (°)	90	90	79.314(3)
β (°)	90	103.581(3)	87.748(3)
γ (°)	120	90	71.287(2)
Volume ($Å^3$)	2663.0(5)	2181.6(5)	509.98(5)
Z	6	4	1
D_{cal} (g/cm^3)	1.526	1.503	1.548
μ (mm^{-1})	1.274	1.166	0.905
$F(000)$	1266	1016	249
Reflections collected	6440	3255	2665
Independent reflected	3051 ($R_{int} = 5.81\%$)	1937 ($R_{int} = 6.26\%$)	1797 ($R_{int} = 3.56\%$)
GOF on F^2	1.178	1.139	1.150
$R1$, $wR2$ ($[I > 2\sigma(I)]$)	0.0618/0.1184	0.0851/0.1832	0.0704/0.1541
$R1$, $wR2$ (all data)	0.1025/0.1386	0.1311/0.2155	0.0864/0.1662

Table 2
Selected bond lengths (Å) and angles (°) for complexes **1**, **2** and **3**

1			
Cu(1)–O(1)#1	1.958(6)	Cu(1)–O(2)	1.961(6)
Cu(1)–N(2)	2.002(5)	Cu(1)–N(1)#2	2.019(5)
Cu(1)–O(1W)	2.544(8)	Cu(1)–O(2W)	2.535(8)
Hydrogen bonds:			
O(1W)···O(4)#1	2.700(9)	O(1W)···O(2W)#5	2.869(8)
O(1W)···O(3W)#6	2.84(1)	O(2W)···O(3)	2.708(9)
O(2W)···O(4W)	2.83(1)	O(3W)···O(3)#5	2.75(1)
O(3W)···O(4W)#7	2.85(1)	O(4W)···O(4)#8	2.74(1)
O(1)#1–Cu(1)–N(2)	91.3(3)	O(2)–Cu(1)–N(2)	91.5(2)
O(1)#1–Cu(1)–N(1)#2	88.7(2)	O(2)–Cu(1)–N(1)#2	88.4(2)
O(1W)–Cu(1)–O(1)#1	93.2(3)	O(1W)–Cu(1)–O(2)	87.0(3)
O(1W)–Cu(1)–N(2)	89.0(3)	O(1W)–Cu(1)–N(1)#2	91.3(3)
O(2W)–Cu(1)–O(1)#1	86.6(2)	O(2W)–Cu(1)–O(2)	93.4(3)
O(2W)–Cu(1)–N(2)	88.4(3)	O(2W)–Cu(1)–N(1)#2	91.3(3)
2			
Zn(1)–O(1)	2.046(5)	Zn(1)–N(1)	2.097(6)
Zn(1)–O(2)	2.295(5)	O(1)–Zn(1)–N(1)	100.1(2)
O(1)#1–Zn(1)–N(1)	95.9(2)	N(1)–Zn(1)–N(1)#1	96.6(3)
O(1)–Zn(1)–O(2)	60.0(2)	N(1)–Zn(1)–O(2)	91.5(2)
O(1)–Zn(1)–O(2)#1	101.8(2)	O(2)–Zn(1)–O(2)#1	90.4(3)
3			
Co(1)–O(1W)	2.052(3)	Co(1)–N(1)	2.140(4)
Co(1)–O(2W)	2.146(4)		
Hydrogen bonds:			
O(1W)···O(1)	2.590(4)	O(1W)···O(4W)#4	2.762(5)
O(2W)···O(3W)#1	2.826(6)	O(2W)···O(4W)#5	2.780(4)
O(3W)···O(2)	2.751(3)	O(3W)···O(2)#6	2.817(4)
O(3W)···O(4W)#5	2.930(5)	O(4W)···O(1)	2.703(4)
O(1W)–Co(1)–N(1)	90.43(16)	N(1)–Co(1)–O(2W)#1	89.66(15)
O(1W)#1–Co(1)–O(2W)	91.73(15)	O(1W)–Co(1)–O(2W)	88.27(15)
N(1)–Co(1)–O(2W)	90.34(15)		

Symmetry transformations used to generate equivalent atoms:
For **1**: #1 $y+1, -x+y+1, z+1/6$ #2, $x-1, y, z$ #3 $x-y, x-1, z-1/6$ #4 $x+1, y, z$ #5 $y, -x+y, 1/6+z$ #6 $1+y, -x+y, 1/6+z$ #7 $-1+x, -1+y, z$ #8 $x-y, x, -1/6+z$.
For **2**: #1 $-x+3/2, y, -z+1$ #2 $-x+1, -y+1, -z+1$.
For **3**: #1 $-x, -y+2, -z$ #2 $-x, -y+1, -z+1$ #3 $-x+1, -y+1, -z-1$ #4 $1-x, 1-y, -z$ #5 $x, 1+y, z$ #6 $1-x, 2-y, -1-z$.

crystallographic studies as well as atomic parameters are given in the Supplementary materials.

3. Results and discussion

As shown in Fig. 1, the structure of **1** contains two types of 1D chains: the Cu(bipy) chain along the diagonal axis of *b* and −*c* (Fig. 1a), and the Cu($C_4H_4O_4$) helix along the *c*-axis (Fig. 1b). The interconnection of these chains and helixes through Cu(II) ions results in a novel 3D open framework with micropores (Fig. 2). Each Cu(II) ion is octahedrally coordinated by two carboxylate oxygen atoms from two succinate ligands, two nitrogen atoms from two bipy ligands and two aqua ligands. The Cu–N distances are slightly larger than those of Cu–O(carboxylate) distances (Table 2), and both are comparable to those reported in the copper(II) complex with maleic acid and phen [23]. The Cu–O(aqua) distances are in the range of 2.535(8)–2.544(8) Å, much longer than those of Cu–O(carboxylate) and Cu–N(bipy) bonds. The coordination geometry around the Cu(II) ions can be best described as a "Jahn–Teller" distorted octahedron with elongated axial distances that is well-established for copper(II) complexes [24]. The succinate ligand adopts a bis-monodentate bridging coordination mode, as in its zinc phen complexes. The other two carboxylate oxygen atoms remain non-coordinated and are available for hydrogen bonding.

The lattice water molecules are located in the micropores of the framework (Fig. 2), forming a number of hydrogen bonds with the aqua ligands and non-coordinated carboxylate oxygen atoms. In addition, there is also hydrogen bonding between aqua ligands and non-coordinated carboxylate oxygen atoms (Table 2).

The structure of **2** features a 1D Zn(bipy)($C_4H_4O_4$) chain along the diagonal axis of *b* and -*c* (Fig. 3). Each zinc(II) ion is six-coordinated by two N atoms from two

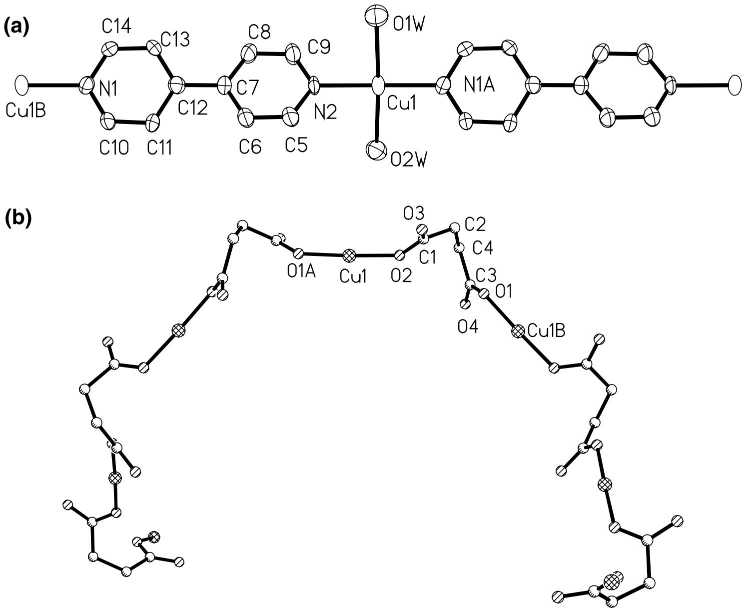

Fig. 1. (a) ORTEP representation of the 1D chain formed by the bridging of Cu(II) ions via 4,4′ bipy ligands, the thermal ellipsoids are drawn with 50% probability; (b) helix along the *c*-axis formed by the $Cu(C_4H_4O_4)$ units.

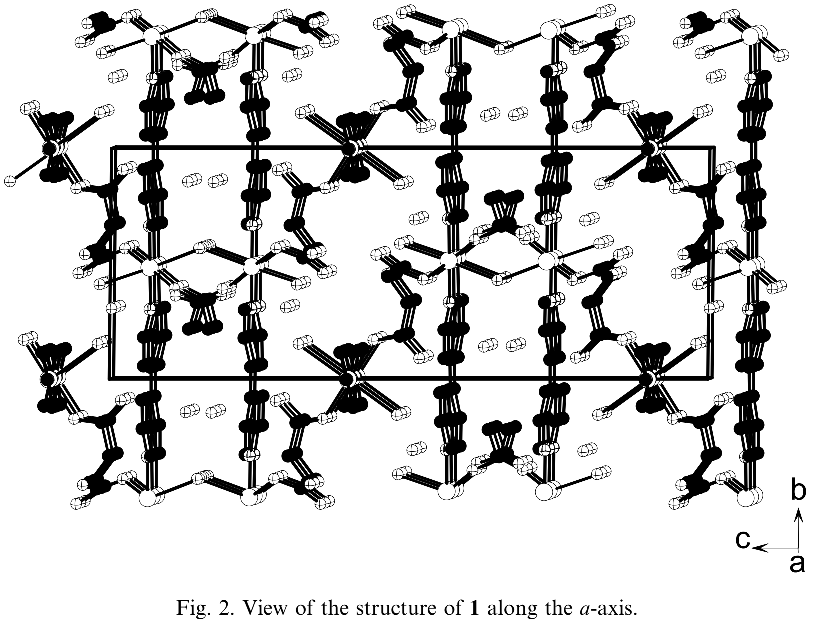

Fig. 2. View of the structure of **1** along the *a*-axis.

bipy molecules and two bidentate chelating carboxylate groups from two succinate ligands. The Zn–N distance is 2.097(6) Å, comparable to those reported for zinc complexes of bipy [18,19,25,26]. The $Zn–O_2$ distance is about 0.2 Å longer than that of $Zn–O_1$. Based on the bond lengths and angles (Table 2), the zinc coordination polyhedron is a severely distorted octahedron. Unlike that in **1**, the succinate ligand adopts a bis-bidentate coordination mode that has been reported in the dimeric zinc-phen succinate [17]. The bipy ligand is monodentate, and reports on monodentate bipy metal complexes are relatively few [27]. Neighboring 1D chains are interconnected through π–π interaction between the pyridine rings into a ⟨0 1 1⟩ layer (Fig. 4). The distance from the ring formed by N1, C1, C2, C3, C9, C10 to the ring formed by N2, C4, C5, C6, C7, C8 from the neighboring chain is 4.11 Å. The dihedral angle between these two rings is 4.9°. Similar π–π interaction between pyridine rings has also been reported in a number of transition metal phen succinates [14–17]. The ⟨0 1 1⟩ metal succinate layers are held together via a weak van der Waals' force.

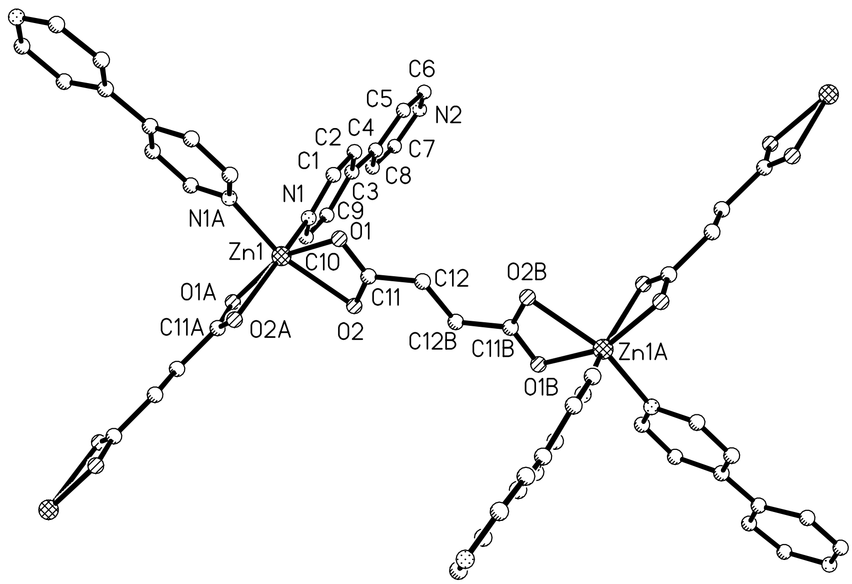

Fig. 3. 1D chain of **2** along the ⟨0 1 1⟩ direction.

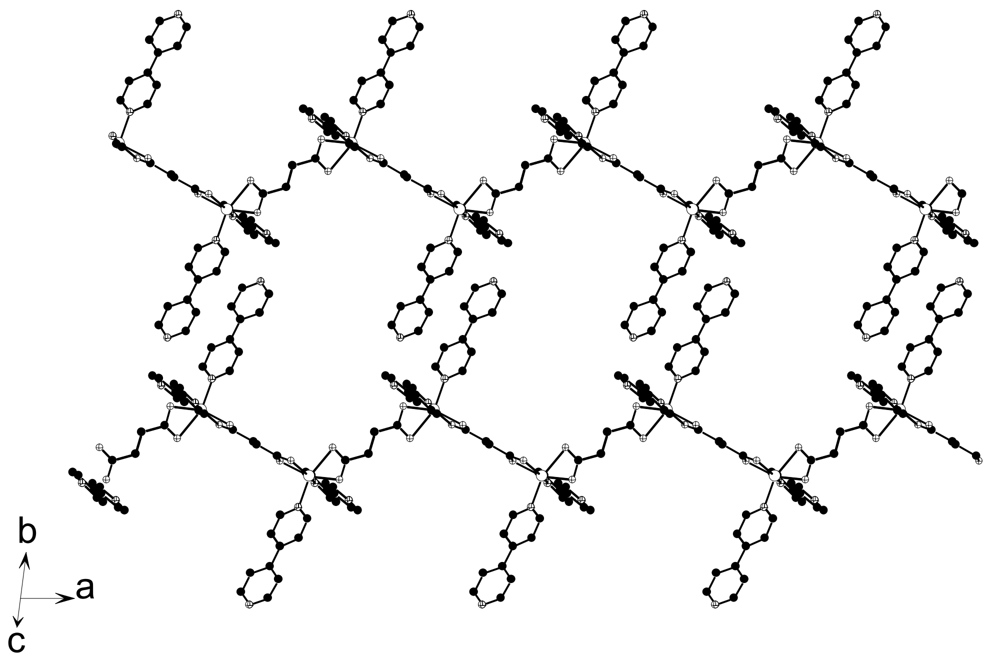

Fig. 4. ⟨0 1 1⟩ layer built from 1D chains through π–π interaction of the pyridine rings in **2**.

The structure of **3** contains a 1D $[Co(bipy)(H_2O)_4]^{2+}$ chain along the diagonal of the *b* and -*c* axes, a succinate anion and four lattice water molecules. As shown in Fig. 5, the Co(II) in the chain is octahedrally coordinated by two N atoms of two bipy molecules and four aqua ligands. The Co–O and Co–N distances are quite close and are comparable to those reported in the literature (Table 2) [9–11,28]. Each pair of CoN_2O_4 octahedra are bridged by a bipy ligand, resulting in a 1D chain.

Unlike those in **1** and **2**, the succinate anion is not bound to the metal ion, but forms hydrogen bonds with the aqua ligands as well as lattice water molecules (Table 2). Non-coordinated succinate anion and succinic acid has been reported in Zn-phen succinates [17]. The succinate anions are sandwiched between $[Co(bipy)(H_2O)_4]^{2+}$ chains, which are interconnected through the lattice water molecules via hydrogen bonds, thus forming a ⟨0 1 1⟩ hydrogen bonded layer (Fig. 6). Neighboring layers are further interlinked into a 3D network through hydrogen

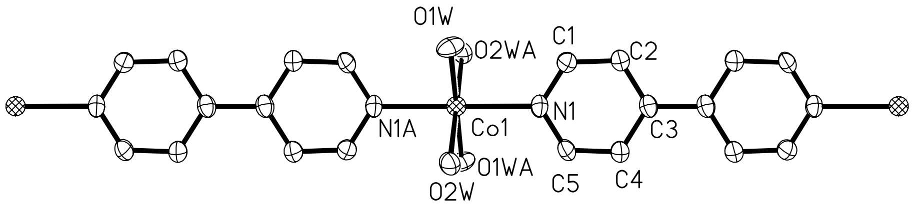

Fig. 5. ORTEP representation of the 1D chain built from Co(bipy)$(H_2O)_4$ units in **3**. The thermal ellipsoids are drawn with 50% probability.

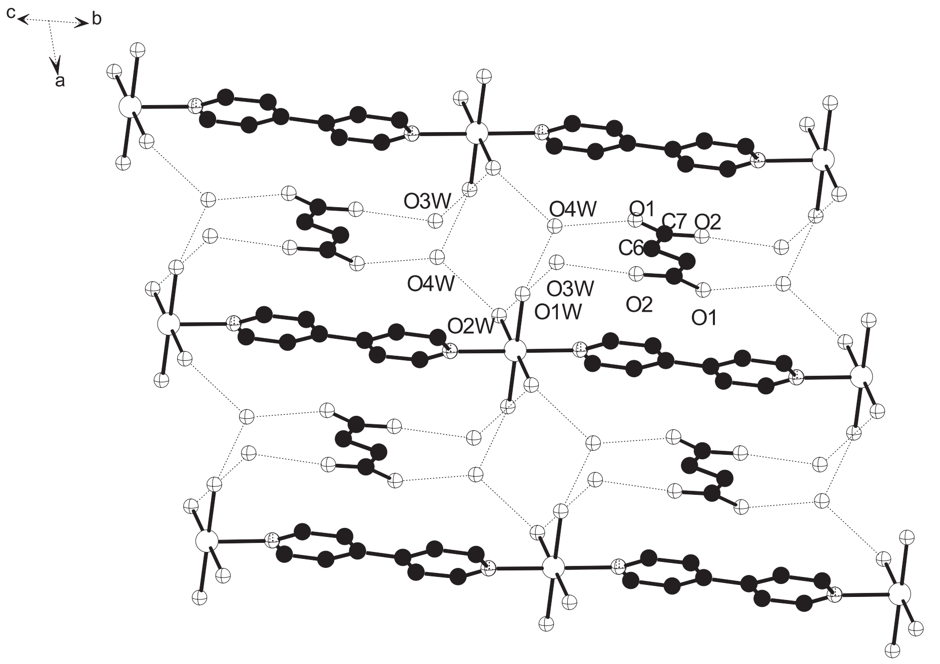

Fig. 6. ⟨0 1 1⟩ hydrogen bonded layer of **3**.

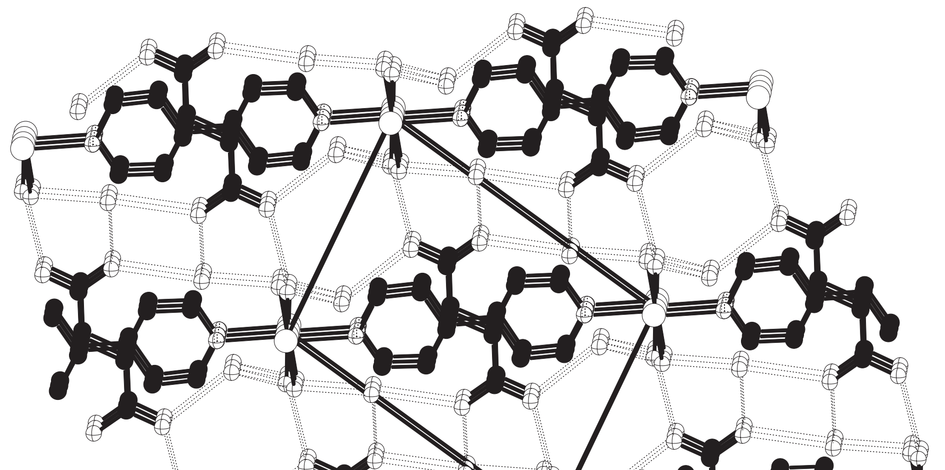

Fig. 7. View of the hydrogen bonded 3D network of **3** along the *a*-axis.

bonds between carboxylate oxygen atoms, aqua ligands as well as lattice water molecules (Fig. 7). The O···O distances range from 2.590(4) to 2.930(5) Å.

TGA curves of complex **1** indicate three steps of weight losses. The first weight loss starts at 50 °C and is complete at 108 °C, which corresponds to the release of two lattice water molecules. The observed weight loss of 9.5% is close to the calculated one (8.8%). The second weight loss from 130 to 265 °C corresponds to the loss of two aqua ligands and the coordination bipy molecule, the weight loss of 49.5% is in agreement with the calculated one (47.1%). The third weight loss corresponds to the decomposition of the carboxylate ligand, which is complete at 360 °C. The final product is copper(II) oxide. Complex **2** is stable up to 220 °C, then it starts to decompose, which is complete at 320 °C. The final product is zinc(II) oxide. The total weight loss of 85.2% is close to the calculated value (83.5%). The cobalt(II) complex shows only one weight loss which starts at 160 °C and is completed at 290 °C. The release of lattice water molecules at such a high temperature is probably due to the strong hydrogen bonds among lattice water molecules, aqua ligands and non-coordinated carboxylate ligands. The final product is cobalt(II) oxide since the TGA experiments were carried out under a nitrogen atmosphere.

4. Supplementary materials

Crystallographic data for complexes **1**, **2**, and **3** have been deposited with the Cambridge Crystallographic Center, CCDC No. 203888, 203889, 203890. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK (fax: +44-1233-336-033, email: deposit@ccdc.cam.ac.uk or www:http//www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Innovative Project (No. IP021038) and the Introduction of Overseas Elitists Program (No. IB021036), Chinese Academy of Sciences.

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