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Hydrothermal synthesis, structures and properties of coordination polymers based on μ_4-bridging benzene-1,2,4,5-tetracarboxylate: $[Co(Him)_2(\mu_4\text{-bta})_{1/2}]_n$ and $\{[Cu(phen)(\mu_4\text{-bta})_{1/2}]\cdot H_2O\}_n$ (bta = benzene-1,2,4,5-tetracarboxylate, Him = imidazole, phen = 1,10-phenanthroline)

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Abstract

The complexes $[Co(Him)_2(\mu_4\text{-bta})_{1/2}]_n$ 1 and $\{[Cu(phen)(\mu_4\text{-bta})_{1/2}]\cdot H_2O\}_n$ 2 were hydrothermally synthesized at 160°C and their structures were determined by single-crystal X-ray diffraction. Complex 1 was triclinic, space group $P-1$, $a = 7.9294(11)$ Å, $b = 9.621(3)$ Å, $c = 9.6461(16)$ Å, $\alpha = 116.772(19)^\circ$, $\beta = 96.791(13)^\circ$, $\gamma = 102.787(19)^\circ$, $Z = 2$, $V = 620.3(2)$ Å^3, $R_1 = 0.0252$ and w$R_2 = 0.0640$ $[I > 2\sigma(I)]$; complex 2 was monoclinic, space group $P2_1/c$, $a = 7.386(3)$ Å, $b = 12.723(4)$ Å, $c = 15.831(3)$ Å, $\beta = 102.66(2)^\circ$, $Z = 4$, $V = 1451.5(7)$ Å^3, $R_1 = 0.0389$ and w$R_2 = 0.1033$ $[I > 2\sigma(I)]$. In both of the structures the metal ions were linked by the μ_4-bridging benzene-1,2,4,5-tetracarboxylate ligands, resulting in one-dimensional double-metal chains. The synthesized products were characterized by IR spectroscopy, UV–VIS spectra, inductively coupled plasma (ICP), elemental, thermogravimetric (TGA) and magnetic analyses.

Keywords: Hydrothermal synthesis; Crystal structure; Copper(II) complex; Cobalt(II) complex; Benzene-1,2,4,5-tetracarboxylate complexes

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1. Introduction

Self-assembled extended metal complexes as functional solid materials with specific network topologies are of great interest due to their fascinating molecular structures and their potential application to magnetism [1,2], electrical conductivity [3], ion exchange [4], separation [5], biology [6] and catalysis [7]. Especially, the assembly of organic molecules and metal-ion building blocks can yield a new generation of multi-dimensional networks, which contain channels, or cavities of various sizes and shapes [8]. Hydrogen bonding has been widely used to construct extended organic–inorganic solids with condensed and open structures [9].

The bridging ligand is one of the important factors that greatly influence the structures of coordination polymers. So far a variety of coordination polymers with different structures and different bridging ligands have been synthesized, especially the synthesis and the structures of coordination polymers containing organic diamine (including bipyridine) as bridging ligands have been reported more and more often [10–13]. Comparatively, transition metals coordination polymers containing organic polycarboxylate as bridging ligands have been reported obviously seldom. In fact, organic polycarboxylate is one of the most widely used bridging ligands for designing polynuclear complexes with interesting magnetic properties. The coordination chemistry of aromatic polycarboxylate-transition metal complexes attracts considerable interest in inorganic chemistry and in some applied sciences. So far some of the supramolecular structures based on one of the multi-dentate aromatic polycarboxylate bridging ligands such as rigid 1,4-benzenedicarboxylate [14], rigid benzene-1,3,5-tricarboxylate [15], rigid benzene-1,2,4-tricarboxylate [16] and rigid benzene-1,2,4,5-tetracarboxylate [17], have

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been reported. Among these ligands benzene-1,2,4,5-tetracarboxylate has four carboxylate groups that may be completely or partially deprotonated, inducing a lot of coordination modes and interesting structures with higher dimensions. Moreover, it can act not only as hydrogen-bond acceptor but also as hydrogen-bond donor to form new extended structures by hydrogen bonding interactions. Scheme 1 illustrates the versatile coordination abilities of the bta ion.

In this paper, we report on the synthesis and characterization of two three-dimensional supramolecular network structures $[Co(Him)_2(\mu_4\text{-bta})_{1/2}]_n$ **1** and $\{[Cu(phen)(\mu_4\text{-bta})_{1/2}]\cdot H_2O\}_n$ **2**. The structure **2** is novel, and the structure **1** is isomorphic with the structure $[Zn_2(imi)_4(bta)(H_2O)_2]_n$ (17d) reported previously.

2. Experimental

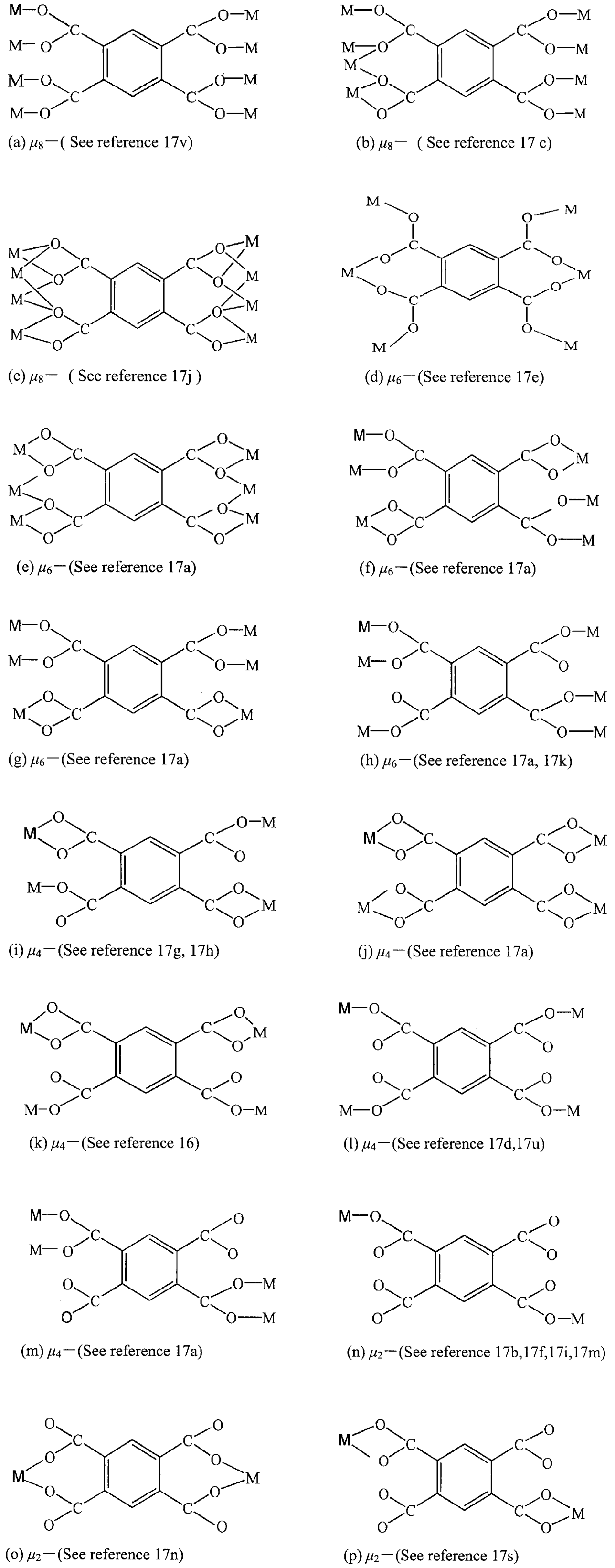
2.1. Synthesis of $[Co(Him)_2(\mu_4\text{-bta})_{1/2}]_n$ 1

A mixture of Him (0.50 g, 7.4 mmol), $CoCl_2\cdot 6H_2O$ (0.85 g, 3.6 mmol) and $Na_4(bta)$ (1.0 g, 2.9 mmol) was dissolved in 20 mL of water and stirred for 30 min. The resulting solution was sealed and heated at 160°C for 120 h under autogenous pressure. After cooling to room temperature, the mauve columnar product was obtained and washed with distilled water. The yield of the crystal material was based on Co(II) by approximately 65 wt%. **IR** (KBr, cm^{-1}): $\tilde{\nu} = 3275$ w, 3165w, 3067w, 2928w, 2639w, 1859b, 1599vs, 1483s, 1440 m, 1367vs, 1323 m, 1311m, 1262s, 1190w, 1172m, 1143w, 1132w, 1108m, 1070vs, 954m, 934m, 910m, 864s, 823s, 743vs, 657vs, 620s, 610s, 512s, 474m.

2.2. Synthesis of $\{[Cu(phen)(\mu_4\text{-bta})_{1/2}]\cdot H_2O\}_n$ 2

A mixture of $CuCl_2\cdot 2H_2O$ (0.50 g, 2.9 mmol), 1,10-phen (0.50 g, 2.5 mmol), $Na_4(bta)$ (0.50 g, 1.5 mmol) was dissolved in 20 mL of water and stirred for 30 min The resulting solution was sealed and heated at 160°C for 72 h. After cooling to room temperature a light green columnar product was obtained. The yield of the crystal material was based on Cu(II) by approximately 78 wt%. **IR** (KBr, cm^{-1}): $\tilde{\nu} = 3526$ m, 3429m, 3051w, 1592m, 1519m, 1494s, 1429s, 1403m, 1372m, 1344m, 1327s, 1221s, 1147s, 1128vs, 1111m, 1055m, 1018m, 928s, 954 m, 857vs, 824vs, 791s, 763s, 739 s, 723vs, 677s, 652s, 573s, 465m.

The ICP analysis and elemental analysis are in good agreement with the theoretical values: for **1**, Co, 18.32 wt%; C, 41.19 wt%; H, 2.84 wt%; N, 17.40 wt% (calculated: Co, 18.40 wt%; C, 41.23 wt%; H, 2.80 wt%;



(a) μ_8—(See reference 17v)
(b) μ_8— (See reference 17 c)
(c) μ_8— (See reference 17j)
(d) μ_6—(See reference 17e)
(e) μ_6—(See reference 17a)
(f) μ_6—(See reference 17a)
(g) μ_6—(See reference 17a)
(h) μ_6—(See reference 17a, 17k)
(i) μ_4—(See reference 17g, 17h)
(j) μ_4—(See reference 17a)
(k) μ_4—(See reference 16)
(l) μ_4—(See reference 17d,17u)
(m) μ_4—(See reference 17a)
(n) μ_2—(See reference 17b,17f,17i,17m)
(o) μ_2—(See reference 17n)
(p) μ_2—(See reference 17s)

Scheme 1. Typical coordination modes for the benzene-1,2,4,5-tetracarboxylate ligand.

N, 17.49 wt%), and for **2**, Cu, 16.49 wt%; C, 52.68 wt%; H, 2.87 wt%; N, 7.20 wt%, (calculated: Cu, 16.55 wt%; C, 52.74 wt%; H, 2.84 wt%; N, 7.24 wt%).

2.3. *Characterization*

Elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer. Inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300DV ICP spectrometer. IR spectra were measured on a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr pellets. The UV–VIS spectra were performed on a UV-3100 UV–VIS–NIR recording spectrophotometer. Thermogravimetric analysis was performed on a Perkin-Elmer TGA-7 analyzer with a heating rate of $20^\circ\mathrm{C\,min^{-1}}$ in air. Magnetic measurements were obtained using an MPMS-XL magnetometer at $H = 5000\,\mathrm{Oe}$ in the temperature range 4–300 K.

2.4. *Determination of crystal structure*

Crystals of **1** and **2** with size 0.28 mm × 0.32 mm × 0.48 mm and 0.16 mm × 0.28 mm × 0.34 mm, respectively, suitable for single-crystal X-ray diffraction, were selected. The data collections were made at room temperature on a Siemens P4 four-circle diffractometer with graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) and $\omega{-}2\theta$ scans. For **1,** a total of 2622 reflections were collected, of which 2052 were unique ($R_{\mathrm{int}} = 0.0192$) and 1951 were considered to be observed with $I > 2\sigma(I)$. Systematic absence and statistics of intensity distribution resulted in a space group of $P{-}1$ for **1**. For **2,** a total of 3617 reflections were collected, of which 2557 were unique ($R_{\mathrm{int}} = 0.0264$) and 2041 were considered to be observed with $I > 2\sigma(I)$. Systematic absence and statistics of intensity distribution resulted in a space group of $P2(1)/c$ for **2**. The two structures were solved by direct methods with SHELXTL (Version 5.1, 1997) program [18]. The refinement was performed by full-matrix least-squares refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically. Experimental X-ray data for structures **1** and **2** were listed in Table 1; selected bond lengths and angles of **1** and **2** were listed respectively in Tables 2 and 3.

3. Results and discussion

3.1. *Synthesis*

The complexes $[\mathrm{Co(Him)_2(\mu_4\text{-}bta)_{1/2}}]_n$ **1** and $\{[\mathrm{Cu(phen)(\mu_4\text{-}bta)_{1/2}}]\cdot\mathrm{H_2O}\}_n$ **2** were constructed via a self-assembly process under mid-temperature hydro-

Table 1
Crystal data and structure refinement for 1 and 2

	1	**2**
Empirical formula	$C_{11}H_9CoN_4O_4$	$C_{17}H_{11}CuN_2O_5$
Formula weight	320.15	386.82
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
a (Å)	7.9294(11)	7.386(3)
b (Å)	9.621(3)	12.723(4)
c (Å)	9.6461(16)	15.831(3)
α (°)	116.772(19)	
β (°)	96.791(13)	102.66(2)
γ (°)	102.787(19)	
V (Å^3)	620.3(2)	1451.5(7)
Z	2	4
ρ(calcd.) (g cm^{-3})	1.714	1.770
μ (mm^{-1})	1.403	1.539
$F(000)$	324	784
Crystal size (mm)	0.28 × 0.32 × 0.48	0.16 × 0.28 × 0.34
θ range [°]	2.44–25.02	2.07–25.02
Index ranges	$-1 \leqslant h \leqslant 9$ $-9 \leqslant k \leqslant 9$ $-11 \leqslant l \leqslant 11$	$-1 \leqslant h \leqslant 8$ $-1 \leqslant k \leqslant 15$ $-18 \leqslant l \leqslant 18$
Reflections collected	2622	3617
Independent reflections	2052 [R(int) = 0.0192]	2557 [R(int) = 0.0264]
Obs. Refl [$I > 2\sigma(I)$]	1951	2041
Parameters	181	226
Goodness-of-fit on F^2	1.090	1.067
Final R indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0252$, $wR_2 = 0.0640$	$R_1 = 0.0389$, $wR_2 = 0.1033$
R indices (all data)	$R_1 = 0.0264$, $wR_2 = 0.0646$	$R_1 = 0.0516$, $wR_2 = 0.1084$
Largest diff. Peak and hole [e/Å^{-3}]	0.311/−0.287	0.559/−0.286

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

Table 2
Selected bond lengths (Å) and angles (°) for $[\mathrm{Co(Him)_2(\mu_4\text{-}bta)_{1/2}}]_n$ (1)

Co(1)–O(1)	1.9770(17)	C(3)–N(2)	1.327(3)
Co(1)–O(4)	1.9813(15)	C(4)–C(5)	1.344(4)
Co(1)–N(3)	2.0067(18)	C(4)–N(3)	1.377(3)
Co(1)–N(1)	2.035(2)	C(5)–N(4)	1.352(4)
C(1)–C(2)	1.342(4)	C(6)–N(3)	1.317(3)
C(1)–N(1)	1.370(3)	C(6)–N(4)	1.329(3)
C(2)–N(2)	1.355(4)	C(7)–O(2)	1.233(3)
C(3)–N(1)	1.315(3)	C(7)–O(1)	1.276(3)
C(11)–O(3)	1.237(3)	C(11)–O(4)	1.275(3)
O(1)–Co(1)–O(4)	102.82(7)	O(1)–Co(1)–N(3)	120.45(8)
O(4)–Co(1)–N(3)	115.33(7)	O(1)–Co(1)–N(1)	115.83(8)
O(4)–Co(1)–N(1)	97.15(7)	N(3)–Co(1)–N(1)	103.23(8)
C(2)–C(1)–N(1)	109.5(2)	C(1)–C(2)–N(2)	106.7(2)
N(1)–C(3)–N(2)	111.8(2)	C(5)–C(4)–N(3)	108.6(3)
C(4)–C(5)–N(4)	107.0(3)	N(3)–C(6)–N(4)	110.9(2)
C(3)–N(1)–C(1)	104.9(2)	C(3)–N(1)–Co(1)	128.94(16)
C(1)–N(1)–Co(1)	126.14(16)	C(3)–N(2)–C(2)	107.0(2)
C(6)–N(3)–C(4)	105.8(2)	C(6)–N(3)–Co(1)	132.45(17)
C(4)–N(3)–Co(1)	121.74(16)	C(6)–N(4)–C(5)	107.7(2)

Table 3
Selected bond lengths (Å) and angles (°) for $\{[Cu(phen)(\mu_4\text{-bta})_{1/2}]\cdot H_2O\}_n$ (2)

Cu(1)–O(1)	1.942(3)	C(2)–O(2)	1.221(4)
Cu(1)–O(3)	1.982(2)	C(2)–O(1)	1.272(4)
Cu(1)–N(2)	1.984(3)	C(6)–N(2)	1.326(5)
Cu(1)–N(1)	1.990(3)	C(15)–N(1)	1.316(5)
C(1)–O(4)	1.234(4)	C(16)–N(1)	1.366(4)
C(1)–O(3)	1.280(4)	C(17)–N(2)	1.366(4)
O(1)–Cu(1)–O(3)	89.48(11)	N(1)–C(15)–C(14)	122.2(4)
O(1)–Cu(1)–N(2)	97.18(13)	N(1)–C(16)–C(12)	123.4(4)
O(3)–Cu(1)–N(2)	158.32(11)	N(1)–C(16)–C(17)	115.6(3)
O(1)–Cu(1)–N(1)	159.21(12)	N(2)–C(17)–C(9)	122.7(4)
O(3)–Cu(1)–N(1)	98.40(11)	N(2)–C(17)–C(16)	116.6(3)
N(2)–Cu(1)–N(1)	82.55(12)	C(15)–N(1)–C(16)	117.8(3)
O(4)–C(1)–O(3)	122.76(19)	C(15)–N(1)–Cu(1)	129.4(2)
O(2)–C(2)–O(1)	125.1(3)	C(16)–N(1)–Cu(1)	112.7(2)
O(2)–C(2)–C(3)	119.5(3)	C(6)–N(2)–C(17)	118.4(3)
O(1)–C(2)–C(3)	115.3(3)	C(6)–N(2)–Cu(1)	129.1(3)
N(2)–C(6)–C(7)	122.7(4)	C(17)–N(2)–Cu(1)	112.3(2)
C(2)–O(1)–Cu(1)	112.0(2)	C(1)–O(3)–Cu(1)	100.68(18)

thermal conditions. The formation of supramolecular frameworks was influenced by factors such as the solvent system, templates, counterions, ligand geometry, temperature, reaction time, pH level and the ratio between the metal salt and the ligand, etc. [19–24].

During the exploration of the below-mentioned system the molar ratio of Him and Co^{II} was maintained at less than 3:1 and that of phen and Cu^{II} less than 1.7:1, thus making easy the formation of complexes **1** and **2**. As the ratio got larger, $[Co(Him)_6]^{2+}$ cations and $[Cu(phen)_3]^{2+}$ were formed more easily, resulting in the formation of low dimensional products, but no coordination polymers could be formed. The pH value of the reaction system was also an important factor. The experimental results indicated that the pH value of the two reactions must be maintained about 7 and about 10 to obtain the complexes **1** and **2**, respectively. For entropic reasons, the synthesis at higher temperature could promote the formation of polymer frameworks of higher dimensionality through the loss of terminal ancillary ligands. This can be justified by the following reactions. From the viewpoint of thermodynamics, the self-assembled structures represented thermodynamic minima.

$$0.5n\,[\mathrm{bta}]^{4-} + n[\mathrm{Co(H_2O)_6}]^{2+} + 2n\,\mathrm{Him} \rightarrow [\mathrm{Co(Him)_2}(\mu_4\text{-bta})_{1/2}]_n + 6n\,\mathrm{H_2O}\ (\mathbf{1}),$$

$$0.5n\,[\mathrm{bta}]^{4-} + n[\mathrm{Cu(H_2O)_6}]^{2+} + n\,\mathrm{phen} \rightarrow \{[\mathrm{Cu(phen)}(\mu_4\text{-bta})_{1/2}]\cdot \mathrm{H_2O}\}_n + 5n\,\mathrm{H_2O}\ (\mathbf{2}).$$

3.2. Structure description

Fig. 1a shows the fundamental building block of complex **1**. Each Cobalt (II) site is coordinated by two nitrogen atoms of two single Him ligand (Co–N,

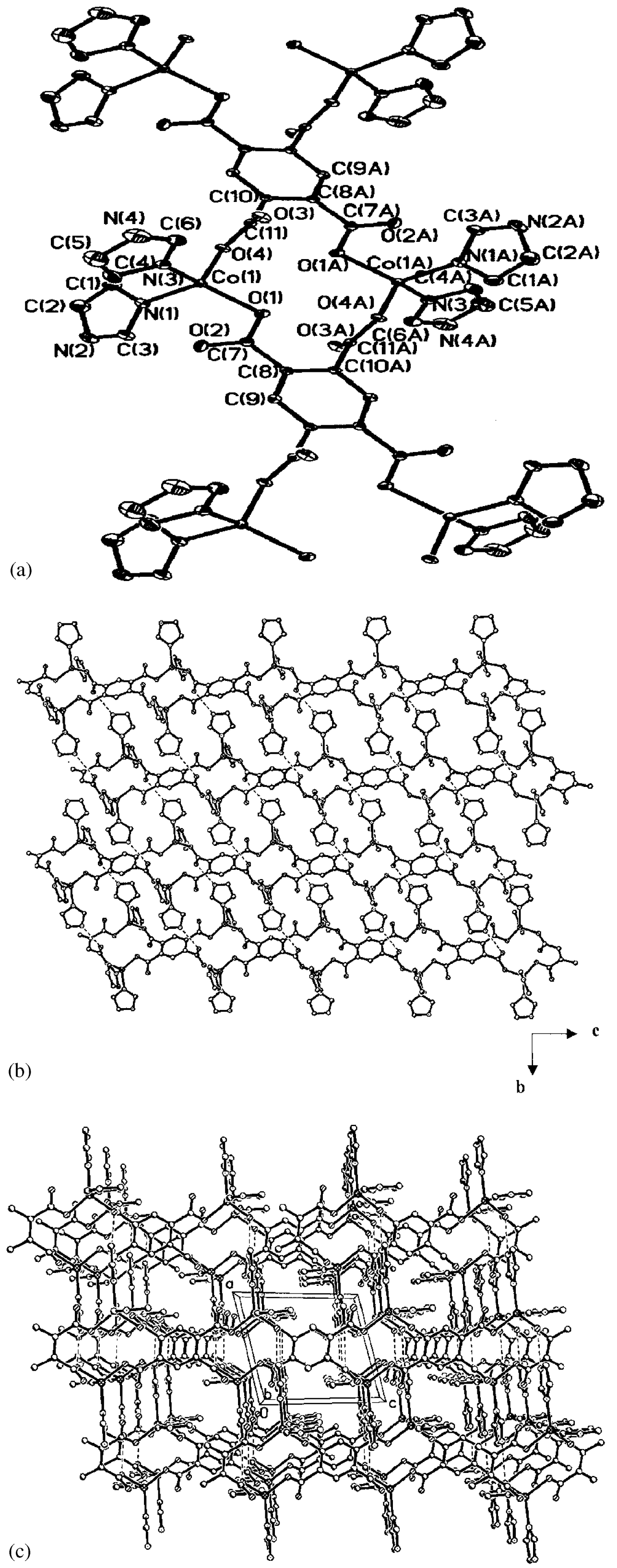


Fig. 1. (a) Molecular structure of **1** showing all non-hydrogen atoms and the atom numbering scheme. 30% probability amplitude displacement ellipsoids are shown. (b) 2-D sheet of **1** formed through hydrogen bonding in the *bc* plane. (c) A view of the 3-D network of **1** along the *b*-axis.

2.035(2) Å, 2.007(2) Å, respectively) and two oxygen atoms from carboxylate groups of two different bta ligands, (Co–O, 1.977(2) Å, 1.981 (2) Å, respectively). The coordination geometry of the Co(II) atom is a distorted tetrahedral with coordination angles O–Co–O of 102.82(7)° and N–Co–N of 103.23(8)° as well as O–Co–N angles ranging from 97.15(7)° to 120.45(8)°. All carboxyl groups of bta are coordinated with Co ions through monodentate interactions. The dihedral angles between each of the four planes of the carboxyl groups and the plane of benzene ring of the bta are, respectively, 93.6°, 14.1°, 14.1°, and 93.6°. The dihedral angles between benzene and each of the two Him rings are 80.5° and 113.2°, respectively, and the dihedral angle between two Him rings is 91.5°. The crystallographic independent units are then linked together via bta to form a 1-D double-metal chain in which 14-membered rings are regularly arranged.

These adjacent double-metal chains along the *b* axis are further connected through hydrogen bonding [N(2)–H···O(3) $(x, y-1, z)$, N(2)···O(3) distance of 2.770 Å and N(2)–H···O(3) angle of 178.10°] between the carboxylate groups and Him of neighboring chains, which leads to a 2-D structural motif in the *bc* plane as illustrated in Fig. 1b. These 2-D sheets along the *a*-axis are linked into a 3-D network through hydrogen bonding [N(4)–H···O(4) $(x-1, y, z)$, N(4)···O(4) distance of 2.929 Å and N(4)–H···O(4) angle of 150.58°] between the carboxylate groups and Him of neighboring chains, as a result, the 14-membered rings constitute parallel channels along *b* axis regularly arranged in the 3-D supramolecular framework (Fig. 1c). The size of 14-membered ring is about 5.415 Å × 7.261 Å.

The molecular structure of **2** is displayed in Fig. 2a. Each copper(II) site is coordinated by two nitrogen atoms of a single phen ligand (Cu–N, 1.984(3) Å, 1.990(3) Å, respectively) and two oxygen atoms from the carboxylate groups of two bta anions in monodentate fashion (Cu–O, 1.942(3) Å, 1.982(2) Å, respectively), forming a linear double-metal chain via μ_4-bta linkage in which 16-membered rings are arranged regularly. The square-planar coordination environment of copper is distorted, with O–Cu–O angle of 89.48(1)°, the N–Cu–N angle of 82.55(1)° and N–Cu–O angles ranging from 97.18(3)° to 159.21(2)°. The four carboxylate groups of the bta are coordinated with four copper ions through the same kind of coordination mode. The four dihedral angles between each of the corresponding carboxylate groups and the C_6 ring plane of the bta are 115.3°, 33.1°, 115.3° and 33.1°, respectively. The dihedral angle between the phen ligand and the benzene plane of bta is 66.4°. In the neighboring two blocks, the phen rings are parallel. There are four copper (II) atoms around the bta ion and each copper (II) atom is coordinated by the two adjacent bta units, so there are two copper (II) ions in each bta unit. Additional water molecules act as space filling particles and contribute to stabilization of the crystal structure by hydrogen bonding.

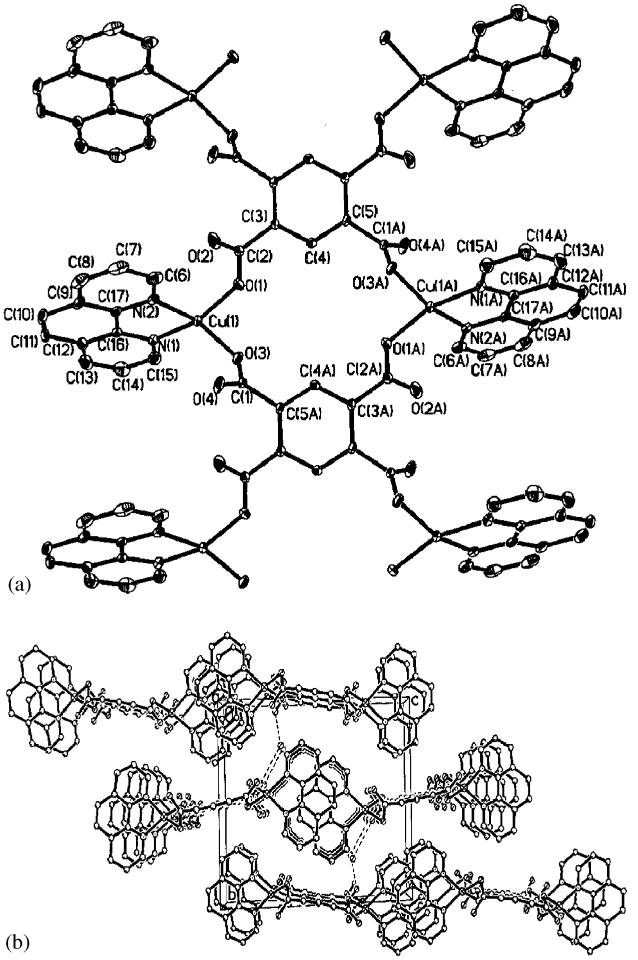


Fig. 2. (a) Molecular structure of **2** showing all non-hydrogen atoms and the atom numbering scheme. 30% probability amplitude displacement ellipsoids are shown. (b) A view of the 3-D network of **2** along the *a*-axis.

The crystal packing diagram of the **2** is shown in Fig. 2b. There exist hydrogen bondings between crystal water molecules and oxygen atoms of non-coordinated carboxyl of bta groups of adjacent chains along the *b*-axis. For example, bond length for Ow1···O4 is 2.860 Å and for Ow1···O2 is 2.836 Å. The phen rings of neighboring chains along the *c*-axis direction are interdigital with each other, and there are strong face-to-face $\pi-\pi$ stacking interactions (running along the *a*-axis direction) between the phen rings. The distance between phen rings of the adjacent chains is ca. 3.27 Å. Through this secondary bonding (including hydrogen bonding and $\pi-\pi$ interaction), a 3-D network is formed from the chains.

3.3. Characterization

The IR spectral data of the two complexes were given in Section 2. In both of the complexes **1** and **2** the absorption bands of the asymmetric and symmetric vibration of carboxylate appeared between 1600 and 1320 cm^{-1}. The $\Delta\nu$ ($\nu_{\text{asym}}(CO_2)$—$\nu_{\text{sym}}(CO_2)$) values of 232 and 265 cm^{-1} in complexes **1** and **2**, respectively, suggested the monodentate coordination of the carboxylate groups [25]. That was also in agreement with the crystal structures.

The solid-state diffuse reflection spectra complex **1** showed the peaks of a strong triplet at 520, 564 and 579 nm. The three maxima at 520, 564 and 579 nm were caused by spin–orbit coupling and transitions to doublet states during the spin-allowed $^4A_2 \rightarrow {}^4T_1$ transition. The characteristics of tetrahedral-coordinated Co(II) with a d^7 configuration [26] were greatly different from those of penta-coordinated [27] and octahedral-coordinated Co(II) [28]. The solid-state diffuse reflection spectra complex **2** showed the two strong bands at 617 nm and 717 nm. The broad band centered at 717 nm was assigned to $d_z^2 \rightarrow d_{x-y}^{2-2}$ transition and a resolved shoulder band at 617 nm was assigned to d_{xy}, d_{xz}, $d_{yz} \rightarrow d_{x-y}^{2-2}$ transition in distorted square-planar symmetry [29].

The thermal behavior of complex **1** was studied from 30°C to 570°C. The TGA curve (see Fig. 3) indicated almost only one stage of weight-loss. Complex **1** was thermally stable until around 330°C and then began to decompose. The TGA of complex **1** showed that the weight loss was 75.2 wt% during the temperature 330–510°C. The step corresponded to the release of organic components (Him and bta)(calculated value of 81.5 wt%). After decomposition of complex **1** at high temperature, the residues were cobalt oxides that constituted 24.8 wt% (calculated value of 23.4 wt%). Several mass loss regions were seen in TGA curve of the complex **2** (Fig. 4). The first mass loss between 30°C and 150°C was 4.2 wt% and corresponded to 1 mol of H_2O per formula unit (calcd. 4.65 wt%). The next mass loss (≈270°C) was that of phen ligand between 170°C and 330°C (loss calculated 46.5 wt%, observed 48.7 wt%). The final step (330–510°C) corresponded to the release of bta ligand, giving copper oxides as the final decomposition products which constituted 22.7 wt% (calcd. 20.68 wt%).

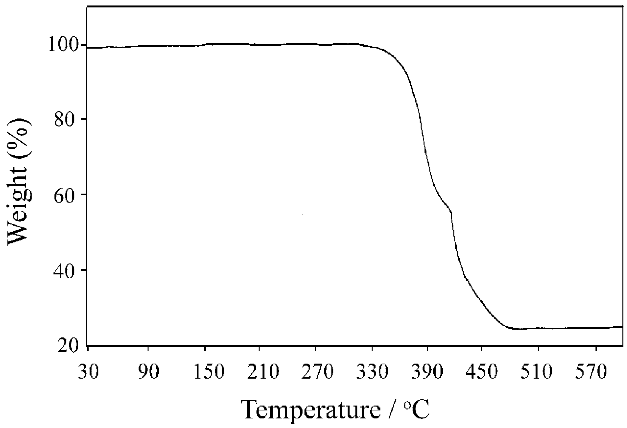


Fig. 3. Thermogravimetric analysis for **1**.

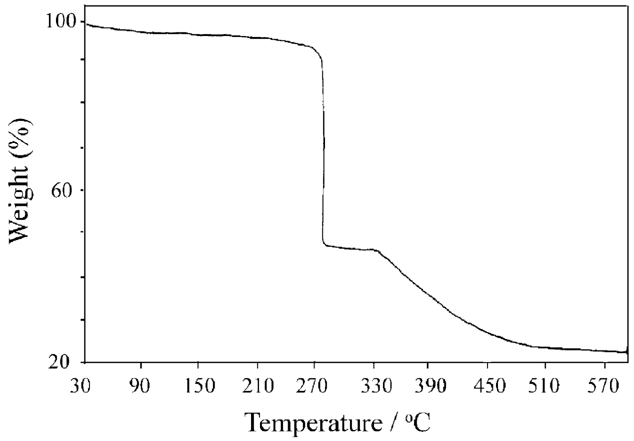


Fig. 4. Thermogravimetric analysis for **2**.

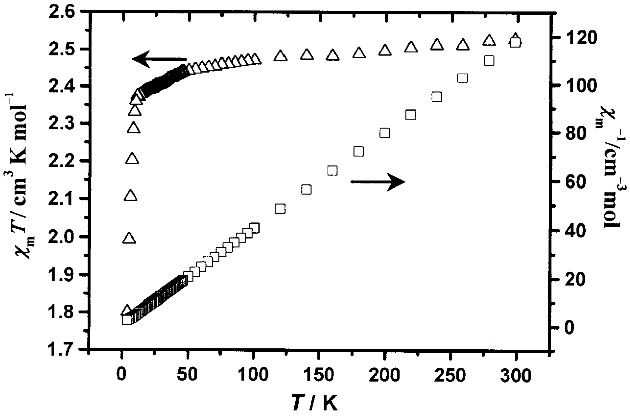


Fig. 5. Plots of $\chi_m T$ and χ_m^{-1} vs temperature for **1**.

3.4. *Magnetic properties of* **1** *and* **2**

Plots of $\chi_m T$ and χ_m^{-1} vs. T for **1** and **2** are shown in Figs. 5 and 6, respectively.

Complex **1**. At 298 K, the $\chi_m T$ value is ca. 2.52 $\text{cm}^3\,\text{K}\,\text{mol}^{-1}$, larger than that (1.88 $\text{cm}^3\,\text{K}\,\text{mol}^{-1}$) of an isolated Co^{2+} ion ($S = 3/2$, $g = 2.0$). The $\chi_m T$ value decreases slowly and then abruptly below 11 K to reach a value of 1.80 $\text{cm}^3\,\text{K}\,\text{mol}^{-1}$and that was a typical antiferromagnetic behavior. The magnetic susceptibilities follow the Curie–Weiss law [$\chi_m = 1/(T-\theta)$] in the whole range of 4–298 K, with a Weiss constant $\theta = -1.39$ K and a Curie constant $C = 2.52\,\text{cm}^3\,\text{mol}^{-1}$ K, corresponding to a g value of 2.31. The more distant Co···Co separation along the chain (9.7 Å) can contribute to very weak antiferromagnetic interaction [30].

Complex **2**. The $\chi_m T$ value at 298 K is ca. 0.52 $\text{cm}^3\,\text{K}\,\text{mol}^{-1}$, higher than that (0.38 $\text{cm}^3\,\text{K}\,\text{mol}^{-1}$) of an isolated Cu^{2+} ion ($S = 1/2$, $g = 2.0$). As the

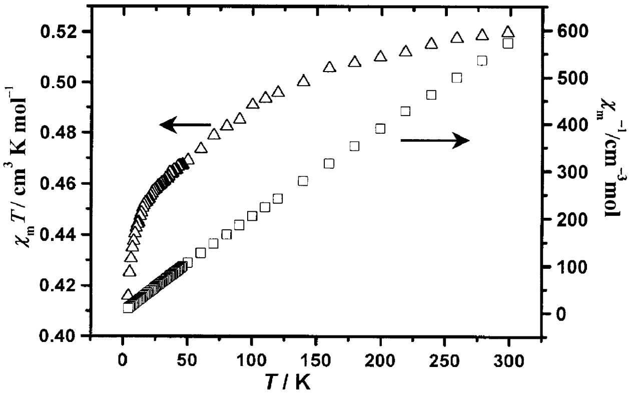


Fig. 6. Plots of $\chi_m T$ and χ_m^{-1} vs temperature for **2**.

temperature decreases, the $\chi_m T$ value decreases continuously, reaching a value of 0.42 cm^3 K mol^{-1} at 4.0 K. This indicates that an antiferromagnetic coupling occurs. The shorter Cu···Cu distance along the chain (7.38 Å) can contribute to antiferromagnetic superexchange coupling [14d, 31]. The magnetic susceptibilities follows the Curie–Weiss law in the whole range of 4–298 K, giving a Weiss constant $\theta = -3.62$ K and a Curie constant $C = 0.52$ cm^3 mol^{-1} K, corresponding to a g value of 2.36.

4. Conclusion

This work shows that four carboxylate groups of bta are coordinated with metal ions through monodentate interactions. The two structures based on covalent interactions exhibit one-dimensional double-metal chains. In the structure of **1**, the chains are linked by different directional hydrogen bondings between the carboxylate groups of bta and Him of neighboring chains, giving rise to a 3-D network. In the structure of **2**, the chains are linked by hydrogen bonding between crystal water molecules and oxygen atoms of non-coordinated carboxylate groups of bta and the chains have $\pi - \pi$ interaction among the phen rings, forming a 3-D network. The experimental verification of complexes **1** and **2** may help understand more about polycarboxylate ligands and engineer new supramolecular architectures. The hydrogen bonding and π–π interaction are of great importance to the construction of open-frameworks with diverse architectures and functions. Our further research plan is to design and prepare polymetallic materials with extended polydimensional structures containing 1,2,4,5-benzenetetracarboxylate ligands and other organic polycarboxylates as bridging ligands, and study their functional performances such as magnetic properties, adsorption and catalysis, etc.

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