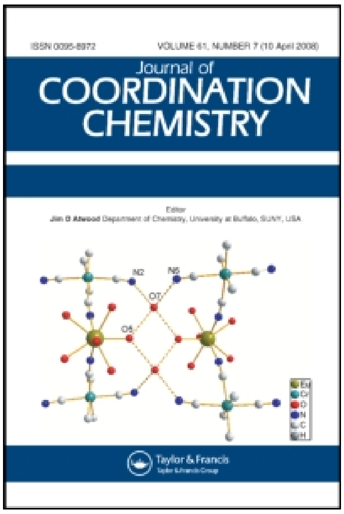

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Different aliphatic acid controlled assembly of coordination polymers constructed from cobalt

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Different aliphatic acid controlled assembly of coordination polymers constructed from cobalt

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Three new Co containing coordination polymers $\{Co_2(suc)_2(1,10'\text{-phen})_2\}_n$ (**1**), $\{Co_2(glu)_2(1,10'\text{-phen})_2\}_n$ (**2**), $\{Co(adip)(1,10'\text{-phen})(H_2O)\}_n$ (**3**), have been synthesized under the hydrothermal condition and characterized by elemental analysis, IR, TG analysis and single crystal X-ray diffraction. Complex **1** exhibits a novel two-dimensional layer framework, in which the bi-nuclear Co clusters are linked by succinic anions. Complex **2** has a one-dimensional chain-like structure. Complex **3** is also a one-dimensional chain-like structure, which is further connected by hydrogen bonds to generate a two-dimensional, layer-like structure. Furthermore, the thermal properties of the above three complexes are studied.

Keywords: Co-containing coordination polymer; Aliphatic acid; Hydrothermal reaction

1. Introduction

The investigation of novel metal–organic hybrid compounds has attracted considerable interest and importance in recent years, not only due to their intriguing structural motifs but also their potential applications in catalysis, medicine, host–guest chemistry and the promising photo-, electro-and magnetic properties [1–6]. In this respect, as the d-block transition metals have different valences, the selection of special inorganic and organic building blocks possessing specific features to fulfill special needs, such as versatile binding modes and coordination abilities to form hydrogen bonds, is the key to construction of a desired framework [7, 8]. Dicarboxylates such as malonate, fumarate and 1,4-benzenedicarboxylate have been widely used in constructing different dimensional metal–organic hybrid compounds [9]; other dicarboxylate ligands are rarely used. There are at least three intriguing structural features for the adipate and glutaric ligands. In the first place, they contain two bridging moieties, which lead to a variety of connection modes with transition metal centers and provides abundant structural motifs. In the second place, they can act as hydrogen bond donors and also as acceptors. Thus they are excellent candidates for construction of multidimensional coordination polymers, especially 2-, 3-D open framework and helical structures. However, introduction of an N-donor chelate ligand such as 2,2′-bpy or 1,10′-phen in

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the {M/adipate} {M/glutaric} (M = transition metal) system may induce new structural evolution. Althrough several interesting examples have been reported on adipate by Jung, Ribas, Bakalbassis and their co-workers [10–11], chelate containing N-donors, for example 2,2′-bpy, 1,10′-phen have seldom been explored. It is well known that chelate ligands are capable of "passivating" metal sites via the N donors of the organic groups. However the syntheses of compounds containing mixed ligands are expected to be more difficult to control than those of compounds containing only one ligand due to different solubility of mixed organic ligands and the coordination competition of organic ligands with the transition metal centers [7].

Hydrothermal synthesis is a powerful method for construction of such organic–inorganic hybrid materials. In such a relatively low temperature and autogenous pressure environment, problems of different solubility for various ligands are minimized, and appropriate O-donor and N-donor ligands may be selected by the metal centers for efficient molecular building during the crystallization process.

In this article, we report three novel Co-containing coordination polymers $\{Co_2(suc)_2(1,10'\text{-phen})_2\}_n$ (**1**), $\{Co_2(glu)_2(1,10'\text{-phen})_2\}_n$ (**2**), $\{Co(adip)(1,10'\text{-phen})(H_2O)\}_n$ (**3**). Complex **1** exhibits an interesting 2-D structure in which the binuclear Co clusters are linked by succinate anions. Complex **2** has an interesting 1-D structure along the *c* axis. Complex **3** is also a one-dimensional, chain-like structure, further connected by hydrogen bonds to generate a two-dimensional, layer-like structure (scheme 1).

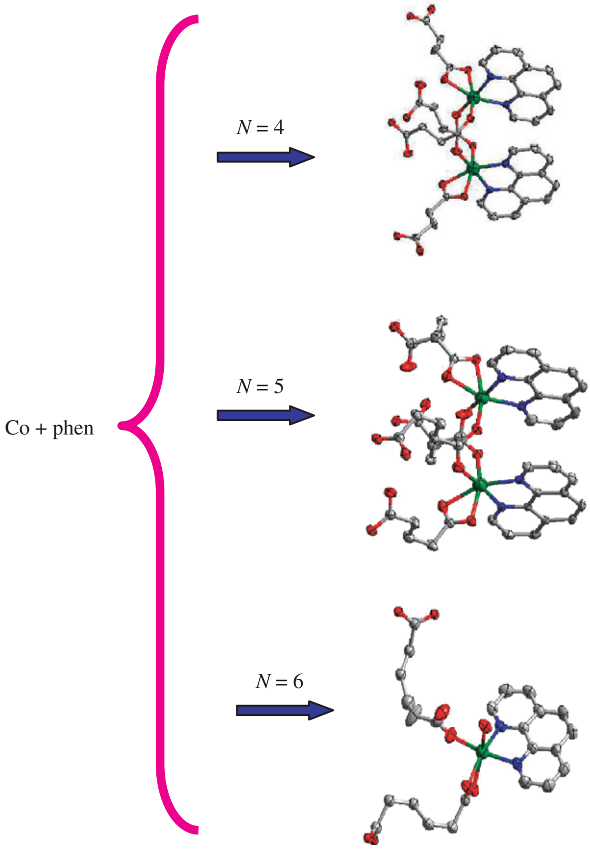
2. Experimental

2.1. *Materials and methods*

All chemicals were purchased of reagent grade and used without further purification. Elemental analyses (C, N, H) were performed on a Perkin-Elemer 2400 CHN elemental analyzer. FT/IR spectra were recorded in the range 4000–400 cm^{-1} on an Alpha Centaut FT/IR spectrophotometer using a KBr pellet. TG analyses were performed on Perkin-Elemer TGA7 instrument in flowing N_2 with a heating rate of 10°C min^{-1}. All measurements were performed at room temperature.

2.2. *Syntheses of complexes*

2.2.1. $\{Co_2(suc)_2(1,10'\text{-phen})_2\}_n$ (1). Complex **1** was prepared from a mixture of $Co(OAc)_2 \cdot 4H_2O$, (0.050 g, 0.20 mmol), succinic acid (0.047 g, 0.40 mmol) and 1,10′-phen (0.036 g, 0.2 mmol) in 6 mL H_2O. The mixture was stirred for 25 min, and pH was then adjusted to 6 with 1 M NaOH. After stirring for a further 25 min, the mixture was transferred to a 23 mL Teflon-lined stainless steel bomb, and kept at 150°C under autogenous pressure for 4 days. After cooling the reaction system to room temperature during 24 h, red block crystals of **1** were obtained. Yield: 0.078 g (55% based on Co). Elem. Anal. Calcd: C, 54.05%; H, 3.38%; N, 7.88%; Co, 16.59%. Found: C, 54.10%; H, 3.45%; N, 7.96% Co, 16.71%. IR: 3061(w), 1574(s), 1536(m), 1509(s), 1441(s),



Scheme 1. Three new Co(II) containing coordination polymers, $\{Co_2(suc)_2(1,10'\text{-}phen)2\}_n$ (**1**), $\{Co_2(glu)_2(1,10'\text{-}phen)_2\}_n$ (**2**), $\{Co(adip)(phen)(H_2O)\}_n$ (**3**), have been synthesized under the hydrothermal condition.

1419(s), 1401(s), 1227(m), 1149(m), 1101(w), 1078(w), 1052(w), 978(m), 942(m), 908(w), 871(s), 778(w), 719(s), 644(m), 593(m), 555(w), 526(w), 422(w).

2.2.2. $\{Co_2(glu)_2(1,10'\text{-}phen)_2\}_n$ (2). In the similar procedure to complex **1**, $Co(OAc)_2 \cdot 4H_2O$, (0.050 g, 0.20 mmol), glutaric acid (0.066 g, 0.50 mmol) and 1,10′-phen (0.090 g, 0.50 mmol) were dissolved in 6 mL water, then pH was adjusted to 6.0 by 1 M NaOH. The mixture was stirred in air for 30 min and then transferred to a 23 mL. Teflon reactor and kept at 170°C for 5 days under autogenous pressure; red crystals of **2** were obtained. Yield: 0.079 g (53% based on Co). Elem. Anal. Calcd: C, 54.95%; H, 4.34%; N, 7.54%; Co, 15.87%. Found: C, 54.80%; H, 4.45%; N, 7.66% Co, 16.01%. IR spectrum (cm^{-1}): 3434(m), 3055(m), 3010(w), 2952(m), 2931(m), 2893(m), 1587(s), 1546(m), 1504(m), 1461(m), 1421(s), 1345(w), 1324(m), 1292(m), 1161(m), 1154(m), 856(s), 827(m), 728(s).

2.2.3. $\{Co(adip)(phen)(H_2O)\}_n$ (3).

$Co(OAc)_2 \cdot 4H_2O$, (0.050 g, 0.20 mmol), adipate (0.073 g, 0.50 mmol) and 1,10′-phen (0.090 g, 0.50 mmol) were dissolved in 6 mL water, then pH was adjusted to 5.5 by 1 M NaOH. The mixture was stirred in air for 30 min and then transferred to a 23 mL Teflon reactor and kept at 180°C for 5 days under autogenous pressure; complex **3** was obtained. Yield: 0.055 g (67%based on Co). Elem. Anal. Calcd: C, 53.83%; H, 4.52%; N, 6.98%; Co, 14.69%. Found: C, 54.01%; H, 4.45%; N, 6.96% Co, 14.71%. IR spectrum (cm^{-1}): 3058(w), 2948(w), 2856(w), 1624(w), 1583(s), 1511(s), 1459(s), 1402(s), 1303(m), 1131(m), 1007(w), 931(w), 855(s), 812(w), 788(w), 728(s), 666(w) 643(m), 625(m).

2.3. *X-ray crystallography*

Single crystals of all the above three complexes were glued on a glass fiber. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer at 293 K using graphite monochromate Mo-Kα radiation ($\lambda = 0.71073$ Å) and IP technique. Empirical absorption correction was applied. The structure was solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXTL 97 crystallographic software package [12]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps. Further details of the X-ray structural analysis are given in table 1. Selected bond lengths and angles are listed in tables 2–4. Crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters are available in supplementary crystallographic data.

Table 1. Crystal data and structure refinement for complexes **1** to **3**.

Empirical formula	$C_{32}H_{24}Co_2N_4O_8$	$C_{34}H_{32}Co_2N_4O_8$	$C_{18}H_{18}CoN_2O_5$
Formula weight	710.41	742.50	401.27
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2/*c*	*P*2(1)/*c*	*C*2/*c*
Unit cell dimensions (Å, °)			
a	12.308(3)	10.537(2)	22.553(5)
b	10.106(2)	20.780(4)	9.1149(18)
c	22.684(5)	13.471(3)	17.494(4)
β	97.62(3)	100.63(3)	103.32(3)
Volume ($Å^3$)	2796.6(10)	2899.0(5)	3499.5(12)
Z	4	4	8
Calculated density ($g\,cm^{-3}$)	1.687	1.701	1.523
Data/restraints/parameters	6395/0/415	6607/0/433	3058/6/255
Reflections collected/unique	26359/6395 [$R(int) = 0.0366$]	27705/6607 [$R(int) = 0.0427$]	12843/3058 [$R(int) = 0.0522$]
Completeness to $\theta = 27.48$	99.7%	99.3%	99.2%
Goodness-of-fit on F^2	0.919	0.956	1.085
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0303$, $wR_2 = 0.0840$	$R_1 = 0.0411$, $wR_2 = 0.1190$	$R_1 = 0.0438$, $wR_2 = 0.1351$
R indices (all data)	$R_1 = 0.0382$, $wR_2 = 0.0902$	$R_1 = 0.0547$, $wR_2 = 0.1258$	$R_1 = 0.0569$, $wR_2 = 0.1407$

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

3. Results and discussion

3.1. *Structure descriptions*

The single crystal structural analysis shows that the structure of **1** is a unique two-dimensional framework. The fundamental unit is shown in figure 1(a). There are two crystallographic independent Co(II) centers in the fundamental unit that are linked by succinic acid ligands, exhibiting two coordination modes. One adopts a bis-chelating

Table 2. Bond lengths (Å) and angles (°) for **1**.

Co(1)–O(4)	2.0366(14)	Co(l)–O(2)	2.0443(15)
Co(1)–N(2)	2.1284(17)	Co(l)–N(1)	2.1552(17)
Co(1)–O(6)	2.1760(15)	Co(1)–O(5)	2.1862(13)
Co(2)–O(1)	2.0133(14)	Co(2)–O(3)	2.0730(15)
Co(2)–N(3)	2.1197(17)	Co(2)–N(4)	2.1448(16)
Co(2)–O(7)	2.1676(14)	Co(2)–O(8)	2.1735(15)
O(7)–Co(2)–O(8)	60.55(5)	N(4)–Co(2)–O(8)	90.39(6)
N(3)–Co(2)–O(8)	160.83(6)	O(3)–Co(2)–O(8)	87.04(7)
O(1)–Co(2)–O(8)	101.07(5)	N(4)–Co(2)–O(7)	87.02(6)
N(3)–Co(2)–O(7)	103.33(6)	O(3)–Co(2)–O(7)	86.01(6)
O(1)–Co(2)–O(7)	161.22(6)	N(3)–Co(2)–N(4)	77.76(6)
O(3)–Co(2)–N(4)	172.96(6)	O(1)–Co(2)–N(4)	89.43(6)
O(3)–Co(2)–N(3)	102.92(7)	O(1)–Co(2)–N(3)	93.91(6)
O(1)–Co(2)–O(3)	97.49(6)	O(6)–Co(1)–O(5)	60.21(5)
N(1)–Co(1)–O(5)	86.30(6)	N(2)–Co(1)–O(5)	100.26(5)
O(2)–Co(1)–O(5)	86.61(6)	O(4)–Co(1)–O(5)	158.50(6)
N(1)–Co(1)–O(6)	91.11(6)	N(2)–Co(1)–O(6)	158.35(5)
O(2)–Co(1)–O(6)	85.16(7)	O(4)–Co(1)–O(6)	99.18(5)
N(2)–Co(1)–N(1)	77.49(6)	O(2)–Co(1)–N(1)	172.90(6)
O(4)–Co(1)–N(1)	88.18(6)	O(2)–Co(1)–N(2)	104.03(7)
O(4)–Co(1)–N(2)	98.80(6)	O(4)–Co(1)–O(2)	98.37(6)

Table 3. Bond lengths (Å) and angles (°) for **2**.[a]

Co(1)–O(6)	2.0434(19)	Co(2)–O(8)	2.0362(19)
Co(1)–O(7)	2.053(2)	Co(2)–O(5)	2.0528(19)
Co(1)–N(4)	2.117(2)	Co(2)–N(2)	2.137(2)
Co(1)–O(2)#1	2.1195(18)	Co(2)–O(2)	2.1186(18)
Co(1)–O(3)#1	2.1532(19)	Co(2)–N(1)	2.153(2)
O(6)–Co(1)–O(7)	93.63(9)	O(8)–Co(2)–O(5)	94.33(8)
O(6)–Co(1)–N(4)	94.91(7)	O(8)–Co(2)–N(2)	98.63(8)
O(7)–Co(1)–N(4)	100.82(10)	O(5)–Co(2)–N(2)	104.21(9)
O(6)–Co(1)–N(3)	91.77(8)	O(8)–Co(2)–O(2)	160.88(8)
O(7)–Co(1)–N(3)	174.54(8)	O(5)–Co(2)–O(2)	87.19(8)
N(4)–Co(1)–N(3)	77.92(8)	N(2)–Co(2)–O(2)	99.46(7)
O(6)–Co(1)–O(3)	101.43(7)	O(8)–Co(2)–N(1)	90.28(8)
O(7)–Co(1)–O(3)	87.76(9)	O(5)–Co(2)–N(1)	174.76(7)
N(4)–Co(1)–O(3)	161.05(8)	N(2)–Co(2)–N(1)	77.49(8)
N(3)–Co(1)–O(3)	91.92(8)	O(2)–Co(2)–N(1)	87.64(8)
O(6)–Co(1)–O(4)	161.64(7)	O(8)–Co(2)–O(1)	101.62(7)
O(7)–Co(1)–O(4)	87.77(8)	O(5)–Co(2)–O(1)	83.99(8)
N(4)–Co(1)–O(4)	102.82(7)	N(2)–Co(2)–O(1)	157.50(8)
N(3)–Co(1)–O(4)	87.35(8)	O(2)–Co(2)–O(1)	59.52(7)
O(3)–Co(1)–O(4)	60.30(7)	N(1)–Co(2)–O(1)	92.66(7)

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

Table 4. Bond lengths (Å) and angles (°) for **3**.

Co(1)–O(1)	2.057(2)	Co(1)–O(1)	2.096(2)
Co(1)–N(1)	2.111(2)	Co(1)–N(1)	2.154(3)
Co(1)–O(4)	2.158(2)	Co(1)–O(3)	2.191(2)
O(1)–Co(1)–O(5)	91.30(10)	O(1)–Co(1)–N(1)	94.99(10)
O(5)–Co(1)–N(1)	97.62(9)	O(1)–Co(1)–N(2)	172.26(10)
O(5)–Co(1)–N(2)	86.31(10)	N(1)–Co(1)–N(2)	78.05(10)
O(1)–Co(1)–O(4)	93.42(9)	O(5)–Co(1)–O(4)	96.85(8)
N(1)–Co(1)–O(4)	163.07(9)	N(2)–Co(1)–O(4)	94.17(10)
O(1)–Co(1)–O(3)	89.50(9)	O(5)–Co(1)–O(3)	156.99(8)
N(1)–Co(1)–O(3)	105.22(8)	N(2)–Co(1)–O(3)	95.58(9)
O(4)–Co(1)–O(3)	60.15(8)		

mode and the other is bis-bridging mode. These coordination modes are often found in this kind of complex. Co(1) adopts distorted octahedral coordination with four oxygen atoms and two nitrogen atoms. The Co(1)–O bond lengths are in the range of 2.036 Å (Co(1)–O(4)) to 2.186 Å (Co(1)–O(5)), and the Co(1)–N bond lengths are 2.129 Å, and 2.155 Å for Co(1)–N(2), and Co(1)–N(1) respectively. The O–Co–O bond angles are in the range 60.21 to 158.50°. The Co(2) ion adopts the same coordination mode as Co(1), but with different bond lengths and angles. The succinic acid ligands in this complex adopt two kinds of coordination modes, bis-chelating, and bis-bridging. Succinic acid ligands link adjacent Co ions together to form a binuclear Co(II) unit. The binuclear Co(II) units are further connected by organic ligand to form a one-dimensional chain as shown in figure 1(b). The adjacent one-dimensional chains are connected by bis-bridging succinic acid ligand to form two-dimensional 4,4′-net structure as shown in figure 1(c).

X-ray crystallographic analysis reveals that complex **2** exhibits an interesting one-dimensional network. The fundamental unit is shown in figure 2(a). There is one crystallographically unique Co(II) center in the asymmetric unit. The Co(1) center is defined by two nitrogen atom of one phen ring with Co(1)–N average bond distance of 2.126 Å, two oxygen atoms (Co(1)–O(5) = 2.193 Å, Co(1)–O(3) = 2.151 Å) of one chelating carboxylate group and two oxygen atoms of the other two bridging carboxylate groups (Co(1)–O(2) = 2.051 Å, Co(1)–O(8) = 2.043 Å). The Co(II) center displays distorted octahedral coordination geometry. Such two $\{CoN_2O_4\}$ octahedra units are connected together to form a linear binuclear Co(II) dimer via two carboxal groups of two different glutaric ligands in the edge-sharing mode. In addition, two carboxylate groups of a glutaric anion exhibit different coordination modes with Co(II) centers. One carboxylate group acts as a bidentate ligand to link two Co(II) centers, while another carboxylate group exhibits a bis-chelating mode to bridge one Co(II) center. On the basis of such a coordination mode, a one-dimensional covalently bonded framework is formed, as shown in figure 2(b).

Complex **3** is a two-dimensional supramolecular network composed of one-dimensional chains. The fundamental unit is shown in figure 3(a). There is only one crystallographic independent Co(II) ions in the structure, and it adopts distorted octahedral geometry with three oxygen atoms (two from a chelating carboxylate group and the other from a monodentate carboxylate group) two nitrogen atoms from 1,10′-phen, the other coordination site occupied by water. The Co–O distances range from 2.057 to 2.191 Å, and the O–Co–O bond angles are in the range of 60.15° to

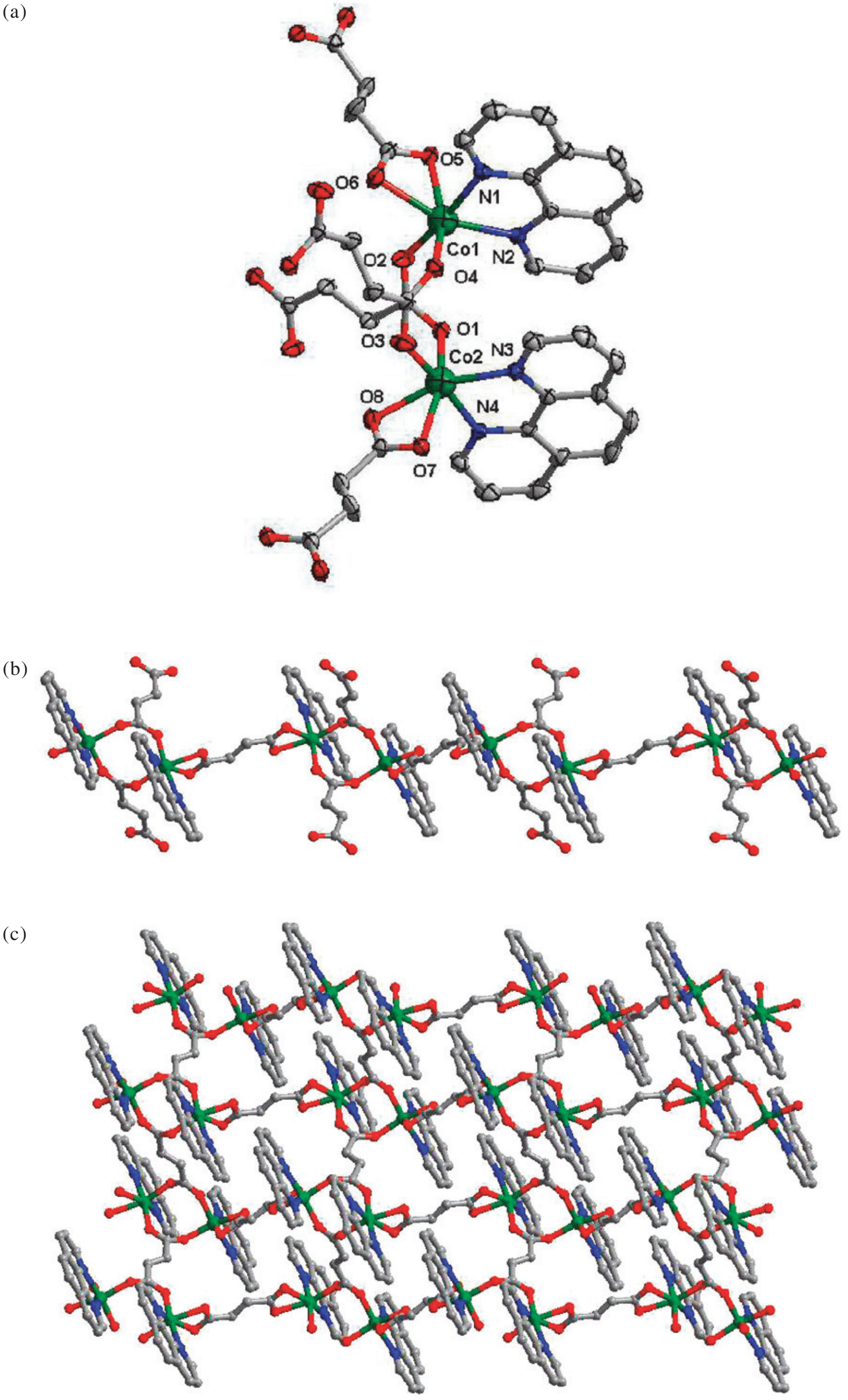


Figure 1. (a) ORTEP drawing of the Co(II) coordination environment in complex **1**. (b) A view of the one-dimensional chain structure of **1**. (c) The two-dimensional 4,4-net layer network of **1**.

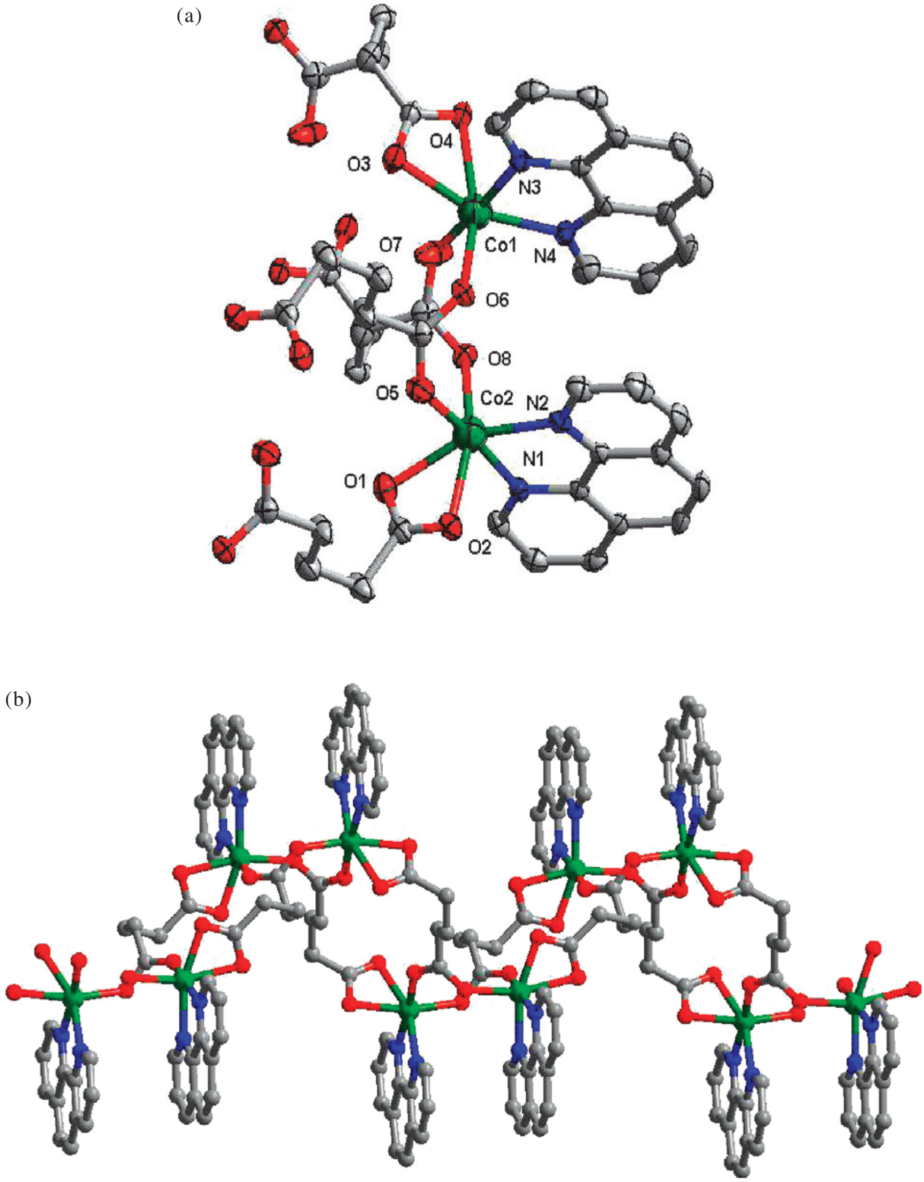


Figure 2. (a) ORTEP drawing of the Co(II) coordination environment in complex **2**. (b) The one-dimensional chain structure of **2**.

156.99°. The adipic acid ligand adopts coordination modes, one bis-chelating and the other bis-monodentate. The Co(II) ions are connected by these adipate ligands to form a one-dimensional, chain-like structure along the (1, 0, 1) axis as shown in figure 3b. Two adjacent chains are connected by hydrogen bonds to form a two-dimensional supramolecular network with O(4)–H(1)–O(5) = 1.882 Å as shown in figure 3c.

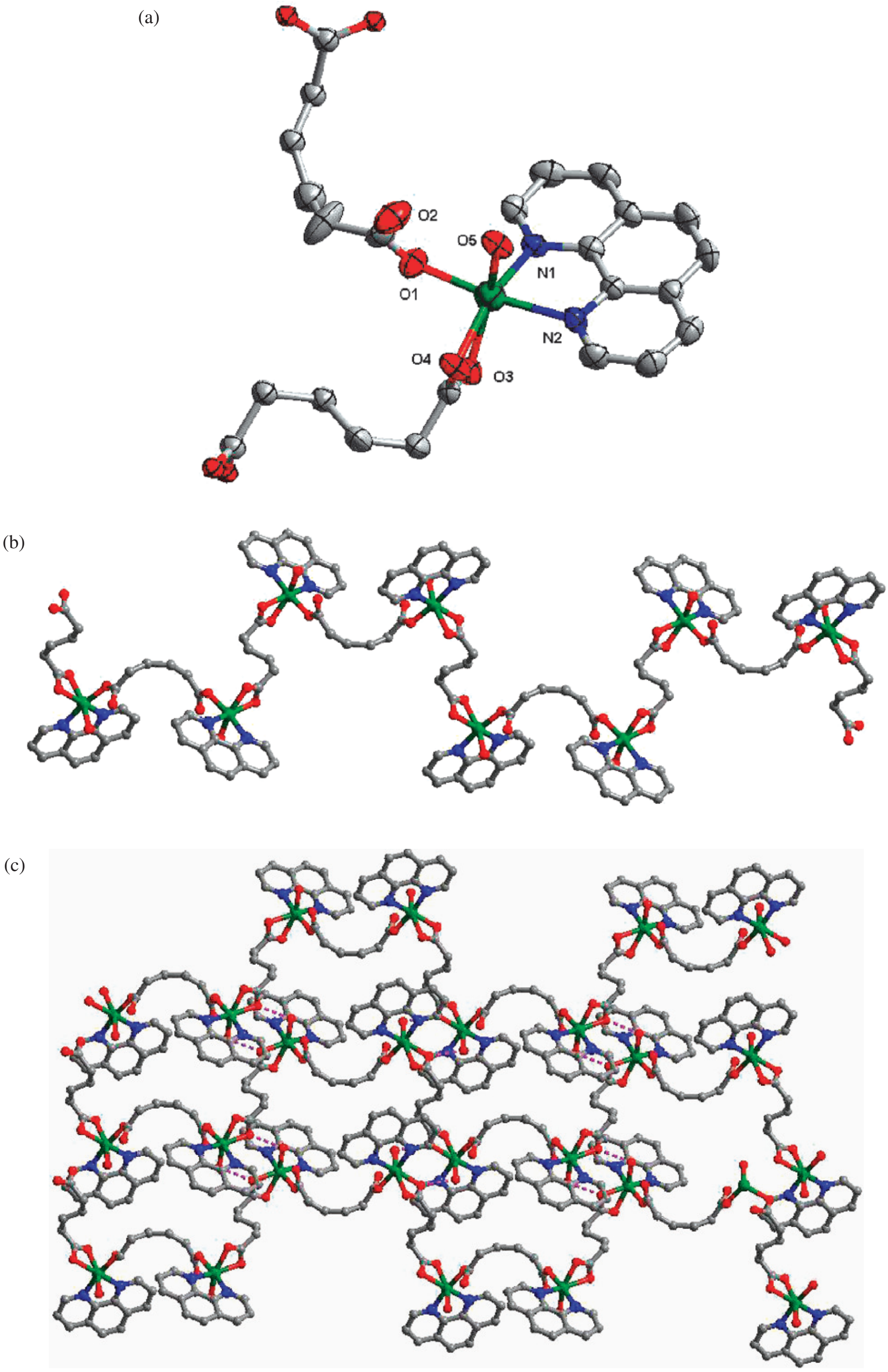


Figure 3. (a) ORTEP drawing of the Co(II) coordination environment in complex **3**. (b) View of the one-dimensional chain structure of **3**. (c) A view of the two-dimensional supramolecular structure of **3**.

3.2. *IR spectroscopy*

The IR spectrum of complex **1** shows characteristic bands of carboxyl group 1574, 1509 cm^{-1} for the anti symmetric stretch and 1441, 1401 cm^{-1} for the symmetric stretch. The separation (Δ) between γ_{asym} (CO_2) and γ_{sym} (CO_2) indicate the coordination modes in complex **1**. The IR spectrum of complex **2** shows characteristic bands of carboxyl at 1587 cm^{-1} for the antisymmetric stretch and 1504 and 1421 cm^{-1} for symmetric stretching. The separations (Δ) between γ_{asym} (CO_2) and γ_{sym} (CO_2) indicate the presence of chelating (83 cm^{-1}) and bridging (166 cm^{-1}) coordination modes of carboxyl groups in complex **2**. For complex **3**, characteristic bands of carboxyl at 1583, 1511 and 1459 cm^{-1}, 1402 cm^{-1} represent the antisymmetric stretching and symmetric stretching, respectively. The separations (Δ) between γ_{asym} (CO_2) and γ_{sym} (CO_2) indicate the presence of chelating (52 cm^{-1}) and bridging (181 cm^{-1}) coordination modes of carboxyl groups in complex **3**. The peak appears at 3058 cm^{-1} represents the existence of water molecules [13].

3.3. *Thermo gravimetric analyses*

For complex **1**, the weight loss of 83.47% from 345–480°C is equivalent to the loss of coordinated ligands (Calcd: 83.33%). TG curve of complex **2** also exhibits only one weight loss stage. The weight loss of 83.34% in the range of 365–560°C corresponds to the concomitant release of 1,10′-phen and glutaric ligands (Calcd 83.50%). For complex **3**, the first weight loss of 4.57% (Calcd 4.49%) represents the loss of water, and the next weight loss represents the loss of 80.56% (Calcd 80.74%).

4. Conclusions

In this article, we successfully combined Co and succinate, glutarate, and adipate with other organic ligands and synthesized three novel coordination polymers. The successful synthesis of the new compound **1**, **2** and **3** proves the capability of hydrothermal reaction in preparing organic–inorganic hybrid materials and shows the strong coordination capacity of adipate. The rational combination of the two aspects enriches the chemistry of metal-based coordination polymers.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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