

Two New Cd(II) and Co(II) Coordination Polymers Based on a 1,10-Phenanthroline Derivative and Tri- or Tetra-Carboxylates: Syntheses, Structures and Photoluminescence

Xiu-Yan Wang^{a,b}, Yu He^{a,b} and Fei-Fei Liu^{a,b}

^a College of Chemistry, Jilin Normal University, Siping 136000, People's Republic of China

^b Key Laboratory of Preparation and Applications of Environmental Friendly Materials, Ministry of Education, Siping 136000, People's Republic of China

Reprint requests to Prof. Xiu-Yan Wang. E-mail: wangxiuyan2001@yahoo.com.cn

Z. Naturforsch. **2012**, 67b, 459–464 / DOI: 10.5560/ZNB.2012-0029

Received January 27, 2012

Two new coordination polymers constructed with the 1,10-phenanthroline derivative 2-(2-chloro-6-fluorophenyl)-1H-imidazo[4,5-f][1,10]-phenanthroline (L) and different carboxylates, namely, $[\text{Cd}_2(\text{L})_2(1,3,5\text{-BTC})(\text{Cl})]\cdot\text{H}_2\text{O}$ (**1**) and $[\text{Co}_2(\text{L})_2(1,2,4,5\text{-BTC})(\text{H}_2\text{O})_2]$ (**2**), have been synthesized under hydrothermal conditions (1,3,5-BTC = 1,3,5-benzenetricarboxylate anion and 1,2,4,5-BTC = 1,2,4,5-benzenetetracarboxylate anion). Crystal data for **1**: $\text{C}_{47}\text{H}_{25}\text{Cd}_2\text{Cl}_3\text{F}_2\text{N}_8\text{O}_7$, triclinic, space group $P\bar{1}$, $a = 10.1084(5)$, $b = 14.9285(7)$, $c = 15.2930(4)$ Å, $\alpha = 72.1050(10)$, $\beta = 86.160(2)$, $\gamma = 79.6000(10)^\circ$, $V = 2159.88(16)$ Å³, $Z = 2$. Crystal data for **2**: $\text{C}_{24}\text{H}_{13}\text{ClCoFN}_4\text{O}_5$, triclinic, space group $P\bar{1}$, $a = 7.4767(15)$, $b = 10.094(2)$, $c = 14.772(3)$ Å, $\alpha = 91.23(3)$, $\beta = 100.95(3)$, $\gamma = 106.57(3)^\circ$, $V = 1045.8(4)$ Å³, $Z = 2$. Their crystal structures have been determined by single-crystal X-ray diffraction analyses, and the compounds further characterized by physico-chemical and spectroscopic methods. In **1**, each 1,3,5-BTC anion connects five Cd(II) atoms to form a double chain. These chains are extended into 2D supramolecular networks through $\pi-\pi$ interactions. $\text{N}-\text{H}\cdots\text{Cl}$, $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonding interactions further stabilize the network of **1**. In **2**, each 1,2,4,5-BTC anion bridges four Co(II) atoms to yield a chain. $\pi-\pi$ interactions among adjacent chains result in a 2D supramolecular architecture.

Key words: Crystal Structure, 2-(2-Chloro-6-fluorophenyl)-1H-imidazo[4,5-f][1,10]-phenanthroline, 1,3,5-Benzenetricarboxylate, 1,2,4,5-Benzenetetracarboxylate

Introduction

Current interest in coordination polymers based on the assembly of metal ions and multifunctional organic ligands is rapidly expanding owing to their intriguing architectures and potential applications [1–5]. A variety of coordination polymers with fascinating structure topologies have been prepared by taking certain factors into account, such as the coordination mode of the metal ion and the shape, flexibility, functionality, and symmetry of the organic ligands, of which many are derived from multicarboxylic acids due to their interesting structural characteristics [6–8]. Organic ligands with carboxylate groups are especially interesting because of their various coordination modes to metal ions, resulting from completely or partially deprotonated sites allowing for the large diversity of topologies [9–11].

On the other hand, chelating *N*-donor ligands have been intensely investigated as auxiliary ligands for the construction of novel coordination polymers [12]. In this regard, 1,10-phenanthroline (phen) has been widely utilized to build up supramolecular architectures because of its excellent coordination ability and its large conjugated system that can easily form $\pi-\pi$ interactions [13]. As far as we know, less attention has so far been given to its important derivative 2-(2-chloro-6-fluorophenyl)-1H-imidazo[4,5-f][1,10]-phenanthroline (L) [14–17]. It possesses an aromatic system and is a good candidate for the construction of supramolecular architectures. In this work, two new coordination polymers $[\text{Cd}_2(\text{L})_2(1,3,5\text{-BTC})(\text{Cl})]\cdot\text{H}_2\text{O}$ (**1**) and $[\text{Co}_2(\text{L})_2(1,2,4,5\text{-BTC})(\text{H}_2\text{O})_2]$ (**2**) have been synthesized under hydrothermal conditions (1,3,5-BTC = 1,3,5-benzenetricarboxylate anion and 1,2,4,5-BTC =

1,2,4,5-benzenetetracarboxylate anion). Their composition and structures have been determined by single-crystal X-ray diffraction analyses, IR spectra, and elemental analyses. In addition, the thermal and luminescence properties of the complexes have also been investigated in the solid state at room temperature.

Results and Discussion

Structure description of **1**

Selected bond lengths and angles for [Cd₂(L)₂(1,3,5-BTC)(Cl)]·H₂O (**1**) and [Co₂(L)₂(1,2,4,5-BTC)(H₂O)₂] (**2**) are listed in Table 1. Single-crystal X-ray structure analysis has shown that compound **1** has a two-dimensional

supramolecular network structure. As shown in Fig. 1, the asymmetric unit of **1** contains two unique Cd(II) atoms, one 1,3,5-BTC anion, one chloride anion, and two kinds of L ligands. The Cd1 atom is six-coordinated by two nitrogen atoms from one L ligand and four carboxylate oxygen atoms from three different 1,3,5-BTC anions in an octahedral coordination sphere. The Cd2 atom is five-coordinated by two nitrogen atoms from one L ligand, two carboxylate oxygen atoms from two different 1,3,5-BTC anions, and one chloride anion in a trigonal-bipyramidal arrangement. The Cd–O bond lengths range from 2.211(2) to 2.434(2) Å, and the Cd–N distances vary from 1.989(6) to 2.125(3) Å. These values are near to the data reported for [Cd₂(DFDA)₂(L)₂] (DFDA = 9,9-dipropylfluorene-2,7-dicarboxylate anion and

Compound 1			
Distances			
Cd(1)–N(1)	2.366(3)	Cd(1)–N(2)	2.300(3)
Cd(1)–O(2)	2.357(3)	Cd(1)–O(5) ^{#2}	2.234(2)
Cd(1)–O(3) ^{#1}	2.321(3)	Cd(1)–O(4) ^{#1}	2.434(2)
Cd(2)–N(5)	2.351(3)	Cd(2)–N(6)	2.344(3)
Cd(2)–O(6)	2.283(2)	Cd(2)–Cl(1)	2.4950(10)
Cd(2)–O(1) ^{#2}	2.211(2)		
Angles			
O(5) ^{#2} –Cd(1)–N(2)	139.63(9)	O(5) ^{#2} –Cd(1)–O(3) ^{#1}	100.02(10)
N(2)–Cd(1)–O(3) ^{#1}	116.62(11)	O(5) ^{#2} –Cd(1)–O(2)	83.33(10)
N(2)–Cd(1)–O(2)	80.03(10)	O(3) ^{#1} –Cd(1)–O(2)	90.70(9)
O(5) ^{#2} –Cd(1)–N(1)	98.28(10)	N(2)–Cd(1)–N(1)	71.48(10)
O(3) ^{#1} –Cd(1)–N(1)	130.12(10)	O(2)–Cd(1)–N(1)	137.43(9)
O(5) ^{#2} –Cd(1)–O(4) ^{#1}	118.26(9)	N(2)–Cd(1)–O(4) ^{#1}	97.62(10)
O(3) ^{#1} –Cd(1)–O(4) ^{#1}	54.23(9)	O(2)–Cd(1)–O(4) ^{#1}	139.84(9)
N(1)–Cd(1)–O(4) ^{#1}	76.23(9)	O(1) ^{#2} –Cd(2)–O(6)	94.01(9)
O(1) ^{#2} –Cd(2)–N(6)	101.21(10)	O(6)–Cd(2)–N(6)	146.25(10)
O(1) ^{#2} –Cd(2)–N(5)	159.28(10)	O(6)–Cd(2)–N(5)	84.03(9)
N(6)–Cd(2)–N(5)	71.16(10)	O(1) ^{#2} –Cd(2)–Cl(1)	109.45(7)
O(6)–Cd(2)–Cl(1)	105.36(7)	N(6)–Cd(2)–Cl(1)	97.72(8)
N(5)–Cd(2)–Cl(1)	90.89(7)		
Compound 2			
Distances			
Co(1)–N(1)	2.150(4)	Co(1)–N(2)	2.120(4)
Co(1)–O(1)	2.068(3)	Co(1)–O(1W)	2.095(4)
Co(1)–O(4) ^{#1}	2.169(3)	Co(1)–O(3) ^{#1}	2.174(4)
Angles			
O(1)–Co(1)–O(1W)	88.41(14)	O(1)–Co(1)–N(2)	106.31(13)
O(1W)–Co(1)–N(2)	97.30(15)	O(1)–Co(1)–N(1)	171.44(15)
O(1W)–Co(1)–N(1)	83.42(14)	N(2)–Co(1)–N(1)	77.37(14)
O(1)–Co(1)–O(4) ^{#1}	93.73(12)	O(1W)–Co(1)–O(4) ^{#1}	115.38(15)
N(2)–Co(1)–O(4) ^{#1}	142.16(14)	N(1)–Co(1)–O(4) ^{#1}	87.51(13)
O(1)–Co(1)–O(3) ^{#1}	91.26(13)	O(1W)–Co(1)–O(3) ^{#1}	175.80(13)
N(2)–Co(1)–O(3) ^{#1}	86.82(14)	N(1)–Co(1)–O(3) ^{#1}	96.70(14)
O(4) ^{#1} –Co(1)–O(3) ^{#1}	60.45(13)		

Table 1. Selected bond lengths (Å) and angles (deg) for **1** and **2** with estimated standard deviations in parentheses.

Symmetry transformations used to generate equivalent atoms for **1**: ^{#1} $-x, -y, -z + 2$; ^{#2} $-x + 1, -y, -z + 2$; for **2**: ^{#1} $x + 1, y, z$.

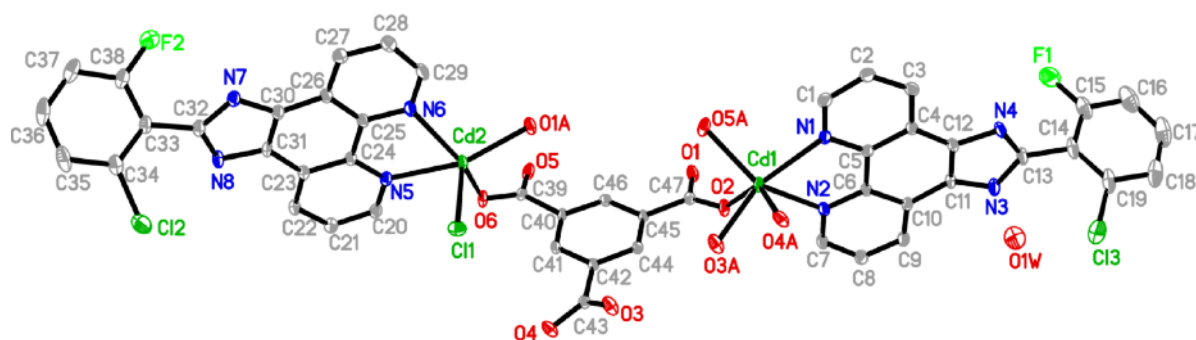


Fig. 1 (color online). ORTEP view of **1** showing the local coordination environments of the Cd(II) centers with hydrogen atoms and water molecules omitted for clarity (displacement ellipsoids at the 30 % probability level).

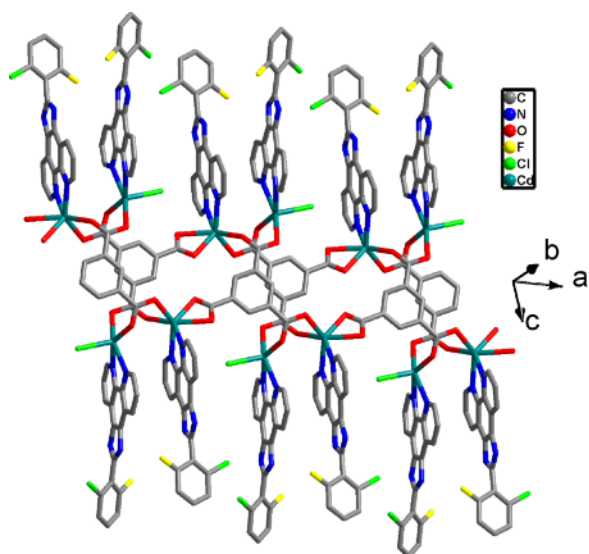


Fig. 2 (color online). View of the double chain structure of **1**.

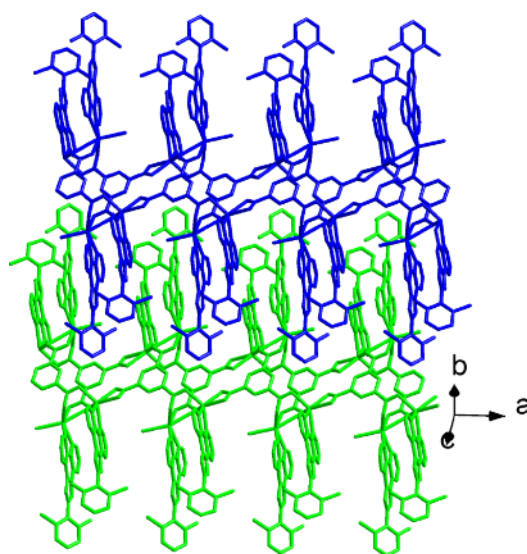


Fig. 3 (color online). View of the 2D supramolecular architecture of **1** formed by π – π interactions.

L1 = 1,4-bis(imidazol-1-ylmethyl)benzene) [18]. Each 1,3,5-BTC anion connects five Cd(II) atoms to form a double chain structure (Fig. 2). Notably, the L ligands are located on both sides of the double chains. The lateral L ligands from adjacent chains are paired to furnish strong π – π interactions (centroid-to-centroid distance 3.47(2) Å and face-to-face distance 3.39(3) Å). Therefore, the chains are extended into two-dimensional supramolecular networks through these π – π interactions (Fig. 3). Obviously, the π – π stacking interactions play an important role in the formation and stabilization of the supramolecular network structure. In addition, hydrogen bonding interactions, such as the O–H...N between the water

molecule and the nitrogen atoms of L, N–H...Cl between the nitrogen atom of L and the chlorine atom of L, and N–H...O between the nitrogen atoms of L and carboxylate oxygen atoms of 1,3,5-BTC, further stabilize the structure of **1**.

Structure description of **2**

Single-crystal X-ray structure analysis has shown that the asymmetric unit of **2** consists of one Co(II) atom, one L molecule, half a 1,2,4,5-BTC ligand, and one coordinated water molecule (Fig. 4). Each Co(II) atom is six-coordinated by four oxygen atoms from two different 1,2,4,5-BTC anions and the water

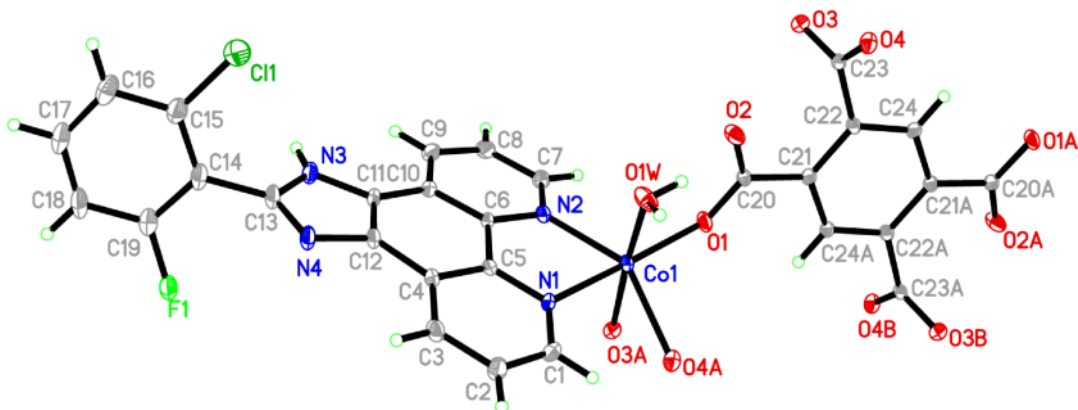


Fig. 4 (color online). ORTEP view of **2** showing the local coordination environment of the Co(II) center with hydrogen atoms and non-coordinated water molecules omitted for clarity (displacement ellipsoids at the 30% probability level; H atoms as spheres with arbitrary radii).

molecule, and two nitrogen atoms from one L ligand in a distorted octahedral mode. The two carboxylate oxygen atoms (O1 and O4A) from two 1,2,4,5-BTC anions and two nitrogen atoms (N1 and N2) from one L ligand make up the basal plane, and the axial positions are occupied by two oxygen atoms (O1W and O3A). The Co–O distances vary from 2.068(3) to 2.174(4) Å. The four carboxylate units of the 1,2,4,5-BTC anion show two kinds of coordination modes: two are linked to Co(II) atoms in a monodentate mode, while the other two chelate one Co(II) atom (Fig. 4). In these modes, each 1,2,4,5-BTC anion connects four Co(II) atoms to yield a double chain structure (Fig. 5). The L ligands are attached at both sides of the chains. The most in-

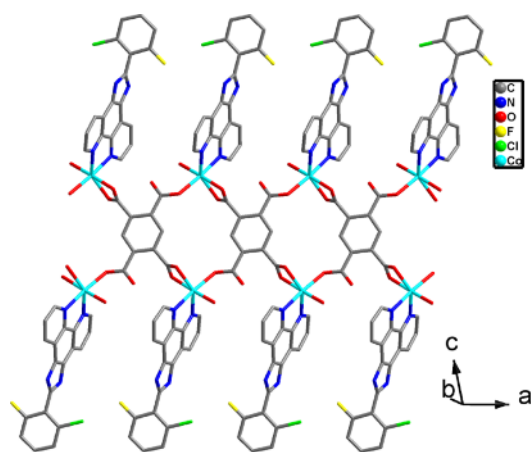


Fig. 5 (color online). View of the double chain structure of **2**.

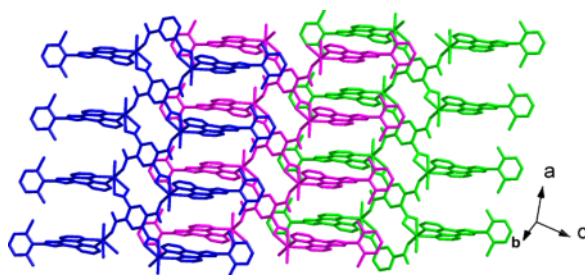


Fig. 6 (color online). View of the layer architecture of **2** formed by π – π interactions.

teresting feature of the compound is the presence of π – π stacking interactions among neighboring chains (centroid-centroid distance of 3.58(4) Å and face-to-face distance of 3.40(3) Å), which extend the adjacent chains into a two-dimensional supramolecular network (Fig. 6).

Luminescence properties

Luminescence properties of Cd(II) coordination polymers are very attractive because of their various applications in chemical sensors, electroluminescence and photochemistry [19]. The solid-state photoluminescent properties of the free ligand L and of compound **1** were investigated in the solid state at room temperature. As shown in Fig. 7, the emission peaks of the free ligand L are observed at about 400 and 550 nm with the excitation peak at 325 nm, probably attributable to $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions [19].

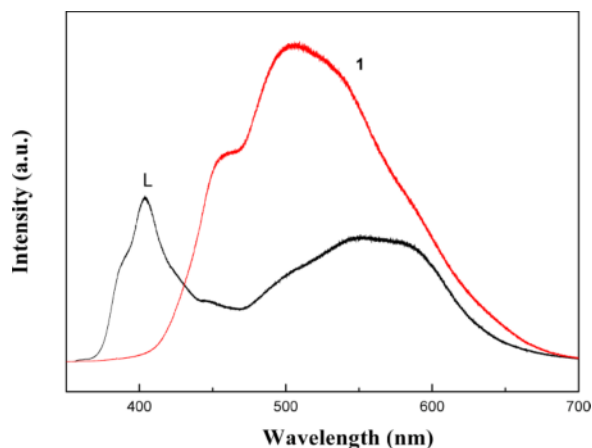


Fig. 7 (color online). Emission spectra of the ligand **L** and of **1** at room temperature.

Compound **1** exhibits fluorescence at room temperature, and the emission peak appears at 515 nm upon excitation at 325 nm. The emission of **1** can be essentially ascribed to the luminescence of its ligand **L**, since a similar emission was observed in the free **L** ligand. The red-shifts observed for compound **1** are due to the coordination of the ligand to the metal atom [19].

Experimental Section

General

All materials were of analytical or reagent grade and used as received from commercial suppliers without further purification. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer. The photoluminescence properties of the ligands and compounds were measured on a Perkin-Elmer FLS-920 spectrometer.

Syntheses of compounds **1** and **2**

A mixture of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.228 g, 1 mmol), **L** (0.348 g, 1 mmol) and 1,3,5- H_3BTC (0.210 g, 1 mmol) was dissolved in 10 mL distilled water, followed by addition of triethylamine until the pH value of the system was adjusted to between 5 and 6. The resulting solution was stirred for about 2 h at room temperature, sealed in a 23 mL Teflon-lined stainless-steel autoclave and heated at 448 K for 7 d under autogeneous pressure. After the mixture had been cooled to room temperature at a rate of 10°C h^{-1} , blue crystals of **1** were obtained. Yield: 24% based on Cd(II). – Anal. for $\text{C}_{47}\text{H}_{25}\text{Cd}_2\text{Cl}_3\text{F}_2\text{N}_8\text{O}_7$ (%): calcd. C 47.7, H 2.1, N 9.5; found C 47.3, H 2.4, N 9.7. – IR (KBr, cm^{-1}): $\nu = 3369\text{m}, 1666\text{s}, 1554\text{w}, 1429\text{m}, 1105\text{w}, 1008\text{w}, 835\text{m}, 744\text{w}, 702\text{w}, 620\text{w}, 558\text{w}$. The preparation of **2** was similar to that of **1** except that 1,2,4,5- H_4BTC (0.224 g, 1 mmol)

Compound	1	2
Formula	$\text{C}_{47}\text{H}_{25}\text{Cd}_2\text{Cl}_3\text{F}_2\text{N}_8\text{O}_7$	$\text{C}_{24}\text{H}_{13}\text{ClCoFN}_4\text{O}_5$
M_r	1182.90	550.76
Crystal size, mm ³	$0.19 \times 0.16 \times 0.13$	$0.20 \times 0.18 \times 0.14$
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a , Å	10.1084(5)	7.4767(15)
b , Å	14.9285(7)	10.094(2)
c , Å	15.2930(4)	14.772(3)
α , deg	72.1050(10)	91.23(3)
β , deg	86.160(2)	100.95(3)
γ , deg	79.600(1)	106.57(3)
V , Å ³	2159.88(16)	1045.8(4)
Z	2	2
D_{calcd} , g cm ^{−3}	1.82	1.75
μ (Mo $K\alpha$), mm ^{−1}	1.2	1.0
$F(000)$, e	1168	556
hkl range	$-12 \leq h \leq 11$ $-17 \leq k \leq 18$ $-18 \leq l \leq 17$	$-9 \leq h \leq 8$ $-13 \leq k \leq 13$ $-18 \leq l \leq 19$
θ range, deg	1.40–26.04	3.05–27.47
Refl. collect./unique/ R_{int}	11942/6610/0.0187	10191/3067/0.0563
Data/ref. parameters	8405/622	4724/325
$R1/wR2$ [$I > 2\sigma(I)$]	0.0348/0.0728	0.0617/0.1599
$R1/wR2$ (all data)	0.0499/0.0805	0.1010/0.1984
GoF (F^2)	1.027	1.084
$\Delta\rho_{\text{max/min}}$, e Å ^{−3}	0.47/−0.72	0.56/−1.25

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

and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.238 g, 1 mmol) were used instead of 1,3,5- H_3BTC and $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ for **1**. Crystals of **2** suitable for single-crystal X-ray diffraction analysis were collected by filtration, washed several times with distilled water and dried in air at ambient temperature. Yield 47 % based on Co(II). – Anal. for $\text{C}_{24}\text{H}_{13}\text{ClCoFN}_4\text{O}_5$ (%): calcd. C 52.3, H 2.4, N 10.2; found C 52.6, H 2.0, N 10.6. – IR (KBr, cm^{-1}): $\nu = 3459\text{m}$, 1655s , 1449m , 1104m , 1008m , 848w , 702w , 619m , 557w .

X-Ray structure determinations

Single-crystal X-ray diffraction data for **1** were recorded on a Bruker APEX diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. Single-crystal X-ray diffraction data for **2** were recorded on a Rigaku R-Axis RAPID image plate diffractometer likewise with graphite-monochromatized $\text{MoK}\alpha$ radiation at 293 K. The structures were solved by Direct Methods with SHELXS-97 [20] and refined by full-matrix

least-squares techniques using SHELXL-97 [21]. Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms attached to the carbon atoms were generated geometrically. Water H atoms of **1** were located in a difference Fourier map and refined as riding atoms with $d(\text{O}-\text{H}) = 0.85 \pm 0.01 \text{ \AA}$ and $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{O})$. Water H atoms of **2** were not located in a difference Fourier map. Selected bond lengths and angles of **1** and **2** and details of the structure determinations are listed in Tables 1 and 2.

CCDC 840266 and 840267 for **1** and **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

This work was supported by the Key Project of the Chinese Ministry of Education (no. 210053) and the Technology Development Program of Jilin Province (no. 20100549).

- [1] B. F. Abrahams, S. R. Batten, M. J. Grannas, H. Hamit, B. F. Hoskins, R. Robson, *Angew. Chem.* **1999**, *111*, 1538–1540; *Angew. Chem. Int. Ed.* **1999**, *38*, 1475–1477.
- [2] S. R. Batten, *Cryst. Eng. Commun.* **2001**, *18*, 1–7.
- [3] O. M. Yaghi, M. O’Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714.
- [4] M. Dinca, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann, J. R. Long, *J. Am. Chem. Soc.* **2006**, *128*, 16876–16883.
- [5] L. Carlucci, G. Ciani, D. M. Proserpio, *Coord. Chem. Rev.* **2003**, *246*, 247–289.
- [6] H. Wu, H.-Y. Liu, Y.-Y. Liu, J. Yang, B. Liu, J.-F. Ma, *Chem. Commun.* **2011**, *47*, 1818–1820.
- [7] R. J. Hill, D. L. Long, N. R. Champness, P. Hubberstey, M. Schroder, *Acc. Chem. Res.* **2005**, *38*, 335–348.
- [8] N. W. Ockwig, O. Delgado-Friederichs, M. O’Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176–182.
- [9] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–16581.
- [10] Y. P. Ren, X. J. Kong, X. Y. Hu, M. Sun, L. S. Long, R. B. Huang, L. S. Zheng, *Inorg. Chem.* **2006**, *45*, 4016–4023.
- [11] C. J. Kepert, T. J. Prior, M. J. Rosseinsky, *J. Am. Chem. Soc.* **2000**, *122*, 5158–5168.
- [12] Z.-G. Kong, X.-Y. Wang, L. Carlucci, *Inorg. Chem. Commun.* **2009**, *12*, 691–694.
- [13] X.-Y. Wang, S. Ma, T. Li, S. W. Ng, *Z. Naturforsch.* **2011**, *66b*, 103–106.
- [14] Z.-L. Xu, Y. He, S. Ma, X.-Y. Wang, *Trans. Met. Chem.* **2011**, *36*, 585–591.
- [15] J. Yang, G. D. Li, J. J. Cao, Q. Yue, G. H. Li, J. S. Chen, *Chem. Eur. J.* **2007**, *13*, 3248–3261.
- [16] Z.-G. Kong, X.-Y. Ma, Z.-L. Xu, *Z. Naturforsch.* **2010**, *65b*, 1173–1176.
- [17] X.-Y. Wang, Y. He, L.-N. Zhao, Z.-G. Kong, *Inorg. Chem. Commun.* **2011**, *14*, 1186–1189.
- [18] H. D. Guo, X. M. Guo, S. R. Batten, J. F. Song, S. Y. Song, S. Dang, G. L. Zheng, J. K. Tang, H. J. Zhang, *Cryst. Growth Des.* **2009**, *9*, 1394–1401.
- [19] W. Chen, J.-Y. Wang, C. Chen, Q. Yue, H.-M. Yuan, J.-S. Chen, S.-N. Wang, *Inorg. Chem.* **2003**, *42*, 944–946.
- [20] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473.
- [21] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.