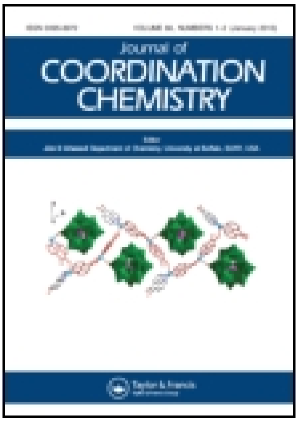
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:47
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Two cobalt(II) complexes with 5-(1H-benzotriazol-1-ylmethyl)isophthalate: synthesis, structural characterization and magnetism

Hai-Wei Kuai [a] , Xiao-Chun Cheng [a] & Xiao-Hong Zhu [a]
[a] Faculty of Life Science and Chemical Engineering , Huaiyin Institute of Technology , Huaian , China

Accepted author version posted online: 03 Apr 2013.Published online: 02 May 2013.

To cite this article: Hai-Wei Kuai , Xiao-Chun Cheng & Xiao-Hong Zhu (2013) Two cobalt(II) complexes with 5-(1H-benzotriazol-1-ylmethyl)isophthalate: synthesis, structural characterization and magnetism, Journal of Coordination Chemistry, 66:10, 1795-1804, DOI: 10.1080/00958972.2013.792335

To link to this article: http://dx.doi.org/10.1080/00958972.2013.792335

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Journal of Coordination Chemistry, 2013
Vol. 66, No. 10, 1795–1804, http://dx.doi.org/10.1080/00958972.2013.792335

Two cobalt(II) complexes with 5-(1H-benzotriazol-1-ylmethyl) isophthalate: synthesis, structural characterization and magnetism

HAI-WEI KUAI*, XIAO-CHUN CHENG and XIAO-HONG ZHU

Faculty of Life Science and Chemical Engineering, Huaiyin Institute of Technology, Huaian, China

(*Received 17 November 2012; in final form 6 February 2013*)

Co(II) salts react with 5-(1H-benzotriazol-1-ylmethyl)isophthalic acid (H_2L) under hydrothermal conditions to yield [Co(L)(py)(H_2O)] (**1**) and [Co(L)] (**2**) [py = pyridine], which have been characterized by single crystal and powder X-ray diffractions, Infrared, elemental and thermogravimetric analysis. The two complexes have structures dependent on the different experimental conditions. As a result, **1** has a 1-D ladder structure, which can be further linked to build a 3-D framework through hydrogen bonding and π–π interactions; **2** is a binodal (3,6)-connected 2-D **kgd** network with $(4^3)_2(4^6.6^6.8^3)$ topology. Synthetic strategies on coordination modes of ligand and structures of resultant complexes are discussed. Magnetism of **2** was investigated.

Keywords: Cobalt; Metal-organic framework; Characterization; Magnetic property

1. Introduction

Design and synthesis of metal-organic frameworks have attracted attention for their intriguing structures and interesting properties [1]. Exploration of such hybrid materials has become a goal of crystal engineering [2]. Functional properties of complexes are dependent on the nature of metal centers, bridging ligands, and their architectures. For example, complexes with porous architectures may show sorption or catalytic properties [3], and metal ions containing unpaired electrons such as Co(II) could be bridged by ligands to form polynuclear subunits which may mediate magnetic interactions [4]. Structural diversity may be achieved by different experimental conditions even though it is still a challenge to assemble complexes with target structures because of uncertainty in the assembly process [5]. Among many factors, the nature of ligands plays a decisive role in the formation of complexes [6].

In previous research, most coordination frameworks are formed via multidentate ligands bridging metals [7]. Coordination polymers with aromatic polycarboxylates such as terephthalate and isophthalate have been well studied due to their rigidness, diverse coordination modes and high thermal stability [8]. Linkers with an amalgamation of heterocyclic and carboxylates have been a hot research theme for construction of

---

*Corresponding author. Email: kuaihaiwei@hyit.edu.cn coordination frameworks [9]. Recently, we selected a mixed N- and O-donor ligand combining with 1,2,3-benzotriazole and aromatic carboxylates as building blocks, namely 5-(1H-benzotriazol-1-ylmethyl)isophthalic acid (H_2L), to synthesize complexes with interesting properties. Apart from anticorrosion properties [10], benzotriazole and its derivatives may perform well in crystal engineering for their peculiar structural characteristics: (1) steric hindrance of benzotriazolyl might engender subtle impact on the formation of complexes; (2) more potential coordination sites may endow them to adopt variable coordination modes to satisfy geometric requirements of metal centers. Moreover, H_2L combines carboxylate and benzotriazolyl groups. Given the coordination modes of carboxylates [11], H_2L can act as a multi-connector in assembly of complexes with various structures. Flexible benzotriazolylmethyl arm in H_2L has freedom to adopt different orientations [12] from its axial rotation to satisfy coordination requirements. Herein, we report synthesis and characterization of two new Co(II) coordination polymers, $[Co(L)(py)(H_2O)]$ (**1**) and [Co(L)] (**2**). The H_2L ligand exhibits varied coordination modes in **1** and **2** (scheme 1). The magnetic properties of **2** were investigated.

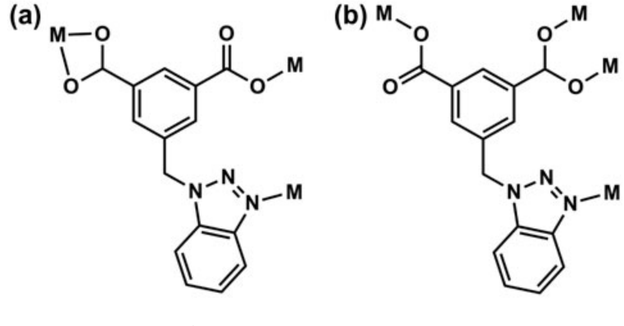
2. Experimental

2.1. *Materials and methods*

All commercially available chemicals are of reagent grade and used as received. According to the literature [13], a slightly revised experimental procedure was used to synthesize H_2L. Elemental analyses of C, H, and N were taken on a Perkin-Elmer 240C elemental analyzer. Infrared spectra (IR) were recorded on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) was performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of $10\,^{\circ}C\,min^{-1}$. Powder X-ray diffraction (PXRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα ($\lambda = 1.5418$ Å) radiation at room temperature. The magnetic measurements from 1.8 to 300 K were carried out on a Quantum Design MPMS7 SQUID magnetometer in a field of 2000 Oe.

2.2. *Preparation of $[Co(L)(py)(H_2O)]$ (1)*

A solution of $Co(NO_3)_2 \cdot 6H_2O$ (87.3 mg, 0.3 mM) and H_2L (29.6 mg, 0.1 mM) in pyridine/H_2O (2:8, 10 mL) was stirred for 30 min and then placed in a 16 mL Teflon-lined



Scheme 1. The coordination modes of L^{2-} in **1** (A) and **2** (B).

stainless steel container and heated at 180 °C for 72 h. Then the oven was shut off and cooled naturally at ambient temperature. After cooling to room temperature, light red platelet crystals of **1** were obtained with an approximate yield of 20% based on H_2L. Anal. Calcd for $C_{20}H_{16}N_4O_5Co$ (%): C, 53.23; H, 3.57; N, 12.41. Found (%): C, 53.51; H, 3.80; N, 12.66. IR (KBr pellet, cm^{-1}): 3315 (m, br), 1,602 (m), 1,553 (s), 1504 (w), 1,485 (w), 1,456 (s), 1,441 (s), 1,377 (s), 1,353 (s), 1,314 (m), 1,275 (w), 1,240 (w), 1,226 (m), 1,163 (w), 1,143 (w), 1,114 (w), 792 (m), 762 (s), 753 (s), 718 (s), 694 (s).

2.3. *Preparation of [Co(L)] (2)*

Reaction mixture of $Co(NO_3)_2·6H_2O$ (87.3 mg, 0.3 mM), H_2L (29.6 mg, 0.1 mM) and KOH (11.2 mg, 0.2 mM) in 10 mL H_2O was sealed in a 16 mL Teflon-lined stainless steel container and heated at 210 °C for 48 h. The oven cooled at a rate of 20 °C/h giving dark purple slender crystals of **2** with an approximate yield of 20% based on H_2L. Anal. Calcd for $C_{15}H_9N_3O_4Co$ (%): C, 50.87; H, 2.56; N, 11.86. Found (%): C, 50.62; H, 2.83; N, 12.12. IR (KBr pellet, cm^{-1}): 1,619 (s), 1,556 (s), 1,498 (m), 1,454 (s), 1,429 (w), 1,381 (s), 1,356 (m), 1,317 (w), 1,302 (w), 1,282 (m), 1,249 (w), 1,219 (m), 1,170 (m), 1,156 (w), 951 (w), 804 (m), 780 (m), 765 (s), 740 (s), 722 (s), 594 (m).

2.4. *X-ray crystallography*

The crystallographic data collections for **1** and **2** were carried out on a Bruker Smart Apex CCD area-detector diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K. The diffraction data were integrated by using SAINT [14], which was also used for intensity corrections for Lorentz and polarization effects.

Table 1. Crystallographic data and structure refinement details for **1** and **2**.

	1	**2**
Empirical formula	$C_{20}H_{16}N_4O_5Co$	$C_{15}H_9N_3O_4Co$
Formula weight	451.30	354.18
Temperature/K	293(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	*P*–1	*P*2$_1$/c
a/Å	10.0073(7)	8.3839(6)
b/Å	10.1073(7)	11.1671(8)
c/Å	11.6425(8)	16.8776(10)
α/°	77.4990(10)	90.00
β/°	65.0560(10)	119.785(3)
γ/°	61.4580(10)	90.00
V (Å^3)	937.82(11)	1371.40(16)
Z, D_{calcd} (Mg/m^3)	2, 1.598	4, 1.715
F(0 0 0)	462	716
θ range/°	1.93–28.37	2.29–28.34
Reflections collected	6,825	9,734
Independent reflections	4,656	3,418
Goodness-of-fit on F^2	1.054	1.052
R_1 [$I > 2\sigma(I)$]^a	0.0294	0.0405
wR_2 [$I > 2\sigma(I)$]^b	0.0776	0.1131

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_O^2) + (aP)^2 + bP]$, $P = (F_O^2 + 2F_C^2)/3$.

Table 2. Selected bond lengths [Å] and angles [°] for **1** and **2**.

1			
Co(1)–O(1)	2.0309(11)	Co(1)–O(5)	2.1132(11)
Co(1)–N(21)	2.1481(13)	Co(1)–O(3)#1	2.1746(11)
Co(1)–O(4)#1	2.1454(11)	Co(1)–N(1)#2	2.1739(14)
O(1)–Co(1)–O(5)	95.92(5)	O(1)–Co(1)–N(21)	88.61(5)
O(1)–Co(1)–O(3)#1	164.85(4)	O(1)–Co(1)–O(4)#1	104.04(4)
O(1)–Co(1)–N(1)#2	90.32(5)	O(5)–Co(1)–N(21)	88.64(5)
O(3)#1–Co(1)–O(5)	99.10(4)	O(4)#1–Co(1)–O(5)	159.99(5)
O(5)–Co(1)–N(1)#2	93.37(5)	O(3)#1–Co(1)–N(21)	89.75(5)
O(4)#1–Co(1)–N(21)	90.60(5)	N(1)#2–Co(1)–N(21)	177.82(5)
O(3)#1–Co(1)–O(4)#1	60.91(4)	O(3)#1–Co(1)–N(1)#2	90.78(5)
O(4)#1–Co(1)–N(1)#2	87.81(5)		
2			
Co(1)–O(2)	1.9833(13)	Co(1)–N(1)#1	2.0511(17)
Co(1)–O(1)#2	2.0072(14)	Co(1)–O(4)#3	2.0320(15)
O(2)–Co(1)–N(1)#1	98.08(6)	O(1)#2–Co(1)–O(2)	106.39(6)
O(2)–Co(1)–O(4)#3	101.95(6)	O(1)#2–Co(1)–N(1)#1	108.80(6)
O(4)#3–Co(1)–N(1)#1	111.94(7)	O(1)#2–Co(1)–O(4)#3	125.60(6)

Symmetry transformations used to generate equivalent atoms: for **1**, #1 $1+x$, $-1+y$, z; #2 $1-x$, $1-y$, $-z$; for **2**, #1 $1-x$, $1/2+y$, $3/2-z$; #2 $1-x$, $1-y$, $1-z$; #3 x, $3/2-y$, $-1/2+z$.

Semi-empirical absorption correction was applied using SADABS [15]. The structures of **1** and **2** were solved by direct methods and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares using the SHELXL-97 crystallographic software package [16]. In **1** and **2**, all hydrogens on carbon were generated geometrically, while hydrogens on O5 in **1** could be found at reasonable positions in the difference Fourier maps. The details of crystal parameters, data collection, and refinements for the complexes are summarized in table 1; selected bond lengths and angles are listed in table 2.

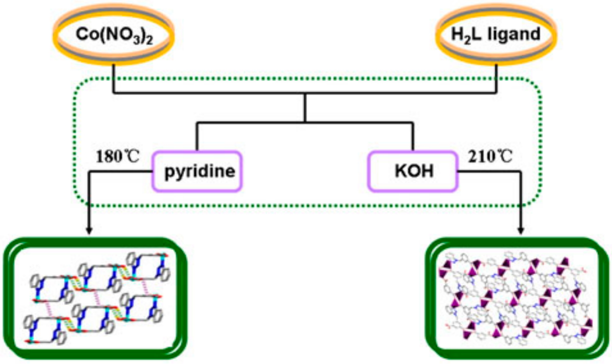
3. Results and discussion

3.1. *Preparation*

As shown in scheme 2, hydrothermal reactions of stoichiometric amount of Co(II) with H_2L under different experimental conditions provided single crystalline materials of **1** and **2**, which are stable in air. H_2L exhibits varied coordination modes in **1** and **2** (scheme 1).

3.2. *Crystal structure description of [Co(L)(py)(H₂O)] (1)*

The hydrothermal reaction of cobalt nitrate hexahydrate and H_2L in the presence of pyridine at 180 °C provided **1**. Single-crystal X-ray structural analysis shows that **1** has a 1-D ladder structure and crystallizes in the triclinic crystal system with *P*–1 space group (table 1). H_2L was completely deprotonated by pyridine to L^{2-}, which could be further confirmed by IR spectrum for the absence of vibration band at 1690–1730 cm^{-1} (see experimental section). The asymmetric unit consists of one Co(II), one L^{2-}, one pyridine and one coordinated water. The coordination environment around Co(II) is shown in figure 1(a) with atom numbering scheme. Co1 is six-coordinate with distorted octahedral coordination geometry by three carboxylate oxygens from two different L^{2-}, one water, one benzotriazolyl nitrogen, and one pyridine. The equatorial plane is occupied by four oxygens with average Co–O bond length of 2.116 Å; two axial positions are held by two



Scheme 2. Simplified schematic representation of synthesis of **1** and **2**.

nitrogens with Co–N bond lengths of 2.1481(13) and 2.1739(14) Å; the coordination bond angles around Co(II) vary from 60.91(4) to 177.82(5)° (table 2). In **1**, two carboxylates in L^{2-} exhibit μ_1–η^1 : η^0-monodentate and μ_1–η^1 : η^1-chelating coordination modes; each benzotriazolyl coordinates to a metal center, and thus the whole L^{2-} ligand adopts μ_3–η^1 : η^0–η^1 : η^1–η^1 mode as three-connector bridge (scheme 1); each metal center is coordinated by three different L^{2-}. The interconnection of metal and ligand extends infinitely to form a 1-D neutral double-stranded chain structure figure 1(b). Apart from coordination bonds, hydrogen bonding and π–π stacking interactions in **1** play a very important role in constructing and stabilizing the structure. According to their function in building the supramolecular framework, we divide the weak interactions into two groups: (1) O(5)–H(16)···O(2)#1 [#1: $1-x$, $1-y$, $1-z$; O(5)···O(2)#1 = 2.7829(19) Å; ∠O(5)–H(16)–O(2)#1 = 163°], the hydrogen bonding interactions between coordinated water and carboxylate O from adjacent chains, which further link the adjacent double-stranded chains to form a 2-D network figure 1(c); (2) π–π stacking interactions with the centroid–centroid distance between the central benzene rings of 3.797 Å, through which adjacent 2-D networks are further linked to yield a 3-D supramolecular framework figure 1(d).

3.3. *Crystal structure description of [Co(L)] (2)*

When KOH was used in the hydrothermal reaction system as alkaline reagent instead of pyridine and reaction temperature was raised to 210 °C, **2** was obtained, which exhibits a 2-D network structure based on Co(II) and L^{2-}. It crystallizes in the monoclinic system with $P2_1/c$ space group. In the asymmetrical unit there are one Co(II) and one L^{2-}. As shown in figure 2(a), each Co(II) is four-coordinate by one benzotriazolyl nitrogen and three carboxylate oxygens from three different L^{2-} to furnish a slightly distorted tetrahedral geometry [$CoNO_3$]. The coordinating bond lengths vary from 1.9833(13) to 2.0511(17) Å; the coordinating bond angles are in the range of 60.57(5)–125.60(6)°. One carboxylate in L^{2-} adopts μ_1–η^1 : η^0-monodentate coordination; the other is μ_2–η^1 : η^1-bridging, with almost identical C–O bond lengths [1.260(2) and 1.263(2) Å] and corresponding Co–O bond distances [1.9833(13) and 2.0072(14) Å], consistent with electronic delocalization from coordination. A binuclear secondary building unit (SBU) [$Co_2(COO)_2$] is formed through carboxylate-bridging two cobalts with Co···Co distance of 3.75 Å figure 2(a), which is shorter than the sum of van der Waals radii (3.84 Å) [17]. In **2**, each L^{2-} bridges

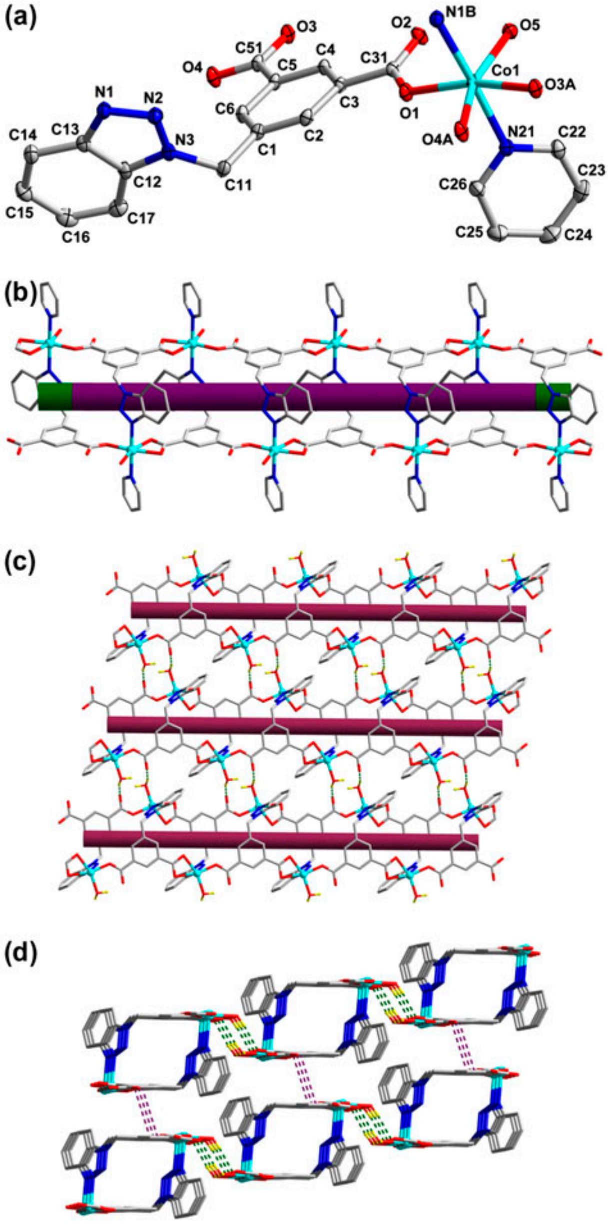


Figure 1. (a) The coordination environment of Co(II) in **1** with 30% probability displacement ellipsoids. Hydrogens were omitted for clarity. (b) View 1-D structure of **1**. (c) 2-D network of **1** extended by hydrogen bonds and (d) the extended 3-D framework of **1**.

three SBUs; each SBU is surrounded by six L^{2-}. This kind of connection proceeds infinitely to generate a 2-D layer structure figure 2(b). If using topology to analyze the structure, each SBU could be regarded as a 6sixconnector node and L^{2-} as a three-connector node

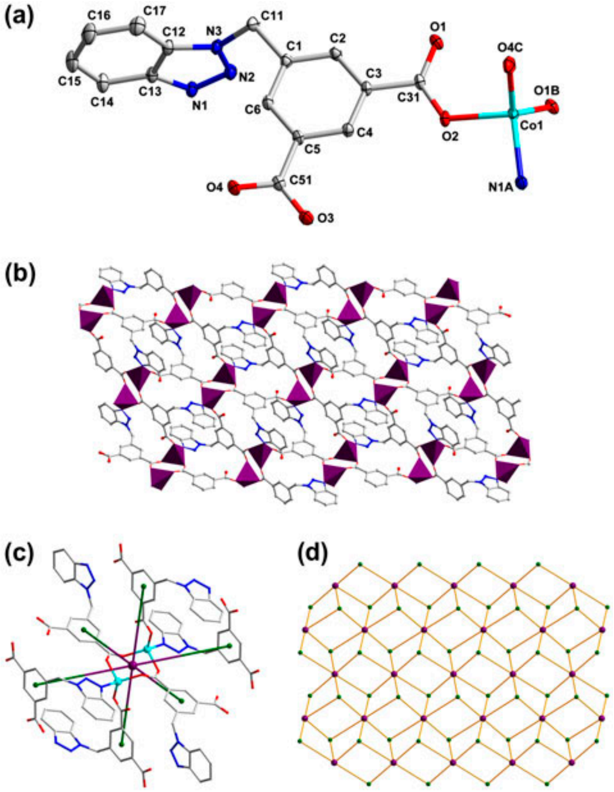


Figure 2. (a) The coordination environment of Co(II) in **2** with 30% probability displacement ellipsoids. Hydrogens were omitted for clarity. (b) 2-D network of **2**. (c) Schematic representation of six-connecting nodes of SBU and (d) schematic representation of the binodal (3,6)-connected 2-D network of **2**.

figure 2(c), and thus, the resultant structure of **2** could be simplified as binodal (3,6)-connected 2-D **kgd** network with $(4^3)_2(4^6.6^6.8^3)$ topology figure 2(d) [18].

3.4. *Coordination modes of H_2L ligand and structural comparison of 1 and 2*

Mixed N- and O-donors are regarded as good candidates for constructing MOFs due to their coordinating capacities and variable coordination modes. H_2L contains a flexible benzotriazolyl, able to adopt more coordination modes and conformations. H_2L was completely deprotonated to L^{2-} and displays different coordination in **1** and **2** (scheme 1). In **1**, the L^{2-} shows $\mu_3\text{–}\eta^1 : \eta^1\text{–}\eta^1 : \eta^0\text{–}\eta^1$ tetradentate coordination as a three-connector to bridge different Co(II) ions to give a 1-D neutral double-stranded chain. In **2**, each L^{2-} with $\mu_4\text{–}\eta^1 : \eta^1\text{–}\eta^1 : \eta^0\text{–}\eta^1$ tetradentate coordination is a three-connected node to link three SBUs $[Co_2(COO)_2]$ to form a 2-D network. The coordination numbers of Co(II) are six and four for the two complexes. Synthetic strategies can influence coordination and structures of resultant complexes. Certainly, the potential variable coordination modes and conformations of H_2L provide the feasibility to assemble complexes with various structures by adjusting experimental conditions.

3.5. *PXRD and TGA*

The phase purity of **1** and **2** could be proved by PXRD analyses. As shown in Supplementary material, each pattern of the bulk sample was in agreement with the simulated pattern from the corresponding single crystal data.

TGA were carried out for **1** and **2** (Supplementary Material). Complex **1** shows continuous weight loss of 21.22% from 150 to 338 °C corresponding to release of coordinated water and pyridine (calcd 21.49%), accompanied by subsequent decomposition of the framework. For **2**, no obvious weight loss can be observed before decomposition of the framework at 457 °C, which further confirms no solvent in the structure.

3.6. *Magnetic property*

Co(II) are bridged by carboxylates to form dinuclear unit [$Co_2(COO)_2$] in **2**, which may mediate magnetic interactions [19]. Thus, the magnetic properties of **2** were investigated from 1.8 to 300 K with a 2,000 Oe applied magnetic field. The magnetic behaviors of **2** as χ_M, χ_M^{-1}, and $\chi_M T$ *versus T* are depicted in figure 3. The $\chi_M T$ value is 2.19 emu K mol^{-1} at 300 K, which is higher than the spin-only value of 1.875 emu K mol^{-1} based on one magnetically isolated Co(II) ($g = 2$ and $S = 3/2$) due to spin-orbital coupling in **2**. As the temperature is lowered, the $\chi_M T$ value decreases slowly and then more rapidly below 75 K to reach 0.090 emu K mol^{-1} at 1.8 K. The χ_M^{-1} value (above 50 K) obeys the Curie-Weiss law well with a Weiss constant (θ) of −32.41 K and a Curie constant (C) of 2.54 emu K mol^{-1}. The negative value of θ and the shape of the $\chi_M T$ *versus T* curve suggests antiferromagnetic interactions between neighboring Co(II) centers, furthermore, the high value of Curie constant (C) [1.875 emu K mol^{-1} for spin-only Co(II)] may be due to spin-orbit coupling, which is comparable to previously reported Co(II) complexes in tetrahedral ligand field [20]. Magnetic analyses for Co(II) complexes are complicated because of their spin-orbital coupling, and some approximate methods may be applied to analyze the magnetic interactions between Co(II) ions. In the present work, the main magnetic interactions may be considered to occur between adjacent Co(II) ions bridged by carboxylate, and the superexchange interactions between the Co(II) ions bridged by L^{2-} can be ignored because

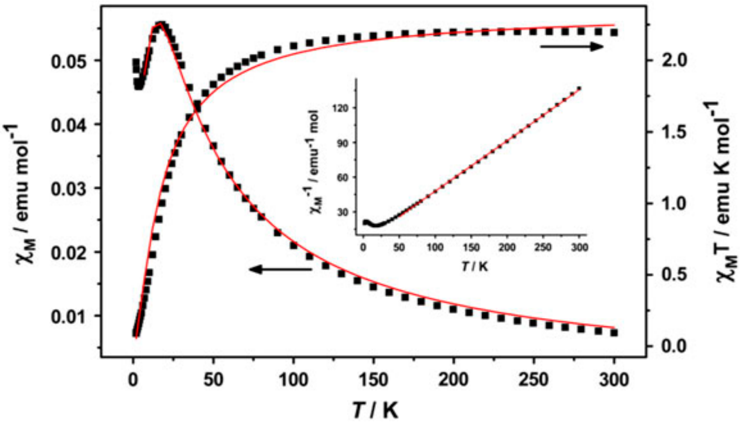


Figure 3. Temperature dependences of magnetic susceptibility of χ_M χ_M^{-1}, and χ_MT for **2**. The red solid line represents the fitted curve.

of the long Co···Co separations of 8.00–10.59 Å. Therefore, the magnetic susceptibility data were fitted assuming that the carboxylate-bridged Co(II) ions form an isolated spin dimer system.

To estimate the strength of the magnetic exchange interaction in **2**, the following simple phenomenological equation was used [21]:

$$\chi_M T = A\exp(-E_1/kT) + B\exp(-E_2/kT)$$

Here, $A+B$ equals the curie constant (C) and E_1, E_2 represent the "activation energies" corresponding to the spin-orbit coupling and the magnetic exchange interaction, respectively. The obtained values of $A+B = 2.58\,\mathrm{cm^3\,mol^{-1}\,K}$ and $E_1/k = 20.32\,\mathrm{K}$ agree with those given in a previous report [21]. The obtained value of $-E_2/k = -2.14\,\mathrm{K}$, corresponding to $J = -4.28\,\mathrm{K}$ with the agreement factor $R = \sum[(\chi_M T)_{\mathrm{obs}} - (\chi_M T)_{\mathrm{calcd}}]^2/\sum[(\chi_M T)_{\mathrm{obs}}]^2 = 2.78\times10^{-4}$, is based on the Ising chain approximation $[\chi T \infty \exp(+J/2kT)]$ [22].

In summary, the negative Weiss constant (θ), the shape of the $\chi_M T$ *versus* T curve, and the negative value of J prove antiferromagnetic interactions between neighboring Co(II) ions within the carboxylate-bridged dinuclear unit $[Co_2(COO)_2]$ in **2**.

4. Conclusion

A carboxylate and benzotriazolyl-containing ligand, 5-(1H-benzotriazol-1-ylmethyl)isophthalic acid (H_2L), was selected with potential variable coordination modes. Hydrothermal reactions of H_2L with Co(II) under different experimental conditions provide two complexes, [Co(L)(py)(H_2O)] (**1**) and [Co(L)] (**2**), exhibiting 1-D and 2-D structure. L^{2-} in the complexes adopt different coordination modes. This study shows that synthetic strategies can influence coordination modes of ligand and structures of complexes, as previously reported for Co(II) coordination polymers with benzenedicarboxylate ligands [23, 24].

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication [CCDC-893791 (for **1**) and CCDC-893792 (for **2**)]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

The authors gratefully acknowledge Huaian Administration of Science & Technology of Jiangsu Province of China (HAG2012022) for financial support of this work.

References

[1] (a) Z. Su, M. Chen, T.A. Okamura, M.S. Chen, S.S. Chen, W.Y. Sun. *Inorg. Chem.*, **50**, 985 (2011); (b) L.J. Li, G. Yuan, L. Chen, D.Y. Du, X.L. Wang, G.J. Xu, H.N. Wang, K.Z. Shao, Z.M. Su. *J. Coord. Chem.*, **64**, 1578 (2011); (c) B. Liu, L.J. Fan, Y.Y. Liu, J. Yang, J.F. Ma. *J. Coord. Chem.*, **64**, 413 (2011); (d) J.P. Zhang, Y.B. Zhang, J.B. Lin, X.M. Chen. *Chem. Rev.*, **112**, 1001 (2012); (e) A. Bétard, R.A. Fischer. *Chem. Rev.*, **112**, 1055 (2012).

[2] (a) J.J. Jiang, M. Pan, J.M. Liu, W. Wang, C.Y. Su. *Inorg. Chem.*, **49**, 10166 (2010); (b) J.J. Jiang, L. Li, M.H. Lan, M. Pan, A. Eichhöfer, D. Fenske, C.Y. Su. *Chem. Eur. J.*, **16**, 1841 (2010); (c) C.H. Jiao, C.H. He, J.C. Geng, G.H. Cui. *J. Coord. Chem.*, **65**, 2852 (2012); (d) H. Xia, X.M. Liu, Q.L. Wu, Y.W. Zhang, W. Gao, Y. Mu. *J. Coord. Chem.*, **65**, 1266 (2012).

[3] (a) J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim. *Nature*, **404**, 982 (2000). (b) J.R. Li, R.J. Kuppler, H.C. Zhou. *Chem. Soc. Rev.*, **38**, 1477 (2009). (c) S.S. Chen, M. Chen, S. Takamizawa, M.S. Chen, Z. Su, W.Y. Sun. *Chem. Commun.*, **47**, 752 (2011).

[4] (a) J. Zhang, J. Ensling, V. Ksenofontov, P. Gütlich, A.J. Epstein, J.S. Miller. *Angew. Chem. Int. Ed.*, **37**, 657 (1998); (b) K.R. Dunbar. *Angew. Chem. Int. Ed.*, **35**, 1659 (1996); (c) H. Zhao, R.A. Heintz, R.D. Rogers, K.R. Dunbar. *J. Am. Chem. Soc.*, **118**, 12844 (1996); (d) J. Milon, M.C. Daniel, A. Kaiba, P. Guionneau, S. Brandès, J.P. Sutter. *J. Am. Chem. Soc.*, **129**, 13872 (2007).

[5] (a) S. Mishra, E. Jeanneau, H. Chermette, S. Daniele, L.G. Hubert-Pfalzgraf. *Dalton Trans.*, 620 (2008); (b) Z. He, C. He, E.Q. Gao, Z.M. Wang, X.F. Yang, C.S. Liao, C.H. Yan. *Inorg. Chem.*, **42**, 2206 (2003); (c) B. Zhao, L. Yi, Y. Dai, X.Y. Chen, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang. *Inorg. Chem.*, **44**, 911 (2005).

[6] (a) G.Z. Liu, S.H. Li, L.Y. Wang. *Cryst. Eng. Commun.*, **14**, 880 (2012); (b) G.X. Liu, Y.Q. Huang, Q. Chu, T.A. Okamura, W.Y. Sun, H. Liang, N. Ueyama. *Cryst. Growth Des.*, **8**, 3233 (2008); (c) R. Cao, D. Sun, Y. Liang, M. Hong, K. Tatsumi, Q. Shi. *Inorg. Chem.*, **41**, 2087 (2002).

[7] (a) A.Y. Robin, K.M. Fromm. *Coord. Chem. Rev.*, **250**, 2127 (2006); (b) S. Kitagawa, R. Kitaura, S.I. Noro. *Angew. Chem. Int. Ed.*, **43**, 2334 (2004).

[8] (a) H. Furukawa, N. Ko, Y.B. Go, N. Aratani, S.B. Choi, E. Choi, A.O. Yazaydin, R.Q. Snurr, M. O'Keeffe, J. Kim, O.M. Yaghi. *Science*, **239**, 424 (2010); (b) H. Deng, C.J. Doonan, H. Furukawa, R.B. Ferreira, J. Towne, C.B. Knobler, B. Wang, O.M. Yaghi. *Science*, **327**, 846 (2010).

[9] (a) Z. Su, J. Fan, T.A. Okamura, M.S. Chen, S.S. Chen, W.Y. Sun, N. Ueyama. *Cryst. Growth Des.*, **10**, 1911 (2010); (b) F. Nouar, J.F. Eubank, T. Bousquet, L. Wojtas, M.J. Zaworotko, M. Eddaoudi. *J. Am. Chem. Soc.*, **130**, 1833 (2008); (c) Z. Su, Z.S. Bai, J. Fan, J. Xu, W.Y. Sun. *Cryst. Growth Des.*, **9**, 5190 (2009); (d) P. Teo, L.L. Koh, T.S.A. Hor. *Inorg. Chem.*, **47**, 6464 (2008).

[10] G.E. Kostakis, P. Xydias, E. Nordlander, J.C. Plakatouras. *Inorg. Chim. Acta*, **383**, 327 (2012).

[11] (a) Z.F. Tian, J.G. Lin, Y. Su, L.L. Wen, Y.M. Liu, H.Z. Zhu, Q.J. Meng. *Cryst. Growth Des.*, **7**, 1863 (2007); (b) Q. Hua, Y. Zhao, G.C. Xu, M.S. Chen, Z. Su, K. Cai, W.Y. Sun. *Cryst. Growth Des.*, **10**, 2553 (2010).

[12] (a) H.W. Kuai, X.C. Cheng, L.D. Feng, X.H. Zhu. *Z. Anorg. Allg. Chem.*, **637**, 1560 (2011); (b) H.W. Kuai, X.C. Cheng, X.H. Zhu. *J. Coord. Chem.*, **64**, 1636 (2011); (c) H.W. Kuai, X.C. Cheng, X.H. Zhu. *J. Coord. Chem.*, **64**, 3323 (2011).

[13] (a) G.C. Xu, Q. Hua, T.A. Okamura, Z.S. Bai, Y.J. Ding, Y.Q. Huang, G.X. Liu, W.Y. Sun, N. Ueyama. *Cryst. Eng. Commun.*, **11**, 261 (2009); (b) J. Fan, B.E. Hanson. *Inorg. Chem.*, **44**, 6998 (2005).

[14] SAINT. *Program for Data Extraction and Reduction*, Bruker AXS Inc., Madison, WI (2002).

[15] G.M. Sheldrick. *SADABS Program for Bruker Area Detector Absorption Correction*, University of Göttingen, Göttingen, Germany (1997).

[16] (a) G.M. Sheldrick. *SHELXS-97*, *Programs for Solution of Crystal Structure*, University of Göttingen, Germany (1997); (b) G.M. Sheldrick. *SHELXL-97*, *Programs of Refinement for Crystal Structure*, University of Göttingen, Germany (1997).

[17] S.Z. Hu, Z.H. Zhou, K.R. Tsai. *Acta Phys.-Chim. Sin.*, **19**, 1073 (2003).

[18] (a) V.A. Blatov. *IUCr Comput. Commun. Newsletter*, **7**, 4 (2006); (b) V.A. Blatov, *TOPOS, A Multipurpose Crystallochemical Analysis with the Program Package*, Samara State University, Russia (2009).

[19] D. Ghoshal, G. Mostafa, T.K. Maji, E. Zangrando, T.H. Lu, J. Ribas, N.R. Chaudhuri. *New J. Chem.*, **28**, 1204 (2004).

[20] (a) J.W. Raebiger, J.L. Manson, R.D. Sommer, U. Geiser, A.L. Rheingold, J.S. Miller. *Inorg. Chem.*, **40**, 2578 (2001); (b) J.M. Herrera, A. Bleuzen, Y. Dromzée, M. Julve, F. Lloret, M. Verdaguer. *Inorg. Chem.*, **42**, 7052 (2003); (c) Z. Su, Z.S. Bai, J. Xu, T. Okamura, G.X. Liu, Q. Chu, X.F. Wang, W.Y. Sun, N. Ueyamab. *Cryst. Eng. Commun*, **11**, 873 (2009); (d) Z. Su, Z.S. Bai, J. Fan, J. Xu, W.Y. Sun. *Cryst. Growth Des.*, **9**, 5190 (2009); (e) M. Chen, S.S. Chen, T.A. Okamura, Z. Su, M.S. Chen, Y. Zhao, W.Y. Sun, N. Ueyama. *Cryst. Growth Des.*, **11**, 1901 (2011).

[21] (a) J.M. Rueff, N. Masciocchi, P. Rabu, A. Sironi, A. Skoulios. *Chem.-Eur. J.*, **8**, 1813 (2002); (b) J.M. Rueff, N. Masciocchi, P. Rabu, A. Sironi, A. Skoulios. *Eur. J. Inorg. Chem.*, 2843 (2001).

[22] (a) R.L. Carlin, *Magnetochemistry*, Springer, Berlin, Heidelberg (1986); (b) O. Kahn, *Molecular Magnetism*, VCH, Weinheim (1993).

[23] (a) D. Tian, Y.H. Zhou, L. Guan, H. Zhang. *J. Coord. Chem.*, **64**, 565 (2011); (b) Z.P. Li, L. Huang, P.X. Xi, H.Y. Liu, Y.J. Shi, G.Q. Xie, M. Xu, F.J. Chen, Z.Z. Zeng. *J. Coord. Chem.*, **64**, 1885 (2011); (c) X.M. Qiu, S.N. Wang, J. Lu, L.Q. Kong, D.C. Li, J.M. Dou. *J. Coord. Chem.*, **65**, 3308 (2012); (d) Y.M. Song, X.F. Feng, F. Luo. *J. Coord. Chem.*, **65**, 2705 (2012); (e) P.X. Chen, G.P. Yang, L. Hou, Y.Y. Wang, Q.Z. Shi. *J. Coord. Chem.*, **65**, 2893 (2012).

[24] (a) S.G. Zhang, H. Li, L.M. Xie, H. Chen, L. Yu, J.M. Shi. *J. Coord. Chem.*, **65**, 2211 (2012); (b) M.L. Liu, Y.X. Wang, W. Shi, J.Z. Cui. *J. Coord. Chem.*, **65**, 1915 (2012); (c) C.B. Liu, L. Gao, J. Wang, X.Y. Li, G.B. Che, Z.L. Xu, Q.W. Wang. *J. Coord. Chem.*, **65**, 4156 (2012); (d) Y.L. Chen, J. Yang, J.F. Ma. *J. Coord. Chem.*, **65**, 3708 (2012); (e) X.L. Zhang, K. Cheng. *J. Coord. Chem.*, **65**, 3019 (2012).