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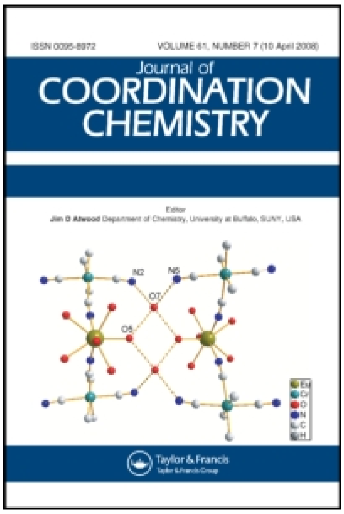

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A 3-D cobalt(II)-coordination polymer with mixed-connected network topology constructed from 4-pyridin-3-yl-benzoic acid

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A 3-D cobalt(II)-coordination polymer with mixed-connected network topology constructed from 4-pyridin-3-yl-benzoic acid

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A new coordination polymer, $[Co_2(\mu\text{-}H_2O)(4,3\text{-pybz})_4]_n$ (**1**), has been hydrothermally synthesized from $Co(NO_3)_2 \cdot 6H_2O$ and an unsymmetrical 4-pyridin-3-yl-benzoic acid (4,3-Hpybz), which is characterized by IR, elemental analysis, thermogravimetric analysis, and single crystal X-ray diffraction. This compound crystallizes in monoclinic, space group $C2/c$ with $a = 11.876(3)$ Å, $b = 15.462(3)$ Å, $c = 21.545(4)$ Å, $\beta = 94.873(5)^\circ$, $V = 3942.0(15)$ Å^3, $Z = 4$, $Dc = 1.565\,\mathrm{g\,cm^{-3}}$, $F(000) = 1904$, GOF = 1.025, $\mu = 0.910\,\mathrm{mm^{-1}}$, $R_1 = 0.0456$, $wR_2 = 0.0983$. Compound **1** shows a 3-D (3,6)-connected coordination framework with $(3.4.5)(3^2.4^4.5^5.6^2.7^2)$ topology, in which cobalt is a six-connected node, and the 4,3-Hpybz ligands serve as two-connected spacers and three-connected nodes. In addition, the magnetic and thermal properties of **1** have also been investigated.

Keywords: Cobalt(II) compound; Crystal structures; Topology; Magnetic properties

1. Introduction

Interest in coordination polymers is based on their intriguing topological architectures and potential applications as functional materials [1–4]. Recently, on the basis of the pioneering work of Zaworotko, Kitagawa, and Yaghi [5–8], large numbers of metal–organic frameworks (MOFs) have been obtained, and many of them exhibit versatile physical and chemical properties. Nevertheless, the rational design and synthesis of MOFs with unique structure and specific function still remains a long-term challenge. The topological analysis of MOFs is an important tool for simplifying complicated compounds and plays an instructive role in the design of functional materials [9]. The topological types found in 3-D MOFs are commonly defined by the vertices (metal ions and/or ligands) and edges (links between vertices), among which three-, four-, five-, six-, seven-, and eight-connected topologies are observed in many reported polymers [10, 11]. Although, some MOFs with mixed-connected topologies have been reported, Pt_3O_4, boracite, twisted boracite, PtS, rutile, pyrite, anatase, etc. [12]. MOFs with high-mixed

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connectivity, such as (3,6)-, (3,9)-, (4,8)-, and (6,8)-connected architectures, are still quite scarce [13].

The key steps in building MOFs are to design appropriate ligands and to choose metal ions with suitable coordination geometries [14]. Asymmetric bridging ligands containing N- or/and O-donors have been widely used. Pyridine carboxylic acids are versatile ligands with multifarious coordination configurations in monoatomic and triatomic syn–syn, syn–anti, and anti–anti conformations. In previous work of our group, several compounds with bipyridine dicarboxylic acids and HIN have been reported [15]. To continue our research, pyridine-benzoic acid, 4-pyridin-3-yl-benzoic acid (4,3-Hpybz), as a multidentate ligand was employed in the self-assembly. Herein, we report a new 3-D coordination polymer, $[Co_2(\mu\text{-}H_2O)(4,3\text{-pybz})_4]_n$ (**1**), assembled from Co^{II} and 4,3-Hpybz, which shows a 3-D (3,6)-connected net with $(3.4.5)(3^2.4^4.5^5.6^2.7^2)$ topology. Additionally, magnetic studies exhibit antiferromagnetic exchange interactions between adjacent Co^{II} centers.

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2. Experimental

2.1. *Materials and methods*

All commercially available solvents and starting materials were used as received. FT-IR spectra were recorded from KBr pellets at 4000–400 cm^{-1} on a Bruker EQUINOX-55 spectrometer. Elemental analysis was determined with an Elementar Vario EL III elemental analyzer. Thermogravimetric analyses (TGA) were performed under nitrogen with a heating rate of 10°C min^{-1} using a NETZSCH STA 449C thermogravimetric analyzer. X-ray powder diffraction (XRPD) was carried out on a Shimadzu XRD-7000 analyzer. Variable temperature magnetic susceptibility measurements were carried out on an Oxford Maglab 2000 magnetometer with an applied field of 10 kOe. Diamagnetic correction was estimated from Pascal's constants.

2.2. *Synthesis*

An aqueous solution (10 mL) containing 4-pyridin-3-yl-benzoic acid (0.10 mmol), and $Co(NO_3)_2 \cdot 6H_2O$ (0.10 mmol) was placed in a Parr Teflon-lined stainless steel vessel (25 mL) under autogenous pressure, heated to 160°C for 5d and subsequently cooled to room temperature at a rate of 5°C h^{-1}. Red block crystalline products were obtained in 48% yield. Anal. Calcd for $C_{48}H_{34}N_4O_9Co_2$(%): C, 62.08; H, 3.69; N, 6.03. Found (%): C, 62.01; H, 3.72; N, 6.11. IR (KBr pellet, cm^{-1}): 3442s, 3224s, 1624s, 1602s, 1547s, 1422s, 1382vs, 1194m, 1134m, 1069w, 1035m, 865m, 815m, 774vs, 705s, 676m, 554m, 474m.

2.3. *X-ray crystallography*

Crystal structure determination of **1** ($0.15 \times 0.10 \times 0.06\ mm^3$) was performed on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. The structure was solved by direct methods and

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

Empirical formula	$C_{48}H_{34}N_4O_9Co_2$
Formula weight	928.65
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions (Å, °)	
a	11.876(3)
b	15.462(3)
c	21.545(5)
β	94.873(5)
Volume (Å^3), *Z*	3942.0(15), 4
Calculated density (g cm^{-3})	1.565
Absorption coefficient (Å) (Mo-Kα)	0.71073
F(000)	1904
θ range for data collection (°)	1.90–25.05
Goodness-of-fit on F^2	1.025
Final R_1, wR_2 [$I > 2\sigma(I)$]^{a,b}	0.0456, 0.0983
R_1, wR_2 (all data)	0.0796, 0.1158

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

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

Co1–O1	2.053(2)	Co1–O5	2.175(2)
Co1–O3	2.083(3)	Co1–N1$^{\#2}$	2.170(3)
Co1–O2$^{\#1}$	2.104(3)	Co1–N2$^{\#3}$	2.183(3)
O(1)–Co(1)–O(3)	175.10(11)	O(1)–Co(1)–O(2)$^{\#1}$	93.28(10)
O(3)–Co(1)–O(2)$^{\#1}$	86.17(10)	O(1)–Co(1)–N(1)$^{\#2}$	91.46(11)
O(3)–Co(1)–N(1)$^{\#2}$	83.66(11)	O(2)$^{\#1}$–Co(1)–N(1)$^{\#2}$	89.31(11)
O(1)–Co(1)–O(5)	95.66(9)	O(3)–Co(1)–O(5)	89.17(10)
O(2)$^{\#1}$–Co(1)–O(5)	86.60(9)	N(1)$^{\#2}$–Co(1)–O(5)	171.97(8)
O(1)–Co(1)–N(2)$^{\#3}$	88.02(10)	O(3)–Co(1)–N(2)$^{\#3}$	92.73(11)
O(2)$^{\#1}$–Co(1)–N(2)$^{\#3}$	177.39(12)	N(1)$^{\#2}$–Co(1)–N(2)$^{\#3}$	92.92(12)
O(5)–Co(1)–N(2)$^{\#3}$	91.02(10)	Co(1)–O(5)–Co(1)$^{\#1}$	115.84(16)

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

successive Fourier difference synthesis (SHELXS-97) and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [16]. Hydrogens were located by geometric calculations. Crystal data and details on refinements for **1** are summarized in table 1. Selected bond distances and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structure*

Single crystal X-ray diffraction analysis shows that the asymmetric unit of **1** consists of one Co^{II}, two 4,3-pybz anions, and half of a coordinated water with two-fold symmetry. Each Co^{II} is six coordinate with two pyridyl nitrogens [Co–N = 2.170(3) and

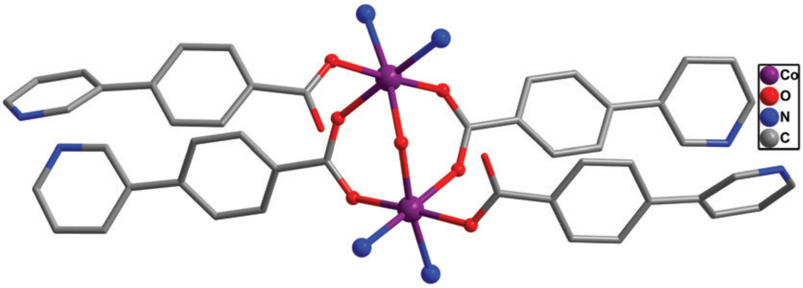

Figure 1. Coordination environment of Co in **1**. Hydrogens are omitted for clarity.

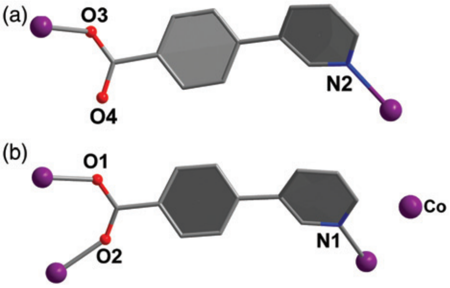

Figure 2. Ball-and-stick representations of coordination modes of two crystallographically independent ligands.

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2.183(3) Å] and three carboxylate oxygens coming from different 4,3-pybz ligands as well as one oxygen from water [Co–O = 2.053(2)–2.175(2) Å], forming a distorted CoN_2O_4 octahedron (figure 1). The Co–$O_{(carboxylate)}$ and Co–$N_{(bipy)}$ bond lengths are in agreement with those in carboxylate- and bipy-containing cobalt(II) complexes [17]. The bond angles range from 83.66(11)° to 177.39(12)° and the Co–O–Co angle is 115.84(16)°.

In this structure, the 4,3-pybz ligands show two different coordination modes, μ_2-unidentate (N_{py})/unidentate (O^-_{COO}) **A** and μ_3-unidentate (N_{py})/bidentate bridging (O^-_{COO}) **B** (figure 2). The phenyl and pyridyl rings are not coplanar with dihedral angles of 37.8° and 43.23° in mode A and B, respectively. With bridging carboxylate and water, two adjacent Co^{II} centers are combined to constitute a $[Co_2(\mu_2\text{-}H_2O)(COO^-)_4]$ dinuclear unit with the Co···Co separation of 3.686 Å. Moreover, a O5W–H5···O4 hydrogen bond forms between water and a pair of uncoordinated carboxylate oxygens [O5···O4 and H5···O4 distances = 2.587(3) and 1.70 Å, respectively; O5–H5···O4 angle = 151.0°], further stabilizing this dinuclear unit. Such dinuclear units can be regarded as secondary building units (SBUs) in the resulting network. Each 4,3-pybz ligand with mode **A** connects two SBUs to result in a 1-D double-chain along the (101) direction (Supplementary material: figure S1a). Synchronously, with mode **B**, the 4,3-pybz ligands also link two SBUs to generate a 1-D double-chain along the (001) direction (figure S1b). As a consequence, such dimeric SBUs are extended by the ligand backbones to afford a 3-D MOFs (figure 3). From a view point of network topology, considering each Co^{II} as a six-connected node (figure 4a), the 4,3-pybz ligands with

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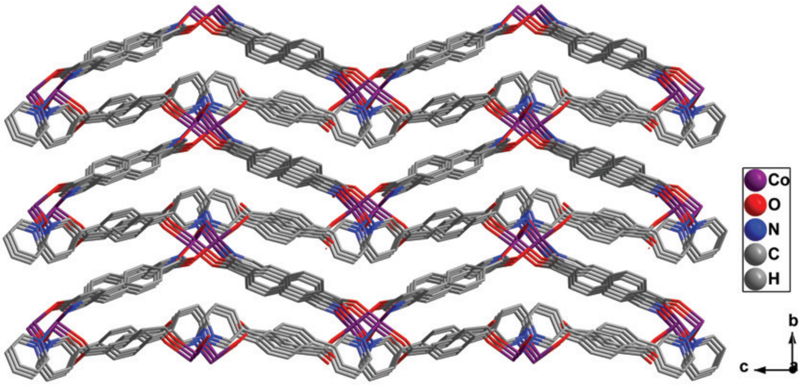

Figure 3. 3-D framework structure of **1** viewed down the *a*-axis.

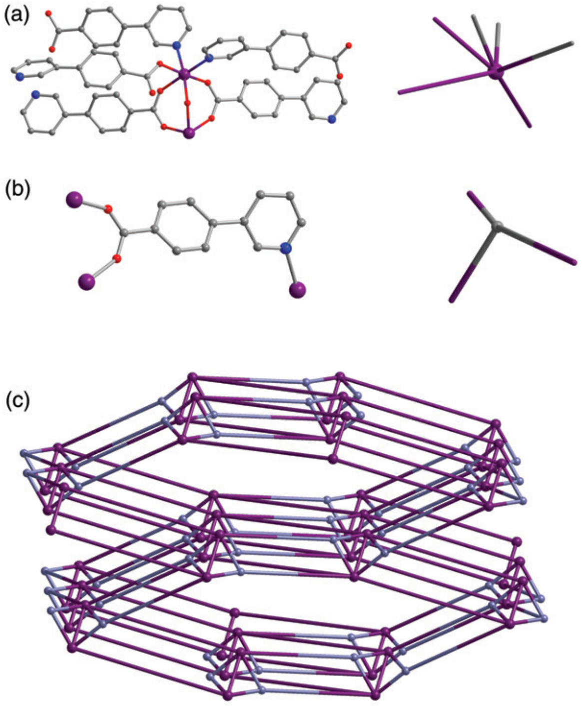

Figure 4. Ball-and-stick and schematic representations of (a) 3-connected and (b) 6-connected nodes. (c) A schematic diagram showing the (3.4.5)($3^2.4^4.5^5.6^2.7^2$) network (gray and wine balls represent three- and six-connected nodes, respectively).

mode A and B are two-connected spacer and three-connected node (figure 4b), respectively. As a result, a 3-D binodal coordination framework with (3,6)-mixed connectivity is formed, as depicted in figure 4(c), which has the Schläfli symbol of (3.4.5)($3^2.4^4.5^5.6^2.7^2$). On the other hand, if we consider the dimeric motifs stated above as the SBUs, this 3-D network can also be simplified to a uninodal four-connected diamond topology (figure 5).

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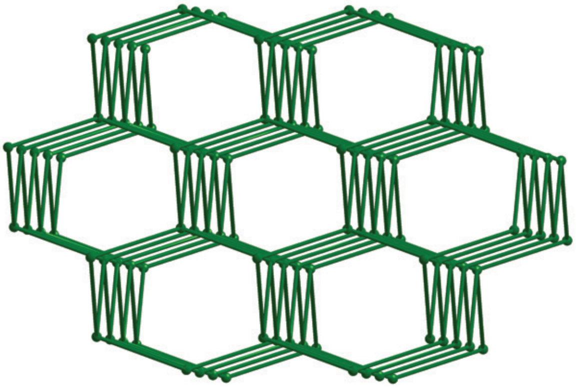

Figure 5. Uninodal four-connected diamond topology of **1**.

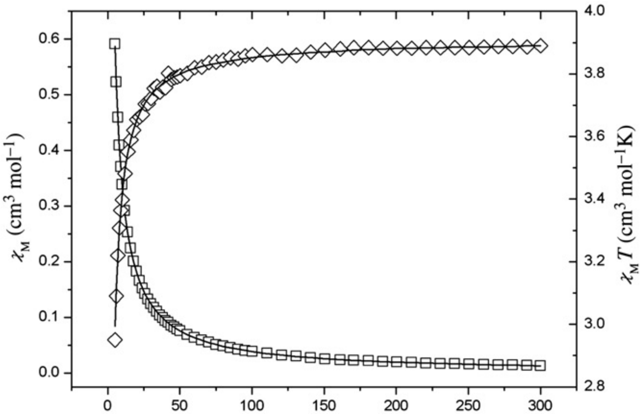

Figure 6. Thermal variation of χ_M and $\chi_M T$ for **1**, □, χ_M experimental values, ◇, $\chi_M T$ experimental values and solid lines, theoretical values.

3.2. *Magnetic properties*

The magnetic properties of **1** were investigated from 5–300 K in a field of 10 kOe. The magnetic susceptibilities χ_M and $\chi_M T$ *versus* T plots are shown in figure 6. At 300 K, the experimental $\chi_M T$ value is 3.89 cm^3 K mol^{-1}, slightly larger than the spin-only value (3.75 cm^3 K mol^{-1}) expected for two isolated spin-only Co^{II} ion ($S = 3/2$, $g = 2.0$). The $\chi_M T$ value of **1** remains almost constant from 300 to 110 K; and then decreases on further cooling, reaching a value of 2.95 cm^3 K mol^{-1} at 5 K. This behavior indicates antiferromagnetic interaction between the Co^{II} ions in the structure. In **1**, the Co $\cdots$ Co distance through the carboxylate of the ligand and water molecule bridge is 3.686 Å. The temperature dependence of the reciprocal susceptibilities ($1/\chi_M$) obeys the Curie–Weiss law above 50 K with $\theta = -15.62$ K, $C = 4.86$ cm^3 K mol^{-1} and $R = 3.247 \times 10^{-5}$ ($R = \sum[(\chi_M)_{obs}-(\chi_M)_{calc}]^2/\sum[(\chi_M)_{obs}]^2$). The moderate negative θ value indicates the antiferromagnetic interactions between adjacent Co^{II} ($S = 3/2$) ions even if a contribution from the spin-orbit coupling of Co^{II} is also present [18].

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Comparable antiferromagnetic interactions between the cobalt ions were also reported in other cobalt compounds [19].

It is well-known that magnetic analyses for Co^{II}-containing compounds will become rather complicated [20], and some approximate methods are often applied to analyze magnetic interactions between Co^{II} ions. The main magnetic interactions may be considered to occur between adjacent Co^{II} ions bridged by carboxylic groups and water, whereas the exchange interactions between Co^{II} ions bridged by the 4,3-pybz ligand can be ignored because of the long $Co \cdots Co$ separations. To simulate the experimental magnetic behavior, we have attempted to fit the experimental susceptibility data assuming that the carboxylic group bridges between Co^{II} ions to form a binuclear unit with coupling constant J and then 4,3-pybz connect the binuclear units to form a 3-D network with an exchange constant zJ'. The susceptibility data were thus analyzed by an isotropic dimer mode of spin $S=3/2$ [21].

$$\chi_{\mathrm{M}} = \frac{Ng^2\beta^2}{KT}\frac{A}{B},$$

where $A = 2\exp[-2J/KT] + 10\exp[-6J/KT] + 28\exp[-12J/KT]$, $B = 1 + 3\exp[-2J/KT] + 5\exp[-6J/KT] + 7\exp[-12J/KT]$.

Finally, the least-squares analysis of magnetic susceptibilities data led to $J=-2.10\,\mathrm{cm}^{-1}$, $g=2.09$, $zJ'=-0.56\,\mathrm{cm}^{-1}$, and $R=2.418\times10^{-4}$ of **1**, where the J value is in agreement with the value of θ deduced above.

3.3. *PXRD and TG analysis*

In order to confirm the phase purity of the bulk materials, the powder X-ray diffraction (PXRD) experiments were carried out for **1** at room temperature (Supplementary material: figure S2). Their peak positions are in good agreement with each other, indicating the phase purity of the products. The thermal stability of **1** has been investigated by TGA and the TG curve is shown in figure S3. The TG curve of **1** illustrates that no weight loss is observed for the ligands up to 320°C; after this, significant weight losses occurred and ended at *ca* 535°C, indicating complete decomposition of the compound to form CoO, which was confirmed by XRPD analysis. This conclusion has been also supported by the percentage of the residues (16.37%), which is in accordance with the expected value (16.14%).

3.4. *IR spectra*

IR spectra of **1** exhibit characteristic bands of carboxylate at 1624 and $1602\,\mathrm{cm}^{-1}$ for the asymmetric stretching and at $1422\,\mathrm{cm}^{-1}$ for symmetric stretching. The separation values between $\nu_{\mathrm{asym}}(CO_2)$ and $\nu_{\mathrm{sym}}(CO_2)$ indicate that the carboxylate groups coordinate monodentate ($202\,\mathrm{cm}^{-1}$) and bis-monodentate ($180\,\mathrm{cm}^{-1}$) [22].

4. Conclusion

We have prepared and characterized a 3-D Co(II) coordination polymer. Compound **1** exhibits a novel (3,6)-connected $(3.4.5)(3^2.4^4.5^5.6^2.7^2)$ topology and has antiferromagnetic interaction.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 757178 for **1**. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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