

A New Six-Connected Double-Layer Metal-Organic Framework Directed by Carboxylate and N-Containing Donor Co-Ligands

Jian-Qiang Liu

Guangdong Medical College, School of Pharmacy, Dongguan, P. R. China

A new polymer, $[Co(fipbb)(bpt).DMF]_n$ (1) $(H_2fipbb = 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) and bpt = 2,5-bis (4-pyridyl)-1,3,4-thiadiazole), has been synthesized and characterized. The polymer presents a two-dimensional (2D) bilayer structure containing dimeric <math>[Co2(COO)4]$ units. In the 2D network, each Co(II) atom is coordinated by four carboxylate oxygen atoms from three different fipbb ligands and two nitrogen atoms from two bpt ligands. The thermogravimetric (TG) and magnetic properties of the compound are also discussed.

Keywords bilayer, magnetism, metal-organic framework, structure

INTRODUCTION

Synthesis and characterization of metal-organic frameworks (MOFs) are of great current interest because of their intriguing structures and potential applications on gas adsorption/separation, microelectronics, nonlinear optics, ion exchange, heterogeneous catalysis, and so on.^[1-5] In this regard, MOFs on the basis of polycarboxylate connectors have been widely focused on due to their versatile coordination capability as well as their sensitivity to acidity of such building blocks, which will be responsible for structural diversity of resulting MOFs.^[6] In contrast to the rigid organic carboxylate ligands, the conformation of flexible ones is variable; thus, they can meet the coordination geometrical requirement of metal ions through changing their conformation, which may provide more possibilities for the construction of novel architectures.^[7] On the other hand, as for the dipyridyl bridging ligands, some analogous sets derived from the proper modification of the classical 4,4'-bipyridine ligand have been employed. Unlike the more commonly used tethering 4,4'-bipyridine ligand, 2,5bis(4-pyridyl)-1,3,4-thiadiazole(bpt) has an angular disposition of its terminal pyridyl spacers because of its central thiadiazole

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ring and two more potential N-donor atoms inducing flexible coordination modes, which favor constructing unexpected, unpredictable, and interesting frameworks.^[8–10] In our previous work, we demonstrated the role of secondary ligands on the resultant MOFs.^[8b] Herein, we report on having synthesized a new compound of [Co(fipbb)(bpt).DMF]n (1), which presents a two-dimensional (2D) bilayer structure containing ring dimeric [Co2 (COO)4] units. Moreover, the thermogravimetric (TG) and magnetic properties of the compound are also discussed.

MATERIALS AND INSTRUMENTS

All reagents were purchased from commercial sources and used as received. Infrared (IR) spectra were recorded with a Perkin–Elmer Spectrum One spectrometer in the region 4000–400 cm⁻¹ using KBr pellets. TGA were carried out with a Metter–Toledo TA 50 in dry dinitrogen (60 mL min⁻¹) at a heating rate of 5°C min⁻¹. X-ray powder diffraction (XRPD) data were recorded on a Rigaku RU200 diffractometer at 60 kV, 300 mA, for Cu K_{\alpha} radiation ($\lambda = 1.5406$ Å), with a scan speed of 2°C/min and a step size of 0.02° in 2 θ . Magnetic susceptibility data of powdered samples restrained in parafilm was measured on Oxford Maglab 2000 magnetic measurement system in the temperature range 300–2 K and at field of 1 kOe. Diamagnetic correction was applied using Pascal's constant.^[11]

Synthesis of the Complex

To a mixture of DMF solution (5 mL) containing H₂fipbb (0.1 mmol) and bpt (0.1 mmol) was added $Co(NO_3)_2 \cdot 4H_2O$ (0.15 mmol) in water at 30°C. The pH of the resulting solution was adjusted to 5.5 using dilute NaOH (0.1 mol/L) and kept at 160°C for 96 h to prepare compound **1**. From that solution, pink crystals suitable for x-ray measurements were obtained. Yield: 40%. Anal.: Calc. (%) for $C_{32}H_{23}CoF_6N_8O_5S$: C, 50.46; N, 9.02; H, 3.22. Found (%): C, 50.40; N, 9.18; H, 3.40. IR (KBr cm⁻¹): 2950 (w), 1688 (s), 1522 (w), 1460(s), 1195 (m), 866(m). CCDC: 800682.

RESULTS AND DISCUSSION

Compound 1 displays an interesting double-layer framework. As shown in Figure 1, each distorted octahedral Co(II)

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Address correspondence to Jian-Qiang Liu, Guangdong Medical College, School of Pharmacy, Dongguan 523808, P. R. China. E-mail: jianqiangliu2010@126.com



FIG. 1. The coordinated geometry of Co(II) ion in **1** (symmetry codes: i = x, y, z + 1; ii = -x + 2, -y + 1, -z + 1, iii = x + 1, y - 1, z) (color figure available online).

center is defined by four carboxylate oxygen atoms from three different fipbb ligands and two nitrogen atoms from two bpt ligands. The two carboxylate groups adopt bidentate chelating and bridging bidentate modes. The Co-O distances fall in the range 2.011(2)-2.182(3) Å, and Co-N bond lengths are 2.175(3)-2.178(3) Å (Table 1), similar to those in others Cocarboxylate coordination polymers.^[12] Each pair of Co(II) ions is connected by a pair of syn-syn fipbb carboxylate groups to form a binuclear subunit, and these are doubly interlinked by the fipbb ligands into an infinite ribbon (Figure 2), which is similar to that observed in [Co(fipbb)(dpp)].MeOH.^[13] The bpt ligand serves as double bridges connecting [Co(fipbb)]_n ribbons into 2D (4,4) noninterpenetrating double layers with two kinds of windows when viewed along the crystallographic a axis (Figure 3). The 2D bilayer framework can also be considered as being constructed by two puckering layers of [Co(fipbb)(bpt)] linked by carboxylato groups of fipbb ligands. This structure is very similar to that of the polymer of [Co(fipbb)(dpp)].MeOH.^[13] The lattice DMF molecule is located at void region. There exist two windows porous. Window A is directed by two binuclear subunits and two fipbb ligands and window B consists of two

TABLE 1Crystallographic data for 1

Empirical formula	$C_{32}H_{23}CoF_6N_8O_5S$
Formula weight	762.54
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	<i>P</i> -1
	a = 8.3070(9) Å
	b = 13.6280(15) Å
Unit cell dimensions	c = 14.8286(15) Å
	$\alpha = 86.2070(10)$
	$\beta = 79.3410(10)^{\circ}$
	$\gamma = 83.8640(10)$
Volume, Z	1638.4(3) Å ³ , 2
Calculated density (kg/m ³)	1.546
Crystal size (mm ³)	$0.26 \times 0.20 \times 0.13$
θ Range for data collection (°)	2.01-25.22
Reflections collected	8288
Independent reflection	5751
Final <i>R</i> indices $[I > 2\sigma (I)]$	$R_1 = 0.0489, wR_2 = 0.1255$
<i>R</i> indices (all data)	$R_1 = 0.0635, wR_2 = 0.1416$

binuclear subunits and bpt ligands (Figure 4). The porous sizes are 8.8 × 9.1 Å (window A) and 12.2×10.2 Å (window B), respectively. A calculation by PLATON indicates that the free volume of channels occupies 15% of the crystal volume.^[14] A fascinating type of 2D \rightarrow three-dimensional (3D) polythreaded motif with different side arms involving nine polymeric units at a time was directed by flexible dicarboxylate and bpt coligands under mild condition.^[15] A three-dimensional, microporous MOF exhibiting reversible water adsorption is constructed from hexagonal Co(II) atoms-dicarboxylate layers and N,N'-pillars of bpt ligands.^[16]

The temperature-dependent molar magnetic susceptibility of **1** was measured at 1000 Oe in the range 2–300 K on a polycrystalline powder sample (Figure 5). At room temperature, $\chi_M T$ is 12.19 cm³ mol⁻¹ K, which is larger than the spin-only value for S = 3/2, indicating the important orbital contribution arising from the high-spin Co(II).^[17] χ_M^{-1} obeys the Curie–Weiss law



FIG. 2. View of the 1D ribbon chain along the bc plane (color figure available online).



FIG. 3. View of Co atoms interlinked by fipbb and bpt co-ligands to generate a 2D bilayer network parallel to (100) plane (color figure available online).

with a Curie constant of 9.88 cm³ K mol⁻¹ and a Weiss constant of $\theta = -0.28$ K. The negative θ value is indicative of a dominant antiferromagnetic interaction between Co²⁺ centers.^[18]

Compound 1 has stability in air and retains its crystalline integrity at ambient conditions. Thermogravimetric analysis of compound 1 shows loss of the DMF molecule (9.9%) within the temperature range of $35-255^{\circ}$ C (calcd. 9.5%) (Figure 6). Further weight loss was observed in the range of $290-510^{\circ}$ C, which is in agreement with the removal of the fipbb and bpt



FIG. 5. Plots $\chi_M T$ and χ_M^{-1} of versus T for 1; solid lines represent fits to the data.

ligands and indicates the network is thermally stable below these temperatures. The pattern that was simulated from the singlecrystal X-ray data of compound 1 was in agreement with those that were observed (Figure 7), which indicates that compound 1 was obtained as a single phase (minor differences can be seen in the positions, intensities, and widths of some peaks).

Crystallographic Data Collection and Structure Determination

Single-crystal data were collected at 298(2) K on a Bruker Smart Apex II diffractometer equipped with graphitemonochromated Mo K α radiation. The structure was solved using direct methods and successive Fourier difference synthesis (SHELXS-97),^[19] and was refined using the full-matrix least-squares method on F² with anisotropic thermal parameters for all nonhydrogen atoms (SHELXL-97).^[20] Metal atoms in



FIG. 4. Schematic representation of the double-layer network (color figure available online).



FIG. 6. The TGA curve of complex 1.



FIG. 7. Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination, with the as-synthesized product of **1** (color figure available online).

all the complexes were located from the E-maps and other nonhydrogen atoms were located in successive difference Fourier syntheses. All other hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. A summary of the crystallographic

TABLE 2Selected bond lengths (Å) and angles (°) for 1

Co1–O4#1 ^a	2.011(2)	O4–Co1–O3	114.29(10)
Co1–O2	2.184(2)	O3-Co1-N1	90.24(10)
Co1–O3	2.030(2)	N1-Co1-N4	177.00(11)
Co1-N4#3	2.175(3)	O4-Co1-O2	155.98(10)
Co1–N1	2.178(3)	O2-Co1-N1	90.24(10)
Co1–O2	2.184(2)	O3–Co1–O2	88.95(9)

^{*a*}Symmetry codes: #1: x, y, z + 1; #2: -x + 2, -y + 1, -z + 1; #3: x + 1, y - 1, z.

data is given in Table 1. Selected bond distances and angles data are given in Table 2.

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