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Polycatenate Structure and Thermal Analysis of a New 2D + 2D Cobalt(II) Coordination Polymer Based on 5-Methoxylisophthalic Acid and 3,5-Bis(imidazole-1-yl)pyridine Co-Ligands[1]

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Abstract—A new Co(II) compound, namely $[Co(CH_3O\text{-}H_2Ip)(Bip)]_n$ (**I**) ($CH_3O\text{-}H_2Ip$ = 5-methoxylisophthalic acid and Bip = 3,5-bis(imidazole-1-yl)pyridine), has been synthesized through combination of $CH_3O\text{-}H_2Ip$, Bip and Co(II) acetate under hydrothermal condition and structurally characterized by IR spectroscopy, elemental analysis and single-crystal X-ray diffraction (CIF file CCDC no. 977220). It crystallizes in triclinic, space group $P\bar{1}$ with $a = 9.764(6)$, $b = 10.106(6)$, $c = 11.673(7)$ Å, $\alpha = 104.12970°$, $\beta = 100.601(7)°$, $\gamma = 105.324(7)°$, $V = 1038.6(11)$ Å^3, $C_{20}H_{16}CoN_5O_5$, $Mr = 465.31$, $Z = 2$, $\rho_{calcd} = 1.488$ g/cm^3, $\mu(MoK_\alpha) = 0.869$ mm^{-1}, $F(000) = 476$, the final $R = 0.0652$ and $wR = 0.1530$. The X-ray analysis demonstrates that compound **I** exhibits a 2D + 2D polyrotaxane (4, 4) net network. Moreover, the thermal analysis of compound **I** has also been investigated.

Keywords: Co(II) complex, crystal structure, thermal analysis

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INTRODUCTION

In recent years, a number of coordination polymers with various structural types and topological characteristics have been documented. The final structures of polymers can be influenced by many factors such as metal centers, ligand, solvent medium, pH values, temperature and so on [1–5]. Through practice of predecessors, a few successful synthetic strategies, such as building block methodology, mixed-ligand strategy, the "pillaring" means, the reticular approach etc. have been exploited [6–9]. Among the strategies, the mixed-ligand strategy is one of the most effective ways to construct new MOFs with unique structures, because mixed-ligand system consisting of two type ligands provides more variability to construct charming topologies. One of the optimal choices is the combination of carboxylic acids and neutral N-containing auxiliary ligands. Among various organic ligands, especially carboxylate-based ligands (such as 1,2-benzene dicarboxylic acid, 1,3-benzene dicarboxylic acid, 1,4-benzene dicarboxylic acid, 1,2,4-benzenetricarboxylicacid, 1,3,5-benzenetricarboxylicacid and so on) have been widely used to construct MOFs owing to their strong coordination abilities and diverse coordination modes [10–14]. In this work, we exploit 5-methoxylisophthalic acid and rigid 3,5-bis(imidazole-1-yl)pyridine ligands to assemble with Co^{2+} ion under solvothermal conditions. Successfully, we obtained a new 2D + 2D polyrotaxane coordination polymer, namely $[Co(CH_3O\text{-}H_2Ip)(Bip)]_n$ (**I**) ($CH_3O\text{-}H_2Ip$ = 5-methoxylisophthalic acid and Bip = 3,5-bis(imidazole-1-yl)pyridine).

EXPERIMENTAL

Materials and general methods. All reagents were of analytical grade and were used without further purification. Elemental analyses for carbon, hydrogen and nitrogen atoms were carried out on a Vario EL III elemental analyzer. The infrared spectrum of a KBr pellet was recorded in the range of 4000–600 cm^{-1} on an Avatar™ 360 E.S.P. IR spectrometer. Thermogravimetric (TG) analyses were carried out in nitrogen at a heating rate of 10°C min^{-1} using a TG/DTA 6300 integration thermal analyzer.

Synthesis of I. The mixture of $Co(OAc)_2 \cdot 4H_2O$ (25 mg, 0.1 mmol), $CH_3O\text{-}H_2Ip$ (19 mg, 0.1 mmol), Bip (21 mg, 0.1 mmol) and distilled water (10 mL) was sealed in a 25 mL stainless-steel reactor with Teflon liner and heated to 150°C and kept at constant temperature for 96 h. Slow cooling of the reaction mixture

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[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement information for **I**

Parameter	Value
Formula weight	465.31
Temperature, K	296(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions:	
a, Å	9.764(6)
b, Å	10.106(6)
c, Å	11.673(7)
α, deg	104.121(7)
β, deg	100.601(7)
γ, deg	105.324(7)
Z; volume, Å^3	2; 1038.6(11)
ρ_{calcd}, mg/m^3	1.488
Absorption coefficient, mm^{-1}	0.869
F(000)	476
θ Range for data collection, deg	2.40–25.50
Reflections collected	7402
Independent reflection (R_{int})	3727 (0.0492)
Data/restraints/parameters	3727/0/281
Goodness-of-fit on F^2	1.001
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0652$, $wR_2 = 0.1530$
R indices (all data)	$R_1 = 0.0957$, $wR_2 = 0.1673$
Largest diff. peak and hole, e/Å^3	0.913 and −0.499

to room temperature at a rate of 5°C/h produced the purple block crystals of **I** in 52% yield (based on Co).

For $C_{20}H_{16}N_5O_5Co$

anal. calcd., %	C, 51.62	H, 3.47	N, 15.05
found, %	C, 51.35	H, 3.43	N, 15.10

Infrared spectrum (KBr; ν, cm^{-1}): 3434 s, 2929 m, 2351 m, 2069 m, 1638 m, 1586 m, 1341 m, 1119 s, 953 m, 775 m, 722 m, 654 m.

X-ray structure determination. Single-crystal X-ray diffraction data for **I** were collected on a Bruker Apex II CCD diffractomete with MoK_α radiation (λ = 0.71073 Å) by using φ/ω scan technique at room temperature. The structure was solved by direct methods with SHELXS-97 [15]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [16]. The empirical absorption corrections were applied by the SADABS program. The H-atoms of carbon were assigned with common isotropic displacement factors and included in the final refinement by the use of geometrical restraints. The crystallographic data for complex **I** are listed in Table 1. Selected bond lengths and angles for **I** are collected in Table 2.

The atomic coordinates and other parameters of the complex have been deposited with the Cambridge

Table 2. Selected bond lengths (Å) and angles (deg) for **I***

Bond	*d*, Å	Bond	*d*, Å
Co(1)–O(4)$^{\#1}$	1.980(3)	Co(1)–N(1)	2.018(4)
Co(1)–O(1)	1.990(3)	Co(1)–N(4)$^{\#2}$	2.025(4)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(4)$^{\#1}$Co(1)O(1)	96.67(14)	O(1)Co(1)N(4)$^{\#2}$	113.00(16)
O(4)$^{\#1}$Co(1)N(1)	108.90(15)	N(1)Co(1)N(4)$^{\#2}$	113.24(17)
O(1)Co(1)N(1)	111.12(15)	C(7)O(1)Co(1)	104.7(3)
O(4)$^{\#1}$Co(1)N(4)$^{\#2}$	112.73(16)	C(8)O(4)Co(1)$^{\#3}$	108.9(3)

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ *x*, *y* – 1, *z*; $^{\#2}$ *x*, *y*, *z* – 1; $^{\#3}$ *x*, *y* + 1, *z*.

Crystallographic Data Center (CCDC no. 977220; deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The asymmetric coordination unit of **I** (Fig. 1) consists of one Co^{2+} ion, one CH_3O-Ip^{2-} ligand and one Bip ligand. Each Co^{2+} ion is four-coordinated by two nitrogen atoms (N(1), N(4)$^{\#2}$) from the two different Bip ligands (Co(1)–N(1) 2.018(4), Co(1)–N(4)$^{\#2}$ 2.025(4) Å) and two oxygen atoms (O(1), O(4)$^{\#1}$) from carboxylate groups of two different CH_3O-Ip^{2-} ligands (Co(1)–O(1) 1.990(3), Co(1)–O(4)$^{\#1}$) 1.980(3) Å). The bond angles Co^{2+} ions around locate in the range of 96.67(14)°–113.24(17)°, which are comparable with those previously reported Co(II)-based complexes [17–19]. The Co^{2+} ion shows a distorted tetrahedron geometry. And there are weak coordinated bonds (Co(1)···O(2) 2.592 and Co(1)···O(3)$^{\#1}$ 2.692 Å) in **I**, resulting to two carboxylate groups of CH_3O-Ip^{2-} ligand nearly coplanar. The dihedral angle of two imidazole ring containing N(1) and N(4) from the central pyridyl ring is 52.429°, in which twist of Bip ligand is observed. Each CH_3O-Ip^{2-} ligands adopts a μ_2-bridging mode to connect two adjacent Co^{2+} ions, in which the carboxylate groups show a μ_1-η^1:η^0 monodentate mode. The CH_3O-Ip^{2-} ligands connect Co(II) atoms to form a 1D chain (Fig. 2). These chains are further linked by bridging Bip ligands along the *z* axis to generate a 2D rectangular (4,4) grid layer (Fig. 3). These identical 2D single nets come in pairs, forming a 2D + 2D (4,4) polyrotaxane net architecture (Fig. 4).

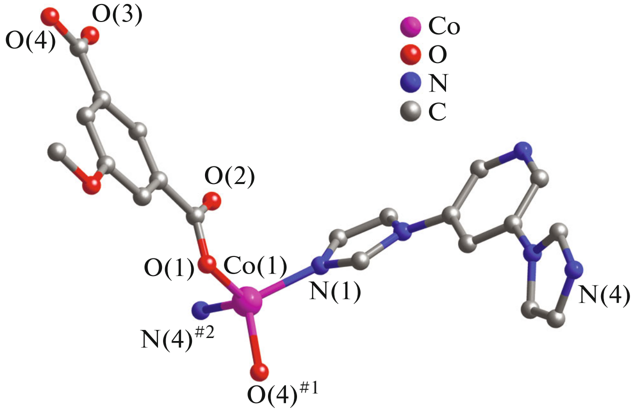

Fig. 1. Coordination environment of Co(II) atom in **I**. Symmetry code: $^{\#1}$ *x*, *y* – 1, *z*; $^{\#2}$ *x*, *y*, *z* – 1.

For the sake of discovering the thermal stability of compound **I**, the thermal weight measurement was carried out in the range of 30–800°C under flowing N_2 atmosphere (Fig. 5). Compound **I** is robust and stable from room temperature to 398°C. Then, a sharp continual weight loss occurred, which is attributed to the decomposition of the framework. And the residue was CoO (obsd. 16.26%, calcd. 16.12%).

In summary, we synthesized a new coordination polymer of Co(II) under hydrothermal conditions through CH_3O-H_2Ip and Bip co-ligands and Co(II) acetate salt. The results revealed that compound **I** shows a 2D layer structure. It is interesting that the 2D + 2D polycatenate structure is observed in **I**. Owing to polycatenate structure in reported coordination polymers are fewer, the exploitation of such structure can be helpful not only for both the design and analysis of crystal structures but also for understanding the relationships between the structure and function of these coordination polymers.

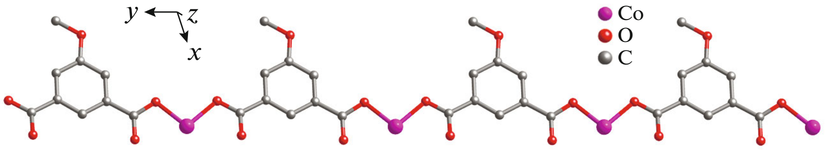

Fig. 2. The 1D chain structure constructed from Co(II) centers and CH_3O-Ip^{2-} ligands in **I**.

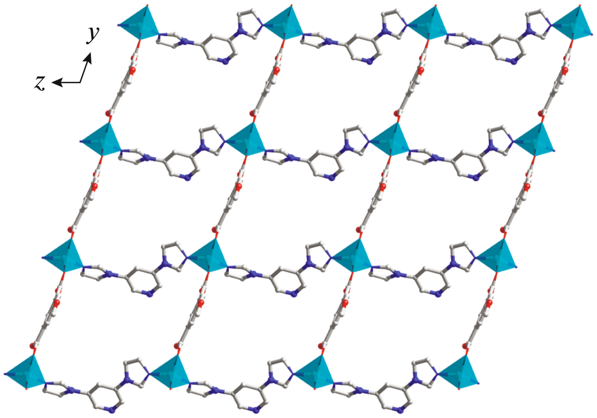

Fig. 3. The single 2D (4,4) net of **I**.

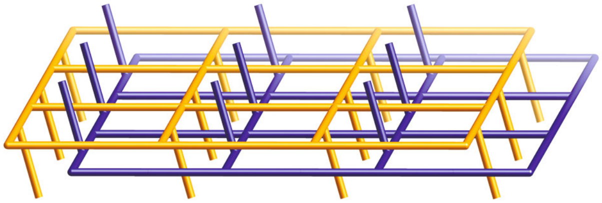

Fig. 4. Parallel 2D + 2D → 2D polyrotaxane structure in **I**.

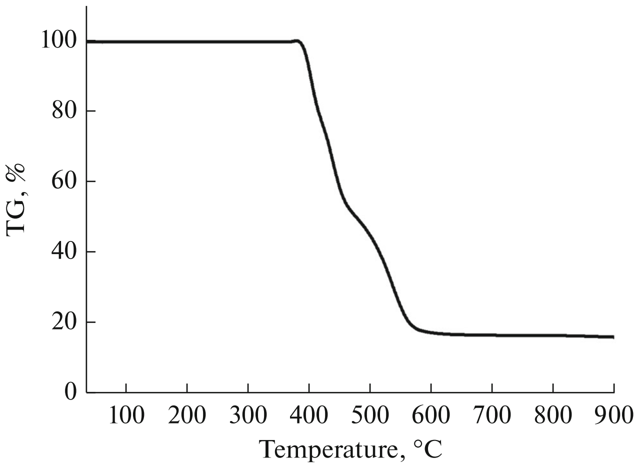

Fig. 5. The TG curve of compound **I**.

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