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Synthesis and Crystal Structure of a 1D Coordination Polymer Constructed by Cobalt with 4-Hydroxypyridine-2,6-Dicarboxylic Acid[1]

C. J. He[a], X. J. Zhou[a], and Y. F. Wang[b]

[a] Life Science Department, Luoyang Normal University Luoyang, Henan, 471022 P.R. China
[b] College of Chemistry and Chemical Engineering, Luoyang Normal University Luoyang, Henan, 471022 P.R. China
*e-mail: wangyf78@163.com

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Abstract—A new one-dimensional chain complex $[Co_3(Hpda)_2(H_2O)_8]_n$ (**I**), where $HpdaH_3$ = 4-hydroxypyridine-2,6-dicarboxylic acid, has been synthesized and characterized structurally. It crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.3718(11)$, $b = 8.4881(13)$, $c = 9.4513(14)$ Å; $\alpha = 110.3300(10)°$, $\beta = 100.7470(10)°$, $\gamma = 95.338(2)°$, $V = 536.77(14)$ Å^3, $C_{14}H_{20}Co_3N_2O_{18}$, $Mr = 681.11$, $Z = 1$, $\rho_c = 2.107$ g/cm^3, $\mu = 2.390$ mm^{-1}, $F(000) = 343$, $R = 0.0182$ and $wR = 0.0486$ for 1893 observed reflections with $I > 2\sigma(I)$. Complex **I** possesses a one-dimensional (1D) chain structure composed of continuous trinuclear Co(II) clusters, which further forms a three-dimensional (3D) supramolecular architecture via hydrogen bonds.

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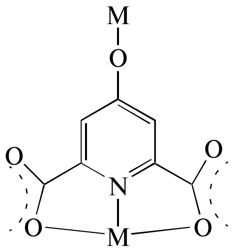
INTRODUCTION

The rational design and construction of novel coordination polymer have attracted much attention in the field of supramolecular chemistry and crystal engineering, due to their intriguing topologies and potential applications as functional materials [1–6]. Over recent decades, a variety of multicarboxylate, triazine, imidazoline, pyridine-based ligands have been extensively studied and are found to exhibit various coordination modes accompanying a diversity of structures with honeycomb, rectangular grid, bilayer lattice, ladder and diamond frameworks being observed, with consequent varying adsorptions, magnetic and luminescent properties [7–12]. Dicarboxylate ligands are widely used to assemble supramolecular network organized by coordination bonds, hydrogen bonds and π–π stacking interaction [13]. Due to the manifold N- and O-donors of pyridine or carboxylic ligands, metal pyridine dicarboxylates can contrast versatile structural motifs, which finally aggregate to generate various supramolecular architectures with interesting properties. As one of the dicarboxylate ligands, 2,6-pyridinedicarboxylic acid have drawn extensive attention. As we know, at present the study of 4-hydroxypyridine-2,6-dicarboxylic acid ($HpdaH_3$) ligand is scarce. In the present paper, we report the syntheses and crystal structure of a new cobalt complex with $HpdaH_3$, $[Co_3(Hpda)_2(H_2O)_8]_n$ (**I**). The coordination modes of ligand observed in complex **I** are the following:



EXPERIMENTAL

Materials and methods. All reagents used in the syntheses were of analytical grade and used without further purification. The C, H, and N elemental analyses were performed on a Vario EL III elemental analyzer. The infrared spectra (4000–600 cm^{-1}) were recorded by using KBr pellet on an Avatar^{TM} 360 E.S.P. IR spectrometer.

Synthesis of complex I. The mixture of $Co(OAc)_2 \cdot 4H_2O$ (25 mg, 0.1 mmol), $HpdaH_3$ (18 mg, 0.1 mmol), 2,2'-bipyridene (15.9 mg, 0.1 mmol), and in distilled water (8 mL) was sealed in a 25 mL stainless-steel reactor with Teflon liner and heated to 130°C and kept at constant temperature for 96 h. Then the autoclave was cooled over a period of 24 h at a rate of 5°C h^{-1}, and the red block crystals suitable for X-ray analysis were obtained. The yield was 42%.

For $C_{14}H_{20}Co_3N_2O_{18}$

anal. calcd., %:	C, 24.69;	H, 2.96;	N, 4.11.
Found, %:	C, 24.58;	H, 3.04;	N, 4.07.

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[1] The article is published in the original.

Infrared spectrum (KBr; ν, cm^{-1}): 3420, 1620, 1585, 1503, 1422, 1391, 1349, 1142, 941.

X-ray crystal determination. Red single crystal of the complex (0.39 × 0.30 × 0.12 mm) was put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using a ϕ/ω scan technique at room temperature, 1981 independent reflections ($R_{int} = 0.0163$) in the range $2.60° < \theta < 25.50°$ with $-8 \le h \le 8$, $-10 \le k \le 10$, $-11 \le l \le 11$ were collected at 295(2) K. The structure was solved by direct methods with SHELXS-97 [14]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains, while the non-hydrogen atoms were treated with common anisotropic displacement factors and included in the final refinement with geometrical restrains. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [15]. The final agreement factor values are $R = 0.0182$ and $wR = 0.0486$. Crystallographic data and refinement parameters are listed in Table 1. The atomic coordinates and other parameters of the complex have been deposited with the Cambridge Crystallographic Data Centre (no. 845887; deposit@ccdc.cam.ac.uk or ttp://www. ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Complex **I** exhibits a 1D coordination motif based on the trimeric $[Co_3(Hpda)_2(H_2O)_8]$ secondary building units (SBUs). The asymmetric unit consists of three Co^{2+} ions, two $Hpda^{3-}$ ligands, eight coordinated water molecules (Fig. 1). In two crystallographically independent Co^{2+} ions. The Co(1) ion locates in an inverse center and is coordinated by one nitrogen atom and three oxygen atoms of two $Hpda^{3-}$ ligands, and two oxygen atoms from two coordinated water molecules. The Co(2) ion possesses a distorted octahedral coordination geometry with two oxygen atoms of two different $Hpda^{3-}$ ligands occupying axis positions and four oxygen atoms of four coordinated water molecules forming an equatorial plane. The Co(1) and its symmetry equivalent Co(1*A*) (*A*: $-x$, $-y$, $-z$) are bridged by two carboxyl oxygen atoms, with a Co(1)···Co(1*A*) distance of 3.467 Å and a Co(1)O(2)Co(1*A*) bond angle of 105.30(5)°. The Co(1)–N(1) bond distance is 2.0400(14) Å. The Co(1)–O(2*A*) bond distance of 2.0921(12) Å is obviously smaller than that of Co(1)–O(4) (2.1975(12) Å) (Table 2). The Co(1)–O(water) bond lengths are 2.0519(12) and 2.1128(12) Å, respectively. The Co(2)–O(8*B*), Co(2)–O(9*A*), Co(2)–O(9*B*) (*B*: $-x + 1$, $-y + 2$, $-z + 1$) bond lengths are 2.0889(12), 2.1317(12), 2.1316(12) Å, respectively, and the Co(2)–O(1*A*) bond length is 2.0921(11) Å. The repeatedly trinuclear Co(II) subunits are linked by $Hpda^{3-}$ ligands in a *syn* coordination mode coordinating to neighboring terminal Co^{2+} ions, generating a 1D linear chain with a period of 16.46 Å. (Fig. 2). In addition, extensive interchain O–H···O hydrogen bonds formed by the coordinated water and the carboxyl group in the $Hpda^{3-}$ ligands link the 1D chain to the 2D layer (Fig. 3). The hydrogen bonds further link adjacent 2D layer into 3D supramolecular network (Fig. 4, Table 3).

Table 1. Crystallographic data and details of the experiment and refinement for complex **I**

Parameter	Value
Color/shape	Brown/block
Formula weight	295(2)
Wavelength, Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions:	
a, Å	7.3718(11)
b, Å	8.4881(13)
c, Å	9.4513(14)
α, deg	110.3300(10)
β, deg	100.7470(10)
γ, deg	95.338(2)
Z; Volume, $Å^3$	1; 536.77(14)
ρ_{calcd}, mg/m^3	2.107
Absorption coefficient, mm^{-1}	2.390
F(000)	343
θ range for data collection, deg	2.60–25.50
Reflections collected	4111
Independent reflections (R_{int})	1981 (0.0163)
Refinement method	Full-matrix least-squares on F^2
Parameters	170
Goodness-of-fit on F^2	1.044
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0182$, $wR_2 = 0.0486$
R indices (all data)	$R_1 = 0.0190$, $wR_2 = 0.0492$
Largest diff. peak and hole, $e/Å^3$	0.275 and –0.329

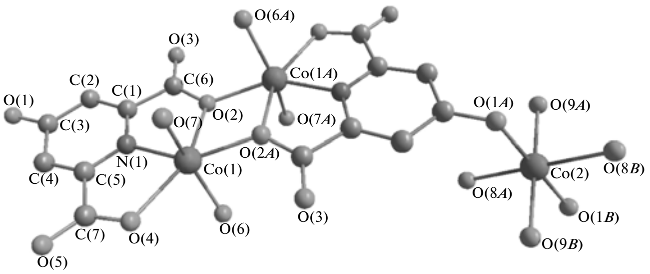

Fig. 1. Coordination environment of Co(II) (symmetry codes: (*A*) $-x$, $-y$, $-z$; (*B*) $-x + 1$, $-y + 2$, $-z + 1$).

Table 2. Selected bond distances and angles for complex **I***

Bond	d, Å	Bond	d, Å
Co(1)–N(1)	2.0400(14)	Co(1)–O(2)	2.2671(12)
Co(1)–O(6)	2.0519(12)	Co(2)–O(8)	2.0889(12)
Co(1)–O(2)$^{\#1}$	2.0921(12)	Co(2)–O(1)	2.0921(11)
Co(1)–O(7)	2.1128(12)	Co(2)–O(9)	2.1317(12)
Co(1)–O(4)	2.1975(12)	O(1)–C(3)	1.3287(19)
Angle	ω, deg	Angle	ω, deg
N(1)Co(1)O(6)	108.32(5)	O(4)Co(1)O(2)	148.74(4)
N(1)Co(1)O(2)$^{\#1}$	146.25(5)	O(8)Co(2)O(1)	92.80(5)
O(6)Co(1)O(2)$^{\#1}$	85.85(5)	O(8)Co(2)O(9)	87.63(5)
N(1)Co(1)O(7)	94.82(5)	O(1)Co(2)O(9)	89.64(5)
O(6)Co(1)O(7)	152.18(5)	C(3)O(1)Co(2)	122.31(10)
O(2)$^{\#1}$Co(1)O(7)	83.02(5)	C(6)O(2)Co(1)$^{\#1}$	133.68(10)
N(1)Co(1)O(4)	76.11(5)	C(6)O(2)Co(1)	115.89(10)
O(6)Co(1)O(4)	86.74(5)	Co(1)$^{\#1}$O(2)Co(1)	105.30(5)
O(2)$^{\#1}$Co(1)O(4)	136.52(4)	C(7)O(4)Co(1)	115.26(10)
O(7)Co(1)O(4)	84.01(5)	O(8)Co(2)O(1)$^{\#2}$	87.20(5)
N(1)Co(1)O(2)	73.49(5)	C(5)N(1)Co(1)	119.16(11)
O(6)Co(1)O(2)	95.96(5)	O(8)Co(2)O(9)$^{\#2}$	92.37(5)
O(2)$^{\#1}$Co(1)O(2)	74.70(5)	O(8)$^{\#2}$Co(2)O(1)$^{\#2}$	92.80(5)
O(7)Co(1)O(2)	105.48(5)	O(1)Co(2)O(1)$^{\#2}$	180.0

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

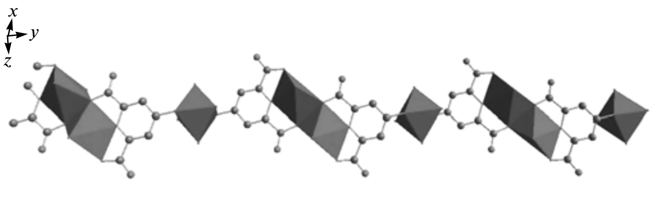

Fig. 2. 1D chain coordination motif.

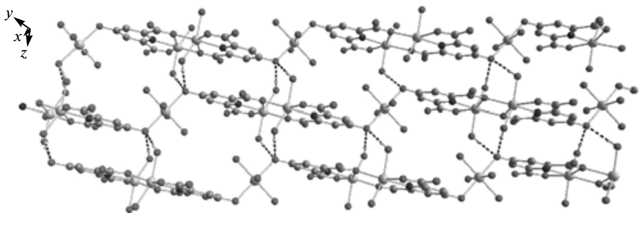

Fig. 3. 2D supramolecular network showing the hydrogen bond interactions (dark red dashed lines).

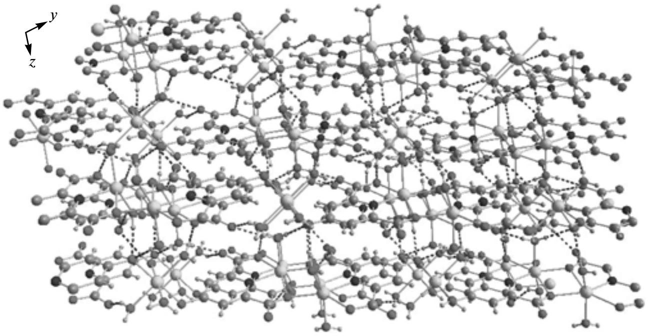

Fig. 4. 3D supramolecular network constructed via O–H···O interactions.

Table 3. Geometric parameters of hydrogen bonds for complex **I***

Contact D–H...A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
O(6)–H(1*w*)···O(3)$^{\#3}$	0.82	2.15	2.8667(18)	146
O(7)–H(3*w*)···O(5)$^{\#4}$	0.82	1.98	2.7984(18)	174
O(8)–H(5*w*)···O(5)$^{\#5}$	0.82	2.02	2.7613(17)	151
O(9)–H(7*w*)···O(7)$^{\#4}$	0.82	2.29	2.9741(18)	141
O(7)–H(4*w*)···O(1)$^{\#6}$	0.83	1.95	2.7848(16)	176
O(6)–H(2*w*)···O(1)$^{\#7}$	0.83	1.83	2.6578(17)	178
O(9)–H(8*w*)···O(3)$^{\#8}$	0.82	1.96	2.7751(18)	176
O(8)–H(6*w*)···O(4)$^{\#4}$	0.81	1.97	2.7635(16)	169

* Symmetry transformations used to generate equivalent atoms: $^{\#3}\ x - 1, y, z$; $^{\#4}\ -x, -y + 1, -z + 1$; $^{\#5}\ x + 1, y, z$; $^{\#6}\ x, y - 1, z$; $^{\#7}\ -x, -y + 1, -z$; $^{\#8}\ x, y + 1, z + 1$.

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