

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF A NOVEL COMPLEX $[\text{Co}(3,3'\text{-bpbc})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ E.-J. Gao, L.-L. Jiang, D. Zhang, W. Jiao, T.-L. Liu, Y.-J. Zhang,
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A novel coordination polymer constructed with $[\text{Co}(3,3'\text{-bpbc})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}(\text{I})$ (3,3'-bpbc = 2,2'-bipyridine-3,3'-dicarboxylic acid) is successfully synthesized at room temperature and characterized by elemental analysis and IR spectra. The crystal structure of the complex is determined by single crystal X-ray diffraction. The unit cell parameters for complex **I** are: $a = 9.9606(11) \text{ \AA}$, $b = 9.2552(10) \text{ \AA}$, $c = 16.0258(17) \text{ \AA}$, $\beta = 96.731(0)^\circ$, $V = 1467.2(3) \text{ \AA}^3$, $Z = 4$, space group $P2(1)/n$. In the crystal, the cobalt(II) ion adopts a hexa-coordinate environment, and the structure units aggregate together to give birth to infinite 1D chains. The 2D and 3D framework is constructed via intermolecular hydrogen bonds.

Keywords: 2,2'-bipyridine-3,3'-dicarboxylic acid (3,3'-bpbc), cobalt(II) complex, crystal structure, coordination

During the past decades, metal complexes containing hydrogen bonded water clusters have received a wide range of attention in the field of supramolecular chemistry and crystal engineering [1—5]. Due to its strength and directionality the hydrogen bond is perhaps the most important intermolecular interaction used in such endeavors. In different chemical environments, the complexes with the same ion and ligand may form different structures [6, 7]. Moreover, ligands containing aromatic rings and multicarboxylate have proved to be a powerful tool in the construction of multidimensional architectures [8] because they can be regarded as not only the hydrogen bond [9, 10] acceptors of carboxylate, but also the strong $\pi-\pi$ stacking [11, 12] ability of aromatic rings. Subsequently, the resultant complexes possess a wide range of chemical and physical properties, such as electrochemical, catalytic, magnetic, photophysical, biochemical and the assembly of supramolecular structures [13—19].

In this paper, we successfully designed the 2,2'-bipyridine-3,3'-dicarboxylic acid (3,3'-bpbc) ligand that consists of two carboxylate groups and aromatic ring systems, and its noncovalent linking sites lead to the aggregation of the neighboring complexes through hydrogen bonds and form a novel complex $[\text{Co}(3,3'\text{-bpbc})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$. In the unit cell, 3,3'-bpbc binds to the cobalt atom in a chelate mode by two N atoms.

Experimental. Materials and measurements. All reagents were of analytical grade, purchased from commercial sources and used without further purification. Elemental analyses (C, H, and N) were performed on a model Finnigan EA 1112 instrument. IR spectra were recorded on a Nicolet IR_470 spectrophotometer using KBr pellets.

Synthesis of I. The concentration of all reagents were 10 mmol/l. An aqueous solution (5 ml) containing $\text{Co}(\text{NO}_3)_2$ (0.05 mmol) was added to an ethanolic solution (10 ml) with 3,3'-bpbc

(0.1 mmol). Stirred in air, the mixture turned to rose pink. The clear solution was obtained after removing turbidness by filtration. Several days later, pink transparent crystals formed by evaporating the solution at room temperature were collected and found suitable for X-ray diffraction.

The FT-IR spectrum (ν , cm^{-1}): 3422 m, 2426 w, 1892 w, 1717 w, 1618 w, 1559 w, 1384 s, 1288 m, 1141 w, 913 w, 766 w, 682 w cm^{-1} .

For $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_8\text{Co}$ anal. calcd, %: C, 38.62; H, 3.78; N, 7.51. Found, %: C, 38.66; H, 3.75; N, 7.54.

X-ray structure determination. The crystal structure of complex **I** was determined by X-ray single crystal diffraction. The sample was isolated from the bulk and mounted on a glass fiber. Data were collected on a Bruker Smart 1000 CCD X-ray single crystal diffractometer with MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The structures were solved by a direct method using the SHELXL-97 package [20, 21]. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms bound to carbon atoms were placed in calculated positions and refined isotropically with a riding model [22]. The crystal data and structure refinement are given in Table 1; selected bond distances (\AA) and bond angles (deg.) are listed in Table 2. The crystal unit structure of complex **I** is shown in Fig. 1.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 873090; deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>)

Results and discussion. Compound **I** possesses an asymmetric unit consisting of one Co atom, one 3,3'-bpbc molecule, three dissociative water molecules, and one crystallization water molecule. An X-ray single crystal analysis revealed that the Co atom allows the formation of a hexa-coordinate environment with one carboxylate oxygen atom O(3), two nitrogen atoms N(1), N(2) from 3,3'-bpbc, and three oxygen atoms O(5), O(6), and O(7) from coordinated water occupying the remaining coordination sites. The coordination angles around the Co atom ranged from 76.17° to 178.88° .

As for the 1D chain in Fig. 2, it is interesting to note that the 1D chain structure was interconnected by oxygen atom associations between subchains. The distance between two neighboring Co

Table 1

Crystallographic data and details of the experiment and refinement of complex I

Parameter	Value
Formula weight	373.18
Crystal system	Monoclinic
Space-group	$P2(1)/n$
Unit cell dimensions: $a, b, c, \text{\AA}$; β , deg.	9.9606(11), 9.2552(10), 16.0258(17); 96.731(0)
$V, \text{\AA}^3$	1467.2(3)
Z	4
$\rho_{\text{calcd}}, \text{g/cm}^{-3}$	1.689
$F(000)$	764.0
θ range for data collection, deg.	$2.29 < \theta < 25.99$
Limiting indices	$-12 \leq h \leq 12, -11 \leq k \leq 9, -19 \leq l \leq 19$
Reflections collected / unique, $I > 2\sigma(I)$	8958 / 2873 ($R_{\text{int}} = 0.0237$)
Number of refined parameters	231
Completeness, %	99.6
Goodness-of-fit on F^2	1.079
Absorption coefficient, mm^{-1}	1.215
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0300, wR2 = 0.0799$
R indices (all data)	$R1 = 0.0344, wR2 = 0.0822$
Largest diffraction peak and hole, e/\AA^{-3}	0.527 and -0.421

Selected bond distances (Å) and bond angles (deg.) for the structure of complex I

Bond	<i>d</i> , Å	Angle	ω, deg.	Angle	ω, deg.
Co(1)—N(1)	2.1575(16)	O(6)Co(1)O(7)	98.83(7)	O(7)Co(1)O(5)	91.41(6)
Co(1)—N(2)	2.1116(15)	O(7)Co(1)N(2)	91.79(7)	O(6)Co(1)O(5)	89.51(6)
Co(1)—O(3)	2.0927(14)	O(7)Co(1)N(1)	166.25(6)	N(2)Co(1)N(1)	76.17(6)
Co(1)—O(5)	2.1227(15)	O(6)Co(1)N(2)	168.90(6)	C(3)C(4)C(5)	116.72(17)
Co(1)—O(6)	2.0646(15)	O(6)Co(1)N(1)	92.90(6)	O(1)C(5)O(2)	125.78(17)
Co(1)—O(7)	2.0549(15)	N(2)Co(1)O(5)	93.49(6)	O(2)C(5)C(4)	116.49(17)
		O(5)Co(1)N(1)	95.88(6)	O(3)C(9)O(4)	126.41(17)
		C(6)C(4)C(5)	124.93(17)	C(6)N(1)Co(1)	111.22(12)
		O(1)C(5)C(4)	117.52(17)	C(12)N(2)Co(1)	123.35(13)
		C(4)C(6)C(7)	126.04(15)	C(1)N(1)Co(1)	121.68(12)
		N(2)C(7)C(6)	113.30(15)	C(12)N(2)C(7)	119.92(16)
		O(3)C(9)C(8)	115.50(15)	C(7)N(2)Co(1)	116.13(12)

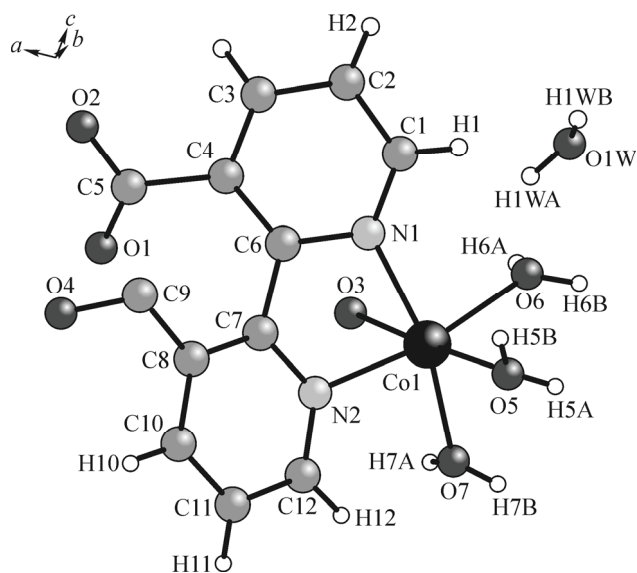
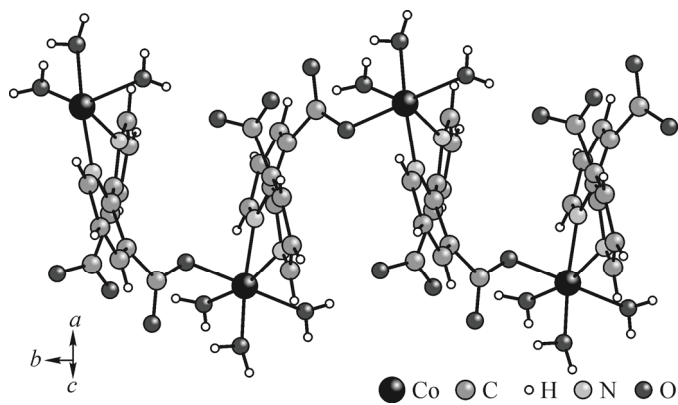
Fig. 1. Crystal unit structure of the $[\text{Co}(3,3'\text{-bpbc})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ complex

Fig. 2. 1D structure of complex I formed by the oxygen atom

Fig. 3. 2D structure of complex **I** formed by hydrogen bonds

atoms is 7.312 Å. The independent units are linked to each other via kinds of hydrogen bonds, resulting in a perfect 2D chain. From the depiction in Fig. 3, it can be seen that the hydrogen bond effect plays an important role in the construction of a 2D structure with a high regularity. Two adjacent 1D chains interact with each other through hydrogen bond interactions (the distances are 1.8796 Å and 2.0257 Å respectively) to form the 2D framework, which is further fabricated into the 3D supramolecular architecture.

Conclusions. The novel coordination cobalt polymer $[\text{Co}(\text{3,3}'\text{-bpbc})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (**I**) has been successfully synthesized at room temperature and characterized by elemental analysis and IR spectra. This study provides important crystallographic information that makes it possible to know about the formation mechanism of the cobalt polymer.

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