

Hydrothermal Synthesis and Crystal Structure of a One-dimensional Cobalt (II) Coordination Polymer with Two Organic Ligands

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A new Co(II) coordination polymer [Co(Hdpa)₂(dpdo)(H₂O)₂] (**1**) (H₂dpa = 2,2'-biphenyldicarboxylic acid, dpdo = 4,4'-bipyridine-*N,N'*-dioxide) has been synthesized and characterized by IR and UV/Vis spectroscopy, elemental analysis, and single-crystal X-ray structure analysis. The Co(II) atom has a distorted octahedral coordination environment with a set of oxygen donors from two Hdpa[−] ligands, two dpdo ligands and two coordinated water molecules. Adjacent cobalt centers are bridged by dpdo ligands thereby generating a chain. In the solid state, the chains further interact with each other and form a 3D supramolecular network *via* C–H... π interactions and multiform hydrogen bonds.

Key words: Hydrothermal Synthesis, Cobalt(II), Crystal Structure

Introduction

Coordination polymers assembled from appropriate multidentate ligands and metal centers are of particular interest showing promise in not only their intriguing structural motifs and physical and chemical properties, but also their potential applications in catalysis, gas storage and separation, magnetism, optical devices, and molecular sensors [1–4]. The key features that determine the overall architectures are the nature of coordinating groups, the ligand topology (such as the number and position of coordinating groups), flexibility or rigidity of the linker groups joining the coordination sites, and the stereochemical preferences of the coordinated metal ions [5–8]. In the design and construction of functional coordination polymers, carboxylic acids containing two or more carboxyl groups are one kind of the most extensively investigated ligands owing to their multiform bonding [9–11]. Among them, 2,2'-biphenyldicarboxylate with a semi-rigid spacer between the two phenyl groups attracts considerable interest in the formation of diverse structures with the metal ion connectors due to its multiform coordina-

tion motifs as well as the twist conformation based on the constraints of the rotation around the C–C bond [12–16].

Besides carboxylates, oligo-pyridyls have been good candidates because they have a readily adjustable length and geometry. 4,4'-Bipyridine-*N,N'*-dioxide (dpdo) is an excellent organic ligand not only as a longer spacer, but also owing to its small diameter which avoids crowding at the metal centers and allows high connectivity and a large volume of voids [17–19]. As a part of our continuing investigations on coordination polymers [20–23], herein, we report the synthesis and crystal structure of a one-dimensional Co(II) coordination polymer [Co(Hdpa)₂(dpdo)(H₂O)₂] (**1**) based on two types of the organic ligands, 2,2'-biphenyldicarboxylic acid (H₂dpa) and 4,4'-bipyridine-*N,N'*-dioxide (dpdo).

Experimental Section

General

Materials: All chemicals were of reagent grade quality obtained from commercial sources and used without further

purification. 4,4'-Bipyridine-*N,N'*-dioxide (dpdo) was prepared according to the literature method [24].

Instrumentation: Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C instrument. IR spectra were recorded from KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000–400 cm^{-1} region. The UV/Vis spectra were obtained on a Shimadzu UV-250 spectrometer in the range of 800 ~ 190 nm in the solid state.

Synthesis

A mixture of $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ (0.125 g, 0.5 mmol), H_2dpa (0.121 g, 0.5 mmol) and dpdo (0.094 g, 0.5 mmol) in 8 mL deionized water was sealed in a 25 mL Teflon-lined stainless-steel container and heated at 120 °C for 3 d. Red block-shaped crystals of **1** were collected in 54% yield. – Anal. for $\text{C}_{38}\text{H}_{30}\text{CoN}_2\text{O}_{12}$: calcd. C 59.60, H 3.95, N 3.66; found C 59.67, H 3.86, N 3.69. – IR (cm^{-1} , KBr pellet): $\nu = 3246(\text{m})$, 3109(*m*), 1699(*s*), 1600(*w*), 1576(*m*), 1541(*s*), 1470(*s*), 1441(*m*), 1414(*s*), 1219(*s*), 1180(*s*), 1025(*w*), 826(*m*), 767(*s*), 555(*m*).

X-Ray crystallographic study

A crystal of size $0.16 \times 0.19 \times 0.26 \text{ mm}^3$ was chosen for the crystallographic study and mounted on a Bruker Smart APEX II CCD diffractometer. All diffraction measurements were performed at room temperature using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by Direct Methods and refined on F^2 by using full-matrix least-squares methods with the SHELXL-97 program [25, 26]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques, and all hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached. Space group, lattice parameters and other relevant information are listed in Table 1, and selected bond lengths and angles are given in Table 2.

CCDC 976287 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Summary of crystal data and refinement results of the polymer **1**.

Empirical formula	$\text{C}_{38}\text{H}_{30}\text{CoN}_2\text{O}_{12}$
Formula weight	765.57
Temperature, K	296(2)
Wavelength	0.71073 \AA
Crystal system	triclinic
Space group	$P\bar{1}$
<i>a</i> , \AA	7.8772(7)
<i>b</i> , \AA	10.1856(9)
<i>c</i> , \AA	10.5138(9)
α , deg	91.923(2)
β , deg	99.969(2)
γ , deg	92.377(2)
Volume, \AA^3	829.40(13)
<i>Z</i>	1
$D_{\text{calcd.}}$, g cm^{-3}	1.53
$F(000)$, e	395
μ , mm^{-1}	0.6
θ range data collection, deg	1.97–25.00
Index ranges	$-9 \leq h \leq 9$, $-12 \leq k \leq 10$ $-12 \leq l \leq 12$
Reflections collected	4273
Independent reflections/ R_{int}	2898/0.0180
Refinement method	Full-matrix least-squares on F^2
Data/parameters	2898/241
Goodness of fit on F^2	1.059
$R_1(F)/wR_2(F^2)$ [$I > 2\sigma(I)$]	0.0363/0.0863
$R_1(F)/wR_2(F^2)$ (all data)	0.0416/0.0891
Largest diff. peak/hole, e \AA^{-3}	0.25/–0.34

Results and Discussion

IR and UV/Vis spectra

In the IR spectrum of polymer **1**, the moderate broad band at 3246 cm^{-1} which is attributed to the $\nu(\text{OH})$ stretching frequency suggests the presence of water molecules. The strong absorption bands at 1699 cm^{-1} is assigned to the stretching frequency $\nu(\text{C}=\text{O})$ indicating the existence of non-coordinated carbonyl groups [27]. The characteristic bands of the carbonyl

Table 2. Selected bond lengths (\AA) and bond angles (deg) for complex **1**^a.

Bond lengths (\AA)			
Co(1)–O(1W)	2.0741(15)	Co(1)–O(1)	2.1531(16)
Co(1)–O(2)	2.1111(14)		
Bond angles (deg)			
O(1)–Co(1)–O(1W)	92.09(6)	O(1)–Co(1)–O(1WA)	87.91(6)
O(1)–Co(1)–O(2)	85.95(6)	O(1)–Co(1)–O(2A)	94.05(6)
O(2)–Co(1)–O(1W)	88.73(6)	O(2)–Co(1)–O(1WA)	91.27(6)

^a Symmetry code A: $1-x, 1-y, 1-z$.

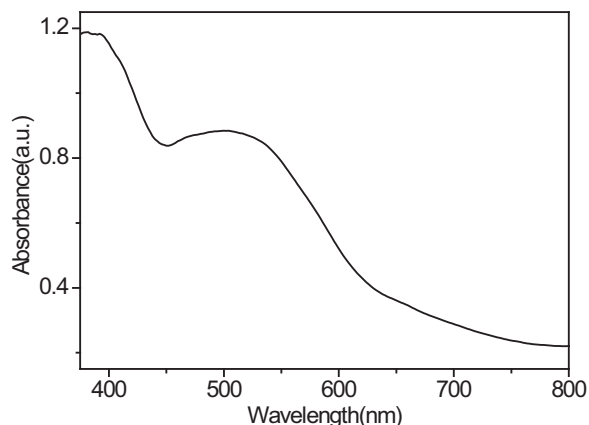


Fig. 1. The electronic spectrum of complex **1** in the solid state at room temperature.

groups are shown at 1541 cm^{-1} for antisymmetric stretching and at 1414 cm^{-1} for symmetric stretching. The separation value of 127 cm^{-1} indicates that the carbonyl groups of the Hdpa^- anion function in the unidentate coordination mode [12]. Two strong bands at 1219 and 1180 cm^{-1} are assigned as $\nu(\text{N-O})$ vibration of dpdo, which agrees well with those of relevant compounds [19, 23]. These results were finally confirmed by X-ray crystallography (see below).

As shown in Fig. 1, the electronic spectrum of the polymer **1** in the solid state displays two absorption peaks at 382 and 504 nm, which can be assigned to

the intraligand charge transfer and a parity-forbidden $d-d$ -type transition of Co(II) [12, 13, 17, 28].

Crystal and molecular structure

Single-crystal X-ray structural analysis has revealed that the structure of **1** exhibits a three-dimensional supramolecular framework based on polymeric chains, which are formed through the coordinative interactions between Co(II) cations and dpdo ligands. The compound crystallizes in the triclinic space group $P\bar{1}$, and the asymmetric unit consists of one Co(II) cation, one monoprotonated 2,2'-biphenyldicarboxylate (Hdpa^-), one half dpdo ligand and one coordinated water molecule. As shown in Fig. 2, the Co(1) atom lies on a crystallographic center of inversion in a distorted octahedron. The six oxygen donors comprise two monodentate carboxylate oxygen atoms O(2) and O(2A) from two Hdpa^- ligands, two atoms O(1) and O(1A) from two dpdo ligands, and a pair of oxygen atoms O(1W) and O(1WA) from two coordinated water molecules (symmetry code A: $1-x, 1-y, 1-z$). The Co–O distances are in the range of $2.0741(15)$ – $2.1531(15)\text{ \AA}$. Adjacent cobalt cations are linked by bridging dpdo ligands to generate a chain structure. The shortest Co...Co distance is 12.62 \AA within the chain. Moreover, a C–H... π interaction between the carbon atom C(8) and an adjacent pyridine ring [N(1)C(1)–C(5)] is found in the chain with a C...M separation of 3.83 \AA and a C–H...M

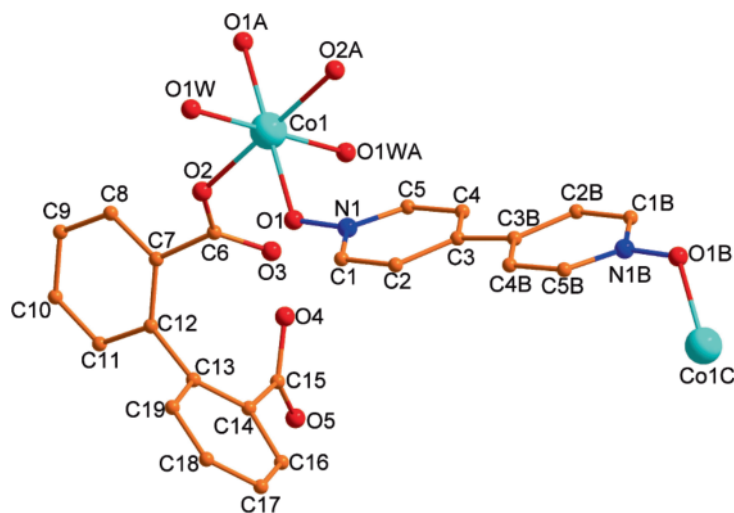


Fig. 2 (color online). The coordination environment of Co(II) in complex **1**. Hydrogen atoms and solvate water molecules are omitted for clarity (symmetry codes: A: $1-x, 1-y, 1-z$; B: $-x, -y, 1-z$; C: $-1+x, -1+y, z$).

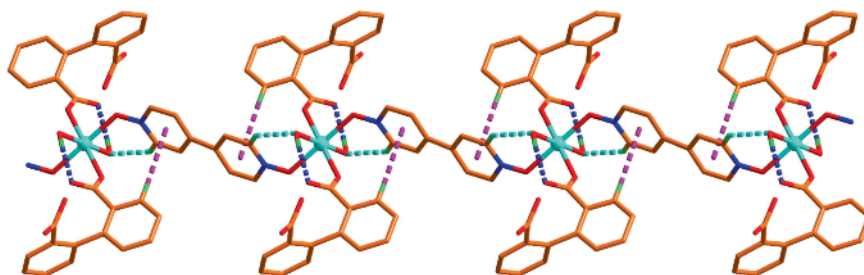


Fig. 3 (color online). Illustration of the chain in polymer **1** showing C-H $\cdots\pi$ interactions (pink) and C(5)-H(5A) \cdots O(1W) (turquoise) and O(1W)-H(1WD) \cdots O(3) (blue) hydrogen bonds in dashed lines.

Table 3. Hydrogen bonding interactions (\AA and deg) for **1**.

D-H \cdots A	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle(\text{DHA})$	Symmetry codes of atom A
O(1W)-H(1WC) \cdots O(5)	0.85	1.93	2.770(2)	168	$x, y, 1+z$
O(1W)-H(1WD) \cdots O(3)	0.85	1.87	2.695(2)	164	$1-x, 1-y, 1-z$
O(4)-H(4B) \cdots O(3)	0.82	1.77	2.583(2)	172	
C(1)-H(1A) \cdots O(1)	0.93	2.45	3.361(3)	165	$-x, 1-y, 1-z$
C(5)-H(5A) \cdots O(1W)	0.93	2.42	3.194(3)	140	$1-x, 1-y, 1-z$
C(17)-H(17A) \cdots O(4)	0.93	2.53	3.241(3)	134	$-1+x, y, z$
C(17)-H(17A) \cdots O(3)	0.93	2.52	3.179(3)	128	$-x, 1-y, -z$

angle of 169.1° . Two types of C(5)-H(5A) \cdots O(1W) and O(1W)-H(1WD) \cdots O(3) hydrogen bonds are also found in the chain, which play a role in stabilizing the network (Fig. 3, Table 3). Due to steric hindrance, each Hdpa $^-$ ligand adopts a twist conformation with the dihedral angle of the two phenyl rings at 84.6° , which agrees well with that in related complexes [15, 16].

Adjacent chains form a layer structure through the combination of C-H $\cdots\pi$ interactions and two types of C-H \cdots O hydrogen bonds (Fig. 4). The C-H $\cdots\pi$ interactions between the carbon atom C(4) and the adjacent benzene ring [C(7)-C(12)] have a C(4) \cdots M sep-

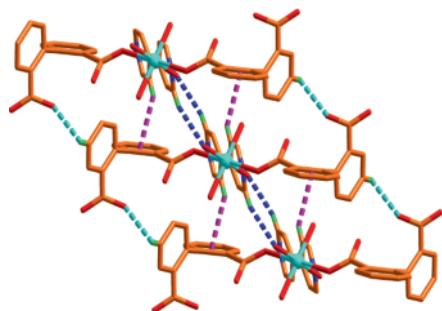


Fig. 4 (color online). A view of a sheet in the polymer **1** showing C-H $\cdots\pi$ interactions (pink) and C(1)-H(1A) \cdots O(1) (blue) and C(17)-H(17A) \cdots O(4) (turquoise) hydrogen bonds in dashed lines.

aration of 3.63 \AA and a C-H \cdots M angle of 140.3° . The C(1) and C(17) atoms of the Hdpa $^-$ ligand form C(1)-H(1A) \cdots O(1) and C(17)-H(17A) \cdots O(4) hydrogen bonds with O(1) and O(4) of dpdo and Hdpa $^-$ ligands, respectively. The layers are further connected into a three-dimensional network through multiform hydrogen bonding interactions. The O-H \cdots O interaction involving the O(1W) atom from the coordinated water molecule and the O(5) atom from the COOH

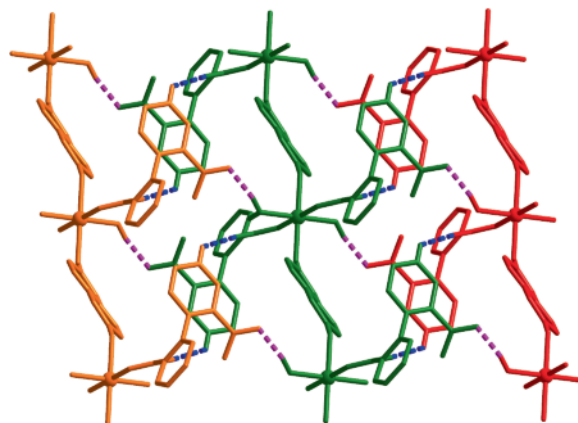


Fig. 5 (color online). The 3D supramolecular framework in the polymer **1** showing C(17)-H(17A) \cdots O(3) (pink) and O(1W)-H(1WC) \cdots O(5) (blue) hydrogen bonds in dashed lines.

group is characterized by an O(1W)⋯O(5) separation of 2.77 Å and an O–H⋯O angle of 168.4°. Another C–H⋯O interaction leads to the C(17)⋯O(3) separation of 3.18 Å with a C–H⋯O angle of 128.0° (Fig. 5). Although these hydrogen bonds are weak compared to the metal-oxygen coordinative bonds, it is suggested that these interactions are important in molecular packing.

Conclusions

In this paper, a polymer [Co(Hdpa)₂(dpdo)(H₂O)₂] (**1**) containing two organic components, dpdo (4,4'-bipyridine-*N,N'*-dioxide) and Hdpa[−] (protonated 2,2'-biphenyldicarboxylate), has been synthesized. Its

structure has been established by single-crystal X-ray diffraction analysis, and the compound has also been characterized by IR and UV/Vis spectroscopy, and elemental analysis. In the solid state, **1** exhibits a three-dimensional supramolecular framework based on chains that are formed by connecting Co(II) centers with dpdo ligands.

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