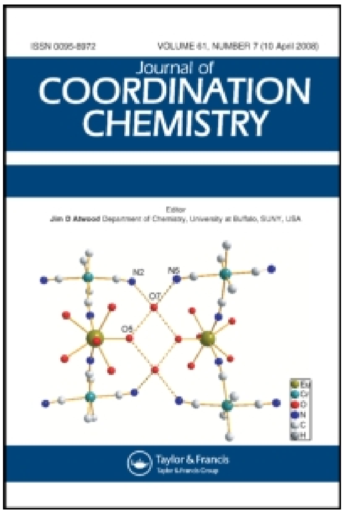

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A two-dimensional strong hydrogen-bond network constructed from a transition metal with a polycarboxylato ligand

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A two-dimensional strong hydrogen-bond network constructed from a transition metal with a polycarboxylato ligand

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The supramolecular complex with mixed-ligands $[Co_2(1,2,4,5\text{-btec})(2,2'\text{-bipy})_2(H_2O)_6] \cdot 2H_2O$ (1,2,4,5-btec = benzene-1,2,4,5-tetracarboxylic acid; 2,2′-bipy = 2,2′-bipyridine) was prepared and characterized by elemental analyses, IR spectra and X-ray single-crystal diffraction analysis. X-ray crystal structural analysis reveals that the compound belongs to the monoclinic system. $C_{30}H_{34}Co_2N_4O_{16}$, $P2_1/n$, $a = 12.2998(5)$ Å, $b = 7.5943(3)$ Å, $c = 17.9100(5)$ Å, $\alpha = 90.00°$, $\beta = 100.0790(3)°$, $\gamma = 90.00°$, $V = 1647.13(10)$ Å^3, $Z = 2$. The complex is dinuclear with two Co atoms linked by two O atoms from one 1,2,4,5-benzenetetracarboxylate. In the unit of the structure, the two bipys are in same plane, and the dihedral angle with the benzene ring is 64.1°. There exist strong hydrogen bonds between the carboxylate oxygen atoms and coordinated water in the plane and weak H-bonding between the carboxylate oxygen atoms and H–C in the aromatic ring perpendicular to the plane.

Keywords: 3D hydrogen-bonding network; Cobalt (II) complex; mixed ligands; polycaboxylato ligand; dihedral angle

1. Introduction

Design and synthesis of supramolecular coordination polymers have received much attention in recent years due to their intriguing structural features and potential applications in catalysis, ion-exchange, nonlinear optics, chemical absorption, electroconductivity and magnetism [1–8]. The vast majority of reported work is based on the use of polydentate ligands to bind to d-block transition metal ions to build novel coordination architectures by hydrogen bonding and π–π stacking interactions [9–11].

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1,2,4,5-benzenetetracarboxylate has attracted interest as a potential bridging ligand with a variety of connection modes with transition metal centers and abundant structural motifs [12–14]. The chelate ligand 2,2′-bipy usually inhibits expansion of the polymeric framework by "passivation" of metal sites *via* the N donors [15–16]. Some structures of coordination polymers constructed from btec and N-containing chelate ligands have been reported [17–22]. Here we report the preparation and crystal structure characterization of $[Co_2(1,2,4,5\text{-btec})(2,2'\text{-bipy})_2(H_2O)_6]\cdot 2H_2O$ **(1)**.

2. Experimental

2.1. *General procedures*

All reagents were purchased commercially and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Co is determined by ICP-AES analysis. The infrared spectra were recorded on an Alpha Centauri FT/IR spectrometer with KBr pellets in the 4000–500 cm^{-1} region.

2.2. *Synthesis of $[Co_2(1,2,4,5\text{-btec})(2,2'\text{-bipy})_2(H_2O)_6]\cdot 2H_2O$ (1)*

A 5 mL aqueous solution of $CoCl_2 \cdot 6H_2O$ (0.2379 g, 1 mmol) was slowly added to a 25 ml alcohol solution of 1,2,4,5-benzenetetracarboxylate (0.3272 g, 1.5 mmol) and 2,2′-pyridine (0.2342 g, 1.5 mmol); the pH was adjusted to 6.5 by addition of NaOH, with stirring at 100°C for 90 min. The mixture was cooled slowly to room temperature, and was filtered to give a pink solution. After a few days, pink crystals formed. Elemental analyses: Co 12.45%, C 44.55%, H 4.21%, N 6.93%; Found: Co 14.60%, C 44.50%, H 4.18%, N 6.87%. IR (KBr, cm^{-1}): 3422.13, 1602.42(C=O), 1556.47(C=O), 1487.90, 1442.90, 1379.84, 764.26.

2.3. *X-ray crystallography*

Structural measurement of (**1**) is performed on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation at 293 K, and the ω scan mode in the range of $2.48° < \theta < 27.48°$. Cell parameters were obtained by global refinement of the positions of all collected reflections. An empirical absorption correction was applied. The structure was solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL-97 program. All of the non-hydrogen atoms were refined anisotropically. Crystallographic details of the structure are summarized in table 1. Selected bond lengths and angles are given in table 2.

The CIF files of **1** have been deposited at the Cambridge Crystallographic Data Center and allocated the deposition numbers: CCDC 229723.

3. Results and discussion

As shown in figure 1(a), $Co(bipy)(H_2O)_3$ entities are linked by a 1,2,4,5-btec bridge ligand. Each Co atom is coordinated by two N atoms from 2,2′-pyridine, three aqua

Table 1. Crystal data and structure refinement for $[Co_2(1,2,4,5\text{-btec})(2,2'\text{-bipy})_2(H_2O)_6] \cdot 2H_2O$ **(1)**.

Empirical formula	$C_{30}H_{34}Co_2N_4O_{16}$
Formula weight	824.47
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	12.2998(5)
b (Å)	7.5943(3)
c (Å)	17.9100(5)
α (°)	90.00
β (°)	100.0790(10)
γ (°)	90.00
Volume (Å^3)	1647.13(10)
Z	2
Absorption coefficient (mm^{-1})	1.091
$F(000)$	848
Crystal size (mm^3)	$0.480 \times 0.126 \times 0.105$
θ range for data collection (°)	2.20 to 27.48
Limiting indices	$-15 \le h \le 15$, $-9 \le k \le 9$, $-23 \le l \le 23$
Reflections collected	7059
Independent reflections	3770 ($R_{\text{int}} = 0.0504$)
Data/restraints/parameters	3770/0/235
Goodness-of-fit on F^2	0.992
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0804$, $wR2 = 0.1049$

Table 2. Selected bond lengths (Å) and angles (°) for (**1**).

Bond lengths			
Co–OW(1)	2.076(2)	Co–N(1)	2.116(3)
Co–OW(2)	2.127(2)	Co–OW(3)	2.129(2)
Co–N(2)	2.136(3)	Co–O(1)	2.140(2)
O(1-)–C(14)	1.257(4)	O(2)–C(14)	1.262(4)
O(3)–C(15)	1.248(4)	O(4)–C(15)	1.245(4)
N(1)–C(1)	1.338(4)	N(1)–C(5)	1.346(4)
N(2)–C(10)	1.334(4)	N(2)–C(6)	1.346(4)
C(1)–C(2)	1.384(5)	C(2)–C(3)	1.363(6)
C(3)–C(4)	1.373(5)	C(4)–C(5)	1.390(4)
C(5)–C(6)	1.485(4)	C(6)–C(7)	1.387(5)
Bond angles			
OW(1)–Co–N(1)	95.63(10)	OW(1)–Co–OW(2)	175.19(8)
N(1)–Co–OW(2)	89.03(10)	OW(1)–Co–OW(3)	90.67(9)
N(1)–Co–OW(3)	170.43(10)	OW(2)–Co–OW(3)	84.55(8)
OW(1)–Co–N(2)	86.21(10)	N(1)–Co–N(2)	77.08(10)
OW(2)–Co–N(2)	93.70(9)	OW(3)–Co–N(2)	96.22(9)
OW(1)–Co–O(1)	88.09(9)	N1–Co–O(1)	93.54(9)
OW(2)–Co–O(1)	92.82(8)	OW(3)–Co–O(1)	93.86(8)
N(2)–Co–O(1)	168.46(9)	C(14)–O(1)–Co	126.78(19)
C(1)–N(1)–C(5)	118.3(3)	C(1)–N(1)–Co	125.5(2)
C(5)–N(1)–Co	116.2(2)	C(10)–N(2)–C(6)	118.4(3)
C(10)–N(2)–Co	126.1(2)	C(6)–N(2)–Co	115.5(2)
N(1)–C(1)–C(2)	122.4(4)	C(3)–C(2)–C(1)	119.0(3)
C(2)–C(3)–C(4)	119.6(3)	C(3)–C(4)–C(5)	118.9(4)
N(1)–C(5)–C(4)	121.7(3)	N(1)–C(5)–C(6)	115.6(3) .
C(4)–C(5)–C(6)	122.6(3)	N(2)–C(6)–C(7)	121.8(3)
N(2)–C(6)–C(5)	115.6(3)	C(7)–C(6)–C(5)	122.6(3)
C(6)–C(7)–C(8)	119.1(3)	C(9)–C(8)–C(7)	119.3(3)
C(8)–C(9)–C(10)	118.7(3)	N(2)–C(10)–C(9)	122.8(3)

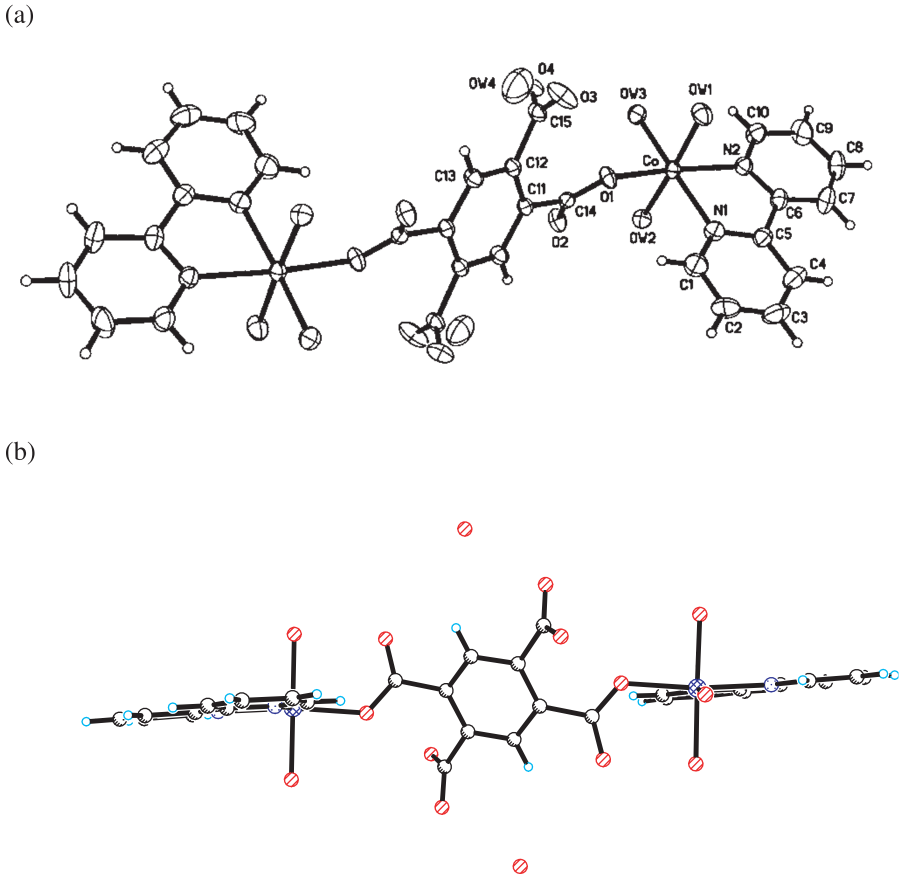
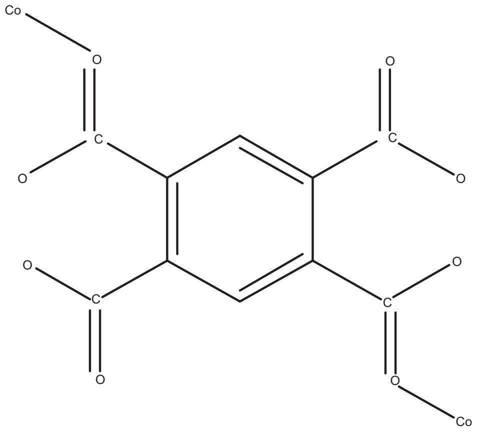


Figure 1. (a) ORTEP drawing (50% thermal) of molecular structure of (1), (b). Two bipys are in the same plane. The dihedral angle with the middle ring is 64.1°.

ligands and one O atom from the benzenetetractracarboxylate ligand. It has a distorted octahedron (Co–O(W1) = 2.076(2) Å; Co–O(W2) = 2.127(2) Å; Co–N(1) = 2.116(3) Å; Co–O(W3) = 2.129(2) Å; Co–N(2) = 2.136(3) Å; Co–O(1) = 2.140(2) Å).

The ligand 1,2,4,5-btec is centro-symmetrically bonded to two Co atoms, coordinated in a *bis* monodentate manner. So, 1,2,4,5-btec acts as a bidentate ligand (scheme 1), as observed previously [23]. In the unit structure of the compound, two bipys are in the same plane, and the dihedral angle with the aromatic rings is 64.1° (figure 1b).

There are multiple strong hydrogen bonds formed between coordinated water molecules and carboxyl oxygen atoms [O4 ⋯ Ow2, O3 ⋯ Ow3, O2 ⋯ Ow3, and O4 ⋯ Ow1], with lengths 2.702, 2.647, 2.664 and 2.732 Å, respectively. Therefore, the complex is extended to a 2D layer structure (figure 2). Weak H-bond interactions between the carboxylate oxygen atoms and C–H, extend the compound to a 3D framework (figure 3a). The details of the H-bonds are shown in (figure 3b). The solvent water molecules are all located in the 2D layers and have no interactions in the 3D direction.



Scheme 1. The coordination mode of btec in **1**.

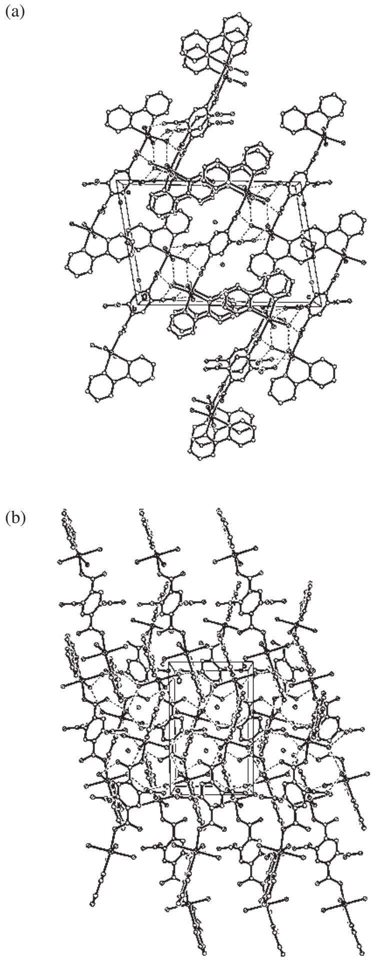


Figure 2. The view of the crystal packing down from b axis (a) and c axis (b).

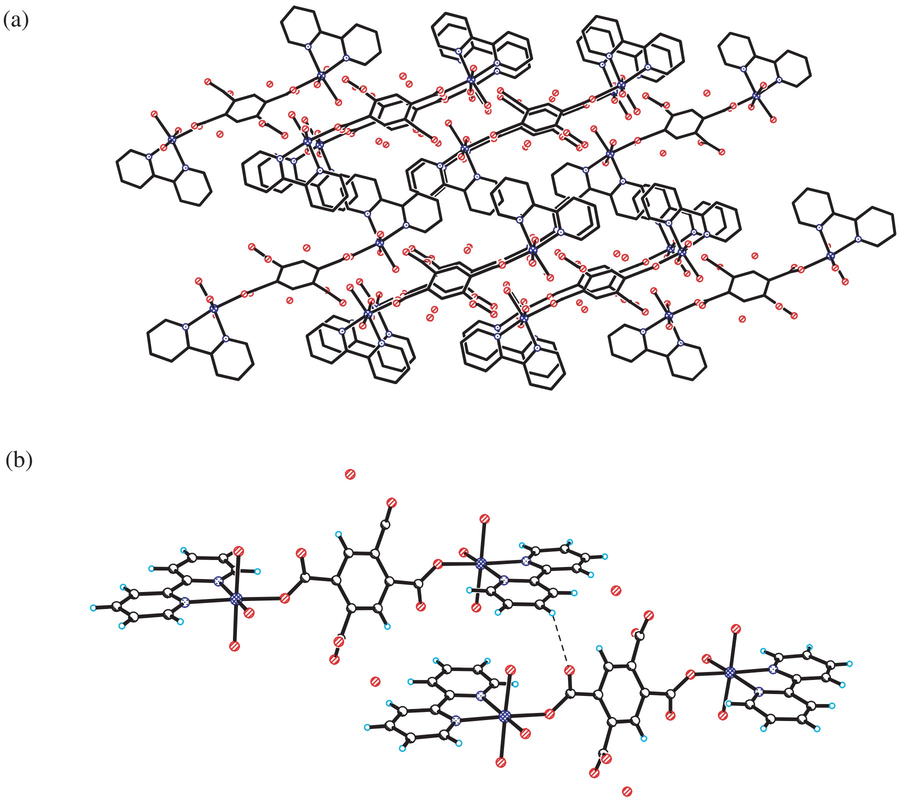


Figure 3. Molecular packing view down the b axis (a) and the H-bond detail (b).

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