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# A hydrogen-bonded 3D coordination network of $Co^{II}$ with 4-(*p*-benzoxy)-1,2,4-triazole: hydrothermal synthesis, characterization, crystal structure and emission property

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### Abstract

A six-coordinated monomeric  $Co^{II}$  complex,  $[Co(L)_2(H_2O)_4] \cdot 10H_2O(1)$ , where  $HL=4 \cdot (p-benzoxy) \cdot 1,2,4$ -triazole, has been synthesized and characterized by elemental analyses, IR, thermogravimetric analysis and X-ray diffraction technique. Structural analyses reveal that the  $Co^{II}$  center has a  $CoN_2O_4$  octahedral environment with four O atoms of coordinated water molecules constituting the equatorial plane and two N atoms of two distinct L ligands occupying the two axial sites in **1**. A striking structural feature of **1** resides in the formation of a threedimensional (3D) supramolecular architecture through intermolecular  $O-H \cdots O$  hydrogen-bonding interactions. Complex **1** displays strong blue emission in the solid state.

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Keywords: Hydrothermal synthesis; Cobalt(II) complex; 4-(p-benzoxy)-1,2,4-triazole; Crystal structure; Emission property

## 1. Introduction

Metallosupramolecular complexes with novel structures and properties assembling from transition metal junctions and bridging ligands have been rapidly developed due to their intriguing structural diversity and potential applications as functional materials [1–5]. However, the rational design on preparation of new materials for special applications is still at an early evolutionary stage with the current focus mainly on understanding the factors that determine crystal packing. During the passing decades, several types of forces, such as coordination bonding [6–11], versatile hydrogen bonding interactions [12–15],  $\pi$ – $\pi$  stacking [16,17] and electrostatic interactions [18] have been recognized and used in constructing extended networks. Up to now, the most important driving forces in crystal engineering are coordination bonding and hydrogen bonding interactions. Many classes of networks assembled from mono- or poly-nuclear metal complexes via hydrogen bonding interactions have been reported [19]. The unique strength, directionality, and complementarity of noncovalent hydrogen bonding play a central role in the creation of a variety of architectures for molecular selfassembly and recognition in chemical, physical and biological sciences [20–22]. Carboxylic derivatives are important members in hydrogen bonding coordination chemistry family due to their intriguing hydrophilic COO<sup>-</sup> group [23].

Polynuclear coordination compounds containing derivatives of 1,2,4-triazole have been of increasing interest during the last decade. A series of novel polynuclear metal complexes with 1,2,4-triazole ligands were reported by Carcia et al. [24]. Triazoles have played a notable role in the development of transition metal coordination chemistry because of their rich chemistry and variety of bonding modes: terminal, bridging and chelating coordination modes. On the other hand, several studies have dealt with the search for magneto-structural correlations for transition

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metal(II) compounds containing N1,N2-1,2,4-triazole bridges [25]. Combining all aspects stated above, thus, we anticipated that the incorporation of the triazole groups on the backbone of benzoic acid would lead to the novel complexes when treated with the metal ions. In this paper, we report the synthesis, characterization, spectra and of a mononuclear Co<sup>II</sup> complex with L ligand, [Co(L)<sub>2</sub>(H<sub>2</sub> O)<sub>4</sub>]·10H<sub>2</sub>O (1), where HL=4-(*p*-benzoxy)-1,2,4-triazole (Scheme 1), which features a three-dimensional network through intermolecular O–H···O hydrogen bonding interactions.

### 2. Experimental

### 2.1. Materials and general methods

All reagents for syntheses and analyses were of analytical grade. FT-IR spectra (KBr pellets) were taken on a FT-IR 170SX (Nicolet) spectrometer. C, H and N analyses were performed on a Perkin-Elmer 240C analyzer. Thermal stability (TG-DTA) studies were carried out on a Dupont thermal analyzer from room temperature to 600 °C. Emission spectra were taken on a Cary Eclipse Fluorescence Spectrophotometer.

### 2.2. Preparation of ligand

4-(*p*-benzoxy)-1,2,4-triazole (HL). HL was prepared from monoformylhydrazine, triethyl orthoformate and para aminobenzoic acid according to the similar method described by Bayer et al. [26]. Yield: 55%. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O):  $\delta$  11.3 (s, 1H), 8.6 (s, 2H), 8.2 (d, 2H), 7.5 (d, 2H).

## 2.3. Preparation of $[Co(L)_2(H_2O)_4] \cdot 10H_2O$

The title complex was prepared by reacting an aqueous solution of  $Co(NO_3)_2$  with 4-(*p*-benzoxy)-1,2,4-triazole (HL) in a 1:2 molar ratio. Suitable NaOH was added to this solution (pH 7) and it was stirred at room temperature for 3 h until a homogeneous solution was obtained. And then it was sealed in 20 ml acid digestion bomb at 140 °C for 3 days. Faint red block crystals were obtained by filtration and dried in air. The yield of the target complex is ca. 50% (based on Co). Anal. Calcd for  $C_{18}H_{40}CoN_6O_{18}$ : C, 31.43; H, 5.87; N, 12.23%. Found: C, 31.02; H, 5.44; N, 12.55%. IR (KBr pellet, cm<sup>-1</sup>) spectra: 3485(br)s, 3112s, 3018m, 3011w, 1919w, 1693m, 1605vs,1536vs, 1505m, 1474w,

1384vs, 1371vs, 1308s, 1248s, 1227m, 1209m, 1091s, 1012m, 979w, 966w, 864m, 784s, 693m.

# 2.4. Crystallographic data collection and structure determination

Single-crystal X-ray diffraction of **1** was performed on a BRUKER SMART 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo/K radiation ( $\lambda$ =0.71073 Å) by  $\varpi$  scan mode in the range of 3.15 <  $\theta$  < 25.02° at 293(2) K. All data were corrected by semi-empirical method using SADABS program. The program SAINT [27] was used for integration of the diffraction profiles.

The structure was solved by the direct methods using SHELXS program of the SHELXL-97 package and refined with SHELXL [28]. The Co<sup>II</sup> center was located from the *E*-map and other non-hydrogen atoms were discovered through subsequent successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on  $F^2$ . The hydrogen atoms of the ligand were placed in the geometrically calculated positions. Meanwhile, the hydrogen atoms of water molecules were first found in a difference electron density map, and then placed in the final refinement in the riding model approximation with displacement parameters derived from

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Crystal data and structure refinement summary for complex 1

	$[Co(H_2O)_4(L)_2] \cdot 10H_2O$
Empirical formula	C <sub>18</sub> H <sub>40</sub> CoN <sub>6</sub> O <sub>18</sub>
Formula weight	687.49
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions (Å, °)	
Α	25.872(7)
В	7.908(2)
С	16.906(4)
β	112.854(4)
Volume (Å <sup>3</sup> )	3187.1(14)
Ζ	4
$D_{\text{calcd}} (\text{g/cm}^3)$	1.433
$\mu (\mathrm{mm}^{-1})$	0.621
F (000)	1444
Range of $h, k, l$	-30/26, -5/9, -20/16
Reflections collected	5040
Unique/observed reflections	$2761(R_{int}=0.0252)/2379$
Max. and min. transmission	0.8859 and 0.8357
Data/restraints/parameters	2761/0/252
Goodness-of-fit on $F^2$	1.084
$R^{\rm a}$ and $R_{\rm w}^{\rm b}$	0.0279 and 0.0677
Largest diff. peak and hole $(e/Å^3)$	0.344 and $-0.272$

<sup>a</sup>  $R = \sum (||F_0| - F_C||) / \sum |F_0|.$ 

<sup>b</sup>  $wR = \left[\sum w(|F_0|^2 - |F_C|^2)^2 / \sum w(F_0^2)\right]^{1/2}.$ 

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

Co(1)-N(1)	2.154(2)	Co(1)-O(3W)	2.058(2)
Co(1)-O(2W)	2.079(2)	Co(1)-O(1W)	2.084(2)
O(3W)-Co(1)-	180.00	O(3W)-Co(1)-O(1W)	93.87(5)
O(2W)			
O(2W)-Co(1)-	86.13(5)	O(3W)-Co(1)-	93.87(5)
O(1W)		O(1W)#1	
O(2W)-Co(1)-	86.13(5)	O(1W)#1-Co(1)-	172.27(9)
O(1W)#1		O(1W)	
O(3W)-Co(1)-	89.72(4)	O(2W)-Co(1)-N(1)#1	90.28(4)
N(1)#1			
O(1W)-Co(1)-	91.88(6)	O(3)#1-Co(1)-N(1)#1	88.16(5)
N(1)#1			
O(3W)-Co(1)-N(1)	89.72(4)	O(2W)-Co(1)-N(1)	90.28(4)
O(3)-Co(1)-N(1)	88.16(5)	O(1W)#1-Co(1)-N(1)	91.88(6)
N(1)-Co(1)-N(1)#1	179.44(8)		

Symmetry codes: #1 2-x, y, 1.5-z.

the parent atoms to which they were bonded. The refinement converged to final R=0.0279, wR=0.0677, S=1.084,  $(\Delta/\sigma)_{max}=0.000$ . The ratio of minimum to maximum apparent transmission is 0.9433. Molecular graphics were drawn with the program package XP. Further crystallographic data and experimental details for structural analyses of 1 are summarized in Table 1, and the selected bond lengths and angles with their estimated standard deviations in Table 2. No. CCDC 231274.

### 3. Results and discussion

## 3.1. Description of the crystal structure of 1

The structure of **1** consists of neutral isolated  $[Co(L)_2(H_2O)_4]$  units and lattice water molecules. The ORTEP view of **1** with atom labeling is shown in Fig. 1a with lattice water molecules being omitted for clarity. The  $[Co(L)_2(H_2O)_4]$  unit possess crystallographically imposed  $C_2$  symmetry with the Co(1), O(2w) and O(3w) atoms on the two-fold axis. The coordination geometry around the Co<sup>II</sup> center could be described as an octahedron generated by O(1w)-O(2w)-O(3w)-O(1w)#1 on the basal plane, two nitrogen atoms of L on the axial sites, and the Co<sup>II</sup> ion sits at the center of the basal plane.

In this complex, ligand L adopts the unique Co–N coordination mode although another N atom of triazole and two O atoms of carboxylate group have strong coordination abilities to Co<sup>II</sup>. The Co–N and Co–O bond distances lie in the normal ranges of 2.154(1) and 2.058(2)–2.083(1) Å, respectively (Table 2). All crystallization water molecules are including in the asymmetric unit of **1**.

The related hydrogen-bonding geometry is given in Table 3. All values involved with hydrogen bonds fall in normal range. The intermolecular O–H···O hydrogen-bonding interactions (O(2w)–H(2wA)····O2#4 and O(3w)–H(3wA)····O2#3) from the coordinated H<sub>2</sub>O and –COO<sup>–</sup>



(c) (d)

Fig. 1. (a) ORTEP view with atom labeling (displacement ellipsoids drawn at 30% probability) of the structure of **1** (free water molecules omitted for clarity); (b) View of the  $[Co(L)_2(H_2O)_4]$  layer formed through O–H···O hydrogen-bonding interactions in **1** along *c*-axis; (c) View of the crystallization H<sub>2</sub>O layer formed through O–H···O hydrogen-bonding interactions in **1** along *c*-axis; (d) View of the 3D network formed through O–H···O hydrogen-bonding interactions in **1**.

Table 3 Hydrogen-bonding geometry (Å, °) for complex 1

D–H···A	D–H	Н…А	D····A	D−H…A
O1W-H1WB····O8W#5	0.73(3)	2.06(3)	2.772(2)	167(3)
O1W-H1WA…O4W	0.85(3)	1.83(3)	2.674(2)	170(3)
O2W-H2WA···O2#4	0.80(2)	1.92(2)	2.7089(17)	168(2)
O3W-H3WA····O2#3	0.81(2)	1.97(2)	2.7691(19)	168(2)
O4W-H4WA…O1#7	0.86(3)	1.83(3)	2.685(2)	172(3)
O4W-H4WB…O6W	0.86(3)	1.88(3)	2.736(3)	171(3)
O5W-H5WB···O4W#8	0.80(4)	1.99(4)	2.782(3)	169(3)
O5W-H5WA…O7W	0.82(4)	1.94(4)	2.762(3)	174(3)
O6W-H6WBO2#3	0.77(3)	2.00(3)	2.769(2)	178(3)
O6W-H6WA…O8W#6	0.86(4)	1.92(4)	2.768(2)	168(3)
O7W-H7WA…O6W	0.75(3)	2.02(3)	2.756(3)	168(3)
O7W-H7WB···O5W#2	0.93(3)	1.79(3)	2.708(3)	168(3)
O8W-H8WA…N2#9	0.78(3)	2.25(3)	2.975(2)	155(2)
O8W–H8WB…O1	0.85(3)	1.93(3)	2.771(2)	172(3)

Symmetry codes: #2 1.5-x, -0.5+y, 1.5-z; #3 1.5-x, 0.5-y, 1-z; #4 1.5-x, -0.5-y, 1-z; #5 0.5+x, -0.5-y, 0.5+z; #6 0.5+x, 0.5-y, 0.5+z; #7 1.5-x, 0.5+y, 1.5-z; #8 x, 1+y, z; #9 -0.5+x, -0.5+y, z.

group of  $[Co(L)_2(H_2O)_4]$  units leads to the formation of the two-dimensional network, parallel to the [010] and [101] directions, as illustrated in Fig. 1b. It is interesting that the resultant hydrogen-bonding eight-membered ring patterns can be regarded as quasi-quadrangle consisting of oxygen atoms. As we know, such hydrogen bonding eightmembered rings are very important for the synthetic investigation of clay-like and zeolite-like compounds [29]. Between two adjacent L, the center-to-center of aryl-aryl separation of 3.709 Å indicates that  $\pi$ - $\pi$  stacking interactions further stabilize the 2D hydrogen-bonding network. The type of  $\pi$ - $\pi$  stacking interactions may be of interest to the designing of advanced materials [30]. The extensive hydrogen bonds from the crystallization water molecules give rise to infinite 1D chains, which are parallel to the *b*-axis. The crystallization water chains are then connected by the hydrogen bonds (O(8w)-H(8wB)...O1 and O(4w)-H(4wa)····O1#7) between the crystallization water molecules and O(1) atoms of the -COO<sup>-</sup> group to construct infinite layers, which are also parallel to the [010] and [101] directions, as shown in Fig. 1c. Likewise, the hydrogen bonding 12-membered rings can be nearly regarded as hexagon and shared O-H···O hydrogen bonds. The adjacent  $[Co(L^1)_2(H_2O)_4]$  and crystallization water layers are linked by the hydrogen bonds between the crystallization water molecules and  $-COO^-$  group along the *c*-axis to form an infinite 3D framework, as plotted in Fig. 1d. Therefore, the Co<sup>II</sup> complex and lattice water layers, which are parallel to each other, pack alternately in the units.

### 3.2. Spectral characterization and thermal properties of 1

The IR spectrum of the title complex exhibits characteristic bands due to the ligand and lattice water vibrations  $(\nu_{O-H}, \nu_{Ar-H}, \nu_{C=N} \text{ and } \nu_{C=O} \text{ at } 3485, 3112-3011, 1693 \text{ and} 1605 \text{ cm}^{-1}$ , respectively). The absorption bands in



Fig. 2. Fluorescent emission spectrum of **1** in the solid state ( $\lambda_{ex}$ =332 nm).

the  $1400-1600 \text{ cm}^{-1}$  region arise from the skeletal vibrations of the aromatic rings of the ligand.

The thermal behaviour of the compound was studied from 30 to 600 °C. The TG–DTA curve indicates that the compound experiences two of weight-loss. It begins to lose water molecules very slowly at 60 °C and ends at about 190 °C, which probably contribute to the coordination water molecules having much stronger bonded energy than the free ones and leading to higher lattice energy. The beginning loss of 4-(*p*-benzoxy)-1,2,4-triazole is at the temperature of 490 °C and ends at a higher temperature of 580 °C. The residue is CoO and will be decomposed at high temperature.

#### 3.3. Emission property of 1

Complex 1 exhibits significant blue fluorescent emission. As shown in Fig. 2, the emission spectrum of 1 is two emission bands with the broad emission bands in the UV-vis region. The emission bands of 1 reveal hypsochromic absorption and significant enhancement of fluorescent intensities comparing with those of free HL with emission maxima ( $\lambda_{max}$ ) 491.04 and 524.02 nm ( $\lambda_{ex}$ =332 nm), respectively. The emissions of 1 can be assigned as  $\pi$ - $\pi$ \* transitions of the ligand. Generally, the rigidity of the ligand increases more in complex than that in its salt, so the enhanced fluorescence efficiency of the complex is attributed to the more rigidity of the ligand coordination to Co<sup>II</sup> ion that effectively reduces the loss of energy. The shift of the emission is complicated.

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