

One-Pot Synthesis, Crystal Structures and Thermal Properties of Two Three-Dimensional Cobalt(II) Complexes

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Two cobalt(II) compounds $[\text{Co}(2,2'\text{-bipy})(\text{H}_2\text{O})_2(\text{SO}_4)]_n$ (**1**) and $[\text{Co}_2(2,2'\text{-bipy})_2(\text{btec})(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}$ (**2**) (2,2'-bipy = 2,2'-bipyridine, H_4btec = 1,2,4,5-benzenetetracarboxylic acid), have been simultaneously synthesized by a one-pot slow solvent evaporation reaction. Their structures were determined by single-crystal X-ray diffraction and further characterized by X-ray powder diffraction (XRPD), IR, elemental and thermogravimetric analysis (TGA). The structural analysis reveals that compound **1** exhibits an infinite 1D chain structure with the octahedral Co(II) centers bridging by the tetrahedral $\mu_2\text{-SO}_4^{2-}$ ligands, while compound **2** possesses a dinuclear $\text{Co}_2(2,2'\text{-bipy})_2(\text{btec})(\text{H}_2\text{O})_6$ unit and the two adjacent octahedral Co(II) ions are linked by the bimonodentately coordinated btec ligand. Additionally, compound **2** exhibits blue fluorescent emission in the solid state at room temperature.

Key Words : Cobalt (II) complexes, One-pot synthesis, Crystal structure, Thermal properties, Supramolecular

Introduction

The design and synthesis of supramolecular polymers have attracted extensive attention owing to their potential as functional materials and intriguing topologies.¹⁻⁹ It is widely acknowledged that the coordinative bonding is the primary interaction to sustain the network, while supramolecular interactions, such as hydrogen bonding, π - π stacking interactions and Van der Waals forces are also believed to play important roles.¹⁰⁻¹⁷ To date, a variety of supramolecular polymers with complicated architectures and interesting properties based on different bridging ligands especially aromatic polycarboxylate ligands have been synthesized successfully.¹⁸⁻²⁴ Among these ligands, H_4btec is especially of interest for the construction of novel supramolecular polymers thanks to its following interesting characteristics:^{14,25-28} (i) it has four carboxyl groups which can be fully or partially deprotonated, inducing rich coordination modes and allowing interesting structures with higher dimensions; (ii) it can act not only as hydrogen bond donors but also as hydrogen bond acceptors, owing to the number of deprotonated carboxyl groups and (iii) some of the carboxyl groups can be tilted from the phenyl ring plane upon coordination to metal ions, thus it may connect metal ions in different directions. Therefore, it is regarded as a good candidate of bridging ligands to construct different kinds of polymeric structures. Furthermore, the introduction of another kind of aromatic N-containing chelating bidentate ligand such as 2,2'-bipyridine or 1,10-phenanthroline is also important in the metal-btec system which may provide potential supramolecular recognition sites for π - π stacking interactions to form interesting structures.^{11,19,29,30}

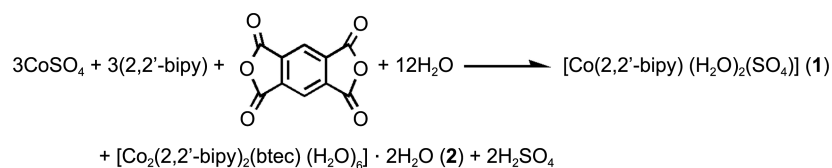
On the other hand, cobalt compounds have attracted extensive interest in recent years owing to their intriguing

structures and biomedical properties.^{18,31-34} On the basis of the aforementioned points, we have attempted to synthesize new cobalt supramolecular complexes with mixed ligands containing H_4btec and 2,2'-bipy. In this paper, we report the synthesis, structure, and thermal properties of two 3D cobalt(II) compounds $[\text{Co}(2,2'\text{-bipy})(\text{H}_2\text{O})_2(\text{SO}_4)]_n$ (**1**) and $[\text{Co}_2(2,2'\text{-bipy})_2(\text{btec})(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}$ (**2**).

Experimental Section

Materials and Methods. All reagents were purchased commercially. Elemental analyses (C, H and N) were performed using a vario EL cube CHNS/O elemental analyzer. FT/IR spectra were recorded in the 4000-400 cm^{-1} regions on a Nicolet-Avatar 370 infrared spectroscopy, using KBr pellets. XRPD patterns were recorded on a Shimadzu D/MAX-3BX diffractometer with $\text{Cu-K}\alpha$ radiation. The simulation of XRPD spectrum was carried out with the Mercury software. TGA was performed on a NETZSCH equipment in air with a heating rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$. Fluorescence spectrum was recorded with a Horiba FluoroMax-4 spectrofluorometer at room temperature.

Synthesis of Compounds 1 and 2. A dimethylformamide solution (10 mL) containing pyromellitic dianhydride (0.055 g, 0.25 mmol) and 2,2'-bipy (0.117 g, 0.75 mmol) was added to an aqueous solution (10 mL) of $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (0.070 g, 0.25 mmol), orange-yellow color was observed immediately. Then the mixture was stirred for 30 minutes and filtered. The filtrate was allowed to store at room temperature. After two months of slow evaporation, a few red crystals with different shapes were obtained, **1** needle and **2** lump. The obviously different physical shapes complexes were separated by hand picking, then washed with distilled water and dried in the air. Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_6\text{S}\text{Co}$: C, 34.59; H, 3.48; N, 8.07.



Scheme 1. The possible chemical reaction of compounds **1** and **2**.

Found: C, 34.27; H, 3.54; N, 8.32%. IR (KBr, cm^{-1}) 3595 m, 3543 m, 3503 m, 3443 m, 3370 m, 1636 s, 1399 m, 1109 m, 767 w, 614 m. Anal. Calcd. for $\text{C}_{30}\text{H}_{34}\text{N}_4\text{O}_{16}\text{Co}_2$: C, 43.70; H, 4.16; N, 6.80. Found: C, 43.77; H, 4.10; N, 6.78%. IR (KBr, cm^{-1}) 3593 m, 3376 m, 3190 m, 3074 s, 1674 w, 1547 s, 1378 s, 1320 m, 1169 m, 1135 m, 1019 m, 915 s, 810 s, 763 s, 728 w, 642 m, 524 m, 443 m.

X-ray Data Collection and Structure Refinement. Suitable single crystals with dimensions of $0.16 \times 0.12 \times 0.10 \text{ mm}^3$ for **1** and $0.32 \times 0.26 \times 0.25 \text{ mm}^3$ for **2** were selected for single-crystal X-ray diffraction analysis. Data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) in the ω scanning mode at 293(2) K for **1** and 273(2) K for **2**. The structures were solved by direct methods using SHELXS-97³⁵ and refined by full-matrix least-squares methods against F^2 (SHELXL-97).³⁶ All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located geometrically and refined isotropically. The crystal data and structure refinement of compounds **1** and **2** were summarized in Table S1. Selected bond lengths and angles of compounds **1** and **2** were listed in Table S2. Crystallographic data in cif format have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 797095 for **1**, CCDC 802071 for **2**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Results and Discussion

Synthesis and Characterization. Compounds **1** and **2** were synthesized by a slow solvent evaporation reaction of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, pyromellitic dianhydride and 2,2'-bipy ligand at a molar ratio of 1:1:3. The possible chemical reaction of compounds **1** and **2** is shown in Scheme 1. Originally, we tried to synthesize tetracarboxylate cobalt(II) complexes by the hydrolytic ring opening reactions of pyromellitic dianhydride. Interestingly, we report here a one-pot synthesis in which two complexes are simultaneously formed, and this phenomenon is relatively rare in synthetic chemistry.³⁷⁻⁴⁰ Compound **1**, using a similar method with 5-hydroxyisophthalic acid instead of pyromellitic dianhydride, has been reported by Li *et al.*⁴¹ However, no the corresponding 5-hydroxyisophthalate cobalt(II) complex was obtained. Therefore, we think that H_4btcc has a stronger coordination ability than 5-hydroxyisophthalic acid to Co(II) ion. The hydrolytic ring opening reactions of pyromellitic dianhydride give H_4btcc under room temperature, which further aggregates

with cobalt(II) ions to produce compound **2**. It has also been reported by Qi *et al.* using a different synthetic approach with a higher R-value than ours.⁴² Therefore, only the structure of compound **1** is described in detail in the paper.

Complexes **1** and **2** are stable in air, and almost insoluble in common solvents, such as water, methanol, alcohol and acetonitrile. The simulated and experimental XRPD patterns of compounds **1** and **2**, obtained at room temperature, are shown in Figure 1. Their peak positions are in good consistency with each other, indicating the phase purity of the as-synthesized samples. The IR spectra diagram of **1** and **2** are shown in Figure S1. The IR spectra of the two complexes with a broad band centered at *ca.* 3000-3600 cm^{-1} , which is attributed to the O-H stretching vibration modes of water molecules.⁴³ The bands at 1399 and 767 cm^{-1} for **1**,

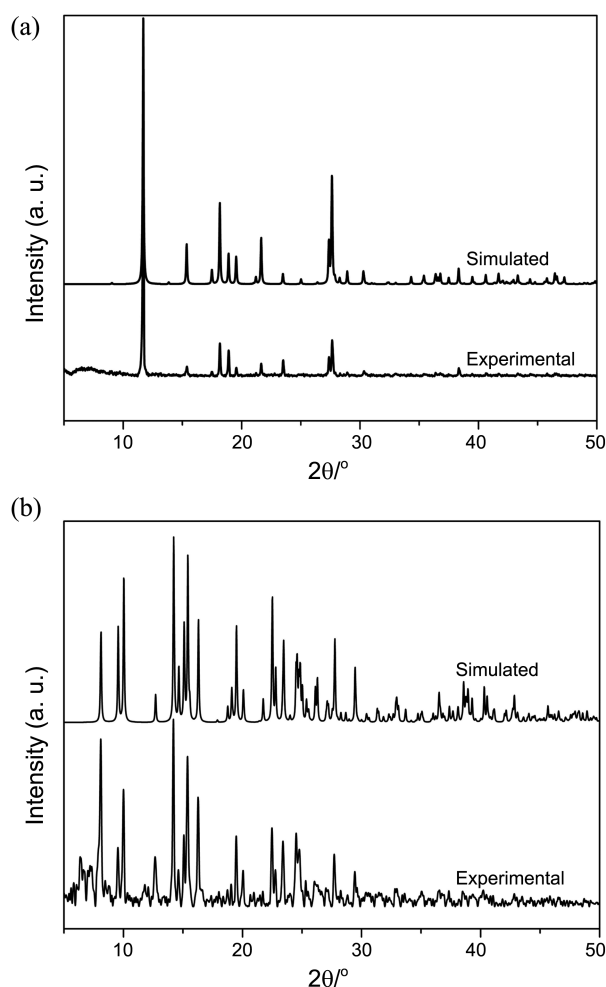


Figure 1. (a) The XRPD pattern of compound **1**. (b) The XRPD pattern of compound **2**.

and 1320, 1169, 763, 728 cm^{-1} for **2**, respectively, which are attributed to the characteristic peaks of 2,2'-bipy (similar to the peaks in free 2,2'-bipy in Figure S1). Compound **1** that exhibited two medium peaks at 1399 and 614 cm^{-1} are attributed to the stretching of the coordination SO_4^{2-} anions, which is consistent with that of free SO_4^{2-} in sample $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (Figure S1). In complex **2**, there is no absorption peak between 1730 and 1690 cm^{-1} , indicates that all the carboxyl groups are deprotonated.⁴⁴ The difference value ($\Delta\nu$) of $\nu_{\text{as}}(\text{COO}^-)$ (1547 cm^{-1}) and $\nu_{\text{s}}(\text{COO}^-)$ (1378 cm^{-1}) is 169 cm^{-1} , which shows that the carboxylate groups coordinate to the Co(II) ions in monodentate mode.⁴⁵

TGA of complexes **1** and **2** were carried out in air with a heating rate of 10 $^\circ\text{C} \cdot \text{min}^{-1}$. As shown in Figure 2, the TG diagram of **1** shows that the decomposition of the mixed ligands complex undergoes three stages. The first weight-loss, 10.84%, was in the range of 108–200 $^\circ\text{C}$ with a peak at 166 $^\circ\text{C}$, corresponding to the loss of two water molecules (calc. 10.38%). The residue at the first stage was found to may be $[\text{Co}(2,2'\text{-bipy})(\text{SO}_4)]_n$. The second weight-loss (45.09%) was in the range of 300–495 $^\circ\text{C}$, attributed to the loss of coordinated 2,2'-bipy ligand (calc. 44.96%). The third stage, which occurred in the range of 500–800 $^\circ\text{C}$, the weight-loss (22.30%) was coincided with the loss of a SO_3 gas molecule (calc. 23.05%). After decomposition of **1** at high temperature, the weight of the residue (20.85%) is responded to cobalt oxide (calc. 21.60%). The TG curve of **2** exhibits two continuous weight loss stages in the temperature range of 30–570 $^\circ\text{C}$. The first weight-loss, 17.52%, was in the range of 57–200 $^\circ\text{C}$, corresponding to the loss of two lattice water and six coordination water molecules (calc. 17.47%). The second weight-loss (61.94%) was in the range of 240–400 $^\circ\text{C}$, which was attributed to the loss of coordinated 2,2'-bipy and btec ligands (calc. 62.34%). The final residue, estimated as dicobalt trioxide, has the observed mass 20.66% against the theoretical value of 20.14%.

Crystal Structure of Complex 1. The X-ray single crystal structure determination reveals that compound **1** exists as a neutral 1D infinite chain with a basic $[\text{Co}(2,2'\text{-bipy})(\text{H}_2\text{O})_2-$

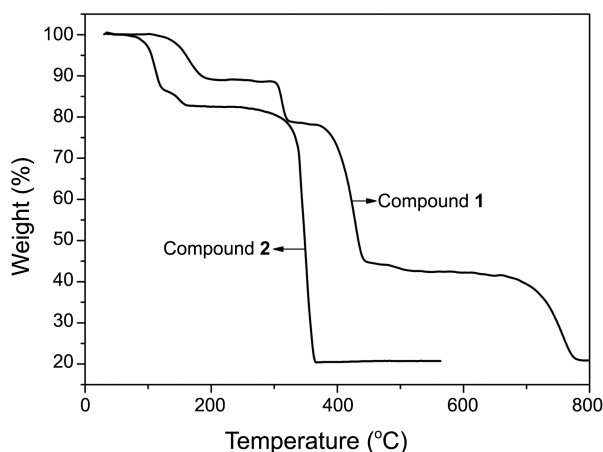


Figure 2. Thermogravimetric analysis (TGA) diagrams of compounds **1** and **2**.

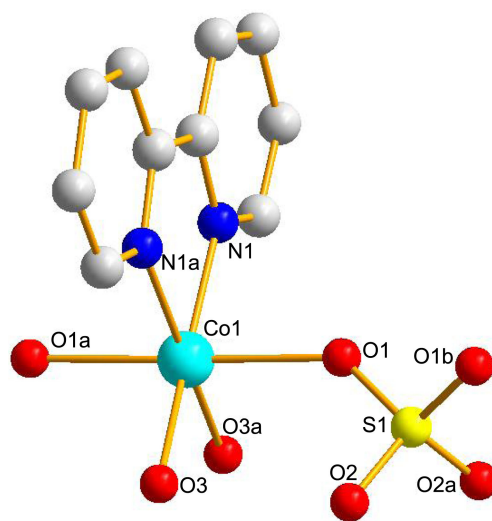


Figure 3. A monomer fragment of the 1D chain with the atomic labeling scheme in **1** (H atoms have been omitted for clarity).

(SO_4) unit (Figure 3). Each Co(II) ion adopts the coordination geometry of $\{\text{CoN}_2\text{O}_4\}$, which was defined by two nitrogen atoms (N1, N1a) from one 2,2'-bipy molecule, two *cis*-oxygen atoms (O3, O3a) from two water molecules and two *trans*-oxygen atoms (O1, O1a) from two μ_2 - SO_4^{2-} anions. In each octahedral Co(II) unit, N1, N1a, O3 and O3a form the equatorial plane and the axial positions are occupied by O1 and O1a. The axial Co-O distance (2.1691 Å) is *ca.* 0.0768 Å longer than the equatorial Co-O bands, which indicates that the Co(II) ion adopts an axially elongated octahedral geometry.

The geometry sulfate ion is a distorted tetrahedral. The S-O bond lengths of the coordinated oxygen atoms [1.4748(11) Å] are shorter than those of the uncoordinated oxygen atoms [1.4757(12) Å]. A distortion of the sulfate tetrahedral is also shown by the O-S-O bond angles which are between 108.89(7) and 110.14(8) $^\circ$. Sulfate anions in **1** are acting as μ_2 -bridging ligands by two oxygen atoms connected with two cobalt centers, forming a -Co-O-SO₂-O-Co- 1D chain along *b* axis, as shown in Figure 4(a). The individual chain contains octahedral $[\text{CoN}_2\text{O}_4]$ and tetrahedral $[\text{SO}_4]$ are joined by common vertices. Within a linear chain, the shortest Co...Co distance is 6.607 Å.

It is worth noting that each 2,2'-bipy ligand in a mono-chain is inserted into the interspaces of the closest two 2,2'-bipy ligands of the other mono-chain, generating a novel double 1D chain structures. These double 1D chains are parallel to each other along the *a* axis, as shown in Figure 4(b). The interdigitation structures of 2,2'-bipy ligands in **1** result in the formation of a 2D supramolecular layer structure. The shortest distance between two 2,2'-bipy rings is 3.2874 Å, showing that there are π - π stacking interactions between the planar 2,2'-bipy ligands in the neighboring layers. There are hydrogen bonds involving 2,2'-bipy ligands, sulfate anions and coordinated water molecules. The neighboring polymeric chains possess strong interchain H-bonding interactions between the coordinated water O(W) mole-

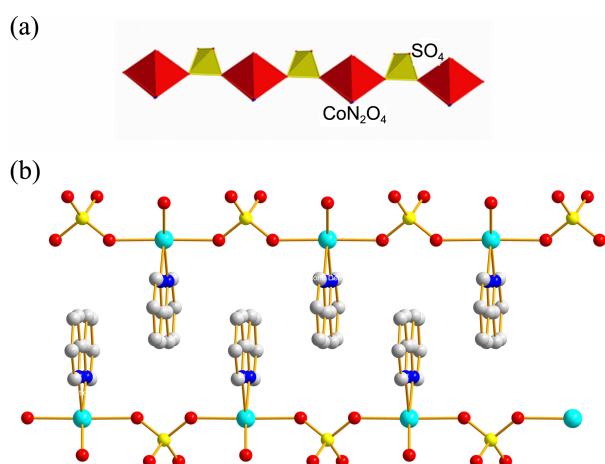


Figure 4. (a) Strands of CoN_2O_4 octahedra and SO_4 tetrahedra forming wire like chains in **1**. (b) The double one-dimensional chains structure of **1**.

cules and the uncoordinated O(2) atoms from sulfates [$\text{O}(3)\text{--H}(3\text{A})\cdots\text{O}(2) = 2.6747(18) \text{ \AA}$, $168(2)^\circ$; $\text{O}(3)\text{--H}(3\text{B})\cdots\text{O}(2)\#5 = 2.7276(17) \text{ \AA}$, $166(3)^\circ$; symmetry codes: #5 $x, -y, z-1/2$]. Through the interchain hydrogen bonds, the 2D supramolecular layers are interlinked to form 3D supramolecular framework. In addition, weak hydrogen bonds also exist between the neighboring layers [$\text{C}(4)\text{--H}(4)\cdots\text{O}(2)\#3 = 3.409(2) \text{ \AA}$, 147.3° ; $\text{C}(2)\text{--H}(2)\cdots\text{O}(1)\#4 = 3.370(2) \text{ \AA}$, 152.1° ; symmetry codes: #3 $x+1/2, -y+1/2, z-1/2$; #4 $x, -y+1, z-1/2$].

Fluorescence Spectroscopy of Complex 2. The solid state luminescence property of **2** was investigated at room temperature and the result is provided in Figure 5. It can be observed that the compound **2** exhibits blue fluorescence with two emission bands at 435 and 466 nm under excitation of 320 nm. According to the reported literatures, the free H_4btcc and 2,2'-bipy exhibit fluorescent emission peaks at 342 nm ($\lambda_{\text{ex}} = 308 \text{ nm}$)⁴⁶ and 365 nm ($\lambda_{\text{ex}} = 352 \text{ nm}$),⁴⁷ respectively. Comparing with the emission of free H_4btcc and 2,2'-bipy ligands, the emission peaks at 435 and 466 nm

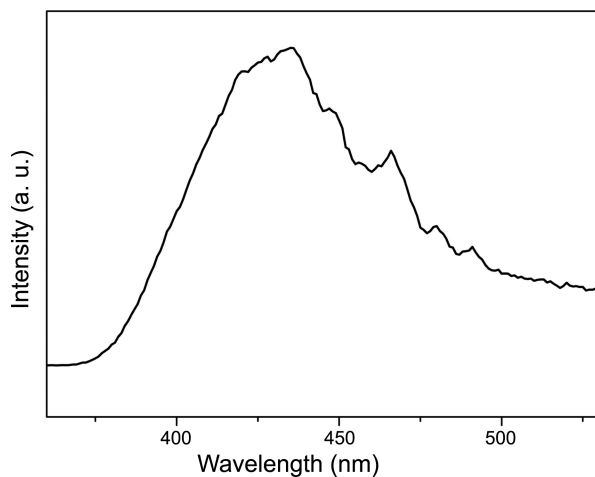


Figure 5. Fluorescence spectrum for complex **2** in the solid state at room temperature ($\lambda_{\text{ex}} = 320 \text{ nm}$).

are tentatively attributed to the emission of ligand-to-metal charge transfer (LMCT). Compound **2** may be used as a potential photoactive material because it is highly thermally stable and insoluble in common polar and nonpolar solvents.

Conclusion

In conclusion, two cobalt(II) supramolecular complexes have been simultaneously synthesized by a one-pot solvent evaporation reaction of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 2,2'-bipy and pyromellitic dianhydride in a water-dimethylformamide mixed solvent system. Complex **1** exhibits a 1D linear chain structure, while complex **2** displays a neutral dinuclear structure. The differences are attributed to the different bridging ligands in **1** and **2**. In addition, compounds **1** and **2** extend their structures to 3D supramolecular framework through the π - π stacking and hydrogen bonding interactions. This work illustrates again that the combination of coordination covalent and noncovalent bonds is an important tool to construct interesting supramolecular frameworks.

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