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

Bo Tao, Wen Lei, Feiran Cheng, and Hua Xia*

Faculty of Material Science and Chemistry Engineering, China University of Geosciences, Wuhan 430074, China

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Two cobalt(II) compounds [Co(2,2'-bipy)(H$_2$O)$_2$(SO$_4$)$_2$]$_n$(1) and [Co$_2$(2,2'-bipy)$_2$(btec)(H$_2$O)$_6$]·2H$_2$O (2) (2,2'-bipy = 2,2'-bipyridine, H$_2$btec = 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 μ$_2$-SO$_4$$^-$ ligands, while compound 2 possesses a dinuclear Co$_2$(2,2'-bipy)$_2$(btec)(H$_2$O)$_6$ unit and the two adjacent octahedral Co(II) ions are linked by the bismonodentately 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 structures and biomedical properties. On the basis of the aforementioned points, we have attempted to synthesize new cobalt supramolecular complexes with mixed ligands containing H$_2$btec and 2,2'-bipy. In this paper, we report the synthesis, structure, and thermal properties of two 3D cobalt(II) compounds [Co(2,2'-bipy)(H$_2$O)$_2$(SO$_4$)$_2$]$_n$(1) and [Co$_2$(2,2'-bipy)$_2$(btec)(H$_2$O)$_6$]·2H$_2$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 CHN/S/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 Cu-Kα 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 °C·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 CoSO$_4$·7H$_2$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.

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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 C\(_{30}\)H\(_{34}\)N\(_4\)O\(_{16}\)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 × 0.12 × 0.10 mm\(^3\) for 1 and 0.32 × 0.26 × 0.25 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\(_\alpha\) radiation (\(\lambda = 0.71073\) Å) in the \(\omega\) scanning mode at 293(2) K for 1 and 273(2) K for 2. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares methods against F\(^2\) (SHELXL-97). 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 CoSO\(_4\)·7H\(_2\)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\(_4\)btec has a stronger coordination ability than 5-hydroxyisophthalic acid to Co(II) ion. The hydrolytic ring opening reactions of pyromellitic dianhydride give H\(_2\)btec 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.

Compounds 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,
and 1320, 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\(^4\) anions, which is consistent with that of free SO\(^4\) in sample CoSO\(_4\)-7H\(_2\)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 °C\(\text{min}^{-1}\). 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 °C with a peak at 166 °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 °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 °C, the weight-loss (22.30%) was coincided with the loss of a SO\(_4\) 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 °C. The first weight-loss, 17.52%, was in the range of 57-200 °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 °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 \([\text{Co}(2,2’\text{-bipy})(\text{H}_2\text{O})_2]\)\(-\mu_2\text{-oxygen atoms (O3, O3a)}\) from two water molecules and two \(\text{trans}\)-oxygen atoms (O1, O1a) from two \(\mu_2\text{-SO}_4\) 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 bonds, 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)°. Sulfate anions in 1 are acting as \(\mu_2\)-bridging ligands by two oxygen atoms connected with two cobalt centers, forming a -Co-O-SO\(_4\)-Co- 1D chain along \(b\) axis, as shown in Figure 4(a). The individual chain contains octahedral [CoN\(_4\)O\(_4\)] and tetrahedral [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 2. Thermogravimetric analysis (TGA) diagrams of compounds 1 and 2.](image-url)

![Figure 3. A monomer fragment of the 1D chain with the atomic labeling scheme in 1 (H atoms have been omitted for clarity).](image-url)
respectively. Comparing with the emission of free H\[O(3)\]cules and the uncoordinated O(2) atoms from sulfates [O(3)–H(3A)–O(2) = 2.6747(18) Å, 168(2)°; O(3)–H(3B) –O(2)#5 = 2.7276(17) Å, 166(3)°; 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 [C(4)–H(4)–O(2)#3 = 3.409(2) Å, 147.3°; C(2)–H(2)–O(1)#4 = 3.370(2) Å, 152.1°; symmetry codes: #3 x+1/2, –y+1/2, z–1/2; #4 x, –y+1, 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 [C(4)–H(4)–O(2)#3 = 3.409(2) Å, 147.3°; C(2)–H(2)–O(1)#4 = 3.370(2) Å, 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 342 nm. According to the reported literatures, the free H\[btec\] and 2,2′-bipy exhibit fluorescent emission peaks at 342 nm (\(\lambda_{ex} = 308\) nm)\(^{46}\) and 365 nm (\(\lambda_{ex} = 352\) nm)\(^{47}\) respectively. Comparing with the emission of free H\[btec\] and 2,2′-bipy ligands, the emission peaks at 435 and 466 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) supramolecualr complexes have been simultaneously synthesized by a one-pot solvent evaporation reaction of CoSO\(_4\)-7H\(_2\)O, 2,2′-bipy and pyromellitic dianhydride in a water-dimethylformamide mixed solvent system. Complex 1 exhibits a 1D linear 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 \(\pi-\pi\) 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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**References**

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