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One-Dimensional Coordination Polymers of Cobalt with 4,4′-Bipyridine: Syntheses and Structures

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Several new one-dimensional coordination polymers were obtained by reactions of different simple cobalt salts with 4,4′-bipyridine. $Co(SO_4)(H_2O)_3(4,4'\text{-bipy})\cdot 2H_2O$ (**1**) was obtained by reacting $CoSO_4$ with 4,4′-bipy in a water/ethanol solvent system: hexagonal, $P6_5$, $a = 11.435(2)$ Å, $c = 20.886(4)$ Å, $Z = 6$. $CoCl_2(DMSO)_2(4,4'\text{-bipy})$ (**2**) was crystallized from the reaction of an aqueous solution of $CoCl_2$ with a DMSO solution of 4,4′-bipy: orthorhombic, *Pbcn*, $a = 11.470(2)$ Å, $b = 11.390(2)$ Å, $c = 14.753(1)$ Å, $Z = 4$. Reaction of $Co(CH_3COO)_2$ with 4,4′-bipy in water/acetonitrile under hydrothermal conditions yielded $Co(CH_3COO)_2(4,4'\text{-bipy})$ (**3**): triclinic, $P\bar{1}$, $a = 7.996(1)$ Å, $b = 9.128(1)$ Å, $c = 10.676(1)$ Å, $\alpha = 109.79(1)°$, $\beta = 99.90(1)°$, $\gamma = 100.98(1)°$, $Z = 2$. **1** and **2** have structures containing linear Co−bipy−Co chains. In **1**, the chains are connected by a network of hydrogen bonds. The structure of **3** contains linear double Co−bipy−Co chains bridged by CH_3COO^- groups. The reaction chemistry observed in different solvent systems and under hydrothermal conditions is discussed.

Introduction

We and others have studied the syntheses and structures of coordination polymers in which ligands such as pyrazine and 4,4′-bipyridine are used to bridge metal centers to form one-, two-, and three-dimensionally connected polymer networks. Some examples are reviewed in recent papers by Lu et al.[1,2] A general objective of these studies has been to develop methods for the synthesis of three-dimensionally connected open framework solids with potential as sorbents or catalysts. The synthesis and structural chemistry of one- or two-dimensional polymer systems, however, also provides insight into the role of specific solvents and counterion effects on the polymerization process. In the present work, we describe the synthesis, structure, and reactivity of three new one-dimensional polymers formed by coordination of 4,4′-bipy to Co(II) ions. The compounds were obtained by using $CoSO_4$, $CoCl_2$, and $Co(OAc)_2$ as starting materials and are unusual in that in all cases the anions are directly coordinated to the metal centers.

Structures containing one-dimensional polymer chains are formed in a variety of ways by coordination of ligands such as pyrazine (pyz), 4,4′-bipy, and their derivatives to metal centers or to dimetal centers with metal−metal bonds. Examples of dimetal systems include $Mo_2(OAc)_4(4,4'\text{-bipy})$,[3] $Mo_2(OAc)_4(pyz)$,[3] $Mo_2(O_2CCF_3)_4(4,4'\text{-bipy})$,[4] $Cr_2(OAc)_4(pyz)$,[5] $Rh_2(O_2CC_2H_5)_4(phz)$ (phz = phenazine),[6] and $Ru_2(O_2CC_2H_5)_4(phz)BF_4$.[7] Chain structures formed by halide-bridged dinuclear Cu(I) dimers connected by pyz, 4,4′-bipy, and phz have been reported,[2,8,9] and there is one example of a structure containing dinuclear Cu(II) units bridged by 4,4′-bipy.[10]

Most of the known examples of chain structures, however, contain single metal centers. For example, Cu(I) and Ag(I) ions normally adopt a pseudotetrahedral geometry and form zigzag chains with 4,4-bipy, pyrazine, and pyrazine derivatives.[11a−f] The compounds $Mn(4,4'\text{-bipy})(N(SiMe_3)_2)_2$ and $Cu(2,2'\text{-bipy})(4,4'\text{-bipy})(ClO_4)_2$ both have nonlinear chains with the M(II) ions present in pseudotetrahedral geometry.[12,13] Compounds with octahedrally coordinated metal centers generally have linear chain structures, for example compounds containing Cu(II),[14a−d] Cd(II),[15] Mn(II),[16a,b] Fe(II),[17] Ni(II),[18] and Co(II).[1,17,19a,b] Linear

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chain structures are also formed by Ag(I) with a coordination number of 2 with pyrazine and pyrazine derivatives.[11b,20]

The linear chain structures that are formed by coordination of pyrazine (pyz) and 4,4′-bipy to metal centers can be further elaborated to form 2D and/or 3D polymers through other connections. For example, metal−metal interactions in Ag(4,4′-bipy)NO_3 link all Ag−bipy−Ag chains into a 3D network.[21] Halide ions are often involved in the extension of chain structures.[9,22−25] For example, the double chain structure of $Cu(C_8H_6N_2)Cl_2$ can be regarded as a limited extension of a single-chain polymer.[25] Other ligands used to connect metal−pyz−metal chains include $C_2O_4^{2-}$ for Cu(II), CN^- for Cd(II), and NO_3^- for Ag(I) ions.[26−29]

Experimental Section

All chemicals were obtained from Aldrich and were used as received. Infrared data were collected on a Galaxy FTIR 5000 series spectrometer using the KBr pellet method. X-ray powder diffraction (XRD) measurements used a Scintag XDS 2000 automated powder diffractometer ($\theta-\theta$ geometry, Cu Kα radiation, flat plate sample). The Lazy-Pulverix program[30] was used to simulate powder patterns from the single-crystal X-ray data. Thermogravimetric analysis data were collected on a DuPont 9900 TG analyzer in flowing nitrogen at a heating rate of 10 °C/min. X-ray powder diffraction data were obtained for bulk polycrystalline samples of all of the compounds synthesized. Sample purity was confirmed by comparison of the measured data with the simulated diffraction patterns.

$Co(SO_4)(H_2O)_3$(4,4′-bipy)·$2H_2O$ (1). A solution of 0.313 g (2.0 mmol) of 4,4′-bipyridine in ethanol was slowly diffused into an aqueous solution of 0.155 g (∼1 mmol) of $CoSO_4\cdot xH_2O$. Pink needle-shaped single crystals of **1** slowly formed around the solution interface. Using ether as the solvent for 4,4′-bipy gave the same result. Product yields based on $CoSO_4$ were typically >60%. The purity of the product was confirmed by powder X-ray diffraction. Eliminating water from the solvent system yielded a different compound. Layering an ethanol solution of 4,4′-bipy with a DMSO (dimethyl sulfoxide) solution of $CoSO_4$ gave light purple square crystals of $CoSO_4$(4,4′-bipy)$_2$.[31] Due to decay in crystal quality, only preliminary results were obtained for this phase (see below).

1 can also be synthesized by hydrothermal reaction. A 0.155 g (∼1 mmol) amount of $CoSO_4$ and 0.312 g (2.0 mmol) of 4,4′-bypyridine were added to a mixture of 7 mL of water and 3 mL of ethanol in a PTFE-lined Parr bomb. The bomb was heated to 160 °C and held for 72 h. After being slowly cooled to ambient temperature, the bomb was opened, and the product was filtered off and washed with water and diethyl ether to remove any excess starting material. The crystals were dried in air. Variation of the solvent composition resulted in different shapes and sizes of the single crystals. If acetone was used instead of ethanol, the resulting crystals were smaller and a second unidentified phase appeared. IR for **1**: 3396 m, 3094 w, 1608 s, 1514 w, 1486 m, 1413 s, 1174 m, 116 vs, 1105 m, 1098 w, 1010 w, 804 s, 723 w, 619 m, 512 w cm^{-1}.

$CoCl_2(DMSO)_2$(4,4′-bipy) (2). **2** was synthesized by using a three-layer method. The bottom layer consisted a solution of 0.065 g (0.5 mmol) of $CoCl_2$ in 10 mL of dimethyl sulfoxide (DMSO). The middle layer was a mixture of 5 mL of DMSO and 5 mL of diethyl ether. The top layer was a solution of 0.156 g (1.0 mmol) of 4,4′-bipyridine in 10 mL of diethyl ether. Purple square single crystals of **2** were formed around the middle layer in about 1 week. Product yields based on $CoCl_2$ were typically 20−30%. The use of ethanol or methanol as the solvent for 4,4′-bipy resulted in the same product but with smaller crystal size. When water or DMF (dimethylformamide) was used as the solvent for $CoCl_2$, only purple precipitates were formed. IR for **2**: 3418 s, 2043 m, 2009 m, 2956 w, 2912 w, 1604 vs, 1535 m, 1491 w, 1418 vs, 1307 w, 1212 m, 1004 w, 997 vs, 949 vs, 8333 s, 828 m, 704 w, 632 s, 513 w cm^{-1}.

$Co(OAc)_2$(4,4′-bipyridine) (3). This compound can be synthesized by using both solution and hydrothermal methods. Hydrothermal reactions were carried out by adding 0.249 g (1.0 mmol) of $Co(CH_3COO)_2\cdot 4H_2O$ and 0.468 g (3.0 mmol) of 4,4′-bipyridine to a mixture of 4 mL of water and 4 mL of acetonitrile in a PTFE-lined Parr bomb. The bomb was heated to 160 °C and held at that temperature for 3 days. The bomb was then allowed to cool to room temperature in the oven after the oven was turned off. The product, maroon rod crystals of **3**, was filtered off and washed with water and diethyl ether and dried. Product yields based on $Co(CH_3COO)_2\cdot 4H_2O$ were typically >80%. Other solvents, for example water/acetone and water/methanol, give crystalline **3**, but the purity and crystal quality declined. No crystalline product was obtained in pure water. Interestingly, we observed that if pyrazine was present in the reaction as a competing ligand for 4,4′-bipy, the crystal quality of **3** was greatly enhanced even though the corresponding pyrazine compound was not formed.

Crystals of **3** were obtained in several solvent systems by the interdiffusion method as used for **2**. For example, water (for $Co(OAc)_2$)/acetonitrile (for 4,4′-bipy), water/methanol, and water/acetone solvents all produced single-phase crystalline **3**. Product yields based on $Co(CH_3COO)_2\cdot 4H_2O$ were typically >70%. IR for **3**: 3075 w, 3049 w, 3019 w, 2924 w, 1603 vs, 1562 vs, 1487 m, 1441 vs, 1339 w, 1217 m, 1088 m, 1045 m, 1004 w, 935 w, 885 w, 818 s, 733 w, 671 m, 631 m cm^{-1}.

X-ray Crystallography. A suitable crystal of **1** was mounted with epoxy glue on the tip of a glass fiber and transferred to an Enraf Nonius CAD4 four-circle diffractometer. Data were collected with Mo Kα radiation (λ = 0.710 73 Å). A single crystal of **2** was attached to the tip of a glass fiber and quickly mounted on a Nicolet R3 diffractometer under a cold nitrogen stream (−50 °C). A typical procedure involved centering 25 reflections (20° ≤ 2θ ≤ 40°) to determine the unit cell. For **1** and **2**, the Laue symmetries were confirmed by checking the intensities of equivalent reflections, and data were collected using the $\omega-2\theta$ scan method. Data for **1** and **2** were corrected for Lorentz and polarization effects. Empirical absorption corrections based on ψ scans were applied. The structures of **1** and **2** were solved by direct methods and standard difference Fourier technique using SHELXS-86[32] and SHELXL-93[33] programs. Space group $P6_5$ was chosen for **1** over $P6_1$ on the basis of comparison of Flack parameters. For **2**, *Pbcn* was uniquely determined from systematic absences. Hydrogen atoms have been placed on calculated positions and were not refined. For clarity they are omitted in the figures and the tables. A maroon rod crystal of **3** having approximate dimensions 0.05 × 0.05 × 0.4 mm was mounted in a random orientation on a Siemens SMART platform diffractometer

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Table 1. Crystallographic Data for $CoSO_4(H_2O)_3$(4,4′-bipy)·$2H_2O$ (**1**), $CoCl_2((DMSO)_2$(4,4′-bipy) (**2**), and $Co(OAc)_2$(4,4′-bipy) (**3**)

	1	**2**	**3**
formula	$CoSN_2O_9C_{10}H_{18}$	$CoCl_2S_2N_2O_2C_{14}H_{20}$	$CoO_4N_2C_{14}H_{14}$
fw	401.25	442.27	333.20
space group	$P6_5$	*Pbcn*	$P\bar{1}$
a, Å	11.435(2)	11.470(2)	7.996(1)
b, Å	11.435(2)	11.390(2)	9.128(1)
c, Å	20.886(4)	14.753(1)	10.676(1)
α, deg	90	90	109.79(1)
β, deg	90	90	99.90(1)
γ, deg	120	90	100.98(1)
V, Å^3	2365.1(7)	1927.4(5)	695.8(1)
Z	6	4	2
T, °C	25	−50	−50
ρ(calcd), g cm^{-3}	1.690	1.524	1.591
μ, mm^{-1}	1.268	1.392	1.25
R_1 ($I > 2\sigma(I)$)^a	0.0470	0.0254	0.0256
wR_2 ($I > 2\sigma(I)$)^b	0.1246	0.0614	0.0694

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**−**3**

$Co(H_2O)_3$(4,4′-bipy)SO_4·$2H_2O$ (**1**)			
Co−O(6)	2.046(8)	Co−O(4)	2.252(7)
Co−O(5)	2.084(8)	S−O(4)	1.499(7)
Co−O(7)	2.143(7)	S−O(3)	1.468(7)
Co−N(2)	2.165(8)	S−O(1)	1.468(8)
Co−N(1)	2.172(8)	S−O(2)	1.481(9)
O(6)−Co−O(5)	176.0(4)	O(6)−Co−O(4)	88.7(3)
O(6)−Co−O(7)	89.9(3)	O(5)−Co−O(4)	87.2(3)
O(5)−Co−O(7)	94.2(3)	O(7)−Co−O(4)	178.5(3)
N(2)−Co−N(1)	176.9(3)		
$CoCl_2$(4,4′-bipy)$(DMSO)_2$ (**2**)			
Co−O(1)	2.129(2)	Co−Cl	2.4707(5)
Co−N(1)	2.152(2)	S−O	1.527(2)
Co−N(2)	2.152(2)	S−C(7)	1.775(3)
S−C(8)	1.792(3)		
O−Co−O	175.85(8)	O(1)−Co−Cl	90.86(4)
O−Co−N(2)	92.08(4)	O−Co−Cl	89.31(4)
O−Co−N(1)	87.92(4)	N(2)−Co−Cl	87.706(13)
N(2)−Co−N(1)	180.0	N(1)−Co−Cl	92.295(13)
$Co(OAc)_2$(4,4′-bipy) (**3**)			
Co−O(1)	2.022(1)	Co−O(2)	2.017(1)
Co−O(3)	2.175(1)	Co−O(4)	2.211(1)
Co−N(1)	2.168(1)	Co−N(2)	2.166(1)
O(1)−C(11)	1.251(2)	O(2)−C(11)	1.255(2)
O(3)−C(13)	1.256(2)	O(4)−C(13)	1.252(2)
C(11)−C(12)	1.504(2)	C(13)−C(14)	1.494(3)
O(1)−Co−O(2)	120.4(1)	O(1)−Co−O(3)	88.3(1)
O(1)−Co−O(4)	147.8(1)	O(2)−Co−O(3)	151.1(1)
O(2)−Co−O(4)	91.7(1)	O(3)−Co−O(4)	59.5(1)
N(1)−Co−N(2)	177.2(1)		

equipped with a 1K CCD area detector.[34] The sample was placed in a stream of dry nitrogen gas at −50 °C, and the radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. A hemisphere of data (1271 frames at 5 cm detector distance) was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 20 s/frame. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability, and the maximum correction on *I* was <1%. The data were integrated using the Siemens SAINT program,[35] with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A ψ scan absorption correction was applied on the basis of the entire data set using the SADABS program.[36] Redundant reflections were averaged. The structure of **3** was solved in the triclinic space group $P\bar{1}$ using Patterson methods and refined using SHELXTL.[37] Detailed information can be found in Table 1.

Results and Discussion

Structures. Selected bond distances and angles for **1**−**3** are given in Table 2. All three structures contain linear chains formed by 4,4′-bipyridine ligands connecting Co atoms. In **3** CH_3COO^- groups bridge Co atoms in parallel Co−bipy−Co chains to form double chains, as shown in Figure 3. All Co atoms are octahedrally coordinated and are divalent.

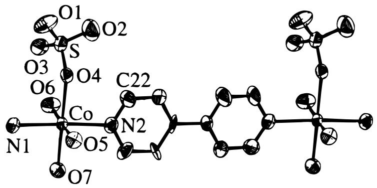

Figure 1. View of the infinite linear chain of $Co(H_2O)_3$(4,4′-bipy)-SO_4·$2H_2O$ (**1**).

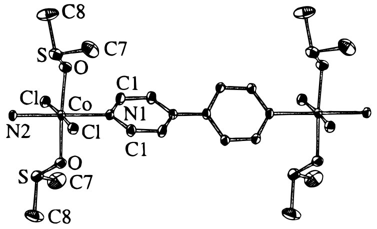

Figure 2. View of the infinite linear chain of $Co(DMSO)_2$(4,4′-bipy)-Cl_2 (**2**).

Part of the structure of **1** is shown in Figure 1. In **1**, each Co atom is coordinated to two 4,4′-bipyridine ligands, one of the oxygen atoms in a SO_4^{2-} anion, and three water molecules from the solvent. The other two water molecules occupy space in the structure between the chains. All of the water molecules and the SO_4^{2-} anions are interconnected through hydrogen bonds. In each unit cell, the Co−bipy−Co chains lie in the *ab* plane along the *a*, *b*, and (110) axes. There are six infinite chains stacked perpendicular to the *c* axis in the unit cell related by the 6_5-screw axes. The chains are spaced at 3.48 Å intervals along the *c* axis. The phenyl rings in the 4,4′-bipyridine ligands are nearly coplanar (the interplanar angle is 4.0°), and there are no bipyridine interactions between chains. The length of the bond between the Co(II) ion and the oxygen of the sulfate group is 2.252(7) Å and is the longest among the Co−O distances. The two water molecules are trans to each other and are tightly bonded to Co with Co−O distances of 2.046(8) and 2.084(8) Å. The water molecule coordinated trans to the SO_4^{2-} is less strongly bonded to Co with a Co−O distance of 2.143(7) Å. The Co−N bond distances are 2.165(8) and 2.172 (8) Å similar to the distances found in **2** and **3**. The presence of a coordinated sulfate group is somewhat unexpected. In the related compound, $Co(pz)(H_2O)_4SO_4$·$2H_2O$,[19a] an additional water molecule rather than the SO_4^{2-} anion completes the local coordination around the Co ion.

In the structure of **2**, the Co center is coordinated to two 4,4′-bipyridine ligands, the two Cl anions, and two DMSO molecules (Figure 2). The Cl^- anions are located trans to each other as are the DMSO molecules. The unit cell contains four infinite chains that lie along the *b* axis. The Co−Cl bond length is

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(34) *SMART*, version 4.05; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1995.

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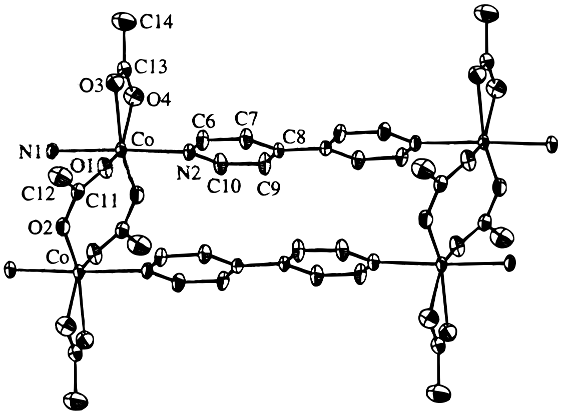

Figure 3. View of the infinite double chain of Co(4,4′-bipy)($CH_3COO)_2$ (**3**).

2.4707(5) Å. The distance between the Co atom and the oxygen of the DMSO molecule is 2.120(2) Å, close to the value found for the Co−N bond length (2.152 Å) suggesting that the bonding contributions from the solvent and the 4,4′-bipyridine ligands are similar. In this structure the two phenyl rings of the 4,4′-bipyridine are not coplanar. The dihedral angle is 34.3°.

The structure of **3** contains no solvent molecules. Acetate groups coordinate to the Co atoms in two different ways (Figure 3). One anion type uses two oxygen atoms to chelate to a Co ion forming a four-membered Co−O−C−O ring. The other anion type forms a bridge using two oxygen atoms between the Co centers in two parallel linear chains. The structure of **3** contains double rather than the single linear chains found in **1** and **2**. The Co−O bond lengths for the bridging oxygen atoms are shorter (2.022(1) and 2.017(1) Å for **3**) than the Co−O bond lengths involving the chelating oxygen atoms. The bond distances between the chelating oxygen atoms and the Co center are 2.175(1) and 2.211(1) Å for **3**. The distances between the cobalt atoms bridged by the CH_3COO^- groups are 4.02(1) Å. There are no Co−Co bonds. To our knowledge, **3** is the first example of a double chain structures with 4,4′-bipyridine. The only other example in the pyrazine/bipy family of complexes is $Cu(C_8H_6N_2)Cl_2$, a double chain structure formed by single chains of Cu−quinoxaline−Cu bridged by Cl atoms.[25]

Reaction Chemistry. In a previous paper,[1] we described the influence of solvents on the structures of 2D and 3D metal coordination polymers formed with pyrazine and 4,4′-bipyridine. The influence of the solvent chemistry and the reactions conditions is again seen in the 1D compounds. Compounds **1** and **3** can be prepared using both solution and hydrothermal conditions. Compound **2** was formed only under solution conditions.

In water, $CoSO_4$ reacts with 4,4′-bipy to form **1**. In solution reactions, the selection of the second solvent only affects the crystal quality. In nonaqueous conditions, a different compound, $CoSO_4$(4,4′-bipy)$_2$, is formed. Although a detailed structure could not be obtained due to poor crystal stability, preliminary results clearly showed that the structure contains an infinite 2D square net of composition Co(bipy)$_2^{2+}$ interconnected by SO_4^{2-} groups through Co−O bonds. The structures of $CoSO_4$(4,4′-bipy)$_2$ and Zn(4,4′-bipy)$_2$(SiF_6) are similar.[38] In the latter, the Zn(bipy)$_2$ layers are joined by bridging SiF_6^{2-} anions. Although Co−SO_4 and Zn−SiF_6 bipy systems behave similarly in nonaqueous conditions, in aqueous systems their reaction products with 4,4′-bipy are different. SO_4^{2-} is coordinated to Co under both conditions, while SiF_6^{2-} is not coordinated to Zn when water is used.[39] As mentioned above, SO_4^{2-} is also not coordinated to Co in the product of the reaction of $CoSO_4$ with pyrazine under aqueous conditions.[19a]

2 is only obtained in the presence of DMSO using solution reaction conditions. Attempts to synthesize **2** hydrothermally were unsuccessful, and the expected 4,4′-bipy analogue of Co(pyz)$_2$Cl$_2$ was not obtained. Both hydrothermal and solution conditions can be used to synthesize **3**.

Thermogravimetric Analysis. **1** and **2** were heated to 600 °C, and **3** was heated to 400 °C in N_2. For **1**, TGA shows a weight loss of 22.26% from 80 to 150 °C corresponding to the loss of five water molecules (calc 22.43%). A second weight loss of 38.75% from 250 to 415 °C corresponds to removal of one 4,4′-bipyridine (calc 38.88%). The final residue was amorphous by powder XRD. The thermal decomposition behavior of **2** is much like that observed for **1**. The compound loses coordinated solvent molecules below 110 °C. The observed weight loss (35.38%) corresponds to the loss of two molecules of DMSO (calc 35.28%). From 350 to 480 °C the compound lost an additional 35.76% weight corresponding to one molecule of 4,4′-bipyridine (calc 35.29%).

The thermal decomposition behavior of **3** is quite different. The loss of the coordinated bipyridine ligands and the decomposition of Co(OAc)$_2$ occurs simultaneously. No weight loss was observed below 180 °C. A single-step weight loss was observed between 210 and 340 °C corresponding to 77.50% for Co(OAc)$_2$(4,4′-bipy). The weight loss corresponds to one 4,4′-bipyridine molecule and two acetate groups assuming that the residue is CoO (calc 77.51%).

Although the Co−N(bipy) bond lengths for **1**−**3** are similar, the temperatures at which bipyridine molecules are evolved from the structures are quite different due to differences in the local Co coordination environment and the possibility of different decomposition pathways and intermediates.

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Supporting Information Available: Three X-ray crystallographic files, in CIF format, for the compounds Co(SO_4)(H_2O)$_3$(4,4′-bipy)·2H_2O (**1**), $CoCl_2$(DMSO)$_2$(4,4′-bipy) (**2**), and Co(CH_3COO)$_2$(4,4′-bipy) (**3**) are available on the Internet only. Access information is given on any current masthead page.

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