Coordination polymers of cobalt(II): $[Co(4,4'\text{-}bpy)_2(O_2CCF_3)_2]_n$ and $[Co(4,4'\text{-}bpy)(O_2CCH_3)_2(H_2O)_2]_n$

You-Sheng Zhang,[a] Gary D. Enright,[b] Steven R. Breeze[b] and Suning Wang*[a]

[a] *Department of Chemistry, Queen's University, Kingston, ONT K7L 3N6, Canada*
[b] *Steacies Institute for Molecular Science, National Research Council, 100 Sussex Dr., Ottawa, ONT K1A 0R6, Canada*

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Two novel coordination polymers of cobalt(II) have been synthesized and characterized structurally. The first compound, $[Co(4,4'\text{-}bpy)_2(O_2CCF_3)_2]$ (**1**), was obtained from the reaction of $Co(O_2CCF_3)_2$ with 4,4′-bipyridine. Compound **1** has a covalently linked, two-dimensional, fishing-net-like structure. The fishing nets of **1** stack in the lattice, allowing the formation of extended channels that host diethyl ether solvent molecules in the solid state. The second compound, $[Co(4,4'\text{-}bpy)(O_2CCH_3)_2(H_2O)_2]$ (**2**), was obtained from the reaction of $Co(CH_3CO_2)_2 \cdot 4H_2O$ with 4,4′-bipyridine. Compound **2** has a covalently linked one-dimensional chain structure. In the crystal lattice of **2** the one-dimensional chains form an interpenetrating, three-dimensional structure *via* interchain hydrogen bonds between acetate and H_2O ligands. There are channels parallel to the *b* axis in the lattice of **2** that appear to host small guest molecules such as methanol and H_2O.

Coordination polymers are an important class of materials because of their potential applications in catalysis and advanced materials (*e.g.*, sensors, liquid crystals, magnetic materials, and nonlinear optical materials).[1] We have been interested in the synthesis of coordination polymers containing paramagnetic and redox active metal ions such as Co(II). The strategies employed by our group involve using both covalent and hydrogen bonds in the construction of polymeric coordination compounds. Recently, we reported that by using bridging ligands that have a ∼90° twist such as tetraacetylethane dianion, polynuclear compounds with chiral structures can be obtained.[2] Bridging ligands such as 4,4′-bipyridine (4,4′-bpy), widely used in coordination polymers, do not promote the formation of chrial structures. However, they have been found to be very effective in the formation of various interesting extended structures.[3] We report herein two new cobalt(II) coordination polymers where 4,4′-bipyridine is used as the bridging ligand.

Experimental

All chemicals were obtained from Aldrich and used as received. Elemental analyses were performed at Canadian Microanalytical Service Ltd., Delta, BC. Magnetic susceptibility measurements were performed by using a Gouy balance (Johnson Matthey) at 23 °C.

Synthesis of $[Co(4,4'\text{-}bpy)_2(CF_3CO_2)_2]$ (1)

$Co(CF_3CO_2)_2$ (200 mg, 0.70 mmol), obtained from the stoichiometric reaction of $CoCl_2$ with $Ag(O_2CCF_3)$, was dissolved in 10 ml of methanol. With stirring, a methanol solution of 4,4′-bpy (218 mg, 1.40 mmol) was added into the flask slowly. After a few hours, the solution was concentrated to 5 ml *in vacuo*. Orange-red crystals formed after slow diffusion of diethyl ether vapor into the solution for a week. The yield was 81% based on $Co(CF_3CO_2)_2$. Anal. calcd for the vacuum-dried sample, $C_{24}H_{16}N_4O_4F_6Co$: C, 48.24; H, 2.68; N, 9.38. Found: C, 47.87; H, 2.86; N, 9.18.

Synthesis of $[Co(4,4'\text{-}bpy)(CH_3CO_2)_2(H_2O)_2]$ (2)

A methanol solution of 4,4′-bpy (109 mg, 0.7 mmol) was slowly added to a methanol solution of $Co(CH_3CO_2)_2 \cdot 4H_2O$ (200 mg, 0.70 mmol) with stirring. A light orange precipitation formed immediately. After a few hours, the solution was filtered. The clear filtrate was kept under diethyl ether vapor for a week. Light-orange crystals were obtained. The yield of compound **2** varied from 20%–60%, depending on the concentration of the solution and the rate of crystallization. Anal. calcd for the vacuum-dried sample, $C_{14}H_{18}N_2O_6Co$: C, 45.54; H, 4.87; N, 7.59. Found: C, 40.81; H, 5.06; N, 4.83. No satisfactory CHN analysis results could be obtained despite repeated attempts. The poor agreement between the observed and calculated CHN values is likely caused by the presence of water molecules in the crystal lattice of **2**.

X-Ray crystallographic analyses

Single crystals of compounds **1** and **2** were obtained from a solution of methanol and diethyl ether and sealed inside glass capillaries along with solution. Data of **1** were collected over the 2θ range of 3.00–56.5° at −100 °C on a Siemens CCD X-ray diffractometer with Mo-Kα radiation while the data of **2** were collected over the 2θ range of 3.00–50° at 23 °C on a Siemens P4 X-ray diffractometer with Mo-Kα radiation. All data were processed on a pentium PC using Siemens SHELXTL software package (5.0). The crystals of both compounds belong to monoclinic crystal systems. The space groups, *C*2/*c* and *P*2/*n*, were established based on systematic absences, statistics of intensity distributions, and the successful solution and refinements of the structures. The structures of both compounds were solved by direct methods. The lattice of **2** has two independent Co(II) units with similar structures, each of which has an inversion center of symmetry. The positions of hydrogen atoms are either located directly from the difference Fourier maps or calculated. Their contributions in structure factor calculations were included. There are two diethyl ether solvent molecules per Co_2 unit in **1**. The occupancy factor for each diethyl ether was found to be 0.70. All non-hydrogen atoms in **1** were refined anisotropically. Water

Table 1 Crystallographic data

Compound	1	2
Formula	$C_{24}H_{16}N_4O_4F_6Co \cdot 1.5C_2H_5OC_2H_5$	$C_{14}H_{18}N_2O_6Co \cdot (CH_3OH)_x(H_2O)_y$
FW	708.5	368.9+
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2/n$
a/Å	27.173(3)	11.8538(14)
b/Å	15.280(2)	7.4146(8)
c/Å	17.026(2)	19.448(6)
α/°	90	90
β/°	107.06(2)	90.06(2)
γ/°	90	90
U/Å^3	6758.1(12)	1709.3(6)
Z	8	4
T/°C	−100	23
μ/cm^{-1}	5.85	10.4
Reflns measured	19534	3168
Reflns used (R_{int})	8570 (0.090)	3015 (0.029)
Final $R[I > 2\sigma(I)]$	$R_1{}^a = 0.0784$ $wR_2{}^b = 0.1838$	$R_1 = 0.0680$ $wR_2 = 0.1910$
R (all data)	$R_1 = 0.2041$ $wR_2 = 0.2435$	$R_1 = 0.0867$ $wR_2 = 0.2319$

^{a} $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. ^{b} $wR_2 = \{\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\mathrm{Max}\,(F_o^2, 0) + 2F_c^2]/3$.

and methanol solvent molecules appeared to be present in the lattice of **2**. Some of the residual electron densities in the difference Fourier map of **2** that are likely to arise from disordered methanol solvent molecules or water molecules were assigned to carbon atoms and refined with a partial occupancy. All non-hydrogen atoms except those of the disordered solvent molecule in **2** were refined anisotropically. The details of crystal data are provided in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC reference number 440/109. See http://www.rsc.org/suppdata/nj/1999/625/ for crystallographic files in .cif format.

Results and discussion

Compound 1

Compound **1** was obtained from a stoichiometric reaction of $Co(O_2CCF_3)_2$ with 4,4′-bipyridine in methanol. The composition and structure of **1** were established by elemental and X-ray diffraction analysis. Magnetic susceptibility measurements using a Gouy balance revealed that the cobalt(II) ion in **1** has a high-spin configuration (the magnetic moment of **1** at 25 °C was determined to be 4.32 BM, consistent with a high spin d^7 Co(II) ion).[4]

Table 2 Selected bond lengths (Å) and angles (deg)

	Compound 1		
Co–O(3)	2.066(4)	Co–N(4)	2.180(4)
Co–O(1)	2.071(4)	O(3)–Co–O(1)	178.9(2)
Co–N(1)	2.166(4)	N(2)–Co–N(3)	177.8(2)
Co–N(2)	2.176(4)	N(1)–Co–N(4)	177.7(2)
Co–N(3)	2.178(4)		
	Compound 2		
Co(1)–O(3)	2.066(4)	N(1A)–Co(1)–O(1A)	94.2(2)
Co(1)–N(1)	2.144(4)	N(1)–Co(1)–O(1A)	85.8(2)
Co(1)–O(1)	2.154(4)	O(3)–Co(1)–O(1)	98.8(2)
Co(2)–O(6)	2.068(4)	O(6A)–Co(2)–N(2)	91.7(2)
Co(2)–N(2)	2.147(4)	O(6)–Co(2)–N(2)	88.3(2)
Co(2)–O(4)	2.159(4)	N(2)–Co(2)–N(2A)	180.0
O(3)–Co(1)–N(1A)	88.3(2)	O(6A)–Co(2)–O(4)	81.2(2)
O(3)–Co(1)–N(1)	91.7(2)	O(6)–Co(2)–O(4)	98.8(2)
O(3)–Co(1)–O(1A)	81.2(2)	N(2)–Co(2)–O(4)	85.7(2)
O(3A)–Co(1)–O(1A)	98.8(2)	N(2A)–Co(2)–O(4)	94.3(2)

The structure of the unique mononuclear portion of compound **1** is shown in Fig. 1, along with the portion related by a twofold rotation axis. The geometry around the Co(II) ion is a typical octahedron [O(1)–Co–O(3) = 178.9(2)°, N(2)–Co–N(3) = 177.8(2)°, N(1)–Co–N(4) = 177.7(2)°]. The Co–O(1) and Co–O(3) bond lengths are shorter than the Co–N bond lengths. One could attribute the bond length difference to the fact that O(1) and O(3) are negatively charged, hence forming a stronger bond with Co(II) than those of the neutral nitrogen donor atoms of the 4,4′-bpy ligands. The other factor for the bond length discrepancy is likely due to Jahn–Teller distortion,[5] which is known to be present in a high spin d^7 octahedral metal complex. Each of the four 4,4′-bpy ligands around the Co(II) ion is bound to a second Co(II) center. As a result, compound **1** forms a two-dimensional, covalently linked network. The Co–Co separation distance is 11.43 Å, which results in very little magnetic interactions between the two cobalt(II) centers as confirmed by the magnetic data.

As shown in Figs. 2 and 3, the two-dimensional, fishing-net-like sheets are staggered in the crystal lattice, resulting in the formation of one-dimensional channels in the lattice. Similar non-interpenetrating two-dimensional structures based on 4,4′-bipyridine have been observed previously in $Co(NCS)_2(4,4'\text{-bpy})_2$,[3a] $Cd(4,4'\text{-bpy})_2(NO_3)_2$,[3d] and $[Zn(4,4'\text{-bpy})_2(SiF_6)_2]$.[3i] Unlike $Co(NCS)_2(4,4'\text{-bpy})_2$, in which the two pyridyl groups of the 4,4′-bpy ligand are twisted by 56°, the two pyridyl groups of 4,4′-bpy in **1** are close to being coplanar (the dihedral angle is 13.5°). The atomic separation distances

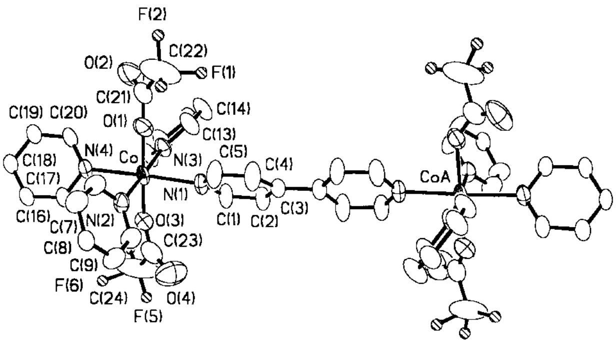

Fig. 1 Coordination environment around the unique cobalt(II) ion of **1** with 50% thermal ellipsoids and labeling scheme. Hydrogen atoms are omitted for clarity. Fluorine atoms are shown as ideal spheres.

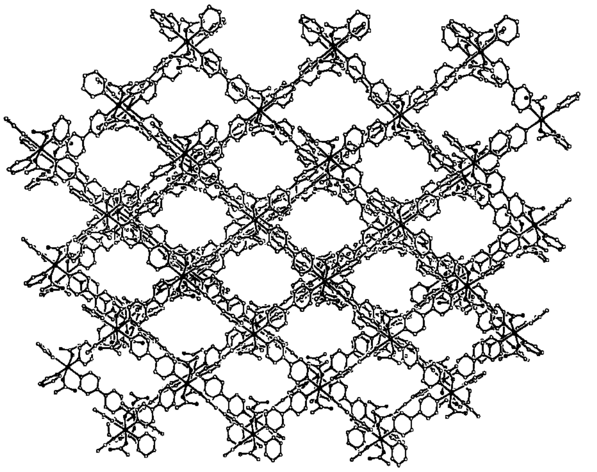

Fig. 2 A view projected down the *a* axis, showing the two-dimensional structure of **1**. The guest diethyl ether molecules are located inside the channels but are omitted for clarity.

between the two neighboring 2D sheets in **1** are 8.96 and 9.15 Å, respectively, much longer than[3d] that in $Co(NCS)_2(4,4'\text{-}bpy)_2$ (6.49 Å), due to the fact that the CF_3COO^- ligand is much bigger than NCS^-. The effective dimension of the diamond-shaped cavity in **1** is approximately 8.43 × 8.43 Å. Diethyl ether solvent molecules are located inside these channels. These diethyl ether guest molecules readily escape from the lattice at ambient temperature. The vacuum-dried sample of **1** appears to absorb ethyl acetate molecules reversibly [one ethyl acetate per $Co(4,4'\text{-}bpy)_2(CF_3CO_2)_2$] as evidenced by a TGA study. The absorbed ethyl acetate molecules escape from the lattice in the temperature range of ~50–120 °C. The utility of compound **1** in hosting small organic molecules is currently being further investigated in our laboratory.

Compound 2

Compound 2 was obtained from the reaction of $Co(CH_3CO_2)_2 \cdot 4H_2O$ with one equivalent of 4,4′-bipyridine. The composition of **2** could not be conclusively established by elemental analysis due to the presence of water and perhaps methanol solvent molecules in the crystal lattice. Magnetic susceptibility measurements using a Gouy balance confirmed that the cobalt(II) ion in **2** also has a high-spin configuration (the magnetic moment of **2** at 25 °C was found to be 4.1 BM).

The structure of compound **2** was determined by single-crystal X-ray diffraction analysis, which established unambiguously that **2** has the formula $[Co(4,4'\text{-}bpy)(CH_3CO_2)_2(H_2O)_2]$ plus noncoordinating H_2O and CH_3OH. There are two independent but similar mononuclear Co(II) moieties in the asymmetric unit. The structure of one of the mononuclear units of **2** is shown in Fig. 4. The cobalt(II) ion is situated on an inversion center with an octahedral geometry. The Co–N bond lengths are similar to those in **1**. The most unexpected feature is that the $Co–O(H_2O)$ bond lengths [Co(1)–O(3) = 2.066(4), Co(2)–O(6) = 2.068(4) Å] are shorter than those of Co–O(acetate) [Co(1)–O(1) = 2.154(4), Co(2)–O(4) = 2.159(4) Å]. Because of the negative charge of the acetate ligand, one would expect it to form a shorter Co–O bond than the water ligand. The discrepancy of the Co–O bond lengths in **2** could again be attributed to Jahn–Teller distortion of a high spin d^7 metal ion. The two pyridyl rings of the 4,4′-bpy ligand are not coplanar, with a dihedral angle of 20°.

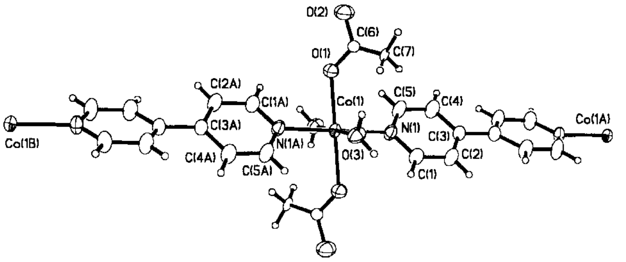

Fig. 4 Coordination environment around Co(1) in compound **2** with 50% thermal ellipsoids and labeling scheme.

As observed in **1**, the 4,4′-bpy ligand functions as a bridging ligand to two cobalt(II) ions, leading to the formation of a one-dimensional covalently linked chain. The one-dimensional chain of **1** resembles that of $Co(4,4'\text{-}bpy)(H_2O)_3(SO_4)$ and $Co(4,4'\text{-}bpy)(DMSO)_2Cl_2$, reported recently by Jacobson and coworkers.[3c] However, unlike Jacobson's compounds where no interchain linkages were reported, the one-dimensional chains of **2** are further linked together through hydrogen bonds to form an unusual extended 3D structure. The chains made of repeating Co(1) units stack in the crystal lattice with an interchain separation distance of 7.42 Å. The same is true for the chains made of repeating Co(2) units, as shown in Fig. 5. There are interchain hydrogen bonds[6] within the stack of Co(1) chains or Co(2) chains. The hydrogen bonds are between the H_2O ligand and the noncoordinating oxygen atom of the acetate ligand as indicated by the distances of O(2)···O(3A) = 2.789 Å and O(5)···O(6A) = 2.787 Å. As a result of the interchain hydrogen bonds, there are rectangular channels within each stack of chains with dimensions of

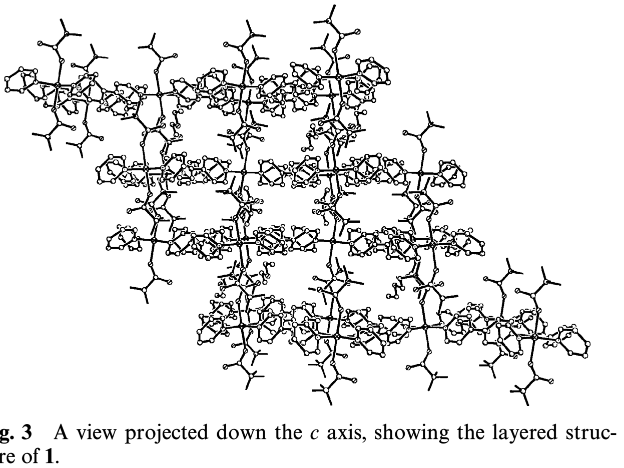

Fig. 3 A view projected down the *c* axis, showing the layered structure of **1**.

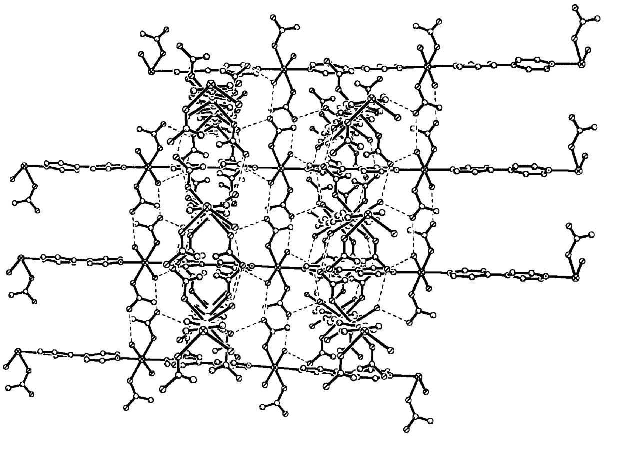

Fig. 5 A diagram showing the stacking and interpenetration of one-dimensional chains in **2**.

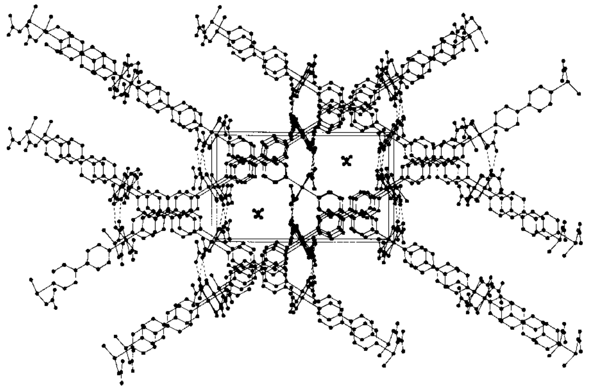

Fig. 6 A view projected down the *b* axis showing the relative orientation of the interpenetrating chains, the one-dimensional channels, and the location of the guest molecules in the lattice of **2**.

7.43 × 11.39 Å. Most interestingly, these channels are filled by the second set of chains, which are linked to the first set of chains by additional hydrogen bonds [O(2)···O(6) = 2.773 Å and O(3)···O(5) = 2.782 Å] between the acetate and the H_2O ligands. As a result, compound **2** has a lattice made of two sets of interpenetrating chains. Hydrogen bonds clearly play a key role in the formation of such a lattice. There are channels formed by the interpenetrating chains along the *b* axis as shown in Fig. 6. The effective dimension of these channels is approximately 2.92 × 5.03 Å. Guest molecules, which are likely to be either H_2O or methanol, were found inside these channels. The nature of the guest molecules could not be established unambiguously by X-ray diffraction or TGA analysis. The paramagnetism and insolubility of **2** in common solvents precluded the characterization of the guest molecules by NMR and mass spectrometry.

In summary, two new coordination polymers of cobalt(II) compounds have been synthesized and characterized structurally. The crystal lattice of the covalently linked 2D polymer of **1** can function as a host for molecules such as diethyl ether and ethyl acetate. The 1D polymer of **2** forms a hydrogen-bound extended structure in the crystal lattice, which appears to host small guest molecules but the nature of the guest molecules could not be established conclusively at this time.

Acknowledgements

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