Crystal Structure and Magnetic Property of Two Novel 1-D Cobalt(II) Assemblies

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Two novel one-dimensional (1-D) cobalt(II) self-assemblies, [Co(pyterpy)$(NCS)_2$] (**1**) and [Co(pyterpy)(SO_4)]•$(CH_3OH)(C_2H_5OH)(H_2O)$ (**2**) (pyterpy = 4′-(4‴-pyridyl)-2,2′:6′,2″-terpyridine) were synthesized and characterized. Compound **1** forms a linear chain, and compound **2** forms a zigzag chain. It is thought that the structural differences are caused by binding counter anions as coligands.

The design of coordination polymer has been extensively studied because of promising applications in porous materials, molecule-based magnetic materials, and so on.[1] The dimensionalities for coordination compounds are controlled by a various metal ions, ligands and inter- and intramolecular interactions (hydrogen bonds, π–π interactions), which control the physical properties. In particularly, 1-D compounds have exhibited unusual magnetism, conductivity and nonlinear effects.[2] Molecule-based 1-D compounds have a potential for generating novel and interesting physical properties. Herein, we report the syntheses, crystal structures and magnetic properties of two novel 1-D cobalt(II) self-assemblies.

The ligand pyterpy (pyterpy = 4′-(4‴-pyridyl)-2,2′:6′,2″-terpyridine) was synthesized by the method reported previously.[3] The compound **1** was prepared by the reaction of the pyterpy and $Co(NCS)_2$, and $CoSO_4$ was used for the compound **2**. The single crystals of **1** were obtained by slow diffusion method in EtOH, and the crystals of **2** were obtained in a mixture of MeOH and EtOH.

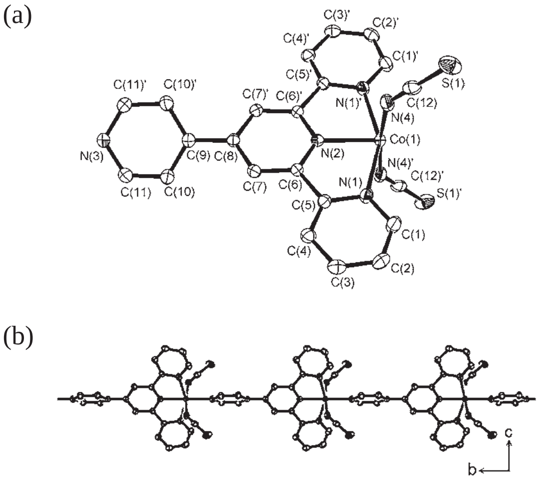

Figure 1. Perspective views of (a) the compound **1**, showing 50% probability displacement ellipsoids and (b) its 1-D structure at *bc* plane. H atoms are omitted for clarity.

Figure 1a shows ORTEP drawing for **1**, and Figure 1b shows the 1-D arrangement along the *b* axis.[5] The compound **1** forms 1-D linear chain, and terpyridine and pyridine moieties in pyterpy, and two NCS^- counter anions coordinate to a cobalt(II) ion. The terpyridine moiety in pyterpy is coplanar, and the dihedral angle between the terpyridine and pyridine planes is 39.6(2)°. The bond lengths, Co–N, for **1** are similar to those of high-spin cobalt(II) compounds reported previously.[4] Co(1)–N(1) and Co(1)–N(2) distances in Co–terpyridine unit are 2.186(3) and 2.053(4) Å, respectively. Co(1)–N(3) distance in Co–pyridine unit is 2.127(4) Å, and Co(1)–N(4) distance in $Co–NCS^-$ unit is 2.117(3) Å. Two NCS^- ligands diagonally coordinate to a cobalt(II) ion, and Co(1)–N(4)–C(12) angle is 145.5(2)°. N(1)–Co(1)–N(1)′ angle is 153.4(1)°, and the N(2)–Co(1)–N(3) and N(4)–Co(1)–N(4)′ bonds are almost linear, which induce a pronounced distortion of the CoN_6 octahedron. C(4)···S(1) distance between the 1-D molecules is 3.275(3) Å, which is shorter than van der Waals radius and indicates π-chalcogen intermolecular interaction. The shortest inter- and intrachain Co···Co distances are 8.73 and 11.20 Å, respectively, and the distances are similar to previous data.[4b]

Figure 2a shows ORTEP drawing for **2**, and Figure 2b shows the 1-D crystal packing structure in the *ac* plane. The compound **2** contains MeOH, EtOH, and water molecules in the crystal and forms zigzag chain.

The coordinating fashion for **2** is completely different from that for **1**. Two oxygen atoms of the SO_4^{2-} ligand coordinate to a

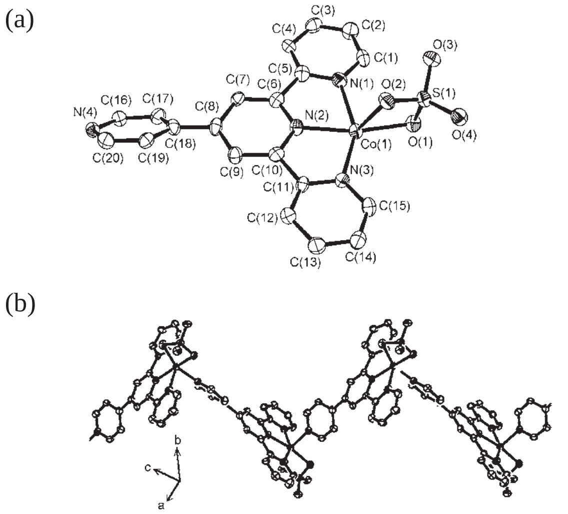

Figure 2. Perspective views of (a) the compound **2**, showing 50% probability displacement ellipsoids and (b) its 1-D zigzag structure. H atoms and solvent molecules are omitted for clarity.

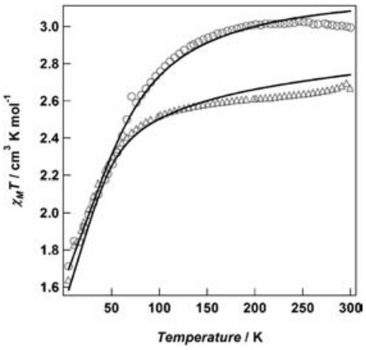

Figure 3. Temperature dependences of $\chi_m T$ versus T plots for **1** (○) and **2** (△) at 1 T. The solid lines indicate that the best fit for experimental data.

cobalt(II) ion at the cis in the equatorial and the axial position. The bond lengths and angles of surrounding cobalt(II) ion show that the structure for **2** is considerably distorted than that for **1**. The angle of N(2)–Co(1)–N(4) is 93.8(2)° and the S(1)–O(1) and S(1)–O(2) distances are longer than the S(1)–O(3) and S(1)–O(4) distances,[6] indicating coordinating effect. The pyridine in the pyterpy coordinate to cobalt(II) ion for the Co-terpy square perpendicularly. The shortest inter- and intrachain Co···Co distances are 9.22 and 11.21 Å, respectively.

Furthermore the compound **2** exhibited the guest exchange property reported previously.[4b] After removing MeOH, EtOH, and water molecules by annealing, **2** incorporated five water molecules. As a result, the compound [Co(pyterpy)SO$_4$]·5H$_2$O (**2′**) was obtained.[6] TG analysis also shows that the removing the guest molecules and incorporation of five water molecules were retained in successive cycles for **2′**.

The temperature dependences of $\chi_m T$ plots for **1** and **2** are shown in Figure 3. The $\chi_m T$ values at 300 K is equal to 2.99 cm^3 K mol^{-1} for **1** and 2.70 cm^3 K mol^{-1} for **2**, which are larger than that expected for the spin-only value (1.875 cm^3 K mol^{-1}, high-spin Co$^{\mathrm{II}}$; $S = 3/2$). The $\chi_m T$ values gradually decrease on cooling mode. When the Curie–Weiss law was applied in the range of 100–300 K, the Curie constant, C, is 3.18 cm^3 K mol^{-1} and the Curie temperature, θ, is -13.5 K for **1**, and $C =$ 2.74 cm^3 K mol^{-1} and $\theta = -9.6$ K for **2**. Both the Curie constants are in usual range of octahedral high-spin cobalt(II) ion (2.8–3.4 cm^3 K mol^{-1}).[7] The data were fitted by the expressions accounting for spin–orbit coupling λ on high-spin cobalt(II) ion which has a $^4T_{1g}$ ground state (eq 1), where A is a crystal field parameter, $x = \lambda/k_B T$ ($A = 1.5$ is weak-field limit and $1.0 =$ strong-field limit).[7] The best fitting parameters were obtained with the values of $A = 1.3$ and $\lambda = -117\,\mathrm{cm}^{-1}$ for **1**, and $A =$ 1.0 and $\lambda = -104\,\mathrm{cm}^{-1}$ for **2**. Both of slight deviations at high temperature can be caused by the anisotropy of octahedral environment.[7d] Additionally, the values of λ smaller than that for cobalt(II) free ion ($\lambda = -170\,\mathrm{cm}^{-1}$) can be attributed to the covalency of the Co–N bond. The magnetic property for **2′** was also measured, and the property is similar to that for **2**.[6]

$$\mu^2 = \frac{\left[\begin{array}{l}\dfrac{7(3-A)^2x}{5} + \dfrac{12(A+2)^2}{25A} + \left\{\dfrac{2(11-2A)^2x}{45} + \dfrac{176(A+2)^2}{675A}\right\}\exp\left(-\dfrac{5Ax}{2}\right) \\ + \left\{\dfrac{(A+5)^2x}{9} - \dfrac{20(A+2)^2}{27A}\right\}\exp(-4Ax)\end{array}\right]}{\dfrac{x}{3}\left[3 + 2\exp\left(-\dfrac{5Ax}{2}\right) + \exp(-4Ax)\right]} \tag{1}$$

In conclusion, we synthesized two novel 1-D high-spin cobalt(II) compounds **1** and **2**. The compound **1** with NCS$^-$ anion forms 1-D linear chain with a mean crystal field. But the compound **2** with SO$_4{}^{2-}$ anion forms 1-D zigzag chain with a strong field. It is suggested that the differences of the structural and magnetic properties are caused by coordinated counter anions. The results will provide an indicator constructing novel 1-D cobalt(II) compounds.

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5 Crystal data for **1**; $C_{22}H_{14}N_6S_2Co$ (485.45), monoclinic, $C2/c$ (No. 15), $a = 15.5751(9)$ Å, $b = 11.202(1)$ Å, $c =$ 11.9673(6) Å, $\beta = 102.490(1)°$, $V = 2038.6(2)$ Å^3, $Z = 4$, $D_{\mathrm{calcd.}} = 1.582\,\mathrm{g\,cm^{-1}}$, μ (Mo Kα) $= 10.70\,\mathrm{cm^{-1}}$, 2339 unique reflections measured, $R_1 = 0.042$ ($I > 3.2\sigma(I)$), $Rw = 0.106$. For **2**; $C_{23}H_{26}O_7N_4SCo$ (561.47), monoclinic, $P2_1/n$ (No. 14), $a = 9.629(1)$ Å, $b = 16.286(2)$ Å, $c =$ 15.267(2) Å, $\beta = 105.031(4)°$, $V = 2312.3(6)$ Å^3, $Z = 4$, $D_{\mathrm{calcd.}} = 1.613\,\mathrm{g\,cm^{-1}}$, μ (Mo Kα) $= 8.87\,\mathrm{cm^{-1}}$, 4824 unique reflections measured, $R_1 = 0.065$ ($I > 3.0\sigma(I)$), $Rw = 0.153$.

6 The crystallographic and magnetic data for **1** and **2** and the characterized data for **2′** are listed in Supporting Information. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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