Three-Dimensional Polymers with Metal–Oxygen and Metal–Ligand Chains: $[Mn(II)(4,4'\text{-bipy})_2(Cr_2O_7)(H_2O)_2]$ and $[Co(II)(4,4'\text{-bipy})_2(Cr_2O_7)]$

Yoshihito Hayashi,* Tomoko Tagami, Hidesato Mano, and Akira Uehara*
Department of Chemistry, Faculty of Science, Kanazawa University, Kakuma-machi, Kanazawa 920-1192

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Reaction of aqueous solutions of $[M(H_2O)_6](ClO_4)_2$ (M = Mn(II) and Co(II)) and dichromate ion with 4,4'-bipy provides coordination polymers with metal–oxygen chain. The structure of $[Mn(4,4'\text{-bipy})_2(Cr_2O_7)(H_2O)_2]$ reveals the 2D sheet structure which is constructed by hydrogen bonding between 1D chains, while $[Co(4,4'\text{-bipy})_2(Cr_2O_7)]$ shows hybrid 3D polymers which have metal–bipy square grid and the dichromate pillar forms an interpenetrated cuboidal 3D structure.

Inorganic coordination polymers and those novel solid-state structures have been developed to offer the rational strategies for design of new crystalline materials.[1] Especially, bifunctional rod-like molecules of the polypyridine type have been proved to be suitable for 2D and 3D grids network. These porous compounds have cavities to encapsulate guest molecules and show the potential for catalysis. Polyoxometalate-based 3D framework materials have also been investigated recently.[2] To introduce an oxidation ability to the network material, we started to design the hybrid polymers with typical coordination grid by 4,4'-bipy system and with oxometalate chains by dichromate[3] which is known as representative oxidizing reagent. We present here the synthesis and structural characterization of the dichromate-bridged two-dimensional coordination polymer $[Mn(4,4'\text{-bipy})_2(Cr_2O_7)(H_2O)_2]$ (**1**) and higher dimensional interpenetrated polymer $[Co(4,4'\text{-bipy})_2(Cr_2O_7)]$ (**2**).

Compound **1** is prepared as follows: The mixture of 4,4'-bipy (47 mg) and $MnCl_2 \cdot 4H_2O$ (59 mg) in 5 cm^3 of water was heated to 80 °C for 10 min. After addition of $K_2Cr_2O_7$ (88 mg) in 5 cm^3 of hot water, the orange solution was filtered. After a day, the resulting black crystals were collected and washed with hot water then dried. Yields, 30 mg (16%).[4]

The structure of $[Mn(4,4'\text{-bipy})_2(Cr_2O_7)(H_2O)_2]$ **1** (Figure 1) is constructed from the dichromate-bridge linked through $[Mn(4,4'\text{-bipy})_2(H_2O)_2]$ octahedra into a one-dimensional chain.[5] The relative propagation direction of the chain lies parallel to one another. The manganese site is defined by two nitrogen donors from two 4,4'-bipy ligands (Mn1–N1, 2.255(3)), *trans*-oxo groups from dichromate (Mn1–O1, 2.211(3)), and two water molecules (Mn1–O2, 2.143(2)). The conformation of coordinated dichromate is distinct from that of discrete compound $[Mn_2(bipy)_4(Cr_2O_7)_2]$,[6] suggesting that the steric constraints imposed by the 4,4'-bipy ligand are distinct from those of the 2,2'-bipy. The one end of the 4,4'-bipy ligand is coordinated to the manganese center. The other, at the opposite end of the 4,4'-bipy ligand, forms hydrogen bond with the neighboring chain through the coordinated water molecules (N(2)–O(1') = 2.808(3) Å). As a result of two hydrogen bonds between Mn and Mn'(Figure 1), the 2D sheet structure was formed by linking 1D chains.[7] The interplanar separation between those sheets is ca. 5.70 Å. The torsion angle between the bipyridyl ring was 24.8(5)°.

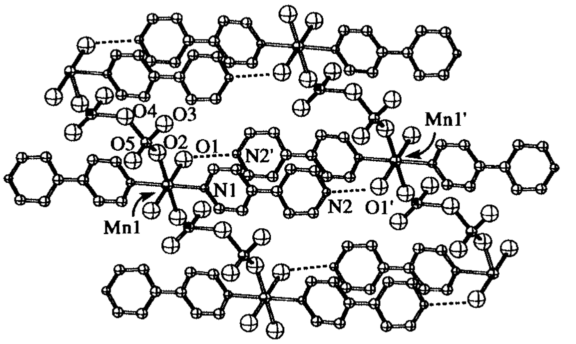

Figure 1. Structure of $[Mn(4,4'\text{-bipy})(H_2O)(Cr_2O_7)]$ (**1**). Selected distances (Å) and angles(°) are as follows: Mn(1)–O(1), 2.211(3); Mn(1)–O(2), 2.143(2); Mn(1)–N(1), 2.255(3); Cr(1)–O(2), 1.628(2); Cr(1)–O(3), 1.541(5); Cr(1)–O(4), 1.819(5); Cr(1')–O(4), 1.792(5); Cr(1)–O(5), 1.47(1); O(1)–N(2'), 2.808(3); O(1)–Mn(1)-O(2), 92.27(8); O(1)–Mn(1)-N(1), 92.67(9); O(2)–Mn(1)-N(1), 90.35(8); Mn(1)–O(2)-Cr(1), 145.7(2); Cr(1)–O(4)-Cr'(1), 132.3(3).

The manganese coordination site occupied by weakly coordinated water molecules suggests that further condensation at the metal center into multi-dimensional polymer should be feasible. In fact, the use of Co(II) in place of Mn(II) ions afforded the 3D-core structure. The synthesis of compound **2** is carried out as follows: The solution of 4,4'-bipy (47 mg) in 20 cm^3 of hot water was mixed with 20 cm^3 of the hot water solution of $CoCl_2 \cdot 6H_2O$ (36 mg). After addition of $K_2Cr_2O_7$ (44 mg) in 20 cm^3 of hot water, the orange mixture was heated for 20 min. After several days, the resulting black crystals were collected and washed with hot water. Yields, 46 mg (51%).[8]

The structure of interpenetrated $[Co(4,4'\text{-bipy})_2(Cr_2O_7)]$ **2** (Figure 2)[9] is constructed from two-fold interpenetrating 3D cuboidal networks. The cobalt atom is in octahedral geometry, being coordinated by two *trans*-oxygen atoms of dichromate (Co1–O1, 2.058(4); Co1–O7, 2.068(4) Å) and four nitrogens of bipy ligands (Co1–N1, 2.226(4); Co1–N2, 2.119(4); Co1–N3, 2.219(4); Co1–N4, 2.142(3) Å). The interesting structural feature in **2** is that the cobalt atoms have been bridged by four 4,4'-bipy and two dichromate ligands to generate an infinite 3D-framework featuring cuboidal $[Co_8(4,4'\text{-bipy})_8(Cr_2O_7)_4]$ structural units with the dimensions of 8.772(1) × 11.367(1) × 11.419(1) Å, as shown in Figure 2(a). The 4,4'-bipy ligands along the axis exhibit a torsion angle of 33.8(2)°, and those in the other direction, a torsion angle of 34.0(2)°.

Compound **2** can be regarded as having been generated from square grid 2D sheets that are cross-linked by dichromate anions like the pillar in clays. Each dichromate was located on the center of the square formed by cobalt atoms and 4,4'-bipy ligands. The interpenetration of $[Co_8(4,4'\text{-bipy})_8(Cr_2O_7)_4]$

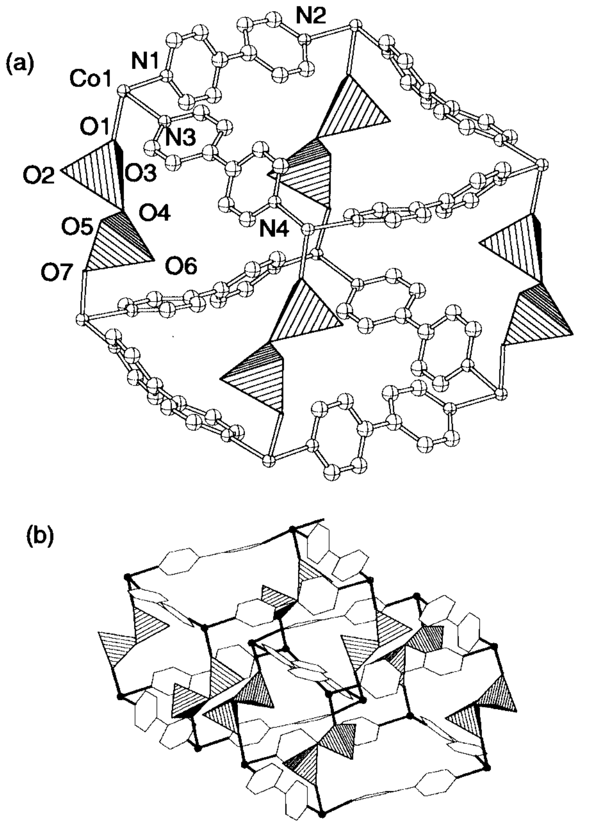

Figure 2. Illustrations for the crystal structure of $[Co(4,4'\text{-bipy})_2Cr_2O_7]$ (**2**). (a) Representation of the cuboidal unit. (b) Representation of interpenetrating structure. Selected distances (Å) and angles(°) are as follows: Co(1)–O(1), 2.058(4); Co(1)–O(7), 2.068(4); Co(1)–N(1), 2.226(4); Co(1)–N(2), 2.119(4); Co(1)–N(3), 2.219(4); Co(1)–N(4), 2.142(3); Cr(1)–O(1), 1.630(4); Cr(1)–O(2), 1.775(3); Cr(1)–O(3), 1.605(4); Cr(1)–O(4), 1.583(4); O(1)–N(2'), 2.808(3); O(1)–Co(1)-O(7), 175.7(2); Co(1)–O(1)-Cr(1), 158.0(3); Cr(1)–O(4)-Cr(2), 128.6(3).

cubes is illustrated in Figure 2(b). No special contact between two independent frameworks of interpenetration was observed. The relative position of Co_8 cube interpenetration is parallel to each other, and the similar twofold interpenetration has been reported by using terephthalate(tp) ligand, [M(tp)(4,4'-bipy)].[10] It is noted that diagonal interpenetration of 2D sheet has been common in planar (4,4) networks.[11]

We also examined the temperature dependence of the bond parameters to estimate the thermal expansion behavior of the cuboidal framework.[12] At –150 °C, the dimension of the $[Co_8(4,4'\text{-bipy})_8(Cr_2O_7)_4]$ cube was shrunk. The Co–Co distances between dichromate bridge were shrunk for more than 0.11 Å.[13] The Co–Co distances bridged by 4,4'-bipy ligands were almost identical (11.358 and 11.420 Å). In a simple picture, the coordination grid by 4,4'-bipy ligands is relatively stiff (stronger M–N bonds and constant lengths of organic components) but the dichromate pillars are joined by relatively loose hinges. The relative position of the interpenetration was not changed and no phase transfer to break the inversion center on the center of the interpenetration was observed in the temperature range of –150 to 25 °C.

In summary, the dichromate-bridged 3D polymer has been prepared, which represents the first example of dichromate pillared structures containing cobalt-bipy square grid layers.

References and Notes

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4 Anal. Calcd for $[Mn(4,4'\text{-bipy})_2(Cr_2O_7)(H_2O)_2]$: C, 38.78; H, 3.25; N, 9.05%. Found: C, 38.74; H, 3.18; N, 9.04%. IR (KBr, 500–1100 cm^{-1}): 960 (s, br), 929 (s, sh), 873 (m), 811 (m), 783 (m), 673, 624, 574, 484.

5 Crystal data for **1**: fw = 619.3, triclinic, space group $P\bar{1}$, a = 8.263(1), b = 10.259(1), c = 7.5042(7) Å, α = 94.008(9)°, β = 109.022(8)°, γ = 82.75(1)°, V = 596.3(1) $Å^3$, Z = 1, Mo Kα radiation (λ = 0.71070 Å), T = 24 °C. R_1 = 0.037 (wR_2 = 0.058) for 2100 independent reflections (R_{int} = 0.011) with $I > 3\sigma(I)$ and 178 parameters. Highest residual electron density 0.47 $e \cdot Å^{-3}$. The O4 and O5 atoms were disordered over two positions with a site occupancy ratio 0.5/0.5.

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8 Anal. Calcd for $[Co(4,4'\text{-bipy})_2(Cr_2O_7)]$: C, 40.9; H, 2.75; N, 9.54%. Found: C, 40.09; H, 2.78; N, 9.39%. IR (KBr, 500–1100 cm^{-1}): 958 (s, br), 935 (s, sh), 889 (m), 860 (m), 812 (m), 758, 733, 671, 633.

9 Crystal data for **2**: fw = 587.3, monoclinic, space group $C2/c$, a =21.518(2), b = 15.304(1), c = 16.881(2) Å, β = 127.300(2)°, V = 4422.1(8) $Å^3$, Z = 8, Mo Kα radiation (λ = 0.71070 Å), T = 24 °C. R_1 = 0.069 (wR_2 = 0.103) for 3416 independent reflections with $I > 3\sigma(I)$ and 307 parameters. Highest residual electron density 0.48 $e \cdot Å^{-3}$.

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12 Crystal data for **2**: fw = 1396.9, monoclinic, space group $C2/c$, a = 21.3569(3), b = 15.3164(2), c = 16.8602(2) Å, β = 127.402(1)°, V = 4381.2(1) $Å^3$, Z = 4, Mo Kα radiation (λ = 0.71070 Å), T = –150°C. R_1 = 0.052 (wR_2 = 0.076) for 3366 independent reflections with $I > 3\sigma(I)$ and 307 parameters. Highest residual electron density 0.83 $e \cdot Å^{-3}$.

13 The thermal expansion factor has been estimated as: $\alpha_l = (l_T - l_{T_o})/l_o(T - T_o) = 4.7 \times 10^{-5}\ K^{-1}$.