Molecular-assembled Complexes of Mixed-valent Ruthenium Dimer with Hexacyanoferrate(III) and Hexacyanocobaltate(III) Ions

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The three-dimensional coordination polymers, $[\{Ru_2(piv)_4\}_3(H_2O)M(CN)_6]$ [M=Fe (**1**) and Co (**2**), Hpiv = pivalic acid], have been synthesized and characterized by X-ray crystallography, electronic spectroscopy and magnetic susceptibility measurement.

Cyano-bridged metal complexes have been subjected to intensive study for the past decades. Using a hexacyanometalate ion as building block in combination with another paramagnetic metal ion is now an attractive approach to build molecular based magnetic materials.[1] We are interested in extending this approach to dinuclear metal-metal bond systems, since the metal-metal bond has many electrons which might be available for enhanced magnetic interaction. An earlier attempt to obtain such compounds produced diamagnetic one because both the dinuclear metal unit and the hexacyano metalate ion have not any unpaired electrons.[2] Our strategy is to use paramagnetic ruthenium(II,III) dinuclear system which has 3/2 spins in their metal-metal bonding.[3a] So far, we prepared dinuclear, tetranuclear, and polynuclear adducts by the use of organic bridging groups such as nitronyl nitroxide radicals,[3] tcnq (7,7,8,8-tetracyano-quinodimethane),[4] and quinone[5] molecules. In these adducts, the organic bridging group occupies the axial position of the ruthenium dimer and the magnetic interaction with the ruthenium(II,III) spins is mostly antiferromagnetic except for the ferromagnetic chain compound with the pyridyl nitronyl nitroxide.[3c] It might be possible that these spins interact ferrimagnetically if the paramagnetic hexacyanometalate ions and the ruthenium dimers bearing different numbers of spins are arranged alternately. Therefore, we have prepared new adducts of ruthenium(II,III) carboxylate dimers by introducing hexacyanoferrate(III) and hexacyanocobaltate(III) bridges. We report here the first example of mixed-metal complexes containing paramagnetic metal-metal bonds, $[\{Ru_2(piv)_4\}_3(H_2O)M(CN)_6]$ (M=Fe (**1**) and Co (**2**), Hpiv = pivalic acid).

Reaction of $[Ru_2(piv)_4(H_2O)_2]BF_4$ with potassium hexacyanoferrate(III) results in the formation of **1** as a yellow brown powder.[6] Similarly, treatment of $[Ru_2(piv)_4(H_2O)_2]BF_4$ with potassium hexacyanocobaltate(III) led to red brown powder.[7] Analytical data of these complexes are consistent with the formulation of heteronuclear species, **1**•$2H_2O$ and **2**•$2H_2O$.[6,7] Infrared spectra of **1**•$2H_2O$ and **2**•$2H_2O$ show a sharp CN stretching band at 2115 or 2126 cm^{-1}, respectively, which is close to those of $K_3[M(CN)_6]$ (M=Fe, Co).[8] The *syn-syn* bridging mode of the carboxylato groups can be also confirmed by the infrared spectra [**1**•$2H_2O$, $\nu_{as}(COO)$ 1488, $\nu_s(COO)$ 1420 cm^{-1}; **2**•$2H_2O$, $\nu_{as}(COO)$ 1488, $\nu_s(COO)$ 1420 cm^{-1}].[8] Diffuse reflectance spectra of these complexes show a distinctive band at 451 (for **1**•$2H_2O$) and 447 (for **2**•$2H_2O$) nm, which is characteristic of ruthenium(II,III) carboxylate dimer core,[9] and a shoulder band at around 620 nm for **1**•$2H_2O$, which can be assigned to δ–δ^* transition band, although this shoulder band is obscured by the strong band at 447 nm in the case of **2**•$2H_2O$.

It was hard to grow crystals for this system. After many efforts, diffusion of DMF solution of $[Ru_2(piv)_4(H_2O)_2]BF_4$ and aqueous solution of potassium hexacyanoferrate(III) gave brown crystals, **1**•$4H_2O$ and **2**•$4H_2O$. The X-ray crystallographic studies show that the crystal structures of **1**•$4H_2O$ and **2**•$4H_2O$ are isostructural, although the former did not give a good-quality data.[10] A perspective view of the structure of **1**•$4H_2O$ is shown in Figure 1. The Fe1 atom is located on a four-fold axis and the $Fe(CN)_6^{3-}$ anion has an almost regular octahedral geometry. The Fe1 center uses four cyano groups (C2–N2) within the *ab* plane to connect the Ru atoms (Ru3) of the $Ru_2(piv)_4$ dimer units, giving rise to a two-dimensional sheet made up of 28-membered [-Fe-CN-Ru_2-NC-]$_4$ rings (Figure 2), while one (C1–N1) of the remaining two *trans*-cyano ligands coordinates to the Ru atom

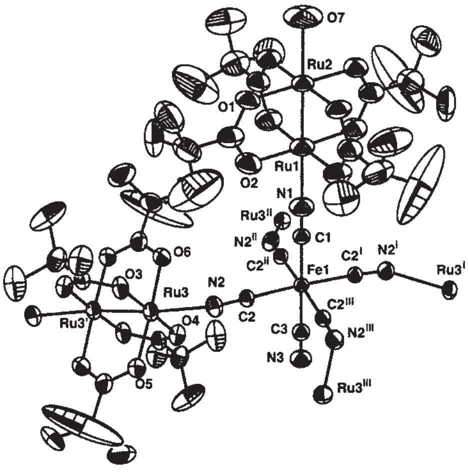

Figure 1. Perspective view of **1**•$4H_2O$. Hydrogen atoms of pivalate are omitted for clarity. Selected bond distances (l/Å) and angles (ϕ/°): Ru1–Ru2 2.273(5), Ru3–Ru3′ 2.292(3), Ru1···Fe1 5.322(11), Ru3···Fe1 5.153(8), Ru1–N1 2.219(13), Ru1–O2 2.020(8), Ru2–O1 2.009(7), Ru2–O7 2.254(13), Ru3–N2 2.267(7), Ru3–O3 2.029(6), Ru3–O4 2.008(6), Ru3–O5 2.015(6), Ru3–O6 2.010(6), Fe1–C1 1.952(12), Fe1–C2 1.960(7), Fe1–C3 1.945(14), C1–N1 1.150(17), C2–N2 1.132(8), C3–N3 1.136(18); Ru3–N2–C2 149.8(5), N2–Ru3–Ru3′ 167.63(17), Fe1–C2–N2 176.6(6). i: $-x + 1/2$, $-y + 1/2$, z; ii: $-y + 1/2$, x, z; iii: y, $-x + 1/2$, z.

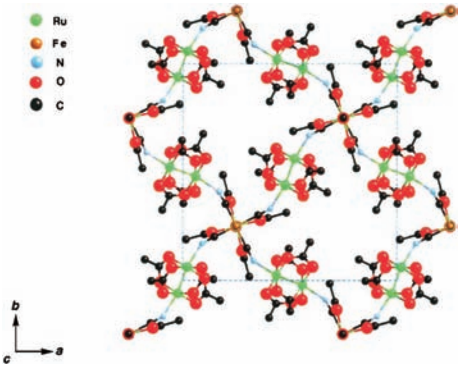

Figure 2. Extended structure of **1**•4H_2O. The view is along the *c* axis. Methyl groups and H atoms are omitted for clarity.

(Ru1) of the $Ru_2(piv)_4$ dimer unit and the other is terminal (C3–N3) along the *c* direction. The complex has two types of dinuclear ruthenium(II,III) units, one is axially coordinated by two cyano groups, the other by cyano group and water molecule. The former has the crystallographic inversion center at the center of the Ru_2 core (Ru3–Ru3′), and the latter has the four-fold axis along the Ru1–Ru2 bond. The Ru–Ru distances (Ru3–Ru3′ 2.292(3), Ru1–Ru2 2.273(5) Å) are comparable to those of ruthenium(II,III) carboxylate dimers.[3–5] The Ru3–N2 and Ru1–N1 distances are 2.267(7) and 2.219(13) Å, respectively. The Ru3–N2–C2 angle is 149.8(5)°, whereas the Ru1–N1–C1 angle is 180°. In the crystal, the nitrogen atom (N3) of the terminal CN group is hydrogen-bonded to the neighboring water molecule coordinated to the ruthenium atom of the neighboring carboxylate dimer [N3···O7 $(x, y, 1+z)$, 2.610(2) Å] to link the two-dimensional sheets into a three-dimensional network through extensive hydrogen bondings. We believe that the powder samples of **1**•2H_2O and **2**•2H_2O have almost the same three-dimensional network to the present crystal structures.

The temperature dependence of the magnetic susceptibilities of **1**•2H_2O and **2**•2H_2O was measured in the range 4.5–300 K. The effective magnetic moment for **1**•2H_2O (7.52 μ_B per $(Ru_2)_3Fe$ unit at 300 K) is a little higher than the spin-only value (6.93 μ_B) for noninteracting three 3/2 spins and one 1/2 spin. The magnetic moment gradually decreases with lowering of temperature and reaches a minimum value around 20 K (Figure 3). Upon further cooling, the magnetic moment increases abruptly, reaching a maximum value of 10.34 μ_B at 8 K, and then decreases. This type of variation of the μ_{eff} vs temperature suggests a ferrimagnetic behavior of **1**•2H_2O with a $Ru_2^{II,III}$–Fe^{III} antiferromagnetic interaction. Above 100 K the magnetic susceptibility data can be fitted to the Curie–Weiss expression $\chi_M = C/(T - \theta)$ with $\theta = -34.8$ K, which is consistent with the presence of the antiferromagnetic coupling. On the other hand, the antiferromagnetic behavior is expected for **2**•2H_2O, because the hexacyanocobalt(III) moieties are diamagnetic low-spin d^6 and the $S = 3/2$ spins of the $Ru_2(piv)_4$ units can interact through the hexacyanocobalt(III) bridges each other. The effective magnetic moment for **2**•2H_2O (7.44 μ_B per molecule at 300 K) is a little higher than the spin-only value (6.71 μ_B) for noninteracting three 3/2 spins. The magnetic moment monotonically decreases with lowering of temperature and reaches a value of 5.72 μ_B at 4.5 K. The magnetic susceptibility data above 10 K can be fitted to the Curie–Weiss expression with $\theta = -23.0$ K, which also proves the presence of antiferromagnetic coupling in **2**•2H_2O, although zero-field splitting contribution is not considered in this expression.[3a] The present results show that the combination of dinuclear unit and hexacyanometalate ion is important to produce a designed magnetic property. Further studies are now in progress.

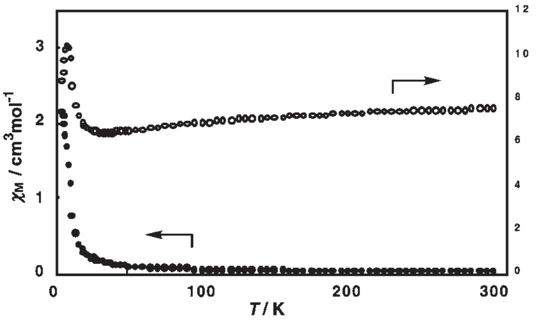

Figure 3. Temperature dependence of magnetic moment (○) and magnetic susceptibility (●) of **1**•2H_2O.

References and Notes

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6 $[Ru_2(O_2CCMe_3)_4(H_2O)_2]BF_4$ (50 mg, 69 mmol) was dissolved in methanol (10 cm^3), then added an aqueous solution (10 cm^3) of potassium hexacyanoferrate(III) (23 mg, 70 mmol) with stirring. After stirring for 3 h, yellow brown precipitate was filtered and washed with methanol/water (1 : 1), followed by drying in vacuo. Yield 26 mg (54%). Found: C, 37.98; H, 5.22; N, 4.08%. Calcd for $C_{66}H_{114}FeN_6O_{27}Ru_6$ C, 37.99; H, 5.51; N, 4.03%. IR (KBr, cm^{-1}): ν_{as}(COO) 1488, ν_s(COO) 1420, ν(CN) 2115.

7 Compound **2** was prepared in the same way as that for **1**, except for using potassium hexacyanocobaltate(III) instead of potassium hexacyanoferrate(III). Yield, 23 mg (33%). Found: C, 37.99; H, 5.30; N, 4.01%. Calcd for $C_{66}H_{114}CoN_6O_{27}Ru_6$ C, 37.94; H, 5.50; N, 4.02%. IR (KBr, cm^{-1}): ν_{as}(COO) 1488, ν_s(COO) 1420, ν(CN) 2126.

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10 Crystallographic data: for **1**·4H_2O; $C_{66}H_{118}FeN_6O_{29}Ru_6$, fw = 2121.93, tetragonal, space group *P*4/*n*, $a = 17.23(3)$, $c = 15.54(3)$ Å, $V = 4616(14)$ Å^3, $Z = 2$, $D_m = 1.49$, $D_{calcd} = 1.53$ g cm^{-3}, μ(Mo Kα) = 11.79 cm^{-1}, crystal dimensions 0.28 × 0.15 × 0.07 mm^3, 25992 reflections measured ($2\theta_{max} = 53.34°$), 3158 [$I \geq 2\sigma(I)$] used in the refinement, $R1 = 0.1047$, $wR2 = 0.2448$. For **2**•4H_2O; $C_{66}H_{118}CoN_6O_{29}Ru_6$, fw = 2125.01, tetragonal, space group *P*4/*n*, $a = 17.176(9)$, $c = 15.494(12)$ Å, $V = 4571(5)$ Å^3, $Z = 2$, $D_m = 1.52$, $D_{calcd} = 1.54$ g cm^{-3}, μ(Mo Kα) = 12.14 cm^{-1}, crystal dimensions 0.25 × 0.25× 0.10 mm^3, 19899 reflections measured ($2\theta_{max} = 46.62°$), 2412 [$I \geq 2\sigma(I)$] used in the refinement, $R1 = 0.0454$, $wR2 = 0.1095$. Intensity data were collected on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation. All the structures were solved by the direct method and refined by the full-matrix least-squares method using the SHELXTL software package.