Self-assembly of Mixed-valent Ruthenium(II,III) Pivalate and Octacyanotungstate(V) Building Blocks

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One-dimensional coordination polymer of $[Ru_2(piv)_4(\mu\text{-}CN)W(CN)_7]_n^{2n-}$ (Hpiv = pivalic acid) has been synthesized in the presence of PPh_4^+. The X-ray crystal structure reveals an alternating arrangement of ruthenium(II,III) dimers and $[W(CN)_8]^{3-}$ ions in a 1-D chain. The magnetic susceptibility data (4.5–300 K) shows a ferrimagnetic behavior of this complex.

Dinuclear ruthenium carboxylates with "paddle wheel" structures have been subjected to intensive study for the past three decades because of their unique properties.[1] These dinuclear ruthenium carboxylates, especially, mixed-valent ruthenium(II,III) dimers exhibit two axial labile sites as well as a higher spin state of three unpaired electrons ($S = 3/2$) that might be available for enhanced magnetic properties.[2–5] On the other hand, cyanometalates have attracted much interest due to their useful applications in the field of molecule-based magnetism.[6] Therefore, Ru_2 carboxylates and cyanometalates make a good combination for supramolecular assembly to produce new coordination polymers with unique structures and interesting magnetic properties. As the first stage of such studies, we prepared metal-assembled complexes of $Ru_2^{II,III}$ pivalate dimer with hexacyanometalate ions $[M(CN)_6]^{3-}$ (M = Fe and Co) and found a ferrimagnetic behavior for $[Ru_2(piv)_4]_3[Fe(CN)_6]$.[5a] The analogous systems with ruthenium(II,III) acetate, $[Ru_2(CH_3COO)_4]_3[M(CN)_6]$ (M = Cr, Fe, Co, and Mn) were characterized magnetically.[5b,5c] In order to fully utilize the magnetic potentialities of $Ru_2^{II,III}$ dimers in combination with cyanometalates and develop this type of molecule-based magnetic materials, we have examined octacyanometalate building blocks for our systems. The $[M(CN)_8]^{3-/4-}$ ions (M = Mo and W) were successfully used for the self-assembly of supramolecular 0-D, 1-D, 2-D, and 3-D coordination compounds.[7] Herein, we report the synthetic strategy, structure, and magnetic properties of the $Ru_2^{II,III}$–W^V chain system formed in the reaction of $[Ru_2(piv)_4]^+$ and $[W(CN)_8]^{4-}$ precursors.

When the reaction was performed under an equimolar stoichiometry of Ru_2:W, we obtained green precipitate which could not be crystallized. The IR spectrum exhibited a weak ν(CN) band of $[W(CN)_8]^{3-}$ together with strong ν_{as}(COO) and ν_s(COO) bands of $[Ru_2(piv)_4]^+$, suggesting a very low ratio of W:Ru_2 for this sample. Therefore, we treated $[Ru_2(piv)_4(thf)_2]BF_4$ with excess amount of $K_4[W(CN)_8]\cdot 2H_2O$ in water in the presence of PPh_4^+, resulting in the deposition of orange microcrystals.[8] The analytical data were consistent with the formulation of heterometallic $(PPh_4)_2[Ru_2(piv)_4(\mu\text{-}NC)W(CN)_7]\cdot 5H_2O$ ($\mathbf{1}\cdot 5H_2O$). The introducing of nonstraightforward Ru_2:W stoichiometry (1:10) together with appropriate counter cations (PPh_4^+) allowed the self-assembly process to the desired alternating Ru_2–W 1-D chain structure.

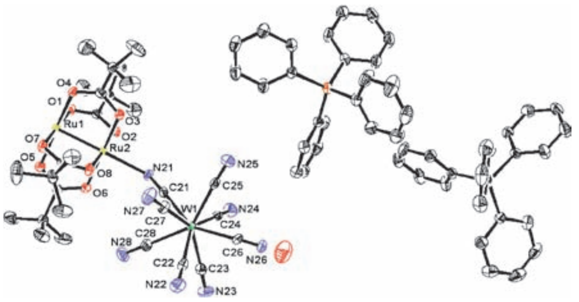

Figure 1. ORTEP drawing for the asymmetric part of the unit cell of $\mathbf{1}\cdot 0.5H_2O$ showing 30% probability ellipsoids. H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ru1–Ru2 2.2852(6), Ru1–O1 2.035(4), Ru1–O4 2.035(4), Ru1–O5 2.028(4), Ru1–O7 2.015(4), Ru1–N26 2.273(5), Ru2–O2 2.029(4), Ru2–O3 2.016(4), Ru2–O6 2.002(4), Ru2–O8 2.026(4), Ru2–N21 2.266(4); Ru1–Ru2–N21 172.2(1), Ru2–Ru1–N26′ 174.3(1), Ru1–N26′–C26′ 164.0(5), W1–C26–N26 177.9(5).

The IR spectrum of $\mathbf{1}\cdot 5H_2O$ shows a sharp ν(CN) band at 2148 cm^{-1} which indicates relatively high symmetry of $[W(CN)_8]^{3-}$. The spectrum also contains two distinctive ν_{as}(COO) and ν_s(COO) bands of syn-syn-bridging carboxylato group at 1485 and 1417 cm^{-1}, respectively, confirming the preserving of the $[Ru_2(piv)_4]^+$ core.[3b] The diffuse reflectance spectrum of $\mathbf{1}\cdot 5H_2O$ exhibits a $\delta(Ru_2) \rightarrow \delta^*(Ru_2)$ transition band at 1039 nm with a red shift from that of $[Ru_2(piv)_4(H_2O)_2]BF_4$, being the result of the axial coordination of the nitrogen atom of the cyano group.[3b] The red prismatic crystals of $\mathbf{1}\cdot 0.5H_2O$, suitable for X-ray crystallography, were grown by slow diffusion of aqueous solutions of $[Ru_2(piv)_4(thf)_2]BF_4$ and $K_4[W(CN)_8]\cdot 2H_2O$ with PPh_4Cl in an H-tube over four days in the dark at 18 °C.[9] A perspective view of the asymmetric part is presented

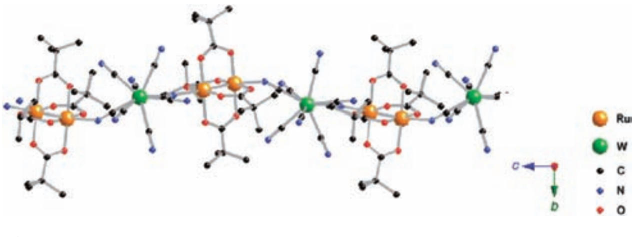

Figure 2. Projection of zigzag chain of $\mathbf{1}\cdot 0.5H_2O$ on *bc* plane. PPh_4^+ cations, water molecules, and H atoms are omitted for clarity.

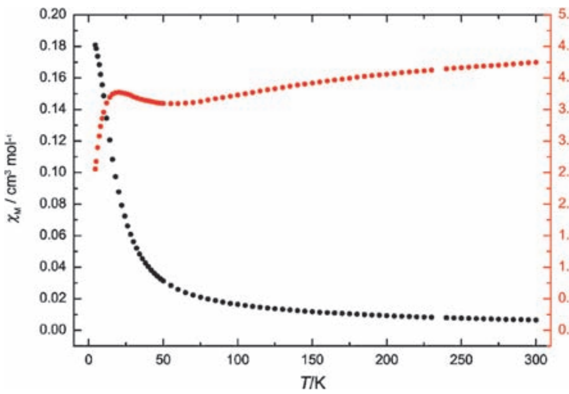

Figure 3. Temperature dependence of effective magnetic moment (in red) and magnetic susceptibility (in black) of **1**$\cdot 5H_2O$.

in Figure 1. The coordination geometries of Ru (Ru1 and Ru2) and W sites are axially elongated octahedron and square antiprism, respectively. The Ru–Ru bond length (2.2852(6) Å) is similar to those found for other ruthenium(II,III) carboxylate dimers. The W–C–N angles are nearly linear with a mean value of 178.7° and maximum deviation from the linearity no longer than 2.6°. The average values of W–C and C–N bond distances are 2.17 and 1.14 Å which are typical for cyano-bridged assemblies based on octacyanometalates. Two cyano ligands of each octacyanotungstate(V) (N21–C21 and N26–C26) coordinate to the adjacent Ru_2 clusters forming a 1-D zigzag chain propagating along $[10\bar{1}]$ lattice vector (Figure 2). Both cyano bridges are significantly bent (C21–N21–Ru2 angle $= 152.8(4)°$ and C26′–N26′–Ru1 angle $= 164.0(5)°$) and the closest intrachain metallic distances, Ru···W are equal to 5.42 and 5.54 Å, respectively. Since these chains are separated from each other by bulky aromatic cations, the corresponding interchain distances (M···M) are considerably longer with values exceeding 10 Å. This is the first example of structurally characterized cyano-bridged polymer based on mixed-valent $Ru_2^{II,III}$ dimers and octacyanometalate precursors.

The effective magnetic moment for **1**$\cdot 5H_2O$ at 300 K (4.25 μ_B) is comparable to the expected spin-only value (4.24 μ_B) for uncoupled 3/2 (for $Ru_2^{II,III}$) and 1/2 spins (for W^V). Upon cooling, the magnetic moment gradually decreases to a minimum value of 3.59 μ_B at 55 K, then increases reaching the maximum value of 3.77 μ_B at 20 K, and upon further cooling, it finally decreases (Figure 3). This type of μ_{eff} temperature dependence indicates a ferrimagnetic behavior of **1**$\cdot 5H_2O$ with a antiferromagnetic interaction between $Ru_2^{II,III}$ and W^V centers through the cyano bridge. The Curie–Weiss plot, $\chi_M = C/(T - \theta)$, above 100 K forms a straight line with a negative Weiss constant of $\theta = -57(1)$ K, supporting the ferrimagnetism. It is to be noted that the increase in μ_{eff} begins at 55 K when the temperature is lowered, which is much higher than those (2.1 and 20 K) for the 2-D and 3-D polymers of $[Ru_2(RCOO)_4]_3[Fe(CN)_6]$ (R = CH_3 and $(CH_3)_3C$) having similar 3/2–1/2 spin systems.[5] This may be due to the larger θ value of **1**$\cdot 5H_2O$ (cf. $\theta = -34.8$ K for $[Ru_2((CH_3)_3CCOO)_4]_3[Fe(CN)_6]^{5a)}$). The stronger antiferromagnetic interaction could be induced by the introduction of $W(CN)_8$ which has a large diffusion of the 5d magnetic orbitals. The decrease below 20 K may come from the large zero-field splitting of the present complex.

Further work on the construction of supramolecular systems based on Ru_2 clusters and octacyanometalates is now in progress.

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References and Notes

1 a) F. A. Cotton and R. A. Walton, "Multiple Bonds between Metal Atoms," 2nd ed., Oxford Univ. Press, New York (1993). b) M. A. S. Aquino, *Coord. Chem. Rev.*, **170**, 141 (1998). c) M. A. S. Aquino, *Coord. Chem. Rev.*, **248**, 1023 (2004).

2 a) M. Handa, Y. Sayama, M. Mikuriya, R. Nukada, I. Hiromitsu, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **71**, 119 (1998). b) Y. Sayama, M. Handa, M. Mikuriya, I. Hiromitsu, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **73**, 2499 (2000). c) Y. Sayama, M. Handa, M. Mikuriya, I. Hiromitsu, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **76**, 769 (2003).

3 a) F. D. Cukiernik, A.-M. G.-Godquin, R. Maldivi, and J.-C. Marchon, *Inorg. Chim. Acta*, **215**, 203 (1994). b) D. Yoshioka, M. Mikuriya, and M. Handa, *Bull. Chem. Soc. Jpn.*, **77**, 2205 (2004).

4 a) H. Miyasaka, C. S. C.-Fernandez, R. Clerac, and K. R. Dunbar, *Angew. Chem., Int. Ed.*, **39**, 3831 (2000). b) H. Miyasaka, R. Clerac, C. S. C.-Fernandez, and K. R. Dunbar, *Inorg. Chem.*, **40**, 1663 (2001).

5 a) D. Yoshioka, M. Mikuriya, and M. Handa, *Chem. Lett.*, **2002**, 1044. b) Y. Liao, W. W. Shum, and J. S. Miller, *J. Am. Chem. Soc.*, **124**, 9336 (2002). c) T. E. Vos, Y. Liao, W. W. Shum, J.-H. Her, P. W. Stephens, W. M. Reiff, and J. S. Miller, *J. Am. Chem. Soc.*, **126**, 11630 (2004).

6 M. Pilkington and S. Decurtins in "Comprehensive Coordination Chemistry II: from Biology to Nanotechnology," ed. by J. A. McCleverty and T. J. Meyer, Elsevier, Oxford (2004), Vol. 7, Chap. 7.4, p 177.

7 a) T. Kashiwagi, S. Ohkoshi, H. Seino, Y. Mizobe, and K. Hashimoto, *J. Am. Chem. Soc.*, **126**, 5024 (2004). b) T. Korzeniak, K. Stadnicka, M. Rams, and B. Sieklucka, *Inorg. Chem.*, **43**, 4811 (2004). c) P. Przychodzen, K. Lewinski, M. Balanda, R. Pelka, M. Rams, T. Wasiutynski, C. Guyard-Duhayon, and B. Sieklucka, *Inorg. Chem.*, **43**, 2967 (2004).

8 Synthesis of **1**$\cdot 5H_2O$: $K_4[W(CN)_8]\cdot 2H_2O$ (209.3 mg, 0.358 mmol) was dissolved in water (40 cm^3) and the aqueous solution (40 cm^3) of $[Ru_2(piv)_4(thf)_2]BF_4$ (30.0 mg, 0.0358 mmol) was added with stirring. Then aqueous solution of PPh_4Cl (28.2 mg, 0.752 mmol) was successively added. The resulting orange precipitate was filtered off, washed with water, and dried in vacuo. During the synthesis, the solution was protected from light due to the photosensitivity of octacyanotungstate(IV). Yield, 34 mg (58%). Found: C, 51.39; H, 4.18; N, 6.53%. Calcd for $C_{76}H_{86}N_8O_{13}P_2Ru_2W$: C, 51.65; H, 4.90; N, 6.34%. Diffuse reflectance spectrum: 257, 379, 428, 476, and 1039 (br).

9 Crystal data for **1**$\cdot 0.5H_2O$: $C_{76}H_{77}N_8O_{8.5}P_2Ru_2W$, $M_r = 1686.39$, monoclinic, space group $P2_1/n$, $a = 13.866(2)$, $b = 25.341(4)$, $c = 20.971(3)$ Å, $\beta = 93.641(3)°$, $V = 7354.0(18)$ Å^3, $T = 291(2)$ K, $Z = 4$, $D_{calcd} = 1.523$ Mg m^{-3}, $\mu = 2.070$ mm^{-1}, 45553 reflections measured, 17030 unique ($R_{int} = 0.0432$), 12978 observed [$I > 2\sigma(I)$] used in the refinement. The data were collected on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo Kα radiation. All the calculations were performed using SHELXTL software package. The final refinement gave: $R1 = 0.0542$ and $wR2 = 0.0928$ [for 12978 reflections with $I > 2\sigma(I)$].

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