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Magnetic Material Based on Mixed-Valent Dinuclear Pivalate and Cyanidometalate

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Mixed-metal complex consisting of ruthenium(II,III) pivalate, $[\text{Ru}_2(\text{piv})_4]^+$ (Hpiv = pivalic acid), tetraethylammonium and octacyanidotungstate(V) ions, $(\text{Et}_4\text{N})\{[\text{Ru}_2(\text{piv})_4]_2\text{W}(\text{CN})_8\} \cdot 4\text{H}_2\text{O}$, was synthesized and characterized by elemental analysis, infrared and UV-vis spectra and temperature dependence of magnetic susceptibilities (2–300 K). The magnetic susceptibilities, zero-field-cooled and field-cooled magnetizations, and AC susceptibility data showed that the present complex is ferrimagnetic with T_c value of 80 K. The field dependence of magnetization exhibited a hysteresis with a coercive field of 17000 Oe at 5 K.

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1. Introduction

Lantern-type metal carboxylates such as copper(II) acetate have attracted much attention for the past six decades because of their dinuclear core made up by four carboxylate-bridges and unique properties [1, 2]. In case of ruthenium, mixed-valent dinuclear ruthenium(II)–ruthenium(III) state is stable and the $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ carboxylates, $[\text{Ru}_2(\text{O}_2\text{CR})_4]^+$, afford a 3/2 spin system [1, 3–5]. This 3/2 spin system can be considered as a good spin source for molecular magnetic materials [5–26]. In order to understand the magnetic properties of these compounds, systematic investigations were needed for mixed-metal complexes based on dinuclear ruthenium carboxylates and cyanidometalate ions. Recently, we reported on magnetic properties of mixed-metal complexes of dinuclear ruthenium(II,III) carboxylates with dicyanidoargentate(I) $\text{Ag}(\text{CN})_2^-$ [23], tetracyanonickelate(II) $\text{Ni}(\text{CN})_4^{2-}$ [24], and tetracyanoplatinate(II) $\text{Pt}(\text{CN})_4^{2-}$ [25, 26] and hexacyanidocobaltate(III) $\text{Co}(\text{CN})_6^{3-}$ [17]. These compounds showed a weak antiferromagnetic interaction between 3/2 spins of dinuclear ruthenium units through the cyanidometalate groups. On the other hand, mixed-metal systems with hexacyanidoferrate(III) $\text{Fe}(\text{CN})_6^{3-}$ [17–20], hexacyanidochromate(III) [19, 20] and octacyanidotungstate(V) $\text{W}(\text{CN})_8^{3-}$ [21, 22] show a ferrimagnetic behavior. It should be noticeable that mixed-metal complex $[\{\text{Ru}_2(\text{piv})_4\}_3(\text{H}_2\text{O})\text{W}(\text{CN})_8]$ of ruthenium pi-

valate $[\text{Ru}_2(\text{piv})_4]^+$ (H-piv = pivalic acid) with octacyanidotungstate $[\text{W}(\text{CN})_8]^{3-}$ has a high T_c value of 44 K, whereas an analogous mixed-metal complex $(\text{PPh}_4)_2[\text{Ru}_2(\text{piv})_4\text{W}(\text{CN})_8]$ with octacyanidotungstate and tetraphenylphosphonium ion did not show a ferrimagnetic behavior [22]. In this regard, the presence of tetraphenylphosphonium cation may be a key factor determining the magnetic properties in the mixed-metal systems. In this study, we synthesized new mixed-metal complex of ruthenium(II)–ruthenium(III) pivalate and octacyanidotungstate as shown in Fig. 1 by using tetraethylammonium ion (Et_4N^+) as a cation in the hope of obtaining new magnetic materials. The isolated mixed-metal complex $(\text{Et}_4\text{N})\{[\text{Ru}_2(\text{piv})_4]_2\text{W}(\text{CN})_8\} \cdot 4\text{H}_2\text{O}$ (1) was characterized by using elemental analysis, infrared and UV-vis spectroscopies, and temperature dependence of magnetic susceptibilities.

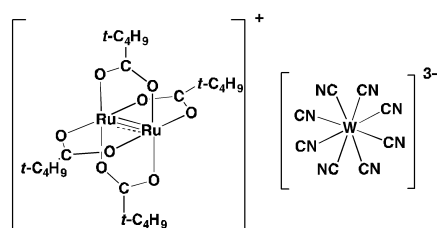


Fig. 1. Chemical structures of $[\text{Ru}_2(\text{piv})_4]^+$ (left) and $[\text{W}(\text{CN})_8]^{3-}$ (right).

2. Experimental details

2.1. Materials

Tetrafluoroborate of dinuclear ruthenium(II,III) and potassium octacyanidotungstate(IV) were prepared by a

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method described in the literature [11, 22]. All of other reagents were commercially available and used as received.

2.2. Synthesis of $(Et_4N)[\{Ru_2(piv)_4\}_2W(CN)_8] \cdot 4H_2O$

To an aqueous solution (7 ml) of $K_4W(CN)_8 \cdot 2H_2O$ (21 mg, 0.036 mmol), an aqueous solution (7 ml) of $[Ru_2(piv)_4(H_2O)_2]BF_4$ (30 mg, 0.23 mmol) and aqueous solution (7 ml) of Et_4NCl (36 mg, 0.05 mmol) were added. The reaction mixture was stirred overnight in the dark, the resulting brown precipitate was filtered off, washed with water and dried in vacuum. Yield, 22.3 mg (52%). Analytically found: C, 37.43; H, 5.50; N, 6.21%. Calculated for $C_{30}H_{44}N_2O_8Ru_2W$: C, 37.21; H, 5.58; N, 6.97%. IR (KBr, cm^{-1}): 1581 ($\nu_{as}COO$), 1417 (ν_sCOO). Diffuse reflectance spectra: λ_{max} 273, 437, 574, and 1026 nm.

2.3. Characterization

Infrared spectra were recorded on a JASCO MFT-2000 spectrometer as a KBr pellet. Solid-state UV-Vis spectra were recorded in the range of 200–2000 nm on a Shimadzu UV-3100 spectrophotometer (reflection method). Elemental analyses were performed on a Thermo Finnigan FLASH EA1112 analyzer. DC and AC magnetic data were measured using a Quantum Design MPMS XL SQUID magnetometer. The magnetic measurements were carried out at University Claude Bernard Lyon 1 on polycrystalline samples. To avoid orientation in the magnetic field, the samples were pressed in a home-made Teflon sample holder equipped with a piston. The data were corrected for diamagnetism of the sample holder and the constituent atoms using Pascal's constants [27].

3. Results and discussion

Elemental analysis of the isolated complex showed the 1:2:1 ($Et_4N:Ru_2(piv)_4:W(CN)_8$) formulation (Et_4N)[$\{Ru_2(piv)_4\}_2W(CN)_8$] $\cdot 4H_2O$ (**1**). IR data showed a strong $\nu(CN)$ band of $W(CN)_8^{5-}$ moiety at 2146 cm^{-1} and two COO stretching bands at 1487 and 1420 cm^{-1} with the difference in energy characteristic of syn-syn bridging carboxylate [28].

As shown in Fig. 2, the diffuse reflectance spectrum of **1** showed a broad band at 1026 nm in the near-infrared region. The band can be assigned to the $\delta(Ru_2) \rightarrow \delta^*(Ru_2)$ transition band and showed a red shift compa-

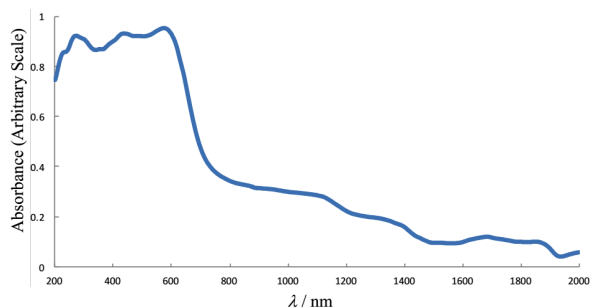


Fig. 2. Diffused reflectance spectra of **1**.

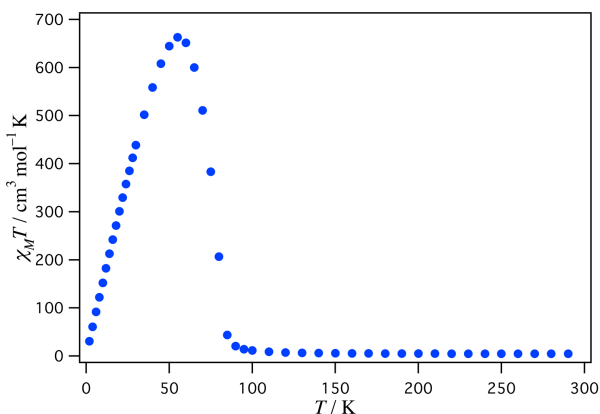


Fig. 3. Temperature dependence of $\chi_M T$ of **1**.

red with that of $[Ru_2(piv)_4(H_2O)_2]BF_4$ (990 nm), suggesting the axial coordination of the cyanide group of $W(CN)_8^{3-}$ moiety.

Magnetic susceptibility measurements were made in the temperature range of 2–300 K. The magnetic data of **1** are shown in Fig. 3 in the form of $\chi_M T$ plots, where χ_M is the molar magnetic susceptibility per $(Ru_2)_2W$ unit. As shown in Fig. 3, $\chi_M T$ at 300 K is $4.67\text{ cm}^3\text{ K mol}^{-1}$ corresponding to the effective magnetic moment of $6.11\ \mu_B$, which is comparable to that expected for magnetically isolated two dinuclear $Ru_2^{II,III}S = 3/2$ ions and a $W^V S = 1/2$ ion (theoretical value for $g = 2$). As the temperature is lowered, $\chi_M T$ decreases down to a minimum value of $4.62\text{ cm}^3\text{ K mol}^{-1}$ at 250 K then below it gradually increases until 95 K, then more rapidly up to a maximum of $663\text{ cm}^3\text{ K mol}^{-1}$ ($72.8\ \mu_B$) at 55 K and then decreases gradually down to $15.3\text{ cm}^3\text{ K mol}^{-1}$ ($11.1\ \mu_B$) at 2 K. The magnetic behavior is characteristic of ferrimagnetic behavior due to antiferromagnetic interaction between $Ru_2^{II,III}$ and W^V ions through the cyanide bridges.

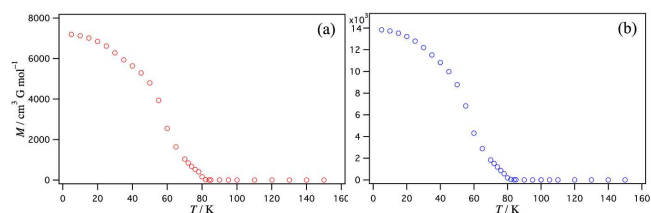


Fig. 4. ZFC (a) and FC (b) magnetization curves measured in 27 G for **1**.

The zero-field-cooled (ZFC) and field-cooled (FC) magnetizations, $M(T)_{ZFC}$ and $M(T)_{FC}$, respectively, rise below 80 K (Fig. 4), indicative of T_c at 80 K.

Magnetic ordering at 80 K was confirmed from the presence of peaks in both the real (χ'_M) and imaginary (χ''_M) parts of AC susceptibility (Fig. 5). This temperature is definitely higher than that of $[\{Ru_2(piv)_4\}_3(H_2O)W(CN)_8]$ ($T_c = 44\text{ K}$, [22]) and those found in the analogous complexes of ruthenium carboxylates with hexacyanidometalates $[\{Ru_2(CH_3CO_2)_4\}_3M(CN)_6]_n$ ($M = Fe$ ($T_c =$

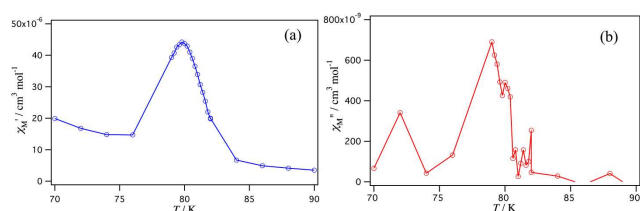


Fig. 5. Real part $\chi'_M(T)$ (a) and imaginary part $\chi''_M(T)$ (b) of AC susceptibility data for **1**.

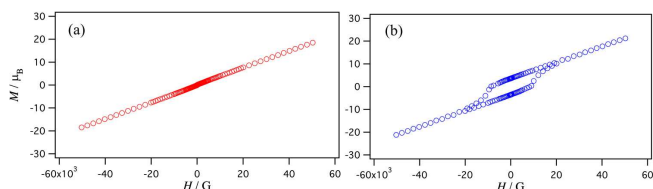


Fig. 6. Magnetic hysteresis loops at 80 K (a) and 5 K (b) for **1**.

2.1 K, [18]), Cr ($T_c = 33, 34.5$ K, [18]), Mn ($T_c = 9.6$ K, [18]); [$\{\text{Ru}_2(\text{piv})_4\}_3\text{M}(\text{CN})_6\}_n \cdot 2n\text{H}_2\text{O}$ (M=Fe ($T_c = 4.8$ K, [19]), Cr ($T_c = 37.5$ K, [19])). It seems that the Ru_2 carboxylate and octacyanidotungstate systems have more advantage for attaining the high T_c value than the Ru_2 carboxylate systems with the first-transition-metal cyanides.

Below T_c , the field dependence of the magnetization, $M(H)$, exhibits hysteresis (Fig. 6). The hysteresis curves at different temperatures show that the coercive field increases as the temperature decreases as expected for a magnet. The coercive field is 17000 Oe at 5 K. The large coercivity may be related with the 2D layer structure and the large anisotropies of the diruthenium cations and tungstate ions similarly to the case for [$\{\text{Ru}_2(\text{piv})_4\}_3(\text{H}_2\text{O})\text{W}(\text{CN})_8$]. Such 2D motif can be hold for the present case, because we found a 2D sheet structure in the similar 2:1 mixed-metal complex, [$\{\text{Ru}_2(\text{CH}_3\text{COO})_4\}_2\text{Pt}(\text{CN})_4\} \cdot 2\text{H}_2\text{O}$ [26]. The high T_c and the large coercive field values can be ascribed to the introduction of the large diffusion of the 5d magnetic orbitals to the metal-metal bonding in the ruthenium carboxylate clusters.

4. Conclusion

A new mixed-metal complex was synthesized by introducing the cation, tetraethylammonium ion. The isolated mixed-metal system showed a ferrimagnetic behavior and the T_c value was estimated to be of 80 K from the ZFC and FC studies and AC susceptibility measurements. The mixed-metal systems containing ruthenium carboxylate and octacyanidotungstate are promising for constructing new magnetic materials.

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