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Synthesis and Magnetic Properties of 3-D $[Ru^{II/III}{}_2(O_2CMe)_4]_3[M^{III}(CN)_6]$ (M = Cr, Fe, Co)

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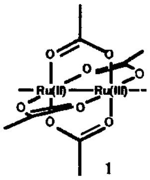

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In the pursuit of new molecule-based magnets,[1] the diruthenium tetraacetate cation, $[Ru^{II/III}{}_2(O_2CMe)_4]^+$ (**1**), is an intriguing building block. **1** has a high-spin $S = {}^3/_2$ ground state due to the accidental degeneracy of the π^* and δ^* HOMOs,[2] an unusually large zero-field splitting, $D = +53 \pm 24$ cm^{-1},[2b,3] and the ability to add one or two ligands axial to the Ru−Ru bond. Several extended structures based on **1** have been reported.[4−6] However, even when the structure is bridged with organic radicals such as nitroxides, albeit antiferromagnetically coupled, magnetic ordering does not occur.[6a] We report herein $[Ru^{II/III}{}_2(O_2CMe)_4]_3[M^{III}(CN)_6]$ [M = Cr (**2**), Fe (**3**), Co (**4**)] and their magnetic properties, including magnetic ordering at 33 K for **2**, a rare example of a magnet containing a second-row transition metal.

Compounds **2**−**4** form upon addition of an aqueous solution of $K_3[M^{III}(CN)_6]$ to a freshly prepared aqueous solution containing a stoichiometric amount of $[Ru^{II/III}{}_2(O_2CMe)_4]Cl$ in an inert atmosphere.[7] The ν_{CN} IR spectrum shows single sharp absorptions at 2138, 2116, and 2125 cm^{-1} for **2**−**4**, respectively, consistent with maintaining octahedral symmetry about the M^{III} site. In addition, all three compounds show characteristic asymmetric and symmetric ν(OCO) bands at 1444 and 1403 cm^{-1} and a $\delta(CO_2)$ band at 691 cm^{-1} for **1**.[8] On the basis of the stoichiometry and ability of **1** to axially coordinate to the N of cyanide, **2**−**4** are proposed to form a 3-D network structure with −M−C≡N−Ru=Ru−N≡C−M− linkages along all three Cartesian axes, as illustrated in Figure 1. A related motif is observed for the Prussian blue family of magnetic materials.[9]

The powder diffraction patterns of **2**−**4** can be indexed[10] to isomorphous body-centered cubic structures with a = 13.34, 13.30, and 13.10 Å, respectively. On the basis of the structures of $[M(CN)_6]^{3-}$ [11] and **1**,[3] the M···M linkage separation $a \approx 13$ Å and $a_{Co} < a_{Fe} < a_{Cr}$ are expected, as observed. Hence, the diffraction data are consistent with the structure in Figure 1. The body-centered space group indicates a second independent lattice interpenetrating the first lattice, as observed, for example for $Mn[C(CN)_3]_2$.[12]

The magnetic susceptibilities, χ, of **2**−**4** were studied using a SQUID magnetometer between 2 and 300 K. The effective moments, μ_{eff} [$=(8\chi T)^{1/2}$] at 300 K for **2**−**4** are 7.72, 7.30, and 7.26 μ_B, respectively. These values are in good agreement for the summation of independent spins based on the Curie−Weiss equation, eq 1, i.e., 7.75, 6.93, and 6.71 μ_B. Modeling of $\mu_{eff}(T)$ (Figure 2) is more complex, as although the M site can be modeled

$$\chi_M = \frac{Ng^2\mu_B{}^2}{3k_B(T-\theta)}[S(S+1)] \qquad (1)$$

with eq 1, the ruthenium(II/III) dimer is known to have a large zero-field splitting (D) and a temperature-independent paramagnetic (TIP) component, and its contribution to $\chi(T)$ can be described by eq 2;[2b,6,13] eq 3 can be used to model the expected $\chi(T)$ for **2**−**4**. The Weiss constant, θ, is introduced to roughly simulate the magnetic interactions between the paramagnetic species.

$$\chi_{Ru_2} = \frac{Ng^2\mu_B{}^2}{k_B(T-\theta)}\left[\frac{1}{3}\,\frac{1+9e^{-2D/k_BT}}{4(1+e^{-2D/k_BT})} + \frac{2}{3}\,\frac{1+(3k_BT/4D)(1-e^{-2D/k_BT})}{1+e^{-2D/k_BT}}\right] + \mathrm{TIP} \qquad (2)$$

$$\chi_{Tot} = 3\chi_{Ru_2} + \chi_M \qquad (3)$$

As Co^{III} is diamagnetic, for $T > 2$ K, $\mu_{eff}(T)$ for **4** can be fit by eq 2, with $D = 69.4$ cm^{-1}, $\mathrm{TIP}_{Ru_2} = 800 \times 10^{-6}$ emu/mol, $\theta = 0$ K, $g_{Ru_2} = 2.04$, and the chi-squared agreement factor[14] is $\sum(\mu_{exp} - \mu_{calc})^2/\mu_{exp} = 2.823 \times 10^{-3}$ (Figure 2). This is in accord with magnetic behavior observed for several other complexes containing **1**.[6]

In contrast to the case for **4**, eq 3 fits $\mu_{eff}(T)$ only above 120 and 8 K for **2** and **3**, respectively (Figure 2). For **2**, the data can be fit with $D = 69.4$ cm^{-1}, $\theta = -40$ K, $g_{Ru_2} = 2$, $g_{Fe} = 2$, and $\mathrm{TIP}_{Ru_2} = 700 \times 10^{-6}$ emu/mol (chi-squared $= 5.511 \times 10^{-3}$). The fitting parameters indicate significant antiferromagnetic coupling between adjacent spin sites. Upon decreasing T for **2**, $\mu_{eff}(T)$ increases below ~50 K, reaching a maximum value of 30.9 μ_B at 32 K prior to abruptly decreasing to 3.65 μ_B at 2 K (Figure 2).

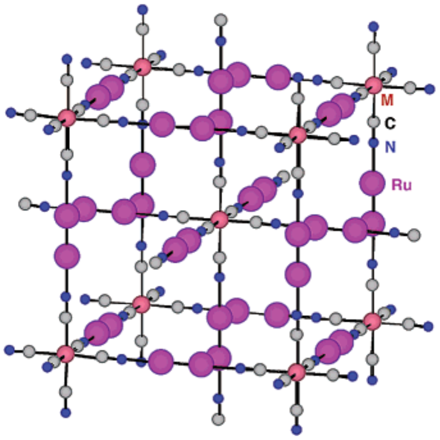

Figure 1. Proposed 3-D body-centered, interpenetrating network structure for $[Ru_2(O_2CMe)_4]_3[M^{III}(CN)_6]$ (M = Cr, Fe, Co); the bridging acetates, rotated 45° with respect to $[M^{III}(CN)_6]^{3-}$, are not shown for clarity.

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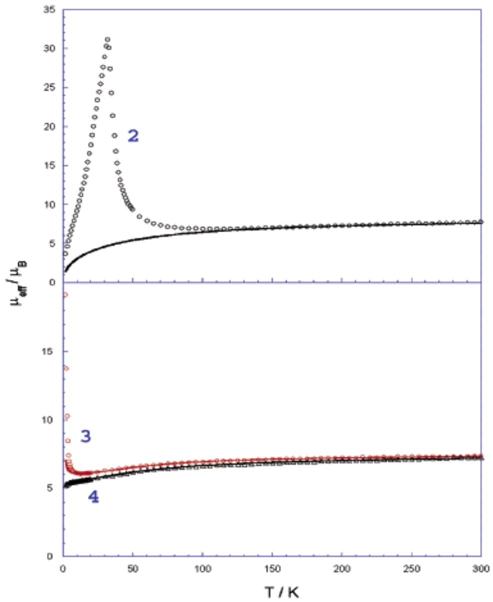

Figure 2. $\mu_{eff}(T)$ and the fit to the higher temperature data with eqs 2 and 3 for **2** (top) and **3** and **4** (bottom).

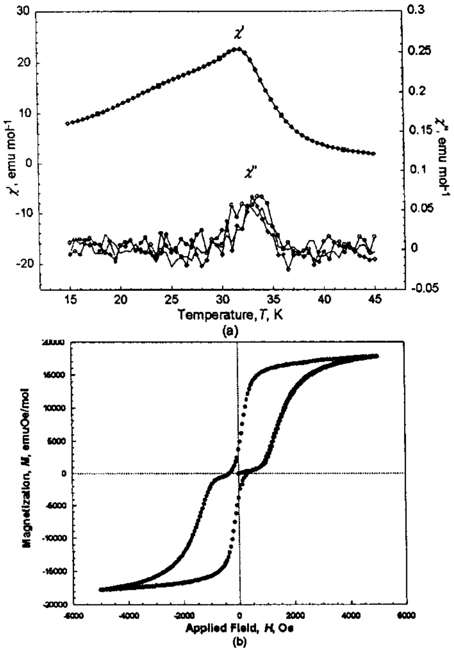

Figure 3. (a) Alternating current $\chi'(T)$ and $\chi''(T)$ at 9.9, 99, and 999 Hz. (b) $M(H)$ showing a constricted hysteresis loop for **2**.

This behavior is indicative of magnetic ordering. To confirm that **2** magnetically orders, the in-phase (χ') and out-of-phase (χ'') alternating current susceptibilities were taken and show frequency-independent peaks for both $\chi'(T)$ at 32 K and $\chi''(T)$ at 34 K, confirming that **1** orders with $T_c = 33 \pm 1$ K (Figure 3a). The field dependence of the magnetization, $M(H)$, approaches saturation at 2 kOe and saturates to a value of 17 870 emu·Oe/mol at 2 K (Figure 3b). Assuming $g = 2$, a saturation magnetization, M_s, of 67 000 emu·Oe/mol is expected for ferromagnetic coupling, while a value of 33 500 emu·Oe/mol is expected for antiferromagnetic coupling. Antiferromagnetic coupling as observed for the 1-D chain of **1**(NITPh) (NITPh = phenyl nitronyl nitroxide),[6a] leading to ordering as a ferrimagnet, is expected for **2**. The observed value is one-half the expectation for the latter, and this low value may be due to the large D of the ruthenium dimer, since for $T \ll D$, only the $S = {}^1/_2$ state is significantly populated at 2 K. An applied field leads to a small increase in M, which for a metamagnet increases above ~800 Oe prior to saturation. Hysteresis with a very unusual constricted shape is observed at 2 K (Figure 3b). The remanent magnetization at 2 K is 3700 emu·Oe/mol. Constricted hysteretic behavior and reduced M_s have been attributed to metamagnetism caused by canted spins,[11b] and this phenomenon is under further study.

Above 8 K, $\mu_{eff}(T)$ for **3** can be fit by eq 3 (Figure 3). The data can be fit with $D = 69.4$ cm^{-1}, $\theta = 0.7$ K, $g_{Ru_2} = 2.075$, $g_{Fe} = 2$, and $TIP_{Ru_2} = 400 \times 10^{-6}$ emu/mol (chi-squared = 2.448×10^{-3}). The divergence at 8 K suggests a transition from short-range ferromagnetic interaction to long-range magnetic ordering. Upon decreasing T for **3**, $\mu_{eff}(T)$ increases sharply at ~10 K, reaching 19.2 μ_B at 2 K (Figure 3). $\chi'(T)$ and $\chi''(T)$ increase with decreasing temperature, but peaks are not present above 2 K. These data suggest that the onset of magnetic ordering occurs below 2 K.

These initial studies show that **1** can be used as a building block for the formation of molecule-based magnets.

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(7) After the solution was stirred for 2 h, the product was collected by filtration and dried in a vacuum. Once separated, the products are stable in air. Elemental analysis gave satisfactory results. (Calcd for **2**: C, 23.66; H, 2.38; N, 5.52. Obsd: C, 23.82; H, 2.48; N, 5.72. Calcd for **3**: C, 23.60; H, 2.38; N, 5.50. Obsd: C, 23.68; H, 2.41; N, 5.14. Calcd for **4**: C, 23.55; H, 2.37; N, 5.49. Obsd: C, 23.37; H, 2.13; N, 5.28.)

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