Magnetic Properties

Building Blocks for 2D Molecule-Based Magnets: The Diruthenium Tetrapivalate Monocation $[Ru^{II/III}_2(O_2CtBu)_4]^+$**

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The development of molecule-based magnets has made significant progress with a variety of spin-bearing organic as well as inorganic building blocks.[1] One building block that has garnered attention in molecule-based magnets is the diruthenium tetracarboxylate cation, $[Ru_2(O_2CMe)_4]^+$ (**1**).[2–4] Ion **1** has an $S = 3/2$ ground state with the $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*2}$ valence electronic configuration, owing to near degeneracy of the π^* and δ^* orbitals.[5] Besides the unusually high spin state for a second-row coordination complex, diruthenium tetracarboxylate species have large zero-field splittings, $D = +63 \pm 11\ \text{cm}^{-1}$,[6,7] and are able to coordinate up to two axial ligands a property that is essential for building extended network structures. Many 1D extended structures based on diruthenium tetracarboxylate compounds have been explored by using organic bridging ligands,[2] such as nitroxide radicals, TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane), quinone, phenazine, $[N(CN)_2]^-$, and $[C(CN)_3]^-$. These extended network structures exhibit weak antiferromagnetic interactions between spin sites, but not long-range magnetic ordering.

$[Ru_2(O_2CMe)_4]^+$ has been incorporated into cubic 3D networks with metal hexacyanometallate(III), $[M(CN)_6]^{3-}$ (M = Co, Fe, Mn, Cr). $[Ru_2(O_2CMe)_4]_3[M^{III}(CN)_6]$ (M = Co (**2**), Fe (**3**), Cr (**4**)) have a 3D body-centered, interpenetrating network structure (Figure 1) that magnetically orders at 2.1 K for **3** and 33 K for **4**.[3] Using pivalate, Yoshioka et al. obtained $[Ru_2(O_2CtBu)_4]_3[M^{III}(CN)_6]\cdot 2H_2O$ (M = Co (**5**), Fe(**6**)), which formed a 2D layered network (Figure 2).[4] Tris(oxalato)metallate(III) species also form 2D and 3D extended networks depending on synthetic conditions and have been studied to understand the magnetostructural relationship of these materials.[8] While the temperature dependence of the magnetic susceptibilities, $\chi(T)$, of **5** and **6** were reported, ferrimagnetic behavior was suggested for **6**, but not established. Owing to the high T_c observed for **4**, we sought to prepare $[Ru_2(O_2CtBu)_4]_3[Cr^{III}(CN)_6]\cdot 2H_2O$ (**7**), for which modeling suggests should form a non-interpenetrating, primitive cubic lattice.[9] Herein we report its magnetic behavior as well as our detailed investigation of the magnetic properties of $[Ru_2(O_2CtBu)_4]_3[M^{III}(CN)_6]\cdot 2H_2O$ [M = Co (**5**), Fe (**6**), Cr (**7**)].

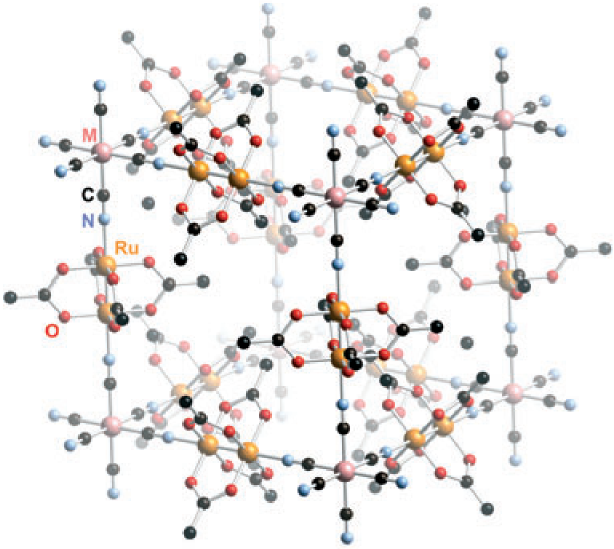

Figure 1. 3D network structure of $[Ru_2(O_2CMe)_4]_3[M^{III}(CN)_6]$ (M = Cr (**2**), Co (**3**), Fe(**4**)).[3] The hydrogen atoms are omitted for clarity. A second network structure interpenetrates this lattice, but it is omitted for clarity.

Orange-brown **5**,[4] **6**,[4] and **7**[10] were synthesized in a similar manner to the published procedure. Compounds **5** and **6** were verified by X-ray powder diffraction[11] and IR data.[4] The X-ray powder diffraction data of **7** was indexed to a

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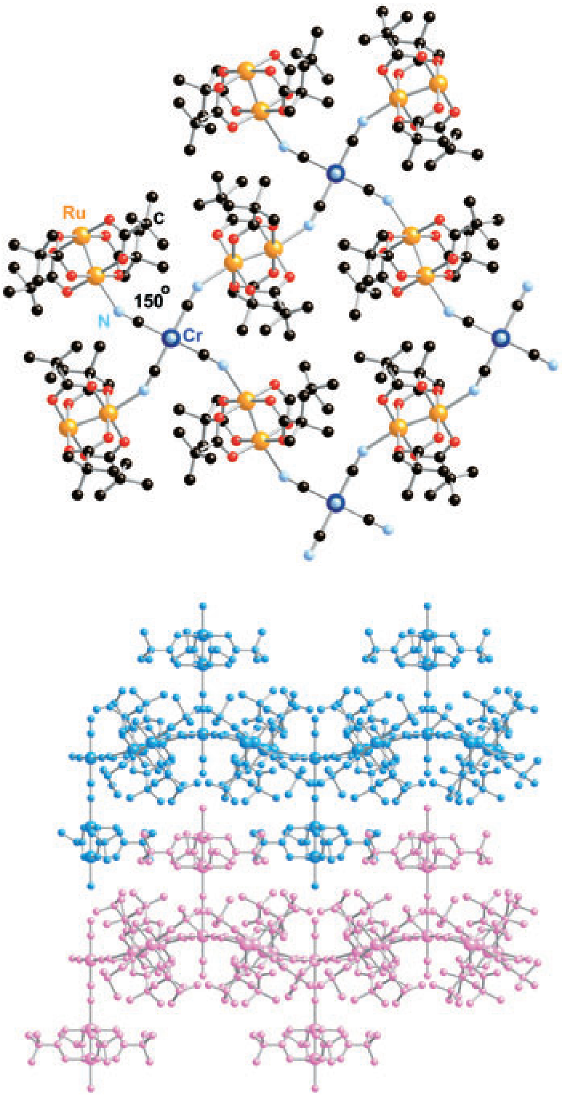

Figure 2. 2D layer structure of $[Ru_2(O_2C\mathit{t}Bu)_4]_3[M^{III}(CN)_6]$ (M = Cr (**7**), Co (**5**),[4] Fe (**6**)[4]) viewed from the *c* axis to show the 2D layer connectivity (top) and viewed from the *b* axis to show the stacking of the 2D layers (bottom).

tetragonal unit cell[10,11] and found to be isomorphous to **6** indicating that **7** was a 2D layered compound similar to **6**.

The 4 to 300 K magnetic susceptibilities, χ, of **5**–**7** were determined on a Quantum Design MPMS-5XL magnetometer at 50 Oe (Figure 3).[12] The 298 K effective moments, μ_{eff} $[=(8\chi T)^{1/2}]$, 7.35 μ_B for **5**, 7.57 μ_B for **6**, and 7.51 μ_B for **7**. The $\mu_{\mathrm{eff}}(T)$ for **5** decreases slightly to 5.49 μ_B at 4 K while for **6** it decreases until around 25 K where upon μ_{eff} abruptly increases to a maximum of 36 μ_B at 5 K. The $\mu_{\mathrm{eff}}(T)$ for **7** also decreases with lowering of the temperature until around 125 K where upon μ_{eff} increases to a maximum of 137 μ_B at 34 K and then abruptly decreases to 17 μ_B at 4 K. The abrupt peaks in $\mu_{\mathrm{eff}}(T)$ plots suggests that **6** and **7** magnetically ordered.

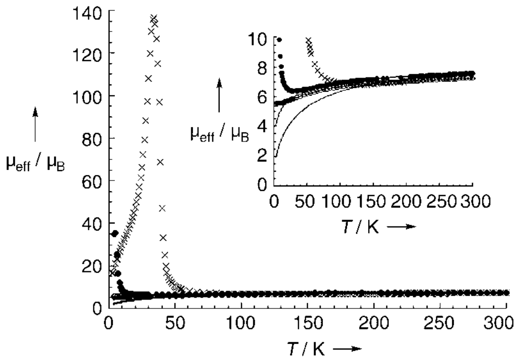

Figure 3. $\mu_{\mathrm{eff}}(T)$ for **5** (○), **6** (●), and **7** (×) and the fits to the high-temperature data with Equation (2) as the solid black lines. The insert highlights the region below 10 μ_B.

Since the diruthenium tetracarboxylate dimer has a large zero-field splitting (D) and a temperature-independent paramagnetic (TIP) component, fitting the $\chi(T)$ to a simple Curie–Weiss model would not be appropriate; therefore, their contributions were incorporated into Equation (1).[13] The $\mu_{\mathrm{eff}}(T)$ for **5**–**7** were modeled with Equation (2) which accounts for D and in addition incorporates the contribution of the paramagnetic metal hexacyanide.[3]

$$\chi_{\mathrm{Ru}_2} = \frac{N g_{\mathrm{Ru}_2}^2 \mu_B^2}{k_B(T-\theta)}\left[\frac{1}{3}\frac{1+9\,e^{\frac{-2D}{k_B T}}}{4(1+e^{\frac{-2D}{k_B T}})}+\frac{2}{3}\frac{1+\frac{3k_B T}{4D}(1-e^{\frac{-2D}{k_B T}})}{1+e^{\frac{-2D}{k_B T}}}\right] + \mathrm{TIP}\ \text{for}\ T>\theta \qquad (1)$$

$$\chi_{\mathrm{Tot}} = 3\chi_{\mathrm{Ru}_2} + \chi_M\ \text{where}\ \chi_M = \frac{N g_M^2 \mu_B^2}{3k_B(T-\theta)}[S(S+1)] \qquad (2)$$

The $\mu_{\mathrm{eff}}(T)$ for **5** was fitted with $\theta = 0$ K, $g_{\mathrm{Ru}_2} = 2.04$, $\mathrm{TIP}_{\mathrm{Ru}_2} = 800\times10^{-6}$ emu mol^{-1}, and the same D value, 69.4 cm^{-1} as was used for fitting **2**–**4**,[3] (χ^2 agreement factor $=\Sigma(\mu_{\mathrm{obs}}-\mu_{\mathrm{calcd}})^2\ \mu_{\mathrm{obs}}^{-1}$[14] $= 2.6\times10^{-3}$). The D value and g_{Ru_2} were kept constant in fitting **6** and **7**. The $\mu_{\mathrm{eff}}(T)$ for **6** was fitted above 50 K with $\theta = -5$ K, $g_{\mathrm{Ru}_2} = 2.04$, $g_{\mathrm{Fe}} = 3.0$,[15] $\mathrm{TIP}_{\mathrm{Ru}_2} = 600\times10^{-6}$ emu mol^{-1} ($\chi^2 = 1.5\times10^{-3}$). The fitting parameters for **6** indicate some antiferromagnetic coupling between adjacent spin sites. This situation is in contrast to **3**, which needed no antiferromagnetic coupling between adjacent spin sites to fit the observed data.[3] Similarly, the $\mu_{\mathrm{eff}}(T)$ was fitted above 150 K for **7** with $D = 69.4$ cm^{-1}, $\theta = -45$ K, $g_{\mathrm{Ru}_2} = 2.04$, $g_{\mathrm{Cr}} = 2.0$, $\mathrm{TIP}_{\mathrm{Ru}_2} = 300\times10^{-6}$ emu mol^{-1} ($\chi^2 = 2.9\times10^{-3}$). The -40 K θ value obtained for **4** to fit the observed data,[3] is similar to $\theta = -45$ K found for **7**, and the trend of having a stronger magnetic coupling between adjacent spin sites for **6** and **7** than in **3** and **4** correlates with their higher T_cs.

As a result of deviation from Equation (2) at lower temperature, **6** and **7** warranted further study to ascertain evidence of magnetic ordering. Zero-field/field cooled (ZFC/FC) $M(T)$ (M = magnetization) studies revealed bifurcation temperatures, T_b, at 6.5 K for **6** and 39.5 K for **7** (Figure 4) indicative of magnetic ordering.

Magnetic ordering of **6** and **7** was confirmed from the presence of absorptions in both the real (χ') and imaginary (χ'') alternating current (ac) susceptibilities (Figure 5). Compound **6** has a slight frequency dependence for both $\chi'(T)$ and $\chi''(T)$ peaks. The peak in $\chi'(T)$ shifts from 4.8 K at 10 Hz to

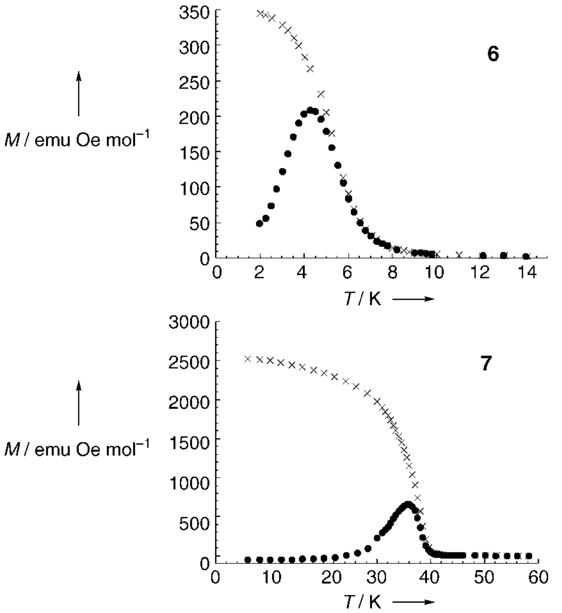

Figure 4. Field cooled (FC, ×) and zero field cooled (ZFC, ●) $M(T)$ data for **6** and **7**.

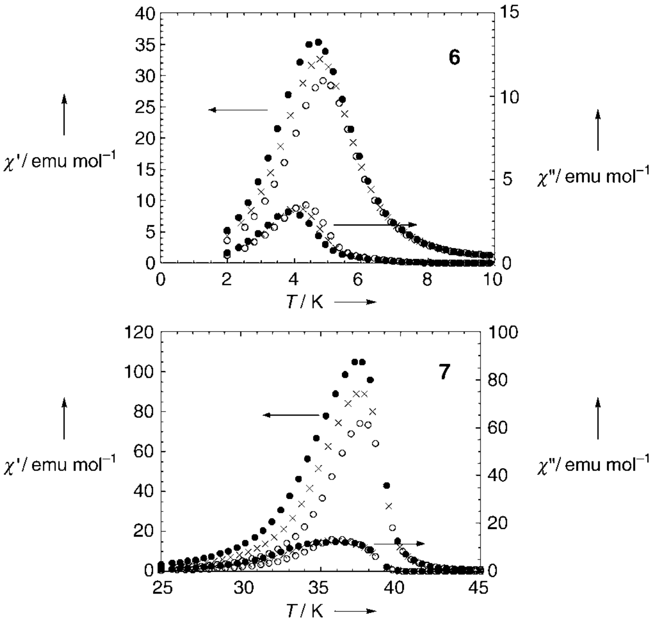

Figure 5. $\chi'(T)$ (left axis) and $\chi''(T)$ (right axis) at 10 (●), 100 (×), and 1000 (○) Hz for **6** and **7**.

4.7 K at 1000 Hz. Compound **7** has nearly frequency independent peaks for both $\chi'(T)$ at 37.5 K and $\chi''(T)$ at 36.5 K.

The 2 K field dependence of the magnetization, $M(H)$, for **6** and **7** exhibit hysteresis (Figure 6). The coercive fields of **6** was 190 Oe and **7** 20000 Oe, which are larger coercive fields (H_{cr}) than the analogous acetate 3D structures, **3** (10 Oe) and **4** (470 Oe). The large coercive fields are probably related to the 2D layer structure and the large anisotropy of the diruthenium cations. Enormous coercivity of approximately 27000 Oe were reported for [Mn^{III}(porphyrin)][TCNE] family of molecule-based magnets at 2 K, but they are only about 2% of that value at 5 K,[16] Hence, although raising the temperature for **7** to 5 K reduces H_{cr} to 13000 Oe, this value is still substantially greater than observed for the [Mn^{III}(porphyrin)][TCNE] family of magnets and the genesis is under investigation.

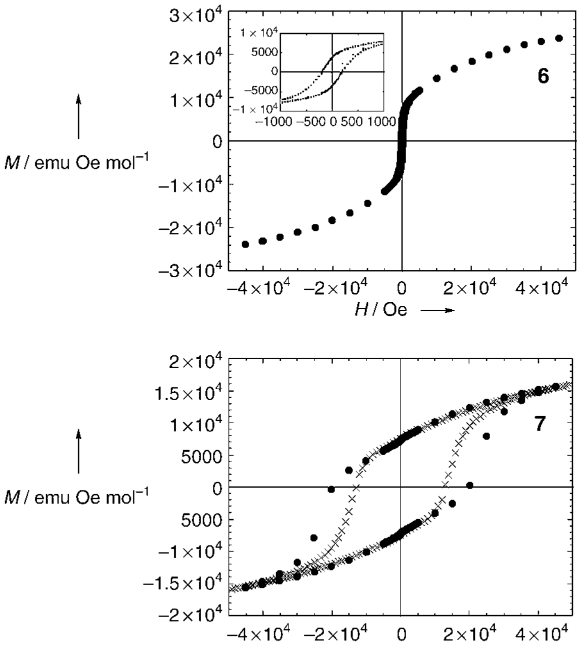

Figure 6. $M(H)$ of **6** at 2 K (●) and **7** at 2 K (●) and 5 K (×) taken from ±50000 Oe. Insert for **6** is an expansion of the region between ±1000 Oe.

The T_c values for **6** and **7** exceed those of their 3D analogous **3** and **4** (Table 1). This result is contrast to 2D

Table 1: Summary of the ν_{CN} IR absorptions and magnetic properties for $[Ru_2(O_2CMe)_4]_3[M^{III}(CN)_6]$[3] and $[Ru_2(O_2CtBu)_4]_3[M^{III}(CN)_6]\cdot 2H_2O$ (M = Cr, Fe, Co).

	M	ν_{CN} [cm^{-1}]	μ_{eff} [μ_B]	T_b [K]	T_c [K][a]	M_s [emu Oe mol^{-1}][b]	M_r [emu Oe mol^{-1}]	H_{cr} [Oe]
2[3]	Co	2125	7.26	–	–	–	–	–
5	Co	2126	7.35	–	–	–	–	–
3[3]	Fe	2116	7.30	3.0	2.1	22700[c]	40[c]	10[c]
6	Fe	2115	7.57	6.5	4.8	24400[c]	3600[c]	190[c]
4[3]	Cr	2138	7.72	32.0	33.0	20800[c]	3840[c]	470[c]
7	Cr	2133	7.57	39.5	37.5	16200[c]	7500[c]	20000[c]
						15800[d]	7500[d]	13000[d]

[a] T_c determined from the peak in $\chi'(T)$ at 10 Hz. [b] M_s is the magnetization at 5 T. [c] Value at 2 K. [d] Value at 5 K.

(racemic) and 3D (chiral) network structured (cation)M^{II}-[$M^{III}ox_3$] (ox = oxalato) materials that have similar T_c values.[8] In addition to having a differing dimensionality (2D layer and 3D cubic structures), the angle between CN and diruthenium dimer was 150.5(10)° in the 2D layer structure and 180° in the cubic 3D structure (compare Figure 1 and Figure 2 top). Also, the 3D cubic structure has an interpenetrating lattice not found in the 2D layer. In addition, pivalate is more electron donating into the diruthenium core than the acetate ligand, which might enhance the magnetic coupling between the diruthenium dimer and the metal hexacyanide unit. The structural and/or electronic reasons why **6** and **7** have a higher T_c than **3** and **4** are still under investigation.

Understanding the magnetostructural relationship of this new class of materials incorporating a relatively large zero-field-splitting ligand and metal hexacyanides would provide important information for molecule-based materials. These compounds highlight the importance of determining magnetostructural relationships for rationally design molecule-based magnets with desired physical properties.

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[10] $K_3[Cr(CN)_6]$ (18 mg, 55 mmol) was dissolved in water (5 mL) and was added to a stirred methanol solution (10 mL) of $[Ru_2(O_2CtBu)_4]Cl$ (100 mg, 156 mmol). After 1 h, an orange brown precipitate was isolated by centrifugation, washed with water, then dried in vacuo (Yield 78%; 84 mg). IR (KBr): 2133 cm^{-1} (ν_{CN}). Elemental analysis (%) calcd for $C_{66}H_{112}CrN_6O_{26}Ru_6$: C 38.41, H 5.47, N 4.07; found: C 38.14, H 5.49, N 4.07. The powder diffraction data was indexed to a tetragonal space group: $a = b = 17.39(6)$ Å; $c = 15.67(6)$ Å; $V = 4739(40)$ Å^3.

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