Zero-Field Splitting, Field-Dependent Magnetization of Mixed-Valent $S = {}^{3}/_{2}$ Diruthenium(II,III) Tetracarboxylates

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The 2 K field-dependent magnetization, $M(H)$, of $S = {}^{3}/_{2}$ $[Ru^{II/III}{}_2(OAc)_4]^+$ was studied. $[Ru^{II/III}{}_2(OAc)_4]^+$ exhibits an unusually low magnetization with respect to that predicted by the classical Brillouin function. This reduced value is a consequence of the large anisotropy arising from the large zero-field splitting (ZFS), D (+63 ± 11 cm^{-1}), of the $[Ru^{II/III}{}_2(OAc)_4]^+$ cation, which alters the energy levels with respect to the isotropic energy levels used to derive the Brillouin function. Analytical expressions for the parallel and perpendicular components of $M(H)$ that include zero-field splitting (ZFS), D, and interdimer coupling, θ, are presented for $S = {}^{3}/_{2}$. The expression was derived from second-order perturbation theory for $|D| \gg g\mu_B H$. The experimental data fit very well with $g = 2.24 \pm 0.01$, $D = +69.5$ cm^{-1} ($D/k_B = +100$ K), and $0 > \theta > -0.6$ K indicative of very weak interdimer interactions for both $[Ru^{II/III}{}_2(OAc)_4]Cl$ and $[Ru^{II/III}{}_2(OAc)_4]_3[Co^{III}(CN)_6]$.

Introduction

Field-dependent magnetization, $M(H)$, studies are frequently relied upon to ascertain the spin state of a paramagnetic site via fitting the data to the Brillouin function, as was first reported by Henry.[1] This is best established for isolated paramagnetic centers that do not have contributions to the magnetization from orbital angular momentum, spin−orbit coupling, and/or zero-field splitting, as analytical expressions that include these contributions have not been reported. Nonetheless, numerical methods have been developed principally to identify isolated paramagnetic centers present in some proteins.[2] Likewise, to understand the magnetic couplings (ferro- or antiferromagnetic) and the ground state of molecule-based magnets, $M(H)$ studies are important. In particular we sought to identify the nature of the coupling present in $[Ru^{II/III}{}_2(OAc)_4]_3[Cr^{III}(CN)_6]$ ($T_c = 33$ K). This magnet possesses $S = {}^{3}/_{2}$ $[Ru^{II/III}{}_2(OAc)_4]^+$ and $S = {}^{3}/_{2}$ $[Cr^{III}(CN)_6]^{3-}$ spin sites;[3] however, octahedral Cr^{III} is well modeled by the Brillouin function, and $[Ru^{II/III}{}_2(OAc)_4]^+$ is not.

The physical properties of the mixed-valent, D_{4h} $[Ru^{II/III}{}_2(OAc)_4]^+$ have been extensively studied. This cation has a $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*2}$ $S = {}^{3}/_{2}$ valence electronic configuration[4,5] with spins fully delocalized between the two ruthenium centers. However, $[Ru^{II/III}{}_2(OAc)_4]^+$ has an unusually large zero-field splitting (ZFS), D (+63 ± 11 cm^{-1}; $D/k_B = 90.6 \pm 15.8$ K).[5−7] $[Ru^{II/III}{}_2(OAc)_4]_3[Cr^{III}(CN)_6]$ has $D = 69.4$ cm^{-1} ($D/k_B = 100$ K); hence, at low temperature ($\leq T_c$) only the $m_s = {}^{1}/_{2}$ state is significantly populated, complicating the analysis of the field-dependent magnetization, $M(H)$ including an anomalous hysteresis loop.[3] Due to the presence of zero-field splitting, the Brillouin function cannot be used to model the $M(H)$ data. Nonetheless, there are analytical models for anisotropic temperature-dependent magnetization, $M(T,D)$,[6a] and herein we extend the methodology used to derive analytical expressions for $M(T,D)$ to derive expressions for $M(H,D)$, and the derived expressions are used to fit the observed $M(H)$ data for $[Ru_2(OAc)_4]Cl$ and $[Ru_2(OAc)_4]_3[Co(CN)_6]$ with excellent agreement.

Experimental Section

$[Ru_2(OAc)_4]Cl$, **1**, and $[Ru_2(OAc)_4]_3[Co(CN)_6]$, **2**, were prepared as previously described.[3] Field-dependent magnetization measurements were carried out on either a Quantum Design MPMS-5XL SQUID magnetometer from 0 to 5 T or a Quantum Design PPMS Model 9 T susceptometer from 0 to 7.4 T at 2 K as previously described.[8]

Results and Discussion

At 2 K the $M(H)$ of **1** and **2** were observed to be 10 270 and 10 262 emu·Oe Ru$_2$-eq^{-1} at 5 T, respectively (Figure 1). These values are lower than predicted from the Brillouin function, eq 1 for $S = {}^{3}/_{2}$ (i.e., 16 755 emu·Oe mol^{-1}) due, as discussed above, to the extremely large ZFS of $[Ru_2(OAc)_4]^+$ [5−7] that depopulates the $m_s = {}^{3}/_{2}$ energy level at 2 K.[9] Thus, the only populated state is $m_s = {}^{1}/_{2}$. This is in contrast to a 1:1 state occupation for the $m_s = {}^{3}/_{2}$ and $m_s = {}^{1}/_{2}$ states when the system is isotropic, i.e., $D = 0$. Hence, data were fit to the Brillouin function for $S = {}^{1}/_{2}$ that includes a term to account for intradimer interactions θ.[10]

$$M(H,\theta)_{\text{Brillouin}} = N g \mu_B S \left[(2S+1)\coth\left(\frac{g\mu_B S H}{k_B(T-\theta)} \frac{2S+1}{2S} \right) - \coth\left(\frac{g\mu_B S H}{k_B(T-\theta)} \frac{1}{2S} \right) \right] \frac{1}{2S} \quad (1)$$

where N is Avogadro's number, g is the Landé factor, μ_B is the Bohr magneton, S is the spin quantum number, and H is the magnetic field, with $g = 3.69$, $\theta = -0.35$ K for **1**, and $g = 3.69$, $\theta = -0.12$ K and for **2** (Figure 1). The small θ values indicate very weak intradimer antiferromagnetic coupling. Weaker coupling is expected via the three diamagnetic five-atom $-NCCo^{III}CN-$ bridges for **2** with respect to the diamagnetic single-atom Cl^- bridge for **1**, as observed.

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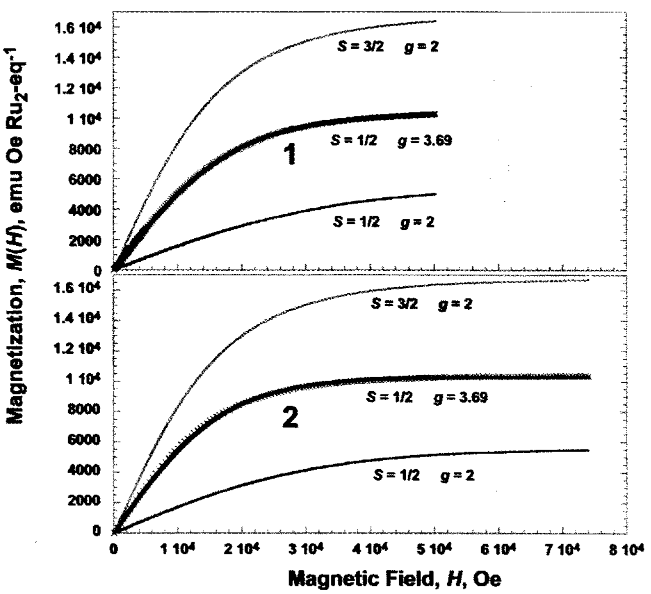

Figure 1. $S = {}^1/_2$ Brillouin function fit, eq 1, with the data of **1** ($S = {}^1/_2$, $g = 3.69$, $\theta = -0.35$ K), and **2** ($S = {}^1/_2$, $g = 3.69$, $\theta = -0.12$ K). The calculated $M(H)$ for $g = 2$, $S = {}^1/_2$, and $S = {}^3/_2$ from eq 1 are shown for comparison. The observed data are plotted as x's.

The large unphysical 3.69 g-value fit to the Brillouin function emphasizes the inappropriateness of eq 1, which is attributed to the different splitting magnitudes of the $m_s = {}^1/_2$ states arising from the ZFS. The Zeeman splitting used to derive the Brillouin function is $E = \pm g\mu_B H/2$ for $S = {}^1/_2$ but is not valid due to ZFS. Taking into account the anisotropy arising from the ZFS, the splitting for $m_s = {}^1/_2$ is $E_\parallel = \pm g_\parallel \mu_B H_\parallel/2$, and $E_\perp = \pm g_\perp \mu_B H_\perp - 3g_\perp{}^2\mu_B{}^2 H_\perp{}^2/(8D)$,[11a] Figure 2. Since $\mu_B = 9.274 \times 10^{-24}$ J T^{-1} is small, the latter term for $E_\perp$ is negligible. Hence, the perpendicular splitting is twice that of the parallel for $M(H,D)$, thus $g_{M(H,D)\perp} = 2g_{M(H,D)\parallel}$. Given that the Brillouin function is isotropic, $g_{Brillouin} = g_{Brillouin\perp} = g_{Brillouin\parallel}$. The average g value for $M(H,D)$ is $g_{M(H,D)}$ where $g_{M(H,D)} = (2g_{M(H,D)\perp} + g_{M(H,D)\parallel})/3 = (5g_{M(H,D)\parallel})/3$. $g_\parallel$ for the Brillouin and $M(H,D)$ expressions are the same, i.e., $g_{M(H,D)\parallel} = g_{Brillouin\parallel} = g_{Brillouin} = \pm g_\parallel \mu_B H_\parallel/2$. Thus, $g_{M(H,D)} = (5/3)g_{Brillouin} = 2.2$; hence, an alternative model is required. Consequently, we sought to fit the data with an analytical expression for $M(H,D,\theta)$.

Analytical expressions for $M(H,D,\theta)$ are not readily available, but numerical methods have been used.[12a] The $M(H,D)$ calculation by numerical methods takes into account the integration over all space. The integration ensures that all orientations of the sample are included,[12b] but analytical expressions for this have not been reported. Nonetheless, the structure of diruthenium complex is 3-D body centered, interpenetrating cubic lattice, and the orientation of the crystal at all directions are equivalent, and consequently an analytical expression for $M(H,D,\theta)$ was derived.

Analytical Expression for $M(H,D,\theta)$. $[Ru_2(OAc)_4]^+$ possesses an ${}^4B_{2u}$ ground state and ${}^2A_{1u}$, ${}^2A_{2u}$, ${}^2B_{2u}$, ${}^2B_{1u}$ excited states; however, the excited states do not contribute to the paramagnetism.[5b] Thus, the excited states are neglected. In the case of isotropic $S = {}^3/_2$, both the $m_s = \pm{}^3/_2$ and $\pm{}^1/_2$ energy levels are essentially equally populated. These states, however, are not evenly populated due to the ZFS, D, arising from the tetragonal distortion, and the larger the $|D|$, the greater the difference in the population of the states, especially for $T \approx |D|$. The ZFS Hamiltonian, $\hat{H}_{ZFS}$, in an octahedral crystal field with Zeeman effect is used to describe this phenomenon.

$$\hat{H}_{ZFS} = g\mu_B \underline{\hat{S}}\cdot\underline{H} + D\left[\hat{S}_z{}^2 - \frac{S(S+1)}{3}\right] + E(\hat{S}_x{}^2 - \hat{S}_y{}^2) \quad (2)$$

where D is the axial ZFS tensor, E is the rhombic ZFS tensor, S_z is the spin at parallel direction with respect to H, while S_x and S_y are the spins perpendicular with respect to H. Since there is no rhombic distortion in the system (i.e., $E = 0$),[6] the Hamiltonian reduces to:

$$\hat{H}_{ZFS} = g_z\mu_B\hat{S}_z\cdot H_z + g_x\mu_B\hat{S}_x\cdot H_x + g_y\mu_B\hat{S}_y\cdot H_y + D\left[\hat{S}_z{}^2 - \frac{S(S+1)}{3}\right] \quad (3)$$

and the energy of the ZFS Hamiltonian can be expressed by the secular determinant as:

$$\begin{array}{c|cccc} & |{}^3/_2\rangle & |-{}^3/_2\rangle & |{}^1/_2\rangle & |-{}^1/_2\rangle \\ \hline \langle{}^3/_2| & 2D + \frac{3}{2}g_z\mu_B H_z & 0 & \frac{\sqrt{3}}{2}(g_x\mu_B H_x + ig_y\mu_B H_y) & 0 \\ \langle-{}^3/_2| & 0 & 2D - \frac{3}{2}g_z\mu_B H_z & 0 & \frac{\sqrt{3}}{2}(g_x\mu_B H_x + ig_y\mu_B H_y) \\ \langle{}^1/_2| & \frac{\sqrt{3}}{2}(g_x\mu_B H_x - ig_y\mu_B H_y) & 0 & \frac{1}{2}g_z\mu_B H_z & g_x\mu_B H_x - ig_y\mu_B H_y \\ \langle-{}^1/_2| & 0 & \frac{\sqrt{3}}{2}(g_x\mu_B H_x - ig_y\mu_B H_y) & g_x\mu_B H_x + ig_y\mu_B H_y & -\frac{1}{2}g_z\mu_B H_z \end{array} = E_{ZFS} \quad (4)$$

The anisotropic magnetization function, $M(H,D,\theta)$, for $S = {}^3/_2$ is derived from the ZFS Hamiltonian, eq 3, and magnetization equation. We introduce the Weiss constant, θ, to account for weak intermolecular coupling.[11b]

$$M(H,D,\theta)_\parallel = N\left[3g\mu_B \sinh\left(\frac{3}{2}\frac{g\mu_B H}{k_B(T-\theta)}\right)\exp(-2D/k_BT) + g\mu_B \sinh\left(\frac{g\mu_B H}{2k_B(T-\theta)}\right)\right] \Bigg/ \left[2\cosh\left(\frac{3}{2}\frac{g\mu_B H}{k_B(T-\theta)}\right) \times \exp(-2D/k_BT) + 2\cosh\left(\frac{g\mu_B H}{2k_B(T-\theta)}\right)\right] \quad (5a)$$

$$M(H,D,\theta)_\perp = N\left[\frac{-3}{2D}g^2\mu_B{}^2 H \exp\left(\frac{-2D - \left[\frac{3}{8D}g^2\mu_B{}^2H^2\right]}{k_BT}\right) + \frac{3}{2D}g^2\mu_B{}^2 H \cosh\left(\frac{-g\mu_B H}{k_B(T-\theta)}\right) - 2g\mu_B \sinh\left(\frac{-g\mu_B H}{k_B(T-\theta)}\right)\right] \Bigg/ \left[2\exp\left(\frac{-2D - \left[\frac{3}{8D}g^2\mu_B{}^2H^2\right]}{k_BT}\right) + 2\cosh\left(\frac{-g\mu_B H}{k_B(T-\theta)}\right)\right] \quad (5b)$$

$$M(H,D,\theta)_{AVERAGE} = \frac{M(H)_\parallel + 2M(H)_\perp}{3} \quad (5c)$$

Indeed, using eq 5, $M(H,D,\theta)$ gave the best fit for **1** with $g = 2.253$, $D = 69.4$ cm^{-1} ($D/k_B = 100$ K), and $\theta = -0.56$ K, with a χ^2 agreement factor[13] $= \Sigma(M_{observed} - M_{calc})^2/M_{observed}{}^2 = 1.0046$. The best fit for **2** with $g = 2.235$, $D = 69.4$ cm^{-1}

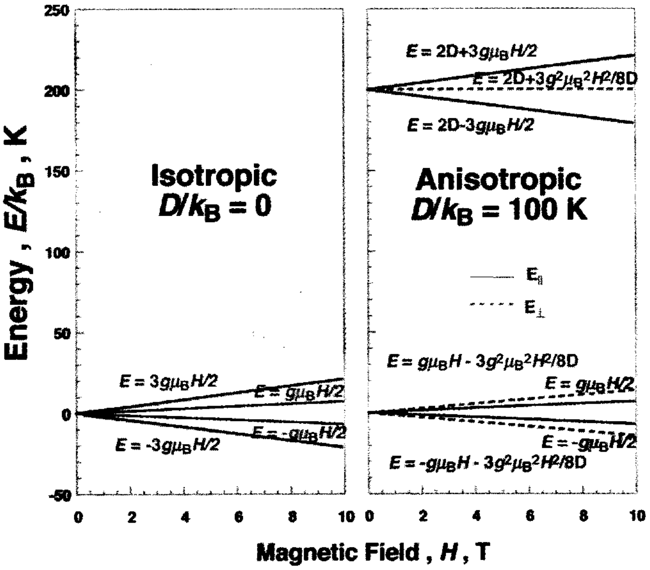

Figure 2. Energy spectra of $S = {}^3/_2$ energy levels with Zeeman effect, and isotropic and anisotropic for $D = 69.4$ cm^{-1} ($D/k_B = 100$ K).

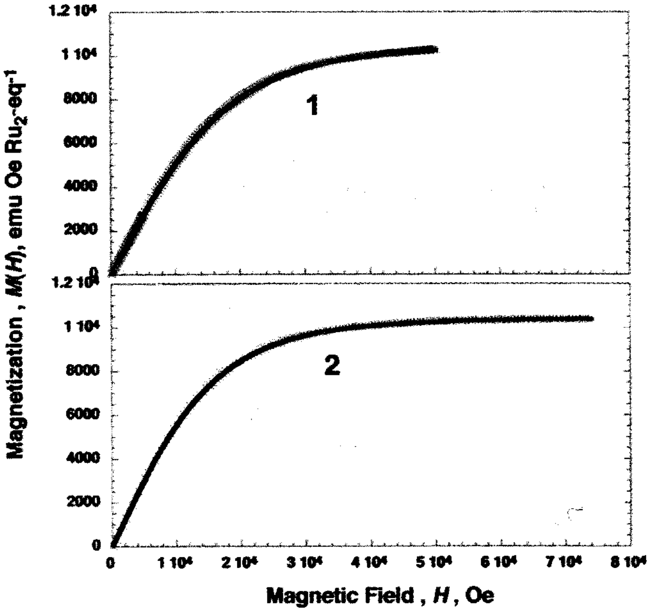

Figure 3. Observed $M(H,D,\theta)$ (×) for **1** ($g = 2.253$, $D = 69.4$ cm^{-1} ($D/k_B = 100$ K), and $\theta = -0.56$ K) and **2** ($g = 2.235$, $D = 69.4$ cm^{-1} ($D/k_B = 100$ K), $\theta = -0.24$ K), and their fits to eq 5.

($D/k_B = 100$ K), $\theta = -0.24$ K ($\chi^2 = 0.93$) (Figure 3). Again, the small θ values indicate very weak intradimer antiferromagnetic coupling.

The observed magnetizations 10,270 and 10,262 emu·Oe Ru_2-eq^{-1} at 5 T for **1** and **2**, respectively, are consistent with only the $m_s = {}^1/_2$ energy level being populated. The observed magnetization is the first plateau, and it should eventually rise to about 18,900 emu·Oe Ru_2-eq^{-1} when saturation occurs. This saturation magnetization is predicted to be the same value as that predicted by the Brillouin function, i.e., 18,880 and 18,725 emu·Oe Ru_2-eq^{-1} for **1** and **2**, respectively.

Since the anisotropic magnetization function is derived from second-order degenerate perturbation, $|D| \gg g\mu_BH$ was assumed. For large applied magnetic fields, $D \approx g\mu_BH$; hence, second-order perturbation is not valid. Consequently, there will be energy crossing when $D \approx g\mu_BH$, but to fully understand and to predict this energy-crossing phenomena, which results in the magnetization steps, an exact solution of the Hamiltonian, or higher-order perturbations, is required. This is a focus of ongoing studies, which will predict both energy-crossing and noncrossing effects. The noncrossing energy is due to the noncrossing rule, in which energy from spins that possess the same symmetry does not cross, and as a consequence, the energy-level mixing should occur.

Conclusion

Extension of the classical Brillouin function, $M(H)$, to include zero-field splitting (ZFS), D, [$|D| \gg g\mu_BH$] [and an intermolecular interaction (θ)], to a general analytical expression for the anisotropic magnetization function, $M(H,D,\theta)$, has been derived. This equation describes the unusually low values of the observed magnetization for $[Ru^{II/III}{}_2(OAc)_4]^+$. Deviations from the classical Brillouin function are a consequence of differing energy levels with respect to the isotropic energy levels used to derive the Brillouin function. However, further theoretical studies and high-field experiments will enable the understanding of the spin behavior upon saturation and energy-level crossover for materials with zero-field splitting.

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