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Initial Use of Dioximate Ligands in 3d/4f Cluster Chemistry: Synthesis, Structure, and Magnetic Studies of an Unusual $[Gd^{III}_2Mn^{IV}O]^{8+}$ Complex

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An unusual $[Mn^{IV}Gd^{III}_2(\mu_3\text{-}O^{2-})]^{8+}$ triangular complex has been prepared from the initial use of 2,6-diacetylpyridine dioxime ($dapdoH_2$) in 3d/4f cluster chemistry. The complex has an $S = {}^{13}/_2$ ground state, with exchange parameters $J = +0.49$ cm^{-1} and $J' = -0.12$ cm^{-1} [$\mathscr{H} = -2J(\hat{S}_i \cdot \hat{S}_j)$ convention] for the $Gd^{III}\cdots Mn^{IV}$ and $Gd^{III}\cdots Gd^{III}$ interactions, respectively. The origin of this ground state has been rationalized by consideration of the spin frustration occurring within the complex as a function of the relative magnitude of the competing interactions.

Intense attention has been directed in the recent years toward the synthesis of polynuclear 3d metal clusters.[1] This field has particularly flourished because of the realization that such molecular species will often possess very interesting magnetic properties and that some of them are single-molecule magnets (SMMs). SMMs are molecules that function as magnets below a critical temperature, providing a new "bottom-up" approach to nanoscale magnetic materials.[2] Several groups have since explored mixed 3d/4f compounds, and particularly Mn/Ln ones, as attractive routes to new SMMs, encouraged by the report of a Cu_2Tb_2 SMM by Matsumoto and co-workers.[3] The hope has been that a lanthanide's often significant spin and/or its often large anisotropy will lead to 3d/4f SMMs with properties significantly different from those of homometallic 3d ones. Indeed, this approach has successfully led to several Mn/Ln SMMs, including $Mn_{11}Ln_4$,[4] $Mn_{11}Gd_2$,[5] Mn_5Ln_4,[6] and Mn_6Dy_6[7] examples.

The Mn/Ln complexes obtained to date have not usually been amenable to detailed studies that can yield the magnitudes of the intramolecular exchange interactions and a resulting rationalization of how these lead to the observed ground state S value. Reasons for this are varied and include (i) the usually high nuclearity of these molecules and the consequently large number of pairwise exchange interactions (J_{ij}), many of which are competing and lead to spin frustration effects, (ii) the weak nature of the Mn−Ln and Ln−Ln exchange interactions, and (iii) spin−orbit coupling effects, which preclude accurate magnetic susceptibility fits for polynuclear systems.[8] For such reasons, we are targeting new synthetic routes that might yield small-nuclearity Mn/Ln complexes that are more amenable to an analysis of the sign and nature of their exchange interactions. We have recently been employing 2,6-diacetylpyridine dioxime ($dapdoH_2$) in 3d/4f chemistry, and we can report that this has led to a new $Gd^{III}_2Mn^{IV}$ complex with an unusual mix of metal oxidation states; we herein describe the synthesis, structure, and magnetochemical characterization of this compound. This also represents the initial use of $dapdoH_2$ in mixed-metal cluster chemistry, having been employed to date only in homometallic $Mn^{II/III}$ [9] and heterometallic Cr^{III}−Cu^{II} [10] complexes.

The reaction of $Mn(O_2CPh)_2\cdot 2H_2O$, $Gd(NO_3)_3\cdot 6H_2O$, $dapdoH_2$, and NEt_3 in a 1:1:2:4 molar ratio in MeCN gave a dark-brown solution, from which were subsequently isolated brown crystals of $[MnGd_2O(O_2CPh)_3(O_2CMe)(dapdo)(dapdoH)_2]$ (**1**) in 60% yield as **1**·10MeCN.[11] The acetate anion very likely comes from Mn^{III}- or Mn^{IV}-catalyzed aerial oxidation of MeCN. Dried

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(11) Anal. Calcd (found) for dried **1** (solvent-free): C, 48.74 (48.62); H, 4.34 (4.39); N, 10.23 (10.09). Crystal structure data for **1**·10MeCN: $C_{70}H_{75}Gd_2MnN_{19}O_{15}$, 1791.93 g mol^{-1}, monoclinic, *I2/a*, $a = 19.424(2)$ Å, $b = 27.132(3)$ Å, $c = 30.071(3)$ Å, $\beta = 90.155(2)°$, $Z = 8$, $V = 15848(3)$ Å^3, $d_{calc} = 1.502$ g cm^{-3}, $T = 173(2)$ K. Final R1 = 8.87 and wR2 = 19.76.

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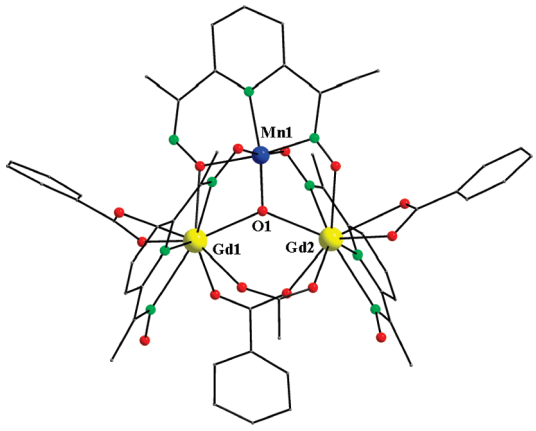

Figure 1. Molecular structure of **1**. Color code: Mn^{IV}, blue; Gd^{III}, yellow; O, red; N, green; C, gray. Hydrogen atoms are omitted for clarity.

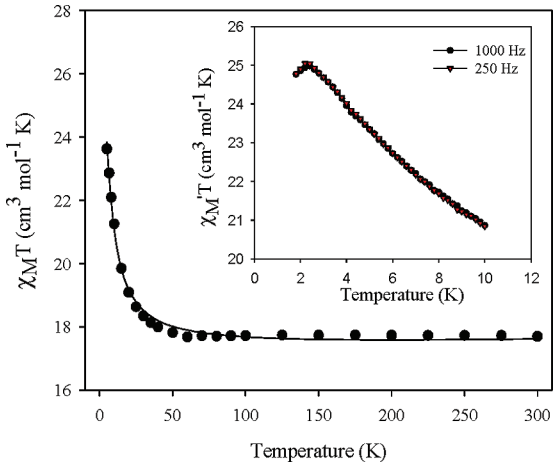

Figure 2. $\chi_M T$ vs T plot for complex **1** in a 1 kG field. The solid line is the fit of the data to the theoretical expression; see the text for the fit parameters. Inset: Plot of the in-phase ac susceptibility (χ'_M, as $\chi'_M T$) of **1** in a 3.5 G field oscillating at the indicated frequencies.

solid analyzed satisfactorily (C, H, and N) as solvent-free,[11] ruling out the possibility that the acetate is in reality a NO_3^- group; the same reaction in a different solvent does not give complex **1**. The structure of **1** (Figure 1) consists of an isosceles $Gd^{III}_2Mn^{IV}$ triangle with a central μ_3-O^{2-} ion O1, which is slightly (0.034 Å) above the $MnGd_2$ plane. Each dapdoH$^-$ group is a tridentate chelate on a Gd atom and forms a diatomic Gd−N−O−Mn bridge to Mn1 with its deprotonated NO^- arm. The dapdo^{2-} group is a tridentate chelate on Mn1 and bridges asymmetrically to the Gd atoms: one NO^- arm forms a diatomic Mn−N−O−Gd bridge to one Gd atom, whereas the other forms a monatomic Mn−O−Gd bridge to the other Gd atom. This asymmetric bridging mode is statically disordered in the crystal. The Gd···Gd edge is bridged by a benzoate and an acetate group. Ligation is completed by a chelating (η^2) benzoate group on each Gd atom. The Mn^{IV} oxidation state and O^{2-} protonation level were established by bond valence sum (BVS) calculations,[12] charge considerations, and inspection of the metric parameters. Mn1 is six-coordinate with distorted octahedral geometry, whereas each Gd^{3+} ion is nine-coordinate with a distorted capped square-antiprismatic geometry. Compound **1** is the first Mn/Ln complex with a triangular topology and the first 3d/4f cluster with a dioximate ligand.

Solid-state direct current magnetic susceptibility (χ_M) data on dried **1** were collected in a 1 kG (0.1 T) field in the 5.0−300 K range and are plotted as $\chi_M T$ vs T in Figure 2. $\chi_M T$ has a value of 17.60 cm^3Kmol^{-1} at 300 K, and it remains essentially constant down to 50 K and then rapidly increases to 23.62 cm^3Kmol^{-1} at 5 K. The $\chi_M T$ value at 300 K is essentially the same as the spin-only ($g = 2$) value of 17.64 cm^3Kmol^{-1} for one Mn^{IV} ($S = {}^3/_2$) and two Gd^{III} ($S = {}^7/_2$, $L = 0$) noninteracting ions. The essentially constant value down to 50 K is consistent with very weak exchange interactions in the molecule, as expected when Ln ions are involved. To determine the individual pairwise exchange parameters J and J' between the Gd−Mn and Gd−Gd pairs, respectively, the $\chi_M T$ vs T data were fit to the appropriate theoretical expression for an isosceles $Gd^{III}_2Mn^{IV}$ triangle of C_{2v} symmetry; i.e., we assumed that the Gd−Mn interactions would be very weak and essentially identical despite the slightly different bridges described above. The isotropic spin Hamiltonian describing the exchange interactions within **1** is given by eq 1, where $\hat{S}_i$ is the spin operator for metal atom M_i ($i = 1$ for Mn and 2 and 3 for Gd).

$$\mathscr{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3) - 2J'\hat{S}_2 \cdot \hat{S}_3 \quad (1)$$

The eigenvalues of this spin Hamiltonian can be determined analytically with the Kambe vector coupling method.[13] Thus, using the substitutions $\hat{S}_A = \hat{S}_2 + \hat{S}_3$ and $\hat{S}_T = \hat{S}_A + \hat{S}_1$, where S_T is the total spin of the molecule, allows the spin Hamiltonian to be transformed into the equivalent form given by eq 2. The eigenvalues of eq 2 are given by eq 3, where $E(S_T,S_A)$ is the energy of state S_T arising from S_A, and constant terms contributing to all states have been omitted.

$$\mathscr{H} = -2J(\hat{S}_T{}^2 - \hat{S}_A{}^2 - \hat{S}_1{}^2) - 2J'(\hat{S}_A{}^2 - \hat{S}_2{}^2 - \hat{S}_3{}^2) \quad (2)$$

$$E(S_T, S_A) = -J[S_T(S_T + 1) - S_A(S_A + 1)] - J'[S_A(S_A + 1)] \quad (3)$$

For complex **1**, the overall multiplicity of the spin system is 256, made up of 28 spin states ranging from $S_T = {}^1/_2$ to ${}^{17}/_2$. Derivation of the appropriate Van Vleck equation and its use to fit the $\chi_M T$ vs T data (shown as the solid line in Figure 2) gave $J = +0.49(2)$ cm^{-1}, $J' = -0.12(3)$ cm^{-1}, and $g = 1.98(1)$. A temperature-independent paramagnetism term was included and held constant at 900×10^{-6} cm^3 mol^{-1}.[8,14] The exchange interactions are thus both very weak, and of different sign, and predict the complex to have an intermediate $S_T = {}^{13}/_2$ ground state, the $|S_T, S_A\rangle = |{}^{13}/_2, 5\rangle$ state, with low-lying $S_T = {}^{11}/_2$ and ${}^{15}/_2$ excited states at 5.32 and 5.62 cm^{-1}, respectively, above the ground state.

In order to confirm the ground state of **1**, alternating current (ac) magnetic susceptibility studies were performed in the 1.8−10 K temperature range using a 3.5 G ac field oscillating at 250−1000 Hz. The in-phase $\chi'_M T$ signal (inset

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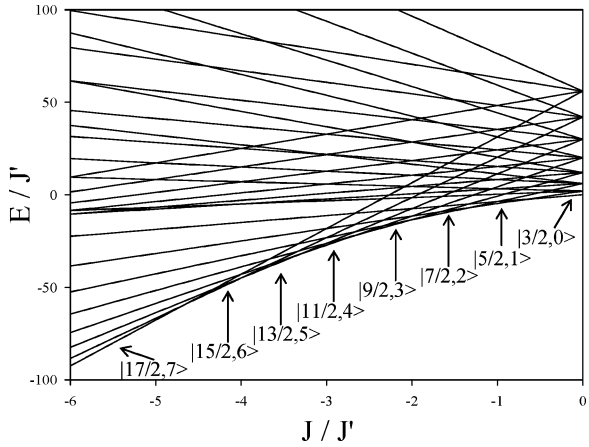

Figure 3. Variation of the spin-state energies of **1** with the J/J' ratio, showing multiple changes in the ground state; the states are labeled as $|S_T, S_A\rangle$.

of Figure 2) rapidly increases with decreasing temperature, indicating depopulation of excited states with S values smaller than the ground state, and reaches a maximum at 25.2 cm^3Kmol^{-1} before then decreasing slightly, to 24.7 cm^3Kmol^{-1} at 1.8 K. The lowest temperature data thus confirm an $S = {}^{13}/_2$ state with $g \sim 2$; $\chi'_M T$ values for $S = {}^{11}/_2$, ${}^{13}/_2$, and ${}^{15}/_2$ with $g = 2.0$ are 17.9, 24.4, and 31.9 cm^3Kmol^{-1}, respectively. There were no out-of-phase ac signals down to 1.8 K, and **1** is thus not an SMM.

A ferromagnetic $J = +0.49(2)$ cm^{-1} and an antiferromagnetic $J' = -0.12(3)$ cm^{-1} for the Gd−Mn and Gd−Gd interactions, respectively, indicate the presence of competing interactions and spin-frustration effects. This is consistent with the observed $S = {}^{13}/_2$ ground state, which does not correspond to a simple "spin up/spin down" picture of spin alignments. Instead, this value indicates some intermediate (frustrated) alignments resulting from the competing interactions, as is also indicated by the $S_A = 5$ value of the $|S_T, S_A\rangle = |{}^{13}/_2, 5\rangle$ ground state.[15] In such situations, the ground state is extremely sensitive to the relative magnitudes of the competing exchange interactions. Because there has been no theoretical analysis to date of the spin-state energies as a ratio of the J values in an isosceles triangle comprising one $S = {}^3/_2$ and two $S = {}^7/_2$ spins, we have carried one out in order to rationalize the observed ground state of **1**.

In Figure 3 are plotted the energies, in units of J', of the 28 spin states of complex **1** as a function of the J/J' ratio, for J ferromagnetic and J' antiferromagnetic values. Several important conclusions can be drawn: (i) as expected for a spin-frustrated system, the ground state is indeed very sensitive to the J/J' ratio, with eight different ground states spanning $S_T = {}^3/_2 - {}^{17}/_2$ being possible for this combination of signs for J and J'; (ii) when $J \gg J'$ and as a result $|J/J'| > \sim 4.65$, the ground state is described by $S_T = {}^{17}/_2$ and $S_A = 7$, i.e., the $|{}^{17}/_2, 7\rangle$ state, arising from J, totally overwhelming J', and aligning the two Gd spins parallel to the Mn spin

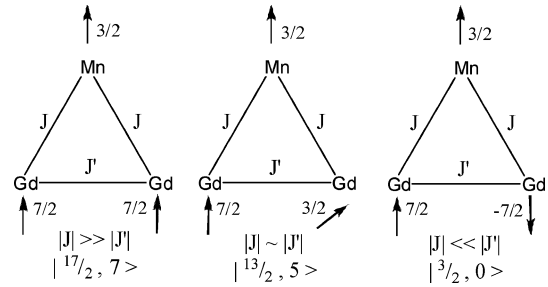

Figure 4. Depictions of the indicated $|S_T, S_A\rangle$ states, showing (left) the complete frustration of J' and the resultant $S_T = {}^{17}/_2$ ground state, (middle) the intermediate situation, giving the $S = {}^{13}/_2$ ground state of **1**, and (right) the complete frustration of J and the resultant $S_T = {}^3/_2$ ground state.

and thus to each other. This is depicted in Figure 4, left, and corresponds to the antiferromagnetic J' interaction being totally frustrated. As $|J'|$ increases relative to $|J|$, the Gd spins are no longer perfectly parallel but, at some intermediate alignment, are determined by the relative magnitudes of J and J', i.e., the $|J/J'|$ ratio. Thus, as this ratio gets progressively smaller, the Gd spins align less and less parallel and then more and more antiparallel. When $4.65 > |J/J'| > 4.2$, the ground state is $|{}^{15}/_2, 6\rangle$, and when $\sim 4.2 > |J/J'| > \sim 3.2$, the ground state is $|{}^{13}/_2, 5\rangle$, found experimentally for **1** (Figure 4, middle). Finally, when $J \ll J'$ and $\sim 0.65 > |J/J'| > 0$, the J interaction is completely frustrated, the Gd spins are perfectly antiparallel, and the ground state is thus $|{}^3/_2, 0\rangle$ (Figure 4, right).

The fit shown in Figure 2 gave $J = +0.49(2)$ cm^{-1}, $J' = -0.12(3)$ cm^{-1}, and thus $|J/J'| = 4.08$, which is within the range for a $|{}^{13}/_2, 5\rangle$ ground state. Note that if J and J' were (i) both ferromagnetic, (ii) antiferro- and ferromagnetic, respectively, or (iii) both antiferromagnetic, they could not yield an $S = {}^{13}/_2$ ground state: the first two cases would give $S = {}^{17}/_2$ and ${}^{11}/_2$ ground states, respectively, for all J/J' ratios, and the third could give a ground state only in the $S = {}^1/_2 - {}^{11}/_2$ range. Thus, although we were originally wary about the reliability of the exchange parameters obtained from the fit, it does appear that the opposite sign and relative magnitudes of J and J' are indeed correct.

In summary, a $Gd^{III}{}_2Mn^{IV}$ triangular complex has resulted from the initial use of a dioximate ligand in 3d/4f cluster chemistry. The complex has an $S = {}^{13}/_2$ ground state, resulting from a ferromagnetic $Gd^{III}-Mn^{IV}$ interaction and an antiferromagnetic Gd−Gd one. We are now exploring the incorporation of an anisotropic Ln^{III} ion in place of the Gd^{III} ion and the further use of $dapdoH_2$ in higher-nuclearity 3d/4f clusters.

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Supporting Information Available: Crystallographic data (CIF format) for **1** and structural and magnetism figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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