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

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An unusual $[\text{Mn}^{IV}\text{Gd}^{III}(\mu_2-\text{O}^2-)]^{8+}$ triangular complex has been prepared from the initial use of 2,6-diacyetylpyridine 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$^{-1}$ [where $J = -2\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ 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. 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 new “bottom-up” approach to nanoscale magnetic materials. 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$_4$Tb$_2$ SMM by Matsumoto and co-workers. The hope has been that a 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-diacyetylpyridine dioxime (dapdoH$_2$) in 3d/4f chemistry, and we can report that this has led to a new Gd$^{III} \cdots$ Mn$^{IV}$ 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$^{II/III}$ and heterometallic Cu$^{II} \cdots$ Cu$^{II}$ complexes.

The reaction of Mn(O$_2$CPh)$_2$·2H$_2$O, Gd(NO$_3$)$_3$·6H$_2$O, 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 $[\text{MnGd}_{3}(\text{O}_2\text{CPh})_3\cdot(\text{O}_2\text{CMe})(\text{dapdo})(\text{dapdoH})_2]$ (1) in 60% yield as $\cdot$10MeCN.$^{11}$ The acetate anion very likely comes from Mn$^{III}$ or Mn$^{IV}$-catalyzed aerial oxidation of MeCN. Dried
solid analyzed satisfactorily (C, H, and N) as solvent-free,

ruling out the possibility that the acetate is in reality a NO₃⁻
group; the same reaction in a different solvent does not give
complex 1. The structure of 1 (Figure 1) consists of an
isosceles Gd₃MnIV triangle with a central µ_v-O²⁻ ion O₁,
which is slightly (0.034 Å) above the MnGd₂ 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
deprontonated NO group is a tridentate chelate on a Gd atom and
-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 (η⁵) benzolate group
on each Gd atom. The MnIV oxidation state and O²⁻
protonation level were established by bond valence sum
(BVS) calculations, and inspection of the metric parameters. Mn1 is six-coordinate with distorted
octahedral geometry, whereas each Gd³⁺ 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 dioxime
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 χ_m/T vs T in Figure 2. χ_m/T has a value of 17.60 cm³Kmol⁻¹ at 300 K, and it remains
essentially constant down to 50 K and then rapidly increases
to 23.62 cm³Kmol⁻¹ at 5 K. The χ_m/T value at 300 K is
essentially the same as the spin-only (g = 2) value of 17.64
cm³Kmol⁻¹ for one Mn⁴⁺ (S = 1/2) and two Gd³⁺ (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
χ_m/T vs T data were fit to the appropriate theoretical expression for an isosceles Gd₃MnIV triangle of C_{2v}.

\( \mathcal{H} = -2J(\hat{S}_1^2 - \hat{S}_2^2 - \hat{S}_3^2) - 2J'(\hat{S}_1^2 - \hat{S}_2^2 - \hat{S}_3^2) \) (2)

\( E(S_1, S_2, S_3) = -J[\hat{S}_1(\hat{S}_1 + 1) - S_2(S_2 + 1)] - J'[S_2(S_2 + 1)] \) (3)

For complex 1, the overall multiplicity of the spin system is
256, made up of 28 spin states ranging from S₁ = 1/2 to 17/2.
Derivation of the appropriate Van Vleck equation and its
use to fit the χ_m/T vs T data (as shown in 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 cm³ mol⁻¹.²,¹⁴ The exchange interactions are thus both very weak, and of
different sign, and predict the complex to have an intermediate
S₁ = 17/2 ground state, the IS₁, S₁ = 17/2, 5) state, with
low-lying S₁ = 11/2 and 13/2 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 χ'ₘ/T signal

the Mn⁴⁺ and O²⁻ ions were 3.91 and 1.97, respectively.


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$^3$Kmol$^{-1}$ before then decreasing slightly, to 24.7 cm$^3$Kmol$^{-1}$ at 1.8 K. The lowest temperature data thus confirm an $S = \frac{11}{2}$ state with $g \sim 2$; $\chi_M T$ values for $S = \frac{11}{2}, \frac{13}{2}$, and $\frac{15}{2}$ with $g = 2.0$ are 17.9, 24.4, and 31.9 cm$^3$Kmol$^{-1}$, respectively. There were no out-of-phase ac signals down to 1.8 K, and $\mathbf{1}$ 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 $S = \frac{13}{2}$ 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 $S(\mathbf{1})$, $S(\mathbf{2})$ = $\frac{11}{2}, 5$ 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 $S = \frac{1}{2}$ and two $S = \frac{3}{2}$ spins, we have carried one out in order to rationalize the observed ground state of $\mathbf{1}$.

In Figure 3 are plotted the energies, in units of $J'$, of the 28 spin states of complex $\mathbf{1}$ 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 $S_T = \frac{1}{2} - \frac{3}{2}$ being possible for this combination of signs for $J$ and $J'$; (ii) when $J > J'$ and as a result $|U/J'| > \sim 4.65$, the ground state is described by $S_T = \frac{17}{2}$ and $S_A = 7$, i.e., the $|\frac{17}{2}, 7\rangle$ state, arising from $J$, totally overwhelming $J'$, and aligning the two Gd spins parallel to the Mn spin and thus to each other. This is depicted in Figure 4, left, and corresponds to the antiferromagnetic $J'$ interaction being totally frustrated. As $U/J'$ increases relative to $|U|$, 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 $|U/J'|$ ratio. Thus, as this ratio gets progressively smaller, the Gd spins align less and less parallel and then more and more antiparallel. When $4.65 > |U/J'| > 4.2$, the ground state is $|\frac{13}{2}, 6\rangle$, and when $\sim 4.2 > |U/J'| > \sim 3.2$, the ground state is $|\frac{13}{2}, 5\rangle$, found experimentally for $\mathbf{1}$ (Figure 4, middle). Finally, when $J < J'$ and $\sim 0.65 > |U/J'| > 0$, the $J$ interaction is completely frustrated, the Gd spins are perfectly antiparallel, and the ground state is thus $|\frac{13}{2}, 0\rangle$ (Figure 4, right).

The fit shown in Figure 2 gave $J = +0.49(2)$ cm$^{-1}$, $J' = -0.12(3)$ cm$^{-1}$, and thus $|U/J'| = 4.08$, which is within the range for a $|\frac{13}{2}, 5\rangle$ 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 $S = \frac{13}{2}$ ground state: the first two cases would give $S = \frac{11}{2}$ and $\frac{13}{2}$ ground states, respectively, for all $J/J'$ ratios, and the third could give a ground state only in the $S = \frac{1}{2} - \frac{1}{2}$ 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$^{3+}$–Mn$^{4+}$ triangular complex has resulted from the initial use of a dioximate ligand in 3d/4f cluster chemistry. The complex has an antiferromagnetic Gd$^{3+}$–Mn$^{4+}$ interaction and the resultant $|U/J'| = 4.08$ for the $S(\mathbf{1})$, $S(\mathbf{2})$ = $\frac{11}{2}, 5$ ground state, resulting from a ferromagnetic Gd$^{3+}$–Mn$^{4+}$ interaction and an antiferromagnetic Gd–Gd one. We are now exploring the incorporation of an anisotropic Ln$^{3+}$ ion in place of the Gd$^{3+}$ 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 $\mathbf{1}$ and structural and magnetism figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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