

Slow Magnetization Relaxation in Unprecedented $\text{Mn}^{\text{III}}_4\text{Dy}^{\text{III}}_3$ and $\text{Mn}^{\text{III}}_4\text{Dy}^{\text{III}}_5$ Clusters from the Use of *N*-Salicylidene-*o*-aminophenol

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Supporting Information

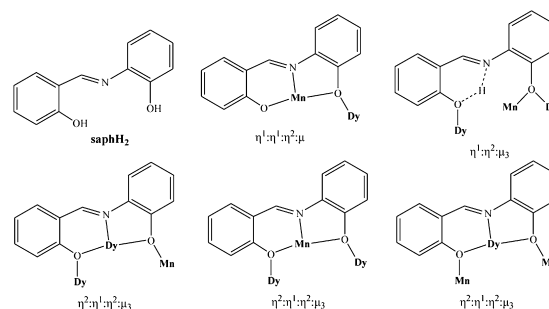
ABSTRACT: The first use of *N*-salicylidene-*o*-aminophenol in 3d/4f chemistry has led to $\text{Mn}^{\text{III}}_4\text{Dy}^{\text{III}}_5$ and $\text{Mn}^{\text{III}}_4\text{Dy}^{\text{III}}_3$ clusters with unprecedented metal topologies and stoichiometries; both compounds exhibit out-of-phase signals indicative of the slow magnetization relaxation of a single-molecule magnet.

In the molecular chemistry arena, polynuclear 3d/4f complexes occupy a special position among mixed-metal molecular magnetic materials because they present an alternative to homometallic transition-metal and lanthanide clusters.¹ The choice of the 4f metal ion is of great importance because it directs the interest regarding the potential applications. 3d/4f metal clusters have shown a pronounced ability to act either as single-molecule magnets (SMMs)² when the f-block ions are highly anisotropic and possess a significant spin (i.e., Dy^{III} , Tb^{III} , Ho^{III}) or as magnetic refrigerants³ when the molecules are isotropic and high-spin, conditions that are fulfilled by employment of the Gd^{III} ion. Furthermore, “hybrid” molecular materials exhibiting both intriguing magnetic and optical properties could result when the 4f metal ion is one of the most intensely photoluminescent, such as Eu^{III} and Tb^{III} .⁴

Our group, and others, has had a long-standing interest in the synthesis of heterometallic 3d/4f SMMs,⁵ which are molecular species exhibiting an energy barrier to the relaxation of magnetization due to the combination of a large ground-state spin multiplicity (*S*) and a significant negative zero-field splitting (*D*) of that ground state. The hope has been that the copresence of two different anisotropic and high-spin metal ions within the same species will lead to SMMs with unprecedented structural motifs and exciting magnetic properties, such as enhanced energy barriers⁶ and/or irregular quantum behaviors.⁷ For such reasons, we are targeting new synthetic routes that might yield large-nuclearity 3d/4f clusters, and the combination of Mn^{III} / Dy^{III} ions appears to be a promising pathway to achieve the desired structural and magnetic properties. Indeed, this approach has successfully led to various $\{\text{Mn}_x\text{Dy}_y\}$ cluster combinations ($x = 2-21$; $y = 1-8$) and SMMs, albeit not many of which containing solely Mn^{III} atoms.^{5,8}

Toward this end, synthetic methods must be developed to combine the preferred 3d and 4f ions within a cluster. Among the various routes employed to date, the “one-pot” reactions involving a mixture of 3d and 4f metal salts and a ligand possessing a distinct coordination affinity for preferential binding to the two different types of ions appear as an ideal strategy to be followed. The design and synthesis of new multidentate chelating/bridging organic ligands is undoubtedly an attractive route to isolating new 3f/4f clusters and SMMs.⁹ On the other hand, one of the most important challenges for synthetic inorganic chemists is the reemployment of “old” well-known ligands in modern fields of coordination chemistry. Among these, Schiff base ligands, and particularly *N*-salicylidene-*o*-aminophenol (saphH_2 , Chart 1), should favor the formation of 3d/4f

Chart 1. Structural Formula and Abbreviation of the Ligand *N*-Salicylidene-*o*-aminophenol (saphH_2) and the Crystallographically Established Coordination Modes of Its Deprotonated Forms in Complexes 1 and 2



metal species via binding through the relatively soft N atom and the two hard, deprotonated O atoms. Note that the saphH_2 ligand has been widely used for the isolation of mono- and dinuclear metal complexes¹⁰ but with almost negligible presence in metal cluster chemistry.¹¹

With all of the above in mind, we decided to employ, for the first time, saphH_2 in Mn/Dy chemistry as a means of obtaining

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high-nuclearity heterometallic clusters with exciting structures, uncommon $\{\text{Mn}_x\text{Dy}_y\}$ combinations, and interesting magnetic properties. The reaction of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, saphH_2 , and NET_3 in a 1:2:2:2 molar ratio in MeCN led to a dark-brown suspension, which upon filtration gave a dark-red filtrate and a brown microcrystalline solid. The former solution was allowed to slowly evaporate at room temperature, yielding after 2 days dark-red prismatic crystals of $(\text{NH}_4\text{Et}_3)_2[\text{Mn}_4\text{Dy}_5\text{O}_2(\text{OH})_4(\text{NO}_3)_4(\text{saph})_8(\text{H}_2\text{O})_4]$ (**1**) in 40% yield.¹² The freshly prepared brown solid was dissolved in CH_2Cl_2 , and the resulting dark-brown solution was layered with MeCN to give after 3 days brown platelike crystals of $[\text{Mn}_4\text{Dy}_3\text{O}_2(\text{OH})_4(\text{NO}_3)_3(\text{saph})_6(\text{saphH})(\text{H}_2\text{O})]$ (**2**) in 30% yield.

The anion of **1** (Figure 1, top) consists of four Mn^{III} and five Dy^{III} atoms held together by two $\mu_4\text{-O}^{2-}$ (O3 and O3'), four $\mu_3\text{-OH}^-$ (O4, O4', O5, and O5'), and eight saph^{2-} ligands. The latter are of two types: $\eta^1:\eta^1:\eta^2:\mu$, with the Mn atom belonging to the chelating part of the ligand and one of the alkoxido arms bridging a Dy atom, and $\eta^2:\eta^1:\eta^2:\mu_3$, with the Dy atom positioned in the chelating part and each of the alkoxido groups bridging a Mn atom or a Dy atom (Chart 1). The complex thus contains an overall $[\text{Mn}_4\text{Dy}_5(\mu_4\text{-O})_2(\mu_3\text{-OH})_4]^{19+}$ core (purple thick lines), emphasizing the fused "tetrahedra-to-bowtie" description (black dashed lines). Color scheme: Mn^{III} , blue; Dy^{III} , yellow; O, red; N, green; C, gray.

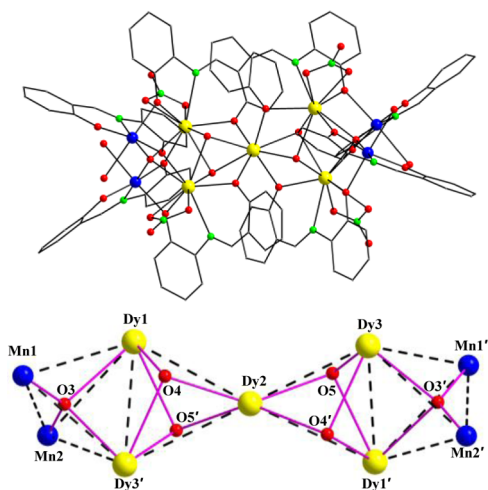


Figure 1. (top) Structure of the anion of **1** and (bottom) its simplified $[\text{Mn}_4\text{Dy}_5(\mu_4\text{-O})_2(\mu_3\text{-OH})_4]^{19+}$ core (purple thick lines), emphasizing the fused "tetrahedra-to-bowtie" description (black dashed lines). Color scheme: Mn^{III} , blue; Dy^{III} , yellow; O, red; N, green; C, gray.

OH^- (O4, O4', O5, and O5'), and eight saph^{2-} ligands. The latter are of two types: $\eta^1:\eta^1:\eta^2:\mu$, with the Mn atom belonging to the chelating part of the ligand and one of the alkoxido arms bridging a Dy atom, and $\eta^2:\eta^1:\eta^2:\mu_3$, with the Dy atom positioned in the chelating part and each of the alkoxido groups bridging a Mn atom or a Dy atom (Chart 1). The complex thus contains an overall $[\text{Mn}_4\text{Dy}_5(\mu_4\text{-O})_2(\mu_3\text{-OH})_4(\mu\text{-OR})_{12}]^{7+}$ core, with peripheral ligation provided by four bidentate-chelating NO_3^- groups and four terminal H_2O molecules, each bound to a Mn atom. A description of the metal topology of **1** is as two central $\{\text{Dy}_3(\mu_3\text{-OH})_2\}^{7+}$ equilateral triangles with a common vertex (a "bowtie") fused to two external $\{\text{Mn}_2\text{Dy}_2(\mu_4\text{-O})\}^{10+}$ edge-sharing tetrahedra (Figure 1, bottom). All Mn atoms are six-coordinate with distorted octahedral geometries, exhibiting pronounced Jahn–Teller (JT) axial elongations; the four JT axes are essentially perpendicular to each other. All of the Dy atoms are nine-coordinate, except the central Dy2 atom, which is eight-coordinate. The metal oxidation states and protonation levels of $\text{O}^{2-}/\text{OH}^-/\text{OR}^-/\text{H}_2\text{O}$ groups (as well as those of complex **2**) were all confirmed by inspection of the metric parameters and bond-valence-sum¹³ calculations.

Powell et al. have recently reported two structurally and magnetically intriguing compounds, namely, a discrete $\{\text{Dy}_3(\mu_3\text{-OH})_2\}^{7+}$ triangle with SMM behavior of thermally excited spin states¹⁴ and its dimerized $\{\text{Dy}_6(\mu_3\text{-OH})_4\}^{14+}$ version with

enhanced slow magnetization relaxation.¹⁵ Among the many structurally characterized pentanuclear Ln^{III} clusters with a square-pyramidal topology and impressive magnetic properties,¹⁶ the topology of the Dy_5 subunit within **1** is unprecedented and reminiscent of a new type of triangular-linked species.

Complex **2** crystallizes in monoclinic space group $P2_1/c$ with two independent molecules in the asymmetric unit, but these are structurally very similar, and therefore only one (Figure 2, left)

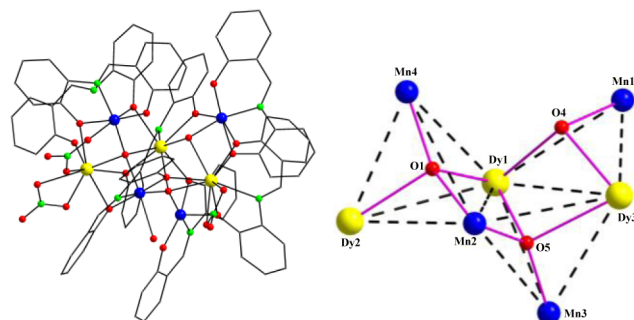


Figure 2. (left) Structure of one of the two crystallographically independent molecules in **2** and (right) its simplified $[\text{Mn}_4\text{Dy}_3(\mu_4\text{-O})_2(\mu_3\text{-OH})]^{16+}$ core (purple thick lines), emphasizing the fused "bitetrahedral-to-triangle" description (black dashed lines). Color scheme as in Figure 1.

will be discussed. The core of **2** comprises four Mn^{III} and three Dy^{III} atoms arranged as two $\{\text{Mn}_2\text{Dy}_2(\mu_4\text{-O})\}^{10+}$ edge-sharing tetrahedra, with one of them sharing an additional edge with a $\{\text{MnDy}_2(\mu_3\text{-OH})\}^{8+}$ triangle (Figure 2, right). The metal atoms are additionally bridged by 10 OR^- alkoxido groups of six saph^{2-} and one saphH^- chelates to give a complete $[\text{Mn}_4\text{Dy}_3(\mu_4\text{-O})_2(\mu_3\text{-OH})(\mu\text{-OR})_{10}]^{6+}$ core. Peripheral ligation about the core is provided by an $\eta^1:\eta^1:\mu$ and two bidentate-chelating NO_3^- groups, and a terminal H_2O molecule. The saph^{2-} groups are tridentate-chelating to either a Mn atom or a Dy atom, with each of their alkoxido arms also bridging adjacent Dy or Mn atoms, respectively; these groups are thus $\eta^2:\eta^1:\eta^2:\mu_3$ and $\eta^1:\eta^1:\eta^2:\mu$ (Chart 1). The only saphH^- group adopts a quite unusual, for such a Schiff base ligand, $\eta^1:\eta^2:\mu_3$ coordination mode (Chart 1), with the existence of a strong intraligand hydrogen bond ($\text{O}\cdots\text{H}\cdots\text{N}$ 2.683 Å). The Dy atoms are eight- (Dy1 and Dy2) and nine-coordinate (Dy3) with very distorted geometries, while Mn(1,2,4) and Mn3 are six- and five-coordinate, respectively, with distorted octahedral and square-pyramidal ($\tau = 0.06^{17}$) geometries, respectively.

Complexes **1** and **2** are the first structurally characterized, very high-nuclearity metal clusters to contain any form of the *N*-salicylidene-*o*-aminophenol ligand and the first and second¹⁸ examples of clusters exhibiting Mn_4Dy_5 and Mn_4Dy_3 stoichiometries, respectively.

Solid-state direct-current (dc) magnetic susceptibility (χ_M) data were collected in the 5.0–300 K range in a 1 kG (0.1 T) field (Figure S3 in the Supporting Information). At 300 K, the $\chi_M T$ values are 68.82 and 55.85 $\text{cm}^3 \text{mol}^{-1} \text{K}$ for **1**·2 H_2O and **2**, respectively, which are lower and slightly higher than the expected values of 82.85 and 54.51 $\text{cm}^3 \text{mol}^{-1} \text{K}$ for uncoupled $\text{Mn}^{\text{III}}_4\text{Dy}^{\text{III}}_5$ and $\text{Mn}^{\text{III}}_4\text{Dy}^{\text{III}}_3$ systems (Mn^{III} , $S = 2$, $g = 2$; Dy^{III} , $S = 5/2$, $L = 5$, $g_J = 4/3$, ${}^6\text{H}_{15/2}$), respectively.^{5,8} Upon lowering of the temperature, the $\chi_M T$ value of **1**·2 H_2O gradually decreases to a minimum value of 49.35 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 5.0 K, suggesting dominant antiferromagnetic exchange interactions between the

metal centers and an appreciable ground-state spin value. The magnetic behavior of **2** is very different from that of **1** but again indicates a large ground-state spin value. Thus, the $\chi_M T$ value of **2** first steadily increases to $60.53 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 40 K and then rapidly decreases to a minimum value of $38.18 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 5 K, which is likely attributed to competition between ferro- and antiferromagnetic coupling and/or crystal-field effects of Dy^{III} .^{5,8} To investigate whether **1** and **2** are SMMs, alternating-current (ac) susceptibility data were collected in a 3.5 G ac field oscillating at various frequencies and with a zero dc field (Figure 3). Frequency-dependent decreases in the in-phase (χ_M')

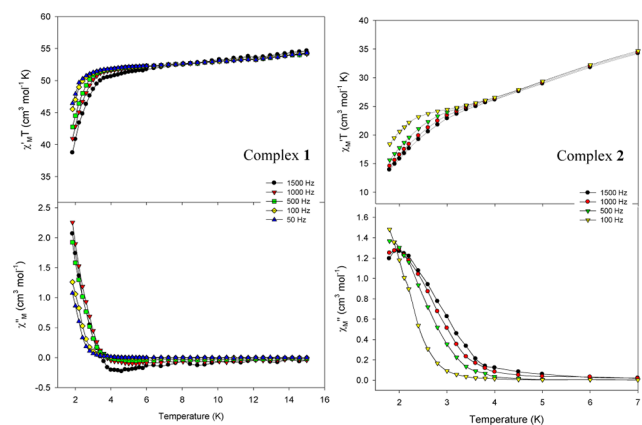


Figure 3. Plots of the in-phase ($\chi_M' T$, top) and out-of-phase (χ_M'' , bottom) ac susceptibility signals versus T for $1 \cdot 2\text{H}_2\text{O}$ (left) and **2** (right).

signals with concomitant increases in the out-of-phase (χ_M'') signals were observed for both complexes, indicative of the slow magnetization relaxation of a SMM.

In conclusion, we have shown that an “old”, in coordination chemistry, ligand, such as the simple Schiff base saphH₂, can indeed yield high-nuclearity 3d/4f metal clusters with new structures and interesting magnetic properties, without requiring the copresence of ancillary organic groups. We are currently investigating the photoluminescent properties of **1** and **2**, as well as the preparation of several Mn_4Ln_5 and Mn_4Ln_4 analogues, to provide deeper insight into the nature of the intramolecular exchange interactions. Finally, given the intriguing magnetic behavior of the Dy_3 triangles, it would be magnetically, and also optically, interesting to synthesize analogues of **1** with diamagnetic 3d metal ions (i.e., Ga^{III}) in place of Mn^{III} .

ASSOCIATED CONTENT

Supporting Information

Crystallographic data (CIF format), synthetic details, and various structural and magnetism figures for complexes **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (12) Anal. Calcd (found) for $1 \cdot 2\text{H}_2\text{O}$: C, 40.28 (40.15); H, 3.20 (3.13); N, 5.55 (5.76). Crystal structure data for $1 \cdot 10\text{MeCN}$: $\text{C}_{130}\text{H}_{130}\text{Mn}_4\text{Dy}_5\text{N}_{23}\text{O}_{38}$, $M_w = 3654.83$, orthorhombic, space group *Pccn* with $a = 21.8064(11) \text{ \AA}$, $b = 23.8797(13) \text{ \AA}$, $c = 26.3457(14) \text{ \AA}$, $V = 13719.0(13) \text{ \AA}^3$, $T = 150(2) \text{ K}$, $Z = 4$, $R_1 [I > 2\sigma(I)] = 0.0364$, $wR_2 = 0.0848$ (F^2 , all data). Anal. Calcd (found) for **2** (solvent-free): C, 44.80 (44.92); H, 2.77 (2.83); N, 5.74 (5.61). Crystal structure data for $2 \cdot 5\text{MeCN}$: $\text{C}_{101}\text{H}_{82}\text{Mn}_4\text{Dy}_3\text{N}_{15}\text{O}_{27}$, $M_w = 2645.08$, monoclinic, space group *P2₁/c* with $a = 29.146(5) \text{ \AA}$, $b = 21.095(3) \text{ \AA}$, $c = 32.414(5) \text{ \AA}$, $V = 19447(5) \text{ \AA}^3$, $T = 150(2) \text{ K}$, $Z = 8$, $R_1 [I > 2\sigma(I)] = 0.0518$, $wR_2 = 0.1381$ (F^2 , all data). CCDC deposition numbers for **1** and **2**: 909501 and 909502.
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