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Structure and Properties of New Mixed-Valent $[Mn^{III}_2Mn^{IV}_3Ln^{III}_5O_5]$ Complexes (Ln^{III} = Tm^{III}, Lu^{III}, and Yb^{III})

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Supporting Information

ABSTRACT: By using 2′-hydroxyacetophenoxime, a new family of complexes with an $[Mn^{III}_2Mn^{IV}_3Ln_5O_5]$ core was obtained with Ln = Tm (**1**), Lu (**2**), and Yb (**3**). Heterometallic Mn/Tm and Mn/Lu combinations have had no precedence so far. Studies of the magnetic properties indicate the presence of intracomplex antiferromagnetic interactions in **1** and **3**, as well as a dominating ferromagnetic interaction between Mn^{III} and Mn^{IV} spins in **2**, leading to an $S_T = {}^5/_2$ ground state.

The chemistry of polynuclear manganese complexes is a rapidly developing branch of science, motivated by their interesting magnetic properties, including single-molecule-magnet (SMM) behavior,[1] which may result in applications like high-density information storage.[2] Recently, lanthanide (Ln) ions were introduced into the complex molecules because of their high magnetic anisotropy.[3] When mixed with 3d metal ions, the capability of Ln ions to adopt large coordination numbers (CNs) often results in interesting topologies and high-nuclearity heterometallic complexes, like $[Mn^{III}_9Mn^{II}_2Gd_2O_8(OH)_2(piv)_{10.6}(fca)_{6.4}(NO_3)_2(H_2O)]\cdot 13CH_3CN\cdot H_2O$.[4a] The use of Ln ions in manganese chemistry to obtain large aggregates has so far been reported in many systems including La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Yb.[4−15] No examples of manganese complexes including Tm or Lu ions have been published to date. In this paper, we report on two examples of a new family of mixed-valent complexes with an $[Mn_5Ln_5O_5]$ core (Ln = Tm (**1**) and Lu (**2**), respectively). To our knowledge, both elemental combinations are novel in manganese chemistry. Additionally, the isomorphous Yb analogue (**3**) was obtained, the full structural determination of which has been hampered so far by the poor quality of the obtained crystals (see the Supporting Information, SI).

1−**3** were obtained by a two-step reaction of a methanol solution of $MnCl_2\cdot 4H_2O$ and 2′-hydroxyacetophenoxime with NEt_4OH and 2 equiv of lanthanide nitrate (Scheme 1).

Black crystals of **1** and **2** were structurally characterized by means of single-crystal X-ray diffraction (XRD). Both compounds are isomorphous and contain isostructural cationic complexes $[(Ph(CMe)(NO)O)_8(Ph(CMe)(NOH)O)(CH_3O)_4O_5Mn_5Ln_5(CH_3OH)_4(H_2O)]^{2+}$ (Figure 1) beside two Cl^- anions and two solvent molecules per formula unit.

Scheme 1. Synthesis of Compounds 1−3

Mn^{2+} + 2′-hydroxyacetophenoxime (1:1 eq in MeOH)

↓ + NEt_4OH (3 eq), stirring (0.5 h)
+ Ln^{3+} (2 eq), stirring (12 h)
work-up, layering by Et_2O

$[(Ph(CMe)(NO)O)_8(Ph(CMe)(NOH)O)(CH_3O)_4O_5Mn_5Ln_5(CH_3OH)_4(H_2O)]Cl_2$
(**1**·2MeOH: Ln = Tm, 18%; **2**·2MeOH: Ln = Lu, 29%; **3**: Ln = Yb, 30%)

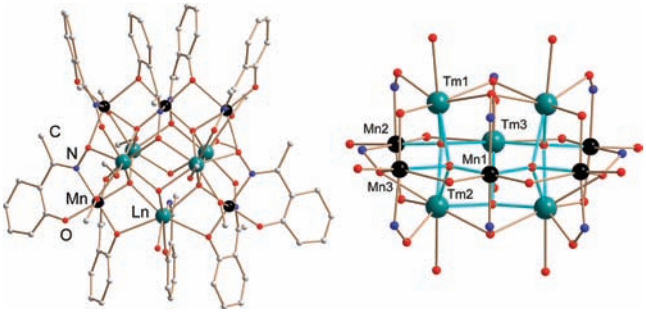

Figure 1. Left: Structure of the cationic complex in **1**, as an example of the isostructural complexes in **1** and **2**. H atoms and disorder of one ligand are omitted for clarity (see the SI for further details). Right: Magnification of the central core of the complex highlighting the $[Mn_5Ln_5O_5]$ unit by bold cyan bonds.

The central structural motif in the complex cations is an unprecedented $[Mn_5Ln_5O_5]$ core. Bond-valence-sum calculations and bond-length analyses regarding the presence/lack of Jahn−Teller distortions (Tables S2 and S3 in the SI) suggest that the title compounds comprise mixed-valent complexes with three Mn^{IV} ions (Mn1, Mn2, and Mn2′ with ′ = *x*, 1.5 − *y*, *z*) and two Mn^{III} ions (Mn3 and Mn3′), all with a distorted-octahedral coordination sphere. The coordination sphere of four of the five Ln^{III} ions with CN = 7 (Ln1 and Ln1′) or 8 (Ln2 and Ln2′) includes one methanol ligand, whereas for the remaining Ln^{III} ion with CN = 8 (Ln3), the terminal ligand is apparently a water molecule.

The Ln^{III} and Mn ions are interconnected by five oxido bridges (O2−O5). O2 acts as a μ_3-bridging ligand to Ln2, Ln3, and Ln2′, whereas O3 and O4 are μ_4-bridging ligands to Ln1,

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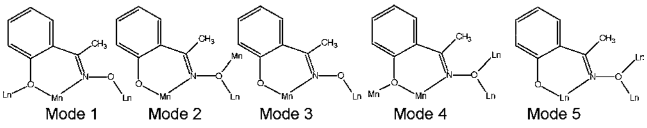
Ln2, Ln3, and Mn2 and to Ln1, Ln2, Mn1, and Mn3, respectively. Moreover, the complex core also includes four methoxido ligands (with O7, O9, O7′, and O9′), bridging the Ln2···Mn2 and Ln1···Mn3 pairs, respectively. The complexes contain nine oxime ligands, one of which should be protonated for charge balance. Alternatively, one of the oxido ligands might be protonated. Eight oxime molecules participate in coordination to both Mn and Ln ions, exhibiting four different coordination modes, whereas one oxime molecule coordinates only to Ln ions (Scheme 2).

Scheme 2. Ligand Coordination Modes in 1 and 2



In coordination modes 1−4 (Scheme 2; see Table S3 in the SI for selected angles), the ligand chelates one Mn ion via an oxime N atom and a phenolate O atom. In modes 2 and 3, the phenolate O atom does not participate in any further coordination, whereas in modes 1 and 4, it μ-bridges to another Ln or Mn ion, respectively. The oxime O atoms coordinate to Ln or Mn ions. In coordination mode 5, only Ln ions are involved (Scheme 2).

The chloride anions are involved as acceptors in O−H···Cl hydrogen bonds with methanol ligands bonded to $\mathrm{Ln^{III}}$ centers as donors. The $[\mathrm{Mn_5Ln_5O_5}]$ cations along with the interacting chloride anions form undulating layers perpendicular to the [001] axis (Table S4 and Figure S1 in the SI).

The magnetic properties of the three compounds were investigated (Figures 2 and 3 and S2 in the SI). At room temperature, the χT product is 53.3, 11.9, and 24.9 $\mathrm{cm^3 \cdot K/mol}$ for **1**−**3**, respectively, in good agreement with the expected values (47.375, 11.625, and 24.475 $\mathrm{cm^3 \cdot K/mol}$) for three $\mathrm{Mn^{IV}}$ ions ($S = {}^3/_2$, $g = 2$, and $C = 1.875$ $\mathrm{cm^3 \cdot K/mol}$), two $\mathrm{Mn^{III}}$ ions ($S = 2$, $g = 2$, $C = 3$ $\mathrm{cm^3 \cdot K/mol}$) and five $\mathrm{Tm^{III}}$ ions ($S = 1$, $L = 5$, ${}^3H_6$, $g = {}^7/_6$, $C = 7.15$ $\mathrm{cm^3 \cdot K/mol}$) for **1** or five diamagnetic $\mathrm{Lu^{III}}$ ions for **2** or five $\mathrm{Yb^{III}}$ ions ($S = 1/2$, $L = 3$, ${}^2F_{7/2}$, $g = {}^8/_7$, $C = 2.57$ $\mathrm{cm^3 \cdot K/mol}$) for **3**, respectively. Upon lowering of the temperature, the χT product at 1000 Oe (Figure 3) decreases to 21.5 and 7.3 $\mathrm{cm^3 \cdot K/mol}$ at 1.8 K for **1** and **3**, respectively, probably because of the presence of dominating intracomplex antiferromagnetic interactions, depopulation of the $\mathrm{Ln^{III}}$ excited states, and/or magnetic anisotropy. In the case of **2**, the χT product at 1000 Oe first increases up to a maximum of 12.8 $\mathrm{cm^3 \cdot K/mol}$ at 31 K and decreases at lower temperature to 4.4 $\mathrm{cm^3 \cdot K/mol}$ at 1.8 K (Figure 3). For diamagnetic $\mathrm{Lu^{III}}$ metal ions, this result indicates the presence of dominating ferromagnetic interactions between $\mathrm{Mn^{III}}$ and $\mathrm{Mn^{IV}}$ spins in **2**.

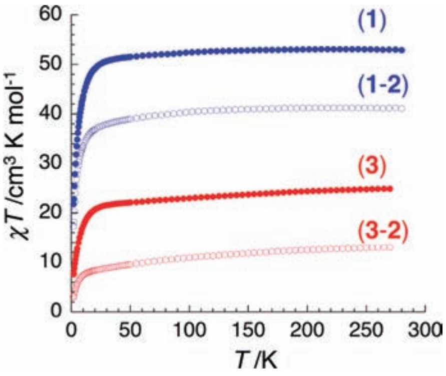


Figure 2. Temperature dependence of the χT product (χ is the magnetic susceptibility defined as M/H per $[\mathrm{Mn_5Ln_5O_5}]$ complex) measured on polycrystalline samples of **1** (blue) and **3** (red) under 1000 Oe. The open dots represent the difference between the magnetic data of **1** and **2** (blue) and **3** and **2** (red).

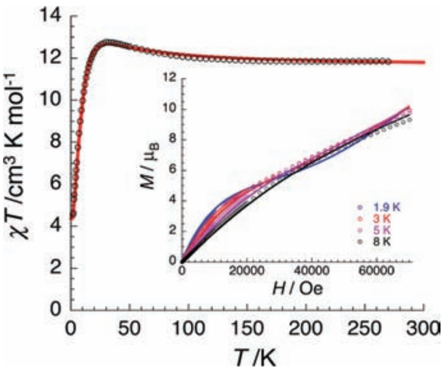


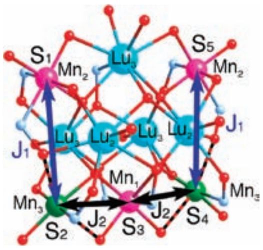
Figure 3. Temperature dependence of the χT product (χ is the magnetic susceptibility defined as M/H per $[\mathrm{Mn_5Lu_5O_5}]$ complex) measured on a polycrystalline sample of **2** under 1000 Oe. Inset: Field dependence of the magnetization measured below 8 K on **2** with sweep rates of 100−200 Oe/min. The solid lines represent the best fit for **2** described in the text.

To model the temperature dependence of the magnetic susceptibility, a simple symmetrical pentanuclear model (Scheme 3) was used as a first approximation. In keeping with the structural motif, the isotropic Heisenberg spin Hamiltonian can be written as follows:

$$H = -2J_1\{S_1 \cdot S_2 + S_4 \cdot S_5\} - 2J_2\{S_2 \cdot S_3 + S_3 \cdot S_4\}$$

where J_1 and J_2 are the average exchange interactions between adjacent $\mathrm{Mn^{IV}}$ and $\mathrm{Mn^{III}}$ spins as defined in Scheme 3; it is worth noting that J_1 is mediated by a single $\mathrm{N{-}O_{ax\text{-}Mn^{III}}}$ bridge while J_2 is mediated by eq-$\mathrm{Mn^{IV}}$ and ax-$\mathrm{Mn^{III}}$ alkoxido and eq-$\mathrm{Mn^{IV}}$ and eq-$\mathrm{Mn^{III}}$ μ_4-oxido links; S_i are the spin operators with $S_1 = S_3 = S_5 = {}^3/_2$ for $\mathrm{Mn^{IV}}$ and $S_2 = S_4 = 2$ for $\mathrm{Mn^{III}}$. The full diagonalization of the spin Hamiltonian and calculation of the magnetic susceptibility have been carried out using the *Magpack* program.[16] As shown in Figure 3, an excellent simulation of the experimental data is obtained using this model with $J_1/k_B = -2.2(1)$ K, $J_2/k_B = +4.0(1)$ K, and $g = 2.00(5)$ to 1.8 K (Figure S14 in the SI). This result confirms the presence of both ferromagnetic and antiferromagnetic couplings between $S = {}^3/_2$ $\mathrm{Mn^{IV}}$ and $S = 2$ $\mathrm{Mn^{III}}$ spins within the $[\mathrm{Mn_5Lu_5}]$ core, leading to an $S_T = {}^5/_2$ spin ground state.

Scheme 3. Scheme of the Spin and Magnetic Interaction Topology in 2 for the $[\mathrm{Mn_5Lu_5}]$ Core



The field dependence of the magnetization for **2** at low temperatures further confirms this model and the estimated interaction parameters. As can be seen in the inset of Figure 3, the same model, employing the exact same J_1, J_2, and g set of parameters to simulate the χT versus T data, also reproduces very well the M versus H data. The magnetization does not saturate at 1.8 K even under 7 T, for which it reaches 10 μ_B. This value is well above the 5 μ_B expected for an $S_T = {}^5/_2$ ground state highlighting the field-induced population of the more magnetic excited states (${}^7/_2$, ${}^9/_2$, ...). As shown by our Heisenberg model, the magnetic anisotropy brought by the Mn^{III} metal ions is probably weak and not detected above 1.8 K. For the Tm and Yb analogues (**1** and **3**), it is impossible to apply a similar approach to model their magnetic susceptibility because of the intrinsic contribution of the paramagnetic Ln ions. In order to get some additional information on these complexes, the magnetic contribution of the Mn ions, measured for **2**, was subtracted from the data of **1** and **3** (Figure 2). The resulting susceptibility thus includes the magnetic contributions of the Ln ions, their intrinsic magnetism, and the Mn···Ln and Ln···Ln magnetic interactions. As shown in Figure 2, the χT product at 1000 Oe decreases continuously with decreasing temperature, which suggests overall dominating Mn···Ln and Ln···Ln antiferromagnetic interactions that are probably superposed with depopulation of the Ln^{III} excited states and the Ln^{III} magnetic anisotropy.

The field dependence of the magnetization in the 1.8–8 K range has also been measured for **1** and **3** (Figure S2a in the SI). For both compounds, the magnetization displays a slow increase with the applied direct-current (dc) field up to 31.2 and 20.0 μ_B, respectively, at 1.8 K and 7 T. The absence of saturation confirms the presence of low-lying excited states, as was already observed for **2**, and also suggests possible magnetic anisotropy. The presentation of the data as M versus H/T plots (Figure S2b in the SI) confirms the presence of these effects because the data are not superposed on a single master curve, as is expected for an isotropic system with a well-defined spin ground state. It is worth noting that no hysteresis on the M versus H data has been observed above 1.8 K with the scan rate used in a traditional magnetometer (100–200 Oe/min). Indeed, in agreement with the M versus H data at 1.8 K that do not show any sign of SMM properties, i.e., slow relaxation of the magnetization/hysteresis effect, the alternating-current susceptibility of these compounds in zero dc field shows a complete absence of the out-of-phase component above 1.8 K.

In conclusion, we present the first examples of a new family of large heterometallic 3d–4f complexes with a novel $[Mn_5Ln_5O_5]$ core that exhibit dominating intra-complex antiferromagnetic interactions in **1** and **3**, or dominating ferromagnetic interactions between Mn^{III} and Mn^{IV} spins in **2**, leading to an $S_T = {}^5/_2$ ground state.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of syntheses and analyses, including X-ray data in CIF format. 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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