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Heterometallic 3d−4f Polyoxometalate Derived from the Weakley-Type Dimeric Structure

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Polyanion $[\{Ce(H_2O)_2\}_2Mn_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{8-}$ (**1**) constitutes the first example of a heterometallic 3d−4f cluster related to the Weakley-type dimeric structure, and it contains an unprecedented $Ce^{III}{}_2Mn^{III}{}_2O_{20}$ rhomblike moiety displaying dominant $Ce^{III}-Mn^{III}$ ferromagnetic interactions.

Polyoxometalates (POMs) are anionic metal−oxygen clusters with a remarkable variety of structures and properties and a multitude of potential applications (e.g., catalysis, materials science, and medicine).[1] Transition-metal-substituted POMs, and more specifically sandwich-type POMs based on lacunary Keggin and Wells−Dawson fragments, have been extensively studied because of their magnetic and catalytic properties.[2] The large family of Weakley-type $[M_4(H_2O)_2(B\text{-}\alpha\text{-}XW_9O_{34})_2]^{n-}$ and $[M_4(H_2O)_2(\alpha\text{-}X_2W_{15}O_{56})_2]^{n-}$ dimers are some of the most representative sandwich POMs.[3] The outer $M(H_2O)$ groups in these tetrasubstituted dimers appear to be labile to a certain degree, as indicated by the isolation of defect di- and trisubstituted derivatives, which can undergo incorporation of M′ ions in the vacancies to form mixed 3d clusters.[4] Exchange of the $M(H_2O)$ groups by transition-metal ions or organotin moieties has also been reported for the related $[M_3W(H_2O)_2(B\text{-}\alpha\text{-}MW_9O_{34})_2]^{12-}$ Tourné POM.[5]

In contrast, little work has been dedicated to the study of heterometallic 3d−4f POMs. To the best of our knowledge, only a few examples have been reported,[6] including a Dy-containing Hervé-like sandwich POM,[6a] two assemblies formed by $Ce^{IV}-Mn^{IV}$ clusters and Wells−Dawson lacunary fragments,[6b,c] a trimeric aggregate of $Ce^{III}-Fe^{III}$-substituted dilacunary Keggin subunits,[6d] and a series of Cu_3 4f cubane moieties stabilized by monolacunary Keggin fragments.[6e]

Therefore, we decided to carry out a systematic study on heterometallic 3d−4f POMs starting from the incorporation of 4f ions to reactive Weakley-type frameworks. Here we report on the interaction between Ce^{IV} and $[Mn^{II}{}_4(H_2O)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{12-}$, which resulted in the first member of this family, namely, $[\{Ce^{III}(H_2O)_2\}_2Mn^{III}{}_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{8-}$ (**1**).

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The $[Mn^{II}_4(H_2O)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{12-}$ POM was prepared as reported by Kortz et al.[7] and isolated as a K^+ salt to use it as the precursor (see the Supporting Information). Polyanion **1** was obtained from the reaction of this precursor with $Ce(NH_4)_2(NO_3)_6$ (1:2 ratio) in water at pH ~ 1, followed by crystallization with aqueous CsCl.[8] Similar reactions with other 4f ions (Ln^{III} = Ce, Eu, Gd, Tb, Er) were not successful, showing that the redox properties of Ce^{IV} might be involved in the formation of **1**. The IR spectrum of **1** (Figure S1 in the Supporting Information) is reminiscent of the precursor with blue shifts of ~30 cm^{-1} for the $\nu_{as}(W-O_t)$ peak (961 cm^{-1}) and ~10 cm^{-1} for the $\nu_{as}(W-O_t) + \nu_{as}(X-O)$ and $\nu_{as}(W-O-W)$ bands (882 and 776 cm^{-1}, respectively) and two new signals at 820 and 738 cm^{-1}. This indicates derivatization of the precursor upon reaction with Ce^{IV} with retention of the sandwich-type framework.

Single-crystal X-ray diffraction[9] shows that the novel polyanion **1** can be described as the product of the substitution of the two outer Mn^{II} atoms in the precursor by two $Ce^{III}(H_2O)_2$ groups, together with internal Mn^{II} to Mn^{III} oxidation. This results in a sandwich assembly of ideal C_{2h} symmetry, which represents the first heterometallic 3d−4f POM derived from the Weakley-type dimeric structure (Figure 1). Polyanion **1** contains an unprecedented $Ce_2Mn_2O_{20}$ rhomblike cluster composed of two internal $Mn^{III}O_6$ octahedra and two external $Ce^{III}O_6(H_2O)_2$ square antiprisms, all edge-sharing (Figure 2). The $Mn^{III}-O$ bonding consists of four short bonds with two corner-shared W_2O_{11} dimers and two longer, cis-related Mn−O(Ge) bonds. These bonds are significantly shorter than those of the Mn^{II} precursor.[7] The $Ce^{III}-O$ bonding is in agreement with other Ce^{III}-containing POMs,[10] and it is composed of two short bonds with a corner-shared W_2O_{11} dimer, three short bonds with an edge-shared W_2O_{10} dimer, two long $Ce-O_w$ bonds, and one very long Ce−O(Ge) bond.

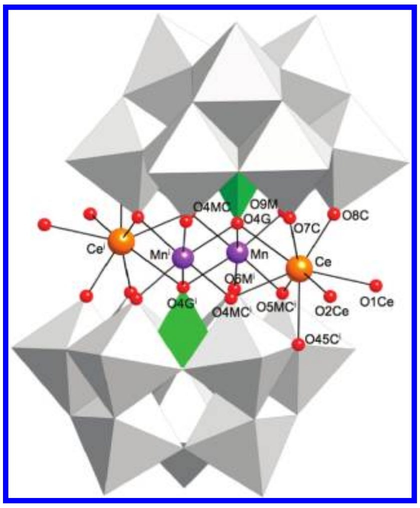

Figure 1. Polyhedral/ball-and-stick representation of the centrosymmetric **1** with atom labeling (i: $-x$, $-y$, $1-z$). Selected bond lengths and interatomic distances (Å): Mn−O6M^i, 1.967(14); Mn−O9M, 2.033(12); Mn−O4MC, 2.037(11); Mn−O5MC^i, 2.044(11); Mn−O4G, 2.090(12); Mn−O4G^i, 2.180(11); Ce−O7C, 2.170(14); Ce−O8C, 2.206(11); Ce−O4MC^i, 2.321(11); Ce−O5MC^i, 2.322(12); Ce−O45C^i, 2.330(12); Ce−O1Ce, 2.390(13); Ce−O2Ce, 2.467(12); Ce−O4G, 2.603(11); Mn···Mn^i, 3.281(4); Mn···Ce^i, 3.568(3); Mn···Ce, 3.578(3); Ce···Ce^i, 6.347(3).

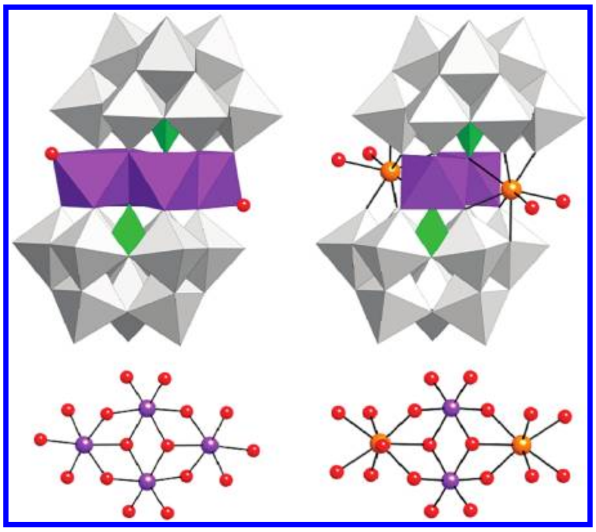

Figure 2. Structural relationship between the $[Mn_4(H_2O)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{12-}$ precursor[7] (left) and **1** (right), including details of the central $Mn^{II}_4O_{16}$ and $Ce^{III}_2Mn^{III}_2O_{20}$ clusters. Color code: same as that in Figure 1.

Close inspection of the lacunary−central cluster junctions reveals an αα configuration,[4b] which differs from the $\beta\beta$ one of the precursor, where the internal $Mn^{II}O_6$ octahedra share corners with edge-shared W_2O_{10} dimers (Figure 2). This indicates that the formation of **1** might proceed via the release of the outer $Mn(H_2O)$ groups, most likely as a result of the Mn^{II} to Mn^{III} oxidation at the central cluster by Ce^{IV}, followed by subsequent rearrangement of the sandwich skeleton and the incorporation of $Ce^{III}(H_2O)_2$ moieties in the vacancies to stabilize the POM framework. This is reminiscent of the disubstituted $[\{Na(H_2O)\}_2Fe^{III}_2(\alpha\text{-}P_2W_{15}O_{56})_2]^{16-}$ Weakley POM, formed by air oxidation of the parent $[Fe^{II}_4(H_2O)_2(\alpha\text{-}P_2W_{15}O_{56})_2]^{16-}$ cluster, which undergoes a loss of $Fe(H_2O)$ groups, $\beta\beta$ to αα isomerization, and incorporation of Na^+ in the vacancies.[4a] Despite being known to suitably oxidize Mn^{II} up to Mn^{IV},[11] Ce^{IV} has scarcely been employed as a Mn oxidant in POM chemistry. In our case, the use of Ce^{IV} as an oxidizing and coordinating agent in a 2:1 Ce/POM ratio allowed us to stabilize both the

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(8) To a suspension of $K_{12}[Mn_4(H_2O)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]$ (0.28 g, 0.05 mmol) in water (20 mL) was added aqueous 0.1 M $Ce(NH_4)_2(NO_3)_6$ (1 mL, 0.10 mmol), and a dark-brown solution was obtained (pH 1.1). After the addition of aqueous 1 M CsCl (0.5 mL), the solution was left to slowly evaporate at room temperature. Brown, rodlike single crystals of **1** suitable for X-ray diffraction formed after a few weeks (yield: 0.08 g, 26% based on Ge). Anal. Calcd (found) for $Ce_2Cs_6Ge_2H_{28}K_2Mn_2O_{82}W_{18}$: Ce, 4.62 (4.47); Cs, 13.16 (12.91); Ge, 2.40 (2.40); Mn, 1.81 (1.81); W, 54.60 (52.34). IR (cm^{-1}): 961 (m), 882 (s), 820 (m), 776 (vs), 699 (s), 514 (w), 456 (m). TGA: thermal analysis (Figure S2 in the Supporting Information) shows the endothermic release of ~14 water molecules below 110 °C [calcd (found): 4.34 (4.25)].

(9) Crystal data: $Ce_2Cs_6Ge_2H_{28}K_2Mn_2O_{82}W_{18}$, fw = 6060.5 g mol^{-1}, monoclinic, $P2_1/n$; a = 16.8768(7) Å, b = 12.7160(4) Å, c = 19.6800(8) Å, β = 109.085(4)°, V = 3991.3(3) Å^3, Z = 2, ρ_{calcd} = 5.043 g cm^{-3}, μ = 30.890 mm^{-1}; 14 177 collected reflections, 4730 unique (R_{int} = 0.037), 3689 observed [$I > 2\sigma(I)$]; 307 parameters, $R(F)$ = 0.033 [$I > 2\sigma(I)$], $wR(F)^2$ = 0.081 (all data), GOF = 1.009.

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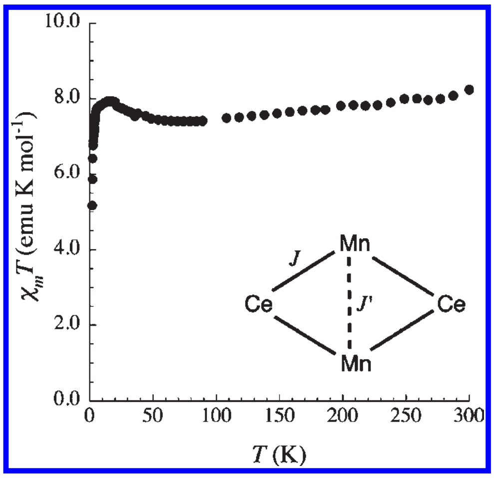

Figure 3. Thermal dependence of the χT product for **1** and schematic representation of the magnetic interactions in the $Ce^{III}{}_2Mn^{III}{}_2O_{20}$ cluster.

final Mn^{III} state and the resulting defect POM framework in the absence of Na^+ cations.

According to the literature, lacunary−central cluster junctions of αα, α*β*, and *ββ* configurations are observed for di-, tri-, and tetrasubstituted Weakley-type dimers, respectively (including mixed 3d species).[4] From this point of view, polyanion **1** can be considered as a Mn^{III}-disubstituted Weakley-type tungstogermanate stabilized by coordination of $Ce^{III}(H_2O)_2$ groups in the vacant sites instead of the usually observed Na^+ cations. Therefore, polyanion **1** constitutes the first POM comprising a defect Weakley-type tungstogermanate subunit to date. No disubstituted analogues of this subunit containing trilacunary Keggin fragments or Mn in the central cluster can be found in the literature to our knowledge.

The χT product of **1** at room temperature is 8.2 emu K mol^{-1}, in good agreement with that expected for a magnetically diluted sample containing two octahedral high-spin Mn^{III} ions (each one contributing a spin-only value of ∼3 emu K mol^{-1}) and two Ce^{III} (each one contributing ∼0.8 emu K mol^{-1}).[11b] The χT product decreases with T down to a value of 7.4 emu K mol^{-1} around 60 K, where it increases again up to a maximum of 7.9 emu K mol^{-1} at 15 K (Figure 3). Although this high-temperature decrease could suggest the presence of antiferromagnetic (AF) interactions between paramagnetic centers, its magnitude actually corresponds to the behavior of the single ions due to the spin−orbit coupling of the Ce^{III} centers. Their χT product (which corresponds to a single unpaired electron but with an unquenched angular momentum) typically decreases from its room temperature value down to ∼0.2 emu K mol^{-1} (Figure S5 in the Supporting Information). On the other hand, the increase in the magnetic moment below 60 K can only be attributed to the presence of dominant ferromagnetic (F) interactions in the cluster. Unfortunately, the spin−orbit coupling plus strong single-ion anisotropy in this system does not allow us to use a simple magnetic model to quantify the magnetic exchange because such an analysis is clearly beyond the scope of this work.

In such a rhomblike magnetic distribution, two different J values are expected (Figure 3). It has been well established in analogous systems that J is always greater than J'[12] and also that octahedral Mn^{III} ions connected through oxo or hydroxo bridges show AF interactions,[13] as in the Mn^{III} derivative of the precursor.[13c] Therefore, J' must be negative in this system, and the dominant F interactions need to be due to J being positive ($Ce^{III}-Mn^{III}$ interaction). The coexistence of J's of opposite sign is also supported by the field dependence of the magnetization at 2 K (Figure S4 in the Supporting Information). It shows a rapid increase for low fields because of the dominant F interactions, but then it reaches a saturation value of 6 μB at 5 T, below the pure F, high-spin state (10 μB for $S = 5$). This feature suggests a ground state with six unpaired electrons ($S = 3$), intermediate between the pure F and AF energy levels and also affected by the spin frustration expected for such a rhomblike array with competing magnetic interactions.

In summary, this work shows that Weakley-type POMs are reactive toward 4f ions, resulting in POM systems that can be used as molecular models for a detailed study of the interactions between magnetic 3d and 4f centers. In our case, the reaction of Ce^{IV} with $[Mn^{II}{}_4(H_2O)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{12-}$ led to the first heterometallic 3d−4f POM derived from the Weakley-type dimeric structure, $[\{Ce^{III}(H_2O)_2\}_2Mn^{III}{}_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{8-}$ (**1**). The stabilizing capability of $Ce^{III}(H_2O)_2$ groups upon coordination to the vacant sites allowed us to isolate a POM comprising a defect Weakley-type tungstogermanate subunit for the first time. No disubstituted analogues of this subunit containing trilacunary Keggin fragments or Mn in the central cluster can be found in the literature to our knowledge. The unprecedented $Ce^{III}{}_2Mn^{III}{}_2O_{20}$ rhomblike cluster displays dominant $Ce^{III}-Mn^{III}$ F interactions. We plan to extend this work to the systematic incorporation of other 4f ions into Weakley-type frameworks in order to achieve a better understanding of the reactivity and magnetism in this POM family.

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Supporting Information Available: Experimental section including synthesis of the precursor, FT-IR spectrum (Figure S1), TGA curve (Figure S2), ORTEP view (Figure S3), and field-dependent magnetization at 2 K (Figure S4) of **1**, χT vs T curve of $Ce(NO_3)_3 \cdot 6H_2O$ (Figure S5), and X-ray crystallographic data of **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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