SHORT COMMUNICATION

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An Unexpected Ferromagnetic Coupling in a Dinuclear Manganese(II) Linked Trivacant Heteropolymolybdate Derivative

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An unexpected ferromagnetically coupled dinuclear manganese(II) linked trivacant heteropolymolybdate $[HN(CH_3)_3]_{10}[Mn_2(V^VMo_9O_{33})_2]\cdot 10H_2O$ (**1**) has been synthesized in aqueous solution and characterized by elemental analysis, IR spectroscopy, thermal gravimetric analysis, and single-crystal X-ray diffraction. A new kind of heteropolymolybdate $[VMo_9O_{33}]^{7-}$ anion is shown. The magnetic properties of **1** indicate typical ferromagnetic interactions through the Mn^{II}–O–Mn^{II} bridge unit.

Introduction

Polyoxometalates (POMs) are a well-known class of metal–oxygen clusters with a large variety of compositions and structures, and their structures together with their properties are of considerable interest because of the potential application in areas of catalysis, materials science, medicine, etc.[1–7] In virtue of a great family of POM building blocks, significant effort has been directed to the creation of rational assemblies for obtaining new compounds with desired functional properties. In the class of POMs, the complexes consisting of POMs and transition-metal ions are an important subfamily because of their structural and magnetic diversity.[8–12] Recently, a large number of POM-based magnetic clusters with various nuclearities were synthesized, and many complexes containing dinuclear manganese(II) are well documented. However, to the best of our knowledge, a POM with ferromagnetically coupled dinuclear manganese(II) centers has never been reported until now.

Herein we report the synthesis, characterization, and magnetic properties of $[HN(CH_3)_3]_{10}[Mn_2(V^VMo_9O_{33})_2]\cdot 10H_2O$ (**1**), in which dinuclear manganese(II) clusters exhibit ferromagnetic interactions. In contrast to previously reported complexes in which there are similar structures with antiferromagnetic coupling interactions,[13] complex **1** is a rare example of a ferromagnetically coupled dinuclear manganese(II) complex.

Results and Discussion

Crystal Structure

A single-crystal X-ray diffraction analysis revealed that complex **1** consists of three kinds of subunits: the $[Mn_2(V^VMo_9O_{33})_2]^{10-}$ anion (see Figure 1), the $[HN(CH_3)_3]^+$ cation and isolated water molecules.[14] By considering the XPS data (see Figure S2), the bond valence sum (BVS) calculations,[15] the charge balance, and elemental analysis, compound **1** is formulated as $[HN(CH_3)_3]_{10}[Mn^{II}_2(V^VMo^{VI}_9O_{33})_2]\cdot 10H_2O$. The BVS values for eighteen Mo atoms are in the range 6.182–5.931 with an average value of 6.087, while those for the Mn and V atoms are 2.14 and 4.967, respectively. The calculated results are in agreement with the expected +6, +2, and +5 oxidation state for Mo, Mn, and V, respectively.

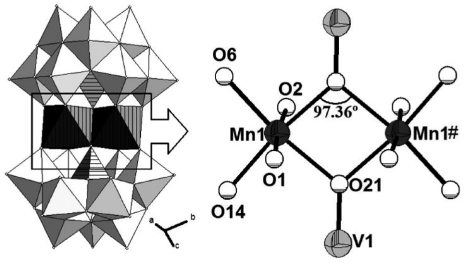

Figure 1. Representation of the $[Mn_2(V^VMo_9O_{33})_2]^{10-}$ anion in **1**. The $[Mn_2(V^VMo_9O_{33})_2]^{10-}$ anions are shown as polyhedra, and the central $\{Mn_2O_{10}\}$ cluster and the connecting heteroatoms are shown as ball-and-stick models. (White: MoO_6 and O, light gray: VO_4 and V, dark gray: MnO_6 and Mn).

The structure of complex **1** is similar to that of $(H_2NCNH_2NH_2)_8(H_3O)_2[Mn_2(As^VMo_9O_{33})_2]\cdot 9H_2O$.[13] The new $\{VMo_9O_{33}\}$ polyanion in **1** derives from the Keggin

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(B-β-VMo_9O_{33}) structure, and a $\{Mn_2O_{10}\}$ group is located in the central belt. There are four types of coordinated oxygen atoms in the cluster: the terminal oxygen atom O_t, the bridging oxygen atom O_b linked to Mn and Mo, the bridging oxygen atom O_b linked to two Mo centers, and the central oxygen atom O_c. The Mo–O distances are in the range 1.694(7)–1.725(7) Å for O_t, 1.756(6)–2.220(7) Å for the bridging oxygen atoms O_b linked to two Mo atoms, 1.737(6)–1.745(6) Å for the bridging oxygen atoms O_b linked to the Mn and Mo atoms, and 1.957(6)–2.447(5) Å for O_c. The V–O distances vary from 1.681(6) to 1.737(6) Å, which are longer than the As–O distances 1.666(5)–1.700(5) Å in the As^V-centered analogue.[13]

In complex **1**, the manganese(II) ion has a significantly distorted octahedron coordination geometry; the oxygen atoms are provided by four MoO_6 octahedra and two VO_4 tetrahedra. The bond length between the manganese(II) ion and the VO_4 tetrahedron [Mn1–O21 2.225(7) Å] is slightly longer than those between the manganese(II) ion and the MoO_6 octahedra [Mn1–O1 2.147(8), Mn1–O2 2.143(8), Mn1–O6 2.145(7) and Mn1–O14 2.145(6) Å]. The two manganese(II) ions are doubly bridged by the VO_4 tetrahedron with a Mn···Mn separation of 3.328 Å. The Mn1–O21–Mn1#1 bridging angle with a value of 97.36(28)° is smaller than the corresponding angle in the As^V-centered complex [98.25(22)°].[13]

Magnetic Properties

The magnetic susceptibility of complex **1** was measured with an applied field of H = 100 Oe in the temperature range 2–300 K, and the magnetic data are shown in Figures 2, 3, and 4. The $1/\chi_M$ vs. T plot displays Curie–Weiss behavior from 8 to 300 K. The best linear fit of the $\chi_M^{-1}(T)$ data above 8 K yields C = 8.75 emu K mol^{-1} and θ = 3.00 K for 100 Oe (see Figure 2).

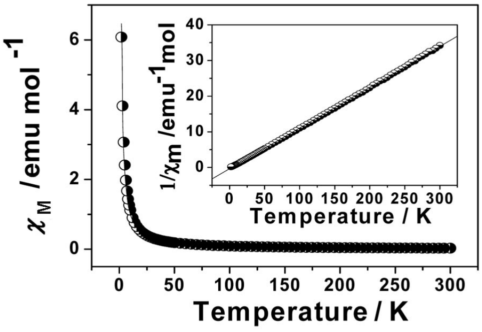

Figure 2. Temperature dependence of the inverse magnetic susceptibility (χ_M^{-1}) for **1** between 2 and 300 K. Solid lines are generated from the best fit by the Curie–Weiss expression.

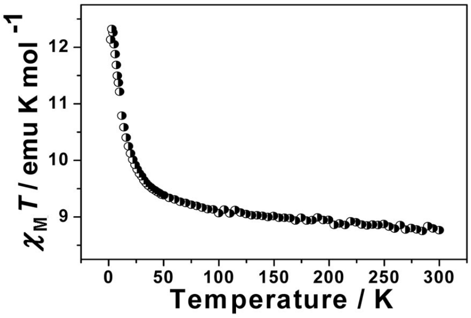

Figure 3. Plots of $\chi_M T$ vs. T in the temperature range 2–300 K for **1** under an applied magnetic field of 100 Oe.

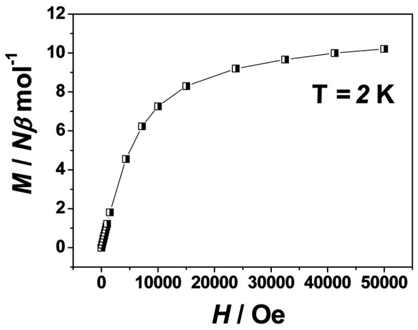

Figure 4. Magnetization as a function of the applied field recorded at 2 K.

The experimental data can be fitted to a modified Heisenberg–Dirac–van Vleck $S_A = S_B = 5/2$ spin-coupled model (see Supporting Information).[16] The least-squares fit gives a magnetic coupling constant of $J = 0.14$ cm^{-1} by assuming $g = 2.0$, with an agreement factor R {defined as $\Sigma_i[(\chi_M T)_{obs}(i) - (\chi_M T)_{calc}(i)]^2/\Sigma_i[(\chi_M T)_{obs}(i)]^2$} of 6.24×10^{-3}. The J value suggests the occurrence of a ferromagnetic Mn^{II}–Mn^{II} interaction in **1**, which is in good agreement with the result of linear fitting based on the Curie–Weiss equation.

At room temperature, the value of $\chi_M T$ per $[Mn_2(V^VMo_9O_{33})_2]^{10-}$ unit is 8.77 emu K mol^{-1} (8.37 μ_B, H = 100 Oe) and is slightly higher than the expected value of 8.36 μ_B for the two isolated Mn^{II} ions (S = 5/2, g = 2.00). The $\chi_M T$ product increases slightly on lowering the temperature from 300 to 50 K, and at lower temperatures, it steadily increases to reach a value of 12.13 emu K mol at 2 K. This behavior is typical of a ferrimagnetic spin arrangement. The magnetization data for **1** has also been measured as a function of the applied magnetic field up to 5000 Oe at 2 K, as shown in Figure 4. The M values increase with increasing magnetic field and reach a value of 10.21 at 5 T, which suggests an S = 5 spin ground state for **1**.

A ferromagnetic interaction between the Mn^{II} ions bridged by the oxygen atoms from the two V^VO_4 tetrahedra in **1** is unexpected because a dinuclear Mn^{II} complex bridged by the oxygen atom of the As^VO_4 tetrahedra is generally antiferromagnetic.[13] Although some Mn^{II} complexes bridged by alkoxido or phenoxido oxygen atoms show ferromagnetic interactions,[17] the reason for the occurrence of ferromagnetic interactions in complex **1** remains unclear. This ferromagnetic interaction might occur by a superexchange mechanism through the oxygen atoms of the VO_4

tetrahedron in the complex. According to the structural data, the central $Mn_2–(\mu\text{-}O)_2$ moiety in complex **1** has smaller Mn–O–Mn angles and longer Mn–O bonds than those of the $\{Mn_2(As^VMo_9O_{33})_2\}$ unit, which may be responsible for the ferromagnetic interaction. But further analysis for the reason for this behavior is hindered because of a lack of available data for dinuclear manganese(II) complexes with oxygen bridges from a V^VO_4 tetrahedron. An in-depth magnetic investigation will be done in due course.

IR Spectrum and Thermal Analysis

In the IR spectrum of **1** (Figure S2), the bands at 984, 936, 855, 753, 668 cm^{-1} are assigned to the $\nu(V–O_a)$, $\nu(Mo–O_t)$, $\nu(Mo–O_c)$, and $\nu(Mo–O_b)$ modes of the $[VMo_9O_{33}]^{7–}$ fragment. The bands in the 3434–1477 cm^{-1} region are attributed to characteristic vibrations of the $[HN(CH_3)_3]^+$ groups.

The thermal gravimetric curve of **1** exhibits two weight loss steps in the temperature range 30–600 °C (see Figure 5). The first weight loss of 4.54% in the temperature range 30–120 °C corresponds to the release of 10 crystalline water molecules. The second stage, which occurs from 228 to 467 °C, is attributed to the loss of 10 organic molecules. The observed weight loss (18.31%) is in agreement with the calculated value (17.01%). By considering the residue of V_2O_5, MnO, and MoO_3, the observed total weight loss (76.29%) is also similar to the calculated value (77.59%).

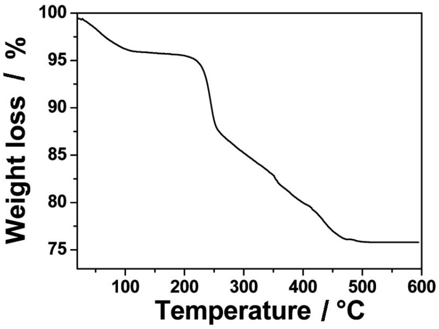

Figure 5. The thermogravimetric curve of **1** measured in the range 30–600 °C under a dry atmosphere of air with a heating rate of 10 °C min^{-1}.

Conclusions

In summary, we prepared a ferromagnetically coupled dinuclear manganese(II) complex, $[HN(CH_3)_3]_{10}[Mn_2(V^VMo_9O_{33})_2]\cdot 10H_2O$ (**1**), assembled from the trivacant heteropolymolybdates, and its structure and magnetic properties were studied. It represents the first example of ferromagnetically coupled heteropolymolybdate complex based on the $[VMo_9O_{33}]^{7–}$ fragment. In contrast to the complex $(H_2NCNH_2NH_2)_8(H_3O)_2[Mn_2(As^VMo_9O_{33})_2]\cdot 9H_2O$, whose structure is similar to **1** and is, as usual, antiferromagnetically coupled, complex **1** exhibits unexpected ferromagnetically coupled dinuclear manganese(II) centers. Such a ferromagnetic interaction may occur by the superexchange mechanism through the oxygen atoms of the VO_4 tetrahedron in the complex. This complex provides a new avenue in the molecular magnetism area.

Experimental Section

$NaVO_3\cdot 2H_2O$ (0.158 g, 1 mmol) and $Na_2MoO_4\cdot 2H_2O$ (2.24 g, 9 mmol) were dissolved in H_2O (30 mL), and the pH was adjusted to 3.6 by addition of 1 M hydrochloric acid. The mixture was heated to reflux for 2 h at 60 °C after the addition of $MnSO_4$ (4 mL of a 1 M solution). The solution was cooled to room temperature, and $N(CH_3)_3HCl$ (3 mL of a 1 M solution) was added to the stirred solution. After 4 d, red block crystals formed by evaporation of the filtrate at room temperature. $C_{30}H_{120}N_{10}O_{76}V_2Mn_2Mo_{18}$ (3775.97): calcd. C 9.54, N 3.70, H 3.20, Mn 3.01, Mo 45.73, V 2.69; found C 9.67, N 2.96, H 3.58, Mn 2.91, Mo 44.36, V 2.80.

Supporting Information (see footnote on the first page of this article): Structural figures, IR and XP spectra, and crystallographic data for compound **1** are presented.

Acknowledgments

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[14] Single-crystal structural analysis of **1**: A red crystal of **1** with dimensions of 0.16 × 0.12 × 0.13 mm was glued on a glass fiber. Crystal data for **1**: $C_{30}H_{120}N_{10}O_{76}V_2Mn_2Mo_{18}$, M_r = 3775.97 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 12.9241(14) Å, b = 13.6247(15) Å, c = 17.932(2) Å, α = 72.0290(10)°, β =

69.3680(10)°, $\gamma = 88.2100(10)°$, $V = 2800.2(5)$ Å^3, $Z = 1$, final R factors $R1 = 0.0554$ and $wR2 = 0.0968$. The X-ray crystallographic data were collected at 293 K for **1** on a Bruker SMART CCD single-crystal diffractometer by using Mo-K_α radiation (0.71073 Å). Direct methods were used to solve the structure and to locate the heavy atoms (SHELX97). The hydrogen atoms of the organic molecules were not added in a riding model. CCDC-670568 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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