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$[Mo^{V}_{12}O_{30}(\mu_2\text{-}OH)_{10}H_2\{Ni^{II}(H_2O)_3\}_4]$, a Highly Symmetrical ε-Keggin Unit Capped with Four Ni^{II} Centers: Synthesis and Magnetism

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Polyoxomolybdate clusters and related fragments functioning as diamagnetic frameworks for the deliberate positioning of various exchange-coupled paramagnetic centers have gained considerable interest recently for magnetochemists.[1−4] Our special attention is focused on the comparison of paramagnetic polytopes of the Platonic and Archimedean type (mainly with respect to differences in their low-temperature spin ordering) where novel properties are observed especially in larger systems like the $\{Fe^{III}_{30}Mo_{72}\}$ cluster where the 30 Fe^{III} $S = {}^{5}/_{2}$ centers form an icosidodecahedron.[3] Relevant synthesis strategies, yielding pure and uniform magnetic materials, have been described.[4] Herein we report the synthesis and magnetic properties of a $Ni^{II}-Mo^{V}$ cluster system, $[Mo^{V}_{12}O_{30}(\mu_2\text{-}OH)_{10}H_2\{Ni^{II}_4(H_2O)_{12}\}]\cdot 14H_2O$, **1**, with four Ni^{II} centers positioned at the nucleophilic sites of an ε-Keggin cluster forming a tetrahedron. The compound was characterized by single-crystal X-ray structure analysis, FT-IR and Raman spectroscopy as well as magnetic susceptibility measurements, and elemental analysis including TGA.

The synthesis strategy applied in this work corresponds to our common procedure of initiating a type of molecular growth process based on polyoxometalate units by increasing their negative charge (and thereby the nucleophilicity). This aim can be achieved by the presence of reducing agents and electrophiles which stabilize the product. This approach has also been demonstrated to be a general method for the deliberate placement of electrophilic mono- or polynuclear open- and closed-shell entities on the relevant nucleophilic cluster surfaces.[4]

To a solution of 3.36 g (2.72 mmol) of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ and 11.25 g (45.2 mmol) of $Ni(OOCCH_3)_2\cdot 4H_2O$ in 250 mL of H_2O and 40 mL of acetic acid (50%) was added 620 mg (4.76 mmol) of hydrazinium sulfate with stirring. The resulting green solution was stirred for 10 min and then stored in an Erlenmeyer flask (300 mL, wide necked, covered with a watch glass) in an oil bath at 65 °C for 3 days. Brownish crystals (thin plates) of $[Mo^{V}_{12}O_{30}(\mu_2\text{-}OH)_{10}H_2\{Ni^{II}_4(H_2O)_{12}\}]\cdot 14H_2O$, **1** (**1a**·$14H_2O$),[5−7] were isolated by filtration and washed several times with water (yield 2.5 g; 60% based on Mo). (The Raman spectrum of the filtrate shows the presence of the recently reported spherical cluster of the type $\{Mo_{132}\}$.[8])

The structure of **1a** shows a central ε-Keggin core (Figure 1), which is also present in clusters of the types $\{Mo_{16}\}$,[9] $\{Mo_{37}\}$,[4] and $\{Mo_{43}\}$[10] containing dinuclear, dumbbell-shaped $Mo^{V}-Mo^{V}$ units (Mo−Mo (single bond) = 2.584(1)−2.765(1) Å). The 12 Mo^{V} centers of the ε-Keggin unit, which is formally obtained from the α-isomer $[Mo^{VI}_{12}O_{40}(X^{n+})]^{(8-n)-}$ (X = P, As, Si, Sb, etc.) by rotation of all four Mo_3O_{13} groups by 60°, form a truncated tetrahedron. Probably during the formation of **1a** a highly charged and unstable ε-Keggin fragment $[H_xMo^{V}_{12}O_{40}]^{(20-x)-}$ is stabilized by interaction with four electrophilic $Ni^{II}(H_2O)_3{}^{2+}$ units, which cap four $\{Mo_2\}_3$ hexagons of the Keggin cluster (see also ref 9b), thereby reducing its negative charge, but preserving its T_d symmetry. The structure can also formally be derived from the $\{Mo_{16}\}$-type cluster $[Mo^{V}_{12}O_{28}(\mu_2\text{-}OH)_{12}H_2\{Mo^{VI}O_3\}_4]^{6-}$, **2a**,[9] containing the same ε-Keggin core by replacing four $Mo^{VI}O_3$ units with four $Ni^{II}(H_2O)_3{}^{2+}$ groups, not considering the different types of protonations (see below). The intramolecular Ni···Ni distances are 6.689(1), 6.700(5), 6.616(1), and 6.604(1) Å, respectively. Since each octahedrally coordinated Ni center exhibits three terminal H_2O ligands, **1a** has in principle the potential for further derivatization, e.g., intermolecular linkage through multidentate ligands leading to network structures. Furthermore we were able to isolate the Co^{II} analogue of **1a**.

Despite the high resolution of the crystallographic data collected, the positions of the hydrogen atoms could not be located unambiguously. In order to determine the molecular formula and the charge of **1a**, elemental analysis and Brown's type bond

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(5) Anal. Calcd for $Mo_{12}Ni_4O_{66}H_{64}$ ($M_r = 2506.3$ g/mol): H, 2.57; Ni, 9.4; crystal H_2O, 10.1; coordinated H_2O, 8.6. Found: H, 2.60; Ni, 9.3; H_2O (TG), 18.3.

(6) Spectroscopic data (main bands) for **1**: IR (KBr pellet; $\nu(cm^{-1})$) 1615 (m, $\delta(H_2O)$), 957 (vs, $\nu(Mo{=}O)$), 801 (s), 763 (s), 665 (sh), 599 (sh), 527 (s) 419 (w), 399 (w); Raman (KBr dilution matrix; $\lambda_e = 1064$ nm; $\nu(cm^{-1})$) 976 (m, $\nu(Mo{=}O)$), 944 (sh), 912 (sh, $\nu(Mo{=}O)$), 776 (w), 460 (m), 292 (w), 220 (w), 164 (m).

(7) Crystal data for **1**: thin brownish plates, 0.4 × 0.25 × 0.1 mm, monoclinic space group $C2/m$ (No. 12), $a = 29.755(1)$ Å, $b = 18.0498(9)$ Å, $c = 12.2258(6)$ Å, $\beta = 111.14(1)°$, $Z = 4$, $D_{calcd} = 2.719$ mg/mm³, $\mu(Mo\ K\alpha) = 3.69$ mm^{-1}. The data were collected at 183 K using a Siemens AXS three-circle diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å, graphite monochromator) with 1K-CCD detector (ω scan frames). Of the 17825 reflections ($1.79° \leq \Theta \leq 27.0°$), 6711 unique reflections ($R_{int} = 0.029$) were used to solve the structure by direct methods (SHELXTL version 5), and it was refined on F^2 by least-squares techniques. At convergence, R1 = 0.0345 for 5588 reflections with $I > 2\sigma(I)$ and the goodness of fit on F^2 is 0.871. Each crystal water molecule was found to be disordered over two positions.

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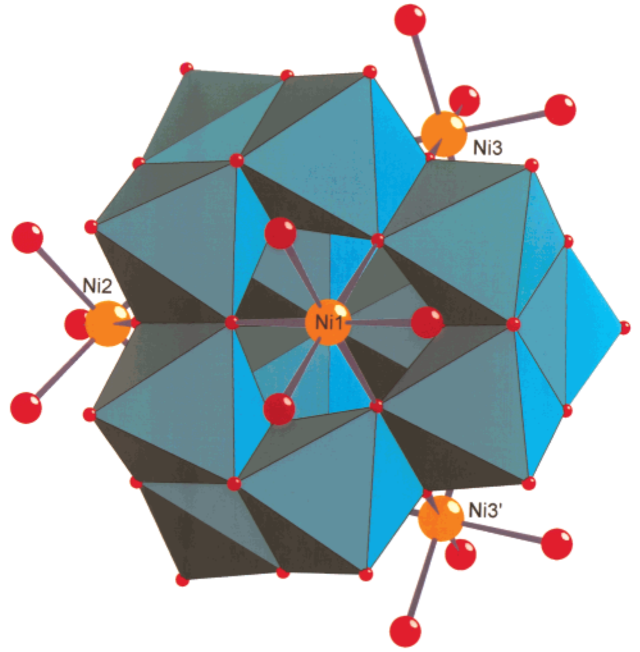

Figure 1. View of the structure of **1a** in crystals of **1** along the crystallographic *a* axis (ϵ-{$Mo^V{}_{12}O_{40}H_{12}$} core in polyhedral and Ni^{II}-$(H_2O)_3$ caps in ball-and-stick presentation).

valence sum (BVS) calculations for the relevant O atoms had to be performed. In **2a**[9] all 12 μ_2-O atoms linking {$Mo^V{}_2$} pairs show uniform BVS values (1.05 ± 0.07) indicating monoprotonation. However, in **1a** some corresponding μ_2-O atoms exhibit larger BVS values (1.15 (2×), 1.16, 1.35 (2×); the other values range from 0.92 to 1.11), which implies a lower degree of (disordered) protonation. The four μ_3-O atoms spanning the cavity of **1a** exhibit BVS values of 1.29 (3×) and 0.95, respectively. This is in good agreement with **2a**, which has two disordered protons in the cavity in addition to the 12 protons associated with the μ_2-O atoms.[9] The BVS values for the Mo centers (4.86−5.26) clearly indicate the presence of 12 Mo^V centers. Since the elemental analyses and the IR spectrum of **1** did not show the existence of any further ions (ammonium, acetate, or sulfate), it has to be concluded that **1a** is a neutral cluster, which corresponds to the presence of 12 (10 + 2) protons. This result is in agreement with the BVS calculations (the BVS values for the μ_3-O atoms range from 1.95 to 2.02) and the fact that the compound is completely insoluble in water. It was also observed that there are two short contacts of neighboring units of **1a** (O···O = 2.619(1) Å), which indicates hydrogen bonding.

The magnetic properties of **1a** are dominated by the exchange interactions between the four Ni^{II} centers since the strong interaction between the 12 Mo($4d^1$) centers results in six Mo^V-Mo^V dumbbells with Mo−Mo single bonds, i.e., a diamagnetic ϵ-Keggin core (cf. the susceptibility $\chi = -4.7 \times 10^{-4}$ emu/mol of the diamagnetic compound **2** ≡ $(NH_2(CH_3)_2)_6$**2a**). At room temperature $\chi T = 4.8$ emu K mol^{-1}, which exceeds the spin-only value for $N = 4$ uncorrelated $s = 1$ centers, $\chi_{so}T = NS(S + 1)/2 = 4.0$ emu K mol^{-1}. This difference is caused by the spin−orbit coupling characteristic for nickel(II) complexes with a $^3A_{2g}$ ground state resulting in an increased *g* factor (see below).[11a] Despite the large intramolecular distances, the Ni centers are coupled significantly due to the fact that the polyoxomolybdate framework with high electron density acts as unusually effective ligand transmitting exchange interactions, as has been documented for several other systems with comparable distances between the paramagnetic centers.[1,3] Because of the near equality of the Ni···Ni distances and in order to simplify the mathematical treatment, we used the Heisenberg model for spins $s = 1$ with a single, adjustable exchange energy, J (>0, corresponding to antiferromagnetic exchange), to calculate the weak-field magnetic susceptibility. The magnetic energies per cluster are $E_S = JS(S + 1)/2$, where S (=0, 1, ..., 4) is the total spin, and the corresponding multiplicity factors, G_S (not including the Zeeman degeneracy factor, $2S + 1$), are $G_0 = G_3 = 3$, $G_1 = G_2 = 6$, $G_4 = 1$. For temperatures exceeding $3J/k_B$ the theoretical weak-field susceptibility is very well approximated by a Curie−Weiss formula, $\chi = C/(T + \Theta)$, where $C = (8/3)N_A(g\mu_B)^2/k_B$ and the Weiss temperature is given by $\Theta = 2J$. Here N_A is Avogadro's number, μ_B is the Bohr magneton, k_B is Boltzmann's constant, and *g* is the spectroscopic splitting factor.

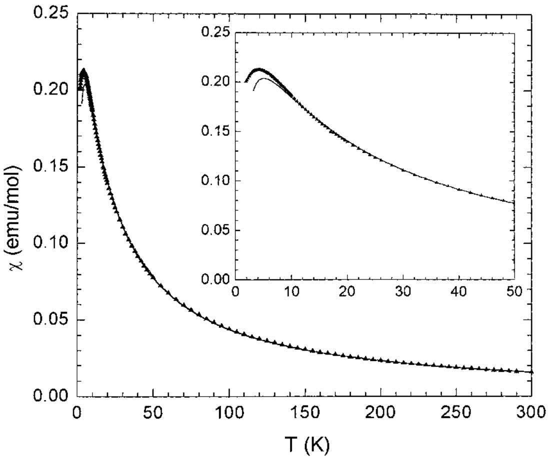

Figure 2. χ_{mol} (corrected for diamagnetism) versus *T* graph for **1** (filled triangles, experiment; continuous curve, theory).

Shown in Figure 2 are the data (triangles) for the dc susceptibility (emu/mol; Quantum Design MPMS-5) measured for 0.5 T as well as the prediction of the Heisenberg model (continuous curve). Above 20 K the experimental data is accurately approximated by the Curie−Weiss formula for the values $C = 4.965$ emu K mol^{-1} and $\Theta = 12.6$ K, corresponding to the choices $J = 6.3$ K and $g = 2.23$. This value for *g* is typical for octahedral $Ni^{II}O_6$-type complexes with relevant spin−orbit coupling.[11] The predictions of the present simplified theory remain in excellent quantitative agreement with the experimental data for all temperatures down to 8 K. As a result of the energy gap between the ground state ($S = 0$) and excited states, the theoretical susceptibility decreases steeply to zero for $T < 5$ K. We believe that this is the mechanism responsible for the sudden drop in the experimental susceptibility data for $T < 4$ K. The most likely source for the modest discrepancy between theory and experiment in the range $T < 8$ K is the existence of a small variation in the exchange energy for the individual Ni−Ni pairs. Another possibility is the existence of a crystal field term to supplement the Heisenberg exchange interaction. The analysis of new experimental data (temperature and field dependence of the magnetization, *T* down to 0.2 K and fields up to 20 T, measurements of R. Modler of Ames Laboratory) can be expected to settle this remaining open issue.

Supporting Information Available: Two X-ray crystallographic files, in CIF format, as well as a labeled ellipsoid plot. This material is available free of charge via the Internet at http://pubs.acs.org.

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