A New Type of Heteropolyoxometalates formed from Lacunary Polyoxotungstate Ions and Europium or Yttrium Cations**

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Polyoxometalates have found applications in catalysis, analytical chemistry, and separation science. A new area of interest is the preparation of novel materials based on polyoxometalate building blocks. Prominent examples in this area can be found in the work by Müller et al.[1] on giant molybdates. Because of their multiple coordination requirements and oxophilicity, lanthanide (Ln) cations are suitable for linking polyoxometalate ions together to form new classes of materials with extended metal–oxygen frameworks. In the case of tungsten, lacunary XW_9 ($SbW_9O_{33}^{7-}$ and $AsW_9O_{34}^{9-}$) ions and $W_5O_{18}^{6-}$ ions have been linked by lanthanide ions to form complexes such as $[Eu_3(H_2O)_3(W_5O_{18})_3(SbW_9O_{33})]^{18-}$,[2] and recently the largest heteropolyoxotungstate ion, containing a cyclic $[Ln_{16}As_{12}W_{148}O_{524}(H_2O)_{36}]^{76-}$, assembly was reported.[3] Extended polymeric structures in the solid state were recently obtained from La and Ce complexes and the lacunary $SiW_{11}O_{39}^{4-}$ ions.[4]

Here we report a new type of heteropolyoxometalates, stable in the solid state and in aqueous solution at pH 7–9, that are assembled from $(PW_9O_{34})^{9-}$ anions and Eu^{III} or Y^{III} cations. The formation of these species is dependent on the countercation that is used. For example, ^{31}P NMR spectra of the $Eu^{3+}/PW_9O_{34}^{9-}$ (2/1) solution (pH 7.0; $PW_9O_{34}^{9-}$ as the Na salt) prior to addition of the new countercation shows the presence of a precursor complex, as yet uncharacterized. Addition of K^+ results in the complex **1** reported herein. Addition of Cs^+ or Rb^+ to the precursor solution yields different products: $[Eu(PW_{11}O_{39})_2]^{12-}$ and a different unknown species, respectively. Addition of Al^{3+} results in $[\{Eu(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{14-}$. Complex **1** can be synthesized from either A-$PW_9O_{34}^{9-}$ or B-$PW_9O_{34}^{9-}$.

$[(PM_2W_{10}O_{38})_4(W_3O_{14})]^{30-}$ (M = Eu, Y; **1**)

Complex **1** is an assembly of 4 $PW_9O_{34}^{9-}$ anions, 8 M^{3+} cations, and 7 additional tungsten atoms that form a $[M_8W_7O_{30}]^{6+}$ network (Figure 1). It can be viewed as composed of two V-shaped asymmetric entities that are symmetry-related by a C_2 axis about a central tungsten atom. Each asymmetric entity (Figure 2) consists of two distorted Keggin-like parts (**L** and **R**), both composed of an A-α-$PW_9O_{34}^{9-}$ cap[5] (see Supporting Information) connected to a distorted M_2W six-membered ring comprising an eight-coordinate (square-antiprismatic) M^{III}, a seven-coordinate M^{III}, and a tungsten atom. The formulation of **1** as $[(PM_2W_{10}O_{38})_4(W_3O_{14})]^{30-}$ reflects the distorted Keggin-like structural parts. Parts **L** and **R** are connected to each other by two bridging WO_6 octahedra (W11 and W12) and the oxygen atoms coordinating the two M^{III} cations (Y1, Y1′).[6] The asymmetric entities are joined together by 6- and 8-membered M–O (M = W, Y) rings about the central tungsten atom W12 (see Supporting Information). Rearrangements of A- and B-XW_9 building groups to form XW_{10} and Keggin structures have been observed previously.[7] The stereochemical requirements of the metal atoms (transition metal, lanthanide or actinide), pH of the solution in which the reaction occurs, and the requirements of the heteroatom (P, As) appear to play a role in this transformation.[8]

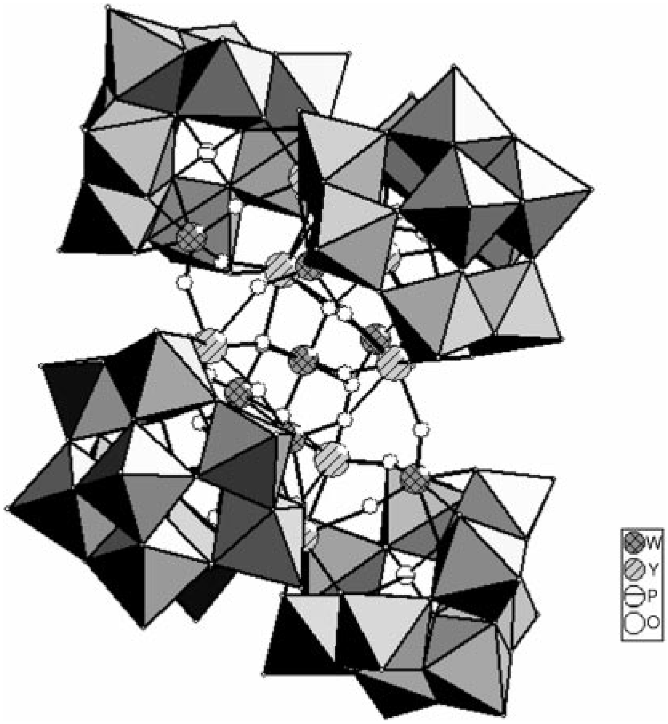

Figure 1. Complex ion **1** comprised of 4 $PW_9O_{34}^{9-}$ ions connected by a network of M–O (M = Y, W) bonds. Eight Y ions and seven W atoms in a $[M_8W_7O_{30}]^{6+}$ network connect the $PW_9O_{34}^{9-}$ anions.

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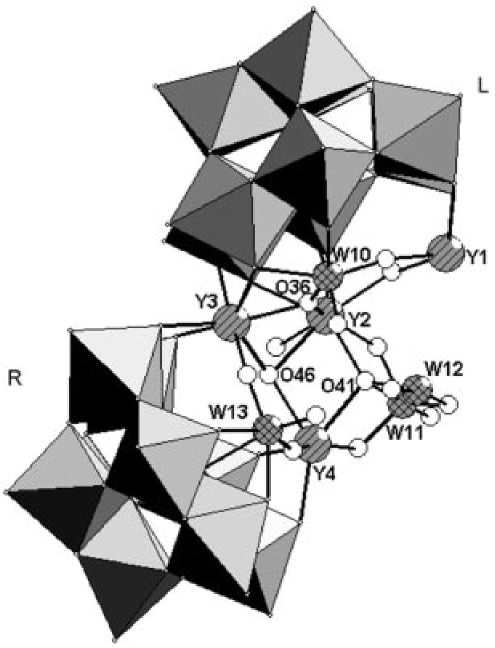

Figure 2. The asymmetric entity of **1** consists of two distorted Keggin-like parts $[(PY_2W_{10}O_{38})^{5-}]$ connected to each other and to the symmetry equivalent entity by bridging oxygen atoms and tungstate units.

The strong involvement of the potassium countercations, seen in the three-dimensional "tertiary" structure of the complex salt, influences the formation of this particular structure. Packing of the anions perpendicular to the crystallographic *a* axis shows a zigzag ribbonlike geometry; potassium cations sew together the strands to form a two-dimensional network. Packing along the *c* axis shows an interlocking structure; potassium cations tie together the heteropolyanions to form linear strands, and tie together the strands as well (Figure 3)

The complex ion **1** bears a charge of -30. This charge is compensated by 15 potassium and six sodium cations from the reaction mixture, as well as nine oxonium ions. On the basis of simple angular considerations, it is likely that three triply bridging hydroxo ligands (μ_3-OH) connect the M and W ions in the M,W,O core of **1**.(Figure 2) The sum of the M-O-M angles is close to the value of 328.4° expected for pure sp^3-hybridized oxygen atoms (the three oxygen atoms connecting the $PW_9O_{34}^{9-}$ anions of **L** and **R** in each asymmetric entity).[9] The sum of the M-O-M angles for the other triply bridging oxygen atoms is close to the 360° for a μ_3-O bonding situation. The M–O bond lengths for μ_3-O, μ_3-OH, μ_2-O, and OH_2 are close to those found in other lanthanide oxygen clusters.[10]

Both ^{183}W and ^{31}P NMR spectroscopy on $K_{15}Na_6(H_3O)_9[(PY_2W_{10}O_{38})_4(W_3O_{14})]$ provide evidence that the complex remains intact in aqueous solution. The $PW_9O_{34}^{9-}$ group itself is not stable under aqueous conditions and forms other polyoxoanions upon decomposition.[11] The M^{III},W,O network apparently holds the PW_9 units together tightly. Two signals are observed in the ^{31}P NMR spectrum, consistent with the C_2 symmetry. The ^{183}W NMR spectrum of the Y analogue shows 19 signals (see Supporting Information), one with a relative intensity of unity and three with about twice the intensity of the other fifteen; this suggests overlapping signals. In total, 22 signals are expected as the complex contains 22 nonequivalent tungsten atoms.

Complex **1** is stable at pH 7–9, according to ^{31}P NMR spectroscopy on the Eu compound. Below pH 6, decomposition to a species with one ^{31}P signal at $\delta = 5.3$ (structure unknown as yet), is observed; at pH 6, the two signals characteristic of **1** and the signal at $\delta = 5.3$ are observed; the signals for **1** alone are observed at pH 7–9. Above pH 10, signals attributed to phosphate are observed.

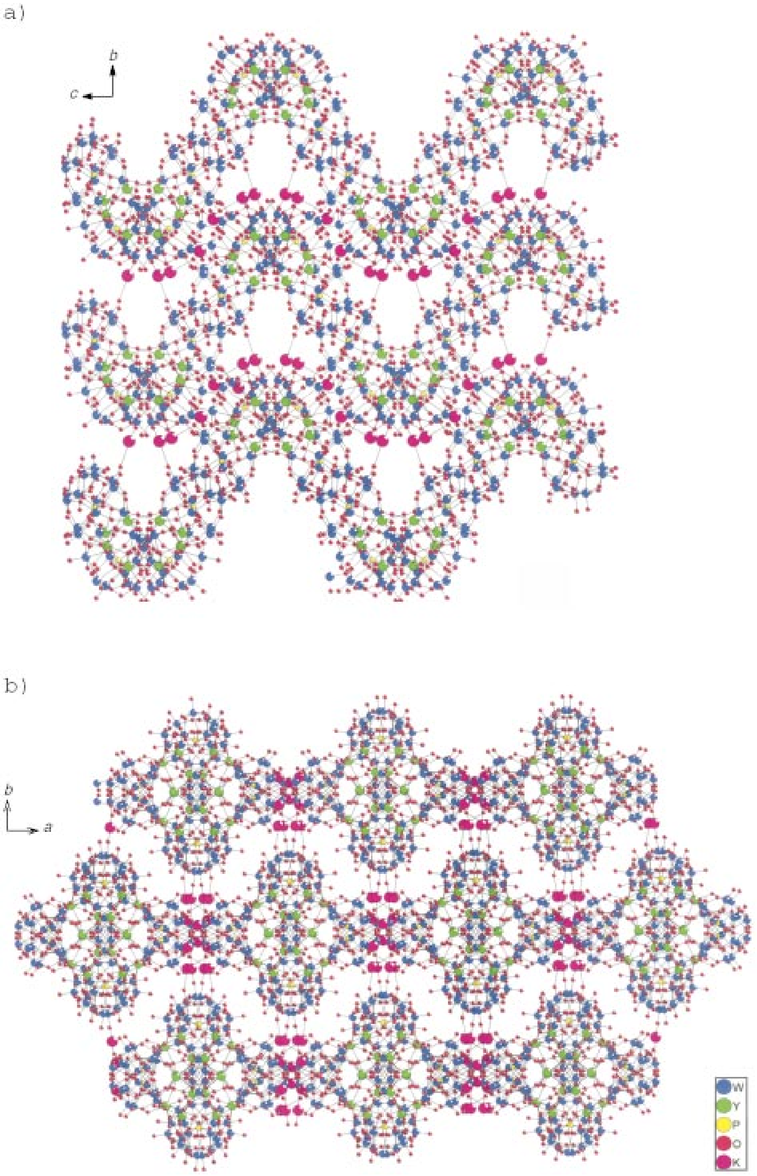

Figure 3. Packing of **1** and K^+ cations along the crystallographic *a* axis (a) and *c* axis (b). The K^+ counterions binding to the surface oxygen atoms of the complex ion link them to form the zigzag and rosette structures shown.

The excitation spectrum of the Eu^{III} compound in aqueous solution showed four transitions at 579.6, 579.9, 580.2, and 580.5 nm, corresponding to the $^7F_0$ to $^5D_0$ transitions of the four unique Eu^{3+} sites (Figure 4). Due to the overlap of the transitions, it was difficult to determine the lifetime of each Eu^{III} site in D_2O and H_2O solutions in order to calculate the number of coordinated H_2O molecules.[12] Excitation into the tungsten bands of a solid sample of the Eu^{III} compound leads to Eu^{III} emission. The luminescence lifetimes for solid samples, prepared in H_2O and D_2O ($\lambda = 590$ nm), resulted in $q = 0.7 \pm 0.5\,H_2O$ per Eu ion;[12] this is consistent with the crystallographic data, which show two water molecules, one each bound to Eu4, per 8 Eu^{III} ions in the molecule.

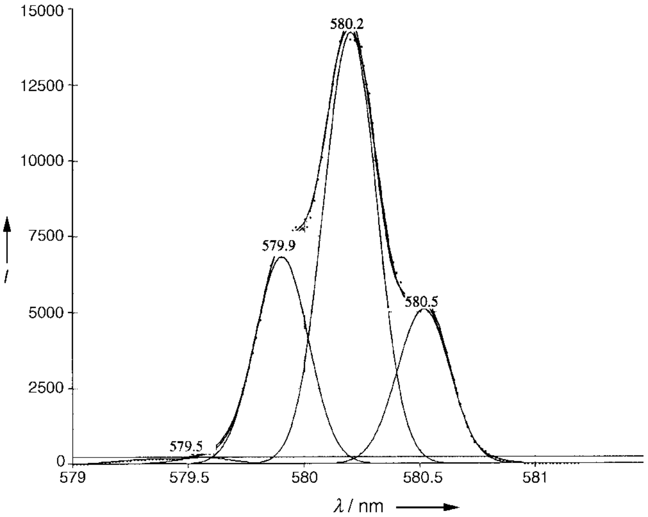

Figure 4. Laser Excitation spectrum of the Eu^{3+} compound showing the overlapping excitation bands of the four different Eu^{3+} sites. The Eu^{3+} emission due to the $^5D_0$ to $^7F_2$ transition was monitored.

Experimental Section

$K_{15}Na_6(H_3O)_9[(PY_2W_{10}O_{38})_4(W_3O_{14})]^{30-}$: Solid powdered $Na_9PW_9O_{34}\cdot 15H_2O$[13] (2.2 g, 0.81 mmol) was added to a solution of $YCl_3\cdot 6H_2O$ (0.57 g, 1.9 mmol) in H_2O (7.5 mL). The resulting suspension was heated to about 80 °C, and a clear solution formed. Solid KCl (1.4 g, 19 mmol) was added to the hot solution, and the solution heated for an additional 10 min. The resulting slurry was cooled to room temperature and then in an ice bath. The solid was collected by filtration, washed with cold H_2O, and recrystallized from hot H_2O (yield: 2.1 g, 72% based on YCl_3). X-ray-quality crystals of $K_{15}Na_6(H_3O)_9[(PY_2W_{10}O_{38})_4(W_3O_{14})]$ were grown at −10 °C from a clear solution of $K_{15}Na_6(H_3O)_9[(PY_2W_{10}O_{38})_4(W_3O_{14})]$ in H_2O saturated with KCl. The europium complex was prepared in a similar manner from $EuCl_3\cdot 6H_2O$.

Elemental analysis (%) calcd (based on crystal structure) for $K_{15}Na_6(H_3O)_9[(PY_2W_{10}O_{38})_4(W_3O_{14})]\cdot 9H_2O$: Y 5.71, W 63.40, P 0.99, K 4.71, Na 1.11; found: Y 5.7, W 62.8, P 1.0, K 5.9, Na 0.2. Elemental anaysis (%) calcd (based on crystal structure) for $K_{16.5}(H_3O)_{13.5}[(PEu_2W_{10}O_{38})_4(W_3O_{14})]\cdot 26H_2O$: Eu 9.22, W 59.6, P 0.93, K 4.7%, H_2O 5.4; found: Eu 9.7, W 62.3, P 1.1, K 5.1, Na 0.3, H_2O 4.9. The elemental analyses are consistent with the formulations. The major differences between calculated and found weight percentages are for the countercations and the water of hydration, as expected. IR (KBr disk) for both complexes showed metal–oxygen stretches at $\tilde{\nu} = 1092$ (m), 1055 (m), 1025 (m), 951 (s), 935 (s), 820(vs), 790 cm^{-1} (s).

^{31}P NMR (161.8 MHz, D_2O) of $K_{15}Na_6(H_3O)_9[(PY_2W_{10}O_{38})_4(W_3O_{14})]$: $\delta = -9.68, -10.53$; ^{31}P NMR (D_2O) of $K_{16.5}(H_3O)_{13.5}[(PEu_2W_{10}O_{38})_4(W_3O_{14})]$: $\delta = 31.76, 23.24$; ^{183}W NMR (16.7 MHz, D_2O) of $K_{15}Na_6(H_3O)_9[(PY_2W_{10}O_{38})_4(W_3O_{14})]$: $\delta = -30.8, -99.8, -103.4, -110.8, -124.2, -129.8, -131.1, -133.8, -134.6, -135.8, -139.2, -141.3, -145.9, -149.7, -157.9, -159.8, -174.7, -187.8, -225.7$.

Crystal structure analysis for $K_{15}Na_6(H_3O)_9[(PY_2W_{10}O_{38})_4(W_3O_{14})]\cdot 9H_2O$: Crystal dimensions 0.4 × 0.2 × 0.2 mm, monoclinic, space group $C2/c$, $a = 22.236(8)$, $b = 34.264(12)$, $c = 26.698(9)$ Å, $\beta = 96.271(6)°$, $V = 20219(18)$ Å^3, $\rho_{calcd} = 4.08$ g cm^{-3}, total collected reflections 51 638, unique reflections 23 150, $R_{int} = 0.0725$, $\mu = 75.805$ mm^{-1}, $R_1 = 0.0824$ for $I < 2\sigma(I)$ and $wR_2 = 0.1999$ for all reflections, total parameters 709, max residual electron density 6.823 e A^{-3}.

Crystal structure analysis for $K_{16.5}(H_3O)_{13.5}[(PEu_2W_{10}O_{38})_4(W_3O_{14})]\cdot 26H_2O$: Crystal dimensions 0.3 × 0.3 × 0.2 mm, triclinic, space group $P/1$, $a = 20.27270(10)$, $b = 22.62970(10)$, $c = 25.88400(10)$ Å, $\alpha = 68.33$, $\beta = 85.21$, $\gamma = 85.52°$, $V = 10982(8)$ Å^3, $\rho_{calcd} = 3.98$ g cm^{-3}, total collected reflections 71 178, unique reflections 45 571, $R_{int} = 0.1046$, $\mu = 25.106$ mm^{-1}, $R_1 = 0.1448$ for $I < 2\sigma(I)$ and $wR_2 = 0.3439$ for all reflections, total parameters 1365, max residual electron density 8.977 e A^{-3}.

Differences in the anion charge and number of cations found in both $K_{15}Na_6(H_3O)_9[(PY_2W_{10}O_{38})_4(W_3O_{14})]$ and $K_{16.5}(H_3O)_{13.5}[(PEu_2W_{10}O_{38})_4(W_3O_{14})]$ of 9$^-$ and 13$^-$, respectively, are most likely compensated by protons. The high residual electron densities in both structures, due to W atom noise, are found within an Ångstrom of W atoms and are accompanied by other W atom noise peaks of similar intensity. Single crystal X-ray diffraction data on $K_{15}Na_6(H_3O)_9[(PY_2W_{10}O_{38})_4(W_3O_{14})]$ and $K_{16.5}(H_3O)_{13.5}[(PEu_2W_{10}O_{38})_4(W_3O_{14})]$ were collected at 298 K and 153 K, respectively, on a Bruker P4 diffractometer equipped with a SMART CCD detector and a graphite monochromator ($\lambda(Mo_{K\alpha}) = 0.71073$ Å). The structures were solved by direct methods and standard difference-map techniques, and refined by full-matrix least-squares procedures (SHELXTL).[14] No hydrogen atoms were included.

Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-391092 ($K_{15}Na_6(H_3O)_9[(PY_2W_{10}O_{38})_4(W_3O_{14})]$) and CSD-411918 ($K_{16.5}(H_3O)_{13.5}[(PEu_2W_{10}O_{38})_4(W_3O_{14})]$).

Elemental analysis was performed at Hunter College by inductively coupled plasma analysis on a Spectro Spectroflame M120 E spectrometer and by Kanti Technologies Inc, Tonawanda, NY. IR spectra were recorded on a Perkin Elmer Series 1600 FTIR spectrometer. ^{31}P and ^{183}W NMR were recorded on a JEOL 400 MHz with 85% H_3PO_4 and 2 M Na_2WO_4, respectively, as external standards.

Laser luminescence studies were performed at Pennsylvania State University with a Continuum YG581 pulsed Nd:YAG laser, pumping a TDL50 tunable dye laser. The $^7F_0$ to $^5D_0$ transitions of the Eu^{3+} ions were excited while the $^5D_0$ to $^7F_2$ emission band was monitored. Measurements were carried out at 25.0 ± 0.1 °C. The commercially available Peakfit program, which employs a nonlinear regression method, was used for data analyses. The concentrations of the samples used to obtain the excitation and the luminescence decay lifetime spectra were 20 mM.

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[5] Y3, Y4, and W13 of **R** belong to three different edge-shared $Y(3,4)W_2O_{12}$ and $W(13)W_2O_{13}$ groups and are linked to the others through corner-shared oxygen atoms to give an A-type positional isomer. The fourth edge-shared W_3O_{13} group is not rotated with respect to the parent α-Keggin part (see Supporting Information); this defines the second type of isomerism as α.

[6] A detailed description of the bonding in **L** and **R** (Figure 2) follows: Y1 (7-coordinate) and Y2 (8-coordinate) are both bound to oxygen atoms of **L**. Y1 is also bound to one oxygen atom in each of the symmetry-equivalent **L** (μ_2-O (2.264(17) Å) to W10A) and **R** (μ_2-O (2.275(19) Å) to W13A) and μ_2-O (2.301(17) Å) to W12. The other four coordination sites of the eight-coordinate Y2, which connect **L** to **R**, are occupied by μ_3-O (2.483(17) Å) to Y3 and Y4, μ_2-O to W12 (2.310 Å), μ_2-O to W11 (2.39 Å) and a terminal O atom (2.44 Å). Similarly, Y3 and Y4 are bound to O atoms of **R**. Y3 is connected to **L** by μ_3-O (2.442(17) Å) to W4 and W5, μ_3-O (2.556(18) Å) to W5 and W10, μ_3-O (2.464 (18) Å) to W4 and Y2, and the fourth remaining site to μ_3-O (2.337(17) Å) to Y2 and Y4. The three remaining coordination sites on Y4, connecting Y4 to **L**, are occupied by μ_2-O (2.341(18) Å) to W12, μ_2-O (2.368(19) Å) to W11, and μ_3-O (2.335(17) Å) to W12 and Y2.

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"Nanoobjects" by Self-Assembly Concomitant with Modifications under Alterable Boundary Conditions: Incorporation of Paramagnetic Metal Centers (Cu^{2+}) in Ring-Shaped Molybdenum-Oxide Based Clusters[**]

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Dedicated to Professor Dr. Hansgeorg Schnöckel on the occasion of his 60th birthday

Until now it has been a tremendous and ongoing challenge to initiate a variety of chemical reactions at *well-defined* positions even of the same and structurally *well-defined* nanoobject, especially if significant property changes or novel functionalities are intended.[1] This aim has now been achieved for giant ring-shaped molybdenum oxide based clusters of the type $\{Mo_{154}\}$ and $\{Mo_{176}\}$ which can be obtained in related crystalline salts in a facile high-yield synthesis and exhibit nanosized cavities, a variety of sites with different well-defined functional groups, and overall are comparable to a nanostructured landscape.[2, 3] Here we report the incorporation of paramagnetic metal centers, that is, Cu^{2+} ions, in cavities of these rings—which are spanned by four O atoms and have the corresponding appropriate size—according to a basic type of self-assembly process leading to nanoobjects all of which have the ring topology. Important in this context is that this allows a variety of deliberate concomitant modifications under alterable boundary conditions—such as the pH, temperature, and/or presence of different substrates—corresponding to the different sites.[4] The procedure opens perspectives not only for a new type of nanochemistry but also for an understanding of a basic reaction type of material organization (see below).

The reduction of an acidified aqueous polymolybdate solution with copper powder leads to the crystalline black compound **1**, which was characterized by elemental analyses

$$(NH_4)_{26}[(H_4Cu^{II}_5)Mo^{V}_{28}Mo^{VI}_{114}O_{432}(H_2O)_{58}]\cdot{\approx}300\,H_2O \qquad \mathbf{1}$$

(including cerimetric titration to determine the formal number of Mo^V centers), thermogravimetry (to determine the amount of crystal water), spectroscopy (UV/Vis/NIR, infrared (IR), resonance-Raman, ESR), single-crystal X-ray structure analysis,[5] and bond valence sum (BVS)[6] calculations (to determine the positions of the H_2O molecules and to

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