$\beta = 97.542(1)$, $\gamma = 97.410(1)^\circ$, $V = 35\,592(3)$ Å^3, $Z = 1$, $\rho = 2.466$ g cm^{-3}, $\mu = 2.907$ mm^{-1}, $F(000) = 25\,484$, crystal size $= 0.35 \times 0.20 \times 0.05$ mm^3. Crystals of **1** were removed from the mother liquor and immediately cooled to 183(2) K on a Bruker AXS SMART diffractometer (three-circle goniometer with 1 K CCD detector, $Mo_{K\alpha}$ radiation, graphite monochromator; sphere data collection in ω at 0.3° scan width in four runs with 606, 500, 606, and 500 frames ($\phi = 0$, 88, 180 and 268°) at a detector distance of 5.00 cm). A total of 371 523 reflections ($0.66 < \Theta < 27.05^\circ$) were collected of which 153 584 reflections were unique ($R_{int} = 0.0511$). An empirical absorption correction using equivalent reflections was performed with the program SADABS. The structure was solved with the program SHELXS-97 and refined using SHELXL-93 to $R = 0.0559$ for 96 134 reflections with $I > 2\sigma(I)$, $R = 0.1066$ for all reflections; max./min. residual electron density 3.680 and -2.844 e Å^{-3}. (SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen 1993/97; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, 2001.) Further details on the crystal structure investigation 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 number CSD-411984.

[10] I. D. Brown in *Structure and Bonding in Crystals, Vol. II* (Eds.: M. O'Keeffe, A. Navrotsky), Academic Press, New York, **1981**, pp. 1–30.

[11] EXAFS measurements were performed at the beamline A1 at HASYLAB (Hamburg) on samples ground together with suprapure polyethylene and subsequently pressed into pellets with a thickness of 300 μm. Spectra were obtained in the transmission mode at the Eu-L_{III} edge covering the range from 6.75–8.00 keV. The magnitude of the Fourier transform of the EXAFS after background and phase correction shows a distinct and symmetric maximum at 243 pm which is clearly a result of almost only (!) one kind of oxygen coordination to the Eu absorber. A second coordination shell at about 350 pm is assigned to Eu ⋯ Mo separations.

[12] Although the total number of molybdenum centers is certain, the (formal) number of Mo^V centers has a slight uncertainty, though the given number of 24 is the most reasonable one according to the comparison with previous related structures, that is, parts of the well known $\{Mo_{154}\}$ and $\{Mo_{176}\}$ clusters with respect to the related BVS values of comparable protonation sites and Mo_5O_6-type building blocks.[1b, 6] This assignment results in a charge of -20 per "dimer" **1a** by referring to the number of abundant protons and Mo^V centers (note: the related electron spins are paired here as in the reduced Keggin ions[13]). Despite the nonmagnetic $^7F_0$ ground state, the Eu^{III}-ions yield a temperature-dependent paramagnetism (TIP) since the weak spin-orbit splitting of the ^7F term ($\lambda \approx 300$ cm^{-1}) allows excited ^7F_J states ($J = 1, 2, \cdots$) to be thermally populated.[14] As the relevant states are not significantly perturbed by ligand-field effects, the magnetism of a system containing N Eu^{III} positions corresponds very well to N times the free Eu^{III} ion contribution (typical $\chi_{mol}T$ value for an Eu^{III} ion at room temperature: 1.53 emu K mol^{-1} [14b]). The observed paramagnetism of **1** ($\chi_{mol}T = 23.2$ emu K mol^{-1} at 290 K, corrected for diamagnetism and an estimated TIP value of the polyoxomolybdate ring) corresponds to 15 (±1) individual Eu^{III} centers per formula unit which is in agreement with the Eu analysis (calcd (%) for **1** with X = H: Eu 4.03; found: Eu 3.9). While eight of these are definitely constituents of the $\{Mo_{256}\}$-type cluster dimer, the remaining six Eu^{III} cations per formula unit are strongly disordered in the crystal lattice and cannot be localized exactly. (The observed temperature dependence of $\chi_{mol}T$ for **1** also rules out the presence of Eu^{II} centers.) Thus, the resulting problem is to explain the charge difference between -20 (see above) and -18 corresponding to the presence of six Eu^{III} lattice cations. This might be a result of the (corresponding) presence of two alkali cations (found (%) ca. 0.07) or two H^+ ions which is a more reasonable explanation (see formula). Based on the extremely small values of the potassium (and sodium) analyses this problem cannot be solved without doubt. Location of the water ligands was by comparison with previous structures while the related oxygen BVS indicate the presence of two "new type" water ligands per ring of **1a** on the building blocks adjacent to the new $\{Mo_2^*\}$ groups (see, Figure 2). The given crystal-water content corresponds to the maximum number with respect to the unit-cell volume according to our usual procedure (note: the rapid release of crystal water!).

[13] M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56–70; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34–48.

[14] a) O. Kahn, *Molecular Magnetism*, VCH, Weinheim, **1993**, p. 43; b) H. Lueken, *Magnetochemie*, Teubner, Stuttgart, **1999**, p. 38.

[15] A. Müller, C. Beugholt, H. Bögge, M. Schmidtmann, *Inorg. Chem.* **2000**, *39*, 3112–3113.

[16] Investigating the O-BVS values of the equatorial μ_3-O atoms it turns out that, firstly, (exactly only) one atom per compartment is protonated and, secondly, moving from one equatorial bridging ligand (H_2O1) of the ("new") $\{Mo_2^*\}$ unit to the corresponding other $\{Mo_2^*\}$ type bridging (H_2O2) ligand and passing six compartments of half a cluster ring, the sequence of protonated (p) and unprotonated (u) equatorial μ_3-O atoms is: H_2O1 u-p u-p u-p u-p u-p u-u H_2O2. The alternating occupation of these positions is caused by the repulsive forces between the H atoms of adjacent compartments. That the above sequence is favored over the other possible sequence H_2O1 u-u p-u p-u p-u p-u p-u H_2O2 or to a 50:50 disordered situation as in the parent cluster type is caused by two Eu^{III} ions positioned close to the "u-u" compartment. Our present results support our earlier conclusion (correct formula): one μ_3-OH group per compartment.[1b, 6]

[17] U. Simon, G. Schön in *Handbook of Nanostructured Materials and Nanotechnology, Vol. 3* (Ed.: H. S. Nalwa), Academic Press, New York, **1999**, p. 131; G. Schön, U. Simon, *Colloid Polym. Sci.* **1995**, *273*, 101–217; G. Schön, U. Simon, *Colloid Polym. Sci.* **1995**, *273*, 202–218; G. L. Snider, A. O. Orlov, I. Amlani, X. Zuo, G. H. Bernstein, C. S. Lent, J. L. Merz, W. Porod, *J. Appl. Phys.* **1999**, *85*, 4283–4285.

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[19] The IR spectrum is practically identical to that of the related Pr^{III} molybdate educt used in ref. [15] and to that of a compound formulated there as $Eu_2O_3 \cdot 7\,MoO_3 \cdot n\,H_2O$ ($n = 6$ and 8) and obtained according to a preparation method given in the literature (*Gmelin Handbook of Inorganic Chemistry, Mo Suppl., Vol. B4*, Springer, Berlin, **1985**, p. 262 and *Chem. Abstr.* **1973**, *78*, 10950).

[20] See C. Beugholt, *Dissertation*, Fakultät für Chemie, Universität Bielefeld, **2001**, with a preliminary formula.

Mo^V/Pyrophosphate Polyoxometalate: An Inorganic Cryptate

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Polyoxometalate chemistry continues to be a subject of great interest, since the wide and fascinating variety of structures and properties of these objects gives rise to numerous applications.[1] Polyoxoanions containing phosphato groups constitute the largest class of heteropolyanions, with structures ranging from molecular complexes to extended frameworks.[2] In contrast, very few polyoxometalate-containing polyphosphato groups have been structurally characterized. In 1994, Kortz and Pope reported the first X-ray structure of a polyoxomolybdate(VI) containing the pyrophosphato $(P_2O_7)^{4-}$ ligand.[3] Since then, only two other structures

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have been reported.[4] For these three compounds, the $(P_2O_7)^{4-}$:Mo^{VI} ratio is between 1:6 and 1:18. The lack of information concerning this class of compound and the absence of Mo^{V} pyrophosphate complexes can be justified by the observations of Weil-Malherbe and Green.[5] Indeed, they have shown that the hydrolysis of pyrophosphate into monophosphate is catalyzed in water by molybdenum. Moreover, this reaction is enhanced by Mo^{V} rather than by Mo^{VI}, and is optimal at pH 2 with a secondary maximum at pH 5.5. We are currently investigating the interaction between (poly)phosphate and Mo^{V} either under hydrothermal conditions[6] or usual "bench" conditions. We have tried to determine a domain where the hydrolysis of pyrophosphate by Mo^{V} would be minimal. This work led us to the isolation and characterization of the first pyrophosphate/Mo^{V} complex **1**, a highly charged and highly hydrated complex which comprises two nearly perpendicularly interconnected wheels, an unprecedented topology for an inorganic compound.

$\mathrm{Na_{24}[Na_4(H_2O)_6 \subset \{(Mo_2O_4)_{10}(P_2O_7)_{10}(CH_3COO)_8(H_2O)_4\}] \cdot 97\,H_2O}$ **1**

The synthesis has been performed in sodium acetate buffer. The success of this approach can be explained by considering that 1) the rate of hydrolysis of the $(P_2O_7)^{4-}$ ion must be lower at the pH of the acetate buffer and that 2) acetate can lead to the formation of the stable $[\mathrm{Mo}^{V}_{2}O_4(\mu\text{-}CH_3COO)]^{+}$ dimer,[7] which possesses two free sites in *cis* positions on each Mo^{V} center. This arrangement must permit the formation of large rings in presence of bridging ligands. Compound **1** was synthesized by mixing sodium molybdate, pyrophosphate, and hydrazine and stirring the mixture for three hours. Then, the solution was allowed to crystallize at room temperature. The final yield is not affected if the Mo^{VI} species is first reduced by hydrazine before the addition of pyrophosphate, or if all the reagents are added simultaneously. This situation is evidence of the stability of pyrophosphate in this medium. Similar experiments have been performed in lithium, potassium, or cesium acetate buffer. The role of the alkaline cation seems crucial since compound **1** has not been obtain under these conditions.

Complex **1** is built up by two nonequivalent interconnected wheels (Figure 1). The largest wheel (noted $\{\mathrm{Mo}_{12}\}$) is formed by twelve Mo^{V} centers (Figure 2a), and the smallest (noted $\{\mathrm{Mo}_{8}\}$) contains eight Mo^{V} atoms (Figure 2b). All the molybdenum centers are in a distorted octahedral environment and have an Mo=O bond, that is, they contain a terminal oxygen atom. As usually observed,[6, 7] the Mo^{V} atoms are arranged by pairs, forming the diamagnetic dinuclear unit $\{\mathrm{Mo}^{V}_{2}(\mu\text{-}O)_2O_2\}$, with an average Mo···Mo separation of 2.54 Å. These dimers are bridged by two types of pyrophosphate groups. Six pyrophosphate unitss connect two dimers, and four are bridging three dimers, ensuring the connection between the two wheels. These two wheels are nearly perpendicular (Figure 2c), with an angle of 92.8° (calculated considering the least-square planes defined by the metallic atoms). It follows that **1** can then be described as an inorganic cryptate of an overall D_{2d} symmetry. The coordination spheres of four of the six dimers of the $\{\mathrm{Mo}_{12}\}$ entity is completed by a μ-O_2 acetato anion, while those of the two remaining dimers are completed by water molecules (Figure 2a). The role of these exogenous ligands is crucial since it strongly influences the curvature of the dimers and thus the topology of the whole edifice. This effect can be emphasized by the distances between the axial ligands in a $\{\mathrm{Mo}^{V}_{2}O_4(H_2O)_2\}$ dimer ($d(O_t \cdots O_t) = 2.910(9)$ Å and $d(O_{H_2} \cdots O_{H_2}) = 3.144(9)$ Å) and in the $\{\mathrm{Mo}^{V}_{2}O_4(CH_3COO)_2\}$ dimers ($d(O_t \cdots O_t) = 3.172(9)$–

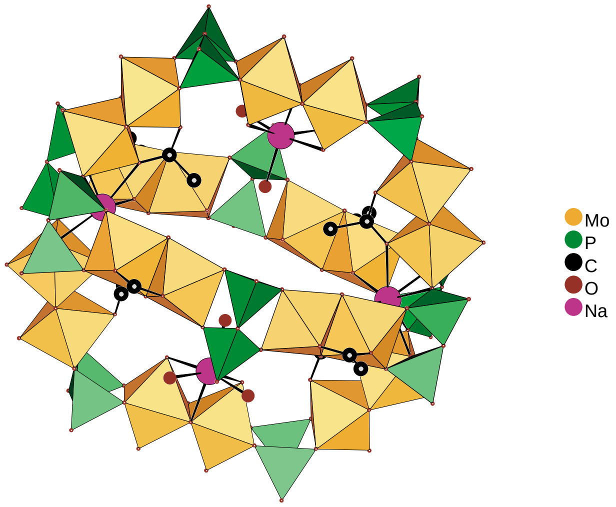

Figure 1. Polyhedral representation of **1**. Lengths range (average lengths) [Å]: Mo=O 1.659(7)-1.681(6) (1.668); Mo-O(Mo) 1.910(6)-1.937(6) (1.922); Mo-O(P) 2.055(8)-2.095(6) (2.076); Mo-O(C) 2.215(6)-2.331(6) (2.275); Mo-OH_2 2.324(6)-2.328(6) (2.326); P=O 1.455(6)-1.487(6) (1.473); P-O(P) 1.578(8)-1.614(6) (1.605); P-O(Mo) 1.499(7)-1.520(6) (1.511); C-O 1.239(11)-1.262(10) (1.250); C-C 1.481(14)-1.498(13) (1.491).

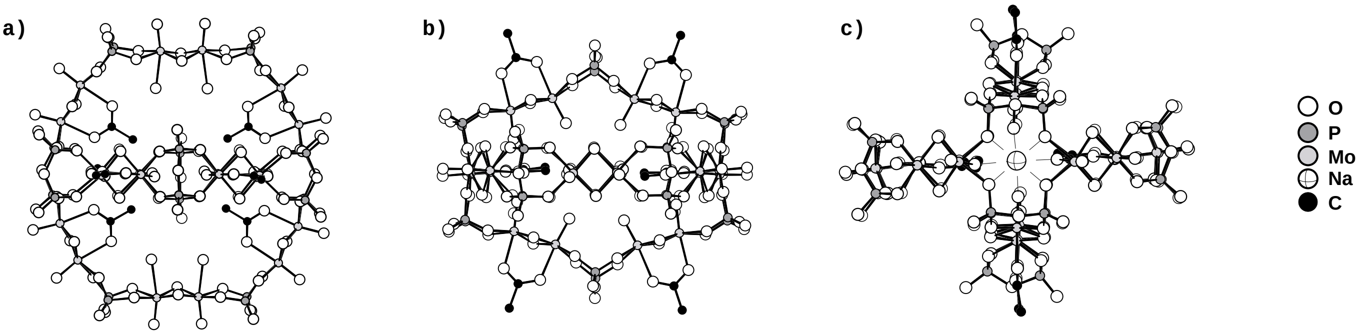

Figure 2. Ball-and-stick representations of **1** highlighting a) the $\{\mathrm{Mo}_{12}\}$ ring and the inner acetate groups b) the $\{\mathrm{Mo}_{8}\}$ ring and the outer acetate groups c) the near perpendicular arrangement of the $\{\mathrm{Mo}_{12}\}$ and the $\{\mathrm{Mo}_{8}\}$ planes.

3.254(10) Å and $d(O_{OCH_3}\cdots O_{OCH_3}) = 2.171(9)-2.207(10)$ Å. In $\{Mo_{12}\}$, all the Mo=O groups are directed towards the outside of the cavity. The situation is different for the $\{Mo_8\}$ wheel, where each dimer is coordinated to an acetate anion, and the Mo=O groups are directed towards the inside of the cavity. Valence bond summations (VBS) have been applied on all the atoms.[8] These calculations confirmed the oxidation state of molybdenum atoms and permitted us to conclude that all the pyrophosphato groups are fully deprotonated, which is consistent with the presence of the 28 sodium cations determined by elemental analysis. Four of these counterions have been found inside the cavity. Two are located at the intersections of the wheels, connecting four $\{Mo^{V}_2O_4(CH_3COO)_2\}$ fragments through eight oxygen atoms (d(Na-O) = 2.403(7)-2.516(7) Å). These two tightly bound sodium cations must play a key role in the stability of the receptor which acts as a cryptand anion (Figure 1).[9] Two additional alkaline cations have been found linked to the water molecules of the $\{Mo^{V}_2O_4(H_2O)_2\}$ dimers, the remaining counterions being located outside the cage. Finally, a vacant site is available at the center of the polyanion.

The NMR spectrum of **1** at room temperature (Figure 3) exhibits three resonances located at $\delta_1 = 3.03$ ppm, $\delta_2 = 1.66$ ppm, and $\delta_3 = -0.64$ ppm with relative intensity of 2:1:2. This result is in agreement with the structure determined by X-ray diffraction. The spectrum of this solution remains unchanged over several weeks, which shows the high stability of **1** in this medium. The ^{31}P NMR spectrum has also been recorded in water and gives a complex pattern, which indicates decomposition of compound **1**. Among the large number of species observed, free phosphato groups and the well-known $[P_4Mo_6(OH)_3O_{28}]^{9-}$ complex,[6b, 10] which results from the hydrolysis of the polyphosphate moieties, have been identified. Indeed the pyrophosphate ligands in **1** are highly available to direct attack by the solvent compared to the only water-stable example of a Mo^{VI}–pyrophosphate compound, the Dawson-like $[(P_2O_7)Mo_{18}O_{54}]^{4-}$ ion, where the pyrophosphate group is encapsulated.[3]

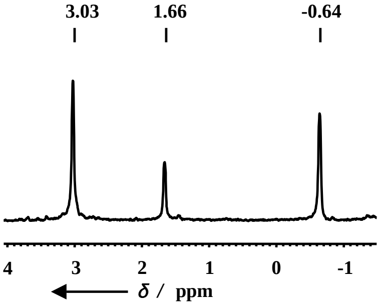

Figure 3. ^{31}P NMR spectrum of **1** in acetate buffer at room temperature.

In conclusion, we have characterized the first Mo^{V}–pyrophosphate complex which possesses a unique double-wheel topology and a high $(P_2O_7)^{4-}$:Mo^{V} ratio. This complex has been obtained in an acetate buffer medium. We are now investigating the possibility to insert a guest cation in the central cavity of **1**, and the behavior of Mo^{V} and pyrophosphate in various mono- and dicarboxylate buffers.

Experimental Section

$Na_2MoO_4\cdot 2H_2O$ (10.33 mmol, 2.5 g) was dissolved in a 4 M sodium acetate/acetic acid buffer (pH 4.67, 100 mL), to which $N_2H_4\cdot H_2O$ (3.08 mmol, 150 μL) and $Na_4P_2O_7$ (5.6 mmol, 2.5 g) were added. The obtained green solution was stirred for 3 h and then allowed to stand at room temperature. Orange parallelepipedic crystals were collected by filtration after 3 days. Yield: 1.12 g (32 % based on Mo); elemental analysis (%) calcd for **1**: Mo 26.15, P 8.45, C 2.62, Na 8.78; found: Mo 26.86 P 8.23, C 2.86, Na 9.06. IR (KBr pellet): $\tilde{\nu}$ = 1638 (s), 1549 (m), 1454 (w), 1424 (sh), 1203 (s), 1087 (s), 1036 (s), 969 (m), 748 (w), 678 (w), 581 (m), 522 (m), 483 cm^{-1} (m); UV/Vis (4 M sodium acetate/acetic acid buffer): $\lambda_{max}(\varepsilon) = 301$ (104700), 402 nm (1950), 465 (1000); ^{31}P NMR (121.5 MHz, 25 °C, H_3PO_4 85 %): $\delta = 3.03$, 1.66, -0.64 ppm.

Crystal data and structure refinement for **1**: an orange parallelepipedic crystal (0.12 × 0.10 × 0.02 mm) was analyzed with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector using $Mo_{K\alpha}$ monochromatized radiation ($\lambda = 0.71073$ Å). Monoclinic, space group $P2(1)/n$, $a = 20.8051(1)$, $b = 21.3293(1)$, $c = 22.6197(2)$ Å, $\beta = 94.270(1)^\circ$, $V = 10009.81(11)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.306$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.567$ mm^{-1}, F(000) = 6860, 70617 reflections measured, of which 26891 were independent, 1377 refined parameters, $R = 0.0771$, $wR_2 = 0.1518$. Data reduction was performed with the SAINT software. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program based on the method of Blessing. The structure was solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package. As crystal structure shows disorder in the range of water molecules and sodium cation, the exact formula and molecular weight have been established from thermogravimetry (TG) studies and the elemental analysis. The hydrogen atoms of the acetate groups were located and refined using a constrained "riding" model. CCDC-178291 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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