Formation of a "less stable" polyanion directed and protected by electrophilic internal surface functionalities of a capsule in growth: $[\{Mo_6O_{19}\}^{2-}\subset\{Mo^{VI}{}_{72}Fe^{III}{}_{30}O_{252}(ac)_{20}(H_2O)_{92}\}]^{4-}$

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The spherical capsule skeleton of the host–guest system $[\{Mo_6O_{19}\}^{2-}\subset\{Mo^{VI}{}_{72}Fe^{III}{}_{30}O_{252}(CH_3COO)_{20}(H_2O)_{92}\}]^{4-}$ 1a—built up by 12 $\{(Mo^{VI})Mo^{VI}{}_5\}$ type pentagonal units linked by 30 Fe^{III} centers which span the unique icosahedral Archimedean solid, the icosidodecahedron—can now be constructed deliberately and with a simpler composition than before from an acidified aqueous molybdate solution containing the mentioned (virtual) pentagonal units; the encapsulated hexamolybdate—normally not formed in water—is built up in an unprecedented way concomitant with capsule growth, while being directed by the corresponding internal electrophilic surface functionalities.

It is well known that aesthetically beautiful spherical objects can, geometrically speaking, be constructed from pentagons according to the related building block principle known for instance from virology, architecture (geodesic domes) as well as from daily life. But the use of this principle in synthetic chemistry has not been deliberately exploited. Though it became known that pentagonal units of the type $\{(Mo^{VI})Mo^{VI}{}_5\}$ occur in spherical capsules/Keplerates of the general formula $\{(Mo)Mo_5\}_{12}\{Linker\}_{30}$ (the linker can be of a mononuclear (M) or dinuclear metal type (M_2)[1–4]) it could only be proven in the particular case of $M \equiv VO^{2+}$ [4] that the spherical capsules can be directly synthesized by the addition of linkers to the dynamic library containing (virtual) pentagonal units† (see also ref. 5 regarding general remarks). The related cluster type with the skeleton $\{(Mo)Mo_5\}_{12}\{Fe^{III}\}_{30}$ could until now not be synthesized in a straightforward reaction and contains inside the capsule—due to the specific preparation process—complex units of the type $\{Mo_2O_{8/9}\}^{n-}$ as ligands,[6] which complicates the structure and, in principle, the interpretation of its (magnetic) properties.

Herein we report on the synthesis of the $\{(Mo)Mo_5\}_{12}\{Fe^{III}\}_{30}$ type cluster **1a** exhibiting several new features: (1) the spherical capsule/Keplerate can be directly constructed based on an appropriate molybdate library containing the above mentioned virtual pentagonal units, (2) the mentioned $\{Mo_2O_{8/9}\}^{n-}$ units[6] are not present, and most important (3) the hexamolybdate $[Mo_6O_{19}]^{2-}$ anion is encapsulated noncovalently bonded, a discovery which will have implications for future theoretical and synthetic work. Furthermore, it should be noted that the inorganic skeleton of **1a** is of tremendous interest because of its unique magnetic properties.[8,9a–c]

$Na_4[\{Mo_6O_{19}\}^{2-}\subset\{Mo^{VI}{}_{72}Fe^{III}{}_{30}O_{252}(CH_3COO)_{20}(H_2O)_{92}\}]\cdot$*ca.* 120 $H_2O \equiv Na_4\cdot$**1a**$\cdot$*ca.* 120 H_2O **1**

If an acidified aqueous solution of sodium molybdate which contains a rather high concentration of acetic acid is treated with iron(III) chloride, yellow crystals of **1** precipitate after some days.‡ Compound **1**, which crystallizes in the space group $R\bar{3}$, was characterized by elemental analysis (including ESCA), thermogravimetry (to determine the actual(!) crystal water content), spectroscopy (IR, Raman, UV-Vis), and single-crystal X-ray structure analysis (including bond valence sum (BVS) calculations)§ and magnetic susceptibility measurements.

The cluster anion **1a** (the anions occupy in **1** two crystallographically independent positions $\bar{1}$ and $\bar{3}$) is of the expected spherical $\{(Mo)Mo_5\}_{12}\{Linker\}_{30}$ type mentioned above. Correspondingly, the heptacoordinated Mo centers of the 12 pentagonal $\{(Mo^{VI})Mo^{VI}{}_5\}$ type units span an icosahedron, and the 30 Fe^{III} linkers, the quasi-regular icosidodecahedron (Fig. 1) which is a hybrid of the icosahedron and the dodecahedron and contains correspondingly 20 trigonal and 12 pentagonal faces[7] (Fig. 1). The 20 acetate ligands in **1a**, some of which are disordered, are located inside the sphere and are coordinated in a bidentate fashion to the metal centers, preferentially bridging Fe and Mo sites. **1a** does not contain the $\{Mo_2O_{8/9}\}^{n-}$ type units in contrast to the former reported $\{Fe\}_{30}$ type compound.[6]

The most interesting aspect of the present work is the encapsulation of the hexamolybdate $[Mo_6O_{19}]^{2-}$ in the cavity of the capsule (Fig. 2). This polyanion cannot be obtained as other polymolybdates simply in water and is preferably formed in organic solvents, thereby crystallizing together with organic cations.[10] In the present system it is stabilized/protected by the comparably large number of acetates inside the cavity of **1a**, which form a hydrophobic environment. It is important to note that negatively charged polyoxometalates cannot be encapsulated in (highly) negatively charged Keplerates/capsules like the $\{Mo_{132}\}$ cluster.[3] In the present case **1a** is "approximately neutral" and the pure inorganic part/skeleton, *i.e.* without the acetate ligands, is even positively charged. (Note: a few deprotonated H_2O ligands coordinated to the Fe centers cause a small negative charge.) This allows attraction/collection of small anionic fragments with the consequence that the stepwise formation of $[Mo_6O_{19}]^{2-}$ can occur

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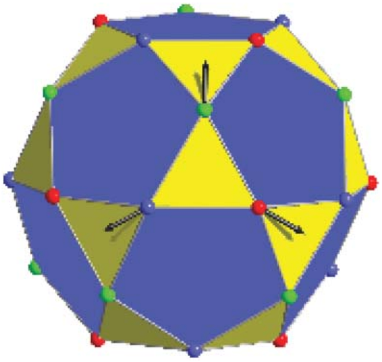

Fig. 1 The unique Archimedean solid: the $\mathrm{Fe^{III}}$ centers (small colored spheres) of the $\{(\mathrm{Mo^{VI}})\mathrm{Mo^{VI}}_5\}_{12}\{\mathrm{Fe^{III}}\}_{30}$ type Keplerate **1a** (but also of the corresponding $\{\mathrm{OV^{IV}}\}_{30}$ system[4]) span the shown icosidodecahedron which is unique among the Archimedean solids.† (Note: in the Kagomé lattice, every vertex has the same surroundings in the sense that the polygons meeting at each vertex are in sequence: pentagon (hexagon in the Kagomé case), triangle, pentagon (hexagon), triangle; see ref. 7*a*, p. 13.) There are three groups (“sublattices”) of 10 spins (red, blue, green, respectively), with all spins of a sublattice having parallel spin vectors, while nearest-neighbor spin vectors (three highlighted) differ in angular orientation by 120° (see text and ref. 9*a*).

concomitantly with the growth of the capsule skeleton, *i.e.* on its internal electrophilic surface.

With respect to the synthesis the following aspect is important: in aqueous solution, the pentagonal $\{(\mathrm{Mo^{VI}})\mathrm{Mo^{VI}}_5\}$ unit “occurs” relatively weakly bound in the $[\mathrm{Mo^{VI}}_{36}\mathrm{O}_{112}(\mathrm{H_2O})_{16}]^{8-}$ anion[11] (see Fig. 14a of ref. 11*b*), which is practically the only abundant species at low pH values and furthermore the largest isopolymolybdate to be obtained under non-reducing conditions.[11] Correspondingly $\{(\mathrm{Mo})\mathrm{Mo}_5\}_{12}\{\mathrm{Linker}\}_{30}$ type Keplerates, which have—because of their spherical shape (minimum surface–volume ratio)—a high formation tendency, are formed from that solution in the presence of (potential) linkers like $\mathrm{Fe^{III}}$ ions. The reaction is based on a “split-and-link” mechanism with the $\{(\mathrm{Mo^{VI}})\mathrm{Mo^{VI}}_5\}$ unit being abstracted from the $\{\mathrm{Mo}_{36}\}$ type species.¶ (Related results regarding mixed metal species like $\{\mathrm{Mo^{V}}_4\mathrm{V^{IV}}_{26}\}$, or $\{\mathrm{Fe^{III}}_{22}\mathrm{V^{IV}}_8\}$[12] will be reported later.) As pentagonal $\{(\mathrm{Mo^{VI}})\mathrm{Mo^{VI}}_5\}$ building blocks of the $\{\mathrm{Pentagon}\}_{12}\{\mathrm{Linker}\}_{30}$ type occur in spherical capsules/Keplerates also with the binuclear linkers $\{\mathrm{Mo^{V}}_2\mathrm{O}_4\}^{2+}$ [1–4] it is possible to apply also to them the synthetic principle outlined here for the mononuclear linkers.[13]

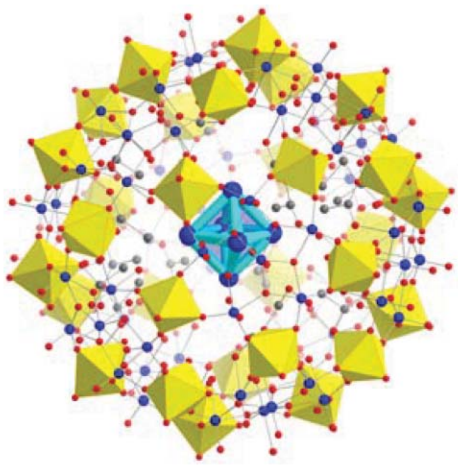

Fig. 2 Structure of **1a** emphasizing the $\mathrm{Mo^{VI}}$ positions of the encapsulated hexamolybdate ion within the metal oxide skeleton of the capsule **1a** (Mo blue, O red spheres) and the linkers in the form of $\mathrm{FeO_6}$ octahedra (yellow).

To characterize the magnetic properties of **1**, the magnetic susceptibility *versus* temperature as well as the magnetization as a function of field were measured (this had to be done in order to prove whether an influence of the $[\mathrm{Mo_2O_{8/9}}]^{n-}$ units exists; see above). The room temperature value $\chi T = 120.1\ \mathrm{cm^3\ K\ mol^{-1}}$ is slightly smaller than that expected for 30 noninteracting iron(III) ions ($\chi T = 131.3\ \mathrm{cm^3\ K\ mol^{-1}}$, assuming $g = 2.00$). On lowering the temperature, the χT product decreases, reaching a value of $\chi T = 10.3\ \mathrm{cm^3\ K\ mol^{-1}}$ at $T = 1.8$ K, which is indicative of predominant antiferromagnetic exchange interactions. A Curie–Weiss plot of χ^{-1} *versus* T yields a Curie constant of $C = 128.4 \pm 0.2\ \mathrm{cm^3\ K\ mol^{-1}}$ and a Weiss temperature of $\theta = -22.3 \pm 0.3$ K. This Weiss temperature is virtually identical to that found for the earlier $\{\mathrm{Mo_{72}Fe_{30}}\}$ cluster,[9a] which shows that the magnetic properties of the cluster have not been affected by the changed synthetic procedure. This is confirmed by the magnetization curve which is virtually linear as a function of field. The numerical derivative shows the typical minimum at about 5.5 T, which was shown to be due to competing spin configurations.[9b] Also the low-temperature field-dependence of the magnetization (0–24 Tesla, 0.42 K) of **1** is identical to that of the previously described $\{\mathrm{Mo_{72}Fe_{30}}\}$[9a,b] (see Acknowledgements).

It has been demonstrated that it is possible to “use” pentagonal “building units” which play, geometrically speaking, in spherical molecules the same role as in spherical constructions in general. In the present context they can be used as a glue for trapping 30 magnetic centers M (*e.g.* M = $\mathrm{V^{IV}O^{2+}}$, $\mathrm{Fe^{III}}$) to form the icosidodecahedron $\{\mathrm{M}\}_{30}$. As the resulting frustrated magnetic systems share topological features with the highly celebrated Kagomé lattice[14] (see Fig. 1) these types of studies are expected to provide a deeper understanding of basic aspects of geometrical/magnetic frustration and the related role of the spin sizes of the metal centers.[4a,14] Correspondingly, the method will be extended by us to other magnetic centers in the future, too. The most important aspect of the work refers to the possibility to encapsulate quantum dots like polyoxometalates existing with different electron distributions in host systems. In this context it is important to note that there seems to be a general tendency for practically neutral spherical molybdenum oxide based capsules—but positively charged without the organic ligands—to have a high affinity for the (integration of) polyoxomolybdates.[15] Interestingly, metal oxide cluster encapsulation is also possible in virus cavities (see: Viral Cage Directed Synthesis of Nanoclusters, chapter 10.9, p. 482 in ref. 16).

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Notes and references

† In this context it is worthwhile to mention that different linkers in the Keplerates with approximately icosahedral symmetry span (distorted) Archimedean solids:[3b,6] in the case of dinuclear metal linkers a (distorted) truncated icosahedron, $\{M_2\}_{30}$, and in the case of mononuclear linkers the unique icosidodecahedron $\{M\}_{30}$ with a highly "isotropic" surface (of importance for the magnetic behavior) due to the fact that all edges and dihedral angles are equal[7] (Fig. 1). In the $\{M\}_{30}$ situation, a network of corner-shared triangles exists on the sphere surface (Fig. 1), which can cause in special spin situations like in the $\{Fe^{III}\}_{30}$ case a unique magnetic frustration.[8,9a–c] These $\{Fe^{III}\}_{30}$ type clusters show furthermore a novel type of assembly process in solution.[9d]

‡ *Synthesis of* **1**: $Na_4[\{Mo_6O_{19}\}\subset\{Mo^{VI}{}_{72}Fe^{III}{}_{30}O_{252}(CH_3COO)_{20}(H_2O)_{92}\}]\cdot$*ca.* 120 H_2O ≡ $Na_4\cdot$**1a**$\cdot$*ca.* 120 H_2O. 0.5 g $FeCl_3\cdot 6H_2O$ (1.85 mmol) were added to a solution of 3.0 g $Na_2MoO_4\cdot 2H_2O$ (12.4 mmol) in a mixture of 25 mL H_2O and 15 mL CH_3COOH 100%. After acidification with 12.5 mL 1 M hydrochloric acid the solution (pH ≈ 2) was heated to 90–95 °C, stirred briefly and cooled to room temperature while after 6 h the yellow microcrystalline precipitate was filtered off. The yellow crystals of the pure compound precipitated from the filtrate after 5 days, were filtered off, washed with cold water and dried in air. Yield: 0.24 g (22% based on Fe). (The microcrystalline precipitate has approximately the same IR and Raman spectra but is much less soluble; it should contain the $\{Mo_{72}Fe_{30}\}$ type capsules linked in a non-ordered way, furthermore with different amounts of acetate ligands and without the hexamolybdate guest.)

Elemental analysis (%) calc.: Mo 40.26, C 2.58, H 2.62, Na 0.48%. Found: Mo 39.0, C 2.6, H 2.8, Na 0.5%. (The (not given) ESCA data obtained from Prof. M. Neumann (Osnabrück) correspond to the theoretical Mo to Fe ratio. There is a small error limit with respect to the charge/number of acetates.)

Characteristic IR bands: ν/cm^{-1} (KBr pellet): 1622m ($\delta(H_2O)$), 1541m ($\nu_{as}(COO)$), 1421w ($\nu_s(COO)$), 955m ($\nu(Mo{=}O)$), 854m, 778s, 627m, 573s, 445m.

Characteristic Raman bands: ν/cm^{-1} (solid state, KBr dilution, λ_e = 1064 nm): 950s, 908w ($\nu(Mo{=}O)$), 838s, 518m, 451w, 370m, 238 w-m.

§ *Crystal data for* **1**: $C_{40}H_{484}Fe_{30}Mo_{78}Na_4O_{523}$, M = 18587.05 g mol^{-1}, rhombohedral, space group $R\bar{3}$, a = 54.607(2), c = 60.034(3) Å, V = 155033(10) $Å^3$, Z = 12, ρ = 2.389 g cm^{-3}, μ = 2.763 mm^{-1}, F (000) = 108096, crystal size = 0.25 × 0.25 × 0.20 mm. Crystals of **1** were removed from the mother liquor and immediately cooled to 188(2) K on a Bruker AXS SMART diffractometer (three circle goniometer with 1 K CCD detector, Mo-Kα radiation, graphite monochromator; hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435 and 230 frames (Φ = 0, 88 and 180°) at a detector distance of 5.00 cm). A total of 173057 reflections ($1.59 < \Theta < 22.49°$) were collected of which 43683 reflections were unique (R(int) = 0.0795). An empirical absorption correction using equivalent reflections was performed with the program SADABS-2.10. The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to R = 0. 0975 for 23116 reflections with $I > 2\sigma(I)$, R = 0.1851 for all reflections; max./min. residual electron density 1.29 and −0.85 e $Å^{-3}$ (SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen, 1997, 2003; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, 2001). CCDC 298078. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604977j. The $\{Mo_6\}$ type clusters are disordered over six positions while the sum of the occupancy factors for each Mo atom is, as expected, one. The situation is the same for the sites $\bar{1}$ and $\bar{3}$.

¶ Generally speaking, molybdenum oxide based building units—present as virtual ingredients in a dynamic library in aqueous solution—display a unique type of flexibility and can adjust their size and shape depending on the boundary conditions. This flexibility is especially nicely proven by the reaction of a solution of $[PMo_{12}O_{40}]^{3-}$ with Fe^{III} leading primarily to a fragmentation of the Keggin ions while the formed fragments and the Fe^{III} ions build up the spherical system $\{(Mo^{VI})Mo^{VI}{}_5\}_{12}\{Fe^{III}\}_{30}$ with a non-decomposed Keggin ion encapsulated (A. Müller, S. K. Das, H. Bögge, M. Schmidtmann, A. Botar and A. Patrut, *Chem. Commun.*, 2001, 657). This means in that case the intact rather stable Keggin ion is an educt, in contrast to the present investigation where the hexamolybdate is a "reaction product" (the formation of which again proves the flexibility of the system). In the former case the number of acetate ligands inside the cavity is smaller than in **1a**, because the Keggin ion is larger than the hexamolybdate.

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