

Generation of cluster capsules (I_h) from decomposition products of a smaller cluster (Keggin- T_d) while surviving ones get encapsulated: species with core-shell topology formed by a fundamental symmetry-driven reaction

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A novel and fundamental reaction system of matter following a type of 'supramolecular Darwinism' leads to the formation of giant spherical nano-sized cluster capsules as kinetically controlled destination having the highest possible symmetry (I_h) and formed directly from the decomposition products of the well known but less symmetrical Keggin anions (T_d) in aqueous medium in the presence of Fe^{III} —acting as a type of environmental influence—under conditions where Keggin anions are known to be extremely stable; remarkably the remaining non-decomposed Keggin anions finally get (non-covalently) encapsulated protected by the formed spherical capsules of the new supramolecular compound $[PMo_{12}O_{40} \subset \{(Mo^{VI})Mo^{VI}_5\}_{12} Fe^{III}_{30}O_{252} \cdot (H_2O)_{102}(MeCO_2)_{15}] \cdot xH_2O$ ($x \approx 120$).

The fact that self-assembly processes—based on simple (mainly highly symmetrical) building blocks or preorganized units—preferentially lead to higher symmetrical reaction products is an interesting phenomenon, *e.g.* in cluster chemistry which has not been explored in detail until now. Examples are the well known Keggin type anions, like $[PMo_{12}O_{40}]^{3-}$ (T_d) formed from molybdate and phosphate, models for the Fe_4S_4 type ferredoxin, like $[Fe_4S_4(SH)_4]^{2-}$ (T_d), the molybdenum-oxide-based giant wheels ($\approx D_{7d}$) as well as spheres (I_h). Therefore, the question arises as to why highest (possible) symmetrical species are the targets, and furthermore, whether we can elucidate this phenomenon or solve the problem by means of a model reaction system. In a novel fundamental type of reaction, which can be related to a type of 'Supramolecular Darwinism' (see below), it can be shown that tetrahedral Keggin anions 'lose—at least partly—the competition' with higher symmetrical, *i.e.* icosahedral capsule type species as kinetic target in aqueous solution even under conditions where they are quantitatively formed. The formation of the latter occurs at the expense of the former.

In the presence of Fe^{III} ($FeCl_3 \cdot 6H_2O$), *i.e.* formally in a kind of 'environmental attack', the Keggin anions¹ decompose in solution with the formation of the pentagonal $\{(Mo^{VI})Mo^{VI}_5O_{21}\}$ type building blocks which get linked by $\{Fe^{III}(H_2O)_2\}^{3+}$ groups. This leads finally to the formation of novel composites consisting of discrete icosahedral nanocluster capsules with the encapsulated Keggin anions $[PMo_{12}O_{40}]^{3-}$, which are abundant in the new compound $[PMo_{12}O_{40} \subset \{(Mo^{VI})Mo^{VI}_5\}_{12} Fe^{III}_{30}O_{252}(H_2O)_{102}(MeCO_2)_{15}] \cdot xH_2O$ **1** ($x \approx 120$).[†] Upon drying, **1** shows a fast solid-state reaction with the consequence that the composites **1a** get covalently linked leading to the formation of $\{PMo_{12}O_{40} \subset H_4[(Mo^{VI})Mo^{VI}_5]_{12} Fe^{III}_{30}O_{254}(H_2O)_{98}(MeCO_2)_{15}\} \cdot xH_2O$ **2** ($x \approx 60$), see refs. 2–4. This condensation process is only important in the present context as the relevant dry (!) product can be more easily structurally characterized compared to **1**. Using Fe^{II} instead of Fe^{III} the related compounds $[H_yPMo_{12}O_{40} \subset \{(Mo^{VI})Mo^{VI}_5\}_{12} Fe^{III}_{30}O_{252}(H_2O)_{102}(MeCO_2)_{15}] \cdot xH_2O$ **3** ($x \approx 120$) and $[H_yPMo_{12}O_{40} \subset H_4\{(Mo^{VI})Mo^{VI}_5\}_{12} Fe^{III}_{30}O_{254}(H_2O)_{98}(MeCO_2)_{15}\} \cdot xH_2O$ **4** ($x \approx 60$) are obtained which contain the one- or two-

electron reduced Keggin anions $[H_yPMo_{12}O_{40}]^{3-}$.[‡] Compound **4** can be obtained not only by the present new fundamental type of reaction but also in a facile synthesis starting from the simple ingredients phosphate, molybdate, acetate, and Fe^{II} .²

Compound **2** with the cross-linked composites having core-shell topology and partly also **1**, *i.e.* the 'corresponding' non-dried crystals, were characterized by elemental analyses, thermogravimetry (to determine the crystal water content), single-crystal X-ray structure analysis§ [including the calculation of bond valence sums in order to distinguish between (terminal) O and OH_2 ligands] and spectroscopic methods (IR, Raman, UV–VIS, NIR) as well as magnetic measurements.¶ Whereas the complete structural characterization of **4**, obtained with another reaction, has already been reported (see ref. 2), the corresponding non-dried new compound **3** was characterized, like **1**, spectroscopically and by its crystal data (see below).|| Compounds **1** and **3** with discrete cluster units (space group $P2_1/n$) as well as **2** and **4** with their corresponding layer structures (space group $Cmca$) are isostructural and have, as expected, practically the same unit cell dimensions. The crystal structures of **2** and **4** show the icosahedral capsule/nucleus type composites, abundant in **1** and **3**, cross-linked to 2D type assemblies *via* the formation of four $Fe^{III}-O-Fe^{III}$ bonds per unit (see footnote ||). Whereas the capsules of **1** and **2** have, as mentioned above, non-covalently bonded classical non-reduced Keggin anions $[PMo_{12}O_{40}]^{3-}$ (Fig. 1) those of **3** and **4** have the reduced Keggin anions $[H_yPMo_{12}O_{40}]^{3-}$ encapsulated. The acetate ligands, which are highly disordered, are located inside the spheres and coordinate as bidentate ligands bridging Mo and Fe sites. As the non-dried compounds **1** and **3** with the discrete cluster composites and different electron populations have, as expected, the same space group and practically the same unit cell dimensions as the compound $\{[(Mo^{VI})Mo^{VI}_5]_{12} Fe^{III}_{30}O_{252}(MeCO_2)_{10}\{Mo_2O_7(H_2O)\}\{H_2Mo_2O_8(H_2O)\}_3(H_2O)_{91}\} \cdot xH_2O$ **5** ($x \approx 140$) containing the same $\{(Mo)Mo_5O_{21}\}_{12} Fe_{30}$ cluster capsules without Keggin ions, and for which the complete single crystal X-ray analysis has been performed.⁸ **1** and **3** can easily be identified from the relevant crystal data.§ (Note that in the present case the non-dried crystals of **1** and **3** do not diffract sufficiently.)

The important result of this investigation is that the Keggin ions are not stable in the presence of Fe^{III} (or Fe^{II} and air) as they decompose, while $\{(Mo^{VI})Mo^{VI}_5O_{21}\}$ type pentagons are formed which are subsequently linked by $\{Fe^{III}(H_2O)_2\}^{3+}$ groups. The remarkable fact is that the remaining non-decomposed Keggin ions (reduced or not reduced) appear in the reaction product encapsulated. Interestingly, the Keggin ions even seem to accelerate the formation of their cage around them as templates. This models the observation that assembly processes of simple linkable units lead preferably to highly symmetrical species. The process can be correlated with a general symmetry formalism or symmetry-evolution principle for a quasi isolated (!) system; in this respect, the second law of thermodynamics and the symmetry-evolution principle are isomorphic (see ref. 6). The degree of symmetry cannot decrease as the system evolves, but either remains constant or

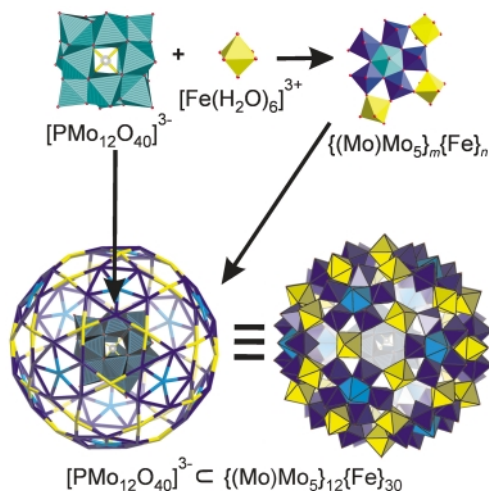


Fig. 1 Reaction scheme showing the decomposition of a part of the Keggin anions (top left, polyhedral representation) in the presence of Fe^{III} forming thereby fragments of the type $\{(Mo)Mo_5\}_m\{Fe\}_n$ which function as building blocks (top right, polyhedral representation) and leading finally to the formation of the $\{(Mo)Mo_5\}_{12}\{Fe\}_{30}$ type cage (bottom left with wire-frame representation of the capsule's metal atoms in blue and yellow (Fe part), and bottom right with polyhedral representation of the capsule), which subsequently encapsulates the remaining non-decomposed Keggin anions (polyhedral representation) to form the supramolecular species with core-shell topology: guest \subset (pentagon)₁₂(linker)₃₀ \equiv $[PMo_{12}O_{40}]^{3-} \subset \{(Mo)Mo_5\}_{12}\{Fe\}_{30}$ (colour code MoO₆/7 polyhedra: blue/turquoise, FeO₆ octahedra: yellow).

increases. (The effect is at least as symmetric as the cause.) This corresponds to the fact that causal relations exist between states of cause subsystems and states of effect subsystems, while states of the subsystems are determined by the states of the whole system. In other words, equivalent initial states must evolve into equivalent final states (see also ref. 5).

To express the related general aspect: two competing molecular systems model a type of 'Supramolecular Darwinism' principle.** Spherical shell type molecules with highest possible (icosahedral) symmetry are for symmetry reasons the kinetically controlled destination and best adapted to the environment.

Notes and references

† *Syntheses*: **1**: to an aqueous solution (60 mL) of $H_3[PMo_{12}O_{40}] \cdot xH_2O$ (4.0 g, 2.2 mmol), $MeCO_2H$ (15 mL, 100%) and $FeCl_3 \cdot 6H_2O$ (2.5 g, 9.2 mmol) 20 mL of NaOH solution (1 M) was added. The resulting clear brownish solution was kept in an open beaker for one week at 20 °C. Yellow plates of **1** precipitated during this time.

2: The wet crystals of **1** were filtered off, washed with water and kept at room temp. The condensation reaction was complete after ca. 1 h. Yield: 1.0 g (17.5% based on the starting Keggin type compound). (Note: single crystals suitable for X-ray structure analysis were obtained under more dilute conditions.)

3: To an aqueous solution (25 mL) of $H_3[PMo_{12}O_{40}] \cdot xH_2O$ (5.0 g, 2.7 mmol) and $MeCO_2H$ (10 mL, 100%), $FeCl_2 \cdot 4H_2O$ (1.0 g, 5 mmol) was added (colour change to blue-green). 15 mL of NaOH solution (1 M) was subsequently added and the resulting clear solution was kept in an open flask for 2 weeks at 20 °C while greenish plates precipitated.

4: The wet crystals of **3** were filtered off, washed with water and kept at room temp. for the solid-state condensation reaction. Yield: 0.25 g (3.5% based on the starting Keggin type compound).

‡ For **3** or **4** it is difficult to distinguish between a one- and two-electron reduced system (even to position the electrons) which is mainly due to the presence of a large number (12 + 102) of metal atoms in connection with apparent analytical problems and due to disorder phenomena.

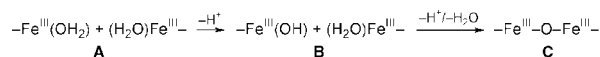
§ *Unit cell parameters for 1*: monoclinic, space group $P2_1/n$, $a = 26.548(4)$, $b = 34.737(9)$, $c = 28.910(4)$ Å, $\beta = 97.194(3)^\circ$, $U = 26.452(30)$ Å³.

Crystal data for 2: $C_{30}H_{365}Fe_{30}Mo_{84}O_{482}P$, $M = 18\,205.65$, orthorhombic, space group $Cmca$, $a = 36.847(1)$, $b = 34.936(1)$, $c = 34.859(1)$ Å, $U = 44\,874(3)$ Å³, $Z = 4$, $D_c = 2.695$ g cm⁻³, $\mu = 3.328$ mm⁻¹, $F(000) = 34\,896$, crystal size = $0.22 \times 0.12 \times 0.02$ mm. Dry crystals of **2** were measured at 183(2) K on a Bruker AXS SMART diffractometer (Mo-K α , graphite monochromator). A total of 113 792 (1.71 < θ < 25.0°) reflections were collected of which 20 083 unique reflections ($R_{int} = 0.155$) were used. The structure was solved using the program SHELXS-97 and refined using the program SHELXL-97 to $R = 0.073$ for 10 583 reflections with $I > 2\sigma(I)$. Several crystal water molecules could not be located due to their disorder. For the encapsulated Keggin ion only the central P atom and (partly disordered) Mo atoms (but not the O atoms because of the disorder) could be detected for which the occupancy factors, however, add up to 12. These data together with the analysis, vibrational spectrum and the employed pH support the presence of a complete Keggin anion rather than a lacunary type one. Due to the disorder and related basic analytical problems in connection with the error limit of the number of acetate ligands, differently protonated Keggin ions cannot be completely excluded. CCDC 153129. See <http://www.rsc.org/suppdata/cc/b0/b009518b/> for crystallographic data in .cif or other electronic format.

Unit cell parameters for 3: monoclinic, space group $P2_1/n$, $a = 26.388(8)$, $b = 34.698(3)$, $c = 28.852(1)$ Å, $\beta = 96.958(4)^\circ$; $U = 26.224(36)$ Å³.

¶ *Selected physical and spectroscopic data for 2*: IR (KBr pellet) (ν/cm^{-1}): 1618m $\{\delta(H_2O)\}$, 1535m $\{\nu_{as}(CO_2)\}$, 1422m $\{\nu_s(CO_2)\}$, 1068w $\{\nu_{as}(PO)\}$, 960m $\{\nu(Mo=O)\}$, 775s, 623s, 567m, 433w. Raman (KBr dilution, $\lambda_c = 1064$ nm) (ν/cm^{-1}): 950s $\{\nu(Mo=O)\}$, 836w, 512w, 371w, 241w. UV-VIS (solid state reflectance spectrum) λ_{max}/nm : ca. 285 (sh), ca. 370 (br). The magnetic susceptibility data are identical to those of **4** (see ref. 2).

|| The crystals have to be taken from the corresponding mother-liquors and immediately investigated, because **2** and **4** with the characteristic layer structures are formed very fast even at room temperature due to a classical inorganic condensation process (see refs. 3 and 4). In the present case this corresponds to the following process (in schematic representation) which



takes place after the capsules come closer together due to partial loss of crystal water. The related steps can be observed easily through the shrinking of the unit cell volumes. **A** denotes here the discrete composites and **C** the final product. Under the present mild conditions the content of each capsule remains of course unchanged.

** The term Darwinism is not only used in the literature in the sense of Darwin's *The Origin of Species by Means of Natural Selection*, but also for non-biological systems under (dissipative) stationary non-equilibrium conditions: (H. Haken uses it in his synergetics approach: H. Haken, *Synergetics*, Springer, Berlin, 1983; see especially: H. Haken, *Erfolgsgeschichte der Natur—Synergetik: Die Lehre vom Zusammenwirken*, Rowohlt, Reinbek, Hamburg, 1995, pp. 91, 94, 289 and H. Haken and A. Wunderlin, *Die Selbststrukturierung der Materie*, Vieweg, Braunschweig, 1991, p. 448 and additionally E. Ben-Jakob and H. Levine, *Nature*, 2001, **409**, 985 [*'Patterning via competition'*]). In classical chemical reactions in general, a 'competition' between (molecular) species can be addressed. However, this is hardly detectable, in contrast to the present case where the different (kinetic) stabilities of two species can easily be referred to / explained by their different symmetry.

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