Water in Polyoxometalate Capsules

Drawing Small Cations into Highly Charged Porous Nanocontainers Reveals "Water" Assembly and Related Interaction Problems**

Achim Müller, Erich Krickemeyer, Hartmut Bögge, Marc Schmidtmann, Bogdan Botar, and Marina O. Talismanova*

Dedicated to Professor Michael T. Pope on the occasion of his 70th birthday

Herein we report a series of easily accessible, soluble, spherical, porous nanocapsules with internal surfaces that are tunable with respect to charge and hydrophilicity/phobicity. These systems are based on a very robust fundamental cluster skeleton $\{(\text{pent})_{12}(\text{link})_{30}\} = \{(\text{Mo})\text{Mo}_5\}_{12}\{\text{link}\}_{30}$[1,2] where pent is the basic pentagonal $\{(\text{Mo})\text{Mo}_5\}$ type of unit and link refers to linker groups. This general formula describes, for example, the new compound **1** where

$$(\text{NH}_4)_{72-n}\,[(\text{H}_2\text{O})_{81-n} + (\text{NH}_4)_n \subset \{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{SO}_4)\}_{30}]\cdot \approx 200\,\text{H}_2\text{O} \quad \mathbf{1}$$

the cluster anion has an extremely high negative charge (an increase from 42− in the educt **2a** (that is, the anion of compound **2**) to 72− without counting encapsulations), and shows a well-constructed hydrophilic internal surface.

$$(\text{NH}_4)_{42}\,[\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{CH}_3\text{COO})\}_{30}]\cdot \approx 300\,\text{H}_2\text{O}\cdot \approx 10\,\text{CH}_3\text{COONH}_4 \quad \mathbf{2}^{[2b,7]}$$

In this type of capsule, for the first time several well-defined water molecule assemblies can be observed (for general aspects see refs. [3,4]) some of which agree with those obtained from molecular-dynamics calculations for liquid water.[4b] As the *discrete* assemblies contain the $\{\text{H}_2\text{O}\}_{20}$ dodecahedron with 30 hydrogen bonds, this offers the chance to get a deeper understanding of the structure of crystalline clathrate hydrates, also in connection with their role in essential industrial processes,[5] and to study the hydrophobic effect (Figure 1). Furthermore, because the nanocapsules are soluble, stable, porous, and manipulatable several other options for their use in nanotechnology are conceivable.[6]

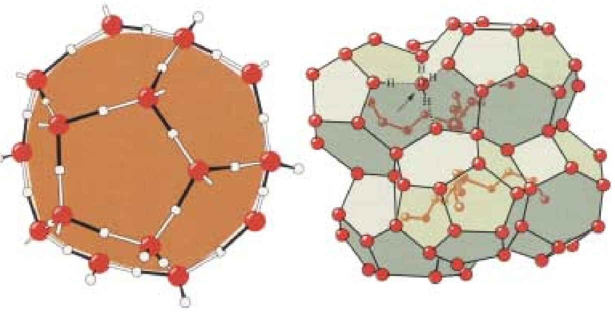

Figure 1. Two examples of H_2O assemblies/cages: The important $\{\text{H}_2\text{O}\}_{20}$ dodecahedron,[5] which is also found in the discrete water assemblies in the cluster cavities described here (left), and a related enlarged cavity (with dodecahedra being involved) from which water is excluded by the presence of an encapsulated nonpolar molecule (right), which demonstrates the fundamental hydrophobic effect also present in some of the clusters discussed here (reproduced with permission from D. Voet, J. G. Voet, *Biochemistry*, 2nd ed., Wiley, New York, **1995**).

Compound **1** was obtained by the reaction of an aqueous solution of **2**[2b,7] with $(\text{NH}_4)_2\text{SO}_4$ at pH ≈ 1 thereby introducing $30\,\text{SO}_4^{\,2-}$ ligands which increases the negative cluster charge by 30 units, and therefore its affinity to cation uptake. Compound **3** was prepared from **2** by replacing not all of the acetate ligands and thereby maintaining a hydrophobic part in contrast to **1**. Compound **4** was prepared in a similar way to **1**, but such that an increase in the negative cluster charge is achieved while allowing a well-defined number of Na^+ ions to become encapsulated. This was done in the presence of another larger cation that could not be encapsulated, with the ability to influence the uptake. Compounds **5**[8] and **6**[9] contain the novel structurally well-defined encapsulated H_2O clusters, $\{\text{H}_2\text{O}\}_{40}$ and $\{\text{H}_2\text{O}\}_{80}$, which were not identified previously,[8,9] while **7**[10] is mentioned here to facilitate comparisons of encapsulations. Clusters **1**, **3**, and **4** were characterized by elemental analysis, thermoanalysis, mass spectrometry, potentiometric titrations (to determine the number of Mo^{V} centers), IR spectroscopy, and single-crystal X-ray structure analysis[11] including bond-valence-sum (BVS) calculations.[12]

$$(\text{NH}_4)_{60}[\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{SO}_4)\}_{18}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{CH}_3\text{COO})\}_{12}]\cdot \approx 300\,\text{H}_2\text{O} \quad \mathbf{3}$$

$$[(\text{CH}_3)_2\text{NH}_2]_{52}\,\text{Na}_8[\text{Na}_6 + (\text{H}_2\text{O})_n \subset \{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{SO}_4)\}_{24}\{\text{Mo}^{\text{V}}_2\text{O}_4(\text{CH}_3\text{COO})\}_6]\cdot \approx (250-n)\text{H}_2\text{O} \quad \mathbf{4}$$

$$[(\text{H}_2\text{O})_{40+1} \subset \{(\text{Mo})\text{Mo}_5\text{O}_{21}(\text{H}_2\text{O})_4\text{CH}_3\text{COO}\}_{12}\{\text{Mo}^{\text{V}}\text{O}(\text{H}_2\text{O})\}_{30}]\cdot \approx 110\,\text{H}_2\text{O} \quad \mathbf{5}^{[8]}$$

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[*] Prof. Dr. A. Müller, E. Krickemeyer, Dr. H. Bögge, M. Schmidtmann, Dr. B. Botar, M. O. Talismanova
Lehrstuhl für Anorganische Chemie I
Fakultät für Chemie der Universität
Postfach 100131, 33501 Bielefeld (Germany)
Fax: (+49) 521-106-6003
E-mail: a.mueller@uni-bielefeld.de

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$$(NH_4)_{42}[(H_2O)_{80} \subset \{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}_2O_4(H_2PO_2)\}_{30}] \cdot \approx 220\,H_2O \quad \mathbf{6}^{[9]}$$

$$[(NH_2)_3C^+]_{32}[(H_2O)_{100} + \{(NH_2)_3C^+\}_{20} \subset \{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}_2O_4(SO_4)\}_{10}\{Mo^{V}_2O_4(H_2PO_2)\}_{20}] \cdot \approx 100\,H_2O \quad \mathbf{7}^{[10]}$$

The cluster anions of **1**, **3**, and **4** (**1a**, **3a**, and **4a**) are based on a robust $\{(pent)_{12}(link)_{30}\}$ type skeleton with 20 nanosized pores, and contain different encapsulated species, including electrolytes, which influence the water structure. The spherical capsules[2,13,14] have 30 bidentate ligands coordinated to the $30\{Mo^{V}_2O_4\}^{2+}$ groups which link the 12 basic structure-determining pentagonal $\{(Mo)Mo_5\}$ units each of which has six H_2O ligands. In **1a**, there is an internal shell built up by 132 hydrophilic components, that is, O atoms and H_2O ligands. This cluster, with open pores, has a two-shell water structure with integrated NH_4^+ ions inside the capsule (Figure 2). The first shell, that is, the central dodecahedron, is similar in shape to the "normal" $(H_2O)_{20}$ dodecahedron (see Figure 1)—as in **7a** (O···O: ≈2.85 Å)[10]—but "expanded" (O/N···O/N: ≈3.48 Å) because of the presence of two NH_4^+ ions, one in the center and one at the shell, or alternatively, both at the shell, replacing water molecules in both positions.[15,16a] Thermogravimetry and elemental analyses studies carried out on samples obtained at different temperatures, show that two NH_3 molecules are released together with encapsulated water in a well-defined step at approximately 410 °C while this high temperature indicates that the NH_3 is from the decomposition of encapsulated NH_4^+ ions. This situation is supported by a mass spectrometry study measuring the 17/18 mass ratio up to 450 °C.[16b] Remarkably, this type of cage structure is also postulated for related gas-phase species.[15,17] The positively charged and enlarged first-shell central dodecahedron forms strong hydrogen bonds with the $12\,X_5$ ($X = H_2O$ or NH_4^+) pentagons (O/N···O/N: ca. 2.97 Å) forming the second shell. This second shell which can also be formally considered to be a strongly distorted rhombicosidodecahedron, is practically identical to the third shell of **7a**,[10] and is built up mostly by water molecules. The number of possible NH_3 molecules released well below 400 °C arising from encapsulated NH_4^+ ions cannot be determined as the lattice NH_4^+ ions decompose at similar temperatures. The mentioned $12 \times 5 = 60$ members of the second shell form hydrogen bonds with the 30×2 terminal sulfate ligand O atoms (O/N···O: ca. 3.06 Å).

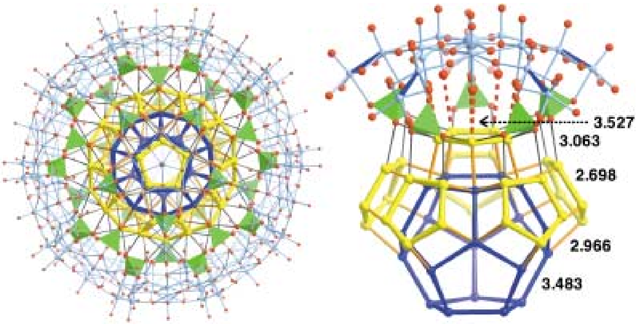

Figure 2. The structure of the spherical cluster **1a** showing the encapsulated water and electrolyte (left). A related segment (right) together with some representative average interatomic distances [Å] is also shown (Mo atoms light blue; O red; SO_4^{2-} green tetrahedra; inner $(H_2O)_{20}$ shell blue; outer $(H_2O)_{60}$ shell yellow).

When small Na^+ cations with rather high charge density are present in solution, a different situation leading to **4a** is observed (Figure 3): The Na^+ ions, which contrary to NH_4^+, can clearly be identified by single-crystal structure analysis, are encapsulated differently than the NH_4^+ ions in **1a** but do not allow the formation of a structurally well-defined water cluster (this effect is even more pronounced in case of Li^+ ions). Important is that the uptake of Na^+ ions can be drastically increased if Na_2SO_4 is available in higher concentration and if the cluster charge is increased to 72− by replacing all acetate ligands (note that the Na^+ positions are under occupied, that is, there are more pores than Na^+ ions, see molecular formula). Interestingly, a comparable situation regarding the relative role of Na^+ and NH_4^+ ions was detected by mass spectrometry studies on related electrolyte solutions.[18,19] The Na^+ ions in **4a** are "coordinated" to three H_2O molecules and to three oxygen atoms of the sulfate ligands thereby nicely modeling ion-pair formation known for (concentrated) aqueous electrolyte solutions. If only a smaller number of the acetate ligands of **2a** are replaced, which leads

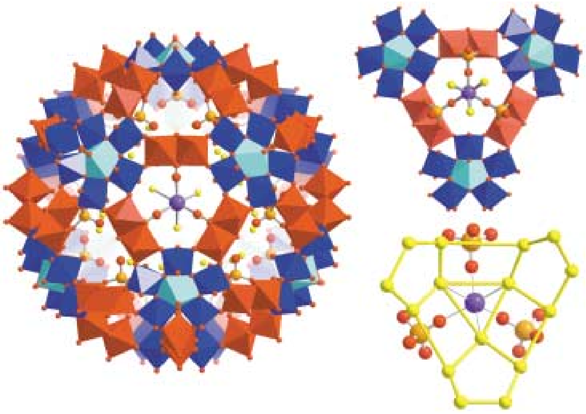

Figure 3. Left: structure of **4a** in polyhedral representation viewed along a C_3 symmetry axis and highlighting the cluster surface nicely showing four of the 20 nanoscale pores (see also ref. [10a]). Only one encapsulated Na^+ ion (violet), which is coordinated to sulfate groups (S orange; O red) and water oxygen atoms (yellow) is shown, the others are omitted for clarity. A segment of the structure corresponding to the pore area but now viewed from the cluster center is shown in two representations. Top right: an encapsulated Na^+ ion "coordinated" to three SO_4^{2-} ligands and three H_2O molecules, with this $Na(SO_4)_3(H_2O)_3$ group shown together with three $\{(Mo)Mo_5\}$ (blue polyhedra and central turquoise pentagonal bipyramid) and three $\{Mo_2\}$ building units (red polyhedra). Bottom right: the same $Na(SO_4)_3(H_2O)_3$ group without the Mo-based building units but shown in relation to a segment of the incomplete H_2O shell with the three coordinating H_2O molecules in the center (for details of under occupation, see molecular formula).

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to **3a**, the situation is again different: The hydrophobic effect of the acetate ligands dominates and no water assembly, of the kind found in **1a**, is observed.

The introduction of 30 $H_2PO_2^-$ ligands—instead of the SO_4^{2-} ions as in **6a**,[9] that is, with 60 H instead of 60 O atoms—offers the possibility to generate an unusual incompletely covered (perforated) hydrophilic internal surface (a special aspect not considered in the previously reported compound[9]). This leads to a situation where 20 H_2O molecules can be "fixed" in a well-defined way in 20 trigonal holes built up by the 30 PH_2 groups (Figure 4 and Figure 5). The 20 trapped H_2O molecules, which do not interact with one another, show strong hydrogen bonds to the next $\{H_2O\}_{60}$ shell spanning a strongly distorted Archimedean solid while creating a novel $(H_2O)_{80}$ cluster (O···O: ca. 2.70 Å).

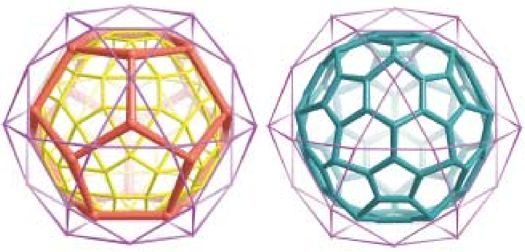

Figure 4. The encapsulated water cluster of **6a**: the inner $(H_2O)_{60}$ shell (yellow) together with the 20 H_2O molecules (red)—embedded in the perforated internal cluster-shell surface (left; see also Figure 5)—forms a novel completely hydrogen-bonded $(H_2O)_{80}$ cluster with an average O···O separation of approximately 2.70 Å (turquoise; right). Shown additionally in both cases: the shell envelope spanned by the 30 $P(H_2)$ centers (lilac).

Figure 5. Models demonstrating the tuning of the internal shell surfaces of the spherical nanocapsule. Left: closed hydrophilic surface as in **1a**. Middle: hydrophobic surface as in **2a**. Right: perforated hydrophilic surface spanned by 3×20 H(P) atoms forming 20 holes as in **6a**, in which 20 H_2O molecules can be trapped (O red; S green; H_2O brown; C black; H yellow; P lilac).

The fundamental procedure outlined here is based on capsule differences regarding 1) size, 2) overall charge, 3) (related) pore situations (larger, smaller, open or shut,[20a] and with different electron densities), 4) structure of the internal surfaces (hydrophilic, hydrophobic, covered or not covered, different functionalities). Referring to (1): As the cluster capsules **1a**–**7a**, except **5a**, have the same type of binuclear linker between the pentagonal units, that is, $\{Mo^V{}_2O_4\}^{2+}$ units,[2,13,14] they are of equal size, while the capsule of **5a** is smaller because of the mononuclear spacer $\{OMo^VH_2O\}^{3+}$.[8] The size-influence on the encapsulations can be nicely shown by comparing **5a** (shell sequence: dodecahedron, dodecahedron) with **7a**[10] (shell sequence: dodecahedron, dodecahedron, rhombicosidodecahedron): Both show the same type of water assembly, however, in the smaller cluster capsule **5a** the third (largest) outer shell ($\{H_2O\}_{60}$) is missing (Figure 6). The formation of well-defined water clusters is mainly because the pores are either nearly closed (in **5a**) or closed (in **7a**). In addition, as a result of the relatively low cluster charge, no disturbing cations and internal surfaces are present. The acetate ligands, besides the ((12×6)−12) water ligands at the pentagons in **5a**, do not influence the assembly because of their small number, disorder, and positions. Referring to (2): The encapsulation of cations, that is, NH_4^+ in **1a** and Na^+ in **4a**, proves the influence of the (high) overall negative charge on cation uptake. Referring to (3): It turns out that the pores can be closed very easily if related shape- and size-complementarity is fulfilled, as in case of **7a**.[10] In clusters with high negative charges, such as **1a** and **4a**, smaller cations such as NH_4^+ and Na^+ will get drawn into the cavity. Referring to (4): The internal surface has an important influence on the structure of the encapsulated units. If the surface is hydrophilic, for example, similar to that of a (possible) liquid water segment as in **1a**—with 132 components, that is, 60 O sulfate atoms and 72 H_2O ligands of the {(Mo)Mo$_5$} type pentagons—or **6a**—with 60 $PO_2H_2^-$ H atoms and also the 72 H_2O ligands at the pentagons and with no structure-destroying cations, such as Na^+ or Li^+, present—we find very well-defined symmetrical water clusters encapsulated (Figures 2, 5, 6). This phenomenon is especially supported by closed pores as in **7a**. If the pores are not closed, as in the case of **6a**, the influence of the hydrophilic shell is still present but it is not so pronounced. In contrast to this situation, that is, in case of open pores and a

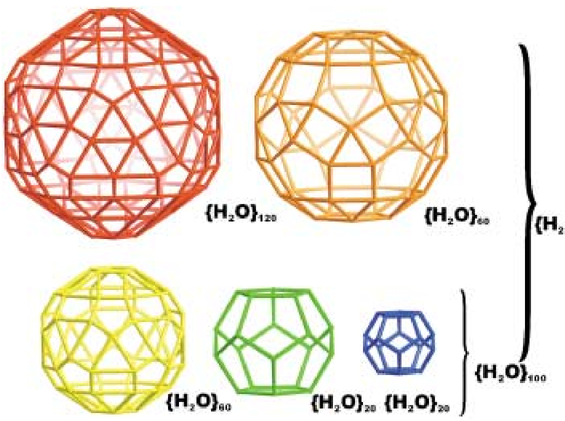

Figure 6. The hierarchy of water shells: $\{H_2O\}_{280}$ as obtained from molecular-dynamics calculations for liquid water[4b] and corresponding to a combination of all five properly connected shells shown. $\{H_2O\}_{100}$ is based on the three shells of **7a** (shown in the bottom row), and $\{H_2O\}_{40}$ corresponds to the two different-sized $\{H_2O\}_{20}$ dodecahedra of **5a** shown in green and blue. Thus the $\{H_2O\}_{100}$ cluster represents the center of $\{H_2O\}_{280}$.

rather large number of hydrophobic acetate ligands located at crucial structure-influencing positions, as in **3a**, the encapsulated water cluster is disordered, as is that of **2a** with only acetate ligands. Remarkably, the large number of hydrophobic ligands of **2a** leads to an unusual type of encapsulated water assembly that a very dense packing of H_2O molecules results.[20b] Additionally, there is the option also to investigate more complex water assemblies in the nanocontainers and even to generate new clusters therein.[21]

The fundamental route, based on the changeable properties of nanocontainers with their robust skeleton kept intact, provides the possibility to study encapsulated assemblies of molecules under well-defined reproducible conditions. As liquid water has a short-range order, in agreement with a prominent peak at approximately 2.8 Å due to the O–O vector in the X-ray diffraction radial distribution curve showing approximately four nearest oxygen neighbors, a so-called tetrahedrality concept for water was developed[4a] with the intention to reflect collective rather than pair behavior. Tetrahedrality, which is observed in **1a**, **4a**, and especially **7a**, is the important intrinsic property of "water" which can, in principle, cause the formation of highly symmetrical icosahedral aggregates under different conditions in different states but with the exclusion of the formation of a crystalline order because of the presence of the five-fold axis. Important in this context is that according to molecular-dynamics calculations[4b] a fluctuating network of water molecules, with localized icosahedral symmetry, is proposed to exist derived from clusters containing, if complete, 280 fully hydrogen-bonded molecules all tetrahedrally coordinated (Figure 6). The $\{H_2O\}_{280}$ assembly contains in its center exactly the same icosahedral $\{H_2O\}_{100}$ cluster found in **7a** (Figure 6). But as in the three-dimensional bulk water, hydrogen-bonds are permanently broken and rebuilt on a picosecond time scale, the consideration of flickering water clusters with approximate icosahedral symmetry as snap-shots is of course an approximation. Furthermore, it is possible to study the influence of ions on water structures in confined spaces, that is, in capsules in general.[22] As it is also possible to generate mostly hydrophobic internal surfaces, novel weakly hydrogen-bonded water assemblies can be studied,[20b] and in this connection also some aspects of the important hydrophobic effect.[23,24] Referring to two general aspects: First, "water" can be studied as a probe to investigate "complex system" behavior in general ("water" is an extremely complex system but less so on a nanoscale), and second, a "new state of inorganic ions" involved in the formation of a novel type of aggregates[25] of interest for "soft-matter physics"[26] can be generated from molybdenum-oxide based clusters with hydrophilic surfaces, even allowing the control of the aggregate size by the change in the cluster charge.[27]

Experimental Section

1: A solution of **2**[7] (5.0 g, 0.17 mmol) and $(NH_4)_2SO_4$ (20.0 g, 151 mmol) in H_2O (400 mL) was adjusted with 16% HCl (about 20 mL) to pH ≈ 1 and heated under reflux for 2 h in an oil bath (ca. 125 °C) without stirring. The hot solution was purified by filtration and the dark-brown filtrate stored at 20 °C in an open 600-mL beaker (wide necked) for crystallization. After one week the dark-brown crystals of **1** were collected by filtration, washed quickly with ice-cold 2-propanol and dried in air. Yield: 4.3 g (89% based on Mo). Characteristic IR bands (KBr pellet): $\tilde{\nu} = 1618$ (m, δ (H_2O)), ≈ 1425 (sh), 1400 (s) ($\delta_{as}(NH_4)$), 1188 (m), 1136 (m), 1038 (w-m, $\tilde{\nu}_{as}(SO_4)$), 970 (s), 935 (w-m, $\tilde{\nu}$ (Mo=O)), 856 (s), 800 (vs), 727 (s), 633 (w-m), 571 cm^{-1} (m-s). Elemental analysis (%) calcd: N 3.64; found: N 3.6.

3: A solution of **2**[7] (5.0 g, 0.17 mmol) and $(NH_4)_2SO_4$ (20.0 g, 151 mmol) in H_2O (400 mL) was adjusted with 1 N HCl to pH ≈ 3 and heated under reflux for 2 h in an oil bath without stirring. The hot solution was purified by filtration and the dark-brown filtrate stored at 20 °C in an open 600-mL beaker (wide necked) for crystallization. After one week the dark-brown crystals of **3** were collected by filtration, washed quickly with ice-cold 2-propanol and dried in air. Yield: 2.6 g (55% based on Mo). Characteristic IR bands (KBr pellet): $\tilde{\nu} = 1618$ (m, δ (H_2O)), 1533 (w-m, $\tilde{\nu}_{as}$(COO)), ca. 1425 (sh), 1402 (s, $\delta_{as}(NH_4)$), 1184 (m), 1132 (m), 1040 (w-m, $\tilde{\nu}_{as}$ (SO_4)), 972 (s), 935 (w-m, $\tilde{\nu}$ (Mo=O)), 858 (s), 800 (vs), 727 (s), 633 (w-m), 571 cm^{-1} (m-s). Elemental analysis (%) calcd for **3**: C 1.07, N 2.96, S 2.14; found: C 1.1, N 3.1, S 2.2.

4: A solution of **2**[7] (2.0 g, 0.068 mmol) and Na_2SO_4 (3.4 g, 23.9 mmol) in H_2O (80 mL) was adjusted with H_2SO_4 (2 mol L^{-1}) to pH ≈ 2.5 and stirred for 24 h at room temperature. After increasing the temperature to 70 °C for 30 min and addition of $(CH_3)_2NH_2Cl$ (1.5 g, 18.4 mmol) the solution was stirred again for 20 min at 70 °C. After filtration of the hot solution the dark-brown filtrate was stored at 20 °C for crystallization. After one day the dark-brown, paralelpipedic crystals of **4** were collected by filtration, washed quickly with ice-cold water and dried in air. Yield: 1.4 g (70% based on Mo). Crystals suitable for single-crystal X-ray structure analysis were obtained by recrystallizing the sample from water. Final yield after recrystallization: ca. 40%. Characteristic IR bands (KBr pellet): $\tilde{\nu} = 1622$ (m, $\delta(H_2O)$), 1545 (w, $\tilde{\nu}_{as}$(COO)), 1464 (w-m, $\delta_{as}(CH_3)$), 1190 (w), 1138 (m-w), 1040 (w, $\tilde{\nu}_{as}(SO_4)$ triplet), 1020 (w, $\tilde{\nu}$ (CN)), 972 (s), 939 (m, $\tilde{\nu}$ (Mo=O)), 860 (s), 802 (vs), 729 (s), 634 (m), 573 cm^{-1} (s). Elemental analysis (%) calcd for **4**: C 4.67, N 2.44 Na 1.08, S 2.58; found: C 4.4, N 2.4, Na 1.0, S 2.6.

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Keywords: cluster chemistry · nanostructures · polyoxometalates · porous materials · water

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[3] Water is highly structured but with random hydrogen-bonded links which results in medium-range regions disaggregating and reforming, a phenomenon generally described with so-called *flickering clusters*, which can be considered as a version of the mixture-model of water (G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, **1997**). Femtosecond spectroscopy investigations support this picture (see S. Woutersen, U. Emmerichs, H. J. Bakker, *Science* **1997**, *278*, 658–660; see also S. W. Benson, E. D. Siebert, *J. Am. Chem. Soc.* **1992**, *114*, 4269–4276).

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[5] In these hydrates, guests are encapsulated in polyhedral cages, the faces of which are mainly built up by five-membered rings of water molecules (Figure 1). These which correspond to those believed to exist in liquid water[4] and which are also abundant in discrete assemblies in some of the clusters presented here. Clathrate hydrates have been investigated from several scientific points of view, for example, for understanding of the basic principles of structural chemistry, and also for their industrial use (see *Gas Hydrates: Challenges for the Future* (Eds.: G. D. Holder, P. R. Bishnoi), *Ann. N. Y. Acad. Sci.* **2000**, *912* and G. A. Jeffrey in *Inclusion Compounds, Vol. 1* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol), Academic Press, New York, **1984**, pp. 135–190.

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[11] Crystal data for **1**: $H_{994}Mo_{132}N_{72}O_{845}S_{30}$, $M_r = 29156.55\ \mathrm{g\,mol^{-1}}$, rhombohedral, space group $R\bar{3}$, $a = 32.7248(7)$, $c = 73.668(2)$ Å, $V = 68323(3)$ Å^3, $Z = 3$, $\rho = 2.126\ \mathrm{g\,cm^{-3}}$, $\mu = 1.938\ \mathrm{mm^{-1}}$, $F(000) = 42846$, crystal size $= 0.30 \times 0.30 \times 0.15\ \mathrm{mm^3}$. A total of 134220 reflections ($0.77 < \Theta < 27.03°$) were collected of which 33139 reflections were unique ($R(\mathrm{int}) = 0.0296$). $R = 0.0419$ for 27415 reflections with $I > 2\sigma(I)$, $R = 0.0543$ for all reflections; max./min. residual electron density 2.246 and $-1.017\ \mathrm{e\,Å^{-3}}$. Crystal data for **3**: $C_{24}H_{1020}Mo_{132}N_{60}O_{840}S_{18}$, $M_r = 28838.16\ \mathrm{g\,mol^{-1}}$, rhombohedral, space group $R\bar{3}$, $a = 32.7356(7)$, $c = 73.627(2)$ Å, $V = 68330(3)$ Å^3, $Z = 3$, $\rho = 2.102\ \mathrm{g\,cm^{-3}}$, $\mu = 1.910\ \mathrm{mm^{-1}}$, $F(000) = 42408$, crystal size $= 0.40 \times 0.30 \times 0.20\ \mathrm{mm^3}$. A total of 132551 reflections ($0.77 < \Theta < 27.00°$) were collected of which 33009 reflections were unique ($R(\mathrm{int}) = 0.0287$). $R = 0.0404$ for 27614 reflections with $I > 2\sigma(I)$, $R = 0.0526$ for all reflections; max./min. residual electron density 2.130 and $-1.109\ \mathrm{e\,Å^{-3}}$. Crystal data for **4**: $C_{116}H_{1078}Mo_{132}N_{52}Na_{14}O_{802}S_{24}$, $M_r = 29795.68\ \mathrm{g\,mol^{-1}}$, rhombohedral, space group $R\bar{3}$, $a = 32.791(2)$, $c = 74.231(6)$ Å, $V = 69121.9(84)$ Å^3, $Z = 3$, $\rho = 2.147\ \mathrm{g\,cm^{-3}}$, $\mu = 1.907\ \mathrm{mm^{-1}}$, $F(000) = 43908$, crystal size $= 0.40 \times 0.30 \times 0.20\ \mathrm{mm^3}$. A total of 119085 reflections ($0.77 < \Theta < 27.06°$) were collected of which 33381 reflections were unique ($R(\mathrm{int}) = 0.0536$). $R = 0.0687$ for 24268 reflections with $I > 2\sigma(I)$, $R = 0.1067$ for all reflections; max./min. residual electron density 2.342 and $-1.252\ \mathrm{e\,Å^{-3}}$. Crystals of **1, 3** and **4** 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, $Mo_{K\alpha}$ radiation, graphite monochromator; hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435, and 230 frames ($\phi = 0$, 88 and 180°) at a detector distance of 5.0 cm). For all structures empirical absorption corrections were performed using equivalent reflections with the program SADABS. The structures were solved with the program SHELXS-97 and refined using SHELXL-93. (SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen, Göttingen (Germany), **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-412950 (**1**). Crystallographic data (excluding structure factors) for **3** and **4** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-202399 (**3**) and CCDC-202400 (**4**). 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 CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[12] 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.

[13] A. Müller, P. Kögerler, A. Dress, *Coord. Chem. Rev.* **2001**, *222*, 193–218.

[14] A. Müller, P. Kögerler, H. Bögge, *Struct. Bonding (Berlin)* **2000**, *96*, 203–236.

[15] It was argued according to mass spectrometry studies that especially $H_3O^+(H_2O)_{20}$ and $NH_4^+(H_2O)_{20}$ should have similar structures with a central hydronium or ammonium ion (see: G. Hulthe, G. Stenhagen, O. Wennerström, C.-H. Ottosson, *J. Chromatogr. A* **1997**, *777*, 155–165). The dodecahedral water clusters collapse if the voids are not occupied by the guest molecules. Whether this is the case in our encapsulated water clusters where the $\{H_2O\}_{20}$ dodecahedron is necessarily connected with the next shell is not clear. Interestingly, in **1** and **5**, we find electron density in the center of the first-shell dodecahedron which should be a result of H_2O or NH_4^+ ions in **1** and of H_2O in **5** (see formula).

[16] a) This view is supported by the following fact: A capsule of a compound obtained with a lower concentration of NH_4^+ ions in the reaction medium than for **1a**, has a smaller-sized central dodecahedron because there is a smaller number of encapsulated NH_4^+ ions while the distance to the second shell is correspondingly larger; b) A. Malecki, A. Bielanski, E. Diemann, A. Müller, to be published in connection with related studies on the release of encapsulated components.

[17] Quantum-mechanical studies on $NH_4^+(H_2O)_{20}$ have demonstrated that the cluster with an NH_4^+ ion in the dodecahedral cavity has the same energy as the cluster with an NH_4^+ ion on the surface of the cage and a neutral water molecule in the cavity (A. Khan, *Chem. Phys. Lett.* **2001**, *338*, 201–207).

[18] Whereas clathrate-like cage structures with the magic number 20 in the case of NH_4^+, K^+, Cs^+ hydrates have been detected with LILBID (laser-induced liquid beam ionization/desorption) mass spectrometry of supercooled aqueous solutions, this was not the case for Li^+ and Na^+ ions.[19] This result means that a thermodynamically stable, icosahedral cage of water molecules can only be expected around the larger cations.

[19] F. Sobott, A. Wattenberg, H.-D. Barth, B. Brutschy, *Int. J. Mass Spectrom.* **1999**, *185–187*, 271–279, and references therein.

[20] a) Pore closing seems to have an influence on the type of "water structure": In **7a** we find a compact $\{H_2O\}_{100}$ cluster with the central O atoms tetrahedrally coordinated (for a proposed separation into shells see Figure 6); b) M. Henry, *ChemPhysChem* **2002**, *3*, 607–616.

[21] An interesting shell/solid sequence is found in an NH_4^+ salt of the cluster anion $[(H_2O)_n + \text{"polymolybdate"} \subset \{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_4(CH_3COO)\}_{30}]^{m-}$: (icosahedron +) dodecahedron + icosahedron which has larger electron densities than in the other mentioned cases. This is caused by the presence of Mo atoms of an encapsulated disordered polyoxomolybdate "swimming in water" with an as yet unknown

structure and corresponds to a new state of encapsulated inorganic ions.

[22] In context of the present work it should be mentioned that general ionic behavior in solution as well as in the present nanocontainers parallels, at least formally, the *relative* positions of the ions of the not fully understood Hofmeister series[23] (the series for cations and anions show opposite behavior; see also A. A. Zavitsas, *J. Phys. Chem. B* **2001**, *105*, 7805–7817). The series describes the order of effectiveness of different ions in stabilizing a protein and their ability to salt the protein out arises from several effects.[23b] Referring to our present problem, encapsulated cations with high charge density (starting from the right part of the series) prevent the formation of well-defined encapsulated water clusters. This can be nicely observed with encapsulated Li^+ ions (A. Müller, A. Clapa, H. Bögge, M. Schmidtmann, unpublished results).

[23] a) D. Voet, J. G. Voet, *Biochemistry*, 2nd ed., Wiley, New York, **1995**; b) T. E. Creighton, *Proteins: Structures and Molecular Properties*, 2nd ed., Freeman, New York, **1997**, pp. 156, 263–264, 295–296.

[24] The hydrophobic effect is the name given to influences that cause nonpolar substances to minimize their contacts with water.[23]

[25] a) A. Müller, E. Diemann, C. Kuhlmann, W. Eimer, C. Serain, T. Tak, A. Knöchel, P. K. Pranzas, *Chem. Commun.* **2001**, 1928–1929; b) T. Liu, S. K. Das, E. Diemann, A. W. M. Dress, A. Müller, unpublished results.

[26] *Soft Matter Physics* (Eds.: M. Daoud, C. E. Williams), Springer, Berlin, **1999**.

[27] In this context it is important to realize that we have the remarkable situation of "charged water assemblies": The hydrophilic nanoobjects, for example, the anionic sphere and wheel-type species with their hydrophilic surfaces covered with H_2O ligands, behave like charged water assemblies as their surface is covered with a strongly fixed water skin/hydration shell which has a well-defined structure.