Supramolecular Chemistry

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"Gating" the Pores of a Metal Oxide Based Capsule: After Initial Cation Uptake Subsequent Cations Are Found Hydrated and Supramolecularly Fixed above the Pores**

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Dedicated to Professor Dante Gatteschi
on the occasion of his 60th birthday

Biological cell contact with the outer world depends essentially on ion fluxes, the cations involved follow—during passive transport through transmembrane channels—a route in the direction of the electrochemical gradient ("downhill").[1] They travel through the membrane channel and come to a halt when the electrochemical gradient reaches zero. (The electrochemical gradient is based on the combination of the voltage and concentration gradient for the ion under consideration.) The gradients are maintained by active transporters and pumps, which enable/facilitate rapid membrane voltage changes to be produced by the passive transport. The cations can be initially attracted by negatively charged carboxylate functional groups of amino acids pointing towards the entrance of the channel, as in the case of the bacterial K^+ ion channel.[1a] The question arises whether this type of gating mechanism can be modeled with porous capsules/artificial cells, that is, on the basis of rather robust, spherical, highly negatively charged nanosized capsules of the type $[\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}_2O_4(\text{ligand})\}_{30}]^{x-}$[2] ($x = 72$ for the SO_4^{2-} ligand, as for the anion **1a** in **1**),[3a] which has 20 pores and a cavity, linked together by 20 channels.[2] The capsules are comparable with biological cells in the sense that they are busy areas showing traffic in both directions through the channels, from the surface to the interior and back. For an

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understanding of the influx it is important to know that the negative charge density increases from the capsule periphery to the 30 sulfate ligands at the internal (tunable) cavity surface where, after entering, the cations are finally positioned.[3,4] This type of cation transport/uptake process based on the capsules can optimally be studied if highly charged cations are chosen, such as the Pr^{3+} ion, which, because of their high charge, have a high affinity to the negatively charged capsule (though a few NH_4^+ ions are also integrated[5]). In addition the Pr^{3+} ions have a moderate dehydration energy (allowing us to detect cation entrance as well as trapping of the hydrate complex), and the favorable crystallographic attribute of a high electron density. In this investigation, evidence is obtained that with sufficient uptake of the highly positively charged Pr^{3+} ions, the pores and channels block further uptake as a result of the lowering of the charge, that is, the (formal) electrochemical gradient approaches zero. (The consideration of the electrochemical gradient is in this case of course formal, because of the small number of ions involved.) As a consequence, further $[Pr(H_2O)_9]^{3+}$ complexes present in solution are trapped above the pores forming a new type of supramolecular species corresponding to a sphere-surface coordination chemistry.

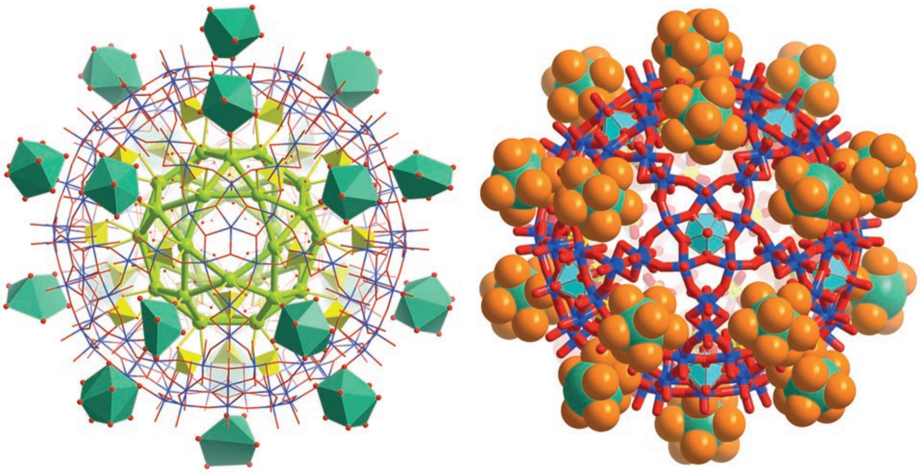

Figure 1. Left: Structure of **2a** emphasizing the outer, hydrated Pr^{3+} ions (dark green polyhedra) as well as the inner Pr^{3+} ions forming an under-occupied icosidodecahedron (light green); additionally shown: the metal oxide skeleton of the capsule (wire-frame model; Mo blue, O red) and the SO_4^{2-} ions (yellow tetrahedra); selected bond lengths in Å. Right: Space-filling representation of the outer, hydrated Pr^{3+} ions with the metal oxide capsule skeleton shown as a wire-frame model (same color code as on the left) with the central pentagonal bipyramids of the pentagonal units in polyhedral representation (light blue; see also text).

$$(NH_4)_{72-n}[\{(H_2O)_{81-n}+(NH_4)_n\}\subset\{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6\}_{12}-\{Mo^{V}{}_2O_4(SO_4)\}_{30}]\cdot\approx 200\,H_2O\equiv(NH_4)_{72-n}\,\mathbf{1a}\cdot\approx 200\,H_2O\quad\mathbf{1}$$

Crystals of **2** (space group $R\bar{3}c$)[6,7] can be obtained by interaction of **1a** with Pr^{3+} ions under (deliberately chosen) high-concentration conditions which should guarantee a comparably high uptake of Pr^{3+} ions. In this context it should be realized that in biological situations the ion-concentration differences between the outside of the cell and its interior (as in the case of Na^+ and K^+ ions) is a basic condition for several fundamental life processes, such as signal transduction, also the ion flux into the channel, which is limited by the narrowest part of the channel, increases with high ion concentrations outside the cell.[1a]

$$(NH_4)_{27}[Pr(H_2O)_9]_{10}[(Pr)_5\subset\{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6\}_{12}-\{Mo^{V}{}_2O_4(SO_4)\}_{30}]\cdot\approx[185\,H_2O+12\,Cl^-+3\,Pr^{3+}+3\,NH_4^+]-\equiv(NH_4)_{27}[Pr(H_2O)_9]_{10}\,\mathbf{2a}\cdot[\text{cocrystallized components}]\quad\mathbf{2}$$

Capsule **2** was characterized by elemental analyses, thermogravimetry (to determine the amount of crystal water), and spectroscopic methods (IR, Raman) as well as single-crystal X-ray diffraction analyses (including bond valence sum (BVS) calculations).[7] The release of NH_4^+ ions from **1a**, which occurs during the formation of **2a**, was studied by ^{15}N-HSQC NMR (^{15}N-decoupled) spectroscopy.

The structure analysis shows that **2a** has—as does **1a**[3a] and several other related capsules[2]—the "classical" approximate icosahedral $\{pentagon\}_{12}\{linker\}_{30}$ skeleton. This structure can also be easily demonstrated by Raman spectroscopy as **2a** shows the characteristic "few-line" spectrum in which the highest intensity band at 876 cm^{-1} is assigned to the interesting, totally symmetric A_g breathing vibration of the (large number of) 240 bridging oxygen atoms in the capsule. Remarkably, in **2a**, Pr^{3+} centers are found inside as well as in hydrated form outside the capsule (Figure 1). Each of the five encapsulated Pr^{3+} ions, which are disordered over 30 equivalent positions forming an icosidodecahedron, is coordinated to a sulfate group that acts as a bidentate ligand to a $\{Mo_2\}$ linker. The coordination sphere of the internal Pr^{3+} ions is completed by the oxygen atoms of the encapsulated water molecules. In this sense the water molecules, which are formally organized in shells and linked by strong hydrogen bonds, "behave" as polydentate/macrocyclic ligands;[8a] structurally speaking the encapsulated water molecules in **2a** form a partially occupied $\{H_2O\}_{60+20}$ type shell.[8b] Additionally, in this case the $\{H_2O\}_{60+20}$ shell, together with the Pr positions inside the cavity, form an interesting spherical shell type aggregate; the Pr positions are located a little below/inside the water cage (Figure 2).

The important discovery is that in crystals of **2** ten Pr^{3+} ions are, as a result of a kind of pore closing, found located above the pores, which does not happen with lower Pr^{3+} ion concentrations; in those cases the Pr^{3+} ions are only found encapsulated within the cavity (see details in ref. [9] and the Note added in proof ref. [20]). The non-encapsulated Pr^{3+} ions are found mostly with classical ninefold hydration[10a–d]

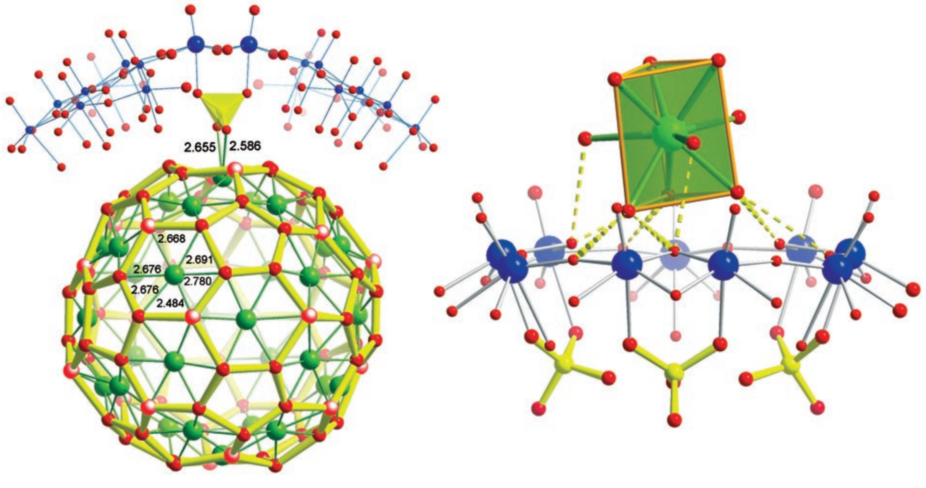

Figure 2. Left: Part of the structure of **2a**: The under-occupied 30 Pr^{3+} ion positions inside the capsule form, together with the $\{H_2O\}_{80}$ cluster shell positions [formally described as $\{H_2O\}_{60}$ (distorted rhombicosidodecahedron in red) + $\{H_2O\}_{20}$ (dodecahedron in pale red)], a new type of spherical cluster shell which is emphasized (Pr green, O red and pale red). The pale red positions are located on the C_3-axis (partly occupied by the $\{H_2O\}_{20}$ water molecules). A fragment of the metal oxide skeleton of the capsule is also shown (ball-and-stick representation; Mo blue, O red) symmetrically coordinated to one sulfate group (yellow tetrahedron). Right: Structure of a $[Pr(H_2O)_9]^{3+}$ complex above a pore (not all are so well-defined as in this case), highlighting the H-bonds (broken yellow lines) between the water ligands and oxygen atoms of the $\{Mo_9O_9\}$ pore (Pr green, Mo blue, S yellow, O red).

while the water ligands are hydrogen bonded to the O atoms of the $\{Mo_9O_9\}$ pores/rings. This can formally be considered as an outer sphere complex situation (see ref. [10e]) with the capsule acting as polydentate ligand. In any case, **2a** can be considered as a new type of supramolecular species with the "guests" located at the sphere surface (see Figure 1 and Figure 2, right; O···O distances: approximately 2.8 to 3.0 Å).[3d] The situation is a consequence of the following process: After initial uptake of the five highly charged Pr^{3+} ions and their positioning at the internal cavity functional groups, the formal electrochemical gradient,[11] which can be generally speaking correlated with the driving force for the uptake of the cation under consideration, decreases owing to the decrease in the overall negative charge of the capsule. The consequence is that finally no more cations can pass through the "closed" pores/channels,[12] which corresponds to a type of modeling of voltage gating.[1]

In this context we considered the presence of the NH_4^+ ions encapsulated in **1a** in more detail. From earlier X-ray crystallography investigations there was only indirect evidence that a few encapsulated NH_4^+ ions are present in **1a**.[3a] But these ions are rather strongly fixed in the capsule cavity and cannot easily be removed; this result follows from combined thermogravimetry, mass spectroscopy, and temperature-dependent elemental analyses studies up to 450 °C. Remarkably, the release of the "last" NH_3 molecules out of the capsules upon heating occurs at comparably high temperature (i.e. 420 °C). This NH_3 release is favored by an interesting cavity internal reaction occurring at 360 °C by which the $\{Mo^V_2\}$ linkers reduce the sulfate ligands while the SO_2 formed is released; [13a] the redox process increases the size of the channels drastically. Information on the basic responsive behavior of the encapsulated NH_4^+ ions upon cation uptake has now been obtained: The ^{15}N-HSQC spectrum[13b] of ^{15}N enriched **1** dissolved in DMSO[13c] (Figure 3) shows the existence of a few internal sites occupied with NH_4^+ ions[13d]—a situation comparable with the observation of different sites occupied with encapsulated Li^+ ions in the corresponding capsule according to information obtained not only from X-ray crystallography but also from ^7Li NMR spectra[14])—whereas the related broadened ^1H signals are, as expected, all shifted upfield (as are the Li^+ signals in the corresponding system). Of the various ^{15}N signals some are shifted upfield, and some downfield compared to the external ammonium signal. There is a slow proton exchange between the encapsulated NH_4^+ ions at different sites with the external ammonium ions present in solution. To understand the behavior of the encapsulated $^{15}NH_4^+$ ions in **1a** as a response to the entrance of cations in general (**1a** is always used in these type of ion transport studies), Ca^{2+} ions were added which are known to be easily encapsulated and firmly fixed at as many as 20 equivalent positions below the channels.[4] $CaBr_2$ was used instead of the paramagnetic praseodymium salt to enable NMR spectroscopy monitoring of the effect of metal uptake on the mobility of encapsulated NH_4^+ ions. The important result is that with the addition of small amounts of $CaBr_2$, all the signals caused by the presence of the small

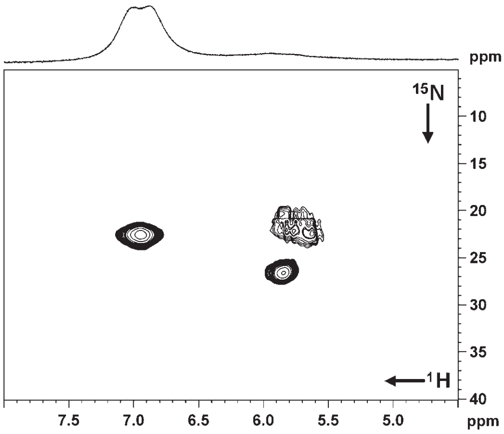

Figure 3. ^{15}N-HSQC NMR (^{15}N-decoupled) spectrum of a solution of ^{15}N-enriched **1** in DMSO showing the presence of the encapsulated NH_4^+ ions. The correlation peak (7/23 ppm) for the intense ^1H doublet for the free, solvated ammonium ions is accompanied by additional correlations (which disappear after cation uptake) with exclusively upfield proton (5.5–6 ppm) and up-and downfield nitrogen chemical shifts (21–26 ppm) corresponding to the encapsulated NH_4^+ ions. The shapes of the signals of the 1D-^1H NMR spectrum are due to a slow H^+ exchange which is responsible for the broadening of the signal of the "free" and encapsulated ammonium cations. Extended ^{15}N-NMR studies demonstrate that the shape of these signals also depends on the amount of water present.

number of encapsulated NH_4^+ ions vanish. Clearly, this change is due to breaking of the equilibria and release of the internal ammonium cations. This result can be clearly transferred not only to our Pr^{3+} situation but also to other cation uptakes related to counterion transport in general. The term "gating" is justified as the first cations taken up eject the few NH_4^+ ions from the cavity,[13c] with increasing Pr^{3+} ion concentrations trapping occurs, and furthermore, each ion has its own characteristic chemical potential.[11]

We also examined other exchange processes occurring within the capsule, such as the exchange of acetate by (hydrogen) sulfate in the preparation of **1** (see Experimental Section): Addition of protons to the aqueous solution leads to the formation of acetic acid which is easily released. The consequence is a drastic increase of the channel size allowing the entrance of SO_4^{2-} ions. A formally related situation of interest is another acid–base system inside the capsule, that is, the ammonium/ammonia equilibrium. By increasing the "pH" of a solution of **1**, that is, by avoiding capsule decomposition, some NH_3 can be formed in small amounts which could, in principle, easily pass through the pores. Interestingly, NH_3 gas channels are presently being discussed in biological systems. (We considered this problem because the NH_4^+ ion transport through the pores is involved in the Pr^{3+} uptake.) In this context some general facts should be mentioned: Ammonium is one of the most important nitrogen sources in nature, that is, for bacteria, fungi, and plants whereas it is toxic in high concentrations to animals. Though it has long been known that the ammonium-transport proteins are present in all domains of life, only recent functional studies with members of this family have yielded controversial results with respect to the chemical nature of the transported species (NH_4^+ or NH_3). In a special case, structural data and energetic considerations strongly indicated the presence of hydrophobic functioning ammonia gas channels.[15] In this sense an interesting aspect was pointed out by Heitman and Agre[16] as to whether it is possible that ammonia has other important physiological roles, possibly as a signaling molecule.

The present studies with varying ion concentrations inside and outside the capsule are interesting in relation to the fact that living cells can only function properly if the inner-cell ion concentrations are different from those in the surrounding local environments, that is, under non-equilibrium conditions.[1] Finally, our porous capsules, because of their basic container function (see for example, ref. [17]), can offer the chance to perform a variety of encapsulation chemistry processes,[18] and to carry out coordination chemistry under confined conditions and on nanosized sphere surfaces. Generally speaking, the capsules can be considered as nano test-tubes; in this context recent related discussions on "*record breaking test tubes*" may be referred to.[19]

Experimental Section

1: (same compound as in ref. [3a], but obtained with a simpler synthetic method as heating is avoided): $(NH_4)_2SO_4$ (8.0 g, 60.5 mmol) and subsequently H_2SO_4 (21 mL, 2 M) was added under stirring to a solution of $(NH_4)_{42}[Mo_{132}O_{372}(H_2O)_{72}(CH_3COO)_{30}]\cdot\approx(10\,CH_3COONH_4+300\,H_2O)$ (2.0 g, 0.07 mmol)[2e,f] in water (160 mL). The mixture was kept in an open beaker for crystallization. After 2 weeks the precipitated brown crystals were collected by filtration and washed with a small amount of 2-propanol, and then with diethyl ether. Yield: 1.8 g. Characteristic IR bands (KBr disk): $\tilde{\nu}=1618$ [m, $\delta(H_2O)$], 1400 [s, $\delta_{as}(NH_4)$], 1195 (w), 1136 (m), 1038 (w) [$\nu_{as}(SO_4)$], 970 (s), 935 (w) [ν (Mo=O)], 856 (w), 800 (vs), 727 (s), 631 (w), 571 cm^{-1} (m). Characteristic Raman bands (solid state, KBr dilution, $\lambda_e\approx1064$ nm): $\tilde{\nu}=949$ [m, ν (Mo=O)], 876 [s, $\nu(O_{bri}$ breathing/$A_{1g})$] 374 (m), 304 cm^{-1} (w). Elemental analysis (%) calcd: N 3.5, S 3.35; found: N 3.5, S 3.6.

2: H_2SO_4 (1.5 mL, 0.5 M) was added under stirring to a solution of **1** (1.26 g, 0.034 mmol) in water (16 mL), shortly afterwards a solution of $PrCl_3\cdot6\,H_2O$ (1.85 g, 5.20 mmol) in water (4 mL) was added. (Note the deliberate use of a high concentration in contrast to normal synthetic conditions.) The resulting mixture was stirred for one minute and then immediately filtered into an open beaker for crystallization. After four days the precipitated dark brown crystals were separated out and washed with ice-cold water. Yield: 1.0 g (74 % based on **1**). Characteristic IR bands (KBr disk): $\tilde{\nu}=1622$ [m, $\delta(H_2O)$], 1400 [m, $\delta_{as}(NH_4)$], 1190 (sh), 1138 (m), 1055 (sh), 970 (s), 940 (sh) [ν(Mo=O)], 856 (w), 800 (s), 725 (s), 633 (w), 571 cm^{-1} (m). Characteristic Raman bands (solid state, KBr dilution, $\lambda_e\approx1064$ nm): $\tilde{\nu}=951$ [m, ν (Mo=O)], 876 [s, $\nu(O_{bri}$ breathing/$A_{1g})$] 375 (m), 309 cm^{-1} (w). Elemental analysis (%; see ref. [6]) calcd: Pr 8.22, N 1.36, Cl 1.37; found: Pr 8.3, N 1.4, Cl 1.5.

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[5] The charge of 72− given for **1a** does not consider the encapsulated NH_4^+ ions, the number and position of which cannot be determined by single-crystal X-ray studies because the ions occur at the same positions as the encapsulated H_2O molecules. The exchange of NH_4^+ with the added Pr^{3+} ions does not influence the conclusion of "gating" as the influence of increasing Pr^{3+} concentration on the primary uptake and subsequent trapping could be demonstrated unequivocally by different experiments; the general behavior of NH_4^+ ions upon cation uptake is discussed in the text.

[6] The chemical formula of **2** refers to the maximum possible number of water molecules and is calculated from the cell volume and that of all cell components, not considering the crystal water molecules. The given calculated values for Cl, N, Pr are related to a formula with 25 crystal water molecules less than given (note: **2**, as found for all similar compounds, shows slow weathering and loses water of crystallization). Furthermore, the number of encapsulated NH_4^+/H_2O units is not referred to in the formula, as it is not possible to distinguish between these by X-ray crystallography. The presence of the disordered small ion lattice components (see formula of **2**) is typical for these types of spherical clusters containing large voids. They occur especially in the present case as a result of the high concentration condition of the synthesis. In the case of **1** the additional lattice components (the NH_4^+ and CH_3OO^- ions) could be determined in detail with NMR spectroscopy (F. Taulelle, L. Allouche, A. Senouci, M. Henry, A. Müller, unpublished results).

[7] Crystal data for **2**: $H_{814}Cl_{12}Mo_{132}N_{30}O_{839}Pr_{18}S_{30}$, $M_r = 31252.47\,\mathrm{g\,mol^{-1}}$, rhombohedral, space group $R\bar{3}c$, $a = 50.3036(11)$, $c = 61.3381(18)$ Å, $V = 134418(6)$ Å^3, $Z = 6$, $\rho = 2.316\,\mathrm{g\,cm^{-3}}$, $\mu = 2.958\,\mathrm{mm^{-1}}$, $F(000) = 90156$, crystal size $= 0.40 \times 0.30 \times 0.25\,\mathrm{mm^3}$. Crystals of **2** 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; hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435, and 230 frames ($\varphi = 0$, 88, and 180°) at a detector distance of 5.00 cm). A total of 265004 reflections ($1.62° < \Theta < 26.99°$) were collected of which 32585 reflections were unique ($R_{int} = 0.0416$). 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-97 to $R = 0.0625$ for 24263 reflections with $I > 2\sigma(I)$, $R = 0.0939$ for all reflections; max./min. residual electron density 2.440 and $-2.380\,\mathrm{e\,Å^{-3}}$ (SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen, **1997/2003**; structure graphics with DIAMOND 2.1/3.0 from K. Brandenburg, Crystal Impact GbR, 2001/2004). 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 number CSD-415386.

[8] a) F. A. Hart in *Comprehensive Coordination Chemistry, Vol. 3* (Ed.: G. Wilkinson), Pergamon, Oxford, **1987**, pp. 1091–1099; b) This is comparable to the situation within the capsule cavity containing $H_2PO_2^-$ ligands;[3a] see also: M. Henry, H. Bögge, E. Diemann, A. Müller, *J. Mol. Liq.* **2005**, *118*, 155–162.

[9] Important in the context of pore/channel gating is that under more dilute concentrations **1a** "attracts" only a smaller number of Pr^{3+} ions, which does not lead to the corresponding pore closing discussed herein. One related example refers to the compound with the stoichiometry $(NH_4)_{25}(NH_2CHNH_2)_6Pr_3[\{(NH_2CHNH_2)_{20} + (Pr)_4\} \subset \{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_4(SO_4)\}_{30}]\cdot \approx 280\,H_2O$ (**3**). For the capsule anion **3a**, three encapsulated Pr^{3+} ions are found disordered over the same thirty equivalent positions found in **2a**; see: A. Müller, Y. Zhou, L. Zhang, H. Bögge, M. Schmidtmann, M. Dressel, J. van Slageren, *Chem. Commun.* **2004**, 2038–2039.

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[11] The following formulation described in biophysical and biochemical text books (e.g. ref. [1a]) is representative for biological ion membrane processes; we can only give a simplified illustrative view of the present ion transport as it is based on a relatively small inorganic capsule system compared to the biological case: A solute tends to move from a region of high to a region of low concentration which finally results in an equilibrium. Consequently, movement down a concentration gradient is accompanied by a favorable free-energy change ($\Delta G < 0$). The free-energy change per mole of solute moved across a membrane (ΔG_{conc}), is equal to $-RT\ln C_o/C_i$ (C_o and C_i are the outside and inside concentrations of the ion, respectively). If the solute is an ion, moving it into a cell across a membrane whose inside is at a voltage V relative to the outside will cause an additional free-energy change (per mole of solute moved) of $\Delta G_{volt} = zFV$. Just where the concentration and voltage gradients are equal, $\Delta G_{conc} + \Delta G_{volt} = 0$, the ion distribution across the membrane is at equilibrium.[12] (In the present case, this is formally the situation the after the five Pr^{3+} have been taken up.) In other words, the equilibrium corresponds to the situation where the electrochemical potential, that is, the chemical potential of the ion in the presence of an electrical potential (corresponding additional term zFV to which all encapsulated ions contribute) inside and outside is equal (see especially: P. Atkins, J. de Paula, *Atkins' Physical Chemistry*, 7th ed., Oxford University Press, Oxford, **2002**, p. 1023). In the present type of experiment the chemical potential of the encapsulated Pr^{3+} ions depends strongly on their interactions with the sulfate receptors.

[12] In biological cells a part of the "channel protein" blocks the passive ion channel owing to a minor conformational change as an effect of decreased electrochemical gradient.[1]

[13] a) A. Malecki, A. Bielanski, Cracow, unpublished results; b) The gradient selected ^{15}N-HSQC spectrum was measured with the sensitivity enhanced version of the pulse sequence on a Bruker AVANCE 400 spectrometer, adjusted to a ^{1}H–^{15}N coupling constant of 75 Hz. The measurement time was 36 min with 8 scans and 128 increments of a saturated solution of the ^{15}N-enriched compound **1** in DMSO (for the method see: L. E. Kay, P. Keifer, T. Saarinen, *J. Am. Chem. Soc.* **1992**, *114*, 10663–10665). To study the influence of cation uptake approximately 30 mg $CaBr_2$ were added to 0.7 mL saturated solution of **1**; c) The ^{15}N-NMR spectrum was measured in DMSO and not in water to avoid increased H exchange, which would complicate the results; d) The correct number of encapsulated NH_4^+ ions will be determined with a higher field instrument in the near future.

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[20] Note added in proof, November 23, 2005: In the case of the interaction of a solution of **1a** with increasing concentrations of Ca^{2+}, practically continuous increasing cation uptake (with subsequent gating) occurs, which is easily demonstrated by the "blue shift" of the lowest wavenumber band of the three $\nu_{as}(SO_4)$ signals measured in the IR spectrum of the resulting precipitate.