Cation behavior at an artificial cell interface: binding distinguished by ion hydration energetics and size†‡

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The unique molybdenum oxide-based nucleophilic porous capsule/artificial cell $[\{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_4(SO_4)_{30}\}]^{72-}$, according to an X-ray crystallographic study, traps $[Al(H_2O)_6]^{3+}$ complexes above the pores while interacting with the latter *via* hydrogen bonds; this is supported by ^{27}Al NMR studies of the interaction of the capsule with hydrated Al^{3+} cations in aqueous solution.

In a nice, small book entitled *Nanophysics and Nanotechnology: An Introduction to Modern Concepts in Nanoscience*,[1] in the section "Ion Channels", attractive aspects of the application of nanoobjects containing channels/pores are presented. Here we refer to this type of object, *i.e.* the spherical nanocapsules $(\text{pentagon})_{12}(\text{linker})_{30}$ [2a–e] which react differently/specifically with strongly- and less strongly-bonded water ligands. The nanocapsules (Keplerates) exhibit 20 pores/channels and are stable in solution under well-defined conditions (proofs below). We refer here specifically to the interaction of an aqueous solution containing the "hard" Al^{3+} ions (see below) with the spherical nanosized capsules (**1a**) which leads to an unusual supramolecular species showing the $[Al(H_2O)_6]^{3+}$ ions trapped at the capsule pores. It is noteworthy that the Keplerate-type capsules allow a variety of investigations ranging from the modelling of biological ion transport[2f] to the observation of unprecedented self-assembly processes.[2g] For the definition of a Keplerate see ref. 2*h*).

$$(NH_4)_{72-n}\,[\{(H_2O)_{81-n} + (NH_4)_n\} \subset \{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_4(SO_4)\}_{30}]\cdot ca.\ 200H_2O \equiv (NH_4)_{72-n}\ \mathbf{1a}\cdot ca.\ 200H_2O\ \text{[ref. 3]} \qquad (1)$$

The reaction of an aqueous solution of **1** (obtainable in high yield in a facile synthesis[3b]) with hydrated Al^{3+} leads to the formation of **2** containing the capsule anion **2a**.§ Compound **2** was characterised by elemental analyses, thermogravimetry (to determine the amount of water of crystallisation), redox titration (to determine the number of Mo^{V} centres) and spectroscopic methods (IR, Raman, UV-Vis) as well as single-crystal X-ray structure analysis† (including bond valence sum calculations). (see ESI‡)

$$(NH_4)_{15}[Al(H_2O)_6]_9[Al(H_2O)_6]^{\text{trap}}_{10}[\{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_4(SO_4)\}_{30}]\cdot ca.\ 250H_2O \equiv (NH_4)_{15}[Al(H_2O)_6]_{19}\ \mathbf{2a}\cdot ca.\ 250H_2O \qquad (2)$$

The compound crystallises in the space group $C2/c$ (encapsulated disordered H_2O molecules are included in the $250H_2O$ part). The anionic capsule **2a** is built up, like **1a**, by 12 pentagonal units of the type $\{(Mo^{VI})Mo^{VI}{}_5\}$ which are positioned at the vertices of an icosahedron and connected by 30 $\{Mo^{V}{}_2O_4(SO_4)\}$ linking groups (Fig. 1). The capsule contains 20 $\{Mo_9O_9\}$-type pores and, due to the presence of sulfates, a functionalised cavity shell (see *e.g.* ref. 4). The most important result is that the H_2O ligands of ten $[Al(H_2O)_6]^{3+}$ complexes—found distributed over all 20 $\{Mo_9O_9\}$ (underoccupied) pore positions—interact rather strongly with the pore O atoms *via* hydrogen bonds (Fig. 1b). The related Al–O–H···O distances occur in the range 2.6–3.2 Å.

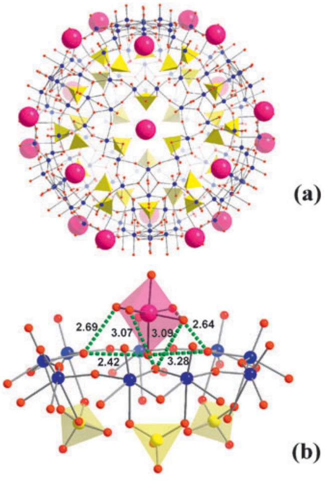

Fig. 1 (a) Structure of the anion **2a** (mostly in ball-and-stick representation) showing the sulfate ligands as yellow tetrahedra and highlighting the Al^{3+} cations (large pink spheres) found hydrated above all the 20 pores in underoccupied fashion (see text; colour code: Mo blue, O red); (b) one pore area showing the $\{Mo_9O_9\}$ ring–$[Al(H_2O)_6]^{3+}$ (pink octahedron) interaction *via* hydrogen bonds (distances in Å).

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‡ Electronic supplementary information (ESI) available: More details about NMR, solution Raman spectra with reference to stabilities and encapsulated water clusters as well as the Acknowledgements. Crystal data for **2**. See DOI: 10.1039/b718260k

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According to our recent studies special cations present in solution can—after the removal of their hydration shells—traverse the pores/channels of the capsule type under investigation and ultimately position themselves in the interior.[4,5] In the case of the Al^{3+} cations, however, this was not *a priori* predictable because the water ligands in $[Al(H_2O)_6]^{3+}$ are rather strongly bound.[6a,b] As a consequence of this we find the complexes fixed at the pores and no Al^{3+} ions taken up into the cavity[6d] (no NH_4^+–Al^{3+} countertransport) in spite of the large amount of these present in the reaction medium. In contrast, larger univalent cations such as Na^+, important for biological ion transport processes (r_i = 1.16 Å for Na^+; for comparison r_i = 0.68 Å for Al^{3+}, both distance values for C. N. = 6)[6b] form much less stable aqua complexes and therefore easily shed their water coat and cross the pores/channels while recomposing their ligand shells with oxygen donors; these are available from the SO_4^{2-} ligands as well as from the encapsulated H_2O molecules (see *e.g.* ref. 3–5).

The present investigation refers to one of the possible applications of the mentioned capsule type, besides others like modelling biological cation transport,[2f,5] such as the study of the strength of the interaction between the capsule and hydrated metal ions (see below). The present result is obtained due to the rather slow rate of H_2O ligand exchange in $[Al(H_2O)_6]^{3+}$ equivalent to the related large mean residence time[6a,b] which even facilitates the investigation by ^{17}O NMR.[6a] Al^{3+} has, besides that, one of the largest hydration enthalpies for cations.[6c]

To address the interaction of Al^{3+} with the present Keplerate, we have investigated the system by ^{27}Al NMR (Fig. 2). However, the near insolubility of **2** in water and polar organic solvents resulting from the presence of a rather large number of Al^{3+} cations required the use of the soluble compound **3**¶ and/or the study of the direct interaction of solutions of **1a** with Al^{3+}. The spectrum of a moderately heated solution of **3** in D_2O shows peaks at −1.0 and −0.2 ppm which have different temperature dependencies (Fig. 2, first and second spectra from the bottom).‖ When larger amounts of Al^{3+} were added to the solution of **3** the peak at −0.2 ppm increased in intensity, but the addition of increased amounts of the complexing agent hydroxypyridine-1-oxide removed that signal (the related intensity decrease started immediately after addition). In contrast to that, we find the decrease of the intensity of the peak at −1.0 ppm to be remarkably slow, but it also disappears completely after some time in case of an excess of pyrh (not shown here). (The ^{27}Al NMR spectra of a solution of **1** after addition of Al^{3+} are similar to those of Fig. 2.) Based on all facts we assign the signal at −1.0 ppm to hydrated Al^{3+} ions in contact with the pores (see Fig. 1b) taking into account that these Al^{3+} ions are more protected against the complexing agent than the Al^{3+} in free $[Al(H_2O)_6]^{3+}$ (peak at −0.2 ppm). In spite of many experiments we were not able to detect resonance(s) for encapsulated Al^{3+} ions, which is in agreement with the crystallographic results and the discussion above.

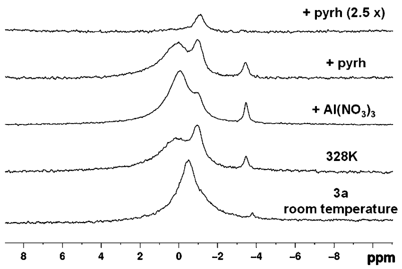

Fig. 2 ^{27}Al-NMR spectra of a solution of **3** in D_2O under varying conditions (the four upper spectra were measured at 328 K, the bottom one at *ca.* 295 K). Spectra have been measured after addition of highly polarizing Al^{3+} (10 μL 1M $Al(NO_3)_3 \cdot 9H_2O$ in D_2O) and different amounts of 2-hydroxypyridine-1-oxide (pyrh (Aldrich), 20 wt% in H_2O; 10 and 25 μL); for further details see text and this footnote.‖

$$[(CH_3)_2NH_2]_{54}Al_6\,[\{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_4(SO_4)\}_{30}]\cdot ca.\ 200H_2O \equiv [(CH_3)_2NH_2]_{54}Al_6\ \mathbf{3a}\cdot ca.\ 200H_2O\ \text{(simplified formulation; see text)} \qquad (3)$$

The situation in which Al^{3+} ions do not enter the capsule is the opposite to that of alkali cations like Li^+ where fast uptake–release exchange processes dominate in water (but not in DMSO!) and prevent the observation of separate NMR signals in that solvent.[5b,c] The present result is in agreement with the stability of the spherical capsule under well-defined conditions** as well as that of the Al^{3+} aqua complex. If a reversible release of the pentagonal (Mo)Mo_5 units (which can be considered in capsules of the present type as ligands in a coordination polymer with spherical periodicity[7]) occurred, this would lead to an uptake of the Al^{3+}.

To summarize: the interaction of a capsule of the type **1a** with metal aqua complexes can be studied systematically in order to provide information regarding the extent to which water ligands can be released from the ligand spheres of metal

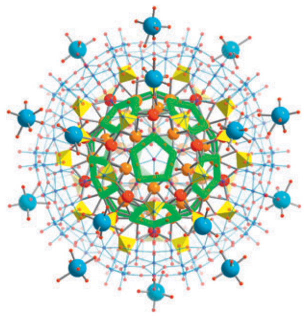

Fig. 3 Structure of the capsule-related product obtained by the reaction of an aqueous solution of **1** with Mn^{2+} ions (mostly in ball-and-stick representation; encapsulated $\{H_2O\}_{60}$ shell shown in green). The cations are found inside (five) as well as outside (eight) the capsule. Inside they are positioned on two different types of equivalent (underoccupied) positions: (i) over 30 equivalent positions (orange), while the Mn^{2+} ions are coordinated in a bidentate fashion to the 30 SO_4^{2-} ligands (yellow polyhedra); and (ii) over 20 equivalent positions (red) forming a dodecahedron corresponding to sites at the C_3-axis, *i.e.* in the centre of triangles spanned by three oxygen atoms of three equivalent SO_4^{2-} ligands (see *e.g.* ref. 5*c* and *d*). Regarding the positions outside, the eight cations (blue spheres) are found mostly in hydrated form located above all of the 20 pores in underoccupied fashion (weak interactions/links between a few Mn^{2+} and terminal O atoms of the pentagonal $\{(Mo^{VI})Mo^{VI}{}_5\}$-type units of neighbouring capsules are not shown).

cations, in the sense that this can subsequently lead to uptake of the latter. An instructive example is the different "behavior" of Mn^{2+} (no crystal field stabilisation energy) and Ni^{2+} hexaaqua complexes. Whereas a few Mn^{2+} get encapsulated (Fig. 3) all Ni^{2+} ions are found with their six H_2O ligands having a larger residence time[6a,b] trapped above the pores. (Structural details for the two cases will be published later.[8]) In any case, this type of work opens up new perspectives for coordination chemistry under confined geometries, *i.e.* on surfaces, in pores and cavities (encapsulation chemistry[9]) of porous nanocapsules. As Al^{3+} is a strongly polarizing, "hard" (and therefore rather reactive) cation, according to the high charge-to-radius ratio investigations of that cation with respect to its affinities to different oxygen donors—in the present case to water and the capsule O atoms—are especially interesting (see also ESI‡). The mentioned property of Al^{3+} has serious consequences for toxicity with respect to aquatic life (see *e.g.* ref. 10).

Notes and references

§ Synthesis of **2**: To a solution of compound **1** (0.5 g, 0.017 mmol) in 30 ml H_2O in a 100 ml beaker, $AlCl_3\cdot6H_2O$ (5 g, 21 mmol) was added (pH ≈ 2) and the reaction medium was stirred for 1 h. After 10 d the precipitated dark-brown crystals of **2** were filtered and washed with cold 2-propanol. Yield: 0.4 g. Found: Al (gravimetrically), 1.6; N, 0.4%. Calc.: Al, 1.70; N, 0.69%. An investigation of the Al^{3+} uptake was also performed at varying pH values (from *ca.* 1.5 to 2.5) while no significant changes were observed.
Characteristic IR bands: ν/cm^{-1} (KBr pellet) 1629 (m, $\delta(H_2O)$), 1404 (w-m, $\delta(NH_4)$), 1185 (w), 1128 (m-w), 1051 (w) (all $\nu_{as}(SO_4)$), 977 (s), 948 (m) (ν(Mo=O)), 858 (s), 802 (vs), 725 (s), 630 (m), 569 (s), 478 (m).
Characteristic Raman bands: ν/cm^{-1} (solid state, KBr dilution, $\lambda_e \sim$ 1064 nm) 951 (w) (ν(Mo=O)), 880 (s), $\nu(O_{bri}$-breathing), 479 (w), 430 (w), 375 (m), 304 (w-m) (see ESI;‡ comparison to the solution spectrum of **1**).

¶ The preparation method of **3** was identical to that of **2**, the only difference being that $[(CH_3)_2NH_2]Cl_2$ (1 g) was added. The formula of **3** was established by elemental (found: Al, 0.4; C, 4.0; N, 2.1%; calc.: Al, 0.55; C, 4.46; N, 2.59%) and partial single-crystal X-ray structure analysis† as well as spectroscopic methods (IR, Raman, UV-Vis). As the related skeleton is exactly identical to that of **2a** and the positioning of Al^{3+} cations cannot be proven crystallographically because of the small number of cations and the related disorder (see text above regarding **2**), no further details about the structure of **3** are presented.
Characteristic IR bands: ν/cm^{-1} (KBr pellet) 1624 (m, $\delta(H_2O)$), 1461 (w-m, $\delta(NH_2)$), 1180 (w), 1130 (m-w), 1045 (w) (all $\nu_{as}(SO_4)$), 1022 (w, ν(CN)) 972 (s), 948 (m) (ν(Mo=O)), 860 (w), 802 (s), 729 (s), 633 (w), 570 (s), 474 (m). Crystal data for **3**: $H_{976}Mo_{132}N_{54}C_{108}O_{764}Al_6S_{30}$, $M = 29\,048.75$ g mol^{-1}, space group $R\bar{3}$, $a = 32.8888(8)$, $c = 74.251(3)$ Å, $V = 69\,555(3)$ Å^3, $Z = 3$, $\rho = 2.010$ g cm^{-3}, $\mu = 1.90$ mm^{-1}, $F(000) = 39\,720$, crystal size = 0.40 × 0.20 × 0.20 mm.
^{27}Al NMR spectra of **3** were collected at 156.2 MHz on a Varian UNITY 600 MHz spectrometer and a Bruker AVANCE 400 at 104.2 MHz. Peak positions are given relative to the internal reference list of the spectrometer, corresponding to 1.1 m $Al(NO_3)_3$ in D_2O (ref. 11). **3** (25 mg, 6.5 × 10^{-7} mol) was dissolved in 1 mL D_2O (initial pH 2.4).

‖ The peaks in the spectra are accompanied under special conditions, *i.e.* mainly upon aging and heating, by two additional weak signals with variable intensities: one at *ca.* 15.5 ppm (due to the presence of $[Al(OH)_6Mo_6O_{18}]^{3-}$ with an extremely high formation tendency) and another at 3.3 ppm upfield of the $[Al(H_2O)_6]^{3+}$ signal. The latter peak can be unequivocally assigned to the presence of $[Al(H_2O)_5SO_4]^+$; both peaks depend strongly on concentration and temperature (see ESI‡ containing relevant details, references and information about the stability of **1a**).

** The fact that the spherical porous capsules/Keplerates of the type $\{(Mo)Mo_5\}_{12}(linker)_{30}$ are stable in solutions—of course under well-defined(!) conditions, *e.g.* avoiding very long-term exposure to O_2—is the basis for the present type of investigation. The stability has been proven by (i) ultracentrifugation referring to **1a** (ref. 12); (ii) the few line Raman spectra[2a,5a] which are characteristic for the high symmetry of the skeleton and which are practically identical for related solution and solid-state cases (convincing examples are found in the ESI‡ as well as in ref. 13; and (iii) small angle scattering studies as well as (iv) by the isolation of the capsules from solutions with cationic surfactants and subsequent analyses of the stoichiometrically well-defined neutral compounds formed including related TEM studies/images.[14] A nice proof refers to ^7Li-EXSY spectra of the Li^+ capsule in DMSO which show numerous slow exchange processes related to a cation uptake and release equilibrium,[5a,b] while in the case that the 20 pores of the capsule are closed with formamidinium (or guanidinium) cations (leading to an extreme capsule stabilization), the cation exchange is suppressed up to 400 K.[5c] Furthermore, a ^7Li-DOSY spectrum of the same capped capsule shows one signal for Li^+ with a low value of the diffusion coefficient which proves that the corresponding Li-cations move with the intact closed capsules (unpublished results).

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