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En route to coordination chemistry under confined conditions in a porous capsule: Pr^{3+} with different coordination shells†

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The highly charged nanocontainer capsule of the type $\{\text{pentagon}\}_{12}\{\text{linker}\}_{30} \equiv \{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SO_4)\}_{30}$ with 20 nanosized pores and channels allows the entrance of cations like Pr^{3+}: the latter are positioned at two different sites and have two different coordination shells, corresponding to a coordination chemistry under confined conditions; a fascinating aspect is that capsule encapsulated water shells fixed by hydrogen bonds act formally as polydentate ligands.

Among the self-assembled molecular containers with different shapes and sizes, designed as constrained environments for the encapsulation of guest molecules showing in principle potential applications in several aspects,[1] spherical nanoscale cluster capsules/nanocontainers of the type $\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}[\text{linker/ligand}]_{30}\}$ have special unique properties, like 20 sizeable pores, finely sculpturable cavity interiors and, in between, 20 tuneable functionalizable channels.[1b,1c] Here we show the interesting phenomenon of metal cations like Pr^{3+} entering into channels and the inner capsule, thereby constituting a novel situation with a metal center in two different environments corresponding to a coordination chemistry under confined conditions, or in other words, cation transfer in a controlled and specific fashion.

Exposure of an acidified aqueous solution of **1**,[2d]‡ exhibiting the above mentioned capsule properties, to Pr^{3+} and formamidinium cations yielded compound **2**§ which was characterized by elemental analyses, thermogravimetry (to determine the amount of water of crystallization), IR- and Raman-spectroscopy, magnetic measurements¶ and single-crystal X-ray diffraction analyses (including bond valence sum (BVS) calculations for the distinction of Mo^{V}/Mo^{VI}).‖

$$(NH_4)_{72-n}[\{(H_2O)_{81-n} + (NH_4)_n\} \subset \{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_4(SO_4)\}_{30}]\cdot ca.\ 200H_2O \equiv (NH_4)_{72-n}\cdot\mathbf{1a}\cdot ca.\ 200H_2O\ \mathbf{1}^{2d}$$

$$(NH_4)_{25}(NH_2CHNH_2)_6Pr_3[\{(NH_2CHNH_2)_{20} + Pr_4\} \subset \{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_4(SO_4)\}_{30}]\cdot ca.\ 280H_2O \equiv (NH_4)_{25}(NH_2CHNH_2)_6Pr_3\cdot\mathbf{2a}\cdot ca.\ 280H_2O\ \mathbf{2}$$

The crystal structure of **2** (space group $R\bar{3}$) shows anions corresponding to the above mentioned capsule type while the 20 pores of the $\{Mo_9O_9\}$ type are covered by the total number of 20 $HC(NH_2)_2^+$ guest cations noncovalently bonded to the ring oxygen atoms corresponding to a type of super–supramolecular chemistry in respect to the large number of host sites. Because of their smaller size and lower affinity to the ring compared to the guanidinium cation situation,[2c] they are located in average *ca.* 0.3 Å below the centers of the $\{Mo_9O_9\}$ rings. Inside the capsule, a water cluster is located, which consists of two shells, an outer $\{H_2O\}_{60}$ Archimedean solid and an inner $\{H_2O\}_{20}$ dodecahedron, *i.e.* with a structure comparable to that of **1a** but in this case only half occupied (see Fig. 1). The coordination of the Pr^{3+} cations to the sulfate ligands is nicely proven by the cation influence on the characteristic splitting of the $\nu_{as}(SO_4) = \nu_3(F_2)$ band.§

Four disordered Pr^{3+} cations are found to be encapsulated while remarkably situated at two different positions:

(1) Three Pr^{3+} cations are disordered over 30 equivalent positions forming an (underoccupied) icosidodecahedron (Figs. 1 and 2) where each underoccupied Pr^{3+} center is coordinated in a bidentate fashion to only one SO_4^{2-} ligand (average occupancy factor 0.1 for each position) comparable to the Ce^{3+} case.[2e]

(2) One Pr^{3+} is disordered over 20 equivalent positions forming a dodecahedron at the lower part of the channel area. These positions correspond to well-defined sites at the C_3-axes, in the center of triangles spanned by three oxygen atoms of three different SO_4^{2-} ligands (see Figs. 1 and 2). The diameter of the dodecahedron is of course larger than that of the above mentioned icosidodecahedron (average occupancy factor one twentieth for each position).

The two cation sites are typical for capsules with sulfate ligands but have not been found until now both occupied in the same capsule.[1c,2d,2e]

Referring now to the type of coordination environment, including the different H_2O ligands belonging to different shells, the Pr^{3+} inside the capsule cavity which coordinates symmetrically in a bidentate fashion to two O atoms of a SO_4^{2-} ligand, has four O atoms of the $\{H_2O\}_{60}$-type H_2O shell as well as two O atoms of the $\{H_2O\}_{20}$-type shell as ligands, thus forming a distorted cubane-type coordination (see also ref. 2*e*). On the other hand, each Pr^{3+} in the lower channel area coordinating to three O atoms of three different SO_4^{2-} ligands, has three O atoms of the $\{H_2O\}_{60}$-type water

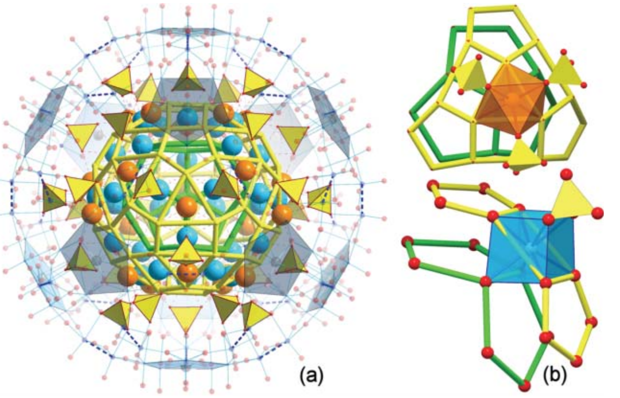

Fig. 1 (a) Structure of **2a** emphasizing the outer $\{H_2O\}_{60}$ (yellow) and inner $\{H_2O\}_{20}$ (green) shell as well as the 30 eightfold coordinated (light blue) and the 20 sevenfold coordinated (orange) Pr positions together with the SO_4 tetrahedra (yellow); the capsule itself without guests in the pores is given as partially transparent ball-and-stick model (pentagonal and linker units highlighted; Mo blue, O red). (b) Two sections from **2a** emphasizing the distorted capped-octahedron-like (top) and distorted cubane-like (bottom) environments of the Pr^{3+} cations (colour code as in (a)).

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† Dedicated to Professor Bernt Krebs on the occasion of his 65th birthday

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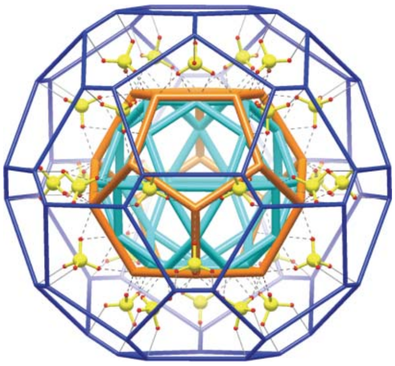

Fig. 2 Ball-and-stick representation of the polyhedra spanned by the Pr positions inside the nanocapsule **2a**. (1) An icosidodecahedron (cyan) formed by 30 equivalent Pr positions with each Pr coordinated symmetrically in a bidentate fashion to only one SO_4^{2-} ligand in the cavity. (2) A dodecahedron (orange) formed by 20 equivalent Pr positions in the lower channel area with each Pr coordinated to three O atoms of three different SO_4^{2-} ligands. Additionally shown: the observed truncated icosahedral $\{Mo^{V}_2\}_{30}$ fragment (blue) and 30 SO_4^{2-} ligands (yellow) (only O atoms coordinating to S are shown for clarity).

molecules and one O atom of the dodecahedral $\{H_2O\}_{20}$-type shell as ligands, while a distorted mono-capped octahedron is formed.

In known praseodymium compounds, the sevenfold (distorted mono-capped octahedron/trigonal prism)[3] and eightfold (cubane-type)[4] coordinations are found, though those examples are not very typical for the present case as the coordination polyhedra of f-element complexes are not governed, as in the case of d-elements, by covalency or ligand-field considerations. Lanthanide coordination geometries are governed by a minimization of the repulsive ligand–ligand interactions and steric requirements in case of polydentate ligands.[5] It is certainly fascinating that the latter point is relevant in the present case as water polyhedra, *i.e.* shells connected by hydrogen bonds, act as ligands.

The work opens up perspectives for a special type of encapsulation chemistry,[1*b*,1*c*] *i.e.* coordination chemistry under confined conditions. This can be extended to 1) a variety of ligands like the present one, 2) different capsule charges, 3) different types of porosity, 4) different solvent molecules like water, and finally 5) different metal centers. In addition, the presence of cations like Pr^{3+} in two different coordination geometries gives a unique opportunity to study the ligand influence on the electronic structure of rare earth compounds.

Notes and references

‡ According to the high negative charge of the sulfate-type capsules a high affinity to cations exists. But the total number of encapsulated cations, like in the case of NH_4^+, which may occur disordered with H_2O in the capsule (see ref. 2*d*) or disordered in the pore area, cannot be given in all cases. The charge 72− refers to the pure capsule skeleton without encapsulated metal cations. With each related encapsulation—lowering the capsule charge—the affinity to cations is decreased, in the present case due to the abundance of organic cations in the pores (note: the Pr^{3+} uptake, like that of Eu^{3+}, can be increased in principle under other/different conditions; in case of Ca^{2+} even 20 cations can be encapsulated).

§ *Synthesis* of **2**: a solution of **1** (3.80 g, 0.13 mmol) in H_2O (40 ml), to which 2 M H_2SO_4 (5 ml) and $PrCl_3·6H_2O$ (1.85 g, 5.21 mmol) dissolved in H_2O (20 ml) is added, is stirred at room temperature for 5 min. After addition of $NH_2CH(=NH)·HCl$ (0.48 g, 5.98 mmol), the solution is stirred for 30 min and subsequently NH_4Cl (1.00 g, 18.69 mmol) is added. After stirring again for 30 min, the solution is filtered and stored in an open 250 ml beaker. The dark brown crystals which precipitated after 1 day were filtered, washed with ice-cold water and dried in air. Yield: 2.1 g. Found: C 1.1; H 2.6; N 3.5; Pr 3.4; Mo 42.8%. Calc. for **2**: C 1.03; H 3.09; N 3.54; Pr 3.24; Mo 41.59%. The formula was given by taking into account the whole available volume of the unit cell for occupation with crystal water, but the analytical data are given for **2** after a characteristic loss of 80 crystal water molecules. *Characteristic IR bands*: ν/cm^{-1} (KBr pellet) 1718 (m), 1622 (m,$\delta(H_2O)$), 1402 (m–w, $\delta(NH_4)$), 1191 (w), 1136 (m–w), 1095 (w), ($\nu_{as}(SO_4)$), 975, 945 (sh) (s, ν(Mo=O)), 856 (s), 800 (vs), 725 (vs), 632 (m), 569 (s) cm^{-1}. *Characteristic Raman bands*: ν/cm^{-1} [solid state, KBr dilution, λ_e = 1064 nm]: 954 (w), 947 (w), 877 (s), 476 (w), 432 (w), 373 (m), 303 (w–m); [in H_2O]: 950 (w), 876 (s), 435 (m), 369 (s), 305 (m).

¶ Magnetic susceptibility curves were recorded for **2**. The analysis of the magnetic properties of Pr^{3+} compounds is not straightforward.[6] For rare earth ions spin–orbit coupling is more important than exchange or crystal field interactions. That means that the magnetic properties cannot be described in a spin only framework. Praseodymium(III) has a $4f^2$ configuration corresponding to a $^3H_4$ ground state for the free ion, which in complexes is split by the crystal field. The non-Kramers doublet ground state can be treated as an effective spin at low temperatures with $g_{\|} = 1.5$ and $g_{\perp} = 0$ according to theory. Mixing between the ground $J = 4$ and the excited $J = 5$ states has been found, which complicates the analysis. A detailed study involving not only susceptibility measurements but also X-band EPR and frequency domain magnetic resonance spectroscopy is in progress.

‖ *Crystal data for* **2**: $C_{26}H_{934}Mo_{132}N_{77}O_{844}Pr_7S_{30}$, M = 30448.75 g mol^{-1}, rhombohedral, space group $R\bar{3}$, a = 32.8976(8), c = 74.076(3) Å, V = 69429(3) $Å^3$, Z = 3, ρ = 2.185 g cm^{-3}, μ = 2.269 mm^{-1}, F (000) = 44454, crystal size = 0.22 × 0.22 × 0.10 mm^3. Crystals of **2** were removed from the mother liquor and immediately cooled to 188(2) K on a Bruker AXS SMART diffractometer (three circle goniometer with 1K CCD detector, Mo–K_α 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 120563 reflections ($1.53 < \theta < 26.99°$) were collected of which 33529 reflections were unique (R(int) = 0.0328). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.03.[7] The structure was solved with the program SHELXS-97[7] and refined using SHELXL-97 to R = 0.0460 for 26361 reflections with $I > 2\sigma(I)$, R = 0.0643 for all reflections; max./min. residual electron density 2.032 and −1.481 e $Å^{-3}$ (structure graphics with DIAMOND 2.1[8]). CCDC 239438. See http://www.rsc.org/suppdata/cc/b4/b407753a/ for crystallographic data in .cif format.

1 (*a*) J. Kang and J. Rebek, Jr., *Nature*, 1997, **385**, 50; (*b*) M. Gross, *Chem. Br.*, 2003, **39**(8), 18; (*c*) W. G. Klemperer and G. Westwood, *Nat. Mater.*, 2003, **2**, 780.
2 (*a*) A. Müller, P. Kögerler and C. Kuhlmann, *Chem. Commun.*, 1999, 1347; (*b*) N. Hall, *Chem. Commun.*, 2003, 803; (*c*) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, S. Roy and A. Berkle, *Angew. Chem. Int. Ed.*, 2002, **41**, 3509; (*d*) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, B. Botar and M. O. Talismanova, *Angew. Chem. Int. Ed.*, 2003, **42**, 2085; (*e*) A. Müller, S. K. Das, S. Talismanov, S. Roy, E. Beckmann, H. Bögge, M. Schmidtmann, A. Merca, A. Berkle, Y. Zhou and L. Zhang, *Angew. Chem. Int. Ed.*, 2003, **42**, 5039; (*f*) A. Müller, *Science*, 2003, **300**, 749.
3 O. Greis, R. Ziel, B. Breidenstein, A. Haase and T. Petzel, *J. Alloy Compd.*, 1995, **216**, 255.
4 M. Schmidt, H. Oppermann, C. Hennig, R. W. Henn, E. Gmelin, N. Söger and M. Binnewies, *Z. Anorg. Allg. Chem.*, 2000, **626**, 125.
5 F. A. Hart, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon Press, Oxford, 1987, **vol. 3**, p. 1059.
6 R. L. Carlin, *Magnetochemistry*, Springer, Berlin, 1986.
7 *SHELXS/L*, *SADABS*, G. M. Sheldrick, University of Göttingen, 1997.
8 *DIAMOND 2.1*, K. Brandenburg, Crystal Impact GbR, 2001.