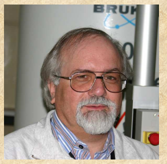

Porous inorganic capsules in action

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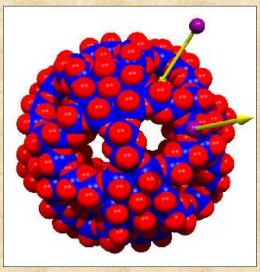
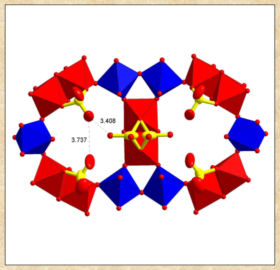
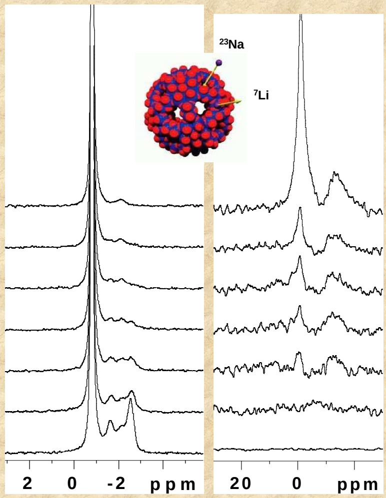


Spherical nanosized capsules (figure left) based on molybdenum oxide containing building blocks of the type $(pent)_{12}(linker)_{30} \equiv \{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(ligand)\}_{30}$ yield surprisingly stable structures, even in solution, with sizeable pores (figure right), finely sculptured interiors and, in between, tuneable functionalized channels with unprecedented molecular-scale filter properties.

The channel functionalities as well as the capsule size and charge can be extensively varied, with charge modulations leading to related changes in the affinity for cations, which can be extreme for highly charged species. This allows to study transfer processes and other interactions in a controlled and specific fashion.

A multinuclear NMR study has demonstrated [1)], that an exchange exists for small cations between the interior and surrounding of the capsules. These studies are extended here to investigate the influence of the environment on these processes [2)].

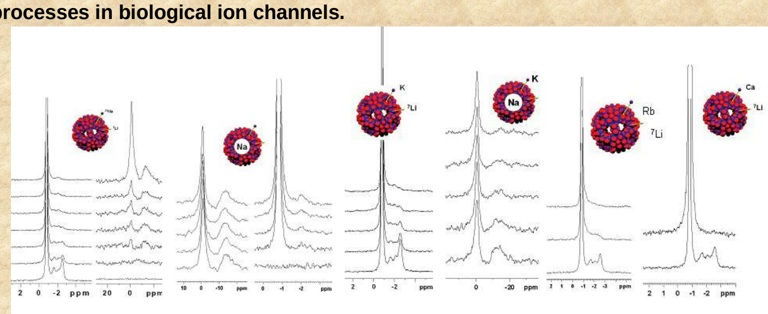


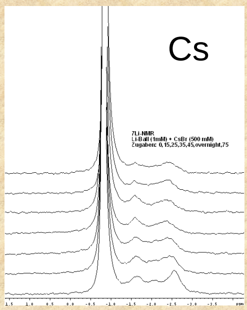


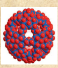
Basically, ^{7}Li-NMR was used to study the interactions of Li-cations with the target capsule

$$(Me_2NH_2)_{44}Li_n[Li_{28-n} \subset \{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^V_2O_4(SO_4)\}_{30}]\cdot ca.200\ H_2O$$

and to demonstrate the exchange of cations between the interior and the surrounding solution, e.g. in DMSO. Meanwhile, it could be demonstrated by multinuclear NMR that controlled cation exchanges take place where Na replaces Li and K replaces Li as well as Na. This can be continued up to Rb, while with Cs some new, yet unexplained results are observed, obviously due to the increased radius of the cation resulting in a completely different solvation behavior. Thus, this system may be useful as a model to simulate and study cation exchange processes in biological ion channels.

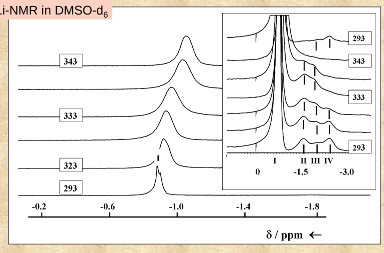


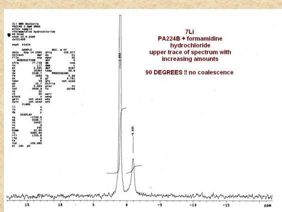


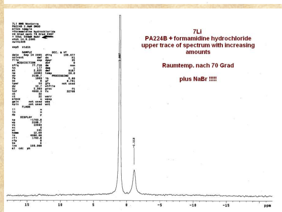


Angew. Chem. 2004, 116, 4566 – 4570 (corr.: 116, 5225)
Angew. Chem. Int. Ed. 2004, 43, 4466 – 4470 (corr.:43, 5115)

^{7}Li-NMR in DMSO-d_6



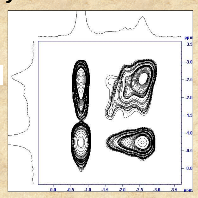




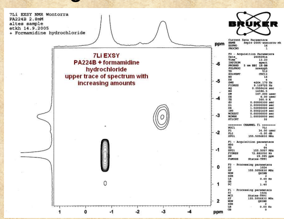
In contrary, the addition of pore fitting substances like formamidinium-hydrochloride allows to break the numerous equilibria and yields only a limited number of signals, obviously due to the interior and exterior cations.

Under these conditions, and the addition of a well defined amount of stoppers, we no longer observe a coalescence of the signals or an exchange of Li against Na. Thus, by using appropriate compounds, the interier of the capsules can be secured against the surrounding and thus be used as a transport system.

^{7}Li-NMR in DMSO-d_6



EXSY



Spherical nanosized capsules based on molybdenum oxide containing building blocks are stable in solution, exhibit numerous and designable exchange processes for different types of cations, strongly depending on the environment (solvent) and the properties of the cations (dimensions, charges).

Numerous heteronuclear NMR experiments allow to study especially the exchange behavior of the different types of cations and the important contribution of water as the transporting medium.

The influx and efflux processes can be interrupted by molecular corks and result in a clear separation of signals for the inner and outer cations. Variable temperature measurements document, that with formamidinium-hydrochloride molecules as corks a very stable sitiation is achieved up to temperatures around 90 degrees and exchange against other cations is definitely prevented.

Consequently, these cluster molecules can be viewed as “inorganic (artificial) cells” which mimic some processes occuring in nature and allow to study the exchange processes in great detail, avoiding contributions from conformational changes.

The corked capsules can be viewed as “nanocontainers” with an interior secured against the environment, thus, in favorable cases, being able to “transport” e.g. special cations.

1) A. Müller, D. Rehder, E.T.K. Haupt, A. Merca, H. Bögge, M. Schmidtmann, G. Heinze-Brückner
Angew. Chem., 2004, 116, 4566 / Angew. Chem. Int. Ed., 2004, 43, 4466 *(highlighted in Chemistry World 11/2004)*
2) E.T.K. Haupt, C. Wontorra, D. Rehder, A. Müller Chem. Commun. 2005, 3912-3914 *(highlighted in spectrallines 50/2005)*
3) D. Rehder, E.T.K. Haupt, H. Bögge, A. Müller Chem. Asian. J. 1-2, 76-81 (2006)

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