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A Unique Fluoride Nanocontainer: Porous Molecular Capsules Can Accommodate an Unusually High Number of “Rather Labile” Fluoride Anions**

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Dedicated to Professor Jean-Marie Lehn on the occasion of his 75th birthday

Abstract: *The present work refers to the challenging issue of fluoride anion recognition/binding in water by taking advantage of the unique possibilities offered by the porous molecular nanocontainers of the $\{Mo_{132}\}$ Keplerate type allowing the study of a variety of new phenomena. Reaction of the highly reactive carbonate-type capsule with aqueous HF results in the release of carbon dioxide and integration of an unprecedentedly large number of fluoride anions—partly as coordinated ligands at both the pentagonal units and the linkers, partly as a disordered water/fluoride assembly inside the cavity. The internal assembly and some of the fluoride ligands are easily released, which provides interesting options for future studies regarding coordination chemistry and catalysis under confined conditions.*

Fluorine is ubiquitous in the environment as the fluoride ion and is often considered an essential trace element owing to the effectiveness of fluoride as a cariostatic agent.[1,2] However, no vital biochemical role has been identified yet for fluoride. Moreover the optimal concentration range between deficiency and toxicity is quite narrow[2] and cumulative fluoride uptake may result in severe adverse effects on cellular metabolism.[3,4] In this context, it may be noted that i12fluoride-sensing riboswitches have been recently discovered in bacterial and archaeal messenger RNAs where they regulate expression of genes that encode fluoride transporters thereby counteracting the toxicity of fluoride.[5]

Owing to the dual role of the fluoride anion as both a beneficial and harmful species, its recognition, sensing, and encapsulation/fixation in water is attracting interest in the scientific community.[6] It is a most challenging task especially because of the high hydration energy of the fluoride ions,[6] and in spite of many related scientific reports (for reviews see Refs. [6a,b] and for a selection of quite a number of special-case studies see Refs. [7–15]), only a few systems display affinity and selectivity high enough to allow practical applications. While several hydrogen-type bonding receptors have been found to enclose well-defined fluoride/water clusters,[13–15] it has also been suggested that inorganic cages could provide effective fluoride receptors.[6a] This option has been considered in the present study through a special type of metallo-receptor, that is, porous water-soluble spherically shaped molybdenum oxide-based capsules of the type $\{(Mo)^{VI}Mo^{VI}_{5}\}_{12}\{Mo^{V}_{2}(ligand)\}_{30}$ known as Keplerates,[16] which have intriguing properties especially with respect to specific interactions with their environment and controlled internal transport.[17a] These molecular capsules can be obtained with a variety of anionic ligands that undergo easy inside–outside exchange, which makes them a unique class of anion receptors and carriers.[17b] In addition the capsules can act as cation receptors in case of sulfate or phosphate ligands.[17] In the context it is also worth noting that surfactant-encapsulated capsules can be integrated in supported liquid or lipid bilayer membranes.[18]

We report herein the synthesis, X-ray crystal structure analysis, and NMR spectroscopic characterization of an unprecedented $\{Mo_{132}\}$-type capsule (for stability of the general type see Supporting Information) containing approximately 60 fluoride ions. It should be emphasized that this compound is quite different from other reported fluorooxomolybdates.[19] The acetate-type capsule **1a**[16] is often used to obtain new capsules through exchange of acetate ligands,[20] but complete replacement of the acetate ligands is sometimes difficult to achieve and above all the method does not apply to weakly coordinating ligands. Fortunately the carbonate-type capsule **2a**[21] provides a convenient way to extend the scope of $\{Mo_{132}\}$-type capsules because of the easy decomposition of the CO_3^{2-} ligands. Though the capsule **2a** is stable in an aqueous solution in a limited range of pH values, CO_2 is released upon acidification which leads to a highly

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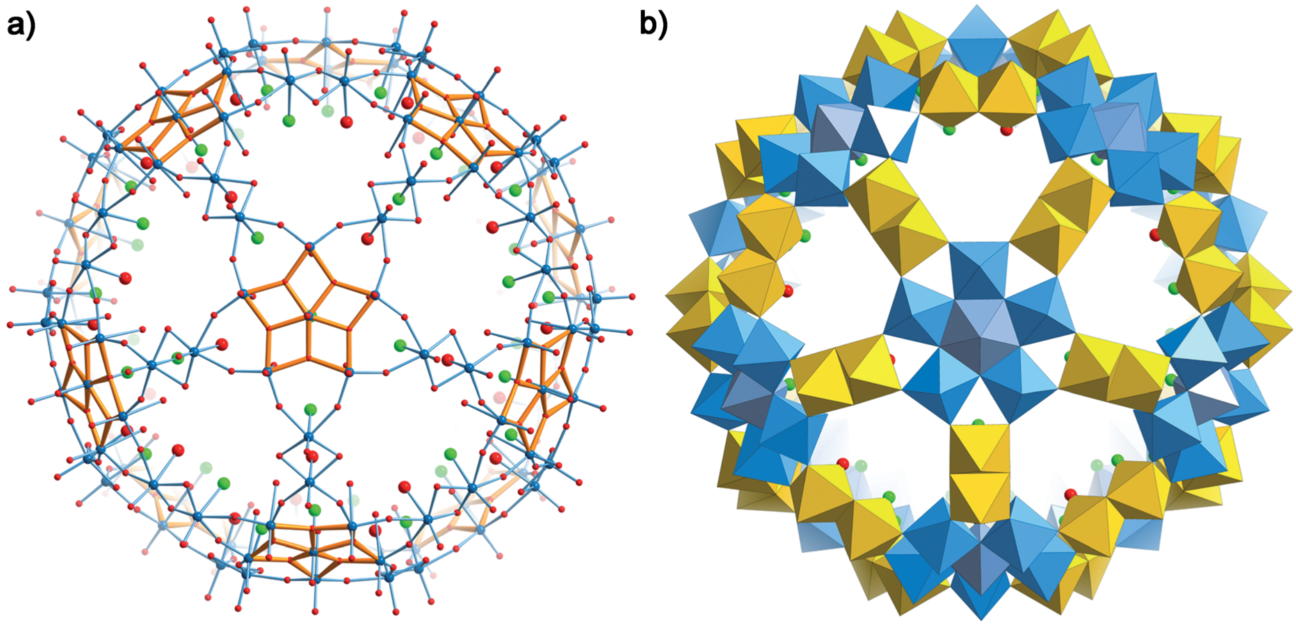

Figure 1. a) Ball-and-stick representation of the capsule **3a** highlighting the $\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_5(F)\}$ pentagonal units in orange. The H_2O ligands coordinated to Mo^V centers of the linkers and the F^- ions coordinated to Mo^V centers of the linkers and the central Mo^{VI} atoms of the pentagonal units are shown as enlarged red and green spheres, respectively (one possible H_2O/F^- ligand distribution scenario at the linker sites of cluster **3a** is shown; for the H_2O/F^- disorder at the linkers and related distances see the Supporting Information, Figure S3). Color code of the skeleton: Mo blue, O red. b) Polyhedral representation highlighting the pentagonal units (blue and violet) and the $\{Mo^V_2O_4\}$ linkers (yellow).

reactive capsule with a large number of Mo^V-type Lewis acid centers that are either coordinatively unsaturated or bound to easily exchangeable H_2O ligands and are therefore prone to bind a large diversity of ligands even if these ligands are only weakly coordinating. For example, the addition of an aqueous solution of HF and $(CH_3)_2NH_2F$ to a solution of **2** in water leads to the crystallization of compound **3** while the related compound **4** is obtained by pseudo-recrystallization of **3** in water (see Experimental Section).

$[NH_4]_{42}[\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^V_2O_4(CH_3COO)\}_{30}]\cdot$
ca. $10\,CH_3COONH_4 \cdot$ ca. $300\,H_2O \equiv$
$[NH_4]_{42}[\mathbf{1a}] \cdot$ ca. $10\,CH_3COONH_4 \cdot$ ca. $300\,H_2O \equiv \mathbf{1}$

$[NH_4]_{72}[\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo^V_2O_4(CO_3)\}_{30}]\cdot$
ca. $260\,H_2O \equiv [NH_4]_{72}[\mathbf{2a}] \cdot$ ca. $260\,H_2O \equiv \mathbf{2}$

$[NH_4]_{22}[(CH_3)_2NH_2]_{47}[((H_2O)_{18}\ +\ 15\,F^-) \subset$
$\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_5F\}_{12}\{Mo^V_2O_4(F)(H_2O)\}_{30}] \cdot$ ca. $250\,H_2O \equiv$
$[NH_4]_{22}[(CH_3)_2NH_2]_{47}[\mathbf{3a}] \cdot$ ca. $250\,H_2O \equiv \mathbf{3}$

$[(CH_3)NH_3]_{51}[(CH_3)_2NH_2]_{10}[Mo^{VI}_{72}Mo^V_{60}O_{372}F_{35}(H_2O)_{81}(MoO_4)_7]\cdot$
ca. $250\,H_2O \equiv [(CH_3)NH_3]_{51}[(CH_3)_2NH_2]_{10}[\mathbf{4a}] \cdot$ ca. $250\,H_2O \equiv \mathbf{4}$

Compounds **3** and **4** were characterized by elemental analysis, spectroscopic methods (IR, Raman and, to some extent, ^{19}F NMR) and X-ray crystallography. Compound **4** was primarily investigated to gain information about the behavior of **3a** in solution (easy release of the integrated water/fluoride species). The IR spectra of **3** and **4** (Supporting Information, Figure S1) show the characteristic band pattern of $\{Mo_{132}\}$-type capsules.[16b] Single-crystal structure analyses have confirmed that both capsules **3a** (Figure 1) and **4a** have the archetypal spherical skeleton consisting of 12 $\{(Mo^{VI})Mo^{VI}_5\}$ pentagonal units positioned at the vertices of an icosahedron and connected by 30 $\{Mo^V_2O_2(\mu\text{-}O)_2\}$ linkers. However, they differ in the composition of the inner wall and the content of the internal cavity. The related 132 internal coordination sites, in *trans* position to the doubly bonded oxo ligands, are occupied by water and fluoride ligands which may not be easily distinguished especially if both of them are disordered over the same site as is the case with the linkers. However, the related Mo–OH_2 and Mo–F bond lengths are significantly different (see part 3 of the Supporting Information and references therein) which allows fairly reliable structural models to be proposed.

Remarkably, the analysis of internal metal–ligand bond lengths shows that the capsule **3a** contains pentagonal units of the type $\{Mo^{VI}_6O_{21}(H_2O)_5F\}^{7-}$ instead of $\{Mo^{VI}_6O_{21}(H_2O)_6\}^{6-}$ which are commonly present in the $\{Mo_{132}\}$-type Keplerates (see Ref. [22] for another special case of the $\{(Mo^{VI})Mo^{VI}_5\}$ pentagonal unit). In contrast to the pentagonal units where the fluoride ion is clearly localized on the central seven-coordinate Mo^{VI} center (Figure S3a), the internal Mo^V–ligand bond lengths are half-way between those expected for Mo^V–F and Mo^V–OH_2 (Figure S3b), which is consistent with water and fluoride ligands equally disordered over the 60 related sites. Therefore the capsule **3a** features an internal hydrophilic ligand wall comprising altogether of approximately 42 fluoride ions and 90 H_2O ligands (error limit ± 2; cf. analytical data).

As in other $\{Mo_{132}\}$-type capsules with hydrophilic interiors, concentric shells of water molecules exist within the cavity of **3a**. Specifically, there are three under-occupied shells with diameters of 2.39–2.43, 4.10–4.36, and 7.90–8.26 Å, respectively (Figure S4), that most probably include the 15 remaining fluoride ions (see formula of **3** above) besides water molecules. Though the distinction between fluorine and oxygen is problematical in the present case, it should be noted that a fluoride ion can play the topological role of a water molecule as shown for example by the comparison of cyclic $[F(H_2O)]_4^{4-}$[15] and $(H_2O)_8$[23] assemblies. The largest shell is attracted towards the spherical ligand wall as shown by the corresponding hydrogen-bonding distances; for details, see Figure S4.

The intriguing structural features of **3a** reflect the influence of several factors including the *trans*-influence of Mo=O bonds and the high tendency of fluoride to form hydrogen bonds with water molecules. Also worth mentioning is the presence of well-defined water dimers, which are situated in the pores of the cluster **3a** (Figure 2). Water dimers are important members of a class of water polymers,[24a] which were recently clearly identified in the vapor phase at room temperature.[24b,c]

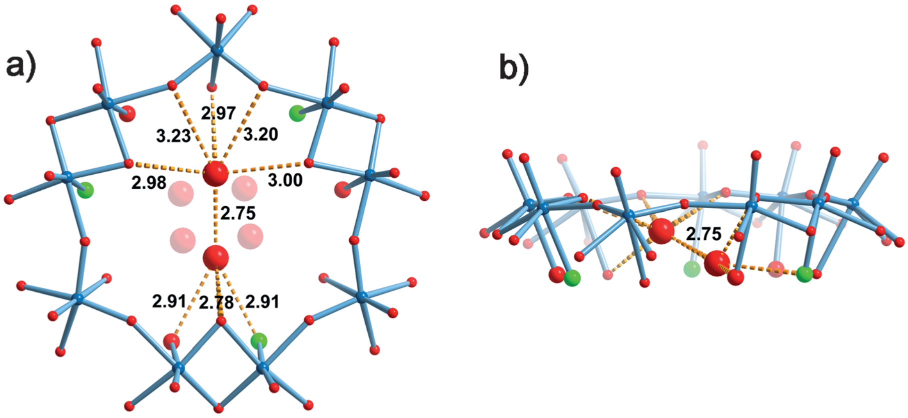

Figure 2. Top (a) and side views (b), in ball-and-stick representation, of one $\{Mo_9O_9\}$ pore of **3a** with a water dimer trapped inside. A water dimer is present in 12 of the 20 $\{Mo_9O_9\}$ pores of **3a**. In each case, they are disordered inside the pore over three nearly equivalent positions. For clarity, only one position (occupancy 33.3 %) is highlighted; the two others are shown transparent in the top view. Mo blue, O red, F green; interatomic distances in Å. The O···O distance (2.75 Å) compares well with those for water dimers in other inorganic materials (see for example, Ref. [24d]).

The capsule **4a** differs significantly from the parent one, **3a**, in the following: a) the absence of the water/fluoride shells in the internal cavity as well as of the water dimers in the pores, and b) the presence of the MoO_4^{2-} ligands replacing part of the internal F^-/H_2O ligands of **3a**. All together there are seven disordered MoO_4^{2-} ligands per capsule, three of which bind to the linkers in a μ_2-mode, two bind to the pentagonal units in a μ_3-mode, and the last two bridge pentagonal units and linkers in a μ_2-mode (for details see Figure S5). The observed structural change between the capsules **3a** and **4a** was partly anticipated and is easily explained: The unbound fluoride ions are easily removed from the interior of the negatively charged capsule upon dissolution of **3** in water while dissociation of some internal ligands may also occur as commonly observed, for example, for acetate ligands.[20] This dissociation weakens the capsule skeleton which undergoes partial decomposition while the resulting molybdate fragments are trapped as MoO_4^{2-} ligands at the internal capsule wall (see Supporting Information).

As expected, the Raman spectra of aqueous solutions of **3** and **4** are nearly the same; they are dominated by a few intense lines that are characteristic for each icosahedral $\{Mo_{132}\}$ oxide skeleton (see Figure S2).[25] Further insight into the transformation of **3a** in aqueous solution could in principle be obtained by using ^{19}F NMR spectroscopy which, however, proved to be difficult as interactions between the integrated fluoride guests and the host are rather weak: A preliminary study has confirmed the presence of different types of fluoride ions within the capsule while the system evolves over time (see Supporting Information, part 5).

In summary, the successful synthesis of **3** from **2** in solution demonstrates the potential of the carbonate-type capsule as a convenient starting reagent for the easy synthesis of novel capsules. Generally speaking, the controlled release of CO_2 from **2** in the presence of specific ligands opens new avenues in the field of $\{Mo_{132}\}$-type capsules. Furthermore, the fluoride-type capsule **3a** itself provides interesting options regarding solution/coordination chemistry under confined conditions as fluoride ions are present simultaneously at the linkers, the pentagonal units, as well as in the internal water shells. Easy exchange of internal ligands in $\{Mo_{132}\}$-type Keplerates is due in part to the *trans*-influence of the Mo=O bonds. It has been previously demonstrated that controlled removal of the internal ligands of the acetate ball **1a** generates exposed, catalytically active, $\{Mo^V_2O_4(H_2O)_2\}^{2+}$ units with labile water ligands and Lewis and Brønsted acid properties allowing catalytic reactions to be performed inside the cavity.[26] We are currently exploring the reactivity of the fluoride balls **3a** and **4a** to further assess the potential of Keplerates as nanoreactors. A preliminary result refers to hydrolysis of methyl acetate; the related complete results will be reported as soon as possible.

Experimental Section

For general information about materials and methods, see part 1 of the Supporting Information. For basic considerations about the stability of $\{Mo_{132}\}$ Keplerates, see part 6 of the Supporting Information.

3: A mixture of 1 M aqueous HF (10 mL) and aqueous dimethylammonium fluoride (1.6 mL, 7.04 mmol) was added under stirring to a solution of **2** (0.5 g, 0.019 mmol) in water (30 mL); stirring was continued for a further 10 min. The solution was subsequently left for crystallization in open air. After 5 days the precipitated dark-brown rhombohedral crystals were collected by filtration and washed with isopropanol and diethyl ether. Yield: 0.35 g (66% based on Mo). Elemental analysis calcd (%) $C_{94}H_{1080}F_{57}Mo_{132}N_{69}O_{680}$ (considering 200 molecules of water of crystallization): C 4.06, N 3.47, F 3.89; found: C 3.9, N 3.4, F 3.8; for the IR spectrum see Figure S1.

4: Methylammonium chloride (0.2 g, 2.45 mmol) was added to a stirred solution of **3** (0.5 g, 0.018 mmol) in water (20 mL); stirring was continued for a further 10 min. After 10 h the mixture was filtered and the filtrate left for crystallization in the open air. The brown crystals that formed over 3–5 days were collected by filtration, washed with ethanol and dried in air. Yield: 0.2 g (40% based on Mo). Elemental anal calcd (%) for $C_{71}H_{948}F_{35}Mo_{139}N_{61}O_{681}$ (considering 200 molecules of water of crystallization): C 3.09, N 3.10, F 2.41; found: C 3.0, N 2.9, F 2.4; for the IR spectrum see Figure S1.

Crystal data of **3**: $C_{94}H_{1180}F_{57}Mo_{132}N_{69}O_{730}$, $M_r = 28712.08\ \text{g mol}^{-1}$, rhombohedral, space group $R\bar{3}$, $a = 32.761(2)$, $c = 73.865(4)$ Å, $V = 68657(9)$ Å^3, $Z = 3$, $\rho = 2.083\ \text{g cm}^{-3}$, $\mu = 1.861\ \text{mm}^{-1}$, $F(000) = 42372$, crystal size $= 0.32 \times 0.24 \times 0.22\ \text{mm}^3$. A total of 410721 reflections ($1.92 < \Theta < 30.12°$) were collected of which 44945 reflections were unique ($R(\text{int}) = 0.0406$). $R = 0.0648$ for 31212 reflections with $I > 2\sigma(I)$, $R = 0.1086$ for all reflections; max/min residual electron density 1.77 and -1.18 e Å^{-3}.

Crystal data of **4**: $C_{71}H_{1048}F_{35}Mo_{139}N_{61}O_{731}$, $M_r = 28460.30\ \text{g mol}^{-1}$, rhombohedral, space group $R\bar{3}$, $a = 32.7482(11)$, $c = 73.724(3)$ Å, $V = 68472(5)$ Å^3, $Z = 3$, $\rho = 2.071\ \text{g cm}^{-3}$, $\mu = 1.951\ \text{mm}^{-1}$, $F(000) = 41706$, crystal size $= 0.38 \times 0.18 \times 0.16\ \text{mm}^3$. A total of 665302 reflections ($1.92 < \Theta < 30.15°$) were collected of which 44832 reflections were unique ($R(\text{int}) = 0.0502$). $R = 0.0939$ for 28007 reflections with $I > 2\sigma(I)$, $R = 0.1658$ for all reflections; max/min residual electron density 2.08 and -1.63 e Å^{-3}.

CCDC 1020226 (**3**) and 1020225 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Keywords: fluorides · polyoxometalates · porous capsules · receptors · water dimers

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