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An Inclusion Complex of Hexamolybdate inside a Supramolecular Cage and Its Structural Conversion

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Supporting Information

ABSTRACT: A self-assembled cage compound consisting of four concave ligands and two square-planar-coordinated Pd^{II} ions was found to quantitatively encapsulate a hexamolybdate dianion $[Mo_6O_{19}]^{2-}$ in solution. The addition of 1 equiv more of $[Mo_6O_{19}]^{2-}$ to the inclusion complex resulted in the formation of a precipitate from which single crystals were grown. X-ray analysis showed that a structural conversion had taken place upon crystallization: one hexamolybdate anion was found to be wrapped in a chiral, cyclic arrangement of three ligands in the absence of any Pd^{II} ions to give a compound of the formula $\{[Mo_6O_{19}]^{2-}@(ligand)_3+2H^+\}$. We postulate the stabilization of this arrangement by attractive C−H···O and CF_3−pyridine interactions.

The anionic polyoxometalates (POMs) formed from early transition metals, such as molybdenum, show a rich structural diversity as well as interesting electrical and optical properties with potential applications in catalysis, medicine, and materials science.[1] Examples include heteronuclear clusters,[2] giant wheels,[3] cages,[4] dendrimers,[5] and extended framework materials.[6] In particular, the covalent organic functionalization of POMs[7] has generated hybrid compounds with new properties such as light-induced electron transfer,[8] guest uptake,[9] and gel formation.[10] Furthermore, the versatile use of POMs as building blocks in supramolecular assembly has been demonstrated by the synthesis of chiral nanorods,[11] discrete rotaxanes,[12] and cucurbit[*n*]uril-based hybrids.[13] In the field of host−guest chemistry, POMs have been employed as large counteranions,[14] as redox-active nodes in framework solids,[6a] and as guests inside a metal−organic framework[15] and associated with bowl-shaped cyclotriveratrylenes and their metal−organic analogues.[16] The full encapsulation of a POM anion inside a discrete host compound, however, has only been rarely reported.[17]

We have recently introduced a new coordination cage **1** consisting of four concave, rigid bis-monodentate pyridyl ligands and two square-planar-coordinated metal ions, such as Pd^{II} (Figure 1d).[18] The positioning of the two metal ions on the opposite sides of the spherical cage compound generates a hollow cavity large enough to encapsulate a variety of negatively charged guests in between the positively charged metal centers.[19] We further found that the addition of excess amounts of dianionic guests to the host−guest complexes of **1** leads to aggregation and crystallization of the assembly.[20]

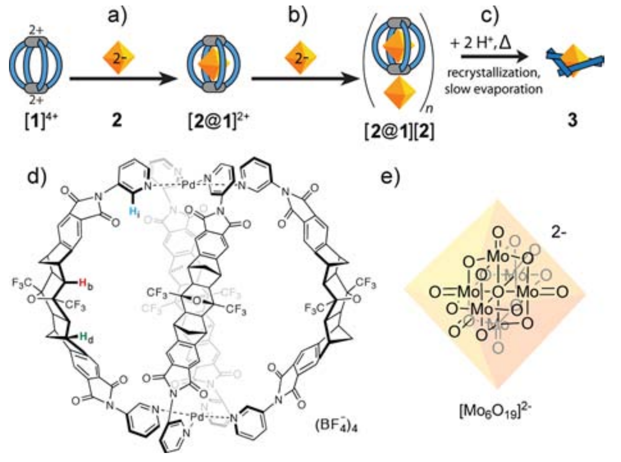

Figure 1. Schematic representation of the formation of (a) a soluble inclusion complex $[\mathbf{2}@\mathbf{1}]^{2+}$ and (b) the precipitate $[\mathbf{2}@\mathbf{1}][\mathbf{2}]$ which forms upon the addition of a second 1 equiv of **2**. (c) Recrystallization leads to conversion into the adduct **3**. Structures of (d) cage **1** and (e) hexamolybdate **2**.

The elucidation of the prerequisites for guest encapsulation sets the basis for the design of a system for light-initiated crystallization[21] and a new strategy for rotaxane formation[22] based on cage **1** and disulfonated aromatic guest molecules. Whereas the latter examples were based on the two-point electrostatic anchoring of the guests to the two oppositely arranged metal centers via both of their sulfonate groups, we show here that guests of suitable size featuring a spherical, delocalized negative charge can likewise be encapsulated inside the cavity of **1** (Figure 1a). We chose the octahedral hexamolybdate anion $[Mo_6O_{19}]^{2-}$ (**2**) as a candidate for the encapsulation study.[23]

Indeed, an NMR spectroscopic titration study using acetonitrile solutions containing cage **1** and the tetra-*n*-butylammonium salt of **2**, $(N^nBu_4)_2[Mo_6O_{19}]$, indicated the formation of a soluble inclusion complex $[\mathbf{2}@\mathbf{1}]^{2+}$ through the observation of a signal shifting of certain protons of cage **1**. In particular, the signal of the cage's inward-pointing hydrogen atoms H_b (red in Figures 1d and 2) was found to shift

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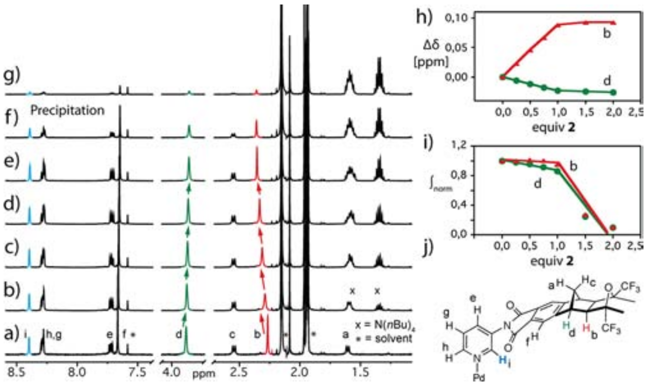

Figure 2. ^{1}H NMR titration of (a) a 0.7 mM solution of cage **1** in CD_3CN with (b) 0.25, (c) 0.50, (d) 0.75, (e) 1.00, (f) 1.50, and (g) 2.00 equiv of guest **2** (298 K, 500 MHz, $N^nBu_4^+$ signals at 0.9 and 3.1 ppm omitted). The plotting of (h) the change in the chemical shift $\Delta\delta$ and (i) the relative integral values of the ligand's proton signals H_b and H_d shows the sharp transition between guest uptake and guest-induced precipitation after the addition of 1 equiv of **2**. (j) Signal assignment to the structure of cage **1**.

downfield upon the addition of up to 1 equiv of guest **2**. Proton H_d (green in Figures 1d and 2) was concomitantly found to shift upfield. The relative chemical shift $\Delta\delta$ of both signals ceased after the addition of the first 1 equiv of guest **2** was completed, in accordance with the conception that all cages have been saturated with guest **2** upon the addition of an equimolar amount of **2** (Figure 2h). It is interesting to note that the signal of the cage's inward-pointing hydrogen atom H_i, which is located near the two Pd^{II} ions (blue in Figures 1d and 2), does not undergo a significant shift upon the addition of guest **2**, which is in contrast to the behavior caused by our previously examined dianionic aromatic guests.[20] This observation can be explained by comparing the structure and charge localization of the disulfonates and the spherical hexamolybdate anion: whereas the former are pointing their sulfonate groups toward H_i, guest **2** gets in closer contact with the ligand backbone's protons H_b. A molecular model (PM6) supports this assumption (Supporting Information, Figure S1). In well accordance with our previous findings[18] further is the observation that the addition of more than 1 equiv of guest **2** to the soluble host–guest complex [**2**@**1**]$^{2+}$ leads to the immediate formation of a microcrystalline precipitate of anticipated composition [**2**@**1**][**2**]. The precipitation is going along with a gradual decrease in the signal intensities of the cage's proton signals in the ^{1}H NMR spectrum (Figure 2i). The addition of 2 equiv of **2** to **1** thus results in the almost complete vanishing of the cage's NMR signals (Figure 2g), and the further addition of **2** does not result in any additional precipitation.

Furthermore, the formation of a soluble host–guest complex [**2**@**1**]$^{2+}$ was confirmed by electrospray ionization mass spectrometry (ESI-MS; Figure 3). The spectrum shows the signal for [**2**@**1**]$^{2+}$ as the largest peak, accompanied by smaller peaks of the free ligand and cage **1**.

Our attempts to obtain single crystals of the species [**2**@**1**][**2**] reproducibly delivered crystals whose X-ray structure determination revealed a surprising result: upon recrystallization, the host–guest complex of the Pd^{II}-based coordination cage comprising four organic ligands was found to transform into assembly {**2**@(ligand)$_3$+2H$^+$} (**3**), thus in the absence of any Pd^{II} ions. We suspect that the protons present in **3** result from residual water under the formation of $Pd(OH)_2$, driven by the high stability of aggregate **3**.

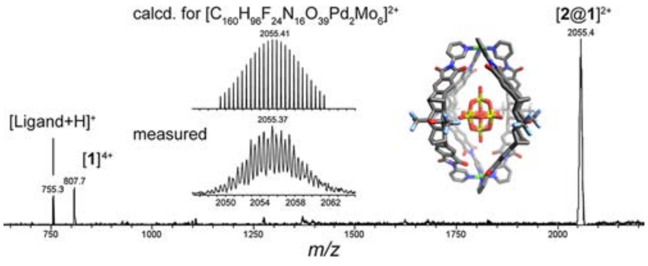

Figure 3. ESI-MS spectrum of the host–guest complex [**2**@**1**]$^{2+}$ (including the result of the PM6 structure optimization).

The structure of **3** reveals that a hexamolybdate anion is wrapped into a chiral, cyclic arrangement of three ligands in an "egg in a nest" shape of approximate D_3 symmetry (Figure 4).

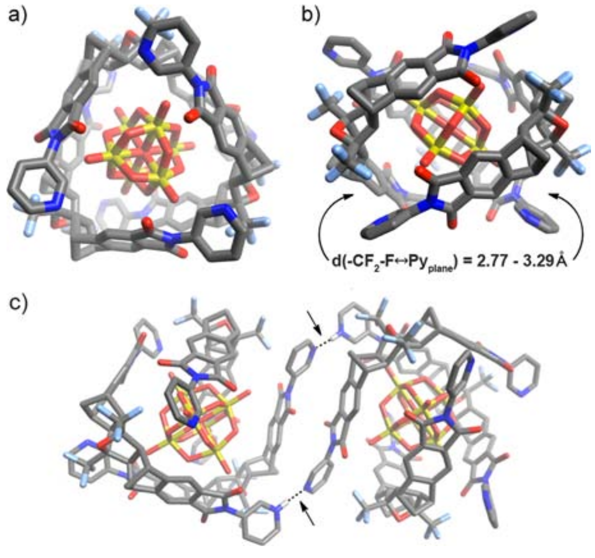

Figure 4. X-ray crystal structure of **3**: (a) top view and (b) side view highlighting two of the six close CF_3–pyridine contacts. (c) Two aggregates of **3** form a dimer via two pyridinium–H···pyridine hydrogen bonds (indicated by arrows). Other hydrogen atoms and solvent molecules have been omitted for clarity. See the Supporting Information for detailed crystallographic data (CCDC 857446). Color code: C, gray; N, dark blue; O, red; F, light blue; Mo, orange.

Two of the six pyridine nitrogen atoms were found to be protonated. Intermolecular hydrogen bonds to a nonprotonated pyridyl moiety of a neighboring aggregate (Figure 4c) and an acetonitrile molecule are observed involving these hydrogen atoms, respectively (Supporting Information, Figure S2). The remaining four pyridyl nitrogen atoms could not be identified as possible hydrogen-bond donors. Close C–H···O contacts are observed between the hydrogen atoms of the [7]oxabicyclo[2.2.1]heptane moieties of the ligands and the hexamolybdate cluster, with the smallest H–O distance being 2.54 Å (Supporting Information, Figures S3 and S4).[24] Eye-catching is the further observation of six rather close CF_3–pyridine contacts (F–ring plane distance 2.77–3.29 Å) between all three ligands that might contribute to the stabilization of the supramolecular aggregate. In order to be able to judge the significance of this observation, we performed a CCDC crystal structure database survey. We found more than 2000 hit structures with CF_3 groups positioned over pyridine ring planes, showing that five out of the six distances found in the X-ray structure of **3** are clearly on the short to very short side (Supporting Information, Figure S5). Gas-phase quantum mechanical (QM) calculations on the MP2/6-311++G(d,p) level of theory further indicated that a CF_3 group (of CH_3CF_3) positioned over the middle of a pyridine ring in a distance (F—ring plane) of 2.9 Å represents a minimum on the potential energy surface, thus delivering an energetic stabilization of about 11.4 kJ/mol (2.8 Å and 20.4 kJ/mol for the corresponding protonated pyridinium model; Supporting Information, Figures S6—S9). This result is in well accordance with previously reported data including X-ray structural analysis and QM calculations of a variety of C—F···π contacts involving electron-deficient aromatic systems such as pyridine.[25] Thus, the cyclic arrangement of six of these noncovalent interactions and the multiple C—H···O hydrogen bonds are expected to be, at least partially, responsible for the structural conversion of [**2**@**1**][**2**] into **3** upon recrystallization [going along with the protonation of two pyridine nitrogen atoms and the formation of a $Pd(OH)_2$ precipitate].

In conclusion, we presented that the hexamolybdate dianion can be incorporated into a metal—organic coordination cage showing a preference for the binding of anionic guest molecules in solution. The encapsulation of the prototypical Lindqvist-type compound **2** inside a discrete host compound may open the possibility of modulating the cluster's electronic and optical properties and the accessibility of substrates to the POM core in catalytically active systems by the design of the surrounding cage structure. Together with the recent advances in the covalent organic functionalization of POMs, this noncovalent approach of covering an organic shell around an inorganic cluster compound may lead to the generation of hybrid materials with new properties and functions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data of **3** in CIF format, a CCDC database survey, synthetic procedures and characterization, NMR spectra, X-ray crystal structure of **3**, and QM calculation results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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