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Changing the Oxothiomolybdate Ring from an Anionic to a Cationic Receptor

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The ionic recognition properties of neutral oxothiomolybdenum wheels can be changed from anionic to cationic through ionization of the internal aquo ligands. In the solid state, $[Mo_8O_8S_8(OH)_{10}(H_2O)]^{2-}$ (**1**) interacts with two Cs^+ cations to give a close supramolecular host–guest arrangement. Such interactions appear to be maintained in solution as a labile association.

The polycondensation of the dioxothio cation $[Mo_2O_2S_2(OH_2)_6]^{2+}$ originates a family of compounds based on the simple linear chaining of the dinuclear building block through double hydroxo bridges.[1,2] In a polar medium, the oligomeric strings loop to give molecular inorganic cycles. The self-assembly process can be controlled by means of templating agents, mainly anionic groups such as phosphates, metalates, or polycarboxylates, which are found to be encapsulated covalently as guests in the adapted central cavity.[2] In the presence of soft bases, such as halides (Cl^-, Br^-, and I^-), supramolecular assemblies based on hydrogen bonding were evidenced either in the solid state or in solution, thus highlighting anionic recognition properties for this class of compounds.[2a,d] Here, we report on the interactions between the inorganic cycle and two Cs^+ cations after ionization of the polarized inner aquo ligands, thus evidencing that the inorganic ring can be changed from an anionic receptor to a cationic one.

The addition of a strong base to the neutral inorganic cycle $[Mo_{10}O_{10}S_{10}(OH)_{10}(H_2O)_5]$ in water leads to partial depro-tonation of the inner H_2O molecules.[3] In the presence of Cs^+ cations, a reorganization occurs and a dianionic octameric ring bicapped by two Cs^+ cations with formula $[Cs_2Mo_8O_8S_8(OH)_{10}(H_2O)]\cdot33H_2O$ (**1**) is formed.

The synthesis of **1** was obtained by suspending the precursor $K_2[I_2Mo_{10}S_{10}O_{10}(OH)_{10}(OH_2)_5]\cdot15H_2O$ (1 g, 0.4 mmol)[2] in 60 mL of deionized water. The pH was adjusted at about 6 through slow addition of a 1 mol·L^{-1} sodium hydroxide solution (1.2 mL). The cloudy solution was clarified by centrifugation. Then, cesium chloride (0.33 g, 2 mmol) was added, provoking the precipitation of a yellow solid (**1**). After filtration and drying with EtOH and diethyl ether, 1 g of crude product **1** was obtained. Yield: 91%. IR [KBr pellet, $\bar{\nu}$ (cm^{-1})]: 960 (s), 937 (sh), 511 (s), 488 (s). Anal. Calcd for **1** ($[Cs_2Mo_8O_8S_8(OH)_{10}(H_2O)]\cdot33H_2O$): Cs, 12.08; Mo, 34.88; S, 11.66; H, 3.57. Found: Cs, 12.11; Mo, 34.41; S, 11.69; H, 3.71. A total of 1 g of **1** was dissolved in 130 mL of *N,N*-dimethylformamide (DMF), and the resulting solution allowed to stand in air for crystallyzation.

After 24 h, thin orange air-sensitive crystals of **1′** suitable for X-ray diffraction analysis[4] were collected. Yield: 45%. IR [KBr pellet, $\bar{\nu}$ (cm^{-1})]: 1473 (w, DMF), 1384 (w, DMF), 960 (s), 1107 (w, DMF), 938 (s), 506 (s). Anal. Calcd for

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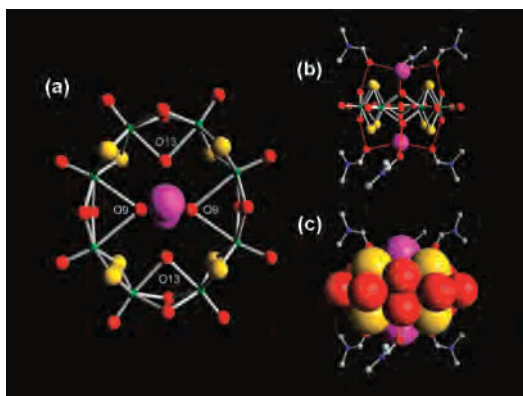(3) Cadot, E.; Dolbecq, A.; Salignac, B.; Sécheresse, F. *J. Phys. Chem. Solids* **2001**, *62*, 1533.
(4) Crystal data for **1′**: formula $[Cs_2Mo_8O_8S_8(OH)_{10}(OH_2)]\cdot7DMF\cdot2H_2O$; crystal dimensions 0.35 × 0.06 × 0.06 mm, mounted in paratone oil at *T* = 100 K; Bruker X8 CCD crystal single-crystal diffractometer equipped with a Mo anode and a graphite monochomator (λ = 0.710 73 Å). Data were collected out to a $2\theta_{max}$ value of 50°; ω scan; Lorentzian and polarization correction; semiempirical (*SADABS* program) absorption 2.417 mm^{-1}; min/max transmission 0.4850/0.8685; total reflections collected, 67 364; *R*(int) = 0.0606; system, trigonal, space group $R\bar{3}$; *a* = 38.626(2) Å, *c* = 13.6978(16) Å; *V* = 17699(2) Å^3; *Z* = 9; ρ_{calc} = 1.805 g·cm^{-3}; structure solution by direct methods, refinement parameters over all reflections, R1 = 0.0874 for 6922 independent reflections with *I* > 2σ(*I*) and 363 parameters, R1 = 0.1143 for all reflections; software used, Bruker X8, *SAINT*, *SHELXTL*; no H atoms were included. Note that several disordered DMF molecules were ultimately removed from the structure and the data set was corrected with the program *PLATON SQUEEZE*. Further details on the crystal structure investigations may be obtained in the CIF file (see the Supporting Information).

Figure 1. Supramolecular assembly of [Cs₂Mo₈O₈S₈(OH)₁₀(H₂O)]·6DMF: (a) top view (without DMF) showing the two capping Cs⁺ cations (purple spheres) and the inner components of the elliptical ring; (b) side view showing the six DMF molecules spanning the bridging hydroxo groups and the Cs⁺ cations; (c) space-filling model highlighting the penetration of the Cs⁺ ion within both sides of the open cavity.

$[Cs_2Mo_8O_8S_8(OH)_{10}(H_2O)]\cdot 8DMF\cdot 2H_2O$:[5] Cs, 11.93; Mo, 34.47; S, 11.52; C, 12.93; H, 3.26; N, 5.03. Found: Cs, 10.82; Mo, 35.13; S, 11.60; C, 13.28; H, 3.07; N, 5.13. ESI-MS (DMF/CH₃CN, negative mode): m/z 643 ($[Mo_8]^{2-}$ − 2H₂O), 673 ($[Mo_8]^{2-}$), 698 ($[Mo_8]^{2-}$·3H₂O), 720 ($[Mo_8]^{2-}$·H₂O·2CH₃CN), 769 ($[Mo_8]^{2-}$·3H₂O·2DMF), 789 ($[Mo_8]^{2-}$·H₂O·3DMF), 817 ($[Mo_8]^{2-}$·4DMF), 1582 ($[CsMo_8]^-$·2H₂O·DMF).

X-ray diffraction analysis reveals an elliptical octameric ring associated with two Cs⁺ cations (Figure 1). The inorganic cycle consists of four $\{Mo_2O_2S_2\}$ units connected to each other by double hydroxo bridges. The charge balance is ensured by the presence inside the ring of two opposite hydroxo bridges with characteristic short Mo−O bond distances [2.24(1)−2.25(1) Å]. The presence of two Cs⁺ cations on both sides of the ring is a striking feature of the structure. Using the common terminology, such an association corresponds to an exclusive cesium−cryptate association,[6] denoted as $2Cs^+\cap\{Mo_8\}$. Both Cs⁺ ions are related by an inversion center and appear slightly displaced from the center of the cavity to give short distances with two S atoms [3.66(1)−3.67(1) Å], close to the sum of the ionic radii (3.58 Å). The supramolecular arrangement between the ring and the Cs⁺ cations involves three DMF molecules bridging the Cs⁺ cations [3.03(1)−3.16(1) Å] and hydroxo groups of the ring [2.67(3)−2.77(2) Å] through the formamide C=O groups. The coordination sphere of the Cs⁺ cations is completed by a terminal O atom belonging to the adjacent $\{Mo_8\}$ cyclic unit. The cavity of the molecular receptor contains one H₂O molecule coordinated to two adjacent Mo atoms [Mo−OH₂ = 2.78(3)−2.81(4) Å] and symmetrically disordered over two main sites (SOF = 0.5). This H₂O molecule contracts strong hydrogen bonds with the adjacent OH groups [O···O = 2.59(3)−2.64(4) Å] in
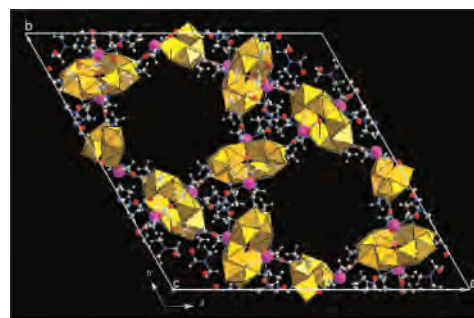
(5) The small discrepancy of one DMF molecule between formulas determined by elemental analysis and X-ray structure is due to the difficulty in locating the last DMF solvate highly disordered in the solid-state structure.
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Figure 2. Structural view of **1** in the *a/b* plane showing the large void channels containing H₂O and free DMF molecules (not shown for clarity).
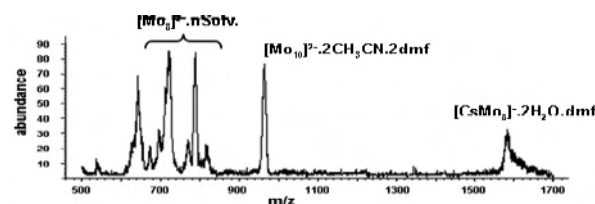

Figure 3. ESI-MS spectrum of **1′** in DMF/CH₃CN. The assignments are given in the experimental section.

fair agreement with distances obtained from density functional theory (DFT) calculations (2.55 Å).

In the solid state, **1** crystallizes in the $R\bar{3}$ space group to give a 3D hexagonal network through the direct connections of the Cs⁺ ion and terminal O atom belonging to the adjacent $\{Mo_8\}$ ring [Cs−O = 3.18(2) Å]. The 3D network along the (001) projection shows large channels that reach about 16 Å in diameter (Figure 2). These large channels are partially filled by H₂O molecules and a disordered DMF solvent (according to the elemental analysis, half of a DMF molecule per asymmetric unit is missing).

Electrospray ionization mass spectrometry (ESI-MS) has been carried out on **1′** in a DMF/CH₃CN mixture under soft experimental conditions. Despite a low ionization yield, the m/z peaks are fully consistent with the presence of the $[Mo_8O_8S_8(OH)_{10}(H_2O)]^{2-}$ anion surrounded with variable amounts of solvent, i.e., H₂O, CH₃CN, or DMF (Figure 3). The broad peak at m/z 1582 was assigned to the ion-pairing species $[Cs-Mo_8]^-$, showing that the exclusive association between $[Mo_8]^{2-}$ and Cs⁺ can be maintained under ESI-MS conditions. The peak at m/z 964 is attributed to the presence of the dianionic $[Mo_{10}O_{10}S_{10}(OH)_{12}(H_2O)_3]^{2-}$ species. Such results evidence that, under ESI-MS conditions (about 10^{-4} mol·L⁻¹), equilibria take place, involving several species such as $\{Mo_{10}\}^{2-}$, $\{Mo_8\}^{2-}$, and a Cs⁺ cation.

¹H NMR characterization in DMF-d_7 (Figure 4a) at 215 K yields two sharp lines ($\Delta\nu_{1/2}$ = 2 Hz) at 11.02 and 11.98 ppm, which correspond to the two distinct hydroxo bridges connecting the $\{Mo_2O_2S_2\}$ units within the frozen elliptical ring. As the temperature increases, both lines shift toward low frequency and collapse at 285 K to give a broad line ($\Delta\nu_{1/2}$ = 50 Hz at ∼10.1 ppm). Such behavior is consistent with a "flip-flop" motion between two equivalent elliptical conformations of the ring, leading at high temperature to an averaged D_{4h} symmetry. No other ¹H NMR resonances were observed, meaning that a fast exchange occurs between the protons of the inner hydroxo groups and those of the attached
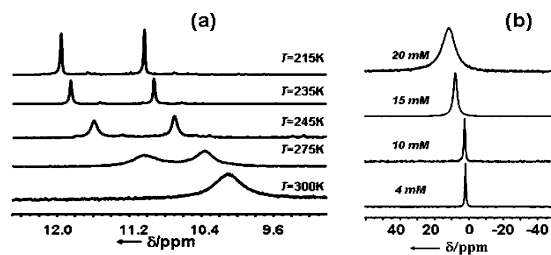
Figure 4. (a) Variable-temperature ^{1}H NMR of **1'** in DMF (hydroxo resonances). (b) Variable-concentration ^{133}Cs NMR at 300 K consistent with exclusive anion−cation associations, such as {Cs−Mo$_8$}$^-$ and {Cs$_2$−Mo$_8$} involved in an equilibrium process.

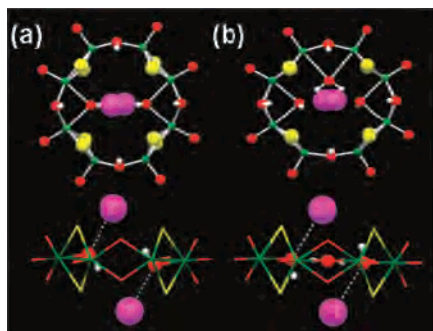**Figure 5.** Top (up) and side (bottom) views of DFT-optimized geometries of the complexes [Cs$_2$Mo$_8$] (a) and H$_2$O@[Cs$_2$Mo$_8$] (b) in the gas phase.

water over the temperature range 215−350 K. The line shapes of the ^{1}H NMR spectra were analyzed according to a two-site exchange process, using the Bloch equations. The activation parameters were derived by an Eyring analysis and yield $\Delta G^{\ddagger} \approx \Delta H^{\ddagger} = 50$ kJ·mol^{-1} and $\Delta S^{\ddagger} \sim 0$. The enthalpic component of the fluxional barrier could be assigned to the internal proton transfer from water to hydroxo groups, while the $\sim$0 value obtained for $\Delta S^{\ddagger}$ means that no significant change in solvation occurs between the elliptical structure and the activated conformations.

^{133}Cs NMR experiments carried out at variable concentration from 4 to 20 mmol·L^{-1} of **1'** in DMF (Figure 4b) reveal a single line where the chemical shift and line width vary gradually from 1.9 to 12.5 ppm and from 40 to 560 Hz, respectively. Such behavior demonstrates qualitatively that interactions between Cs$^+$ cations and the ring exist in solution through a fast exchange process.[6,7] The increase of the concentration would favor interactions between the ion pairs. The systematic shift to downfield is in agreement with Cs complex formation.[8] The weak paramagnetic shift (10.6 ppm) is consistent with a weak overlap between the orbitals of the donor S atoms and the outer p orbitals of the Cs ions.[6b] Therefore, the main effect of the exclusive complex formation upon ^{133}Cs NMR parameters lies in the significant increase of the line width from about 2 Hz for the uncom-

plexed Cs$^+$ cation (CsNO$_3$ in DMF) to 560 Hz for the NMR line of ^{133}Cs in the 20 mmol·L^{-1} solution. Because electric field gradient anisotropy is the principal origin of relaxation for quadrupolar nuclei, the observed increase of the relaxation rate reflects the anisotropy of the coordination sphere of Cs$^+$ in the exclusive complex, which consists of three S atoms belonging to the ring moiety and of three labile DMF molecules.

Finally, geometry optimizations have been carried out with DFT[9] on five model molecules, namely, the isolated dianionic ring [Mo$_8$O$_8$S$_8$(OH)$_{10}$]$^{2-}$, hereafter abbreviated as [Mo$_8$]$^{2-}$, [Cs$_2$Mo$_8$], and the same complexes encapsulating either one or two H$_2$O molecule(s): H$_2$O@[Mo$_8$]$^{2-}$, H$_2$O@[Cs$_2$Mo$_8$], and (H$_2$O)$_2$@[Cs$_2$Mo$_8$]. No significant elliptical deformation of the Mo$_8$ framework is obtained for the free dianion, showing that the repulsion between the hydroxo groups is not the driving force to this distortion. Surprisingly, the presence of the counterions in [Cs$_2$Mo$_8$] induces an elliptical deformation reversed with respect to observation (Figure 5a). This is explained by the attraction exerted by Cs$^+$ (Cs···O = 2.945 Å), which pulls the hydroxo O atoms out of the average molecular plane and drags the attached metal atoms. The encapsulation of one H$_2$O molecule in the position shown in Figure 5b maintains the (OH)$^-$ close to the average plane and reverses the elliptical distortion according to the crystal structure, even though the computed deformation is much smaller. The bond energy of one H$_2$O molecule encapsulated in [Cs$_2$Mo$_8$] was calculated to be 17.6 kJ·mol^{-1} with respect to separate [Cs$_2$Mo$_8$] and H$_2$O. The encapsulation of a second H$_2$O molecule inside [Cs$_2$Mo$_8$] is computed to be exothermic by 35.8 kJ·mol^{-1} with respect to separate fragments. Nevertheless, (H$_2$O)$_2$@[Cs$_2$Mo$_8$] exhibits a circular geometry analogous to that of [Mo$_8$]^2. Therefore, DFT calculations show that the elliptical conformation of the molybdic cycle is mainly induced by the presence of a single inner H$_2$O molecule, thus consistent with the crystallographic data.

In conclusion, we evidenced the formation of a new exclusive cesium−cryptate complex by changing the ionic character of an oxothiomolybdate ring. This result emphasizes the high modularity and flexibility of this class of inorganic cycles for a fine-tuning of their host−guest properties.

Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) DFT calculations have been carried out with the 2004 version of the ADF program (ADF2004.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com., 2004) using the BP86 exchange-correlation functional. All atoms are described with the Slater basis sets referred to as TZP (triple-ζ polarized for the valence shell) in the User's Guide.