Polyoxometalates

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Supramolecular Chemistry on a Cluster Surface: Fixation/Complexation of Potassium and Ammonium Ions with Crown-Ether-Like Rings**

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Dedicated to Professor C. N. R. Rao on the occasion of his 75th birthday

Ion pairing in aqueous solution orchestrates a variety of processes occurring in several areas of science, including polyoxometalate chemistry.[1] Our present interest refers to the anionic cluster $[H_3Mo_{57}V_6(NO)_6O_{183}(H_2O)_{18}]^{21-}$ (**1a**) of $(NH_4)_{21}[H_3Mo_{57}V_6(NO)_6O_{183}(H_2O)_{18}]\cdot 65\,H_2O$ (**1**).[2,3] Cluster **1a** not only has very interesting magnetic and electronic properties,[4] but also exhibits a wide range of unique nucleophilic surface functionalities, which are the basis for a novel type of molecular growth process that occurs in six external holes.[5a–c] Regarding its multifunctionality, this highly charged cluster, which is an especially interesting member of the polyoxometalate family,[5d–j] should be an appropriate object for the investigation of its interactions with cations.[6] Whereas the structure of **1a** was previously determined by single-crystal diffraction studies of the ammonium salt,[2,8] we intended to use experimental and theoretical studies to gain more insight into the distributions of different cations on the cluster surface, and in particular in the external holes. Therefore we synthesized compound **2**, which contains potassium along with ammonium cations. These cations were selected as they have the appropriate sizes to interact with the surface functionalities. Furthermore, we discovered a remarkable separation/selective complexation process of these cations on the surface of **2a**, which was unprecedented in inorganic supramolecular chemistry and in ion-pairing research. The latter aspect should have consequences for the understanding of the self-assembly processes for the present type of giant polyoxometalates.

$$[H_3Mo_{57}V_6(NO)_6O_{183}(H_2O)_{18}]^{21-} \qquad (\mathbf{1a} = \mathbf{2a})$$

$$(NH_4)_{21}\cdot \mathbf{1a}\cdot 65\,H_2O \qquad (\mathbf{1})$$

$$(NH_4)_{11}K_{10}\cdot \mathbf{2a}\cdot 70\,H_2O \qquad (\mathbf{2})$$

Compound **2** with the two different cations (Figure 1) was prepared in a similar fashion to **1**, but in presence of K^+ ions in

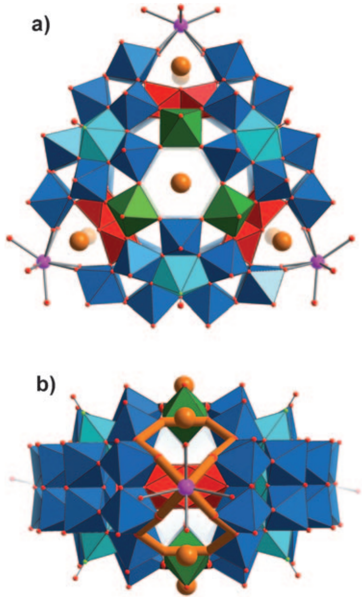

Figure 1. a) Polyhedral (cluster skeleton) and ball-and-stick representation (coordinated cations) of **2a** including the characteristic surface area (view in the direction of the C_3 axis). The skeleton is built up by three $\{Mo_{17}\}$ units (MoO_6 octahedra in blue, and the central $MoNO_6$ pentagonal bipyramid in cyan) connected through three $\{Mo_2\}$ groups (built up by two face-sharing MoO_6 octahedra; red) and six $V^{IV}O_6$ octahedra (green). For all structural details of **1a**, including the $O{=}V(H_2O)^{2+}$ groups, see Ref. [2]. b) The corresponding side view (i.e., approximately perpendicular to the C_3 axis). The region of two of the six $\{Mo_4VKO_6\}$ rings with a shared potassium ion is emphasized. An independent formula for the arrangement in (a) and (b) is not given as it corresponds to part of the solid state structure. Spheres: O red, N (of NH_4^+) orange, K pink.

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the reaction medium (see the Experimental Section). It crystallizes in the space group $P6_3/mmc$, and was characterized by elemental analyses, thermogravimetry (to determine the number of crystal water molecules), redox titrations (to determine the number of V^{IV} and Mo^V centers), IR and UV/Vis spectroscopy, single-crystal X-ray structure analysis, and bond valence sum (BVS) calculations (see Experimental Section).

According to the single-crystal X-ray structure analysis, the basic cluster skeleton of the anion **2a** without the coordinated cations corresponds, as expected, to that of the previously published anion **1a**.[2] The cluster comprises three large $\{Mo_{17}\}$ fragments linked by six vanadium(IV) centers and three $\{Mo^V_2\}$ type units such that external holes are generated (Figure 1).[2] The interesting result is that two $\{Mo_3V_3O_6\}$ crown-ether-like pores (Figure 2a) and the functional groups of the six external holes of **2a** interact differently with potassium and ammonium ions, which leads to their separation/selective complexation whereby the $\{Mo_4VKO_6\}$ rings play a key role. (For arguments for the positioning of the ammonium ions, see below and reference [9]).

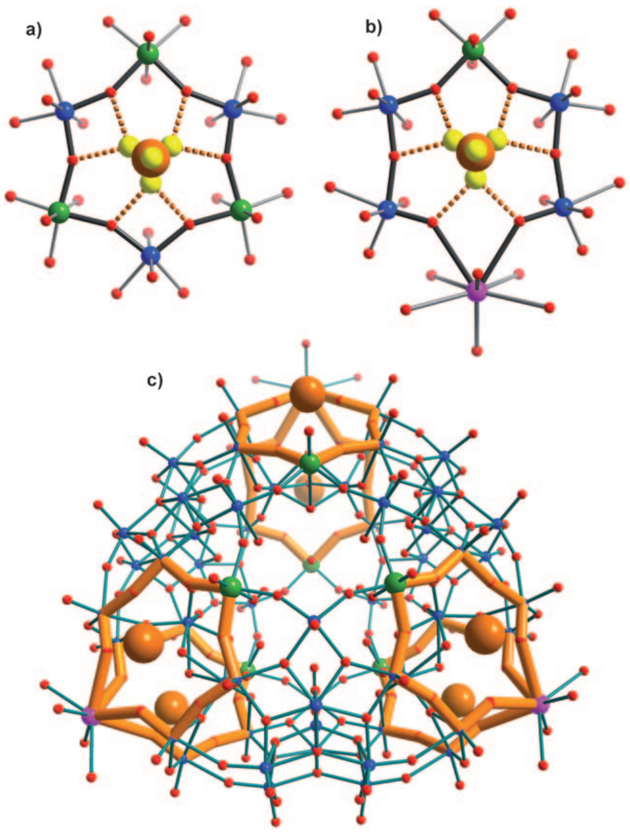

Figure 2. a) Ball-and-stick representation of one of the two $\{Mo_3V_3O_6\}$ pores of **2** containing an ammonium cation (hydrogen atoms modeled). N···O distances: 3.15 Å. b) One of the six $\{Mo_4VKO_6\}$ rings each formed by four skeletal bridging and two terminal oxygen atoms (see text) as well as a vanadium and potassium atom. N···O distances: 3.14–3.28 Å. c) The incorporation of the six $\{Mo_4VKO_6\}$ rings in the cluster holes. The region of two rings with one common potassium ion is also shown in Figure 1b. Mo blue, V green, K pink, O red; NH_4^+: N orange, H yellow.

There are three symmetry-independent positions for the cations at the cluster surface. The first type involves two equivalent positions slightly above the centers of the two $\{Mo_3V_3O_6\}$ pores that have not been considered until now (Figure 1a and Figure 2a). These two sites are occupied by ammonium cations, which are fixed by six O···H−N hydrogen bonds (Figure 2a). The N···O distances correspond to those of the related [18]crown-6 species.[9c,d]

The second type of position involves the three equatorial positions occupied by potassium ions (Figure 1a). Each cation is coordinated to four symmetry-equivalent terminal oxygen atoms of two neighboring $\{Mo_{17}\}$ units, which leads to the generation of two $\{Mo_4VKO_6\}$ crown-ether-like rings[9c] (Figure 1b and Figure 2b,c). The third type refers to six symmetry-equivalent sites in the holes (Figure 2c), where six $\{MoO\}^{4+}$ groups were found in a subsequent growth process from **1a**.[5a,b] In the present case of **2**, six ammonium ions are found there, positioned slightly above the six $\{Mo_4VKO_6\}$ rings (Figure 1b, Figure 2b,c); each site is formed by four bridging and two terminal oxygen cluster atoms and the corresponding metal atoms (N···O = 3.14–3.28 Å; Figure 2b). The coordination of potassium renders the two attached oxygen atoms more nucleophilic, as bridging oxygen atoms are considered more nucleophilic than terminal ones.

This distribution of the cations is fully consistent with the results obtained from a computational investigation giving information for the attractor areas for cations, when the size difference between the cations under consideration is not considered. Indeed, analysis of both the electronic structure and the molecular electrostatic potential determined using DFT-based methods clearly showed that the most nucleophilic sites on the surface of **1a** are the bridging V-O-Mo oxygen atoms that define the two crown-ether-like rings, where the two NH_4^+ cations are found in the present crystal structure. Furthermore, a set of atomic charges derived from the DFT calculations was used to carry out classical molecular dynamics simulations of **1a** in H_2O solution in the presence of lithium ions (Figure 3) using the DLPOLY2 program, developed in Daresbury Laboratory by Smith and Forester.[10] The computed trajectories enabled the average distribution of lithium counterions around **1a** to be visualized while no cation entered through the (rigid) pores under the calculation conditions. Figure 3 shows an isosurface of the space distribution function (SDF), which indicates the regions where the counterions spent most time during the simulation. The lithium ions are preferably found slightly above the two $\{Mo_3V_6O_6\}$ pores and in the area of the four terminal oxygen atoms (Figure 3) where the potassium ions are positioned in **2**; the difference of the size of lithium and potassium ions has consequences for the type of coordination. Full details about this computational study in connection with the different cations, and a comparison with the experimental results, will be published in a full paper.[11]

To summarize and conclude: The two $\{Mo_3V_3O_6\}$ pores in **2a** function like the [18]crown-6[9c,d] and interact with ammonium ions. This scenario corresponds completely to that of the porous $M'_{30}\{(M)M_5\}_{12}$ ($M' = Fe^{III}$, Cr^{III}, V^{IV}; M = Mo, W) Keplerates in which appropriate cations can be fixed in the 20 (analogous) $\{(metal)_6O_6\}$ capsule pores;[12] this has

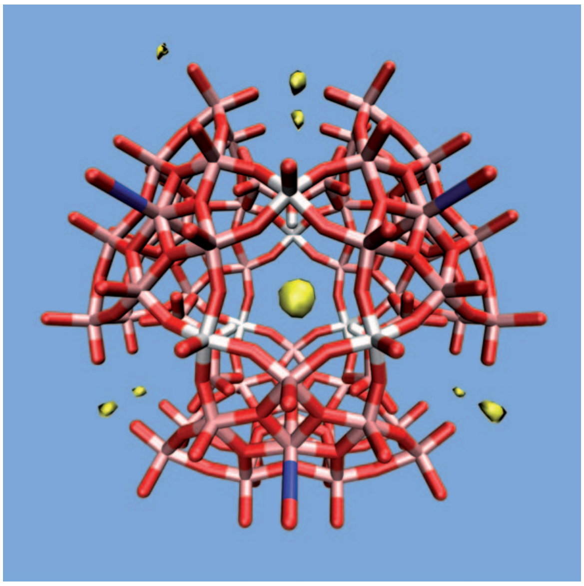

Figure 3. Isosurface of the space distribution function (SDF) for lithium counterions around **1a** computed according to a classical molecular dynamics simulation using explicit water solvent molecules (not shown). The yellow isosurface regions enclose the regions of highest probability of finding lithium cations around the cluster surface.

been unequivocally shown for example for 20 ammonium ions located in the 20 $\{W_3Fe_3O_6\}$ pores of the $Fe_{30}\{(W)W_5\}_{12}$ type cluster.[9b] Of note in the present study is the selective complexation/separation of ammonium and potassium ions by a synergetic process, and in particular the location of six ammonium ions through hydrogen bonds to the six $\{Mo_4VKO_6\}$ crown-ether-like rings in the external cluster holes.

The present result could initiate new investigations regarding the study of counterion distributions on surfaces of large metal-oxide-based clusters[5e–j] having specific surface functionalities such that selective nanoscale complexation of cations is possible. A challenging aspect is to be able to distinguish between specific cation coordination, as in the present case, and types of non-specific ion-pairing, as both facilitate the formation of giant assemblies of metal-oxide based macroanions owing to a decrease of repulsion.[13] Importantly, the two different scenarios should influence the assembly processes differently; this is presently considered as an interesting research area.[13] A further interesting aspect is that the six VO^{2+} ions in **2a** can be replaced by other 3d ions, which leads to different electron delocalizations[4] and therefore different cluster surface properties.

Experimental Section

Synthesis of **2**: A mixture of $K_2MoO_4{\cdot}5H_2O$ (15.16 g, 46.2 mmol), NH_4VO_3 (1.79 g, 15.3 mmol) $NH_2OH{\cdot}HCl$ (15 g, 215.9 mmol), aqueous hydrochloric acid (3.5%, 30 mL), and of water (650 mL) was refluxed without stirring for 2 h. The grey precipitate was filtered from the hot solution and the filtrate was stored for crystallization in a closed flask at 20 °C. Dark blue-violet crystals precipitated from the filtrate after 3 days, were collected by filtration, washed with cold water, and dried in air. Yield: 1.2 g (13% based on Mo). Elemental analysis (%) for $H_{223}K_{10}Mo_{57}N_{17}O_{277}V_6$ calcd: N 2.15, K 3.54, V 2.76, Mo 5.20; found: N 1.9, K 3.9, V 2.9, Mo 5.5. Characteristic IR bands (KBr pellet): $\tilde{\nu} = 1616$ (m), 1593 (m, ν(NO)), 1404 (m, $\delta_{as}(NH_4^+)$), 982 (w-m) and 939 (w-m) (both ν(V=O) and ν(Mo=O)), 887/874 (vs), 787 (vs), 667 (s), 613 (s), 576 (s), 544 (m) cm^{-1}. UV/Vis (in H_2O): $\lambda = 560$, 840 nm (IVCT transition).

Crystal data for **2**: $H_{223}K_{10}Mo_{57}N_{17}O_{277}V_6$, $M_r = 11\,060.17$; hexagonal, space group $P6_3/mmc$, $a = 23.5733(7)$, $c = 27.0113(11)$ Å, $V = 12\,999.2(8)$ Å^3, $Z = 2$, $\rho = 2.826$ g cm^{-3}, $\mu = 3.141$ mm^{-1} , $F(000) = 10\,560$, crystal size $= 0.40 \times 0.35 \times 0.12$ mm^3. A total of 74 197 reflections ($1.73 < \theta < 26.98°$) were collected of which 5181 reflections were unique ($R(\text{int}) = 0.0267$). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.10. The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to $R = 0.0404$ for 4612 reflections with $I > 2\sigma(I)$, $R = 0.0475$ for all reflections; max/min residual electron density 2.704 and -2.670 e Å^{-3}. Crystals of **2** were removed from the mother liquor and immediately cooled to 183(2) K on a Bruker AXS SMART diffractometer (three circle goniometer with 1 K CCD detector, $Mo_{K\alpha}$ radiation, graphite monochromator; hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435 and 230 frames ($\phi = 0$, 88 and 180°) at a detector distance of 5 cm). (SHELXS/L, SADABS from G.M. Sheldrick, University of Göttingen 1997/2003; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, 2001).

Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-420489.

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