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A potassium selective 'nanosponge' with well defined pores†‡

Achim Müller,*[a] Bogdan Botar,[a] Hartmut Bögge,[a] Paul Kögerler[b] and Alois Berkle[a]
[a] *Fakultät für Chemie der Universität, Lehrstuhl für Anorganische Chemie I, Postfach 100131, D 33501 Bielefeld, Germany. E-mail: a.mueller@uni-bielefeld.de*
[b] *Ames Laboratory, Iowa State University, Ames, IA 50014, USA*

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The novel spherical cluster-compound $K_2Na_6[K_{20}\subset Mo_{80}V_{22}O_{282}(SO_4)_{12}(H_2O)_{66}]\cdot\approx 140H_2O$ 1 has been obtained in a 'one-pot' reaction and exhibits several remarkable structural features: 30 open shell centers, *i.e.* 8 Mo^V and 22 V^{IV} spanning an icosidodecahedron, the incorporation of 20 K^+ cations capping 20 appropriate $\{M_6O_6\}$ pores/rings present at the surface of the spherical cluster-anion, and an encapsulated aggregate of water molecules.

Using specific reaction routes, recent insights into polyoxomolybdate chemistry has allowed the deliberate design of ball-shaped clusters with icosahedral symmetry some of which exhibit unusual magnetic and electronic properties (for general aspects see ref. 1). These species can be obtained by connecting pentagonal $\{(Mo)Mo_5\}$-type building units—present in all large molybdenum–oxide based clusters—with linkers of different size and composition leading to differently sized pores.[2] Several members of this cluster family, namely $\{Mo_{72}Fe^{III}_{30}\}$[3] and $\{Mo_{75}V^{IV}_{20}\}$,[4] of interest for magnetochemistry, were obtained. In this context we report here the novel, heterometallic (Mo/V), mixed-valence ($Mo^{V/VI}$) compound containing 30 d^1 metal centers $K_2Na_6[K_{20}\subset Mo_{80}V_{22}O_{282}(SO_4)_{12}(H_2O)_{66}]\cdot\approx 140H_2O$ = $K_2Na_6[K_{20}\subset\{(Mo^{VI})Mo^{VI}_5O_{21}(SO_4)(H_2O)_3\}_{12}(V^{IV}O(H_2O))_{22}(Mo^VO(H_2O))_8]\cdot\approx 140H_2O$ **1** (= K_2Na_6**1a**$\cdot\approx$ $140H_2O$). The cluster anion **1a** contains 20 $\{M_6O_6\}$ rings capped by *ca.* 20 K^+ cations and an encapsulated aggregate of water molecules.

Complex **1** was obtained in a self-assembly process from aqueous molybdate and vanadyl sulfate solutions in the different stoichiometric ratios given in the ESI† in the presence of dithionite as reducing agent and potassium cations. The compound was characterized by elemental analysis, thermogravimetry (to determine the lattice water content), potentiometric titrations (to determine the number of V^{IV} and Mo^V centers), spectroscopic methods (IR, VIS-NIR) (ESI†), as well as magnetic measurements and single-crystal X-ray structure analysis [including bond valence sum (BVS) calculations].†§

The anion **1a** belongs to the family of icosahedral polyoxometalates having the general formula $(pentagon)_{12}(linker)_{30}$. The 12 pentagonal units are positioned at the vertices of an icosahedron and are connected by 22 ± 1 $\{V^{IV}O(H_2O)\}^{2+}$ and 8 ± 1 $\{Mo^VO(H_2O)\}^{3+}$ linking groups as shown in Fig. 1 (a corresponding error limit has to be taken into account). The d^1 metal centers are statistically distributed over the 30 vertices of an icosidodecahedron and adopt a distorted octahedral coordination including their terminal oxygen atoms which are mainly directed towards the interior of the cluster. Remarkably, **1a** incorporates 20 potassium cations located *ca.* 1.0 Å above the centers of the 20 $\{M_6O_6\}$ rings/pores of the anion (Figs. 1 and 2; there seems to be a slight under-occupation which is balanced by disorder of the K atoms with the H_2O molecules, which are located about 2.9 Å below the main K positions). Our investigation demonstrates that each of the $\{M_6O_6\}$ rings has receptor properties that in principle resemble those of the crown ethers of supramolecular chemistry. (Remarkably, the pores of a spherical cluster can be tuned by using different linkers/spacers.) The 12 sulfate ligands attached in a tridentate manner to the pentagonal units inside the cluster cavity are disordered with the 72 H_2O ligands.

A key requirement for the preparation of **1** is the use of a reducing agent leading to the formation of $\{Mo^VO(H_2O)\}^{3+}$ linking groups, which are stronger electrophiles towards the negatively charged pentagonal units than the $\{V^{IV}O(H_2O)\}^{2+}$

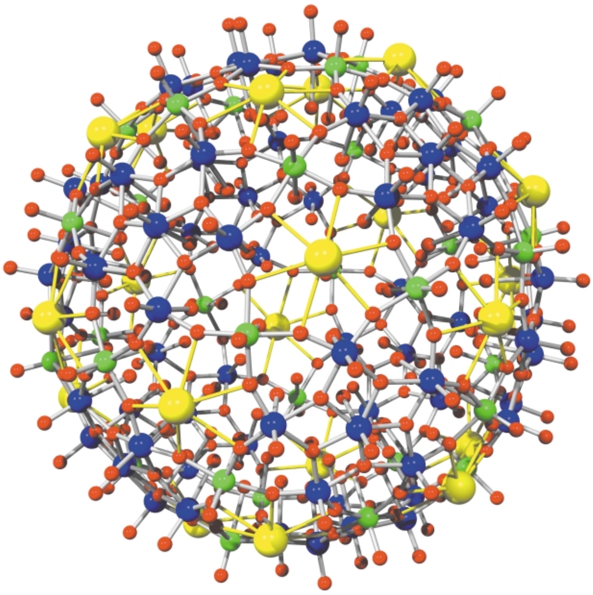

Fig. 1 Structure of the icosahedral cluster-anion **1a** in ball and stick representation (colour code: Mo^{VI} blue, V^{IV} /Mo^V green, O red, K yellow; the disordered SO_4^{2-} ligands are omitted for clarity).

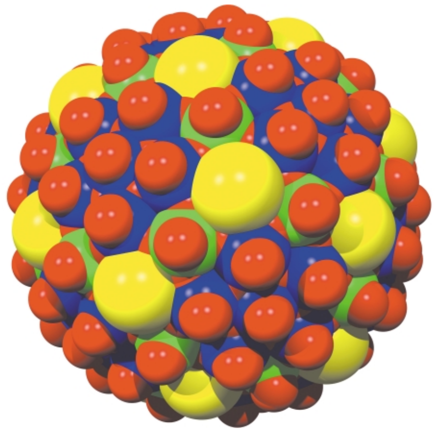

Fig. 2 Space filling representation of **1a** highlighting the nanosponge affinity to the K^+ cations located on the C_3-axes (colour code as in Fig. 1).

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† Electronic supplementary information (ESI) available: synthesis, selected data, and crystal data for **1**. See http://www.rsc.org/suppdata/cc/b2/b210523n/

‡ Dedicated to Professor C. N. R. Rao on the occasion of his 70th birthday.

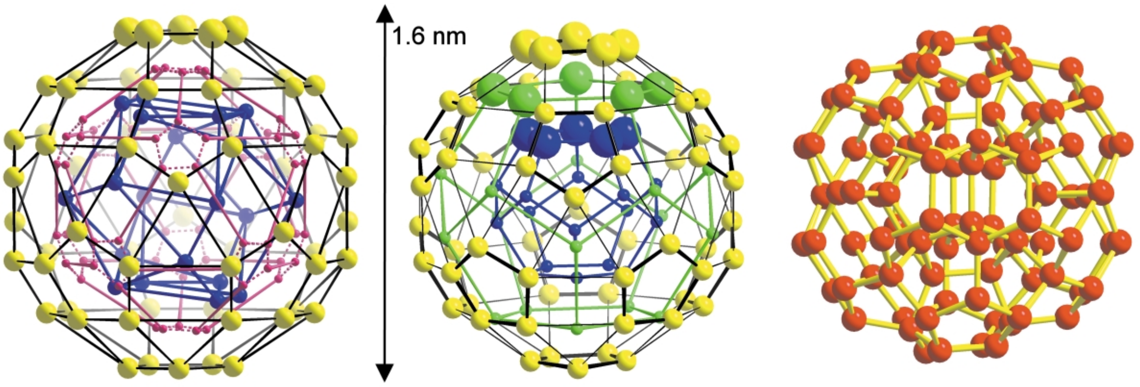

Fig. 3 Comparison of three shells within the cluster cavity of **1a** (left) with those of **2a** (middle). The third shell (yellow) corresponds to a rhombicosidodecahedron with 60 vertices. In the case of **1a** it is formed by water molecules attached as ligands to the pentagonal units but also by bridging oxygen atoms of disordered sulfate ligands and in the case of **2a** only by encapsulated and non-coordinated water molecules. The second shell is formed by the terminal oxygen atoms (violet) of the SO_4^{2-} ligands in **1a** and water molecules (green) in **2a** (the dashed violet lines connect the five positions over which each of the oxygen atoms in **1a** is disordered like the corresponding sulfur atoms). The first shell (blue) consists of water molecules in both anions but is not as well-organized for **1a** as the corresponding shell of **2a**. The overall structure of the encapsulated water molecules of **2a** (right) is icosahedral with all O atoms nearly tetrahedrally coordinated and could be a snapshot of liquid water (not expressed in ref. 7*a*).

groups (comparable to the $\{Mo_{102}\}$-type species[5]). This allows in principle to tune the electron density at the receptor sites. Interestingly, the amount of reducing agent in the present case does not seem to influence strongly the number of Mo^V centers in the cluster (see experimental section in ESI†) indicating that we can rule out the possible existence of other related clusters in the reaction product having varying V^{IV}/Mo^V ratios. The presence of Mo^V linkers also decreases the overall negative charge of the cluster-anion compared to a hypothetical less stable $\{Mo_{72}V_{30}(SO_4)_{12}\}$-type cluster which would have a negative charge of 36−.

The electronic spectrum of **1** in the VIS-NIR region shows a broad absorption band at ~1100 nm due to $Mo^V \rightarrow Mo^{VI}$ intervalence charge transfer transitions and a more intense band with a maximum at 540 nm assigned to heteronuclear $V^{IV} \rightarrow Mo^{VI}$ charge transfer transitions in agreement with the differences in optical electronegativity between the atoms involved.[6]

In the case of the present types of giant spherical clusters with large cavities, not only the shell is interesting but also the organization of the encapsulated water molecules which can in principle be directed by the ligands attached to the internal cluster surface[2] as well as by the sizes of the pores. Whereas a highly-symmetrical, icosahedral $(H_2O)_{100}$ aggregate was observed for the larger spherical cluster $\{(Mo^{VI})Mo^{VI}_5\}_{12}\{(Mo^V)_2\}_{30}$ **2a** having completely closed pores[7] the situation here is different (see Fig. 3) as the cluster cavity is smaller and the cluster shell is less symmetrical because of different types of disorder (*i.e.*, V/Mo and SO_4^{2-}/H_2O).

Extended Hückel MO calculations indicate that the eight Mo 4d electrons of the (formal) Mo^V linker positions in **1a** are partially delocalized over the Mo positions of the $\{(Mo)Mo_5\}$-type pentagonal building blocks, resulting in strong spin pairing, and favour ring configurations in which the Mo^V linkers occupy neighbouring sites. Due to these strong correlations the Mo 4d electrons increase only the temperature independent paramagnetism (TIP). The observed magnetism of **1**[8] therefore reflects very strong antiferromagnetic exchange interactions between the 22 $S = 1/2$ VO^{2+} linker groups that are mediated by the –O–$Mo^{V/VI}$–O– groups; χT steadily decreases from 4.2 emu K mol^{-1} at room temperature (compared to the spin-only value of 8.25 emu K mol^{-1} for 22 uncorrelated $S = 1/2$ centers with $g = 2.0$) to 0.35 emu K mol^{-1} at 2 K. Interestingly, the room-temperature value per V^{IV} center in **1**, 0.19 emu K mol^{-1}, is nearly identical to the corresponding value found for the $\{Mo_{75}V_{20}\}$-type system.[4]

This work opens perspectives for the preparation of a new series of giant spherical mixed-valence clusters of interest for magnetochemistry but also for a new type of supramolecular chemistry, or in other words for a novel porous-cluster chemistry with a manifold of receptors tunable regarding size and electron density, which can be formally related to classical supramolecular chemistry based on monotopic receptors.[9,10] Finally there is a chance to look at the encapsulated water clusters the structure of which can be influenced by the type of cluster shell organization. This can lead to a better understanding of H_2O type interactions.[11]

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