COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Synergetic activation of “silent receptor” sites leading to a new type of inclusion complex: integration of a 64-membered ring comprising K^+ and SO_4^{2-} ions into a molybdenum oxide-based nanoobject†‡

Achim Müller,* Liviu Toma, Hartmut Bögge, Marc Schmidtmann and Paul Kögerler
Fakultät für Chemie der Universität, Lehrstuhl für Anorganische Chemie I, Postfach 100131, D 33501 Bielefeld, Germany. E-mail: a.mueller@uni-bielefeld

Received (in Cambridge, UK) 15th May 2003, Accepted 20th June 2003
First published as an Advance Article on the web 11th July 2003

The new type of inclusion species $[Mo^{VI}_{114}Mo^{V}_{32}O_{429}(H_2O)_{50}(KSO_4)_{16}]^{30-}$ comprising 16 encapsulated K^+ and SO_4^{2-} ions shows an unusual 64-membered $\{K(SO_4)\}_{16}$ ring integrated into a wheel-shaped type nanocluster host; it is formed by a synergetically induced functional complementarity and represents a text-book example of a very complex non-biological material.

The manipulation of *well defined* objects is currently an eminent challenge in the field of nanoscience. An related task in this context is the study of cooperativity phenomena, in particular when a manifold of ingredients—as a special case also nanodots—can be positioned at equivalent sites. This cooperativity situation—formally comparable to that in extended structures showing translational invariance—can render new/important information, *e.g.* if large ring systems are considered.[1] Such rings can, in principle, also be investigated in order to extrapolate properties of infinite chains. In the present case, a suitable nanoobject is available in the form of the hexadecameric molybdenum oxide-based ring-shaped cluster of the $\{Mo_{11}\}_{16} = \{Mo_{176}\}$ type, which shows a variety of functionalities and even manifold equivalent neighbouring sites.[2] Here we report a related novel inclusion species[3] of high complexity comprising 16 integrated K^+ and SO_4^{2-} ions leading to the formation of an unusual encapsulated 64-membered ring system with distances comparable to those of solid K_2SO_4.

The nanosized system in question was obtained from a reaction mixture from which usually discrete nanosized wheel-shaped cluster species like $[Mo^{VI}_{144}Mo^{V}_{32}O_{528}H_{16}(H_2O)_{80}]^{16-} \equiv [\{Mo^{VI}_2O_5(H_2O)_2\}\{Mo^{VI/V}_8O_{26}(\mu_3\text{–}O)_2H(H_2O)_3Mo^{VI/V}\}]_{16}^{16-} \equiv [\{Mo_2\}\{Mo_8\}\{Mo_1\}]_{16}^{16-}$ **2a** are formed[2] (referred to here as $\{Mo_{176}\}$), while in presence of high K^+ and SO_4^{2-} concentrations, cluster **1a** is formed thereby integrating the corresponding ions at adjacent “receptor” type sites for anions and cations (formally considered; see below).† **1** was characterized by elemental and thermogravimetric analysis (to determine the crystal water content), cerimetric titrations [for the determination of the (formal) number of the Mo^V centers], bond valence sum (BVS) calculations (to determine the number and positions of H_2O/OH ligands as well as the formal number of Mo^V centers), spectroscopic methods (IR, resonance-Raman, Vis-NIR), EHMO calculations, and single crystal X-ray structure analysis.§ $K_{14}Na_{16}[Mo^{VI}_{114}Mo^{V}_{32}O_{429}(H_2O)_{50}\{KSO_4\}_{16}]\cdot$*ca.* 500 $H_2O \equiv K_{14}Na_{16}[\{Mo^{VI}_2O_5(H_2O)_2\}_9\{Mo^{VI/V}_8O_{24}(H_2O)_2\}_{16}\{KSO_4\}_{16}] \cdot$ *ca.* 500 H_2O **1**.

The tetragonal unit cell of **1** (space group *P* 4/*n*) shows the abundance of anionic nanosized ring-shaped units **1a**. (The defects in all $\{Mo_1\}$ and seven of the $\{Mo^{VI}\}_2$ type units occurred as usual due to increasing the pH values.†) These correspond to the parent $\{Mo_{176}\}$ type cluster **2a** and represent a new type of inclusion species (see Fig. 1). In comparison to the original $\{Mo_{176}\}$ ring the cluster anion **1a** shows the following remarkable features.

The hexadecameric parent ring system shows 16 $\{O_4\}$ tetrahedra (comparable to the well-known central $\{O_4\}$ unit of Keggin type ions, see Fig. 2) between the $\{Mo_4O_6\}$ segments encapsulating formally S^{6+} instead of H^{+2} or Cu^{2+},[4] situations already known from the completely analogous tetradecameric parent cluster $\{Mo_{11}\}_{14}$. In fact we observe, as in Keggin ions, the abundance of encapsulated SO_4^{2-} anions (S–O: 1.47–1.53 Å). Note in this context that in the central O_4 cavity of the classical Keggin ions H^+, P^{5+}, S^{6+} or M^{n+} can (formally) be correspondingly positioned.[5]

The 16 K^+ cations interact with 16 $\{Mo_6O_6\}$ crown-ether type ring systems (Fig. 2) having nucleophilic properties.[3] This interaction is supported (synergetically) by the “encapsulation” of the SO_4^{2-} anions which increases the negative charge, and thereby the nucleophilicity. To some extent referring only to the K^+ centers, a similar situation occurs for spherical nanoobjects, where *e.g.* each K^+ interacts with a slightly smaller and planar M_6O_6 type ring/pore (see ref. 6 and Fig. 1). (It was this latter fact that stimulated us to do the present type of experiment.)

The uniqueness is the presence of adjacent different specific sites, which leads to the formation and integration of an unusual

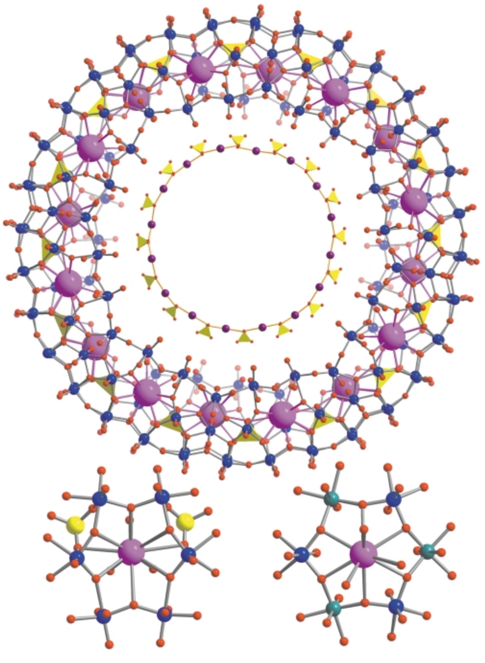

Fig. 1 Structure of **1a** in crystals of **1** in ball and stick representation but highlighting the K centers (pink spheres; for a more detailed presentation of the environment see Fig. 3) and SO_4^{2-} units (yellow; polyhedral representation). The interaction of K^+ with one $\{Mo_6O_6\}$ receptor type site in **1a** (bottom left) and the approximately comparable situation of a M_6O_6 (M = Mo, V) pore in a spherical molybdenum oxide-based system[6] (bottom right) is additionally presented. For a better demonstration of the K^+–SO_4^{2-} type interaction, the structure of the $\{K(SO_4)\}_{16}$ ring on a smaller scale and removed from its environment is shown in the center (O red, Mo blue, V/Mo turquoise).

---

† Electronic supplementary information (ESI) available: experimental and further crystallographic details. See http://www.rsc.org/suppdata/cc/b3/b305447k/

‡ Dedicated to Prof. Pierre Gouzerh on the occasion of his 60th birthday.

DOI: 10.1039/b305447k

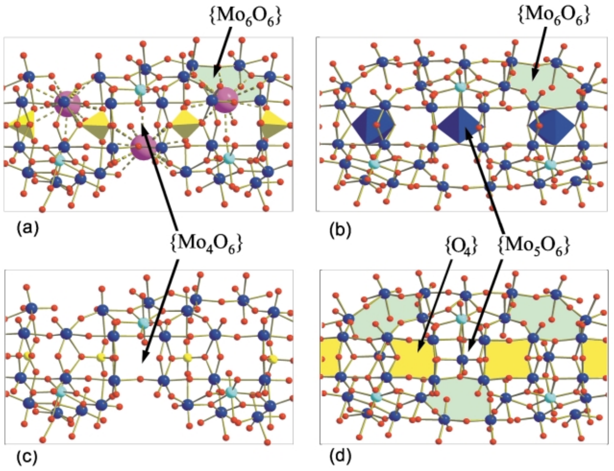

Fig. 2 Simplified demonstration of: (1) the multitude of specific adjacent "receptors" forming a zig-zag ring for K^+ ($\{Mo_6O_6\}$ rings highlighted in green) and for SO_4^{2-} ions (sites between $\{Mo_5O_6\}$ compartments schematically highlighted in yellow) (d), and (2) the change from the parent $\{Mo_2Mo_8Mo_1\}_n$ type (b, d) [2] to the $\{Mo_2\}_{n-x}\{Mo_8\}_n$ type (a, c) ring structure with the change of the $\{Mo_5O_6\}$[2] to the $\{Mo_4O_6\}$ compartments (released $\{Mo_1\}$ as blue octahedra in (b); SO_4^{2-} tetrahedra and K^+ highlighted in (a)) (colour code as in Fig. 1 with the pentagonal bipyramidal Mo type centers in cyan).

64-membered $\{KOSO\}_{16}$ type ring showing two relevant K···O distances of the order of 3.1 Å (Figs. 1 and 2). (The other two K···O(S) distances are longer.) All 16 $\{Mo_1\}$ units of the $\{Mo_5O_6\}$[2] compartments and seven $\{Mo_2\}$ building blocks of the parent $\{Mo_{176}\}$ type cluster **2a** are pushed out due to the use of the appropriate pH (for reasons see ESI†) while correspondingly 16 $\{Mo_4O_6\}$ segments are formed (Fig. 2). This has consequences for the electronic structure (as shown below). The reference to receptors is of course a simplification as the K^+ cations are also coordinated to other functions like SO_4^{2-} and to additional H_2O ligands (as shown in Fig. 3) and, correspondingly, are located *ca.* 1.5 Å below the Mo_6O_6 ring.

The IR spectrum of **1** also shows the abundance of SO_4^{2-} ions due to bands at 1176, 1118, 1043 cm^{-1}, while a comparison of the resonance Raman spectrum of the parent cluster **2a** of the type $\{Mo_{176}\}$ or $\{Mo_{154}\}$ (these are practically identical: bands at 795, 536, 462, 324, 214 cm^{-1}) with that of **1a** (793, 444, 307, 216 cm^{-1}) proves the (significant) change of the electronic structure. In both cases (*i.e.* **1a** and **2a**) the resonance Raman spectra (λ_e = 1064 nm) depend on the $Mo^V \rightarrow Mo^{VI}$ IVCT but these take place in case of **2a** within the well defined small $\{Mo_5O_6\}$ compartments.[2] The band at 536 cm^{-1} (missing in **1a**) can be tentatively assigned to a ν_s $(Mo_1(O_{br})_4)$ type vibration.

Whereas in the parent cluster **2a** two Mo-4d electrons are localized within each $\{Mo_5O_6\}$ compartment with virtually no electronic inter-compartment interactions,[7] the 32 Mo-4d electrons in **1a** are delocalized over that part of the ring system which is built up by the 16 $\{Mo_4O_6\}$ segments. Extended Hückel MO calculations† of **1a** and **2a** both reveal a set of 16 nearly degenerated molecular orbitals to form the energetically highest occupied MOs (HOMOs). These consist mostly of Mo(4d) functions of the Mo positions found in the 16 $\{Mo_4O_6\}$ segments and are separated by a significant energy gap from the lowest unoccupied MO (LUMO).[8] Compared to the parent $\{Mo_{176}\}$ cluster anion **2a**, the further delocalization of these 16 HOMOs in **1a** results in a significant decrease (*ca.* 10%) of the HOMO–LUMO gap. This decrease causes a significant increase of the temperature-independent paramagnetic contribution to the overall magnetism of **1** observed in preliminary experiments.[9,10]

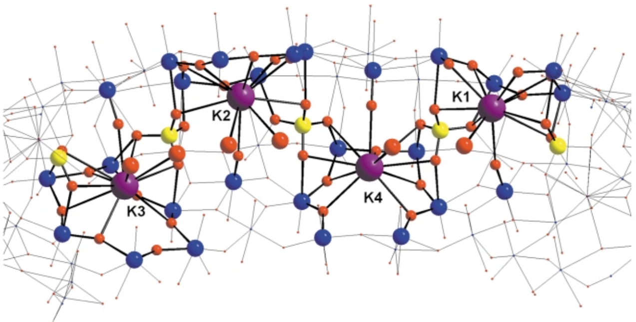

Fig. 3 Four crystallographic independent environments ($\{Mo_6O_6\}$ (or $\{Mo_4O_5\}$ in case of missing $\{Mo_2\}$ units), SO_4^{2-}, H_2O, O of $\{(Mo)Mo_5\}$) of the K^+ cations (colour code as in Fig. 1).

The present case proves that we are to some extent on the route to elucidate how reactions can be performed at non-equivalent sites of structurally *well defined* but very complex metal oxide-based nanoobjects. The related complex nanostructured landscape has a multitude of functions, *e.g.* potential "receptors" for anions and cations which have to be synergetically activated by the ions with opposite charge. This corresponds to synergetically induced functional complementarity, a situation comparable with an allosteric effect, *i.e.* the modulation of sites at distant locations due to interactions. Moreover, the present cluster system offers the potential to act polytopically for different substrates thus allowing, in principle, the study of ring-structure-based complex cooperative effects between different guests like cations and anions.

Financial support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the European Union (HPRN-CT 1999-00012) is gratefully acknowledged. L. T. thanks the Graduiertenkolleg "Strukturbildungsprozesse" of the University of Bielefeld for a fellowship.

Notes and references

§ *Crystal data* for **1a**: $H_{1100}K_{30}Mo_{146}Na_{16}O_{1043}S_{16}$, M = 33857.84 g mol^{-1}, tetragonal, space group *P*4/*n*, a = 51.726(2), c = 21.747(1) Å, V = 58185(4) $Å^3$, Z = 2, ρ = 1.933 g/cm^3, μ = 1.768 mm^{-1}, $F(000)$ = 33156, crystal size = 0.20 × 0.10 × 0.06 mm^3. Total reflections 159990 ($1.11 < \theta < 20.04°$), 27280 unique ($R(\text{int})$ = 0.1144). The structure was refined using SHELXL-93[11] to R = 0.0843 for 16975 reflections with $I > 2\sigma(I)$, R = 0.1427 for all reflections. CSD 412534. See http://www.rsc.org/suppdata/cc/b3/b305447k/ for crystallographic files in .cif format.

1 For a classical textbook seeI. Haiduc, *The Chemistry of Inorganic Ring Systems*, Vols. 1 and 2, Wiley, London, 1970.
2 A. Müller, P. Kögerler and C. Kuhlmann, *Chem. Commun.*, 1999, 1347–1368; A. Müller and C. Serain, *Acc. Chem. Res.*, 2000, **33**, 2–10.
3 J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley, New York, 2000; J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; G. A. Jeffrey, in *Inclusion Compounds*, ed. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Academic Press, New York, 1984.
4 A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, P. Kögerler, C. Rosu and E. Beckmann, *Angew. Chem., Int. Ed*, 2001, **40**, 4034–4037.
5 M. T. Pope and A. Müller, *Angew. Chem., Int. Ed*, 1991, **30**, 34–48.
6 A. Müller, B. Botar, H. Bögge, P. Kögerler and A. Berkle, *Chem. Commun.*, 2002, 2944–2945.
7 A typical consequence of the high degree of localization of the two Mo-centered electrons per compartment is *e.g.* the high similarity of the resonance Raman spectra of the $\{Mo_{176}\}$ and the $\{Mo_{154}\}$ type clusters and the (linear) relation between the extinction coefficient of the Mo(V) → Mo(VI) type IVCT absorption bands of molybdenum blue compounds and the formal number of Mo(V) centers.
8 This behaviour of the frontier orbitals also supports the fact that both structures **1a** and **2a** favour an electronic configuration with formally 32 Mo(V) centers.
9 P. Köyerler and A. Müller, to be published.
10 The Mulliken net charges (derived from the EHMO electronic configuration) of the molybdenum centers of the $\{Mo_4O_6\}$ segments in **1a** are non-uniform and alternate depending on their relative position with respect to the pentagonal MoO_7 bipyramids within the $\{Mo_8\}$ groups. These patterns agree well with BVS values from the corresponding single-crystal X-ray analysis.
11 SHELXS/L, G. M. Sheldrick, University of Göttingen, 1993/97.