On the option of generating novel type surfaces with multiphilic ligands within the cavity of a giant metal–oxide based wheel type cluster: chemical reactions with well-defined nanoobjects

Achim Müller,*[a] Samar K. Das,[a] Christoph Kuhlmann,[a] Hartmut Bögge,[a] Marc Schmidtmann,[a] Ekkehard Diemann,[a] Erich Krickemeyer,[a] Josef Hormes,[b] Hartwig Modrow[b] and Matthias Schindler[b]

[a] *Lehrstuhl für Anorganische Chemie I, Fakultät für Chemie, Universität Bielefeld, Postfach 100131, D-33501 Bielefeld, Germany. E-mail: a.mueller@uni-bielefeld.de*
[b] *Physikalisches Institut, Universität Bonn, D-53115 Bonn, Germany*

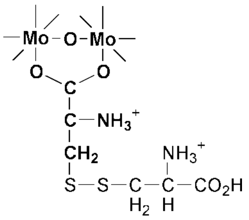
Received (in Cambridge, UK) 9th January 2001, Accepted 21st February 2001
First published as an Advance Article on the web 16th March 2001

The reaction of an aqueous solution of sodium molybdate with cysteine hydrochloride acting as educt and reducing agent at rather low pH values (≈ 1.5) results in the formation of $Na_3[Mo_{154}O_{462}H_{14}(H_2O)_{48}(HO_2C–(NH_3^+)HC–CH_2–S–S–CH_2–CH(NH_3^+)–COO^-)_{11}]\cdot x\ H_2O$ 1 ($x \approx 250$) containing nanosized ring-shaped clusters which capture the oxidation product of cysteine, *i.e.* the diprotonated cystine ligands (H_2cystine$^+$) at the inner wall of their cavities; interestingly, the multiphilic ligands containing different types of functional groups (two $–NH_3^+$, one $–CO_2^-$, one $–CO_2H$ and one –S–S–) attach to the inner wall of the cluster through one of the two carboxylate groups thereby demonstrating the possibility to generate novel type surfaces within the cavity of a nanostructured ring-shaped cluster.

The design of multifunctional and especially of well ordered micro- and meso-porous materials which can incorporate guest molecules is a challenging task of modern chemistry.[1–3] Guests which may be reversibly and specifically bound at different appropriate sites of the host are of special interest. In particular this type of interaction may be significant for the synthesis of specially designed porous materials and may play a key role in catalysis and especially in separation methods. Polyoxometalates, formed by self-assembly processes are ideal systems in this respect as they can form crystalline materials with well-defined cavities and pores.[4]

Our recent interests in this field include the design of cavities within networks built up by giant wheel type species which can be opened and closed again as required.[5,6] Here we report a novel compound, in which cystine ligands (H_2cystine$^+$) are coordinated at the inner wall of a relevant nanosized car-tire shaped cluster anion.

If an aqueous acidified solution of Na_2MoO_4 is reduced with cysteine at *ca.* 55 °C, blue crystals of **1** precipitate after 1–2 days.† Compound **1** was characterized by elemental analysis‡ (including cerimetric titration to determine the formal number of Mo^V centers), thermogravimetry (for the determination of the crystal water content), bond valence sum (BVS) calculations[7] (to determine the positions of the H_2O ligands and to distinguish between Mo^{VI} and Mo^V centers), spectroscopic methods (IR, resonance-Raman, UV–VIS, XANES)§ and finally by single crystal X-ray structure analysis.¶ For the synthesis of **1**, cysteine acts as reducing agent at rather low pH values (≈ 1.5) resulting in the formation of the mixed-valent $\{Mo_{154}\}$ type cluster with 28 Mo^V centers (formal consideration) while the protonated form of the oxidized product, *i.e.* cystine, gets coordinated to the inner surface of the giant cluster through one of its carboxylate ends (Scheme 1).



Scheme 1 Atoms found in the crystal structure shown in bold.

The single crystal X-ray structure of **1** revealed the tetradecameric ring-shaped structure (Fig. 1) of the anion **1a** of **1**, which can be compared to that of the related parent host anion **2a**[5e] by substituting 2 × 11 = 22 H_2O ligands with 11 cystine (H_2cystine$^+$, see Scheme 1). According to the related building-block principle, **1a** and **2a** can be formulated generally as $[\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}]$ or specifically as $[\{(O)_2{=}Mo^{VI}(\mu\text{-}O)L_iMo^{VI}{=}(O)_2\}_{14}\{Mo^{VI/V}{}_8O_{26}(\mu_3\text{-}O)_2H(H_2O)_3\text{-}Mo^{VI/V}\}^{3-}{}_{14}]^{3-}$ **1a** and $[\{(O)_2{=}Mo^{VI}(H_2O)(\mu\text{-}O)(H_2O)Mo^{VI}{=}(O)_2\}^{2+}{}_{14}\{Mo^{VI/V}{}_8O_{26}(\mu_3\text{-}O)_2H(H_2O)_3Mo^{VI/V}\}^{3-}{}_{14}]^{14-}$ **2a** (ΣL_i = 11 μ-$HO_2C–(NH_3^+)HC–CH_2–S–S–CH_2–CH(NH_3^+)–CO_2^-$ + 6 H_2O).

While the basic $\{Mo_8\}$ and $\{Mo_1\}$ units are identical in both clusters, this is not the case for all of the $\{Mo_2\}$ groups because of the substitution of some H_2O ligands. The complete structure of the cystine ligands is—as expected—not found in the crystal structure due to the related high degree of disorder of the long chains which show an extreme flexibility and are attached to the inner wall through one of the two 'carboxylate ends'.‖ However, the experimental results of numerous carbon, hydrogen, nitrogen and sulfur analyses‡ together with spectroscopic data establish the fact that the cystine ligands are intact. The

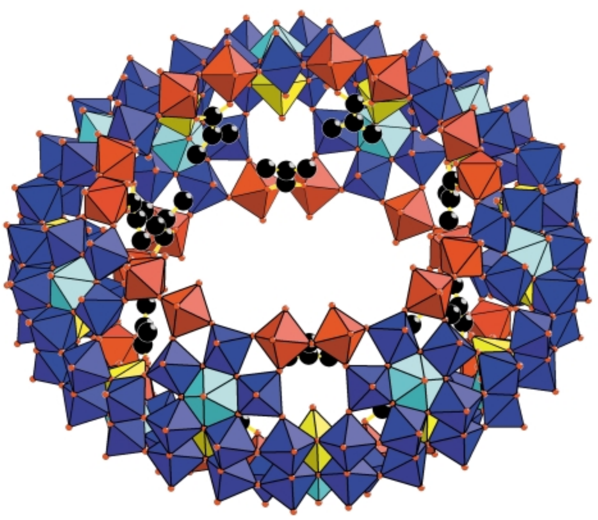


Fig. 1 Inclined view into the giant wheel type cluster anion **1a** in crystals of **1** in polyhedral (polyoxomolybdate part) and partly in ball-and-stick representation ($\{Mo_2\}$: red; $\{Mo_8\}$: blue (central pentagonal bipyramids: cyan); $\{Mo_1\}$: yellow; oxygen: small red circles; carbon and (disordered) nitrogen: enlarged black circles).

DOI: 10.1039/b100362n

This journal is © The Royal Society of Chemistry 2001

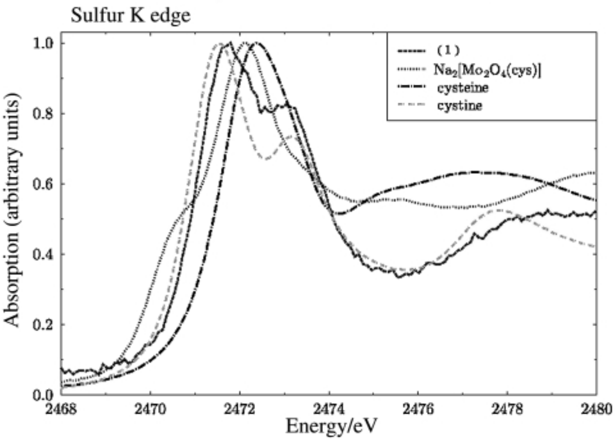


Fig. 2 S K-edge XANES spectra.

abundance of coordinated H_2cystine$^+$ is mainly supported by the IR and XANES spectral studies. In particular, a comparison of the S K-edge spectra of **1** (Fig. 2) and authentic cystine with those of cysteine and a cysteine molybdenum complex provides clear support for the presence of the former ligands. The absorptions at *ca.* 2472 eV are assigned to excitations of S 1s electrons to the first unoccupied electronic states of either the complexes or the free ligands. In the case of the complexes there are also unoccupied states centered on the molybdenum–oxygen part, but these are spatially significantly separated. Therefore, only ligand-internal transitions exhibit higher probabilities. The patterns for cystine and cysteine however, free or complexed, differ characteristically. The IR spectrum proves the abundance of cystinium cations which is indicated by the presence of a medium intensity band at 1495 cm^{-1} assigned to the $\delta(NH_3^+)$ mode of the cation as well as by the characteristic ν(C=O) band at 1730 cm^{-1} of the –CO$_2$H group.[8] The diprotonation of the cystine ligands is supported by the experimental results of Na analyses since each replacement of a H_2O ligand by H_2cystine$^+$ reduces the negative charge of the original cluster **2a** by one unit. (However, the presence of one monoprotonated instead of diprotonated cystine in connection with four instead of three (highly disordered) Na$^+$ cations could not be excluded.) The resulting low charge is consistent with the very low solubility of **1**.

The 11 H_2cystine$^+$ ligands, coordinated to {Mo$_2$} units through their carboxylate functions, are located quite disordered near the inner wall of the cavity (Fig. 1). Such a situation is also suggested by molecular modelling using the MM+ force field approach.** When all positions known from the crystal structure determination are kept fixed the remaining energy hypersurface turns out to be rather flat.

To summarize the interesting aspects: it is possible to place molecules at the inner wall of the cavity of a giant metal–oxide based wheel type cluster by replacing H_2O ligands. With the use of ambiphilic and/or multiphilic ligands, new characteristic surface structures inside the cavity can be generated. This process, which has been employed here with the cystine attached to the inner wall, creates an interesting type of (inner) surface with –NH$_3^+$, –CO$_2$H and –S–S– functions, which we are currently attempting to construct. This type of research work has special relevance for the construction of novel silica hybride materials containing these types of clusters.

Notes and references

† To an aqueous solution (35 mL) of $Na_2MoO_4\cdot 2H_2O$ (3.0 g, 12.4 mmol) and hydrochloric acid (25 mL, 1.1 M) in a 100 mL Erlenmeyer flask, L-cysteine hydrochloride monohydrate (0.41 g, 2.3 mmol) was added and the reaction medium was stirred for 5 min at room temperature. The yellow color, which developed immediately after addition of cysteine, changed to bright green within 2–3 min and after a further 5 min to blue–grey. The suspension was subsequently heated in an oil bath at 55 °C under constant stirring for 2 h (flask covered with a watch glass) resulting in a dark blue solution which was kept at 20 °C for another 2 h. The amorphous blue material, separated after this time, was filtered off and the blue filtrate was kept at room temperature for 2 d in a 100 mL Erlenmeyer flask at 15–20 °C (note: the storing temperature should not exceed 20 °C). The precipitated blue crystals were filtered from the mother-liquor, washed with cold water and dried at room temperature. Yield: 0.9 g ($\approx$37% based on Mo).

‡ Anal. Calc. for $C_{66}H_{753}Mo_{154}N_{22}Na_3O_{804}S_{22}$ (M = 30272.96): C, 2.62; H, 2.51; N, 1.02; S, 2.33; Na, 0.23. Found: C, 2.7; H, 2.4; N, 1.0; S, 2.4; Na, 0.3%.

§ *Selected spectroscopic data* for **1**: IR (KBr pellet) (ν/cm^{-1}): 1730w {ν(C=O)}, 1607m {$\nu_{asym}(CO_2^-) + \delta(H_2O)$}, 1494m {$\delta(NH_3^+)$}, 1412w, 1346w, 1135w, 991m, 975m, 905wm {ν(Mo=O)}, 861w, 755bw, 630s, 558s. Resonance-Raman (KBr dilution, λ_e = 1064 nm) (ν/cm^{-1}): 800s, 534s, 460s, 325s, 214s. VIS–NIR (water) (λ_{max} /nm): 748 (IVCT), 1072 (IVCT).

¶ *Crystal data* for **1**: $C_{66}H_{753}Mo_{154}N_{22}Na_3O_{804}S_{22}$, M = 30272.96 g mol^{-1}, monoclinic, space group $C2/m$, a = 36.243(2), b = 42.788(2), c = 31.541(1) Å, β = 107.886(1)°, U = 46549(4) Å^3, Z = 2, D_c = 2.160 g cm^3, μ = 2.156 mm^{-1}, $F(000)$ = 29176, crystal size = 0.40 × 0.20 × 0.20 mm. Crystals of **1** 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-Kα radiation, graphite monochromator). Hemisphere data were collected in ω at 0.3° scan width in three runs with 606, 435 and 230 frames (ϕ = 0, 88 and 180°) at a detector distance of 5 cm. A total of 138023 reflections (1.50 < Θ < 27.06°) were collected of which 50782 unique reflections (R_{int} = 0.072) were used. An empirical absorption correction using equivalent reflections was performed with the program SADABS. The structure was solved with the program SHELXS-97 and refined using SHELXL-93 to R = 0.065 for 25857 reflections with $I > 2\sigma(I)$; max./min. residual electron density 2.141 and -1.701 e Å^{-3}. (SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen 1993/1997; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, 1999.) CCDC 154874. See http://www.rsc.org/suppdata/cc/b1/b100362n/ for crystallographic data in .cif or other electronic format.

‖ In the meantime we have isolated and characterized (including crystal structure determination) an analogous compound with valine amino acid ligands—also attached to the inner wall of the ring *via* the carboxylate oxygen atoms—which show the same type of disorder.

** Molecular modelling was performed with the Hyperchem 6 Pro program from Hypercube Inc. employing the MM+ force field. The parameters implemented in this program were used without change.

1 *Multifunctional Mesoporous Inorganic Solids*, ed. C. A. C. Sequeira and M. J. Hudson, Kluwer, Dordrecht, 1993; *Comprehensive Supramolecular Chemistry, Vol. 6, Solid-state Supramolecular Chemistry: Crystal Engineering* and *Vol. 7, Solid-state Supramolecular Chemistry: Two- and Three-dimensional Inorganic Networks*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle and J-M. Lehn, Pergamon/Elsevier, Oxford, 1996.

2 G. Férey and A. K. Cheetham, *Science*, 1999, **283**, 1125; H. Li, A. Laine, M. O'Keeffe and O. M. Yaghi, *Science*, 1999, **283**, 1145.

3 M. E. Davis, *Chem. Eur. J.*, 1997, **3**, 1745 and references therein.

4 A. Müller, F. Peters, M. T. Pope and D. Gatteschi, *Chem. Rev.*, 1998, **98**, 239.

5 (*a*) A. Müller, E. Krickemeyer, J. Meyer, H. Bögge, F. Peters, W. Plass, E. Diemann, S. Dillinger, F. Nonnenbruch, M. Randerath and C. Menke, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2122; (*b*) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, C. Beugholt, P. Kögerler and C. Lu, *Angew. Chem., Int. Ed.*, 1998, **37**, 1220; (*c*) A. Müller, M. Koop, H. Bögge, M. Schmidtmann and C. Beugholt, *Chem. Commun.*, 1998, 1501; (*d*) A. Müller, S. K. Das, H. Bögge, C. Beugholt and M. Schmidtmann, *Chem. Commun.*, 1999, 1035; (*e*) A. Müller, S. K. Das, V. P. Fedin, E. Krickemeyer, C. Beugholt, H. Bögge, M. Schmidtmann and B. Hauptfleisch, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1187; (*f*) A. Müller, S. Q. N. Shah, H. Bögge and M. Schmidtmann, *Nature*, 1999, **397**, 48.

6 A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann and F. Peters, *Angew. Chem., Int. Ed.*, 1998, **37**, 3360; A. Müller, V. P. Fedin, C. Kuhlmann, H. Bögge and M. Schmidtmann, *Chem. Commun.*, 1999, 927; A. Müller, S. Polarz, S. K. Das, E. Krickemeyer, H. Bögge, M. Schmidtmann and B. Hauptfleisch, *Angew. Chem., Int. Ed.*, 1999, **38**, 3241.

7 I. D. Brown, in *Structure and Bonding in Crystals*, ed. M. O'Keeffe and A. Navrotsky, Academic Press, New York, 1981, vol. II, pp. 1–30.

8 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 4th edn., 1986.

9 S. Polarz, B. Smarsly, C. Göltner and M. Antonietti, *Adv. Mater.*, 2000, **12**, 1503.