Exchanged ligands on the surface of a giant cluster: $[(MoO_3)_{176}(H_2O)_{63}(CH_3OH)_{17}H_n]^{(32 - n)-}$

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The synthesis of 1a·(32 − *n*)Na^+·*ca.* 600 H_2O·*ca.* 30 CH_3OH 1 containing the ring-shaped, mixed-valence (Mo^V/Mo^{VI}) cluster $[(MoO_3)_{176}(H_2O)_{63}(CH_3OH)_{17}H_n]^{(32 - n)-}$ 1a as a discrete unit in the crystal lattice is reported, which for the first time yields a compound of this type *via* a facile synthetic method and without amorphous reaction products; remarkably, H_2O ligands can be replaced by CH_3OH on the surface of a giant metal-oxide based cluster which has a nanometer sized cavity and, in contrast to zeolites, reducing properties.

Early reports on the giant reduced ring-shaped, metal-oxide cluster $[Mo_{154}(NO)_{14}O_{420}(\mu_3\text{-}O)_{28}(H_m)_{14}(H_2O)_{70}]^{(42 - n)-}$ **2**[1,2] and more recently on the even larger analogue $[(MoO_3)_{176}(H_2O)_{80}H_n]^{(32 - n)-}$ **3**[3] (a reduced, protonated giant molecular molybdenum oxide with H_2O ligands), have shown the difficulties associated with the synthesis, isolation, identification and characterization of such systems, especially of the *m* and *n* values which correspond to the different protonations; see below.[1–4] Here we report a facile synthetic method for the pure crystalline blue mixed-valence compound (type III according to the Robin–Day classification)[5] **1a**·(32 − *n*)Na^+·*ca.* 600 H_2O·*ca.* 30 CH_3OH **1** containing the discrete cluster $[(MoO_3)_{176}(H_2O)_{63}(CH_3OH)_{17}H_n]^{(32 - n)-}$ **1a** with CH_3OH ligands.‡ In contrast, all previously reported compounds of this type were obtained only under less lucid reaction conditions and not completely in crystalline form.

1 was simply prepared by addition of a methanolic solution of $MoCl_5$ to an acidified solution of molybdate§ and characterized by elemental analysis, single crystal X-ray structure analysis¶ [including bond valence sum (BVS) calculations for determination of the positions of the H atoms and the (formal) number of Mo^V centres], vibrational as well as VIS–NIR spectra, and redox titrations for the (additional) determination of the (formal) number of Mo^V centres.

The single crystal X-ray structure analysis¶ of compound **1** shows eight ring-shaped clusters in the unit cell, the (large) volume of which is comparable to that of protein structures (Fig. 1). The rings are packed only approximately parallel to the *a*,*b* plane, whereby they are tilted slightly relative to one another along the *a* and *b* axes. The cluster **1a** (Fig. 2) consists of sixteen sets of the three characteristic building blocks[2,6] $\{Mo_2\}$, $\{Mo_8\}$ and $\{Mo_1\}$ corresponding to the formula of the hexadecameric cluster $[\{Mo_2\}\{Mo_8\}\{Mo_1\}]_{16}$ ($\equiv[\{Mo^{VI}_2O_5(H_2O)_2\}\{Mo^{VI/V}_8O_{26}(\mu_3\text{-}O)_2(H_m)L_3Mo^{VI/V}\}]_{16}$ with L = H_2O, CH_3OH and m = 0, 1 or 2 corresponding to the overall charge related to n = 0, 16 or 32).‡ The positions of the CH_3OH ligands in **1a** can be best described by referring to the sixteen characteristic Mo_6O_6 rings which are formed by two adjacent $\{Mo_8\}$-type units and one $\{Mo_2\}$ group. In every such Mo_6O_6 ring but three, a CH_3OH ligand is found coordinated to one or two Mo centres, respectively (for details see Fig. 2; referring to the packing in the crystal structure, the CH_3OH ligands are located at regions in the direct neighbourhood of adjacent rings).

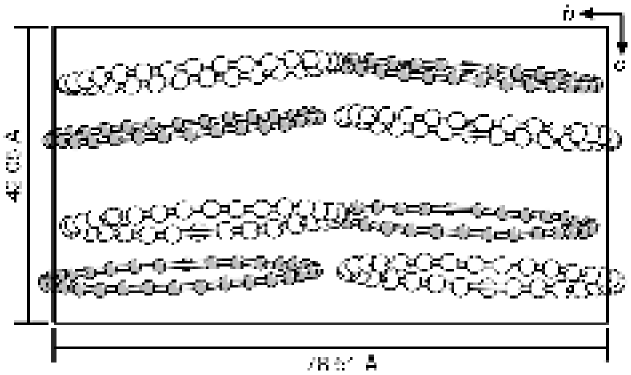

Fig. 1 Unit cell of **1** viewed along the *a* axis showing the packing of the rings. For the sake of clarity only the equatorial $\{Mo_1\}$-type atoms are shown (rings at the rear of the unit cell: grey).

Whereas **1a** is a mixed-valence cluster with an $S = 0$ spin ground state but no metal–metal bonds, the (rather) large diamagnetic mixed-valence $\{Mo_{43}\}$-type cluster[7] $[H_{13}Mo_{43}O_{112}\{(OCH_2)_3CCH_3\}_7]^{9-}$ contains 'dumb-bells' or pairs of covalently bonded Mo^V centres. On the other hand, in the largest reported polyoxotungstate $[Ln_{16}As_{12}W_{148}O_{524}(H_2O)_{36}]^{76-}$ all the W centres exist in completely oxidized W^{VI} form.[8]

The fast formation of cluster **1a** as well as the subsequent crystallization of compound **1**, free from amorphous precipitates, is facilitated not only by the use of aqueous methanol as solvent (with lower solubility than in water, as was used in previous preparation methods) but also by the addition of a solution containing Mo^V centres which become direct constituents of the reaction product **1**. In this context it should be mentioned that generations of chemists have tried to isolate crystals from molybdenum-blue solutions without success.[9,10] Another important result of the present study is that it is in principle possible to substitute ligands on the reducing surface of a giant metal-oxide based cluster with the possible consequence of influencing the activation of the ligands.

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Notes and References

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‡ The cluster charge 32 − *n* corresponds to the difference between the (formal) number of Mo^V centres (32 according to redox titrations and Mo-BVS values) and the number of protonations at the 32 μ_3-O atoms having BVS values of 1.20 ± 0.05. As these are practically constant in *ca.* 20 related structures in the corresponding $(\mu_3\text{-}O)_2O_2$ tetrahedra (see Fig. 2) we have an identical situation in all compounds which have either two, one or no protons in each such tetrahedron corresponding to n = 32, 16 or 0; but n = 28, 14 or 0 in tetradecameric species like **2**. The determination of the exact formula and the charge of the large investigated protonated mixed-valence cluster by single-crystal X-ray structure analysis therefore presents an almost invincible problem, in particular as charged lattice components like Na^+ located in cavities and channels and large amounts of crystal water molecules or solvent molecules cannot be clearly localized due to disorder phenomena. The analytical data, however, also have only limited accuracy because the concentration of the mentioned charged lattice components is very small (but not the number of ions in the formula unit!) and because the

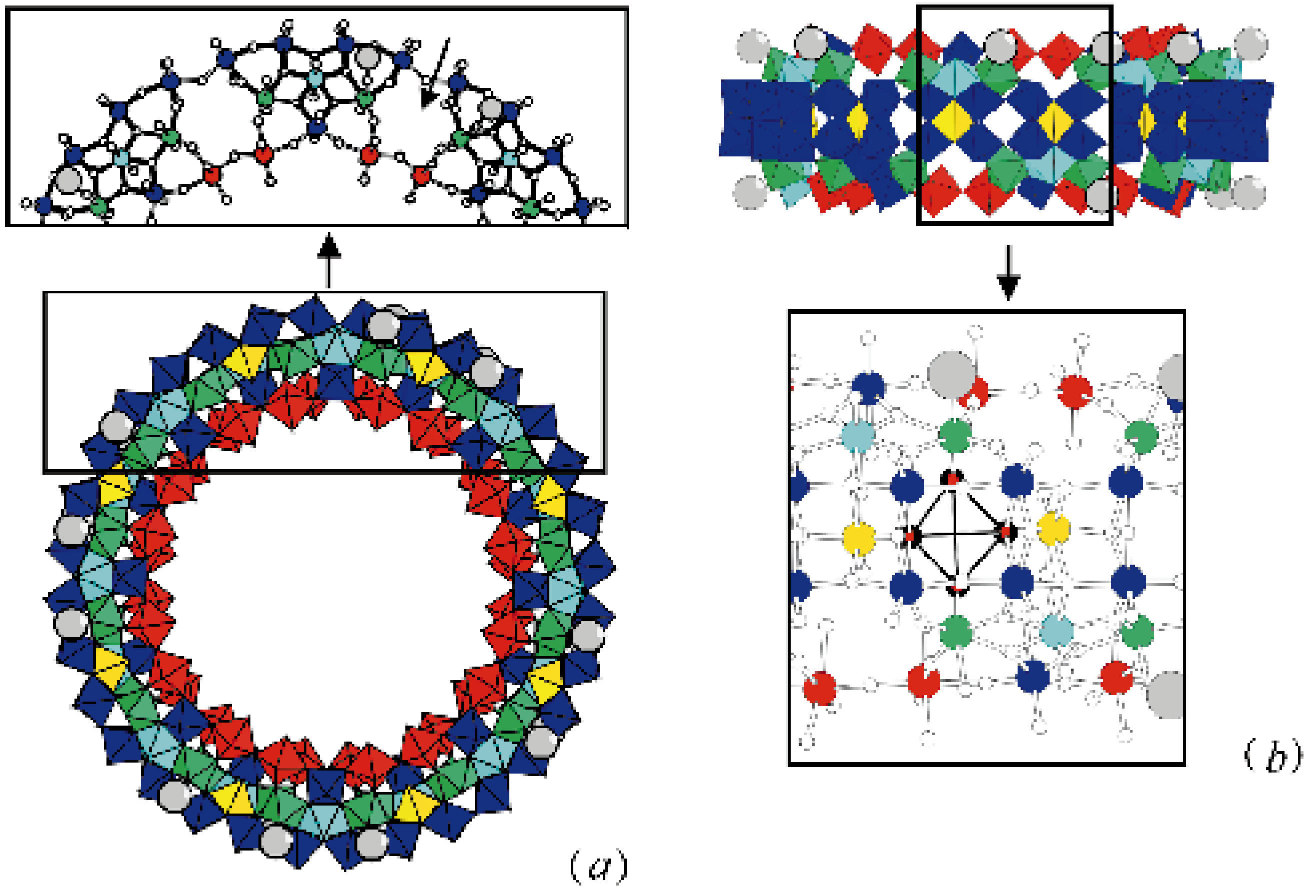

Fig. 2 Polyhedral representations of the structure of **1a** in two perspectives. (*a*) Top view, including an additional enlarged segment in ball-and-stick representation depicting the {Mo_8}-type units and {Mo_2} groups forming the Mo_6O_6 rings (see arrow) on the upper half of the cluster structure, showing the typical positions of the CH_3OH ligands with respect to the {Mo_8} units, as well as the twelve–membered rings. (*b*) Side view including an enlarged segment in ball-and-stick representation showing one of the sixteen $(\mu_3\text{-}O)_2O_2$ tetrahedra (highlighted by black lines) between two incomplete double-cubane-type fragments formed by five Mo and the related six O atoms of the {Mo_8} and {Mo_1} units, whereby the two μ_3-O atoms, highly accessible for protonation, are coordinated to (partly reduced) Mo centres. ({Mo_8} units: blue with the central pentagonal bipyramids (light blue) and the MoO_6 octahedra (green) at the right and left sides of these as (possible) coordination sites for the CH_3OH ligands; {Mo_2} units: red; {Mo_1} units: yellow; C atoms of CH_3OH ligands: grey; O atoms forming the $(\mu_3\text{-}O)_2O_2$ tetrahedron in the enlarged segment of (*b*): red connected by black lines).

large content of solvent molecules in the structure varies due to pronounced weathering. In any event, we consider an *n* value of 16 for the hexadecameric clusters **1a** and **3** (n = 14 for tetradecameric species) to be most suitable according to the sodium analysis together with the (only) possible *n* values.

§ A solution of $MoCl_5$ (0.5g; 1.83 mmol in 13.2 ml dry CH_3OH) was added dropwise to a stirred aqueous solution of $Na_2MoO_4{\cdot}2H_2O$ (2.01 g; 8.3 mmol in 18.5 ml H_2O) acidified with 1.0 ml 25% hydrochloric acid. The resulting blue solution was subsequently adjusted with 10% hydrochloric acid to pH 1.4 and stored under exclusion of air. Blue tetragonal-prismatic crystals which precipitated from the filtrate within 4 days were filtered and dried quickly in an argon stream. Yield: 0.64 g, 31.6% based on $MoCl_5$ used. Found: Na, 1.00; C, 1.51; H, 3.85 (Cl, 0.2). Calc.: Na, 0.94 (for 16 Na); C, 1.44; H, 3.94%. Subtraction of the estimated volume of the structurally localized atoms (using increments) from the total volume of the unit cell shows that a maximum of *ca.* 600 crystal water molecules can in principle be present per formula unit. **1**, however, loses a large amount of solvent molecules (about 60%) due to extremely strong and rapid weathering even at room temperature within 2 h. The analytical data which could therefore only be obtained for the partly weathered compound are corrected for this effect (based on time-dependent TG measurements), so that they can be compared to the calculated values which refer to the compound with the maximum crystal water content. IR ν/cm^{-1} (KBr pellet prepared under argon, 1700–400 cm^{-1}): 970m, 910wm [ν(Mo=O)], 820sh, 747s, 669sh, 634s, 559s. Resonance-Raman ν/cm^{-1} (KBr matrix, λ_e = 1064 nm): 804s, 536m, 465m, 325m, 217m. UV–VIS λ_{max}/nm (methanol): 743 (IVCT), 1072 (IVCT).

¶ *Crystal data* for **1**: $C_{47}H_{1530}Mo_{176}Na_{16}O_{1238}$, M = 39166.5 g mol^{-1}, tetragonal, space group $P42_1c$, a = 78.508(5), c = 42.050(3) Å, U = 259180(30) Å^3, Z = 8, D_c = 2.008 g cm^{-3}, μ = 1.76 mm^{-1}, $F(000)$ = 154270, crystal size = 0.35 × 0.35 × 0.35 mm^3. Crystals of **1** were removed from the mother liquor and immediately cooled to 198(2) K on a Bruker AXS SMART diffractometer (Mo-Kα, graphite monochromator). A total of 861055 reflections (1.70 < θ < 22.49°) were collected of which 168666 unique reflections (R_{int} = 0.1277) were used. The structure was solved using the program SHELXS-97 and refined using the program SHELXL-97 to R = 0.0951 for 111621 reflections with $I > 2\sigma(I)$. CCDC 182/911.

1 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.
2 A. Müller, F. Peters, M.T. Pope and D. Gatteschi, *Chem. Rev*., 1998, **98**, 239.
3 A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, C. Beugholt, P. Kögerler and C. Lu, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1220.
4 A. Müller, J. Meyer, E. Krickemeyer and E. Diemann, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1206.
5 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.
6 A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, F. Peters, C. Menke and J. Meyer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 484.
7 M. I. Khan and J. Zubieta, *J. Am. Chem. Soc.*, 1992, **114**, 10058; H. K. Chea, W. G. Klemperer and T. A. Marquart, *Coord. Chem. Rev.*, 1993, **128**, 209.
8 K. Wassermann, M. H. Dickman and M. T. Pope, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1445.
9 *Gmelins Handbuch der Anorganischen Chemie*, Verlag Chemie, Berlin, 1935: Mo, pp.134–137.
10 *Gmelin Handbook of Inorganic Chemistry*, Springer, Berlin, 1989: Mo Suppl. B3, pp. 61–68.

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