A hydrogen-bonded cluster with 'onion-type' structure, encapsulated and induced by a spherical cluster shell: $[(H_2O)_n\subset Mo^{VI}_{72}Mo^{V}_{60}O_{372}(HCO_2)_{30}(H_2O)_{72}]^{42-}$

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By reacting an aqueous solution of ammonium heptamolybdate with formic acid in the presence of hydrazinium sulfate at pH ≈ 4.2 the compound $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(HCO_2)_{30}(H_2O)_{72}]\cdot xHCO_2Na\cdot yH_2O$ 1 ($x \approx 30$, $y \approx 250$) with spherically shaped stable cluster anions is obtained; owing to the spherical shape of the cluster–shell template, the anion 1a (with the small 'nondisturbing' bidentate HCO_2^- ligand) exhibits a remarkable overall 'onion-type' structure, thereby revealing also a novel type of inclusion: a hydrogen-bonded cluster with 'onion-type' structure, which suggests interesting aspects for a new type of supramolecular chemistry.

Linking elementary building blocks in different ways in order to synthesize a large variety of different molecular constructions, in particular those of the nanoworld is still a formidable challenge for the inorganic chemist.[1] Recently we succeeded in developing a synthetic route for an inorganic superfullerene or a giant ball-shaped cluster anion.[2] Here we report on the synthesis of a new related compound **1** which shows a novel structural feature: an unusual hydrogen-bonded cluster of guest molecules encapsulated as a part of the overall 'onion-type' structure.

Compound **1** which crystallizes in the space group $R\bar{3}$ was synthesized by reducing an aqueous molybdate solution with hydrazinium sulfate in the presence of formic acid (pH ≈ 4.2).‡§ The spherical icosahedral cluster shell of the anion **1a** is built up by 12 $\{Mo_{11}\}$ fragments of the type $\{(Mo)Mo_5\}\{Mo^{V}_1\}_5$ with a central bipyramidal pentagonal $\{MoO_7\}$ unit (Fig.1). (Throughout, the oxidation state of the molybdenum center is only given if different from VI.) Each central $\{MoO_7\}$ unit is connected *via* edges to five $\{MoO_6\}$ octahedra which are linked in pairs to the five surrounding Mo^V atoms. Each of the latter is bonded to a Mo^V center of one of the five neighbouring $\{Mo_{11}\}$ fragments thus forming a $\{Mo^{V}_2\}$ unit. All oxygen atoms of the 132 $Mo–O_{term}$ groups lie on the surface of the ball-shaped cluster and accordingly the *trans*-orientated H_2O ligands of the 72 Mo centers as also the carboxylate ligands bonded to the $\{Mo^{V}_2\}$ groups point towards the center of the ball. To give an alternative description, the twelve $\{(Mo)Mo_5\}$ pentagons of **1a** are bridged *via* the 30 well known $\{Mo^{V}_2\}$ groups with Mo–Mo single bonds which themselves are stabilized by the bidentate carboxylate ligands. The corresponding formulation is $[\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}_2O_4(HCO_2)\}_{30}]^{42-}$.

Most interestingly, the small carboxylate ligand used here allows a special type of organization of the encapsulated H_2O molecules resulting in a hydrogen-bonded cluster as guest system with an 'onion-type' structure[3] (see Fig. 2 with space filling representation). Six H_2O molecules with nearly trigonal antiprismatic ordering (in violet) form the innermost shell with a distance of *ca.* 3.5 Å from the (unoccupied) center of the 'onion'. The second shell (6.2–6.9 Å, highlighted as green spheres) is approximately close packed and contains *ca.* 35 H_2O molecules. The third shell (8.2–8.7 Å, shown as yellow spheres) contains a smaller number of H_2O molecules. This unusual arrangement which is induced by the spherical cluster shell spanned by the 132 molybdenum atoms is obviously only possible in the presence of the comparatively small formate ligands coordinating to the $\{Mo^{V}_2\}$ groups. This allows the H_2O molecules of the third shell to occupy positions between the bidentate ligands in the region of the 'pores'.

To evaluate the influence of the carboxylate ligands on the structure of the encapsulated molecules we also used other carboxylate ligands. The analogous reaction of sodium molybdate with monochloroacetic acid, for instance, led to the formation of a spherically shaped cluster anion and the related compound $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(ClCH_2CO_2)_{30}(H_2O)_{72}]\cdot xClCH_2COONa\cdot yH_2O$ ($x \approx 15$, $y \approx 250$) which crystallizes in the space group $Fm\bar{3}$. However, due to the poor crystal quality and disorder problems we were unable to locate in detail the arrangement of guest molecules inside the cavity.¶ Interestingly, the spherical anion was possibly abundant in a solution investigated by Ostrowetsky in the early 1960s as the UV–VIS spectrum reported there is identical with that obtained by us.[4]

The high stability of **1** is remarkable and allows the development of a chemistry similar to that of the Keggin-ion type, for instance a new type of host–guest chemistry. In the

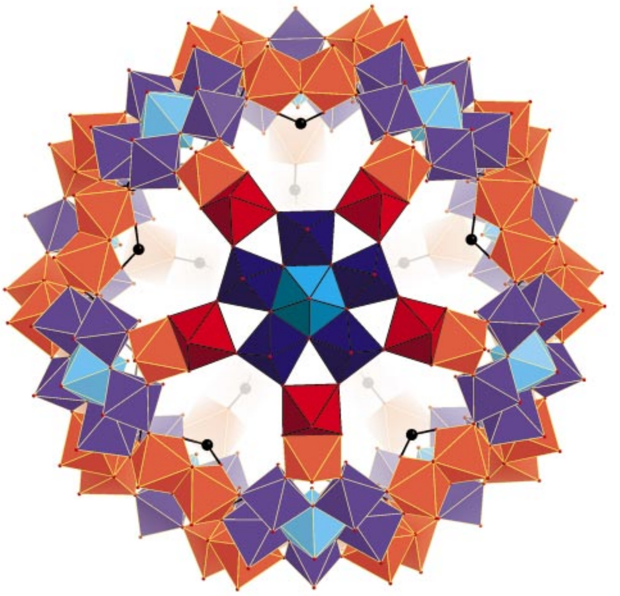

Fig. 1 Illustration of the structure of **1a** with perspective view along a fivefold symmetry axis highlighting a pentagonal $\{Mo_{11}\}$ unit owing to the structural complexity of the spherical shape shown in polyhedral representation. The five peripheral atoms of a $\{Mo_{11}\}$ unit are formed by the Mo centers of the five related $\{Mo^{V}_2O_4\}^{2+} = \{Mo^{V}_2\}$ groups attached to the $\{(Mo)Mo_5\}$ pentagons ($\{(Mo)Mo_5\}$ groups blue with the central MoO_7 bipyramids cyan; $\{Mo^{V}_2\}$ bridge red).

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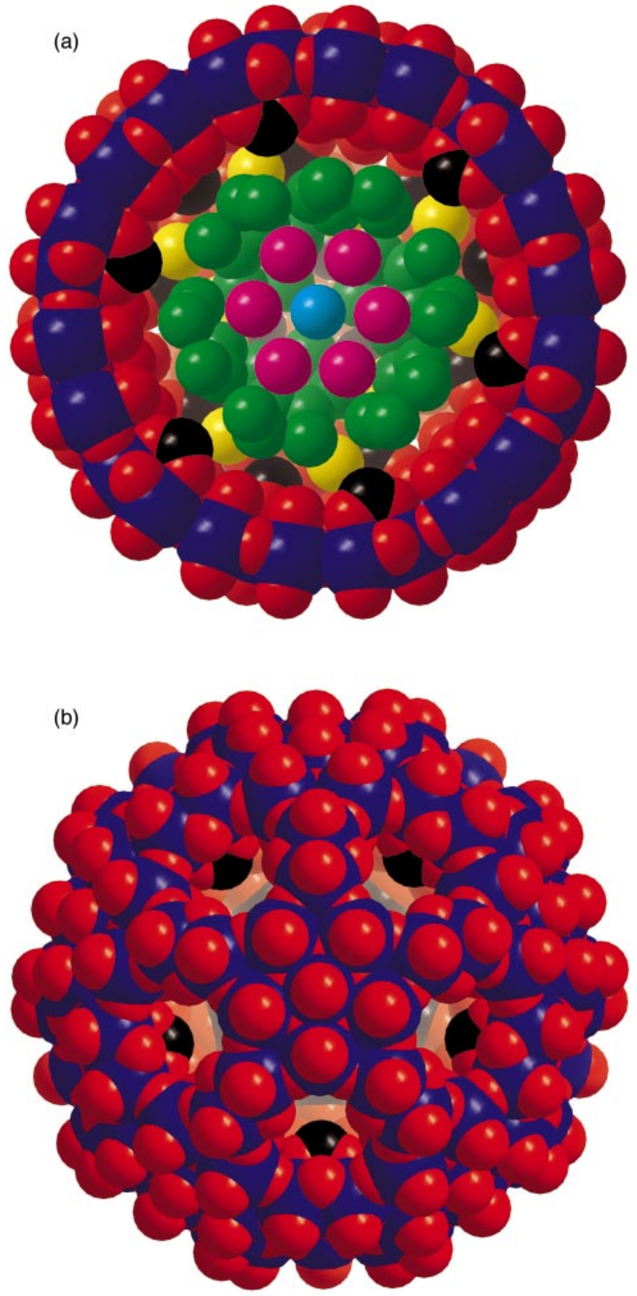

Fig. 2 Cross section through the equator of **1a** (shown in space filling representation) allowing a view into its cavity and highlighting the hydrogen-bonded cluster of the encapsulated H_2O molecules (only oxygen atoms are shown) (*a*). While the empty central region is marked by a light-blue circle, the different shells spanned by encapsulated H_2O molecules are represented by spheres with different colours: violet shell (radius *ca.* 3.5 Å), green shell (6.2–6.9 Å) and yellow shell (8.2–8.7 Å). Interestingly, the onion-like structure of the whole anion is completed by the three successive outer shells consisting of (1) that of the 72 H_2O and 30 formate ligands coordinated to molybdenum atoms and pointing into the cavity (*ca.* 10.5 Å), (2) that of the 132 molybdenum atoms (*ca.*13.1 Å) and (3) that of the terminal 132 oxygen atoms (*ca.* 14.7 Å) (molybdenum atoms blue, oxygen red, carbon black). For comparison, the whole spherical cluster anion is shown in space filling representation (*b*) (molybdenum atoms blue, oxygen red, carbon black).

present case it would be of special interest, theoretically, to study the influence of the outer spherical shell (including that with differently coordinated ligands) on the organization of the complementary inner-shells of hydrogen-bonded-type clusters, such as observed in compound **1**. The structures of the discrete $(H_2O)_n$-type clusters and related hydrogen-bonded aggregates are, of course, also interesting (see for instance ref. 5 and papers cited therein).

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Notes and references

‡ *Synthesis of* $(NH_4)_{42}[Mo^{VI}{}_{72}Mo^{V}{}_{60}O_{372}(HCO_2)_{30}(H_2O)_{72}]\cdot xHCO_2$-$Na\cdot yH_2O$ **1** ($x \approx 30, y \approx 250$): to a solution of NaOH (4.24 g), HCO_2H (5.00 ml; 98%) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (5.30 g) in 50 ml of water, $N_2H_4\cdot H_2SO_4$ (0.76 g) was added under continuous stirring, resulting in a green–blue colouration of the reaction mixture. After 10 min the pH value of the solution was adjusted to 4.2 by adding 10% HCO_2H dropwise. The solution was kept at room temperature for 4 days. The red–brown crystals which precipitated were filtered off, washed with MeOH and dried at room temperature. Yield: 1.90 g (32%). Correct elemental analyses for C, H, N, Na and H_2O. IR (solid, KBr pellet, ν/cm^{-1}): 1618m [$\delta(H_2O)$], 1562s [$\nu_{as}(CO_2)$], 1401s [$\delta_{as}(NH_4^+)$], 1350w [$\nu_s(CO_2)$], 972s and 938w [ν(Mo=O)], 858m, 801vs, 727vs, 633w, 572s, 474w, 414w. FT-Raman [solid (λ = 1064 nm), ν/cm^{-1}]: 923m and 880s [ν(Mo=O)], 695w, 477w, 434w, 375s, 316 m, 255w, 123w. UV–VIS [H_2O, absorption, λ/nm ($\varepsilon/\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}$)]: 450 (22000).

§ *Crystal data* for **1**: $C_{60}H_{872}Mo_{132}N_{42}Na_{30}O_{814}$, M = 28565.20, hexagonal, space group $R\bar{3}$, a = 32.4214(10), c = 73.249(3) Å, U = 66679.9(39) Å^3, Z = 3, D_c = 2.134 g cm^{-3}, μ = 1.93 mm^{-1}, $F(000)$ = 41736.0, crystal size = 0.25 × 0.20 × 0.15 mm^3. 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 1K CCD detector, Mo-Kα radiation, graphite monochromator). Hemisphere data collection 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 5.00 cm. A total of 115045 reflections ($0.78 < \theta < 25.01°$) were collected of which 25930 unique reflections (R_{int} = 0.1066) 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-97 to R = 0.0784 for 12308 reflections with $I > 2\sigma(I)$ (all programs from G. M. Sheldrick, University of Göttingen). Max./min. residual electron density 2.629 and −1.367 e Å^{-3} . CCDC 182/1216. See http://www.rsc.org/suppdata/cc/1999/927/ for crystallographic files in .cif format.

¶ *Synthesis of* $(NH_4)_{42}[Mo^{VI}{}_{72}Mo^{V}{}_{60}O_{372}(ClCH_2CO_2)_{30}(H_2O)_{72}]\cdot xClCH_2$-$CO_2Na\cdot yH_2O$ ($x \approx 15$, $y \approx 250$). To a solution of NaOH (4.00 g), $ClCH_2CO_2H$ (9.45 g) and $Na_2MoO_4\cdot 2H_2O$ (5.00 g) in 50 ml of water, $N_2H_4\cdot H_2SO_4$ (0.610 g) was added under continuous stirring, resulting in a green–blue colouration of the reaction mixture. After 10 min the pH of the solution was adjusted to 4.2 by adding 20% $ClCH_2CO_2H$ dropwise and kept at room temperature for 4 days. H_2O (50 ml) and NH_4Cl (8.0 g) were subsequently added to the filtrate and the solution allowed to stand for a further 2 days. The red–brown crystals which precipitated were filtered off, washed with MeOH and dried at room temperature. Yield: 1.05 g (24%). Correct elemental analyses for C, H, N, Na and H_2O. IR (solid, KBr pellet, ν/cm^{-1}): 1758w, 1618sh [$\delta(H_2O)$], 1579s, [$\nu_{as}(CO_2)$], 1407s [$\delta_{as}(NH_4^+)$], (1259w, 1172w, 1085w), 969s and 938sh [ν(Mo=O)], 852m, 795s, 725s, 630w, 570s, 486w, 414w. FT-Raman [solid (λ 1064 nm), ν/cm^{-1}]: 942m and 873s [ν(Mo=O)], 465w, 437w, 373s, 316m, 251w, 212w, 132w. UV–VIS [H_2O, absorption, λ/nm ($\varepsilon/\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}$)]: 452 (21000). *Crystal data*: $C_{90}Cl_{45}Mo_{132}N_{42}Na_{15}O_{784}$, M = 29726.32, cubic, space group $Fm\bar{3}$, a = 46.06 Å, U = 97703 Å^3, Z = 4, T = 173(2) K. The structure was not fully reported because of the poor crystal quality.

The figures were prepared with the program DIAMOND (K. Brandenburg, *Diamond—Informationssystem für Kristallstrukturen*, Crystal Impact GbR, Germany).

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3 Compare with MS_2-based onion-type structures (M = Mo, W), *e.g.* R. Tenne, L. Margulis, M. Genut and G. Hodes, *Nature*, 1992, **360**, 444.

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