A novel acetated 54-member crown-shaped polyoxomolybdate with unprecedented structural features: $Na_{26}[\{Na(H_2O)_2\}_6(\{\mu_3\text{-}OH)_4Mo^{V}_{20}Mo^{VI}_{34}O_{164}(\mu_2\text{-}CH_3COO)_4\}]\cdot\approx 120H_2O$

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The EPR silent acetated 54-member crown-shaped polyoxomolybdate $Na_{26}[\{Na(H_2O)_2\}_6(\{\mu_3\text{-}OH)_4Mo^{V}_{20}Mo^{VI}_{34}O_{164}(\mu_2\text{-}CH_3COO)_4\}]\cdot\approx 120H_2O$ (1), constructed from two different but related building blocks in a new mode, is synthesized in high yield by reducing an acidified aqueous solution of $Na_2MoO_4\cdot 2H_2O$ and $CH_3COONa\cdot 3H_2O$.

Ever since interest was sparked by the biological activity of the sodium cryptate $[NaW_{21}Sb_9O_{86}]^{18-}$, a species that has been subsequently applied as HAP23 in AIDS therapy,[1,2] there has been an enormous growth in the area of inorganic 'host–guest' polyoxometalates, partly motivated by their potential applications in catalysis, biology, medicine and materials science.[3,4] Generally, the guests are linked to the *endo* oxygen atoms of the host shells *via* valence bonds or intermolecular interactions such as hydrogen bonding.[5–7] One among many examples is that the N_3^- or NO_3^- anion is encapsulated within an approximately spherical $\{H_{12}V_{18}O_{44}\}^{n-}$ polyoxovanadate 'host' cage.[8]

Octamolybdates exhibit various structural patterns in the solid-state and these isomers can interconvert with each other by 'bond-making/breaking' in solution.[9,10] Although a number of corresponding oxide-based composite solid-state materials were synthesized in the presence of structure-directing organic ligands such as diamines, few nanometered polyoxomolybdates constructed from these octamolybdates have been reported. We report here the synthesis and characterization of a novel acetated 54-member crown-shaped polyoxomolybdate, which contains unprecedented building blocks, and exhibits interesting structural features.

$$Na_{26}[\{Na(H_2O)_2\}_6(\{(\mu_3\text{-}OH)_4Mo^{V}_{20}Mo^{VI}_{34}O_{164}\text{-}(\mu_2\text{-}CH_3COO)_4\}]\cdot\approx 120H_2O \qquad (1)$$

Compound **1** was synthesized in high yield by reducing an acidified aqueous solution of Na_2MoO_4,† and characterized by elemental analysis, cerimetric titration (to determine the number of Mo^V), thermogravimetric analysis (to determine the amount of crystallized water), bond valence sum (BVS) calculations[11,12] (to determine the number and the positions of OH groups, as well as the number of Mo^V centers), spectroscopic methods (IR, Raman and UV–VIS)‡ and single-crystal X-ray structure analysis.§

The structure of **1** consists of a discrete 54-member crown-shaped $[\{Na(H_2O)_2\}_6(\{(\mu_3\text{-}OH)_4Mo^{V}_{20}Mo^{VI}_{34}O_{164}(\mu_2\text{-}CH_3COO)_4\}]^{26-}$ **1a** nanoanion (containing four bridging acetate groups and six encapsulated seven-coordinated sodium cations as 'guests'), and 26 Na^+ cations. As shown in Figs. 1 and 2, two different but related building blocks have been found in **1a**. The first building block is the centrosymmetric octamolybdate $\{Mo_8O_{28}\}$ ($\equiv[Mo^{V}_2Mo^{VI}_6O_{28}]^{10-}$) moiety, which consists of eight distorted edge-shared molybdenum–oxygen octahedra. The structure of this centrosymmetric octamolybdate is very similar to other reported octamolybdate anions, which can be described as $[Mo_8O_{26}(X)_2]^{2n-4}$, for example, $[(HO)_2Mo_8O_{26}]^{6-}$, where *n* is the normal charge of coordinated base X.[12–14] However, in addition to long interblock distances existing within this octamolybdate unit, rather short metal–metal bonds are also found between two neighboring $\{Mo_8O_{28}\}$ units (Mo(7)–Mo(27), 2.58216(18), Mo(19)–Mo(20), 2.5985(16) Å). To the best of our knowledge, such short Mo–Mo distances have rarely been observed in other polyoxomolybdates, particularly in nano-size systems. The second feature is the unprecedented asymmetric $\{Mo_9O_{30}(X)_2\}$ ($\equiv[(\mu_3\text{-}OH)_2Mo^{V}_4Mo^{VI}_5\text{-}\ O_{28}(CH_3COO)_2]^{10-}$) unit, which is constructed by nine molybdenum atoms (four Mo^V and five Mo^{VI} centers). Each molybdenum is coordinated by six oxygen atoms in distorted octahedral arrangement with one short Mo=O bond for Mo^V and two for Mo^{VI}. Again, long Mo–Mo distances (around 3.21 Å) and short Mo–Mo bonds (shorter than 2.6 Å) are also formed within the new $\{Mo_9O_{30}(X)_2\}$ unit. In summary, each crown-shaped anion **1a** contains ten short Mo–Mo bonds and eight long interblock Mo–Mo distances, which are listed in the caption to Fig. 1.

The two building blocks are connected to each other into a spiral $[(HO)_4Mo^{V}_{16}Mo^{VI}_{34}\text{-}\ O_{160}(CH_3COO)_4]^{44-}$ ring, in which the linkage between the two neighboring $\{Mo_8O_{28}\}$ units is edge-shared, while that between $\{Mo_8O_{28}\}$ and $\{Mo_9O_{30}(X)_2\}$ is corner-shared (Fig. 2). Four additional $\{Mo_1\}$ ($\equiv[Mo^{V}O]^{3+}$) groups, which cap the linking Mo atoms between $\{Mo_8O_{28}\}$ and $\{Mo_9O_{30}(X)_2\}$ units, are bridged by four acetate ligands to complete the crown-shaped 'host' nanoanion. Six seven-coordinated Na^+ cations with (distorted) pentagonal-

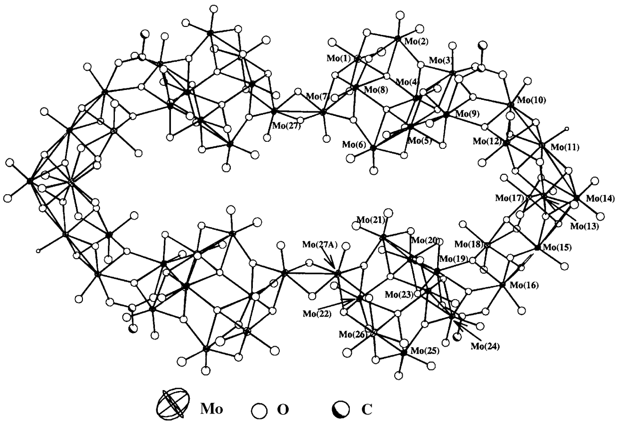

Fig. 1 (*a*) Perspective drawing of **1a** constructed by two different building blocks: $\{Mo_8O_{28}\}$ ($\equiv[Mo^{V}_2Mo^{VI}_6O_{28}]^{10-}$) and novel unprecedented $\{Mo_9O_{30}(X)_2\}$ ($\equiv[(\mu_3\text{-}OH)_2Mo^{V}_4Mo^{VI}_5O_{28}[(CH_3COO)_{2/2}]_2]^{10-}$) moieties. According to BVS calculations, the following molybdenum centers are Mo^V: Mo(5), Mo(7), Mo(9), Mo(10), Mo(11), Mo(15), Mo(16), Mo(19), Mo(20) and Mo(27). Selected Mo–Mo distances: Mo(5)–Mo(9) 2.5974(18), Mo(5)–Mo(6) 3.2146(18), Mo(7)–Mo(27) 2.5816(18), Mo(10)–Mo(11) 2.5962(17), Mo(11)–Mo(14) 3.2185(17), Mo(14)–Mo(15) 3.2143(18), Mo(15)–Mo(16) 2.5933(18), Mo(19)–Mo(20) 2.5985(16), Mo(20)–Mo(21) 3.2096(17) Å.

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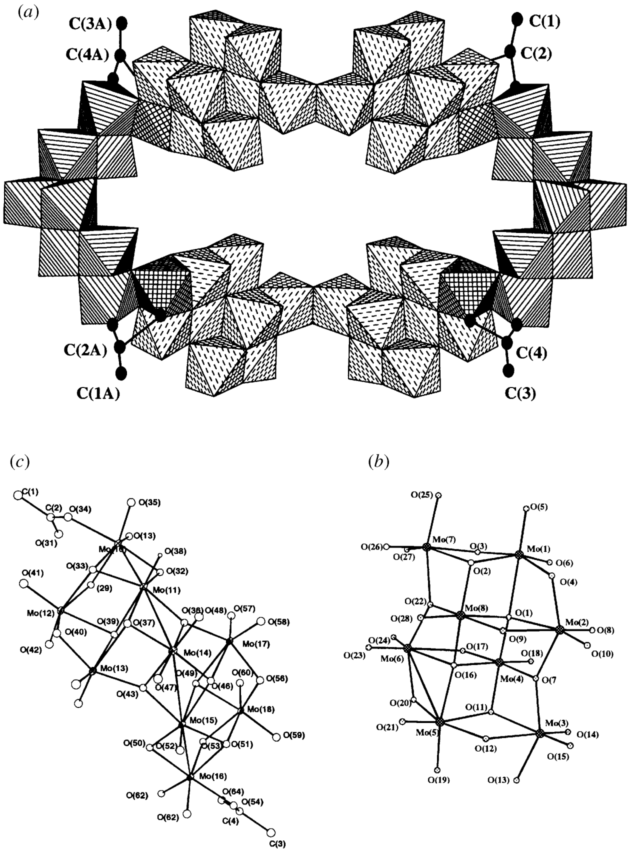

Fig. 2 (*a*) Polyhedral representation of **1a** (all encapuslated Na^+ cations are deleted for clarity). The linkage between two neighboring $\{Mo_8O_{28}\}$ moieties (having a pattern of dashed lines) is edge-shared, while that between $\{Mo_8O_{28}\}$ and $\{Mo_9O_{30}(X)_2\}$ units (marked with parallel lines) are corner-shared. $\{Mo^VO\}^{3+}$ units are cross-hatched; (*b*) the $\{Mo_8O_{28}\}$ unit in **1a**; (*c*) the $\{Mo_9O_{30}(X)_2\}$ (X=CH_3COO) moiety in **1a**.

bipyramid environments are held inside the 'host' nanoanion by linking to five *endo* oxygen atoms with Na–O distances of 2.264–3.010 Å. These encapsulated Na^+ cations are located near Mo atoms (Na(1)–Mo(10), 3.691, Na(2)–Mo(16), 3.697, and Na(3)–Mo(6), 3.989 Å), and may play an important template role in the formation of the crown-shaped anion **1a**.

The silent EPR spectrum of compound **1** indicates that the unpaired electrons of the two neighboring Mo^V atoms are completely coupled, which is consistent with structural analysis. The IR spectrum of **1** exhibits strong bands at 962 (s), 947 (s) and 901 (s) attributed to ν(Mo=O), and a series of characteristic bands for bridging acetate groups in the range 1550–1200 cm^{-1}.

The positions of OH^- and Mo^V sites are assigned on the basis of the *s* values, in which *s* is the bond strength derived from the expression $s = (R/1.882)^{-6.0}$ (R = Mo–O distances).[11] According to this procedure, the O(39), O(39A), O(49) and O(49A) ascribed to OH^- sites, have *s* values (0.9875–0.9927) are significant smaller than that of the others (1.5707–2.0930) which are normal for the O^{2-} sites.

In summary, a novel 54-member crown-shaped polyoxomolybdate has been synthesized and characterized crystallographically. It seems that there exists various building blocks in solution, and it is possible to link those building blocks to a variety of crown-shaped polyoxomolybdates. This has been confirmed recently by our preliminary experiments.

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Notes and references

† *Synthesis of* **1**: to a solution of $Na_2MoO_4{\cdot}2H_2O$ (40 mmol, 9.68 g) and $CH_3COONa{\cdot}3H_2O$ (50 mmol) in H_2O (55 ml) acidified by 8.5 ml of 17% HCl (pH = 4.15), $NH_2NH_2{\cdot}2HCl$ (4.8 mmol, 0.5 g) was added under continuous stirring for 5 min. The resulting reaction mixture was then kept at room temperature in a wide-necked Erlenmeyer-flask for ten days (color changed from green to dark brown). Black–red columnar crystals of **1** were filtrated from the mother liquor, washed with cooled propan-2-ol, and finally dried in air (4.95 g, yield 59.54%). Anal. calcd. for $C_8H_{280}Mo_{54}Na_{32}O_{308}$: Mo, 46.16, Na, 6.56, C, 0.86, H, 2.51. Found: Mo, 46.62, Na, 6.59 (atomic absorption method), C, 0.79, H, 2.71% (determination was carried out on EA1110 (CHNS-0 CE instruments). Cerimetric titration was carried out to determine the number of Mo^V (~ 20 ± 2 electrons), which is consistent with the results of BVS calculations.

‡ Characteristic IR bands for **1** (KBr pellet, ν/cm^{-1}): 1630 (s, $\delta(H_2O)$), 1541 (s-m, ν_{as}(COO)), 1444 (m, ν_s(COO)), 962 (s), 947 (s), 901 (s) (ν(Mo=O)), 862(s), 721 (s), 727 (s), 494 (m): Characteristic FT-Raman bands (λ_e = 1064 nm, ν/cm^{-1}): 969 (vs), 940 (s), 927 (m), 912 (w) (ν(Mo=O)), 875 (w), 796 (w), 472 (m), 352 (m), 323 (m), 281 (m). Characteristic UV/VIS bands (λ/nm): 308.00 ($\varepsilon = 6.71 \times 10^4\ M^{-1}\ cm^{-1}$) and 209.50 ($\varepsilon = 3.59 \times 10^5\ M^{-1}\ cm^{-1}$).

§ *Crystal data*: $C_8H_{280}Mo_{54}Na_{32}O_{308}$, 11222.76, triclinic, $P\bar{1}$, a = 17.6814(6), b = 19.8620(7), c = 23.4663(8) Å, α = 90.0210(10), β = 102.6740(10), γ = 100.41°, V = 7902.0(5) Å^3 and Z = 1. The diffraction data were collected on a Simens SMART CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature. A total of 41201 reflections (0.89 to 25.02°) were collected, of which 27539 independent reflections [R(int) = 0.0507] were used. The coordinates of molybdenum atoms were determined by direct methods, and the remaining non-hydrogen atoms were located and refined by a usual procedure of a combination of the difference Fourier synthesis and least-squares technique. All molybdenum atoms and partial other non-hydrogen atoms were refined with anisotropic thermal parameters giving rise to convergence with R_1 = 0.0718 and wR_2 = 0.1969 ($I > 2((I))$). CCDC182/1725. See http://www.rsc.org/suppdata/cc/b0/b004948o/ for crystallographic files in .cif format.

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