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Novel Acetate Polyoxomolybdate “Host” Accommodating a Zigzag-Chainlike “Guest” of Five Edge-Shared Sodium Cations: $Na_{21}\{[Na_5(H_2O)_{14}]\subset[Mo_{46}O_{134}(OH)_{10}(\mu\text{-}CH_3COO)_4]\}\cdot CH_3COONa\cdot\approx 95H_2O$

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A novel ESR-silent polyoxomolybdate $Na_{21}\{[Na_5(H_2O)_{14}]\subset[Mo^{V}_{20}Mo^{VI}_{26}O_{134}(OH)_{10}(\mu\text{-}CH_3COO)_4]\}\cdot CH_3COONa\cdot\approx 90H_2O$ (**3**) was simply synthesized in high yield by reducing an acidified aqueous solution of $Na_2MoO_4\cdot 2H_2O$ and $CH_3COONa\cdot 3H_2O$. The structure of **3** is constructed by a 46-member crown-shaped anion, $[Na_5(H_2O)_{14}]\subset[Mo^{V}_{20}Mo^{VI}_{26}O_{134}(OH)_{10}(\mu\text{-}CH_3COO)_4]^{21-}$, **3a**, which is built up by three different but related building blocks in a new mode and further connected into layers via Na^+ and hydrogen bonds. Crystal data of compound **3**: triclinic space group P(–1); $a = 16.4065(3)$, $b = 17.4236(2)$, $c = 20.8247(3)$ Å; $\alpha = 87.57$, $\beta = 67.9810(10)$, $\gamma = 80.6970(10)°$; $V = 5445.08(14)$ Å^3; $Z = 1$; $D_{calcd} = 2.902$. Structure solution and refinement are based on 19 014 reflections, $R = 0.0750$.

Since the biologically active sodium cryptate $[NaW_{21}Sb_9O_{86}]^{18-}$ was reported,[1] an enormous growth in the area of inorganic “host−guest” polyoxometalates has been achieved.[2] Nowadays, the number of such “host−guest” complexes known to contain “guest” anions, cations, molecules such as CH_3CN, or cation/anion aggregates such as $NH_4^+Cl^-$, is very vast.[3] However, such complexes in this field will certainly continue to attract greater attention, because of their enormous structural diversity and potential applications in catalysis, biology, and medicine.[4]

The employment of some organic ligands such as carboxylic acids and organodiamines, which can be extensively linked to inorganic oxide backbones and have a dramatically profound impact on the oxide structures, offers a powerful synthetic route for the design of novel materials.[5] For example, CH_3COOH and HCOOH were introduced into the molybdenum-blue systems, giving rise to the formation of giant ball-shaped, nanometer-sized basket-shaped, or onion-shaped polyoxomolybdate anions based on interesting $\{Mo_{11}\}$ blocks. In a previous paper, we showed that the crown-shaped (twisted) anion **1a** ($\equiv[\{Na(H_2O)_2\}_6\subset\{(\mu_3\text{-}OH)_4Mo^{V}_{20}Mo^{VI}_{34}O_{164}(\mu_2\text{-}CH_3COO)_4\}]^{26-}$) is constructed from blocks $\{Mo_8\}$ and $\{Mo_9\}$.[7] Using a similar reaction system, we have now succeeded in selectively isolating another acetate crown-shaped, mixed-valence, ESR-silent polyoxomolybdate, **3**, which exhibits some interesting structural features: (1) the host shells are constructed from three different but related building blocks; (2) each “host” accommodates a zigzag-chainlike “guest” of five edge-shared sodium cations; and (3) weak Mo−Mo interactions and rather strong Mo−Mo bonds (shorter than 2.61 Å) are found in the compound.

$$Na_{26}[\{Na(H_2O)_2\}_6\subset\{(\mu_3\text{-}OH)_4Mo^{V}_{20}Mo^{VI}_{34}O_{164}(\mu_2\text{-}CH_3COO)_4\}]\cdot\approx 120H_2O\ (\mathbf{1})^{7}$$

$$Na_9[\{Na(H_2O)_2\}\subset\{(\mu_3\text{-}OH)_4Mo^{V}_{8}Mo^{VI}_{10}O_{52}(CH_3COO)_2\}]\cdot\approx 45H_2O\ (\mathbf{2})^{8}$$

$$Na_{21}[\{Na_5(H_2O)_{14}\}\subset\{Mo^{V}_{20}Mo^{VI}_{26}O_{134}(OH)_{10}(\mu\text{-}CH_3COO)_4\}]\cdot CH_3COONa\cdot\approx 95H_2O\ (\mathbf{3})$$

Compound **3** was simply synthesized in high yield by reducing an acidified aqueous solution of Na_2MoO_4[9] and

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characterized by elemental analysis,[10] cerimetric titration (to determine the number of Mo^{V}), thermogravimetric analysis (to determine the amount of crystallized water), bond valence sum (BVS) calculations[11] (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),[12] and single-crystal X-ray structure analysis.[13]

One of the most challenging problems the chemists in the POMs (polyoxometalates) field confront is how to control the equilibria among different species in one reaction pot and then, of course, isolate desirable products. Recently, our interest has been focusing on seeking a simple synthetic route to isolate novel "host−guest" compounds with desirable properties. Our preliminary work shows that the main factors that affect these equilibria are acidity, temperature, and the concentration of reagents. Several reactions in a controllable manner to isolate different crown-shaped acetate polyoxomolybdates were carried out under different pH values and concentrations. The results indicated that, at higher acidity or higher concentration of Na_2MoO_4, the equilibria are favorable for the higher nuclearity product. At pH = 4.2, $c(Na_2MoO_4) = 0.5$ M, and $c(CH_3COO) = 1.22$ M, black-brown plates of the 18-member ring crown-shaped polyoxomolybdate **2**,[8] of which the structure is slightly different from that reported by Müller et al.,[6b] were precipitated. At pH = 3.5, $c(Na_2MoO_4) = 0.5$ M, $c(CH_3COO) = 1.22$ M, and adding a certain amount of electrolyte NaCl, the 46-member inorganic crown **3**, isolated as black-brown needles, is the only product, while at pH = 4.2, $c(Na_2MoO_4) = 0.68$ M, and $c(CH_3COO) = 0.86$ M, 54-member ring polyoxoanion **1** enclosing six seven-coordinated Na^+ is obtained predominantly.[7]

The compound **3** is constructed by 46-member crown-shaped anions, $[Na_5(H_2O)_{14}]\subset[Mo^{V}_{20}Mo^{VI}_{26}O_{134}(OH)_{10}(\mu\text{-}CH_3COO)_4]^{21-}$ **3a**, which is built up by the three different but related building blocks, $\{Mo_8O_{28}\}(\equiv[Mo^{V}_2Mo^{VI}_6O_{28}]^{10-})$, $\{Mo_9O_{30}(X)_2\}(\equiv[(OH)_2Mo^{V}_4Mo^{VI}_5\{(CH_3COO)_{2/2}\}_2]^{10-})$, and $\{Mo_4O_{15}(X)\}$ $(\equiv[(OH)_3Mo^{V}_2Mo^{VI}_2O_{12}(CH_3COO)_{2/2}]^{6-})$ (Figure 1). The structures of $\{Mo_8O_{28}\}$ and $\{Mo_9O_{30}(X)_2\}$ units had been described in details in our previous paper,[7] and the relationships among the three units are further illustrated in Supporting Information.

The first kind of building blocks, centrosymmetric octamolybdate $\{Mo_8O_{28}\}$ $(\equiv[Mo^{V}_2Mo^{VI}_6O_{28}]^{10-})$ moiety, consists of eight distorted edge-shared molybdenum−oxygen octahedra. This octamolybate unit is structurally similar to other octamolybdate anions described as $[Mo_8O_{26}(X)_2]^{2n-4}$ (where n is the normal charge of coordinated base X).[14] More interestingly, each crown-shaped anion **3a** contains two asymmetric $\{Mo_9O_{30}(X)_2\}$ $(\equiv[(OH)_2Mo^{V}_4Mo^{VI}_5O_{28}[(CH_3COO)_{2/2}]_2]^{10-})$ units. The asymmetric $\{Mo_9O_{30}(X)_2\}$ unit is constructed by nine molybdenum atoms, of which each Mo is coordinated by six oxygen atoms in distorted octahedral arrangement with one short Mo═O bond for Mo^{V} and two for Mo^{VI}. Short Mo─Mo bonds (∼2.6 Å) are formed between any two Mo^{V} atoms, while weak metal−metal interactions with Mo─Mo distances of about 3.21 Å are found between any Mo^{V} and Mo^{VI} centers. In addition, novel $\{Mo_4O_{15}(X)\}$ $(\equiv[(OH)_3Mo^{V}_2Mo^{VI}_2O_{12}(CH_3COO)_{2/2}]^{6-})$ subunits are also found in 46-member ring **3a**. This building block is constructed from four edge-shared molybdenum−oxygen octahedral, and it exhibits similar polyhedral representation to that of the $\{Mo_4O_{13}\}^{2-}$ units of the parent β-$[Mo_8O_{26}]^{4-}$ anion.[15]

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(8) Crystal data: $C_4H_{104}Mo_{18}Na_{10}O_{107}$, monoclinic, space group $C2/c$; $a = 25.9907(8)$, $b = 16.5992(3)$, $c = 22.8473(7)$ Å; $\beta = 93.4370(10)°$; $V = 9839.2(5)$ Å^3; final $R = 0.0416$ $[I > 2\sigma(I)]$ based on 8666 independent reflections [R(int) = 0.0252] with max/min electron density 1.814 and −1.298 e/Å^3. Details of the structure and related reaction of the 18-membered ring crown-shaped polyoxomolybdate will be discussed elsewhere.

(9) Synthesis of compound **3**: To a solution of $Na_2MoO_4{\cdot}2H_2O$ (27 mmol, 6.53 g) and $CH_3COONa{\cdot}3H_2O$ (65.70 mmol, 8.94 g) in H_2O (34 mL) (the pH value was adjusted to 3.5 with 20 mL of 10% HCl) was added $NH_2NH_2{\cdot}2HCl$ (4.1 mmol, 0.43 g) under continuous stirring within 5 min. The reaction mixture (the color changed from green to dark brown) was filtrated the next day, and after 1.50 g NaCl was added, the filtrate was then kept in a wide-necked Erlenmeyer flask without further disturbance for two weeks. The mainly precipitated black-brown columnar crystals of **3** were filtered, washed with cooled 2-propanol, and finally dried in air (yield: 3.62 g, 65.41% based on Mo).

(10) Anal. Calcd for $C_{10}H_{243}Mo_{46}Na_{27}O_{263}$: Mo, 45.94; Na, 6.46; C, 1.25; H, 2.53. Found: Mo, 46.12; Na, 5.96 (atomic absorption method); C, 1.21; H, 2.71 (determination was carried out on EA1110 CHNS-0 CE instruments). A total of 21 Na^+ ions were successfully found in per unit cell on the basis of electron density, which is slightly less than the number expected from elemental analyses. Additionally, an acetic molecule of crystallization was located by fixing C−O and C−C distances, which is consistent with elemental analysis. Just as for other extremely large structures (e. g., $\{Mo_{144}\}$, $\{Mo_{146}\}$, and $\{Mo_{176}\}$ reported by Prof. Müller), only part of Na^+ cations expected from elemental analyses can be successfully found in structure solving because of disorder. However, the main structures of the anions seem not to be affected by disorder. In this case, the formula including the charge can be determined within an error limit if analytical data and the charges of all ingredients are taken into account. Several sodium analyses have been carried out. However, because of the extremely high content of crystallization water, which may vary to some extent even at room temperature as a result of facile weathering, the analytical data cannot be very accurate. Thus, the detected Na value is somewhat lower than expected from the given formula for **3**. Cerimetric titration has been carried out to determine the number of Mo^{V} (∼20 ± 1 electrons), which is rather consistent with the results of BVS calculations.

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(12) Characteristic IR bands for **3** (KBr pellet, ν[cm^{-1}]): 1635(m, $\delta(H_2O)$), 1558(m), 1541(m) (ν_{as}(COO)), 1506(w), 1444(m) (ν_s(COO)), 964, 947(s), 901(m s) (ν(Mo═O)), 868(m), 831(w), 781(m), 725, 619(s), 561(m), 490(s), 465(m). Characteristic FT-Raman bands ($\lambda_e = 1064$ nm, ν[cm^{-1}]): 969(m), 950(m), 935(w), 910(w) (ν(Mo═O)), 796 (w), 468(s). Characteristic UV−vis bands (λ, nm): 210 ($\epsilon = 2.77 \times 10^5$ M^{-1} cm^{-1}), 291 ($\epsilon = 3.76 \times 10^4$ M^{-1} cm^{-1}), and 297 ($\epsilon = 3.76 \times 10^4$ M^{-1} cm^{-1}).

(13) Crystal data: $C_{10}H_{243}Mo_{46}Na_{27}O_{263}$; 9607.01; triclinic; $P(-1)$; $a = 16.4065(3)$, $b = 17.4236(2)$, $c = 20.8247(3)$ Å; $\alpha = 87.57$, $\beta = 67.9810(10)$, $\gamma = 80.6970(10)°$; $V = 5445.08(14)$ Å^3; and $Z = 1$. The diffraction data were collected on a Siemens SMART CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at room temperature. A total of 28 434 reflections (1.05−25.04°) were collected, of which independent reflections 19 014 [R(int) = 0.0588] were used. An empirical absorption correction was performed with the program SADABS. 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. The structure was solved with the program SHELXS-97 and refined using SHELXL-93 to R1 = 0.0750 and wR2 = 0.1925 ($I > 2\sigma(I)$) for 19 014 reflections with max/min residual electron density 2.167 and −1.702 e/Å^3. Final atomic coordinates, displacement parameters, and full bond lengths of the structures are given as the Supporting Information. Selected metal−metal bond distances are given in figure captions.

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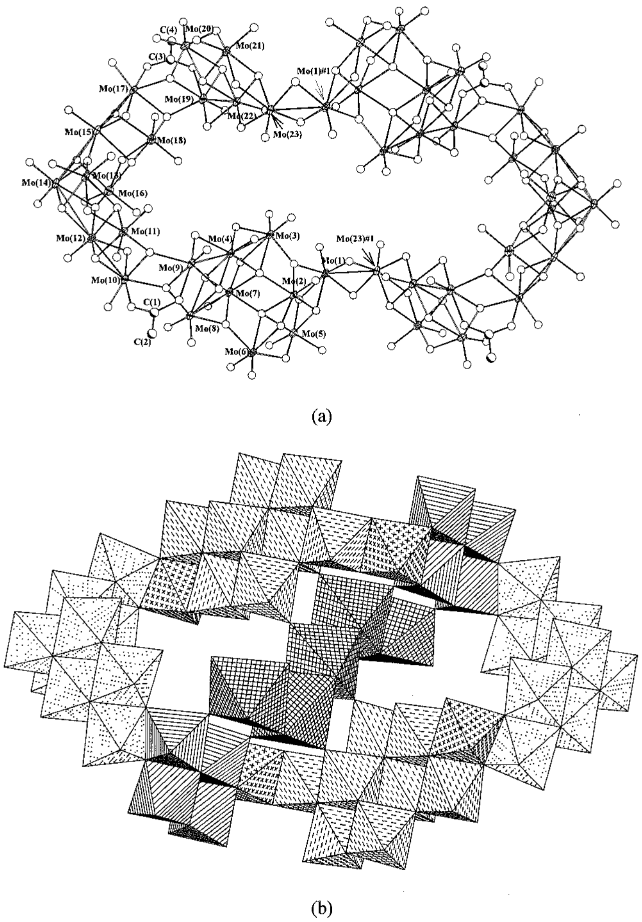

Figure 1. (a) Ball−stick representation of spiral ring of **3a** (all encapsulated Na^+ cations are omitted for clarity). Selected Mo−Mo distances: Mo(1)−Mo(23)#, 2.571(2); Mo(3)−Mo(4), 3.216(2); Mo(4)−Mo(9), 2.601(2); Mo(10)−Mo(12), 2.607(2); Mo(14)−Mo(15), 3.214(2); Mo(15)−Mo(17), 2.592(2); Mo(19)−Mo(22), 2.597(2); Mo(23)−Mo(1)#1, 2.571(2) Å. (b) Polyhedral representation of the crown-shaped anion **3a**. The linkage mode between$\{Mo_9O_{30}(X)_2\}$ (marked with regular dots) and $\{Mo_8O_{28}\}$ (dashed lines) is corner-shared, while that between any moieties $\{Mo_9O_{30}(X)_2\}$ and $\{Mo_4O_{15}(X)\}$ units (parallel) is edge-shared. $\{Mo_1\}$ units are marked with crosses, while the Na_5 "guest" has a hatching pattern.

Three types of the described building blocks in **3a** are connected to each other into a larger subunit and further linked by $\{Mo_1\}$ ($\equiv[Mo^VO]^{3+}$) units into the 46-member twisted ring structure. The linkage between any $\{Mo_9O_{30}(X)_2\}$ and $\{Mo_4O_{15}(X)\}$ units is edge-shared, while that between any $\{Mo_9O_{30}(X)_2\}$ and $\{Mo_8O_{30}\}$ moieties is corner-shared. The cavity of it is about 4.742 (O(13)−O(13A)) × 9.878 (O(75)−O(75A)) × 19.974 (O(36)−O(36A)) $Å^3$, which makes the spiral ring accommodate a zigzag-chainlike "guest" of five edge-shared six-coordinated Na^+ in the following sequence: Na(3)(μ_2-OH_2)Na(2)(μ_2-OH_2)Na(1)(μ_2-OH_2)Na(2A)(μ_2-OH_2)Na(3A). The corresponding Na−Na distances are 3.614(13), 3.467(7), 3.467(7), and 3.614(13) Å, respectively. The large cationic aggregate acting as a big "guest" is linked to the eight endo oxygen atoms of the twisted ring ($Na-O_{endo}$ distances are in the range 3.370(14)−3.460(15) Å). Moreover, the crown-shaped anions **3a** are connected into three-dimensional chains via Na^+ cations with different coordinators and topologies (Na−O, 2.363−2.825 Å, $Na-OH_2$, 2.254−2.708 Å).

The positions of OH^- and Mo^V sites are assigned on the basis of the $\sum s$ values, in which the s is the bond strength derived from the Brown equation, $s = \exp[(R_0-R)/B]$ ($R_0 = 1.907$ for Mo, and $B = 0.37$). According to this procedure, the O(36), O(50), O(66), O(73), and O(74) sites (and corresponding symmetric positions) are ascribed to OH^- sites, whose $\sum s$ values (1.094−1.273) are significantly smaller than those of the others (1.613−2.181) that are normal for the O^{2-} sites. The silent ESR spectrum of compound **3** indicates that the unpaired electrons of two neighboring Mo^V atoms are completely coupled, which is consistent with structural analysis.

In summary, besides $\{Mo_{54}\}$ and $\{Mo_{18}\}$,[6b,8] another crown-shaped polyoxomolybdate with a novel configuration has been synthesized and characterized crystallographically. Obviously, there exist various building blocks in one reaction pot, and these blocks can be self-assembled into a related set of crown-shaped or cyclic polyoxomolybdate anions under different boundary conditions. These successful syntheses might lead to the synthesis of some other larger rings using larger cations, cluster molecules other than Na^+. Furthermore, the various linkage modes between these moieties are expected to give rise to a variety of crown-shaped polyoxomolybdates. Indeed, this has been confirmed recently by our preliminary experiments by introducing magnetic ions into the crown-shaped system.

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Supporting Information Available: Text and figure depicting relationships among building blocks. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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