

Synthesis and Structural Characterization of Three New Inorganic “Host-guest” Polyoxomolybdates

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Since two interesting inorganic “host-guest” polyoxomolybdates **1** and **2** have been reported previously, we have now succeeded in selectively isolating three new acetated “host-guest” polyoxomolybdates **3**–**5**, which considerably extend the range of structures in the cyclic polyoxomolybdate catalogue. **3** crystallizes in the triclinic space group $P\bar{1}$ with $a = 1.22235(1)$ nm, $b = 1.52977(2)$ nm, $c = 1.54022(1)$ nm, $\alpha = 113.746(1)^\circ$, $\beta = 96.742(1)^\circ$, $\gamma = 101.564(1)^\circ$, $V = 2.51892(4)$ nm³, $Z = 1$, $D_c = 2.568$ g·cm⁻³. **4** and **5** crystallize in the monoclinic system: $P2(1)/n$, $a = 1.08298(2)$ nm, $b = 1.54029(1)$ nm, $c = 2.78893(5)$ nm, $\beta = 94.2730(10)^\circ$, $V = 4.63929(12)$ nm³, $Z = 2$ and $D_c = 2.671$ g·cm⁻³ for **4**, and $C2/c$, $a = 2.59907(8)$ nm, $b = 1.65992(3)$ nm, $c = 2.28473(7)$ nm, $\beta = 93.4370(10)^\circ$, $V = 9.8392(5)$ nm³, $Z = 4$ and $D_c = 2.556$ g·cm⁻³ for **5**. The structures of **3**, **4** and **5** consist of 18-membered “host-guest” polyoxoanions $[\{\text{Na}(\text{X})_2\} \subset \{(\mu_3\text{-OH})_4\text{Mo}_8\text{Mo}_{10}^{\text{VI}}\text{O}_{52}(\mu_2\text{-CH}_3\text{COO})_2\}]^{-(n+9)}$ ($\text{X} = \text{CH}_3\text{COO}^-$ for **3**, DMF for **4** and H_2O for **5**), which are connected via Na^+ ions or hydrogen bonds into infinite extended frameworks.

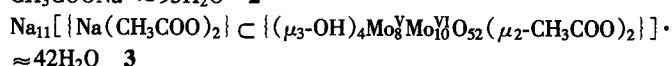
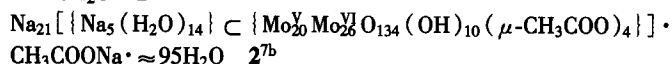
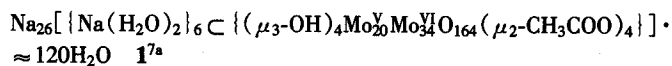
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Introduction

Stimulated by various and alluring topologies and driven by potential applications in catalysis, biology, medicine and materials science, inorganic “polyoxometalate chemistry has recently witnessed some remarkable achievements.¹ Nowadays, a wide variety of such complexes containing “guest” anions like Cl^- , N_3^- and NO_3^- , cations like Na^+ and K^+ , molecules like CH_3CN , or cation/anion aggregates like $\text{NH}_4^+/\text{Cl}^-$, have been synthesized and structurally characterized.² Generally, these guests are attached to the *endo* oxygen atoms of “host” cages via valence bonds or intermolecular interactions such as hydrogen bonding.²

Although the employment of carboxylic acids and organodiamines offers a powerful synthetic route for the de-

sign of novel materials,³ only few polyoxometalate clusters containing coordinated carboxyls have been isolated, including Keplerate spheres,⁴ acetated cyclic polyoxomolybdates⁵ and the first cyclic polyoxothiotungstate⁶ with two encapsulated glutarate ions $[\text{OOC}(\text{CH}_2)_3\text{COO}]^{2-}$. In recent years, significant efforts in our research group have been carried out toward the self-assembly processes of such well-defined polyoxomolybdates, generating two novel crown-shaped polyoxomolybdates **1** and **2** with fascinating structural topologies.⁷ Using similar reaction system, we have now succeeded in selectively isolating three new acetated crown-shaped polyoxomolybdates **3**–**5**, which considerably extend the range of structures in the cyclic polyoxomolybdate catalogue.



Experimental

Synthesis

Compounds **1** and **2** can be synthesized as the methods reported in literature.⁷

Compound 3 To a solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (20 mmol, 4.84 g), $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (48.87 mmol, 6.65 g) in H_2O (40 mL) (the pH value was adjusted to 4.2 with 10% HCl), $\text{NH}_2\text{NH}_2 \cdot 2\text{HCl}$ (2.0 mmol, 0.21 g) was added under continuous stirring within 5 min. The reaction mixture (the color changed from green to dark

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brown) was kept in a wide-necked Erlenmeyer-flask without further disturbance for two weeks, resulting in black brown plate crystals of **3**. Yield 0.54 g, 12.48% based on Mo. IR (KBr) ν : 3451 (br), 1637 (m), 1541 (m), 1444 (m), 960, 937 (s), 903 (m-s), 735, 648 (s), 561, 496, 465 (m) cm^{-1} . Anal. calcd for $\text{C}_8\text{H}_{100}\text{Mo}_{18}\text{Na}_{12}\text{O}_{106}$: Mo 44.33, Na 7.08, C 2.47, H 2.59; found Mo 43.75, Na 7.25, C 2.35, H 2.43.

Compound 4 DMF (2.5 mL) was slowly added into an aqueous solution of **3** (0.1 mmol, 0.39 g) in H_2O (15 mL) under continuous stirring. Red-brown crystals of **4** were precipitated from the resulting solution kept at room temperature in a wide-necked Erlenmeyer-flask for two months, washed with cooled EtOH and dried in air. Yield 0.18 g, 48.24% based on Mo. IR (KBr) ν : 3465 (br), 1641 (s), 1537 (m), 1437 (m), 1393 (m), 1259 (w), 1117 (w), 1018 (w), 958 (vs), 937 (vs), 910 (vs), 768 (m), 741 (s), 708 (m), 688 (s), 627 (m), 569 (m), 496 (m) cm^{-1} . Anal. calcd for $\text{C}_{10}\text{H}_{90}\text{Mo}_{18}\text{N}_2\text{Na}_{10}\text{O}_{96}$: Mo 46.28, Na 6.16, C 3.22, H 2.43, N 0.75; found Mo 46.34, Na 6.13, C 3.18, H 2.41, N 0.81.

Compound 5 To a solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (10.0 mmol, 2.42 g) and $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (22.06 mmol, 3.0 g), CH_3COOH (2.5 mL) in H_2O (45 mL), $\text{NH}_2\text{NH}_2 \cdot 2\text{HCl}$ (1.44 mmol, 0.15 g) was added under continuous stirring within 5 min. After filtration the next day, the reaction mixture (the color changed from green to dark brown) was transferred into a schlenk-flask, then a solution of $\text{H}_2\text{NCH}_2\text{CHNH}_2$ (4 mL) in EtOH (20 mL) was slowly diffused via vapor into the filtrate at room temperature, resulting in red needle crystals of **5** within two weeks. Yield 0.18 g, 48.24% based on Mo. IR (KBr) ν : 3454 (br), 1630 (m), 1537 (m), 1446 (m), 957 (s), 935 (vs), 904 (vs), 739 (vs), 704 (vs), 654 (s), 565 (s), 499 (s) cm^{-1} . Anal. calcd for $\text{C}_4\text{H}_{100}\text{Mo}_{18}\text{Na}_{10}\text{O}_{105}$: Mo 45.62, Na 6.07, C 1.27, H 2.66; found Mo 45.39, Na 6.10, C 1.25, H 2.58.

X-Ray crystallography

Crystals were taken directly from the mother liquor and sealed in glass capillary together with a bit of mother liquor before data collections. Diffraction data were collected on a Siemens SMART CCD diffractometer with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.071073$ nm) at room temperature. An empirical absorption correction by SADABS was applied to the intensity data. All structures were solved using direct methods by locating molybdenum atoms, and the remaining non-hydrogen atoms were located from afterward Fourier syntheses. All refinements were carried out using full-matrix least squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms except non-coordinated H_2O molecules. The crystallographic data for **3**–**5**, are presented in Table 1. Selected bond lengths and angles for **3**–**5** are listed in Tables 2 and 3, respectively.

Results and discussion

One of the most prominent features of the chemistry of polyoxometalates is the simultaneous formation of different species in an aqueous solution. How to control the equilibria among different species in one reaction pot and then, of course, to isolate desirable products, has become one of the most challenges for the chemists in the POMs field. Recently, we have been interested in seeking a simple synthetic route to isolate "host-guest" compounds with desirable properties, and isolated two novel cyclic polyoxomolybdates **1** and **2**.⁷ We have now extended our exploration in this system under different pH values and concentrations. Our preliminary results show that the main affecting factors on these equilibria are acidity and temperature, and the concentration of reagents. At higher acidity or higher concentration of Na_2MoO_4 , the equilibria are favorable for the higher nuclearity products. Interestingly, it is possible to vary the packing of the cluster anions by adding different organic reagents, and therefore to obtain new compounds, *e. g.* addition of DMF led to **4** crystallizing in the monoclinic space $P2(1)/n$ ($Z = 2$, $V = 4.63929(12)$ nm^3); vapor diffusion of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ resulted in **5** crystallizing in the monoclinic space group $C2/c$ ($Z = 4$ and $V = 9.8392(5)$ nm^3).

All compounds were characterized by elemental analysis, cerimetric titration (to determine the number of Mo^{V}), thermogravimetric analysis (to determine the amount of crystallized water), spectroscopic methods (IR, Raman and UV-vis) and single-crystal X-ray analysis. Valence bond sum calculations based on the Brown equation $S = \exp[(R_0 - R)/B]$ ($R_0 = 1.907$ for Mo, and $B = 0.37$)⁸, have been applied on all atoms to confirm the valence of the metal centres and to locate the positions of OH groups. The assignment of Mo^{V} and Mo^{VI} centers based on BVS calculations is in agreement with the charges of the cluster anions and the fact that all the Mo^{V} centres form covalent Mo—Mo single bonds. Just as for other large structures such as "molybdenum blue" giant wheels reported by Müller and his co-workers,⁹ only part of Na^+ cations expected from elemental analyses can be successfully located in structure solving due to disorder. However, the main structures of the anions appear not to be effected by disorder.

The poly-membered rings of **3**–**5** are built up from two following building blocks: *cis*- $\{\text{Mo}_9\}$ ($\equiv [(\text{OH})_2\text{Mo}_4^{\text{V}}\text{Mo}_5^{\text{VI}}\{(\text{CH}_3\text{COO})_{2/2}\}_2]^{10-}$). This asymmetric unit is constructed by five edge-sharing MoO_6 octahedra and two dumb-bell-type $[\text{Mo}_2^{\text{V}}\text{O}_4]^{2+}$ subunits in *cis*-positions with a short Mo—Mo bond (*ca.* 0.26 nm) within the $\{\text{Mo}_2\text{O}_4\}$ dimmers (Table 2), and non-bonding $\text{Mo} \cdots \text{Mo}$ contacts (*ca.* 0.35 nm) between the $\{\text{Mo}_2\text{O}_4\}$ subunits and neighboring Mo^{VI} centers. Each Mo atom has a slightly distorted octahedral geometry with one short terminal $\text{Mo} = \text{O}$ for Mo^{V} (0.1675–0.1692 nm) and two terminals for Mo^{VI} (0.1684–0.1723 nm).

Table 1 Crystallographic data for compounds 3, 4 and 5

Compound	3	4	5
Empirical formula	C ₈ H ₁₀₀ Mo ₁₈ Na ₁₂ O ₁₀₆	C ₁₀ H ₉₀ Mo ₁₈ N ₂ Na ₁₀ O ₉₆	C ₄ H ₁₀₀ Mo ₁₈ Na ₁₀ O ₁₀₅
M_r (g·mol ⁻¹)	3895.68	3731.66	3785.66
Crystal size (mm ³)	0.40 × 0.22 × 0.16	0.43 × 0.30 × 0.28	0.52 × 0.28 × 0.28
Color/shape	Red/lozenge	Red/block	Red/block
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> ₂ (1)/ <i>n</i>	<i>C</i> ₂ / <i>c</i>
<i>a</i> (nm)	1.22235(1)	1.08298(2)	2.59907(8)
<i>b</i> (nm)	1.52977(2)	1.54029(1)	1.65992(3)
<i>c</i> (nm)	1.54022(1)	2.78893(5)	2.28473(7)
α (°)	113.746(1)	90	90
β (°)	96.742(1)	94.2730(10)	93.4370(10)
γ (°)	101.564(1)	90	90
Volume (nm ³)	2.51892(4)	4.63929(12)	9.8392(5)
<i>Z</i>	1	2	4
D_c (g·cm ⁻³)	2.568	2.671	2.556
<i>F</i> (000)	1884	3596	7320
μ (mm ⁻¹)	2.341	2.552	2.386
θ Range (°)	1.48 to 25.07	1.46 to 25.01	1.46 to 25.05
<i>h</i> , <i>k</i> , <i>l</i> Ranges	-14 ≤ <i>h</i> ≤ 14, -17 ≤ <i>k</i> ≤ 18, -18 ≤ <i>l</i> ≤ 9	-12 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 18, -33 ≤ <i>l</i> ≤ 24	-30 ≤ <i>h</i> ≤ 30, -15 ≤ <i>k</i> ≤ 19, -12 ≤ <i>l</i> ≤ 27
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Absorption correction	SADABS	SADABS	SADABS
Reflections collected	13075	15896	15361
Unique reflections (<i>R</i> _{int})	8729 (0.0389)	8034 (0.0204)	8666 (0.0252)
Refined parameters	570	611	605
<i>GOF</i>	0.0998	1.063	1.039
Max. shift in final cycle	0.001	0.001	0.001
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0550, <i>wR</i> ₂ = 0.1429	<i>R</i> ₁ = 0.0316, <i>wR</i> ₂ = 0.0800	<i>R</i> ₁ = 0.0400, <i>wR</i> ₂ = 0.1063
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0762, <i>wR</i> ₂ = 0.1583	<i>R</i> ₁ = 0.0390, <i>wR</i> ₂ = 0.0850	<i>R</i> ₁ = 0.0530, <i>wR</i> ₂ = 0.1175
Max. and min. residual electron density (e ⁻ ·nm ⁻³)	1475 and -1863	1960 and -715	1820 and -1345

The crystal structures of 3–5 consist of 18-membered ring crown-shaped polyoxoanions [Na(X)₂(μ₃-OH)₄-Mo₈^{VI}Mo₁₀^{VI}O₅₂(μ₂-CH₃COO)₂]⁻⁽ⁿ⁺⁹⁾ (where *n* is the normal charge of coordinated base X, X = CH₃COO⁻ for 3, DMF for 4 and H₂O for 5), Na cations and crystal water molecules. Each 18-membered ring contains two *cis*-{Mo₉} units (Fig. 1), which are linked to each other via two shared edges to form a ramped ring (Fig. 2a). Alternatively, the cluster ring can be described as that two oval octagons are staged to form a ramped ring with two additional Mo^{VI}O octahedra situating on the outer edges along the long axis of the ring (Fig. 2b). A Na⁺ cation is located right at the symmetric center of the ring, and coordinated to four *endo* bridging oxygen groups of the same ring (Na—O distance of 0.236–0.247 nm) and two base X (X = CH₃COO⁻ for 3, DMN for 4 and H₂O for 5).

Comparing 3 and the crown-shaped polyoxomolybdate

Na₉[{Na(H₂O)₂}] ⊂ {H₄Mo₁₈O₅₆(CH₃COO)₂} · 3CH₃COOH · 36H₂O (6),^{5a} it is found that both compounds crystallize in the same triclinic space group *P*(-1) with similar cell parameters. However, two water molecules coordinated to the central Na ions enclosed in the 18-membered ring of 6 are replaced by two deprotonated acetate groups in 3, and two additional Na⁺ cations are therefore required for overall neutrality. Anion 3a is connected into a two-dimensional framework via Na ions and hydrogen bonds, while 4a is linked via Na bridges into an infinite chain (Fig. 3). The crystal structure of 5 is more complicated than those of 3 and 4. As shown in Fig. 4, the crown-shaped anions 5a are first linked via an edge-sharing V-shaped [Na₅(OH₂)₁₇]⁵⁺ aggregate into a chain along the [001] direction. In this aggregate, there are four [NaO(OH₂)₅] octahedra and one Na(OH₂)₆ triangular prism. Perpendicular to the *a*-axis, each 5a bonds to four edge-sharing

Table 2 Selected bond lengths ($\times 10^{-1}$ nm) for compounds 3, 4 and 5

3 ^a	Mo(1)—O(6)	1.676(6)	Mo(3)—O(1)	2.253(6)	Mo(6)—O(23)	1.693(7)	Mo(8)—O(24)	1.976(6)
	Mo(1)—O(5)	1.961(6)	Mo(3)—O(4)	2.306(6)	Mo(6)—O(22)	1.716(7)	Mo(8)—O(7) # 1	2.063(6)
	Mo(1)—O(3)	1.975(6)	Mo(4)—O(16)	1.706(6)	Mo(6)—O(21)	1.927(7)	Mo(8)—O(27)	2.158(6)
	Mo(1)—O(4)	2.018(6)	Mo(4)—O(15)	1.715(6)	Mo(6)—O(14)	1.962(6)	Mo(8)—O(8) # 1	2.200(6)
	Mo(1)—O(2)	2.114(6)	Mo(4)—O(11)	1.933(6)	Mo(6)—O(20)	2.225(6)	Mo(9)—O(29)	1.700(7)
	Mo(1)—O(1)	2.321(5)	Mo(4)—O(14)	1.945(6)	Mo(6)—O(17)	2.333(7)	Mo(9)—O(30)	1.704(7)
	Mo(2)—O(9)	1.677(6)	Mo(4)—O(1)	2.215(6)	Mo(7)—O(26)	1.682(6)	Mo(9)—O(8) # 1	1.930(6)
	Mo(2)—O(5)	1.957(6)	Mo(4)—O(2)	2.296(6)	Mo(7)—O(25)	1.946(5)	Mo(9)—O(21)	1.942(6)
	Mo(2)—O(4)	1.979(6)	Mo(5)—O(18)	1.723(6)	Mo(7)—O(3)	1.999(6)	Mo(9)—O(20)	2.238(6)
	Mo(2)—O(8)	2.038(5)	Mo(5)—O(19)	1.723(6)	Mo(7)—O(24)	2.004(6)	Mo(9)—O(24)	2.356(6)
	Mo(2)—O(10)	2.150(6)	Mo(5)—O(17)	1.944(6)	Mo(7)—O(17)	2.134(6)	Mo(1)—Mo(2)	2.6337(10)
	Mo(2)—O(7)	2.179(6)	Mo(5)—O(2)	1.960(6)	Mo(7)—O(20)	2.333(6)	Mo(1)—Mo(5)	3.2032(10)
	Mo(3)—O(13)	1.703(7)	Mo(5)—O(3)	2.227(6)	Mo(8)—O(28)	1.675(7)	Mo(5)—Mo(7)	3.2112(10)
	Mo(3)—O(12)	1.717(7)	Mo(5)—O(14)	2.238(6)	Mo(8)—O(25)	1.944(6)	Mo(7)—Mo(8)	2.6129(10)
	Mo(3)—O(7)	1.936(6)	C(1)—C(2)	1.448(17)	C(3)—C(4)	1.508(13)		
	Mo(3)—O(11)	1.957(6)	C(3)—O(10) # 1	1.263(11)				
4 ^b	Mo(1)—O(3)	1.692(4)	Mo(3)—O(13)	2.112(4)	Mo(6)—O(18)	1.946(4)	Mo(8)—O(13)	2.332(4)
	Mo(1)—O(1)	1.946(4)	Mo(3)—O(12)	2.380(4)	Mo(6)—O(23)	1.954(4)	Mo(9)—O(30)	1.702(4)
	Mo(1)—O(2)	1.976(4)	Mo(4)—O(17)	1.690(4)	Mo(6)—O(9)	2.212(4)	Mo(9)—O(29)	1.721(4)
	Mo(1)—O(4) # 1	2.051(4)	Mo(4)—O(15)	1.946(4)	Mo(6)—O(8)	2.315(4)	Mo(9)—O(28)	1.934(4)
	Mo(1)—O(6)	2.176(4)	Mo(4)—O(14)	1.967(4)	Mo(7)—O(25)	1.709(4)	Mo(9)—O(4)	1.936(4)
	Mo(1)—O(5)	2.181(4)	Mo(4)—O(6) # 1	2.068(4)	Mo(7)—O(24)	1.729(4)	Mo(9)—O(12)	2.227(4)
	Mo(2)—O(10)	1.698(4)	Mo(4)—O(16)	2.170(4)	Mo(7)—O(8)	1.936(4)	Mo(9)—O(14)	2.333(4)
	Mo(2)—O(1)	1.941(4)	Mo(4)—O(4)	2.179(4)	Mo(7)—O(13)	1.954(4)	Mo(1)—Mo(2)	2.6181(6)
	Mo(2)—O(7)	1.974(4)	Mo(5)—O(20)	1.709(4)	Mo(7)—O(7)	2.232(4)	Mo(2)—Mo(7)	3.2037(6)
	Mo(2)—O(2)	2.015(4)	Mo(5)—O(19)	1.716(4)	Mo(7)—O(23)	2.264(4)	Mo(3)—Mo(4)	2.6075(6)
	Mo(2)—O(8)	2.125(4)	Mo(5)—O(6)	1.930(4)	Mo(8)—O(26)	1.699(4)	Mo(3)—Mo(7)	3.2159(6)
	Mo(2)—O(9)	2.309(4)	Mo(5)—O(18)	1.943(4)	Mo(8)—O(27)	1.714(4)	N(1)—C(3)	1.327(8)
	Mo(3)—O(11)	1.692(4)	Mo(5)—O(9)	2.232(4)	Mo(8)—O(28)	1.942(4)	N(1)—C(5)	1.453(8)
	Mo(3)—O(15)	1.944(4)	Mo(5)—O(2)	2.294(4)	Mo(8)—O(23)	1.962(4)	N(1)—C(4)	1.469(8)
	Mo(3)—O(7)	1.992(4)	Mo(6)—O(21)	1.712(4)	Mo(8)—O(12)	2.225(4)	C(1)—O(5) # 1	1.266(7)
	Mo(3)—O(14)	2.010(4)	Mo(6)—O(22)	1.713(4)			C(1)—C(2)	1.497(8)
5 ^c	Mo(1)—O(2)	1.687(5)	Mo(3)—O(6)	2.018(5)	Mo(6)—O(23)	1.684(5)	Mo(8)—O(26)	1.947(5)
	Mo(1)—O(1)	1.952(5)	Mo(3)—O(12)	2.131(5)	Mo(6)—O(21)	1.940(5)	Mo(8)—O(20)	2.216(5)
	Mo(1)—O(6)	1.967(5)	Mo(3)—O(7)	2.325(5)	Mo(6)—O(11)	1.975(5)	Mo(8)—O(22)	2.303(5)
	Mo(1)—O(4) # 1	2.040(5)	Mo(4)—O(16)	1.710(5)	Mo(6)—O(22)	2.017(5)	Mo(9)—O(29)	1.684(5)
	Mo(1)—O(5)	2.163(5)	Mo(4)—O(15)	1.712(5)	Mo(6)—O(17)	2.142(5)	Mo(9)—O(21)	1.955(5)
	Mo(1)—O(3)	2.203(4)	Mo(4)—O(8)	1.938(5)	Mo(6)—O(20)	2.280(4)	Mo(9)—O(22)	1.980(5)
	Mo(2)—O(10)	1.706(5)	Mo(4)—O(14)	1.962(5)	Mo(7)—O(25)	1.698(5)	Mo(9)—O(3) # 1	2.039(4)
	Mo(2)—O(9)	1.718(5)	Mo(4)—O(7)	2.224(5)	Mo(7)—O(24)	1.720(5)	Mo(9)—O(30)	2.150(5)
	Mo(2)—O(8)	1.926(5)	Mo(4)—O(12)	2.296(5)	Mo(7)—O(26)	1.940(5)	Mo(9)—O(4)	2.192(5)d
	Mo(2)—O(3)	1.928(4)	Mo(5)—O(19)	1.713(5)	Mo(7)—O(14)	1.960(5)	Mo(1)—Mo(3)	2.6165(8)
	Mo(2)—O(7)	2.230(5)	Mo(5)—O(18)	1.723(5)	Mo(7)—O(20)	2.174(4)	Mo(5)—O(6)	3.2091(8)
	Mo(2)—O(6)	2.321(5)	Mo(5)—O(17)	1.950(5)	Mo(7)—O(17)	2.298(5)	Mo(6)—Mo(9)	2.6072(8)
	Mo(3)—O(13)	1.683(5)	Mo(5)—O(12)	1.959(5)	Mo(8)—O(27)	1.701(5)	O(5)—C(1) # 1	1.265(9)
	Mo(3)—O(1)	1.957(5)	Mo(5)—O(14)	2.218(5)	Mo(8)—O(28)	1.708(6)	O(30)—C(1)	1.265(9)
	Mo(3)—O(11)	1.994(5)	Mo(5)—O(11)	2.220(4)	Mo(8)—O(4)	1.933(5)	C(1)—O(5) # 1	1.265(9)
							C(1)—C(2)	1.514(10)

^a Symmetry mode: # 1 -x, -y-1, -z+1. ^b Symmetry mode: # 1 -x+1, -y, -z. ^c Symmetry mode: # 1 -x+1/2, -y+3/2, -z.

Table 3 Selected bond angles (°) for compounds 3, 4 and 5

3	O(6)-Mo(1)-O(5)	104.5(3)	O(12)-Mo(3)-O(11)	97.4(3)	O(17)-Mo(5)-O(3)	75.3(2)	O(25)-Mo(8)-O(24)	93.9(2)
	O(6)-Mo(1)-O(3)	101.1(3)	O(7)-Mo(3)-O(11)	147.6(3)	O(3)-Mo(5)-O(14)	79.9(2)	O(28)-Mo(8)-O(27)	89.0(3)
	O(6)-Mo(1)-O(4)	100.6(3)	O(11)-Mo(3)-O(1)	71.7(2)	O(23)-Mo(6)-O(22)	105.0(4)	O(28)-Mo(8)-O(25)	105.0(3)
	O(6)-Mo(1)-O(2)	95.3(3)	O(13)-Mo(3)-O(4)	163.9(3)	O(22)-Mo(6)-O(21)	96.4(3)	O(28)-Mo(8)-O(24)	108.3(3)
	O(6)-Mo(1)-O(1)	166.6(3)	O(1)-Mo(3)-O(4)	70.1(2)	O(23)-Mo(6)-O(14)	95.4(3)	O(29)-Mo(9)-O(30)	105.8(4)
	O(9)-Mo(2)-O(5)	103.6(3)	O(16)-Mo(4)-O(15)	104.7(3)	O(23)-Mo(6)-O(20)	97.3(3)	O(29)-Mo(9)-O(21)	100.9(3)
	O(9)-Mo(2)-O(4)	106.3(3)	O(16)-Mo(4)-O(11)	98.3(3)	O(23)-Mo(6)-O(17)	163.4(3)	O(8) # 1-Mo(9)-O(21)	147.3(3)
	O(5)-Mo(2)-O(4)	94.4(2)	O(15)-Mo(4)-O(11)	96.7(3)	O(26)-Mo(7)-O(25)	106.1(3)	O(29)-Mo(9)-O(24)	162.3(3)
	O(9)-Mo(2)-O(8)	100.4(3)	O(16)-Mo(4)-O(14)	95.3(3)	O(26)-Mo(7)-O(3)	99.5(3)	O(35)-C(1)-O(30)	124.1(17)
	O(9)-Mo(2)-O(10)	87.6(3)	O(16)-Mo(4)-O(1)	94.5(3)	O(26)-Mo(7)-O(24)	102.5(3)	O(35)-C(1)-C(2)	119.2(19)
	O(9)-Mo(2)-O(7)	167.1(3)	O(16)-Mo(4)-O(2)	162.4(3)	O(3)-Mo(7)-O(24)	155.6(2)	O(64)-C(3)-O(58)	124.1(18)
	O(13)-Mo(3)-O(12)	104.0(4)	O(1)-Mo(4)-O(2)	71.8(2)	O(26)-Mo(7)-O(17)	94.8(3)	O(64)-C(3)-C(4)	117.2(18)
	O(13)-Mo(3)-O(7)	98.8(3)	O(18)-Mo(5)-O(19)	103.4(3)	O(3)-Mo(7)-O(17)	76.4(2)	O(145)-C(6)-O(146)	119(7)
O(13)-Mo(3)-O(11)	99.5(3)	O(18)-Mo(5)-O(3)	89.9(3)	O(26)-Mo(7)-O(20)	166.5(3)	O(145)-C(6)-C(5)	145(5)	
4	O(3)-Mo(1)-O(1)	105.95(17)	O(11)-Mo(3)-O(14)	103.29(18)	O(20)-Mo(5)-O(18)	100.00(18)	O(25)-Mo(7)-O(23)	171.34(17)
	O(3)-Mo(1)-O(2)	106.32(18)	O(11)-Mo(3)-O(13)	96.40(17)	O(20)-Mo(5)-O(9)	94.22(17)	O(26)-Mo(8)-O(28)	99.4(2)
	O(2)-Mo(1)-O(6)	76.58(14)	O(7)-Mo(3)-O(13)	76.62(15)	O(20)-Mo(5)-O(2)	164.06(17)	O(26)-Mo(8)-O(23)	95.95(19)
	O(3)-Mo(1)-O(5)	86.76(17)	O(11)-Mo(3)-O(12)	168.10(17)	O(21)-Mo(6)-O(18)	96.79(19)	O(26)-Mo(8)-O(12)	98.03(19)
	O(6)-Mo(1)-O(5)	79.96(15)	O(17)-Mo(4)-O(15)	105.92(18)	O(21)-Mo(6)-O(23)	100.55(19)	O(26)-Mo(8)-O(13)	165.37(18)
	O(10)-Mo(2)-O(1)	106.59(18)	O(17)-Mo(4)-O(14)	108.13(19)	O(21)-Mo(6)-O(8)	158.05(19)	O(30)-Mo(9)-O(29)	104.8(2)
	O(10)-Mo(2)-O(7)	100.37(18)	O(17)-Mo(4)-O(16)	87.39(18)	O(21)-Mo(6)-O(9)	89.94(18)	O(30)-Mo(9)-O(28)	101.47(19)
	O(10)-Mo(2)-O(2)	101.38(18)	O(17)-Mo(4)-O(4)	166.12(17)	O(9)-Mo(6)-O(8)	70.69(13)	C(3)-N(1)-C(5)	122.2(5)
	O(10)-Mo(2)-O(8)	94.49(17)	O(20)-Mo(5)-O(19)	105.0(2)	O(25)-Mo(7)-O(24)	103.2(2)	C(3)-N(1)-C(4)	120.3(5)
	O(10)-Mo(2)-O(9)	165.69(17)	O(20)-Mo(5)-O(6)	98.23(18)	O(25)-Mo(7)-O(8)	103.53(18)	C(5)-N(1)-C(4)	117.2(5)
5	O(2)-Mo(1)-O(1)	104.3(2)	O(13)-Mo(3)-O(12)	94.3(2)	O(19)-Mo(5)-O(14)	87.5(2)	O(25)-Mo(7)-O(17)	162.3(2)
	O(2)-Mo(1)-O(6)	107.2(2)	O(1)-Mo(3)-O(12)	158.28(19)	O(19)-Mo(5)-O(11)	167.8(2)	O(27)-Mo(8)-O(28)	105.2(3)
	O(1)-Mo(1)-O(6)	94.96(19)	O(6)-Mo(3)-O(12)	91.82(18)	O(23)-Mo(6)-O(21)	105.9(2)	O(27)-Mo(8)-O(4)	98.5(2)
	O(2)-Mo(1)-O(5)	88.2(2)	O(13)-Mo(3)-O(7)	165.7(2)	O(23)-Mo(6)-O(11)	101.0(2)	O(27)-Mo(8)-O(26)	99.7(2)
	O(6)-Mo(1)-O(3)	76.56(18)	O(16)-Mo(4)-O(15)	104.8(3)	O(23)-Mo(6)-O(22)	99.2(2)	O(27)-Mo(8)-O(20)	95.2(2)
	O(10)-Mo(2)-O(9)	104.2(3)	O(15)-Mo(4)-O(8)	100.0(2)	O(23)-Mo(6)-O(17)	93.4(2)	O(27)-Mo(8)-O(22)	164.5(2)
	O(9)-Mo(2)-O(8)	100.9(2)	O(16)-Mo(4)-O(14)	101.0(2)	O(23)-Mo(6)-O(20)	164.2(2)	O(28)-Mo(8)-O(22)	89.9(2)
	O(3)-Mo(2)-O(7)	80.85(18)	O(16)-Mo(4)-O(7)	158.4(2)	O(25)-Mo(7)-O(24)	105.0(3)	O(4)-Mo(8)-O(22)	74.40(18)
	O(7)-Mo(2)-O(6)	70.88(16)	O(16)-Mo(4)-O(12)	89.4(2)	O(25)-Mo(7)-O(26)	99.4(2)	O(29)-Mo(9)-O(21)	103.9(2)
	O(13)-Mo(3)-O(1)	105.4(2)	O(19)-Mo(5)-O(18)	103.1(3)	O(25)-Mo(7)-O(14)	94.4(2)	O(29)-Mo(9)-O(22)	107.0(2)
	O(11)-Mo(3)-O(6)	156.66(19)	O(17)-Mo(5)-O(12)	140.59(19)	O(25)-Mo(7)-O(20)	95.1(2)	O(29)-Mo(9)-O(30)	87.3(2)

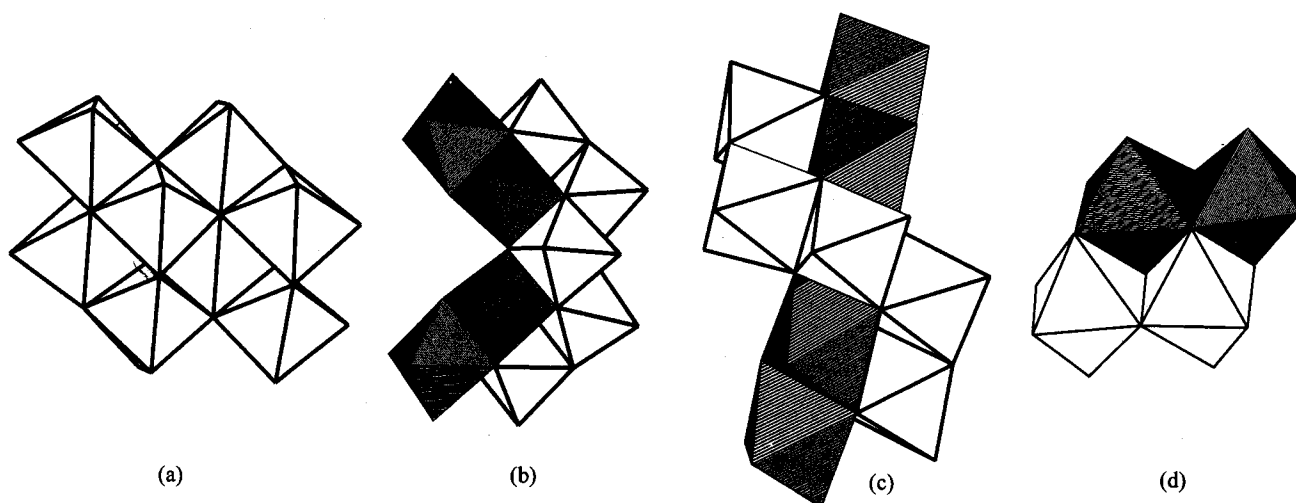


Fig. 1 Polyhedral representation of building blocks encountered in 1–5: (a) {Mo₈}, (b) *cis*-{Mo₉}, (c) *trans*-{Mo₉} and (d) {Mo₄} units. Dumb-bell-type [Mo₂O₄]²⁺ subunits are marked as parallel lines, while other oxomolybdenum octahedra have a blank mode.

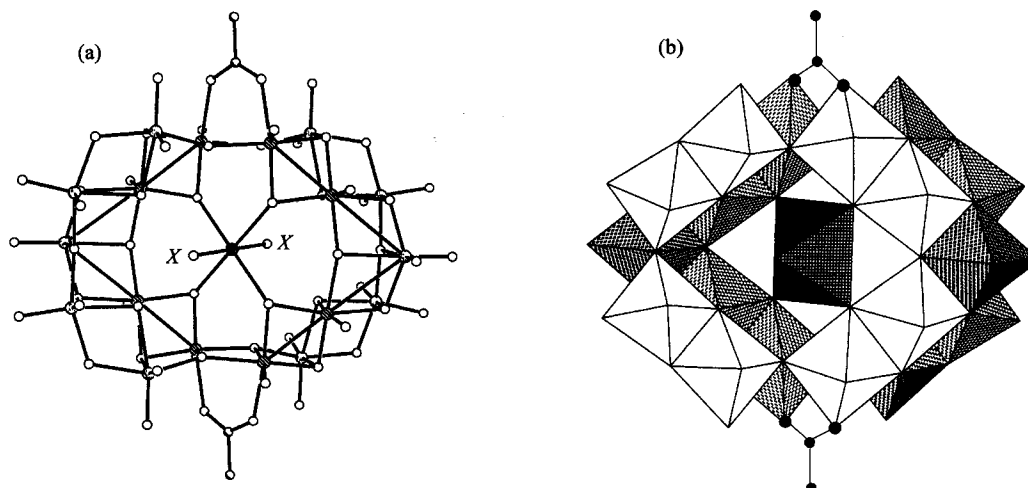


Fig. 2 (a) Structure of $[\{Na(X)_2\} \subset \{(\mu_3-OH)_4Mo_8^V Mo_{10}^{VI} O_{52}(\mu_2-CH_3COO)_2\}]^{-(n+9)}$ ($X = CH_3COO^-$ for **3**, DMF for **4** and H_2O for **5**) built up by two *cis*- $\{Mo_9\}$ units. (b) Polyhedral representation showing that the $\{Mo_{18}\}$ ring can be described as that two oval octagons are staged to form ramped ring with two additional $Mo^{VI}O$ octahedra situating on the outer edges along the long axis of the ring.

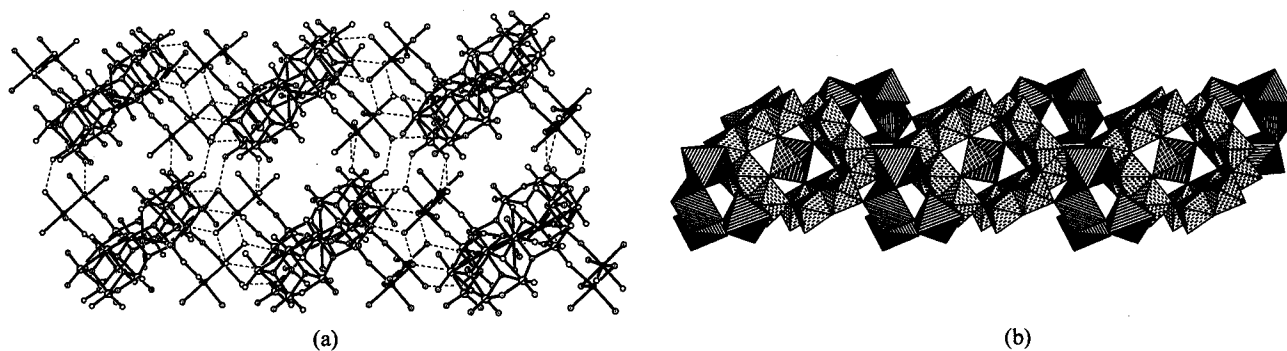


Fig. 3 (a) Cluster anions **3a** are connected into a layer via hydrogen bonds. (b) Cluster anions **4a** are linked into an infinite chain via Na^+ bridges.

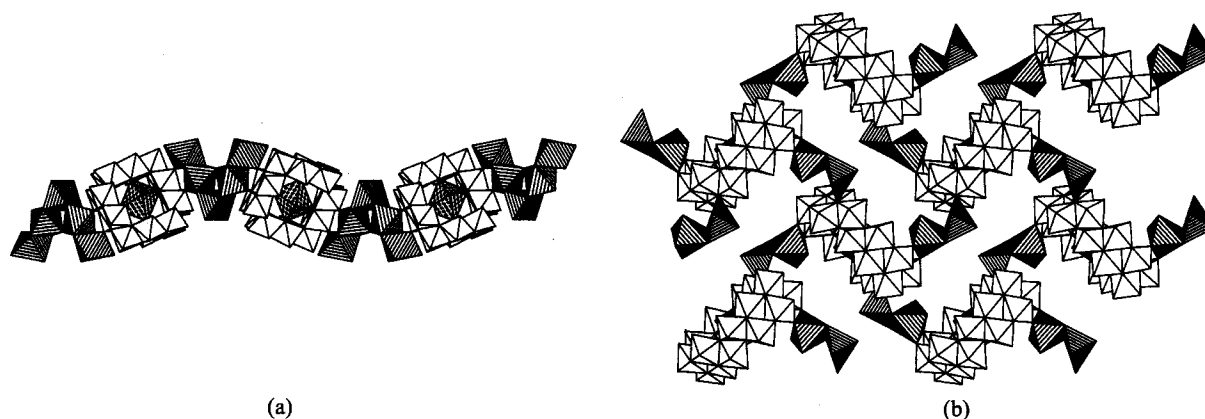


Fig. 4 (a) Cluster anions **5a** are first linked via *V*-shaped $[Na_5(OH_2)_{17}]^{5+}$ moieties into an infinite chain along *c*-axis. (b) Perpendicular to the *a*-axis, cluster anions **5a** are lined via $[Na_2(OH_2)_6]^{2+}$ moieties into a 2-D sheet. Through these interactions towards different directions, anions **5a** are linked into a very complicated 3-D network.

$[Na_2(OH_2)_6]^{2+}$ moieties (consisting of a distorted $NaO_2(OH_2)_4$ octahedron and a distorted $NaO(OH_2)_4$ square pyramid) to form a 2-D sheet. Thus, crown-shaped anions **5a** are connected into a very complicated 3-D network through several interactions between anions and cations towards different directions.

The IR spectra of **3–5** show similar characteristics

features, namely, absorptions in the range of $970–900\text{ cm}^{-1}$ are attributed to $\nu(Mo=O)$; a series of bands in the $870–490\text{ cm}^{-1}$ range are associated to $\nu(\mu_3-O-Mo_3)$ or $\nu_{as}(Mo-O-Mo)$. Medium absorptions are observed at 1541 cm^{-1} for **3**, 1537 cm^{-1} for **4** and **5**, corresponding to the $\nu_{as}(COO)$. The $\nu_s(COO)$ vibrations appear round 1445 cm^{-1} .

Conclusions

A series of crown-shaped polyoxomolybdates with attractive structures have been synthesized and their structures were characterized. Obviously, there exist various building blocks in each reaction solution. These successful syntheses might lead to the synthesis of some other larger rings using larger even cations, cluster molecules than Na^+ . Furthermore, the various linkage modes between these moieties are expected to give rise to a variety of crown-shaped polyoxomolybdates. Compared with $\{\text{Mo}_{18}\}$ compounds **3**–**6**, an interesting conclusion can be drawn, namely, it is possible to vary the packing of the cluster anions by adding other reagents, and novel crown-shaped analogues may be obtained under different mixed-solvents. Relevant investigations are presently in progress in our laboratory.

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