$Mo^V{}_2O_4{}^{2+}$ Directs the Formation and Subsequent Linking of Potential Building Blocks under Different Boundary Conditions: A Related Set of Novel Cyclic Polyoxomolybdates

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Dedicated to Prof. Dieter Sellmann on the occasion of his 60th birthday

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The synthesis and structural characterization of a novel series of deep-red mixed-valence (Mo^{VI}/Mo^V) compounds with nano-sized spherically shaped cluster anions containing 18, 40, or 54 Mo atoms, respectively, is reported: $Na_{10}[H_4Mo_{18}O_{56}(CH_3COO)_2]$ × ca. 36 H_2O × 3 CH_3COOH (**1**), $(NH_4)_{12}Na_{12}[Mo_{40}O_{128}]$ × ca. 70 H_2O (**2**), $(NH_4)_{12}Na_{20}[H_4Mo_{54}O_{168}(CH_3COO)_4]$ × ca. 64 H_2O (**3**), $Na_{32}[H_4Mo_{54}O_{168}(CH_3COO)_4]$ × ca. 128 H_2O (**4**), and $Na_{32}[H_4Mo_{54}O_{168}(CH_3COO)_4]$ × ca. 98 H_2O (**5**). Clusters **3**, **4**, and **5** differ in the packing of the rings in the lattice. The anions are easily formed by reduction of an acidified aqueous molybdate solution while the deliberately generated $Mo^V_2O_4{}^{2+}$ group – abundant in all clusters – has a directing influence on the formation of the preliminary building blocks. Furthermore, it is possible to control the ratio of the $\{Mo^V_2\}$ units to the Mo^{VI} centres by adjusting the specific concentration of the employed reducing agent.

Introduction

Obtaining a strategy for the formation of complex molecular systems with desired properties − constructed from simple building blocks by conservative self-assembly processes − is an ambitious endeavour in contemporary chemistry. In this context, the polyoxomolybdate system under consideration shows a variety of units (either as existing or virtual species), whose linking can be controlled by the deliberate generation of stable and transferable fragments.[1] An important step for us in this regard was, for example, the use of pentagonal $\{(Mo)Mo_5\}$-type units that allowed us not only to adjust the size of giant spherical species, but also to generate such types of molecules with practically 150 unpaired electrons at their periphery by linking these pentagonal units with Fe^{III} ($S = {}^5/_2$) centres.

A prominent feature of the chemistry of molybdenum is the formation of numerous polyoxomolybdate(VI) anions in aqueous solutions. Depending on the boundary conditions, the large number of species existing simultaneously in strongly overlapping equilibria can be considered − in this context − as an extensive library of building blocks, accessible on demand. The equilibria (the dynamics of aggregation reactions) are mostly characterized by the degree of acidity. On the other hand, the negative charge and therefore the nucleophilicity of intermediate cluster fragments can be increased by reduction, resulting in further attraction of electrophiles and thus in growth of the molecular systems.[2]

Reducing an acidified aqueous solution of ammonium heptamolybdate with sodium dithionite − under conditions that favour the generation of $Mo^V_2O_4{}^{2+}$ [= $Mo^V_2O_4(H_2O)_6{}^{2+}$ = $\{Mo^V_2\}$] units (controlled pH and redox potential), led to the simultaneous precipitation of two compounds, $(NH_4)_{12}Na_{12}[Mo_{40}O_{128}]$ × ca. 70 H_2O (**2**) and $(NH_4)_{12}Na_{20}[H_4Mo_{54}O_{168}(CH_3COO)_4]$ × ca. 64 H_2O (**3**), which are easily distinguishable by their different crystal shapes.[3]

Since the ratio of the red lozenge-shaped crystals of **2** relative to the red needle-shaped ones of **3** depends upon the amount of reducing agent, our challenge was thus to find suitable conditions − based on our knowledge of the different Mo^V/Mo^{VI} ratios in **2a** and **3a** − for obtaining both compounds in a pure form. These experiments led to the discovery of a series of related new compounds.[4]

Results and Discussion

All mentioned cluster anions were formed by stepwise growth processes, initiated and directed by the in situ generated $Mo^V_2O_4{}^{2+}$ units. (During the last decade, several other compounds containing one, two, or more $\{Mo^V_2\}$ units have been reported.[5]) The important result, however, in the context of our a priori intention, is that all the clusters with $\{Mo^V_2\}$ groups reported here are distinguishable by their $\{Mo^V_2\}/Mo^{VI}$ ratios that result from the different redox equivalents of reducing agent used and from the proton concentration or acidity of the reaction medium. Table 1 summarizes these trends and includes clusters of the type $\{Mo_{48}\}$[6] and $\{Mo_{132}\}$[7] that also contain $\{Mo^V_2\}$ building

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Table 1. Some properties of the cluster anions isolated from aqueous molybdate solution (pH ≈ 4) in presence of acetate; the asterisk stands in all cases for the reduced form

	Building blocks	Mo^{V} centres	Mo^{VI} centres	Mo^{V}/Mo	Charge per Mo	O/Mo
$[Mo_{40}O_{128}]^{24-}$	$\{Mo_2{*}\}_4\{Mo_8\}_4$	8	32	0.20	0.60	3.2
$[H_4Mo_{54}O_{168}(CH_3COO)_4]^{32-}$	$\{Mo_2{*}\}_2\{Mo_8{*}\}_4\{Mo_9{*}\}_2$	20	34	0.37	0.59	3.3
$[Mo_{48}O_{148}]^{28-}$ [a]	$\{Mo_2{*}\}_2\{Mo_4\}_2\{Mo_9{*}\}_4$	20	28	0.42	0.58	3.1
$[Mo_{116}O_{331}(CH_3COO)_{30}(H_2O)_{56}]^{46-}$ [b]	$\{Mo_2{*}\}_{25}\{(Mo)Mo_5\}_{11}$	50	66	0.43	0.40	3.1
$[H_4Mo_{18}O_{56}(H_3CCOO)_2]^{10-}$ [b]	$\{Mo_9{*}\}_2$	8	10	0.44	0.56	3.3
$[Mo_{132}O_{372}(H_3CCOO)_{30}(H_2O)_{72}]^{42-}$ [c]	$\{Mo_2{*}\}_{30}\{(Mo)Mo_5\}_{12}$	60	72	0.45	0.32	3.3

[a] To be published. – [b] See ref.[9] – [c] See ref.[7]

blocks. Notably, at *lower* pH values, molybdenum blue species like the ring-shaped $\{Mo_{154}\}$ cluster are formed where no $\{Mo^{V}_{2}\}$ units are present.[8]

All compounds were characterized by elemental analyses [including cerimetric titration for the determination of the (formal) number of reduced centres], thermogravimetry (to determine the amount of crystal water), spectroscopy (UV/Vis, IR, Raman), and single-crystal X-ray structure analyses [including bond valence sum (BVS) calculations for the determination of the position of the H_2O ligands, as well as for the distinction between Mo^{VI} and Mo^{V} centres]. The crystallographic data for the diamagnetic, mixed-valence compounds $Na_{10}[H_4Mo_{18}O_{56}(CH_3COO)_2] \times$ ca. 36 $H_2O \times$ 3 CH_3COOH (**1**), $(NH_4)_{12}Na_{12}[Mo_{40}O_{128}] \times$ ca. 70 H_2O (**2**), $(NH_4)_{12}Na_{20}[H_4Mo_{54}O_{168}(CH_3COO)_4] \times$ ca. 64 H_2O (**3**), $Na_{32}[H_4Mo_{54}O_{168}(CH_3COO)_4] \times$ ca. 128 H_2O (**4**), and $Na_{32}[H_4Mo_{54}O_{168}(CH_3COO)_4] \times$ ca. 98 H_2O (**5**) are given in Tables 2 and 3.

Detailed structural information can be obtained from Figures 1–4. Figure 1 illustrates the importance of the mentioned $Mo^{V}_{2}O_4^{2+}$ dumb-bell-type "linkers" (equivalent to the $\{Mo^{V}_{2}O_{10}\}$ structural building block in the solids, which of course does not exist in solution) for the $\{Mo_{18}\}$-, $\{Mo_{40}\}$-, and $\{Mo_{54}\}$-type clusters. These units have a high formation tendency in molybdate solutions in the presence of reducing agents at pH values relevant for the present investigations.

As an example, the $\{Mo_{18}\}$ cluster anion **1a**[9] (Figures 1 and 4) reflects the tendency of even small polyoxomolybdates to adopt ring-shaped structures. The anion itself has approximately C_{2h} symmetry, and consists of two identical building blocks – denoted as *cis*-$\{Mo_9{*}\}$ – each containing five Mo^{VI} centres and two $\{Mo^{V}_{2}\}$ units (the asterisk * denotes the presence of reduced centres, i.e. of $\{Mo^{V}_{2}O_{10}\}$ groups, either as $\{Mo_2{*}\}$ units or as part of the $\{Mo_8{*}\}$ or $\{Mo_9{*}\}$ framework). These four $\{Mo^{V}_{2}\}$ units

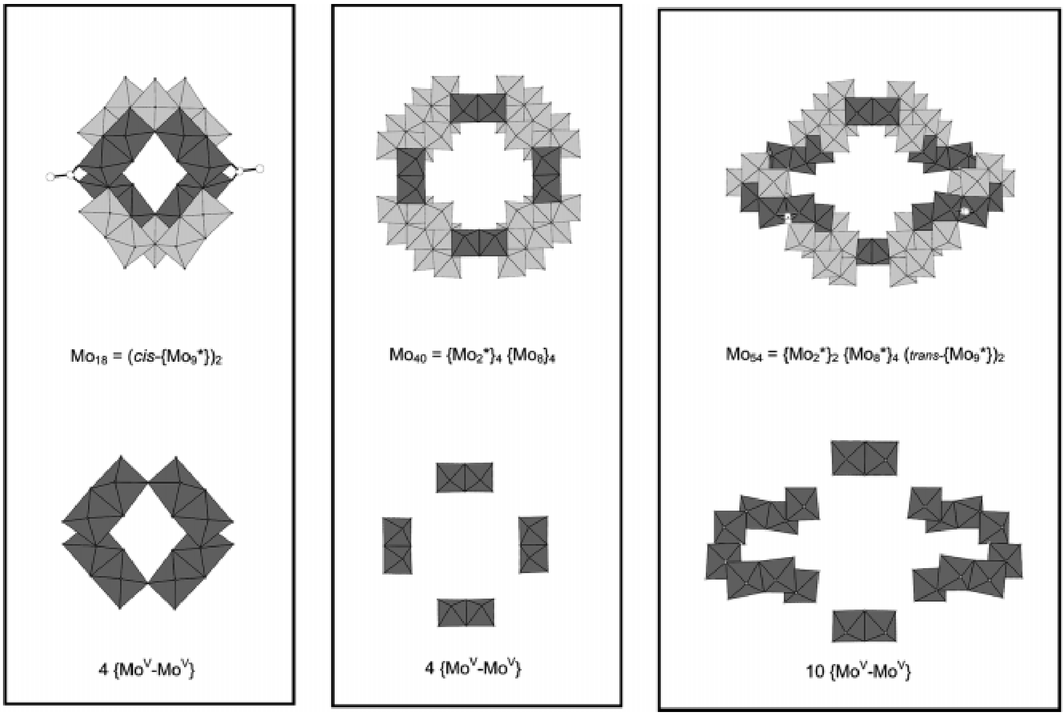

Figure 1. Polyhedral representations of the complete $\{Mo_{18}\}$ (**1a**) (left), $\{Mo_{40}\}$ (**2a**) (centre), and $\{Mo_{54}\}$ (**3a**–**5a**) (right) clusters based on the $\{Mo_2{*}\}$ dumb-bells with $Mo^{V}-Mo^{V}$ single bonds, highlighted in dark-grey (top); for clarity, the abundant $\{Mo_2{*}\}$ groups are also shown separately (bottom)

form an oxomolybdenum(V) core fragment (see Figure 1, bottom) with a puckered cyclic framework comparable to that of the compound $Mo_8O_{16}(OMe)_8(PMe_3)_4$.[10] A more detailed view can be obtained from Figure 4, which also elucidates the notation *cis*- and *trans*-$\{Mo_9{}^*\}$ (occurring in the $\{Mo_{54}\}$ cluster anion) regarding the different positions of the two molybdenum octahedra directed towards the central $\{Mo_7\}$ moiety (note that the local symmetry of the *cis*-$\{Mo_9{}^*\}$ unit is C_s).

The polymorphic compound **2** crystallizes in two different space groups, $P2_1/m$ and *Pnma*. Its ring-shaped anions form layers that are separated by the cations. Depending on the orientation of the anions of two layers towards each other, either the monoclinic or the orthorhombic polymorph results.[11] The $\{Mo_{40}\}$ anion **2a** (Figure 1) consists of 168 non-hydrogen atoms, i.e. 40 molybdenum centres (including eight Mo^V) and 128 oxygen atoms, and has approximately C_{4v} symmetry whereby eight $\{Mo^{VI}O_6\}$ and two $\{Mo^VO_6\}$ octahedra form one $\{Mo_{10}\}$ unit possessing a mirror plane. Cleaving two of the terminal octahedra of this $\{Mo_{10}\}$ unit leads to an $\{Mo_8\}$ framework resembling the γ-octamolybdate that was recently isolated as a main constituent of a nonamolybdate formed under a comparable proton concentration.[12] Here we prefer the alternative description: Four $\{Mo_2^V\}$ groups link four $\{Mo_8\}$ units (note that these units are not identical with the above-mentioned γ-octamolybdate), corresponding to the formula given above (Figure 1). Whereas in the case of **2** [containing the $\{Mo_{40}\}$ (= $\{Mo_2{}^*\}_4\{Mo_8\}_4$) cluster anion **2a**] the $\{Mo_2^V\}$ building units are not the dominating structural feature, this is actually the case for the $\{Mo_{54}\}$ (= $\{Mo_9{}^*\}_2$-$\{Mo_8{}^*\}_4\{Mo_2{}^*\}_2$) cluster anion of **3**, **4**, and **5**, as well as for the $\{Mo_{18}\}$ = $\{Mo_9{}^*\}_2$ cluster anion of **1**, where all such units are directly connected (see Figures 1−4).

The crown-shaped (twisted) anion $\{Mo_{54}\}$ (= $\{Mo_9{}^*\}_2\{Mo_8{}^*\}_4\{Mo_2{}^*\}_2$, see Figure 2), abundant in compounds **3**, **4**, and **5**, consists of 238 non-hydrogen atoms, i.e. 54 molybdenum atoms (including 20 Mo^V), 176 oxygen, and eight carbon atoms, and has approximately C_{2v} symmetry (in the crystal lattice the site symmetry of the twisted anion is in all cases *i*). The formulation based on the three different building blocks ($\{Mo_2{}^*\}$, $\{Mo_8{}^*\}$, $\{Mo_9{}^*\}$) − shown in Figure 2 − corresponds to the above-mentioned formula. Figures 3 and 4 show a comparison of the latter two building blocks with the two other related cluster anions **1a** and **2a**. The $\{Mo_8{}^*\}$ unit, containing six $Mo^{VI}O_6$ as well as two Mo^VO_6 octahedra, can be (formally) derived from the corresponding $\{Mo_8\}$ unit of the $\{Mo_{40}\}$ anion by a two-electron reduction step, i.e. by formation of an $\{Mo_2^V\}$ group (Figure 3). The other building block (denoted *trans*-$\{Mo_9{}^*\}$), present twice in the $\{Mo_{54}\}$ cluster, consists of nine molybdenum−oxygen octahedra, and has approximately C_2 symmetry. Four Mo^V centres form two $\{Mo_2^V\}$ units and point to opposite sites thereby enabling an interesting comparison with the *cis*-$\{Mo_9{}^*\}$ unit of the $\{Mo_{18}\}$ cluster (Figure 4). Due to the different orientation of the $\{Mo_2^V\}$ units towards each other (compared to the *cis*-$\{Mo_9{}^*\}$ units), the further linking of these structural building blocks is already fixed.

The $\{Mo_{54}\}$ cluster anion can be "constructed" in the following way: Two of the $\{Mo_8{}^*\}$ units are linked by an $\{Mo_2^V\}$ unit resulting in a super-unit of the type $\{Mo_8{}^*\}$

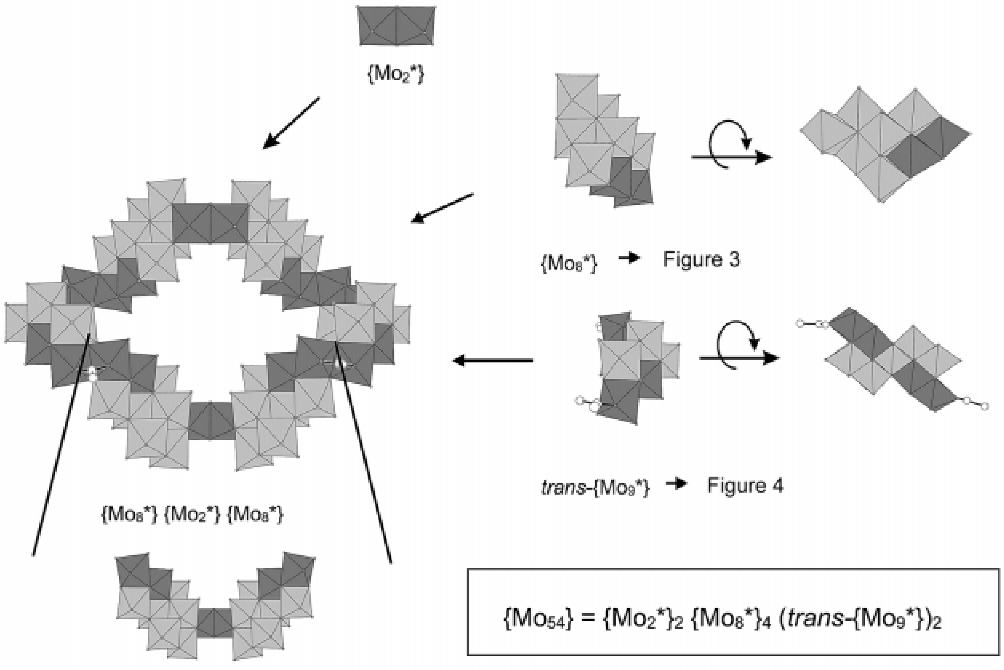

Figure 2. Polyhedral representation of the $\{Mo_{54}\}$ cluster (left) and its three formal building blocks (right): $\{Mo_2{}^*\}$, $\{Mo_8{}^*\}$, and $\{Mo_9{}^*\}$ ($\{Mo_2{}^*\}$ = $[Mo_2^VO_4O_6]^{10-}$, $\{Mo_8{}^*\}$ = $[Mo_2^VMo_6^{VI}O_{28}]^{10-}$, and $\{Mo_9{}^*\}$ =$[(\mu_3\text{-}OH)_2Mo_4^VMo_5^{VI}O_{26}(CH_3COO)_2]^{10-}$); one super-unit of the type $\{Mo_8{}^*\}\{Mo_2{}^*\}\{Mo_8{}^*\}$ is also shown (bottom)

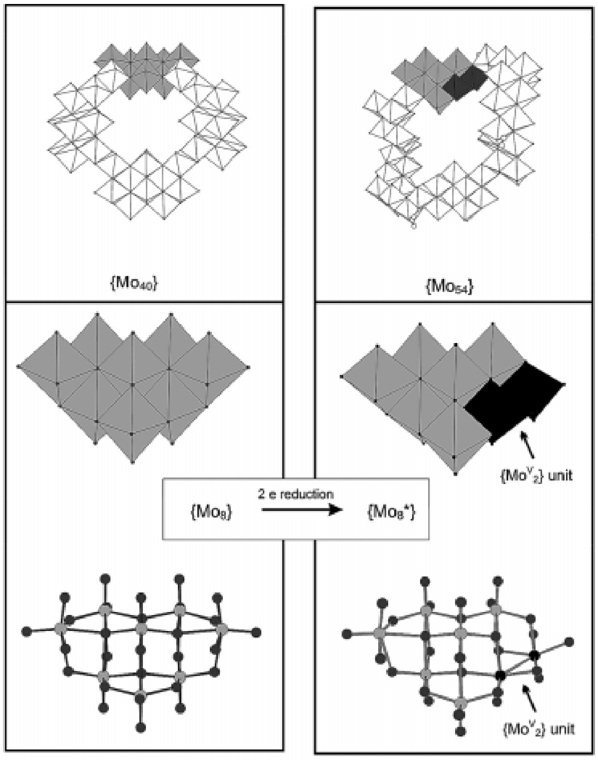

Figure 3. Structural comparison of an $\{Mo_8\}$ unit derived from $\{Mo_{40}\}$ (left) with the corresponding $\{Mo_8*\}$ unit (containing one $\{Mo^V-Mo^V\}$ type unit) of the $\{Mo_{54}\}$ (right) cluster in polyhedral representation (top) and as ball-and-stick model (bottom); ball-and-stick representation: Mo^V dark-grey, Mo^{VI} light-grey, O atoms medium grey; polyhedral representation: $\{Mo_2^V\}$ units dark-grey, $\{Mo^{VI}{}_mO_n\}$ moieties light-grey

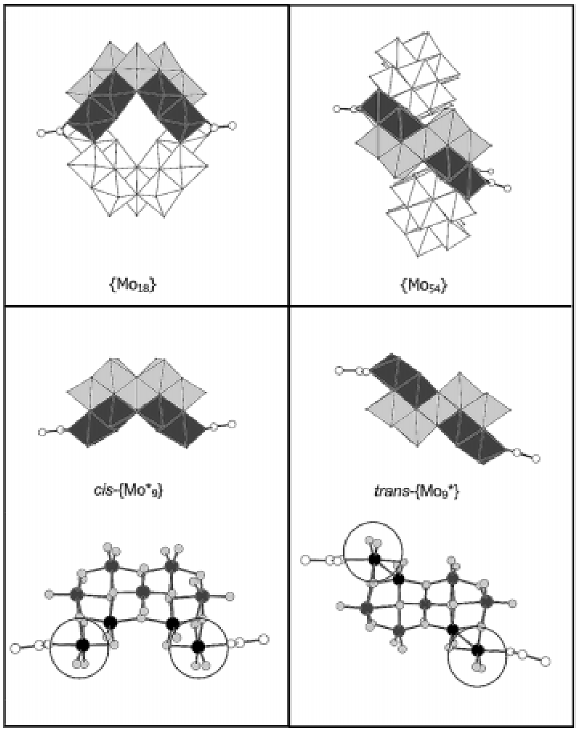

Figure 4. Structural comparison of $\{Mo_9*\}$ units − derived from the $\{Mo_{18}\}$ (top, left) and from the $\{Mo_{54}\}$ cluster (top, right) − in polyhedral and ball-and-stick representation; the classification of *cis* and *trans* corresponds to the position of the $\{Mo^V-Mo^V\}$ units relative to each other; ball-and-stick representation: Mo^V black, Mo^{VI} light-grey, O atoms medium grey; polyhedral representation: $\{Mo_2^V\}$ units dark-grey, $\{Mo^{VI}{}_mO_n\}$ moiety light-grey; the acetate ligands (carbon: open circle) are shown in both cases in ball-and-stick representation)

$\{Mo_2*\}\{Mo_8*\}$. Two of these are finally bridged at both ends through edge-sharing with the two *trans*-$\{Mo_9*\}$ building blocks and by an acetate ligand (Figures 2 and 4). Remarkably, the construction of the $\{Mo_{40}\}$ cluster can be described in the same way: Two super-units of the type $\{Mo_8\}\{Mo_2*\}\{Mo_8\}$ (i.e., the aforementioned non-reduced $\{Mo_8\}$ groups!) are linked by additional $\{Mo_2*\}$ groups resulting in the bowl-shaped anion.

Interestingly, it is possible to vary the packing of the cluster units by adding different reagents, e.g., acetylacetone or sodium chloride. Comparing the sodium salts of the $\{Mo_{54}\}$ compounds **4** and **5**, it is obvious that the crystal water content, and thus the unit cell volume, is reduced by ca. 1:7 through replacing sodium chloride by acetylacetone during the crystallization process. Adding other cations, e.g. ammonium leads to a further shrinking of the cell and relevant investigations are presently in progress.

Looking at the charge per Mo atom and the value $R = \Sigma O/\Sigma Mo$ for all aggregates shows values that are practically constant, except for the charge per Mo atom in case of the $\{Mo_{132}\}$ ball-type species and its derivative. A value of $R \approx 3$ is observed in many cases, and even for large aggregates like the big wheel $[(MoO_3)_{154}H_{14}]^{14-}$.

Conclusions

Our synthetic route has as its aim the deliberate synthesis of clusters based on the use of $\{Mo_2^V\}$ units under different boundary conditions. In this context, it is interesting to note that the $\{Mo_8^{VI}\}$ building block, which is important for the present preparation conditions,[13] can at least formally be reduced to the actual $\{Mo_8*\}$ building block containing one $\{Mo_2^V\}$ dumb-bell unit (Figure 4) and, in the presence of additional molybdenum and reducing agent, to the $\{Mo_9*\}$ building block. The general strategic approach to control molecular growth by conservative self-organization processes offers, in principle, a wide variety of new species that can be constructed from simple building blocks.

Experimental Section

General Techniques: All reactions were performed using 100-mL Erlenmeyer flasks where no attempts were made to exclude oxygen. All chemicals except sodium dithionite were at least of reagent grade, and were used as supplied. Note, that sodium dithionite (85% iodometrically) should be fresh and powdered prior to use. The use of aged charges, which contain more water and might be partly decomposed, will result in lower yields and gives less crystalline materials. − Elemental analyses (C,H,N) were performed using a LECO CHN 920 analyzer. The nitrogen values were determined by the Kjeldahl method, the sodium content by flame photometry. (The error limits for the determination of the sodium and ammonium cations in **2** and **3** restrict somewhat the reliability of their quantity in the formula unit by ±1.) − Vibrational spectroscopy was carried out with a Bruker IFS66/FRA106. − The amounts of crystal water were determined thermogravimetrically with a Shimadzu TA-60WSI thermo-balance under argon. − The UV/Vis spectra were measured using either a Shimadzu UV-160A or a Beckman Acta M IV instrument (solid with cellulose as reference). The compounds are stable in dry air but decompose easily while dissolving in water.

Preparation of 1: To a solution of 7.70 g of sodium molybdate dihydrate (31.8 mmol), 50.0 g of sodium acetate trihydrate (367.4 mmol), and 5.0 g of sodium chloride (85.6 mmol) in 300 mL of H_2O, an aqueous hydrazine sulfate solution (0.1 M, 61 mL) and afterwards 75 mL of acetic acid (100%) were added. The reaction medium was heated whilst stirring for 4 d at 35 °C (slow colour change from green to brownish-green) while the volume of the solution was kept constant by adding water. The solution was subsequently cooled to room temperature and filtered. The filtrate was kept in an open beaker and the volume of the solution was reduced by slow evaporation (up to 130 mL). Crystalline **1** was filtered off after 1 week and dried with $CaCl_2$. Yield 2.0 g (30% based on Mo). − IR (KBr pellet): $\tilde{\nu}$ = 3440 (s), 3162 (s), 1636 (m) [$\delta(H_2O)$], 1541 (m), 1443 (m), 1394 (sh), 1330 (m), 1028 (w), 960 (sh), 935 (s), 898 (m), 712, 636, 565, 498, 411. − Raman (λ_e = 1064 nm, undiluted powder): $\tilde{\nu}$ = 966, 930 [$\nu(Mo{=}O)$], 747, 774, 662, 574, 507, 358, 330, 286, 200, 157 cm^{-1}. − UV/Vis (cellulose): λ_{max} = ca. 260, ca. 340, ca. 395, ca. 535, ca. 1040 nm. − $C_{10}H_{94}Mo_{18}Na_{10}O_{102}$ (3803.6): calcd. C 3.16, H 2.49, Na 6.04, H_2O 17.0; found C 3.3, H 2.4, Na 8.2, H_2O 14. − Cerimetric titration: 8±1 e.

Preparation of 2. − (a) After a solution of 3.00 g of ammonium heptamolybdate tetrahydrate (2.4 mmol) in 25 mL of water was acidified with 0.8 mL of acetic acid (100%), 0.20 g of sodium dithionite (1.1 mmol) were added (colour change to deep-green). After stirring the solution for 5 min, 3.00 g of sodium chloride was dissolved and the resulting solution was allowed to stand for 4.5 h for crystallization. The precipitated red lozenge-shaped crystals were filtered off, washed with aqueous acetone (50 vol-%) and finally dried in air. Yield 0.28 g (9% based on Mo). ***Note:*** After 5 h, crystals of **3** also start to precipitate. Pure crystalline **2**, i.e. an $\{Mo_{54}\}$-free product, can be obtained by replacing acetic acid by hydrochloric acid (**2** does not contain acetate ligands!). − **(b)** After a solution of 3.00 g of ammonium heptamolybdate tetrahydrate (2.4 mmol) in 25 mL of water was acidified with 3.0 mL of hydrochloric acid (1 M), 0.20 g of sodium dithionite (1.1 mmol) was added (colour change to deep-green). After stirring the solution for 5 min, 3.00 g of sodium chloride was dissolved and the resulting solution was allowed to stand for 4.5 h for crystallization. The precipitated red lozenge-shaped crystals were filtered off, washed with aqueous acetone (50-vol%) and finally dried in air. − Yield 0.58 g (18% based on Mo). ***Note:*** Comparing the two preparation methods the total yield was higher when hydrochloric acid was used, but the crystals were less suitable for single-crystal X-ray structure analysis. − IR (KBr pellet): $\tilde{\nu}$ = 3440 (s), 3162 (s), 1617 (m) [$\delta(H_2O)$], 1400 (s) [$\delta_{as}(NH_4{}^+)$], 946 (s) [$\nu(Mo{=}O)$], 903 (sh), 869 (s), 765 (m), 724 (s), 652 (s), 486 (m) cm^{-1}. − Raman (λ_e = 1064 nm, undiluted powder): $\tilde{\nu}$ = 965, 937 [$\nu(Mo{=}O)$], 909, 989, 842, 774, 723, 489, 375, 347, 276, 203, 143 cm^{-1}. − UV/Vis (cellulose): λ_{max} = ca. 285, ca. 380 nm. − $H_{188}Mo_{40}N_{12}Na_{12}O_{198}$ (7638.9): calcd. H 2.46, N 2.20, Na 3.61, H_2O 16.5; found H 2.08, N 2.22, Na 3.8, H_2O 14 (calcd. for compound containing 70 H_2O). − Cerimetric titration: 8±1 e.

Preparation of 3. − (a) After acidifying a solution of 3.00 g of ammonium heptamolybdate tetrahydrate (2.4 mmol) and 0.5 g of sodium acetate trihydrate in 25 mL of water with 3.0 mL of hydrochloric acid (1 M), 0.30 g of sodium dithionite (1.7 mmol) was added (colour change to deep-green). After stirring for 5 min, 3.00 g of sodium chloride was added and the resulting solution was allowed to stand for crystallization for 15−18 h. The precipitated red needle-shaped crystals were filtered off, washed with acetone and finally dried in air. Yield 0.67 g (20% based on Mo). − **(b)** After a solution of 3.00 g of ammonium heptamolybdate tetrahydrate (2.4 mmol) in 25 mL of water was acidified with 0.8 mL of acetic acid (100%), 0.30 g of sodium dithionite (1.7 mmol) was added (colour change to deep-green). After stirring the solution for 5 min, 3.00 g of sodium chloride was dissolved and the resulting solution was allowed to stand for 12−15 h for crystallization. The precipitated red needle-shaped crystals were filtered off, washed with aqueous acetone (50-Vol%), and finally dried in air. − Yield 0.3 g (8% based on Mo). ***Note:*** Comparing the two preparation methods, the total yield is higher when hydrochloric acid is used (similar to compound **2**), but the crystals are less suitable for single-crystal X-ray structure analysis. − IR (KBr pellet): $\tilde{\nu}$ = 3459 (s), 1624 (m) [$\delta(H_2O)$], 1540 (m) [$\nu_{as}(COO^-)$], 1436 (sh), 1402 (s), 962 (m), 944 (m) [ν (Mo=O)], 899 (m), 860 (m), 716 (m), 660 (m), 624 (m), 490 (m) cm^{-1}. − Raman (λ_e = 1064 nm, undiluted powder): $\tilde{\nu}$ = 969, 945, 936 [$\nu(Mo{=}O)$], 765, 660, 491, 380, 357, 280, 242, 204 cm^{-1}. − UV/Vis (cellulose): λ_{max} = ca. 270, ca. 325, ca. 360 nm. − $C_8H_{192}Mo_{54}N_{12}Na_{20}O_{240}$ (9938.3): calcd. C 0.97, H 1.93, N 1.68, Na 4.63, H_2O 11.6; found C 0.94, H 2.38, N 1.68, Na 4.3, H_2O 11. − Cerimetric titration: 20±1 e.

Preparation of 4: To a solution of 4.50 g of sodium molybdate dihydrate (18.6 mmol) and 1.00 g of sodium acetate trihydrate in 25 mL of water, 1.00 g of sodium dithionite (5.75 mmol) was added (colour change to deep-brown). After stirring for 5 min, the solution was acidified with 3.00 mL of hydrochloric acid (1 M), stirred for an additional 15 min and finally allowed to stand for crystallization. The red needle-shaped crystals were filtered off after 7 d, washed with acetone and subsequently dried in air. − Yield 0.37 g (10% based on Mo). − IR (KBr pellet): $\tilde{\nu}$ = 3459 (s), 1635 (m) [$\delta(H_2O)$], 1541 (m) [$\nu_{as}(COO^-)$], 1445 (m), 961 (m), 944 (m) [$\nu(Mo{=}O)$], 900 (m), 861 (m), 718 (m), 667 (m), 620 (m), 491 (m) cm^{-1}. − Raman (λ_e = 1064 nm, undiluted powder): $\tilde{\nu}$ = 975, 947, 936 [$\nu(Mo{=}O)$], 838, 762, 663, 509, 478, 358, 284, 243, 205 cm^{-1}. − UV/Vis (cellulose): λ_{max} = ca. 280, 320, 360 nm. − $C_8H_{272}Mo_{54}Na_{32}O_{304}$ (11150.7): calcd. C 0.86, H 2.44, Na 6.60, H_2O 20.6; found C 0.88, H 2.10, Na 6.8, H_2O 18. − Cerimetric titration: 20±1 e.

Preparation of 5: To a solution of 4.50 g of sodium molybdate dihydrate (18.6 mmol) in 25 mL of water, 2.0 mL of acetylacetone was added dropwise (colour change to yellow) followed by 1.00 g of sodium dithionite (5.75 mmol) (colour change to deep-brown). After stirring for 5 min, the reaction medium was acidified with 2.0 mL of acetic acid (100%) and stirred for an additional 15 min. After 3 d, the red needle-shaped crystals were filtered off, washed with aqueous acetone (70 vol-%) and finally dried in air. − Yield 0.33 g (10% based on Mo). − IR (KBr): $\tilde{\nu}$ = 3459 (s), 1635 (m) [$\delta(H_2O)$], 1541 (m) [$\nu_{as}(COO^-)$], 1445 (m), 961 (m), 944 (m) [$\nu(Mo{=}O)$], 900 (m), 861 (m), 718 (m), 667 (m), 620 (m), 491 (m) cm^{-1}. − Raman (λ_e = 1064 nm, undiluted powder): $\tilde{\nu}$ = 974, 952,

Table 2. Crystallographic data of compounds **1** and **2**

Compound	**1** $Na_{10}[H_4Mo_{18}O_{56}(CH_3COO)_2]$ $\times$ 36 H_2O $\times$ 3 CH_3COOH	$Na_{12}(NH_4)_{12}[Mo_{40}O_{128}]$ $\times$ 74 H_2O	**2** $Na_{12}(NH_4)_{12}[Mo_{40}O_{128}]$ $\times$ 70 H_2O
Color and shape	red	red lozenge	red lozenge
Ratio $Mo^V/\Sigma Mo$	0.44	0.25	0.25
M [g mol^{-1}]	3803.67	7711.17	7639.10
Empirical formula	$C_{10}H_{94}Mo_{18}Na_{10}O_{102}$	$H_{196}Mo_{40}N_{12}Na_{12}O_{202}$	$H_{188}Mo_{40}N_{12}Na_{12}O_{198}$
Crystal system	triclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/m$	$Pnma$
a [Å]	12.1293(5)	13.1752(6)	24.5144(15)
b [Å]	15.2523(6)	34.922(2)	34.940(2)
c [Å]	15.2852(6)	22.0247(10)	23.3214(14)
α [°]	114.911(1)		
β [°]	94.227(1)	101.378(1)	
γ [°]	101.647(1)		
Volume [Å^3]	2471.4(2)	9934.4(8)	19976(2)
Z	1	2	4
$\rho_{calcd.}$ [Mgm^{-3}]	2.556	2.578	2.540
μ [mm^{-1}]	2.373	2.583	2.567
Crystal size [mm^3]	0.40 × 0.22 × 0.16	0.24 × 0.20 × 0.06	0.20 × 0.10 × 0.02
2θ range	1.52 to 30.02°	0.94 to 27.01°	1.66 to 26.99°
Reflections collected	33526	58486	115056
Reflections observed	12493	16617	10726
$[I > 2\sigma(I)]$	(R_{int}= 0.0219)	(R_{int}= 0.0383)	(R_{int}= 0.1348)
Refined parameters	643	1175	1028
$R1$ $[I > 2\sigma(I)]$	0.0356	0.0490	0.0643
$wR2$ $[(I > 2\sigma(I)]$	0.0997	0.1272	0.1532
max. and min. residual electron density [eÅ^{-3}]	2.138 and −1.828	2.916 and −1.582	2.883 and −1.324

Table 3. Crystallographic data of compound **3−5**

Compound	**3** $Na_{20}(NH_4)_{12}[H_4Mo_{54}O_{168}(CH_3COO)_4]$ $\times$ 64 H_2O	**4** $Na_{32}[H_4Mo_{54}O_{168}(CH_3COO)_4]$ $\times$ 128 H_2O	**5** $Na_{32}[H_4Mo_{54}O_{168}(CH_3COO)_4]$ $\times$ 98 H_2O
Color and shape	red needles	red needles	red needles
Ratio $Mo^V/\Sigma Mo$	0.37	0.37	0.37
M [g mol^{-1}]	9938.30	11150.70	10610.22
Empirical formula	$C_8H_{192}Mo_{54}N_{12}Na_{20}O_{240}$	$C_8H_{272}Mo_{54}Na_{32}O_{304}$	$C_8H_{212}Mo_{54}Na_{32}O_{274}$
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	13.4911(10)	17.3511(7)	17.8483(5)
b [Å]	21.729(2)	20.2180(8)	18.0932(6)
c [Å]	23.149(2)	23.0180(10)	21.7368(7)
α [°]	67.827(1)	91.574(1)	84.032(1)
β [°]	76.448(1)	103.591(1)	71.598(1)
γ [°]	73.341(1)	98.215(1)	85.337(1)
Volume [Å^3]	5959.3(8)	7752.5(6)	6615.7(4)
Z	1	1	1
$\rho_{calcd.}$ [Mgm^{-3}]	2.769	2.388	2.663
μ [mm^{-1}]	2.896	2.268	2.643
Crystal size [mm^3]	0.22 × 0.06 × 0.06	0.45 × 0.20 × 0.15	0.20 × 0.14 × 0.08
2θ range	0.96 to 27.01°	1.6 to 29.99°	0.99 to 27.02°
Reflections collected	57485	104693	63938
Reflections observed	15162	31157	19328
$[I > 2\sigma(I)]$	(R_{int}= 0.0685)	(R_{int}= 0.0541)	(R_{int}= 0.0460)
Refined parameters	1337	1534	1457
$R1$ $[I > 2\sigma(I)]$	0.0596	0.0582	0.0490
$wR2$ $[(I > 2\sigma(I)]$	0.1446	0.1452	0.1289
max. and min. residual electron density [eÅ^{-3}]	3.040 and −1.924	3.027 and −1.776 eÅ $^{-3}$	2.825 and −2.107

936 [ν(Mo=O)], 765, 661, 491, 380, 357, 280, 242, 204, 182, 150 cm^{-1}. − UV/Vis (cellulose): λ_{max} = ca. 270, ca. 325, ca. 360 nm. − $C_8H_{212}Mo_{54}Na_{32}O_{274}$ (10610.2): calcd. C 0.90, H 2.00, Na 6.94, H_2O 16.6; found C 1.15, H 2.00, Na 6.50, H_2O 14. − Cerimetric titration: 20±1 e.

X-ray Crystallography: Crystals were taken directly from the mother liquor and mounted on a glass fibre at 183 K. In case of **3**, the crystals were first dried and then mounted for X-ray investigations. Diffraction data were collected with a Bruker AXS three-circle diffractometer with a 1 K-CCD detector. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares with SHELXL-93/97. All non-hydrogen atoms were refined anisotropically. The assignment of Mo^V and Mo^{VI} centres, as well as the protonation, clearly follows from bond valence sum calculations[14] and is in agreement with the charge on the cluster anions and the fact that all the Mo^V centres form dumbbell-type $\{Mo_2^V\}$ units with covalent Mo−Mo single bonds. Due to disorder, not all cations could be localized. The crystallographic data for **1** and **2** are given in Table 2, for **3**, **4**, and **5** in Table 3. Further details on the crystal structure investigation of **2** may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [Fax: (internat.) + 49-(0)7247/808-666; E-mail: crysdata@fiz-karlsruhe.de] on quoting the depository numbers CSD-411693 and 411694. Crystallographic data (excluding structure factors) for compounds **1** and **3−5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156640 (**1**), -156641 (**3**), -156642 (**4**), and -156643 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] A. Müller, P. Kögerler, C. Kuhlmann, *Chem. Commun.* **1999**, 1347.

[2] A. Müller, J. Meyer, E. Krickemeyer, C. Beugholt, H. Bögge, F. Peters, M. Schmidtmann, P. Kögerler, M. J. Koop, *Chem. Eur. J.* **1998**, *4*, 1000.

[3] M. Baumann, Diploma Thesis, University of Bielefeld, **1999**.

[4] While preparing this publication, C. Lu − a former Alexander von Humboldt fellow in our group at Bielefeld − obtained the compound $Na_{32}[H_4Mo_{54}O_{168}(H_3CCOO)_4]$ × ca. 120 H_2O, using a different preparation method (similar to that of our $\{Mo_{132}\}$-type keplerate $\{Mo_{132}\}$); the structural description, in spite of the correct structure determination, is different to that described here: W. Yang, C. Lu, X. Lin, H. Zhuang, *Chem. Commun.* **2000**, 1623.

[5] H. K. Chae, W. G. Klemperer, T. A. Marquart, *Coord. Chem. Rev.* **1993**, *128*, 209.

[6] Recently, we isolated crystals of another ring-shaped polyoxomolybdate. Preliminary investigations led to the (empirical) formula $Na_{28}[Mo^V_{20}Mo^{VI}_{28}O_{148}]$. The anion is built up from the three different building blocks $\{Mo_2*\}$, $\{Mo_4\}$, and $\{Mo_9*\}$.

[7] A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, F. Peters, *Angew. Chem.* **1998**, *110*, 3567; *Angew. Chem. Int. Ed.* **1998**, *37*, 3360−3363. Structural and topological features can be found in the following review article: A. Müller, H. Bögge, P. Kögerler, *Struct. Bonding* **2000**, *96*, 203.

[8] A. Müller, C. Serain, *Acc. Chem. Res.* **2000**, *33*, 1.

[9] This compound was isolated and reported for the first time as a by-product of the "open" keplerate, i. e. the basket-type analogue of the spherical $\{Mo_{132}\}$-type cluster (see also ref.[7]): A. Müller, S. Polarz, S. K. Das, E. Krickemeyer, H. Bögge, M. Schmidtmann, B. Hauptfleisch, *Angew. Chem.* **1999**, *111*, 3439; *Angew. Chem. Int. Ed.* **1999**, *38*, 3241−3245. An improved synthetic method is currently under investigation. Recently, S.-W. Zhang and co-workers isolated an isostructural compound with the acetate ligands being replaced by L-alanine (G. Liu, Y.-G. Wei, J. Liu, Q. Liu, S.-W. Zhang, Y.-Q. Tang, *J. Chem. Soc., Dalton Trans.* **2000**, 1013).

[10] D. J. Darensbourg, R. L. Gray, T. Delord, *Inorg. Chim. Acta* **1985**, *98*, L39.

[11] Furthermore, we succeeded in isolating a sodium salt of **2**, revealing a fascinating solid-state structure that will be discussed elsewhere in context with the different packing of the cluster anions in the respective lattices.

[12] T. Yamase, M. Sugeta, E. Ishikawa, *Acta Crystallogr., Sect. C* **1996**, *52*, 1869. The γ-$[Mo_8O_{28}]^{4-}$ anion has been postulated to be an intermediate in the related α−β interconversion: W. G. Klemperer, W. Shum, *J. Am. Chem. Soc.* **1976**, *98*, 8291.

[13] Preliminary mass spectra (ESI) of such solutions indicate the presence of hexa-, hepta-, and octamolybdate species.

[14] I. D. Brown, in: *Structure and Bonding in Crystals*, vol. II (Eds.: M. O'Keeffe, A. Navrotsky), Academic Press, New York, **1981**, p. 1−30.

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