Coordination Chemistry Reviews, 128 (1993) 209–224

High-nuclearity oxomolybdenum(V) complexes*

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(Received 26 January 1993)

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ABSTRACT

During the past decade, a new family of high nuclearity oxometalates has emerged, oxomolybdenum(V) complexes whose d-electrons are localized in Mo^V–Mo^V bonds. The structure types of all known complexes in this family are reviewed, including nine different (Mo^V–Mo^V) monomer, dimer, trimer, tetramer, hexamer, and octadecamer structures, with an emphasis on high-nuclearity structures. In each case, oxomolybdenum(V) core structures are identified and analyzed with regard to degree of polymerization, degree of condensation, and oxygen packing, and an effort is made to identify smaller complexes as subunits of larger structures.

1. INTRODUCTION

High-nuclearity oxomolybdenum complexes have traditionally contained Mo^{VI} centers only (iso- and heteropolymolybates) or both Mo^V and Mo^{VI} centers with

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* Dedicated to the memory of Professor John C. Bailar, Jr.

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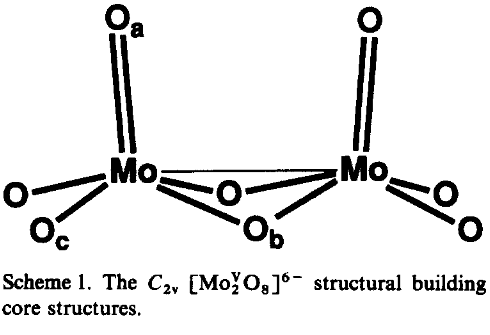
delocalized d-electrons (heteropoly blues) [1]. More recently, however, a new family of high-nuclearity oxomolybdenum complexes has emerged, one whose Mo^V d-electrons are localized in Mo^V—Mo^V single bonds. These complexes have appeared in various contexts, including organometallic chemistry ($[(C_5Me_5Rh)_8(Mo_{13}O_{40})]\cdot Cl_2\cdot 13H_2O$ [2]), alkoxide chemistry ($(Me_3NH)_2(Et_4N)Na_4[Na(H_2O)_3H_{15}Mo_{42}O_{109}\{(OCH_2)_3CCH_2OH\}_7]\cdot 15H_2O$ [3]), and coordination chemistry $(PPh_4)_2(H_3O)_2Na[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]\cdot 5H_2O$ [4]). Moreover, their stoichiometries and structures are complicated, and structural interrelationships are far from obvious. The present review aims to address the situation through a systematic review of polynuclear Mo^V oxo complexes containing Mo^V—Mo^V units, with an emphasis on the structures of high-nuclearity species, i.e. those containing more than four Mo^V centers.

The Mo^V—Mo^V unit in molybdenum oxo complexes is known to occupy the ligand environment shown in Scheme 1 [5–10]. Within this $[Mo_2^VO_8]^{6-}$ structural building unit, the Mo^V—Mo^V bond distance lies in the 2.5–2.7 Å range, while Mo^V—O bond distances are in the 1.6–1.8 Å range for O_a, the 1.9–2.0 Å range for O_b, and the 2.0–2.2 Å range for O_c. Frequently, but not always, a sixth oxygen ligand is weakly bonded to each Mo^V center trans to the O_a ligand. Here, complex oxomolybdenum(V) structures will be simplified by extracting from them core structures comprised of $[Mo_2^VO_8]^{6-}$ building units of the type shown in Scheme 1, and then showing how these units are linked together. As with organic polymers, linkage of $[Mo_2^VO_8]^{6-}$ units can be achieved either by addition or by condensation. In the former case, the core structures have formulas $Mo_{2n}O_{8n}^{6n-}$, corresponding to degree of polymerization n. In the latter case, condensation yields core structure formulas $Mo_{2n}O_{8n-p}^{(6n-2p)-}$ corresponding to a degree of polymerization n and a degree of condensation Z:

$$n\mathrm{Mo}_2^{V}\mathrm{O}_8^{6-} = \mathrm{Mo}_{2n}^{V}\mathrm{O}_{8n-p}^{(6n-2p)-} + p\mathrm{O}^{2-} \qquad (1)$$

$$Z = p/n \qquad (2)$$

According to eqn. (2), the degree of condensation is the number of O^{2-} ligands eliminated upon condensation per $[Mo_2^VO_8]^{6-}$ building unit. This definition is in



Scheme 1. The C_{2v} $[Mo_2^VO_8]^{6-}$ structural building unit observed in polynuclear oxomolybdenum(V) core structures.

complete accord with the classical definition of Z^+ [11] obtained when polyoxoanions are viewed as condensates of tetrahedral oxoanions obtained upon acidification:

$$x\mathrm{Mo^VO_4^{3-}} + y\mathrm{H^+} = \mathrm{Mo_x^VO_{4x-(y/2)}^{(3x-y)-}} + (y/2)\mathrm{H_2O} \tag{3}$$

$$Z^+ = y/x \tag{4}$$

If protons are removed from eqn. (3), x is set equal to $2n$, and y is set equal to $2p$, then $Z = Z^+$ and eqns. (3) and (4) are converted into eqns. (1) and (2), respectively. For purposes of calibration, $Z = 0$ for $\mathrm{Mo_2^VO_8^{6-}}$, $Z = 1$ for $\mathrm{Mo_2^VO_7^{4-}}$, $Z = 2$ for $\mathrm{Mo_2^VO_6^{2-}}$, and $Z = 3$ for $\mathrm{Mo_2^VO_5}$. In this review, oxomolybdenum(V) complexes will be regarded as those complexes containing $\mathrm{Mo^V}$ bonded only to oxygen ligands, and related complexes containing other types of ligand will be treated as derivatives. These derivatives have been reviewed extensively elsewhere [5–10], and will be discussed here only when the parent complex is unknown.

2. ($\mathrm{Mo^V}$–$\mathrm{Mo^V}$) MONOMERS

Numerous oxomolybdenum(V) complexes and derivatives having monomeric $[\mathrm{Mo_2^VO_8}]^{6-}$ core structures are known [5–10], and the single example treated here was selected on the basis of its apparent complexity. The centrosymmetric $[\mathrm{Mg_2Mo_8O_{22}(OMe)_6(MeOH)_4}]^{2-}$ anion shown in Fig. 1(a) has been observed in the solid state as a solvated $[\mathrm{Mg(MeOH)_6}]^{2+}$ salt [12]. When $[\mathrm{Mo_2^VO_8}]^{6-}$ units (see Scheme 1) are extracted from the anion structure as shown in Fig. 1(b), the structure is seen to contain two isolated $[\mathrm{Mo_2^VO_8}]^{6-}$ units, i.e. two ($\mathrm{Mo^V}$–$\mathrm{Mo^V}$) monomers. The anion structure can be regenerated by dimethylating each $[\mathrm{Mo_2^VO_8}]^{6-}$ unit to form two $[\mathrm{Mo_2^VO_6(OMe)_2}]^{4-}$ units, interconnecting the $\mathrm{Mo^V}$ centers with two $\mathrm{O^{2-}}$ ligands, interconnecting the $\mathrm{O_c}$ oxygens (see Scheme 1) with

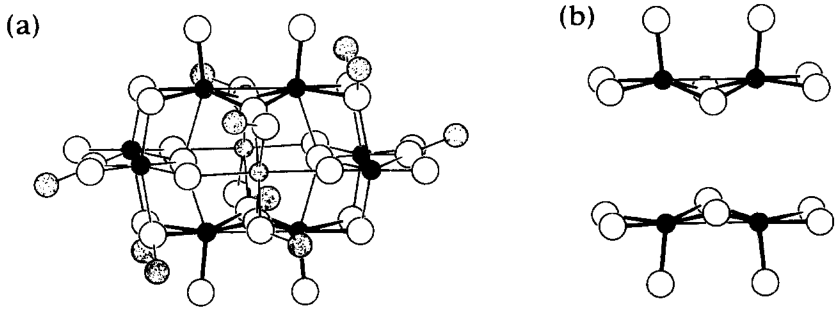


Fig. 1. The C_i $[\mathrm{Mg_2Mo_8O_{22}(OMe)_6(MeOH)_4}]^{2-}$ anion (a), and its D_{2h} oxomolybdenum(V) core structure (b) comprised of two isolated $[\mathrm{Mo_2^VO_8}]^{6-}$ building units. Molybdenum atoms are drawn as small filled circles, magnesium atoms as small shaded circles, oxygen atoms as large open circles, and carbon atoms as large shaded circles; hydrogen atoms have been omitted for purposes of clarity. Molybdenum–oxygen bonds within the $[\mathrm{Mo_2^VO_8}]^{6-}$ structural building units are drawn as thick bonds, and all the remaining bonds are drawn as thin bonds.

two $[(Mo^{VI}O_2)_2(\mu\text{-OMe})]^{3+}$ units, and interconnecting the O_b oxygens with two $[Mg(MeOH)_2]^{2+}$ units.

3. $(Mo^V-Mo^V)_2$ DIMERS

As was the case for (Mo^V-Mo^V) monomers, numerous structures are known to contain $(Mo^V-Mo^V)_2$ dimers in their oxomolybdenum(V) core structures [5–10]. These structures fall into three classes, and one member from each has been selected for discussion. The first two classes include $Mo_4^VO_{16}^{12-}$ oxomolybdenum(V) core structures that are $[Mo_2^VO_8]^{6-}$ dimers and are formally addition polymers. In the third class, two $[Mo_2^VO_8]^{6-}$ units have two oxygen atoms in common, and the $Mo_4^VO_{14}^{8-}$ oxomolybdenum(V) core structure is formally a condensation polymer.

3.1 Rhombic complexes

The squarate complex $[Mo_4O_8(OMe)_2(C_4O_4)_2(C_4O_4H)_2]^{4-}$ shown in Fig. 2(a) is known as a solvated $Bu_4^nN^+$ salt [13]. This complex contains two $(Mo^V-Mo^V)^{10+}$ units, eight O^{2-} oxide ligands, two CH_3O^- bridging ligands, two bridging $C_4O_4^{2-}$ squarate ligands, and two terminal $C_4O_4H^-$ hydrogensquarate ligands. Extraction of $[Mo_2^VO_8]^{6-}$ building units yields the $Mo_4^VO_{16}^{12-}$ oxomolybdenum(V) core structure shown in Fig. 2(b), in which the Mo^V centers occupy the vertices of a distorted rhomb (rhomboid). Note the compactness of this core structure: the oxygen atoms form a cubic closest-packed array and the molybdenum centers occupy octahedral holes within that array.

3.2 Tetrahedral complexes

Several phosphomolybdate lattice compounds contain the $[Mo_4O_8(PO_4)_4]^{8-}$ fragment shown in Fig. 3(a) where some or all of the PO_4^{3-} groups serve as bridging

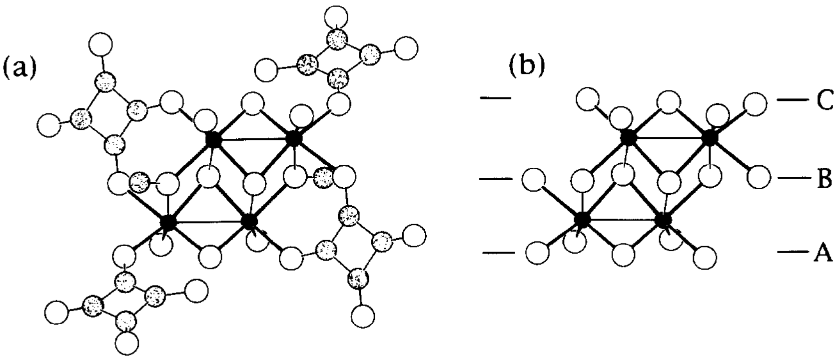


Fig. 2. The C_i $[Mo_4O_8(OMe)_2(C_4O_4)_2(C_4O_4H)_2]^{4-}$ anion (a) and its C_i $Mo_4^VO_{16}^{12-}$ oxomolybdenum core structure (b). Atoms and bonds are drawn as explained in the Fig. 1 caption.

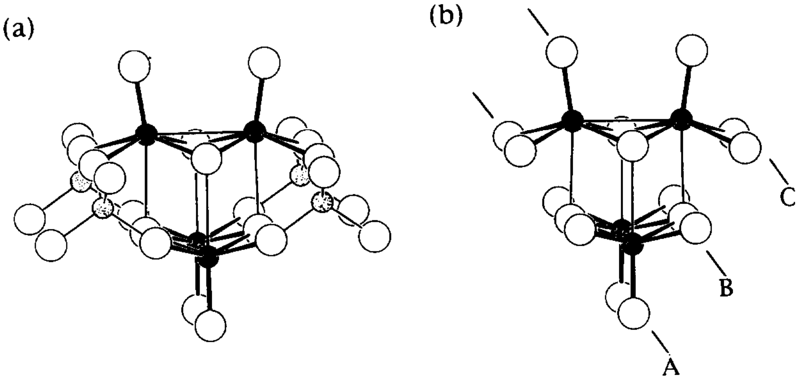


Fig. 3. The D_{2d} $[\mathrm{Mo_4O_8(PO_4)_4}]^{8-}$ anion (a) in $\mathrm{(Pr_4N)(NH_4)[Mo_4O_8(PO_4)_{4/2}]}$ and its D_{2d} $\mathrm{Mo_4^VO_{16}^{12-}}$ oxomolybdenum(V) core structure (b). Molybdenum atoms are drawn as small filled circles, phosphorus atoms as small shaded circles, and oxygen atoms as large open circles. Molybdenum–oxygen bonds within the $[\mathrm{Mo_2^VO_8}]^{6-}$ structural building units are drawn as thick bonds, and all the remaining bonds as thin bonds.

ligands between $\mathrm{Mo_4^VO_8^{4+}}$ units. The compounds include $\mathrm{(Et_4N)_2[Mo_4O_8(PO_4)_{2/2}(H_{1.5}PO_4)_2]\cdot 2H_2O}$ [9], containing one-dimensional polymers; $\mathrm{(Et_2NH_2)_2[Mo_4O_8(PO_4)_{4/2}]}$ [14], (4-phenylpyridinium)$_2$$\mathrm{[Mo_4O_8(PO_4)_{4/2}]}$ [14], and $\mathrm{(Pr_4N)(NH_4)[Mo_4O_8(PO_4)_{4/2}]}$ [15], containing two-dimensional sheets; and $\mathrm{(Me_4N)_{1.3}(H_3O)_{0.7}[Mo_4O_8(PO_4)_{4/2}]\cdot 2H_2O}$ [16], containing a three-dimensional phosphomolybdate framework. A closely-related molecular "cubane" structure where four bidentate $\mathrm{(CH_3)_2POS^-}$ ligands are all bonded to the same $\mathrm{Mo_4O_8}$ core is found in the oxomolybdenum(V) derivative $\mathrm{[Mo_4O_8(Me_2POS)_4]}$ [17].

When $[\mathrm{Mo_2^VO_8}]^{6-}$ units are extracted from the $[\mathrm{Mo_4O_8(PO_4)_4}]^{8-}$ structure, the $\mathrm{Mo_4^VO_{16}^{12-}}$ oxomolybdenum(V) core structure shown in Fig. 3(b) is obtained. Here, the $\mathrm{Mo^V}$ centers lie at the vertices of a distorted tetrahedron (disphenoid). This tetrahedral complex is isomeric with the $\mathrm{Mo_4^VO_{16}^{12-}}$ complex shown in Fig. 2(b), and is also a very compact structure comprised of cubic closest-packed oxygen atoms with $\mathrm{Mo^V}$ centers occupying octahedral holes.

3.3 Linear complex

The $\mathrm{Mo_6O_{10}(OPr^i)_{12}}$ structure [18] and its oxomolybdenum(V) core structure are shown in Fig. 4(a) and (b), respectively. The $\mathrm{Mo_4^VO_{14}^{8-}}$ core structure is comprised of two $[\mathrm{Mo_2^VO_8}]^{6-}$ building units fused together at two $\mathrm{O_c}$ sites. Since they have two oxygens in common, the degree of condensation is 1 according to eqns. (1) and (2). Comparison of Fig. 4(b) with Fig. 4(a) shows that all six of the $\mathrm{O_c}$ oxygens in the $\mathrm{Mo_4^VO_{14}^{8-}}$ core structure are alkoxide oxygens; the $\mathrm{O_c}$ oxygens at each end of the structure are, in addition, coordinated to an $\mathrm{Mo^{VI}O(OPr^i)_3}$ group.

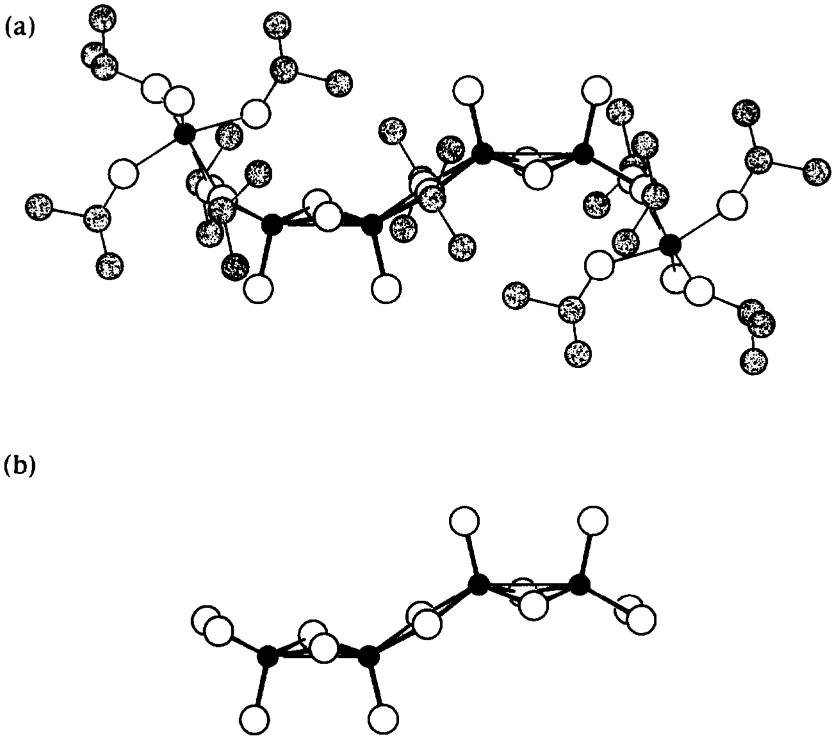


Fig. 4. The C_i $Mo_6O_{10}(OPr^i)_{12}$ structure (a) and its C_{2h} $Mo_4^VO_{14}^{8-}$ oxomolybdenum(V) core structure (b). Atoms and bonds are drawn as explained in the Fig. 1 caption.

4. $(Mo^V–Mo^V)_3$ TRIMERS

The $[Mo_6O_{15}(PO_4)_4]^{12-}$ complex illustrated in Fig. 5(a) is observed in several salts as a protonated polyanion: $(PPh_4)_2(H_3O)_2Na[Mo_6O_{15}(HPO_4)(H_2PO_4)_3] \cdot 5H_2O$ [4], $(H_3PO_4)Na_8In_4(H_2O)_4[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]_4$ [9], $(H_3PO_4)Na_{14}(Et_4N)_6[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]_4 \cdot xH_2O$ [19], and (4-phenylpiperidinium)$_4$Na$_{2.5}$$[Mo_6O_{15}(H_{1.4}PO_4)_4] \cdot 4H_2O$ [14]. Its $Mo_6O_{21}^{12-}$ oxomolybdenum(V) core structure, shown in Fig. 5(b), has a degree of condensation equal to 1, since each of the three $[Mo_2^VO_8]^{6-}$ subunits shares two O_c oxygens with neighboring $[Mo_2^VO_8]^{6-}$ subunits.

5. $(Mo^V–Mo^V)_4$ TETRAMERS

Two types of $(Mo^V–Mo^V)_4$ tetramer are known, and both are cyclic. The first is a homologue of the cyclic trimers just discussed in that its degree of condensation is also 1. The second is more highly condensed ($Z = 2$) in that each $[Mo_2^VO_8]^{6-}$

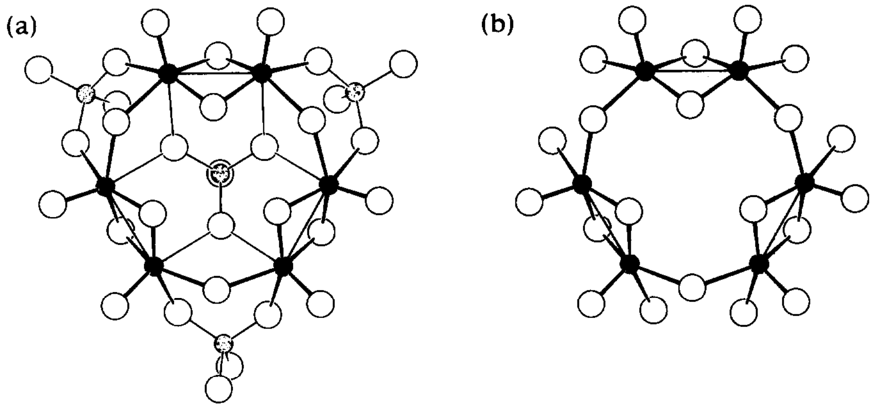


Fig. 5. The approximately C_{3v} symmetric $[Mo_6O_{15}(PO_4)_4]^{12-}$ anion (a) in $(PPh_4)_2(H_3O)_2Na[Mo_6O_{15}(HPO_4)(H_2PO_4)_3] \cdot 5H_2O$ and its C_{3v} $Mo_6O_{21}^{12-}$ oxomolybdenum(V) core structure (b). Atoms and bonds are drawn as explained in the Fig. 3 caption.

building unit shares all four of its O_c oxygens (see Scheme 1) with its neighbors in the ring structure.

5.1 Puckered cyclic complex

The $Mo_8O_{16}(OMe)_8(PMe_3)_4$ molecule shown in Fig. 6(a) contains oxide, methoxide and trimethylphosphine ligands coordinated to Mo^V—Mo^V units, and is thus an oxomolybdenum(V) derivative [20]. A hypothetical oxomolybdenum(V) parent core structure can be obtained, however, by replacing the $P(CH_3)_3$ ligand with an

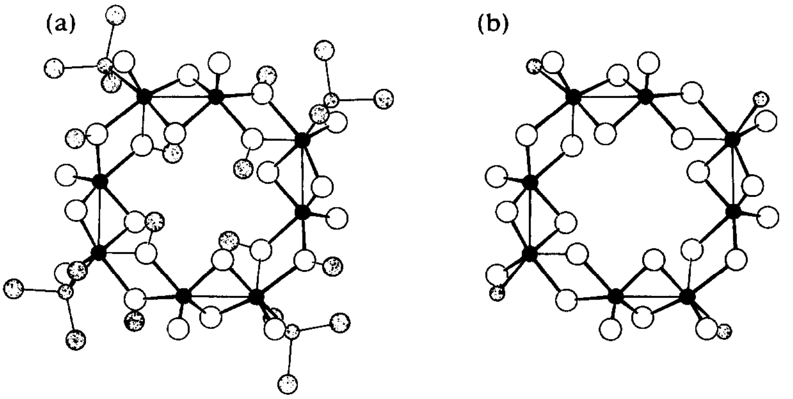


Fig. 6. The S_4 $Mo_8O_{16}(OMe)_8(PMe_3)_4$ molecule (a) and its oxomolybdenum(V) derivative core structure (b). Molybdenum atoms are drawn as small filled circles, phosphorus atoms as small shaded circles, carbon atoms as large shaded circles, and oxygen atoms as large open circles; hydrogen atoms are omitted for purposes of clarity. Molybdenum—ligand bonds within the phosphorus-substituted $[Mo_2^VO_8]^{6-}$ structural building units are drawn as thick bonds, and all the remaining bonds as thin bonds.

oxygen ligand and extracting the four $[Mo_2^VO_8]^{6-}$ structural building units present to obtain the $Mo_8^VO_{28}^{16-}$ structure shown in Fig. 6(b).

5.2 *Planar cyclic complex*

The $[Mo_8O_{16}(OMe)_8(C_2O_4)]^{2-}$ anion (see Fig. 7(a)) is known as an $Bu_4^nN^+$ salt [21]. Its $Mo_8^VO_{24}^{8-}$ oxomolybdenum(V) core structure is shown in Fig. 7(b). Here, all O_a and O_b oxygens are oxide oxygens and all O_c oxygens are alkoxide oxygens.

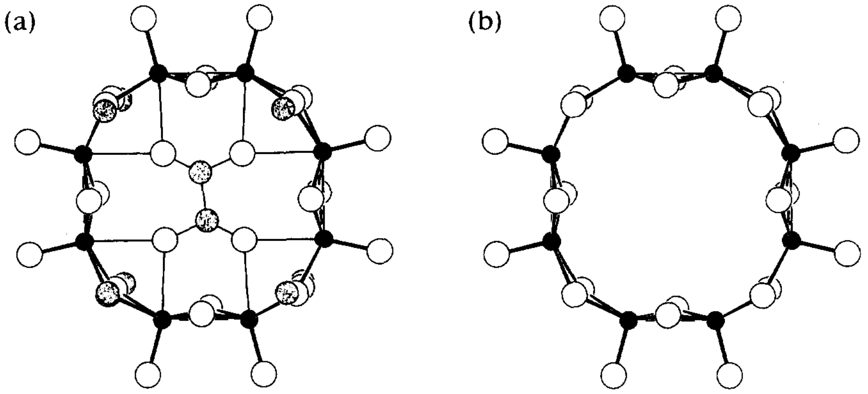


Fig. 7. The D_{4h} $[Mo_8O_{16}(OMe)_8(C_2O_4)]^{2-}$ anion (a) and its D_{4h} $Mo_8^VO_{24}^{8-}$ oxomolybdenum(V) core structure (b). Atoms and bonds are drawn as explained in the Fig. 1 caption.

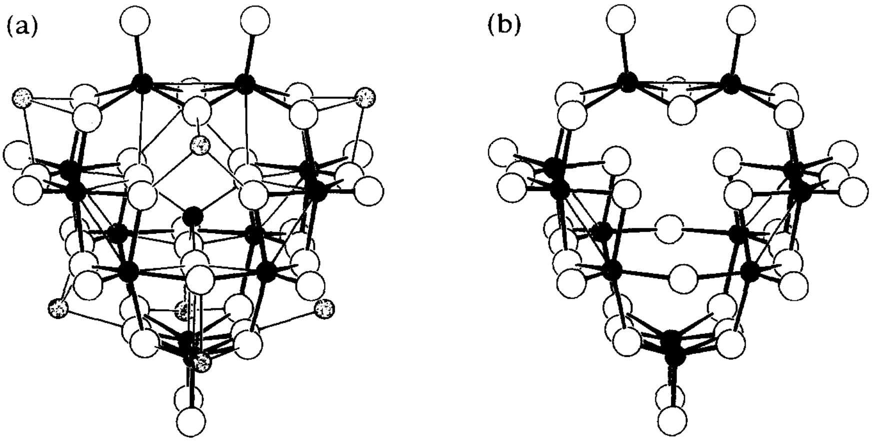


Fig. 8. The T_d $Rh_8Mo_{13}O_{40}^{10+}$ fragment of the $[(C_5Me_5Rh)_8(Mo_{13}O_{40})]^{2+}$ cation structure and its T_d $Mo_{12}^VO_{36}^{12-}$ oxomolybdenum(V) core structure (b). Molybdenum atoms are drawn as small filled circles, rhodium atoms as small shaded circles, and oxygen atoms as large open circles. Molybdenum–oxygen bonds within the $[Mo_2^VO_8]^{6-}$ structural building units are drawn as thick bonds, and all the remaining bonds as thin bonds.

6. $(Mo^V{-}Mo^V)_6$ HEXAMERS

The $[(C_5Me_5Rh)_8(Mo_{13}O_{40})]^{2+}$ cation has been prepared as a hydrated, hydroxide/chloride salt [2]. As shown in Fig. 8(a), a tetrahedral $Mo^{VI}O_4^{2-}$ anion lies at the center of the structure, and this anion is surrounded by an $Mo^V_{12}O_{36}^{12-}$ cage (Fig. 8(b)), which in turn is bonded to the rhodium centers of eight $C_5Me_5Rh^{III\,2+}$ groups. The $Mo^V_{12}O_{36}^{12-}$ cage is, in fact, an oxomolybdenum(V) core structure comprised entirely of $[Mo^V_2O_8]^{6-}$ units of the type shown in Scheme 1. Each of the $[Mo^V_2O_8]^{6-}$ units shares each of its four O_c oxygens with a neighboring unit; the degree of polymerization is six and the degree of condensation is two.

For future reference, it is useful to re-examine the $[(C_5Me_5Rh)_8(Mo_{13}O_{40})]^{2+}$ cation and its $Mo^V_{12}O_{36}^{12-}$ core from the alternative viewpoint shown in Fig. 9(a) and (b). Here, the molybdenum oxide framework is seen to be a cubic closest-packed array of oxygens with Mo^V centers occupying octahedral holes. Moreover, the

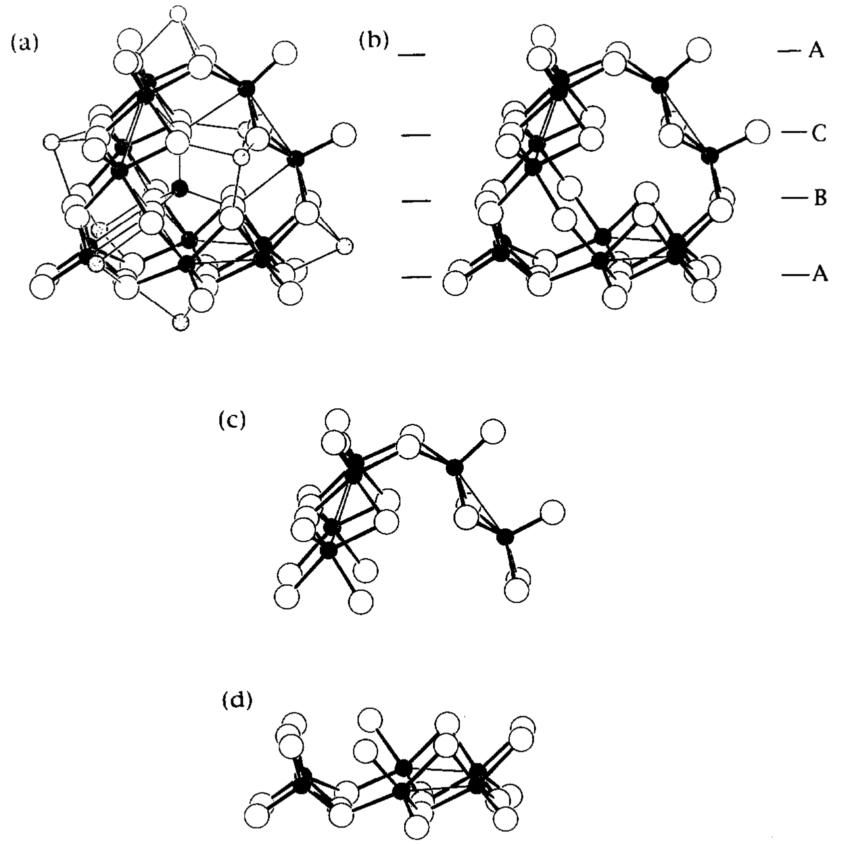


Fig. 9. Alternative views of Fig. 8(a) and (b) are shown in (a) and (b), respectively; two isomeric $Mo^V_6O_{21}^{12-}$ subunits of the $Mo^V_{12}O_{36}^{12-}$ oxomolybdenum(V) core structure are shown in (c) and (d).

$Mo^{V}_{12}O^{12-}_{36}$ core structure is seen to result from fusion of the two isomeric $Mo^{V}_{6}O^{12-}_{21}$ units shown in Fig. 9(c) and (d). The cyclic structure in Fig. 9(d) is identical to the structure shown in Fig. 5(b).

7. $(Mo^{V}–Mo^{V})_{18}$ OCTADECAMERS

The mixed-valence compound $(Me_3NH)_2(Et_4N)Na_4[Na(H_2O)_3H_{15}Mo_{42}O_{109}\{(OCH_2)_3CCH_2OH\}_7]\cdot15H_2O$ [3] contains the $[Mo^{V}_{36}Mo^{VI}_{6}O_{109}\{(OCH_2)_3CCH_2OH\}_7]^{23-}$ polyoxoalkoxide shown in Fig. 10. The $Mo^{V}_{36}O^{30-}_{105}$ oxomolybdenum(V) core structure (see Fig. 11(a)) has the most highly condensed oxomolybdenum(V) framework observed to date ($Z = 2.17$). As illustrated in Fig. 11(b) and (c), the core structure can be simplified considerably by breaking it down into a $Mo^{V}_{12}O^{12-}_{36}$ cage subunit and a $Mo^{V}_{24}O^{42-}_{81}$ ring subunit which have 12

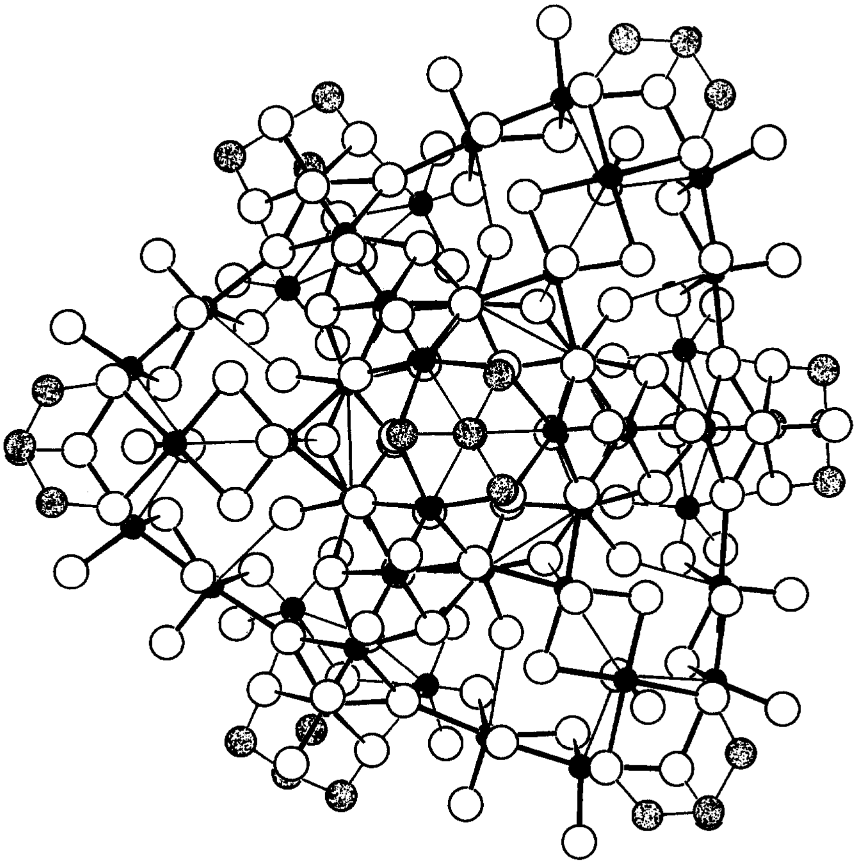


Fig. 10. The C_{3v} $[Mo^{V}_{36}Mo^{VI}_{6}O_{109}\{(OCH_2)_3CCH_2OH\}_7]^{23-}$ structure, with atoms and bonds drawn as explained in the Fig. 1 caption. All of the CH_2OH moieties have been deleted from $(CH_2)_3CCH_2OH$ groups for purposes of clarity.

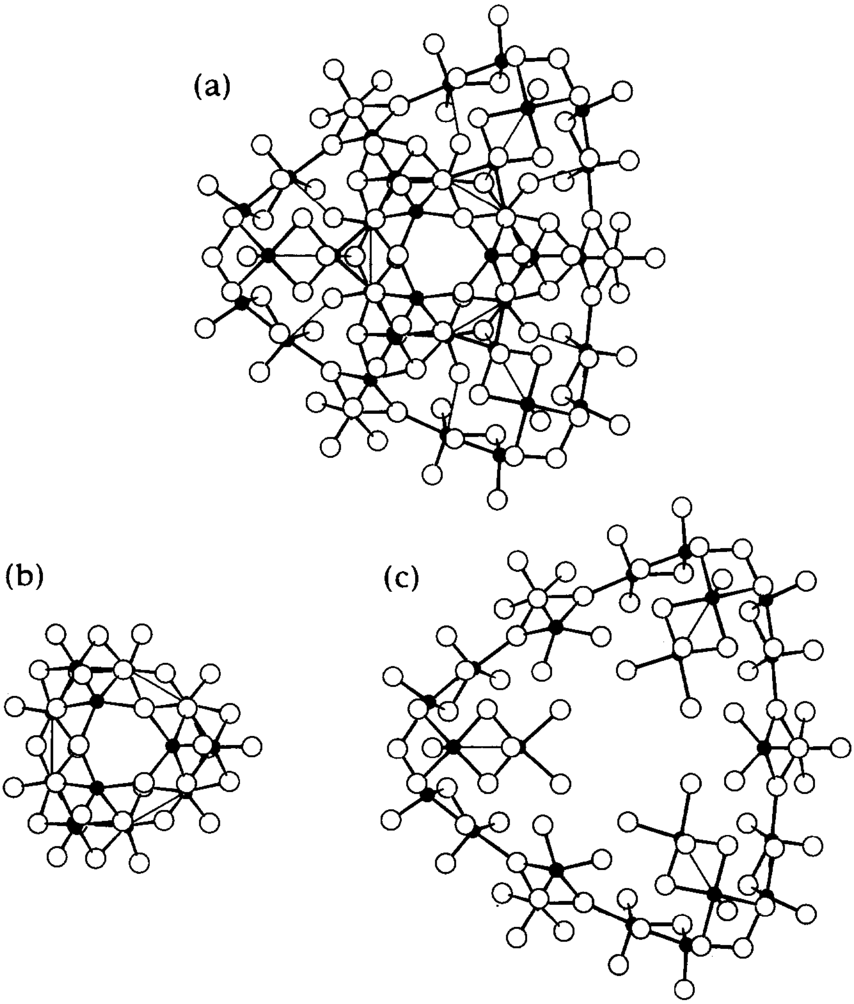


Fig. 11. The C_{3v} $\mathrm{Mo}^{\mathrm{V}}_{36}\mathrm{O}^{30-}_{105}$ oxomolybdenum(V) core structure of the $[\mathrm{Mo}^{\mathrm{V}}_{36}\mathrm{Mo}^{\mathrm{VI}}_{6}\mathrm{O}_{109}\{(\mathrm{OCH}_2)_3\text{-}\mathrm{CCH}_2\mathrm{OH}\}_7]^{23-}$ ion is shown in (a); its $\mathrm{Mo}^{\mathrm{V}}_{12}\mathrm{O}^{12-}_{36}$ and $\mathrm{Mo}_{24}\mathrm{O}^{42-}_{81}$ subunits are shown in (b) and (c), respectively. Atoms and bonds are drawn as explained in the Fig. 1 caption. The same viewing perspective is adopted for Figs. 10 and 11.

oxygen atoms in common. The $\mathrm{Mo}^{\mathrm{V}}_{12}\mathrm{O}^{12-}_{36}$ cage in Fig. 11(b) is the same species observed as the oxomolybdenum(V) core structure of $[(\mathrm{C}_5\mathrm{Me}_5\mathrm{Rh})_8(\mathrm{Mo}_{13}\mathrm{O}_{40})]^{2+}$ (see Fig. 9(b)): Fig. 11(b) shows a "top" view and Fig. 9(b) shows a "side" view. The $\mathrm{Mo}^{\mathrm{V}}_{24}\mathrm{O}^{42-}_{81}$ ring in Fig. 11(c) is seen to be comprised of three $\mathrm{Mo}^{\mathrm{V}}_{2}\mathrm{O}^{6-}_{8}$ subunits (Scheme 1) and three $\mathrm{Mo}^{\mathrm{V}}_{6}\mathrm{O}^{12-}_{21}$ subunits (Fig. 9(c)) which share a total of six oxygen atoms. The nature of the $\mathrm{Mo}^{\mathrm{V}}_{2}\mathrm{O}^{6-}_{8}/\mathrm{Mo}^{\mathrm{V}}_{6}\mathrm{O}^{12-}_{21}$ linkage is evident in Fig. 11(c): each $\mathrm{Mo}_2\mathrm{O}^{6-}_{8}$ subunit shares each of its two O_b atoms (see Scheme 1) with a neighboring $\mathrm{Mo}^{\mathrm{V}}_{6}\mathrm{O}^{12-}_{21}$ subunit where the same oxygen serves as an O_c oxygen. The linkages between the central $\mathrm{Mo}_{12}^{V}\mathrm{O}_{36}^{12-}$ subunit and the peripheral $\mathrm{Mo}_{6}^{V}\mathrm{O}_{21}^{12-}$ and $\mathrm{Mo}_{2}^{V}\mathrm{O}_{8}^{6-}$ subunits is difficult to see in the "top" view shown in Fig. 11(a), but can be clearly seen in Fig. 12 where the same "side" view adopted for Fig. 9(b) is employed. In Fig. 12, two $\mathrm{O_c}$ oxygens (see Scheme 1) in each $\mathrm{Mo}_{6}^{V}\mathrm{O}_{21}^{12-}$ subunit are seen to be shared with the central $\mathrm{Mo}_{12}^{V}\mathrm{O}_{36}^{12-}$ subunit where they serve as $\mathrm{O_b}$ oxygens; two $\mathrm{Mo}_{2}^{V}\mathrm{O}_{8}^{6-}$ $\mathrm{O_c}$ oxygens also serve as $\mathrm{Mo}_{12}^{V}\mathrm{O}_{36}^{12-}$ $\mathrm{O_c}$ oxygens. Two $\mathrm{O_a}$ oxygens plus an $\mathrm{O_b}$ oxygen in the $\mathrm{Mo}_{12}^{V}\mathrm{O}_{36}^{12-}$ subunit also form weak bonds to three molybdenum centers in each $\mathrm{Mo}_{6}^{V}\mathrm{O}_{21}^{12-}$ subunit, occupying coordination sites trans to $\mathrm{O_a}$ oxygens (see Scheme 1). One $\mathrm{Mo}_{12}^{V}\mathrm{O}_{36}^{12-}$ $\mathrm{O_c}$ oxygen is similarly bonded to one molybdenum center in each $\mathrm{Mo}_{2}^{V}\mathrm{O}_{8}^{6-}$ subunit, trans to an $\mathrm{O_a}$ oxygen. Comparison of Fig. 12 with Fig. 9(a) is instructive in that tridentate binding of the central $\mathrm{Mo}_{12}^{V}\mathrm{O}_{36}^{12-}$ cage to peripheral $\mathrm{Mo^V}$ centers (Fig. 12) and $\mathrm{Rh^{III}}$ centers (Fig. 9(a)) is seen to occur in the same two ways, using either a triangle of $\mathrm{O_b}$ oxygen atoms or a triangle of $\mathrm{O_c}$ oxygen atoms.

The $\mathrm{Mo}_{36}^{V}\mathrm{O}_{105}^{30-}$ oxomolybdenum(V) core structure has a seemingly irregular geometry when described as a central $\mathrm{Mo}_{12}^{V}\mathrm{O}_{36}^{12-}$ core joined to three $\mathrm{Mo}_{2}^{V}\mathrm{O}_{8}^{6-}$ and three $\mathrm{Mo}_{6}^{V}\mathrm{O}_{21}^{12-}$ subunits. A far more regular pattern becomes evident, however, upon examination of the oxygen atom packing geometry. As mentioned above in Sect. 6, the 36 oxygen atoms in the $\mathrm{Mo}_{12}^{V}\mathrm{O}_{36}^{12-}$ unit are cubic closest-packed, and

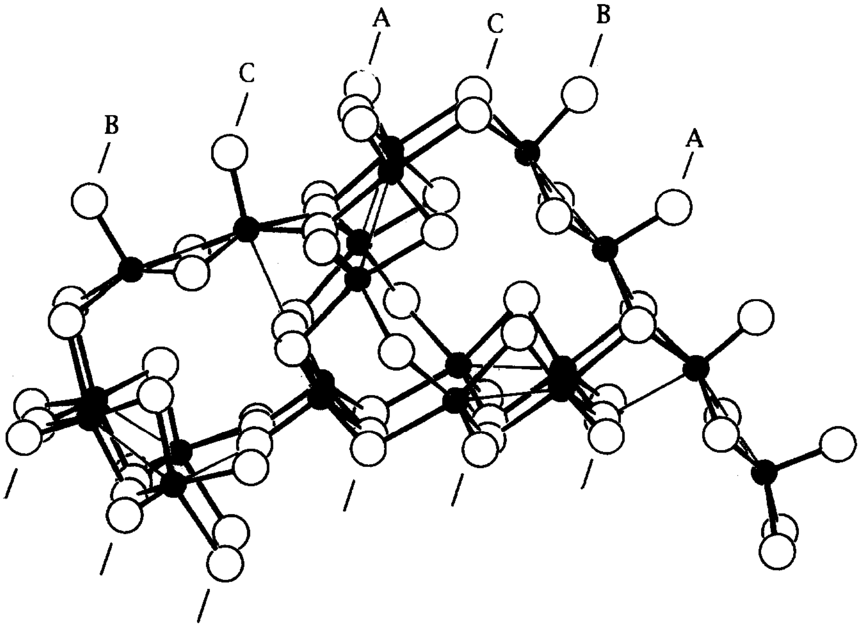


Fig. 12. Substructure of the $\mathrm{Mo}_{36}^{V}\mathrm{O}_{105}^{30-}$ structure showing the linkages between the central $\mathrm{Mo}_{12}^{V}\mathrm{O}_{36}^{12-}$ subunit and the $\mathrm{Mo}_{2}^{V}\mathrm{O}_{8}^{6-}$ and $\mathrm{Mo}_{6}^{V}\mathrm{O}_{21}^{12-}$ subunits. Atoms and bonds are drawn as explained in the Fig. 1 caption.

this packing is shown in Fig. 13(a) in the same orientation employed in Fig. 11(b), i.e. perpendicular to a set of closest-packed planes. When the three $\mathrm{Mo}^{\mathrm{V}}_{2}\mathrm{O}_{8}^{6-}$ subunits are joined to the $\mathrm{Mo}^{\mathrm{V}}_{12}\mathrm{O}_{36}^{12-}$ unit, each of the three groups of six oxygen atoms added extends the closest-packing as shown in Fig. 13(b), such that all 54 oxygen atoms in the $\mathrm{Mo}^{\mathrm{V}}_{18}\mathrm{O}_{54}^{18-}$ subunit shown form cubic closest-packed array. When the $\mathrm{Mo}^{\mathrm{V}}_{36}\mathrm{O}_{105}^{30-}$ core structure is completed by joining three $\mathrm{Mo}^{\mathrm{V}}_{6}\mathrm{O}_{21}^{12-}$ subunits, each of the three groups of 17 oxygen atoms added further extends the closest-packing of the 54 oxygen atoms shown in Fig. 13(b). The resulting array of 105 oxygen atoms shown in Fig. 13(c) is *not* cubic closest-packed, however. Instead, each set of 17 oxygen atoms adds two layers of oxygen atoms to the ABCA cubic closest-packed layer sequence of the 54 oxygen atom array to generate an ABCACB mixture of cubic and hexagonal closest-packing. This type of hybrid cubic/hexagonal closest-packing of oxygen atoms is not unusual in polyoxoanion chemistry and is observed, for example, in the Keggin structure, albeit on a smaller scale [22].

We finally turn to the problem of generating the $[\mathrm{Mo}^{\mathrm{V}}_{36}\mathrm{Mo}^{\mathrm{VI}}_{6}\mathrm{O}_{109}\text{-}\{(\mathrm{OCH_2})_3\mathrm{CCH_2OH}\}_7]^{23-}$ structure from its $\mathrm{Mo}^{\mathrm{V}}_{36}\mathrm{O}_{105}^{30-}$ oxomolybdenum(V) core structure though addition of six $\mathrm{Mo}^{\mathrm{VI}}$ centers, 25 O^{2-} ligands, and seven $[(\mathrm{CH_2})_3\mathrm{CCH_2OH}]^{3+}$ moieties. This is achieved as shown in Fig. 14. First a

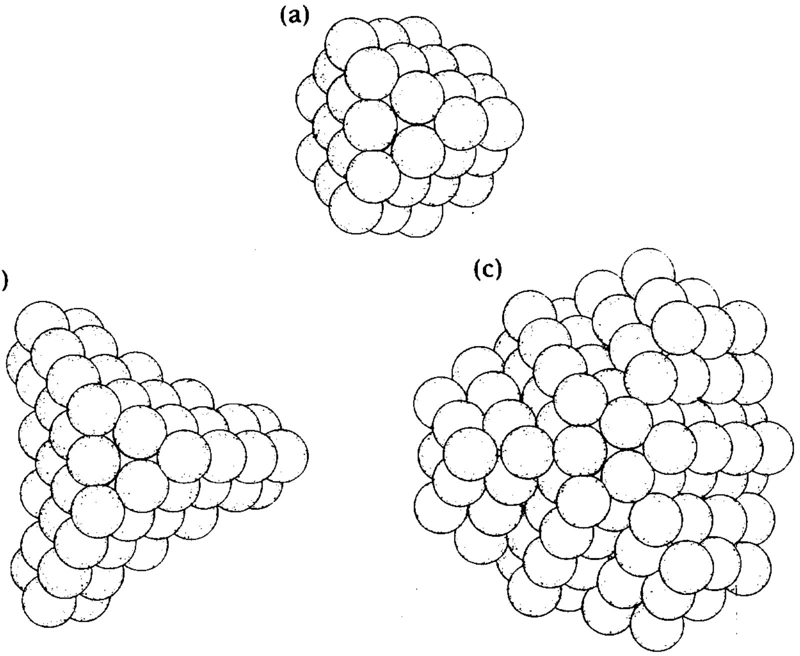


Fig. 13. Spacefilling representations of the $\mathrm{Mo}^{\mathrm{V}}_{12}\mathrm{O}_{36}^{12-}$ (a) and $\mathrm{Mo}^{\mathrm{V}}_{18}\mathrm{O}_{54}^{18-}$ (b) subunits of the $\mathrm{Mo}^{\mathrm{V}}_{36}\mathrm{O}_{105}^{30-}$ oxomolybdenum(V) core structure (c). The viewing perspective adopted is the same as that employed in Figs. 10 and 11.

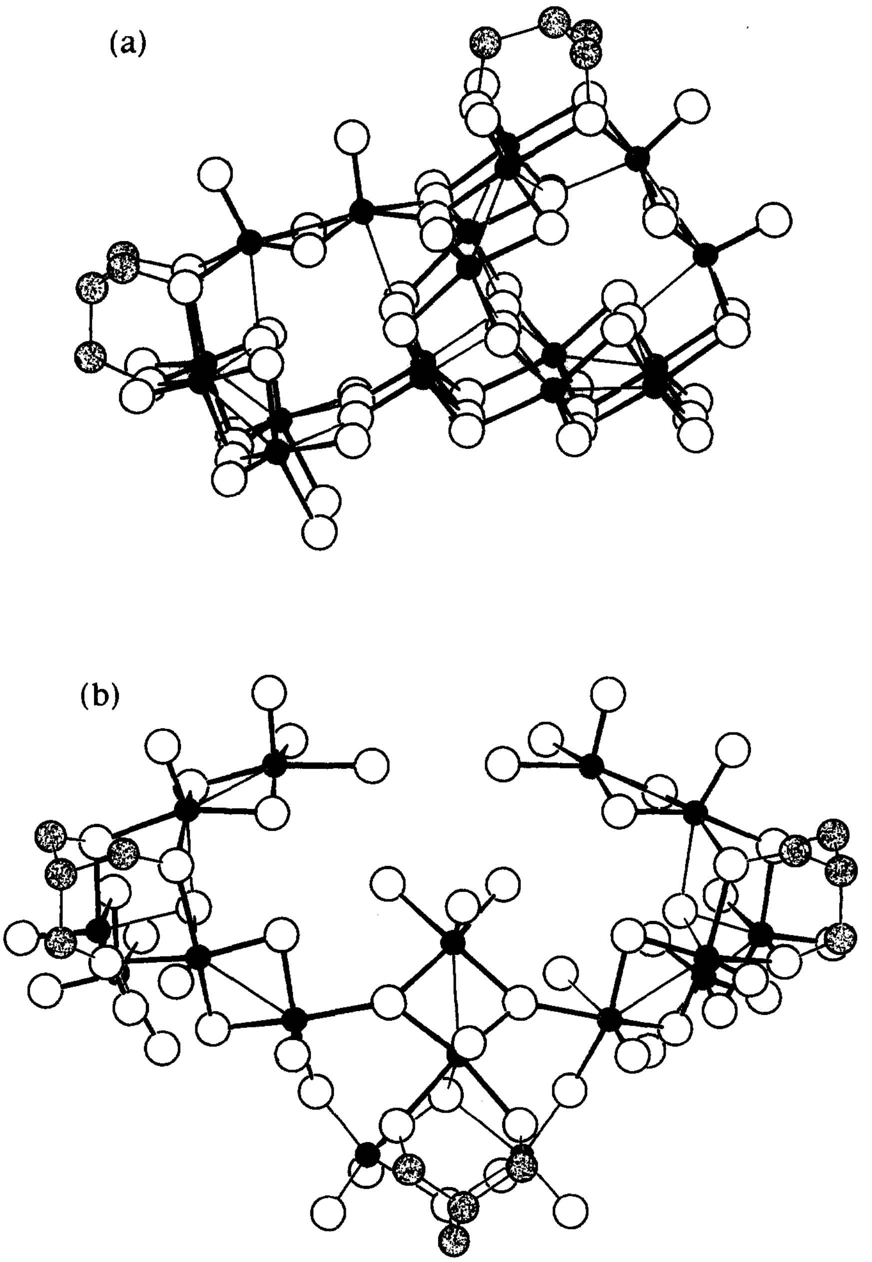


Fig. 14. Fragments of the $[\mathrm{Mo}^{\mathrm{V}}_{36}\mathrm{Mo}^{\mathrm{VI}}_{6}\mathrm{O}_{109}\{(\mathrm{OCH}_2)_3\mathrm{CCH}_2\mathrm{OH}\}_7]^{23-}$ structure discussed in the text. Atoms and bonds are drawn as explained in the Fig. 1 caption. All of the $\mathrm{CH}_2\mathrm{OH}$ moieties have been deleted from $(\mathrm{CH}_2)_3\mathrm{CCH}_2\mathrm{OH}$ groups for purposes of clarity.

$[(CH_2)_2CCH_2OH]^{3+}$ group is added to the "top" of the $Mo^V_{12}O_{36}^{12-}$ cage, and four O^{2-} ligands are placed in its central cavity (Fig. 14(a)). These four atoms occupy the same positions occupied by the four $Mo^{VI}O_4^{2-}$ oxygens in the $[(C_5Me_5Rh)_8(Mo_{13}O_{40})]^{2+}$ cation (Fig. 9(a)). Next, each of the three $Mo^V_6O_{21}^{12-}$ subunits is modified by adding a central O^{2-} ligand plus a $[(CH_2)_3CCH_2OH]^{3+}$ group as shown in Fig. 14(a). Finally, an $Mo^{VI}_2O_6$ group plus a $[(CH_2)_3CCH_2OH]^{3+}$ group is added "below" each $Mo^V_2O_8^{6-}$ subunit as shown in Fig. 14(b). Note that each $Mo^{VI}_2O_6$ group is actually bonded an $Mo^V_2O_8^{6-}$ subunit and its two neighboring $Mo^V_6O_{21}^{12-}$ subunits.

8. CONCLUSIONS

The family of nine polynuclear oxomolybdenum(V) core structures reviewed above resembles related families of structures such as oxomolybdenum(VI) and oxovanadium(V) structures in that structural building units can be readily identified [8,10]. The family of oxomolybdenum(V) compounds containing Mo^V—Mo^V units is unique, however, in that only finite oxomolybdenum(V) core structures are observed, whereas infinite chains, sheets, and lattice frameworks are routinely observed in oxovanadium(V) and oxomolybdenum(VI) chemistry [8,10]. Even the parent compound $Mo^V_2O_5$ is unknown! One can, of course, easily rationalize this state of affairs by pointing to the large family of mixed-valence Mo(V/VI) lattice compounds, the molybdenum bronzes and oxides [23], and assuming that compounds with delocalized d-electrons are energetically favored in extended systems relative to compounds whose d-electrons are localized in Mo^V—Mo^V bonds. Nonetheless, the preparation of extended oxomolybdenum(V) structures based on the $[Mo^V_2O_8]^{6-}$ structural building unit of Scheme 1 appears to be feasible and stands as a challenge to the synthetic chemist.

ACKNOWLEDGEMENT

We are grateful to the National Science Foundation for support of this research.

REFERENCES

1 M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer-Verlag, Heidelberg, 1983.
2 H.K. Chae, W.G. Klemperer, D.E. Páez Loyo, V.W. Day and T.A. Eberspacher, Inorg. Chem., 31 (1992) 3187.
3 M.I. Khan and J. Zubieta, J. Am. Chem. Soc., 114 (1992) 10058.
4 R.C. Haushalter and F.W. Lai, Inorg. Chem., 28 (1989) 2904.
5 B. Spivak and Z. Dori, Coord. Chem. Rev., 17 (1975) 99.
6 E.I. Stiefel, Prog. Inorg. Chem., 22 (2977) 1.
7 A.G. Sykes, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, Vol. 3, Pergamon Press, Oxford, 1987, p. 1229.

8 M.T. Pope, Prog. Inorg. Chem, 39 (1991) 181.
9 R.C. Haushalter and L.A. Mundi, Chem. Mater., 4 (1992) 31.
10 Q. Chen and J. Zubieta, Coord. Chem. Rev., 114 (1992) 107.
11 K.-H. Tytko and O. Glemser, Adv. Inorg. Chem. Radiochem., 19 (1976) 239.
12 M. Yu. Antipin, L.P. Didenko, L.M. Kachapina, A.E. Shilov, A.K. Shilova and Y.T. Struchkov, J. Chem. Soc. Chem. Commun., (1989) 1467.
13 Q. Chen, S. Liu and J. Zubieta, Inorg. Chim. Acta, 164 (1989) 115.
14 R.C. Haushalter and L.A. Mundi, Mater. Res. Soc. Symp. Proc., 233 (1991) 255.
15 E.W. Corcoran, Jr., Inorg. Chem., 29 (1990) 157.
16 R.C. Haushalter, K.G. Strohmaier and F.W. Lai, Science, 246 (1989) 1289.
17 R. Mattes and K. Mühlsiepen, Z. Natursforsch. Teil B, 35 (1980) 265.
18 M.H. Chisholm, K. Folting, J.C. Huffman and C.C. Kirkpatrick, Inorg. Chem., 23 (1984) 1021.
19 R.C. Haushalter and F.W. Lai, Angew. Chem. Int. Ed. Engl., 28 (1989) 743.
20 D.J. Darensbourg, R.L. Gray and T. Delord, Inorg. Chim. Acta, 98 (1985) L39.
21 Q. Chen, S. Liu and J. Zubieta, Angew. Chem. Int. Ed. Engl., 27 (1988) 1724.
22 J.W. Linnett, J. Chem. Soc., (1961) 3796.
23 H. Vincent and M. Marezio, in C. Schlenker (Ed.), Low-Dimensional Electronic Properties of Molybdenum Bronzes and Oxides, Kluwer, Dordrecht, 1989, p. 49.