ligand competition effects must be considered.

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Interconversion of Polyoxometallates

Sir:

The interface between the chemistry of solid-state lattices and discrete cluster molecules is becoming less sharply defined as parallels emerge[1] between the principles which determine the structural features of the two classes. The advantages of viewing cluster molecules as fragments of close-packed arrays, rather than as assemblies of atoms joined by directed bonds, is one interesting aspect.[1b,c] One of the "oldest" classes of metal clusters is the polyoxometallates, and interest in their chemistry is sustained by their complex (and incompletely understood) structural and reactivity patterns.[2] Interconversion of these large anions in solution is an intriguing feature of their chemistry,[3] and a mechanism for the isomerization of α- and β-$[Mo_8O_{26}]^{4-}$ via a series of intermediates has been presented[4] recently. The two isomers can be viewed as distorted arrays of cubic close-packed oxygen atoms with molybdenum atoms occupying interstitial sites.

This paper considers an alternative isomerization mechanism based upon concerted translations of close-packed fragments along molecular mirror planes. The process is reminiscent of the crystallographic shear concept which accounts for the structural features of certain molybdenum, and other early transition-metal, oxide phases.[5] This alternative mechanism (i) is consistent with current literature data and our ^{95}Mo NMR studies on the α and β forms and (ii) suggests that similar interconversions are possible in the paramolybdate $[Mo_7O_{24}]^{6-}$ and other systems. Although such processes have not been unequivocally detected for these systems as yet, we start by considering $[Mo_7O_{24}]^{6-}$ as the argument is developed most simply from that molecule.

In principle, paramolybdate could have either of the molecular structures of Figure 1. The observed[6] solid-state structure (designated P; C_{2v} point symmetry) is idealized in Figure 1b with use of the condensed polyhedron convention.[7] Figure 1a illustrates an alternative structure (designated A; D_{3d}) actually observed[8] for $[Cr^{III}Mo_6O_{24}]^{9-}$.

Interconversion of A and P can be achieved by concerted translation of an eight-oxygen, two-molybdenum fragment (O_8, Mo_2; idealized in Figure 2a as a pair of edge-shared, incomplete octahedra) along a mirror plane common to A and P. This translation is conveniently monitored by following[9] the
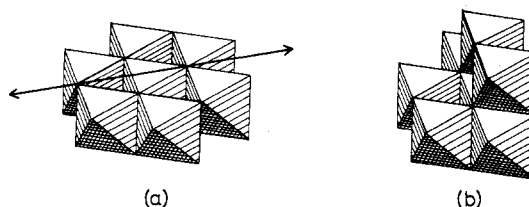

Figure 1. Idealized molecular structures of (a) $[CrMo_6O_{24}]^{9-}$ (structure A) and (b) $[Mo_7O_{24}]^{6-}$ (structure P) represented as condensed MO_6 octahedra. The common mirror plane is highlighted by the arrow.
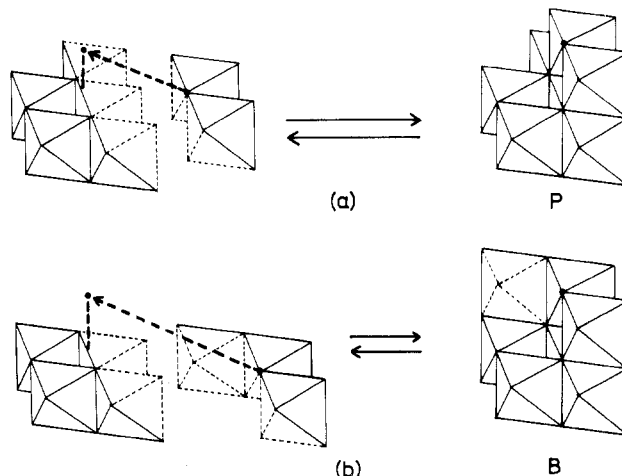

Figure 2. Schematic representation of the proposed (a) A $\rightleftharpoons$ P interconversion and (b) A $\rightleftharpoons$ B interconversion illustrating the (a) eight-oxygen, two-molybdenum (O_8, Mo_2) and (b) ten-oxygen, three-molybdenum (O_{10}, Mo_3) translations. The fragments, represented as incomplete (dashed lines) octahedra, are separated here for clarity *only* but are in contact throughout the translation. Marker oxygens are indicated by ●.
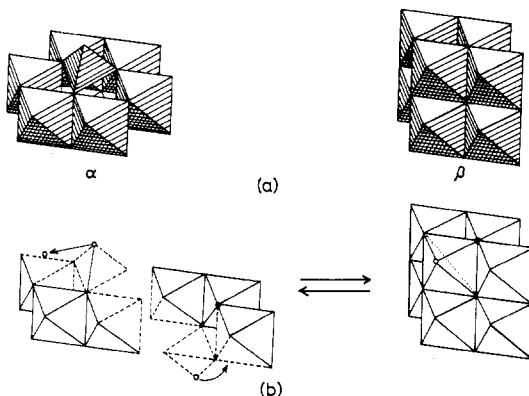

Figure 3. (a) Idealized molecular structures of α- and β-$[Mo_8O_{26}]^{4-}$. (b) Proposed interconversion $\alpha \rightleftharpoons \beta$ via concerted translation of a (O_{12}, Mo_3) fragment and the accompanying conversion of the tetrahedral Mo sites in α to octahedral sites in β. The fragments are separated for clarity *only*. Open circles represent the capping oxygens of α. The final positions of the four oxygens which define a capping "tetrahedron" in α are indicated by dotted lines in β.

marker oxygen highlighted in Figure 2, which is converted from a triply bridging (in A) to a doubly bridging (in P) ligand. In fact, multiple conversions of P → A followed by A → P *along a different mirror plane* scramble six of the seven mo-

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(2) Tsigdinos, G. A. *Top. Curr. Chem.* **1978**, *76*, 1–64. (b) Tytko, K.-H.; Glemser, O. *Adv. Inorg. Chem. Radiochem.* **1976**, *19*, 239–315.
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(5) Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Oxford University Press: London, 1975; pp 184–6.
(6) Evans, H. T., Jr.; Gatehouse, B. M.; Leverett, P. *J. Chem. Soc., Dalton Trans.* **1975**, 505–514.
(7) The idealized condensed polyhedron model is used here for illustrative convenience in two dimensions. However, we emphasize that many of the points are best appreciated by consideration of spatial and, particularly, cubic close-packed hard-sphere models.
(8) Perloff, A. *Inorg. Chem.* **1970**, *9*, 2228–2239.
(9) If a right-handed coordinate system is defined in Figures 1a and 2a with the origin at the marker oxygen, the z axis parallel to the C_3 symmetry axis, the y axis defined by the translational mirror plane, and octahedral edges defining unit length, the marker oxygen is translated to $(0, 3^{1/2}/2, 1/2)$.
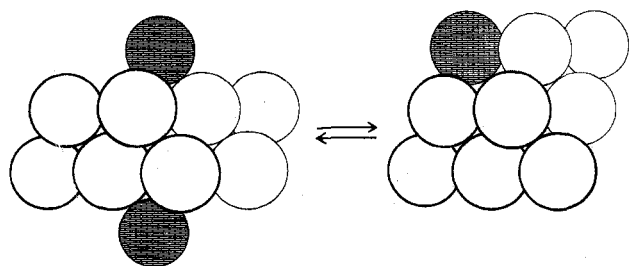
Figure 4. $\alpha \rightleftharpoons \beta$ isomerization as represented by cubic close-packing of oxygens viewed along a C_2 axis in the α form. The capping oxygens are shaded. The oxygen atoms from one side of the appropriate cleaving mirror plane are heavily outlined.
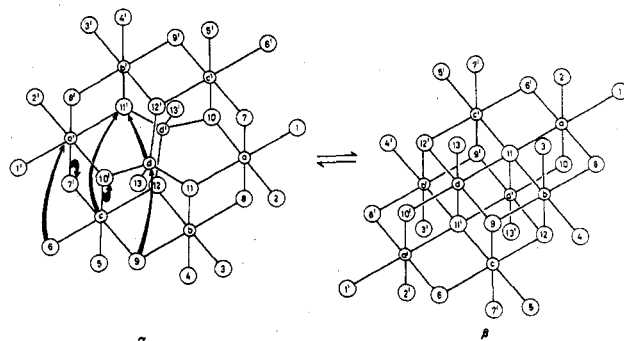

Figure 5. Idealized representation of one of three equivalent interconversions (translation across the α plane of symmetry defined by atoms 10, 10', 7, and 7') between α- and β-$[Mo_8O_{26}]^{4-}$, illustrating the β sites to which α atoms move. The notation in the α form is that of ref 4. Arrows illustrate the fragment translation; the symmetry-related arrows are not shown.

lybdenum atoms and all of the oxygen atoms (since bridging and terminal oxygens are also exchanged by this mechanism). The recent ^{17}O NMR data[10] for P-$[Mo_7O_{24}]^{6-}$ in H_2O is not inconsistent with such intramolecular exchange being one of possibly several solution processes.

A related concerted translation of a (O_{10}, Mo_3) close-packed fragment (shown in Figure 2b as three edge-shared, incomplete octahedra), in which the marker oxygen undergoes the *same* translation as previously described for A → P, generates a new structure[11] B, of point symmetry C_s (Figure 2b). This structure, however, has a five-coordinate ("coordinatively unsaturated") molybdenum site, and, although such sites are not unknown in solid-state Mo^{VI} oxide phases, the B-$[Mo_7O_{24}]^{6-}$ isomer remains unobserved to date. However, we note that P-$[Mo_7O_{24}]^{6-}$ is reported[12] to yield adducts "[M'-$(Mo_7O_{24})]^{4-}$" with M' = Mn^{II}, Co^{II}, and Cu^{II}. These heteroatoms M' may stabilize the B structure by inserting into the site which is available on the mirror plane, thereby coordinatively saturating the five-coordinate molybdenum with a solvent-based ligand (OH^- or O^{2-}) and bonding to the four oxygens which define the site.

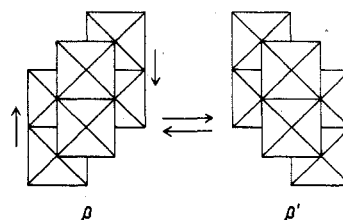In this context, $[Mo_8O_{26}]^{4-}$ can be regarded as the adduct $[(MoO_2)(Mo_7O_{24})]^{4-}$ and the known structure[13,14] of β-$[Mo_8O_{26}]^{4-}$ (C_{2h}; Figure 3a) is just the B structure with MoO_2 now occupying the M' site on the mirror plane. This arrangment ensures six-coordination for all molybdenum atoms.

Similarly, α-$[Mo_8O_{26}]^{4-}$ (D_{3d}; Figure 3a)[15,16] is formally derived from the A structure by removing the unique metal atom and symmetrically capping the resultant octahedral hole with two MoO units. The idealized A and α structures differ only in atoms which are located on the C_3 axis, and consequently both exhibit D_{3d} point symmetry.

The isomerisation $\alpha \rightleftharpoons \beta$ is a feature of the chemistry of $[Mo_8O_{26}]^{4-}$. Interconversion of α and β can be achieved by concerted translation of the same three molybdenum atoms which interconvert A and B, this time as part of a (O_{12}, Mo_3) close-packed fragment (Figure 3b). The marker oxygen undergoes the same translation suggested for the A $\rightleftharpoons$ P and A $\rightleftharpoons$ B interconversions. *This translation causes the smooth transition of the tetrahedral capping sites of α to octahedral sites in β.*[17] This crucial point is most elegantly demonstrated by cubic close-packed sphere models (Figure 4).

Figure 6. Interconversion of β- and β'-$[Mo_8O_{26}]^{4-}$. The mirror plane is the plane of the paper.

The process is envisaged as a *concerted* mechanism in which bond breaking and making occur synchronously via a thermally accessible transition state—one part of the molecule slides smoothly and continuously past the other, and there are no chemically well-defined intemediates.

The simplicity of this concerted process contrasts with the other suggested mechanism[4] which proposes a series of consecutive bond-breaking and -making steps occurring via several identifiable intermediates ($\alpha \rightleftharpoons \alpha-\gamma \rightleftharpoons \gamma \rightleftharpoons \gamma-\beta \rightleftharpoons \beta$). Importantly, the mechanisms differ in the β sites to which α atoms move (Figure 5).

Interconversion of $\beta \rightarrow \alpha$ followed by $\alpha \rightarrow \beta$ along different mirror planes scrambles all of the oxygen and molybdenum atoms not located on the C_3 axis of α-$[Mo_8O_{26}]^{4-}$, but the two MoO capping groups on that axis cannot be exchanged with the other molybdenum and oxygen atoms via these processes. However the ^{95}Mo NMR spectra[18] of α- and β-$[Mo_8O_{26}]^{4-}$ (enriched to 96.47% in ^{95}Mo for maximum sensitivity) in MeCN exhibit the *same* single, narrow resonance at room temperature, implying exchange of *all* molybdenum atoms. This can be achieved via additional concerted translations of molybdenum and peripheral oxygen atoms on the mirror plane of the β structure in a process reminiscent of the "merry-go-round" mechanisms which equilibrate organometallic carbonyls.[19] Thus, $\alpha \rightarrow \beta$ places the two "on-axis" MoO capping units and two other molybdenum atoms and associated oxygens on the mirror plane of the β structure. Then, in the condensed polyhedron convention, a concerted translation of the two pairs of "MoO$_6$ octahedra" *in opposite directions* along the mirror plane leads to an equivalent structure, β' (Figure 6), and

(10) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Schum, W. *Inorg. Chem.* **1979**, *18*, 93–103.
(11) This A → B process is a (O_{10}, Mo_3) translation. A (O_{12}, Mo_3) translation generates a related structure.
(12) Malik, A.; Zubairi, S. A.; Khan, A. S. *J. Chem. Soc., Dalton Trans.* **1977**, 1049–1050.
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(17) When the two capping MoO units are included, the process involves concerted movement of a total of 14 oxygen and their five associated molybdenum atoms.

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effectively scrambles the MoO capping units. Consequently, $\alpha \rightleftharpoons \beta \rightleftharpoons \beta' \rightleftharpoons \alpha$ interconversions permit intramolecular exchange of all molybdenum (and oxygen) atoms, consistent with the ^{95}Mo NMR results. The existing ^{17}O NMR data[10,15] for these complex systems is not so clear-cut. In wet MeCN close to room temperature, α-$[Mo_8O_{26}]^{4-}$ shows oxygen exchange not involving water, although coalescence apparently has not been reached. The data are consistent[15] with a MoO_4 reorientation process at the capping site and may indeed represent an additional, lower energy process to those considered above.

Concerted translations of other molybdenum/oxygen fragments along mirror planes can also be considered for the highly symmetric[20,21] (O_h) $[Mo_6O_{19}]^{2-}$ ion but result in structures containing five-coordinate molybdenum atoms. These isomeric forms appear to be thermally inaccessible as, in solution and over a wide temperature range, $[Mo_6O_{19}]^{2-}$ exhibits[10,18] the single ^{95}Mo and the three ^{17}O resonances expected from the crystal structure. Similar conclusions can be drawn concerning $[V_{10}O_{28}]^{6-}$ from ^{51}V and ^{17}O NMR studies.[10,22]

Intramolecular translations of close-packed fragments might be expected in polyoxometallate solution chemistry generally. A crucial role will be played by ^{17}O and the relevant metal NMR data in establishing if predicted interconverting isomers are thermally accessible. As anticipated in the discussion of the $[M'(Mo_7O_{24})]^{4-}$ adducts above, the presence of heteroatoms would be expected to profoundly influence those processes. If the heteroatom is itself stereochemically labile (e.g., many metal ions), the translation processes may not be hindered and fluxional heteropolymetallates can result. On the other hand, molecules such as $[(OAs)_2Mo_6O_{24}]^{6-}$ and $[(PhAs)_2Mo_6O_{24}]^{4-}$, with structures[23,24] based upon the labile α-$[Mo_8O_{26}]^{4-}$, show no ^{17}O NMR evidence[24] of oxygen scrambling, even at elevated temperature.

Registry No. $[Mo_8O_{26}]^{4-}$, 12346-58-6.

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