Cluster Fragmentation and Orbital Analysis: A Theoretical Study of Cohesive Interactions and Electronic Properties of Polyoxometalates with the Keggin Structure

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Multiple oxide clusters have been utilized as catalysts for several types of reactions, including oxidation and hydrocarbon cracking. Most notable are the solid acid catalysts which include zeolites and the Keggin ions. The α-Keggin ion is of the form $M_{12}O_{40}{}^{n-}$, where the charge depends on the metal selected. When M = Mo, the Keggin ion is chemically derived from molybdenum trioxide. In this work we focus on the structural and electronic relationship of the Keggin ion to MoO_3 and analyze the "electronic" mechanism for the stability and catalytic properties of the Keggin ion.

Introduction

Ever since the synthesis of the first heteropolyacid, the unusual chemistry of the material has been studied. It has been shown that the compound is extremely simple to prepare and appears to be stable under ambient conditions.[1] Its characteristics result from the unique assembly of a set of metal oxide octahedra through the sharing of bridging oxygens and bound in the center by some high-valent cation.[1–4] The structure stabilizes a large negative charge possibly through a high degree of delocalization and has been described as lacunar-like as a result of the number and size of the cavities arranged around the central ion.[5] Most common of all structures is that formed from twelve metal oxide "octahedra" and is referred to as the α-Keggin structure.[1]

Apart from its use as a source of electrons in charge-transfer (CT) matrixes,[6] heteropolyacids exhibit a high catalytic activity. The bridging oxygens are active sites in the promotion of specific oxidation reactions.[5,7–12] In addition, there exists at least one labile electron which produces a "hopping" effect (the frequency of this "hopping" is believed to be on the order of 10^8 s^{-1} (see ref 14) and may be the reason behind the excellent CT effects and the strong acidity observed. Electron "hopping" has been used to explain the fast electron exchange which leads to temperature-dependent line broadening in the EPR spectra of these materials[13,14] and can be understood to be a consequence of high electron mobility between octahedral subunits through the presence of the bridging oxygens. It is also possible that there may be some metal–metal coupling given the distance between metal centers is on the order of 3 Å.

Metal oxides have been always used in heterogeneous catalysis and, as a result, have been extensively studied with the aim of determining the source of activity and the factors influencing catalytic behavior.[15] More specifically, much computational analysis has been done on these structures to correlate electronic orbital interactions with reactivity. Both "one"- and "two"-dimensional structures have been examined theoretically.[16] The one-dimensional studies were really band structure analyses for a single chain of molybdenum oxide octahedra, while the two-dimensional studies focused on the electronic properties of MoO_3, a metal oxide characterized by an assembly of layered molybdenum oxide octahedra. Little has been accomplished as far as understanding the three-dimensional structure represented by heteropolyacids; whatever experimental work done on these materials has been confined to structural elucidation and catalytic activity in various reaction systems. In this work, "three"-dimensional structure refers to the real molecular geometry of the $XMo_{12}O_{40}{}^{n-}$. In this rather large cluster, the molybdenum oxide octahedra are assembled to form a tetrahedral cluster with structural components reminiscent of MoO_3. The relevance of the molecular structure of the Keggin ion to the structural motif represented in MoO_3 is realized by consideration of experimental and structural effects. First, phosphomolybdic acid is prepared from the reaction of phosphoric acid with MoO_3; and MoO_3 and phosphoric acid are the primary decomposition products of the phosphomolybdic acid which occurs upon heating at ca. 500 °C. The second point of interest is that the molecular constitution of the Keggin ion is made of two primary structural components, one is a tetrameric arrangement of molybdenum oxide octahedra, and the other is a trimeric

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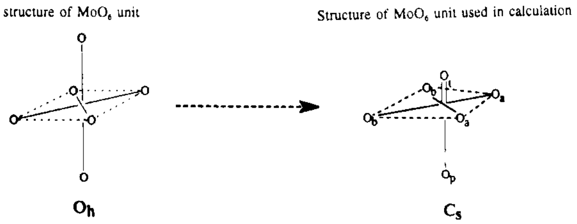

Figure 1. Octahedral distortion in the MoO_6 subunit in the Keggin cluster. The local structure of the unit in the Keggin cluster has C_s symmetry, while the corresponding unit in MoO_3 has C_{4v} symmetry.

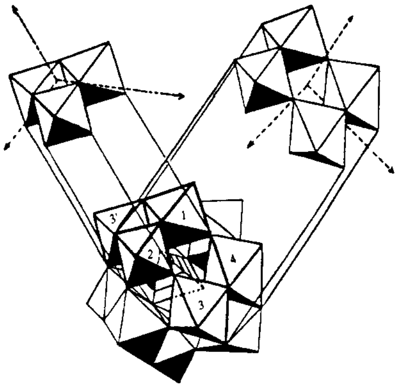

Figure 2. Keggin unit and the subunits from which it may be constructed. The cluster can be considered to consist of a conglomeration of three tetramers or four trimers.

assembly. The tetrameric unit is a harbinger of the MoO_3 structure.

There is therefore a great deal to be learned regarding the correlation of electronic interactions with structure, understanding the electronic forces that drive catalytic activity, and determining the cationic substitution effects in the material. This is especially interesting as the cluster can also be envisaged as an agglomeration of distorted metal oxide octahedra similar to those found in the more commonly studied layer structures (Figure 1).

The unique nature of these materials is represented by the Keggin unit (Figure 2). The entire entity may be fragmented into trimeric subunits as shown. Within each trimer, three metal oxide subunits are anchored through a shared oxygen (O_p, Figure 1) to a central cation of high formal charge. The atom O_p occupies a site along a 3-fold rotation axis and disrupts the expected 4-fold symmetry normally expected in 2-dimensional metal oxides.[4,17] It is through the linkage of three metal oxide octahedra by O_p that the basal bridging oxygens become dissimilar to the corresponding oxygens in 2-D metal oxides such as MoO_3. There is therefore a distortion in the structure, and the basic unit possesses C_s symmetry. An entirely different class of metal oxides can be built up from these and similar types of reactions.[18-20]

Another important property of heteropolyacids is the ability to maintain structural integrity upon metal ion substitution.[21] This is affected during synthesis, and the result is that a cluster is almost geometrically identical to the single metal ion analog. Moreover, it is possible in many instances to reduce the material extensively without undergoing structural degradation.[5] Reduction is normally achieved in several ways including replacement of the metal ion or central cation with one of lower oxidation state or by standard electrochemical means. The latter is a reversible process and may be used to induce temporary reduction in the cluster to facilitate certain reactions. The first method induces an intrinsic reduction in the cluster, producing significant changes in reactivity.

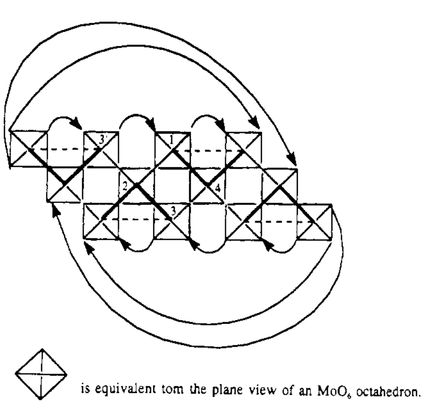

Figure 3. Equivalent two-dimensional layer from which the Keggin unit may be generated. The trimeric subunits are highlighted. Note the periodicity of the appearance of these units. The octahedra are numbered in the MoO_3 and Keggin ion to show the development of the three-dimensional structure.

Assembling the Keggin Unit

In this study, phosphomolybdic acid, $H_3PMo_{12}O_{40}$, will be used to model the behavior of the Keggin unit. Using a method described by Klemperer,[22] it is possible to "flatten" the Keggin cluster, i.e., the real three-dimensional molecular structure of phosphomolybdic acid, into a two-dimensional sheet of MoO_6 units (loosely referred to as octahedra), which mimics the exact conformation found in MoO_3 (Figure 3). To reverse the process and reform the three-dimensional cluster, the layer may be systematically wrapped onto itself as shown by the arrows. This produces the strained 3-fold oxygen center, while two out of every three "apical" oxygens are lost. The result is the sharing of the remaining oxygen among three molybdenum ions. Furthermore, each octahedron suffers an identical set of distortions to satisfy the structural requirements of the unit. Distortion in the basal plane is expected to be secondary in nature, as the "driving force" of the process is trimerization through a shared apical oxygen ion. Thus, it is not surprising that the oxide structure of MoO_3 is easily restored at moderate heating.

As the metal oxide layer is linked together, two octahedra each from two adjacent trimers form a tetrameric unit as illustrated in Figure 1. This produces a secondary interaction, i.e., between two pairs of trimers through a bridging oxygen, O_b. This particular interaction is characteristic only of this tetrameric conformation and also helps to define the character of the Keggin unit. The changes in the bond angles in the former basal plane of the metal oxide are very significant, and the dihedral angles

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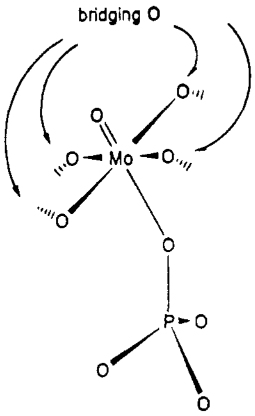

Figure 4. Link between the central PO_4^{3-} and a metal oxide octahedron. O_p is shared between P and Mo.

in the trimers and between the two pairs of octahedra in the tetramers change from a value of 180° each to 52° and 60°, respectively.

The seeming gross strain is exaggerated as the real bond angle of Mo–O–Mo is 90°, and the originally flat structure is puckered upward. The influence of these changes will be discussed.

Phosphomolybdic acid is easily prepared from a slurry of MoO_3 in H_2O on addition of excess H_3PO_4 and refluxes until all of the insoluble material disappears.[23] The high oxidation state of Mo is preserved by adding some oxidizing agent such as H_2O_2.[24] While the mechanism is unknown, it is likely that the acidic medium protonates the apical O^{2-} ligand (O_p), inducing elimination of H_2O as it interacts with a neighboring protonated O_p and causing the flat structure to warp. The end result from protonation and elimination may lead to formation of the stable Keggin unit.

Ion Substitution

From the stoichiometry of the heteropolyacid $H_3PMo_{12}O_{40}$, a formal oxidation state of +5 may be assigned to phosphorus. This is the treatment common for most oxoanions in which the central atom shows a decreased electronegativity with respect to oxygen. This convention assists the discussion of further heteroatom substitutions as it provides a formalism for the treatment of charge in the cluster. In some ways the Keggin unit may be described as a clathratic structure surrounding a tetrahedral PO_4^{3-} unit. Bonding between PO_4^{3-} and an octahedral unit is illustrated in Figure 4. The corresponding formula for this compound will then be $H_3PO_4 \cdot 12MoO_3$, where the P–O bond distance is similar to that in other phosphates, being of the order of 1.52 Å.[25] A set of analogs of this material can be described, where P is replaced with Si, S, Ge, etc. This will be examined to determine how size, effective nuclear charge, and residual electronic population on the central ion stabilize the heteropolyacid; in addition, the possible effects on catalysis will be considered.

One of the most interesting features of heteropolyacids and their corresponding salts is the variety of cationic metal ion substitution that the unit tolerates. Mono- and disubstituted material are routinely produced. There is some evidence, however, that the higher substituted materials become increasingly unstable.[26] Polyoxoanions have been found for several other materials including W(VI), Re(VI), Ru(VI), Os(VI), Cr(V), Ti(IV), V(IV),[27] etc., and may even involve mixed metal systems such as $XV_xMo_{12-x}O_{40}^{n-}$, $XW_xMo_{12-x}O_{40}^{n-}$, and $XSi_xMo_{12-x}O_{40}^{n-}$,[27,28] where X = P, Si, etc. Of particular importance is the vanado-substituted material as the replacement of any Mo with V provides a probe by which the cluster may be extensively studied.[29]

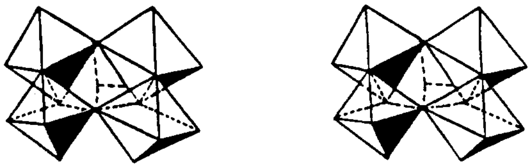

Figure 5. Unique positions of a pair of metal ions (V) in the tetrameric unit. Only the conformation in which the pair is located in the trimeric unit (a) will be considered.

The equivalency of the Mo ions is lost on substituting another metal ion into the system. When replacing two metal ions, there are six possible positions for the second ion after the first one is substituted. Of these, only one orientation will be considered (Figure 5) as it is believed that this is sufficient to establish arguments regarding metal–metal interactions between and across subunits.

Method of Approach

The extended Hückel formalism[30] was used in this study and is believed to be sufficient to illustrate the orbital interactions that drive the unique cluster behavior and to provide several clues as to the possible nature of catalysis. The method and computational program has been previously described in the reference cited. The orbital parameters[31] used in the calculation are summarized in Table 1. Bond distances used in the calculation are listed in Table 2.[32] Coordinates of a single MoO_6 unit were determined and then used to generate the position of the rest of the 11 Mo and 36 O atoms through the use of the symmetry relations extant in the Keggin cluster. The resulting structure ensures an overall T_d symmetry in the $PMo_{12}O_{40}^{3-}$ unit, plus local C_{3v} and C_{2v} symmetries in the trimeric and tetrameric units, respectively.

In this work, we have considered the stabilization observed in the distorted octahedra and have analyzed stability factors for the real three-dimensional molecular geometry of $PMo_{12}O_{40}^{3-}$. To achieve this, the cluster was decomposed into its basic tetrameric and trimeric structural fragments to simplify the orbital analysis and help to understand the characteristic differences in the electronic structure of the Keggin ion and the oxide from which

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Table 1. Extended Hückel Parameters

atom	orbital	H_{ii} (eV)	Slater exponent
B	2s	−15.2	1.3
	2p	−8.5	1.3
Si	3s	−16.3	1.383
	3p	−8.5	1.383
Ge	4s	−16.0	2.16
	4p	−9.0	1.85
P	3s	−14.5	1.6
	3p	−9.7	1.6
S	3s	−18.0	1.817
	3p	−11.3	1.817
O	2s	−27.6	2.28
	2p	−11.0	2.275
Mo	5s	−7.3	1.96
	5p	−3.6	1.96
	4d	−7.9	4.54(0.590)[a] 1.96(0.590)[b]
V	4s	−6.7	1.6
	4p	−3.4	1.6
	3d	−6.7	4.75(0.456)[a] 1.50(0.752)[b]

[a] Orbital coefficient c_1. [b] Orbital coefficient c_2 for the double-ζ functions.

Table 2. Bond Distances Used in Calculation

ion pair	dist (Å)
Mo–O_t	1.65
Mo–O_a	1.88
Mo–O_b	1.95
Mo–O_p	2.43
P–O_p	1.53

it was prepared. The contribution of interactions within and between these fragments to the stability of the parent cluster is discussed.

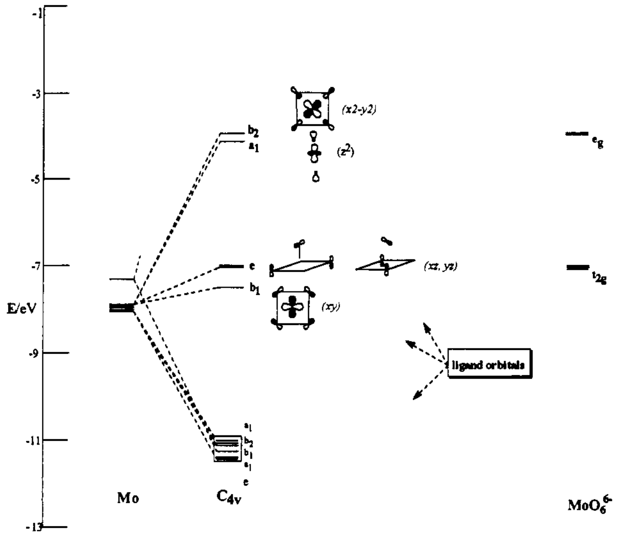
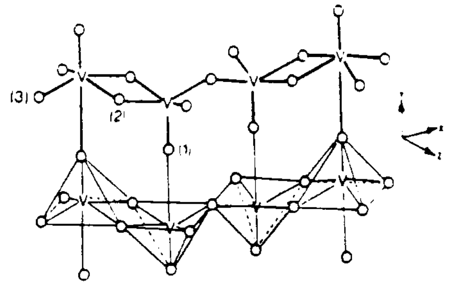


Figure 6. Molecular orbital diagram showing the effects of tetragonal distortion on the d-orbitals of Mo in $MoO_6{}^{6-}$. Focus is on the orbital contribution from the d-orbitals.

Results and Discussion

Keggin Unit Decomposition. (*a*) *Distortion in the Octahedral Units.* In reality the so-called MoO_6 octahedron is tetragonally distorted in the two-dimensional MoO_3 lattice. An apical or terminal O is doubly bonded to the metal ion center, inducing a weakening of the Mo–O bond in the trans position. This distortion may be considered to be driven by a "solid-state" second-order Jahn–Teller perturbation or Peierl's distortion,[33] leading to a molecular orbital distribution illustrated in Figure 6. A similar effect is observed in the molecular structure of the Keggin ion and in other two-dimensional oxides such as V_2O_5. The energetic effects driving this distortion can be seen in Figure 6 which shows the development of the "octahedral" states from the metal d- and ligand-orbital states. This distortion relieves the antibonding σ and π interactions along the z axis. For these particular materials, the total d-orbital occupation is low, and thus it is the π stabilization that is most important. In Figure 6, a decomposition of states of the distorted octahedron is provided. On the left, the metal contribution to the states is schematically represented, with the states of the undistorted octahedron appearing on the right. It can be seen that, for the distorted octahedron, the antibonding π states are stabilized relative to the t_{2g} of the "regular" octahedron. A parallel effect is seen in the σ states; the e_g are destabilized to a higher energy in comparison with the regular octahedron. It is interesting that the assymmetric lengthening of Mo–O bonds increases the stability in the octahedron at low levels of reduction or metal d-orbital population and provides a link between the two-dimensional layers of the oxide. Each O of a lengthened Mo–O bond is actually the "terminal" oxygen, Mo = O bond in the next layer, so that a chain develops between layers. This distortion which stabilizes the octahedral unit, providing one of the cleavage planes for MoO_3 as the long Mo–O can be severed, preserving the main bonding features in the molybdenum oxide octahedra. This sort of behavior is fairly common and is also observed in V_2O_5.[34] The difference in this oxide is that the distortion is more severe. The "terminal" V=O is considerably shorter and the "long" bond is about 2.7 Å. Here, the chain develops, but a structural twist occurs. Instead of a simple two-dimensional network forming from these distorted octahedra, the actually structure has a "twist" to it:



This effect assists in the cohesive interaction between the two-dimensional layers as long as short vanadium–oxygen bonds occur in pairs between the planes. Again, a cleavage plane is created between the layers as in the case of molybdenum trioxide.

It is not surprising that this stabilizing distortion is retained in the Keggin ion as the octahedra are chemically derived from MoO_3 and such stabilizing effects can be observed for even low levels of d-orbital occupation. In the case of molybdenum oxide, structural stabilization occurs for low levels of population but is increasingly destabilized on reduction. When the Fermi energy rises as a result of more severe reduction, destabilization of the

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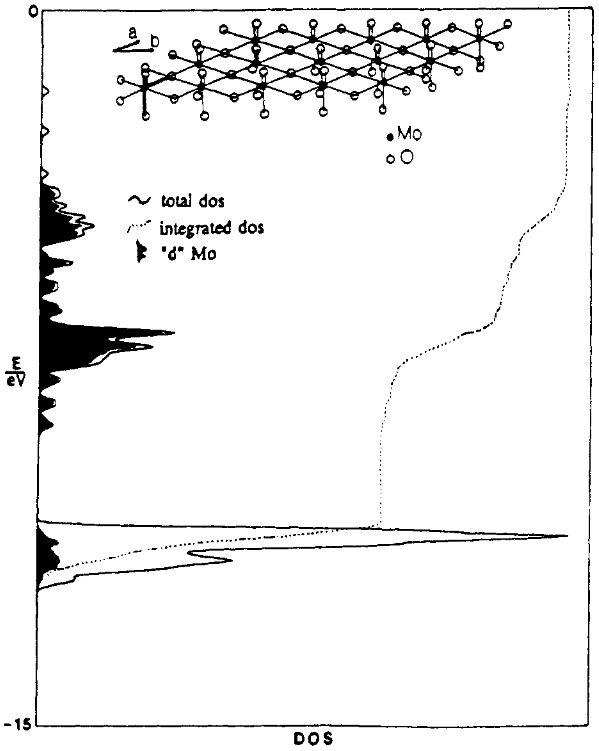

Figure 7. Density of states (DOS) for MoO_3. The structure of the metal oxide is given inset. The unit in bold was used as the generating set for the two-dimensional layer produced by projecting in the *a* and *b* directions.

basal oxygen–metal bond is induced as the respective antibonding orbitals become filled.

(*b*) *Decomposition of the Keggin Ion.* Figure 6 also shows the d-orbital contribution to each discrete molecular orbital. We can extrapolate this interaction to the two-dimensional crystal structure and develop a density of electronic states (DOS) which would represent the distribution of the electronic orbital energies for the crystal and plot out the corresponding d-orbital contributions versus energy (Figure 7). This represents the reference point from which the α-Keggin unit will be built. While the symmetry of the cluster will not allow for a resolution of the contributions of the respective d-orbitals, crystal orbital calculations will be sufficient to extract the necessary information.

The "density of states" for the subunits or clusters are not exactly the same as in the metal oxide lattice described by Figure 7. Since the units are discrete molecular units and are not extended infinitely, the so-called density of states is really just a histogram of molecular states. This is appropriate for comparison for several reasons. First, owing to the size of the Keggin ion, a large number of molecular states per cluster is observed with many states localized to a fairly narrow energy window. For example, most of the oxygen states occur in the range from −12.0 to −10.0 eV and the metal d-states are centered at −7.6 eV. This construct allows for greater ease of comparison of orbital states between the subunits of the oxide and the MoO_3. This histogram/density of states can be obtained by treating each structural component as though it represents the unit cell of a model subunit with large translation vectors >20 Å. The orbital overlap truncation implicit in this method will effectively reduce the "crystal" to a single unit. We can therefore discuss an equivalent "DOS" resulting from orbital interaction as it represents the orbital distribution with energy in the molecular cluster or a simple histogram of molecular states.

Figure 8 illustrates the DOS for the subunits $Mo_3O_{13}^{n-}$, $Mo_4O_{18}^{m-}$, and $PMo_{12}O_{40}^{3-}$. In each, the d-orbital contribution is also given. The metal orbital contribution in the frontier region is primarily from the d-orbitals, and hence the area left unshaded mostly represents the contribution from the O ligands. Comparing the subunits, the d-orbital concentration increases with the number of metal ions because the ratio of metal to oxygen increases. One of the primary points is that the typical metal oxide DOS exhibited, with the O "band" below the metal "band", is separated by a gap of the order of 3.0–3.5 eV. This is very similar to that in MoO_3, where the distribution is of the same order of magnitude.[35]

There is an interesting difference between the "DOS" distributions of the three-dimensional molecular unit versus the two-dimensional MoO_3 layer. As is typical with such metal oxides,[34] there is a significant degree of nonbonding character in MoO_3 originating from the d_{xy} orbital. This is not the case in any of the 3-D subunits or clusters, where the orbital in question is mixed into the others and develops bonding/antibonding characteristics. The bandgap of 1.8 eV present in MoO_3 is then increased to the characteristic value for HOMO–LUMO splitting energy for the three-dimensional molecular cluster, and the overall electronic population of the Mo d-orbitals decreases as a result of orbital rearrangement. (HOMO: highest occupied molecular orbital. LUMO: lowest unoccupied molecular orbital.) In general, the bandgap for solids or the HOMO–LUMO splitting for molecular species is indicative of stability factors influenced by covalent bonding. The greater stabilization of bonding orbitals and the corresponding destabilization of antibonding levels occur as the covalent bonding character increases opens the gap for molecular or solid-state structures.

The extreme orbital mixing, effected by the low-point symmetry in $Mo_{12}O_{40}^{8-}$, limits the extent by which orbital decomposition can be executed as each molecular orbital consists of a complex blend of the atomic orbitals from the respective atoms. Symmetry assignment is therefore very difficult and does not provide information for the cluster as a whole. No simple correlation diagram can be drawn to illustrate cluster formation from the sheet of MoO_3. However, from a comparison of the DOS of the various "surfaces", it can be expected that the orbital interaction extant in the two-dimensional array of MoO_3 (Figures 6 and 7) will be indicative of similar interactions in the three-dimensional cluster.

The process of "electron hopping" presupposes that there is some degree of interunit coupling, probably through the bridging oxygens. The mechanism for this unique behavior is believed to be vibronic in nature,[36] as a result of the coupling of vibrational and electronic states. Absorption of energy of the order of 3–3.2 eV (ca. 24 000–25 000 cm^1) will cause the material to appear yellow as it does. This is an excellent justification of the applicability of the extended Hückel theory and the parameters used in the calculation. On reduction the actual color changes to green or blue, indicative of a lowering of the "HOMO–

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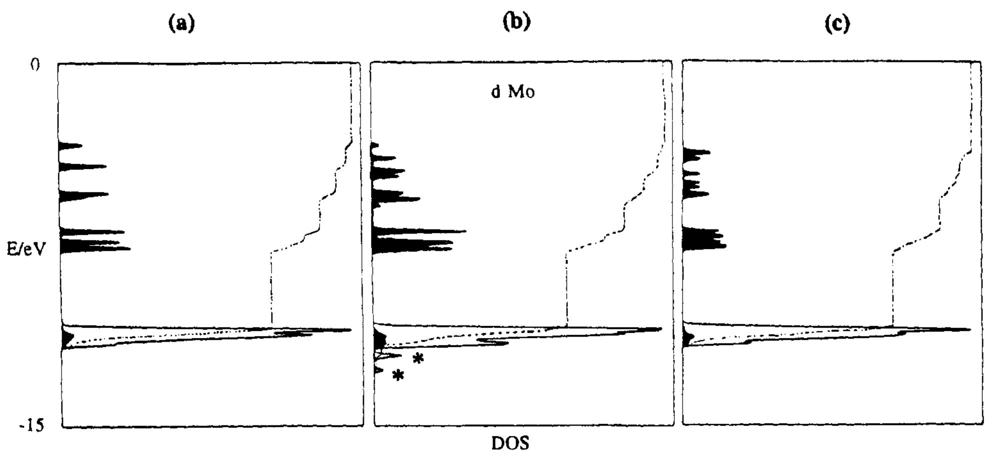

Figure 8. DOS for (a) $Mo_3O_{13}^{8-}$, (b) $PMo_{12}O_{40}^{3-}$, and (c) $Mo_4O_{18}O^{12-}$. The contributions marked by asterisks in (b) indicate the influence of P; cf. Figure 10.

LUMO" gap and an overall increase of the number of electronically active states. Reduction populates π-antibonding levels between the metal and the corresponding apical oxygen and therefore some M → L charge transfer can occur. This is also evident in the DOS, where states ca. 7.6 eV are populated, and the gap is reduced. Even under such conditions, however, the degree of direct M–M coupling is minimal, and furthermore, there is experimental evidence to support a ground-state localization of a single electron on Mo.[17b]

While the formal oxidation state assigned to each molybdenum atom is given as +6, our calculations assign a charge of +4.2 to +4.3 to the metal ion. This is probably a more accurate description of the nature of the metal ion, as it is almost impossible to obtain a purely ionic bond. The partial occupancy of the metal orbitals underscores the contribution of the metal orbitals to the "valence band" (Figure 8). Consequent to the synchronicity in the energy distribution of metal and oxygen orbitals, symmetry-allowed orbital interaction occurs, producing significant metal–oxygen orbital overlap. As stated previously, it is believed that an analysis of the interactions in the subunits will be indicative of similar behavior in the Keggin cluster. There is an overall consistency in this argument as the oxidation state of the metal ion in the subunits is of the same order as in the cluster. In fact, the overlap may be underestimated as the charge on the metal ion is slightly higher (more positive) than in the cluster, and orbital phase relationships are bonding overall in this energy region. This may be a result of the presence of "dangling" singly bonded O_a and O_b which will have a higher electronic localization than if they were bridged.

The magnitude of orbital interaction appears to be limited by the metal orbital contribution to the valence band. This is clear from the d-orbital distribution given in the DOS. Moreover, the electronic population increase per Mo in the valence band is only on the order of 0.05 on increasing the total subunit electron count by 9–10 electrons/Mo. This is in contrast to that in the respective bridging oxygens where the corresponding increase in electronic population is between 1 and 2 electrons/O, emphasizing the fact that the frontier levels are dominated by oxygen and that it is the anions that are more susceptible to redox processes.

To evaluate the extent of orbital overlap and bonding within the subunits, the weighted population of the molecular orbitals produced by interaction of a pair of atoms may be found. This will be described as the "weighted orbital overlap population" between two bonded atoms (WOOP). This is equivalent to the COOP curve, e.g., crystal orbital overlap population, however, this acronym is normally reserved for solids in which interactions between the units are preserved in the development of "infinite" structure. In this work, the overlap population data are restricted to analysis of states within the subunit or molecular structure of the Keggin ion. A lowering of the value of the summed overlap population is indicative of either a depopulation of bonding orbitals or population of antibonding orbitals and thus a weakening of the bond. Table 3 summarizes the WOOP between pairs of atoms in the trimeric and tetrameric subunits. It is possible to compare values within a specific unit as this will indicate the important trends which explain its electronic properties.

Table 3. Bonding Properties in the Trimeric and Tetrameric Units of the Keggin Cluster

	Mo_3O_{13} (trimer)		Mo_4O_{18} (tetramer)	
	a	**b**	**a**	**b**
charge on unit	−8	−10	−12	−14
no. of e^-/no. of Mo[a]	34.7	35.3	36.0	36.5
Fermi energy (eV)	−10.89	−7.59	−10.82	−7.63
WOOP				
($Mo–O_a–Mo^b$)	0.2814	0.2832	0.2791	0.2791
($Mo–O_b–Mo^c$)			0.3085	0.3086
($Mo–O_a{}^d$)			0.2962	0.2958
($Mo–O_b{}^d$)	0.2941	0.2935	0.2940	0.2940
($Mo–O_p$)	0.1400	0.1398	0.1459	0.1476

[a] Number of electrons in subunit per Mo ion. [b] WOOP for metal–oxygen bond where the coordination of the oxygen is fully satisfied. O_a represents the O shared by two octahedra in a single trimer. [c] WOOP for the metal–oxygen bond where the coordination of the oxygen is fully satisfied. O_b represents the O linking two octahedra in separate trimers to form the tetramer. [d] WOOP for Mo–O for the "dangling" oxygen; the oxygen ligand is singly bonded to the metal and hence has an unsatisfied coordination.

From the table it is clear that the Mo–O_a (bridging) bonding is distinctly different from the Mo–O_b (bridging) interaction, with the latter being stronger. This trend appears to be reversed in the "dangling" oxygens where the stronger localization of electrons around these oxygens is compensated by the greater availability of the metal orbitals in the trimer as a result of weaker interaction with the "bridging" O_a. These interactions will not be discussed further as they are not representative of any equivalent site in the Keggin cluster. It stated previously that the Mo–O–Mo angle for O = O_a is 52° compared to

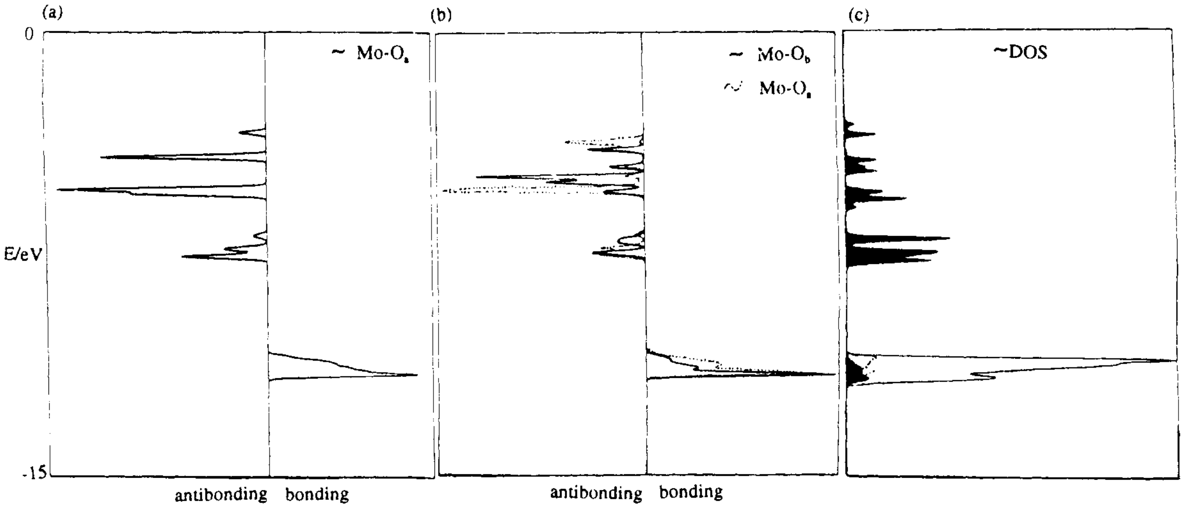

Figure 9. Weighted orbital overlap population (WOOP) between Mo and O in (a) $Mo_3O_{13}^{8-}$ and (b) $Mo_4O_{18}^{12-}$. Interaction is bonding for unreduced units. (c) (—) DOS; (- - -) O_p; shaded, Mo of $PMo_{12}O_{40}^{3-}$.

59.6° for O = O_b, where the latter will possess less steric strain as it is less acute. (The bridging O atom is sp^3 hybridized and will therefore prefer a bond angle of 109.5°.) The relative bond orders given in the table appear to confirm the greater degree of bonding found in Mo–O_b–Mo. Reduction will produce significant changes in the Mo–O bonding characteristics as these orbitals become antibonding above 7.6 eV. This is easily seen by plotting the orbital overlap population distribution versus energy (Figure 9).[37] While this promotes an increasing instability in the cluster, it is not sufficient to induce cluster fragmentation under reasonably mild reduction. Once again the distribution does not represent a solid-state crystal distribution, as the cluster demonstrates localized orbital interactions, only. Furthermore, consideration of the DOS shows that the states populated through reduction are antibonding in nature, the actual number of these states is small relative to the number of bonding states. In this region, there are a large number of nonbinding metal states which accommodates a significant portion of the increase electron density, and this is shown in Figure 9 as well.

No significant decrease in Mo–O stability occurs on reduction. Supporting data are provided in Table 3. This is superficial as a closer look at the position of the Fermi energy in Figure 9 indicates that it lies at the top of the oxygen p "band" in a Mo–O bonding region. In this analysis, we focus on the effect of the redox character on the stability of the complex as these materials display multiple stable redox states. Thus, it is necessary to consider the states near the anticipated Fermi energy and those immediately affected by reduction. Just below the Fermi level, that is, the top of the oxygen "band". Most interactions are π bonding between metal and oxygen. Therefore, a maximum in bond strength will occur when this band is fully occupied. The actually orbital occupation of the Keggin ion strongly depends on its environment and complexation. Furthermore, reduction commonly occurs when these materials are utilized in catalytic processes; in many cases the reduced Keggin ions are "reoxidized" with peroxide. In fact, peroxide is added in the synthetic protocol to prevent unwanted reductions. For such "oxidized" materials, the actual filling of the oxygen p "band" is expected to be "incomplete". In such cases, reduction will therefore initially strengthen and *then* weaken the bond as π-bonding states become populated to saturation and then nonbonding and antibonding states at higher energies become increasingly populated. Though the effect is small. The data shown in Table 3 suggest that little overall effect is observed with reduction. The net change for these two redox factors is essentially the combination of two effects: first, saturation of π-bonding orbitals and then the population of nonbonding and π-antibonding states. The reduction in bond strength is affected by the latter. In Figure 6 these states were shown for the Keggin ion. These orbitals are strongly localized on the metal. The effect is further muted as there are really three states of similar energy and thus a two-electron reduction per octahedral unit really distributes electron density over three states comprised to a large degree of metal character, through the orbital phase relationship is antibonding. This explains the bonding/antibonding characteristics of the WOOP curve. The lowest lying of these three is the orbital state implicated in the basal plane. The others affect the Mo═O terminal bond, not the bridging oxygen states. Some competitive features in bond strength are therefore expected, and there is a real decrease in Mo–O bonding at higher levels of reduction after the nonbonding metal states are occupied. Very little effect is seen in either the Mo–O_a (bridging) bonding for the trimer or tetramer. This is shown in Table 3. Further reduction will serve to destabilize both Mo–O bonds. Overall, these results illustrate the stability of the Keggin ion toward moderate reduction and thus allow a further understanding of its stability in oxidative processes.

What is of importance in the preceding observation is the provision of a possible pathway for electronic hopping, facilitated by the indirect coupling of metal ion centers through the bridging oxygens. The smaller overlap population, ~10% between Mo and O_a relative to Mo–O_b may lead to a shallower vibrational potential well and a greater chance for vibronic coupling with an adjacent metal ion center. In addition, the greater overlap population between the metal ion and O_b indicates a higher stability or lower lability of this species for sacrificial loss in the process of catalysis. This suggest that O_a may be more catalytically important. Furthermore, in support of the

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(37) This is analogous to the Hoffmann type integrated Crystal Orbital Overlap Population (COOP) for extended structures (ref 16, pp 42–55).

previous argument, the tetramer appears to generate a higher reduced state in O_a than in O_b. While O_b shows a calculated charge of −1.45 and −1.47 on 2-e$^-$ reduction (charge of −14 on tetramer), the O_a charge is −1.52 and remains at this value on reduction. Although there is a small degree of Mo–O destabilization leading to a higher lability of the O_b species, this is offset first by the decrease in overlap population between Mo and O_a and the higher negative charge on O_a. Furthermore, a portion of this electron density becomes localized on metal orbitals and indeed this is verified by the data in Table 3 which shows that 25–30% of the increased electron density becomes localized at the metal site and thus cannot contribute significantly to the destabilization of the Keggin ion. It therefore appears that O_a is the favored reaction site in oxidation reactions, where the incoming reactant moiety binds to the bridging O through an electrophilic carbonyl carbon.[8] Indeed, preliminary calculations show that O_a "loses" 0.5 electrons when H_2CO approaches it.

The relatively poor Mo–O_p interaction is a result of the distance separating the two ions. A definite conclusion cannot be drawn regarding the presence of a clathratic-type Keggin cluster, as O_p is not fully coordinated in the α-Keggin unit. The effect of the central cation may be so significant that the M–O bond is drastically reduced.

The foregoing discussion demonstrates that it is possible to analyze the Keggin unit by decomposing it into its respective tetramers and trimers and observing each individually. The existence of the trimeric building block is supported by the occurrence of many complexes with an Mo_3 central entity containing Mo–O–Mo bonds.[20,38] While the tetramer appears to be the basic unit for construction, it is only on forming intertrimeric links that the Keggin unit appears stable and develops its unique electronic and catalytic properties. Both the trimer and tetramer are proven to be useful subunits for analysis of the electronic interactions in the cluster. It is clear, however, that a seemingly complex structure can be decomposed into manageable components which may be analyzed to shed light on the behavior of the parent species.

Central Ion Substitution. One process of heteropoly-acid catalysis involves a direct link between the Keggin unit and an electrophilic carbon. Because of the position of O_p and moreso the central cation, there is little chance of direct interaction involving these species. Various workers have posited that the lacunary-like structure allows some penetration of small moieties into the cage, thus assisting in subsequent chemical reaction.[19,39] While this is possible, our discussion will focus more on the effect of the central cation on the overall stability and Mo–O interaction, rather than on the provision of better binding sites for intercalating molecules. This analysis will help to characterize the "vacancy" in the molybdenum oxide shell and thus is a natural place to undertake the initial study of the clathratic nature of the Keggin unit. Table 4 summarizes the effect of central ion substitution on various factors and includes the calculated charge and residual population of each cation (X) (pop.). The "stabilization energy", E, reflects the stabilization of the Keggin unit induced by the presence of X, relative to $Mo_{12}O_{40}^{8-}$. The results clearly indicate that there is a high level of covalency in the bonding between X and O_p, as observed from the number of electrons involved in the X–O_p bond as given in the table. In addition, a trend in the stabilization energy with X replacement is established.

Table 4. Effect of Cationic Substitution on the Keggin Unit

X	group	charge	pop.[a]	Z^b	O_p–X[c]	O_p–Mo[d]	E^e/eV
B	3	1.04	1.96	0.53	0.578	0.146	−13.53
Si	4	2.08	1.92	0.92	0.627	0.134	−14.20
Ge	4	1.87	2.13	0.88	0.652	0.142	−16.33
P	5	2.87	2.13	1.4	0.648	0.143	−15.43
S	6	3.27	2.73	1.2	0.672	0.150	−22.66

[a] The effective number of electrons in the valence shell of the cation. This includes those both in nonbonding orbitals and shared in covalent bonding. [b] A measure of the effective nuclear charge; found by taking the ratio charge/pop. [c] Number of electrons between O_p and X. This indicates not the degree of bonding but rather the extent of covalent interaction. [d] Number of electrons shared between O_p and Mo to which it is bonded. [e] This was found by subtracting the total energy of the $Mo_{12}O_{40}^{8-}$ moiety from the total energy of $XMo_{12}O_{40}^{n-}$ as found from the calculation. The number of electrons was kept constant at 320, and the central ion was initially entered *into the calculation with zero population.*

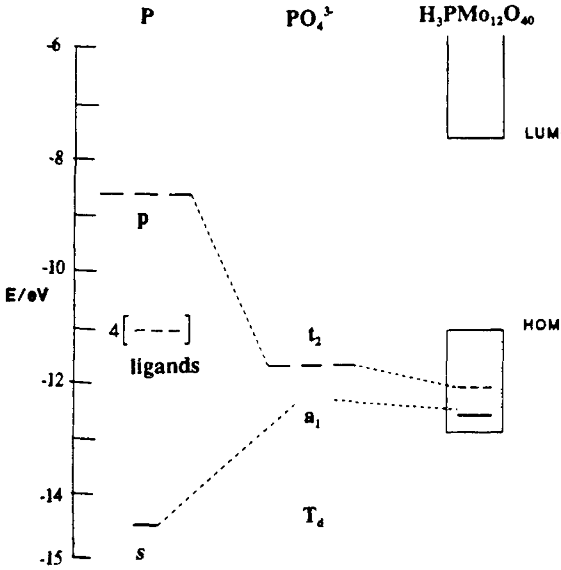

Figure 10. Correlation diagram illustrating the behavior of the orbitals of P on interaction of PO_4^{3-} in the Keggin unit in the frontier region. Orbitals are P–O_p bonding in character and appear to be buried below the HOMO of the cluster, making them insensitive to redox processes. There is, however, a growth of stability as the orbitals are shifted downward in energy.

On the whole there is a strong interaction between X and O_p regardless of the charge on X. In the first instance the interaction may be envisaged to be typical of a local XO_4^{n-} tetrahedral complex. This is perturbed symmetrically to the Mo attached to each O_p, inducing a depopulating effect on XO_4^{n-}. More specifically, however, the population of X increases as is observed for X = P, where P is reduced by as much as 0.20 electron (when compared to PO_4^{3-}), while the population of O_p decreases by 0.44 electron/ion (i.e., O_p is oxidized through loss of 0.44 electron). Figure 10 illustrates the effect of the three-dimensional cluster, represented by $PMo_{12}O_{40}^{3-}$. Only the X orbital contributions of significance to stability have been drawn, and hence the figure does not represent the complete molecular orbital diagram. It may be noted that the orbital distribution is characteristic of a T_d structure, and this is preserved in the Keggin unit. Furthermore,

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Table 5. Summary of the Electronic Population between Atom Pairs of a Fragmented Keggin Unit

bond pair	isolated unit	Keggin unit
P–O_p	0.608 (PO_4^{3-})	0.648
M–O_p	0.142 ($Mo_{12}O_{40}^{8-}$)	0.143

the reduction of P can be easily appreciated as the X orbitals are stabilized well below the HOMO.

It was stated earlier that the Keggin unit can be formulated as $H_3PO_4\cdot12MoO_3$, hinting that a clathrate structure may issue from the PO_4^{3-} moiety trapped in a $(MoO_3)_{12}$ cage. In fact, an examination of a fragment decomposition based on the encapsulation of PO_4^{3-} in the dodecahedral cage shows that the binding or "stabilization" energy is on the order of 5.29 eV. This can be compared to the stabilization energy of 15.43 eV encountered for the P^{5+} ion in $Mo_{12}O_{40}^{8-}$ quoted in Table 4. It has been suggested that it is the PO_4^{3-} unit that is trapped in the cage and "tumbles" with a relatively small energy input in the UV region. Our arguments are further substantiated by an examination of the electronic population between bonded atoms (Table 5). The trapping of PO_4^{3-} in the $(MoO_3)_{12}$ cage appears to increase the electronic population of the bond between P and O_p. Bonding orbital interactions are observed in the energy region as seen in Figure 10 and consequently represent an increasing stability of the PO_4^{3-} moiety, supporting the theory of a clathratic structure. The calculation was repeated for SO_4^{2-} which shown the highest S^{n+} stabilization energy and it was found that the SO_4^{2-} stabilization energy was of the same order as the PO_4^{3-}, being 5.81 eV.

It is observed that the number of electrons between Mo and O_p is of the same order of magnitude as determined from the WOOP for the trimeric and tetrameric subunits. No firm conclusion can be drawn from this. The WOOP shows little change in the total number of electrons between Mo and O_p on introduction of P (Table 5) and, moreover, the contribution of the P orbitals to the molecular orbital distribution is far below the HOMO (Figure 8); it is most probable that there is little perturbation of the Mo–O_p bond by P.

Substitution of Metal Ion. It is suspected that the substitution of one of the metal ions with another in one or more octahedral subunit has the effect of lowering the extent of electron hopping normally associated with these materials.[40,41] This appears to be the result of the perturbation of the molecular orbitals of the Keggin unit, whereby the symmetry of the cluster is removed and the degeneracies are lifted. The so-called "valence trapping" will lead to a localization of electron density on reduction which has been observed with several other techniques.[41] From analysis of the DOS of the substituted $PMo_{12}O_{40}^{3-}$, not obviously, the energy region for atomic orbital interaction is almost the same. The electronic localization is therefore symmetry driven. EPR analysis confirms that substitution of one or two Mo with V increases the spin density remarkably. While this is a result of many other factors, it is still indicative of the existence of an unpaired localized electron.

Figure 11 illustrates the DOS associated with the mono- and disubstituted materials. In both instances, there is little overall perturbation of the electronic states especially at the frontier level; this is substantiated by the constant "HOMO–LUMO" gap regardless of cationic substitution. The bonding contribution from V appears to be distributed evenly over the same region as the Mo orbitals (as given in Figure 8). When comparing the total energies of these systems with the 12-molybdic species, there appears to be a destabilization of the order of 0.72 eV/vanadium, it is difficult to observe this phenomenon in Figure 11 but may be attributed to a greater level of discreteness and hence less overlap between V and O in the bonding region of the DOS. This occurs below the Fermi energy and therefore the result manifests itself as a net destabilization of the cluster. On the other hand, the absence of V orbitals in the region directly above the Fermi energy means that the substituted metal cation will not be directly involved in the destabilization of the Keggin unit. However, because the number of Mo–O (antibonding) interactions just above the Fermi level is reduced, the level of destabilization normally expected from reduction will be lower. A tendency for destabilization of the strong bonding Mo d-orbitals leads to a growth of nonbonding or even antibonding metal–oxygen interaction. This supports earlier arguments concerning the effect of V.

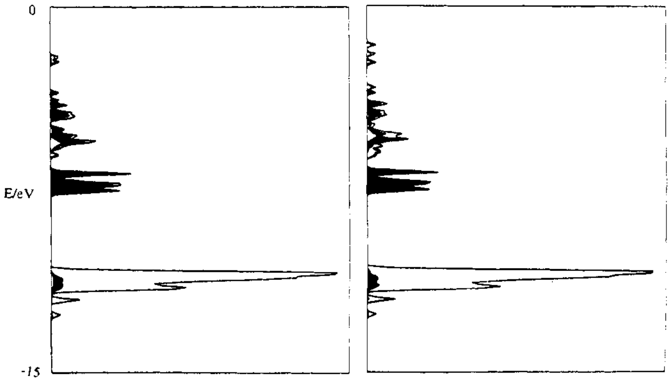

Figure 11. DOS for (a) $PVMo_{11}O_{40}^{4-}$ and (b) $PV_2Mo_{10}O_{40}^{5-}$. The overall distribution for the unreduced forms remain the same. However, the effects of substitution will become evident on reduction.

An insight into the valence trapping in reduced mixed heteropolyanions such as $PVMo_{11}O_{40}^{4-}$, where there is a localization of charge about V may be gained from observation of the orbital localization in the $MoVO_{10}^{n-}$ cluster. This phenomenon may result from a polarization of charge produced by orbital interaction between V and the orbitals of the Keggin unit. This localization is induced by simple electronic effects. First, as the d-orbital states are significantly higher in energy, they contribute less to the overall bonding stability of the cluster and tend to interact less strongly with the oxygen. In addition, a significant number of nonbonding states are localized well above the Fermi level. These states have a sizeable contribution from vanadium, and because of their more limited interaction with anions in the cluster, they tend to be more strongly localized on the vanadium. This may provide for the valence trapping that occurs upon substitution of vanadium into the lattice. This effect can be seen in Figure 11.

Conclusions

A number of interesting points have been raised concerning the α-Keggin unit. It has been demonstrated

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that it was possible to assemble the cluster electronically from a two-dimensional sheet of edge-sharing metal oxide "octahedra". The typical interactions found in the assembled cluster are produced after the octahedra are linked together to form the three-dimensional structure, where groups of three metal ions share an inner "apical" oxygen. It is therefore salient to compare the Keggin unit with its corresponding metal oxide, especially the former is an equally active catalyst as the latter for various reactions. The activity of the cluster may be a result of a high reactivity of a particular bridging oxygen, induced by the linking of a pair of trimeric subunits.

Central ion and metal ion substitution appear to affect both the stability and the redox properties of the Keggin unit. Here we have shown that while the tetrahedral center is relatively loosely held to the surrounding metal ion cage, it does add stability, probably as a result of satisfying the coordination sphere of each metal ion. In addition, it may act as an electronic well from which or to which electrons may redistribute. Metal ion substitution may induce higher site activity by effectively decreasing the level of metal–oxygen interaction with little expense to the overall stability of the cluster.

The chemistry of the Keggin ion provides a fertile ground for the development of novel catalytic sites, lacunary compounds, and even charge-transfer complexes. Its inherent stability, substitutional tolerance and ability to withstand high levels of reduction make the possible variations inexhaustible. Here, we have demonstrated the effectiveness of molecular orbital calculations to probe the cluster. This work provides a mechanism of understanding complex structures by decomposing them into simple units. Future considerations will be directed at analysis of the crystal chemistry of such ions and the lattice induced electronic effects.

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