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Electronic Structure of the Highly Reduced Polyoxoanion [PMo$_{12}$O$_{40}$(VO)$_2$]$^{5-}$: A DFT Study

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Introduction

The chemistry of polyoxoanions has been studied extensively.[1−12] A large body of experimental knowledge has been accumulated on these oxide clusters, which can in many instances be reduced, maintaining their integrity with only subtle changes in their structure.[7a,12] Trends in the obtention of blue reduced species have been empirically established over time, and the nature of electronic delocalization within the cluster has been discussed. Both hopping and ground-state delocalization mechanisms have been proposed to explain their electronic structure.[1] However, there is still a need for a systematic analysis of the effects of reduction on the molecular and electronic structure, stability, and reactivity of these clusters. Ab initio theoretical studies in this field are still scarce and are restricted to some fully oxidized polyanions.[13−15] The aim of this note is to present the first theoretical calculations of this type on the redox properties of a Keggin anion. For that, a bicapped, highly reduced Keggin complex [PMo$_{12}$O$_{40}$(VO)$_2$],$^{5-}$ **1**, whose synthesis and characterization have been reported recently by Hill et al.,[16] was chosen. In contrast with the isostructural [V$_{15}$O$_{42}$]$^{9-}$ cluster,[17] in which all of the vanadium atoms are formally d^0 metals, in anion **1** the metal centers contain eight electrons (see Figure 1 for a 3D representation of the anion). In their study Hill suggests, on the basis of valence bond calculations, that two of the electrons are in vanadium centers while the other six electrons are on molybdenum. The results of our density functional calculations (DFT) on the bicapped cluster [PMo$_{12}$O$_{40}$(VO)$_2$]$^{5-}$ agree with this.

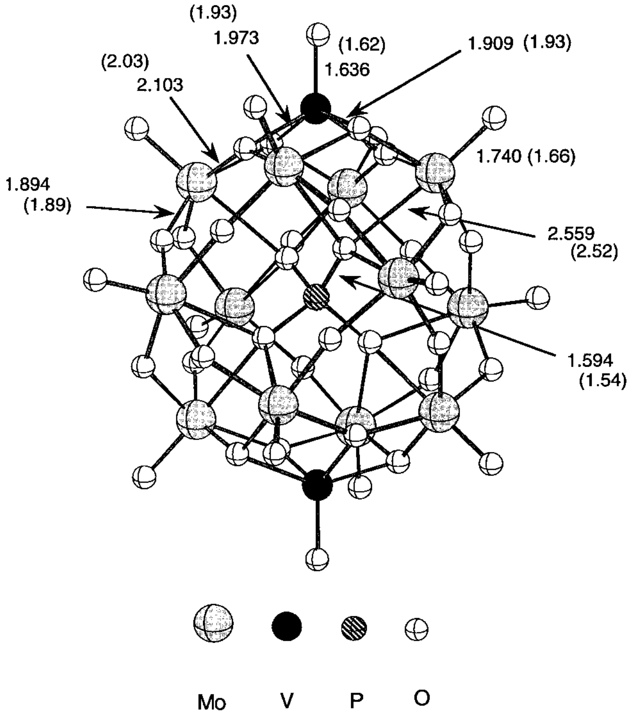

Figure 1. Optimized bond distances (in Å) for the ground state of the anion [PMo$_{12}$O$_{40}$(VO)$_2$]$^{5-}$ compared with the experimental values (in parentheses). The geometry of the cluster with net charge 2−, the most stable free anion, was found very similar to that of the anion with charge 5−. The electron addition to the cluster slightly elongates the metal−oxygen bond lengths. The largest difference between the clusters with charges 2− and 5− is not higher than 0.03 Å.

Theoretical Details

All of the calculations were carried out with the ADF program[18] using a triple-ζ + polarization Slater basis set to describe the valence electrons of O. For vanadium a frozen core composed of the 1s, 2s, and 2p levels was described by double-ζ Slater functions, 3d and 4s by triple-ζ functions, and 4p by a single orbital. An equivalent basis set was used for molybdenum. The valence electrons of P were described by triple-ζ + polarization functions. The geometries and binding energies were calculated using gradient corrections. We used the local spin density approximation characterized by the electron gas exchange ($X\alpha$ with $\alpha = {}^2/_3$) together with Vosko−Wilk−Nusair parametrization[19] for correlation. Becke's nonlocal corrections[20] to the exchange energy and Perdew's nonlocal corrections[21] to the correlation

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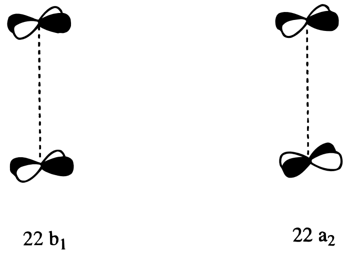


Figure 2. Schematic representation of the vanadium orbitals $22b_1$ and $22a_2$. The contribution of the two vanadium atoms is 60% and 80% for the orbitals $22b_1$ and $22a_2$, respectively.

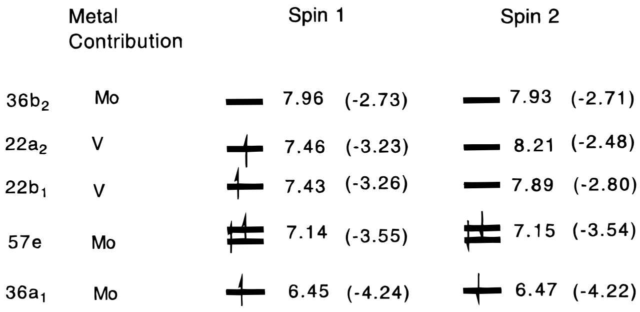


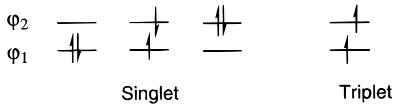
Figure 3. Symmetry, occupations, and energies (in eV) of the metal orbitals for the optimized triplet ground state of $[PMo_{12}O_{40}(VO)_2]^{5-}$. In parentheses are given the orbital energies of the triplet ground state structure in the presence of a sphere of diameter equal to 20 Å which generates at the center of the molecule a potential of 0.393 au, the estimated potential due to the crystal.

energy were added. The geometry optimizations on the bicapped cluster were performed under the constraints of the D_{2d} point symmetry group. Some calculations were also carried out with the X-ray geometry using the C_1 symmetry group. Spin-unrestricted calculations were used for the open-shell configurations.

Results and Discussion

The Isolated Cluster. In a polyoxometalate, the oxygen atoms can be formally considered as O^{2-}. Moreover, in a fully oxidized cluster the metal atoms do not have d electrons. Therefore, the occupied orbitals can be seen as oxygen orbitals, and the unoccupied orbitals as metal orbitals. Obviously, this representation corresponds to the ionic model, and in fact the occupied orbitals have a metal contribution and the empty orbitals have a nonnegligible oxygen contribution. The calculations show that for anion **1** the ground state is a triplet in which two of the eight metal electrons occupy the quasi degenerate vanadium orbitals $22b_1$ and $22a_2$. A schematic representation of these d-symmetry adapted vanadium orbitals is given in Figure 2. The other six of the eight d electrons fill the orbitals $36a_1$ and 57e, which are linear atomic combinations of the d orbitals of the 12 Mo atoms. Figure 3 shows the computed energies of the occupied metal orbitals and the energy of the LUMO. The high positive orbital energies are due to the absence of the counterions in the calculations. We will discuss this point below. Figure 1 compares the optimized bond distances for anion **1** with the X-ray values. We can see that the experimental and theoretical bond lengths are, in general, in excellent agreement. The highest discrepancy (0.08 Å) was found for the $Mo-O_t$ (terminal oxygen) bond.

In an attempt to analyze the magnetic properties of the cluster, the energy of the lowest singlet was also computed for $[PMo_{12}O_{40}(VO)_2]^{5-}$. For two magnetic orbitals φ_1 and φ_2 with two electrons there are four configurations, as is shown in **2**.



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While one configuration is involved in the triplet state, three configurations contribute significantly to the lowest singlet. In this situation the triplet state is well described by means of a monodeterminantal wave function, but the calculation of the lowest singlet requires a multideterminantal wave function to be considered. An approach to the use of multideterminantal techniques has been proposed by Noodleman et al.[22] This approach makes use of an unrestricted formalism and a broken-symmetry solution. In contrast to the delocalized nature of the $22b_1$ and $22a_2$ orbitals in the broken-symmetry solution, the magnetic orbitals are localized on each metallic center, and each orbital is occupied by one electron of different spin. With this procedure, the low-spin solution is not a pure spin state but represents an averaged aligment of spins (see Noodleman[23]). Ruiz et al. have shown that DFT methods combined with the broken-symmetry approach provide an accurate description of the magnetic coupling constants in transition metal systems.[24] Very recently, Caballol et al. reported that the broken symmetry approach underestimates the singlet−triplet energy gap and that in fact this method provides a lower limit to the singlet−triplet energy gap.[25] In the broken-symmetry approach the relative energy of the lowest singlet with respect to the ground state was computed to be 379 cm^{-1} using the geometry of the triplet state. This value decreases to 269 cm^{-1} for the optimal structure of the singlet state. We can conclude from these calculations that the anion $[PMo_{12}O_{40}(VO)_2]^{5-}$ should have *paramagnetic* behavior.

The energy of the triplet structure with the configuration ...$36a_1^2$ $57e^2$ $22b_1^2$ 22 a_2^2 which corresponds to an electronic structure with four vanadium and four molybdenum electrons was also computed. The relative energy of this triplet structure with respect to the structure of minimum energy was found to be 1.41 eV. This considerable energy difference fully confirms the predictions made by Hill,[16] who suggested that two of the eight metal electrons are localized on the vanadium centers, whereas the other six electrons are primarily localized on the molybdenum centers.

In order to analyze the redox properties of the metal oxide clusters with the structure $[PMo_{12}O_{40}(VO)_2]$, we studied the relative stabilities of the various reduced species as a function of the number n of the metal electrons. Figure 4 shows the total energy of the cluster versus the net charge of the compound. Each energy point in Figure 4 was computed after a complete geometry optimization of the cluster. The most interesting feature in this curve is that a region of minimal energy is obtained for anions with net charges 2− and 3−, corresponding to $n = 5$ or 6 metal electrons, respectively. For $n = 6$ the energy of the cluster is higher than the structure of minimum energy ($n = 5$) by only 0.4 eV. The addition of electrons to the cluster strongly modifies the absolute energy of the molecular orbitals,

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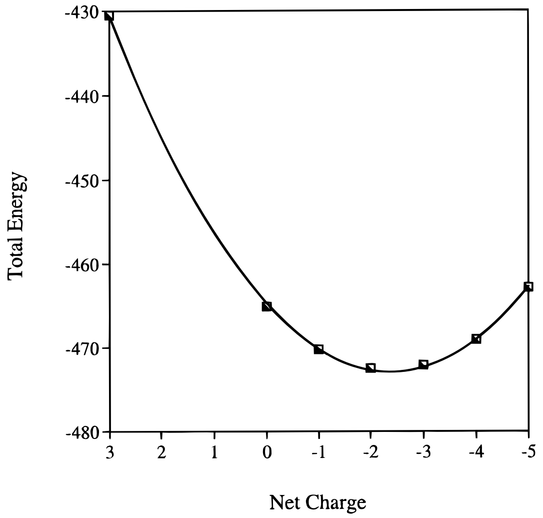

Figure 4. Total energy (in eV) vs the net charge of the anion for the isolated cluster (see the text).

but the relative energy between them remains approximately constant. One consequence is that the first metal electrons (up to $n = 4$) are accommodated in the molybdenum orbitals $36a_1$ and 57e, the most stable metal orbitals in the $[PMo_{12}O_{40}(VO)_2]$ cage. When another electron is added to the cluster, it does not go to the semifilled 57e orbital since for $n = 5$ the configuration of lowest energy is ...$36a_1^2\ 57e^2\ 22b_1^1$. For $n = 6$ the ground state is a triplet with the configuration $36a_1^2\ 57e^3\ 22b_1^1$. To sum up, the calculations carried out on the isolated system show the propensity of the molybdenovanadophosphate cage to accept metal electrons, but they can hardly reproduce the optimal number of electrons to be accommodated in the real molecular environment since the presence of counterions around the anion will generate a stabilizing potential and increase the tendency of the cluster to accept electrons until an equilibrium is reached, giving rise to the observed cluster.

Modeling the Crystal Field. Two procedures were used to model the crystal field. One of these was the procedure developed by Benard and co-workers[26] which they used to study electrostatic potential distributions in polyoxoanions. This procedure, which we denote as model I in the present work, can be summarized in the following way:

(i) The atoms of the surrounding crystal (cations and anions) are modeled using point charges obtained by Mulliken population analysis.

(ii) The electrostatic potential generated at the center of the molecule is determined by the model crystal field in successive shells until convergence is reached. Benard's group has shown that small changes in the values of the point charges do not significantly modify the crystal field on the anion.

(iii) A new DFT calculation is carried out in the presence of a charged sphere with a diameter equal to 20 Å, which is defined to reproduce the potential at the center of the anion obtained in the previous step.

In anion $[PMo_{12}O_{40}(VO)_2]^{5-}$ the value of the potential due to the crystal was estimated to be 0.393 au. The potential converged after including 13 shells with a total of 755 424 point charges. The DFT calculations carried out on $[PMo_{12}O_{40}(VO)_2]^{5-}$ in the presence of the charged sphere show that the crystal field strongly stabilizes the cluster but does not modify the magnetic properties of the anion. The major difference appears in the orbital energies, which dramatically decrease. In the absence of the crystal field the energies of the frontier orbitals are 7.46 and 7.43 eV for the magnetic orbitals and 7.96 eV for the LUMO. The corresponding values after including the crystal field are −3.23, −3.26, and −2.73 eV, respectively (Figure 3). It should be pointed out that the HOMO−LUMO energy gap is not altered by the presence of the electric field.

A second procedure (model II) was used to study the anion $[PMo_{12}O_{40}(VO)_2]^{5-}$. It consisted of the anion at the X-ray geometry surrounded by 14 point charges at the mass center of the 14 Et_3NH counterions that form the first shell of counterions. In model II, the electroneutrality of the global system was maintained by attributing a fractional value of $+(5/14)e$ to each point charge. In contrast to the model of the charged sphere, in model II the potential generated by the positive charges on the anion is not isotropic. In spite of this difference and of the fact that no symmetry restrictions were used in the calculations, the frontier orbitals for the lowest triplet are very similar to those orbitals of the free anion and of the anion surrounded by a charged sphere. In model II the HOMO−LUMO gap was computed to be 0.58 eV.

The influence of the crystal environment on the profile energy in Figure 4 was analyzed using models I and II. Both models confirmed that the crystal field indeed increases the tendency of the cluster to accept electrons. With model II the energy minimum with respect to the number n of metal electrons was reached exactly for $n = 8$. This value corresponds to the observed species (anion **1**). In this model the energy for $n = 7$ and $n = 9$ was computed to be higher than the minimum by 2.8 and 0.56 eV, respectively. With the model of the charged sphere, equilibrium is reached further away since the energy of the cluster with $n = 9$ is lower than the energy of anion **1** by 1.48 eV. According to this model, removing one electron from anion **1** to give the cluster with seven metal electrons requires an energy of 4.8 eV. The calculations carried out with models I and II confirm the importance of the crystal field, which shifts the number of metal electrons that can be accommodated in the framework $[PMo_{12}O_{40}(VO)_2]$ from 5 or 6 in the free cluster to 8 in the observed crystal and possibly more in a different crystal environment.

Conclusions

In the present work DFT calculations were carried out on $[PMo_{12}O_{40}(VO)_2]^{5-}$ and other related anions. Two main conclusions emerge. The first is that this polyoxometalate tends not to be completely oxidized. The second conclusion concerns the electronic structure of $[PMo_{12}O_{40}(VO)_2]^{5-}$. Six of the eight d electrons of this highly reduced anion are accommodated in three symmetry-adapted Mo orbitals, while the other two d electrons are in quasi degenerate linear combinations of the d vanadium orbitals. The triplet state was found to be the ground state, and the singlet−triplet energy gap was computed to be 269 cm^{-1}. These values clearly suggest that the anion $[PMo_{12}O_{40}(VO)_2]^{5-}$ should be paramagnetic. The calculations show the high propensity of the $[PMo_{12}O_{40}(VO)_2]$ cage to have metal electrons. The crystal environment, which was included in the calculations by means of two models, increases this tendency.

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