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Iron−Molybdenum Electron Delocalization in Substituted Keggin Polyoxoanions

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The quantum-chemical DFT calculations of fragments of molybdophosphoric Keggin polyoxoanion and its iron-substituted derivative are performed. It is shown that fragment calculations reproduce well local geometry and charge distribution in the whole polyoxoanion. It is found that the equilibrium $Fe^{II} + Mo^{VI} \leftrightarrow Fe^{III} + Mo^{V}$ can be realized in iron-substituted Keggin polyoxoanions. It gives an interesting example of participation of heteroatoms in polyoxoanion addenda in the electron delocalization processes.

I. Introduction

Polyoxoanions (POA) have attracted much attention in recent years.[1−4] A large body of experimental data has been accumulated on these large metal−oxygen clusters, formed usually by Mo, W, and V and widely used in such different fields as catalysis, electronic and magnetic materials, medicine, etc. One inherent property of POA containing metal−oxygen octahedra with only one nonshared oxygen atom (type I in the Pope classification[1]) is their ability to be reduced by one or several electrons with only small changes in the structure.[5−9] The reduced species frequently possess a deep blue color, which justifies their name "heteropoly blues". The added "blue" electrons are delocalized according to various time scales, over numerous addenda atoms. Both hopping and ground state delocalization mechanisms have been proposed[6−8] to explain their electronic structure.

The substitution of POA addenda metal atoms by another transition metal allows one to modulate the properties of POA and, thus, presents a special interest.[3,4,10,11] Another way to change the properties of POA appears in the secondary structure, where counterions in POA containing solids can be substituted. It seems natural that the substitution of addenda atoms perturbs the delocalization pattern. The reducing electron can be either trapped at the substituting atom or delocalized over the rest of the POA. In this context, the couple iron−molybdenum occupies a special place. As it was noted by Goodenough[12] several years ago, the closeness of redox potentials Mo^{VI}/Mo^{V} and Fe^{III}/Fe^{II} in an octahedral environment allows one to anticipate an equilibrium $Fe^{II} + Mo^{VI} \leftrightarrow Fe^{III} + Mo^{V}$ in oxides containing both ions at octahedral sites.

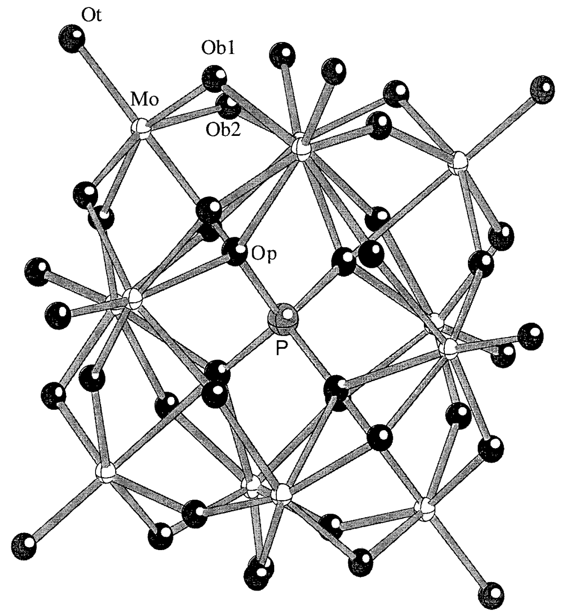

Figure 1. Ball-and-stick representation of the Keggin structure. The different types of oxygen atoms are indicated (O_t is a terminal oxygen; O_{b1} and O_{b2} are bridging oxygens in one trimer and between two trimers, respectively; O_P stands for the oxygen in a phosphorus tetrahedral environment).

Recent experiments seem to support this hypothesis for POA with a Keggin structure (Figure 1). Molybdophosphoric acid (MPA) and its salts are extensively studied as active catalysts in the oxidation of alkanes.[11,13] They contain the Keggin POA $PMo_{12}O_{40}{}^{3-}$. The addition of a large enough amount of iron into the MPA cesium salt leads to the partial substitutions of

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both Cs counterion and molybdenum atoms in the addenda of the POA.[14−16] The ^{57}Fe Mössbauer spectrum at room temperature presents two quadrupole doublets attributed to iron(III) either in a counterion position or incorporated into the Keggin unit. However, at 4.2 K some of the intensity of the second doublet is transferred to a new doublet characteristic for iron(II). It suggests that one can have a coexistence of valence configurations $Fe^{II} + Mo^{VI}$ and $Fe^{III} + Mo^{V}$.

In the present paper we study the possibility of iron−molybdenum electron transfer within a Keggin unit on the basis of quantum-chemical DFT calculations of the electronic structure. Several theoretical studies of the POA electronic structure are known in the literature including some recent ones using ab initio and DFT methods.[17−26] The fully optimized calculations of such large molecules as a Keggin unit by first-principles methods present rather difficult issues and can be achieved only by assuming some symmetry. However, the substitution in the addenda position and structural relaxation accompanying electronic redistribution lead to loss of symmetry. As a result, the calculations become more complex and cost much more CPU time. Therefore, we model the whole Keggin unit by subunits, representing a quarter or a half of the whole cluster. As it will be shown, these models reproduce in a rather satisfactory way the structural characteristics of the full molecule and are suitable for the description of the local electron transfer between adjacent metal ions.

II. Theoretical Details

All electronic structure calculations in this work were performed with the DFT method implemented in the Gaussian-94 program.[27] Geometry optimizations were carried out using the combined B3LYP method.[28,29] Constraints of the symmetry group were taken into account if a molecule possessed a particular symmetry. Since the high-spin configuration for iron is favored in oxides, all calculations of substituted clusters were done by the spin-unrestricted method.

The basis used for the calculations is the LANL2DZ one which includes the Huzinaga−Dunning double-ζ basis set[30] for the oxygen and hydrogen atoms, and the Hay and Wadt effective core potentials (ecp's),[31] accounting for the Mo relativistic effects, with a double-ζ valence basis set for phosphorus and transition-metal atoms.

Table 1. Optimized Bond Distances for Model Clusters

	$Mo-O_t$	$Mo-O_{b1}$	$Mo-O_{b2}$	$Mo-O_p$	$P-O_p$
cluster A	1.71	1.93	1.94	2.58	1.60
cluster B	1.72	1.94	1.93	2.44	1.57
expt (ref 34)	1.66	1.96	1.97	2.43	1.53

The influence of polarization functions on oxygen and phosphorus was also investigated. Single point calculations of model clusters at the B3LYP level indicate that the share of electronic charge between different metallic atoms does not change upon inclusion of these extra polarization functions.

III. Results and Discussion

(a) Nonsubstituted Keggin Anion. The Keggin structure (Figure 1) can be considered as containing four trimeric metal−oxygen subsets. Each octahedron MoO_6 shares two edges with two octahedra of the same trimer and is connected by two corners with octahedra from other trimers. Three octahedra from the same trimer have one common oxygen atom, and four such atoms form a tetrahedral environment of the phosphorus. Two pathways for the electron transfer between nearest-neighbor metal sites can be suggested. They correspond to the two types of contacts of the adjacent MoO_6 octahedra: through an edge and through a corner. There is no agreement in the literature about a dominating electron transfer pathway. In their earliest work,[32] Kozik and Baker gave preference to edge-shared electron transfer in $PW_{12}O_{40}{}^{4-}$. Later, on the basis of the NMR data, the same authors concluded that the preferred electron hopping route is via corner-sharing octahedra.[7] However, their data deal with doubly reduced polytungstates with Co as a heteroatom in the Keggin cluster. In our case, the average Mo−Mo distance within a trimer is 3.41 Å, whereas that between corner-sharing Mo atoms is 3.71 Å. Also, the nuclear factor is important for the electron transfer. The frequency corresponding to the $Mo-O_{b2}-Mo$ stretching vibration is higher than that for $Mo-O_{b1}-Mo$,[33] favoring electron transfer via edge. So, the Mo_3O_{13} trimer can be chosen as an elementary unit to study the intramolecular electron transfer. To represent the rest of the Keggin unit we also add the phosphorus atom, for which coordination is completed to tetrahedral by three OH groups. Hanging bonds were saturated by hydrogen atoms. The model cluster we study has the formula $PMo_3O_{16}H_9$ and possesses the symmetry group C_{3v} (cluster A, Figure 2a). To evaluate the influence of the cluster size on modeling of the Keggin unit we also studied the molecule of the C_{2v} symmetry containing two trimers and representing one half of the POA $(PMo_6O_{26}H_{10})^-$ (cluster B, Figure 2b).

Table 1 compares the optimized bond distances for the two clusters with experimental values of the Keggin unit obtained from X-ray crystallography.[34] For cluster B, the experimental and theoretical distances are in general in good agreement. The highest deviation was found for the $Mo-O_P$ bond (0.06 Å). For cluster A, the bond lengths in the cycle of the three Mo nicely fit the experimental values. The distances $Mo-O_P$ and $P-O_P$ are overestimated. This result can be explained by the fact that in the triplet we partly lost the rigidity of the Keggin unit around the heteroatom.

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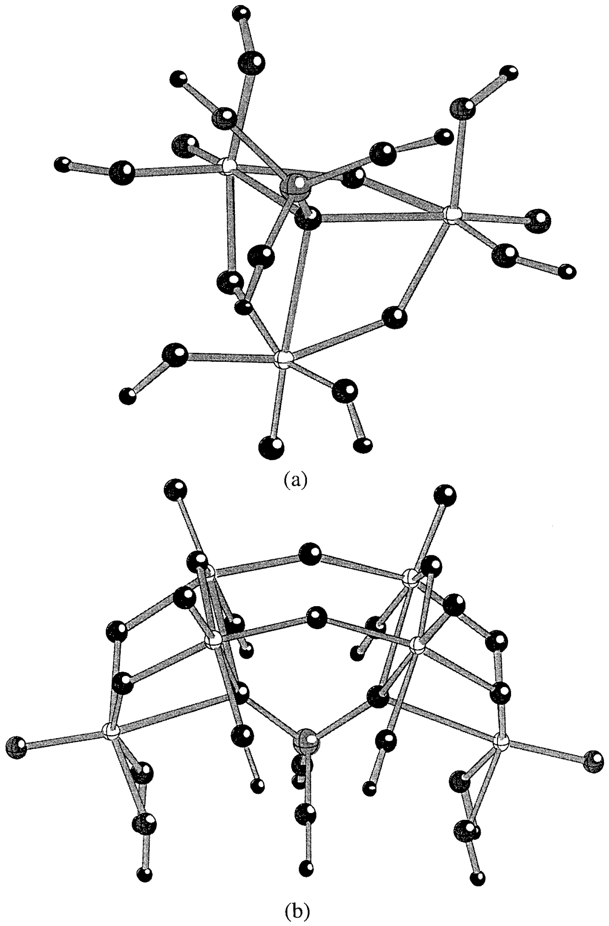

Figure 2. Model clusters used to represent the Keggin unit: (a) trimeric cluster (cluster A); (b) six-nuclear cluster (cluster B).

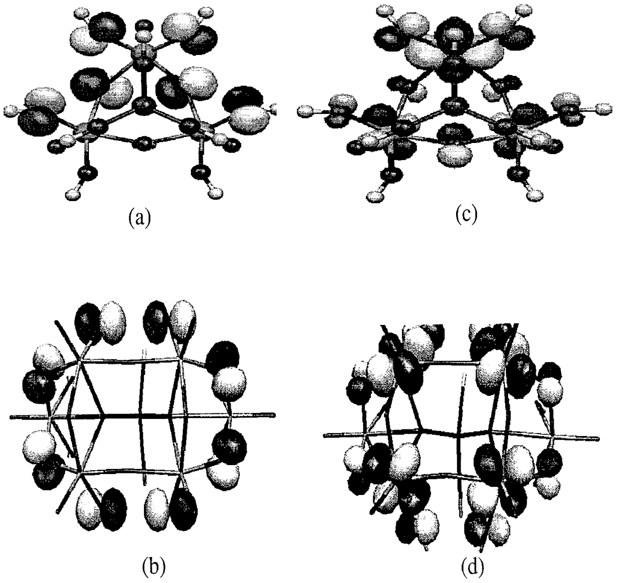

Figure 3. Composition of HOMO and LUMO for clusters A and B: (a) HOMO of cluster A ($E = -0.2807$ hartree); (b) LUMO of cluster A ($E = -0.1353$ hartree); (c) HOMO of cluster B ($E = -0.18457$ hartree); (d) LUMO of cluster B ($E = -0.05702$ hartree).

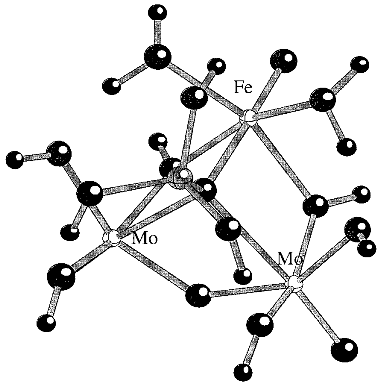

Figure 4. Model cluster used to represent the iron-substituted Keggin unit (cluster C).

The composition of the blocks of highest occupied and lowest free orbitals of our model clusters is the same as for the complete Keggin unit.[17] The former are composed of oxygen orbitals, and the latter contain mainly metal orbitals. Figure 3 presents the HOMO and LUMO of clusters A and B. The value of the HOMO–LUMO gap in the two model clusters A and B is strongly overestimated if we compare with the value given for the full unit.[17] It can be explained by the reduction of the number of interactions in model clusters. The Mulliken charges of Mo atoms were found equal to 1.51 for the cluster A, 1.40 and 1.66 for the cluster B. These values are references for Mo charge corresponding to the formal oxidation state +VI within different models.

The analysis of optimized distances and orbital structure shows a good agreement between our model clusters and the Keggin unit. They can be used to study the local perturbations resulting from the substitution of one molybdenum atom by iron.

(b) Iron-Substituted Keggin Anion. The nonstoichiometric iron-substituted cesium salt of molybdophosphoric acid studied experimentally[14] contains about 0.6 Fe atom as a counterion and 0.9 Fe atom substituting for molybdenum per Keggin unit. (The synthesis of iron-doped salt with excess Fe is similar to that described in ref 15.) The probability of finding two neighboring Fe atoms within a POA is negligibly small. Therefore we considered the substitution of only one molybdenum atom in our model clusters.

Although it is commonly admitted that the general structure of POA is preserved, the environment of the iron atom is not known in detail. In solution, depending on the pH, hydroxo or water ligands may replace terminal oxygen in the coordination sphere of substituted atom.[10,35,36] Unfortunately, there is no data for complex salts with the substitution in addenda and counterion positions. As both clusters A and B give a satisfactory description of the total Keggin unit, we considered only the simplest cluster A, where an iron atom simply substitutes molybdenum. To compensate the negative extra charge corresponding to the valence configuration $Fe^{II} + Mo^{VI}$ four protons were added (cluster C, see Figure 4). The symmetry group of the resulting cluster is C_s. We also tried to perform calculations for the substituted cluster in which the O_t atom is replaced by H_2O. However, some difficulties described below appeared for such a model. The electronic structure calculations were done supposing the electronic total spin equal to 2. It corresponds either to Fe^{II} high spin in the valence configuration $Fe^{II} + Mo^{VI}$ or antiferromagnetically coupled spins $^5/_2$ (Fe^{III}) and $^1/_2$ (Mo^V) in the electronic configuration $Fe^{III} + Mo^V$. The high-spin state of iron is confirmed by Mössbauer studies,[14] and antiferromagnetic exchange interaction is typical for different magnetic spins in heteropoly complexes.[37]

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Table 2. Optimized Bond Distances for the Two Minima of Iron-Substituted Cluster C

	$Fe-O_t$	$Fe-O_{b1}$	$Fe-O_{b2}$	$Fe-O_p$	$Mo-O_t$	$Mo-O_{b1}$	$Mo-O_{b2}$	$Mo-O_p$
minimum 1	1.64	2.14	2.14	2.14	1.70	1.96, 1.92	2.02	2.55
minimum 2	1.63	2.06	2.02	2.05	1.70	2.06, 1.90	2.06	2.58

Table 3. Energies[a] of Frontier Orbitals for Iron-Substituted Cluster C

	HOMO α	HOMO β	LUMO α	LUMO β
minimum 1	−0.235 67	−0.212 00	−0.163 35	−0.159 40
minimum 2	−0.212 21	−0.211 60	−0.169 11	−0.148 88

[a] In hartrees.

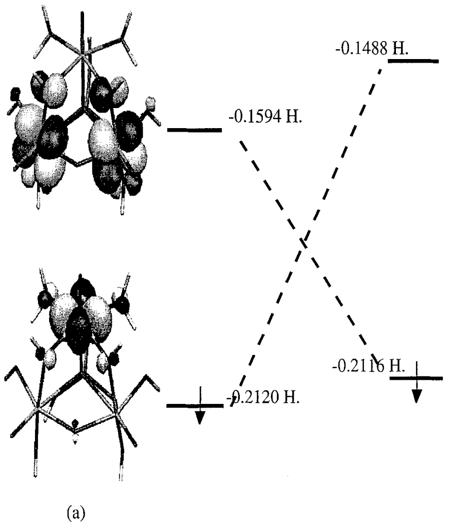

Figure 5. Composition of HOMO and LUMO of cluster C in minimum 1 (a) and minimum 2 (b).

Table 2 summarizes the main distances found for cluster C. This equilibrium geometry was obtained by the optimization procedure in which the geometry of cluster A (Table 1) was taken as the starting point. It can be noted that all the distances in the coordination spheres around the Mo atoms besides $Mo-O_{b2}$ change slightly. The Mulliken charges for Mo atoms are equal to 1.52, i.e., very close to the value found for cluster A (1.51). One can conclude that the energy minimum found describes Mo atoms in the oxidation state Mo^{VI}, and the calculated iron charge 0.57 corresponds to Fe^{II}.

Iron d orbitals fall into the energy gap between nonbonding oxygen and antibonding $Mo-O_b$ orbitals. The energies of few frontier orbitals are presented in Table 3. The spin β HOMO is localized on iron and oxygens and is followed by the LUMO containing Mo and bridging oxygen orbitals (Figure 5a). The most straightforward way to produce the electron transfer between Fe and Mo is to interchange these two orbitals. It is difficult to specify a priori a distortion which can result in this inversion. Recent studies of heterobimetallic oxygen-bridged complexes suggested that some kind of resonance can occur in these species between the structures $M^{IV}{=}O\cdots M'^{II}$ and $M^{II}\cdots O{=}M'^{IV}$.[38] The bridging oxygen atoms play a dominating role in such dynamics. Following these ideas we forced bridging oxygens to shift toward iron and used this new departure point in the geometry optimization procedure. A new minimum was found by this way in which total energy (−1476.8187 hartrees) is very close to that of the previous one (−1476.8177 hartrees). However, the structures and charge distributions corresponding to the two minima are quite different. The distances for the second minimum (Table 2) clearly indicate the contraction of the coordination sphere around the iron atom, which is in agreement with the increase of its Mulliken population which changes to 0.73. Correspondingly, the populations of the two equivalent Mo atoms decrease to 1.40. The average Mo−O distance in the first coordination sphere passes from 2.03 to 2.06 Å. The composition of the spin β HOMO and LUMO clearly indicates their inversion comparatively to minimum 1 (Figure 5b). A certain transfer of the electronic density toward Mo is also found in α orbitals. One can conclude that minimum 2 describes a state where an electron has been transferred from Fe to two Mo atoms. The less pronounced change of the average Mo−O distance occurs due to the delocalization of the transferred charge between two metal atoms. The presence of two potential surface minima with different localization of an “extra” electron is reminescent of multiminima surfaces of class II mixed-valence compounds.[39]

Since the energies of the two minima are very close, fast electron transfer is likely to occur at room temperature. We tried to localize a transition state for this transfer to estimate the barrier energy. However, we did not succeed in this research, probably due to the complexity of our model system. We may assume that the potential surface is flat enough, corresponding to a flexible structure.

We also tried to perform similar calculations for the model where O_t linked with iron is replaced by water molecule. During the optimizations starting from different points the calculations first converge in the directions of two minima, similar to minima 1 and 2. However, after several iteration steps, the different parts of the model cluster begun to move apart. This dissociation shows that the cluster model with the terminal water ligand does not give an adequate description of the substituted Keggin unit.

The existence of two minima corresponding to different localization patterns for the electronic charge agrees with the experimental data. At low temperature two possible states of Keggin-unit-substituted iron atom are observed by the Mössbauer spectroscopy. At room temperature the fast electronic jumps between two minima lead to the merging of these two spectra into one. Contrary to the well-described cases of the electronic delocalization between similar atoms (for example, in trinuclear mixed-valence iron carboxylates[40]), here the electron transfer between different atoms is encountered. It also cannot be excluded that the equilibrium $Fe^{II} + Mo^{VI} \leftrightarrow Fe^{III} + Mo^{V}$ could occur in other mixed-metal oxygen-bridged complexes.

IV. Conclusions

Two main conclusions can be drawn from this work. The first one concerns the applicability of small fragments to model electronic properties of such large clusters as POA. Our analysis shows that such models can be useful in the analysis of local structure and local charge redistribution. However, if one is

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interested in such global properties of Keggin POA as stability and redox potentials, the whole structure must be considered, sometimes with account of the crystal field.[25]

The second point refers to substituted Keggin POA. Our calculations confirm that a substituted atom such as Fe can actively participate in the electron delocalization processes within molybdenum Keggin POA, as it was previously suggested by Mössbauer spectroscopy.[14] As substitution of POA by other transition metals is often used to tune their redox properties, the analysis of reactivity of iron-containing POA should give special consideration to this effect.

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