Atomic and Electronic Structures of Hydrated Polymolybdates by First Principles Calculations

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First principles calculations of hydrated polymolybdates complexes have been made with an atomic orbital basis molecular orbital method. Hydration effects are taken into account by the conductor-like screening model (COSMO) using dielectric constant of water. Hydrated heptapolymolybdate, $\text{Mo}_7\text{O}_{24}^{5-}$, shows a low symmetry structure, which agrees well to experimental results, i.e., X-ray diffraction of crystalline salts and X-ray absorption fine structure of the hydrated complex. Contrary to that, the hydrated heteropolyanion, NiMo$_6$O$_{24}^{10-}$ prefer to exhibit the high symmetry structure. Inspection of the electronic states found that the Ni ion exhibits trivalent state or $d^6$ formal sense. Jahn-Teller distortion around Ni is therefore evident. Such distortion cannot be found in CrMo$_6$O$_{24}^{10-}$.

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Keywords: first principles calculation, conductor-like screening model, polymolybdates

1. Introduction

Hexavalent molybdenum species, which are dissolving as orthomolybdate ions MoO$_4^{2-}$ in basic aqueous media, are known to be condensed into a series of cluster ions called iso-polymolybdates, e.g., heptamolybdate Mo$_7$O$_{24}^{5-}$ and octamolybdate Mo$_8$O$_{24}^{4-}$, in concert with their protonation. The structure of the polymolybdate ions have been determined traditionally with X-ray analyses of their crystalline salts, such as $M_2(M_2O_3)$_4$-\cdot$H$_2$O (M$^+$ = Na$^+$, K$^+$, NH$_4^+$, etc.). Recently, atomic structure of Mo$_7$O$_{24}^{5-}$ ion in aqueous solutions were experimentally studied in-situ by combing X-ray absorption spectroscopy (XAS), anomalous X-ray scattering (AXS), and small-angle X-ray scattering (SAXS) by the present authors.$^{1,2}$ The study showed that the local structure of Mo$_7$O$_{24}^{5-}$ (aq) is almost the same as that of its salt crystals such as (NH$_4$)$_6$(Mo$_7$O$_{24}$)$_4$-4H$_2$O.$^3$ They are composed of distorted Mo$_6$ octahedrons with three different Mo-O bond lengths ranging from 0.17 to 0.23 nm. The structure of the distorted octahedron is similar to that can be found in Mo$_3$O$_7$ crystal.$^4$

In the presence of second metal ions, molybdate ions form another series of complex polymolybdates, e.g. AlMo$_6$O$_{24}^{9-}$ and CoMo$_6$O$_{24}^{9-}$, which are called heteropolyanions. Recently, Murase et al. have reported the formation of heteropolyanion involving Ni$^{2+}$ ions at around pH 5 using the factor analysis, a multivariate analysis, of visible absorption spectra for the Ni$^{2+}$-MoO$_4^{2-}$ system.$^5$ Assessed from the spectral change, the heteropolyanion had the composition NiMo$_6$O$_{24}^{10-}$. Since the salts of NiMo$_6$O$_{24}^{10-}$ have not been prepared successfully, the structure of NiMo$_6$O$_{24}^{10-}$ ion has not been clarified by means of X-ray diffraction. According to the analysis of XAFS (X-ray absorption fine structure) for the Ni$^{2+}$-MoO$_4^{2-}$ solution, however, the present authors have found the configuration of NiMo$_6$O$_{24}^{10-}$ ion to be one Ni$^{2+}$ ion surrounded by six sets of distorted MoO$_6$ octahedron with three different Mo-O bond lengths.

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2. Computational Procedure

Calculations were made using a first principles molecular orbital method. A program code DMOL$^{3,8,9}$ has been adopted. It uses numerical basis functions as values on an atomic-centered spherical-polar mesh. The radial part of the basis functions were obtained by solving the atomic Kohn-Sham equations numerically. Greater variational freedom was obtained by doubling the basis-set size, namely by generation of an entire second set of functions. A 3d orbital was also included for oxygen. The basis sets are called DND (double numerical plus d-functions) that is equivalent to 6-31G* basis sets used in Gaussian code.$^{10}$ Generalized gradient corrected functional (GGA)$^{11}$ was used to treat exchange and correlation potential. Spin polarization was taken into account only for molecules. Geometry optimization was truncated when the maximum displacement was smaller than 0.5 pm. Hydration effects were included by COSMO, which will be explained in detail in the next chapter.

3. Effects of Hydration on the Atomic Arrangements

When a charged molecule or solute is present in water, it is surrounded by a shell of highly ordered water molecules, which is known as hydration. The phenomenon can be
described by a charged species embedded in a dielectric medium from the macroscopic viewpoint. The medium or solvent polarized at the surface of the cavity that accommodates the charged solute. COSMO is a popular approach to include the solvation effects in quantum mechanical calculations. Its usefulness to accurately reproduce geometry and energetics of solvated molecules has been well confirmed.

The effect of hydration on the optimized geometry can be clearly demonstrated in a complicated molecule. In a simple system, such as in MoO$_4^{2-}$, neither optimized geometry nor electronic structure was significantly modified by applying the hydration effect. It simply translated energy eigenvalues because of the compensation of the extra charge in a molecule.

As an example of a complicated molecule, we have examined structures of a Mo(VI)-citrate complex MoO$_4$-(cit)$^4^-$, (cit$^{4^-} = C_6H_4O_7^{4^-}$) with and without the hydration. The dielectric constant of water, $\varepsilon = 78.4$ was used. In order to examine the hydration effects, other computational conditions such as basis functions and initial structure for geometry optimization were kept to be identical. Figure 1 shows structures with and without the hydration after geometrical optimization. Two structures look quite different especially around the Mo ion. When the hydration effect is taken into account, Mo is six fold coordinated. The Mo-O bond lengths are 180 pm, 205 pm, 233 pm and 250 pm. The atomic arrangement is analogous to that of the anion structure of MoO$_3$(cit)$^4^-$ in a crystal $K_2$[MoO$_3$(cit)] $\cdot$2H$_2$O reported in Ref. 12. The Mo-O bond lengths in the crystal are 173, 174, 205, 224, and 241 pm. On the other hand, one of the Mo-O bonds is broken when the hydration effects are not taken into account. The structure without the hydration is far from that of the crystal. The need of the hydration effects on the structural optimization of such a complicated molecule can be clearly demonstrated. COSMO is confirmed to be a quite successful approach to include the effect.

4. Geometry and Charge Distribution of Hydrated Heptapolyoxomolybdate, Mo$_7$O$_{24}^{6-}$

It has been widely accepted that atomic structure of the Mo$_7$O$_{24}^{6-}$ (aq) is basically the same as that in its salt crystal. It shows approximately $C_{2v}$ point symmetry, which is rather low. As will be mentioned in the next chapter, some heteropolyoxomolybdates MMO$_8$O$_{24}^{n-}$ with transition metal ions such as Cr$^{3+}$ and Co$^{3+}$ are known to exhibit higher point symmetry $D_{3d}$ with the alloying element at the center of the cluster. Figure 2 shows two kinds of geometry with the same composition of Mo$_7$O$_{24}^{6-}$ in comparison to experimental data of (NH$_4$)$_3$(Mo$_7$O$_{24}$)$^{4+}$-4H$_2$O.

![Fig. 1 Theoretically optimized structures of MoO$_3$(cit)$^{2+}$ with and without the hydration.](image1)

![Fig. 2 High and low symmetry structures of MMO$_8$O$_{24}^{n-}$.](image2)

### Table 1 Bond lengths of Mo-O and O-M-O angle by the present calculations in high and low symmetry Mo$_7$O$_{24}^{n-}$ in comparison to experimental data of (NH$_4$)$_3$(Mo$_7$O$_{24}$)$^{4+}$-4H$_2$O.

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<th>High symmetry</th>
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The structure of the hydrated Mo$_7$O$_{24}^{6-}$ complex optimized in the present study agrees well with that in the salt crystal such as (NH$_4$)$_6$(Mo$_7$O$_{24}$)$\cdot$4H$_2$O as can be found in Table 1. Difference in Mo-O distances in the two complexes is smaller than 6%. In-situ XAFS study by Shinoda et al. found that the Mo-O distances of the hydrated Mo$_7$O$_{24}^{6-}$ complex can be classified into three groups, i.e., 173, 193 and 224 nm. The number of bonds in each group is the same. The present theoretical results are consistent to the XAFS results, too.

Mulliken charge of Mo and O atoms are summarized in Table 2. The cationic charge is larger in the central Mo than that of the outer Mo in both structures. However, the difference is much larger in the high symmetry structure. The Mulliken charge of Mo in the hydrated Mo$_7$O$_{24}^{6-}$ molecule as discussed in the previous chapter is +0.82, which is significantly lower than that in the present hydrated heptapolymolybdate, Mo$_7$O$_{24}^{6-}$, although the formal charges of Mo in two molecules are the same as +6.

### 5. Structure of Heteropolymolybdate, NiMo$_6$O$_{24}^{10-}$ (aq)

Structure of the heteropolymolybdate, NiMo$_6$O$_{24}^{10-}$ (aq) is also examined with two different point symmetries fixing the position of the Ni ion at the center of the complex. In contrast to the hydrated heptapolymolybdate, Mo$_7$O$_{24}^{6-}$, we found that the high symmetry structure shows 1.24 eV lower energy than the low symmetry structure. The Mo-O distances and Mulliken charges are summarized in Table 3. It is interesting that the NiO$_6^{10-}$ octahedron located at the center of the complex is elongated from the regular one. Such distortion cannot be observed in the MoO$_6^{2-}$ octahedron located at the center of the hydrated high symmetry Mo$_7$O$_{24}^{6-}$ as described in the previous chapter.

The density of states for NiMo$_6$O$_{24}^{10-}$ (aq) near HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) is shown in Fig. 3. It looks complicated, which arises not merely from the size of the system but from the mixture of Mo-4d and O-2p orbitals with Ni-3d orbitals. Both of HOMO and LUMO are mainly composed of Mo-4d mixed with O-2p orbitals. Molecular orbital energies of some of these Mo-4d + O-2p type molecular orbitals are located close to the Ni-3d bands with majority and minority spins. It is very interesting to note that the Ni-$e_g$ orbital splits into two with only one occupied orbital. This means that the Ni ion is in $d^8$ configuration as Ni(II), not in $d^9$ configuration as in Ni(II). The electronic structure is schematically drawn in Fig. 3. The distortion can therefore be clearly explained by the presence of the Ni(III) with partially occupied $e_g$ orbital which can exhibit Jahn-Teller distortion.

In the present calculation, the number of electrons have been chosen assuming Ni(II), Mo(VI) and O(II). Nevertheless, the computational result show Ni(III), not Ni(II). This means that Mo$_6$O$_{24}^{12-}$ has more electron affinity than Ni(II) in the given environment. In the following chapter, we show results of NiMo$_6$O$_{24}^{7-}$ (aq) on the basis of assumption of Ni(III) in order to examine the difference between NiMo$_6$O$_{24}^{10-}$ (aq) and NiMo$_6$O$_{24}^{9-}$ (aq).

### 6. Structures of Heteropolymolybdate, MM$_6$O$_{24}^{9-}$ (aq), (M = Cr, Co, Ni)

Crystal structures of salts with CrMo$_6$O$_{24}^{9-}$ (aq) and CoMo$_6$O$_{24}^{9-}$ (aq) ions have been reported in literature. But
that for M = Ni has not been reported in the authors’ best knowledge. Cr(III) and Co(III) are \( d^3 \) and \( d^6 \) configurations in a formal sense. They are thus expected not to show the Jahn-Teller distortion assuming that Co(III) is in the low spin configuration. As a matter of fact, their crystals do not show such distortion. The computed results are compared to the experimental results on salt crystals in Table 4. The agreements are satisfactory. Co ion does not show magnetic moments and therefore it is in the low spin state. It is worthwhile to note that the O-M-O angle is slightly deviated from that of the regular octahedron similar to the case of \( \text{Mo}_7\text{O}_{24}^{6−} \) (aq) as described previously. Certainly the distortion cannot be ascribed to the Jahn-Teller distortion.

Computed results of \( \text{NiMoO}_6\text{O}_{24}^{6−} \) (aq) as shown together in Table 4 are qualitatively the same as that of \( \text{NiMo}_6\text{O}_{24}^{10−} \) (aq). Ni ion shows electronic configuration of Ni(III) or \( d^8 \) displaying Jahn-Teller distortion. A small distortion of the O-Ni-O angle is also evident in this case.

### 7. Summary

First principles calculations of hydrated polymolybdates complexes have been made with an atomic orbital basis molecular orbital method with GGA. Major results can be summarized as follows:

1. Hydration effects on the structure of a \( \text{MoO}_4\text{Cit}_4^{1−} \), \( \text{cit}^{4−} = \text{C}_6\text{H}_{12}\text{O}_7^{4−} \) complex can be well taken into account by COSMO using dielectric constant of water.

2. Energies of hydrated heptapolymolybdate, \( \text{Mo}_7\text{O}_{24}^{6−} \), with low and high symmetry structures were compared. The low symmetry structure is found to be preferable by 0.84 eV. The presence of a nearly regular octahedron that is forced to be present in the high symmetry structure is concluded as the origin of the hindrance of the high symmetry structure of \( \text{Mo}_7\text{O}_{24}^{6−} \).

3. Contrary to that, the hydrated heteropolymolybdate, \( \text{NiMoO}_6\text{O}_{24}^{10−} \), is found to prefer the high symmetry structure. It is more stable than the low symmetry structure by 1.24 eV. The Ni atom in the complex is spin-polarized with antiferromagnetic coupling to the surrounding Mo atoms. It exhibits Ni(III) configuration in a formal sense and displays Jahn-Teller distortion.

4. Other heteropolymolybdate with Cr(III) and Co(III) are present instead of Ni(III) do not show such a distortion, because they are in \( d^3 \) and \( d^6 \) (low spin) configurations, respectively.
Acknowledgements

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REFERENCES

10) Gaussian is a code name of popular first principles program. See the web site at http://www.gaussian.com.