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Studies on the Structure of Cationic Dimer of Molybdenum(VI) in Acidic Solution by XANES and EXAFS

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Structure of the cationic dimer of molybdenum(VI) species in acidic solution was investigated by the use of XANES and EXAFS. It was found that each Mo atom in the dimer has two terminal oxygens and Mo-O-Mo bond angle is ca. 125°.

Hexavalent molybdenum exists as a monomeric form of MoO_4^{2-} in neutral or alkaline solution. In weakly acidic solution the ion exists as $Mo_7O_{24}^{6-}$, $Mo_8O_{26}^{4-}$, or $Mo_6O_{19}^{2-}$ as a function of acidity of the solution. These species have been identified by pH titration,[1] spectrophotometry[2] and Raman spectroscopy.[3] In further acidic ($pH \lesssim 1$) solution, cationic species have been considered to be present.[4,5] However, their structures remain to be established.

In order to clarify the structure of the cationic species, X-ray absorption spectra were measured for solid and solution samples of Mo(VI) complexes and X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were analyzed.

$Na_2MoO_4 \cdot 2H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and other chemicals of guaranteed reagent grade were used without further purification. (dien)MoO_3 (dien = diethylenetriamine) and $[(C_2H_5)_4N]_2Mo_6O_{19}$ were prepared according to the literatures.[6,7] The Mo(VI) solutions were prepared from $Na_2MoO_4 \cdot 2H_2O$. The concentration of Mo(VI) was adjusted to 0.1 M (M = mol dm^{-3}) unless otherwise noted. The spectra were obtained at beam line 10B of the 2.5 GeV storage ring of Photon Factory. A Si(311) channel-cut-crystal monochromator was used. The sample solutions were held in polyethylene bags during the measurement. The solid samples were powdered and loaded on adhesive tapes. The energy scale E in the spectra was calibrated by using the pre-edge peak of $Na_2MoO_4 \cdot 2H_2O$ at 20007.0 eV. The threshold energy, E_0, was determined from the position of the half height of the absorption edge at around 20040 eV. The XANES spectra were normalized in intensity at higher energy side of EXAFS region.

Pre-edge peaks in the XANES spectra are shown in Fig.1 for solid samples of $[(C_2H_5)_4N]_2Mo_6O_{19}$ (1), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (2), and $Na_2MoO_4 \cdot 2H_2O$ (3). In the compounds

two types of oxygen atoms make bonds to Mo(VI), i.e. bridged (Mo-O-Mo) and terminal (Mo=O) oxygen. Cramer et al.[8] have pointed out that Mo(VI) complexes having Mo=O bond show the pre-edge peak which is assigned to 1s-4d transition and that the peak intensity increases with the number of terminal oxygens per molybdenum atom, n. The relative intensity, p, of the pre-edge peak referred to that of sample 1 and the value of n are listed in Table 1. Our result also indicates that the peak intensity correlates with the number of the Mo=O bond per Mo(VI) atom. Introduction of nitrogen atoms to the coordination sphere of Mo(VI) reduces the p value. The correlation is also observed for the species in solutions. (dien)MoO_3 in aqueous solution has quite a large value of n as compared with that for the solid and this results from hydrolysis of (dien)MoO_3 producing MoO_4^{2-}.[9] The p values for strongly acidic solutions, where the cationic species of Mo(VI) is considered to be present, correspond to about two Mo=O bonds per Mo(VI) in the cation.

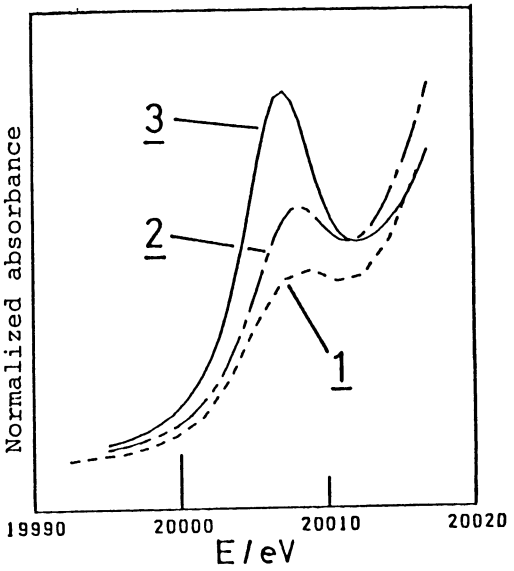

Fig.1. Pre-edge peaks for Mo(VI) solid samples.

The pre-edge peak for the cation is observed at 20008.8 eV. The positions are 20007.0 and 20008.5 eV for MoO_4^{2-} of tetrahedral symmetry around Mo(VI) and for $Mo_6O_{19}^{2-}$, $Mo_7O_{24}^{6-}$, and (dien)MoO_3 of octahedral (somewhat distorted) symmetry, respectively. Therefore, the cation seems to take octahedral symmetry around Mo(VI).

Figure 2 shows Fourier transform (FT) of the EXAFS for 0.4 M Mo(VI) in 2 M $HClO_4$, in which it is known that over 90% Mo(VI) form the dimeric species.[4] In the FT, the corrections for the phase shift and the backscattering amplitude were performed by using the parameters for Mo-O bond given by Teo and Lee.[10] A peak at about 1.7 Å corresponds to Mo=O bond. The number of oxygen atoms, N_O, in the coordination sphere of Mo(VI) in the dimer can be estimated by using the relation, $hR^2 = kN$, where h is the peak height in FT, R the bond length and k the proportional constant.[11] In this case the root-mean-square relative deviation (RMSRD) of R is assumed to be constant. The reference sample used to determine the value of k is MoO_4^{2-} (pH 7.28). The values of N_O and R_O determined are listed in Table 2.

Table 1. Intensity of pre-edge peak p and n value

		p	n
solid	1	1.00	1
	2	1.30	1.71
	3	1.85	4
(dien)MoO_3		1.32	3
MoO_2(oxine)$_2$		1.20	2
solutions			
$Mo_6O_{19}^{2-}$ in CH[a]		1.12	(1)
$Mo_7O_{24}^{6-}$ (pH4.63)		1.22	(1.71)
(dien)MoO_3		1.63	
MoO_4^{2-} (pH 7.28)		1.63	(4)
Mo(VI) in	1 M HCl	1.26	
	3 M HCl	1.24	
	1 M $HClO_4$	1.26	
	3 M $HClO_4$	1.23	
	1 M HNO_3	1.27	
	3 M HNO_3	1.27	
	1 M H_2SO_4	1.21	
	3 M H_2SO_4	1.26	

a) CH = cyclohexanone.

In four different 2 M acid solutions, N_O is around two, which is in agreement with the conclusion derived from the analysis of XANES. In these solutions, major species is reported to be the dimer having a μ-oxo bridge.[4,12] In Fig.2, a small peak at 3.37 Å (this value was obtained by using the parameters for Mo-Mo bond[13]) corresponding to Mo-Mo bond appears but the bridged oxygen, O_b, is obscured by the large peak corresponding to Mo=O. Assuming that the Mo-O_b distance is 1.9 Å, which is the averaged Mo-O_b value obtained from the literatures[14,15] for crystals of Mo(VI) compounds, it is concluded that the dimeric cation has a bent Mo-O-Mo bond with the angle of ca. 125°.

From the position of the pre-edge peak in XANES spectra, the dimeric cation is considered to take octahedral symmetry. Therefore, three water molecules may coordinate to each Mo(VI). However, oxygen atoms of water molecule which should appear at about 2.2-2.3 Å in FT could not be observed clearly. This may be caused by rapid exchange of coordinated water molecule, i.e. the labile character of Mo(VI).[16] Indeed, for Mo(V) which is known to be labile, no coordinated water molecule has been observed by EXAFS.[17] The intensity of the peak at 3.37 Å (Mo-Mo) is relatively small in comparison with other dimers having Mo-Mo bond length of ca. 2.1-2.6 Å,[17] which indicates the large RMSRD resulted from the weak bond between Mo(VI) atoms.

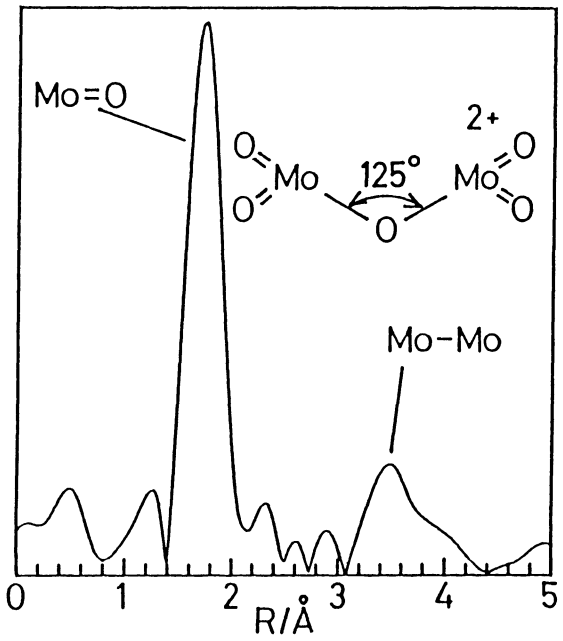

Fig.2. FT of EXAFS for Mo(VI) in 2 M $HClO_4$.

Table 2. Results of EXAFS FT

		R_O/Å	N_O	E_O/eV
solid	1	b)	---	20016.6
	2	1.74	2.0	20016.5
	3	1.77	3.8	20018.2
(dien)MoO_3		1.78	3.2	20015.4
solutions				
$Mo_6O_{19}^{2-}$ in CH[a]		b)	---	20016.8
$Mo_7O_{24}^{6-}$ (pH 4.63)		1.75	1.8	20016.3
(dien)MoO_3 in H_2O		1.76	4.3	20018.0
MoO_4^{2-} (pH 7.28)		1.78	4.0	20017.8
Mo(VI) in 2 M HCl		1.70	1.7	20016.9
2 M $HClO_4$		1.72	1.8	20016.3
2 M HNO_3		1.71	1.9	20017.7
2 M H_2SO_4		1.73	1.8	20016.1

a) CH = cyclohexanone.
b) No detectable peak at 1.7 Å.

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