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EXAFS Study on Polynuclear Molybdenum and Tungsten Compounds

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EXAFS (Extended X-ray Absorption Fine Structure) spectra were analyzed for various polynuclear molybdates and tungstates in order to examine the feasibility of this method for the structural study of complex polynuclear compounds. We found an unusual phenomenon that Mo-O peaks in Fourier transforms of $Mo_6O_{19}{}^{2-}$ and $PMo_{12}O_{40}{}^{3-}$ are hardly discernible while the corresponding tungstates give the W-O peaks clearly and normally.

In recent years, EXAFS spectroscopy has been proved to be useful for the study of short range order of atoms in polynuclear compounds.[1-3)]

Hexavalent molybdenum forms such polynuclear isopoly compounds as $X_6Mo_7O_{24}$, $X_4Mo_8O_{26}$ or $X_2Mo_6O_{19}$ (X : counter ion or proton) and also heteropoly compounds as $X_3PMo_{12}O_{40}$. The polytungstates are also known having similar structures in which molybdenum atoms are replaced with tungsten atoms.

In order to examine the feasibility of EXAFS for the structral study of molybdenum and tungsten polynuclear compounds, Fourier transforms of EXAFS measured for solid samples of various molybdates and tungstates are compared with the known data of X-ray structure analysis.

$Na_2MoO_4 \cdot 2H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were purchased from Wako Pure Chemical Industry, LTD. $[(C_4H_9)_4N]_2Mo_6O_{19}$,[4)] $[(C_4H_9)_4N]_3PMo_{12}O_{40}$,[5)] $[(C_4H_9)_4N]_2W_6O_{19}$,[6)] and $[(C_2H_5)_4N]_3PW_{12}O_{40}$ 7) were prepared according to the literatures.

The X-ray absorption spectra of Mo K-edge and W L_{III}-edge were obtained at BL 7C of the 2.5 GeV storage ring of Photon Factory of the National Laboratory for High Energy Physics (KEK). A Si(111) double monochromator was used. The solid samples were powdered and loaded on adhesive tapes.

According to the data obtained from X-ray structure analysis, molybdenum in MoO_4^{2-} compound coordinates to four oxygen atoms in which Mo-O distances are 1.75-1.78 Å.8) $Mo_7O_{24}^{6-}$ 9) and $Mo_6O_{19}^{2-}$ 10) compounds are composed of seven and six MoO_6 distorted octahedra, respectively. The octahedra have terminal oxygen (double bond, ca.1.68 Å for Mo-O distance in $Mo_6O_{19}^{2-}$ compound10) and ca.1.71-1.76 Å in $Mo_7O_{24}^{6-}$ compound9)) and bridging oxygen atoms (with 1.86-2.01 Å and 2.32 Å for the Mo-O distances in the former compound and 1.73-2.55 Å for the latter). The ionic radius

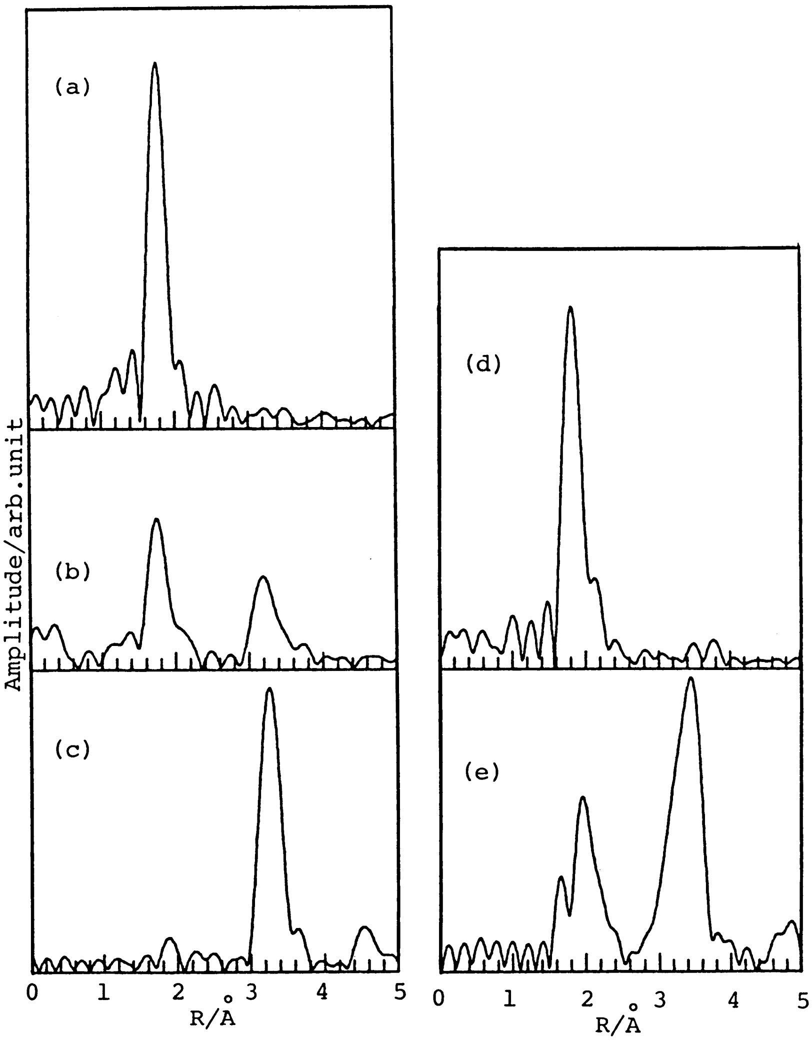

Fig. 1. Fourier transforms of Mo K-edge for (a) $Na_2MoO_4 \cdot 2H_2O$, (b) $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, (c) $[(C_4H_9)_4N]_2Mo_6O_{19}$, and W L_{III}-edge for (d) $Na_2WO_4 \cdot 2H_2O$ and (e) $[(C_4H_9)_4N]_2W_6O_{19}$.

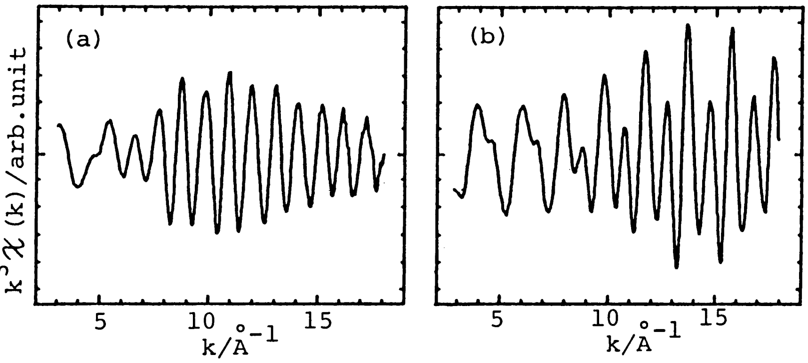

Fig. 2. Extracted oscillations of EXAFS for (a) $[(C_4H_9)_4N]_2Mo_6O_{19}$ and (b) $[(C_4H_9)_4N]_2W_6O_{19}$.

of hexavalent tungsten is similar to that of molybdenum (0.62 Å). Although the interatomic distances are not exactly the same, the geometrical structures of their polynuclear complexes are also quite similar to the corresponding molybdates, respectively.¹¹⁾

Figure 1 shows Fourier transforms of Mo K-edge EXAFS data for MoO_4^{2-} (a), $Mo_7O_{24}^{6-}$ (b), and $Mo_6O_{19}^{2-}$ compound (c), and W L_{III}-edge for WO_4^{2-} (d) and $W_6O_{19}^{2-}$ compound (e). The correction of phase shift and backscattering amplitude was performed by use of the calculated values by Teo and Lee.12) The k-range for Fourier transform is 4-18 $Å^{-1}$. The peak corresponding to Mo-O in MoO_4^{2-} compound is present at 1.77 Å in Fig. 1 (a). For $Mo_7O_{24}^{6-}$ (b), a Mo-Mo peak is present at about 3.20 Å in addition to a Mo-O peak at 1.77 Å. Although the bond lengths for Mo-O or Mo-Mo bonds are distributing in the crystal according to the results of X-ray diffraction analysis,9) each bond gives only single peak in the Fourier transform.

In Fig. 1 (c), we found an unusual phenomenon in Fourier transform spectrum which has never been known in the literature yet. The Mo-O peaks for $Mo_6O_{19}^{2-}$ compound which should appear at somewhere around 1.7 Å, 1.9 Å, and 2.3 Å, are hardly discernible, but a strong peak at 3.26 Å appears corresponding to the oxygen-bridged Mo-Mo distance. Considering from the X-ray structure analysis data, both Mo-O and Mo-Mo peaks for $Mo_6O_{19}^{2-}$ should be stronger than those of more dispersed form for $Mo_7O_{24}^{6-}$. In contrast to the result of the molybdates, the spectra for tungstates are different and quite normal. There are two apparent peaks corresponding to terminal W=O (1.66 Å) and bridging W-O (1.96 Å) bonds in addition to W-W peak (3.45 Å) in Fig. 1 (e). Figure 2 shows the extracted oscillations of EXAFS for $Mo_6O_{19}^{2-}$ (a) and $W_6O_{19}^{2-}$ (b) compounds.

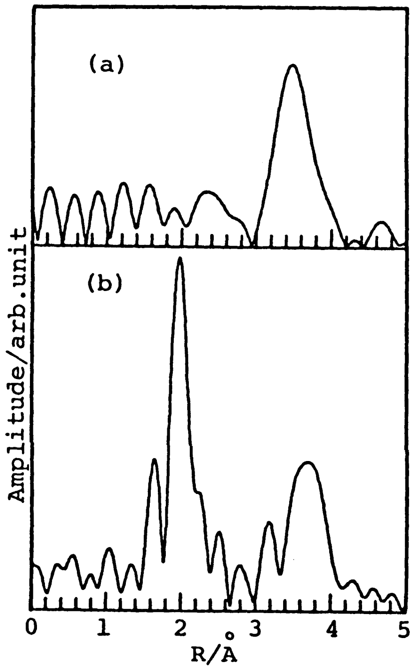

Fig. 3. Fourier transforms of (a) Mo K-edge for $PMo_{12}O_{40}^{3-}$ compound and (b) W L_{III}-edge for $PW_{12}O_{40}^{3-}$ compound.

An analogous phenomenon appears in heteropoly molybdate, $PMo_{12}O_{40}^{3-}$, and tungstate, $PW_{12}O_{40}^{3-}$ as shown in Fig. 3. The W-O peaks appear clearly in the spectrum for $PW_{12}O_{40}{}^{3-}$ but the Mo-O peaks do not for $PMo_{12}O_{40}{}^{3-}$.

Two reasons could be derived for such unusual results, firstly the large Debye-Waller factor for Mo-O bonds and secondly multiple scattering effect. In our preliminary calculation, the multiple scattering effect taking into account Mo-O-Mo atoms is more pronounced in rather high k-range (10-17 $Å^{-1}$) for $Mo_6O_{19}{}^{2-}$ model than $Mo_7O_{24}{}^{6-}$ model. The further detailed analysis is now under the investigation.

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