934 © *1989 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **62**, 934—935 (1989) [Vol. 62, No. 3

# XPS Study of Binuclear Mo(V) Complexes with Di-μ-oxo, μ-Oxo-μ-sulfido, and Di-μ-sulfido Bridges

Hideaki Takahashi,† Takashi Shibahara,†† and Yoshihisa Yamamoto*
Faculty of Pharmaceutical Sciences, Higashi Nippon Gakuen University,
Ishikari-Tobetsu, Hokkaido 061-02
†Faculty of Engineering, Hokkaido University, Sapporo 060
††Department of Chemistry, Okayama University of Science, 1-1 Ridai-cho, Okayama 700

(Received August 4, 1988)

**Synopsis.** X-Ray photoelectron spectroscopy (XPS) was applied to three binuclear molybdenum(V) complexes of di-μ-oxo-, μ-oxo-μ-sulfido-, and di-μ-sulfido-bis[(cysteinato)-oxomolybdate(V)]$^{2-}$, $[Mo_2(\mu\text{-}O)_x(\mu\text{-}S)_yO_2(cys)_2]^{2-}$ ($x=2$, $y=0$; $x=y=1$; and $x=0$, $y=2$), and the electronic state for Mo atom of the $(\mu\text{-}O)_2$ bridge, (μ-O, μ-S) bridge and $(\mu\text{-}S)_2$ bridge complexes was studied. It has been found that the binding energy of the Mo $3d_{5/2,3/2}$ peaks shifts to a lower value by at most 0.5 eV with increasing the number of μ-S bridges from 0 to 2. On the other hand, those of O 1s, C 1s, N 1s, and S 2s peaks are not significantly affected by bridge substitution. The change in the electronic state of Mo atoms is discussed in terms of the low electronegativity of the S atom.

The structures of binuclear molybdenum(V)–cysteine complexes with oxo and sulfide bridges, $[Mo_2(\mu\text{-}X)(\mu\text{-}Y)O_2(cys)_2]^{2-}$ (X,Y=O or S, cys: $SCH_2CH(NH_2)CO_2$), have been examined though X-ray analyses (Fig. 1) by several investigators, Knox et al.[1] have determined the structure of $Na_2[Mo_2(\mu\text{-}O)_2O_2(cys)_2]\cdot 2H_2O$ (abbreviation: $(\mu\text{-}O)_2$ bridge), Brown et al.[2] have dealt with $Na_2[Mo_2(\mu\text{-}S)_2O_2(cys)_2]\cdot 5H_2O$ (abbreviation: $(\mu\text{-}S)_2$ bridge), and Shibahara et al.[3] have elucidated the structure of $Ca[Mo_2(\mu\text{-}O)(\mu\text{-}S)O_2(cys)_2]\cdot 3H_2O$ (abbreviation: (μ-O)(μ-S) bridge). A comparison of data between $(\mu\text{-}O)_2$ and $(\mu\text{-}S)_2$ bridge complexes for the structure allows us to recognize that a complex with a $(\mu\text{-}S)_2$ bridge has longer distances between Mo–Mo and Mo–$O_{cys}$, and a shorter distance between Mo–$O_t$ than does a complex with a $(\mu\text{-}O)_2$ bridge. This may be due to a difference in the electronic state of Mo atoms between these two complexes.

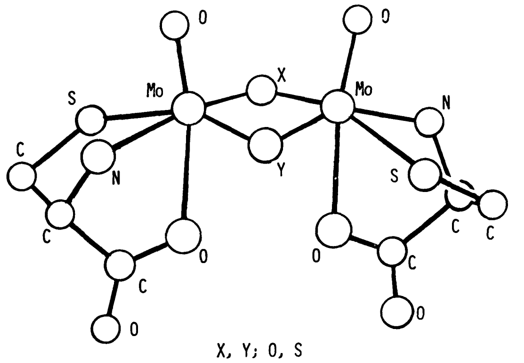

Fig. 1. The structure of $[Mo_2(\mu\text{-}X)(\mu\text{-}Y)O_2(cys)_2]^{2-}$.

The present paper deals with the electronic state of the $(\mu\text{-}O)_2$ bridge, the (μ-O)(μ-S) bridge and $(\mu\text{-}S)_2$ bridge complexes by XPS measurements.

## Experimental

**Preparation of Complexes.** $Na_2[Mo_2(\mu\text{-}O)(\mu\text{-}O)O_2(cys)_2]\cdot 5H_2O$, $Na_2[Mo_2(\mu\text{-}O)(\mu\text{-}S)O_2(cys)_2]\cdot 4H_2O$ and $Na_2[Mo_2(\mu\text{-}S)(\mu\text{-}S)O_2(cys)_2]\cdot 5H_2O$ were prepared according to published procedures.[4]

**Measurements.** XPS measurements were carried out in a vacuum of around $1.3\times10^{-7}$ Pa with irradiation of Mg *Kα* X-rays ($h\nu=1253.6$ eV) to the sample mounted on a holder with Au-mesh, using a VG ESCA 3 electron spectrometer. The binding energes ($E_B$) of all peaks was corrected by taking the kinetic energy ($=h\nu-E_B$) of the Na KLL Auger peak to be 990.0 eV, in order to avoid any ambiguity in accurately determining the value of $E_B$ of broad C 1s peaks.

## Results and Discussion

In spectra for $Na_2[Mo_2(\mu\text{-}O)(\mu\text{-}O)O_2(cys)_2]\cdot 5H_2O$, $Na_2[Mo_2(\mu\text{-}O)(\mu\text{-}S)O_2(cys)_2]\cdot 4H_2O$, and $Na_2[Mo_2(\mu\text{-}S)(\mu\text{-}S)O_2(cys)_2]\cdot 5H_2O$, there appeared to be O 1s, C 1s, N 1s, S 2p, S 2s, Mo $3d_{5/2}$, Mo $3d_{3/2}$, Mo $3p_{3/2}$, and Mo $3p_{1/2}$ ESCA-peaks and O(KLL), and Na(KLL) Auger-peaks. The binding energy ($E_B$) and the full width at half

Table 1. Binding Energy ($E_B$)[a] and Full Width at Half Maximum (FWHM)[b] of Peaks Obtained for Binuclear Molybdenum(V)–Cysteine Complexes

| Complex | | C 1s | O 1s | S 2p | N 1s | Mo 3d | | Mo 3p | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 5/2 | 3/2 | 3/2 | 1/2 |
| $Na_2[Mo_2(\mu\text{-}O)(\mu\text{-}O)O_2(cys)_2]\cdot 5H_2O$ | $E_B$ (eV) | 285.2 | 531.5 | 162.4 | 400.0 | 231.3 | 234.4 | 397.2 | 414.7 |
| | FWHM (eV) | 3.4 | 2.7 | 2.8 | 2.5 | 3.0 | 2.4 | 3.4 | 3.3 |
| $Na_2[Mo_2(\mu\text{-}O)(\mu\text{-}S)O_2(cys)_2]\cdot 4H_2O$ | $E_B$ (eV) | 285.2 | 531.6 | 162.4 | 400.2 | 231.2 | 234.4 | 396.9 | 414.5 |
| | FWHM (eV) | 3.2 | 2.6 | 2.7 | 2.6 | 3.0 | 2.2 | 3.8 | 3.4 |
| $Na_2[Mo_2(\mu\text{-}S)(\mu\text{-}S)O_2(cys)_2]\cdot 5H_2O$ | $E_B$ (eV) | 285.4 | 531.6 | 162.3 | 400.1 | 230.8 | 233.9 | 396.6 | 414.3 |
| | FWHM (eV) | 3.3 | 2.6 | 2.6 | 2.7 | 2.8 | 2.0 | 3.7 | 3.4 |

a) The value of $E_B$ for all peaks was corrected by using the kinetic energy of Na KLL Auger peak to be 990.0 eV.
b) The value of FWHM for N 1s, Mo $3d_{5/2}$, Mo $3d_{3/2}$, and Mo $3p_{3/2}$ was obtained by a peak deconvolution with computer analysis.

maximum (FWHM) of the ESCA-peaks are shown in Table 1. All of the examined complexes have relatively broad C 1s peaks, because of a difference in $E_B$ of C 1s between hydrocarbon and carbonyl group in the cysteine ligand. Each complex shows relatively sharp peaks of N 1s, O 1s, and S 2p; these peaks have similar values of $E_B$ and FWHM. This suggests that the O and S atoms included in a different functional group have similar electronic states, and that the electronic states of N, O, and S atoms are not significantly affected by bridge substitution.

The binding energy of Mo $3d_{5/2}$ and Mo $3d_{3/2}$ peaks for the $(\mu\text{-S})_2$ complex is lower by about 0.4 and 0.5 eV than those for the $(\mu\text{-O})(\mu\text{-S})$ and $(\mu\text{-O})_2$ complexes, respectively, and Mo $3p_{3/2,1/2}$ peaks also show about 0.3 eV of chemical shift to the lower binding energy side by substituting $(\mu\text{-S})_2$ for a $(\mu\text{-O})_2$ bridge.[5] This strongly suggests that the electron density for Mo atoms in a $(\mu\text{-S})_2$ complex is higher than that in $(\mu\text{-O})(\mu\text{-S})$ and $(\mu\text{-O})_2$ complexes. The lower electronegativity of the S atom, compared with that of the O atom, could make the electron density for Mo atoms higher, leading to an enhancement of the covalent bonding characteristics of the bridge.

Recently, similar effects of the S atom have been reported for other type of complexes. Ikari et al.[6] examined $[M_2(\mu\text{-X})(\mu\text{-Y})O_2(\text{edta})]^{2-}$ complexes (M: Mo or W; X, Y: O or S) by XPS. They reported that $E_B$ of Mo $3d_{5/2}$ peak for the $(\mu\text{-O})(\mu\text{-S})$ complexes is lower by 1.2 eV than that for the $(\mu\text{-O})_2$ complex, and that W $4f_{7/2}$ peak shifts 1.1 eV lower by substituting $(\mu\text{-S})_2$ bridge for $(\mu\text{-O})_2$ bridge. Shibahara et al.[7] showed a decrease of ca. 2 eV in $E_B$ of the Mo $3d_{5/2}$ peak by replacing O-bridge with S-bridge for $[Mo_3O_{4-n}S_n(NCS)_9]^{5-}$ ($n$=0—3). Ansari et al.[8] reported that $E_B$ of W $4d_{5/2}$ for $[W_2O_2(\mu\text{-S})_2(S_2CNEt_2)_2]$ is higher by 0.5 eV than that for $[W_2S_2(\mu\text{-S})_2(S_2CNEt_2)_2]$. The chemical shift of the Mo 3d peak observed in this investigation by the bridge substitution seems to be smaller than that reported for the other type of complexes stated above. Thus, the electronic state of the central metal atoms can be appreciably affected by the electronic effect, steric effect, coordination number or configuration of the coordinated ligands in complexes.

## References

1) J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, **25**, 1857 (1969).

2) D. H. Brown and J. A. D. Jeffreys, *J. Chem. Soc., Dalton Trans.*, **1973**, 732.

3) T. Shibahara, H. Kuroya, K. Matsumoto, and S. Ooi, *Bull. Chem. Soc. Jpn.*, **60**, 2277 (1987).

4) V. R. Ott, D. S. Swieter, and F. A. Schultz, *Inorg. Chem.*, **16**, 2538 (1977), and references therein.

5) The lower chemical shift in Mo $3p_{3/2,1/2}$ peaks compared with that in Mo $3d_{5/2,3/2}$ peaks may be due to a less effect of charge density change for Mo atom on $E_B$ of the more inner orbital of Mo.

6) S. Ikari, Y. Sasaki, and T. Ito, *Inorg. Chem.*, in press.

7) T. Shibahara, H. Tsuru, and H. Kuroya, *Inorg. Chim. Acta*, **150**, 167 (1988). The following values (eV) of $E_B$ of Mo $3d_{5/2}$ were obtained: $[Mo_3(\mu_3\text{-O})(\mu\text{-O})_3(NCS)_9]^{5-}$, 231.8; $[Mo_3(\mu_3\text{-S})(\mu\text{-O})_3(NCS)_9]^{5-}$, 229.8; $[Mo_3(\mu_3\text{-S})(\mu\text{-O})_2(\mu\text{-S})(NCS)_9]^{5-}$, 229.6; $[Mo_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})_2(NCS)_9]^{5-}$, 229.5; $[Mo_3(\mu_3\text{-S})(\mu\text{-S})_3(NCS)_8(H_2O)]^{4-}$, 229.2.

8) M. A. Ansari, J. Chandrasekaran, and S. Sarkar, *Bull. Chem. Soc. Jpn.*, **61**, 2265 (1988).