XPS Spectra of Incomplete Cubane-type Cluster with $Mo_3O_{4-n}S_n^{4+}$ Core ($n = 0–4$)

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Preparation, structure, and properties of incomplete cubane-type cluster complexes with [1] and without [2] sulfur bridge(s) have been published and it has been shown that the substitution of sulfur(s) for oxygen(s) in the bridge(s) causes red-shifting of the absorption peak of the electronic spectrum in the visible region and lengthening of Mo–Mo distances.

We now report the XPS spectral change on the introduction of sulfur(s) into the incomplete cubane-type core. Although several XPS studies on molybdenum complexes have been made [3], nothing has been discussed on the change of Mo-$3d_{5/2}$ (or -$3d_{3/2}$) binding energies by the introduction of sulfur(s) into the bridge(s).

Aqua ions, $Mo_3O_{4-n}S_n(aq)^{4+}$ (**A**$_n$; $n = 0–4$), were prepared by the published procedures [1a–d], while the thiocyanato complexes, $[Mo_3O_{4-n}S_n(NCS)_9]^{5-}$ (**B**$_n$; $n = 0–3$) and $[Mo_3S_4(NCS)_8(H_2O)]^{4-}$ (**B**$_4$) were prepared as follows. To **A**$_n$ (*ca.* 0.05 M per trimer in 2 M HCl) was added solid KSCN so as to make its concentration one molar. Then, the resultant solution was heated at *ca.* 40 °C for 1 h. Addition of pyridine to the solution gave crystals[**] of **B**$_n$ ($n = 0–4$) as pyridinium salts.

XPS measurements were carried out on a Shimadzu ESCA-850 electron spectrometer using the Mg Kα (1253.6 eV) radiation taking carbon ($1s_{1/2}$) binding energy (285.0 eV) as standard[†]. A sample dissolved in acetone was put onto a sample table, dried and transferred into the photo-emission chamber of the apparatus. The peak positions of the binding energies of Mo-$3d_{5/2}$ and Mo-$3d_{3/2}$ are shown in Fig. 1. It can be seen that, as the number of sulfur in the $Mo_3O_{4-n}S_n$ core increases, the binding energies of Mo-$3d_{5/2}$ and Mo-$3d_{3/2}$ decrease. This can be qualitatively explained by the difference of electronegativity between oxygen and sulfur; oxygen, the electronegativity of which is larger than that of sulfur, attracts electrons of molybdenum to itself more than sulfur does, consequently making molybdenum rather positive with the result that electrons are harder to remove from molybdenum. Introduction of one sulfur into the core gives rise to a shift relatively large as compared to ones in the case of introducing two to four sulfurs. The first sulfur occupies the μ_3 position, while the second to fourth take μ_2 positions; this may account for the cause of the phenomenon. However, electronic spectral change on the formation of μ_3-S is only slight when compared to the case of μ_2-S [1a–d]; more elaborate studies are required for a consistent answer to these problems.

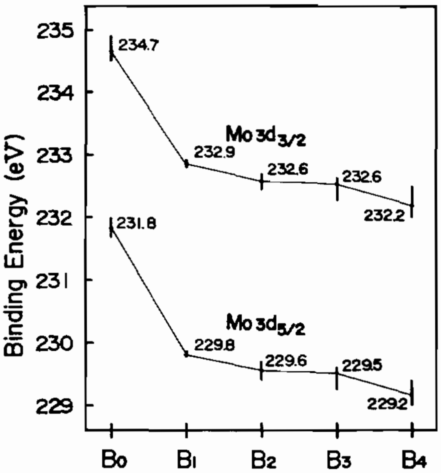

Fig. 1. Dependence of the Mo-$3d_{5/2}$ and Mo-$3d_{3/2}$ binding energies on the number of sulfurs in the $Mo_3O_{4-n}S_n$ core $n = 0–4$).

Positions of the binding energies of S-2p of NCS^- and the $Mo_3O_{4-n}S_n$ core overlap each other. Our attempts to separate the overlapped bands into the components with a reasonable intensity ratio were unsuccessful.

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[**] Found (calc.): N, 15.11(15.16); C, 31.48(31.58); H, 2.40(2.49) for $(pyH)_5B_0 \cdot H_2O$; N, 14.81(14.78); C, 30.03(30.77); H, 2.42(2.58) for $(pyH)_5B_1 \cdot 2H_2O$; N, 14.58(14.59); C, 29.95(30.40); H, 2.28(2.55) for $(pyH)_5B_2 \cdot 2H_2O$; N, 14.52(14.43); C, 29.77(30.04); H, 2.39(2.52) for $(pyH)_5B_3 \cdot 2H_2O$; N, 13.26(13.01); C, 25.17(26.04); H, 1.80(2.65) for $(pyH)_4B_4 \cdot 4H_2O$.

[†] It was impossible to separate the C-$1s_{1/2}$ band of pyridinium carbon from that of thiocyanate carbon and the peak position of the band was taken as standard.

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