Determination of Oxidation States of Pt in mixed-metal Clusters by X-ray Emission Spectroscopy

S. Nanao[a,3303], Y. Watanabe[a,3323], H. Hayashi[b,7277], N. Kawamura[c,1205], Y. Udagawa[b,7366], and Y. Mizobe[a]

[a]IIS, Univ. of Tokyo, [b]Tohoku Univ. [c]JASRI

The molecular mixed-metal clusters have been attracting significant attention in relevance of synthesizing catalysts and metalloenzymes. Sulfido-bridged mixed metal complexes having a $Pt(\mu\text{-}S)_2WS$ core are the basic compounds of them and Pt is the most important metallic element in them. The valence number of Pt, however, is still unknown.

The objective of the present study is to estimate the valence number of Pt in the sulfido-bridged mixed metal complexes by x-ray emission spectroscopy at Pt $L\alpha_1$.

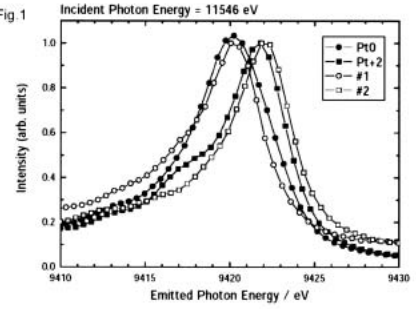
The measurements were performed at BL47U using x-ray emission spectrometer designed by the present authors (Tohoku Univ. group). The samples are $[NEt_4][Tp^*WS_3Pt(PPh_3)]$ and $[NEt_4][Tp^*WS_3PtCl_2]$, which are denoted in this report as #1 and #2, respectively. The structures are shown in ref. 1.

The spectra of $[Pt\ Cl_2(PPh_3)_2]$, $[Pt\ (PPh_3)_3]$ were also measured as references. $[Pt\ Cl_2(PPh_3)_2]$ and $[Pt\ (PPh_3)_3]$ are denoted as Pt+2 and Pt0, respectively. The valence number of them are known as +2 and 0, respectively.

Figure 1 shows a portion of the emission spectra for the incident x-rays of 11.546 keV. These spectra and others indicate the valence numbers of Pt for the samples #1 and #2 are 0 and +2, respectively.

Interesting dependence of the spectra on the incident x-ray energy has been found. The analyses in detail are in progress.

Fig.1



1) Preparation of Mononuclear Tungsten Tris(sulfide) and Molybdenum Sulfido-Tetrasulfido Complexes with Hydridotris(pyrazolyl)borate Coligand and Conversion of the Former into Sulfido-Bridged Bimetallic Complex Having $Pt(\mu\text{-}S)_2WS$ core, H.Seino, Y.Arai, N.Iwata, S.Nagao, Y.Mizobe and M.Hidai, Inorganic Chem. **40**, 1677-1682(2001).

Analysis of molecular composition and imaging of *Nanobacteria.*

Kumon* Hiromi (8523)[1], Tomochika Ken-ichi (8531)[2], Uesugi Ken-tarou (1544)[3], and Yagi Naoto (1129)[3]

1. Okayama Univ., 2. Okayama Gakuin Univ. 3. Spring-8 / JASRI

Urinary stone-like precipitates derived from a long culture of several strains of *Nanobacteria*-like organisms (NLO) and packed single cells of NLO were analyzed by a high resolution monochrome X-ray CT. CT images of stone-like precipitates were obtained at resolution power of about 1 mm. Despite the average size of single culture cells (less than 1 mm), the packed cells collected by centrifugation were visible. However, clear CT images of packed cells in a glass capillary tube were not obtained. We need to develop a more suitable method of sample preparation for NLO analysis.