Systematically Observation of Electronic States for Sulfur-hexacoordinating Nickel Complexes by X-ray Absorption Spectroscopy

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Recently synthesized Rh-Ni trinuclear complexes hexacoordinated with sulfur ions, 3-aminopropanethiolate (apt) metalloligand [Ni{Rh(apt)3}2](NO3)n (n = 2, 3, 4), are found to be chemically interconvertible between Ni2+ and Ni4+ [1]. S K-edge X-ray absorption spectroscopy (XAS) indicates that the Ni ions have hybridization with sulfur ions. In addition, this effect depends on n [2]. On the other hand, Furthermore, new synthesized Ir-Ni trinuclear complexes hexacoordinated with sulfur ions from Rh(L)3 metalloligand (L = aminothiolate ligand) are also found to be chemically interconvertible between Ni2+ and Ni4+. In order to clarify the electronic states of their interconvertible nature of Ni ions from the physical point of view, we have systematically investigated the electronic structures of Ir-Ni trinuclear complexes by means of S K-edge XAS.

The XAS measurements were carried out at BL-10 of Synchrotron Radiation Center in Ritsumeikan University, Japan. The S K-edge XAS spectra were taken simultaneously in the total electron yield (TEY) and partial fluorescence yield (PFY) modes with a photon energy resolution of ∼1 eV.

These micro-crystal samples were thinly expanded on the conductive carbon tape attached on the sample holder in the air before transferring them into the vacuum chamber. We repeatedly measured the spectra on the same and different sample positions, confirming the data reproducibility with neither serious radiation damage nor sample-position dependence of the S K-edge XAS spectra. Photon energy was calibrated by the top of the S K-edge peak of K2SO4 (2481.7 eV). All measurements were performed at room temperature.

Figure 1 shows the S K-edge XAS spectra for Rh-Ni trinuclear complexes in the TEY mode. The S K-edge XAS spectra for Rh-Ni trinuclear complexes [Ni{Rh(apt)3}2](NO3)n (n = 2, 3, 4) and [Ni{Rh(aet)3}2](NO3)2 are also shown. The characteristic spectral peaks at 2473 eV, 2476 eV, and 2480 eV were observed. In particular, the peak at 2473 eV was shifted to higher photon energy with increasing n. Comparing with the S K-edge XAS studies for [Ni{Rh(apt)3}2](NO3)n [2], show that the spectral peaks at 2473 eV, 2476 eV, and 2480 eV are the S 1s→C-coordinating S π bonding transition originating from the apt molecules and the S 1s→S 4p transitions respectively. On the other hand, the observed peak at 2470 eV is independent of n and developed with increasing n. This peak corresponds to the singly occupied molecular orbital (SOMO), which indicates that there is hybridization between Ni and S ions. The larger intensity of SOMO for Ir-Ni trinuclear complexes than that of [Ni{Rh(apt)3}2](NO3)n clearly shows that the molecular structure for Ir-Ni trinuclear complexes is more stable as the [NiS6]2-n cluster under the octahedral-like symmetry than that of [Ni{Rh(apt)3}2](NO3)n.

References

Fig. 1 The S K-edge XAS spectra of Ni trinuclear complexes in the TEY mode at room temperature.