Systematically Observation of Hybridization Effects for Sulfur-coordinating Nickel Complexes by Soft X-ray Absorption Spectroscopy

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Recently synthesized Rh-Ni trinuclear complexes hexacoordinated with sulfur ions, 3-aminopropanethiolate (apt) metalloligand $[\mathrm{Ni}\{\mathrm{Rh(apt)_3}\}_2](\mathrm{NO_3})_n$ (n = 2, 3, 4), are found to be chemically interconvertible between Ni^{2+} and Ni^{4+} [1]. Furthermore, new synthesized Ir-Ni trinuclear complexes hexacoordinated with sulfur ions from $\mathrm{Rh(L)_3}$ metalloligand (L = aminothiolate ligand) are also found to be chemically interconvertible between Ni^{2+} and Ni^{4+}. In order to clarify the origins of their interconvertible nature and the stability of such a high oxidation state as the tetravalency from the physical point of view, we have systematically investigated the local 3*d* electronic structures of Ir-Ni trinuclear complexes as well as the Rh-Ni and Rh-Co trinuclear complexes hexacoordinated with sulfur ions, 2-aminoethanethiolate (aet) and apt metalloligand $[\mathrm{Ni}\{\mathrm{Rh(aet)_3}\}_2](\mathrm{NO_3})_2$. $[\mathrm{Co}\{\mathrm{Rh(aet)_3}\}_2](\mathrm{NO_3})_2$ by means of soft X-ray absorption spectroscopy (XAS).

The XAS measurements were carried out at BL-11 of Synchrotron Radiation Center in Ritsumeikan University, Japan. The Ni and Co $L_{2,3}$-edge XAS spectra were taken simultaneously in the total electron yield (TEY), partial fluorescence yield (PFY), and partial electron yield (PEY) modes with a photon energy resolution of ~500 meV.

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 $L_{2,3}$-edge XAS spectra. Photon energy was calibrated by the top of the L_3-edge peak of $\mathrm{LiCoO_2}$ (780.2 eV) and NiO (854.0 eV) respectively. All measurements were performed at room temperature.

Figure1 shows the Ni $L_{2,3}$-edge XAS spectra for Ir-Ni trinuclear complexes, $[\mathrm{Ni}\{\mathrm{Rh(apt)_3}\}_2](\mathrm{NO_3})_n$ (n = 2, 3, 4) and $[\mathrm{Ni}\{\mathrm{Rh(aet)_3}\}_2](\mathrm{NO_3})_2$ in the PEY mode which is the most reliable for the quantitative discussion even though it is relatively surface sensitive reported by the previous XAS studies [2]. Since the edge jump at L_3-edge is shifted to the high Photon Energy side, the covalency of Ni ions of Ir-Ni trinuclear complexes is 2+, 3+ and 4+, respectively. On the other hand, as with $[\mathrm{Ni}\{\mathrm{Rh(apt)_3}\}_2](\mathrm{NO_3})_n$ and $[\mathrm{Ni}\{\mathrm{Rh(aet)_3}\}_2](\mathrm{NO_3})_2$, a satellite structure reflecting the hybridization effects between Ni and sulfur ions can be observed. We considered that these effects are different from $[\mathrm{Ni}\{\mathrm{Rh(apt)_3}\}_2](\mathrm{NO_3})_n$ and $[\mathrm{Ni}\{\mathrm{Rh(aet)_3}\}_2](\mathrm{NO_3})_2$ because the spectral shape including in the satellite structure is different.

References

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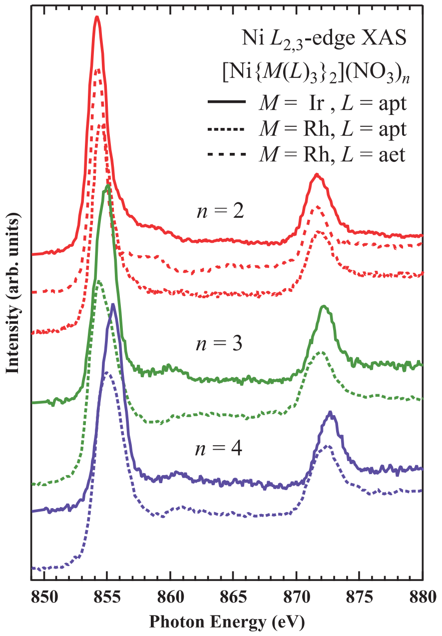

Fig. 1 The Ni $L_{2,3}$-edge XAS spectra of Ni trinuclear complexes in the PEY mode at room temperature.