Soft X-ray core-level absorption study of Ni-based trinuclear complexes [Ni{Rh(apt)$_3$}$_2$](NO$_3$)$_n$ (n = 2, 3, 4)

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The Ni-Rh trinuclear complexes with 3-aminopropanethiolate (apt) [Ni{Rh(apt)$_3$}$_2$](NO$_3$)$_n$ (n = 2, 3, 4) have been successfully synthesized as a valence interconversion system [Fig.1(a)] [1]. The nickel ions are in an octahedral coordination with six sulfur ions. The chemical analysis indicates that the Ni ions in [Ni{Rh(apt)$_3$}$_2$](NO$_3$)$_n$ are stable as a HS-Ni^{2+} (d^8) state for n = 2, a LS-Ni^{3+} (d^7) state for n = 3, and a LS-Ni^{4+} (d^6) state for n = 4, respectively.

The importance of hybridization effects between the transition-metal (TM) and sulfur ions in inorganic sulfides for their physical properties have conventionally been recognized because of the fact that the radial distribution of S 3p orbital is larger than that of O and N 2p orbitals. Actually, the hybridization effects in NiS and NiS$_2$ have been reported on the basis of Ni 2p core-level photoemission and Ni $L_{2,3}$-edge x-ray absorption (XAS) [2,3]. However, the direct verifications of the local Ni 3d electronic states in [Ni{Rh(apt)$_3$}$_2$](NO$_3$)$_n$ are still lacking. We have thus examined the 3d electronic states of [Ni{Rh(apt)$_3$}$_2$](NO$_3$)$_n$ probed by the Ni $L_{2,3}$-edge XAS.

The Ni $L_{2,3}$-edge XAS measurements were carried out at BL-11 of Synchrotron Radiation Center in Ritsumeikan University, Japan. The Ni $L_{2,3}$-edge XAS spectra were taken in the partial electron yield (PEY) with a photon energy resolution of about 600 meV. In the PEY mode, we applied the voltage of 550 V to the Au mesh, installed in the front of microchannel plate (MCP), for the Ni $L_{2,3}$-edge measurements in order to suppress a strong background caused by the C, N and O K-edge absorptions in the spectra [4].

We have also performed spectral simulations of a [NiS$_6$]$^{12-n}$ configuration-interaction cluster model under the O_h symmetry by using the XTLS 9.0 program [5]. We have reproduced the Ni $L_{2,3}$-edge XAS spectra by optimizing the charge transfer energy from S 3p to Ni 3d orbitals: Δ and the hybridization strength described as a Slater-Coster parameter: $(pd\sigma)$.

Figure 1(b) shows the Ni $L_{2,3}$-edge XAS spectra of [Ni{Rh(apt)$_3$}$_2$](NO$_3$)$_n$. The satellite structure, which reflects the explicit hybridization effects between the Ni 3d and S 3p orbitals, has been observed at higher photon energy side of ~ 6 eV in all complexes. Simulated XAS spectra by the cluster model are also shown in Fig. 1(b), by which the hybridization parameters in Table 1 have been optimized. We have found that a so-called negative charge-transfer-energy ($\Delta < 0$) state is realized for n = 4, in which the total energy of the d^{7}L state is lower than that of the d^6 state (L stands for a hole in the sulfur sites).
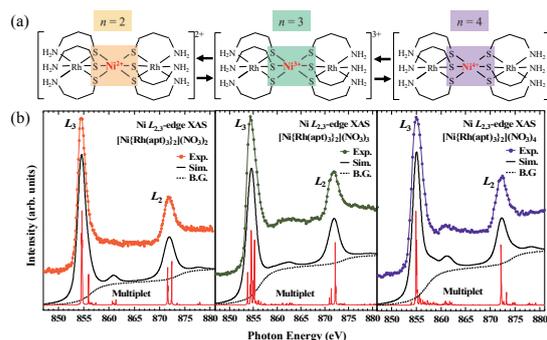
Fig. 1 (a) Molecular structure of [Ni{Rh(apt)$_3$}$_2$](NO$_3$)$_n$. (b) Ni $L_{2,3}$-edge XAS spectra and spectral simulations of [Ni{Rh(apt)$_3$}$_2$](NO$_3$)$_n$.

Table 1 Hybridization parameters obtained by the cluster-model calculations.

	n = 2	n = 3	n = 4
Δ	3.5 eV	1.0 eV	**-4.0 eV**
$(pd\sigma)$	1.2 eV	**1.8 eV**	0.9 eV

References

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