The hybridization effects in NiS and NiS$_2$ have larger than that of O and N$_2$ p in inorganic sulfides for their physical properties between the transition-metal (TM) and sulfur ions. However, the direct verifications and O suppress a strong background caused by the C, N applied the voltage of 550 V to the Au mesh, resolution of about 600 meV. In the PEY mode, we electron yield (PEY) with a photon energy (3) Synchrotron Radiation Center, Ritsumeikan University, Kusatsu, Shiga 525-0058, Japan.

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The Ni-Rh trinuclear complexes with 3-aminopropanethiolate (apt) [Ni{Rh(apt)$_3$}]$_2$$(NO_3)_n$ ($n = 2, 3, 4$) have been synthesized as a valence interconversion system [Fig.1(a)] [1]. The nickel ions are in an octahedral coordination with six sulfur ions. The chemical analysis indicates that the Ni ions in [Ni{Rh(apt)$_3$}]$_2$$(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$_3$]$_{12-n}$ configuration-interaction cluster model under the $O_n$ 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: $\Delta$ and the hybridization strength described as a Slater-Coster parameter: ($\Delta_{pd}$).

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$^0$L state is lower than that of the d$^0$ state (L stands for a hole in the sulfur sites).

![Fig. 1](image)

(a) Molecular structure of [Ni{Rh(apt)$_3$}]$_2$$(NO_3)_4$.

(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.

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<th>$n$</th>
<th>$\Delta$ (eV)</th>
<th>$\Delta_{pd}$ (eV)</th>
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<td>2</td>
<td>3.5</td>
<td>1.2</td>
</tr>
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<td>3</td>
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<tr>
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**References**


