

X-ray absorption spectroscopy of bis(dithiolene) complexes

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1 Introduction

Metal dithiolene complexes have been extensively investigated for more than half a century [1] because of their unique chemical and physical properties and also variety of applications such as photo energy conversion, non-linear optics, and electronic or photonic devices [2]. Nevertheless, oxidation states of the complexes are still less understood due to redox non-innocent nature of ligands. Therefore in order to investigate the oxidation or chemical states of Ni dithiolene complexes, we used sulfur *K*-edge X-ray absorption spectroscopy (XAS).

2 Experiment

Experiments were performed at beamline BL-27A with an InSb(111) double-crystal monochromator with an energy resolution of ca. 0.8 eV around S *K*-edge. The XAS spectra of polycrystalline TBA[Ni^{III}(mnt)₂] and Ni^{II}(S₂C₂Ph₂)₂ (mnt = maleonitriledithiolate, TBA = tetra n-butyl ammonium, as shown inset of Fig. 1) were measured using monitoring sample drain current near the S *K*-edge (2465–2505 eV) and normalized to the incident flux with thin aluminum films. Such energies were chosen to excite the S 1s core electron to 3*p* and 4*p* unoccupied orbitals.

3 Results and Discussion

Fig. 1 shows S *K*-edge XAS spectra of polycrystalline neutral form of Ni(S₂C₂Ph₂)₂ and one-electron oxidized form of [Ni^{III}(mnt)₂]⁻. Based on previous study [3], peak A is assigned to S 1s → b_{1g}^{*}(Ni 3*d*_{xy}^{*} - L_{xy}) transition. Peak B and C are assigned to S 1s → σ^{*}(S-C-CN) and S 1s → σ^{*}(S-C) transitions, respectively. Peak D is attributed to S 1s → 4*p*. Features of peak A in both samples are resemble in each other but the peak position of [Ni^{III}(mnt)₂]⁻ is slightly shifted to higher energy (~0.3eV) than that of Ni^{II}(S₂C₂Ph₂)₂. This shift would be caused by difference in Ni oxidation states, where effective nuclear charge (Z_{eff}) of Ni is larger for the [Ni^{III}(mnt)₂]⁻.

Although a chemical component [Ni(mnt)₂]⁻ in the TBA[Ni^{III}(mnt)₂] is similar to that in [(n-C₄H₉N)[Ni^{III}(mnt)₂]⁻ [3], it was found that S *K*-edge XAS features are different. Especially, SOMO (Singly Occupied Molecular Orbital) at lower energy position of peak A has not been observed in the TBA[Ni^{III}(mnt)₂]. This suggests that ligand π^{*}contribution in SOMO may be much smaller in the TBA[Ni^{III}(mnt)₂]. However, in general, such different contribution is not plausible for the

same chemicals. Therefore, further consideration is needed to understand this contradiction. Also a low-lying out-of-plane ligand π^{*} orbital corresponding to S 1s → b_{3g}^{*}(L_{yz}) transition emerging between peaks A and B has not been observed, differently from the XAS of the [(n-C₄H₉N)[Ni^{III}(mnt)₂]⁻ [3].

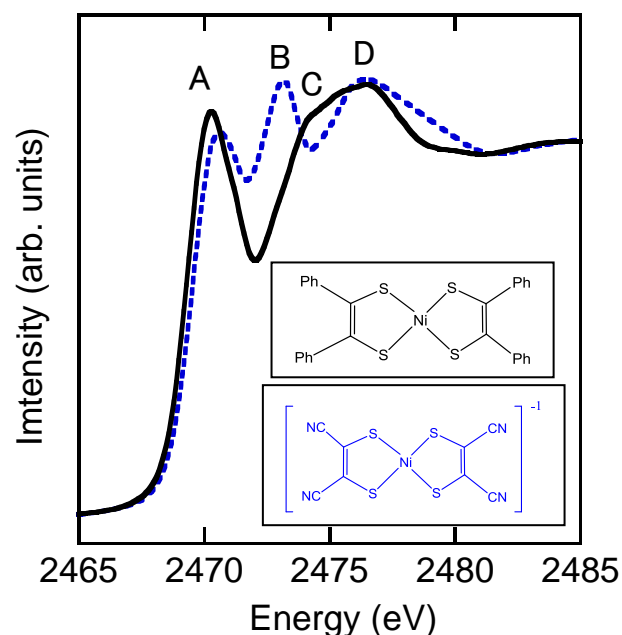


Fig. 1: S *K*-edge XAS spectra of polycrystalline samples of Ni^{II}(S₂C₂Ph₂)₂ (black solid line, black chemical formula) and TBA[Ni^{III}(mnt)₂]⁻ (blue dot line, blue chemical formula).

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References

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