

Strong metal-to-ligand charge transfer bands observed in Ni *K*- and *L*-edge XANES of planar Ni complexes

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Polarized Ni *K*-edge and *L*-edge XANES spectra were measured for some planar Ni complexes with low-spin $3d^8$ configuration, $K_2Ni(CN)_4 \cdot H_2O$, $Ni(Hdmg)_2$ (Hdmg: 2,3-butanedione dioximato) and $[(n-C_4H_9)_4N]_2[Ni(mnt)_2]$ (mnt: 1,2-dicyanovinylene-1,2-dithiolato). In all the spectra, strong satellite bands are found in addition to the lowest Ni $1s, 2p \rightarrow 3d^*$ atomic lines. These are mostly assigned to the metal-to-ligand charge transfer (MLCT) transitions to unoccupied states with dominant ligand π^* components, in good agreement with *ab initio* molecular orbital predictions. The low-lying ligand π^* orbital is essential in interpreting the metal *K*-edge and *L*-edge XANES of $3d$ transition metal compounds.

Keywords: metal-to-ligand charge transfer; XANES; linear polarization dependence; molecular orbital.

1. Introduction

Metal *K*- and *L*-edge XANES spectra of transition metal compounds with π backbonding such as organometallics are difficult to understand because ligand orbitals are covalently combined with metal $3d$ and $4p$ orbitals. The presence of excitation to unoccupied ligand orbitals mixed with metal $4p$ orbitals, namely metal-to-ligand charge transfer (MLCT) transition, was clearly revealed in polarized Ni *K*-edge XANES of $K_2Ni(CN)_4 \cdot H_2O$ (Kosugi *et al.*, 1986). Possibility of the MLCT transition was also discussed in metal *L*-edge XANES (Hitchcock *et al.*, 1990; Rühl *et al.*, 1993; Arrio *et al.*, 1996).

In order to elucidate the MLCT transition more clearly and systematically, we have measured Ni *K*-edge and *L*-edge XANES of some planar Ni complexes, $K_2Ni(CN)_4 \cdot H_2O$, $Ni(Hdmg)_2$ (Hdmg: 2,3-butanedione dioximato) and $[(n-C_4H_9)_4N]_2[Ni(mnt)_2]$ (mnt: 1,2-dicyanovinylene-1,2-dithiolato). These low-spin “ $3d^8$ ” complexes have strong covalency hybridization, and ligand field, resulting in reduction of many-electron effects. The symmetry of the core-excited states is investigated by measuring the polarization dependence of the XANES spectra for their single crystals. The polarized Ni *K*-edge XANES spectra were measured in transmission mode at BL-10B of the Photon Factory. On the other hand, the polarized Ni *L*-edge XANES spectra were measured by total electron yields at BL1A of the UVSOR facility. *Ab initio* quantum chemical calculations were performed by using the GSCF3 code (Kosugi & Kuroda, 1980; Kosugi, 1987).

2. Polarized Ni *K*-edge and *L*-edge XANES of $K_2Ni(CN)_4 \cdot H_2O$

Figure 1(a) shows polarized Ni *K*-edge XANES spectra of $K_2Ni(CN)_4 \cdot H_2O$ (Kosugi *et al.*, 1986) for the electric vector *E* parallel and perpendicular to the molecular *z* axis (*E*//*z* and *E*⊥*z*), which is perpendicular to the $[Ni(CN)_4]^{2-}$ molecular plane (*xy*) of D_{4h} symmetry. A weak feature A and some strong features b_1 , b_2 , *c*, and *d* are observed. Feature A is assigned to a quadrupole

transition to Ni $3d_{x^2-y^2}^*(b_{1g}^*)$. Features b_1 and b_2 observed only in the *E*//*z* spectrum are assigned to dipole-allowed Ni $1s \rightarrow 4p\pi^*$

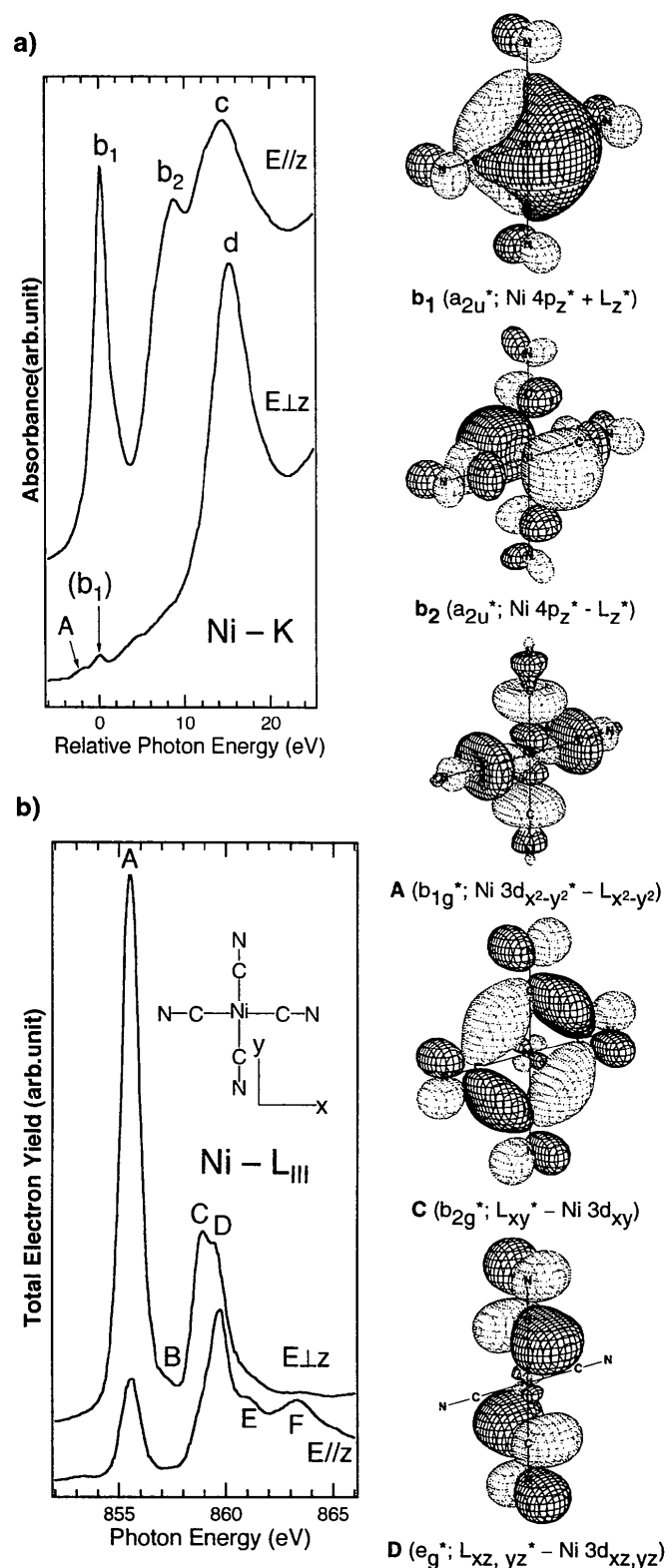


Figure 1

Polarized XANES spectra at (a) the Ni *K*-edge and (b) the Ni *L*-edge of $K_2Ni(CN)_4 \cdot H_2O$ and some molecular orbitals related to XANES.

transitions with MLCT character (Kosugi, 1988, 1996), where the Ni $4p_z^*(a_{2u}^*)$ orbital is split through mixing with the ligand π^* orbital (L_z^*) in in-phase and out-of-phase combinations as $4p_z^*+L_z^*$ and $4p_z^*-L_z^*$, as shown in Fig. 1.

Figure 1(b) shows polarized Ni L -edge XANES of $K_2Ni(CN)_4 \cdot H_2O$. A main peak A and strong satellite bands C and D are observed. The lowest main absorption peak A is assigned to a dipole-allowed transition to Ni $3d_{x^2-y^2}(b_{1g}^*)$ with antibonding character as shown in Fig. 1. Feature A is also observed for the forbidden polarization direction $E//z$; this is because the sample had significant disorder of $[Ni(CN)_4]^{2-}$ due to dehydration under vacuum. Features C and D observed predominantly in the $E \perp z$ and $E//z$ spectra are assigned to in-plane and out-of-plane MLCT transitions, respectively (Hatsui *et al.*, 1998a), where the in-plane excited orbital b_{2g}^* has a dominant in-plane CN π^* (L_{xy}^*) component with a small $3d_{xy}$ contribution, and the out-of-plane excited orbital e_g^* has a dominant CN π^* (L_{xz}, yz^*) component with a small $3d_{xz, yz}$ contribution, as shown in Fig. 1.

3. Polarized Ni K -edge and L -edge XANES of $Ni(Hdmg)_2$

Figure 2(a) shows polarized Ni K -edge XANES spectra in the $E//z$ and $E \perp z$ directions of $Ni(Hdmg)_2$, where the coordinate is chosen as in inset of Fig. 2(b). $Ni(Hdmg)_2$ with D_{2h} symmetry would show trichroism in the dipole transition. However, $Ni(Hdmg)_2$ molecules are rotated by 90° to one another in the single crystal (Williams *et al.*, 1959), and the $E \perp z$ spectrum should be an average of the $E//x$ and $E//y$ spectra. A weak feature A and some strong features b_1 , b_2 , c, and d are observed. Feature A is assigned to a quadrupole transition to Ni $3d_{xy}(b_{1g}^*)$. Features b_1 and b_2 observed only in the $E//z$ spectrum are assigned to dipole-allowed Ni $1s \rightarrow 4p\pi^*$ transition with MLCT character, where the Ni $4p_z^*(b_{1u}^*)$ orbital is split through mixing with the ligand π^* orbital (L_z^*) in in-phase and out-of-phase combinations as $4p_z^*+L_z^*$ and $4p_z^*-L_z^*$, as shown in Fig. 2. Yamashita *et al.* (1989) reported the Ni K -edge XANES of $Ni(Hdmg)_2$ and assigned the band b_1 to Ni $1s \rightarrow 3d_{xy}^*$. Their assignment is, however, unacceptable because the observed polarization dependence indicates that band b_1 is a dipole-allowed $E//z$ transition but neither quadrupole nor $E \perp z$ one such as $1s \rightarrow 3d_{xy}^*$.

Figure 2(b) shows polarized Ni L -edge XANES of $Ni(Hdmg)_2$. A main peak A and strong satellite bands B and D are observed. The lowest main absorption peak A is assigned to the transition to Ni $3d_{xy}(b_{1g}^*)$ with antibonding character as shown in Fig. 2. Features B and D observed predominantly in the $E//z$ spectrum are assigned to out-of-plane MLCT transitions (Hatsui *et al.*, 1998b), where there are two low-lying π^* ligand orbitals, b_{2g}^* (L_{xz}^*) and b_{3g}^* (L_{yz}^*) with small $3d_{xz}$ and $3d_{yz}$ components, as shown in Fig. 2, and the former is lower in energy than the latter.

4. Polarized Ni K -edge and L -edge XANES of $[Ni(mnt)_2]^{2-}$

Figure 3(a) shows polarized Ni K -edge XANES spectra of $[(n-C_4H_9)_4N]_2[Ni(mnt)_2]$ for ($E//x, k//y$), ($E//y, k//x$) and ($E//z, k//x$) directions, where the coordinate is chosen as in inset of Fig. 3(b) and k denotes the wave vector of the incident light. All the $[Ni(mnt)_2]^{2-}$ anions with D_{2h} symmetry are parallel in the single crystal (Kobayashi & Sasaki, 1977); therefore, several polarized spectra are measurable for different polarization directions. Feature A is observed in the ($E//x, k//y$) and ($E//y, k//x$) spectra and is undoubtedly assigned to a quadrupole transition to Ni $3d_{xy}(b_{1g}^*)$. Feature b is observed in the $E//z$ spectrum and is assigned to a dipole-allowed Ni $1s \rightarrow 4p\pi^*$ transition with no MLCT character, as shown in Fig. 3; in contrast to

$K_2Ni(CN)_4 \cdot H_2O$ and $Ni(Hdmg)_2$, there is no splitting of the Ni $1s \rightarrow 4p_z^*(b_{1u}^*)$ transition because of absence of low-lying $b_{1u}^*(L_z^*)$ ligand orbitals combined with Ni $4p_z^*$. On the other hand, weak features c and d are observed in the $E//y$ and $E//x$ spectra, respectively, and are assigned to the MLCT transitions to the in-plane CN π^* (b_{2u}^*, L_y^*) and CN σ^* (b_{3u}^*, L_x^*) orbitals. Noh *et al.* (1997) reported the Ni K -edge XANES spectra of some

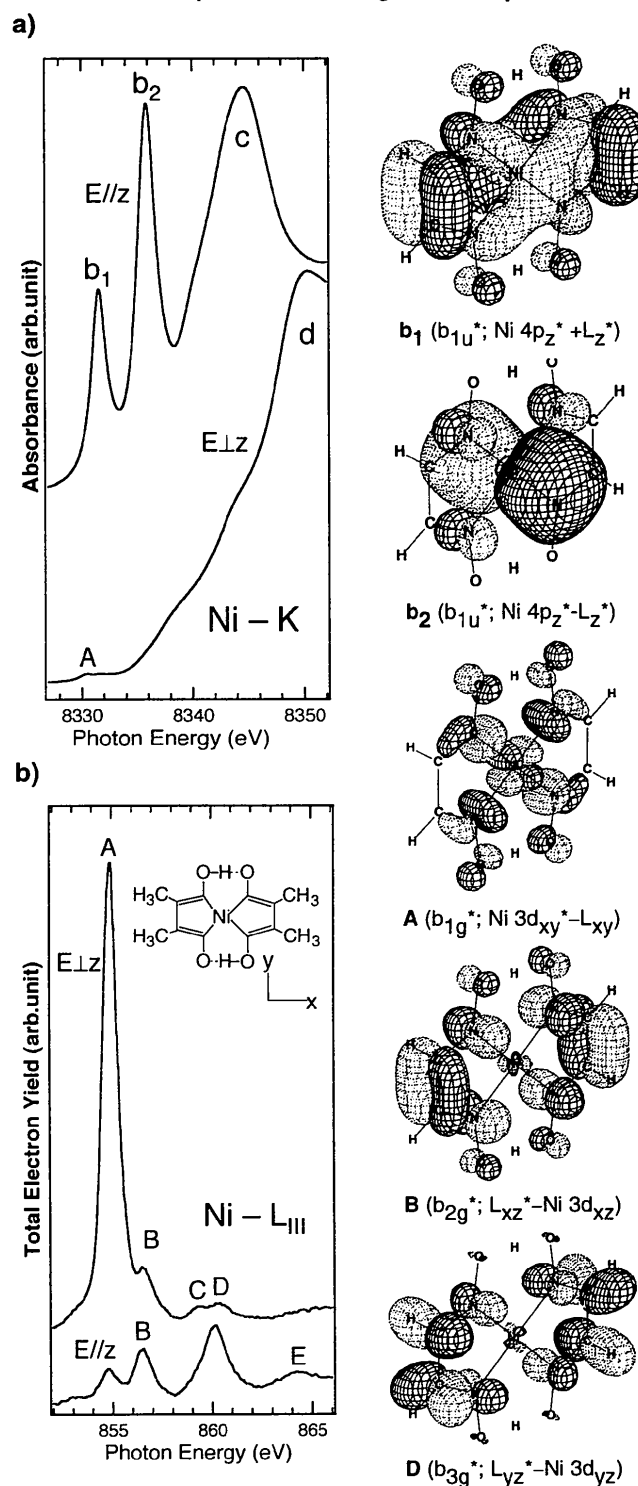


Figure 2
Polarized XANES spectra at (a) the Ni K -edge and (b) the Ni L -edge of $Ni(Hdmg)_2$ and some molecular orbitals related to XANES.

Ni dithiolene complexes and assigned bands b and f to the transitions to $1s^1[3d^{10}L^{-1}]4p_z^{*1}$ and $1s^1[3d^2]4p_z^1$ states with the same symmetry, respectively (L^{-1} stands for a hole in ligand orbital). In Figure 2, however, bands b and f show different polarization dependence, $E//z$ and $E \perp z$, respectively. The assignment reported by Noh *et al.* (1997) is, therefore, incorrect.

Figure 3(b) shows polarized Ni *L*-edge XANES of $[\text{Ni}(\text{mnt})_2]^{2-}$. The lowest main absorption peak A is assigned to the transition to Ni $3d_{xy}^*(b_{1g}^*)$ with antibonding character as shown in Fig. 3. Feature B is very weak in the $E//x$ spectrum and feature C is not observed in the $E//z$ spectrum; it is possible that B and C have $3d_{yz}$ and $3d_{xy}$ or $3d_{x^2-y^2}$ components, respectively. As shown in Fig. 3, there are two low-lying unoccupied ligand orbitals with $b_{3g}^*(L_{yz}^*)$ and $a_g^*(L_{x^2-y^2}^*)$ orbitals; therefore, features B and C can be assigned to MLCT transitions to these orbitals.

5. Conclusion

Polarized Ni *K*-edge and *L*-edge XANES spectra were measured for the planar Ni complexes, $[\text{Ni}(\text{CN})_4]^{2-}$, $\text{Ni}(\text{Hmg})_2$, and $[\text{Ni}(\text{mnt})_2]^{2-}$. All the spectra show strong extra absorption features in addition to the Ni $1s \rightarrow 3d^*$, $4p^*$ and Ni $2p \rightarrow 3d^*$ intra-atomic lines. Based on the observed polarization dependence and *ab initio* molecular orbital calculations, these satellite bands are attributable to one-electron MLCT (metal-to-ligand charge transfer) transitions to ligand π^* orbitals. The satellite bands gain their intensities from covalency hybridization between the Ni $4p^*/3d$ orbitals and the ligand π^* orbitals. These results reveal that the low-lying ligand unoccupied orbitals are essential to interpret the metal *K*-edge and *L*-edge XANES of transition metal complexes with molecular ligands.

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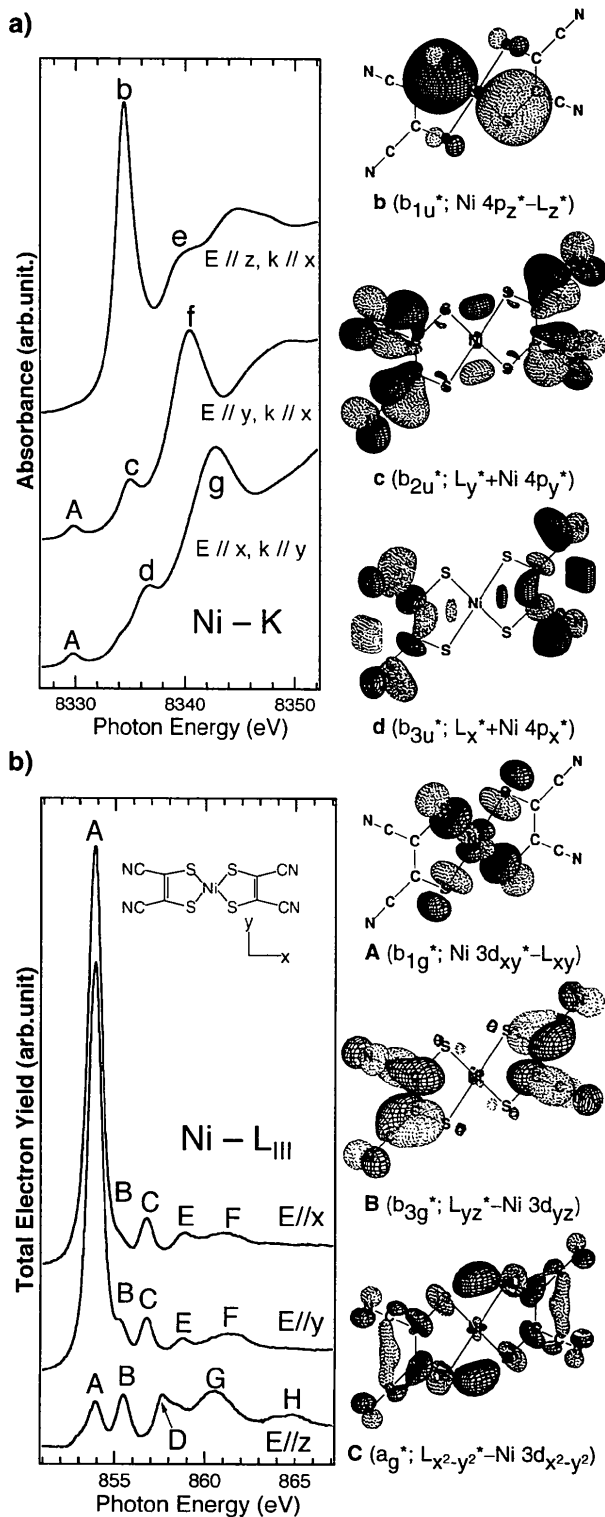


Figure 3

Polarized XANES spectra at (a) the Ni *K*-edge and (b) the Ni *L*-edge of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Ni}(\text{mnt})_2]$ and some molecular orbitals related to XANES.

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