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Abstract. XAFS measurements have been carried out at both room temperature and 100 K on complexes of general form of Co^{III}(N-N)(DBQ), where N-N is 1,10-phenanthroline(phen), *N,N,N',N'*-tetramethylethlenediammine(tmeda), and DBQ is the 3,6-di-*tert*-butylcatechol or 3,6-di-*tert*-semiquinone ligands. Co K-edge XAFS spectra disclosed that Co(tmeda)(DBQ)$_2$ is locked in a charge distribution of Co^{III}(tmeda)(3,6-DBSQ)(3,6-DBCat), while Co(phen)(DBQ)$_2$ is accompanied by the transition of Co^{III}/Co^{II} dependent on temperature.

1. INTRODUCTION

Transition metal complexes containing quinone ligands have been shown to have metal- and quinone-localized electronic levels that are close in energy.[1] As a consequence, intramolecular charge transfer between metal and ligand occurs at low energy, and, in some cases, under conditions of thermal equilibrium.[2,3] Structural changes that accompany shifts in metal oxidation state have been applied to materials that exhibit photomechanical properties and optical switching effects.[4] The most extensively studied equilibria of this type occur for complexes of cobalt of general formula Co(N-N)(DBQ)$_2$, where DBQ is the semiquinone or catecholate form of either 3,5- or 3,6-di-*tert*-butyl-1,2-benzoquinone and N-N is a bidentate nitrogen-donor coligand. Temperature - dependent equilibria (eq. 1) may be observed in the solid state as well as in solution by monitoring

$$Co^{III}(N\text{-}N)(DBSQ)(DBCat) \leftrightarrow Co^{II}(N\text{-}N)(DBSQ)_2 \qquad (1)$$

changes in either optical spectrum or magnetism with the shift from low-spin Co^{III} to high-spin Co^{II}. Although the spectroscopic studies on the transition of oxidation state have been elucidated for both solution and the solid state, the direct measurements of the structural changes associated with the transition of oxidation state have been limited to crystalline samples. In this respect, X-ray absorption spectroscopy has become a powerful tool for probing both electronic and geometric structures for any types of samples.[5] In this paper, XAFS studies are established on two cobalt complexes [Co(tmeda)(3,6-DBQ)$_2$ (sample A) and Co(phen)(3,6-DBQ)$_2$ (sample B)] in crystalline state, which will be applicable to compounds in noncrystalline states such as polymer or solution samples.

2. EXPERIMENTAL

Synthetic procedures to form the title complexes followed the previously reported ones.[2] The XAFS spectra at the cobalt K-edge were recorded on beam line 10B of the Photon Factory in the transmission mode at room temperature and 100 K. For XAFS spectra, a linear background was subtracted from the experimental spectra by extrapolating the least-square fitting of the pre-edge experimental points, and the edge jump was set to unity. In order to determine the structural parameters, a curve fitting was performed with the UWXAFS code[6] for the first shell in the Fourier transform (FT), using theoretical functions calculated by the FEFF 5 code[7] for all scattering paths.

3. RESULTS AND DISCUSSION

Fig. 1 shows the Co K-edge XANES spectra recorded at both room temperature and 100 K for the present compounds. Sample B shows an overall spectral shift of about 1.5 eV to a higher energy side at 100 K, while sample A shows the same spectra irrespective of temperature. These spectral changes indicate that sample B undergoes the oxidation state transition of $Co^{II} \rightarrow Co^{III}$ such as eq. (1) due to electron transfer from metal to ligand as the temperature decreases. These results are in good agreement with the fact that the transition temperature of eq. (1) is 410 K and 250 K for sample A and sample B, respectively. FTs of the Co K-edge EXAFS spectra in Fig. 2 represent the same pattern as XANES spectra. That is, FTs for sample A are almost the same at both temperatures, but room temperature FT of sample B is completely different from low temperature FT. Especially, the shape of first-shell peak, which is due to N and O backscatters around cobalt atom, indicates that the local symmetry on Co^{III} ions is almost octahedral, but Co^{II} ions have lower local symmetry. The Fourier filtered spectra of the first-shell peak and the best fits are shown in Fig. 3, and the fitted structural parameters are summarized in Table 1. Bond distances between cobalt and N/O atoms fitted for sample A are consistent with those (d(Co-O$_{av}$) = 1.872 Å; d(Co-N$_{av}$) = 2.026 Å) determined by means of single crystal X-ray diffraction at RT.[2] In addition, Co-N/O bond distances of sample A are very similar to those of sample A at low temperature, in which Co^{III} ions are stabilized. On the other hand, sample B at RT was not
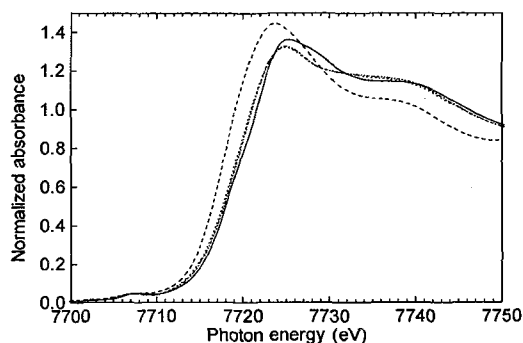
Figure 1: Co K-edge XANES spectra for sample A (RT;—·—, 100K;–···–) and sample B (RT;----, 100K;—–).

Table 1. Curve-fitting Results for Co K-edge EXAFS.

sample	shell	N[a]	$R(\text{Å})$[a]	$\sigma^2(\text{Å}^2)$[a]	$\Delta E_0(\text{eV})$[a]
A	Co-N	2.0	2.03	0.0066	-13.7
(RT)	Co-O	3.7	1.86	0.0038	-12.9
B	Co-N	1.0	2.03	0.0052	-22.9
(100 K)	Co-O	4.2	1.87	0.0029	-16.8
B	Co-N	2.1	2.15	0.0111	-7.7
(RT)	Co-O	2.2	2.06	0.0059	0.2
	Co-O	2.2	1.90	0.0034	0.2

[a] N is the number of scatterers. R is the metal-scatterer distance. σ^2 is a mean square deviation in R. ΔE_0 is the shift in E_0 for the theoretical scattering function.

only well fitted with the addition of a third backscattering term but also presents larger bond distances Co-N/O, which is due to the presence of Co^{II} ions. From the comparison of the bond distances of sample B at RT with those (d(Co-O_{av})=2.066 Å and d(Co-N_{av})=2.165 Å) of another Co^{II}-complex, $Co^{II}(NO_2$-phen)(3,6-DBSQ)$_2$ [8], suggest that the local symmetry around Co ions is changed from octahedral structure to trigonal prismatic one with the transition of $Co^{III} \rightarrow Co^{II}$.

4. Conclusion

The present temperature-dependent XAFS studies for cobalt semiquinonate/catecholate complexes have shown that the ligand-to metal charge transfer results in the Co^{III}/Co^{II} transition and accompanying local structural change. XAFS is also expected to give a useful information on temperature-dependent electronic and structural changes of tautomeric forms of complex in polymer state that is industrially potential due to their photochemical properties and optical switching effects.
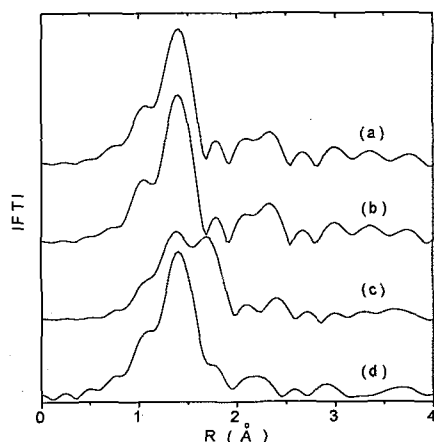

Figure 2: FTs of Co K-edge EXAFS for sample A at RT (a) and 100 K (b), and sample B at RT (c) and 100 K (d)
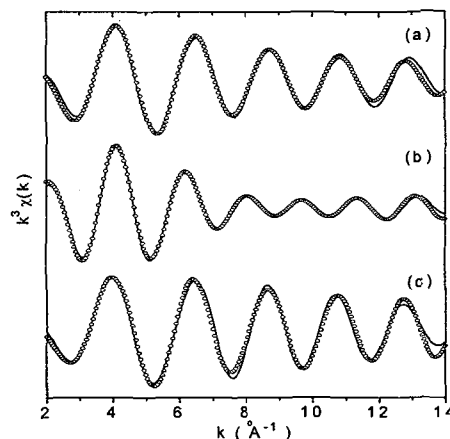

Figure 3: Experimental Fourier filtered $k^3\chi(k)$ (O) of the first peak in FTs and the best fits (–) for sample A at RT (a), sample B at RT (b) and 100 K (c).

Acknowdelgments

References

[1] Pierpont C. G., Lange C. W., *Prog. Inorg. Chem.* **41** (1993) 381.
[2] Jung O. -S., Pierpont C. G., *Inorg. Chem.* **33** (1994) 2227.
[3] Attia A. S., Pierpont C. G., *Inorg. Chem.* **34** (1995) 1172.
[4] Jung O. -S., Pierpont C. G., *J. Am. Chem. Soc.* **116** (1994) 2229.
[5] Choy J. -H, Yoon J. -B, Kim D. -K, Hwang S. -H, *Inorg. Chem.* **34** (1995) 6524.
[6] Newville M.,Livins P., Yocoby Y., Rehr J. J., Stern E. A., *Phys. Rev. B* **47** (1993) 14126.
[7] Rehr J. J., Mustre de Leon J., Zabinsky S. I., Albers R. C., *J. Am. Chem. Soc.* **113** (1991) 5135.
[8] Jung O. -S, Pierpont C. G., *J. Am. Chem. Soc.* **116** (1994) 1127.