XANES Spectra of $Co(ala)_3$ and $Co(acac)_3$ in Solid and Solution

Mitsuru SANO
Department of Chemistry, College of General Education, Nagoya University,
Nagoya 464-01
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Synopsis. XANES spectra of $[Co(ala)_3]$ and $[Co(acac)_3]$ have been measured in solid and solution. Comparisons of spectra of the species in solid and solution give a basis for the spectral change being attributable to intermolecular interactions.

X-Ray absorption spectra near K-edge have been measured for many years. The relations between XANES features and electronic structures of the absorbing atom have been extensively studied. In spite of some successful studies,[1] full understanding still remains for further systematic studies.

In recent papers,[2,3] the author reported that systematic measurements of Co K-edge XANES for Co(III) complexes showed counter-ion effect for $[Co(NH_3)_6]X_3$ (X=Cl, Br, and I), and that the Co XANES spectra of $[Co(H_2O)_6](ClO_4)_2$, $[Co(H_2O)_6]SO_4$, and $[Co(NH_3)_6]Br_3$ in solid are different from those in solution. These findings suggest that "the counter ion effect" in solid does not originate from a long-range effect as ejected electrons directly interact with counter ions but from a short range effect where XANES is influenced by slight distortion of a local electronic and geometrical structure induced by counter ions. Then, if this suggestion is correct, it is expected that XANES spectra of non-charged compounds without counter ions in solution will differ from those in the crystal in which a strong intermolecular interaction such as hydrogen-bonding exists. In order to make sure this, I measured XANES spectra of (+)mer-$[Co(ala)_3]$ (ala^-=alaninate) which has hydrogen bonds in the crystal and those of $[Co(acac)_3]$ ($acac^-$=4-pentanedionate) which has no strong intermolecular interaction in the solid, and compared them with those in solution.

The cobalt(III) complexes were prepared and recrystalized according to standard methods.[4] Organic solvents were purified by distillation. A solid sample was ground and diluted with boron nitride and contained in a plastic cell. A small volume of each sample solution (0.1 M, 1 M=1 mol dm^{-3}) was contained in a teflon cell with teflon windows. X-Ray absorption measurements were carried out at the BL-10B on the storage ring of Photon Factory (KEK). Synchrotorn radiation (2.5 GeV, 120—280 mA) was monochromatized with a chnnel-cut Si(311) monochromater. Other instrumental details are given in Ref. 5. The absorption spectra were measured in the transmission mode at room temperature. All spectra have been normalized to give an edge jump of 1.0.

Figure 1 shows the XANES spectra and their first

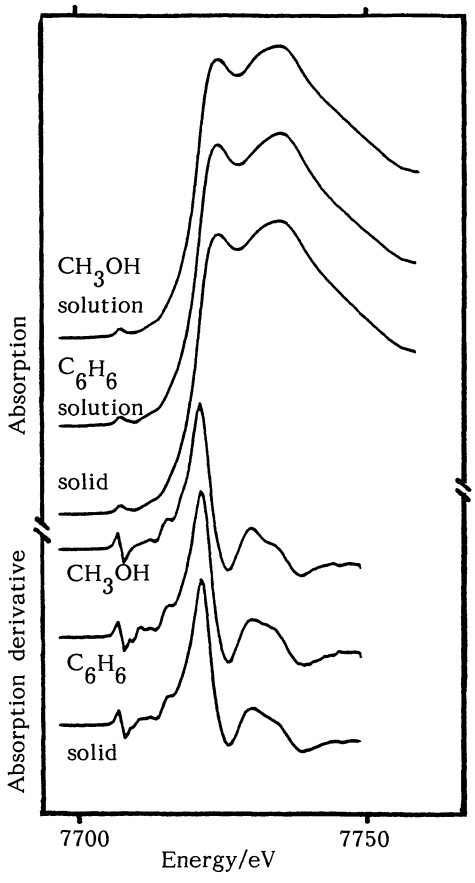


Fig. 1. Co K edge spectra and their derivatives of $[Co(acac)_3]$ in solid and solutions.

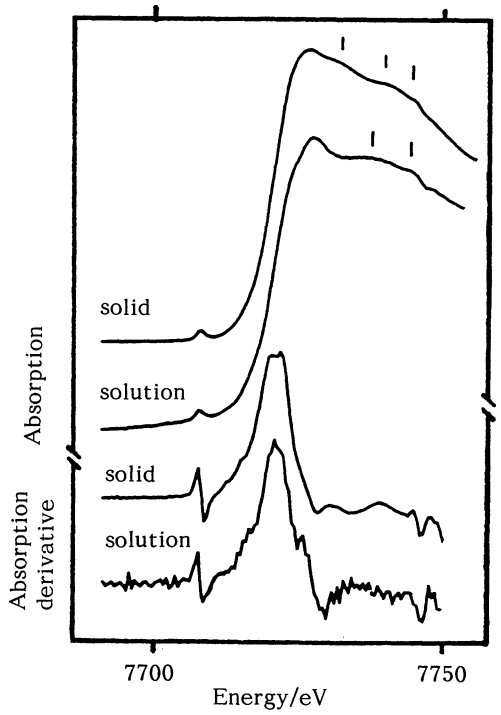
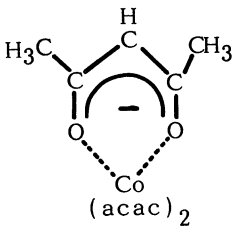
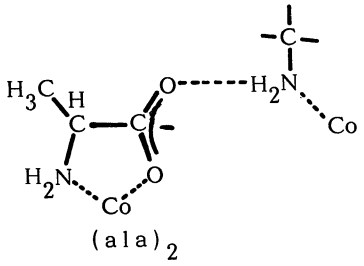


Fig. 2. Co K edge spectra and derivatives of mer-$[Co(ala)_3]$ in solid and aqueous solutions.



Scheme 1.



Scheme 2.

derivatives of $[Co(acac)_3]$ in crystal and solution, and Fig. 2 the corresponding spectra of $[Co(ala)_3]$. The spectra of $[Co(acac)_3]$ are similar to each other and also similar to those of its acetonitrile and dimethylformamide solutions. Although the XANES spectrum of $[Co(ala)_3]$ in crystal generally resembles that in aqueous solution, some small differences are found in 7725—7750 eV; two absorptions can be observed in solution and three absorptions in solid.

The crystal structures of both complexes have been well studied.[6-7] The coordination form for $[Co(acac)_3]$ is schematically shown by Scheme 1 and six Co–O bond lengths are practically the same (Co–O=1.883—1.892 Å).[5] This suggests the absence of strong intermolecular interactions in solid $[Co(acac)_3]$. This is also supported by the fact that the compound easily sublimes. Since there is no strong intermolecular interaction in solid $[Co(acac)_3]$, it is expected that the conditions of geometrical and electronic structures are the same in solid and in solution. This can be the reason for the XANES spectra being similar to each other. In $[Co(ala)_3]$,[7] the alaninate ions coordinate to a cobalt ion as shown in Scheme 2. Strong hydrogen bonds exist between the complexes in the crystal in Scheme 2. This strong interaction between the molecules causes a change in the geometrical arrangement and charge distribution within the molecule, which will result in a change in the electronic state. The interaction between the complex and water in aqueous solution is much weaker than that between the complexes in solid. The intermolecular interaction in crystal different from that in solution results in a change in a different geometrical and electronic structure and thus a change in the spectra of $[Co(ala)_3]$.

The present result exemplifies that the XANES spectral change is attributable to the intermolecular interaction associated with a geometrical and electronic local change rather than direct interactions of the electron wave with surrounding atoms. It also discloses what is "the counter-ion effect". Yamashita et al.[8] reported a correlation between XANES patterns and crystal packing structures. These findings demonstrate how much change of XANES in solid by intermolecular interaction. It is useful to compare with XANES of solid compounds and theoretical consideration.

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