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EXAFS and XANES Spectra of Cobalt(III) EDTA Complexes in Solids and Solutions

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The Co K-edge XANES (X-ray Absorption Near-Edge Structure) of $[Co(edta)]^-$ ($edta^{4-}$=ethylenediamine-*N,N,N′,N′*-tetraacetate) complex in crystal varies with the kind of counter cations and it also varies with the kind of solvents when it is dissolved. The amplitude of the oscillation in its EXAFS (Extended X-ray Absorption Fine Structure), or the peak height in its Fourier transform, also varies as much as threefold depending on the kind of counter cations or solvents. The most plausible cause for the variations is the difference in the thermal disorder of the bonds which is enhanced by the formation of hydrogen bonding between carboxylato groups in the complex and the water molecules in crystal or the solvent molecules in solution.

The structures of metal–edta complexes are not necessarily the same. They are known to take various coordination structures.[1] The structures can also vary with the environments, i.e. in crystals[2] or in solutions.[3,4] The EXAFS and XANES techniques appear to be suitable for the structural studies of such complexes since these spectroscopic techniques extract the information regarding the local structure around the central metal irrespective of the environments. The complex treated in this work is $[Co(edta)]^-$ which is considered to be so stable that no structural change in its inner sphere would occur against the variation of the environments. In spite of the expected rigidity of the complex, it was found that its EXAFS and XANES spectra are highly sensitive to the environments. This paper reports the X-ray absorption spectra of the complex in various environments and the possible effects of hydrogen bonding on the Debye–Waller factors or the EXAFS oscillation amplitudes.

Experimental

Samples. $Li[Co(III)(edta)]\cdot 3H_2O$ and $Na[Co(III)(edta)]\cdot 4H_2O$ were prepared according to the literatures.[5,6] $Rb[Co(III)(edta)]\cdot 2H_2O$ was synthesized in the following way; Rb_2CO_3 was added to a warm slurry solution containing RbCl, $(CH_3COO)_2Co\cdot 4H_2O$, and H_4edta until the pH of the solution became 4. The $[Co(II)(edta)]^{2-}$ ion was oxidized by adding 3% H_2O_2 aqueous solution. After filtration, this solution was concentrated and cooled, and ethanol was added to crystallize $Rb[Co(edta)]\cdot 2H_2O$. $NH_4[Co(III)(edta)]\cdot 2H_2O$ was synthesized using a similar method from $Co(NO_3)_2\cdot 6H_2O$, H_4edta, and NH_4OH. All the solid samples were recrystallized twice or more from water and ethanol. Elemental analysis: Found for $Li[Co(edta)]\cdot 3H_2O$: C, 29.32; H, 4.55; N, 6.85%. $Na[Co(edta)]\cdot 4H_2O$: C, 26.56; H, 4.26; N, 6.19%. $Rb[Co(edta)]\cdot 2H_2O$: C, 24.21; H, 3.49; N, 5.65%. $NH_4[Co(edta)]\cdot 2H_2O$: C, 29.63; H, 5.06; N, 10.41%.

Aqueous solutions of $0.1\ mol\cdot dm^{-3}$ $[Co(edta)]^-$ were prepared from the above Na salt. HNO_3 or NaOH were used to adjust their pH to 3.0, 5.0, 7.0, and 9.0. The solutions of pH 7.0 and 9.0 turned to be pH 6.9 and 8.1, respectively, after the X-ray absorption measurements. DMF (*N,N*-dimethylformamide) solution was prepared from $K[Co(edta)]\cdot 2H_2O$ which was synthesized by the conventional method.[6] Excess of 18-crown-6 ether was added to raise the solubility of the complex. KBr disks of solid samples were prepared for the measurements of infrared absorption spectra.

Measurements and Calculations. Co K-edge X-ray absorption spectra were obtained at BL-7C of the Photon Factory in the National Laboratory for High Energy Physics using a Si(111) double crystal monochromator. Powder samples of ca. 0.5 mm thick were held between two sheets of adhesive tape. Solution samples were placed in polyethylene pouches. Fourier transform calculations of EXAFS were performed by using the phase shift and scattering amplitude parameters tabulated by Teo and Lee.[7] Transformations were performed over the k range of 2.9—16.75 Å^{-1}. In order to reduce ripple peaks in Fourier transforms, Hamming window function was used.

Results and Discussion

Figure 1 shows XANES spectra and Fourier transforms of EXAFS for aqueous solutions. Both spectra show no dependence on pH. Their Raman scattering and UV-Visible absorption spectra were also measured and showed no dependence on pH. According to Higginson et al.,[4] the form of Co(III)–EDTA is either $[Co(Hedta)(H_2O)]$, $[Co(edta)(H_2O)]^-$, $[Co(edta)]^-$, or $[Co(edta)(OH)]^{2-}$ depending on pH of the solution. In the pH range of 3.0 to 8.1, most of the complex has been known to form $[Co(edta)]^-$. The present results indicate that the structure of $[Co(edta)]^-$ in aqueous solutions is very stable over this pH range.

Figure 2 shows Co K-edge XANES spectra for (a) aqueous solution, (b) $Na[Co(edta)]\cdot 4H_2O$, (c) $NH_4[Co(edta)]\cdot 2H_2O$, (d) $Rb[Co(edta)]\cdot 2H_2O$, (e) $Li[Co(edta)]\cdot 3H_2O$, and (f) DMF solution. They can be classified into three groups; (A) aqueous solution and Na salt, (B) NH_4 and Rb salts, and (C) Li salt and DMF solution. The spectra for group A have the lowest threshold energies and the lowest peak heights at around 7740 eV. In contrast, group C has the highest

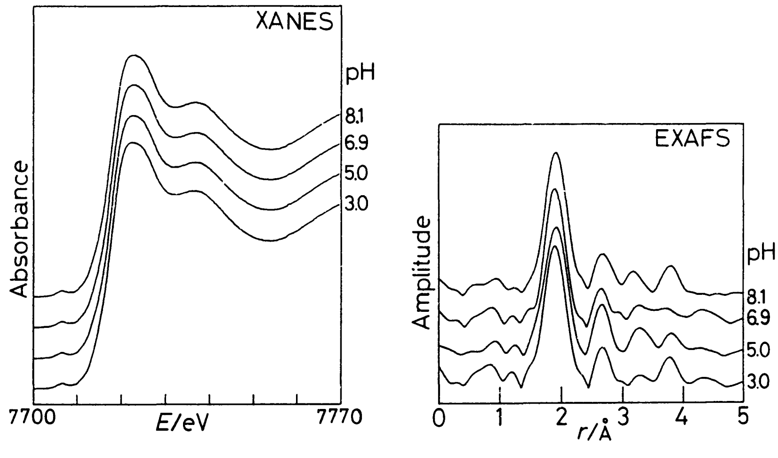

Fig. 1. Co K-edge XANES spectra and Fourier transforms of EXAFS for [Co(edta)]$^-$ in different pH aqueous solutions.

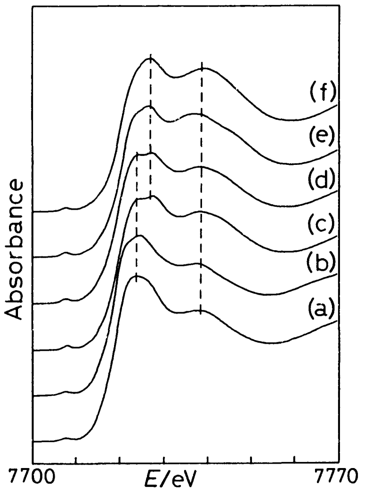

Fig. 2. Co K-edge XANES spectra for (a) aqueous solution, (b) Na[Co(edta)]·4H_2O, (c) NH_4[Co(edta)]·2H_2O, (d) Rb[Co(edta)]·2H_2O, (e) Li[Co(edta)]·3H_2O, and (f) DMF solution.

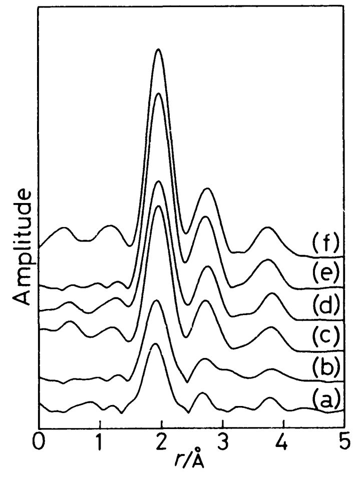

Fig. 3. Fourier transforms of Co K-edge EXAFS for (a) aqueous solution, (b) Na[Co(edta)]·4H_2O, (c) NH_4[Co(edta)]·2H_2O, (d) Rb[Co(edta)]·2H_2O, (e) Li[Co(edta)]·3H_2O, and (f) DMF solution.

threshold energies and the highest peak heights at 7740 eV. Group B is intermediate between A and C. The highest peaks, so called white line, in A or C are composed of a single peak possibly accompanying a shoulder, while those of B are composed of double peaks and the position of its higher energy component agrees with the position of the peak in C.

There are two possibilities which may contribute to the differences in the XANES spectra of three groups. One is the photoelectron scattering by the counter cations or solvent molecules. The other is the indirect effects of the cations or the solvents on the electronic and/or structural conditions of the complex anion, [Co(edta)]$^-$. There is a reason to reject the former possibility, i.e. although the N in NH_3 and Rb are quite different photoelectron scatterers in respect to the amplitude and phase shift (the distances of Co–N and Co–Rb are similar 5.68 and 5.81 Å, respectively[5]), the XANES spectra of the samples having these atoms as counter cations are almost the same. In addition to this, there seems to be no systematic correlation between the XANES spectrum and the kind of counter cation. Therefore, it is almost impossible to consider that the variety of XANES spectra is caused by the direct photoelectron scattering by the counter cation.

Fourier transforms of EXAFS for [Co(edta)]$^-$ in various environments are shown in Fig. 3. One easily finds three peaks in each of the Fourier transforms. By referring to the crystallographic data for NH_4 salt,[5] these peaks are assigned to the bond distances between Co and the scatterers as follows; the most intense peaks at around 1.9 Å correspond to four oxygens (O_1 in Fig. 4) and two nitrogens, the second peaks at around 2.7 Å to ten carbons, and the third peaks at around 3.8 Å to

Table 1. Peak Positions and Their Heights in Fourier Transforms of Co K-edge EXAFS for $[Co(edta)]^-$ Complexes

Sample	Peak position/Å			Peak height[a]		
	1st	2nd	3rd	1st	2nd	3rd
(a) Average of aqueous solution	1.92	2.69	—	0.5	0.4	—
(b) $Na[Co(edta)]\cdot 4H_2O$	1.92	2.75	3.80	0.5	0.5	0.5
(c) $NH_4[Co(edta)]\cdot 2H_2O$	1.96	2.76	3.79	1.0	1.0	1.0
(d) $Rb[Co(edta)]\cdot 2H_2O$	1.95	2.76	3.83	1.0	1.1	1.1
(e) $Li[Co(edta)]\cdot 3H_2O$	1.97	2.75	3.77	1.4	1.4	1.1
(f) DMF solution	1.97	2.78	3.75	1.5	1.3	1.2
$NH_4[Co(edta)]\cdot 2H_2O$	1.91[b]	2.73[b]	3.85[b]	—	—	—
$[Co(sarmp)(NH_3)_3][Co(edta)]\cdot H_2O$	1.92[c]	2.74[c]	3.89[c]	—	—	—

a) Relative intensity. b) and c) The average of the distances of corresponding bonds for $[Co(edta)]^-$ from crystallographic data of Refs. 5 and 9, respectively. $sarmp^{2-}$=sarcosinate-*N*-propionate.

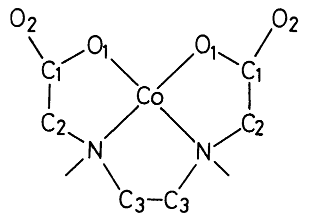

Fig. 4. Numbering on some atoms in $[Co(edta)]^-$ complex.

four oxygens (O_2) not coordinating to Co. In spite of its long distance, the third peaks due to O_2 appear with an unusual intensity, particularly for the samples of groups B and C. Binsted et al.[8] studied EXAFS of cobalt carbonyls such as $[Co(CO)_4]^-$ and found that the linear configuration of Co–C–O atoms enhances the peak corresponding to Co–O bond because of the multiple scattering effect. In the present case, it is plausible that the intensity of the third peak results from the same multiple scattering effect because the angles of Co–C_1–O_2 are known to be about 160° and those of Co–O_2–C_1 about 14° from the crystallographic data for NH_4 salt.[5]

Table 1 lists the peak positions in each Fourier transform and the mean distances of corresponding bonds taken from the crystallographic data.[5,9] The third peaks are not clear for some samples of aqueous solutions.

There are large differences in the amplitude of EXAFS oscillation. The ratio of the heights of the first peaks in Fourier transforms is roughly 1:2:3 between groups A, B, and C, respectively. Since the coordination numbers of Co in all the samples are known to be constantly six,[10] the large differences in peak heights must be resulted from the differences in the root-mean-square displacement of Debye-Waller factor. The Debye-Waller factor of a peak originates from two contributions, static bond length distribution and dynamic or thermal disorder. In order to examine the contribution of static distribution, some simulation calculations were performed. The simulated EXAFS spectra were obtained by using a constant value of Debye-Waller factor to each kind of bonds and distributed bond lengths limited within reasonable ranges. However, the spectra could not give such large differences in peak heights in Fourier transforms as shown in experimental spectra. Therefore there must be some large differences in thermal disorder among the samples of group A, B, and C.

One of the origins for the large differences in thermal disorder may be the presence of hydrogen bonding which donates electrons from carboxylato group to water molecule. A water molecule can approach to O_2 and even to O_1 to form hydrogen bonding. This effect appears in other experimental phenomena, e.g. UV absorption spectra[11] and ^{13}C NMR spectra.[12] The presence of such hydrogen bonding has also been known in the $[Co(edta)]^-$ crystals[9] and in an analogous complex, $[Co(III)(trdta)]^-$ ($trdta^{4-}$=trimethylenediamine-*N,N,N′,N′*-tetraacetate) crystal.[13] $NH_4[Co(edta)]\cdot 2H_2O$ crystal must have such hydrogen bonding, since some distances between O in water molecule and O_2 or O_1 are less than 3.0 Å. More hydrogen bonding may exist in Na salt than in NH_4 salt, because the volume of an unit cell of Na salt is larger only about 10% than that of NH_4 salt and the number of waters of crystallization are twice as much. The fact that the spectrum for DMF solution sample is most intense should be due to the absence of the hydrogen bonding.

It is quite interesting to note that the weaker the peak in the Fourier transform, the shorter the bond length read from the first peak position. This may be due to the fact that the Debye-Waller factors for Co–O bonds of longer lengths increase more than the shorter ones upon the hydrogen bonding formation. (cf. the bond lengths are 1.870, 1.896, 1.913, 1.922 Å for Co–O and 1.921 and 1.925 Å for Co–N in NH_4 salt.[5])

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