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Structures of Fe(III) complexes with EDTA and EDDDA in aqueous solution by EXAFS and XANES

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Abstract

The Fe K-edge X-ray absorption spectra of Fe(III) complexes with EDTA (ethylenediaminetetraacetic acid) and EDDDA (ethylenediamine-*N*,*N*-diacetic-*N*,*N*′-dipropionic acid) in weakly acidic or neutral aqueous solutions are measured. The spectra of powdered crystalline samples of these complexes are also measured as the reference materials. The comparisons of the XANES spectra, including their pre-edge peak, and the EXAFS Fourier transforms conclude that in aqueous solution a seven-coordinate structure is predominant for the Fe(III)–EDTA complex and a six-coordinate one for the Fe(III)–EDDDA complex.

Introduction

It is known that Fe(III)–EDTA takes either a six- [1] or seven-coordinate [2] structure when it crystallizes from neutral or weakly acidic solution. The latter structure is similar to that of the Mn(II)–EDTA complex [3], in which the seventh coordination site is occupied by H_2O. While the structure of Fe(III)–EDTA in the crystal phase has been established by reliable diffraction techniques, little is known about the structure in the solution phase due to the lack of adequate analytical techniques. It is also due to the fact that the Fe(III)–EDTA complex undergoes a rapid ligand substitution reaction in aqueous solution [4]. In order to study the structure of the complex in solution, or its coordination number, its EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near edge structure) spectra will be reported in this paper. The spectra of crystalline samples, of which structures are known, have also been measured as the reference materials. The spectra of Fe(III) complexes with EDDDA (ethylenediamine-*N*,*N*′-diacetic-*N*,*N*′-dipropionic acid) were also measured. The EXAFS and XANES techniques are suitable for determining the coordination numbers of such complexes since these techniques extract information regarding the local structure around the central metal irrespective of the environments.

Experimental

Sample preparation

Fe(III) complexes studied in this work are: (a) $Na[Fe(edta)H_2O]\cdot 2H_2O$, (b) $Li[Fe(edta)H_2O]\cdot 2H_2O$, (c) Li[Fe(edta)], (d) $[Fe(Hedta)H_2O]\cdot 2H_2O$, (e) $Li[Fe(eddda)]\cdot 2H_2O$, (f1) Fe(III)–EDTA aqueous solution at pH 1, (f2) Fe(III)–EDTA aqueous solution at pH 3, (f3) Fe(III)–EDTA aqueous solution at pH 5, and (g) Fe(III)–EDDDA aqueous solution at pH 7. $Li[Fe(edta)H_2O]\cdot 2H_2O$

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[2], $Na[Fe(edta)H_2O]\cdot 2H_2O$ [2], $[Fe(Hedta)H_2O]\cdot 2H_2O$ [5], and $Li[Fe(eddda)]\cdot 2H_2O$ [6] (bright yellow) were prepared according to the literature references with slight modifications. Elemental analyses confirmed the above compositions for the respective complexes. $Li[Fe(edta)]$ (light yellow powder) was obtained by drying $Li[Fe(edta)H_2O]\cdot 2H_2O$ (dark brown crystals) at 100–110 °C and was identified by its decrease in weight and elemental analysis. Aqueous solutions of *c*. 0.1 mol dm^{-3} Fe(III) complex were prepared by dissolving each solid sample. Hydrochloric acid and hydrogen sodium carbonate were used to adjust the pH values.

Measurements and calculations

The Fe K-edge X-ray absorption spectra were obtained at BL-10B and BL-7C of the Photon Factory in the National Laboratory for High Energy Physics using a Si(111) double crystal monochromator. Powdered solid samples were loaded on adhesive tapes. Polyethylene pouches with a thickness of 3–5 mm were used for solution samples. Fourier transform calculations of EXAFS were performed by using the phase shift and scattering amplitude parameters tabulated by Teo and Lee [7]. The calculations were performed over the k range of 2.6–12.6 $Å^{-1}$. In order to reduce ripple peaks in Fourier transforms, a Hamming window function was used. A curve-fitting procedure was also applied to the EXAFS spectra. However, it could not provide reliable results, possibly because of the presence of too many shells to be considered for the Fe–EDTA complex and large disorder among its coordination bonds.

The spectra are so drawn that the ordinate scales are in common between Figs. 1 and 2, 3 and 4, and 5 and 6, thus the relative magnitudes are to be read from these Figures.

Results and discussion

Figure 1 shows Fe K-edge XANES spectra for solid samples. Noticeable variations are found in the region around the largest peak. There is a strong sharp peak B in the seven-coordinate complexes of (a) $Na[Fe(edta)H_2O]\cdot 2H_2O$ [2] and (b) $Li[Fe(edta)H_2O]\cdot 2H_2O$ [2], while the peak is weak or almost absent in six-coordinate complexes of (c) $Li[Fe(edta)]$, (d) $[Fe(Hedta)H_2O]\cdot 2H_2O$ [5], and (e) $Li[Fe(eddda)]\cdot 2H_2O$.

The six-coordinate structure of (c) was confirmed by diffuse reflectance spectroscopy. The diffuse reflectance spectra of (b) and (c) were obtained and compared with the results of Garbett *et al.* [8]. The comparison, and the dark brown color of (b) and the bright yellow color of (c) indicate that the former complex is seven-coordinate and the latter six-coordinate. For the Fe(III)–EDDDA complexes [6], it has been reported that only the *trans*(O_5) six-coordinate isomer with two oygens (O_5) of five membered N–O rings at the *trans* position was isolated and there is little room for a seventh coordination site in the *trans*(O_5) isomer.

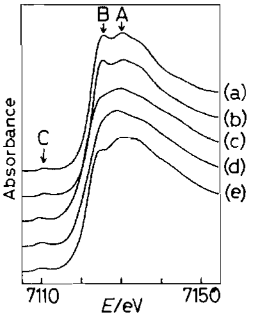

Fig. 1. Fe K-edge XANES spectra for (a) $Na[Fe(edta)H_2O]\cdot 2H_2O$, (b) $Li[Fe(edta)H_2O]\cdot 2H_2O$, (c) $Li[Fe(edta)]$, (d) $[Fe(Hedta)H_2O]\cdot 2H_2O$ and (e) $Li[Fe(eddda)]\cdot 2H_2O$.

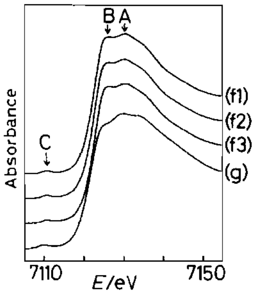

Fig. 2. Fe K-edge XANES spectra for Fe(III)–EDTA in aqueous solution at pH of 1 (f1), 3 (f2) and 5 (f3), and (g) Fe(III)–EDDDA at pH 7.

Now one can compare XANES spectra for solid samples in Fig 1 with those for aqueous solutions of Fe(III)–EDTA, (f1–f3) in Fig. 2. It is quite obvious that the spectral features for solution do not depend on its pH value, and that they are the same as those for solid samples (a) and (b). Therefore, one can conclude that the coordination number of the complex in aqueous solution is seven. Since the spectrum of the EDDDA complex in solution (g) is similar to that in the solid state, (e), and does not contain the peak B, this complex in solution must be a six-coordinate structure.

One can also use the shape of peak C (indicated in Figs. 1 and 2) to determine the symmetries of the complexes. The expanded spectra for peak C are shown in Fig. 3 and 4. Since the spectra were collected on different occasions, the calibration error in photon energy for these spectra may amount to a few tenths of an eV. Therefore we do not use

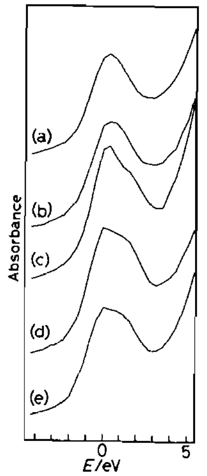

Fig. 3. Expanded spectra for peak C. Photon energies are relative scale and may contain some uncertainty. The notations are the same as in Fig. 1.

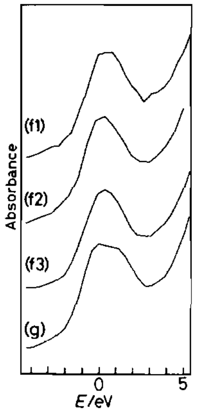

Fig. 4. Expanded spectra for peak C. The notations are the same as in Fig. 2.

the absolute photon energy scale here. Careful inspection of Fig. 3 leads to the fact that the six-coordinate complexes (c, d, and e) show the peaks with unsymmetrical shape while the seven-coordinate ones (a and b) show a smooth peak with Gaussian shape. The peak C is due to the $1s \rightarrow 3d$ transition [9] with two components, $1s \rightarrow t_{2g}$ and $1s \rightarrow e_g$. The two components are resolved indistinctly in the spectra for the six-coordinate complexes with almost octahedral symmetry, but they are not resolved at all for the seven-coordinate complexes with lower symmetry. The results for solution samples (f1), (f2) and (f3) in Fig. 4 look similar to those for (a) and (b) with seven coordination.

Fourier transforms of EXAFS for the Fe(III) complexes in the solid state are shown in Fig. 5. By referring to the EXAFS of $[Co(edta)]^-$ [10] and by consideration of the crystallographic data for Na and Li salts of $[Fe(edta)H_2O]^-$ [2] and $[Fe(Hedta)H_2O]$ [5], one may expect that the Fe–EDTA complexes give three peaks in their Fourier transforms; the most intense peak (the first peak) at around 2.1 Å corresponding to the bonds Fe–O and Fe–N, the second peaks at 2.8–3.2 Å to Fe–C, and the third peaks at around 4 Å to Fe–O of uncoordinated oxygen atoms of carboxylato group.

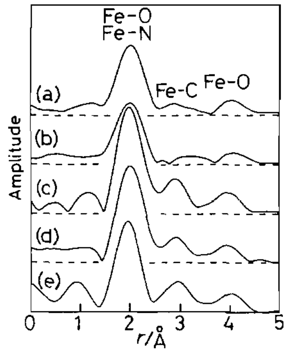

Fig. 5. Fourier transforms of Fe K-edge EXAFS. The notations are the same as in Fig. 1.

For the six-coordinate Fe complexes, i.e. (c) $[Fe(edta)]^-$, (d) $[Fe(Hedta)H_2O]$ and (e) $[Fe(eddda)]^-$, the Fourier transforms show the expected three peaks, while for the seven-coordinate complexes, $[Fe(edta)H_2O]^-$ salts, i.e. (a) and (b), the second peak can hardly be observed. Further, the first peaks of the seven-coordinate complexes are obviously weaker than those of the six-coordinate complexes. The static disorders for the first peaks of the seven- and six-coordinate complexes are estimated to be 0.13 and 0.11–0.12 Å, respectively, from the root-mean-square standard deviation of Fe–O,N bond lengths of their crystallographic data [2, 5, 6]. Because the effect of the static disorder on the peak strength is partly cancelled out by the coordination number, 6 or 7, the thermal disorder of the Fe–O and/or Fe–N bond in seven-coordinate complexes must be considerably larger than that of six-coordinate ones.

Now we can study the Fourier transforms for aqueous solution samples shown in Fig. 6. The first and the second peaks for the EDTA complex solution are weak if compared to that for the solution of the EDDDA complex and those for six-coordinate solid samples of (c), (d) and (e). This observation again suggests that the structure of the Fe(III)–EDTA complex in aqueous solution is mainly seven-coordinate. The conclusion derived from the present XANES and EXAFS studies agrees with the recent Raman study [11].

The spectra for the Fe(III)–EDDDA in solid and in solution are compared and both spectra are iden-

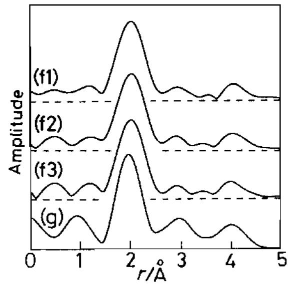

Fig. 6. Fourier transforms of Fe K-edge EXAFS for Fe(III) complex aqueous solutions. The notations are the same as in Fig. 2.

tical with respect to the XANES pre-edge peak (e) in Fig. 3 and (g) in Fig. 4, and Fourier transform (e) in Fig. 5 and (g) in Fig. 6. Thus the coordination number in solution must be six.

Strictly speaking, the EDTA or the EDDDA complex in solution must not necessarily take only the seven- or only the six-coordinate structure, respectively. They can be a mixture of six- and seven-coordinate species. But it seems that the major portion of the EDTA and the EDDDA complexes in solution take the seven- and six-coordinate structure, respectively.

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