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Structure and properties of iron(III) 1,3-propanediaminetetraacetate complex in aqueous solutions

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Abstract

The structure of iron(III) 1,3-propanediaminetetraacetate (1,3-pdta) in aqueous solutions was studied on the basis of Raman spectroscopy, nuclear magnetic relaxation, and pH titration. It has been found that, in aqueous solution, $Fe(1,3\text{-pdta})^-$ exists in a normal sexidentate hexacoordinate geometry. The six-membered chelate ring formed by the diamine moiety of the 1,3-pdta ligand does not adopt a skew-boat conformation having C_2 symmetry (as found in sodium salt crystals) but a twist-boat one having no C_2 symmetry (as in the lithium salt crystals). Although edta complexes of iron(III) form a dimeric complex in slightly alkaline solutions, the 1,3-pdta complex of Fe(III) does not show such a tendency. The 1,3-pdta complex is stable only in the pH region of 2–7.5; the corresponding edta complex is stable even in a strongly acidic solution.

Introduction

Ethylenediaminetetraacetate (edta) forms stable complexes with a variety of first-row transition metals. Among these, iron(III) [1–4], manganese(II) [5] and vanadium(III) [6] complexes prefer to adopt a sexidentate heptacoordinate geometry, since the size of the chelate ring is not large enough to encircle larger central ions.

The diamine ring of the 1,3-propanediaminetetraacetate ($(^-OOCCH_2)_2NCH_2CH_2CH_2N(CH_2COO^-)_2$; 1,3-pdta) complexes is larger than that of edta complexes. The whole chelate ring system of the 1,3-pdta complexes is less strained than that of the edta complexes. According to the X-ray analyses of $Li[Fe(1,3\text{-pdta})]\cdot 3H_2O$ [7] and $Na[Fe(1,3\text{-pdta})]\cdot 3H_2O$ [8], $Fe(1,3\text{-pdta})^-$ takes a normal sexidentate hexacoordinate geometry and the constraints of the chelate ring are relaxed to some extent.

The 1,3-pdta complexes have some other behaviour different from that of complexes having different diamino polycarboxylate ligands. Choppin and Muscatello [9] have reported that the stability constants of $M(1,3\text{-pdta})^-$ (M = Am, Cm, Bk and Cf) are much lower than those expected from the value of ΣpK_a of the 1,3-pdta acid. Ogino *et al.* [10] have determined the thermodynamic parameter, $\Delta G°$, $\Delta H°$, $\Delta S°$, for (diamino polycarboxylato)–metal(III/II) redox couples (metal = V, Cr, Fe and Ru) and found that the $[Fe(1,3\text{-pdta})]^{-/2-}$ couple gives parameters quite different from those of the other iron complexes. This unusual behaviour of the 1,3-pdta complexes has not yet been explained sufficiently.

In order to clarify the structure of the Fe(III) 1,3-pdta complex in aqueous solution, we studied the Raman spectra and nuclear magnetic relaxation.

Experimental

Preparation

1,3-propanediaminetetraacetic acid ($1,3\text{-pdtaH}_4$) and its barium salt were prepared by the method of Weyh and Hamm [11]. Lithium and sodium salts of $Fe(1,3\text{-pdta})^-$ were prepared by the method of Kanamori *et al.* [12].

Measurements

The Raman spectra were recorded on a JASCO R-800 laser Raman spectrophotometer. An Ar^+ ion laser (488.0 nm) was used as an excitation source. The spectral band width was set at 5 cm^{-1}. The

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powdered samples were shaped into disks. The disks were spun to avoid thermal decomposition induced by local illumination of the laser light. The sample solutions with a concentration of 0.1 mol/dm^3 were prepared for the Raman spectroscopy.

^{1}H spin-lattice relaxation times (T_1s) were measured at 20 MHz by using a JEOL (FSE-60SS) pulsed NMR spectrometer. In order to determine T_1 at room temperature, we applied a train of $\pi/2$ pulse–π–single $\pi/2$ pulse sequence generated by a computer program. The observed magnetization recovery can then be reproduced by an exponential curve with a time constant of T_1. Aqueous solutions of 6×10^{-3} mol/dm^3 were used for the T_1 measurements.

The pH titration was carried out as follows. The standard 0.01 mol/dm^3 NaOH solution was prepared from CO_2 free sodium hydroxide. The ionic strength of the Fe(III) 1,3-pdta complex solution and the NaOH solution was maintained at 1.0 with KCl. The pH of the solution was measured with a glass–Ag/AgCl electrode system equipped with a Mitsubishi chemical automatic titrator model GT-05. All titrations were performed at 20 ± 1 °C. After the desired components (40 dm^3) were transferred into a cell, the solution was degassed for 15 min with argon gas. pH values were determined as a function of the volume of standard NaOH added. Argon gas was bubbled slowly through the solution during the entire titration. A range of the complex concentration between 1.00 and 6.00×10^{-2} mol/dm^3 was checked. The titration speeds were 1.9, 3.5, 4.9 and 6.2 cm^3/min for the complex solutions of 1.00, 2.00, 4.00 and 6.00×10^{-2} mol/dm^3, respectively.

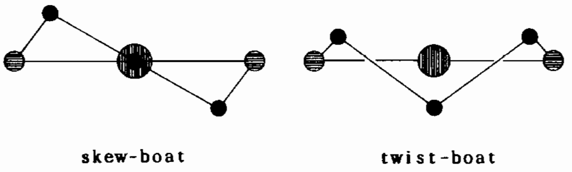

Fig. 1. Schematic representation of symmetrical skew-boat and twist-boat conformations of the six-membered chelate ring of the trimethylenediamine backbone in the Fe(1,3-pdta)$^-$ complex: ◍, iron; ⊜ , nitrogen; ●, carbon atom.

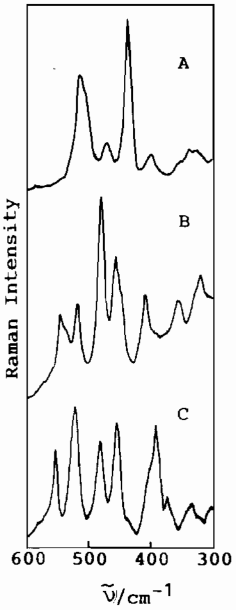

Fig. 2. Raman spectra of Na[Fe(1,3-pdta)]·$3H_2O$ (A), Li[Fe(1,3-pdta)]·$3H_2O$ (B) and [Fe(edtaH)(H_2O)]·H_2O (C).

Results and discussion

Solid state structures of lithium and sodium salts of Fe(1,3-pdta)$^-$

Single crystal X-ray analyses of the lithium [7] and sodium [8] salts of Fe(1,3-pdta)$^-$ show that Fe(1,3-pdta)$^-$ exists in a sexidentate hexacoordinate geometry. The most noticeable difference between these two salts has been found in the conformation of the six-membered diamine chelate ring: the trimethylenediamine moiety takes a symmetric skew-boat conformation in the sodium salt while a twist-boat one in the lithium salt. These two conformations are illustrated schematically in Fig. 1. The skew-boat form has C_2 symmetry, on the other hand the twist-boat form lacks it.

The Raman spectrum in the 300–600 cm^{-1} region, in which the skeletal vibrations of the coordination polyhedron are expected to appear, characterizes the structure of the Fe(III) edta complexes [12]. One can expect a similar feature for the Raman spectra of the Fe(III) 1,3-pdta complex, since 1,3-pdta is a close analogue of edta. Figure 2 shows the Raman spectra of the sodium (A) and lithium (B) salts of Fe(1,3-pdta)$^-$. In the 400–500 cm^{-1} region, the sodium salt has an intense band at 445 cm^{-1} and a weak one at 475 cm^{-1} whereas the lithium salt has two intense bands. Similar splittings are observed in the region above 510 cm^{-1}. Such splitting can be explained as a result of the lack of C_2 symmetry in the lithium salt. Figure 2, C corresponds to the Raman spectrum of [Fe(edtaH)(H_2O)] containing a quinquedentate edta ligand with a free carboxyl group. Consequently the complex does not have C_2 symmetry. It should be noted that losing C_2 symmetry results in a similar spectrum regardless of its origin. Potassium, rubidium, caesium and ammonium salts of Fe(1,3-pdta)$^-$ show spectra very similar to that observed for the sodium salt [12].

The Raman spectral features observed for the lithium and sodium salts of Fe(1,3-pdta)$^-$ are in agreement with the results of the X-ray analyses [7, 8]. It also appears that the six-membered diamine chelate ring of Fe(1,3-pdta)$^-$ in the potassium, rubidium, caesium and ammonium salts takes the symmetric skew-boat conformation.

Structure of Fe(1,3-pdta)$^-$ complex in aqueous solutions

It is well known that the iron(III) edta complex forms a dimeric complex containing a μ-oxo bridge in slightly alkaline solutions [13–16]. A pH titration was carried out to examine the formation of dimeric complexes and the hydrolysis behaviour of the Fe(III) 1,3-pdta complex in the region from slightly acidic to alkaline. A pK_a value of 7.29 has been obtained for the following hydrolysis reaction:

$$\mathrm{Fe(1,3\text{-}pdta)^- + H_2O \rightleftharpoons Fe(1,3\text{-}pdta)(OH)^{2-} + H^+}$$

It has also been found that the titration curves do not depend on the complex concentration in the range of 1.00–6.00$\times 10^{-2}$ mol/dm^3, suggesting the absence of dimerization of the complex. Beyond pH = 7.9, a small amount of precipitate appeared in all solutions and the reproducibility of the titration curve became slightly poor. Probably the monohydrized complex easily decomposed at higher pHs.

Figure 3 shows the Raman spectra of the Fe(1,3-pdta)$^-$ complex in aqueous solution as a function of pH. Aqueous solutions of Fe(1,3-pdta)$^-$ give almost the same Raman spectra in the pH = 2–7 region. The observed spectral feature in this pH region rather resembles that of the lithium salt (see Fig. 2), though some differences are found in the relative intensities of the Raman bands, especially of the 552 cm^{-1} band (see Figs. 2 and 3). Two intense bands in the 400–500 cm^{-1} region indicate the lack of C_2 symmetry of the Fe(1,3-pdta)$^-$ complex in aqueous solutions.

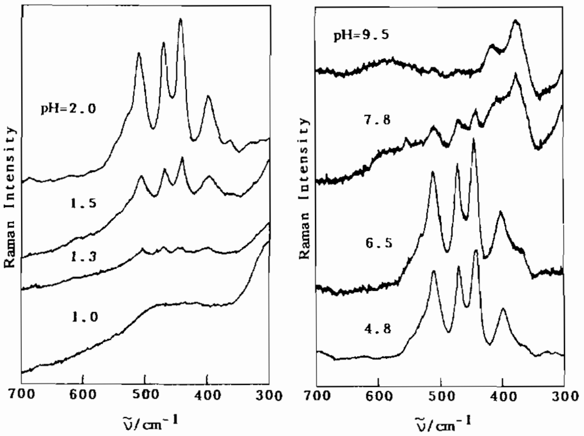

Fig. 3. Raman spectra of the aqueous solution of Fe(1,3-pdta)$^-$ as a function of pH.

The Raman bands due to the Fe(1,3-pdta)$^-$ complex become very weak and indistinguishable above pH = 7. This behaviour suggests that the monohydroxo iron(III) complex with 1,3-pdta, formed in a slightly basic solution, is unstable and easily hydrized further to a non-chelate complex. These observations are consistent with the results of the titration study. On the contrary, Fe(edta)$^-$ forms a fairly stable dimeric complex in alkaline solutions.

In acidic solutions, the Fe(III) complex with a monoprotonated 1,3-pdta has the formation constant pK_H = 2.4 [17, 18], where K_H = [MHL]/[H][ML]. No detectable changes of the Raman band have been observed down to the pH = 2 region. However, on decreasing the value of pH below 2 the intensities of the Raman bands due to the Fe(1,3-pdta)$^-$ complex decrease considerably. Bands assignable to Fe(1,3-pdtaH)(H$_2$O) could not be detected. At pH = 1.0 the bands are weak and diffused in the 400–600 cm^{-1} region. This spectral feature agrees well with that of the hexaaquairon(III) complex.

In order to clarify the reason for the symmetry lowering of the complex observed in the pH = 2–7 region and to confirm the result of the Raman spectral study below pH = 2, the pH dependence of the ^{1}H spin-lattice relaxation times was examined.

Measurements of spin-lattice relaxation time, T_1, of water protons have successfully estimated the coordination number of water in several paramagnetic complexes containing diamino polycarboxylate ligands [19–23]. The relaxation rate, $[T_1^{-1}]_{obs}$, observed for paramagnetic complexes can be expressed as follows

$$[T_1^{-1}]_{obs} = [T_1^{-1}]_p + [T_1^{-1}]_s + [T_1^{-1}]_b$$

where the first term is the contribution from water molecules in the primary coordination sphere and the second term the secondary one. The third term means the relaxation rate of bulk water, which usually can be neglected since $[T_1^{-1}]_b \ll [T_1^{-1}]_p$, $[T_1^{-1}]_s$.

T_1 versus pH relation is shown in Fig. 4. The constant value of T_1 (*c.* 216 ms) in the pH = 2–7.5 region is consistent with the results of the Raman spectral study. This value relative to the Fe(III) 1,3-pdta complex is much larger than the value of 75 ms observed for the [Fe(edta)(H$_2$O)]$^-$ complex containing a single water molecule in the primary coordination sphere. Since 1,3-pdta is a close analogue of edta, the contribution from the second coordination sphere of the Fe(III) 1,3-pdta complex must be analogous to that of the edta complex. Accordingly,

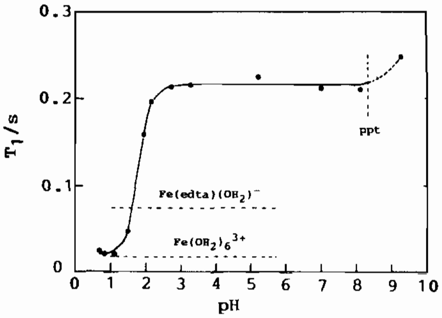

Fig. 4. ^{1}H spin-lattice relaxation time, T_1, observed in the aqueous solution of Fe(1,3-pdta)$^-$ as a function of pH.

the difference in T_1 described above indicates that the Fe(III) 1,3-pdta complex has no water molecule in the primary coordination sphere in the pH region concerned, taking a normal sexidentate hexacoordinate geometry as found in the solid state. The measurements of the spin-lattice relaxation times suggest that the Raman band splitting in the 400–500 cm^{-1} region in Fig. 3 is caused by a twist-boat conformation of the six-membered chelate ring of the trimethylenediamine moiety (not by a quinquedentate coordination of the 1,3-pdta ligand).

The spin-lattice relaxation time, T_1, of the complex solution becomes short with decreasing the value of pH below 2. Finally (at pH = 1), T_1 gives the value of $Fe(OH_2)_6^{3+}$.

The Raman spectral and NMR behaviour of the Fe(III) 1,3-pdta complex, in acidic solutions, implies that the Fe(III) complex with a monoprotonated 1,3-pdta is not stable and the Fe(III) ion releases the free 1,3-pdta ligand in the pH region below 2. This property is also in contrast to that of the Fe(III) edta complex which is stable even in strongly acidic solutions [12].

It is noteworthy that the six-membered chelate ring formed by 1,3-pdta brings out a considerable decrease in the stability of the iron(III) complex in both acidic and alkaline solutions though the steric constraints are relaxed in the 1,3-pdta complex compared with in the edta complex. This instability of the 1,3-pdta complex may be related to the difference in the pK_a values (6.11 for edta and 7.96 for 1,3-pdta [24]) for protonation of the N donor in the ligands as suggested by Choppin and Muscatello [9].

To conclude, in aqueous solutions in the range of pH = 2–7, the Fe(III) 1,3-pdta complex exists in the sexidentate hexacoordinate geometry and the six-membered chelate ring of the trimethylenediamine backbone prefers a twist-boat conformation.

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