# The Raman Spectral Study on the Solution Structure of Iron(III)-edta Complexes

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The Raman spectra of iron(III) complexes with ethylenediaminetetraacetate were observed for the purpose of elucidating the structure of the complexes in solution. In a Raman spectral study on the solid complexes, the spectra in the 300—600 $cm^{-1}$ region were found to be diagnostic to coordination geometry. Namely, the coordination number can be determined on the basis of the wavenumber difference of the two major bands observed in the 450—600 $cm^{-1}$ region; the wavenumber differences observed for heptacoordinate complexes lie between 32 and 42 $cm^{-1}$, while that for the hexacoordinate complex is 62 $cm^{-1}$. Complexes containing a sexidentate edta exhibit a single intense band around 470 $cm^{-1}$ in the 450—500 $cm^{-1}$ region, while complexes containing a quinquedentate edta exhibit two intense bands in this region. These Raman spectral criteria were then applied for the determination of the solution structure. The Raman spectral features observed for solutions of Fe(III)-edta complexes indicate that the any alkali metal salts and acid salts of $Fe^{III}(edta)^-$ give sexidentate heptacoordinate complex ions in water. The dimeric complex which is formed in an alkaline solution was characterized as being a dinuclear complex consisting of two quinquedentate hexacoordinate iron(III) moieties with a Fe–O–Fe bridging unit.

Iron(III) complexes with ethylenediaminetetraacetate (edta) have been extensively studied, especially in relation to their catalytic activities. An iron(III)-edta system shows both catalase and peroxidase activities.[1—6] This system also catalyses superoxide dismutation.[7—9] Detailed information about the structure of Fe(III)-edta complexes in solution is indispensable for any understanding of such catalytic activities. In the crystalline states of Fe(III)-edta complexes, three different geometries have been found by X-ray analyses. The sexidentate heptacoordinate geometry has been commonly found in amber Li, Na, K, Ag, and Tl salts.[10—12] These unique heptacoordinate complexes have a distorted pentagonal bipyramidal geometry. The pentagonal plane consists of two amino nitrogens, two carboxylato oxygens, and a water molecule, while the axial positions are occupied by the remaining two carboxylato oxygens. The sexidentate hexacoordinate geometry has been found in yellow lithium salt.[13,14] In addition, the quinquedentate hexacoordinate monoaqua complex, $[Fe^{III}(edtaH)(H_2O)]$, has been found in yellow acid salt.[15]

Although the structures of the Fe(III)-edta complexes in crystalline states have been clearly determined, the structure in solution has not been well-characterized. One of the reasons is that the structure in the solid states is not necessarily retained in solution, since high-spin iron(III) complexes are substitution labile in solution.

Although visible-near-infrared spectra[16] in solution have been used to differentiate between hexa- and heptacoordination of Fe(III)-edta complexes, those spectra are of little use for determining the coordination mode (quinque- or sexidentate) of edta. Nuclear magnetic resonance (NMR) is of great use in elucidating the solution structure of diamagnetic transition metal complexes. The applicability of NMR, however, is greatly limited in determining the solution structure of Fe(III)-edta complexes because of the paramagnetic properties of iron(III). Very recently, EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near edge structure) techniques have been applied to distinguish hexa- and heptacoordination of Fe(III)-edta complexes in solution.[17]

In our previous work,[18] the Raman spectral method was successfully applied for the structural determination of Cr(III)-edta complex in solution. The Raman spectra in the 300—600 $cm^{-1}$ region, in which skeletal vibrations of the coordination polyhedron occur, have been found to be particularly informative concerning the coordination geometry. Herein we apply the Raman spectral method in order to establish the structure of Fe(III)-edta complexes in solution.

## Experimental

**Preparation. $Fe^{III}$-edta Complexes:** The yellow acid salt, $HFe^{III}(edta)\cdot H_2O$, and amber acid salt, $HFe^{III}(edta)\cdot 2.5H_2O$, were prepared according to a method of Lambert, Godsey, and Seitz.[19] The alkali metal salts were obtained by the modified method of Hoard et al.[10] as follows: The solution of the acid salt was neutralized by adding a solution of an equivalent amount of alkali metal hydroxide (sodium or potassium) or carbonate (lithium, rubidium, or cesium). After filtering the resulting solution, the filtrate was concentrated with a rotary evaporator. Crystals were obtained by spontaneous evaporation of the concentrated solution at room temperature. The lithium salt crystallized into the yellow or amber form; sometimes, a mixture of the two forms. It is uncertain what conditions of crystallization govern the crystal forms of the lithium salt. Formulations of the alkali metal salts were confirmed by elemental analyses and are as follows: $LiFe^{III}(edta)\cdot 3H_2O$ (yellow and amber),

$NaFe^{III}(edta)\cdot 3H_2O$, $KFe^{III}(edta)\cdot 2H_2O$, $RbFe^{III}(edta)\cdot 2.5H_2O$, and $CsFe^{III}(edta)\cdot 2H_2O$. Dimeric complex, $Na_4[Fe^{III}_2(edta)_2O]\cdot 3H_2O$ was isolated by the method of Schugar, Walling, Jones, and Gray.[20)]

**$Fe^{III}$-1,3-pdta Complexes:** 1,3-propanediaminetetraacetic acid ($1,3\text{-pdtaH}_4$) and its barium salt were prepared by a method of Weyh and Hamm.[21)] Potassium salt of $Fe^{III}(1,3\text{-pdta})^-$ was prepared as follows. A mixture containing 5.76 g of barium salt of 1,3-pdta, 4.72 g of iron(III) sulfate, and 1.74 g of potassium sulfate in 50 $cm^3$ of water was stirred at room temperature for 2 h. After the precipitate was removed by filtration, the filtrate was evaporated to 10—20 $cm^3$ with a rotary evaporator. Yellow crystals were obtained by spontaneous evaporation of the concentrated solution at room temperature. Sodium, rubidium, and cesium salts were prepared by the same method by using an equivalent amount of respective alkali metal sulfates.

**Analysis.** Calcd for $NaFe(1,3\text{-pdta})\cdot 3H_2O$: C, 30.36; H, 4.63; N, 6.44%. Found: C, 30.30; H, 4.64; N, 6.40%. Calcd for $KFe(1,3\text{-pdta})\cdot 0.5H_2O$: C, 32.53; H, 3.72; N, 6.90%. Found: C, 32.57; H, 3.68; N, 6.96%. Calcd for $Rb(1,3\text{-pdta})\cdot 0.5H_2O$: C, 29.20; H, 3.34; N, 6.19%. Found: C, 29.15; H, 3.30; N, 6.27%. Calcd for $CsFe(1,3\text{-pdta})\cdot 2.5H_2O$: C, 24.65; H, 3.57; N, 5.23%. Found: C, 24.41; H, 3.34; N, 5.08%.

**Measurements.** The solid samples used for Raman measurements were in the forms of disks. The disks were spun so as to avoid any thermal decomposition induced by local laser illumination. The Raman spectra were recorded on a JASCO R-800 laser Raman spectrophotometer with an $Ar^+$ ion laser (514.5 or 488.0 nm). The spectral band width was set at 5 $cm^{-1}$. The concentrations of neutral and acidic solutions were 0.1 mol $dm^{-3}$. The concentrations of the alkaline solutions were less than 0.05 mol $dm^{-3}$ because of the high absorbances of the complex in the alkaline solution.

**Calculations.** Normal coordinate analysis was performed using computer programs, BGLZ and LSMB, developed by Shimanouchi laboratory, Department of Chemistry of the University of Tokyo.

## Results and Discussion

**Solid State Structures of the Alkali Metal Salts of $Fe^{III}(edta)^-$.** Of the alkali metal salts, the amber Li, Na, K, and Rb salts have been characterized to have a sexidentate heptacoordinate complex ion[10—12)] and the yellow Li salt to have a sexidentate hexacoordinate complex ion[13,14)] by X-ray analyses. As noted in the Experimental Section, the crystallization conditions which give the yellow or amber lithium salt selectively was not found. However, recrystallization of relatively purified lithium salt tends to give the yellow salt in most cases. Coexisting ions in the crystallization solvent may, therefore, influence the crystalline form of the lithium salt.

At first, we examined the Raman spectra of the solid alkali metal salts in order to determine the spectral difference between the hexa- and heptacoordinate complexes. It was found that the 300—600 $cm^{-1}$ region is most diagnostic to the coordination geometry. The observed spectra in this region are shown

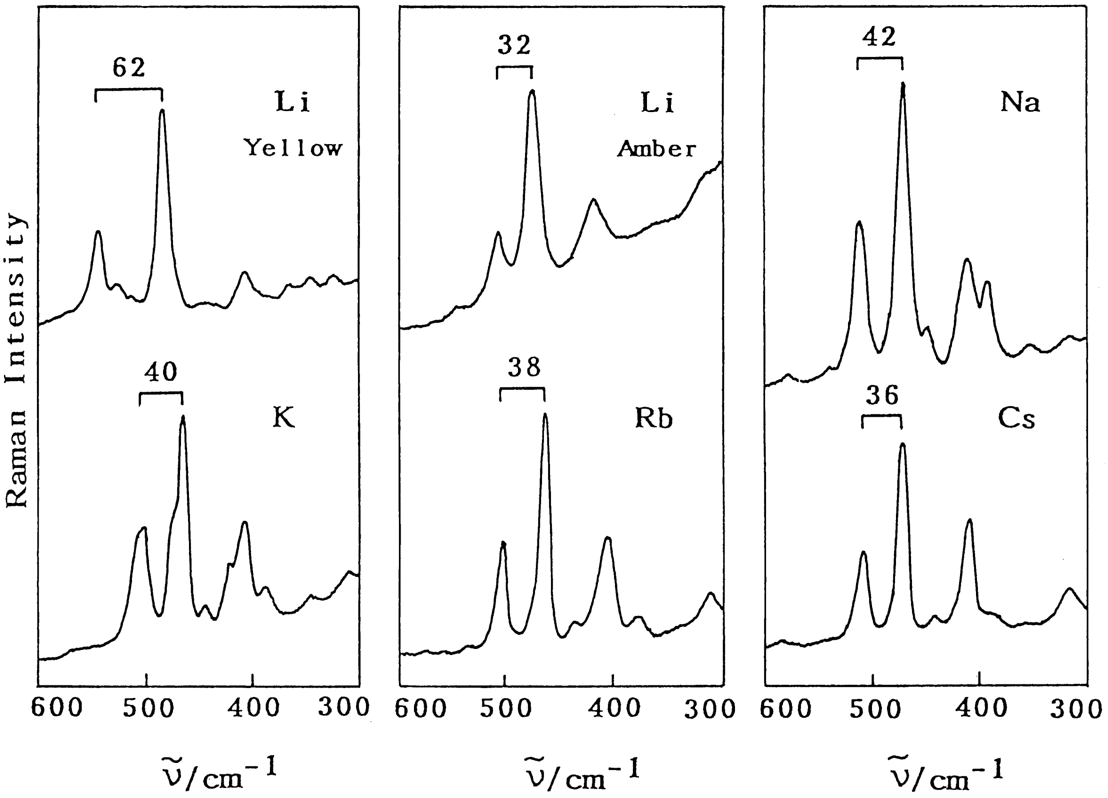

Fig. 1. Raman spectra of alkali metal salts of $Fe^{III}(edta)^-$ in solid states.

Table 1. Observed and Calculated Wavenumbers (cm$^{-1}$), and Vibrational Assignments for $[\mathrm{Fe(edta)}]^-$ and $[\mathrm{Fe(edta)(H_2O)}]^-$ in the 300—600 cm$^{-1}$ Region

| $[\mathrm{Fe(edta)}]^-$ | | | $[\mathrm{Fe(edta)(H_2O)}]^-$ | | |
|---|---|---|---|---|---|
| Obsd[a)] | Calcd[b)] | Assignments[c)] | Obsd[a)] | Calcd[b)] | Assignments[c)] |
| 565 vw | 544 B | Fe-N, C-N-C | 534 vw | 548 B | Fe-N, C-C=O |
| 545 s | | | | | |
| | | | 502 s | 518 A | Fe-N, C-N-C |
| 526 w | 521 A | Fe-N, O-Fe-N | | | |
| 510 vw | | | | | |
| | | | 470 vs | 496 A | Fe-N, O-Fe-N, Fe-W, O-Fe-W |
| | | | | 480 B | Fe-N, O-Fe-O |
| 483 vs | 486 B | Fe-N, N-Fe-N, Fe-N-C | | | |
| | 484 A | C-N-C, O-Fe-N, Fe-O | 447 w | 446 B | O-Fe-N |
| | 480 B | O-Fe-O, Fe-N-C | | 428 B | O-Fe-O |
| | | | | 427 A | O-Fe-O, O-Fe-N, Fe-O |
| 443 vw | 414 A | N-Fe-O, C-C=O | | | |
| 409 m | 413 B | Fe-O, C-N, O-C=O | 408 m | 404 B | Fe-O, C-N-C, O-Fe-N, O-Fe-O |
| | | | | 403 A | O-Fe-N, O-Fe-O |
| 390 sh | 389 B | C-N-C | | | |
| | 388 A | C-N-C, O-Fe-O | 391 m | 380 B | O-Fe-W, O-Fe-O, Fe-O, C-N-C |
| | 368 A | C-N-C, Fe-O | 350 w | 358 A | Fe-W, C-N-C |
| 364 w | 355 B | C-N-C | | 349 A | Fe-N-C, C-N-C, Fe-W |
| 346 w | 352 A | O-Fe-O, Fe-O | | 345 B | C-N-C, Fe-O |
| | 346 A | Fe-O, O-Fe-O, O-Fe-N | | | |
| | | | 316 vw | 329 B | C-N-C, N-Fe-O, Fe-N-C, O-Fe-W |
| 325 w | 322 B | O-Fe-O, Fe-O | | 318 A | C-N-C, Fe-W |
| | 309 A | O-Fe-O, Fe-O | | 305 B | O-Fe-W, Fe-O |

Force constants: K(Fe-N) 0.85; K(Fe-O) 0.6; K(N-C) 3.9; K(C-C) 2.3; K(C=O) 7.7; K(C-O) 7.6; H(N-Fe-N) 0.15; F(N-Fe-N) 0.12; H(N-Fe-O) 0.45; F(N-Fe-O) 0.12; H(O-Fe-O) 0.2; F(O-Fe-O) 0.3; H(Fe-N-C) 0.1; F(Fe-N-C) 0.2; H(N-C-C) 0.45; F(N-C-C) 0.25; H(C-C-O) 0.23; F(C-C-O) 0.67; H(C-C=O) 0.6; F(C-C=O) 0.9; H(C-N-C) 0.3; F(C-N-C) 0.15; (mdyn Å$^{-1}$). a) Data for the lithium salts. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. b) A and B stand for symmetry species under $C_{2v}$ point group. c) Symmetry coordinates of which potential energy distributions are more than 10%.

in Fig. 1. The edta complexes give fairly intense Raman bands in the 300—600 cm$^{-1}$ region, while the Raman spectrum of edta, itself, has only weak bands in this region. Most of the observed bands in the 300—600 cm$^{-1}$ region can, therefore, be assigned to such skeletal vibrations as Fe–N and Fe–O stretching and bending of the coordination polyhedron. In order to make sure of this assignment, normal coordinate analyses were performed for $[\mathrm{Fe(edta)}]^-$ and $[\mathrm{Fe(edta)(H_2O)}]^-$ complexes. The results are summarized in Table 1 for vibrations in the 300—600 cm$^{-1}$ region. In a normal coordinate calculation, protons were neglected and a simplified force field was employed. The bending and repulsive force constants for the N–Fe–N, Fe–N–O, and C–N–C angles were set, as shown in the footnote of Table 1. The other force constants were transferred from those obtained for $[\mathrm{M(gly)_2}]$ (M=Ni$^{\mathrm{II}}$, Cu$^{\mathrm{II}}$, and Co$^{\mathrm{II}}$).[22)] Table 1 shows that the vibrations in the 450—550 cm$^{-1}$ region have a larger contribution of Fe–N stretching, and those in the 300—450 cm$^{-1}$ region have a dominant contribution of Fe–O stretching, and skeletal and C–N–C bendings.

As can be seen from Fig. 1, there are some minor differences among the spectra of the heptacoordinate Li, Na, K, and Rb ion in the 300—450 cm$^{-1}$ region in which skeletal bending has a larger contribution. A close spectral resemblance is, however, clearly recognized in the 450—600 cm$^{-1}$ region, in which Fe–N stretching dominates. That is, all of the spectra have a most intense band around 470 cm$^{-1}$ and a second intense band around 510 cm$^{-1}$. The hexacoordinate Li salt also shows the most intense band around 470 cm$^{-1}$, with a second intense band at higher wavenumbers. This apparent spectral resemblance between the hexa- and heptacoordinate iron(III)-edta complexes is expectable since both complexes have the same $C_{2v}$ symmetry. However, a detailed examination of the spectra indicates that the wavenumber differences between the most intense and second intense bands in the 450—600 cm$^{-1}$ region are definitely different between the hepta- and hexacoordinate complexes. That is, the wavenumber differences observed for the heptacoordinate Li, Na, K, and Rb salts lie between 32 and 42 cm$^{-1}$. On the other hand, the wavenumber difference observed for the hexacoordinate lithium salt is 62 cm$^{-1}$. Predicting such a difference based on a normal coordinate analysis is not meaningful because of poor knowledge regarding the potential field for transition metal complexes containing a large organic ligand, such as $[\mathrm{Fe^{III}(edta)}]^-$. Furthermore, no useful information concerning the band intensity could be obtained from a normal coordinate analysis. There-

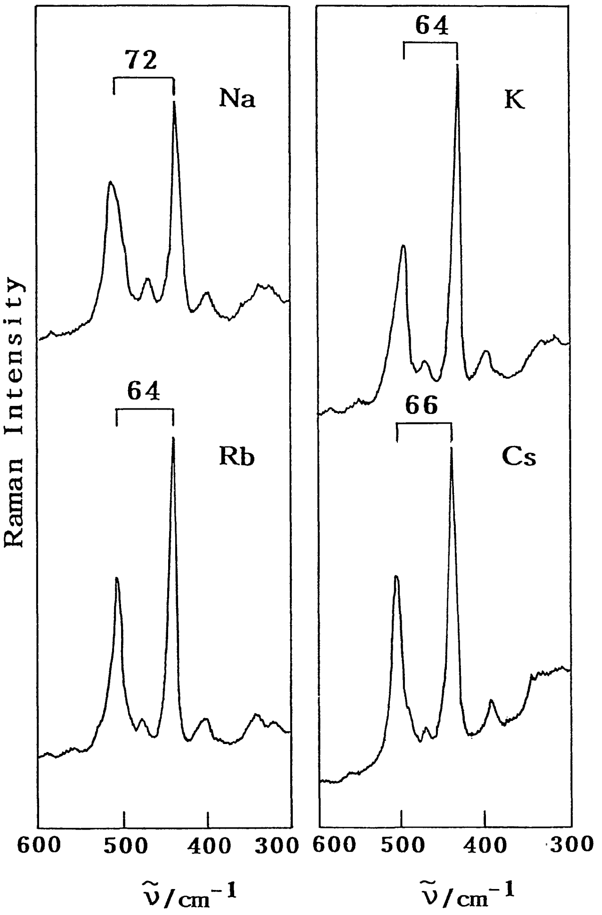

Fig. 2. Raman spectra of alkali metal salts of [$\mathrm{Fe^{III}}$(1,3-pdta)]$^-$ in solid state.

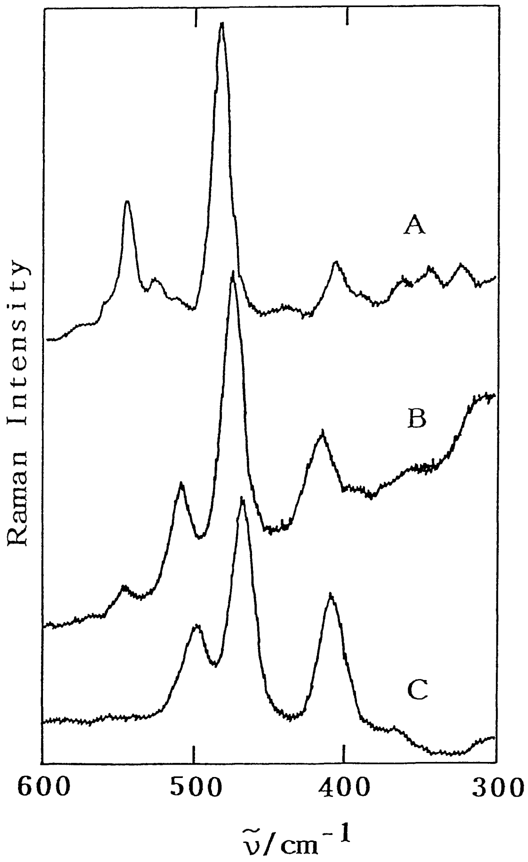

Fig. 3. Raman spectra of acid salt of $\mathrm{Fe^{III}}$(edta)$^-$; A: the yellow form in solid state; B: the amber form in solid state; C: aqueous solution.

fore, we observed the Raman spectra of some alkali metal salts of Fe(III)-1,3-pdta$^-$ (1,3-pdta: 1,3-propanediaminetetraacetate) in order to ascertain the above criterion experimentally. The 1,3-pdta ligand favorably takes a sexidentate hexacoordinate geometry. The observed Raman spectra are shown in Fig. 2. Of the salts in Fig. 2, the sodium salt was confirmed to take a sexidentate hexacoordinate geometry by X-ray analysis.[23] A close resemblance is clearly recognized among the Raman spectra of the Na, K, Rb, and Cs salts, indicating that the K, Rb, and Cs salts also take the sexidentate hexacoordinate geometry. It is reasonably expected that the Raman spectral feature in the 300—600 cm$^{-1}$ region for [$\mathrm{Fe^{III}}$(1,3-pdta)]$^-$ complexes would resemble that for the sexidentate hexacoordinate [$\mathrm{Fe^{III}}$(edta)]$^-$ complexes, since the elongation of the diamine ring should hardly influence the vibrations observed in the 300—600 cm$^{-1}$ region. In fact, the Raman spectra of [$\mathrm{Fe^{III}}$(1,3-pdta)]$^-$ have a very similar feature to that of the sexidentate hexacoordinate [$\mathrm{Fe^{III}}$(edta)]$^-$. The wavenumber differences between the most intense and second intense bands in the 450—600 cm$^{-1}$ region for the 1,3-pdta complexes lie between 64 and 72 cm$^{-1}$, being consistent with the criterion proposed for differentiating hexa- and heptacoordinate geometry for [$\mathrm{Fe^{III}}$(edta)]$^-$ Then, it is reasonably assumed that the wavenumber difference of the two major bands in the 450—600 cm$^{-1}$ region is diagnostic to the coordination number of the complexes with edta and an edta-like ligand.

For the cesium salt, which has not been characterized by X-ray analysis, the wavenumber difference is 36 cm$^{-1}$. The complex ion in the cesium salt is, therefore, concluded to be in a sexidentate heptacoordinate geometry.

No noticeable systematic difference due to the cation size was found in the Raman spectra in the region of 300—600 cm$^{-1}$.

**Structures of the Acid Salt.** The two different crystalline forms (yellow and amber) of the acid salt, H$\mathrm{Fe^{III}}$(edta), have been isolated. X-ray analysis of the yellow acid salt shows that the complex is in a hexacoordinate geometry and that edta coordinates as a quinquedentate ligand.[15] The sixth position is occupied by a water molecule. The quinquedentate edta ligand leaves a carboxyl group uncoordinated. Infrared studies have also indicated the presence of an uncoordinate -COOH group in the yellow acid salt.[19,24] Figure 3-A shows the Raman spectrum of the yellow acid salt in the 300—600 and 1600—1800 cm$^{-1}$ regions. The existence of the uncoordinate carboxyl group in the yellow acid salt has been confirmed by an observation of the 1745 cm$^{-1}$ band due to the C=O stretching of the -COOH group. The spectral feature in the 300—600 cm$^{-1}$ region is completely different from those observed for the alkali metal salts (cf. Fig. 1). Especially, the spectral difference in the 450—500 cm$^{-1}$ region was found to be most diagnostic to the coordination mode of edta. That is, a single intense band appears around 470 cm$^{-1}$ for the complexes with a sexidentate edta ligand, whereas two intense bands appear in this region for a complex with a quinquedentate edta ligand. This band splitting may be the result of a lack of symmetry in the quinquedentate edta complex. A similar spectral feature has been found in the quinquedentate hexacoordinate Cr$^{III}$(edta)$^-$ complex.[18)]

The structure of the amber acid salt has not been well-characterized, though its color suggests a heptacoordinate iron(III) complex. Figure 3-B shows the Raman spectra of the amber acid salt. The spectral feature in the 300—600 cm$^{-1}$ region quite resembles those observed for the amber alkali metal salts which contain a sexidentate heptacoordinate monoaqua iron(III) complex ion. In addition, the spectrum in the 1600—1800 cm$^{-1}$ region has no bands which are attributable to a carboxyl group. These observations indicate that the amber acid salt is highly likely to contain a sexidentate heptacoordinate monoaqua complex ion. A similar structure has been found in $H_2Mn_3(edta)_2\cdot 10H_2O$.[25)] In this complex, the acid hydrogens are located between two [Mn$^{II}$(edta)(H$_2$O)]$^{2-}$ units, linking them by hydrogen bonding.

**Structure in Neutral Aqueous Solutions.** The structure of Fe(III)-edta complexes in solutions has been studied by several methods with various degrees of certainty. Several geometries have been proposed for the complex in neutral aqueous solutions. Hoard, Kennard, and Smith[26)] have pointed out that the complex ion takes a quinquedentate heptacoordinate geometry in aqueous solutions. Garbet, Lang, and Williams[16)] have suggested the same geometry based on their visible-near-infrared study. On the other hand, Higginson and Khan[27)] have proposed a sexidentate hexacoordinate geometry based on their spectrophotometric measurements. Oakes and Smith[28)] have shown that the complex has a single water molecule in its coordination sphere, based on their NMR relaxation study, implying a sexidentate heptacoordinate geometry. Several other NMR relaxation studies[29,30)] have also indicated the presence of a single coordinate water in the complex in aqueous solutions. Sawyer and Tackett[31)] have investigated the infrared spectra of iron(III)-edta complex in D$_2$O as a function of pD. They observed a single peak in the 1500—1700 cm$^{-1}$ region in the pD range of 2.4—7.5 and indicated that all the carboxylate groups of edta coordinate to iron(III). Sakane et al.[17)] have pointed out that the complex ion is in a heptacoordinate geometry based on the EXAFS and XANES spectra.

Raman spectra of solution samples have almost the same quality as those of solid samples. Therefore, one can compare directly the structure in solution with that in the solid state by comparing the Raman spectra obtained for both states. Figure 3-C presents the Raman spectrum of an aqueous solution of the hexa- or heptacoordinate lithium salt. Any other alkali metal salts, of course, give the same spectra in aqueous solution. The spectra of the solid samples are also shown for a comparison. The Raman spectrum of the solution quite resembles those observed for the sexidentate heptacoordinate complex ions in the solid state. Namely, a single band was observed at 468 cm$^{-1}$ and the observed wavenumber difference between this band and the one at higher wavenumber was 31 cm$^{-1}$. These facts clearly indicate that the Fe(III)-edta$^-$ complex exists dominantly in a sexidentate heptacoordinate geometry in neutral aqueous solutions.

**Structures in Acidic Solutions.** In acidic solutions a protonation of the coordinate carboxyl group would be expected for the iron(III)-edta complex. Schwarzenbach and Heller[32)] have reported the equilibrium constant, p*K*, for this protonation to be less than 1.5. Lambert, Godsey, and Seitz[19)] have obtained 2.2 for this p*K* value, and suggested that the complex exists in a quinquedentate heptacoordinate geometry. Sawyer and Tackett[31)] observed the infrared spectrum of the complex in D$_2$O at pD=1.5 and assigned the very faint absorption around 1720 cm$^{-1}$ to the vibration of

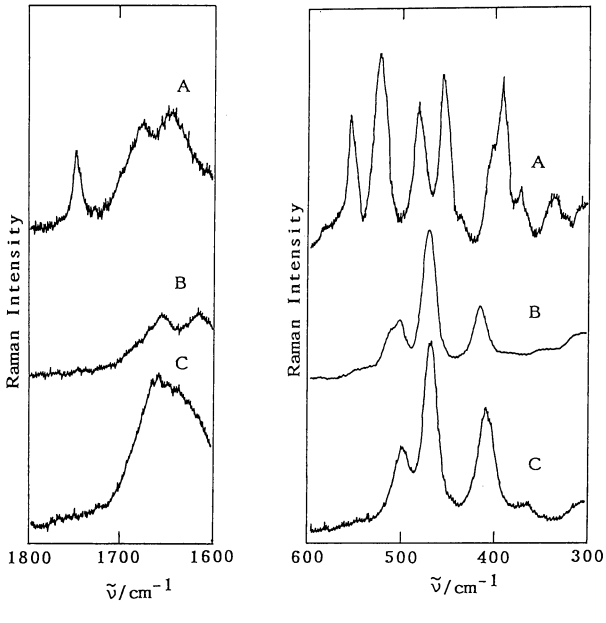

Fig. 4. Raman spectra of LiFe$^{III}$(edta)$\cdot$3H$_2$O; A: the yellow form in solid state; B: the amber form in solid state; C: aqueous solution.

an uncoordinate carboxyl group.

The Raman spectrum of the yellow or amber acid salt in aqueous solution is shown in Fig. 4-C. The pH of the solution was 1.2. The spectrum in the 300—600 $cm^{-1}$ region is very similar to that of the sexidentate heptacoordinate acid salt but is completely different from that of the quinquedentate hexacoordinate acid salt. There is no band which is assignable to a C=O stretching of the uncoordinated carboxyl group in the 1700—1800 $cm^{-1}$ region. These observations indicate that the complex is ionized and unambiguously takes a sexidentate heptacoordinate geometry, even at pH=1.2.

The iron(III)-edta complex is fairly stable even in strongly acidic solutions. In order to determine the structure in strongly acidic solutions, the Raman spectra in 1 and 2 mol $dm^{-3}$ HCl solutions were observed (Fig. 5). The weak shoulder which is observed around 1730 $cm^{-1}$ in a 1 mol $dm^{-3}$ HCl solution becomes clear upon increasing the acidity of the solution. This band is attributable to C=O stretching of the -COOH group. In the 300—600 $cm^{-1}$ region, new bands appear around 390, 450, and 520 $cm^{-1}$ in the 1 mol $dm^{-3}$ HCl solution; the intensities of these bands increase with increasing the HCl concentration. Regarding the positions, these new bands correspond well to the bands observed in the quinquedentate hexacoordinate acid salt in the solid state. These observations suggest that the protonated complex is formed in HCl solutions and is in a quinquedentate hexacoordinate geometry. In contrast to the HCl solutions, even in 2 mol $dm^{-3}$ $HClO_4$, no new bands were observed in the 300—600 $cm^{-1}$ region. Since the perchlorate ion has little tendency to coordination, the coordination of a chloride ion may be responsible for the formation of the quinquedentate hexacoordinate complex in HCl solutions. The band at 312 $cm^{-1}$, clearly observed in the Raman spectrum of the 2 mol $dm^{-3}$ HCl solution, may be due to Fe–Cl stretching.[33]

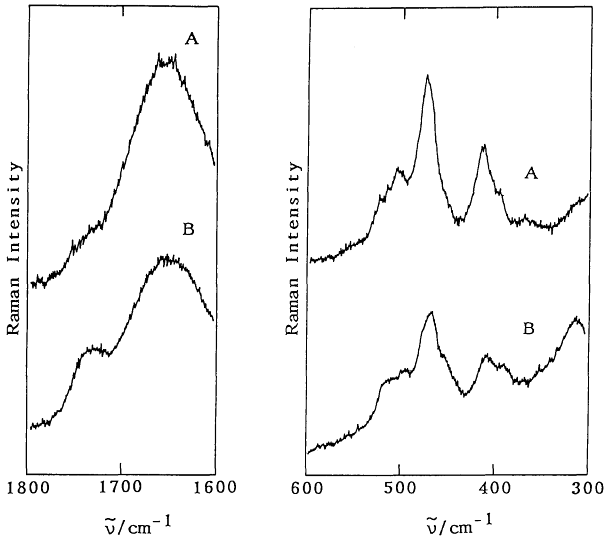

Fig. 5. Raman spectra of $Fe^{III}(edta)^-$ in HCl solutions; A: 1 mol $dm^{-3}$ HCl solution; B: 2 mol $dm^{-3}$ HCl solution.

**Structures in Alkaline Solutions.** Schwarzenbach and Heller[32] have reported equilibrium constants corresponding to the formation of mono-, di-, and trihydroxo species: p$K$=7.5, 9.4, and 12.3, respectively. Of these hydroxo species, the existence of the di- and trihydroxo complexes is questionable. Dimerization also occurs in basic solutions, and its formation constant has been reported.[4,34–36] The crystalline dimer has been isolated[20] but not characterized by X-ray analysis. An X-ray analysis of the dimer with hedta ($N$-hydroxyethylenediamine-$N,N',N'$-triacetate) shows that the dimer consists of two hexacoordinate iron(III) units surrounded by a bridging oxygen and a quinquedentate hedta ligand.[37] An analogous structure has been proposed for the dimeric complex with edta.[36]

Figure 6 shows the Raman spectrum of the solid sodium salt of the dimeric complex with edta. If the monomeric unit in the dimer has a quinquedentate hexacoordinate geometry, the Raman bands due to the monomeric unit should appear in the similar positions to those of the quinquedentate hexacoordinate acid salt, since it is reasonably expected that the deprotonation of the uncoordinate carboxyl group in the quinquedentate hexacoordinate acid salt hardly affects the skeletal vibrations of the coordination polyhedron. In fact, the bands at 522, 478, 457, and 390 $cm^{-1}$ observed for the dimer correspond well with respect to their positions to the bands at 523, 481, 455, and 392 $cm^{-1}$ observed for the quinquedentate hexacoordinate acid salt. The band at 422 $cm^{-1}$ observed for the dimer may be assigned to the symmetric

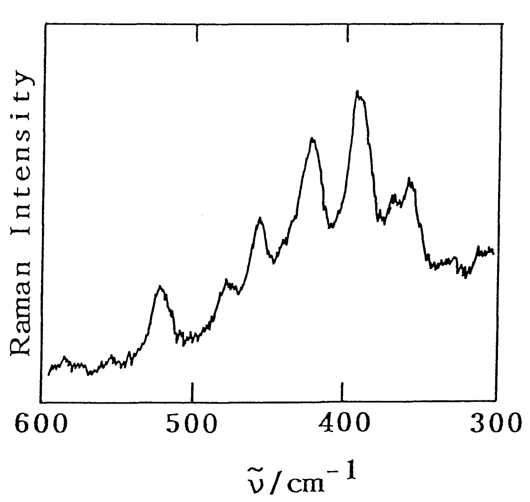

Fig. 6. Raman spectrum of $Na_4[Fe_2(edta)_2O]\cdot 3H_2O$ in solid state.

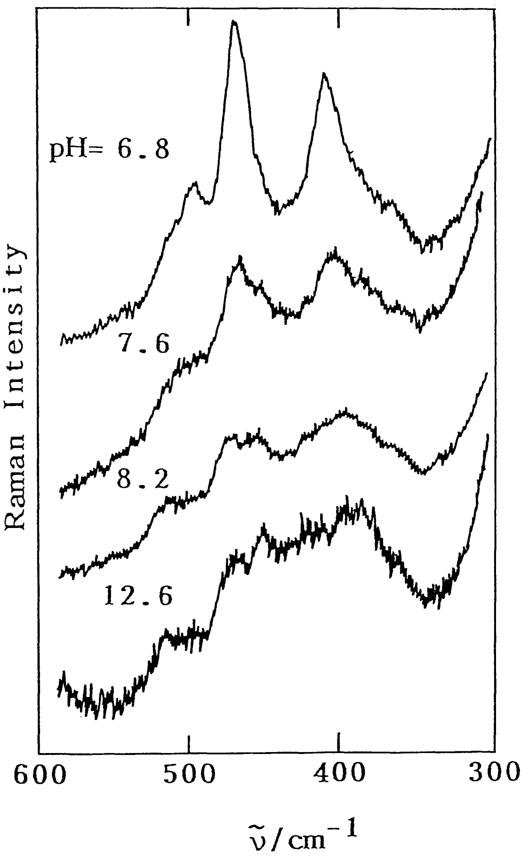

Fig. 7. Raman spectra of alkali metal salt of $Fe^{III}(edta)^-$ in aqueous solution as a function of pH.

stretching of the Fe–O–Fe unit.[38,39]

Figure 7 shows the Raman spectra of the iron(III)-edta complex as a function of pH. The solution becomes dark red when the pH increases. A 0.1 mol dm$^{-3}$ solution of the complex, which was employed for the Raman measurement of neutral and acidic solutions, completely absorbs laser light. The Raman spectra at a higher pH region were, therefore, obtained with ca a 0.01 mol dm$^{-3}$ solution and, as a result, the observed spectra have low signal-to-noise ratios. In the Raman spectra at higher pHs several new bands are discernible around 520, 480, 450, 410 and 360 cm$^{-1}$. These bands correspond nicely to those observed for the solid dimer, indicating that the structure of the dimer in the solid state is retained in aqueous solutions. In conclusion, the monomeric unit in the dimer takes a quinquedentate hexacoordinate geometry both in the solid state and aqueous solution.

The existence of the monomeric monohydroxo complex was not confirmed by the present Raman measurements. The monomeric monohydroxo complex, $[Fe(OH)(edta)]^{2-}$, would have either the sexidentate heptacoordinate geometry or the quinquedentate hexacoordinate geometry. It is therefore anticipated that the Raman bands due to the monohydroxo complex are superimposed on those of the monoaqua complex or those of the dimer.

### References

1) P. M. Mader, *J. Am. Chem. Soc.*, **82**, 2956 (1960).

2) G. L. Kochanny and A. Timmick, *J. Am. Chem. Soc.*, **83**, 2777 (1961).

3) Zh. P. Kochanova and A. P. Purmal, *Russ. J. Phys. Chem.*, **38**, 1342 (1964).

4) C. Walling, M. Kurz, and H. J. Schugar, *Inorg. Chem.*, **9**, 93 (1970).

5) R. E. Hester and E. M. Nour, *J. Raman Spectrosc.*, **11**, 35 (1981).

6) E. N. Rizkalla, O. H. El-Shafey, and N. M. Guindy, *Inorg. Chim. Acta*, **57**, 199 (1982).

7) G. J. McClune, J. A. Fee, G. A. McCluskey, and J. T. Groves, *J. Am. Chem. Soc.*, **99**, 5220 (1977).

8) B. Halliwell, *FEBS Lett.*, **92**, 321 (1978).

9) C. Bull, G. M. McClune, and J. A. Fee, *J. Am. Chem. Soc.*, **105**, 5290 (1983).

10) J. L. Hoard, M. Lind, and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 2770 (1961); M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, **3**, 34 (1963).

11) X. Solans and M. Font Altaba, *Acta Cryst., Sect. C*, **40**, 635 (1984).

12) J. M. Lopez-Alcala, M. C. Puetra-Vizcaino, F. Gonzalez-Vilchez, E. N. Duesler, and R. E. Tapscott, *Acta Cryst., Sect. C*, **40**, 939 (1984).

13) N. V. Novozhilova, T. N. Polynova, M. A. Porai-Koshits, N. I. Pechurova, L. I. Martynenko, and A. Khadi, *Zh. Struct. Khim.*, **14**, 745 (1973).

14) Y. Kushi, K. Morimasa, K. Yoshitsugu, and H. Yoneda, Abstracts of Papers, The 35th Symposium on Coordination Chemistry of Japan, Hiroshima, 1985; Abstr., No. 2B01.

15) C. H. Kennard, *Inorg. Chim. Acta*, **1**, 347 (1967).

16) K. Garbet, G. Lang, and R. J. P. Williams, *J. Chem. Soc. A*, **1971**, 3433.

17) H. Sakane, I. Watanabe, K. Ono, S. Ikeda, S. Kaizaki, and Y. Kushi, *Bull. Chem. Soc. Jpn.*, to be published.

18) K. Kanamori and K. Kawai, *Inorg. Chem.*, **25**, 3711 (1986).

19) J. L. Lambert, C. E. Godsey, and L. M. Seitz, *Inorg. Chem.*, **2**, 127 (1963).

20) H. Schugar, C. Walling, R. B. Jones, and H. B. Gray, *J. Am. Chem. Soc.*, **89**, 3712 (1967).

21) J. A. Weyh and R. E. Hamm, *Inorg. Chem.*, **7**, 2431 (1968).

22) J. R. Kincaid and K. Nakamoto, *Spectrochim. Acta*, **32A**, 277 (1976).

23) K. Okamoto, K. Kanamori, and J. Hidaka, *Acta Cryst.*, in press.

24) L. H. Hall and J. L. Lambert, *J. Am. Chem. Soc.*, **90**, 2036 (1968).

25) S. Richards, B. Pederson, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964).

26) J. L. Hoard, C. H. L. Kennard, and G. S. Smith, *Inorg. Chem.*, **2**, 1316 (1963).

27) W. C. E. Higginson and A. H. Khan, *J. Chem. Soc. Pak.*, **5**, 93 (1983).

28) J. Oakes and E. G. Smith, *J. Chem. Soc., Faraday Trans. 1*, **79**, 543 (1983).

29) J. F. Whidby and D. E. Leydon, *Anal. Chim. Acta*, **51**, 25 (1970).

30) J. Bloch and G. Navon, *J. Inorg. Nucl. Chem.*, **42**, 693 (1980).

31) D. T. Sawyer and J. E. Tackett, *J. Am. Chem. Soc.*, **85**, 2390 (1963).

32) G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 576 (1951).

33) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed, John Wiley & Sons, New York (1978), pp. 317—324.

34) R. L. Gustafson and A. E. Martell, *J. Phys. Chem.*, **67**, 576 (1963).

35) H. J. Schugar, A. T. Hubbard, F. C. Ansonn, and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 71 (1969).

36) C. Manley, *Z. Angew. Phys.*, **32**, 187 (1971).

37) S. J. Lippard, H. Schugar, and C. Walling, *Inorg. Chem.*, **6**, 1825 (1967).

38) D. J. Hewlin and W. P. Griffith, *J. Chem. Soc. A.*, **1966**, 472.

39) R. M. Wing and K. P. Callahan, *Inorg. Chem.*, **8**, 871 (1969).