Electron Spin Resonance Studies of Iron(III) Complexes of Ethylenediaminetetra-acetate and *N*-(2-Hydroxyethyl)ethylenediamine-*NN′N′*-triacetate in Co-ordinating Solvents

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Remarkable solvent dependence of the apparent peak-to-peak linewidth (ΔH_{pp}) has been observed for the rhombic type of e.s.r. spectra of the high-spin Fe^{III}(edta) (edta = ethylenediaminetetra-acetate) and Fe^{III}(hedta) [hedta = *N*-(2-hydroxyethyl)ethylenediamine-*NN′N′*-triacetate] complexes in a series of co-ordinating solvents. Moreover, the order of the solvents which gave the characteristic ΔH_{pp} for each complex was different for the two complex systems: *i.e.* $H_2O \geqslant$ dimethyl sulphoxide (dmso) > *NN*-dimethylformamide (dmf) > CH_3OH for Fe^{III}(edta) and $H_2O > CH_3OH >$ dmf $\geqslant$ dmso for Fe^{III}(hedta). Solvent dependence of the band maxima ($\lambda_{max.}$) corresponding to the *d–d* transition has been also observed for the same series of iron(III) complex–solvent systems although the $\lambda_{max.}$ values obtained were less sensitive to the solvent than the ΔH_{pp} values. In this case, the solvent dependence of $\lambda_{max.}$ for Fe^{III}(edta) and Fe^{III}(hedta) was similar: $\lambda_{max.}$ was smaller for H_2O and CH_3OH (< 600 nm) than for dmf and dmso (> 700 nm). The co-ordination behaviour of the solvent molecules to these iron(III) complexes is discussed in relation to both the ΔH_{pp} and $\lambda_{max.}$ values. It is revealed that in the case of rhombic high-spin iron(III) complexes with such edta and hedta, ΔH_{pp} values obtained by e.s.r. spectroscopy reflect small changes in the co-ordination circumstances; $\lambda_{max.}$ values obtained from electronic spectra did not.

Iron(III) in aqueous solution has been known to form variable co-ordination with multidentate ligands such as ethylenediaminetetra-acetate (edta).[1] This multidentate co-ordination is affected not only by the pH of the solution but also by the type of solvent, as observed through Mössbauer measurements[2] and absorption spectroscopy.[3] However, the structural information about the chelated iron(III) complexes given by the Mössbauer method was not direct nor precise. Absorption spectroscopy has yielded more reliable information, which proposed that the band maximum ($\lambda_{max.}$) corresponding to the *d–d* transition ${}^6A_{1g} \rightarrow {}^4T_{2g}$ can be an indicator of the co-ordination number of Fe^{III}(edta)(solvent) type complexes.[3] However, the $\lambda_{max.}$ values neither depended on the nature of the solvent nor correlated with the Mössbauer parameters. Therefore, to make clear the co-ordination behaviour of Fe^{III}(edta) complexes in co-ordinating solvents, another method is still required.

In this study, e.s.r. spectroscopy was applied because this is one of the most powerful methods to analyse the ligand field in paramagnetic transition metal complexes. Since it is known that Fe^{III}(edta) complexes in frozen aqueous solution are in the rhombic high–spin state,[2,4,5] it was hoped that the e.s.r. spectra may be sensitive to changes in the co-ordination environment.

The e.s.r. measurements were performed for Fe^{III}(edta) and Fe^{III}(hedta) [hedta = *N*-(2-hydroxyethyl)ethylenediamine-*NN′N′*-triacetate] complexes in the frozen co-ordinating solvents water, methanol, *NN*-dimethylformamide (dmf), and dimethyl sulphoxide (dmso).

Experimental

Materials.—Iron(III) ammonium sulphate, $Na[Fe^{III}(edta)]$, $Na_2(H_2edta)$, and $Na_3(hedta)$ were Katayama Chemical reagent grade. Dimethyl sulphoxide, *NN*-dimethylformamide, and methanol solvents were all specially prepared reagents of Nakarai Chemical Limited. Water used as solvent was distilled ion-exchanged.

Sample Preparation.—For the preparation of Fe^{III}(edta) complexes, $Na[Fe^{III}(edta)]$ (1 mmol dm^{-3}) was dissolved into the appropriate solvent. This method ensured that the formation of iron(III) hydroxide was negligible. Fe^{III}(hedta) complex solutions were prepared by dissolving iron(III) ammonium sulphate (1 mmol dm^{-3}) into the $Na_3(hedta)$ solution (3 mmol dm^{-3}). Aqueous solutions were adjusted to pH 7 by mixing citric acid (0.1 mol dm^{-3}) and 0.2 mol dm^{-3} of disodium hydrogenphosphate solutions. For the e.s.r. experiments, 0.3 cm^3 of the complex solution was transferred into a quartz tube (4-mm outside diameter), evacuated, and shielded. In the spectroscopic experiments, complex solutions containing 10 mmol dm^{-3} of Fe^{3+} were measured using a 10-mm quartz cell.

Spectroscopic Method.—First-derivative e.s.r. spectra at *X*-band frequencies (9 150 ± 10 MHz) were obtained using a JEOL JES-ME-IX spectrometer system. E.s.r. measurements were performed at 77 K using a liquid nitrogen dewar. Field calibrations were made with a benzene solution of diphenylpicrylhydrazyl (dpph; $g = 2.003\ 54$).

The absorption spectra were measured with a Hitachi model 100-50 spectrophotometer at ambient temperature.

Results

E.S.R. Spectra of Fe^{III}(edta) *and* Fe^{III}(hedta) *Complexes in Co-ordinating Solvents.*—E.s.r. spectra of Fe^{III}(edta) and Fe^{III}(hedta) complexes in various solvents are shown in Figure 1. The apparent peak-to-peak linewidth (ΔH_{pp}) of these pseudo-singlet spectra varied from 2 to 16 mT depending on the solvent. In addition, two complexes in this study gave almost the same e.s.r. spectra in an aqueous solution of pH 7 but gave completely different ones in other solvents (*i.e.* CH_3OH, dmf, dmso). As a result, the order of solvents with decreasing ΔH_{pp} was $H_2O \geqslant$ dmso > dmf > CH_3OH for Fe^{III}(edta) and $H_2O > CH_3OH >$ dmf $\geqslant$ dmso for Fe^{III}(hedta).

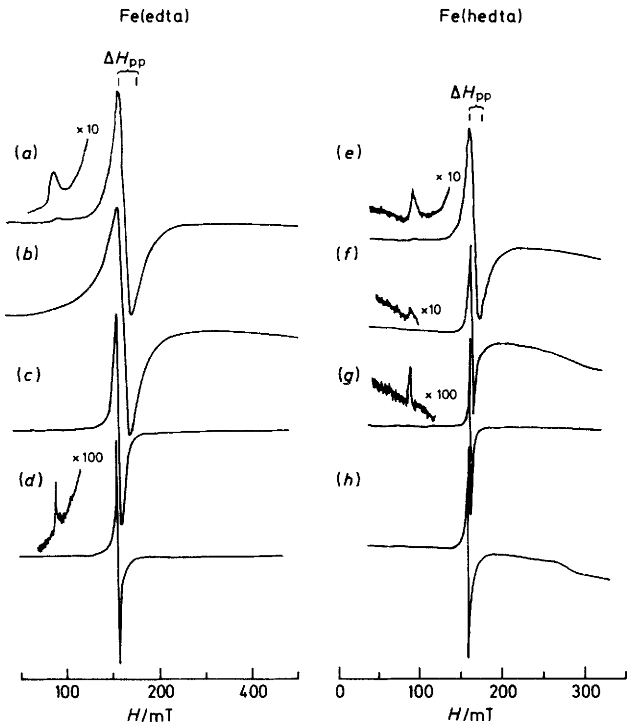

Figure 1. E.s.r. spectra obtained from Na[Fe^{III}(edta)] (1 mmol dm^{-3}) in H_2O (pH 7) (*a*), dmso (*b*), dmf (*c*), methanol (*d*) and from Fe^{III}(hedta) in H_2O (pH 7) (*e*), methanol (*f*), dmf (*g*), dmso (*h*). Recorded at 77 K

An additional weak signal was observed to low field of the main signal in every e.s.r. spectrum of these complexes, which is considered to originate from the transition between another Kramers doublet.[5]

The e.s.r. parameters obtained from Figure 1 are summarized in the Table.

Absorption Spectra.—Absorption spectra of Na[Fe^{III}(edta)] were measured in the same series of solvents used for the e.s.r. experiments (Figure 2). Although the band structure is not as clear beyond 500 nm, similarity of spectral features was found between (*a*) and (*b*), both having $\lambda_{max.}$ around 800 nm, and also between (*c*) and (*d*), and having $\lambda_{max.}$ around 600 nm.

Absorption spectroscopy was also applied for the Fe^{III}(hedta) complex but the band structure of the spectra was too broad and ambiguous to estimate the band maximum.

The absorption data for the Fe^{III}(edta) complex are also listed in the Table together with the results for [Fe^{III}(hedta)$(H_2O)_2$] reported by Garbett *et al.*[3]

E.S.R. Results.—E.s.r. features of the iron(III) edta and hedta complexes in co-ordinating solvents revealed that the ligand field around Fe^{3+} was weak and strongly rhombic. This rhombic high–spin iron(III) is described by the spin Hamiltonian of equation (1); precise reports of theoretical analysis of the e.s.r.

$$\mathscr{H}_s = g\mu_B BS + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) \quad (1)$$

spectra were presented by Aasa and co-workers.[5,6] Here, S, S_x, S_y, and S_z are the spin quantum number and its (x, y, z) components, D and E are zero-field splitting parameters, μ_B is the Bohr magneton, and B is the magnetic flux density at the resonance field.

Using the results of their third-order perturbation calculation for a transition between the middle Kramers doublet, expressions for the principal g values were obtained as in equations (2)—(5).

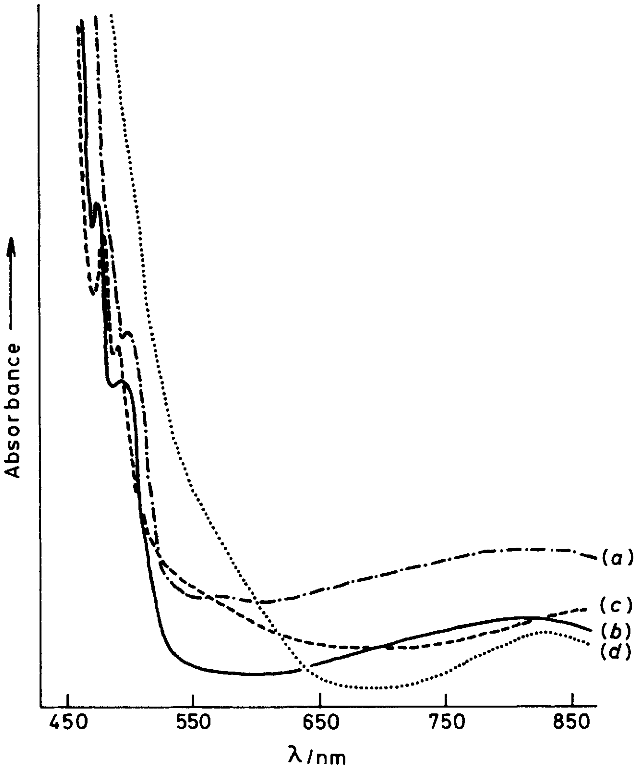

Figure 2. Absorption spectra of Na[Fe^{III}(edta)] in dmf (*a*), dmso (*b*), H_2O (*c*), and methanol (*d*)

$$g_x = 30/7 - (12\,240/2\,401)q^2 - (2\,880/2\,401)r^2 \quad (2)$$

$$g_{z,y} = 30/7 \pm (120/49)q - (1\,320/2\,401)q^2 - (1\,620/2\,401)r^2 \quad (3)$$

where

$$q = (1 - 3E/D)/(1 + E/D) \quad (4)$$

and

$$r = -2(\mu_B B/D)/(1 + E/D) \quad (5)$$

Equations (2)—(5) imply that the principal g values vary with q and r, *i.e.* with the value of E/D. Actually, when the E/D value changes from 0.32 to 0.21, contribution of the second terms of equations (2) and (3) changes from 0.0046 to 0.55 and from 0.07 to 0.81. The rest of the terms contribute one order of magnitude less than these. Wickman *et al.*[7] and Aasa[5] have presented g *versus* E/D and $h\nu$ *versus* g/g' plots, respectively, which are useful to predict the ligand-field dependence of the g anisotropy.

In order to interpret the large apparent linewidth variation (from 2 to 16 mT) observed in this study, we also estimated the g *versus* E/D plot which can simulate the experimental results.

The best-fit parameters of g (4.5, 4.2, 4.1), ΔH_{pp} = 13.9 mT, E/D = 0.3, and D = 0.74 cm^{-1} were obtained for the experimental values of g (4.55, 4.36, 4.11) and ΔH_{pp} = 13.8 mT, which were given by Fe^{III}(edta) complexes made from aerated [Fe^{II}(Hedta)]$^-$ in aqueous solution of pH 7.* For a constant

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* This system gave the best resolved rhombic e.s.r. spectra among the studied systems. Accordingly, estimated g values are the most reliable so that the simulation calculation for this system is worthwhile.

Table. Absorption and e.s.r. spectroscopic data and solvent parameters ε and E_T

	Fe^{III}(edta)		Fe^{III}(hedta)			
Solvent	$10^4\Delta H_{pp}$/T	$\lambda_{max.}$/nm	$10^4\Delta H_{pp}$/T	$\lambda_{max.}{}^a$/nm	ε (25 °C)[b]	$E_T{}^c$/kcal mol^{-1}
H_2O	157	575	155	540	78.4	63.1
Methanol	20	560	47	600	32.6	55.5
dmf	60	810	19	725	37	45.0
dmso	155	810	18.5	725	46.6	43.8

[a] Ref. 3. [b] Dielectric constant, ref. 9. [c] Ref. 8 (cal = 4.184 J).

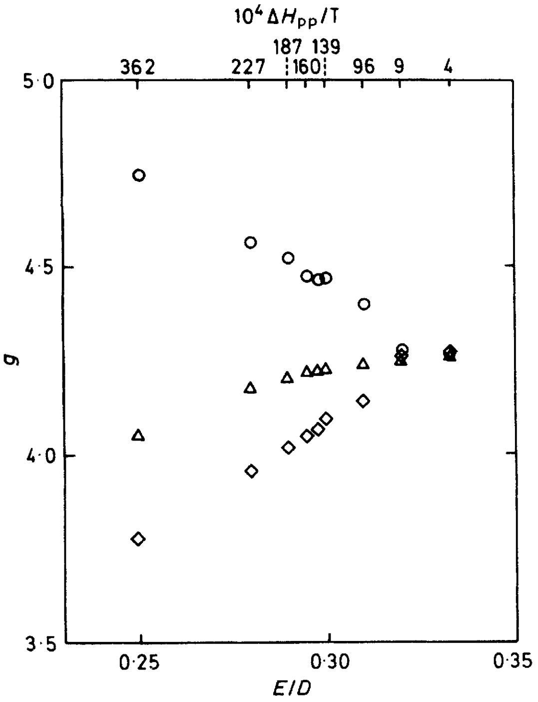

Figure 3. Plot of high-spin iron(III) g values [(△) g_x, (◇) g_y, (○) g_z] for the middle Kramers doublet as a function of the rhombic character of the field (E/D) and the peak-to-peak linewidth, ΔH_{pp}, estimated from the difference of the resonant field corresponding to the largest and the smallest principal g values. $D = 0.74$ cm^{-1}, $B = 0.16$ T

value of E/D, e.g. 0.3, an increase in D from 0.5 to 1.2 cm^{-1} made each of the principal g values increase by ca. 0.03. In contrast, slight change in E/D resulted in a large anisotropy change of the g values (Figure 3).

The apparent peak-to-peak linewidth observed for Fe^{III}(edta) and Fe^{III}(hedta) complexes in this study might be affected by the non-homogeneous broadening owing to the existence of species, differing for example, in the degree of polymerization, or in the displacement of the co-ordinating sites of edta by the solvent. However, these are unlikely because no additional signals were observed characteristic of the polymerized iron(III) complexes and more strongly co-ordinating solvents such as dmso and dmf yielded smaller ΔH_{pp} values for Fe^{III}(hedta) complexes. Moreover, solvent dependence of ΔH_{pp} for Fe^{III}(edta) was completely different from that for Fe^{III}(hedta). Therefore, it seems reasonable to consider that the large solvent dependence of ΔH_{pp} is mainly due to variation of E/D, especially the variation of E.*

Since indistinguishable e.s.r. spectra for Fe^{III}(edta) and Fe^{III}(hedta) in a neutral aqueous solution implied that the edta molecule in this solution was five-co-ordinate, i.e. Hedta^{3-}, the same as hedta, the E/D variation in these complexes in different solvents probably arose from the type and the number of the co-ordinating solvent molecules.

As for the number of the co-ordinating solvent molecules, Garbett et al.[3] have reported that both Fe^{III}(edta) and Fe^{III}(hedta) were seven-co-ordinate in H_2O and methanol and six-co-ordinate in dmf and dmso on the grounds that the absorption peaks, $\lambda_{max.}$, corresponding to the ${}^6A_{1g}\rightarrow{}^4T_{2g}$ transition were characteristic of the co-ordination number: i.e. six-co-ordinate complexes have a $\lambda_{max.} > 700$ nm and the seven-co-ordinate ones <600 nm. As shown in the Table, however, $\lambda_{max.}$ values were not dependent on the type of solvent and represented no difference between edta and hedta complexes.

Variety of the solvent dependence of the g anisotropy observed as an apparent spectral width indicated that the e.s.r. spectrum is very sensitive to the change in the ligand-field symmetry. According to the estimation shown in Figure 3, complexes with smaller ΔH_{pp} values have larger rhombicity of the ligand field. Since we observed completely different results for Fe^{III}(Hedta) from those for the Fe^{III}(hedta) system, it cannot be concluded simply that more strongly co-ordinating solvents cause larger rhombicities. In the hedta system, however, this seems to be true since solvent dependency of $\lambda_{max.}$ and ΔH_{pp} showed an inverse correlation for the studied solvents: the stronger axial ligand will destabilize the ${}^6A_{1g}$ ground state which has half-filled d orbitals more than the excited ${}^4T_{2g}$ state which has a vacant e_g orbital, so that the larger $\lambda_{max.}$ value resulted. Generally, the stronger ligand at the sixth co-ordination site leads to the smaller rhombicity because it would occupy as close a position as possible to the bisector of the x and y axes and destabilize the d_{yz} and d_{zx} orbitals to about the same degree. However, when the configuration of the sixth ligand is fixed out of the bisector, the situation could be inverse because the d_{yz} orbital would be destabilized more than d_{zx}. The co-ordination of the 'stronger' ligand makes the rhombic splitting enlarge more than the tetragonal splitting; that is, the 'stronger' axial ligand possibly causes the larger rhombicity and will give the smaller ΔH_{pp}. This seems to be the case for Fe^{III}(hedta). Interestingly, in the Fe^{III}(hedta) system, the solvation parameter,[8] E_T, showed a good correlation with $\lambda_{max.}$ for the studied solvents (Table). Solvation may work to increase the cubic field strength and destabilize the ${}^4T_{2g}$ state more by the increased pairing energy, and consequently results in a lower $\lambda_{max.}$ for a larger E_T. The smaller rhombicity in the solvents of larger E_T is accord with this.

Unexpected results for the Fe^{III}(Hedta) system can be attributed to the unco-ordinated portion of edta, i.e.

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* Since the studied systems did not provide three accurate principal g values, we could not perform a perfect simulation calculation. However, using the apparent g values, which were estimated at the saddle, crossover, and bottom points of the spectrum, we obtained reasonable figures of E/D: Fe^{III}(edta) in H_2O and in dmso, $E/D = 0.295$; in dmf, 0.318; in methanol, 0.328; Fe^{III}(hedta) in H_2O, $E/D = 0.295$; in methanol, 0.320; in dmf and in dmso, 0.328.

$-CH_2COOH$ (*cf.* $-CH_2CH_2OH$ in hedta). It is likely that the free carboxymethyl group in edta repels polar solvent molecules more strongly than the less polar ones and interferes with tight co-ordination of the solvent. Supporting this, the dielectric constant (ε)[9] showed good correspondence with the ΔH_{pp} values in the Fe^{III}(Hedta) system (see Table). This is in contrast to the Fe^{III}(hedta) system whose non-co-ordinating group is less polar and which did not show such a correspondence.

On the basis that ΔH_{pp} of Fe^{III}(hedta) in a methanol solution was 2.5 times larger than that of Fe^{III}(Hedta) as well as $\lambda_{max.}$ for the former being larger than for the latter, we suspect that the Fe^{III}(hedta) complex is a mixture of six- and seven-co-ordinate complexes in methanol, different from Garbett's proposal[3] of a single species with the seven-co-ordination.

In conclusion, it can be stated that as a result of the solvent co-ordination to Fe^{III}(Hedta) or its derivative complexes in a rhombic high-spin state, where the solvents have slightly different co-ordinating ability, an apparent peak-to-peak linewidth of the e.s.r. spectra reflects the ligand-field symmetry very sensitively, whereas the *d–d* transition band only reflects a difference in the ligand-field strength due to different co-ordination numbers.

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