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Nuclear Magnetic Resonance Study of Praseodymium, Europium and Ytterbium Ethylenediaminetetraacetates*†

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Proton NMR has been used to study the structural and kinetic behaviour in D_2O solution, of the ethylenediaminetetraacetates of praseodymium, europium and ytterbium. The constants $K^H_{LnEDTA^-}$ for the following equilibrium have been measured

$$\mathrm{LnOH(EDTA)(H_2O)}^{2-}_{n-1} + \mathrm{H}^+ \rightleftharpoons \mathrm{Ln(EDTA)(H_2O)}^-_n$$

(log $K^H_{LnEDTA^-}$ = 12.86 (Pr), 12.48 (Eu) and 12.3 (Yb) at 20 °C). In the case of ytterbium, the rate of interconversion of YbEDTA⁻ and the hydroxo complex has been estimated, and is of the order of 10^4 sec^{-1}. Finally, evidence has been given for the existence of 1:2 and 2:3 complexes in a solution of europium with an excess of EDTA; in the 1:2 complex the second EDTA molecule is bound by only one iminodiacetate group, whereas in the 2:3 complex, one EDTA molecule acts as a bridging ligand.

Introduction

A previous publication from this laboratory [3] treated the ligand exchange reaction of several rare earth ethylenediaminetetraacetates ($LnEDTA^-$) with EDTA in excess. The system was interpreted as being a simple two site exchange between $LnEDTA^-$ and free EDTA. However, the coordination of a second EDTA molecule has been suggested by Kostromina and Ternovaya [4], on the basis of proton NMR data, and more recently, Brucher *et al.* [5] have shown by spectrophotometric and potentiometric methods the existence of a 1:2 $Ln(EDTA)_2^{5-}$ complex and also a bridged complex $Ln_2EDTA_3^{6-}$; the above mentioned interpretation did not take into account such species.

Merbach and Gnaegi's NMR study [3] was carried out on diamagnetic rare earths. In this work, three paramagnetic lanthanides have been chosen, in the hope that the much larger range of chemical shift differences between bound and free ligands would enable identification of 1:2 and 2:3 metal/EDTA complexes.

Much interest has focussed on the 1:1 $LnEDTA^-$ complexes, especially since their introduction as lanthanide shift reagents for aqueous solutions [6, 7]. Their usefulness as shift reagents lies in the fact that they may be used between pH 6 and 10, *i.e.* much higher than for the uncomplexed aquo ions which precipitate near neutral pH. Thus, before proceeding to a study of the systems with ligand in excess, the pH and temperature dependence of the proton NMR spectra of solutions of praseodymium, europium and ytterbium ethylenediaminetetraacetate have been investigated. These particular lanthanides were chosen because of their representative behaviour as chemical shift reagents. $PrEDTA^-$ causes downfield shifts, whereas $YbEDTA^-$ induces upfield shifts and also broadens resonances. The existence of the controversial structural change shown by the $LnEDTA^-$ complexes across the lanthanide series [8, 9] prompted us to also study the behaviour of $EuEDTA^-$, which is intermediate in the series, and induces upfield shifts.

The behaviour of lanthanide EDTA complexes is complicated at high pH by the formation of hydroxo species of the type $LnOH(EDTA)^{2-}$. The protonation constants for these hydroxo complexes have been measured for europium by polarography [10], for neodymium by absorption spectroscopy [11] and for several diamagnetic rare earths by NMR [3]. We shall report values for praseodymium, europium and ytterbium.

Experimental

The lanthanide ethylenediaminetetraacetates ($KLnEDTA \cdot nD_2O$) were prepared as described in reference [3], and recrystallised twice from D_2O. The ratio rare earth/EDTA was confirmed to be 1:1 by titration (in the presence of xylene orange indicator and urotropine buffer) with a solution of EDTA or rare earth nitrate in the appropriate case [12]. In

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every case, one drop caused the colour change. The amount of D_2O of crystallisation was determined by means of Karl Fischer titrations in dry methanol, using Metrohm apparatus E452.

All solutions for proton NMR were made up in D_2O (99.9% D): for solutions with excess of ligand the appropriate amount of D_4EDTA was added to the KLnEDTA·nD_2O. The pH was adjusted at 20 °C in a thermostated jacket Metrohm EA876-1, using a Metrohm E457 microburette containing solutions of 4M KOD or DNO_3. The KOD was prepared by carefully reacting potassium metal with D_2O under nitrogen. The DNO_3 (83% D) was made by diluting fuming nitric acid in D_2O.

The electrodes were standardised in H_2O medium, using the method described in [13], and since the measurements have been carried out using D_2O as solvent, the meter readings have been corrected to the pD scale using the relationship pD = pH(meter reading) + 0.4 [14]. Since pD is the generalised equivalent of pH in deuterated solvents, the term pH will henceforth be used for the corrected values.

NMR measurements were made on a Bruker WP-60 spectrometer using Fourier transform mode with internal deuterium lock. As internal reference, either tetramethylammonium chloride (TMAC) or tertiary butanol (t-butOH) were used as secondary standards in concentration <1%. However, chemical shift values are reported with respect to the sodium salt of 3-trimethylsilyl-1-propane sulfonate (TMS*), with $\delta_{\text{t-butOH}} = 1.233$ ppm and $\delta_{\text{TMAC}} = 3.166$ ppm. Temperatures, accurate to ±1 °C, were measured with a Hewlett Packard platinum resistor thermometer No 2802A using the substitution technique.

Results and Discussion

The proton NMR spectrum of free EDTA consists of two singlets with intensity ratio 2:1, corresponding to the acetate and ethylenic protons. Once the EDTA is coordinated to a metal ion, the appearance of the spectrum depends on the labilities of the metal–oxygen and metal–nitrogen bonds. In all cases studied here, the metal–nitrogen bond is relatively inert, resulting in an AX pattern for the inequivalent acetate protons. Thus a typical spectrum at low pH consists of a singlet due to the ethylenic protons, and two doublets with $J \simeq 16$ Hz for the acetate protons.

Solutions with Ratio Ln/EDTA 1:1

The pH dependence of the chemical shift at 20 °C in a 0.053 m solution of KPrEDTA in D_2O is depicted in Figure 1. It can be seen that no significant change in the chemical shift occurs until pH 11.2, where an important change in δ begins to take place. The slight chemical shift change seen below pH 4.4 is due to formation of the acid complex HPrEDTA. The downfield shifts at high pH are attributed to the formation of a monohydroxo complex*. This is most conveniently treated as a simple protonation reaction (1) for which

$$\underset{\text{B}}{\text{LnOH(EDTA)(H}_2\text{O)}^{2-}_{n-1}} + \text{H}^+ \rightleftharpoons \underset{\text{A}}{\text{Ln(EDTA)(H}_2\text{O)}^{-}_{n}} \qquad (1)$$

the equilibrium constant is $K^{H}_{\text{LnEDTA}^-}$. Spectra of both PrEDTA$^-$ and the hydroxo complex are also shown in Figure 1. Exchange between the species A and B in 1:1 solutions is rapid, and the chemical shift of the single peak observed is the population weighted mean of the chemical shifts of species A and B. Taking into account the law of mass action for reaction (1), one obtains the relation (2).

$$\delta^{\text{obs}}_{\text{LnEDTA}^-} = \frac{1}{1 + K^{H}_{\text{LnEDTA}^-}[\text{H}^+]} (\delta_{\text{B}} + K^{H}_{\text{LnEDTA}^-}[\text{H}^+]\,\delta_{\text{A}}) \qquad (2)$$

By fitting the experimental data to equation (2) using a non linear regression program, we were able to calculate $K^{H}_{\text{LnEDTA}^-}$. In Table I we report this quantity for the three lanthanides studied, together with the results of other authors for comparison. The results for europium and ytterbium were obtained from the plots of pH *versus* chemical shift depicted in Figures 2 and 3, in which are also shown spectra of the corresponding LnEDTA$^-$ and hydroxo complexes.

One interesting feature that is apparent for ytterbium (Figure 3) is the "turning back" of the chemical shift for acetate peak c at highly alkaline pH. This was not observed for the other two lanthanides studied, perhaps because of the smaller difference in chemical shift for the various species, but it shows clearly that there are other species present besides the proposed monohydroxo complex. It is suggested that these could include a double hydroxo complex of the form Yb(EDTA)(OH)$_2^{3-}$. However, the data do not allow quantitative calculations for this, so they have been interpreted by assuming that the first step is formation of YbOH(EDTA)$^{2-}$.

The protonation constants $K^{H}_{\text{LnEDTA}^-}$ for the hydroxo complex of LnEDTA$^-$ (Table I), show that the stability of the hydroxo complexes increases across the series. The decrease in log $K^{H}_{\text{LnEDTA}^-}$ from praseodymium through europium to ytterbium is to be expected because the smaller rare earth ions cause

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*It is noted at this stage that although we consider the hydroxo complex to be of the form LnOH(EDTA)$^{2-}$, we cannot exclude the possibility of other species such as a bridged dimeric complex of the form {Ln(EDTA)–OH–(EDTA)Ln}$^{3-}$.

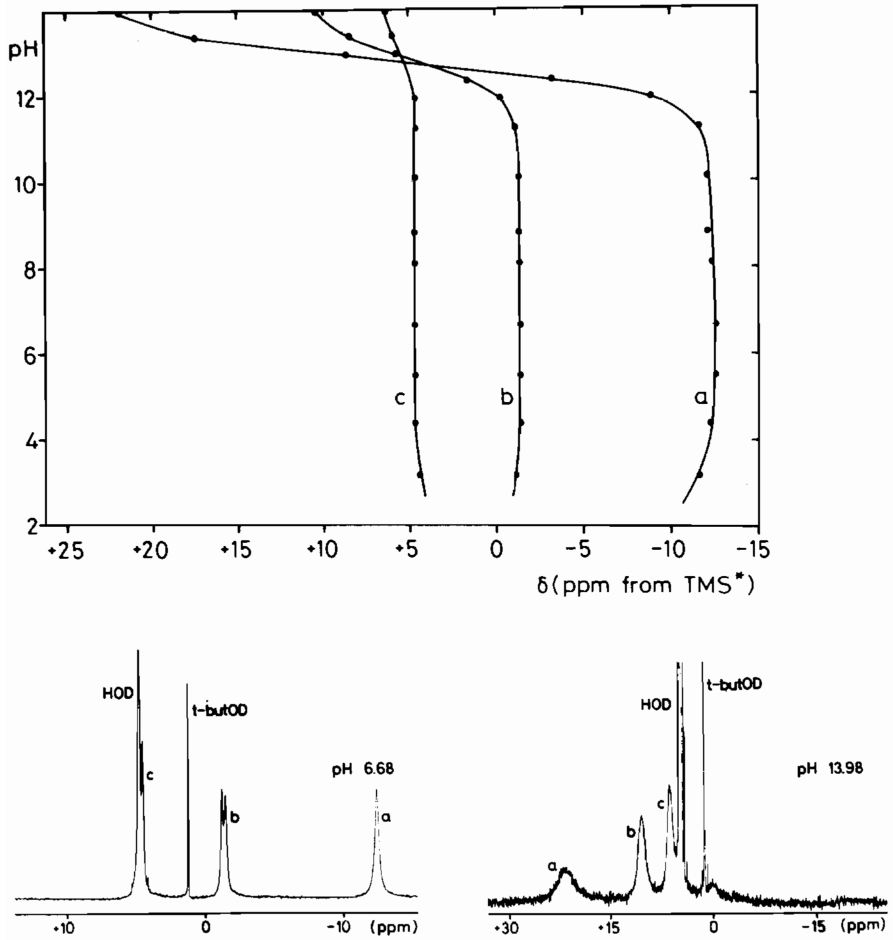


Figure 1. pH dependence of chemical shift for KPrEDTA, 0.053m, at 20 °C, with typical spectra. Assignments: a) ethylenic protons; b), c) acetate protons.

TABLE I. Logarithms of the Protonation Constants $K^{H}_{LnEDTA^-}$ of $LnOH(EDTA)(H_2O)^-_{n-1}$ at 20 °C.

Sc	Y	La	Pr	Nd	Eu	Yb	Lu
10.6[a]	11.9[a]	>11[a]	12.86[b]	≃12.2[c]	12.48[b] 12.64[d]	12.3[b]	11.7[a]

[a] By NMR, [KLnEDTA] = 0.1m [3]. [b] By NMR, this work, [KLnEDTA] = 0.05m for Pr^{3+}, Eu^{3+}, 0.1m for Yb^{3+}. [c] By polarography, [Eu] = 0.001m [10]. [d] By spectrophotometry, [KNdEDTA] = 0.01 to 0.03m; for the reaction $NdEDTA^- + OH^- \rightleftharpoons NdOH(EDTA)^{2-}$, log K = 1.78 [11].

a larger polarisation of the coordinated water molecules, increasing the stability of the complex. This is consistent with the results of other authors for other lanthanides, taking into account experimental error.

In the case of praseodymium and europium, reaction (1) occurs at a rate that is too rapid to be measured by NMR. However, for ytterbium, it was possible to determine the pseudo first order rate constant, k, for the conversion of the hydroxo species to $YbEDTA^-$. These are given in Table II, and it is seen that at 20 °C and at a pH where $YbEDTA^-$ and $YbOH(EDTA)^{2-}$ are in almost equal concentrations, k would be of the order of 10^4 sec^{-1}. This is too slow to be simply a proton jump (which is effectively a substitution of OH^- by H_2O), but could be explained by one of a number of mechanisms, such as the decrease of the coordination number by one, with the departure of an OH^- molecule, or a mechanism whereby the unbound carboxylate group of a five

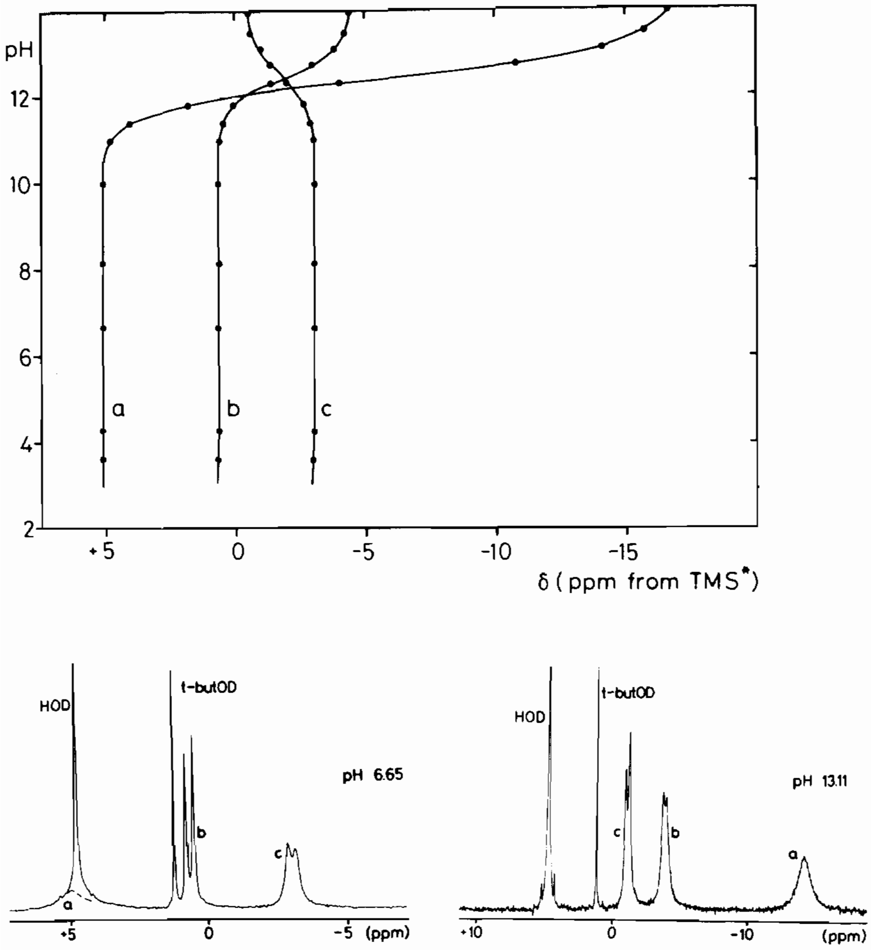


Figure 2. pH dependence of chemical shift for KEuEDTA, 0.047m, at 20 °C, with typical spectra. Assignments: a) ethylenic protons; b), c) acetate protons.

TABLE II. Estimated Pseudo First Order Rate Constants, $k = -d[\mathrm{YbOH(EDTA)^{2-}}]/dt[\mathrm{YbOH(EDTA)^{2-}}]$, for the Interconversion of the Hydroxo Complex and $\mathrm{YbEDTA^-}$.

pH	P[a]	k (sec^{-1})		
		0 °C[b]	50 °C[c]	80 °C[c]
11.99	0.33	2.7 × 10^3	–	9.5 × 10^4
12.14	0.41	–	3.0 × 10^4	–
12.62	0.68	1.3 × 10^3	–	5.5 × 10^4
12.67	0.70	–	1.7 × 10^4	–

[a] $P = [\mathrm{YbOH(EDTA)^{2-}}]/([\mathrm{YbEDTA^-}] + [\mathrm{YbOH(EDTA)^{2-}}])$. [b] Measured on an acetate resonance. [c] Measured on ethylenic resonance.

coordinated EDTA molecule replaces an $\mathrm{OH^-}$ group to regain its usual six coordination. For praseodymium and europium, the mechanism is probably the same, despite the fact that the faster rate of conversion prevented quantitative measurements.

We next consider how the proton NMR spectra of the 1:1 complex are modified when an excess of EDTA is present, using as an example, europium.

Solution with Ratio Eu/EDTA 1:2

The pH dependence of the proton chemical shifts for a solution of Eu/EDTA in the ratio 1:2 are shown at 50 °C in Figure 4. It is easier to distinguish the ethylenic peaks at 50 °C than at 20 °C and so the former temperature reflects better the physical behaviour of the system. Throughout the pH range, two non-equivalent EDTA molecules are present. For purposes of comparison, broken lines have been added to the diagram to show the behaviour of the corresponding 1:1 complex at 50 °C.

At low pH (≃4.4), the chemical shifts of the two sets of EDTA signals are the same as for the 1:1 complex and the free ligand. Considering first the set of EDTA signals with chemical shifts close to those of $\mathrm{EuEDTA^-}$, these diverge from the broken lines between pH 4.4 and 7.5, and then remain constant until

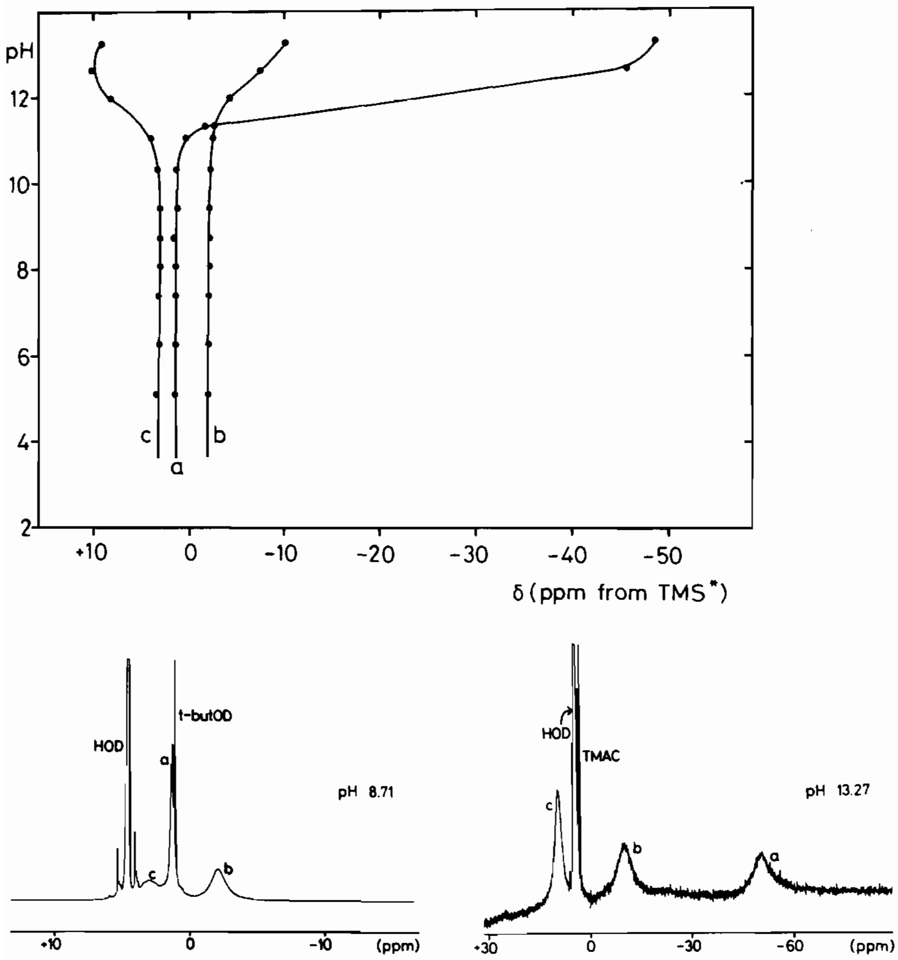


Figure 3. pH dependence of chemical shift for KYbEDTA, 0.1m, at 20 °C, with typical spectra. Assignments: a) ethylenic protons; b), c) acetate protons.

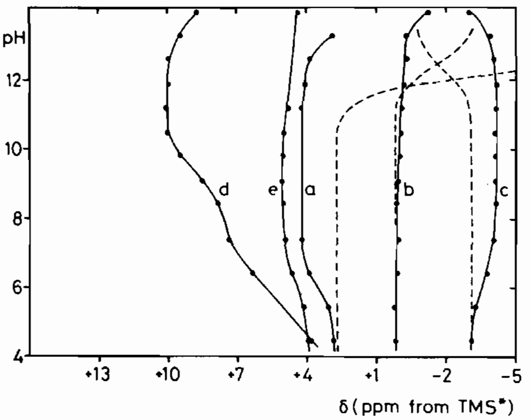


Figure 4. pH dependence of chemical shift at 50 °C for a solution [Eu] = 0.043m, [EDTA] = 0.085m. Assignments: a) ethylenic; b), c) acetate protons of entirely coordinated EDTA; d) ethylenic; e) acetate protons of partially coordinated EDTA. Broken lines represent the corresponding EuEDTA$^-$ complex.

pH ≃ 13. Until this pH, there are no hydroxo complexes formed, unlike for the 1:1 stoichiometry.

The variation of δ for the second EDTA molecule (which does not correspond to the δ pattern of free EDTA), as well as the modified chemical shifts of the 1:1 complex mentioned above, can be explained if we assume that a 1:2 complex, $Eu(EDTA)_2^{5-}$ forms. The first molecule is entirely coordinated as in EuEDTA$^-$, but its peak positions are modified by the presence of a second molecule which is coordinated by only one of its iminodiacetate groups, $-N(CH_2-COO^-)_2$, the other one remaining free. The fact that only a single resonance for the acetate protons of the second molecule can be seen shows that the exchange rate between the free and coordinated iminodiacetate groups is fast on the NMR time scale. The chemical shift curve for the ethylenic protons (d) shows a variation between pH 7 and 10 which is typical of an equilibrium between two species, and may be an indication of protonation of the nitrogen of the free iminodiacetate group, according to equation (3). Brucher's [5] values for the stability constants of the

$$Eu(EDTA)_2^{5-} + H^+ \rightleftharpoons Eu(EDTA)H(EDTA)^{4-} \quad (3)$$

protonated complex $Ln(EDTA)H(EDTA)^{4-}$ and the 1:2 complex $Ln(EDTA)_2^{5-}$, combined with the first protonation constant of free EDTA, predict a value of log K for equation (3) of 8.66 for europium, which agrees reasonably well with Figure 4.

Finally, there are no hydroxo complexes formed because there are probably no water molecules in the first coordination sphere of $Eu(EDTA)_2^{5-}$ which may be deprotonated, and this is why no chemical shift change is seen until pH > 13.

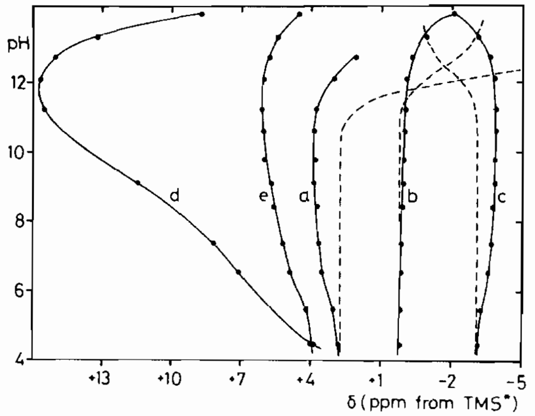
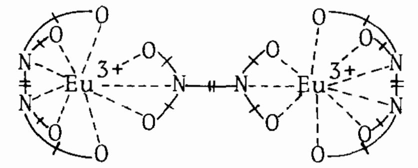


Figure 5. pH dependence of chemical shift at 50 °C for a solution [Eu] = 0.047m, [EDTA] = 0.070m. Assignments: a) ethylenic; b), c) acetate protons of entirely coordinated EDTA; d) ethylenic; e) acetate protons of bridged EDTA. Broken lines represent the corresponding $EuEDTA^-$ complex.

Solution with Ratio Eu/EDTA 2:3

A plot of pH *versus* δ similar to the diagram for the ratio 1:2 is given in Figure 5. As previously, above pH 4.4 there is no free ligand observed. Thus, for the given stoichiometry 2:3 there are two possibilities: either there is 50% 1:1 and 50% 1:2 complex, if we assume that these are the only species present, or there are species such as the bridged $Ln_2EDTA_3^{6-}$ complex proposed by Brucher *et al.* [5] in the solution. In the first case, one would expect approximately the same chemical shifts for the signals of the second molecule of EDTA (d and e) as in Figure 4. Thus the second case seems to be the more likely, since comparison of Figures 4 and 5 shows that the ethylenic protons (d) have a much larger chemical shift than in the solution with 1:2 ratio. This indicates that both iminodiacetate groups of the second EDTA molecules are coordinated symmetrically to a paramagnetic centre. These facts confirm the existence of $Ln_2EDTA_3^{6-}$, for which the assumed structure is shown here:



The chemical shift curve (d) goes through a maximum near pH 12, which corresponds to the region of maximum $Ln_2EDTA_3^{6-}$ formation reported by Brucher in his distribution curve. From a kinetic point of view, the bridging EDTA is more labile than the other two, as witnessed by the fact that its acetate groups appear as a singlet (e) in the NMR spectrum.

The existence of other than 1:1 complexes was not seen by Merbach and Gnaegi [3] and Rhyl [15] in their studies of the diamagnetic rare earth ethylenediaminetetraacetates. In these cases the difference between the resonance for the free and bound iminodiacetate groups was very small and therefore imperceptible. What does become clear from the study of the paramagnetic lanthanide EDTA systems is that the kinetic behaviour in the presence of an excess of EDTA is much more complicated than the scheme presented earlier [3], due to the existence of both 1:2 and 2:3 complexes, and hence we are at this stage unable to proceed to a more quantitative kinetic study.

Acknowledgments

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