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NMR Study of Ternary Complexes of Some Paramagnetic Lanthanide Ethylenediaminetetraacetates with Iminodiacetate, Methyliminodiacetate and cetate*† Nitrilotriacetate*†

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Ternary complex formation of lanthanide ethylenediaminetetraacetates ($LnEDTA^-$) with other polyaminocarboxylate ligands L in D_2O solution has been confirmed by ^1H NMR. For $Ln(EDTA)IDA^{3-}$, the stability is maximum in the middle of the series: log K = 3.27 (Pr), 4.28 (Eu) and 2.67 (Yb), and for Eu(EDTA)L the stability is greatest for NTA^-: log K = 4.28 (IDA), 4.33 (MIDA) and 5.05 (NTA). In the case of $LnEDTA^-$ with excess of NTA, other competing reactions occur with formation of $Ln(NTA)_2^{3-}$, $Ln(EDTA)_2^{5-}$ and $Ln_2EDTA_3^{6-}$.

The ligand exchange reaction

$$Ln(EDTA)L + {}^*L \rightleftharpoons Ln(EDTA){}^*L + L$$

has also been investigated for these complexes, and pseudo first order rate constants k_L estimated. For L = IDA, the rate of exchange decreases across the lanthanide series, and for europium, $k_{MIDA} \cong k_{IDA} > k_{NTA}$.

Introduction

The existence of ternary complexes formed by the rare earth ethylenediaminetetraacetates with a second polyaminocarboxylate ligand such as iminodiacetate (IDA), methyliminodiacetate (MIDA) and nitrilotriacetate (NTA), has been demonstrated previously by potentiometry [3] and absorption spectroscopy [4] [5]. An attempt to predict the mechanism of formation has been made by proton NMR [6]; however, for diamagnetic ions the chemical shift changes are small and it is not possible to obtain formation constants for these complexes. We report here a proton NMR study of several paramagnetic rare earths, which was undertaken in the hope of revealing further information concerning the formation and exchange reactions undergone by these complexes. The work was done as a function of both pH and temperature, and since the presence of the paramagnetic ion causes large chemical shifts, many interesting features which were not obvious with diamagnetic ions appeared. For example, the exchange of the second polyaminocarboxylate ligand, previously thought too fast to be measured, shows itself to be slow on the NMR time scale.

The behaviour of $LnEDTA^-$ in the presence of NTA is particularly interesting. Tananaeva *et al.* [4] had already noticed that the species $Nd(NTA)_2^{3-}$ was present in a solution of $NdEDTA^-$ with an excess of NTA, and preliminary results by Chastellain [7] showed that any ternary complex ($Ln(EDTA)NTA^{4-}$) formation is complicated by the $Ln(NTA)_2^{3-}$/free NTA exchange [8]. This means that some free EDTA will also be present, and the behaviour of $LnEDTA^-$ with an excess of EDTA has been the subject of a recent publication [2].

The behaviour of the various species as followed by NMR help to elucidate the structural and kinetic problems of the ternary complex formation.

Experimental

The preparation and analysis of the lanthanide ethylenediaminetetraacetates ($KLnEDTA \cdot xD_2O$) and the preparation of samples for NMR, as well as the experimental details concerning NMR and pH measurements have been described in the preceding article [2].

The polyaminocarboxylate ligands: iminodiacetic acid (H_4IDA, Fluka), methyliminodiacetic acid (H_4-MIDA, Schuchardt, Munich) and nitrilotriacetic acid (H_3NTA, Siegfried) were recrystallised from D_2O and the water content determined by the Karl Fischer method.

All solutions for NMR were prepared in D_2O, and tertio-butanol (t-butOH) was used as internal reference in concentration <1%. Chemical shift values are reported with respect to the sodium salt of 3-trimethylsilyl-1-propane sulfonate (*TMS): $\delta_{tbutOH} = 1.233$ ppm.

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*Abstracted from Ph.D. thesis of R. V. Southwood-Jones [1].

†Part VI of series. For part V see reference [2].

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TABLE I Logarithms of Stability Constants at 20 °C for Ternary Complex Formation

$$\mathrm{LnEDTA} + \mathrm{L} \rightleftharpoons \mathrm{Ln(EDTA)L}$$

where L is IDA, MIDA and NTA

Metal Ion	Ln(EDTA)IDA			Ln(EDTA)MIDA		Ln(EDTA)NTA	
	a	b	c	b	c	a	c
Pr	3 48		3 27			4 67	
Eu	4 23		4 28		4 33	5 03	5 05
Yb	2 55		2 67			2 85	
Lu	2 51	2 4				2 81	
Y	3 24	3 2		2 8		3 73	

[a] By potentiometry, μ = 0 1*M* KNO_3, [3] [b] By NMR, [13] [c] By NMR, this work, [LnEDTA] = 0 05–0 1*m*, [L] = 0 09–0 25*m*

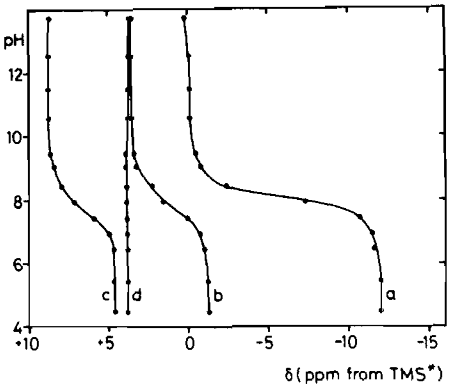

Figure 1 pH dependence of chemical shift at 20 °C for a solution [PrEDTA] = 0 053*m*, [IDA] = 0 133*m* Assignments a) ethylenic b), c) acetate protons of EDTA, d) unique IDA resonance observed

Results

Ln(EDTA)IDA^{3-}

An NMR study of solutions of $PrEDTA^-$, $EuEDTA^-$ and $YbEDTA^-$ with IDA as a second ligand has been undertaken as a function of pH and temperature We shall report here the main features common to the three lanthanides, with particular reference to praseodymium, and shall then describe the different kinetic observations for each rare earth in detail

The pH dependence of chemical shift for the EDTA and IDA resonances in a 1 2 5 solution of $PrEDTA^-/IDA^{2-}$ is shown in Figure 1 A typical spectrum consists of a singlet (a) corresponding to the ethylenic protons of EDTA, an AX spectrum (two widely separated doublets, b and c) corresponding to the non-equivalent acetate protons of EDTA, and a singlet (d) for the IDA protons The sharp change in chemical shift of the EDTA peaks between pH 6 5 and 10 is evidence for the formation of ternary complexes, which proceeds according to the reaction (1) As expected, no hydroxo complexes are evident at high pH, showing that the first coordination sphere

$$\mathrm{LnEDTA^-} + \mathrm{IDA^{2-}} \rightleftharpoons \mathrm{Ln(EDTA)IDA^{3-}} \quad (1)$$

is entirely occupied by EDTA and IDA It is recalled that this was also shown to be the case for $Ln(EDTA)_2^{5-}$ and $Ln_2EDTA_3^{6-}$ [2] There is no peak corresponding either to free EDTA or to a second coordinated molecule of EDTA, showing that $Ln(IDA)_2^{3-}$ cannot be present either However, since the IDA is present in excess, one would expect an exchange reaction to take place between free and complexed IDA according to equation (2) For praseodymium, the linewidths of IDA

$$\mathrm{Ln(EDTA)IDA^{3-}} + {}^{*}\mathrm{IDA^{2-}} \rightleftharpoons \mathrm{Ln(EDTA)^{*}IDA^{3-}} + \mathrm{IDA^{2-}} \quad (2)$$

(at any pH above the point of ternary complex formation) decrease with increasing temperature from 0 °C to 80 °C, and integration of the peaks indicates that the single peak observed contains all the IDA The exchange (2) is therefore rapid on the NMR time scale A slight upfield shift of the IDA peak is apparent near pH 10, and is due to deprotonation of the free IDA

The formation constant K_{Ln} for the ternary complex formation (1) is related to the first protonation constant $1/K_a$ for IDA, and the equilibrium constant K′ for the reaction (3) by the equation $K_{Ln} = K'/K_a$

$$\mathrm{LnEDTA^-} + \mathrm{H(IDA)^-} \rightleftharpoons \mathrm{Ln(EDTA)IDA^{3-}} + \mathrm{H^+} \quad (3)$$

One may obtain K′ from the equivalence point of the chemical shift change as a function of pH (Figure 1), and the initial concentrations of rare earth and ligand† The values found at 20 °C for praseodymium, europium and ytterbium are reported in Table I

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†If the fraction of rare earth in the mixed complex is x, and the initial concentration of Ln^{3+} is c, and of $H(IDA)^-$ is d, then $K' = cx[H^+]/c(1 - x)(d - cx)$, which simplifies to $K' = [H^+]/(d - c/2)$ at the equivalence point

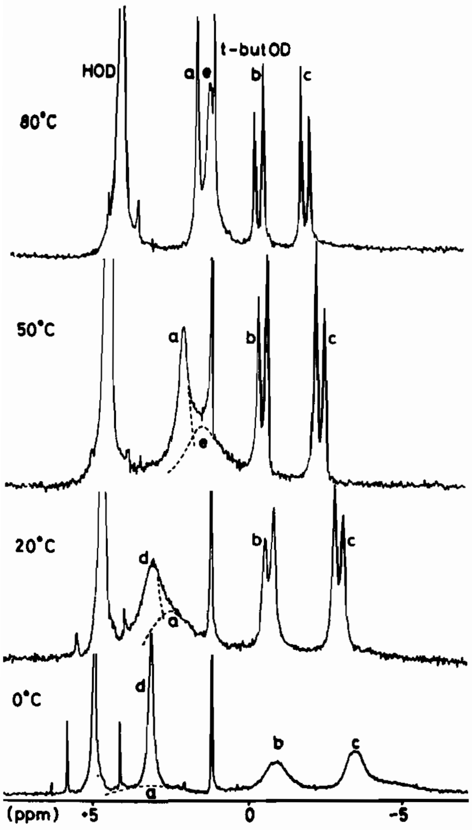

Figure 2. Temperature dependence of ^{1}H NMR spectra for a solution [EuEDTA] = 0.047*m*, [IDA] = 0.118*m* at pH 11.54. Proton peak assignments: a) EDTA ethylenic in Eu(*EDTA*)IDA^{3-}, b), c) EDTA acetate in Eu(*EDTA*)IDA^{3-}, d) free IDA, e) IDA exchanging rapidly between free and coordinated sites. IDA coordinated in Eu(EDTA)*IDA*$^{3-}$ is too broad to be seen.

Both the reaction of formation (1) and the exchange reaction (2) are too fast in the case of praseodymium to be measured by NMR. For europium, because of its smaller ionic radius and higher stability for the mixed complex, one would expect a slower dissociation rate (1) of Eu(EDTA)IDA^{3-} in the pH range where EuEDTA^{-} and Eu(EDTA)-IDA^{3-} are in equilibrium, and also a slower exchange rate (2) for IDA at higher pH if one assumes a dissociative rate determining step for the latter process. In Figure 2 are shown spectra at four different temperatures for europium at pH 11.54. The ternary complex is fully formed so there will be no complication from reaction (1). Considering first the EDTA acetate peaks, we observe that as we decrease the temperature from 80 °C, the doublets resulting from AX coupling first broaden and then become unresolved. This is an expected effect and is due to paramagnetic broadening. The same trend is seen for the ethylenic peak, with an even more marked effect, so that at 0 °C, we are only able to predict its position.

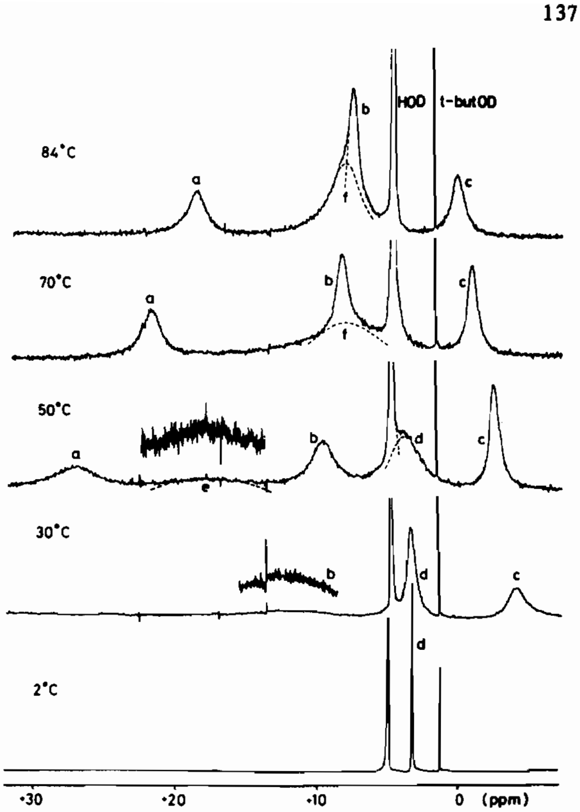

Figure 3. Temperature dependence of ^{1}H NMR spectra for a solution [YbEDTA] = 0.1*m*, [IDA] = 0.25*m* at pH 11.53. Proton peak assignments: a) EDTA ethylenic in Yb(*EDTA*)-IDA^{3-}, b), c) EDTA acetate in Yb(*EDTA*)IDA^{3-}, d) free IDA, e) IDA coordinated in Yb(EDTA)*IDA*$^{3-}$, f) rapid exchange coalescence of peaks d) and e).

An increase in linewidth on lowering of temperature is also observed for IDA. The broadening is greatest at 50 °C, and is attributed to a second effect which is present in addition to paramagnetic broadening, that of slowing down of the IDA exchange between free and complexed sites. In fact, if we consider the spectrum at 0 °C, the IDA peak is again quite narrow and its chemical shift corresponds to the expected population of free IDA sites. The bound IDA, which may be quite broad, could not be positively identified, but because of the upfield shift of the fast exchanging IDA at high temperature must also be upfield.

For ytterbium, depicted at pH 11.53 in Figure 3 as a function of temperature, the same general features as seen for europium are visible. The EDTA peaks become wider with decreasing temperature until they are completely broadened out at 2 °C. The free IDA peak shows increasing exchange broadening from 2° to 50 °C. Furthermore, it is easy to see from these spectra that as the exchange (2) becomes faster, this peak moves downfield. The coordinated IDA is seen as a very broad signal at 50 °C at δ = 17.9 ppm. At lower temperatures, paramagne-

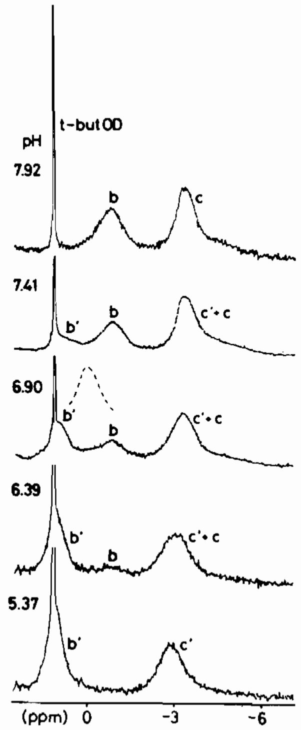

Figure 4. Selection of spectra as a function of pH at 0 °C for a solution [EuEDTA] = 0.047*m*, [IDA] = 0.118*m*. The simultaneous presence of peaks b'), c') EDTA acetate protons in EuEDTA^-, and b), c) EDTA acetate protons in Eu(*EDTA*)IDA^{3-} shows that mixed complex formation is slow on the NMR time scale. The dotted line at pH 6.9 represents the spectrum at 20 °C. See text for details.

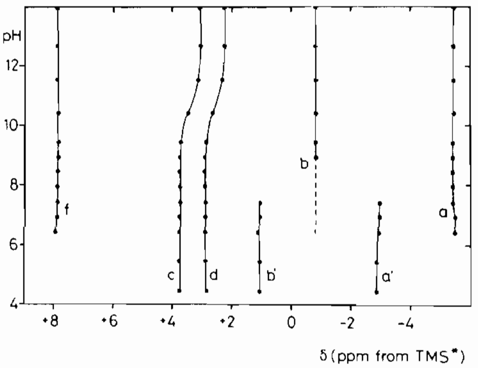

Figure 5. pH Dependence of chemical shift at 1 °C for a solution [EuEDTA] = 0.047*m*, [MIDA] = 0.118*m*. Proton peak assignments: a'), b') EDTA acetate in EuEDTA^-, a), b) EDTA acetate in Eu(*EDTA*)MIDA^{3-}, c) free MIDA acetate, d) free MIDA methyl, f) MIDA methyl coordinated in Eu(EDTA)*MIDA*$^{3-}$. EDTA acetate protons between pH 7 and 9, as well as ethylenic protons over the whole pH range, are too broad to be seen.

tism causes it to be too broad to be distinguished at all. On increasing the temperature to 80 °C, one observes the coalescence, which appears as a shoulder at δ = 7.75 ppm.

Measurement of the free IDA linewidth at 20 °C (under slow exchange conditions and at pH 11.53 where the mixed complex is completely formed) yields a pseudo first order rate constant k_L for the exchange reaction (2), given by $k_L = -d[\mathrm{Ln(EDTA)L}]/dt[\mathrm{Ln(EDTA)L}]$, which for Eu(EDTA)$\mathrm{IDA}^{3-}$ is found to be 210 ± 20 sec^{-1}, and for Yb(EDTA)-IDA^{3-} is 119 ± 20 sec^{-1}.

At lower pH (*e.g.* from 8.5 to 5.5 for Eu^{3+}), the situation is complicated by the dissociation of the ternary complex. By considering the behaviour of the EDTA peaks as a function of pH, we conclude that reaction (1) is slow on the NMR time scale near 0 °C. Figure 4 shows the spectra at 0 °C, where it is noticed that one of the acetate peaks of the mixed complex (b) grows in at the expense of the corresponding acetate peak in 1:1 EuEDTA^- (b'). The other acetate peak has very similar chemical shifts for both species, so the effect is not apparent in this case (c and c'). The dotted line at pH 6.9 represents the corresponding single peak observed for the same pH at 20 °C, showing clearly the coalescence over this temperature range; the peak is however wider during complex formation than at low or high pH. By 80 °C, the EDTA acetate peaks remain narrow throughout the pH range.

Ternovaya and Kostromina [6] in their study of several diamagnetic rare earth mixed complexes with EDTA and IDA have attributed the difference in bound EDTA resonance upon complexation with IDA to an increase in metal–nitrogen bond lengths. They also saw only one resonance for IDA, but they did not work as a function of temperature and so could make no further comment apart from its being a fast exchange. However, it must be noted that even a slow exchange rate could demonstrate itself as a 'fast' exchange on the NMR time scale for diamagnetic substances, since the chemical shift difference between bound and free ligand is very small, and our earlier observation that the exchange rate decreases across the series is not contradicted. One further difference they noticed was that for Lu^{3+} the AB spectrum characteristic of the EDTA acetate protons disappears upon complexation, indicating that the Lu–N bonds have become labile. We have found that for the three rare earths studied in this work, the AX spectrum remains sharp even at high pH; thus the Ln–N bonds remain inert.

Ln(EDTA)MIDA^{3-}

The MIDA ligand is different from IDA only in the methyl group which replaces the proton attached to the nitrogen atom, and a slightly higher first protonation constant. The NMR spectrum of MIDA shows two resonances having an intensity ratio of 4:3, corresponding to the acetate and methyl protons, with the former appearing at lower field. The general appearance of the spectra where the ternary complex $Eu(EDTA)MIDA^{3-}$ is present is very similar to those of the corresponding IDA complex discussed above. A solution containing $EuEDTA^-$ and MIDA in the ratio 1:2.5 has been used to study the pH and temperature dependence of the $Eu(EDTA)MIDA^{3-}$ system. Figure 5 shows the pH dependence of the chemical shifts at 1 °C. Below pH 6.43, the EDTA acetate resonances are those of $EuEDTA^-$. From pH 6.43 to 7.41 a second set of EDTA acetate signals, assigned to $Eu(\mathit{EDTA})MIDA^{3-}$, is also present, increasing in size with pH at the expense of the first set, which become smaller. The formation reaction (4) is

$$EuEDTA^- + MIDA^{2-} \rightleftharpoons Eu(EDTA)MIDA^{3-} \qquad (4)$$

therefore slow for this temperature and pH range, as was the case for $Eu(EDTA)IDA^{3-}$. Above pH 7.41, only the acetate resonances for the mixed complex are present.

The pK obtained from a titration curve of the acetate signals at 20 °C has been used with the first protonation constant of $MIDA^{2-}$ to estimate the stability constant of $Eu(EDTA)MIDA^{3-}$. This gives a log K_{Eu} value of 4.33, which is of the same order of stability as for the corresponding IDA complex (log K_{Eu} = 4.28).

Examination of the spectra as a function of temperature, shown for pH 11.38 in Figure 6, indicates that the exchange reaction (5) is quite slow at the

$$Eu(EDTA)MIDA^{3-} + {}^*MIDA^{2-} \rightleftharpoons Eu(EDTA){}^*MIDA^{3-} + MIDA^{2-} \qquad (5)$$

lowest temperature measured, 2 °C. The bound methyl peak of MIDA (f) was identified by integration with respect to the free ligand. Considering the bound (f) and free (d) methyl peaks of MIDA, they both broaden and approach each other until 31 °C, when they are widest. At higher temperature they are visible as a coalesced peak (i) at δ = 3.4 ppm at 84 °C. Following the free MIDA acetate (c), one sees that it broadens from 2 °C to 31 °C, and then narrows down until high temperature. This indicates that until 31 °C, there is slow exchange with bound acetate protons, and the fact that the chemical shift of peak c changes by only a very small amount is evidence that the bound peak must be situated very close to c and be very wide. It is shown as the dotted peak e in the spectrum at 2 °C.

Measurement of the linewidth of the MIDA methyl peak bound in the mixed complex enables us to estimate directly, using the slow exchange approximation, the pseudo first order rate constant k_{MIDA} for the process of MIDA exchange (5) at 20 °C. This yielded $k_{MIDA} = 250 \pm 20\ sec^{-1}$.

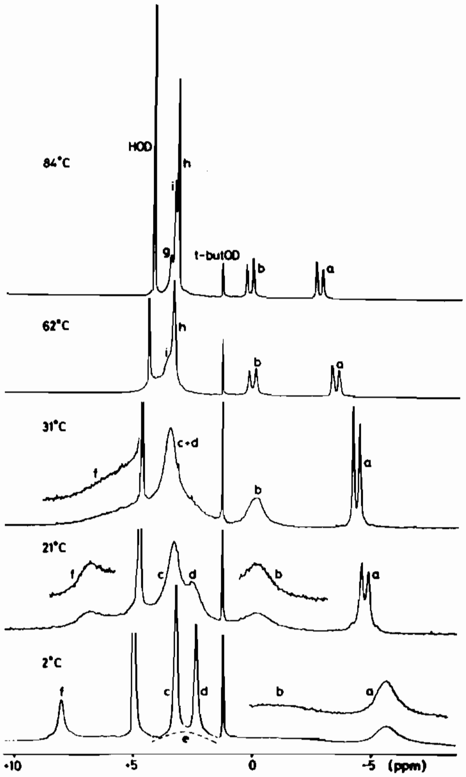

Figure 6. Temperature dependence of ^1H NMR spectra for a solution [EuEDTA] = 0.047*m*, [MIDA] = 0.118*m* at pH 11.38. Proton peak assignments: a), b) EDTA acetate in $Eu(\mathit{EDTA})MIDA^{3-}$, c) free MIDA acetate, d) free MIDA methyl, e) MIDA acetate, f) MIDA methyl in $Eu(EDTA)\mathit{MIDA}^{3-}$, g) EDTA ethylenic in $Eu(\mathit{EDTA})MIDA^{3-}$, h) rapid exchange coalescence of peaks c) and e), i) rapid exchange coalescence of peaks d) and f).

Ln(EDTA)NTA^{4-}

Chastellain [7], in a study of the diamagnetic rare earths, showed that in solutions of stoichiometry $LnEDTA^-/NTA^{3-}$ 1:2, there was partial formation of the complex $Ln(NTA)_2^{3-}$ in the whole pH range studied, which results in the liberation of an EDTA molecule according to the reaction (6). In addition,

$$LnEDTA^- + 2NTA^{3-} \rightleftharpoons Ln(NTA)_2^{3-} + EDTA^{4-} \qquad (6)$$

if there is formation of free EDTA, one must take into account our earlier study, and assume that there may be formation of 2:3 and 1:2 complexes [2]. The ternary complex $Ln(EDTA)NTA^{4-}$ would also be expected. We therefore propose that the reactions (7) to (9) take place in addition to (6). Furthermore, since NTA is in excess, the spectra may be complicated by the exchange reactions (10) and (11) and other combinations.

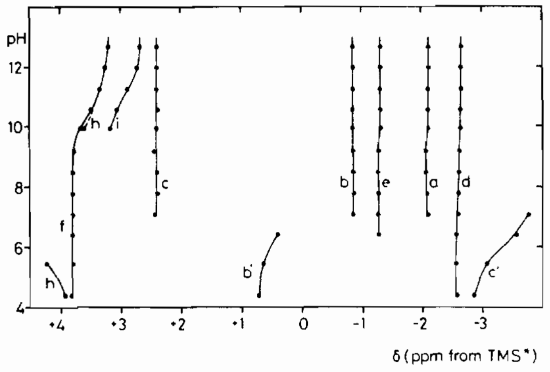

Figure 7. pH dependence of chemical shift at 20 °C for a solution [EuEDTA] = 0.047*m*, [NTA] = 0.094*m*. Proton peak assignments: a) Eu(*EDTA*)NTA^{4-} ethylenic, b') c') Eu*EDTA*$^-$ acetate, b), c) Eu(*EDTA*)NTA^{4-} acetate, d) Eu(*NTA*)$_2^{3-}$, e) Eu(EDTA)*NTA*$^{4-}$, f) free NTA, h) free EDTA ethylenic, i) free EDTA acetate. The Eu*EDTA*$^-$ ethylenic peak is hidden by the HOD peak.

$$\mathrm{2LnEDTA^{4-} + EDTA^{4-} \rightleftharpoons Ln_2EDTA_3^{6-}} \tag{7}$$

$$\mathrm{LnEDTA^{-} + EDTA^{4-} \rightleftharpoons Ln(EDTA)_2^{5-}} \tag{8}$$

$$\mathrm{LnEDTA^{-} + NTA^{3-} \rightleftharpoons Ln(EDTA)NTA^{4-}} \tag{9}$$

$$\mathrm{Ln(EDTA)NTA^{4-} + {*NTA^{3-}} \rightleftharpoons Ln(EDTA){*NTA^{4-}} + NTA^{3-}} \tag{10}$$

$$\mathrm{Ln(NTA)_2^{3-} + {*NTA^{3-}} \rightleftharpoons Ln(NTA){*NTA^{3-}} + NTA^{3-}} \tag{11}$$

We have studied Eu(EDTA)NTA^{4-} and Yb(EDTA)-NTA^{4-} as a function of temperature and pH. Figure 7 shows the pH dependence of chemical shifts at 20 °C for a solution [EuEDTA]/[NTA] in ratio 1:2. With this ratio, we are close to the optimum ratio of 1:2.5 found by Tananaeva *et al.* [4] for formation of the ternary complex. There are several remarks to be made concerning the assignments in this figure. The first is the presence of peak d at δ = –2.6 ppm, which has been assigned to Eu(NTA)$_2^{3-}$ by comparison with the work of Gfeller and Merbach [8]. The presence of Eu(NTA)$_2^{3-}$, whereas no peak for Eu-(IDA)$_2^-$ had been seen, is not surprising when we consider that the stability constant of the former is much larger. As in the case of Eu(EDTA)IDA^{3-} and Eu(EDTA)MIDA^{3-}, the formation reaction (9) is slow on the NMR time scale. Indeed, we note the presence of two signals (b' and c') corresponding to the acetate protons in EuEDTA$^-$ which diminish in intensity with pH as the ternary complex is formed, while two further signals (b and c), corresponding to acetate protons in Eu(*EDTA*)NTA^{4-} increase in intensity. The signals a and e may be assigned either to the EDTA ethylenic protons or to the NTA protons bound in the ternary complex. However, it will by shown below that signal e will be assigned to the bound NTA; in addition, the behaviour of the peak a with temperature (see Figure 8) shows the normal paramagnetic shift and broadening with decreasing temperature from 80° to 0 °C for bound ethylenic protons.

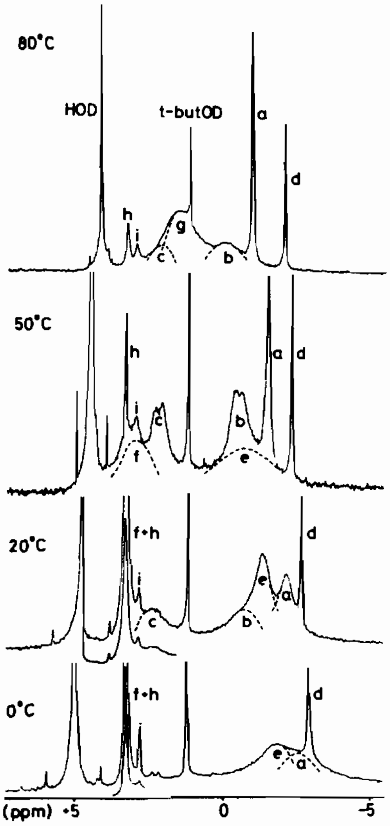

Figure 8. Temperature dependence of ^{1}H NMR spectra for a solution [EuEDTA] = 0.047*m*, [NTA] = 0.094*m* at pH 11.24. Peak assignments: a) Eu(*EDTA*)NTA^{4-} ethylenic, b), c) Eu(*EDTA*)NTA^{4-} acetate, d) Eu(*NTA*)$_2^{3-}$, e) Eu(EDTA)-*NTA*$^{4-}$, f) free NTA, g) coalescence of peaks e) and f) under fast exchange conditions, h) free EDTA acetate, i) free EDTA ethylenic.

Simultaneously to (9), reactions (7) and (8) will take place to some extent. In fact, contrary to the preceding cases studied, one sees that the acetate peaks of EuEDTA$^-$ undergo a high field shift between pH 4 and 7. This is most probably due to the formation of Eu(EDTA)$_2^{5-}$ and/or Eu$_2$EDTA$_3^{6-}$, and in fact such a shift has been observed for peak c' in Figures 4 and 5 of reference [2] for solutions containing an excess of EDTA. This is further supported by the fact that to low field we see the signal h which corresponds to the acetate peak of free EDTA at pH 4.4; this signal shifts to lower field as a result of formation of the complexes mentioned above. Even more compelling evidence is available only at 50 °C, pH 6.4 to 7.2 (not shown), where both acetate and ethylenic peaks corresponding to a second bound molecule of EDTA [2] are visible. These peaks are paramagnetically broadened at lower temperatures. The formation of 1:2 and 2:3 complexes explains the lack of free EDTA at intermediate pH values. It is emphasised that above pH 8.4 at all temperatures, the peaks due to a second bound molecule of EDTA no longer occur, and are replaced by free EDTA peaks; this indicates that reaction (9) predominates over (7) and (8). The ethylenic peak of free EDTA (i) is clearly visible from pH 9.9 upwards, but the acetate peak of free EDTA (h) becomes hidden under the free NTA resonance (f).

Geier and Karlen [3] have measured the stability constants of the $Ln(EDTA)NTA^{4-}$ complexes by potentiometry, using solutions much more dilute than those used in this work. However, in view of our proton NMR data, it must be assumed that reaction (9) is not the only reaction occuring, and the other reactions shown above must be taken into account to make any quantitative measurements strictly correct. The equilibrium constant for reaction (6) may be calculated from the formation constants of $EuEDTA^-$ (pK 17.35, 20 °C, 0.1 KNO_3, [9]) and $Eu(NTA)_2^{3-}$ (pK 20.76, 0.1 KNO_3, [10]) and is 2.6 X 10^3 which is quite sizeable. In view of this, it is interesting to consider the equilibrium constant for the reaction (12). This may be estimated at high pH (where the mixed complex is favoured and there is

$$Eu(EDTA)NTA^{4-} + NTA^{3-} \rightleftharpoons Eu(NTA)_2^{3-} + EDTA^{4-} \qquad (12)$$

no competition from (7) and (8)) from the initial concentrations of $EuEDTA^-$ and NTA, and the relative concentrations of $Eu(EDTA)NTA^{4-}$ and $Eu(NTA)_2^{3-}$ determined by integration of the appropriate NMR peaks (a and d in Figure 8). This gives values of 2.97 X 10^{-2} at 80 °C (15% of the europium is in the form $Eu(NTA)_2^{3-}$) and 2.28 X 10^{-2} at 50 °C (13% in the form $Eu(NTA)_2^{3-}$), but at lower temperatures paramagnetic broadening prevents accurate estimates. These results confirm that the mixed complex is strongly favoured over $Eu(NTA)_2^{3-}$ at high pH. As shown by equation (12) a large excess of NTA disfavours formation of the ternary complex, as seen by Tananaeva *et al.* [4]. The stability constant for mixed complex formation (9) may be obtained by combining the equilibrium constants for reactions (6) and (12), for which the pK values estimated above are 3.41 and −1.64 respectively. This gives an estimated value of 5.05, which is close to Geier and Karlen's value of 5.03. The greater stability of $Eu(EDTA)NTA^{4-}$ compared to $Eu(EDTA)IDA^{3-}$ is reflected in the fact that the NMR peaks remain virtually constant from pH 7.8 upwards, indicating that mixed complex formation is already complete at this low pH.

We have seen that the rate of formation of $Eu(EDTA)NTA^{4-}$ is slower than that of $Eu(EDTA)IDA^{3-}$ and $Eu(EDTA)MIDA^{3-}$, because for the last two complexes, the EDTA signals are already chemically exchange broadened at 20 °C, which is not yet the case for the NTA system. In consequence, we expect the ligand exchange reaction (10) to be slower for NTA, which may be confirmed by considering the change of a particular spectrum (above pH ≅ 8) as a function of temperature. Figure 8 depicts this for pH 11.24. We assign peak e to bound NTA protons in the ternary complex. At 0 °C, this peak is broadened by paramagnetism; at 20 °C it is narrower, while at 50 °C it is exchange broadened. The corresponding free NTA peak becomes broader until 50°C, and at 80 °C the broad coalesced peak g is due to NTA exchanging rapidly between sites e and f, whereas the only free ligand signals visible are those of acetate (h) and ethylenic (i) EDTA protons. The possibility of (11) being a fast exchange is discounted because the $Eu(NTA)_2^{3-}$ peak decreases in linewidth with temperature, and at 80 °C is very narrow, showing that (10) is much faster than (11).

Qualitatively, NTA appears to exchange slower than IDA or MIDA, because the NTA linewidth is very broad at 80 °C and at a similar pH to the others. Linewidth measurements on the free ligand have been made at 20 °C and pH 11.24. Assuming equal concentrations of $Eu(EDTA)NTA^{4-}$ and free NTA, which is necessarily the case for an initial ratio of 1:2, even though the exact concentrations are not known, yields a pseudo first order rate constant $k_{NTA} = d[Eu(EDTA)NTA^{4-}]/dt[Eu(EDTA)NTA^{4-}] = 25 \pm 8$ sec^{-1}.

Ytterbium, because of the broadness of its peaks, does not allow as many interesting features to be distinguished as for europium. However, the general behaviour is the same, and the pseudo first order rate constant k_{NTA} found at 20 °C and pH 10.6 is 31 ± 8 sec^{-1}.

Discussion

The stability constants found in this work for the reaction (13) are presented in Table I, together with

$$LnEDTA + L \rightleftharpoons Ln(EDTA)L \qquad (13)$$

the values of Geier and Karlen [3] and Brücher [11] for comparison. It is seen that for IDA, all three lanthanides studied agree well with Geier and Karlen's values. For MIDA, the only point of comparison we have is that of Brücher, who finds that for yttrium, $Y(EDTA)MIDA^{3-}$ is only 0.4 log K units less stable than $Y(EDTA)IDA^{3-}$. One would expect the constants of stability for the two complexes $Ln(EDTA)MIDA^{3-}$ and $Ln(EDTA)IDA^{3-}$ to be almost the same, because of the similarity of the ligands; or slightly higher for the MIDA complex because of greater basicity of the ligand. This is verified for europium, where we find that the MIDA complex is more stable than $Eu(EDTA)IDA^{3-}$ by 0.05 log K units.

In the case of NTA, we have shown the presence of $Ln(NTA)_2^{3-}$ in a solution of $LnEDTA^-$ with excess NTA, which has reacted according to equation (6).

$$LnEDTA^- + 2NTA^{3-} \rightleftharpoons Ln(NTA)_2^{3-} + EDTA^{4-} \quad (6)$$

Hence it is not clear from potentiometry whether the H^+ consumed by KOH in the titration of a mixture of $LnEDTA^-$ and $H(NTA)^{2-}$ result from reaction (6) or from formation of the mixed complex (9). We

$$LnEDTA^- + NTA^{3-} \rightleftharpoons Ln(EDTA)NTA^{4-} \quad (9)$$

have measured the equilibrium constant for the competing reation (13) for europium at 20 °C, high

$$Ln(EDTA)NTA^{4-} + NTA^{3-} \rightleftharpoons Ln(NTA)_2^{3-} + EDTA^{4-} \quad (13)$$

pH, which yields the value of log K = –1.64. This value is consistent with the log K value of –1.78 found for neodymium by Tananaeva *et al.* [4] from absorption spectra. At low pH, one must also take into account the formation of 2:3 and 1:2 complexes, according to the equilibria (7) and (8). In their potentiometric determinations of the formation constants of the ternary NTA complex, Geier

$$2LnEDTA^- + H(EDTA)^{3-} \rightleftharpoons Ln_2EDTA_3^{6-} + H^+ \quad (7)$$

$$LnEDTA^- + H(EDTA)^{3-} \rightleftharpoons Ln(EDTA)H(EDTA)^{4-} \quad (8)$$

and Karlen [3] did not consider these numerous equilibria. In spite of this, the correspondence between their value for europium and ours is excellent. The reason for this is that they worked with a ratio $LnEDTA^-/NTA$ of 1:1, and under these conditions there is not much formation of $Ln(NTA)_2^{3-}$ especially near the end of the titration. It is recalled that for the 1:2 stoichiometry about 13% of the rare earth was in this latter form at high pH.

It is of interest to consider if there is a relationship between the structure of the ternary complex Ln(EDTA)L and the properties of the ligand L for L = NTA and IDA, which can explain the different behaviour of the two complexes. The most important difference between NTA and IDA is that the former is tetradentate, the latter tridentate. Thus formation of a complex $Ln(NTA)_2^{3-}$ is greatly favoured over $Ln(IDA)_2^-$. Formation of $Ln(EDTA)NTA^{4-}$ if all ligand arms coordinate would involve expansion of the inner coordination sphere to ten, which would especially exert a strain on the rare earths towards the end of the series; these complexes are nevertheless more stable than $Ln(EDTA)IDA^{3-}$ or $Ln(EDTA)MIDA^{3-}$. To explain this fact, Tananaeva *et al.* [4] have proposed that for $Nd(EDTA)IDA^{3-}$, the EDTA is pentacoordinated, while for $Nd(EDTA)NTA^{4-}$ the EDTA is five coordinated and NTA only tricoordinated. Our results show that at 80 °C, high pH, the EDTA acetate NMR signals are wider than at 50 °C, which can only be due to faster rate of breaking the Eu–N bond than was seen for the other mixed complexes, causing exchange between the two acetate resonances. This is consistent with Tananaeva's suggestion, as in a strained complex metal–nitrogen bonds would also be likely to break.

The reaction of formation (13) has been shown to be slow on the NMR time scale in acid media; the formation of Ln(EDTA)L is slower for L = NTA than for IDA or MIDA. The NMR technique does not lend itself to direct measurement of the rate of formation of $Eu(EDTA)NTA^{4-}$ because complexation takes place in a region where several reactions occur. However, it was possible to estimate a rate of formation for the complex $Eu(EDTA)IDA^{3-}$ at 20 °C. The rate observed by NMR was transformed to the second order rate constant for the formation of the mixed complex. In this form it is directly comparable with Karlen's [12] rate of formation k_{41}. However, he investigated the formation reaction only for the $Ln(EDTA)Oxs^{3-}$ mixed complex, and his value of $k_{41} = 6.0 \times 10^5\ M^{-1}\ sec^{-1}$ for europium is somewhat smaller than our estimate of $\cong 1 \times 10^7\ M^{-1}\ sec^{-1}$.

A study as a function of temperature has revealed that the exchange reaction (14) is slow on the NMR time scale at high pH below about 50 °C. The

$$Ln(EDTA)L + {}^*L \rightleftharpoons Ln(EDTA){}^*L + L \quad (14)$$

mechanism of exchange was not determined because we have not studied the reaction as a function of ligand concentration. However, we have been able to measure several pseudo first order rate constants k_L for (14), where $k_L = -d[Ln(EDTA)L]/dt[Ln(EDTA)L]$, either by measuring directly the bound ligand linewidth, or by measuring free ligand linewidths and taking into account population factors. These are summarised for 20 °C in Table II, and we may distinguish two trends. The first is a decrease in rate across the rare earth series, as seen for IDA; this is interesting because it shows that in spite of the fact that $Eu(EDTA)IDA^{3-}$ is more stable than $Yb(EDTA)IDA^{3-}$, the IDA exchange is still faster in the former case. This suggests that the rate deter-

TABLE II. Pseudo First Order Rate Constants k_L at 20 °C, for the Exchange Reaction:

$$\mathrm{Ln(EDTA)L} + {}^*\mathrm{L} \rightleftharpoons \mathrm{Ln(EDTA)}{}^*\mathrm{L} + \mathrm{L}$$

where L is IDA, MIDA and NTA.

Metal Ion	k_L (sec^{-1})		
	IDA	MIDA	NTA
Pr	[a]	–	–
Eu	210 ± 20	250 ± 20	25 ± 8
Yb	119 ± 20	–	31 ± 8

[a] Too fast to be measured by NMR.

mining step for the overall exchange mechanism is dissociative in nature. In the case of Ln(EDTA)-NTA^{4-} the relative uncertainties are greater due to smaller line broadening; furthermore, no measurements have been made on the praseodymium ternary complex. It is therefore not possible to conclude a trend for this ligand.

The europium results for the three ligands enable us to classify them in order of exchange rate. We see that $k_{MIDA} \cong k_{IDA} > k_{NTA}$. It would have been interesting to see how the rate of exchange of one iminodiacetate group of an EDTA molecule would compare in this series. However, the studies having this aim showed the presence of Ln(EDTA)$_2^{5-}$ *etc.* and ratios of EDTA/Ln > 3 would be necessary to study the exchange.

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