Kinetic Studies of Lanthanoid Carboxylate Complexes

II. A PMR Investigation of the Lanthanum and Lutetium EDTA Complexes

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The labilities of the coordinative bonds in the lanthanum and lutetium EDTA complexes have been studied by PMR measurements. The metal-oxygen bonds were found to be labile in both complexes as well as the metal-nitrogen bonds in the lanthanum complex. Only the metal-nitrogen bonds in the lutetium complex have long life-times in the PMR time-scale. The rate of ligand exchange of the lanthanum EDTA complex in slightly alkaline solutions has been determined by PMR line shape analysis. This exchange was found to be catalysed by hydroxide ions.

In an earlier paper,[1] the rate constants for the dissociation of some lanthanoid EDTA complexes were reported. The rates were determined from reactions, in which the ligand was exchanged between two different metal ions in a slightly acid medium. This method is not applicable to neutral and alkaline solutions because of hydrolysis. Such solutions may instead be studied by nuclear magnetic resonance methods to give information of the rate of exchange of EDTA between the free and complex-bonded states. A prerequisite for the method is that the concentrations of the free EDTA and of the LnEDTA complex are of similar magnitude. The dominating species in the solutions used are the unhydrolysed complex and mono- and di-protonated EDTA.

The PMR spectra of complex-bonded EDTA may be of different type, depending on the configuration of the complex and on the lability of the bonds between EDTA and the central ion. Hence, the spectra may be used to obtain some structural information as well as some rate data.

EXPERIMENTAL

Chemicals. All chemicals were of analytical grade. Standard solutions of $LaCl_3$ and $LuCl_3$ were prepared by dissolving the corresponding oxides (from Potash & Chemical Corp.) in hydrochloric acid. The solutions were standardized as described before.[1] Solution of potassium chloride and EDTA were prepared as in Ref. 1.

Instrumental. The PMR spectra were recorded at 60 MHz, using a Varian A 60 A spectrometer. The shifts were measured with the usual side band technique by means of a Hewlett Packard audio frequency oscillator, model 202, and a frequency counter, model 5216 A.

The shifts are given relative to tetramethylsilane, TMS, which was used as an external reference. No corrections for bulk susceptibilities were made.

All spectra were recorded at the probe temperature, measured by the methanol shift. The temperature was found to be $44.9 \pm 0.3°C$. Dissolved oxygen was removed from the solutions just before recording the spectra.

Labilities of the coordinative bonds. In free EDTA, the four ethylene protons and the eight acetate protons are equivalent within each group, and thus two singlets of relative intensities $1:2$ are observed in the PMR spectrum. When complexing EDTA with a metal ion, different signal patterns will be obtained, depending on the lability of the metal-oxygen and the metal-nitrogen bonds, and on the structure of the complex.

Reilly *et al.*[2] have given an exhaustive discussion of the four possible cases for an octahedral complex, *viz.* (i) the lifetimes of both the metal-oxygen and metal-nitrogen bonds are short; (ii) the life-time of the metal-oxygen bond is short, while that of the metal-nitrogen bond is long; (iii) the reversed situation; the lifetime of the metal-oxygen bond is long and that of the metal-nitrogen bond is short; and (iv) the lifetimes of both bonds are long.

Hoard *et al.*[3,4] have determined the structure of the solids $La(OH_2)_4(EDTA)H$ and $MLa(OH_2)_3EDTA$ ($M = K$, Na, or NH_4) by X-ray diffraction. The lanthanum ion co-ordinates with four oxygen and two nitrogen atoms of EDTA. The plane through the lanthanum and the two nitrogen atoms forms a quasi-mirror plane for the coordinated ligand. The ethylenediamine group in the ligand is slightly puckered.

If the ethylenediamine group is puckered also in solution then Reilly's discussion is relevant for lanthanoid EDTA complexes. Hence (i) gives a PMR spectrum consisting of two singlets, one for the ethylene protons and the other for the acetate protons; (ii) gives an AB-type multiplet for the acetate protons and a singlet for the ethylene protons; (iii) is improbable for structural reasons, and (iv) gives a complicated spectrum where both the acetate and ethylene protons give rise to multiplets.

Spectra of a solution containing about 180 mM lutetium EDTA complex were recorded in the pH range $2 < pH < 12$. Outside this range precipitation occurs. It was not necessary to add neutral salt to obtain information about the labilities of the bonds. The pH of the solution was varied by adding 1 M potassium hydroxide. The hydrogen ion concentration was determined at 25°C by a glass electrode.

For the lutetium complex, the signal from the acetate protons is split into an AB quartet (Fig. 1). This indicates a metal-nitrogen bond of long lifetime. The metal-oxygen bond, on the other hand, probably has a short lifetime, since the ethylene protons give rise to a singlet. However, when the pH of the solution is increased to about 12, the AB pattern gradually disappears and a singlet appears. Furthermore, the chemical shifts for both the acetate protons and the ethylene protons change in this pH range (Table 1). This might be due to the formation of a mixed complex, *viz.* Lu(OH)EDTA. If such
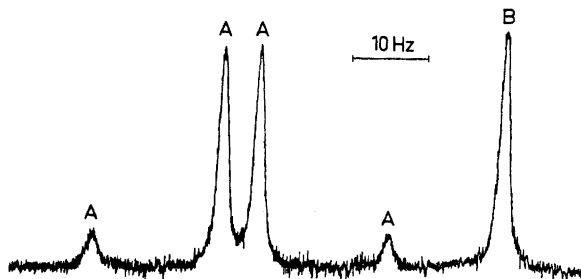

Fig. 1. The recorded spectrum of 180 mM lutetium EDTA complex at pH = 6.43.

Table 1. The chemical shifts for the acetate, A, and ethylene, E, protons of the lutetium EDTA complex. Reference TMS.

pH, $-\delta_A$, $-\delta_E$; 1.98, 3.62, 3.04; 2.33, 3.62, 3.04; 3.19, 3.62, 3.04; 3.76, 3.63, 3.05; 4.29, 3.63, 3.04; 6.43, 3.62, 3.04; 8.24, 3.63, 3.04; 9.16, 3.61, 3.04; 9.86, 3.62, 3.04; 10.60, 3.60, 3.01; 11.47, 3.57, 2.95; 12.22, 3.55, 2.92.

a complex is formed it is almost certain that the hydroxide ion is directly bound to the metal atom. Then it would be expected that the metal-nitrogen bonds, and hence the shift for the ethylene proton, are more sensitive for the deprotonation of the aqua complex than are the metal-oxygen bonds, which are labile already in the aqua complex itself. The numbers in Table 1 support this view, since they show that the change in shift of the ethylene protons is larger than that of the acetate protons.

It seems also very reasonable that the formation of a hydroxo complex leads to labilisation of the metal-nitrogen bond. This gives rise to a singlet instead of an AB quartet in the PMR spectrum. Hence, all PMR data are concordant with the formation of a hydroxo complex.

The coupling constant for the AB quartet was calculated by the procedure given in Ref. 5, and was found to be (17.1 ± 0.3) Hz.
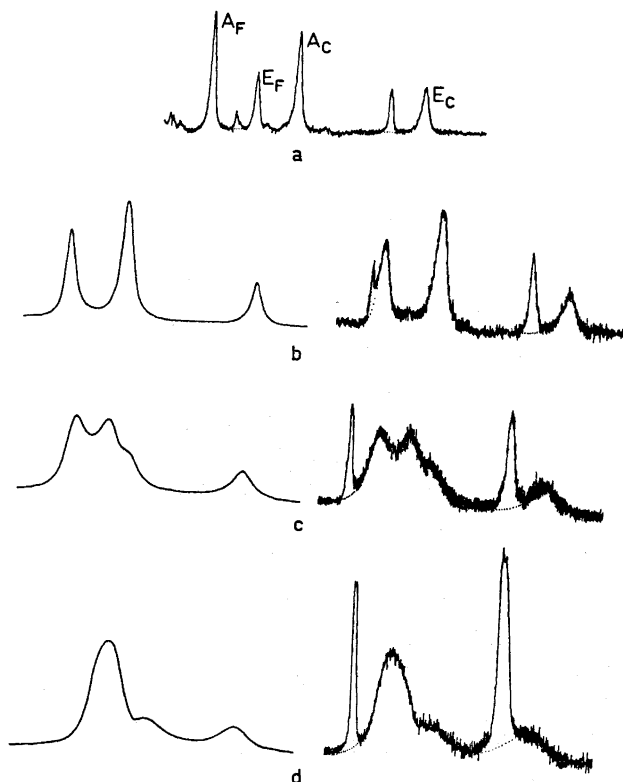

Fig. 2. Recorded and calculated spectra of free EDTA and lanthanum EDTA complex in about equal concentrations. (a) No exchange, (b) $\tau_C = 0.160$ s, (c) $\tau_C = 0.0523$ s, and (d) $\tau_C = 0.0360$ s.

From the measured shifts, the equilibrium constant, $K_{\mathrm{LnA(OH)}}$ (eqn. 1), for the formation of the mixed lutetium hydroxide complex could be estimated to be about 10^2 M^{-1}, in accordance with the estimate given by Merbach and Gnägi.[6]

The PMR spectrum of the lanthanum EDTA complex consists of two singlets (Fig. 2a). Thus, the lanthanum-nitrogen and lanthanum-oxygen bonds are both labile.

The conclusions above concerning the labilities of the metal-oxygen bonds are relevant only if the ethylenediamine group is puckered. If this group were planar the spectra would not give any information about the labilities of the metal-oxygen bonds, since all four acetate groups would then be equivalent. Thus a singlet would be obtained from the protons independent of the lability of the metal-oxygen bond. However, all information available about the structure of EDTA complexes seems to support a puckered ethylenediamine group.

Kinetics of the lanthanum EDTA exchange. When studying the exchange between the diamagnetic complex and the free ligand, it is favourable to have both these species in about equal concentrations. In order to obtain a large signal to noise ratio, concentrations in the order of 0.5 M are desirable. However, this was impossible in the present investigation because of the limited solubility of both the lanthanum complex and the free EDTA. The following solutions of varying pH were used:

$$\left\{\begin{array}{l} 50 \text{ mM LaEDTA} \\ 50 \text{ mM EDTA} \\ I = 1.0 \text{ M (KCl)} \end{array}\right.$$

The hydrogen ion concentration was adjusted by 1 M potassium hydroxide. In these solutions, the ionic strength was chosen as 1.0 M instead of 0.5 M, since the large concentrations of ligand would otherwise make the major contribution to the ionic strength a contribution which also varies strongly with the pH of the solution.

Fig. 2a shows the spectra of free EDTA and the lanthanum EDTA complex in the absence of exchange. This was established by lowering the pH of the solutions until the signals did not narrow any more. The peaks labelled A result from the protons in the acetate group of EDTA and those labelled E arise from the protons in its ethylene group. Indices F and C are used for free and complexed EDTA, respectively. A large signal in the spectra originates from a 50 Hz overtone to the water signal, corresponding to the frequency of the main current. This is due to the high amplification of the spectrometer, which is necessary because of the low EDTA concentrations.

The resolution of the spectrometer was adjusted so that the same linewidth (0.6 Hz) was always obtained from the water signal. Each spectrum was recorded at least twice.

The hydrogen ion concentration was measured at 25°C by a glass electrode.

Calculation. Instead of using the approximative formulae for exchange processes, which can lead to rather large systematic errors,[7] the mean lifetime of the free EDTA, τ_{F}, was calculated by line shape analysis. The exchange pattern can be described as two overlapping two-site cases, where each site shows a singlet. By using the full expressions derived by Gutowsky and Holm,[8] line shapes have been calculated by a computer. By means of an iterative procedure,[9,10] the parameters were adjusted so as to give the least error square sum to the observed spectrum.

The recorded spectra were digitized by measuring the heights from the base line in steps of 0.5 Hz for 200 points. By this procedure it was possible to subtract the overtone peaks of the water signal when they did not interfere too much. However, these "extra" signals limited the useful range of exchange rates. For lifetimes less than 0.03 s it was impossible to obtain any reliable results.

The following parameters have been adjusted in the calculations: K, a normalizing constant; τ_{F}, the mean lifetime of free EDTA; p_{F}, the mol fraction of free EDTA, and the shifts δ_1 and δ_2, *i.e.* the separation in Hz between A_{F} and E_{F} and between A_{C} and E_{C}, respectively. The apparent transverse relaxation times, $T_{2\mathrm{F}}$ and $T_{2\mathrm{C}}$, were determined from the line widths of the four peaks in the absence of exchange. Thus, $T_{2\mathrm{F}}$ for the signals A_{F} and E_{F} was found to be 0.187 s and 0.188 s, respectively, whereas $T_{2\mathrm{C}}$ for the peaks A_{C} and E_{C} showed a greater difference, *viz.* 0.159 s and 0.146 s. This might indicate that the acetate groups are more labile than the ethylene group. The mean value of $T_{2\mathrm{C}}$, 0.153 s, was used in the calculations.
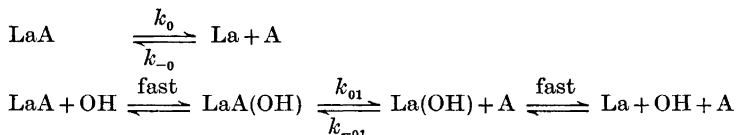
In Fig. 3 the adjusted values of δ_1, *i.e.* the separation in Hz between the acetate and ethylene protons in free EDTA, are plotted *vs.* the hydroxide ion concentration. The

adjustment of the parameters was repeated with fixed values of δ_1 taken from the curve $\delta_1([OH^-])$. The results of the calculations are given in Table 2. Some examples of calculated and recorded spectra are given in Fig. 2, b−d.

Table 2. Rate data for the exchange LaEDTA $\rightleftharpoons$ La + EDTA.

$[OH^-] \times 10^8/M$, p_F, δ_1/Hz, τ_C/s; 1.56, 0.521, 16.9, 0.275; 2.06, 0.498, 17.5, 0.256; 2.20, 0.461, 17.6, 0.237; 2.85, 0.488, 18.1, 0.160; 3.35, 0.480, 18.5, 0.187; 5.33, 0.513, 19.1, 0.0995; 5.40, 0.479, 19.2, 0.0932; 7.46, 0.502, 19.2, 0.0639, 8.73, 0.500, 19.3, 0.0523; 9.21, 0.505, 19.3, 0.0512; 11.0, 0.500, 19.4, 0.0435; 13.6, 0.492, 19.4, 0.0360.

The stoichiometric reaction mechanism. The following reactions are regarded:

$$LaA \quad \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} \quad La + A$$

$$LaA + OH \underset{}{\overset{fast}{\rightleftharpoons}} LaA(OH) \underset{k_{-01}}{\overset{k_{01}}{\rightleftharpoons}} La(OH) + A \overset{fast}{\rightleftharpoons} La + OH + A$$

The first and the last steps in the hydroxide ion dependent path are rapid equilibria. Their equilibrium constants are defined by

$$K_{LaA(OH)} = \frac{[LaA(OH)]}{[LaA][OH]} \text{ and } K_{La(OH)} = \frac{[La(OH)]}{[La][OH]} \tag{1}$$
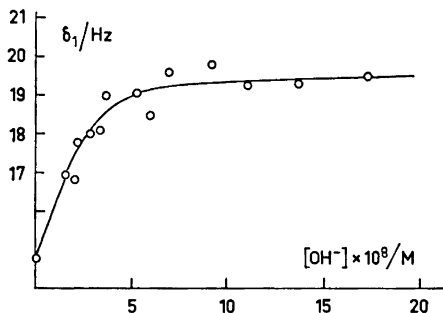

Fig. 3. The separation in Hz, δ_1, between the acetate and ethylene protons in free EDTA, as a function of the hydroxide ion concentration.
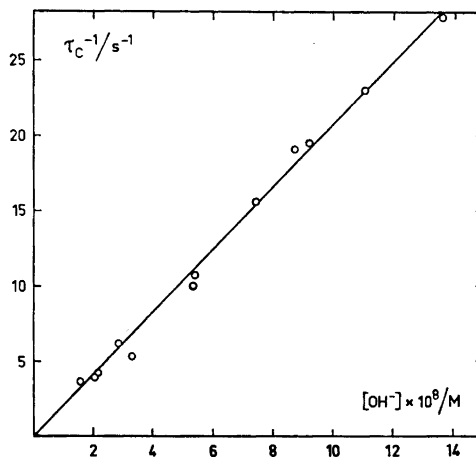
Fig. 4. The observed rate constant, τ_C^{-1}, as a function of the hydroxide ion concentration.

At equilibrium the rate equation becomes

$$-\frac{d[LaA]}{dt} = k_0[LaA] - k_{-0}[La][A] + k_{01}[LaA(OH)] - k_{-01}[La(OH)][A] = 0 \tag{2}$$

Combination of eqns. (1) and (2) gives

$$[\text{LaA}](k_0 + k_{01}\,K_{\text{LaA(OH)}}[\text{OH}]) = [\text{A}]\,(k_{-0}[\text{La}] + k_{-01}K_{\text{La(OH)}}[\text{La}][\text{OH}]) \tag{3}$$

Thus
$$\frac{[\text{LaA}]}{\tau_C} = \frac{[\text{A}]}{\tau_F} \tag{4}$$

where $\tau_C^{-1} = k_0 + k_{01}\,K_{\text{LaA(OH)}}\,[\text{OH}]$

and $\tau_F^{-1} = [\text{La}]\,(k_{-0} + k_{-01}\,K_{\text{La(OH)}}\,[\text{OH}])$

Hence, τ_C^{-1} is a linear function of the hydroxide ion concentration.

The line shape analysis gives τ_F, but τ_C is related to τ_F by the following expression:

$$\frac{p_F}{\tau_F} = \frac{p_C}{\tau_C} \tag{5}$$

Fig. 4 shows τ_C^{-1} as a function of the hydroxide ion concentration.

RESULTS

From the PMR spectra of the fast dissociating lanthanum EDTA and the much slower dissociating lutetium EDTA, it can be concluded that the cleavage of the metal-nitrogen bond is rate determining for the dissociation of the complexes. The metal-oxygen bonds seem to be labile compared with the metal-nitrogen bonds. The same conclusion has been drawn by Margerum [11] from exchange reactions of copper and nickel with EDTA and hydroxy-ethylethylenediaminetriacetate.

The dissociation of the lanthanum EDTA complex was found to be catalysed by hydroxide ions. The following rate constant was found:

$$\tau_C^{-1} = k_0 + k_{01}\,K_{\text{LaA(OH)}}[\text{OH}^-]$$

with $k_0 = (0 \pm 1)$ s^{-1} and $k_{01}\,K_{\text{LaA(OH)}} = (2.0 \pm 0.4)10^8$ s^{-1} M^{-1}. The errors given are the confidence limits on the 99 % level. Merbach and Gnägi [6] give a value of $K_{\text{LaA(OH)}} < 1000$ M^{-1}. Hence, the rate constant $k_{01} > (2.0 \pm 0.4)10^5$ s^{-1} for the dissociation of the hydrolysed complex, La(OH) EDTA.

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