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The synthesis of polyhydroxycarboxylates
Part III. Lanthanide(III) catalyzed addition of glycolate to maleate – a kinetic study

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Abstract

The reaction mechanism of a Michael-like addition of glycolate (ga, **1**) to maleate (male, **2**) catalyzed by lanthanide(III) ions in aqueous solution giving carboxymethoxysuccinate (cmos, **3**) is discussed with respect to its reaction kinetics. The reaction takes place in a ternary complex of Ln(male)(ga) with the addition of the ionized Ln(III) coordinated hydroxy group of **1** to the olefinic bond of **2** as the rate determining step. The first order rate constant in the ternary complex is around 1 min^{-1}. Since exchange of the ligands is fast, the amount of the ternary complex Ln(male)(ga) formed in the mixed ligand system has to be calculated by its stability constant. The stability constants of $Ln(ga)_n$, $Ln(male)_n$, $Ln(cmos)_n$ ($n=1$, 2) and Ln(male)(ga) were determined potentiometrically. The pK_a for the ionization of the Ln(III) coordinated hydroxyl group of **1** could be obtained indirectly from the reaction kinetics. The existence of the Ln(III) coordinated $H_{-1}ga$ ligand was supported by ^{13}C NMR. The effective charge density of the cation plays an important role in decreasing the pK_a of the hydroxyl group of **1** upon coordination. This effect is somewhat counteracted by a concomitant decrease of the nucleophilicity of the resulting alcoholate group in the addition reaction. The La(III) catalyzed reverse reaction ($\mathbf{3} \rightarrow \mathbf{1}+\mathbf{2}$) was found to be stereoselective, resembling enzyme catalysis.

Introduction

The complexes of lanthanide(III) ions (Ln(III)) are among the most exchange labile metal complexes, in particular for the 3+ oxidation state. The predominant electrostatic nature of the metal–ligand interaction and the high formal charge in combination with the high coordination number (8–9 in aqueous solution) [1, 2] may provide unique properties for homogeneous catalysis. In the aqueous reaction systems, the metal ion usually exerts its influence via polarization of chemical bonds and, in addition, it has the possibility to bring about intramolecular group transfer because of its capability to form ternary complexes [3]. Information on the influence of the ionic radius on intramolecular group transfer reactions can be obtained for the Ln(III) ions, as these ions consist of a family of 15 chemically similar metal ions, wherein the ionic radius decreases going through the series [4].

A transferable group in the complex can be the hydroxide ligand, which acts as an intramolecular general base. A coordinated hydroxyl ligand is essential in several biologically important reactions such as the metal ion catalyzed hydrolysis of amides [5–7] and esters [7–9], in trans-phosphorylations [10–20], and in the hydration of unsaturated olefinic bonds [3, 21]. The latter metal ion promoted reaction show similarities with the previously described La(III) catalyzed addition of glycolate (ga, **1**) to maleate (male, **2**) yielding carboxymethoxysuccinate (cmos, **3**) (Scheme 1) [22].

On the basis of an NMR study of the complexes that are present in the reaction medium, we have postulated a mechanism in which La(III) acts as a template by forming a ternary complex with **1** and **2** [22]. La(III) probably brings about the ionization of the hydroxyl group of **1** upon coordination (**4**, see Scheme 2), and then an intramolecular nucleophilic addition of the di-ionized glycolate ligand ($H_{-1}ga$) to **2** in the La(III) complex, results in the formation of **3**.

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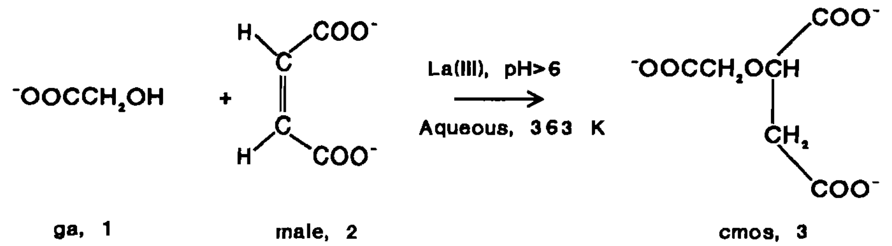


Scheme 1.

The reaction is marked by a strong product inhibition; upon formation of two molecules of **3** per La(III) cation, the reaction rate drastically reduces. Apparently, the La(cmos)$_n$ ($n = 1$, 2) complexes formed are stronger than the La(III) complexes of the starting compounds. The La(cmos) complex is still capable of promoting the addition reaction, although, the reaction rate is reduced significantly as a result of the occupation of four coordination sites [22].

Recently, we have shown that addition reactions of diols and polyols to α,β-unsaturated dicarboxylates are also possible in the presence of multivalent metal ions and that a variety of new chelating agents is accessible with this synthetic route [23, 24].

This paper describes the results of a more detailed study of the mechanism of the addition reaction of **1** to **2**. Special attention was paid to the stereochemistry of the reaction and the ionization of Ln(III)-coordinated **1**. The stabilities of the intermediate ternary Ln(III) complexes were determined potentiometrically and then used in the analysis of the kinetics of the reaction.

Experimental

Equipment

HPLC analyses were carried out using a 8×100 mm 10 μm Nucleosil C18 cartridge, containing a Waters RCM100 module. An aqueous solution (0.01 M) of trifluoroacetic acid as the mobile phase was used at a flow rate of 1.0 ml/min. A Waters Assoc. R401 detector in conjunction with a Spectra-Physics SP4270 Computing Integration was used for detection. For preparative HPLC a Waters LC-500 with two Waters PrePAK-500/C18 columns was used with 0.01% (vol./vol.) trifluoroacetic acid in water as the eluent.

All potentiometric measurements were performed in double distilled water with a Metrohm 605 pH meter, a combined pH electrode equipped with a Teflon ground joint (sleeve) diagram and an Argenthal reference system (type HA 405-60-88TE-S7, Ingold) in which the 3 M KCl of the reference compartment was replaced by a saturated NaCl solution. The titrations were performed at 25 °C in a thermostatted reaction vessel (50 ml) with two inlets, for electrode and buret. The pH meter was standardized by pH 4.008 (N.B.S. buffer 2.5305 g potassium phthalic acid in 250 ml) and by pH 6.865 (N.B.S. buffer 0.8825 g Na_2HPO_4 and 0.8475 g KH_2PO_4 in 250 ml). The hydrogen activity coefficient was determined by measuring the hydrogen ion activity for a set of titration data of a standardized $HClO_4$ solution at an ionic strength of 1.0 M ($NaClO_4$). A value of 1.835 was found.

For the kinetic measurements at 90 °C, the pH was measured with a high temperature electrode (Ingold, 405-60-S7, standard combined electrode with Argenthal high-temperature reference system). A Metrohm 654 pH meter was used with automatic temperature correction via a Pt100 ceramics. A thermostatted reaction vessel (270 ml) equipped with a cooler, a pH electrode, Pt100, and an automatic buret was used in the reactions. The pH of the reaction mixture was kept constant by a pH-stat consisting of a Metrohm impulsomat 614 and a Metrohm dosimat 655.

The pD values are direct readings of a pH meter equipped with an electrode, which was standardized by aqueous buffer solutions at 25 °C.

All ^1H NMR data were recorded on a Varian VXR-400 S spectrometer. The ^{13}C NMR spectra were recorded on a Varian VXR-400 S, on a IBM/ Bruker WP2705Y NMR spectrometer at 67.93 MHz (FSU facility), or on a Nicolet NT-200 WB spectrometer.

Compounds

The Ln(III) chlorides were purchased as hydrates from Alfa Products. The Ln(III) oxides were purchased from Janssen. The $Ln(ClO_4)_3$ solutions were prepared by dissolving the oxides in concentrated $HClO_4$ (60–62%), Baker a.r.) by heating. The excess of $HClO_4$ was removed by evaporation (fuming) close to dryness. The residue was diluted with water (double distilled). The Ln(III) contents of the salts of the stock solutions obtained were determined by an

EDTA titration with Xylenol Orange as the indicator and hexamethylenetetramine (urotropine) as buffer. The concentration of stock solutions of maleic acid (H_2male), glycolic acid (Hga) (both Merck-Schuchardt, a.r.) and H_3cmos were determined by titration with 0.1 M NaOH solution.

H_3cmos was synthesized according to a modification of the previously described procedure [22]. An aqueous solution (250 ml) of Na_2male (0.5 M), Naga (1.0 M) and $LaCl_3$ (0.25 M) was prepared at pH 7.3 and 90 °C. After 4 h of heating at 90 °C another portion of $LaCl_3 \cdot 7.1H_2O$ (13.4 mmol) was added. The heating was continued for 16 h. HPLC analysis showed 90% conversion of **2** to **3**. The reaction mixture was acidified with trifluoroacetic acid and purified by preparative HPLC. The volume of the collected fractions was reduced by evaporation and the residue was lyophilized. The transparent oil was dried *in vacuo* over NaOH. After 4 days the oil started to crystallize, and after one week no more trifluoroacetic acid could be detected in the product. Yield 30% (38 mmol, 7.39 g) of pure H_3cmos. *Anal.* Calc. for $C_6H_8O_7 \cdot 0.12H_2O$: C, 37.07; H, 4.32. Found C, 37.00, H 4.20%. ^{1}H NMR δ(ppm) (D_2O, pD 1.7, t-BuOH at 1.2 ppm): 4.45 (dd, 1H, $J_{3,4}=4.6$ Hz, $J_{3,4'}=6.8$ Hz, H_3), 4.36, 4.26 (AA′-system, 2H, $J_{1,1'}=-16.8$ Hz, $H_{1,1'}$), 2.97 (dd, 1H, $J_{4,4'}=-16.8$ Hz, $J_{3,4}=4.6$ Hz, H_4), 2.89 (dd, 1H, $J_{4,4'}=-16.8$ Hz, $J_{3,4'}=6.8$ Hz, $H_{4'}$).

Potentiometry

The ionic strengths of all solutions used were adjusted to 1.0 M using $NaClO_4$. For the determination of the stability constants of the binary and ternary complexes of **1** and **2** two titrations at different concentrations were made. One set of titrations was performed at a Ln(III) concentration of 0.002 M. For the 1:1 and 1:2 binary complexes of **1**, a solution containing both Naga (0.01 M) and Hga (0.01 M) was titrated to the $Ln(ClO_4)_3$ solution (50 ml) at 25 °C. For the 1:1 binary complex of **2**, a solution containing both Na_2male (0.02 M) and NaHmale (0.016 M) was used. Another set of titrations was performed with 50 ml of a $Ln(ClO_4)_3$ solution (0.005 M) containing Na_2male (0.004 M) and NaHmale (0.001 M). For the 1:2 binary complex of **2**, a solution containing both Na_2male (0.04 M) and NaHmale (0.01 M) was titrated to this solution. The same procedure was used for the 1:1:1 ternary complex, where a solution containing Naga (0.03 M) and Hga (0.01 M) was titrated to the lanthanide(III)–**2** solution. For the 1:1 and 1:2 binary complexes of **1** a solution containing Naga (0.03 M) and Hga (0.01 M) was titrated to 50 ml of a $Ln(ClO_4)_3$ (0.002 M) solution containing Naga (0.0015 M) and Hga (0.0005 M). For the synthesized ligand **3**, the pK_as at $I=1.0$ M ($NaClO_4$) were determined in duplicate by titrating a sodium hydroxide solution (0.03 M) to a H_3cmos solution (0.002 M) at 25 °C. The stabilities of the 1:1 and 1:2 complexes were determined in duplicate by a titration of a solution of Na_3cmos (0.014 M) and HNa_2cmos (0.016 M) to a $Ln(ClO_4)_3$ solution (0.002 M) at $I=1.0$ M ($NaClO_4$).

Computations of the stability constants

The proton stability constants of **3** were calculated with a BASIC computer program written for polyprotic weak acid equilibrium calculations. The stability constants for the binary complexes and the Ln(male)(ga) ternary complex were calculated with a BASIC computer program written by Cacheris [25]. The programs utilize a combined Simplex/Marquardt algorithm for evaluation of the equilibrium constants. A modified Newton–Raphson algorithm [26] is used to calculate $-\log[H^+]$ for each data point that is compared to the observed value. In all titrations the average deviation between calculated and observed $-\log[H^+]$ was smaller than 0.01. The association constants for the 1:1 and 1:2 binary complexes were treated as constants in the calculation of the 1:1:1 ternary complex.

Kinetics — pH variation

The pH electrode was standardized with the buffers of pH 7 and 9 (Merck) at 25 °C. Prior to calibration the electrode was kept at room temperature for 16 h. The electrode was replaced when the asymmetric potential was out of the millivolt range set by Metrohm (+45 to −35 mV at pH 7).

A solution (250 ml, pH 8) of Naga (0.510 M) and Na_2male (0.102 M) was heated to 90 °C. The pH of this solution was adjusted to the desired value with hydrochloric acid (1 M) or sodium hydroxide (0.5 M). Then $LnCl_3$ (2.55 M, 5 ml) was added. The pH of the reaction mixture was kept constant, when necessary, by addition of hydrochloric acid (1.0 M). The maximum addition needed was 2 ml. No volume corrections were made. At certain time intervals samples of 0.5 ml were taken and acidified with 2 M trifluoroacetic acid solution. HPLC analysis was used to determine the amounts of **2** and **3** formed. Compound **3** was the only product formed in all cases. Therefore, the mass balance equation was used to calculate the conversion . The data were processed by a Lotus 1-2-3 spreadsheet. The initial rates were obtained from the curve of the formation of **3** versus time by determining the initial slope.

Kinetics — variation of the concentration of 2

A solution (250 ml) of Naga (0.510 M) and Na_2male (0.204–0.0102 M) was heated to 90 °C. Then a $LaCl_3$

solution (2.55 M, 5 ml) was added and the pH was adjusted to 6.55. A precipitate was formed in the experiments at concentrations less than 0.02 M.

Reaction in D_2O

Naga and Na_2male were prepared by neutralization of aqueous solutions of the acids with NaOH, followed by precipitation with ethanol. The precipitates were dried *in vacuo* over H_2SO_4. $LaCl_3 \cdot 7.1H_2O$ (0.37 g, 0.99 mmol) was dried *in vacuo* at 80 °C to yield $LaCl_3 \cdot 2.3H_2O$. Na_2male (0.49 g, 2.5 mmol) and Naga (1.45 g, 5 mmol) were dissolved in D_2O (25 ml). A total of 20 ml of this solution was added to $LaCl_3 \cdot 2.3H_2O$. The reaction mixture was heated up to 90 °C. The pD of the reaction mixture was 7.48. After 3 h the reaction mixture was analyzed by HPLC and ^{1}H NMR.

^{1}H NMR of **3**, δ(ppm) (D_2O, pD 1.7, t-BuOH at 1.2 ppm): 4.43 (broad d, 1H, $J_{3,4}=4.58$ $J_{3,4'}=5.06$ Hz, H_3), 4.35, 4.22 (AA'-system, 2H, $J_{1,1'}=-15.5$ Hz, $H_{1,1'}$), 2.98 (d, $J_{3,4}=4.58$ Hz, H_4), 2.92 (d, $J_{3,4'}=5.06$ Hz, $H_{4'}$). After removing La(III) by Dowex 50W (H^+) and neutralization with sodium hydroxide: ^{1}H NMR of **3**, δ(ppm) (D_2O, pD 7.5, t-BuOH at 1.2 ppm): 2.56 (d, $J_{3,4}=3.4$ Hz, H_4), 2.45 (d, $J_{3,4'}=8.9$ Hz, $H_{4'}$) [27]. The integral ratio of $H_4/H_{4'}=1.5$.

H–D exchange of 3

A solution of H_3cmos (0.1416 g, 0.728 mmol) in 10 ml D_2O was neutralized with 3 equiv. NaOD. Then $LaCl_3$ (0.1869 g, 0.501 mmol) was added and the pD of the solution was adjusted to 8.0. After 24 h at 90 °C, the reaction mixture was acidified with a DCl solution. ^{1}H NMR δ(ppm) (D_2O, pD 1.6, t-BuOH at 1.2 ppm): 6.31 (s, 0.24 H, male), 4.40 (m, 1H, H_3 cmos), 4.40, 4.15 (AA'-system, 2H, $J_{1,1'}=-14.9$ Hz, $H_{1,1'}$ cmos),4.16 (s, 0.4 H, ga), 3.02 (dd, $J_{4,4'}=-17.4$ Hz, $J_{3,4}=4.6$ Hz, H_4H cmos), 2.98 (d, $J_{3,4}=4.5$ Hz, H_4D cmos), 2.90 (d, $J_{3,4'}=3.7$ Hz, $H_{4'}$D cmos), 2.90 (dd, $J_{4,4'}=-17.4$ Hz, $J_{3,4}=3.7$ Hz, $H_{4'}$H cmos).

No fumarate was detected. About 20% of **3** was decomposed into **2** and **1**. The lower intensity of the peak for **2** in the ^{1}H NMR spectrum in comparison to that for **1** suggests that **2** is partly deuterated (40%). About 85% of H_4 or $H_{4'}$ of **3** has been replaced by deuterium. A low amount of H–D exchange (<5%) had occurred on the H_3 position of **3**. No H–D exchange was found in Hga, and on positions H_1 and $H_{1'}$ of **3**.

Results and discussion

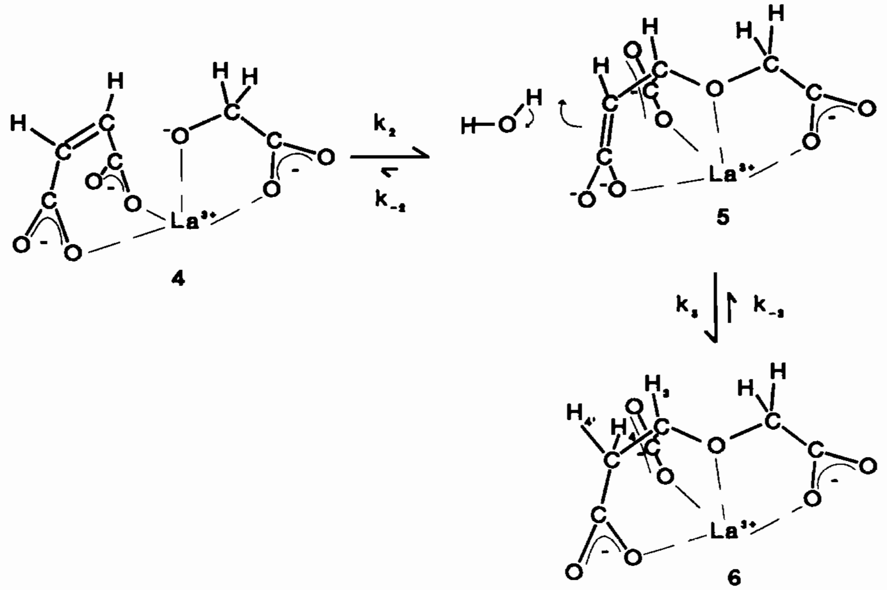
Description of the reaction

In the absence of a multivalent metal ion, no addition reaction of **1** to **2** occurs. When La(III) is added, however, an addition reaction yielding **3** takes place. At 90 °C a solution of **1** (1.0 M) and **2** (0.5 M), in the presence of La(III) (0.25 M), showed 90% conversion of **2**, after 24 h. The reaction is reversible: heating a solution of **3** in the presence of La(III) gave partial decomposition of **3** into **1** and **2**. After 24 h, the reaction mixture had about the same composition as that obtained starting from **1** and **2**. The reaction is highly stereoselective as negligible amounts of the thermodynamically more stable fumarate were formed. Apparently, coordination of **3** by La(III) favors the elimination reaction towards **2** by holding the carboxylate groups of the succinate part in the '*cis*'-configuration. Because of this remarkable stereoselectivity the reaction resembles the hydration of Z-aconitate catalyzed by the enzyme aconitase in the Krebs cycle [28–30].

The protonation of the carbanion (**5**) (see Scheme 2) is stereoselective to some extent as was reflected in the results of experiments performed in D_2O. Starting from **1** and **2**, **3** was obtained with about equal amounts of deuterium and hydrogen at the methylene positions 4 and 4'. The ratio D_4 and $D_{4'}$ was 2:3. The same preference for deuteration of the 4' position was observed starting from pure **3**. In this reaction the total amount of deuterium at 4 and 4' was 42%, whereas **2** contained 40% D in total. Almost no H–D exchange had occurred for the proton positions 3 (<10%), 1, 1' (both <5%) in **3** and in compound **1**.

The selectivity observed in the H–D exchange at the 4 position, with respect to that at the 4' position indicates that the protonation–deprotonation of carbanion **5** in the reaction mechanism (see Scheme 2) occurs from one side with some preference, obviously the sterically less hindered one. Most likely, this step occurs via water in the second coordination sphere.

In this addition reaction the assignment of the rate limiting step is complicated by fast exchange of the Ln(III) complexes formed, which makes an exact determination of the concentration of the 'reactive complex' troublesome. A similar reaction, the intramolecular addition of a coordinated ethylenediamine to **2** in an isolated inert ternary complex of Co(III) [21], shows no general base catalysis. In that case the addition is rate limiting. The resulting Co(III)-coordinated carbanion is rapidly protonated, since no general acid catalysis was observed using buffer acids much more acidic than H_2O. Therefore, we suppose that also in the Ln(III) catalyzed addition of **1** to **2**, the addition of H_{-1}ga to coordinated **2** in a ternary complex is rate limiting and is followed by fast protonation of the carbanion (**5**).



Scheme 2.

Stabilities of ternary complexes of Ln(III) with 1 and 2 (I = 1.0 M NaClO$_4$, 25 °C)

Gd(III)-induced ^{13}C relaxation rate enhancements and Dy(III)-induced ^{17}O shifts have revealed the presence of considerable amounts of ternary complexes with both **1** and **2** in the reaction medium at 25 °C [22]. The extent to which ternary complexes are formed, however, cannot be obtained quantitatively from NMR. Therefore, the conditional stability constants (β) for these ternary complexes must be determined, which are defined as:

$$\beta_{pqrs} = [\mathrm{Ln}_p(\mathrm{H})_q(\mathrm{male})_r(\mathrm{ga})_s]/[\mathrm{Ln(III)}]^p \cdot [\mathrm{H}]^q \cdot [\mathrm{male}]^r \cdot [\mathrm{ga}]^s \qquad (1)$$

The stability constants were measured at an ionic strength of 1.0 M in order to be able to use these data in the analysis of the kinetic measurements (see below). No addition reaction of **1** to **2** occurred under the conditions applied for the determination of the stability constants (pH < 6, 25 °C). The stability constants of Ln(ga), Ln(ga)$_2$, Ln(male), Ln(male)$_2$ and Ln(male)(ga) were determined independently at two different concentrations. The stability constants obtained are shown in Table 1.

The stability constants β_{1001} and β_{1010} are in agreement with those reported in the literature [31]. The second stepwise stability constant of Ln(ga)$_2$, K_{1002} ($\beta_{1002}/\beta_{1001}$), is only 0.63 times smaller than that of the first. The ligand present in the La(ga) complex apparently has a small influence on the second incoming ligand **1**. The ligand **2** present in the Ln(III) complex, on the contrary, has a big effect on the second incoming ligand, as the stepwise stability constant of Ln(male)$_2$, K_{1020}, is about 10 times smaller than β_{1010}.

TABLE 1. Stability constants of Ln(III)-**1** and Ln(III)-**2** complexes[a]

Ln	**1**		**2**		**1+2**	
	β_{1001}[b]	β_{1002}[b]	β_{1010}[c]	β_{1020}[c]	β_{1011}	β_{1011}(stat)[d]
La	2.13	4.09	2.64	4.19	4.45	4.44
Pr	2.39	4.46	2.81	4.47	4.74	4.77
Nd	2.46	4.54	2.87	4.67	4.90	4.91
Eu	2.44	4.80	2.99	4.68	5.09	5.04
Dy	2.48	4.73	2.91	4.36	5.01	4.85
Er	2.52	4.92	2.81	4.31	4.94	4.92
Yb	2.65	5.12	2.82	4.41	5.10	5.07

[a] Log values are given; $I = 1.0$ M NaClO$_4$, 25 °C. [b] For **1**: p$K_a = 3.62$ (ref. 31). [c] For **2**: p$K_{a1} = 1.63$, p$K_{a2} = 5.62$ (ref. 31). [d] Calculated with the use of eqn. (2).

The statistical value of the stability constant of the ternary complex Ln(male)(ga) (β_{1011}(stat)), which is the value of the stability constant if there were no interactions between the ligands **1** and **2**, is calculated from the stability constants of the individual binary complexes (β_{1002} and β_{1020}) with the use of eqn. (2) [32]

$$\beta_{1011}(\mathrm{stat}) = 2(\beta_{1002} \cdot \beta_{1020})^{1/2} \qquad (2)$$

The observed stability constants are, within experimental error, the same as those calculated with eqn. (2) (see Table 1). The ternary complex formation apparently is governed by statistical factors. This implies that the geometry of the coordinated ligands in the ternary complex is similar to that of the binary

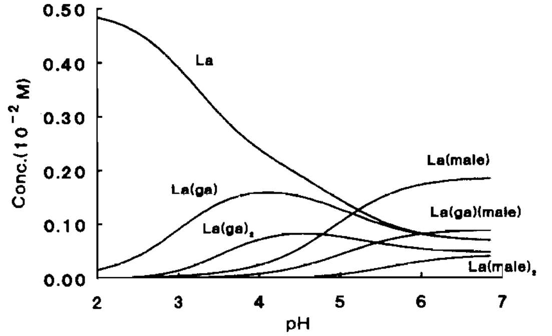


Fig. 1. Speciation in the La(III)-**1**-**2** mixed ligand system vs. pH. $La_{tot} = 0.5 \times 10^{-3}$ M, $male_{tot} = ga_{tot} = 10^{-2}$ M.

complexes, which is in agreement with the results of the Ln(III)-induced NMR experiments [22]. There is no indication of synergic cooperation of the ligands in the ternary complex, in contrast to what is often observed for the d-block transition metal ions [32].

The predominance of statistical contributions to the stabilities of the complexes of the Ln(III) cations with **1** and **2** is probably due to the large ionic radius of the Ln(III) ion in combination with the purely electrostatic coordinative bonds. The same probably holds for other small ligands and this is in our view very promising for extending the scope of the intramolecular catalysis of Ln(III) ions as no special ligand–ligand interactions will restrict the ternary complex formation.

A plot of the distribution of the species as a function of the pH calculated with the use of the stability constants determined for the La(III)–male–ga mixed ligand system (see Table 1) is given in Fig. 1.

An estimation of the stability constants at 90 °C can be made by using the Van't Hoff equation, assuming that $\Delta C_p = 0$ (Table 2) [31]. The stability constants measured for the binary complexes can be used in combination with the literature values of ΔH_{25} (measured with calorimetry) [31]. No value of ΔH_{25} is available for the Ln(male)(ga) complex formation. Therefore, the stability of the ternary complex is determined from β_{1002} and β_{1020} at 90 °C using eqn. (2). The stability constants calculated this way are compiled in Table 2.

Stability constants of Ln(III)-3 complexes (I = 1.0 M NaClO$_4$, 25 °C)

The product **3** displaces **1** and **2** from the La(III) complexes upon its formation due to the difference in stability constants. The ligand **3** can form 1:1 and 1:2 complexes [27]. Polynuclear complexes are formed at concentrations higher than 0.01 M as shown by ^{1}H NMR [27]. Both β_{101} and β_{102} were determined (Table 3).

The stability constants of the Ln(cmos) complexes are about 10^3 times higher than the Ln(male) or Ln(ga) complexes.

For all Ln(III) measured, the stability constant β_{101} of **3** is about 10 times higher than that of the ternary complex Ln(male)(ga). For the formation of Ln(male)(ga) versus Ln(cmos) there is a difference in entropy as the first has three particles forming one, while the second has only two forming one. According to Rossotti this cratic effect corresponds with a $\Delta S°$ difference of 7.9 e.u. [33], log β_{101} − log β_{1011} would be 1.7 ($\Delta(T\Delta S°)/(2.3RT)$), which reasonably agrees with the observed difference. This entropy effect mainly contributes in shifting the equilibrium of the reaction to the side of **3**. The strive for stronger complexes in metal ion catalyzed reactions is, for example, also observed for the metal ion catalyzed enolization and hydration of oxaloacetate [34] and for the addition of the enolic form of pyruvate to its keto form in the dimerization of pyruvate [35]. In these reactions, the metal ion stabilizes the final products with respect to the starting

TABLE 2. Calculated stability constants for 90 °C[a]

Complex	Pr(III)			Eu(III)			Er(III)		
	ΔH[b]	K_{25}	K_{90}	ΔH[b]	K_{25}	K_{90}	ΔH[b]	K_{25}	K_{90}
Ln(male)	10.5	2.81	3.2	10.5[c]	2.99	3.4	15.5[d]	2.82	3.4
Ln(male)$_2$	20.1	4.47	5.2	19.7[c]	4.68	5.4	23.8[d]	4.41	5.4
Ln(ga)	−5.0[e]	2.39	2.2	−3.3	2.44	2.3	−0.8	2.65	2.6
Ln(ga)$_2$	−9.2[e]	4.46	4.1	−5.9	4.80	4.5	−2.5	5.12	5.0
Ln(male)(ga)		4.74	5.0[f]		5.09	5.3[f]		5.10	5.5[f]

[a] $I = 1.0$ M NaClO$_4$, 25 °C. Using the following data from ref. 31: ΔH (kJ/mol): 0.84 (Hmale), 0.42 (H$_2$male), −2.34 (Hga, $I = 2.0$ M NaClO$_4$). At 90 °C for **2**: $pK_{a_1} = 1.65$, $pK_{a_2} = 5.65$; for **1**: $pK_a = 3.53$. [b] ΔH (kJ/mol) at 25 °C at $I = 1.0$ M NaClO$_4$ for **2** and $I = 2.0$ M NaClO$_4$ for **1**. For the calculation of K_{90}, it is assumed that $\Delta C_p = 0$. [c] Values for Sm(III). [d] Values for Ho(III). [e] Values for Nd(III). [f] Statistical value calculated according to eqn. (2).

TABLE 3. Stability constants of Ln–**3** complexes[a]

	β_{101}	β_{102}		β_{101}	β_{102}
La	5.72	9.05	Tb	6.20	10.64
Pr	5.80	9.49	Dy	5.83	9.94
Nd	5.93	9.75	Ho	6.05	9.99
Sm	6.11	10.23	Er	6.25	10.40
Eu	5.85	9.98	Yb	6.11	10.10
Gd	6.08	10.28			

[a]Log values are given. $I = 1.0$ NaClO$_4$, 25 °C. p$K_{a1} = 2.46$, p$K_{a2} = 3.60$, p$K_{a3} = 4.64$.

compounds, which is supposed to be a quantitative measure for the activation by the metal ion in the reactions [34, 35].

*Ionization of Ln(III)-coordinated **1** (H$_{-1}$ga)*

Some indications for the formation of Ln(III)-coordinated H$_{-1}$ga can be found in the literature. The crystal structure of Er(ga)(H$_{-1}$ga) shows unambiguously the presence of the H$_{-1}$ga ligand in the solid state [36]. The structure is a three-dimensional network in which the alcoholate group of H$_{-1}$ga acts as a bridge between two erbium ions. Comparison of IR data of this crystal structure with IR data of an alkaline solution containing a ratio of Er(III)/**1** of 1/3 also shows the C–O$^-$ vibration of the H$_{-1}$ga ligand in solution [37]. From anion exchange experiments, the existence of the Eu(ga)$_2$(H$_{-1}$ga) complex has been proposed [38]. The use of potentiometric methods to determine the pK_{ion} of a coordinated ga ligand cannot be decisive due to concomitant ionization of a coordinated water [39]. ^{1}H NMR has been valuable for studying the ionization of the hydroxyl group of La(2-hydroxyethylethylenediaminetriacetate) [40]. Therefore, we have chosen NMR to determine the pH range in which the ionization of the hydroxyl of Ln(III)-coordinated **1** occurs. ^{13}C NMR was used because **1** contains two different carbon atoms that are connected to the donor groups in the La(III) complex. The La(nitrilotriacetate) (La(nta)) complex was used as a model for the reactive ternary complex La(male)(ga)$_n$ ($n = 1$, 2) and to prevent La(OH)$_3$ precipitation. The diamagnetic La(III) coordinates firmly with the nta ligand ($\beta_{101} = 10.47$, $I = 0.1$ M, 25 °C) [31], and is able to coordinate simultaneously with **1** as five coordination sites are still available [41].

In the mixed ligand system La/nta/**1** (molar ratio 1/1/2) no change in the ^{13}C NMR chemical shifts was observed until pH 7.7. At pH 8.2 precipitation occurred during the measurement. Upon raising the pH to 8.9 the precipitate dissolved again. At the same time an upfield shift of 0.5 and 0.3 ppm was observed for the methylene and carboxylate carbons of **1**, respectively (Fig. 2). The chemical shifts of these ligands were then close to those of the free ligand.

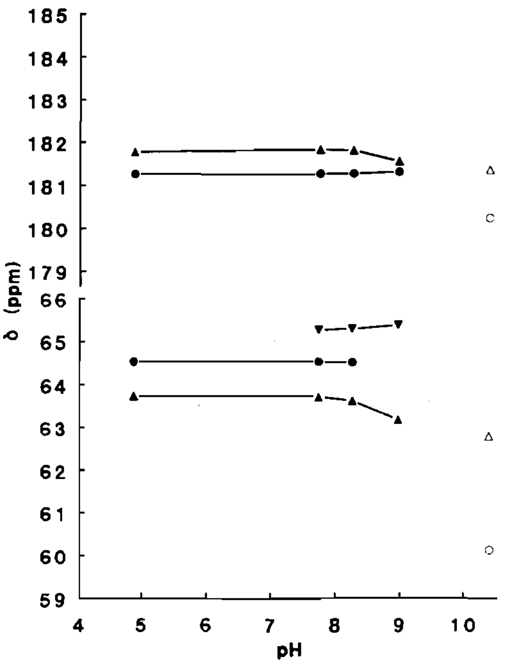


Fig. 2. ^{13}C chemical shift (ppm) in the La(III)–nta–**1** ternary complex system 0.1 M La(III), 0.1 M nta, 0.2 M **1**, in aqueous solution containing 10% D$_2$O at 25 °C vs. pH. **1**: CH$_2$ (▲), COO$^-$ (▲); nta: CH$_2$ (●), COO$^-$ (●) of La(nta) and CH$_2$ (▼) of La(nta)$_2$. For comparison the chemical shift of the free ligands at pH 10.4 are included (open symbols).

Some changes also occurred in the spectrum of the nta ligand. At pH 7.7 a second signal of the methylene carbons of nta was observed, which became the only signal present at pH 8.9 (Fig. 2). The formation of a second nta complex is supported by ^{139}La NMR. A second La(III) signal appeared at pH > 7.7 that is shifted 120 ppm downfield from the signal for the La(nta)(ga) complex. At pH 9 the latter signal disappeared. The chemical shift of the new signal indicates that a La(nta)$_2$ complex is formed [42] upon formation of La(III) complexes of H$_{-1}$ga or OH$^-$ ligands. The same change of the ^{139}La spectrum as a function of the pH was observed in the absence of **1**, when La(III) hydroxo complexes were formed. Apparently, ionization of the ga and water ligand is accompanied by a disproportionation of the La(III) complexes towards La(nta)$_2$ and probably relatively stable dimeric or polynuclear La(III) complexes involving OH$^-$ or H$_{-1}$ga ligands, which escape observation due to excessive linewidths.

Support for the involvement of the H$_{-1}$ga ligand in these complexes was obtained from a ^{13}C NMR experiment analogous to that described above but

TABLE 4. Stability constants of **1**[a]

log β_{0101}	3.63
log $\beta_{0\text{-}101}$	-13.8^{b}
log $\beta_{0\text{-}100}$	-13.78
log $\beta_{1\text{-}100}$	-9.1^{c}
log β_{1001}	2.55
log $\beta_{1\text{-}101}$	-5.8^{d}

[a] $I = 0.1$, 25 °C. [b] See text. [c] $I = 0.3$, 25 °C (ref. 51). [d] See text.

now with the diamagnetic Y(III). The signals for **1** at pH higher than 7 appeared to be broadened beyond detection, whereas those for nta remained sharp. Even at pH 9 no free **1** could be detected. This can be ascribed to a decrease of the exchange rate of **1** between the bound and free form, upon deprotonation of the coordinated OH group*.

Obviously, $H_{-1}ga$ will coordinate the La(III) stronger than **1**. Its stability constant $\beta(H_{-1}ga)$ can be deduced from Table 4 with the use of $\beta(H_{-1}ga) = K_{ion}\beta_{1001}/\beta_{0\text{-}101}$, where K_{ion} is the ionization constant of the Ln(III) coordinated hydroxyl group of **1**. For the calculation of $\beta(H_{-1}ga)$, $\beta_{0\text{-}101}$ is needed. Beck *et al.* have determined by optical rotation the pK_a of the first hydroxyl group of tartaric acid to be 13.8 [45]. The same value was obtained for the pK_{a3} of gluconic acid [46]. For pK_{ion} we took the value determined kinetically (see below), which is in agreement with the results of the ^{13}C NMR study on the La/nta/ga mixed ligand system. Using these data the stability constant $\beta(H_{-1}ga)$ is calculated to be 8.0.

With the estimated stability constants that are compiled in Table 4, the distribution of the various species as function of the pH was calculated (see Fig. 3). The concentration of LaOH is small with respect to that of La(H_{-1}ga), which is in agreement with the insignificance of the addition of the water to **2**, as a side reaction of the addition of **1** to **2**.

Reaction kinetics

The reaction mechanism outlined in Scheme 2 needs further kinetic support. Initial reaction rates were used in order to limit the number of species that have to be taken into account. A ten times excess of **1** with respect to Ln(III) was used in order to keep the amount of hydroxide coordinated to the Ln(III) low (see above) and to diminish the change of the overall concentration of Ln(III) bound **1** (Ga_{tot} − ga), upon formation of H_{-1}ga. Furthermore, the reaction can then be considered as pseudo zero order in **1** and the range of pHs used can be extended without the risk of precipitation.

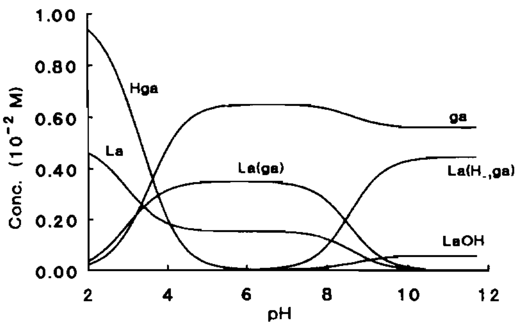


Fig. 3. Speciation in the La(III)–**1** ligand system as a function of the pH, calculated with the association constants given in Table 4. 0.005 M La(III), 0.010 M **1** at 25 °C.

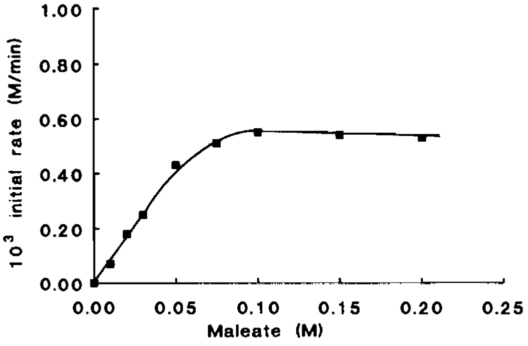


Fig. 4. Dependence of the initial rate of the addition of **1** to **2** on the concentration of **2** in a reaction mixture containing 0.05 M La(III) and 0.5 M **1**. pH is maintained at 6.55 (90 °C), reaction temperature 90 °C.

First, the concentration of **2** in a La(III) catalyzed reaction was varied at constant pH in order to determine the molar ratio **2**/Ln(III), where the reaction rate is optimal. These experiments were performed at pH 6.5 (90 °C). Small variations of the pH around 6.5 have almost no influence on the reaction rate. Figure 4 shows the initial reaction rate as a function of the concentration of **2**. The maximum initial rate (5.5 10^{-4} M min^{-1}) was obtained at ratios of **2**/Ln(III) higher than 1.5. This suggests that in the 'reactive' ternary complex one ligand of **2** is present.

For the sake of simplicity La(male)(ga) is considered the only 'reactive' ternary complex present. If it is assumed, as already discussed, that the reaction from compound **4** to **5** (see Scheme 2) is the rate

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*An alternative explanation would be that at pH > 7 an exchange via $Ln(nta)(ga) + OH^{+} \rightleftharpoons Ln(nta)(OH) + ga$ becomes predominant (cf. ref. 43), with a smaller exchange rate (on the NMR time-scale) than the corresponding substitution reaction with water at lower pH. It should be expected, however, that if that would be the case a further increase of the pH would lead to a shift of the above mentioned equilibrium to the right and then it would be possible to observe free ga [44].

limiting step and that $k_{-2} \ll k_3$ then the initial rate can be given by eqn. (3).

$$r = k_2[\mathrm{Ln(male)(H_{-1}ga)}] \qquad (3)$$

Since an excess of **1** was employed, one can neglect the $\mathrm{Ln(male)}_n$ ($n=1$, 2) complexes under the conditions applied (molar ratio Ln(III)/**2** of 1/2). Then with substitution of the ionization constants of **4** (eqn. (4))

$$K_{\mathrm{ion}} = [\mathrm{Ln(male)(H_{-1}ga)}][\mathrm{H^+}]/[\mathrm{Ln(male)(ga)}] \qquad (4)$$

and the mass balance (eqn. (5))

$$\mathrm{male_{tot}} = [\mathrm{Ln(male)(ga)}] + [\mathrm{Ln(male)(H_{-1}ga)}] + [\mathrm{male}] + [\mathrm{Ln(male)}] + 2[\mathrm{Ln(male)_2}] \qquad (5)$$

into eqn. (3) gives

$$r = k_2C/(1 + \mathrm{H^+}/K_{\mathrm{ion}}) \qquad (6)$$

which can be rearranged to

$$1/r = \mathrm{H^+}/(K_{\mathrm{ion}}Ck_2) + 1/k_2C \qquad (7)$$

wherein $C = \mathrm{male_{tot}} - \mathrm{male} \approx [\mathrm{Ln(male)(ga)}]$, which holds as the concentration of bound **1** ($\mathrm{Ga_{tot}} - \mathrm{ga}$) is constant.

The initial reaction rate as a function of the pH of the La(III) catalyzed reaction is shown in Fig. 5. A precipitate was present above pH 7.3. The rate of the addition increased upon raising the pH.

In Fig. 6 the reciprocal of the initial rate for various Ln(III) ions is given as a function of the $\mathrm{H^+}$ concentration. At a free proton concentration of 0.41×10^{-6} (pH 6.4) Dy(III) and Er(III) are the best catalysts among the Ln(III) ions (Fig. 6). A good correlation with eqn. (7) is consistent with the assignment of the rate limiting step (Scheme 2). From the slopes and intercepts of these lines, the $\mathrm{p}K_{\mathrm{ion}}$ values were calculated, using eqn. (7) (see Table 5).

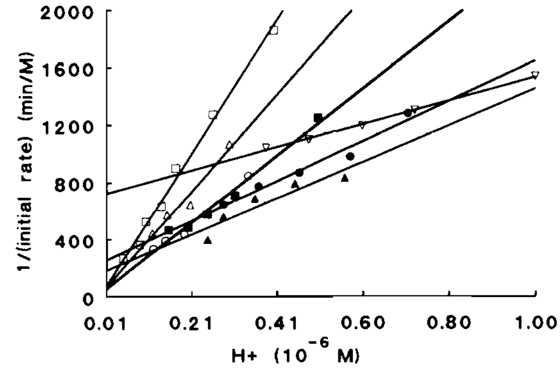

Fig. 6. The reciprocal initial rate of the addition of **1** to **2** as a function of $[\mathrm{H^+}]$ at 90 °C. 0.50 M **1**, 0.10 M **2** and 0.05 M $\mathrm{LnCl_3}$. La(III) (□), Pr(III) (△), Nd(III) (○), Eu(III) (■), Dy(III) (▲), Er(III) (●), Yb(III) (▽).

TABLE 5. Addition of **1** and **2** catalyzed by various Ln(III) ions

	$10^{-9}/K_{\mathrm{ion}}k_2C$[a]	$1/k_2C$[a]	$\mathrm{p}K_{\mathrm{ion}}$	k_2C
La	4.7	21	8.4	0.048
Pr	3.4	26	8.1	0.039
Nd	2.4	27	7.9	0.037
Eu	2.4	33	7.9	0.030
Dy	1.3	170	6.9	0.006
Er	1.4	240	6.8	0.004
Yb	0.8	716	6.1	0.001

[a]See eqn. (7).

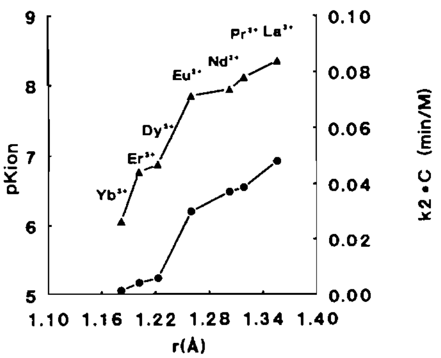

Fig. 7. $\mathrm{p}K_{\mathrm{ion}}$ (▲) and k_2C (●) (see eqn. (7)) vs. the ionic radius of the Ln(III) ion.

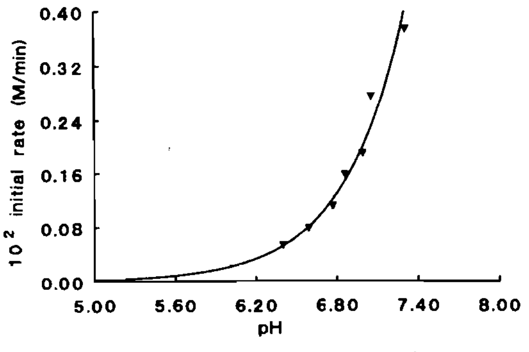

Fig. 5. Dependence of the initial rate of the addition of **1** to **2** on the pH in the La(III) catalyzed reaction at 90 °C. 0.50 M **1**, 0.10 M **2** and 0.05 M $\mathrm{LaCl_3}$.

The $\mathrm{p}K_{\mathrm{ion}}$ shows a decreasing trend when going through the Ln(III) series (Fig. 7) The $\mathrm{p}K_{\mathrm{ion}}$ is related to the effective charge density of the Ln(III) ion in question, which increases going from La(III) to Lu(III) [47]. At higher effective charge density the polarization of the hydroxyl group of Ln(III)-bound **1** becomes larger and consequently the $\mathrm{p}K_{\mathrm{ion}}$ decreases when going through the Ln(III) series. A 'Gd-break' seems to be present for the $\mathrm{p}K_{\mathrm{ion}}$ and, thus, for the stability constant of the ternary complex $\mathrm{La(male)(H_{-1}ga)}$. Similar breaks are observed for the stability constants of many other Ln(III) complexes [48, 49], including those of **1** and **2**.

An estimation of the rate constant k_2 can be obtained with $C = [\text{Ln(male)(ga)}]$*. Using the data from Table 2, C at pH 6 (90 °C) can be calculated to be 0.0212 (Pr(III)), 0.0198 (Eu(III)) and 0.0146 (Er(III)) M. From these concentrations and k_2C (Table 5) k_2 can be calculated: 1.8 Pr(III), 1.5 Eu(III) and 0.07 Er(III) min^{-1}.

Apparently, the decrease of pK_{ion} of the hydroxyl group of **1** upon coordination to the Ln(III) ion, which leads to an increase of the concentration of the reactive H_{-1}ga ligand at a given pH, is counteracted by a decrease of its nucleophilicity, which is in agreement with the known reduction of nucleophilic capability of the hydroxide ion upon coordination to a metal ion [3, 50].

Conclusions

The formation of **3** from **1** and **2** catalyzed by Ln(III) ions is an equilibrium reaction, in which the driving force is the stronger complexation of the product **3**. The reaction takes place in a ternary complex of Ln(male)(ga) with the addition of the ionized Ln(III)-coordinated hydroxyl group of **1** to the olefinic bond of **2** as the rate determining step. The first order rate constant of the reaction is around 1 min^{-1} for the Ln(III) ions at 90 °C. The effective charge density of the Ln(III) ion plays an important role in decreasing the pK_a of a hydroxyl group of **1** upon coordination. This effect is somewhat counteracted by a concomitant decrease of the nucleophilicity of the resulting alcoholate group.

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*It is assumed that the concentrations of the Ln(ga)_3 and Ln(male)(ga)_2 complexes are negligible.

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