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Nuclear Magnetic Resonance Studies of Rare Earths Polyaminocarboxylates. IV. Nitrilotriacetates [1, 2]

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^{1}H-NMR has been used to study the rare earth bis(nitrilotriacetates) (M = La, Ce, Pr, Nd, Sm, Eu, Tm, Yb, Lu, Y) in the presence of an excess of ligand as a function of pH. Three kinetic pathways are observed for the intermolecular ligand exchange reaction:

1. $$M(NTA)_2^{3-} \underset{k_{-o}}{\overset{k_o}{\rightleftarrows}} M(NTA) + NTA^{3-}$$

The rate constants k_{-o}, for the formation of the bis-complexes, are in agreement with a mechanism involving outer-sphere complex formation, followed by a dissociative interchange of the outer-sphere NTA^{3-} with an inner-sphere water molecule.

2. $$M(NTA)_2^{3-} + H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} M(NTA) + HNTA^{2-}$$

(acidic medium)

Along the rare earth series, the rate constants k_{-3} are nearly constant (2×10^3 to 6×10^3 s^{-1} M^{-1}) and 0.7×10^4 to 1.3×10^4 smaller than k_{-o}. Two mechanisms may be invoked for the formation of M-$(NTA)_2^{3-}$. In the first one, the rate determining step is again the rate of loss of a water molecule from the inner-sphere, with $HNTA^{2-}$ protonated on a carboxylate group as the reacting species. In the second one, it is proposed that the decrease in rate is due to the relatively slow rate of proton migration from the nitrogen atom in a partially bonded reaction intermediate.

3. $$M(NTA)_2^{3-} + {}^*NTA^{3-} \overset{k_1}{\rightleftarrows} M(NTA)({}^*NTA)^{3-} + NTA^{3-} \quad \text{(basic medium)}$$

The symmetric ligand exchange occurs through a progressive chelation of the entering ligand and simultaneous dechelation of the leaving ligand. The rate constants k_1 decrease strongly along the series, whereas the stability constants K_{ML_2} increase.

Introduction

The mechanisms of reaction between rare earth ions and polyaminocarboxylates involve several steps. Numerous kinetic studies have been carried out in the presence of an excess of metal ion, a case where the reactions are relatively slow and may be followed by spectrophotometry or by tracer techniques [3]. In the case of an excess of ligand, the reactions are faster and nuclear magnetic resonance has shown to be a useful technique. The ligand exchange reactions on the diamagnetic rare earth ethylenediaminetetraacetates [4] and nitrilotriacetates [5], as well as on the praseodymium hydroxyethyliminodiacetate [1], have been studied as a function of ligand concentration and pH. Our objective is to extend the nitrilotriacetate study to the whole rare earth series by looking at the paramagnetic ions and also to redetermine the stability constants of the rare earth nitrilotriacetates at the high concentrations necessary for the NMR measurements, in order to calculate more precisely the concentrations of the various species in equilibrium which have to be known to obtain precise rate constant data.

Experimental

Preparation

The hydrated rare earth nitrates were obtained by attack of the oxides (purity > 99.9%) with concentrated nitric acid. The mononitrilotriacetates $M(NTA)\cdot nH_2O$ were prepared by mixing stoichiometric quantities of $M(NO_3)_3\cdot xH_2O$ with a concentrated solution of $K_2H(NTA)$ (prepared from H_3NTA, Siegfried). The protons liberated by complex formation were neutralized by potassium hydroxide. The complex $M(NTA)\cdot nH_2O$ precipitated, and the mixture was stirred mechanically for 24 hours, then cooled to 5 °C. The pH of the solution was between 4 and 6, depending on the nature of the rare earth. Care must be taken to avoid adding an excess of potassium hydroxide which would result in precipitation of the rare earth hydroxide or the formation

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of very soluble hydroxocomplexes. The product obtained was washed twice with water and dried under vacuum (18 mmHg). Analysis of the lanthanide complexes M(NTA) was carried out as described in a previous paper [5]. The metal/nitrogen ratio in the complexes was one within experimental error (0.5%), and the hydration number is between 2.5 and 4.5.

pH Measurements

They were carried out with a METROHM E 388 Compensator, equipped with a combined glass electrode, which was calibrated* by titration of a solution of nitric acid with decarbonated potassium hydroxide [7], at ionic strength 1.0 *M*(KNO_3). The measurements were made at 20.0 ± 0.1 °C under a nitrogen atmosphere free of CO_2.

Determination of Stability Constants

The first protonation constant of the nitrilotriacetate anion was determined by titrating 0.2 *M* K_2H(NTA) solution with 0.7 *M* decarbonated potassium hydroxide. Since H_3(NTA) and KH_2(NTA) are only slightly soluble, the second and third protonation constants were estimated by titration of a 6×10^{-3} *M* solution of H_3(NTA) (ionic strength 1.0 *M*, KNO_3) with 0.7 *M* KOH.

To determine the stability constants of the 1:2 complex, 0.15 *M* solutions of $K_3M(NTA)_2$ were prepared by mixing M(NTA) and K_3(NTA) in stoichiometric quantities. The solutions were titrated with 2 *M* nitric acid until precipitation of the neutral complex M(NTA). The titration curve allowed the precise determination of the stability constant K_{ML_2} of the 1:2 complex. Work in supersaturated M(NTA) solution gave good estimates of the stability constants K_{ML} of the 1:1 complexes.

Calculations

The simultaneous calculation of several stability constants from the titration curve was done by means of the program VARIAT [8], with approximate constants introduced as initial values. The subprograms APPROX [9] and NEWRAP [8] evaluate the theoretical quantities of base or acid required to obtain the pH values measured during the titration.

^{1}H-NMR Measurements

Spectra were obtained at 90 MHz using a Bruker HX-90 spectrometer equipped with a B-ST 100 variable-temperature accessory. Temperature measurements were made in the usual way with the calibrated charts supplied by Varian. t-Butanol was used as an internal reference for the measure of instrumental broadening and chemical shift. The protons of t-butanol resonate at 1.233 ppm downfield from those of sodium 3-(trimethylsilyl)-1-propanesulfonate (TMS*) and all chemical shifts are reported with respect to TMS*. The solutions contained 1% of D_2O which was used as an internal deuterium lock signal. To minimize the effect of instrumental line broadening, the line width at half-height is given by

$$W = W^{measd} - W^{measd}_{t\text{-}ButOH} \qquad (1)$$

where W^{measd} is the actual width on the spectrum. The values of τ_C^r and τ_F^r, the residence times of NTA in the complexed and free sites, were obtained in the slow-exchange region [10] according to

$$1/\tau = \pi(W - W^o) \qquad (2)$$

where W^o is the line-width at half-height in absence of exchange. W_L^o was measured in solutions of NTA only, at the same concentration and pH as those studied for the kinetic measurements. The residence times τ_C^r and τ_F^r are related to the populations P_C and P_F of the sites by

$$P_C \cdot \tau_F^r = P_F \cdot \tau_C^r \quad \text{with} \quad P_C + P_F = 1 \qquad (3)$$

The mean lifetime τ_C of the species ML_n is related to the residence time τ_C^r of L in the site ML_n by equation (4):

$$\tau_C^r = n\,\tau_C \qquad (4)$$

From a kinetic point of view the mean lifetime τ_C of ML_n is linked to the rate of exchange by relation (5):

$$1/\tau_C = d[ML_n]/[ML_n]\,dt \qquad (5)$$

Results

Nitrilotriacetic Acid

The protonation of the nitrilotriacetate anion has been studied by IR and NMR by Chapman *et al.* [11]. The first proton attaches itself to the nitrogen and the three carboxylate groups are linked by hydrogen bridges, which, according to these authors, give the $H(NTA)^{2-}$ anion a tricyclic structure. The further protonations take place on the carboxylate groups, breaking the hydrogen bonds. We have determined the protonation constants of the nitrilotriacetate anion at the high concentration required for the NMR kinetic study. By potentiometry, we obtain at 20 °C a log K_1^H value of 9.55 ± 0.03 (0.2 *M* NTA) in good agreement with the value of 9.58 ± 0.05 (0.4 *M* NTA) calculated from an NMR titration curve reported previously [5]. For the determination of the second

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*In paper II of this series [5] the buffer solutions of McIlvaine [6] were used for the calibration. In order to compare all these results with the former ones for the rare earth nitrilotriacetates, we have corrected the older results to adapt them to the new pH scale.

TABLE I. Stability Constants K_{ML_2} of Rare Earth Bis(nitrilotriacetates) Determined by Titration of $K_3M(NTA)_2$ 0.15 *M* with Nitric Acid 2 *M* at 20 °C.

Rare Earth	La	Ce	Pr	Nd	Sm	Eu	Tb
$\log K_{ML_2}$	6.64	7.27	7.66	7.86	8.09	8.15	8.28
Rare Earth	Dy	Ho	Er	Tm	Yb	Lu	Y
$\log K_{ML_2}$	8.36	8.30	8.20	8.47	8.53	8.60	8.02

TABLE II. ^{1}H-NMR Chemical Shifts (ppm) and Line Width $W^o_{M(NTA)_2}$ (Hz) of 0.15 *M* Rare-earth Bis(nitrilotriacetates) at 20 °C.

Rare Earth	δ	$W^o_{M(NTA)_2}$	Rare Earth	δ	$W^o_{M(NTA)_2}$
La	3.41[a]	0.85	Ho	−7.21	170
Ce	7.66	6.1	Er	−4.25	160
Pr	11.66	7.1	Tm	−17.41	80
Nd	6.68	11.3	Yb	−8.00[b]	13.1
Sm	3.55	1.4	Lu	3.51[a]	0.7
Eu	−2.55	1.6	Y	3.43[a]	0.9
Tb	−5.71	190	Sc	3.50[a]	0.7

[a] Measured by Merbach and Gnaegi [5], $\delta_{NTA} = 3.19$ ppm. [b] $\delta_{Yb(NTA)}$: −8.01 ppm; $\delta_{Yb(NTA)(OH)^-}$: −8.95 ppm.

and third protonation constants the ionic strength was fixed at 1.0 *M* with KNO_3 because of the low solubility of nitrilotriacetic acid at low pH. The values obtained are $\log K^H_2 = 2.2 \pm 0.1$ and $\log K^H_3 = 1.0$ (<1.6).

Rare Earth Mono- and Bis(nitrilotriacetates)

The nitrilotriacetate anion is a potentially tetradentate ligand and forms stable M(NTA) and $M(NTA)_2^{3-}$ complexes with the rare earth ions. The stability constants of the bis(nitrilotriacetates) have been determined by potentiometric titration of 0.15 *M* solutions of $K_3M(NTA)_2$ (Table I). The ^{1}H-NMR signals of the nitrilotriacetate ion in the diamagnetic M(NTA) and $M(NTA)_2^{3-}$ complexes (M = La, Y, Lu, Sc) are downfield from the signal of free NTA^{3-} [5]. The downfield shift increases with a decrease in the ionic radii, but the maximum effect is less than 0.4 ppm (Table II). For the paramagnetic lanthanides, the isotropic shift induced by the metal strongly influences the chemical shift of coordinated NTA, as well as that of water. In solutions containing $M(NTA)_2^{3-}$ and an excess of ligand one observes two distinct signals, which implies a nitrilotriacetate exchange slow on the NMR time scale. On the other hand the proton exchange from coordinated and free water is rapid. The chemical shift of the water protons is therefore the weighted average of the individual chemical shifts. In the case of erbium, dysprosium and holmium, the solvent peak is shifted towards high field, which masks the signal of free NTA and prevents the study of the exchange reaction between free and coordinated NTA for these three lanthanides. For the other lanthanides the solvent peak is shifted to low field. The long electronic relaxation time of gadolinium broadens the ^{1}H-NMR signals too much to allow a study of $Gd(NTA)_2^{3-}$ solutions.

The formation of complexes other than M(NTA) and $M(NTA)_2^{3-}$ has been considered by several authors. Noddack *et al.* [12], in a polarographic study, proposed the existence of binuclear complexes $M_2(NTA)_3^{3-}$, whose existence was refuted by Anderegg [13]. In solutions of pH less than 2, Ternovaya *et al.* [14] showed the presence of the protonated complex $NdH(NTA)^+$. By titration of M(NTA) with a strong base the existence of hydroxo-complexes $M(NTA)(OH)^-$ was shown [15]. We have verified the formation of $Yb(NTA)(OH)^-$ by titration of a 0.043 *M* solution of Yb(NTA) with 2*M* KOH. The protonation constant K^H_{ML} (= $[Yb(NTA)]/[Yb(NTA)(OH)^-][H^+]$) was found to be 10^7. The titration was carried out between n = 0.3 and 0.8 (n = equiv KOH/equiv Yb(NTA)). At low pH, the complex Yb(NTA) precipitates, while at high pH, there is a precipitate of ytterbium hydroxide. During the course of the titration, the chemical shift of the coordinated NTA peak is displaced. The presence of only one signal implies a rapid exchange of hydroxylic protons between Yb(NTA) and $Yb(NTA)(OH)^-$. Figure 1 shows that there exists a linear correlation between the chemical shift of coordinated NTA and the titration factor. If we extrapolate the chemical shift measurements to values of n = 0 and n = 1, we obtain the shifts of Yb(NTA) = −8.01 ± 0.05 ppm and $Yb(NTA)(OH)^-$ = −8.95 ± 0.03 ppm. Protonated or hydrocomplexes of the bis(nitrilotriacetates) are unknown and were not observed in our NMR study.

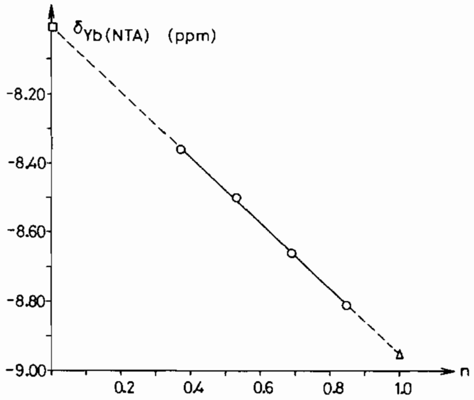


Figure 1. ^{1}H-NMR titration curve of 0.043 *M* Yb(NTA) with 2 *M* KOH at 20 °C. Chemical shift of coordinated NTA as a function of the titration factor n. □: $\delta_{Yb(NTA)}$ (extrapolated) = −8.01 ± 0.05 ppm. △: $\delta_{Yb(NTA)(OH)^-}$ (extrapolated) = −8.95 ± 0.03 ppm.

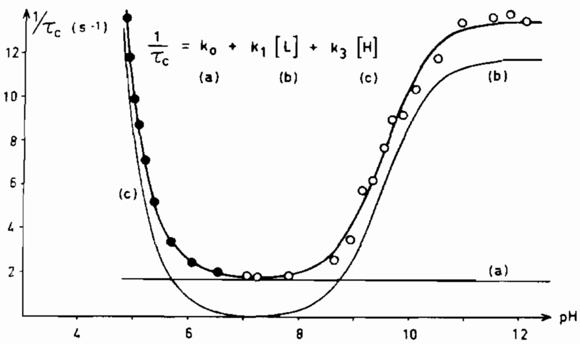


Figure 2. Ligand exchange reaction between $Ce(NTA)_2^{3-}$ and an excess of NTA at 20 °C. The solid lines (a), (b) and (c) represent the contribution of the three corresponding kinetic paths to the overall exchange reaction. The solid line through the experimental data represents the sum of the three contributions. ○ $[Ce(NTA)_2^{3-}]$ = 0.10 *M* and $[NTA_f]$ = 0.20 *M*. ● $[Ce(NTA)_2^{3-}]$ = 0.15 *M* and $[NTA_f]$ = 0.12 *M*.

Kinetic Study

In their study of the diamagnetic rare earth nitrilotriacetates Merbach and Gnaegi [5] proposed the following kinetic paths for the ligand exchange between the bis(nitrilotriacetate) complex and an excess of nitrilotriacetate:

$$M(NTA)(^*NTA)^{3-} \underset{k_{-o}}{\overset{k_o}{\rightleftharpoons}} M(NTA) + (^*NTA)^{3-} \qquad (6)$$

$$M(NTA)(^*NTA)^{3-} + (NTA)^{3-} \overset{k_1}{\rightleftharpoons} M(NTA)_2^{3-} + (^*NTA)^{3-} \qquad (7)$$

$$M(NTA)(^*NTA)^{3-} + H(NTA)^{2-} \overset{k_2}{\rightleftharpoons} M(NTA)_2^{3-} + H(^*NTA)^{2-} \qquad (8)$$

$$M(NTA)(^*NTA)^{3-} + H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} M(NTA) + H(^*NTA)^{2-} \qquad (9)$$

Their study has now been extended to the paramagnetic rare earths. The measurements of exchange rates were carried out with an excess of ligand and the metal ion complexed for more than 99% in the form of $M(NTA)_2^{3-}$. The ligand exchange rates can be determined from the linewidths of the NMR signals of $M(NTA)_2^{3-}$. However the natural linewidth of the paramagnetic $M(NTA)_2^{3-}$ is usually larger than the exchange broadening, therefore the measurements were carried out on the diamagnetic site of the free NTA. In the case of the samarium and europium complexes, for which the paramagnetic broadening is small, we checked that the exchange rates determined from the coordinated and free NTA were identical. On the basis of the equations developed in the experimental section we can derive the relation (10) which may be used to calculate the mean lifetime τ_C of the complex $M(NTA)_2^{3-}$.

$$1/\tau_C = \pi(W_{NTA} - W_{NTA}^o)[NTA_f]/[M(NTA)_2^{3-}] \qquad (10)$$

where W_{NTA} and W_{NTA}^o are the linewidths of free NTA in the presence and the absence of exchange respectively, and $[NTA_f]$ is the total concentration of noncomplexed NTA. When the linewidths of $M(NTA)_2^{3-}$ were measured, equation (11) was used.

$$1/\tau_C = 2\pi(W_{M(NTA)_2} - W_{M(NTA)_2}^o) \qquad (11)$$

Combination of equation (5) with the rate laws for the kinetic paths (6) to (9) leads to the overall kinetic equation (12) for the ligand exchange.

$$1/\tau_C = k_o + k_1[NTA^{3-}] + k_2[H(NTA)^{2-}] + k_3[H^+] \qquad (12)$$

It follows that by an appropriate choice of pH and free ligand concentration, it becomes possible to determine independently the different rate constants.

Figure 2 shows, for cerium, the experimental $1/\tau_C$ values as a function of the pH. The overall exchange rate shows a minimum at intermediate pH. At low pH the contribution of the acid catalysed path (equation 9) becomes important and at high pH the symmetric exchange of NTA^{3-} (equation 7) is the predominant contribution to the overall exchange rate. At intermediate pH's the term $k_o + k_2[H(NTA)^{2-}]$ contributes mainly to the exchange, and Table III shows that $1/\tau_C$ is independent of the concentration of free NTA. This indicates that the contribution of the symmetric exchange of $H(NTA)^{2-}$ according to equation (8) is negligible. An upper limit of 5 s^{-1} M^{-1} can be estimated for k_2.

TABLE III. $1/\tau_C$ at Intermediate pH's for Cerium and Praseodymium at 20 °C.

Cerium					Praseodymium				
$[Ce(NTA)_2^{3-}]$ (*M*)	$[NTA_f]$ (*M*)	pH	$1/\tau_C$ (s^{-1})	k_o [a] (s^{-1})	$[Pr(NTA)_2^{3-}]$ (*M*)	$[NTA_f]$ (*M*)	pH	$1/\tau_C$ (s^{-1})	k_o [a] (s^{-1})
0.198	0.149	7.27	2.0	1.9	0.150	0.247	6.63	1.0	1.0
0.100	0.200	7.06	1.9	1.8	0.175	0.227	6.65	0.6	0.6
0.100	0.200	7.26	1.8	1.7	0.200	0.203	6.63	0.8	0.8
0.100	0.200	7.82	1.7	1.5	0.225	0.177	6.73	0.8	0.8
0.150	0.120	–	–	1.9[b]	0.250	0.150	6.49	0.7	0.7
0.100	0.200	–	–	1.5[c]	0.147	0.103	6.90	0.7	0.7

[a] $k_o = 1/\tau_C - k_1[NTA^{3-}] - k_3[H^+]$. [b] Extrapolation of measurements in acid media (from data in Table IV). [c] Extrapolation of measurements in slightly alkaline media (from data in Table V).

TABLE IV. $1/\tau_C$ (s^{-1}) at Low pH's and 20 °C for Ce, Pr, Nd, Sm, Eu, Tm and Yb.

Cerium		Praseodymium		Neodymium		Samarium		Europium		Thulium		Ytterbium	
[C][a] : 0.150 *M* [L][b] : 0.120 *M*		[C] : 0.147 *M* [L] : 0.103 *M*		[C] : 0.149 *M* [L] : 0.100 *M*		[C] : 0.150 *M* [L] : 0.150 *M*		[C] : 0.148 *M* [L] : 0.122 *M*		[C] : 0.151 *M* [L] : 0.101 *M*		[C] : 0.145 *M* [L] : 0.101 *M*	
pH	$1/\tau_C$	pH	$1/\tau_C$	pH	$1/\tau_C$	pH	$1/\tau_C$	pH	$1/\tau_C$	pH	$1/\tau_C$	pH	$1/\tau_C$
6.11	2.5	6.39	0.7	6.89	0.5	6.91	0.4	5.34	0.5	3.92	3.1	4.31	0.9
5.71	3.4	5.42	1.5	5.38	0.9	4.99	1.2	4.95	0.9	3.87	3.5	4.19	1.3
5.38	5.2	5.22	2.1	5.09	1.8	4.83	1.5	4.52	1.8	3.82	3.9	4.14	1.3
5.22	7.1	5.00	2.9	4.97	2.1	4.57	2.6	4.38	2.5	3.78	4.4	4.03	1.9
5.10	8.7	4.82	3.8	4.74	2.9	4.32	4.5	4.32	2.9	3.74	4.7	3.97	1.9
5.00	9.9	4.67	5.6	4.73	3.1	4.21	6.2	4.18	4.1	3.71	5.4	3.92	2.3
4.92	11.8	4.60	5.8	4.63	3.7	4.07	7.8	3.99	5.8	3.68	5.6	3.83	2.8
4.85	13.6	4.59	6.3	4.53	4.2			3.87	8.4	3.65	6.0	3.73	3.8
				4.43	5.4							3.65	4.5
				4.33	7.4								

[a] Concentration of $M(NTA)_2^{3-}$. [b] Total concentration of the ligand in noncoordinated form.

TABLE V. $1/\tau_C$ (s^{-1}) in Slightly Basic Medium for Cerium at 20 °C. A linear least squares fit of $1/\tau_C$ as a function of $[NTA^{3-}]$ gives: $k_o = 1.5 \pm 0.7\ s^{-1}$ and $k_1 = 61 \pm 6\ s^{-1}\ M^{-1}$.

$[Ce(NTA)_2^{3-}]$ (*M*)	$[NTA_f]$[a] (*M*)	pH	$[NTA^{3-}]$[b] (*M*)	$1/\tau_C$ (s^{-1})
0.0995	0.199	8.61	0.020	2.6
0.0990	0.198	8.95	0.040	3.5
0.0985	0.197	9.18	0.059	5.6
0.0980	0.196	9.37	0.078	6.2
0.0975	0.195	9.55	0.098	7.7
0.0970	0.194	9.72	0.116	9.0
0.0965	0.193	9.92	0.135	9.2
0.0960	0.192	10.15	0.154	10.4
0.0955	0.191	10.56	0.174	11.7
0.0950	0.190	12.20	0.190	13.5

[a] Total concentration of the ligand in noncoordinated form. [b] Calculated from the relation: $[NTA^{3-}] = [NTA_f]/(K_1^H[H^+] + 1)$.

Therefore the line broadenings measured at these intermediate pH's have been assigned to exchange according to reaction (6) with rate constants k_o (Table VIII).

In acidic medium the rate constants k_3 and k_o were obtained by a linear least squares fit of the experimental data (Table IV) according to the simplified equation (13):

$$\text{pH} < 7: \qquad 1/\tau_C = k_o + k_3[H^+] \qquad (13)$$

For lanthanides heavier than neodymium, k_o is less than 0.3 s^{-1} which is too small to be determined by NMR and only an upper limit may be given.

In basic medium the rate constant k_1 is obtained from the simplified equation (14):

$$\text{pH} > 8: \qquad 1/\tau_C = k_o + k_1[NTA^{3-}] \qquad (14)$$

For the measurements in slightly basic medium (Table V) the total concentration of free ligand is approximately constant and the concentration of

TABLE VI. $1/\tau_C$ (s^{-1}) in Basic Medium at 20 °C.

	$[M(NTA)_2^{3-}]$ (*M*)	$[NTA^{3-}]$ (*M*)	pH	$1/\tau_C$ (s^{-1})	k_1[a] (s^{-1} M^{-1})
Cerium	0.095	0.190	11.02	13.4	62
			11.59	13.7	63
			11.90	13.8	64
			12.20	13.5	62
	0.185	0.139	11.78	11.1	68
			12.03	11.2	68
			12.36	11.4	69
			12.81	11.2	68
Praseodymium	0.135	0.222	12.18	9.0	37
	0.158	0.204	12.06	8.2	36
	0.180	0.183	12.16	7.4	36
	0.203	0.159	12.24	6.6	36
	0.225	0.135	11.84	5.9	38
Neodymium	0.136	0.224	11.96	4.4	17
	0.158	0.203	11.76	3.9	17
	0.181	0.182	11.78	3.5	16
	0.203	0.156	11.88	3.2	17
	0.224	0.137	12.08	3.2	19

[a] Calculated from the relation: $k_1 = (1/\tau_C - k_o)/[NTA_2^{3-}]$.

TABLE VII. Determination of k_1 as a Function of Temperature for Samarium and Europium.

$[Sm(NTA)_2^{3-}] = 0.150\,M$ and $[NTA_f] = 0.150\,M$				$[Eu(NTA)_2^{3-}] = 0.151\,M$ and $[NTA_f] = 0.151\,M$			
$1/\tau_C^o$[a] (s^{-1})	$1/\tau_C$[b] (s^{-1})	t (°)	k_1[c] (s^{-1} M^{-1})	$1/\tau_C^o$[a] (s^{-1})	$1/\tau_C$[b] (s^{-1})	t (°)	k_1[c] (s^{-1} M^{-1})
2.6	17.9	60	102	2.0	15.8	60	91
1.2	12.7	55	77	1.5	11.5	55	66
0.4	10.1	49	65	0.9	6.5	49	37
0.4	4.7	42	27	0.4	4.9	43	30
0.2	3.6	36	23	0.2	3.1	36	19

[a] Measured at pH 6.8. [b] Measured at pH 12.0. [c] Calculated from the relation: $k_1 = (1/\tau_C - k_o)/[NTA_2^{3-}]$.

NTA^{3-} varies as a function of the pH by deprotonation of $H(NTA)^{2-}$. At pH greater than 11.5, the free ligand is more than 99% in the form of NTA^{3-} and the concentration of free ligand is then varied (Table VI). For samarium and europium the broadening measured in basic medium at 20 °C is negligible; however, k_1 at this temperature was obtained by extrapolation of values measured between 36 °C and 60°C (Table VII) using an Arrhenius plot. Table VIII summarizes all the rate constants obtained.

Discussion

In the present NMR study the rate constants (Figure 3) for the formation of $M(NTA)_2^{3-}$ complexes according to (15) have been measured. For the formation of a metal chelate from a hydrated metal ion and

$$M(NTA) + NTA^{3-} \underset{k_o}{\overset{k_{-o}}{\rightleftharpoons}} M(NTA)_2^{3-} \qquad (15)$$

a multidentate ligand, Geier [16], on the basis of Eigen's work [17], proposed a multistep mechanism. Merbach and Gnaegi [5] have suggested a similar scheme for the formation of $M(NTA)_2^{3-}$ from M(NTA) and NTA^{3-}, where M is a diamagnetic rare earth ion. Firstly, NTA^{3-} and the M(NTA) complex diffuse together to form an outer-sphere complex. Secondly, in a concerted step, a water molecule dissociates from the metal chelate and a donor group of the tetradentate ligand coordinates with the metal ion at the vacated site. Thirdly, in

TABLE VIII. Rate Constants for the Ligand Exchange between $M(NTA)_2^{3-}$ and an Excess of NTA at 20 °C.

	k_o (s^{-1})	$k_{-o} \times 10^{-7}$ [b] (s^{-1} M^{-1})	$k_3 \times 10^{-4}$ (s^{-1} M^{-1})	$k_{-3} \times 10^{-3}$ [c] (s^{-1} M^{-1})	k_1 (s^{-1} M^{-1})
La	13 ± 1[a]	5.7	500 ± 100[a]	6.0	(6.7 ± 1.7) × 10^2 [a]
Ce	1.7 ± 0.5	3.2	83 ± 4	4.4	65 ± 5
Pr	0.8 ± 0.5	3.7	22 ± 2	2.8	37 ± 4
Nd	0.5 ± 0.3	3.6	14 ± 1	2.9	17 ± 4
Sm	<0.3	–	9 ± 0.7	3.1	6.5
Eu	–	–	5.9 ± 0.4	2.3	5.6
Tm	–	–	2.8 ± 0.3	2.3	–
Yb	–	–	2.1 ± 0.2	2.0	–
Lu	–	–	1.9 ± 0.2[a]	2.1	–
Y	–	–	11 ± 2[a]	3.2	–
Sc	–	–	0.8 ± 0.1[a]	–	–

[a] Measured by Merbach and Gnaegi [5] and adapted to our pH scale. [b] $k_{-o} = k_o \cdot K_{ML_2}$. [c] $k_{-3} = k_3 \cdot K_{ML_2}/K_1^H$.

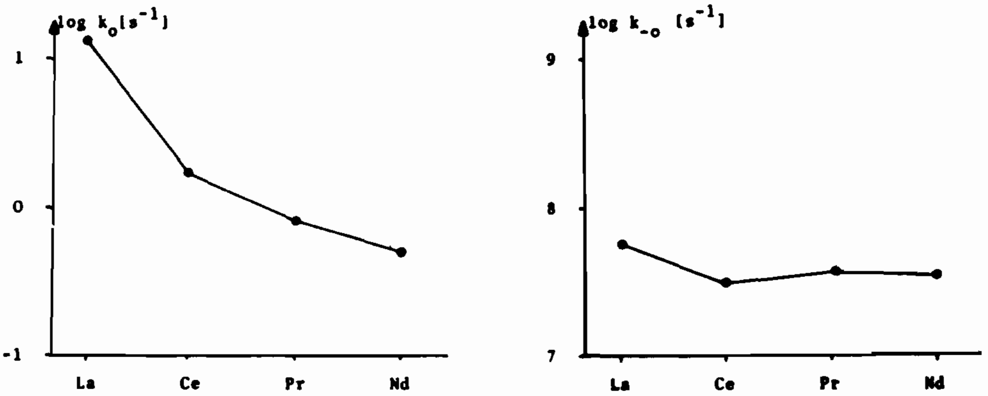


Figure 3. Rate constants for the spontaneous dissociation (k_o) and the formation (k_{-o}) of the bis(nitrilotriacetates) at 20 °C.

$$M(NTA)_2^{3-} \underset{k_{-o}}{\overset{k_o}{\rightleftarrows}} M(NTA) + NTA^{3-}$$

successive concerted steps water molecules are substituted by the remaining donor atoms of the NTA ligand. Depending on the case, the first or one of the next bond formations of the tetradentate ligand, determines the overall rate of complex formation. This multistep mechanism can be represented by the simplified scheme (16). K_{os} is often calculated either by the equations of Fuoss [18] or diffusion equations [19]; because of the high metal chelate concentration used in this study, such a calculation

$$M(NTA)_{aq} + NTA_{aq}^{3-} \underset{K_{os}}{\overset{fast}{\rightleftarrows}} \qquad (16)$$

$$[(NTA)M(H_2O)\cdots(NTA)]^{3-} \underset{k_o}{\overset{k'_{-o}}{\rightleftarrows}} M(NTA)_2^{3-}$$

makes no sense. However, K_{os} should not be too different from unity as shown earlier [5]. It is therefore of interest to compare the rate constants k_{-o} with the rates of departure of a water molecule during the formation of rare earth complexes from aquoions. The rates of formation of the bis(nitrilotriacetates) from the mono(nitrilotriacetates) and NTA^{3-} is nearly constant and of the same order of magnitude as the value of 8 × 10^7 to 9 × 10^7 s^{-1} found for the formation of murexide [20] and oxalate [21] complexes of the light rare earths. We conclude that the presence of a multidentate ligand in the first coordination sphere does not seem to change significantly the rate of loss of a water molecule in the first coordination sphere of a rare earth ion. The decrease in the rate constant k_o for the spontaneous dissociation of NTA^{3-} from $M(NTA)_2^{3-}$ reflects the increase in the stability constant K_{ML_2} along the rare earth series.

Another formation reaction to account for the global kinetic behaviour is the reaction (17). As already shown by Kula and Rabenstein [22] for the formation reaction of the cadmium and zinc bis(nitrilotriacetates), one observes a decrease in the rate

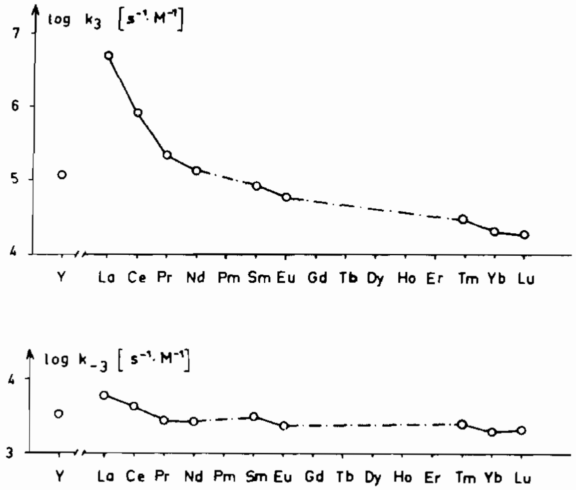


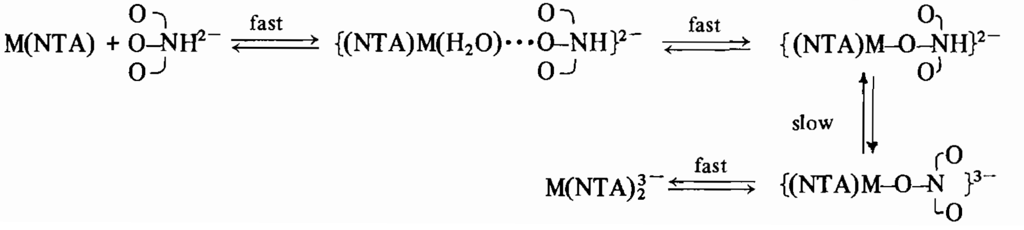
Figure 4. Rate constants for the acid catalysed dissociation (k_3) and the formation (k_{-3}) of the bis(nitrilotriacetates) at 20 °C.

$$M(NTA)_2^{3-} + H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} M(NTA) + H(NTA)^{2-}$$

of reaction of M(NTA) with the free ligand by protonation of the latter (Figure 4). The ratio k_{-0}/k_{-3}

$$M(NTA) + HNTA^{2-} \underset{k_3}{\overset{k_{-3}}{\rightleftharpoons}} M(NTA)_2^{3-} + H^+ \quad (17)$$

of the rate constants for the formation of $M(NTA)_2^{3-}$ from the unprotonated and protonated ligand is 0.7 X 10^4 to 1.3 X 10^4. To explain this decrease in reactivity, Cassat and Wilkins [23] have proposed a mechanism where the rate determining step is the departure of a water molecule from the metal inner coordination sphere with, as the reacting species, the nitrilotriacetate protonated on a carboxylate group; this species has a nitrogen atom with a lone pair to coordinate to the metal ion. The ratio of the concentrations of $HNTA^{2-}$ protonated on the nitrogen atom and on a carboxylate group can be obtained from the relative basicity of the nitrogen ($\log K_1^H$ of NTA^{3-} = 9.55) and of the acetate anion ($\log K_1^H$ of CH_3COO^- = 4.60) and by taking into account the different multiplicities of the two protonation sites.The calculated ratio of 3 X 10^4 is in agreement with Cassat and Wilkin's mechanism proposal. However, the slow rate of formation can also be explained if one admits that $HNTA^{2-}$ protonated on nitrogen is the reacting species using the reaction scheme (18). The first two steps are fast and result in the coordination of one carboxylate group.



(18)

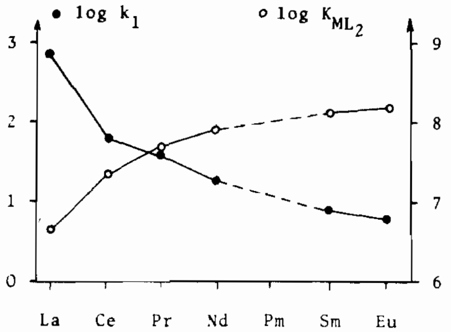


Figure 5. Rate constants (k_1) for the symmetric NTA^{3-} exchange on $M(NTA)_2^{3-}$ and stability constants (K_{ML_2}) of $M(NTA)_2^{3-}$ at 20 °C.

$$M(NTA)(^*NTA)^{3-} + NTA^{3-} \overset{k_1}{\rightleftharpoons} M(NTA)_2^{3-} + {}^*NTA^{3-}$$

The next steps are fast, consisting first in the loss of a second water molecule and formation of a metal–nitrogen bond to close a chelate ring, and then in the formation of a fully chelated bis(nitrilotriacetate) complex. The rate constant k_3 for the acid catalysed dissociation of NTA^{3-} from $M(NTA)_2^{3-}$ decreases strongly, reflecting, as previously for k_o, the increase in the stability of the bis(nitrilotriacetates) along the rare earth series.

The symmetric NTA^{3-} exchange on $M(NTA)_2^{3-}$, a bimolecular reaction characterized by the rate constant k_1, occurs with the formation of an intermediate of formula $M(NTA)_3^{6-}$ (see scheme 19). The high coordination numbers, eight to ten usually,

$$\begin{aligned} &M(NTA)_2^{3-} + {}^*NTA^{3-} \rightleftharpoons \\ &\qquad \{NTA\cdots M(NTA)\cdots {}^*NTA\}^{6-} \rightleftharpoons \\ &\qquad M(NTA)(^*NTA)^{3-} + NTA^{3-} \end{aligned} \quad (19)$$

of the lanthanide ions in their complexes facilitates the formation of intermediates where the cation is simultaneously coordinated to three nitrilotriacetates. The mechanism involves the progressive chelation of the entering ligand and simultaneous dechelation of the leaving one. In the intermediates, one nitrilotriacetate is fully chelated and the two others partially. The rate constant k_1 decreases while the stability constant K_{ML_2} increases along the series, which supposes that the rupture of a metal–ligand bond is the rate determining step.

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