investigation, were for the moment unsuccessful.

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Kinetics of the Exchange Reactions and the Formation Rate of the Lanthanide(III)-Ethylenediamine-Tetraacetate Complexes

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The kinetics of the substitution reactions of the metal ions in the lanthanide(III)-ethylenediamine-tetraacetate ($\text{Lnedta}^- = \text{LnY}$) complexes have been investigated in detail by isotopic-exchange [1–4] and spectrophotometric methods [5–7]. As a result, the main features of the mechanisms of the reactions are known. The exchange can take place by the proton catalyzed dissociation of complexes as well as by the direct attack of the exchanging metal on the complex. In the interval $3 < \text{pH} < 6$ the dissociative path predominates and it is assumed that the relatively slow dissociation of complexes is followed by a fast reaction of the free ligand with the exchanging metal. The intimate mechanisms of these processes are not known and the possible role of the water-exchange rate of the metal ions has hardly been investigated.

Recently studying the kinetics of the exchange reactions between the Ceedta and Ni^{2+} or Co^{2+} ions we have shown [7] that the reactions of the free ligand formed by dissociation, depend on the water-exchange rate of both the outcoming and incoming metal ions. As a result the dissociation of the complex must be regarded as reversible reaction as it is described in the following scheme:

$$\text{Ceedta}^- + \text{H}^+ \overset{K^{\text{H}}}{\rightleftharpoons} \text{CeHedta} \qquad (1)$$

$$\begin{array}{lcl} \text{CeHedta} & \underset{k_{\text{H}_i\text{Y}}^{\text{Ce}}}{\overset{k_{\text{CeHY}}}{\rightleftharpoons}} & \text{Ce}^{3+} + \text{Hedta}^{3-} \\ & & \qquad\quad \text{H}^+ \Big\downarrow\!\Big\uparrow \\ & & \qquad \text{H}_i\text{edta}^{(4-i)-} \end{array} \qquad (2)$$

$$\text{H}_i\text{edta}^{(4-i)-} + \text{M}^{2+} \xrightarrow{k_{\text{H}_i\text{Y}}^{\text{M}}} \text{Medta}^{2-} + i\text{H}^+ \qquad (3)$$

where the degree of protonation of the ligand, i, depends on the pH of the solution.

In the presence of Ce^{3+} and M^{2+} ion excess pseudo-first-order rate constants k_p can be obtained and from the dependence of the k_p values on the concentration of the H^+, Ce^{3+} and M^{2+} ions, the formation rate constants $k_{H_iY}^{M}$ of the Medta^{2-} complex can be calculated [7]. With the application of this principle the formation rate constants of some Lnedta complexes have been determined, since in spite of the interest of these complexes their rate of formation has not been investigated [6].

For the determination of the formation rate constants $k_{H_iY}^{Ln}$ the kinetics of the following exchange reaction was investigated:

$$\text{Ceedta}^- + \text{Ln}^{3+} \rightleftharpoons \text{Ce}^{3+} + \text{Lnedta}^- \qquad (4)$$

where Ln = Nd, Gd, Er and Y.

The formation rate constants can be determined only when the rate of formation of the Lnedta complexes can be slowed down with the increase of the concentration of the Ce^{3+} ions. This condition fulfills if $k_{Ce}^{-H_2O}[Ce^{3+}] > k_{Ln}^{-H_2O}[Ln^{3+}]/10$ ($k_{Ce}^{-H_2O}$ and $k_{Ln}^{-H_2O}$ are the characteristic water-exchange rate constants of the Ce^{3+} and the Ln^{3+} ions).

The exchange reactions (4) were followed by spectrophotometry at 280 nm (25 °C, I = 1 *M* KCl, cell length 4 cm). The concentration of the Ceedta was 4×10^{-4} *M*, while the pH as well as the concentration of the Ce^{3+} and Ln^{3+} ions were varied between 8×10^{-3} and 6×10^{-2} *M*. The concentration of the Ln^{3+} ions was always high enough ($[Ln^{3+}] > [Ce^{3+}]$) to make the exchange practically complete. With the application of these conditions the exchange reaction (4) can be treated as a first order one and its rate can be expressed as follows:

$$-\frac{d[\text{CeY}]_t}{dt} = k_p[\text{CeY}]_t \qquad (5)$$

Taking into consideration all the possible reaction paths of the exchange the pseudo-first-order rate constant can be expressed with the following equation:

$$k_p = \frac{k_{\text{CeY}}^{\text{Ln}} + k_{\text{CeHY}}^{\text{Ln}} K_{\text{CeY}}^{\text{H}}[\text{H}^+] +}{1 + K_{\text{CeY}}^{\text{H}}[\text{H}^+]}$$
$$+ \frac{\sum_i k_{\text{H}_i\text{Y}}^{\text{Ln}} \beta_i [\text{H}^+]^i \;/ K_{\text{CeY}}[\text{Ce}^{3+}]}{1 + K_{\text{CeY}}^{\text{H}}[\text{H}^+]} [\text{Ln}^{3+}] \qquad (6)$$

where k_{CeY}^{Ln} and k_{CeHY}^{Ln} are the rate constants of the reactions taking place by the direct attack of the Ln^{3+} ions on the Ceedta^- and CeHedta complexes. K_{CeY} is the stability constant, K_{CeY}^{H} is the protonation constant of the Ceedta^-. β_i is the i-th protonation constant of the edta^{4-} ligand.

The formation rate constants have been calculated using eqn. (6) to computer fit the k_p values obtained at various H^+, Ce^{3+} and Ln^{3+} concentrations. The results of the calculations indicated an appropriate fitting with the use of i = 1 and 2. The contribution

TABLE I. The formation rate constants of the Lnedta complexes and the k^{Ln}_{CeY} values.

k (M^{-1} s^{-1})	Nd	Gd	Er	Y
$10^8 \times k^{Ln}_{HY}$	2.7	3.0	1.8	0.9
$10^6 \times k^{Ln}_{H_2Y}$	1.1	1.1	0.54	0.18
k^{Ln}_{CeY}	0.35	0.28	0.22	0.14

of the reaction taking place by the direct attack of the Ln^{3+} ions on the protonated complex CeHedta has some importance only in the reaction with Y^{3+} ($k^{Y}_{CeHY} = 200\ M^{-1}\ s^{-1}$). The rate constants obtained are listed in Table I.

If the formation of complexes takes place by the Eigen-mechanisms, the second-order rate constants can be expressed as the product of the water-exchange rate constant of the metal ion and the outer sphere association constant K_{os} of the ions: $k^{Ln}_{HY} = k^{-H_2O}_{Ln} \times K_{os}$. The water-exchange rate constants of the Ln^{3+}·aq ions are quite uncertain but their order of magnitude is about 10^8 [6]. A more accurate value is known for the Gd^{3+}·aq, $k^{-H_2O}_{Gd} = 10{\cdot}6 \times 10^8\ s^{-1}$ [8]. Taking into account the value $k^{Gd}_{HY} = 3 \times 10^8\ M^{-1}\ s^{-1}$ (Table I) the association constant K_{os} can be calculated as $K_{os} = 0.28\ M^{-1}$. For 3+ and 3− ions the predicted K_{os} value is about 100, that is much higher [9]. This suggests that the formation rate constants obtained are too low to assume the rate determining role of the water-exchange from the first coordination sphere. It seems more probable that the rate controlling step in the reaction between the Ln^{3+} ion and the monoprotonated $Hedta^{3-}$ ligand is the ring closure because one of the iminodiacetate groups of the ligand is deprotonated. The $k^{Ln}_{H_2Y}$ values are about 2 orders of magnitude lower than the k^{Ln}_{HY} values which can be interpreted assuming a slower, rate controlling proton transfer step (or deprotonation) making possible the coordination of a deprotonated iminodiacetate group.

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About Some Mixed Molecular Complexes of the Dithiooxalate Anion with Lanthanides and Some Transition Elements

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The dithiooxalate anion, $S_2C_2O_2^{2-}$, has been previously shown to give low dimensional compounds, such as:

$$MM'(S_2C_2O_2)_2 \text{ with } \begin{array}{l} M = Ca, Ba, Zn, Mn(II) \\ M' = Ni(II), Pd(II), Pt(II), Cu(II) \end{array}$$

A particular interest has been afforded to the compound with M = Mn, M′ = Cu, because of its one-dimensional structure constituted of ordered extended chains, –Mn–L–Cu–L–Mn– ($L = S_2C_2O_2$); and moreover because of its very interesting magnetic properties.

The substitution of lanthanide elements (Ln(III)) to the metal M, led to a new family characterized by a structural entity:

$$Ln_2(Solvent)_{2n}M'_3(S_2C_2O_2)_6$$

i.e. a neutral centrosymmetric heteropentanuclear unit.

This family has been particularly studied for M′ = Ni, Solvent = H_2O, and Ln(III) = La, Ce, Nd, Sm, Eu, Gd, Y, Dy, Er, Yb. Within this series a modification of the lanthanide environment occurs between Dy and Er. The coordination polyhedron is a tricapped trigonal prism (CN = 9, n = 5) for the bulkiest lanthanides while it is only a bicapped trigonal prism (CN = 8, n = 4) for the other lanthanides. The loss of one water molecule in the coordination sphere of the lanthanide can be attributed to steric effects in relation with the decrease of the lanthanide radius. The CN modification induces a rearrangement of the ligand ($O_2C_2S_2$) around the lanthanide, and a change of structure. Bulkiest lanthanides, up to Dy, crystallize in the monoclinic system ($P2_1/c$) and their lattice looks like a channels structure with inserted water molecules within the channels; while the less bulky lanthanides crystallize in the triclinic system