Aminopolycarboxylates of Rare Earths.
16. Kinetics of Metal Ion-exchange Reactions between Cerium(III) *meso*- and *racemic*-2,3-Diaminobutane-*N*,*N*,*N*′,*N*′-tetraacetate Complexes and the Cobalt(II), Nickel(II), Copper(II) and Lead(II) Ions

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Abstract

A spectrophotometric method was used to study the kinetics of the metal ion-exchange reactions between the complexes *rac*-Cedbta and *meso*-Cedbta and Pb^{2+}, Cu^{2+}, Co^{2+} or Ni^{2+}. These exchange reactions proceed predominantly through proton-catalysed dissociation of the complexes. A minor role of the reaction involving direct attack by the exchanging metal ion is observed only for *meso*-Cedbta. In the reactions with Co^{2+} and Ni^{2+}, the proton-catalysed dissociations of *rac*-Cedbta and *meso*-Cedbta are to be considered as reversible processes; on the basis of the resulting rate equation, the rate constants may be calculated for the formation reactions of the Co^{2+} and Ni^{2+} complexes. The rate constants for the dissociation of the complexes vary in the sequence *rac*-Cedbta < *meso*-Cedbta < Ceedta. This sequence is explained in terms of the spatial requirements of the methyl groups in the ligands *rac*-dbta and *meso*-dbta, the lower flexibility of the coordinated ligand, and the lower mobility of the functional groups relative to those in edta.

Introduction

The equilibrium properties of the complexes formed between the lanthanide(III) ions (Ln^{3+}) and various aminopolycarboxylic acids have been investigated in great detail. These complexes are of considerable importance in the separation of the rare earths by ion-exchange chromatography and in their complexometric determination [1]. The aminopolycarboxylic acid most widely used for this purpose is ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (H_4edta), and its complexes have therefore been particularly studied from many aspects. Besides the stability constants and the bonding conditions, much work has been devoted to studies of the kinetic behaviour of the complexes Lnedta$^-$, which involve both metal ion-exchange [2–10] and ligand-exchange reactions [7, 11, 12]. These studies have revealed that the metal ion-exchange reactions may take place through both associative and dissociative pathways (through the direct attack of the exchanging metal ions on the complex or through the proton-catalysed dissociation of the complexes) [2–10].

Substantially less is known of the kinetic behaviour of the complexes formed with the various aminopolycarboxylic acid analogues of edta, though the effects of variations in the structure of the ligand, manifested in the modification of the kinetic properties of the complexes, may provide information of value towards a deeper understanding of the behaviour of the edta complexes.

If one of the hydrogen atoms on each of the carbon atoms of the ethylene group in H_4edta is replaced by a methyl group, two ligands can be obtained: *meso*-2,3-diaminobutane-*N*,*N*,*N*′,*N*′-tetraacetic acid (*meso*-H_4dbta) and *racemic*-2,3-diaminobutane-*N*,*N*,*N*′,*N*′-tetraacetic acid (*rac*-H_4dbta). The lanthanide(III) ions form complexes of high stability with both of these ligands, but the complexes of *rac*-dbta have essentially larger stability constants than those of *meso*-dbta [13, 14]. The sequence of stability constants for the complexes, including those of edta, is *rac*-dbta > edta > *meso*-dbta. The differences in stability of the complexes have been explained in terms of the spatial requirements of the two methyl groups [13, 14], which result in more strained chelate rings and longer Ln–N bond lengths, particularly for the complexes of *meso*-dbta.

The kinetic behaviour of the complexes of *meso*-dbta and *rac*-dbta has not been examined previously. With a view to obtaining data on the effects of the presence of the methyl groups on the rates of formation and dissociation of the complexes, in order to be able to compare the kinetic properties of the complexes of *meso*-dbta and *rac*-dbta (less flexible

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than edta) with those of the corresponding complexes of edta, we have therefore studied the kinetics of the metal ion-exchange reactions

$$CeY^{-} + M^{2+} \rightleftharpoons MY^{2-} + Ce^{3+} \qquad (1)$$

where Y^{4-} = *meso*-$dbta^{4-}$ or *rac*-$dbta^{4-}$, and M^{2+} = Co^{2+}, Ni^{2+}. Cu^{2+} or Pb^{2+}.

Experimental

The chemicals used in the experiments were of highest analytical purity. The solutions of $Co(ClO_4)_2$, $Ni(ClO_4)_2$ and $Pb(ClO_4)_2$ employed were prepared from the corresponding carbonates. $Cd(ClO_4)_3$ was a product of Aldrich. The concentrations of these perchlorate solutions were controlled by means of complexometric titration. *meso*-H_4dbta and *rac*-H_4dbta were prepared as described earlier [15]. Solutions of composition NaCeY were prepared from equivalent amounts of solutions of $Ce(ClO_4)_3$ and Na_2H_2Y by adjustment of the pH to approximately 6.

Experiments were performed at 25 °C at constant ionic strength (1 M $NaClO_4$). When reactions (1) took place, the pH remained practically unchanged and therefore no buffer was applied.

pH was measured with a Radiometer pHM-84 pH-meter, with glass and Calomel electrodes, the latter filled with saturated NaCl solution. The H^+ ion concentration was found from the measured pH by the method suggested by Irving *et al.* [16].

The metal ion-exchange reactions were followed in 40 mm quartz cells with a Beckman DB-GT spectrophotometer: at 285 nm for *meso*-Cedbta and Pb^{2+}, Ni^{2+} or Co^{2+}; at 326 nm for *meso*-Cedbta and Cu^{2+}; at 300 nm for *rac*-Cedbta and Pb^{2+}, Ni^{2+} or Co^{2+}; and at 323 nm for *rac*-Cedbta and Cu^{2+}.

The concentrations of the ionic species involved in the reaction were selected so that reaction (1) should go practically quantitatively, when it could be regarded as pseudo-first-order. The concentration of the exchanging metal ion was chosen to be at least 20 times higher than that of the complex CeY. In the reactions with Co^{2+} and Ni^{2+}, the Ce^{3+} had to be taken in excess too, in order to achieve the conditions of a pseudo-first-order reaction.

Under such conditions, the rate of exchange can be given by the following equation:

$$-\frac{d[CeY]}{dt} = k_p[CeY] \qquad (2)$$

where k_p is the pseudo-first-order rate constant, and [CeY] is the total concentration of the complex.

The pseudo-first-order rate constants k_p were determined with the method of non-linear least squares from pairs of data read off the absorbance *versus* time plots after equal time intervals, by means of computer fitting [8].

TABLE I. Pseudo-first-order Rate Constants of the Reaction between *meso*-Cedbta and Pb^{2+}

pH	k_p (s^{-1})	pH	k_p (s^{-1})
c_{Pb} =	0.008 M	c_{Pb} =	0.032 M
3.69	0.057	4.20	0.040
3.48	0.083	3.75	0.067
3.48	0.084	3.48	0.099
3.32	0.11	3.42	0.11
3.30	0.11	3.21	0.15
3.27	0.12	3.17	0.16
3.22	0.13	3.09	0.18
3.21	0.13	3.03	0.19
3.19	0.14		
3.05	0.17		
c_{Pb} =	0.016 M	c_{Pb} =	0.040 M
3.64	0.067	5.09	0.032
3.56	0.077	4.08	0.050
3.26	0.13	3.45	0.11
3.26	0.13	3.37	0.12
3.21	0.14	3.33	0.13
3.20	0.14	3.13	0.17
3.17	0.15	3.04	0.19
3.17	0.15	3.03	0.20
3.10	0.17	3.03	0.20
3.04	0.18	3.00	0.20
c_{Pb} =	0.024 M		
4.67	0.023		
4.00	0.043		
3.54	0.085		
3.17	0.15		
3.17	0.15		
3.16	0.15		
3.10	0.17		
3.05	0.18		
3.00	0.20		
2.98	0.20		

Results and Discussion

The rates of the metal ion-exchange reactions between *meso*-$Cedbta^-$ or *rac*-$Cedbta^-$ and Pb^{2+}, Cu^{2+}, Co^{2+} or Ni^{2+} were studied as a function of pH at various exchanging metal ion concentrations. In the studies on the reactions with Ni^{2+} and Co^{2+}, the Ce^{3+} concentration too was varied. The pseudo-first-order rate constants k_p determined at the different concentrations are listed in Table I–VIII.

The k_p data in these Tables reveal that, as found earlier in studies of the Lnedta complexes [2–10], the rates of the metal ion-exchange reactions increase as the H^+ concentration is raised. The k_p values increase slightly as the exchanging Cu^{2+} or Pb^{2+} concentration is elevated in the reactions with the

TABLE II. Pseudo-first-order Rate Constants of the Reaction between *rac*-Cedbta and Pb^{2+}

pH	k_p (s^{-1})	pH	k_p (s^{-1})
c_{Pb} =	0.040 M	c_{Pb} =	0.016 M
5.27	0.0069	5.58	0.0028
5.08	0.0071	3.33	0.037
5.06	0.0072	3.18	0.049
5.04	0.0072	2.98	0.067
5.02	0.0073	2.82	0.082
2.85	0.081	2.78	0.087
2.80	0.087	2.56	0.11
2.76	0.091		
2.59	0.11	c_{Pb} =	0.008 M
2.32	0.14	5.80	0.0014
		5.75	0.0014
c_{Pb} =	0.032 M	5.54	0.0015
5.38	0.0055	3.57	0.023
5.12	0.0058	3.28	0.040
5.12	0.0058	3.07	0.057
5.08	0.0059	2.87	0.076
2.84	0.082	2.65	0.10
2.50	0.12	2.58	0.11
2.48	0.12	2.44	0.12
c_{Pb} =	0.024 M		
5.58	0.0041		
5.47	0.0041		
2.82	0.084		
2.56	0.11		
2.52	0.11		
2.44	0.12		
2.40	0.13		
2.31	0.14		
2.28	0.14		

TABLE III. Pseudo-first-order Rate Constants of the Reaction between *meso*-Cedbta and Cu^{2+}

pH	k_p (s^{-1})	pH	k_p (s^{-1})
c_{Cu} =	0.04 M	c_{Cu} =	0.016 M
4.52	0.0045	4.78	0.0070
4.18	0.024	4.78	0.0071
3.99	0.033	4.41	0.013
3.99	0.038	3.66	0.057
3.90	0.068	3.36	0.10
3.59	0.069	3.17	0.14
3.54	0.075		
c_{Cu} =	0.032 M	c_{Cu} =	0.008 M
4.58	0.012	5.20	0.0031
4.40	0.016	4.96	0.0043
4.16	0.023	4.92	0.0046
4.14	0.024	4.42	0.012
3.98	0.032	4.06	0.024
3.55	0.072	3.98	0.028
3.33	0.11	3.85	0.038
3.18	0.14	3.54	0.070
		3.54	0.071
c_{Cu} =	0.024 M		
4.66	0.0097		
4.60	0.011		
4.39	0.015		
4.20	0.020		
4.13	0.023		
3.96	0.032		
3.51	0.077		
3.14	0.15		

meso-Cedbta complex, but the rate of exchange reaction of *rac*-Cedbta is practically independent of the concentration of the Pb^{2+} or Cu^{2+} ions.

In the exchanges with Co^{2+} and Ni^{2+}, the k_p data cannot be used to draw conclusions on the extent of exchange through the direct attack by the exchanging metal ions, since the exchanging metal ion and the Ce^{3+} are in competition, because of the Ce^{3+} excess applied. At the same time, it is known from previous investigations that, for the exchange with $Ceedta^-$, for example, Co^{2+} and Ni^{2+} are less active than Cu^{2+} [8]; we therefore assumed that exchange involving direct attack by Co^{2+} or Ni^{2+} makes a negligible contribution to the exchange reactions of *meso*-Cedbta and *rac*-Cedbta.

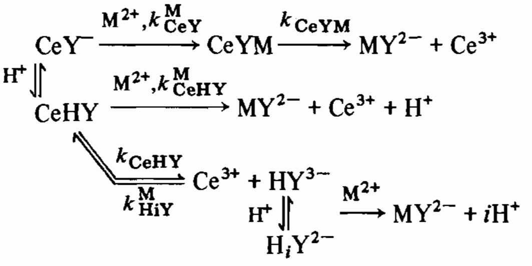
With regard to the appreciable pH-dependence of the rates of the examined metal ion-exchange reactions, on the basis of the earlier results [2–10] we assumed that the exchange occurs predominantly via proton-catalysed dissociation of the complexes. Exchange involving direct attack by the exchanging metal ion has a minor role only in the case of the reactions of *meso*-Cedbta with Pb^{2+} or Cu^{2+}.

The proton-catalysed dissociation of the complexes is followed by a very fast reaction between the free ligand and the Pb^{2+} or Cu^{2+}. In the exchange reactions involving Co^{2+} or Ni^{2+}, the free ligand formed by dissociation of the protonated complex CeHY may interact with the liberated Ce^{3+} ion to reform the CeY^- complex. This latter possibility is demonstrated by the finding that pseudo-first-order rate constants can be obtained only in the presence of a Ce^{3+} excess, for only in this case can the Ce^{3+} concentration be regarded as constant. The reforming of CeY^-, *i.e.* the competition between Ce^{3+} and Co^{2+} or Ni^{2+}, is also indicated by the fact that the rate of exchange decreases when the Ce^{3+} concentration is increased (Tables V–VIII). Such different behaviour of Co^{2+} and Ni^{2+} has been explained by their having substantially lower water-exchange rates than that of Ce^{3+} [8] ($k_{Co}^{H_2O} = 2.6 \times 10^6$ s^{-1}, $k_{Ni}^{H_2O} = 3.4 \times 10^4$ s^{-1}, $k_{Ce}^{H_2O} = 2.5 \times 10^8$ s^{-1}, $k_{Pb}^{H_2O} = 7.5 \times 10^9$ s^{-1}, and $k_{Cu}^{H_2O} = 2 \times 10^8$ s^{-1} [7]).

TABLE IV. Pseudo-first-order Rate Constants of the Reaction between *rac*-Cedbta and Cu^{2+}

pH	k_p (s^{-1})	pH	k_p (s^{-1})
c_{Cu} =	0.040 M	c_{Cu} =	0.024 M
4.84	0.0020	5.10	0.0011
4.80	0.0021	4.83	0.0018
4.55	0.0033	4.65	0.0025
4.45	0.0039	4.62	0.0026
3.61	0.021	4.58	0.0028
3.55	0.023	4.36	0.0044
3.25	0.042	4.06	0.0081
3.19	0.046	4.00	0.0092
3.16	0.049	3.87	0.012
3.12	0.052	3.80	0.014
3.07	0.057	3.64	0.020
3.01	0.062	3.38	0.033
2.98	0.065	3.30	0.038
2.90	0.073	3.18	0.046
2.88	0.075	3.10	0.054
2.79	0.084	2.97	0.066
		2.90	0.073
c_{Cu} =	0.032 M	c_{Cu} =	0.016 M
4.60	0.0029	5.31	0.00073
4.54	0.0032	5.30	0.00073
4.53	0.0032	5.12	0.00097
4.42	0.0040	5.09	0.0010
3.89	0.012	4.87	0.0015
3.81	0.014	3.51	0.025
3.30	0.038	3.33	0.036
3.28	0.039	3.07	0.056
3.10	0.054	3.05	0.058
3.08	0.056	2.96	0.067
2.99	0.063		
2.89	0.074	c_{Cu} =	0.008 M
2.78	0.085	5.55	0.00040
2.77	0.086	5.50	0.00043
2.70	0.094	5.48	0.00044
2.58	0.11	4.37	0.0040
		4.34	0.0043
		2.93	0.070
		2.48	0.12

These findings and the earlier results [8] led us to assume that the exchange reactions (1) may take place via the pathways given in the general reaction scheme (3):



(3)

where $i = 1, 2$ or 3 (in the pH range investigated, the ligands are predominantly present in the forms H_2Y^{2-} and H_3Y^{-}, and the protonation equilibria of the ligand presumably develop very quickly).

The exchange reactions of *rac*-Cedbta occur practically exclusively through the dissociation of the protonated complex CeHY formed in the equilibrium reaction. In the cases of the reactions with Co^{2+} and Ni^{2+}, the dissociation of the protonated complex must be regarded as reversible.

If all of the possible reaction pathways are taken into consideration on the basis of scheme (3), the rate equation for the metal ion-exchange reactions is as follows:

$$-\frac{d[CeY]}{dt} = k^{M}_{CeY}[CeY][M] + k^{M}_{CeHY}[CeHY][M] + k_{CeHY}[CeHY] - \sum_{1}^{3} k^{Ce}_{H_iY}[Ce][H_iY] \quad (4)$$

In the reactions with Pb^{2+} and Cu^{2+}, the CeY^{-} complex is not reformed; in these cases, therefore, the final term in rate equation (4) can be neglected. Accordingly, from eqns. (1) and (4), the equation $[CeY] = [CeY^{-}] + [CeHY] + [CeYM]$ expressing the total concentration of the complex, and the equations $K_{CeHY} = [CeHY]/[CeY][H^{+}]$ and $K_{CeYM} = [CeYM]/[CeY][M]$ defining the stability constants of the protonated and the binuclear complex, respectively, the connection may be written between the pseudo-first-order rate constant k_p and the rate constants relating to the exchange via the various reaction pathways:

$$k_p = \frac{k_1[M] + k_2[H^{+}] + k_3[M][H^{+}]}{1 + K_{CeHY}[H^{+}] + K_{CeYM}[M]} \quad (5)$$

where $k_1 = k^{M}_{CeY}$, $k_2 = k_{CeHY}K_{CeHY}$ and $k_3 = k^{M}_{CeHY} \cdot K_{CeHY}$.

The values of the constants k_1, k_2, k_3, K_{CeHY} and K_{CeYM} in the exchange of *meso*-Cedbta were established by fitting the k_p values obtained at the various H^{+} and Pb^{2+} or Cu^{2+} concentrations (Tables I and III) on the basis of eqn. (5) [8]. The standard error in the constants K_{CeYM} and k_3 calculated in this way was larger than the values of the constants. It may therefore be assumed that the exchange via the pathway with rate constant k^{M}_{CeHY} makes a negligible contribution and the stability constant of the binuclear complex is very low. The values found for k_1, k_2 and K_{CeHY} are presented in Table IX, together with the results obtained from studies of the similar exchange reactions of Ceedta [8].

In the case of the exchange reaction involving *rac*-Cedbta, the value of the terms containing the metal ion concentration [M] in eqn. (5) is zero, as the reaction rate is independent of the metal concentration. Thus, the values of constants k_2 were calculated from the least-squares fitting (Table IX).

Since we assume that the reaction involving the direct attack by the exchanging metal ion plays no

TABLE V. Pseudo-first-order Rate Constants of the Reaction between *meso*-Cedbta and Co^{2+}

c_{Ce} = 0.016 M				c_{Co} = 0.040 M	
pH	k_p (s^{-1})	pH	k_p (s^{-1})	pH	k_p (s^{-1})
c_{Co} =	0.040 M	c_{Co} =	0.024 M	c_{Ce} =	0.032 M
5.78	0.00052	5.43	0.00055	5.58	0.00045
5.77	0.00053	4.20	0.0080	5.04	0.0011
5.54	0.00078	3.82	0.019	3.67	0.022
5.26	0.0013	3.65	0.028	3.60	0.026
4.82	0.0033	3.35	0.055	3.34	0.047
4.01	0.021	3.16	0.084	3.32	0.049
3.65	0.046	3.10	0.096	3.31	0.050
3.41	0.079	3.03	0.11	3.29	0.052
3.38	0.086	2.97	0.13	3.13	0.75
3.31	0.10				
3.26	0.11	c_{Co} =	0.016 M	c_{Ce} =	0.024 M
3.25	0.11	5.40	0.00040	5.60	0.00053
3.14	0.15	3.96	0.0092	3.63	0.033
3.13	0.15	3.90	0.011	3.34	0.062
3.13	0.15	3.00	0.080	3.32	0.065
3.11	0.15	2.87	0.11	3.24	0.079
		2.82	0.12	3.11	0.10
c_{Co} =	0.032 M	2.75	0.14	3.09	0.11
5.88	0.00036	2.55	0.21		
5.87	0,00037			c_{Ce} =	0.008 M
4.28	0.0089			5.99	0.00060
4.23	0.0099			5.29	0.0023
3.39	0.066			4.14	0.030
3.33	0.075			3.87	0.055
				3.86	0.057
				3.63	0.095

role in the cases of Co^{2+} and Ni^{2+} either, eqn. (4) can be written in the following form:

$$-\frac{d[CeY]}{dt} = k_{CeHY}[CeHY] - \sum_{1}^{3} k^{Ce}_{H_iY}[Ce][H_iY] \qquad (6)$$

In the studies of the exchange reactions, the concentrations of Ce^{3+} and Co^{2+} or Ni^{2+} were much higher than that of the complex *rac*-Cedbta or *meso*-Cedbta. Hence, the concentration of the free ligand $H_iY^{-(4-i)}$ is always extremely low and can be regarded as constant. Thus, the principle of steady state may be applied to the exchange reactions; by introducing $d[H_iY]/dt \approx 0$ and rearranging eqn. (6), we obtain

$$-\frac{d[CeY]}{dt} = \sum_{1}^{3} k^{M}_{H_iY}[M][H_iY] \qquad (7)$$

From eqns. (1) and (7), and the equation $[CeY] = [CeY^-] + [CeHY]$ expressing the total concentration of the complex, the pseudo-first-order rate constant may be given as follows:

$$k_p = \frac{[M]\sum_{1}^{3} k^{M}_{H_iY}\beta_i[H^+]^i}{K_{CeY}[Ce^{3+}](1 + K_{CeHY}[H^+])} \qquad (8)$$

where K_{CeY} is the stability constant of the complex *rac*-$Cedbta^-$ or *meso*-$Cedbta^-$, and β_i is the protonation constant of the ligand ($\beta_i = [H_iY]/[Y^{4-}][H^+]^i$).

The rate constants in eqn. (8) were determined by fitting the pseudo-first-order rate constants k_p obtained at the various H^+, Ce^{3+} and Co^{2+} or Ni^{2+} concentrations on the basis of eqn. (8). The standard error in the constant $k^{M}_{H_3Y}$ exceeded the values of the constants, and neglect of the terms containing these constants did not influence the good fit. It is probable, therefore, that the Co^{2+} and Ni^{2+} complexes are formed via participation of the species HY^{3-} and H_2Y^{2-}. The values obtained for the rate constants of formation of the complexes through the solution of eqn. (8) are given in Table X, together with the formation rate constants found during studies of the similar metal ion-exchange reactions of Ceedta [8].

TABLE VI. Pseudo-first-order Rate Constants of the Reaction between *rac*-Cedbta and Co^{2+}

c_{Ce} = 0.016 M				c_{Co} = 0.040 M	
pH	k_p (s^{-1})	pH	k_p (s^{-1})	pH	k_p (s^{-1})
c_{Co} =	0.040 M	c_{Co} =	0.024 M	c_{Ce} =	0.032 M
5.81	0.000074	5.40	0.00010	5.43	0.000088
5.36	0.00019	5.16	0.00018	4.55	0.00059
4.35	0.0019	5.13	0.00019	3.85	0.0030
4.33	0.0020	2.77	0.055	3.53	0.0066
3.77	0.0074	2.57	0.094	3.50	0.0072
3.75	0.0077	2.53	0.10	3.25	0.013
3.51	0.014	2.31	0.18	3.18	0.016
3.40	0.018			3.07	0.021
3.16	0.033	c_{Co} =	0.016 M	2.99	0.026
3.14	0.035	5.11	0.00013		
3.07	0.042	4.11	0.0013	c_{Ce} =	0.024 M
3.00	0.057	3.77	0.0029	3.88	0.0038
2.90	0.066	3.67	0.0037	3.80	0.0045
2.68	0.12	3.66	0.0038	3.67	0.0059
2.51	0.18	3.56	0.0049	3.68	0.0061
		2.65	0.050	3.52	0.0090
c_{Co} =	0.032 M	2.53	0.067	3.46	0.010
5.24	0.00020	2.40	0.096	3.19	0.021
4.75	0.00060	2.33	0.11	3.16	0.022
4.67	0.00071			3.16	0.023
3.31	0.018	c_{Co} =	0.008 M		
3.25	0.022	3.07	0.0082		
2.80	0.069	2.94	0.012		
2.79	0.071	2.89	0.013		
2.37	0.21	2.76	0.019		
		2.24	0.071		
		2.04	0.12		

From a comparison of the rate constants in Tables IX and X, it may be stated in general that the presence of the methyl groups and their steric position in the *meso*-dbta and *rac*-dbta ligands exert considerable effects on the rates of the metal ion-exchange reactions of the complexes. We shall attempt to explain their kinetic behaviour by means of a comparison with those of the complexes of edta. Attention must be paid to the higher basicities of their nitrogen atoms, and also to the modifications of the structures, which can be expected to alter their kinetic properties in different ways. Thus, the higher basicity of the nitrogen atoms would result in higher stability constants, but the modification in the structure, e.g. the strain in the chelate rings in the complexes of *meso*-dbta [14], leads to a change in the opposite direction. The sequence of the stability constants of the edta and *meso*-dbta complexes may be a result of such opposite effects. The edta ligand forms more stable complexes with the large Ln^{3+} ions than those of *meso*-dbta, but for the transition metal ions, where a larger role is played by the more covalent bonding with the N atom, the *meso*-dbta complexes are the more stable [21].

From a comparison of the rates of exchange proceeding through the proton-catalysed dissociation of the complexes (Table IX), it can be seen that the k_2 values decrease in the sequence edta > *meso*-dbta > *rac*-dbta. This sequence is surprising if we compare it with the sequence *rac*-dbta > edta > *meso*-dbta for the stability constants of the Ce^{3+} complexes, since the thermodynamic and kinetic stabilities vary in parallel for the various Ln(III)–aminopolycarboxylate complexes examined so far [2–10, 22]. The reason for the different behaviour of *meso*-Cedbta, *i.e.* the fact that its dissociation is slower than expected, is presumably the presence of the two methyl groups. As a consequence of the unfavourable steric situation of the methyl groups and the repulsion between them, the stability-enhancing effect of the chelate rings in the complex is smaller [14]; at the same time, the coordinated ligand is less flexible and the functional groups are less mobile, and therefore the frequency of rupture of the bonds and hence the probability of dissociation of the complex are lower.

Our ^1H NMR spectroscopic studies indicate that the rate-determining step in the proton-catalysed

TABLE VII. Pseudo-first-order Rate Constants of the Reaction between *meso*-Cedbta and Ni^{2+}

c_{Ce} = 0.016 M				c_{Ni} = 0.040 M	
pH	k_p (s^{-1})	pH	k_p (s^{-1})	pH	k_p (s^{-1})
c_{Ni} =	0.008 M	c_{Ni} =	0.032 M	c_{Ce} =	0.008 M
3.52	0.0018	4.13	0.0018	5.76	0.00018
3.32	0.0029	3.26	0.014	3.05	0.054
3.28	0.0031	3.06	0.021	3.03	0.057
3.07	0.0052	3.04	0.022	2.98	0.064
2.60	0.015	2.79	0.041	2.94	0.071
2.25	0.035	2.68	0.052	2.84	0.089
2.02	0.060	2.41	0.097	2.58	0.16
1.99	0.064	2.38	0.105	2.47	0.21
		2.32	0.12		
c_{Ni} =	0.016 M			c_{Ce} =	0.024 M
3.61	0.0029	c_{Ni} =	0.04 M	5.35	0.00017
3.47	0.0041	5.82	0.00012	4.20	0.0014
3.10	0.0098	5.58	0.00015	3.90	0.0026
2.83	0.019	5.22	0.00026	3.51	0.0064
2.80	0.020	3.62	0.0074	3.27	0.011
2.71	0.024	3.55	0.0087	3.20	0.013
2.67	0.027	3.47	0.010	3.15	0.015
2.59	0.032	3.42	0.012		
2.45	0.045	3.29	0.016	c_{Ce} =	0.032 M
2.37	0.053	3.28	0.016	4.66	0.00041
2.34	0.057	3.21	0.019	3.49	0.0051
2.31	0.061	3.07	0.026	3.33	0.0073
2.10	0.1	2.99	0.031	3.16	0.011
		2.91	0.038	3.10	0.012
c_{Ni} =	0.0024 M	2.75	0.055	2.90	0.02
3.73	0.0034	2.71	0.061	2.85	0.022
3.60	0.0046	2.63	0.073	2.76	0.026
3.48	0.0061	2.47	0.11	2.30	0.08
3.42	0.0069	2.33	0.15		
3.24	0.011	2.28	0.17		
3.14	0.013	2.22	0.19		
3.12	0.014	2.20	0.20		
2.90	0.024				
2.76	0.033				
2.64	0.042				
2.46	0.065				
2.44	0.069				

dissociation of the $Ceedta^-$ complex is the formation of an intermediate in which one of the iminodiacetate (imda) groups of the edta is coordinated to the Ce^{3+}, while the other, protonated imda group is free [23]. The protonation constants of the complexes *rac*-Cedbta and *meso*-Cedbta are higher than that of $Ceedta^-$ (Table IX), but it is probable that, due to the steric requirement of the methyl groups, the protonated half-unwrapped intermediates can be formed with more difficulty and with lower probability in the cases of *meso*-Cedbta and *rac*-Cedbta; accordingly, the rates of their proton-assisted dissociation will also be lower than that of $Ceedta^-$.

The rate constants characterizing the efficiency of the exchange reactions taking place by the direct attack of the metal ions of the complex decrease in the sequence Cedta > *meso*-Cedbta > *rac*-Cedbta (for *rac*-Cedbta the contribution of this reaction pathway can practically be neglected). The observed sequence of the rate constants can be interpreted by the mechanisms assumed for the exchange of Ceedta [8]. The attacking metal ion forms a binuclear complex of low stability, $CeYM^+$, by binding to one of the carboxylate groups of the complex. The stability of the binuclear complexes formed with the more flexible ligand edta is relatively higher, but it is extremely low for the 'rigid' complex *rac*-Cedbta. In the *meso*-Cedbta complex the ligand is also not flexible, but due to the steric hindrance as a result of the unfavourable position of the methyl groups,

TABLE VIII. Pseudo-first-order Rate Constants of the Reaction between *rac*-Cedbta and Ni^{2+}

c_{Ni} = 0.040 M				c_{Ce} = 0.016 M	
pH	k_p (s^{-1})	pH	k_p (s^{-1})	pH	k_p (s^{-1})
c_{Ce} =	0.008 M	c_{Ce} =	0.024 M	c_{Ni} =	0.032 M
5.28	0.000070	2.83	0.0045	3.45	0.0016
3.20	0.0067	2.67	0.0059	3.18	0.0028
3.12	0.0077	2.62	0.0065	2.79	0.0057
2.82	0.14	2.52	0.0076	2.72	0.0064
2.51	0.023	2.34	0.0095	2.54	0.0087
2.50	0.023	2.28	0.011	2.33	0.013
2.49	0.024	2.25	0.012	2.16	0.017
2.39	0.028	2.11	0.015	2.16	0.017
2.26	0.035				
		c_{Ce} =	0.032 M	c_{Ni} =	0.024 M
c_{Ce} =	0.016 M	2.76	0.0038	2.88	0.0037
3.53	0.0017	2.40	0.0070	2.74	0.0047
2.92	0.0057	2.31	0.0081	2.58	0.0062
2.91	0.0058	2.22	0.0094	2.41	0.0082
2.75	0.0077	2.13	0.011	2.37	0.0087
2.69	0.0086	2.11	0.011	2.32	0.0095
2.63	0.0095	2.10	0.012	2.28	0.010
2.54	0.011	2.10	0.013	2.27	0.010
2.53	0.011			2.23	0.011
2.52	0.011				
2.41	0.014			c_{Ni} =	0.016 M
2.39	0.014			2.94	0.0022
2.17	0.021			2.33	0.0062
2.12	0.022			2.24	0.0072
2.07	0.024			2.11	0.0091
				2.10	0.0092
				2.09	0.0094
				2.03	0.010
				c_{Ni} =	0.008 M
				2.01	0.0053
				2.00	0.0054

TABLE IX. Rate Constants of the Exchange Reactions between *meso*-Cedbta, *rac*-Cedbta, Ceedta and Pb^{2+} as well as Cu^{2+} Ions

Complex	Pb^{2+}			Cu^{2+}		
	k_1 ($M^{-1} s^{-1}$)	k_2 ($M^{-1} s^{-1}$)	K_{CeHY}	k_1 ($M^{-1} s^{-1}$)	k_2 ($M^{-1} s^{-1}$)	K_{CeHY}
meso-Cedbta	0.77 ± 0.06	271 ± 8	480 ± 45	0.16 ± 0.02	275 ± 10	500 ± 30
rac-Cedbta		96 ± 6	498 ± 40		93 ± 5	482 ± 20
Ceedta	3.7	2900 [8]		0.37	1400 [17]	

TABLE X. Formation Rate Constants of the *rac*-Nidbta, *meso*-Nidbta, *rac*-Codbta and *meso*-Codbta Complexes

Ligand	Ni^{2+}		Co^{2+}	
	k^{M}_{HY} ($M^{-1} s^{-1}$)	$k^{M}_{H_2Y}$ ($M^{-1} s^{-1}$)	k^{M}_{HY} ($M^{-1} s^{-1}$)	$k^{M}_{H_2Y}$ ($M^{-1} s^{-1}$)
rac-dbta	(4.8 ± 0.5) × 10^5	(2.7 ± 0.5) × 10^2	(3.3 ± 0.3) × 10^6	(1.5 ± 0.2) × 10^3
meso-dbta	(1.7 ± 0.2) × 10^6	(4.2 ± 0.8) × 10^2	(1.2 ± 0.2) × 10^7	(1.4 ± 0.2) × 10^4
edta [8]	9 × 10^5	1.1 × 10^3	4.8 × 10^7	1.6 × 10^4
	1.9 × 10^5	3 × 10^3 [19]	1 × 10^7 [18]	
	1 × 10^6 [20]			

the interaction between the donor atoms and the Ce^{3+} ion is weaker, and the formation of binuclear complexes of low stability is possible. This binuclear complex can slowly be transformed to an intermediate in which one of the imda groups of the ligand is coordinated to the Ce^{3+} and the other to the attacking metal. This symmetrical intermediate leads relatively quickly to the formation of the *meso*-Pbdbta or *meso*-Cudbta complex, the rate-determining step of the exchange being some step giving rise to the formation of this intermediate.

The rates of complex formation with Co^{2+} and Ni^{2+} generally decrease in the sequence edta > *rac*-dbta > *meso*-dbta (Table X), though the rates of the reactions with edta and with *rac*-dbta do not differ substantially. This sequence demonstrates that the reactions take place most rapidly with the most flexible ligand, edta, while the complexes of *meso*-dbta are formed most slowly; in the latter, the steric hindrance between the methyl groups means that the highly strained chelate rings are probably formed more slowly. Hence, in the complex formation involving the ligands HY^{3-}, parts are played in the development of the reaction rate by the rate of water exchange by the metal ions, and by the rate of formation of the chelate rings.

For the formation of the Co^{2+} and Ni^{2+} complexes, the rate constants $k^{M}_{H_2Y}$ are considerably lower, which indicates that, besides the rates of water exchange by the metal ions, a more important role in the development of the rates of the reactions with the doubly protonated ligand may be played by some deprotonation or proton-migration reaction, in the course of which the reacting intermediate is produced.

To summarize the results, it may be stated that the rates of formation and dissociation of the complexes *rac*-Cedbta and *meso*-Cedbta are lower than those of Ceedta. The deciding role in the observed behaviour of the *rac*-dbta and *meso*-dbta complexes may be played by the spatial requirements of the methyl groups; this has the result that, in spite of the strain in the chelate rings, the functional groups (acetate and imda) in their complexes are less mobile than in the corresponding edta complexes. Accordingly, through the introduction of appropriate substituents, the polyfunctional aminopolycarboxylates can be transformed to ligands that are less flexible and hence form complexes that are more inert.

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