Inorganica Chimica Acta, *127* (1987) 113–119

Aminopolycarboxylates of Rare Earths.
15. Kinetic Study of Metal Ion Exchange Reactions Between Cerium(III)–1,2-Diaminopropane-*N*,*N*,*N*′,*N*′-tetraacetate Complexes and Cobalt(II), Nickel(II), Lead(II) and Copper(II) Ions

G. LAURENCZY and E. BRÜCHER*

Department of Inorganic and Analytical Chemistry, Kossuth Lajos University, Debrecen, H-4010, Hungary

(Received May 26, 1986)

Abstract

The rate of the exchange reactions occurring between the $Cedpta^-$ complex and Pb^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+} ions generally increases with an increase in the concentration of the H^+ and metal ions. The interpretation of the results was based on the assumption that the exchange reaction can take place either by the slow, proton-assisted dissociation of $Cedpta^-$, followed by the fast reaction between the exchanging metal ion and the free ligand, or by direct attack by the metal ion on the $Cedpta^-$ complex and the protonated CeHdpta complex. The reaction between the $Cedpta^-$ and Pb^{2+} ions predominantly occurs through the fast formation of a dinuclear intermediate $[CedptaPb]^+$, in which a carboxylate group is coordinated to the Pb^{2+}, and the other functional groups of the ligand are progressively transferred from the Ce^{3+} to the Pb^{2+} ion. The values of the rate constants characteristic for the direct attack by Pb^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+} are linearly proportional to the water exchange rate of these ions, indicating an exchange mechanism similar to that assumed for the exchange reactions of $Ceedta^-$.

In the reactions with Co^{2+} and Ni^{2+} ions, the free ligand formed by the proton-assisted dissociation of $Cedpta^-$ can react with the Ce^{3+} ions to form $Cedpta^-$ again, due to the lower water exchange rate of Ni^{2+} and Co^{2+}. In these cases the rate constants of the formation reactions of $Nidpta^{2-}$ and $Codpta^{2-}$ can be calculated from the rate equation obtained for the exchange reactions.

Introduction

The stability constants of the ethylenediaminetetraacetate ($edta^{4-}$) complexes of the transition metal(II) ions (M^{2+}) and the lanthanide(III) ions (Ln^{3+}) are well known [1]. Detailed studies have been made of their kinetic behaviour, and particularly of the rates of their metal ion exchange reactions [2]. Nevertheless, information available on the mechanisms of these exchange reactions is still rather limited. One way of acquiring additional information is to study the behaviour of complexes involving aminopolycarboxylic acids analogous to H_4edta, and to attempt to correlate any differences observed in the behaviour of the corresponding edta complexes with differences between the structures of the ligands.

The two nitrogen atoms in edta differ in basicity: the values of the protonation constants are $\log K_1^H = 10.26$ and $\log K_2^H = 6.16$ [1]. The difference between the two constants can be increased if one of the ethylene hydrogen atoms is replaced by a methyl group. In the resulting compound, 1,2-diaminopropane-*N*,*N*,*N*′,*N*′-tetraacetic acid (H_4dpta), the protonation constants of the two nitrogen atoms are $\log K_1^H = 10.86$ and $\log K_2^H = 6.25$ [3]. Because of the greater basicity, the stability constants of the $Lndpta^-$ complexes are higher than those of $Lnedta^-$ [3]. Due to the presence of the methyl group, the dpta ligand is asymmetrical in structure relative to edta; this will presumably influence the structures of its complexes and hence their kinetic behaviour.

The kinetic behaviour of the $Lndpta^-$ complexes has not yet been studied, but during the determination of their stability constants by a method involving competition it was found that the metal ion exchange reactions proceed slowly at $pH > 4$ [4]. On this basis we have carried out a spectrophotometric study of the kinetics of the following metal ion exchange reactions:

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

where $M^{2+} = Co^{2+}$, Cu^{2+}, Ni^{2+} or Pb^{2+}. In this way, information may be obtained on the effects of the nature of the exchanging metal ion on the kinetics of the reaction.

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*Author to whom correspondence should be addressed.

0020-1693/87/$3.50

Experimental

Compounds of the highest analytical purity were used. The NaCedpta solution was prepared by mixing equivalent quantities of $Ce(ClO_4)_3$ (Alfa Chem. Co.) and H_4dpta (Aldrich) solutions and neutralizing the resulting solution. The concentrations of the solutions were measured complexometrically. $Co(ClO_4)_2$, $Cu(ClO_4)_2$, $Ni(ClO_4)_2$ and $Pb(ClO_4)_2$ solutions were prepared by dissolving the corresponding carbonates in $HClO_4$.

Experiments were performed at 25 °C, at constant ionic strength (1.0 M $NaClO_4$). No buffer was used, as the pH of the solutions remained practically constant throughout the reaction. pH was measured with a Radiometer pHM 84 pH-meter, with glass and NaCl-saturated Calomel electrodes. H^+ ion concentrations were calculated from the measured pH values by the procedure given by Irving *et al.* [5].

The protonation constant of the $Cedpta^-$ complex ($K_{HCeY} = [HCeY]/[CeY][H^+]$) was determined by means of a pH-potentiometric titration under similar conditions: $K_{HCeY} = 35 \pm 6$.

The reactions were followed with a Beckman DB-GT spectrophotometer using 4 cm cells at 281 nm for Co^{2+}, Ni^{2+} and Pb^{2+}, and at 324 nm for Cu^{2+}.

The concentration of the exchanging metal ion was always at least 20 times the concentration of $Cedpta^-$. Thus, exchange reaction (1) proceeded practically to completion and could be regarded as a pseudo-first-order reaction. Under such conditions, the rate of exchange can be described by the following relation:

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

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

The absorbance of the solutions can be given by the following equation:

$$A_t = A_p + (A_r - A_p)e^{-k_p t} \qquad (3)$$

where A_p is the absorbance of the products, A_r is the absorbance of the reactants, and A_t is the absorbance after time t.

The pseudo-first-order rate constants k_p were determined by computer fitting. Pairs of data were read off the absorbance *vs.* time curves at equal time intervals, and three-parameter fitting (k_p, A_p and $(A_r - A_p)$) was carried out by the method of non-linear least squares; the square sum of the differences in the measured and calculated absorbance values was minimized.

Results and Discussion

Studies of the kinetics of metal ion exchange reactions of Ln(III)–aminopolycarboxylate complexes have revealed that the reactions are of first order with respect to the complexes taking part in the exchange [6–12]. Accordingly, the rates of reactions (1) were studied as a function of pH at constant $Cedpta^-$ concentration and at various exchanging metal ion concentrations. Similarly, as observed in the reactions with $Ceedta^-$ [11], the exchanges involving Co^{2+} and Ni^{2+} can be treated as pseudo-first-order reactions only if the Ce^{3+} ions in the solution are also in excess compared to the $Cedpta^-$ complex.

The rate constants k_p found are listed in Tables I–IV. The tabulated data show that the rates of the metal ion exchange reactions increase as the concentration of H^+ is increased, just as was demonstrated in earlier investigations with other aminopolycarboxylates [6–12]. At $pH > 4.5$, the k_p values also increase slightly with an increase in the concentration of Pb^{2+} or Cu^{2+}. At $pH < 4$, however, a rise in the Pb^{2+} concentration leads to a definite decrease in the rate of the exchange reaction, as was observed in the reaction between $Ceedta^-$ and Pb^{2+} [11].

From the effects of variations in the concentrations of H^+ and the exchanging metal ions on the rates of the reactions, conclusions could be drawn as to their roles in the exchange reactions [11]. Thus, we assume that the exchange proceeds via the proton-catalysed dissociation of the $Cedpta^-$ complex followed by the fast reaction between the liberated ligand $H_i dpta^{i-4}$ and the exchanging metal ion M^{2+}. As to the reactions with Ni^{2+} and Co^{2+}, their relatively low water exchange rates ($k_{Co}^{-H_2O} = 2.6 \times 10^6$ s^{-1} and $k_{Ni}^{-H_2O} = 3.4 \times 10^4$ s^{-1} [2]) mean that there is a possibility for $Cedpta^-$ to be reformed because of the much higher water exchange rate of Ce^{3+} ($k_{Ce}^{-H_2O} = 2.5 \times 10^8$ s^{-1} [2]). This means that Ce^{3+} must be in excess in the experiments, in order to ensure a constant Ce^{3+} concentration. The water exchange rate of Pb^{2+} is higher ($k_{Pb}^{-H_2O} = 7.5 \times 10^9$ s^{-1}), while that of Cu^{2+} is approximately the same as that of Ce^{3+} ($k_{Cu}^{-H_2O} = 2 \times 10^8$ s^{-1} [2]); in the presence of an excess of Pb^{2+} or Cu^{2+}, therefore, reaction (1) proceeds practically completely in the direction of the upper arrow.

Besides the proton-catalysed dissociation of $Cedpta^-$, the exchange may take place through a direct reaction between the complex and the exchanging metal ion, when the formation of an intermediate binuclear species $CedptaM^+$ must be assumed. In the reactions between $Cedpta^-$ and Pb^{2+}, formation of the $CedptaPb^+$ intermediate is definitely indicated by the finding that at higher H^+ concentration ($pH < 4$) an increase in the Pb^{2+} concentration is accompanied by a reduction in the rate of the exchange (Table I). This is presumably a consequence of

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

pH	k_p (s^{-1})	pH	k_p (s^{-1})	pH	k_p (s^{-1})
c_{Pb} = 0.065 M		c_{Pb} = 0.032 M		c_{Pb} = 0.016 M	
4.88	0.019	5.41	0.012	5.83	0.0073
4.81	0.019	5.39	0.012	5.77	0.0074
4.77	0.019	5.34	0.012	5.73	0.0075
3.87	0.043	5.36	0.012	5.67	0.0076
3.67	0.058	5.26	0.013	5.52	0.0079
3.46	0.082	5.23	0.013	5.51	0.0079
3.09	0.160	5.18	0.013	5.45	0.0081
		5.17	0.013	5.00	0.010
		5.12	0.013	4.93	0.011
c_{Pb} = 0.052 M		3.37	0.120	4.21	0.029
		3.25	0.150	3.47	0.120
4.93	0.017	3.15	0.180	3.30	0.160
4.85	0.018			3.28	0.170
4.75	0.018			3.12	0.220
4.33	0.025	c_{Pb} = 0.026 M			
3.36	0.110				
		5.36	0.011	c_{Pb} = 0.013 M	
		5.19	0.012		
c_{Pb} = 0.040 M		5.18	0.012	5.35	0.0075
		5.11	0.012	4.83	0.0110
5.34	0.014	4.09	0.034	4.05	0.0390
5.31	0.014			3.57	0.0980
5.30	0.014				
5.24	0.014	c_{Pb} = 0.024 M			
5.19	0.014			c_{Pb} = 0.008 M	
5.14	0.014	5.59	0.0099		
5.11	0.014	5.57	0.0099	6.12	0.0042
5.05	0.015	5.51	0.010	6.11	0.0042
5.04	0.015	5.51	0.010	6.03	0.0043
4.92	0.016	5.48	0.010	5.91	0.0044
3.62	0.072	5.28	0.011	5.86	0.0044
3.46	0.095	5.11	0.012	5.84	0.0045
		4.83	0.014	5.77	0.0046
		3.07	0.220	5.62	0.0049
c_{Pb} = 0.039 M				3.51	0.1200
				3.44	0.1300
5.07	0.015			3.39	0.1500
4.99	0.015			3.20	0.2100
4.90	0.016				
3.76	0.056				
3.30	0.130				
3.30	0.130				
3.26	0.140				
3.18	0.160				

TABLE II. Pseudo-first-order Rate Constants of the Reaction between $Cedpta^-$ and Cu^{2+}

pH	k_p (s^{-1})	pH	k_p (s^{-1})	pH	k_p (s^{-1})
c_{Cu} = 0.040 M		c_{Cu} = 0.024 M		c_{Cu} = 0.008 M	
5.36	0.0050	5.18	0.0049	5.49	0.0021
5.09	0.0068	5.15	0.0051	5.34	0.0028
5.07	0.0069	4.97	0.0069	5.28	0.0031
5.07	0.0069	4.96	0.0069	5.20	0.0036
4.99	0.0078	4.93	0.0074	5.10	0.0044
4.86	0.0094	4.84	0.0086	4.10	0.037
4.75	0.011	4.73	0.010	3.98	0.049
4.46	0.019	4.70	0.011	3.93	0.054
3.72	0.087	4.62	0.013	3.90	0.057
3.49	0.140	4.56	0.015	3.82	0.068
		4.33	0.024	3.71	0.086
		3.94	0.054	3.66	0.095
c_{Cu} = 0.032 M		3.86	0.063	3.45	0.150
		3.81	0.070	3.43	0.150
5.08	0.0063	3.65	0.098	3.37	0.170
5.05	0.0066	3.58	0.110		
4.99	0.0071				
4.92	0.0080				
4.87	0.0087	c_{Cu} = 0.016 M			
4.76	0.010				
4.26	0.028	5.27	0.0037		
3.91	0.058	4.95	0.0065		
3.80	0.073	4.94	0.0066		
3.71	0.088	4.92	0.0069		
3.45	0.150	4.85	0.0078		
3.43	0.150	4.40	0.020		
3.28	0.200	4.08	0.040		
		3.86	0.064		
		3.85	0.064		
		3.73	0.084		
		3.51	0.130		

the binuclear complex being formed very quickly, whereas its further transformation occurs relatively slowly. At the same time, protonation of the binuclear complex is inhibited by the presence of the two metal ions; at a higher Pb^{2+} concentration, therefore, when the binuclear complex too is formed in a greater amount, the extent of exchange proceeding by proton-catalysed dissociation is lower. The low rate of further transformation of the binuclear complex may be explained by the fact that when $CedptaPb^+$ is rapidly formed, the ligand is probably bound to the Pb^{2+} through only one acetate group [11]; while the bonds between the Ce^{3+} and the other functional groups break only slowly and progressively, the bonds between the Pb^{2+} and the other functional groups of the ligand are formed slowly in parallel with this [2]. In the exchanges involving Co^{2+} and Ni^{2+}, the exchange occurring via the direct reaction of the complex and the exchanging metal ion is of comparatively low significance, as the binuclear intermediate is also formed slowly because of the low water exchange rates of the metal ions.

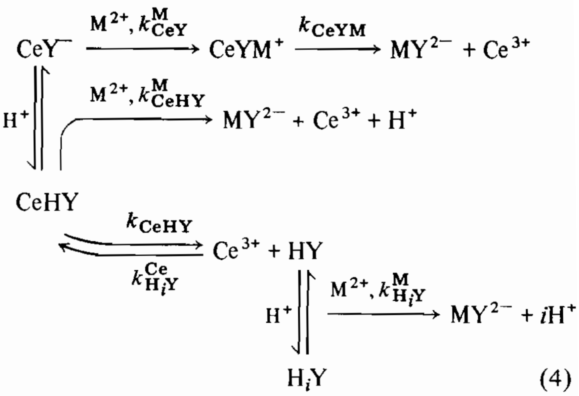
When the above results and the earlier ones are taken into consideration, the following reaction scheme [11], which contains both the possible and the probable reaction pathways, may be used to describe the metal ion exchange reaction (1) and to establish the rate equation eqn. (4) where i = 1, 2 or

TABLE III. Pseudo-first-order Rate Constants of the Reaction between Cedpta$^-$ 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	
5.69	0.00027	4.70	0.0012	4.52	0.0015
5.09	0.00086	4.51	0.0018	4.46	0.0017
4.23	0.0056	3.37	0.021	3.35	0.019
4.18	0.0063	3.36	0.021	3.14	0.028
4.18	0.0063	2.91	0.049	2.92	0.041
3.84	0.013	2.87	0.053	2.87	0.046
3.76	0.086	2.56	0.085	2.71	0.058
3.66	0.019	2.52	0.090		
3.52	0.026	2.32	0.120		
3.48	0.028			c_{Ce} = 0.024 M	
3.47	0.029				
3.33	0.039	c_{Co} = 0.016 M		3.42	0.021
3.20	0.049			3.41	0.022
3.13	0.056	5.86	0.000084	2.98	0.049
2.89	0.085	4.95	0.00045	2.81	0.065
2.89	0.086	3.91	0.0045	2.79	0.067
2.87	0.089	3.52	0.010	2.79	0.068
2.68	0.120	3.43	0.012	2.78	0.068
2.63	0.130	3.32	0.015	2.74	0.073
2.56	0.140	3.21	0.019	2.68	0.080
2.55	0.140	3.05	0.026	2.68	0.081
2.54	0.150	3.01	0.027		
2.33	0.200	3.01	0.028		
		2.82	0.038	c_{Ce} = 0.008 M	
		2.73	0.044		
c_{Co} = 0.032 M		2.63	0.051	5.45	0.00075
		2.54	0.059	3.48	0.056
5.04	0.00075	2.45	0.067	3.41	0.064
4.74	0.0015			3.40	0.066
4.45	0.0027			3.07	0.120
4.35	0.0034	c_{Co} = 0.008 M		2.89	0.170
3.73	0.014				
3.63	0.017	5.59	0.000064		
3.14	0.044	5.16	0.00015		
3.10	0.047	3.66	0.0038		
3.02	0.054	3.28	0.0083		
2.97	0.059	3.18	0.0099		
2.90	0.068	3.05	0.013		
2.75	0.085	3.03	0.013		
2.60	0.110	3.01	0.014		
2.57	0.110	2.96	0.015		
2.39	0.150	2.95	0.015		
2.27	0.170	2.73	0.022		
		2.64	0.025		
		2.37	0.037		
		2.35	0.038		
		2.13	0.053		

3, as practically only the protonated ligand forms HY^{3-}, H_2Y^{2-} and H_3Y^- are present in the pH range in question.

The stability constants of the binuclear complexes formed in the systems are defined by eqn. (5).



(4)

$$K_{CeYM} = \frac{[CeYM^+]}{[CeY^-][M^{2+}]} \tag{5}$$

TABLE IV. Pseudo-first-order Rate Constants of the Reaction between Cedpta$^-$ and Ni^{2+}

c_{Ni} = 0.040 M		c_{Ce} = 0.0107 M			
pH	k_p (s^{-1})	pH	k_p (s^{-1})	pH	k_p (s^{-1})
c_{Ce} = 0.008 M		c_{Ni} = 0.012 M		c_{Ni} = 0.060 M	
5.18	0.000035	4.63	0.00028	4.92	0.000073
3.66	0.0011	3.14	0.0083	3.51	0.0018
2.94	0.0057	2.70	0.021	3.15	0.0041
2.72	0.0091	2.67	0.023	3.08	0.0047
2.68	0.0098	2.64	0.024	2.74	0.0097
2.62	0.011	2.38	0.043	2.46	0.018
2.54	0.013	2.26	0.055	2.42	0.019
2.40	0.018	2.24	0.058	2.39	0.021
2.37	0.019	2.06	0.086	2.18	0.033
2.14	0.032			2.08	0.041
c_{Ce} = 0.016 M		c_{Ni} = 0.090 M		c_{Ni} = 0.030 M	
2.63	0.0055	3.24	0.0050	3.27	0.0015
2.63	0.0056	2.91	0.010	2.97	0.0029
2.43	0.0085	2.57	0.021	2.85	0.0038
2.40	0.0091	2.57	0.021	2.81	0.0042
2.36	0.010	2.27	0.041	2.61	0.0065
2.29	0.012	2.23	0.044	2.47	0.0088
2.14	0.016	2.23	0.044	2.38	0.011
2.03	0.020	2.13	0.055	2.25	0.014
				2.16	0.017
c_{Ce} = 0.024 M					
2.94	0.0019				
2.53	0.0046				
2.19	0.0097				
2.10	0.012				
2.05	0.013				
2.03	0.014				
2.01	0.014				
1.81	0.022				

TABLE V. Rate Constants of the Exchange Reactions between Cedpta, Ceedta and Pb^{2+} as well as Cu^{2+} Ions

M^{2+} Y	Pb^{2+}			Cu^{2+}		
	k_1 (M^{-1} s^{-1})	k_2 (M^{-1} s^{-1})	K_{CeYPb}	k_1 (M^{-1} s^{-1})	k_2 (M^{-1} s^{-1})	K_{CeYCu}
dpta	0.56 ± 0.02	840 ± 20	19 ± 3	0.083 ± 0.004	901 ± 50	5
edta [11]	3.7	2900	35	0.37	1400	

The metal ion exchange proceeding through the various reaction pathways outlined in the reaction scheme eqn. (4) can be described by the following rate equation:

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

In the exchanges involving Pb^{2+} and Cu^{2+}, experimental experience indicates that the negative terms in eqn. (6) make only a negligible contribution. Thus, from eqns. (1), (5) and (6), together with the relation $[CeY] = [CeY^-] + [CeHY] + [CeYM^+]$, the dependence of the pseudo-first-order rate constant k_p on the concentrations of the ionic species taking part in the reaction may be given by the following equation:

$$k_p = \frac{k_1[M] + k_2[H^+] + k_3[M][H^+]}{1 + K_{CeHY}[H^+] + K_{CeYM}[M]} \qquad (7)$$

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

In the exchange involving Pb^{2+}, and to a lesser extent in that involving Cu^{2+}, the binuclear intermediate $CeYM^+$ accumulates; it may therefore be assumed that the rate-determining step is not the formation of the binuclear complex, but its further transformation. Thus, k^{M}_{CeY} may be expressed in terms of the stability constant of the binuclear complex: $k^{M}_{CeY} = K_{CeYM}k_{CeYM}$.

The values of the constants k_1, k_2, k_3 and K_{CeYM} were determined by using eqn. (7) to fit the k_p values (Tables I and II) obtained at the various H^+ and M^{2+} concentrations. The calculated constants k_3 had very high standard deviations, and the correlation was practically independent of whether the final term in the numerator of eqn. (7) was included or not. Hence, it is probable that the exchange involving direct attack of the exchanging metal ion on the protonated CeHdpta complex makes only a negligible contribution to the reaction. The rate constants calculated are given in Table V.

The rates of metal ion exchange in the systems $Cedpta^-$–Co^{2+} and $Cedpta^-$–Ni^{2+} can be expressed by eqn. (6). The presence of a large excess of Ce^{3+} and Co^{2+} or Ni^{2+} obviously means that the concentration of the free ligand $H_i$dpta is extremely low and can be regarded as practically constant. Accordingly, through application of the principle of stationarity ($d[H_iY]/dt = 0$), eqn. (6) may be written in the following form [11]:

$$-\frac{d[CeY]}{dt} = k^{M}_{CeY}[CeY][M] + k^{M}_{CeHY}[CeHY][M] + \sum_{1}^{3} k^{M}_{H_iY}[M][H_iY] \qquad (8)$$

where $[CeY] = [CeY^-] + [CeHY]$.

From eqns. (1), (5) and (8), the value of k_p can be expressed as follows:

$$k_p = \frac{k_1 + k_3[H^+] + k_4[H^+]/[Ce] + k_5[H^+]^2/[Ce] + k_6[H^+]^3/[Ce]}{1 + K_{CeHY}[H^+]}[M] \qquad (9)$$

TABLE VI. Rate Constants Obtained from the Study of the Exchange Reactions between Cedpta, Ceedta and Ni^{2+} as well as Co^{2+}

	k_1 (dm^3 mol^{-1} s^{-1})	k_4 (dm^3 mol^{-1} s^{-1})	k_5 (dm^6 mol^{-2} s^{-1})	k^{M}_{HY} (dm^3 mol^{-1} s^{-1})	$k^{M}_{H_2Y}$ (dm^3 mol^{-1} s^{-1})
Ni^{2+}					
dpta	$(2 \pm 1) \times 10^{-6}$	2.2 ± 0.3	$(1.7 \pm 0.3) \times 10^{3}$	1.9×10^{6}	8.3×10^{2}
edta [11]	5.4×10^{-5}	1.3	2.3×10^{3}	9×10^{5}	1.1×10^{3}
Co^{2+}					
dpta	$(2.1 \pm 0.3) \times 10^{-3}$	79 ± 5	$(1.5 \pm 0.3) \times 10^{4}$	6.8×10^{7}	7.3×10^{3}
edta [11]	2.2×10^{-3}	70	3.4×10^{4}	4.8×10^{7}	1.6×10^{4}

where $k_1 = k^{\mathrm{M}}_{\mathrm{CeY}}$, $k_3 = k^{\mathrm{M}}_{\mathrm{CeHY}} K_{\mathrm{CeHY}}$, $k_4 = k^{\mathrm{M}}_{\mathrm{HY}} K^{\mathrm{H}}_1 / K_{\mathrm{CeY}}$, $k_5 = k^{\mathrm{M}}_{\mathrm{H_2Y}} K^{\mathrm{H}}_1 K^{\mathrm{H}}_2 / K_{\mathrm{CeY}}$, $k_6 = k^{\mathrm{M}}_{\mathrm{H_3Y}} K^{\mathrm{H}}_1 K^{\mathrm{H}}_2 K^{\mathrm{H}}_3 / K_{\mathrm{CeY}}$, K^{H}_1, K^{H}_2 and K^{H}_3 are the first, second and third protonation constants of dpta^{4-}, and K_{CeY} is the stability constant of Cedpta$^-$.

The rate constants k_1, k_4 and k_5 were determined by using eqn. (9) to fit the pseudo-first-order rate constants k_{p} obtained at various concentrations of H$^+$, Ce^{3+} and Co^{2+} or Ni^{2+}. The standard deviations in the constants k_3 and k_6 were larger than their values. Thus, the fitting was not influenced by their inclusion or their omission; *i.e.* the exchanges proceeding via reaction pathways characterized by the rate constants k_3 and k_6 make only negligible contributions to the overall reaction. The rate constants found are listed in Table VI. This Table contains the rate constants $k^{\mathrm{M}}_{\mathrm{H}_i\mathrm{Y}}$ corresponding to the rates of formation of the Codpta^{2-} and Nidpta^{2-} complexes.

A comparison of the rate constants in Tables V and VI permits the following conclusions concerning the course of the metal ion exchange reactions.

The stability constant of the Cedpta$^-$ complex is larger than that of the Ceedta$^-$ complex; as in other cases, this results in a higher kinetic stability. The metal ion exchange reaction of Cedpta$^-$ takes place more slowly than that of Ceedta$^-$, as regards both the direct attack by the exchanging metal ion (k_1) and the proton-catalysed dissociation of the complex (the rate constants for the dissociation of CeHedta and CeHdpta are $k_{\mathrm{CeHX}} = 52.3$ s^{-1} and $k_{\mathrm{CeHY}} = 28$ s^{-1}). The slower dissociation of the protonated CeHdpta complex is presumably a consequence of the fact that the basicity of one of the nitrogen atoms of the dpta ligand is higher because of the inductive effect of the methyl group, and thus the ethylenediamine chelate ring is bonded more strongly to the Ce^{3+}, which lowers the frequency of liberation of one of the iminodiacetate groups of the ligand. ^{1}H NMR studies on Ceedta$^-$ have revealed that the rate-determining step in the dissociation of the complex is the formation of a half-dissociated, protonated intermediate, *i.e.* the cessation of coordination of one of the iminodiacetate groups of the edta molecule [12]. Our results indicate that the presence of the methyl group does not cause a fundamental change in the kinetic behaviour of the complex. Thus, as with CeHedta, the dissociation of CeHdpta may occur through the formation of a protonated intermediate in which the ligand is coordinated via only one of the iminodiacetate groups. However, this is less likely to be formed than in the case of Ceedta$^-$.

The rate constants $k^{\mathrm{M}}_{\mathrm{CeY}}$ ($= k_1$) relating to the rates of exchange through direct attack by the exchanging metal ions vary very considerably with the rate of metal ion water exchange (Fig. 1).

The data presented in Fig. 1 demonstrate that the rate of exchange involving direct reaction between Cedpta$^-$ and the metal ions is directly proportional to the rate of water exchange by the exchanging metal ions, *i.e.* $k^{\mathrm{M}}_{\mathrm{CeY}} = b k^{-\mathrm{H_2O}}_{\mathrm{M}}$ and $b = 10^{-9.6}$. Constant b has an equivalent meaning to that of the similar constant obtained from the essentially identical results in the investigation of the metal ion exchange reactions of the Ceedta$^-$ complex (Fig. 1) [11]. The value of b gives an approximate expression of the probability of formation of the non-protonated intermediate containing the ligand coordinated through only one of the iminodiacetate groups. If the free iminodiacetate group in such an intermediate is coordinated to the attacking metal ion, a nearly symmetrical binuclear intermediate is formed in which the functional groups are progressively bound to the attacking metal ion. Formation of the binuclear complex [Ce(OOCCH$_2$)$_2$NCH(CH$_3$)CH$_2$N(CH$_2$COO)$_2$M]$^+$ is probably the rate-determining process in the exchange occurring via the associative reaction pathway. The structure of the binuclear complex formed in this manner is not the same as that of the previously mentioned binuclear complex CedptaM$^+$, that is rapidly formed in the first step of the exchange involving attack by Pb^{2+} or Cu^{2+}. In the latter case, the relatively low value of the stability constant K_{CeYM} indicates that the ligand is bonded to the attacking metal ion via only one of its carboxylate groups, the nearly symmetrical intermediate being produced by the slower rearrangement of the functional groups in the intermediate formed earlier. Thus, the first steps are different in the exchanges involving direct attack by Pb^{2+} and Cu^{2+} or by Co^{2+} and Ni^{2+}, but both of these different reaction pathways lead to the formation of nearly symmetrical binuclear intermediates with the same structures, following which the exchange takes place in an identical manner.

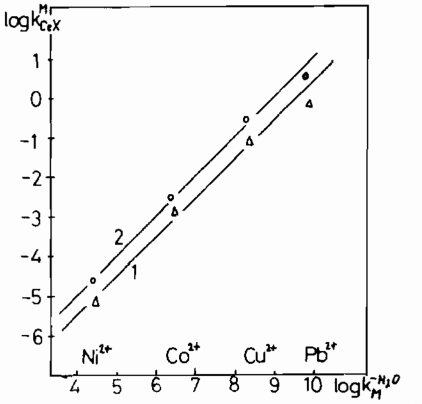


Fig. 1. Dependence of the rate constant $k^{\mathrm{M}}_{\mathrm{CeY}}$ on the characteristic water exchange rate of the attacking metal ions: Cedpta (1) and Ceedta (2).

The values of the rate constants for the formation of the Codpta^{2-} and Nidpta^{2-} complexes are practically the same as those for Coedta^{2-} and Niedta^{2-} [11]. This shows that the presence of the methyl group and the slightly different basicities of the nitrogen atoms do not lead to very appreciable changes in the rates of the complex-formation reactions in which the ligands with related structures, $Hedta^{3-}$ and $Hdpta^{3-}$, or H_2edta^{2-} and H_2dpta^{2-}, take part. The rates of the complex-formation reactions depend on the rate of metal ion water exchange, on the structure of the ligand, and on the rates of chelate ring closure and deprotonation. The reason why the rate of complex formation with the diprotonated ligand H_2dpta^{2-} ($k^{M}_{H_2Y}$) is low is presumably because the reaction necessitates deprotonation of the two nitrogen atoms, and either this, or possibly the proton migration, proceeds relatively slowly.

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