

## Aminopolycarboxylates of Rare Earths. 9. Kinetic Study of Exchange Reactions between the Cerium(III)-Ethylenediaminetetraacetate Complex and Lead(II), Nickel(II), and Cobalt(II) Ions

E. BRÜCHER\* and G. LAURENCZY

Received January 4, 1982

The rate of exchange reactions taking place between the  $\text{Ce}(\text{edta})^-$  complex and  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Co}^{2+}$  ions in general increases with increasing  $\text{H}^+$  and metal ion concentration. On the basis of the rate equations obtained, it was assumed that the exchange reactions proceed via the dissociation of the protonated  $\text{Ce}(\text{Hedta})$  complex as well as by the direct attack of the metal ions on the  $\text{Ce}(\text{edta})^-$  and  $\text{Ce}(\text{Hedta})$  complexes. In the  $\text{Ce}(\text{edta})^-$ - $\text{Pb}^{2+}$  system the results have been explained by the fast formation and slow transformation of the binuclear complex  $\text{Ce}(\text{edta})\text{Pb}^+$ , in which presumably only an acetate group is coordinated to the  $\text{Pb}^{2+}$  ion. The rate of exchange between  $\text{Ce}(\text{edta})^-$  and  $\text{Ni}^{2+}$  (as well as  $\text{Co}^{2+}$ ) is inversely proportional to the  $\text{Ce}^{3+}$  ion concentration. This has been explained by the much lower water-exchange rate of the  $\text{Ni}^{2+}(\text{aq})$  and  $\text{Co}^{2+}(\text{aq})$  ions compared to that of the  $\text{Ce}^{3+}(\text{aq})$  ion. The rate of exchange taking place by the direct attack of the metal ions on the complex is linearly proportional to the water-exchange rate of these ions. This presumably resulted from the formation of an intermediate complex, where one of the iminodiacetate groups of edta is coordinated to the  $\text{Ce}^{3+}$  ion while the other one is coordinated to the attacking  $\text{Ni}^{2+}$  or  $\text{Co}^{2+}$  ion.

Complex formation between ethylenediaminetetraacetate ( $\text{edta}^{4-}$ ) and lanthanide(III) ions ( $\text{Ln}^{3+}$ ) is of great importance in the ion-exchange chromatographic separation of the lanthanides, and the equilibrium conditions and kinetic behavior of the  $\text{Ln}(\text{edta})^-$  complexes have therefore been investigated in detail. In the interval  $3 < \text{pH} < 6$ , the exchange reactions of the central ions of the complexes occur predominantly by  $\text{H}^+$  ion-catalyzed dissociation of the complexes, while direct attack of the exchanging metal ions plays a relatively minor role.<sup>1-7</sup> At the same time, in the reactions of transition-metal edta complexes a substantially higher contribution is made to the exchange by direct attack of the exchanging metal ion.<sup>8,9</sup>

The contribution of the reaction involving the direct encounter of the  $\text{Ln}(\text{edta})^-$  complexes and the exchanging metal ion is known to decrease as the atomic number of the central ion increases;<sup>7,10</sup> accordingly, as regards elucidation of the structure of the intermediate playing the decisive role in the exchange, investigations with complexes of the elements with lower atomic numbers offer the greatest promise.

With a view to obtaining more detailed information on the mechanism of the associative exchange between the  $\text{Ln}(\text{edta})^-$  complex and the exchanging metal ion, we have studied the kinetics of the exchange reactions between  $\text{Ce}(\text{edta})^-$  and  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$ . The characteristic water-exchange rates of the  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  ions are very different:  $7.5 \times 10^9$ ,  $2.6 \times 10^6$ , and  $3.4 \times 10^4 \text{ s}^{-1}$ , respectively.<sup>11</sup> Hence, it was hoped that the planned kinetic investigations would permit conclusions on the role of the rate of water loss from the exchanging metal ion in the exchange process.

### Experimental Section

The  $\text{KCe}(\text{edta}) \cdot 8\text{H}_2\text{O}$  complex was prepared by mixing solutions

of  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  (99.9%, Koch-Light) and  $\text{K}_2\text{H}_2\text{edta}$  and then neutralizing; the  $\text{K}_2\text{H}_2\text{edta}$  was made from  $\text{H}_4\text{edta}$  (p.A., Reanal).  $\text{Pb}(\text{ClO}_4)_2$ ,  $\text{Co}(\text{ClO}_4)_2$ , and  $\text{Ni}(\text{ClO}_4)_2$  were prepared by dissolution of the corresponding carbonates, of the highest analytical purity, in perchloric acid. Both the complex and the perchlorate salts were purified by repeated recrystallization before being used in the experiments.

Experiments were performed at 25 °C at constant ionic strength ( $0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$ ). the concentrations of the  $\text{Pb}(\text{II})$ ,  $\text{Co}(\text{II})$ , or  $\text{Ni}(\text{II})$  perchlorates were taken into consideration in the calculation of the ionic strength. No buffer was used in the investigations, since the pH of the solution undergoes practically no change in the course of the exchange.

A Radiometer pHM-26 pH meter, with glass and saturated calomel ( $\text{NaCl}$ ) electrodes, was used for pH measurement. The  $\text{H}^+$  ion concentration was established from the measured pH value by the procedure recommended by Irving et al.<sup>12</sup> ( $\text{pH}_c = \text{pH} + 0.198$ ). The progress of the exchange reactions was followed at 280 nm in 40-mm quartz cells with a Beckman DB-GT spectrophotometer. At this wavelength the absorbance due to the  $\text{Pb}(\text{edta})^{2-}$ ,  $\text{Co}(\text{edta})^{2-}$ , and  $\text{Ni}(\text{edta})^{2-}$  complexes is negligible, and the absorbance of the  $\text{Ce}^{3+}$  ion is also far lower than that of the  $\text{Ce}(\text{edta})^-$  complex.

Given the knowledge of the stability constants of the complexes,<sup>13</sup> the concentrations of the  $\text{Ce}(\text{edta})^-$  and of the  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , or  $\text{Ni}^{2+}$  ions were chosen so that the exchange reaction should take place essentially quantitatively. Under such conditions, the rate of the exchange can be given as

$$-\frac{d[\text{Ce}(\text{edta})^-]_t}{dt} = k_p[\text{Ce}(\text{edta})^-]_t \quad (1)$$

where  $k_p$  is a pseudo-first-order rate constant and  $[\text{Ce}(\text{edta})^-]_t$  is the total concentration of the complex at a given time. Since the reaction is first order, the absorbance ( $A_t$ ) of the solution at a time  $t$  after the beginning of the reaction may be expressed in the following way:

$$A_t = A_p + (A_r - A_p)e^{-k_p t} \quad (2)$$

where  $A_p$  and  $A_r$  are the absorbances of the products and the reactants, respectively. The values of the pseudo-first-order rate constants,  $k_p$ , were determined by computer fitting on the basis of expression 2. The program first computed an approximate value of  $k_p$  by the method of Kezdy and Swinbourne<sup>14</sup> (from values read off the absorbance vs. time graph at equal time intervals), and the resulting value was then refined further by the method of nonlinear squares (the square sum of the differences between the measured and the calculated absorbance values being minimized).

- (1) R. H. Betts, O. F. Dahlinger, and D. M. Munro, in "Radioisotopes in Scientific Research", Vol. 2, R. C. Exterman, Ed., Pergamon Press, Elmsford, NY, 1958, p 326.
- (2) P. Glentworth, B. Wiseall, C. L. Wright, and A. J. Mahmood, *J. Inorg. Nucl. Chem.*, **30**, 967 (1968).
- (3) P. Glentworth and D. A. Newton, *J. Inorg. Nucl. Chem.*, **33**, 1701 (1971).
- (4) T. Asano, S. Okada, and S. Taniguchi, *J. Inorg. Nucl. Chem.*, **32**, 1287 (1970).
- (5) E. Brücher and P. Szarvas, *Inorg. Chim. Acta*, **4**, 632 (1970).
- (6) T. Ryhi, *Acta Chem. Scand.*, **26**, 3955 (1972).
- (7) T. Ryhi, *Acta Chem. Scand.*, **27**, 303 (1973).
- (8) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **1**, 852 (1962).
- (9) D. W. Margerum, D. L. Janes, and H. M. Rosen, *J. Am. Chem. Soc.*, **87**, 4463 (1965).
- (10) E. Brücher and L. Boros, *Proc. Int. Conf. Coord. Chem.*, **15**, 420 (1973).
- (11) D. W. Margerum, D. R. Cayley, D. C. Weatherburn, and G. K. Pagenkopf, "Coordination Chemistry", Vol. 2, A. E. Martell, Ed., American Chemical Society, Washington, DC, 1978, ACS Monogr. No. 174, p 1.

- (12) H. M. Irving, M. G. Miles, and L. D. Pettit, *Anal. Chim. Acta*, **38**, 475 (1967).
- (13) L. G. Sillen and A. E. Martell, *Spec. Publ.-Chem. Soc.*, No. 17 (1964) (Suppl. No. 1); No. 25 (1971).
- (14) E. S. Swinbourne, "Analysis of Kinetic Data", Nelson, London, 1971, p 81.

Table I. Pseudo-First-Order Rate Constants of the Reaction between Ce(edta)<sup>-</sup> and Pb<sup>2+</sup>

pH	10 <sup>2</sup> k <sub>p</sub> , s <sup>-1</sup>	pH	10 <sup>2</sup> k <sub>p</sub> , s <sup>-1</sup>	pH	10 <sup>2</sup> k <sub>p</sub> , s <sup>-1</sup>
c <sub>Pb<sup>2+</sup></sub> = 0.004 mol/dm <sup>3</sup>					
6.541	1.28	5.220	2.23	4.522	5.84
6.514	1.35	5.181	2.32	4.202	13.0
6.480	1.27	4.662	4.86	4.122	12.9
6.129	1.45	4.586	5.67	4.083	15.5
5.878	1.69				
c <sub>Pb<sup>2+</sup></sub> = 0.006 mol/dm <sup>3</sup>					
6.492	1.61	6.270	1.80	4.074	15.4
6.313	1.86	5.924	2.04	3.704	30.9
c <sub>Pb<sup>2+</sup></sub> = 0.008 mol/dm <sup>3</sup>					
6.101	2.42	5.321	3.08	4.468	7.81
5.962	2.37	5.222	3.17	4.404	8.40
5.839	2.69	4.922	4.42	4.380	8.59
5.706	2.57	4.816	4.69	4.183	12.3
5.473	3.07	4.505	7.79	4.067	15.5
c <sub>Pb<sup>2+</sup></sub> = 0.01 mol/dm <sup>3</sup>					
5.781	3.21	5.378	3.57	4.171	12.1
5.734	3.01	5.075	4.38	4.132	13.0
5.716	3.12	4.889	4.46	4.127	15.7
5.429	3.27	4.186	12.5	3.943	18.7
c <sub>Pb<sup>2+</sup></sub> = 0.012 mol/dm <sup>3</sup>					
5.786	3.58	4.901	6.04	4.177	13.9
5.693	3.65	4.425	9.33	4.112	14.8
5.497	3.84	4.237	12.3	3.859	22.5
5.241	4.36				
c <sub>Pb<sup>2+</sup></sub> = 0.016 mol/dm <sup>3</sup>					
5.668	3.93	4.998	5.21	3.950	22.2
5.582	4.04	4.961	5.59	3.938	20.7
5.563	4.27	4.679	7.48	3.750	27.8
5.466	4.23	4.312	12.5		
c <sub>Pb<sup>2+</sup></sub> = 0.02 mol/dm <sup>3</sup>					
5.846	4.26	4.837	6.21	4.208	11.8
5.719	4.36	4.786	6.66	4.113	12.8
5.684	4.32	4.563	7.37	4.059	15.4
5.559	4.41	4.508	8.08	4.008	16.4
5.056	5.64	4.297	13.4	3.842	20.6
c <sub>Pb<sup>2+</sup></sub> = 0.024 mol/dm <sup>3</sup>					
5.600	5.24	5.389	5.22	5.286	5.32
5.487	5.15	5.345	5.31	5.265	5.62
5.487	5.14				

## Results and Discussion

The rate of exchange was studied at constant Ce(edta)<sup>-</sup> concentration, at given Pb<sup>2+</sup>, Ni<sup>2+</sup>, or Co<sup>2+</sup> ion concentration, and at various pH values. In the reactions with Ni<sup>2+</sup> and Co<sup>2+</sup> ions pseudo-first-order rate constants, *k<sub>p</sub>*, have been obtained only when there was a 20–40-fold Ce<sup>3+</sup> ion excess in the system compared to the concentration of Ce(edta)<sup>-</sup>, which suggests that the exchange process includes a reversible reaction step. The concentration of the exchanging metal ion was always chosen to be sufficiently larger than the concentration of the free Ce<sup>3+</sup> ion for the exchange to be virtually complete. The resulting *k<sub>p</sub>* values are contained in Tables I–III.

The pseudo-first-order rate constants listed in Tables I–III increase with increasing H<sup>+</sup> ion concentration and in general with the rise of the concentration of the exchanging metal. If the earlier results are also taken into consideration,<sup>1–7,10</sup> the increase observed in the exchange rate with increasing H<sup>+</sup> ion concentration can be explained by the proton-catalyzed dissociation of the Ce(edta)<sup>-</sup> complex. The protonated Ce(Hedta) complex formed in the equilibrium reaction undergoes faster dissociation than the nonprotonated Ce(edta)<sup>-</sup>. The Hedta<sup>3-</sup> ligand formed interacts rapidly with the M<sup>2+</sup> exchanging metal ion, to yield M(edta)<sup>2-</sup>. The increase of the *k<sub>p</sub>* values with increasing concentration of the M<sup>2+</sup> exchanging metal ions indicates that the exchange may also take place via the formation of a binuclear complex, following the direct attack of the M<sup>2+</sup> ion on the Ce(edta)<sup>-</sup> and Ce(Hedta) complexes.

Table II. Pseudo-First-Order Rate Constants of the Reaction between Ce(edta)<sup>-</sup> and Ni<sup>2+</sup>

pH	10 <sup>4</sup> k <sub>p</sub> , s <sup>-1</sup>	pH	10 <sup>4</sup> k <sub>p</sub> , s <sup>-1</sup>	pH	10 <sup>4</sup> k <sub>p</sub> , s <sup>-1</sup>
c <sub>Ce<sup>3+</sup></sub> = 0.01 mol/dm <sup>3</sup>					
c <sub>Ni<sup>2+</sup></sub> = 0.02 mol/dm <sup>3</sup>					
5.598	0.052	3.189	19.5	2.882	56.6
3.508	4.83	3.132	25.5	2.722	98.6
3.478	7.49	3.108	26.5	2.600	166
c <sub>Ni<sup>2+</sup></sub> = 0.03 mol/dm <sup>3</sup>					
3.928	3.44	2.860	84.9	2.697	154
3.212	30.0	2.847	91.2	2.553	289
2.921	66.1				
c <sub>Ni<sup>2+</sup></sub> = 0.04 mol/dm <sup>3</sup>					
6.103	0.044	3.522	12.2	2.961	79.9
5.488	0.156	3.223	32.4	2.784	163
3.769	5.95	2.986	69.8	2.711	183
c <sub>Ni<sup>2+</sup></sub> = 0.05 mol/dm <sup>3</sup>					
5.409	0.198	3.300	30.6	2.910	123
4.424	1.98	3.021	78.2	2.611	338
3.761	8.50	2.948	103		
c <sub>Ce<sup>3+</sup></sub> = 0.018 mol/dm <sup>3</sup>					
c <sub>Ni<sup>2+</sup></sub> = 0.03 mol/dm <sup>3</sup>					
5.206	0.102	2.956	33.8	2.593	120
4.326	0.661	2.909	37.5	2.399	237
3.583	4.43	2.852	48.7	2.252	415
3.206	14.7				
c <sub>Ce<sup>3+</sup></sub> = 0.014 mol/dm <sup>3</sup>					
4.883	0.274	2.893	58.9	2.339	378
4.687	0.329	2.683	125	2.299	462
3.196	21.3	2.579	171	2.186	704
c <sub>Ce<sup>3+</sup></sub> = 0.012 mol/dm <sup>3</sup>					
4.346	0.967	3.134	26.3	2.305	562
4.213	1.95	2.841	76.7	2.173	847
3.488	8.83				
c <sub>Ce<sup>3+</sup></sub> = 0.008 mol/dm <sup>3</sup>					
4.903	0.356	4.017	3.06	3.249	27.4
4.812	0.503	3.640	8.08	2.912	89.0
4.159	2.09	3.286	25.9	2.784	136

Table III. Pseudo-First-Order Rate Constants of the Reaction between Ce(edta)<sup>-</sup> and Co<sup>2+</sup>

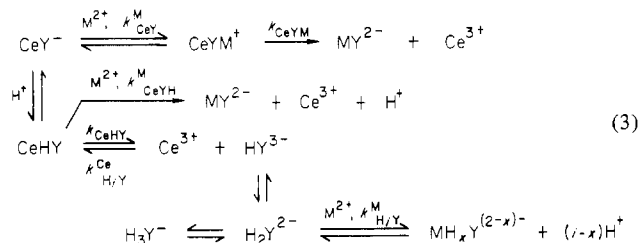
c <sub>Ce<sup>3+</sup></sub> = 0.01 mol/dm <sup>3</sup>					
c <sub>Co<sup>2+</sup></sub> = 0.03 mol/dm <sup>3</sup>		c <sub>Co<sup>2+</sup></sub> = 0.04 mol/dm <sup>3</sup>		c <sub>Co<sup>2+</sup></sub> = 0.05 mol/dm <sup>3</sup>	
pH	10 <sup>3</sup> k <sub>p</sub> , s <sup>-1</sup>	pH	10 <sup>3</sup> k <sub>p</sub> , s <sup>-1</sup>	pH	10 <sup>3</sup> k <sub>p</sub> , s <sup>-1</sup>
6.272	0.191	5.835	0.392	6.004	0.392
6.261	0.134	5.318	1.64	5.790	0.442
6.109	0.317	5.193	2.07	5.519	0.846
4.254	13.6	4.258	12.7	4.765	5.31
3.681	45.7	4.112	21.9	4.699	9.75
3.573	54.5	3.757	48.5	4.697	6.29
3.523	66.8	3.544	73.9	4.153	15.7
				4.039	37.1
				3.828	35.3
				3.586	65.0
c <sub>Co<sup>2+</sup></sub> = 0.04 mol/dm <sup>3</sup>					
c <sub>Ce<sup>3+</sup></sub> = 0.008 mol/dm <sup>3</sup>			c <sub>Ce<sup>3+</sup></sub> = 0.02 mol/dm <sup>3</sup>		
pH	10 <sup>3</sup> k <sub>p</sub> , s <sup>-1</sup>	pH	10 <sup>3</sup> k <sub>p</sub> , s <sup>-1</sup>	pH	10 <sup>3</sup> k <sub>p</sub> , s <sup>-1</sup>
5.921	0.638	4.271	7.86		
5.861	0.676	3.615	38.4		
4.363	11.7	3.380	69.5		
3.563	81.1	3.255	95.6		
3.528	78.9	3.238	107		

The inspection of the data tabulated in Table I shows that at higher H<sup>+</sup> ion concentrations (at about pH < 4.5) the *k<sub>p</sub>* values do not increase with increasing Pb<sup>2+</sup> ion concentrations, as may be predicted from the results obtained at higher pH values. The relative decrease of the rate of exchange can be

explained by assuming the formation of the  $\text{Ce}(\text{edta})\text{Pb}^+$  binuclear complex.<sup>15,16</sup> If the formation of this complex is very fast and its stability constant ( $K_{\text{CeY Pb}}$ , where  $\text{Y} = \text{edta}$ ) is not too low, then at higher  $\text{Pb}^{2+}$  concentrations the concentration of the binuclear complex is significant and thus the protonation of  $\text{Ce}(\text{edta})^-$  is hindered. This reduces the contribution of the proton-catalyzed dissociation to the exchange and results in the relative decrease of the reaction rate. Since the stability constant of the protonated complex is not too large ( $K_{\text{CeHY}} = 54^{17}$ ), the effect of the  $\text{Pb}^{2+}$  ions may be appreciable even in the case where  $K_{\text{CeY Pb}} \approx 1$ . The stability constants are defined by the equations

$$K_{\text{CeHY}} = \frac{[\text{Ce}(\text{Hedta})]}{[\text{Ce}(\text{edta})^-][\text{H}^+]} \quad K_{\text{CeY Pb}} = \frac{[\text{Ce}(\text{edta})\text{Pb}^+]}{[\text{Ce}(\text{edta})^-][\text{Pb}^{2+}]}$$

On the basis of the above considerations and previous experiences,<sup>1-11,18</sup> we assume that the exchange reactions take place in the manner described in eq 3, where  $i = 1, 2$ , or 3



and  $x = 0$  to 1. In (3) the exchange through the direct dissociation of  $\text{Ce}(\text{edta})^-$  was neglected, because it was found to be very slow.<sup>2,18</sup> The protonation of the  $\text{Ce}(\text{edta})\text{M}^+$  binuclear complex was not taken into account either, since this can occur only with very low probability.

From the reaction scheme (3) the rate equation of the exchange reactions can be given as

$$-\frac{d[\text{CeY}]_t}{dt} = k_{\text{CeY}}^{\text{M}}[\text{CeY}][\text{M}] + k_{\text{CeHY}}^{\text{M}}[\text{CeHY}][\text{M}] + k_{\text{CeHY}}^{\text{Ce}}[\text{CeHY}] - \sum_1^3 k_{\text{H}_i\text{Y}}^{\text{Ce}}[\text{Ce}][\text{H}_i\text{Y}] \quad (4)$$

In the  $\text{Ce}(\text{edta})^-$ - $\text{Pb}^{2+}$  system the contribution of the last term in eq 4 can be neglected, because the experimental results do not show the contribution of the reactions, characterized by the rate constants  $k_{\text{H}_i\text{Y}}^{\text{Ce}}$ . This is probably a result of the higher water-exchange rate of the  $\text{Pb}^{2+}$  ion than of the  $\text{Ce}^{3+}$  ion ( $k_{\text{H}_2\text{O}}^{\text{Ce}} = 2.5 \times 10^8 \text{ s}^{-1}$ ). From rate equations (1) and (4), from the relation  $[\text{CeY}]_t = [\text{CeY}^-] + [\text{CeHY}] + [\text{CeY Pb}^+]$ , and from the equation defining the stability constants  $K_{\text{CeHY}}$  and  $K_{\text{CeY Pb}}$  the pseudo-first-order rate constant  $k_p$  may be given as

$$k_p = \frac{k_1[\text{Pb}^{2+}] + k_2[\text{H}^+] + k_3[\text{Pb}^{2+}][\text{H}^+]}{1 + K_{\text{CeHY}}[\text{H}^+] + K_{\text{CeY Pb}}[\text{Pb}^{2+}]} \quad (5)$$

where  $k_1 = K_{\text{CeY Pb}}k_{\text{CeY Pb}}$ ,  $k_2 = K_{\text{H CeY}}k_{\text{CeHY}}$ , and  $k_3 = K_{\text{CeHY}}k_{\text{Pb CeHY}}$ . The rate constants  $k_1$ ,  $k_2$ , and  $k_3$  and the stability constant  $K_{\text{CeY Pb}}$  were calculated by using eq 5 for the computer fitting of the  $k_p$  values shown in Table I. In the

**Table IV.** Rate Constants of the Exchange Reaction between  $\text{Ce}(\text{edta})^-$  and  $\text{Pb}^{2+}$  Ion and the Value of  $K_{\text{CeY Pb}}$

$k_1$ , $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$	$10^{-3}k_2$ , $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$	$10^{-4}k_3$ , $\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$	$K_{\text{CeY Pb}}$ , $\text{mol}^{-1} \text{ dm}^3$
$3.7 \pm 0.1$	$2.9 \pm 0.1$	$3.4 \pm 0.9$	$35 \pm 3$
$k_{\text{CeY Pb}}$ , $\text{s}^{-1}$	$k_{\text{CeHY}}$ , $\text{s}^{-1}$	$k_{\text{Pb CeHY}}$ , $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$	
0.11	53.7	630	

calculation the square sum of the relative differences of experimentally found and calculated  $k_p$  values was minimized. The resulting constants are given in Table IV.

From a comparison of the stability constants of the  $\text{Pb}(\text{II})$ -acetate complex ( $\log K_1 = 2.15^{13}$ ) and the binuclear  $\text{Ce}(\text{edta})\text{Pb}^+$  complex ( $\log K_{\text{CeY Pb}} = 1.54$ ), it may be assumed that in the binuclear complex one of the carboxylate groups of edta is coordinated to the  $\text{Pb}^{2+}$  ion.

The occurrence of the reversible reaction step in the exchange reactions with  $\text{Ni}^{2+}$  or  $\text{Co}^{2+}$  ions (eq 3) is probably a consequence of the fact that the water-exchange rate of the  $\text{Ce}^{3+}$  ion is much higher than those for the  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions. As a result, the rates of formation of the  $\text{Ni}(\text{edta})^{2-}$  and  $\text{Co}(\text{edta})^{2-}$  complexes are substantially lower than the rate of formation of the  $\text{Ce}(\text{edta})^-$  complex ( $k_{\text{CeHY}}^{\text{Ce}} \gg k_{\text{H}_2\text{Y}}^{\text{Ni}}$  and  $k_{\text{H}_2\text{Y}}^{\text{Ce}} \gg k_{\text{H}_2\text{Y}}^{\text{Co}}$ ), and therefore the  $\text{Hedta}^{3-}$  anion released on dissociation of the protonated  $\text{Ce}(\text{Hedta})$  (this anion may take up further protons in the pH range in question) very probably interacts with the  $\text{Ce}^{3+}$  ion, even if it is present at a considerably lower concentration than the  $\text{Ni}^{2+}$  or  $\text{Co}^{2+}$  ion.

In the  $\text{Ce}(\text{edta})^-$ - $\text{Ni}^{2+}$  and  $\text{Ce}(\text{edta})^-$ - $\text{Co}^{2+}$  systems the concentration of the free ligands formed,  $\text{H}_i\text{edta}^{(4-i)-}$ , varies as follows:

$$\frac{d[\text{H}_i\text{Y}]}{dt} = k_{\text{CeHY}}[\text{CeHY}] - \sum_1^3 k_{\text{H}_i\text{Y}}^{\text{Ce}}[\text{H}_i\text{Y}][\text{Ce}^{3+}] - \sum_1^3 k_{\text{H}_i\text{Y}}^{\text{M}}[\text{H}_i\text{Y}][\text{M}^{2+}] \quad (6)$$

Because of the presence of the large metal ion excess, the concentration of the ligands  $\text{H}_i\text{Y}$  is extremely low and approximately constant. Accordingly, it is possible to apply the steady-state principle, with  $d[\text{H}_i\text{Y}]/dt \approx 0$ . On this basis, from a comparison of eq 4 and 6, the rate of exchange can be written as

$$-\frac{d[\text{CeY}]_t}{dt} = k_{\text{CeY}}^{\text{M}}[\text{CeY}][\text{M}] + k_{\text{CeHY}}^{\text{M}}[\text{CeHY}][\text{M}] + \sum_1^3 k_{\text{H}_i\text{Y}}^{\text{M}}[\text{M}][\text{H}_i\text{Y}] \quad (7)$$

where  $[\text{CeY}]_t = [\text{CeY}^-] + [\text{CeHY}]$ .

The concentrations of the free ligand species,  $\text{H}_i\text{edta}$ , present in small amounts in the system can be expressed in terms of their protonation constants  $K_{\text{H}_1}^{\text{H}}$ ,  $K_{\text{H}_2}^{\text{H}}$ , and  $K_{\text{H}_3}^{\text{H}}$  and the stability constant  $K_{\text{CeY}}$  for the  $\text{Ce}(\text{edta})^-$  complex.

If these relations are introduced into rate equation (7), a comparison of eq 1 and that relaxation leads to the following expression for the value of  $k_p$ :

$$k_p = \left\{ (k_1 + k_2[\text{H}^+] + k_3[\text{H}^+]/[\text{Ce}^{3+}] + k_4[\text{H}^+]^2/[\text{Ce}^{3+}] + k_5[\text{H}^+]^3/[\text{Ce}^{3+}]) / (1 + K_{\text{CeHY}}[\text{H}^+]) \right\} [\text{M}^{2+}] \quad (8)$$

where  $k_1 = k_{\text{CeY}}^{\text{M}}$ ,  $k_2 = K_{\text{H CeY}}^{\text{M}}K_{\text{CeHY}}$ ,  $k_3 = k_{\text{H}_2\text{Y}}^{\text{M}}K_{\text{H}_1}^{\text{H}}/K_{\text{CeY}}$ ,  $k_4 = k_{\text{H}_3\text{Y}}^{\text{M}}K_{\text{H}_1}^{\text{H}}K_{\text{H}_2}^{\text{H}}/K_{\text{CeY}}$ , and  $k_5 = k_{\text{H}_3\text{Y}}^{\text{M}}K_{\text{H}_1}^{\text{H}}K_{\text{H}_2}^{\text{H}}K_{\text{H}_3}^{\text{H}}/K_{\text{CeY}}$ .

The values of the rate constants  $k_1$ ,  $k_2$ ,  $k_3$ ,  $k_4$ , and  $k_5$  were determined with use of eq 8 to computer fit the pseudo-first-order rate constants,  $k_p$ , at the various  $\text{H}^+$ ,  $\text{Ni}^{2+}$  or  $\text{Co}^{2+}$ , and  $\text{Ce}^{3+}$  ion concentrations. The calculations indicated that the contribution made to the total exchange by the reaction

(15) D. W. Margerum, P. J. Menardi, and D. L. Janes, *Inorg. Chem.*, **6**, 283 (1967).

(16) E. Brücher and G. Laurency, *J. Inorg. Nucl. Chem.*, **43**, 2089 (1981).

(17) R. Király, Dissertation, Kossuth University, Debrecen, Hungary, 1975.

(18) G. Laurency, Dissertation, Kossuth Lajos University, Debrecen, Hungary, 1980.

(19) J. C. Cassatt and R. G. Wilkins, *J. Am. Chem. Soc.*, **90**, 6045 (1968).

(20) D. W. Margerum and B. A. Zabin, *J. Phys. Chem.*, **66**, 2214 (1962).

(21) A. Schlundt and H. Wendt, *Ber. Bunsenges. Phys. Chem.*, **72**, 652 (1968).

(22) T. R. Bhat, and D. Raahama, and J. Snakar, *Inorg. Chem.*, **5**, 1132 (1966).

(23) N. Tanaka, *Bull. Chem. Soc. Jpn.*, **36**, 73 (1963).

Table V. Rate Constants Obtained from the Study of the Exchange Reactions between Ce(edta)<sup>-</sup> and Ni<sup>2+</sup> as well as Co<sup>2+</sup>

M <sup>2+</sup>	$k_{1,2}$ , mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup>	$k_{2,3}$ , mol <sup>-2</sup> dm <sup>6</sup> s <sup>-1</sup>	$k_{3,4}$ , mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup>	$k_{4,5}$ , mol <sup>-2</sup> dm <sup>6</sup> s <sup>-1</sup>
Ni <sup>2+</sup>	$(5.4 \pm 0.4) \times 10^{-5}$	$2 \pm 1$	$1.3 \pm 0.1$	$(2.3 \pm 0.1) \times 10^3$
Co <sup>2+</sup>	$(2.2 \pm 0.8) \times 10^{-3}$	$(2.7 \pm 1.7) \times 10^3$	$70 \pm 20$	$(3.4 \pm 2.0) \times 10^4$

M <sup>2+</sup>	$k_{\text{CeHY}}^M$ , mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup>	$k_{\text{CeH}_2\text{Y}}^M$ , mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup>
Ni <sup>2+</sup>	$9 \times 10^5$	$1.1 \times 10^3$
	$1.9 \times 10^5$ <sup>19</sup>	$3 \times 10^3$ <sup>19</sup>
	$1.8 \times 10^5$ <sup>20</sup>	$2 \times 10^3$ <sup>20</sup>
	$1.0 \times 10^6$ <sup>21</sup>	
	$1.7 \times 10^6$ <sup>22</sup>	
Co <sup>2+</sup>	$4.8 \times 10^7$	$1.6 \times 10^4$
	$1 \times 10^7$ <sup>23</sup>	

pathway characterized by  $k_5$  never attained even 3%; accordingly, this reaction was subsequently neglected. The rate constants found are listed in Table V.

The investigation of the exchange occurring in the Ce(edta)<sup>-</sup>-Ni<sup>2+</sup> and Ce(edta)<sup>-</sup>-Co<sup>2+</sup> systems also provided a possibility for the determination of the rate constants of the relatively fast reactions between the Ni<sup>2+</sup> and Co<sup>2+</sup> ions and the ligands Hedta<sup>3-</sup> and H<sub>2</sub>edta<sup>2-</sup>. If the different conditions are taken into consideration, there is a comparatively good agreement between the resulting rate constants and those reported for similar reactions in the literature (Table V).

**Mechanism of the Exchange Reactions.** Mainly on the basis of studies with complexes of the transition metals, a general mechanism has been proposed by Margerum et al.<sup>9,11</sup> for the course of the exchange reactions of edta complexes; this mechanism can also be applied to the reactions of the lanthanide(III) complexes of edta, but attention must then be paid to the differences in coordination chemical behavior between Ln<sup>3+</sup> and the transition-metal ions. It is particularly important that the Ln<sup>3+</sup> ions favor the negatively charged oxygen donor atoms rather than the nitrogen donor atoms. Consequently, there are great differences between the structures and reactivities of the complexes Ln(Hedta) and, for example, Ni(Hedta)<sup>-</sup>, which are important from the aspect of the occurrence of the exchange reactions. The protonation of Ni(edta)<sup>2-</sup> takes place on the noncoordinated carboxylate group; thus, both of the nitrogen atoms are coordinated and the dissociation of the complex is very slow.<sup>24</sup> The contribution of exchanges taking place by the proton-catalyzed dissociation of Ce(edta)<sup>-</sup> is always significant. The structure of the protonated Ce(Hedta) complex formed in solution is not known, but on the basis of the comparatively high rate of its dissociation ( $k_{\text{CeHY}} = 53.7 \text{ s}^{-1}$ ) it may be assumed that protonation results in a more considerable decrease in the number of coordinated functional groups and the dissociation is preceded by the formation of an intermediate in which only one iminodiacetate group of the edta is coordinated to the Ce<sup>3+</sup> ion.

The values of the rate constants  $k_{\text{CeY}}^M$  and  $k_{\text{CeHY}}^M$  obtained with the various metal ions are different (Tables IV and V), and therefore the relative extent of the exchange proceeding by the direct attack of the metal ion also dependent on the nature of the exchanging metal ion. Figure 1 presents the rate constants  $k_{\text{CeY}}^M$  as a function of the water-exchange rate  $k_{\text{H}_2\text{O}}^M$  of the exchanging metal ions. The figure also shows the values of  $k_{\text{CeY}}^{\text{Cu}} = 0.37 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ <sup>10</sup> and  $k_{\text{CeY}}^{\text{Nd}} = 0.39 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ <sup>18</sup> obtained for the Cu<sup>2+</sup> and Nd<sup>3+</sup> ions ( $k_{\text{H}_2\text{O}}^{\text{Cu}}$

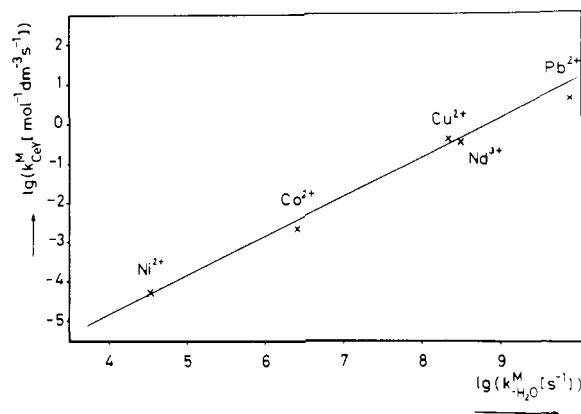


Figure 1. Dependence of the rate constants  $k_{\text{CeY}}^M$  on the rate of the water loss of the exchanging ions.

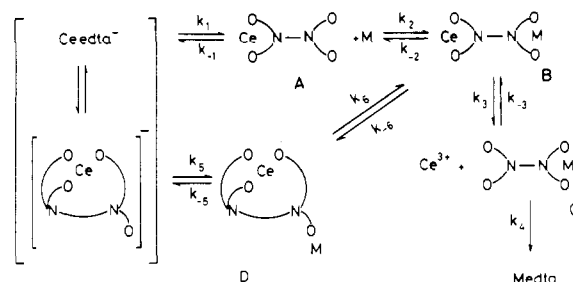


Figure 2. Assumed mechanism for transfer of edta from Ce(edta)<sup>-</sup> to the attacking metal ion.

$= 2 \times 10^8 \text{ s}^{-1}$  and  $k_{\text{H}_2\text{O}}^{\text{Nd}} = 3.1 \times 10^8 \text{ s}^{-1}$ <sup>11</sup>). In the case of the Pb<sup>2+</sup> ion,  $k_{\text{CeY}}^{\text{Pb}} = k_{\text{CeYPb}} K_{\text{CeYPb}}$ .

It can be seen from Figure 1 that the effectiveness of direct attack of the metal ion is directly proportional to the water-exchange rate of the metal ion. The linear variation of  $k_{\text{CeY}}^M$  with the rate of water loss from the exchanging metal ion can be interpreted on the basis of the general mechanism relating to the exchanging reactions of edta complexes.<sup>9,11</sup> The reaction scheme given in Figure 2 shows the assumed elementary steps taking place by the direct attack of the metal ions on the complex Ce(edta).

The concentrations of the reaction intermediates A, B, and C (Figure 2) are very low, and for the prediction of their role and importance in the exchange process, the following considerations have to be taken into account: (i) The probability of the dissociation of an iminodiacetate segment of the coordinated edta ligand is very low, because of the necessity of the cleavage of three Ln<sup>3+</sup> ion-donor atom bonds. (ii) The rate of the coordination of the iminodiacetate segment to the central metal ion in the half-unwrapped intermediates (A and C) is probably very high. (iii) In the further transformation of the binuclear and half-unwrapped intermediates their stability constants, as well as the average lifetimes of the bonds, play an important role. The average lifetime of the N-Ni and N-Co bond is much higher than that of the N-Ce bond.

With use of these considerations the following relationships can be assumed for the rate constants:  $k_{-1} \gg k_1$ ,  $k_{-1} \gg k_2$ ,  $k_3 \gg k_{-6}$ , and  $k_4 \gg k_{-3}$ . According to these relationships and the reaction scheme in Figure 2, the rate of the reaction is directly proportional to the concentration of the intermediate B. Since the rate of the formation of the intermediate B was relatively low and its accumulation was not observed, with use of the steady-state principle ( $d[B]/dt \approx 0$ ) its concentration can be expressed as

$$[B] = \frac{k_2[A][M^{2+}]}{k_{-2} + k_3} \quad (9)$$

Since species A and Ce(edta)<sup>-</sup> are in equilibrium, the rate of

(24) M. W. Grant, H. W. Dodgen, and J. P. Hunt, *J. Am. Chem. Soc.*, **93**, 6828 (1971).

(25) T. J. Bydalek and D. W. Margerum, *J. Am. Chem. Soc.*, **83**, 4326 (1961).

the exchange reaction proceeding by the direct attack of the metal ions on the complex ( $v_a$ ), through intermediates A, B, and C, is

$$v_a = \frac{k_1}{k_{-1}} \frac{k_2 k_3}{k_{-2} + k_3} [\text{Ce}(\text{edta})][\text{M}^{2+}] \quad (10)$$

Rate equation (10) can be simplified by taking into account the following considerations. With X = iminodiacetate, we have  $k_1/k_{-1} \approx K_{\text{CeX}}/K_{\text{CeY}} \approx 10^{-9.9}$  and  $k_2 \approx K^{-\text{H}_2\text{O}}_{\text{M}} K_{\text{Oe}}$ , where  $K_{\text{Oe}}$  is the stability constant of the outer-sphere complex formed by the interaction of species A and  $\text{M}^{2+}$  ( $K_{\text{Oe}} \approx 1$ ). The relative values of  $k_{-2}$  and  $k_3$  may be compared by calculating the values  $k_{-2} \approx k^{-\text{H}_2\text{O}}_{\text{M}}/K_{\text{MX}}$  and  $k_3 \approx k^{-\text{H}_2\text{O}}_{\text{Ce}}/K_{\text{CeX}}$ .<sup>11,13</sup> With consideration to these values, rate equation (10) can be written in the following simpler form for the cases of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Co}^{2+}$  as exchanging ion:

$$v_a = k^{-\text{H}_2\text{O}}_{\text{M}} \frac{K_{\text{CeX}}}{K_{\text{CeY}}} [\text{Ce}(\text{edta})][\text{M}^{2+}] \quad (11)$$

The significance of the constant  $b$  can be established from eq 11. Since this equation gives the exchange rate for the direct attack of the metal ion, the rate constant  $k^{\text{M}}_{\text{CeY}} \approx k^{-\text{M}_2\text{O}}_{\text{M}} K_{\text{CeX}}/K_{\text{CeY}}$ , and thus  $b \approx K_{\text{CeX}}/K_{\text{CeY}}$ . This implies that the constant  $b$  expresses the probability of the formation of the half-unwrapped intermediates A, which can be approximately given as the ratio of the stability constants of the complexes  $\text{Ce}(\text{imda})^+$  and  $\text{Ce}(\text{edta})^-$ . When the approximations are taken into account, the agreement between the value  $b = 10^{-9.1}$ , obtained from the slope in Figure 1, and the ratio  $K_{\text{CeX}}/K_{\text{CeY}} = 10^{-9.9}$  is acceptable.

According to these results the rate of the water loss from the exchanging metal ion plays an important role in the rate-limiting step of the exchange reactions. Similar results were found by Margerum et al. for the exchange reactions of the edta complexes of transition metals.<sup>20</sup>

The protonation of  $\text{Ce}(\text{edta})^-$  can increase the rate of the formation of the intermediate A. The rate of the exchange

proceeding by this pathway is proportional to the concentration of both the  $\text{M}^{2+}$  and the  $\text{H}^+$  ions.

The reaction between  $\text{Ce}(\text{edta})^-$  and the  $\text{Pb}^{2+}$  ion proceeds through the formation of the intermediate D. It is known from the results of  $^1\text{H}$  NMR studies that the carboxylate- $\text{Ln}^{3+}$  ion bonds are labile but that the lifetime of the "free" carboxylate group is very short.<sup>26</sup> As a result of the very high water-exchange rate of the  $\text{Pb}^{2+}(\text{aq})$  ion the probability of an encounter of a  $\text{Pb}^{2+}(\text{aq})$  ion that has lost a water molecule with the "free" carboxylate group of  $\text{Ce}(\text{edta})^-$  in an appropriate position is relatively high, when the binuclear complex D is formed. The rate of transformation of the binuclear complex D into the intermediate B is also low (but probably higher than the rate of formation of B from the intermediate A), and when the concentration of the  $\text{Pb}^{2+}$  ion is high, the concentration of the binuclear complex D can be significant. Thus the rate-determining step of the reaction here is probably connected with the formation of species B from species D.

Besides the primary importance of water-exchange rates of the attacking metal ion in the exchange reaction, some minor role is played by the concentration ratio of the complex and the metal ion.<sup>9</sup> The exchange reactions can take place in principle through intermediates A, B, and C as well as D, B, and C. If the rate of the water loss of the attacking metal ion is higher than that of the central ion and the concentration of the complex is lower than the concentration of the metal ion, then the exchange takes place predominantly through the intermediates D, B, and C. But when the rate of the water loss of the attacking metal ion is lower and its concentration is not extremely high, then the exchange is slow and predominantly proceeds by the formation of the intermediates A, B, and C.

**Registry No.** Ce, 7440-45-1; Pb, 7439-92-1; Ni, 7440-02-0; Co, 7440-48-4.

(26) T. H. Sidall and W. E. Stewart, *Inorg. Nucl. Chem. Lett.*, **4**, 421 (1969).

Contribution from the Departments of Chemistry, The Florida State University, Tallahassee, Florida 32306, and University of Houston, Houston, Texas 77004

## Solvent and Ligand Effects on the Electroreduction of Chromium Porphyrins<sup>1,2</sup>

LAWRENCE A. BOTTOMLEY and KARL M. KADISH\*

Received April 12, 1982

The electroreduction of chloro(5,10,15,20-tetraphenylporphinato)chromium(III) was investigated as a function of solvent, and the identities of all electrode reactants and products were determined via voltammetric and spectroelectrochemical experiments. Detailed oxidation-reduction mechanisms and half-wave potentials are reported for reactions in 10 different nonaqueous solvents. In dichloroethane and DMF both the Cr(II) and Cr(II)-anion-radical species were shown to axially coordinate two substituted pyridine molecules. Formation constants for these adducts were computed from electrochemical titration data. The magnitude of the formation constants was shown to be linearly related to the  $\text{p}K_a$  of the pyridine nitrogen atom.

### Introduction

Despite the recent interest in the chemistry of Cr porphyrins,<sup>3-15</sup> little has been published on the electrochemistry of this system. Ten years ago Fuhrhop, Kadish, and Davis<sup>16,17</sup>

reported that (OEP)CrOH could be oxidized in PrCN with single-electron-transfer steps at potentials of 0.79, 0.99, and 1.22 V at a Pt-button electrode. Similarly, single-electron reductions were observed at -1.14 and -1.35 V in  $\text{Me}_2\text{SO}$ . The electron transfers observed at 0.99 and -1.35 V were assigned as the electrogeneration of the  $\pi$  cation and  $\pi$  anion radicals, respectively. These assignments were based in large part on the observed  $2.25 \pm 0.15$  V difference between half-wave potentials for formation of the  $\pi$  anion and  $\pi$  cation radicals with 25 other octaethylporphyrins.<sup>16,17</sup>

\* To whom correspondence should be addressed at the University of Houston.

(1) Presented in part at the 157th Meeting of the Electrochemical Society, St. Louis, MO, May 1980 (No. 473), and in part at the 181st Meeting of the American Chemical Society, Atlanta, GA, March 1981 (INOR No. 147).