Kinetics of Ligand Exchange Between Ethylenedinitrilotetra-acetato-cuprate(II) and Triethylenetetra-aminecadmium(II)

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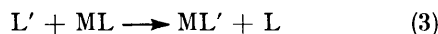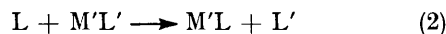
The double-ligand exchange between ethylenedinitrilotetra-acetatocuprate(II) and triethylenetetra-aminecadmium(II), $[Cu(edta)]^{2-} + [Cd(trien)]^{2+} \longrightarrow [Cu(trien)]^{2+} + [Cd(edta)]^{2-}$, has been investigated kinetically, by the stopped-flow technique, at 25.0 °C, $I = 0.2$ mol dm^{-3}, and pH 8.0—10.5, in the absence of added free ligands edta or trien. The reaction proceeds through two different pathways, (*i*) a chain-reaction mechanism {first order in $[Cu(edta)^{2-}]$ and half order in $[Cd(trien)^{2+}]$} and (*ii*) a direct double-ligand exchange (first order in both complexes). By operating under different experimental conditions it is possible to enhance the relative contribution of each pathway and to evaluate the single kinetic parameters.

THE ligand exchange between two multidentate ligand (L and L′) complexes [equation (1)] has been shown to

$$ML + M'L' \longrightarrow ML' + M'L \qquad (1)$$

proceed by a chain-reaction mechanism.[1-3] A dissociative mechanism would be governed by the rates of dissociation of either reacting complex, which, for multidentate ligand complexes, are generally slow.

Free ligands, which are in equilibrium with their complexes, can initiate the overall reaction through the chain sequence [equations (2) and (3)]. If the individual

$$L + M'L' \longrightarrow M'L + L' \qquad (2)$$

$$L' + ML \longrightarrow ML' + L \qquad (3)$$

propagating steps (2) and (3) are faster than the single dissociation steps of either ML or M′L′, the ligand-exchange rate can then be strongly enhanced by the catalytic effect of adding free ligand, L and L′, and analytical applications to the determination of trace-metal ions can be developed.[4,5]

In this paper the kinetics and mechanism of the ligand-substitution reaction between ethylenedinitrilotetra-acetatocuprate(II) $[Cu(edta)]^{2-}$ and triethylenetetra-aminecadmium(II) $[Cd(trien)]^{2+}$ are described.

Data on the reaction of $[Cu(edta)]^{2-}$ with $[Cd(trien)]^{2+}$ have been reported recently.[6] This study, conducted in the presence of an excess of free edta, refers to the catalyzed ligand-substitution reaction of $[Cd(trien)]^{2+}$ with edta.

EXPERIMENTAL

Reagents.—Ethylenedinitrilotetra-acetic acid (H_4edta) (reagent grade) was supplied by Carlo Erba. Triethylene-tetra-amine (trien) was supplied by Eastman and its aqueous solutions were prepared from the product freshly purified by distillation *in vacuo*.

Copper and cadmium perchlorates were obtained by dissolution of their carbonates in aqueous perchloric acid and successive crystallizations from water. Their solutions were titrated by standard methods. Solutions of $[Cu(edta)]$ and $[Cd(trien)]$ (charges are omitted hereafter for the sake of simplicity) were obtained by adding a slight excess (3—5%) of the desired metal to a known amount of the ligand. Excess of the metal was precipitated by increasing the pH to 10.0 and the filtered solution was then brought to pH 7.0.

Sodium perchlorate was used to bring all the solutions to ionic strength $I = 0.2$ mol dm^{-3} and borate buffer was added in order to maintain the desired pH.

Apparatus.—All kinetic runs were performed with a Durrum–Gibson stopped-flow spectrophotometer (2.00-cm path length) equipped with a Tektronix model 564 storage oscilloscope. Equilibrium spectrophotometric data were obtained with an Hitachi–Perkin-Elmer EPS 3T spectrophotometer. pH Measurements were performed with a Metrohm 388 pH meter.

Procedure.—The reaction was studied by mixing different solutions of one of the reacting complexes (3×10^{-3}—12×10^{-3} mol dm^{-3}) in turn with a solution of the other complex (3×10^{-4} mol dm^{-3}) so that the concentration of the reactant in excess could be considered as constant. Both solutions were brought to the same pH and ionic strength. The temperature was kept constant at 25.0 °C and the investigated pH range was 8.0—10.5. The progress of the reaction was monitored at 550 nm by following the formation of [Cu(trien)] ($\varepsilon = 142$ dm^3 mol^{-1} cm^{-1}).[1] At this wavelength the only other absorbing species was [Cu(edta)] ($\varepsilon = 6.02$ dm^3 mol^{-1} cm^{-1}).[1] Some measurements were performed in the presence of free ligand, *i.e.* trien for runs where [Cu(edta)] > [Cd(trien)], and edta in the other case. The ligand was added to the solution containing its complex.

RESULTS AND DISCUSSION

Reaction (4) is highly favoured to proceed to the right and the reverse reaction can be neglected; in fact the
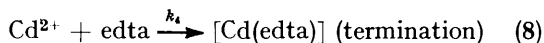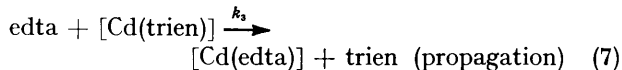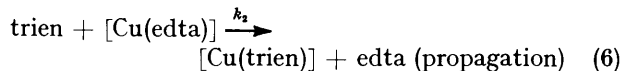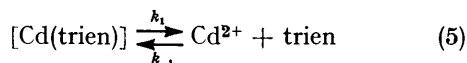
$$[Cu(edta)] + [Cd(trien)] \longrightarrow [Cu(trien)] + [Cd(edta)] \qquad (4)$$
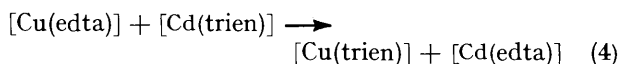
trien complexes of Cd^{II} and Cu^{II} have stability constants (log K) of 10.8 and 20.4 respectively and the edta complexes of Cu^{II} and Cd^{II} both have a value of log $K =$ 16.[7,8] Thus, the equilibrium constant of reaction (4) has the value log $K = 9.6$.

The dissociation rates of [Cu(edta)] and [Cd(trien)] can be obtained from their formation rates,[1,9] computed according to the Eigen mechanism,[10] and from their conditional stability constants: log $K_{cond.}$ are 16 and 9, at pH 9, for [Cu(edta)] and [Cd(trien)] respectively.[7] Their formation rate is governed by the water-exchange rate at the metals (log k *ca.* 8 for both metal ions);[10] therefore $k_{diss.} = k_{form.}/K_{cond.} \approx 10^{-8}$ s^{-1} for [Cu(edta)] and 0.1 s^{-1} for [Cd(trien)]. A dissociative mechanism would be governed by the slower rate, *i.e.* [Cu(edta)] decomplex-

ation, which appears to be much slower than the presently investigated rates (stopped-flow range).

Moreover, addition of free ligands has a strongly accelerating effect. These observations are consistent with a chain mechanism according to equations (5)—(8).

$$[\text{Cd(trien)}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Cd}^{2+} + \text{trien} \qquad (5)$$

$$\text{trien} + [\text{Cu(edta)}] \xrightarrow{k_2}$$
$$[\text{Cu(trien)}] + \text{edta (propagation)} \quad (6)$$

$$\text{edta} + [\text{Cd(trien)}] \xrightarrow{k_3}$$
$$[\text{Cd(edta)}] + \text{trien (propagation)} \quad (7)$$

$$\text{Cd}^{2+} + \text{edta} \xrightarrow{k_4} [\text{Cd(edta)}] \text{ (termination)} \quad (8)$$

Reaction (5) is the initiating step which produces small amounts of free trien, reactions (6) and (7) are the chain propagating steps, and reaction (8) is the terminating step. The rate of exchange is governed by the rate of one of the propagating steps, equation (9). Application

$$\text{Rate} = \frac{d[\text{Cd(edta)}]}{dt} = \frac{d[\text{Cu(trien)}]}{dt} =$$
$$k_2[\text{Cu(edta)}][\text{trien}] \quad (9)$$

of the steady-state condition to the sequence (5)—(8) enables us to obtain [edta] and [trien] which yield equation (10). Experimental runs, performed with

$$\text{Rate} =$$
$$\frac{k_1k_2[\text{Cu(edta)}][\text{Cd(trien)}](k_3[\text{Cd(trien)}] + k_4[\text{Cd}^{2+}])}{k_2k_4[\text{Cu(edta)}][\text{Cd}^{2+}] + k_{-1}[\text{Cd}^{2+}](k_3[\text{Cd(trien)}] + k_4[\text{Cd}^{2+}])}$$
$$(10)$$

[Cu(edta)] in excess, showed the reaction to be of pseudo-half order according to equation (11). In fact, plots of

$$\text{Rate} = k_a[\text{Cd(trien)}]^{\frac{1}{2}} \quad (11)$$

$(1 - \alpha^{\frac{1}{2}})$ against time {where α, the fraction of reactant remaining at time t,[11] is given by $(A_\infty - A_t)/(A_\infty - A_0)$ and A_0, A_t, and A_∞ are the absorbances at time zero, due to the absorption by [Cu(edta)], at time t, and at the end of the reaction respectively}, after a small induction period, were linear up to at least 90% completion; a test according to Powell's plot was also in agreement with an order of 0.5.[12,13]

From the slope of the above plots, k_a can be computed [11] [equation (12)]. These rate constants were found to be a

$$k_a/2 = \text{slope} \times [\text{Cd(trien)}]_0^{\frac{1}{2}} \quad (12)$$

linear function of [Cu(edta)], the reactant in excess, and decreased with pH; thus we obtain equation (13).

$$\text{Rate} = k_0[\text{Cu(edta)}][\text{Cd(trien)}]^{\frac{1}{2}} \quad (13)$$

Figure 1 shows some half-order plots for runs performed at different [Cu(edta)] values. Table 1 lists values of k_a and $k_0 = k_a/[\text{Cu(edta)}]$ under different experimental conditions.

In order to fit the observed behaviour (13) with the

general equation (10), the condition that $k_3[\text{Cd(trien)}]$ is the predominant term in the denominator of equation (10) must be assumed, and consequently the same term
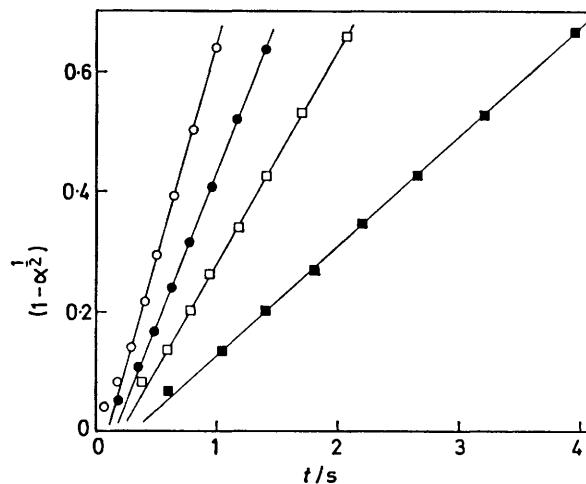

FIGURE 1 Half-order plots (see text) for reaction of an excess of [Cu(edta)] with [Cd(trien)]; pH = 9.0, [Cd(trien)] = 3 × 10⁻⁴ mol dm⁻³, 25.0 °C, [Cu(edta)] = 3 × 10⁻³ (■), 6 × 10⁻³ (□), 9 × 10⁻³ (●), 1.2 × 10⁻² (○) mol dm⁻³

will predominate in the numerator. These assumptions are reasonable, in fact k_3 (attack of edta to a cadmium

$$\text{Rate} = \frac{k_1k_2k_3[\text{Cu(edta)}][\text{Cd(trien)}]^2}{k_{-1}k_3[\text{Cd(trien)}][\text{Cd}^{2+}]} =$$
$$K_1k_2[\text{Cu(edta)}][\text{Cd(trien)}]/[\text{Cd}^{2+}] \quad (14)$$

complex) should be fairly high,[14,15] whereas [Cd²⁺] is low. Then equation (10) reduces to (14) where k_1 (see ref. 7 and

TABLE 1

Observed kinetic parameters for the reaction of an excess of [Cu(edta)] with [Cd(trien)] under different experimental conditions [a]

$10^3 S$ [b]		$10^3[\text{Cu(edta)}]$	$10^3 k_a$	k_0
s⁻¹	pH	mol dm⁻³	mol$^{\frac{1}{2}}$ dm⁻$^{\frac{3}{2}}$ s⁻¹	dm$^{\frac{3}{2}}$ mol⁻$^{\frac{1}{2}}$ s⁻¹
31	8.0	3.0	1.07	0.36
55	8.0	6.0	1.91	0.32
73	8.0	9.0	2.53	0.28
111	8.0	12.0	3.84	0.32
60	8.5	3.0	2.08	0.69
118	8.5	6.0	4.09	0.68
178	8.5	9.0	6.17	0.69
226	8.5	12.0	7.82	0.65
183	9.0	3.0	6.34	2.1
356	9.0	6.0	12.3	2.1
528	9.0	9.0	18.3	2.0
759	9.0	12.0	26.3	2.2
480	9.5	3.0	16.6	5.5
930	9.5	6.0	32.2	5.4
1 460	9.5	9.0	50.5	5.6
1 860	9.5	12.0	64.5	5.4
895	10.0	3.0	31.0	10.3
1 720	10.0	6.0	59.6	9.9
2 450	10.0	9.0	84.7	9.4
3 290	10.0	12.0	114	9.5
1 380	10.5	3.0	47.8	15.9
2 700	10.5	6.0	93.5	15.6
4 100	10.5	9.0	142	15.8
5 200	10.5	12.0	180	15.0

[a] [Cd(trien)] = 3 × 10⁻⁴ mol dm⁻³, θ_c = 25.0 °C, and I = 0.2 mol dm⁻³ (Na[ClO₄]). [b] S = Slope of the plots of $(1 - \alpha^{\frac{1}{2}})$ against time (see text).

Table 2) is the conditional instability constant of [Cd(trien)]; the concentration of Cd^{2+} and total free trien must be equal, in fact the trien subtracted by equation (6) is then replaced by equation (7); these reactions reach a common rate, depending on the extent of the dissociation (5) and consequently the rate of disappearance of trien is equal to the rate of its appearance through reaction (7). The termination step lowers both the concentration of Cd^{2+} and edta, and consequently of trien.

$$[Cd^{2+}] = [trien] = [Cd(trien)]^{\frac{1}{2}}K_1^{\frac{1}{2}} \qquad (15)$$

$$Rate = K_1^{\frac{1}{2}}k_2[Cu(edta)][Cd(trien)]^{\frac{1}{2}} \qquad (16)$$

Thus we obtain equation (15), and equation (14) becomes equation (16). Thus, $k_0 = K_1^{\frac{1}{2}}k_2$. By knowing $K_1^{\frac{1}{2}}$ it is

(trien)] in excess. Under these conditions, the assumptions made in deriving equations (14) and (16) should be even more valid and pseudo-first-order requirements should be fulfilled. Figure 2 shows some pseudo-first-order plots which show excellent linearity and Table 3 gives the derived pseudo-first-order rate constants ($k_{obs.} = 2.303 \times$ slope). Equation (16) predicts that the rate should be of half order with respect to [Cd(trien)], whereas the data show that the order is intermediate between 0.5 and unity, and that the rates are higher than those predicted by equation (16) with the values of K_1 and k_2 reported above.

Thus, another pathway must be present whose rate becomes detectable when [Cd(trien)] is in excess, and

TABLE 2

Kinetic and equilibrium parameters for the reaction of [Cd(trien)] with an excess of [Cu(edta)] [a]

pH	$\dfrac{k_0}{dm^{\frac{3}{2}} mol^{-\frac{1}{2}} s^{-1}}$	log K [b]	log $\alpha_{Cd[OH]}$ [b]	log $\alpha_{trien(H)}$ [b,c]	log $K_{cond.}$	$\dfrac{k_0(K_{cond.})^{-\frac{1}{2}}}{dm^3 mol^{-1} s^{-1}}$	$\dfrac{k_{trien}^{[Cu(edta)]}{}^{d}}{dm^3 mol^{-1} s^{-1}}$
8.0	0.32	10.75		3.3	7.45	1.7×10^3	3.5×10^3
8.5	0.68	10.75	0.2	2.4	8.15	8.1×10^3	8.0×10^3
9.0	2.1	10.75	0.4	1.5	8.85	5.6×10^4	4.5×10^4
9.5	5.5	10.75	0.8	0.8	9.15	2.0×10^5	1.4×10^5
10.0	9.8	10.75	1.6	0.3	8.85	2.6×10^5	2.7×10^5
10.5	15.6	10.75	2.4	0.1	8.25	2.1×10^5	3.6×10^5

[a] $\theta_c = 25.0$ °C, $I = 0.2$ mol dm^{-3}. [b] From ref. 7. [c] Computed with the following protonation constants for trien: log $K_1 = 10.0$, log $K_2 = 9.28$, log $K_3 = 6.75$, log $K_4 = 3.40$, from ref. 7. [d] Taken from ref. 16.

possible to compute k_2, the rate of displacement of edta by trien on Cu^{2+}. Table 2 lists the experimental k_0 values, K_1, and the computed k_2; the agreement with the
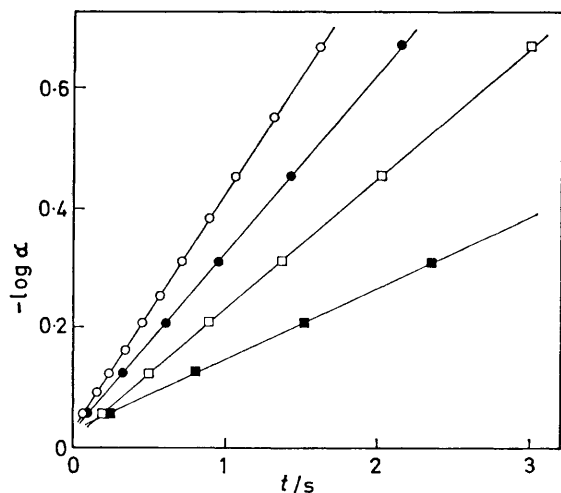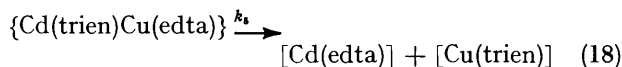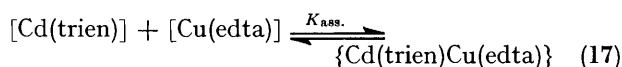

FIGURE 2 Pseudo-first-order plots (see text) for reaction of an excess of [Cd(trien)] with [Cu(edta)]; pH 9.0, [Cu(edta)] = 3×10^{-4} mol dm^{-3}, 25.0 °C, [Cd(trien)] = 3×10^{-3} (■), 6×10^{-3} (□), 9×10^{-3} (●), 1.2×10^{-2} (○) mol dm^{-3}

k_2 values obtained by Margerum and co-workers [1,16] is satisfactory and gives support to the present mechanism.*

Additional measurements were performed with [Cd-

* The value of k_2 has been obtained as a sum of the contribution of the reactions [Cu(edta)] + trien ($k = 4.3 \times 10^5$), [Cu(edta)] +Htrien+ ($k = 3.5 \times 10^4$), and [Cu(edta)] + H_2trien^{2+} ($k = 2.1 \times 10^2$ dm^3 mol^{-1} cm^{-1})[16] and with the protonation constants reported in ref. 16 (the same protonation constants used for the computer resolution of the above rate constants).

whose contribution increases the reaction order with respect to [Cd(trien)] toward unity. This could be accounted for by considering an exchange of ligands through a direct interaction of the complexes [equations (17) and (18)]. The addition of this sequence to reactions (5)—(8) yields equations (19)—(21). When [Cd(trien)] is

$$[Cd(trien)] + [Cu(edta)] \underset{}{\overset{K_{ass.}}{\rightleftharpoons}} \{Cd(trien)Cu(edta)\} \qquad (17)$$

$$\{Cd(trien)Cu(edta)\} \xrightarrow{k_5} [Cd(edta)] + [Cu(trien)] \qquad (18)$$

$$Rate = k_0[Cd(trien)]^{\frac{1}{2}}[Cu(edta)] + k_0'[Cd(trien)][Cu(edta)] = k_{obs.}[Cu(edta)] \qquad (19)$$

$$k_{obs.} = k_0[Cd(trien)]^{\frac{1}{2}} + k_0'[Cd(trien)] \qquad (20)$$

$$k_0' = K_{ass.}k_5 \qquad (21)$$

increased, the relative contribution of the second term of equation (19) becomes predominant and the order with respect to [Cd(trien)] increases toward unity; whereas when [Cu(edta)] is in excess, the first term is the major contributor, according to the half-order term.†

Figure 3 shows some plots of $k_{obs.}[Cd(trien)]^{-\frac{1}{2}}$ as a function of $[Cd(trien)]^{\frac{1}{2}}$ according to equation (20) rewritten in the linearized form [equation (22)]. Table 3

$$k_{obs.}[Cd(trien)]^{-\frac{1}{2}} = k_0 + k_0'[Cd(trien)]^{\frac{1}{2}} \qquad (22)$$

reports also the values of k_0 and k_0' obtained from such plots. The agreement between the intercepts of

† The contribution of the direct exchange of the ligands [paths (17) + (18)], for the measurements performed with [Cu(edta)] in excess, is always smaller than the contribution of the chain mechanism: the latter is favoured by a factor ranging between 5 and 15 at $\alpha = 0.5$.

TABLE 3

Pseudo-first-order rate constants $k_{obs.}$ (s^{-1}), k_0 ($dm^{\frac{3}{2}} mol^{-\frac{1}{2}} s^{-1}$), and k_0'/($dm^3 mol^{-1} s^{-1}$) for the reaction of [Cu(edta)] with an excess of [Cd(trien)] *

pH	8.0	8.5	9.0	9.5	10.0	10.5
10^3[Cd(trien)]/mol dm^{-3}						
3.0	0.055	0.103	0.27	0.64	0.86	1.18
6.0	0.101	0.186	0.50	1.01	1.43	1.94
9.0	0.128	0.261	0.68	1.54	2.00	2.55
12.0	0.175	0.32	0.91	1.90	2.46	3.36
$k_0 = $	0.5	1	2	6	9	14
$k_0' = $	10	20	55	110	125	140

* [Cu(edta)] = 3×10^{-4} mol dm^{-3}, $\theta_c = 25.0$ °C, $I = 0.2$ mol dm^{-3}.

the above plots and the k_0 values obtained in the reversed conditions gives further support to the advanced mechanism. Figure 4 shows the dependence of the rate of sequences (17) and (18) on pH. A fast detachment of one end of trien and of a carboxylato-group of edta* could be responsible for a precursor association between the complexes (2+ and 2− overall charges) with a preferential co-ordination of one end of trien to Cu at the co-ordination sites free from detached carboxylato-groups. The direct ligand exchange (17) and (18) was considered but not detected in the [Ni(trien)] + [Cu(edta)] reaction.[1] The present behaviour is then to be ascribed mainly to [Cd(trien)] which can partially

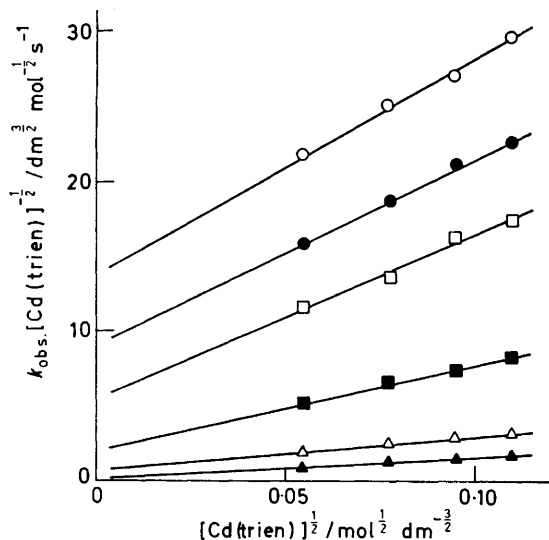FIGURE 4   Variation of k_0 (●) and of k_0' (○) as functions of pH

10^{-6}—50×10^{-6} mol dm^{-3}) the rates were greatly increased; in fact free ligands enhance the effectiveness of the chain-propagation steps. Analytical applications of this effect to the kinetic determination of metal ions in solution could be developed according to previously described procedures.[4,5]

FIGURE 3   Plots of $k_{obs.}$[Cd(trien)]$^{-\frac{1}{2}}$ as a function of [Cd(trien)]$^{\frac{1}{2}}$ for reaction of an excess of [Cd(trien)] with [Cu(edta)]; 25.0 °C, [Cu(edta)] = 3×10^{-4} mol dm^{-3}, pH = 10.5 (○), 10.0 (●), 9.5 (□), 9.0 (■), 8.5 (△), 8.0 (▲)

dissociate to a larger extent than [Ni(trien)] to give the intermediate of reaction (17).

Additional measurements were performed by adding free edta or trien to the reaction mixtures (see the Experimental section). In both cases (additions of 5 ×

* It has been shown that, in the displacement from one metal ion to another in a polyaminopolycarboxylic ligand complex, the first dissociation steps involve very fast detachment of co-ordinated groups from the outgoing metal (see E. Mentasti and E. Pelizzetti, *Inorg. Chem.*, 1978, **17**, 3133, and refs. therein).
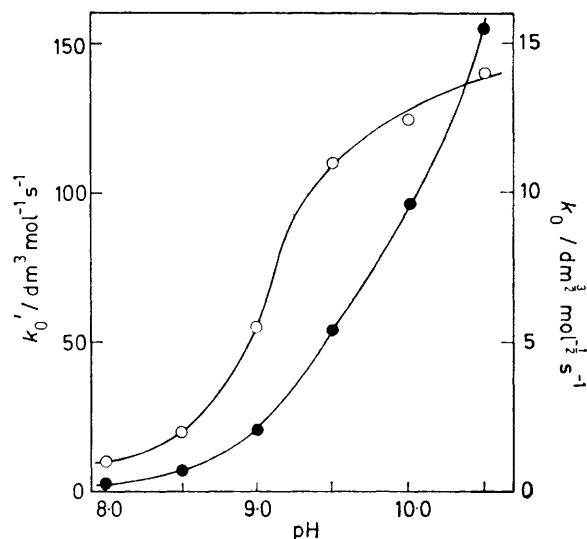
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