

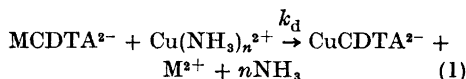
Exchange Reactions of *trans*-1,2-Diaminocyclohexanetetraacetate Complexes of Alkaline Earth Ions in the pH Range 8.5–10.5

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The exchange reactions between the alkaline earth complexes of *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetate (CDTA) and Cu(II) or Pb(II) have been studied by Margerum *et al.*¹ and Pausch and Margerum.² The reaction rate was shown to be independent of the Cu(II) and Pb(II) concentrations. Furthermore, a linear relation was found between the reaction rate constant and the hydrogen ion concentration. The pH range investigated was 5.5–7.6 for Mg-, Ca- and SrCDTA and 7.0–7.6 for BaCDTA.

The present communication describes the exchange reaction between the alkaline earth complexes of CDTA and Cu(II) in the pH range 8.5–10.5. The overall reaction is shown in (1). The rate of reaction was measured at 380 or 800 nm on a Durrum-Gibson stopped flow spec-



trophotometer for M=Ba²⁺ or Sr²⁺ and on a Beckman DK-2 spectrophotometer for M=Ca²⁺ or Mg²⁺. The initial concentration of MCDTA²⁻ was 10⁻³ M, and the ionic strength and pH were adjusted using NH₄NO₃ and NH₃.

The rate of reaction (1) is independent of the concentration of Cu(NH₃)_n²⁺ when Cu²⁺ is used in an excess of 50–100. Reaction (1) is accordingly pseudo first order at constant pH with the rate constant *k*_d.

A plot of *k*_d versus [H⁺] for M=Ca²⁺ (cf. Fig. 1) indicates in the investigated pH range a linear relationship between *k*_d and [H⁺] which agrees with eqns. (2) and (3) as stated by Margerum *et al.*¹ and Pausch and Margerum.² Furthermore, titration curves of MCDTA²⁻ (M=Mg²⁺, Ca²⁺, Sr²⁺ or Ba²⁺) show that MHCDTA⁻ and M(OH)CDTA³⁻ are not found in the solutions used in the present investigation

where the hydrogen ion concentration is low.

$$\frac{d[\text{CuCDTA}^{2-}]}{dt} = k_d[\text{MCDTA}^{2-}] = k^{\text{MCDTA}}[\text{MCDTA}^{2-}] + k_{\text{H}}^{\text{MCDTA}}[\text{H}^+][\text{MCDTA}^{2-}] \quad (2)$$

$$k_d = k^{\text{MCDTA}} + k_{\text{H}}^{\text{MCDTA}}[\text{H}^+] \quad (3)$$

Figs. 2, 3, and 4 show plots of *k*_d versus [H⁺] for M=Mg²⁺, Sr²⁺, and Ba²⁺, respectively. From these plots it is seen that eqn. (2) is quantitatively correct only in the pH range 8.5–9.2.

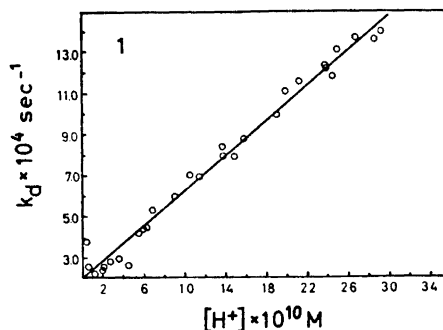
k^{MCDTA} and *k*_H^{MCDTA} in Table 1 have been calculated from Figs. 1, 2, 3, and 4 using the relationship given in eqn. (3). The calculation for M=Mg²⁺, Sr²⁺, and Ba²⁺ has been carried out in the pH range mentioned above where the linear

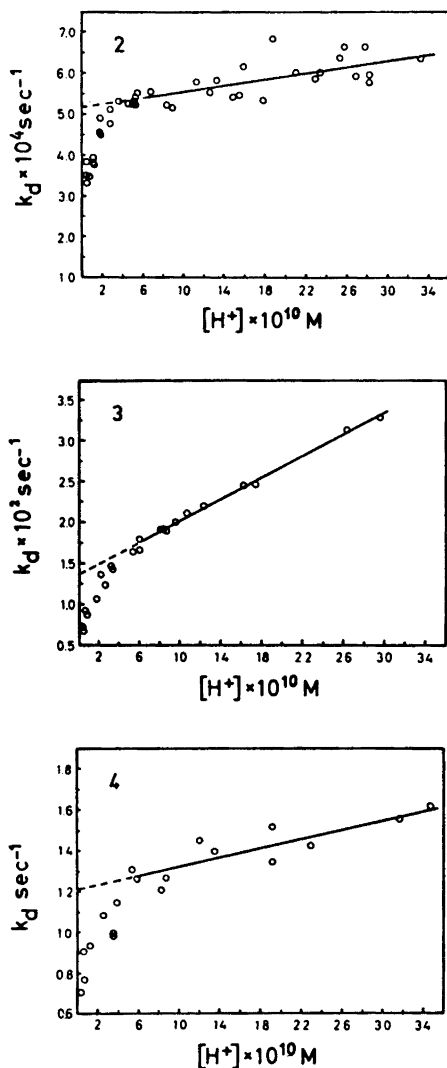
Table 1. Rate constants for the dissociation of MCDTA²⁻ complexes.^a

M ²⁺	<i>k</i> ^{MCDTA} sec ⁻¹	<i>k</i> _H ^{MCDTA} M ⁻¹ sec ⁻¹	pH range
Mg	5.2 × 10 ⁻⁴ (0) ^b	3.8 × 10 ⁴ (6.33 × 10 ⁴) ^b	8.5–9.2 (5.5–7.6) ^b
Ca	2.1 × 10 ⁻⁴ (0) ^b	4.2 × 10 ⁵ (4.14 × 10 ⁵) ^b	8.5–10.5 (5.5–7.6) ^b
Sr	1.4 × 10 ⁻² (3.0 × 10 ⁻²) ^b	6.7 × 10 ⁶ (6.06 × 10 ⁶) ^b	8.5–9.2 (5.5–7.6) ^b
Ba	1.2 (4.4) ^b	1.1 × 10 ⁸ (1.05 × 10 ⁸) ^b	8.5–9.2 (7.0–7.6) ^b

^a Calculated from eqn. (3) by a least squares method; for the calculation of *k*^{MCDTA} see text; initial [MCDTA²⁻] = 10⁻³ M; [Cu(NH₃)_n²⁺] = 10⁻¹ M; NH₄⁺/NH₃ buffer; μ = 0.5; 25.0°C.

^b From Ref. 2; μ = 0.5; 25.0°C.





Figs. 1–4. Hydrogen ion dependence on the observed first-order rate constants k_d for, respectively, CaCDTA^{2-} , MgCDTA^{2-} , SrCDTA^{2-} , and BaCDTA^{2-} .

relation between k_d and $[\text{H}^+]$ exists. These two rate constants have also been determined by Pausch and Margerum.² Satisfactory agreement was found between their values and the constants calculated in the present work (Table 1).

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Figs. 2, 3, and 4 also show that the plots of k_d versus $[\text{H}^+]$ deviate from the straight line in the pH range 9.2–10.5 for $\text{M}=\text{Mg}^{2+}$, Sr^{2+} or Ba^{2+} . Eqn. (3) is therefore not correct. $k_{\text{H}^{\text{MCDTA}}}$, when interpreted as the rate constant for the direct dissociation of the CDTA complex, is accordingly smaller than stated in Table 1.

From the observed $[\text{H}^+]$ profile, it is reasonable to conclude that $k_{\text{H}^{\text{MCDTA}}}$ is probably a complex function of the hydrogen ion concentration. The $[\text{H}^+]$ dependence of $k_{\text{H}^{\text{MCDTA}}}$ is negligible for $\text{pH} < 9.2$; cf. Table 1.

Nyssen and Margerum³ have studied the kinetics of both dissociation and formation of LaCDTA^- in the pH range 4.2–6.0. Eqn. (3) was found to be valid for the dissociation. These authors³ have shown that the rate-determining step for the formation of LaCDTA^- had to be placed after a fast formation of a reaction intermediate. The rate-determining step of formation of LaCDTA^- , as well as of the alkaline earth complexes of CDTA,² is not the characteristic water exchange rate of the hydrated metal ion. Furthermore, the rate of formation of LaCDTA^- was found to increase with decreasing $[\text{H}^+]$.³

The $[\text{H}^+]$ profile in Figs. 2, 3, and 4 may possibly be explained by assuming the same kinetics of formation for LaCDTA^- and for MCDTA^{2-} ($\text{M}^{2+}=\text{Mg}^{2+}$, Sr^{2+} or Ba^{2+}). The complexity of $k_{\text{H}^{\text{MCDTA}}}$ in this investigation may then be rendered more comprehensible by using a “Steady State” approximation for the reaction intermediate similar to that described for LaCDTA^- .

Parallel studies⁴ on the rate of dissociation of these complexes are being carried out in this laboratory using the exchange of optically active CDTA instead of metal ion exchange. The studies confirm the $[\text{H}^+]$ profile of these reactions for $\text{M}^{2+}=\text{Mg}^{2+}$, Ca^{2+} , Sr^{2+} or Ba^{2+} .

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