TABLE III

ANALYTICAL DATA FOR THE COMPLEXES OF THE TYPE [Au(N–N)Cl₂]X

(N–N)	X⁻	Au, % Calcd	Au, % Found	C, % Calcd	C, % Found	N, % Calcd	N, % Found	H, % Calcd	H, % Found
1,10-phen	Cl⁻	40.77	40.1	29.79	29.3	5.79	5.75	1.67	1.60
bipy	Cl⁻	42.89	43.5	26.12	25.9	6.09	5.89	1.75	1.80
5-NO₂-1,10-phen	ClO₄⁻	33.26	32.50	24.31	23.7	7.09	6.43	1.19	1.11

lytical data for all of the complexes required are collected in Table III. Acetone was purified and dried by successive distillation over $KMnO_4$ and K_2CO_3, respectively. The substituted pyridines were commercial samples which were purified by distillation over KOH pellets.

Kinetics.—Freshly prepared solutions of the complex and the amine were brought to the reaction temperature separately and mixed in the thermostated cell of an Optica-CF4 double-beam recording spectrophotometer. The changes in optical density were followed by scanning the near-ultraviolet spectrum in the range 315–360 mμ at various times or, after preliminary experiments, by following the optical density change at a wavelength where

there was a maximum change and where rate constants could be conveniently calculated. All the experiments were carried out in the presence of an excess of amine in order to avoid possible equilibria and to have first-order kinetics. The observed rate constants for each experiment were calculated from the plot of log $(D_\infty - D_t)$ against time. Some reactions were repeated several times under the same conditions and the reproducibility was better than 5%. Conductivity measurements were carried out by means of an LKB 3216B conductivity bridge.

Multidentate Ligand Kinetics. X. Exchange Reactions of Metal(II)–Cyclohexylenediaminetetraacetate Complexes

BY DALE W. MARGERUM, P. J. MENARDI, AND D. L. JANES

The exchange reactions of divalent metal ion complexes of *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate (CyDTA) with aquometal ions are sluggish compared to the corresponding reactions of EDTA complexes. Nine metal(II)–CyDTA complexes are studied and in each case the rate of exchange is independent of the concentration of the aquometal ion and depends only upon the acid-dissociation rate of the complex. Second-order rate constants (M^{-1} sec^{-1}, 25°, 0.1 μ) for the reaction of hydrogen ion with metal(II)–CyDTA are 5.6 × 10⁴ (Mg), 7.1 × 10⁵ (Ca), 320 (Mn), 3.2 (Co), 3.5 × 10⁻⁴ (Ni), 3.9 (Cu), 170 (Zn), 23 (Pb), and 3.1 (Hg). The rate constants for Co, Ni, Cu, and Zn are consistent with a stepwise-dissociation path in which a proton adds to one of the CyDTA nitrogen atoms before the second metal–nitrogen bond breaks. Thus, the values for the rate constants are in remarkable agreement with values predicted from the characteristic water substitution rate constants of the metal ions and the CyDTA stability constants for hydrogen ion and the metal ions. In contrast Mn, Mg, and Ca depart significantly from this behavior and the rate constants are ¹/₁₀ to ¹/₆₀₀ as large as would be predicted. A mechanism is proposed for these complexes in which two metal–nitrogen bonds are broken in succession as a proton is added to one nitrogen. In this mechanism the water substitution rate constant of the metal ion is no longer applicable because several coordinate bonds are broken in the rate-determining step and the kinetics are not characteristic of a stepwise process.

Introduction

The cyclohexane ring in CyDTA prevents this multidentate ligand from undergoing a process of simultaneous unwrapping and transfer of its coordinating groups from one metal ion to another which is characteristic of EDTA.[1,2] Earlier papers in this series showed that nickel–CyDTA[1] and mercury–CyDTA[3] complexes exchange with copper and other metal ions at a rate which depends on the hydrogen ion concentration but not on the concentration of aquometal ions. In the present work the CyDTA complexes of seven other divalent metal ions from various groups of the periodic table show the same type of kinetic behavior.
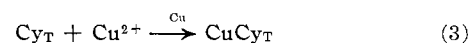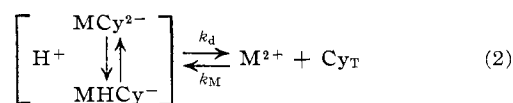
The general exchange reaction with copper is

(1) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **2**, 683 (1963).
(2) D. W. Margerum, D. L. Janes, and H. M. Rosen, *J. Am. Chem. Soc.*, **87**, 4463 (1965).
(3) D. L. Janes and D. W. Margerum, *Inorg. Chem.*, **5**, 1135 (1966).

$$MCy^{2-} + Cu^{2+} \longrightarrow CuCy^{2-} + M^{2+} \qquad (1)$$
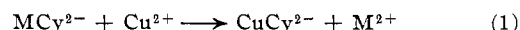
where M^{2+} is Mg, Ca, Mn, Co, Ni, Cu (exchanging with Pb), Zn, Hg, or Pb, and Cy^{4-} is *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate (CyDTA). However, no direct kinetic interaction between Cu^{2+} and MCy^{2-} is observed, and the kinetic system is

$$\left[H^+ \begin{array}{c} MCy^{2-} \\ \updownarrow \\ MHCy^- \end{array} \right] \underset{k_M}{\overset{k_d}{\rightleftarrows}} M^{2+} + Cy_T \qquad (2)$$

$$Cy_T + Cu^{2+} \xrightarrow{Cu} CuCy_T \qquad (3)$$

where $Cy_T = Cy^{4-} + HCy^{3-} + H_2Cy^{2-} + H_3Cy^-$ and $MCy_T = MCy^{2-} + MHCy^-$. A steady-state approximation is appropriate for Cy_T because its concentration is extremely small in the presence of excess copper ion. Equation 4 can be simplified to eq 5 if

$$\text{exchange rate} = \frac{k_d k_{Cu}[Cu^{2+}][MCy_T]}{k_{Cu}[Cu^{2+}] + k_M[M^{2+}]} \quad (4)$$

the experimental conditions are adjusted to give $k_{Cu}[Cu^{2+}] \gg k_M[M^{2+}]$.

$$\frac{d[CuCy_T]}{dt} = \frac{-d[MCy_T]}{dt} = k_d[MCy_T] \quad (5)$$

The value of the dissociation rate constant, k_d, depends on the hydrogen ion concentration with the general relation given in eq 6. The value of k^{MCy} is so

$$k_d[MCy_T] = k^{MCy}[MCy^{2-}] + k_H^{MCy}[H^+][MCy^{2-}] + k_H^{MHCy}[H^+][MHCy^-] \quad (6)$$

small that for most metals the contribution from this term is negligible. The value of k_H^{MCy} is determined for each of the nine metal(II)–CyDTA complexes. The values of k_H^{MHCy} are determined for several cases to assure accurate values for k_H^{MCy}.

Experimental Section

The acid form of CyDTA was reagent grade material obtained from LaMont Laboratories and from Fluka Chemical Co. It was recrystallized twice by dissolving in dilute base followed by the addition of $HClO_4$. Solutions were standardized with copper using Murexide indicator.

Perchlorate salts were used in all of the experiments. The metal(II) perchlorates were prepared from the corresponding carbonates or oxides and recrystallized. Solutions were standardized by complexometric titration with EDTA or CyDTA. Solutions of Na_2CaCy, Na_2HgCy, and Na_2PbCy were prepared by stoichiometric addition of H_4Cy, $M(ClO_4)_2$, and NaOH. The $MgCy^{2-}$ solution was prepared with a 10% excess of $Mg(ClO_4)_2$. Solutions of Na_2MnCy, Na_2CoCy, Na_2NiCy, Na_2CuCy, and Na_2ZnCy were prepared by adding a slight excess of metal perchlorate to H_4Cy followed by the addition of NaOH first to give the complex and then to precipitate the excess metal. The solutions were filtered and stored at pH 10.

Recrystallized $NaClO_4$ was used to keep the ionic strength constant at 0.10 M (except for 0.050 M for zinc–CyDTA). In general, the buffer was 2,6-lutidinium perchlorate (5.0 × 10^{-3} M with NaOH added to adjust the pH). Practical grade 2,6-lutidine (Matheson Coleman and Bell) was distilled (142.5–143.5°) and crystals of the perchlorate salt were prepared. In a few cases a borate–mannitol buffer was used (5.0 × 10^{-3} to 1.2 × 10^{-2} M borate with mannitol added to adjust the pH).

Reactions were followed spectrophotometrically by measuring the absorbance of copper–CyDTA at 310 mμ or in a few cases at 270 mμ. With cobalt as a scavenger, 240 mμ was used. The rate of formation of nickel–CyDTA was studied at 230 mμ (ϵ_{Cy} 424, ϵ_{Ni} <1.0, ϵ_{NiCy} 1613). A Cary 14 (or a Beckman DU) spectrophotometer, thermostated to ±0.1°, was used for the exchange studies. Most reactions were followed to completion or for at least 2 half-lives. First-order rate constants in agreement with eq 5 were obtained from plots of log $(A_\infty - A)$ against time where A_∞ is the absorbance when the reaction is complete. Conditions were adjusted to make the reverse reaction in eq 2 negligible compared to the reaction with copper ion acting as the scavenger.

Some reactions were very fast including the exchange of copper with magnesium–CyDTA, calcium–CyDTA, and the formation reaction of nickel–CyDTA. A stopped-flow mixing system[4,5] with mixing times of a few milliseconds was attached to a Beckman DU and a Tektronix 564 storage oscilloscope. A few of the Mg–CyDTA reactions with copper were followed with

the Cary 14 using a small plastic plunger to mix reactants in a rectangular cell in less than 10 sec.

The exchange reaction of Ni–CyDTA was extremely slow. At pH 5 the reaction half-life is calculated to be 6.5 years. Only the first 5% of the exchange was followed, but this still required days or weeks depending on the pH. This study gave a sensitive way of detecting impurities in the CyDTA. Thus, one source of CyDTA showed a minor component to be present representing 0.2% of the total nickel–CyDTA. This impurity reacted with copper in the first few hours. Following a little burst of absorbance, the reaction proceeded for an entire week at a rate attributed to Ni–CyDTA itself. The initial rate had both a copper and a hydrogen ion dependence. Another source of recrystallized CyDTA did not show the same behavior but had a slight absorbance jump on mixing. The faster reacting component is attributed to some more labile derivative of CyDTA. It is present in such small amounts that it could not be observed in the reactions of the other metals, which were based on several half-lives rather than a few per cent reaction. The slower reaction of the nickel complex had a reproducible rate with no copper dependence and it was the major component. Hence, it was used to give the dissociation rate constant.

The stability constants for the CyDTA complexes were taken from Anderegg[6] (20.0°, 0.10 μ) and were corrected to values at 25° using his heats of formation. This gave the following log K stability constants of interest to the present study: HCy^{3-} (12.27), H_2Cy^{2-} (6.09), $MgCy^{2-}$ (11.02), $CaCy^{2-}$ (13.10), $MnCy^{2-}$ (17.38), $CoCy^{2-}$ (19.53), $CuCy^{2-}$ (21.87), $ZnCy^{2-}$ (19.30), $HgCy^{2-}$ (24.74), $PbCy^{2-}$ (20.19). Constants for the protonated complexes were used from work[7] at 0.1 μ and 20°.

Results

Exchanging Metal Ion as a Scavenger.—Each metal–CyDTA complex was studied in an exchange reaction such as eq 1 and gave a first-order kinetic dependence in accord with eq 5. Variation of the scavenger metal ion concentration was tested in each case to prove that the observed rate constant was, in fact, independent of the exchanging metal ion concentration. Two scavengers, cobalt and copper, were tested with manganese–CyDTA and gave the same results. In the case of copper–CyDTA the scavenger was lead ion. In all other cases it was Cu(II) and the general requirement was that $k_{Cu}[Cu^{2+}] \gg k_M[M^{2+}]$ in order to give dissociation rate constants. The characteristic rate constant reported[8] for substitution in the first coordination sphere of copper is 2 × 10^8 sec^{-1} while the values for nickel, magnesium, and cobalt are from 2 × 10^4 to 10^6 sec^{-1}. Hence, a large excess of copper is not needed to make the $k_{Cu}[Cu^{2+}]$ term much larger than $k_M[M^{2+}]$. On the other hand, the characteristic rate constants for water substitution of manganese, calcium, zinc, and mercury are from 3 × 10^7 to 2 × 10^9 sec^{-1} so that a large excess of copper would seem to be required. This was true with zinc–CyDTA where reactions below pH 5 with only 25% excess copper showed a copper dependence. Therefore, a 50-fold excess of copper was used. However, at higher pH a large excess of copper was not required. This appears to be due to an increase in the ratio k_{Cu}/k_{Zn}. Enhanced kinetic reactivity of hydrolyzed copper has been observed in several systems.[9,10] In the

(4) J. M. Sturtevant in "Rapid Mixing and Sampling Techniques in Biochemistry," B. Chance, *et al.*, Ed., Academic Press Inc., New York, N. Y., 1964, p 89.

(5) D. W. Margerum and J. D. Carr, *J. Am. Chem. Soc.*, **88**, 1639 (1966).

(6) G. Anderegg, *Helv. Chim. Acta*, **46**, 1833 (1963).

(7) G. Schwarzenbach, R. Gut, and G. Anderegg, *ibid.*, **37**, 937 (1954).

(8) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

(9) D. W. Margerum, B. A. Zabin, and D. L. Janes, *Inorg. Chem.*, **5**, 250 (1966).

(10) P. J. Menardi, Ph.D. Thesis, Purdue University, 1966.

reaction of copper with mercury–CyDTA a similar pH effect was found, but the enhanced reactivity of copper is not sufficient to account for the effect, and the ratio k_{Cu}/k_{Hg} must be affected by hydrolysis of mercury. Calcium ion has a fast water exchange rate and it does not hydrolyze so it was a surprise that in the exchange with calcium–CyDTA there was no copper dependence even when copper was at low concentrations. This is indirect evidence for a k_{Ca} value much less than the characteristic substitution of water in the aquo calcium ion. Other evidence supports a slower than expected reaction with CyDTA in the work which follows. A similar situation was the exchange of cobalt and Mn–CyDTA where a 10- to 30-fold excess of cobalt was sufficient to make $k_{Co}[Co^{2+}] \gg k_M [Mn^{2+}]$. As will be seen, the manganese reaction with CyDTA also is slower than the water substitution rate constant would predict, or else this would not be possible.

Resolution of Rate Constants with $[H^+]$.—In each exchange reaction the rate of the exchange decreased as the pH increased and the rate was independent of the concentration of the metal ion scavenger. Figure 1 shows that the observed rate constants for calcium–CyDTA and magnesium–CyDTA have a first-order hydrogen ion dependence. The concentrations of MgHCy⁻ and CaHCy⁻ were negligible and the last term in eq 6 did not contribute to the rate. In Figure 1 the intercepts are zero so the k^{MCy} terms also are negligible. The slopes give k_H^{MgCy} and k_H^{CaCy}, and these rate constants fully describe the kinetic behavior of the exchange reaction. Similar plots were obtained for the CyDTA complexes of Mn, Ni, Zn, and Pb. The reactions of cobalt–CyDTA and copper–CyDTA were studied at sufficiently low pH to give a significant kinetic contribution from CoHCy⁻ and CuHCy⁻. Data for these systems were resolved using eq 7 where K_{MHCy}

$$k_0(1 + K_{MHCy}[H^+])/[H^+] = k_H^{MCy} + k_H^{MHCy}K_{MHCy}[H^+] \quad (7)$$

is the protonation constant[7] of MCy^{2-}. Figure 2 shows the resolution for the cobalt system.

In every case except mercury–CyDTA the first term in eq 6 was negligible and only the proton-assisted dissociation path was observed even at pH 6–7. As discussed earlier[3] there may be a reaction between H⁺ and HgCyOH³⁻ in the case of mercury, which accounts for its different behavior.

The resolved rate constants (Table I) give a value for the proton reaction with each metal–CyDTA complex. Earlier work[1] gave k_H^{NiCy}, k_H^{NiHCy}, and $k_H^{NiH_2Cy}$ values at an ionic strength of 1.25. The present work determined the k_H^{NiCy} constant at 0.10 μ and verified the behavior in the pH range of 4–5.

Temperature Dependence.—Three of the kinetic systems (Mn, Zn, and Pb) were chosen for temperature studies and a complete pH study was done at each temperature. The k_H^{MCy} values gave excellent Arrhenius plots. The results are summarized in Table II.[11] These three CyDTA complexes were picked because their k_H^{MCy} values at 25° were of the same order of magnitude. There is a striking difference in the
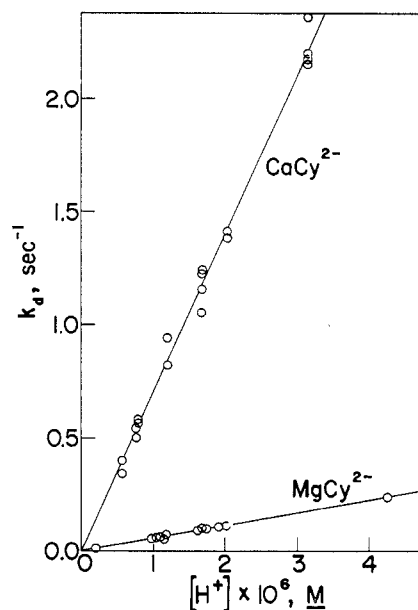

Figure 1.—Effect of hydrogen ion concentration on the dissociation rate constant of $CaCy^{2-}$ and $MgCy^{2-}$ at 25.0°, μ = 0.1. Initial $[CaCy^{2-}] = 2.50 \times 10^{-4}$, initial $[MgCy^{2-}] = 2.02 \times 10^{-4}$, and $[Cu^{2+}]$ varied from 4×10^{-4} to 1.2×10^{-3} M.
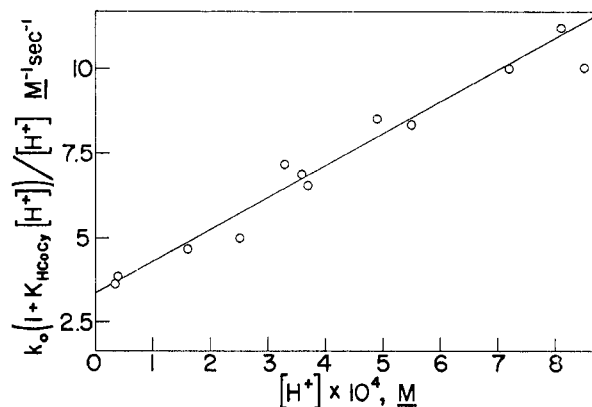

Figure 2.—Effect of hydrogen ion concentration on the dissociation constant of Co-CyDTA at 25.0°, μ = 0.1.

kinetic parameters for the proton reaction with zinc–CyDTA compared to manganese– or lead–CyDTA.

Kinetics of Formation of Ni-CyDTA and its Stability Constants.—The rate of formation of nickel–CyDTA was measured with a stopped-flow mixing apparatus in the pH range 7.49–7.87. At this pH HCy^{3-} is the main species of free CyDTA present with smaller concentrations of H_2Cy^{2-}. To a first approximation the observed rate constant equals k_{Ni}^{HCy}, but the rate constants were evaluated in terms of both HCy^{3-} and H_2Cy^{2-} using eq 8, which is plotted in Figure 3.

$$k_0\left(1 + \frac{1}{[H^+]K_{H_2Cy}}\right) = k_{Ni}^{H_2Cy} + \frac{k_{Ni}^{HCy}}{K_{H_2Cy}[H^+]} \quad (8)$$

The reaction half-lives were in the vicinity of 30 msec and there was some scatter in the data at each pH.

CyDTA Complex of	pH range	Temp, °C	k_H^{MCy}, M^{-1} sec^{-1}	k_H^{MHCy}, M^{-1} sec^{-1}
Mg	5.3–6.7	25.0	5.6×10^4	...
Ca	5.5–6.3	25.0	7.1×10^5	...
Mn	4.6–6.3	10.0	66	...
	4.7–6.1	25.0	315	...
	5.1–5.9	25.0	317[a]	...
	4.4–5.6	39.3	1180	...
Co	3.1–5.5	25.0	3.2	12
Ni	4.0–5.2	25.0	3.4×10^{-4}	...
Cu[b]	2.9–4.8	25.0	3.9	4.9
Zn[c]	4.2–5.9	15.0	103	...
	4.5–6.8	25.0	169	...
	4.5–5.9	35.3	280	...
Hg	3.6–5.7	25.0	3.1	...
Pb	4.6–5.9	10.0	4.0	...
	4.3–5.8	25.0	23	...
	4.3–5.7	39.3	78	...

[a] Co(II) as scavenger.   [b] Pb(II) as scavenger.   [c] 0.05 μ.

TABLE II
KINETIC PARAMETERS FOR H$^+$ REACTION WITH MCy^{2-}

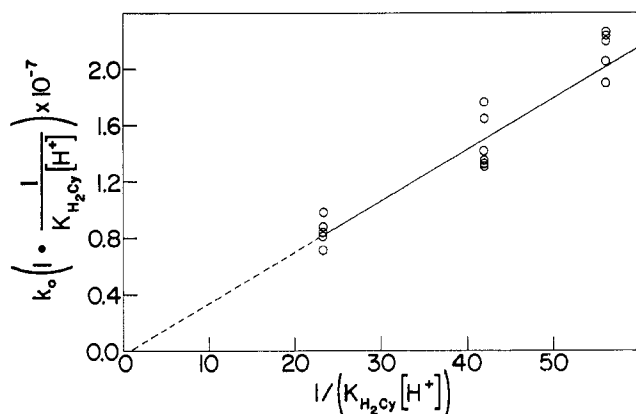|	k_H^{MnCy}	k_H^{ZnCy}	k_H^{PbCy}
E_a, kcal	17.0	8.7	17.3
A, M^{-1} sec^{-1}	1.0×10^{15}	4.0×10^8	1.2×10^{14}
$\Delta H^\ddagger$, kcal	16.4	8.1	16.7
$\Delta S^\ddagger$, eu	+10	−21	+5.8

Figure 3.—Resolution of the rate constants for the formation reaction of nickel(II) with CyDTA at 25.0°, μ = 0.1. Initial [Ni^{2+}] = [CyDTA] = 9.45×10^{-5}.

The line in Figure 3 is a least-squares fit of the data which gives a value of $(3.6 \pm 0.3) \times 10^5 \, M^{-1}$ sec^{-1} for k_{Ni}^{HCy} and indicates that by comparison the value of $k_{Ni}^{H_2Cy}$ is negligible. This gives a direct measure of the rate constant for the reaction with HCy^{3-} rather than extrapolating a value from lower pH. Nickel hydrolysis[12] is not of concern in this pH region (log K_h = −10.1). It is interesting that the rate constant for the reaction with EDTA (Ni^{2+} + HY^{3-}) is $1.8 \times 10^5 \, M^{-1}$ sec^{-1}.[13]

Anderegg[6] did not report the stability constant for NiCy^{2-} because of its extreme sluggishness, but the

(12) D. D. Perrin, *J. Chem. Soc.*, 3644 (1964).
(13) D. W. Margerum and B. A. Zabin, *J. Phys. Chem.*, **66**, 2214 (1962).

present kinetic data plus the acidity constant for HCy^{3-} give log K_{NiCy} = 21.35 ± 0.03 (25.0°, 0.10 μ). This is consistent with the values Anderegg found for the other transition metals. It also is consistent with the value determined kinetically[1] at μ = 1.25 which is log K_{NiCy} = 20.5 (corrected from the reported value of 19.9 because of the change of log K_{HCy} from 11.7[14] to 12.3[6]). Another determination of the stability constant of NiCyDTA from equilibrium measurements[15] gave log K_{NiCy} = 20.0 at 25°, 0.1 μ (corrected from 19.4), but it seems very probable that the extreme sluggishness of the equilibration might have caused errors. The kinetically determined constant is not subject to the errors caused by a pseudo equilibrium state and it is used for the subsequent discussions.

Discussion

Predicted Rate Constants.—In the CyDTA exchange kinetics, the same reaction (eq 9) can be studied

$$MCy^{2-} + H^+ \underset{k_M^{HCy}}{\overset{k_H^{MCy}}{\rightleftharpoons}} HCy^{3-} + M^{2-} \qquad (9)$$
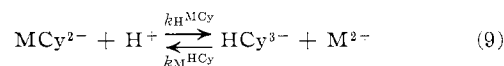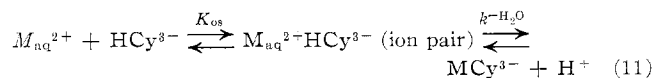
for many metal ions and a direct comparison can be made of the effect of the metal ion on the reaction rate. Furthermore, the experimental values of k_H^{MCy} can be compared to calculated values (eq 10) using the known stability constants and the formation rate constant (k_M^{HCy})

$$k_H^{MCy} = k_M^{HCy}\frac{K_{HCy}}{K_{MCy}} = k_M^{-H_2O}K_{os}\frac{K_{HCy}}{K_{MCy}} \qquad (10)$$

expected for the reaction of each aquo metal ion with HCy^{3-}.

Ion-Pair Mechanism.—Formation rate constants of many complexes have been observed to correspond to the product of the characteristic water substitution rate constant $(k_M^{-H_2O})$ and the outer-sphere association constant (K_{os}) of the reacting ions.[16] The experimental formation rate constant, k_{Ni}^{HCy} = 3.6×10^5 M^{-1} sec^{-1}, can serve as a reference to calculate the K_{os} value (eq 11) because the characteristic water sub-

$$M_{aq}^{2+} + HCy^{3-} \underset{}{\overset{K_{os}}{\rightleftharpoons}} M_{aq}^{2-}\cdot HCy^{3-} \text{ (ion pair)} \overset{k^{-H_2O}}{\rightleftharpoons}$$
$$MCy^{3-} + H^+ \quad (11)$$

stitution constant for nickel is well known ($k_{Ni}^{-H_2O}$ = 2.7×10^4 sec^{-1}).[8,17] This gives a K_{os} value of 13 which is reasonable for an outer-sphere association of 2+ and 3− ions. Thus, the outer-sphere association constant for Cr(H$_2$O)$_6^{3+}$ with SO$_4^{2-}$ is equal to 12[18] and the constants for [Co(NH$_3$)$_5$H$_2$O]$^{3+}$ with SCN$^-$, SO$_4^{2-}$, H$_2$PO$_4^-$ are 2–12 at moderate ionic strengths.[19] If K_{os} values are calculated from the EDTA reaction

(14) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **32**, 1682 (1949).
(15) J. H. Holloway and C. N. Reilley, *Anal. Chem.*, **32**, 249 (1960).
(16) M. Eigen and R. G. Wilkins, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1965, p 55.
(17) The value reported by M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 107 (1962), at 20° agrees with ref 8 when corrected to 25°.
(18) M. Yasuda, K. Yamsaki, and H. Ohtaki, *Bull. Chem. Soc. Japan*, **33**, 1067 (1960).
(19) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

(HY^{3-}) with Co,[20] Ni,[13] Cu,[21] and Cd,[22] the values are 10, 9, 16, and 16, respectively. Table III lists the experimental and predicted[8,17,23] values of k_H^{MCy} based on the ion-pair mechanism using $K_{os} = 13$.

Prior Acetate Bond Formation.—Another set of predicted constants is listed in Table III for what is termed the acetate mechanism which is shown in eq 12. Two metal ions never have been observed to react simultaneously with CyDTA, so the transition state should be one which will not accommodate coordination to two metals. Hence, coordination to a nitrogen atom rather than to one of the acetate groups must be involved in the transition state. If the rate-determining step (rds)

$$M^{2+} + HCy^{3-} \rightleftharpoons \underset{M}{\overset{\bar{O}}{\rightleftharpoons}} {}^+ \quad \xrightarrow{rds} \quad MCy^{2-} + H^+ \quad (12)$$
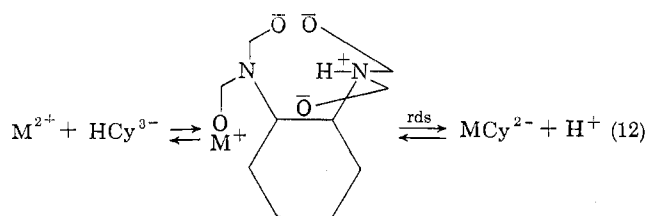
was metal coordination to an acetate group, there is no reason why one metal could not help another to dissociate. Nevertheless, the acetate groups are readily available for coordination and it is logical to assume that metal–acetate bond formation (eq 12) could precede the rate-determining step. This can be treated as a prior equilibrium because metal acetate dissociation would be fast compared to nitrogen bond formation. An acetate preequilibrium mechanism best explains a number of EDTA reaction mechanisms.[24] If this is the case, then the value for k_M^{HCy} is more correctly expressed as $k_M^{-H_2O} K_{MAc} K'$ where K_{MAc} is the metal acetate stability constant and K' includes thermodynamic and kinetic factors such as electrostatic attraction of the remaining negative groups, repulsion of the NH^+ group, and steric repulsion in nitrogen bond formation. With nickel, K_{NiAc} is 10 and therefore K' is 1.3. To a first approximation K' can be considered constant for the +2 metals, and therefore k_M^{HCy} can be calculated for each, using this value, the acetate stability constants, and the characteristic water substitution rate constant.

Group 1, Stepwise Mechanism.—Table III indicates good agreement between the predicted and experimental values for Co, Cu, and Zn using nickel as the reference. The mechanism with prior acetate bond formation seems to fit a little better than the ion-pair mechanism. Values used for the metal acetate stability constants were log K_{MAc} equal to 0.51 (Mg),[25] 0.53 (Ca),[25] 0.61 (Mn),[26] 1.52 (Co),[27] 1.0 (Ni),[28] 1.8 (Cu),[28] 1.28 (Zn),[29] 5.55 (Hg),[30] and 2.1 (Pb).[28]

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TABLE III

COMPARISON OF EXPERIMENTAL RATE CONSTANTS AND PREDICTED VALUES FOR THE REACTION OF HYDROGEN ION WITH METAL–CyDTA COMPLEXES USING NICKEL AS A REFERENCE AT 25° AND 0.1 μ

Metal	k_H^{MCy}(exptl), M^{-1} sec^{-1}	k_H^{MCy} (predicted),[a] M^{-1} sec^{-1}	k_H^{MCy} (predicted),[b] M^{-1} sec^{-1}	$k_M^{-H_2O}$, sec^{-1}
Group 1. Agreement with Stepwise Mechanism and Individual Bond-Breaking Steps				
Co	3.2	0.8	2.6	1.1×10^6 [8]
Ni	3.6×10^{-4}	3.6×10^{-4}	3.6×10^{-4}	2.7×10^4 [8,17]
Cu	3.9	0.6	4.1	2×10^8 [8]
Zn	1.7×10^2	0.4×10^2	0.7×10^2	3×10^7 [23]
Group 2. Disagreement with Stepwise Mechanism. Simultaneous Bond Breaking Proposed				
Mg	5.6×10^4	2.3×10^7	0.7×10^7	1×10^5 [17]
Ca	7.1×10^5	4.8×10^8	1.6×10^8	2.5×10^8 [23]
Mn	3.2×10^2	3.1×10^3	1.3×10^3	3.1×10^7 [8]
Group 3. Assignment Uncertain				
Pb	23	...	...	...
Hg	3.1	4.7×10^{-3}	...	2×10^9 [23]

[a] Ion-pair mechanism.   [b] Acetate mechanism.

Group 2, Simultaneous Bond Dissociation.—However, the metals in group 2 have experimental values of k_H^{MCy} which are $1/10$ to $1/600$ as large as predicted. The calcium and magnesium complexes deviate the most. Obviously the formation rate constants, k_{Ca}^{HCy} and k_{Mg}^{HCy}, also must be about $1/600$ as large as would be predicted from the $k_{Ca}^{-H_2O}$ and $k_{Mg}^{-H_2O}$ values. This accounts for the earlier observation that there was no copper ion dependence of the type expected from eq 4 in the reaction with calcium–CyDTA. The rate of reaction for calcium and CyDTA is much slower than for copper and CyDTA. We propose that the reactions of magnesium and calcium with CyDTA require the simultaneous loss of more than one water molecule before reaching the transition state. Another way of stating this mechanism is that there is no appreciable stabilization of a reaction intermediate between successive steps involving two (or more) coordination sites. Therefore, the coordination around the metal undergoes a greater change in the transition state than is the case for monodentate substitution. The same reaction path could be involved for ions in group 1 and group 2, but in group 1 each change of coordination is preceded and followed by a reaction intermediate. Hence, the reactions in group 1 proceed step by step whereas the reactions in group 2 require at least two steps at a time.

The reaction with manganese gives a k_H^{MnCy} value which is $1/5$ to $1/10$ as large as predicted by eq 12. The agreement between experiment and prediction for the other transition metals was so much better that a mechanism similar to that for calcium and magnesium was suspected. The temperature study gives supporting evidence. Although the $k_H^{MnCy} \simeq 2 \times k_H^{ZnCy}$ at

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25°, the activation energy for the manganese reaction is 8.3 kcal/mole greater than for the zinc reaction. The stepwise path proposed for zinc would be expected to represent a highly ordered transition state. This is reflected in the low value for A and the negative $\Delta S^{\ddagger}$. The manganese reaction has a high E_a (or $\Delta H^{\ddagger}$) barrier to overcome, but the transition state is much less ordered. Hence, manganese is placed in group 2.

Group 3, Unassigned.—The kinetic parameters for the lead–CyDTA reaction suggest that it too belongs in group 2, but rate constants for monodentate substitution of aquo lead ion are not available for comparison. The fact that the value for k_H^{PbCy} is in excellent agreement with a value of 20 M^{-1} sec^{-1} reported[31] for the corresponding reaction with EDTA seems to rule out a special role for CyDTA. Estimated values of $k_{Pb}^{-H_2O}$ are 1.2 × 10^7 and 1.5 × 10^8 sec^{-1} for the acetate and ion-pair mechanism, respectively. These values represent a relatively fast water substitution rate. This suggests lead reacts by a stepwise mechanism. The facts seem contradictory so lead is placed in group 3. In any case the value of $k_{Pb}^{-H_2O}$ must be at least 10^7 sec^{-1}.

With mercury, the ion-pair mechanism predicts a much smaller constant than is observed and the acetate mechanism predicts too large a constant. The difficulty is that the value of k_{Hg}^{HCy} calculated directly from the experimental value $(k_H^{HgCy}K_{HgCy}/K_{HCy})$ equals 9 × 10^{12} M^{-1} sec^{-1}, which is faster than the ions can diffuse together. The reaction probably is complicated by hydrolysis of mercury. Therefore, no mechanism is assigned to mercury–CyDTA.

Proposed Reaction Structures.—A nuclear magnetic resonance study[32] of CyDTA and its protonated species gives information on the configuration of the ligand and shows that the nitrogen atoms are the sites protonated in HCy^{3-} and H$_2$Cy^{2-}. The work of Muller and Tosch[33] with cyclohexane and Sudmeier and Reilley with CyDTA shows that a single conformation of the cyclohexane ring, the chair form, is preferred. As the number of protons on CyDTA varies from 0 to 2, no major change occurs in the conformation of the iminodiacetate groups which occupy diequatorial positions.

The mutual repulsion of the protons in H$_2$Cy^{2-} could be reduced either by partial rotation ($\sim$60°) of each iminodiacetate group as in structure I or by 180° rotation of one group as in structure II. The structure diagrams make no attempt to show the detailed conformation. The dashed arrows indicate the proposed direction of the N–H bond. Intermediate structures are less likely because of rotational barriers. The possible rapid interconversion of structures I and II by proton exchange and nitrogen inversion prevents the nmr data from indicating the relative population of these rotomers. As discussed earlier, a structure with 180° rotation of both iminodiacetate groups (so that the N–H bonds point in opposite directions) is very

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unfavorable owing to interference of the acetate hydrogens from opposite groups.

I   II
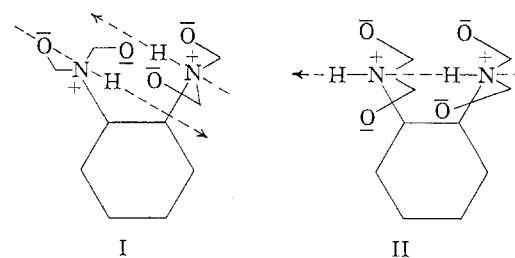
The configuration of the reaction intermediate consisting of H$^+$ and MCy^{2-} also must involve twisting of the nitrogen atoms because of the repulsion of the proton and the metal ion. The proton must go to a nitrogen atom in order to explain the predominant proton dissociation path at pH values where even a free acetate group no longer is protonated. Therefore, structure III is proposed where an N–M bond and an N–H bond are rotated away from one another and their charge repulsion is partially shielded by acetate groups. The ligand groups which are removed from the metal ion are replaced by coordinated water. Structure IV is a less likely reaction intermediate because steric blocking makes the 180° rotation from III to IV difficult and the inversion path is impossible as long as the metal is coordinated to either nitrogen. Structure IV itself has ring hydrogen atoms which would be in the way of coordinated water.
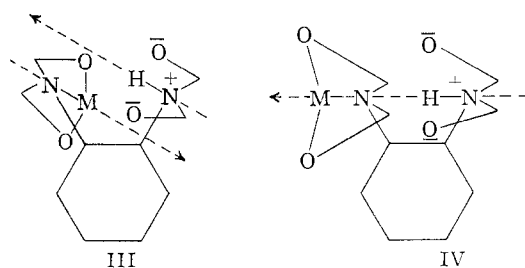
III   IV
proposed reaction intermediate   less likely reaction
for group 1 metals   intermediate

Relation of Proposed Structure to Groups 1 and 2.—Structure III is proposed as a reaction intermediate in the dissociation reaction of metal ions in group 1. To complete the dissociation one more acetate group must dissociate, and the rate-determining step is metal–nitrogen bond dissociation from the remaining glycinate chelate. This is the acetate mechanism which is given as a formation reaction in eq 12 where one acetate is bonded and the transition state is the coordination of one nitrogen to the metal. The stability of this intermediate is sufficient to make the rest of the steps required to complete the complex of lower energy.

For the group 2 metals, structure III or a structure similar to it is proposed as the transition state in which the metal leaves as the proton enters. The metals in group 2 form weaker nitrogen bonds and Mg^{2+} and Ca^{2+} may have a lower coordination number. As a result, there is no energy minimum for structure III. As the proton enters, the metal ion must leave both nitrogens. Two metal–nitrogen bonds are broken in

succession as the proton is added to one nitrogen. Hence, the kinetics are not characteristic of a stepwise mechanism.

The restricted rotation of CyDTA results in a rather small coordination cage for metal ions. Large metal ions should have greater steric hindrance in moving in and out of the cage and be less likely to proceed in a stepwise mechanism. The ionic radii (A) calculated from Goldschmidt values for crystal radii according to the method of Couture and Laidler[34] are Cu^{2+} (0.87), Ni^{2+} (0.97), Mg^{2+} (0.98), Co^{2+} (1.03), Zn^{2+} (1.04), Mn^{2+} (1.14), Ca^{2+} (1.33), Hg^{2+} (1.40), and Pb^{2+} (1.65). Although calcium and manganese are larger than the metal ions in group 1, magnesium is not and the mechanism for mercury and lead is uncertain. Ionic size alone cannot explain the difference in behavior.

Recent measurements[35] report primary hydration numbers for some of these metal ions: Mg^{2+} (3.8), Ca^{2+} (4.3), Zn^{2+} (3.9), Hg^{2+} (4.7), and Pb^{2+} (5.7). The anomalous behavior of Mg^{2+} and Ca^{2+} cannot be correlated directly to their low coordination number because Zn^{2+} also has a low hydration number.

A simple correlation which does appear to be valid is based on the relative stabilities of the metal glycinate or metal iminodiacetate complexes. The metals in group 1 form more stable complexes with these segments of CyDTA than those in group 2. If the stability is greater than the electrostatic repulsion between the metal and the protonated nitrogen, then structure III is a reaction intermediate and a stepwise path is observed. If the stability is less than the electrostatic repulsion, both metal–nitrogen bonds break when the one nitrogen is protonated and the simultaneous bond

dissociation mechanism is observed. Accordingly, the steric requirements of CyDTA, the size of the metal ion, and its coordination number may all affect the degree to which the proton–metal repulsion is shielded. Recent nmr studies[36] of the ligand-exchange kinetics of calcium–EDTA indicate that the $HEDTA^{3-}$ reaction with Ca^{2+} is much slower than with $EDTA^{4-}$. The $HEDTA^{3-}$ reaction is more sluggish than the $k_{Ca}^{-H_2O}$ value would predict. Hence, protonation of the ligand may be an important effect as well as the size of the coordination cage.

The fact that one metal ion cannot kinetically participate in the replacement of another metal in the CyDTA complexes but that a proton can take part in the reaction is a direct result of steric hindrance. It is known that rigid chelates such as the porphyrins are very sluggish in their reactions. Thus, the formation reactions of Mn, Co, Ni, Cu, and Zn with a porphyrin-type chelating agent[37] are much slower than individual water substitution reactions. In the CyDTA reactions some metals show such an effect. As the coordination cage of a ligand becomes more confined and rigid, more metal ions would be expected to deviate from their characteristic water substitution rates. However, with CyDTA the shift in mechanism appears to be due to changes in the relative stabilities of protonated intermediates rather than a direct function of size or coordination numbers of the cation.

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Absolute Infrared Intensities and Bonding in Metal Carbonyls. I. Decacarbonyl Manganese—Its Isoelectronic Analogs and Derivatives[1]

BY R. M. WING AND D. C. CROCKER

Absolute infrared intensity data are given for several metal carbonyls of the type $M_2(CO)_{10}$ in the carbonyl stretching region. These data as well as cross metal–metal bond C–O stretch–stretch interaction constants are explained using a model based on electrostatic interaction between $d\pi$ orbitals on opposite metal atoms. The effect of replacing the apical carbonyl groups by nonback-bonding ligands is discussed. Some comment is made concerning the value of infrared intensity data as a structural tool.

Introduction

There has been considerable discussion recently concerning the infrared spectra of binuclear metal carbonyls of the dimanganese decacarbonyl type.[2–6] While

endeavoring to learn more about the interactions between the metal carbonyl moieties and, in particular,

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