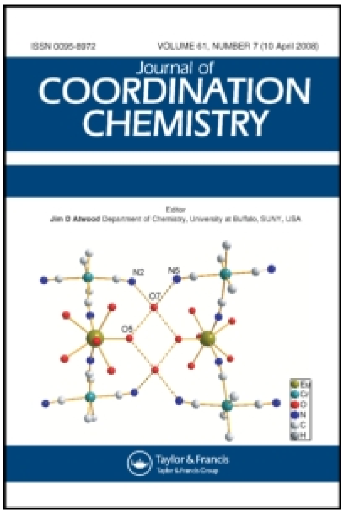

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Pearson, Ralph G. and Dewit, David G.(1973) 'KINETIC BEHAVIOR OF AMINOPOLYCARBOXYLATE LIGANDS IN SUBSTITUTION REACTIONS OF Zn(II) COMPLEXES', Journal of Coordination Chemistry, 2: 3, 175 — 184
To link to this Article: DOI: 10.1080/00958977308072969
URL: http://dx.doi.org/10.1080/00958977308072969

J. Coord. Chem., 1973, Vol. 2, pp. 175–184

Printed in Woking, England

KINETIC BEHAVIOR OF AMINOPOLYCARBOXYLATE LIGANDS IN SUBSTITUTION REACTIONS OF Zn(II) COMPLEXES[1]

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(*Received June* 28, 1972)

Kinetic results are reported for reactions of hexa-aquozinc(II) ion and several zinc(II) complexes with aminopolycarboxylate ligands and some bidentate ligands. Factors which alter "normal" kinetic behavior in these systems are demonstrated and discussed: the effect of complex geometry, of proton transfer, and of six-membered ring closure. Other features of these reactions and mechanisms are also discussed. Differences in kinetic behavior observed for reaction of maleonitriledithiolate (mnt^{2-}) with $Zn(NTA)^-$ and for similar reactions with $Cu(NTA)^-$ and $Ni(NTA)^-$ suggest differences in structure for the respective NTA complexes (NTA^{3-} = nitrilotriacetate). Proton transfer from $NTAH^{2-}$ is believed to control the rates of reaction with $Zn(H_2O)_6{}^{2+}$ and $Zn(dto)_2{}^{2-}$ (dto^{2-} = dithiooxalate). The behavior of EDTA in reaction with zinc complexes is compared with that of two analogues that form six-membered chelate rings.

INTRODUCTION

Since the establishment of the "dissociative interchange" mechanism for metal complex formation,[2,3] attention has been directed to factors in substitution reactions which result in departures from predicted kinetic behavior.[4] These anomalies are usually attributed to some feature of the chemical system which alters the rate-controlling step.

A substitution reaction which involves a change in coordination number and geometry about the metal ion may exhibit anomalous kinetic behavior if the configurational change is the rate-determining step. This phenomenon has been proposed to explain anomalous reactivity in a Cu(II) substitution reaction[5] and in a Zn(II) complex formation reaction,[6] and it may explain catalytic effects of certain metal ions in biochemical reactions.[7] A further departure from the usual complex formation mechanism may arise when a rate-determining proton transfer must occur prior to coordination of the donor atom to the metal. This situation has been documented in formation reactions of Ni(II)[8] and Cu(II)[9] complexes, and measured rate constants for proton transfer from glycine zwitterion to solvent[10] indicate that this process may be rate-controlling for complex formation with many metal ions. Chelate ring size may affect the kinetic behavior in certain substitution reactions. Closure of five-membered rings is considered to be very rapid and since initial ligand coordination usually labilizes remaining coordinated solvent molecules, coordination of the first donor atom is rate-controlling. Closure of six- and seven-membered chelate rings, however, has been found to be rate-determining in reactions with labile aquometal ions.[11]

This paper describes kinetic studies of reactions of aminopolycarboxylate ligands with various types of Zn(II) complexes. The intention was to examine the effect on kinetic behavior of (1) complex geometry, (2) proton transfer, and (3) six-membered ring closure in a system where crystal field effects do not interfere. We also hoped to establish information about the coordination sequence of aminopolycarboxylate ligands in these types of reactions as compared with that in other studies.[12]

EXPERIMENTAL SECTION

Materials

Zinc perchlorate, $Zn(ClO_4)_2 \cdot 6H_2O$, was purchased from G. F. Smith. Solutions of $Cd(ClO_4)_2$ were prepared by dissolving $CdCl_2$ in water, adding $AgClO_4$ (G. F. Smith) until all chloride was precipitated, and removing the AgCl by filtration. Solutions of the metal perchlorates were standardized by titrating with a standard solution of EDTA using published procedures.[13]

The disodium salt of nitrilotriacetic acid, Na_2NTAH, was purchased from Eastman. This salt was recrystallized from 50% ethanol-water and a solution was standardized by titrating with a standard NaOH solution. The disodium salt of EDTA, $Na_2EDTAH_2 \cdot H_2O$ (Fisher), assay 100%, was not further purified. The ligand 1,3-propanediaminetetraacetic acid, $PDTAH_4$, was prepared and purified by a published method.[14] *Anal.* Calcd for $C_{11}H_{18}N_2O_8$: C, 43.1; H, 5.92; N, 9.15. Found: C, 43.1; H, 6.16; N, 9.09. A sample of ethylenediaminetetrapropionic acid (EDTP) was kindly provided by other workers.[15] The ligand 8-hydroxyquinoline-5-sulfonic acid, H_2sox, was purchased from Eastman and recrystallized from water-methanol. Sodium maleonitriledithiolate, Na_2mnt, prepared by a published method,[16] was recrystallized from ethanol-ethyl ether, washed with ethyl ether, and dried under vacuum at 80°C for several hours. Potassium dithiooxalate, K_2dto (Eastman), was crystallized three times from aqueous solution by adding methanol and dried under vacuum at 80°C. The purity of both Na_2mnt and K_2dto was determined by spectrophotometric titration with a standard nickel perchlorate solution. The indicators Chlorphenol Red (CPR) (Eastman Kodak) and Thymol Blue (TB) (National Aniline) were used without further purification.

Instrumentation

Kinetic runs were made using a commercially available stopped-flow device which has been described in the literature.[17] Visible and ultraviolet spectra were obtained with a Cary Model 14 spectrophotometer. A Beckman DU-2 spectrophotometer was used to determine stability constants. Infrared spectra were run on a Perkin-Elmer Model 337 spectrophotometer using KBr disks. All *p*H measurements were made with a Radiometer Model 25 *p*H meter employing the G222B glass electrode and the K401 calomel reference electrode.

Stability Constants

Values of the stability constants $\beta_2 = [ML_2{}^{2-}]/[M^{2+}][L^{2-}]^2$ for $Zn(mnt)_2{}^{2-}$, $Zn(dto)_2{}^{2-}$, and $Cd(dto)_2{}^{2-}$ were estimated using the following method. To solutions of these complexes, EDTA (for $Zn(mnt)_2{}^{2-}$) or NTA (for $Zn(dto)_2{}^{2-}$ and $Cd(dto)_2{}^{2-}$) was added and in each case the concentrations and *p*H were adjusted so that the displacement of mnt^{2-} (or dto^{2-}) from the metal proceeded only part way. Since ligand concentrations were always much greater than that of metal and since very stable complexes are formed in all cases, it was assumed that no free metal ion was present. Furthermore, it was assumed that no mixed species formed and hence, in the case of $Zn(mnt)_2{}^{2-}$, for example, only the species $Zn(mnt)_2{}^{2-}$, $Zn(EDTA)^{2-}$, mnt^{2-}, and $EDTAH^{3-}$ were present at equilibrium. The equilibrium *p*H was adjusted so that virtually all of the free EDTA or NTA was present as the monoprotonated species. The ionic strength of the solutions was 0.1 *M* ($NaClO_4$) at 25°C. Using $Zn(mnt)_2{}^{2-}$ as an example, the absorbance at a given wavelength is given by

$$\begin{aligned} A = e_1[mnt^{2-}] &+ e_2[Zn(mnt)_2^{2-}] \\ &+ e_3[EDTAH^{3-}] \\ &+ e_4[Zn(EDTA)^{2-}] \end{aligned} \tag{1}$$

The extinction coefficients, e_1, were measured independently, and measuring A, equation (1) was solved simultaneously with three conservation equations based on the initial concentrations of Zn^{2+}, EDTA, and mnt^{2-}. This permits calculation of the constant

$$K = \frac{[Zn(EDTA)^{2-}][mnt^{2-}]^2[H^+]}{[Zn(mnt)_2{}^{2-}][EDTAH^{3-}]}$$

which is related to known constants[18] (Table I) and β_2. In general, measurements were made using at least two widely separated wavelengths and different values of $[H^+]$. Values of log β_2 obtained (Table I) were reproducible to within 0.3 log units.

Kinetic Runs

Kinetic data were obtained using the stopped-flow device mentioned previously. All reactions were run at 25 + 0.1°C. and the ionic strength was held constant at 0.1 *M* using $NaClO_4$. When necessary, *p*H adjustments of reactant solutions were made immediately preceding each run using dilute, freshly-prepared solutions of NaOH and $HClO_4$. Solutions of mnt^{2-}, dto^{2-}, and complexes of these ligands were freshly prepared immediately before each run, and the runs were made as quickly as possible since decomposition occurs over long periods. The reactions were monitored at wavelengths at which the absorbance differed most between reactants and products, *i.e.*, for reactions involving dto^{2-} at 258 nm; sox^{2-} at 365 nm;

$Zn(mnt)_2^{2-}$ at 378 nm; CPR at 575 nm; and TB at 595 nm. The visible and ultraviolet spectra of product solutions were identical to spectra of solutions containing the expected products prepared independently.

In cases for which the reaction resulted in no suitable spectral changes, or for which proton release was to be monitored directly, an indicator was coupled to the system.

$$M + LH \overset{k}{\rightleftharpoons} ML + H^+$$

$$H^+ + I \underset{k_2}{\overset{k_1}{\rightleftharpoons}} HI \qquad K = k_1/k_2$$

M denotes a metal ion, LH a protonated ligand, and HI the protonated form of the indicator. Charges on the complexes and indicator are omitted. With M in excess over LH, the observed pseudo-first-order rate constant $k[M]$ is to be measured although the rate of formation of HI is observed. Clearly, the indicator equilibrium must be rapid relative to the proton release reaction, but in addition, the effect of the reverse (k_2) step in the equilibrium must be negligible. One way to achieve the latter condition is to drive the indicator equilibrium to completion by making the initial concentration of LH (and thus $[H^+]$) very much greater than the initial concentration of I. This is often experimentally unfeasible. Alternatively, it can be shown that if $K(b—[HI]) \gg 1$ (where b is the total indicator concentration), the observed rate constant reduces to the desired value $k[M]$. Thus for normal indicators experimental conditions must be adjusted so that the total indicator concentration is sufficiently great and that $[I] > [HI]$ throughout the reaction.

In each indicator-coupled reaction, concentrations and pH were adjusted to fulfil these conditions as rigorously as possible. Furthermore, it was verified that the indicator equilibria were indeed rapid with respect to the reactions of interest by reacting the indicators with acid independently on the stopped-flow. Finally, it was shown that the reaction rates were independent of indicator concentration.

Treatment of Data

Reactions were always run with one reactant in pseudo-first-order excess, *i.e.* in at least a ten-fold excess over the other. Thus each reaction generally followed a first-order rate law and a first-order rate constant k_{obsd} was extracted from each run. A kinetic study involved varying the concentration of the excess reactant and determining the dependence of k_{obsd} on the concentration of this reactant.

Some of the reactions studied consist of two steps as indicated by a fast absorbance change followed by a slower one. In these cases, accurate values of A_∞ for the first step often could not be determined directly, and the method employed was to set A_∞ at an apparently reasonable value and then to vary it in small increments until a best straight line ($\ln(A - A_\infty)$ *v.* time) was obtained. When the two steps were fairly close in rate, only the very first portion of the first step and the very last portion of the second step were analyzed, in order to avoid complications arising from possible mixing in the intermediate region.

All rate constants reported are average values of at least three, and usually more, determinations. The maximum variation of these determinations was seldom more than 15% and most often about 10%.

RESULTS AND DISCUSSION

Stability Constants and Structures

Formation constants for complexes involved in this study are listed in Table I. These stabilities dictate the feasibility of ligand substitution reactions. Some of the displacement equilibria can be driven to

TABLE I

Equilibrium constants for reactions involved in this Study[a]

Equilibrium	log K, or log β_2
$H^+ + EDTA^{4-} = EDTAH^{3-}$	10.27
$H^+ + EDTAH^{3-} = EDTAH_2^{2-}$	6.16
$H^+ + NTA^{3-} = NTAH^{2-}$	9.73
$N^+ + NTAH^{2-} = NTAH_2^-$	2.49
$H^+ + sox^{2-} = Hsox^-$	8.3
$Zn^{2+} + EDTA^{4-} = Zn(EDTA)^{2-}$	16.40
$Zn^{2+} + NTA^3 = Zn(NTA)^-$	10.66
$Cd^{2+} + NTA^{3-} = Cd(NTA)^-$	9.80
$Zn^{2+} + 2sox^{2-} = Zn(sox)_2^{2-}$	14.3
$Zn^{2+} + 2mnt^{2-} = Zn(mnt)_2^{2-}$	17.6[b]
$Zn^{2+} + 2dto^{2-} = Zn(dto)_2^{2-}$	10.6[b]
$Cd^{2+} + 2dto^{2-} = Cd(dto)_2^{2-}$	12.7[b]

[a] Taken from reference 18 at 25° C unless otherwise noted.

[b] Determined in this work at 25° C, ionic strength = 0.1 *M*; log β_2 ± 0.3 log units.

TABLE II

Summary of reactions studied[a]

Reaction	Initial pH	k_{obsd}, sec^{-1}
1. $Zn(H_2O)_6^{2+}$ + 2mnt^{2-}		> 500[b]
2. + 2dto^{2-}		> 500[b]
3. + 2sox^{2-}		> 500[b]
4. + NTA	6.7	$2.7 \times 10^5[NTAH^{2-}]$
5. + EDTA	varied	> 500[b]
6. + EDTP	6.1	200[c]
7. + PDTA	6.1	~ 500
8. $Cd(dto)_2^{2-}$ + NTA	6.8	Step 1: $5.1 \times 10^4[NTAH^{2-}]$ Step 2: 0.54
9. $Zn(dto)_2^{2-}$ + NTA	6.8	Step 1: 11.5 + $4.1 \times 10^4[NTAH^{2-}]$ Step 2: ~10 (complex)
10. + EDTA	6.1	> 500[b]
11. + EDTP	6.1	45[c]
12. + PDTA	6.1	20.9
13. $Zn(mnt)_2^{2-}$ + EDTA	7.0, 8.2	5[c]
14. $Zn(sox)_2^{2-}$ + EDTA	7.0	33.3
	8.2	16.7
15. $Zn(NTA)^-$ + 2dto^{2-}	7.0	1.73
16. + 2mnt^{2-}	7.0	27.9

[a] All reactions carried out at 25.0°C and ionic strength = 0.1 *M*.
[b] Too fast to measure by stopped flow.
[c] Limiting behavior observed with increasing concentration. Value given is estimated limiting value of k_{obsd}.

completion in either direction by appropriately adjusting initial conditions. Table II summarizes the reactions studied.

Information is limited concerning structures of complexes in solution and can often be inferred only from solid-state structures. $Zn(mnt)_2^{2-}$ and most other Zn(II) dithiolates appear to be tetrahedral in the solid state.[19] $Zn(sox)_2^{2-}$ (H_2sox = 8-hydroxyquinoline-5-sulfonic acid) may be square-planar as is $Zn(ox)_2 \cdot 2H_2O$ (Hox = 8-hydroxyquinoline).[20] We have studied the infrared spectrum of $K_2Zn(dto)_2$ in KBr disks, and comparison with spectra of $K_2Ni(dto)_2$ and $K_2Pt(dto)_2$, the structures[21] and spectra[22, 23] of which are well characterized, suggests that coordination is through sulfur for the zinc complex. Raman and nmr evidence indicates that the complex $Zn(EDTA)^{2-}$ in aqueous solution is six-coordinated from pH 3 to 11[24] with labile carboxylate groups.[25] Similar evidence indicates that all four groups are coordinated in $Zn(NTA)^-$ and the three methylene groups are equivalent by nmr,[26] consistent with a tetrahedral structure or with *cis*-$Zn(NTA)(H_2O)_2^-$ provided carboxylate exchange is rapid.

Effect of Complex Geometry

Reactions 1–4, 15, and 16 (Table II) were studied in an attempt to document anomalous kinetic behavior attributable to rate-determining changes in coordination number or structure. Since the aquozinc ion is known to be six-coordinated,[27] formation reactions of tetrahedral complexes could be anomalously slow. Formation of complexes $Zn(L\text{–}L)_2^{2-}$ (reactions 1–3) were too fast to measure by stopped flow methods ($k_{obsd} > 500$ sec^{-1}). It is possible that (*a*) none of these complexes is tetrahedral; (*b*) the structural change, octahedral ⇌ tetrahedral, is still too fast to measure; or (*c*) the structural change is not rate-controlling.

Formation of $Zn(NTA)^-$ (reaction 4) is anomalously slow but may be explained on the basis of rate-determining proton transfer (below).

Reactions 15 and 16, displacement of NTA by dto^{2-} and mnt^{2-}, are analogous to the previously reported reaction of $Cu(NTA)^-$ with mnt^{2-} for which anomalous kinetic behavior was explained in terms of a structural interconversion.[5] With $[Zn(NTA)^-] = 5.00 \times 10^{-5}$ *M* and the bidentate ligand varied in first-order excess, the initial pH was adjusted to 7.0 and an indicator (TB) was coupled to the system which was sensitive to the *p*H increase as the NTA nitrogen was displaced. The values of k_{obsd} in Table III indicate that nitrogen displacement is independent of the concentration of entering ligand but markedly dependent upon the nature of the nucleophile.

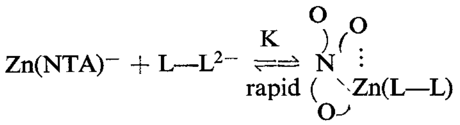
TABLE III

Rate constants[a] for the reaction of Zn(NTA)− with dto2− and mnt2−.

L—L^{2-}	[L—L^{2-}], $M \times 10^3$	k_{obsd}, sec^{-1}
dto^{2-}	2.00	1.73
dto^{2-}	3.00	1.73
dto^{2-}	4.00	1.74
dto^{2-}	5.00	1.73
mnt^{2-}	1.00	27.3
mnt^{2-}	2.00	27.6
mnt^{2-}	3.00	28.4
mnt^{2-}	5.00	28.1

[a] 25° C. Ionic strength = 0.1 *M*.

This behavior contrasts with that of Cu(NTA)$^-$ reacting with mnt^{2-}. In that case, the rate law and spectral changes indicate that coordination of the first mnt^{2-} is rate-determining.[5] For the Zn(NTA)$^-$ reaction, the dependence of the magnitude of k_{obsd} on the nature of the added nucleophile but not on concentration is consistent with rapid addition of the first entering ligand to form an adduct from which rate-determining dissociation of NTA occurs:



$$\text{Zn(NTA)}^- + \text{L—L}^{2-} \underset{\text{rapid}}{\overset{K}{\rightleftharpoons}} \text{N}\cdots\text{Zn(L—L)}$$

For k_{obsd} to be independent of [L—L^{2-}], K[L—L^{2-}] $\gg 1$. Dissociation of NTA from this adduct (k) can be succeeded by rapid reaction with a second ligand to form the product Zn(L—L)$_2^{2-}$ and drive the reaction to completion. The greater labilizing influence of mnt^{2-} may result from the greater electron density it places on the metal by increased covalent bonding relative to dto^{2-}.

It was proposed that Cu(NTA)$^-$ is tetrahedral or distorted toward such a structure on the basis of relative reactivities of the NTA and EDTA complexes of Cu(II) and Ni(II) with mnt^{2-}.[1,5] The difference in behavior for the Zn(II) system may be explained by invoking a *cis*-octahedral structure for Zn(NTA)(H$_2$O)$_2^-$, as for Ni(NTA)(H$_2$O)$_2^-$,[28] so that addition of the first mnt^{2-}, unlike the case of Cu(NTA)$^-$, is relatively unimpeded at the aquated coordination sites.

Effect of Proton Transfer

The formation of Zn(NTA)$^-$ from the zwitterion NTAH^{2-} (reaction 4) was measured by coupling an indicator (CPR) to the system and monitoring the release of H$^+$ as the NTA nitrogen coordinated. The Zn^{2+}, in first-order excess, was varied from 1.25×10^{-4} to 1.00×10^{-3} *M*, the experimentally feasible range. Initially the *p*H was adjusted to 6.7 and it remained in the range (4.5 to 7.0) where NTA exists virtually 100% as the NTAH^{2-} zwitterion.[29] The concentration of indicator was 5×10^{-5} *M*. Simple first-order behavior was observed with $k_{obsd}(\text{sec}^{-1}) = 2.7 \times 10^5[\text{Zn}^{2+}]$. Our result is in fair agreement with the value obtained by nmr methods (5.1×10^5 M^{-1}sec^{-1} at ionic strength = 1 *M*).[26]

The dissociative interchange mechanism predicts a second-order rate constant of 1.5×10^9 M^{-1}sec^{-1} for this reaction.[26] Figure 1 depicts a mechanism for this formation reaction which is similar to that proposed previously[26] to explain this anomalous result and similar behavior for formation of Ni(NTA)$^-$.[12b] This mechanism predicts $k_{\text{obsd}} = k_1\text{K}[\text{Zn}^{2+}]$ in the limit $\text{K}[\text{Zn}^{2+}] \ll 1$. Since linear behavior is observed, $\text{K} < 10^2\ \text{M}^{-1}$, and employing a value of about 10 M^{-1}, the formation constant for mono(acetato)zinc(II) ion,[18] the value of k_1 is estimated to be 10^4 sec^{-1}.

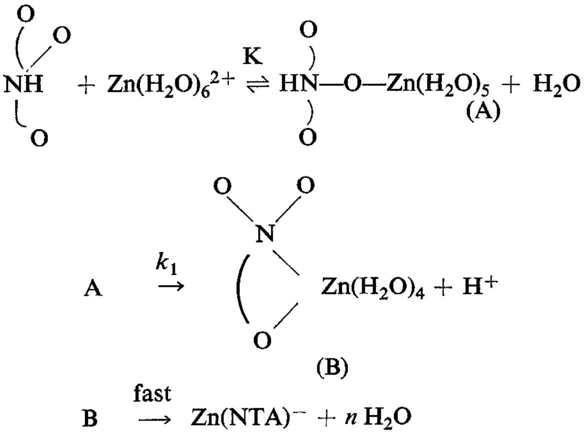


FIGURE 1 Proposed mechanism for the formation reaction of Zn(NTA)−. Charges are omitted.

This rate-controlling step (k_1) involves transfer of the proton followed by coordination of the nitrogen atom, although the exact mode of this transfer is not specified. Assistance from uncoordinated carboxylate groups can occur,[10] but comparison with the result for Ni(NTA)$^-$ formation ($k = 7.5\ \mathrm{M^{-1}\ sec^{-1}}$) suggests metal ion participation after adduct formation. The rate constants for Zn(NTA)$^-$ and Ni(NTA)$^-$ formation parallel the labilities of coordinated water molecules even though both rates are much slower than the dissociative interchange mechanism predicts. Expulsion of the proton could be directly assisted by the aquometal ion, and the effectiveness of this assistance would depend upon the lability of the remaining coordinated water molecules.

Reaction 5, formation of Zn(EDTA)$^{2-}$, was carried out under the same conditions as reaction 4 except that the pH was varied to give EDTAH^{3-} and EDTAH$_2{}^{2-}$ in solution. The reaction was too rapid to detect on the stopped flow ($k_{obsd} > 500\ \mathrm{sec^{-1}}$) regardless of pH. This result is not inconsistent with the rate-determining proton transfer mechanism because consideration of the protonation equilibrium constants involved (Table I) indicates a difference in the ease of proton transfer for each case. Log $K = -9.73$ for

$$\mathrm{H_2O + NTAH^{2-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_3O^+ + NTA^{3-}}$$

Values of k_2 are typically 10^9 to $10^{10}\ \mathrm{M^{-1}sec^{-1}}$ or less for these systems[3] which places an upper limit of approximately $1\ \mathrm{sec^{-1}}$ for $k_1[\mathrm{H_2O}]$. For EDTAH$_2{}^{2-}$ proton transfer will be considerably more facile than from NTAH^{2-} even though pathways other than transfer to solvent can operate.[10]

Reactions of NTA and EDTA zwitterions with dto complexes (reactions 8–10) supply information that the reactions with aquozinc ion do not provide. The release of dto^{2-} was monitored at a wavelength characteristic of uncoordinated ligand and [NTA] was varied in first-order excess. For Zn(dto)$_2{}^{2-}$ and Cd(dto)$_2{}^{2-}$ the initial pH was adjusted to 6.8 and it remained in the range where NTA exists as virtually 100% NTAH^{2-}. Buffers interfered with the reactions by displacing dto^{2-}.

Kinetic results for Zn(dto)$_2{}^{2-}$ and Cd(dto)$_2{}^{2-}$ are consistent with the stability difference for the complexes (Table I) and the importance of proton transfer. Displacement of dto^{2-} by NTAH^{2-} is a two-step reaction in both cases. For Zn(dto)$_2{}^{2-}$, in solutions containing from 3.5×10^{-4} to 4.2×10^{-3} M NTAH^{2-}, the first step obeys the rate law $k_{\mathrm{obsd}}(\mathrm{sec^{-1}}) = 11.5 + 4.1 \times 10^4[\mathrm{NTAH^{2-}}]$. The second step exhibits complicating factors as [NTAH^{2-}] increases. Up to 1.25×10^{-3} M NTAH^{2-}, the second step is roughly independent of [NTAH^{2-}] with $k_{\mathrm{obsd}} \cong 10\ \mathrm{sec^{-1}}$. At higher NTA concentrations this step begins mixing with faster processes. This is believed to result from interaction with a second NTA which assists in removing the second dto^{2-} from the metal. A weak interaction of Zn(NTA)$^-$ with a second NTA is known to occur with excess ligand.[26]

For Cd(dto)$_2{}^{2-}$, from 1×10^{-3} to 3×10^{-3} M, the first step obeys the rate law $k_{\mathrm{obsd}}(\mathrm{sec^{-1}}) = 5.1 \times 10^4[\mathrm{NTAH^{2-}}]$. The NTA concentration range is smaller in this case because higher concentrations are required to drive the reaction to completion whereas the rate exceeds the stopped flow range above 3×10^{-3} M NTA. The second step is strictly independent of [NTAH^{2-}] with $k_{\mathrm{obsd}} = 0.54\ \mathrm{sec^{-1}}$.

Figure 2 shows the mechanism proposed for the first step of the substitution reaction. In accordance with the two term rate law observed, the mechanism contains two pathways and predicts $k_{\mathrm{obsd}} =$

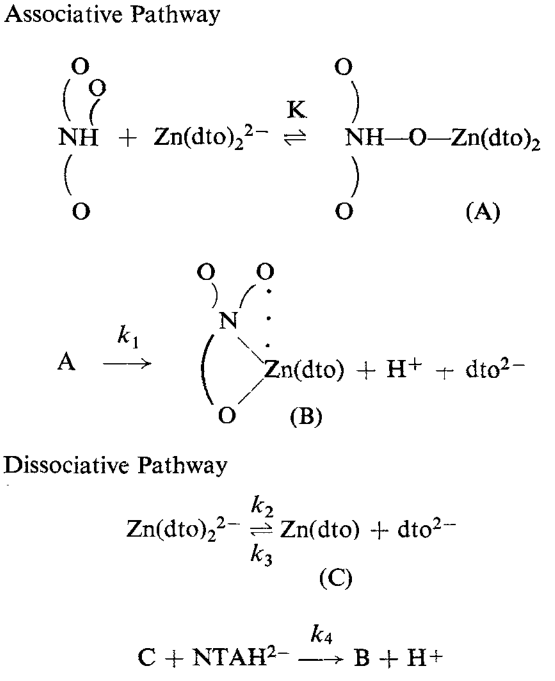


FIGURE 2 Proposed mechanism for the first step of the reaction of Zn(dto)$_2{}^{2-}$ (or Cd(dto)$_2{}^{2-}$) with NTAH^{2-}. Charges are omitted.

$k_2 + k_1K[NTAH^{2-}]$ when a steady-state is assumed for species C and in the range where $k_4[NTAH^{2-}] \gg k_3[dto^{2-}]$. The relative unimportance of the dissociative pathway (k_2) for $Cd(dto)_2^{2-}$ is consistent with the greater stability of this complex (Table I). The marked similarity of the second-order terms (k_1K) for $Zn(dto)_2^{2-}$ ($4.1 \times 10^4\ M^{-1}sec^{-1}$) and for $Cd(dto)_2^{2-}$ ($5.1 \times 10^4\ M^{-1}sec^{-1}$) is significant. As for aquozinc ion (Figure 1), initial coordination likely occurs through oxygen,[8, 30a,b] and although $Cd(dto)_2^{2-}$ is more stable than $Zn(dto)_2^{2-}$, the dto^{2-} is displaced by NTA at least as rapidly from Cd(II) as from Zn(II). This implies that rate-controlling transfer of the proton precedes coordination of nitrogen and rapid departure of dto^{2-}. The value of k_1K should correlate with that for $Zn(H_2O)_6^{2+}$ ($2.7 \times 10^5\ M^{-1}sec^{-1}$). The smaller value may reflect less favorable adduct formation (K) and less effective assistance in proton transfer (k_1) with the more negative metal center in the dto complex.

The second step in the substitution reactions probably involves dissociation of the second dto^{2-} followed by complete coordination of NTA. The relative magnitudes of k_{obsd} are consistent with the stability difference for the two complexes if this step is dissociative in nature.

Substitution of $Zn(dto)_2^{2-}$ by EDTA at $pH = 6.1$ (reaction 10) is too rapid to detect by stopped flow methods. This is reasonable since proton transfer should be more facile from EDTA. The behavior of $EDTAH^{3-}$ and NTA^{3-} should be similar because in each case coordination of a nitrogen atom, regarded as the kinetically important step in these systems,[12d] is unimpeded. As the pH for reaction 9 was raised to 7.5 and above, the spectral change observed became less as more NTA^{3-} was formed and eventually the entire reaction became too rapid to observe.

Effect of Six-Membered Ring Closure

The reactions of EDTA with $Zn(H_2O)_6^{2+}$ and $Zn(dto)_2^{2-}$ are too fast to follow with the stopped flow. Two EDTA analogues which form six-membered chelate rings in a metal complex show different kinetic behavior. EDTP, which contains four propionate groups, and PDTA, which contains a 1,3-propanediamine group, were studied in formation reactions with $Zn(H_2O)_6^{2+}$ (reactions 6 and 7) by coupling an indicator (CPR) and monitoring proton release. $[CPR] = 2 \times 10^{-4}\ M$. For excess Zn^{2+}, the $[Zn^{2+}]$ was varied from 2.5×10^{-4} to $1.0 \times 10^{-3}\ M$. The initial pH was set at 6.1. For EDTP, the dependence of k_{obsd} on $[Zn^{2+}]$ is shown in Figure 3. The value of k_{obsd} increases with $[Zn^{2+}]$ but begins to approach a limiting value in the region of 200 sec^{-1}. The rate for the PDTA reaction is just at the limit of detection for the stopped flow. This means that $k_{obsd} = 500\ sec^{-1}$, and no apparent change in rate with $[Zn^{2+}]$ occurred.

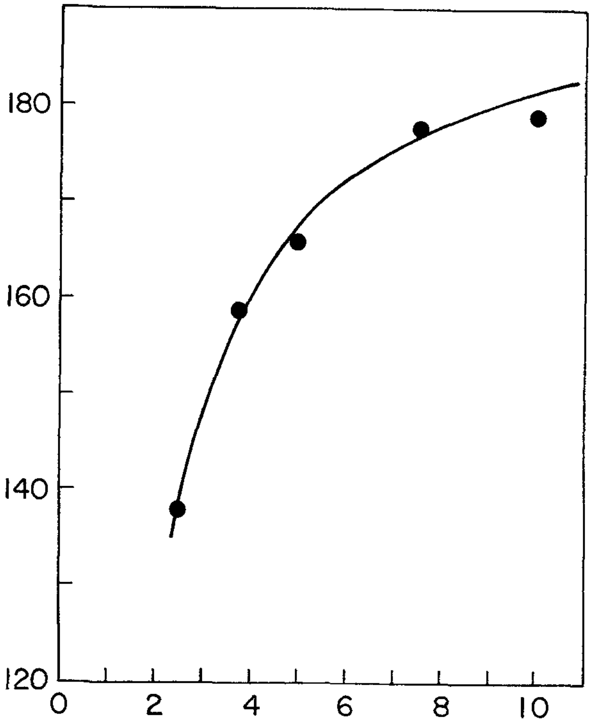


FIGURE 3 The dependence of k_{obsd} on $[Zn^{2+}]$ for the formation of $Zn(EDTP)^{2-}$ at 25°c. Ionic strength = 0.1 M.

Substitution reactions (11 and 12) of $Zn(dto)_2^{2-}$ with the same two ligands were followed by monitoring release of dto^{2-} at 258 nm. The runs were made with EDTP and PDTA in excess. The pH was adjusted to 6.1, at which one nitrogen is protonated and the other is approximately half protonated,[18, 31] and effective buffering is maintained throughout the reaction. For EDTP, the dependence of k_{obsd} on [EDTP] from 2.5×10^{-4} to $3.0 \times 10^{-3}\ M$ is shown in Figure 4. The observed reaction proceeds in one step and k_{obsd} approaches a limiting value of approximately 45 sec^{-1}. For PDTA the one step reaction is independent of [PDTA] in the same concentration range, and $k_{obsd} = 20.9\ \text{sec}^{-1}$.

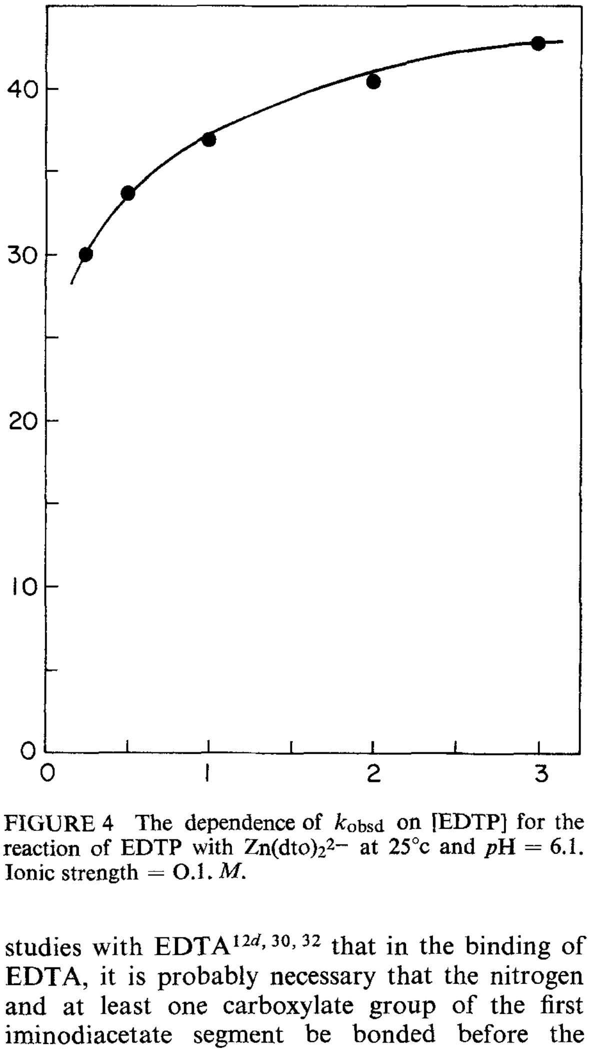


FIGURE 4 The dependence of k_{obsd} on [EDTP] for the reaction of EDTP with $Zn(dto)_2^{2-}$ at 25°c and $pH = 6.1$. Ionic strength = 0.1. *M*.

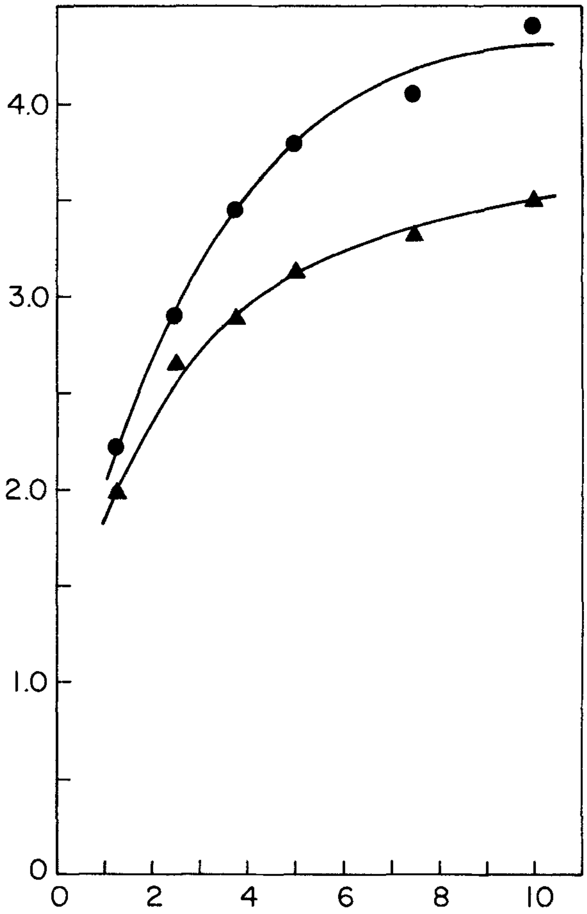


FIGURE 5 The dependence of k_{obsd} on [EDTA] for the reaction of EDTA with $Zn(mnt)_2^{2-}$ at 25°c. Ionic strength = 0.1. *M*. O, $pH = 8.2$; Δ, $pH = 7.0$.

To postulate how six-membered ring closure alters the kinetic behavior, a general coordination sequence must be established for EDTA and similar ligands. One may conclude from the many kinetic studies with EDTA[12d, 30, 32] that in the binding of EDTA, it is probably necessary that the nitrogen and at least one carboxylate group of the first iminodiacetate segment be bonded before the diamine ring closes and coordination of the second nitrogen occurs. We have reacted EDTA with $Zn(mnt)_2^{2-}$ and $Zn(sox)_2^{2-}$, which are more stable than $Zn(dto)_2^{2-}$ (EDTP and PDTA will not displace these ligands), and these reactions (13 and 14) are easily measurable. With EDTA in excess, the dependence of k_{obsd} on [EDTA] is shown in Figure 5 when the initial pH is adjusted to 8.2 (~100% $EDTAH^{3-}$) and to 7.0 for reaction with $Zn(mnt)_2^{2-}$. The limiting behavior suggests an adduct formation equilibrium which "saturates" at high [EDTA]. As more nitrogens are protonated, this association becomes less favorable and k_{obsd} levels off less readily at pH 7.0. For $Zn(sox)_2^{2-}$ the reaction is faster and Table IV shows that k_{obsd} is independent of [EDTA] in the range studied, suggesting that formation of the adduct is more favorable with $Zn(sox)_2^{2-}$.

Subsequent departure of ligands is more rapid for less stable complexes. Substitution of sox^{2-} is more rapid at low pH since it is a basic ligand (Table I) and in general, rate substitution by EDTA decreases in the order
$Zn(dto)_2^{2-} > Zn(sox)_2^{2-} > Zn(mnt)_2^{2-}$.

The reactions of PDTA with both $Zn(H_2O)_6^{2+}$ and $Zn(dto)_2^{2-}$ are similar in the sense that no dependence of k_{obsd} on [PDTA] is observed. The

TABLE IV

Rate constants[a] for the reaction of EDTA with Zn $(sox)_2{}^{2-}$

Initial pH	EDTA, $M \times 10^3$	k_{obsd}, sec^{-1}
7.0	1.25	33.0
7.0	2.50	32.8
7.0	3.75	32.6
7.0	5.00	33.9
7.0	7.50	34.0
8.2	1.25	16.8
8.2	2.50	16.5
8.2	3.75	16.8
8.2	5.00	16.7
8.2	6.25	16.7
8.2	7.50	16.7

[a] 25°C. Ionic Strength = 0.1 *M*.

coordination of the first iminodiacetate segment requires closure of at least one five-membered ring and this must occur as easily as for EDTA. Further reaction requires closure of the six-membered 1,3-propanediamine ring rather than a five-membered ethylenediamine ring and this must account for the reduced reactivity of PDTA. The behavior of EDTP, Figures 3 and 4, suggests initial formation of an adduct which is not as stable as that of PDTA, for which k_{obsd} is independent of [PDTA] in the same concentration range. Adduct formation, in the sense described above, requires closure of a six-membered iminopropionate ring for EDTP rather than five-membered rings as for PDTA and EDTA. The most important subsequent step is closure of the ethylenediamine ring, which should occur with the same facility as for EDTA, although other propionate rings must close to complete the coordination of EDTP.

It is doubtful whether quantitative comparisons may be made regarding closure rates for the different six-membered rings. Attempts to assign rate constants to these processes from these results would be unwarranted. Nevertheless, the striking kinetic effect of ring size in each case can be explained in terms of a reasonable coordination scheme for these ligands.

Summary

A useful summary of other kinetic studies on zinc complexes is given by Cayley and Hague.[33] Second-order rate constants for aquozinc ion reacting with ligands of all kinds is normally 10^6 to 10^7 $M^{-1}sec^{-1}$, and most rates are beyond the range of the stopped flow. Pyridine-2-azo-*p*-dimethylaniline (PADA) was found[33] to react with $Zn(NTA)^-$ and other zinc complexes at similar high rates. This is in contrast to the behavior of $Zn(NTA)^-$ reacting with mnt^{2-} and to our observation that aquozinc ion reacted notably faster than other zinc complexes in substitution reactions. We have attempted to document some factors which alter the "normal" behavior for Zn(II) and other systems.

Proposal of detailed mechanisms for coordination of aminopolycarboxylate ligands is not justified on the basis of our results, but it is possible to make some over-simplified statements about the coordination sequence which help to understand the effects observed. Coordination of nitrogen and probably one carboxylate group is the important initial step and formation of this adduct may be inhibited when rearrangement of the complex is required, when proton transfer must occur, or when the sterically difficult closure of six-membered rings is required. For EDTA and its analogues, closure of the diamine ring is the most important subsequent step, and this step is very rapid except when a six-membered chelate ring is formed.

*

ACKNOWLEDGEMENTS

Financial support for this work came from Grant 6431x from the National Science Foundation and from a predoctoral NIH fellowship to D.G.D.W. Thanks are due to Professor A. E. Martell for a gift of ethylenediaminetetrapropionic acid.

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