

iodine series show on the contrary<sup>2,20</sup> an actual destabilizing effect of increased halogen substitution. Thus in the chlorine series, we have  $\Delta H_f^\circ(\text{CH}_4) = -17.8$ ,  $\Delta H_f^\circ(\text{CH}_3\text{Cl}) = -20.7$ ,  $\Delta H_f^\circ(\text{CH}_2\text{Cl}_2) = -22.4$ ,  $\Delta H_f^\circ(\text{CHCl}_3) = -25$ , and  $\Delta H_f^\circ(\text{CCl}_4) = -26.0$ , all in kcal/mole.

It appears from this that the data presented here are compatible with a nonbonded electrostatic interaction arising from alternate polarity of atoms in *gauche* conformations. If this is correct, we should expect to see similar interactions in other related compounds. For example,

(20) S. W. Benson, "Thermochemical Kinetics," John Wiley and Sons, Inc., New York, N. Y., 1968. (See Appendix for group and thermochemical data.)

1,3-dichloro, or difluoro, or dicyano compounds might be expected to show a preference for *gauche* conformations with the negative halogen near the positive carbon. Effects in these compounds will not be as great as with the present types because of the compensating effects of increased halogen-halogen repulsion in the *gauche* conformations.

From our results we can calculate  $\Delta H_f^\circ$  and  $S^\circ$  contributions for the following groups.<sup>2</sup>

	$\Delta H_f^\circ$ , kcal/mole	$S^\circ_{298}$ , gibbs/mole
C-(H <sub>2</sub> )O(I)	+3.8	40.7 <sup>a</sup>
C-(H)(C)O(Cl)	-22.3	15.9

<sup>a</sup> Value assigned.

## Ligand-Exchange Kinetics and Solution Equilibria of Cadmium, Zinc, and Lead Nitrilotriacetate Complexes<sup>1a-c</sup>

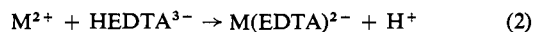
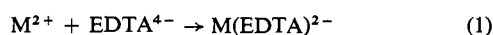
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**Abstract:** Proton nuclear magnetic resonance (nmr) techniques have been used to study the aqueous solution chemistry of the nitrilotriacetate (NTA) complexes of cadmium, zinc, and lead. Complexes having NTA-to-metal ratios of 1 and 2 are present, depending upon the solution conditions, and their formation constants were evaluated from chemical shift data. The kinetics of ligand exchange between the free and the complexed forms were measured using nmr line-broadening techniques. Exchange was found to occur by both first-order dissociation of the metal-ligand complexes and by second-order processes involving free ligand and metal-ligand complexes. The rate constants for each of the reactions resulting in ligand exchange were evaluated from the dependence of the exchange rate upon ligand concentration and pH. It was observed that, when the free NTA is in the monoprotonated form, the rate of ligand exchange is significantly less than the rate when the NTA is in the totally ionized form. From comparisons of the rate constants in these and in other systems, mechanisms to explain the dependence of the exchange rate on the degree of protonation of the reacting ligand are discussed. It is proposed that the decrease in rate is due to the relatively slow rate of proton migration from the nitrogen atom in a partially bonded reaction intermediate. Possible structures for the NTA complexes are discussed based on the kinetic rate constants, the equilibrium formation constants, and the heteronuclear coupling observed in the nmr spectra for several of the complexes.

In earlier papers, proton nuclear magnetic resonance (nmr) line-broadening studies of the ligand-exchange kinetics in the strontium-ethylenediaminetetraacetic acid (EDTA) and calcium-EDTA systems were reported.<sup>2,3</sup> The rate of EDTA exchange between the free and complexed forms was measured, and the reactions resulting in exchange were established. In those systems, exchange occurs by first-order dissociation of the metal-EDTA complex and by second-order processes involving direct reaction of the free EDTA with the metal-EDTA complex. From the measured dissociation rate constants and the appropriate equilibrium constants, rate constants were calculated for the formation of the metal-EDTA

complexes by reaction of the aquated metal ion with the EDTA tetraanion (eq 1) and with monoprotonated EDTA (eq 2). Rate constants calculated for reaction 1 are



approximately those predicted for a mechanism in which water loss from the aquated metal ion is rate determining. However, the rate constants calculated for reaction 2 are from two to three orders of magnitude smaller than predicted for a similar rate-determining mechanism. This is in contrast to the reactions of Ni(II), Co(II), Cu(II), Zn(II), and Cd(II) with HEDTA<sup>3-</sup> to form the corresponding M(EDTA)<sup>2-</sup> complexes.<sup>4-8</sup> For the latter reactions, the observed rate constants all agree with the

(1) (a) This work was supported in part by a grant (GP4423) from the National Science Foundation and by a National Institutes of Health Predoctoral Fellowship (D. L. R.). (b) Abstracted in part from the Ph.D. thesis of D. L. Rabenstein. (c) Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967. (d) Author to whom inquiries should be addressed at Chevron Research Co., Richmond, Calif. 94802.

(2) R. J. Kula and D. L. Rabenstein, *J. Am. Chem. Soc.*, **89**, 552 (1967).

(3) R. J. Kula and G. H. Reed, *Anal. Chem.*, **38**, 697 (1966).

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

(5) N. Tanaka, *Bull. Chem. Soc. Japan*, **36**, 67 (1963).

(6) N. Tanaka, H. Osawa, and M. Kamada, *ibid.*, **36**, 530 (1963).

(7) K. Bril, S. Bril, and P. Krumholz, *J. Phys. Chem.*, **59**, 596 (1955).

(8) N. Tanaka, R. Tamamushi, and M. Kodama, *Z. Physik. Chem. (Frankfurt)*, **14**, 141 (1958).

values predicted for a mechanism where water loss from the aquated metal ion is the rate-determining step. The results for the alkaline earth-EDTA systems were discussed in terms of an intermediate in which the alkaline earth ion is bonded to one iminodiacetate segment of EDTA and the proton to the other.<sup>2,3</sup> However, no conclusions could be drawn regarding the relative importance of proton migration and metal ion dissociation processes in governing the reaction rate.

In the present paper, the results of nmr line-broadening studies of the ligand exchange kinetics in the Cd(II)-, Zn(II)-, and Pb(II)-nitrilotriacetic acid (NTA) systems are reported. These systems have been investigated to elucidate the mechanism of the reaction of protonated multidentate aminocarboxylic acid ligands with aquated metal ions. The structurally simpler NTA ligand possesses four coordinating groups, three carboxylate oxygens and one nitrogen; and in the monoprotonated ligand, the proton is on the nitrogen atom.<sup>9,10</sup> Since there are fewer metal-coordinating groups in NTA than in EDTA, the importance of proton transfer in the reactions of the monoprotonated ligand should be more readily ascertainable.

Also included in the present paper are the results of nmr investigations of the complex formation equilibria for these metal-NTA systems, including complexes with NTA-to-metal ratios of 1 and 2.

## Experimental Section

**Chemicals.** Nitrilotriacetic acid (Geigy Chemical Co.) was purified by recrystallizing it three times from aqueous solution. The crystalline potassium salts of the complexes, KMNTA, were synthesized using H<sub>3</sub>NTA and the appropriate reagent grade metal carbonate. The general procedure was to prepare a solution approximately 0.2 M in metal carbonate and in H<sub>3</sub>NTA. After the solution was stirred vigorously with the evolution of carbon dioxide, KOH was added to bring the pH to approximately 8.0. Ethanol was added to crystallize the potassium salts of the 1:1 complexes which were redissolved in water and crystallized again by adding ethanol. After drying in a vacuum oven at 60°, the crystalline complexes had the following compositions: KZnNTA·H<sub>2</sub>O, KCdNTA·0.5H<sub>2</sub>O, and KPbNTA. A previously described nmr technique for determining hydration numbers was employed to determine the extent of hydration of the crystalline complexes.<sup>11</sup>

For the nmr studies, weighed amounts of the crystalline complex and H<sub>3</sub>NTA were mixed to give the desired concentrations, and KOH was added to bring the solution to the appropriate pH. All solutions were prepared using triply distilled water. Tetramethylammonium (TMA) nitrate, prepared by titration of a 25% aqueous solution of TMA hydroxide (Matheson Coleman and Bell) with HNO<sub>3</sub> to a neutral pH, was the source of TMA for chemical shift measurements.

**pH Measurements.** All pH measurements were made with a Sargent Model DR pH meter equipped with a standard glass electrode and a fiber tip, saturated calomel reference electrode. Before making measurements, the pH meter was standardized using both saturated potassium acid tartrate buffer (pH 3.56) and 0.01 M sodium tetraborate buffer (pH 9.18). The potentiometric pH titration procedure used for determining the acid ionization constants of NTA has been described previously.<sup>12</sup> The ionic strength was maintained constant with 1.0 M KNO<sub>3</sub>, and the titration was performed at 25°. The acid ionization constants were reevaluated at this high ionic strength to make them compatible with the nmr data which are obtained on solutions of high ionic strength (normally between 1 and 2 M).

(9) D. Chapman, D. R. Lloyd, and R. Prince, *J. Chem. Soc.*, 3645 (1963).

(10) V. L. Hughes and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 1319 (1956).

(11) R. J. Kula, D. L. Rabenstein, and G. H. Reed, *Anal. Chem.*, **37**, 1783 (1964).

(12) R. J. Kula and D. L. Rabenstein, *ibid.*, **38**, 1934 (1966).

**Nmr Measurements.** Proton nmr measurements were made on a Varian A-60A high-resolution spectrometer at a probe temperature of 25 ± 1°. Spectra were recorded at sweep rates of 0.2 Hz/sec both for chemical shift measurements and for resonance line-width measurements. Sweep widths of 50 and 100 Hz were employed. For line-width measurements, each spectrum was recorded four or five times, and the individual values were averaged. The experimental line widths reported are the averaged values. For line widths less than 5 Hz, the precision of the measurements was ± 0.2 Hz; for line widths greater than 5 Hz, the precision was ± 0.4 Hz.

All chemical shift measurements are reported in hertz from the central resonance of the TMA triplet, a negative shift indicating that the resonance is downfield from TMA. The TMA resonances are near the resonances of the nonlabile protons of NTA allowing narrow regions of the spectrum to be expanded and increasing the accuracy of the measured chemical shifts and line widths.

**Rate Measurements.** To quantitatively evaluate the exchange rate constants, the NTA-to-metal ratio was varied from 1 to 2 at constant values of pH, and the lifetimes of the NTA in the complexed and free environments were calculated from the observed nmr spectra. The exchange kinetics are considered to be in the slow, intermediate, or fast exchange region according to the following criteria. In the extreme of slow exchange, separate resonances are observed for the free and for the complexed NTA. In the extreme of fast exchange, one averaged, broadened resonance is observed for the NTA in the two forms. For intermediate rates of exchange, the transition from separate resonances for the free and for the complexed NTA to one averaged resonance occurs.

In the extreme of slow exchange, the mean lifetime,  $\tau_{\text{complex}}$ , of a given metal NTA species between events which lead to exchange of ligand between free and complexed forms was calculated from the width of the complexed NTA resonance using eq 3.<sup>13</sup>

$$\frac{1}{\tau_{\text{complex}}} = \pi(W_{1/2}' - W_{1/2}) \quad (3)$$

$W_{1/2}'$  is the line width of the exchange-broadened, complexed NTA resonance (in hertz), and  $W_{1/2}$  is the line width of the complexed NTA resonance in the absence of exchange.  $W_{1/2}$  was obtained from the nmr spectrum for a solution containing equimolar concentrations of NTA and metal at the same pH as that at which the exchange measurement was made.

For the intermediate exchange situation, the mean lifetime of the metal complex was calculated from the observed separation (in hertz) of the two overlapping resonances using eq 4.<sup>13</sup>  $\Delta\nu_0$  is the

$$\frac{1}{\tau_{\text{complex}}} = \frac{\sqrt{2}\pi(\Delta\nu_0^2 - \Delta\nu_{\text{exch}}^2)^{1/2}}{2} \quad (4)$$

separation of the free and complexed NTA resonances in the absence of exchange, and  $\Delta\nu_{\text{exch}}$  is the observed separation of the resonances under conditions where exchange between the two forms is occurring. Equation 4 is applicable only to the case in which the populations of the free and complexed NTA are equal.

In the extreme of rapid exchange, one resonance is observed at a mean chemical shift given by

$$\nu_{\text{mean}} = P_{\text{free}}\nu_{\text{free}} + P_{\text{complex}}\nu_{\text{complex}} \quad (5)$$

$P$  represents the fractional population and  $\nu$  the chemical shift of the ligand resonances in each form.  $P_{\text{free}} = [\text{NTA}]_{\text{free}}/[\text{NTA}]_{\text{total}}$  where  $[\text{NTA}]_{\text{total}} = [\text{NTA}]_{\text{complex}} + [\text{NTA}]_{\text{free}}$  and  $P_{\text{free}} + P_{\text{complex}} = 1$ . As  $\tau_{\text{free}}$  and  $\tau_{\text{complex}}$  decrease, the line width of the resonance at  $\nu_{\text{mean}}$  decreases, reaching a limiting value given by eq 6.  $W_{1/2, \text{free}}$

$$W_{1/2}^{\text{limiting}} = P_{\text{free}}W_{1/2, \text{free}} + P_{\text{complex}}W_{1/2, \text{complex}} \quad (6)$$

and  $W_{1/2, \text{complex}}$  are the line widths of the free and complexed NTA in the absence of exchange. For line widths greater than  $W_{1/2}^{\text{limiting}}$ , the mean lifetime of the complexed species was calculated from the observed line width,  $W_{1/2}^{\text{obsd}}$ , using eq 7.<sup>13</sup>

(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 221-223.

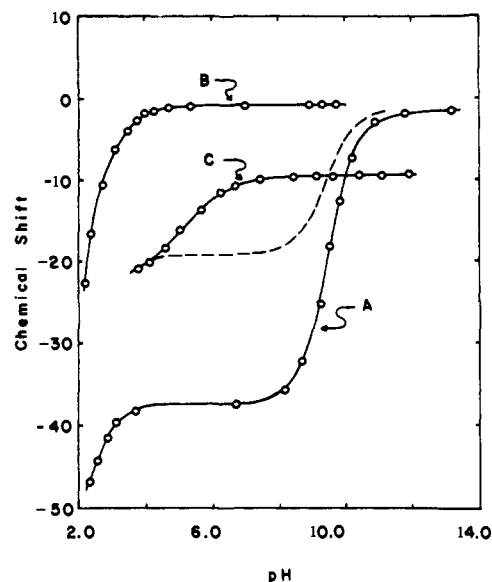


Figure 1. pH dependence of the chemical shifts for acetate resonances in Cd-NTA solutions: curve A, 0.30 M H<sub>3</sub>NTA above pH 4, 0.05 M H<sub>3</sub>NTA below pH 4; curve B, 0.10 M KCdNTA; curve C, 0.60 M H<sub>3</sub>NTA, 0.30 M Cd(NO<sub>3</sub>)<sub>2</sub>. Dashed line is the predicted chemical shift behavior for a solution containing 0.60 M H<sub>3</sub>NTA, 0.30 M Cd(NO<sub>3</sub>)<sub>2</sub> if no Cd(NTA)<sub>2</sub><sup>4-</sup> complex were formed and ligand exchange is rapid (temperature 25°).

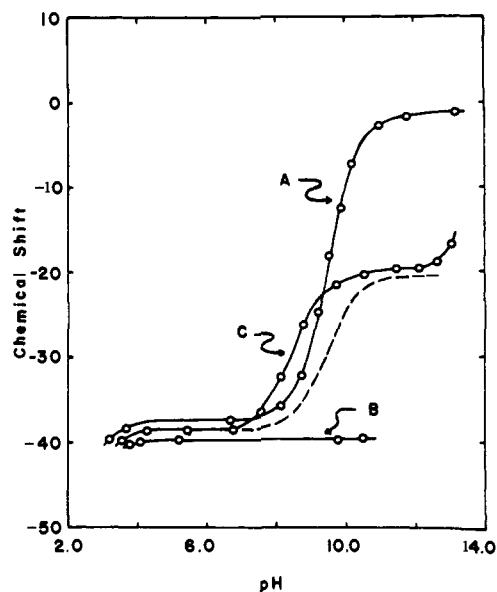


Figure 2. pH dependence of the chemical shifts for acetate resonances in Pb-NTA solutions: curve A, 0.30 M H<sub>3</sub>NTA; curve B, 0.15 M KPbNTA; curve C, 0.30 M H<sub>3</sub>NTA, 0.15 M Pb(NO<sub>3</sub>)<sub>2</sub>. Dashed line is the predicted chemical shift behavior for a solution containing 0.30 M H<sub>3</sub>NTA, 0.15 M Pb(NO<sub>3</sub>)<sub>2</sub> if no Pb(NTA)<sub>2</sub><sup>4-</sup> complex were formed and ligand exchange is rapid (temperature 25°).

$$\frac{1}{\tau_{\text{complex}}} = \frac{P_{\text{free}}^2 P_{\text{complex}} 4\pi(\nu_{\text{free}} - \nu_{\text{complex}})^2}{W_{1/2}^{\text{obsd}} - (P_{\text{free}} W_{1/2, \text{free}}) - (P_{\text{complex}} W_{1/2, \text{complex}})} \quad (7)$$

## Results

**Nmr Behavior of Metal-Nitrilotriacetate Systems.** The proton nmr spectrum for the six equivalent, nonlabile CH<sub>2</sub> (acetate) protons of NTA consists of a single resonance in the absence of a complexing metal ion. The chemical shift of this resonance is pH dependent, as shown by curve A in Figure 1. Above pH 12, the chemical shift approaches a constant value corresponding to the chemical shift of the NTA trianion, NTA<sup>3-</sup>. Between pH 12 and 7, the chemical shift decreases, corresponding to the addition of one proton to form the monoprotonated dianion, HNTA<sup>2-</sup>. The acidic proton adds to the nitrogen atom to form the nitrogen-protonated zwitterion.<sup>9,10</sup> Below pH 4, the acetate proton resonance is shifted further downfield, corresponding to protonation of the carboxylate groups. From the chemical shift behavior, it is evident that in the pH range 4–7, the major species present is HNTA<sup>2-</sup>. In those pH regions where the NTA is present in more than one form, only one averaged resonance is observed, indicating that the acidic proton exchange is rapid on the nmr time scale.

The proton nmr spectra of the metal-NTA systems were observed as a function of pH. The accessible pH ranges for solutions having a metal-to-NTA ratio of 1 are pH 2–10 for Cd-NTA, pH 3.5–11 for Pb-NTA, and pH 2–8 for Zn-NTA. Below pH 2, H<sub>3</sub>NTA precipitates. Above pH 8, Zn(OH)<sub>2</sub> precipitates in the Zn system, and above pH 10, Cd(OH)<sub>2</sub> precipitates in the Cd system. In the Pb system, a precipitate containing Pb and NTA forms

below pH 3.5, and above pH 11, Pb precipitates either as the hydroxide or the hydrous oxide.

The chemical shift of the acetate protons in the Cd-NTA and Pb-NTA systems depends upon the solution pH, as shown in Figures 1 and 2, respectively. For a metal-to-ligand ratio of 1 in the Cd-NTA and Pb-NTA systems, the nmr spectra consist of a narrow, single resonance flanked symmetrically by two smaller satellite resonances over a wide pH range (pH 3.6–10 for Cd-NTA and pH 3.7–9 for Pb-NTA). The chemical shift behavior of the central resonance is shown by the curves labeled B in Figures 1 and 2. Below pH 4, the chemical shift of the central resonance is pH dependent due to partial dissociation of the 1:1 complexes and exchange of NTA between the free and the complexed forms. Above pH 4 for both systems, the chemical shift remains constant, corresponding to the chemical shifts of the M(NTA)<sup>-</sup> complexes (-0.8 Hz for Cd(NTA)<sup>-</sup> and -39.8 Hz for Pb(NTA)<sup>-</sup>). The chemical shift difference between Pb(NTA)<sup>-</sup> and NTA<sup>3-</sup> measured in the present study (38.0 Hz) differs from a previously reported value (30 Hz).<sup>14</sup> The present measurement was made under conditions where the NTA-to-metal ratio was 1 so that only the Pb(NTA)<sup>-</sup> complex was present. For a ratio greater than 1, some Pb(NTA)<sub>2</sub><sup>4-</sup> forms, resulting in a chemical shift difference between Pb(NTA)<sup>-</sup> and NTA<sup>3-</sup> of less than 38.0 Hz.

The Cd(NTA)<sup>-</sup> spectrum is shown in Figure 3. The satellite resonances which symmetrically flank the central resonance arise from spin-spin coupling of the magnetically active Cd<sup>111</sup> and Cd<sup>113</sup> nuclei (natural abundance of 25%; nuclear spins of 1/2) with the acetate protons. *J*<sub>CH<sub>2</sub>-Cd</sub>, the metal proton coupling constant, is small compared to the difference between the resonance frequencies

(14) R. J. Day and C. N. Reiley, *Anal. Chem.*, **38**, 1323 (1966).

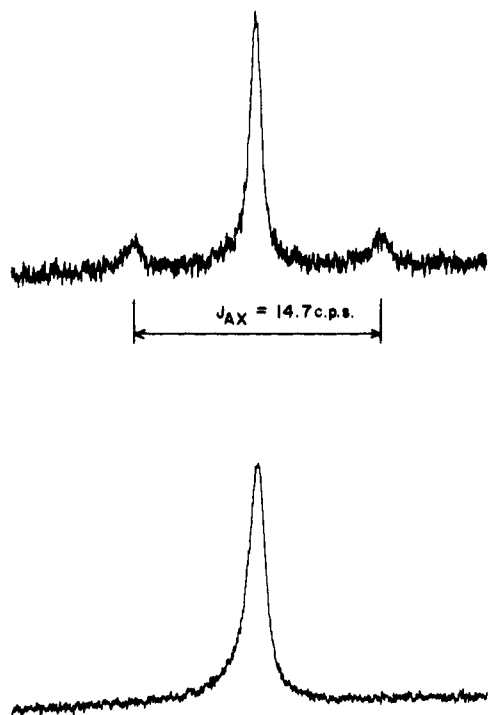
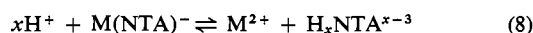


Figure 3. Nmr spectra (60-MHz) of Cd-NTA complexes: upper, 0.10  $M$   $\text{Cd}(\text{NTA})^-$ , pH 6.5; lower, 0.10  $M$   $\text{Cd}(\text{NTA})_2^{4-}$ , pH 11.2 (temperature 25°).

of the ligand protons and the magnetically active nuclei<sup>15</sup> so that the spin-spin coupling in  $\text{Cd}(\text{NTA})^-$  can be described as an  $A_6X$  situation. Analysis of the spectrum shows that  $J_{\text{CH}_2-\text{Cd}}$  is equal to 14.7 Hz for  $\text{Cd}(\text{NTA})^-$ . Similar spectra are observed for the  $\text{Pb}(\text{NTA})^-$  complex due to spin-spin coupling of the  $\text{Pb}^{207}$  nuclei (natural abundance of 21%; nuclear spin of  $1/2$ ) with the acetate protons.  $J_{\text{CH}_2-\text{Pb}}$  is equal to 18.9 Hz for  $\text{Pb}(\text{NTA})^-$ . The satellite resonances for  $\text{Cd}(\text{NTA})^-$  are broadened at the extremes of the pH region over which they are observed. For  $\text{Pb}(\text{NTA})^-$ , the satellite resonances are broadened at the lower pH limit of 3.7 and are collapsed above pH 9.

The chemical shift behavior for the Zn-NTA system is shown in Figure 4. For a metal-to-ligand ratio of 1, a single averaged pH-dependent resonance was observed over the pH range studied (2–8). Above pH 4, the chemical shift remains constant at a value of  $-16.0$  Hz, corresponding to the chemical shift of the  $\text{Zn}(\text{NTA})^-$  complex.

For the  $\text{Cd}(\text{NTA})^-$  and  $\text{Zn}(\text{NTA})^-$  complexes, as the pH is decreased below a certain value, the resonance (curve B) shifts in the direction of free NTA resonances at that pH (curve A). This chemical shift behavior suggests dissociation of the  $\text{M}(\text{NTA})^-$  complex into free ligand and aquated metal ion according to eq 8. In these pH regions, NTA is present in both free and complexed forms



and must be exchanging rapidly between these two forms because only one averaged resonance is observed. The

(15) Reference 13, p 480.

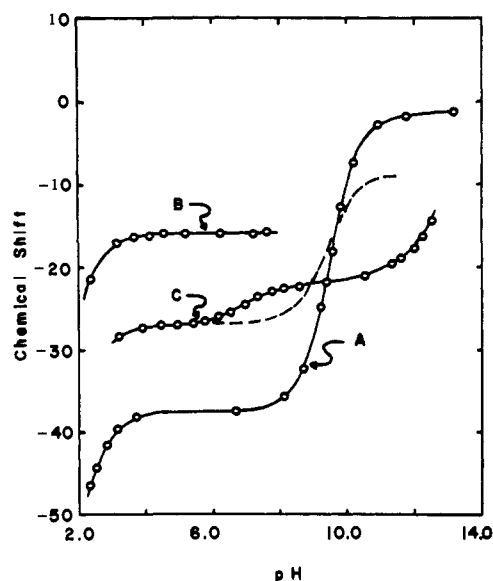


Figure 4. pH dependence of the chemical shifts for acetate resonances in Zn-NTA solutions: curve A, 0.30  $M$   $\text{H}_3\text{NTA}$  above pH 4, 0.05  $M$   $\text{H}_3\text{NTA}$  below pH 4; curve B, 0.15  $M$   $\text{KZnNTA}$ ; curve C, 0.30  $M$   $\text{H}_3\text{NTA}$ , 0.15  $M$   $\text{Zn}(\text{NO}_3)_2$ . Dashed line is the predicted chemical shift behavior for a solution containing 0.30  $M$   $\text{H}_3\text{NTA}$ , 0.15  $M$   $\text{Zn}(\text{NO}_3)_2$  if no  $\text{Zn}(\text{NTA})_2^{4-}$  complex were formed and ligand exchange is rapid (temperature 25°).

formation constants of the 1:1  $\text{M}(\text{NTA})^-$  complexes, defined by eq 9, can be calculated from the pH dependence

$$K_{f1} = \frac{[\text{M}(\text{NTA})^-]}{[\text{M}^{2+}][\text{NTA}^{3-}]} \quad (9)$$

of the chemical shift curves. At a certain pH, the conditional formation constant,  $K'_{f1}$ , is defined by eq 10, and the observed chemical shift,  $\nu_{\text{obsd}}$ , is given by eq 11.

$$K'_{f1} = \frac{[\text{M}(\text{NTA})^-]}{[\text{M}^{2+}][\text{NTA}]_{\text{free}}} \quad (10)$$

$$\nu_{\text{obsd}} = P_{1:1}\nu_{1:1} + P_{\text{NTAfree}}\nu_{\text{NTAfree}} \quad (11)$$

$P$  is the fractional population and  $\nu$  the chemical shift of the ligand in a given form,  $P_{1:1} = [\text{M}(\text{NTA})^-]/[\text{NTA}]_{\text{total}}$  where  $[\text{NTA}]_{\text{total}} = [\text{M}(\text{NTA})^-] + [\text{NTA}]_{\text{free}}$ ,  $P_{1:1} + P_{\text{NTAfree}} = 1$ , and  $\nu_{\text{obsd}}$  is obtained from curve B at each pH under consideration.

By rearranging eq 11, the fractional populations can be expressed in terms of  $\nu_{\text{obsd}}$  as

$$P_{1:1} = \frac{\nu_{\text{obsd}} - \nu_{\text{NTAfree}}}{\nu_{1:1} - \nu_{\text{NTAfree}}} \quad (12)$$

$$P_{\text{NTAfree}} = \frac{\nu_{\text{obsd}} - \nu_{1:1}}{\nu_{\text{NTAfree}} - \nu_{1:1}} \quad (13)$$

Substitution of eq 12 and 13 into eq 10 yields eq 14, which expresses  $K'_{f1}$  in terms of  $\nu_{\text{obsd}}$ . The formation constant

$$K'_{f1} = \frac{\left( \frac{\nu_{\text{obsd}} - \nu_{\text{NTAfree}}}{\nu_{1:1} - \nu_{\text{NTAfree}}} \right)}{\left( \frac{\nu_{\text{obsd}} - \nu_{1:1}}{\nu_{\text{NTAfree}} - \nu_{1:1}} \right)^2} [\text{NTA}]_{\text{total}} \quad (14)$$

**Table I.** Experimentally Determined Equilibrium Constants<sup>a</sup>

	CdNTA <sup>b</sup>	ZnNTA <sup>b</sup>	PbNTA
Log $K_{f1}$	9.4	10.0	11.4 <sup>c</sup>
Log $K_{f2}$	4.9	3.5	2.0 <sup>b</sup>

<sup>a</sup> At 25°. <sup>b</sup> Determined from nmr measurements under high ionic strength conditions. <sup>c</sup> Under low ionic strength conditions; see ref 16.

$K_{f1}$  is then calculated from  $K_{f1}'$  using eq 15, where  $\alpha_3$  is the fraction of free NTA present as  $\text{NTA}^{3-}$  at the pH value for which  $K_{f1}'$  was determined.  $\alpha_3$  was calculated using acid ionization constants determined potentiometrically in 1.0 M ionic strength solution ( $\text{p}K_1 = 1.54$ ,  $\text{p}K_2 = 2.26$ ,  $\text{p}K_3 = 9.55$ ). The formation constants for the  $\text{Cd}(\text{NTA})^-$  and  $\text{Zn}(\text{NTA})^-$  complexes given in Table I<sup>16</sup> were calculated

$$K_{f1} = K_{f1}'/\alpha_3 \quad (15)$$

from the data in Figures 1 and 4. The formation constant for the  $\text{Pb}(\text{NTA})^-$  complex could not be calculated from the nmr data because the complex is stable over the accessible pH range, and no shift in the resonance because of complex dissociation is observed.

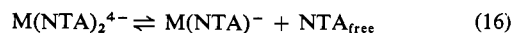
For a metal-to-ligand ratio of 2 in all three systems, only one averaged pH-dependent resonance was observed in the pH regions studied. The chemical shift behavior of these averaged resonances is shown by the curves labeled C in Figures 1, 2, and 4. This indicates that the NTA is exchanging rapidly between the free and complexed forms. If, however, the NTA were exchanging only between the free form and the 1:1 complexed form, the experimental curves would follow the curves given by the dashed lines since the NTA would be exchanging between two different chemical environments whose chemical shifts are given by curves A and B. The population of each of the environments would be equal so that the observed chemical shift would be midway between curves A and B. In none of the systems studied does the experimental chemical shift curve follow the behavior predicted if NTA were present only as  $\text{NTA}_{\text{free}}$  and  $\text{M}(\text{NTA})^-$ . Rather, the curves are shifted, indicating that at least one additional complexed species is formed. Because NTA is a tetradentate ligand, and because these metals are all capable of octahedral coordination,<sup>17</sup> there may be at least two coordination sites on the metal ion occupied by water molecules in the  $\text{M}(\text{NTA})^-$  complex. Thus, a second NTA ligand can add to  $\text{M}(\text{NTA})^-$  to form the  $\text{M}(\text{NTA})_2^{4-}$  complex. Evidence for  $\text{M}(\text{NTA})_2^{4-}$  complexes with Cd and Zn has previously been obtained from potentiometric pH titration data.<sup>18</sup>

The chemical shifts given by curve C for the Cd and Pb systems, in which the NTA-to-metal ratio is 2 (Figures 1 and 2), reach a plateau above pH 7 and 11, respectively, and these plateaus are presumably the chemical shifts of the  $\text{M}(\text{NTA})_2^{4-}$  complexes ( $-9.6$  Hz for  $\text{Cd}(\text{NTA})_2^{4-}$  and  $-19.5$  Hz for  $\text{Pb}(\text{NTA})_2^{4-}$ ). Below these pH's the  $\text{M}(\text{NTA})_2^{4-}$  complexes dissociate according to eq 16.

(16) L. G. Sillén and A. E. Martell, "The Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

(17) B. E. Douglas and D. H. McDaniel, "Concepts and Models of Inorganic Chemistry," Blaisdell Publishing Co., Waltham, Mass., 1965, p 370.

(18) G. Schwarzenbach and W. Beidermann, *Helv. Chim. Acta*, **31**, 331 (1948).



The chemical shift of the averaged resonance (curve C) is determined by the fractional population and chemical shift of NTA in each of the three forms ( $\text{NTA}_{\text{free}}$ ,  $\text{M}(\text{NTA})^-$ , and  $\text{M}(\text{NTA})_2^{4-}$ ) and can be used to calculate the conditional formation constant (defined by eq 17).

$$K_{f2}' = \frac{[\text{M}(\text{NTA})_2^{4-}]}{[\text{M}(\text{NTA})^-][\text{NTA}]_{\text{free}}} \quad (17)$$

The observed chemical shift is described by an equation analogous to eq 11. By considerations similar to those employed in the derivation of eq 14, the conditional formation constant is expressed in terms of the observed chemical shift by eq 18. The formation constant for the  $K_{f2}' =$

$$2 \left( \frac{2v_{\text{obsd}} - v_{\text{M}(\text{NTA})^-} - v_{\text{NTA}_{\text{free}}}}{2v_{\text{M}(\text{NTA})_2^{4-}} - v_{\text{M}(\text{NTA})^-} - v_{\text{NTA}_{\text{free}}}} \right)^2 [\text{NTA}]_{\text{total}} \quad (18)$$

$\text{M}(\text{NTA})_2^{4-}$  complexes,  $K_{f2}$  (defined by eq 19), can then be calculated from  $K_{f2}'$  using eq 20.  $K_{f2}$  has been

$$K_{f2} = \frac{[\text{M}(\text{NTA})_2^{4-}]}{[\text{M}(\text{NTA})^-][\text{NTA}^{3-}]} \quad (19)$$

$$K_{f2} = K_{f2}'/\alpha_3 \quad (20)$$

calculated for the Cd-NTA and Pb-NTA systems using the data in Figures 1 and 2. The results are given in Table I.

For the Zn-NTA system (Figure 4), curve C continues to shift upfield and never reaches a constant value assignable to the chemical shift of  $\text{Zn}(\text{NTA})_2^{4-}$ . The upfield chemical shift is attributed to the formation of  $\text{Zn}(\text{NTA})(\text{OH})^{2-}$ . Without  $v_{\text{Zn}(\text{NTA})_2}$ ,  $K_{f2}$  cannot be evaluated directly from eq 18 and 20. However, from the observed chemical shift at two pH values, the above equations can be employed simultaneously to determine  $K_{f2}$  and  $v_{\text{Zn}(\text{NTA})_2}$ . By this method a value of  $-21.7$  Hz for  $v_{\text{Zn}(\text{NTA})_2}$  and the value of  $K_{f2}$  in Table I for  $\text{Zn}(\text{NTA})_2^{4-}$  are calculated.

The nmr spectra observed for the  $\text{M}(\text{NTA})_2^{4-}$  complexes consist of a single, sharp resonance. This is illustrated in Figure 3 by the spectrum for the  $\text{Cd}(\text{NTA})_2^{4-}$  complex. Of interest is the absence of the cadmium-proton and lead-proton couplings which are observed in the spectra for the 1:1  $\text{Cd}(\text{NTA})^-$  and  $\text{Pb}(\text{NTA})^-$  complexes.

#### Exchange Reactions Involving Monoprotonated NTA.

The nmr spectra of the three metal-NTA systems investigated each gave a single resonance for the solution conditions of Figures 1, 2, and 4, except for the satellite peaks present in the Cd-NTA and Pb-NTA systems when the NTA-to-metal ratio is 1. Resonance broadening was observed in certain pH regions for the Cd-NTA and Zn-NTA systems, indicating that ligand exchange was occurring and that the exchange rate constants for these systems were accessible by nmr techniques.

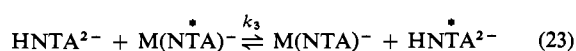
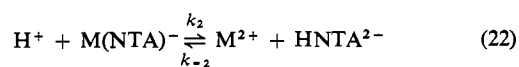
Below pH 7, noncomplexed NTA is present predominantly as  $\text{HNTA}^{2-}$ , and in the pH region below which appreciable amounts of  $\text{M}(\text{NTA})_2^{4-}$  complexes begin to form, exchange can be considered as occurring between  $\text{M}(\text{NTA})^-$  and  $\text{HNTA}^{2-}$ . On the basis of the species

**Table II.** Nmr Kinetic Data for the Cd-NTA System in the Low pH Region<sup>a</sup>

pH	[CdNTA], <i>M</i>	[NTA] <sub>free</sub> , <i>M</i>	<i>W</i> <sub>1/2, CdNTA</sub> <sup>b</sup>	$\Delta v_{\text{exch}}$ <sup>c</sup>	<i>W</i> <sub>1/2, (av)</sub> <sup>d</sup>	1/ $\tau_{\text{CdNTA}}$
4.40	0.04	0.04	8.6			24.4
4.40	0.07	0.07	11.2			32.7
4.40	0.10	0.10		32.4		36.5
4.40	0.13	0.13		27.9		53.2
4.40	0.16	0.16		23.9		61.0
4.40	0.20	0.20		18.4		70.0
4.10	0.04	0.04	12.6			37.1
4.10	0.07	0.07		31.4		39.6
4.10	0.10	0.10		27.8		51.0
4.10	0.13	0.13		25.0		58.0
4.10	0.16	0.16		19.4		68.0
3.80	0.30	0.30			19.2	108
3.99	0.30	0.30			23.7	90.0
4.10	0.30	0.30			26.4	83.4
4.21	0.30	0.30			28.1	78.5
4.29	0.30	0.30			29.3	75.0

<sup>a</sup> 25°. <sup>b</sup> Ligand-exchange rate slow; 1/ $\tau_{\text{CdNTA}}$  calculated using eq 3. <sup>c</sup> Ligand-exchange rate intermediate; 1/ $\tau_{\text{CdNTA}}$  calculated using eq 4. <sup>d</sup> Ligand-exchange rate rapid; 1/ $\tau_{\text{CdNTA}}$  calculated using eq 7.

present, the following exchange reaction paths were considered in the kinetic analysis for these pH regions.



Since the reactions are studied under equilibrium conditions, NTA = NT\*A, and the reverse rate constant in eq 23 is equal to the forward rate constant. Rate constant  $k_{-1}$  is related to  $k_1$ , and  $k_{-2}$  is related to  $k_2$  by the appropriate formation and acid dissociation constants. The resulting rate equation for the complexed NTA is

$$-\frac{d[\text{complex}]}{dt} = k_1[\text{M(NTA)}^-] + k_2[\text{M(NTA)}^-][\text{H}^+] + k_3[\text{M(NTA)}^-][\text{HNTA}^{2-}] \quad (24)$$

The reciprocal of the mean lifetime of the metal-NTA complex, 1/ $\tau_{\text{complex}}$ , is related to the exchange rate,  $-d[\text{complex}]/dt$ , by

$$\frac{1}{\tau_{\text{complex}}} = -\frac{d[\text{complex}]}{dt} \frac{1}{[\text{complex}]}$$

which leads to

$$\frac{1}{\tau_{\text{complex}}} = k_1 + k_2[\text{H}^+] + k_3[\text{HNTA}^{2-}] \quad (25)$$

The individual rate constants were evaluated by determining 1/ $\tau_{\text{complex}}$  as a function of [HNTA<sup>2-</sup>] at constant pH values and by determining 1/ $\tau_{\text{complex}}$  as a function of [H<sup>+</sup>] at constant [HNTA<sup>2-</sup>]. 1/ $\tau_{\text{complex}}$  was calculated from the measured line widths of the exchange broadened acetate resonances. For the data at constant pH values, plots of 1/ $\tau_{\text{complex}}$  vs. [HNTA<sup>2-</sup>] yielded  $k_3$  as the slope and  $k_1 + k_2[\text{H}^+]$  as the intercept. Rate constants  $k_1$  and  $k_2$  were obtained from the intercepts at several pH

**Table III.** Experimentally Determined Ligand-Exchange Rate Constants for NTA Complexes<sup>a,b</sup>

	CdNTA	ZnNTA
$k_1, \text{sec}^{-1}$	< 1	< 1
$k_2, M^{-1} \text{sec}^{-1}$	$2.9 \pm 0.5 \times 10^5$	$1.8 \pm 0.8 \times 10^5$
$k_{-2}, M^{-1} \text{sec}^{-1}$	$2.1 \pm 0.4 \times 10^5$	$5.1 \pm 1.0 \times 10^5$
$k_{-2}^{\text{predicted}}, M^{-1} \text{sec}^{-1}$	$1.2 \times 10^{10}$	$1.5 \times 10^9$
$k_3, M^{-1} \text{sec}^{-1}$	$2.9 \pm 1.0 \times 10^2$	$5.3 \pm 0.6 \times 10^2$
$k_4, M^{-1} \text{sec}^{-1}$	$1.8 \pm 0.3 \times 10^7$	$2.0 \pm 0.3 \times 10^6$
$k_5, M^{-1} \text{sec}^{-1}$	$1.3 \pm 0.4 \times 10^7$	$6.0 \pm 0.6 \times 10^8$
$k_6, \text{sec}^{-1}$	$2.2 \pm 0.4 \times 10^2$	$6.3 \pm 0.8 \times 10^2$
$k_7, M^{-1} \text{sec}^{-1}$	$1.4 \pm 0.2 \times 10^2$	
$k_8, M^{-1} \text{sec}^{-1}$	$1.2 \pm 0.3 \times 10^3$	

<sup>a</sup> 25°. <sup>b</sup> Error limits are the range of experimental values.

values by plotting the intercept vs. [H<sup>+</sup>]. For the data at constant [HNTA<sup>2-</sup>], plots of 1/ $\tau_{\text{complex}}$  vs. [H<sup>+</sup>] yielded  $k_2$  as the slope and  $k_1 + k_3[\text{HNTA}^{2-}]$  as the intercept;  $k_1$  and  $k_3$  were obtained from the intercepts by using data at several [HNTA<sup>2-</sup>] values.

**Cadmium-NTA.** Nmr kinetic data for the Cd-NTA system are presented in Table II. For the solution conditions used, the ligand-exchange rates varied from slow to rapid, and 1/ $\tau_{\text{complex}}$  was calculated using either eq 3, 4, or 7. The rate constants for the reactions which lead to exchange of NTA were resolved using eq 25 as discussed above. The results are presented in Table III.

The proton-assisted dissociation rate constant,  $k_2$ , has also been measured by electrochemical methods for the Cd(NTA)<sup>-</sup> complex. The reported values<sup>19</sup> range from  $6.5 \times 10^4$  to  $1.5 \times 10^6 M^{-1} \text{sec}^{-1}$ . The rate constant measured for this reaction in the present study is in good agreement with the value obtained by Shuman,  $4.1 \pm 0.5 \times 10^5 M^{-1} \text{sec}^{-1}$ , using stationary electrode polarography.<sup>20</sup>

**Zinc-NTA.** Nmr kinetic data for the Zn-NTA

(19) J. Koryta, *Z. Elektrochem.*, **64**, 196 (1960).

(20) M. Shuman, Ph.D. Dissertation, University of Wisconsin, Madison, Wis., 1966.

**Table IV.** Nmr Kinetic Data for the Zn-NTA System for the Low pH Region<sup>a</sup>

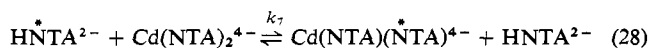
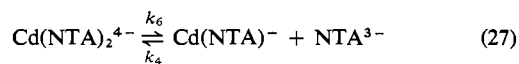
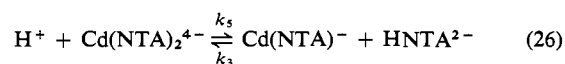
pH	[ZnNTA], <i>M</i>	[NTA] <sub>free</sub> , <i>M</i>	<i>W</i> <sub>1/2</sub> , (av)	1/τ <sub>ZnNTA</sub>
4.00	0.15	0.03	4.85	33.5
4.00	0.15	0.05	6.9	45.5
4.00	0.15	0.07	7.9	58.1
4.00	0.15	0.09	8.9	64.6
4.00	0.15	0.11	8.35	82.0
4.00	0.15	0.13	8.3	91.5
4.00	0.15	0.15	7.5	109
4.00	0.20	0.20	6.15	138
3.81	0.15	0.15	6.90	118
4.02	0.15	0.15	7.9	103
4.20	0.15	0.15	8.4	95.4
4.50	0.15	0.15	9.15	87.0
3.85	0.20	0.20	5.90	147
3.99	0.20	0.20	6.15	138
4.18	0.20	0.20	6.52	129
4.35	0.20	0.20	6.75	123
4.51	0.20	0.20	6.77	121
4.65	0.20	0.20	6.82	120

<sup>a</sup> 25°.

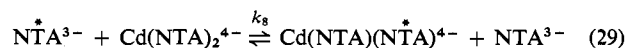
system are given in Table IV. The rate of ligand exchange for all the solutions listed in Table IV was rapid on the nmr time scale, and eq 7 was used to evaluate the lifetimes. The rate constants for the reactions resulting in ligand exchange were resolved using eq 25 and are listed in Table III.

**Lead-NTA.** The proton resonance of Pb(NTA)<sup>-</sup> is separated from the resonance of HNTA<sup>2-</sup> by only 2.5 Hz. In order that the nmr method be applicable to the study of exchange kinetics, the chemical shift separation of the two nonequivalent forms must be much greater than the line width in the absence of exchange.<sup>21</sup> The line widths of both the Pb(NTA)<sup>-</sup> and the HNTA<sup>2-</sup> proton resonances in the absence of exchange are 0.6 Hz, and, consequently, the ligand-exchange kinetics of Pb(NTA)<sup>-</sup> in the low pH region cannot be studied by nmr line-broadening methods.

**Exchange Reactions Involving the NTA Trianion.**  
**Cadmium-NTA.** For an NTA-to-Cd ratio of 2, the chemical shift data presented in curve C of Figure 1 indicate that the formation of Cd(NTA)<sub>2</sub><sup>4-</sup> is complete above pH 8.5. Below pH 8.5, exchange broadening was observed for the solution conditions of Figure 1, while above this pH the line width remained constant. When the NTA-to-Cd ratio was increased to 3, exchange broadening was observed up to pH 10. For these solution conditions, excess NTA is present, and exchange is occurring between the free and the complexed forms. Knowing the species present in this pH region, the following reactions have been considered in the kinetic analysis when the NTA-to-Cd ratio is greater than 2.



(21) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).



Equation 30 is the resulting rate expression for the non-complexed NTA.

$$-\frac{d[\text{NTA}]}{dt} = k_3[\text{Cd}(\text{NTA})^-][\text{HNTA}^{2-}] + k_4[\text{Cd}(\text{NTA})^-][\text{NTA}^{3-}] + k_7[\text{HNTA}^{2-}][\text{Cd}(\text{NTA})_2^{4-}] + k_8[\text{NTA}^{3-}][\text{Cd}(\text{NTA})_2^{4-}] \quad (30)$$

Converting this to an expression in terms of the mean lifetime of the noncomplexed NTA, τ<sub>NTA</sub>, leads to

$$\frac{1}{\tau_{\text{NTA}}} = k_3 \frac{\alpha_2[\text{Cd}(\text{NTA})_2^{4-}]}{K_{f2}\alpha_3[\text{NTA}]_{\text{free}}} + k_4 \frac{\alpha_3[\text{Cd}(\text{NTA})_2^{4-}]}{K_{f2}\alpha_3[\text{NTA}]_{\text{free}}} + k_7[\text{Cd}(\text{NTA})_2^{4-}]\alpha_2 + k_8[\text{Cd}(\text{NTA})_2^{4-}]\alpha_3 \quad (31)$$

where α<sub>3</sub> = [NTA<sup>3-</sup>]/[NTA]<sub>free</sub> and α<sub>2</sub> = [HNTA<sup>2-</sup>]/[NTA]<sub>free</sub> at the pH of the measurement. Plots of 1/(τ<sub>NTA</sub>[Cd(NTA)<sub>2</sub><sup>4-</sup>]) vs. 1/(K<sub>f2</sub>α<sub>3</sub>[NTA]<sub>free</sub>) at constant pH give straight lines whose slopes, *S*, are k<sub>3</sub>α<sub>2</sub> + k<sub>4</sub>α<sub>3</sub> and whose intercepts, *I*, are k<sub>7</sub>α<sub>2</sub> + k<sub>8</sub>α<sub>3</sub>. By analysis of data at different pH values, the various rate constants were resolved using eq 32 and 33.

$$\frac{S}{\alpha_3} = k_3 \left( \frac{\alpha_2}{\alpha_3} \right) + k_4 \quad (32)$$

$$\frac{I}{\alpha_2} = k_7 + k_8 \left( \frac{\alpha_3}{\alpha_2} \right) \quad (33)$$

The data for the Cd-NTA system listed in Table V were plotted according to eq 31. The following values (*M*<sup>-1</sup> sec<sup>-1</sup>) were obtained for *S*/α<sub>3</sub>: pH 8.50, 1.5 × 10<sup>7</sup>; pH 9.00, 1.8 × 10<sup>7</sup>; pH 9.40, 2.0 × 10<sup>7</sup>. Rate constant k<sub>3</sub> was previously determined (Table III) to be equal to 2.9 × 10<sup>2</sup> *M*<sup>-1</sup> sec<sup>-1</sup>. This rate constant is much smaller than the value measured for *S*/α<sub>3</sub> and, consequently, the contribution of k<sub>3</sub>(α<sub>2</sub>/α<sub>3</sub>) to *S*/α<sub>3</sub> must be negligible. *S*/α<sub>3</sub> is then equal to k<sub>4</sub>, and the average value of k<sub>4</sub> for the data presented is listed in Table III. Rate constant k<sub>6</sub> was calculated from k<sub>4</sub> using the relationship k<sub>6</sub> = k<sub>4</sub>/K<sub>f2</sub>.

The following values (*M*<sup>-1</sup> sec<sup>-1</sup>) were measured for *I*/α<sub>2</sub>: pH 8.50, 2.75 × 10<sup>2</sup>; pH 9.00, 5.0 × 10<sup>2</sup>; pH 9.40, 13.0 × 10<sup>2</sup>. The values of k<sub>7</sub> and k<sub>8</sub>, listed in Table III, were obtained from a plot of *I*/α<sub>2</sub> vs. α<sub>3</sub>/α<sub>2</sub>.

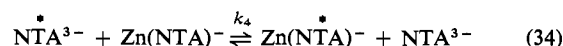
**Zinc-NTA.** Curve C in Figure 4 shows that at pH 5.6 Zn(NTA)<sub>2</sub><sup>4-</sup> begins to form. Below this pH, the predominant species present are Zn(NTA)<sup>-</sup> and HNTA<sup>2-</sup>. For a solution containing equal concentrations of the 1:1 complex and free NTA, eq 25 predicts that as the pH is increased upward from 4.0 toward 5.6, 1/τ<sub>complex</sub> will decrease ([H<sup>+</sup>] decreases; [HNTA<sup>2-</sup>] remains constant). As 1/τ<sub>complex</sub> decreases, the width of the averaged resonance will increase according to eq 7. If, however, exchange processes in addition to those considered in eq 25 are occurring, 1/τ<sub>complex</sub> will be larger than predicted by eq 25, and the width of the averaged resonance will be less than predicted. Such behavior is observed above pH 4.90 for the solution whose chemical shifts are plotted in curve C, Figure 4. The reaction

Table V. Nmr Kinetic Data for the Cd-NTA System in the High pH Region<sup>a</sup>

pH	[Cd] <sub>total</sub> M	[NTA] <sub>total</sub> M	α <sub>3</sub>	α <sub>2</sub>	W <sub>1/2</sub> (av)	1	
						τ <sub>NTAfree</sub> [Cd(NTA) <sub>2</sub> <sup>4-</sup> ]	K <sub>f2</sub> α <sub>3</sub> [NTA] <sub>free</sub>
8.50	0.10	0.26	0.091	0.909	5.00	3280	2.27 × 10 <sup>-3</sup>
8.50	0.10	0.29	0.091	0.909	6.70	2300	1.51 × 10 <sup>-3</sup>
8.50	0.10	0.32	0.091	0.909	8.10	1785	1.14 × 10 <sup>-3</sup>
8.50	0.10	0.35	0.091	0.909	9.35	1410	0.91 × 10 <sup>-3</sup>
9.00	0.10	0.26	0.24	0.76	3.60	3940	8.55 × 10 <sup>-4</sup>
9.00	0.10	0.29	0.24	0.76	4.47	2880	5.69 × 10 <sup>-4</sup>
9.00	0.10	0.32	0.24	0.76	5.35	2140	4.27 × 10 <sup>-4</sup>
9.00	0.10	0.35	0.24	0.76	6.00	1740	3.42 × 10 <sup>-4</sup>
9.40	0.10	0.26	0.50	0.50	2.42	4610	4.12 × 10 <sup>-4</sup>
9.40	0.10	0.29	0.50	0.50	2.80	3140	2.74 × 10 <sup>-4</sup>
9.40	0.10	0.32	0.50	0.50	3.05	2490	2.06 × 10 <sup>-4</sup>
9.40	0.10	0.35	0.50	0.50	3.16	2140	1.65 × 10 <sup>-4</sup>

<sup>a</sup> 25°.

which begins to contribute appreciably to the total exchange at this pH is



Including a term for this exchange path in eq 25 and rearranging leads to

$$\frac{1}{\tau_{\text{Zn}(\text{NTA})}} - k_2[\text{H}^+] - k_3[\text{HNNTA}^{2-}] = k_4\alpha_3[\text{NTA}]_{\text{free}} \quad (35)$$

A plot of the left side of eq 35 vs. α<sub>3</sub>[NTA]<sub>free</sub> yields a straight line with k<sub>4</sub> as the slope. Data from curve C, Figure 4, are plotted in Figure 5, and the value determined for k<sub>4</sub> is given in Table III. Rate constant k<sub>6</sub> is calculated from k<sub>4</sub> as in the Cd-NTA system.

**Lead-NTA.** The ligand-exchange kinetics for the Pb(NTA)<sub>2</sub><sup>4-</sup> complex could not be obtained from the nmr data. In the pH region where Pb(NTA)<sub>2</sub><sup>4-</sup> is present (pH 8–13), it was found that the line widths for the exchange-averaged resonance for a solution containing NTA-to-Pb in a ratio of 3 was only 0.7 Hz up to pH 13. This indicates that for the Pb-NTA system the rate of ligand exchange in the high pH region is extremely fast and outside the range observable by nmr. Assuming that an increase in line width of 0.2 Hz can be observed, the lifetime of Pb(NTA)<sub>2</sub><sup>4-</sup> is less than 6.6 × 10<sup>-4</sup> sec and the lifetime of NTA<sub>free</sub> is less than 3.2 × 10<sup>-4</sup> sec for the above solution at a pH of 12.

## Discussion

**Equilibrium Stability and Structures of the Metal-NTA Complexes.** The metal ions studied are presumably capable of both octahedral and tetrahedral coordination.<sup>17</sup> Assuming octahedral coordination in the M(NTA)<sup>-</sup> complexes and that all four of the NTA donor groups are metal coordinated, the M(NTA)<sup>-</sup> complexes would have the structure shown in Figure 6. The formation constants with the tetradentate NTA ligand (Table I) are larger than the formation constants for the corresponding tridentate N-methyliminodiacetic acid (MIDA) complexes<sup>16</sup> (log K<sub>f</sub> = 6.8 for Cd(MIDA), log K<sub>f</sub> = 7.7 for Zn(MIDA), and log K<sub>f</sub> = 8.0 for Pb(MIDA)), sup-

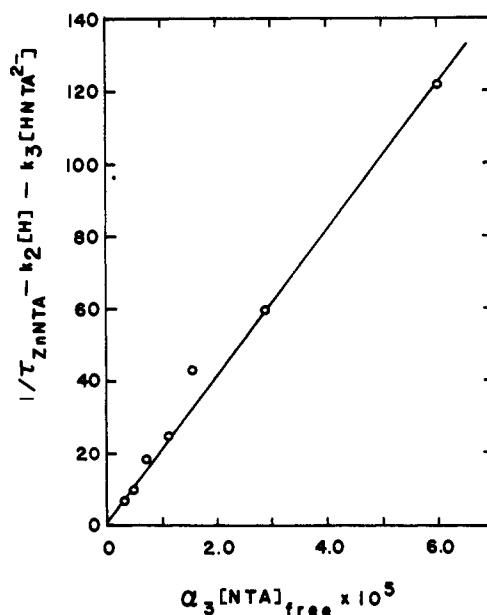


Figure 5. Nmr kinetic data for the Zn(NTA)<sup>-</sup> + NTA<sup>3-</sup> exchange reaction. H<sub>3</sub>NTA = 0.30 M, Zn(NO<sub>3</sub>)<sub>2</sub> = 0.15 M (temperature 25°).

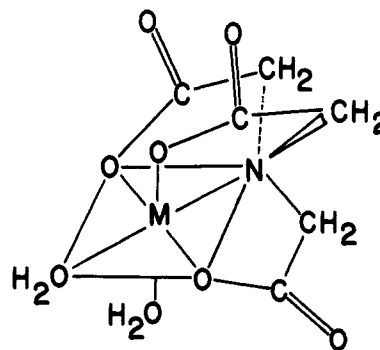


Figure 6. Possible structure of the 1:1 metal-NTA complexes.



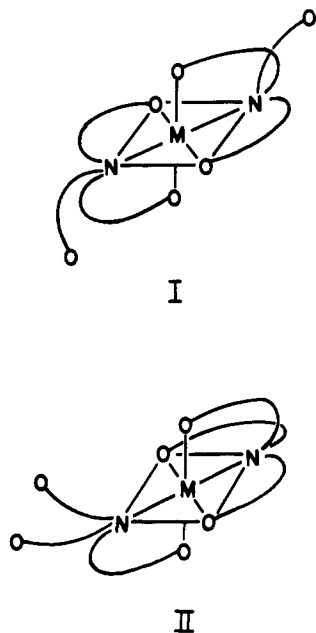


Figure 7. Possible structures of NTA complexes containing two NTA ligands.

porting the assumption that all four groups in NTA are metal coordinated.

In the  $M(\text{NTA})_2^{4-}$  complexes, there are eight possible ligand donor groups but, presumably, only six metal coordination sites. In one possible structure for the  $M(\text{NTA})_2^{4-}$  complexes (structure I in Figure 7), each of the NTA ligands is tridentate. The complex formed is then comparable to the  $M(\text{MIDA})_2^{2-}$  complexes in which all six coordination sites are presumably occupied. The over-all formation constants,  $K$ , for the  $M(\text{NTA})_2^{4-}$  complexes ( $K = K_{f1}K_{f2}$ ) are:  $\log K = 14.3$  for  $\text{Cd}(\text{NTA})_2^{4-}$ ,  $\log K = 13.5$  for  $\text{Zn}(\text{NTA})_2^{4-}$ , and  $\log K = 13.4$  for  $\text{Pb}(\text{NTA})_2^{4-}$ , compared to the over-all formation constants for the  $M(\text{MIDA})_2^{2-}$  complexes,<sup>16</sup>  $\log K = 12.5$  for  $\text{Cd}(\text{MIDA})_2^{2-}$ ,  $\log K = 14.1$  for  $\text{Zn}(\text{MIDA})_2^{2-}$ , and  $\log K = 12.1$  for  $\text{Pb}(\text{MIDA})_2^{2-}$ . Another possible structure for the  $M(\text{NTA})_2^{4-}$  complexes (structure II, Figure 7) has one NTA tetradentate and the other bidentate with a glycine segment complexed. Formation constants  $K_{f, \text{GI}}$  have been reported<sup>22</sup> for the glycine (GI) complexes of  $\text{Zn}(\text{NTA})^-$  and  $\text{Pb}(\text{NTA})^-$ , where  $K_{f, \text{GI}} = [\text{M}(\text{NTA})(\text{GI})]/[\text{M}(\text{NTA})][\text{GI}]$ . Using these data, over-all formation constants,  $K$ , are calculated for the glycine complexes ( $K = K_{f1}K_{f, \text{GI}}$ ):  $\log K = 13.6$  for  $\text{Zn}(\text{NTA})(\text{GI})^{2-}$  and  $\log K = 13.3$  for  $\text{Pb}(\text{NTA})(\text{GI})^{2-}$ . The formation constants for both the  $M(\text{NTA})(\text{GI})^{2-}$  complexes and the  $M(\text{MIDA})_2^{2-}$  complexes are in reasonable agreement with the formation constants for the  $M(\text{NTA})_2^{4-}$  complexes. Consequently, the equilibrium data do not indicate if one of the structures proposed in Figure 7 is favored.

The proton nmr spectra for the  $\text{Cd}(\text{NTA})^-$  and  $\text{Cd}(\text{NTA})_2^{4-}$  complexes and for the  $\text{Pb}(\text{NTA})^-$  and  $\text{Pb}(\text{NTA})_2^{4-}$  complexes provide additional insight into the structure of the  $M(\text{NTA})_2^{4-}$  complexes. For the  $\text{Cd}(\text{NTA})^-$  and  $\text{Pb}(\text{NTA})^-$  complexes, spin-spin coupling

of the NTA protons with the magnetically active Cd and Pb nuclei is observed, while it is absent in the spectra of the corresponding 2:1 complexes (Figure 3). Metal-proton coupling has previously been observed for the metal chelates of EDTA and several related ligands.<sup>23,24</sup> It has been proposed for the EDTA complexes that, even if the lifetime of individual metal EDTA bonds is short, the metal-proton coupling is not relaxed so long as the chelated EDTA does not exchange rapidly with the free EDTA.<sup>23</sup> The metal-proton coupling should be observed even if the ligand partially unwraps from a metal ion and then rebonds to the same metal ion because all nuclei remain in the same spin states, and the coupling is not relaxed. Thus, the presence of isotopic coupling in the  $\text{Pb}(\text{NTA})^-$  and  $\text{Cd}(\text{NTA})^-$  complexes implies that the first-order dissociation rate constants of these complexes are less than  $2\pi J_{\text{CH}_2-\text{M}}$  (experimentally  $2\pi J_{\text{CH}_2-\text{Cd}} = 92.5 \text{ sec}^{-1}$  for  $\text{Cd}(\text{NTA})^-$ ;  $2\pi J_{\text{CH}_2-\text{Pb}} = 119 \text{ sec}^{-1}$  for  $\text{Pb}(\text{NTA})^-$ ). Dissociation of the complexes at rates faster than this would lead to relaxation of the coupling.<sup>13</sup> This is in agreement with the upper limit determined for the dissociation rate constant of  $\text{Cd}(\text{NTA})^-$ .

The absence of metal-proton coupling for the  $\text{Cd}(\text{NTA})_2^{4-}$  and  $\text{Pb}(\text{NTA})_2^{4-}$  complexes means that the average rate constant for the dissociation of NTA from these complexes is greater than  $2\pi J_{\text{CH}_2-\text{M}}$ . In agreement with this, the rate constant for the dissociation of  $\text{Cd}(\text{NTA})_2^{4-}$  to form  $\text{Cd}(\text{NTA})^-$  is found to be approximately a factor of 2 larger than  $2\pi J_{\text{CH}_2-\text{Cd}}$ . The dissociation rate constant for  $\text{Pb}(\text{NTA})_2^{4-}$  could not be measured because the ligand exchange was too rapid, but, by analogy with the Cd-NTA system, it can be concluded from the absence of isotope coupling in  $\text{Pb}(\text{NTA})_2^{4-}$  that the first-order dissociation rate constant of  $\text{Pb}(\text{NTA})_2^{4-}$  is considerably larger than that of  $\text{Pb}(\text{NTA})^-$  and must be greater than  $119 \text{ sec}^{-1}$ . The absence of isotope coupling for both of these  $M(\text{NTA})_2^{4-}$  complexes seems to support structure I in Figure 7 where both NTA's are equivalent, and there is an equal probability for either to dissociate. Only three of the four available donor groups of each NTA are metal bonded, and the average lifetime of NTA complexed to the metal would be less than if all four coordinating groups were bonded (as in  $M(\text{NTA})^-$ ), which could result in a collapse of the isotope coupling. If the 2:1 complexes formed from  $M(\text{NTA})^-$  and  $\text{NTA}^{3-}$  by adding a glycine segment of  $\text{NTA}^{3-}$  to the metal ion (structure II in Figure 7), the bidentate  $\text{NTA}^{3-}$  would probably dissociate and should not result in the collapse of the tetradentate NTA metal-proton coupling. However, the bonding of the bidentate segment might result in weaker metal bonding to the tetradentate ligand, and a lifetime which would be decreased below  $1/2\pi J_{\text{CH}_2-\text{M}}$ . Studies of metal-proton coupling in metal-NTA-glycine mixed complexes should provide valuable information concerning the effect of a bidentate ligand upon the bonding of tetradentate NTA and the structure of the  $M(\text{NTA})_2^{4-}$  complexes.

The absence of AB patterns in the nmr spectra for the acetate protons of complexed NTA suggests that the individual metal carboxylate oxygen bonds are labile. If the bonding were inert, the different acetate protons would be magnetically nonequivalent, resulting in AB splitting of

(23) R. J. Day and C. N. Reilly, *Anal. Chem.*, **36**, 1073 (1964).

(22) D. Hopgood and R. J. Angelici, *J. Am. Chem. Soc.*, **90**, 2508 (1968).

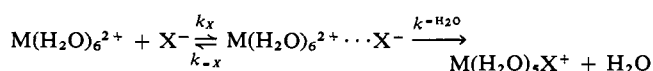
(24) G. H. Reed, Ph.D. Dissertation, University of Wisconsin, Madison, Wis., 1968.

these protons. Such AB splitting has been reported for the Co(III)-NTA complex which does have inert metal carboxylate oxygen bonding.<sup>25</sup> However, the absence of AB patterns does not indicate the lability of the metal nitrogen bonds in the complexes studied because AB patterns will not be observed even for inert metal nitrogen bonding when the metal carboxylate oxygen bonding is labile.<sup>26</sup>

**pH Dependence of Isotopic Coupling.** Metal-proton coupling is observed for Cd(NTA)<sup>-</sup> over the pH region 3.6-10 and for Pb(NTA)<sup>-</sup> over the pH region 3.7-9. At a pH of 3.6 for Cd(NTA)<sup>-</sup>, the isotope peaks are broad and are beginning to coalesce. Using the proton-assisted dissociation rate constant listed in Table III, the apparent first-order dissociation rate constant,  $k$  ( $k = k_1 + k_2[\text{H}^+]$ ), at pH 3.6 is calculated to be 72.5 sec<sup>-1</sup>. This agrees with the conclusion that the apparent first-order rate constant must be less than  $1/2\pi J_{\text{CH}_2-\text{Cd}}$  for the isotope coupling to still be observed ( $1/2\pi J_{\text{CH}_2-\text{Cd}} = 92.5 \text{ sec}^{-1}$ ). Below pH 3.6, the isotope peaks coalesce into the central resonance. At the lower pH limit of 3.7 for Pb(NTA)<sup>-</sup>, the coupling is broad but not yet completely relaxed. Koryta<sup>19</sup> reports a proton-assisted dissociation rate constant of  $2.5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$  for Pb(NTA)<sup>-</sup>. Using this rate constant, the apparent first-order dissociation rate constant at pH 3.7 is calculated to be 500 sec<sup>-1</sup>. This is much larger than the rate constant for which the isotope coupling would disappear ( $1/2\pi J_{\text{CH}_2-\text{Pb}} = 119 \text{ sec}^{-1}$ ), which suggests that Koryta's reported value for the proton-assisted dissociation rate constant is too large.

In the intermediate pH region for both Cd(NTA)<sup>-</sup> and Pb(NTA)<sup>-</sup>, the isotope peaks are sharp. At the upper limit of pH 10 for Cd(NTA)<sup>-</sup>, the coupling is again broad, indicating that the dissociation rate in this pH region is more rapid, possibly due to the greater lability of the Cd(NTA)(OH)<sup>2-</sup> complex which begins to form.<sup>18</sup> Above pH 9, the Pb(NTA)<sup>-</sup> isotope peaks disappear. This may be caused by the formation of a Pb(NTA)(OH)<sup>2-</sup> complex or by the reaction of free NTA (produced by the formation of lead hydroxide species) with Pb(NTA)<sup>-</sup>. The formation of lead hydroxide species also causes curve C in Figure 2 to shift upfield above pH 12. However, the stoichiometry of the species formed could not be established from the nmr data.

**Mechanism of Formation of NTA Complexes.** In the mechanism commonly proposed for the reaction of an aquated metal ion with a ligand to form a metal complex, the metal ion and the ligand first diffuse together to form an outer-sphere or association complex.<sup>27</sup> A water molecule then dissociates from the aquated metal ion, and a donor group of the ligand coordinates with the metal ion at the vacated site. When steric and electrostatic effects are negligible, the rate-determining step in this reaction mechanism is the water loss from the aquated metal ion. For a monodentate ligand, this mechanism may be depicted as



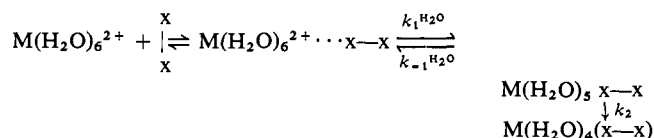
(25) B. B. Smith and D. T. Sawyer, *Inorg. Chem.*, **7**, 922 (1968).

(26) D. L. Rabenstein, Ph.D. Dissertation, University of Wisconsin, Madison, Wis., 1968.

(27) M. Eigen and R. G. Wilkins, "Mechanisms of Inorganic Reactions," *Advances in Chemistry Series*, No. 49, R. K. Murmann, R. T. M. Fraser, and J. Bauman, Ed., American Chemical Society, Washington, D. C., 1965, pp 55-65.

Steady-state approximations can be applied to this sequence to express the observed formation rate constant,  $k_f$ , in terms of the individual steps. The result is that  $k_f = K_{\text{os}}k_{-\text{H}_2\text{O}}$ , where  $K_{\text{os}}$  is the outer-sphere association constant ( $k_x/k_{-x}$ ) and  $k_{-\text{H}_2\text{O}}$  the rate of water loss from the aquated metal ion. The rates of water loss for many metals have been measured,<sup>28</sup> and  $K_{\text{os}}$  can be approximated using either the equations of Fuoss<sup>29</sup> or diffusion equations.<sup>30</sup>

For a multidentate ligand, the previously outlined reaction scheme has to be modified to account for the stepwise nature of complex formation with multidentate ligands.<sup>31-35</sup> This is illustrated by the reaction scheme for a bidentate ligand.

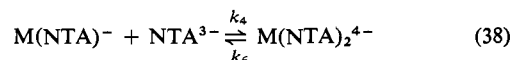
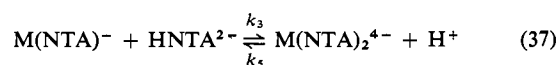


As in the case of a monodentate ligand, the bidentate ligand forms an outer-sphere complex with the metal ion followed by water loss from the metal ion and the formation of the first metal-ligand bond. A second water molecule then dissociates from the metal ion in a position *cis* to the first metal-ligand bond, and the second metal-ligand bond forms. The rate of this second bond formation process is represented by  $k_2$  in the above reaction sequence. Depending upon the relative magnitudes of  $k_{-1\text{H}_2\text{O}}$  and  $k_2$ , the first or second bond formation to the bidentate ligand determines the over-all rate of complex formation. For the tetradentate NTA ligand, the reaction sequence for complex formation would include steps for each of the successive bond formations.

In the present study, rate constants have been measured for the formation of the M(NTA)<sup>-</sup> complexes according to



and for the formation of the M(NTA)<sub>2</sub><sup>4-</sup> complexes according to



The necessary data are available to predict rate constant  $k_{-2}$  for the Cd and Zn systems for the mechanism in which loss of the first water molecule from the aquated metal ion is the rate-determining step. The predicted values,  $k_{-2}^{\text{predicted}}$ , are listed in Table III. The rates of water loss used for Cd<sup>2+</sup> and Zn<sup>2+</sup> are  $4 \times 10^8$  and  $5 \times 10^7 \text{ sec}^{-1}$ , respectively.<sup>28</sup> The ratio of the predicted  $k_{-2}$  to the observed  $k_{-2}$  is  $5 \times 10^4$  for Cd<sup>2+</sup> and  $3 \times 10^3$  for Zn<sup>2+</sup>. These data suggest that, in the reaction of Cd<sup>2+</sup> and Zn<sup>2+</sup> with HNTA<sup>2-</sup>, the rate-determining step is not loss of the

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(29) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

(30) M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, *Progr. Reaction Kinetics*, **2**, 287 (1964).

(31) G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

(32) A. K. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 3700 (1959).

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(34) D. B. Rorabacher and D. W. Margerum, *ibid.*, **3**, 382 (1964).

(35) D. W. Margerum and H. M. Rosen, *ibid.*, **7**, 299 (1968).

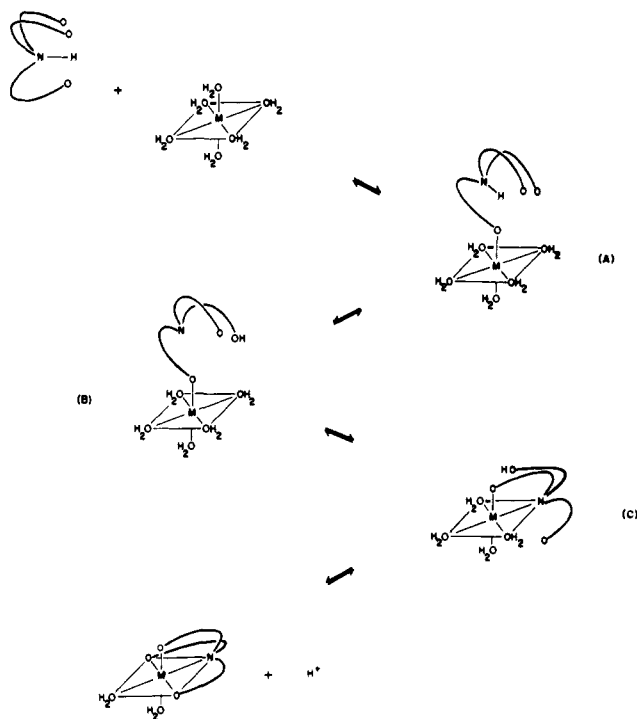


Figure 8. Proposed stepwise reaction mechanism for the formation of  $M(NTA)^-$  from the aquated metal ion and  $HNTA^{2-}$ .

first water molecule from the aquated metal ion. A large decrease in the rate of reaction of aquated  $Ni^{2+}$  with NTA upon protonation of the NTA has previously been reported.<sup>36</sup>

The rate of the reaction of  $M(NTA)^-$  with free NTA is also found to decrease if the reacting NTA is protonated. The ratio of  $k_4/k_3$  is  $6 \times 10^4$  for  $Cd^{2+}$  and  $4 \times 10^3$  for  $Zn^{2+}$ , within experimental error the same ratios as for  $k_{-2}^{predicted}/k_{-2}$ . In the formation of  $M(NTA)^-$  and  $M(NTA)_2^{4-}$  from  $HNTA^{2-}$ , then, the proton is important in governing the rates of the reactions.

In addition to the nitrogen-protonated  $HNTA^{2-}$  isomer in solution, a small equilibrium amount of carboxylate-protonated  $HNTA^{2-}$  can also be present. It may be that this is the reactive species rather than the nitrogen-protonated isomer due to blocking of the nitrogen atom by the proton.<sup>37,38</sup> Similar reactive species have been proposed for the reaction of diprotonated EDTA,<sup>38,39</sup> diprotonated analogs of EDTA and  $HNTA^{2-}$ , and monoprotonated iminodiacetate anion<sup>39</sup> with  $Ni^{2+}$ . The relative amount of carboxylate-protonated  $HNTA^{2-}$  should be governed by the relative basicities of the nitrogen and carboxylate oxygen groups of NTA.  $K_3^{-1}$  for  $HNTA^{2-}$  represents the basicity of the nitrogen, and  $K_a^{-1}$  for acetic acid should approximate the basicity of the carboxylate group in  $HNTA^{2-}$ . The estimated relative stability of the protonated carboxylate form, corrected statistically, is then  $3K_3/K_a \approx 1/(3 \times 10^4)$ . Based on these approximations, one out of every  $3 \times 10^4$

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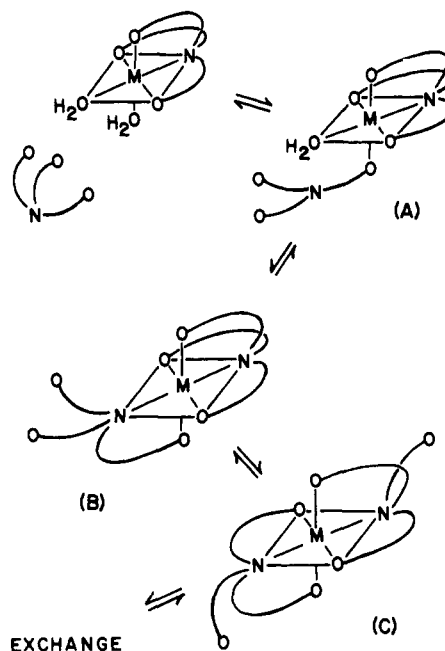


Figure 9. Proposed stepwise reaction mechanism for the symmetrical  $M(NTA)^- + NTA^{3-}$  ligand-exchange reaction.

$HNTA^{2-}$  ions is carboxylate protonated. If this is the reactive isomer,  $k_{-2}$  would be  $1/(3 \times 10^4)$  of  $k_{-2}^{predicted}$  and  $k_3$  would be  $1/(3 \times 10^4)$  of  $k_4$ . In each case this is approximately the ratio observed for Cd but is about 15 times greater than the ratio observed for  $Zn^{2+}$ . If the carboxylate-protonated isomer were the only reactive  $HNTA^{2-}$  species, these rate constants should decrease by the same amount for both the Cd and the Zn systems.

An alternative formation reaction mechanism to account for the observed kinetic behavior in the reaction of  $M^{2+}$  with  $HNTA^{2-}$  is shown in Figure 8. Assuming the nitrogen-protonated isomer is the reacting ligand, the first group to bond is presumably a carboxylate group, and intermediate A is formed. The next step is the loss of another water molecule and formation of the metal-nitrogen bond to close the chelate ring (intermediate C). Before this can happen, however, the proton must migrate from the nitrogen group to either solvent water or to a carboxylate group, the latter giving intermediate B. This process must be rapid relative to the rate at which intermediate A can dissociate back to reactants if the  $M(NTA)-(H_2O)_2^-$  complex is to form. If the proton transfer is slow relative to dissociation of intermediate A back to reactants,  $k_{-2}$  will be smaller than predicted.

Rate data are available for reactions similar to the two reactions possible for intermediate A. The dissociation rate constants for the Zn-(acetate) and Cd-(acetate) complexes are calculated to be  $\approx 2 \times 10^6$  and  $\approx 10^7$   $sec^{-1}$ , respectively.<sup>27</sup> Because of charge-charge interactions between the proton and the metal ion, the dissociation rate of the carboxylate-bonded intermediate back to reactants is presumably slightly different from these values. The reaction by which the proton is removed from the nitrogen to permit the complex to form could be either a direct reaction with solvent water or migration from the nitrogen to a neighboring carboxylate group.

The kinetics of these two reactions for glycine have been studied by Sheinblatt and Gutowsky, who report a pseudo-first-order rate constant of  $5 \text{ sec}^{-1}$  for the transfer of the proton to  $\text{H}_2\text{O}$  and a rate constant of  $175 \text{ sec}^{-1}$  for migration of the proton to the carboxylate group.<sup>40</sup> The rate constant for the process by which the proton leaves the nitrogen atom in intermediate A would probably be slightly different from either of these rate constants for glycine because of charge-charge interaction between the metal ion and the proton. However, the rate constants for the dissociation of the metal acetate complexes are much larger than the rate constants for the proton-transfer reactions. These considerations suggest that formation of the metal-nitrogen bond is rate determining in the complex formation reactions represented by eq 36 because of the slow rate of proton transfer.

A possible reaction path for the formation of  $\text{M}(\text{NTA})_2^{4-}$  by eq 38, on the basis of the stepwise nature of multidentate ligand reactions, is shown in Figure 9. The over-all reaction is the exchange of ligand between the free and the complexed forms through  $\text{M}(\text{NTA})_2^{4-}$ , shown here as a symmetrical complex (intermediate C). Forma-

tion of the symmetrical complex by the proposed mechanism involves three steps: (a) loss of a water molecule from  $\text{M}(\text{NTA})^-$  and formation of a first metal-carboxylate bond to the incoming NTA (intermediate A), (b) loss of the second water molecule and formation of the metal-nitrogen bond (intermediate B), and (c) displacement of a carboxylate group of the bound NTA and formation of the second carboxylate bond to the incoming NTA (intermediate C). A similar mechanism is proposed for the analogous reaction involving the monoprotonated NTA (eq 37). However, because the proton is on the nitrogen in  $\text{HNTA}^{2-}$ , proton transfer must occur before intermediate B can form from intermediate A. If the dissociation of intermediate A to reactants is rapid relative to the proton migration and formation of the metal-nitrogen bond, the formation of the metal-nitrogen bond becomes rate determining. On the basis of the rate constants discussed previously for metal-acetate dissociation and proton transfer, the proton transfer is slower and accounts for the large differences between the rates of reaction of  $\text{NTA}^{3-}$  ( $k_4$ ) and  $\text{HNTA}^{2-}$  ( $k_3$ ) with the  $\text{M}(\text{NTA})^-$  complexes. From these considerations, it is proposed that proton transfer from the nitrogen atom of  $\text{HNTA}^{2-}$  governs the rates of the reaction of  $\text{HNTA}^{2-}$  with both  $\text{M}^{2+}$  and  $\text{M}(\text{NTA})^-$ .

(40) M. Sheinblatt and H. S. Gutowsky, *J. Am. Chem. Soc.*, **86**, 4814 (1964).