

dentate ligand whereas the remaining two ligands behaved as bidentates. They concluded that increasing *N*-alkyl substitution leads to decreasing stability constants for second bond formation and attributed this trend to metal-ligand steric effects.

In the present study the larger charge on the Au(III) relative to Cu(II) and Ni(II) tends to oppose these metal-ligand steric effects and apparently is sufficient to enable the Et₂dien-H to behave as a tridentate ligand. However, the inherent weakness of the bond between the metal and the terminal tertiary nitrogen of the Et₂dien-H ligand favors the formation of species I in eq 5. This bidentate species is much more open to bromide ion attack and can easily pass through the distorted tetrahedral intermediate¹⁶ depicted in eq 5 to form the product.

Registry No. [Au(Me₂dien-H)Cl]PF₆, 40354-46-9;

[Au(Me₂dien-H)Br]⁺, 40272-97-7; [Au(Me₂dien-H)OH]⁺, 40477-30-3; [Au(Me₂dien)Cl]²⁺, 40272-98-8; [Au(Et₂dien-H)Cl]PF₆, 40272-99-9; [Au(Et₂dien-H)Br]⁺, 40273-00-5; [Au(Et₂dien-H)OH]⁺, 40273-01-6; [Au(Et₂dien)Cl]²⁺, 40273-02-7; [Au(Me₄dien-H)Cl]PF₆, 40273-03-8; [Au-(Me₄dien-H)Br]⁺, 40273-04-9; [Au(Me₄dien-H)OH]⁺, 40273-05-0; [Au(Me₄dien)Cl]²⁺, 40354-47-0; Br₂, 7726-95-6.

Acknowledgment. The authors are indebted to the Electrical Engineering Department of Union College for the loan of the Polaroid oscilloscope camera.

(16) The dihalogenated species is shown as a distorted tetrahedron with the "loose end" lying in the same plane as the Au-N bonds. Such a symmetrical intermediate is necessary to avoid violation of microscopic reversibility.

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada

Nuclear Magnetic Resonance Studies of the Solution Chemistry of Metal Complexes. VIII.¹ Ligand-Exchange Kinetics of the 1,3-Propylenediaminetetraacetic Acid and Ethylenediamine-*N,N'*-diacetic-*N,N'*-dipropionic Acid Complexes of Cadmium, Zinc, and Lead

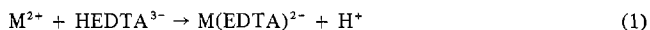
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Received October 31, 1972

The kinetics of the ligand-exchange reactions of the 1,3-propylenediaminetetraacetic acid (1,3-PDTA) and ethylenediamine-*N,N'*-diacetic-*N,N'*-dipropionic acid (EDDDA) complexes of cadmium, zinc, and lead have been measured by nmr line-broadening methods. Rate constants were obtained for the proton-assisted dissociation of each of the complexes and for the displacement of complexed ligand by free ligand for several of the complexes. The rates of first-order dissociation of all of the complexes are too slow to measure by nmr line-broadening methods. Rate constants for the reaction of cadmium and zinc with monoprotonated 1,3-PDTA are approximately equal to those of the analogous reactions with monoprotonated ethylenediaminetetraacetic acid, while the rate constants for reaction of cadmium, zinc, and lead with monoprotonated EDDDA are from 2.5 to 10 times slower than the rate constants for reaction with monoprotonated 1,3-PDTA. Mechanisms are proposed for the complexation reactions of the monoprotonated ligands.

Introduction

The rates of complexation of divalent Cd,² Zn,³ Co,⁴ Cu,⁵ and Ni⁶ by the monoprotonated form of EDTA⁷



are all approximately equal to those predicted by the mechanism⁸ in which dissociation of water from the aquated metal ions is rate determining.⁹ However, the rates of complexation of Ca¹⁰ and Sr¹¹ by the tetraanion of EDTA



are factors of $\leq 2.5 \times 10^2$ and 1.6×10^3 greater than their rates of complexation by HEDTA³⁻. Similarly, the rates of complexation of Ni¹² and Cd^{13,14} by the trianion of NTA are 7×10^4 times greater than their rates of complexation by HNTA²⁻, while the rates of reaction of Zn¹³ and Pb¹⁵ with monoprotonated NTA (eq 3) are 3-4 orders of magnitude



less than the approximate values predicted by the mechanism in which dissociation of water is rate determining.¹⁶ Mechanisms proposed to account for these decreased rates either

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(7) Abbreviations used: EDTA, ethylenediaminetetraacetic acid; 1,3-PDTA or L, 1,3-propylenediaminetetraacetic acid; EDDDA or L, ethylenediamine-*N,N'*-diacetic-*N,N'*-dipropionic acid; NTA, nitrilotriacetic acid.

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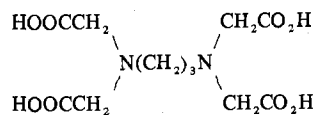
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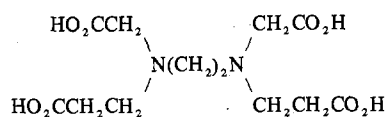
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visualize the reaction as proceeding through a partially coordinated, nitrogen-protonated intermediate with proton transfer from the nitrogen to carboxylate oxygen or solvent molecule as the rate-determining step^{11,13} or consider the carboxylate-protonated isomer to be the only reactive isomer of the monoprotinated ligand.^{13,17,18} In many cases the rates of second-order ligand-displacement reactions also decrease with increasing protonation of the noncomplexed ligand.^{10,11,13,15,19,20}

In the present paper, the results of nuclear magnetic resonance (nmr) line-broadening studies of the ligand-exchange kinetics of the 1,3-propylenediaminetetraacetic acid (1,3-PDTA)⁷



and ethylenediamine-*N,N'*-diacetic-*N,N'*-dipropionic acid (EDDDA)



complexes of Cd, Zn, and Pb are reported. These systems have been investigated with the objective of elucidating the mechanisms of ligand-exchange reactions of Cd, Zn, and Pb complexes of aminocarboxylic acid ligands, with emphasis on the complexation reactions of the monoprotinated forms of the ligands. These ligands were chosen in order to observe the effects of slight structural changes on the rates of reactions of aminocarboxylic acids of the EDTA type. The predominant pathways by which ligand exchanges between the free and complexed forms have been established and their rate constants have been measured.

Experimental Section

Chemicals. 1,3-PDTA was synthesized by the method of Weyh and Hamm.²¹ EDDDA (Lamont Laboratories), cadmium nitrate, lead nitrate (Fisher Certified reagents), and zinc nitrate (Baker Analyzed reagent) were used as received. A stock solution of tetramethylammonium (TMA) nitrate was prepared by titration of a 25% aqueous solution of TMA hydroxide (Eastman Organic Chemicals) with concentrated HNO₃ to a neutral pH.

pH Measurements. All pH measurements were made at 25° with an Orion Model 801 pH meter equipped with a standard glass electrode and a fiber-tip saturated-calomel reference electrode. Saturated potassium acid tartrate and 0.01 M sodium tetraborate, pH 3.56 and 9.18 at 25°, were used to standardize the meter.

Nmr Measurements. Nmr spectra were obtained on a Varian A-60D at a probe temperature of 25 ± 1° or on a Varian HR 220-MHz high-resolution spectrometer at a probe temperature of 23 ± 1°. At 60 MHz, spectra were recorded at sweep rates of 0.1 Hz/sec for both chemical shift and line shape measurements; sweep widths of 50 Hz were used. For line shape measurements each spectrum was recorded at least four times and the widths at half-height of the individual spectra were averaged. Chemical shifts are reported in ppm relative to the central resonance of the TMA triplet; positive shifts indicate resonances upfield from TMA. The central resonance of TMA is 3.17 ppm downfield from the methyl resonance of sodium 3-(trimethylsilyl)-1-propanesulfonate (TMS*).

Solutions used in the nmr measurements were prepared in triply distilled water from the appropriate amounts of metal salt and 1,3-

PDTA or EDDDA. Potassium hydroxide and nitric acid were used to bring the solutions to the desired pH. Most solutions were between 0.1 and 0.2 M in metal salt and ligand, varying in ionic strength from ~0.4 to ~0.8 M. Because of the high concentrations necessary in the nmr experiment, inert electrolyte was not added to control the ionic strength. Tetramethylammonium nitrate (TMA) was added as a reference compound for chemical shift measurements.

Results

Proton Nmr Spectra of the Ligands. The proton nmr spectrum of 1,3-PDTA consists of a sharp singlet for the acetate methylenic protons, a broad triplet-like pattern for the protons of the two nitrogen-bonded methylenic groups of the propylene part of the ligand, and a broad quintet-like pattern for the protons of the central methylenic group of the propylene part of the ligand over the pH range 2-13. The lack of any broadening of the acetate methylenic resonance indicates exchange of the acidic nitrogen-bonded and carboxylate-bonded protons is fast on the nmr time scale. The resonances due to the protons of the propylene part of the ligand, which form an A₄B₂ spin system, were not used in the ligand-exchange studies because of their complexity. The chemical shifts of the 1,3-PDTA resonances are pH dependent, as illustrated by the chemical shift vs. pH data for the acetate methylenic protons in Figure 1. By analogy with EDTA, the two nitrogen atoms of the tetra-anion of 1,3-PDTA are protonated first, followed by protonation of the carboxylate groups.^{22,23}

From the chemical shift vs. pH data, values were determined for the third and fourth ionization constants of 1,3-PDTA (defined by eq 4 and 5) by methods described pre-

$$K_3 = a_{\text{H}}[\text{HL}^{3-}]/[\text{H}_2\text{L}^{2-}] \quad (4)$$

$$K_4 = a_{\text{H}}[\text{L}^{4-}]/[\text{HL}^{3-}] \quad (5)$$

viously.^{13,24} These constants are mixed-mode constants involving hydrogen ion activity and 1,3-PDTA concentrations. The values so obtained are given in Table I, along with literature data.^{25,26}

Over the pH range 3-13, the proton nmr spectrum of EDDDA consists of a sharp singlet for the acetate methylenic protons, a sharp singlet for the ethylenic protons between the two nitrogen atoms, and a complex multiplet for the carbon-bonded protons of the two propionate groups. The spectrum of a pH 10 solution has been described previously.²⁷ On the basis of chemical shifts of structurally related protons in other aminocarboxylic acids,^{23,28} the downfield singlet was assigned to the acetate methylenic protons. The chemical shifts of the EDDDA resonances are pH dependent, as illustrated by the chemical shift data for the acetate methylenic protons in Figure 2. The third and fourth ionization constants of EDDDA were determined from these data; the results are given in Table I.

Nmr Spectra of the Metal Complexes. AB patterns are observed for the acetate methylenic protons of all the complexes studied except those of Pb(1,3-PDTA)²⁷. Satellite peaks due to proton coupling to ¹¹¹Cd and ¹¹³Cd (*I* = 1/2, natural abundance 25%) and ²⁰⁷Pb (*I* = 1/2, natural abundance

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Table I. Acid Ionization Constants of 1,3-PDTA and EDDDA

	1,3-PDTA		EDDDA	
	This work ^a	Lit. ^b	This work ^a	Lit. ^c
pK ₁		1.88		3.00
pK ₂		2.57		3.79
pK ₃	7.93	8.02	6.00	5.98
pK ₄	10.25	10.46	9.88	9.83

^a Temperature 25°; ionic strength ~0.6 M. ^b Reference 25. Ionic strength 0.1 M; mixed-mode constants. ^c Reference 26. Ionic strength 0.1 M; mixed-mode constants.

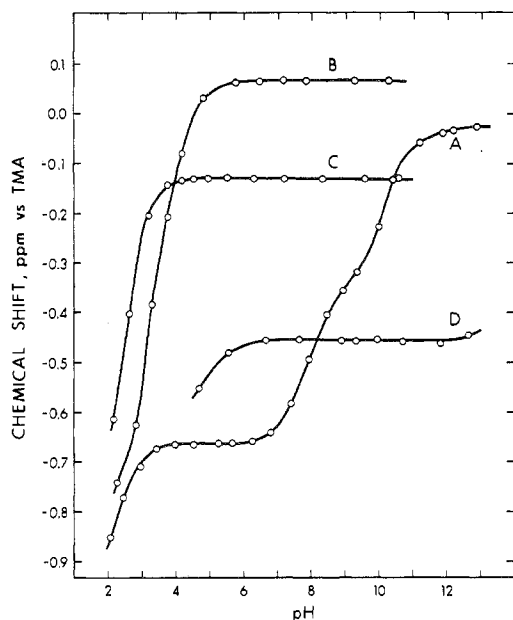


Figure 1. pH dependence of the chemical shift of the acetate methylenic resonance of 1,3-PDTA: curve A, 0.20 M 1,3-PDTA; curve B, 0.20 M Cd(NO₃)₂, 0.20 M 1,3-PDTA; curve C, 0.20 M Zn(NO₃)₂, 0.20 M 1,3-PDTA; curve D, 0.20 M Pb(NO₃)₂, 0.20 M 1,3-PDTA. The experimental points in B and C are the chemical shifts at the center of the AB patterns.

21%) are also observed in the spectra of the cadmium and lead complexes, resulting in multiplet patterns that are comprised of the AB part of an ABX pattern superimposed on an AB pattern for Cd(1,3-PDTA)²⁻, Cd(EDDDA)²⁻, and Pb(EDDDA)²⁻.^{29,30} The multiplet patterns of the acetate methylenic protons of Cd(1,3-PDTA)²⁻ and Zn(1,3-PDTA)²⁻ have been presented in an earlier paper.²⁹ The resonance pattern of the acetate methylenic protons of Pb(1,3-PDTA)²⁻ is a singlet (at 60, 100, and 220 MHz) flanked symmetrically by satellites due to coupling to ²⁰⁷Pb. The AB patterns of the Cd and Zn complexes of 1,3-PDTA and the Zn complex of EDDDA are well resolved and analyzable³¹ at 60 MHz and 25°, whereas the AB patterns of the Cd and Pb complexes of EDDDA are partially collapsed at 60 and 100 MHz due to smaller chemical shift differences and faster rates of AB interchange. The multiplet patterns of the latter two complexes are sufficiently resolved at 220 MHz that a complete analysis was possible for Pb(EDDDA)²⁻ and a partial analysis for Cd(EDDDA)²⁻. The spectral parameters are summarized in Table II.

The chemical shift behavior of the proton resonances for the metal complexes is pH dependent, as illustrated by the

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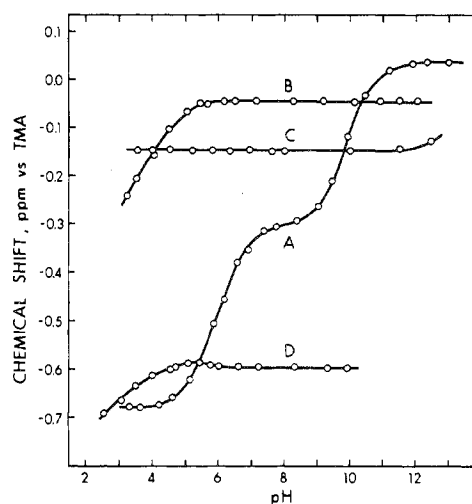


Figure 2. pH dependence of the chemical shift of the acetate methylenic resonance of EDDDA: curve A, 0.20 M EDDDA; curve B, 0.20 M Cd(NO₃)₂, 0.20 M EDDDA; curve C, 0.20 M Zn(NO₃)₂, 0.20 M EDDDA; curve D, 0.20 M Pb(NO₃)₂, 0.20 M EDDDA. The experimental points in curves B-D are the chemical shifts at the center of the AB patterns.

Table II. Nmr Spectral Parameters for the M(1,3-PDTA)²⁻ and M(EDDDA)²⁻ Complexes^a

	$\Delta\delta_{AB}$	J_{AB}	$ J_{AX} $	$ J_{BX} $
Cd(1,3-PDTA) ²⁻	0.192	-16.3	11.8	15.0
Pb(1,3-PDTA) ²⁻			19.2	
Zn(1,3-PDTA) ²⁻	0.220	-16.3		
Cd(EDDDA) ²⁻	<i>b</i>	<i>b</i>	13.5	12.5
Pb(EDDDA) ²⁻	0.221	-16.7	22.6	17.5
Zn(EDDDA) ²⁻	0.453	-18.3		

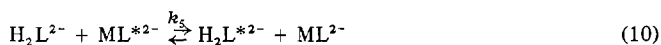
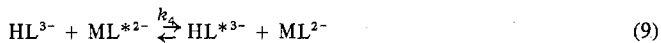
^a δ values in ppm; J values in Hz. ^b Could not be determined because of apparent overlap of the weak lines of the AB pattern and the satellite lines.

data in Figures 1 and 2. In all cases, the chemical shifts remain constant above a certain pH when the metal-to-ligand ratio is 1, corresponding to the chemical shifts of the 1:1 complexes. Below this pH, the resonances move toward those of the free ligand and are exchange broadened. Calculations on the species present in the 1,3-PDTA systems using the ionization constants in Table I and literature formation constants²⁵ indicate that this results from dissociation of the 1:1 complexes and formation of protonated complexes. For example, calculations indicate that in a Cd-1,3-PDTA solution with a metal-to-ligand ratio of 1 dissociation of the complex and formation of a protonated complex takes place at pH less than 5.5. For the EDDDA systems, no formation constants are available for the protonated complexes, but a species of this type is indicated by the chemical shift data.

Ligand-Exchange Kinetics of the 1,3-PDTA Complexes.

Ligand-exchange broadening was observed in the nmr spectra of each of the 1,3-PDTA complexes under conditions where some noncomplexed ligand was present. From the exchange broadening for a given set of experimental conditions, the mean lifetime τ_{LF} between events which lead to exchange of ligand from the free form to the complexed form was determined. The following reactions were considered to be pathways by which exchange could occur





The AB multiplet patterns observed for the acetate methylenic protons of Cd(1,3-PDTA)²⁻ and Zn(1,3-PDTA)²⁻ at intermediate pH values in the absence of noncomplexed ligand indicate that for these conditions the mean lifetime of the complexes before dissociation is long on the nmr time scale ($\tau_{\text{complex}} > 0.1$ sec) and, consequently, that the rate of the reaction represented by eq 6 is too slow to be measured by the nmr line-broadening method. Similarly, the metal-proton spin-spin coupling observed in the Cd and Pb complexes of 1,3-PDTA indicates that for these complexes the reaction represented by eq 6 contributes a negligible amount to the exchange broadening.¹⁵ Neglecting the reaction represented by eq 6, the rate equation for exchange of ligand from the free form to the complexed form is

$$-d[L_f]/dt = k_{-2}[M^{2+}][HL^{3-}] + k_3[L^{4-}][ML^{2-}] + k_4[HL^{3-}][ML^{2-}] + k_5[H_2L^{2-}][ML^{2-}] \quad (11)$$

where $[L_f]$ represents the sum of the concentrations of the free ligand in the various protonated forms. The reciprocal of the mean lifetime of the free form, $1/\tau_{L_f}$, is related to the exchange rate, $-d[L_f]/dt$, by

$$\frac{1}{\tau_{L_f}} = -\frac{d[L_f]}{dt} \frac{1}{[L_f]} \quad (12)$$

which yields

$$\frac{1}{\tau_{L_f}} = k_{-2}\alpha_3[M^{2+}] + k_3\alpha_4[ML^{2-}] + k_4\alpha_3[ML^{2-}] + k_5\alpha_2[ML^{2-}] \quad (13)$$

where $\alpha_2 = [H_2L^{2-}]/[L_f]$, $\alpha_3 = [HL^{3-}]/[L_f]$, and $\alpha_4 = [L^{4-}]/[L_f]$. Expressing the concentrations in eq 13 in terms of fractional concentrations and the term for the contribution from the reaction represented by eq 7 in terms of $[ML^{2-}]$ by the relation $k_{-2}[M^{2+}] = k_2[H^+][ML^{2-}]/\alpha_3[L_f]$ yields

$$P_{L_f}/\tau_{L_f}P_{ML} = k_2[H^+] + (k_3\alpha_4 + k_4\alpha_3 + k_5\alpha_2)[L_f] \quad (14)$$

where P_{L_f} and P_{ML} are the fractional concentrations of ligand in the free and complexed forms ($P_{L_f} + P_{ML} = 1$). The individual rate constants were evaluated from the dependence of τ_{L_f} on $[H^+]$ and $[L_f]$.

In the Cd-1,3-PDTA system, τ_{L_f} was calculated from the exchange broadening of the free-ligand resonance in slow-exchange³² spectra with eq 15,³³ where $W_{1/2}'$ is the width

$$1/\tau_{L_f} = \pi(W_{1/2}' - W_{1/2}) \quad (15)$$

at half-height (in hertz) of the exchange-broadened free-ligand resonance and $W_{1/2}$ is the width of the free ligand resonance in the absence of exchange. Lifetime data are given in Table III for experiments in which the pH was held constant and the concentration of free ligand was varied. According to eq 15, the slope of a plot of $P_{L_f}/\tau_{L_f}P_{ML}$ vs. $[L_f]$ at constant pH is equal to $k_3\alpha_4 + k_4\alpha_3 + k_5\alpha_2$ and the intercept is equal to $k_2[H^+]$. At the pH values listed in

Table III. Kinetic Data for the Cd-1,3-PDTA System at Constant pH Values as a Function of Free-Ligand Concentration^a

pH	$[L_f], M$	P_{L_f}/P_{CdL}	$1/\tau_{L_f}$	
5.52	0.180	11.5	0.816	
	0.162	5.28	1.48	
	0.143	3.15	2.36	
	0.125	2.10	3.39	
	0.107	1.46	4.30	
	0.090	1.04	5.34	
	0.073	0.726	6.41	
	0.057	0.497	8.10	
	5.72	0.180	11.5	0.691
		0.161	5.25	1.22
0.143		3.16	1.95	
0.125		2.08	2.57	
0.107		1.45	3.05	
0.090		1.03	4.27	
0.073		0.724	5.06	
0.055		0.476	6.25	
6.00		0.163	5.67	0.879
		0.145	3.39	1.19
	0.127	2.19	1.63	
	0.109	1.53	2.23	
	0.092	1.08	2.83	
	0.075	0.763	3.36	
	0.058	0.515	4.49	
	6.51	0.162	5.35	1.10
		0.143	3.13	1.76
		0.125	2.08	2.23
0.107		1.45	3.05	
0.091		1.05	3.74	
0.074		0.742	4.33	
0.058		0.510	4.96	
7.09		0.181	11.76	0.88
		0.162	5.32	1.92
		0.145	3.29	2.86
	0.127	2.18	3.49	
	0.109	1.51	4.46	
	0.092	1.08	5.21	
	0.075	0.758	6.31	
	0.059	0.527	7.13	
	8.03	0.182	12.43	2.79
		0.162	5.41	5.62
0.144		3.21	8.13	
0.125		2.12	10.2	
0.108		1.48	12.1	
0.091		1.05	14.4	
0.074		0.740	16.1	
0.057		0.510	18.9	

^a At 25°.

Table III, α_3 ranges from factors of 10^5 to 3×10^2 greater than α_4 while k_3 has been found to be only 10-20 times larger than k_4 in similar reactions of EDTA complexes,^{10,11} suggesting that the term $k_3\alpha_4$ contributes a negligible amount to the slopes of the $P_{L_f}/\tau_{L_f}P_{ML}$ vs. $[L_f]$ plots for the data in Table III. Thus the slope m is equal to $k_4\alpha_3 + k_5\alpha_2$ which can be rearranged to give

$$m/\alpha_2 = k_4\alpha_3/\alpha_2 + k_5 \quad (16)$$

Rate constants k_4 and k_5 were evaluated from the least-squares slope and intercept of a plot of m/α_2 vs. α_3/α_2 ; the values so obtained and their standard deviations are given in Table IV. The uncertainty in the intercepts of the plots of $P_{L_f}/\tau_{L_f}P_{ML}$ vs. $[L_f]$ was too large to allow evaluation of k_2 from these data.

Lifetime data are given in Table V as a function of pH for a solution 0.1 M in both Cd(1,3-PDTA)²⁻ and free 1,3-PDTA. The rate of ligand exchange decreases as the pH is increased from pH 4.80, goes through a minimum at pH 6.4, and then increases as the pH is increased further. Above pH 8.5, the rate of ligand exchange is so fast that the line shapes are of the intermediate to fast³² types. Since exchange occurs among a single line, an AB pattern, and the AB part of an

(32) Ligand exchange is defined as slow on the nmr time scale when separate resonances are observed for free and complexed ligand, as intermediate when the separate resonances are partially coalesced and as fast when a single, averaged resonance is observed.

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Table IV. Experimentally Determined Ligand-Exchange Rate Constants ($M^{-1} \text{ sec}^{-1}$) for 1,3-PDTA and EDDDA Complexes^a

	Cd(1,3-PDTA) ²⁻	Pb(1,3-PDTA) ²⁻	Zn(1,3-PDTA) ²⁻	Cd(EDDDA) ²⁻	Pb(EDDDA) ²⁻	Zn(EDDDA) ²⁻
k_2	$9.1 (\pm 0.3) \times 10^5$	$2.0 (\pm 0.1) \times 10^7$	$3.9 (\pm 0.1) \times 10^4$	$4.8 (\pm 0.2) \times 10^6$	$1.2 (\pm 0.1) \times 10^7$	$2.0 (\pm 0.1) \times 10^4$
k_{-2}	$4.1 (\pm 0.1) \times 10^9$	$6.8 (\pm 0.3) \times 10^{10}$	$4.0 (\pm 0.1) \times 10^9$	$4.0 (\pm 0.2) \times 10^8$	$2.5 (\pm 0.2) \times 10^{10}$	$8.3 (\pm 0.4) \times 10^8$
k_3		$2.0 (\pm 0.9) \times 10^4$		$1.5 (\pm 0.3) \times 10^3$	$2.0 (\pm 0.1) \times 10^4$	
k_4	$3.5 (\pm 0.1) \times 10^2$ ^b $2.5 (\pm 0.1) \times 10^2$ ^c	$1.5 (\pm 0.2) \times 10^3$	6.5 ± 0.2			
k_5	$2.6 (\pm 1.0) \times 10^b$ $3.2 (\pm 0.3) \times 10^c$	$1.7 (\pm 0.4) \times 10^2$	$2.5 (\pm 0.1) \times 10$			

^a At 25°. ^b From experiments at constant pH and varying $[L_f]$. ^c From experiments at constant $[L_f]$ and varying pH.

Table V. Free-Ligand Lifetime as a Function of pH for the Cd-1,3-PDTA System^a

pH	$1/\tau_{L_f}$, sec ⁻¹		$1/\tau_{L_f}$, sec ⁻¹		$1/\tau_{L_f}$, sec ⁻¹	
4.80	17.3	5.76	4.62	6.51	3.84	
4.99	12.7	6.00	4.12	6.84	5.09	
5.23	8.80	6.24	3.84	7.14	6.28	
5.49	6.64	6.42	3.51	7.68	12.1	
				8.24	17.3	

^a With 0.1 M Cd(1,3-PDTA)²⁻ and 0.1 M free 1,3-PDTA. $W_{1/2}$ of free resonance for no ligand exchange is 0.73 Hz. Temperature 25°.

ABX pattern, no attempt was made to evaluate lifetimes from data at pH greater than 8.5.

Rate constant k_2 was obtained from the data in Table V. At pH values less than 6.4, α_4 is negligible relative to α_2 and α_3 and the contribution to exchange by the reaction represented by eq 8 can be neglected. Since P_{L_f} equals P_{ML} , rearrangement of eq 14 leads to

$$\frac{1}{\tau_{L_f}} - (k_4\alpha_3 + k_5\alpha_2)[L_f] = k_2[H^+] \quad (17)$$

The value given in Table IV for k_2 was obtained from the slope of a plot of $1/\tau_{L_f} - (k_4\alpha_3 + k_5\alpha_2)[L_f]$ vs. $[H^+]$ using the data in Table V and the values determined above for k_4 and k_5 . Rate constant k_{-2} was obtained from k_2 using the relation $k_{-2} = k_2 K_4 K_f$ where K_f is the formation constant of Cd(1,3-PDTA)²⁻. Rate constants k_4 and k_5 were also evaluated from the data in Table V. In the pH range 6.4–8.5, the amount of ligand exchange via the reaction represented by eq 7 is negligible. α_4 is small relative to α_2 and α_3 over this pH range so that the reaction represented by eq 8 can be neglected for the reasons given previously. Thus, eq 14 can be rearranged to give

$$1/\tau_{L_f}[L_f]\alpha_2 = k_4\alpha_3/\alpha_2 + k_5 \quad (18)$$

The values obtained for k_4 and k_5 from a plot of $1/\tau_{L_f}[L_f]\alpha_2$ vs. α_3/α_2 for the data in Table V are given in Table IV.

Above pH 8.5, the increased rate of ligand exchange is presumably due to increased contributions from the reactions represented by eq 8 and 9.

Kinetic data for the Zn-1,3-PDTA system³⁴ were obtained from the width at half-height of exchange-broadened free-ligand resonances for experiments in which the free-ligand concentration was held constant and the pH was varied. Rate constants k_2 , k_4 , and k_5 were obtained from these data by procedures similar to those used in the analysis of the data in Table V; the results are given in Table IV. Because

of the fast³² ligand exchange and the complexity of the exchange case, kinetic data for the Pb-1,3-PDTA system were obtained from exchange-broadened spectra by comparison with computer-simulated spectra. The system is a four-site, random intermolecular exchange case since 1,3-PDTA exchanges between the noncomplexed form and lead ions in three nuclear spin states, $+1/2$ and $-1/2$ for lead-207 and zero for the other isotopes of lead. Spectra were simulated with a program described previously.¹⁵ Lifetime data were obtained from experiments in which the pH was held constant and the free-ligand concentration was varied.³⁴ From the slopes of plots of $P_{L_f}/(\tau_{L_f}P_{ML})$ vs. $[L_f]$, the values for k_3 , k_4 , and k_5 given in Table IV were obtained. From the intercepts, an approximate value of $2.2 \times 10^7 M^{-1} \text{ sec}^{-1}$ was obtained for k_2 . The more precise value for k_2 given in Table IV was obtained from the pH dependence of the exchange rate of a solution containing 0.10 M Pb(1,3-PDTA)²⁻ and 0.10 M free 1,3-PDTA³⁴ using the procedure described previously for the evaluation of k_2 for Cd(1,3-PDTA)²⁻. The simulated spectra in Figure 3 were calculated using lifetimes predicted from the rate constants in Table IV for the free-ligand concentrations in Figure 3. The agreement between experimental and simulated spectra is representative of the fits obtained in the lifetime determinations.

Ligand-Exchange Kinetics of the EDDDA Complexes. The reactions represented by eq 6–10 were considered to be the predominant pathways by which EDDDA exchanges between the free and complexed forms for the solution conditions used in the present work. The AB multiplet patterns observed for the acetate methylenic protons of the EDDDA complexes at intermediate pH values in the absence of non-complexed ligand indicate that the mean lifetime of the complexes before first-order dissociation by the reaction represented by eq 6 is long on the nmr time scale ($\tau_{\text{complex}} > 0.1 \text{ sec}$). Thus the rate of this reaction is too slow to be measured by the nmr line-broadening method. Free-ligand lifetimes were determined from the width at half-height of the exchange-broadened acetate resonance of the free ligand.

Lifetime data³⁴ for the Cd-EDDDA system for experiments in which pH was held constant and free-ligand concentration was varied yielded the value given in Table IV for k_3 and a value of zero within experimental error for k_4 , indicating that k_4 is too small to be determined by this method. From lifetime data³⁴ as a function of pH for a solution 0.1 M in both Cd(EDDDA)²⁻ and free EDDDA, the value for k_2 in Table IV was obtained.

Lifetime data³⁴ were taken for the Pb-EDDDA system at constant pH values as a function of free-ligand concentration and at a constant free-ligand concentration as a function of pH. From these data, the rate constants given for Pb(EDDDA)²⁻ in Table IV were obtained.

For the Zn-EDDDA system, lifetime data as a function of pH for a solution 0.10 M in both Zn(EDDDA)²⁻ and free EDDDA indicate that the rates of the reactions represented by eq 8–10 are too slow to measure by the nmr line-

(34) Tables of experimental data will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-1868.

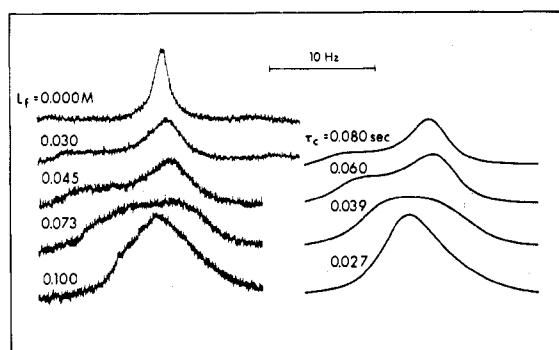


Figure 3. Experimental and theoretical nmr spectra for the acetate methylenic protons of $\text{Pb}(1,3\text{-PDTA})^{2-}$ at pH 7.00 with varying excess concentrations of 1,3-PDTA. Theoretical spectra were calculated for the lifetimes indicated, which were obtained from the rate constants given in Table IV and the free-ligand concentrations given by the experimental spectra. $\text{Pb}(1,3\text{-PDTA})$ concentration was 0.10 M.

broadening method. The value given for k_2 in Table IV was obtained from these data.

Discussion

Mechanism of Formation of the $\text{M}(1,3\text{-PDTA})^{2-}$ and $\text{M}(\text{EDDDA})^{2-}$ Complexes. The rates of complexation of Cd^{2+} and Zn^{2+} by monoprotated 1,3-PDTA are essentially the same as the rates of reaction with monoprotated EDTA.^{2,3} No value for the rate of complexation of Pb^{2+} by monoprotated EDTA is available for comparison. The rates of complexation of Cd^{2+} , Zn^{2+} , and Pb^{2+} by monoprotated EDDDA, however, are from 2.5 to 10 times slower than the rates with monoprotated 1,3-PDTA.

In the dissociative mechanism⁸ of complex formation from an aquated metal ion and a multidentate ligand, the reaction takes place in a stepwise fashion, with metal ion and ligand first diffusing together to form an outer-sphere or association complex. A water molecule then dissociates from the aquated metal ion, and a donor group of the multidentate ligand coordinates at the vacated coordination site. A second water molecule then dissociates at a position cis to the metal-ligand bond, and the second bond forms. The reaction continues with a separate step for each of the metal-ligand bonds. Depending on the structure of the ligand, the rate of formation of a specific metal-ligand bond will govern the overall complexation rate. For the majority of complexes whose formation kinetics have been studied, formation of the first metal-ligand bond is rate determining,⁸ its rate being governed by the rate of water dissociation from the aquated metal ion in the outer-sphere complex.

A stepwise sequence for the reaction of aquated metal ions with monoprotated hexadentate ligands of the EDTA type is shown in Figure 4. Reaction proceeds by dissociation of water molecules followed by metal-ligand bond formation to yield an intermediate in which the three dentates of one end of the ligand are metal coordinated while coordination of the other end is blocked by the proton on the nitrogen. For further coordination to occur, the second metal-nitrogen bond has to form before the intermediate dissociates to reactants. Presumably the second metal-nitrogen bond can form only after the proton has been transferred to a carboxylate oxygen or to a solvent molecule.

The similarity of the rate constants for the reactions of monoprotated EDTA and 1,3-PDTA with aquated Cd^{2+} and Zn^{2+} suggests that, once the nitrogen-protonated intermediate has formed with these ligands, coordination of the remaining dentates is not rate determining. If it were rate-

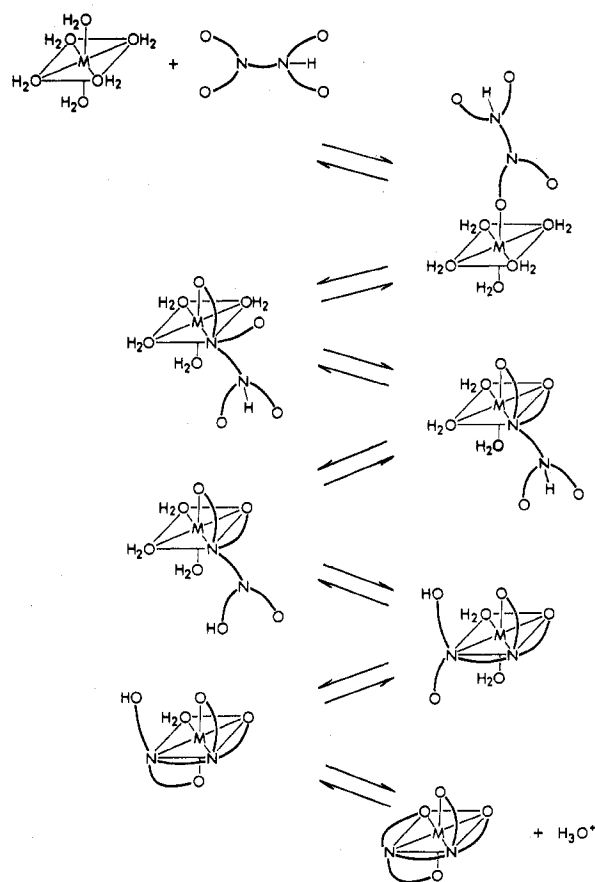


Figure 4. Proposed stepwise reaction mechanism for the formation of ML^{2-} complexes from M^{2+} and HL^{3-} , where HL^{3-} is the monoprotated form of EDTA-type ligands.

determining, it is likely the overall complexation rate constants for monoprotated 1,3-PDTA would be less than those of monoprotated EDTA due to the six-membered ring in the $\text{M}(1,3\text{-PDTA})^{2-}$ complexes.^{35,36} These results are consistent with the rate-determining step being the formation of one of the first three metal-ligand bonds.

The smaller rate constants for reaction with monoprotated EDDDA suggest the rate-determining step is different in these reactions. It is possible that, when the first ligand dentate to bond is a propionate carboxylate oxygen, the rate of formation of the metal-nitrogen bond to close the six-membered chelate ring is less than when the first ligand dentate to bond is an acetate carboxylate oxygen. Kustin, Pasternack, and coworkers^{35,36} have shown that formation of a six-membered chelate ring can be slower than formation of a five-membered ring. If this were the only factor responsible for the decrease, the rates of complexation with monoprotated EDDDA should be at least half those with monoprotated 1,3-PDTA. A larger decrease, the magnitude of which would be metal ion dependent, might result if the rates of dissociation of the nitrogen-protonated intermediates in the EDDDA reactions are sufficiently large that a significant amount of intermediate dissociates to reactants prior to proton transfer from the nitrogen. Kinetic data are not available for model tridentate complexes from which the rates of dissociation of the nitrogen-protonated, tridentate intermediates of 1,3-PDTA and EDDDA can be obtained. However, assuming the rate constants for formation of the

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nitrogen-protonated intermediates to be equal to the rate constants for reaction with monoprotonated 1,3-PDPA and the formation constants for the intermediates to be approximately those of complexes of model tridentate ligands, order-of-magnitude rates of intermediate dissociation can be predicted. The rate constant for dissociation, k_d , is given by k_{-2}/K_f , where K_f is the formation constant. Using the formation constants³⁷ of the iminodiacetic acid (IDA) complexes as approximate values for tridentate coordination to monoprotonated 1,3-PDPA and assuming the formation constants for tridentate coordination to monoprotonated EDDDA lie somewhere between those for IDA and those for iminodipropionic acid, the predicted value for the dissociation rate constant of the Cd^{2+} intermediate with 1,3-PDPA is $1.8 \times 10^4 \text{ sec}^{-1}$ while that of the Cd^{2+} intermediate with EDDDA is between 1.8×10^4 and $1.1 \times 10^6 \text{ sec}^{-1}$. The predicted value for the dissociation rate constant of the Zn^{2+} intermediate with 1,3-PDPA is $3.7 \times 10^2 \text{ sec}^{-1}$ while that of the intermediate with EDDDA is between 3.7×10^2 and $4.5 \times 10^4 \text{ sec}^{-1}$. The formation constant of the Pb^{2+} complex of iminodipropionic acid is not available. The reaction by which the proton leaves the nitrogen to permit formation of the second metal-nitrogen bond could involve either direct transfer to solvent water or migration to a neighboring carboxylate group. The kinetics of these two reactions for the nitrogen-protonated isomer of neutral glycine have been studied by Sheinblatt and Gutowsky,³⁸ who reported a pseudo-first-order rate constant of 5 sec^{-1} for the transfer of the nitrogen-bonded proton to H_2O and a rate constant of 175 sec^{-1} for migration of the proton to the carboxylate group. The rate constant for the process by which the proton leaves the nitrogen atom in the nitrogen-protonated intermediates would probably be somewhat larger than either of these rate constants for glycine because of charge-charge interaction between the metal ion and the proton and the additional carboxylate group to which proton transfer can occur. These considerations suggest that the rates of dissociation of the metal ions from the Cd^{2+} and Zn^{2+} intermediates of EDDDA are larger than from the corresponding intermediates of 1,3-PDPA and may be comparable to the rate of proton transfer from the nitrogen atom. These considerations also predict that, if this is a rate-determining factor, the rate of reaction with Cd^{2+} should be decreased more than with Zn^{2+} , as observed experimentally. If these conclusions are correct, a further decrease would be predicted for the complexation reactions of the monoprotonated form of ethylenediaminetetrapropionic acid.

Spin-Spin Coupling. The AB patterns observed for the

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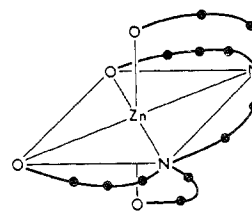


Figure 5. Possible structure of $\text{Zn}(\text{EDDDA})^{2-}$.

acetate proton resonances of all the complexes except $\text{Pb}(1,3\text{-PDPA})^{2-}$ indicate nonlabile metal-nitrogen bonding on the nmr time scale.^{29,30} The absence of an AB pattern for $\text{Pb}(1,3\text{-PDPA})^{2-}$, even at 220 MHz, may be due to more labile metal-nitrogen bonding or to the chemical shifts of the two acetate methylenic protons being accidentally equivalent.

The magnitude of the geminal coupling constant, J_{AB} , is approximately the same for $\text{Cd}(1,3\text{-PDPA})^{2-}$, $\text{Zn}(1,3\text{-PDPA})^{2-}$, and $\text{Pb}(\text{EDDDA})^{2-}$ but substantially different for $\text{Zn}(\text{EDDDA})^{2-}$. Sudmeier and coworkers³⁹ have reported the magnitude of the geminal coupling constants of methylenic protons of acetate groups bonding in the plane and out of the plane formed by $\text{Co}(\text{III})$ and the two nitrogens of amino-carboxylate ligands to be -16 ± 0.5 and -18 ± 0.5 Hz. Because of the sensitivity of geminal coupling to the electronegativity of substituents, the magnitudes of in-plane and out-of-plane geminal coupling constants of aminocarboxylate ligands coordinated to divalent metal ions may be different. Assuming the relative magnitudes to be in the same direction as those of $\text{Co}(\text{III})$ complexes, the results in Table II suggest the structure in Figure 5 for $\text{Zn}(\text{EDDDA})^{2-}$. Support for this structure also comes from the observation of Legg and coworkers⁴⁰ that $\Delta\delta_{AB}$ for out-of-plane acetate methylenic groups of cobalt(III) aminocarboxylate complexes is larger than for in-plane groups and the results of Byers and Douglas²⁷ which show the structure of one isomer of $\text{Co}(\text{EDDDA})^-$ to be similar to that shown in Figure 5.

Registry No. 1,3-PDPA, 1939-36-2; EDDA, 32701-19-2; $[\text{Cd}(1,3\text{-PDPA})]^{2-}$, 40273-08-3; $[\text{Pb}(1,3\text{-PDPA})]^{2-}$, 16787-03-4; $[\text{Zn}(1,3\text{-PDPA})]^{2-}$, 40273-09-4; $[\text{Cd}(\text{EDDA})]^{2-}$, 40273-10-7; $[\text{Pb}(\text{EDDA})]^{2-}$, 40299-72-7; $[\text{Zn}(\text{EDDA})]^{2-}$, 40354-48-1.

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