amount of N-bonded product arising from nitrogen attack would account for the slight rate increase actually observed, or it could simply be due to a salt effect. In summary, a dependence upon the size of the reagent is consistent with the second mechanism but should not be a factor in the ring-opening mechanism.[21]

Registry No. $[Pd(Et_4dien)SCN][B(C_6H_5)_4]$, 22143-00-6; $[Pd(Et_4dien)NCS][B(C_6H_5)_4]$, 22142-99-0; Br^-, 24959-67-9; $[Pd(Et_4dien)SeCN][B(C_6H_5)_4]$, 19599-79-2; $[Pd(Et_4dien)NCSe][B(C_6H_5)_4]$, 18024-40-3; I^-, 2046-154-5; N_3^-, 14343-69-2; CN^-, 57-12-5; $SeCN^-$, 5749-48-4.

Acknowledgment. The authors wish to express their sincere appreciation to the National Science Foundation for the support of this research (Grants GP-8327 and GP-20607) and to Professor Harry Gray for supplying us with a copy of his paper prior to publication.

(21) A referee suggested that the strain on the bent $SeCN^-$ group by the tridentate amine, without distortion of the Pd–amine bonds, is a more probable explanation of its special position among leaving groups; *i.e.*, a relatively weak interaction of the palladium(II) with a potential entering group might be enough to remove a strained $-SeCN^-$. We do not find this explanation to be compelling. Its logical extension suggests that the strained, angular Pd–SCN group should also be susceptible to attack by an incoming group for it, too, is destabilized by the presence of the ethyl groups and isomerizes at rates only slightly slower than those of the Pd–SeCN isomer. In point of fact, only the Pd–SeCN isomer exhibits the second-order pathway.

Contribution from the Department of Chemistry,
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Nuclear Magnetic Resonance Studies of the Solution Chemistry of Metal Complexes. VI. Stability Constants of Some Cadmium and Zinc Polyamine and Aminocarboxylate Mixed-Ligand Complexes[1,2]

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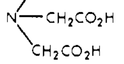
Stability constants, $K^{ML}{}_{MLX}$, for the complexation reaction $ML + X \rightleftharpoons MLX$ have been determined from proton magnetic resonance chemical shift measurements for a series of complexes where M is cadmium or zinc, L is nitrilotriacetic acid (nta) or β, β', β''-triaminotriethylamine (tren), and X is ethylenediamine (en), glycine (gly), malonic acid (ma), or iminodiacetic acid (ida). The log $K^{ML}{}_{MLX}$ values are as follows: 5.00, $Zn(nta)(en)^-$; 5.05, $Cd(nta)(en)^-$; 1.15, $Zn(tren)(en)^{2+}$; 2.83, $Cd(tren)(en)^{2+}$; 3.62, $Zn(nta)(gly)^{2-}$; 2.93, $Cd(nta)(gly)^{2-}$; 1.00, $Zn(tren)(gly)^+$; 2.59, $Cd(tren)(gly)^+$; 3.61, $Zn(nta)(ida)^{3-}$; 4.01, $Cd(nta)(ida)^{3-}$; 1.34, $Zn(nta)(ma)^{3-}$. The stability constants of the monohydroxy complexes of $Zn(nta)^-$ and $Zn(tren)^{2+}$ were also determined; the log $K^{ZnL}{}_{ZnL(OH)}$ values are 4.01 for $Zn(nta)(OH)^{2-}$ and 2.90 for $Zn(tren)(OH)^+$. The results indicate the tendency of $Zn(tren)^{2+}$ to form mixed complexes with en and gly is significantly less than that of the other complexes studied, suggesting that the structure of $Zn(tren)^{2+}$ is different from the structures of the other 1:1 complexes. The structures of the $M(nta)(gly)^{2-}$, $M(nta)(ida)^{3-}$, and $M(nta)_2{}^{4-}$ complexes are discussed on the basis of the formation constants of the ternary complexes.

Introduction

There has been considerable recent interest in the formation of mixed-ligand complexes in solution, in part due to the use of such complexes as models in studies of metalloenzyme–substrate interactions.[3-9] In the present work, the stability constants of the mixed-ligand complexes resulting from the addition of glycine (gly) or ethylenediamine (en) to the cadmium and zinc complexes of nitrilotriacetic acid (nta, I) and β, β', β''-triaminotriethylamine (tren, II) have been determined from proton nuclear magnetic resonance (nmr) chemical shift measurements. The stability constant of the complex formed from $Zn(nta)^-$ and malonic acid (ma) and the stoichiometry and equilibrium constants for the interaction of hydroxide ions with $Zn(nta)^-$ and $Zn(tren)^{2+}$ have also been determined.



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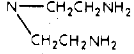

II

The structures of nta and tren are such that, if $M(nta)^-$ and $M(tren)^{2+}$ complexes are six-coordinate in aqueous solution, the two water molecules which complete the inner coordination shell will be in cis positions. Evidence supporting the cis-octahedral arrangement in $Ni(tren)(H_2O)_2{}^{2+}$ has recently been obtained from solvent-exchange studies;[10] however thermochemical data[11] suggest that $Zn(tren)^{2+}$ is less hydrated and exists as a four- or five-coordinate complex.

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(2) Supported in part by a grant from the National Research Council of Canada.

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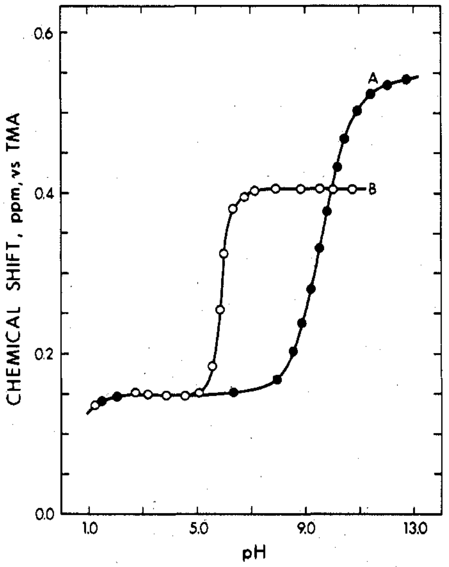

Figure 1. pH dependence (25°) of the chemical shift at the center of the multiplet pattern for the carbon-bonded protons of tren: curve A, 0.198 *M* tren + 0.4 *M* KNO_3; curve B, 0.198 *M* tren + 0.198 *M* $Cd(NO_3)_2$.

The stability constants of the mixed complexes resulting from the addition of iminodiacetic acid (ida) to the cadmium and zinc complexes of nta are also reported. These complexes were studied in an attempt to elucidate the structures of previously described[12] complexes in which the nta-to-metal ratio is 2. In the $M(nta)_2{}^{4-}$ complexes, several structures are possible because the number of ligand dentates exceeds the coordination number of the metal, assuming the maximum coordination numbers of cadmium and zinc to be 6. Attempts were made previously to ascertain structural information from the stability constants of the $M(nta)_2{}^{4-}$ complexes; however stability constants for appropriate model systems had not been reported.

Experimental Section

Chemicals. The metal nitrate salts and the ligands, with the exception of tren, were of the highest purity commercially available and were used as received. tren was separated from technical grade triethylenetetramine (Baker Chemical Co.) by fractional crystallization as the trihydrochloride salt (tren·3HCl).[13,14] To eliminate interferences from the formation of chloro complexes, the chloride ion was removed by passing a solution of tren·3HCl through an anion-exchange column in the hydroxide form. The resulting solution was standardized by titration with HNO_3. The crystalline potassium salts of the nta complexes, $KM(nta)\cdot xH_2O$, were prepared as described previously.[12] Stock solutions of $Cd(NO_3)_2$ and $Zn(NO_3)_2$ were standardized by edta titration,[15] and a stock solution of ethylenediamine was standardized by titration with HNO_3. A stock solution of tetramethylammonium (TMA) nitrate was prepared by titration of a 25% aqueous solution of TMA hydroxide (Eastman Organic Chemicals) with concentrated HNO_3 to a neutral pH.

pH Measurements. 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 standards, pH 3.56 and 9.18 at 25°, were used to calibrate the pH meter.

Nmr Measurements. Nmr spectra were obtained on a Varian A-60-D spectrometer or on a Varian HA-100 spectrometer at a probe temperature of 25 ± 1°. Solutions used in the nmr studies were prepared in distilled water from the requisite amounts of either crystalline material or standard solution. KNO_3 was added to solutions containing only ligand to give an ionic strength comparable to that of solutions containing metal ions. Solutions used in the determination of the stability constants of the complexes MLX contained equimolar amounts of M, L, and X. HNO_3 or KOH was added to bring the solutions to the desired pH's. TMA nitrate was added to each solution as a reference compound for chemical shift measurements; positive shifts in ppm indicate resonances upfield from the central resonance of the TMA triplet. The central resonance of TMA is 3.17 ppm downfield from the methyl resonance of sodium 3-(trimethylsilyl)-1-propanesulfonic acid (TMS*).

Results

The mixed complexes studied in this work are formed by the binding of ligand X to metal complex ML, where L is nta^{3-} or tren. Previous results[12] indicate that virtually all

$$ML + X \rightleftarrows MLX \qquad (1)$$

$$K^{ML}{}_{MLX} = [MLX]/[ML][X] \qquad (2)$$

the nta^{3-} is coordinated to form $Cd(nta)^-$ and $Zn(nta)^-$ at pH >4 when the solution contains equimolar concentrations of metal ion and ligand. In the present work, the Cd^{2+} and Zn^{2+} complexes of tren were investigated in a similar manner to determine at what pH's coordination to form $Cd(tren)^{2+}$ and $Zn(tren)^{2+}$ is complete. The pH dependence of the nmr spectrum of the carbon-bonded protons of tren, which consists of a complex multiplet pattern of the AA′BB′ type, was studied in aqueous solutions containing KNO_3 and in aqueous solutions containing equimolar concentrations of $Cd(NO_3)_2$ or $Zn(NO_3)_2$ and tren. At most pH values and in the presence of Cd^{2+} and Zn^{2+} the lines of the multiplet are broad and overlapping. Consequently the chemical shift at the center of the multiplet pattern was measured rather than fully analyzing each spectrum. The chemical shift at the center of the multiplet in the absence of a complexing metal ion is pH dependent (curve A in Figure 1) due to nitrogen protonation. An averaged multiplet was also observed for the carbon-bonded protons of tren in cadmium-containing solutions, with some exchange broadening in the pH range 5.5–7.0. The results are shown by curve B in Figure 1. At pH values less than ~7.5, the complex is dissociated, the extent of dissociation depending on pH. A formation constant of $\log K_f = 11.8$ ($K_f = [Cd(tren)^{2+}]/[Cd^{2+}][tren]$) was determined from the averaged chemical shifts at pH <7.5 by methods described previously.[12] Prue and Schwarzenbach reported a value of $\log K_f = 12.3$ from potentiometric titration measurements.[16] For the zinc system, separate multiplet patterns were observed for the complexed and free tren due to slow ligand exchange. The complex is partially dissociated at pH values less than ~5.5. From the relative intensities of the complexed and free resonances at pH's less than 5.5, a formation constant of $\log K_f = 14.53$ was determined; Prue and Schwarzenbach reported a value of $\log K_f = 14.65$.[16]

Nmr spectra of the carbon-bonded protons of the ligands ida, gly, en, and ma consist of a single exchange-averaged resonance, the chemical shift of which is pH dependent due to ionization of acidic protons. For glycine, the resonance for the CH_2 protons shifts upfield by 0.387 ppm (curve A, Figure 2) as the pH increases from 7 to 12 due to ionization of the amino proton. Protonation constants (Table I) were determined from the chemical shifts of the

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Table I. Ligand Protonation Constants and Mixed-Ligand Complex Stability Constants^{a-c}

	Ethylenediamine	Glycine	Iminodiacetic acid	Nitrilotri-acetic acid	Malonic acid
$pK_1{}^d$	7.35	2.38	2.65^e		2.50
pK_2	10.20	9.70	9.48		5.10
$\log K^{\mathrm{Zn(nta)^-}}{}_{\mathrm{Zn(nta)(L)}}$	5.00 ± 0.07	3.62 ± 0.04	3.61 ± 0.07	3.5^f	1.34 ± 0.11
$\log K^{\mathrm{Cd(nta)^-}}{}_{\mathrm{Cd(nta)(L)}}$	5.05 ± 0.05	2.93 ± 0.17	4.01 ± 0.05	4.9^f	
$\log K^{\mathrm{Zn(tren)^{2+}}}{}_{\mathrm{Zn(tren)(L)}}$	1.15 ± 0.10	1.00 ± 0.05			
$\log K^{\mathrm{Cd(tren)^{2+}}}{}_{\mathrm{Cd(tren)(L)}}$	2.83 ± 0.05	2.59 ± 0.03			

^{a} At 25°. ^{b} Unless otherwise indicated, determined from nmr measurements at ionic strengths of ~0.4–0.6 *M*; see Experimental Section for details. ^{c} Error limits are standard deviations. ^{d} $K_1 = [H^+][HL]/[H_2L]$; $K_2 = [H^+][L]/[HL]$; $pK_1 = -\log K_1$. ^{e} G. Schwarzenbach and H. Senn, quoted in ref 21. ^{f} Reference 12.

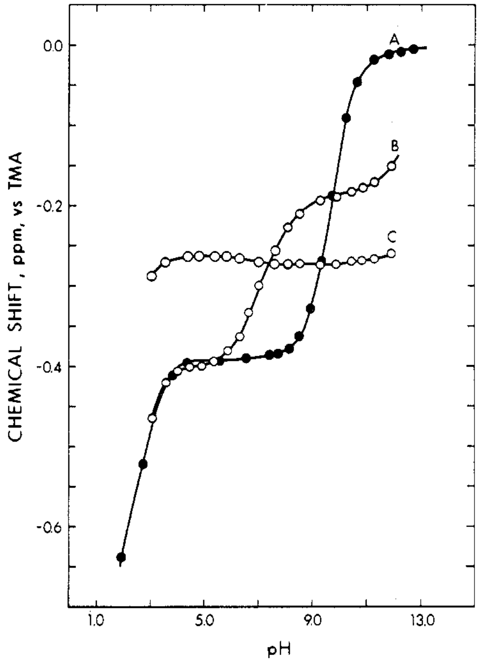

Figure 2. pH dependence (25°) of the chemical shift of (A) the methylene protons of glycine in a solution containing 0.20 *M* glycine + 0.6 *M* KNO_3, (B) the methylene protons of glycine in a solution containing 0.20 *M* glycine + 0.20 *M* $Zn(nta)^-$, and (C) the methylene protons of nta in a solution containing 0.20 *M* glycine + 0.20 *M* $Zn(nta)^-$.

carbon-bonded ligand protons using methods described previously.[17]

The formation constants of the mixed-ligand complexes were determined from the chemical shifts of the carbon-bonded protons of ida, gly, en, or ma in solutions which also contained $M(nta)^-$ or $M(tren)^{2+}$. The method used will be illustrated by the Zn(nta)-gly system. The averaged chemical shift of the glycine protons is the sum of the chemical shifts of the glycine in the complexed and uncomplexed forms, weighted according to the relative concentration of each form (eq 3), where $\mathrm{gly_f}$ represents the sum of the concentrations of the various protonated forms of uncomplexed

$$\nu_{\mathrm{av}} = P_{\mathrm{gly_f}}\nu_{\mathrm{gly_f}} + P_{\mathrm{M(nta)(gly)}}\nu_{\mathrm{M(nta)(gly)}} \tag{3}$$

glycine, ν represents the chemical shift, and P is the mole fraction ($P_{\mathrm{gly_f}} + P_{\mathrm{M(nta)(gly)}} = 1$) of glycine in the forms indicated. The chemical shift of glycine in $Zn(nta)(gly)^{2-}$ is the chemical shift at the point where the chemical shift *vs.* pH curve for the glycine solution containing $Zn(nta)^-$ intersects the chemical shift *vs.* pH curve for the glycine solution that contains no complexing metal ion.[17] Combination of eq 3 and the equation relating mole fractions leads to

$$P_{\mathrm{M(nta)(gly)}} = \frac{\nu_{\mathrm{gly_f}} - \nu_{\mathrm{av}}}{\nu_{\mathrm{gly_f}} - \nu_{\mathrm{M(nta)(gly)}}} \tag{4}$$

The mole fraction of complexed glycine at a particular pH was calculated from the averaged chemical shift using eq 4. The concentration of $M(nta)(gly)^{2-}$ was then calculated from the mole fraction of this species ($[M(nta)(gly)^{2-}] = P_{\mathrm{M(nta)(gly)}}[\mathrm{gly}]_t$), and the concentrations of $M(nta)^-$ and uncomplexed glycine were obtained by difference. These concentrations yielded a conditional stability constant $K_f{}^c$ ($=[M(nta)(gly)^{2-}]/[M(nta)^-][\mathrm{gly}]_f$), from which the pH-independent stability constant defined by eq 5 and 6 was obtained: $K^{\mathrm{M(nta)^-}}{}_{\mathrm{M(nta)(gly)^{2-}}} = K_f{}^c/\alpha$ where α is the fraction of uncomplexed glycine in the ionized form at the pH of the measurement.[18] The stability constants obtained in this way are listed in Table I. For comparison, Hopgood and Angelici[19] reported a $\log K^{\mathrm{Zn(nta)^-}}{}_{\mathrm{Zn(nta)(gly)^{2-}}}$ of 3.64 from potentiometric titration data.

$$M(nta)^- + gly \rightleftarrows M(nta)(gly)^{2-} \tag{5}$$

$$K^{\mathrm{M(nta)^-}}{}_{\mathrm{M(nta)(gly)^{2-}}} = \frac{[M(nta)(gly)^{2-}]}{[M(nta)^-][gly^-]} \tag{6}$$

The chemical shift behavior of the ligand protons at pH's > 10.5 in the Zn(nta)(ligand) and Zn(tren)(ligand) systems indicates that in this pH range hydroxide ion is displacing some ligand from the mixed complex with the formation of Zn(nta)(hydroxy) and Zn(tren)(hydroxy) complexes. For example, at pH >10.5 the chemical shift of glycine in the presence of $Zn(nta)^-$ (Figure 2) moves in the direction of the chemical shift of uncomplexed glycine, due to hydroxide ions displacing glycine as described by eq 7 and 8.

$$Zn(nta)(gly)^{2-} + xOH^- \rightleftarrows Zn(nta)(OH)_x{}^{(1+x)-} + gly^- \tag{7}$$

$$K_{\mathrm{eq}} = \frac{[Zn(nta)(OH)_x{}^{(1+x)-}][gly^-]}{[Zn(nta)(gly)^{2-}][OH]^x} \tag{8}$$

Similar behavior was observed for the complexes of Cd^{2+}; however precipitation of presumably $Cd(OH)_2$ precluded a detailed study of the interaction of hydroxide ion with cadmium.

The stability constants and stoichiometries of the $Zn(nta)(OH)_x{}^{(1+x)-}$ and $Zn(tren)(OH)_x{}^{(2-x)}$ complexes were determined from the pH dependence of the chemical shift of the second ligand in the high pH region. The method used is illustrated by the following for the $Zn(nta)(gly)^{2-}$ system. Rearrangement of eq 8 followed by taking logarithms leads to eq 9, where $\mathrm{pOH} = -\log[OH^-]$. K_{eq} was obtained from

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the pOH 0 intercept and the number of hydroxide ions from the slope of a plot of the left side of eq 9 *vs.* pOH. The

$$\log \frac{[\mathrm{Zn(nta)(OH)}_x{}^{(1+x)-}][\mathrm{gly}^-]}{[\mathrm{Zn(nta)(gly)}^{2-}]} = -x\ \mathrm{pOH} + \log K_{\mathrm{eq}} \quad (9)$$

concentration of $\mathrm{Zn(nta)(gly)}^{2-}$ at a particular pOH was calculated from the averaged chemical shift of the glycine resonance using eq 4, and the concentrations of Zn(nta)-$\mathrm{(OH)}^{(1+x)-}$ and gly^- were then obtained by difference. For the Zn(nta)-gly system, a value of 0.9 was obtained for x and 2.5 for K_{eq}. For the Zn(nta)-ida system, a value of 1.1 was obtained for x and 2.5 for K_{eq}, indicating the stoichiometry of the complex to be $\mathrm{Zn(nta)(OH)}^{2-}$. The formation constant of $\mathrm{Zn(nta)(OH)}^{2-}$, defined by eq 10 and 11, was obtained from K_{eq} using the relationship $K^{\mathrm{Zn(nta)}^-}{}_{\mathrm{Zn(nta)(OH)}^{2-}} = K_{\mathrm{eq}}K^{\mathrm{Zn(nta)}}{}_{\mathrm{Zn(nta)(L)}}$. The value log $K^{\mathrm{Zn(nta)}^-}{}_{\mathrm{Zn(nta)(OH)}^{2-}} = 4.01$ was obtained from both systems. A value of 1.1 for the number of hydroxide ions involved and 4.14 for the value of log $K^{\mathrm{Zn(nta)}^-}{}_{\mathrm{Zn(nta)(OH)}^{2-}}$ was previously obtained from chemical shift measurements on a solution containing nta and Zn^{2+} in the ratio of 2:1.[20] For comparison, Schwarzenbach[21] reported an approximate value of 4 and Hopgood and Angelici[19] reported a value of 3.55 for log $K^{\mathrm{Zn(nta)}^-}{}_{\mathrm{Zn(nta)(OH)}^{2-}}$, although Courtney, *et al.*,[22] reported that $\mathrm{Zn(nta)}^-$ does not form a hydroxy complex. Treatment of the Zn(tren)-gly system by the above method yielded a value of 1.0 for the number of hydroxide ions involved and 79.4 for K_{eq}, from which the value log $K^{\mathrm{Zn(tren)}^{2+}}{}_{\mathrm{Zn(tren)(OH)}^+} = 2.90$ was calculated.

$$\mathrm{Zn(nta)^- + OH^- \rightleftarrows Zn(nta)(OH)^{2-}} \quad (10)$$

$$K^{\mathrm{Zn(nta)}^-}{}_{\mathrm{Zn(nta)(OH)}^{2-}} = \frac{[\mathrm{Zn(nta)(OH)}^{2-}]}{[\mathrm{Zn(nta)}^-][\mathrm{OH}^-]} \quad (11)$$

The methylene protons of nta in the glycine solution containing $\mathrm{Zn(nta)}^-$ give rise to a single, sharp resonance whose chemical shift (curve C, Figure 2) changes only slightly in the pH region where complexation of glycine by $\mathrm{Zn(nta)}^-$ is occurring and then levels off at a constant value up to the pH region where hydroxide displaces the glycine. Similar behavior was observed for the other complexes studied, indicating that virtually all the nta^{3-} or tren is complexed at the pH's where the stability constants were determined.

Discussion

Mixed-Ligand Complexes of Glycine and Ethylenediamine. The nta^{3-} and tren complexes of Cd^{2+} and Zn^{2+} all form mixed complexes with the bidentate ligands glycine and ethylenediamine; however, the tendency toward mixed complex formation varies considerably. The difference between the stability constant for complexation of glycine or ethylenediamine by $\mathrm{M(nta)}^-$ or $\mathrm{M(tren)}^{2+}$ and for complexation by the fully aquated metal ion, Δ log K (see eq 12), reflects the tendency for addition of the bidentate ligand to form the mixed complex. Negative values are expected because fewer coordination sites are available in the $\mathrm{M(nta)}^-$ and $\mathrm{M(tren)}^{2+}$ complexes. Δ log K values for the glycine and ethylenediamine complexes are listed in Table II.

$$\Delta \log K = \log K^{\mathrm{ML}}{}_{\mathrm{MLX}} - \log K^{\mathrm{M}}{}_{\mathrm{MX}} \quad (12)$$

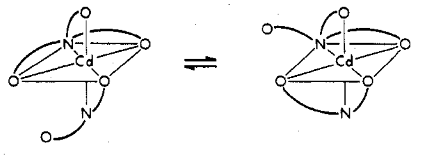
Table II. Values of Δ log K for the Glycine and Ethylenediamine Mixed-Ligand Complexes[a]

	Δ log K	
	Ethylenediamine	Glycine
Zn(nta)(X)	−1.00[b]	−1.80[d]
Cd(nta)(X)	−0.42[c]	−1.72[e]
Zn(tren)(X)	−4.85	−4.42
Cd(tren)(X)	−2.64	−2.06

[a] Δ log K is defined by eq 13. [b] Log $K^{\mathrm{Zn}}{}_{\mathrm{Zn(en)}} = 6.00$: C. J. Nyman, E. W. Murbach, and G. B. Millard, *J. Amer. Chem. Soc.*, 77, 4194 (1955). [c] Log $K^{\mathrm{Cd}}{}_{\mathrm{Cd(en)}} = 5.47$: G. A. Carlson, J. P. McReynolds, and F. H. Verhoek, *J. Amer. Chem. Soc.*, 67, 1334 (1945). [d] Log $K^{\mathrm{Zn}}{}_{\mathrm{Zn(gly)}} = 5.42$: N. C. Li and R. A. Manning, *J. Amer. Chem. Soc.*, 77, 5225 (1955). [e] Log $K^{\mathrm{Cd}}{}_{\mathrm{Cd(gly)}} = 4.65$: H. Mackenzie, quoted in ref 21.

The most striking conclusion from the results in Table II is that the tendency for $\mathrm{Zn(tren)}^{2+}$ to form mixed complexes with glycine and ethylenediamine is significantly less than that of the other complexes. This may be an indication that the coordination number of Zn^{2+} in the $\mathrm{Zn(tren)}^{2+}$ complex is different from the coordination numbers in the $\mathrm{Cd(tren)}^{2+}$, $\mathrm{Zn(nta)}^-$, and $\mathrm{Cd(nta)}^-$ complexes. This is consistent with the thermochemical studies of Paoletti, *et al.*,[11] which suggest that in aqueous solution $\mathrm{Zn(tren)}^{2+}$ is less hydrated than are the $\mathrm{Mn(tren)}^{2+}$, $\mathrm{Fe(tren)}^{2+}$, $\mathrm{Ni(tren)}^{2+}$, and $\mathrm{Cu(tren)}^{2+}$ complexes and probably is either tetrahedral or five-coordinate. Recent water-exchange studies suggest that Ni^{2+} in $\mathrm{Ni(tren)}^{2+}$ is octahedrally coordinated with two water molecules cis in the fifth and sixth coordination positions.[10] Ciampolini, *et al.*,[23,24] also concluded from thermochemical studies that the complexes $\mathrm{Zn(en)_2}^{2+}$ and $\mathrm{Zn(dien)}^{2+}$, where dien is diethylenetriamine, are tetrahedral in aqueous solution. If Zn^{2+} is less than six-coordinate in $\mathrm{Zn(tren)}^{2+}$, formation of mixed-ligand complexes in which all six dentates are coordinated would require an expansion of the coordination sphere to accommodate the larger number of dentates or, alternatively, the number of ligand dentates coordinated in the $\mathrm{Zn(tren)}^{2+}$ mixed complexes might be less than 6, as has been proposed[24] for the complex $\mathrm{Zn(dien)_2}^{2+}$. Tetrahedral coordination in $\mathrm{Zn(nta)}^-$ is likely to be less favored due to electrostatic repulsion between the carboxylate groups of nta^{3-}. The significantly smaller stability constant for $\mathrm{Zn(tren)(OH)}^+$ compared to that of $\mathrm{Zn(nta)(OH)}^{2-}$ is consistent with different numbers of water molecules coordinated in $\mathrm{Zn(tren)}^{2+}$ and $\mathrm{Zn(nta)}^-$.

Mixed-Ligand Complexes of $\mathrm{M(nta)}^-$ and Aminocarboxylate Ligands. The stability constants of the ternary complexes formed from $\mathrm{Cd(nta)}^-$ and gly^-, ida^{2-}, and nta^{3-} increase as the number of ligand dentates increases, opposite to the trend expected from electrostatic considerations if each of the second ligands coordinated to the Cd^{2+} through the same number of dentates. These data suggest that if gly^- is bidentate in $\mathrm{Cd(nta)(gly)}^{2-}$, ida^{2-} in $\mathrm{Cd(nta)(ida)}^{2-}$ is tridentate, as represented by IV, at least part of the time,



III IV

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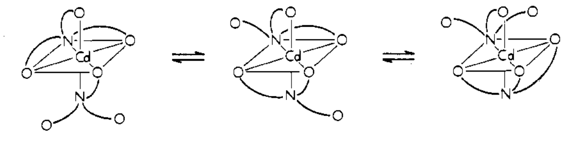
and that the second nta^{3-} of Cd(nta)$^{4-}$ is more than bidentate, as represented by VI and VII, at least part of the time.


V VI VII

$K^{\text{Cd(nta)}^-}{}_{\text{Cd(nta)(X)}}$ is equal to the ratio of the formation (k_f) and dissociation (K_d) rate constants for the reaction described by eq 5. If complexation of ligand X by Cd(nta)$^-$ occurs *via* the dissociative mechanism,[25] K_f for the ligands gly$^-$, ida^{2-}, and nta^{3-} will decrease as the charge on the ligand increases due to electrostatic effects. k_d has to decrease in this same order for the stability constants to increase in the order

$$K^{\text{Cd(nta)}^-}{}_{\text{Cd(nta)(gly)}^{2-}} < K^{\text{Cd(nta)}^-}{}_{\text{Cd(nta)(ida)}^{3-}} < K^{\text{Cd(nta)}^-}{}_{\text{Cd(nta)}_2{}^{4-}}$$

which is consistent with an increasing degree of coordination by the second ligand. The small change in $K^{\text{Zn(nta)}^-}{}_{\text{Zn(nta)(X)}}$ as the charge on X increases suggests the structures of the gly$^-$, ida^{2-}, and nta^{3-} complexes of Zn(nta)$^-$ are similar to those proposed above for the Cd(nta)(X) complexes.

Registry No. nta, 139-13-9; tren, 4097-89-6; en, 107-15-3; gly, 56-40-6; ma, 141-82-2; ida, 142-73-4; Zn(nta)(en)$^-$, 36245-45-1; Cd(nta)(en)$^-$, 36191-48-7; Cd(tren)(en)$^{2+}$, 36191-49-8; Zn(nta)(gly)$^{2-}$, 36191-50-1; Cd(nta)(gly)$^{2-}$, 36191-51-2; Cd(tren)(gly)$^+$, 36191-52-3; Zn(nta)(ida)$^{3-}$, 12717-57-6; Cd(nta)(ida)$^{3-}$, 12717-56-5; Zn(nta)(ma)$^{3-}$, 36191-53-4.

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An Improved Synthesis and a Structural Study of Six-Coordinate Tin Tropolonates by Dipole Moments and Kerr Constants in Solution

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Dipole moments and molar Kerr constants determined at 25° for tropolone in cyclohexane and carbon tetrachloride have been used to estimate the optical anisotropy of the tropolonate ligand. A comparison of dipole moments and Kerr constants calculated for the various candidate structures with those obtained from experiment indicates that the tin tropolonates $R_2Sn(trop)_2$ (where R = Cl, CH_3, or C_6H_5) exist preferentially in solution as the cis form. An improved method of synthesis is also described.

The existence of monomeric, neutral, six-coordinate organotin chelate compounds of the type R_2SnCh_2 has been an established fact for a number of years.[1,2] The organic substituent R can be either an alkyl or an aromatic group while the ligand Ch$^-$ can be one of a variety of bidentate types. Because of the possible involvement of tin "d" orbitals and a lingering uncertainty concerning molecular geometries of tin complexes,[3] the structures of these molecules remain the object of considerable interest.

Recent solution- and crystal-state investigations have strongly supported the assignment of cis-type structures. Electric polarization studies[3-6] have clearly shown that such configurations are favored for a wide variety of β-keto enolates. An X-ray analysis[7] of dimethyltin bis(8-hydroxyquinolinolate) has indicated a distorted octahedral structure with a C-Sn-C bond angle of 111°. Mossbauer spectra[8-11] of solids tend to be interpreted in terms of similar cis structures, although crystalline bis(2,4-pentanedionato)-dimethyltin(IV) has been assigned a trans configuration on the basis of quadrupole splitting. The nmr spectra of analogous tropolonates have also been interpreted in terms of a favored cis arrangement.[12,13]

β-Keto enolates have frequently been used in structural studies because of their stability and the relative ease of interpretation of their spectra. However, it has been suggested[14,15] that in solution the β-keto enolate groups may be nonrigid and for that reason structural information derived from spectral and dielectric measurements may be

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