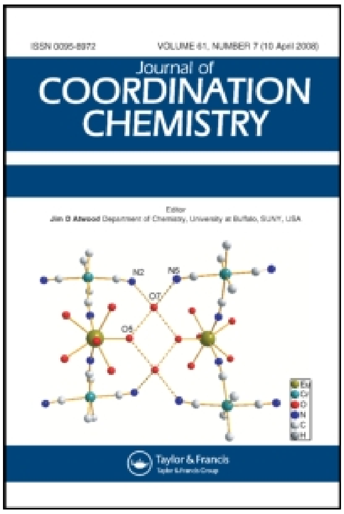

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STABILITIES OF COMPLEX FORMATION BETWEEN TRIETHYLENETETRAAMINE-N^2, N^3-DIACETIC ACID AND SOME TRANSITION METAL IONS

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The protonation and stability constants of Ni(II), Cu(II), and Zn(II) complexes of a new sexidentate ligand, triethylenetetraamine-N^2,N^3-diacetic acid tetrahydrochloride (H_2ttda·4HCl), have been determined using pH titration techniques at $\mu = 0.10$. The complexes of ttda^{2-} with Ni(II), Cu(II), and Zn(II) are more stable than those of edta and the Ni(II) and Zn(II) ttda complexes are more stable than those of penten.

INTRODUCTION

Recently the stereochemistry of inert cobalt(III) complexes of *triethylenetetraamine-N^2,N^3-diacetate* (ttda^{2-}) ion has been studied using circular dichroism[1] and carbon-13 and proton nuclear magnetic resonance techniques.[2] In comparison with its structural analogues, i.e. edta^{4-} (ethylenediaminetetraacetate ion) and penten (*N,N,N′,N′*-tetrakis(*β*-aminoethyl)ethylenediamine), ttda^{2-} is expected to be an effective sequestering agent for many metal ions (Figure 1). It has the advantage over polyamines in having a doubly negative charge. It also has an advantage over edta^{4-} since ttda^{2-} has four nitrogen donor atoms compared to two nitrogens for edta^{4-}. Complexes are generally more stable with ligands having strongly basic donor atoms. The lower charge of ttda^{2-} should be an advantage over edta^{4-} since there is complete charge neutralization for ttda^{2-} complexes of divalent metal ions. In order to evaluate ttda^{2-} as a ligand it is necessary to determine the stabilities of complexes of many metal ions. In this paper we report the study with nickel(II), copper(II), and zinc(II) ions.

EXPERIMENTAL SECTION

Materials and Standard Solutions

Triethylenetetraamine-N^2,N^3-diacetic acid (H_2ttda) was synthesized by the method of Igi[3] and isolated as a tetrahydrochloride salt (H_2ttda·4HCl). The crude compound was recrystallized several times from ethanol–water solution. A 1×10^{-2} M solution was prepared and standardized first by potentiometric precipitation titration of chloride ions in acidic media using a silver electrode and a calomel reference electrode using standard silver nitrate solution, then the concentration was checked by titration with standard KOH solution. The standard silver nitrate solution was prepared from dried reagent grade silver nitrate. Carbonate-free KOH solution (0.1 M) was prepared from reagent grade KOH. The KOH solution was standardized using potassium hydrogen phthalate. The standard metal salt solutions, having a concentration of about 2×10^{-2} were prepared from reagent grade nitrates and were standardized by complexometric titrations. 1 M solution of KNO_3 was prepared and determined by passing aliquots of the solution into a cation exchange (Dowex 50W-X8 resin) column in the H^+ form, and titrating the displaced H^+ with standard KOH solution.

Potentiometric Titrations

All titrations were carried out at constant ionic strength of 0.1 M KNO_3. A Corning Model 101 digital pH meter in conjunction with a Corning pH electrode and a Corning calomel reference electrode were employed. The sample was prepared by pipeting

10 ml of 1×10^{-2} M of $H_2ttda{\cdot}4HCl$ solution and 10 ml of 1 M KNO_3 solution into a 100 ml volumetric flask and diluting to 100 ml with carbonate-free deionized water in the absence and presence of 5 ml 2×10^{-2} M metal salt solutions. The final mixture was transferred into a 200 ml home-made titration vessel fitted with an outer constant temperature water circulating jacket and a 5-hole cover. Electrodes, buret, gas-inlet and outlet were fitted into these holes. Prior to each titration, the pH meter was standardized at pH 4.00, 7.00 and 10.00 ± 0.02 pH using Fisher buffer solutions. The assembly was thermostated at 25.0 ± 0.10°C with oxygen-free nitrogen gas bubbling through the solution and with stirring. KOH solution was delivered from a 5 ml buret with a reading accuracy of ±0.01 ml.

All equilibrium calculations were performed using computer programs available in our laboratories. The determination of the protonation constants of both the ligand and the metal chelate was achieved using a nonlinear least squares routine. The complex formation constants were calculated using a program provided by Professor A. E. Martell and Dr. R. J. Motekaitis of Texas A & M University. The activity coefficient, f_H^+ was calculated by titrating a HCl solution of known concentration with 0.1 M KNO_3 using 0.1 M KOH solution. The measured pH was then converted to hydrogen ion concentration, $[H^+]$, according to Eq. (1).

$$-\log_{10}[H^+] = pH + \log_{10} f_H^+ \qquad (1)$$

A value of 13.791 was employed for the pKw at 25°C, ionic strength 0.10.

Other Physical Measurements

Visible and IR absorption spectra were recorded using a Cary Model 118 spectrophotometer and a Beckman IR 8 spectrophotometer, respectively.

RESULTS AND DISCUSSION

Ligand Protonation Constants

The ligand potentiometric titration curve (L of Figure 2) shows three buffer regions: one from pH 2.5 to pH 5 which corresponds to the dissociation of first three strong acid protons; another from pH 5 to pH 7.5 which corresponds to the dissociation of the fourth proton, and the third from pH 7.5 to over pH 10.5, the dissociation of the last two protons. It is intuitive that the first two acidic protons are the two carboxylic acid protons and the last four protons bear a similarity of those of the triethylenetetraamine (trien).[4] The deprotonation scheme of $H_2ttda{\cdot}4HCl$ is shown in Figure 3. The calculated ligand protonation constants of $H_2ttda{\cdot}4HCl$ are given in Table I according to the definition: $K^H_{H_nL} = [H_nL]/[H][H_{n-1}L]$. Also listed in Table I are protonation constants of some other ligands of interest. The first two protonation constants of $ttda^{2-}$ (K^H_{HL} and $K^H_{H_2L}$) are quite high compared to those of trien which may reflect both the higher electrondensity on the tertiary nitrogen of $ttda^{2-}$ relative to the secondary nitrogen of trien and the inductive and charge effects of the deprotonated negatively charged acetate substituents. The two low log K values of acetate arms of

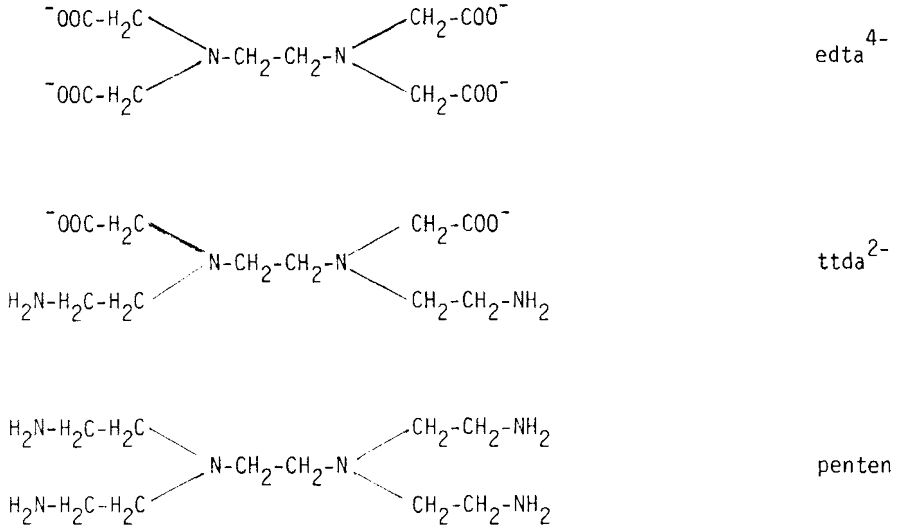

FIGURE 1 Structure of $edta^{4-}$, $ttda^{2-}$, penten. (For abbreviation, see text.)

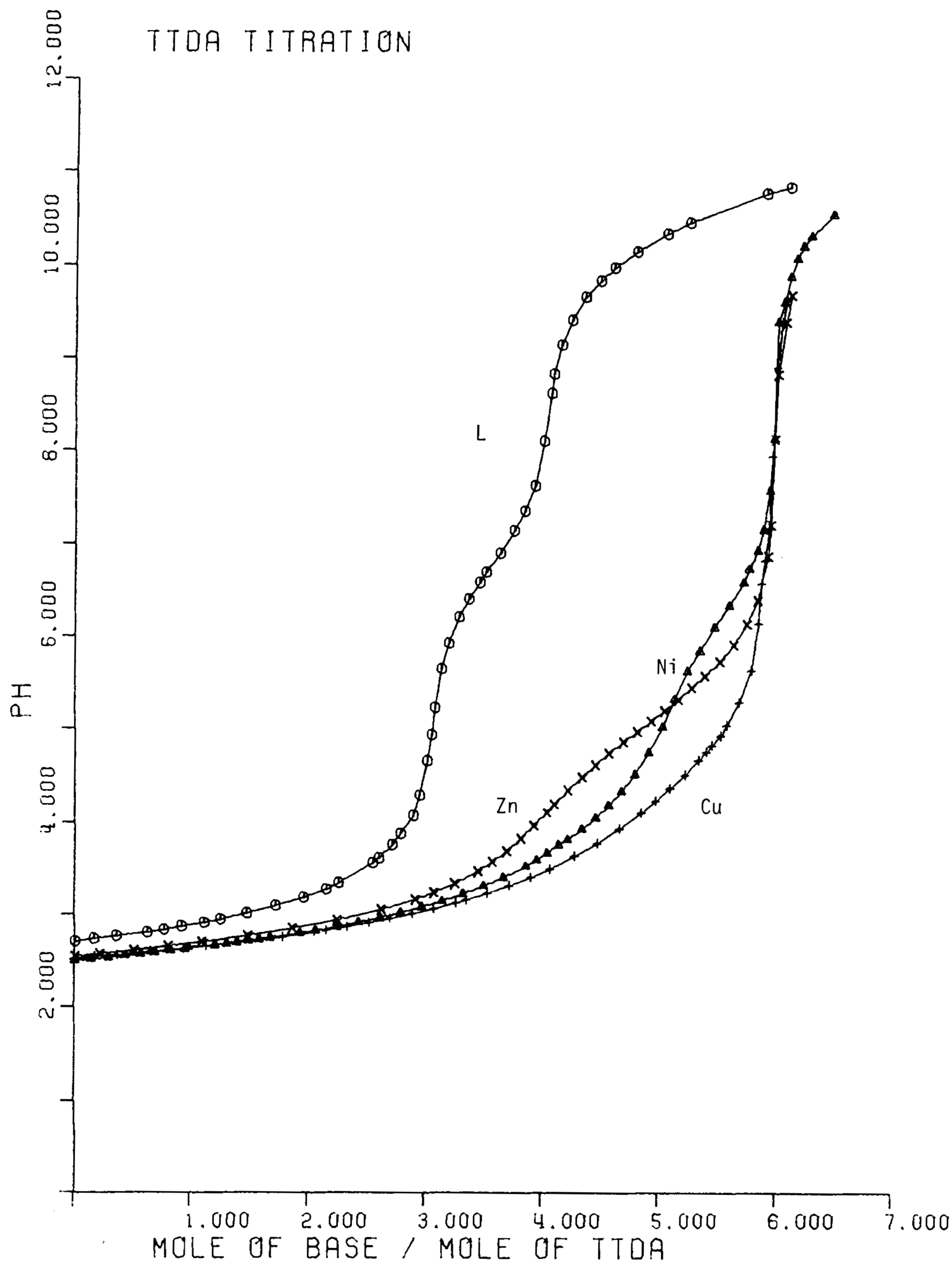

FIGURE 2 Potentiometric equilibrium curves for H_2ttda·4HCl (L, -O-O-O-O-) and 1 : 1 ratios of H_2ttda 4HCl with Ni^{2+} (-Δ-Δ-Δ-Δ-), Cu^{2+} (-+-+-+-+-), and Zn^{2+} (-×-×-×-×-). [H_2ttda·4HCl] = [M^{2+}] ≃ 1.000 × 10^{-3} M; T = 25°C; μ = 0.10 M (KNO_3).

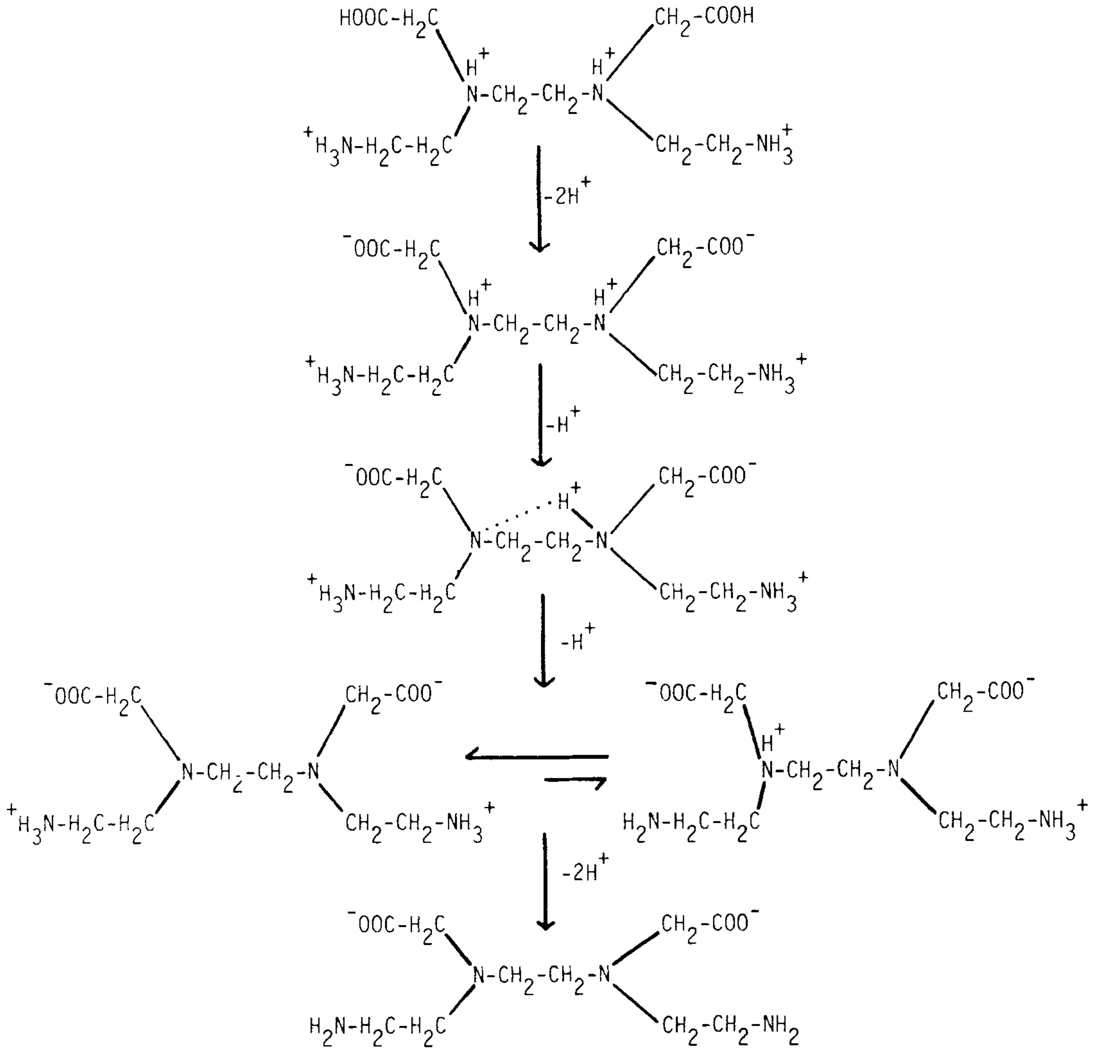

FIGURE 3 Probable deprotonation scheme of H_2ttda·4HCl.

TABLE I
Ttda ligand protonation constants.[8] $\mu = 0.10$, $T = 25°C$

	log K^H_{HL}	log $K^H_{H_2L}$	log $K^H_{H_3L}$	log $K^H_{H_4L}$	log $K^H_{H_5L}$	log $K^H_{H_6L}$
edta	10.17	6.11	2.68	2.0	1.5	0.0
ttda	10.54 ± 0.02	9.86 ± 0.02	6.70 ± 0.03	3.78 ± 0.06	(2.76)	(1.87)
trien	9.74	9.08	6.56	3.25	—	—
penten	10.08	9.58	8.99	8.42	1.33	—

$H_2ttda \cdot 4HCl$ cannot be determined very accurately due to the greater degree of dissociation at small ligand concentration. However, they are expected to be close to the corresponding ones of $edta^{4-}$. The high positive charge accumulated on the ligand after protonation would also be responsible for the lower log K values.

Determination of the Stability Constants

The metal complex formation equilibrium curves obtained are shown in Figure 2. The higher pH buffer zone of Zn(II) system between $a = 0$ and $a = 4$ indicates that Zn(II) ion forms the least stable complex with $ttda^{2-}$ (a = mole of base added/mole of ligand). *The same conclusion can be drawn from the calculated average protonation number* $\bar{n}$, defined by Eq. (2).[5]

$$\bar{n} = \frac{\text{Total dissociable hydrogen ion concentration bound to ligand species}}{\text{Total ligand concentration}} \qquad (2)$$

In general, for all three metal-ttda systems, if the total ligand concentrations are the same, Zn-ttda system always has the greatest $\bar{n}$ value before any base is added. This indicates that Zn(II) ion competes less favorably than Cu(II) and Ni(II) against H^+ ion to bind $ttda^{2-}$. *It has been found that for the three* metal-ttda systems, all the beginning $\bar{n}$ values are in between 2.00 and 3.00 indicating that the complexation reaction is

$$M^{2+} + H_4ttda^{2+} + 2H^+ \rightleftharpoons MH_2ttda^{2+} + 4H^+ \qquad (3)$$

For Zn(II) ion, the deprotonation of ZnH_2ttda^{2+} *occurs after four equivalents of base are added and* two additional equilibria can be seen from the titration curve (equations 4 and 5) and the corresponding chelate protonation constants, $K^H_{MH_2L}$ and K^H_{MHL}, can be determined easily.

$$MH_2ttda^{2+} \xrightleftharpoons{K^H_{MH_2L}} MHttda^+ + H^+ \qquad (4)$$

$$MHttda^+ \xrightleftharpoons{K^H_{MHL}} Mttda + H^+ \qquad (5)$$

In the case of Ni^{2+} and Cu^{2+} ions, the three equilibria (Eqs. (3)–(5)) overlap with one another, therefore, the two chelate protonation constants (Eqs. 4 and 5) are determined by carefully selecting data points with $\bar{n}$ values less than 1.500. In doing this, log $K^H_{MH_2L}$ and log K^H_{MHL} values can be determined with standard deviations less than 0.05 or better. After the values of $K^H_{MH_2L}$ and K^H_{MHL} are known, the calculation of stability constant of complex formation, K^M_{ML} (Eq. (6)), is straightforward.[6]

$$M^{2+} + ttda^{2-} \xrightleftharpoons{K^M_{ML}} Mttda \qquad (6)$$

Table II lists the logarithms of values of $K^H_{MH_2L}$, K^H_{MHL} and additional formation constants $K^M_{MH_2L}$ and K^M_{MHL} defined by Eqs. (7) and (8),

$$M^{2+} + H_2ttda \xrightleftharpoons{K^M_{MH_2L}} MH_2ttda^{2+} \qquad (7)$$

$$M^{2+} + Httda \xrightleftharpoons{K^M_{MHL}} MHttda^+ \qquad (8)$$

Table III lists the log K^M_{ML} values of Mttda complexes and other ligands of interest.

Stability of Metal-ttda Chelates

As one can see, metal-ttda chelates have formation constants comparable to those of metal-edta and penten complexes. The factors contributing to the stability have not been studied yet. However, there is much information from earlier studies of thermo-

TABLE III
Formation constants of some ligands of interest;[8]
$\mu = 0.10(KNO_3)$, $T = 25°C$

log K^M_{ML} L =	edta	ttda	trien	penten
Ni^{2+}	18.52	19.95 ± 0.15	13.8	19.10
Cu^{2+}	18.70	21.78 ± 0.02	20.1	22.10
Zn^{2+}	16.44	19.13 ± 0.22	12.03	16.06

TABLE II
Metal-ttda protonation and formation constants; $\mu = 0.10(KNO_3)$, $T = 25°C$

	log $K^H_{MH_2L}$	log K^H_{MHL}	log $K^M_{MH_2L}$	log K^M_{MHL}	log K^M_{ML}
Ni^{2+}	3.88 ± 0.03	6.16 ± 0.02	9.59	15.57	19.95 ± 0.15
Cu^{2+}	3.45 ± 0.05	4.79 ± 0.04	9.62	16.03	21.78 ± 0.02
Zn^{2+}	4.62 ± 0.01	5.53 ± 0.01	8.88	14.12	19.13 ± 0.22

TABLE IV
Thermodynamic data for the formation of edta, ttda, trien, and penten with Ni(II), Cu(II) and Zn(II);[7,8] $\mu = 0.10$, $T = 25°C$

	$\Delta G°$ (Kcal mole^{-1})			$\Delta H°$ (Kcal mole^{-1})			$\Delta S°$ (eu)		
	Ni(II)	Cu(II)	Zn(II)	Ni(II)	Cu(II)	Zn(II)	Ni(II)	Cu(II)	Zn(II)
edta	−25.18	−25.43	−22.36	−8.40	−8.70	−5.60	57.3	56.0	56.0
ttda	−27.21	−29.70	−26.09	—	—	—	—	—	—
trien	−18.8	−27.4	−16.4	−14.00	−21.55	−8.90	16.0	19.5	25.0
penten	−26.06	−30.16	−21.59	−19.65	−24.50	−14.50	21.5	19.0	25.0

dynamic parameters of complex formation.[7,8] These results can be utilized to provide some rationalizations. In Table IV are listed thermodynamic parameters of complex formation of Ni(II), Cu(II) and Zn(II) with ligands edta^{4-}, trien, and penten.

As seen from Table IV, the entropy factor dominates the stabilities of edta complexes and the enthalpy factor dominates the stabilities of polyamine complexes. It is probably true that for the first row transition metal ions, the entropy of complex formation is largely dependent upon the ligand itself, the size of the metal ion, and particularly the neutralization of charge. The enthalpy factor is largely dependent upon the nature of the ligand atom (N or O). Based on these, the thermodynamic parameters of complex formation of Ni(II), Cu(II), and Zn(II) with ttda^{2-} might not be difficult to estimate. Examining the ligand structure, we know edta^{4-}, ttda^{2-}, and penten all have an ethylenediamine backbone with different number of acetate and aminoethyl arms attached to the end nitrogens. Edta^{4-} has four acetate arms and penten has four aminoethyl arms with ttda^{2-} in between of the two which has two of each. It has been shown by NMR technique in aqueous solution[10] that if pH is high enough, the structure of Niedta^{2-} is predominantly octahedral with each of the six donor atoms of edta^{4-} occupying one binding site. This is different from the solid state structure in which the ligand is quinquedentate-chelated to the metal ion with one free equatorial acetate arm because of the chelate ring strain. The sixth coordination site is occupied by a water molecule.[10] Since the two aminoethyl arms replacing acetate arms of edta^{4-} should be less strained, ttda^{2-} provides a better octahedral environment in aqueous solution than edta^{4-} does. Therefore it is reasonable to assume that the structure of M(II)-ttda complex has predominantly an octahedral structure in aqueous solution.

Substitution of a carboxylate oxygen for a water molecule contributes little to the enthalpy of formation of transition metal complexes. We expect the $\Delta H°$ of the complexes of ttda^{2-} to be higher than those edta^{4-} and comparable to those of trien, which is also a 4 N donor. Because of the neutralization of charge on complex formation, the $\Delta S°$ values should be high, as in the case of edta^{4-} complexes compared to those of trien. Since Cu^{2+} has a greater preference for N donors than do Ni^{2+} and Zn^{2+}, the only complex of those considered which is more stable than the ttda^{2-} complex is Cu(penten)$^{2+}$ where the ligand provides six N donors.

In summary, among the three metal-ttda complexes, Cuttda with the greatest enthalpy contribution turns out to be the most thermodynamically stable complex. The zinc complex, Znttda, with less enthalpy contribution is the least stable complex. Nevertheless, comparing the complex formation of these metal ions with edta^{4-}, and penten, ttda^{2-} is the ligand which by far forms the most thermodynamically stable complexes for both Ni(II) and Zn(II) ions. This is in agreement with our early expectations. Presumably Cuttda is a little less stable than Cupenten because the gain in entropy by substituting two acetate groups for aminoethyl groups cannot compensate the concomitant enthalpy loss.

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