

greatly reduced (e.g. dimethyl sulfoxide ( $\log K_1 = 1.04$ )<sup>27</sup> or carbon monoxide (no reaction observed)).<sup>28</sup> The relatively low equilibrium constants observed for good  $\pi$ -acceptor ligands such as  $P(OPh)_3$  and CO indicate that the contribution of  $\pi$ -back-bonding interactions to the stability of the Rh-L bond is relatively insignificant. These findings are consistent with theoretical and experimental indications of a lack of  $\pi$ -stabilization in dirhodium(II) tetraacetate complexes.<sup>24-26</sup> Drago and co-workers, however, have observed that the properties of dirhodium(II) butyrate<sup>14</sup> and perfluorobutyrate<sup>15</sup> complexes with axial  $\pi$ -acceptor ligands cannot be interpreted on the basis of  $\sigma$  contributions alone and must include some metal-to-ligand  $\pi$ -back-bonding interactions. The presence of  $\pi$  interactions has also been observed to a certain extent in dirhodium(II) complexes in which the bridging acetates have been replaced by more electron-donating ligands such as the acetamide anion.<sup>27,28</sup> For the complexes in this study there appear to be no significant steric effects on the stability of the phosphine

adducts or on the rates of their formation. The trend in the cone angles,<sup>29</sup>  $PPh_3$  ( $150^\circ$ ) >  $AsPh_3$  ( $147^\circ$ ) >  $P(CH_2CH_2CN)_3$  ( $137^\circ$ ) >  $P(OPh)_3$  ( $133^\circ$ ) >  $P(OCH_3)_3$  ( $112^\circ$ ), is not reflected in the orders of  $k_1$  or  $K_1$ .

The results of the present study indicated that axial-ligand substitution on  $Rh_2(O_2CCH_3)_4(CH_3CN)_2$  proceeds by a dissociative (D) mechanism. The relative stability constants of the phosphine and phosphite adducts may be rationalized on the basis of their  $\sigma$ -donor abilities, with  $\pi$ -back-bonding of only minor importance. The kinetics of the axial-solvent substitution in aqueous media suggest that the process may involve an interchange dissociative ( $I_d$ ) mechanism, and further studies on the kinetics of axial substitution by water-soluble phosphines are in progress to clarify the mechanism.

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## Equilibrium and Thermodynamic Study of the Aqueous Complexation of 1,4,7-Triazacyclononane- $N,N',N''$ -triacetic Acid with Protons, Alkaline-Earth-Metal Cations, and Copper(II)

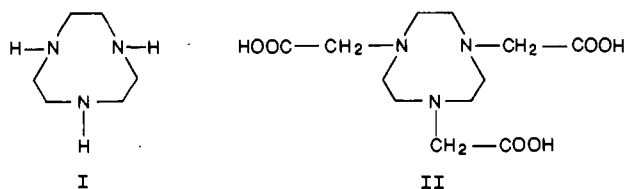
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pH potentiometric titrations are employed to estimate temperature-dependent equilibrium constants for reactions of the amino acid 1,4,7-triazacyclononane- $N,N',N''$ -triacetic acid ( $H_3T$ ) with  $H^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ , and  $Ba^{2+}$ . Additionally, reactions of  $H_3T$  with  $Cu^{2+}$  are studied by both pH potentiometry and spectrophotometry. The equilibrium constant data serve to calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  for the various reactions via a van't Hoff analysis. Interpretation of the thermodynamic data leads to several conclusions: (1) First and second protonation reactions of  $T^{3-}$  seem localized to nitrogen sites while addition of a third and fourth proton involve carboxylate groups. (2)  $Mg^{2+}$  complexation of  $T^{3-}$  is distinct from that of the other alkaline-earth-metal ions studied. It appears that  $T^{3-}$  forms only four or five bonds with  $Mg^{2+}$  whereas the congener ions likely form six bonds.  $Mg^{2+}$  is however the most stable of the group IIA (group 2<sup>3+</sup>) metal complexes apparently because of the formation of fewer but stronger metal to ligand bonds. (3)  $Cu^{2+}$  forms an unusually stable 1:1 complex with  $T^{3-}$ . The protonated form of the complex is dominant in the pH range from 0 to 2.7. The stability and properties of alkaline-earth-metal and  $Cu^{2+}$  complexes with  $T^{3-}$  are discussed and compared to those of other polyamino polycarboxylic acids in the light of the available thermodynamic, spectroscopic, and X-ray crystallographic data.

Complexation reactions of metal ions with macrocyclic polyamine ligands have been subjects of numerous investigations in recent years. These complexes have unusual stability, structural, spectroscopic, and magnetic properties. Additionally, some of the macrocycles are found to form kinetically inert complexes compared with their noncyclic analogues. As an example a number of unusual complexation properties of 1,4,7-triazacyclononane (I), abbreviated as [9]ane $N_3$ , have been reported by several workers.<sup>1-4</sup>

The synthesis of a triacetic acid derivative of [9]ane $N_3$ , 1,4,7-triazacyclononane- $N,N',N''$ -triacetic acid, was first reported by Takamoto and coworkers in 1973.<sup>5</sup> This compound (II), abbreviated here by the symbol  $H_3T$ , appears to share some of the macrocyclic complexing properties of the parent compound.<sup>6</sup> In particular, complexes with divalent metal ions have unusual stability in spite of a highly strained coordination geometry.<sup>7,8</sup>



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**Table I.** Temperature-Dependent  $pK_a$  Values of  $H_3T$  and Their Uncertainties

$t, ^\circ C$	$H_4T^+ = H_3T + H^+$	STD, <sup>b</sup> mL	$H_3T + H_2T^- + H^+$	$H_2T^- = HT^{2-} + H^+$	$HT^- = T^{3-} + H^+$	STD, mL
Ionic Strength = 1.0 M <sup>c</sup>						
15	1.893 ± 0.003	0.002	3.122 ± 0.003	6.115 ± 0.003	11.092 ± 0.004	0.028
25	1.955 ± 0.003	0.003	3.163 ± 0.003	6.032 ± 0.004	10.773 ± 0.007	0.019
35	2.015 ± 0.012	0.012	3.185 ± 0.003	5.926 ± 0.003	10.535 ± 0.007	0.027
45	2.052 ± 0.004	0.004	3.208 ± 0.008	5.832 ± 0.006	10.192 ± 0.006	0.031
55	1.978 ± 0.004	0.004	3.245 ± 0.004	5.765 ± 0.005	10.115 ± 0.007	0.028
Ionic Strength = 0.1 M <sup>c</sup>						
15			3.081 ± 0.006	5.762 ± 0.006	11.878 ± 0.017	0.021
25			3.160 ± 0.004	5.742 ± 0.005	11.730 ± 0.017	0.018
35			3.165 ± 0.004	5.671 ± 0.004	11.581 ± 0.018	0.015
45			3.198 ± 0.003	5.627 ± 0.004	11.184 ± 0.012	0.012
55			3.229 ± 0.002	5.578 ± 0.004	10.859 ± 0.008	0.009

<sup>a</sup> Background electrolyte 1.0 M NaClO<sub>4</sub>. <sup>b</sup> Rms value of differences between calculated and experimental volume data expressed in milliliters of titrant. Typical titration volumes were 2–5 mL. <sup>c</sup> Background electrolyte 0.10 M NaNO<sub>3</sub>.

Thus, a detailed study of the complexation properties of  $H_3T$  should provide some information about the steric, bonding, and solvation factors relevant to macrocyclic complexation reactions. In this connection we now report a thermodynamic study of  $H_3T$  acid–base and complexation properties with Mg(II), Ca(II), Ba(II), Sr(II), and Cu(II). Our purpose is to characterize the reactions of  $H_3T$  in terms of the enthalpy and entropy changes, which may then be interpreted in terms of bonding, structural strain, and solvation. In order to obtain the necessary data we made pH potentiometric titration experiments to determine temperature dependent equilibrium constants whose analysis provides estimates of the thermodynamic functions. The pH potentiometric experiments were not suited to formation constant determination for the strong complex with Cu(II), and a spectrophotometric method was employed instead. We begin with a description of experimental procedures and data analysis methods.

### Experimental Section

**Materials.** All reagents and solvents were reagent grade and were used without further purification. Metal ion solutions were prepared directly from the nitrate or perchlorate salts and were standardized by complexometric titrations with commercial 0.1000 M Na<sub>2</sub>H<sub>2</sub>EDTA reagent by standard methods.<sup>9</sup>

**1,4,7-Triazacyclononane**, [9]aneN<sub>3</sub>, was prepared according to the method of Richman and Atkins.<sup>10</sup> The crude product was recrystallized as the trihydrochloride salt and used without further purification.

**1,4,7-Triazacyclononane-*N,N,N'*-triacetic acid**,  $H_3T$ , was prepared according to the method of Takahashi and Takamoto.<sup>5</sup> [9]aneN<sub>3</sub>·3HCl (2.64 g, 11.2 mmol), chloroacetic acid (3.31 g, 35 mmol), and LiOH·0.5H<sub>2</sub>O (3.2 g, 75 mmol) were dissolved in 30 mL of water and maintained at 45 °C for 7 h. The pH was maintained near 10 ± 0.5 by intermittent addition of small portions of solid LiOH·0.5H<sub>2</sub>O. Addition of 12 M HCl adjusted the solution to pH 2.8. After evaporation, a clear yellow oil was taken up with a minimum of hot ethanol, and slow cooling to 0 °C yielded a white hygroscopic product. This product was recrystallized from a minimum of hot water, affording colorless hexagonal plates of the acid. Weighed portions of the product were titrated with NaOH. Two sharp endpoints were obtained corresponding to  $a = 1$  mol of NaOH/mol of  $H_3T$  and  $a = 2$  mol of NaOH/mol of  $H_3T$ . At times this method produced a product that consisted of a mixture of  $H_3T$  and its HCl salt,  $H_4TCl$ . In order to avoid this complication in later work, ligand samples of well-defined stoichiometry were prepared by the method below.

**Lithium Dihydrogen 1,4,7-Triazacyclononane-*N,N,N'*-triacetate Dihydrate.** The synthesis procedure above was repeated with the reaction mixture carefully acidified to a pH near 3.5. Cooling gave the monolithium salt, LiH<sub>2</sub>T·2H<sub>2</sub>O. NaOH titration of air-dried samples of the product yielded equivalent weight values always less than 1% different from the value of 345 calculated for C<sub>12</sub>H<sub>20</sub>N<sub>3</sub>O<sub>6</sub>Li·2H<sub>2</sub>O. KBr pellet preparations of this material showed IR absorption at 1640 cm<sup>-1</sup>, which we ascribe to the presence of carboxylate groups. However absorption

peaks near 1700 cm<sup>-1</sup>, which corresponded to protonated carboxylic acid groups and were present in the earlier preparation, were absent from the LiH<sub>2</sub>T·2H<sub>2</sub>O spectrum. Anal. Calcd for C<sub>12</sub>H<sub>24</sub>N<sub>3</sub>O<sub>6</sub>Li: C, 47.07; H, 7.01; N, 13.72. Found: C, 46.68, H, 7.13, N, 13.45. <sup>1</sup>H NMR (D<sub>2</sub>O) showed singlets at 3.34 (12 H) and 3.78 ppm (6 H). Solutions of the ligand were generally prepared from weighed samples of the monolithium salt but were nonetheless standardized by pH potentiometric titration with NaOH.

### pH Potentiometric Titrations

Our experimental method for determining temperature-dependent complexation constants of T<sup>3-</sup> with metal ions consists of NaOH titrations with solutions composed by metal salts and equivalent amounts of complexing agent added as LiH<sub>2</sub>T or  $H_3T$  solutions. We employ supporting electrolyte media of 0.10 M NaNO<sub>3</sub> or 1.0 M NaClO<sub>4</sub> in these experiments. In order to assure conditions of essentially constant ionic strength during titration we employ a 0.100 M NaOH titrant with the  $I = 0.10$  M analyte solutions or a 0.100 M NaOH, 0.90 M NaClO<sub>4</sub> titrant with the  $I = 1.0$  M solutions. These experiments provide pH vs. volume of titrant data whose appropriate analysis yield metal, T<sup>3-</sup> complexation constants. In order to make this analysis we first require independent and precise estimates of  $H_3T$  acidity constants under the same conditions of ionic strength and temperature to be employed in complexation experiments.

**Determination of  $H_3T$  Acidity Constants.** Acidity constants defined by eq 1 ( $n = 1-3$ ) were determined from a series of pH potentiometric titration experiments.  $H_3T$  solutions, typically

$$K_{a_n} = \frac{[H^+][H_{3-n}T^{n-}]}{[H_{2-n}T^{1-n}]} \quad (1)$$

2–5 nM, were made up in either 0.10 M NaNO<sub>3</sub> or 1.0 M NaClO<sub>4</sub> and titrated with appropriate 0.10 M NaOH reagent solutions. pH vs. volume of titrant data were obtained during addition of approximately 30 portions of titrant to the analyte solution maintained under a nitrogen atmosphere in a thermostated cell. Titrations were always continued beyond  $a = 3$  mol of NaOH/mol of  $H_3T$ . An Orion Model 801 pH meter was calibrated at each measurement temperature by previously described methods.<sup>11,12</sup> The calibration allowed direct interpretation of pH data in terms of H<sup>+</sup> concentration. Values of temperature-dependent  $K_w' = [H^+][OH^-]$ , also required for analysis of the titration data, were obtained from additional measurements with dilute NaOH solutions in 0.10 M NaNO<sub>3</sub> and 1.0 M NaClO<sub>4</sub> media.

Corrected pH vs. volume of titrant data along with  $pK_w'$  estimates were analyzed with the aid of the program SCOGS<sup>13</sup> suitably adapted to a local Control Data Corp. Cyber facility. In order to use the program  $H_3T$  was modeled as a triprotic acid with acidity constants defined above. However, these equations do not

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Table II.  $\Delta H$  and  $\Delta S$  Values for Protonation of  $T^{3-}$  and Related Compounds

base	reaction	$\Delta H^\circ$ , kcal mol <sup>-1</sup>	$\Delta S^\circ$ , cal mol <sup>-1</sup> K <sup>-1</sup>
	$B^{3-} + H^+ = BH^{2-}$	-7.29	21.0
	$BH^{2-} + H^+ = BH_2^-$	-2.83	15.1
	$BH^- + H^+ = BH_3$	+0.34	12.1
	$B^{3-} + H^+ = BH^{2-}$	-6.65	22.5
	$B^{2-} + H^+ = BH_2^-$	-3.09	14.2
	$BH_2^- + H^+ = BH_3$	+1.12	15.8
[9]aneN <sub>3</sub> <sup>b</sup>	$B + H^+ = BH^+$	-10.4 ± 0.1	13.0 ± 0.2
	$BH^+ + H^+ = BH_2^{2+}$	-9.9 ± 0.1	-2.1 ± 0.3

base	reaction	$\Delta H^\circ$ , kcal mol <sup>-1</sup>		$\Delta S^\circ$ , cal mol <sup>-1</sup> K <sup>-1</sup>	
		<i>I</i> = 0.10 M	<i>I</i> = 1.0 M	<i>I</i> = 0.10 M	<i>I</i> = 1.0 M
$T^{3-c}$	$T^{3-} + H^+ = HT^{2-}$	-11.1 ± 1.6	-11.0 ± 0.9	16.3 ± 5.3	12.4 ± 2.9
	$HT^{2-} + H^+ = H_2T^-$	-2.1 ± 0.2	-3.9 ± 0.1	19.2 ± 0.6	14.5 ± 0.4
	$H_2T^- + H^+ = H_3T$	-1.4 ± 0.2	-1.3 ± 0.1	19.2 ± 0.8	18.7 ± 0.3
	$H_3T + H^+ = H_4T^+$		+1.2 ± 0.6		12.9 ± 2.1

<sup>a</sup>Reference 18. *I* = 0.10 M. <sup>b</sup>Reference 19. *I* = 0.10 M. <sup>c</sup>This work. Uncertainties represent standard error estimates.

account for possible protonation of  $H_3T$  to form  $H_4T^+$  solution species, defined by eq 2. Hancock and co-workers<sup>8</sup> have estimated

$$K_{a-1} = \frac{[H^+][H_3T]}{[H_4T^+]} \quad (2)$$

$pK_{a-1} = 1.7$  at 25 °C in *I* = 0.1 M media. In order to avoid the complication represented by  $H_4T^+$  formation, our analysis was restricted to data with pH > 3.4 where the concentration of this species could be neglected. The results of our calculations appear in Table I. The data analysis program provides standard error estimates for each calculated acidity constant, and these values appear below the  $pK$  entries. As an additional output the program calculates the "residual in titer", which corresponds to the difference between calculated and experimental titrant volumes. The values of these point by point residuals seemed to be randomly scattered and were comparable to our a priori estimate of ±0.010 mL buret precision. The magnitude of titer residuals is reflected by the rms value entered in Table I and labeled STD.

Multiple entries at a given temperature correspond to replicate titrations made with different  $H_3T$  or  $LiH_2T$  preparations and employment of different electrodes. However, the third entry at 25 °C corresponds to averages and standard errors derived from a total of five different titration experiments. These 25 °C values are compared to those reported by Hancock and co-workers,<sup>8</sup> which are 3.16, 5.74, and 11.41 for  $pK_{a1}$ ,  $pK_{a2}$ , and  $pK_{a3}$ , respectively, for  $H_3T$ . While values of  $pK_{a1}$  and  $pK_{a2}$  seem to be in agreement, the earlier  $pK_{a3}$  value is sufficiently different from the present results to warrant some further investigation. A pH potentiometric technique reported elsewhere<sup>2c</sup> provided an independent estimate of the discrepant  $pK_{a3}$  value. Briefly, this method relies on a comparison between a titration of the weak acid  $HT^{2-}$  with NaOH and a second blank titration of the supporting electrolyte with NaOH. The blank titration provides a working curve of pH vs.  $[OH^-]$  in the appropriate pH region and does not rely on a linear glass electrode response. The experimental working curve along with appropriate mass and charge balance equations allows estimation of species concentrations which in turn provide  $pK_{a3}$  values. The results of such experiments provided values of  $11.78 \pm 0.11$  (five determinations). These results are interpreted as confirming the data in Table I, which values will be used in subsequent calculations. In addition to these acidity constants estimates of  $H_3T$  protonation constants ( $pK_{a-1}$ ) defined by eq 2 are also required. Temperature-dependent  $pK_{a-1}$  values were determined by NaOH titration of ~10 mM  $H_3T$  solutions in 1.0 M  $NaClO_4$  previously treated with  $HClO_4$ . SCOGS analysis of the titration data yields both  $pK_{a1}$  and  $pK_{a-1}$  values.  $pK_{a1}$  values obtained in this way always agreed with the earlier values to within ±0.02 log units.  $pK_{a-1}$  results appear in Table I.

Data in Table I serve as a basis for estimating  $\Delta H^\circ$  and  $\Delta S^\circ$ , the enthalpy and entropy changes, respectively, for  $H_3T$  acidic

dissociation and protonation reactions. ( $\Delta H^\circ$  and  $\Delta S^\circ$  do not represent standard values of these parameters in the usual sense but relate to 0.10 M  $NaNO_3$  or 1.0 M  $NaClO_4$  electrolyte media as the standard-state solvents.) A least-squares regression analysis of  $R \ln K$  vs. *T* has slope and intercept related to the values of the thermodynamic parameters. The plots were linear and points scattered in an apparently random fashion about the regression lines.  $\Delta H^\circ$  and  $\Delta S^\circ$  values along with derived standard error estimates are compared with corresponding data for related compounds in Table II. Discussion of these data are deferred to a later section, and metal ion complexation studies are now described.

**Determination of Complexation Constants.** NaOH titrations of solutions containing 1.0–8.0 mM Ca(II), Sr(II), or Ba(II) and equivalent or excess  $H_3T$  provided pH vs. volume of titrant data for analysis via the program SCOGS. The same pH calibration and correction techniques as described earlier were employed. The results of these calculations indicate that both Ca(II) and Sr(II) form appreciable concentrations of protonated complex species  $H[CaT]$  and  $H[SrT]$ . That is, the pH vs. composition data could not be adequately fit to model equations accounting for only  $CaT^-$  and  $SrT^-$  complexes. Residuals were unacceptably large and showed systematic trends. However, when protonated complex species were included in the model equations the resulting computer output indicated an apparently random pattern of residuals in titer whose rms value was comparable to our a priori estimate of ±0.010 mL buret precision. Temperature-dependent calcium and strontium complexation constants and their uncertainties appear in Table III.

Titration data with barium mixtures could be adequately fit with model equations accounting for  $BaT^-$  as the only complex species. We repeated these calculations allowing for the formation of a protonated barium complex, but the improvement in fit between calculated and experimental data as reflected by the rms value of residuals in titer could not be regarded as significant. We conclude that protonated  $BaT^-$  complexes play no significant role in the present experiments if such complexes exist at all.

Titrations with magnesium solutions did not give stable pH readings even after several hours. Consequently, we abandoned a direct titration procedure and employed an "out-of-cell" titration technique as follows. Portions of a single stock solution containing equimolar quantities of  $H_3T$  and  $Mg^{2+}$  along with an amount of NaOH corresponding to "titration" points between *a* = 0 and *a* = 3 mol of NaOH/mol of  $H_3T$  and an appropriate amount of  $NaNO_3$  were diluted in volumetric flasks and equilibrated for 1–2 days at each measurement temperature. pH values were then recorded along with meter calibrations. Each of the approximately 10 measurement solutions was returned to the storage flask after measurement and the procedure repeated daily. Consecutive pH readings identical within ±0.004 pH unit were taken as equilibrium

**Table III.** Temperature-Dependent Formation Constants and Acidic Dissociation Constants of  $T^{3-}$  Complexes with Group IIA Cations

<i>t</i> , °C	log <i>K</i> for $M^{2+} + T^{3-} = MT^{-}$			
	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
15		9.01 ± 0.01 <sup>a</sup> (0.003) <sup>b</sup>	6.88 ± 0.01 (0.005)	5.12 ± 0.01 (0.003)
25	9.69 ± 0.03 (0.02)	8.92 ± 0.01 (0.003)	6.83 ± 0.01 (0.004)	5.10 ± 0.01 (0.001)
35	9.66 ± 0.03 (0.02)	8.74 ± 0.01 (0.003)	6.76 ± 0.01 (0.005)	5.06 ± 0.01 (0.001)
45	9.64 ± 0.02 (0.01)	8.61 ± 0.01 (0.003)	6.75 ± 0.01 (0.006)	5.02 ± 0.01 (0.003)
55	9.73 ± 0.02 (0.01)	8.49 ± 0.01 (0.002)	6.68 ± 0.01 (0.004)	5.00 ± 0.01 (0.001)

<i>t</i> , °C	-log <i>K</i> for $MHT = MT^{-} + H^{+}$		
	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>
15		4.92 ± 0.06	6.3 ± 0.2
25	4.6 ± 0.2 <sup>a,c</sup>	5.06 ± 0.03	6.1 ± 0.1
35	4.4 ± 0.3	5.17 ± 0.05	6.0 ± 0.1
45	4.4 ± 0.2	4.93 ± 0.03	6.1 ± 0.1
55	4.1 ± 0.2	4.88 ± 0.03	5.9 ± 0.1

<sup>a</sup>Uncertainties represent standard error estimates derived from program SCOGS. These estimates account for statistical uncertainties in  $pK_a$  values used as input parameters in the data analysis and are derived by standard propagation-of-variance methods. <sup>b</sup>Parentetical entries represent rms fits in titer in milliliters and are to be compared with typical titration volumes of 1.5–3 mL. <sup>c</sup>Rms titer fit are the same as those for corresponding entries above.

values, which were generally achieved within 3–4 days after solution preparation. Our pH calibration measurements varied by about ±0.004 pH unit during the period of the experiment. The corrected pH vs. composition data obtained in this way were analyzed with SCOGS and the resultant equilibrium constant data appear in Table III. We make no estimate of Mg(II) complexation constants at 15 °C. Equilibrium at this temperature was sufficiently slow to make it difficult to distinguish between slow pH drift and random fluctuations and so we abandoned these experiments. However, Mg(II) complexation constants at 25 °C reported here ( $\log K_{MgT} = 9.69$  and  $\log K_{H[MgT]} = 14.2$ ) are significantly at variance with the estimate of  $\log K_{MgT}$  of 8.93 given in ref 8. It appears that the discrepant values result from inadequate equilibration times in the earlier experiments, which were carried out on a time scale of minutes. The present results indicate a need for much longer equilibration times. As a confirmation to the experiments above, several of the titrations with solutions containing excess amounts of  $H_3T$  were repeated. In each case calculated equilibrium constants were essentially identical with previously obtained values and residuals in titer were always randomly scattered and acceptably small. We infer that only 1:1 metal/ligand stoichiometries are present in these solutions. The 25 °C complexation constant for Ca(II) with  $T^{3-}$  obtained here

( $\log K_{CaT} = 8.92$ ) seems in reasonable agreement with an earlier estimate of 8.81.<sup>8</sup>

Equilibrium constant data in Table III allow estimation of  $\Delta H^\circ$  and  $\Delta S^\circ$  for a variety of complexation reactions via van't Hoff analysis. The results of the least-squares estimates along with standard error estimates appear in Table IV.

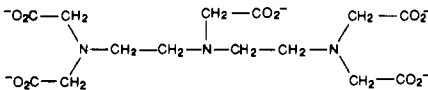
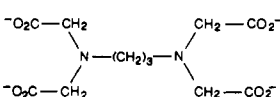
Attempts were made to extend our pH potentiometric titration experiments to include  $T^{3-}$  complexation of Cu(II). However, examination of the titration data indicated that Cu(II) complexes with  $T^{3-}$  were essentially completely formed even at the lowest pH region of the experiment. That is, the initial branch of the titration curve observed with 1:1 Cu(II) mixtures with  $H_3T$  were superimposable with curves resulting from titration of strong acids with concentration of 2 mol of  $H^+$ /mol of Cu(II). This leads to a conclusion that the reaction  $Cu^{2+} + H_3T = H[CuT] + 2H^+$  is essentially complete even at pH values near 2.0. The titration curve deviates significantly from that of a strong acid in the region from  $a = 2$  to  $a = 3$  mol of NaOH/mol of  $H_3T$ , and this behavior is interpreted as resulting from the acid/base equilibrium dissociation of the weak acid  $H[CuT]$ . Data corresponding to this region of the titration curve in  $I = 1.0$  M  $NaClO_4$  medium allowed estimation of the acidic dissociation constant for  $H[CuT]$  by means of the calculational procedures above. The 25 °C value for this acidity constant is included in Table VI.

Two sets of spectrophotometric experiments with  $CuT^{-}$  solutions are now described. The first of these estimates  $H[CuT]$  acidity constants while the second provides values for  $CuT^{-}$  formation constants.

### Spectrophotometric Experiments

$Cu^{2+}$ ,  $H[CuT]$ , and  $CuT^{-}$  solution species exhibit markedly different spectra in the wavelength region between 600 and 800 nm. Consequently, absorbance vs. composition data may lead to estimates of  $H[CuT]$  acidity constants and  $CuT^{-}$  formation constants. In order to obtain values for the first of these we made spectrophotometric titration experiments in which ~4 mM  $CuT^{-}$  solutions ( $I = 1.0$  M) initially neutralized to pH ~6 were titrated with  $HClO_4$  made up to  $I = 1.0$  M with  $NaClO_4$ . An approximately 25-mL portion of the  $CuT^{-}$  solution was contained in a thermostated vessel connected to a separately thermostated cuvet via a flow-through arrangement. A Cary 14 spectrophotometer recorded the spectrum between 600 and 800 nm after each of about eight additions of acid with the final solution pH near 2.0. Results obtained during a typical experiment appear in Figure 1. We interpret the appearance of a single isosbestic point near 720 nm as confirming the presence of only two complex species in the pH range of these experiments, namely  $CuT^{-}$  and  $H[CuT]$ . Composition vs. absorbance data at several wavelengths were analyzed by using the program SQUAD,<sup>14</sup> which provided the

**Table IV.**  $\Delta H^\circ$  and  $\Delta S^\circ$  Values for Complexation Reactions of  $T^{3-}$  and Model Amino Acid Ligands with Group IIA Cations at an Ionic Strength of 0.1 M

ligand	Mg <sup>2+</sup>		Ca <sup>2+</sup>		Sr <sup>2+</sup>		Ba <sup>2+</sup>	
	$\Delta H^\circ$ , kcal mol <sup>-1</sup>	$\Delta S^\circ$ , cal mol <sup>-1</sup> K <sup>-1</sup>	$\Delta H^\circ$ , kcal mol <sup>-1</sup>	$\Delta S^\circ$ , cal mol <sup>-1</sup> K <sup>-1</sup>	$\Delta H^\circ$ , kcal mol <sup>-1</sup>	$\Delta S^\circ$ , cal mol <sup>-1</sup> K <sup>-1</sup>	$\Delta H^\circ$ , kcal mol <sup>-1</sup>	$\Delta S^\circ$ , cal mol <sup>-1</sup> K <sup>-1</sup>
$T^{3-}$ <sup>a</sup>	+0.4 ± 0.9	45 ± 3	-5.9 ± 0.3	21 ± 1	-2.1 ± 0.3	24 ± 1	-1.38 ± 0.11	18.6 ± 0.4
EDTA <sup>4-</sup> <sup>b</sup>	3.49	51	-6.55	27	-4.08	26	-4.93	19
	3.6	54	-6.1	29	-7.5	19	-7.3	14
DTPA <sup>5-</sup> <sup>c</sup>								
	9.09	59	-1.74	27				
TMDTA <sup>4-</sup> <sup>d</sup>								

<sup>a</sup>This work. <sup>b</sup>Reference 20. <sup>c</sup>Reference 21. <sup>d</sup>Reference 22.

**Table V.**  $\Delta H^\circ$  and  $\Delta S^\circ$  for Acidic Dissociation Reactions of H[MgT], H[CaT], and H[SrT] Complexes and Corresponding Data for Metal-EDTA Complexes

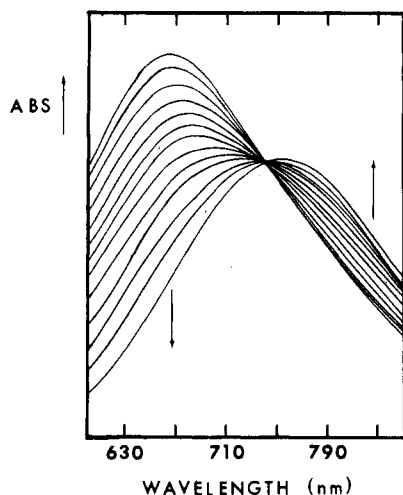
reaction	M <sup>2+</sup>	$\Delta H^\circ$ , kcal mol <sup>-1</sup>	$\Delta S^\circ$ , cal mol <sup>-1</sup> K <sup>-1</sup>
H[MT] = H <sup>+</sup> + MT <sup>-</sup>	Mg <sup>2+</sup>	7.7 ± 2.1 <sup>a</sup>	5 ± 6 <sup>a</sup>
	Ca <sup>2+</sup>	0.8 ± 1.8	-20 ± 6
	Sr <sup>2+</sup>	4.1 ± 1.2	-14 ± 4
H[M(EDTA)] <sup>-</sup> = H <sup>+</sup> + M(EDTA) <sup>2-</sup> <sup>b</sup>	Mn <sup>2+</sup>	1.2 ± 0.3	-10 ± 2
	Co <sup>2+</sup>	1.9 ± 0.3	-7 ± 2
	Ni <sup>2+</sup>	1.8 ± 0.3	-9 ± 3
	Zn <sup>2+</sup>	2.2 ± 0.3	-6 ± 3
	Cd <sup>2+</sup>	0.4 ± 0.3	-12 ± 3

<sup>a</sup>Uncertainties represent standard error estimates derived from uncertainties in slopes of least-squares van't Hoff lines. <sup>b</sup>Reference 16.

**Table VI.** Temperature-Dependent Conditional  $pK_a$  Values for H[CuT] Proton Dissociation at Various Temperatures

<i>t</i> , °C	$pK_a$	<i>t</i> , °C	$pK_a$
15	2.73 ± 0.03 <sup>a</sup>	35	2.72 ± 0.01
25	2.77 ± 0.02	45	2.68 ± 0.01
25	2.71 ± 0.04 <sup>b</sup>	55	2.79 ± 0.03

<sup>a</sup>Uncertainties represent standard error estimates and are derived by propagation-of-variance techniques applied to the observed scatter in the absorbance vs. composition data. <sup>b</sup>pH potentiometric value. The standard error estimate is based on a pH uncertainty of ±0.004 pH unit.

**Figure 1.** Plot of absorbance vs. wavelength for CuT<sup>-</sup> solutions at *I* = 1.0 and 25 °C. Arrows indicate change in absorbance with increasing pH. [CuT<sup>-</sup>] ~ 0.005 M, and pH is varied between 2.0 and 3.4.

temperature-dependent H[CuT] acidity constants and their uncertainties listed in Table VI. We note the apparent agreement between pH potentiometric and spectrophotometric  $pK_a$  values at 25 °C (2.71 ± 0.04 and 2.77 ± 0.02, respectively), which seems to confirm the procedures used here. As an additional output of these experiments we obtain 25 °C extinction coefficients for CuT<sup>-</sup> and H[CuT] species, which are 98 ± 1 and 110 ± 1 L mol<sup>-1</sup> cm<sup>-1</sup> at their respective  $\lambda_{max}$  values of 750 and 660 nm. The data analysis also yields values for the rms residual, which corresponds to the rms difference between calculated and observed absorbance values, and these were always less than our ±0.01 *A* a priori precision estimate in these experiments.

In order to obtain CuT<sup>-</sup> formation constants we made a second series of experiments in which six ~4 mM CuT<sup>-</sup> solutions were made up in strongly acidic media between 0.1 M HClO<sub>4</sub> and 0.5 M HClO<sub>4</sub> with *I* = 1.0 M. A Beckman Acta CIII spectrophotometer equipped with a thermostated cell compartment served

**Table VII.** Temperature-Dependent Conditional Formation Constants for CuT<sup>-</sup> and H[CuT] at an Ionic Strength of 1.0 M<sup>a</sup>

<i>t</i> , °C	log <i>K</i>		STD, <sup>b</sup> <i>A</i>
	Cu <sup>2+</sup> + T <sup>3-</sup> = CuT <sup>-</sup>	Cu <sup>2+</sup> + H <sup>+</sup> + T <sup>3-</sup> = H[CuT]	
15	21.97 ± 0.02 <sup>c</sup>	24.70 ± 0.02 <sup>c</sup>	0.002
25	21.63 ± 0.03	24.37 ± 0.03	0.004
35	21.30 ± 0.03	24.04 ± 0.03	0.004
45	21.02 ± 0.03	23.76 ± 0.03	0.004
55	20.73 ± 0.02	23.47 ± 0.02	0.004

<sup>a</sup>Ionic strength of 1.0 M made up with NaClO<sub>4</sub>, HClO<sub>4</sub> mixtures. <sup>b</sup>Entries represent rms scatter of absorbance data and are to be compared with typical absorbance values between 0.3 and 0.5. <sup>c</sup>Standard error estimates derived from program SQUAD. These values do not take account of uncertainties in  $pK_a$  estimates for H<sub>4</sub>T<sup>+</sup> or H[CuT] whose values are input parameters in the data analysis. The  $pK_a$  estimates employed here were always "smoothed" values obtained from least-squares analysis of  $pK_a$  vs. 1/*T* data.

**Table VIII.**  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and 25 °C log *K* Values for Cu<sup>2+</sup> Complexation with Amino Acid Ligands: Acidic Dissociation of the Complexes

ligand, L <sup>n-</sup>	log <i>K</i> at 25 °C	$\Delta H^\circ$ , kcal mol <sup>-1</sup>	$\Delta S^\circ$ , cal mol <sup>-1</sup> K <sup>-1</sup>
Reaction: Cu <sup>2+</sup> + L <sup>n-</sup> = CuL <sup>2-n</sup>			
T <sup>3-a</sup>	21.63 ± 0.02	-13.4 ± 0.8	54 ± 2
EDTA <sup>4-b</sup>	18.9 ± 0.1	-8.2 ± 0.2	59 ± 2
cDOTA <sup>4-c,d</sup>	22.2 ± 0.2	-14.3 ± 0.2	54 ± 0.05
cTRITA <sup>4-c,e</sup>	21.6 ± 0.2	-13.6 ± 0.2	53 ± 0.05
cTETA <sup>4-c,f</sup>	21.6 ± 0.2	-12.9 ± 0.2	56 ± 0.05
Reaction: H[CuL] <sup>3-n</sup> = H <sup>+</sup> + CuL <sup>2-n</sup>			
T <sup>3-a</sup>	-2.74 ± 0.02	0.1 ± 0.6	-13 ± 2
EDTA <sup>4-b</sup>	-3.0 ± 0.1	2.0 ± 0.3	-7 ± 3

<sup>a</sup>This work, *I* = 1.0. log *K* values are smoothed values obtained from van't Hoff plots. Uncertainties represent rms scatter of points around the regression lines. <sup>b</sup>Reference 16, *I* = 0.10. <sup>c</sup>Reference 17, *I* = 0.10. <sup>d</sup>1,4,7,10-Tetraazacyclododecane-*N,N',N'',N'''*-tetraacetate or [12]aneN<sub>4</sub>.<sup>4ac</sup>. <sup>e</sup>1,4,7,10-Tetraazacyclotridecane-*N,N',N'',N'''*-tetraacetate or [13]aneN<sub>4</sub>.<sup>4ac</sup>. <sup>f</sup>1,4,8,11-Tetraazacyclotetradecane-*N,N',N'',N'''*-tetraacetate or [14]aneN<sub>4</sub>.<sup>4ac</sup>.

to make absorbance measurements at four wavelengths between 660 and 750 nm. At each wavelength the absorbance decreased continuously with increasing acidity, corresponding to dissociation of the H[CuT] complex present in these solutions to form the weakly absorbing Cu<sup>2+</sup> ion. Absorbance vs. composition data obtained in this way were analyzed by the program SQUAD with results indicated in Table VII. Also included are the rms values of residuals between calculated and observed absorbances. The values are consistent with our a priori estimate of ±0.004*A*. Moreover, the residuals between calculated and experimental absorbances appeared randomly scattered. We conclude that the behavior of acidic CuT<sup>-</sup> solutions may be adequately described by the protonation and dissociation equilibria detailed above. As one important consequence of this conclusion, we surmise that H<sub>4</sub>T<sup>+</sup> present in these solutions is not further protonated even in 0.5 M HClO<sub>4</sub>. That is, appreciable protonation of H<sub>4</sub>T<sup>+</sup> would result in a systematic discrepancy between calculated and measured absorbances, which was not observed. We have made calculations which indicate that even a 10% protonation of H<sub>4</sub>T<sup>+</sup> to form H<sub>5</sub>T<sup>2+</sup> would have resulted in a clearly detectable trend in the data. Thus, we estimate an upper limit of  $pK_{a,2}$  of -0.6.

Finally, temperature-dependent equilibrium constant data in Table VII along with those listed earlier allow estimation of  $\Delta H^\circ$  and  $\Delta S^\circ$  for various reactions of Cu<sup>2+</sup> with H<sub>3</sub>T species. These are summarized and compared with other Cu<sup>2+</sup>-amino acid complexations in Table VIII.

### Discussion

**Protonation Reactions of T<sup>3-</sup>.** Results of acidity constant calculations given in Table I indicate that T<sup>3-</sup> is capable of reaction with as many as 4 mol of H<sup>+</sup>/mol of T<sup>3-</sup>. We examine the sequence of protonation reactions at nitrogen atom and carboxylate

basic sites and refer to Table II, which compares  $\Delta H^\circ$  and  $\Delta S^\circ$  values for  $T^{3-}$  stepwise protonation with corresponding values for related bases. Each of the model compounds listed features initial protonation at a nitrogen site, and this process is uniformly exothermic and entropy producing. We connect the negative values of  $\Delta H^\circ$  with decreased internal energy in the protonated products compared with the unprotonated base and hydronium ion reactants. That is, formation of strong N-H bonds results in an exothermic protonation reaction.  $\Delta H^\circ$  for  $T^{3-}$  protonation more closely resembles that for [9]ane $N_3$  than that for the model amino acids. This seems to be a consequence of a stronger overall N-H bonding in the three-nitrogen  $T^{3-}$  and [9]ane $N_3$  bases than in the two-nitrogen amino acids. Positive  $\Delta S^\circ$  values reflect solvent release from both the hydronium ion reactant and from the solvation sphere of the highly charged bases. Strongly solvated 3- bases have decreased charge upon protonation with consequent loss of solvation, and this provides a positive contribution to the entropy change. Thus, differential solvation accounts for the more positive  $\Delta S^\circ$  values observed with the 3- bases than with [9]ane $N_3$ . Because  $\Delta H^\circ$  and  $\Delta S^\circ$  for primary  $T^{3-}$  protonation appear to follow the pattern for nitrogen protonation described above, we conclude that the proton in  $HT^{2-}$  is likewise localized to nitrogen atoms.

Addition of a proton to  $HT^{2-}$  has  $\Delta H^\circ$  and  $\Delta S^\circ$  values very similar to those for the amino acid models in Table II, and the second proton appears also to add to a nitrogen site. In contrast to this behavior, the third protonation reaction to form  $H_3T$  has  $\Delta H^\circ = +1.4 \text{ kcal mol}^{-1}$ , intermediate between the small positive  $\Delta H^\circ$  values characteristic of the third (carboxylate) protonation in the model amino acid compounds containing only two nitrogen atoms and the larger negative value expected for nitrogen protonation. It seems likely that  $H_3T$  may consist of a tautomeric mixture of protonated nitrogen and carboxylate sites or may involve proton bonding between proximal nitrogen and carboxylate bases. The latter of these structures is favored by the unusually positive value of  $\Delta S^\circ$  for the third protonation. Presumably an intermolecular hydrogen-bonded structure would be less strongly solvated than a zwitterion and its formation would provide a positive contribution to the entropy change. In any case it appears that carboxylate as well as nitrogen sites distribute protons in  $H_3T$ .

Addition of a fourth proton to form  $H_4T^+$  has  $\Delta H^\circ$  and  $\Delta S^\circ$  very similar to corresponding values for carboxylate protonation in model bases, and we conclude that addition of this proton is localized to carboxylate sites. These observations appear to be in general agreement with some derived in an earlier investigation of  $T^{3-}$  protonation properties.<sup>15</sup> In that study  $^1\text{H}$  NMR chemical shift displacements of methylenic hydrogen atoms were interpreted in terms of proton distributions in T species. The results indicated that acidic protons in  $H_3T$  interact substantially with carboxylate sites and are not localized to nitrogen atoms. Furthermore the  $^1\text{H}$  NMR results indicate that the three nitrogen atoms are not fully protonated even in solutions containing 5 mol of  $\text{H}^+$ /mol of  $T^{3-}$ . This is in keeping with our interpretation of  $H_4T^+$  formation as resulting from carboxylate protonation. Partially

protonated nitrogen atoms in  $H_3T$  are not significantly affected by addition of a fourth proton at a carboxylate site and so remain only fractionally protonated in  $H_4T^+$ . In order to visualize the unusual protonation sequence we made space-filling models of protonated  $T^{3-}$  species. We account for primary solvent interactions by attaching a water molecule to each protonated site, thus adding protons as  $\text{H}_3\text{O}^+$ . Our construction suggests two possible conformations of T species. One of these has three acetate groups situated on one side of the ring plane and a second has two acetate groups opposing a third. Each conformer features vicinal  $-\text{N}-\text{H}_3\text{O}^+$ ,  $-\text{CO}_2^-$  internal hydrogen bonding interactions analogous to those in glycine. However, the staggered conformer also allows hydrogen-bonding interactions between an acetate group on one nitrogen and an adjacent  $-\text{N}-\text{H}_3\text{O}^+$  site. Apparently, the net effect of these combined interactions is to effectively distribute the protons between nitrogen and carboxylate sites in  $H_4T^+$ . Finally, the construction provides an interesting speculation regarding our failure to detect  $H_5T^{2+}$  species even in 0.5 M  $\text{HClO}_4$  medium. Internal hydrogen-bonding interactions between acetate and adjacent protonated nitrogen sites effectively block both potential basic sites from further protonation since this process would result in loss of the internal bonding interaction and would also require an increase in overall solvation. Such pairwise interaction is possible for only two nitrogen and two carboxylate sites and would thus allow protonation at the remaining nitrogen and carboxylate sites and account for all four protons in  $H_4T^+$ . Thus, it seems possible that the unusual  $T^{3-}$  protonation reactions may be a consequence of the geometric arrangement of the basic sites in this molecule.

#### Complexation Reactions with Group IIA (Group 2<sup>23</sup>) Cations.

Temperature-dependent formation constants of  $T^{3-}$  with group IIA cations appear in Table III along with equilibrium constant data for acid dissociation reactions of  $\text{H}[\text{MT}]$  type complexes. van't Hoff analysis of these data provides  $\Delta H^\circ$  and  $\Delta S^\circ$  values, and these are compared with thermodynamic data for similar complexation equilibria in Table IV. These data seem to indicate a number of differences between  $T^{3-}$  complexations and those of related complexing agents, particularly with  $\text{Mg}^{2+}$ . These include an unusual relatively exothermic formation of  $\text{MgT}^-$  which has  $\Delta H^\circ = +0.4 \text{ kcal mol}^{-1}$  compared with  $\Delta H^\circ = +3.47 \text{ kcal mol}^{-1}$  for  $\text{Mg}(\text{EDTA})^{2-}$  and  $+3.6 \text{ kcal mol}^{-1}$  for  $\text{Mg}(\text{DTPA})^{3-}$  formation. At the same time  $\Delta S^\circ$  for  $\text{MgT}^-$  formation is substantially less positive than that for other  $\text{Mg}^{2+}$  complexes. In contrast to this behavior  $T^{3-}$  complexations with  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  are less exothermic than expected but have  $\Delta S^\circ$  values remarkably similar to those for EDTA and DTPA complexes with these ions. We rationalize these data by envisioning the complexation process in terms of stepwise metal-ligand bond formation. Formation of each M-L bond may be construed as consisting of two primary processes—release of solvation water from  $\text{M}^{2+}$  and subsequent M-L bond formation. Admittedly, other processes relating to changes in outer-sphere solvent interaction with isolated or partially bound product vs. reactant species must occur, but these are likely to be similar in the series of reactions we examine and so we omit these for the sake of simplicity.

Release of each water molecule initially bound to  $\text{M}^{2+}$  makes a positive contribution to both the complexation enthalpy and entropy. A strong  $\text{M}^{2+}-\text{H}_2\text{O}$  bond is broken while a water molecule is released into the solvent, increasing system disorder. Subsequent formation of a metal-ligand bond provides a negative contribution to  $\Delta H^\circ$  as well as a negative contribution to  $\Delta S^\circ$  since the bound ligand presumably has fewer degrees of internal freedom. In light of the very similar  $\Delta S^\circ$  values for formation of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  complexes with each of the model ligands in Table IV, it seems likely that the last of these effects, loss of internal freedom, represents only a small contribution to the overall entropy change. We associate the positive  $\Delta S^\circ$  values that characterize the metal complexations as resulting primarily from expulsion of solvation water. The observed inverse relationship between  $\Delta S^\circ$  and atomic number is in keeping with the general observation that the extent of solvation, hence the degree of hydration in the uncomplexed metal ion, decreases with atomic

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- (23) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III  $\rightarrow$  3 and 13.)

number. Loss of weakly bound water from the larger cations provides a smaller positive contribution to the entropy, and  $\Delta S^\circ$  is less positive for these complexations. We infer from these arguments that  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  complexes with  $\text{T}^{3-}$  feature the same degree of solvent release as their complexes with the model ligands. Thus,  $\text{T}^{3-}$  complexes of these ions appear also to have hexadentate metal-ligand coordination, similar to that in their complexes with the model compounds.

$\Delta H^\circ$  values for  $\text{T}^{3-}$  complexation of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  are systematically less exothermic than values for corresponding complexes with EDTA or DTPA. For example,  $\Delta H^\circ$  for  $\text{CaT}^-$  formation differs from that for  $\text{Ca}(\text{EDTA})^{2-}$  by about 2 kcal mol<sup>-1</sup> while  $\Delta H^\circ = -1.4$  kcal mol<sup>-1</sup> compared to  $-4.9$  kcal mol<sup>-1</sup> for  $\text{Ba}(\text{EDTA})^{2-}$ . These data are most easily compared by examining the metathesis reaction:  $\text{Ba}(\text{EDTA})^{2-} + \text{T}^{3-} = \text{BaT}^- + \text{EDTA}^{4-}$  for which  $\Delta H^\circ = +3.5$  kcal mol<sup>-1</sup> and  $\Delta S^\circ \sim 0$  cal mol<sup>-1</sup> K<sup>-1</sup>. Evidently, bonding in  $\text{Ba}(\text{EDTA})^{2-}$  is substantially stronger than in the  $\text{T}^{3-}$  complex. This is partially accounted for on the basis of strain in the cyclic  $\text{T}^{3-}$  system consequent to conformational changes required to provide six coordination positions for the central metal ion. The data seem to indicate that much of the strain interaction in  $\text{MT}^-$  complexes is provided by formation of the sixth metal-ligand coordination. We compare  $\Delta H^\circ$  and  $\Delta S^\circ$  for  $\text{H}[\text{MT}]$  acidic dissociations with those for  $\text{H}[\text{M}(\text{EDTA})]^-$  in Table V. Presumably, the dissociation reactions feature similar mechanisms involving proton loss from a carboxylate group with subsequent metal-carboxylate bonding. The negative entropy change may be associated with  $\text{H}^+$  solvation and loss of internal freedom in the hexacoordinate reaction product. This is partially offset by release of solvent water from the sixth coordination site in  $\text{H}[\text{MT}]$  and  $\text{H}[\text{M}(\text{EDTA})]$ . The similar  $\Delta S^\circ$  values observed for both EDTA and T complexes reflect the like nature of these acidic dissociation reactions. We ascribe the more positive  $\Delta H^\circ$  values for  $\text{H}[\text{CaT}]$  and  $\text{H}[\text{SrT}]$  to increased strain in  $\text{SrT}^-$  and  $\text{CaT}^-$  compared with that in the EDTA complexes. Thus,  $\text{H}[\text{CaT}]$  and  $\text{H}[\text{SrT}]$  are substantially weaker acids than  $\text{H}[\text{M}(\text{EDTA})]^-$  species because of strain interactions in the hexacoordinate  $\text{CaT}^-$  and  $\text{SrT}^-$  species. In summary,  $\text{T}^{3-}$  complexes of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  appear to follow familiar patterns and their behavior may be rationalized in terms of steric constraints in the ligand ring system. However,  $\text{Mg}^{2+}$  complexation with  $\text{T}^{3-}$  seems to differ markedly from the typical pattern of polyamino acid complexations as discussed below.

$\Delta H^\circ$  and  $\Delta S^\circ$  for  $\text{MgT}^-$  formation are  $+0.4$  kcal mol<sup>-1</sup> and  $+46$  cal mol<sup>-1</sup> K<sup>-1</sup>, respectively. Following the discussions above, we interpret that the observed  $\Delta S^\circ$  value, which is about 10 cal mol<sup>-1</sup> K<sup>-1</sup> less positive than that for model ligands, may indicate a lower degree of solvent stripping from  $\text{Mg}^{2+}$  in the complex. In other words  $\Delta S^\circ$  is less positive because less solvation water is expelled from  $\text{Mg}^{2+}$ , which in turn is a result of forming fewer than six  $\text{Mg}^{2+}$ - $\text{T}^{3-}$  bonds. Apparently, the relatively exothermic value of  $\Delta H^\circ$  results from fewer but stronger  $\text{Mg}^{2+}$ - $\text{T}^{3-}$  bonds than the bonds in six-coordinate  $\text{Mg}(\text{EDTA})^{2-}$ , for example. In an attempt to understand this behavior, we examine the acidic dissociation reaction of  $\text{H}[\text{MgT}]$  as it compares with those of other group IIA  $\text{H}[\text{MT}]$  and similar  $\text{H}[\text{M}(\text{EDTA})]^-$  dissociations. Relevant data are given in Table V. We interpret  $\Delta H^\circ = +8$  kcal mol<sup>-1</sup> for  $\text{H}[\text{MgT}]$  dissociation as resulting from cleavage of at least one or two strong bonds in this species. That is, overall bonding forces in  $\text{H}[\text{MgT}]$  are substantially stronger than those in  $\text{MgT}^-$ . The larger positive  $\Delta S^\circ$  value for  $\text{H}[\text{MgT}]$  dissociation is consistent with solvent loss from the partially coordinated  $\text{Mg}^{2+}$  ion present in the protonated complex and suggests formation of at least one new  $\text{Mg}^{2+}$ -ligand bond after proton loss. Thus, we envision  $\text{H}[\text{MgT}]$  acidic dissociation as consisting of proton loss followed by a bond formation reaction between the ligand and partially coordinated cation. However, observed  $\Delta H^\circ$  and  $\Delta S^\circ$  values for this process are inconsistent with the carboxylate dissociation mechanism discussed above. Instead, it appears likely that  $\text{H}[\text{MgT}]$  acidic dissociation proton loss occurs from a nitrogen site in the complex. This process is likely to be markedly more endothermic than proton dissociation from a carboxylate group.

We have already noted that  $>\text{N}-\text{H}^+$  dissociations are endothermic by roughly 10 kcal mol<sup>-1</sup> while  $\Delta H^\circ$  values near 0 kcal mol<sup>-1</sup> are observed for proton loss from carboxylic acids. Furthermore ammonium dissociations are characterized by substantially less negative  $\Delta S^\circ$  values than those for carboxylic acids, which allows for the observed positive  $\Delta S^\circ$  values for  $\text{H}[\text{MgT}]$  proton loss. In this connection it is useful to examine the complexation reaction  $\text{Mg}^{2+} + \text{HT}^{2-} = \text{H}[\text{MgT}]$  for which we calculate  $\Delta H^\circ = +4$  kcal mol<sup>-1</sup> and  $\Delta S^\circ = +24$  cal mol<sup>-1</sup> K<sup>-1</sup>. The reaction features  $\text{Mg}^{2+}$  complexation with a T species already strongly bound at a nitrogen site. The small (compared with  $\text{Mg}(\text{EDTA})^{2-}$  formation)  $\Delta S^\circ$  value suggests a low degree of solvent expulsion and coordination of  $\text{Mg}^{2+}$ . The relatively small positive value of  $\Delta H^\circ$  seems to indicate protonation of  $\text{H}[\text{MgT}]$  at a nitrogen site in that the observed value of  $\Delta H^\circ$  seems inconsistent with cleavage of a strong  $>\text{N}-\text{H}^+$  bond. Instead it seems likely that  $\Delta H^\circ$  for this reaction can be accounted for partially by loss of internal hydrogen-bonding interactions present in  $\text{HT}^{2-}$  but not in  $\text{H}[\text{MgT}]$  and partially by loss in secondary solvent interaction in  $\text{H}[\text{MgT}]$  compared with that for  $\text{Mg}^{2+}$  and  $\text{HT}^{2-}$  reactants. If our earlier arguments that only four or five metal-ligand coordinations are present in  $\text{MgT}^-$  and that  $\text{H}[\text{MgT}]$  proton loss involves formation of a new metal-ligand coordination are recalled, it seems possible that bonding in  $\text{H}[\text{MgT}]$  consists only of  $\text{Mg}^{2+}$ -carboxylate interactions and does not involve  $\text{Mg}^{2+}$ -nitrogen bonding. This behavior would rationalize the much more negative  $\Delta H^\circ$  value observed for  $\text{MgT}^-$  formation with that for  $\text{Mg}(\text{EDTA})^{2-}$ , for example. In spite of these arguments we regard the foregoing analysis as speculative. The detailed nature of metal-ligand coordination in  $\text{MgT}^-$  and  $\text{H}[\text{MgT}]$  remains a subject for further investigation. We now turn our attention to a discussion of  $\text{Cu}^{2+}$  complexes of  $\text{T}^{3-}$ .

**Complexation Reactions with  $\text{Cu}(\text{II})$ .** Spectrophotometric and pH potentiometric experiments with  $\text{Cu}^{2+}$ - $\text{H}_3\text{T}$  solutions indicate the presence of only  $\text{CuT}^-$  and  $\text{H}[\text{CuT}]$  complexes in the pH range from 0.3 to 12. Both complexes are unusually stable with log  $K_f$  values of  $21.63 \pm 0.03$  and  $24.37 \pm 0.03$  at  $I = 1.0$  M and 25 °C (Table VII), which are to be compared with corresponding EDTA log  $K_f$  values of  $18.91 \pm 0.07$  and  $21.9 \pm 0.1$  at  $I = 0.10$  M at the same temperature.<sup>16</sup> The  $\text{CuT}^-$  formation constant is similar to those reported for  $\text{Cu}^{2+}$  complexes with several cyclic tetraaza tetraacetic acids whose log  $K_f$  values at  $I = 0.10$  and 25 °C are 22.2, 21.6, and 21.6 for cDOTA, cTRITA, and cTETA, respectively.<sup>17</sup> Additionally,  $\Delta H^\circ$  and  $\Delta S^\circ$  values for  $\text{CuT}^-$  formation closely resemble those for the tetraaza tetraacetate acid complexes. For example  $\Delta H^\circ$  and  $\Delta S^\circ$  for  $\text{CuT}^-$  formation are  $-13.4 \pm 0.8$  kcal mol<sup>-1</sup> and  $54 \pm 2$  cal mol<sup>-1</sup> K<sup>-1</sup>, respectively, compared with  $-14.3$  kcal mol<sup>-1</sup> and  $54$  cal mol<sup>-1</sup> K<sup>-1</sup>, respectively, for  $\text{Cu}[\text{cDOTA}]^{2-}$  formation. Additionally, corresponding data for  $\text{Cu}(\text{EDTA})^{2-}$  formation are  $-8.2 \pm 0.2$  kcal mol<sup>-1</sup> and  $59 \pm 2$  cal mol<sup>-1</sup> K<sup>-1</sup>. We ascribe the substantially more exothermic  $\text{Cu}^{2+}$  complexation with  $\text{T}^{3-}$  and the tetraaza tetraacetate cDOTA compared with that with EDTA to formation of additional strong  $\text{Cu}-\text{N}<$  bonds in these species. The similarity of reaction entropies points to similar copper-ligand bonding, namely one in which the  $\text{Cu}^{2+}$  solvation sphere is stripped to allow hexacoordinate interaction between  $\text{Cu}^{2+}$  and the ligand. This observation is in accord with a recent X-ray crystallographic study of  $\text{CuT}^-$ , which indicated that all six  $\text{Cu}^{2+}$  coordinations are bonded to  $\text{T}^{3-}$  sites.<sup>8</sup> The present results seem to indicate that the coordination structure of  $\text{CuT}^-$  in solution resembles that in the solid phase. This supposition provides an explanation for the unusually differing  $\lambda_{\text{max}}$  values for  $\text{CuT}^-$  and  $\text{H}[\text{CuT}]$  species (750 and 660 nm, respectively) as follows. First, we note that the thermodynamic properties for acidic dissociation of  $\text{H}[\text{CuT}]$  are somewhat different from those for  $\text{H}[\text{Cu}(\text{EDTA})]^-$  dissociation.  $\Delta H^\circ$  values for  $\text{H}[\text{CuT}]$  and  $\text{H}[\text{Cu}(\text{EDTA})]^-$  dissociations are  $-0.1 \pm 0.6$  kcal mol<sup>-1</sup> and  $+2.0 \pm 0.3$  kcal mol<sup>-1</sup>, respectively, while  $\Delta S^\circ$  for the corresponding reactions are  $-13 \pm 2$  cal mol<sup>-1</sup> K<sup>-1</sup> and  $-7 \pm 3$  cal mol<sup>-1</sup> K<sup>-1</sup>, respectively. It seems that both dissociation processes involve proton dissociation from a carboxylate site with subsequent  $\text{Cu}^{2+}$ - $\text{CO}_2^-$  coordination. Because these processes are likely to have similar energetics in the two dissociation reactions, we must

ascribe the difference in reaction enthalpies to a bonding interaction more favorable in  $\text{CuT}^-$  than in  $\text{H}[\text{CuT}]$  compared with the change in overall bonding between  $\text{Cu}(\text{EDTA})^{2-}$  and  $\text{H}[\text{Cu}(\text{EDTA})]^-$ . This might result from a reorientation of metal-ligand bonds in the  $\text{CuT}^-$  species resulting in either release of strain or more effective metal-ligand interaction. Some internal reorientation is consistent with the more negative  $\Delta S^\circ$  value for  $\text{H}[\text{CuT}]$  acidic dissociation compared with that for  $\text{H}[\text{Cu}(\text{EDTA})]^-$ . Both processes restrict internal motion by binding a carboxylate group, but this restriction seems larger in the case of  $\text{H}[\text{CuT}]$ .  $\Delta S^\circ$  for the acidic dissociation reactions consists of contributions from several processes: (1) solvent ordering around  $\text{H}^+$ , common to both reactions; (2) increased secondary solvation around the copper complexes, a process that provides a larger negative contribution to  $\text{H}[\text{Cu}(\text{EDTA})]^-$  dissociation than to  $\text{H}[\text{CuT}]$  dissociation; (3) positive contributions due to solvent release from the sixth copper coordination; (4) loss of internal freedom. Of these factors the last might account for the more negative  $\Delta S^\circ$  value observed for  $\text{H}[\text{CuT}]$  dissociation. That is, differences in solvent binding at the sixth copper coordination site might result in a relatively more negative contribution to  $\Delta S^\circ$  for  $\text{H}[\text{CuT}]$  dissociation. However, the sixth coordination position on  $\text{Cu}^{2+}$  is known to be only weakly solvated so that differences between weakly solvated sites are not

likely to provide for the observed result. Consequently, it appears possible that some distortion of  $\text{Cu}^{2+}$  ligation occurs upon  $\text{CuT}^-$  formation. This proposition seems supported by the X-ray crystallographic data, which indicate an unusually large trigonal distortion in  $\text{CuT}^-$  in which the locus of nitrogen atoms is twisted away from the carboxylate locus by about  $30^\circ$  from the idealized octahedral orientation. A large trigonal distortion of this kind would certainly influence the ligand field near  $\text{Cu}^{2+}$  and might profoundly effect the magnitude of the ligand field, thus accounting for the unusual difference between spectral properties of  $\text{H}[\text{CuT}]$  and  $\text{CuT}^-$ . As a final comparison we note that  $\lambda_{\text{max}} = 660 \text{ nm}^{2c}$  for aqueous  $\text{Cu}[\text{9}] \text{aneN}_3^{2+}$ , which we presume exists as a hexacoordinate species. Unfortunately, no crystallographic data is available for this complex. Nevertheless it seems unlikely that large trigonal distortions would be present and that the similar  $\lambda_{\text{max}}$  values of  $\text{H}[\text{CuT}]$  and  $\text{Cu}[\text{9}] \text{aneN}_3(\text{H}_2\text{O})_3^{2+}$  reflect approximately octahedral coordination. Thus, it appears that the large displacement of  $\lambda_{\text{max}}$  from 660 nm for  $\text{H}[\text{CuT}]$  to a value near 750 nm for  $\text{CuT}^-$  results from a substantial distortion of the ligand field in  $\text{CuT}^-$ , which we connect with a release of strain interactions in  $\text{H}[\text{CuT}]$ . The importance of these interactions is consistent with thermodynamic, X-ray crystallographic, and spectral evidence.

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## Kinetics and Mechanism of General-Acid-Assisted Oxidation of Bromide by Hypochlorite and Hypochlorous Acid

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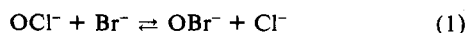
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The rate expression for the oxidation of bromide by  $\text{HOCl}$  and  $\text{OCl}^-$  is  $-\text{d}[\text{OCl}^-]_{\text{T}}/\text{dt} = k_{\text{HA}}[\text{HA}][\text{OCl}^-]_{\text{T}}[\text{Br}^-]$ , where  $[\text{OCl}^-]_{\text{T}} = [\text{OCl}^-] + [\text{HOCl}]$  and  $\text{HA}$  is a general acid ( $\text{H}_2\text{O}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{ClCH}_2\text{COOH}$ , or  $\text{H}_3\text{O}^+$ ). The  $k_{\text{HA}}$  value for  $\text{H}_3\text{O}^+ + \text{OCl}^- + \text{Br}^-$  is  $3.65 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$  (this path requires  $\text{HOCl}$  as an intermediate), while the  $k_{\text{HA}}$  value for  $\text{H}_3\text{O}^+ + \text{HOCl} + \text{Br}^-$  is  $1.32 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$ . In terms of second-order expressions, the rate constant for  $\text{HOCl} + \text{Br}^-$  is  $1.55 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , while the rate constant for  $\text{OCl}^- + \text{Br}^-$  is only  $0.90 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ . The proposed mechanism for the acid-assisted reactions (except for  $\text{H}_3\text{O}^+ + \text{OCl}^-$ ) is a simultaneous proton transfer (from  $\text{HA}$  to  $\text{OCl}^-$  or to  $\text{HOCl}$ ) and  $\text{Cl}^+$  transfer to  $\text{Br}^-$  (to give  $\text{BrCl}$ , which reacts rapidly to give  $\text{OBr}^-$  or  $\text{Br}_2$  and  $\text{Br}_3^-$ ). The Brønsted  $\alpha$  value is 0.75 for the reactions of  $\text{HA}$  with  $\text{OCl}^-$  and  $\text{Br}^-$ , and the  $\alpha$  value is 0.27 for the reactions of  $\text{HA}$  with  $\text{HOCl}$  and  $\text{Br}^-$ . The  $\alpha$  values reflect the degree of proton transfer in the transition state.

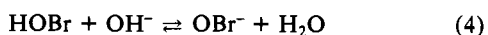
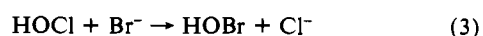
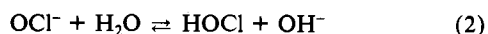
### Introduction

Many non-metal redox reactions take place by atom-transfer or ion-transfer processes. However, much less attention has been paid to the kinetics and mechanisms of these reactions than to electron-transfer reactions. This lack of study may have left the impression that the reactions are well understood. In reality, detailed knowledge of non-metal redox reaction kinetics and mechanisms is limited.

The oxidation of bromide ion by hypochlorite ion was studied by Farkas, Lewin, and Bloch<sup>1</sup> in the pH range 10.8–13.2 under second-order conditions. They verified the stoichiometry of eq 1 and studied the progress of the reaction by titrimetric methods.



They reported the rate-determining step to be the reaction between  $\text{HOCl}$  and  $\text{Br}^-$  with a rate constant of  $2.95 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C. Their proposed mechanism (eq 2–4) implies nucleophilic



attack by  $\text{Br}^-$  at oxygen, which is equivalent to an  $\text{OH}^+$  transfer between  $\text{Cl}^-$  and  $\text{Br}^-$ .

Recent studies in our laboratory indicate that  $\text{Cl}^+$  transfer occurs in the reactions of  $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$  with iodide<sup>2</sup> and in the reaction of  $\text{NH}_2\text{Cl}$  with sulfite.<sup>3</sup> All of these reactions are general-acid assisted. (General-acid-catalyzed reactions can be considered to be a special case of general-acid-assisted reactions in which no acid is consumed or released.) The reaction of  $\text{OCl}^-$  with  $\text{I}^-$  is also general-acid assisted and appears to have a  $\text{Cl}^+$ -transfer mechanism.<sup>2</sup> We propose  $\text{ICl}$  as an intermediate in all the reactions with iodide. Recent pulsed-accelerated-flow studies<sup>4</sup> show that the reaction between  $\text{ICl}$  and  $\text{I}^-$  to form  $\text{I}_2$  and  $\text{I}_3^-$  is extremely rapid.

Eigen and Kustin<sup>5</sup> determined the kinetics of halogen hydrolysis by temperature-jump relaxation methods. Their work shows that  $\text{H}_3\text{O}^+$  assists the rate of reaction between  $\text{Br}^-$  and  $\text{HOBr}$  to form  $\text{Br}_2$ . Thus,  $\text{H}_3\text{O}^+$  might well be expected to assist the reaction between  $\text{Br}^-$  and  $\text{HOCl}$ , but this has not been studied previously.

In the present work, we report the kinetics of the reaction in eq 1 in base (from 0.45 M  $\text{NaOH}$  to pH 9.5) and show that the

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