

# Equilibrium Studies of Polynucleating Ligands. II. Metal Complexes of Tetrakis(aminomethyl)methane

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**Abstract:** The interactions of tetrakis(aminomethyl)methane (tam) with Mn(II), Fe(II), Co(II), Ni(II), Zn(II), and Cd(II) have been studied. Equilibrium constants were determined by potentiometric methods in aqueous 0.1 M KNO<sub>3</sub> at 25°. The species MH(tam)<sup>3+</sup> was stable in all systems with the exception of Mn(II) and Fe(II) where hydrolysis of the metal ions resulted in precipitation and prevented equilibrium studies. All the metal-ligand association constants follow the Irving-Williams order. The monoprotic dissociation of MH(tam)<sup>3+</sup> was determined for Co(II) and Ni(II). In the case of Zn(II), hydrolysis occurs in an overlapping step and results in the formation of Zn(tam)OH<sup>+</sup> which slowly polymerizes. The measured and derived equilibrium constants obtained in the study are compared to constants previously determined with HC(CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>. Trends in electrostatic interactions and entropy effects are discussed.

Equilibrium studies of tetrakis(aminomethyl)methane (tam) with Cu(II) revealed that many interesting complex ionic species were formed because of the geometric arrangement of the four coordinating amine groups on the ligand.<sup>1</sup> This paper reports on the complexes formed by tam with Mn(II), Fe(II), Co(II), Ni(II), Zn(II), and Cd(II). A comparison of the stabilities of metal complexes formed by the ligand 2-aminomethyl-1,3-diaminopropane is also discussed and provides many correlations involving both charge and statistical effects.

## Experimental Section

**Procedures.** Potentiometric measurements were made on a Radiometer pHM4 pH meter in the Ni(II)-tam study. A Radiometer pHM26 was used to study other metal-tam systems. The meter-electrode system was calibrated to provide  $-\log [H^+]$  values directly, as previously described.<sup>2</sup>

**Materials.** The preparation of the tetraammonium nitrate salt of tam, H<sub>4</sub>tam(NO<sub>3</sub>)<sub>4</sub>, has been reported previously.<sup>1</sup> Two or three recrystallizations of crude H<sub>4</sub>tam(NO<sub>3</sub>)<sub>4</sub> from hot 2 M nitric acid yielded crystals of primary standard purity.

Stock solutions of manganese(II) nitrate, iron(II) sulfate, cobalt(II) nitrate, nickel(II) nitrate, zinc(II) nitrate, and cadmium(II) nitrate were prepared from reagent grade chemicals. Metal concentrations were determined for the most part by EDTA titrations.<sup>3</sup> FeSO<sub>4</sub> solutions were standardized by permanganate titration.

The titrant solutions of carbonate-free sodium hydroxide were standardized against potassium acid phthalate.

**Calculations.** Equilibrium constants were determined from experimental data according to the method outlined by Schwarzenbach and Heller<sup>4</sup> with some modification. The constants were calculated for concentrations in moles/liter and refer to 25.0° and an ionic strength of 0.1 M adjusted with KNO<sub>3</sub>. The uncertainties in mathematical values which appear on certain constants are standard deviations. On the average, three titrations were performed for each system with concentrations of ligand ranging from 2 × 10<sup>-3</sup> to 1 × 10<sup>-2</sup> M.

## Results and Interpretation

The four pK<sub>a</sub>'s of H<sub>4</sub>tam<sup>4+</sup> have been determined previously and are listed in Table I with constants obtained in this study.

(1) L. J. Zompa and R. F. Bogucki, *J. Am. Chem. Soc.*, **88**, 5186 (1966).

(2) R. F. Bogucki and A. E. Martell, *ibid.*, **80**, 4170 (1958).

(3) H. A. Flaschka, "EDTA Titrations," Pergamon Press, New York, N. Y., 1959.

(4) G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 119 (1951).

**Ni(II)-tam (1:1).** When equimolar amounts of Ni(NO<sub>3</sub>)<sub>2</sub> and H<sub>4</sub>tam(NO<sub>3</sub>)<sub>4</sub> were titrated with standard base, a single steep inflection occurred at  $a = 3$ , where  $a$  represents the moles of base added per mole of tam (Figure 1). Beyond the inflection the slope of the titration curve resembles that of a weak acid. The concentration independence of pH values in the region from  $a = 3$  to 4 indicates that no polynuclear species are formed. Beyond  $a = 4$  the solution becomes turbid, and after approximately 20 min a pale blue precipitate forms.

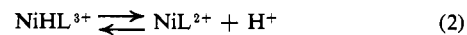
The application of charge and mass balance expressions to a single-step reaction between  $a = 0$  and 3



in which L represents tam gives consistent values for the equilibrium constant calculated between  $a = 1.0$  and 2.7.

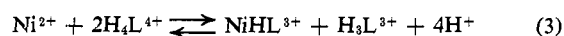
$$K_1 = \frac{[NiHL^{3+}][H^+]^3}{[Ni^{2+}][H_4L^{4+}]} = 10^{-8.40 \pm 0.02}$$

The region from  $a = 3$  to 4 is consistent with the monoprotic acid dissociation



$$K_2 = \frac{[NiL^{2+}][H^+]}{[NiHL^{3+}]} = 10^{-7.63 \pm 0.03}$$

**Ni(II)-tam (1:2).** When solutions containing 2:1 molar ratios of H<sub>4</sub>tam(NO<sub>3</sub>)<sub>4</sub> to Ni(NO<sub>3</sub>)<sub>2</sub> were titrated with standard base, inflections occurred in the titration curve at  $a$  values of 2, 3, and 4 (Figure 2). The reaction presumed to occur between  $a = 0$  and 2 is



Application of charge and mass balance expressions in this region produced values for  $K_3$  which drifted significantly with changing  $a$  values, probably because of other, unaccounted-for protonated chelate species. The value of  $K_3$  listed in Table I was derived, instead, as the product of  $K_1$  and  $K_{a1}$ , both of which are known with good precision.

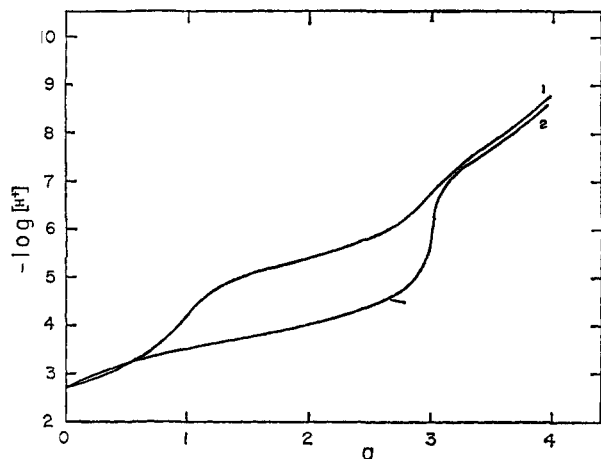
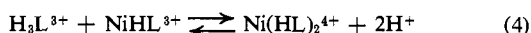
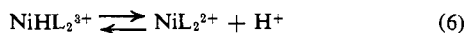
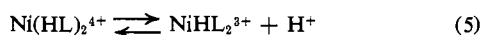


Figure 1. (1) Co(II)-tam (1:1), [tam] =  $5.59 \times 10^{-3}$  M. (2) Ni(II)-tam (1:1), [tam] =  $6.57 \times 10^{-3}$  M.

In the region from  $a = 2$  to 3, a second mole of tam combines with  $\text{NiHL}^{3+}$  according to the reaction



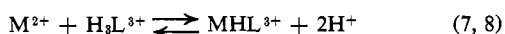
An equilibrium constant of  $10^{-7.72 \pm 0.05}$  was calculated for this reaction. The final step in the sequence is a diprotic dissociation of the species  $\text{Ni}(\text{HL})_2^{4+}$ .



The constants calculated for reactions 5 and 6 are  $10^{-7.57 \pm 0.05}$  and  $10^{-8.00 \pm 0.06}$ , respectively.

**Zn(II)-tam (1:1) and Co(II)-tam (1:1).** The titration of  $\text{Zn}(\text{NO}_3)_2\text{-H}_4\text{tam}(\text{NO}_3)_4$  and  $\text{Co}(\text{NO}_3)_2\text{-H}_4\text{tam}(\text{NO}_3)_4$  in 1:1 molar ratios with standard base produced inflections at  $a = 1$  and 3. The Zn(II)-tam system also gave an inflection at  $a = 5$ ; however, this was accompanied by precipitation and drifting of pH values which prohibited calculations in this region.

The region between  $a = 0$  and 1 is identical with the titration of the protonated ligand,  $\text{H}_4\text{tam}^{4+}$ , alone in the case of both Zn(II) and Co(II). After the first inflection, a significant lowering of the metal-ligand curve below that of the free ligand indicates a strong metal-ligand interaction. Calculations were made for the direct formation of  $\text{MHL}^{3+}$  in a single step



The results obtained in the Zn(II)-tam and Co(II)-tam systems were  $K_7 = 10^{-8.84 \pm 0.03}$  and  $K_8 = 10^{-8.32 \pm 0.04}$ , respectively. The  $K$  values tended to drift in the most acid region of the curve, which suggests further protonation of  $\text{MHL}^{3+}$ , probably to form  $\text{MH}_2\text{L}^{4+}$  in small amounts. Equilibrium calculations applied in the region between  $a = 1.3$  and 2 gave

$$K_9 = \frac{[\text{ZnH}_2\text{L}^{4+}][\text{H}^+]}{[\text{Zn}^{2+}][\text{H}_3\text{L}^{3+}]} = 10^{-2.52 \pm 0.08}$$

$$K_{10} = \frac{[\text{CoH}_2\text{L}^{4+}][\text{H}^+]}{[\text{Co}^{2+}][\text{H}_3\text{L}^{3+}]} = 10^{-2.87 \pm 0.08}$$

With the equilibrium constants for the diprotonated complexes of Zn(II) and Co(II) and  $K_7$  and  $K_8$ , the acidity constants of  $\text{MH}_2\text{L}^{4+}$  can be evaluated ( $K_{11}$  and  $K_{12}$  in Table I).

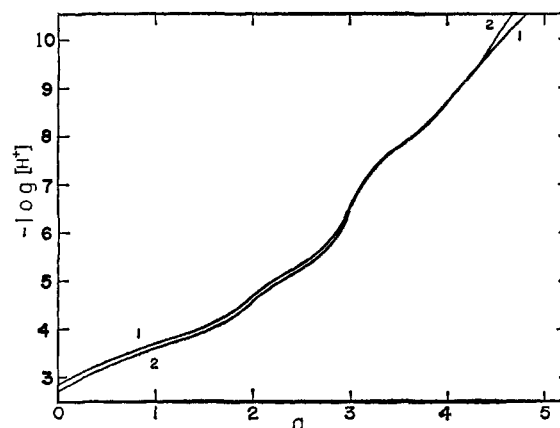


Figure 2. Ni(II)-tam (1:2): (1) [tam] =  $3.57 \times 10^{-3}$  M; (2) [tam] =  $6.67 \times 10^{-3}$  M.

After 3  $a$  values of base was added, the Co(II)-tam titration curve behaved like the Ni(II)-tam (1:1) curve; a concentration-independent region between 3 and 4  $a$  values followed immediately by precipitate formation.

Table I

$K$ value	Reaction	$-\text{Log } K$
$K_{a1}$	$\text{H}_4\text{L}^{4+} \rightleftharpoons \text{H}_3\text{L}^{3+} + \text{H}^+$	$3.03 \pm 0.01$
$K_{a2}$	$\text{H}_3\text{L}^{3+} \rightleftharpoons \text{H}_2\text{L}^{2+} + \text{H}^+$	$5.67 \pm 0.01$
$K_{a3}$	$\text{H}_2\text{L}^{2+} \rightleftharpoons \text{HL}^+ + \text{H}^+$	$8.17 \pm 0.02$
$K_{a4}$	$\text{HL}^+ \rightleftharpoons \text{L} + \text{H}^+$	$9.89 \pm 0.03$
$K_1$	(1) $\text{Ni}^{2+} + \text{H}_4\text{L}^{4+} \rightleftharpoons \text{NiHL}^{3+} + 3\text{H}^+$	$8.40 \pm 0.02$
$K_2$	(2) $\text{NiHL}^{3+} \rightleftharpoons \text{NiL}^{2+} + \text{H}^+$	$7.62 \pm 0.03$
$K_3$	(3) $\text{Ni}^{2+} + 2\text{H}_4\text{L}^{4+} \rightleftharpoons \text{NiHL}_2^{3+} + \text{H}_3\text{L}^{3+} + 4\text{H}^+$	$11.43 \pm 0.02^a$
$K_4$	(4) $\text{NiHL}^{3+} + \text{H}_3\text{L}^{3+} \rightleftharpoons \text{Ni}(\text{HL})_2^{4+} + 2\text{H}^+$	$7.72 \pm 0.05$
$K_5$	(5) $\text{Ni}(\text{HL})_2^{4+} \rightleftharpoons \text{NiHL}_2^{3+} + \text{H}^+$	$7.57 \pm 0.05$
$K_6$	(6) $\text{NiHL}_2^{3+} \rightleftharpoons \text{NiL}_2^{2+} + \text{H}^+$	$8.00 \pm 0.06$
$K_7$	(7) $\text{Zn}^{2+} + \text{H}_3\text{L}^{3+} \rightleftharpoons \text{ZnHL}^{3+} + 2\text{H}^+$	$8.84 \pm 0.03$
$K_8$	(8) $\text{Co}^{2+} + \text{H}_3\text{L}^{3+} \rightleftharpoons \text{CoHL}^{3+} + 2\text{H}^+$	$8.32 \pm 0.04$
$K_9$	(9) $\text{Zn}^{2+} + \text{H}_3\text{L}^{3+} \rightleftharpoons \text{ZnH}_2\text{L}^{4+} + \text{H}^+$	$2.25 \pm 0.08$
$K_{10}$	(10) $\text{Co}^{2+} + \text{H}_3\text{L}^{3+} \rightleftharpoons \text{CoH}_2\text{L}^{4+} + \text{H}^+$	$2.87 \pm 0.08$
$K_{11}$	(11) $\text{ZnH}_2\text{L}^{4+} \rightleftharpoons \text{ZnHL}^{3+} + \text{H}^+$	$6.32 \pm 0.08$
$K_{12}$	(12) $\text{CoH}_2\text{L}^{4+} \rightleftharpoons \text{CoHL}^{3+} + \text{H}^+$	$5.45 \pm 0.08$
$K_{13}$	(13) $\text{CoHL}^{3+} \rightleftharpoons \text{CoL}^{2+} + \text{H}^+$	$7.82 \pm 0.01$
$K_{14}$	(14) $\text{Zn}^{2+} + 2\text{H}_3\text{L}^{3+} \rightleftharpoons \text{ZnHL}^{3+} + \text{H}_2\text{L}^{2+} + 3\text{H}^+$	$14.51 \pm 0.02^b$
$K_{15}$	(15) $\text{Co}^{2+} + 2\text{H}_3\text{L}^{3+} \rightleftharpoons \text{CoHL}^{3+} + \text{H}_2\text{L}^{2+} + 3\text{H}^+$	$13.99 \pm 0.04^b$
$K_{16}$	(16) $\text{Cd}^{2+} + \text{H}_2\text{L}^{2+} \rightleftharpoons \text{CdHL}^{3+} + \text{H}^+$	$4.48 \pm 0.18$

<sup>a</sup> Evaluated from product of  $K_1$  and  $K_{a1}$ . <sup>b</sup> Evaluated from the products of constants determined in the 1:1 systems and  $K_{a2}$ . These numbers are listed because their precision is better than those determined in the 1:2 systems (see text).

The region from  $a = 3$  to 4 in the Co(II)-tam (1:1) system was consistent with the monoprotic dissociation of the species  $\text{CoHL}^{3+}$ .

$$K_{13} = \frac{[\text{CoL}^{2+}][\text{H}^+]}{[\text{CoHL}^{3+}]} = 10^{-7.82 \pm 0.01}$$

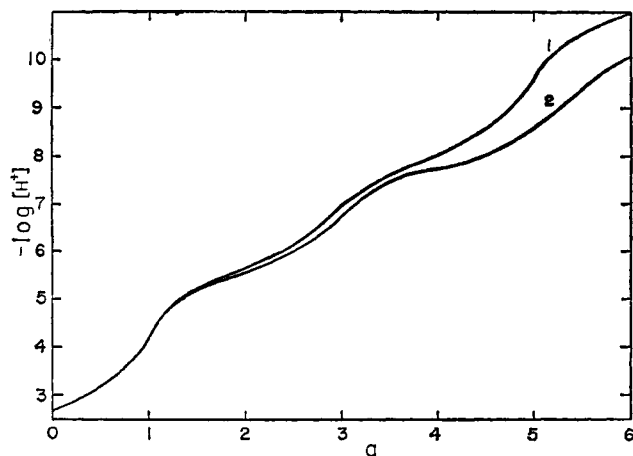


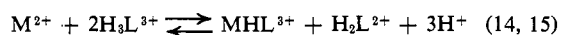
Figure 3. Zn(II)-tam (1:1): (1) rapid titration,  $[\text{tam}] = 6.63 \times 10^{-3} M$ ; (2) equilibrium titration,  $[\text{tam}] = 6.96 \times 10^{-3} M$ .

This reaction might also be interpreted as



In the Zn(II)-tam (1:1) system beyond  $a = 3$ , the pH drifted toward more acid values after each addition of an increment of base. The titration curves obtained first by rapid titration and then by allowing the solution to attain equilibrium after each increment of base was added are shown in Figure 3. The inflection at  $a = 5$  in the rapid titration most probably indicates the formation of  $\text{ZnL}(\text{OH})^+$ . This species may then form polynuclear olation complexes responsible for the lower pH values obtained in the equilibrium curve and the shift of the inflection to an  $a$  value of approximately 5.2. Equilibrium calculations were not made in this region because of drifting pH values and precipitate formation.

**Zn(II)-tam (1:2) and Co(II)-tam (1:2).** When 1:2 molar ratios of  $\text{M}(\text{NO}_3)_2$  (where M represents either Zn(II) or Co(II)) and  $\text{H}_4\text{tam}(\text{NO}_3)_4$  are titrated with standard base, three inflections are observed in the titration curves (Figures 4 and 5). These inflections occur at  $a$  values of 1, 2.5, and 4. The region from  $a = 0$  to 1 represents the acidic dissociation of  $\text{H}_4\text{L}^{4+}$  to  $\text{H}_3\text{L}^{3+}$ . The section of titration curve from  $a$  values 1 to 2.5 corresponds to the reaction



Equilibrium constants calculated in the usual manner at ligand concentrations from  $2 \times 10^{-3}$  to  $10^{-2} M$  gave  $K_{14} = 10^{-14.58 \pm 0.08}$  and  $K_{15} = 10^{-13.97 \pm 0.08}$  in the Zn(II) and Co(II) systems, respectively. The reaction above represents the summation of reaction 7 or 8 with the second acid dissociation reaction of  $\text{H}_4\text{tam}^{4+}$ . Thus the constants  $K_{14}$  and  $K_{15}$  should be equal in value to the products  $K_7 K_{a2} = 10^{-14.51}$  and  $K_8 K_{a2} = 10^{-13.99}$ , respectively. The agreements in values are well within experimental error and lend confidence in the essential correctness of the assumptions. Further equilibrium constants were not obtained in these systems because of the prohibitively numerous complex species which could be present in the buffer region above  $a = 2.5$ .

**Cd(II)-tam (1:1 and 1:2).** When equimolar ratios of  $\text{Cd}(\text{NO}_3)_2$  and  $\text{H}_4\text{tam}(\text{NO}_3)_4$  were titrated with standard base, the titration curve obtained was similar to that of the free  $\text{H}_4\text{tam}(\text{NO}_3)_4$  from  $a = 0$  to 2. Be-

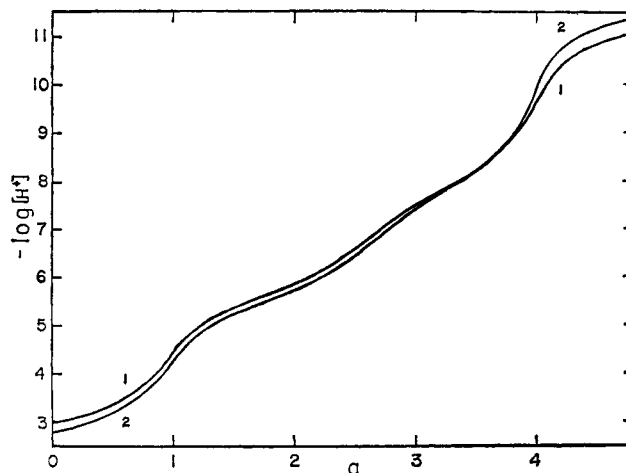


Figure 4. Co(II)-tam (1:2): (1)  $[\text{tam}] = 2.79 \times 10^{-3} M$ ; (2)  $[\text{tam}] = 5.59 \times 10^{-3} M$ .

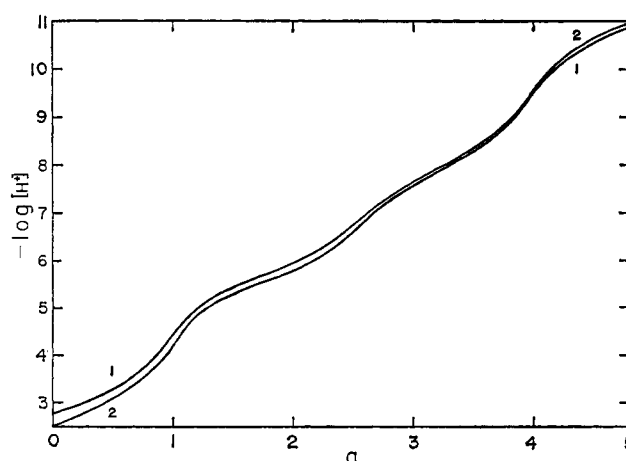


Figure 5. Zn(II)-tam (1:2): (1)  $[\text{tam}] = 4.90 \times 10^{-3} M$ ; (2)  $[\text{tam}] = 9.90 \times 10^{-3} M$ .

yond  $a = 2$  the metal-ligand curve drops to pH values lower than the free-ligand curve and also gives a weak inflection at  $a = 3$ . Calculations based on the reaction



gave  $K_{16} = 10^{-4.48 \pm 0.18}$ . After 3.5  $a$  values of base was added, a precipitate formed which prevented further studies in the system.

The titration curve obtained for the 1:2 system gives a weak inflection at  $a = 2$  and a steep inflection at  $a = 4$ . No precipitate was observed during the titration. From the stoichiometry it appears that  $\text{CdL}_2^{2+}$  is formed, but quantitative calculations were not possible because as in the Zn(II)- and Co(II)-tam 1:2 systems many protonated complex species are probably present in the buffer region beyond  $a = 2$ . The number of these complexes gives rise to an abundance of variables in the simultaneous equations used in equilibrium expressions, thereby prohibiting solution of these equations.

**Fe(II)-tam (1:1) and Mn(II)-tam (1:1).** In titrations containing equimolar amounts of Fe(II) or Mn(II) with  $\text{H}_4\text{tam}(\text{NO}_3)_4$ , there were no observable metal-ligand interactions at  $a$  values 0 to 2. Beyond  $a = 2$  (pH 6.5-7.5), hydrolysis of the metal ions resulting in precipitation prevented further study in these systems.

Table II

Reaction	Log K				
	Co(II)	Ni(II)	Cu(II) <sup>a</sup>	Zn(II)	Cd(II)
(17) $M^{2+} + L \rightleftharpoons ML^{2+}$	7.6 (6.3) <sup>d</sup>	10.7 (9.9)	11.0 (10.9)	...	5.7 (5.4)
(18) $M^{2+} + HL^+ \rightleftharpoons MHL^{3+}$	5.5 (3.8)	8.5 (5.6)	8.6 <sup>b</sup> (8.7)	5.0 (3.8)	3.7 (3.4)
(19) $M^{2+} + H_2L^{2+} \rightleftharpoons MH_2L^{4+}$	2.8 (1.6)	...	5.4 (3.6)	3.2 (1.7)	... (1.6)
(20) $ML^{2+} + L \rightleftharpoons ML_2^{2+}$	...	8.1	8.4	...	...
(21) $ML^{2+} + HL^+ \rightleftharpoons ML(HL)^{3+}$	...	6.4	6.9	...	...
(22) $ML^{2+} + H_2L^{2+} \rightleftharpoons M(HL)_2^{4+}$	...	5.8	6.3	...	...
(23) $MHL^{3+} + HL^+ \rightleftharpoons M(HL)_2^{4+}$	...	6.1	6.9 <sup>b</sup>	...	...
(24) $MH_2L^{4+} + L \rightleftharpoons M(HL)_2^{4+}$	...	...	11.9	...	...
(25) $MHL^{3+} + L \rightleftharpoons ML(HL)^{3+}$	...	8.4	9.3 <sup>b</sup>	...	...
(26) $MHL^{3+} + H^+ \rightleftharpoons MH_2L^{4+}$	5.5	...	5.0 <sup>b</sup>	6.3	...
(27) $ML^{2+} + H^+ \rightleftharpoons MHL^{3+}$	7.8	7.6	...	...	7.9 <sup>c</sup>
(28) $ML(HL)^{3+} + H^+ \rightleftharpoons M(HL)_2^{4+}$	...	7.6	7.6	...	...
(29) $ML_2^{2+} + H^+ \rightleftharpoons ML(HL)^{3+}$	...	8.0	8.3	...	...

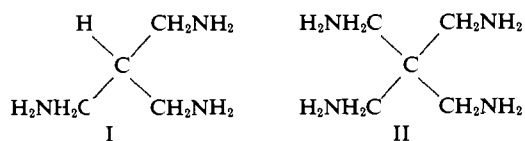
<sup>a</sup> Values for Cu(II) were taken from ref 1 except as noted in b. <sup>b</sup> These values are different by 1 log unit from those reported in ref 1 (see discussion in text). <sup>c</sup> Value estimated on the basis of the related values for Co and Ni. <sup>d</sup> Values enclosed in parentheses refer to adap.

Table I is a compilation of the equilibrium constants determined in this study. The four acidity constants of  $H_4tam^{4+}$  are also listed.

### Discussion

Table II lists a number of association reactions and their corresponding association constants which may be derived from the equilibrium constants reported in Table I. The values for Cu(II) were taken from ref 1 with some changes. On the basis of data in this study, we have changed the estimated value for the first acid dissociation constant of  $CuH_2L^{4+}$  from  $10^{-6}$  to  $10^{-5}$ . This value seems more reasonable in view of the values of  $10^{-6.3}$  and  $10^{-5.5}$  for the less strongly complexed  $ZnH_2L^{4+}$  and  $CoH_2L^{4+}$ , respectively. As a result of this change, the derived values listed for Cu in reactions 18, 23, and 25 are 8.6, 6.9, and 9.3 rather than the previously reported values of 7.6, 7.9, and 10.3, respectively. It is important to note that this change does not alter any of the trends noted in ref 1, nor does it necessitate any change in the interpretations of these trends. In fact, the new values fit better in the various trends in each case.

The values in parentheses for reactions 17, 18, and 19 are the values reported by Anderegg<sup>5</sup> for 2-amino-methyl-1,3-diaminopropane (adap, structure I), the structure of which allows interesting comparisons to be made between metal complexes of adap and tam (structure II). Both ligands are potentially tridentate for



metal ions with octahedral or tetrahedral coordination requirements, but only bidentate for square-planar metal ions.

It should be noted that Anderegg's studies with adap<sup>5</sup> were performed in 0.1 M  $KNO_3$  at 20°. At this temperature, all of the proton and metal association constants for adap will be a bit larger (on the average by 0.1 to 0.3 log unit) than they would be at 25°. With a reasonable correction of -0.15 log unit for the differential of 5°, the three proton association constants (as logs) for adap at 25° would be 10.23, 8.41, and 6.28,

(5) G. Anderegg, *Helv. Chim. Acta*, 45, 1303 (1962).

whereas the corresponding values for tam are 9.89, 8.17, and 5.67. The somewhat greater basicity of the adap amine groups would predict correspondingly larger association constants with metal ions for adap than tam. On the other hand, the statistical factor would tend to make metal-tam association constants somewhat larger than the corresponding metal-adap values inasmuch as tam has a statistically larger number of ways of bonding to the metal ion in each comparable compound. Thus these two, relatively small, opposing tendencies, as well as the temperature differential, will make it difficult to assign any significance to small differences (a few tenths of a log unit) between association constants for similar tam and adap chelates. However, large differences (greater than 1 log unit) are certainly significant and can be employed to evaluate trends and especially changes in the dentate number of a chelating agent. In reaction 18,  $HL^+$  may be tridentate for tam and only bidentate for adap. Thus the significant drop in stabilities for the adap chelates of Co, Ni, and Zn as compared to the tam chelates indicates that these complexes drop from tridentate to bidentate and thereby lose the stability of one donor atom and one chelate ring in going from tam to adap. The very small differences between the values of Cu and Cd, on the other hand, suggest that these chelates are only bidentate in both cases. In reaction 19, Co, Zn, and Cu all show a sharp decrease for the adap chelate because  $H_2(adap)^{2+}$  can be only a unidentate donor, whereas  $H_2(tam)^{2+}$  may be bidentate.

In a vertical comparison of reactions 17, 18, and 19, in that order, the large decreases in stabilities for all metal ions and both ligands reflect the increase in electrostatic repulsion between metal and ligand as well as the decrease in the number of available donor groups as the ligand becomes protonated. The same effect is seen in the analogous reactions 20, 21, and 22 except that whereas Cu showed a decrease of 3.2 log units in going from reaction 18 to reaction 19, it decreased by only 0.6 log unit in the corresponding sequence 21 to 22. The reason for this difference of 2.6 log units is readily understood if we consider that the complex  $ML(H_2L)^{4+}$  (analogous to  $MH_2L^{4+}$ ) is not stable but transfers a hydrogen ion from the more acidic  $H_2L^{2+}$  portion of the complex to the more remote and much more basic amine portion, L, and thus forms the stable complex  $M(HL)_2^{4+}$ . The acid pK value in Table II for  $CuH_2L^{4+}$

is estimated as 5.0, whereas for  $\text{Cu}(\text{HL})_2^{4+}$  the value is 7.6. Therefore, we can expect that the association constants for reaction 22 and also for reaction 24 include approximately 2.5 log units of stability which are provided by this energetically favored proton transfer, in addition to the stability due to the association of the species in the reaction. This effect is seen more dramatically, perhaps, in the comparison of the corresponding pairs of reactions, (17) with (20), (18) with (21), and (19) with (22). In the first two pairs, the stabilities show the expected decrease between the addition of the first and second ligand, whereas in going from reaction 19 to reaction 22 the constant for Cu actually increases because the added stability caused by the proton transfer is larger than the normal decrease between the addition of the second and third ligands.

Many other trends are apparent and will be discussed briefly. The end products formed in the sequence (20), (21), (22) are the same as those formed in (20), (25), (24), respectively, but whereas the constants follow the order (20) > (21) > (22) in the first series, we find that in the second series (20) < (25) < (24) because in this case the increasing positive charge resides not on the ligand but on the metal complex and thus facilitates association with the nucleophilic ligand. Likewise, in the series (22), (23), (24), the same end product,  $\text{M}(\text{HL})_2^{4+}$ ,

is formed in each case, but the constants follow the order (22) < (23) < (24), because in this order, the extra positive charges are switched from the ligand to the metal complex. This again favors stronger association. In addition if we allow for the (approximately) 2.5 log units of extra stability in the values for (22) and (24), the increase obtained is quite regular, being 3.3, 6.1 for Ni and 3.8, 6.3, 9.4 for Cu.

Finally, Anderegg<sup>5</sup> did not report the formation constant for the tricoordinated complex  $\text{Zn}(\text{adap})^{2+}$ , apparently because of the formation of hydrolysis products in an overlapping step as the bidentate  $\text{ZnH}(\text{adap})^{3+}$  was being converted to  $\text{Zn}(\text{adap})^{2+}$ . In this study, we were able to obtain a formation constant for the tricoordinated complex  $\text{ZnH}(\text{tam})^{3+}$  but unable to obtain a constant for  $\text{Zn}(\text{tam})^{2+}$  because of hydrolytic polynucleation which resulted in precipitate formation. Thus the appearance of hydrolysis in these Zn complexes seems to depend more on the charge of the complex than on the number of ligand donor groups bound.

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## Metal Ion Catalysis of Oxygen Transfer Reactions. I. Vanadium Catalysis of the Epoxidation of Cyclohexene<sup>1</sup>

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**Abstract:** The reaction of *t*-butyl hydroperoxide with cyclohexene, in the presence of catalytic quantities of the vanadium acetylacetonates  $\text{VO}(\text{acac})_2$  and  $\text{V}(\text{acac})_3$  or the octoate  $\text{V}(\text{oct})_3$ , gives quantitative yields of cyclohexene oxide at temperatures up to 84°, but this epoxidation is not catalyzed by the corresponding cobalt(II) derivatives or by di-*t*-butyl peroxalate. The reaction, as catalyzed by  $\text{VO}(\text{acac})_2$ , is first order in catalyst (in the range  $6 \times 10^{-5}$  to  $1.2 \times 10^{-3}$  M chelate), and, with cyclohexane as the major solvent component, is first order also in olefin (in the range 0.088–1.8 M). The epoxidation is strongly inhibited by *t*-butyl alcohol, a reaction product. Initial rates (extrapolated values) in cyclohexene conform to the rate law,  $\text{rate} = k[\text{V}_0]/\{1/[\text{P}]K_p + 1\}$ , where  $[\text{V}_0]$  is the concentration of added vanadium and  $[\text{P}]$  is the concentration of hydroperoxide. This is consistent with reaction *via* a hydroperoxide–vanadium complex (VP) having an association constant  $K_p$  and a specific rate  $k$ . Values of  $k$  lie between  $7.3 \text{ min}^{-1}$  (24.1°) and  $39.3 \text{ min}^{-1}$  (50.6°); activation parameters are  $\Delta H^\ddagger = 12.7 \text{ kcal/mole}$  and  $\Delta S^\ddagger = -19.8 \text{ eu}$ . Values of  $K_p$  are  $15.3 \text{ M}^{-1}$  at 24.1° and  $10.3 \text{ M}^{-1}$  at 50.6°. Rates in the presence of *t*-BuOH follow a more complex rate law (eq 3 in the text) of the type which indicates competitive inhibition by alcohol through two alcohol–vanadium complexes, VA and VA<sub>2</sub>, having association constants  $119 \text{ M}^{-1}$  and  $2.1 \times 10^4 \text{ M}^{-2}$  at 41.3°. The proposed mechanism involves neither a free-radical chain process nor a recycling of the metal between two oxidation states, but rather a rate-determining heterolysis of the O–O bond in a vanadium(V)–hydroperoxide complex. The structural requirements for this type of metal catalysis are considered.

It is widely recognized that the reactions of hydrogen peroxide and alkyl hydroperoxides may be strongly influenced by catalytic quantities of compounds of the

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transition metals; decomposition rates may increase dramatically, and the manner in which these oxidants react with oxidizable substrates may be seriously

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