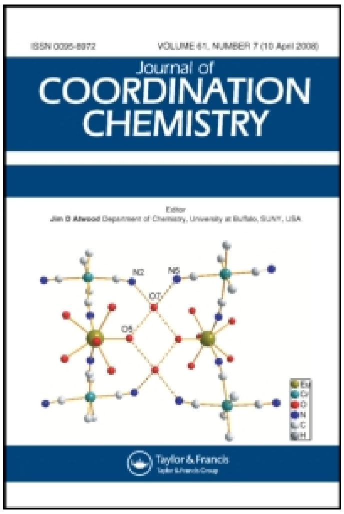

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THE SYNTHESIS OF 1,1,1-TRIS(AMINOMETHYL)ETHANE-N, N',N"-TRIACETIC ACID AND A STUDY OF THE STABILITY AND SPECTROSCOPIC PROPERTIES OF SEVERAL OF ITS METAL COMPLEXES

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THE SYNTHESIS OF 1,1,1-TRIS(AMINOMETHYL)ETHANE-N,N′,N″-TRIACETIC ACID AND A STUDY OF THE STABILITY AND SPECTROSCOPIC PROPERTIES OF SEVERAL OF ITS METAL COMPLEXES

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A potentially sexadentate amino acid 1,1,1-tris(aminomethyl)ethane-N,N′,N″-triacetic acid (TAMETA) was prepared by reacting its precursor amine 1,1,1-tris(aminomethyl)ethane (tame) with bromoacetic acid. The new amino acid TAMETA was characterized by elemental analysis, ir and nmr spectroscopy. Also, its Co(III) complex was prepared, isolated as a red solid, and characterized by elemental and spectroscopic analyses. In order to compare TAMETA with work reported previously on a related amino acid *cis,cis*-1,3,5-triaminocyclohexane-N,N′,N″-triacetic acid (TACHTA), equilibrium studies in aqueous solution with Co(II), Ni(II), Cu(II), and Zn(II), and electronic solution spectra with Co(II), Ni(II), and Cu(II) were performed. The details of the preparation of the solid [Co(III)-(TACHTA)] complex which had not been reported in the earlier paper on TACHTA complexes is included here.

INTRODUCTION

Metal complexes of the tripod ligands 1,1,1-tris-(aminomethyl)ethane (tame) and *cis,cis*-1,3,5-triaminocyclohexane (*cis,cis*-tach) have been studied extensively.[1–4] When bound to a metal ion, the three nitrogen atoms of these ligands occupy a face of the coordination polyhedron. Because of this stereochemical feature, derivatives of these amines have proven to be quite useful in studying metal complexes of unusual coordinative geometry.[5–7]

Previously, we reported[8,9] the synthesis of the amino acid derivative of *cis,cis*-tach, *cis,cis*-1,3,5-triaminocyclohexane-N,N′N″-triacetic acid (TACHTA). Our studies indicated that this ligand formed stable metal complexes in which three amine nitrogen and three carboxylate oxygen donor atoms occupy opposing faces on the metal. Because of the lack of other amino acids which produce coordinative environments similar to TACHTA, and which allow meaningful comparison of complex equilibria and spectroscopic data, we prepared the amino acid derivative of tame, 1,1,1-tris(aminomethyl)ethane-N,N′,N″-triacetic acid (TAMETA).

Now we report the synthesis and characterization of TAMETA and its Co(III) complex. The Co(II), Ni(II), and Zn(II) complexes of TAMETA were studied in solution by potentiometric pH titration, and in some cases by infrared and visible spectroscopy of solution and solid states. Comparison of the equilibrium constants and spectra of these TAMETA complexes with those of TACHTA and other related amino acids provided information about the stereochemistry of TAMETA complexes in solution as well as that of TACHTA complexes. Also, the details of the synthesis of the Co(III) complex are included here.

EXPERIMENTAL SECTION

1,1,1-Tris(aminomethyl)ethane (tame) – Fleischer's method which was previously reported[10] was employed with some modification for the synthesis of tame.[11] After catalytic reduction of the 1,1,1-tris-(azidomethyl)ethane, the ethanolic solution of tame was filtered and evaporated to give a yellow oil.[12] When this oil was distilled in vacuo,[10] a yield of approximately 90% of the pure amine (based on the weight of azide) was obtained as an almost colorless viscous oil. Nmr: $\delta^{CDCl_3}_{TMS}$ 0.75 (s,1,CH_3), 1.23 (s,2,NH_2), 2.50 (s,2,CH_2).

1,1,1-Tris(aminomethyl)ethane-N,N′,N″-triacetic acid Hydrobromide (TAMETA·3HBr). A solution of 874 mg. (7.45 mmol) of tame in 30 ml of boiled distilled water was heated to 50° and purged with nitrogen. A solution of 3.10g (22.4 mmol) of bromoacetic acid in 10 ml of water was neutralized with sodium hydroxide and then added dropwise over a fifteen-minute period to the solution of tame. The resulting mixture was stirred under nitrogen at a temperature between 50–60° for two days. During this period small additions of sodium hydroxide solution were necessary to keep the pH in the 7–8 range. Then the mixture was cooled, filtered, and treated with 5 ml of 48% hydrobromic acid. The amino acid hydrobromide salt (TAMETA·3HBr) was separated from the inorganic salt (sodium bromide) by fractional crystallization. The crude TAMETA·3HBr was recrystallized from 48% hydrobromic acid yielding 2.0g (3.5 mmol, 47%) TAMETA·3HBr·$2H_2O$ as off-white crystals, m.p. 180° dec. *Anal.* Calcd. for $C_{11}H_{21}N_3O_6 \cdot 3HBr \cdot 2H_2O$: C, 23.18; H, 5.11; N, 7.37; Br, 42.05. Found: C, 22.91; H, 5.01; N, 7.56; Br, 42.25. Nmr: $\delta^{D_2O}_{TMS}$ 2.00 (s,1, CH_3), 4.04 (s, 2, CH_2), 4.64 (s, 2, $CH_{2\,(glycyl)}$).

1,1,1-Tris(aminomethyl)ethane-N,N′N″-triacetato-cobalt(III) sesquihydrate, [Co(TAMETA]·1.5H₂O and cis,cis-*1,3,5-Triaminocyclohexane-N,N′,N″-triacetatocobalt(III) sesquihydrate, [Co(TACHTA)]·1.5H₂O.*[8] A solution containing an equimolar ratio of sodium tris(carbonato)cobaltate(III) trihydrate[13] and the appropriate amino acid salt (ca. 0.05*F*) was stirred at 50° for 8–10 hr. In the case of the TACHTA complex some red solid formed during this period. The precipitation of the Co(III) complexes was completed by the addition of ethanol (15 ml) and a small quantity of ether giving nearly theoretical yields. *Anal.[Co(TAMETA)]·1.5H₂O.* Calcd. for $C_{11}H_{18}N_3O_6Co \cdot 1.5H_2O$: C, 35.30; H, 5.66; N, 11.23; Co, 15.75. Found: C, 35.64; H, 5.55; N, 10.86; Co, 15.48. *[Co(TACHTA)]·1.5H₂O.* Calcd. for $C_{12}H_{18}N_3O_6Co \cdot 1.5H_2O$: C, 37.31; H, 5.48; N, 10.88; Co, 15.26. Found: C, 37.44; H, 5.72; N, 10.63; Co, 15.30.

Materials Solutions of TAMETA·3HBr were prepared from the recrystallized salt and standardized by titration with a standard sodium hydroxide solution. The number of moles of base required between the strong acid inflection (titration of three carboxylate protons) and the first weak acid inflection (titration of the first amine proton) was assumed to be equal to the number of moles of TAMETA·3HBr present.

Metal nitrate solutions prepared from reagent grade chemicals were standardized with EDTA.[14]

The titrant solution of 0.1 *N* ± 0.00005 sodium hydroxide obtained from Fisher Scientific Company was used without further standardization.

Procedures In general, titrations of metal-ligand systems were performed at concentrations ranging from $1.5 - 8 \times 10^{-3}$ *F* with equimolar quantities of metal and ligand although in some cases the metal-ligand ratio was varied. An alternate titration procedure was used in the Ni(II)-TAMETA system because of the relatively slow establishment of equilibrium. Each of the titration points in this system was obtained from a single solution. Each solution was prepared by adding equimolar amounts of metal and ligand, sufficient solid potassium nitrate for a 0.1 *F* solution, the amount of base required to achieve a specific *a* value (*a* equals the moles of base added per mole of ligand present), and water to the appropriate volume in a volumetric flask. These solutions were stored in a constant temperature bath (25°) and their pH values were recorded at 2-3 day intervals until they remained constant.

Solutions in the titration cell were protected from air by a stream of humidified, prepurified nitrogen. Special precautions were necessary to exclude oxygen from the Co(II)-TAMETA titration. These included placing two Cr(II) scrubbers in series in the nitrogen line, and presaturating the sodium hydroxide titrant solution with nitrogen.

Physical Measurements An Orion 801 pH meter was used in combination with Beckman glass and calomel electrodes. Calibration of the meter-electrode system was described previously.[9] The titrant was added by a Radiometer ABU 12 Autoburet. All measurements were done at 25° in 0.1 *F* KNO_3.

Electronic spectra were recorded with a Cary Model 14 spectrophotometer. Spectra were run on 1:1 solutions of TAMETA and Co(II), Ni(II), and Cu(II). Solid state spectra were obtained using the nujol mull technique.[15]

Infrared spectra were recorded with a Perkin-Elmer

225 spectrophotometer. Solids were run as KBr discs, and solutions of solids in D_2O were run between silver chloride plates.

Nmr spectra were recorded with a Varian A-60 spectrometer and the chemical shifts are relative to TMS (external capillary in the case of D_2O solvent).

Calculations Equilibrium constants were calculated from titration data by means of the generalized program SCOGS[16] adapted for a time-sharing Control Data Corp. 6600 facility and modified as described previously.[9]

RESULTS

Titrations The potentiometric titration curve of TAMETA·3HBr, H_6L^{3+}, contains three inflections, one at $a = 3$ corresponding to the titration of the three strongly acidic carboxylate protons, and two other inflections at $a = 4$ and $a = 5$, respectively. These latter two inflections correspond to the neutralization of two weakly acidic protonated amine groups. The Ka of the third amine proton is so small that no inflection for it is seen on the titration curve. The acidity constants are listed in Table I.

Titration curves obtained with equimolar mixtures of TAMETA·3HBr with Co(II) and Zn(II) are superimposable on the titration curve of the free acid alone between $a = 0$ and $a = 3$. This behaviour indicates that complexes of these metal ions with TAMETA are not present in appreciable concentrations until all the carboxylate protons have been neutralized. Between $a = 3$ and $a = 6$ the curves are depressed well below that of the free acid indicating complex formation. That complex formation occurs in two distinct steps is indicated by a weak inflection at $a = 5$ and a very steep inflection at $a = 6$.

Both Cu(II)- and Ni(II)-TAMETA titration curves feature inflections at $a = 5$ and $a = 6$, and in that respect are similar to the Co(II)- and Zn(II)-TAMETA curves. However, these curves are depressed below that of the free acid throughout the entire $a = 0$ to $a = 6$ region to the extent that the inflection at $a = 5$ is quite steep.

In general, calculations for metal-complex formation were made from data in the $a = 3$ to $a = 6$ region of the titration curve. In the case of the Cu(II)-TAMETA system where a significant amount of complex formation occurs below $a = 3$, a wider range of a values was used in the computation of the formation constants. Originally, the titration data was analyzed assuming the presence of many protonated and hydrolyzed species. However, computer analysis rejected many of these complex species,[9,17] and in all of the 1:1 metal-TAMETA systems studied, only two complex species ML^- and MHL are required to fit the experimental data within the estimated uncertainty in measurement. The stability constants obtained in this study are summarized in Table I.

Infrared spectra – Cobalt(III) complexes The infrared spectrum of solid $[Co(TAMETA)] \cdot 1.5H_2O$ shows an intense absorption band in the antisymmetric carboxylate stretching region with maxima at 1635 and 1600 cm^{-1}. Assuming that these maxima represent the only major absorptions for this complex

TABLE I
Acidity constants of TAMETA[a]

Reaction	–Log Ka
$H_3L \rightleftarrows H_2L^- + H^+$	4.69 ± 0.02
$H_2L^- \rightleftarrows HL^{2-} + H^+$	7.73 ± 0.01
$HL^{2-} \rightleftarrows L^{3-} + H^+$	10.73 ± 0.01

Stability constants of metal-TAMETA complexes[a]

	Log K			
Reaction	Co(II)	Ni(II)	Cu(II)	Zn(II)
$M^{2+} + L^{3-} \rightleftarrows ML^-$	12.56 ± 0.08	15.67 ± 0.04	16.32 ± 0.09	12.78 ± 0.03
$M^{2+} + HL^{2-} \rightleftarrows MHL$	7.64 ± 0.02	9.62 ± 0.02	12.74 ± 0.07	7.90 ± 0.01

[a] $\mu = 0.1$ (KNO_3) and temperature is 25.0°

in this region of the spectrum, the ratio of the band areas is calculated to be approximately 2:1 based on the 1635 cm^{-1} band as the major component. The spectrum of solid [Co(TACHTA)]·1.5H$_2$O shows only a single absorption peak at 1639 cm^{-1}. In contrast to the solid state spectra, the solution spectra in D$_2$O of both complexes feature only single sharp absorption maxima 1628 cm^{-1} for [Co(TACHTA)], and 1630 cm^{-1} for [Co(TAMETA)].

Electronic spectra The aqueous solution spectra of [Co(TACHTA)] and [Co(TAMETA)] are nearly identical. The red solutions exhibit two symmetrical absorption bands one in the visible and the other in the u.v. region (see Table II). These bands appear at positions similar to those reported for the β (facial-N) isomer of tris(glycinato)cobalt(III).[18] In octahedral symmetry these bands may be assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively. With respect to band positions, the solid state electronic spectra for both Co(III) complexes differ only slightly from their solution spectra. However, the intensity ratio of the high to low energy band increases significantly (ca. 45% for the [Co(TAMETA)]·1.5H$_2$O).

The spectrum of the [Co(TAMETA)]$^-$solution at pH = 11 shows two absorption bands, one at 19,600 cm^{-1} may be assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transitions, while the band at 9,350 cm^{-1} may arise from the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition. Computation of Dq[19] for [Co(TAMETA)]$^-$based upon the above assignments gives a value of 1010 cm^{-1}. A similar calculation of Dq for [Co(TAMETA)]$^-$in a previous work[9] gave a value of 1080 cm^{-1}.

A solution spectrum of [Ni(TAMETA)]$^-$is independent of pH in the 7 to 11 range and may be interpreted on the basis of an octahedral ligand field. The values of Dq and B (1100 cm^{-1} and 907 cm^{-1}, respectively) are based on the assignments ν_1 ($^3A_{2g} \rightarrow {}^3T_{2g}$) = 11,000 cm^{-1}, ν_2 ($^3A_{2g} \rightarrow {}^3T_{1g}$) = 17,900 cm^{-1}, and ν_3 ($^3A_{2g} \rightarrow {}^3T_{1g}(P)$) = 28,700 cm^{-1}. Corresponding values of Dq and B for [Ni(TACHTA)]$^-$are 1090 cm^{-1} and 907 cm^{-1}.[20] In both complexes absorption band positions calculated from the values of Dq and B are in close agreement with the observed positions[21] (see Table III). Because of the nonoverlapping equilibria between [Ni(TAMETA)]$^-$and [NiH(TAMETA)], it is possible to obtain a spectrum of the protonated complex (i.e. at pH = 4 75% of Ni(II) is present as [NiH(TAMETA)]). The absorption bands for this complex are broadened considerably, and band positions for ν_2 and ν_3 calculated on the basis of an octahedral model are in 10% error.

The [Cu(TAMETA)]$^-$spectrum at pH = 11 features a single absorption band centred at 16,400 cm^{-1} The position of this band is quite insensitive to changes in pH ($\nu_{\max}$ shifts by approximately 100 cm^{-1} as the pH is varied from 1.5 to 11.5).

The electronic absorption spectra of the complexes are summarized in Table II.

DISCUSSION

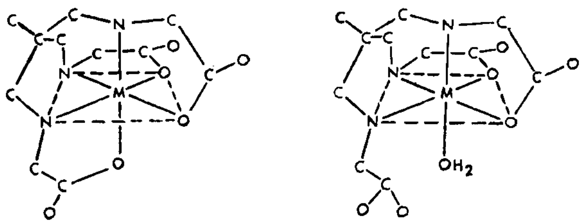
Cobalt(III) complexes Both TACHTA and TAMETA appear to form sexadentate octahedral Co(III) complexes in aqueous solution. Because of the stereochemistry of these ligands, the three amine nitrogen donor atoms must occupy one face of the octahedron while the three carboxylate oxygen donor atoms occupy the opposite face (I). These structures are supported by infrared spectra of the complexes in D$_2$O solution which show a single absorption band in the antisymmetric carboxylate stretching region at a position generally assigned to COO–Co(III).[22] Both complexes in aqueous solution show nearly identical electronic spectra (see Table II) while the absorption maxima and relative peak intensities are quite similar to that observed for the β (N-facial) isomer of [Co(gly)$_3$].[18]

TABLE II
Electronic absorption spectra (cm^{-1}) of the cobalt(III), cobalt(II), nickel(II), and copper(II) complexes[a,b]

Co(TACHTA)	19,500 (193), 27,200 (148)
CoTAMETA)	19,500 (193), 26,700 (155)
Co(TAMETA)$^-$	19,600 (10), 9,350 (4)
Ni(TAMETA)$^-$	11,000 (20), 12,700 sh, 17,900 (10), 28,700 (13)
NiH(TAMETA)	11,100 (15), 11,800 sh, 15,400 (10), 27,200 (11)
Cu(TAMETA)$^-$	16,400 (71)

[a] Numbers in parentheses are molar extinction coefficients.
[b] Spectra were recorded in aqueous solution at 20°C.

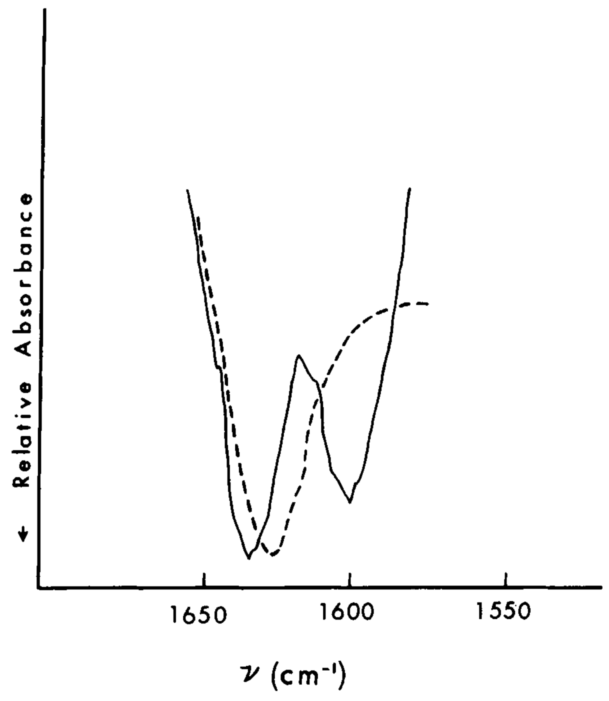
In the solid state the mode of complexation of TACHTA and TAMETA on Co(III) differs. The infrared spectrum of [Co(TACHTA)]$\cdot$1.5H_2O (KBr pellet) shows a single band at 1639 cm^{-1} which may be assigned to an antisymmetric carboxylate stretch of the COO–Co(III) type. The electronic spectrum of the same solid (nujol suspension) shows no appreciable shift in band position or change in relative peak intensity ratio ($^A\nu_1/^A\nu_2$) from the aqueous solution spectrum. For [Co(TACHTA)]$\cdot$ $\cdot$ 5H_2O it appears there is no change in coordination environment between solid and solution states. In contrast, the infrared spectrum of [Co(TAMETA)] $\cdot$ 1.5H_2O (KBr pellet) shows two well-resolved maxima in the ν_{asym} COO^- region (Figure). The larger band at 1635 cm^{-1} may be assigned to COO–Co(III), while the lower energy, less intense band at 1600 cm^{-1} may be assigned to free carboxylate COO^-, the latter assignment indicating that possibly one carboxylate group is unattached in the solid. Support for this conclusion derives from a comparison of the electronic spectra of solid (nujol suspension) and solution. Although no appreciable band shift is observed, a significant change does occur in relative peak intensity ratios: $^A\nu_1/^A\nu_2$ (solution) $>$ $^A\nu_1/^A\nu_2$ (solid). The structures postulated for [Co(TAMETA)] in the solid state and in aqueous solution are illustrated below.



I
Solution

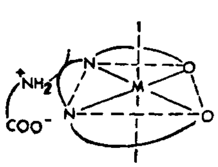
II
Solid

Proposed Stereochemistry of [Co(TAMETA)]

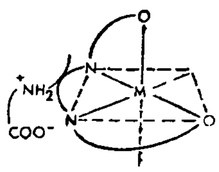


Infrared Spectra of [Co(TAMETA)]$\cdot$1.5H_2O solid (———) and D_2O solution (- - - -)

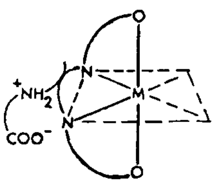
Stereochemistry of M(II) complexes Neutral MHL complexes in both the TAMETA and TACHTA systems may contain an uncoordinated glycine moiety ($-\overset{+}{N}H_2CH_2COO^-$). Assuming octahedral symmetry for the complexes, three structures for MHL based on the stereochemistry of the ligands (III, IV, V)† are possible.



III



IV



V

When the proton is removed from MHL, the ligand may assume either a sexa- or pentadentate function.

Co(II) complexes The electronic spectra of $[Co(TAMETA)]^-$ and $[Co(TACHTA)]^-$ are consistent with octahedral stereochemistry. The greater molar absorptivity for $[Co(TACHTA)]^-$ may be indicative of a larger degree of distortion imposed on the metal by the sterically rigid TACHTA.

Ni(II) complexes The electronic spectra of $[Ni(TAMETA)]^-$ and $[Ni(TACHTA)]^-$ are nearly identical. Observed band positions (Table III) are in agreement with the band positions calculated on the basis of Dq and B for an octahedral model.[19] However, the electronic spectrum of [NiH(TAMETA)] when compared with that for $[Ni(TAMETA)]^-$ shows the low energy band, ν_1, broadened and apparently shifted to slightly higher energy, and both ν_2 and ν_3 shifted to lower energies. In general, Dq values for NiN_2O_4 chromophores are found at lower energies

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†Structures are illustrated with TAMETA

TABLE III
Electronic spectral assignments for Ni(II)–amino acid complexes

Ni(TAMETA)$^-$		Ni(TACHTA)$^{-a}$		
ν(cm^{-1})	νcalc'd(cm^{-1})	ν(cm^{-1})	νcalc'd(cm^{-1})	Assignment(O$_h$)
11,000	–	10,900	–	$^3A_2g \dashrightarrow {}^3T_2g(\nu_1)$
12,700	–	12,800	–	$^3A_2g \longrightarrow {}^1E_g$
17,900	17,700	17,900	17,500	$^3A_2g \longrightarrow {}^3T_1g(F)(\nu_2)$
28,700	28,900	28,400	28,800	$^3A_2g \longrightarrow {}^3T_1g(P)(\nu_3)$
Dq = 1,100 cm^{-1} B = 927 cm^{-1}		Dq = 1,090 cm^{-1} B = 908 cm^{-1}		

Band (cm^{-1})	NiH(TAMETA)	Ni(EDDA)(H$_2$O)$_2$^{b}	Ni(gly)$_2$(H$_2$O)$_2$^{c}	Ni(DACODA)(H$_2$O)^b
ν_1	11,100	9,900	9,900	12,300 13,100^d
ν_2	16,500	16,400	16,200	15,800
ν_3	27,200	27,000	27,000	26,400

[a] See ref. 9.
[b] See ref. 24.
[c] See ref. 23b.
[d] Band splits in square pyramidal, five-coordinate geometry. See ref. 24 for assignments.

than those for the NiN_3O_3 type.[23] We suggest that the shift of ν_1 (10 Dq for O$_h$ Ni(II) complexes) to higher energies in [NiH(TAMETA)] is caused by the partial blocking of an axial site by a dangling carboxylate group which results in a distortion of the complex. The large error obtained in calculating the ν_2 and ν_3 band positions based on an octahedral model seems to support this theory. The octahedral complexes [Ni(EDDA)$(H_2O)_2$] and [Ni(gly)$_2$$(H_2O)_2$] have values of ν_2 and ν_3 similar to those in [NiH(TAMETA)]. The [Ni(DACODA)] complex, most likely a five-coordinate complex in solution, shows a trend similar to that for [NiH-TAMETA)] in position of absorption bands.[24] Although it is unlikely that [NiH(TAMETA)] is a five-coordinate species, it may be distorted from octahedral stereochemistry ($O_h \rightarrow C_{4v}$) in which the $^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$ splits giving rise to $B_1 \rightarrow B_2$ and $B_1 \rightarrow E$ components (band broadening effect) of which the higher energy component is more intense and this may account for its observed spectral properties (Table III).

Cu(II) complexes The electronic spectrum of 1:1 solutions of TAMETA and Cu(II) at low pH(1–3) shows a single absorption maximum at 16,300 cm^{-1}. The rule of average environment for tetragonally distorted Cu(II) complexes containing two N(amino) and two O(carboxylate) donors and two axially-coordinated water molecules predicts an absorption maximum at ca. 15,900 cm^{-1}.[25] Although this value seems to rule out the tetragonally-distorted structure proposed for [CuH(TAMETA)], (III), recent work[26] suggests that steric factors must be taken into consideration in analyzing the spectral data of tetragonally distorted Cu(II) complexes, and that the observed absorption maximum is consistent with the proposed structure.[27] [Cu(TAMETA)]$^-$absorbs at a slightly lower energy than [CuH(TAMETA)]. This behavior is expected for the Cu(II)-TAMETA system because the coordination of a nitrogen donor atom to a fifth coordination position (axial) will produce a bathochromic shift–"the pentaamine effect."[28] An analysis of the spectral data in the [Cu(TACHTA)]$^-$system similar to that done for [Cu(TAMETA)]$^-$could not be made because of the overlapping equilibrium between the ML and MHL species.

Based on the characteristic behavior of Cu(II) complexes in solution,[28,29] it is thought unlikely that either TAMETA or TACHTA function as sexadentate ligands with Cu(II).

Zn(II) complexes Zn(II) is known to form complexes with coordination numbers four and six. In both [Zn(TAMETA)]$^-$and [Zn(TACHTA)]$^-$, the potentiometric data (i.e. magnitude of pKa for MHL) suggest that Zn(II) has a coordination number greater than four.

Equilibrium studies The acidity constants of TAMETA are listed in Table I. As expected, it is a stronger acid than its protonated amine precursor

(H_3tame^{3+}).[1] A comparison of the acidity constants of TAMETA and TACHTA indicates that TAMETA is the stronger acid (pKa_3 for TACHTA = 7.17).[9] This acidity difference is attributed to the effectiveness of charge separation in the TACHTA molecule when it exists in the equatorial form. This same conformational effect prevents efficient intramolecular hydrogen bonding and may be responsible for reversing the trend for pKa_1 (pKa_1 for TACHTA = 9.60).[9]

The formation constants for TAMETA complexes with Co(II), Ni(II), Cu(II), and Zn(II) (Table I) follow the expected Irving-Williams order. When these constants are compared with similar constants obtained with TACHTA (Table IV) some interesting observations can be made. The overall formation constants (β_{ML}) obtained for TAMETA are approximately an order of magnitude less than those for TACHTA, and the acidity constants of the protonated metal complexes, MHL, are significantly lower with TACHTA. These differences are illustrated by the titration curves of the 1:1 metal(II)-ligand systems. The metal(II)-TAMETA curves all show an inflection at *a* = 5, while those of the metal(II)-TACHTA systems are smooth in this region. The differences in pKa's for the [MH(TAMETA)] and [MH(TACHTA)] complexes may be due to the difference in flexibility of the two ligands. The binding of the third nitrogen atom to the metal in the TACHTA complexes is accomplished easily since its degree of freedom is restricted by the stereochemistry of the cyclohexane ring. This effect is greatest in the case of Cu(II)($\Delta pKa_{MHL} \simeq 3.5$) but exists for all the M(II) systems studied.

Equilibrium constants for the formation of MHL from M^{2+} and HL^{2-} show that TACHTA forms more stable Co(II) and Ni(II) complexes, TAMETA forms a more stable Cu(II) complex, while neither ligand enhances the stability of the Zn(II) complex (Table IV). Although TACHTA must undergo a conformational change (equatorial (chair) to axial (chair) or skew (boat)) in order to form the protonated complexes, this conformational energy barrier is apparently not large enough to compensate for the basicity difference between the two amino acids. Thus, TACHTA forms more stable protonated complexes with Co(II) and Ni(II). With Cu(II) stereochemical effects cause a reversal in the order of stability [CuH(TAMETA)]>[CuH(TACHTA)]. Stereomodels indicate that if [CuH(TACHTA)] has a planar structure similar to that proposed for [CuH(TAMETA)], III, nonbonded contacts will tend to destabilize this complex. Since both Co(II) and Ni(II) complexes of TACHTA may assume less strained conformations in solution, i.e. IV and V, the expected order of stability is observed. Apparently, Zn(II) complexes possess some kind of intermediate stereochemistry in solution in which basicity and stereochemical factors effectively cancel out.

The [M(DACODA)] complexes are similar to the protonated TAMETA and TACHTA complexes in that they will contain two coordinated amine and

TABLE IV

Stability constants of amino acid complexes

Reaction: $M^{2+} + L^{q-} \rightleftarrows ML^{2-q}$

	log β_{ML}		
	TAMETA	TACHTA[a]	DACODA[b]
Co(II)	12.6	13.8	8.6
Ni(II)	15.7	16.6	10.3
Cu(II)	16.3	17.1	18.6
Zn(II)	12.8	13.4	11.3

Reaction: $M^{2+} + HL^{2-} \rightleftarrows MHL$ Reaction: $MHL \rightleftarrows ML^- + H^+$

	log K_{MHL}		−log Ka	
	TAMETA	TACHTA[a]	TAMETA	TACHTA[a]
Co(II)	7.6	8.3	5.8	4.1
Ni(II)	9.6	10.8	4.7	3.8
Cu(II)	12.7	11.2	7.2	3.7
Zn(II)	7.9	7.9	5.9	4.1

[a] Ref. 9
[b] Ref. 30

carboxylate groups.[24] A comparison of the formation constants log K_{MHL} for M(II) complexes of TAMETA and TACHTA with log β_{ML} for an analogous set of DACODA complexes (Table IV) shows that DACODA forms more stable Cu(II) and Zn(II) complexes and, within an order of magnitude, equally stable Ni(II) and Co(II) complexes.[30] Legg and coworkers[24] have demonstrated that when DACODA coordinates to Co(II), Ni(II), Cu(II), and Zn(II) the donor nitrogen and oxygen atoms are situated approximately in a square plane. A similar coordination environment may be found in the Cu(II) complexes of TAMETA and TACHTA (III), but their stability is lowered over that of [CuDACODA] possibly by stereochemical effects caused by a noncoordinated glycine moiety. This destabilizing steric effect is minimized in the corresponding Co(II) and Ni(II) complexes if we assume structures IV and V which differ from the square planar structures found for Co(II) and Ni(II) DACODA complexes. Although we are uncertain about the ligand coordinative environment of the protonated Zn(II) complexes of TAMETA and TACHTA, it is probably closer to square planar as indicated by the difference between their stability constants and that of [ZnDACODA].

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