

Complex Formation Equilibria between 1,1,1-Tris(N-methylaminomethyl)ethane and Nickel(II), Copper(II), Zinc(II) and Hydrogen Ions

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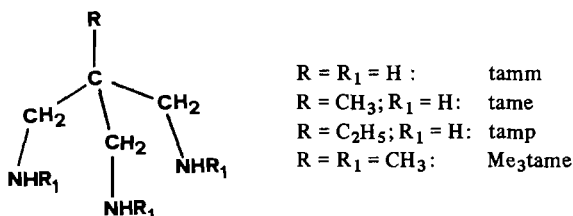
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The reactions of 1,1,1-tris(N-methylaminomethyl)ethane (Me_3tame) with nickel(II), copper(II), zinc(II) and hydrogen ions have been studied at 298 K in aqueous solution ($0.5 \text{ mol dm}^{-3} \text{ KNO}_3$) using potentiometric techniques. The equilibrium constants have been calculated using the computer program MIQUV. The stepwise equilibrium constants were obtained by combining the cumulative constants. Both basicity and stability constants have been compared with those previously reported for the similar non-methylated triamine 1,1,1-tris(aminomethyl)ethane (tame). Me_3tame is more basic than tame and forms less stable metal complexes. The ligand Me_3tame has little tendency to form protonated complexes and only $[\text{Cu}(\text{Me}_3\text{tame})\text{H}]^{3+}$ was found.

Introduction

Metal complexes with tripod-like ligands tamm, tame and tamp of general formula:



have been thoroughly investigated both from the synthetic and thermodynamic point of view [1–4]. In particular, thermodynamic data relative to the complex formation of the ligands 1,1,1-tris(aminomethyl)ethane, tame, and 1,1,1-tris(aminomethyl)propane, tamp, have been previously published by this laboratory [2–4].

We have now studied the equilibria of complex formation of the ligand Me_3tame and Ni(II), Cu(II) and Zn(II) ions. A comparison of both basicity and stability constants of this ligand with those of the related ligand tame is made to examine the influence of the N-methylation on the ability of the ligand to bind to hydrogen and/or metal ions.

Experimental

Preparation of the Ligand Me_3tame

$\text{Me}_3\text{tame} \cdot 3\text{HCl}$ was prepared as follows: 1,1,1-tris(chloromethyl)ethane (I) was prepared in 85% yield by reaction of 1,1,1-tris(hydroxymethyl)ethane with SOCl_2 in pyridine.

A solution of 10.5 g (0.06 mol) of (I) and 1.5 g of NaI in 70 cm^3 of anhydrous ethyl alcohol was then cooled and placed in an autoclave, 25 g of anhydrous methylamine (0.8 mol) was cooled and added to the reaction mixture, which was stirred and heated to 160 °C for 24 hours. The cooled reaction mixture was then concentrated under reduced pressure to yield a yellowish oil. The ligand Me_3tame was isolated as the hydrochloride derivative by bubbling gaseous HCl through a solution of the above crude product in diethyl ether. The white crystals of $\text{Me}_3\text{tame} \cdot 3\text{HCl}$ were filtered off and recrystallized twice from hot ethanol. The solid was dried under vacuum and the yield was 5.8 g of $\text{Me}_3\text{tame} \cdot 3\text{HCl}$ (36%). *Anal.* Calcd for $\text{C}_8\text{H}_{24}\text{N}_3\text{Cl}_3$: C, 35.77; H, 9.00; N, 15.64; Cl, 39.59%. Found: C, 35.9; H, 9.0; N, 15.8; Cl, 39.6%.

Materials

The potentiometric measurements were carried out in an ionic medium of $0.5 \text{ mol dm}^{-3} \text{ KNO}_3$. Merck products (Suprapur Grade) were used without purification. Standardized, CO_2 -free solutions of NaOH were prepared as before [3]. The concentration of metal ion solutions was determined gravimetrically by standard methods.

Emf Measurements

The potentiometric titrations were carried out using the fully automatic apparatus described elsewhere [5]. The experimental readings of the emf were not corrected for the liquid junction potential because this effect was negligible in the pH range investigated [6]. Experimental details concerning the emf titrations are shown in Table I.

TABLE I. Experimental Details of the Emf Measurements.

Curve	Ion	Initial Concentrations (mM)			pH Range	Number of Data Points
		MCl ₂	Me ₃ tame · 3HCl	HCl		
1	H ⁺		5.688	6.603	2.7–11.2	66
2	H ⁺		2.360	6.431	2.4–11.3	48
3	H ⁺		5.700	6.651	2.5–11.2	69
4	Cu ²⁺	2.266	8.969	3.384	4.4–11.0	89
5	Cu ²⁺	3.445	7.104	3.423	4.4–11.3	89
6	Cu ²⁺	0.800	9.759	3.397	4.4–11.0	89
7	Ni ²⁺	0.804	7.881	0.0	3.8–11.4	86
8	Ni ²⁺	1.720	8.419	0.0	3.8–10.0	61
9	Ni ²⁺	3.224	7.170	0.0	3.9–11.4	81
10	Zn ²⁺	0.883	7.948	0.0	6.4–11.6	80
11	Zn ²⁺	1.721	7.114	0.0	6.4–11.6	82
12	Zn ²⁺	4.113	8.808	6.637	6.5–7.8	25

Calculations

The new computer program MIQUV [7] was used to process the potentiometric data, and to calculate both basicity and stability constants. The criteria adopted in the procedure for selecting the species formed in the equilibria are discussed in detail elsewhere [3]. The errors associated with the stepwise constants have been calculated taking into account the standard deviations of the overall constants and the correlation coefficients between them.

Results and Discussion

Basicity Constants

Basicity constants of ligand Me₃tame are given in Table II and the basicity constants of the related ligand tame are given for the purpose of comparison in Table III. For the first protonation step Me₃tame is more basic than tame, for the second step it is only slightly more basic than tame, whereas for the third step of protonation tame is slightly more basic than Me₃tame. This makes the overall basicity constant of Me₃tame higher than that of tame. This is not unexpected because secondary polyamines have been found to be more basic than the corresponding primary polyamines [8, 9].

TABLE II. Logarithms of the Cumulative Formation Constants of the Species not Containing Metal, and Their Standard Deviations.

Formation Constant of Me ₃ tame (L)	log β
β _{HL}	10.641 ± 0.001
β _{H₂L}	19.006 ± 0.001
β _{H₃L}	24.616 ± 0.001
β _{OH}	-13.746 ± 0.001

TABLE III. Logarithms of the Stepwise Protonation Constants at 25 °C in 0.5 M KNO₃.^a

Reaction	Log K	
	L = Me ₃ tame	L = tame
H ⁺ + L ⇌ HL ⁺	10.641(1)	10.157(1)
H ⁺ + HL ⁺ ⇌ H ₂ L ²⁺	8.365(1)	8.252(3)
H ⁺ + H ₂ L ²⁺ ⇌ H ₃ L ³⁺	5.610(1)	5.854(6)
3H ⁺ + L ⇌ H ₃ L ³⁺	24.616(1)	24.263(3)

^a Values in parentheses are standard deviations on the last significant figure.

TABLE IV. Logarithms of the Cumulative Formation Constants of the Species Present in the Systems Nickel(II)–, Copper(II)– and Zinc(II)–Me₃tame and Their Standard Deviations.

Formation Constant	log β
β _{NiL}	9.369 ± 0.002
β _{CuL}	9.558 ± 0.003
β _{CuHL}	15.959 ± 0.003
β _{Cu(OH)L}	1.08 ± 0.01
β _{Cu(OH)₂L}	-10.60 ± 0.01
β _{Cu₂(OH)₂L₂}	5.02 ± 0.01
β _{ZnL}	5.888 ± 0.003
β _{Zn(OH)L}	-3.072 ± 0.009
β _{Zn(OH)₂L}	-12.575 ± 0.008

Nickel(II) Complexes

The stability constant for the system Ni(II)/Me₃tame is given in Table IV. The chemical model which best fits our experimental data is the one based on the formation of the single complex [Ni(Me₃tame)]²⁺. Other chemical models were tried but each new species introduced was rejected with

TABLE V. Logarithms of the Equilibrium Constants for Reactions of Complex Formation at 25 °C in 0.5 M KNO₃.^a

	L = Me ₃ tame			L = tame		
	M = Ni	M = Cu	M = Zn	M = Ni	M = Cu	M = Zn
M ²⁺ + L ⇌ ML ²⁺	9.369(2)	9.558(3)	5.888(3)	10.149(6)	10.97(1)	6.615(6)
M ²⁺ + HL ⁺ ⇌ MLH ³⁺		5.318(3)			8.234(5)	
ML ²⁺ + H ⁺ ⇌ MLH ³⁺		6.401(4)			7.42(1)	
ML ²⁺ + OH ⁻ ⇌ M(OH)L ⁺		5.27(1)	4.786(9)		5.51(2)	4.98(1)
M(OH)L ⁺ + OH ⁻ ⇌ M(OH) ₂ L		2.07(2)	4.24(1)			3.46(1)

^a Values in parentheses are standard deviations on the last significant figure.

a negative formation constant, except for the species [Ni(Me₃tame)₂]²⁺ which was retained (though without significant effect upon the value of the formation constant of [Ni(Me₃tame)]²⁺). The low value of Log β₂ (9.8) with respect to Log β₁ (9.3) and the low degree of formation of the [ML₂]²⁺ species (1% maximum in curve 7) allow us also to discard this species without significant deterioration in the fit. The logarithms of the stepwise equilibrium constants are shown in Table V so that we can compare and discuss the relative stability of the complexes of Me₃tame and tame. The single complex formed with Ni(II) and the ligand Me₃tame, namely [Ni(Me₃tame)]²⁺, is less stable than the corresponding complex with tame. This follows the pattern that secondary polyamines are more basic than primary polyamines and form less stable metal complexes. For the tame system no protonated species are formed. In general it can be seen that the less stable the metal complexes, the higher the pH required to form protonated species.

Copper(II) Complexes

The stability constants for the system Copper(II) Me₃tame are given in Table IV. The Copper(II) complexes with Me₃tame are much less stable than the corresponding complexes with tame. For example the constants for the 1:1 complexes are Log β₁ = 9.56 and 10.97 and for the addition of one proton to the complex [CuL]²⁺ to form [CuLH]³⁺ (see Table V) Log K = 6.40 and 7.42 for Me₃tame and tame respectively. Since the free ligand Me₃tame is more basic than tame, one might have expected the contrary. Because of the probable steric hindrance in complexes of Me₃tame it seems unlikely that the complex [Cu(Me₃tame)₂]²⁺ will be formed. At high pH values hydroxo-complexes are expected. Indeed the ligand Me₃tame does not form the species [Cu(Me₃tame)₂]²⁺ and the hydroxo species [Cu(Me₃tame)OH]⁺, Cu(Me₃tame)(OH)₂ and [Cu₂(Me₃tame)₂(OH)₂]²⁺ have been found. The equilibrium constant for the reaction involving the addition of a hydroxide ion to the complex [CuL]²⁺ is about the same for the two ligands Me₃tame and tame. The binuclear species

[Cu₂(Me₃tame)₂(OH)₂]²⁺ found in this system has been often found in other systems involving Cu(II) and sterically hindered polyamines [10].

Zinc(II) Complexes

The stability constants for the system Zinc(II)/Me₃tame are given in Table IV. They follow the same trend as observed for Ni(II) and Cu(II), [Zn(Me₃tame)]²⁺ being less stable than the corresponding complex [Zn(tame)]²⁺. Neither protonated species nor [Zn(Me₃tame)₂]²⁺ complexes were formed, but hydroxo species were present. The equilibrium constants for the stepwise addition of hydroxide ion to [Zn(Me₃tame)]²⁺ and [Zn(Me₃tame)(OH)]⁺ to form [Zn(Me₃tame)(OH)]⁺ and Zn(Me₃tame)(OH)₂ respectively are similar to those of tame.

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