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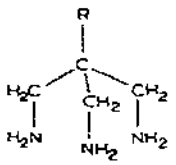
COMPLEX FORMATION EQUILIBRIA BETWEEN 1,1,1-TRIS(AMINOMETHYL)ETHANE AND DIVALENT TRANSITION METAL IONS: THE CHEMICAL MODEL AND THERMODYNAMIC QUANTITIES

A. SABATINI and A. VACCA

Laboratorio CNR, Istituto di Chimica Generale dell'Università, Via J. Nardi 39, 50132 Florence (Italy)

The ligand 1,1,1-tris(aminomethyl)ethane (hereafter abbreviated as tame) has three equivalent primary amino groups disposed at the base of a "tripod". This triamine and the two similar triamines, differing only in the substituent at the apical carbon atom, 1,1,1-tris(aminomethyl)methane (tamm) and 1,1,1-tris(aminomethyl)propane (tamp),



R = H tamm
R = CH_3 tame
R = C_2H_5 tamp

form complexes with transition metal ions which have been the subject of at least four previous studies [1—4]. The intramolecular bonds in these ligands force the three nitrogen atoms to occupy adjacent positions in the coordination sphere of the metal ion. If all three are bound to the metal they occupy a triangular face of the coordination polyhedron. Each pair of coordinated nitrogen atoms gives rise to a six-membered chelate ring.

Formation constants have previously been determined for some tamm and tame complexes [2—4]. A common feature of these reports is the absence of any formation constant for a species containing more than one ligand per metal ion. This is in obvious contrast with the fact that the solid compounds of tamm and tamp which have been isolated contain two molecules of ligand per metal ion [1,2]. Another point of discussion is the widely-held belief that tridentate ligands which contain peripheral amino groups only do not easily coordinate with all the donor atoms simultaneously [5].

The equivocal nature of the previous results has led us to study further the aqueous solution equilibria involving tame and the 3*d* transition metal ions Ni^{2+}, Cu^{2+} and Zn^{2+}. The scope of this work is twofold: (i) to verify the existence in solution of the 1 : 2 complexes that can be obtained as crystals,

and (ii) to find out what effect the relatively inflexible structure of the ligand and the system of six-membered chelate rings has upon the stereochemistry and stability of the complexes formed.

This is the first part of a complete thermodynamic study and in it we consider two strictly interconnected problems: the determination of the nature of the complex species which exist in the solution equilibria, usually referred to as the problem of species selection, and the determination of the species concentrations which in practice means the determination of the formation constants of the species selected. For the selection of species we used statistical methods [6] and for the computation of the formation constants we used our computer program MINIQUAD [7]. Thus the work also served to evaluate the speed, robustness and power of the computer program and statistical methods.

EXPERIMENTAL

tame. 3HCl was prepared by a published procedure and recrystallised from water and methanol [8]. The potentiometric measurements were carried out at 25°C in 0.5 *M* KNO_3 as previously described [9]. The standard potential of the cell was calculated for each titration curve by applying Gran's method [10] to the initial part of the curve and further Gran plots obtained at the end of the titration were used to check the analytical concentrations of the reagents for internal consistency. The concentration of metal ion and ligand and the $-\log [H^+]$ range for each titration curve are shown in Table 1.

CALCULATIONS

The equilibrium constants reported in this communication were obtained by simultaneous refinement relative to data from at least two different titra-

TABLE 1

Experimental details of the potentiometric measurements

Curve	Ion	Initial concentrations (m*M*)			$-\log [H^+]$ range	Number of data points
		$M(NO_3)_2$	tame.3HCl	HNO_3		
1	H^+	—	1.301	0.667	4.4—10.9	64
2	H^+	—	1.432	0.735	4.3—10.9	72
3	Ni^{2+}	0.975	1.179	0.613	4.8—8.1	26
4	Ni^{2+}	0.591	1.222	0.634	4.9—9.5	27
5	Ni^{2+}	0.732	1.191	0.619	4.9—10.9	36
6	Cu^{2+}	0.552	1.187	0.614	3.6—10.4	49
7	Cu^{2+}	0.325	1.196	0.658	3.7—10.5	42
8	Cu^{2+}	0.910	1.262	0.664	3.6—10.4	43
9	Zn^{2+}	0.397	1.198	0.615	4.8—10.9	45
10	Zn^{2+}	0.846	1.194	0.618	5.3—10.9	53

tion curves. The number of data points in each curve is shown in Table 1. The program MINIQUAD was run on an IBM 360/67 computer, using starting values of the formation constants estimated without the aid of preliminary computations.

There is, in our opinion, no problem of species selection in the determination of ligand protonation constants, since an excellent fit of the observed data was obtained postulating the presence of tameH$^+$, tameH_2^{2+} and tameH_3^{3+}. The other species containing metal ions were subjected to the following selection process.

The first calculation was based on a model consisting of the complexes which had previously been identified [4]. Other species were then introduced one after another in addition to the original species. The formation constants corresponding to each hypothesis advanced were obtained by least square refinement, along with their standard deviations and an agreement index R [11]:

$$R = \sqrt{\frac{\sum_i (f_i^{obs} - f_i^{calc})^2}{\sum_i (f_i^{obs})^2}}$$

In addition, MINIQUAD calculates a χ^2 statistic which is a measure of the normality of the distribution of the residuals $(f_i^{obs} - f_i^{calc})$ [7].

We reject a model as unsatisfactory if the R factor is greater than 0.004, which is the largest value that can be regarded as significantly different from zero when the errors in the observations are taken into account. The acceptable value of χ^2 at the 95% confidence level for 6 degrees of freedom [7], should be less than the expected value 12.6 [11]. In these systems, however, we were forced to accept a hypothesis with χ^2 greater than this value, presumably because of the inevitable systematic errors present in the data.

The overall stability constants are defined as follows:

$$\beta(MH_pL_r) = \frac{[MH_pL_r]}{[M][H]^p[L]^r} \quad \text{and} \quad \beta(M(OH)_qL_r) = \frac{[M(OH)_qL_r][H]^q}{[M][L]^r}$$

The convention regarding hydrolysed species follows that defined in Stability Constants [12].

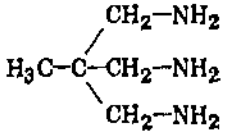
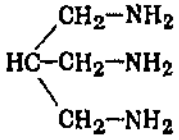
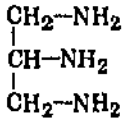
DISCUSSION

Basicity constants

The basicity constants of the ligands are shown in Table 2. The agreement between our values and those obtained previously is satisfactory in view of the different conditions of temperature and ionic strength used. The values for tamm are higher than for tame; since tame should be the more basic

TABLE 2

Basicity constants of 1,1,1-tris(aminomethyl)ethane, 1,1,1-tris(aminomethyl)methane) and 1,2,3-triaminopropane[a]

	Ionic strength	Temp. (°C)	log K_1	log K_2	log K_3	Ref.
	0.5 *M* KNO_3	25	10.157 (1)	8.252 (3)	5.854 (6)	this work
	0.1 *M*	20	10.48	8.48	5.80	[b]
	1 *M* KNO_3	22	10.61	8.86	6.90	[c]
	0.1 *M* $NaNO_3$	20	10.38	8.56	6.43	[d]
	0.1 *M* $NaNO_3$	20	9.59	7.95	3.72	[e]

[a] Values in parentheses are standard deviations on the last significant figure.
[b] Ref. 4.
[c] Ref. 2
[d] Ref. 3.
[e] Ref. 13.

amine on account of the inductive effect of the apical substituent, we surmise that steric effects may be important. The basicity constants of 1,2,3-triaminopropane [13] are lower than those of tame and tamm. This is in line with the fact that there is a carbon atom less in the aliphatic chain between the nitrogen atoms, bringing them both electronically and sterically closer together.

Nickel complexes

A summary of the selection process is given in Table 3. The species $Ni(H_2tame)^{4+}$, $Ni(Htame)^{3+}$ and $Nitame^{2+}$ selected in Ref. 4 gave a very poor fit ($R = 0.048$). In the next model, $Nitame_2^{2+}$ was included. This had two effects: the species $Ni(H_2tame)^{4+}$ was eliminated and both R and χ^2 improved drastically. This caused us to use this model as a base for the successive hypotheses — the introduction of $Ni(Htame)_2^{4+}$ and $Ni(Htame)tame^{3+}$ in succession. An even lower agreement index resulted and χ^2 also decreased significantly. The species $Nitamm_2^{2+}$, $Ni(Htamm)tamm^{3+}$ and $Ni(Htamm)_2^{4+}$ were inferred by Spiro and Ballhausen [2]. However they were not able to determine formation constants both for the lack, at that period, of suitable computational methods and because they only had a small quantity of ligand. A final trial including the species $Ni(H_2tame)^{4+}$ was unsuccesfull since the formation constant became negative and had consequently to be eliminated.

Copper complexes

The results of the species selection are shown in Table 4. The model Cu/1 based on previously reported results [4] is decidedly unsatisfactory. The introduction of other species has reduced the agreement index R and we can consider the last two as the better hypotheses. These differ in the presence of the copper hydroxide complex $Cu(OH)_2tame$, which is, at best, only a minor species. Because of this its inclusion has an insignificant effect upon the values of R, χ^2 and the formation constants, and the constant $\beta(Cu(OH)_2tame)$ comes out with a high standard deviation. We are inclined, as a general principle, to choose the simplest model when hypotheses do not differ significantly in respect of R and χ^2. In this case, therefore, we select Cu/8.

Zinc complexes

The results for the various models are shown in Table 5. The agreement index for the model selected by Kitajiri et al. [4] is decidedly unsatisfactory. The best values for R and χ^2 are obtained with Zn/4, which differs from the model accepted for copper(II) in the presence of a well defined bis-hydroxo mono-ligand complex, and the absence of the two protonated bis-ligand complexes. The inclusion of these two complexes did not bring about a significant improvement in the fit, and the χ^2 statistic was higher than for Zn/4. In one case the monoprotonated complex $Zn(Htame)^{3+}$ was rejected with a negative formation constant. We therefore select the model Zn/4.

TABLE 3

Logarithms of the formation constants of the Nickel(II)–tame complexes obtained using different hypotheses[a]

Hypothesis	MH_2L	MHL	ML	MH_2L_2	MHL_2	ML_2	R	χ^2
Ni/1	21[b]	15[b]	10.2(2)	—	—	—	0.0483	275
Ni/2	rejected	15.48(3)	10.161(5)	—	—	17.25(1)	0.0030	53
Ni/3	—	15.46(3)	10.14(1)	30.7(3)	—	17.27(2)	0.0029	87
Ni/4	—	15.54(2)	10.149(4)	—	24.05(8)	17.27(1)	0.0024	20
Ni/5	—	15.50(2)	10.104(9)	31.06(9)	24.19(6)	17.31(1)	0.0021	14

[a] M = Ni; L = tame; charges are omitted for simplicity; values in parentheses are standard deviations on the last significant figure.
[b] The standard deviation is greater than the value of the constant.

TABLE 4

Logarithms of the formation constants of the Copper(II)–tame complexes obtained using different hypotheses[a]

Hypothesis	MH_2L	MHL	ML	M(OH)L	$M(OH)_2L$	MH_2L_2	MHL_2	ML_2	R	χ^2
Cu/1	22[b]	18.3(2)	12.4(8)	—	—	—	—	—	0.0667	243
Cu/2	22[b]	18.37(6)	12.3(1)	4.3(2)	—	—	—	—	0.0202	121
Cu/3	—	18.36(6)	12.3(1)	4.3(2)	—	—	—	—	0.0202	116
Cu/4	—	18.36(3)	12.33(6)	3.67(9)	—	—	—	18.26(9)	0.0109	43
Cu/5	—	18.37(3)	12.29(6)	3.58(9)	—	—	25.86(9)	18.24(9)	0.0106	54
Cu/6	—	18.39(2)	11.40(8)	2.68(9)	—	34.41(6)	—	18.84(7)	0.0088	213
Cu/7	—	18.40(5)	10.9(4)	3.4(1)	—	34.3(1)	26.8(1)	—	0.0179	213
Cu/8	—	18.392(4)	10.97(1)	2.75(1)	—	34.37(1)	27.04(1)	18.70(1)	0.0015	21
Cu/9	—	18.392(4)	10.97(1)	2.75(1)	−9.0(2)	34.37(1)	27.06(1)	18.69(2)	0.0015	23

[a] M = Cu; L = tame; charges are omitted for simplicity; values in parentheses are standard deviations on the last significant figure.
[b] The standard deviation is greater than the value of the constant.

TABLE 5

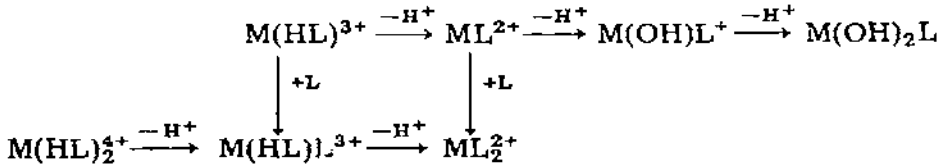
Logarithms of the formation constants of the Zinc(II)—tame complexes obtained using different hypotheses[a]

Hypothesis	MH_2L	MHL	ML	M(OH)L	$M(OH)_2L$	MH_2L_2	MHL_2	ML_2	R	χ^2
Zn/1	22[b]	rejected	7[b]	—	—	—	—	—	0.2516	208
Zn/2	rejected	13[b]	6.5(2)	−1.8(4)	—	—	—	—	0.0623	355
Zn/3	—	13.54(5)	6.613(8)	−2.05(1)	−12.40(2)	—	—	—	0.0033	45
Zn/4	—	13.54(4)	6.618(6)	−2.13(2)	−12.39(1)	—	—	10.88(7)	0.0025	21
Zn/5	—	13.57(5)	6.60(1)	−2.13(2)	−12.39(1)	—	19.0(8)	10.87(7)	0.0025	32
Zn/6	—	rejected	6.52(3)	−2.08(2)	−12.42(2)	27.67(8)	19.3(4)	—	0.0038	35

[a] M = Zn; L = tame; charges are omitted for simplicity; values in parentheses are standard deviations on the last significant figure.
[b] The standard deviation is greater than the value of the constant.

CONCLUSIONS

The complexes identified in this study are all mononuclear and can be organised in two deprotonation series:



With nickel(II) no evidence was obtained for the presence of a hydroxy complex. This result agrees with all previous studies of nickel(II) polyamine complexes. The $Cu(OH)_2$tame complex is extremely doubtful, and no serious error will be made if it is not considered. The two protonated bis-ligand complexes were not characterised in the zinc(II) system. We are unable to affirm the presence of species with the formula MH_2L^{4+} which other authors have reported in the case of tame [4] and similar systems [2,3]. This finding illustrates a general point. When a complex is rejected during the process of species selection, this signifies only that the complex is not formed in appreciable concentration under the given experimental conditions. It is possible, however, that upon changing drastically the experimental conditions a rejected complex is formed in larger amount and becomes well-defined.

The logarithms of the equilibrium constants for selected reactions are shown in Table 6. As will be seen, the simple copper(II) complexes are only slightly more stable than the corresponding nickel(II) complexes. This can be attributed to the particular inflexible structure of the ligand tame which imposes fac coordination, which is particularly unfavorable in the case of copper (II). Other structural deductions could be inferred from the values in Table 6,

TABLE 6

Logarithms of the equilibrium constants of some selected reactions[a]

Reaction	M = Ni	M = Cu	M = Zn
M^{2+} + tame → $Mtame^{2+}$	10.104(9)	10.97(1)	6.618(6)
$Mtame^{2+}$ + tame → $Mtame_2^{2+}$	7.21(2)	7.72(3)	4.26(8)
M^{2+} + $Htame^{+}$ → $M(Htame)^{3+}$	5.34(2)	8.235(5)	3.38(4)
$M(Htame)^{3+}$ + $Htame^{+}$ → $M(Htame)_2^{4+}$	5.4(1)	5.82(2)	
$M(Htame)^{3+}$ + tame → $M(Htame)tame^{3+}$	8.69(8)	8.66(1)	
$Mtame^{2+}$ + OH^- → $M(OH)tame^{+}$		5.51(2)	4.98(3)
$M(OH)tame^{+}$ + OH^- → $M(OH)_2$tame			3.47(3)

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

but it is well known that when such conclusions are based only on stability constant information they are rarely definitive. Calorimetric measurements are under way which will allow both the enthalpy and the entropy of each reaction to be determined, and this should lead to a sounder understanding of the factors involved in the equilibria.

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