Reactions of 1,1,1-Tris(aminomethyl)alkanes with Nickel(II), Copper(II), Zinc(II), and Hydrogen Ions. A Calorimetric and Spectrophotometric Investigation

By **Antonio Sabatini** * and **Alberto Vacca**, Istituto di Chimica Generale ed Inorganica, Laboratorio C.N.R., Via J. Nardi 39, 50132 Florence, Italy

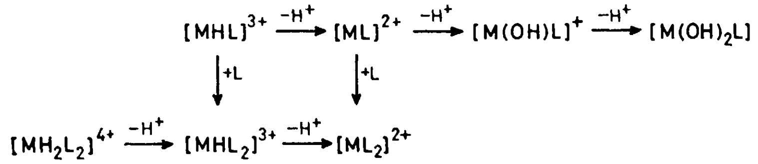
The enthalpy changes for the reactions of Ni^{2+}, Cu^{2+}, Zn^{2+}, and H^+ with $CH_3C(CH_2NH_2)_3$ and $CH_3CH_2C(CH_2NH_2)_3$ at 298 K in aqueous solution (0.5 mol dm^{-3} $K[NO_3]$) have been determined using continuous calorimetric titrations. The LKB–8700 calorimeter has been suitably modified for this purpose. A FORTRAN IV computer program has been employed to obtain the heats of formation of the complex species from the experimental data. By combination of the values of the enthalpy changes with the corresponding free-energy changes, reported elsewhere, values of the entropy of reactions have been calculated. Inspection of these thermodynamic quantities allows conclusions to be made about the co-ordinating properties of the two ligands. The visible spectra of the copper(II) complexes have been determined in order to get additional information about their structures.

THE formation of transition-metal complexes of 1,1,1-tris(aminomethyl)alkanes, of general formula $RC(CH_2NH_2)_3$, has been the subject of several previous papers.[1-4] These amines are potentially tridentate ligands containing peripheral primary amino-groups only. If all three nitrogen atoms are co-ordinated to the metal they are forced to occupy the corners of a triangular face of the co-ordination polyhedron, giving rise to the formation of a condensed system of six-membered chelate rings.

Crystalline complexes of 1,1,1-tris(aminomethyl)methane (tamm), 1,1,1-tris(aminomethyl)ethane (tame), and 1,1,1-tris(aminomethyl)propane (tamp) with 3*d* metal ions have been isolated and characterized,[1,4] and recently the *X*-ray analyses of two cobalt(III)–tame complexes were reported.[5]

Stability constants have previously been determined for some metal complexes of these ligands,[2] and we have recently investigated the complex-formation equilibria of tame and tamp with nickel(II), copper(II), and zinc(II) ions.[3] The formation constants of these metal complexes were determined at 25 °C in 0.5 mol dm^{-3} $K[NO_3]$. The complexes identified are all mononuclear and can be classified in two distinct deprotonation series (Scheme 1). All of the above complexes are formed by copper(II) with the exception of $[Cu(OH)_2L]$, no evidence was obtained for the presence at equilibrium of the protonated zinc(II) complexes $[ZnHL_2]^{3+}$ and $[ZnH_2L_2]^{4+}$, and with nickel(II) the two hydroxy-species and the complex $[NiH_2L_2]^{4+}$ have not been identified.

It is well known that definitive conclusions about the structure of complexes in solution cannot be drawn from $\Delta G^{\ominus}$ values only. Thus, in order to derive other valuable information about the co-ordination features of this type of ligand, the enthalpies of formation of nickel(II), copper(II), and zinc(II) complexes have been determined using calorimetric techniques. The visible spectra of the copper(II) complexes of tame and tamp have also been obtained and analysed.



$$\begin{tikzcd}
 & {[MHL]^{3+}} \arrow[r, "-H^+"] \arrow[d, "+L"] & {[ML]^{2+}} \arrow[r, "-H^+"] \arrow[d, "+L"] & {[M(OH)L]^{+}} \arrow[r, "-H^+"] & {[M(OH)_2L]} \\
{[MH_2L_2]^{4+}} \arrow[r, "-H^+"] & {[MHL_2]^{3+}} \arrow[r, "-H^+"] & {[ML_2]^{2+}} & &
\end{tikzcd}$$

SCHEME 1

EXPERIMENTAL

Materials.—The compounds tame·3HCl and tamp·3HCl were prepared as previously described.[2]

Aqueous solutions of sodium hydroxide, hydrochloric acid, nickel(II), copper(II), and zinc(II) chlorides were prepared and standardized as before.[3]

A 0.5 mol dm^{-3} potassium nitrate stock solution was made up from the reagent grade (Erba) chemical and used as the ionic medium for the calorimetric and spectrophotometric measurements. The amount of protolytic impurities contained in this solution was found to be negligible, as shown by Gran plots [6] obtained from strong acid–strong base pH titrations.

Calorimetric Measurements.—The LKB-8700 calorimetry system was modified in order to perform continuous titration experiments. The value of the thermistor resistance in the reaction vessel was obtained by measuring the output voltage of the unbalanced Wheatstone bridge. For this purpose, the electronic galvanometer and the null detector were replaced by a high-accuracy Schlumberger A200 digital voltmeter. During the calorimetric measurements the variable resistance of the Wheatstone bridge was kept constant (2 020 ohm). Under these conditions the output voltage of the unbalanced bridge was always within the range −0.600 to 1.600 mV.

A thermistor was incorporated into the precision thermostat bath in order to measure its temperature before and after each calorimetric titration. This thermistor can be inserted in the Wheatstone bridge circuit in place of the vessel thermistor using a suitable switch. Care was taken to maintain a constant room temperature (24.7 ± 0.2 °C), in order to avoid fluctuations of the bath temperature greater than 0.0005 °C.

In the continuous thermometric titrations a sodium hydroxide solution was added to the solution of the reagents in the calorimetric vessel. The titrant was introduced at a rigorously constant rate using a precision piston burette. The experimental details of the titrations performed are in Table 1.

TABLE 1

Experimental details of the calorimetric measurements

Ligand (L)	Metal ion	Initial quantities (mmol) MCl$_2$	L	HCl	Volume of initial solution/cm^3	Na[OH] added / mmol	Rate / mmol min^{-1}
tame			0.3346	1.0140	83.0	1.0958	0.1429
			0.2588	0.7956	80.4	0.9049	0.1429
			0.3018	0.8980	82.1	0.9543	0.1432
			0.3082	0.9009	81.5	0.9540	0.1431
	Ni^{2+}	0.2902	0.3121	1.5849	84.1	1.4154	0.1415
		0.2144	0.2862	1.4971	87.2	1.4241	0.1424
		0.1313	0.3065	1.5547	79.5	1.8395	0.1415
		0.1643	0.4358	1.9458	81.7	1.5509	0.1410
	Cu^{2+}	0.2185	0.3161	1.3866	81.7	1.3396	0.1435
		0.1381	0.3151	1.3840	84.3	1.5800	0.1436
		0.2595	0.3119	1.3649	83.4	1.2857	0.1429
		0.1539	0.2981	1.5339	83.1	1.8528	0.1425
	Zn^{2+}	0.3037	0.3021	1.3439	76.9	1.3040	0.1449
		0.2599	0.5552	2.8444	83.0	3.0217	0.1439
		0.1399	0.3009	1.5417	80.3	1.8576	0.1429
		0.1528	0.4738	2.0494	81.9	2.4053	0.1415
tamp			0.3484	0.9828	78.5	1.1435	0.1429
			0.3481	1.0505	81.9	1.1443	0.1430
			0.2997	0.8860	81.6	0.9525	0.1429
	Ni^{2+}	0.2869	0.2913	1.5163	87.0	1.4155	0.1415
		0.1244	0.2451	1.3546	86.3	1.6891	0.1408
		0.2091	0.2957	1.5249	83.8	1.4070	0.1407
		0.1606	0.4198	1.8816	82.6	1.5473	0.1407
	Cu^{2+}	0.2167	0.2808	1.2790	84.6	1.2238	0.1412
		0.1944	0.2913	1.3122	81.6	1.5746	0.1431
		0.3259	0.3236	1.4077	81.3	1.2820	0.1424
		0.1405	0.3006	1.3398	79.4	1.5702	0.1427
		0.3184	0.3275	1.4215	83.2	1.2959	0.1440
	Zn^{2+}	0.2034	0.7192	2.9662	83.2	2.7349	0.1439
		0.2824	0.3929	1.6138	80.8	1.5830	0.1439
		0.2999	0.5647	2.8709	78.1	3.0232	0.1440
		0.1399	0.2981	1.5241	79.8	1.8412	0.1416

A typical measurement consisted of seven stages: (*a*) pre-calibration, for *ca.* 5 min, in which no titrant was added; (*b*) electrical calibration, when a constant current, accurately measured, was applied through the resistance heater over a measured period of time (usually 5 min); (*c*) pre-reaction similar to (*a*); (*d*) reaction in which the reagent was added at constant rate; (*e*) post-reaction similar to (*a*); (*f*) electrical calibration similar to (*b*); and (*g*) post-calibration similar to (*a*).

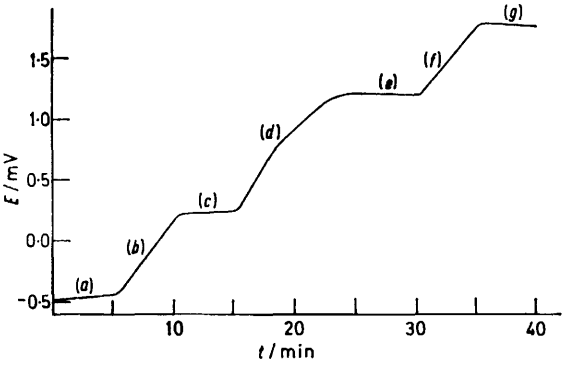


FIGURE 1 Voltage-time plot obtained from a typical calorimetric measurement. For steps (*a*)—(*g*) see text

Readings of the output voltage of the Wheatstone bridge were taken every 20 s. A voltage–time plot obtained from a typical measurement is shown in Figure 1.

Spectrophotometric Measurements.—Absorption spectra of solutions containing tame– and tamp–copper(II) complexes in 0.5 mol dm^{-3} K[NO$_3$] were recorded between 400 and 1 200 nm at room temperature on a Beckmann DK2 spectrophotometer fitted with 1-cm silica cells.

Eight different solutions were prepared for each system: weighed amounts of metal chloride, ligand trihydrochloride, and sodium hydroxide were mixed in order to achieve the most favourable conditions for the formation of all the complex species investigated. The analytical concen-

TABLE 2

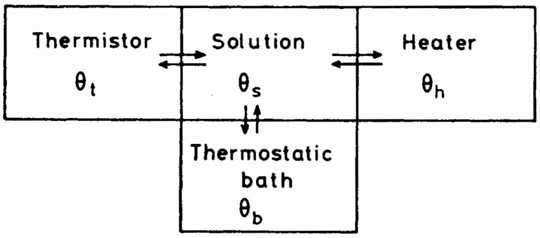
Experimental details of the spectrophotometric measurements

Ligand (L)	Concentrations (mol m^{-3}) CuCl$_2$	L	HCl	Na[OH]
tame	8.949	10.838	14.527	
	8.722	10.561	4.979	
	9.110	12.976		5.833
	9.569	13.630	3.951	
	8.635	19.006	12.380	
	8.302	18.278		1.920
	9.416	22.718	27.575	
	9.102	21.954	14.484	
tamp	7.610	9.361	14.125	
	7.484	9.205	4.672	
	9.410	13.370		5.761
	9.585	13.623	4.519	
	10.091	22.358	14.246	
	9.201	20.385	0.761	
	10.099	23.749	28.397	
	9.871	23.209	15.242	

trations of the reagents present in the above solutions are listed in Table 2.

CALCULATIONS AND RESULTS

Calorimetric Data.—The thermistor resistance and hence its temperature is obtained from the output voltage of the Wheatstone bridge. The temperature of the thermistor, θ_t, is usually somewhat different from that of the surrounding solution, θ_s, due to the finite value of the thermal leakage constant. A similar effect also operates between the solution and the heater at temperature θ_h. As a consequence, heat is exchanged between the solution and the thermistor as well as between the solution and the heater. There is also heat exchange between the solution in the vessel and the thermostat bath. The heat flow inside the calorimeter thus takes place between four different regions at different temperatures according to Scheme 2.



SCHEME 2

The differential change in heat content of any region is given by equation (1), where C is the heat capacity of the

$$dQ = Cd\theta = [W + K(\theta_e - \theta)]dt \qquad (1)$$

region, $d\theta$ is the differential temperature change of the region over the time interval dt, W is the power generated inside the region, and K is the thermal leakage constant for an external region at temperature θ_e. Equation (1) can be reformulated as (2). A system of three linear differential

$$d\theta/dt = \theta' = [W + K(\theta_e - \theta)]/C \qquad (2)$$

equations, (3)—(5), which describes the behaviour of

$$\theta_t' = [W_t + K_{ts}(\theta_s - \theta_t)]/C_t \qquad (3)$$

$$\theta_h' = [W_h + K_{hs}(\theta_s - \theta_h)]/C_h \qquad (4)$$

$$\theta_s' = [W_s + K_{ts}(\theta_t - \theta_s) + K_{hs}(\theta_h - \theta_s) + K_s(\theta_b - \theta_s)]/C_s \qquad (5)$$

thermistor, heater, and solution regions is obtained if θ_b is constant and θ_b' is consequently zero. Here C_t, C_h, and C_s are the heat capacities of the thermistor, heater, and solution respectively, W_t, W_h, and W_s are the powers which are generated in the thermistor, heater, and solution, and K_{ts}, K_{hs}, and K_s are the heat conduction constants between solution and thermistor, solution and heater, and solution and thermostat bath, respectively. In equation (5) W_s is the resultant of several terms [equation (6)] where W_{st},

$$W_s = W_{st} + W_r + W_{dil} + W_{tit} \qquad (6)$$

W_r, W_{dil}, and W_{tit} are power contributions generated in the solution due to mechanical stirring, chemical reactions, dilution of the titrant, and temperature difference between titrant and solution, respectively.

The set of differential equations can be solved by using a Taylor series expansion. This procedure allows calculation of values of the thermistor temperature as a function of time, which can be compared with the experimental data. A number of FORTRAN IV least-squares computer programs have thus been written to determine the parameter set which gives the best fit between observed and calculated values. Only parameters which cannot be evaluated by separate calibration experiments and are specific to each experimental run (*e.g.* heat capacity of the solution, enthalpy of reaction, *etc.*) are refined by the least-squares method. The whole calculation procedure will be described in detail elsewhere.[7]

Chemical calibration of the calorimeter was accomplished by measuring the heat of neutralization of hydrochloric acid with sodium hydroxide in 0.5 mol dm^{-3} potassium nitrate. The value obtained, 13.535 ± 0.004 kcal mol^{-1},[*] is in excellent agreement with a previously reported value.[8]

Table 3 shows the thermodynamic functions $\Delta G^\ominus$, $\Delta H^\ominus$, and $\Delta S^\ominus$ for some reactions. The algorithm used to derive the standard deviations of $\Delta G^\ominus$ values was described previously.[3] The standard deviations of $\Delta H^\ominus$ values were obtained analogously. Finally, the standard deviations of $T\Delta S^\ominus$ values were calculated by simply adding the standard deviations of the corresponding $\Delta G^\ominus$ and $\Delta H^\ominus$ values.

Spectrophotometric Data.—The concentrations of the species present in each solution of Table 2 were calculated by solving the three simultaneous mass-balance equations. The values of the equilibrium constants used in the calculations were those previously reported [3] and molar absorption coefficients of the complexes were obtained by a least-squares procedure. The calculated spectra are shown in Figure 2.

DISCUSSION

Table 3 shows the values of the thermodynamic functions $-\Delta G^\ominus$, $-\Delta H^\ominus$, and $\Delta S^\ominus$ for the protonation of tame and tamp.

All the heats of stepwise protonation are nearly equal for both amines. The values increase slightly for tamp but are coincident within two standard deviations for tame. Such behaviour has not been found previously for aliphatic triamines.[9] Another interesting feature is that the total heat of protonation is the same for these two amines and very similar to the corresponding value reported for tach (*cis,cis,cis*-1,3,5-triaminocyclohexane),[10] which also contains three equivalent primary amino-groups.

The compound tamp is slightly more basic than tame for the first protonation step on account of the more favourable entropy term which outweighs the less favourable enthalpy contribution. This fact can be explained by assuming that the Htamp$^+$ species is less hydrated than Htame$^+$ as a consequence of the more bulky alkyl group present. The compound tame becomes progressively more basic than tamp in the two successive protonation steps, particularly the third. This result can be explained by considering the structural differences between the two amines. Thus, the greater size of the aliphatic chain, going from tame to tamp, produces a decrease in the local dielectric constant: the repulsion between the protonated amino-groups present

---

[*] Throughout this paper: 1 cal = 4.184 J.

in the polycharged cation is greater for tamp, which is accordingly less basic. Furthermore, the lower effective dielectric constant for tamp causes a more marked stiffening of the aliphatic chain and a greater interaction with water molecules, as shown by the lower entropy changes.

Nickel(II) *Complexes*.—As shown by the $-\Delta G^\ominus$ values reported in Table 3, the addition of one ligand molecule is more favoured for tamp than for tame. The greater stability of the $[\mathrm{Ni(tamp)}]^{2+}$ complex is due to the more favourable entropy contribution which outweighs the less favourable enthalpy term. For the second formation step the two enthalpy values are coincident within the standard deviations and the formation of the tamp complex is mainly favoured by the entropy contribution.

TABLE 3

Thermodynamic functions $\Delta G^\ominus$, $\Delta H^\ominus$ (kcal mol^{-1}), and $\Delta S^\ominus$ (cal K^{-1} mol^{-1}) for the reactions of tame and tamp with H^+, Ni^{2+}, Cu^{2+}, and Zn^{2+} at 25 °C in 0.5 mol dm^{-3} K[NO$_3$] *

	L = tame			L = tamp		
Reaction	$-\Delta G^\ominus$	$-\Delta H^\ominus$	$\Delta S^\ominus$	$-\Delta G^\ominus$	$-\Delta H^\ominus$	$\Delta S^\ominus$
$\mathrm{L + H^+ \longrightarrow HL^+}$	13.856(2)	11.72(4)	7.2(1)	13.956(2)	11.48(2)	8.3(1)
$\mathrm{HL^+ + H^+ \longrightarrow H_2L^{2+}}$	11.259(3)	11.65(3)	−1.3(1)	11.146(3)	11.68(2)	−1.8(1)
$\mathrm{H_2L^{2+} + H^+ \longrightarrow H_3L^{3+}}$	7.983(4)	11.71(2)	−12.5(1)	7.542(4)	11.94(1)	−14.7(1)
$\mathrm{L + 3H^+ \longrightarrow H_3L^{3+}}$	33.098(5)	35.08(2)	−6.65(9)	32.644(5)	35.10(1)	−8.24(6)
$\mathrm{Ni^{2+} + L \longrightarrow [NiL]^{2+}}$	13.85(1)	10.66(7)	10.7(3)	14.28(1)	10.11(5)	14.0(2)
$\mathrm{[NiL]^{2+} + L \longrightarrow [NiL_2]^{2+}}$	9.71(2)	10.99(8)	−4.3(3)	10.23(1)	11.07(6)	−2.8(2)
$\mathrm{[NiHL]^{3+} + L \longrightarrow [NiHL_2]^{3+}}$	11.62(8)	9.6(3)	7(1)	12.20(8)	10.7(4)	5(2)
$\mathrm{Ni^{2+} + HL^+ \longrightarrow [NiHL]^{3+}}$	7.34(3)	7.5(2)	−0.5(6)	7.01(3)	7.2(2)	−0.5(8)
$\mathrm{[NiL]^{2+} + HL^+ \longrightarrow [NiHL_2]^{3+}}$	5.1(1)	6.4(4)	−5(2)	4.9(1)	7.7(5)	−9(2)
$\mathrm{[NiL]^{2+} + H^+ \longrightarrow [NiHL]^{3+}}$	7.34(3)	8.6(2)	−4.1(8)	6.70(3)	8.5(2)	−6(1)
$\mathrm{[NiL_2]^{2+} + H^+ \longrightarrow [NiHL_2]^{3+}}$	9.25(8)	7.2(4)	7(2)	8.65(8)	8.1(4)	2(2)
$\mathrm{Cu^{2+} + L \longrightarrow [CuL]^{2+}}$	14.97(2)	15.2(2)	−0.8(7)	15.23(2)	13.4(1)	6.1(5)
$\mathrm{[CuL]^{2+} + L \longrightarrow [CuL_2]^{2+}}$	10.54(3)	7.6(2)	9.9(7)	11.12(3)	8.7(1)	8.2(6)
$\mathrm{[CuHL]^{3+} + L \longrightarrow [CuHL_2]^{3+}}$	11.81(2)	10.2(1)	5.4(4)	12.43(3)	9.8(2)	8.8(6)
$\mathrm{Cu^{2+} + HL^+ \longrightarrow [CuHL]^{3+}}$	11.23(1)	12.46(3)	−4.5(1)	11.18(1)	12.53(3)	−4.5(1)
$\mathrm{[CuL]^{2+} + HL^+ \longrightarrow [CuHL_2]^{3+}}$	8.07(3)	7.4(2)	2.2(8)	8.38(3)	8.9(2)	−1.8(9)
$\mathrm{[CuHL]^{3+} + HL^+ \longrightarrow [CuH_2L_2]^{4+}}$	7.93(2)	11.1(1)	−10.6(4)	8.06(3)	11.1(1)	−9.8(6)
$\mathrm{[CuL]^{2+} + H^+ \longrightarrow [CuHL]^{3+}}$	10.12(2)	9.0(2)	3.8(7)	9.90(2)	10.6(1)	−2.3(5)
$\mathrm{[CuL_2]^{2+} + H^+ \longrightarrow [CuHL_2]^{3+}}$	11.39(2)	11.6(1)	−0.7(5)	11.21(3)	11.7(2)	−1.7(7)
$\mathrm{[CuHL_2]^{3+} + H^+ \longrightarrow [CuH_2L_2]^{4+}}$	9.98(2)	12.7(2)	−9.1(8)	9.59(2)	12.7(2)	−10.3(9)
$\mathrm{[CuL]^{2+} + OH^- \longrightarrow [Cu(OH)L]^+}$	7.52(3)	0.4(8)	24(3)	7.87(3)	3.3(2)	15.4(9)
$\mathrm{Zn^{2+} + L \longrightarrow [ZnL]^{2+}}$	9.02(1)	6.08(6)	9.9(2)	9.41(1)	5.44(3)	13.3(1)
$\mathrm{[ZnL]^{2+} + L \longrightarrow [ZnL_2]^{2+}}$	5.80(8)	5.0(3)	3(1)	5.93(3)	5.0(1)	3.2(5)
$\mathrm{Zn^{2+} + HL^+ \longrightarrow [ZnHL]^{3+}}$	4.60(4)	4.7(2)	−0.2(7)	4.52(3)	4.8(1)	−1.0(5)
$\mathrm{[ZnL]^{2+} + H^+ \longrightarrow [ZnHL]^{3+}}$	9.43(4)	10.3(2)	−2.8(8)	9.10(3)	10.9(1)	−5.9(5)
$\mathrm{[ZnL]^{2+} + OH^- \longrightarrow [Zn(OH)L]^+}$	6.79(1)	0.9(4)	20(1)	6.85(1)	0.4(2)	21.7(6)
$\mathrm{[Zn(OH)L]^+ + OH^- \longrightarrow [Zn(OH)_2L]}$	4.72(1)	3.5(5)	4(2)	4.42(3)	3.4(3)	4(1)

* Values in parentheses are standard deviations in the last significant figure.

The enthalpy changes for the reactions involving addition of the bidentate HL^+ ligand are nearly equal and markedly lower than the corresponding values obtained for the reactions with the unprotonated amine. This result shows clearly that tame and tamp behave as tridentate ligands with respect to the nickel ion, and is confirmed by the values of the thermodynamic functions for protonation of the co-ordinated ligand. Both $-\Delta G^\ominus$ and $-\Delta H^\ominus$ values for these reactions are noticeably lower than the corresponding values for the first stage of protonation of the free ligands.

Copper(II) *Complexes*.—The reactions involving addition of one ligand molecule are more favoured for tamp than for tame, as for the nickel(II) complexes.

As far as the formation of the 1 : 1 complexes is concerned, the greater stability of the $[\mathrm{Cu(tamp)}]^{2+}$ complex is due to the entropy contribution which outweighs the less favourable enthalpy change. These reactions are, as expected, more exothermic than those of nickel(II). The associated entropy changes are extremely low, particularly for the formation of $[\mathrm{Cu(tame)}]^{2+}$ (−0.8 cal K^{-1} mol^{-1}). Negative values of entropy changes have never been found for similar reactions of copper(II) with aliphatic polyamines.[9]

The second step of complex formation for both ligands is less exothermic than the first. The increase of $\Delta S^\ominus$ values on going from the first to the second stage of complex formation is just the opposite of what has been previously found for similar systems.[9]

The addition of one ligand molecule to the protonated complex $[\mathrm{CuHL}]^{3+}$ is more exothermic than the corresponding reaction with the $[\mathrm{CuL}]^{2+}$ complex.

The $-\Delta H^\ominus$ values for protonation of the co-ordinated ligand are close to the corresponding values for protonation of the free ligand. From these results it may be inferred that one nitrogen atom is either not bonded or weakly bonded to the copper(II) ion.

In order to get additional information about the structure of these complexes, their visible spectra were examined (Figure 2). The absorption spectra of corresponding complexes of the two ligands are almost superimposable, except for the 1 : 1 complexes. This result is in agreement with the thermochemical quantities, which, for these complexes, exhibit the largest differences. The spectrum of the diprotonated species $[\mathrm{Cu(HL)_2}]^{4+}$ is clearly different from that of $[\mathrm{Cu(HL)L}]^{3+}$, which shows a shoulder at *ca.* 12 000 cm^{-1}. This result can be attributed to the different structures of the two complexes. The complex ion $[\mathrm{Cu(HL)_2}]^{4+}$ should have four nitrogen atoms bonded to the metal in the equatorial plane of the co-ordination octahedron. Therefore a fifth metal–nitrogen bond should be present in the species [Cu(HL)L]$^{3+}$ in an axial position. The spectra of [Cu(HL)L]$^{3+}$ and [CuL$_2$]$^{2+}$ are quite similar, implying that these species should have the same type of co-ordination. The spectrum of the complex [Cu(tame)$_2$]$^{2+}$ has been recently described,[4] the reported data being in excellent agreement with our values.

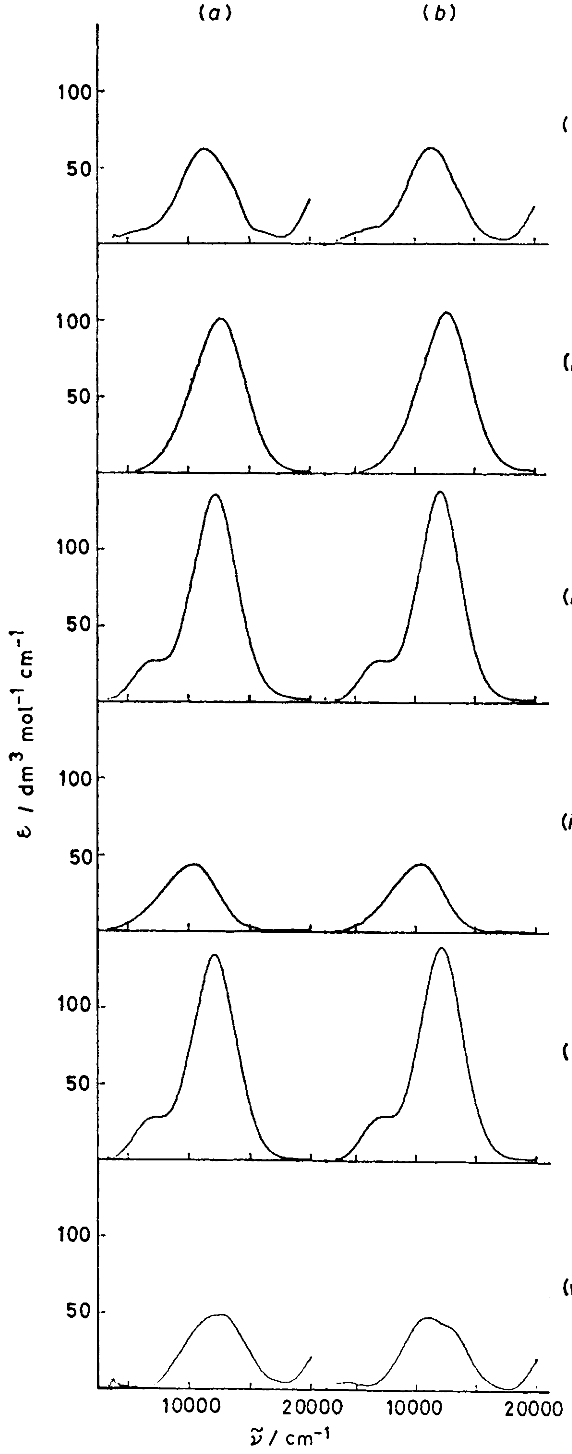


FIGURE 2 Absorption spectra of copper(II) complexes formed by tame (a) and tamp (b) in 0.5 mol dm^{-3} K[NO$_3$]. Species: (i) [Cu(OH)L]$^+$; (ii) [CuH$_2$L$_2$]$^{4+}$; (iii) [CuHL$_2$]$^{3+}$; (iv) [CuHL]$^{3+}$; (v) [CuL$_2$]$^{2+}$; (vi) [CuL]$^{2+}$

The reaction of hydroxide ion with the [CuL]$^{2+}$ complex is slightly more favoured for tamp than for tame. This is due to the enthalpy contribution which prevails over the less favourable entropy term.

Zinc(II) *Complexes*.—As far as the stepwise reactions of complex formation for [ZnL]$^{2+}$ and [ZnL$_2$]$^{2+}$ are concerned, a regular decrease of the $-\Delta G^{\ominus}$ values, a decrease of the $-\Delta H^{\ominus}$ values, and the usual decreasing trend of the entropy changes are found.

The enthalpy changes for the reactions of the bidentate ligands HL$^+$ with the zinc ion are less negative than those found for the formation of [ZnL]$^{2+}$, and are very close to those obtained for the stepwise formation of [ZnL$_2$]$^{2+}$. This can be explained by assuming that the first ligand molecule acts as a tridentate chelate, whilst the second one is bound to the metal with only two nitrogen atoms.

The $\Delta S^{\ominus}$ values for the formation of the complexes [ZnL]$^{2+}$ are very similar to those observed for the corresponding reactions of nickel(II). This strongly suggests that the corresponding complexes have the same structure. The entropy changes for the stepwise formation of the complexes [ZnL$_2$]$^{2+}$ are markedly greater than those observed for the nickel(II) complexes. This can be explained by assuming that the zinc in [ZnL$_2$]$^{2+}$ is five-co-ordinated: only two nitrogen atoms of the second ligand molecule are co-ordinated, replacing three water molecules in the co-ordination sphere of the zinc(II) ion.

The addition of hydroxide ion to [ZnL]$^{2+}$ occurs for both ligands with a very small enthalpy change and a large positive entropy change, in agreement with the interpretation that bonding of hydroxide ion to [ZnL]$^{2+}$ occurs with release of more than one water molecule. The second addition of hydroxide ion is more exothermic than the first, indicating that in this case the formation of the complex does not imply the removal of more than one water molecule.

Conclusions.—The behaviour of the two ligands, tame and tamp, is quite different from that observed for other aliphatic triamines. This is not surprising since these two amines differ from the others in the presence of three equivalent primary amino-groups. The triamine tach, which has been the subject of recent investigations,[10,11] possesses similar structural properties. Unfortunately, few complex-formation enthalpies are reported in the literature for this amine.[10]

The small structural difference between tame and tamp (a CH$_2$ group) is responsible for the significant differences in the thermodynamic quantities for both protonation and complex-formation reactions of the two ligands. Addition of the neutral ligand to positive ions (H$^+$, M^{2+}, [ML]$^{2+}$, [MHL]$^{3+}$) is always favoured for tamp, due to the entropy term which outweighs the less favourable enthalpy change. This result can be explained by assuming that such reactions occur with the release of more water molecules for tamp than for tame.

In contrast, reactions between the protonated ligand and positive ions are favoured for tame. This is due to the fact that the electrostatic repulsion between the positive charges present in the species formed is greater in the case of tamp, because of the lower local dielectric constant associated with the more bulky aliphatic skeleton. The stronger electrostatic field around these tamp complexes gives rise to a greater ordering of the solvation water molecules and this is reflected in the less favourable entropy term.

The thermodynamic functions are consistent with full co-ordination of both ligands in the nickel complexes. All these species should have octahedral configurations as shown in Figure 3.

The complexes $[ZnL]^{2+}$ and $[ZnHL]^{3+}$ are presumably octahedral, whilst the zinc in $[ZnL_2]^{2+}$ should be five-co-ordinated. The thermodynamic functions show clearly that in the first hydrolysis step of $[ZnL]^{2+}$ there is a decrease of the metal co-ordination number. The metal ion in the monohydroxo-complex is probably also five-co-ordinated. Tentatively, it can be assumed that further hydrolysis occurs with no change in the co-ordination number of the zinc(II) ion, as shown in Figure 3.

It is difficult to propose structures for the copper(II) complexes on the basis of the thermodynamic results. The entropy change for the formation of $[Cu(tame)]^{2+}$ is exceptionally low, *ca.* 10 cal K^{-1} mol^{-1} less than the corresponding values reported for other aliphatic triamines.[9] Going from the first to the second formation step of the copper(II) complexes of both tame and tamp, an increase of the entropy change is observed: exactly the opposite of what usually occurs. This anomalous behaviour is presumably due to the different structure of these amines with respect to those previously investigated. The compounds tame and tamp contain three equivalent primary amino-groups and the three nitrogen atoms are forced to occupy the corners of a triangular face of the co-ordination polyhedron of the metal ion. Such a facial co-ordination is not the most favourable for copper(II) ion.

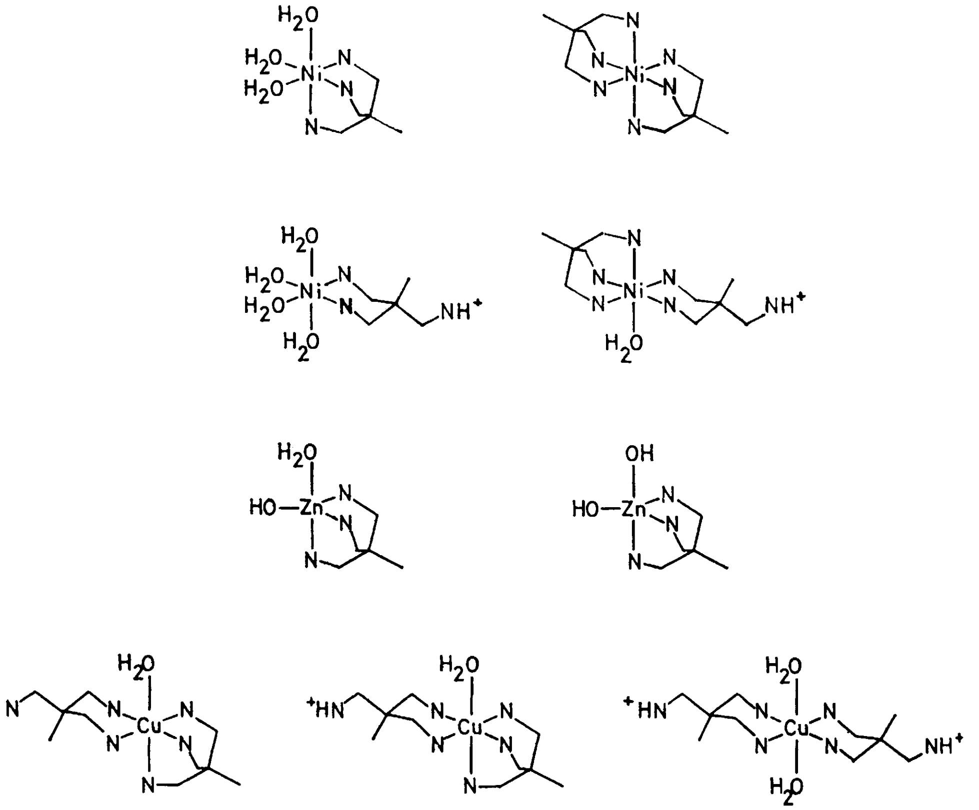


FIGURE 3 Schematic representation of the suggested structures for the metal complexes of tame and tamp

The structures of the 1 : 2 copper(II) complexes can be assigned with greater confidence. The spectral data are consistent with a tetragonally distorted octahedral co-ordination, where one ligand in the axial position is always a water molecule as shown in Figure 3.

We wish to acknowledge the help received from Professor P. Paoletti through valuable discussions and the assistance of Dr. L. Bologni who carried out the calorimetric experiments.

[9/681 *Received, 1st May,* 1979]

REFERENCES

[1] F. Hein and R. Burkhardt, *Chem. Ber.*, 1957, **90**, 928; T. G. Spiro and C. J. Ballhausen, *Acta Chem. Scand.*, 1961, **15**, 1707.

[2] G. Anderegg, *Helv. Chim. Acta*, 1962, **45**, 1303; N. Kitajiri, T. Arishima, and S. Takamoto, *Nippon Kagaku Zasshi*, 1970, **91**,

240; A. Sabatini and A. Vacca, *Co-ordination Chem. Rev.*, 1975, **16**, 161.

[3] M. Micheloni, A. Sabatini, and A. Vacca, *Inorg. Chim. Acta*, 1977, **25**, 41.

[4] J. R. Flückiger, Dissertation Thesis, Metallkomplexe mit aliphatischen Triaminen und ihren Schiffschen Basen, University of Freiburg, Switzerland, 1977.

[5] R. J. Geue and M. R. Snow, *Inorg. Chem.*, 1977, **16**, 231; J. Flückiger and C. W. Schläpfer, *Proc. XIX Internat. Conf. Co-ordination Chem.*, 1978, **2**, 42.

[6] G. Gran, *Analyst*, 1952, **77**, 661.

[7] A. Vacca, A. Sabatini, and L. Bologni, unpublished work.

[8] M. Micheloni, P. Paoletti, and A. Vacca, *J.C.S. Perkin II*, 1978, 945.

[9] J. J. Christensen and R. M. Izatt, 'Handbook of Metal Ligand Heats,' Marcel Dekker, New York, 1970.

[10] L. Fabbrizzi, M. Micheloni, and P. Paoletti, *Inorg. Chem.*, 1976, **15**, 1451.

[11] R. F. Childers, R. A. D. Wentworth, and L. J. Zompa, *Inorg. Chem.*, 1971, **10**, 302.