Thermochemistry of Metal Complexes with the Rigid Ligand 1,3,5-*cis,cis*-Triaminocyclohexane

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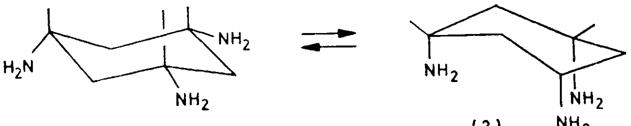
The heats of formation of nickel(II) and copper(II) complexes with the title ligand have been determined by microcalorimetric techniques, and the corresponding entropy values have been obtained by the appropriate combination with the reported free-energy data. Comparison with complexation of more flexible triamines emphasizes the role of the rigidity of the ligand in co-ordination to metal ions, from a thermodynamic standpoint.

MUCH of the reported co-ordination chemistry of chelating agents deals with aliphatic polyamines (ethylenediamine being the first member of the series), which are particularly suitable for forming complexes with 3*d* metal cations in aqueous solution. The pioneering work of Schwarzenbach [1] on the chelate effect was based on equilibrium data for the formation of metal complexes with open-chain polyamines.

Most of the multidentate amine ligands which have been studied are of the open-chain type, the flexibility of which is essential for satisfying the stereochemical requirements of the co-ordinated metal ion, and also for the formation of stable metal complexes.[2] An exception is provided by the terdentate ligand 1,3,5-*cis,cis*-triaminocyclohexane (tach), in which the amino-groups are attached to the comparatively rigid framework of cyclohexane. Furthermore, when not co-ordinated, tach is expected to exist as the more stable triequatorial conformer (1), whereas the co-ordinated ligand is forced to adopt the intrinsically less favourable triaxial conformation (2). *Facial* co-ordination is also enforced, in contrast to the situation with most thermochemically investigated amines, for which *meridional* co-ordination is possible.



(1) (2)

Equilibrium studies on the complexes of tach were first reported by Brauner and Schwarzenbach [3] and, after synthesis of a more purified *cis,cis* isomer,[4] log *K* values were reported for tach complexes with Ni^{II}, Cu^{II}, and Zn^{II}.[5] More recently, a complete investigation of the co-ordination chemistry of tach and some related ligands in solution has been reported.[6] Log *K* values were found to be quite different from those with corresponding open-chain triamines, but correlation of stability and ligand structure was difficult in the absence of more complete thermodynamic data, such as changes in $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$. We therefore decided to investigate the complexation of tach with 3*d* metal ions, using calorimetric techniques. This study has made available the complete set of thermodynamic functions, $\Delta G^{\ominus}$, $\Delta H^{\ominus}$, and $\Delta S^{\ominus}$, associated with the reactions of tach with Ni^{II} and Cu^{II}. A preliminary account of the corresponding zinc(II) complexes has been made.[7]

EXPERIMENTAL

Reagents.—The ligand tach was prepared and purified by sublimation according to a method reported in ref. 6. The purity of the substance was checked by C, H, and N analyses and pH titrations. The salts $[Ni(tach)(OH_2)_3][NO_3]_2$ and $[Ni(tach)_2][NO_3]_2$ were also prepared as described previously.[6] Samples of the free ligand and of the nickel(II) complexes were kindly provided by the late Professor Gerold Schwarzenbach {Found: C, 19.8; H, 5.90; N, 19.3. Calc. for $[Ni(tach)(OH_2)_3][NO_3]_2$: C, 19.7; H, 5.80; N, 19.15. Found: C, 32.9; H, 6.90; N, 25.8. Calc. for $[Ni(tach)_2][NO_3]_2$: C, 32.65; H, 6.85; N, 25.4%}.

A solution of $CuCl_2$ was prepared and the copper content determined gravimetrically by electrodeposition. The tach solution (0.1 mol dm^{-3}) was prepared by dissolving the ligand in CO_2-free water and was kept under nitrogen. The solution of alkaline cyanide was prepared by adding appropriate quantities of Na[OH] (Erba RP) and Na[CN] (Erba RP) to CO_2-free twice-distilled water, and the same solution was used throughout all batch-microcalorimetric experiments. A standard Na[OH] solution (*ca.* 0.3 mol dm^{-3}) was prepared by washing Na[OH] pellets several times under nitrogen with carbon dioxide-free water. The solution from the third washing was collected. The normality and purity of the Na[OH] solution was determined by pH titrations following the Gran method.[8] Two more dilute solutions of Na[OH] (0.01 and 0.02 mol dm^{-3}), as required in the flow-microcalorimetric apparatus, were obtained by diluting the standard Na[OH] solution with carbon dioxide-free water. The concentrations of the dilute solutions were checked calorimetrically by neutralization ($H^+ + OH^-$) in 0.1 mol dm^{-3} $Na[ClO_4]$; the heat of this reaction (-13.395 ± 0.016 kcal mol^{-1}) has been determined in previous experiments and it is in good agreement with the reported values.[9]

Standard HCl solutions were prepared by diluting the azeotropic mixture and standardized by potentiometric titration.

Calorimetric Procedures.—*Flow technique*. Because reactions between Cu^{II} and the ligand tach are fast this technique can be applied to determine the enthalpies of complex formation. The calorimetric apparatus was an LKB 10700-1 flow microcalorimeter, equipped with a Keithley model 150B microvolt ammeter. Solutions were injected in the calorimeter by high-precision electronic burettes (Mettler model DV 10) equipped with 50-cm^3 glass cylinders

(Mettler model DV 105). The flow rate from each burette was varied by a resistance box. The design of the experiment and the calibration of the apparatus have been described in detail.[10] In a typical experiment, burette (A) injected a solution containing the ligand tach, an excess of hydrochloric acid, and an appropriate amount of a copper(II) salt. Burette (B) was used for injecting Na[OH] solution. All solutions used in the flow-calorimetric experiments were adjusted to an ionic strength of 0.1 mol dm^{-3}, using Na[ClO$_4$] (Erba CGS). The procedure used to obtain $\Delta H^{\ominus}$ has been previously described.[10] The values of the equilibrium constant β_{pqr} used in the calculation were those reported in ref. 6. A value of $K_w = 1.63 \times 10^{-14}$ was employed for the ionic product of water. The calculations were made with a Fortran program written for an IBM 168-370 computer system.[11]

Batch technique. An LKB batch microcalorimeter (10700-2) was used. A full description of this apparatus, its calibration, and its mode of operation for slow reactions has already been given in detail.[12] Ultraviolet spectral measurements were made on a Varian Cary 17 spectrophotometer equipped with quartz cells of 1 mm path length. Because the reactions between nickel(II) ion and tach are too slow to be monitored directly by calorimetry we chose to examine the decomposition reaction of nickel(II)–tach complexes with excess of Na[CN] in strong alkaline solution, *i.e.* as in equation (1) where L = tach and n = 1 or 2.

$$[NiL_n]^{2+} + 4CN^- \longrightarrow [Ni(CN)_4]^{2-} + nL \tag{1}$$

$\Delta H^{\ominus}$ values for the case L = OH$_2$, n = 6 have been reported previously.[12] In a batch-microcalorimetric experiment the nickel complex solution (0.4 cm^3, 0.005—0.01 mol dm^{-3}) was introduced by weight into one side of the calorimetric cell and the Na[OH]–Na[CN] solution (2.5 cm^3; 0.9 mol dm^{-3} Na[OH], 0.1 mol dm^{-3} Na[CN]) was introduced into the other by a precision pipette (PIPETMAN). The calorimeter was allowed to equilibrate overnight until a steady baseline was obtained at the sensitivity range chosen, and then the reaction was started by mixing the reactants.

The reaction cells were coated with paraffin wax to prevent creeping, this coating being renewed after 10—15 determinations. The reactions was considered complete when no further heat effect could be detected. Furthermore, to confirm that a reaction was complete, and that equilibrium had been reached, the concentration of [Ni(CN)$_4$]$^{2-}$ was determined spectrophotometrically in the reaction mixture as soon as thermal measurements were completed. This was done by using the sharp absorption band at 268 nm ($\varepsilon = 1.21 \times 10^4$ dm^3 mol^{-1} cm^{-1}). In all cases the concentration of [Ni(CN)$_4$]$^{2-}$ was close to the equilibrium value expected.[13] Under the reaction conditions used, and by employing values of previously determined stability constants, the percentages of the species present at equilibrium before and after mixing were calculated by means of the DISPOL computer program[11] (Table 1). Correction for the enthalpy of dilution of the Na[OH]–Na[CN] solution was made to each measurement by introducing this solution (2.5 cm^3) into one side of the cell and pure water (0.4 cm^3) into the other. The experimental results were corrected for the presence of the species [Ni(CN)$_5$]$^{3-}$ as indicated in Table 1. For reaction (2) a value of 3.1 kcal mol^{-1} has been previously reported.[14,15,*]

$$[Ni(CN)_4]^{2-} + CN^- \rightleftharpoons [Ni(CN)_5]^{3-} \tag{2}$$

TABLE 1

Percentage of the species at equilibrium

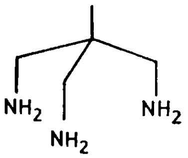
	Ni^{2+}	[NiL]$^{2+}$	[NiL$_2$]$^{2+}$	[Ni(CN)$_4$]$^{2-}$	[Ni(CN)$_5$]$^{3-}$
On dissolving [NiL(OH$_2$)$_3$][NO$_3$]$_2$ in water	0.5	98.2	1.3		
On dissolving [NiL$_2$][NO$_3$]$_2$ in water	0	1.7	98.3		
After mixing with excess of Na[CN]–Na[OH]	0	0	0	97.4	2.6

log β values: [NiL]$^{2+}$, 10.40; [NiL$_2$]$^{2+}$, 18.90; [Ni(CN)$_4$]$^{2-}$, 30.5; [Ni(CN)$_5$]$^{3-}$, 30.0; L = tach.

DISCUSSION

The thermodynamic quantities, $\Delta G^{\ominus}$, $\Delta H^{\ominus}$, and $\Delta S^{\ominus}$, associated with the formation of 1 : 1 and 1 : 2 complexes of tach with Ni^{II} and Cu^{II} are reported in the Table 2. In each case the reactions are exothermic and are characterized by a positive entropy change, as is usually observed for complexation by polyamines in aqueous solution.

To assist in evaluating the extent to which the rigidity of the ligand tach influences the thermodynamics of complexation, each value in the Table is compared with that associated with the corresponding complex of tame (3),[16] which, like tach, possesses three amine groups and is forced to adopt *facial* co-ordination, but which differs in having a greater degree of flexibility.



(3)

The crystal structure of the compound [Ni(tach)$_2$][NO$_3$]$_2$ has recently been reported[17] and it has been shown that in the [Ni(tach)$_2$]$^{2+}$ ions the nickel is six-co-ordinate with octahedral geometry. In solution the ions [Ni(tach)]$^{2+}$ and [Ni(tach)$_2$]$^{2+}$ have electronic spectra typical of octahedral co-ordination;[6] in the species [Ni(tach)]$^{2+}$ the remaining co-ordination sites must be occupied by three water molecules. The compound [Ni(tach)(OH$_2$)$_3$][NO$_3$]$_2$ has been isolated and the spectrum of the solid resembles that of the ion [Ni(tach)]$^{2+}$ in solution. Both the first and the second steps of complexation with tach are 2—3 kcal mol^{-1} less exothermic than with tame, but each step is characterized by a more positive entropy change (Table 1).

Analogous changes are observed for the 1 : 1 and 1 : 2 complexes with Cu^{II}, but in this case the differences

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

between tach and tame are more marked: the enthalpy contribution more strongly favours complexation of the more flexible tame (by 5—6 kcal mol^{-1}) and the entropy change is very much more positive for co-ordination of the more rigid tach.

It is not possible to obtain detailed stereochemical information from the spectra of these complexes in solution, which show only typical unstructured absorption bands.[6] Nevertheless, the tendency of Cu^{II} towards elongated octahedral co-ordination, due to the Jahn–Teller effect, is well known. In the complexes $[CuL]^{2+}$ (L = tach or tame) two donor atoms of the *facial* ligand would occupy equatorial positions, while the third would be forced to occupy an axial position, with formation of a weaker Cu–N bond.

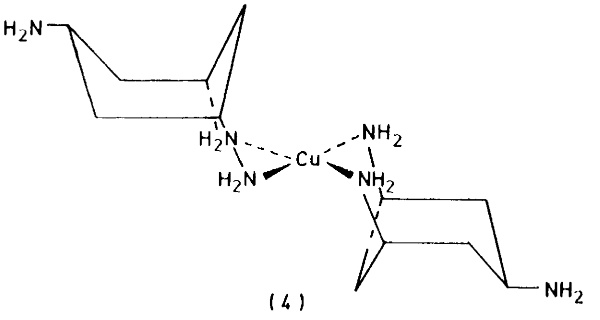
TABLE 2

Thermodynamic quantities [a] for complex formation with aliphatic triamines, in aqueous solution at 25 °C

	Ni			Cu			Zn		
Reactions	$-\Delta G^{\ominus}$	$-\Delta H^{\ominus}$	$\Delta S^{\ominus}$	$-\Delta G^{\ominus}$	$-\Delta H^{\ominus}$	$\Delta S^{\ominus}$	$-\Delta G^{\ominus}$	$-\Delta H^{\ominus}$	$\Delta S^{\ominus}$
M^{2+} + tach	14.04 [b]	8.8(1) [c]	17.6(3) [c]	14.593 [b]	9.6(1) [c]	16.7(3) [c]	9.41 [d]	0.1 [d]	31 [d]
M^{2+} + tame [e]	13.85	10.66	10.7	14.97	15.2	−0.8	9.02	6.08	9.9
M^{2+} + dpt [f]	12.53	10.56	6.6	19.38	16.1	11	10.80	5.4	18
$[M(tach)]^{2+}$ + tach	8.44 [b]	8.6(1) [c]	−0.5(6) [c]	6.56 [b]	1.1(6) [c]	18.0(1) [c]			
$[M(tame)]^{2+}$ + tame [e]	9.71	10.99	−4.3	10.54	7.6	9.9	5.80	5.0	3
$[M(dpt)]^{2+}$ + dpt [f]	4.61	7.0	−8						
$[M(tach)]^{2+}$ + OH^-				7.99 [b]	7.7(2) [c]	1(2) [c]	7.98 [d]	4.2 [d]	13 [d]
$[M(tame)]^{2+}$ + OH^-				7.52	0.4	24	6.79	0.9	20
$[M(dpt)]^{2+}$ + OH^-				5.65	2.28	11	7.10	3.77	11.2

[a] Units of $\Delta G^{\ominus}$ and $\Delta H^{\ominus}$ are kcal mol^{-1}, of $\Delta S^{\ominus}$ are cal K^{-1} mol^{-1}. [b] At $I = 0.1$ mol dm^{-3} Na[ClO$_4$]; data from ref. 6, corrected to 25 °C through ΔH. [c] This work, $I = 0.1$ mol dm^{-3} Na[ClO$_4$]. [d] At $I = 0.1$ mol dm^{-3} KCl, refs. 5 and 7. [e] Data from ref. 16. [f] Data from ref. 18.

The values of $\Delta H^{\ominus}$ for the nickel(II) complexes of tach or tame are roughly equal for both the first and second steps of complexation, showing that even in the second step the ligand is fully co-ordinated. In the case of Cu^{II}, however, the second step exhibits a much smaller heat effect; in particular, the reaction $[Cu(tach)]^{2+}$ + tach is athermic within the limits of experimental error. This could be explained by supposing that the copper in the species $[CuL_2]^{2+}$ is essentially four-co-ordinate, each molecule of ligand acting in a bidentate manner (4). In this way the addition of a second molecule of triamine produces a net increase in co-ordination of only one nitrogen atom. In the case of tach the situation is particularly unfavourable because such a rearrangement must also include the change in configuration of the cyclohexane ring from the chair to the boat form, a process known to be endothermic. The presence of two free amine residues in the species $[CuL_2]^{2+}$ explains why $\Delta S_2 \gg \Delta S_1$ for the complexes of Cu^{II}, a unique observation in the stepwise co-ordination of polyamines where normally $\Delta S_2 < \Delta S_1$.



(4)

The solid complexes $[Cu(tach)_2][NO_3]_2$ and $[Cu(tach)_2][ClO_4]_2$ have also been isolated and crystallographic studies have shown that each ligand molecule is fully co-ordinated according to a distorted octahedral stereochemistry. However, it is well known that, for many copper(II) polyamine complexes having a high co-ordination number, dissolution in water can induce the detachment of some amine groups.

The less exothermic complexation of tach compared to tame, both for Cu^{II} and Ni^{II}, can be attributed to several factors: (*a*) the conversion of the triequatorial conformer of tach into triaxial before complexation [this endothermic effect must surely be always less than that calculated for the conversion in the gas phase (11 kcal mol^{-1})];[4] (*b*) the greater rigidity of tach compared to tame and the consequent difficulty of satisfying the geometrical requirements of the metal ion. In fact both tach and tame are able to present their donor atoms at the corners of an equilateral triangle in a strain-free configuration, a situation particularly favourable for nickel(II) ions, whose co-ordination polyhedron, an octahedron, has regular equilateral triangular faces. The lower exothermicity of formation of the complexes $[Ni(tach)]^{2+}$ and $[Ni(tach)_2]^{2+}$ compared to the corresponding tame complexes (2 kcal mol^{-1}) is probably attributable to the endothermic contribution of the interconversion triequatorial ⟶ triaxial. For a complex $[CuL]^{2+}$, because of the tetragonal distortion, the arrangement of donor atoms of the triamine ligand must be distorted towards an isosceles triangle: such a process is acceptable for the flexible tame, but must be much more difficult for tach, rigidly pre-oriented to equilateral triangular co-ordination. This could explain the fact that for the species $[CuL]^{2+}$ the exothermic advantage of tame compared to tach (*ca.* 6 kcal mol^{-1}) is far greater than that observed in the corresponding nickel compounds.

It may also be noted that in the case of the flexible ligand tame $\Delta H^{\ominus}(CuL)/\Delta H^{\ominus}(NiL)$ is 1.5, a value found for complexes with non-sterically hindered multidentate amines. For the ligand tach this quantity is smaller (*ca.* 1.1), a testimony to the difficulty with which tach co-ordinates to Cu^{II}.

The different degrees of rigidity of the ligands tach and tame have the opposite effect on the entropy term. While the flexible tame passes from a mixture of many possible configurations to the rigidity of the co-ordinated ligand, thus losing a large amount of configurational entropy, tach, in its triaxial configuration, possesses the same arrangement when co-ordinated and the loss of entropy is very small (presumably the $\Delta S^{\ominus}$ associated with the triequatorial-triaxial conversion is quite small). The experimental values of the entropy of complexation are in complete agreement with this model. The opposing effects of the enthalpy and entropy terms in the complexation of tach and tame is shown by the calculated data for reaction (3). Thus it can be seen (Table 3)

$$[M(tach)]^{2+} + tame \longrightarrow [M(tame)]^{2+} + tach \quad (3)$$

that neither the replacement of tame by tach, nor the reverse, is favoured ($\Delta G^{\ominus} \simeq 0$), but this balance is the result of opposite and nearly equal $\Delta H^{\ominus}$ and $T\Delta S^{\ominus}$ terms.

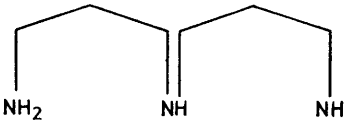
TABLE 3

Metathetic reactions involving rigid (tach) and flexible (tame) ligands

	$[M(tach)]^{2+}$ + tame		$[M(tame)]^{2+}$ + tach
M	$\Delta G^{\ominus}$	$\Delta H^{\ominus}$	$-T\Delta S^{\ominus}$
Ni	0.2	−1.9	2.1
Cu	−0.4	−5.6	5.2
Zn	0.4	−6.0	6.4

Thermodynamic quantities, in kcal mol^{-1}, have been obtained from data in Table 2.

A second comparison which may be made is with the linear triamine dipropylenetriamine (dpt) (5),[18] which, like tach and tame, forms six-membered chelate rings but has the ability for *meridional* co-ordination. An *X*-ray study[19] has shown that in the complex ion $[Ni(dpt)_2]^{2+}$ the two ligand molecules are disposed meridionally and their donor atoms are at the vertices of an octahedron. The value of $\Delta H^{\ominus}(Ni^{2+} + dpt)$ is equal to $\Delta H^{\ominus}(Ni^{2+} + tame)$ showing that with flexible ligands there is no enthalpy advantage for *facial* (tame) or *meridional* (dpt) co-ordination in regular octahedral complexes. However, such an advantage appears in the second step where it can be seen that the addition of a second molecule of dpt provokes a sharp decrease in the enthalpy effect. It seems possible to attribute this to greater steric repulsion between meridionally co-ordinated ligands.[18,19]

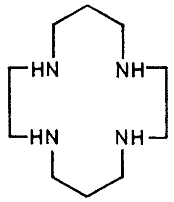


(5)

In the case of Cu^{II}, dpt has a more exothermic co-ordination than tame in the first step, probably because it can occupy three equatorial sites, known to be preferred by copper. However, as far as the second step is concerned, the interligand repulsions are such that the species $[Cu(dpt)_2]^{2+}$ is not formed in aqueous solution, in contrast to the case with the other two ligands considered in this work.

As far as the hydrolysis reactions $[CuL]^{2+} + OH^- \longrightarrow [CuL(OH)]^+$ are concerned, tame and tach behave quite differently: while the reaction of $[Cu(tame)]^{2+}$ is characterized by a small thermal effect and a large positive entropy change (analogous to that found with corresponding complexes of linear triamines of various lengths),[2] the hydrolysis of $[Cu(tach)]^{2+}$ is strongly exothermic and characterized by a moderately positive $\Delta S^{\ominus}$. This difference in behaviour may probably be attributed to different structures of the species produced, $[Cu(tach)(OH)]^+$ and $[Cu(tame)(OH)]^+$, but at present there are insufficient data on which to base hypotheses.

Conclusions.—This work shows that the rigidity of the ligand favours the formation of complexes because of the entropy term ($\Delta S^{\ominus} > 0$). In the case of tach, the slight flexibility may prevent the ligand from completely satisfying the stereochemical preference of the metal ion co-ordinated, thus lessening the entropic advantage because of the reduced enthalpy term. The ideal ligand would be a rigid one in which the donor atoms are pre-arranged in the ideal way for co-ordination. Such a situation is indeed found in the tetra-aza macrocycles. Thus the 14-membered macrocycle, cyclam (6), has the right dimensions to incorporate a 3*d* metal ion such as Cu^{II} and high-spin Ni^{II}. Its complexes are exceptionally stable as a result of particularly favourable contributions from both $\Delta H^{\ominus}$ (strong M–N interactions) and $T\Delta S^{\ominus}$ (rigidity of the 'closed' ligand).[12,20]



(6)

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