Thermodynamics of Complex Formation of Aliphatic Linear Tetra-amines. ΔH and ΔS for the Reactions of 1,5,9,13-Tetra-azatridecane with Protons and Some Bivalent Transition-metal Ions

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Complexes with aliphatic multidentate polyamine ligands, containing five-membered rings, are more stable than the corresponding complexes containing six-membered rings, for systems with separated and linked rings. This greater stability must be solely ascribed to a more exothermic heat of reaction. The heats of protonation and of formation of nickel(II), copper(II), and zinc(II) complexes of the quadridentate ligand 1,5,9,13-tetra-azatridecane (tt) have been determined calorimetrically at 25° in 0·1M-sodium nitrate and used to calculate the entropies of protonation and complex formation. The complexes of such a ligand contain a system of three linked six-membered rings. In order to point out the different effect of steric constraints in five- and six-membered ring systems ΔH and ΔS of complex formation of several linear aliphatic polyamines have been reviewed. The comparison of appropriate thermodynamic functions brings the evidence for two different types of steric constraints: those present in an individual chelate ring and those arising from the progressive linking of chelate rings. The individual ring strain is greater in six-membered rings, while the cumulative ring strain has a greater destabilising effect on linked five-membered rings. Moreover in the case of complexes containing six-membered rings the standard molar entropies of metal complexes have been found to be linearly related to standard molar entropies of the free ligand.

METAL-ION complexes with aliphatic polyamines have been extensively studied and much work on the thermodynamics of formation of these complexes in aqueous solution has been reported.[1] Their high stability has been mainly interpreted in terms of a favourable entropy change (the ' chelate effect ').[2] Further, it is well known that complexes with five-membered chelate rings are more stable than the analogous complexes with six-membered rings. Such a difference in stability, which is generally explained in terms of a higher strain in six-membered compared with five-membered rings, is ascribed to a more exothermic heat of formation.[3] On the other hand, criteria of conformational analysis [4] account for energetic terms, which are responsible for the stability of metal diamine rings. These terms are mainly enthalpies. Aliphatic quadridentate ligands, analogues of 1,4,7,10-tetra-azadecane (trien) [5], are currently receiving much attention.[6] These ligands are able to form complexes with a system of three consecutive chelate rings. The bulkiness of the ligand, the conformations, and the steric constraints of the rings in the metal-ion complex give rise to very interesting spectroscopic and thermodynamic properties.

Previous papers have reported the stability constants of some metal ions with some of these ligands.[7] As the stability of five- and six-membered chelate rings is due to the enthalpy changes, we have determined calorimetrically the heats of formation of metal-ion complexes with these tetra-amines. This paper reports the enthalpy and the entropy of the reaction of 1,5,9,13-tetra-azatridecane (tt), with some bivalent transition-metal ions. The determination of the thermodynamic functions for the protonation of the polyamine was of further interest in order to determine, by comparison with trien, the effect of the increased number of methylene groups on the heats and the entropies of neutralisation.

EXPERIMENTAL

1,5,9,13-Tetra-azatridecane (tt) was obtained commercially. It was purified as the hydrochloride, formed by adding hydrochloric acid to an aqueous alcoholic solution of the amine. The product was recrystallised from aqueous alcohol and then dried to constant weight at 60° *in vacuo* (Found: Cl, 47·5. Calc. for $C_9H_{28}Cl_4N_4$: Cl, 47·6%). The

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solutions of metal ions and of potassium hydroxide were prepared and stored as previously described.[8]

Calorimetric Measurements.—Calorimetric measurements were carried out in a titration calorimeter LKB 8700/2 by the technique previously described.[9]

For the protonation measurements, different volumes of a standard solution of potassium hydroxide were added to *ca.* 90 ml of a solution containing the tetra-amine hydrochloride and a slight excess of hydrochloric acid. For the formation of metal complexes the calorimetric ampoule contained also an equimolar amount of metal ion. The heat of formation of the complex $[Ni(tt)]^{2+}$ was determined by an indirect method as already described.[10]

TABLE 1

Calorimetric results for the protonation of 1,5,9,13-tetra-azatridecane in 0·1M-$NaNO_3$ at 25·0°

Calorimetric ampoule			KOH added [a]		
H^+ (mmol)	tt (mmol)	vol. (ml)	vol. (ml)	(mmol)	Q [b] (cal)
2·1418	0·5123	91·65	1·00	0·4890	2·268
1·6528	0·5123	92·65	1·00	0·4890	0·946
1·1638	0·5123	93·65	1·00	0·4890	0·597
3·7918	0·8970	89·46	2·00	0·9780	4·629
2·8183	0·8970	91·46	2·00	0·9780	1·812
1·8358	0·8970	93·46	2·00	0·9780	1·163
3·8185	0·9026	90·02	2·00	0·9780	4·633
2·8378	0·9026	92·02	2·00	0·9780	1·848
1·8598	0·9026	94·02	2·00	0·9780	1·145
0·8818	0·9026	96·02	2·00	0·9780	0·890
3·8757	0·9166	91·41	2·00	0·9780	4·824
2·8977	0·9166	93·41	2·00	0·9780	1·861
1·9197	0·9166	95·41	2·00	0·9780	1·173
0·9417	0·9166	97·41	2·00	0·9780	0·926

[a] The concentration of titrant solution was 0·4890 mmol ml^{-1}. [b] Corrected for the heat of dilution of KOH 0·4890M in 0·1M-$NaNO_3$.

TABLE 2

Calorimetric results for metal complex formation with 1,5,9,13-tetra-azatridecane, tt, in 0·1M-$NaNO_3$ at 25·0°

	Calorimetric ampoule				Titrant added [a] KOH		
Metal	H^+ (mmol)	M^{2+} (mmol)	tt (mmol)	vol. (ml)	(ml)	(mmol)	Q [b] (cal)
Cu	3·7931	0·9079	0·8973	91·85	7·30	3·5697	24·710
	2·4163	0·5016	0·4969	92·31	4·90	2·3961	18·645
	2·4158	0·4949	0·4968	92·50	4·90	2·3961	18·586
Zn	2·2237	0·5308	0·5495	89·47	4·20	2·1500	7·736
	2·2808	0·5898	0·5632	91·79	4·20	2·1500	7·740
	2·2251	0·5315	0·5501	90·52	4·20	2·1500	7·750
					HCl		
Ni	0·0173	0·5171	0·5490	90·68	8·00	2·2640	18·686
	0·0171	0·5123	0·5440	89·85	8·00	2·2640	18·676
	0·0169	0·5053	0·5365	88·61	8·00	2·2640	18·663

[a] The concentration of KOH was 0·4890 mmol ml^{-1} for measurements on copper(II)–tt system and 0·5118 mmol ml^{-1} for measurements on the Zn^{II}–tt system; the HCl used in the destruction of nickel(II) complex was 0·2830M. [b] Corrected for the heat of dilution of the titrant in 0·1M-$NaNO_3$.

All the measurements were carried out with the reaction system thermostatted at 25·000 ± 0·001 °C. The heats of formation were calculated with an I.B.M. 1130 computer and an appropriate program. The concentration equilibrium constants used with (tt) were those reported in 0·1M-$NaNO_3$ at 20 °C,[11] corrected to 25 °C using our ΔH values. The detailed results are shown in Tables 1 and 2.

Spectrophotometric Measurements.—The spectra of the complexes were recorded on a Beckman DK2-A spectrophotometer fitted with stoppered silica cells.

RESULTS AND DISCUSSION

Protonation.—Table 3 shows the values of the thermodynamic functions ΔG, ΔH, and ΔS for the stepwise protonation of (tt); for comparison, the corresponding values for (trien)[12] are shown in parentheses. For the first step the heat of protonation of (tt) is greater than that of (trien) by *ca.* 1·2 kcal mol^{-1}. This can be attributed to the inductive effect of the larger number of methylene groups present in the aliphatic chain of the former polyamine. As observed for the protonation of other aliphatic amines[3,12–15] ΔH_2 is greater than ΔH_1.

TABLE 3

Thermodynamic functions for the neutralisation and complex formation of 1,5,9,13-tetra-azatridecane, tt, in 0·1M-$NaNO_3$ at 25·0°

	$-\Delta H°$ [a] (kcal mol^{-1})	$-\Delta G°$ [b] (kcal mol^{-1}	$\Delta S°$ [a] (cal deg^{-1} mol^{-1})
$tt + H^+ \rightleftharpoons tt\,H^+$	12·20 ± 0·06 (11·01)	14·26	6·9 (7·8)
$tt\,H^+ + H^+ \rightleftharpoons tt\,H_2^+$	12·47 ± 0·11 (11·27)	13·40	3·2 (3·7)
$tt\,H_2^+ + H^+ \rightleftharpoons tt\,H_3^+$	11·65 ± 0·17 (9·53)	11·65	0·0 (−2·0)
$tt\,H_3^+ + H^+ \rightleftharpoons tt\,H_4^+$	10·88 ± 0·23 (6·83)	9·85	−3·5 (−8·1)
$Ni^{2+} + tt \rightleftharpoons [Ni(tt)]^{2+}$	13·2 ± 0·2	14·30 ± 0·07	3·7 ± 0·9
$Cu^{2+} + tt \rightleftharpoons [Cu(tt)]^{2+}$	19·45 ± 0·05	23·26 ± 0·14	12·8 ± 0·5
$Zn^{2+} + tt \leftrightharpoons [Zn(tt)]^{2+}$	7·35 ± 0·01	12·71 ± 0·05	18·0 ± 0·2

[a] Values in parentheses refer to (trien) (ref. 12). [b] Values at 20° taken from ref. 11 and corrected at 25° by using the enthalpy values obtained in this work.

The two main factors to be considered are: (i) The first stage of protonation involves a tautomeric equilibrium[16] between species protonated on the primary or secondary nitrogen atoms. In the second stage of protonation the most favourable arrangement is that where the protons are as far apart as possible, *i.e.* on the primary nitrogen atoms. This results in an

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overall exothermic process; (ii) The increase in 'electrostriction'[17] in going from the mono- to the bi-protonated form.

The difference $\Delta H_2 - \Delta H_1$ is of the same order of magnitude for the tetra-amine with ethylenic chains. We can observe this constancy also in the protonation of the linear triamines 1,4,7-triazaheptane (dien)[13] and 1,5,9-triazanonane (dpt)[3] (0·70 kcal mol^{-1}). In the third stage the difference between the heats for the two tetra-amines becomes larger (2·1 kcal mol^{-1}). This is due to the greater distance between the protonated groups in (tt), so that the electrostatic repulsion on the third proton is weaker. The 'electrostriction' acts in the same way. In fact the effective dielectric constant ε_e and its temperature coefficient $-\frac{\delta\varepsilon}{\delta T}$ increase with increasing bulkiness of the organic part between the charges,[17] then the electrostatic work A_{el} decreases and we have a lower heat of reaction:

$$\Delta H = -A_{el}[1 + (T/\varepsilon_e)(\delta\varepsilon/\delta T)]$$

The markedly large difference between the heats of protonation of (tt) and (trien) in the fourth stage can be explained in the same way. The entropy change in the four stages of protonation decreases, passing from a positive to a negative value. The same trend was also found in (trien).[12] The ΔS_1 and ΔS_2 values are comparable in the two tetra-amines while ΔS_3 and ΔS_4 have less negative values than those of (trien). This fact can be explained by the stiffening of the aliphatic chain caused by the electrostatic repulsion between the two charged amine groups.[9] Such a stiffening effect is greater in (trien) where the NH_3^+ groups are nearest.

Complex Formation.—The spectrum of the complex $[Cu(tt)]^{2+}$ ($\nu_{max.} = 17{\cdot}0$ kK, $\varepsilon = 157$) shows a remarkable similarity to that of $[Cu(trien)]^{2+}$ ($\nu_{max.} = 17{\cdot}4$ kK, $\varepsilon = 150$).[5] A six-fold distorted octahedral co-ordination with a planar arrangement of the four nitrogen atoms around the metal ion has been suggested for $[Cu(trien)]^{2+}$ in aqueous solution.[5] The spectrum of the complex $[Ni(tt)]^{2+}$ seems to indicate an octahedral configuration because the frequencies of the absorption maxima and the ε values are of the right order for complexes of this stereochemistry[18] ($\nu = 8{\cdot}7$ kK, $\varepsilon = 5{\cdot}6$; $\nu = 19{\cdot}0$ kK, $\varepsilon = 6{\cdot}6$; $\nu = 27{\cdot}6$ kK, $\varepsilon = 15{\cdot}6$).

Enthalpy Changes.—Table 3 shows the heats of the reactions of tt with Ni^{II}, Cu^{II}, and Zn^{II} ions. The polyamine tt is more basic than (trien) and the heats of the stepwise protonation, as previously reported, are also higher. In spite of this the enthalpies of complex formation are less exothermic than those of (trien).[5] The heat of formation of a metal polyamine complex is affected by two main factors. (i) The steric constraints which are present in the whole chelate ring or individual ring strain. (ii) The steric constraints arising from the linked metal–diamine rings or cumulative ring strain.[19]

In order to elucidate the two different effects, the ΔH and ΔS values of complex formation of Ni^{II} and Cu^{II} ions with the polyamines, ethylenediamine (en),[20] dien,[21] and trien[5] are compared to the corresponding values with 1,3-diaminopropane,[22] (dpt)[3] and (tt) in Table 4.

TABLE 4

ΔH (kcal mol^{-1}) and ΔS (cal deg^{-1} mol^{-1}) of formation of copper(II) and nickel(II) complexes with linear aliphatic polyamines

	Five-membered rings			Six-membered rings		
Copper(II)	en [b]	dien [c]	trien [d]	pn [e]	dpt [f]	tt [g]
$-\Delta H$	12·6	18·0	21·6	11·0	16·1	19·4
$-\Delta H_{calc}$ [a]	12·6	18·9 (0·9) [h]	25·2 (3·6) [h]	11·0	16·5 (0·4) [h]	22·0 (2·6) [h]
ΔS	6·3	12·0	19·5	9·6	11·0	12·8
		+5·7	+7·5		+1·4	+2·8
Nickel(II)						
$-\Delta H$	9·3 [e]	11·8	14·0	7·2	10·6	13·2
$-\Delta H_{calc}$	9·3	13·8 (2·0) [h]	18·4 (4·4) [h]	7·2	10·8 (0·2) [h]	14·4 (1·2) [h]
ΔS	3·3	8·5	16·0	7·3	6·6	3·7
		+5·2	+7·5		−0·7	−2·9

[a] $\Delta H_{calc} = n_N \cdot \Delta H$ (M diamine)/2, where: n_N is the number of co-ordinated nitrogen atoms, M is Cu^{II} or Ni^{II} ion and diamine is ethylenediamine (en) for complexes with five-membered rings and 1,3-diaminopropene (pn) for complexes with six-membered rings. [b] Ref. 20. [c] Ref. 21. [d] Ref. 5. [e] Ref. 22. [f] Ref. 3. [g] This work. [h] Values in parentheses are the differences ($\Delta H_{calc} - \Delta H_{exp}$).

The heats of reaction of Ni^{II} and Cu^{II} ions with 1,3-diaminopropane are lower than the corresponding (en) values, in other words, the steric constraints in the six-membered chelate ring are larger than in the five-membered ring. Examination of the crystallographic data shows that the six-membered rings exhibits larger distortions from the normal values than the five-membered. For example, the $C\hat{N}M$ angle in ethylenediamine complexes is near to the normal value of 109°[23] but, in contrast, the diaminopropane complexes present the much distorted value of *ca.* 120°.[24] Therefore, this ring strain forces the donor atoms to assume orientations different by those preferred in a strain-free configuration.

The heats of formation of metal complexes with the tetra-amine tt are lower than those of the corresponding bis-1,3-diaminopropane (pn) complexes, having two separated six-membered rings and the same set of donor atoms ($[Ni(pn)_2]^{2+}$, $\Delta H = 14{\cdot}6$ kcal mol^{-1} [22]; $[Cu(pn)_2]^{2+}$, $\Delta H = 23{\cdot}6$ kcal mol^{-1} [22]). The same trend has been observed in the metal–(trien) and (en) complexes, having

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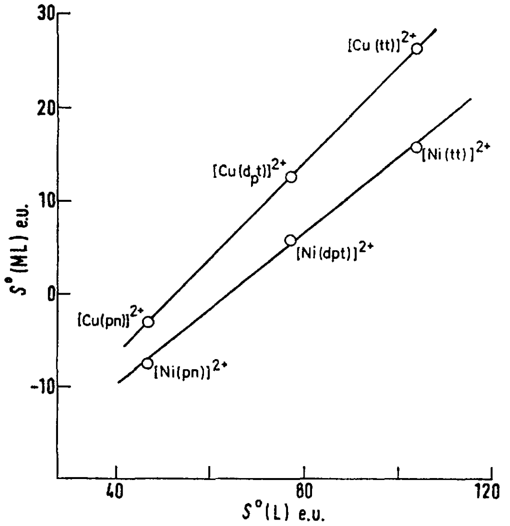
five-membered rings, both linked and separated ([Ni(en)$_2$], ΔH = 18·4 kcal mol^{-1} [22]; [Cu(en)$_2$]$^{2+}$, ΔH = 23·6 kcal mol^{-1};[20] the data concerning (trien) complexes are reported in Table 4). This lower thermal effect must be ascribed to steric constraints arising from the linked chelate rings in the metal tetra-amine complexes. In order to give a rough evaluation of the magnitude of these steric constraints we have compared ΔH_{exp} against ΔH_{calc} obtained by halving the enthalpy of formation of the complexes: [Cu(en)]$^{2+}$, [Cu(pn)]$^{2+}$, [Ni(en)]$^{2+}$, and [Ni(pn)]$^{2+}$ and multiplying this value by the number of co-ordinated nitrogens. The ΔH_{calc} is the enthalpy of formation of a complex with a cumulative ring strain-free configuration and is greater than ΔH_{exp}. The differences $\Delta H_{\text{calc}} - \Delta H_{\text{exp}}$ (Table 4) reflect the steric constraints arisen from the progressive linking of chelate rings and are greater in five-membered linked rings. The values of ΔH_{calc} are related to formation of co-ordinate bonds with all primary nitrogens and they are incorrectly compared to experimental values involving the formation of bonds with secondary nitrogens. However ΔH_{calc}, calculated by considering the real number of secondary nitrogens, are always greater than experimental values: for example ΔH obtained by adding up the complex formation enthalpy of [Cu(en)]$^{2+}$ to [Cu-(*NN'*-dimethylethylenediamine)]$^{2+}$ [20] is clearly greater than ΔH_{exp} of [Cu(trien)]$^{2+}$ (23·8 against 21·6 kcal mol^{-1}). All the ΔH_{calc} values reported in Table 4 refer to formation of co-ordinate bonds with primary nitrogens, owing to the greater availability of thermodynamic data.

The structure of the complex [Ni(dien)$_2$]$^{2+}$ shows a $\mathrm{N{-}\hat{Ni}{-}N}$ angle more markedly distorted (82°) whilst in the complex [Ni(dpt)$_2$]$^{2+}$ this angle approaches the normal value (91°).[25] Thus the cumulative effect of a second ring leads to, for the five-membered rings, an enhanced incompatibility between the real positions of the donor atoms and those preferred by acceptor metal ion. The deviations from the calculated enthalpies (Table 4) are different for Ni$^{\text{II}}$ or Cu$^{\text{II}}$ complexes. The linking of five-membered rings causes larger strains and consequently greater differences in the enthalpy of Ni$^{\text{II}}$ than of Cu$^{\text{II}}$ complexes, whilst in six-membered chelate rings the reverse occurs. In other words the steric constraints of the ring system depend also on the electronic and geometric requirements of the central metal ion.

Entropy of Complex Formation.—The values of the entropies of formation of Ni$^{\text{II}}$, Cu$^{\text{II}}$, and Zn$^{\text{II}}$ complexes with the ligand tt are reported in Table 3. These values are compared, in Table 4, with those of formation of five-membered ring complexes with the ligands: (en), (dien), and (trien) and with those of formation of six-membered ring complexes with the ligands: (pn) and (dpt). As is well known, each ΔS of formation, *i.e.* the entropy change of the metathetic reaction:

$$\mathrm{M^{2+}{}_{aq} + L \rightleftharpoons ML^{2+}{}_{aq} + \mathit{x}H_2O} \qquad (1)$$

is always positive and contributes to the high stability of the polyamine complexes (the 'chelate effect').[2] This favourable entropy change is mainly due to two contributions of opposite sign. One, negative, can be ascribed to the loss in total entropy of the ligand when its donor atoms are frozen in the co-ordination sites of the metal ion; the other, positive, is due to the release of water molecules. The latter term generally overcomes the former. The aqueous metal ion retains and orientates other water molecules in addition to those disposed in the co-ordination sites. These are retained by hydrogen bonding to the co-ordinated water molecules. The formation of this solvent lattice is probably responsible for the high stability of the aqueous metal ion, in spite of the poor basicity of the water. The introduction of a ligand molecule, particularly if it is a bulky ligand or a chelating agent, not only displaces the water molecules from the co-ordination sites, but destroys, more or less extensively, the solvent lattice (compare for instance the values of the ΔS_1 of formation of copper(II)–ethylenediamine complex (6·3 cal deg.$^{-1}$ mol^{-1}) with that of formation of the analogous complex with the much more bulky *NNN'N'*-tetramethylethylenediamine (13·0 cal deg^{-1} mol^{-1}).[20,26] The introduction of a second ligand molecule in the already greatly 'dehydrated' complex ion displaces a small number of water molecules, probably only those co-ordinated. This hypothesis, for instance, accounts for the values of ΔS_2 of the reactions of the $3d^{5-10}$ metal ions with (en) [20,27] or (dien) [13]; these ΔS_2 are markedly lower than those predicted on the basis of statistical contributions, with respect to ΔS_1. In a chelating agent the hydrocarbon chain has the same dehydrating effect and this obviously increases with the increasing length of the chain. Therefore the nickel(II)



Plot of standard molar entropies for Ni$^{\text{II}}$ and Cu$^{\text{II}}$ complex ions against the standard molar entropies for the polyamines in aqueous solution

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and copper(II) complexes with the ligand (pn) show more positive ΔS of formation than the analogous complexes with (en) (see Table 4). However in the case of the triamine and even more so with the tetra-amine complexes the ΔS values of complex formation with propylenic ligands are less positive than with ethylenic ligands (see Table 4). This means that the loss of translational vibrational, and rotational entropy of the propylenic ligand, in comparison with the ethylenic one, is greater than the contribution arising from dehydration. In the case of nickel(II) complexes with propylenic ligands the former effect overcomes the latter; therefore the entropy of complex formation decreases in the order: $[\mathrm{Ni(pn)}]^{2+} > [\mathrm{Ni(dpt)}]^{2+} > [\mathrm{Ni(tt)}]^{2+}$. In the Figure the standard molar entropies for complex ions $S°(\mathrm{ML})$, calculated by method previously reported,[28] are plotted against the standard molar entropies of the ligand, calculated from Cobble's equation.[29] Values of $S°(\mathrm{ML})$ are related linearly to $S°(\mathrm{L})$ and increase in the following order: $S°[\mathrm{M{-}(pn)}] < S°[\mathrm{M{-}(dpt)}] < S°[\mathrm{M{-}(tt)}]$. Therefore for six-membered chelate rings the entropy of each complex results mainly from the possible arrangements of the aliphatic chains, *i.e.* from the conformation contribution of the chelated rings.

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