Thermodynamics of Complex Formation with Linear Aliphatic Tetra-amines. Part III.[1] Enthalpy and Entropy Contributions to the Stability of Metal Complexes of 4,7-Diazadecane-1,10-diamine

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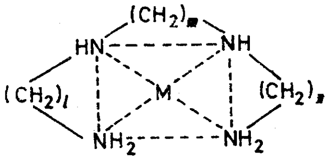
The enthalpies of the reactions, in 0·5M-KNO_3 at 25 °C, between the linear tetra-amine 4,7-diazadecane-1,10-diamine (3,2,3-tet) and the hydrogen, copper(II), nickel(II), and zinc(II) ions have been determined by means of direct calorimetric titrations. By use of the ΔG values reported elsewhere the corresponding ΔS values have been calculated. Complexes of 3,2,3-tet, which contains a system of condensed chelate rings with the ring-size sequence 6,5,6, have heats of formation higher than those of the corresponding complexes of 2,2,2-tet (ring-size sequence 5,5,5) and of 3,3,3-tet (sequence 6,6,6). However copper(II) and zinc(II) complexes have a less negative ΔH than the complexes of 2,3,2-tet which has the ring-size sequence 5,6,5.

THE complexes formed by the 3*d* metal ions with the ligand 2,3,2-tet with a ring sequence 5,6,5 are more stable[2] than either the complexes with 2,2,2-tet[3] (sometimes called trien) with the ring-size sequence 5,5,5 or those with 3,3,3-tet[4] with the ring-size sequence 6,6,6. This higher stability is due to a markedly more favourable enthalpic contribution.[1] This reflects the ability of the ligand to co-ordinate in a configuration having almost no steric strain.



		Ring-size sequence in the complex
$l = m = n = 2$	2,2,2-tet	5,5,5
$l = n = 2$; $m = 3$	2,3,2-tet	5,6,5
$l = n = 3$; $m = 2$	3,2,3-tet	6,5,6
$l = m = n = 3$	3,3,3-tet	6,6,6

The stability constants of a number of metal ions with the ligand 3,2,3-tet have recently been determined.[5] These complexes have the ring-size sequence 6,5,6 and are more stable than the corresponding complexes with the sequence 5,5,5 (2,2,2-tet) and 6,6,6 (3,3,3-tet). However, the complexes of 3,2,3-tet are less stable than those of 2,3,2-tet.

In order to determine the relative effects of the enthalpy and entropy terms on the stability of these complexes we have measured the enthalpies of formation directly by calorimetric titration. Combining these values with the reported values of ΔG, we readily calculate the corresponding values of ΔS.

The ΔH and ΔS values for the successive stages in the neutralization of 3,2,3-tet have also been determined. These data taken with those previously reported for other systems give interesting information on the

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[1] Part II, L. Fabbrizzi, R. Barbucci, and P. Paoletti, *J.C.S. Dalton*, 1972, 1529.

[2] D. C. Weatherburn, E. J. Billo, J. P. Jones, and D. W. Margerum, *Inorg. Chem.*, 1970, **9**, 1557.

[3] G. Schwarzenbach, *Helv. Chim. Acta*, 1970, **33**, 974.

[4] P. Teyssié, G. Anderegg, and G. Schwarzenbach, *Bull. Soc. chim. belges*, 1962, **71**, 177.

[5] P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chem.*, in the press.

nature of the interaction of polyamines with the hydrogen ion in aqueous solution.

EXPERIMENTAL

Materials.—The tetra-amine 3,2,3-tet was prepared as described elsewhere[5] and distilled under vacuum. The middle fraction, collected at 170 °C and 4 mmHg, was used to prepare the hydrochloride. The hydrochloride was prepared by adding an excess of hydrochloric acid to a cooled and continuously stirred alcoholic solution of the amine. 3,2,3-Tet,4HCl was recrystallised twice from water–alcohol and dried to constant weight at 60 °C (Found: Cl 44·1%. Calc. for $C_8H_{26}Cl_4N_4$: Cl, 44·3%). Solutions of potassium hydroxide, nitric acid, and metal nitrate were obtained and standardized as described.[6]

Calorimetric Measurements.—Calorimetric measurements were performed with a titration calorimeter LKB 8700-2. Titrant solution was added by a Metrhom Dosimat E 415 burette, in conjunction with a Metrhom Dosifix E 442 programmer. All measurements were carried out with the calorimetric system thermostatted at 25·000 ± 0·001 °C. A so-called 'potentiometric method' was employed; in the protonation measurements different volumes of a standard KOH solution (*ca.* 0·5M) were added to *ca.* 90 ml of a 0·5M-KNO_3 solution containing 0·5—1·0 mmol of the tetra-amine hydrochloride and occasionally a slight excess of acid (0·1—0·4 mmol).

In order to study the formation of complexes with copper(II) and zinc(II), standard KOH was added to a 0·5M-KNO_3 solution containing the amine hydrochloride and the metal nitrate. The heats of formation of the nickel(II) complexes were determined by an indirect method: the calorimetric vessel contained *ca.* 90 ml of a 0·5M-KNO_3 solution of the complex prepared 24 h earlier. The complexes were destroyed by adding an excess of nitric acid. The heat of formation of water (25 °C and 0·5M-KNO_3) was determined by adding the standard KOH solution to a 0·5M-KNO_3 solution containing an excess of nitric acid.*

Calculation of the Enthalpies.—The so-called 'potentiometric method' of the determination of the enthalpy changes applies to the study of reactions of metal ions with basic ligands in aqueous solution. This method requires four types of measurement: (i) determination of Q_{dil}, heat of dilution of the titrating solution (in our case the dilution of the titrant solution in a 0·5M-KNO_3 solution); (ii) determination of the heat of formation of water, ΔH_w. These measurements are carried out by adding a solution of a strong base to a solution of a strong acid in excess (in our case standard KOH to a solution of HNO_3 in 0·5M-KNO_3); (iii) determination of the heats of protonation of the ligand. These measurements are carried out by titrating a solution of the amine hydrochloride with a strong base (in our case a standard KOH solution is added to a 0·5M-KNO_3 solution of the tetra-amine hydrochloride); and (iv) determination of the heats of complex formation. These measurements are carried out by titrating, with a strong base, solutions containing variable amounts of the amine hydrochloride and a soluble salt of the metal (a nitrate in our case). In the case of nickel(II) the indirect method described above is used: nickel(II) polyamine complexes are destroyed by addition of excess of acid (HNO_3 in our case).

The heat evolved in one of these reactions and calorimetrically determined is to be corrected for the thermal effects due to the dilution of the titrating solution and eventual secondary reactions: for example in the determination (iv) the secondary reactions are the formation of water and the deprotonation of the ligand. The determination of the enthalpies from the calorimetric measurements (ii), (iii), and (iv) requires the knowledge of the concentrations of the reactant species before and after the reaction.

In the reaction (ii) it is assumed that all hydroxyl ions added react with the excess of hydrogen ions contained in the solution in the ampoule to give water. Thus, ΔH_w is simply given by the ratio of the measured heat [corrected for (i)] and the number of moles of added base.

In the cases (iii) and (iv) the concentrations of the species are obtained by solving the system of the mass-balance equations (1) where T_M, T_H, and T_L are the total concentration of the metal, acid, and ligand and β_{pqr} the appropriate equilibrium constant (for symbolism used see ref. 7).

$$\begin{aligned} T_M &= [M] + \Sigma p\beta_{pqr}[M]^p[H]^q[L]^r \\ T_H &= [H] + \Sigma q\beta_{pqr}[M]^p[H]^q[L]^r \\ T_L &= [L] + \Sigma r\beta_{pqr}[M]^p[H]^q[L]^r \end{aligned} \quad (1)$$

The system of three non-linear equations in the unknown [M], [H], and [L] is solved by the reiterative method of Newton–Raphson[8] [for the protonation of the ligand ($T_M = 0$) the system is reduced to two equations]. Thus, the concentration of a species of formula $M_pH_qL_r$ is obtained from equation (2). The thermal effect (iii) is expressed by equation (3). In this equation n_{OH} is the number of moles of OH^- added during the titration.

$$[M_pH_qL_r] = \beta_{pqr}[M]^p[H]^q[L]^r \quad (2)$$

$$Q = Q_{dil} + n_{OH}\Delta H_w + \delta n_{OH}\Delta H_w - \sum_{q=1}^{s} \delta n_{H_qL}\Delta H(L + qH^+) \quad (3)$$

The term n_{OH} ΔH_w is introduced for computational advantages: in fact, the addition of hydroxyl ions is represented as an equivalent decrease of the total number of moles of acid (T_H decreases). This involves the formation of an equivalent number of molecules of water and the thermal effect of this reaction is to be considered; δn_{OH} is the change of the number of moles of free OH^- during the reaction; δn_{H_qL} is the change of the number of moles of the different protonated species of the ligand, *s* being the highest number of protons bonded to the ligand; obviously the number of the measurements will be higher than *s*, the number of unknowns. A number of type (3) equations equal to the number of type (iii) measurements is written and the linear simultaneous equations in the *q* unknowns $\Delta H(L + qH^+)$ are solved by the least-squares method.

For the type (iv) reactions (complex formation) the

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* Experimental details of the calorimetric measurements (the quantities of the reagents and the volume of the solution before and after the reaction and the heat evolved) have been deposited with the National Lending Library in Supplementary Publication SUP 20727 (4 pp.). For details of the Supplementary Publication Scheme see *J. Chem. Soc.* (*A*), 1971, Index issue.

[6] A. Dei, P. Paoletti, and A. Vacca, *Inorg. Chem.*, 1968, **7**, 865.

[7] E. Arenare, P. Paoletti, A. Dei, and A. Vacca, *J.C.S. Dalton*, 1972, 736.

[8] H. Margenau and G. M. Murphy, 'The Mathematics of Physics and Chemistry,' 2nd edn., Van Nostrand, New York, 1956, p. 492.

measured heat Q is expressed by (4). ΔH_{pqr} represents the

$$Q = Q_{\text{dil}} + n_{\text{OH}}\Delta H_{\text{w}} + \delta n_{\text{OH}}\Delta H_{\text{w}} - \sum_{q=1}^{s} \delta n_{\text{H}_q\text{L}}\Delta H(\text{L} + q\text{H}^+) - \sum \delta n_{\text{M}_p\text{H}_q\text{L}_r}\Delta H_{pqr} \qquad (4)$$

enthalpy of the general reaction (5).

$$p\text{M} + q\text{H} + r\text{L} + x\text{H}_2\text{O} \rightleftharpoons [\text{M}_p\text{H}_q\text{L}_r] \qquad (5)$$

The system of the equations of the type (4) is solved by the least-squares method. In the case of formation of protonated metal complexes or those containing hydroxyl ions ($q \gtrless 0$) the values reported in Table 3 do not refer to reaction (5) but are relative to a combined reaction and are obtained by an appropriate thermodynamic cycle. For example the heat of the hydrolysis of ZnL is obtained by the cycle shown in Scheme 1 and equation (6).

$$\Delta H(\text{ZnL}^{2+} + \text{OH}^-) = \Delta H_{1,-1,1} - \Delta H_{1,0,1} + \Delta H_{\text{w}} \qquad (6)$$

For the reactions involving nickel(II) ions, where an indirect method is employed as described above, enthalpy changes are obtained from (4) where the term $n_{\text{OH}}\Delta H_{\text{w}}$ is obviously zero (acid is added).

SCHEME 1

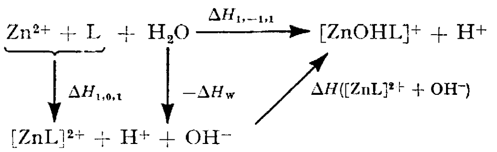

TABLE 1

Thermodynamic functions of the reactions of 3,2,3-tet with hydrogen ions and copper(II), nickel(II), and zinc(II) ions at 25 °C in 0·5M-KNO$_3$

	$-\Delta H°$/kcal mol^{-1}	$-\Delta G°$ [a]/kcal mol^{-1}	$\Delta S°$/cal mol^{-1} K^{-1}
$\text{L} + \text{H}^+ \rightleftharpoons \text{HL}^+$	12·23 ± 0·07	14·54 ± 0·01	7·8 ± 0·3
$\text{HL}^+ + \text{H}^+ \rightleftharpoons \text{H}_2\text{L}^{2+}$	12·79 ± 0·10	13·58 ± 0·01	2·6 ± 0·4
$\text{H}_2\text{L}^{2+} + \text{H}^+ \rightleftharpoons \text{H}_3\text{L}^{3+}$	10·71 ± 0·13	11·64 ± 0·01	3·1 ± 0·5
$\text{H}_3\text{L}^{3+} + \text{H}^+ \rightleftharpoons \text{H}_4\text{L}^{4+}$	9·77 ± 0·17	7·96 ± 0·01	−6·1 ± 0·7
$\text{Cu}^{2+} + \text{HL}^+ \rightleftharpoons [\text{CuHL}]^{3+}$	18·1 ± 0·1	20·1 ± 0·1	6·7 ± 0·7
$\text{Cu}^{2+} + \text{L} \rightleftharpoons [\text{CuL}]^{2+}$	25·89 ± 0·03	29·78 ± 0·01	13·1 ± 0·1
$\text{Ni}^{2+} + \text{HL}^+ \rightleftharpoons [\text{NiHL}]^{3+}$	12·0 ± 0·4	13·3 ± 0·1	4·4 ± 1·7
$\text{Ni}^{2+} + \text{L} \rightleftharpoons [\text{NiL}]^{2+}$	19·19 ± 0·07	20·04 ± 0·01	2·9 ± 0·5
$\text{Zn}^{2+} + \text{HL}^+ \rightleftharpoons [\text{ZnHL}]^{3+}$	7·7 ± 0·2	9·8 ± 1	7·0 ± 1·0
$\text{Zn}^{2+} + \text{L} \rightleftharpoons [\text{ZnL}]^{2+}$	10·62 ± 0·08	15·35 ± 0·01	15·9 ± 0·3
$[\text{ZnL}]^{2+} + \text{OH}^- \rightleftharpoons [\text{ZnOHL}]^+$	2·0 ± 0·1	5·5 ± 0·1	11·7 ± 0·7

[a] Values taken from ref. 5; standard state: 1 mol l^{-1}.

All these calculations were performed with an appropriate FORTRAN programme written for an IBM 1130 computer.

RESULTS AND DISCUSSION

Enthalpies of Protonation.—Table 1 reports the enthalpies of the stepwise protonation of 3,2,3-tet. ΔH_1 exhibits a more negative value than the corresponding one for protonation of the homologous tetra-amines 2,2,2-tet [9] and 2,3,2-tet,[1] which contain a smaller number of methylene groups. However, the first step does not involve the exclusive protonation of a primary or a secondary nitrogen atom, but more realistically both types of nitrogen atom should be protonated to a different extent, depending on the structure of the tetra-amine. The different percentage is related to the values of the basic microconstants of the different nitrogen atoms: the appropriate values can be estimated by the formula of Clark and Perrin [10] and the percentages of the primary nitrogen atoms protonated so evaluated are: 2,2,2-tet, 69·4; 2,3,2-tet, 48·3; and 3,2,3-tet, 74·7.

The highest ΔH_1 value found for 3,2,3-tet is to be attributed both to the large protonation of the primary nitrogen atom (reaction more exothermic than that involving a secondary nitrogen atom) and to the remarkable inductive effect due to the largest number of methylene groups. In the following steps owing to the electrostatic repulsion for each tetra-amine the nitrogen atoms furthest apart are protonated (*e.g.*, in the second step the two outer primary nitrogen atoms are involved).

For each step the observed sequence of ΔH is 3,2,3-tet > 2,3,2-tet > 2,2,2-tet: the exothermicity of the protonation increases with the length of the aliphatic chain, *i.e.*, with the distance between ammonium ions.

The simultaneous protonation of the primary and secondary nitrogen atoms in the first step accounts for the higher exothermicity of the second step (ΔH_2 more negative than ΔH_1) for these tetra-amines [1,9,11] and other polyamines too.[12] In the double-charged species H_2L^{2+}, as we have seen, the two primary nitrogen atoms are mostly protonated: therefore the reaction $\text{HL}^+ + \text{H}^+$ involves in part the transfer of a hydrogen ion from a secondary to a primary nitrogen atom and this is an exothermic process.

Schwarzenbach [13] suggested an alternative explanation for this phenomenon: he applied to the ion–dipole interactions (such as the protonation of a polyamine) the electrostatic model suggested by Prue.[14] The electrostatic contributions depend on the structure of the amine and also on the values of ε_e and $\partial\varepsilon_e/\partial T$, that is, on the dielectric constant and on its variation with temperature in the immediate neighbourhood of the reaction centres.

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[9] P. Paoletti, M. Ciampolini, and A. Vacca, *J. Phys. Chem.*, 1963, **67**, 1065.

[10] J. Clark and D. D. Perrin, *Quart. Rev.*, 1964, **18**, 295.

[11] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *J.C.S. Dalton*, 1972, 745.

[12] P. Paoletti, R. Walser, A. Vacca, and G. Schwarzenbach, *Helv. Chim. Acta*, 1971, **54**, 243.

[13] G. Schwarzenbach, *Pure Appl. Chem.*, 1970, 307.

[14] J. E. Prue, *J. Chem. Educ.*, 1969, **46**, 12.

The value of ΔH for an electrostatic interaction in a solvent of dielectric constant ε is given by equation (7)

$$\Delta H_{\mathrm{el}} = -A_{\mathrm{el}}\left\{1+\frac{\partial \ln \varepsilon}{\partial \ln T}\right\} \qquad (7)$$

where A_{el}, the electrostatic work, is the energy change when the two charged species are brought from infinity to the bond distance apart. $\partial \ln \varepsilon/\partial \ln T$ is negative and greater than unity (macroscopic value −1·32) so that since A_{el} is negative (repulsion between positive charges) the elecrostatic contribution is exothermic.

With increasing charge on the polyammonium ion the molecules of water involved in solvation assume an ever more ordered structure. The local polarizability of the solvent becomes much less dependent on temperature so that $\partial \ln \varepsilon/\partial \ln T$ becomes less negative and less than unity. As a result ΔH_{el} becomes positive and thus the electrostatic contribution becomes endothermic. As this endothermicity becomes more noticeable with increasing charge on the polyammonium ion so the ΔH values become progressively less negative for successive stages of protonation (3rd and 4th), as is experimentally observed.

Complexes of Copper(II).—Table 2 shows that the greater stability of the complex $[\mathrm{Cu(3,2,3\text{-}tet)}]^{2+}$, which has the chelate ring-size sequence 6,5,6, than of complexes having either all five-membered rings $[\mathrm{Cu(2,2,2\text{-}tet)}]^{2+}$ or all six-membered rings $[\mathrm{Cu(3,3,3\text{-}tet)}]^{2+}$, can be attributed to a more exothermic heat of formation. Further $[\mathrm{Cu(3,2,3\text{-}tet)}]^{2+}$ is less stable than the complex $[\mathrm{Cu(2,3,2\text{-}tet)}]^{2+}$ which has a different sequence of alternating rings, and this too can be attributed to a less negative value of the heat of reaction.

TABLE 2

Thermodynamic functions of the formation of metal complexes with four-co-ordinating polyamines in aqueous solution at 25 °C [a]

	Metal	2,2,2-tet [b]	2,3,2-tet [c]	3,2,3-tet [d]	3,3,3-tet [e]	$(\mathrm{en})_2$	$(\mathrm{tn})_2$ [i]
$-\Delta G°/$	Ni	18·8	22·4	20·0	14·3	18·9 [f]	16·7
kcal mol⁻¹	Cu	27·4	32·6	29·8	23·3	26·9 [g]	23·6
	Zn	16·4	17·5	15·4	12·7	14·4 [h]	
$-\Delta H°/$	Ni	14·0	17·9	19·2	13·2	17·9 [f]	14·6
kcal mol⁻¹	Cu	21·6	27·7	25·9	19·5	25·2 [g]	22·0
	Zn	8·9	11·9	10·6	7·4	13·7 [h]	
$\Delta S°/$	Ni	16·0	15·0	2·9	3·7	3·5 [f]	7·1
cal mol⁻¹ K⁻¹	Cu	19·5	16·5	13·1	12·8	5·8 [g]	5·4
	Zn	25·0	18·8	15·9	18·0	2·0 [h]	

[a] Standard state: 1 mol l⁻¹. [b] Ref. 15: $I = 0{\cdot}1$ (KCl). [c] Ref. 1,2: $I = 0{\cdot}5$ (KCl). [d] This work: $I = 0{\cdot}5$ ($\mathrm{KNO_3}$). [e] Ref. 4, 11: $I = 0{\cdot}1$ ($\mathrm{NaNO_3}$). [f] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 1960, 4553: $I = 1$ ($\mathrm{KNO_3}$). [g] R. Barbucci, L. Fabbrizzi, P. Paoletti, and A. Vacca, *J.C.S. Dalton*, 1972, 740: $I = 0{\cdot}5$ ($\mathrm{KNO_3}$). [h] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 1960, 4553; $I = 1$ (KCl). [i] F. Holmes and D. R. Williams, *J. Chem. Soc.* (*A*), 1967, 1702; $I = 0{\cdot}3$ ($\mathrm{NaClO_4}$).

Copper(II) complexes with these tetra-amines have a distorted octahedral structure, probably with the four nitrogens in the equatorial plane and with two molecules of water in the axial positions.[15,16] An examination of molecular models shows that the ligand 2,2,2-tet and even more so the ligand 3,3,3-tet are sterically constrained when they co-ordinate to the metal ion and that there are considerable strains present in a system of linked chelate rings which are either all five-membered or all six-membered. Ligands which are able to form complexes containing a sequence of rings of alternating size, 5,6,5 (2,3,2-tet) and 6,5,6 (3,2,3-tet), place the donor atoms in positions which better suit the requirements of the acceptor ion giving a configuration with less steric strain. Thus the more marked thermal effect relative to the reactions involving 2,3,2-tet and 3,2,3-tet reflects the ability of the two ligands to form stronger co-ordinate bonds.

The effect on ΔH of introducing an aliphatic chain between two nitrogens in *cis* positions in $[\mathrm{Cu(en)_2}]^{2+}$ is known.[1,17] Thus the introduction of an ethylenic chain (as in the complex $[\mathrm{Cu(2,2,2\text{-}tet)}]^{2+}$) produces steric strain and makes the ΔH of formation less negative, but the introduction of a propylenic chain {as in the complex $[\mathrm{Cu(2,3,2\text{-}tet)}]^{2+}$} not only does not produce steric strain in the system of linked rings but actually favours the formation of co-ordinate bonds (ΔH more negative) (see Table 2). This is probably due to the nitrogens being forced into a position which is more favourable for co-ordination. With the complex $[\mathrm{Cu(tn)_2}]^{2+}$ on the other hand the opposite happens: the introduction of a propylenic chain {the complex $[\mathrm{Cu(3,3,3\text{-}tet)}]^{2+}$} leads to a decrease in the enthalpy whilst the introduction of an ethylenic chain {$[\mathrm{Cu(3,2,3\text{-}tet)}]^{2+}$} raises the heat of formation (Table 2). In this case it is probable that the ethylenic chain forces the nitrogens into a more favourable orientation for donation.

In the complex $[\mathrm{Cu(H\ 3,2,3\text{-}tet)}]^{3+}$ the tetra-amine ligand is only terdentate and the complex contains two linked rings, one five-membered and the other six-membered. Thus its heat of formation should be similar to that of the triamine 3-azahexane-1,6-diamine[18] (2,3-tri) but in fact it is smaller (18·1 as against 19·2 kcal mol⁻¹) probably due to the repulsion between the metal ion and the ammonium ion. Nevertheless $[\mathrm{Cu(H\ 3,2,3\text{-}tet)}]^{3+}$ has a higher heat of formation than the complexes with the triamines 3-azapentane-1,5-diamine:[19] (2,2-tri) 18·0 kcal mol⁻¹ and 4-azaheptane-1,7-diamine:[20] (3,3-tri) 16·1 kcal mol⁻¹ and this can probably be attributed to the 5,6 ring combination being more favourable for co-ordination than either the 5,5 or the 6,6 combination. That a ring sequence 5,6 is more favourable than a 5,5 sequence is clearly demonstrated by the fact that the heat of formation

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[15] L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 1961, 5115.

[16] M. D. Alexander, P. C. Harrington, and A. Van Heuvelen, *J. Phys. Chem.*, 1971, **75**, 3355.

[17] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *Co-ordination Chem. Rev.*, 1972, **8**, 31.

[18] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *Inorg. Chim. Acta*, 1973, 157.

[19] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 1961, 2994.

[20] P. Paoletti, F. Nuzzi, and A. Vacca, *J. Chem. Soc.* (*A*), 1966, 1385.

of [Cu(H 3,2,3-tet)]$^{3+}$ is more exothermic than that of the analogous complex [Cu(H 2,2,2-tet)]$^{3+}$ (15·8 kcal mol^{-1}).[15] However the difference between these ΔH values (2·3 kcal mol^{-1}) is greater than the difference between the ΔH values for the complexes [Cu(2,3-tri)]$^{2+}$ and [Cu(2,2-tri)]$^{2+}$ (1·2 kcal mol^{-1}). This is attributed to the fact that in the complex [Cu(H 2,2,2-tet)]$^{3+}$, where the ammonium group is joined to an ethylenic chain, the electrostatic repulsion is greater than in the complex [Cu(H 3,2,3-tet)]$^{3+}$, where the charged group is one propylenic chain length away.

Complexes of Nickel(II).—For nickel(II) the interpretation of the thermodynamic data is more complicated. Nickel(II) tetra-amine complexes can exist in solution in two forms, a square planar yellow form and a blue octahedral form.[21,22] The equilibrium (8) depends both on

$$\underset{\text{Octahedral}}{[\mathrm{NiL(H_2O)_2}]^{2+}} \rightleftharpoons \underset{\text{Square}}{[\mathrm{NiL}]^{2+}} + 2\mathrm{H_2O} \qquad (8)$$

the ionic strength I and on the temperature T. Increasing either I or T favours the formation of the planar species.

Table 2 shows the thermodynamic data for the formation of nickel(II) complexes with all four tetra-amines. The order of the ΔH values is not the same as that found for the copper(II) complexes, *i.e.*, 2,3,2-tet > 3,2,3-tet > 2,2,2-tet > 3,3,3-tet. In this case it is found that the formation of the 3,2,3-tet complex is more exothermic than that of the 2,3,2-tet complex. This behaviour must result from the different concentrations of the yellow and blue species in the two system. Under the experimental conditions $I = 0{\cdot}5$ and $T = 25$ °C it is found from spectrophotometric measurements that for 2,3,2-tet [22] 25% of the yellow planar species is present whilst for 3,2,3-tet [23] only 10% of this species is present. The conversion of the blue octahedral form into the yellow planar form is endothermic; that is to say the formation of the planar species is less exothermic than the formation of the octahedral form. The higher concentration of the planar species present in the [Ni(2,3,2-tet)]$^{2+}$ system accounts for the smaller heat of complexation relative to the reaction with 3,2,3-tet.

Nickel(II) like copper(II) forms a protonated complex [Ni(H 3,2,3-tet)]$^{3+}$ and as for the corresponding copper(II) complex its heat of formation is distinctly less negative than that of the 2,3-tri complex (13·5 kcal mol^{-1}) [18] and more negative than those of the 2,2-tri [19] and 3,3-tri [20] complexes (11·9 and 10·5 kcal mol^{-1}).

Zinc(II) *Complexes*.—The greater stability of the complexes having alternately five- and six-membered rings than of those having either all five-membered or all six-membered rings can only be rationalized for octahedral co-ordination. From molecular models it is clear that with this geometry the ligands 2,3,2-tet and 3,2,3-tet are able to co-ordinate giving a configuration with less steric strain.

Zinc(II) polyamine complexes are usually believed to be tetrahedrally co-ordinated in solution and a tetrahedral configuration was assigned to [Zn(2,2,2-tet)]$^{2+}$ on the basis of the very large entropy change (25·0 cal mol K^{-1}).[15]

With this geometry one would not expect removal of strain in the complexes having alternately five- and six-membered rings. However zinc(II) complexes with 2,3,2-tet and 3,2,3-tet exhibit a higher heat of formation than [Zn(2,2,2-tet)]$^{2+}$ (Table 2). Further the entropy changes involved in reactions with 2,3,2-tet and 3,2,3-tet are less conspicuous than with 2,2,2-tet. This suggests that zinc(II) ion in the complexes having alternately five- and six-membered rings is not tetrahedrally co-ordinated, but more probably exhibits a co-ordination number greater than four. The smaller number of water molecules released during the reaction should account for the smaller ΔS value. The conformation of the ligands would favour an octahedral or a square pyramidal geometry as is shown by molecular models and on the other hand the formation of octahedral and square pyramidal complexes is more exothermic than that of a complex with tetrahedral geometry.

[Zn(2,3,2-tet)]$^{2+}$ and [Zn(3,2,3-tet)]$^{2+}$ have a less negative ΔH value than the [Zn(en)$_2$]$^{2+}$ complex (Table 2), opposite to what was found for copper(II) tetra-amine complexes. [Zn(H 3,2,3-tet)]$^{3+}$ (Table 1) exhibits a greater heat of formation than the tetrahedral complex [Zn(2,2-tri)]$^{2+}$ [20] (6·5 kcal mol^{-1}) and this supports the hypothesis of a geometry different from the tetrahedron in the protonated complex, too.

Finally, the complex [Zn(3,2,3-tet)]$^{2+}$ is also capable of taking up a hydroxide ion to give the species [ZnOH-(3,2,3-tet)]$^{+}$ and the thermodynamic functions for this reaction are shown in Table 1. Two mechanisms can be suggested for this reaction according to the geometry assumed for the complex [Zn(3,2,3-tet)]$^{2+}$. In the case of tetrahedral co-ordination it is necessary to suppose that an amine group becomes detached and is replaced by a hydroxide ion. On the other hand in the case of octahedral or square pyramidal co-ordination the species [ZnOH(3,2,3-tet)]$^{+}$ will be formed by simple deprotonation of a molecule of co-ordinated water.

The fact that the thermodynamic functions for this reaction are comparable with those of the analogous deprotonation of a zinc(II) polyamine complex, *i.e.*, [Zn(3,3-tri)]$^{2+}$ + OH^{-} $\rightleftharpoons$ [ZnOH(3,3-tri)]$^{2+}$ ($\Delta H = -3{\cdot}8$ kcal mol^{-1}; $\Delta S = 11{\cdot}2$ cal mol K^{-1}) [20] seems to support the second hypothesis.

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