Thermodynamics of Complex Formation with Linear Aliphatic Tetramines. Part II.[1] Heats and Entropies of the Reactions of 3,7-Diazanonane-1,9-diamine with Hydrogen Ions and Some Bivalent Transition-metal Ions [2]

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Heats of formation of Ni^{II}, Cu^{II}, Zn^{II}, and proton complexes of 3,7-diazanonane-1,9-diamine (2,3,2-tet) have been measured calorimetrically. These thermodynamic data show that the high stability of the metal complexes is mainly due to the enthalpy term even if the entropy term is favourable.

THE greater stability of metal ion complexes with aliphatic multidentate ligands containing five-membered rather than six-membered chelate rings is generally attributed to the greater strain present in the latter.[3,4] Ring strain explains all the unfavourable effects of chelation: (i) the more or less strong co-ordinate bond of the donor atoms; and (ii) steric constraints in the aliphatic chain (eclipsing of the hydrogens, non-bonded interactions, and angle and bond-length distortions).[5] These contributions are enthalpy terms; the higher stability of complexes containing five-membered rings [*e.g.*, bis(ethylenediamine) in comparison with bis(trimethylenediamine) complexes] [6] has been ascribed solely to a larger heat of formation.

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

[2] Presented in part at the 'Conference on the Stability and Reactivity of Co-ordination Compounds,' Bressanone, September 1971.

[3] H. M. Irving, R. J. P. Williams, D. J. Ferrett, and A. E. Williams, *J. Chem. Soc.*, 1954, 3494.

[4] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.

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In the reaction with ter- or quadri-dentate ligands, the complexes containing fused five-membered rings are more stable than those containing fused six-membered rings.[1] However the chelate ring introduces further steric constraints (cumulative ring strain) [1,7,8] so these complexes show a lower heat of formation than those having separated rings.

TABLE 1

Calorimetric results for the protonation of *NN'*-bis-(2-aminoethyl)propane-1,3-diamine (2,3,2-tet) in 0·5M-KCl at 25 °C

Calorimetric vessel			KOH added		
H^+/mmol	(2,3,2)-tet/ mmol	Vol./ml	Vol./ml	mmol	*Q* [a]/cal
2·1282	0·5256	90·70	1·00	0·5118	2·352
1·6164	0·5256	91·70	1·00	0·5118	1·825
1·1046	0·5256	92·70	1·00	0·5118	1·208
0·5928	0·5256	93·70	1·00	0·5118	1·028
2·1192	0·5253	90·32	1·00	0·5118	2·401
1·6074	0·5235	91·32	1·00	0·5118	1·807
1·0956	0·5235	92·32	1·00	0·5118	1·190
0·5838	0·5235	93·32	1·00	0·5118	1·062
2·1544	0·5319	91·79	1·00	0·5118	2·428
1·6426	0·5319	92·79	1·00	0·5118	1·867
1·1308	0·5319	93·79	1·00	0·5118	1·218
0·6190	0·5319	94·79	1·00	0·5118	1·073

[a] Corrected for the heat of dilution of KOH (0·5118M) in 0·5M-KCl.

TABLE 2

Calorimetric results for the metal complex formation of *NN'*-bis-(2-aminoethyl)propane-1,3-diamine (2,3,2-tet) in 0·5M-KCl at 25 °C

	Calorimetric vessel				Titrant added [a]		
	H^+	M^{2+}	(2,3,2)-tet		KOH		
Metal	mmol	mmol	mmol	Vol/ml	ml	mmol	*Q* [b]/cal
Cu							
	2·0348	0·4769	0·5031	88·03	3·80	1·9448	20·090
	2·4013	0·4702	0·5232	92·48	4·50	2·3031	23·574
	2·4747	0·4837	0·5418	91·68	4·70	2·4055	24·241
Zn							
	1·9919	0·4728	0·4790	90·66	3·70	1·8937	12·003
	2·0276	0·4803	0·4876	94·12	3·80	1·9448	12·330
	2·0010	0·4738	0·4812	92·89	3·70	1·8937	12·156
Ni					HCl		
	0·0658	0·2500	0·4966	88·90	10·00	2·8300	14·879
	0·0656	0·2492	0·4950	88·60	10·00	2·8300	14·784
	0·0669	0·2542	0·5050	90·40	10·00	2·8300	15·034
	0·1114	0·4485	0·4786	88·83	10·00	2·8300	10·704
	0·1125	0·4526	0·4829	89·64	10·00	2·8300	10·768
	0·1132	0·4557	0·4863	90·25	10·00	2·8300	10·870

[a] The concentration of KOH was 0·5118 mmol/ml; the HCl used in the nickel(II) complex destruction was 0·2830M. [b] Corrected for the heat of dilution of the titrant in 0·5M-KCl.

The stability constants of the Cu^{II}, Ni^{II}, and Zn^{II} complexes with 3,7-diazanonane-1,9-diamine (2,3,2-tet) have been reported.[9] These complexes, with a sequence of five-, six-, and five-membered rings, are more stable than those of the linear aliphatic tetra-amines, previously investigated, *i.e.*, triethylenetetra-amine (trien) [10,11] which can form only five-membered rings and 4,8-diazaundecane-1,11-diamine(3,3,3-tet) [1,12] with only six-membered rings.

To investigate whether the exceptional stability of complexes of (2,3,2-tet) is due to a favourable enthalpy or entropy term we determined ΔH and ΔS values for the formation of Ni^{II}, Cu^{II}, and Zn^{II} complexes. ΔH And ΔS of the stepwise protonation have been determined and, by comparison with the values reported for the homologous tetramines (trien) [13] and (3,3,3-tet),[1] the effect of the length of the aliphatic chain on the thermodynamic functions of protonation has been evaluated.

EXPERIMENTAL

Materials.—(2,3,2-tet) was prepared by the method of Van Alphen [14] and distilled under vacuum. The middle fraction was purified as the *hydrochloride*, which was recrystallised from aqueous alcohol and dried to constant weight at 60 °C *in vacuo* (Found: Cl, 46·4. $C_7H_{24}N_4Cl_4$ requires Cl, 46·3%). Solutions of potassium hydroxide, hydrochloric acid, and metal chloride were obtained and standardised as described.[15]

Calorimetric Measurements.—The measurements were carried out [16] with an LKB 8700/2 titration calorimeter. In the protonation measurements standard KOH was added stepwise to *ca.* 90 ml of a solution containing the tetramine hydrochloride and a trace of hydrochloric acid. For the copper(II) and zinc(II) complexes the calorimetric

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[8] J. G. Gibson and E. D. McKenzie, *J. Chem. Soc.* (*A*), 1971, 1666.

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

[10] G. Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 974.

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

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

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

[14] J. Van Alphen, *Rec. Trav. chim.*, 1936, **55**, 835.

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

[16] R. Barbucci, P. Paoletti, and A. Vacca, *J. Chem. Soc.* (*A*), 1970, 2202.

vessel contained also an equimolar amount of metal chloride. The heats of formation of the complexes $[Ni(2,3,2\text{-tet})]^{2+}$ and $[Ni(2,3,2\text{-tet})_2]^{2+}$ were determined by an indirect method. The calorimetric vessel contained *ca.* 90 ml of a solution of the complexes prepared 24 hours earlier. The complex was destroyed by adding excess of hydrochloric acid. All the measurements were carried out with the reaction system thermostatted at 25·000 ± 0·001 °C. The heat changes were determined with an IBM 1130 programme and were corrected for the heat of dilution, determined under the same conditions. The composition of the solutions at equilibrium and before and after the reaction was calculated with a computer programme.[17] The equilibrium constants used were those determined by Margerum and his co-workers.[9] The ionic product of water (0·5M-KCl; 25 °C) reported by Harned and Owen [18] was used (pK = 13·72). The heats of formation were obtained by a least-squares method.[16] The heat of formation of water (0·5M-KCl at 25 °C) was determined by adding standard KOH to a solution of hydrochloric acid containing 0·5M-KCl. The value from five different measurements, 13·48 ± 0·01 kcal mol⁻¹, disagrees with that calculated by Harned and Hamer [19] from the temperature dependence of the ionization constant of water in 0·5M-KCl (13·77 kcal mol⁻¹). Better agreement is obtained by substituting for the value of the heat at infinite dilution in the Harned equation that calorimetrically determined [20] (with $\Delta H_i^{25} = 13{\cdot}34$, $\Delta H^{25}_{0\cdot 5M-KCl}$ becomes 13·62 kcal mol⁻¹).

TABLE 3

Thermodynamic functions of the neutralisation and complex formation of *NN'*-bis-(2-aminoethyl)propane-1,3-diamine (2,3,2-tet) at 25 °C in 0·5M-KCl

	$-\Delta H$ kcal mol⁻¹	$-\Delta G$ [a] kcal mol⁻¹	ΔS cal mol⁻¹ K⁻¹
$(2,3,2\text{-tet}) + H^+ \rightleftharpoons (2,3,2\text{-tet } H^+)$	10·96 ± 0·06	13·96 ± 0·03	10·1 ± 0·3
$(2,3,2\text{-tet}) + 2H^+ \rightleftharpoons (2,3,2\text{-tet } H_2^{2+})$	22·29 ± 0·04	26·91 ± 0·07	15·5 ± 0·4
$(2,3,2\text{-tet}) + 3H^+ \rightleftharpoons (2,3,2\text{-tet } H_3^{3+})$	32·32 ± 0·06	36·81 ± 0·03	15·1 ± 0·3
$(2,3,2\text{-tet}) + 4H^+ \rightleftharpoons (2,3,2\text{-tet } H_4^{4+})$	41·50 ± 0·06	45·01 ± 0·03	11·8 ± 0·3
$Cu^{2+} + (2,3,2\text{-tet}) \rightleftharpoons [Cu(2,3,2\text{-tet})]^{2+}$	27·7 ± 0·1	32·6 ± 0·1	16·4 ± 0·1
$Ni^{2+} + (2,3,2\text{-tet}) \rightleftharpoons [Ni(2,3,2\text{-tet})]^{2+}$	17·9 ± 0·1	22·4 ± 0·1	15·1 ± 0·5
$[Ni(2,3,2\text{-tet})]^{2+} + 2,3,2\text{-tet} \rightleftharpoons [Ni(2,3,2\text{-tet})_2]^{2+}$	4·1 ± 0·2	5·0 ± 0·3	3·0 ± 1·7
$Zn^{2+} + (2,3,2\text{-tet}) \rightleftharpoons [Zn(2,3,2\text{-tet})]^{2+}$	11·9 ± 0·1	17·5 ± 0·1	18·8 ± 0·1

[a] Values from ref. 9.

TABLE 4

Thermodynamic functions of the protonation of linear aliphatic tetramines in aqueous solution at 25 °C

	Step	(trien) [a]	(2,3,2-tet) [b]	(3,3,3-tet) [c]
$-\Delta G$/kcal mol⁻¹	1	13·3	14·0	14·3
	2	12·4	13·0	13·4
	3	8·9	9·9	11·7
	4	4·4	8·2	9·8
$-\Delta H$/kcal mol⁻¹	1	11·0	11·0	11·2
	2	11·3	11·3	12·5
	3	9·5	10·0	11·7
	4	6·8	9·2	10·9
ΔS/cal mol⁻¹ K⁻¹	1	7·8	10·1	6·9
	2	3·7	5·4	3·2
	3	−2·0	−0·4	0·0
	4	−8·1	−3·3	−3·5

[a] Ref. 13; μ = 0·1M (KCl). [b] This work. [c] Ref. 12; μ = 0·1M (NaNO₃).

Results of the calorimetric measurements are in Tables 1 (protonation) and 2 (complex-formation).

RESULTS AND DISCUSSION

Protonation of the Amines.—Table 3 shows the values of ΔG, ΔH, and ΔS for the four successive stages of protonation. The corresponding values of the tetra-amine ligands (3,3,3-tet) and (trien) are reported in Table 4. A gradual decrease of $-\Delta H$ and ΔS with the stepwise protonation is observed for all three tetramines. Therefore the conclusions drawn for (3,3,3-tet) [1] and (trien) [11] apply to (2,3,2-tet). Further all the heats of the stepwise protonation are lower than the corresponding values of (3,3,3-tet): the lack of two methylene groups in the external chains leads to a decrease in the enthalpy of protonation by a lower inductive effect. The two enthalpies of protonation ΔH_1 and ΔH_2 are equal, within experimental error, while ΔH_3 and ΔH_4 of (2,3,2-tet) are more exothermic than those of (trien) by 0·5 and 2·4 kcal mol⁻¹ respectively. Therefore the introduction of a methylene group in the central aliphatic chain does not increase the heats of protonation of the two primary nitrogens but it considerably affects the protonation of the two secondary nitrogens. The longer central chain also causes a greater shielding of the electrostatic repulsion between the two positive nitrogens, particularly evident on protonation of the last nitrogen.

Complex Formation.—Ethylenediamine (en) complexes, containing five-membered rings, are more stable than trimethylenediamine (tn) complexes containing six-membered rings.[21] For instance, $[M(en)_2]^{2+}$ complexes (M = Ni or Cu) exhibit a more negative free-energy

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[18] H. S. Harned and B. B. Owen, ' Physical Chemistry of Electrolytic Solutions,' 3rd edn., Reinhold Publishing Corp., New York, 1958, pp. 638—752.

[19] H. S. Harned and W. J. Hamer, *J. Amer. Chem. Soc.*, 1935, **57**, 27.

[20] L. Sacconi, P. Paoletti, and M. Ciampolini, *Ricerca sci.*, 1959, **29**, 2412; J. D. Hale, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, 1963, **67**, 2605; C. E. Vanderzee and J. A. Swanson, *ibid.*, p. 2608.

[21] L. G. Sillèn and A. E. Martell, ' Stability Constants,' Special Publication, No. 25, The Chemical Society, London, 1970.

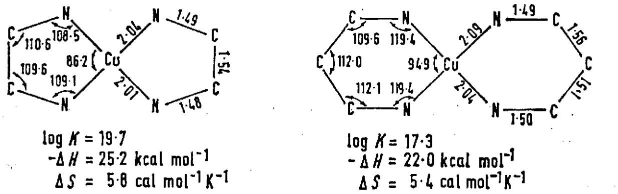
change than $[M(tn)_2]^{2+}$complexes (see Table 5). Thermodynamic data[22-24] show that the more negative free-energy change is due to a more negative enthalpy change. This higher heat of complex formation is related to the greater ability of ethylenediamine to arrange its donor atoms in the co-ordination sites required by the acceptor metal ion.

TABLE 5

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

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

[a] Ref. 11; μ = 0·1M (KCl). [b] This work. [c] Ref. 1; μ = 0·1M ($NaNO_3$). [d] Ref. 24; μ = 1M (KNO_3). [e] Ref. 23; μ = 0·5M (KNO_3). Ref. 24; μ = 1M (KCl). [g] Ref. 22; μ = 0·3M ($NaClO_4$).



Size and stability of chelate rings. Thermodynamic[a] and structural[b] parameters for the complexes $[Cu(en)_2]^{2+}$ and $[Cu(tn)_2]^{2+}$. Whereas in the ethylenediamine ring bond angles are only slightly distorted from the normal values, the trimethylenediamine ring shows appreciable distortion: ∠CCC = 112°, ∠CNCu = 119°. Moreover Cu–N bonds are shorter and presumably stronger in the five-membered ring

[a] Refs. 22 and 23. [b] Refs. 25 and 26.

X-Ray structures[25] show that the six-membered rings are more strained than the five-membered, exhibiting great deviations of bond angles and lengths from the normal values. The Figure reports some structural parameters of $[Cu(en)_2]^{2+}$[26] and $[Cu(tn)_2]^{2+}$,[27] with their thermodynamic functions;[22,23] the six-membered rings show the largest bond distortions from the expected values.

Steric constraints increase in ter- and quadri-dentate polyamine complexes containing a system of two or three fused chelate rings (cumulative ring strain),[1,7,8] so a decrease of heat of formation with respect to the corresponding complexes with separated rings is observed (Table 5). However the decrease of enthalpy is outweighed by a favourable change in translation entropy (responsible for the chelate effect).[27] Then the formation of fused five-membered ring complexes is favoured in comparison with the complexes containing separated rings, hence the stability constant is higher {compare, for example, in Table 5 $[Me(en)_2]^{2+}$ with [M(trien)]$^{2+}$, where M = Cu or Zn; and also the six-co-ordinate Ni^{II} complexes: $[Ni(en)_3]^{2+}$[22] $\Delta G = -24{\cdot}6$ kcal mol^{-1}, $\Delta H = -27{\cdot}9$ kcal mol^{-1}, $\Delta S = 11$ cal mol K^{-1}; with $[Ni(den)_2]^{2+}$[28] (den = diethylenetriamine) $\Delta G = -25{\cdot}4$ kcal mol^{-1}, $\Delta H = -25{\cdot}3$ kcal mol^{-1}, $\Delta S = 0$ cal mol^{-1} K^{-1}; and with Ni(penten)]$^{2+}$ [penten = *NNN'N'*-tetra(2-aminoethyl)ethylenediamine][29] $\Delta G = -26{\cdot}1$ kcal mol^{-1}, $\Delta H = -19{\cdot}7$ kcal mol^{-1}, $\Delta S = 21{\cdot}5$ cal mol K^{-1}}.

The steric constraints produced by linking of chelate rings are more conspicuous in the six-membered rings and the related decrease of the enthalpy term is so remarkable that it cancels the favourable entropy change {compare in Table 5 $[Cu(tn)_2]^{2+}$ and [Cu(3,3,3-tet)]$^{2+}$ and also the six-co-ordinate complexes $[Ni(tn)_3]^{2+}$:[22] $\Delta G = -20{\cdot}8$ kcal mol^{-1}; $\Delta H = -21{\cdot}7$ kcal mol^{-1}; $\Delta S = -3{\cdot}0$ cal mol^{-1} K^{-1} with $[Ni(dpt)_2]^{2+}$[17] (dpt = 3,3'-diaminodipropylamine): $\Delta G = -17{\cdot}6$ kcal mol^{-1}; $\Delta H = -16{\cdot}4$ kcal mol^{-1}; $\Delta S = -0{\cdot}9$ cal mol^{-1} K^{-1}}. The complexes with fused six-membered rings do not exhibit a chelate effect.

The enthalpy values of the five-, six-, and five-membered complexes with (2,3,2-tet) allow comparison with those previously reported. As an example the introduction of a methylene group in the central hydrocarbon chain relieves the stretch of the (trien) ligand and allows a less strained co-ordination of the donor atoms. The heat of formation is therefore higher. The formation of [Cu(2,3,2-tet)]$^{2+}$ is more exothermic than that of $[Cu(en)_2]^{2+}$. In the formation of [Cu(2,3,2-tet)]$^{2+}$ the more favourable change in translational entropy, responsible for the chelate effect, is not balanced by a decrease of the enthalpy term with respect to $[Cu(en)_2]^{2+}$. On the contrary, the large negative enthalpy change markedly contributes to the large negative free-energy change. The sum of the favourable ΔH and ΔS values explains the exceptionally high stability of [Cu(2,3,2-tet)]$^{2+}$.

Copper(II) *Complexes*.—The energy terms which define the enthalpies of formation of the polyamine complexes are: (1) strength of the M–N bonds; (2) steric constraints which may act both to decrease the strength of the M–N bonds and to produce repulsive non-bonded interactions; (3) replacement of the water molecules from both the first and the second hydration sphere; (4) tetragonal distortion; and (5) partial dehydration of the polyamine ligand.

The visible spectra of the aqueous solutions[7,11] and

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[22] F. Holmes and D. R. Williams, *J. Chem. Soc.* (*A*), 1967, 1702.

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[24] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 1960, 4553.

[25] Y. Komiyama and E. C. Lingafelter, *Acta Cryst.*, 1964, **17**, 1145.

[26] A. Pajunen, *Suomen Kem.*, 1969, *B*, **42**, 15.

[27] G. Schwarzenbach, *Helv. Chim. Acta*, 1952, **35**, 2344.

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

[29] L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 1964, 5046.

structural investigations[25] of the solid compounds show that the complexes $[Cu(en)_2]^{2+}$, $[Cu(trien)]^{2+}$, and $[Cu(2,3,2\text{-tet})]^{2+}$ arrange the four nitrogen atoms of the ligand on a basal plane in which the Cu^{II} ion occupies the centre. In aqueous solution the two axial positions are occupied by molecules of water. The heats of complex formation follow the order: $[Cu(2,3,2\text{-tet})]^{2+} > [Cu(en)_2^{2+} > [Cu(trien)]^{2+}$. The same trend was found for the absorption maxima of these complexes in aqueous solution[7,11] {$\nu_{max.}$ 19·0 kK $[Cu(2,3,2\text{-tet})]^{2+}$, 18·2 kK $[Cu(en)_2]^{2+}$, and 17·4 kK $[Cu(trien)]^{2+}$}. We think that this sequence is mainly due to the decreasing strength of the Cu–N bond. The tetragonal distortion may increase both with the equatorial ligand field, and with the non-bonded interactions between the hydrophobic chains and the water molecules axially bonded, but these non-bonded interactions would decrease in the order $[Cu(2,3,2\text{-tet})]^{2+} > [Cu(trien)]^{2+} > [Cu(en)_2]^{2+}$.

The sequence of the entropy change of copper(II) reactions with linear aliphatic tetramines is $[Cu(trien)]^{2+} > [Cu(2,3,2\text{-tet})]^{2+} > [Cu(3,3,3\text{-tet})]^{2+}$ (Table 5). On co-ordination the chelating agents, especially aliphatic ligands, will largely lose their flexibility. This negative entropy contribution is overcome by the large positive contribution due to the release of the water molecules from the first and second hydration sphere of the metal ion. This favourable entropy change is responsible for the high stability of multidentate ligand complexes. The loss of flexibility of a polyamine ligand increases with increasing length of aliphatic chain. Consequently, ΔS of complex formation decreases with the size of the chelate ring.[30] The complex $[Cu(2,3,2\text{-tet})]^{2+}$ with two five-membered and a six-membered ring exhibits an entropy change intermediate between that of the 5,5,5-membered ring complex $[Cu(trien)]^{2+}$ and that of the 6,6,6-membered ring complex $[Cu(3,3,3\text{-tet})]^{2+}$.

Nickel(II) *Complexes*.—As observed for nickel(II) polyamine complexes,[31-33] $[Ni(2,3,2\text{-tet})]^{2+}$ exists in solution in both yellow planar diamagnetic and blue octahedral paramagnetic forms. The equilibrium is shifted in favour of the diamagnetic species on increasing the temperature and the ionic strength. By spectral measurements, it was estimated that in the experimental conditions of our calorimetric titrations the amount of the planar species was *ca.* 25%.[34] As the transformation from the octahedral to the planar form is endothermic, the heat of formation of the octahedral complex alone must be higher than the experimentally determined heat (17·9 kcal mol^{-1}). The heat of formation of the octahedral $[Ni(2,3,2\text{-tet})]^{2+}$ (Table 5) complex should be higher than that of formation of the $[Ni(en)_2]^{2+}$ complex. Thus, in the nickel(II) reactions, as for copper(II), the enthalpy of the (2,3,2-tet) complex would be more negative than the corresponding bisethylenediamine complex, so that the $-\Delta H$ sequence is again $[Ni(2,3,2\text{-tet})]^{2} > [Ni(en)_2]^{2+} > [Ni(trien)]^{2+}$. We may suppose that the M–N bonds are stronger as the co-ordination square is more regular. Of course this regularity depends on the length of the aliphatic chain between the two nitrogen atoms too.

The structure of a yellow planar species of $[Ni(trien)]^{2+}$[35] was reported, but not of an octahedral one. The equatorial square of the octahedral complex $[Ni(en)_2(NCS)_2]$[36] is greatly distorted; the angle N–Ni–N of the chelate ring is 82° whereas the adjacent angle, out of the ethylenediamine ring, is 98°. Unfortunately the structure of a (2,3,2-tet) complex has not been determined, but we can make a useful comparison with the octahedral complex $[Ni(cyclam)Cl_2]$[37] (cyclam = 1,4,8,11-tetra-azacyclotetradecane). This ligand is a closed-chain polyamine and the N–Ni–N angles show smaller deviations from the expected value (85·7° in the five-membered and 94·3 in the six-membered ring instead of 90°).

The entropy values also depend on the 25% planar form. Its entropy would be greater than that of the diaquo-octahedral form; *i.e.*, the last one would exhibit a lower ΔS than that reported in Table 5, and lower than the corresponding value of (trien). Therefore the sequence of the entropies of the octahedral nickel(II) complexes would be $[Ni(en)_2]^{2+} > [Ni(trien)]^{2+} > [Ni(2,3,2\text{-tet})]^{2+}$, similar to that shown in the copper(II) complexes.

The $[Ni(2,3,2\text{-tet})]^{2+}$ complex can react with another polyamine molecule to form the complex $[Ni(2,3,2\text{-tet})_2]^{2+}$ in which all the vertices of the co-ordination octahedron around the nickel(II) ion are occupied by nitrogen atoms.

The two polyamine molecules in $[Ni(2,3,2\text{-tet})_2]^{2+}$ may be arranged in two different ways: (i) one (2,3,2-tet) molecule acts as a four-co-ordinating ligand in a *cis*-octahedral environment, whereas the other, acting as bidentate ligand, occupies the two remaining co-ordination sites on two adjacent nitrogens; (ii) each of the two (2,3,2-tet) molecules acts as a three-co-ordinating ligand.

According to the hypothesis (i) the reaction: $[Ni(2,3,2\text{-tet})]^{2+} + (2,3,2\text{-tet})$ should be compared with the analogous reaction $[Ni(en)_2]^{2+} + (en)$. The heat of the former reaction is markedly lower than that of the latter (4 *vs.* 10 kcal mol^{-1} [22]).

If the model (ii) is assumed, we might compare the overall reaction $Ni^{2+} + 2(2,3,2\text{-tet})$ with the analogous addition of two terdentate polyamines: $Ni^{2+} + 2(den)$. Also in this case the heat of the reaction involving (2,3,2-tet) is the lowest (22·0 *vs.* 25·3 kcal mol^{-1} [28]). Probably the non-co-ordinating amine groups in $[Ni(2,3,2\text{-tet})_2]^{2+}$ affect the co-ordination bonds of the

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adjacent nitrogens and lower the heat of reaction. The overall heat of $[Ni(2,3,2\text{-tet})_2]^{2+}$ formation, even if lower than that of $[Ni(den)_2]^{2+}$ [28] and $[Ni(en)_3]^{2+}$,[22] is always higher than that of $[Ni(penten)]^{2+}$ [29] [penten = $(NH_2{\cdot}CH_2{\cdot}CH_2)_2N{\cdot}(CH_2)_2{\cdot}N(CH_2{\cdot}CH_2{\cdot}NH_2)_2$] and [Ni(*p*-tetraen)]$^{2+}$ [38] [*p*-tetraen = $(NH_2{\cdot}CH_2{\cdot}CH_2)_2N{\cdot}(CH_2)_3{\cdot}N(CH_2{\cdot}CH_2{\cdot}NH_2)_2$]. The steric constraints present in the fused ring system of the two last complexes destabilize the Ni–N bonds more markedly.

Zinc(II) *Complexes*.—The sequence of the enthalpies of complex formation is now $[Zn(en)_2]^{2+} > [Zn(2,3,2\text{-tet})]^{2+} > [Zn(trien)]^{2+}$. This unusual behaviour may be explained by the different stereochemistry in the Zn^{II} complexes. If we agree to tetrahedral co-ordination, where the angle N–Me–N is *ca.* 109°, then neither trimethylenic chains of (2,3,2-tet) can span the co-ordination sites easily. Then we do not get an overall strain-free complex, even if the arrangement of the nitrogen atoms around the zinc(II) ion is better than that of (trien).

General Conclusions and the Macrocyclic Effect.—Some papers [11,28,29,39] showed that in the complexation of multidentate ligands the heat of reaction decreases with increasing denticity of the ligand; it was suggested that metal–secondary or tertiary nitrogen bonds, present in fused-ring complexes, are weaker than metal–primary nitrogen bonds, present in separated-ring complexes. However, in the complexation of the quadridentate ligand (2,3,2-tet), the heat of complex formation equals or exceeds the heat of formation of the bisethylenediamine complex which has all primary nitrogens. Thus the thermal effect and also the co-ordinate bond strength in polyamine complexes are not related to the type of nitrogen atom (primary or secondary) but are likely to be related to the capability of the ligand to arrange its nitrogen atoms to suit the electronic demands of the metal ion. The extent of the steric constraints arising depends upon the hydrocarbon chain length and changes with the stereochemistry of the complex.

In the complexation of the two sexidentate polyamines (penten) [29] and (*p*-tetraen) [38] an opposite result is observed: the complexes with the ligand (*p*-tetraen), which has the sequence 5,6,5 in equatorial rings, exhibit a lower heat of formation than the corresponding (penten) complexes in which all the rings are five-membered. The expansion of the middle chelate ring should favour the co-ordination of the in-plane nitrogens, but markedly disfavour the co-ordination of the apical nitrogens. In other words, the positive enthalpy contribution, owing to the removal of the strain in the equatorial ring system, is overcome by the unfavourable steric effects produced in the axial rings. Further, the addition of another six-membered ring to the five-, six-, five-membered complexes of (2,3,2-tet) increases the stability. Thus, the stability constant of the copper(II) complex with the cyclic amine (tet-a) [40] [(tet-a) = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane] is *ca.* 4 log units larger than that of the $[Cu(2,3,2\text{-tet})]^{2+}$ complex. To emphasize the exceptional stability of these complexes, the term 'macrocyclic effect' has been introduced.[40] Because of the kinetic inertness of these macrocyclic compounds a full thermodynamic investigation is not easy to carry out.

However, on the basis of the previous arguments we suggest that the macrocyclic effect is not a more extensive chelate effect, *i.e.*, solely due to a favourable change in translational entropy; but it must be mainly ascribed to the enthalpy term.

The formation of metal complexes with open-chain tetramines causes a noteworthy loss of translational and vibrational entropy of the ligand, when the donor atoms are frozen in the co-ordination sites. By contrast, the complexation of the more rigid macrocyclic ligand causes a lesser entropy loss so that the entropy change of the reaction is more positive. Thus, the entropy term should also partly contribute to the larger stability of the macrocyclic complexes.

We thank the Italian Consiglio Nazionale delle Ricerche for financial assistance.

[1/2344 *Received*, 7*th December*, 1971]

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