Thermodynamics of Complex Formation of 1,5,8,12-Tetra-azadodecane with Copper(II) Ions and Protons in Aqueous Solution

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Thermodynamic data are reported for the protonation of the tetra-amine 1,5,8,12-tetra-azadodecane (3,2,3-tet) and for the formation of the complexes $Cu(3,2,3\text{-tet})^{2+}$ and $Cu(3,2,3\text{-tet}.H)^{3+}$. Data for the respective copper complexes are $\Delta G = -123{\cdot}8 \pm 0{\cdot}5, -83{\cdot}8 \pm 0{\cdot}5$ kJ mol^{-1}; ΔH(calorimetric) $= -104{\cdot}0 \pm 0{\cdot}9, -70{\cdot}3 \pm 1{\cdot}2$ kJ mol^{-1}; $\Delta S = 66{\cdot}3 \pm 5, 45{\cdot}5 \pm 5$ J mol^{-1} K^{-1} at 25 °C, $I = 0{\cdot}10$M-NaCl. In comparison with related tetra-amines the sequence of basicities ($\sum_1^4 \log k_i$) is 3,3,3-tet > 3,2,3-tet > 2,3,2-tet > 2,2,2-tet and for stabilities of 1 : 1 copper(II) complexes is 3,2,3-tet > 2,2,2-tet > 3,3,3-tet.

THERMODYNAMIC data have been reported for complex formation by the tetra-amine ligands 1,4,7,10-tetra-azadecane (2,2,2-tet, trien)[1,2] and 1,5,9,13-tetra-azatridecane (3,3,3-tet)[3] with protons and some transition-metal ions. The results for the complex formation with copper(II) ions were interpreted in terms of steric constraints in the chelate rings.[2,3] These ligands are an extension to the lower homologous series en, tmd, dien, dpt † which have been studied widely.[4]

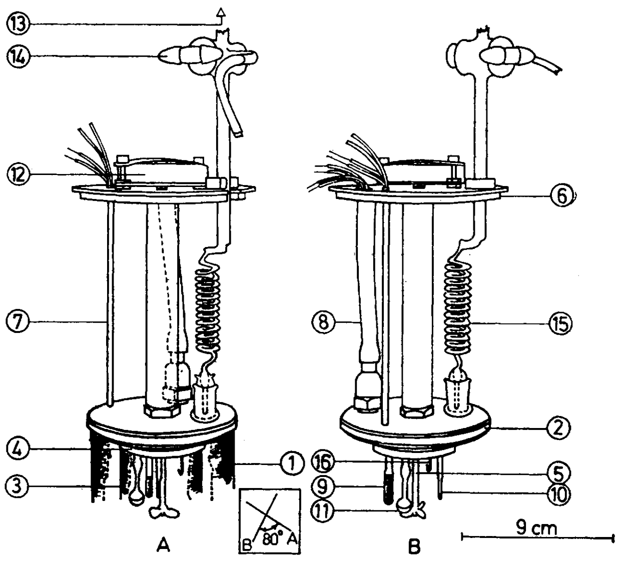
The protonation constants[5] and preliminary copper–ligand stability constants[6] have been reported for the title compound, the analogous tetra-amine ligand 1,5,8,12-tetra-azadodecane (3,2,3-tet). Here, we report the thermodynamic constants for the formation of the copper complexes $Cu(3,2,3\text{-tet})^{2+}$ and $Cu(3,2,3\text{-tetH})^{3+}$, and the determination of the enthalpy changes for complex formation of 3,2,3-tet with protons and copper(II) ions at 25 °C and $I = 0{\cdot}10$M (NaCl).

EXPERIMENTAL

Materials.—The preparation of the ligand 3,2,3-tet has been described previously.[5] Acidified copper chloride solutions, prepared from B.D.H. AnalaR reagent, were standardised by gravimetric analysis as copper salicylaldoximate[7] and by complexometric titrations[8] against EDTA.

p[H$^+$] *Measurements.*—p[H$^+$] Data were obtained by potentiometric titrations using the apparatus, and [H$^+$] calibration method described previously.

Calorimetric Measurements.—The main features of the incremental titration calorimeter are shown in the Figure. The calorimeter consisted of an outer brass can (1) and lid (2) and an inner thin-walled glass vessel (3) with a brass lid of thin cross-section (4). The glass vessel was silvered on the outer wall and covered with a layer of thin reflecting tin foil. A threaded brass ring was sealed with an epoxy resin glue (Araldite) to the outer rim of the glass. The underneath face of the lid (4) was coated with a layer of polyurethane enamel. The maximum capacity of the glass vessel was *ca.* 110 ml. The two lids (2) and (4) were permanently joined by a short nylon shaft through which the hollow glass stirrer shaft (5) passed. The outer lid (2) was fastened to a Tufnal disc (6) by way of three connecting tubes; a central brass tube, through which the stirrer passed, and two other tubes (7) and (8) which carried the leads to the heater (9) and thermistor (10), and the tubes to the cooler (11). The glass propeller stirrer was connected to a synchronous motor (12) (Philips type AU5100/22, 250 rev min^{-1}) mounted on the disc (6).



Titration calorimeter

The cooler consisted of a thin-walled glass tube, with a small bulb at the lower end which contained *ca.* 0·2 ml of water. Cooling was effected by passing air (at room temperature) over the surface of the water.

The heater consisted of cotton-covered Manganin wire wound around the outside of the lower half of a thin-walled glass tube. The wire was insulated from the solution by a thin coating of Araldite.

Titrant was dispensed manually, at a constant rate, from

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† en = Ethylenediamine; tmd = 1,3-diaminopropane; dien = bis(2-aminoethyl)amine; dpt = bis(3-aminopropyl)amine.

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

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

[3] R. Barbucci, L. Fabbrizzi, P. Paoletti, and A. Vacca, *J.C.S. Dalton*, 1972, 740.

[4] L. G. Sillén and A. E. Martell, 'Stability Constants,' Special publication No. 17, 1964, and No. 25, 1971, The Chemical Society, London.

[5] G. R. Hedwig and H. K. J. Powell, *Analyt. Chem.*, 1971, **43**, 1206.

[6] G. R. Hedwig, J. L. Love, and H. K. J. Powell, *Austral. J. Chem.*, 1970, **23**, 981.

[7] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' Longmans, London, 3rd edn., 1961.

[8] G. Schwarzenbach and H. Flaschka, 'Complexometric Titrations,' 2nd Eng. edn., Methuen, London, 1969.

an Agla micrometer glass syringe (13) of total volume 0·5 ml. The titrant was added in increments of *ca.* 0·3 ml and passed through a thin-walled glass spiral (15) (volume *ca.* 0·9 ml), which allowed efficient thermostatting of the solution, then entered the calorimeter through a fine glass tube (16). A three-way tap (14) enabled the syringe to be refilled from a titrant reservoir.

The temperature inside the calorimeter was measured using a single NTC thermistor (Philips type 2322 627 11103, $R_{25\,°\mathrm{C}} = 8950\ \Omega$) which was one arm of an AC transformer bridge (operated at a r.m.s. voltage of *ca.* 0·2V); another arm contained resistance (a decade box, H. W. Sullivan, London, tolerance ±0·05%) and capacitance balances.

The out-of-balance potential of the bridge was amplified, rectified and fed to a Honeywell Electronik 194 Lab/Test Recorder, the chart of which constituted a resistance–time scale. The usual working sensitivity was *ca.* 12 chart divisions for a 0·1 Ω change in thermistor resistance or *ca.* 2×10^{-5} °C division^{-1}. (The temperature coefficient of resistance of the thermistor was $368 \pm 5\ \Omega\ °\mathrm{C}^{-1}$.)

Electrical calibrations were performed using a conventional heater curcuit.[9] The precision resistors used in the heater circuit were H. W. Sullivan non-reactive resistances, tolerance ±0·1% and ERG precision wire wound resistors, tolerance ±0·05%. All voltage measurements were made using a Cambridge Slide Wire potentiometer, type 44244/3 (readability 0·001 mV), a Muirhead standard cell, and a sensitive galvanometer (H. Tinsley and Co. type SR4/45). The heating time was determined as the time between the switching on and switching off of a microswitch operated by a synchronous motor driven cam. The heating time was 63·70 ± 0·03 s, determined using a Levell Universal counter-timer type TM 51B.

The calorimeter was immersed in a bath containing *ca.* 55 l of water at 25·0 °C, controlled to ±0·001 °C.

The operation of the calorimeter was as follows. The titrant line was filled with solution at room temperature, to such a position which allowed for volume expansion (*ca.* 0·0005 ml) when placed into the thermostat bath. After the calorimeter was assembled, heating was applied to bring the temperature of the calorimeter approximately to that of the thermostat bath. (Calorimeter equilibrium temperature was *ca.* 0·01 to 0·02 °C above bath temperature.) Before the addition of titrant, the temperature of the calorimetric solution was adjusted to be *ca.* 0·005 °C higher than bath temperature. Corrections for the temperature difference between the titrant and calorimetric solution were negligible.

The corrected resistance changes were obtained by linear extrapolation from the fore and after recorder traces to a time equal to half the heating (or reaction) time. The heat changes during a reaction were evaluated from the resistance changes by reference to electrical calibrations. During these electrical calibrations, the heat inputs were matched as closely as possible to those of the reactions. After a reaction, the time required for the calorimeter to attain thermal equilibrium, as judged from thermal leakage constant determinations, was *ca.* 6 min. This compares favourably with values obtained for calorimeters of this type.[10]

The precision of the calorimeter, determined from many electrical calibrations, was to ±0·2% for heat changes of *ca.* 8 J.

The accuracy of the system was checked by determining the enthalpy change for NaOH–HCl neutralisation and for the protonation of Tris (aq) with HCl. The mean and standard deviation of eight determinations of the enthalpy of protonation of Tris was $-47{\cdot}83 \pm 0{\cdot}05$ kJ mol^{-1} (from heat changes of 7 to 8 J). This value is 0·7% higher than previous literature values [10,11] of −47·48 and −47·44 kJ mol^{-1}, and is just outside the total experimental error of 0·6%. The results for NaOH/HCl were consistent with those for Tris protonation.

RESULTS AND CALCULATIONS

Stability Constants.—Representative data from the pH titrations of NaOH against solutions of copper ions, 3,2,3-tet, and acid are deposited with the National Lending Library.[12] p[H$^+$] Data could not be satisfactorily interpreted in terms of only one complex CuL^{2+}. Spectrophotometric measurements as a function of pH indicated an increase in $\lambda_{\mathrm{max.}}$ as the pH decreased, which suggested the formation of a protonated complex in the pH range 3·5 to 5. Stability constants for the formation of the complexes, were calculated using a non-linear least-squares procedure.[5]

$$\mathrm{Cu}^{2+} + \mathrm{L} \rightleftharpoons \mathrm{CuL}^{2+}(K_1)$$
$$\mathrm{Cu}^{2+} + \mathrm{HL}^{+} \rightleftharpoons \mathrm{CuHL}^{3+}(K_2)$$

The results of the stability constant calculations for titrations at different M : L ratios ($T_{\mathrm{M}} : T_{\mathrm{L}}$ *ca.* 1 : 1, 1 : 1·5, and 10 : 1) showed satisfactory agreement [12] and concurred with the results from the analysis of the 10 : 1 and 1 : 1 titration data using Schwarzenbach's method.[13]

Enthalpy Data.—For the ligand protonation reactions, titrant HCl was added to solutions of ligand, acid, and NaCl. From the mass balance equations for T_{H} and T_{L},

$$T_{\mathrm{H}} = [\mathrm{H}] - K_{\mathrm{w}}/[\mathrm{H}] + T_{\mathrm{L}} \frac{\sum\limits_{n=1}^{4} n\beta_n[\mathrm{H}]^n}{\sum\limits_{n=0}^{4} \beta_n[\mathrm{H}]^n} \qquad (1)$$

where $\beta_n = \prod\limits_{i=1}^{n} k_i$, k_i being the concentration quotient for the stepwise protonation $\mathrm{LH}_{i-1}^{(i-1)+} + \mathrm{H}^{+} \rightleftharpoons \mathrm{LH}_{i}^{i+}$, and where $\beta_0 = 1$. The solution composition at each calorimetric titration point was calculated by solving the polynomial in $[\mathrm{H}]^6$, formed on rearrangement of equation (1), using the Newton–Rapson method.[14] For each titration point, the required approximate solution for the polynomial was interpolated from a previously determined formation curve. The calorimetric data from titrations of 3,2,3-tet with HCl are deposited as a Supplementary publication.[12] The measured exothermic

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[9] J. M. Sturtevant, in 'Techniques of Organic Chemistry,' Part I, 'Physical Methods,' ed. A. Weissberger, vol. I, p. 523.

[10] I. Grenthe, H. Ots, and O. Ginstrup, *Acta Chem. Scand.*, 1970, **24**, 1067.

[11] G. Ojelund and I. Wadsö, *Acta Chem. Scand.*, 1968, **22**, 2691.

[12] Material deposited as Supplementary Publication No. 20639, 4 pp. For details of the Supplementary Publication scheme, see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[13] G. Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 947.

[14] N. I. Vilenkin, 'Successive Approximations,' Pergamon Press, Oxford, 1964.

heat changes between successive titration points were corrected for the heat of dilution of HCl, and for the secondary reaction[10] $H^+ + OH^- \rightleftharpoons H_2O$, $\Delta H° = -55{\cdot}84$ kJ mol^{-1}. The enthalpy changes for the stepwise protonation reactions, $(LH_{i-1}^{(i-1)+} + H^+ \rightleftharpoons LH_i^{i+}$, $\Delta H_i)$ were calculated by a least-squares procedure using a suitable computer program. If Q_{corr} is the corrected incremental heat change and if $Q_{calc} = r\Delta H_1 + s\Delta H_2 + t\Delta H_3 + u\Delta H_4$ where *r*, *s*, *t*, *u* are respectively the changes in the number of mmol of the species LH, LH_2, LH_3, and LH_4 between successive titration points, and Q_{calc} is the calculated heat change in joules, then the least-squares process varied the parameters ΔH_i so as to minimise the error square sum $\sum_{j=1}^{n} W_j(Q_{corr} - Q_{calc})_j^2$. The weighting factor W_j for the j_{th} measurement of Q_{corr} was taken as unity.

TABLE 1

Thermodynamic functions for the stepwise protonation of tetra-amine ligands [a] at 25 °C, $I = 0{\cdot}10$M

n [b]	log k_n	$-\Delta G$/kJ mol^{-1}	$-\Delta H$/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
1,5,8,12-Tetra-azadodecane (3,2,3-tet)				
1	10·53 ± 0·02	60·10 ± 0·1	$51{\cdot}68 \pm 0{\cdot}2_7$	28·3 ± 1·2
2	9·77 ± 0·02	55·76 ± 0·1	$51{\cdot}80 \pm 0{\cdot}2_0$	13·3 ± 1·0
3	8·30 ± 0·02	47·37 ± 0·1	$43{\cdot}18 \pm 0{\cdot}1_4$	14·1 ± 0·8
4	5·59 ± 0·02	$31{\cdot}90 \pm 0{\cdot}0_6$	$34{\cdot}16 \pm 0{\cdot}1_3$	−7·6 ± 0·6
	34·2			
1,5,9,13-Tetra-azatridecane (3,3,3-tet) [c]				
1	10·45	59·66	$51{\cdot}04 \pm 0{\cdot}2_5$	28·9
2	9·82	56·07	52·17 ± 0·4	13·4
3	8·54	48·74	48·74 ± 0·7	0·0
4	7·22	41·21	45·52 ± 0·8	−14·6
	36·0			
1,4,7,10-Tetra-azadecane (trien, 2,2,2-tet) [d]				
1	9·78	55·81	46·07	32·7
2	9·06	51·71	47·15	15·3
3	6·55	37·38	39·87	−8·4
4	3·24	18·49	28·58	−33·8
	28·6			

[a] Log k_i data for protonation of 2,3,2-tet at 0·5M-KCl, 25 °C are 10·25, 9·50, 7·28, 6·02 ($\sum_{i=1}^{4} \log k_i = 33{\cdot}1$); D. C. Weatherburn, E. J. Billo, J. P. Jones, and D. W. Margerum, *Inorg. Chem.*, 1970, **9**, 1557. [b] Data refers to the reaction $H_{n-1}L^{(n-1)+} + H^+ \rightleftharpoons H_nL^{n+}$. [c] Data from ref. 3, 0·1M-NaNO$_3$. [d] Data from ref. 1, 0·1M-KCl.

For the determination of the enthalpy changes for the reactions $Cu^{2+} + L \rightleftharpoons CuL^{2+}$ (ΔH_1) and $Cu^{2+} + HL^+ \rightleftharpoons CuHL^{3+}$ (ΔH_2), solutions made from the solid complex Cu(3,2,3-tet)$(ClO_4)_2$[6] were titrated with HCl. The solution composition at each titration point was obtained by solving the three mass-balance equations (T_M, T_H, and T_L) using a successive approximations method incorporated into a suitable computer program. Calorimetric data from the titrations are also treated as a Supplementary publication.[12] The enthalpy changes were calculated using a least-squares process, $Q_{calc} = R\Delta H_1 + S\Delta H_2$, where *R* and *S* are the number of mmol of CuL and CuHL formed between successive titration points.

The thermodynamic functions ΔG, ΔH, and ΔS, relative to a 0·1M-NaCl standard state, for the stepwise protonation of 3,2,3-tet and for other tetra-amines are shown in Table 1. Data for the formation of the corresponding copper complexes are shown in Table 2.

DISCUSSION

Protonation.—The free-energy change on protonation of an amine nitrogen in the presence of a charge (or a dipole) elsewhere in the molecule will become more negative as the distance of the charge (or dipole) from the protonation centre increases. For the methylenediamines $NH_2(CH_2)_nNH_2$, both log k_1 and log k_2 increase as *n* increases from $n = 2$ (ethylenediamine) to $n = 6$ (hexamethylenediamine).[15] Linear tetra-amines have three methylene chains joining the four nitrogen atoms. The predicted basicity sequence ($\sum_{i=1}^{4} \log k_i$) for the tetra-amines with combinations of two- and three-membered methylene chains would be 3,3,3-tet > 3,2,3-tet > 2,3,2-tet > 2,2,2-tet where 2,3,2-tet is the amine $NH_2{\cdot}[CH_2]_2{\cdot}NH{\cdot}[CH_2]_3{\cdot}NH{\cdot}[CH_2]_2{\cdot}NH_2$. The available data for these tetra-amines (Table 1) show that this predicted sequence is observed.

TABLE 2

Thermodynamic data for the formation of copper(II) complexes with tetra-amine ligands at 25 °C, $I = 0{\cdot}10$M

Reaction	log K	$-\Delta G$/kJ mol^{-1}	$-\Delta H$/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
1,5,8,12-Tetra-azadodecane (3,2,3-tet)				
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	21·69 ± 0·08	123·8 ± 0·5	104·0 ± 0·9	66·3 ± 5
$Cu^{2+} + HL^+ \rightleftharpoons CuHL^{3+}$	14·69 ± 0·08	83·8 ± 0·5	$70{\cdot}2_7 \pm 1{\cdot}2$	45·5 ± 5
1,5,9,13-Tetra-azatridecane (3,3,3-tet) [a]				
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	$17{\cdot}0_5 \pm 0{\cdot}1$	97·3 ± 0·6	$81{\cdot}3_8 \pm 0{\cdot}2$	53·6 ± 2
1,4,7,10-Tetra-azadecane (2,2,2-tet) [b]				
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	20·08	114·6	$90{\cdot}1_6$	81·6
$Cu^{2+} + HL^+ \rightleftharpoons CuHL^{3+}$	13·8	78·7	66·1	41·8

[a] Data from ref. 3, 0·1M-NaNO$_3$. [b] Data from ref. 2, 0·1M-KCl.

For the protonation of diamines, the stepwise enthalpy changes are more exothermic for primary amines than for secondary amines. For example, the $-\Delta H_1$ value for ethylenediamine[16] protonation is 50·96 kJ mol^{-1}

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

[16] P. Paoletti, R. Barbucci, A. Vacca, and A. Dei, *J. Chem. Soc.* (*A*), 1971, 310.

whereas that for *NN′*-dimethylethylenediamine[16] is 44·94 kJ mol^{-1} (both at $I = 0{\cdot}5\text{M}$-KCl and 25 °C). The enthalpy change for the first stepwise protonation of *N*-methylethylenediamine lies between that for ethylenediamine and that for *NN′*-dimethylethylenediamine which suggests a tautomeric equilibrium in the neutralisation of the asymmetric diamine.[16] A comparison of $-\Delta H_1$ for the protonation of the tetra-amines (Table 1) with $-\Delta H_1$ for the protonation of ethylenediamine, trimethylenediamine,[16] and *NN′*-dimethylethylenediamine suggests that for the tetra-amines also, the initial protonation does not occur entirely on the primary nitrogen. A similar deduction can be made for the triamines dien and dpt.[17]

The difference between the successive stepwise enthalpy changes for protonation of the methylenediamines $NH_2\cdot[CH_2]_n\cdot NH_2$ decreases as the chain-length increases[15] and is very small for hexamethylenediamine, $\Delta H_1 = -58{\cdot}2$ kJ mol^{-1} and $\Delta H_2 = -57{\cdot}4$ kJ mol^{-1}. The enthalpy data for protonation of 3,2,3-tet (Table 1) show that $\Delta H_1 \sim \Delta H_2$. This result suggests that the first and second protonation steps involve an addition of protons onto both primary and secondary amine nitrogens and that the dication has structures with minimal repulsion between charge centres; *i.e.* the dominant tautomers in equilibrium will be

$$\overset{+}{N}H_3\cdot[CH_2]_3\cdot NH\cdot[CH_2]_2\cdot NH\cdot[CH_2]_3\cdot\overset{+}{N}H_3$$

and

$$\overset{+}{N}H_3\cdot[CH_2]_3\cdot NH\cdot[CH_2]_2\cdot\overset{+}{N}H_2\cdot[CH_2]_3\cdot NH_2$$

For successive protonations of these tetra-amines, charge repulsion will lead to a decrease in the exothermic heat of protonation. As the distances between the charges increase with increasing chain length, (the electrostriction decreases;[18] the effective dielectric constant increases[18]) the electrostatic interaction will decrease, resulting in a more exothermic change. The effect of interaction between adjacent like charges will be important for the third and fourth protonation steps; the $-\Delta H_3$ and $-\Delta H_4$ values (Table 1) increase in the order 2,2,2-tet < 3,2,3-tet < 3,3,3-tet.

For the fourth stepwise protonation of these tetra-amines, protonation of the ion $\overset{+}{N}H_3\cdot[CH_2]_x\cdot\overset{+}{N}H_2\cdot[CH_2]_y\cdot NH\cdot[CH_2]_x\cdot\overset{+}{N}H_3$ is likely to be the dominant reaction. As the charges of closest proximity to the protonation site will be of greatest importance, it might be expected that the $-\Delta H_4$ for the tetra-amines will be comparable with $-\Delta H_3$ for dien and dpt. The data in Table 1 and for these triamines[17] increase in the order 2,2,2-tet < dien < 3,2,3-tet < 3,3,3-tet ∼ dpt.

The entropy change for the protonation of alkyl monoamines increases in the order $RNH_2 < R_2NH < R_3N$; for R = methyl there is an almost constant increase[19] (*ca.* 20 J mol^{-1} K^{-1}). A similar trend (in ΔS_1) has also been observed for the diamines ethylenediamine, piperazine, and triethylenediamine.[20] The data in Table 1, and the data for the triamines dien and dpt,[17] show that the ΔS_1 values for all the polyamines are of a similar magnitude (values vary from a smallest of 28·3 to a largest of 32·7 J mol^{-1} K^{-1}) and lie between the value for ethylenediamine, 23·8 J mol^{-1} K^{-1}, and that for piperazine, 43·1 J mol^{-1} K^{-1}.[21] This suggests, as does the enthalpy data, that for these tri- and tetra-amines the protonation in the first stepwise process occurs neither exclusively on a primary nor exclusively on a secondary nitrogen atom.

For subsequent stepwise protonations, the entropy changes decrease. This trend results from (i) chain stiffening due to charge repulsion[22,15] and (ii) an increased solvent ordering ability of the charged ion due to the close proximity of the charges.[22]

Copper Complexes.—It is well known that a labile complex with a five-membered chelate ring is more stable than that with a six-membered chelate ring.[23,24] For example, the free-energy change for the formation of the 1 : 1 copper complex with 1,3-diaminopropane is less negative than that with 1,2-diaminoethane,[25] even though 1,3-diaminopropane is the stronger base. Similarly, the 1 : 1 copper complex with dien is more stable than that with dpt. For the tetra-amines, the data in Table 3 show that the stabilities of the complexes increase in the sequence Cu(3,3,3-tet) < Cu(2,2,2-tet) < Cu(3,2,3-tet).

The most stable complex results from a combination of five- and six-membered chelate rings. In square co-ordination 3,2,3-tet can have each chelate ring in a stable non-eclipsed configuration and gives an apparently strain-free system.[6] In contrast, for the co-ordination of 2,2,2-tet in a planar configuration the chelate rings cannot all adopt the favoured *gauche* form without considerable strain (distortion of the bond angles).[26] Also models show that for 3,3,3-tet there is considerable strain in the metal–secondary nitrogen bonds if each chelate ring is in the favoured chair configuration.[6] Any ring strain in a complex will contribute to the enthalpy change of complex formation, as it is the enthalpy term which is most directly related to the change in the number and strength of bonds.[27]

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[26] B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc.* (*A*), 1966, 1331.

[27] G. H. Nancollas, 'Interactions in Electrolyte Solutions,' Elsevier, London, 1966.

TABLE 3

Temperature-independent (ΔH_c) and temperature-dependent (ΔH_e) enthalpy data for the formation of some copper(II)–amine complexes

Amine, reaction	$-\Delta H$/kJ mol^{-1}	$\lambda_{max.}$/nm	$-\Delta n$	ΔH_e/kJ mol^{-1}	$-\Delta H_c$/kJ mol^{-1}	($-\Delta H_c/p$) kJ mol^{-1} [a]
$Cu^{2+} + 2en \longrightarrow Cu(en)_2^{2+}$	105·3 [b]	549 [c]	2	7·6	112·9	28·3
Cu^{2+} + 3,2,3-tet $\longrightarrow$ Cu(3,2,3-tet)$^{2+}$	104·0	545 [d]	1	7·9	111·9	28·0
Cu^{2+} + 2,2,2-tet $\longrightarrow$ Cu(2,2,2-tet)$^{2+}$	90·2 [e]	575 [e]	1	7·1	97·3	24·3
Cu^{2+} + 3,3,3-tet $\longrightarrow$ Cu(3,3,3-tet)$^{2+}$	81·4 [f]	588 [f]	1	6·9	88·3	22·1
Cu^{2} + dien $\longrightarrow$ Cu(dien)$^{2+}$	75·3 [g]	611 [c]	1	6·6	81·9	27·3

[a] p Is the number of nitrogen atoms bonded to the copper ion. [b] From T. Davies, S. S. Singer, and L. A. K. Stavely, *J. Chem. Soc.*, 1954, 2304. [c] From C. K. Jorgensen, *Acta Chem. Scand.*, 1955, **9**, 1362. [d] From ref. 6. [e] From ref. 2. [f] From ref. 3. [g] From ref. 17.

The enthalpy change on co-ordination of a ligand to a metal ion can be expressed in terms of two quantities;[28] a temperature-dependent term which incorporates long-range electrostatic forces which are dependent on the medium, and a temperature-independent term representing short range or quantum mechanical (covalent) forces independent of the environment. The temperature-dependent enthalpy change ΔH_e is given by the equation[28] $\Delta H_e = (T - \nu)(\Delta S - \Delta nRln55{\cdot}5)$ where ν is a temperature characteristic of the solvent (219 K for water) and Δn is the increase in the number of solute species on co-ordination. The temperature-independent enthalpy change, ΔH_c, is given by $\Delta H = \Delta H_e + \Delta H_c$. ΔH_c and ΔH_e contributions to the enthalpy data for the formation of the copper(II) complexes of some polyamines are shown in Table 3. The $-\Delta H_c/p$ value [p = number of nitrogen atoms bonded to the copper(II) ion] for 3,2,3-tet is close to that for ethylenediamine, which indicates that the copper complex with 3,2,3-tet is almost strain free (assuming this is the case for ethylenediamine for which the C–N–M angle is close to 109° in co-ordination[3]). The more endothermic values for 2,2,2-tet and 3,3,3-tet compared with en, indicate the increased strain (cumulative ring strain[26]) in the formation of the *linked* chelate rings. The $\lambda_{max.}$ data for the copper(II)–tetra-amine complexes are also shown in Table 3. The value of $\lambda_{max.}$ will depend on the donor strength of the nitrogen atoms and on the degree of tetragonal distortion in the complex, *i.e.* the value will be closely related to the temperature-independent enthalpy term ΔH_c. The data in Table 3 show that both the ligand-field strength and ΔH_c increase in the order $Cu(dien)^{2+} <$ Cu(3,3,3-tet)$^{2+}$ $<$ Cu(2,2,2-tet)$^{2+}$ $<$ $Cu(en)_2^{2+} \sim$ Cu(3,2,3-tet)$^{2+}$; the correlation is approximately linear.

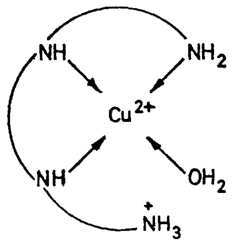
For the reaction

$$M(H_2O)_n^{2+}(aq) + L(aq) \rightleftharpoons M(H_2O)_xL^{2+}(aq) + (n - x)H_2O$$

dominant contributions to the entropy change arise from (i) the release of water molecules from the inner co-ordination sphere of the metal ion, (ii) changes in the number of degrees of freedom of the ligand on co-ordination, (iii) changes in the ' solvation lattice ' of the metal ion on co-ordination. The data in Table 2 show that the entropy changes for the formation of copper complexes with the tetra-amines increase in the order 3,3,3-tet < 3,2,3-tet < 2,2,2-tet.

The position of 3,2,3-tet in this sequence is consistent with the postulate[3] that the loss of translational, vibrational, and rotational entropy of the propylenic ligand, 3,3,3-tet, in comparison with the ethylenic ligand 2,2,2-tet, is greater than the contribution from changes in the ' solvation lattice '.

Spectrophotometric and potentiometric data suggested the formation of a protonated complex $CuHL^{3+}$ with the ligand 3,2,3-tet. A similar complex was also observed with the tetra-amine ligand 2,2,2-tet.[2] The most likely structure for these complexes is where one primary and two secondary nitrogen atoms are co-ordinated to the metal ion and the remaining terminal nitrogen atom is protonated. The thermodynamic data for the formation of protonated copper(II) complexes with these tetra-amine ligands are shown in Table 2. The larger separation between the charged centres Cu^{2+} and $-NH_3^+$ for 3,2,3-tet is expected to contribute to the observed more exothermic ΔH for this ligand.



Although 3,3,3-tet is a stronger base than either 2,2,2-tet or 3,2,3-tet, it does not give a protonated complex $CuHL^{3+}$. This is because the Cu(3,3,3-tet)$^{2+}$ complex, with its cumulative ring strain and a lower stability constant, is formed in a higher pH range (5·3 to 6·2;[29] *cf.* 3·5 to 4·2 for 3,2,3-tet).

Log k° and Log K° Data.—For both the protonation and copper complexing reactions equilibrium constants were determined in NaCl solutions at $I = 0{\cdot}20$, 0·15, 0·10, and 0·04M. These constants were extrapolated to zero ionic strength to give the thermodynamic equilibrium constants $k_i°$ and $K_i°$. The protonation data have been reported.[5] Data for the copper complexes at $I = 0{\cdot}20$ through 0·0M are: $\log K_1 = 21{\cdot}81$, 21·69, 21·69, 21·53 ± 0·08, $\log K_1° = 21{\cdot}2_2 \pm 0{\cdot}1$ from a plot of $\log K_1 - [I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})]$ against I; $\log K_2 = 14{\cdot}80$, 14·73, 14·69, 14·50 ± 0·08, $\log K_2° = 14{\cdot}18 \pm 0{\cdot}1$ from a plot of $\log K_2 - [2I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})]$ against I.

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