Thermochemical Study of the Stepwise Protonation of 3-Azaheptane-1,7-diamine and 4-Azaoctane-1,8-diamine, and of Complex Formation between Copper(II) and 3-Azaheptane-1,7-diamine and 4,9-Diazadodecane-1,12-diamine †

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Calorimetric enthalpy data [at 25 °C and I = 0.1 mol dm^{-3} (NaCl)] are reported for stepwise protonation of the tribasic ligands 3-azaheptane-1,7-diamine (3NH-hd) and 4-azaoctane-1,8-diamine (4NH-od, spermidine) and for the formation of the copper complexes [CuL]$^{2+}$, [Cu(HL)]$^{3+}$, and [Cu(OH)L]$^{+}$ (L = 3NH-hd) and [CuL]$^{2+}$ and [Cu(HL)]$^{3+}$ [L = the tetrabasic ligand 4,9-diazadodecane-1,12-diamine (4,9NH-ddd, spermine)]. By comparison with data for homologous linear triamines and tetra-amines, the relative importance of enthalpy and entropy terms in stabilising large chelate rings is assessed.

RECENT papers [1,2] have reported equilibrium constants for the complexing reaction between copper (II) and three linear polyamine ligands which contain a tetramethylene linkage (and which therefore give metal complexes containing one seven-membered chelate ring). The ligands give the complexes (*i*) [CuL]$^{2+}$, [Cu(HL)]$^{3+}$, [Cu(HL)$_2$]$^{4+}$, and [Cu(OH)L]$^{+}$ [L = 3-azaheptane-1,7-diamine (3NH-hd)], (*ii*) [CuL]$^{2+}$, [Cu(HL)]$^{3+}$, and [Cu(OH)L]$^{+}$ [L = 4-azaoctane-1,8-diamine (4NH-od)], and (*iii*) [CuL]$^{2+}$ and [Cu(HL)]$^{3+}$ [L = 4,9-diazadodecane-1,12-diamine (4,9NH-ddd)]. For the two triamine ligands the seven-membered chelate ring contributes *ca.* 10^2—10^3 dm^3 mol^{-1} to the formation constant for [CuL]$^{2+}$ [measured relative to the formation constants for copper(II) complexes of ethylenediamine and propane-1,3-diamine respectively]. In contrast, the quadridentate ligand, both in its protonation reactions ($\Delta G,\Delta H$) and copper complexing (ΔG), displays properties similar to those shown by two isolated propane-1,3-diamine ligands and the net contribution of the seven-membered ring to the stability of [CuL]$^{2+}$ is approximately zero.

This paper presents the first enthalpy and entropy data for copper(II) complexing by polyamine ligands having a tetramethylene linkage. Data are reported for the formation of [CuL]$^{2+}$, [Cu(HL)]$^{3+}$, and [Cu(OH)L]$^{+}$ (L = 3NH-hd) and [CuL]$^{2+}$ and [Cu(HL)]$^{3+}$ (L = 4,9NH-ddd), and for the stepwise protonation of 3NH-hd and 4NH-od. For the series of homologous linear triamine ligands $H_2N{\cdot}[CH_2]_2{\cdot}NH{\cdot}[CH_2]_x{\cdot}NH_2$ in their copper complexes [CuL]$^{2+}$, the low stability of the complex with a seven-membered chelate ring ($x = 4$) arises from a low enthalpy term (the entropy terms being approximately equal). In contrast, for the homologous linear tetra-amine ligands $H_2N{\cdot}[CH_2]_3{\cdot}NH{\cdot}[CH_2]_x{\cdot}NH{\cdot}[CH_2]_3{\cdot}NH_2$, the low stability of the complex with $x = 4$ arises from a very low (negative) entropy term, the enthalpy term being very favourable and reflecting the high basicity of this ligand.

EXPERIMENTAL

Materials.—3-Azaheptane-1,7-diamine (3NH-hd) (purum; Fluka) and 4-azaoctane-1,8-diamine (4NH-od) (pure; Koch-Light) were purified as their tris(hydrochloride) salts [2,3] and 4,9-diazadodecane-1,12-diamine (4,9NH-ddd) (puriss; Koch-Light) was purified as its tetrakis(hydrochloride) salt [3] (Found: C, 29.4; H, 8.1; N, 17.5. Calc. for $C_6H_{20}Cl_3N_3$: C, 29.9; H, 8.4; N, 17.5. Found: C, 33.1; H, 8.7; N, 16.6. Calc. for $C_7H_{22}Cl_3N_3$: C, 33.0; H, 8.7; N, 16.5. Found: C, 34.5; H, 8.7; N, 16.3. Calc. for $C_{10}H_{30}Cl_4N_4$: C, 34.5; H, 8.7; N, 16.1%).

pH *Measurements*.—pH Data were obtained by potentiometric titrations with the apparatus and [H$^+$]-calibration method previously described.[4]

Calorimetric Measurements.—The calorimeter has been described.[5] The accuracy of the system was checked again [2,5] by determining the enthalpy change for protonation of aqueous aminotri(hydroxymethyl)methane (Tris) with HCl; the mean and standard deviation of three measurements (measured heat change *ca.* 8 J) was -47.77 ± 0.26 kJ mol^{-1} (lit.,[6,7] -47.48 and -47.44 kJ mol^{-1}). For the protonation of 3NH-hd and 4NH-od, solutions of the ligand (c_L *ca.* 3×10^{-3} mol dm^{-3}, $\bar{n}_H$ *ca.* 0.3)‡ were titrated in the calorimeter with HCl (*ca.* 1 mol dm^{-3}).

For the complexes [CuL]$^{2+}$ and [Cu(HL)]$^{3+}$, and for [Cu(OH)L]$^{+}$ (L = 3NH-hd), calorimetric measurements involved titration of HCl (*ca.* 1 mol dm^{-3}) into solutions of copper dichloride (*ca.* 3×10^{-3} mol dm^{-3}) and ligand (*ca.* 4×10^{-3} mol dm^{-3}) starting at pH *ca.* 6.2—6.6 and 9.6 respectively (*cf.* distribution curves [2]); *i.e.* the enthalpy change for dissociation (or protonation) of the complex was determined. A similar procedure was used for the complexes [CuL]$^{2+}$ and [Cu(HL)]$^{3+}$ (L = 4,9NH-ddd) ($c_M = 0.7 \times 10^{-3}$—1×10^{-3}, $c_L = 0.5 \times 10^{-2}$—1×10^{-2} mol dm^{-3}, pH *ca.* 6.8); also the formation of [CuL]$^{2+}$ was studied by titration of $CuCl_2$ solution (*ca.* 0.1 mol dm^{-3}) into a buffered solution of the ligand (c_L *ca.* 8×10^{-3} mol dm^{-3}, $\bar{n}_H$ *ca.* 1.3). All measurements were for I = 0.10 mol dm^{-3} NaCl at 25 °C.

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† No reprints available.

‡ c_L = Total concentration of the ligand; $\bar{n}_H$ = average number of protons bound per ligand molecule.

[1] B. N. Palmer and H. K. J. Powell, *J.C.S. Dalton*, 1974, 2086.

[2] B. N. Palmer and H. K. J. Powell, *J.C.S. Dalton*, 1974, 2089.

[3] E. Giglio, A. M. Liquori, R. Puliti, and A. Ripamonti, *Acta Cryst.*, 1966, **20**, 683.

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

[5] G. R. Hedwig and H. K. J. Powell, *J.C.S. Dalton*, 1973, 793.

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

[7] G. Ojelund and I. Wadso, *Acta Chem. Scand.*, 1968, **22**, 2691.

RESULTS AND CALCULATIONS

Representative data for all the enthalpimetric titrations are in Supplementary Publication No. SUP 21596 (10 pp.).*

TABLE 1

Thermodynamic functions for stepwise protonation of triamine ligands at 25 °C and $I = 0.10$ mol dm^{-3}

n	log K_n	$-\Delta G_n$ / kJ mol^{-1}	$-\Delta H_n$ / kJ mol^{-1}	ΔS_n / J K^{-1} mol^{-1}
3-Azapentane-1,5-diamine (3NH-pd)[a,b]				
1	9.79	55.80	46.82	30.1
2	8.98	51.21	49.95	4.2
3	4.25	24.24	30.10	−19.6
3-Azaheptane-1,7-diamine (3NH-hd)[c,d]				
1	10.65	60.8 ± 0.1	51.2 ± 0.3	32.2 ± 1.3
2	9.42	53.80 ± 0.05	48.6 ± 0.3	17.4 ± 1.2
3	6.71	38.30 ± 0.05	40.8 ± 0.2	−8.4 ± 0.9
4-Azaheptane-1,7-diamine (4NH-hd)[e,f]				
1	10.65	60.74	51.37	31.4
2	9.57	54.55	54.30	0.8
3	7.72	44.02	43.76	0.8
4-Azaoctane-1,8-diamine (4NH-od)[c,d]				
1	10.89	62.2 ± 0.3	56.7 ± 0.7	18.5 ± 3.5
2	9.81	56.0 ± 0.1	53.5 ± 0.4	8.4 ± 1.7
3	8.34	47.6 ± 0.2	48.9 ± 0.5	−4.4 ± 2.5
3-Azahexane-1,6-diamine (3NH-hxd)[g]				
1	10.44	59.6	50.9	29.2
2	9.36	53.7	50.7	9.1
3	6.37	36.7	41.6	−17.5

[a] M. Ciampolini and P. Paoletti, *J. Phys. Chem.*, 1961, **65**, 1224; 0.1 mol dm^{-3} KCl. [b] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 1961, 2994. [c] This work. [d] Ref. 2; 0.1 mol dm^{-3} NaCl. [e] A. Vacca, D. Arenare, and P. Paoletti, *Inorg. Chem.*, 1966, **5**, 1384. [f] Ref. 11; 0.1 mol dm^{-3} KCl. [g] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *J.C.S. Dalton*, 1974, 2403; 0.5 mol dm^{-3} K[NO$_3$].

Calculations to determine the solution composition at each calorimetric titration point, and calculations of ΔH_i values from the corrected heat changes and the changes in solution composition between successive titration points followed procedures detailed previously.[5] For the protonation of 3NH-hd and 4NH-od, stepwise enthalpy changes were determined from 16 data points (three titrations) and 20 data points (five titrations) respectively. ΔH_i Values are given in Table 1 and compared with data for analogous triamines.

TABLE 2

Thermodynamic functions for the formation of copper(II) complexes with triamine ligands at 25 °C and $I = 0.10$ mol dm^{-3}

Reaction	log K	$-\Delta G$ / kJ mol^{-1}	$-\Delta H$ / kJ mol^{-1}	ΔS / J K^{-1} mol^{-1}
3-Azaheptane-1,7-diamine (3NH-hd) [a,b]				
$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	13.44 ± 0.02	76.7 ± 0.1	64.0 ± 0.3	42.6 ± 1.5
$Cu^{2+} + [HL]^+ \rightleftharpoons [Cu(HL)]^{3+}$	8.94 ± 0.02	51.0 ± 0.1	44.7 ± 0.2	21 ± 1
$[CuL]^{2+} + OH^- \rightleftharpoons [Cu(OH)L]^+$	4.42 ± 0.03	25.2 ± 0.2	5.4 ± 0.7	66 ± 3
4-Azaheptane-1,7-diamine (4NH-hd) [c,d]				
$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	14.20	81.0	67.2	46.0
$[CuL]^{2+} + OH^- \rightleftharpoons [Cu(OH)L]^+$	4.1	23.6	9.5	47.2
3-Azahexane-1,6-diamine (3NH-hxd) [e]				
$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	16.60	94.7	80.4	48.1
3-Azapentane-1,5-diamine (3NH-pd) [c,f]				
$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	15.80	90.1	75.2	50.2
$[CuL]^{2+} + OH^- \rightleftharpoons [Cu(OH)L]^+$	4.50	25.6	11.3	48.1

[a] Ref.2; 0.10 mol dm^{-3} NaCl. [b] This work. [c] A. Vacca, D. Arenare, and P. Paoletti, *Inorg. Chem.*, 1966, **5**, 1384; 0.1 mol dm^{-3} KCl. [d] Ref. 11; 0.1 mol dm^{-3} KCl. [e] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *J.C.S. Dalton*, 1974, 2403; 0.5 mol dm^{-3} K[NO$_3$]. [f] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 1961, 2994.

For the enthalpimetric titration of HCl against solutions of copper dichloride, 3NH-hd, and NaCl ($I = 0.10$ mol dm^{-3}), the measured heat change was corrected for the heat of dilution of HCl,[8] the reaction $H^+ + OH^- \longrightarrow H_2O$ (ΔH_{H_2O}),[9] and for the stepwise protonation reactions of ligand not co-ordinated to the metal. The enthalpy changes for $Cu^{2+} + L \longrightarrow [CuL]^{2+}$ (ΔH_1) and $Cu^{2+} + HL^+ \longrightarrow [Cu(HL)]^{3+}$ (ΔH_2) were calculated from 13 data points (four titrations) by use of the least-squares expression $Q_{corr.} = r\Delta H_1 + s\Delta H_2$, in which r and s are the changes in the number of moles of $[CuL]^{2+}$ and $[Cu(HL)]^{3+}$ respectively between successive titration points. Results are given in Table 2 and compared with those for analogous systems. A similar procedure was adopted for the reaction $[Cu(OH)L]^+ + [H_3O]^+ \longrightarrow [CuL]^{2+} + H_2O$ ($\Delta H_{H_2O} - \Delta H_{OH}$), using four data points in the pH range 9.6—8.3 [where no other copper(II)–ligand reaction occurs] and the expression $Q_{corr.} = t\Delta H_{OH}$ where t is the change in the number of moles of $[Cu(OH)L]^+$ between successive titration points $\{[CuL]^{2+} + [OH]^- \longrightarrow [Cu(OH)L]^+ (\Delta H_{OH})\}$.

The complexes $[CuL]^{2+}$ and $[Cu(HL)]^{3+}$ (L = 4,9NH-ddd) are stable only in solutions containing a large excess of ligand.[1] Therefore in the enthalpimetric titration of HCl against very dilute solutions of copper dichloride and excess of ligand the measured exothermic heat change was small (*ca.* 3.5 J) and much of it (*ca.* 160%) arose from protonation of excess of ligand, with the result that values of $Q_{corr.}$ were small and carried a significant error. Values of ΔH_1 and ΔH_2 (−92 ± 5 and −62 ± 11 kJ mol^{-1} respectively) were determined as described for 3NH-hd; ΔH_1 was also determined by the more accurate method of direct titration of $CuCl_2$ solution into a buffered solution of the ligand (pH *ca.* 10); the measured heat change was corrected for the heat of dilution of $CuCl_2$ titrant [8,10] and for the redistribution

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue.

[8] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, N.B.S. Technical Note 270—3, 1968.

[9] P. Gerding, I. Leden, and S. Sunner, *Acta Chem. Scand.*, 1963, **17**, 2190

[10] G. R. Hedwig, Ph.D. Thesis, University of Canterbury, New Zealand, 1972.

(amongst protonated ligand species) of protons released in the reaction $Cu^{2+} + H_{\tilde{n}_H}L \longrightarrow [CuL]^{2+} + \tilde{n}_H H$. The solution composition at each titration point was calculated using a suitable iterative computer program, with trial values of pH interpolated from a non-calorimetric titration under similar conditions. ΔH Values are given in Table 3.

TABLE 3

Thermodynamic functions for the formation of copper(II)-tetra-amine complexes $[CuL]^{2+}$ and $[Cu(HL)]^{3+}$ at 25 °C and $I = 0.10$ mol dm^{-3}

Tetra-amine	log K_1 [a]	$-\Delta H_1$ / kJ mol^{-1}	ΔS_1 / J K^{-1} mol^{-1}	log K_2 [b]	$-\Delta H_2$ / kJ mol^{-1}	ΔS_2 / J K^{-1} mol^{-1}
3,6NH-od [c]	20.08	90.1	81.6	13.8	66.1	41.8
4,7NH-dd [d]	21.69	104.0	66	14.69	70.3	45.5
4,8NH-ud [e]	17.05	81.4	53.6			
4,9NH-ddd [f]	14.70	88.1 ± 1.7 (92 ± 5)	−14 ± 7	9.99	 (62 ± 11)	

[a] For the reaction $Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$. [b] For the reaction $Cu^{2+} + [HL]^+ \rightleftharpoons [Cu(HL)]^{3+}$. [c] 3,6-Diazaoctane-1,8-diamine; L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 1961, 5115; 0.1 mol dm^{-3} KCl. [d] Ref. 5; 0.1 mol dm^{-3} NaCl. [e] Ref. 18; 0.1 mol dm^{-3} Na[NO$_3$]. [f] This work, 0.10 mol dm^{-3} NaCl. The values in parentheses are from titration of HCl into a solution of $[CuL]^{2+}$ in excess of ligand (see text).

DISCUSSION

Protonation.—Equilibrium constants for the protonation of 3NH-hd and 4NH-od have been reported [2] and compared with data for homologous linear triamines. The overall basicities ($\Sigma \log K_i$) were in accord with those expected for polyamines on the basis of their chain length, *viz.* 3-azahexane-1,6-diamine (3NH-hxd) < 4-azaheptane-1,7-diamine (4NH-hd) < 4NH-od, and 3-azapentane-1,5-diamine (3NH-pd) < 3NH-hxd < 3NH-hd. From Table 1 it is seen that the overall enthalpy changes $\Sigma(\Delta H_i)$ become increasingly exothermic with increasing chain length. The values of ΔH_3 clearly reflect the effect of chain length, with 4NH-od having the highest value (−48.9 kJ mol^{-1}) and 3NH-pd the lowest (−30.1 kJ mol^{-1}). This arises because the third protonation will be on to a cation for which the dominant tautomeric form has the ammonium groups widely separated, *viz.* in each case on to the secondary nitrogen of $H_3\overset{+}{N}\cdot[CH_2]_x\cdot NH\cdot[CH_2]_y\cdot\overset{+}{N}H_3$. In contrast, the values of ΔH_1 and ΔH_2 will reflect the effects both of (*i*) protonation occurring on both primary and secondary nitrogen centres to give species involving a tautomeric distribution of protons,[5,11] and (*ii*) the varying chain length between the site of protonation and the other amine or ammonium centres.[12,13]

The site (or sites) of amine protonation can be inferred from both the enthalpy change (which will be more exothermic for a primary than for a secondary or tertiary nitrogen) [14] and the entropy change which has been shown to increase regularly in going from primary to tertiary amines,[15] typical values being 23.8 J K^{-1} mol^{-1} for a primary alkylamine (ethylenediamine) and *ca.* 43 J K^{-1} mol^{-1} for a secondary alkylamine (2,5-diazahexane [14] and piperazine [16]). For 3NH-hd, ΔH_1 (−51.2 kJ mol^{-1}) is less exothermic than expected for protonation of the more basic terminal nitrogen (*cf.* butane-1,4-diamine, $\Delta H_1 = -56.8$ kJ mol^{-1}),[12] but more exothermic than expected for protonation of the secondary nitrogen (*cf.* 2,5-diazahexane, $\Delta H_1 = -44.9$ kJ mol^{-1}).[14] Also ΔS_1 (32.3 J K^{-1} mol^{-1}) is intermediate to values typical for protonation of primary and secondary amines; it is therefore inferred that for this polyamine (as is the case for many others [5]) the initial protonation gives a tautomeric distribution of protons over both primary and secondary amino-groups.

In contrast, for 4NH-od it is inferred that the initial protonation is predominantly on the more basic of the primary nitrogens, since ΔH_1 is the same as that for butane-1,4-diamine [12] and ΔS_1 is close to that for ethylenediamine and its higher homologues.[12] The compound 4,9NH-ddd shows a similar property; [2] further, for both of these longer chain polyamines, ΔH_2 values indicate that the second stepwise protonation is predominantly on the second primary amino-group. The reason for the distinctive pattern of protonation shown by these two polyamines (but not by any of their lower homologues) is not clear. The problem is not resolved by reference to empirical rules (for calculation of basicities) such as those of Clark and Perrin.[17] These rules predict that for 3NH-hd the respective log K_i values for initial protonation on a terminal nitrogen or on the secondary nitrogen will differ by *ca.* 0.4; for 4NH-od the predicted difference is *ca.* 0.1. For both of these triamines a distribution of protons over both amine sites is anticipated, but it is only for 3NH-hd that the ΔH_1 and ΔS_1 values support this prediction.

If the dominant diammonium cation is $H_3\overset{+}{N}\cdot[CH_2]_x\cdot NH\cdot[CH_2]_y\cdot\overset{+}{N}H_3$ the sum of ΔH_1 and ΔH_2 should reflect the effect of varying chain length between the charged centres (becoming more exothermic with increasing chain length)

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

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

[13] G. Schwarzenbach, 'Electrostatic and Non-Electrostatic Contributions to Ion Association in Solution,' Plenary Lectures, 12th Internat. Conf. on Co-ordination Chem., Sydney, 1969, Butterworths, London, 1969.

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

[15] A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, 1951, **47**, 34.

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

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

even though the individual ΔH_i values may not (because a distribution of protons on and off the secondary nitrogen centre is involved in the separate steps). Observed values are -96.8, -99.8, -105.7, and -110.2 kJ mol^{-1} for 3NH-pd, 3NH-hd, 4NH-hd, and 4NH-od respectively. For 4NH-od, $\Delta H_1 + \Delta H_2$ is equal to the sum of ΔH_1 for protonation of propane-1,3-diamine plus ΔH_1 for protonation of butane-1,4-diamine (*viz.* 110.4 kJ mol^{-1});[12] it can be inferred that for this long-chain polyamine there is negligible transmission of inductive effects between the terminal amine groups. This is consistent with observations on the two protonation steps for the diamines $H_2N\cdot[CH_2]_n\cdot NH_2 (n = 2–6)$.[12]

Copper Complexes.—Equilibrium constants have been reported for the formation of copper complexes with 3NH-hd and 4NH-od.[2] The low values of log K(CuL) relative to those for 3NH-pd and 4NH-hd have been discussed in terms of decreased stability of seven-membered chelate rings. (This lower stability arises despite the higher basicity of long-chain polyamines.) The measured ΔH for formation of $[Cu(3NH\text{-}hd)]^{2+}$ (Table 2) indicates that this decreased stability arises primarily from an enthalpy effect. This may be rationalised in terms of the repulsion which occurs between adjacent polar amine groups when they must be brought closer together (than in the free 3NH-hd molecule) in order to effect co-ordination to the metal ion.[1] In contrast, for 3NH-pd, the separation between these amine groups is already similar to that adopted on co-ordination. The entropy change for co-ordination of 3NH-hd to Cu^{II} is slightly less than that for 3NH-pd and 4NH-hd; this is consistent with the postulate [18] that co-ordination causes a net loss in ligand entropy, and that this loss is greater for aliphatic amines with longer chains.

Equilibrium constants for the protonation and copper complexing,[1] and calorimetric data for the protonation [2] of 4,9NH-ddd, have been reported. From the enthalpy data reported here it is seen that the low stability of the copper complex of 4,9NH-ddd cannot be ascribed to the enthalpy term. Rather, the data indicate that it is primarily an entropy effect, the ΔS term being negative in contrast to positive ΔS terms for other copper tri- and tetra-amines. It was expected that the entropy change for complex formation of 4,9NH-ddd would be smaller than that for 4,7-diazadecane-1,10-diamine (4,7NH-dd) and for 4,8-diazaundecane-1,11-diamine (4,8NH-ud);[18] however, the very low value of -14 J K^{-1} mol^{-1} is difficult to explain since it implies that the loss of vibrational, translational, and rotational entropy for the ligand is greater than the entropy increase due to release of co-ordinated water molecules and changes in the solvation lattice.[18]

The large value of ΔH for formation of $[Cu(4,9NH\text{-}ddd)]^{2+}$ parallels the very high basicity for this ligand. In order to assess the contribution to ΔH which relates to the stability of the chelate rings (as distinct from the basicity of the ligand), it is useful to examine $\Delta H'$ for the reaction $[CuL]^{2+} + 4H^+ \longrightarrow Cu^{2+}(aq) + [H_4L]^{4+}$, where $\Delta H' = \Sigma\Delta H_i(\text{protonation}) - \Delta H(\text{CuL})$. For the ligands in Table 2 the order of $\Delta H'$ values is 3,6NH-od $(-71.7) <$ 4,7NH-dd $(-76.9) <$ 4,8NH-ud $(-116.1) <$ 4,9NH-ddd $(-118.1$ kJ mol$^{-1})$. These values indicate that (*i*) $[Cu(4,9NH\text{-}ddd)]^{2+}$ and $[Cu(4,8NH\text{-}ud)]^{2+}$ have similar low ring stabilities, and (*ii*) the unexpectedly large value of ΔH for $[Cu(4,9NH\text{-}ddd)]^{2+}$ is primarily related to the high basicity of the ligand. They also support an earlier prediction [1] (based on log K values for copper–triamine and –tetra-amine complexes) that in polyamine complexes, as for simple diamines, five-membered chelate rings are more stable than six- and seven-membered rings; the same result is obtained from a consideration of $\Delta H'$ values for the linear triamine ligands.

From thermodynamic data it has been deduced that 4,9NH-ddd has protonation properties approaching those of two isolated propane-1,3-diamine (pd) molecules.[2] Further, the complexes $[Cu(4,9NH\text{-}ddd)]^{2+}$ and $[Cu(pd)_2]^{2+}$ have similar stability constants and it was inferred that 4,9NH-ddd shows a much reduced chelate effect relative to other tetra-amines. These deductions are supported by the similar ΔH values for formation of $[Cu(4,9NH\text{-}ddd)]^{2+}$ (*ca.* -88 kJ mol^{-1}) and $[Cu(pd)_2]^{2+}$ (-92.2 kJ mol^{-1}).[19] However, the negative ΔS for formation of the former complex does not compare well with the value for the latter (22.5 J K^{-1} mol^{-1}) and it may be inferred that the very low value of ΔS relates to loss of entropy by the central tetramethylene linkage within 4,9NH-ddd. A crystal-structure analysis [20] on $[Cu(4,9NH\text{-}ddd)][ClO_4]_2$ revealed a short C–C bond and an associated large torsion angle within the seven-membered ring, indicative of ring strain.

From consideration of the two ligands 3NH-hd and 4,9NH-ddd it appears that the low stability of complexes containing a seven-membered chelate ring could arise from either a small value for $-\Delta H$ or a small value for ΔS, depending on the structure of the ligand.

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

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

[20] R. Boggs and J. Donohue, *Acta Cryst.*, 1975, **B31**, 320.