Complex Formation with a *C*-Alkyl-substituted Linear Tetra-amine. Free Energy, Enthalpy, and Entropy Changes for the Reactions of 4,4,9,9-Tetramethyl-5,8-diazadodecane-2,11-diamine with Copper(II) Ions and Protons in Aqueous Solution

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Thermodynamic data are reported for the protonation of the hexamethyl-substituted tetra-amine 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-diamine (hm-3,2,3-tet) and for the formation of the copper complex Cu(hm-3,2,3-tet)$^{2+}$. Data are compared with those for the unsubstituted tetra-amine, 3,2,3-tet; small differences in stepwise protonation constants and in copper complex stabilities relate mainly to differences in ΔS values.

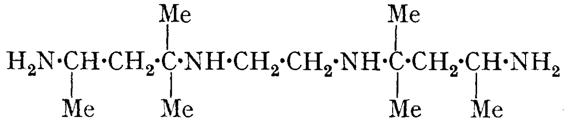
We recently reported[1] thermodynamic data for complex formation of the tetra-amine 4,7-diazadecane-1,10-diamine (3,2,3-tet) (I) with protons and copper(II) ions. This ligand is a further member of a homologous series of tetra-amines (2,2,2-tet, 3,3,3-tet, and 2,3,2-tet) which have been the subject of recent thermodynamic studies.[2,3] We now report thermodynamic data for complex formation of the homologous hexamethyl-substituted tetra-amine 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-diamine (hm-3,2,3-tet) (II) with protons and copper(II) ions at 25 °C and at $I = 0{\cdot}10\,\text{M}$ (NaCl).

3,2,3-tet

$\mathrm{H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2}$

(I)

hm-3,2,3-tet



$$\mathrm{H_2N{\cdot}\underset{Me}{CH}{\cdot}CH_2{\cdot}\overset{Me}{\underset{Me}{C}}{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}\overset{Me}{\underset{Me}{C}}{\cdot}CH_2{\cdot}\underset{Me}{CH}{\cdot}NH_2}$$

(II)

EXPERIMENTAL

Materials.—The ligand hm-3,2,3-tet was prepared by a sodium-in-pentyl alcohol reduction of the diamine–dioxime 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione dioxime[4,5] and isolated as the dihydroperchlorate salt by the addition of $HClO_4$ to pH *ca.* 8·5. The product was recrystallised from hot water (Found: C, 36·7; H, 8·0; N, 12·2. Calc. for $C_{14}H_{36}Cl_2N_4O_8$: C, 36·6; H, 7·8; N, 12·2%). Standard solutions of copper chloride were obtained as previously described.[1]

p[H$^+$] *Measurements.*—p[H$^+$] data were obtained by potentiometric titrations with the apparatus and the [H$^+$] calibration method described.[6]

Calorimetric Measurements.—The calorimeter and its operation have been described.[1] For the ligand protonation measurements, solutions of the ligand ($T_L \sim 4 \times 10^{-3}\,\text{M}$) were titrated with standard HCl (*ca.* 0·5M), and for the formation of the copper complex, solutions of ligand and HCl ($T_L \sim 5 \times 10^{-3}\,\text{M}$, $T_H \sim 1 \times 10^{-3}\,\text{M}$) were titrated with standard copper chloride (*ca.* 0·6M).

RESULTS AND CALCULATIONS

Stability Constants.—Representative p[H$^+$] data from the pH titrations of NaOH against solutions of hm-3,2,3-tet and HCl are deposited in Supplementary Publication No. 20746 (9 pp.).* Protonation constants were calculated from the $\bar{n}$, p[H$^+$] data by use of the weighted least-squares procedure previously described.[6] The differences between sets of constants, calculated with use of both unit and non-unit weighting of the $\bar{n}$ data in the least-squares process ($\sigma^{\bar{n}}$ was calculated both by using the equation for propagation of variance,[7] and from the experimental $\bar{n}$ data of a number of titrations) were well within the estimated uncertainties of the constants. This result has also been observed by other workers.[8] The stepwise protonation constants are shown in Table 1.

In titrations of NaOH against solutions of copper(II) ions, ligand, and HCl, the solution pH at each titration point attained a steady value after *ca.* 10 min. Representative titration data are deposited with N.L.L. Spectrophotometric measurements on 1 : 1 copper : ligand solutions, as a function of pH, indicated no change in $\lambda_{\text{max.}}$ as the pH increased from 3 to 11 [$\lambda_{\text{max.}}$ 534 nm, $I = 0{\cdot}10\,\text{M}$ (NaCl)], and it was deduced that neither hydroxo-, CuL(OH)$^+$, nor protonated, CuHL^{3+}, complexes are formed. For the single complex species CuL^{2+} the stability constant was calculated from the data at each titration point. For each titration, the calculated log K values fluctuated about a mean value; the mean and standard deviation of a measurement from the mean for the titrations of $T_M \sim 1 \times 10^{-3}$ and $T_M \sim 6 \times 10^{-4}$ (ratio $T_L : T_M$ *ca.* 1 : 1) were 22·43 ± 0·02 and 22·38 ± 0·02 respectively.

Enthalpy Data.—Calorimetric data from the titrations of hm-3,2,3-tet with HCl are deposited with N.L.L. The procedures used to calculate the solution composition at each titration point, and the stepwise enthalpies of protonation, were described previously.[1] The stepwise enthalpy changes are shown in Table 1.

Data from a calorimetric titration of copper chloride

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* For details of the Supplementary Publications scheme see Notice to Authors No. 7, *J.C.S. Dalton*, 1972, Index Issue. (Items less than 10 pp. are sent as full-sized copies.)

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

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

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

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

[5] M. Burgess, J. F. Lewin, and H. K. J. Powell, unpublished work.

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

[7] P. C. Jurs, *Analyt. Chem.*, 1970, **42**, 747.

[8] F. J. C. Rossotti, H. S. Rossotti, and R. J. Whewell, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2051, and references therein.

against a solution of hm-3,2,3-tet, HCl, and NaCl are deposited with N.L.L. Use of an alkaline solution with high [L] increased the rate of reaction between Cu^{2+} and L; reaction was complete within 3 min of titrant addition. The solution composition at each titration point was calculated by use of a successive approximations method. The thermodynamic functions for the formation of the copper complex with hm-3,2,3-tet are shown in Table 2.

DISCUSSION

Protonation.—The log k data in Table 1 show that the overall basicity ($\sum_{i=1}^{4} \log k_i$) of hm-3,2,3-tet is slightly lower than that of 3,2,3-tet. This difference in basicity is due to (opposing) small differences in both the overall enthalpy and overall entropy changes.

TABLE 1

Thermodynamic [a] data for the stepwise protonation of hm-3,2,3-tet and 3,2,3-tet in aqueous solution, 25 °C, I = 0·10M

Reaction	log k_n [b]	$-\Delta G$/kJ mol^{-1}	$-\Delta H$ [c]/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
		hm-3,2,3-tet		
$L + H^+ \rightleftharpoons LH^+$	11·09 ± 0·03	63·29 ± 0·1$_7$	51·22 ± 0·1$_2$	40·5 ± 1·3
$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	10·06 ± 0·02	57·41 ± 0·1	53·03 ± 0·3	14·6 ± 1·3
$LH_2^{2+} + H^+ \rightleftharpoons LH_3^{3+}$	7·61 ± 0·01	43·45 ± 0·1	46·38 ± 0·2$_5$	−9·8 ± 1·1
$LH_3^{3+} + H^+ \rightleftharpoons LH_4^{4+}$	4·90 ± 0·01	27·98 ± 0·0$_6$	33·25 ± 0·3	−17·7 ± 1·2
	33·66	192·13	183·9	27·6

Reaction	log k_n	$-\Delta G$/kJ mol^{-1}	$-\Delta H$/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
		3,2,3-tet [d]		
$L + H^+ \rightleftharpoons LH^+$	10·53 ± 0·02	60·10 ± 0·1	51·68 ± 0·2$_7$	28·3 ± 1·2
$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	9·77 ± 0·02	55·76 ± 0·1	51·80 ± 0·2$_0$	13·3 ± 1·0
$LH_2^{2+} + H^+ \rightleftharpoons LH_3^{3+}$	8·30 ± 0·02	47·37 ± 0·1	43·18 ± 0·1$_4$	14·1 ± 0·8
$LH_3^{3+} + H \rightleftharpoons LH_4^{4+}$	5·59 ± 0·02	31·90 ± 0·0$_6$	34·16 ± 0·1$_3$	−7·6 ± 0·6
	34·2	195·1	180·8	48·1

[a] With reference to a standard state of 0·1M-NaCl. [b] Computed from 39 data points. [c] Computed from 30 data points. [d] Data from ref. 1.

TABLE 2

Thermodynamic [a] data for the formation of copper complexes with hm-3,2,3-tet and 3,2,3-tet [b] at 25 °C and I = 0·10M (NaCl)

Reaction	log K	$-\Delta G$/kJ mol^{-1}	$-\Delta H$/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
Cu^{2+} + hm-3,2,3-tet $\rightleftharpoons$ Cu(hm-3,2,3-tet)$^{2+}$	22·41 ± 0·06 [c]	127·8$_9$ ± 0·3	104·0 ± 0·9 [d]	80·2 ± 4
Cu^{2+} + 3,2,3-tet $\rightleftharpoons$ Cu(3,2,3-tet)$^{2+}$	21·69 ± 0·08	123·8 ± 0·5	104·0 ± 0·9	66·3 ± 5

[a] With reference to a standard state of 0·10M-NaCl. [b] Data from ref. 1. [c] Computed from 24 data points. [d] Computed from 4 data points.

The first stepwise enthalpy of protonation of hm-3,2,3-tet, ΔH_1, is less exothermic than ΔH_2. This trend has been observed for other polyamines.[1,2,9] As concluded for 3,2,3-tet,[1] both the first and second stepwise protonations of hm-3,2,3-tet will give a tautomeric equilibrium between species protonated on the primary and on the secondary nitrogen atoms. For successive stepwise protonations increasing repulsion between adjacent ammonium sites causes a decrease in the exothermic enthalpy change. This has also been observed for other polyamines.[1,9]

The enthalpy change for a stepwise protonation in aqueous solution can be separated into a gas-phase protonation enthalpy and hydration enthalpies of the species in equilibrium. For the gas-phase protonation of some *N*-alkyl-substituted monoamines, the enthalpy changes follow the inductive order.[10] Similarly, the inductive effect of the six methyl substituents on hm-3,2,3-tet will increase the electron density on the nitrogen atoms thus producing more exothermic enthalpy changes for this gas-phase protonation than those for the protonation of the unsubstituted ligand 3,2,3-tet. However, whether these differences will be apparent in aqueous solution will depend on the hydration enthalpies of the species involved. As the differences between the stepwise enthalpies of protonation, in aqueous solution, of hm-3,2,3-tet and 3,2,3-tet are not large (Table 1) it appears that differences between gas-phase enthalpies and differences between the hydration enthalpies are largely compensatory. A similar result was reported for a series of *C*-alkyl-substituted ethylenediamines.[11]

The first stepwise entropy of protonation of hm-3,2,3-tet is 12·2 J mol^{-1} K^{-1} greater than that for 3,2,3-tet. This may result from the decreased electrostriction of the solvent owing to the methyl substituents on hm-3,2,3-tet shielding the solvent from the charge on the ion. For subsequent stepwise protonations of hm-3,2,3-tet, there is a gradual decrease in the entropy change ΔS_i.

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

[10] E. M. Arnett, F. M. Jones, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 4724.

[11] H. K. J. Powell and N. F. Curtis, *J. Chem. Soc.* (*B*), 1966, 1205.

Similar trends have been reported for other tetraamines[1-3] and are attributed to chain stiffening and increased electrostriction by the multicharged ions. The ΔS_3 and ΔS_4 values are more negative for hm-3,2,3-tet than for 3,2,3-tet. This could be explained by the decrease in the number of degrees of freedom of the *gem*-dimethyl groups of hm-3,2,3-tet, which arises through solvent ordering about the protonated secondary nitrogen atoms.

Complex Formation with Copper(II) *Ions*.—The thermodynamic data in Table 2 show that the Cu(hm-3,2,3-tet)$^{2+}$ complex is slightly more stable than Cu(3,2,3-tet)$^{2+}$ and that this difference in stability arises entirely from the entropy term.

The structures of copper complexes with linear tetraamine ligands are regarded as square planar or tetragonally distorted with a planar arrangement of nitrogen atoms about the metal ion.[3,4] For the Cu(hm-3,2,3-tet)$^{2+}$ complex in this structural form, there are both axial and equatorial methyl groups and from models it is apparent that non-bonded interactions occur between these axial groups and the solvent molecules in the *trans*-planar sites. These interactions will weaken the binding of the solvent molecules to the copper ion; this in turn will contribute to an increased ΔS change for the formation of Cu(hm-3,2,3-tet)$^{2+}$ compared with Cu(3,2,3-tet)$^{2+}$. This is supported by the visible spectrophotometric data[4] which show that the degree of tetragonal distortion is indeed greater for Cu(hm-3,2,3-tet)$^{2+}$ than for Cu(3,2,3-tet)$^{2+}$.[12]

It is interesting that despite the similar basicity for hm-3,2,3-tet and 3,2,3-tet and the similar stability for their copper(II) complexes, only 3,2,3-tet forms a protonated complex Cu(HL)$^{3+}$ in which the ligand is terdentate with respect to the metal ion.

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