Equilibrium Studies. Complex Formation of 4-Azaheptane-1,7-diamine, 4,8-Diazanonamine, and 4-Aza-4-methylheptane-1,7-diamine with Copper(II) Ions and Protons in Aqueous Solution †

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Equilibrium constants are reported for the protonation of the linear triamine, 4-azaheptane-1,7-diamine (4NH-hd), and its *N*-methyl analogues, 4,8-diazanonamine (4,8NH-nam) and 4-aza-4-methylheptane-1,7-diamine (4NH-4Me-hd), I = 0·1M(NaCl), 25°C. Formation constants and spectrophotometric data are presented for the complexes $[CuL(H_2O)]^{2+}$ and $[CuL(OH)]^{3+}$ formed by each ligand. Data are compared with those for analogous triamines.

THERMODYNAMIC data have been reported for the formation of proton and metal-ion complexes with homologous triamines $NH_2(CH_2)_xNH(CH_2)_yNH_2$, *viz.* 3-azapentane-1,5-diamine (3NH-pd; $x = y = 2$),[1-3] 3-azahexane-1,6-diamine (3NH-hxd; $x = 2$, $y = 3$),[4,5] 3-azaheptane-1,7-diamine (3NH-hd; $x = 2$, $y = 4$),[6] 4-azaheptane-1,7-diamine (4NH-hd; $x = 3$, $y = 3$),[7,8] and 4-azaoctane-1,8-diamine (4NH-od; $x = 3$, $y = 4$).[6] With copper(II), complexes of the form $[CuL(H_2O)]^{2+}$,[1,5-7] $[CuL_2]^{2+}$,[1,5] $[CuHL(H_2O)_2]^{2+}$,[5,6] $[Cu(HL)L]^{3+}$,[5] and $[CuL(OH)]^{3+}$ [1,5-7] have been characterised. For the triamine 3NH-pd, protonation constants were determined for a series of 1,5-di-*N*-alkyl substituted derivatives[9] and protonation and copper-complex formation constants have been determined for an extensive series of mono-, di-, tri-, tetra-, and penta-*N*-alkyl substituted derivatives.[10]

We now report equilibrium data for two mono-*N*-methyl substituted derivatives of 4NH-hd for (i) ligand protonation, and (ii) formation of $[CuL(H_2O)]^{2+}$ and $[CuL(OH)]^{+}$. Neither spectrophotometric nor potentiometric data provided evidence for the formation of $[CuHL(H_2O)_2]^{2+}$ or $[CuL_2]^{2+}$ complexes. The observed effect of *N*-alkyl substitution was a small decrease in the basicity of the ligand and a greater decrease in the stability of $[CuL(H_2O)]^{2+}$, relative to 4NH-hd.

EXPERIMENTAL

Materials.—The triamines (Fluka, commercial grade) were purified by triple vacuum distillation through a 5-cm Vigreaux column in a nitrogen atmosphere. The fraction distilling at 80—85 °C (*ca.* 0·5 Torr) was collected each time. 4-Azaheptane-1,7-diamine was converted into its trihydrochloride salt and twice recrystallised from aqueous methanol (Found: C, 30·1; H, 8·5. Calc. for $C_6H_{20}Cl_3N_3$: C, 30·0; H, 8·4%). 4,8-Diazanonamine and 4-aza-4-methylheptane-1,7-diamine were dissolved in an excess of dilute HCl and the amine molarity was determined by potentiometric titration against standard NaOH; the end-points for $\bar{n}_H$ = 3·0 and 2·0 were located accurately by Gran's plots[11] using data on both the high and low pH side of the end-point.

$p[H^+]$ *Measurements.*—$p[H^+]$ Data were obtained for potentiometric titrations with the apparatus and $[H^+]$ calibration method previously described.[12] All measurements were for solutions at 25 °C, I = 0·1M (NaCl).

RESULTS AND CALCULATIONS

Representative $p[H^+]$ data from the titration of NaOH (*ca.* 1M) against solutions of the three triamines, HCl and NaCl (I = 0·10M) are deposited in Supplementary Publi-

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† No reprints available.

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cation No. 21251 (6 pp.).* For the two *N*-substituted triamines the plot of pH against titre had a well defined inflexion (end-point) at pH *ca.* 7·6—8·9 after the addition of 1 mol of alkali ($\bar{n}_H = 2{\cdot}0$) per mol of triamine trihydrochloride. In contrast the plot for 4NH-hd showed a poorly defined inflexion near pH 8·5, indicative of a smaller difference between log k_3 and log k_2 for protonation of this amine (1·9; *cf.* 2·6, 2·7 for substituted amines, Table 1). The stepwise protonation constants in Table 1 were computed from the derived $\bar{n}_H$(obs) and p[H$^+$] data by use of the least-squares procedure previously described.[12] Each calculation used 40—60 data points in the range $\bar{n}_H$ = 0·5—2·9; data for which $T_H < K_W/[H^+]$ were not used.† The least-squares calculation achieved *R* factors[13] of *ca.* 0·2—0·7%. The quoted errors relate to the least-squares fit and to the uncertainty in the stoicheiometries of all solutions.

TABLE 1

Equilibrium constants for the stepwise protonation of triamine ligands at 25 °C, $I = 0{\cdot}10$M

$R^1NH(CH_2)_xNH(R^2)(CH_2)_yNH_2$		log k_1	log k_2	log k_3	$\sum_i \log k_i$
$x = y = 2$	$R^1 = R^2 = H$ [a]	9·79	8·98	4·25	23·0
$x = y = 2$	R^1 = Me, R^2 = H [b]	9·86 ± 0·06	9·18 ± 0·02	3·30 ± 0·03	22·3
$x = y = 2$	$R^1 = R^2$ = Me [b]	10·03 ± 0·02	9·35 ± 0·02	2·82 ± 0·03	22·2
$x = 2, y = 3$	$R^1 = R^2 = H$ [c]	10·44 ± 0·01	9·36 ± 0·01	6·37 ± 0·01	26·2
$x = 2, y = 4$	$R^1 = R^2 = H$ [d]	10·65 ± 0·02	9·42 ± 0·01	6·71 ± 0·01	26·8
$x = 3, y = 3$	$R^1 = R^2 = H$ [e]	10·65 ± 0·02	9·57 ± 0·03	7·72 ± 0·03	27·9
$x = 3, y = 3$	$R^1 = R^2 = H$ [f]	10·56 ± 0·04	9·53 ± 0·03	7·65 ± 0·02	27·7
$x = 3, y = 3$	R^1 = Me, R^2 = H [f]	10·68 ± 0·06	9·69 ± 0·04	7·03 ± 0·03	27·4
$x = 3, y = 3$	R^1 = H, R^2 = Me [f]	10·50 ± 0·03	9·60 ± 0·02	6·98 ± 0·02	27·1
x = 3, $y = 4$	$R^1 = R^2 = H$ [d]	10·89 ± 0·05	9·81 ± 0·02	8·34 ± 0·03	29·0

[a] Ref. 3, 0·10M-KCl. [b] Ref. 10, 0·11M-KNO$_3$. [c] Ref. 5, 0·5M-KNO$_3$. [d] Ref. 6, 0·10M-NaCl. [e] Ref. 7, 0·1M-KCl. [f] This work, 0·10M-NaCl.

TABLE 2

Equilibrium constants, log *K*, for the formation of copper(II) complexes with linear triamine ligands, 25 °C, $I = 0{\cdot}10$M

	Triamine					
Reaction	4NH-hd [a]	4,8NH-nam [a]	4NH-4Me-hd [a]	3NH-hxd [b]	3NH-pd [c]	3,6NH-ham [c]
$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$ log K_1	14·09 ± 0·01 (14·20 ± 0·06) [d]	12·94 ± 0·02	12·86 ± 0·02 (12·71) [e]	16·60 ± 0·01	15·91 ± 0·03 (15·8) [f]	15·32 ± 0·03
$[CuL]^{2+} + OH^- \rightleftharpoons [CuL(OH)]^+$ log K_{OH}	4·19 ± 0·05 (4·14 ± 0·16) [d]	3·95 ± 0·08	4·32 ± 0·08	4·72 ± 0·01	5·17 ± 0·06	5·07 ± 0·08
$Cu^{2+} + HL \rightleftharpoons [CuHL]^{3+}$ log K_{HL}				9·02 ± 0·02		
$[CuL]^{2+} + L \rightleftharpoons [CuL_2]^{2+}$ log K_2				3·28 ± 0·02	(5·21) [f]	
$[CuL]^{2+} + 3H^+ \rightleftharpoons Cu^{2+} + [LH_3]^{3+}$ log K' [g]	13·65	14·46	14·22	9·57	7·11	7·02

[a] This work, $I = 0{\cdot}10$M-NaCl; mean ± standard deviation from mean. [b] Ref. 5, 0·5M-KNO$_3$. [c] Ref. 10, 0·13M-KNO$_3$; 3,6NH-ham = 3,6-diazaheptamine. [d] Ref. 7, 0·1M-KCl. [e] Ref. 18, 1M-KNO$_3$, 20 °C. [f] Ref. 2, 0·1M-KCl. [g] $\sum_i \log k_i - \log K$ ($Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$).

For titrations of NaOH against solutions of the protonated triamines, copper(II) chloride ($c_L : c_M$ *ca.* 1·05—1·10), and NaCl ($I = 0{\cdot}10$M) the pH against titre curve showed two buffer regions separated by a distinct end-point (pH *ca.* 7·0—8·5) which corresponded to completion of the reaction $Cu^{2+} + LH_3^{3+} + 3OH^- \longrightarrow [CuL]^{2+} + 3H_2O$ (plus loss of one proton from each mole of excess ligand) at the end of the first buffer region. Spectrophotometric measurements on solutions in the first buffer region showed development of a single absorption maximum at 630, 645, and 640 nm for 4NH-hd, 4,8NH-nam, and 4NH-4Me-hd respectively corresponding to the formation of a single complex with 3 N-donor atoms co-ordinated, and which can be formulated $[CuL(H_2O)]^{2+}$ if only the stronger in-plane metal-ligand bonds are considered ($\varepsilon_{max.}$ = 101, 107, and 114 respectively when $\bar{n} = 1{\cdot}00$). These pH data were interpreted in terms of a single equilibrium, $Cu^{2+} + L \rightleftharpoons [CuL(H_2O)]^{2+}$: the log K_1 values (Table 2) calculated at each data point were invariant through the data set (see Supplementary Data).

The second buffer region arose from the formation of the deprotonated complex $[CuL(OH)]^+$ from $[CuL(H_2O)]^{2+}$. The absorption maximum for the complex $[CuL(OH)]^+$ was shifted *ca.* 20—40 nm toward shorter wavelengths[6,8] relative to $[CuL(H_2O)]^{2+}$. The value of $K_{OH} = [CuL(OH)^+]/[CuL(H_2O)^{2+}][OH^-]$ was determined for each data point as described previously;[6] the average values (± standard deviation) are reported in Table 2.

Potentiometric and spectrophotometric measurements were made on titrations of NaOH into solutions containing a 10 : 1 ratio of $c_L : c_M$ (c_L *ca.* 1 × 10^{-2}M), $I = 0{\cdot}10$M-NaCl. The pH against titre curve showed a buffer region spanning *ca.* 0·5 pH in the range pH 5—6, followed by an end-point (0·5—1·0 pH) after addition of three equivalents of alkali per mole of metal; the curve then showed the characteristics of a titration against excess ligand. Spectrophotometric measurements on solutions taken from the buffer region showed development of a single absorption maximum as described above. The titration data for the pH 5—6 range was interpreted satisfactorily in terms of a single

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* For details of Supplementary Publications Scheme see Notice to Authors, No. 7, *J.C.S. Dalton*, 1974, Index issue.

† $\bar{n}_H$ = Average number of protons bound per ligand molecule; $\bar{n}_H(obs.) = \{(c_H)_i\text{-NaOH-}[H^+] + K_W/[H^+]\}/c_L$; $T_H = (c_H)_i$-NaOH; c_L = total concentration of the ligand; $(c_H)_i$ = initial concentration of ionisable acid.

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equilibrium reaction $Cu^{2+} + L \rightleftharpoons [CuL(H_2O)]^{2+}$ and gave an invariant constant K_1 which was in agreement with that obtained from 1 : 1 titrations. Up to the onset of the reaction $[CuL(H_2O)]^{2+} + OH^- \rightleftharpoons [CuL(OH)]^+$ at pH *ca.* 9·3 the calculated $\bar{n}$ did not exceed 1·00 ± 0·02.

For titrations of metal–ligand solutions, representative data are deposited in the Supplementary Publication.

DISCUSSION

Protonation.—Studies on the protonation of primary, secondary, and tertiary amines have established that the order of basicity is tertiary < primary < secondary.[14-16] This sequence results from two opposing effects, (i) an entropy change which favours protonation in the sequence tertiary > secondary > primary, the increments in ΔS being *ca.* 20 J mol^{-1} K^{-1},[15] and (ii) an enthalpy change which favours protonation in the sequence primary > secondary > tertiary.[14,16] Thus, for the protonation of ethylenediamine and its *NN'*-dimethyl and *NNN'N'*-tetramethyl derivatives log k_1 values are 9·98, 10·17, and 9·28 respectively.[16] Further, for the protonation of polyamines each protonation stage is best represented by a mixture of tautomeric forms involving a distribution of protons over primary, secondary, and tertiary nitrogen centres.[16,17] This distribution can be established from the observed enthalpy and entropy changes when compared with those for isolated primary, secondary, and tertiary amino-groups,[17] or by deducing microconstants inter-relating the tautomeric forms.[16] Thus it has been estimated on the basis of ΔH_{obs}, that for the protonation of $MeNHCH_2CH_2NH_2$ the initial protonation is *ca.* 54—64% on the secondary amino nitrogen while for $Me_2NCH_2CH_2NH_2$ the initial protonation is 58—63% on the primary amino-nitrogen.[16] The uncertainty in these procedures is illustrated by the fact that estimates based on microconstants suggest 86—93% primary nitrogen protonation for the latter amine.[16]

For the triamines studied in this work the overall basicities ($\sum_i \log k_i$) are 27·7, 27·4, and 27·1 for 4NH-hd, 4,8NH-nam, and 4NH-4Me-hd respectively. The low value for 4NH-4Me-hd relates to the occurrence of a tertiary amino-group in this ligand, although k_3, which may be considered to relate predominantly to protonation on the central amino-group [1,17] is not significantly lower than for the other ligands. The overall basicity could be expected to be larger for 4,8NH-nam as this contains two secondary amino-centres, but the trend is not observed. However the larger values determined for k_1 and k_2 (involving protonation mainly on the terminal groups) may be related to this effect.

The observed lack of contrast in both stepwise and overall basicities of these triamines was also observed for the related ligands 3-azapentane-1,5-diamine and its *N*-methyl and *NN'*-dimethyl derivatives,[10] and differs from the situation for related diamines.[16] We conclude that a complex set of tautomeric equilibria is involved in the protonation steps and that the stepwise distribution of protons between amino-groups is difficult to estimate.

Copper Complexes.—The general result that complexes involving six-membered chelate rings are thermodynamically less stable than those involving five-membered chelate rings is borne out in a comparison of the copper(II) complexes of 4-azaheptane-1,7-diamine and 3-azapentane-1,5-diamine (log K_1 = 14·09 and 15·9 respectively). This order of stabilities occurs despite the greater overall basicity of 4NH-hd ($\sum_i \log k_i$ = 27·7 compared with 23·0) and has been related to the necessity to draw the mutually repelling polar amine groups together in ligands producing six-membered chelate rings before the donor atoms are suitably situated for co-ordination to a metal centre. The values of log K' for the reaction $[CuL(H_2O)]^{2+} + 3H^+ \rightleftharpoons [Cu(aq)]^{2+} + [LH_3]^{3+}$ (Table 2), which give a measure of ring stability for triamine ligands of different basicity, indicate that stability is greatest for two linked five-membered chelate rings > a linked five- and six-membered ring > two linked six-membered rings.

The decrease in stability of the $[CuL(H_2O)]^{2+}$ complexes going from L = 4NH-hd to 4,8NH-nam and 4NH-4Me-hd (log K_1 = 14·09, 12·94, and 12·86 respectively) exceeds that predicted on the basis of the overall basicities of the ligands (Table 1). It appears that the substitution of a single methyl group on a primary or secondary nitrogen donor has a small destabilizing effect on the chelate ring system. This is seen most clearly by considering the log K' values (Table 2) which indicate that the chelate ring system is least stable for 4,8NH-nam.

Table 2 compares results obtained from this work with those reported previously by Vacca *et al.*[7] for 4-azaheptane-1,7-diamine (0·1M-KCl) and by Goldberg and Fernelius [18] for 4-aza-4-methylheptane-1,7-diamine (20 °C, 1M-KNO_3). The two results for the first ligand are in close agreement.

In their reactions with copper(II) the triamine ligands 3-azahexane-1,6-diamine [5] and 3-azaheptane-1,7-diamine and 4-azaoctane-1,8-diamine [6] give protonated complexes $[CuHL(H_2O)_2]^{3+}$ in the more acidic part of the first buffer region. The formation of such complexes becomes apparent from (i) a drift in log K values, decreasing with increasing $\bar{n}$, and (ii) the development of a long wavelength absorption in the visible absorption spectrum ($[CuHL(H_2O)_2]^{3+}$ absorbs at a wavelength *ca.* 30 nm longer than does $[CuL(H_2O)]^{2+}$).[6] No such evidence was obtained for the three ligands

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studied here. To enhance the formation of protonated complexes the titrations were performed at a lower pH by using a 10 : 1 ratio of $c_L : c_M$. Neither spectrophotometric nor log K data supported the existence of either protonated species or of bis complexes, $[CuL_2]^{2+}$, in aqueous solution. The bis complexes with L = 3-azahexane-1,6-diamine and 3-azapentane-1,5-diamine are of low stability (log K = 3·28 and 5·21 respectively) and a complex with L = 4-azaheptane-1,7-diamine would be of even lower stability.

The log K_{OH} values span a small range, 3·95—4·32, and for a wide selection of triamine ligands log K_{OH} values lie within or near this range and show no clear relationship to the basicity or substitution pattern of linear triamine ligands.

[4/1391 *Received*, 10*th July*, 1974]