Thermodynamic, Electronic, and Electron Paramagnetic Resonance Investigation of the Co-ordinating Properties of 3-Azaheptane-1,7-diamine in Aqueous Solution

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The heats of protonation and of complex formation with Cu^{II} of the ligand 3-azaheptane-1,7 diamine (L) have been measured calorimetrically at 25 °C in 0.5 mol dm^{-3} $K[NO_3]$ solution, and the corresponding entropy values have been calculated. The results are compared with those from previously investigated systems with homologous triamines. The present system has also been examined by electronic absorption and e.p.r. spectroscopy. For the simple complex $[CuL]^{2+}$, evidence is presented for a structure with two fused chelate rings, one five-membered and the other seven-membered. The complexes $[Cu(HL)_2]^{4+}$, $[CuL(HL)]^{3+}$, and $[CuL_2]^{2+}$ contain only two five-membered chelate rings, both the molecules of the ligand acting as bidentates. The difference between the enthalpies of formation of the complexes is attributed to different desolvation processes.

COMPLEXES formed by the 3*d* metal ions with ligands which have five- and six-membered chelate rings have far less strain than analogous systems in which all the chelate rings are either five- or six-membered.[1] This has been verified by thermodynamic data for complexes formed both by tri-[2] and quadri-dentate[3] ligands. A recent e.p.r. study, however, has shown that the complexes formed by Cu^{2+} with a homologous series of triamine ligands 3-azapentane-1,5-diamine, 3-azahexane-1,6-diamine, and 4-azaheptane-1,7-diamine have $g_{\parallel}$ values which increase regularly with the aliphatic chain length and $A_{\parallel}$ values which decrease in the same order.[4] This might be explained by supposing that there is a different geometric arrangement of each of the three ligands about the acceptor metal ion.

A previous potentiometric study[5] has shown that the triamine 3-azaheptane-1,7-diamine forms a remarkable number of complexes in aqueous solution, *viz.* $[Cu(HL)]^{3+}$, $[CuL]^{2+}$, $[Cu(HL)_2]^{4+}$, $[CuL(HL)]^{3+}$, $[CuL_2]^{2+}$, and $[CuL(OH)]^{+}$ of which half are protonated. The complex $[CuL]^{2+}$ seems to contain two chelate rings, one five- and the other seven-membered, whilst the three complexes with a metal to ligand ratio of 1 : 2 all seem to have the same structure at least in aqueous solution.[5] In order to obtain more definite information on the stereochemistry of these latter complexes, we have investigated them further by means of both calorimetric and (e.p.r. and electronic) spectroscopic measurements. We have isolated the solid complexes $[Cu(HL)_2][ClO_4]_4$, $[CuL(HL)][ClO_4]_3$, and $[CuL_2][ClO_4]_2$ and have studied their properties both in the solid state and in aqueous solution. The protonation of the free ligand has also been studied calorimetrically and the values of $\Delta H^{\ominus}$ have been compared with those previously found for analogous triamines.

EXPERIMENTAL

3-Azaheptane-1,7-diamine is commercially available (Eastman Organic Chemicals). The product was twice crystallised as the hydrochloride from ethanol and dried *in vacuo* at 60 °C (Found: C, 29.9; H, 8.4; Cl, 44.2; N, 17.5. Calc. for $C_6H_{20}Cl_3N_3$: C, 29.9; H, 8.2; Cl, 44.2; N, 17.5%). The potassium hydroxide solution (0.5 mol dm^{-3}) was prepared from K[OH] pellets as previously described.[5]

Solid Complexes.—*Bis*(3-*azaheptane*-1,7-*diamine*)*copper*(II) *perchlorate*, $[CuL_2][ClO_4]_2$. The complex was prepared by adding an excess of ligand to a solution obtained by dissolving 2.0 mmol of $Cu[ClO_4]_2 \cdot 6H_2O$ (molar ratio Cu : L = 1 : 3) in ethanol (15 cm^3). The blue precipitate was recrystallised from methanol and dried *in vacuo* at 60 °C (Found: C, 27.35; H, 6.70; Cu, 12.35; N, 15.95. Calc. for $C_{12}H_{34}Cl_2CuN_6O_8$: C, 27.45; H, 6.55; Cu, 12.1; N, 16.0%).

(3-*Azaheptane*-1,7-*diamine*)(3-*azaheptane*-1-*amine*-7-*aminium*)*copper*(II) *perchlorate*, $[CuL(HL)][ClO_4]_3$. The ligand was added dropwise to 2.0 mmol of an ethanolic solution of $Cu[ClO_4]_2 \cdot 6H_2O$ which had been adjusted to pH *ca.* 7 by addition of a small amount of 70% $HClO_4$. The resulting dark violet precipitate was recrystallised from methanol and dried *in vacuo* at 60 °C (Found: C, 22.65; H, 5.75; Cu, 10.4; N, 13.35. Calc. for $C_{12}H_{35}Cl_3CuN_6O_{12}$: C, 23.05; H, 5.65; Cu, 10.15; N, 13.45%).

Bis(3-*azaheptane*-1,7-*diaminium*)*copper*(II) *perchlorate*, $[Cu(HL)_2][ClO_4]_4$. The method used was similar to that for the monoprotonated species but involves addition of rather more $HClO_4$ such that the copper(II) solution was at pH *ca.* 4. The reddish violet product obtained was recrystallised from methanol and dried *in vacuo* at 60° C (Found: C, 19.85; H, 5.35; Cu, 8.65; N, 11.4. Calc. for $C_{12}H_{36}Cl_4CuN_6O_{16}$: C, 19.85; H, 5.00; Cu, 8.75; N, 11.6%).

Spectroscopic Measurements.—Infrared spectra from 400 to 4 000 cm^{-1} were recorded as Nujol mulls on a Perkin-Elmer model 337 spectrophotometer. The electronic spectra were determined at 25 °C using a Beckmann DK 2A instrument. The e.p.r. spectra were recorded on a Varian E9 spectrometer and were calibrated using diphenylpicrylhydrazyl (dpph) as a *g* marker. Glassy e.p.r. spectra were obtained at −140 °C and solution spectra at room temperature. The spectra were measured on solutions 10^{-2}—10^{-3} mol dm^{-3} in Cu^{II} with ethylene glycol–water (1 : 3) as solvent. The procedure for identifying the species present in solution has already been described.[4] Simulated spectra for a Lorentzian lineshape were obtained using Venable's

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[1] P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chim. Acta Rev.*, 1973, **7**, 43.

[2] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *J.C.S. Dalton*, 1974, 2403.

[3] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *J.C.S. Dalton*, 1973, 1763; L. Fabbrizzi, R. Barbucci, and P. Paoletti, *ibid.*, 1972, 1529.

[4] R. Barbucci and M. J. M. Campbell, *Inorg. Chim. Acta*, 1976, **16**, 113.

[5] R. Barbucci, P. Paoletti, and A. Vacca, *Inorg. Chem.*, 1975, **14**, 302.

program[6] and in all cases it was possible to fit the experimental spectra extremely closely. The e.p.r. parameters given in Table 2 are the best-fit parameters for the final simulation.

Calorimetric Measurements.—An LKB 8700/2 titration calorimeter was used. In the protonation measurements the K[OH] solution was added to *ca.* 90 cm^3 of a 0.5 mol dm^{-3} K[NO$_3$] solution containing the triamine trihydrochloride (0.5—1.0 mmol) and in some cases a slight excess of acid. In order to study the formation of complexes with Cu^{II}, K[OH] was added to a 0.5 mol dm^{-3} K[NO$_3$] solution containing the amine trihydrochloride and the metal nitrate. The technique adopted involved continuous addition of K[OH] to the solution in the vessel and this will be reported elsewhere.

TABLE 1

Thermodynamic functions for the protonation of aliphatic triamines in 0.5 mol dm^{-3} K[NO$_3$] at 25 °C

Reaction		3-Azaheptane-1,7-diamine	3-Azahexane-1,6-diamine [a]	3-Azapentane-1,5-diamine [b]	4-Azaheptane-1,7-diamine [c]
$L + H^+ \rightleftharpoons HL^+$	$-\Delta G^{\ominus}$/kcal mol^{-1}	14.551 (3)	14.233	13.351	14.523
	$-\Delta H^{\ominus}$/kcal mol^{-1}	12.86 (8)	12.18	11.20	12.29
	$\Delta S^{\ominus}$/cal K^{-1} mol^{-1}	5.7 (2)	6.89	7.2	7.5
$HL^+ + H^+ \rightleftharpoons H_2L^{2+}$	$-\Delta G^{\ominus}$/kcal mol^{-1}	13.081 (5)	12.759	12.246	13.051
	$-\Delta H^{\ominus}$/kcal mol^{-1}	12.13 (16)	12.14	11.95	12.99
	$\Delta S^{\ominus}$/cal K^{-1} mol^{-1}	3.2 (2)	2.08	1.0	0.2
$H_2L^{2+} + H^+ \rightleftharpoons H_3L^{3+}$	$-\Delta G^{\ominus}$/kcal mol^{-1}	9.525 (9)	8.692	5.796	10.528
	$-\Delta H^{\ominus}$/kcal mol^{-1}	10.71 (25)	9.95	7.20	10.47
	$\Delta S^{\ominus}$/cal K^{-1} mol^{-1}	−4.0 (4)	−4.22	−4.7	0.2

[a] Ref. 2. [b] Ref. 8. [c] Ref. 9.

TABLE 2

Electronic, e.p.r., and i.r. spectra of the copper(II)–3-azaheptane-1,7-diamine (L) complexes

	Solid		Aqueous solution								
				E.p.r. spectra							
Complex	Electronic spectra (10^3 cm^{-1})	I.r. spectra [a] (bands due to ClO$_4^-$)	Electronic spectra [b] (10^3 cm^{-1})	$g_{\parallel}$	$g_{\perp}$	$g_{\perp}'$ [c]	$g_{iso.}$	$A_{\parallel}$	$A_{\perp}$	$A_{\perp}'$ [c]	$A_{iso.}$
[Cu(HL)]$^{3+}$			15.2 (47)	2.281	2.060	2.053	2.129	176	10	17	70
[Cu(HL)$_2$][ClO$_4$]$_4$	19.2	1 130—1 040vb, 930s, 622s	17.5 (90)	2.206	2.044	2.044	2.098	193	19	26	82
[CuL(HL)][ClO$_4$]$_3$	19.7	1 130—1 040vb, 931s, 625s, 615s									
[CuL$_2$][ClO$_4$]$_2$	16.9	1 160—1 030vb, 620s									

[a] s = Strong, b = broad, and vb = very broad. [b] Values in parentheses are the molar absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}). [c] Calculated from $g_{iso.} = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$ or $A_{iso.} = \frac{1}{3}(A_{\parallel} + 2A_{\perp})$.

RESULTS AND DISCUSSION

Protonation.—The results obtained from the protonation measurements are shown in Table 1. It is to be noted that the enthalpy of the first step is larger than that of the second which in turn is larger than that of the third, *i.e.* $-\Delta H_1^{\ominus} > -\Delta H_2^{\ominus} > -\Delta H_3^{\ominus}$. This differs from the usual trend for linear polyamines having more than two basic sites which is $-\Delta H_2^{\ominus} > -\Delta H_1^{\ominus} > -\Delta H_3^{\ominus}$. This latter trend is usually explained by invoking a tautomeric process.[7] The result obtained for 3-azaheptane-1,7-diamine is however consistent with that obtained for the analogous 3-azahexane-1,6-diamine for which it was found that $-\Delta H_1^{\ominus} \geqslant -\Delta H_2^{\ominus} > -\Delta H_3^{\ominus}$.[2] If we consider the three analogous triamines 3-azapentane-1,5-diamine,[8] 3-azahexane-1,6-diamine, and 3-azaheptane-1,7-diamine we find that $-\Delta H_1^{\ominus}$ increases as the length of one of the ' arms ' of the aliphatic chain increases (Table 1). On the other hand, the value of $-\Delta H_2^{\ominus}$ remains practically constant, whilst $-\Delta H_3^{\ominus}$ also increases progressively. This may be explained by supposing that the first step in the protonation process is attack on the more basic primary nitrogen, *i.e.* on the nitrogen at the end of the longer aliphatic chain. It is found that $-\Delta H_1^{\ominus}$ increases from 3-azapentane-1,5-diamine to 3-azahexane-1,6-diamine to 3-azaheptane-1,7-diamine. The second proton attacks the nitrogen atom furthest away from the protonated one in order to minimise the repulsion between the positive charges, *i.e.* the second step involves protonation of the other primary nitrogen. However, this nitrogen atom is influenced by the secondary nitrogen atom, which in the three amines under consideration is always the same distance away from it so that $-\Delta H_2^{\ominus}$ is about the same in each case. Finally the third step protonation involves attack on the secondary nitrogen atom which is at varying distances from the first protonated primary nitrogen so that the trend observed is as for $-\Delta H_1^{\ominus}$.

Comparison with 4-azaheptane-1,7-diamine[9] lends support to this mechanism of protonation since its $-\Delta H_1^{\ominus}$ is equal to that of 3-azahexane-1,6-diamine to within experimental error, while its $-\Delta H_2^{\ominus}$ is larger than the values found for the three amines considered, presumably because the primary nitrogen atom involved is further away from the secondary nitrogen (three methylene groups instead of two). Its $-\Delta H_3^{\ominus}$ value (protonation of the central nitrogen) is equal to that of 3-azaheptane-1,7-diamine, which is reasonable since the distance between the secondary and primary nitrogen atoms is the

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[6] J. H. Venable, Ph.D. Thesis, Yale University, 1965.

[7] M. Ciampolini and P. Paoletti, *Ricerca Sci.*, 1963, A405.

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

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

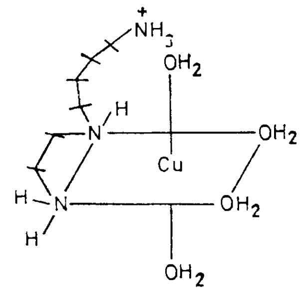
average of the two such distances present in 3-azaheptane-1,7-diamine.

1 : 1 *Complexes of* Cu^{2+}.—Two complexes having this metal : ligand ratio were formed, $[Cu(HL)]^{3+}$ and $[CuL]^{2+}$. E.p.r. parameters were obtained for the protonated species both at room temperature and at low temperature (glassy state). The electronic spectrum was also obtained (Table 2). The parameters are typical of a tetragonally distorted octahedral complex with a $d_{x^2-y^2}$ ground state and are essentially the same as those found for other complexes with diamine ligands.[4] This shows that the presence of the charge on the protonated nitrogen atom does not affect the co-ordinating capacity of the two remaining nitrogen atoms. It is clear that the protonated nitrogen involved is that at the end of the longer aliphatic chain since spectroscopic parameters are influenced by the size of the chelate ring [10] and the values found for the complex $[Cu(HL)]^{3+}$ are typical of complexes with a five-membered chelate ring, (I).

TABLE 3

Thermodynamic functions for the reactions of 3-azaheptane-1,7-diamine (L) with Cu^{II}

	3-Azaheptane-1,7-diamine			3-Azahexane-1,6-diamine		
Reaction	$-\Delta G^\ominus$ kcal mol^{-1}	$-\Delta H^\ominus$ kcal mol^{-1}	$\Delta S^\ominus$ cal K^{-1} mol^{-1}	$-\Delta G^\ominus$ kcal mol^{-1}	$-\Delta H^\ominus$ kcal mol^{-1}	$\Delta S^\ominus$ cal K^{-1} mol^{-1}
$Cu^{2+} + HL^+ \rightleftharpoons [Cu(HL)]^{3+}$	12.533 (5)	11.69 (7)	2.83 (0.25)	12.30	11.5	2.7
$[CuL]^{2+} + H^+ \rightleftharpoons [Cu(HL)]^{3+}$	9.29	9.26	0.1	3.89	4.46	−1.9
$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	17.797 (15)	15.28 (0.14)	8.43 (0.51)	22.639	19.22	11.5
$Cu^{2+} + 2HL^+ \rightleftharpoons]Cu(HL)_2]^{4+}$	22.629 (11)	23.91 (0.10)	−4.31 (0.38)			
$[CuL_2]^{2+} + 2H^+ \rightleftharpoons [Cu(HL)_2]^{4+}$	27.64	27.43	0.7			
$Cu^{2+} + HL^+ + L \rightleftharpoons [CuL(HL)]^{3+}$	23.777 (15)	23.36 (0.16)	1.39 (0.60)	26.059	25.12	3.2
$[CuL_2]^{2+} + H^+ \rightleftharpoons [CuL(HL)]^{3+}$	14.25	14.03	0.7	13.18	11.98	4.1
$Cu^{2+} + 2L \rightleftharpoons [CuL_2]^{2+}$	24.086 (17)	22.19 (0.24)	6.34 (0.86)	27.11	25.32	6.0
$[CuL]^{2+} + L \rightleftharpoons [CuL_2]^{2+}$	6.29 (3)	6.91 (0.38)	−2.1 (1.4)	4.47	6.1	−5.5
$[CuL]^{2+} + OH^- \rightleftharpoons [CuL(OH)]^+$	5.94(0.13)	2.58 (0.18)	11.27 (0.67)	6.44	2.28	13.9



(I)

The thermodynamic parameters for the reaction $Cu^{2+} + HL^+ \rightleftharpoons [Cu(HL)]^{3+}$ are the same as those for the analogous reaction with 3-azahexane-1,6-diamine,[2] showing the negligible influence of the external positive charge on the properties of the complex (Table 3). Although the percentage of the simple complex $[CuL]^{2+}$ which is formed is always low,[5] regardless of the metal: ligand ratio, it was possible to measure its heat of formation. The value of $-\Delta H^\ominus$ is higher than that for the corresponding protonated complex by 3.6 kcal mol^{-1} and this difference is only explainable in terms of a larger number of co-ordinated nitrogen atoms.* Thus the complex $[CuL]^{2+}$ must have two chelate rings, one five- and the other seven-membered. Since copper(II) complexes involving saturated chelate rings of this size (seven-membered) are not known, it can be argued that the presence of the stable five-membered ring favours further chelation and the formation of a second less-stable ring. Given the length of the aliphatic chain, the terminal nitrogen could be co-ordinated either axially or equatorially. In fact an examination of Stuart models shows that there is little strain involved with either of these ligand configurations. If we now consider the series of copper(II) complexes, $[CuL]^{2+}$, with tridentate amines, we find the following trend in the $-\Delta H^\ominus$ values:[2,8,9] 3-azahexane-1,6-diamine > 3-azapentane-1,5-diamine > 4-azaheptane-1,7-diamine > 3-azaheptane-1,7-diamine. Thus the complex with both a five-membered and a seven-membered chelate ring is the least favoured, with an enthalpy change smaller even than that for the complex having two six-membered rings.

The thermodynamic data for the binding of a hydroxide ion to the complexes $[CuL]^{2+}$ are shown in Table 3. Comparison with the data for the 3-azahexane-1,6-diamine complex shows that there is little difference between them. For this latter complex it was previously suggested that the introduction of the OH^- group involves only the removal of water molecules without the least disturbance of the co-ordinated ligand.[2] This hypothesis can also account for the behaviour of the 3-azaheptane-1,7-diamine complex. This similarity between the two complexes also reinforces the belief that the ligand 3-azaheptane-1,7-diamine is completely co-ordinated, *i.e.* through all three nitrogen atoms, to the metal ion in the acceptor complex $[CuL]^{2+}$.

1 : 2 *Complexes of* Cu^{2+}.—Three complexes having this metal : ligand ratio are found in aqueous solution, $[Cu(HL)_2]^{4+}$, $[CuL(HL)]^{3+}$, and $[CuL_2]^{2+}$.[5] They have also been isolated in the solid state and their i.r. and electronic reflectance spectral data are shown in Table 2. The bands in the 3 150—3 300 cm^{-1} region show the presence in the first two complexes of protonated amine groups, the bands being more intense in the case of the diprotonated complex. The spectrum of the complex

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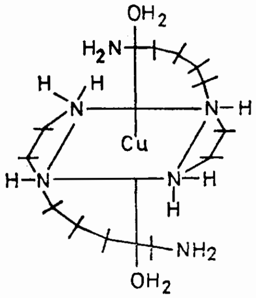
* 1 cal = 4.184 J.

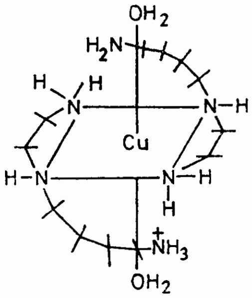
[10] R. Barbucci, P. Paoletti, and M. J. M. Campbell, *Inorg. Chim. Acta*, 1974, **10**, 69.

$[CuL_2]^{2+}$ does not have any bands at higher frequency, which is indicative of free amine groups. For all three complexes, the characteristic bands of the ClO_4^- ion do not seem to indicate co-ordination of this group.[11] This is particularly noticeable in the case of the simple complex $[CuL_2][ClO_4]_2$ for which even the very sensitive ν_4 bending mode at 620 cm^{-1} is not split. Relative to the simple complex, the maxima in the solid-state electronic spectra of the two protonated species show a displacement to higher frequencies indicative of a smaller axial interaction. The results of the i.r. spectra and the position of the maximum in the solid-state spectrum of the simple complex can only be explained by assuming that in the solid state there is an axial interaction with the amine groups of the neutral ligands.

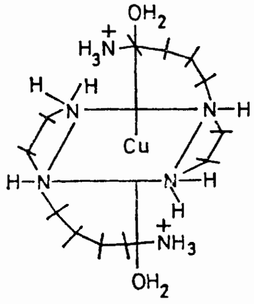
In aqueous solution the maxima in the electronic spectra remained the same over a wide range of pH (4—8) (Table 2). Similarly, both the shape of the e.p.r. spectra and the parameters obtained from them remained unaltered over the same range of pH. This was also the case when the metal to ligand ratio was varied in such a way as to obtain the maximum concentration of each of the three complexes. This behaviour can be explained by supposing that all the species have the same structure and hence the same spectrum. The e.p.r. parameters found are typical of tetragonally distorted octahedral complexes having the chromophore CuN_4O_2.[4] As an example, the complex $[Cu(dmen)_2(OH_2)_2]^{2+}$ (dmen = *NN*-dimethylethylenediamine) gives a similar spectrum as regards shape and parameters.[4] Thus all the three complexes $[Cu(HL)_2]^{4+}$, $[CuL(HL)]^{3+}$, and $[CuL_2]^{2+}$ retain the same structure in aqueous solution with four nitrogen atoms co-ordinated to the metal ion and two free amine groups more or less protonated according to the type of complex, (II)—(IV).



(II)



(III)



(IV)

This shows yet again that the presence of charged nitrogen atoms does not affect the co-ordinate bond strength of the remaining nitrogens. Thus the differences found in the enthalpies of complex formation must be attributed to effects other than the co-ordination process (Table 3). The complex-formation reaction in aqueous solution involves liberation of a certain number of water molecules both from the metal ion and from the free ligand, so that it would be more accurate to formulate the reaction as in (1). The number of water

$$[Cu(OH_2)_6]^{2+}\cdot lH_2O + L\cdot xH_2O \rightleftharpoons [CuL(OH_2)_m]^{2+}\cdot nH_2O + yH_2O \quad (1)$$

molecules liberated will vary with the type of complex formed. Desolvation is an endothermic process which counterbalances the larger exothermic term associated with formation of the Cu–N bonds. In the case of the protonated complexes, the number of water molecules liberated will be less since some of them will remain linked to the protonated nitrogen(s). The endothermic contribution is therefore smaller and the value of $-\Delta H^\ominus$ correspondingly larger. This is confirmed by the lower values of $\Delta S^\ominus$ found for the protonated complexes (due to a smaller contribution from the translational entropy). The difference between the enthalpies of formation of the diprotonated complex and the simple complex (1.7 kcal mol^{-1}) is significant and can only be attributed to the desolvation process.

The formation of the protonated complex can also be regarded as resulting from the protonation $[ML_2]^{2+} + H^+ \rightleftharpoons [ML(HL)]^{3+}$. In complexes with only partially co-ordinated ligands, *i.e.* with one or more free ' arms ', protonation will occur on basic sites not involved in co-ordination, leading to thermodynamic functions very similar to those for protonation of the free ligand. On the other hand, if the ligand is completely co-ordinated it will be more difficult to form the protonated complex.[12] This will be reflected in the values of the thermodynamic functions and in particular in the enthalpy, which should be smaller than the value found for protonation of the free ligand because of the heat required to break the Cu–N bond.

In the case of the ligand 3-azaheptane-1,7-diamine there are three protonated complexes $[Cu(HL)]^{3+}$, $[Cu(HL)_2]^{4+}$, and $[CuL(HL)]^{3+}$, but only for the last two does protonation occur on the free nitrogens. The enthalpy for binding of the proton to the complex $[CuL_2]^{2+}$ (Table 3) is similar to that for the first step in protonation of the free ligand (Table 1). The enthalpy associated with the binding of two protons is almost double that for the first step. This implies that (*i*) protonation occurs on two equivalent basic sites, (*ii*) the nitrogen being proton-

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[11] R. Barbucci, P. Paoletti, and G. Ponticelli, *J. Chem. Soc.* (*A*), **1971**, 1637.

[12] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *Inorg. Chim. Acta*, 1973, **7**, 157.

ated is terminal on the longer aliphatic chain, and (*iii*) the charge on the metal ion does not affect the protonation. It is useful to compare the data for this reaction with those for the analogous reaction of 3-azahexane-1,6-diamine (Table 3). The enthalpy change for this reaction is less than that for 3-azaheptane-1,7-diamine, solely because of the lower heat of protonation of the free ligand. The longer aliphatic chain length in 3-azaheptane-1,7-diamine does not have a noticeable effect.

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