Copper-(I) and -(II) complexes with tertiary linear polyamines of the type $Me_2NCH_2(CH_2NMeCH_2)_nCH_2NMe_2$ (n = 1–4)

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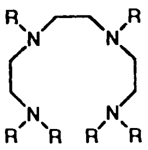
2,5,8,11-Tetramethyl-2,5,8,11-tetraazadodecane, 2,5,8,11,14-pentamethyl-2,5,8,11,14-pentaazapentadecane, and 2,5,8,11,14,17-hexamethyl-2,5,8,11,14,17-hexaazaoctadecane, form stable complexes with Cu^I in aqueous solutions. On the other hand 2,5,8-trimethyl-2,5,8-triazanonane, does not. This indicates that the stabilization of Cu^I by tertiary amine ligands in aqueous solutions requires at least four nitrogens. The electronic spectra and the electrochemical properties of the $[CuL^i]^{2+}$ complexes over a wide pH range were studied and potentiometric titrations were made of solutions containing equimolar concentrations of Cu^{II} and L^i. The nature of the complexes present in these solutions is discussed.

N-Methylation of tetraaza macrocyclic ligands has been shown to stabilize a variety of low-valent transition-metal complexes, *e.g.* Ni^I,[1] Cu^I,[2] Pd^I[3] and Cr^{II}.[4] The effect on the properties of these complexes was attributed mainly to the increased hydrophobic nature, *i.e.* to the lack of hydrogen bonds of the type M–N–H • • • O in these complexes and to their increased radii which decreases their solvation energies.[5] Clearly other factors, *e.g.* distortions induced by the steric strain due to the added methyl groups, contribute to the observed effects.[5b] Recently it was shown that also the open-chain tetraamines L^2, L^{10} and L^{12} inhibit disproportionation of copper(I) in aqueous solutions whereas L^1, L^9 and L^{11} do not.[5b] On the other hand the triamine L^8 does not inhibit this disproportionation in aqueous solutions.[6] It therefore seemed of interest to study the effect of the chain length, *i.e.* of the number of ligating tertiary amine groups, on the properties of copper-(II) and -(I) complexes in aqueous solutions.

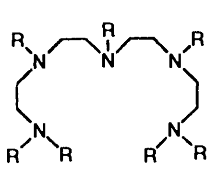
We decided to study the properties of the complexes with L^4 and L^6 in aqueous solutions. It was hoped that light would be shed on the reasons why tertiary amine ligands are poor σ donors,[7] though alkyls are electron-donating substituents. Furthermore the development of ligands which stabilize Cu^I in aqueous solutions is also of interest in the framework of the recent interest in the chemistry of copper(I) complexes in aqueous solutions. This interest stems from the role of copper(I) in catalysis, in biological systems, and in free-radical reactions.

Compounds with chains containing more than six tertiary nitrogen-donor groups were not chosen for two reasons: their ability to bind more than one copper ion[8] and the coordination number of copper usually does not exceed six.[9] The effect of extending the chain length, *i.e.* the number of donor nitrogen atoms, on the properties of copper(II) complexes with the corresponding unmethylated amines L^1, L^3, L^5 and L^7 was previously studied. The conclusions of this study were:[10] at least three of the amine groups are bound to the copper(II) ion, the rest might be protonated depending upon the pH of the solution; at most five copper–nitrogen bonds are formed in complexes with these types of amines even if more nitrogen-donor atoms are available (the fourth nitrogen in the chain contributes $10^{4.2}$, the fifth $10^{2.7}$ and the sixth only $10^{0.9}$ to the stability constant of the complex respectively).

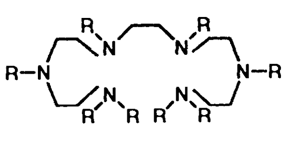
The results obtained in the present study indicate that also the tertiary linear polyamines form at most five co-ordinated complexes with Cu^{II} and probably also with Cu^I.



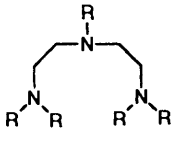
R = H L^1
R = CH_3 L^2



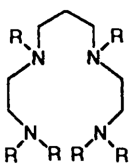
L^3
L^4



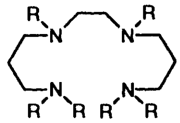
R = H L^5
R = CH_3 L^6



L^7
L^8



R = H L^9
R = CH_3 L^{10}



L^{11}
L^{12}

Experimental

Materials

All solutions were prepared from A. R. grade chemicals and from distilled water further purified by passage through a Milli Q Millipore set-up, final resistivity > 10 MΩ cm^{-1}. The amines L^2, L^5 and L^6 were prepared by N-methylation of the unmethylated L^1, L^3 and L^5 using formaldehyde and formic acid according to literature methods,[11] and crystallized as their HCl salts; all were used as their HCl salts. The extent of N-methylation was verified by elemental analysis and by ^1H and ^{13}C NMR spectroscopy. Both techniques indicated that in over 97% of the molecules all the nitrogen donors were tertiary ones.

Physical measurements

Electrochemical measurements were carried out using a EG&G model 263 potentiostat/galvanostat. EG&G parc model 303A SMDE working electrode and model 270/250 research electrochemistry 4.00 software.

Some of the preliminary experiments were carried out using a Bioanalytical Systems inc. CV-1B cyclic voltammograph, a three-electrode cell and a Yokogawa Hokushin Electric type 3080 X-Y recorder. A saturated calomel electrode (SCE) served as a reference and a hanging mercury drop electrode was the working electrode. All experiments were carried out in 0.5 mol dm^{-3} solutions. The redox potentials given are the averages of the peak potentials of the cathodic and anodic waves. No correction for activity coefficients was introduced. These measurements were carried out in solutions containing a ratio of 2:1 amine to copper in order to ensure that no free Cu^{2+} ions were present which would cause disproportionation following reduction. The pH was measured with a Corning 220 pH meter.

Potentiometric measurements were carried out in 0.15 mol dm^{-3} $NaClO_4$ (C. Erba ACS grade, purified according to a described procedure[12]). Standardized CO_2-free solutions of NaOH, used in the potentiometric titrations, were prepared by following the procedure described in ref. 13. Potentiometric titrations were carried out by using equipment (potentiometer, burette, stirrer, cell, microcomputer, *etc.*) fully described previously.[14] The computer program SUPERQUAD[15] was used to process the data and calculate both basicity and stability constants. The latter were calculated using only concentrations without correction for activity coefficient effects. Therefore they are concentration stability constants and not thermodynamic ones.

The measurements were carried out in solutions containing a 1:1 ratio of amine to copper which simplifies the analysis of the data and increases the accuracy of the calculated stability constants.

The UV/VIS spectra were recorded using a Hewlett-Packard 8452A diode-array spectrophotometer.

Computer model calculations

These were carried out with a Tektronix CAChe system, the software used being MM2 which computes molecular mechanical values for optimum geometries. The strain in the ligands in the complexes was determined by subtracting the calculated energy of the free amine from that of the ligand calculated when its geometry was frozen to the optimum configuration in the copper(II) complex.

Results

In order to obtain a detailed characterization of the species in the solutions used in this study, potentiometric titrations of solutions containing the amines L^2, L^4 and L^6 and of solutions containing equimolar mixtures of these and $CuSO_4$ were performed. The results obtained are summarized in Table 1 and Figs. 1 and 2. For comparison purposes literature data concerning L^1, L^3, L^7 and L^8 and their copper complexes are included in the table. No comparable data are available for L^5; the only study of the stability constant of its copper complex performed to date used an electrochemical approach and states that the stability constant of $[CuL^5]^{2+}$ is only slightly higher than that of $[CuL^3]^{2+}$.[10] However all the values obtained are considerably higher than those accepted today.[16]

The results presented in Table 1 clearly indicate that N-methylation decreases the basicity of the amines studied. This finding is in accord with literature data concerning other tertiary amines and is commonly attributed to the lower solvation of the acidic form of the tertiary amine.[5]

The redox properties of the copper complexes with these amines were studied using cyclic voltammetry. A typical result is shown in Fig. 3. Reversible electrochemical waves are obtained in these systems. The measurements were carried out over a wide range of pH. The results summarized in Table 2

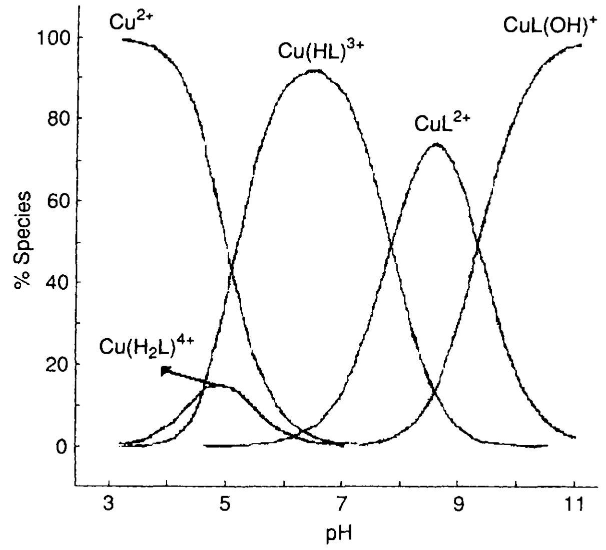


Fig. 1 Distribution diagrams of the species formed by Cu^{2+} and L^4, as a function of pH at 25 °C in 0.15 mol dm^{-3} $NaClO_4$

Table 1 Basicity and formation constants for the system copper(II)–L^i (i = 2, 4, 6 or 8) in aqueous solutions[a]

	log K						
Reaction	L^{7b}	L^{8c}	L^{1b}	L^2	L^{3b}	L^4	L^6
$L + H^+ \rightleftharpoons HL^+$	9.84	9.22(1)	9.74	9.23(1)	9.70	9.42(1)	9.70(3)
$HL^+ + H^+ \rightleftharpoons H_2L^{2+}$	9.02	8.41(3)	9.07	8.47(1)	9.14	8.74(1)	8.64(3)
$H_2L^{2+} + H^+ \rightleftharpoons H_3L^{3+}$	4.23	2.09(3)	6.56	5.36(2)	8.05	7.67(1)	8.12(3)
$H_3L^{3+} + H^+ \rightleftharpoons H_4L^{4+}$			3.25	1.68(3)	4.70	3.12(1)	5.90(6)
$H_4L^{4+} + H^+ \rightleftharpoons H_5L^{5+}$					2.97	1.67(3)	2.60(6)
$L + Cu^{2+} \xrightleftharpoons{(K_{II})} [CuL]^{2+}$	15.9	12.16(3)	20.1	12.60(1)	22.8	12.20(2)	12.8(1)
$[CuL]^{2+} + H^+ \rightleftharpoons [Cu(HL)]^{3+}$			3.6	6.16(1)	5.2	7.98(4)	8.46(4)
$[Cu(HL)]^{3+} + H^+ \rightleftharpoons [Cu(H_2L)]^{4+}$					3.8	4.61(3)	6.88(4)
$[Cu(H_2L)]^{4+} + H^+ \rightleftharpoons [Cu(H_3L)]^{5+}$							3.86(5)
$[CuL]^{2+} + OH^- \rightleftharpoons [CuL(OH)]^+$		5.14(4)	3.3	6.43(3)		4.42(2)	4.08(5)
$L + Cu^+ \xrightleftharpoons{(K_I)} [CuL]^+$	< 10[d]	< 8[d]	< 12[d]	11.0(3)[e]	< 13.4[d]	10.9(3)[e]	10.5(3)[e]

[a] There are no comparable data for L^5 and its copper complex, see text. [b] Taken from ref. 16. [c] Ref. 17. [d] Upper limit for K_I; calculation is based on the fact that no comproportionation is observed. The procedure for this calculation is given in ref. 5(*b*). [e] Calculated from the electrochemical data according to the procedure given in ref. 5(*b*).

Table 2 Redox potentials (mV) of the copper complexes obtained by cyclic and square-wave voltammetry at a hanging mercury drop electrode *vs.* NHE; scan rate 20 mV s^{-1}, $[Cu^{II}]$ = 0.001 mol dm^{-3}, [L] = 0.002 mol dm^{-3}, $[ClO_4^-]$ = 0.5 mol dm^{-3}

	pH															
	5		6		7		8		9		10		11		12	
Amine	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2
L^2	116	−101	80	−118	65	−118	60	−118	45	−137	12	−145	−48	−145	−105	−148
L^4	110	−118	109	−125	105	−181	90	−202	75	−202	14	−194	−39	−195	−88	−205
L^6	140	−104	130	−113	120	−158	70	−193	22	−198	−23	−203	−63	−203	−98	−203

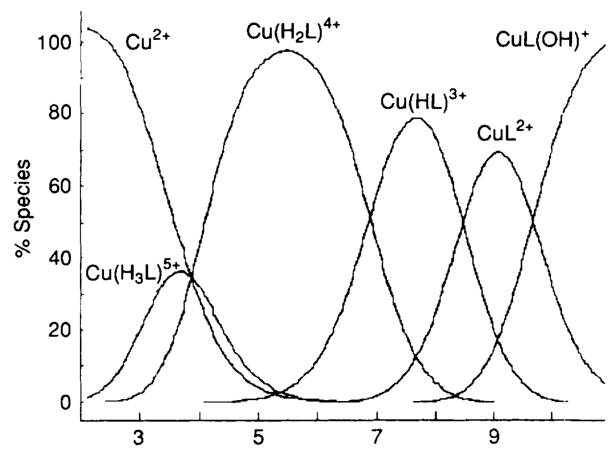


Fig. 2 Distribution diagrams of the species formed by Cu^{2+} and L^6 as a function of pH at 25 °C in 0.15 mol dm^{-3} $NaClO_4$

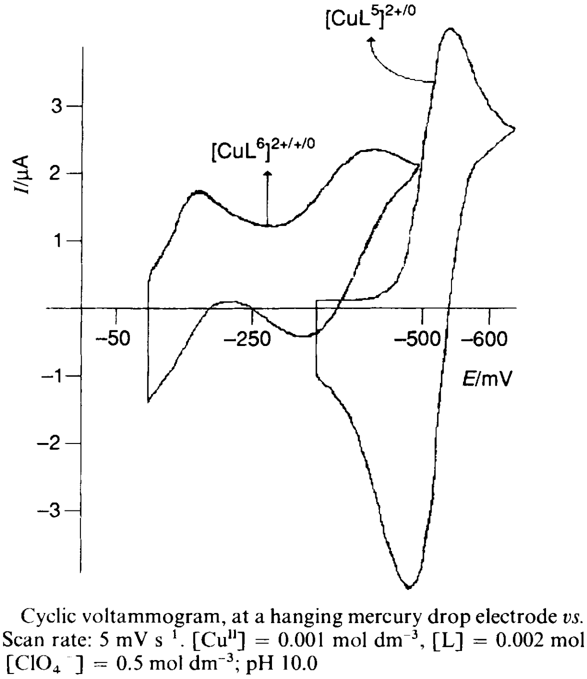


Fig. 3 Cyclic voltammogram, at a hanging mercury drop electrode *vs.* SCE. Scan rate: 5 mV s^{-1}. $[Cu^{II}]$ = 0.001 mol dm^{-3}, [L] = 0.002 mol dm^{-3}, $[ClO_4^-]$ = 0.5 mol dm^{-3}; pH 10.0

clearly demonstrate that $[CuL^i]^{2+}$ (i = 2, 4 or 6) are reduced *via* two consecutive single-electron processes whereas $[CuL^i]^{2+}$ (i = 1, 3 or 5) are reduced *via* a single two-electron process; for the latter complexes the redox potentials are considerably more cathodic.[10]

The electrochemical results clearly suggest that the comproportionation process (1) should occur for $[CuL^i]^{2+}$

$$[CuL^i]^{2+} + Cu^0 + L^i \rightleftharpoons 2[CuL^i]^+ \qquad (1)$$

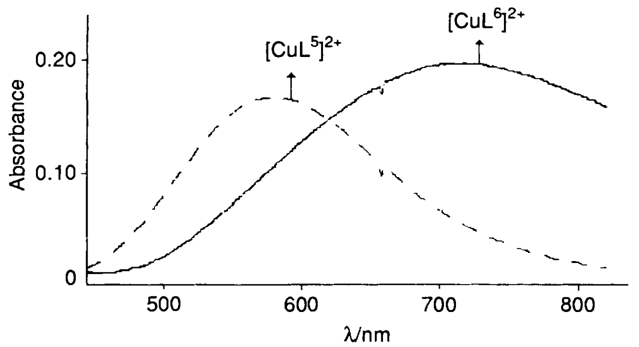


Fig. 4 Spectral band due to the d–d transition. $[Cu^{II}]$ = 0.001 mol dm^{-3}, [L] = 0.002 mol dm^{-3}; pH 10.0

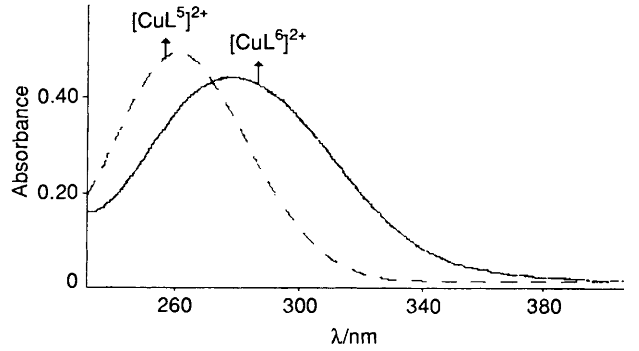


Fig. 5 Spectral band due to a charge-transfer transition. $[Cu^{II}]$ = 0.0001 mol dm^{-3}, [L] = 0.0002 mol dm^{-3}; pH 10

(i = 2, 4 or 6). Indeed, when a copper plate is added to a deaerated solution containing $[CuL^i]^{2+}$ and excess of amine at different pH values the comproportionation reaction occurs within a few hours and the solution loses its colour. When dioxygen is added, equation (2), to the latter solutions they

$$2[CuL^i]^+ + 0.5O_2 \longrightarrow 2[CuL^i]^{2+} \qquad (2)$$

turn blue and the concentration of $[CuL^i]^{2+}$ is double that initially introduced.

The UV/VIS spectra of the $[CuL^i]^{2+}$ complexes were measured over a wide pH range. These consist of two bands, one attributed to a ligand-to-metal charge-transfer (l.m.c.t.) transition and one due to a d–d transition. Typical spectra are shown in Figs. 4 and 5, the results are summarized in Table 3. The spectra due to the d–d transition clearly indicate that the nature of the complexes is affected by the pH in accord with the potentiometric results. The bands due to the l.m.c.t. transitions are shifted to shorter wavelengths at higher pH. The effect of pH on the spectra is considerably more pronounced for the complexes with the methylated ligands compared to those of corresponding complexes with non-methylated ligands, again in accord with the potentiometric results. The results clearly show that N-methylation shifts

Table 3 The UV/VIS spectral data [λ_{max}/nm (10^{-3} ε/cm^2 mol^{-1})] for the copper(II) complexes. $2[Cu^{II}] = [L]$; $I = 0.5$ mol dm^{-3}

	pH							
Amine	5	6	7	8	9	10	11	12
L^1	568 (140)	568 (140)	568 (140)	568 (140)	568 (140)	570 (140)	571 (135)	572 (130)
	258 (4650)	258 (4650)	258 (4650)	258 (4650)	258 (4600)	258 (4650)	258 (4550)	258 (4500)
L^2	634 (50)	634 (200)	636 (210)	636 (210)	638 (200)	646 (190)	644 (160)	642 (120)
	298 (4900)	300 (5100)	302 (5250)	300 (5150)	298 (5000)	296 (4850)	294 (4650)	282 (4560)
L^3	614 (170)	626 (170)	626 (170)	628 (170)	630 (165)	632 (165)	632 (160)	632 (155)
	268 (4400)	268 (4200)	268 (4100)	268 (4050)	268 (4000)	268 (4000)	268 (3900)	268 (3900)
L^4	674 (250)	674 (240)	682 (265)	700 (245)	710 (250)	714 (250)	714 (240)	714 (200)
	296 (4400)	296 (4600)	296 (4850)	298 (5050)	298 (5150)	298 (5150)	296 (5100)	294 (4800)
L^5	576 (155)	576 (155)	576 (155)	576 (155)	576 (150)	576 (150)	576 (150)	580 (140)
	260 (4450)	260 (4450)	260 (4400)	260 (4400)	260 (4400)	260 (4350)	260 (4300)	260 (4300)
L^6	676 (225)	680 (220)	684 (215)	690 (200)	696 (180)	718 (220)	718 (165)	714 (140)
	296 (4500)	296 (4500)	296 (4450)	294 (4450)	292 (4400)	288 (4250)	280 (4050)	272 (4300)

Table 4 Results of MM2 calculations of the strain in the ligand in the copper(II) complexes

Amine	No. of nitrogens bound to Cu	No. of H_2O bound to Cu	Strain/kJ mol^{-1}
L^8	3	3	74
L^2	3	2	91
	3	3	123
	4	2	137
L^4	4	1	140
	4	2	164
	5	0	238
	5	1	325
L^6	4	0	160
	4	1	203
	4	2	193
	5	0	305
	5	1	330
	6	0	763

both the d–d and the l.m.c.t. bands to longer wavelengths in accord with earlier reports.[5]

As strain energy in the ligand might be a major contributing factor to the stability of the complexes studied it was decided to calculate it approximately in the gas phase. For this purpose it was assumed that the co-ordination number of Cu^{II} is six, or plausibly five in the more sterically hindered complexes. The results of such MM2 calculations are summarized in Table 4. They show that increasing the number of nitrogen-donor atoms bound to the central copper cation increases the strain of the complex dramatically. Furthermore the strain energy increases considerably with the number of CH_2CH_2NMe groups even if they are not bound to the copper.

Discussion

The results clearly demonstrate that the N-methylated amines L^4 and L^6, in analogy to L^2,[5b] stabilize Cu^I in aqueous solutions. An analysis of the data in Table 1 shows that, as for L^2, L^{10} and L^{12}, the stability constants of $[CuL^4]^{2+}$ and $[CuL^6]^{2+}$ are not considerably higher than those of $[CuL^4]^+$ and $[CuL^6]^+$ in contrast to the observations for the complexes of the corresponding non-methylated amines $L^{1,3,5}$. The following conclusions can also be drawn. (1) The N-methylated amines are weaker bases than the corresponding non-methylated ones, in accord with previous results.[5] (2) N-Methylation causes a considerable decrease in K_{II} and has only a minor effect on K_I. Only an upper limit of the latter can be determined for the non-methylated amines from the electrochemical results.[5b] (3) N-Methylation transforms the $[CuL^i]^{2+}$ complexes into considerably stronger acids, *i.e.* the stability constant for binding OH^- increases. This observation is also in accord with previous results[5] and was attributed to the lack of $Cu^{II}–N–H\cdots O$ hydrogen bonds in the complexes with tertiary nitrogen donors which inhibits charge delocalization. (4) The value of K_{II} for the non-methylated amines increases considerably with the number of nitrogen donor atoms, up to five,[10] which indicates that all the nitrogens are bound to the Cu^{II} in $[CuL^i]^{2+}$, $i = 1$, 3 or 7. On the other it seems to be nearly independent of the number of tertiary nitrogen donor atoms, compare K_{II} for L^i ($i = 2, 4, 6$ or 8). This result indicates that either only three or four tertiary nitrogens are bound to the central Cu^{II} or that the binding of the fourth and fifth ones weakens the other Cu–N bonds, and/or that the desolvation effects are compensated by the formation of the Cu–N bond. Previous results clearly demonstrate that in $[CuL^2]^{2+}$ the ligand is bound to the central copper in a tetradentate mode.[5b] (5) A comparison of the equilibria constants of the reactions $[CuL]^{2+} + H^+ \rightleftharpoons [Cu(HL)]^{3+}$ clearly demonstrates that N-methylation of the ligands shifts the equilibrium to the right. This also indicates that either only three or four tertiary nitrogens are bound to the central Cu^{II} or that the binding of the fourth and fifth ones is very weak.

The smaller equilibrium constant of the reaction $[CuL^i]^{2+} + OH^- \rightleftharpoons [CuL^i(OH)]^+$ for $i = 4$ and 6 than for $i = 2$, by *ca.* two orders of magnitude, probably stems from the competition between the OH^- ligand and the binding of the fifth nitrogen donor to the copper. The minor difference in the corresponding values for $[CuL^4]^{2+}$ and $[CuL^6]^{2+}$ might be due to a weak interaction between the sixth nitrogen and the copper or to a steric effect caused by the sixth nitrogen. The fact that the binding constant of OH^- to $[CuL^2]^{2+}$ is higher than that to $[CuL^8]^{2+}$ is probably due to the difference in the hydrophobicity of the ligands and/or to the ligation site. Hydroxide clearly is bound to an axial site in $[CuL^2(OH)]^+$, whereas in the case of $[CuL^8(OH)]^+$ the ligation site could be axial or equatorial.

The suggestion that the ligands in $[CuL^4]^{2+}$ and $[CuL^6]^{2+}$ are five-co-ordinated is corroborated by the pH effect on the d–d bands, Fig. 6. These results clearly show that the behaviour of $[CuL^2]^{2+}$ differs from that of $[CuL^4]^{2+}$ and $[CuL^6]^{2+}$. The large decrease in the ligand-field splitting at high pH for the last two complexes, which occurs at a pH significantly below that of hydroxide binding (Figs. 1 and 2), is attributed to the binding of the fifth nitrogen to the central Cu^{II}.

The electrochemical studies clearly demonstrate that the effect of N-methylation on the redox potential of the $[CuL^i]^{2+/+}$ couples is similar for the three ligands studied, Table 2. The pH effect on the first redox process E_1 is in accord with that on the composition of the solution, Table 1.

It is of interest that the pH dependence of the redox couples $[CuL^i]^{+/0}$ for $i = 4$ or 6 differs considerably from that of the couple $[CuL^2]^{+/0}$, Fig. 7. As L^2 is a tetradentate ligand in $[CuL^2]^+$, this results suggests that the ligands L^4 and L^6 are

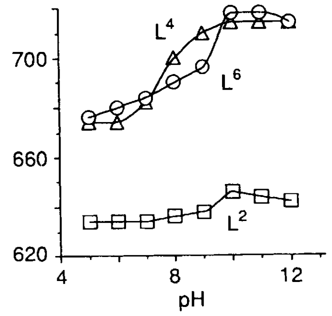


Fig. 6 Shift of the maxima of the spectral bands due to the d–d transition as a function of pH

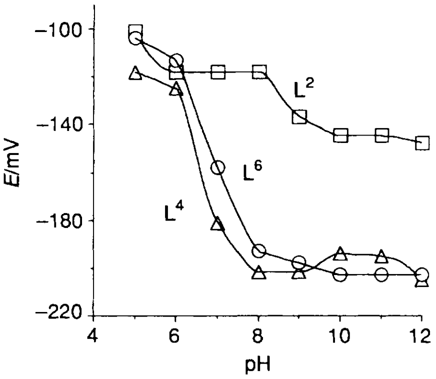


Fig. 7 Plots of the $[\mathrm{Cu^{I}L}^{i}]$–Cu^0 redox potentials *vs.* pH for $i = 2$, 4 and 6

probably pentadentate $[\mathrm{CuL}^i]^+$ (L^8 does not stabilize $\mathrm{Cu^I}$ in aqueous solutions^6).

The red shift of the d–d band upon N-methylation, Fig. 4, indicates that the ligand-field splittings in $[\mathrm{CuL}^i]^{2+}$, $i = 2$, 4 or 6, are smaller than when $i = 1$, 3 or 5. Thus tertiary amines are less good σ donors than secondary amines though methyls are electron-donating substituents. However this observation is in accord with previous reports.^{5} Recently it was proposed that this effect stems from the lack of hydrogen bonds of the type Cu–N–H ··· O in complexes of ligands with tertiary amine donor groups.^{5} A major contribution of a tetrahedral distortion, caused by steric hindrance in $[\mathrm{CuL}^i]^{2+}$, $i = 2$, 4 or 6, was ruled out by EPR spectroscopy.^{5b}

The red shift of the charge-transfer band upon N-methylation, Fig. 5, suggests that either the tertiary amines are better electron donors than secondary amines and/or that the copper(II) ions are stronger oxidants in the N-methylated complexes. The effect of the N-methylation on the d–d band indicates that the second argument is the correct one.^{5}

As the results seem to indicate that L^4 and L^6 are five-co-ordinated to $\mathrm{Cu^{II}}$ and probably also to $\mathrm{Cu^{I}}$, though the stability constants of their complexes are not higher than those of L^2 and L^8, it was decided to calculate the strain energies in the ligands in the copper(II) complexes using the MM2 program. The results are summarized in Table 4, and the following conclusions can be drawn. (1) The binding of a fifth nitrogen to the $\mathrm{Cu^{II}}$ contributes approximately 100 kJ mol^{-1} to the strain in the ligands both in $[\mathrm{CuL}^4]^{2+}$ and in $[\mathrm{CuL}^6]^{2+}$. (2) Binding of the sixth nitrogen in $[\mathrm{CuL}^6]^{2+}$ would increase considerably the strain in the ligand and is therefore not likely to occur. However a weak interaction between the sixth nitrogen and the copper due to their geometric arrangement cannot be ruled out. (3) The addition of a water molecule in the sixth co-ordination site has usually only a minor effect on the strain energy of the tertiary amine ligand. These conclusions show that the observation that the stability constants, K_{II}, do not increase with the number of tertiary nitrogen donor atoms stems at least partially from a compensation between the increase in the binding energy and the strain energy.

Conclusion

The results lead to the following conclusions.

(1) Stabilization of copper(I) complexes by tertiary linear polyamine ligands in aqueous solutions requires at least four tertiary nitrogen-donor atoms. An increase in the number of donor nitrogens to five or six does not change the extent of this stabilization significantly.

(2) The stability constants K_{II} do not increase with the number of tertiary nitrogen donor groups in contrast to those for the complexes with L^i, $i = 1$, 3, 5 or 7.^{10} This is probably due to the considerably larger strain energy of the N-methylated ligands, though the smaller solvation of the N-methylated complexes might contribute to the observed effect.

(3) Amines L^4 and L^6 are pentadentate in their complexes with $\mathrm{Cu^{II}}$ and probably also with $\mathrm{Cu^{I}}$.

(4) Potentiometric titrations are not sufficient for identifying the nature of species formed in the solutions and it is advantageous to augment them with other measurements, *e.g.* electrochemical and spectrophotometric ones.

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