Macro-inorganics. Part 3.† Chelation of Copper(II) Ion with Some Polymers having a Poly(amido-amine) Structure and their Non-macromolecular Models

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Copper(II) complex formation with some poly(amido-amines) and their non-macromolecular models has been studied by potentiometric and spectrophotometric (electronic and e.s.r.) techniques. Real stability constants could be determined for the macromolecular ligands. The presence of complexes such as $[CuL]^{2+}$, $[Cu(OH)L]^+$, and $[Cu(OH)_2L]$ (where in the case of polymeric ligands L represents the repeating unit) could be ascertained in aqueous solution. The stability constants of the $[CuL]^{2+}$ complexes with macromolecular ligands are slightly lower than those of their non-macromolecular models. Some of the complexes have been obtained and studied in the solid state. They have clear-cut stoicheiometries and their electronic spectra are identical to those obtained in solution. In order to elucidate the mechanism of complex formation, low-molecular-weight models of the polymers have also been studied. The complexes of the polymers and their corresponding models show identical electronic and e.s.r. spectra.

COMPLEX formation between metal ions and synthetic polymers containing suitable functional groups has received little attention until recently. As a rule, complex formation is a very intriguing process when macromolecular ligands are involved. It is generally concerned with the co-ordination of the metal ion by functional groups belonging to different monomeric units.[1] Therefore, the only realistic way of describing polymeric complexing systems involves the use of averaged $K_{\text{app.}}$ values.[2]

A new class of multifunctional polymers, poly(amido-amines) (see below), show interesting properties as complexing agents for natural polysaccharides.[3] Some of them are also capable of forming stable complexes with several metal ions.[4] In a previous paper we reported some results on the protonation of poly(amido-amines).[5] We found that *real* basicity constants could be determined, while only *apparent* constants can be obtained for most polyelectrolytes.[2]

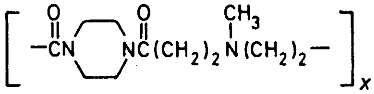
The aim of the present paper is to report some results on the complex formation between copper(II) and poly(amido-amines). This study has been carried out by a number of different physicochemical techniques, such as potentiometry, electronic spectrophotometry, and e.s.r. spectroscopy.

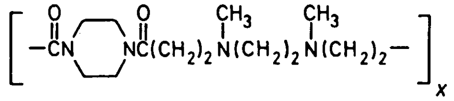
EXPERIMENTAL

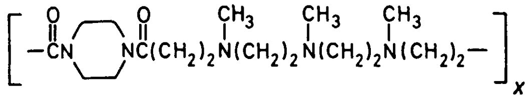
Materials.—The poly(amido-amines) and their non-macromolecular models were prepared as previously described.[3,5]

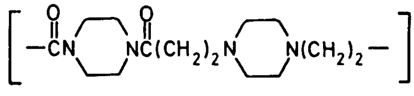
Solid complexes. All the solid complexes were prepared by mixing ethanol solutions of $Cu[NO_3]_2\cdot3H_2O$ and ligand in 1 : 1 mol ratio. A small volume of acetone was then added and the solution cooled to −5 °C. The copper(II) complexes were then usually precipitated and those with the models were then recrystallized from ethanol. All the compounds were dried *in vacuo* at 50 °C [Found: C, 32.1; H, 5.7; Cu, 12.0; N, 15.9. Calc. for $CuL^2(NO_3)_2\cdot3H_2O$: C, 32.1; H, 6.15; Cu, 12.15; N, 16.05. Found: C, 37.4; H, 6.6; Cu, 10.9; N, 14.7. Calc. for $CuL^6(NO_3)_2\cdot H_2O$: C, 37.55; H, 6.30; Cu, 11.05; N, 14.6. Found: C, 35.0; H, 6.5; Cu, 10.7; N, 16.7. Calc. for $CuL^3(NO_3)_2\cdot3H_2O$: C, 35.15; H, 6.75; Cu, 10.95; N, 16.85. Found: C, 38.5; H, 5.9; Cu, 11.3; N, 15.0. Calc. for $CuL^8(NO_3)_2$: C, 38.9; H, 5.80; Cu, 11.45; N, 15.1%].

Polymeric ligands

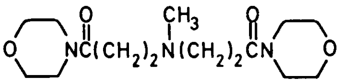
(L^1)


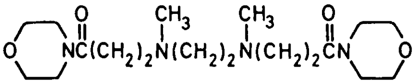
(L^2)


(L^3)


(L^4)


Models

(L^5)


(L^6)


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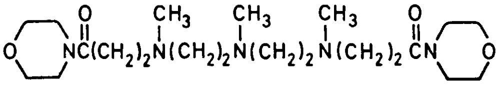
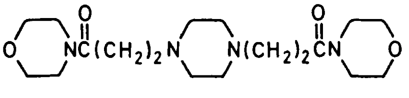


(L^8)


Methods.—E.m.f. measurements. Potentiometric titrations were performed according to a previously described procedure,[6] using a Beckman Research potentio-

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† Parts 1 and 2 are references 5 and 15 respectively.

meter, an Ag–AgCl reference electrode, an Orion 91-01-00 glass electrode, and a salt bridge containing 0.1 mol dm^{-3} NaCl solution. All the potentiometric measurements were carried out at 25 °C in 0.1 mol dm^{-3} NaCl. The stability constants were calculated from at least three different titration curves. The ligand : metal ratios varied from 1 : 0.6 to 1 : 0.1; the pH range was 2.5—9.0. The program MINIQUAD-76A, which was used to calculate the constants, has been described elsewhere.[7] The protonation constants and the experimentally measured ionic product of water were held constant during the calculation of the complex-formation constants. Details of the potentiometric titrations are reported in Table 1.

TABLE 1

Experimental details of the potentiometric measurements in 0.1 mol dm^{-3} NaCl solution at 25 °C

Ligand	Ability to form copper(II) complexes in aqueous solution	Initial amount mmol		No. of points
		L	Cu	
L^1	No			
L^2	Yes	0.148 7	0.047 1	39
		0.234 1	0.041 9	41
		0.122 9	0.049 9	29
		0.217 4	0.039 4	31
L^3	Yes	0.326 8	0.073 1	47
		0.259 3	0.147 7	37
		0.225 3	0.040 4	45
		0.274 8	0.062 0	36
L^4	No			
L^5	No			
L^6	Yes	0.120 4	0.045 8	35
		0.228 9	0.066 5	39
		0.247 8	0.054 2	39
L^7	Yes	0.178 3	0.080 1	31
		0.207 4	0.020 3	21
		0.383 8	0.106 4	36
L^8	No			

Electronic spectra. Absorption spectra were recorded at room temperature with a Cary model 14 spectrophotometer using 1 cm silica cells. Reflectance spectra were obtained by a method analogous to that reported by Venanzi and co-workers.[8]

TABLE 2

Electronic and e.s.r. spectral data

Compound	Electronic spectra[a] (10^3 cm^{-1})		E.s.r. spectra of aqueous solution					
	Solid	aqueous solution	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$[b]	$A_{\perp}$[b]	$g_{iso.}$	$A_{iso.}$
$[CuL^2][NO_3]_2\cdot3H_2O$	15.1	14.8 (174)	2.252	2.062	178	12.5	*c*	*c*
$[CuL^6][NO_3]_2\cdot H_2O$	14.8	14.8 (176)	2.252	2.056	178	12	2.127	68
$[CuL^3][NO_3]_2\cdot3H_2O$	16.4	16.1 (244)	2.221	2.050	181	12.5	*c*	*c*
$[CuL^7]^{2+}$	*d*	16.1 (244)	2.221	2.050	181	12.5	2.115	74
$[CuL^8][NO_3]_2$	15.8, 18.2 (sh)	*e*	*e*		*e*		*e*	

[a] The molar absorption coefficients (dm^3 mol^{-1} cm^{-1}) are given in parentheses. [b] All hyperfine coupling constants are in units 10^{-4} cm^{-1}. [c] Anisotropic spectrum at r.t. [d] Not obtained in the solid state. [e] Not stable in solution.

E.s.r. spectra. First derivative *X*-band e.s.r. spectra were recorded at room temperature and at −140 °C using a Varian E-9 spectrometer and were calibrated using diphenylpicrylhydrazyl (dpph) as a *g* marker. Simulated spectra for a Lorentzian lineshape were obtained using our version [9b] of Venable's program [9a] and in all cases it was possible to fit the experimental spectra closely. The e.s.r. parameters given in Table 2 are the best-fit parameters for the final simulation.

RESULTS AND DISCUSSION

Copper(II) *Complexes in Aqueous Solution.*—(*i*) *Stability constants.* The ligating abilities of both polymers and models with respect to copper(II) ion in aqueous solution are summarized in Table 1. The polymeric ligands L^1 and L^4 and their corresponding models L^5 and L^8 do not form any copper(II) complex in aqueous solution. The ligand L^1 contains only one suitable tertiary nitrogen atom in the repeating unit. Therefore, we assume that its inability to form copper(II) complexes may be related to its inability to use a larger number of nitrogen atoms for co-ordination, even when belonging to different monomeric units.[1] This behaviour is similar to that of the non-macromolecular model L^5. As regards the ligands L^4 and L^8, their difficulty in forming copper(II) complexes in aqueous solution may be attributed to the presence of a piperazine ring in the amine part of their structure. The co-ordination of copper(II) ion is possible only by adjusting the piperazine ring into a boat conformation. In fact, it has been shown that substituted piperazines exist mostly in a chair conformation,[10] and the change to the boat conformation involves greater steric hindrance than in the case of analogous open chain diamines.[11] However, in the case of the non-macromolecular model L^8, a solid complex could be isolated in a non-aqueous solvent. The same experiment could not be performed with polymer L^4, which is insoluble in most organic solvents. Nevertheless, the fact that no copper(II) complexes could be obtained in aqueous solution with L^4 gives a further indication that different units do not co-operate in complex formation. All complexes have a well defined stoicheiometry, corresponding to one copper(II) ion for each repeating unit. This behaviour, as far as the macromolecular ligands are concerned, is very unusual.[12]

Real * stability constants [5] could be determined for all the complexes with macromolecular ligands. These are listed in Table 3. The $[CuL]^{2+}$ complexes of both polymer and model with two tertiary nitrogen atoms (L^2 and L^6) are more stable than $[Cu(tmen)]^{2+}$ (tmen = *NNN'N'*-tetramethylethylenediamine), containing two co-ordinated nitrogen atoms; [13] the complexes of L^3 and L^7 are more stable than $[Cu(pmapd)]^{2+}$ (pmapd = *NNN'N''N''*-pentamethyl-3-azapentane-1,5-diamine),[14] containing three co-ordinated nitrogen atoms (Table 3).

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* *Real* means that the constants do not depend on the degree of complexation of the whole macromolecule.

This may be an indication that besides the amine groups, other functions (*e.g.* amide groups) are involved in the co-ordination, even if a different entropy term has to be considered in the two different series of ligands.[15] The poly(amido-amine) complexes are less stable than those of their models. The difference, however, is much smaller than in the case of other polymers.[16]

Of the polymers L^2 and L^3, only L^2 forms a hydroxo-complex, $[Cu(OH)L]^+$. In aqueous solution, the corresponding non-macromolecular model L^6 forms two hydroxo-complexes, namely $[Cu(OH)L]^+$ and $[Cu(OH)_2L]$. Model L^7 forms only one hydroxo-complex, $[Cu(OH)L]^+$. It seems that, as a general rule, the polymers are able to co-ordinate less hydroxo-groups than the corresponding non-polymeric ligands. It is interesting to note that the stability constant of the hydroxo-complex of model L^7 [4.62(8)] is quite similar to those of Cu^{II} with other linear aliphatic triamines, such as 3-azapentane-1,5-diamine (4.50),[17] 4-azaheptane-1,7-diamine (4.1),[18] 3,5-diazaheptylamine (4.7),[19] and 3-azaheptane-1,7-diamine (4.36),[20] showing, as already suggested,[20] that the bulkiness of the polyamine does not affect the process of hydroxo-complex formation. Similarly, the dihydroxo-complex $[Cu(OH)_2L]$ with the ligand L^6 shows a stability constant close to that found for $[Cu(OH)_2(tmen)]$ [13] (Table 3).

TABLE 3

Stability constants of copper(II) complexes with poly(amido-amines) and their corresponding non-macromolecular models at 25 °C

Ligand	Complexing reaction	log β [a]
L^2	$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	8.96(8)
	$[CuL]^{2+} + [OH]^- \rightleftharpoons [Cu(OH)L]^+$	5.52(10)
L^6	$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	9.10(2)
	$[CuL]^{2+} + [OH]^- \rightleftharpoons [Cu(OH)L]^+$ [b]	
	$[CuL]^{2+} + 2[OH]^- \rightleftharpoons [Cu(OH)_2L]$	8.40(13)
tmen [c]	$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	7.37
	$[CuL]^{2+} + 2[OH]^- \rightleftharpoons [Cu(OH)_2L]$	9.12
	$2[CuL]^{2+} + 2[OH]^- \rightleftharpoons [Cu_2(OH)_2L_2]^{2+}$	15.26
L^3	$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	12.19(9)
L^7	$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	13.36(5)
	$[CuL]^{2+} + [OH]^- \rightleftharpoons [Cu(OH)L]^+$	4.62(8)
pmapd [d]	$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	12.16

[a] Estimated standard deviations are given in parentheses. [b] Evidence of its formation in aqueous solution. [c] Ref. 13 in 0.5 mol dm^{-3} $K[NO_3]$. [d] Ref. 14 in 0.13 mol dm^{-3} $K[NO_3]$.

(*ii*) *Electronic and e.s.r. spectra.* In aqueous solution, the electronic and low-temperature e.s.r. spectra of the polymeric $[CuL]^{2+}$ complexes are identical to those of their corresponding models (Table 2). The molar absorption coefficients, the positions of the absorption maxima, and the Hamiltonian parameters are typical of tetragonally distorted octahedral complexes with a $d_{x^2-y^2}$ ground-state electronic configuration and CuN_2O_4 or CuN_3O_3 as chromophores.[9b] Nevertheless, the molar absorption coefficients are much higher than those for analogous *NNN'N'*-tetralkylethylenediamine complexes.[9c] This suggests that there are some contributions from the highly polarizable C=O groups.

A spectrophotometric titration with Cu^{2+} ions has produced a curve for the polymer L^2. It shows that the molar absorption coefficient and the position of the absorption maximum are constant over a wide range of copper(II) ion concentration until a ratio Cu : L of 1 : 1 is reached. This means that the above compound conforms to the Beer–Lambert law. In this respect, the poly(amido-amines) behave differently from most macromolecular ligands, whose metal complexes show spectroscopic parameters which are dependent on the concentration of the complexing ion.[21]

The e.s.r. spectra provide no evidence for exchange coupling. This demonstrates once again that the nitrogen atoms of each monomeric unit of the polymers are far enough apart to allow each complex to behave independently. At room temperature the e.s.r. spectra of the polymeric complexes are anisotropic, while the corresponding non-macromolecular ligands give an isotropic spectrum (Table 2). Table 2 shows that the values of $g_{\parallel}$ decrease as the number of co-ordinated nitrogen atoms increases from two to three. It is well known that the values of $g_{\parallel}$ fall in a fairly narrow range depending on the donor-atom set involved.[9a] Nevertheless, the $g_{\parallel}$ values are lower and the $A_{\parallel}$ values are higher than those obtained for analogous complexes in solution with di- or tri-amine as ligands.[9a] Moreover, it has been shown that *N*-alkylation usually causes an increase in $g_{\parallel}$ and a corresponding decrease in $A_{\parallel}$.[22] For some copper(II) *NN'*-dialkylethylenediamine complexes it was observed that the bulkier amines inhibit the approach of adjacent molecules and decrease the axial interaction, resulting in a stronger in-plane bonding.[23] In this case, $g_{\parallel}$ moves to lower values, and $A_{\parallel}$ to higher ones. This also happens in our case.

Copper(II) *Complexes in the Solid State.*—Solid complexes have been prepared, which correspond to the stoicheiometries reported in the Experimental section. The electronic spectra of the compounds in the solid state are practically identical to those obtained in aqueous solution (Table 2). This suggests that the conformations of the polymeric complexes are similar in solution and the solid state. It may be observed that the polymers themselves are highly regular, and in the complexes the chelated copper ions are evenly distributed along the chains. We emphasize that, to our knowledge, this is the first time that solid complexes with macromolecular ligands, having a definite stoicheiometry, have been isolated.

The shape of the electronic spectrum of the solid compound $CuL^8[NO_3]_2$ is different from that of the other complexes, although the position of the absorption maximum is altered very little. This is probably caused by the difference in nitrogen donor atoms.

Conclusions.—It has been shown that it is possible to obtain *real* stability constants for the copper(II) complexes of some poly(amido-amines). This unusual feature may be ascribed to the substantial independence of the nitrogen atoms belonging to different monomeric units (confirmed by the absence of Cu–Cu coupling in the e.s.r. spectra).

Although definite conclusions have not yet been reached, there are two possible explanations for the independence of monomeric units in the polymers: either (*i*) this independence is simply due to the large distance between nitrogens of different repeating units, irrespective of the particular structure of the polymeric chain, or (*ii*) the independence is due to the presence of a ring structure, namely a 1,4-diacylpiperazine group, between neighbouring monomeric units. In order to elucidate this point, further experiments with specially synthesised poly(amido-amines) are in progress.

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