Spectroscopic and Calorimetric Studies of the Complexing Ability of some Polyamido Polymers containing Amino-acid Residues

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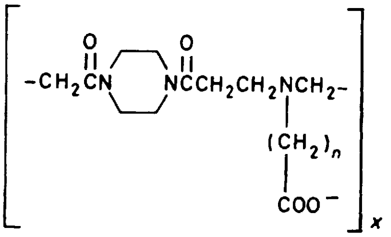
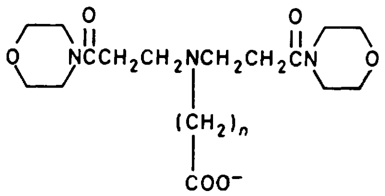
Complexes formed by two polymers L^1 (derived from glycine) and L^2 (derived from β-alanine) and their corresponding non-macromolecular models with copper(II) have been studied in aqueous solution at different pH by e.s.r. and Fourier-transform i.r. (F.t.i.r.) spectroscopy and by calorimetry at 25 °C. The e.s.r. and F.t.i.r. data reveal that L^1 forms a single complex in which co-ordination occurs through one amino nitrogen and one carboxylic group. Each copper(II) ion is co-ordinated to one repeat unit in the polymer. These findings are consistent with the $-\Delta H^\circ$ value of 30 kJ mol^{-1} which is independent of pH, and is very close to that measured for the similar complex with the non-macromolecular model. For L^2 the e.s.r. spectra show the presence of two complexes, one, involving only oxygen donor atoms, formed at low pH and the other, involving one co-ordinated nitrogen atom also, has similar parameters to the complex formed by L^1. The calorimetric data for the first complex, $[Cu(HL)]^{2+}$ (L refers to the repeating monoanionic unit of the polymer), reveal that $-\Delta H^\circ$ is independent of pH but only an approximate value can be obtained because of the small amount of this species formed. The ΔH° value for the second complex, $[CuL]^+$, is very close to that of the simple $[Cu(alaO)]^+$ [alaO = β-alaninate(1−)] complex. F.t.i.r. spectra seem to exclude the participation of the amido carbonyl oxygen to the co-ordination. The dependence of ΔS° on the degree of complex formation is attributed to the statistical entropy contribution.

In our previous papers we reported the protonation [1,2] and Cu^{II} complexing properties [2] of polymers containing amino-acid residues having the structure shown below. In the present work we wish to report spectroscopic evidence [e.s.r., Fourier-transform i.r. (F.t.i.r.), and u.v.] for the nature of the Cu^{II} complexes formed with L^1 (derived from glycine) and L^2 (derived from β-alanine), as well as the enthalpy data for the formation of these complexes.* We have also investigated the corresponding non-macromolecular models L^{1a} and L^{2a} (see below).



L^1; $n = 1$
L^2; $n = 2$



L^{1a}; $n = 1$
L^{2a}; $n = 2$

The pH measurements for the determination of the stability constants of copper(II) complexes showed that the polymer L^1 and model L^{1a} formed only one complex, $[CuL]^+$, whereas L^2 and L^{2a} formed two complexes, $[Cu(HL)]^{2+}$ at low pH, and $[CuL]^+$ at higher pH[1] (L refers to the repeating monoanionic unit of the polymer). The stability constants for the polymeric species $[CuL]^+$ are only 'apparent', *i.e.* log β decreases with pH. In the case of the protonated complex species $[Cu(HL)]^{2+}$, formed by L^2 only, the stability constant is not pH dependent.

Experimental

Preparation of L^1 *['Poly(amido-glycine)'] and* L^2 *['Poly(amido-β-alanine)'].*—These polymers were prepared by a published procedure involving reaction of 1,4-bis(acryloyl)piperazine with the appropriate amino acid in the presence of triethylamine.[1]

Preparation of L^{1a} *(from Glycine) and* L^{2a} *(from β-Alanine).*—The models were synthesized in a similar way to L^1 and L^2, starting with the appropriate amino acid and *N*-acryloylmorpholine in a 1:2 molar ratio, as previously reported.[5]

The purity of all the polymers was checked potentiometrically and calorimetrically, as previously reported.[1]

E.S.R. Measurements.—E.s.r. measurements were carried out at *X*-band frequencies using a Brucker ER-200 spectrometer.

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* Thermodynamic changes for protonation or complex formation of polymeric bases often depend on the degree of protonation or complex formation.[3] In this case the functions are described as 'apparent'; if however any of the functions is independent of the degree of protonation or complex formation then it is described as 'real'.[4]

Table 1. Heats of Cu^{II} complex formation: experimental details of the calorimetric measurements at 25 °C in 0.1 mol dm^{-3} NaCl

L^-	Reaction	pH Range	10^3T_L[a]/mol	10^3T_{Cu}[b]/mol	10^3T_H[c]/mol	C_T[d]/mol dm^{-3}	Method
L^1	$Cu^{2+} + L^- \rightleftharpoons [CuL]^+$	2.2—4.9	0.4006	0.1998	0.5504	−0.1501	Continuous
		2.5—3.5	0.2485	0.1252	0.2734	−0.1076	Incremental
		4.6—1.7	0.9953	0.5017	0.4955	0.5150	Incremental
L^2	$Cu^{2+} + L^- \rightleftharpoons [CuL]^+$	4.8—2.6	0.1290	0.0631	0.0596	0.0995	Continuous
		3.8—4.7	0.1539	0.1498	0.3031	−0.1076	Continuous
		5.1—3.5	0.2568	0.1315	0.1276	0.0995	Continuous
		5.1—3.5	0.2550	0.1300	0.1259	0.0995	Incremental
	$Cu^{2+} + L^- + H^+ \rightleftharpoons [Cu(HL)]^{2+}$	2.3—3.9	0.1498	0.0726	0.4533	−0.1076	Continuous
L^{1a}	$Cu^{2+} + L^- \rightleftharpoons [CuL]^+$	3.42—2.36	0.2482	0	0.2630	0.1009[e]	Isoperibolic
L^{2a}	$Cu^{2+} + L^- \rightleftharpoons [CuL]^+$ $Cu^{2+} + L^- + H^+ \rightleftharpoons [Cu(HL)]^{2+}$	2.70—5.46	0.1815	0.0935	0.4546	−0.1341	Isoperibolic

[a] Initial amount of ligand. [b] Initial amount of copper(II) ion. [c] Initial amount of hydrogen ion. [d] Titrant concentration (negative values indicate titrations with NaOH). [e] Copper(II) titrant solution.

Diphenylpicrylhydrazyl (dpph) was used as a field marker. Ethylene glycol was added to the aqueous solutions of Cu:ligand 1:1 molar ratio to improve glass-forming properties at low temperatures. The Basic computer programs used for the simulation of the spectra are very much modified versions of a program originally written by Venable.[6,*] All simulations were carried out either on a Digital Rainbow 100 with a 62 K memory or on an Olivetti M20 computer with a 128 K memory, both with floating point facilities.

F.T.I.R. Measurements.—Transmission i.r. spectra were recorded in the range 3 000—900 cm^{-1} on a Perkin-Elmer M 1500 F.t.i.r. spectrometer equipped with a Perkin-Elmer 3600 Data Station. The apparatus was purged with nitrogen. Typically, 250 scans at a resolution of 3.2 cm^{-1} were averaged and the spectra were stored on a microfloppy disk. The frequency scale of the instrument was internally calibrated by a reference He–Ne laser to an accuracy of ±0.01 cm^{-1}. The spectra of aqueous solutions were measured in a cell with BaF_2 windows and using a pathlength of *ca.* 13 µm.

The concentration of the polymer solutions was *ca.* 0.2 mol dm^{-3}. To a solution of L^1 an appropriate quantity of $CuCl_2 \cdot 2H_2O$ (Carlo Erba) was added to give a 1:1 copper(II):ligand molar ratio. Then the pH of the solution was adjusted by adding a small amount of a 1 mol dm^{-3} solution of HCl or NaOH. Spectra were recorded at least at two different pH values in the range where the complex species prevailed.

In the case of L^2 it was possible to obtain a 1:1 copper(II):ligand solution up to pH 3.4. In order to record F.t.-i.r. spectra at higher pH values we used solutions of 1:2 copper(II):ligand molar ratio. The strong absorption band of water at 1 640 cm^{-1} obscures some of the polymer bands. The subtraction of water from the polymer spectrum was made with the null criterion, by trying to minimize the water band.

Calorimetric Measurements.—A Tronac model 1250 Isothermal calorimeter, equipped with a 25-cm^3 stainless steel reaction vessel, was used to determine the enthalpy of Cu^{II}–polymer complex formation. Two different types of measurements in the isothermal mode were carried out, one involving continuous titration and the other incremental programmed steps using respectively the programs ISOTHERM and INCREMENTAL ISOTHERM obtained from Tronac Inc.

The same apparatus, operating in the isoperibolic mode, was used to measure the heats for the interaction of copper(II) ions with the non-macromolecular ligands L^{1a} and L^{2a}. In this case a 50-cm^3 Dewar was used as the reaction vessel and our modified version of the program ISOPER controlled the experiments.[7]

A weighed amount of polymer was dissolved in 0.1 mol dm^{-3} NaCl and a $Cu(NO_3)_2$ solution of known titre was added in order to give a 1:2 or 1:1 copper(II):ligand molar ratio. These solutions were titrated by adding either 0.1 mol dm^{-3} HCl or 0.1 mol dm^{-3} NaOH to a 25-ml basic or acidic solution, respectively, prepared at fixed pH values. A CO_2-free NaOH solution was prepared immediately before use. Stock solutions of 0.1 mol dm^{-3} NaCl were prepared from sodium chloride (Suprapur Merck) and used without further purification as the ionic medium for the calorimetric measurements. In the case of L^1 a titration using 0.5 mol dm^{-3} HCl was carried out with a 1:2 copper(II):ligand molar ratio. Even though this results in a variation in ionic strength it was necessary in order to destroy the complex $[CuL^1]^+$ which is extremely stable. A known amount of the non-macromolecular model L^{1a} was titrated with copper(II) nitrate solution until a 1:1 ratio was reached, while the acidic solution of the non-macromolecular model L^{2a} and copper(II) ions in a 2:1 molar ratio was titrated with NaOH solution.

The ΔH° values, corrected for the heats of dilution, were calculated using the program FIT previously described.[7] The ΔS° values were calculated by means of the formula $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$. Experimental details are reported in Table 1.

Results and Discussion

Spectroscopic Measurements.—The 'poly(amido–glycine)' Cu^{II}–L^1 system. At 77 K the e.s.r. spectra are typical of those of elongated tetragonal Cu^{II} species. The spectrum at pH 2 shows the presence of two species one of which has parameters corresponding to those of hydrated Cu^{II} and the other with smaller $g_{\parallel}$ and larger $A_{\parallel}$ values (see Table 2). The concentrations of the two species are approximately equal at this pH. As the pH increases the concentration of uncomplexed copper(II) rapidly decreases and beyond pH 3.5 the copper(II) appears to be entirely in the complexed form. The interpretation of the room-temperature spectra seems to be compatible with the low-temperature data.

The F.t.i.r. spectrum of the 1:1 copper complex at pH 1.8 reveals that bands at 1 737 and 1 616 cm^{-1}, assigned to the C=O stretching of the protonated carboxyl group and to the

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[*] Available on microfilm from University Microfilm Inc. Ann Arbor, Michigan, U.S.A., order no. 66—117.

Table 2. E.s.r. and electronic spectral data

L^-	Species	$g_\parallel$	$g_\perp$	$10^4 A_\parallel/\text{cm}^{-1}$	$10^4 A_\perp/\text{cm}^{-1}$	$10^{-3}\lambda_{max}/\text{cm}^{-1}$ ($\varepsilon/\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$)
—	Cu^{2+}	2.445	2.085	141.7	10.7	12.5 (3)
L^1	$[CuL]^+$	2.335	2.080	177.7	10.7	13.6 (32)
L^2	$[Cu(HL)]^{2+}$	2.395	2.080	167.7	10.7	12.7 (39)
	$[CuL]^+$	2.350	2.075	181.0	10.7	13.4 (53)
L^{2a}	$[Cu(HL)]^{2+}$	2.380	2.065	166.6	8.7	12.7 (35)
	$[CuL]^+$	2.330	2.065	171.8	8.7	13.5 (50)

stretching of the amidic C=O group[2] respectively, no longer appear in the spectrum, whereas two very strong bands appear at 1 630 and 1 582 cm^{-1} respectively (Figure 1 and Table 3). The disappearance of the band at 1 737 cm^{-1} confirms that the carboxyl group is deprotonated in the presence of the metal ion, as also occurs in the case of amino acids[8] and polypeptides.[9]

The new band at 1 582 cm^{-1} can be assigned to the asymmetric stretching of the ionized and co-ordinated carboxyl group. This value is lower than that found in the spectrum of the free ligand L^1 at high pH, as also occurs for metal(II) bis(glycine) complexes in D_2O solution.[8] The band at 1 630 cm^{-1} can be assigned to the stretching of the amidic C=O group. This frequency is higher than that found in the free ligand.[2] The shift of this band to higher frequency does not agree with a C=O group being co-ordinated to the metal ion, as happens in the case of dipeptide and tripeptide complexes.[9] The increase in frequency may be explained by considering the existence in the free ligand of an intramolecular hydrogen bond between the amidic carbonyl and the protonated nitrogen group.[5]

The *d–d* adsorption spectrum of the complex species is shifted to higher energies than that of the hydrated Cu^{II} ion (Table 2). It seems to indicate not too great a tetragonal distortion, but the shift to higher energies of the maximum suggests the presence of at least one donor atom higher than oxygen in the spectrochemical series. This is in agreement with the e.s.r. data. In fact

Table 3. F.t.i.r. frequencies (cm^{-1}) observed for Cu^{II}–L^1 and Cu^{II}–L^2 systems in aqueous solution at different pH

Cu^{II}–L^1 (1:1 molar ratio) pH 1.8	Cu^{II}–L^2 (1:2 molar ratio) pH 5.2
1 630s	1 625s
1 582vs	1 582vs
1 482w	1 482m
1 452m	1 452m
1 425vw	1 420m br
1 390br	—
1 370w	1 375m br
1 320w	1 332w br
1 288w	1 288w
1 250m	1 250s
1 230(sh)	1 230(sh)
—	1 195m
1 180br	1 170(sh)
1 120br	1 112w br
1 050(sh)	1 050(sh)
—	1 030(sh)
1 025m	1 018m
982vw	987vw

Abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, br = broad.

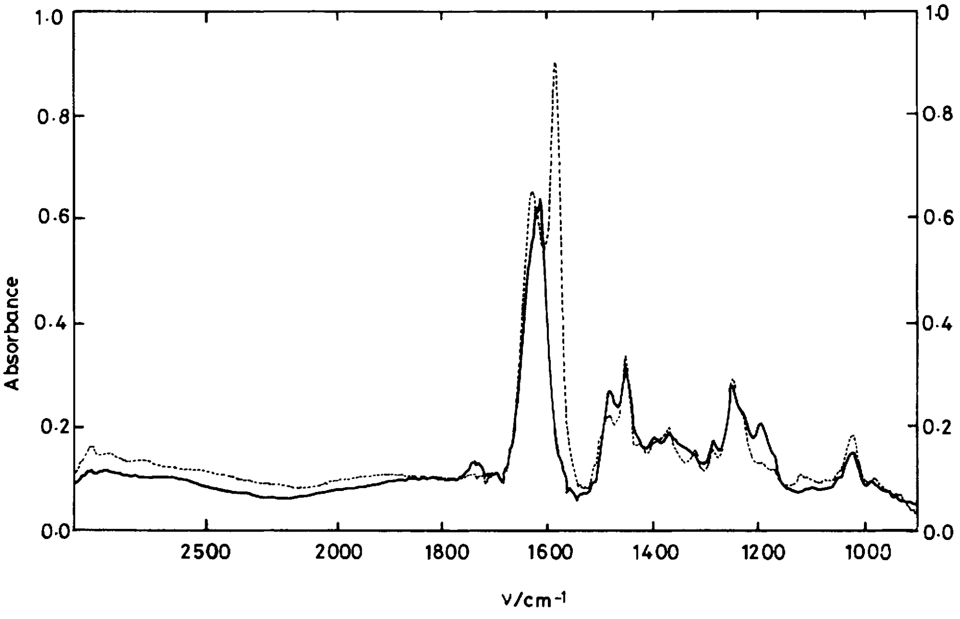

Figure 1. Difference aqueous solution spectra of the free ligand L^1 at pH 2 (——) and of $[CuL^1]^+$ at pH 1.8 (· · · ·) multiplied by a factor 3

the value of $g_{\parallel}$ 2.335 is too high for two co-ordinated nitrogen atoms ($g_{\parallel}$ 2.28)[10] and the most likely hypothesis is that only a single nitrogen atom, the tertiary nitrogen nearest to the carboxylate group, is co-ordinated. Otherwise, the e.s.r. parameters of the $[CuL^1]^+$ species are in good agreement with those obtained for $[Cu(glyO)]^+$ [glyO = glycinate(1−)] in aqueous solution in the vitreous state.[11] The higher value of $A_{\parallel}$ is compatible with an increased field in the equatorial plane.

The 'poly(amido-β-alanine)' Cu^{II}–L^2 system. The low-temperature (77 K) e.s.r. spectrum at pH 2 is that of a single species, hydrated Cu^{II}. However as the pH increases bands indicative of the presence of a new species with smaller $g_{\parallel}$ and larger $A_{\parallel}$ values begin to appear in the parallel (low-field) part of the spectrum. By pH 4 a third species which has similar parameters, though not absolutely identical, to those of the complex species formed by the polymer L^1, is present. At pH 4.5 the concentration of hydrated Cu^{II} is only about half that of each of the two complexes present in roughly equal concentrations (Figure 2). The room-temperature spectra confirm this interpretation.

The *d–d* absorption spectrum of the first complex species (Table 2) is slightly shifted to higher energies in comparison to that of the hydrated Cu^{II} ion, but it is very similar to that observed for the complex [Cu(mal)] [mal = malonate(2−)] which contains a CuO'_2O_2 chromophore (O′ is a carboxylate oxygen) having a $d_{x^2-y^2}$ ground state.[12] The e.s.r. parameters are slightly higher than those of [Cu(mal)].[12] At pH 3.4 and a 1:1 ligand:copper molar ratio, the F.t.i.r. spectrum is quite similar to that of the free ligand, even though at this pH the polymer is present in solution as $[Cu(HL^2)]^{2+}$ but in a very low percentage.[1]

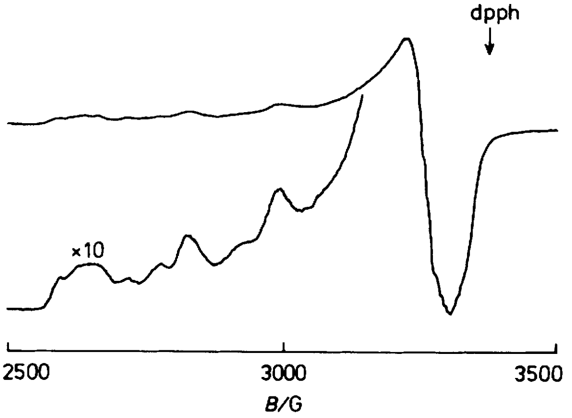

Figure 2. E.s.r. spectrum of a 2:1 L^2:Cu^{II} aqueous solution at 77 K and pH 4.5

The best hypothesis that explains these data is that polymer L^2 co-ordinates to the Cu^{II} ion *via* the negatively charged oxygen of the carboxylate group and one or possibly two amido carbonyl oxygens. The remaining co-ordination positions are almost certainly occupied by water molecules.

For the second complex species the *d–d* and the F.t.i.r. absorption spectra (Tables 2 and 3) are similar to that observed for $[CuL^1]^+$ and taken in conjunction with the e.s.r. parameters this is compatible with the hypothesis of a six-co-ordinate tetragonal complex involving co-ordination of L^2 *via* one nitrogen and one carboxylate oxygen.[10] It seems likely that initially the tertiary nitrogen is protonated and therefore cannot co-ordinate to Cu^{II} while, as the pH rises, deprotonation of this nitrogen leaves it free to bind to the metal. Thus, in the pH range 4—5 there is an equilibrium involving two complex species which may be indicated as $[Cu(HL^2)]^{2+}$ and $[CuL^2]^+$. The slightly higher ε value for $[CuL^2]^+$, compared to that for the corresponding complex $[CuL^1]^+$, can be attributed to the fact that with the β-alanine residue, a six-membered rather than a five-membered chelate ring is formed which results in a more distorted structure. As is well known more distorted species tend to have higher values of ε, presumably because of orbital mixing caused by lower symmetry fields.

We have also recorded the e.s.r. spectra of the non-macromolecular model compound L^{2a} (see Table 2) and the parameters of both $[CuL^{2a}]^+$ and $[Cu(HL^{2a})]^{2+}$ species are very similar to those of the corresponding L^2 spectra. The small differences which are observed can be attributed to the greater flexibility of the monomer. The *d–d* spectra of the two model complexes are virtually identical to those of the corresponding polymer complexes.

Thermodynamics.—Enthalpy changes. The calorimetric results are summarized in Table 4 for the copper(II) complexes. The $\Delta S^{\ominus}$ values were calculated by taking into account the monotonic dependence of $-\Delta G^{\ominus}$ on pH as reported previously[1] because the behaviour of the enthalpic changes is 'real'. In fact the $-\Delta H^{\ominus}$ values do not vary in the overall pH range investigated.

In the case of the interaction between the polymer L^1 and the copper(II) ion only a single complex species $[CuL^1]^+$ is formed. The $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ values found are in good agreement with the thermodynamic functions obtained for the analogous complex with the non-macromolecular model L^{1a}, indicating that co-ordination of Cu^{II} occurs to each single monomeric unit of the polymer. The $-\Delta H^{\ominus}$ value is slightly higher than that of $[Cu(glyO)]^+$ in which co-ordination to the copper(II)

Table 4. Thermodynamic functions of copper(II) complexes at 25 °C in 0.1 mol dm^{-3} NaCl

L^-	Reaction	α Range[a]	$-\Delta G^{\ominus\, b}$/kJ mol^{-1}	$-\Delta H^{\ominus\, b}$/kJ mol^{-1}	$\Delta S^{\ominus\, b}$/J K^{-1} mol^{-1}
L^1	$Cu^{2+} + L^- \rightleftharpoons [CuL]^+$	0.45—0.85	51.5—47.3	30(2)	72—58
L^2	$Cu^{2+} + L^- \rightleftharpoons [CuL]^+$	0.18—0.88	37.2—33.1	16(2)	71—58
	$Cu^{2+} + L^- + H^+ \rightleftharpoons [Cu(HL)]^{2+}$		60	50[c]	33[c]
	$Cu^{2+} + HL \rightleftharpoons [Cu(HL)]^{2+}$		11.3	13[c]	−6[c]
L^{1a}	$Cu^{2+} + L^- \rightleftharpoons [CuL]^+$		57.0(1)	30.0(2)	90(4)
L^{2a}	$Cu^{2+} + L^- \rightleftharpoons [CuL]^+$		34.5(3)	17(2)	58(4)
	$Cu^{2+} + L^- + H^+ \rightleftharpoons [Cu(HL)]^{2+}$		61.5	50[c]	38[c]
	$Cu^{2+} + HL \rightleftharpoons [Cu(HL)]^{2+}$		14.6	13[c]	6[c]

[a] $\alpha = [CuL^+]/[Cu]_{total}$ = degree of complex formation. [b] Values in parentheses are standard deviations. [c] Value determined with low complex concentration.

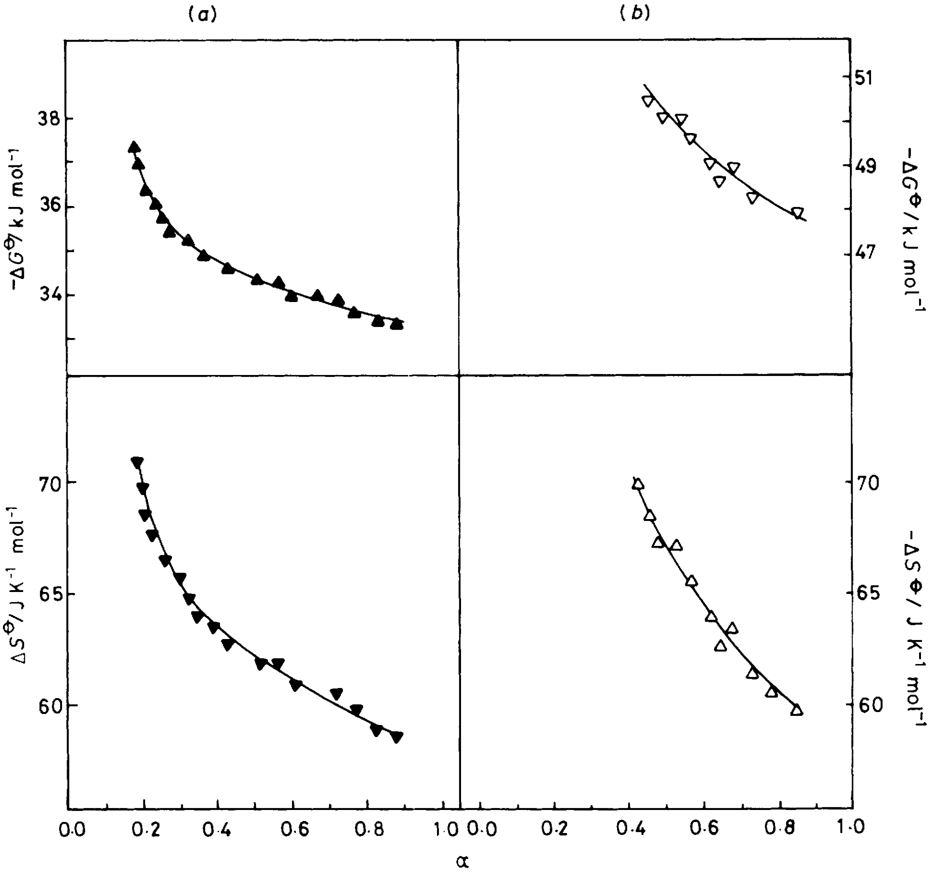

Figure 3. Dependence of the thermodynamic functions at 25 °C in 0.1 mol dm^{-3} NaCl on the degree of copper(II) complex formation α for (*a*) the L^2–Cu^{II} system (2:1 molar ratio), and (*b*) the L^1–Cu^{II} system (1:1 molar ratio)

ion is *via* a primary nitrogen atom and a carboxylate group.[13] By considering that co-ordination of a tertiary nitrogen to a metal ion is generally less exothermic than that of a primary nitrogen, a comparison of the enthalpy changes of $[CuL^1]^+$ and $[Cu(glyO)]^+$ induces us to suppose a structure with the participation of other complexing groups, *i.e.* the amidic carbonyl oxygens, for $[CuL^1]^+$. However two facts are contrary to this hypothesis: the e.s.r. and F.t.i.r. data (see above), and the difficulty of involving the carbonyl groups in the complex if the ligand moiety lies pendant to the main chain of the polymer.[7]

The Cu^{II}–L^2 system seems to behave very differently to the simple copper(II)–β-alanine complex. In fact two complex species are detected in aqueous medium at different pH ranges. At very low pH values a protonated species, $[Cu(HL^2)]^{2+}$, is formed in which co-ordination occurs through the carboxylate group and probably one or both of the adjacent carbonyl groups of the monomeric unit. This species has been detected by e.s.r. measurements (see above) but other authors postulated its existence from pH titration data in solution containing copper(II) ion and glycine[14] or its C-substituted derivatives.[15] Only an approximate $-\Delta H^{\ominus}$ value of the order of 50 kJ mol^{-1} can be determined for this species because of the fact that it is only ever present in relatively small amounts (a maximum of *ca.* 20% with respect to the total amount of polymer present). The $[Cu(HL)]^{2+}$ species is also present with the corresponding non-macromolecular ligand L^{2a} and shows similar thermodynamic parameters. The similarity of results obtained with the two different ligands indicates that the co-ordination of copper(II) is entirely satisfied by employing single monomeric units even if only oxygen groups are involved. However, taking into account essentially electrostatic interactions such as those involving carboxylate groups, endothermic heat changes are to be expected, therefore the anomalous exothermic enthalpy change obtained for the reaction $Cu^{2+} + HL \rightleftharpoons [Cu(HL)]^{2+}$ might be explained by invoking also the co-ordination of one or two amido carbonyl oxygens to Cu^{II}.

At higher pH a new species appears in which the Cu^{II} ion is co-ordinated to the basic nitrogen. The $-\Delta H^{\ominus}$ value for this species is much lower than that observed for $[CuL^1]^+$, but very similar to that for the simple $[Cu(alaO)]^+$ [alaO = alaninate(1−)] complex in which co-ordination clearly occurs through the carboxylate group and a basic nitrogen.[16]

Entropy changes. The $\Delta S^{\ominus}$ values are reported in Figure 3 together with the $-\Delta G^{\ominus}$ values. From the Figure it appears that the trend of $-\Delta G^{\ominus}$ *vs.* α only depends on the entropy factor. $\Delta S^{\ominus}$ Values decrease with α, *i.e.* as the complex formation proceeds the entropy term diminishes. This dependence cannot be attributed to conformational variations of the polymer during complex formation, because no variation in viscosity is observed by adding Cu^{2+} to L^1 or L^2.[1] Besides, interaction between nearest neighbour sites is very low in these polymers as can be deduced by the equality in the $\Delta H^{\ominus}$ values of model and polymer in the complex formation reaction. However we must recognize that all the co-ordinating sites cannot exhibit the same behaviour, in fact a $>N\text{–}COO^-$ group surrounded by other negatively charged groups will attract Cu^{2+} ions more strongly than one which is surrounded by already co-ordinated positive groups. This fact affects not only the energy but also the entropy of complex formation of the polyion. When Cu^{2+} ions are added to the polymer, they will

Table 5. Thermodynamic quantities (S_{st} = statistical entropy term) relative to Cu^{II}–L^2 and Cu^{II}–L^{2a} systems for the reaction $[CuX]^{2+} + Y^- \rightleftharpoons [CuY]^+ + X^-$ ($X = L^{2a}$, $Y = L^2$)

$\Delta \log \beta$	$-\Delta G^\circ$/ kJ mol^{-1}	$-\Delta H^\circ$/ kJ mol^{-1}	TS_{st}°/ kJ mol^{-1}	S_{st}°/ J K^{-1} mol^{-1}
0.65	3.72	0	3.72	12.5
0.45	2.55	0	2.55	8.6
0.31	1.76	0	1.76	5.9
0.22	1.26	0	1.26	4.2
0.06	0.33	0	0.33	1.1
0.01	0.04	0	0.04	0.1
−0.02	−0.13	0	−0.13	−0.4
−0.10	−0.59	0	−0.59	−2.0
−0.13	−0.75	0	−0.75	−2.5
−0.20	−1.13	0	−1.13	−3.8
−0.40	−2.30	0	−2.30	−7.7
−0.49	−2.80	0	−2.80	−9.4
−0.73	−4.18	0	−4.18	−14.0

seek out some co-ordinating sites in preference to others, but without interfering with the co-ordination bond (ΔH°). From a statistical standpoint a remarkable decrease of the entropy value at low α values has to be expected.[17]

At this point it is interesting to consider the reaction $[CuX]^+ + Y^- \rightleftharpoons [CuY]^+ + X^-$ in which the two molecules X^- and Y^- carry identical ligand groups and differ from each other solely by the position of the charge situated on the polymer.

Thus no cratic or translational entropy terms have to be taken into consideration (no variation in the number of species). On reaction the free energy changes depend only on the energy needed to bring the Cu^{2+} ion into the additional field of the charge situated on the polymer. This electrostatic energy[18] can be obtained from equation (1) and is given by equation (2). For

$$\Delta(\log \beta) = \log \beta_{[CuY]^+} - \log \beta_{[CuX]^+} \quad (1)$$

$$\Delta G = -2.305RT\Delta(\log \beta) = -A_{el} - TS_{st} \quad (2)$$

the enthalpy and entropy changes[18] of the process we obtain equations (3) and (4) ($\varepsilon_{eff.}$ = effective dielectric constant). The last term in equation (4) merely takes care of the circumstance

$$\Delta H = -A_{el}\left[1 + \frac{T}{\varepsilon_{eff.}}\frac{\delta\varepsilon_{eff.}}{\delta T}\right] \quad (3)$$

$$\Delta S = -A_{el}\left[\frac{1}{\varepsilon_{eff.}}\frac{\delta\varepsilon_{eff.}}{\delta T}\right] + S_{st} \quad (4)$$

that Cu^{2+} can add to the several and different co-ordinating sites of the polymer.

A combination of the data of Table 4 furnishes the thermodynamic quantities relative to the transfer reaction (Table 5). The enthalpy contribution is zero showing that A_{el}, the electrostatic energy lost by removing to infinity the charge of the cation from the negative charge situated on the neighbouring repeating unit of the polyion, is zero. The entropy term obtained from equation (2) decreases from positive to negative values with the increase in the number of Cu^{2+} ions brought to the polymer. It reaches zero when we have matched half of the negative charges on the polymer with Cu^{2+} ions, *i.e.* we obtain a polymer with the same quantity of negative and positive charges. At this point further addition of Cu^{2+} leads to a situation with a prevailing number of positive charges on the polyion which causes the reverse reaction to occur.

Acknowledgements

This work was supported by the Italian Ministry of Education. We thank Dr. Claudia Zanchini (University of Florence) for recording the e.s.r. spectra.

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Received 3rd *October* 1985; *Paper* 5/1716