Copper(II) complex properties of a basic polymer containing SO₂ groups in the main chain

Rolando Barbucci, Mario Casolaro, Silvia Corezzi and Gianna Reginato

Dipartimento di Chimica, Università di Siena, Piano dei Mantellini 44, 53100 Siena, Italy
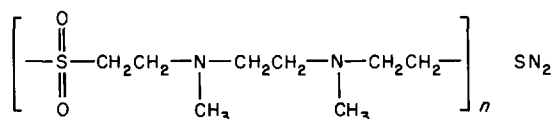
Cu(II) complexes of an aminic polymer containing sulphone have been studied at 25°C in aqueous solution at different pH's by potentiometric, calorimetric, visible and e.p.r. spectroscopic techniques. The potentiometric and spectroscopic data reveal the presence of two different complexes: the first CuL^{2+} (L refers to the repeating unit of the polymer) presents a 'sharp' stability constant. This indicates that $\log \beta$ is unaffected by pH at different polymer/Cu(II) molar ratios. This species reaches a maximum concentration of 30% with respect to the ligand. From e.p.r. measurements, spectrophotometric and calorimetric data we can hypothesize the coordination of one nitrogen and one oxygen probably belonging to the sulphone. The second is a dihydroxo complex $Cu(OH)_2L$ whose stability constant is 'apparent' and decreases with increasing pH, while ΔH^0 is 'sharp'. E.p.r. and visible spectroscopic parameters are reported and the thermodynamic data are discussed.

INTRODUCTION

We have recently studied the basicity and complexing ability in aqueous solution of a new class of polymers having a poly(amido–amino) structure and bearing carboxyl groups as side substituents[1]. These polymers, unlike the poly(amido–amine)s studied previously[2], show both 'apparent' basicity and stability constants towards the Cu(II) ion. The dependence of $\log \beta$ *versus* pH was evaluated by a new method of calculation which permits determination of the value of the stability constant at each titration point, by also taking into account the dependence of the basicity constant vs. pH[1].

The aim of this paper is to widen and deepen the study of complex formation of polyelectrolytes, by reporting the results of the coordinating ability of a polymer carrying sulphone between the amine moiety of the repeating units and having the following structure:

$$\left[-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}} - CH_2CH_2 - \underset{\underset{CH_3}{|}}{N} - CH_2CH_2 - \underset{\underset{CH_3}{|}}{N} - CH_2CH_2 - \right]_n \quad SN_2$$

The sulphone ensures a greater flexibility of the polymeric chain than the bis acryloyl-piperazine ring present in the poly(amido–amine)s and consequently, a pronounced cooperation between different monomeric units and the occurrence of 'apparent' protonation constants, as has been reported in a previous paper[3].

We thought it of some interest to investigate the role of the chain flexibility in the complex formation behaviour towards the Cu(II) ion and the trend of the stability constant *versus* pH, in order to achieve further testing of the polymer stability constant evaluation method proposed by these authors. This study was performed from the thermodynamic (potentiometric and calorimetric) and spectroscopic (visible and e.p.r.) viewpoint.

EXPERIMENTAL

Synthesis

The polymer SN₂ was prepared following a published procedure[3] involving *N,N'*-dimethylethylenediamine and divinylsulphone in aqueous solution in a 1:1 stoichiometric ratio. The polymer was converted to the dihydrochloride compound and the purity checked by potentiometric and calorimetric measurements. The purity was 88%, corresponding to a structure comprising two water molecules for each monomeric unit.

Potentiometric measurements

Potentiometric measurements were performed according to a previously described procedure[4], using a Digital PHM-84 Radiometer potentiometer, an Ag/AgCl reference electrode, an Orion 910100 glass electrode and a salt bridge containing a 0.1 M NaCl solution. The potentiometric and titration apparatus is automatically governed by an Olivetti M 20 minicomputer. All titrations were carried out in a constant temperature cell at 25°C. Presaturated nitrogen was maintained over the surface of the cell to prevent carbon dioxide adsorption. Stability constants for the Cu(II) complexes were determined by adding NaOH 0.1 M to an acidic solution containing 1:1, 1:2 and 1:3 molar ratios of copper nitrate to polymer hydrochloride. All the polymer hydrochloride solutions were prepared immediately before use. E^0 calibrations were performed before and after each titration. The concentration of hydrogen ions was calculated from the e.m.f. values (in mV) employing the formula $[H^+] = \exp(E - E^0)/25.693$. The stability constants were computed for each titration point by the program SUPERFIT as previously described[1] and operating on a Rainbow PC100 minicomputer purchased from Digital Eq. In *Table 1* the experimental conditions of the potentiometric measurements are reported.

Table 1 Experimental details of the potentiometric measurements at 25°C in 0.1 M NaCl

Reaction	Maximum % of complex species formed	pH range	$\log \beta$	T_L (mmol)	T_M (mmol)	T_{H^+} (mmol)	C_{OH^-} (mol dm⁻³)	Points
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	29.8	3.72–4.87	3.72					
	25.9	3.77–5.03	3.73					
	21.4	3.89–5.04	3.95					
		mean value	3.8 (1)	0.2214	0.2203	0.7605	0.1274	23
				0.2240	0.1247	0.7657	0.1274	20
				0.2420	0.0835	0.8017	0.1274	26
$Cu^{2+} + L + 2OH^- \rightleftharpoons Cu(OH)_2L$	61.0	5.50–6.70	20.3–18.3					
	37.2	5.57–6.83	20.0–17.9					
	23.9	5.50–6.71	20.1–18.2					

E.p.r. measurements

E.p.r. measurements were carried out at X-band frequencies using a Brucker ER-200 spectrometer. DPPH was used as the field marker. Ethylene glycol was added to the aqueous solution to improve the glass forming properties at low temperatures. The Basic computer programs used for the simulation of the spectra are a very much modified version of a program originally written by Venable[5]. All simulations were carried out either on a Digital Rainbow PC100 or on an Olivetti M20 both with floating point facilities.

Calorimetric measurements

Calorimetric measurements were performed according to a previously described procedure[6] using a Tronac Model 1250 calorimeter. To determine the enthalpies of complex formation, isothermal calorimetric titrations were performed in a 25 ml reaction vessel. These titrations were performed by adding the titrant solution, either NaOH or $Cu(NO_3)_2$ to a solution of polymer hydrochloride containing Cu(II) or a solution of polymer only, respectively (*Table 2*). The titre was delivered through a Gilmont buret driven by a synchronous motor. For the determination of the enthalpy change relative to the CuL^{2+} complex, the incremental method was used. A solution of the free polymer was titrated with Cu(II) solution over a pH range where the maximum is the formation of the complex, as obtained by the potentiometric curve computation with a single step being used. The final amount of Cu(II) solution added corresponded to a 1 to 3 molar ratio of polymer to copper(II) nitrate. The initial and final pH's were determined by pH meter measurements and compared with those computed by simulating the titration in the same analytical conditions and introducing the stability and basicity constants obtained for the polymer. The agreement between observed pH's and calculated pH's was always better than 0.08 pH units. The enthalpies were obtained by the program FIT previously described[7] which takes into account the variation of the equilibrium constants *versus* pH (*Table 2*).

For the determination of the enthalpy change relative to the $Cu(OH)_2L$ species an isothermal continuous titration was used, either by titrating a solution of the free polymer with Cu(II) solution or by titrating a solution of the polymer hydrochloride containing known amounts of Cu(II) and H^+, with NaOH. Potentiometric measurements on the same aliquot of solution being titrated calorimetrically, were carried out in parallel.

Each amount of the titrant added in the potentiometric measurements coincided with the equal quantity (0.02 ml) of titrant added in the calorimetric measurement. The recorded heat of reaction corresponded to that quantity of titrant added. In this way a perfect correspondence in all the points of the calorimetric and potentiometric curves was obtained. The observed pH's were always in good agreement with the calculated pH's (< 0.08). For each point on the thermometric curve, one ΔH^0 relative to the $Cu(OH)_2L$ complex species was calculated, as described previously[6]. The enthalpy changes reported in *Table 2* are the average values obtained from all the points of the calorimetric curve.

Spectrophotometric measurements

The electronic spectra were recorded at 25°C on a Perkin Elmer 320 spectrophotomer using 1 cm silica cells. To a 5×10^{-3} M aqueous 0.1 M NaCl solution of the hydrochloride $-SN_2-$ polymer, was added a 0.1 M $Cu(NO_3)_2$ solution to obtain a copper(II)/polymer molar ratio of 1:1, 1:2 or 1:3, respectively. The titrations were carried out with 0.1 M NaOH. The electronic parameters for the CuL^{2+} species were calculated by means of the species distribution given by the program FIT described previously[7]. In a similar way, the parameters for the dihydroxo complex species were computed by subtracting the absorption due to Cu^{2+} and CuL^{2+} species. In *Table 3* the electronic parameters of the limiting spectrum for CuL^{2+} and $Cu(OH)_2L$ species are reported.

RESULTS AND DISCUSSION

Spectroscopic data

The 'd-d' absorption spectra and e.p.r. spectra were recorded at several pH values. For pH values lower than 3.7 the presence of the Cu(II) is only observed, then the λ_{max} shifts at a lower value. By varying the pH, an isosbestic point occurs at $\lambda_{max} = 760$ nm which indicates an equilibrium between two different complex species, one with λ_{max} at 709 and the other at 610 nm. The e.p.r. spectra confirm the presence of only two different complexes, whose parameters were well characterized at two different pH's (*Table 3*). Both the e.p.r. spectra can be fitted using an axial spin Hamiltonian although it should be borne in mind that very small anisotropies of the $g_{\parallel}$ values in the xy plane are almost impossible to detect experimentally in solution. Both the species examined in the present work are thought to be tetragonally distorted

Table 2 Experimental details of calorimetric measurements at 25°C in 0.1 M NaCl

Reaction	Titrant conc. C_{OH^-} (mol dm⁻³)	$C_{Cu^{2+}}$ (mol dm⁻³)	T_L (mmol)	T_M (mmol)	T_{H^+} (mmol)	Buret rate (ml min⁻¹)	$\Delta V = V_i - V_0$ (ml)	pH range	L/Cu(II) ratio	$-\Delta H^{a,b}$ (Kcal mol⁻¹)	Method	Points
Cu²⁺ + L ⇌ CuL²⁺		0.4958	0.2493	0.0	0.2086	0.3336	0.167	5.70–4.05	1	3.5	Incremental	1
		0.4958	0.2497	0.0	0.2094	0.3336	0.250	5.88–4.69	2	3.4	Incremental	1
		0.4958	0.2503	0.0	0.1816	0.3336	0.250	5.59–4.28	2	3.6	Incremental	1
		0.4958	0.2500	0.0	0.1999	0.3336	0.500	5.59–4.53	3	3.3	Incremental	1
										mean value 3.4 (1)		
Cu²⁺ + L + 2OH⁻ ⇌ Cu(OH)₂L	0.1274	0.1521	0.1607	0.1535	−0.0029	0.0833	2.50	5.50–6.73	1	20.4(5)	Continuous	25
	0.1268		0.1638	0.0805	0.0410	0.0833	2.50	5.63–6.64	2	20.5(4)	Continuous	8
			0.2573	0.0266	0.0360	0.0833	2.50	6.85–5.53	1	20.7(6)	Continuous	10
										mean value 20.5 (5)		

ᵃ All values are corrected for heats of dilution
ᵇ Values in parentheses are standard deviations

Table 3 E.p.r. and electronic spectral data

Species	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}{}^a$	$A_{\perp}{}^a$	Electronic absorption (kK)
CuL²⁺	2.360	2.090	158.2	14.3	14.1 ($\varepsilon = 36$)ᵇ
Cu(OH)₂L	2.270	2.060	177.0	24.0	16.4 ($\varepsilon = 48$)ᵇ

ᵃ In units of $10^{-4}\,\mathrm{cm^{-1}}$
ᵇ In units of $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$

octahedral geometry species in solution, the ground state is normally $d_{x^2-y^2}$ or more rarely d_{xy}.

The e.p.r. and spectrophotometric parameters of the first species are similar to those of other complexes in which coordination occurs through one basic amino nitrogen and one oxygen atom[8]. This leads to the hypothesis of a six coordinate tetragonal complex in which two coordination sites are occupied, one by a nitrogen atom and the other by an oxygen atom belonging to the sulphone of the polymer, with the formation of a six membered chelate ring, being the remaining coordination sites occupied by water molecules. Recently the coordinating ability of sulphone was studied in N-substituted sulphonamide copper(II) complexes[9], both in the solid state and in solution. It appears that an oxygen atom, even though belonging to sulphonamide group generally occupies axial coordination sites forming polymeric structures which are destroyed in solution. At pH = 6.5 a second copper(II) complex is present with smaller $g_{\parallel}$ and larger $A_{\parallel}$ than the first complex. All the spectroscopic parameters are indicative of a copper(II) complex with at least two basic nitrogens involved in the coordination of a five membered chelate ring[8].

If we compare the e.p.r. parameters of the second complex with those of other tetragonally distorted octahedral Cu(II) complexes containing two tertiary nitrogen atoms and 4 water molecules in the coordination sphere[8], we note a longer $g_{\parallel}$ and a higher $A_{\parallel}$ value. In addition, the maximum of the electronic absorption spectrum is shifted to a higher energy. All this can be interpreted in terms of increased equatorial bonding presumably resulting from a substitution of OH₂ for OH⁻ as the donor atom (see below).

Stability constants

From the e.p.r. and visible spectra, the pH range in which only one complex species is predominant in solution, was determined (*Table 1*). In the first pH range (3.7 < pH < 5.0) different stoichiometries were tested in the computation of the stability constant. As indicated by the spectroscopic data, the first complex species involves only one nitrogen atom and one oxygen of the repeating unit of the polymeric chain, thus the complexes CuHL, Cu₂L, CuL were considered possible. The first, CuHL, was ruled out because the refinement of the stability constant is possible only by decreasing the concentration of this species by increasing pH, to the contrary of that resulting from the e.p.r. and visible spectra. The second, Cu₂L, was not considered because no concordance between pH (observed) and pH (calculated) is possible. In the case of CuL, $\log \beta$ remains constant in the pH range considered and by varying the polymer/Cu(II) molar ratio. Its value ($\log \beta = 3.8$) is in good agreement with the value found in the case of Cu-triethanolamine ($\log \beta = 3.9$)[10] and Cu-tris(hydroxymethyl)methylamine

$(\log \beta = 4.09)^{11}$ where coordination occurs through the nitrogen atom and one alcoholic group.

At pH > 5 the value of $\log \beta$ for the CuL suddenly increases and no concordance in the $\log \beta$ value occurs on changing the polymer/Cu(II) molar ratio, at the same time the visible spectra shows a shift in the λ_{max} value (*Table 3*). All that means that another complex species begins to form in solution. Thus from pH = 5 the titration curves were analysed by taking into account the presence of a second complex. The pH range is typical of hydroxo complexes, therefore similar species were taken into account during the computation of the stability constant. Assuming the $Cu(OH)_2L$ species as complex species, the stability constant permits a fair accord between observed pH's and calculated pH's. Log β decreases with increasing pH (*Figure 1*) but remains unaltered for different polymer/Cu(II) ratios. Similar behaviour was found in the case of CuL$^+$ complexes with polymeric amido–amino acids, but the variations of $\log \beta$'s vs. pH were somewhat reduced[1]. However, we have to remember also that the basicity constants of SN_2^3 are more sensitive to pH than those of polymeric amido-amino acids. The value of the 'apparent' stability constant is decidedly higher than that found for complexes such as $Cu(OH)_2L$ where L in this case is N,N-dimethylethylenediamine or tetramethylethylenediamine[12], but close to the stability constant obtained for the analogue di-hydroxo complex with N,N'-dihydroxoethyl ethylenediamine $(\log \beta = 21.2)$ [13].

Enthalpy and entropy changes

For the CuL^{2+} complex the enthalpy value is close to that found for the corresponding complex with tris(hydroxymethyl)methylamine, (THAM)[14], confirm-
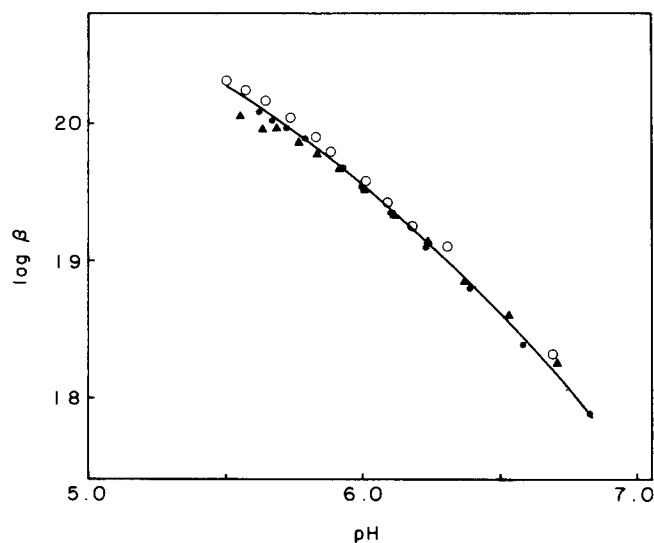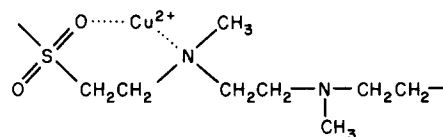
ing the formation of a six membered chelate ring in the complex through the oxygen of the sulphone and the nearer nitrogen. Also the entropy of this complex is similar to that of Cu(THAM)$^{2+}$ (5.5 cal mol^{-1} K^{-1}).[14] Therefore the $Cu(SN_2)^{2+}$ complex can be represented as

As regards the $Cu(OH)_2L$ complex, while the stability constant is 'apparent', the ΔH^0 value is constant *versus* pH. All this means that the variation in $\log \beta$ vs. pH depends only on entropy effects.

The heat of hydrolisis relative to the $Cu(OH)_2L$ complex is markedly larger than the heats of hydrolysis of analogous complexes having two nitrogen atoms in the coordination sphere, such as $Cu(OH)_2$dimeen[15], $Cu(OH)_2$adimeen[15], $Cu(OH)_2$tmen[12] and $Cu(OH)_2$Etolen[16] (dimeen = N,N'-dimethylethylenediamine, adimeen = N,N-dimethylethylenediamine, tmen = N,N,N',N'-tetramethylethylenediamine, Etolen = N-(2-hydroxyethyl)ethylenediamine).

Therefore, we can hypothesize that the reaction $CuL^{2+} + 2OH^- $ leads to the formation of a complex containing two nitrogens and two hydroxyde ions. The enthalpy contribution from the further coordination of a second nitrogen to $Cu(SN_2)^{2+}$, which occurs during the hydrolisis reaction, makes the high ΔH^0 value clear. Indeed, if we consider the overall reaction $Cu^{2+} + L + 2OH^- \rightleftharpoons Cu(OH)_2L$, the thermodynamic functions shift closer to those of dihydroxo complexes of N-substituted ethylenediamine[15] (*Table 4*). At this point the decrease in ΔS^0 on pH can be explained as being due to a cooperative effect among the hydration shells of the repeating units, which determines a lower liberation of water molecules as the complex formation process proceeds. This effect was noted also in other Cu^{2+} complexes with polymers as ligands[6].

CONCLUSIONS

This work represents a further positive test of the method proposed by us for the calculation of stability constants. The decrease of the stability constant vs. pH of the two polymeric amido–amino acid–Cu(II) complexes is confirmed by the trend observed with SN_2 as the ligand with the drop in the stability constant being greater in the latter case.

It is worthwhile mentioning that this trend of $\log \beta$ vs. pH occurs for a complex formation reaction in which a charge neutralization takes place. In addition it seems that a reaction with a full neutralization of charges, such as $CuL^{2+} + 2OH^- \rightleftharpoons Cu(OH)_2L$ provokes a more marked drop than that observed for reactions with a

Figure 1 Variation of the $Cu(OH)_2L$ stability constant $(Cu^{2+} + L + 2OH^- \rightleftharpoons Cu(OH)_2L)$ vs. pH at different ($\bigcirc$, 1/1; *, 2/1; ▲, 3/1) polymer/Cu(II) molar ratios

Table 4 Thermodynamic functions of copper(II) complexes at 25°C in 0.1 M NaCl

Reaction	$\log \beta$	$-\Delta G^0$ (Kcal mol^{-1})	$-\Delta H^0$ (Kcal mol^{-1})	ΔS^0 (cal mol^{-1} K^{-1})
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	3.8 (1)	5.2 (1)	3.4 (1)	6.0 (1)
$\{Cu^{2+} + L + 2OH^- \rightleftharpoons Cu(OH)_2L$	20.2–18.3	27.5–25.0	20.5(5)	23.5–15.0
$\{CuL^{2+} + 2OH^- \rightleftharpoons Cu(OH)_2L$	16.4–14.5	22.4–19.8	17.1(5)	17.6–9.1

partial neutralization, such as $Cu^{2+} + L^- \rightleftharpoons CuL^+$. In complex formation reactions, in which no charge neutralization occurs, the stability constant is independent of pH as in $Cu^{2+} + L \rightleftharpoons CuL^{2+}$. Moreover, the enthalpy changes determined for Cu^{2+}–polymer complexes studied up to now, do not show any dependence on pH, even in cases where the corresponding stability constants largely depend on pH. This means that only the entropy term is responsible for the stability constant variation vs. pH and that no change in the structure or bonds occurs in the complex formation reaction.

ACKNOWLEDGEMENTS

REFERENCES

1   Barbucci, R., Casolaro, M., Nocentini, M., Corezzi, S., Barone, V. and Ferruti, P. *Macromolecules* 1986, **19**, 37
2   Ferruti, P. and Barbucci, R. *Adv. Polym. Sci.* 1984, **58**, 55
3   Barbucci, R., Casolaro, M., Danzo, N., Barone, V., Ferruti, P. and Angeloni, A. *Macromolecules* 1983, **16**, 456
4   Barbucci, R., Casolaro, M., Ferruti, P., Barone, V., Lelj, F. and Oliva, L. *Macromolecules* 1981, **14**, 1203
5   Venable, J. H. *Ph.D. Thesis*, Yale University, 1965, available on microfilm from University Microfilm Inc. Ann Arbor, Michigan, USA, Order n.66–1170
6   Barbucci, R., Campbell, M. J. M., Casolaro, M., Nocentini, M., Reginato, G. and Ferruti, P. *J. Chem. Soc. Dalton* 1986 (in press)
7   Barbucci, R., Casolaro, M., Barone, V., Ferruti, P. and Tramontini, M. *Macromolecules* 1983, **16**, 1159
8   Barbucci, R. and Campbell, M. J. M. *Inorg. Chim. Acta* 1976, **113**, 16
9   Antolini, L., Menabue, L., Pellecani, G., Gaviole, G. B., Grandi, G., Battaglia, L., Corradi, A. B. and Marcotrigiano, G. *J. Chem. Soc. Dalton Trans.* 1984, 1687; Chandhuri, S. *ibid.* 1984, 779
10   Bjerrum, S. *Refn. Nordi. Kemi. Lund.* 1947, 277
11   Bologni, L., Sabatini, A. and Vacca, A. *Inorg. Chim. Acta* 1983, **69**, 71
12   Arenare, E., Paoletti, P., Dei, A. and Vacca, A. *J. Chem. Soc. Dalton* 1972, 736
13   Hall, J. L., Joseph, E. and Gum, M. B. *J. Electroanal. Chem.* 1972, **34**, 529
14   Sabatini, A. and Vacca, A., unpublished results
15   Barbucci, R., Fabbrizzi, L., Paoletti, P. and Vacca, A. *J. Chem. Soc. Dalton* 1972, 740
16   Barbucci, R. *Inorg. Chim. Acta* 1975, **12**, 113