

Applied Macroinorganics. II. Protonation and Heavy Metal Ions Complex-Formation Behavior of Three Crosslinked Resins of Poly(amido-amine) Structure*

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Synopsis

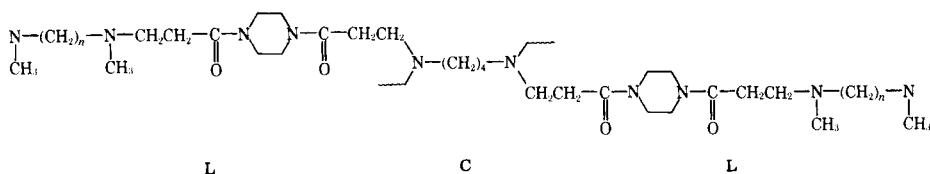
Three resins having a poly(amido-amine) structure have been synthesized. The basicity and complexing ability towards copper(II) have been investigated by potentiometric techniques, and compared with those of the corresponding soluble polymers. The adsorbing capacities of the resins in columns were tested, and a sharp separation between different metal ions is achieved.

INTRODUCTION

We have recently found that a new family of polymers, poly(amido-amines), may act as heavy metal ions complexing agents in aqueous solution.¹ The complexes have well-defined stoichiometries; in particular, one metal ion is coordinated by each repeating unit.² Sharp stability constants have been determined in aqueous solution.^{2,3} In several instances, complexes could be isolated in the solid state, giving elemental analyses quite consistent with the proposed stoichiometries.² This particular behavior, being common to several polymeric ligands, has been recently defined as "macroinorganics."⁴

The above results prompted us to prepare the same poly(amido-amines) in a crosslinked form, in order to investigate a possible application of this class of polymers in the field of the ion exchange resins, and, particularly, to obtain resins able to selectively remove, and recover, traces of heavy metal ions from solutions.

For this purpose, we have prepared three new crosslinked resins having the following structures:

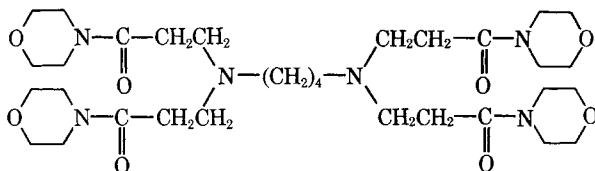


* Part I is Ref. 8

where $n = 2.RN_2$; $3.RN_2L$; $4.RN_2LL$; C = crosslinked amine part and L = linear amine part.

The aim of this paper is to report on some results obtained by studying the protonation and complex formation with Cu(II), of the above resins, as well as their separating ability towards Co(II), Ni(II), and Cu(II).

The basicity constants and the complexing abilities of the above resins have been compared with those of their corresponding linear polymers,⁵ as well as with those of a nonmacromolecular model of the crosslinking units, having the following structure:



This compound has been purposely synthesized.

EXPERIMENTAL

Materials

The resins were prepared by adding bisacryloylpyperazine (2.0 g; 0.010 mol) to a mixture of 1,4-diaminobutane (0.72 g; 0.0020 mol) and *N,N'*-dimethylenediamine (0.55 g; 0.0062 mol) for the resin N_2 , or *N,N'*-dimethylpropanediamine (0.71 g; 0.0069 mol) for the resin N_2L , or *N,N'*-dimethylputrescine (0.72 g; 0.0062 mol) for the resin N_2LL , in 5 cm³ H₂O. The polymerization reaction being a nucleophilic polyaddition, bis primary amines act as tetrafunctional monomers,⁶ thus leading to crosslinked polymers.

The reaction mixture was left at room temperature for 2 days. It set into a gel. It was triturated under water, and repeatedly extracted with water, methanol, and ether. It was then dried at room temperature and 0.1 mm Hg.

The model of crosslinking agent was prepared by adding *N*-acryloylmorpholine (5.86 g; 0.042 mol) to 1,4-diaminobutane (0.92 g; 0.010 mol) as 1-molar methanolic solution.

After standing at RT for 3 days, the reaction mixture was dried under vacuum to constant weight. The residue was dissolved in benzene and, after further drying with anhydrous Na₂SO₄ and filtering, poured into an excess of *n*-heptane. The product separated as heavy oil which failed to crystallize, it was dried at RT and 0.1 mm Hg. The dihydrochloride was prepared by adding concn HCl to a solution of the compound in abs ethanol. White powder mp = 194°C.

ANAL. Found: Cl, 9.64%; C₃₂H₅₈N₆O₈Cl₂ requires Cl, 9.77%.

EMF MEASUREMENTS OF PROTONATION AND CU(II) COMPLEXATION

Crosslinking Model

Potentiometric titration of the model was carried out by means of an Ag/AgCl reference electrode and a salt containing 0.1 mol·dm⁻³ NaCl solution. In each protonation titration the cell was thermostatted at 25°C and filled with ≈100 mL, 0.1 mol·dm⁻³ NaCl solution containing a known amount of model compound (≈10⁻²).

TABLE I
Experimental Details of Potentiometric Measurements in 0.1 mol·dm⁻³ NaCl and at 25°C

Reaction	Concn L (mmol/ g R)	Concn C (mmol/ g R)	Curve	\bar{g}_{resin}	V (mL)	Initial concn Cu ²⁺ (M × 10 ³)	pH range	Num- ber of points
RN ₂ + H ⁺	2.3549	0.7850	1	0.08231	20.30		9.6–2.1	13
			2	0.08024	20.11		9.8–2.2	10
RN ₂ L + H ⁺	2.20	0.7929	1	0.0882	20.29		9.3–2.1	16
			1	0.08581	20.22		10.3–2.2	18
RN ₂ LL + H ⁺	2.1306	0.7102	2	0.09280	30.17		10.1–2.4	16
		Initial concn (M × 10 ³)						
Crosslinking model + H ⁺		6.9911	1				2.4–9.3	197
		2.0049	2				2.4–9.4	89
			1	0.08024	21.39	4.424	2.2–4.4	7
RN ₂ + Cu ²⁺			2	0.08024	22.42	8.442	2.2–5.0	11
			3	0.08024	23.76	1.593	2.2–3.6	7

The solution was titrated with 0.1 mol·dm⁻³ NaOH, added by a Metrohm Dosimat E415 automatic piston burette under CO₂-free nitrogen. The experimental details of the potentiometric measurements are reported in Table I.

The program Miniquad 76A which was used to calculate the constants of model has been described elsewhere.⁷

Resins

The protonation reactions have been investigated by titrating with standard NaOH or HCl a weighed amount of resin, suspended into a measured volume of NaCl 0.1 mol·dm⁻³ aqueous solution ($T = 25^\circ\text{C}$). The titration was followed potentiometrically with a glass electrode. The calculation method and symbols have been reported in a previous paper.⁸

In Table I the conditions are reported. To give an example, a titration for each resin is graphically shown in Figure 1. The continuous curves have been calculated on the basis of the protonation constants values given in Table II.

In the case of RN₂L and RN₂LL, the equivalence points are very sharp and correspond respectively to the protonation of two aminic nitrogens of L (RN₂L), and of two aminic nitrogens of L and one aminic nitrogen of C (RN₂LL). No further protonations of RN₂L occur at higher acidities, after the equivalence point. On the contrary, RN₂LL binds a second proton to the C unit after the equivalence point, at $-\log h$ values of about 3.5.

The titration curve of RN₂ shows only two separated protonation regions, each corresponding to the protonation of one nitrogen of L.

In the case of RN₂LL, the last protonation constant is not sharp.

The proposed value is only an average value (Table II).

TABLE II
 Basicity of Resins, Polymers, and Model Compound of Crosslinking Agent in 0.1 mol·dm⁻³ NaCl at 25°C

System no.	Resin	log K_1^a	log K_2^a	log K_3^a	log K_4^a
1		7.74(10)	4.78(10)		
2		7.94(10)	6.76(10)		
3		8.58(10)	7.44(7)	6.20(10)	≈ 3

Polymer ^b			
1		8.09	4.54
2		8.172	6.691
3		8.715	7.689
	<p>Model</p>	8.341(2)	7.160(5)

^a The values in parentheses are the standard deviations.

^b Ref. 5.

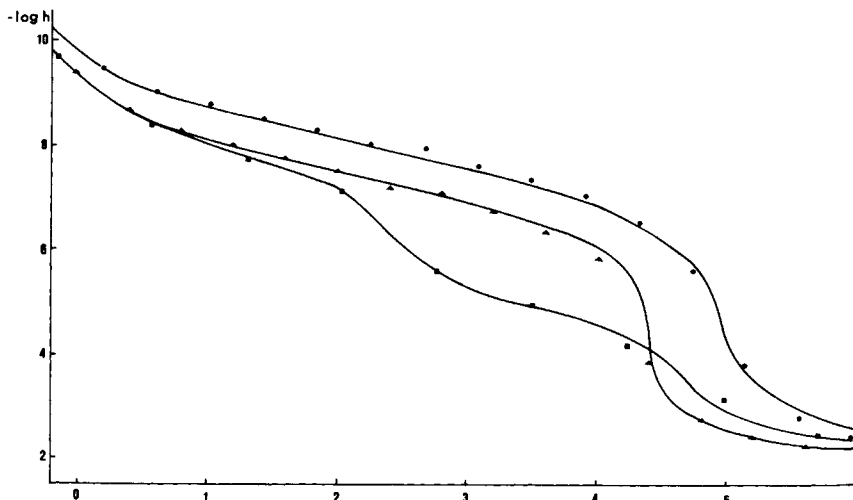


Fig. 1. Titration curves of RN_2 (●), RN_2L (▲), RN_2LL (■). Abscissae: $\log h$; ordinates: $a = C_{\text{HV}}/g$. Conditions: (N_2) $g_{\text{resin}} = 0.08024$, $V = 20.11 \text{ cm}^3$, $\log K_{1,\text{L}} = 7.74$, $\log K_{2,\text{L}} = 4.78$, $C_{\text{L}} = 2.35$. (N_2L) $g_{\text{resin}} = 0.08820$, $V = 20.29 \text{ cm}^3$, $\log K_{1,\text{L}} = 7.94$, $\log K_{2,\text{L}} = 6.76$, $C_{\text{L}} = 2.20$. (N_2LL) $g_{\text{resin}} = 0.08581$, $V = 20.22 \text{ cm}^3$, $\log K_{1,\text{L}} = 8.58$, $\log K_{2,\text{L}} = 7.44$, $\log K_{1,\text{C}} = 6.20$, $\log K_{2,\text{C}} = 3$, $C_{\text{L}} = 2.13$, $C_{\text{C}} = 0.71$.

Cu(II) COMPLEXATION

The complexation reactions have been studied by comparing the potentiometric titration curves of the pure resin with those obtained in the presence of Cu(II).

The experimental method has been extensively described,⁸ and the experimental conditions for different titrations are reported in Table I.

Only $-\log h$ values smaller than 4.5 have been considered in the calculations, because for higher $-\log h$ the precipitation of hydroxy species occurs. RN_2L and RN_2LL don't complex Cu(II) in the acidity range investigated, while RN_2 does, as one can deduce by observing the titration reported in Figure 2. At the same time, a deep blue color is assumed by the resin.

The formation constant of the complex CuRN_2 can be calculated at each titration point and an average value of $\log K = 7.65 \pm 0.10$ is obtained.

RESULTS AND DISCUSSION

Protonation Constants

The protonation behavior of the resins have been investigated first. The results are summarized in Table II. First of all, it may be observed that in the resins RN_2 and RN_2L only the aminic nitrogens of the linear portion seem to be protonated, while the aminic nitrogens of the crosslinking units are inactive in this aspect. The protonation constants are in both cases in good agreement with those previously found in the case of the linear polymers of the same structure (Fig. 3)

The good agreement between the two series of compounds apparently is a further hint than no effects due to the macromolecularity are present as far as the protonation is concerned.⁵

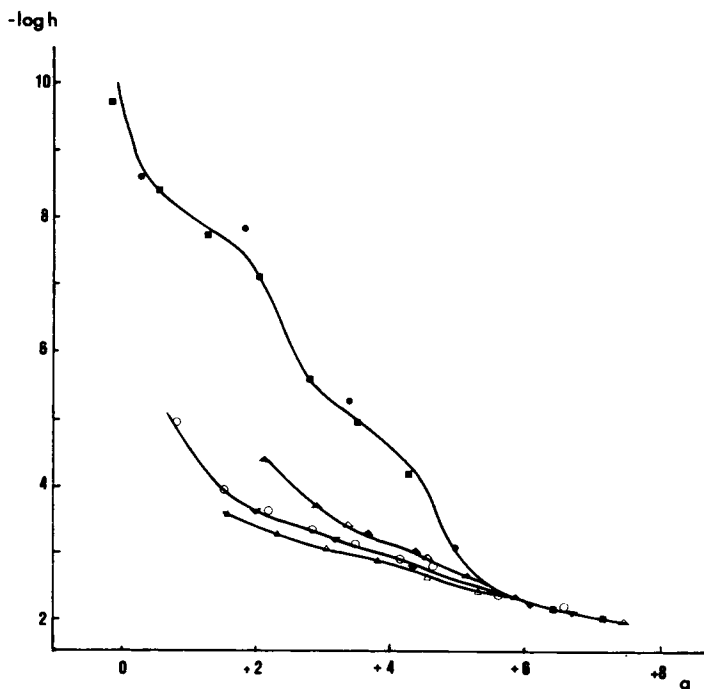


Fig. 2. Titration curves of pure RN_2 (■, ●) and of RN_2 in the presence of Cu(II) . Abscissae: $-\log h$; ordinates: $a = C_{\text{H}}V/g$. Conditions: $g_{\text{resin}} = 0.08024$, $V = 21.39, 22.43, 23.76 \text{ cm}^3$. ($\Delta \blacktriangle$) $C_{\text{Cu}} = 4.424 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$; ($\circ \blacktriangledown$) $C_{\text{Cu}} = 8.442 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$; (\triangle) $C_{\text{Cu}} = 1.593 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$.

By contrast, in the case of resin RN_2LL all aminic nitrogens can be protonated. The titration behavior of this resin may be best interpreted by assuming four basicity constants. The fact that the first two constants are very close to those of the linear polymers, but not so close to those of the crosslinking model, seems to indicate that these constants may be attributed to the linear portion of the resin.

We have no explanation at present for the different behavior between the three resins, as far as the protonation of the crosslinking units is concerned. It may be noticed, however, that in the resin RN_2LL a close similarity exists between the crosslinking units and the repeating units of the linear portion. Further studies on this point are presently in progress.

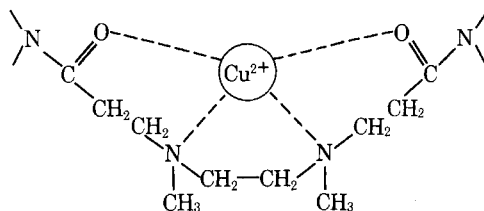
Stability Constants

Only the resin RN_2 gives a complex with Cu(II) ions in aqueous solution. No evidence of complex formation was found with RN_2L and RN_2LL . The stability constant of the CuRN_2 complex is 7.65.

This is considerably lower than the corresponding constant previously obtained with the linear polymer (8.96).²

We think that the above difference is due to the fact that the complex formation in the case of the linear polymer occurs through a cyclic structure around

the copper atom; as previous reported,^{2,9}



The formation of such a cyclic structure is obviously biased in the case of a tightly linked resin.

For the same reason, no complex formation occurs in the case of the resin RN_2L , while the linear polymer gave a complex with $Cu(II)$ having a constant 5.36.²

Column Operations

In order to evaluate the possibility of practical applications of resins RN_2 , studies on the separation of $Co(II)$, $Ni(II)$, and $Cu(II)$ ions on a column of the same resin have been performed.

In Figure 4 the percent of metal ion retained by the resin after elution with 30 cm^3 of buffers at various pH are reported. It may be observed that the elution conditions are sharply different for three ions. In other words, the pH conditions at which each ion is eluted show little or no superimposition.

Therefore, a second set of experiments was performed.

A mixed solution containing 50 g of $Cu(II)$ ions, and 40 g of both $Ni(II)$ ions and $Co(II)$ ions was absorbed on 0.2 g of resin at $pH = 5.75$. After absorption

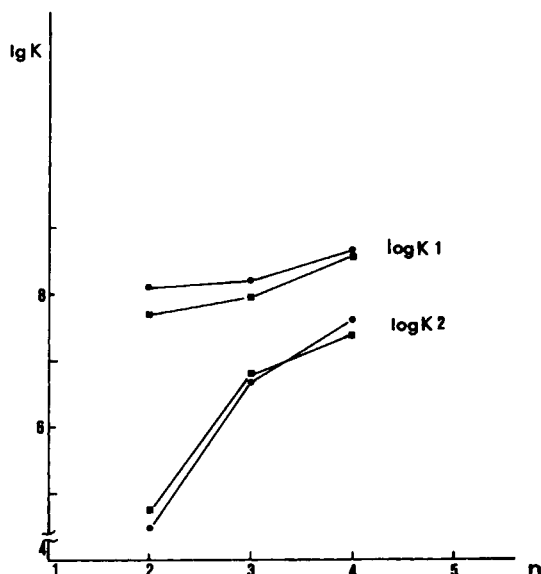


Fig. 3. $\log K$'s of protonation $v n$ (number of $-CH_2-$ groups between the two aminic nitrogens) for poly(amido-amines) in the soluble (●) and in the resin form (■).

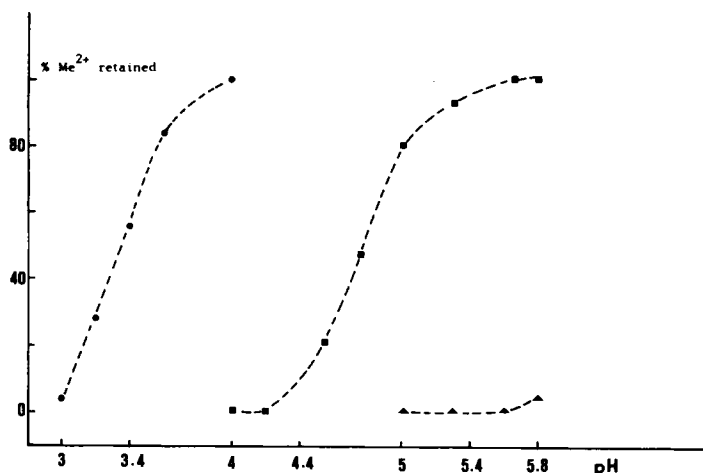


Fig. 4. Plot of the percentage of metal ion retained in the resin N_2 (0.2 g) against pH Cu(II) (100 μg) (●); Ni(II) (100 μg) (■); Co(II) (100 μg) (▲).

the resin was eluted first with 60 cm^3 buffer at pH = 5.75, then with 100 cm^3 of buffer at pH = 4.00, and finally with 30 cm^3 of 1% HCl aqueous solution.

The results are summarized in Figure 5. It may be observed that after 30 cm^3 of buffer at pH = 5.75 all Co(II) ions are eluted, while both Ni(II) and Cu(II) are completely retained even after twice as many cm^3 of the same buffer. Ni(II) is then completely eluted with about 60 cm^3 of buffer at pH = 4; the elution of this ion is "tailed," but there is no danger of Cu(II) elution with this buffer. Consequently, the occurrence of the tail is irrelevant as far of the separation of these two ions is concerned. The slow elution of Ni(II) ions might be ascribed to the fact that the kinetics of the complexation of this ion with this resin is probably slow, as previously observed in the case of the corresponding linear polymer.¹⁰

Finally, the copper ions could be quantitatively eluted with dilute acid. The above absorption-elution cycle could be repeated on the same resin indefinitely.

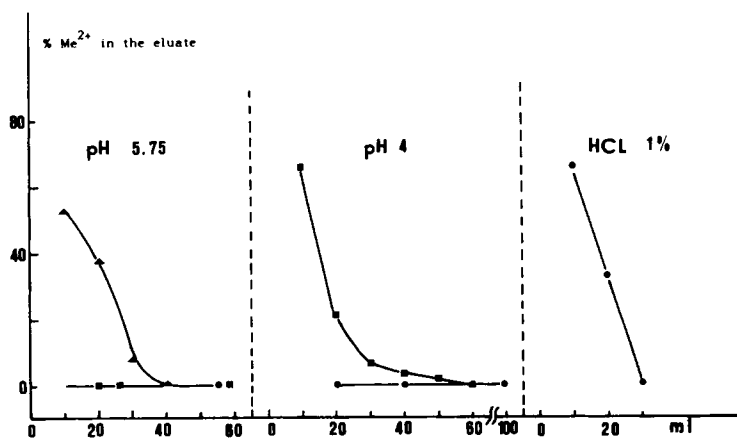


Fig. 5. Plot of the percentage of metal ion retained in the resin (at pH 5.75, 4, and in HCl 1%) against mL of solution eluted. Cu(II) (50 μg) (●); Ni(II) (40 μg) (■); Co(II) (40 μg) (▲).

The recovery of absorbed ions was in all case practically quantitative, the average error being less than 2%.

From the above results the following conclusions may be drawn:

(1) The resin has an unusual capacity for some metal ions, as compared with most commercial resins.¹¹

(2) A sharp separation may be achieved between metal ions of otherwise similar behavior in aqueous solutions. The resin appears to be sufficiently stable in the operating pH conditions to envisage practical applications.

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