Protonation and Complex Formation with Heavy-metal Ions of Two Tetrafunctional Amines and of a New Structurally Related Ion-exchange Resin

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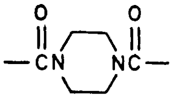
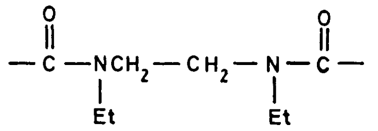
The basicity and complexing ability towards copper(II) of two new tetrafunctional amines containing four basic aliphatic nitrogens (1) and two aliphatic and two heterocyclic nitrogens (2) have been investigated by potentiometric techniques. The basicity constants of the two compounds are different which indicates that the mechanism of protonation is different for the two amines. The presence of complexes [Cu(HL)], [CuL], [Cu(OH)L] for L = (1) and $[Cu(H_2L)]$, [Cu(HL)], [CuL], and [Cu(OH)L] for L = (2) could be detected in aqueous solution. A resin whose repeating unit is structurally related to (2) has been synthesized, and its basicity and stability constants have been compared with those of compound (2).

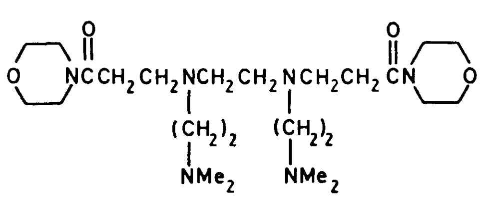
A NEW family of water-soluble tertiary amino-compounds, both high polymers and their non-macromolecular analogues, have recently been synthesized, and their protonation and complexing ability with heavy-metal ions studied.[1] It has been found that, in these respects, the behaviour of the polymeric compounds is similar to that of their non-macromolecular models. This behaviour, which is unusual in the chemistry of polyelectrolytes, has been attributed to the fact that in these polymers the tertiary amino-groups of each repeating unit are separated from those of neighbouring units by bis(aminic) structures such as those shown below.[2,3]



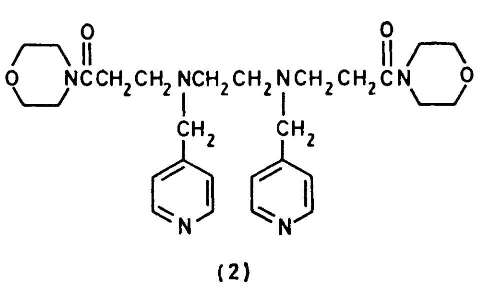


$$-\overset{O}{\overset{\|}{C}}-\underset{Et}{\underset{|}{N}}CH_2-CH_2-\underset{Et}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-$$

This configuration apparently minimizes interactions between aminic groups belonging to different units. Consequently each unit behaves independently, as if it were a small molecule. Hence the name of ' macro-inorganics ' has been proposed for this new branch of chemical research.[4]



(1)



(2)

One of the possible applications of this research is to synthesize hydrophilic ion-exchange resins whose behaviour is predictable from that of their non-macromolecular analogues. We present here some results obtained with two new tetrafunctional amines, (1) and (2), and with a resin whose repeating unit is structurally related to (2).

EXPERIMENTAL

Materials.—The preparation of compound (1) has previously been reported.[5] Compound (2) was prepared by adding *N*-acryloylmorpholine [6] (2.82 g; 0.02 mol) as a 1 molar methanolic solution to *NN'*-di-4-picolylethylenediamine (2.43 g, 0.01 mol) (4-picolyl = 4-methylpyridyl). The reaction mixture was maintained at room temperature for 1 week with occasional stirring. The product was then isolated by evaporating the mixture to dryness *in vacuo* and finally purified by dissolving in warm n-heptane, filtering, and cooling on an ice-bath. The product separated as a heavy oil which was dried at room temperature at a pressure of 0.1 mmHg * [yield 3.9 g (74%)]. It was characterized by i.r. and n.m.r. spectroscopy.

The resin was prepared by adding 1,4-bis(acryloyl)-piperazine (7.5 g, 0.036 mol) to a mixture of *NN'*-di-4-picolylethylenediamine (5.61 g, 0.0232 mol) and 1,4-diaminobutane (0.68 g, 0.007 71 mol) in water (5 cm^3). Being a nucleophilic polyaddition, bis primary amines act as tetrafunctional monomers in the polymerization reaction,[7] thus leading to cross-linked polymers. The reaction mixture was left at room temperature for 2 days, after which it had set into a gel. It was triturated under water, and repeatedly extracted with water, methanol, acetone, and diethyl ether. The product was then dried at room

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

TABLE 1

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

		10^3 Initial concentration/mol dm^{-3}				
Reaction	Curve	L		Cu^{2+}	pH Range	No. of points
Model (1) + H$^+$	1	5.6937			9.69—2.80	46
	2	6.5675			9.69—2.84	44
	3	3 7244			5.97—2.43	20
	4	2.4455			6.50—2.09	31
Model (2) + H$^+$	1	1.4183			8.18—2.45	57
	2	1.3002			2.45—10.76	62
	3	0.7124			8.13—2.39	43
	4	0.6633			2.39—11.34	59
		w/g	V/cm^3			
Resin + H$^+$	1	0.0978	33.17		9.00—3.00	13
	2	0.1151	30.90		8.50—2.80	12
	3	0.1151	30.90		2.80—8.50	10
Model (1) + Cu^{2+}	1	2.1105		0.5223	9.41—2.85	46
	2	1.1621		0.1893	9.44—2.49	40
	3	1.4086		0.4411	9.37—2.40	46
Model (2) + Cu^{2+}	1	0.6946		0.1442	2.8—10.4	59
	2	0.9471		0.1957	3.0—11.0	68
	3	1.056		0.5338	2.7—9.7	56
		w/g	V/cm^3			
Resin + Cu^{2+}	1	0.0762	20.00	5.977	5.50—2.50	12
	2	0.0762	20.00	5.977	2.50—6.00	12

temperature at a pressure of 0.1 mmHg (Found: C, 60.3; H, 8.1; N, 17.5. The sum of monomers requires C, 60.2; H, 7.85; N, 17.55%). The volume of the dry resin increases by a factor of two when put into water. Thus, the water content of the water-equilibrated resin is *ca.* 65% by weight. The structure of the resin is depicted in Table 2.

Electromotive Force Measurements and Calculations.—Models. Potentiometric titrations of the non-macromolecular models (1) and (2) were performed using a Ag–AgCl reference electrode, an Orion 91–01 glass electrode, and a salt bridge containing 0.1 mol dm^{-3} NaCl solution. In each protonation titration the cell was thermostatted at 25 °C and filled with 0.1 mol dm^{-3} NaCl solution (*ca.* 100 cm^3) containing a known amount of the model compound.

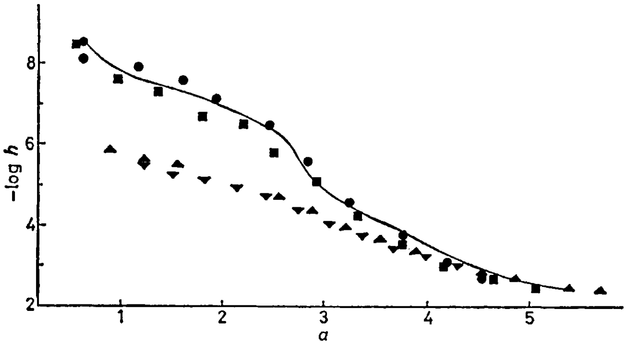


FIGURE 1 Titration curves of the resin in 0.1 mol dm^{-3} NaCl (θ_c = 25 °C, V = 20.00 cm^3, w = 0.076 23 g): resin + acid (■); resin hydrochloride + base (●); resin + acid in the presence of Cu^{II} (▼) ([Cu^{2+}] = 5.98 × 10^{-3} mol dm^{-3}); resin + base in the presence of Cu^{II} (▲) ([Cu^{2+}] = 5.98 × 10^{-3} mol dm^{-3}). $a = C_H V/w$

For the determination of copper(II) stability constants, the cell, at the same temperature as before, was filled with 0.1 mol dm^{-3} NaCl solution (*ca.* 100 cm^3) containing a known amount of ligand and of copper(II) solution. In both cases, the solutions were titrated with a 0.1 mol dm^{-3} hydrochloric acid solution, added by a Metrohm Dosimat E 415 automatic piston burette under CO$_2$-free nitrogen. The experimental details of the potentiometric measurements are reported in Table 1.

The program Miniquad 76A used to calculate the constants of models (1) and (2) has been described elsewhere.[8]

Resin. The potentiometric titrations of the resin were carried out at 25 °C in 0.1 mol dm^{-3} NaCl by titrating the resin suspension (50—200 mg) with a 0.1 mol dm^{-3} hydrochloric acid solution and then back titrating with a 0.1 mol dm^{-3} Na[OH] solution. The junction between the test solution and the NaCl filling solution of the reference electrode was made of fritted glass to prevent diffusion of the resin. After each addition, the potential of the solution was measured and recorded when a steady value was reached (6—8 h, depending on the acidity).

An example of a titration curve is shown in Figure 1. The equivalence point corresponds to the protonation of one nitrogen atom for each linear amine (L) and two nitrogen atoms for each cross-linked amine (C). After the equivalence point, in more acidic solutions (pH 3.3—4.9), further protonation of L occurs. This protonation behaviour agrees well with the capacity of the resin.

$$\bar{n}_{H,L} = \frac{c_{HL} + c_{H_2L} + \dots}{c_L + c_{HL} + c_{H_2L}{}^{+} \dots} = \frac{K_{1,L}h + 2K_{1,L}K_{2,L}h^2 + \dots}{1 + K_{1,L}h + K_{1,L}K_{2,L}h^2 + \dots} \quad (1)$$

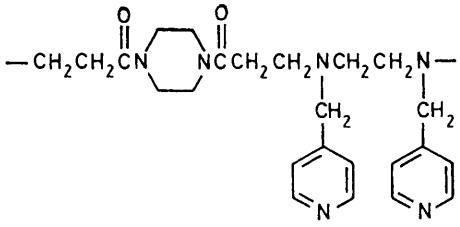
$$\bar{n}_{H,C} = \frac{c_{HC} + c_{H_2C} + \dots}{c_C + c_{CH} + c_{H_2C} + \dots} = \frac{K_{1,C}h + 2K_{1,C}K_{2,C}h^2 + \dots}{1 + K_{1,C}h + K_{1,C}K_{2,C}h^2 + \dots} \quad (2)$$

$$\bar{n}_H = \frac{C_H - h}{(w/V)(C_L + C_C)} \quad (3)$$

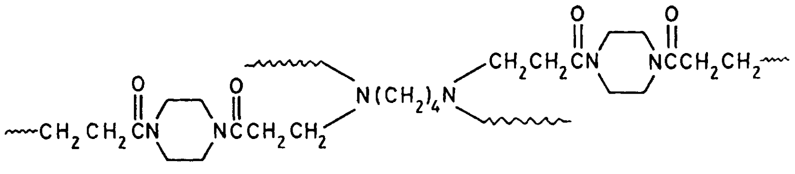
$$K_{i,L} = c_{H_iL}/c_{H_{i-1}L}h \quad (4)$$

$$K_{i,C} = c_{H_iC}/c_{H_{i-1}C}h \quad (5)$$

The basicity constants of the resin have been deduced from the protonation curves ($\bar{n}_{H,L}$ against −log h and $\bar{n}_{H,C}$ against −log h) according to Bjerrum,[9] by comparison with the normalized curves[10] [see equations (1)—(5) where $\bar{n}_H$ =



L



C

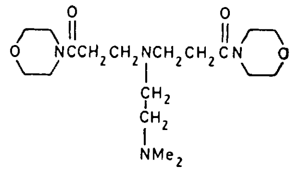
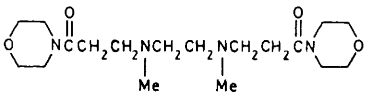
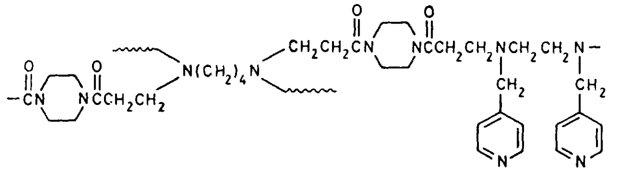
average number of protons linked to each repeating unit (L or C) of the resin, K = basicity constant, h = concentration of free H^+ in the aqueous phase, w = weight (g) of resin titrated, V = volume of aqueous phase (cm^3), C_H and C_M are analytical concentrations of H^+ and M^{n+}, C_L and C_C are total concentrations of L and C in the resin phase (mmol per g of resin) = 1.569 and 0.523, c_M = concentration of free M^{n+} in aqueous phase, c_L, c_{HL}, c_C, c_{HC} *etc.* are the concentrations of the various forms of L and C in the resin phase].

The fact that the experimental points for the plot of $\bar{n}_H$ against $-\log h$ fit satisfactorily with the normalized curves demonstrates that the protonation of the resin is similar to that of simple non-macromolecular amine. In other words in the resin form too, the basicity constants are 'sharp' and not 'apparent' [11] (Table 2).

In Figure 1 two titration curves relating to the complex-formation reaction with the resin are shown. They have been obtained by the method previously described for the protonation investigation, one in the presence of and the other in the absence of copper(II) ions. Evidently, the resin links the metal ions and at the same time releases H^+.

TABLE 2

Basicity of the model compounds and the resin in 0.1 mol dm^{-3} NaCl at 25 °C *

System		log K_1	log K_2	log K_3	log K_4	Ref.
(1)		9.05 (1)	8.34 (1)	4.42 (2)	2.42 (4)	This work
(3)		8.87	4.35			12
(4)	$Me_2NCH_2CH_2NMeCH_2CH_2NMeCH_2CH_2NMe_2$	9.11	8.35	5.26	2.24	13
(2)		7.50 (4)	5.73 (8)	4.31 (23)	4.13 (27)	This work
(5)		8.248	4.80			15
(6)	NC_5H_4Me-4	6.10				16
Resin	 C L	8.6 (2)	7.8 (2)	7.1 (2)	4.1 (1)	This work

* The values in parentheses are the standard deviations.

The concentration of Cu^{2+} in the solution was checked at each titration point in the following way: a small aliquot (10—50 μl) of solution, carefully removed with a micropipette, was transferred into a $[NH_4]Cl$–$[NH_4][OH]$ buffer solution (8 cm³, 0.1 mol dm⁻³) (pH *ca.* 9.3) and analyzed by differential pulse polarography using the standard addition method, or at lower copper(II) concentrations by anodic stripping voltammetry (Polarecord E506 Metrohm voltameter with E607 and E608 control units and a kemula hanging mercury drop electrode). Each analysis was repeated twice, and the agreement was better than 0.5%. By this procedure, we were able to demonstrate that the chelation reaction goes according to equation (6) (where r = resin).

$$Cu^{2+} + (HL)_r \rightleftharpoons (CuL)_r + H^+ \qquad (6)$$

The equilibrium was reached after 6—8 h after each titrant addition (log $K = -2.1 \pm 0.2$).

Column Operations.—The adsorbing capacities of the resin towards heavy-metal ions in columns were tested in the following way. A glass tube with an internal diameter of 0.8 cm was filled with resin (0.4 g). The resin was weighed dry and equilibrated with water before filling the column. The resin was then buffered at the desired pH, and a solution (1 cm³) containing 100 p.p.m. of metal ion was introduced onto the column and eluted with the buffer (25 cm³). The elution rate was 0.1 cm³ min⁻¹. The eluates were collected and polarographically analyzed for metal-ion concentration. The resin was then washed with HCl (0.1 mol dm⁻³) so that the ions previously adsorbed were completely released. This procedure was repeated at several pH values between 2.4 and 6 (the buffers used were acetic acid and acetate, or monochloroacetic acid and monochloroacetate at an ionic strength of 0.1 mol dm⁻³).

Spectrophotometric Measurements.—Electronic spectra were recorded at 25 °C on a Beckman DK-2A spectrometer using 1-cm quartz cells.

RESULTS AND DISCUSSION

Protonation.—Model compounds. The protonation constants of the model compounds (1) and (2) are given in Table 2, together with those of some other amines for comparison. It can be seen that, although the main chains of (1) and (2) are the same length, their constants are markedly different. Specifically, the first two constants of (1) are higher than those of (2), while the opposite is true for the fourth constant. This indicates that the protonation mechanism is not the same in both cases. As far as (1) is concerned, its first protonation constant is similar to that of the bis amine (3) of similar structure,[12] and of (4).[13] In these cases, we have already found that the external nitrogens are protonated first. Hence, we may reasonably presume that this is also true in the case of (1). The difference between the first constants of (1) and (3) may be explained by the fact that in (1), as in (4), two equivalent nitrogens are present, and the first constant will be increased with respect to (3) by the statistical effect.

The second protonation constant of (1) is very similar to that of (4). This apparently means that the second protonation step involves the other external nitrogen.

The third constant of (1) is slightly higher than the second constant of (3), but decidedly lower than the third constant of (4). The third protonation step obviously involves the internal nitrogens and the above differences may readily be explained by the statistical effect [absent in (3)], and by the presence in (1) of carbonyl groups [absent in (4)] which lower the basicity of the internal nitrogens in (1) by the inductive effect, in spite of the possibility of stabilizing the protonated form by hydrogen bonding.[3,14]

The last protonation constant of (1) is similar to that of (4) since in both cases the prevailing effect is the electrostatic one due to the presence of three already protonated nitrogens.

The first protonation of (2) is lower than the corresponding one of (5) [15] but higher than the constant of 4-methylpyridine (6).[16] The latter observation means that in (2) the first protonation step involves the internal aliphatic nitrogens. The presence of an electron-attracting heterocyclic ring in (2) readily explains the difference between (2) and (5).

The second constant of (2) is close to that of (6) and significantly higher than the second constant of (5). This seems to indicate (see also below) that the second protonation step involves the heterocyclic nitrogen.

No definite conclusion can be drawn from examination of the last two constants of (2), as regards the mechanism of protonation. Both of these constants are practically equal and probably involve nitrogen atoms of a different nature.

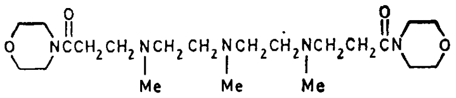
Resin. In principle, the resin should exhibit six different protonation constants, two of which belong to part C and four to part L (see Table 2). However, only four of them could be determined, the last two being too low to allow measurement.

The first two constants have been attributed to the nitrogen atoms of part C on the basis of stoicheiometric considerations (see the calculation method above). The third and fourth constants should be similar to the first two constants of (2). However, they are decidedly lower. This is in contrast to previous findings [1] with another resin of the poly(amido-amine) structure, having a similar cross-linked portion but in which the aminic section of part L is derived from the triamine *NN'N''*-trimethyldiethylenetriamine. In this case, the constants were very similar to those of its non-macromolecular model. We believe that, in the resin studied in the present paper, the bulky substituents induce a very low degree of conformational freedom, resulting in a lower accessibility to the basic sites for the protons. This is confirmed by the fact that the protonation equilibrium is reached only after several hours, while the ' flexible ', previously studied resin reached such an equilibrium after a few minutes.

Copper(II) *Complex Formation.—Model compounds.* The ion Cu^{2+} gives three kinds of complexes with (1), namely [Cu(HL)], [CuL], and [Cu(OH)L]. The stability constants of the complexes are reported in Table 3. For comparison purposes, the stability constants of copper complexes with *NNN'N''N''*-pentamethyldiethylenetriamine (7), with a model compound obtained by addition

TABLE 3

Stability constants of the copper(II) complexes with model compounds (1) and (2), the resin, and some of their analogues

		log K^a		
System		$Cu^{2+} + L \rightleftharpoons$ [CuL]	CuL + $OH^- \rightleftharpoons$ [Cu(OH)L]	Electronic data for [CuL] ^{b}
(1)		12.75 (13)	5.48 (16)	15.4 (260)
(5) ^{c}		9.10		14.8 (176)
(7) ^{d}	$Me_2NCH_2CH_2NMeCH_2CH_2NMe_2$	12.16	5.14	
(8) ^{c}		13.36	4.62	16.1 (244)
(9) ^{e}	$Et_2NCH_2CH_2NEt_2$	8.93	5.49	
(2)		7.3 (8)	5.3 (9)	13.3 (260)
(6) ^{f}		5.39 ^{g}		
Resin		5.0 (2)		

^{a} The values in parentheses are the standard deviations. For $Cu^{2+} + H_2L \rightleftharpoons [Cu(H_2L)]$, log K = 4.0 (1) for L = (2); for Cu^{2+} + $HL \rightleftharpoons$ [Cu(HL)], log K = 9.93 (7) for L = (1), 4.6 (5) for L = (2). ^{b} $\lambda_{max.}$/nm (ϵ/dm^3 mol^{-1} cm^{-1}). ^{c} Ref. 2. ^{d} Ref. 17. ^{e} Ref. 18. ^{f} Ref. 16. ^{g} Relative to the equilibrium $Cu^{2+} + 2\ L \rightleftharpoons [CuL_2]$.

of acryloylmorpholine to *NN'N''*-trimethyldiethylenetriamine (8),[17] and *NNN'N'*-tetraethylethylenediamine (9) [18] have also been reported.

In the case of [CuL], it can be seen that the stability constant is close to that of analogous complexes with (7) [17] and (8),[2] and significantly higher than the constants of the complexes with (5) [2] and (9) [18] containing only two nitrogen atoms. This indicates that only three out of the four basic nitrogens in (1) are involved in copper(II) complex formation. This is confirmed by the electronic spectrum of the [CuL] complex [L = (1)], in which $\lambda_{max.}$ and the value of ϵ are very close to those obtained in the case of (8).[2] On the other hand, by considering the steric hindrance of $N(CH_3)_2$ groups, it appears quite improbable that a co-ordination compound involving all four tertiary amino-groups in the equatorial plane exists in aqueous solution. This is further confirmed by the fact that a [CuL] complex with two molecules of 1,2-bis(dimethylamino)ethane does not exist in aqueous solution, only the 1 : 1 complex.[19]

The stability constant of [Cu(HL)] [L = (1)] is considerably lower than that of [CuL] but higher than that of [CuL] when L = (5) or (9).[18] The constant (log K = 6.13) relative to the protonation of the simple complex (7), L = (1), lies between the second and the third

$$[CuL] + H^+ \rightleftharpoons [Cu(HL)] \qquad (7)$$

protonation constants of the free ligand. That implies, according to Schwarzenbach,[20] that the nitrogen atom to be protonated is free, *i.e.* the [CuL] complex has three nitrogen atoms co-ordinated (see also above). The stability constant of the [Cu(OH)L] complex is close to those of analogous complexes with (7) [17] and (8).[2]

The model compound forms four types of complex, namely $[Cu(H_2L)]$, [Cu(HL)], [CuL], and [Cu(OH)L] in aqueous solution. The relative stability constants are reported in Table 3. The stability constant of [CuL] is markedly lower than those of the analogous complexes with other ligands and in particular is lower than that obtained with (5) [2] and (9) [18] involving only two aliphatic nitrogen atoms in copper(II) co-ordination. We can consider two hypotheses: (*i*) the copper(II) ion co-ordinates to only the two aliphatic nitrogen atoms present in the structure of (2) and the low stability constant of [CuL] [L = (2)] can be explained by the steric hindrance and/or electron-attracting ability of the two picolyl groups which lower the co-ordinating ability of the two remaining nitrogens; or (*ii*) the formation of a [CuL] [L = (2)] complex with the participation of the heterocyclic nitrogens. However, the latter hypothesis can be rejected by comparing the value of the [CuL] [L = (2)] stability constant with that obtained for the complex bis(4-methylpyridine)copper(II) [16] in which two heterocyclic nitrogens are involved.

The stability constants of $[Cu(H_2L)]$ and [Cu(HL)] are considerably lower than that of [CuL], but very close to each other. The latter observation suggests that in both the protonated complexes, two nitrogen atoms are involved in co-ordination, and that they are the same in both cases.

The formation of [Cu(HL)] and $[Cu(H_2L)]$ may occur in three different ways; (*i*) co-ordination with the two aliphatic nitrogens; (*ii*) co-ordination with the two heterocyclic nitrogens; (*iii*) mixed co-ordination with one aliphatic and one heterocyclic nitrogen. The last possibility can be rejected by steric considerations. The skeleton of the heterocyclic ring does not allow the freedom necessary to span the metal ion when the aliphatic nitrogen is already co-ordinated. The second hypothesis implies that the two nitrogens protonated in the [Cu(H_2L)] complex are the aliphatic ones. The constants relative to the stepwise protonation of the complexes, [CuL] + $H^+ \rightleftharpoons$ [Cu(HL)] (log $K = 4.80$) and [Cu(HL)] + $H^+ \rightleftharpoons$ [Cu(H_2L)] (log $K = 5.15$), are almost equal although the second protonation would be expected to be difficult due to the fact that the other nitrogen atom which is very close is already protonated. As a matter of fact the difference between the two protonation constants of the free compound (5) is large (3.4 log units).[15] Thus, the first hypothesis is probably correct.

The stability constant of the [Cu(OH)L] [L = (2)] complex is similar to those with analogous ligands reported in Table 3. It seems, as previously reported,[21] that the introduction of an OH^- ion into the co-ordination sphere of Cu^{2+} practically equalizes the complexing abilities of the aminic ligands.

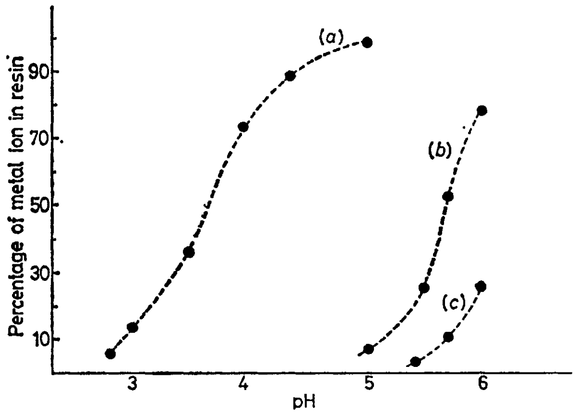


FIGURE 2 Plot of the percentage of metal ion retained in the resin against pH: Cu^{II} (*a*); Ni^{II} (*b*); Co^{II} (*c*)

Resin. The co-ordinating ability of the resin is *ca.* 100 times lower than that of the corresponding model, (2). It is well known that the adsorbing capacity of a resin depends on the cross-linking agent and on the steric hindrance to reaching the co-ordination centres.[22] In the case of this resin, the picolyl groups strongly hinder the introduction of the Cu^{2+} ion. This explains the low stability constant. In real terms, complexation by means of the cross-linking nitrogens may be excluded due to the large distance (4 CH_2) between the two co-ordinating atoms, while the release of one H^+ ion during the complex-formation process agrees with the fact that only one aliphatic nitrogen and one heterocyclic nitrogen out of two are protonated in the pH range 3—5 (see above). At this point we can only think that the Cu^{2+} ion co-ordinates to two identical nitrogen (aliphatic or heterocyclic) atoms of the L part of the resin. Its stability constant is lower than those obtained with ligands containing either two heterocyclic rings (6) or two aliphatic nitrogens (5), but as a rule the resins which exhibit small chain flexibility show a lowering of complex stability.[22] With the aim of finding some practical applications, data have been obtained by passing dilute solutions of several metal ions onto columns filled with the resin in the form of small particles (mesh 25). The results are summarized in Figure 2.

It can be seen that the adsorption of Co^{II} takes place only at pH 5.5. The reduction of Ni^{II} begins at pH 5, while that of Cu^{II} is practically complete at the same pH.

Conclusions.—From the previously reported results for model (1), we thought it pointless to study a cross-linked resin corresponding to this model since results similar (or even worse due to steric effects) to those previously obtained with a triaminic resin [1] could be expected.

From the results obtained with the dipicolyl resin the following conclusions may be drawn. The resin absorbs both Cu^{2+} and Ni^{2+} from aqueous solution. The significantly lower complexing ability of this resin with respect to the previously studied one allows a better selectivity between Cu^{2+} and Ni^{2+} so that a practical application of this resin may be envisaged. It should be noted that this resin also shows better mechanical and thermal stability, and its degree of swelling in aqueous media is sufficiently small and independent of the pH of the solution over a wide range.

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