

## Copper Species Sorbed on Ion-Exchangers. II. The Chelating Iminodiacetate Resin

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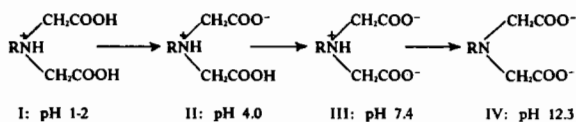
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Copper ions were sorbed from various solutions onto the ion exchangers Dowex-50, Dowex-1, Dowex A-1, and Amberlite IRC-50. The infrared, near infrared visible and electron spin resonance spectra of the various exchangers were measured and compared, and from these spectra some conclusion about the structure and bonding of the various species were drawn.

### Introduction

In a recent study<sup>1</sup> an attempt was made to determine the copper species sorbed on a strong cation and a strong anion exchanger by their electronic and e.s.r. spectra. The study showed this technique to be useful for elucidating the species sorbed. The results are in good agreement with those obtained from similar systems in aqueous and non-aqueous media. In the present paper the bonding of copper on the chelating exchanger Dowex A-1 will be considered, mainly by comparing the electronic, IR and e.s.r. spectra of the sorbed copper species on the exchanger with the spectra of copper species on other exchangers sorbed under similar conditions.

The chelating resin Dowex A-1 has an iminodiacetate functional group which dissociates differently according to the pH of the media.<sup>2,3</sup>



It is evident from the above that these different forms will affect the binding of the copper ions. Thus, in concentrated acid solution, the resin acts as an anion exchanger (structure I) and the species sorbed should be comparable to that sorbed on a strong anion exchanger (e.g. Dowex-1). In slightly acid solutions only chelation by the carboxylic groups would be expected to bond the copper species, similarly to a weak cationic carboxylic exchanger (e.g. IRC-50). The iminodiacetate group should act as a tridentate

ligand only in neutral or alkaline solutions, as Schmuckler<sup>4</sup> asserts.

While the monomeric iminodiacetate (IDA) forms a copper chelate in solution,  $\text{Cu}(\text{IDA})_2$ , it is not very probable that the same complex will be formed on the resin for steric reasons, although such a species was assumed by Marinsky and Egger.<sup>5</sup> If a 1 : 1 complex is sorbed the question arises which monodentate groups will occupy the still available coordination sites on the copper, a problem already discussed by Schmuckler.<sup>4</sup> It is presumed that the spectra presented in this paper will at least partially solve these problems.

### Experimental Section

The methods used for the measurements of the electronic and e.s.r. spectra were described in a previous paper.<sup>1</sup> Infrared spectra were recorded on Perkin-Elmer Recording Infrared Spectrophotometer Model 21 and 33 from KBr pellets or nujol mulls of the exchangers.

### Results and Discussion

**IR Measurements.** In a previous kinetic study it was found<sup>6</sup> that the sorption of copper ions by the Dowex A-1 resin is diffusion-controlled, although the rate of exchange is dependent on the pH of the reaction medium. From the hydrogen form of the resin the exchange is slow, but when the resin is in the sodium form the copper sorbs very rapidly. The question arises whether this difference is due to the slow diffusion of the hydrogen ion or whether a different complex copper species is sorbed in the two cases. The IR spectra were expected to give some information about the bonding of the copper on the exchanger.

Table I shows the carboxyl absorption bands as a function of the ion-exchanger and its loading. From this Table it may be seen that the absorption bands of the carboxyl group are not affected by the fact the iminodiacetate group is linked to the polymeric poly-

(1) C. Heitner-Wirguin and R. Cohen, *J. Phys. Chem.*, **71**, 2556 (1967).

(2) K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, J. Wiley and Sons, 1963.

(3) A. Schwartz, Ph. D. Thesis, Haifa Technion, 1962.

(4) H. Loewenschuss and G. Schmuckler, *Talanta*, **11**, 1399 (1964).

(5) J. A. Marinsky and C. Egger, Proc. 8th Int. Conf. Coord. Chem. Vienna, 1964.

(6) C. Heitner-Wirguin and G. Markovits, *J. Phys. Chem.*, **67**, 2263 (1963).

**Table I.** Infrared absorption bands ( $\text{cm}^{-1}$ ) as a function of ion exchanger and its loading.

Exchanger	Equilibration conditions	Carboxyl groups			Resin form assumed
		-COOH	COO-M	-COOH	
Dowex A-1 H <sup>+</sup>	HCl conc.	1730 vs	1610 w	1210 s	I
A-1 H <sup>+</sup>	CuCl <sub>2</sub> HCl conc.	1740 vs	1610 w	1200 s	I
A-1 H <sup>+</sup>	CuCl <sub>2</sub> 0.25 M 10 min.	1730 w	1620 s	1215 vw	II+III
A-1 H <sup>+</sup>	CuCl <sub>2</sub> 0.25 M 24 hrs. pH = 3 <sup>a</sup>	—	1620	1215 vw	II+III
A-1 H <sup>+</sup>	CuCl <sub>2</sub> 0.25 M 10 days	—	1620	—	III
A-1 Na <sup>+</sup>	—	—	1620	—	III+IV
A-1 Na <sup>+</sup>	CuCl <sub>2</sub> 0.25 M hrs. pH = 9 <sup>a</sup>	—	1620	—	III+IV
A-1 Na <sup>+</sup>	CuCl <sub>2</sub> 0.25 M 10 days	—	1620	—	III+IV
IRC-50 H <sup>+</sup>	—	1710 vs	1550 vw	1250 vs, 1640 vw	
IRC-50 Na <sup>+</sup>	—	1700 m	1550 w	1260 vs, 1630 w	
IRC-50 Na <sup>+</sup>	CuCl <sub>2</sub> 0.25 M	1700 m	1550 s	1200 w, —	

<sup>a</sup> pH of solution at equilibrium. vs, very strong; m, medium; w, weak; s, strong; vw, very weak.

**Table II.** Visible and near infrared absorption bands as a function of the ion exchangers and their loading.

Exchanger	Equilibration conditions	Absorption max $\text{cm}^{-1}$
Dowex A-1 H <sup>+</sup>	CuCl <sub>2</sub> 0.01 M HCl conc.	24600, 7450-10000
Dowex A-1 H <sup>+</sup>	CuCl <sub>2</sub> 0.5 M HCl conc.	20200, 8330
Dowex A-1 H <sup>+</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub> 0.25 M 10 min.	29300, 14300
Dowex A-1 H <sup>+</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub> 0.25 M 24 hrs.	29300, 14300
Dowex A-1 H <sup>+</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub> 0.25 M 10 days	28300, 11700-15300
Dowex A-1 Li <sup>+</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub> 0.25 M 24 hrs.	28600, 11700-15300
Dowex A-1 Li <sup>+</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub> 0.25 M 10 days	28600, 11700-15300
Dowex A-1 Na <sup>+</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub> 0.25 M	28600, 11700-15300
Dowex A-1 Na <sup>+</sup>	CuCl <sub>2</sub> 0.1 M	27000 sh, 24800, 9900-16600
Dowex A-1 Na <sup>+</sup>	CuCl <sub>2</sub> 0.1 M LiCl 1 M	25300, 16600-10300
Dowex A-1 Na <sup>+</sup>	CuCl <sub>2</sub> 0.1 M LiCl 4 M	23000, 15300-7700
IRC-50 H <sup>+</sup>	CuCl <sub>2</sub> 0.1 M	14300 (sharp)
IRC-50 Na <sup>+</sup>	CuCl <sub>2</sub> 0.1 M	14500 (broad)

styrene matrix. It seems somewhat surprising that a solution of copper ions equilibrated with the hydrogen form of the resin for more than twenty-four hours causes the bands associated with the -COOH group to disappear completely. This type of reaction also occurs in solution, *i.e.* strong complexation or chelation occurs generally at a much lower pH than neutralization by a non-chelating agent. Further it has been determined<sup>7</sup> by pH measurements that upon equilibration of the sodium form of the exchanger by a copper chloride solution an equivalent amount of hydrogen ions to the copper ions sorbed are freed. As the sodium form of the resin by itself shows no unionized carboxylic acid band, it must be assumed that structure IV of Dowex A-1 is formed upon adding copper chloride. This structure formation should be better observable in the 800-1100  $\text{cm}^{-1}$  region of the spectrum, but as already mentioned by Nakamoto,<sup>2</sup> the bands in this region can only be attributed to the absorption of the N-C-C-O group as a whole and thus cannot give a definite answer to this question although some changes in this region have been clearly observed. The bottom rows of Table I show the bands of the carboxylic functional group resin IRC-50. Although their frequencies are similar to some of the iminodiacetate bands, the intensities of the various bands indicate that not all of the carboxylic groups (which are weak acids) are dissociated, *i.e.* the band at 1720  $\text{cm}^{-1}$  does not disappear in the presence of copper or sodium ions.

(7) N. Ben-Zwi, M. Sc. Thesis, Jerusalem, 1965.

**Electronic Spectra.** Measurements in the visible and near infrared region of the spectrum should aid the characterization of the sorbed species. In concentrated hydrochloric acid solution it was inferred that the Dowex A-1 resin would act as an anion exchanger and it was thus expected that similar anionic chloride species would be sorbed as on Dowex-1.

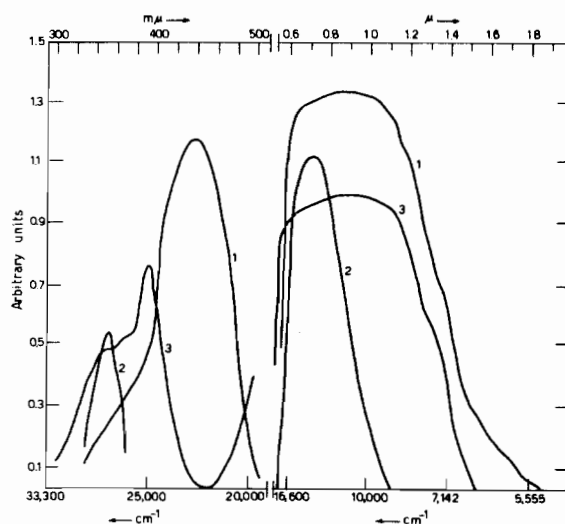


Figure 1. Spectra of copper ions sorbed on Dowex A-1 under various conditions; 1. Dowex A-1/Na<sup>+</sup> after equilibration by CuCl<sub>2</sub> M/2, LiCl 2 M; 2. Dowex A-1/H<sup>+</sup> after equilibration by Cu(NO<sub>3</sub>)<sub>2</sub> M/40 (24 hours); 3. Dowex A-1/Na<sup>+</sup> after equilibration by CuCl<sub>2</sub> M/10.

As may be seen from Table II and Figure 1, two species seem to be sorbed under the experimental conditions. The concentration of the copper ions and hydrochloric acid in the initial solution determine the species (or composition of the mixture of species) sorbed. From a dilute copper solution a yellow species is sorbed. From a concentrated copper solution a brown species (or a mixture of two species) is sorbed. The spectra of these two forms of the acidic exchanger are different, but yet very similar to the spectra obtained from Dowex-1 under the same experimental conditions.<sup>1</sup> These two species were previously identified as  $\text{CuCl}_4^{2-}$  and  $\text{CuCl}_3\text{H}_2\text{O}^-$ .<sup>1</sup> Table II also shows the spectra of the sorbed copper ions on the hydrogen and sodium forms of the exchanger in the absence of excess acid. Some of the phenomena observed were similar to those in the IR spectra, *i.e.* the copper species on the hydrogen form of the resin has a different spectrum from that obtained from the sodium form only during the first 24 hours of equilibration. If the resin is allowed to remain in contact with the copper solution for more than 24 hours, then the spectrum becomes nearly identical with the initial sodium form.

Similar spectra are obtained from solutions of copper ions and the monomeric iminodiacetate and from copper ions sorbed on the carboxylic resin IRC-50. While the d-d band in the spectrum of the copper ions sorbed on the hydrogen form of the resin is a rather sharp one with a maximum at  $14300\text{ cm}^{-1}$ , (this band is usually found for octahedral copper carboxylates<sup>8</sup>) the spectrum obtained from the initial sodium form of the exchangers shows a very strong broadening of the maximum which extends between  $15300\text{--}11700\text{ cm}^{-1}$ , *i.e.* a slight shift to higher energies takes place. This shift may be attributed to the co-ordination of the copper by nitrogen on the chelating functional group (spectrochemical series), although the broadness of the band may also obscure the overlapping spectra of two species, which are sorbed under these conditions. The co-ordination sites on the copper cannot be filled by the IDA group if, as is believed, not more than one IDA group is linked to the copper. Thus, presumably water or some other molecule will satisfy the co-ordination requirement of the copper ion. Spectral measurements have indeed shown that there is a difference between the blue coloured resin obtained by sorbing copper ions from an aqueous solution and the green coloured resin obtained by equilibrating the chelating resin with a solution containing copper in the presence of a high concentration of chloride ions. The maximum absorption region shifts from  $9900\text{--}16600\text{ cm}^{-1}$  to  $7700\text{--}15300\text{ cm}^{-1}$ , showing that the chloride concentration has a strong influence on the spectrum. The charge-transfer band also shifts from  $28600$  to  $25300\text{ cm}^{-1}$ .

**E.S.R. Spectra.** Figure 2 shows the e.s.r. spectra of copper ions sorbed on various ion exchangers and of some frozen copper solutions, all the spectra being

run at  $-160^\circ\text{C}$ . As can be seen from the curves, the resolution obtained is very good. Ion exchangers are thus seen to be good media for measurements of this type, mainly because they enable a satisfactory magnetic dilution to be made. Even at room temperature many of the spectra recorded show a good resolution.

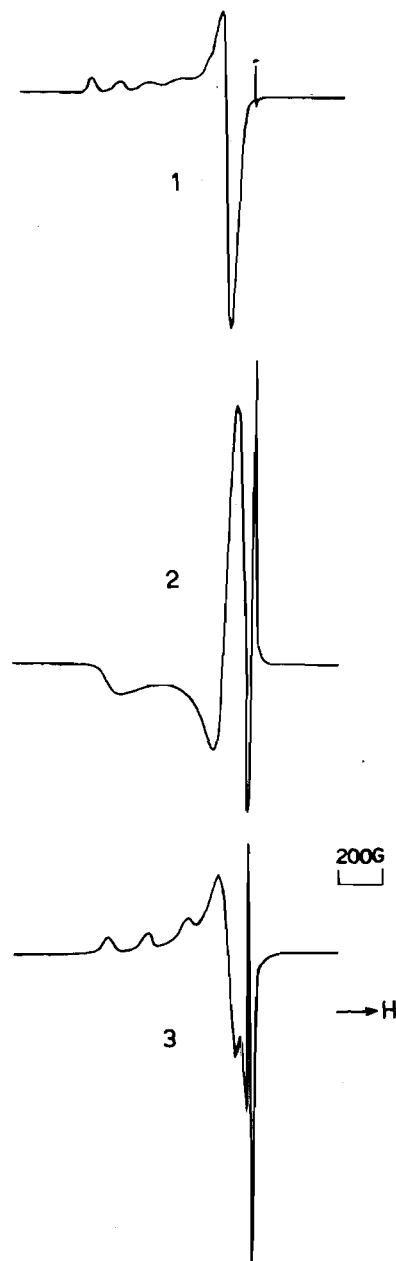


Figure 2. ESR spectra of copper ions sorbed on: 1. Dowex 50 W and IRC-50; 2. Dowex 1 and Dowex A-1 in concentrated hydrochloric acid; 3. Dowex A-1 in neutral solution. \*DPPH peak.

As may be seen from Figure 1, three types of spectra were obtained. The first spectrum is resolved into  $g_{\parallel}$  and  $g_{\perp}$ , and the  $g_{\parallel}$  further shows hyperfine splitting into four lines. The second spectrum

(8) A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier Publ. Comp., 1968, p. 360.

Table III. E.S.R. data for various copper species sorbed on ion exchangers

Resin	Equilibration conditions	Species sorbed assumed	$g_{\parallel}$	$g_{\perp}$	$A_{cm}^{-1}$	$B_{cm}^{-1}$	$\alpha^2$
Dowex-50	$Cu(NO_3)_2$ 0.004 M	$Cu(H_2O)_6^{2+}$	2.405	2.082	0.151	—	0.90
IRC-50	$Cu(NO_3)_2$ 0.002 M	$(H_2O)_4Cu \begin{cases} OOC-R \\ OOC-R \end{cases}$	2.32	2.074	0.142	—	0.79
Dowex-1 yellow	$CuCl_2$ 0.004 M HCl conc.	$CuCl_4^{2-}$	2.365	2.084	—	—	—
Dowex-1 brown <sup>a</sup>	$CuCl_2$ 0.1 M HCl conc.	$CuCl_3H_2O^-$	$g_{ave}$ 2.123	—	—	—	—
Dowex A-1 H <sup>+</sup>	$CuCl_2$ 0.004 M HCl conc.	$CuCl_4^{2-}$	2.365	2.084	—	—	—
Dowex A-1 H <sup>+</sup>	10 min. $CuCl_2$ 0.001 M		2.278	2.088	0.183	0.032	0.86
Dowex A-1 H <sup>+</sup>	24 hrs. $CuCl_2$ 0.001 M		2.257	2.062	0.194	0.031	0.864
Dowex A-1 Na <sup>+</sup>	$Cu(NO_3)_2$ 0.001 M		2.258	2.064	0.194	0.031	0.864
Frozen soln. $CuCl_2$	$CuCl_2$ 0.05 M HCl conc.	$CuCl_4^{2-} + CuCl_3^-$	2.34	2.081	—	—	—
Frozen soln. CuIDA	$Cu(NO_3)_2$ : IDA = 1:5	$Cu(IDA)_2$	2.278	2.067	0.170	0.032	0.812

<sup>a</sup> No splitting into  $g_{\parallel}$  and  $g_{\perp}$  is obtained apparently because of the high copper concentration.

was also resolved into  $g_{\parallel}$  and  $g_{\perp}$ , but the  $g_{\parallel}$  in this case shows three hyperfine lines, while the  $g_{\perp}$  shows a single line splitting. The lowest spectrum is resolved only into  $g_{\parallel}$  and  $g_{\perp}$ . Similar spectra to the above may be found in the literature.<sup>9</sup> The  $g$ ,  $A$ ,  $B$  and  $\alpha^2$  values are presented in Table III. As was expected the  $g$  values calculated for the copper ions sorbed on the Dowex-50 and IRC-50 resins agree well with those determined by Faber and Rogers,<sup>10</sup> and also with the  $g$  values calculated for similar aqueous solutions by Lewis, Alei and Morgan.<sup>9</sup> The  $g$  values evaluated for the Dowex-1, *i.e.* sorbed  $CuCl_4^{2-}$ , are similar to those of Furlani *et al.*<sup>11</sup> and to  $CuCl_2$  in concentrated hydrochloric acid solution as well as being identical with those of the same ion sorbed on Dowex A-1 resin in concentrated hydrochloric acid.

In general, the trend in  $g$  and  $A$  values corresponds to the predicted covalency of the species studied. Gersman and Swalen's<sup>12</sup> relationship was used for the determination of  $\alpha^2$ .

$$\alpha^2 = -\frac{A}{P} + (g_{\parallel}-2) + 3/7(g_{\perp}-2) + 0.04$$

For  $P$  the value of  $0.036 \text{ cm}^{-1}$  was used. This formula does not give big differences in the covalencies of the various species. It would have been preferable to evaluate  $\alpha^2$  with the aid of parameters from the electronic spectra. Unfortunately, in most cases only one broad unresolved d-d absorption band was recorded, thus not allowing any precise calculations.

**Concluding Remarks.** From the experiments carried out in the present study some conclusions may be drawn as to the configuration of the different species sorbed on the Dowex A-1 exchanger. Electronic and e.s.r. spectra demonstrated clearly that

the tetrahedral  $CuCl_4^{2-}$  species is sorbed on this resin from dilute copper solutions in concentrated hydrochloric acid the resin being in form I. From more concentrated copper ion solutions another tetrahedral copper chloride species, probably  $CuCl_3(H_2O)^-$ , is sorbed.<sup>1</sup> The Dowex A-1 resin acts under these conditions only as an anion exchanger,<sup>13</sup> behaving very similarly to the Dowex-1 resin. When the hydrogen form of Dowex A-1 resin is equilibrated with solutions of hydrated copper ions two reactions take place, the first being a fast partial complexation by the carboxylic groups (forms II and III) followed by slow chelation to the nitrogen group (form IV). After equilibration for 24 hours, the spectrum obtained from the hydrogen form becomes identical with that of the initial sodium form. As was found in previous work,<sup>7</sup> an equivalent amount of hydrogen ion is dissociated for each copper atom chelated to the sodium form of the Dowex A-1 resin. These data infer that after 24 hours the hydrogen form of the exchanger as well as the sodium form are exchanged by copper ions linked to the iminodiacetate group as tridentate ligands. In each of these cases it must be assumed that a molecule of water completes the coordination of the copper to some square planar coordination. This molecule of water may be replaced by a chloride ion as may be seen from the electronic spectra (Table II), similarly to the replacement by the aminocarboxylic acids in the work of Schmuckler.<sup>4</sup> An attempt was also made to elucidate the type of bonding by the e.s.r. spectral measurements. An increase in the  $A$  value and a decrease in  $g$  have been related to increasing covalent character.<sup>14</sup> The  $\alpha^2$  values calculated from this data show rather small differences in covalencies. The bonding of copper by the iminodiacetate group seems to be more ionic than covalent ( $\alpha^2 = 0.5$  being purely covalent). This high  $\alpha^2$  is not so surprising when it is considered that an  $\alpha^2$  value has been determined to be 0.84 for Cu-EDTA by Kivelson and Neiman.<sup>15</sup>

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(13) D. G. Birney, E. E. Blake, P. R. Meldrum and P. M. E. Peach, *Talanta*, **15**, 557 (1968).

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(15) D. Kivelson and R. Neiman, *J. Chem. Phys.*, **35**, 149 (1961).