Inorganica Chimica Acta, 154 (1988) 141–155

Synthesis and Characterization of Chelating Ion-exchange Resins: a Spectral Study of Copper(II) Complexes of Chelating Ion-exchange Resins Containing Multidentate Imidazole Moieties

SURESH K. SAHNI*, WILLEM L. DRIESSEN and JAN REEDIJK**

Department of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

(Received April 7, 1988)

Abstract

The synthesis and characterization of several chelating ion-exchange resins incorporating one or more tridentate ligands containing the imidazole group, *i.e.* [bis(benzimidazol-2-ylmethyl)]amine, anchored on microporous and macroporous styrene-DVB copolymers and phenol-formaldehyde condensate matrices, are described. The ligating behaviour of these chelating ion-exchange resins towards copper(II) ions has been studied. The nature of bonding of the chelated/adsorbed species and their structure have been elucidated on the basis of their spectroscopic (infrared, electronic and electron spin resonance) properties. Both five- and six-coordinated copper(II) complexes seem to be formed on the polymeric matrices, and in some cases more than one type of copper(II) species have been found to be present together, as a function of pH. The marked selectivity of one of the resins designated as ES-466B for copper(II) ions has been rationalized in terms of nature of the polymeric matrix and other steric factors responsible for adoption of an unusual stereochemistry in the polymer system.

Introduction

In recent years, an increasing number of chelating ion-exchange resins, containing a variety of chelating groups incorporated in different types of matrices, have been synthesized and evaluated for their selectivity towards different metal ions [1–3]. Some of the important applications of chelating ion-exchange resins include water treatment [4, 5], and recovery of metal ions from metallurgical and industrial effluent solutions [6, 7]. The selective ion-exchange phenomenon in a system mainly depends on a combination of factors, such as the metal–ion chemistry in aqueous solution and polymer phase, the structure of ionogenic functional groups in the polymer phase and the macromolecular structure as present under the separation conditions. Warshawsky [3] pointed out that each of these three major factors has to be adapted for a particular separation problem, and only a successful meeting of the three factors leads to an effective and useful separation system. The structure of ionogenic groups in the cross-linked polymers can be elucidated by studying the spectral properties of metal complexes formed by chelating ion-exchange resins. Such a study is also expected to facilitate the development of a relationship between selectivity and various factors such as steric ones, denticity and nature of the donor atoms present in a chelating ion-exchange resin [8].

Any multidentate ligand system known for its affinity for a particular group of metal ions could be suitable for the development of an efficient chelating ion-exchange resin system, provided such ligands can be incorporated into a polymeric matrix without adding to the already existing cross-linking in the polymeric system by way of inter- and intra-strand cross-linking mechanism. One such group of versatile ligands is that of multidentate imidazole derivatives known for their chelating abilities for transition metal ions. Detailed studies on the nature of bonding and molecular structures of the metal complexes of benzimidazole derivatives are available [9]. However, no attempt appears to have been made to anchor such multidentate benzimidazole ligands on cross-linked polymeric matrices and to study their ligating behavior towards different metal ions to develop new types of chelating ion-exchange resin systems. The development of such polymeric ligands can also be useful as chelating supports for heterogenized homogeneous catalysts [10a] and to study the reaction mechanisms in the biological systems involving imidazole and benzimidazole derivatives [10b]. The good binding properties of benzimidazole have recently been explored to develop polybenzimidazole-supported metal catalysts, because of their remark-

---

*Present address: Department of Chemistry, Polymer Research Institute, State University of New York, Syracuse, N.Y. 13210, U.S.A.

**Author to whom correspondence should be addressed.

0020-1693/88/$3.50

able thermal stability [11a–11c] and also for binding of small organic molecules [11d] and precious metal ions [11e].

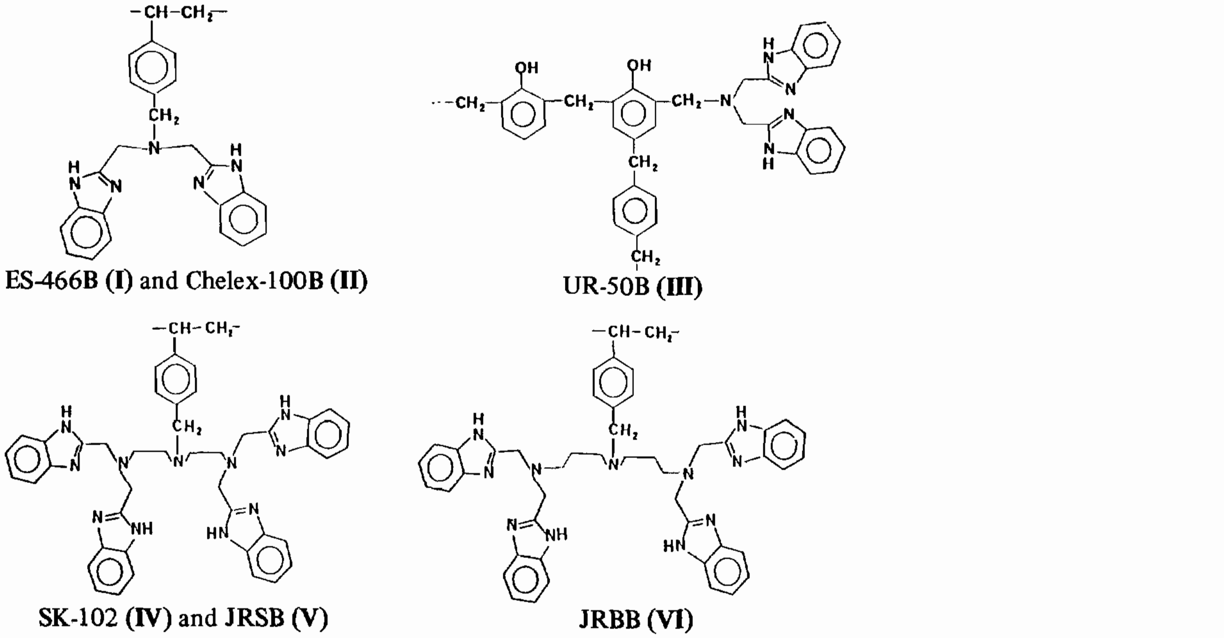
A spectral study of the metal complexes of imidazole supported on a styrene-DVB copolymer matrix has been reported [11f] and some scattered studies on the spectral features of metal complexes of other chelating ion-exchange resins are also available [12]. In continuation to our previous studies on the chelating ion-exchange resins Chelex-100 [13], Spheron Oxine-1000 [14] and ES-467 [15], the synthesis and characterization of novel chelating resins containing one or more tridentate moieties, [bis(benzimidazol-2-ylmethyl)]amine, incorporated into microporous and macroporous styrene-DVB copolymers and phenol-formaldehyde condensates and their ligating behavior towards transition metal ions, particularly copper(II), are described in this paper. The tentative structures of these chelating ion-exchange resins are schematically depicted in Fig. 1.

Experimental

Methods and Materials

Elemental analyses (C, H and N) were performed by microanalytical laboratories of E. Pascher, Bonn, F.R.G. and P. van den Bosch, Technical University, Eindhoven, The Netherlands. The metal analyses were carried out by digesting the metal-containing resins, or beads of resins, with nitric and sulfuric acid, followed by measurements with atomic absorption spectroscopy, employing a Perkin-Elmer 460 atomic absorption and flame spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 580 spectrophotometer equipped with a data station. Ligand field spectra were recorded in the diffuse reflectance mode on a Perkin-Elmer 330 spectrophotometer also equipped with a data station, using a zinc(II) complex of the same resin under study, as a reference [13–15] for both wet and dried samples in the region 5000–33 000 cm^{-1}. The electronic spectra of the high-loaded metal complexes prepared under different conditions were recorded to find out the geometry around the metal ions. In the case of the low-loaded metal complexes, the d–d transitions originating from the ligand field spectra of the metal ions are masked by intra-ligand bands making the assignments of these bands difficult. However, in the case of the high-loaded metal complexes, the d–d transitions can easily be discerned. Electron spin resonance spectra at X-band frequencies at ambient and liquid nitrogen temperature were measured on a Varian E-3 spectrometer.

Analytical grade metal salts were used throughout and well-dried organic solvents were employed for the synthesis. All metal-uptake experiments were carried out in polyethylene bottles. The details of various buffer solutions used are: sodium chloride–hydrochloric acid (pH = 1–1.25), sodium acetate–acetic acid (pH = 3–6) and Tris [tris(hydroxymethyl)-aminoethane]–hydrochloric acid (pH = 7). Below pH 1 pure hydrochloric acid and above pH 7 dilute



ES-466B (I) and Chelex-100B (II)

UR-50B (III)

SK-102 (IV) and JRSB (V)

JRBB (VI)

Fig. 1. Tentative schematic structures of benzimidazole-containing chelating ion-exchange resins derived from ES-466 (ES-466B, I), Chelex-100 (Chelex-100B, II), UR-50 (UR-50B, III), *N*-tetracarboxylic acid derivative of immobilized diethylenetriamine (SK-102, IV), polymer-supported diethylenetriamine (JRSB, V), and immobilized iminobispropylamine derivative (JRBB, IV).

solutions of sodium hydroxide were used, respectively.

The commercial chelating resins ES-466, Chelex-100 and Unicellex UR-50 used as the starting materials for the synthesis of some of the benzimidazole-containing chelating resins were procured from Duolite International Inc., Vitry Sur Seine, Paris, France; Bio.Rad, Richmond, Calif., U.S.A., and Unicellex Division, Unitika Limited, Uji City, Kyoto, Japan, respectively. The other microporous styrene-DVB copolymers used for the preparation of various chelating resins were obtained by suspension polymerization. Chloromethylation of styrene-DVB copolymers was carried out by the method of Pepper *et al.* [16].

Syntheses

The various methods used for the synthesis of benzimidazole-containing resins from iminodiacetic acid resins and polymer-supported diethylenetriamine and iminobispropylamine derivatives are described below.

Synthesis of chelating ion-exchange resins from iminodiacetic acid resins

A general procedure based on the Phillips reaction used for the synthesis of low-molecular weight benzimidazole derivatives [17] was employed for converting commercial iminodiacetic acid containing chelating ion-exchange resins, ES-466, Chelex-100 and Unicellex UR-50, having these groups anchored on macroporous, microporous styrene-DVB copolymers and phenol-formaldehyde condensate matrices, respectively, into benzimidazole derivatives. The corresponding benzimidazole derivatives are designated as ES-466B (**I**), Chelex-100B (**II**) and UR-50B (**III**), respectively. Another chelating ion-exchange resin containing [bis(benzimidazol-2-ylmethyl)]amine groups (abbreviated as IDAB), was also synthesized from an iminodiacetic acid resin prepared by the condensation of dimethyliminodiacetate with chloromethylated microporous styrene-DVB (2%) copolymer according to a published procedure [18]. A resin abbreviated as RR_4B was obtained by the condensation of a chloromethylated polystyrene-DVB (2%) copolymer with [bis(benzimidazol-2-ylmethyl)]amine. A general procedure followed for the preparation of the other chelating ion-exchange resins is described below.

(a) From commercial chelating ion-exchange resins. The appropriate commercial chelating ion-exchange resin containing iminodiacetic acid groups in its H^+ form was suspended in ethylene glycol and to this suspension was added an excess of *o*-phenylenediamine. The reaction contents were refluxed around the boiling point of the solvent (*ca.* 200 °C) in a nitrogen atmosphere for *ca.* 150 h [19]. The mixture was filtered hot and washed with copious amounts of a mixture of ethanol–water, water and ethanol and dried at 60 °C *in vacuo* for 24 h.

(b) From polymer-supported N-polycarboxylic acid resins. The polymer-supported diethylenetriamine (**VII**) and iminobispropylamine-*N*-polycarboxylate resins were prepared essentially by a procedure described by Suzuki *et al.* [20], incorporating a slight modification. A Schiff base, [2-(benzylideneamino)ethyl]amine was used instead of bis[2-(salicylideneamino)ethyl]amine. The appropriate *N*-polycarboxylate resin (**VIII**) was converted into a corresponding benzimidazole derivative using the same method as described above in (a). The resin derived from the diethylenetriamine derivative designated as SK-102 (**IV**) is used for these studies.

(c) From polymer-supported polyamine derivatives. A general procedure involving N-alkylation of a polymer-supported amine was adopted. The polymer-supported diethylenetriamine (**VII**) [on a microporous styrene-DVB copolymer (2% DVB)] (10 g, 27.51 mmol N) was suspended in dried dioxane (200 ml) and to it was added an excess of 2-chloromethylbenzimidazole (6.50 g) [17a] and well dried triethylamine (30 ml). The reaction contents were refluxed while stirring under a nitrogen atmosphere for *ca.* 50 h. The resin so obtained was washed subsequently with dioxane, dioxane–ethanol, dioxane–water mixtures, ethanol and water. Finally, it was washed with ether and dried at 75 °C *in vacuo* for 48 h. This resin is designated as JRSB (**V**) and the resin obtained from iminobispropylamine as JRBB (**VI**); however, only the resin JRSB was studied at length. Analytical data of all the resins are listed in Table I. The amount of ligand incorporated into polystyrene-DVB copolymers and their conversion percent are documented in Table II.

Preparation of samples for spectroscopic studies

Two types of metal-loaded samples were prepared. The one type, containing a low metal content, was prepared by the standard-distribution-coefficient method. The other type, containing higher percentages of metal ions, were prepared through the capacity determination method [15]. In a typical experiment, the appropriate metal salt (100, 50, 25 or 10% of the theoretical capacity of the resin) was added to a weighed amount of the air-dried resin (*ca.* 200 mg) and the reaction contents were buffered at a pH between 3 and 7, and shaken at ambient temperature for 24–36 h. The samples for detection of the presence of counter ions of the metal salts on the polymeric matrix were prepared in demineralized water without using any buffer solutions. The samples were thoroughly washed with ethanol and

TABLE I. Analytical Data of the Chelating Ion-exchange Resins and their Metal Complexes

Sample no.	Compound (pH)	Cu (%)	C (%)	H (%)	N (%)	Cl (%)
I	ES-466B		75.10	7.18	8.33	
II	Chelex-100B		75.65	6.39	9.94	
III	UR-50B		68.38	5.56	5.18	
IV	JRSB		70.52	7.15	10.50	0.52
V	SK-102		76.89	6.97	12.75	0.44
VI	JRBB				11.20	0.46
VII	IDAB				9.60	0.42
1[a]	CuCl$_2$–(ES-466B) (6.6)	2.40			7.83	0.29
2	Cu(NO$_3$)$_2$–(ED-466B) (6.6)	2.27			8.12	
3	CuCl$_2$–(ES-466B) (5.5)	3.40	71.59	6.22	7.99	
4	Cu(NO$_3$)$_2$–(ES-466B) (5.5)	3.10			8.09	
5	CuCl$_2$–(Es-466B) (4.0)	2.90			8.50	
6	Cu(NO$_3$)$_2$–(ES-466B) (4.0)	2.10				
7	CuCl$_2$–(ES-466B) (3.0)	1.80			8.58	
8	Cu(NO$_3$)$_2$–(ES-466B) (3.0)	1.20				
9	CuCl$_2$–(ES-466B) (7.0, D.C)[b]	1.02	73.61	6.22	8.88	
10	Cu(NO$_3$)$_2$–(ES-466B) (7.0, D.C)	0.38	73.23	6.79	8.84	
11	CuCl$_2$–(SK-102) (0.8)	0.42				
12	CuCl$_2$–(ES-102) (1.5)	0.72				
13	CuCl$_2$–(SK-102) (2.4)	0.82			11.81	
14	CuCl$_2$–(SK-102) (3.0)	2.00				
15	CuCl$_2$–(SK-102) (4.0)	0.40			11.92	
16	CuCl$_2$–(SK-102) (6.0)	0.16				
17	CuCl$_2$–JRSB (1.2, D.C)	0.20				
18	CuCl$_2$–JRSB (3.0, D.C)	0.29			10.35	
19	CuCl$_2$–JRSB (5.0, D.C)	0.75			10.30	
20	CuCl$_2$–JRSB (7.0, D.C)	0.57				
21	Cu(NO$_3$)$_2$–(Chelex-100B) (3.5)	1.15			9.31	
22	Cu(NO$_3$)$_2$–(UR-50B) (3.5)	1.02			5.12	
23	CuCl$_2$–RR$_4$B [c]	0.85				
24	CuCl$_2$–RR$_4$B	0.51				
25	CuCl$_2$–IDAB [c]	0.50				0.61

[a] The number given to each complex corresponds to the number given to a particular sample in Table IV. [b] Samples isolated from the distribution coefficient experiment. [c] Samples prepared in ethyl acetate.

TABLE II. Amount of Ligands Incorporated into Polystyrene-DVB Copolymers and their Conversion Percent

Resin	Cl (%) (found) original	Cl (%) (found) residual	N (%) (found)	Amount of ligand incorporated[a] (mmol/g resin)	Conversion[b] (%)
ES-466B			8.33	1.19	
Chelex-100B			9.94	1.42	
UR-50B			5.18	0.74	
JRSB	18.5	0.52	10.50	0.68	51.0
SK-102	18.5	0.44	12.75	0.82	61.7
JRBB	21.5	0.46	11.20	0.73	52.2
IDAB	20.8	0.42	9.60	1.37	61.5

[a] The amount of a ligand incorporated (mmol/g resin) = [%N/14*n*] × 10, where %N = found percent of nitrogen in the product and n is the number of nitrogen atoms in a molecule [20]. [b] The conversion% = [%N/14*n*][(L-35.5)%Cl/100] + 35.5/%Cl/100, where L = ligand molecular weight minus 1 and %Cl is the original amount of chlorine present in chloromethylated polystyrene used as starting material. The %conversion is based on the ratio of the actual ligand content to theoretical value calculated from the total displacement of chlorine by a ligand [20, 26].

ether, and dried at *ca.* 70–80 °C *in vacuo* for *ca.* 24 h and analysed for their metal content. Analytical data of the metal complexes are also included in Table I.

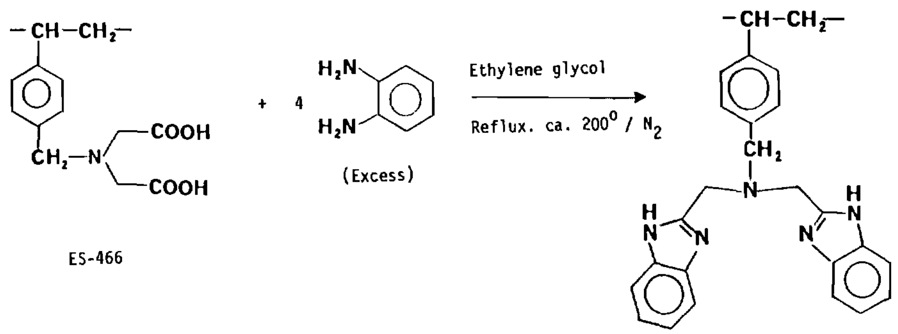
Results and Discussion

Synthesis and Characterization of Chelating Ion-exchange Resins Containing Benzimidazole Derivatives

Various synthetic methods employed for the preparation of low-molecular weight benzimidazoles have been reviewed [17] and the methods for obtaining polybenzimidazoles are also well documented in the literature [21]. The synthesis of vinylbenzimidazole and its derivatives and their copolymers have also been reported [22]. Several examples of imidazole immobilized on the insoluble supports such as cross-linked styrene-DVB copolymers are well known [10, 23]. A number of ion-exchange resins composed basically of cross-linked (divinylbenzene or any other suitable cross-linking agent) recurring units of substituted imidazole and its derivatives have been reported [24]. However, no synthesis of multidentate benzimidazole derivatives anchored on insoluble supports has been reported.

Most of the methods employed for obtaining low molecular weight multidentate benzimidazole ligands can be applicable to the synthesis of the corresponding polymer-supported systems. The low-molecular weight benzimidazole derivatives are generally prepared by the Phillips reaction involving condensation of a carboxylic acid or its derivative with *o*-phenylenediamine in the presence of a mineral acid [17]. A novel approach based on the Phillips reaction has been employed for converting three commercial chelating ion-exchange resins *i.e.* ES-466, Chelex-100 and Unicellex UR-50, all of which contain iminodiacetic acid groups, into their corresponding [bis-(benzimidazol-2-ylmethyl)]amine derivatives, according to a sequence of reactions depicted in Scheme 1.

The progress of the reaction, *i.e.* the conversion of iminodiacetic acid groups into benzimidazole moieties was monitored on the basis of an increase in

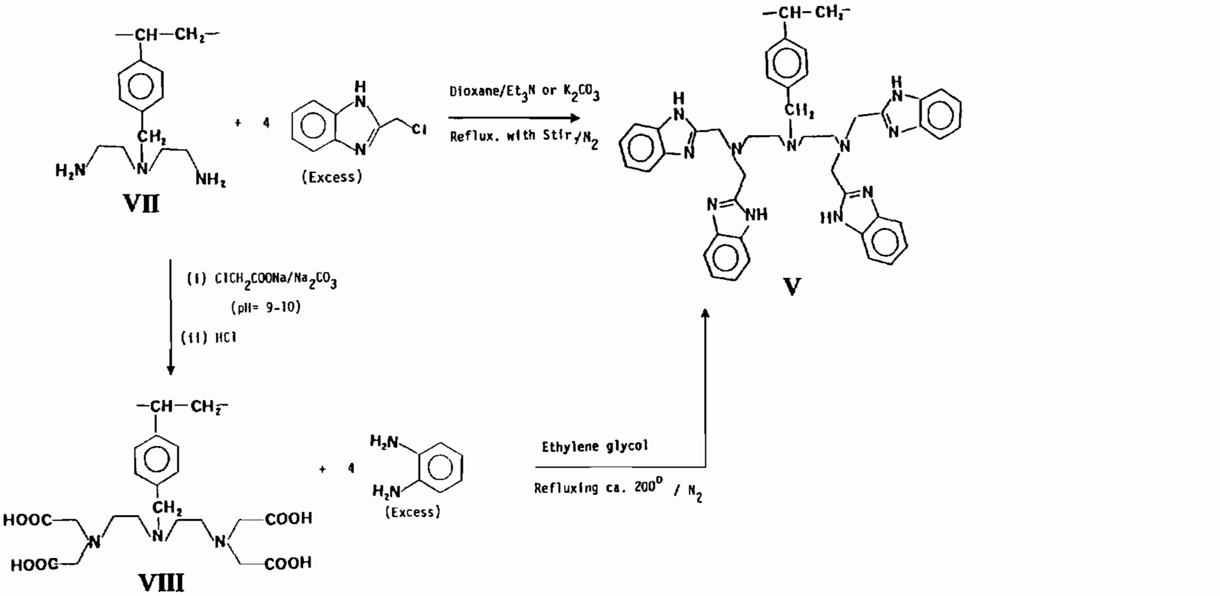


ES-466B (I)

Scheme 1. Reaction sequence depicting the conversion of a commercial chelating ion-exchange resin (ES-466) containing iminodiacetic acid into its corresponding benzimidazole derivative ES-466B (I), employing the Phillips reaction.

the nitrogen content of the product and the infrared spectrum of the sample taken out at regular intervals. A characteristic band of the carboxylic group occurring at *ca.* 1730 cm^{-1} due to m_{asym}CO.O vibrations diminished in intensity as the reaction progressed and the new characteristic bands of benzimidazole derivatives [25] appeared at *ca.* 1650 and 745 cm^{-1} due to C=C and C=N stretching and C—H out-of-plane deformation vibrations, respectively [25]. A stage was reached when no change in the shape and intensity of m_{asym}CO.O vibrations of the iminodiacetic moiety could be observed. The reaction was stopped at this stage. A residual band for the carboxylic acid group was always observed, because of the inaccessibility of all such groups for reaction with *o*-phenylenediamine, probably due to dense nature of the cross-linked polymeric matrix. Various attempts to convert the residual carboxylic acid groups into benzimidazole moieties by employing relatively drastic conditions, *i.e.* refluxing the reaction mixture for longer hours at higher temperatures, very often resulted in breaking and charring of polymeric beads and increased intra-strand cross-linking. The latter was indicated by lack of swelling of the modified resins in various solvents.

The chelating ion-exchange resins designated as SK-102 (**IV**) and JRSB (**V**) were obtained through the modification of the polymer-supported diethylenetriamine and 3,3′-iminobispropylamine derivatives, employing a modified procedure initially suggested by Suzuki *et al.* [20]; the reaction sequences employed for the synthesis of SK-102 and JRSB is depicted in Scheme 2. A benzylidene derivative instead of a salicylidene derivative was used as an intermediate, as phenolic groups are known to react with chloromethylated polystyrene [26]. The polymer-supported amines so obtained show two bands at *ca.* 3380 and 3290 cm^{-1} which can be assigned to m_{asym} and m_{sym} NH_2 vibrations, respectively, and the bands occurring at *ca.* 1620 and 830 cm^{-1} appear to have their origin in bending(NH_2) and $_{wagging}NH_2$ vibrations, respectively. For the preparation of the resin SK-102, an intermediate amine derivative (**VII**) was converted into an *N*-tetracarboxylic acid (**VIII**) which shows characteristic bands at *ca.* 1710 and 1420 cm^{-1} due to m_{asym} and m_{sym}-CO.O vibrations respectively. This resin, like ES-466, was also converted into a benzimidazole derivative through the Phillips reaction. The resin SK-102 shows two characteristic bands of a benzimidazole derivative at *ca.* 1650 and 748 cm^{-1} due to C=C + C=N stretching and C—H out-of-plane deformation vibrations, respectively. The resin JRSB was obtained through N-alkylation of an immobilized amine derivative (**VII**) with 2-chloromethylbenzimidazole in the presence of a base such as triethylamine or anhydrous potassium carbonate (Scheme 2). The N-alkylation of this intermediate (**VII**), having amine functionalities well separated from the benzene ring, was facile; although the N-alkylation of poly(4-aminostyrene) did not proceed well. It appears that the lone pair of electrons present on a nitrogen atom of an amino group directly attached to the benzene ring conjugates with it and hinders the completion of alkylation of such a group. Similar observations have also been made with other low-molecular weight amines.



Scheme 2. Reaction sequences employed for converting an N-tetracarboxylic acid derived from immobilized diethylenetriamine derivative (VIII) into its corresponding benzimidazole derivative (IV) under the Phillips reaction conditions and the immobilized diethylenetriamine itself (VII) into a benzimidazole derivative (V) through its reaction with 2-chloromethylbenzimidazole.

TABLE III. Important Infrared Spectral Bands (cm^{-1}) of Iminodiacetic Acid Chelating Ion-exchange Resins and their Corresponding Benzimidazoles Derivatives

Assignments	ES-466	Chelex-100	UR-50	ES-466B	Chelex-100B	UR-50B	JRSB	Assignment
ν_{asym}CO.O	1740s	1740s	1730s	1735w	1740w	1730w		ν_{asym}CO.O (residual)
νC=C	1600s	1610s	1600s	1640s	1650s	1625s	1648s	νC=C + νC=N
				1610m	1620m	1600m	1630s	
νC–N	1420s	1440s	1418m	1440s	1460s	1470s	1520s	νC=C + νC=N
							1455s	
νC–O + νOH	1250s	1250s	1320m	1420m	1430m	1430m	1430ssh	νC–N
ν_{sym}CO.O	1220s	1210s	1200s	1085s	1090s	1080s	1120s	Benzoid ring breath. vib.
				1040s	1045s	1035s	1025s	
Benzoid ring breath. vib.	1080w	1070m	1080m					
OH	940s		940s	860m	870m	880m	825m	heterocy ring vib.
				770msh	770msh	770wsh	785msh	
δC–H (O.p.[a] benzene ring vib.)	810m	805m		745s	745s	745m	748s	δC–H (o.p. heterocy ring vib.)
δCO.O	650m	660m						

[a] O.p. = out-of-plane vibrations.

Infrared Spectra of Benzimidazole Derivatives and their Metal Complexes

The important bands of different iminodiacetic acid resins and those of the corresponding benzimidazole derivatives are listed in Table III. A number of systematic infrared studies of benzimidazole and its derivatives have been reported [25, 27]. The low-molecular weight benzimidazole derivatives are known to be strongly associated through intermolecular hydrogen bonding and thus show complex spectra. The infrared spectra of benzimidazole exhibit two to three bands in the 1590–1625 cm^{-1} region due to C=C and C=N stretching vibrations. The polymer-supported benzimidazole derivatives also show two such bands at *ca.* 1640 and 1610 cm^{-1}. The 2-substituted benzimidazoles show a characteristic intense band at *ca.* 1550 cm^{-1} [26, 28], though it is not shown by all such compounds; a well-known exception is 2-acetylbenzimidazole [29]. The compounds under study also do not show such a band, instead a rather high intensity band is observed at *ca.* 1350 cm^{-1} due to in-plane skeletal vibrations. In these compounds, the bands occurring at *ca.* 1085–1040 and 860–770 cm^{-1} can be assigned to the benzoid and heterocyclic ring-breathing vibrations, respectively. The most characteristic vibration of 2-substituted benzimidazole derivatives appears to be a high intensity band occurring *ca.* 750 cm^{-1} due to an out-of-plane C–H bending mode [27]. All present immobilized benzimidazole derivatives in fact show a high intensity band at 745–748 cm^{-1}.

The infrared spectra of metal complexes of benzimidazole derivatives have been studied in detail [9a, 30]. Though no striking changes are observed upon coordination, it is well established that the pyridinium tertiary nitrogen atom normally participates in coordination [9d, o]. In copper(II) complexes of the immobilized benzimidazole derivatives, no dramatic changes are observed for any of the characteristic bands; a band occurring at *ca.* 1350 cm^{-1}, however, showed a downward shift of *ca.* 10 cm^{-1}. The infrared spectra of complexes prepared in buffer solutions do not show the presence of counter ions of metal salts. However, in the high-loaded complexes prepared without buffer solutions the presence of such anions as nitrate and sulfate was indicated by elemental analysis and infrared spectra. The charge of copper(II) ions of the complexes prepared in buffer solutions can either be satisfied by the bonding of the benzimidazole moiety in its deprotonated form, by other anionic species still present in the polymeric matrix, by the anions originating from acetate buffers or by ionized residual carboxylic acid groups of iminodiacetic acid resins employed as starting materials. The co-ions or counter ions in such systems have been found to be labile and easily replaceable by other anionic species required for maintaining the electrical neutrality of a polymeric system [31]. The presence of acetate ions (originating from the acetate buffers) in the polymeric matrix of chelating resins has recently been established by infrared spectroscopy [15, 32]. The possibility of the presence of acetate ions in the copper(II) complexes of ES-466B and the other similar resins cannot be ruled out, though examples of coordination of benzimidazole derivatives in deprotonated form are well known [9h, 33].

Electronic and EPR Spectra of Copper(II) Complexes

The ligand field and electron spin resonance spectral data of a selection of copper(II) complexes of the chelating ion-exchange resins containing benzimidazole derivatives, prepared under different conditions of pH and concentration are given in Table IV

TABLE IV. Electronic and Electron Spin Resonance Spectral Data of Copper(II) Complexes of Chelating Ion-exchange Resins Containing Benzimidazole Moieties

Sample no.	Sample (pH)	Ligand field maxima (kK)	EPR parameters		
			$g_\parallel$	$g_\perp$	$A_\parallel$ (G)
1[a]	$CuCl_2$–(ES-466B) (6.6, A.D)[b]	11.63	2.25	2.07	165 (RT)[c]
2	$Cu(NO_3)_2$–(ES-466B) (6.6, A.D)	11.76	2.26	2.06	160 (RT)
3	$CuCl_2$–(ES-466B) (5.5, A.D)	11.50	2.23	2.07	158 (RT)
4	$Cu(NO_3)_2$–(ES-466B) (5.5, dried)	11.76	2.25	2.06	160 (RT)
5	$CuCl_2$–(ES-466B) (4.0, A.D)	11.00	2.24	2.07	160 (77 K)
6	$Cu(NO_3)_2$–(ES-466B) (4.0, dried)	12.00	2.25	2.06	160 (RT)
7	$Cu(NO_3)_2$–(ES-466B) (3.5, A.D)	11.80	2.25	2.06	160 (RT)
8	$CuCl_2$–(ES-466B) (3.5, dried)	11.50	2.26 2.24	2.06 2.07	150 (RT) 160 (77 K)
9	$CuCl_2$–(ES-466B) (7.0, D.C)[d]	11.80	2.24	2.07	155 (RT)
10	$Cu(NO_3)_2$–(ES-466B) (7.0, D.C)	11.76	2.25	2.06	160 (RT)
11	$CuCl_2$–(SK-102) (0.8, A.D.)	15.15, 19.23	2.24	2.09	162 (RT)
12	$CuCl_2$–(SK-102) (1.5, A.D)	13.50, 18.70	2.24 2.24	2.10 2.10	160 (RT) 160 (77 K)
13	$CuCl_2$–(SK-102) (2.40, dried)	13.33, 19.60	2.23 2.23	2.10 2.10	163 (RT) 167 (77 K)
14	$CuCl_2$–(SK-102) (3.0, A.D)	15.27, 19.05	2.22	2.05	175 (RT)
15	$CuCl_2$–(SK-102) (4.0, A.D)	14.26, 23.26	2.24 2.24	2.10 2.10	165 (RT) 155 (77 K)
16	$CuCl_2$–(SL-102) (6.0, dried)	14.39, 23.60	2.25	2.10	150 (RT)
17	$CuCl_2$–JRSB (1.2, D.C)	13.00, 11.20	2.27	2.09	165 (RT)
18	$CuCl_2$–JRSB (3.0, D.C)	13.18	2.24 2.25	2.10 2.09	160 (RT) 160 (77 K)
19	$CuCl_2$–JRSB (5.0, D.C)	13.80	2.24	2.10	160 (RT)
20	$CuCl_2$–JRSB (7.0, D.C)	13.80	2.26 2.27	2.07 2.09	155 (RT) 160 (77 K)
21	$Cu(NO_3)_2$–(Chelex-100B) (3.5, dried)	14.10	2.25	2.10	165 (77 K)
22	$Cu(NO_3)_2$–(UR-50B) (3.5, dried)	11.40	2.27	2.09	160 (RT)
23	$CuCl_2$–RR_4B [e]	10.40, 12.34	2.27	2.09	160 (77 K)
24	$Cu(NO_3)_2$–RR_4B [e] (dried)	10.80, 13.16	2.31	2.11	145 (77 K)
25	$CuCl_2$–IDAB [e] (dried)	14.28	2.27	2.09	160 (RT)

[a] The number of the complex given in this Table corresponds to the number of the complex in Table I. [b] Samples were dried in air only (A.D). [c] Measurements were made at room temperature (RT) or at 77 K. [d] Samples isolated from a distribution coefficient experiment. [e] Samples were prepared in ethyl acetate.

and those of the model and reference compounds in Table V. The EPR spectra recorded at liquid nitrogen temperature do not show any better resolution than those recorded at ambient temperature. The low-loaded copper(II) complexes exhibit well resolved hyperfine splitting patterns contrary to the high-

TABLE V. Electronic and Electron Paramagnetic Resonance (EPR) Spectral Data of some Copper(II) Complexes of Chelating Ion-exchange Resins and Model Compounds

Sample (pH)	Chromophore	Ligand field spectra (kK)	E.P.R. parameters			Reference
$CuCl_2$–Chelex-100[a]	$CuNO_5$	14.50	$g_{av} = 2.14$			13
			$g_\parallel$	$g_\perp$	$A_\parallel$ (G)	
$CuCl_2$–Chelex-100 (low-loading in conc. HCl)	$CuNO_5$	14.50	2.25	2.06	180	13
Cu-Dowex A-1[a]	$CuNO_5$					
hydrated		14.30	2.26	2.06	194	12d
dehydrated	$CuNO_5$	14.30	2.28	2.07	194	
Cu–SphOx-1000[b] (in non-aqueous media)	CuN_2O_2	16.40, 13.90	2.23–2.24		185–195	14
Cu–SphOx-1000 (in aqueous media)	CuN_2O_4	13.90	2.29–2.32		148–160	14
$CuCl_2$ES 467[c] (4.0, low-loading)	CuO_6	11.43	2.34	2.06	135 (77 K)	15
$CuCl_2$–ES-467 (11.5)	CuO_6	11.70	2.28	2.14	140 (RT)	15
$Cu(NO_3)_2$–ES-467	CuO_6	11.76	2.33	2.12	125 (RT)	15
(4.5)			2.33	2.12	130 (77 K)	
$Cu(NO_3)_2$–ES-467 (2.0, low loading)	CuO_6	11.76	2.33	2.07	135	15
Cu–UR-50 (wet)[d]	$CuNO_5$		2.30	2.08	169 (RT)	12a
(3.87) (dried)			2.30	2.08	161 (RT)	
Cu–UR-50 (wet)	$CuNO_5$		2.28	2.07	150 (RT)	12a
(8.60) (dried)			2.28	2.07	169	
$[Cu(NH_3)_6]^{2+}$	$CuN_4N'_2$	11.2, 16.4				34
$[Cu(Im)_6]^{2+}$ [e]	CuN_6	12.5, 16.20				34
$[Cu(edtb)Cl_2]\cdot EtOH\cdot H_2O$ [f]	CuN_3Cl_2	14.10	$g_1 = 2.03, g_2 = 2.14, g_3 = 2.28$			9a
$[Cu(edtb)(NO_3)_2]$	CuN_3O_2	14.30	$g_1 = 2.03, g_2 = 2.12, g_3 = 2.26$			9a
$[Cu_2(edtb)Br_4]$	CuN_3Br_2	14.20	$g_1 = 2.06, g_2 = 2.10, g_3 = 2.28$			9a
$[Cu_2(edtb)(NO_3)_4]$	CuN_3O_2	14.50				9a
$[Cu(ibj)Cl_2]$[g]	CuN_3Cl_2		2.25		164 (77 K)	9b
$[Cu(nnno)Cl]ClO_4$ [h]	CuN_3OCl		2.53		168 (77 K)	9p
$[Cu(nnno)H_2O](NO_3)_2$	CuN_3O_2		2.279		160 (77 K)	9p
$[Cu(bdbz)(NO_3)_2]$ [i]	CuN_3O_2		2.27	2.05	145 (77 K)	9q

[a] Chelex-100 (Bio.Rad) and Dowex A-1 (Dow Chemical Co.) are commercial chelating ion-exchange resins, both of which contain iminodiacetic acid $[(-CH_2-N(CH_2COOH)_2]$ groups anchored on a microporous polystyrene-divinylbenzene (2wt.%) copolymer.

[b] Sphox-1000 is also a commercial chelating ion-exchange resin which contains 8-hydroxyquinoline as chelating groups anchored on poly(hydroxyethylmethacrylate-coethylenedimethacrylate).

[c] ES-467 is another commercial chelating ion-exchange resin containing aminomethylphosphonic acid $[-CH_2NHCH_2P(O)(OH)_2]$ groups anchored on a macroporous polystyrene-DVB copolymer.

[d] UR-50 stands for a commercially available chelating ion-exchange resin Unicellex UR-50 which contains (*o*-hydroxybenzyl)iminodiacetic acid $[HO-C_6H_4-CH_2-N(CH_2COOH)_2]$ groups supported on a phenol-formaldehyde condensate.

[e] Im is imidazole.

[f] edtb is *N,N,N,N'*-tetrakis[(benzimidazol-2-ylmethyl)]-1,2-ethanediamine.

[g] ibj stands for [bis(benzimidazol-2-ylmethyl)]amine.

[h] nnno is *N,N*-[bis(benzimidazol-2-ylmethyl)]ethanolamine.

[i] bdbz stands for [bis(benzimidazol-2-ylmethyl)]benzylamine.

loaded samples, apparently because of some weak Cu–Cu interactions resulting in disappearance of the fine structures in the latter species. There has also been observed considerable line-broadening attributable to dipolar interactions as a result of restricted movement of the copper ions caused by their complexation with a chelating moiety of an ion-exchanger.

The copper(II) complexes of the chelating resin designated as ES-466B prepared in the pH 3–7 range show a band at *ca.* 11 000–12 500 cm^{-1} with a tail on the low energy side and a weak band at *ca.* 21 000–22 000 cm^{-1}. The occurrence of a band at relatively low energy *ca.* 11 000–12 500 cm^{-1} clearly is too low to be associated with a four-coordinated square planar or tetragonal and six-coordinated pseudo octahedral structure. The ligand field spectra of such copper(II) complexes having a chromophore of combination of oxygen and nitrogen donor atoms are known to exhibit a band at higher energy in the range 13000–20000 cm^{-1} [34]. The spectra of the complexes under study seem to be compatible with a five-coordinated stereochemistry, similar to one found for the copper(II) complexes of tridentate [bis(benzimidazol-2-ylmethyl)]amine [9b], the chelating moiety present in the ion-exchange resin ES-466B. It appears that these complexes possess a chromophore CuN_3O_2 in which three nitrogen atoms are provided by the chelating moiety and the coordination sphere is completed by water molecules. This view is also supported by electron resonance spin spectra of these complexes. The values of $g_\perp$, $g_\parallel$ and $A_\parallel$ lie in the range 2.05–2.10, 2.22–2.25 and 150–175 G, respectively, for the copper(II) complexes reported herein. The values observed for different parameters are close to those found for the ammoniated copper(II) complexes adsorbed on different ion-exchange resins [35] and also resemble those observed for the copper(II) complexes of other chelating ion-exchange resin such as Chelex-100 [13], Spheron Oxine-1000 [14], Dowex A-1 [12d] and UR-50 [12b], all of which contain a common chromophore $CuNO_5$. However, the values of various EPR parameters are quite different from those found for copper(II) complexes of Amberlite IRC-50 and ES-467, possessing a chromophore CuO_6 (Table V). It may be pointed that, unlike the high-loaded copper(II) complexes of the other chelating ion-exchange resins with a microporous matrix, the high-loaded complexes of the resin ES-466B show hyperfine splitting, possibly due to their macroporous matrix having copper(II) ions present in rather isolated channels. The possibility, that these complexes contain some six-coordinated species, cannot be completely ruled out, because of their isolation from a predominantly aqueous medium. However, the close proximity of the tertiary imino nitrogen atom to the dense cross-linked polymeric matrix and various steric factors present in the system seem to favor a five-coordinate structure. The ligand field spectra have very often been used for distinguishing the various types of five-coordinated copper(II) complexes, however, a great deal of caution is required in using such empirical criterion [34–37]. Thus, no attempt has been made to assign the stereochemistry of the complexes of chelating ion-exchange resin ES-466B.

The copper(II) complexes of a resin designated as SK-102, containing two units of [bis(benzimidazol-2-ylmethyl)]amine per styrene ring exhibit two types of ligand field spectra. The complexes prepared at lower pH show a band at *ca.* 13300–15200, with a weak band around 18700–19600 cm^{-1}. The lower energy band at *ca.* 13300 cm^{-1} resembles the one also exhibited by the [Cu(edtb)X_2] complexes, where edtb stands for *N,N,N′,N′*-tetrakis[(benzimidazol-2-ylmethyl)]-1,2-ethanediamine and X = Cl, Br or NO_3 [9e]. These complexes have been shown to possess a $d_{x^2-y^2}$ based ground state, usually associated with a distorted square pyramidal geometry, as established on the basis of EPR spectra [38–40]. The g_1 values observed for the SK-102 complexes (Table III) are intermediate of those of g_1 and g_2 found for the edtb complexes. Thus, it appears that the copper complexes of SK-102 might also have some five-coordinated species present on the polymeric matrix of SK-102. The occurrence of a higher energy band at *ca.* 18700–19600 cm^{-1} has also been observed for tetragonal octahedral and square planar copper(II) complexes [41], though the latter type of complexes exhibit ligand field maxima at slightly higher energy *ca.* 18000–20000 cm^{-1} [42]. The occurrence of a higher energy band in the complexes of SK-102 indicates probably the presence of some species with a chromophore CuN_4 characteristic of a tetragonal or a square planar geometry [43]. However, the possibility of these complexes also having a chromophore CuN_2O_2 cannot be ruled out. The square planar copper complexes with a chromophore CuN_2O_2 exhibit a broad structured band in the 13000–20000 cm^{-1} and its intensity has been shown to vary in the order $CuN_4 > CuN_2O_2 > CuO_4$ [44]. In the present complexes, the oxygen donors can either be provided by water molecules, acetate or hydroxide ions known to be present in such systems [31] or the residual carboxylic acid groups of iminodiacetic acid moieties (*vide infra*). Accordingly, the occurrence of a higher energy band can be interpreted in terms of the increased equatorial bonding presumably resulting by the substitution of H_2O with OH^- or acetate ions, as also supported by higher $A_\parallel$ values (Table IV) which lie in the range 165–175 G for the complexes of SK-102 [45]. The coordination through the residual amino group can also be responsible for the higher $A_\parallel$ values [15].

The complexes prepared at the higher pH also show a ligand field maxima at *ca.* 14400, along with a weak band *ca.* 23500 cm^{-1}. The occurrence of the main band at *ca.* 14000 cm^{-1} is consistent with a distorted square pyramidal geometry with a ground state $d_{x^2-y^2}$, like the low-molecular weight [Cu(edtb)-X_2] and [Cu_2(edtb)X_4] complexes which also show a well defined band at *ca.* 14300 cm^{-1} [9e]. A band occurring around 23500 cm^{-1} is too high in energy to have its origin in d–d transitions. Such bands originate in ligand to metal charge-transfer phenomena. Similar bands have also been observed in $[Cu(NCS)_4]^{2-}$ (21000–25000 cm^{-1}) [46] and copper proteins such as azurin and plastocyanin due to copper imidazole (LMCT) [34]. The occurrence of a well defined band at *ca.* 13000–13800 cm^{-1} in the low-loaded complexes of a resin designated as JRSB resemble those of the copper(II) complexes of a tripod ligand [tris(benzimidazol-2-ylmethyl]-amine [9b]. The complexes obtained from the resin UR-50B exhibit maxima at *ca.* 11 400 cm^{-1} which again indicate that some five-coordinated copper(II) species are present on this resin; the copper(II) complexes of Chelex-100B show maxima at much higher energy at *ca.* 14 100 cm^{-1} consistent with a pseudo octahedral structure [34].

From the preceding discussion, it is obvious that the nature of the polymeric matrix of an ion-exchange resin plays an important role in shaping the stereochemistry of metal complexes adsorbed on it. For instance, mainly five-coordinated copper(II) complexes are formed in the highly cross-linked macroporous styrene-DVB (15–20%) copolymer matrix present in the chelating ion-exchange resin ES-466B and also UR-50B having chelating groups incorporated in a condensate of phenol-formaldehyde. These highly cross-linked matrices appear to present more steric constraints in shaping the stereochemistry and configuration of the coordination polyhedra of the chelated species present on them than those on the chelating resins SK-102 and JRSB having benzimidazole derivatives anchored on the lightly cross-linked styrene-DVB (1–2%) copolymers. The latter two resins have been found to form both five- and six-coordinated complexes and resemble closely the ligating behavior of their low-molecular weight analogue, *N,N,N′,N′*-tetrakis[(benzimidazol-2-ylmethyl)]-1,2-ethanediamine. It is apparent that the polymeric matrix of chelating ion-exchange resins contributes significantly to their selectivity.

Stoichiometry and Tentative Structures of the Metal Complexes of Polymer-supported Benzimidazole Derivatives

The fact that the resin, designated as ES-466B, contains approximately 15% DVB indicates that the chelating moiety, [bis(benzimidazol-2-ylmethyl)]-amine present in this resin is not expected to be as flexible as it would be in the unimmobilized state. The resins SK-102 and JRSB, obtained by modification of styrene-DVB copolymers (*ca.* 1–2 wt.% DVB), which contain two such chelating moieties per styrene ring, are expected to be less rigid than such groups present in the ES-466B. The chelating resins Chelex-100B and UR-50B may be expected to possess an intermediate flexibility. The chelating resins like Chelex-100 and Dowex A-1 containing iminodiacetic acid groups anchored on styrene-DVB copolymers (2% DVB) have been shown to form only 1:1 (metal:ligand) complexes; the possibility of formation of 1:2 complexes has been excluded in view of their cross-linked structure. A similar behavior has also been encountered for the metal complexes of the chelating ion-exchange resin ES-467, containing a potentially tridentate moiety aminomethylphosphonic acid anchored on a highly cross-linked macroporous styrene-DVB copolymer [15]. Following the preceeding arguments of rigidness caused by increased cross-linking, it is likely that ES-466B also forms only 1:1 (metal:ligand) complexes. This is also indicated by the elemental analysis of some of its high-loaded copper chloride and nitrate complexes, and it is also adduced from their ligand field and EPR spectra (*vide infra*). The low molecular ligand edtb, containing two tridentate chelating moieties, has not been found to form 1:2 metal complexes with copper either; instead, complexes of the type $[Cu(edtb)X_2]$ and $[Cu_2(edtb)X_4]$ are formed, depending upon the metal to ligand stoichiometry employed. The complexes of SK-102 show a band at *ca.* 18 000–19 000 cm^{-1}, normally present only in the copper complexes with a chromophore CuN_4 [36]. The elemental analysis of these complexes could not be of much help because of their low loading. Thus, it seems that all these chelating ion-exchange resins with multidentate benzimidazole moieties form only 1:1 complexes with copper(II) ions. The chelating moiety, [bis(benzimidazol-2-ylmethyl)]amine acts as a tridentate chelating ligand like its low-molecular weight analogue, and the coordination sphere of the complexes is completed by two or three molecules of water. It is also likely that a metal ion could be chelated through an imino and pyridinium nitrogen atom, along with an oxygen atom of the residual carboxylic acid in the chelating resins derived from the iminodiacetic acid resins (*vide infra*) and the rest of the coordination sphere is again completed by water molecules. The schematic tentative structures of various complexes formed by these chelating ion-exchange resins ES-466B and SK-102 and JRSB are depicted in Figs. 2 and 3, respectively.

Distribution Coefficients and Selectivity

The distribution coefficients of various benzimidazole containing resins were determined for cobalt(II), nickel(II), copper(II), zinc(II) and calcium(II) in the pH range 1–7 at a constant ionic strength at room temperature. The detailed results of this part of the investigation will be published in a separate publication; however, it is worth mentioning here that only the resin ES-466B shows a very high selectivity for copper(II) ions. It is obvious from the plots of log D [where D (distribution coefficient) = amount of metal ion per gram of dry resin/amount of metal ion per ml of solution] *versus* pH that the distribution coefficients for copper(II) ions differ from all the other metal ions studied by a factor of 10^4, which attains an optimum value in the pH range 4.0–5.5 and is larger for copper chloride than for copper nitrate or sulfate. The resin ES-466B hardly takes up any significant amounts of cobalt(II) and nickel(II) in the pH range 1–7, whereas it absorbs a very small

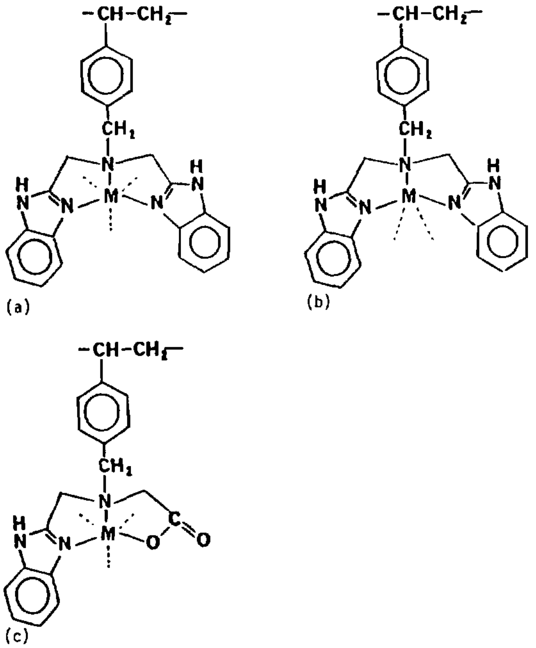


Fig. 2. Tentative schematic structures of copper(II) complexes formed by ES-466B (a) and (b) and its intermediate (c); the broken lines depict the coordination sites to be filled by water molecules or other monodentate ligands and M = Cu(II).

amount of iron(III) and zinc(II). Thus, the chelating resin ES-466B appears to be highly selective for copper(II) ions in the pH range 2–7 and can be used for the separation of copper(II) from a mixture of a number of other metal ions.

The capacity of ES-466B was found to be *ca.* 36 g/kg, about 33% of the theoretical value calculated on the basis of its elemental analysis (Table I). The relatively low capacity of ES-466B can be attributed to (a) incomplete conversion of all the iminodiacetic acid groups present in ES-466 to benzimidazole moieties and (b) inaccessibility of all the benzimidazole groups for complexation with the metal ions. Similar observations have also been made for other chelating polymers containing tri- and tetradentate derivatives of *N,N'*-bis(2-pyridylmethyl)-2,2'-diaminobiphenyl and *N*-(2-pyridylmethyl)-2,2'-diaminobiphenyl [26, 32], which have been shown to possess capacities corresponding to 20 to over 90% utilization of chelating sites, depending upon the structure of the ligand. The low capacity of these chelating resins has been assigned, among other factors, on the polymer attachment site which can result in compression or distortion of ligand site by the contiguous polymer backbone. However, it could not be established whether the various steric factors present in chelating resins affect the stereochemistry

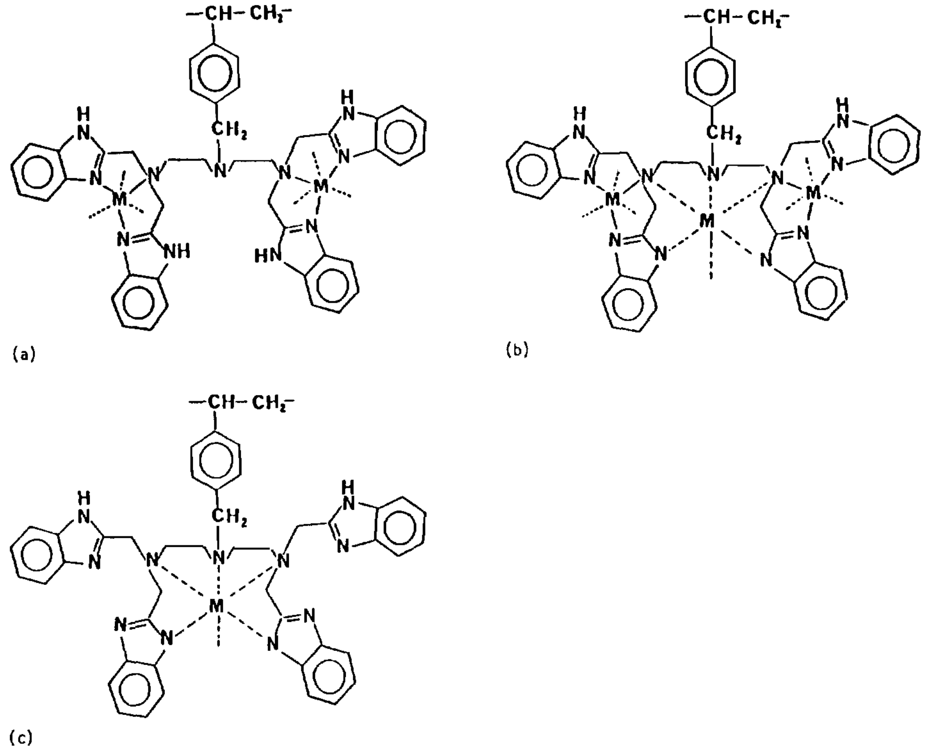


Fig. 3. Possible schematic structures of copper(II) complexes of chelating resins SK-102 and JRSB containing two tridentate [bis-(benzimidazol-2-ylmethyl)]amine moieties per styrene ring; broken lines indicate the potential coordination sites to be filled by water molecules or other monodentate ligands (a) and also depict the other potential coordination sites (b) and (c); M = Cu(II).

of the ligand or whether it is simply a matter of bulk shielding the ion cavity [26]. The same seems to be true for the ES-466B. Further work is in progress to establish the nature of the various factors responsible for relatively low capacity of ES-466B. The capacity of ES-466B is, however, comparable to other commercial chelating resins XF- or XFS-4195 and XFS-43084, having tridentate bispicolylamine and *N*-(2-hydroxypropyl)picolylamine, respectively, attached to macroporous styrene-DVB copolymers [48]. The resin XFS-4195 has been reported to be selective for copper(II) ions only and the resin XFS-43084 having weaker chelating amine groups shows high selectivity for copper, nickel and cobalt as compared to iron, aluminum, calcium and magnesium [47]. The resin ES-466B, besides being more selective than some of the commercially available copper-selective chelating ion-exchange resins, offers some other advantages as well.

A Possible Mechanism of Adsorption of Metal Ions on Chelating Ion-exchange Resins

In highly acidic media the benzimidazole resins like low-molecular weight benzimidazole derivatives exist in the protonated form and can be converted into free base and anionic forms by treatment with alkalis at higher pH as depicted in Fig. 4. The deprotonation constants of (benzimidazoleH$^+$) and its derivatives have been found to lie in the range 5.20–5.80 (pK_{a1}) and around 10.0 (pK_{a2}) [9h, 48]. Thus, the chelating ion-exchange resins containing benzimidazole derivatives can also act as anion exchange resins in the lower pH range, like other chelating resins such as Chelex-100, UR-50, ES-467 and XFS-4195 all of which contain protonating groups. Indeed, the resin ES-466B has been shown to act as an anion exchange resin at lower pH. It is indicated by the infrared spectrum of a sample of this resin treated with potassium nitrate solution which showed a high intensity band at 1380 cm^{-1} due to the presence of ionic nitrate groups [15]. Accordingly, the potential species which can be adsorbed on these chelating ion-exchange resins at lower pH will mainly include negatively charged complexes of the type $[CuCl_3(H_2O)_3]^-$, $[CuCl_4(H_2O)_2]^{2-}$ etc. At relatively higher pH range it is the positively charged and neutral species such as $[Cu(H_2O)_6]^{2+}$ and $[Cu(H_2O)_4Cl_2]$ which can reach the coordination sphere of the chelating moiety present on the polymeric matrix. Once the complexed species are in the vicinity of stronger donors, ligands like water and chloride are replaced and the metal ion is chelated by the polymeric ligand. These species appear to approach the donor sites through the phenomena of diffusion, and the opposite charges also seem to facilitate these processes by electrostatic attraction. The nature of the polymeric matrix (whether microporous or macroporous will be effective in nonaqueous or aqueous media) and the ionic radii of the metal ions are also known to play an important role in the diffusion process and, in turn, to the selectivity of the chelating ion-exchange resins [49].

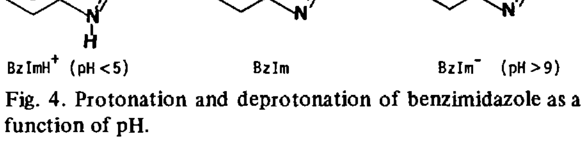


Fig. 4. Protonation and deprotonation of benzimidazole as a function of pH.

Concluding Remarks

Multidentate benzimidazole derivatives, such as [bis(benzimidazol-2-ylmethyl]amine, can be incorporated into highly cross-linked styrene-DVB copolymers by employing (a) the Phillips reaction and (b) N-alkylation of the immobilized polyamines having alkylation sites not directly attached to an aromatic ring. Both these synthetic procedures have been found quite facile and efficient yielding relatively good conversions. Of all the resins described, the resin designated as ES-466B appears to be most selective for copper(II) ions in the pH range 2–6. The high selectivity of this resin, among other things, can be ascribed to various steric factors present in the chelating system and to the flexibility of the copper(II) ions to adapt to various stereochemistries. The presence of more than one type of complexed species on a polymeric matrix can be demonstrated with the aid of electronic and electron spin resonance spectra. The nature and the type of the polymeric matrix of chelating ion exchange resins appear to play an important role in selective binding of metal ions under different conditions. It is also apparent that a chelating resin prepared through two different routes is not expected to behave in the same fashion (as different routes might modify a polymer in different ways: the chelating resins designated as SK-102 and JRSB, for instance, form different type of copper(II) complexes).

Acknowledgements

We thankfully acknowledge the financial support from the Netherlands Organisation for Advancement of Pure Research (Z.W.O) through grant no. 11.28-17 of the Netherlands Foundation for Chemical Research (S.O.N) and Stichting Technische Wetenschappen (S.T.W) through grant no. LCH.011.0144. Thanks are due to Mr René van Bennekom for assistance in experimental work. The continued interest of and useful suggestions by Mr F. B. Hulsbergen, Mr J. W. F. M. Schoonhoven and Mr W. J. van den Boogert are gratefully appreciated. Thanks are also due to Duolite International Inc., France, and Unitika Ltd., Japan, for the gift samples of ES-466 and Unicellex UR-50 resins, respectively.

References

1 S. K. Sahni and J. Reedijk, *Coord. Chem. Rev., 59,* 1 (1984).

2 (a) J. H. Hodgkin, in J. I. Kroschwitz (ed.), 'Encyclopedia of Polymer Science and Engineering', Vol. 3, New York, 1985, p. 363; (b) G. V. Myasoedova and S. B. Savvin, *Russ. J. Anal. Chem., 37,* 383 (1982); (c) G. V. Myasoedova and S. B. Savvin, *Crit. Rev. Anal. Chem., 17,* 1 (1986).

3 A. Warshawsky, *Angew. Makromol. Chem., 109/110,* 171 (1982).

4 (a) C. Calmon, *React. Polym., 4,* 13 (1986); (b) C. Calmon, *J. Am. Water Works Assoc., 73,* 652 (1981).

5 B. A. Bolto, *J. Macromol. Sci. Chem., A14,* 107 (1980).

6 D. S. Flett and D. Pearson, *Chem. Ind., 639* (1975).

7 (a) K. C. Jones and R. R. Grinstead, *Chem. Ind.,* 637 (1977); (b) F. Vernon, *Chem. Ind.,* 630 (1977).

8 S. K. Sahni, W. L. Driessen and J. Reedijk, *Proc. XXIII I.C.C.C.,* Boulder, Colo., U.S.A., 1984, p. 275.

9 (a) H. M. J. Hendriks, 'Copper coordination compounds of imidazoles and chelating imidazole ligands', *Ph.D. Thesis,* Leiden University, The Netherlands, 1981; (b) Y. Nishida, K. Takahashi and S. Kida, *Mem. Fac. Sci. Kyushu Univ. Ser., C 13(1),* 27 (1981); (c) K. Takahashi, Y. Nishida and S. Kida, *Bull. Chem. Soc. Jpn., 57,* 2628 (1984); (d) H. M. J. Hendriks, P. J. M. W. L. Birker, G. C. Verschoor and J. Reedijk, *J. Chem. Soc., Dalton Trans.,* 623 (1982). (e) P. J. M. W. L. Birker, H. J. M. Hendriks, J. Reedijk and G. C. Verschoor, *Inorg. Chem., 20,* 2408 (1981); (f) A. W. Addison, H. M. J. Hendriks, J. Reedijk and L. K. Thompson, *Inorg. Chem., 20,* 103 (1981); (g) L. K. Thompson, B. S. Ramaswamy and E. A. Seymour, *Can. J. Chem., 55,* 878 (1977); (h) R. J. Sundberg and R. B. Martin, *Chem. Rev., 74,* 471 (1974); (i) J. van Rijn, W. L. Driessen, J. Reedijk and J.-M. Lehn, *Inorg. Chem., 23,* 3584 (1984); (j) A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.,* 1349 (1984); (k) H. M. J. Hendriks, P. J. M. W. L. Birker, J. van Rijn, G. C. Verschoor and J. Reedijk, *J. Am. Chem. Soc., 104,* 3607 (1982); (l) M. F. Summers, J. van Rijn, J. Reedijk and L. G. Marzilli, *J. Am. Chem. Soc., 108,* 4254 (1986); (m) J. M. Mdoney, M. Glogowski, D. F. Rohrbach and F. L. Urbach, *Inorg. Chim. Acta, 127,* L33 (1987); (n) Y. Nishida, H. Shimo, H. Maehara and S. Kida, *J. Chem. Soc., Dalton Trans.,* 1945 (1985); (o) J. van Rijn, 'Copper chelates with imidazole-containing ligands', *Ph.D. Thesis,* Leiden University, The Netherlands, 1985; (p) K. Takahashi, E. Ogawa, N. Oishi, Y. Nishida and S. Kida, *Inorg. Chim. Acta, 66,* 97 (1982); (q) K. Takahashi, Y. Nishida and S. Kida, *Bull. Chem. Soc. Jpn., 56,* 339 (1983).

10 (a) C. U. Pitman, Jr., in P. Hodge and D. C. Sherrington (eds.), 'Polymer-supported Reactions in Organic Synthesis', Wiley, New York, 1980, p. 249; (b) P. Hodge, in P. Hodge and D. C. Sherrington (eds.), 'Polymer-supported Reactions in Organic Synthesis', Wiley, New York, 1980, p. 457;

11 (a) J. M. J. Frechet, *Proc. 30th I.U.P.A.C. International Symposium on Macromolecules,* The Hague, The Netherlands, 1985, p. 194; (b) N. H. Li and J. M. J. Frechet, *J. Chem. Soc., Chem. Commun.,* 1100 (1985); (c) J. M. J. Frechet and N. H. Li, *A.C.S., Polym. Prep., 26* (2), (1985); (d) M. Chanda, K. F. O'Driscoll and G. L. Rempel, *React. Polym., 4,* 34 (1986); (e) M. Chanda, K. F. O'Driscoll and G. L. Rempel, *React. Polym., 5,* 157 (1987); (f) J. A. Welleman, F. B. Hulsbergen and J. Reedijk, *Makromol. Chem., 55,* 768 (1982).

12 (a) C. Heitner-Wirguin, in J. A. Marinsky and Y. Marcus (eds.), 'Ion-Exchange and Solvent Extraction', Vol. 7, Marcel Dekker, New York, 1977, p. 83; (b) A. Nakashima, T. Isobe and T. Terutani, *Bull. Chem. Soc. Jpn., 55,* 1811 (1982); (c) A. Deratani, B. Sebille, H. Hommel and A. P. Legrand, *React. Polym., 2,* 261 (1983); (d) K. Umezawa and T. Yamabe, *Bull. Chem. Soc., Jpn., 45,* 56 (1972); (c) S. Laitinen and T. Norita, *Suomen Kemist., B43,* 61, 128 (1970).

13 P. J. Hoek and J. Reedijk, *J. Inorg. Nucl. Chem., 41,* 401 (1979).

14 P. J. Hoek and J. Reedijk, *J. Inorg. Nucl. Chem., 42,* 1759 (1980).

15 S. K. Sahni, R. van Bennekom and J. Reedijk, *Polyhedron, 4,* 1643 (1985).

16 K. W. Pepper, H. M. Paisley and M. A. Young, *J. Chem. Soc.,* 4097 (1953).

17 (a) J. B. Wright, *Chem. Rev., 48,* 437 (1951); (b) P. N. Preston, *Chem. Rev., 79,* 279 (1979); (c) P. N. Preston, in 'The Chemistry of Heterocyclic Compounds, Benzimidazoles and Congeneric Tricyclic Compounds, Part I', Wiley–Interscience, New York, 1981.

18 R. Hering, 'Chelating Ion-Exchangers', Akademik-Verlag, Berlin, 1967.

19 *Nederland Patent Appl. 8602391* (1987) to S. K. Sahni, W. L. Driessen and J. Reedijk.

20 T. M. Suzuki and T. Yokoyama, *Polyhedron, 3,* 939 (1984).

21 (a) C. S. Marvel, *J. Macrobiol. Sci. Rev., Macromol. Chem., C13,* 219 (1975); (b) P. M. Herenrother, in C. E. Schildknecht (ed.), 'Polymerization Process', Wiley–Interscience, New York, 1977, Chap. 4.

22 K. Kunitake, in P. Hodge and D. C. Sherrington (eds.), 'Polymer-supported Reactions in Organic Synthesis', Wiley, New York, 1980, p. 195, and refs. therein.

23 (a) R. H. Gaul and R. S. Drago, *Inorg. Chem., 18,* 2019 (1979); (b) J. P. Collman, R. R. Gagne, J. Kouba and H. Lgusberg, *J. Am. Chem. Soc., 96,* 6800 (1974).

24 *Nederland Pat. 7809083* (1978) to Nat. Inst. Metall., Randburg, S. Africa.

25 D. J. Rabiger and M. M. Joullie, *J. Org. Chem., 29,* 476 (1964).

26 L. R. Melby, *J. Am. Chem. Soc., 97,* 4044 (1975).

27 A. F. Pozharski, A. R. Garnovski and A. M. Simonov, *Russ. Chem. Rev., 35,* 122 (1966).

28 D. J. Rabiger and M. M. Joullie, *J. Org. Chem., 29,* 476 (1964).

29 D. G. O'Sullivan, *Spectrochim. Acta, 16,* 764 (1960).

30 (a) T. J. Lane, I. Nakagawa, J. L. Walters and A. J. Kandathil, *Inorg. Chem., 1,* 267 (1962); (b) K. S. Bose and C. C. Patel, *J. Inorg. Nucl. Chem., 33,* 755 (1971).

31 F. Vernon, *React. Polym., 1,* 51 (1982).

32 S. K. Sahni and J. Reedijk, unpublished results.

33 (a) M. S. Haddad and D. N. Hendrickson, *Inorg. Chem., 17,* 2622 (1978); (b) S. W. Kaiser, R. B. Saillant, W. M. Butler and P. G. Rasmussen, *Inorg. Chem., 15,* 2681, 2688 (1976).

34 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', 2nd edn., Elsevier, Amsterdam, 1984.

35 R. J. Faber and M. J. Rogers, *J. Am. Chem. Soc., 81,* 1849 (1959).

36 (a) D. L. McFadden, A. J. McPhail, C. D. Garner and F. E. Mabbs, *J. Chem. Soc., Dalton Trans.,* 263 (1975); (b) J. W. F. M. Schoonhoven, W. L. Driessen, J. Reedijk and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.,* 1053 (1984).

37 L. K. Thompson, R. G. Ball and J. Trotter, *Can. J. Chem.*, *58*, 1566 (1980).

38 B. J. Hathaway, N. J. Ray, D. Kennedy, N. O'Brian and B. Murphy, *Acta Crystallogr.*, *Sect. B*, *36*, 1371 (1980).

39 B. J. Hathaway, *Coord. Chem. Rev.*, *4*, 143 (1970).

40 B. J. Hathaway, *Coord. Chem. Rev.*, *35*, 211 (1981).

41 (a) H. J. Prochaska, W. F. Schwindinger, M. Schwartz, M. J. Burk, E. Bernarducci, R. A. Lalancrette, J. A. Potenza and H. J. Schugar, *J. Am. Chem. Soc.*, *103*, 3446 (1981); (b) H. Elliot and B. J. Hathaway, *Inorg. Chem.*, *4*, 885 (1965).

42 B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1196 (1972).

43 B. J. Hathaway, *Struct. Bonding (Berlin)*, *57*, 55 (1984).

44 H. Yokoi, *Inorg. Chem.*, *17*, 538 (1978).

45 R. Barbucci, M. Casolaro, S. Corezzi and G. Reginato, *Polymer*, *27*, 1986 (1986).

46 S. Vijaya and P. T. Manoharan, *Inorg. Chem.*, *20*, 1304 (1981).

47 (a) R. R. Grinstead, *Hydrometallurgy*, *12*, 387 (1984); (b) R. R. Grinstead, *J. Metals*, *31(3)*, 13 (1979).

48 (a) M. J. Davies, P. Mamalis, V. Petrov and B. Sturgeon, *J. Pharm. Pharmacol.*, *3*, 420 (1951).

49 P. Meares, in J. Crank and G. S. Park (eds.), 'Diffusion in Polymers', Academic Press, London, 1968, p. 373.