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Spectroscopic Studies of Transition Metal Complexes on Chelating Resins Containing Multidentate Pyridine Derivatives

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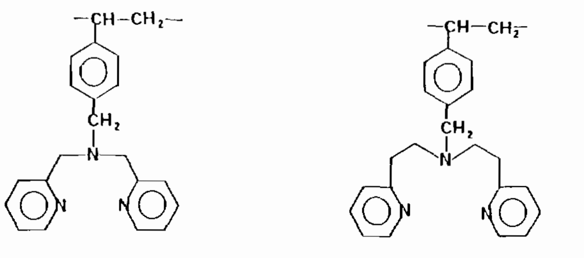
Pyridine derivatives are among the most versatile and thoroughly-studied groups of ligands in coordination chemistry [1, 2]. On account of their pronounced coordinating properties, a number of mono- and multidentate pyridine derivatives have been anchored on various types of polymer matrices [3–5]. Several pyridine-based chelating resins have been found to depict marked selectivity for transition metal ions *vis-à-vis* alkali and alkaline-earth metal ions [6, 7]. Their absorption behavior, selectivity, kinetics, and separation capabilities have been reported [6–9]. However, no concerted effort has been made to study the structural aspects of metal complexes present on such chelating resins (the term 'metal complex' has been used loosely throughout this paper to describe all metal-containing species absorbed on polymers). A structural study of such absorbed species also seems interesting and useful in view of numerous applications that such chelating resins find in analytical chemistry [10], organic synthesis [11], catalysis [12], water treatment [13], affinity chromatography [14] and as speciality polymers [15].

As a part of our investigations on structural aspects of absorbed species [16], the spectroscopic characteristics of some transition metal complexes of chelating resins containing one or two tridentate moieties bis[(2-pyridylmethyl)]amine and bis[2-(2-pyridylethyl)]amine anchored on microporous and macroporous styrene-divinylbenzene copolymers are briefly described in this communication. The tentative structures of various chelating resins are schematically depicted in Fig. 1. The resins designated as P-L$_1$ (I) and P-L$_3$ (III) comprise microporous polystyrene-DVB copolymer matrices, whereas the other two resins P-L$_2$ (II) and P-L$_4$ (IV) possess macroporous matrices.



P-L$_1$ (I) and P-L$_2$ (II)

P-L$_3$ (III) and P-L$_4$ (IV)

Fig. 1. Tentative structures of chelating ion-exchange resins incorporating bis[(2-pyridylmethyl)]amine in microporous (P-L$_1$, I) and macroporous (P-L$_2$, II) and bis[2-(2-pyridylethyl)]amine in microporous (P-L$_2$, III) and macroporous (P-L$_4$) matrices.

These chelating resins were synthesized by condensation of bis[(2-pyridylmethyl)]amine or bis[2-(2-pyridylethyl)]amine with a chloromethylated styrene-DVB copolymer [17], and by N-alkylation of cross-linked poly(aminomethylstyrene)* with a 2-chloroalkylpyridine in well dried dioxane in the presence of triethylamine or anhydrous potassium carbonate in a nitrogen atmosphere [19, 20]. The metal complexes employed for spectroscopic studies were prepared through the methods described earlier [21]. The details of analytical methods and physical measurements are also the same as described in a previous publication [21]. The amount of the incorporated ligand computed through the relationship (mmol/g resin) = [%N/14*n*] X 10, where %N is found percent of nitrogen in the product and *n* is the number of nitrogen atoms in a molecule (7, 19a), amounts to 1.97, 2.36, 2.98, and 2.48 mmol/g resin for P-L$_1$, P-L$_2$, P-L$_3$, and P-L$_4$, respectively.

Results and Discussion

The progress of the resin-modifying reactions was monitored by infrared spectra of the samples scanned at regular intervals. Disappearance or reduction in intensity of two bands occurring at *ca.* 670 and 1250 cm^{-1} due to ν(C–Cl) and ν(CH$_2$–Cl) in chloromethylated polystyrene and ν_{asym} and ν_{sym} (NH$_2$) vibrations appearing at *ca.* 3380 and 3280 cm^{-1} in the immobilized amines indicated the amount of incorporation of pyridine derivatives. These chelating resins exhibit new typical IR bands of pyridine derivatives at *ca.* 1585, 1480, 985, 610 and 400 cm^{-1} which can be assigned to ν(C=C) or ν(C=N), pyridine ring breathing [10a], in-plane deformation [6a], and out-of-plane deformation [16b] vibrations, respectively [22]. In

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*Poly(aminomethylstyrene) was synthesized through a Gabriel phthalimide synthesis [10]. This material is now commercially available in different forms from Bayer AG, Leverkusen, F.R.G. [18].

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the IR spectra of high metal-loaded resins all these bands appear at *ca.* 1610, 1020, 640 and 420 cm^{-1}, respectively. The upward shift in these bands is consistent with pyridine coordination with metal [22].

The ligand field and EPR spectral data of nickel(II) and copper(II) complexes of the chelating resins, along with those of some model compounds are listed in Table I. The ligand field spectra of nickel(II) complexes show three bands at *ca.* 9700, 15 450 and 23 800 cm^{-1} which can be assigned to $^3T_{2g} \leftarrow {}^3A_{2g}$, $^3T_{1g} \leftarrow {}^3A_{2g}$, and $^3T_{1g}(P) \leftarrow {}^3A_{2g}$, in increasing order of energy, in an octahedral field [26]. These band maxima do not agree with those of the six-coordinate nickel(II) complexes $[Ni(DPMA)_2]^{2+}$ of bis[(2pyridylmethyl)]amine (DPMA) [23] and the solid five-coordinate complexes of the type $[Ni(DPEA)X_2]$, where DPEA = bis[2-(2-pyridylethyl)]amine and X = Cl, Br, NO_3 or NCS [23b, 24]. The latter complexes in water exhibit three bands at 10 000, 16 300 and 26 800 cm^{-1}, along with a shoulder at *ca.* 13 300 cm^{-1}. These complexes are formulated as $[Ni(L)(H_2O)_3]^{2+}(X)_2^-$ and agree with a six-coordinated stereochemistry [23]. A similar type of six-coordinated nickel(II) complexes appears to be formed on the present chelating resins. The possibility of formation of 1:2 (M:L) complexes in the resin phase has been eliminated on the basis of relatively lower *Dq* (*ca.* 970 cm^{-1}) of the nickel(II) complexes formed on the chelating resins. A 1:2 complex $[Ni(DPMA)_2]^{2+}(X)_2^-$ of bis[(2-pyridylmethyl)amine] exhibits a much higher *Dq* (1255 cm^{-1}) [23a]. Octahedral nickel(II)–polyamine complexes are known to depict progressively higher *Dq,* with increasing number of pyridine nitrogen atoms in the coordination sphere [23]. Bis[2-(2-pyridylethyl)]amine and several related ligands have not been found to form 1:2 nickel(II) complexes either, because of the steric contraints of these ligands [23a, 24]. So, it appears that the present chelating polymer ligands have steric constraints not allowing two of them chelating to the same nickel(II) ion. Besides, anchored chelating systems lack the flexibitily usually associated with unimmobilized ligands.

TABLE I. Ligand Field and EPR Spectral Data of Nickel(II) and Copper(II) Complexes of Pyridine-based Chelating Resins and those of some Model Compounds

Complex (pH value)	Metal (%)	Ligand field spectra ($10Dq$ in 10^3 cm^{-1})	EPR parameters			Reference
			$g_\perp$	$g_\parallel$	$A_\parallel$(G)	
$NiCl_2$–(P-L_1) (1.3)	1.57	9.70, 15.45, 23.70 (9.70)				this work
$NiCl_2$–(P-L_3) (4.0)	0.15	9.71, 15.30, 23.85 (9.71)				
$[Ni(DPMA)_2]^{2+}$		12.55, 19.60 (12.55)				23a
$[Ni(DPEA)(H_2O)_3]$		10.40, 16.30, 26.80 (10.40)				24
$[Ni(DPEA)Cl_2]$		15.00, 19.80sh, 24.40				24
$CuCl_2$–(P-L_1) (2.0)	7.48	10.00, 11.76	g = 2.08, g = 2.14			this work
$CuCl_2$–(P-L_1) (5.0)	7.12	13.79	g = 2.04, g = 2.13, g = 2.33			
$CuCl_2$–(P-L_2) (1.65)	2.28	10.53, 12.12	g = 2.06, g = 2.15			
$CuCl_2$–(P-L_4) (2.0)	2.12	10.00, 12.35	2.06	2.24	150	
$CuCl_2$–(P-L_2) (6.0)	0.55	13.33	2.095	2.23	160	
$CuCl_2$–(P-L_3) (2.5)	0.40	13.00	2.06	2.26	155	
$[Cu(DPMA)Cl_2]$		13.35	g = 2.05, g = 2.12, g = 2.30			
$[Cu(DPEA)Br_2]$		10.40sh, 13.20				23b
$[Cu(DPEA)Cl_2]$				2.22	157	25d
$[Cu(PVP)_4]Cl_2$[a]		14.50	2.10	2.30	150	4a
$CuCl_2$–Chelex-100		14.50	2.06	2.25	180	16b

[a] PVP = poly(4-vinylpyridine).

High-loaded copper(II) complexes (Cu% > 2 wt.%) exhibit two types of ligand field spectra. The high-loaded copper chloride complexes isolated at pH *ca.* 2 exhibit a broad band at *ca.* 12 000 and another band on the low energy side at *ca.* 10 000 cm^{-1}. A similar complex prepared at higher pH (>4) exhibits a maximum at *ca.* 14 000 cm^{-1}. However, all these complexes exhibit similar EPR spectra (with *g* values lying in the range 2.06–2.08 for $g_\perp$ and 2.13–2.15 for $g_\parallel$) having no fine structure, presumably due to weak metal–metal interactions. The spectra of the complexes prepared at lower pH resemble those of chlorocuprates containing tetragonal octahedral $CuCl_4X_2$ chromophores (where $X = Cl, H_2O$) [27]. It appears that a mixture of such species as $[CuCl_3H_2O]^-$ and $[Cu_2Cl_6]^{2-}$ is present on the polymer matrix of these chelating resins. EPR spectra corroborate these observations, as tetragonal systems are known to exhibit *g* values of $g_\perp = 2.05$ and $g_\parallel = 2.25$ comparable to those of the present copper complexes. The spectra of the latter complexes are comparable to those of copper(II) halide complexes of bis[(2-pyridylmethyl)]amine, bis[2-(2-pyridylethyl)]-amine and dinucleating ligands containing DPEA moieties, all of which are known to form five-coordinated complexes [24a, 25] (Table I). The complexes having a low metal content (<1 wt.%) exhibit a band at *ca.* 13 000–14 000 cm^{-1}. Various EPR parameters $g_\perp$, $g_\parallel$ and $A_\parallel$ computed from the well-resolved spectra fall in the range 2.075–2.105, 2.22–2.26 and 150–165 G, respectively. The ligand field and EPR spectra of these complexes are compatible with a tetragonal geometry having a $d_{x^2-y^2}$ ground state, for which *g* values follow the order $g_\parallel > 2.1 > g_\perp > 2.04$ [28]. Their $A_\parallel$ values (150–165 G) are comparable to those of $[Cu(DPEA)Cl_2]$, $[Cu(PVP)_4]Cl_2$ and other copper complexes of chelating resins containing a chromophore of combination of nitrogen and a few oxygen donor groups [3, 4a] (Table I).

Thus, it is obvious that the absorbed nickel(II) and copper(II) species are coordinated by tridentate chelating moieties anchored on the polymers and the rest of their coordination sphere is completed by water molecules or other monodentate ligands present as counter ions of salts or OH^- groups which usually occur on polymeric matrices. Tentative structures of these complexes are depicted in Fig. 2.

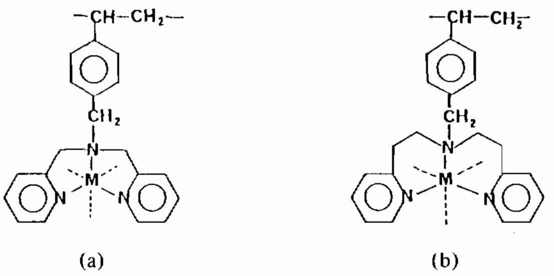

Fig. 2. Tentative schematic structures of metal complexes of chelating resins designated as P-L_1 (a) and P-L_3 (b); the broken lines depict the coordination sites to be occupied by water molecules or other monodentate ligands and M=Ni(II) or Cu(II).

It is interesting to note that different types of EPR spectra are obtained for two equally loaded copper complexes (expressed as meq Cu/g dried resin) of the similar chelating resins having microporous and macroporous matrices. The complexes present on a macroporous matrix exhibit copper hyperfine splitting, whereas the spectra of the complexes present on the microporous matrix are not so well-resolved, as deduced from the total absence of hyperfine splitting, even at subambient temperatures. It appears that copper ions present in macroporous resins remain in relatively isolated channels having the remote possibility of interactions and that aggregation of metal ions in gel type microporous matrix seems to facilitate strong interactions between metal centers. A study of spin–spin exchange interactions of paramagnetic metal ions on a chelating resin designated as Unicellex UR-50 (containing *o*-hydroxybenzyl-iminodiacetic acid groups incorporated in a phenol-formaldehyde condensate) and Dowex A-1 (a resin with iminodiacetic acid groups anchored on a polystyrene-DVB copolymer) also revealed that coordination pores of UR-50 are much closer to one another than those of Dowex A-1 despite the similar loading [29]. Similar observations have also been made with benzimidazole containing resins having microporous and macroporous matrices [16a].

In summary, we have shown that the tridentate pyridine-containing resins, both microporous and macroporous, can chelate to nickel(II) and copper(II), resulting in chromophores $[Ni(N)_3(H_2O)_3]$ and $[Cu(N)_3(H_2O)_n]$ ($n = 2$ or 3). Results are in progress about the selectivity, the capacity and the kinetics of the metal binding.

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