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Masaaki Sato^a; Koichi Kondo^a; Kiichi Takemoto^a

^a Faculty of Engineering, Osaka University Yamadakami, Suita Osaka, Japan

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Functional Monomers and Polymers. LX.* Effects of Counterions on the Structure of Cu(II)-Polyvinylimidazole and Cu(II)-Imidazole Complexes in Aqueous Solution

MASAAKI SATO, KOICHI KONDO, and KIICHI TAKEMOTO

Faculty of Engineering
Osaka University
Yamadakami, Suita
Osaka, Japan

ABSTRACT

The effect of counterion types on the structure of Cu(II) complexes of imidazole and poly-4(5)-vinylimidazole in aqueous solution was studied by spectroscopic and electron spin resonance (ESR) techniques. Visible and ESR spectra of both complexes in aqueous solution containing NaClO₄, KNO₃, KCl, and KBr showed only a slight change from each other in the presence of different counterions. On the other hand, the frequency of the center of absorption band in the visible region (λ_{\max}) and ESR parameters of the complex in aqueous solution did not correspond to those reported for its crystalline state, and in addition, those of the polymeric Cu(II) complex were different from those of the low molecular weight Cu(II) complex. It was proposed that in aqueous solution, water molecules are coordinated to the axial position of the complex where counterion molecules are present in the crystalline state, and that the

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structure of the polymeric Cu(II) complex is different from that of the low molecular weight Cu(II) complex due to steric hindrance of the polymeric ligand.

INTRODUCTION

The structure and properties of the Cu(II) complex of imidazole have received much attention in recent years, since the imidazole group in a histidyl residue has been recognized to play an important role as a ligand in copper-containing proteins [1, 2].

Crystallographic studies have shown that the Cu(II)-imidazole complex has a tetragonally distorted octahedral structure [3-7]. However, the extent to which structures determined in the crystalline state correspond to molecular species existing in solution still seems to remain uncertain. In addition, the structure of polymeric Cu(II) complexes, such as that of polyvinylimidazole in aqueous solution has not previously been studied in detail.

In our previous papers, we reported that the structure of the polymeric Cu(II) complex in aqueous solution, which was different from that of the low molecular weight Cu(II) complex, was changed by the conformational change of the polymeric ligand which was induced by changing pH or ionic strength of the solution [8, 9].

This contribution concerns an investigation of the influence of counterion type upon visible and ESR spectra of the Cu(II) complexes of imidazole and poly-4(5)-vinylimidazole in order to get further information on the structure of the polymeric Cu(II) complexes in aqueous solution.

EXPERIMENTAL

Materials

All solutions were prepared with distilled and deionized water. Commercially available reagents, including copper(II), sodium and potassium salts and sodium hydroxide were of analytical grade and used without further purification. Reagent-grade imidazole was purified by recrystallization from benzene. Poly-4(5)-vinylimidazole [poly-4(5)-VIm] was prepared according to the method reported by Overberger et al. [10]. Concentrations of the polymeric ligand are expressed in unit moles.

Solutions of Cu(II) Complexes

Solutions of the Cu(II)·imidazole complex were prepared by adding aqueous imidazole solution and then neutral salt to aqueous Cu(II)

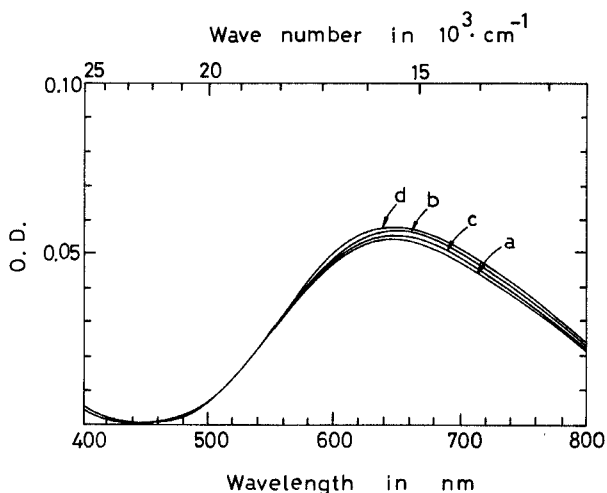


FIG. 1. Visible spectra of Cu(II)·imidazole complex in aqueous solution containing various sorts of neutral salts: (a) NaClO₄; (b) KNO₃; (c) KCl; (d) KBr. [Neutral Salt] = 1.8×10^{-1} M, [Cu(II)] = 1.0×10^{-3} M, [Imidazole] = 1.0×10^{-2} M; pH 7.95.

solution. Solutions of Cu(II)·poly-4(5)-VIm complex, on the other hand, were prepared by adding aqueous Cu(II) solution and then neutral salts to aqueous solution of poly-4(5)-VIm containing small amount of perchloric acid to dissolve the polymeric ligand. The anion of the Cu(II) ion was chosen to be identical with that of the neutral salt added in each case.

Measurements

Spectrophotometric measurements were carried out by using a Union MS-401 type spectrophotometer at 25°C. ESR spectra were recorded as shown in our previous paper [8], except that a microwave frequency of 9.296 GHz was used. pH Values were measured repeatedly within a difference of 0.05 with a Hitachi-Horiba F-7 potentiometer after permitting the complex solution to stand for at least 24 hr.

RESULTS AND DISCUSSION

The effect of counterions on the structure of Cu(II) complexes of imidazole and poly-4(5)-VIm was studied in aqueous solution containing sodium perchlorate, potassium nitrate, potassium chloride, and

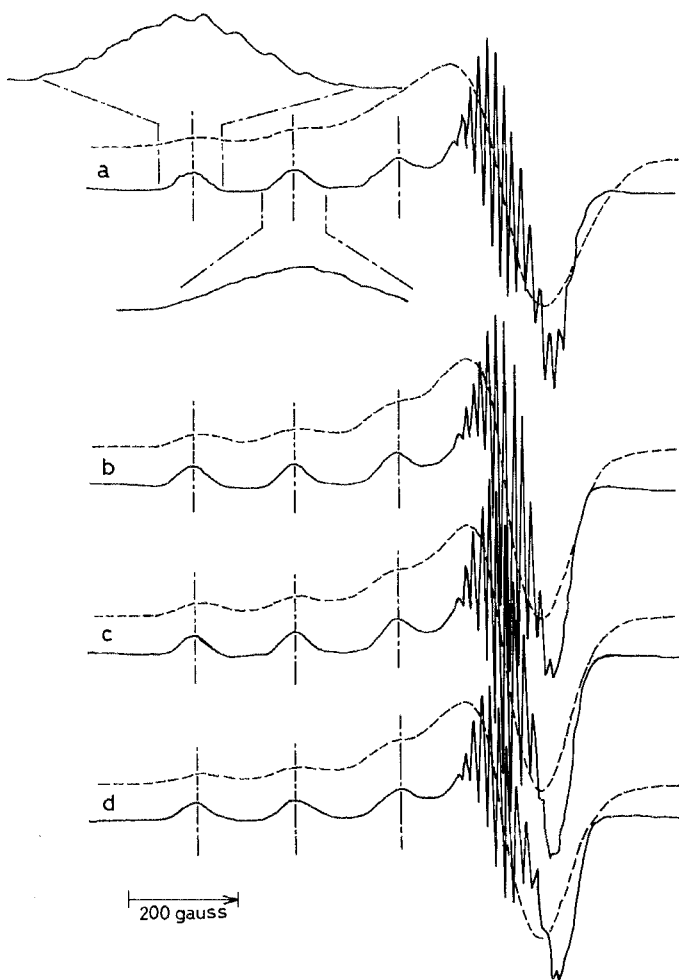


FIG. 2. ESR spectra of Cu(II)-imidazole complex in aqueous solution containing various sorts of neutral salts: (a) NaClO₄; (b) KNO₃; (c) KCl; (d) KBr. [Neutral Salt] = 1.8×10^{-1} M, [Cu(II)] = 1.0×10^{-3} M, [Imidazole] = 1.0×10^{-2} M; pH 7.95. Solid and dashed lines indicate the spectra of the complex in aqueous solution containing 2% and no ethyl alcohol, respectively; 1 gauss (G) = 10^{-4} tesla (T).

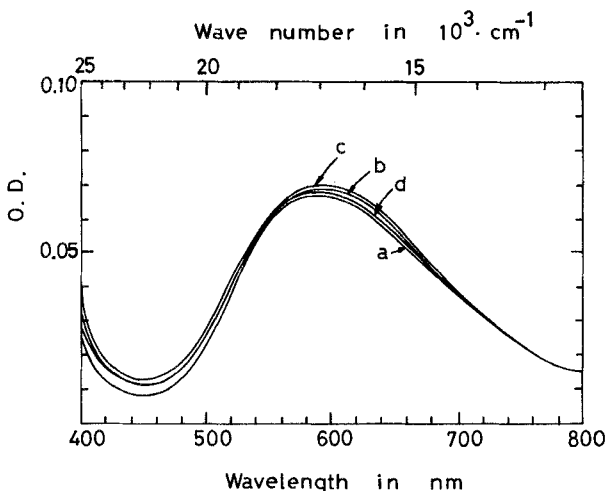


FIG. 3. Visible spectra of Cu(II)·poly-4(5)-VIm complex in aqueous solution containing various sorts of neutral salts: (a) NaClO₄; (b) KNO₃; (c) KCl; (d) KBr. [Neutral Salt] = 9.0×10^{-2} M; [Cu(II)] = 1.0×10^{-3} M; [Poly-4(5)-VIm] = 1.0×10^{-2} M; pH 5.30.

potassium bromide. Figures 1 and 2 show visible and ESR spectra, respectively, of the Cu(II)·imidazole complex and Figs. 3 and 4 show those of the Cu(II)·poly-4(5)-VIm complex.

The different counterions did not cause any marked change in the visible spectra of each complex (Figs. 1 and 3), though λ_{\max} for the former complex was $15.0\text{--}15.6 \times 10^3 \text{ cm}^{-1}$ (640–667 nm) and that for the latter complex was $16.8\text{--}17.0 \times 10^3 \text{ cm}^{-1}$ (588–595 nm). The ESR spectra of these complexes also showed only a small change at different counterions, but ESR parameters for the former complex were different from those for the latter complex, which are summarized in Table 1.

Addition of 2% ethyl alcohol permitted the ESR spectra of the Cu(II)·imidazole complex to be obtained in a highly resolved form having only minor changes in the parameters; thus we are able to observe ligand-nuclear superhyperfine structures. In the case of perchlorate anion, at least nine superhyperfine lines spaced $1.4 \times 10^{-3} \text{ cm}^{-1}$ apart are shown in the low-field edge of the perpendicular signal, which can be attributed to the splitting by four equivalent nitrogen nuclei [11] (Fig. 2). The ESR spectra of Cu(II)·poly-4(5)-VIm complex, on the contrary, are unchanged by the addition of ethyl alcohol, and the superhyperfine structure cannot be obtained.

A few examples of λ_{\max} obtained from the diffuse reflectance

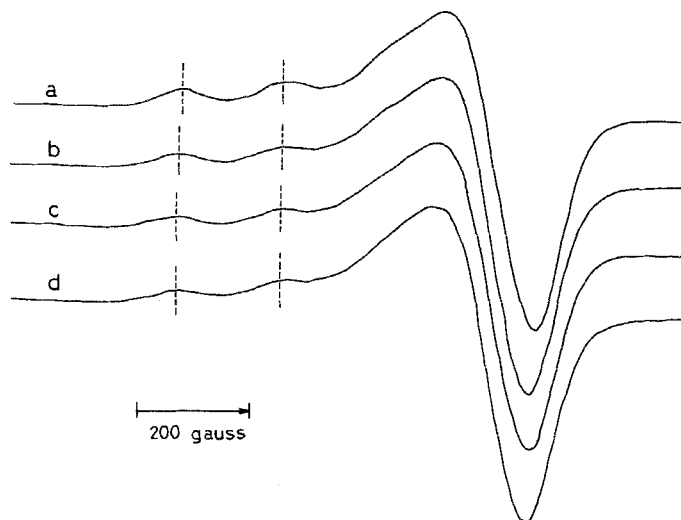


FIG. 4. ESR spectra of Cu(II)·poly-4(5)-VIm complex in aqueous solution containing various sorts of neutral salts. Symbols and conditions same as for Fig. 3 ($1 \text{ G} = 10^{-4} \text{ T}$).

spectra and ESR parameters of Cu(II) complexes of imidazole and substituted imidazoles in the crystalline state reported in the literature are listed in Table 2 [4-7]. The importance of axial ligation to the electronic structures of the Cu(II) complexes is shown from the facts that λ_{max} is changed in the following order by various anions:

$\text{ClO}_4^- > \text{NO}_3^- > \text{Cl}^- > \text{Br}^-$, ranging from 19.6×10^3 to $15.1 \times 10^3 \text{ cm}^{-1}$ in the case of Cu(II)·2-ethylimidazole complex [7], and that λ_{max} and ESR parameters of $[\text{Cu}(\text{Im})_6(\text{NO}_3)_2]$ complex are different from those of $[\text{Cu}(\text{Im})_4(\text{NO}_3)_2]$ complex as a result of replacing the axial N- by O-donor ligands, although the difference in the equatorial Cu-N bond length for these two complexes is within 0.02 \AA [5-6].

The effect of counterions on the spectra of Cu(II)·imidazole complex in aqueous solution, on the contrary, is quite small compared with that in the solid state. The distinction of λ_{max} and ESR parameters between Cu(II)·imidazole complex in aqueous solution containing potassium nitrate, and $[\text{Cu}(\text{Im})_4(\text{NO}_3)_2]$ complex in the crystalline state suggests some differences between these two complexes. The participation of $[\text{Cu}(\text{Im})_6]^{2+}$ type complex in Cu(II)·imidazole complex in aqueous solution, which can be considered to be less affected by counterions than the $[\text{Ni}(\text{Im})_6]^{2+}$ and $[\text{Co}(\text{Im})_6]^{2+}$ complexes [3], could be ruled out, since titration results showed the average coordination number of four [12], and significant differences in the spectra

TABLE 1. Parameters Characterizing ESR and Visible Spectra of Cu(II) Complexes in Aqueous Solution^a

Ligand	Counterion	g_{\perp}	g_{\parallel}	$ A_{\parallel} ^b$ (10^{-3} cm^{-1})	$ A_{\perp} ^b$ (10^{-3} cm^{-1})	$10^{-3} \lambda_{\text{max}}$ (cm^{-1})
Imidazole ^c	ClO_4^-	2.072	2.259	19.5	1.44	15.6
		(2.074)	(2.255)	(19.7)	(1.47)	(15.3)
	NO_3^-	2.068	2.261	19.2	1.36	15.4
		(2.083)	(2.266)	(19.3)	(1.38)	(15.1)
	Cl^-	2.069	2.258	19.4	1.40	15.4
		(2.086)	(2.262)	(19.4)	(1.42)	(15.0)
	Br^-	2.072	2.258	19.4	1.46	15.4
		(2.086)	(2.258)	(19.6)	(1.48)	(15.2)
Poly-4(5)-VIm ^d	ClO_4^-	2.050	2.232	19.4	---	17.0
		2.053	2.234	19.3	---	16.8
	Cl^-	2.055	2.240	18.8	---	16.9
		2.058	2.243	18.8	---	16.8

^a Abbreviations as described in the literature [8, 13]. Cu(II): imidazole concentration ratios were 1:10 and 1:4 (parameters for the latter shown in parentheses).

^b Parameters were obtained from the spectra of the solutions containing 2% ethyl alcohol.

^c pH 7.95; n (average coordination number) = 4; [Neutral Salt] = 0.18 M.

^d pH 5.30; n = 4; [Neutral Salt] = 0.09 M.

^e Could not be observed.

TABLE 2. Parameters Characterizing Visible Spectra of Cu(II) Complexes in the Crystalline State Reported in the Literature^a

Counterion (X ⁻)	10 ⁻³ λ _{max} (cm ⁻¹)		
	[Cu(L) ₄ (X) ₂] ^b	[Cu(L') ₄ (X) ₂] ^c	[Cu(L'') ₄ (X) ₂] ^d
ClO ₄ ⁻	19.6	18.9	— ^e
NO ₃ ⁻	18.9	17.7	18.2
Cl ⁻	16.1	14.6	— ^e
Br ⁻	15.1	16.3	16.4

^aAbbreviations as given in the literature [8, 13].

^bL = 2-Ethylimidazole [7].

^cL' = 2-Ethyl-4(5)-methylimidazole [7].

^dL'': 1,2-dimethylimidazole [4].

^eNot reported.

TABLE 3. Parameters Characterizing ESR Spectra of Cu(II) Imidazole Complexes in the Crystalline State

Complex	10 ⁻³ λ _{max}			
	(cm ⁻¹)	g _x	g _y	g _z
[Cu(Im) ₄ (NO ₃) ₂] ^a	18.8	2.046	2.048	2.230
[Cu(Im) ₆ (NO ₃) ₂] ^b	16.2	2.039	2.068	2.275

^aData of McFadden et al. [5].

^bData of McFadden et al. [6].

observed between [Cu(Im)₄(NO₃)₂] and [Cu(Im)₆(NO₃)₂] complex systems in the solid state were not seen in the case of the complex in aqueous solution, even if the Cu(II): imidazole concentration ratio was changed from 1:4 to 1:10; in addition, λ_{max} and ESR parameters of the Cu(II)-imidazole complex in aqueous solution did not correspond to those of [Cu(Im)₆(NO₃)₂] complex shown in Table 3. Therefore it can be concluded that the structure of Cu(II)-imidazole complex in aqueous solution is different from that in the solid state, although the complexes in these two states take the same stoichiometric form of [Cu(Im)₄]²⁺. That is, the counterion molecules in the axial position may be displaced by the water molecule in aqueous solution.

In the case of Cu(II)-poly-4(5)-VIm complex in aqueous solution, the fact that λ_{max} and ESR parameters are not affected by the type of

counterion present indicates that the structure of the complex is not changed by the counterions and also that the counterion molecules are not coordinated to the copper atom. However, the distinction of λ_{\max} and ESR parameters between the polymeric and low molecular weight Cu(II) complexes seems to be caused by the following two possibilities: participation of the $[\text{Cu}(\text{Im})_6]^{2+}$ type complex in the polymeric Cu(II) complex in aqueous solution and a structural difference between these two complexes. The former possibility seems to be excluded, since the g_{\parallel} value for the polymeric Cu(II) complex is smaller than that for the low molecular weight Cu(II) complex, but the g_z value for the $[\text{Cu}(\text{Im})_6(\text{NO}_3)_2]$ complex is larger than that for the $[\text{Cu}(\text{Im})_4(\text{NO}_3)_2]$ complex. Therefore it can be considered that the structure of the Cu(II):poly4(5)-VIm complex is different from that of the Cu(II)-imidazole complex in aqueous solution. On considering that the imidazolyl groups are linked to a polymer in the case of poly-4(5)-VIm, their complex with Cu(II) may be distorted by the steric hindrance of the polymeric ligand.

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