

ESR Study of the Complex Formation Between $\text{Cu}(\text{ClO}_4)_2$ and a Functionalized Silica Gel Surface

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A formação do complexo entre $\text{Cu}(\text{ClO}_4)_2$ e a superfície da sílica gel modificada com grupos benzimidazol foi estudada por ESR. Os parâmetros de ESR do espectro do complexo formado são usados para determinar a simetria mais provável do complexo na fase sólida. O ajuste das expressões teóricas aos dados experimentais é bem razoável.

The formation of the complex between $\text{Cu}(\text{ClO}_4)_2$ and a silica gel surface grafted with benzimidazole groups has been investigated by ESR. The parameters of the ESR spectrum of the complex obtained are presented and used to determine the most probable immediate environment of the complex formed on the surface of the solid phase. The fit of the theoretical expressions with the experimental data is very reasonable.

Keywords: benzimidazole, functionalization of silica gel

Introduction

In recent years, great interest has been devoted to the preparation and study of organofunctionalized silica gel surface due to its multiple uses in high performance liquid chromatography¹, preconcentration and separation process^{2,4}, ion exchange⁵, biotechnology⁶, and supports for catalysts^{7,9}. The characterization of the surfaces has normally been made by various techniques⁹⁻¹². The technique of electron spin resonance (ESR) has been successfully used to determine the structure of the complex species on the surface^{13,14}.

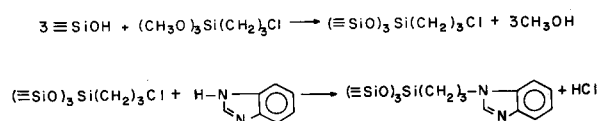
This paper reports the results of an ESR study of the complex formation between copper (II) and benzimidazole groups immobilized on a silica gel surface. Copper (II) ion was chosen because it can form stable complexes with the benzimidazole molecule^{15,16} and also can be used as a paramagnetic probe to determine the structure of the complexes formed¹⁷.

In order to interpret the ESR parameters, Kivelson and Neiman's molecular orbital approach was applied¹⁹.

Experimental Details

Preparations

The process for grafting the benzimidazole molecules on the silica surface is a known procedure¹⁹ and in the present case is represented by the following equations:



where SiOH stands for the silica matrix.

The amount of benzimidazole attached to the silica surface was determined by nitrogen analyses using the Kjeldahl method, giving $0.48 \times 10^{-3} \text{ mol g}^{-1}$. The specific surface area, determined by the BET method, was $383 \text{ m}^2 \text{ g}^{-1}$.

Adsorption of $\text{Cu}(\text{ClO}_4)_2$

A sample of about 2.0 g of the functionalized material (abbreviated here as SiL) was suspended by stirring in 50.0 ml of ethanolic solution with a metal concentration form $1.0 \times 10^{-3} \text{ mol l}^{-1}$. The adsorption was controlled in order to have a ratio of attached benzimidazole group to Copper(II) of $\sim 25:1$ at the surface. The sample obtained under these conditions has a pale blue color. The solid was filtered, washed with ethanol several times and then dried *in vacuo*.

The amount of the sorbed metal was determined ($0.19 \times 10^{-4} \text{ mol g}^{-1}$) in the solid phase. The solid with sorbed metal was washed with pure solvent and dried at about 350 K in an oven. The solid was then weighed and immersed in 50 ml of 0.1 M HCl solution and shaken for 30 min. The released metal ions were analyzed by complexometric titration using EDTA as the titrating reagent.

Electronic spectrum

The electronic absorption spectrum was obtained by immersing the solid in spectroscopic-grade carbon tetrachloride in a quartz cell having a 1 mm path length. The equipment used was a Cary 2300 spectrophotometer.

Electron spin resonance

The ESR spectra were obtained for the Cu^{2+} complex species in the solid phase at 77 K with the samples in quartz tubes. A Varian model E-109, Line Century series, X-band spectrometer with a field modulation frequency of 100 KHz, was used.

Infrared spectra

The infrared spectra were obtained by the transmission technique using a Nicolet FT-IR spectrophotometer. Each sample was ground to obtain disks comprising about 12 mg cm^{-2} of the pulverized material. The spectra were recorded at between 1300-1700 cm^{-1} .

Results and Discussion

In complexes of $\text{Cu}(\text{Methylimidazole})_4\text{X}_2$ the vibrational spectra have shown that coordination of metal imidazole nitrogen shifted the bands belonging to ring vibration modes to higher frequencies in comparison with those of the free ligands⁹. In the present case, the evidence that the copper(II) ion is coordinated to the benzimidazole free nitrogen, and not only physically sorbed on the surface, is shown in the infrared spectrum of $\text{SiL}_m\text{Cu}(\text{ClO}_4)_2$. Figure 1 shows the spectrum of SiL, Fig. 1A, and the spectrum of $\text{SiL}_m\text{Cu}(\text{ClO}_4)_2$, Fig. 1B. Comparing Figs. 1A and B, the

Table 1. Infrared frequencies (cm^{-1}) of $\text{SiL}_m\text{Cu}(\text{ClO}_4)_2$ *

SiL	$\text{SiL}_m\text{Cu}(\text{ClO}_4)_2$	Approximate assignments
1660vw		comb. band
1630 b	1630 b	$\delta \text{ H}_2\text{O}$
1567 m	1569 m	$\nu\text{CC} + \delta\text{CH}$
1500 m	1523 m	$\nu\text{CN} + \nu\text{CC}$
	1487 w	
1458 m	1467 m	$\nu\text{CN} + \delta\text{ring}$
1382 w	1385 w	propyl $\delta \text{ CH}_2$
1353 w	1352 w	

* v = very, m = medium, w = weak, b = broad

band at 1523 cm^{-1} of Fig. 1B is shifted to higher frequencies in relation to that of Fig. 1A by 23 cm^{-1} . The pertinent band is assumed to be due to the plane skeletal vibration of the benzimidazole ring which involves coupled vibration ($\nu\text{CN} + \nu\text{CC}$)^{9, 21, 22}. Table 1 lists the infrared frequencies of SiL and $\text{SiL}_m\text{Cu}(\text{ClO}_4)_2$. We can admit that benzimidazole groups are strongly bonded to copper(II), since the equilibrium constant ($\log K$) of the formation of the surface complex in ethanol solution is 3.37 ¹⁹.

The electronic spectrum of $\text{Cu}(\text{ClO}_4)_2$ adsorbed on the modified silica surface (Fig. 2) showed a broad band, with the maximum peak at about 14285 cm^{-1} . This spectrum is of the general type found for planar or tetragonally distorted octahedral copper(II) complexes with monodentate N-donor ligands, resulting in coordination compounds of the

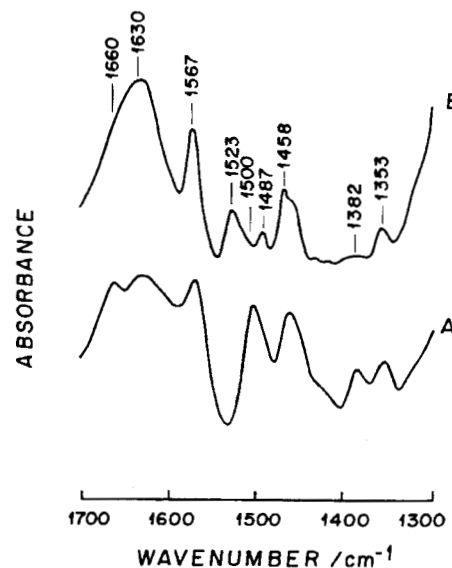


Figure 1. Infrared spectra of the silica surface functionalized with benzimidazole molecule (A) and the $\text{Cu}(\text{ClO}_4)_2$ adsorbed on silica functionalized surface (B).

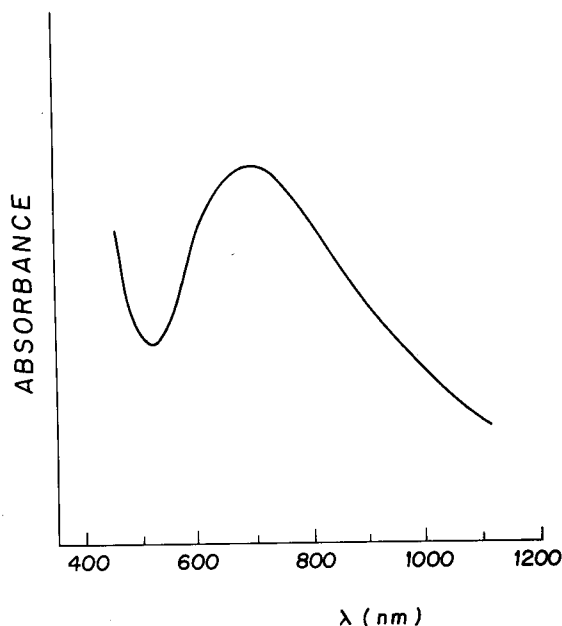


Figure 2. Electronic spectrum of $\text{SiL}_m\text{Cu}(\text{ClO}_4)_2$ immersed in carbon tetrachloride.

type $\text{Cu}(\text{ligand})_4(\text{anion})_2$. In this case the anions are weakly bound to the copper(II)^{15,23,24}.

Figure 3 shows the ESR spectrum of $\text{SiL}_m\text{Cu}(\text{ClO}_4)_2$. The signals invariably consisted of a power spectrum with axial symmetry and resolved low-field components. The ESR spectrum of $\text{SiL}_m\text{Cu}(\text{ClO}_4)_2$ is similar to that observed for analogous non supported copper (II) complexes²³⁻²⁵. In the present case, superhyperfine structure (shfs) due to nitrogen nuclei is observed on the high-field component. In the second derivative spectrum (Fig. 3c), nine absorption peaks can be identified, which are assigned to the shfs interaction between the copper (II) electronic spin ($S=1/2$), and the nitrogen nuclear spin ($I=1$), with separation between the lines of 15 G. The shfs indicate that in this case the equatorial plane of the adsorbed complex incorporates four nitrogen atoms of the benzimidazole groups, which are coordinated to the central copper atom. The other magnetic parameters measured from the spectrum were $g_{\parallel}=2.285$, $g_{\perp}=2.061$ and $A_{\parallel}=160$ G.

In similar complexes^{23,24} the following ESR parameters and ligand field peak maxima have been found: a) $\text{Cu}(\text{EI})_4(\text{ClO}_4)_2$ (EI is ethylimidazole): $g_{\parallel}=2.24$, $A_{\parallel}=180$ Gauss and $\lambda_{\text{max}}=18200$ cm^{-1} . b) $\text{Cu}(\text{PI})_4(\text{ClO}_4)_2$ (PI is propylimidazole): $g_{\parallel}=2.25$, $A_{\parallel}=185$ Gauss and $\lambda_{\text{max}}=18400$ cm^{-1} . The ESR parameters are similar to those of $\text{SiL}_m\text{Cu}(\text{ClO}_4)_2$.

In view of the fact that $\text{Cu}(\text{EI})_4(\text{ClO}_4)_2$ and $\text{Cu}(\text{PI})_4(\text{ClO}_4)_2$ have a distorted tetragonal structure, it is evident that ESR provides a good argument that the copper (II) ion in $\text{SiL}_m\text{Cu}(\text{ClO}_4)_2$ is bonded to four equivalent nitrogen atoms in a D_{4h} symmetry field. This assumption is reason-

able taking into account that, with a loading of about 1,2 molecules per 100 \AA^2 , the average distance between $(\text{CH}_2)_3\text{C}_7\text{H}_6\text{N}_2$ units will be $\sim 9\text{\AA}$. With this separation, is then possible to form a complex which contains four benzimidazole units. Presumably, the perchlorate anion is not coordinated (or is semi-coordinated²³) along the axis perpendicular to the horizontal plane due to the Jahn-Teller effect.

Goodgame and Haines¹⁵ showed that the electronic absorption spectra of $\text{Cu}(\text{Benzimidazole})_4\text{X}_2$ complexes present the following maximum values which are in order (cm^{-1}) of the interaction strength of the metal ion with anion weakly bonded axially: thiocyanate ~ 15600 , chloride and bromide ~ 16000 , nitrate ~ 17500 , perchlorate ~ 19000 . The maximum band value observed at ~ 14285 cm^{-1} in the case of $\text{SiL}_m\text{Cu}(\text{ClO}_4)_2$ is lower than that observed for the corresponding perchlorate complex and higher than that ob-

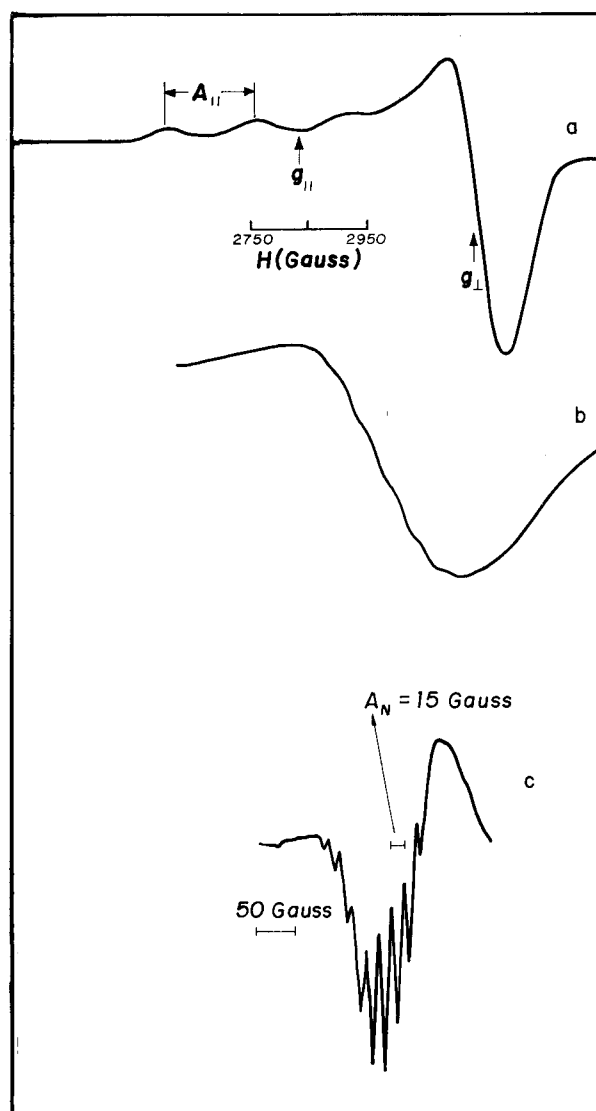


Figure 3. (a) ESR spectrum of $\text{SiL}_m\text{Cu}(\text{ClO}_4)_2$; (b) expanded high-field component of spectrum; (c) second derivative spectrum.

served at $\sim 10400 \text{ cm}^{-1}$ for the copper (II) ion-doped $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$, where the copper (II) ion is in an octahedral field²⁶. In view of this, it can be considered that the perchlorate ions are weakly bonded to copper (II) in $\text{SiL}_m \text{Cu}(\text{ClO}_4)_2$. In this case a possible explanation is the low coordination ability shown by perchlorate anion and then only benzimidazole molecules are bonded to the metal ion.

In order to interpret the ESR parameters, Kivelson and Neiman's molecular orbital approach for copper (II) complexes with D_{4h} symmetry was applied¹⁸.

Considering D_{4h} symmetry in the studied complex, the covalent parameter, α^2 , can be obtained using the following relation^{18,20}

$$\Delta H = 48.25 \alpha^2 \quad (1)$$

where ΔH is the shfs splitting, measured directly from the spectrum. The calculated value of α^2 is 0.31, in this case. α , which is the magnitude of the covalent parameter, gives information about the bond strength since it is proportional to the degree of covalent bonding²⁰.

To evaluate the metal ligand σ -bonding parameter α^2 , the approximate expression below was used¹⁸

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

where P = dipole coefficient = 0.036 cm^{-1} for free Cu^{2+} ion²⁷, or the following normalization condition for the B_{1g} orbital, which is the ground state for a copper (II) complex with D_{4h} symmetry, can be used

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha'S = 1 \quad (3)$$

where S is the integral overlap between $d_{x^2-y^2}$ and the ligand orbitals. Taking $S = 0.093$ ¹⁸ in the latter, the equations give two values of α^2 as 0.74 and 0.78, respectively. These values are in good agreement with data from other related systems²⁸ and they are indicative of appreciable in-plane covalence. The metal ligand in-plane σ -bonding, α^2 , is entirely covalent if $\alpha^2 = 0.5$ and it is entirely ionic if $\alpha^2 = 1$ ¹⁸.

The expression for g_{\perp} in D_{4h} symmetry with ${}^2B_{1g}$ ground state is

$$g_{\perp} = 2.0023 - 2\rho \left[\alpha\beta - \alpha'\beta S - \alpha'(1 - \beta^2)^{1/2} \frac{T(n)}{\sqrt{2}} \right] \quad (4)$$

where $\rho = \alpha\lambda\beta/\Delta E$.

In the present case, an excellent fit between the theoretical expressions and the experimental data can be obtained if we neglect the Π bonding out of the equatorial plane ($\beta = 1$) and take into consideration an effective spin-orbit coupling constant for Cu^{2+} of $\lambda = -579.89 \text{ cm}^{-1}$. This value of λ was reduced from its normal free ion value

of $\lambda = -828 \text{ cm}^{-1}$ by as much as 30%. This reduction of the spin-orbit coupling parameter is normal in the solid state and in frozen solutions of complexes²⁷.

Then, using $\lambda = -579.89 \text{ cm}^{-1}$ the calculated value of ΔE (energy difference between $E_{x^2-y^2}$ and E_{xz}, E_{yz}) = 14285 cm^{-1} is in good agreement with the observed transition as indicated in Fig. 2, which we have assigned to ${}^2E_g \leftarrow {}^2B_{1g}$.

These results are consistent with those obtained by the application of Abragan and Price's model for Cu^{2+} ion in a crystalline field of distorted tetragonal symmetry to interpret the ESR parameters of a series of supported copper(II) benzimidazole complexes¹⁹. In these cases the λ calculated values vary in the range of -418 to -548 cm^{-1} . Therefore, there occurred a reduction of up to 70% in relation to its normal free ion value of $\lambda = -828 \text{ cm}^{-1}$.

Attached benzimidazole molecules can form surface complexes having structures similar to those found for attached imidazole molecules on a silica surface according to previously reported work about an ESR study of the CuCl_2 -imidazole-silica gel system^{9,20}.

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