

## Structure of Cobalt (II) Perchlorate Adsorbed on Silica Gel Surface Chemically Modified with Benzimidazole Molecule

Newton L. Dias Filho<sup>a</sup>, Edson Rodrigues<sup>b</sup>, and Yoshitaka Gushikem<sup>c\*</sup>

<sup>a</sup>Departamento de Física e Química, UNESP, Ilha Solteira, CP 31,  
15378-000 Ilha Solteira - SP, Brazil

<sup>b</sup>Instituto de Física de São Carlos, USP, 13560-250 São Carlos - SP, Brazil

<sup>c</sup>Instituto de Química, Unicamp, CP 6154, 13083-970 Campinas - SP, Brazil

Received: November 4, 1996

Moléculas de benzimidazol covalentemente ligadas à superfície da sílica gel,  $\equiv\text{SiL}$  (onde L = N-propilbenzimidazol), adsorvem  $\text{Co}(\text{ClO}_4)_2$  de solvente não aquoso formando complexos na superfície segundo a reação:  $m \equiv\text{SiL} + \text{Co}(\text{ClO}_4)_2 \rightarrow (\equiv\text{SiL})_m\text{Co}(\text{ClO}_4)_2$ . As constantes de equilíbrio e capacidade de adsorção, foram determinadas aplicando-se a equação de Langmuir fornecendo respectivamente,  $b = 3.0 \times 10^3 \text{ L mol}^{-1}$  e  $N_s = 0.098 \times 10^{-3} \text{ mol g}^{-1}$ . O metal está ligado através do átomo de nitrogênio e o íon perclorato não está coordenado. O estudo de ESR mostrou que o complexo possui essencialmente uma geometria com distorção tetragonal, com os elétrons dos quatro nitrogênios interagindo com o íon metálico central cobalto no plano equatorial. Somente uma espécie complexa foi detectada na superfície.

Covalently attached benzimidazole molecules on silica gel surface,  $\equiv\text{SiL}$  (where L = N-propylbenzimidazole), adsorbs  $\text{Co}(\text{ClO}_4)_2$  from non-aqueous solvent by forming a surface complex according to the reaction:  $m \equiv\text{SiL} + \text{Co}(\text{ClO}_4)_2 \rightarrow (\equiv\text{SiL})_m\text{Co}(\text{ClO}_4)_2$ . The equilibrium constant and the adsorption capacity, determined by applying the Langmuir equation were  $b = 3.0 \times 10^3 \text{ L mol}^{-1}$  and  $N_s = 0.098 \times 10^{-3} \text{ mol g}^{-1}$ , respectively. The metal is bonded through the nitrogen atom and the perchlorate ion is not coordinated. The ESR study indicated that the complex has essentially an octahedral geometry with tetragonal distortion, with the electrons of the four nitrogen atoms interacting with the cobalt central metal ion in the equatorial plane. Only one complex species was detected on the surface.

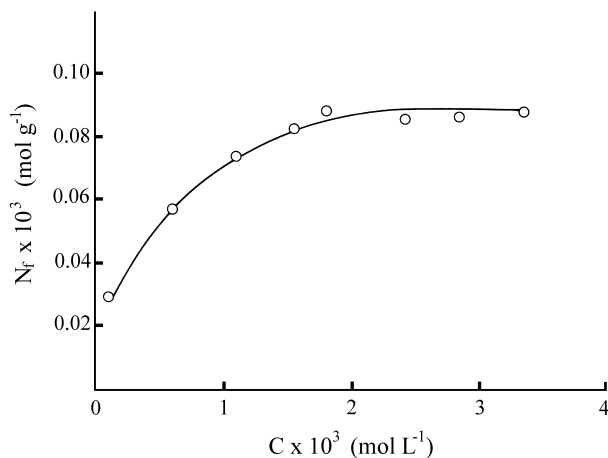
**Keywords:** silica gel, benzimidazole, cobalt-benzimidazole surface complex, cobalt electron spin resonance, silica gel modified with benzimidazole

### Introduction

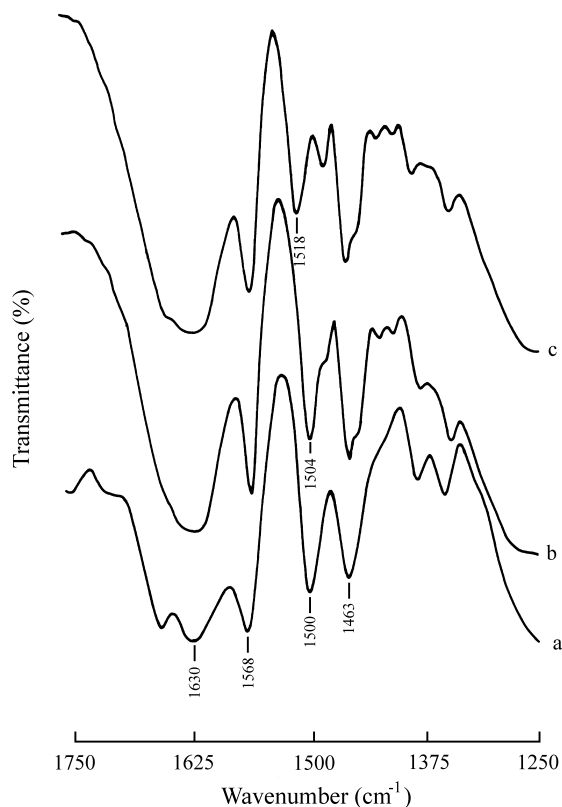
Organic molecules containing nitrogen atoms have been chemically bonded to a silica gel surface in order to adsorb metal ions from aqueous or non aqueous solvents<sup>1-5</sup>. As in solution phase, many complex species may be formed at the solid-solution interface by the reaction of the metal ion with the immobilized functional organic molecule<sup>6-8</sup>. Techniques such as <sup>13</sup>C CPMAS NMR<sup>9,10</sup> and electron spin resonance (ESR)<sup>8,11</sup> have been used to determine the structures of these complex species. The second technique has been particularly useful for copper complexes<sup>10,12</sup>.

Cobalt (II) is adsorbed from acetone solution by the attached benzimidazole yielding a pale blue complex<sup>13</sup>. The adsorption of the metal ion occurs according to the reaction:  $m \equiv\text{SiL} + \text{CoX}_2 \rightarrow (\equiv\text{SiL})_m\text{CoX}_2$ , where  $\equiv\text{SiL}$  is the attached neutral functional organic group on the silica surface. The stepwise complex formation, which consists of a change in the average number of the ligand, m, coordinating one metal ion is a function of the metal loading in the present case because the surface density of attached ligands is constant. The correlation between the structure of the complexes in the solution phase and that on the solid surface is not straightforward because from a steric point of view



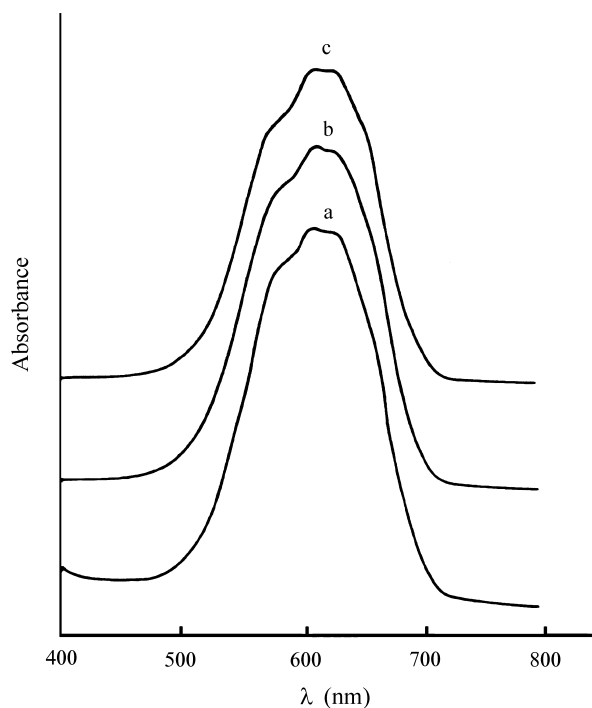


**Figure 1.** Isotherm of adsorption of  $\text{Co}(\text{ClO}_4)_2$  from acetone solution at 298 K by benzimidazole modified silica gel,  $\equiv\text{SiL}$  ( $L = \text{N-propylbenzimidazole}$ ).



**Figure 2.** Infrared spectra of  $(\equiv\text{SiL})_m\text{Co}(\text{ClO}_4)_2$ , pressed disk. Metal loading on the surface ( $N_f/N_o$ ): (a) 0, (b) 0.065 and (c) 0.21.

where  $C$  is the metal concentration in the solution phase in equilibrium with the solid phase. Plotting  $C/N_f$  vs.  $C$  gave a straight line with correlation coefficient  $r = 0.997$  was obtained. The calculated constants were:  $b = 3.0 \times 10^3 \text{ L mol}^{-1}$  and  $N_s = 0.098 \times 10^{-3} \text{ mol g}^{-1}$ . The magnitude of the constant  $b$  is the same as that determined for reaction of the pendant benzimidazole ligand and cobalt (II) in non aqueous solvents<sup>3</sup>. The chemical species formed on the surface is



**Figure 3.** Electronic absorption spectra of  $(\equiv\text{SiL})_m\text{Co}(\text{ClO}_4)_2$  immersed in  $\text{CCl}_4$ : (a)  $N_f/N_o = 0.065$ , (b)  $N_f/N_o = 0.16$  and, (c)  $N_f/N_o = 0.21$ .

thermodynamically stable and adsorption occurs by nitrogen-metal bond formation. The reaction at the surface can be represented by the equation:



The equation shows that when the metal ion diffuses into the solid-solution interface it is followed by the  $\text{ClO}_4^-$  counterion and then, the adsorption occurs as an adsorption of a neutral species. The equation also shows that as the concentration of the metal ion increases at the solid-solution interface, the average number of the attached ligands coordinated to the metal ion decreases because the surface density of the ligands is constant. Therefore, it is very important to study the structure of the species taking into account the quantity of the metal adsorbed on the surface<sup>8</sup>.

#### Infrared spectra

The infrared spectra of  $(\equiv\text{SiL})_m\text{Co}(\text{ClO}_4)_2$  as a function of metal loading is presented in Fig. 2. The bands observed between  $1570$  and  $1450 \text{ cm}^{-1}$  are due to the vibrational modes involving the benzimidazole ring. The band at  $1500 \text{ cm}^{-1}$  observed in Fig. 2a (sample without adsorbed metal,  $N_f/N_o = 0$ ) is slightly shifted to higher frequency,  $1504 \text{ cm}^{-1}$  (Fig. 2b,  $N_f/N_o = 0.065$ ), and for the saturation condition is shifted to  $1518 \text{ cm}^{-1}$  (Fig. 2c,  $N_f/N_o = 0.21$ ). This particular band is assigned to the skeleton vibrational mode of the ring which involves coupled vibrations,  $\nu\text{CN} + \nu\text{CC}$ <sup>15,16</sup>. This band normally is shifted toward higher frequency upon metal-nitrogen bond formation<sup>3,8</sup>. Other

bands observed in the spectra are not sensitive to nitrogen-metal bond formation.

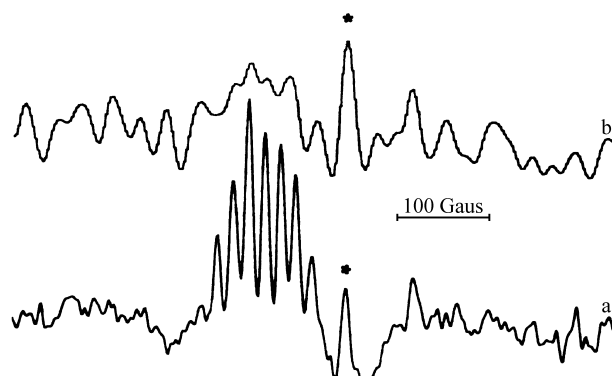
If the adsorption occurs exclusively at the benzimidazole basic site *i.e.*, due to the formation of a nitrogen-metal bond, the saturation value should give an idea of the average number of ligands coordinated to the central metal ion. However, it must be remembered that the surface is heterogeneous and the ligands are not distributed uniformly on this surface and thus, many of them may remain uncoordinated even at surface saturation conditions.

#### Electronic spectra

The electronic spectra for the complex with Nf/No 0.065, 0.16 and 0.21 were recorded. However, no spectral changes (Fig. 3) were observed as the degree of loading was varied, which may suggest that in every case only one chemical species was formed on the surface. A different behavior was observed for Cu(II) complexes adsorbed on benzimidazole-modified silica, where the spectra changed for different degrees of metal loadings<sup>8</sup>. In the last case, more than one species was formed on the surface.

#### ESR spectra

Figure 4 shows the esr spectra obtained for  $(\equiv\text{SiL})_m\text{Co}(\text{ClO}_4)_2$ , under the experimental conditions: Nf/No = 0.065 and 0.21. For Nf/No = 0.21 (Figure 4a) one can distinguish very well nine superhyperfine line structures, characteristic of the interaction of benzimidazole nitrogen atoms with the cobalt unpaired electron, corresponding to the transition  $M_s = -1/2$  to  $1/2$ , and Co nuclear spin  $I = 7/2$ . The other expected transitions are barely seen due to the broadening effects but there are residual broadened superhyperfine lines that may be identified by comparing the second harmonic experimental spectrum with the simulated one. The less concentrated species (Fig. 4b) shows broadened superhyperfine lines in all hyperfine transitions including those of  $M = -1/2$  to  $1/2$ . The spectra (Fig. 4b) as a whole resembles that corresponding to the more concentrated perchlorate species (Fig. 4a). This behavior is indicative that the overall symmetry of the cobalt-benzimidazole complex is not changed when cobalt is diluted *i.e.*, the interaction with four benzimidazole molecules persists. The persistent intense line (starred peaks) with  $g = 2.00$  visible



**Figure 4.** ESR spectra of  $(\equiv\text{SiL})_m\text{Co}(\text{ClO}_4)_2$ : (a) Nf/No = 0.098, (b) Nf/No = 0.065. The starred peaks are due to the  $\text{Fe}^{3+}$  impurity in the silica gel.

in all spectra for  $\equiv\text{SiL}$  or  $(\text{SiL})_m\text{Co}(\text{ClO}_4)_2$ , is due to the  $\text{Fe}^{3+}$  impurity.

The spectra shown in Fig. 4 may be analyzed considering a square planar structure with the metal ion at the origin and four ligands at the equatorial positions. A powder simulation spectrum was generated using the hamiltonian parameters in Table 1 and the line shape consisting of a ratio of Gaussian to Lorentzian equal to 50 percent and line widths of 35 gauss in the parallel and 30 gauss in the perpendicular positions, respectively. The calculations were carried out using the accepted values for  $P = 254 \text{ cm}^{-1}$ <sup>17</sup> and the spin orbit coupling constant  $\lambda = 178 \text{ cm}^{-1}$ <sup>18</sup>. The calculated perpendicular and parallel directions of the superhyperfine coupling constant of the ligand,  $K^N$ , by simulation up to second order in the perturbation treatment for the superhyperfine spectra<sup>19</sup>, gave:  $K^N_{\perp} = 16$  and  $K^N_{\parallel} = 8$  gauss. The resulting simulated spectrum, which agrees fairly well with the experimental spectrum, is shown in Fig. 5.

#### Conclusions

Only one adsorbed complex species is detected for different surface loadings with the metal ion. The ESR study indicated that we have essentially an octahedral complex with tetragonal distortion in a low spin configuration. Under the  $D_{4h}$  crystalline electric field, Co(II) interacts with four nitrogen nuclei of benzimidazole molecules in the equatorial plane. According to the foregoing analysis

**Table 1.**

	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{\text{Co}}$ (gauss)	$A_{\perp}^{\text{Co}}$ (gauss)	$K^N$ (gauss)	Optical transition ( $\text{cm}^{-1}$ )
Experiment	2.0023	2.0650	23	166.0 <sup>a</sup>		17,015
Calculated	2.0023	2.0650	22	-165.5	$K^N_{\perp} = 16$ $K^N_{\parallel} = 8$	17,044

<sup>a</sup> Considering the transition  $M = -1/2$  to  $1/2$  (absolute value).



**Figure 5.** Second harmonic simulated spectrum using data from Table 1. The agreement is fairly good for the central transition ( $M = -1/2$  to  $1/2$ ) where superhyperfine lines 1 to 9 are indicated. In the real spectrum the other transitions are broadened but some structure is visible by comparing with the simulated spectrum.

we have essentially a  $^2A_1$  ground state with the electron in a  $dz^2$  orbital. About 58 percent of the normalized angular variation of this orbital is in  $dx^2-y^2$  and this justifies the observation of superhyperfine lines with the four nitrogen nuclei in the equatorial plane of symmetry of the complex.

### Acknowledgments

Y.G. and E.R. are indebted to FINEP and N.L.D.F. to FAPESP for financial support.

### References

1. Leyden, D.E.; Luttrell, G.H. *Anal. Chem.* **1975**, *47*, 1612.

2. Marshall, M.A.; Mottola, H.A. *Anal. Chem.* **1985**, *57*, 729.
3. Gushikem, Y.; Moreira, J.C. *J. Colloid Interface Sci.* **1985**, *107*, 70.
4. Andreotti, E.I.S.; Gushikem Y. *J. Colloid Interface Sci.* **1991**, *142*, 97.
5. Moreira, W.C.; Gushikem, Y.; Nascimento, O.R. *J. Colloid Interface Sci.* **1992**, *150*, 115.
6. Yatsmirskii, K.B.; Filippov, A.P.; Karpenko, G.A. *Dokl. Phys. Chem.* **1981**, *251*, 251.
7. Kudryavtsev, G.V.; Ivanov, V.M.; Lisichkin, G.V. *Dokl. Inorg. Chem.* **1980**, *250*, 39.
8. Dias Filho, N.L.; Gushikem, Y.; Rodrigues, E.; Moreira, J.C.; Polito W.L. *J. Chem. Soc. Dalton Trans.* **1994**, 1493.
9. Shinoda, S.; Saito Y. *Inorg. Chim. Acta* **1982**, *63*, 23.
10. Rodrigues Filho, U.P.; Gushikem, Y.; Fujiwara, F.Y.; Stadler, E.; Drago V. *Struct. Chem.* **1994**, *5*, 129.
11. Tancredo, A.; Moreira, J.C.; Gushikem, Y.; Nascimento, O.R. *Colloids Surf.* **1986**, *19*, 41.
12. Dias Filho, N.L.; Gushikem Y. *J. Mol. Struct. (Theochem)*, **1995**, *335*, 175.
13. Dias Filho, N.L.; Ph D Thesis, Instituto de Física e Química de São Carlos, USP, 1993.
14. Gushikem, Y.; Iamamoto, M.S. *J. Colloid Interface Sci.* **1990**, *134*, 275.
15. Perchard, C.; Novak, A. *J. Chim. Phys.* **1968**, *65*, 1964.
16. Cordes, M.M.; Walter, J.L. *Spectrochim. Acta Part A* **1968**, *24*, 1421.
17. McGarvey, B.R. *J. Phys. Chem.* **1967**, *71*, 51.
18. McClure, D.S. *Solid. St. Phys.* **1962**, *9*, 399.
19. Chow, C.; Chang, K.; Willet, R.D. *J. Chem. Phys.* **1973**, *59*, 2629.

FAPESP helped in meeting the publication costs of this article