Structure of Copper Complexes Adsorbed on a Silica Gel Surface Chemically Modified with Benzimidazole†

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Silica gel having a particle size between 0.2 and 0.05 mm and a specific surface area, S_{BET} = 473 $m^2 g^{-1}$, was chemically modified with benzimidazole. Adsorption isotherms of CuX_2 (X = Cl, Br or ClO_4) from ethanol and acetone solutions were studied at 298 K. The metal is bonded to the surface through the free nitrogen atom of the attached benzimidazole. The average number of ligands co-ordinated to the central metal ion was shown to depend on the solid surface loading by the solute. At low loading the electronic and ESR spectral parameters indicated that the copper ion is in a distorted-tetragonal symmetry field.

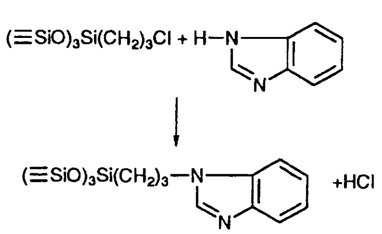
Many organic molecules containing nitrogen have been chemically bonded to silica gel surfaces in order to adsorb metal ions from aqueous and non-aqueous solvents.[1–9] The nature of the complex species adsorbed on the surface of the modified solid has been studied. As in the solution phase, many complex species may be formed on the solid surface by the reaction of the metal ion with the immobilized organic molecules.[10,11] However, some limitations are imposed on the complexes formed at the solid–solution interface because of steric effects, since the attached ligands have limited mobility. The stepwise complex formation, which consists of a change in the number of attached ligands co-ordinating one metal ion, is therefore a function of the surface loading of the support. Techniques such as ^{13}C NMR [using cross polarization magic angle spinning (CP-MAS)],[12] infrared,[4] electronic,[5,7] and electron spin resonance (ESR) spectroscopy,[13] have been used to determine the structures of these complex species on the surface.

The objective of this work is the preparation of a silica chemically modified with benzimidazole molecules and a study of the adsorption of CuX_2 from non-aqueous solvents. This metal was chosen because it can form stable complexes with imidazole and benzimidazole molecules[14–19] and in the present case served also as a probe to determine the geometrical arrangements of the ligands around the central metal ion. Infrared, electronic and ESR techniques were used to characterize the surface complexes.

Experimental

Preparations.—Silica gel 60 (Merck) having a particle size between 0.2 and 0.05 mm was activated at 420 K under vacuum (10^{-3} Torr, *ca.* 0.133 Pa). This silica (*ca.* 50 g) was suspended in dry xylene (200 cm^3), 3-chloropropyltrimethoxysilane (15 cm^3) was added and the mixture stirred for 24 h at 380 K in a nitrogen atmosphere. The resulting modified silica, $\equiv Si(CH_2)_3Cl$, was immersed in pure dimethylformamide (150 cm^3) and benzimidazole (17.5 g, 0.15 mol) was added. The mixture was stirred 24 h at 380 K under a nitrogen atmosphere. The resulting modified silica was filtered off and washed with dimethylformamide and ethanol. The product was heated for 8 h at 353 K under vacuum (10^{-3} Torr).

$$3{\equiv}SiOH + (CH_3O)_3Si(CH_2)_3Cl \longrightarrow ({\equiv}SiO)_3Si(CH_2)_3Cl + 3CH_3OH$$



Scheme 1

The reactions involved in the preparations are shown in Scheme 1 where ≡SiOH stands for the silanol group of the silica matrix.

The amount of benzimidazole attached to the silica surface was determined by nitrogen analyses using the Kjeldahl method. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method using a Micromeritics Flow Sorb 2300 apparatus.

Adsorption Isotherms.—The adsorption isotherms of metal ions on benzimidazole-modified silica, hereafter denoted as SiL, were determined for CuX_2 (X = Cl, Br or ClO_4) in ethanol or acetone solutions (concentrations between 1×10^{-4} and 5×10^{-3} mol dm^{-3}). Solutions of the metal ions were shaken with SiL (0.1 g) at 298.0 ± 0.2 K for 40 min. The supernatants were decanted and the amount of the metal ions was determined by complexometric titration using ethylenediaminetetracetic acid (H_4edta). The quantity of the metal ion sorbed by SiL, N_f, was calculated applying equation (1) where N_a is the initial

$$N_f = (N_a - N_s)/w \qquad (1)$$

number of moles of metal ion in solution, N_s the number in solution at equilibrium with the solid phase and w the sorbent mass.

Surface Complex Formation.—The amount of benzimidazole

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† *Non-SI unit employed:* G = 10^{-4} T.

molecules attached to the silica surface was $N_0 = 0.48 \times 10^{-3}$ mol g^{-1} and the specific surface area, $S_{BET} = 473$ m^2 g^{-1}. Assuming that the molecules uniformly cover the surface, the average molecular density, δ, can be calculated by applying equation (2) where N is Avogadro's number.

$$\delta = N_0N/S_{BET} \qquad (2)$$

The average intermolecular distance, l, can be calculated by using equation (3). The calculated values were $\delta = 0.61$

$$l = (S_{BET}/N_0N)^{\frac{1}{2}} \qquad (3)$$

molecule nm^{-2} and $l = 1.28$ nm. Considering this average intermolecular distance and the propyl spacer between the matrix surface and the benzimidazole group, the attached ligands may have sufficient mobility to co-ordinate with the metal ion and may result in various surface complex species. Assuming that the benzimidazole groups are the exclusive adsorption sites, the complexes formed on the surface can be represented as $(SiL)_mCuX_2$. Therefore, equation (1) can also be expressed as (4) where $N_c[(SiL)_mCuX_2]$ is the number of moles

$$N_f = \sum_m N_c[(SiL)_mCuX_2]/w \qquad (4)$$

of the complex on the surface and the summation is extended for all complex species. The amount of the attached ligand can be written as in equation (5) where $N_L(SiL)$ represents the

$$N_0 = \{N_L(SiL) + \sum_m mN_c[(SiL)_mMX_2]\}/w \qquad (5)$$

number of moles of the unco-ordinated attached ligand. On dividing equation (6) by (7) (see below), the ratio N_f/N_0 gives the fraction of the surface-attached ligand bonded to the metal ion.

Spectroscopy.—The infrared spectra of thin, self-supported solid disks of the samples were obtained by the transmission technique using a Nicolet FT-IR spectrophotometer. The spectra were recorded between 1250 and 1800 cm^{-1}. The electronic absorption spectra were obtained by immersing the solid SiL with MX_2 adsorbed on the surface in spectral-grade carbon tetrachloride in a quartz cell having 1 mm path length. A Cary 2300 spectrophotometer was used. The ESR spectra of CuX_2 complex species sorbed in the solid phase were obtained at 77 K with Cr^{3+} in magnesium oxide as the g marker. Varian E-109, series Line Century X-band and Bruker model 300 spectrometers were used.

Results and Discussion

Adsorption Isotherms.—The adsorption isotherms of CuX_2 on the solid SiL are shown in Fig. 1, as plots of N_f against the concentration c_2 of the solute in equilibrium with the solid phase. The influence of the solvent on the adsorption process is clearly observed. In ethanol solutions the adsorption of $CuCl_2$ [Fig. 1(*b*)] and $Cu(ClO_4)_2$ [Fig. (1(*e*)] is considerably lower than those observed in acetone solutions [Fig. 1(*a*) and 1(*d*)]. The reason is that ethanol, being more polar than acetone, can more strongly solvate the functional groups on the surface and compete with the metal ions for the adsorption sites.[4]

The influence of the counter ion on the adsorption process is also important. The low affinity for $Cu(ClO_4)_2$ towards the solid phase [Fig. 1(*d*) and 1(*e*)] in comparison with those observed for $CuCl_2$ [Fig. 1(*a*) and 1(*b*)] and $CuBr_2$ [Fig. 1(*c*)] is a consequence of the poorer co-ordination ability of ClO_4^-, in comparison with Cl^- and Br^-, to the metal ion in solution phase.

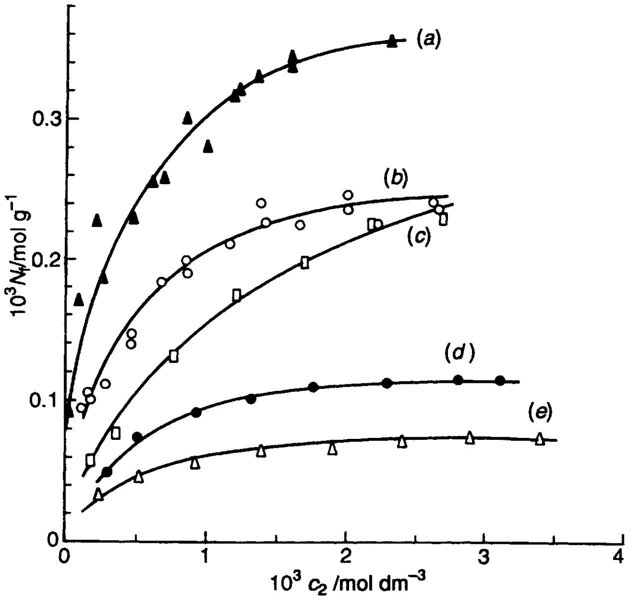

Fig. 1 Adsorption isotherms of CuX_2 on SiL at 298 K: (*a*) $CuCl_2$ from acetone solution, (*b*) $CuCl_2$ from ethanol solution, (*c*) $CuBr_2$ from ethanol solution, (*d*) $Cu(ClO_4)_2$ from acetone solution and (*e*) $Cu(ClO_4)_2$ from ethanol solution

Table 1 Adsorption of CuX_2 by SiL from ethanol and acetone solutions at 298 K

X	Solvent	$10^{-3}\ b$/dm^3 mol^{-1}	$10^3\ N_f^s$/mol g^{-1}	r
Cl	Ethanol	3.4	0.26	0.996
	Acetone	5.7	0.37	0.991
Br	Ethanol	1.1	0.31	0.994
ClO_4	Ethanol	2.3	0.085	0.998
	Acetone	3.1	0.12	0.999

Since the attached ligand is neutral, the adsorption process can be represented by the equilibrium SiL(adsorbed solvent) + CuX_2(solute in solution) $\rightleftharpoons$ SiL·CuX_2(adsorbed solute) + solvent (in solution). Upon diffusion of the metal ion into the solid–solution interface it is accompanied by the counter ion and therefore the solute can also be treated as a neutral species. The equilibrium constant for this process is defined in equation (6)[20] where a_2 and a_1 are, respectively, the activity coefficients

$$K = \frac{N_f a_1}{(N_f^s - N_f)a_2} \qquad (6)$$

of the solute and solvent in the solution phase and N_f^s is the sorption capacity. The value of N_f^s is a constant which depends on the nature of the solvent, solute and temperature. In dilute solution a_1 is also constant so we can write $b = K/a_1$. Equation (6) can be rearranged and written in the form known as the Langmuir equation (7)[20] where concentration c_2 is used

$$\frac{c_2}{N_f} = \frac{1}{bN_f^s} + \frac{c_2}{N_f^s} \qquad (7)$$

instead of activity a_2. The constants b and N_f^s were calculated by plotting c_2/N_f against c_2 and the values are listed in Table 1. The correlation coefficients r of the straight lines were always > 0.99.

The calculated values of b suggest that the sorption of the metal from solution by the solid phase occurs by nitrogen-to-metal bond formation. The magnitude of the constants b and N_f^s are slightly higher in acetone than in ethanol as solvent. These results are consistent with the higher polarity of ethanol which can more strongly solvate the solute and the basic sites on the surface.

Infrared Spectra.—Infrared spectra of $(SiL)_mCu(ClO_4)_2$ for different values of the ratio N_f/N_0 are shown in Fig. 2 and the wavenumbers listed in Table 2. The band at 1500 cm^{-1} observed in Fig. 2(*a*) and 2(*b*) is shifted in Fig. 2(*c*) to 1523 cm^{-1}. This particular band is assigned to the skeleton vibrational mode of the ring which involves coupled vibrations, ν(CN) + ν(CC).[4,21,22] This band has been observed to be shifted toward higher frequency upon metal–nitrogen bond formation.[21] In Fig. 2(*b*) this shift is not observed because N_f/N_0 is very small and most SiL remains unco-ordinated. The weak bands which appear at about 1660 cm^{-1} in Fig. 2(*a*) and (*b*) and disappear in (*c*) is assigned to a combination band.[21,22] Other bands are insensitive to the co-ordination and remain unshifted.

Table 1 presents the infrared bands for all samples as a function of metal loading on the surface. The assignments of the bands observed for $(SiL)_mCuCl_2$ and $(SiL)_mCuBr_2$ at different metal loadings are the same as those made for perchlorate derivatives.

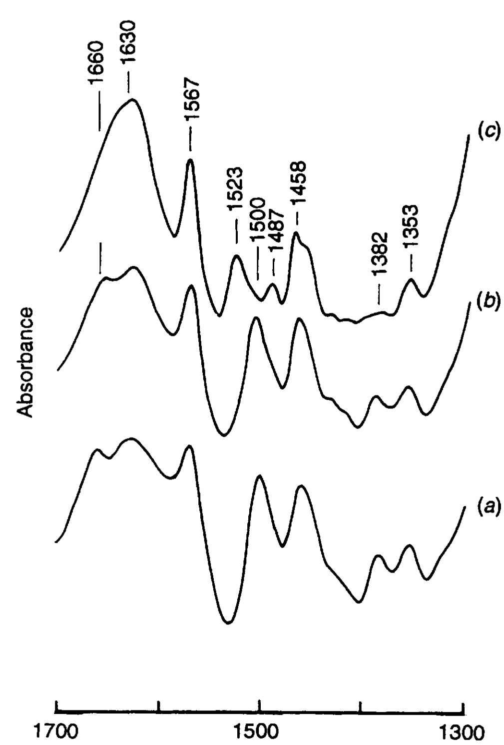

Fig. 2 Infrared spectra of a self-supported disk of $(SiL)_mCu(ClO_4)_2$ as a function of metal loading, N_f/N_0 = 0 (*a*), 0.04 (*b*) and 0.2 : 1 (*c*)

Electronic Spectra.—In Fig. 3 the spectra for $(SiL)_mCuCl_2$ are shown. The peak maximum is shifted to higher energy as the ratio N_f/N_0 decreases, *i.e.* 850, 800 and 700 nm at N_f/N_0 0.5, 0.34 and 0.06 : 1, respectively. The shift of the transition bands to lower energy is very similar to the change in the electronic spectrum of aqueous copper(II) solution which occurs on addition of aqueous ammonia. The absorption maximum increases with successive replacement of water in the complex $[Cu(NH_3)_n(H_2O)_{6-n}]^{2+}$.[23] In the present case the total concentration of the attached organic molecules on the surface is constant and, since they are strong donor bases, at low metal loading they can saturate the co-ordination sites of the metal displacing the chloride ion. It is known that monodentate nitrogen-donor ligands form CuL_4X_2 in which the four ligands L are strongly bound and the two $X(Cl^-$, Br^- or $ClO_4^-)$ are weakly bound to the metal ion in the bulk phase.[18,19] The observed absorption band for the surface complex at lowest loading is similar to those observed for $CuL_4X_2(D_{4h}$ symmetry) and therefore the two gaussian-deconvoluted bands (see last column of Table 3) can be assigned to transitions from the $^2B_{1g}$ ground state to the excited states ^2E_g and $^2B_{2g}$.[24–26] On increasing the metal loading, the average number of ligands attached to the metal ion decreases and the energy difference between the $d_{x^2-y^2}$ orbital (assumed as the ground state although the effective symmetry can change) and d_{xy} and d_{xz}, d_{yz} decreases, shifting the transition bands to lower energy.

For $(SiL)_mCuBr_2$, the peak maximum at N_f/N_0 = 0.18 : 1 is observed at 780 nm and at N_f/N_0 = 0.04 : 1 at 710 nm (Table 3). In this case at higher loading a good-quality spectrum was not

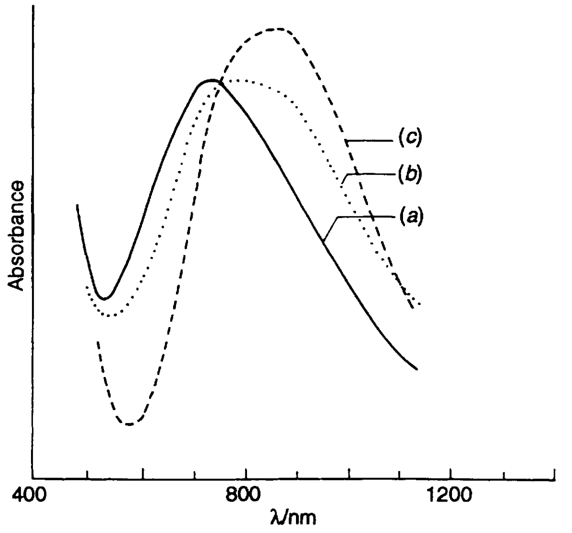

Fig. 3 Electronic spectra of $(SiL)_mCuCl_2$ immersed in carbon tetrachloride. Position of the peak maxima as a function of metal loading, N_f/N_0 = 0.06 (*a*), 0.34 (*b*) and 0.50 : 1 (*c*)

Table 2 Infrared bands (cm^{-1}) of $(SiL)_mCuX_2$*

	$(SiL)_mCuCl_2$		$(SiL)_mCuBr_2$		$(SiL)_mCu(ClO_4)_2$		
SiL	N_f/N_0 0.06	0.5	0.04	0.18	0.04	0.2	Approximate assignment
1660vw	1662w	—	1660vw	—	1660vw	—	Combination band
1630(br)	1630(br)	1630(br)	1630(br)	1630(br)	1630(br)	1630(br)	$\delta(H_2O)$
1567m	1568m	1566m	1568m	1567m	1567m	1569m	ν(CC) + δ(CH)
1500m	1503m	1520m	1502m	1525m	1503m	1523m	ν(CN) + ν(CC)
		1480vw		1485w		1487w	
1458m	1463m	1463m	1464m	1464m	1465m	1467m	ν(CN) + δ(ring)
			1450vw	1450vw		1457vw	
1382w	1385w	1385vw	1385w	—	1385w	1385vw	propyl $\delta(CH_2)$
1353w	1352w	1352w	1350w	1350w	1351w	1352w	

* v = Very, m = medium, w = weak, br = broad.

obtained. For $(SiL)_mCu(ClO_4)_2$, the position of the peak maximum is the same for both metal loading values, *i.e.* 700 nm at $N_f/N_0 = 0.2$ and 0.04. In this case, a possible explanation is that, owing to the low co-ordination ability of the perchlorate anion, only benzimidazole molecules are bonded to the metal ion even at higher loading.

The positions of the gaussian-deconvoluted bands for $(SiL)_mCuCl_2$ and $(SiL)_mCuBr_2$ at lower metal loading (last column in Table 3) are similar to that observed for the perchlorate derivative under the same conditions. Therefore, the assignments made for both transitions are also the same.

ESR Study.—The ESR parameters of $(SiL)_mCuX_2$ (X = Cl, Br or ClO_4) are listed in Table 3 and spectra are shown in Figs. 4–6.

The spectrum for $(SiL)_mCuCl_2$ at $N_f/N_0 = 0.06:1$ is shown in Fig. 4. The hyperfine interaction of the electronic spin ($S = \frac{1}{2}$) with the nuclear spin ($I = \frac{3}{2}$) of copper(II) is observed. In the second-derivative spectrum (shown in detail) the superhyperfine structure can be observed. The separation between the lines is 15 G. At higher metal loading, *i.e.* $N_f/N_0 = 0.5:1$ (spectrum not shown), there was coalescence of the hyperfine structure due to significant dipolar–dipolar interactions which broadened the lines by approximately 70 G (calculated by simulation). The results are consistent with average copper atom densities of 0.016 atoms nm^{-2} at $N_f/N_0 = 0.06:1$ and 0.37 atom nm^{-2} for $N_f/N_0 = 0.5:1$.

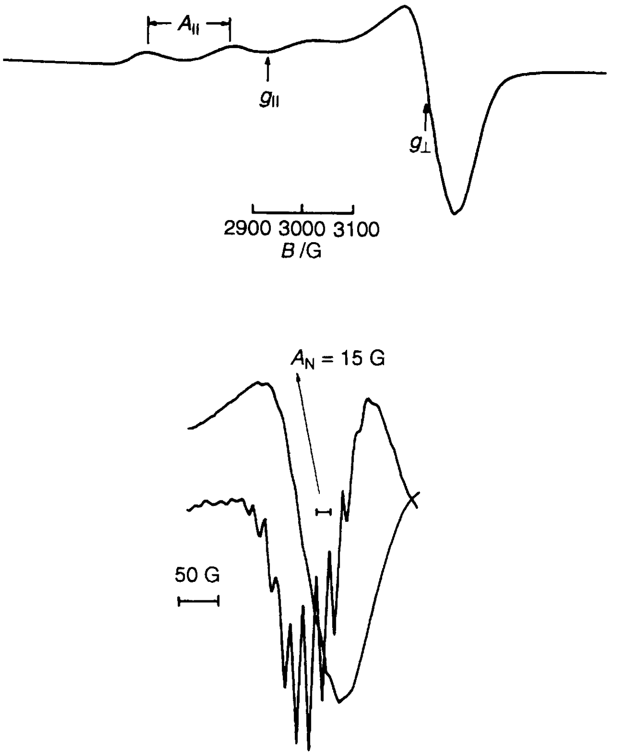

Fig. 4 The ESR spectrum (upper) of $(SiL)_mCuCl_2$ at $N_f/N_0 = 0.06:1$. The expanded spectrum together with the second derivative spectrum is shown below

Fig. 5 shows the ESR spectra of $(SiL)_mCuBr_2$ with different loadings. The spectra at $N_f/N_0 = 0.04$ [Fig. 5(*a*)] and 0.18 : 1 [Fig. 5(*b*)] do not show superhyperfine structures. At higher loading a change in the axial spectrum due to broadening of the resonance was observed (spectrum not shown).

Fig. 6 shows the spectra for $(SiL)_mCu(ClO_4)_2$. The spectrum at $N_f/N_0 = 0.04:1$ [Fig. 6(*a*)] is very similar to that of $(SiL)_mCuCl_2$ at $N_f/N_0 = 0.06:1$ (Fig. 4). In the six-fold expansion shown in detail in Fig. 6 the spectrum also shows superhyperfine structure indicating that the nitrogen atoms are co-ordinated to Cu^{II} in the equatorial plane. Upon increasing the surface loading, $N_f/N_0 = 0.2:1$ [Fig. 6(*b*)], the superhyperfine structure is not observed so clearly.

For similar complexes of CuL_4X_2 (L = *N*-propylimidazole; X = Cl, Br or ClO_4)[18,19] the following ESR parameters and ligand-field peak maxima have been found: (*a*) X = Cl, $g_{\parallel} = 2.28$, $A_{\parallel} = 144$ G and $\lambda_{max} = 630$ nm, (*b*) X = Br, $g_{\parallel} = 2.28$, $A_{\parallel} = 165$ G and $\lambda_{max} = 580$ nm and (*c*) X = ClO_4, $g_{\parallel} = 2.25$, $A_{\parallel} = 185$ G and $\lambda_{max} = 540$ nm. The ESR parameters are very similar with those of $(SiL)_mCuX_2$ listed in Table 3. The ligand-field spectral data for these complexes compared with those given in the text show that the peak maxima of the surface complex are shifted to lower energy. The decrease in energy separation between the $^2B_{1g}$ and ^2E_g and $^2B_{2g}$ states is assigned to the fact that the attached benzimidazole is less basic than imidazole as is found in the free molecule. For benzimidazole $pK_a = 12.3$[27] and for imidazole 14.52.[28]

In order to interpret the ESR parameters, the model of Abragam and Pryce[29] for Cu^{2+} ion in a crystalline field of distorted tetragonal symmetry was applied. The values of $g_{\parallel}$ and $g_{\perp}$ are given by equations (8) and (9) where $x = \lambda/(E_2 - E_0)$, $y = \lambda/(E_3 - E_0)$ and λ = spin–orbit coupling; $E_2 - E_0$ and $E_3 - E_0$ are the electronic energy transitions obtained from absorption spectra. Using the above equations, we may compute the values of the optical transitions corresponding to the tetragonal effect of the crystal field.

$$g_{\parallel} = 2 - 8x + 4x^2 - 8xy + y^2 \tag{8}$$

$$g_{\perp} = 2 - 2y - xy - 2y^2 \tag{9}$$

The computed values of the electronic transition energies in Table 3 correspond to the deconvoluted absorption bands. For the hyperfine constants $A_{\perp}$ and $A_{\parallel}$ we have the equations (10)

Table 3 Electron spin resonance parameters and deconvoluted absorption bands of $(SiL)_mCuX_2$. Calculated values in parentheses

X	N_f/N_0	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$/G	$A_{\perp}$[a]/G	A_N[b]/G	Δ[c]/nm	λ[d]/cm^{-1}	k[e]
Cl	0.06	2.29	2.06	146	—	15	750, 655	−496	0.18
	(0.06)	(2.29)	(2.06)	(−157)	(55.9)		(739, 665)[f]		
Br	0.04	2.23	2.06	158	—	—	734, 674	−418	0.18
	(0.04)	(2.23)	(2.06)	(−179)	(54.5)		(723, 697)		
	0.18	2.31	2.06	157	—	—	833, 729	−474	0.18
	(0.18)	(2.31)	(2.06)	(−148)	(56.7)		(836, 731)		
ClO_4	0.04	2.29	2.06	153	—	15	744, 650	−489	0.18
	(0.04)	(2.29)	(2.06)	(−158)	(55.7)		(738, 666)		
	0.20	2.31	2.07	138	—	—	702, 607	−548	0.18
	(0.20)	(2.31)	(2.07)	(−149)	(56.9)		(717, 638)		

[a] It was not possible to determine the perpendicular component of A. [b] Superhyperfine structure typical for interaction with nitrogen in square-planar configuration. [c] Deconvoluted absorption bands. [d] Reduced or effective spin–orbit coupling parameter in frozen complex. [e] Numerical coefficient connected with admixture of configuration. [f] Calculated absorption bands for the electronic spectrum.

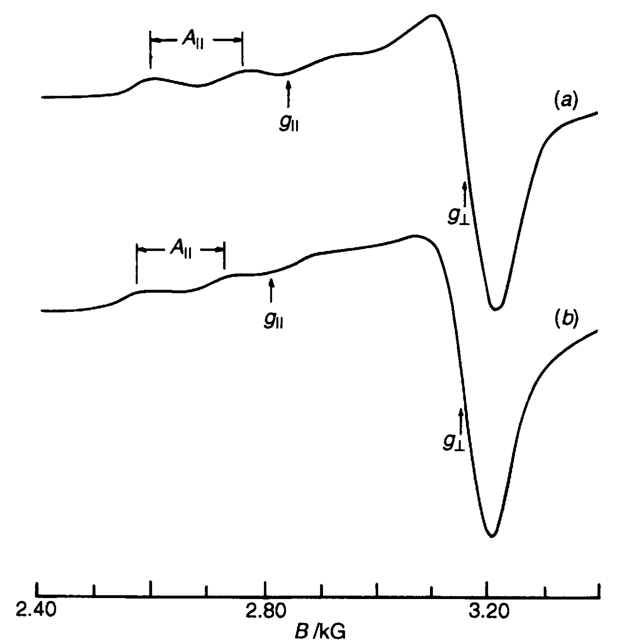

Fig. 5 The ESR spectrum of $(SiL)_mCuBr_2$ as a function of metal loading, N_f/N_0 = 0.04 (*a*) and 0.18:1 (*b*)

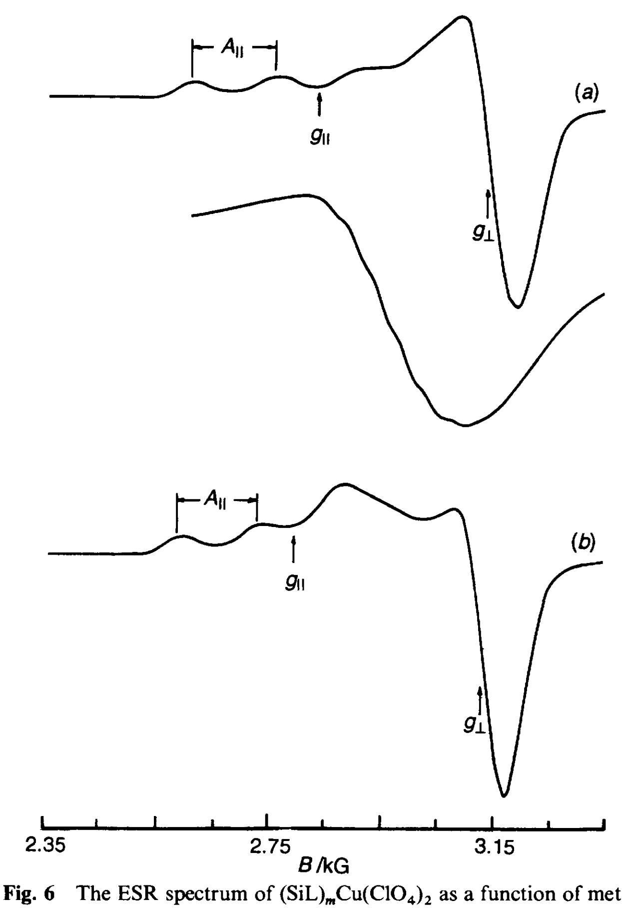

Fig. 6 The ESR spectrum of $(SiL)_mCu(ClO_4)_2$ as a function of metal loading, N_f/N_0 = 0.04 (*a*) (with eight-fold expansion) and 0.20:1 (*b*)

and (11) where $P = 0.036\ cm^{-1}$ for Cu^{2+} and k is a numerical

$$A_{\parallel} = (g_{\parallel} - 2 + \{[3(g_{\perp} - 2) - 4]/7\} - k)P \quad (10)$$

$$A_{\perp} = [g_{\perp} - 2 - (\{[3(g_{\perp} - 2)/2] + 2\}/7) - k]P \quad (11)$$

factor representing the admixture of configurations with s electrons. The fit of the theoretical expressions to the experimental data is very reasonable. The effective spin–orbit coupling constant for Cu^{2+} is reduced from its normal free-ion value of $\lambda = 828\ cm^{-1}$ by as much as 60%. This reduction is normal in the solid state and in frozen solutions of the complexes.[24]

Conclusion

Attached benzimidazole molecules can form surface complexes having similar structures to those found for attached imidazole molecules on silica surfaces.[4] At the lowest loadings the co-ordination sphere in the surface complex species $(SiL)_mCuX_2$ (X = Cl, Br or ClO_4) approximates to square-planar, D_{4h}, symmetry. In this case, the anions X^- are not in the plane determined by the four co-ordinating nitrogen atoms. If semi-co-ordination occurs the anions are placed along the axis perpendicular to the plane, far away from the central metal, due to the Jahn–Teller effect.[19]

Acknowledgements

Y. G. is indebted to Financiadora de Estudos e Projetos (FINEP) for financial support.

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Received 20*th September* 1993; *Paper* 3/05640F