Characterization by EPR spectroscopy of the chiral catalysts bis(oxazoline)-Cu supported in laponites

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An Electron Paramagnetic Resonance study of a chiral Bis(oxazoline)-Cu(II) supported in laponite (synthetic hectorite) is presented. It is concluded that the complex is incorporated into the interlamellar space of the clay giving out isolated Cu(II) entities in which the metal is co-ordinated to oxygen or nitrogen atoms with a symmetry practically planar-square, regardless the solvent used. That point out that the chlorine ligands in the complex are exchanged in the incorporation process in agreement with the previous X-ray absorption spectroscopy data, so that the oxygen atoms of the interlayers and clay surface act as counterions.

Key words: EPR, Cu(II), chiral catalysts

Caracterización, mediante espectroscopia EPR, de los catalizadores quirales bis (Oxazolina)-Cu soportados en Laponitas.

Se presenta un estudio mediante Resonancia Paramagnética Electrónica del complejo quiral Bis(oxazolina)-Cu(II) soportado en laponita (hectorita sintética) (libre de hierro. Del mismo se concluye que el complejo se incorpora en el espacio interlamelar de la arcilla dando lugar a entidades de Cu(II) aisladas en las cuales el metal se coordina a átomos de oxígenos y nitrógenos con una simetría prácticamente planocuadrada, independientemente del disolvente empleado. Ello indica, de acuerdo con los datos previos de espectroscopia de absorción de rayos-X, que los ligandos cloruro del complejo son intercambiados en el proceso de incorporación de forma que los oxígenos de la superficie interlaminar y externa de la arcilla actúan como contraiones.

Palabras clave: EPR, Cu(II), catalizadores quirales

1. INTRODUCTION

Bis(oxazoline)-Cu (BIOX-Cu) complexes (see figure 1) are excellent and versatile chiral catalysts as it has been demonstrated through the results obtained when they are used in several reactions (1). So the heterogenization of such systems results to be very attractive for the preparation of new recoverable catalytic materials for using in obtaining fine chemicals. Since they are cationic complexes one of the ways to reach the heterogenization is by means of the electrostatic interaction with anionic solids. The feasibility of this alternative has been checked by using clays as supports and in this sense the results obtained by using a laponite (hereafter LAP) are noticeable (2). Because of the influence of the environment on the activity and selectivity of this type of catalysts it is need to perform a detailed characterisation of the obtained materials: either of their textural natures or of the identification of the active centres and their environments.

In this regard it has been determined the specific surface and the basal spacing of the solids when the complex is introduced in them, which results indicated that the complex is placed in the interlamellar space. The infrared spectra, when compared with the original complexes, prove that the complex is not modified in the cationic exchange process used in preparing the materials. The X-ray absorption spectroscopy (3) shows that the anionic support acts as the counterion of the cationic complex because the EXAFS spectra of the solid suggests the absence of the chlorine used as counterion in the solution of

BIOX-Cu. Besides the lack of the observation of nearby copper is in agreement with the isolation of the catalytic sites.

Keeping in mind all this ideas and taking into account that Cu(II) complexes are generally paramagnetic, being their Electron Paramagnetic Resonance (EPR) signal very sensitive on the metal co-ordination, we have undertaken an study by means EPR spectroscopy of LAP clays in which the BIOX-Cu

Fig .1.- Formula of the bis(Oxazoline)-Cu complex.

TABLE I. SPIN HAMILTONIAN PARAMETERS OF THE Cu(II) ENTITY IN DIFFERENT SAMPLES

	BIOX-CU		LAPNIT	LAPMET	CuLAP
	solid (RT)*	frozen solution (LNT)	solid RT	solid RT	solid RT
$g_{ }$	2.16	2.28	2.25	2.26	2.38
$g_{\perp}$	2.07	2.09	2.07	2.07	2.08
$A_{ }$ (MHz)	346	430	510	490	410
$A_{\perp}$ (MHz)	-	< 60	< 30	< 30	≈ 65

* In the case of solid BIOX-Cu the determination of the spin Hamiltonian parameters is rather controversial. (see text)

complex have been introduced from solutions in methanol (LAPMET) or nitroethane (LAPNIT) by cation exchange. These spectra have been compared with that observed in LAP clay where Cu(II) has been incorporated from a CuCl₂ solution (CuLAP) as well as with the EPR spectra measured in polycrystalline samples of BIOX-Cu and in a frozen solution of BIOX-Cu in CH₂Cl₂.

2. EXPERIMENTAL PROCEDURE

Preparation of exchanged catalysts. To a solution of bis(oxaline) (1 mmol) in methanol (MET) or nitroethane (NIT) (2 ml) 1 mmol of CuCl₂·H₂O was added. To this solution of green complex 1 g of Na-laponite (LAP) is slowly added and the resulting suspension is stirred for 24 hours. The solid is filtered, washed with the same solvent, then with dichloromethane and dried under air.

Elemental analysis shows the expected N/Cu ratio and a copper content of 0.48 mmol·g⁻¹, for the clay obtained in methanol, and 0.54 mmol·g⁻¹ for the prepared in nitroethane. The surface areas are 189 and 120 m²·g⁻¹ respectively and the basal spacing 16.1 Å and 18.4 Å.

EPR spectra were measured in an ESP380E spectrometer from Bruker working either in X-band or Q-band or in an E112 spectrometer from Varian working in X-band. Powdered samples were examined by introducing them into standard EPR quartz tubes (707-SQ from Wildmad). Spectra were measured at different temperatures between room temperature (RT) and liquid nitrogen temperature (LNT).

3. RESULTS

3.1 EPR spectra of the BIOX-Cu complex.

In figure 2 it is shown the EPR spectrum measured at LNT of a polycrystalline sample of BIOX-Cu (a) and that observed in a frozen solution of this complex in dichloromethane (b). In this last case the EPR signal is a typical one of a Cu(II) entity in a planar-square co-ordination and can be described using the following spin-Hamiltonian (SH):

$$H = \mu_B \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + A_{||} I_z S_z + A_{\perp} (I_x S_x + I_y S_y) \quad [1]$$

TABLE II. RESULTS OBTAINED FROM THE EXAFS ANALYSIS.

	Cu-O			Cu-Cl		
	N	R(Å)	$\Delta\sigma^2(\text{\AA}^2)$	N	R(Å)	$\Delta\sigma^2(\text{\AA}^2)$
BIOX-Cu (polycrystalline)	2	1.96	5.5×10^{-3}	2	2.22	3.5×10^{-3}
BIOX-Cu (nitroethane solution)	2	1.95	8.0×10^{-3}	2	2.22	3.6×10^{-3}
CuLAP (clay)	4	1.97	6.0×10^{-3}	-	-	-
LAPNIT (clay)	4	1.96	7.6×10^{-3}	-	-	-

N (co-ordination number); R (interatomic distance); $\Delta\sigma^2$ relative Debye-Waller factor

with $S = 1/2$ and $I = 3/2$ (in spite that copper has two naturally occurring isotopes: ⁶³Cu in 69.2% and ⁶⁵Cu in 30.8%, their nuclear g-factor are very close and the hyperfine lines for both species are not resolved). μ_B is the Bohr magneton and $g_{||}$, $g_{\perp}$, $A_{||}$, $A_{\perp}$ have the usual meaning. A fitting of the predicted spectrum to the observed one yield for the SH parameters the values depicted in table I.

The situation is more complicated in the case of the spectra measured in polycrystalline BIOX-Cu (figure 2a). In a first approximation, rather conflictive, it can be also described as due to a Cu(II) in an axial symmetry with a SH as given by equation [1] and with its values also shown in table I. These anomalous values together the differences of intensity and

Fig. 2.- EPR spectrum of bis (Oxazolina)-Cu complex measured at LNT temperature in X- band. (a) Polycrystalline sample. (b) A solution in CH₂Cl₂.

width of the “parallel” hyperfine (hf) components likely indicates the existence of intermolecular exchange interactions. That is reinforced by the Q-band EPR spectra in which besides the isolated Cu(II) signal a signal due to copper pairs is also detected. Since we are not particularly interested in the polycrystalline complex signal we do not deal more with this spectrum.

3.2 EPR spectra of Cu(II) in LAP clay.

On figure 3 the spectra measured in X-band at RT of LAPNIT (a), LAPMET (b) and CuLAP (c) are represented. In all the cases it can be associated to Cu(II) in axial symmetry and it is described with the SH given by equation [1]. The best fit of the calculated one to the observed signal is reached with the values for the SH parameter collected in table I. No change are observed in the EPR spectra when measured a liquid nitrogen temperature.

The results found in LAPNIT and LAPMET practically coincide and only a slight diminution of the $A_{\parallel}$ interaction constant is observed in the LAPMET case as compared with the LAPNIT one.

More significant changes are observed in the EPR spectrum measured in CuLAP. When compared with the results obtained in LAPMET and LAPNIT an increase of $g_{\parallel}$ together a diminution of $A_{\parallel}$ is observed, which indicate a more severe change in the electronic distribution.

4. DISCUSSION

Recently Extended X-ray Absorption Spectroscopy (EXAFS) experiments have been performed in these samples (4). The relevant information on the local structure around the copper atom is given in table II. In polycrystalline BIOX-Cu the metal is co-ordinated by two oxygen and two chlorine atoms, being unaltered after solution in nitroethane. The only difference between polycrystalline BIOX-Cu and its nitroethane solution is in the relative Debye-Waller (DW) factors, which, as expected, are larger for the solution

The copper environment is different in the BIOX-Cu solution sample than in the corresponding LAPNIT clay. The Fourier transform (FT) peaks corresponding to the first coordination shell appears at different R values, as can be seen in Figure 4. Both clays, CuLAP and LAPNIT, only show the Cu-O contributions (table II), indicating that the chlorine ions are displaced in the exchange process. LAPNIT shows a higher DW factor than CuLAP, probably due to the presence of Cu-N contribution of the BIOX-Cu complex. On the other hand peaks corresponding to second and further shells (figure 4), which could point out the complex, are very small which makes difficult to perform a reliable fitting of the EXAFS spectrum. However, these spectra are different for both clays indicating a different copper environment, likely due to the presence of the complex into LAPNIT.

These results together the formerly described EPR measurements can be explained with a comprehensive model.

The EPR measurements prove, in first place, that the observed paramagnetic entities in the LAP clay are mainly isolated Cu(II) because the EPR signal shows a well-resolved hyperfine structure. In the LAPNIT and LAPMET the spectra are explained with practically the same values of the SH parameters, which result to be similar to that found for others Cu(II) com-

Fig. 3.- X-band EPR spectra of LAPNIT (a), LAPMET (b) and CuLAP (c) measured at RT.

Fig. 4.- Fourier transform of the EXAFS spectra of BIOX-Cu in nitroethane solution (a), CuLAP (b) and LAPNIT (c).

Fig. 5.- Model for the Cu(II) entities in LAPNIT and LAPMET.

plexes in which the metal is co-ordinated to two nitrogen and two oxygen atoms (5, 6). The slight differences found in the values of the SH parameters for the two samples (LAPNIT and LAPMET) can be understood as a consequence of the solvation effects due to residual solvent molecules.

Taking into account these facts a plausible model for the Cu(II) centres in LAP clay that explains the EPR and X-ray absorption spectroscopy data is shown in figure 5. The chlorine ligands are substituted by bonds with the negative charged inner surface of the clay formed by oxygen ions. These ions together with the nitrogen ligands of the BIOX-Cu molecule define the co-ordination plane of the Cu(II). This substitution also explain the differences observed when the SH parameters in LAPMET and LAPNIT are compared with those found for isolated BIOX-Cu complexes in a CH₂Cl₂ frozen solution.

Let us to consider now the EPR spectrum of CuLAP samples in which Cu(II) have been introduced from a solution of CuCl₂. In this samples the EPR signal also correspond to isolated Cu(II) entities and it can be described by the SH given by equation [1]. On the other hand the SH parameters show more variation as it has been commented above. These values for the SH parameters are in the range of that found by other authors for Cu²⁺ in different clays (7). From these available data up to now it is not possible to get a precise idea about the co-ordination environment of Cu(II) in the CuLAP. The X-ray absorption spectroscopy data point out that the chlorine ions are displaced and the present EPR data indicate that the metal co-ordinates in a tetra co-ordinated environment by bonding to oxygen atoms of the inner surface of the laponite and water

molecules. Besides the EPR data show that Cu(II) in this last samples (CuLAP) also is mainly isolated because of the well-resolved hyperfine structure that indicates the lack of exchange interactions.

5. CONCLUSIONS

The formerly described EPR results let us to draw some conclusions about the copper sites in LAPMET and LAPNIT clays. First the Cu(II) is incorporated mainly as isolated paramagnetic entities. The Cu(II) EPR signals in both cases are practically the same. The similarity of the SH parameters in both cases shows that the Cu(II) site is independent of the solvent used. A comparison of the spin-Hamiltonian parameter values with those found for several compounds in which the Cu(II) is co-ordinate to oxygen or nitrogen atoms reinforces the X-ray absorption conclusion that point out that the chlorine ions are exchanged when the BIOX-Cu complex is incorporated to the clay. Moreover these values point out that the co-ordination of Cu(II) in LAPMET and LAPNIT clays is approximately squared planar.

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