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An EPR study on the enantioselective aziridination properties of a CuNaY zeolite

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A CuNaY catalyst was prepared and used to study the enantioselective aziridination of styrene, with PhI=NTs as the nitrogen source, in the presence of a bis(oxazoline) chiral modifier. The chiral modifier used was a diimine ligand, (*S*)-(−)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline). EPR spectroscopy provides the first direct experimental evidence for the formation of a copper(II)-bis(oxazoline) complex inside the Y zeolite pores after stirring the calcined catalysts with the chiral ligand using acetonitrile as solvent. The copper complexes possess square pyramidal and square planar symmetries, with spin Hamiltonian parameters analogous to those of the equivalent homogeneous complex dissolved in solution. These copper(II) complexes accounted for at least 40% of all available copper within the ion exchanged CuNaY catalyst and represent one Cu(II)-bis(oxazoline) complex per supercage. The remaining uncomplexed Cu(II) ions remain solvated to the acetonitrile molecules. After the aziridination reaction was carried out in the presence of styrene and PhI=NTs, EPR evidenced the selective loss of the signal due to the copper(II)-bis(oxazoline) complex with square pyramidal and square planar symmetries but practically no loss in overall Cu(II) content. This was explained on the grounds of a changing co-ordination environment of the encapsulated complex. However when PhI=NTs was added separately to the catalyst a dramatic loss in Cu(II) signal intensity was observed. These results are discussed in terms of the reaction mechanism in operation.

1. Introduction

For many years zeolites have been successfully used as solid catalysts for large scale industrial processes such as the production of gasoline and related petrochemicals. However in recent years zeolites have taken on a new role as novel enantioselective catalysts for fine chemical synthesis.[1–3] Indeed with increasing demand for optically pure compounds for pharmaceutical and agrochemical applications, enantioselective catalysis is now becoming more and more important. Many experimental approaches have subsequently been developed for the design of new enantioselective systems for heterogeneous catalysis, such as the use of a chiral support for an achiral metal catalyst, immobilisation of an asymmetric catalytically active complex onto an achiral support and modification of an achiral catalyst using a chiral cofactor. The latter approach has been successfully demonstrated by one of us in recent years, for example, in the enantioselective dehydration of butan-2-ol using a chiral dithiane 1-oxide modified HY zeolite.[4,5] Another demonstration of the induced enantioselective properties of modified zeolites, and the purpose of the present investigation, is the enantioselective aziridination of alkenes based on copper exchanged zeolite Y.[6–8]

The importance of developing an effective enantioselective aziridination catalyst is underpinned by the extensive applications of chiral aziridines in fine chemical synthesis since they can be easily converted into chiral diamines and aminoalcohols. Copper catalysts modified with chiral bis(oxazolines) have recently proven to be efficient for the homogeneously catalysed reaction using *N*-(*p*-tolylsulfonyl)iminophenyliodinane (hereafter abbreviated to PhI=NTs) as nitrogen source.[9,10] In the heterogeneous system Langham *et al.*,[6–8] evidenced the successful use of a copper exchanged zeolite Y (CuHY) catalyst for aziridination again using PhI=NTs as the nitrogen source, and found high yields for alkene aziridination without the need for an excess of the alkene. Nevertheless, despite the considerable potential of these catalysts to provide a synthetic method for the asymmetric aziridination of alkenes, the structure of the complex and the mechanistic steps involved in the transformation in the CuY zeolite remain unclear and require further investigation.

Understanding the fundamental mechanistic features of these reactions, and ultimately designing new and better asymmetric solid catalysts, requires detailed knowledge on how the chiral information is transferred to the reactant(s) and whether there is any interaction between the chiral modifier and the catalytically active species. In the current work, we have used EPR spectroscopy to study this problem and to explore at the molecular level the interactions of a CuNaY catalyst with the solvent, the chiral modifier bis(oxazoline) and the reactants themselves. EPR has been widely used for many years to study the bonding, co-ordination and location of copper ions[11–18] and encapsulated copper complexes[19–21] inside the pores of zeolites. However, while EPR is sensitive to changes in the local co-ordination environment of the Cu(II) ion, multiple resonance techniques such as electron nuclear double resonance (ENDOR) or pulsed techniques such as electron spin echo envelope modulation (ESEEM) are required to detect the long range interactions with the surrounding or distant ligand nuclei which are too weak to detect in the normal EPR spectrum. While Kevan *et al.*,[22–24] have successfully applied ESEEM spectroscopy to understand the interactions and spatial co-ordination of transition metal ions

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in microporous materials with various inorganic and organic probe molecules, ENDOR has been less widely applied to these systems.[25] Nevertheless the additional information obtained from these multiple resonance techniques is vital for studies in heterogeneous catalysis since analysis of the ENDOR and ESEEM spectra amounts to identifying the magnetic components of the ligand superhyperfine tensor and thereby provides information on the electronic and geometrical arrangement of the ligands and reactants around the Cu(II) active site.

In the present paper we have used EPR to probe the co-ordination of a CuNaY zeolite in the presence of a chiral bis(oxazoline) modifier and to examine the effects of the reaction solvent (acetonitrile) and different substrates such as PhI=NTs (the nitrogen source) and styrene (the reactant) on the EPR spectra.

Methods

CuNaY sample preparation

CuNaY was prepared using a conventional ion exchange method in which zeolite NaY (*ex* Zeolyst International, CBV100, $n_{Si}/n_{Al} = 2.5$) was treated with an aqueous copper(II) acetate (*ex* Aldrich) solution. The solid was then washed with distilled water and calcined for several hours at 823 K in air prior to use. Elemental analysis of the sample was performed by ICP-AES on a Perkin Elmer Plasma 400 spectrometer.

Catalytic activity

The aziridination reaction was carried out in a batch reactor at 298 K. The chiral modifier or diimine complex used in the current work was (*S*)-(−)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline and will hereafter be referred to as bis(oxazoline). The catalyst ($m_{cat., dry} = 0.329$ g) and the chiral modifier (with a $n_{Cu}/n_{chiral\ modifier}$ ratio of ≈2) were stirred together in 2.5 cm^3 anhydrous acetonitrile (*ex* Aldrich) for 20 min. Then 0.101 g styrene (*ex* Aldrich) and 0.563 g PhI=NTs (prepared according to Yamada *et al.*),[26] were added. After stirring for 24 h, the products were isolated by column chromatography (Matrex Silica 60, Fisher) and analysed using chiral HPLC (column: 25 cm Chiralcel OJ; eluent system: 82 vol.% hexane, 18 vol.% isopropanol; flow rate: 3 cm^3 min^{-1}; wavelength: 235 nm), as described in detail elsewhere.[6–8]

EPR spectroscopy

The zeolite samples for the EPR experiments were prepared according to the procedure used in the catalytic experiments above, *i.e.*, the zeolite was calcined, stirred in anhydrous acetonitrile with or without the chiral modifier, and in some experiments the substrates were added. Afterwards, the suspension was filtered, and the solid was gently dried at 298 K for *ca.* 15 min, placed into an EPR cell and then gently evacuated on a conventional vacuum manifold (10^{-3} Torr).

The homogeneous copper complexes were prepared by adding the appropriate amounts of copper(II) acetate (*ex* Aldrich) or copper(II) perchlorate (*ex* Aldrich) and two different bis(oxazoline) ligands, (*S*)-(−)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) or 2,2′-isopropylidenebis[(4*S*)-4-*tert*-butyl-2-oxazoline] (*ex* Aldrich) ($n_{Cu}/n_{chiral\ modifier} \approx 1$), to ethanol (*ex* Hayman Limited) containing a few drops of water. To obtain a clear solution, the mixture was gently heated (*ca.* 313 K) and/or filtered through a plug of cotton wool. The frozen solution EPR spectra were recorded at 10 K (obtained after adding a drop of dimethyl sulfoxide (*ex* Aldrich) to obtain a good glass).

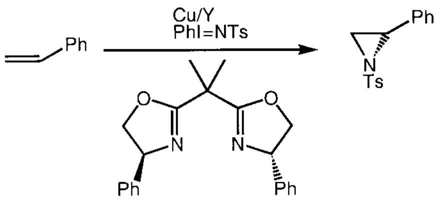
The EPR spectra were recorded on a Varian E109 and a Bruker ESP 300-E Series X-band spectrometer at *ca.* 100 or 10 K. The *g* values were determined using a Bruker NMR gaussmeter calibrated using the perylene radical cation in concentrated H_2SO_4 with $g = 2.00256$. The spin Hamiltonian parameters were determined by simulation of the spectra using the SIM14S software by G. P. Lozos *et al.* (modified by J. M. Lagan, DOS version of 06/09/1991).

Absolute spin concentrations of Cu(II) ions were determined by double integration of the first derivative EPR spectrum, with reference to two different sets of standards ($CuSO_4 \cdot 5H_2O$ and $TiCl_3 \cdot 3THF$) for accurate comparisons.

Results

Catalytic tests

Before the spectroscopic measurements were performed, an experiment using 1.4CuNaY (the numerical prefix indicates the metal content in wt.% of the dry catalyst) as a catalyst in the aziridination of styrene (Scheme 1) was carried out in order to confirm the catalytic activity of the zeolite sample. An isolated yield of aziridine of 75% (based on styrene) and an ee of 52% were observed, which compares well to the extensive results obtained previously by our group in this system[6–8] and demonstrates the appropriate catalytic nature of the samples used in this study.



Scheme 1

EPR spectra of calcined CuNaY

The CuNaY catalyst was prepared as described in the Experimental section and above all in a manner strictly similar to that reported by Langham *et al.*,[6–8] in their aziridination studies on a similar catalyst. The catalyst was calcined in air at 823 K for several hours, evacuated on a conventional vacuum manifold (10^{-3} Torr) at 298 K for *ca.* 1 h, and finally the EPR spectrum was recorded at 100 K (Fig. 1). An identical spectrum was also obtained at 10 K. This spectrum is typical of a d^9 Cu(II) ion in an axial ligand field. The high resolution of both the *g* and *A* components is due to the well-defined co-ordination states of the fully dehydrated ion. Because Cu(II) has a nuclear spin of 3/2, four well-resolved hyperfine lines are expected in the $g_{\parallel}$ region. The additional lines observed in the low field region of Fig. 1, indicate the presence of two different

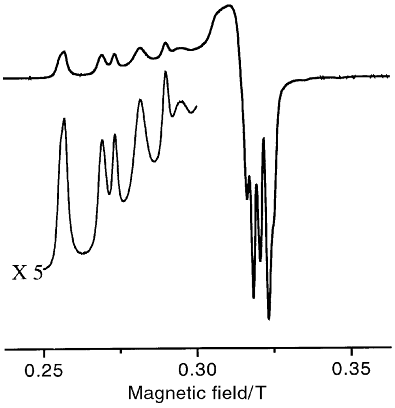


Fig. 1 EPR spectrum of 1.4 CuNaY: calcined at 823 K and degassed at 298 K.

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Cu(II) sites in the calcined/dehydrated CuNaY sample. This assignment will be discussed in detail later.

EPR spectra of calcined CuNaY with acetonitrile and chiral bis(oxazoline)

After calcination, the CuNaY sample was stirred in acetonitrile at 298 K for 30 min. The suspension was then filtered, the solid was gently dried at 298 K for *ca.* 15 min and a small amount of the sample (*ca.* 20 mg) placed into an EPR cell. The sample was subsequently evacuated (10^{-3} Torr) at progressively higher temperatures, while the low temperature EPR spectra (100 K) were recorded at each successive step. The resulting spectra are shown in Fig. 2, while the corresponding g and hyperfine coupling values (A) are listed in Table 1 (along with selected literature values[11–13,18,27]). Evacuation at 298 K creates a single Cu(II) species which is clearly evident in the low temperature spectrum (100 K) and characterised by the $g_{\parallel}$ value of 2.37 and $A_{\parallel}$ value of 12.7 mT. The $A_{\parallel}$ hyperfine splitting is illustrated with the 'stick diagram' in Fig. 2. However, after evacuation at higher temperatures (323 and 373 K) a second Cu(II) species (hereafter labelled species B′) becomes visible in the low temperature spectrum, indicating the presence of a second co-ordination environment for the exchanged copper ions, with a $g_{\parallel}$ value of 2.32 and an $A_{\parallel}$ value of 16.5 mT (Table 1). The intensity of species B′ grows as the evacuation temperature increases.

The spin concentration of Cu(II) ions in the CuNaY sample after stirring in acetonitrile was determined by double integration of the first derivative EPR signal (Fig. 2(a)). This value was compared to the integrated intensities from two different sets of standards. Reproducible and similar results were obtained using both standards. The analysis indicated that 2.18×10^{-4} moles of EPR visible Cu(II) ions are present per gram of catalyst. This corresponds to 1.39 wt.% copper in the catalyst and demonstrates that practically all of the available copper ions exchanged into the NaY zeolite exist as Cu(II) ions. The spectra were also recorded at 10 K and a similar value of the integrated Cu(II) intensity was observed.

The CuNaY sample was then stirred in the acetonitrile solvent containing the chiral bis(oxazoline) modifier, ($n_{\mathrm{Cu}}/n_{\mathrm{chiral\ modifier}} \approx 2$). Prior to recording the spectrum, the suspension was filtered and the solid was allowed to dry in air at 298 K. The resulting EPR spectra of the sample evacuated at different temperatures are shown in Fig. 3. Each spectrum was recorded at 100 K. The addition of the chiral modifier clearly produces a more complex EPR profile (compared to Fig. 2 for CuNaY and acetonitrile only) because, in addition to the peaks ascribed above (arising primarily from species A), two new sets of peaks can now be identified. The first peak (labelled B″ in Table 1) produces g and A values which are very similar to those of species B′, while the second peak (labelled C and identified with the asterisk in Fig. 3) has values which are quite different from the A and B type species. The new peaks were only observable in the presence of the bis(oxazoline) ligand, as no analogous peaks were observed in either the calcined or acetonitrile treated CuNaY sample. Nevertheless, despite the marked changes to the profile of the EPR spectrum, the overall integrated signal intensity remained constant at 100 or 10 K (*i.e.*, no loss in Cu(II) concentration upon addition of the chiral ligand).

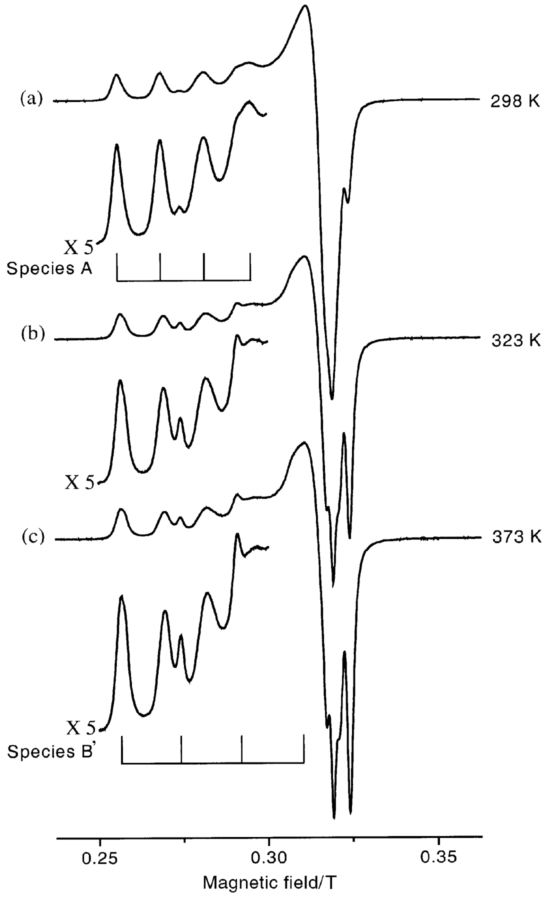

Fig. 2 EPR spectra of 1.4 CuNaY: calcined at 823 K, stirred in acetonitrile and degassed at different temperatures (a)–(c).

Table 1 Measured g and A values for Cu(II) species in ZSM-5 and Y zeolites

Species		$g_{\parallel}$	$A_{\parallel}$/mT	$g_{\perp}$	$A_{\perp}$/mT	Ref.
Pseudo-octahedrally co-ordinated copper in ZSM-5		2.37–2.40	12.0–13.6	2.08–2.09	0.9	13, 18
Pseudo-square-pyramidally co-ordinated copper in ZSM-5		2.31–2.36	14.1–15.6	2.06–2.07	1.4–1.9	13, 18
Pseudo-square planar co-ordinated copper in ZSM-5		2.27–2.29	15.6–17.4	2.05	2.2–2.9	13, 18
Pseudo-octahedrally co-ordinated copper in Y		2.38–2.39	12.4–14.5	2.07	1.3	12, 27
Pseudo-square-pyramidally co-ordinated copper in Y		2.33	15.7–18.2	2.07	1.9–2.0	12, 27
Pseudo-square planar co-ordinated copper in Y		2.24	16.8–17.5			11
1.4 CuNaY (calcined and degassed at 298 K)	A	2.37	12.6–14.3	2.04	1.3	[a]
	B′	2.32	16.5	2.05	2.0	[a]
1.4 CuNaY (stirred in acetonitrile, degassed at 298 K)	A	2.37	12.7	2.07	1.1	[a]
1.4 CuNaY (stirred in acetonitrile with the chiral ligand, (*S*)-(−)-2,2′-isopropylidenebis-(4-phenyl-2-oxazoline), and degassed at 298 K)	A	2.37	12.6–13.9	2.06–2.08	1.3	[a]
	B″	2.31	16.5	2.08	2.0	[a]
	C	2.26	17.3	2.05	1.7	[a]
Cu[(*S*)-(−)-2,2′-isopropylidenebis-(4-phenyl-2-oxazoline)] $(\mathrm{OR})_2$	D	2.29	16.0	2.06	0.5	[a]
Cu[2,2′-isopropylidenebis-((4*S*)-4-*tert*-butyl-2-oxazoline)] $(\mathrm{OR})_2$	D	2.29	14.9	2.06	0.5	[a]

[a] This work.

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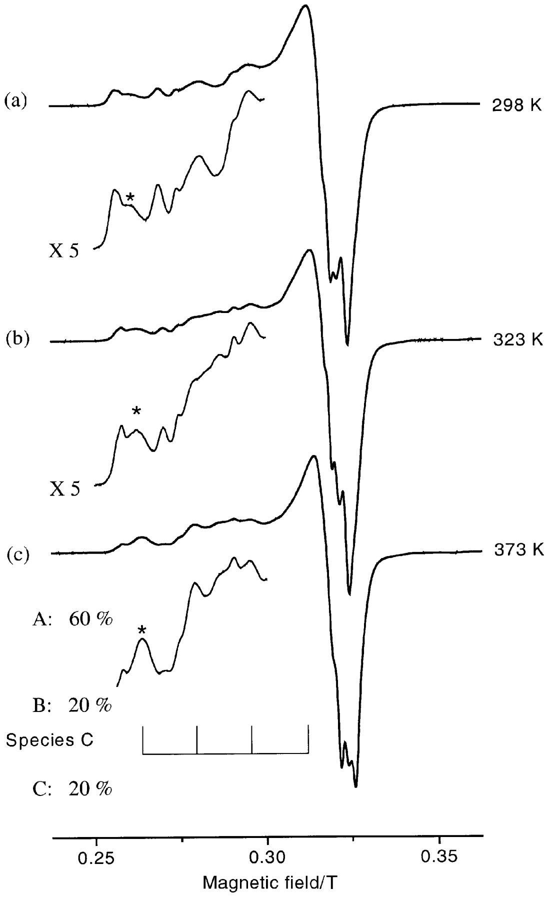

Fig. 3 EPR spectra of 1.4 CuNaY: calcined at 823 K, stirred in acetonitrile with the bis(oxazoline) and degassed at different temperatures (a)–(c).

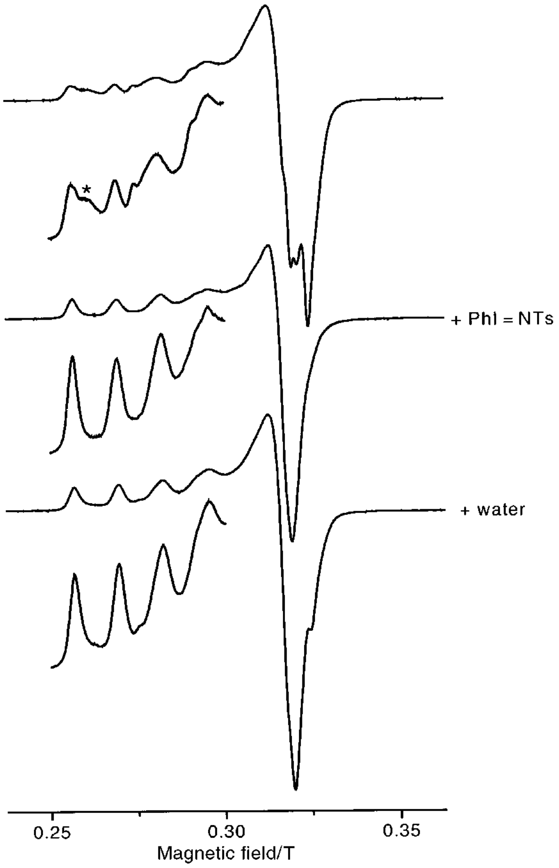

Fig. 4 (a) EPR spectrum of 1.4 CuNaY: calcined at 823 K, stirred in acetonitrile with bis(oxazoline). The spectrum was then recorded after addition of PhI=NTs (b) or water (c) to the catalyst. Each sample was degassed at 298 K.

In order to explore the changes to the co-ordination and oxidation state of the Cu(II) ions, the EPR spectra were measured after various substrates, including PhI=NTs and styrene, had been added to the suspension of the CuNaY catalyst in acetonitrile containing the bis(oxazoline) ligand. The quantities of catalysts and substrates used in these tests were identical to those employed in the catalytic experiments. After 1 h of reaction, the catalyst was filtered and gently dried before evacuation at 298 K in the EPR cell. The resulting EPR spectra are shown in Fig. 4 for the case in which PhI=NTs and styrene only were added. The most pronounced change in the spectra was the complete disappearance of the peaks assigned to species B″ and C and the partial loss of the Cu(II) signal intensity. However, the final Cu(II) concentrations were different depending on the adsorbate used. Based on the initial Cu(II) signal intensity for the CuNaY sample stirred in CH_3CN plus bis(oxazoline) (Fig. 4(a)), the signal intensity decreased after the addition of the various substrates. The extent of reduction in signal intensity is given in Table 2. These measured intensities varied slightly from experiment to experiment and have a ±10% degree of accuracy.

In order to obtain accurate g and A values of the copper species, computer simulations of the EPR spectra were carried out. The experimental and resulting simulated spectra of 1.4CuNaY sample after stirring in acetonitrile and after stirring in acetonitrile with the bis(oxazoline) ligand, are ahown in Fig. 5(a) and (b) respectively.

EPR of copper bis(oxazoline) complex

A series of experiments was also performed on a freshly prepared copper-bis(oxazoline) complex dissolved in acetonitrile, in order to compare the EPR profile (including g and A values) of the homogeneous copper complex in frozen solution with the spectra obtained from the heterogeneous CuNaY system. The dissolved samples were prepared according to the method described in the experimental section. The EPR spectra were recorded at 10 K for two slightly different complexes,[28] namely Cu[(*S*)-(−)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline)]$(OR)_2$ and Cu[2,2′-isopropylidenebis((4*S*)-4-*tert*-butyl-2-oxazoline)]$(OR)_2$ (Fig. 6(a) and (b) respectively). The two bis(oxazoline) ligands differ in the nature of the substituents, which are either the phenyl groups (see structure in

Table 2 Changes to the Cu(II) EPR signal intensity, and absolute Cu(II) concentrations, after addition of various substrates to the CuNaY catalyst stirring in solvent (CH_3CN) and chiral bis(oxazoline) ligand

Sample	EPR signal intensity (%)	Cu(II) concentration moles (g CuNaY)$^{-1}$
(1) CuNaY stirred in CH_3CN with bis(oxazoline)	100	2.2×10^{-4}
(1) + PhI=NTs	55	1.2×10^{-4}
(1) + styrene	75	1.6×10^{-4}
(1) + PhI=NTs/styrene	90	2.0×10^{-4}

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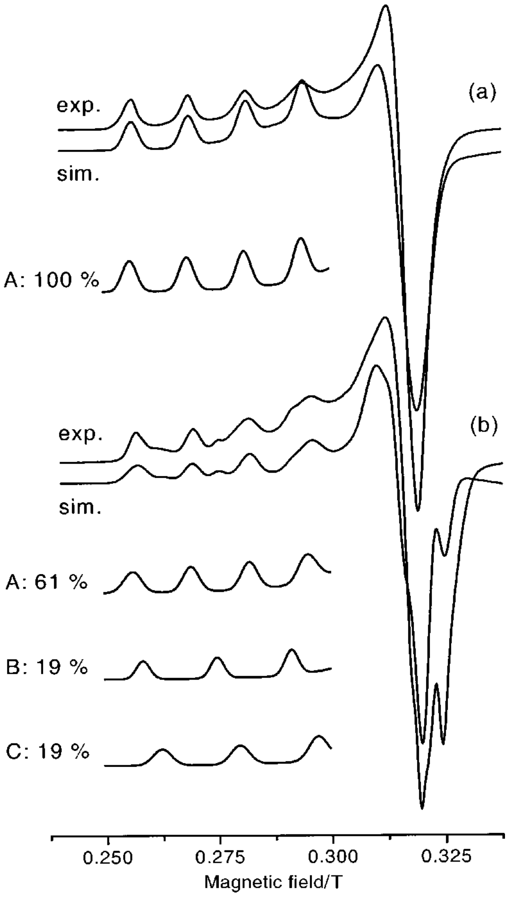

Fig. 5 Experimental and simulated EPR spectra of 1.4 CuNaY: calcined at 823 K: (a) stirred in acetonitrile and degassed at 298 K; (b) stirred in acetonitrile with the bis(oxazoline) ligand and degassed at 298 K.

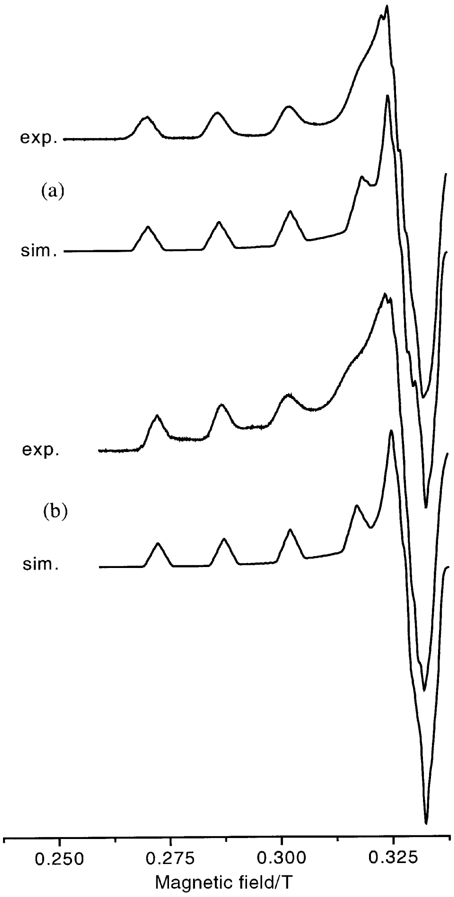

Fig. 6 Experimental and simulated EPR spectra of (a) Cu[(*S*)-(−)2,2′-isopropylidene-bis(4-phenyl-2-oxazoline)](OR)$_2$ and (b) Cu[2,2′isopropylidenebis((4S)-4-*tert*-butyl-2-oxazoline)](OR)$_2$. Note; the simulated linewidths were kept to a minimum to highlight the superimposed superhyperfine structure from the ^{14}N nuclei.

Scheme 1) or the *tert*-butyl groups. The corresponding computer simulations are also shown in Fig. 6. The *g* and *A* values obtained from the simulations are slightly different compared to those observed in the case of CuNaY catalyst containing the chiral diimine modifier. These differences likely arise from the two different environments of the copper ions (*i.e.*, inside the zeolite supercage and in frozen homogeneous solution), indicating that the ion experiences local perturbations which are dissimilar in the two cases. A more accurate analysis of this effect will be studied using 2D-ESEEM experiments to compare the difference in structure of the Cu-complex from the encapsulated NaY zeolite complex to the frozen solution complex.

Only one set of hyperfine components was resolved for the dissolved complexes in frozen solution, indicating the presence of a single Cu(II) co-ordination state and this species will hereafter be labelled D. Owing to the high resolution and anisotropy in the spectra, additional superhyperfine structure associated with the interacting ^{14}N nuclei can be resolved in the parallel and perpendicular features.

In addition, well-resolved c.w. ENDOR spectra were recorded for the homogeneous complex (spectra not shown for brevity) confirming the coordination of the bis(oxazoline) ligand to the Cu(II) ion. In particular the different resonances of the phenyl and *tert*-butyl groups on the ligand (which play an important role in directing the enantioselectivity) were easily identified. The c.w. ENDOR spectra were also recorded on the CuNaY sample containing the bis(oxazoline) ligand for comparison, in an attempt to confirm the formation of a Cu-bis(oxazoline) complex in the Y zeolite supercages. Although ^{1}H resonances were detected which were similar to those observed for the homogeneous complex, the ENDOR spectra of CuNaY were insufficiently resolved to allow an unambiguous assignment. Other EMR methods such as ESEEM or pulsed ENDOR will be required to improve the quality of the spectra.

Discussion

Co-ordination mode of CuNaY: evidence for encapsulated Cu-bis(oxazoline) complexes

The EPR profiles of Cu(II) exchanged zeolites have been thoroughly investigated for many years.[11–18,22–24] Generally, broad structureless spectra are reported at 298 K for the fresh Cu(II) exchanged samples, due to the presence of fully hydrated six-fold co-ordinated Cu(II) ions. Although such a hydrated complex experiences a tetragonally elongated co-ordination environment (due to a Jahn–Teller effect), which produces an asymmetric profile, rapid tumbling of the complex at 298 K results in an averaged and unresolved spectrum. At low temperatures, this rapid tumbling is quenched, so that an anisotropic (axial) EPR profile is instead obtained, with well-resolved *g* and *A* values. As water is progressively removed from the sample, the tumbling complex becomes immobilized on the zeolite pore walls, and eventually after extensive dehydration by thermovacuum treatments the copper ions directly bond to the framework oxygens. This produces low co-ordinated copper species, possessing symmetries such as square pyramidal or in the case of ZSM-5 square planar, and these symmetries are again manifested in the EPR spectra with axial (tetragonal) symmetry corresponding to the unpaired electron located mostly in a d(x^2–y^2) orbital of the copper ion. This situation is clearly exemplified

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in the spectrum of the calcined (823 K) and evacuated CuNaY sample (Fig. 1). The well-resolved and highly anisotropic spectrum is due to the presence of low co-ordinated and dehydrated Cu(II) ions anchored onto the walls of the zeolite host, since most of the water is removed in the calcination and subsequent evacuation steps.

Two copper species (labelled A and B′) can be identified in the EPR spectrum of the calcined material (Fig. 1). Two additional species were identified (labelled B″ and C) in the acetonitrile treated sample containing the bis(oxazoline) ligand. As seen in Table 1, the g and A values of the species A, B and C are significantly different, and this indicates the presence of three distinct groups of copper environments. Species B′ and B″ have very similar EPR parameters, and represent two similar but slightly different square pyramidal co-ordination environments of the copper. In order to understand the origin and symmetry of each species, it is necessary to consider briefly the relationship between the observed g and A values, and the associated molecular symmetry.

Two prevailing copper species have been reported in Cu(II) exchanged Y zeolites, which are pseudo-octahedrally co-ordinated copper ions which exist in the supercages ($g_{\parallel} = 2.38$ to 2.39, $A_{\parallel} = 12.4$ to 14.5 mT, $g_{\perp} = 2.07$, $A_{\perp} = 1.3$ mT) and square-pyramidally co-ordinated copper ions which exist in the sodalite cages ($g_{\parallel} = 2.33$, $A_{\parallel} = 15.7$ to 18.2 mT, $g_{\perp} = 2.07$, $A_{\perp} = 1.9$ to 2.0 mT).[12,27] Similar copper species can also be identified in Cu(II) exchanged ZSM-5 materials, including octahedral ($g_{\parallel} = 2.37$ to 2.40, $A_{\parallel} = 12.0$ to 13.6 mT, $g_{\perp} = 2.08$ to 2.09, $A_{\perp} = 0.9$ mT) and square pyramidal ($g_{\parallel} = 2.31$ to 2.36, $A_{\parallel} = 14.1$ to 15.6 mT, $g_{\perp} = 2.06$ to 2.07, $A_{\perp} = 1.4$ to 1.9 mT) co-ordination.[18] In addition, a square planar co-ordination mode of copper ($g_{\parallel} = 2.27$ to 2.29, $A_{\parallel} = 15.6$ to 17.4 mT, $g_{\perp} = 2.05$, $A_{\perp} = 2.2$ to 2.9 mT) has been observed in this system,[13,18] whereas in faujasites this copper environment was only identified in the presence of N-containing ligands, *e.g.*, NH_3 ($g_{\parallel} = 2.24$, $A_{\parallel} = 16.8$ to 17.5 mT).[11] To the best of our knowledge, there is only one report in the literature on a dehydrated CuY system with spin Hamiltonian parameters typical of square planar symmetries which was assigned to Cu(II) ions in site SI′ co-ordinated with three lattice oxygen atoms and one extra-framework oxygen of a hydroxide forming a deformed tetrahedron.[22] No square planar co-ordination modes of copper are reported for the calcined materials themselves.

It is therefore clear from the above analysis of the literature that species A ($g_{\parallel} = 2.37$; $A_{\parallel} = 12.6$ to 14.3 mT) and B′ ($g_{\parallel} = 2.32$ $A_{\parallel} = 16.5$ mT) can be assigned to a pseudo-octahedral and square pyramidal copper site respectively. These are the only two sites visible in the calcined material after evacuation at 298 K (Fig. 1 and Table 1). Only one species A was visible in the calcined sample after stirring in acetonitrile and evacuation at 298 K (Fig. 2(a)) which can be assigned to a fully solvated copper species with a pseudo-octahedral ligand environment. At higher evacuation temperatures (323 and 373 K; Fig. 2(b) and (c) respectively) some of the acetonitrile molecules are removed from the solvated copper complex, so that lower copper symmetries are observed (*i.e.*, similar to the above mentioned dehydration process; as solvating molecules such as water or acetonitrile are removed, the co-ordination state of the cation is reduced).

However, when the chiral bis(oxazoline) modifier is added to the CuNaY–acetonitrile suspension, the EPR spectra change dramatically (Fig. 3) and at least two new species B″ and C become visible. The g and A values of these species are consistent with a square pyramidal (B″) and square planar (C) co-ordination mode of copper. This strongly indicates that complexation of the copper(II) ions has occurred with the chiral modifier forming copper-bis(oxazoline) complexes with square pyramidal and square planar symmetries. Although species B′ and B″ have both been assigned to a square pyramidal site, in the former case the geometry arises due to co-ordination with the solvent molecules, while in the latter case it clearly arises through complexation with the diimine ligand which have a strong tendency to complex with Cu(II) ions. It should be recalled that species B′ was only visible in the acetonitrile treated CuNaY samples *after* evacuation at 323 K. However, in the presence of the chiral modifier, the square pyramidal species B″ was visible even in the *pre-evacuated* sample, indicating that the ligand is directly responsible for the formation of species B″ and C. In other words, while different Cu(II) locations can exist in the Y zeolite, and may display different reactivities as a function of location and loading, the observed trends clearly arise from the preferential interaction of one copper site with the chiral ligand. Unfortunately no superhyperfine interaction from the ^{1}H or ^{14}N nuclei of the bis(oxazoline) ligand could be identified in the EPR spectra. However, given the fact that only 40% of the entire Cu(II) signal is composed of Cu(II)-bis(oxazoline) complexes (see below), and with the added complexity of line broadening due to the heterogeneous distribution of sites within the CuY zeolite, the absence of resolved superhyperfine splitting is not surprising.

Based on the results of the computer simulations, *ca.* 40% of all the available copper ions co-ordinate with the bis(oxazoline) ligand producing sites with square planar symmetry (species C; 20%) and square pyramidal symmetry (species B″; 20%). This percentage of complexed copper also makes sense considering that a molar ratio of Cu(II) : bis(oxazoline) of 2 : 1 was used in the reaction, and confirms the previous results from our group[8] that not all the Cu(II) cations are modified by the chiral ligand. Knowing that the overall Cu(II) concentration is 2.18×10^{-4} mol (g catalyst)$^{-1}$, this *ca.* 40% contribution of the signal intensity from species B″ and C translates into approximately one copper-bis(oxazoline) complex per supercage. It is not clear if any copper-bis(oxazoline) complexes with octahedral symmetry are formed inside the zeolite, as these sites would produce spin Hamiltonian parameters analogous to the fully solvated copper–acetonitrile ions (species A) and therefore give rise to overlapping signals. Nevertheless it is evident from the EPR data that one copper-bis(oxazoline) complex is indeed formed per supercage either with square planar or square pyramidal symmetry, and considering a 2 : 1 molar ratio of Cu(II) : bis(oxazoline) was used, it is unlikely that any pseudo-octahedral Cu(II)-bis(oxazoline) complexes are formed. This data provides the first direct experimental evidence that a Cu(II)-bis(oxazoline) complex, responsible for the enantioselective aziridination properties, actually forms inside the zeolite supercage.

Interactions of Cu-bis(oxazoline)complex in CuNaY with adsorbates

Having established the formation of copper-bis(oxazoline) complexes inside the supercage of the CuNaY zeolite, we subsequently studied the influence of adsorbates on the co-ordination and oxidation state of the copper ions, to examine if EPR could provide any understanding of the reaction mechanism involved. The CuNaY zeolite was stirred in the usual way with acetonitrile containing the chiral modifier, and afterwards PhI=NTs or styrene were added to the system, as carried out in the catalytic tests. In all cases, two pronounced effects were observed in the EPR spectra. Firstly, the low symmetry Cu(II) species such as the square planar or square pyramidal Cu(II)-bis(oxazoline) sites disappeared (Fig. 4), and secondly the overall Cu(II) concentration decreased to different extents for all added adsorbates with the exception of the co-addition of PhI=NTs/styrene (Table 2). If the interaction of the adsorbate with the copper(II) ions resulted only in a change of co-ordination mode (for example from square

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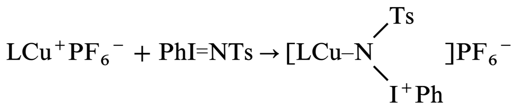
planar to square pyramidal or octahedral) without any change in paramagnetism of the sample, then the integrated Cu(II) signal intensity should remain constant; only the Cu(II) signal profile will change. However, if the copper ions are involved in complex catalytic steps with the reagents involving variable copper valence states, then the Cu(II) concentration would be expected to change.

One must also consider the additional complexity of EPR silent Cu(II) centres, when interpreting changes to the Cu(II) integrated signal intensities, as Cu(II) can be rendered invisible due to spin pairing in dimeric or higher aggregate states or due to fast relaxation processes. For example, a decrease in the EPR signal intensity of Cu(II) in Y and ZSM-5 zeolites was reported following gentle evacuation of the sample at 298 K.[18,19] The decrease in signal intensity for CuY was accounted for, not by reduction of Cu(II) to Cu(I) or strong magnetically interacting states, but due to the presence of specific Cu(II) symmetries such that nearly degenerate ground states occur producing strong spin–lattice relaxation effects which broaden the signal beyond detection.[29] The undetectability of Cu(II) in Cu-ZSM-5 on the other hand was ascribed to magnetic spin–spin relaxation effects *via* Cu–$(OH_2)\cdots(OH)$–Cu fluctuating hydrogen bonds.[18] However as the EPR spectra were recorded at both 10 and 100 K with no apparent differences in intensity, another process must be responsible for the loss of Cu(II) intensity as the reagents are added. Furthermore, because the integrated EPR spectra indicates that most of the Cu(II) is present as EPR visible Cu(II) ions, the possibility of diamagnetic Cu pairs can be eliminated.

The diimine chiral complexes of both Cu(I) and Cu(II) are capable of mediating alkene aziridination[9,10,30] and a number of reports have appeared on the mechanism of the reaction by these complexes. Li *et al.*,[10] considered two possible intermediates in the (diimine)copper(I) catalysed asymmetric aziridination of alkenes in solution. In this first case the role of a discrete Cu(III)-nitrenoid intermediate (Cu=NTs) in the presence of PhI=NTs as nitrogen donor was considered (eqn. (1));

$$\mathrm{LCu^+PF_6^-} + \mathrm{PhI{=}NTs} \rightarrow [\mathrm{LCu{=}NTs}]^+\mathrm{PF_6^-} + \mathrm{PhI} \quad (1)$$

where L represents the different chiral diimine ligands. In this redox process, PhI is fully dissociated from the aziridinating species. However a possible alternative to this redox mechanism involves the copper complex functioning as a Lewis acid, in which the PhI=NTs is covalently attached to the active site;



$$\mathrm{LCu^+PF_6^-} + \mathrm{PhI{=}NTs} \rightarrow [\mathrm{LCu{-}N}(\mathrm{Ts})(\mathrm{I^+Ph})]\mathrm{PF_6^-} \quad (2)$$

Li *et al.*,[10] concluded from their results on Cu(I) that although the catalytic aziridination with PhI=NTs can occur by more than one mechanism, the evidence obtained for the (diimine)copper catalysed reaction strongly implicated the redox mechanism. Experimental data also provided evidence for a common oxidation state of the catalyst irrespective of the oxidation state of the starting copper complex,[31] and that these reactions are being catalysed through Cu(II) rather than Cu(I). It was reported that treatment of an acetonitrile solution of Cu triflate (CuOTf) in the presence of a bis(oxazoline) ligand with PhI=NTs generated a copper species which was indistinguishable from one generated by an identical protocol using $Cu(OTf)_2$ suggesting that a similar catalytically effective complex is accessible from either oxidation state.[9] It was also demonstrated that PhI=NTs oxidises Cu(I)OTf/bis(oxazoline) to a Cu(II) complex and that beginning with either Cu(I)(OTf) or $Cu(II)(OTf)_2$ salts as precursors, gives identical relative reactivities towards various pairs of alkenes.[31] Although Cu(II) can also catalyse the reaction, no details were given on the nature of the intermediate involving Cu(II) and PhI=NTs.

In the current Cu(II)NaY system, when the reaction was carried out in the presence of co-added PhI=NTs/styrene, practically no change in Cu(II) concentration was observed (only *ca.* 10% loss of intensity occurred). However, when PhI=NTs was added separately to the catalyst, a net decrease in the Cu(II) ion concentration (*ca.* 45%) occurred. This *ca.* 45% correlates well with the *ca.* 40% abundance of Cu(II)-bis(oxazoline) complexes formed in the CuNaY system. Regardless of any interaction between PhI=NTs and the remaining 60% of the non-complexed Cu(II), no change occurred in the EPR profile for these ions. These non-complexed cations will be completely solvated by the acetonitrile molecules, and may therefore be unavailable for efficient interaction with PhI=NTs. As Li *et al.*,[32] demonstrated through catalytic studies of copper with tetradentate neutral ligands such as Cu-Salen, the existence of multiple open coordination sites on the copper may be crucial to catalysis of aziridination.

It is difficult to understand how the hypothesised Cu(III)-nitrenoid intermediate (Cu=NTs) can form in the present system (eqn. (1)) unless we invoke an equilibrium state involving Cu(I) and Cu(III) in solution (eqn. (3)). It should be recalled that only 40% of the copper ions are complexed with the bis(oxazoline) so that in the acetonitrile solvent, at least some of the remaining copper ions (60%) will be mobile in the zeolite supercages and may establish the proposed mechanism. Assuming the formation of Cu(I) states *via* eqn. (3), the addition of PhI=NTs should lead to the formation of PhI and a copper nitrenoid species (eqn. (4)), as discussed by Li *et al.*[10] As a result the Cu(II) signal intensity would be expected to decrease, as indeed observed.

$$2\mathrm{Cu(II)} \Leftrightarrow \mathrm{Cu(I)} + \mathrm{Cu(III)} \quad (3)$$

$$\mathrm{PhI{=}NTs} + \mathrm{Cu(I)} \rightarrow \mathrm{PhI} + \mathrm{Cu{=}NTs^+} \quad (4)$$

$$\mathrm{Cu{=}NTs^+} + \mathrm{styrene} \rightarrow \mathrm{Cu(I)} + \mathrm{aziridine} \quad (5)$$

$$\mathrm{Cu(I)} + \mathrm{Cu(III)} \Leftrightarrow 2\mathrm{Cu(II)} \quad (6)$$

When styrene is present in the system, the reaction of the copper nitrenoid intermediate may proceed to produce the aziridine product and regenerate the Cu(I) site (eqn. (5)). Again through a similar equilibrium process as in eqn. (3), the original Cu(II) sites may be reformed (eqn. (6) which is likely to be a slow rate-determining step), so that the overall Cu(II) concentration remains constant at the end of the reaction. In fact the integration data reveals that addition of PhI=NTs/styrene to the catalyst only leads to a 10% loss in Cu(II) signal intensity. If we assume that an equilibrium process (eqn. (3) and (6)) can be established inside the supercages of CuNaY due to the presence of closely interacting Cu(II) pairs or dimers, then the current results, based on eqn. (3)–(6), would support a similar type of redox mechanism for aziridination as suggested by Li *et al.*,[10] since both Cu(I) and Cu(III) intermediates are EPR silent. However it must be clearly pointed out that although this interpretation could account for the EPR data, it is unlikely to occur because it depends on the rate-limiting steps in eqn. (3) and (6). While these reactions can occur in solution, there is no evidence to suggest that they occur within the confined spaces of the zeolite pores, so the actual mechanism remains uncertain.

In addition, the disappearance of an EPR signal must be interpreted with caution, since EPR provides no information on the nature of any resulting diamagnetic state. While the formation of the Cu(III)-nitrene intermediate could account for the observed trends, or possibly the formation of a diamagnetic state formed directly between Cu(II) and the PhI=NTs, one cannot disregard the possibility that a direct interaction between the Cu(II) ions (functioning as a Lewis acid) and the PhI=NTs also proceeds, to produce an unknown diamagnetic intermediate which is responsible for nitrogen

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transfer. In conclusion, we cannot discriminate with confidence between the two proposed reaction pathways in the literature (eqn. (1) and (2)) based on the current EPR data, as both pathways involve a diamagnetic intermediate between the copper complex and the PhI=NTs.

EPR investigation of chiral Cu(II)-bis(oxazoline) complexes

The frozen solution EPR spectra of the Cu[(*S*)-(−)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline)](OR)$_2$ and the Cu[2,2′-isopropylidenebis((4*S*)-4-*tert*-butyl-2-oxazoline)](OR)$_2$ complexes are shown in Fig. 6. The EPR spectra of the two complexes are similar and the *g* and *A* values (Table 1; where $g_{\parallel} = 2.29$ and $A_{\parallel} = 14.9$ to 16.0 mT), indicate the presence of a strong square planar pattern which is consistent with either a square planar or square pyramidal copper geometry (labelled species D). These parameters are also in agreement with EPR results presented by Evans *et al.*,[28] on similar copper complexes. By comparison, the copper species B″ and C observed in the CuNaY samples and formed only in the presence of the bis(oxazoline) ligand are also characterised by low $g_{\parallel}$ values and high $A_{\parallel}$ values similar to species D and indicative of low symmetry copper ions. This similarity in *g* and *A* values for species B″ and C in CuNaY and species D in frozen solution provides further evidence for the formation of copper-bis(oxazoline) complexes inside the zeolite pores.

Conclusions

A CuNaY catalyst (1.4 wt.% Cu) was prepared by conventional ion exchange methods and successfully used for the catalytic aziridination of styrene with PhI=NTs as the nitrogen source. The co-ordination and oxidation state of the copper(II)-containing catalyst was investigated by EPR before and after the catalytic reaction. The EPR spectrum of the calcined and evacuated samples revealed the presence of two copper(II) sites inside the CuNaY zeolite with pseudo-octahedral and square pyramidal geometries. After stirring the calcined catalyst in acetonitrile solvent, a pseudo-octahedral species was predominantly formed due to solvent co-ordination to the copper ion. However, upon addition of the chiral diimine ligand, two new copper(II)-bis(oxazoline) complexes were identified inside the zeolite with a square pyramidal and square planar geometry. Approximately 40% of all the available copper(II) ions in CuNaY were found to exist in these complexed states after incorporation of the chiral ligand, corresponding to one Cu(II)-bis(oxazoline) complex per supercage.

After one hour of reaction with styrene and PhI=NTs, the EPR spectra revealed the preferential loss of the peaks assigned to the square pyramidal and square planar Cu(II)-bis(oxazoline) complexes in the CuNaY catalyst. The rearranged spectrum indicated the presence of pseudo-octahedrally co-ordinated copper ions but the overall Cu(II) integrated intensity remained practically unchanged at the end of the catalytic reaction. However, a selective disappearance of the Cu(II)-bis(oxazoline) peaks was observed after the addition of PhI=NTs only to the catalyst. It is clear from these results that a diamagnetic intermediate is formed which involves PhI=NTs and the Cu(II)-bis(oxazoline) complex, which reacts with styrene to regenerate a paramagnetic Cu(II) complex. The nature of these observations was discussed within the context of the current proposed intermediates involved in the catalytic reaction, but the mechanistic steps remain unclear based on the current data.

A comparative EPR study was also performed on the dissolved Cu[(*S*)-(−)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline)](OR)$_2$ and the Cu[2,2′-isopropylidenebis ((4*S*)-4-*tert*-butyl-2-oxazoline)](OR)$_2$ derivatives in frozen solution. The EPR parameters of the Cu(II) complex were analogous to those observed in the CuNaY catalysts, providing added confirmation for the complexation between ion exchanged Cu(II) and the diimine ligand inside the zeolite.

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