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Use of a Cu^{2+} probe to characterise silica-pillaring in zirconium phosphate by electron paramagnetic resonance spectroscopy

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Copper has been used as an electron paramagnetic resonance (EPR) probe for the interlayer environment of α-zirconium phosphate (α-ZrP) intercalated from hydrolysed/condensed 3-(2-aminoethylamino)propyltrimethoxysilane solutions. These solids are precursors to porous silica-pillared solids. The EPR spectra of the Cu^{2+}–aminosiloxane pillaring solution and of the intercalated solid prepared using this solution are identical. More detailed study of the solution has shown the existence of two types of EPR spectra, when the molar ratio $Si/Cu \geqslant 2$ and when $Si/Cu < 2$. For the former, Cu^{2+} has an environment of nitrogen and oxygen (4+2); at lower Si/Cu ratios, the EPR spectra are characteristic of an oxygen atom environment. On acidification of the aminosiloxane solution, nitrogen coordination to Cu^{2+} is progressively replaced by oxygen, as the amino groups become protonated.

1 Introduction

The modification of layered solids by ion exchange or intercalation is a versatile and powerful synthetic route to new materials demonstrating particular physical or chemical properties depending on the nature of the intercalant.[1] These include enhanced electronic[2] or ionic[3] conduction, non-linear optical properties,[4] molecular recognition,[5] materials with improved mechanical or thermal characteristics,[6] *etc.* In the case of the intercalation or ion-exchange of bulky inorganic or organometallic species, permanent interlayer porosity can be introduced if the expanded phase so formed is treated thermally or chemically in order to consolidate the structure and free interlayer regions occupied by organic or hydroxy groups, or water. From the first reports of alumina- and zirconia-pillared clays in the 1970s,[7] the field has moved forward rapidly in the past 15 years to include pillared layered oxides,[8] hydroxides,[9] phosphates[10] and silicates,[11] and a broad spectrum of pillaring species based on polynuclear metal hydroxo or oxo complex ions obtained by the hydrolysis of metal (Al, Ga, Fe, Cr, Zr) salts, organometallic oligomers, *e.g.* $[H_2N(CH_2)_3SiO_{1.5}]_8$, silicon tris(acetylacetonate), positively charged colloidal particles of titania, silica and, in the case of cationic layers, polyoxometallate ions have been used.

The hydrolytic polycondensation of trialkoxysilanes $RSi(OR')_3$ under defined conditions leads to three-dimensional siloxanes $R(SiO_{1.5})_n$.[12] When R contains a basic function, intercalation of the condensed oligomer into a layered solid acid readily occurs and a silica-pillared compound is formed on elimination of the organic moieties. We have previously reported the synthesis of pillared layered α- and γ-zirconium phosphates using aminopropyl[13] and 3-(2-aminoethylamino)propyltrialkoxides[10] hydrolysed under conditions leading predominantly to octameric silica species in solution. Silica-pillared phosphates of surface area up to 350 $m^2 g^{-1}$ can be obtained in this way, and the nature of the porosity predicted to a certain degree by modifying the charge density of the zirconium phosphate layers. We,[13] and others,[14] have previously studied the nature of the siloxane formed in solution using ^{29}Si NMR spectroscopy, and after intercalation into layered zirconium phosphate. In addition, we have reported[10] that the use of a siloxane, in which the alkyl group has two basic functions, allows the direct incorporation of metal ions during the intercalation step. On calcination, the metal ion, *e.g.* Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Al^{3+}, may remain isolated or may be integrated into the silica cluster forming the pillar but are, at all stages, probe atoms for the interlayer environment using an element-specific technique. This approach is complementary to that in which the residual ion-exchange capacity of a pillared solid is used to insert transition metal ions. Cu^{2+}-containing systems are particularly amenable to study using EPR spectroscopy, and we describe here the characterisation of silica pillaring solutions and the corresponding intercalated zirconium phosphate prepared using 3-(2-aminoethylamino)propylsiloxane in the presence of Cu^{2+}. The results are compared with those in which Cu^{2+} is ion-exchanged into alumina- and zirconia[15]-pillared montmorillonite, hectorite[16] and saponite[17] and with those of a previous study of Cu(II) complexes in organically modified silicate gels using (di)aminotrialkoxysilanes.[18]

2 Experimental

2.1 Synthesis

Controlled hydrolysis of 3-(2-aminoethylamino)propyltrimethoxysilane was performed in ethanol–water (14 : 1 v/v). The solution was aged for 24 h to allow the formation of octameric species[13] (Fig. 1). An aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (10^{-1} mol l^{-1}) was then added to give the desired Si/Cu molar ratio, in the range 0.25–48 before recording EPR spectra, or before contact with the zirconium phosphate host.

α-Zirconium phosphate was prepared according to the method described by Alberti and Torracca.[19] It is characterised by a high degree of crystallinity and an interlayer distance corresponding to the *d*-spacing of the lowest angle diffraction line (d_{002}) in its X-ray diffraction pattern, 7.56 Å. The layer

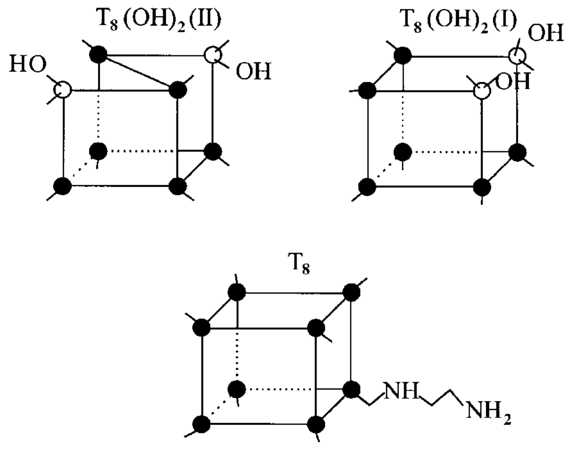

Fig. 1 Schematic representation of dominant species present in an ethanol–water solution of 3-(2-aminoethylamino)propylsiloxane.[10,13]

charge density of pristine α-ZrP was reduced slightly by suspending 1 g in 46 cm^3 of 0.23 mol l^{-1} CH_3NH_2 for 24 h. This mixture was then suspended in the 3-(2-aminoethylamino)propylsiloxane/Cu^{2+} solution, described above, for 7 days. The intercalated solid was recovered by centrifugation, washed several times with water and dried in air. Changes in the interlayer spacing were followed using X-ray diffraction.

2.2 Characterisation

EPR spectra were recorded with a Bruker spectrometer ER100 operating in the X-band ($\nu = 9.6$ GHz). EPR signals of aqueous solutions of paramagnetic salts are frequently difficult to detect at room temperature, consequently all measurements were carried out at 77 K. Measurements of g factors were carried out with maximum accuracy by means of a double cavity using DPPH as a standard ($g = 2.0036$). The tensor components $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ can provide direct information on the environment of the probe ion. The evolution of these parameters is of considerable interest, particularly when the paramagnetic ion is coordinated to nitrogen or oxygen. The most accurate values of the g and A tensors were obtained by a simulation method based on the spin Hamiltonian, taking into account the second order hyperfine interaction (perturbation theory). Solution of the Hamiltonian gives the relation between the experimentally observed quantities and the various coefficients of antibonding molecular orbitals (α^2, β^2 and δ^2). They are connected with the B_{1g}, B_{2g} and E_g orbitals of copper respectively. By using $A_{\parallel}$, $g_{\parallel}$ and $g_{\perp}$, α^2 can be calculated. Parameter β^2 is calculated from the spin–orbit coupling λ of the free electron (-828 cm^{-1}), and E_{xy} determined from the absorption experiments in the visible region. δ^2 is calculated similarly using the value of energy E_{xz}. Parameter α^2 gives the extent of in-plane σ-bonding of the copper ($\alpha^2 = 1$ indicates a pure ionic bond and $\alpha^2 = 0.5$ a totally covalent bond). β^2 shows the extent of in-plane π-bonding ($\beta^2 = 1$ for free copper ion). Parameter δ^2 is directly related to the covalency of the out-of-plane π-bonding. In general, theory shows that the smaller the value of these parameters, the more covalent is the bonding character (σ or π).

^{29}Si NMR spectra were recorded on a Bruker WP 200 SY instrument.

Absorption spectra in the visible region were obtained using a Cary spectrometer.

3 Results and discussion

3.1 EPR spectrum of aqueous solutions of Cu^{2+}

The anisotropy of the g factor of Cu^{2+} in aqueous solution is rarely observed at room temperature.[20] Isotropic thermal motion is usually sufficiently high above 50 K to give rise to a single line.[21,22] In the present study, the observation of a broad signal does not depend on the extent of dilution of the copper nitrate in water and is characteristic[23–25] of the highly mobile octahedral complex $Cu(H_2O)_6{}^{2+}$. The spectrum was simulated using a Lorentzian form, without taking into account the slight anisotropy observed experimentally. The spectroscopic parameters so derived are given in Table 1. The value of g_{iso} for the single line is in agreement with published data[26] and is characteristic of octahedrally coordinated but tetragonally distorted Cu^{2+} ions.

3.2 Copper probe in aqueous ethanolic solutions

A characteristic signal, shown in Fig. 2, is given by Cu^{2+} in water–ethanol at 77 K, where a species with coordination $[Cu(H_2O)_x(EtOH)_{6-x}]^{2+}$ is present;[27] the environment of Cu^{2+} is made up of oxygen atoms from the two solvents. If ethanol molecules participate in the coordination to Cu^{2+}, they induce little spectral modification, except for the observation of hyperfine structure, with respect to the situation in water. The appearance of hyperfine structure is considered to result from the difference in viscosity between water and the water–ethanol mixture.[25,27] The spectrum indicates axial symmetry with good resolution of the hyperfine structure in the low field region (limited resolution at high field). Shoulders are also noted on the signal at low field. These effects are attributed to the influence of a binary solvent system. Simulation of the EPR spectrum was again performed using a Lorentzian form; the results are given in Table 1 and are compared with those of other authors.[26] In agreement with previous studies,[28,29] the g-sequence $g_{\parallel} > g_{\perp} > g_e$ (g_e, free electron) allows us to identify the environment of Cu^{2+} as a tetragonally distorted octahedron, corresponding to D_{4h} symmetry.[30] This spectrum serves as the reference for all the following spectra reported below.

In regularly octahedral CuO_6 copper complexes, the electronic transition between levels $^2E_g \rightarrow {}^2T_g$ gives rise to a broad and intense absorption with a maximum near 13 000 cm^{-1}.[31] In the present work, the maximum, considering aqueous or water–ethanol solution, occurs at 12 300 ± 200 cm^{-1}. Bonding parameters were determined using $\Delta_{\parallel} = \Delta E_{xy} = 13\,000$ cm^{-1} and $\Delta_{\perp} = \Delta E_{xz} = 15\,000$ cm^{-1}, and are reported in Table 2. The value for α^2 of 0.8, notably different from the value indicating pure covalent character (0.5), demonstrates the strongly ionic character of the in-plane σ-bonding. β^2 is close to 1, showing weak in-plane π-character, and the value for δ^2 of 0.95 indicates weak π-character of the out-of-plane bonds. All the parameters lead to the expected conclusion that the Cu^{2+}–oxygen bonds in alcoholic media are ionic in nature. For comparative purposes, the very similar

Table 1 Spectroscopic parameters of Cu^{2+} in various solutions

Solution (77 K)	$\langle g \rangle^a$	$10^4 \langle A \rangle^b$/cm^{-1}	$g_{\parallel}{}^a$	$g_{\perp}{}^c$	$10^4 A_{\parallel}{}^b$/cm^{-1}	$10^4 A_{\perp}{}^d$/cm^{-1}
Cu^{2+} (aq)			$g_{iso} = 2.175$			
Cu^{2+} water–ethanol	2.195	51.5	2.427	2.080	−130.5	−12
Cu^{2+} (aq)^e	2.175	58.0	2.387	2.070	−142.0	−16
Cu^{2+}–methanol^e	2.199	46.5	2.428	2.084	−108.2	−16

[a] ±0.001. [b] ±0.5. [c] ±0.002. [d] ±1. [e] Ref. 26.

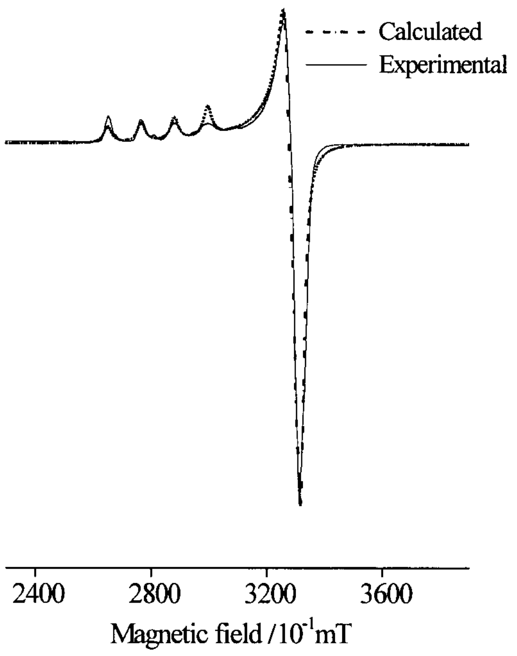

Fig. 2 Cu^{2+} ion in water–ethanol solution: experimental and calculated EPR spectra.

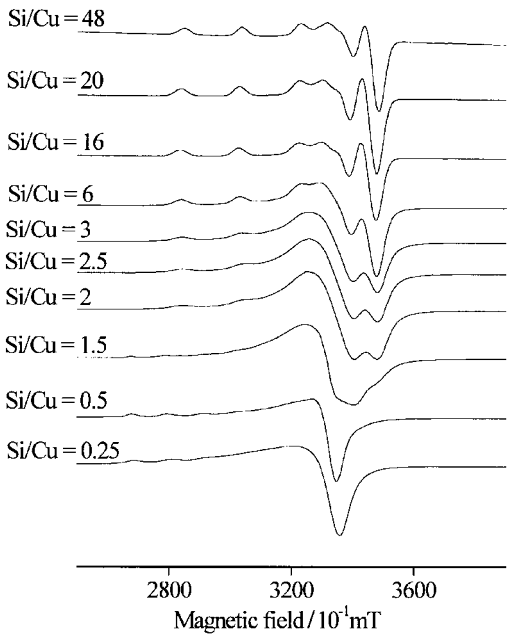

Fig. 3 Evolution of EPR spectra of N_2Si/Cu solutions as a function of Si/Cu ratio.

data for Cu^{2+} in a water–glycerine medium[21] are also given in Table 2.

3.3 Copper probe in ethanol–water siloxane solutions: N_2Si/Cu

The ratio of Si to Cu in the solution was varied between 0.25 and 48 and the EPR spectra recorded at 77 K. Fig. 3 groups the EPR spectra obtained as a function of the Si/Cu molar ratio in the solution.

3.3.1 Ratio Si/Cu = 48–2. The spectrum retains its general features as the Cu^{2+} concentration increases, but a broadening of the various components is observed. Simulation was carried out using a Gaussian form and the hyperfine parameters so derived vary little (Table 3). A solution of ratio Si/Cu = 6, used in the synthesis of copper modified silica pillared phosphates, was selected for more detailed study, and a representative example of an experimental and a simulated spectrum are given in Fig. 4. The conclusions drawn for the solution of this ratio are, nevertheless, valid for others in the range Si/Cu = 48–2. The values of the parallel and perpendicular components of the g and A tensors should be compared with those for Cu^{2+} in ethanol–water mixture. Significant differences are noted, with a strong decrease in value of the $g_{\|}$ and $g_{\perp}$ components, and an increase in $A_{\|}$ and $A_{\perp}$, which implies a drastic change in the environment of copper. Previous studies using a similar solvent TMOS–methanol–3-(2-aminoethylamino)propyltrimethoxysilane with a Cu^{2+} probe have attributed[18] similar evolution in the values of these parameters to the presence of nitrogen in the coordination sphere of Cu^{2+}. It may be concluded that a complex is formed in which four nitrogen atoms coordinate in the equatorial plane; their orientation will create axial symmetry by square-planar type coordination around copper. The coordination sphere is completed by oxygen atoms from the water or ethanol solvent molecules or from nitrate ions.[18,32] Indeed, the spectroscopic parameters reported here are very similar to those given for Cu^{2+} in various nitrogen containing solvents.[18,33,34]

In agreement with the above, in the visible region of the absorption spectrum considering Si/Cu = 6, a broad and asymmetric band is seen, with a maximum at 17 700 ± 300 cm^{-1}, characteristic of copper in tetragonally distorted octahedral coordination. Other work reports bands with maxima in the range 15 200–18 200 cm^{-1} for tetragonally distorted CuN_6, and at higher energy, 18 000–20 000 cm^{-1}, for square planar CuN_4.[35]

Bonding parameters when Si/Cu = 48–2 are almost identical to those calculated, for example, from the spectrum given by a solution with a Si/Cu ratio of 6 (Table 2). The value of α^2 indicates the Cu^{2+}–nitrogen bonds have pronounced ionic character. Compared with its value in water–ethanol solution, the β^2 parameter decreases in value, interpreted in terms of some in-plane π-character arising from delocalisation of electron density and contributing to the stabilisation of the square planar arrangement of nitrogen atoms. The δ^2 parameter is difficult to determine accurately, owing to the presence of both nitrogen and oxygen atoms in the Cu^{2+} coordination sphere. However, calculation of the bonding parameters is performed with values corresponding to Cu–N bonds only. δ^2 indicates that the out-of-plane π-character also increases when Cu^{2+} is dissolved in an aminosiloxane medium. Interpretation of this conclusion is not straightforward, since the axial oxygen bonds are very weak (semi-coordination). Close similarity is observed between the molecular orbital coefficients calculated here, and those reported in a previous study of $[Cu(NH_3)_4]^{2+}$ in ammonia–water–methanol[36] solu-

Table 2 Bonding parameters of Cu^{2+} in different solutions and in an intercalated solid

Solution (77 K)	$A_{\|}/cm^{-1}$	$A_{\perp}/cm^{-1}$	α^{2a}	β^{2a}	δ^{2a}
Cu^{2+} water–ethanol	13 000	15 000	0.80	0.99	0.95
N_2Si/Cu (Si/Cu = 6)	17 700	30 000	0.80	0.77	0.71
Cu^{2+} water–glycerine[b]			0.82	0.98	0.95
$Cu(NH_3)_4^{2+}$ NH_3–H_2O–CH_3OH[c]			0.83	0.77	0.83
α-ZrP/N_2Si/Cu solid (Si/Cu = 6) (300 K)	19 200	25 000	0.78	0.86	0.81

[a] ±0.01. [b] Ref. 21. [c] Ref. 36.

Table 3 Spectroscopic parameters of Cu^{2+} in aminosiloxane solution with various Si/Cu ratios

N_2Si/Cu solution (77 K)	$\langle g\rangle^a$	$10^4\langle A\rangle^b/cm^{-1}$	$g_\parallel^a$	$g_\perp^c$	$10^4A_\parallel^b/cm^{-1}$	$10^4A_\perp^d/cm^{-1}$
Si/Cu = 16	2.087	93.0	2.207	2.028	−199.0	−40
Si/Cu = 6	2.089	91.0	2.210	2.029	−200.5	−36
Si/Cu = 2	2.084	93.0	2.200	2.026	−203.5	−38
Si/Cu = 0.5	2.189	51.5	2.422	2.073	−130.0	−12

$^a\pm0.001$. $^b\pm0.5$. $^c\pm0.002$. $^d\pm1$.

tion (Table 2). The difference in the δ^2 value can be explained considering the interpretation given above.

3.3.2 Ratio Si/Cu < 2. As the amount of Cu^{2+} is increased, the spectroscopic parameters are strongly modified. A Lorentzian form and a second site for copper are required to simulate the experimental spectrum. For the ratio Si/Cu = 0.25, the spectrum is considerably broadened, and interaction between Cu^{2+} and the aminosiloxane appears completely masked by those between Cu^{2+} and the solvents. Indeed, particularly below Si/Cu ratios of around 2, fewer amine groups are available to coordinate to copper and oxygen progressively forms its coordination sphere. Comparison of the EPR spectrum of a solution with Si/Cu = 0.5 with that of copper in ethanol–water solution indicates close similarity, despite the broadening of the former due to strong interactions between the copper centres; the magnetic parameters derived vary only slightly (Table 3).

The evolution of the nature of the site occupied by Cu^{2+} when Si/Cu = 0.25–48 is most clearly seen in the variation of the $g_\parallel$ and $A_\parallel$ parameters as the Si/Cu ratio is varied in the range 0.25–3 (Fig. 5). Similar conclusions are reached using the absorption spectrum.[37]

Bonding parameters for Si/Cu < 2, particularly when Si/Cu = 0.5, are entirely comparable to those in ethanol–water solution, showing the ionic character of the bonding.

3.3.3 Effect of the addition of acid. For a Si/Cu ratio in solution of 6, the pH of the solution was progressively reduced by addition of HCl ($2\ mol\ l^{-1}$). The spectra obtained at different pH values are shown in Fig. 6, and corresponding spectral parameters are given in Table 4. In the range of pH from 10 to 4 there is no observable modification of the hyperfine structure (Fig. 6) and it is concluded that insufficient protonation of the amine groups occurs to perturb the environment around Cu^{2+}. As the solution is further acidified however and below pH 4, profound changes occur in the EPR spectrum, which now shows evidence of two types of Cu^{2+} site (pH 3). The first, now minority site, corresponds to Cu^{2+} coordinated to the siloxane *via* amine functions, and the second is reminiscent of that of Cu^{2+} in ethanol–water solution. Indeed, with the pH of the medium below 4, protonation of the amino groups of the siloxane becomes significant, and their participation in coordination to Cu^{2+} is concomitantly reduced. At pH 2 and below, only one site, now corresponding to that of Cu^{2+} in alcoholic media (*i.e.* Cu^{2+} in an oxygen environment), is observed. Minor differences in the magnetic parameters given by the ethanol solution and the siloxane solution of pH 1 are probably due to the presence in the latter of the siloxane and of chloride ions (a slight shift of the spectrum towards high field is observed in the presence of aminosiloxane, Table 4).

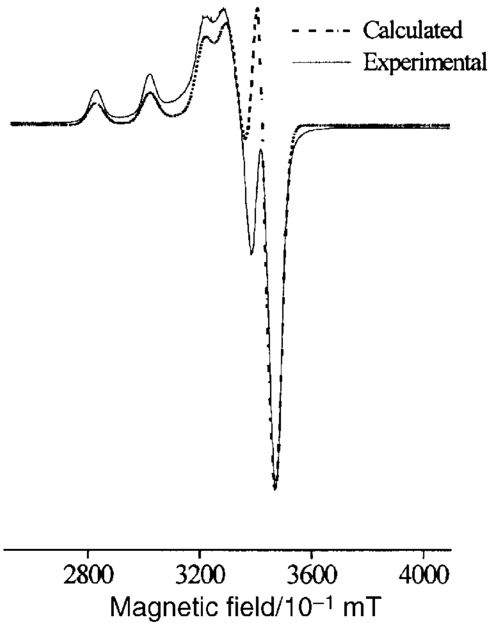

Fig. 4 Experimental and calculated spectra of an N_2Si/Cu solution, with Si/Cu = 6.

This local substitution in the ligands around Cu^{2+} on reducing the pH of the solution seems not to affect significantly, however, the siloxane polyhedron, since the ^{29}Si NMR spectra (for the Cu-free system) of the initial (pH 11) and acidic solutions (pH 2) are unchanged. This is not surprising, since it is known that the formation of octameric siloxane species can be either base- or acid-catalysed.[12] However, on increasing the pH again using NaOH ($1\ mol\ l^{-1}$), a ^{29}Si NMR spectrum characteristic of monomeric and dimeric species is obtained, indicating that depolymerisation has occurred. As it is unlikely that returning to basic pH causes disruption of octa[3-(2-aminoethylamino)propylsiloxane] the depolymerisation is probably due to extensive dilution of the solution.[38] The corresponding EPR spectrum in the Cu^{2+}-containing system becomes once again characteristic of Cu^{2+} in an environment of nitrogen. The evolution of $g_\parallel$ and $A_\parallel$ parameters demonstrate that interactions with the Cu^{2+} probe are significant at short distances and therefore insensitive to the degree of condensation of the siloxane. In particular, the EPR spectrum does not reflect the hydrolysis phenomenon of the siloxane octamer, since it is sensitive only to local effects.

A shift is also observed in the position of the absorption band maximum in the visible region from 17 700 ± 300 for pH 10 to 12 000 ± 200 cm^{-1} for pH 2, this latter is entirely comparable to that given by copper nitrate in ethanol–water solution. This result supports the conclusions given above.

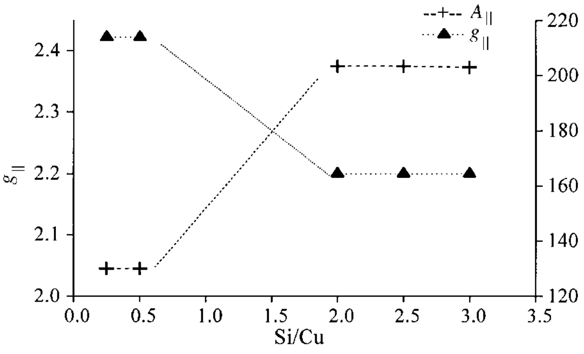

Fig. 5 Evolution of spectroscopic parameters $A_\parallel$ and $g_\parallel$ as a function of Si/Cu ratio, in the range Si/Cu = 0.25–3.

Table 4 Spectroscopic parameters of Cu^{2+} in aminosiloxane solution (Si/Cu = 6), at pH 1, 3 and 10

N_2Si/Cu solution (Si/Cu = 6) (77K)	$\langle g \rangle^a$	$10^4 \langle A \rangle^b$/cm^{-1}	$g_\parallel^a$	$g_\perp^c$	$10^4 A_\parallel^b$/cm^{-1}	$10^4 A_\perp^d$/cm^{-1}
pH 10	2.089	91.0	2.210	2.029	−200.0	−36
pH 3	2.191	53.0	2.420	2.077	−133.0	−12
pH 1	2.189	52.5	2.418	2.075	−133.0	−12

$^a \pm 0.001$. $^b \pm 0.5$. $^c \pm 0.002$. $^d \pm 1$.

Between pH 1 and 3, bonding parameters α^2 and β^2 of Cu–O bonds are identical (within the accuracy limits), and show the clear ionic character of σ-bonding and weak π-character in the equatorial plane. The δ^2 parameter values are also comparable and are indicative of weak out-of-plane π-character. In comparison with the molecular orbital coefficients for solutions at basic pH, *e.g.* pH 10, a slight increase in the ionic character of the σ-bonding and a clear decrease in the in-plane π-character of the bonds is deduced, which can be attributed to the change in nature of the coordination environment of copper, *i.e.* from predominantly nitrogen to predominantly oxygen.

3.3.4 Dried N_2Si/Cu solution. The EPR spectrum of a Cu^{2+}–octa(diaminosiloxane) solution (Si/Cu = 6) dried at 130 °C in air was also recorded (Fig. 7, spectrum b). The signature given by the copper probe is essentially unchanged and it may concluded that its environment in siloxane ethanol–water solution and in the corresponding dried solid are identical; since solvent has been eliminated in the latter case, the Cu coordination sphere of nitrogen atoms must be completed by oxygen atoms from nitrate groups.

3.4 Octa(aminosiloxane)–Cu^{2+} intercalated zirconium phosphate: α-ZrP/N_2Si/Cu

A siloxane–copper nitrate ethanolic solution with a Si/Cu ratio of 6 was selected for intercalation into zirconium phosphate. X-Ray fluorescence spectroscopy showed the Si/Cu molar ratio in the solid to be 3.4. Powder X-ray diffraction showed an expansion from 7.6 Å in the pristine layered host to 24.6 Å in the intercalated solid.[37] Such an increase in interlayer spacing suggests that the octameric arrangement of siloxane in solution has been retained on intercalation. The EPR spectrum of the solid, reproduced in Fig. 7 (spectrum a), shows axial symmetry with medium resolution of the hyperfine structure at low field, and only partial resolution of the perpendicular component. This spectrum qualitatively resembles that given by the Cu^{2+}–octa(diaminosiloxane) solution in ethanol–water at 77 K, and is identical to that obtained after elimination of the solvent from this solution (Fig. 7, spectra c and b respectively). It may be concluded that the environment of Cu^{2+} in all cases is very similar or identical. The hyperfine structure of the spectrum given by the intercalated solid is less resolved with respect to the solution spectra, owing to a lower dispersion of Cu^{2+} ions following intercalation. Although its environment is similarly made up of four nitrogen atoms from diaminosiloxanes and of two oxygen atoms, these latter must now belong either to molecules of co-intercalated solvent, H_2O and EEOH. It may be concluded that the intercalation does not modify the environment of the Cu^{2+}. Moreover, the intercalation of octa(aminosiloxane)/Cu^{2+} cannot be demonstrated by a simple observation of the EPR spectra of the dried N_2Si/Cu solution and the intercalated compound α-ZrP/N_2Si/Cu. This would indicate that the probe is rather far from the α-ZrP layers, *i.e.* the Cu^{2+}–octamer complex is not in direct interaction with the layers. Table 5 gives the *g* and *A* parameters derived from simulation of the spectrum which required the use of a Lorentzian form. These parameters are only slightly different from those of the Cu^{2+}–octa(diaminosiloxane) complex in solution supporting the conclusions given above.

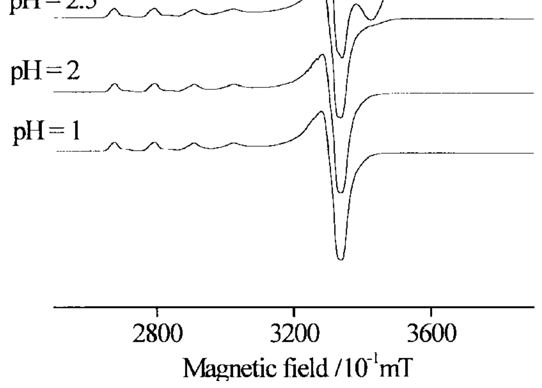

Fig. 6 EPR spectra of N_2Si/Cu solution (Si/Cu = 6) at different pH values.

3.5 Comparison with Cu^{2+}-exchanged α-ZrP (α-ZrP/Cu)

The EPR spectrum of α-ZrP directly exchanged with Cu^{2+} was also recorded for comparison and was found to be totally different from that observed for α-ZrP/N_2Si/Cu. The magnetic parameters (Table 5) clearly reflect this difference, since they are closer to those reported for Cu^{2+} ion-exchanged into

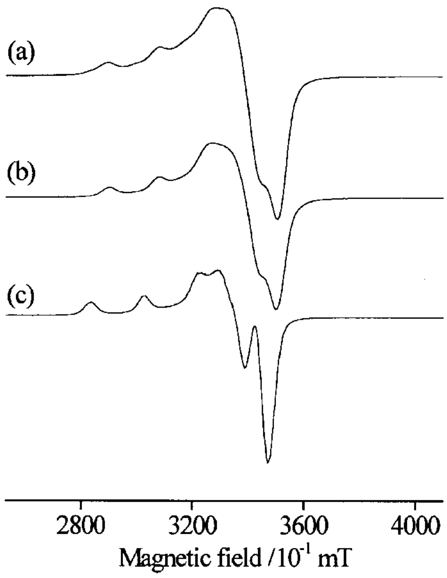

Fig. 7 EPR spectra of (a) intercalated solid α-ZrP/N_2Si/Cu (300 K), (b) N_2Si/Cu solution dried at 130 °C (300 K) and (c) N_2Si/Cu solution (77 K), with Si/Cu = 6.

Table 5 Comparison of spectroscopic parameters for Cu^{2+} in aminosiloxane solution, following intercalation in α-ZrP and direct exchange Cu^{2+}/α-ZrP

Sample	$\langle g\rangle^a$	$10^4\langle A\rangle^b$/cm^{-1}	$g_\parallel^a$	$g_\perp^c$	$10^4A_\parallel^b$/cm^{-1}	$10^4A_\perp^d$/cm^{-1}
N_2Si/Cu solution (Si/Cu = 6) (77 K)	2.094	87.3	2.203	2.039	−193.5	−34
α-ZrP/N_2Si/Cu solid (Si/Cu = 6) (300K)	2.095	89.2	2.208	2.038	−190.0	−39
α-ZrP/Cu solid (300 K)	2.183	51.0	2.410	2.069	−117.0	−18

^{a}±0.001. ^{b}±0.5. ^{c}±0.002. ^{d}±1.

alumina[15,17] or silica[16] pillared clays and where the copper is interacting with oxygen atoms from the pillars and from water molecules. This result implies the presence of two distinct environment around Cu^{2+} ion. We can conclude that there is no evidence for the presence of copper in α-ZrP/N_2Si/Cu in a site similar to that obtained by direct ion-exchange between the host lattice and Cu^{2+}, indicating that the overriding majority of Cu^{2+} ions are carried into the interlayer region as a complex with octa(diaminosiloxane) previously formed in solution.

Absorption in the visible region in the intercalated compound is broad, with a maximum at $19\,200 \pm 100$ cm^{-1}, and a shoulder at $25\,000 \pm 100$ cm^{-1}. These values were attributed to $\Delta_\parallel$ and $\Delta_\perp$ for the purposes of calculating the bonding parameters, given in Table 2. The magnitude of α^2 could indicate the presence of moderate ionic character to the in-plane σ-bonding, those of β^2 and δ^2 moderate π-character, in- and out-of plane respectively. In comparison to the values derived from the Cu^{2+}–siloxane complex in solution, the α^2 coefficient has decreased slightly in value, reflecting a weak reduction in ionic character in the equatorial bonds. The β^2 parameter increases showing a weakness in the in-plane π-character.

4 Conclusion

The local structure around Cu^{2+} in hydrolysed/condensed solutions of 3-(aminoethylamino)propyltrimethoxysilane is conserved on intercalation of the octa(diaminoalkyl)siloxane/Cu^{2+} complex into α-zirconium phosphate. The site occupied by Cu^{2+} within the interlayer region is different from that occupied by Cu^{2+} inserted by direct exchange with α-ZrP.

Studies of the pillared materials obtained after calcination are now underway and will be reported subsequently.

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