as about the fifth power of the bond length, the observed decrease in the vibrational energy implies a bond length of ~1.80 Å in the $^3\pi_g$ excited state.

The increase in bond length in the excited state may also be calculated from the relative intensities of the components of the band,[30] but in the present case, these are not well enough resolved to warrent such an analysis. However, we recently described[31] a simple relationship by which the bond length change δr accompanying an electronic transition may be estimated from the force constant f of the ν_1 vibration, if it is assumed that the energy difference Δ between the d orbitals involved in the transition depends inversely on some arbitrary power n of the bond length:

$$\delta r \approx \Delta nm/(frN)$$

Here, N is the number of ligand atoms (2 in the present case) and m is the number of electrons involved in the transition. This expression has been found to give good agreement with the bond-length changes derived from the analysis of the electronic spectra of a wide range of complexes[30,31] with a value of $n \approx 5$. To a good approximation, for the $^3\pi_g \leftarrow {}^3\pi_g$ transition, a single electron is promoted from the d_{xy}, $d_{x^2-y^2}$ to the d_{z^2} orbital, and substitution of the value $m = 1$ and $\Delta = 13\,000$ cm^{-1} into the above equation, together with $n = 5$, $r = 1.687$ Å, and $f = 5.06$ mdyn Å^{-1} = 2.55×10^5 cm^{-1} Å,$^{-2}$ suggests that each Ni–O bond length should increase by a total of $\delta r \approx 0.0755$ to ~1.76 Å in the $^3\pi_g$ excited state, in fair agreement with the above estimate derived from the decrease in the bond force constant.

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Registry No. NiO_2^{2-}, 37382-01-7; K_2NiO_2, 50811-97-7.

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EPR Reinvestigation of the Copper(II)–Imidazole System

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An EPR reinvestigation of the copper(II)–imidazole system has been carried out. The room-temperature EPR spectrum recorded with a low molar ratio, [Cu^{2+}]:[imidazole] = 1:10, reveals the features of two absorbing species, probably [Cu(imidazole)$_3$]$^{2+}$ and [Cu(imidazole)$_4$]$^{2+}$. The experimental results at high molar ratios at both room and low temperatures give evidence of the formation of a well-characterized four-coordinated species, [Cu(imidazole)$_4$]$^{2+}$. A critical comparison with a recent report in which EPR parameters have been attributed to [Cu(imidazole)$_5$]$^{2+}$ and [Cu(imidazole)$_6$]$^{2+}$ is also made.

Introduction

Recently an EPR characterization of the various species present in the copper(II)–imidazole (imH) system and analogous complexes as well as some mixed complexes having imH as the second ligand has been reported.[1] However, we have set little value on the conclusions reached by the authors of that paper for the following reasons.

(i) They assigned EPR spectra to [Cu(imH)$_n$]$^{2+}$ (n = 4–6) complexes, without having determined the species distribution in the copper(II)–imidazole system; accordingly, the copper–imidazole (and –methylimidazole as well) complexes reported in their paper were not those the authors thought to be present in solution.

(ii) Their hypothesis on the formation of a pentakis(imidazole)copper(II) species was based on the shifts undergone by $g_\parallel$ and $A_\parallel$ values with respect to those of a presumed tetrakis complex; the changes of the magnetic parameters should have been the opposite of those reported.

(iii) Although their EPR spectra showed a well-resolved shf structure, it only appeared in the perpendicular region; furthermore, on the basis of 11 shf lines, they deduced the pentakis(imidazole)copper(II) complex formation, while it is well-known that apical nitrogens contribute to shf interaction in a way different from those bound in the equatorial plane.

(iv) They tried to rationalize trends in rhombic distortion among a series of copper–amine and –polyamine complexes, the EPR spectra of which are essentially axial; they mistook an extra peak for a different resonance line with a peculiar g value.

Therefore, we decided to undertake an EPR reinvestigation of the copper(II)–imidazole system both in water–methanol and in water–dimethyl sulfoxide (Me_2SO) mixtures, the latter mixture being that used in the previous paper.[1]

Experimental Section

$^{63}CuSO_4$ was purchased from Stable Isotope Unit Chemistry Division, Harwell, Oxfordshire, England, and imidazole (Fluka, purissimum) was recrystallized twice from benzene. Twice-distilled water and reagent grade methanol and dimethyl sulfoxide were used to prepare the complex solutions. Three different ratios, [Cu^{2+}]:[imH] = 1:10, 1:100, and 1:200, were used, the concentration of copper(II) ions being 5×10^{-3} mol dm^{-3}. To adjust the solution pH to a value of about 7, imidazole (pK = 7.03) was neutralized up to 50% by adding HNO_3. The calculations associated with the species distribution in the copper(II)–imidazole system have been carried out by using the program DISDI.[2] To get the species distribution as a function of pH, we used the values of log β_n (n = 1–4) reported by James et al.:[3] log β_1 = 4.33, log β_2 = 7.61, log β_3 = 10.31, and log β_4 = 12.2.

EPR spectra were recorded with a conventional X-band spectrometer, Bruker ER 200 D, equipped with a low-temperature control unit. DPPH (g = 2.0036) was used to calibrate the klystron frequency, the magnetic field being continuously measured by means of a Model ER 035 M gauss meter, which gives markers at preselected values. Magnetic parameters were calculated by using a program substantially devised by Pilbrow et al.,[4] which allows one to deal with the shf interaction of one, two, or four nitrogen donors in the equatorial plane.

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Results and Discussion

When measuring EPR spectra on copper(II) complexes present in solution, one must have an exact idea of what is going on by varying the concentration of the various ligands or the pH of the aqueous solution.[5] In other words, a previous speciation study is necessary. In a previously published paper[1] the authors claimed to have the species $[Cu(imH)_5]^{2+}$ (see their Figures 1 and 8), in the copper–imidazole system, using only a $[imH]:[Cu^{2+}]$ ratio ranging from 5 to 10; in order to get the EPR spectrum of $[Cu(imH)_4]^{2+}$, other workers[6,7] previously used $[imH]:[Cu^{2+}]$ ratios ranging from 70 to 120. Though we are aware that freezing could probably change the relative proportions of the species present in the system, the knowledge of the speciation is a good starting point, and a comparison between room-temperature isotropic and frozen-solution anisotropic spectra is of great help.

In fact, the formation of a $[Cu(imH)_5]^{2+}$ species in aqueous solution at 25 °C is not probable under the experimental conditions reported in ref 1. There is only one report[8] in the literature about the existence of this five-coordinated species at $I = 3$ mol dm^{-3} ($NaClO_4$ or NaCl) and with $[imH]:[Cu^{2+}]$ ratios larger than 60. Assuming this five-coordinated species formation and attributing a fictitious $\log \beta_5 \approx 13.7$ (1.5 log units more than the four-coordinated species value) to it, its quantity is almost negligible at pH 7, when the ratio $[Cu^{2+}]:[imH] = 1:10$ is used. Only at $[Cu^{2+}]:[imH] = 1:100$ would it be the predominant species (species distribution diagrams have been added as supplementary material). At pH 7 the system contains both $[Cu(imH)_3]^{2+}$ and $[Cu(imH)_4]^{2+}$ roughly in the same proportions, when a $[Cu^{2+}]:[imH] = 1:10$ ratio is used, while if we consider a $[Cu^{2+}]:[imH] = 1:100$ ratio, the $[Cu(imH)_4]^{2+}$ species is the most abundant one.

The formation of $[Cu(imH)_5]^{2+}$ has been checked by running room-temperature EPR spectra at $[Cu^{2+}]:[imH] = 1:10$, 1:100, and 1:200. As shown in Figure 1, the room-temperature EPR spectra reflect the species distribution discussed above; in fact, at the metal:ligand ratio 1:10 the EPR spectrum is complicated by the presence of more than one species. When a water–methanol mixture is used, the species are probably $[Cu(imH)_3]^{2+}$ and $[Cu(imH)_4]^{2+}$. In water–Me_2SO the behavior of the system is a little more complex, probably because Me_2SO can become a competing ligand toward the already coordinated copper(II) ion. At the other two $[Cu^{2+}]:[imH]$ ratios the room-temperature EPR spectra are virtually identical in both water–methanol and water–Me_2SO. As shown in Figure 1b,c, all the spectra show a well-resolved shf splitting. Nine shf lines can be ascribed to four equivalent in-plane nitrogen donors, giving evidence of the formation of the $[Cu(imH)_4]^{2+}$ species (compare the instrument marker at 340 mT, which falls approximately in the center of the highest field line in the case of the spectrum reported in Figure 1b, with that of Figure 1a; this marker highlights the group of lines belonging to the $[Cu(imH)_4]^{2+}$ species in the spectrum reported in Figure 1a, the other lines belonging to other species present in the system). Hence, with all the $[Cu^{2+}]:[imH]$ ratios used in this study, there is no EPR evidence for $[Cu(imH)_5]^{2+}$ or $[Cu(imH)_6]^{2+}$ at room temperature.

The frozen-solution EPR spectrum, presented in Figure 1d, is representative of the spectral patterns for all the $[Cu^{2+}]:[imH]$ ratios used in this study, either in water–methanol or in water–Me_2SO mixtures. Generally copper complexes in frozen solutions exhibit an axial **g** tensor because it is almost impossible to detect anisotropies in the equatorial plane due to the small hyperfine coupling constants and relatively large line widths. Small differences are reported in the literature ($|g_{xx} - g_{yy}| = 0.02$–0.03),[9-13] but these have sometimes been overestimated by the simulation procedure rather than being effectively true. Among the copper complexes in frozen solution we characterized in the past, the only convincing rhombic distortion we found in an EPR spectrum is that imposed by two 2,2′:6′,2″-terpyridyl molecules on copper ions.[14] Rhombic patterns in copper complexes are easily obtained in the solid state, in which the rigidity of the crystal packing and the favorable small line widths allow the detection of g_{xx} and g_{yy} with relative facility. A copper complex powder EPR spectrum can show two broad peaks in the perpendicular region, but these

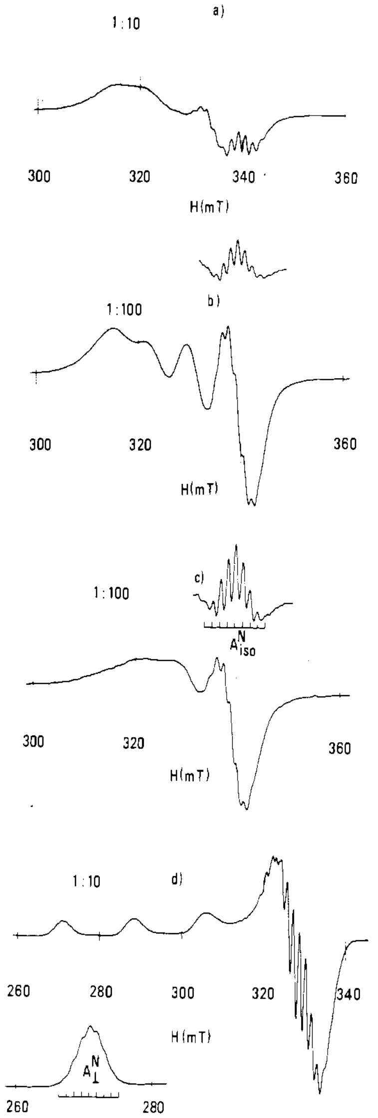

Figure 1. (a–c) Room-temperature liquid-solution EPR spectra of the copper(II)–imidazole system: (a, b) 90% water–10% methanol solvent mixture; (c) 50% water–50% Me_2SO solvent mixture. The $[Cu^{2+}]:[imH]$ molar ratios are shown in each spectrum ($\nu = 9.772$ GHz; modulation frequency 100 kHz; modulation amplitude 0.5 mT; time constant 0.2; microwave power 20 mW). Inserts in (b) and (c) show the second-derivative mode of the highest field line (modulation frequency 12.5 kHz; modulation amplitude 0.5 mT; time constant 0.5 s; microwave power 30–40 mW). (d) Frozen-solution EPR spectrum in the water–methanol mixture. The insert shows the nitrogen shf structure superimposed on the lowest field line ($\nu = 9.405$ GHz; modulation frequency 100 kHz; modulation amplitude 0.5 mT; time constant 0.5 s; microwave power 5 mW).

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Table I. Spin Hamiltonian Parameters Obtained for the Copper(II)–Imidazole System in Water–Methanol and Water–Me_2SO Mixtures

Results from This Work[a]

$[Cu^{2+}]:[imH]$	medium	$g_\parallel$	$A_\parallel$, cm^{-1}	$g_\perp$	$A_\perp$, cm^{-1}	$A^N_\parallel$, cm^{-1}	$A^N_\perp$, cm^{-1}	g_{iso}	A_{iso}, cm^{-1}
1:10	water–methanol	2.260	0.0185	2.054	0.0017	0.0016	0.0012		
1:100	water–methanol	2.264	0.0180	2.057	0.0013	0.0016	0.0012	2.131	0.0079
1:200	water–methanol	2.264	0.0180	2.057	0.0013	0.0016	0.0012	2.131	0.0079
1:10	water–Me_2SO	2.260	0.0187	2.054	0.0017	0.0017	0.0012		
1:100	water–Me_2SO	2.261	0.0186	2.054	0.0017	0.0017	0.0012	2.132	0.0082
1:200	water–Me_2SO	2.262	0.0186	2.054	0.0017	0.0017	0.0012	2.132	0.0084

Results from Other Works

complex	medium	$g_\parallel$	$A_\parallel$, cm^{-1}	$g_\perp$	$A_\perp$, cm^{-1}	$A^N_\parallel$, cm^{-1}	$A^N_\perp$, cm^{-1}	g_{iso}	A_{iso}, cm^{-1}	ref
$[Cu(imH)_4]^{2+}$	water–glycerol	2.255	0.0205	2.060	0.0016	0.0014	0.0012	2.125[b]	0.0079[b]	4
$[Cu(imH)_4]^{2+}$	$[Pd(imH)_4]^{2+}$	2.267	0.0180	2.063						32
$[Cu(imH)_4]^{2+}$	water	2.267	0.0180	2.063						32
$[Cu(imH)_4]^{2+}$	water							2.131	0.0072	3
$[Cu(imH)_4]^{2+}$	water–Me_2SO	2.310	0.0154	2.060		0.0015				1
$[Cu(imH)_5]^{2+}$	water–Me_2SO	2.250	0.0193	2.040		0.0015				1
$[Cu(imH)_6]^{2+}$	water–Me_2SO	2.240	0.0181	2.040		0.0015				1

[a] Errors: $g_\parallel$, 0.001; $A_\parallel$, 0.0001 cm^{-1}; $g_\perp$, 0.003; $A_\perp$, 0.0004 cm^{-1}; A^N, 0.0002 cm^{-1}. [b] $g_{iso} = {}^1/_3(g_\parallel + 2g_\perp)$; $A_{iso} = {}^1/_3(A_\parallel + 2A_\perp)$.

features cannot directly be ascribed to an in-plane rhombic distortion. EPR spectra of copper(II) complexes in frozen solutions can frequently be fitted by an axial spin Hamiltonian, the peak at highest field being an extra peak due to angular anomalies.[15-22]

Spin Hamiltonian parameters obtained by carefully simulating experimental spectra are reported in Table I together with those taken from some relevant literature reports on the same system. As shown in the inset of Figure 1d, one can see well-resolved shf features on the lowest field line: a nine-line pattern can be inferred (suggesting that, when the temperature is lowered, the room-temperature species distribution is slightly modified in favor of the species with a higher coordination number). It is important to point out that the number of nitrogens can be straightforwardly obtained if the shf structure is superimposed on the parallel lines of the spectrum. Very often the shf structure is only resolved in the perpendicular region, so it is very difficult to assess which of the four perpendicular lines it is coming from. A composite pattern is obtained; therefore, it is an ambiguous procedure to count the shf lines appearing in the perpendicular region and state the number of nitrogen donors bound to copper. In the EPR spectrum of Figure 1d at least 12 nitrogen shf lines could be counted in the perpendicular part, but only nine are seen in the parallel region. The best method is to use a multifrequency approach in correlation with computer simulation, since the employment of the S band greatly improves the resolution of the shf lines and in particular those in the parallel region, as shown by Basosi et al.[23] Often room-temperature isotropic spectra can be of great help, if the resolution allows the shf structure to be detected.[24]

Moreover, in pseudooctahedral copper(II) complexes one would expect a shf nine-line pattern if four equivalent (or quasi-equivalent) nitrogen donors were situated at the corners of the equatorial plane with a $d_{x^2-y^2}$ or a d_{xy} ground state. A nitrogen donor linked apically to copper along the z axis would not contribute to the overall shf structure, since very little spin density (only a dipolar coupling is expected) reaches the donor atom. Consequently, the shf contribution of the fifth nitrogen donor to the overall shf interaction is very small and is probably not resolved in the experimental EPR spectrum.[26-28] Thus, it is not possible to distinguish between four- and five-coordinated species on the grounds of shf data only. But, since the EPR spectra of copper(II) complexes are very sensitive to the formation of a $[CuL_5]^{2+}$ adduct when one starts from a $[CuL_4]^{2+}$ species[24-27] (L is a general monodentate ligand), we would expect that on going from the latter to the former the value of $g_\parallel$ should increase and $A_\parallel$ decrease, as a result of the apical interaction. No such shift was observed for the copper–imidazole complexes reported here. The $g_\parallel$ values reported in Table I are practically constant for both solvent mixtures and for all $[imH]:[Cu^{2+}]$ ratios, while a slight decrease of $A_\parallel$ can be seen in the case of the water–methanol mixture. This last fact deserves a brief comment: it can probably be ascribed to a competing axial interaction between the excess imidazole and the solvent molecules. However, the slight increase in $g_\parallel$ values as one goes from the 1:10 to 1:100 or 1:200 molar ratio is not sufficient to account for the existence of a species with definite coordination number larger than 4.

In contrast to the results of Siddiqui et al.[1] our results in both solvent mixtures support the formation of a well-characterized $[Cu(imH)_4]^{2+}$ species when high $[imH]:[Cu^{2+}]$ ratios are used, at both room and low temperatures. When the ligand-to-metal ratio is 10, only at room temperature, in addition to the former species the EPR spectrum also reveals the features of another species, probably $[Cu(imH)_3]^{2+}$.

Registry No. $[Cu(imH)_4]^{2+}$, 47105-83-9; $[Cu(imH)_5]^{2+}$, 95627-61-5; $[Cu(imH)_6]^{2+}$, 35026-25-6.

Supplementary Material Available: Species distribution diagrams for the Cu–imH system (Figure 2) (4 pages). Ordering information is given on any current masthead page.

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