Electron Paramagnetic Resonance and Visible Spectroscopic Studies of Mixed-ligand Complexes of Copper(II) Ion, Salicylate Ion, and a Nitrogen Base in Aqueous Solution*

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The mixed-ligand complex formation of copper(II) ion with salicylate ion and a nitrogen base (ammonia, monoethanolamine, diethanolamine, or triethanolamine) has been studied in aqueous solution at 25 °C and 1.0 mol dm^{-3} ionic strength by means of e.p.r. spectroscopy. The reliability of the proposed e.p.r. method in the study of mixed-ligand systems is verified by comparison of the results obtained with those from visible spectroscopy and potentiometry.

The study of mixed-ligand complex formation is relevant in the field of analytical chemistry, where the use of mixed-ligand complexes allows the development of methods with increased selectivity and sensitivity, and has also great importance in the field of biological and environmental chemistry. A special interest is the study of mixed-ligand complex formation between copper(II) ion, salicylate ion, and a nitrogen base. Metal chelates of aminoalcohols play important roles in nature, for example in the hormones adrenaline and noradrenaline and in aminopolysaccharide chemistry.[1] *ortho*-Hydroxycarboxylic acids and among them, salicylic acid, also have biological significance: they are considered as model compounds in the study of the behaviour of humic and fulvic acids in soils[2,3] and they have pharmaceutical application[4,5] owing to the anti-inflammatory properties of their copper(II) complexes.[6–9] Mixed-ligand complex formation with both kinds of ligands may deeply affect the known properties of these binary systems. The formation constants of these mixed-ligand complexes are also useful for enlarging the descriptive chemistry of complex equilibria.

E.p.r. spectroscopy is a very suitable method for the study of copper(II) complex-formation equilibria in solution.[10,11] In the present work, an e.p.r. titration method[10] is applied to the study of mixed-ligand complex formation between copper(II) ion, salicylate ion (sal), and a mononitrogen base [ammonia, monoethanolamine (mea), diethanolamine (dea), and triethanolamine (tea)] in aqueous solution at 25 °C and 1.0 mol dm^{-3} ionic strength. The reliability of the proposed method is validated by comparison of the results obtained with those obtained from visible spectroscopy, in this work, and from potentiometry.[12–14]

The calculation of reliable values for the stability constants of the mixed-ligand complexes by e.p.r. or visible spectroscopic procedures requires the knowledge of accurate and precise values of the protonation constants for the ligands and the formation constants for their binary complexes with the metal ion, together with the characteristic individual e.p.r. or visible spectra of each of the binary complexes. The binary systems formed by copper(II) ion and the above nitrogen bases were studied previously using the same e.p.r. procedure[15,16] and also by visible spectroscopy.[17] A study of the binary system copper(II)-sal by e.p.r. and visible spectroscopy is included in the present work. The values of the protonation constants for all the ligands were determined previously from e.m.f. data.[12–14]

Experimental

Materials.—Nitric acid, KNO_3, NH_4NO_3, $Cu(NO_3)_2 \cdot 3H_2O$ (Merck, a. r. grade), sodium salicylate (Carlo Erba, a. r. grade), monoethanolamine, diethanolamine, triethanolamine, and ammonia (Fluka puriss.) were used without further purification. All the solutions were prepared using CO_2-free deionized water.

Stock solutions of copper(II) ion were standardized by iodometric titration. Stock solutions of 1.0 mol dm^{-3} mono-, di-, or tri-ethanolammonium ion were prepared by neutralization of known amounts of the ligands with stoicheiometric amounts of a stock 2.0 mol dm^{-3} HNO_3 solution, which was previously standardized volumetrically with tris(hydroxymethyl)aminomethane. Stock solutions of salicylate ion were prepared from a known amount of the sodium salicylate reagent. Carbon dioxide-free potassium hydroxide (Merck, a. r. grade) solutions were prepared and standardized as usual.[18]

The ionic strength of the measured solutions was kept constant at 1.0 mol dm^{-3} by adding, when necessary, the appropriate amount of potassium nitrate.

Apparatus.—E.p.r. solution spectra at 25 °C were recorded on a Varian E-109 E spectrometer in capillary quartz tubes of diameter 1 mm (Wilmad, cat. No. 800). pH Measurements were performed with a Radiometer PHM-64 pH-meter and a combined Ross pH-electrode (Orion 81-02). Visible absorption spectra were recorded on a Beckman DU-7 spectrophotometer interfaced (RS232) to an IBM personal computer. Spectra acquisition was controlled through Beckman data capture software.

E.P.R. and Visible Spectral Determinations.—Solutions for e.p.r. and visible spectroscopic studies were obtained during the potentiometric titration, with a standardized potassium hydroxide solution, of slightly acidic solutions which contain different copper(II) ion concentrations and different ligand-to-metal ion concentration ratios. With the aid of a peristaltic pump the solution being titrated was introduced continuously into the flow cell in the spectrophotometer. After each titrand addition the pH of the solution was measured, the visible spectrum obtained (the absorbance was measured every 20 nm, between 400 and 900 nm), and a sample of 100 μl withdrawn for e.p.r. spectrum determination. In very basic media, the pH was changed by very small additions of a very concentrated base solution, with negligible variations in total volume. For every titration, a previous calibration of the potentiometric cell was carried out by Gran's method.[19]

For all the determinations performed on the copper(II)–sal

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* *Non-S.I. unit employed:* G = 10^{-4} T.

Table 1. Summary of experimental conditions used in the determinations

	Conc. range (mmol l^{-1})			Number of spectra		
System	Cu^{II}	Salicylate	Nitrogen base	E.p.r.	Visible	pH range
Cu–sal	11.1	52.4	—	24	43	3.6—10.2
Cu–sal–NH_3	11.3	77.0	835	27	—	3.8—8.5
Cu–sal–mea	8.18—8.52	15.0—43.0	81.1—83.5	43	52	2.0—8.4
Cu–sal–dea	5.71—10.5	15.1—32.1	93.7—712	74	93	2.0—10.5
Cu–sal–tea	8.2—17.2	46.0—86.2	65.6—83.3	51	51	3.0—11.8

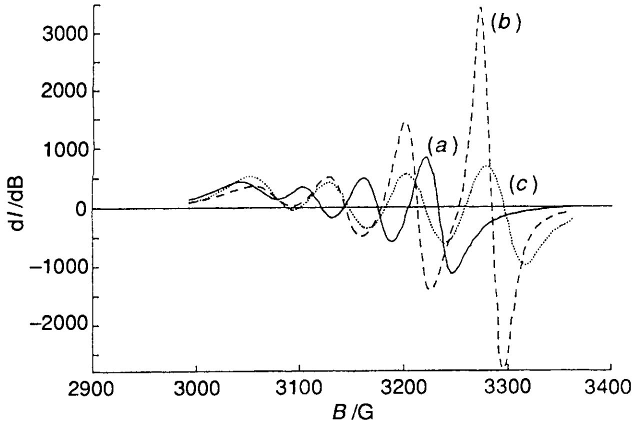

Figure 1. Calculated e.p.r. spectra in the copper(II)–sal and copper(II)–sal–NH_3 systems: (*a*) and (*b*) refer to the 1:1 and 1:2 copper(II):sal species, respectively; $[Cu^{II}] = 1.972 \times 10^{-2}$ mol l^{-1}, gain = 500; (*c*) refers to the 1:1:2 copper(II):sal:NH_3 species; $[Cu^{II}] = 2.026 \times 10^{-2}$ mol l^{-1}, gain = 500

binary system and on the mixed-ligand systems the initial conditions of copper(II) concentration, ligand concentrations, and working pH range are summarized in Table 1.

Data Treatment.—The numerical analysis of the e.p.r. spectra was performed with the FORTRAN ESRDIG2 program described by Kittl and Rode.[10] This program provides the simultaneous determination of the stability constants of the species formed and of their individual e.p.r. spectra.[15,16]

The numerical analysis of the visible spectra was carried out with the computer program SQUAD,[20] which calculates simultaneously the stability constants of the species formed and their individual molar absorptivities in the working wavelength range.

The fit finally achieved in all the studied systems is reasonably good, although the results have been obtained from several different data sets (each from a different titration). The goodness of fit for visible spectroscopy is measured by the standard deviation of the residuals and it is around 0.01 absorbance units. That for e.p.r. spectroscopy is given by the absolute standard deviation of the fit divided by the length of the scale, both in the same arbitrary units and is around 1%. The same level of precision of e.p.r. measurements has been obtained in other related works.[10,11]

Results and Discussion

E.P.R. and Visible Spectral Study of Copper(II)*–Salicylate System*.—At pH values less than 3 no copper(II) complexation is observed since the experimental e.p.r. spectra of the binary copper(II)–salicylate system resemble the spectrum of copper(II) alone at the same background (spectrum consisting of a broad band without hyperfine splitting[21]). When the pH increases there is an increase in resolution of the hyperfine interaction with the copper nucleus ($I_{Cu} = \frac{3}{2}$), which yields evidence of copper(II) complexation. At pH values around 4 the hyperfine splitting into four bands is complete and the spectrum is quite symmetrical. At higher pH values the appearance of a fifth band shows the formation of a second copper(II) complex. At pH $\geqslant$ 8 only the four bands of this second complex appear in the spectrum. This spectrum is very asymmetrical and shifted to higher magnetic fields with respect to those of the other species. So the study of the experimental e.p.r. spectra shows the existence of two different species: one of them predominant at a pH around 4, and the other at pH $\geqslant$ 8. The species detected are the 1:1 and 1:2 copper(II)–sal complexes, in accordance with the spectrophotometric results obtained here and known potentiometric data.[12]

The stability constants obtained for these complexes from the numerical treatment of both the e.p.r. and visible experimental spectra are included in Table 2, and their characteristic e.p.r. spectra are given in Figure 1.

E.P.R. Study of Copper(II)*–Salicylate–Ammonia System*.—In contrast to the binary systems, from only the direct visual observation of the variation in shape of the e.p.r. spectra during the titration of the mixed systems it is usually not possible to assess the number of mixed-ligand species formed, because their individual spectra are obscured by those of the binary species present in the system. By application of the ESRDIG2 program, however, a decision can be reached. Thus, for the copper(II)–sal–ammonia mixed-ligand system, the best fit for all the experimental e.p.r. spectra has been found when only the 1:1:2 Cu:sal:NH_3 mixed-ligand species is included in the model, and the value obtained for the formation constant of this species is given in Table 2. The potentiometric study of this mixed-ligand system has also shown [13] that the only ternary species formed in an appreciable amount is the 1:1:2 Cu:sal:NH_3 complex, which is attributed to the fact that the salicylate ligand adds more easily to the complex previously formed with two ammonia molecules. The characteristic e.p.r. spectrum for the 1:1:2 Cu:sal:NH_3 mixed-ligand species is included in Figure 1.

E.P.R. and Visible Study of Copper(II)*–Salicylate–Ethanolamine Systems*.—In the present work the three mixed-ligand systems containing ethanolamines have been studied by the e.p.r. and the visible spectral titration procedures. For the copper(II)–sal–mea system the best fit of the experimental spectra, both e.p.r. and visible, was obtained with a model containing the 1:1:1:0 and the 1:1:1:−1 copper(II):sal:mea: proton species (the negative value shows the number of hydrogen ions lost in the complex-forming reaction). For the copper(II)–sal–dea and –sal–tea systems the best fit was found with the model which includes the formation of one more species, *i.e.* the three different mixed-ligand species 1:1:1:0, 1:1:1:−1, and 1:1:1:−2 copper(II):sal:L:proton (L = dea or tea). The formation constants evaluated for all the mixed-ligand complexes in the three systems studied are included in Table 2, and, for these systems, the distribution plots as a

Table 2. Formation constants[a] and e.p.r. and visible spectral parameters for the complexes studied at 1.0 mol dm^{-3} ionic strength and 25 °C.

Species	$p:q:r:s$[b]	E.p.r. spectroscopy[c]			Visible spectroscopy[c]			Potentiometry[c]
		$g_{av.}$	$A_{av.}$	log β[d]	$\varepsilon_{opt.}$	$\lambda_{max.}$	log β[e]	log β
$[\mathrm{Cu(sal)}]$	1:1:0:0	2.162	60	10.0(2)	25	740	9.71(3)	9.81
$[\mathrm{Cu(sal)_2}]$	1:2:0:0	2.135	72	17.5(2)	33	660	17.24(7)	17.56
$[\mathrm{Cu(mea)}]$	1:0:1:0	2.155		4.4	24	760	4.63	4.63
$[\mathrm{Cu(mea)_2}]$	1:0:2:0	2.144		8.4	41	670	8.23	8.40
$[\mathrm{Cu(mea)_2H_{-1}}]$	1:0:2: −1	2.132	64	1.5	59	630	0.90	1.49
$[\mathrm{Cu(mea)_2H_{-2}}]$	1:0:2: −2	2.110	88	−8.1	36	590	−8.06	−8.77
$[\mathrm{Cu(dea)}]$	1:0:1:0	2.149		4.2	26	780	4.38	4.38
$[\mathrm{Cu(dea)_2}]$	1:0:2:0	2.147		7.4	37	730	8.39	8.08
$[\mathrm{Cu(dea)_2H_{-1}}]$	1:0:2: −1	2.127	58	0.2	75	680	1.39	1.4
$[\mathrm{Cu(dea)_2H_{-2}}]$	1:0:2: −2	2.114	82	−8.2	54	620	−6.97	−5.9
$[\mathrm{Cu(tea)}]$	1:0:1:0	2.149		4.3	28	800	4.37	4.3
$[\mathrm{Cu(tea)H_{-1}}]$	1:0:1: −1	2.141	61	−1.9	51	750	−1.73	−1.9
$[\mathrm{Cu(tea)H_{-2}}]$	1:0:1: −2	2.129	68	−9.7	70	710	−9.45	−9.7
$[\mathrm{Cu_2(tea)_2H_{-2}}]$	2:0:2: −2	—	—	−1.1	142	750	−1.42	−1.1
$[\mathrm{Cu_2(tea)_2H_{-3}}]$	2:0:2: −3	—	—	−8.2	154	730	−9.02	−8.2
$[\mathrm{Cu_2(tea)_2H_{-4}}]$	2:0:2: −4	—	—	−16.6	197	710	−17.02	−16.6
$[\mathrm{Cu_2(tea)_2H_{-5}}]$	2:0:2: −5	—	—		131	700	−28.50	
$[\mathrm{Cu(tea)_2H_{-2}}]$	1:0:2: −2				41	640	−8.57	
$[\mathrm{Cu(sal)(NH_3)_2}]$	1:1:2:0	2.134	74	16.3(3)				16.67
$[\mathrm{Cu(sal)(mea)}]$	1:1:1:0	2.161	61	16.1(2)	36	740	15.55(3)	13.5
$[\mathrm{Cu(sal)(mea)H_{-1}}]$	1:1:1: −1	2.139	72	9.6(3)	50	660	8.63(4)	
$[\mathrm{Cu(sal)(dea)}]$	1:1:1:0	2.166	61	16.6(6)	40	750	15.73(3)	16.7
$[\mathrm{Cu(sal)(dea)H_{-1}}]$	1:1:1: −1	2.132	69	10.3(6)	64	680	9.23(4)	9.9
$[\mathrm{Cu(sal)(dea)H_{-2}}]$	1:1:1: −2	2.120	75	2.1(3)	58	620	0.74(4)	3.4
$[\mathrm{Cu(sal)(tea)}]$	1:1:1:0	2.161	61	14.8(3)	35	750	14.50(4)	15.4
$[\mathrm{Cu(sal)(tea)H_{-1}}]$	1:1:1: −1	2.143	63	9.0(2)	42	690	8.5(1)	8.5
$[\mathrm{Cu(sal)(tea)H_{-2}}]$	1:1:1: −2	2.131	72	0.9(2)	52	690	0.4(1)	

[a] The values given correspond to the log of the formation constant for the equilibria $p\mathrm{Cu} + q\mathrm{sal} + r\mathrm{L} + s\mathrm{H} \rightleftharpoons \mathrm{Cu}_p(\mathrm{sal})_q\mathrm{L}_r\mathrm{H}_s$, where L is the ligand mea, dea, tea, or NH_3. [b] p, q, r, and s are the stoicheiometric coefficients of the species $\mathrm{Cu}_p(\mathrm{sal})_q\mathrm{L}_r\mathrm{H}_s$; negative values of s mean deprotonation of the hydroxyl groups of the ligand L. [c] For all the systems studied the potentiometric values have been obtained from the literature.[12–14] The e.p.r.[15,16] and visible spectral-values[17] included in the Table for all the binary copper(II)–L (L = mono-, di-, or tri-ethanolamine) systems were obtained previously. The four dimeric 2:2 Cu : tea species do not yield e.p.r. spectra. The protonation constants for the ligands are: salicylic acid,[12] $pK_{a_1} = 2.82$, $pK_{a_2} = 12.92$; NH_3,[13] $pK_a = 9.38$; mea,[14] $pK_a = 9.66$; dea,[14] $pK_a = 9.07$; tea,[14] $pK_a = 7.99$. [d] The value in parentheses indicates which change of the log β value induces a doubling of the error-square function (the sum of the squared differences between calculated and measured spectra, as defined in ESRDIG2[10]). [e] The value in parentheses indicates the standard deviation of log β obtained by the SQUAD treatment.[20]

function of pH for species which contain copper(II) are given in Figure 2.

Figure 3(*a*) illustrates one example of a measured and simulated spectrum and the contribution of the spectra of all species present in solution, whereas Figure 3(*b*) shows a plot of the error between the measured and simulated spectra *versus* field.

As is shown in Figures 4—6, in the three copper(II)–sal–L systems the calculated characteristic individual e.p.r. spectra of all the mixed-ligand species show a completely resolved hyperfine structure. It is also noticeable that, for each system, the loss of each hydrogen atom in the complex-forming reaction causes a shift in the e.p.r. spectrum towards higher magnetic fields. The asymmetry of the calculated e.p.r. spectra also increases with the charge on the complexes for each mixed-ligand system studied. An explanation is that in the present aqueous medium of high ionic strength the complex becomes more highly solvated on increasing its ionic charge, with the consequence of restricted rotation in solution (tumbling).[22]

The anomaly observed in the calculated e.p.r. spectra for the 1:1:1: −1 species in the copper(II)–sal–dea and –sal–tea systems (spectra which show a five-band splitting) can be attributed to the fact that, at the working pH and reagent concentration ranges employed, the 1:1:1: −1 species are always formed simultaneously with other ternary species having different extents of protonation, whose individual e.p.r. spectra must also be determined from the same data set (see distribution plots in Figure 2).

In Table 2 the values obtained using e.p.r. and visible spectroscopy are compared with those obtained from potentiometry.[14] While for the copper(II)–sal–dea system the model evaluated from the experimental e.p.r. and visible spectral data coincides with that obtained from e.m.f. data, for the copper(II)–sal–mea and –sal–tea systems the presence of an additional species through loss of an additional proton is detected at pH values higher than those studied by potentiometry. Thus, the model considered in the evaluation of the stability constants by the spectral procedures is different from that used in the e.m.f. procedure. This explains the differences observed between some of the stability constants obtained from the two procedures. The increased resolving power attained in the spectroscopic experiments can be attributed to the possibility of working in an extended pH range and also to the higher concentration ranges (in ligand and in metal ion) which are used for the e.p.r. spectroscopy.

The values of the isotropic $g_{av.}$ and $A_{av.}$ parameters, which are characteristic for the e.p.r. spectrum of each species, have been calculated for all the mixed-ligand complexes detected and are also given in Table 2, together with the characteristic parameters ($\lambda_{opt.}$ and $\varepsilon_{max.}$) from visible spectroscopy. All these values are dependent on the number and donor strength of the bonded atoms. When the values of $g_{av.}$ and $A_{av.}$ are compared along a series of complexes formed with the same ligands, a trend towards smaller values of $g_{av.}$ and higher values of $A_{av.}$ with increasing deprotonation is observed, which is related to an increasing ligand-field strength.[11,23] In visible spectra a shift

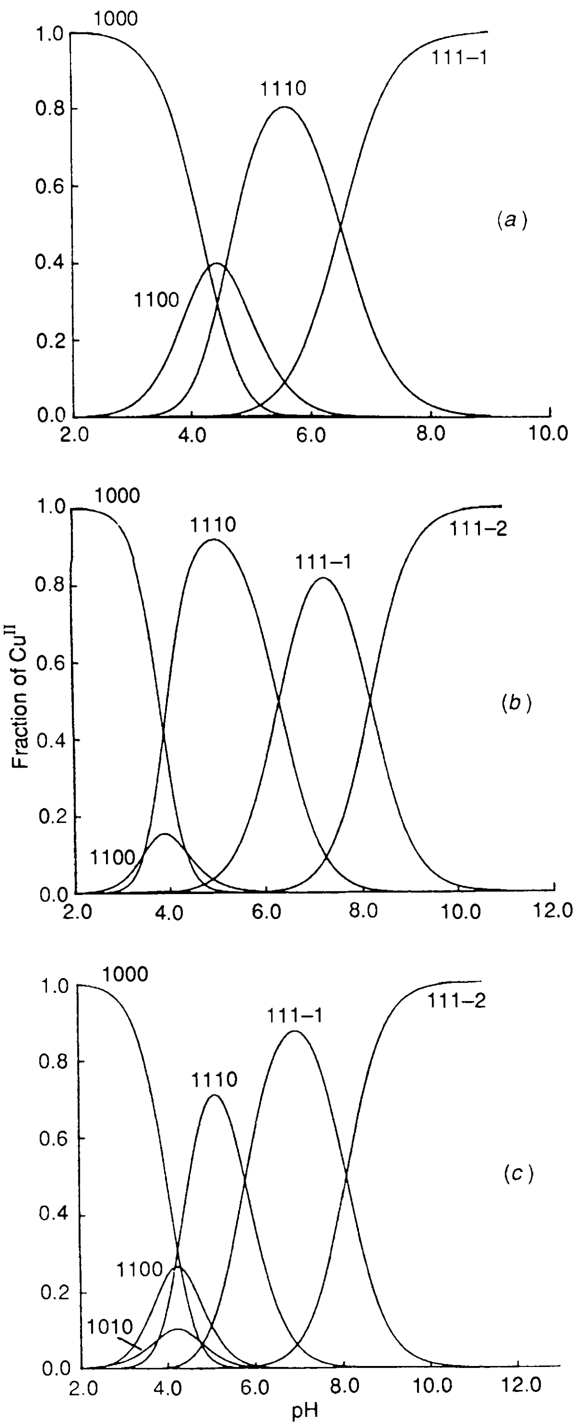

Figure 2. Distribution plots as a function of $-\log[H]$ (evaluated from the values of $\log \beta$ obtained by the e.p.r. technique) for the species which contain copper(II) in the systems (*a*) Cu–sal–mea–proton, (*b*) Cu–sal–dea–proton, (*c*) Cu–sal–tea–proton. $[Cu^{II}] = 0.01$, $[sal] = 0.05$, $[L] = 0.1$ mol l^{-1}; L = mea, dea, or tea

of the *d–d* band to shorter wavelengths is also indicative of an increasing ligand field.[24] The values of $g_{av.}$, $A_{av.}$, and $\lambda_{opt.}$ for all the mixed-ligand complexes detected are consistent with a tetragonally distorted geometry with a gradual increase in the in-plane interaction.

Although the values of $g_{av.}$, $A_{av.}$, and λ_{opt} for each mixed-ligand complex 1:1:1:0 [copper(II):sal:L:proton] are not very different from those for the binary 1:1:0:0 copper(II):sal complex, the shapes of the visible and e.p.r. spectra are significantly different (see Figures 1 and 4—6). They are also completely different from the spectra of the binary 1:0:1:0 copper(II) complexes with ethanolamines, which show a broad band similar to that of copper(II) ion in aqueous solution, shifted to higher magnetic fields.[15,16]

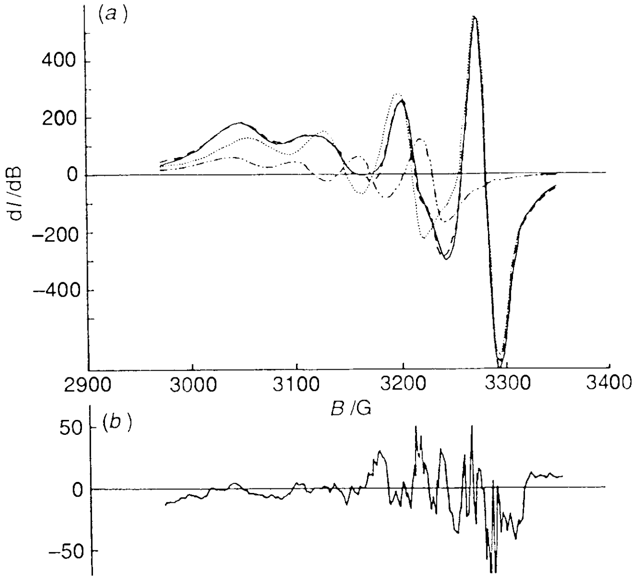

Figure 3. (*a*) Experimental (——) and calculated (– – – –) e.p.r. spectra for the copper(II)–sal–mea system at pH 6.86, together with the contributions of the spectra of the pure species 1:1:1:0 (—· · —) and 1:1:1: −1 (· · · ·). (*b*) Plot of the error between the experimental and calculated spectra *versus* field. $[Cu^{II}] = 8.52 \times 10^{-3}$, $[sal] = 4.30 \times 10^{-2}$, $[mea] = 8.11 \times 10^{-2}$ mol l^{-1}. Gain = 600

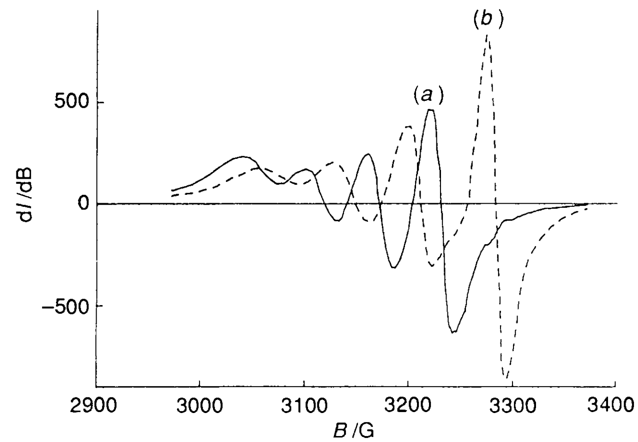

Figure 4. Calculated e.p.r. spectra for the copper(II)–sal–mea system: (*a*) and (*b*) refer to the 1:1:1:0 and 1:1:1: −1 copper(II): sal:mea:proton species, respectively. $[Cu^{II}] = 8.52 \times 10^{-3}$ mol l^{-1}, gain = 600

Conclusion

Although spectroscopic methods are usually considered less precise than potentiometric ones, they provide some additional advantages: they extend the working pH range to strongly acidic or basic solutions, and they also yield some structural information because the results obtained do depend, not only upon pH measurements at individual points of a titration, but also, and more important, upon the shape of the whole experimental spectrum at each of those points. In the study of complex equilibria with copper(II) ions visible spectroscopy is

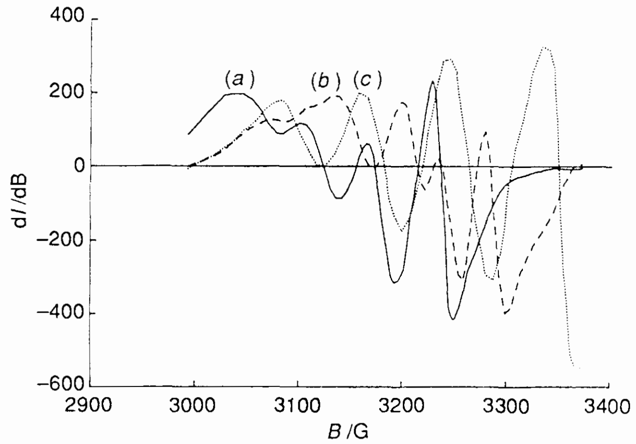

Figure 5. Calculated e.p.r. spectra in the copper(II)–sal–dea system: (*a*), (*b*), and (*c*) refer to the 1:1:1:0, 1:1:1:−1, and 1:1:1:−2 copper(II):sal:dea:proton species, respectively. $[Cu^{II}] = 8.18 \times 10^{-3}$ mol l^{-1}, gain = 425

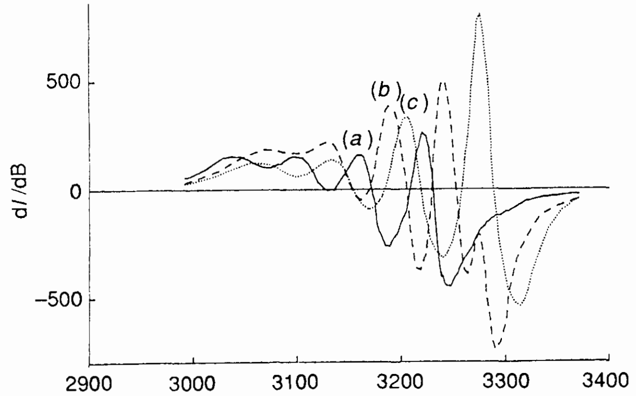

Figure 6. Calculated e.p.r. spectra in the copper(II)–sal–tea system: (*a*), (*b*), and (*c*) refer to the 1:1:1:0, 1:1:1:−1, and 1:1:1:−2 copper(II):sal:tea:proton species, respectively. $[Cu^{II}] = 1.72 \times 10^{-2}$ mol l^{-1}, gain = 370

widely used. However, e.p.r. spectroscopy can give even more information because a more detailed picture of the environment surrounding the metal ion is obtained due to specific hyperfine interactions. As the information obtained by the different techniques (potentiometry, visible spectroscopy, e.p.r. spectroscopy) is in certain aspects complementary, it is worth using these techniques simultaneously in the study of complicated systems, like the mixed-ligand systems investigated here.

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