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The Complex Formation of Cu(II) with Mono- and Di-ethanolamine in Aqueous Solution

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Abstract

The complex formation of Cu(II) with mono- and di-ethanolamine is studied by means of ESR spectroscopy. For both ligands, four complex species with the stoichiometries 110, 120, 12–1 and 12–2 are detected, and their relative stabilities are calculated. From the results obtained, deprotonation of the hydroxyl groups and formation of stable chelate rings are proposed. The similiarities and differences between the complex behaviour of the related compounds tri-ethanolamine, ammonia and β-methoxyethylamine (also studied by ESR spectroscopy) are further analysed.

Introduction

In a previous study about copper complexes with tri-ethanolamine [1], it was shown that this ligand acts as a multidentate via the N and O atoms, forming chelate rings of 5 members. Furthermore, dimerization was found of relevance at neutral and basic pH. The question arises as to whether analogous behaviour can be observed for mono- and di-ethanolamine or if it is specific for tri-ethanolamine.

The coordination chemistry of aminoalcohols with metal ions deserves further study because they play important roles in nature, for example, in hormones [2, 3] and in aminosugars [4, 5]. In solid state studies of aminoalcohol complexes of Cu(II) [6], it was shown that these ligands act as monoanionic, bidentate ligands, and that the complexes formed can be alcoxo-bridged dimers [7. 8]. In the same way, a recent study about the complexes of Cu(II) with D-glucosamine in aqueous solution showed that this ligand molecule bonds to the cupric ion via NH_2 and O^- (deprotonated hydroxyl) groups, giving rise to stable chelate complexes [5].

Ethanolamines can be considered as suitable models to measure the tendency to amino–alcoxo chelate formation. Difficulties arise because in aqueous solution at neutral pH, the hydrolysis and precipitation of copper hydroxide disturbs the equilibria studied. In the study of copper–amine complexes, it is a common procedure [9] to carry out the determinations with a large excess of ligand. Under these conditions, the several complexation steps are displayed without interruptions (precipitation), allowing the determination of the stepwise stability constants. However, a clear disadvantage of this procedure when it is applied to multidentate ligands is that at large excess of ligand, the equilibria involving the release of the same number of protons per metal ion become undistinguishable from pH measurements, preventing the direct determination of the number of bonded ligand molecules. An additional insufficiency of potentiometric methods (pH) is that deprotonation of the ligand in the complexes is analogous to deprotonation of the bonded water molecules (hydrolysis). Some authors [10–13] have assumed that in aqueous solution the hydroxyl groups of aminoalcohols can only be deprotonated at high pH values, acting therefore as very weak bonding moieties. But, on the other hand, the deprotonation of the hydroxyl groups has been proved [5, 13, 14] to occur even at neutral pH, when chelate ring formation is enabled.

In the present work, the complex formation with mono- and di-ethanolamine is studied by means of a recently introduced ESR titration method [15] at 25 °C and 1.0 M ionic strength. For the purpose of comparison, the Cu(II) interaction with ammonia and β-methoxyethylamine has also been studied with the same method. Additionally, the anisotropic ESR and visible absorption spectra of some of the complexes were measured.

Experimental

Materials

NaOH, HNO_3 (Titrisol, Merck); $NaNO_3$, NH_4NO_3, $Cu(NO_3)_2 \cdot 3H_2O$ (Merck, p.a. grade); mono-ethanol-

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amine, di-ethanolamine and β-methoxyethylamine (Fluka, puriss.) were used without further purification. All the solutions were prepared using CO_2-free deionized water. The ionic strength was kept at 1.0 M sodium nitrate. Stock solutions of copper(II) were standardized by iodometric titration. Stock solutions of 1.0 M concentration in mono- and di-ethanolammonium and β-methoxyethylammonium nitrate were prepared by neutralization of the weighed amounts of the ligands with the stoichiometric amounts of a stock 2.0 M HNO_3 solution.

Apparatus

ESR spectra at 25 °C were recorded on a VARIAN E 104 spectrometer (calibrated microwave 9.09 GHz) in tubes of only 1 mm diameter (Wilmad, Cat. Nr. 800), using a 100 kHz field modulation; low temperature ESR spectra (−60 °C) were recorded using a Varian Variable Temperature Controller and the same E-104 Varian spectrometer. Visible absorption spectra were recorded on a Unicam 1800 spectrophotometer and a Beckman Acta M-VII spectrophotometer. pH measurements were performed with a Schott pH-meter CG 803 and a combined Ross pH electrode (Orion 81-02).

ESR Determinations

The ESR titration method was described in ref. 15. The numerical analysis of the ESR spectra was made with the FORTRAN program described in ref. 15. This procedure provides the simultaneous determination of the stability constants of the formed species and of their ESR spectra [1, 16–21].

For di-ethanolamine, 3 titrations with a total set of 44 spectra plus five spectra of basic solutions which contain low ratios of ligand to metal ion (between 2 and 3) were analysed. For mono-ethanolamine, 2 titrations with a total set of 37 spectra plus five ESR spectra of basic solutions which contained low concentration ratios of ligand to metal ion (between 4 and 2) were analysed. For β-methoxyethylamine and ammonia, 2 titrations with 40 and 41 spectra were analysed, respectively.

Results and Discussion

The Number and Nature of the Species in Solution

The determination of the number, nature and stability of the species formed in solution is usually achieved simultaneously, provided that the experimental determinations can be carried out over widespread ratios and concentrations of ligand and metal ion. Unfortunately (see 'Introduction') this is not the case for mono- and di-ethanolamine complexation studies. High ratios of ligand to metal ion should be used to avoid copper hydroxide precipitation at neutral pH. However, at basic pH, when the ratio of ligand to metal ion is higher than two, copper hydroxide redissolves. For tri-ethanolamine, this was observed previously at ratios equal to or higher than one, whereas for ammonia and β-methoxyethylamine much higher ratios should be used. At high pH values, when small amounts of copper are added to solutions which contain mono- and di-ethanolamine in excess (with their amino groups deprotonated), a release of two protons per atom of Cu(II) is observed. These facts are consistent in both cases with the formation of species containing two ligand molecules and having suffered two further deprotonations, which should come from the bonded hydroxyl groups of the ligand or from the bonded water molecules. The latter is less probable due to the high stability of the species formed (see below).

From the numerical analysis of the ESR spectra, four species are formed in the pH range 3–12. As the total number of protons released in the titration studies is also four, under the assumption of stepwise complexation, the proposed species for mono- and di-ethanolamine complexes are* 110, 120, 12–1, 12–2. The results are also in agreement with the obtained ESR and Visible species spectra (see below).

As in the tri-ethanolamine complexes [1], the ^1H NMR spectra of solutions which contain the ligand and small amounts of the metal ion showed strong broadening of the two peaks corresponding to both methylene groups of the ligand. This is in agreement with the metal ion being attached to both terminal amino and hydroxyl groups and, hence, proving chelation.

ESR Titration Determinations

The same patterns of shape changes of the ESR spectra have been observed for mono- and di-ethanolamine complex formation. At acidic pH, the spectra resemble the Cu(II) ESR spectra at the same background. As the pH increases, the ESR spectra change with a shift to higher fields and an increase in resolution of the hyperfine interaction with the Cu nucleus (4 lines, since $I = 3/2$). No decreasing intensity of the experimental spectra was observed over the whole pH range (3–12), showing that in this case no dimers are formed, in contrast with Cu(II) complexation with tri-ethanolamine [1].

ESR spectra of Cu(II)–β-methoxyethylamine solutions display patterns similar to those of the ESR spectra with mono- and di-ethanolamine solutions up to pH 7.5. Above this pH, the ESR spectra become less resolved and not so strongly shifted to higher fields. Only at high pH is the resolution of the hyperfine interaction finally achieved. ESR spectra of Cu(II) ammonia solutions are the broadest and least resolved of all those studied here, although the trends

*pqr refers the stoichiometry of the complex $(Cu)_p(L)_q(H)_r$, where L is the ligand; charges are omitted; negative values of r refer to hydroxyl deprotonation.

observed on increasing pH are similar: a shift to higher fields and a small but appreciable increase in resolution of the hyperfine interaction.

The set of species with the stability constants obtained in the numerical treatment of the ESR spectra [15] are given in Table I.

TABLE I. Overall Summary of Stability Constants at 25 °C and 1.0 M Ionic Strength[a]

pqr[b]	mea	dea	tea[c]	NH_3[d]	β-mea
101[e]	9.66	9.07	7.99	9.38	9.62
110	4.4	4.2	4.4	4.1	4.4
120	8.4	7.4	–	7.6	8.5
130	–	–	–	10.3	10.4
140	–	–	–	12.4	–
12–1	1.5	0.2	–	–	–
12–2	–8.1	–8.2	–	–	–

[a]The values given correspond to the log of the formation constant for the equilibria: $p\mathrm{Cu(II)} + q\mathrm{L} + r\mathrm{H} = (\mathrm{Cu})_p(\mathrm{L})_q(\mathrm{H})_r$ where L is the ligand mea = mono-ethanolamine, dea = di-ethanolamine, tea = tri-ethanolamine and β-mea = β-methoxyethylamine. [b]*pqr* are the stoichiometric coefficients of the species $(\mathrm{Cu})_p(\mathrm{L})_q(\mathrm{H})_r$; negative values of *r* mean deprotonation of the hydroxyl groups of the ligand. [c]Values obtained in a previous work [1]; the other species found were (with the log of their formation constants in parenthesis) 11–1 (–1.9), 11–2 (–9.7), 22–2 (–1.1), 22–3 (–8.2) 22–4 (–16.6). [d]Values obtained potentiometrically [32]. [e]Values obtained potentiometrically at 25 °C and 1.0 M $HLNO_3$ (L = mea, dea, tea, NH_3 or β-mea).

In Figs. 1, 2 and 3 the species distribution of the mono-, di-ethanolamine and β-methoxyethylamine complexes are given.

The stability constant for the formation of the first complex, 110, is similar for the four systems studied and for tri-ethanolamine [1] (also included in Table I), although the protonation constant of the ligands – and therefore the Lewis base strength and

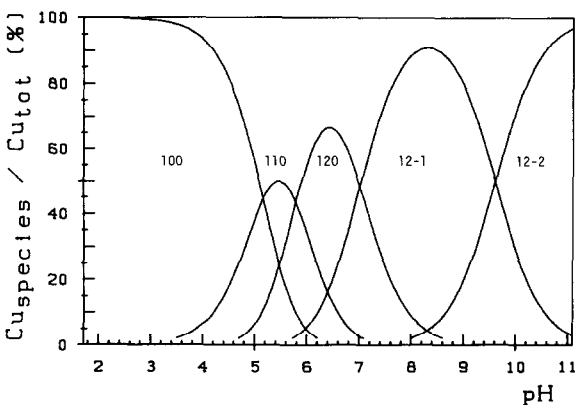

Fig. 1. Distribution of species which contain Cu(II) as a function of pH: 0.01 M Cu(II) + 1.0 M mono-ethanolamine.

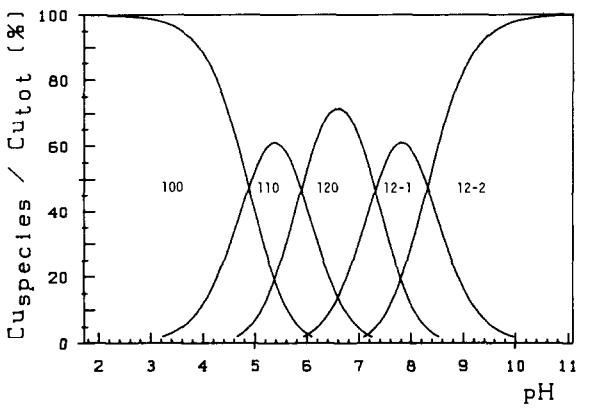

Fig. 2. Distribution of species which contain Cu(II) as a function of pH: 0.01 M Cu(II) + 1.0 M di-ethanolamine.

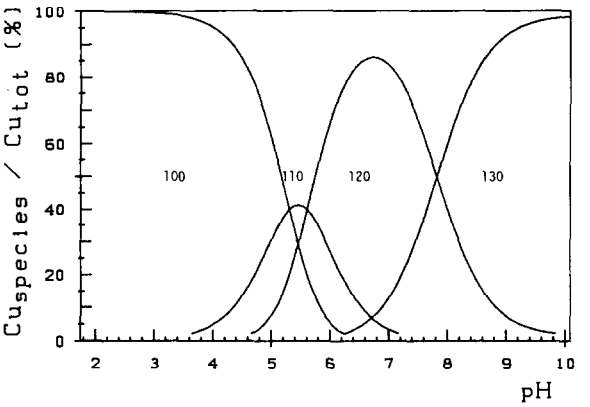

Fig. 3. Distribution of species which contain Cu(II) as a function of pH: 0.01 M Cu(II) + 1.0 M β-methoxyethylamine.

the sigma donor ability of the amino group – are different. Consequently, it should be concluded that other factors contribute to the observed stabilities of the 110 complexes. In particular, an enhancement of complex formation owing to the interaction of the hydroxyl groups is proposed.

The stability of the second complex, 120, which involves the interaction of a second molecule of ligand, is higher for mono-ethanolamine and β-methoxyethylamine than for ammonia complexes, showing that there is no steric hindrance in the formation of such complexes. The complex with di-ethanolamine has somewhat less stability, but the smaller donor strength of its amino group (its protonation constant is a little lower) should be considered in this case.

The formation of the third complex with β-methoxyethylamine, 310, is sterically hindered compared to the formation of the same complex with ammonia, as can be seen from their stepwise stability constants (log K_3 is 1.9 and 2.7, respectively). Furthermore, no formation of a fourth species is

observed for β-methoxyethylamine below pH 11. In contrast, mono- and di-ethanolamine form a third and fourth complex which are not hindered, because they do not involve the entrance of a third molecule of the ligand in the coordination sphere of the metal ion, but, rather, the deprotonation of the already-bonded ligand molecules leading to the complexes 12–1 and 12–2. The first deprotonation seems to be of the same strength for mono- and di-ethanolamine, while the second deprotonation seems to be a little stronger for di-ethanolamine, although definite conclusions cannot be made yet. The consideration of the formation of the species 310 for mono-ethanolamine would have given an unreasonably high value for its stepwise stability constant, higher than for ammonia, and much higher than for β-methoxyethyl-amine. Moreover, for this complex one cannot expect any extra stabilization from a new hydroxyl group, since it could not be involved in the square plane of strong interaction with the metal ion (see below).

Also of interest is the question of why the Cu(II) complexes with tri-ethanolamine dimerize, whereas the complexes with mono- and di-ethanolamine do not. In tri-ethanolamine it was shown [1] that the dimerization involves the formation of two consecutive oxygen bridges between the two metal ions, each of them attached to both oxygen atoms. This arrangement is not possible for di- and mono-ethanolamine because the copper ion is complexed by two molecules of the ligand before the deprotonation of the attached hydroxyl groups takes place, therefore preventing the formation of the two consecutive oxygen bridges present in tri-ethanolamine dimers. Consequently, Cu(II) complexation with mono- and di-ethanolamine gives rise to different species than with tri-ethanolamine.

ESR and Vis Absorption Species Spectra

In Figs. 4, 5 and 6 the ESR species spectra of the Cu(II) complexes with mono-ethanolamine, di-ethanolamine and β-methoxyethylamine are shown. These spectra were calculated from the analysis of the ESR spectra obtained in the experimental titrations with the procedure described previously.

In Table II are given: (a) the ESR isotropic parameters [22] (g_{av}, and A_{av}) of the studied complexes; the value of A_{av} is given only for the complexes in which the hyperfine structure is well resolved; (b) the ESR anisotropic $g_{\parallel}$ and $A_{\parallel}$ parameters for the complexes obtained at high pH values, when they are the only complex species present in solution and, therefore, the assignment is unambiguous; (c) the pH values of the solutions where the considered species are in maximal concentration; and (d) the absorption spectra parameters λ_{max} and ϵ of the solutions at the pH values of maximal concentration of some complexes.

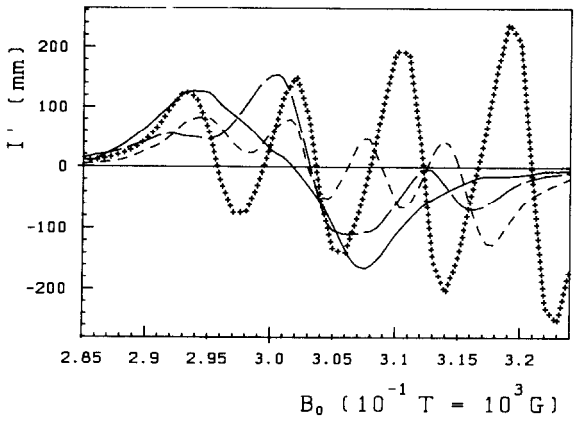

Fig. 4. ESR spectra of Cu(II)–mono-ethanolamine complexes. Species: 110 (——), 120 (— —), 12–1 (– – –), 12–2 (+++++).

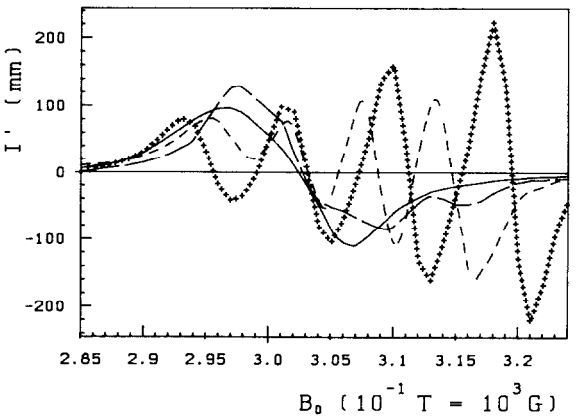

Fig. 5. ESR spectra of Cu(II)–di-ethanolamine complexes. Species: 110 (——), 120 (— —), 12–1 (– – –), 12–2 (+++++).

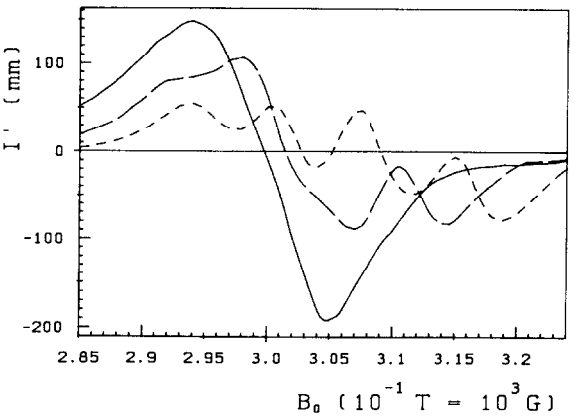

Fig. 6. ESR spectra of Cu(II)–β-methoxyethylamine complexes. Species: 110 (——), 120 (— —), 130 (– – –).

From the values of Table II and the shape of the ESR species spectra of Figs. 4–6, the following considerations can be outlined:

TABLE II. ESR Spectra and Visible Absorption Parameters of the Cu(II) Complexes

Species[a]	g_{av}[b]	A_{av}[b]	$g_{\parallel}$[c]	$A_{\parallel}$[c]	pH[d]	λ_{max}[e]	ϵ[e]
mea							
110	2.155				5.4	730	27
120	2.144				6.4		
12–1	2.132	64			8.4	635	58
12–2	2.110	88	2.22	195	10–12	590	44
dea							
110	2.149				5.3	735	36
120	2.147				6.6		
12–1	2.127	58			7.8	665	70
12–2	2.114	82	2.24	190	10–12	625	63
tea							
110	2.149				4.7	770	
11–1	2.141	61			6.5		
11–2	2.129	68	2.24	175	9–11	705	
β-mea							
110	2.168				5.4	730	
120	2.157				6.8		
130	2.129	72	2.23	180	9–11	624	64
NH_3							
110	2.168				5.5	730	24
120					6.2	680	32
130					7.0	620	43
140	2.123	80			9–11	600	60
Cu(II)aq.							
100	2.190					810	12

[a]Same species notation as in Table I. [b]Values obtained graphically from the ESR solution species spectra (Figs. 4, 5 and 6, and ref. 1) at 25 °C; A_{av} is given in gauss. [c]Values obtained graphically from the ESR frozen solutions at −60 °C (see Figs. 6 and 7); $A_{\parallel}$ is given in gauss. [d]pH values where the concentration of the considered species is maximal. [e]Wavelength λ_{max} (in nanometers) of the absorption maximum, and molar absorptivity ϵ (in mol^{-1} l cm^{-1}) at this maximum for a solution at the given pH.

(1) For all the studied systems, only the room temperature spectra of the higher complexes of each system display a shape with a completely resolved hyperfine structure. The spectra of all 110 complexes have a broad shape similar to the spectra of Cu(II) in aqueous solution, but shifted to higher fields. Formation of the second complex, 120, gives a first split of the high field part of the spectra. In the case of tri-ethanolamine [1] the hyperfine structure was already resolved according to the completely different nature of the species formed, 11–1, with a hydroxyl group already deprotonated, forming a chelate. The third and fourth species have in all the cases the hyperfine structure resolved with four lines, consistent with the interaction of an unpaired electron with a copper nucleus ($I = 3/2$), [22, 23].

(2) The values of g_{av} and A_{av} are dependent on the number and donor strength of the bonded atoms [22–27]. Smaller values of g_{av} and higher values of A_{av} are obtained with increasing ligand field. These are the trends when the values of g_{av} and A_{av} of Table II are compared between the complexes formed with the same ligand. The comparison of the g_{av} and A_{av} values between complexes formed with different ligands is more difficult, probably because opposing factors are involved. The g_{av} values for the 110 complexes with mono-, di- and tri-ethanolamine are lower than the corresponding values for NH_3 and β-methoxyethylamine, although the stability of the complexes is similar (see above). This fact must be a consequence of the coordination of the hydroxyl groups in ethanolamines. The g_{av} values of the second complex, 120, are not very precise due to the structureless spectrum of the corresponding species and because of the overlapping of its shape with the preceding and subsequent species spectra. The values of g_{av} given in Table II for this complex are, therefore, only approximate. (This is the case especially for the complex with di-ethanolamine, where a considerably high value, rather close to the corresponding 110 complex, was obtained.) Although the nature of the third species is different for mono- and di-ethanolamine complexes with regard to ammonia and β-methoxyethylamine, their g_{av} values are similar. This similarity reflects the fact that the bonding of a new molecule of the ligand via the N atom and the deprotonation and chelation of an already attached ligand molecule via the O atom contribute similarly to the g value, and that both processes are difficult to distinguish from the observation of the g_{av} values. On the contrary, however, the formation of the fourth species gives a g_{av} value for the 12–2 complex with mono- and di-ethanolamine lower than that for the 410 complex with ammonia, an observation that is also related to the changes in the absorption spectra (see below). As it has been pointed out by other authors, the values of A_{av} [25] are difficult to correlate, owing to the asymmetry of the ESR spectra. However, a higher A_{av} value is observed for mono-ethanolamine than for di-ethanolamine. This fact is in contradiction with the observed increase of A_{av} values with higher substitution in amines [27], showing again the specifity of the interaction of ethanolamines with Cu(II).

(3) The anisotropic $g_{\parallel}$ values show that the higher complexes are square-planar, tetragonally-distorted structures ($g_{\parallel} > g_{\perp}$; see Fig. 7 for mono-ethanolamine) [22, 25]. ESR spectra of frozen solutions gave further information about the structure of the complexes. In the case of Cu(II) complexes

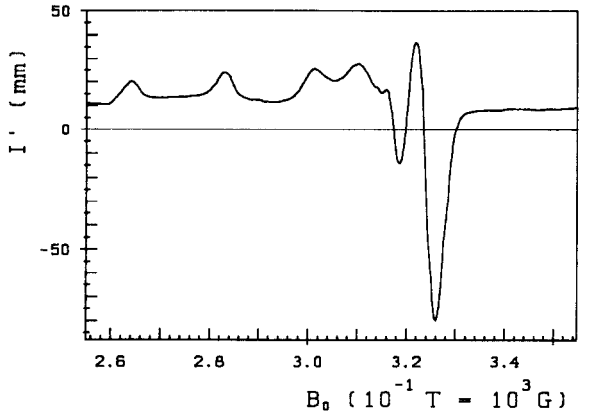

Fig. 7. ESR spectrum of 0.01 M Cu(II) + 0.1 M mono-ethanolamine solution, pH 11.2 (−60 °C).

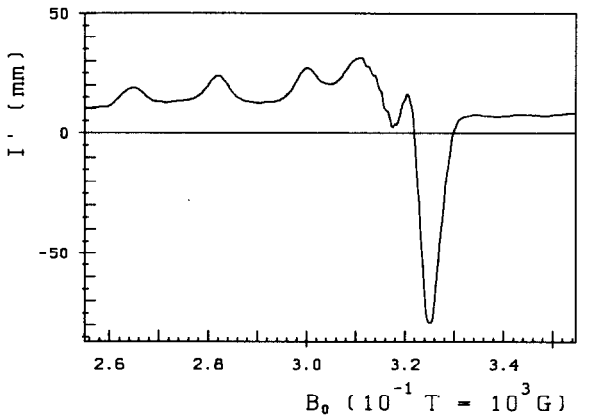

Fig. 8. ESR spectrum of 0.005 M Cu(II) + 0.95 M β-methoxy-ethylamine solution, pH 11.8 (−60 °C).

with β-methoxyethylamine (Fig. 8), a relatively high number of splittings appeared in the high field part of the spectra which should come from the hyperfine interaction with the three N atoms of the ligand. In the case of mono-ethanolamine and di-ethanolamine, the number of splittings is considerably lower, in agreement with the lower number of N-bonded atoms. Nevertheless, precise measurement could not be achieved because the spectra were not completely resolved. Although the room temperature spectra did not show any hyperfine interaction, for mono-ethanolamine this was partially seen at −10 °C in the solution spectrum (Fig. 9).

(4) For the first complex, 110, where there are no ambiguities about which is the strongly bonded atom, it is seen that the maximum of the visible absorption band is similar for Cu(II) complexes with either NH_3, mono-ethanolamine, or β-methoxy-ethylamine, due to the similar donor strength of the N atoms of these ligands. The maximum absorption for the first complex with tri-ethanolamine appears at higher wavelengths in agreement with the lower

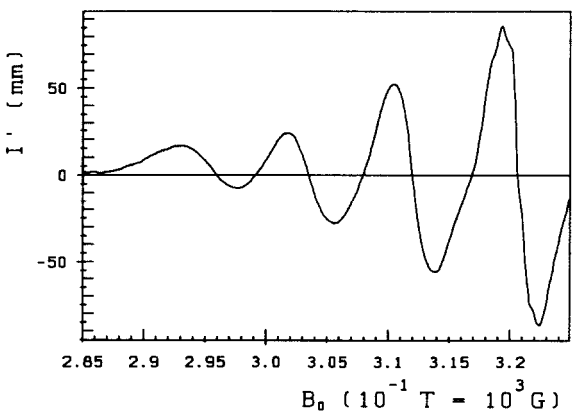

Fig. 9. ESR spectrum of 0.01 M Cu(II) + 0.1 M mono-ethanolamine solution, pH 11.2 (−10 °C).

donor strength of its N atom (log K^H = 8.00 [1]). Consequently the relatively high stability observed in the formation of the complex with tri-ethanolamine should come from an appreciable chelate effect of the hydroxyl groups. This effect can also have a small contribution in the case of mono- and di-ethanolamine, but not more than one hydroxyl group should now be involved.

The deprotonation of the hydroxyl groups of tri-ethanolamine occurs simultaneously with the dimerization of the species formed [1]. The absorption band appears at considerably higher wavelengths than for the complexes with the other ligands. The formation of the second complex with ammonia, mono-ethanolamine and β-methoxyethylamine overlaps with the formation of the first and third complex species, preventing the direct determination of the absorption maxima of their species spectra. It seems, however, that the second complex, 120, for ammonia, mono-ethanolamine and β-methoxyethylamine has the absorption maximum at similar wavelengths. The di-ethanolamine complex absorbs at somewhat higher wavelengths, but this effect should be related to the lower donor strength of its N atom (log K^H 9.07, Table I), here more distinctly observed than in the formation of the first complex. In order to obtain the visible absorption spectra of all the species present in the systems studied here, numerical analysis of the spectra should be performed; some work is planned for this purpose.

Formation of the third complex follows a different complexation path for mono-ethanolamine than for β-methoxyethylamine and ammonia. However, this difference is only slightly distinguishable from the visible absorption spectra, since the absorption maximum is not shifted enough to conclude that there are different donor groups in the complex.

The formation of the fourth complex is the step which reflects a clear difference between mono- and di-ethanolamine on one hand, and ammonia and

β-methoxyethylamine (the latter does not even form a fourth species) on the other hand. The intensity of the spectra decreases considerably, and the shift produced to shorter wavelengths (40–50 nm) is larger than for ammonia. In both complexes the absorption band has a similar shape with a shoulder at 510 nm for mono-ethanolamine and at 530 nm for di-ethanolamine, the spectra being the resultant of two rather separate bands. From the spectrochemical series [30] it is usually assumed that the bonding of a N atom produces a splitting of the d metal orbitals higher than the one produced by the bonding of a negatively charged O atom, and consequently that a N_4 chromophore should absorb at shorter wavelengths than a N_2O_2 chromophore [31]. Ammonia cannot be strictly compared with mono-ethanolamine, because of the different nature of both molecules. But the fact that the 12–2 complex with mono-ethanolamine absorbs at lower wavelengths (higher energy) than the corresponding 410 complex for ammonia gives an additional proof of the strength of the Cu(II) mono-ethanolamine interaction, and therefore, of the assumption that chelation takes place.

Conclusions

In accordance with the results previously obtained for the copper(II) interaction with tri-ethanolamine [1], mono- and di-ethanolamine act as bidentate ligands via the N and O atoms, forming stable five-membered chelate rings. However, while only one molecule of tri-ethanolamine is bonded to Cu(II), mono- and di-ethanolamine form complex species which have two ligand molecules per Cu(II). As a consequence, and also in contrast to tri-ethanolamine, mono- and di-ethanolamine do not form dimer species with Cu(II).

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