

The Complex Formation of Cu(II) with Triethanolamine in Aqueous Solution

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Abstract

The complex formation of Cu(II) ion with triethanolamine in aqueous solution was studied by means of ESR spectroscopy. All the detected species have a ligand-to-metal ratio of one to one. Dimeric species have been found at neutral and basic pH. Values for the stability constants are given*, $\log \beta_{110} = 4.3$, $\log \beta_{11-1} = -1.9$, $\log \beta_{11-2} = -9.7$, $\log \beta_{22-2} = -1.1$, $\log \beta_{22-3} = -8.2$, $\log \beta_{22-4} = -16.2$, and compared with those obtained in a potentiometric study. Deprotonation of hydroxyl groups of the ligand and formation of chelates is proposed from the results of ^1H NMR spectroscopy.

Introduction

As a part of a more general study on mixed ligand complexes of Cu(II) ion with salicylate ion as first ligand and various nitrogen bases as a second ligand [1, 2], a study of copper complexes with triethanolamine was initiated.

There is no agreement about this system in previous studies. Three kinds of complexation models have been proposed: **amination**, where one or more molecules of the ligand are bound to the metal ion only by the nitrogen atom [3–5]; **hydrolysis**, where the complexation involves the deprotonation of the water molecules in the coordination sphere of the metal ion [6–9]; and **chelation**, where the complexation involves the deprotonation of the hydroxyl groups of the triethanolamine, forming a chelate [10]. In the second case, formation of dimers and other polynuclear species has been proposed [6, 7].

From these previous studies, the following conclusions can be drawn:

* β_{pqr} refers to the global formation constant of the equilibrium: $p \text{ Cu(II)} + q \text{ tea} \pm r \text{ H} = (\text{Cu})_p(\text{tea})_q(\text{H})_r$, tea is triethanolamine.

(1) The experimental data could not be interpreted with the formation of amino-complexes; (2) on the basis of potentiometric, polarographic, conductimetric and spectrophotometric studies it seems difficult to establish a satisfactory model of complexation. Although dimeric or other kinds of polynuclear complexes have been proposed by some authors, their existence was difficult to prove with these methods.

The recently introduced ESR technique for the determination of complex equilibria (refs. 11–16) proved to be a useful tool, therefore, to obtain conclusive data for a satisfactory over-all description of this system.

Experimental

Materials and Samples

(a) ESR Experiments

Copper was used as $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (MERCK p.a.). Stock solutions were standardized by iodometric titration. Triethanolamine was obtained from FLUKA (puriss.) and used without further purification. All solutions were prepared using CO_2 -free distilled water. Acid (HNO_3) and base (NaOH) were prepared using Titrisol products (MERCK). The ionic strength of the solutions was kept at 1.0 M potassium nitrate (MERCK p.a.). 72 solutions were prepared for recording ESR spectra and further analysis. These solutions came from (a) three titration experiments with 19, 23 and 17 recorded spectra respectively; (b) two 'dilution' experiments with 4 and 5 recorded spectra; and (c) one 'decreasing ratio' experiment with 2 recorded spectra (see method). The covered range of constituent concentration was: pH 2–10; copper concentration 0.002–0.080 M; triethanolamine concentration 0.005–0.881 M.

(b) ^1H NMR Experiments

Line broadening experiments were performed with solutions containing different amounts of Cu(II) ion by varying the pD. The concentration of the ligand in D_2O (100%; obtained from EGA-Chemie) was kept at 0.5 M in all experiments. Solutions at different ligand to metal-ion ratios (50, 100 and 500) were obtained by dissolving varying amounts of metal salt (CuCl_2), dried at 100°C , MERCK p.a. in the previously prepared ligand solution. The pD was adjusted with concentrated NaOD or DCl (99%; obtained from STOHLER ISOTOPE CHEMICALS).

(c) Potentiometric Experiments

Materials for potentiometric determinations were the same as in the ESR experiments. More experimental details about the potentiometric determinations will be given separately [17].

Apparatus

The spectra were recorded on a VARIAN E 104 spectrometer (calibrated microwave 9.097 GHz) in tubes of only 1 mm diameter (Wilmad Cat. Nr. 800). Further details are given in ref. 11. The ^1H NMR spectra were recorded on a VARIAN EM-360-L 60 MHz spectrometer with a sweep width of 5 ppm and a sweep time of 5 min. Potentiometric apparatus is described in ref. 1.

Methods

ESR Determinations

The ESR titration method was used as described in detail in refs. 11–16.

In this work, special effort has been made in the use of the technique to investigate dimer complexes. Small complex molecules containing two copper ions show a zero ESR spectrum because of the copper–copper interaction. As has been pointed out, the formation of dimers is usually indicated by a loss of intensity of experimental spectra [11, 12, 18, 19]. Consequently, a twofold integration of the ESR signal should give a direct means of measuring the amount of ESR detectable complex molecules with one metal-ion [12]. Although the calculation of the double integral cannot be very accurate because of the experimental errors, it has been used here in two ways: first, in order to see if the assumption that only mononuclear species are formed gives unreliable (too low) values for the double integral of the ESR spectra; second, to estimate values for the stability constants of the species which are formed at the end of the titrations, where the species-spectra and the value of the stability constants cannot be simultaneously obtained with accuracy from the shape of the spectra only.

The ESR titration method [11–17] was extended by including ‘dilution’ experiments. These experi-

ments consist of the recording of the ESR spectra of solutions containing successively decreasing concentrations of metal ion and ligand, at a previously chosen pH value. In the case of doubled metal ion concentration, for instance, nearly double the intensity of the ESR signal should be observed if no polynuclear species were present. In a third kind of experiment, the ratio of ligand-to-metal ion was changed from ten to one, and the experimental spectrum at basic pH was recorded. No precipitation was obtained until the ratio ligand to metal ion decreased below one.

ESR spectra of the three series of experiments (titration, dilution and ratio decreasing experiments) were included in the same numerical analysis of data. The FORTRAN program [11] for the calculations was only modified to handle ESR spectra obtained at different receiver gains of the spectrometer, to take into account the different intensity scale of the recorded spectra in the calculation of the error square function.

^1H NMR Determinations

^1H NMR spectroscopy has been used to assign the coordination sites for the complexation of Cu(II). Paramagnetic ions are known to cause broadening of NMR lines [20–24] because of their influence on the relaxation processes. Two objections have been made to the use of line broadening experiments to determine bonding sites [25, 26]. First, the very different conditions under which these experiments are usually carried out in contrast to those dominating in thermodynamic determinations, and second, the fact that the spin–spin relaxation time (which causes in this case the broadening of the NMR lines) is not entirely due to the distance dependence, but also to the scalar coupling constant between the metal ion and the affected nucleus.

In the case of our investigations these problems seem to be of minor importance because the experimental conditions in the stability constant determinations of the present work are identical with the conditions of the ^1H NMR experiments, and because it is well established that the coupling constant falls off with increasing distance along an aliphatic chain [26, 27] and can be used, therefore, to determine the site of Cu(II) binding to triethanolamine.

Potentiometric Determinations

The potentiometric method was used described in detail in ref. 1.

Results and Discussion

ESR Spectroscopy of Cu(II)–triethanolamine Solutions

Figure 1 shows some representative spectra of Cu(II)–triethanolamine solutions at different pH

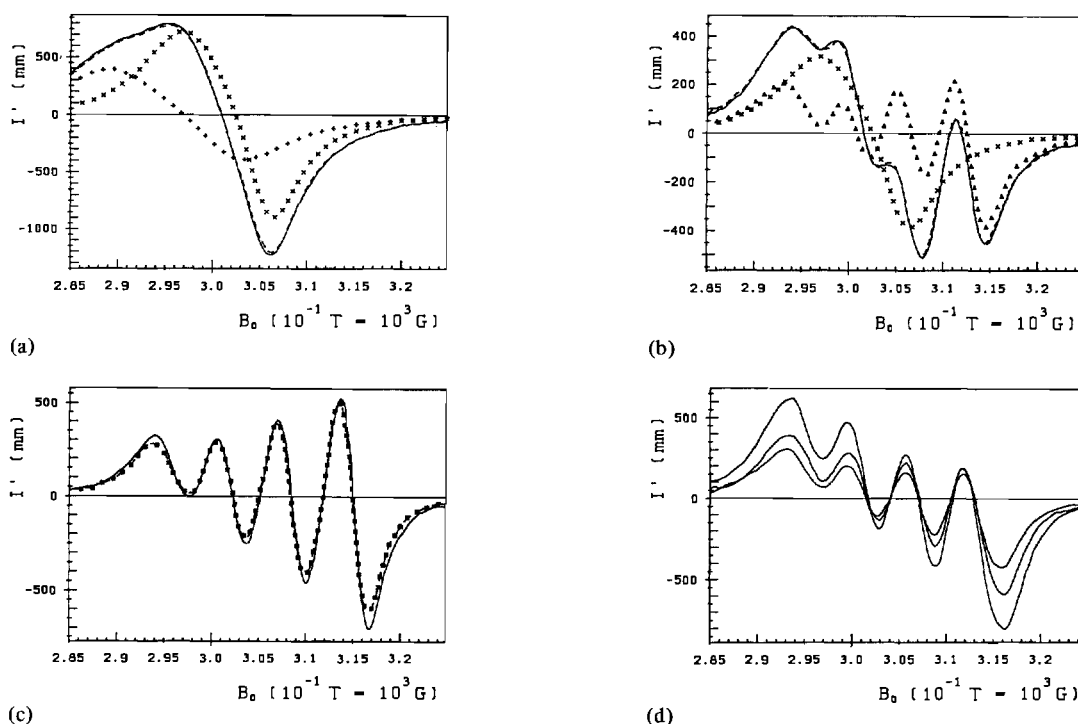


Fig. 1. Some representative ESR spectra: experimental (—), calculated (-----), contribution of species 010 (++++), contribution of species 110 (XXXX), contribution of species 11 - 1 (ΔΔΔΔ), contribution of species 11 - 2 (□□□□). Values of pH, concentration of Cu(II) ion and triethanolamine in moles per litre (in parentheses, ligand-to-metal ratio): (a) 3.69, 0.0086, 0.837 (97.3); (b) 6.20, 0.0075, 0.0411 (5.48); (c) 9.70, 0.0111, 0.0150 (1.35); (d) from up to down 7.46, 0.0515, 0.080 (1.51); 7.50, 0.0257, 0.040 (1.51); 7.54, 0.0129, 0.020 (1.51).

values. The spectra in very acidic media are similar to the spectra of Cu(II) solutions at the same ionic background. Although the experimental solutions were obtained at very different ratios of ligand-to-metal ion, the same characteristic patterns in the shapes of the ESR spectra were observed when the pH was changed. This fact reveals that the same kind of complexes are formed in all cases. At neutral and basic pH the intensity of the experimental spectra decreases considerably. This is interpreted as the formation of stable complexes with more than one copper(II) ion (see method). Spectra of solutions in the dilution experiments (Fig. 1d) reveal clearly the existence of these species.

The set of proposed species, together with the value for their stability constants obtained in the numerical treatment of the data, are shown in Table I. These results have been obtained considering, (1) the best fit for all the experimental spectra within our methodical framework [12]; (2) the assumption of zero spectra for all dimeric species; and (3) sufficient accuracy of the values for the double integral of the species spectra. This latter point is mainly important in the estimation of stability constants of the monomer and dimer formed at high pH (species 11 - 2 and 22 - 4 in Table I).

TABLE I. Results of the Numerical Treatment of the ESR Data in the Cu(II)-triethanolamine System.^a

Species ^b pqr	log of formation constant ^{c,d}
110	4.3(2)
11 - 1	-1.9(4)
11 - 2	-9.7(6)
22 - 2	-1.1(3)
22 - 3	-8.2(3)
22 - 4	-16.6(2)

^aThe value of the protonation constant of the amino group, $\log K = 7.99$, was taken from a potentiometric study [17].

^bpqr refers to the species $(\text{Cu})_p(\text{tea})_q(\text{H})_r$, where tea is triethanolamine; negative values of r mean here the deprotonation of the ligand (see text). ^cValues for the log of the formation constant: $p(\text{Cu(II)}) + q(\text{tea}) + r(\text{H}) = (\text{Cu})_p(\text{tea})_q(\text{H})_r$ at 25 °C and $I = 1.0 \text{ M}$ (I is the ionic strength).

^dValues in parentheses are the deviations in the last figure of the log of the formation constants which cause a double value of the error square function (see ref. 11).

No other set of species could explain the experimental data. Models which imply only monomer species cannot explain the decreasing intensity of

the experimental spectra, mainly in the case of the dilution experiments. Moreover, in the case of only monomer species, the spectra of the pure species 11 - 1 and 11 - 2 have very low values of their double integral. There is no possibility of explaining the experimental data with species of higher amination than the complex 110. The value of the standard deviation of the numerical fit obtained with the set of species and stability constants of Table I is within the expected range of experimental accuracy. This is most remarkable when one considers the extremely different concentrations of the constituents in the different solutions. Figure 2 shows the species distribution of copper complexes with triethanolamine at two different ratios of ligand-to-metal ion, and also at two different total concentrations.

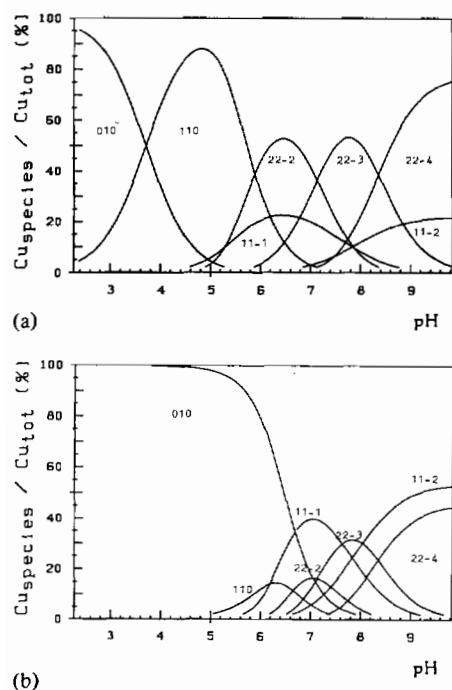


Fig. 2. Distribution of species which contain Cu(II) ion: (a) Cu(II) concentration 0.01 M, triethanolamine concentration 1.0 M, ratio ligand to metal 100; (b) Cu(II) concentration 0.001 M, triethanolamine concentration 0.001 M, ratio ligand to metal 1.

It is seen that dimeric species are predominant when the total concentration of metal ion is higher (Fig. 2a); only at low metal concentrations are the monomers 11 - 1 and 11 - 2 more important than dimers (Fig. 2b). The formation of the first complex is much more favourable when there is a high concentration of the ligand (Fig. 2a). This is the reason why complexation of amines has usually been studied in excess of ligand concentration, *e.g.*, to push forward

amine complex formation at high enough acidity to avoid hydrolysis and precipitation of the species formed upon pH increase [28]. This is not the case for the copper triethanolamine complexes, since no precipitation is observed even at low ligand-to-metal ratio.

ESR spectra of copper(II) ion and of the complex species 110, 11 - 1 and 11 - 2 are shown in Fig. 3.

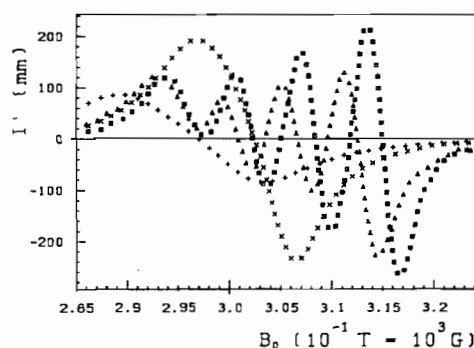


Fig. 3. Shape of ESR species spectra. Species 010 (+++++), 110 (XXXXX), 11 - 1 ($\Delta\Delta\Delta\Delta\Delta$), 11 - 2 ($\square\square\square\square\square$).

The spectrum for the first complex 110 does not show a hyperfine structure, but it is more narrow and intense than are the aquo-copper species spectra. Both 11 - 1 and 11 - 2 species spectra show pronounced hyperfine structures with four signals caused by the nuclear spin of copper ($I_{\text{Cu}} = 3/2$). The spectrum of the species 11 - 2 is more narrow and shifted to the right (higher field) than the spectrum of the species 11 - 1. Double integrals of the three species spectra have similar values, in the expected range of accuracy.

Comparison with Potentiometric Results

Potentiometric results [17] showed the formation of species with a 1:1 ligand-to-metal ratio only, but the method did not allow us to establish an unambiguous model because of the difficulties in the distinction between monomer and dimer species. As it can be seen from mass balance equations, pH determinations can only distinguish the monomer from its dimer in case of high concentrations of the metal ion and a favourable value of the dimerisation constant. Otherwise numerical refinement of stability constants from potentiometric data (pH) will give arbitrary or at least, imprecise values for them.

In Table II the results of numerical analysis of potentiometric data with the MINIQUAD program [29] are shown taking into account the data obtained in the ESR titration experiments and other potentiometric data obtained independently [17]. The results obtained including only monomer species or only dimer species (when there is the corresponding monomer) show a similar fit of the data (*U, R*, Table

TABLE II. Results of MINQUAD [29] Treatment of Potentiometric Data in the Cu(II)-triethanolamine System.^a

Species ^b	log of the constants ^c	U^d	R^d	Comment
110	4.41(6)	2.3 E-5	0.0003	Monomer species
11-1	-1.5(1)			
11-2	-7.9(1)			
110	4.45(6)	2.4 E-5	0.0003	Dimeric species
22-2	-0.3(2)			
22-4	-13.3(1)			
110	4.40(6)	2.2 E-5	0.0003	Mixed model; selection of species became arbitrary
11-1	-1.4(1)			
11-2	rejected			
22-2	rejected			
22-3	-8.0(1.0)			
22-4	-13.4(3)			
110	4.3	3.9 E-5	0.0005	Model taken from ESR determinations; constants are not changed
11-1	-1.9			
11-2	-9.7			
22-2	-1.1			
22-3	-8.2			
22-4	-16.6			

^a10 titration curves and 194 experimental points were analysed. ^bSame notations as in Table I. ^cValues in parentheses refer to three times the standard deviations in the last figure calculated by the MINQUAD program. ^d U and R are respectively the values of the least-squares function and R -factor calculated by MINQUAD.

II). When monomers and dimers are mixed in the same model, the selection became arbitrary, although there was nearly no improvement of the fit. Model

species and stability constants obtained in the ESR determinations give a reasonable fit of the potentiometric data, although it was not the model finally chosen by the program. It should be noted that the ESR data (including the dilution and decreasing ratio experiments) are more complete, since the pH range is extended to higher values and the concentrations of the constituents are varied much more. Therefore, the model finally proposed is the one obtained from the analysis of the ESR data (see Table I) which is made up of 3 monomers and 3 dimers.

From the comparison of potentiometric and ESR results we conclude: (1) potentiometric data, in contrast to ESR data are usually not appropriate for the differentiation of monomer and dimer species; (2) numerical methods for stability constants determination have to include procedures which are based on data allowing the determination of mono- and dimeric species. Potentiometry alone will not be sufficient in many cases.

¹H NMR Spectroscopy of Cu(II)-triethanolamine Solutions

Obtained ¹H NMR spectra are shown in Fig. 4. The peaks corresponding to both kinds of proton methylene groups are strongly broadened. This broadening is the more pronounced the more the amount of Cu(II) and pD increases. The observed peaks at very acidic conditions correspond to those of the protonated ligand in absence of metal. The fact that the lines corresponding to the proton of both methylene groups are broadened to the same extent is interpreted here as the formation of stable chelates where both nitrogen and oxygen atoms are bound to the

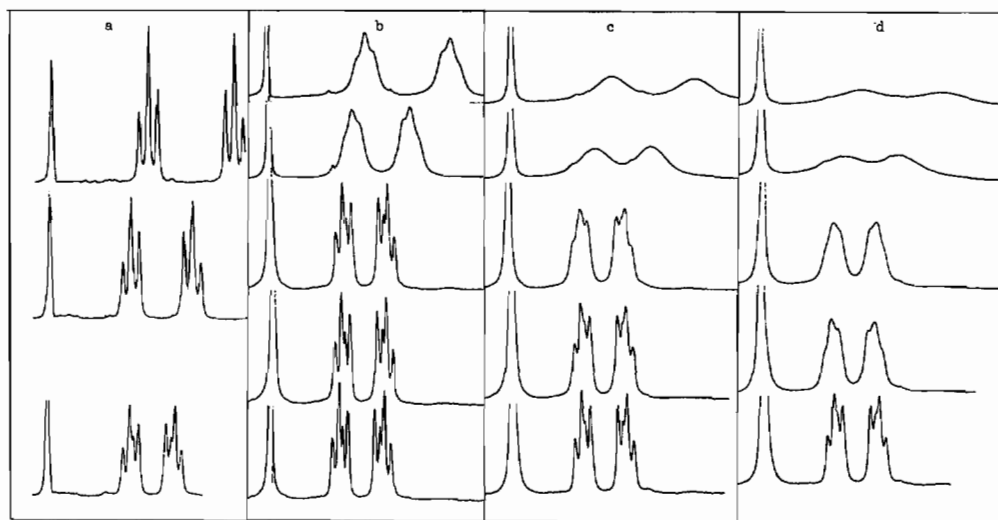


Fig. 4. ¹H NMR spectra. Triethanolamine concentration 0.55 M (a) ligand protonation; from up to down pD 10.0, 6.3 and 1.8; (b), (c) and (d) line broadening experiments; values of pD from up to down 10.0, 8.1, 6.3, 4.6 and 1.8; Cu(II) concentration 0.001 M, 0.005 M and 0.01 M, respectively.

metal ion. Neither amination – which was already discarded to explain the formation of higher complexes at neutral and basic pH – nor the formation of hydroxocomplexes can interpret the strong broadening of both lines simultaneously, since in both cases CH₂ protons adjacent to the nitrogen should principally be relaxed by copper, and consequently give broader NMR lines than CH₂ protons adjacent to the oxygen atoms of the ligand.

Conclusions

Potentiometric and ESR methods proved that only species with a ligand-to-metal ion ratio of one-to-one are needed to explain the data. The ESR method is very suitable for the study of copper complexes in solution, especially when dimeric species are involved and potentiometry gives ambiguous results in the selection of the species. Unfortunately, neither potentiometry nor ESR can give direct proof for the deprotonation of the ligand and formation of chelates. In this work two reasons led to a final proposal of the chelation model: (1) the fact that solutions with low ratios of ligand-to-metal-ion do not precipitate because of the high stability of complex species formed (more stable than usual amine and hydroxoamine complexes, see ref. 3, 28), and (2), the results of the ¹H NMR relaxation experiments.

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