

## Copper Monoethanolamine Complexes

### An Identification of Coordinated Alcoholate and an Estimation of the Acidic Constant of the Alcohol Group in the Ligand

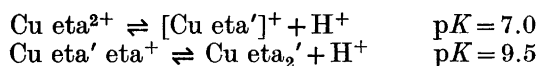
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Dissolved in methanol or DMSO,\* the species  $\text{Cu eta}' \text{ eta ClO}_4$ ,  $\text{Cu eta}' \text{ eta}_2 \text{ ClO}_4$ ,  $\text{Cu eta}' \text{ eta NO}_3$ , and  $\text{Cu eta}_2'^*$  exhibit an absorption at 340 nm, which is absent in water. This suggests that in methanol and DMSO, the alcoholate group of monoethanolamine is coordinated, whereas such coordination does not exist in water. The acidic constant of the alcohol group in coordinated ethanolamine in aqueous solution is tentatively ascribed the value  $10^{-10}$ .

Although various studies on the structure and properties of the copper complexes of ethanolamine in solutions exist in the literature, the present knowledge still seems to be limited.

Flannery *et al.*<sup>1</sup> carried out polarographic studies on these complexes in aqueous solution and found that, with a large excess of the aminoalcohol, complexes of the type  $[\text{Cu}(\text{amine})_4]^{2+}$ , in which only amine groups are coordinated, were the dominating species. This was confirmed by Davies and Patel,<sup>2</sup> with the additional remark that at high pH-values, ethanolamine acts as a chelate, forming the uncharged species  $\text{Cu eta}_2'$ . Based upon potentiometric and spectrophotometric investigations, Davies and Patel<sup>3</sup> recently suggested the following constants to be associated with formation of  $\text{Cu eta}_2'$  in water:



In the visible spectra of the aqueous copper-ethanolamine-system, Ojima and Sone<sup>4</sup> observed a band at 520 nm, increasing in intensity as a function of the aminoalcohol to copper ratio, or when strong base was added to the system; this band was assigned to the formation of the complex  $\text{Cu eta}_2'$ , suggested by Davies and Patel in the explanation of their results.

\* Abbreviations used in this paper: en for ethylenediamine, eta for monoethanolamine, eta' for monoethanolaminolate, and DMSO for dimethylsulfoxide.

The assignment of the band at 520 nm was thought <sup>4</sup> to be confirmed by an electrophoresis study, in which the migration rate of  $\text{Cu}(\text{ClO}_4)_2$  were 20 times as fast on paper strips impregnated with ethylenediamine than with monoethanolamine.

The following information has been obtained from preparative work in nonaqueous media. Udovenko and Artemenko <sup>5</sup> made  $\text{Cu eta}' \text{Cl}$ , and Artemenko <sup>6</sup>  $\text{Cu eta}'_2$  and  $\text{Cu eta}'_2 \cdot \text{H}_2\text{O}$ , all formulated with the aminoalcoholate as chelate. Kida <sup>7</sup> made  $\text{Cu eta}' \text{ eta X}$  ( $\text{X}^- = \text{NO}_3^-, \text{ClO}_4^-$ ),  $\text{Cu eta}'_2$  and  $\text{Cu eta}'_2 \cdot \text{H}_2\text{O}$ , and formulated both the aminoalcohol and the aminoalcoholate as bidentate on the basis of spectrophotometric measurements.

### EXPERIMENTAL

In this study, the spectra in the range 200–400 nm of the following complexes dissolved in methanol, DMSO, and water are considered:  $\text{Cu eta}' \text{ eta ClO}_4$  (I),  $\text{Cu eta}' \text{ eta}_2 \text{ ClO}_4$  (II),  $\text{Cu eta}' \text{ eta NO}_3$  (III),  $\text{Cu eta}'_1$  (IV), and  $\text{Cu en}_2 (\text{ClO}_4)_2$  (V).

I and III are prepared according to Kida,<sup>7</sup> IV according to Artemenko,<sup>6</sup> and II in a way similar to I, but with a greater ratio  $\text{eta}'/\text{Cu}^{2+}$ . V is prepared according to Pfeiffer and Glaser.<sup>8</sup>

The products used in the preparations were all of analytical grade. The analyses of the species involved are given in Table 1.

Absorption spectra were recorded by means of a Cary model 11 MS-50 spectrophotometer.

Table 1.

Species		Cu %	C %	H %	N %
I. $\text{Cu eta}' \text{ eta ClO}_4$ .	Anal.	—	16.74	4.60	9.87
	Calc.	—	16.90	4.58	9.86
II. $\text{Cu eta}' \text{ eta}_2 \text{ ClO}_4$ .	Anal.	—	20.80	5.76	12.18
	Calc.	—	20.87	5.80	12.17
III. $\text{Cu eta}' \text{ eta NO}_3$ .	Anal.	—	19.34	5.29	17.00
	Calc.	—	19.47	5.27	17.04
IV. $\text{Cu eta}'_1$ . <sup>a</sup>	Anal.	34.56	—	—	—
	Calc.	34.63	—	—	—
V. $\text{Cu en}_2 (\text{ClO}_4)_2$ .	Anal.	—	12.70	4.25	14.79
	Calc.	—	12.55	4.18	14.64

<sup>a</sup> As  $\text{Cu eta}'_1$  is extremely hygroscopic, only an iodometric titration was made on the freshly prepared compound. The molar absorbance at 600 nm fits with the value given by Kida.<sup>7</sup>

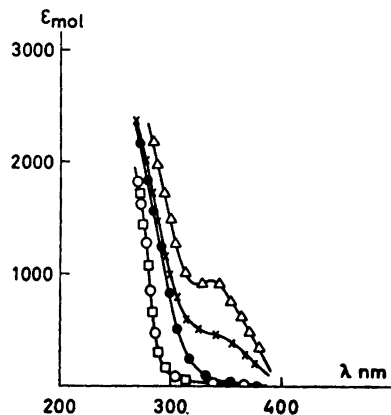
### DISCUSSION

From Fig. 1 is seen that the absorption band at 340 nm, typical of  $\text{Cu eta}' \text{ eta}_2 \text{ ClO}_4$  as well as of  $\text{Cu eta}'_2$  when dissolved in methanol, disappears in the case of  $\text{Cu eta}' \text{ eta}_2 \text{ ClO}_4$  when dissolved in water. Furthermore, the intensity

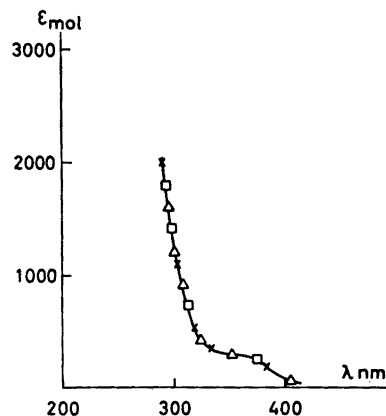
of the band increases by a factor two, when going from  $\text{Cu eta}' \text{ eta}_2 \text{ ClO}_4$  to  $\text{Cu eta}_2'$ .

Comparing these absorption spectra with that of  $\text{Cu en}_2 (\text{ClO}_4)_2$  in methanol, where the band at 340 nm is missing, it may be concluded that this band is typical for coordination through the alcohol group of ethanolamine. To make a further determination whether it is the protonized or deprotonized alcohol group of the aminoalcohol which causes the absorption at 340 nm, spectra of  $\text{Cu eta}' \text{ eta X}$  ( $\text{X}^- = \text{NO}_3^-, \text{ClO}_4^-$ ) and  $\text{Cu eta}' \text{ eta}_2 \text{ ClO}_4$  were measured in DMSO (Fig. 2).

*Fig. 1.*  $\circ$  is used to designate  $\text{Cu en}_2 (\text{ClO}_4)_2$  in  $\text{CH}_3\text{OH}$ ,  $\square$  to designate  $\text{Cu en}_2 (\text{ClO}_4)_2$  in  $\text{H}_2\text{O}$ ,  $\bullet$  to designate  $\text{Cu eta}' \text{ eta}_2 \text{ ClO}_4$  in  $\text{H}_2\text{O}$ ,  $\times$  to designate  $\text{Cu eta}' \text{ eta}_2 \text{ ClO}_4$  in  $\text{CH}_3\text{OH}$ , and  $\triangle$  to designate  $\text{Cu eta}_2'$  in  $\text{CH}_3\text{OH}$ .  $\text{Cu eta}' \text{ eta X}$  ( $\text{X}^- = \text{NO}_3^-, \text{ClO}_4^-$ ) is insoluble in methanol, and unstable in dilute aqueous solution.



*Fig. 2.* Compounds dissolved in DMSO.  $\triangle$  is used to designate  $\text{Cu eta}' \text{ eta}_2 \text{ ClO}_4$ ,  $\square$  to designate  $\text{Cu eta}' \text{ eta ClO}_4$ , and  $\times$  to designate  $\text{Cu eta}' \text{ eta NO}_3$ .  $\text{Cu eta}_2'$  is insoluble in this medium.



It is seen that these species have the band at 340 nm with the same molar absorbance for all three of them, therefore the band is assigned as due to coordinated alcoholate.

Comparing the spectra of  $\text{Cu eta}' \text{ eta}_2 \text{ ClO}_4$  and  $\text{Cu en}_2 (\text{ClO}_4)_2$  dissolved in water (Fig. 1), where the band at 340 nm in both cases is absent, we are led to the tentative conclusion that in water no alcoholate is coordinated to  $\text{Cu}^{2+}$

although the shoulder at 520 nm reported by Ojima and Sone<sup>4</sup> as evidence for this kind of bonding is seen in the spectra of  $\text{Cu eta}' \text{ eta}_2 \text{ ClO}_4$  in water (Fig. 3).

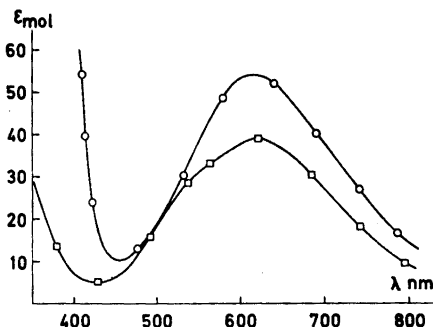


Fig. 3.  $\square$  is used to designate  $\text{Cu eta}' \text{ eta}_2 \text{ ClO}_4$  in  $\text{H}_2\text{O}$ , and  $\circ$  to designate it in  $\text{CH}_3\text{OH}$ .

A point which supports the rejection of the Ojima and Sone assignment of the shoulder at 520 nm is also seen in Fig. 3. The spectrum of  $\text{Cu eta}' \text{ eta}_2 \text{ ClO}_4$  in methanol exhibits no shoulder at 520 nm, although the species is thought to have coordinated alcoholate when dissolved in this medium.

The acidic constant in aqueous solution of the alcohol group in coordinated monoethanolamine is tentatively ascribed the value  $10^{-16}$  on basis of the following arguments:

In the case of  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$  (amine-group bound to copper) we have three monovalent oxy-acids, *i.e.* three acids of the same kind, for which we will expect relative strengths to be almost independent of media. So, as ethanolamine is seen to be a stronger acid than methanol in methanol, this must also be the case in water, but in water, ethanolamine is found to be a weaker acid than water, we then have ( $\text{p}K_A$ 's given at room temperature in water):

$$15.7 < \text{p}K_A^{\text{eta}} < 16.3, \text{ from which } \text{p}K_A^{\text{eta}} \sim 16$$

This result is in striking disagreement with that of Davies and Patel,<sup>3</sup> and it is therefore emphasized that what they have measured is not the dissociation of protons from copper monoethanolamine complexes, but association of hydroxide ions.

That complexes of the form  $\text{Cu eta}_2 (\text{OH})_2$  should exist in water was earlier ruled out<sup>2</sup> by the argument that such species would be semistrong bases — a conclusion reached on comparison with copper ethylenediamine complexes — and would therefore have reasonably great conductance in contradiction to what is actually found. In fact, the comparison between copper complexes of ethylenediamine and monoethanolamine seems a little farfetched, as there is great difference in the ability of the two compounds to act as bidentate ligands.

During this work, efforts were made to prepare the species formulated as  $\text{Cu}(\text{NO}_3)_2 \cdot \text{eta}$  \* by Hieber and Levy.<sup>9</sup> When isolated, the product showed the

\* There is a misprint in the original paper, putting the formula forward as  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{C}_2\text{H}_4 \cdot \text{OHNH}_2$ .

same spectral features as Cu eta' eta NO<sub>3</sub>, and elementary analysis confirmed this formulation. (Found: C 19.42; H 5.32; N 17.16. Calc. C 19.47; H 5.27; N 17.04.)\*

It is therefore suggested that this was also the product Hieber and Levy isolated, as it is difficult to see the difference between Cu eta' eta NO<sub>3</sub> and Cu eta (NO<sub>3</sub>)<sub>2</sub>, getting only analyses on Cu and N. The fact that Cu eta' eta NO<sub>3</sub> can be isolated by Hieber and Levy's method, using a water aminoalcohol mixture as reaction medium, is not in contradiction with the conclusions drawn in the present paper, since the salt is not obtained until almost all the water is removed from the reaction mixture.

The contrast to this is the preparation of Cu eta<sub>3</sub> SO<sub>4</sub> (Found: C 20.85; H 6.14; N 12.34. Calc. C 21.01; H 6.13; N 12.26), also after Hieber and Levy, where the salt is isolated from a reaction mixture still containing water, a fact which is again in agreement with the reached conclusions about the acidic strengths.

Spectral investigations on copper complexes of optically active 1-amino-2-propanol are in progress to give further information about structure in solutions of this type of complexes.

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\* The same conclusion is made by Brannon *et al.*<sup>10</sup>