Copper Monoethanolamine Complexes

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

HANS PETER JENSEN

Chemistry Department A, Technical University of Denmark, DK-2800 Lyngby, Denmark

Dissolved in methanol or DMSO,* the species Cu eta' eta ClO₄⁻, Cu eta' eta₂ ClO₄⁻, Cu eta' eta NO₃⁻, and Cu eta'¹⁺ exhibit an absorption at 340 nm, which is absent in water. This suggests that in methanol and DMSO, the alcoholicate 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 10⁻¹⁰⁻¹².

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.¹ carried out polarographic studies on these complexes in aqueous solution and found that, with a large excess of the aminoalcohol, complexes of the type [Cu(amine)]⁺, in which only amine groups are coordinated, were the dominating species. This was confirmed by Davies and Patel,² with the additional remark that at high pH-values, ethanolamine acts as a chelate, forming the uncharged species Cu eta₂'. Based upon potentiometric and spectrophotometric investigations, Davies and Patel³ recently suggested the following constants to be associated with formation of Cu eta₂' in water:

\[
\begin{align*}
\text{Cu eta}^{2+} & \rightleftharpoons [\text{Cu eta}']^+ + \text{H}^+ & & \text{pK}_1 = 7.0 \\
\text{Cu eta}^-' & \rightleftharpoons \text{Cu eta}^-' + \text{H}^+ & & \text{pK}_2 = 9.5 \\
\end{align*}
\]

In the visible spectra of the aqueous copper-ethanolamine-system, Ojima and Sone ⁴ 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 Cu eta₂', 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 to be confirmed by an electrophoresis study, in which the migration rate of Cu(ClO₄)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 made Cu eta Cl, and Artemenko Cu eta₄ and Cu eta₄.H₂O, all formulated with the aminoaacolate as chelate. Kida made Cu eta eta X (X = NO₃, ClO₄⁻), Cu eta₄ and Cu eta₄.H₂O, and formulated both the aminoaacol and the aminoaacolate 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: Cu eta eta ClO₄ (I), Cu eta eta ClO₄ (II), Cu eta eta NO₃ (III), Cu eta₄ (IV), and Cu en₄ (ClO₄)₄ (V).

I and III are prepared according to Kida, IV according to Artemenko, and II in a way similar to I, but with a greater ratio eta/Cu²⁺. V is prepared according to Pheiffer and Glaser.

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>
<thead>
<tr>
<th>Species</th>
<th>Cu %</th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Cu eta’ eta ClO₄</td>
<td>Anal.</td>
<td>16.74</td>
<td>4.60</td>
<td>9.87</td>
</tr>
<tr>
<td>Calc.</td>
<td>–</td>
<td>16.90</td>
<td>4.58</td>
<td>9.86</td>
</tr>
<tr>
<td>II. Cu eta’ eta ClO₄</td>
<td>Anal.</td>
<td>20.80</td>
<td>5.76</td>
<td>12.18</td>
</tr>
<tr>
<td>Calc.</td>
<td>–</td>
<td>20.87</td>
<td>5.80</td>
<td>12.17</td>
</tr>
<tr>
<td>III. Cu eta’ eta NO₃</td>
<td>Anal.</td>
<td>19.34</td>
<td>5.29</td>
<td>17.00</td>
</tr>
<tr>
<td>Calc.</td>
<td>–</td>
<td>19.47</td>
<td>5.27</td>
<td>17.04</td>
</tr>
<tr>
<td>IV. Cu eta₄’a</td>
<td>Anal.</td>
<td>34.56</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Calc.</td>
<td>34.63</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>V. Cu en₄ (ClO₄)₄</td>
<td>Anal.</td>
<td>12.70</td>
<td>4.25</td>
<td>14.79</td>
</tr>
<tr>
<td>Calc.</td>
<td>12.55</td>
<td>4.18</td>
<td>14.64</td>
<td></td>
</tr>
</tbody>
</table>

*a As Cu eta₄’ 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.

DISCUSSION

From Fig. 1 is seen that the absorption band at 340 nm, typical of Cu eta’ eta₂ ClO₄ as well as of Cu eta₂ when dissolved in methanol, disappears in the case of Cu eta’ eta₂ ClO₄ when dissolved in water. Furthermore, the intensity

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of the band increases by a factor two, when going from Cu eta' eta₂ ClO₄ to Cu eta₂'.

Comparing these absorption spectra with that of Cu en₂ (ClO₄)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 Cu eta' eta X (X⁻ = NO₃⁻, ClO₄⁻) and Cu eta' eta₂ ClO₄ were measured in DMSO (Fig. 2).

![Fig. 1.](image1.png)

*Fig. 1.* ○ is used to designate Cu en₃ (ClO₄)₃ in CH₃OH, □ to designate Cu en₂ (ClO₄)₂ in H₂O, ● to designate Cu eta' eta₂ ClO₄ in H₂O, × to designate Cu eta' eta₂ ClO₄ in CH₃OH, and △ to designate Cu eta' in CH₃OH. Cu eta' eta X (X⁻ = NO₃⁻, ClO₄⁻) is insoluble in methanol, and unstable in dilute aqueous solution.

![Fig. 2.](image2.png)

*Fig. 2.* Compounds dissolved in DMSO. △ is used to designate Cu eta' eta₂ ClO₄, □ to designate Cu eta' eta ClO₄, and × to designate Cu eta' eta NO₃. Cu eta' 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 Cu eta' eta₂ ClO₄ and Cu en₂ (ClO₄)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 Cu³⁺.
although the shoulder at 520 nm reported by Ojima and Sone as evidence for this kind of bonding is seen in the spectra of Cu eta' eta ClO₄ in water (Fig. 3).

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 Cu eta' eta ClO₄ 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 H₂O, CH₃OH, and NH₂CH₂CH₂OH (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 (pKₐ's given at room temperature in water):

15.7 < pKₐ<sub>eta</sub> < 16.3, from which pKₐ<sub>eta</sub> < 16

This result is in striking disagreement with that of Davies and Patel, 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 Cu eta (OH)₂ should exist in water was earlier ruled out by the argument that such species would be semi-strong 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 far-fetched, 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 Cu(NO₃)₃·2C₂H₄·OHNH₄ by Hieber and Levy. When isolated, the product showed the

Fig. 3. □ is used to designate Cu eta' eta ClO₄ in H₂O, and ○ to designate it in CH₃OH.

* There is a misprint in the original paper, putting the formula forward as Cu(NO₃)₃·2C₂H₄·OHNH₄.
same spectral features as Cu eta' eta NO₃, 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 NO₃ and
Cu eta (NO₃)₂, getting only analyses on Cu and N. The fact that Cu eta' eta
NO₃ 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 eta₃ SO₄ (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 solu-
tions of this type of complexes.

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* The same conclusion is made by Brannon et al.¹⁰