The Absorption Spectra of Bis(ethylenediamine)copper(II) Complexes in Various Solutions

By Kôzô SONE

Chemical Laboratory, Department of General Education, Nagoya University, Chikusa-ku, Nagoya

and Shunji UTSUNO

Chemical Laboratory, Aichi Gakugei University, Higashi-ku, Nagoya

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Recently we have carried out a series of measurements of the visible absorption spectra of bis(ethylenediamine)copper(II) complexes in a variety of solvents. Form the results, which are summarized in Table I, we can obtain some information on the states of the complex ion in these media.[1]

Since the perchlorate ion is practically unable to form a complex in a solution, the complex $[Cuen_2](ClO_4)_2$ is considered to be the most favorable for studying the effects of various media on the bis(ethylenediamine)copper(II) ion. The absorption measurements of this complex in water, ethanol, acetone and nitromethane reveal that the λ_{max} and ε_{max} values are not very different in each case, and that the λ_{max} value is shifted toward a shorter wavelength in the order of water→(ethanol and acetone)→nitromethane. In an aqueous solution it may be assumed that two water molecules are loosely bound above and below the copper atom in each planar bis(ethylenediamine)copper(II) ion, forming an elongated octahedral structure; the same situation can also be assumed in ethanol and acetone solutions, but the bondings of the respective solvent molecules will be somewhat weaker than those in an aqueous solution. In a nitromethane solution, the additional coordination of the solvent molecules will be even weaker.[2] Therefore, we can conclude that the weaker the bondings of the solvent molecules are, i. e., the higher the tetragonality of the bis(ethylenediamine)copper(II) ion in a solution is, the shorter will its λ_{max} value be.

TABLE I. ABSORPTION MAXIMA OF $[Cu\ en_2]X_2$ IN VARIOUS SOLUTIONS[a,b]

X	Solvent	λ_{max}(mμ)	ε_{max}
ClO_4	H_2O	550	64
	C_2H_5OH*	547	63
	CH_3COCH_3	547	63
	CH_3NO_2	534	60
	$H_2O+NaClO_4$ (4M)	538	61
	$H_2O+NaClO_4$ (8M)	528	61
	$H_2O+Mg(ClO_4)_2$ (4M)	530	58
	C_5H_5N	582	96
NO_3	H_2O	550	64
	C_2H_5OH*	547	63
	$H_2O+NaNO_3$ (8M)	540	62
Cl	H_2O	550	64
	C_2H_5OH	575	84
	$H_2O+LiCl$ (10M)	553	73

a) Temp.: 20—25°C; chelate concentration: $7\times10^{-3}-8\times10^{-3}$ M (7×10^{-4} M in the cases marked with *).

b) Each absorption curve shows only a simple and approximately symmetrical absorption band.

Of special interest is the effect of concentrated aqueous solutions of sodium perchlorate and magnesium perchlorate. Here we can expect that most of the water molecules will be so strongly attracted by the ions of these salts that the bondings of water molecules above and below the bis(ethylenediamine) copper(II) ions will be more or less disturbed. In fact, we find that the λ_{max} values in these solutions are markedly smaller than that in pure water, and that the value in a 8 M solution of sodium perchlorate is even smaller than that in

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[1] A part of our conclusion does not agree with the opinion of C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York (1963), p. 100. Cf. also F. Rosenblatt, *Z. anorg. u. allgem. Chem.*, **204**, 351 (1932) and H. Ojima and K. Sone, *Naturwiss.*, **51**, 105 (1964).

[2] On the small coordination ability of nitromethane, cf. B. J. Hathaway and D. G. Holah, *J. Chem. Soc.*, **1964**, 2408.

nitromethane.[3] Similar effects can be found also in the case of [Cu en$_2$](NO$_3$)$_2$ in a concentrated sodium nitrate solution (see Table I), and also in solutions of some other copper complexes, e. g., [Cu trien]$^{2+}$ or [Cu glycine$_2$] in the presence of a large amount of sodium perchlorate or sodium nitrate.[4,5]

In pyridine solutions of [Cu en$_2$](ClO$_4$)$_2$ and ethanol solutions of [Cu en$_2$]Cl$_2$ (see Table I), on the other hand, the λ_{max} and ε_{max} values are larger than those described above. In these cases, it is probable that the coordination of pyridine molecules or chloride ions to the bis(ethylenediamine)copper(II) ions takes place, giving the 5- or possibly 6-coordinated complexes, the tetragonalities of which are apparently much lower than those of the more or less solvated complex ions, as has been described above.[6] The spectrum of [Cu en$_2$]Cl$_2$ in concentrated lithium chloride shows, further, that chloro-complex formation also takes place to some extent in this medium.

In summing up all the data in Table I, we can conclude that the higher the tetragonality of the bis(ethylenediamine)copper(II) ion in a solution is, the shorter is its λ_{max} value. It is interesting to note that the powder reflection spectrum of [Cu en$_2$](ClO$_4$)$_2$ reported by Meek and Ehrhardt[7] shows the λ_{max} value of 525 mμ, which is still shorter than all the values in Table I; this indicates that the bis(ethylenediamine)copper(II) ion in this particular case is of the highest tetragonality, since the complex is in contact with only the perchlorate ions, which have only a negligible ability to coordinate.

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[3] In these solutions, and also in nitromethane, we can also expect that the dissociation of [Cu en$_2$](ClO$_4$)$_2$ into bis(ethylenediamine)copper(II) and perchlorate ions is hindered to some extent. However, it is quite certain that the bonding of a perchlorate ion above or below a planar complex ion is much weaker than that of a molecule of water, ethanol or acetone; therefore, we can assume that the tetragonality of the bis(ethylenediamine)copper(II) ions in an aqueous sodium (or magnesium) perchlorate solution or in nitromethane is, at any rate, much higher than that in water, ethanol or acetone (cf. the spectrum of solid [Cu en$_2$](ClO$_4$)$_2$ (see text)).

[4] In the case of [Cu glycine$_2$], for example, the λ_{max} and ε_{max} values in water are 630 mμ and 44, while in a 8 M solution of sodium perchlorate they are 602 mμ and 41 respectively.

[5] A similar effect of sodium perchlorate on some nickel ammines has already been reported by C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 399 (1957) and K. Sone and M. Kato, *Z. anorg. u. allgem. Chem.*, **301**, 277 (1959); in these cases, it was found also that the effect is intensified remarkably by heating. In the case of the bis(ethylenediamine)copper(II) ion, on the other hand, the effect of heating is not so large, and only comparatively small increases in λ_{max} and ε_{max} take place (the values in a 8 M solution of sodium perchlorate at 80°C are ca. 535 mμ and 65 respectively).

[6] Cf. the spectra of [Cu en$_3$]$^{2+}$, [Cu en$_2$NH$_3$]$^{2+}$ and [Cu en$_2$OH]$^+$ reported by J. Bjerrum and E. J. Nielsen, *Acta Chem. Scand.*, **2**, 297 (1948) and H. B. Jonassen, R. E. Reeves and L. Segal, *J. Am. Chem. Soc.*, **77**, 2748 (1955).

[7] D. W. Meek and S. A. Ehrhardt, *Inorg. Chem.*, **4**, 584 (1965). For the absorption spectra of single crystals of some bis(ethylenediamine)copper(II) complexes, see S. Yamada and R. Tsuchida, This Bulletin, **29**, 289 (1956).