

An Spectroscopic Investigation of Complex Formation in Cupric Sulphate Aliphatic Amine System

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Summary

Visible absorption spectra of cupric sulphate and various aliphatic amine solutions were analysed in order to extract information regarding each of amine copper(II) complexes. The presence of four different complexes, i. e. mono, di, tri and tetramine have been indicated by the shift of absorption maxima for these which lie in the vicinity of 750, 685, 640 and 625 μ respectively. The energy changes of these complexes due to exchange of water ligand with amines have been calculated and an interpretation is offered for this shift in the observed position of absorption maxima.

Introduction

A survey of the literature shows that ammonia complexes of cupric sulphate have been investigated in detail very early¹⁾²⁾. However, aliphatic amines, which are substituted ammonia, have been given very little attention, and only a few such complexes have been studied³⁾⁴⁾. In the present paper the results obtained by an systematic spectroscopic investigation of cupric sulphate solutions with different molar quantities of various amines are reported. Amines used are, methyl, ethyl, propyl, butyl, amyl, dimethyl, diethyl, dipropyl and dibutyl amines.

Experimental

The spectra were obtained with a unicam SP 500 recording spectrophotometer on $2 \cdot 10^{-2}$ cupric sulphate solutions with different molar quantities of aliphatic amines. The pH of the solutions was buffered at low value with approximately 2 M ammonium sulphate solution.

Results

The values of calculated absorption maxima, energy in k. cal absorbed per mole and intensity of the various mono, di, tri and tetramine complexes formed by different aliphatic amines, have been given in the following table.

1) G. ANDRÉ, *Compt. Rend.* **100**, 1138 (1885).

2) E. RENCKER, *Bull. Soc. Chem.* (5), 1992 (1937).

3) M. STRAUMANIS, *Z. anorg. allg. Chem.* **230**, 65 (1936).

4) S. PRASAD and P. D. SHARMA, *J. Proc. Inst. Chem.* **30**, 245 (1958).

Table 1

No.	Amine used	Monoamine Complex		Diamine Complex		Triamine Complex		Tetramine Complex		
		λ_{\max}	E_1	λ_{\max}	E_2	λ_{\max}	E_3	λ_{\max}	E_4	ϵ
1.	Ammonia	750 m μ	$3.82 \cdot 10^2$	670 m μ	$4.24 \cdot 10^2$	628 m μ	$4.55 \cdot 10^2$	620 m μ	$4.77 \cdot 10^2$	187.7
2.	Methylamine	750 m μ	$3.82 \cdot 10^2$	685 m μ	$4.17 \cdot 10^2$	640 m μ	$4.47 \cdot 10^2$	625 m μ	$4.57 \cdot 10^2$	177.0
3.	Ethylamine	752 m μ	$3.81 \cdot 10^2$	680 m μ	$4.21 \cdot 10^2$	640 m μ	$4.47 \cdot 10^2$	622 m μ	$4.60 \cdot 10^2$	183.0
4.	Propylamine	750 m μ	$3.82 \cdot 10^2$	680 m μ	$4.21 \cdot 10^2$	641 m μ	$4.46 \cdot 10^2$	625 m μ	$4.57 \cdot 10^2$	180.0
5.	Butylamine	748 m μ	$3.84 \cdot 10^2$	685 m μ	$4.17 \cdot 10^2$	645 m μ	$4.43 \cdot 10^2$	620 m μ	$4.61 \cdot 10^2$	180.0
6.	Amylamine	754 m μ	$3.79 \cdot 10^2$	682 m μ	$4.19 \cdot 10^2$	644 m μ	$4.42 \cdot 10^2$	625 m μ	$4.57 \cdot 10^2$	182.0
7.	Dimethylamine	750 m μ	$3.82 \cdot 10^2$	680 m μ	$4.21 \cdot 10^2$	640 m μ	$4.47 \cdot 10^2$	620 m μ	$4.61 \cdot 10^2$	180.0
8.	Diethylamine	755 m μ	$3.79 \cdot 10^2$	680 m μ	$4.21 \cdot 10^2$	638 m μ	$4.48 \cdot 10^2$	625 m μ	$4.51 \cdot 10^2$	185.0
9.	Dipropylamine	750 m μ	$3.82 \cdot 10^2$	685 m μ	$4.17 \cdot 10^2$	645 m μ	$4.43 \cdot 10^2$	625 m μ	$4.57 \cdot 10^2$	190.0
10.	Dibutylamine	752 m μ	$3.81 \cdot 10^2$	688 m μ	$4.15 \cdot 10^2$	642 m μ	$4.40 \cdot 10^2$	624 m μ	$4.58 \cdot 10^2$	192.0

In the above table: i) E_1, E_2, E_3, E_4 represent energy in K.cals absorbed per mole. ii) ϵ represents extinction.

Discussion

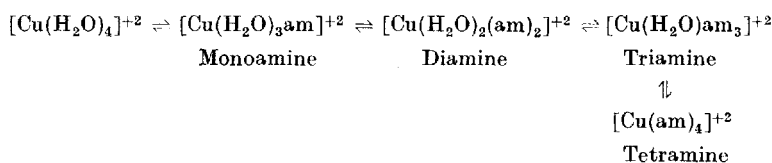
It is reported that complex formation in solution is a stepwise process and many of the complexes formed are quite stable in solution, so that they can be studied upto certain extent⁵). It has therefore, been found that gradual addition of ammonia to a copper sulphate solution results in the formation of atleast 4 different complexes, each of which shows a definite absorption maxima and which are named as mono, di, tri and tetramine complexes respectively⁶).

If other aliphatic amines are gradually added to the copper solution it has been observed that the colour of solution changes which ultimately becomes ink blue and any further addition of amine causes no change in the colour. For spectroscopic study of the solutions exactly one mole of various amines are added to copper sulphate solution in water. Since at each integral ratio, no less than three Cu^{2+} species exist in appreciable quantity the value of the actual absorption maxima was found by plotting true absorptivity against wavelength latter being obtained by solving the equation⁶):

$$AS_i^\lambda = b \sum_k a_k^\lambda C_{ki}$$

AS_i^λ is the absorption at wavelength λ for the i^{th} (Amine)₀/(Cu)₀ ratio, b the cell thickness, a_k^λ is the absorptivity index for the k^{th} species at λ and C_{ki} is the concentration of the K^{th} compound at the i^{th} ratio. Table 1 summarises the spectral maxima for each complex.

Value of the absorption maxima is thus shown to shift from 800 $m\mu$ to 752 $m\mu$, to 685 $m\mu$, to 640 $m\mu$ and lastly to 625 $m\mu$ by subsequent addition of 1, 2, 3, and 4 molar quantities of amine solutions. Later no change occurs even if amine is added in excess. These results indicate the formation of following four compounds



The energy in K. cal absorbed per mole of these complexes (i. e. E_1 , E_2 , E_3 and E_4) have been calculated by the equation $E = Nhc/\lambda$ where N is Avagadros No. h is planks constant C velocity of light and λ the wavelength of absorption maxima of complex under consideration.

It is observed that the energy of copper amine complexes increases gradually as the water ligands in copper ions are replaced, by amines. Consider-

⁵) J. BJERRUM, Metal ammine formation in apens solution F. Hasse & Son. 1941.

⁶) GRANT and KOLLBACK, J. Inorganic & Nucl. Chem. **23**, 25 (1961).

ing the crystal field theory, the blue colouration of copper ions is due to the presence of a single absorption band in 600–900 $m\mu$ region of spectrum. This band occurs due to the light exposure of copper ions, thereby giving them certain energy which is converted into the energy of excitation of an electron from eg to t_{2g} level, during which a absorption band is observed. The ground state is associated with configuration $(t_{2g})^5 (eg)^4$ and excited state with $(t_{2g})^6 (eg)^3$. The magnitude of this excitation energy will eventually depend on the total energy gained by the ion.

It is further clear from the table that the energy values in all the complexes of all the various amines studied here are constant, and that increasing molecular weight of amine causes almost no change in the position of absorption maxima. But there is a change in the E_2 , E_3 and E_4 values of these complexes if compared to the respective value of ammonia complexes, but the E_1 value, i. e. the energy gained by the monoamine complex, remains the same.

For cupric sulphate solutions the absorptions maxima at 800 $m\mu$ is due to $[Cu(H_2O)_4]^{2+}$ and energy value is $3.57 \cdot 10^{-2}$ K. cal/mole. As the water ligands are gradually replaced by 1, 2, 3 or 4 amine ligands the absorption maxima shifts to lower wavelength with a subsequent increase in energy values. Amine produces a much stronger ligand field than water and thus gives rise to an hypsochromic effect which causes the absorption band to shift from the far red to the middle of the red region of spectrum. This ultimately gives rise to a change in the colour of the solutions from faint blue in monoamine to ink blue in tetramine. As the total energy gained by the ion is increased it is expected that the energy which is available for an electron to go from eg to t_{2g} level is also increased. But this can not cause any change in the magnitude of the transition as according to the crystal theory even in cupric sulphate solutions there is an absorption band in the blue region due to $eg \rightarrow t_{2g}$ transition. It can thus be concluded that the deepening of the colour and the shift in the position of absorption maxima is simply due to the stronger ligand field environment produced around the copper ion by the replacement of water ligands with various amines.

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