

Electronic Spectra of Mixed Ligand Complexes of Copper(II) with Different Amino Acids

Mrs. SHAILJA NIGAM* and Miss. HEMLATA MOHABEY†

Department of Chemistry, Government Model Science College, Raipur 492 010, India

Copper(II) complexes were synthesised using methionine as the common ligand and proline and serine as secondary ligands. The mixed ligand complexes are soluble in water. Their electronic spectra was scanned in water. Both the complexes show one asymmetric absorption band around $16,000\text{ cm}^{-1}$, which suggests that these mixed complexes have distorted octahedral geometry. Since single band is observed in the electronic spectra of both the newly synthesised copper(II) complexes, *trans*-geometry is suggested. The value of molar extinction coefficient does not alter by change in concentration hence it is confirmed that complexes do not undergo association or dissociation in solution.

INTRODUCTION

Electronic absorption spectra of transition metal complexes were discussed in detail by Jorgensen¹, Griffiths², Orgel³ and Lever⁴ etc. It is possible to determine the point symmetry in the co-ordination sphere and to assign possible geometry of isomers⁵⁻⁷ on the basis of electronic spectra of the complex.

EXPERIMENTAL

All the chemicals were of AnalaR grade.

Freshly precipitated copper(II) hydroxide was mixed with equimolar solutions of primary ligand *viz* methionine and secondary ligand namely proline or serine, on water bath for 3 h. The pH of the solution was maintained at 7. The reaction mixture was concentrated on water bath at 90–100°C. The solution was filtered while hot. On cooling blue crystals of copper ternary complexes separated out. These were recrystallised with double distilled water. The crystals were dried in vacuum at *ca.* 50°C

RESULTS AND DISCUSSION

Electronic spectra were obtained for characterising the newly synthesised complexes. Both of the complexes show only one asymmetric absorption band around $16,000\text{ cm}^{-1}$.

The electronic spectra are observed in the region 200–800 nm. The region below 200 nm is ultraviolet region and 400 nm to 800 nm is visible region.

†Govt. K.D.M. College, Rajnandgaon, India.

Copper(II) is expected to form distorted octahedral complexes⁸. Copper(II) ion has d^9 configuration. This gives rise to only one free ion in terms of 2D , which is two fold degenerate in spin and orbit, *i.e.*, in any symmetry all the levels belonging to 2D and must have the same inter electronic repulsions. Therefore, all the d-d transitions have energies which are simply the energy difference between the one electronic energy level concerned and independent of inter-electronic repulsions. The degeneracy of the five d-orbitals of free ion is removed^{9, 10} under the influence of cubic crystal field and it splits up into two fold degenerate ground state and the three fold degenerate upper state. The difference between the ground state and excited state directly gives 10 Dq values. For aquo complexes of copper this energy difference is about $13,000\text{ cm}^{-1}$.

Titanium(III) complexes have Ti(III) ion having d^1 configuration. In general a d^n system is equivalent to $d^{(10-n)}$ system with only the level order inverted. Therefore spectral behaviour of copper(II) should be same as spectral behaviour of titanium(III) complexes. Thus copper(II) complexes are expected to give only one band. Due to John-Teller effect, distortion is noticed. Aquo copper(II) complexes¹¹⁻¹³ absorb at $13,000\text{ cm}^{-1}$. Tetragonally distorted octahedral complexes generally give rise to one band at $16,000\text{ cm}^{-1}$. This shift from $13,000\text{ cm}^{-1}$ to $16,000\text{ cm}^{-1}$ confirms the coordination with other ligand. In case of square planar complex a band around $19,000\text{ cm}^{-1}$ is observed, while in distorted octahedral complex this occurs at $16,000\text{ cm}^{-1}$.

Distorted octahedral geometry of both the mixed ligand complexes synthesised in present investigation is proved by an asymmetric absorption band¹⁴⁻¹⁶ around $16,000\text{ cm}^{-1}$. This absorption band is of higher frequency than for tetrahedral geometry. The values as molar extinction coefficient lie between 56 to 70. Therefore tetragonally distorted octahedral geometry is confirmed¹⁷.

Trans isomers give a single band while *cis* isomers give two bands differing by 0.5 kcal/mole. On this basis *trans* configuration for the present complexes may be assumed¹⁸ (Fig. 1 and 2).

The complexes do not undergo dissociation or association as change in concentration does not show any change in ν_{\max} values.

The ν_{\max} values of newly synthesised ternary complexes were compared with ν_{\max} values of binary complexes. In both the cases the value of ν_{\max} of ternary complexes are more than the average ν_{\max} values of binary complexes. This confirms that ternary complexes are more stable than binary complexes.

ACKNOWLEDGEMENT

Authors are thankful to Dr. R.B. Subramaniam, Professor and Head, Department of Chemistry, Government Model Science College, Raipur (M.P.), for providing laboratory facilities and encouraging attitude.

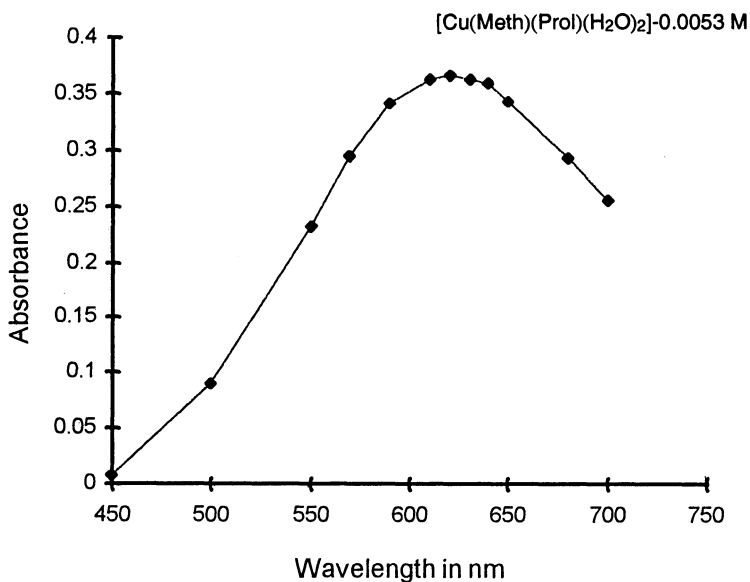


Fig. 1. Absorption spectra in aqueous medium

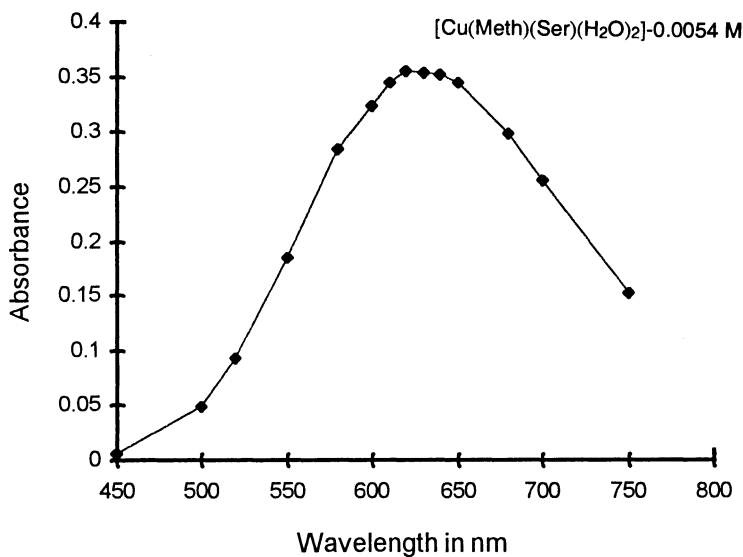


Fig. 2. Absorption spectra in aqueous medium

REFERENCES

- C.K. Jorgensen, *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon Press (1962).
2. J.H. Griffith, *The Theory of Transition Metal Ions*, McGraw-Hill, New York (1961).
 3. L.E. Orgel, *An Introduction to Transition Metal Chemistry*, Wiley, New York (1966).
 4. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, London (1968).
 5. L.N. Ferguson, *The Modern Structural Theory of Organic Chemistry*, Prentice-Hall of India Pvt. Ltd., New Delhi (1966).
 6. H. Hamatava, *Bull. Chem. Soc. (Japan)*, **31**, 95 (1958).
 7. H.H. Joffe and M. Orchin, *Theory and Application of Ultraviolet Spectroscopy*, John Wiley & Sons Inc., p. 284 (1964).
 8. I.M. Procter, B.J. Hathway, D.E. Billing, R.P. Pudley and P.J. Nichil, *J. Chem. Soc.*, 1192 (1964).
 9. C.J. Ballhausan, *Dan. Mat. Fus. Model*, **29**, 4 (1954).
 10. H. Bethe, *Ann. Physik. Chem.*, **197**, 239 (1951).
 11. L.E. Orgel, *J. Chem. Soc.*, 4756 (1952).
 12. O.G. Holmes and D.S. Mac-Clue, *J. Chem. Phys.*, **26**, 1686 (1967).
 13. C.K. Jorgensen, *Acta Chem. Scand.*, **10**, 887 (1956).
 14. G.M. Burrow, R.H. Kruger and F.J. Baxolo, *J. Inorg. Nucl. Chem.*, **2**, 340 (1950).
 15. M.K. Kum and A.E. Martell, *Biochem.*, **3**, 1169 (1964).
 16. H. Sigel and R.B. Martin, *Chem. Rev.*, **82**, 385 (1982).
 17. N. Nichollas and B.A. Warburton, *J. Inorg. Nucl. Chem.*, **33**, 1941 (1971).
 18. P.K. Bhattacharya, *J. Sci. Ind. Res.*, **40**, 382 (1981).

(Received: 15 July 2000; Accepted: 4 October 2000)

AJC-2136