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NOTES

Spectroscopic Studies on Ternary Complexes of Copper(II) with Some Amino Acids

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[Cu(AB)] complex has been prepared where A is primary ligand *i.e.* valine and B is secondary ligand *i.e.* serine.The electronic and ESR spectra of the complex suggest the geometry of the complex to be distorted octahedral and it prossess D_{4h} symmetry.

Keeping in view the increasing importance of mixed ligand complexes in proposed biological systems to synthesise some mixed ligand complexes of copper(II) with amino acids of the type [Cu(AB)] where A is primary ligand valine and B is secondary ligand namely serine. This complex is characterised on the basis of elemental analysis, Infrared spectroscopy, electronic spectra and electron spin resonance studies. The results of elemental analysis suggest that the molecular formula of the complex is [Cu(AB)] type, electronic, IR and ESR studies suggest that these ternary complexes. *i.e.* [Cu(Val)(Ser)] have distorted octahedral geometry[1]. The symmetry of the complex may assumed to be D_4h.

Synthesis of the Complex

An equimolar solution of DL-valine and the secondary ligand serine was heated on water bath for 2 h. with slight excess of freshly precipitated copper hydroxide. The solution was filtered while hot. The filtrate was concentrated on water bath. The pH of the solution was maintained 7 because at pH 7 ternary species are predominant. In the concentrated hot solution a small amount of absolute alcohol was added with constant stirring. Then the complex was allowed to crystallise. Intense blue complex was formed which is soluble in water but insoluble in organic solvents like ether, alcohol etc. It was washed with alcohol and water. It was dried in vacuum at 50°C.

The results of elemental analysis % found (Calc),

$C = 33.93$ (33.86), $H = 5.08$ (5.16) and $N = 9.73$ (9.87) are in conformity with the formulation [Copper (Valine) (Serine)].

An asymmetric broad and weak band is observed at about 16260 cm^{-1}. ν_{max} and extinction coefficient ε_{max} values indicate that the geometry of the complex is tetragonally distorted octahedron[2]. The ν_{max} of the complex is 16260 cm^{-1} which suggest that tetrahedral geometry is not possible as ν_{max} is 8000 to 11500 cm^{-1} for it. This complex may be assumed to be *trans* isomer[1] with D_2h local symmetry based on the apearence of only one band. The symmetry of the complex may be assumed to be D_4h in which N-atoms are taken equivalent to O atoms.

The change in concentration of the solution does not alter the value of ν_{max}, hence the complex does not undergo dissociation or association.

There is an absorption peak observed at about (233) 295 in ultraviolet region for the complex which may be due to charge transfer from amino acid to Cu(II) ion[3]. The coordination of the nitrogen atom of the NH_2 with metal ion is indicated by the downward shift of the NH band to 3250 cm^{-1} in the IR spectra of the complex[4–6]. Nitrogen ligation is further supported by the shift in the δ(NH) frequency which appears at 1650 cm^{-1} in free ligand and in the region 1600 cm^{-1} in the complex. In the far IR spectra ν(M–O) and ν(M–N) modes appear in the ranges 400 cm^{-1} and 320 cm^{-1} respectively.

The ESR spectra of the complex suggest that complex is paramagnetic in nature with one unpaired electron (magnetic moment 1.83 B.M.) The value of both $g_{(av)\,(exp.)}$ and $g_{(av)\,(Theo)}$ are almost equal but they are greater than the value of g_o *i.e.* 2.0036. This indicates that an amount of distortion from the regular octahedron[7] has taken place in the shape of the complex. This supports the conclusion drawn from electronic spectral studies. The values reveals that $g_{11} > g_1 > g_0$ in each case. This indicates[8] that the distortion is due to elongation along Z axis and that the unparied electron is present in $d_{x^2-y^2}$ orbitial (Table 1).

TABLE 1

ESR SPECTRAL PARAMETERS FOR TERNARY COMPLEX OF Cu(II)

H_o for D.P.P.H. = 3414 G

Complex	ESR Parameters							
	g_{av} (Theo)	g_{av} (exp)	g_{11}	$g_{\perp}$	A_{11}	$A_{\perp}$	$\lambda\ cm^{-1}$	μ_{eff} B.M.
[Cu(Val)(Ser)]	2.1238	2.1276	2.1780	2.090	115	57.5	495	1.83

The negative value of λ lie between 450–500 cm^{-1} shows a great delocalization[8] of the unpaired electron and also that the separation between big and other lower lying orbitals decreases[9] as compared to the free ion values.

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