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Synthesis and Characterisation of Some Mixed Ligand Complexs of Cu(II) with 2,2′-Bipyridylamine and Phenols

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Mixed ligand complexes of Cu(II) with 2,2′-bipyridylamine and phenols, *viz.*, catechol, pyrogallol, 2,3-dihydroxynaphthalene or protocatechuic acid have been synthesised and characterised by modern methods like elemental analysis, infrared spectra, thermogravimetric analysis, magnetic moment, electronic spectra and conductivity measurements. All complexes are found to be coloured.

Key Words: Synthesis, Isolation, Cu(II), Mixed ligand chelates, 2,2′-Bipyridylamine, Phenols

INTRODUCTION

Transition metals are well known for their biological relevance[1]. Synthesis, isolation and characterisation of mixed ligand complexes of metal ions is an active field of research now-a-days[2–7]. Copper participates in many biological reactions like bindng of dioxygen, activation of dioxygen, electron transfer, dimutation of superoxide[8] and is found in brain and heart tissue as copper thionein and released in the form of complex with serum albumin[9]. Its biological importance has tempted us to carry out this study. Presently we have synthesised and characterised mixed ligand complexes of Cu(II) with 2,2′-bipyridylamine(A) and phenols, *viz.*, catechol, pyrogallol, 2,3-dihydroxy naphthalene and protocatechuic acid.

EXPERIMENTAL

The primary ligand 2,2′-bipyridylamine (Fluka) and sodium hydroxide (E. Merck) were used. The aromatic phenols such as catechol, pyrogallol, 2,3-dihydroxy naphthalene and protocatechuic acid of BDH Analar grade were used. A stock solution of Cu(II) perchlorate was prepared and standardised by complexometric method[10]. Conductivity water was used throughout the experiment.

Isolation of complexes

The complexes were isolated by adding 0.5 M 10 mL 2,2′-bipyridylamine solution in ethanol to 10 mL 0.5 M aqueous solution of Cu(II) perchlorates at 30°C. After stirring well, 0.5 M 10 mL catechol, pyrogallol, 2,3-dihydroxynaphthalene or protocatechuic acid was added slowly with constant stirring. There was no immediate precipitation. The pH was raised to *ca.* 7.0 using

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0.1 N NaOH solution, resulting in the precipitation of the solid. The complex obtained was washed well in 1 : 1 mixture of ethanol and water so as to remove excess of ligand and unreacted metal. All complexes were dried and kept in vacuum desicator.

Elemental analyses were performed with Column C, H, N analyser. The metal content[11] was determined by titration with standard disodium salt of EDTA after decomposing with a mixture of concentrated nitric acid, perchloric acid and sulphuric acid in the rates of 5 : 2 : 3. The magnetic susceptibilities were measured by the Gouy method at room temperature using $Hg[Co(CNS)_4]$ as calibrant. The IR spectra were recorded on Perkin-Elmer model 983 spectrophotometer. The samples were run as KBr pellets. The UV-visible reflectance spectra were measured on Beckman DK-2A spectrophotometer. Thermal measurements were performed using Du-Pont Thermal Analyser at a 10°C min heating rate.

RESULTS AND DISCUSSION

The analytical data for all the complexes are given in Table-1. All chelates synthesised are coloured air-stable and non-hygroscopic. These chelates are insoluble in water and some other organic solvents like benzene, chloroform, acetonitrile, nitrobenzene etc. but partially soluble in ethanol, DMSO and DMF. The analytical data of complexes (Table-1) indicate 1 : 1 : 1 stoichiometry.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE Cu(II) COMPLEXES

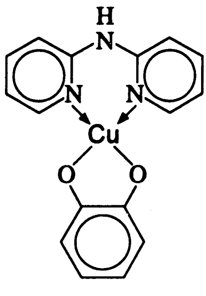
Compound (m.f.) (colour)	Decomp. temp. (°C)	Yield (%)	Analysis %: Found (Calc.)				μ_{eff} (B.M.)
			Cu	C	H	N	
A	200	67	17.55	52.98	4.05	11.23	1.8
$CuC_{16}H_{15}N_3O_3$			(17.60)	(53.18)	(4.15)	(11.63)	
(Dark grey)							
B	210	72	16.77	50.60	4.00	11.00	1.8
$CuC_{16}H_{15}N_3O_4$			(16.85)	(50.92)	(3.97)	(11.14)	
(Dark brown)							
C	225	66	15.41	58.12	4.07	10.09	1.8
$CuC_{20}H_{17}N_3O_3$			(15.46)	(58.39)	(4.13)	(10.21)	
(Dark yellowish brown)							
D	215	68	16.53	52.22	3.70	10.68	1.8
$CuC_{17}H_{15}N_3O_4$			(16.33)	(52.44)	(3.85)	(10.79)	
(Dark brown)							

A = [Cu.·2,2′-bipyridylamine·catechol]·H_2O
B = [Cu·2,2′-bipyridylamine·pyrogallol]·H_2O
C = [Cu·2,2′-bipyridylamine·2,3-dihydroxy naphthalene]·H_2O
D = [Cu·2,2′-bipyridylamine·Protocatechuic acid]·H_2O

IR spectra of the complexes exhibit bands corresponding to 2,2′-bipyridylamine and phenols (*i.e.*, catechol, pyrogallol, 2,3-dihydroxy naphthalene, protocatechuic acid) and metal complexes. In all metal chelates, the presence of water molecules[12] is shown by broad absorptions at 33580–3440 cm^{-1} allowed by some additional bands at 690, 680, 920 cm^{-1} which are assigned to M—OH_2 band[13].

The phenols show a broad IR band at 2750 cm^{-1} which is due to intermolecular hydrogen bonding involving hydrogen of phenolic group[14]. The band has virtually disappeared in the chelates, indicating that the replacement of hydrogen of phenolic group has taken place by the metal ions. The ν(C=N) bands appear at 1670–1665 cm^{-1} in metal complexes as compared to 1660 cm^{-1} in 2,2′-bipyridylamine. The increase (5–10 cm^{-1}) indicates the coordination of nitrogen of 2,2′-bipyridylamine with metal ion. The broad band ν(C=N) at 1230–1220 cm^{-1} in phenols appears at 1240–1230 cm^{-1} in the chelates, thus showing a shift towards higher region by 10 cm^{-1}. This characteristic band supports the formation of (Cu—O) bond[15, 16]. In addition, all the chelates show some more absorptions at 460–420 cm^{-1} and 580–560 cm^{-1} which can be assigned to ν(Cu—O) and ν(Cu—O—C) bonds respectively[17, 18]. The ν(Cu—N) stretching frequencies in 2,2′-bipyridylamine chelates are obtained at higher wave number because of double bond character of Cu—N band due to Cu—N π interaction[19]. The band at 780 cm^{-1} and 640 cm^{-1} in metal chelates corresponds to ν(Cu—N) stretching[20]. The magnetic moment values of all complexes obtained from the corrected magnetic susceptibilities[21] are presented in Table-1. At room temperature the magnetic moment value of the Cu(II) complex (1.86 B.M.) indicates the presence of one free electron. The electronic spectrum exhibits three bands at 14700, 21000 and 25000 cm^{-1} corresponding to $^3B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2E_g$ and charge transfer, respectively[22, 23]. These observations suggest square-planar structure for Cu(II) complexes.

Thermograms of Cu(II) complexes of phenols exhibit endothermic peaks[24] and the percentage mass loss was found to correspond to water molecules. According to Nikolaev *et al.*[25] water eliminated below 140°C can be considered as lattice water and that eliminated above 140°C may be coordinated to metal atom. The TGA study suggests the absence of coordinated water and intermolecular hydrogen bonding in isolated complexes because water molecules are lost at 130°C and decomposition of complexes takes place above 200°C. On the basis of the above study, a tetra-coordinateed square-planar structure is suggested for Cu(II) chelates and the structure proposed for Cu(II)-2,2-bipyridylamine-catechol is as under:



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