

Synthesis and characterization of Copper (II) complexes

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ABSTRACT

The complexes of Cu(II) with Schiff bases viz Bis (2-hydroxynaphthaldehyde) malonoyl dihydrazone (BNHMDH), 5-Chloro salicylaldehyde isonicotinoyl hydrazone (SIH) and 5-Chloro salicylaldehyde morpholine N thiohydrazones, (SMTH) are formed. The schiff base BNHMDH was formed by 2-hydroxy naphthaldehyde and malonoyl dihydrazone, SIH was formed by 5-chloro salicylaldehyde and isonicotinoyl hydrazone and SMTH was formed by 5-chloro salicylaldehyde and morpholine, ESR, electronic and infrared spectral studies and electrical conductivity data suggests square planar geometry.

Key words : Copper (II) complexes, Schiff bases.

INTRODUCTION

The chemistry of copper(II) plays important role in our life. About 4-5mg of copper are required daily. The deficiency of copper in animals results in the inability to use iron stored in the liver. The copper is bound to proteins in the body either as metalloproteins or as enzymes. There are several blue proteins contain copper and act as electron transfer agents by means of $\text{Cu}^{++}/\text{Cu}^+$ couple. These are coloured. eg.: - plastocyanin (occurs in chloroplasts) and azurin (found in bacteria).

The Schiff bases are an important class of ligands in coordination chemistry and have many applications¹ in various fields. The Schiff bases complexes have wide applications in food industry, dyes industry, analytical chemistry, catalysis, fungicidal and agrochemical activity²⁻⁴.

The Schiff base complexes with transition metals have played a prominent role in the development of coordination chemistry⁵. There are many Schiff base metal complexes have been

studied due to their industrial and biological applications⁶⁻⁷.

RESULTS AND DISCUSSION

In this an attempt has been made to characterize and a discussion about various Cu(II) complexes.

IR spectra

The IR spectra of BNHMDH show bands at 1697 cm^{-1} and 1661 cm^{-1} which may be assigned to $\nu\text{C}=\text{O}$ and $\nu\text{C}=\text{N}$ stretching vibrations. The spectrum of the complex shows the absence of bands in the region of $1700-1630\text{ cm}^{-1}$ in combination with the presence of two strong bands of almost equal intensity in the $1630-1597\text{ cm}^{-1}$ region attributable to stretching vibrations of $\nu\text{C}=\text{N}$ group⁸, indicates the condensation of NH_2 group of malonoyl dihydrazine with $>\text{C}=\text{O}$ group of 2-hydroxy-1-naphthaldehyde leading to the formation of $\text{C}=\text{N}$ linkage. Further the complex does not show any band in the region of $3550-3000\text{ cm}^{-1}$ which could be assigned to stretching vibration of either NH group

or NH_2 group of hydrazide such features of IR spectrum of complexes indicates the generation of bis (2-hydroxy-1-naphthaldehyde) malonoyl dihydrazone and its co-ordination to the metal centre in the enol form through $\text{C}=\text{N}$. The ligand appears to acting in bidentate manner.

The ir spectrum of the complexes shows a strong band of 3250cm^{-1} which may be due to νOH vibration of either co-ordinated water molecule or naphtholic OH group.

The ir spectrum of SIH indicates few important bands especially at 1606cm^{-1} which shifts to 1620cm^{-1} in the spectrum of the complex. This indicates the involvement of azomethine nitrogen atom to the metal centre⁹.

The band at 1288cm^{-1} is due to C-O vibration splits in to two components showing shifts to higher frequency indicating co-ordination through phenolate oxygen¹⁰. The pyridyl ring breathing vibrations appearing at 1001cm^{-1} as weak band in free hydrazone remains almost unshifted in position ruling out the possibility in involvement of pyridyl ring nitrogen atom in co-ordination¹¹. Therefore the complex appears to be acting in monobasic bidentate manner co-ordinated through phenolate oxygen atom and azomethine nitrogen atom. The ir spectra of SMTH ligand and their metal complexes have been recorded. The metal complex indicates that in the complex both phenolic OH and $\nu\text{C}=\text{S}$ disappeared and a new band at $760\text{-}745\text{cm}^{-1}$ was observed suggesting co-ordination of metal ion through thiol sulphur and phenolic oxygen via deprotonation¹². The lowering of $\nu\text{C}=\text{N}$ by 15cm^{-1} indicates co-ordination of azomethine nitrogen atom which is further substantiated by the appearance of azine chromophore ($>\text{C}=\text{N}-\text{N}=\text{C}<$) around 1600cm^{-1} ¹³. Thus in these complexes the ligand functions in a dibasic tridentate fashion through O, N and S atoms.

The spectrum of complexes also shows new bands as 3350cm^{-1} , 800cm^{-1} and 900cm^{-1} might be attributed to rocking and wagging modes of co-ordinated water molecules¹⁴⁻¹⁶. The far IR spectrum of the complexes show some additional bands at 400 , 340 , 279 , 200 , 330cm^{-1} which may be assign to M-O, M-N, M-S, M-Cl vibrations respectively.

Table 1: Physical and analytical data of copper (II) complexes

S. No.	Name and Molecular Formula of complexes	colour	m.p.	Element analyses			Magnetic moment in B.M.	Molar conductance $\text{ohm}^{-1}\text{mol}^{-1}\text{cm}^2$	
				C%	H%	N%	M%		
1.	Bis(2-hydroxynaphthaldehyde malonoyl dihydrazone copper (II) Chloride $\text{C}_{24}\text{H}_{16}\text{N}_4\text{O}_4\text{CuCl}_2$)	Greenish blue	320	51.52 (57.90)	2.89 (2.79)	10.01 (11.11)	11.40 (10.00)	1.79	1.55
2.	5-Chloro salicylalddehyde isonicotinoyl hydrazones copper(II) chloride $(\text{C}_{13}\text{H}_9\text{O}_2\text{N}_3\text{Cl})_2\text{Cu}$	Dirty green	305	50.89 (51.90)	2.93 (2.87)	13.70 (14.09)	10.44 (10.05)	1.76	4.93
3.	5-Chloro salicylalddehyde morpholine N thio hydrazone copper(II) chloride $(\text{C}_{21}\text{H}_{15}\text{O}_2\text{N}_2\text{SCl})_2\text{CuCl}_2 \cdot 3\text{H}_2\text{O}$	Greenish blue	310	2.45 (3.41)	4.29 (4.92)	8.58 (8.45)	13.07 (12.05)	1.84	5.92

The electronic spectra of Cu(II) complex exhibit a broad unsymmetric band in the visible region at 15010cm^{-1} and a sharp band to high intensity ($\epsilon=1001\text{ mol}^{-1}\text{ cm}^{-1}$) at 25960 cm^{-1} . The broad unsymmetric band at 15010cm^{-1} may be assigned to ${}^2T_{2g} - {}^2E_g$ transition in the octahedral geometry. The band at 25960 cm^{-1} may be due to ligand metal charge transfer. These bands are characteristics of square planer geometry¹⁷⁻²⁰.

The ESR Spectra of polycrystalline complexes of Cu(II) at 295 and 77K exhibit an axial type of signal with two g values. The Cu(II) hyperfine line could not be resolved in any of these complexes at both these temperature. This may be attributed to the strong dipolar and exchange interactions between Cu(II) ions in the unit cell. The principal g-values were calculated using the procedure of Kncubuhi²¹ which indicate an essentially $dx^2 - y^2$ ground state for the Cu(II) ion. The G parameter is in the range of 3.5-6.5 suggests that the exchange interactions between Cu(II) centre in negligible and the local tetragonal axes of the molecule in the unit cell are aligned parallel or only slightly misaligned²².

Axial symmetry of the complexes and the trend $g_{\parallel} > g_{\perp} > 2.06$ shows that the ground state of copper (II) is predominantly $dx^2 - y^2$. The slight difference in g-values at 295-77K observed in some of these complexes may be attributed to the fluxional nature of geometries or the inaccuracies in the g-value brought about by the broadening effect due to dipolar exchange and unresolved hyperfine interactions²³.

The elemental analysis reveals that the Cu(II) complexes have the compositions BNHMDH $C_{24}H_{16}N_4O_4CuCl_2$, SIH $(C_{13}H_9P_2N_3Cl)_2Cu$ and SMTH $(C_{12}H_{15}O_2N_2SCl)CuC_{12} \cdot 3H_2O$. The electrolytic nature of copper (II) complexes at 10^{-3} M dilution measured in DMF, DMSO and methanol indicate that SIH and SMTH have non electrolytic nature where as BNHMDH has 1:2 electrolytic nature.

The copper (II) complexes are paramagnetic in nature. The value of magnetic moment varies from 1.76 to 1.84BM which is very close to the calculated value of d^1 system. The copper (II) complex appears to have square pyramidal geometry.

EXPERIMENTAL

All the chemical used were of A.R. grade, M.Ps were taken in open capillaries are uncorrected. Elemental analysis was carried out at RSIC CDRI, Lucknow. Conductivity measurements was carried out at Philips conductivity bridge model PR 9500 with a dip type conductivity cell at Dept. of Chemistry, Bareilly College, Bareilly. The conductance of complexes was measured in methanol, DMF and DMSO at 10^{-3} M dilutions (25°). Magnetic susceptibility of the complexes was determined by Gouby method at the Dept. of Chemistry Bareilly. The sample tube was calibrated with $CuSO_4$. The IR spectra of complexes were recorded with Perkin Elmer spectrometer model 651 in KBr phase at RSIC, CDRI Lucknow. The visible spectra were recorded with Beckman Du-2 spectro photometer in the range of 750 cm^{-1} to 300 cm^{-1} at Dept. of Chemistry, Bareilly College, Bareilly.

Preparation of schiff bases

The schiff bases were prepared by the condensation of respective carbonyl and amino compounds. The amino compounds were dissolved in ethanol and refluxed for about half an hour. The requisite amount of carbonyl compounds was added to the flask and this mixture was refluxed for about six hours and kept for 24 hours. The crystals of ligand were obtained and purified by recrystallisation.

Preparation of Cu(II) complexes

Copper (II) acetate monohydrate was dissolved in 50ml. hot methanol. The ligand was heated under reflux in methanol on a water bath for 30 minutes. The schiff base solutions were added to the copper (II) solutions slowly with constant stirring and the mixture was refluxed with magnetic stirring for 2 hours. The separated green ppt. was filtered off, washed thoroughly with methanol and dried *in vacuo* at room temperature.

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