ANALYTICAL and EXPERIMENTAL ANALYSIS of Cu(II) METAL COMPLEXES

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ABSTRACT

Cu(II) metal ions has their own biological importance in medicinal chemistry. we have synthesized Cu(II) complexes of known ligand and were characterized by various physico-chemical analytical methods, such as elemental analysis, conductivity measurements, magnetic susceptibility, electronic spectral studies, infrared spectroscopy studies, ^{1}H NMR spectral studies. This study highlights the analytical and experimental aspects of the synthesized complex and ligand.

KEYWORDS: Ligand, Copper(II) metal complexes.

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INTRODUCTION

Metal complexes are having versatile behavior towards the biological activities, catalyst and etc., among the many ligand systems that can be found in the chemical literature, pincer ligands play an important role and their complexes have attracted tremendous interest due to their high stability, activity, and variability.[1-9] metal alkyl complexes have attracted growing research interest over the past two decades not only because they possess versatile[10] These results prompted additional screening for anti-HIV (human immunodeficiency virus) activity against DNA replication in H_9 lymphocytes and cytotoxic activity against eight tumor cell lines[11] Metal complexes involving organic molecular ligands play key roles in chemical analyses biochemical phenomenaand electrochemical processes. In particular, the detection of metal complexes is significant in analytical chemistry, which provides useful information such as metal ion concentrations in certain chemical systems[12,13].

From above literature survey of metal complexes, Cu(II) metal ions has versatile applications in biological, medicinal, catalytic, optical, luminescence and etc., we have synthesized Cu(II) complexes of known ligand and were characterized by various physico-chemical analytical methods, such as elemental analysis, conductivity measurements, magnetic susceptibility, electronic spectral studies, infrared spectroscopy studies, ^{1}H NMR spectral studies. This study highlights the analytical and experimental aspects of the synthesized complex and ligand.

MATERIALS AND METHODS

All reagents and solvents were purchased from Merck (Darmstadt, Germany) chemical AR grade and were used as provided. DPPH and BHA were purchased from Sigma-Aldrich chemical Co. (St. Louis, MO, USA). TLC analysis was performed on alumina sheets precoated with silica gel 60F-254 and SiO2, 200-400 mesh (Merck) was used for column chromatography. 1H (400 MHz), 13C (100.56 MHz) and 77Se (76.29 MHz) NMR spectra were obtained on a Bruker 400 MHz NMR spectrometer. Chemical shifts are cited with respect to SiMe4 as internal (1H and 13C) and Me2Se as external (77Se) standards. Mass spectral studies were carried out on a Bruker Daltonics 6000 plus mass spectrometer with ESI-MS mode analysis.

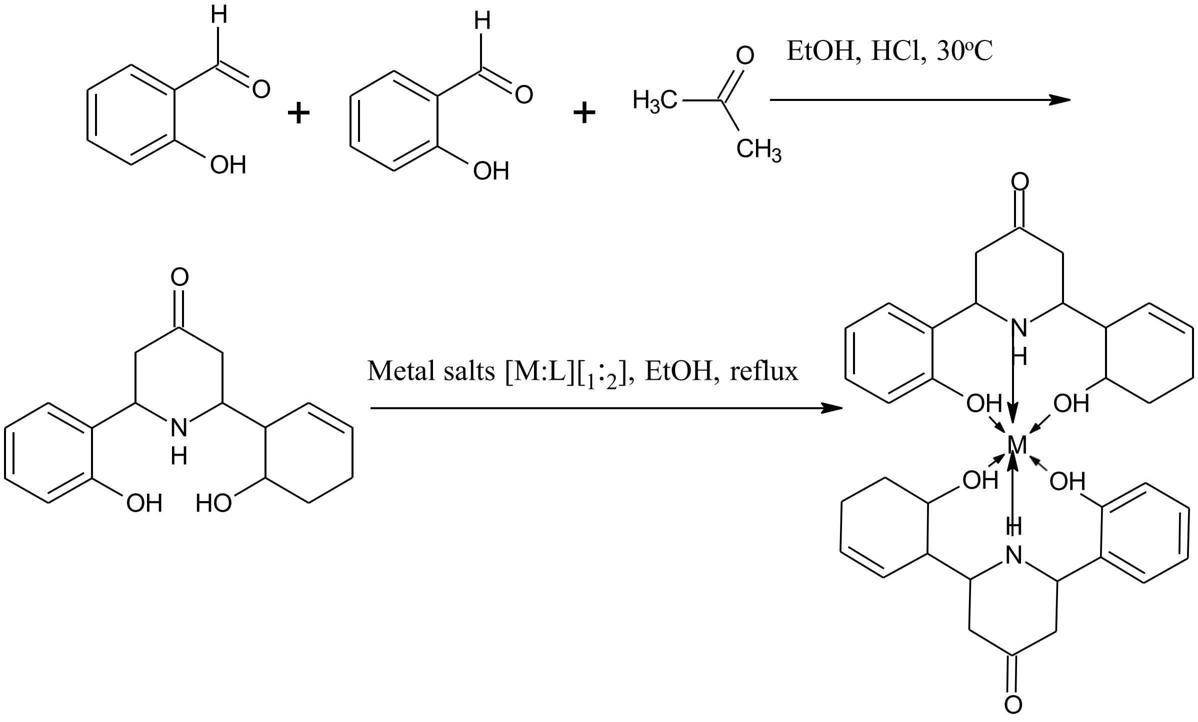
PREPARATION OF LIGAND (L):

Synthesis of 2, 6-bis(2-hydroxyphenyl)piperidin-4-one ligand(L) ($C_{17}H_{17}NO_3$) is similar to that of Niclova et. al., 0.1 mol (7.7 g) of ammonium acetate was dissolved in 30 ml of ethanol and 0.2 mol (21.24 ml) of salicylaldehyde and 0.1 mol (7.35 ml) acetone were added to the solution. The mixture was heated to boiling for 30 min, and set aside for a day. The oily base obtained was converted into its hydrochlorides by the addition of conc. HCl (5 ml) and the separated solid was filtered, dried and recrystallised with liq. NH_3 which upon dilution with water, the free base separated was filtered and recrystallised from absolute ethanol [14].

PREPARATION OF METAL COMPLEXES (M)

Synthesis of metal complexes.

An alcoholic solution of ligand (L) (2 m mol) was refluxed with (1 mmol) of metal chlorides in ethanol on water bath for 2-3 h. Then, to the reaction mixture (2 m mol) of sodium acetate was added and reflux was continued for 3h. The separated complex was filtered, washed thoroughly with water, ethanol and ether. Finally the complexes were dried in vacuum over fused $CaCl_2$[15] .



(L) **M=Cu(II)**

Scheme-1: Synthesis of Ligand (L) and their metal complexes (M)

RESULTS AND DISCUSSION

ANALYTICAL METHODS FOR ANALYSIS

a) Stoichiometry

The stoichiometries of Cu(II) complexes were concluded from their elemental analysis. All the synthesized complexes are colored and are stable in air, non-hygroscopic, have high melting points and are insoluble in water, but soluble in coordinating solvents such as DMF, DMSO, THF as well as acetonitrile. The analytical data are depicted in Table-1. Suggest that the metal : ligand ratio is [1 : 1] & [1 : 2], they can be represented by the general formulae;

$[M(L)_2]$ Where M = Cu(II). L= Ligand,

b) Conductometric studies

All the complexes were anhydrous in nature and insoluble in methanol, ethanol, acetone and benzene. They are soluble in dimethyl sulphoxide and in dimethyl formamide. The general structures of the metal complexes were shown in Scheme-1. The 10^{-3} M solution of the complex in dimethyl sulfoxide (DMSO) was used to determine the molar conductance. The conductivity data reveals that the complexes are non-electrolytic in nature. The metal and anions are estimated using standard procedure (Vogel A. I., 1962). Elemental analysis data are in well agreement with the calculated value and the data are presented in Table-1.

c) Magnetic susceptibility measurements

The magnetic susceptibility measurements of the complexes were obtained at room temperature using Gouy’s balance. Pure $Hg[Co(SCN)_4]$ was synthesized is used as calibration standard. The effective magnetic moment values of the complexes are in Table-2. copper complexes having electronic configuration [Ar] $3d^{10}$ $4s^1$ and Cu(II) ion being a d^9 system has one unpaired electron in 3d shell and its complexes are expected to have magnetic moments close to the spin only value of about 1.91 BM, irrespective of the bond type involved. The magnetic moment of Cu(II) complexes usually lies in the range 1.75-1.91 BM have no major interaction between the unpaired electron on different manganese ions and essentially temperature independent[16].

d) Electronic spectral measurements

The Electronic Absorption Spectral Studies of ligands (L) and some of metal complexes had carried out in the region 250-1100 nm was measured by spectrophotometer. Weighed samples were dissolved in appropriate DMF of HPLC grade at a concentration of 10^{-6} and 10^{-7} M. were measured and carried out at room temperature. The electronic absorption spectrum of the Ligands is depicted in Table-2. and Figure-1. Exhibited two absorption bands around 340 nm and 420 nm respectively. The first band around 340 nm corresponds to Π→Π* of the nitrogen contain group and second band at 420 nm corresponds to n→ Π* transitions. The new Cu(II) complexes are paramagnetic, indicating the presence of copper in the +2 oxidation state. The electronic spectra of all the complexes in DMSO show a band in the 270–285 nm region. This band has been assigned to the charge-transfer transition arising from the excitation of an electron from the metal $t^2{}_g$ level to the unfilled molecular orbitals derived from the p^* level of the ligands, in accordance with the assignments made for other similar octahedral copper(II) complexes[17].

e) FT-IR spectral studies

The structure of ligand confirmed by using IR spectrum. The imported infrared spectral data of prepared Ligands and their metal complexes are represented in Table-3. And spectrums are presented in supplementary data. The IR discussions of ligand and metal complexes are as follows,

Ligand (L); In Ligand (L) showed a broad band at 3000-2500 cm^{-1} indicated the presence of the -O-H group in the ligand which is disappear after the complex formation revels that the M-O bond formation, this band appears near far-infrared region i.e., 500-450 cm^{-1}. A medium band at 1360-1250 cm^{-1}, which was assigned to the formation of the C-O group and also a medium band of the primary amines groups appears at about 1750-1650 cm^{-1} this band frequency slightly shifted to 15-25 cm^{-1} due the formation of complexes of M-N bond this band appears near far-infrared region i.e., 450-410 cm^{-1} [18].

f) ^{1}H NMR spectral studies

The ^{1}H NMR data the ligands and metal complexes are presented in Table-4. The ^{1}H-NMR spectra were recorded in DMSO-d_6 in a multiplet from δ(7.89-8.01) ppm for aromatic protons (Ar-H) in ligand (L). In ligand (L) the signals within the range of δ(1.31-1.55) ppm are attributable to aromatic ring protons and the signal range in between δ(6.98-6.04) ppm for N-H proton, The O-H proton shows peak between δ(7.68-6.64) ppm and at δ(2.78-2.89) signal attributed for the –CH proton[18]

CONCLUSION

Work described here is involved the synthesis and spectroscopic characterization of copper(II) complexes with a new 2, 6-bis(2-hydroxyphenyl)piperidin-4-one ligand. These complexes were characterized by using different physiochemical techniques. These complexes are all neutral and found to have an octahedral geometry with the six donor atoms.

Table-1; Elemental analysis, melting point, molecular weight and molar conductance data of ligand and their metal Complexes

Sl. No.	Compounds	Yield (%)	Mel.point (°C)	Molecular Weight	Elemental analysis Calc. (found) (%)						Molar conduct.(Ohm^{-1}cm^{-2}mol^{-1})
					M	C	H	N	O	anion	
1	L ($C_{17}H_{17}NO_3$)	67	191-193	283	--	72.07 (72.30)	6.05 (6.61)	4.94 (5.01)	16.94 (17.05)	-	10.58
2	$[Ru(C_{17}H_{17}NO_3)_2]$	72	221-222	665	9.77 (9.81)	72.51 (72.55)	6.67 (6.70)	5.00 (5.04)	17.01 (17.10)	-	16.21
3	$[Cu(C_{17}H_{17}NO_3)_2]$	78	205-206	639	8.41 (8.45)	72.81 (72.86)	7.17 (7.18)	5.40 (5.41)	17.13 (17.14)	-	15.47
4	$[Co(C_{17}H_{17}NO_3)_2]$	73	201-203	629	8.30 (8.35)	72.81 (72.83)	8.62 (8.64)	4.51 (4.53)	17.41 (17.42)	-	13.54
5	$[Ru(C_{17}H_{17}NO_3)(Cl)]$	67	224-225	417	12.51 (12.53)	70.62 (70.70)	7.21 (7.22)	4.87 (4.89)	17.70 (17.72)	12.51 (12.55)	12.47
6	$[Cu(C_{17}H_{17}NO_3)(Cl)]$	68	210-211	391	8.30 (8.35)	73.21 (73.24)	7.52 (7.54)	4.28 (4.28)	16.72 (16.74)	8.30 (8.32)	11.64
7	$[Co(C_{17}H_{17}NO_3)(Cl)]$	75	184-185	381	8.30 (8.35)	71.26 (71.30)	5.58 (5.61)	5.03 (5.05)	17.71 (17.78)	8.30 (8.35)	16.41

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