



SPECTROSCOPIC AND ANTIMICROBIAL STUDIES OF MIXED LIGAND COMPLEXES OF TRANSITION METAL (II) IONS WITH NITRO QUINOLINE AND DIBENZOYL METHANE

NEERAJ SHARMA^{*}, RAVI PRAKASH^a and K. CHATURVEDI^b

Department of Chemistry, Institute of Applied Science, GLA University, 17 Km Stone NH-2 Mathura Delhi Road,
P.O. Chaumuha, MATHURA – 281406 (U.P.) INDIA

^aDepartment of Chemistry, B. S. A. College, MATHURA (U.P.) INDIA

^bDepartment of Chemistry, Agra College, AGRA (U.P.) INDIA

(Received : 17.01.2012; Revised : 28.01.2012; Accepted : 30.01.2012)

ABSTRACT

The mixed ligand complexes of Co (II), Ni (II), Cu (II) and Zn (II) with Schiff bases N-(2-hydroxy-1-naphthylidene)-4-chloroaniline (L1H) and N-(2-hydroxybenzylidene)-2,3-dimethylaniline (L2H) have been synthesized and characterized. The resulting complexes were characterized by elemental analysis, thermogravimetric analysis, magnetic moment measurements, conductivity measurements, ¹H NMR, IR, UV-visible and ESR spectral studies. The Schiff bases acts as bidentate monobasic ligands, coordinating through deprotonated phenolic oxygen and azomethine nitrogen atoms. The complexes are non-electrolytic in DMSO. The presence of the two coordinated water molecules in these complexes was indicated by IR spectra and thermogravimetric analysis of the complexes. From the analytical and spectral data the stoichiometry of these complexes have been found to be [M (L1) (L2) (H₂O)₂] {where M = Co (II), Ni (II), Cu (II) and Zn (II)}. It is found that Co (II), Ni (II), Cu (II) and Zn (II) complexes exhibited octahedral geometry. The antimicrobial activities of ligands and their mixed ligand complexes were screened by Disc Diffusion method. It was found that the metal complexes have higher antimicrobial activity than the free ligand.

Key words: Schiff bases, Mixed ligand, Metal complexes, Antimicrobial activity.

INTRODUCTION

In chemistry, a complex, also called a "coordination compounds" or "metal complex", is a structure consisting of a central atom or molecule connected to surrounding atoms or molecules. Originally, a complex implied a reversible association of molecules, atoms, or ions through weak chemical bonds. As applied to coordination chemistry, this meaning has evolved. Some metal complexes are formed virtually irreversibly and many are bound together by bonds that are quite strong.

Copper is a transition metal, which in the zero oxidation state has an electron configuration of [Ar]4s²4p⁶3d⁹. Copper is found in three different oxidation states: Cu (I), Cu (II) and Cu (III). Copper (I) atoms have 10 d electrons. Cu (I) complexes being d¹⁰ have no Jahn-Teller distortion. Cu (I) complexes are diamagnetic and typically colorless. If a Cu (I) complex is colored, the color is a result of a charge transfer

band or an internal transition in a ligand¹⁻⁴. In the copper (II) oxidation state, the metal has 9 d electrons. Jahn-Teller distortion causes a splitting of e_g and t_{2g} orbitals. Most Cu (II) complexes are square planar for this reason. Usually observed in the electronic spectra of Cu (II) complexes is a single broad, poorly resolved band envelope. This envelope is typical of Cu (II) complexes in tetragonal complexes. These complexes are generally blue or green because of an absorption band in the 600-900 nm region of the spectrum.

Reproducing complex biological reactivity within a simple synthetic molecule is a challenging endeavor with both intellectual and aesthetic goals⁵⁻⁸. The sequence of examining biological reactivity, creating similar chemical architectures, and determining functional. Reaction conditions for model systems is a process that allows the biological code of reactivity to be deciphered. In the past years the report on the crystal structures of type 3 copper enzymes (e.g. catechol oxidase, hemocyanins, and tyrosinase), as too type 2 – type 3 copper enzymes (e.g. ascorbate oxidase, laccase, ceruloplasmin) has taken a new turn. The greater availability of such structural information now allows a shift in the role of synthetic modeling from structural and spectroscopic endeavors to development of functional and catalytic models. Functional models can provide an opportunity to examine a biological reactivity at a small-molecule level of detail through systematic and comparative studies. Although one goal of modeling is reproduction of reactivity, extension of this reactivity beyond the scope of the inspiring system is perhaps an even more important objective. Adequate synthetic models that have similar structural, spectroscopic and functional properties of active sites of copper proteins are done. These models provide many elegant examples of selective and environmentally benign oxidants capable of performing interesting organic transformations and many of these are copper complexes that use dioxygen as the ultimate oxidant above all in the catecholase activity.

The coordination chemistry of copper (II) attracts much attention because of its biological relevance and its own interesting coordination chemistry such as geometry, flexible redox property, and oxidation state⁹⁻¹². Nowadays, coordination compounds have been known to be useful in constructing molecular information processing systems, particularly by biological self-organizing processes^{13,14}. Especially for this purpose, synthesis, and structural and chemical characterization of copper complexes has been attempted to mimic metalloenzyme¹⁵⁻¹⁹. Recently, we tried to prepared new materials for electric devices. In a series of those compounds, we have prepared copper (II) complexes containing two nitrato ligands and a 2,2'-dipyridylamine (dpa) derivative ligand²⁰⁻²⁴. The 2,2'-dipyridylamine and its derivatives have been widely used for metal complexes because of their good chelating property, structural flexibility, and feasible reduction property compared with other N,N'-chelating ligand including bipyridine and phenanthroline. Copper (II) complexes ligated by two nitrato ligands and a N,N'-chelating ligand (L), $CuL(NO_3)_2$, are common and some XRD structures have been reported. In those complexes, the coordination numbers varied from 4 to 6 according to nitrato ligating properties.

The aqueous solution coordination chemistry of the transition metal copper is limited to its three accessible oxidation states (I-III)²⁵⁻²⁸. The lowest oxidation state, Cu (I) has a diamagnetic d^{10} configuration and forms complexes without any crystal-field stabilization energy. Complexes of this type are readily prepared using relatively soft polarizable ligands like thioethers, phosphines, nitriles, isonitriles, iodide, cyanide and thiolates. A broad range of coordination geometries is observed. Cu (I) complexes are biologically relevant because they are able to reductively activate molecular oxygen (O_2). However, due to the lability of most Cu (I) complexes, they typically lack sufficient kinetic stability for radiopharmaceutical applications.

Copper (II) exists as a d^9 metal center of borderline softness which favors amines, imines, and bidentate ligands like bipyridine to form square planar, distorted square planar, trigonal pyramidal, square pyramidal, as well as distorted octahedral geometries. Jahn-Teller distortions in six-coordinate Cu (II)

complexes are often observed as an axial elongation or a tetragonal compression. Due to the presence of some crystal-field stabilization energy, Cu (II) is generally less labile toward ligand exchange and is the best candidate for incorporation into radiopharmaceuticals^{29,30}. A third oxidation state Cu (III) is relatively rare and difficult to attain without the use of strong π -donating ligands. These complexes usually adopt a square planar geometry due to the d^8 Cu (III) electron configuration.

Reactions of cupric chloride, nitrate and perchlorate group with dibenzoylmethane and neutral uni and bidentate nitrogen donor ligands in ethanolic medium give series of complexes. The complexes have been characterized on the basis of elemental analysis, molar conductance, magnetic moment, infrared and electronic spectral data.

Copper (II) forms bis- β -diketonate when a cupric salt is treated with a β -diketone in 1 : 2 molar ratio followed by addition of ammonia. However, if the metal ion and β -diketone are taken in 1 : 1 ratio instead of 1 : 2 and then treated with nitrogen donor ligands, mixed ligand complexes are formed. It was therefore thought worthwhile to study the reaction of cupric salts with dibenzoyl methane and some nitrogen donor ligands with a view to preparing mixed ligand complexes.

EXPERIMENTAL

Physical measurements

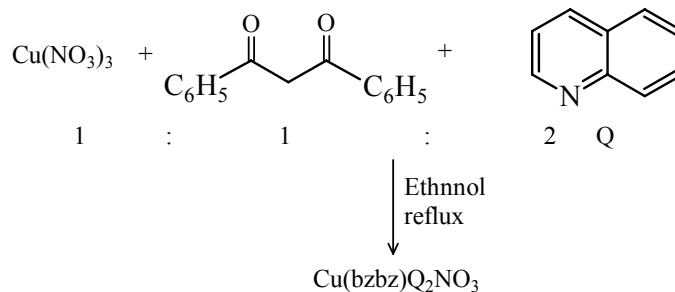
C, H and N analyses were performed by Perkin-Elmer 2400 instrument. FT IR spectra (4000-600 cm^{-1}) as KBr discs of the samples were recorded on a JASCO-460 plus spectrophotometer. Electronic spectra were obtained using a Perkin Elmer Lambda 35 UV/VIS spectrophotometer. Magnetic susceptibility was measured with a Sherwood Scientific MSBMK1 sample magnetometer with Hg [Co (SCN)₄] as calibrant. The molar conductances of $\sim 10^{-3}$ M solution was measured using a systronic direct reading conductivity meter 303.

Chemicals and solvents

All the chemicals used were procured from Merck of AR grade. All solvents used for electrochemical and spectroscopic studies were purified by using standard procedure³¹. Pentane-2,4-dione was purified by double distillation and 1-phenylbutane-1,3-dione, 1,3-diphenylpropane-1,3-dione, pentane-2,4-dione and 5-nitrosalicylaldehyde were purified by recrystallization from ethanol. The complexes were prepared by mixing the molar solutions of metal nitrates & ligands with molar ratio 1:1:1 at pH 6 to 7. The crude obtained were crystallized from ethanol & their purity checked by TLC. The metal nitrates were dissolved in double distilled water and standardized³². The metal content of the complexes were estimated gravimetrically, Cu metal was estimated by ammonium thiocyanate, Ni, Co and Zn metals were estimated by gravimetrically using dimethylglyoxime, ammonium thiocyanate and mercuric thiocyanate respectively³³. The stoichiometric ratio was confirmed by Fengers mass estimation method³⁴.

Synthesis of [Cu(bzbz)Q₂NO₃]

To an ethanolic solution of cupric nitrate, ethanolic solution of dibenzoyl methane was added in 1 : 1 molar ratio. Quinoline was added to this solution in 1 : 2 molar ratio and resulting solution was refluxed for 30 mins. The isolated complex was filtered and washed with ethanol, followed by ether and dried in vacuum desiccator for overnight.



The melting point of the compound was determined.

Compound	Color	M.P. (°C)
Cu (bzbz) Q ₂ NO ₃	shining green	187

RESULTS AND DISCUSSION

Color – The color of the compound was shining green.

Solubility – The compound is insoluble in water but soluble in pyridine and acetone.

Molar conductance

The molar conductance measurement of the Cu (II) complex which was soluble in acetone indicates that the complex is virtually non- electrolytes. The conductance of sample is found to be 0.26 mho cm² mol⁻¹ at 36.5°C.

Magnetic susceptibility

Magnetic susceptibility was determined at room temperature using solid sample by Gouy method. The magnetic susceptibility measurements ($\mu_{\text{eff}} \sim 1.8$ B.M.) indicate that the complex is paramagnetic as expected for a 3 d⁹ ion containing one unpaired electron.

IR Spectra

From the evidence of IR : There is occurrence of NO₂ at 1510 cm⁻¹ and C=C at 1600-1475 cm⁻¹ aromatic (C=C) at 1475 cm⁻¹ and alkene (C=C) at 1600-1680 cm⁻¹, the carbonyl peak at 1654 cm⁻¹ and imine peak (C=N) 1622 cm⁻¹, C=C alkene peak at 1595 cm⁻¹ the NO₂ peak (asymmetric stretching) at 1510 cm⁻¹ and another NO₂ peak (symmetric stretching) at 1313 cm⁻¹.

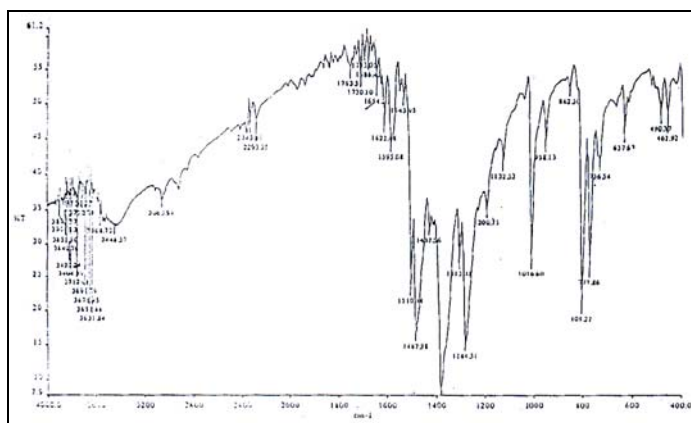


Fig. 1: IR spectra of metal complex Cu (bzbz) Q₂NO₃

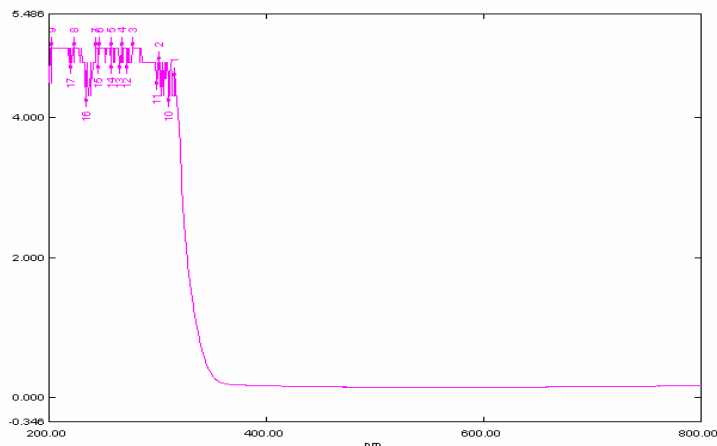


Fig. 2: Electronic spectra of metal complex Cu (bzbz) Q₂NO₃

Electronic spectra

In UV Spectra, the imine peak (C = N) is found at 300-320 nm and carbonyl peak (C=O) peak for dibenzoylmethane is found at 276 nm. The concentration of sample is very less, so there is no peak found centered at 600-639 nm. Therefore, in this region, d-d transition is absent for copper complex^{35,36}.

Expected geometry of metal complex

Since dibenzoylmethane and the nitrogen donors occupy four bonding positions, the complex is definitely a penta-coordinated. Two limiting penta-coordinate geometries for Cu (II) complex are trigonal-bipyramidal and square-pyramidal. Trigonal-bipyramidal Cu (II) complex normally exhibit two distinct bands in the near IR and visible regions. Square-pyramidal Cu (II) complex on the other hand show only one asymmetric absorption in this region³⁷⁻⁴⁰. However, it is difficult to say the type of geometry the complex will adopt only from the electronic spectra. Exact geometry can be established from X-ray crystallographic studies which are now in progress.

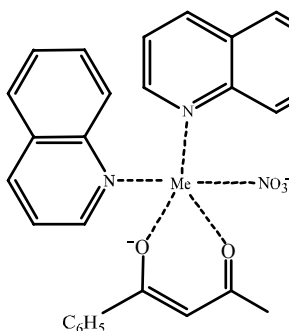


Fig. 3: Structure of expected metal complex of Cu(bzbz) Q₂NO₃

CONCLUSION

We have successfully synthesized the mixed ligand complex of copper (II) containing O-N donor ligands. The complex was also characterized by molar conductance, magnetic susceptibility measurement and also by IR, UV- visible spectroscopy.

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