

A Critical Study of Synthesis, Characterization and Luminescence Studies of Metal-Diimine Complexes

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ABSTRACT

Metal complexes have attracted great interest due to their potential application as luminescent materials in organic light emitting diodes (OLED) in the present technological displays. Through systematic study on the variation of ligands, structural and bonding modes of different metal centers, the structure-property relationships of the various classes of luminescent transition metal complexes can be obtained. The present research reports the synthesis and luminescence studies of some metal-diimine complexes. A diimine ligand namely N,N'-bis- (salicylidene)-4,4'-diaminodiphenylether (3a) was prepared through enamination reaction between diaminodiphenylether with salicylaldehyde in a 1:2 molar ratio. Subsequently, the corresponding Zn(II) (4a) and Cd(II) (4b) complexes were prepared in the presence of base according to a stoichiometric ratio of metal:ligand:NaOH=1:1:2. The synthesized ligand and all the complexes were characterized by CHN elemental analysis, ¹H and ¹³C NMR, UV-Vis and FTIR spectroscopic data and molar conductivity measurements. The spectroscopic data suggested that the ligands acted as N₂O₂-tetradentate, coordinating to the metal atom through both the azomethine N atoms and hydroxyl O atoms. The fluorescence properties of the synthesized metal complexes were investigated. The metal- diimine complexes displayed emission bands centered in the range of 465-490 nm with higher luminescence intensity due to ligand metal-metal charge transfer transitions (LMCT). The relatively large Stoke's shift observed probably indicates that the energy absorbed by the organic ligands was transferred efficiently to the metal ions and merits them to be used as promising emitters in OLED.

Keywords : Synthesis, Characterization, Luminescence Studies, LMCT, OLED

I. INTRODUCTION

Electroluminescent materials have attracted wide attention because of its superiority as emitting materials in latest flat panel displays. In general, there are three different types of electroluminescent materials depending on their structural designs as organic dyes, metal complexes and polymers. Chelated metal complexes which are characteristically heat resistant that resultantly enhance its utility in OLED design as well as their solubility has made them advantageous as it can be fabricated in the form of a layer after solvent evaporation [1,2]. It is well known that 6chi₃ bases

are important compounds not only because of their wide range of biological activities but also as being ligands in complexation with the transition metals. The chelate formation capability of the 6chi₃ base ligands and their different coordination modes with different metal centers through nitrogen atoms of the imine group and other groups attached to the carbonyl compounds such as oxygen atoms have turned them vital in the field of coordination chemistry [3]. These transition metal 6chi₃ base complexes display diverse structural features and, in some instances, exhibit interesting properties namely, anti-bacterial, anti-cancerous, anti-tumorous, analytical reagents, catalytic and luminescent

materials [4-6]. β -diketonate base ligands namely, diimines are able to act as good chelating ligands because of the presence of multiple binding sites which may enhance the luminescence behaviour upon coordinating to two metal ions forming binuclear complexes which exhibit high luminescence behaviour [7,8]. However, reports on the luminescent properties of binuclear β -diketonate base metal complexes are still rare and limited. The studies on binuclear metal complexes in which two metal centres are held in close proximity have attracted considerable interest in metal-metal interaction, spectroscopic properties and luminescence behaviour. These types of complexes still continue to play a very important role in our understanding of various aspects of coordination chemistry of metals. In our attempt to evaluate the luminescence behaviour of binuclear metal complexes, diimine ligand containing a N_2O_2 donor sets and their transition metal complexes of Zn(II) and Cd(II) metal ions were chosen. The diimine ligand synthesized in this study contains a diaminodiphenylether backbone. Coordination of such type of conjugated β -diketonate base ligands with metals increases the rigidity of ligands, which subsequently will reduce the loss of energy via vibrational motions that will subsequently help in improved emission intensity. In addition, the unshared electron pair of nitrogen atoms in the diimines will eventually play a certain role in increasing the luminescence intensity due to the formation of covalent bonds between metal ions and oxygen atoms through π donation of lone pair of electrons on oxygen atoms to the metal ions thus reducing the energy gap between π^* to π orbitals.

Materials and physical measurements All chemicals were purchased commercially either from SigmaAldrich, Merck or Fluka and were used as received without further purifications. Commercial grade solvents used in the preparation of the ligands and metal complexes were distilled according to standard procedures and dried over molecular sieves

before used. All glasswares were thoroughly washed with deionised water and were dried overnight in an oven. All the reactions were carried out in an inert atmosphere of dry nitrogen using degassed solvents. All solid products formed were collected using vacuum filtration and were dried in a desiccator under vacuum before characterization. All the products were characterised by melting point determination, CHN elemental analysis, Fourier Transform Infrared (FTIR) spectroscopy, 1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy, Ultraviolet-Visible (Uv-Vis) spectroscopy and molar conductivity measurements. The melting point of all solid products were determined using an Electrothermal Digital Melting Point apparatus and are not corrected. The CHN elemental analysis for the synthesized samples was determined using Hermo Finnigan EA 1112 series CHN analyzer. FTIR spectra of the synthesized products were recorded as KBr disc using a Perkin Elmer Spectrum One spectrometer at spectral range of 4000 cm^{-1} to 400 cm^{-1} . Solution state Uv-Vis spectra of the samples were recorded on a Shimadzu 1601 spectrophotometer using a quartz cell of 10 mm path length in the wavelength range of 200-800 nm. 1H and ^{13}C NMR spectra of the products were recorded on a Bruker Advance 400 MHz spectrometer using TMS as an internal standard. The NMR samples were dissolved in d_6 -acetone, $CDCl_3$ or d_6 -DMSO. All chemical shifts are reported in ppm relative to TMS. The molar conductivity for the complexes in DMF solution was recorded on a Mettler Toledo FG3/EL3.

II. CONCLUSION

In this research we synthesized symmetrical N_2O_2 diimine (3a) and their Zn(II) and Cd(II) metal complexes displaying dinuclear structure forming the complexes through two nitrogen atoms of azomethine and two oxygen atoms of hydroxyl groups in the tetradentate manner. Metal to ligand stoichiometry in the presence of NaOH as base is 1:1:2. The luminescent

analysis recommends that the large stoke's shift and enhanced luminescence intensity of the complexes enables them to be used as promising electroluminescent emitters in the OLEDs.

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III. REFERENCES

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