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Spectroscopic, electrochemical and biological studies of the metal complexes of the Schiff base derived from pyrrole-2-carbaldehyde and ethylenediamine

Bibhesh K. Singh ^{a,*}, Parashuram Mishra ^b, Anant Prakash ^a, Narendar Bhojak ^c

^a Department of Chemistry, Govt. Post Graduate College, Ranikhet 263645, Uttarakhand, India

^b Bioinorganic & Material Chemistry Laboratory, Tribhuvan University, MMAM Campus, Biratnagar, Nepal

^c Department of Chemistry, Govt. Dungeer College, MGS University, Bikaner, Rajasthan, India

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Abstract The new symmetrical Schiff base *N,N'*bis(pyrrole-2-carbaldehyde)ethylenediamine and its Mn(II), Co(II), Ni(II) and Cu(II) complexes were synthesized and characterized by spectral, magnetic and electrochemical studies. The spectral studies of the complexes reveal that the ligand has coordination through the azomethine nitrogen atoms, pyrrole nitrogen atoms and anions, supported by octahedral geometry. Mass spectrum explains the successive degradation of the molecular species in solution and justifies ML complexes. The electrochemical study indicates that the pyrrole ring stabilizes the metal ion, makes the complex more positively charged, and causes it to be more easily reduced. The molecular structure of the complexes has been optimized by MM2 calculations and suggests an octahedral geometry. Powder X-ray diffraction allows us to determine the cell parameters of the complexes. The bio-efficacy of the ligand and their complexes has been examined against the growth of bacteria in vitro to evaluate their anti-microbial potential.

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1. Introduction

A combination of distinctly different metal ion binding sites within one ligand can lead to materials with interesting new properties such as specific sensors, molecular wires, magnetic and optical devices (Parekh and Patel, 2006). The flexibility

* Corresponding author. Tel.: +91 9760014796; fax: +91 5966220372.

E-mail address: bibheshksingh@yahoo.co.in (B.K. Singh).

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of Schiff base ligands can be improved by hydrogenation of their C=N bonds; they should thus coordinate metal ions more easily. For these reasons, reduced Schiff bases have recently gained considerable attention (Belaid et al., 2008). Schiff base metal complexes attract considerable interest and occupy an important role in the development of the chemistry of chelate systems due to the fact that especially those with N₂O₂ or N₄ tetradentate ligands, closely resemble metallo-proteins (Abd El-Wahab and El-Sarrag, 2004; Anaconda et al., 2009; Bezaatpour et al., 2011; Firdaus et al., 2010). On the other hand, different metal complexes with a wide variety of Schiff bases having such tetradentate donor atoms around the metal ion have been used as catalysts for epoxidation, hydroformylation, hydrogenation, electrochemical investigation and

biological studies of proteins (Abd El-Wahab and El-Sarrag, 2004; Anacona et al., 2009; Bezaatpour et al., 2011; Firdaus et al., 2010). The development in the field of bioinorganic chemistry has been another important factor in spurring the growth of interest in macrocyclic compounds (Valencia et al., 2001; Yang et al., 2009; Raman et al., 2009). Chemically macrocycle containing moieties are of great interest because of their great versatility as ligands, due to the presence of several potential donor atoms, their flexibility and ability to coordinate in either neutral or deprotonated form (Valencia et al., 2001; Yang et al., 2009; Raman et al., 2009; Uysal and Kursunlu, 2011). Many transition metal ions in living systems work as enzymes or carriers in a macrocyclic ligand environment. Meaningful research in this direction might generate simple models for biologically occurring metalloenzymes (Saleh, 2005; Kumar and Alexander, 1999). The behavior of the $>C=N$ bond is strongly dependent on the structure of the amine moiety, which in turn controls the efficiency of the conjugation and may incorporate structural elements able to modulate the steric crowding around the coordination. Various studies have shown that the $>C=N$ group has considerable biological importance (Gudasi et al., 2006).

During the last decade, the coordination chemistry of Schiff bases derived from heterocyclic carbaldehyde has received much attention (Alvarez et al., 2007; Ray et al., 2008; Mohamed et al., 2005; Singh et al., 2010). Recently the stability of N_4 tetradentate Schiff bases in the presence of Sm(II) reagent, determined by the introduction of a pyrrole ring able to coordinate to Sm(II) ion has been studied (Berube et al., 2003). Encouraged by these reports, we have synthesized and characterized the new symmetrical Schiff base N,N' bis(pyrrole-2-carbaldehyde) ethylenediamine and its metal complexes.

2. Experimental

All the chemicals used were of analytical grade and were used as procured. The reagent grade chemicals pyrrole-2-carbaldehyde, ethylenediamine, tetrabutylammonium perchlorate ($n\text{-Bu}_4\text{NaClO}_4$) and metal salts were purchased from Aldrich and Fluka Chemicals Co. and used without further purification. The elemental analyses (C, H and N) of the complexes were performed using Elementar vario EL III model. Metal contents were estimated on an AA-640-13 Shimadzu flame atomic absorption spectrophotometer in solutions prepared by decomposing the complexes in hot concentrated HNO_3 . The molar conductivities of complexes have been measured using a Sybron-Barnstead conductometer in DMSO of 10^{-3} M of their solutions at room temperature. The IR spectra were recorded on a Spectrum BX II model Perkin-Elmer FTIR spectrophotometer in KBr and polyethylene pellets in the range $400\text{--}4000\text{ cm}^{-1}$ and $100\text{--}400\text{ cm}^{-1}$, respectively. The UV-visible spectra were recorded in DMSO on Beckman DU-64 spectrophotometer with quartz cells of 1 cm path length from 200–900 nm and mass spectra (TOF-MS) were recorded on Waters KC-455 model with ES^+ mode in DMSO. ^1H NMR spectra were recorded in DMSO- d_6 solvent on a Bruker Avance 400 MHz instrument. X-band EPR spectra was recorded on a Varian E-112 spectrometer with a variable temperature liquid nitrogen cryostat (The error in g value is ± 0.001) and g factors were quoted relative to the standard marker tetracyanoethylene (TCNE, $g = 2.00277$). Cyclic volta-

metric measurements were carried out with a PC-controlled Eco Chemie-Autolab-12 potentiostat/galvanostat electrochemical analyzing system at 27°C in a three-electrode cell using nitrogen purged DMSO solution containing 0.1 M tetrabutylammonium perchlorate (TBAP) and 10^{-3} M of the complex, in the potential range -1.0 to $+2.0$ V. A Pt wire is used as a working electrode and Ag/AgCl as a reference electrode. Magnetic susceptibility measurements were carried out at room temperature in powder form on a vibrating sample magnetometer PAR 155 with 5000G-field strength, using $\text{Co}[\text{Hg}(\text{SCN})_4]$ as the calibrant (magnetic susceptibility $\approx 1.644 \times 10^{-5}\text{ cm}^3\text{g}^{-1}$). Rigaku model 8150 thermoanalyser was used for simultaneous recording of TG-DTA curves at a heating rate of 10 min^{-1} . For TG, the instrument was calibrated using calcium oxalate, while for DTA, calibration was done using indium metal, both of which were supplied along with the instrument. A flat bed type aluminum crucible was used with α -alumina (99% pure) as the reference material for DTA. The XRD powder pattern was recorded on a vertical type Philips 1130/00 diffractometer, operated at 40 kV and 50 Ma generator using the monochromatized $\text{CuK}\alpha$ line at wavelength 1.54056 \AA as the radiation sources. Sample was scanned between 10° and 70° (2θ) at 25°C . The crystallographic data were analyzed by using the CRYSFIRE – 2000 powder indexing software package and the space group was found by GSAS program. Debye Scherer relation in conjunction with an estimation of 100% peak width was used to estimate the particle size. The density was used to estimate the particle size. The density was determined using Archimedes method.

2.1. Synthesis of ligand and metal complexes

2.1.1. Synthesis of N,N' -bis(pyrrole-2-carbaldehyde) ethylenediamine (Ligand)

Pyrrole-2-carbaldehyde (40 mmol) was dissolved in absolute ethanol (30 ml) added dropwise to a solution of ethylenediamine (20 mmol) in absolute ethanol (30 ml) with constant stirring. Stirring was continued with heating at 60°C for 2 h. A skin colored crystalline powder was collected by vacuum filtration and dried overnight in vacuum.

2.1.2. Synthesis of metal complexes

N,N' -Bis(pyrrole-2-carbaldehyde) ethylenediamine (10 mmol) in 20 ml of absolute ethanol was added dropwise to a solution containing metal salts (10 mmol) in absolute ethanol (20 ml). The mixture was refluxed for 4–6 h on water bath. The precipitate was filtered, washed with cold alcohol and dried under vacuum over silica gel. The metal salts used were Manganese chloride, cobalt nitrate, nickel acetate and copper acetate.

2.2. Molecular modeling

3D molecular modeling of the proposed structure of the complexes was performed using CsChem3D Ultra-11 program package. The correct stereochemistry was assured through the manipulation and modification of the molecular coordinates to obtain reasonable low energy molecular geometries. The potential energy of the molecule was the sum of the following terms (E) = $E_{\text{str}} + E_{\text{ang}} + E_{\text{tor}} + E_{\text{vdw}} + E_{\text{oop}} + E_{\text{ele}}$, where all E s represent the energy values corresponding to the given types of interaction (kcal/mol). The subscripts str, ang, tor,

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