Synthesis, spectroscopic characterization, molecular modeling and potentiometric studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes with 1,1-diaminobutane-Schiff base

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HIGHLIGHTS

- Novel Schiff's base complexes were synthesized.
- The complexes are characterized by different spectroscopic techniques.
- The complexes have different varieties of geometrical structures.
- Schiff's base form complexes with M(II) ions through N_2O_2 donation.
- Protonation equilibria were calculated for Schiff base 50% (v/v) DMSO–water solution.

GRAPHICAL ABSTRACT
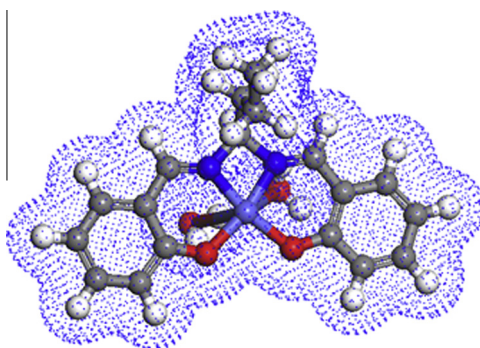
ABSTRACT

Complexes of cobalt(II), nickel(II), copper(II) and zinc(II) of general composition $[M(L)(H_2O)_2] \cdot 2H_2O$ have been synthesized [L = N,N′-bis(2-hydroxybenzylidene)-1,1-diaminobutane]. The elemental analysis, molar conductance measurements, magnetic susceptibility measurements, mass, IR, UV, NMR, SEM, EDX, thermal and EPR spectral studies of the compounds led to the conclusion that the ligand acts as a tetradentate manner. The molar conductance of the complexes in fresh solution of DMSO lies in the range of 7.46–9.13 Ω^{-1} cm^2 mol^{-1} indicating their non-electrolytic behavior. On the basis of analytical and spectroscopic techniques, octahedral geometry of the complexes was proposed. The Schiff base acts as tetradentate ligand, coordinated through deprotonated phenolic oxygen and azomethine nitrogen atoms. The ligand field parameters were calculated for Co(II), Ni(II) and Cu(II) complexes and their values were found in the range reported for a octahedral structure. The molecular parameters of the ligand and its Co(II), Ni(II), Cu(II) and Zn(II) complexes have been calculated. Protonation constants of Schiff base and stability constants of their binary metal complexes have been determined potentiometrically in 50% DMSO–water media at 25 °C and ionic strength 0.10 M sodium perchlorate.

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Introduction

Schiff bases represent one of the most widely utilized classes of ligands in metal coordination chemistry and the chemistry of Schiff bases is an area of increasing interest. Schiff bases are capable of forming coordinate bonds with many metal ions via azomethine or phenolic groups, and so they have been used for synthesis of metal complexes due to their easy formation and strong metal-binding ability. During recent years coordination compounds of biologically active ligands [1–3] have received much attention. Chelation causes drastic change in the biological properties of the

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ligands and also the metal moiety. It has been reported that chelation is the cause and cure of many diseases including cancer. A number of Schiff base complexes [4,5] have been tested for antibacterial activities and they have been found antibacterial [6], antifungal [7], anticancer [8], and herbicidal [9] activities. However, for the period of antibiotics using in clinical practice, steady growth of clinically significant bacteria tolerance to these preparations has been observed. This is likely to be an unavoidable process. Selection of resistant to antibiotic mutants is especially rapid in population of opportunistic pathogenic microorganism [10], which, in turn, often act as donors of resistance genes for particularly dangerous infections agents. Recently, the number of diseases, caused by multidrug resistant gram-positive microorganism, has been continuously increasing. The ability of microorganism to become resistant to major therapies used against them has long been recognized and becomes increasing apparent [11]. Increasing antimicrobial resistance (AMR) presents major threats to public health because it reduces the effectiveness of antimicrobial treatment leading to increased morbidity, mortality and health care expenditure [12].

Thus, in this paper we synthesized a new tridentate Schiff base containing SNO donor atoms and its relevant nickel and palladium complexes. The Schiff base ligand and its complexes were characterized by the FT-IR, ^{1}H NMR, ^{13}C NMR, mass, SEM, EDX, UV–Vis spectroscopy, elemental analysis, magnetic susceptibility, molar conductance and thermal analysis. The geometry of the complexes is characterized by means of spectral and magnetic measurements.

Chemistry

Materials and reagents

The metal salts and the reagents used in this work: $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2 \cdot 2H_2O$, NH_4NO_3, salicylaldehyde and butanal were supplied from Aldrich and Fluka. The solvents used were purchased from Merck and used without further purification.

Instruments

Elemental analysis of ligand and its metal complexes were carried out using Perkin–Elmer elemental analyzer. Molar conductance of the complexes was measured using a coronation digital conductivity meter. IR spectra were recorded using Jasco FTIR-410 spectrometer in KBr pellets from 200 to 4000 cm^{-1}. ^{1}H NMR spectra were recorded with Brucker 300 MHz spectrometer using CDCl$_3$ for ligand and DMSO-d6 for Zn(II) complex with TMS as internal standard. DART-MS spectrum was recorded on a JEOLAccu TOF JMS mass spectrometer. Dry helium was used with 4 LPM flow rate for ionization at 350 °C. Magnetic moments were measured by Guoy method and corrected for diamagnetism of the component using Pascal's constants. UV–Vis spectra were recorded on a JASCO V-570 spectrophotometer in the 190–900 nm. ESR spectrum of the Cu(II) complex was recorded at 300 and 77 K in solid state using Varian, USA E-112 ESR spectrometer. Thermal studies were carried out using Q 600 SDT and Q 20 DSC thermal analyzer. XRD studies were carried out using Bruker AXS D8 advance configuration, X-ray diffractometer. SEM images were recorded in a Hitachi SEM analyzer. Energy Dispersive X-ray Analysis (EDX) (EDAX Falcon System) was conducted to analyze the presence of elements in the specimens that have been sputtered with carbon black.

Synthesis of the ligand

To a mixture of salicylaldehyde (0.4 g, 3.27 mmol) and butanal (0.118 g, 1.64 mmol) was added NH_4NO_3 (0.25 g, 3.27 mmol) in the presence of the NEt$_3$ (1 ml) as a base by stirring in one portion. The mixture was stirred for a further 7 min. The progress of the reaction was monitored by TLC. After the completion of the reaction, a yellow oily substance was obtained. Then, by dissolving the mixture in 2 ml MeOH and cooling overnight, a yellow solid precipitated. The solid product was filtered off and washed with cold MeOH. The crude product was purified by recrystallization in ethanol and the pure Schiff base, N,N'-bis(2-hydroxybenzylidene)-1,1-diaminobutane (H$_2$BHBDAB), was obtained in 96% yield (Scheme 1).

Synthesis of the metal complexes

All complexes were prepared (Scheme 2) by refluxing H$_2$BHB-DAB (0.29 g, 1.0 mmol) and the hydrated metal salts (1.0 mmol), e.g. chloride, in 30 ml ethanol for 2–3 h. The resulting solid complexes were filtered while hot, washed with ethanol followed by diethyl ether and dried in vacuo over CaCl$_2$.

Potentiometric titrations

Potentiometric measurements were made using a Metrohni 686 titroprocessor (Switzerland) equipped with a 665 Dosiniat. The electrode and titroprocessor were calibrated with standard buffer solutions prepared according to NBS specifications [13].

All Potentiometric measurements in this study were carried out in water- DMSO mixtures containing 50% DMSO because of low solubility of Schiff base and possible hydrolysis in aqueous solutions. The pK_w value in this medium was calculated to be 15.48.

Procedure of potentiometric measurements

Potentiometric titrations were carried out at constant temperature and an inert atmosphere of nitrogen with CO$_2$-free standardized 0.1 M NaOH in 40 ml solution containing 0.1 M NaClO$_4$:

(i) 3.0×10^{-3} M HNO$_3$ + 1.5×10^{-3} M Schiff base (for the protonation constant of the Schiff base).

(ii) 3.0×10^{-3} M HNO$_3$ + 1.5×10^{-3} M Schiff base + 7.5×10^{-4} M metal (II or III) ions (for the stability constant of the complexes). The species formed were characterized by the general equilibrium process (1), whereas the formation constants for these generalized species are given by Eq. (2) (charges are omitted for simplicity).

$$pM + qL + rH \rightleftharpoons M_pL_qH_r \tag{1}$$

$$\beta_{pqr} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r} \tag{2}$$

where M, L, H stand for the metal ion, ligand and proton, respectively. The calculations were performed using the computer program MINIQUAD-75 and were conducted on an IBM computer. The stoichiometries and stability constants of the complexes formed were determined by trying various possible composition models for the systems studied.

Molecular modeling

The calculations using DMOL3 program were performed in Materials Studio package [14], which is designed for the realization of large scale density functional theory (DFT) calculations. DFT semi-core pseudo pods calculations (dspp) were performed with the double numerical basis sets plus polarization functional (DNP). The DNP basis sets are of comparable quality to 6-31G Gaussian basis sets [15]. Delley et al. showed that the DNP basis