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Synthesis and characterization of 1,2-bis(2-(5-bromo-2-hydroxybenzilidenamino)-4-chlorophenoxy)ethane and its metal complexes: An experimental, theoretical, electrochemical, antioxidant and antibacterial study

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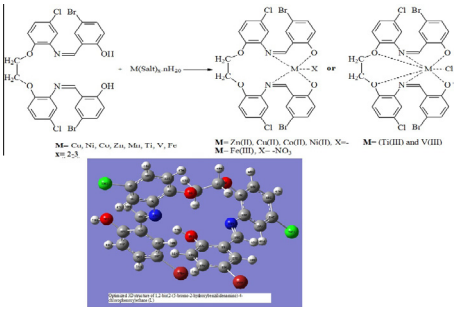
HIGHLIGHTS

- The1,2-bis(2-(5-bromo-2-hydroxybenzilidenamino)-4-chlorophenoxy)ethane synthesized.
- New Cu(II) Ni(II), Co(II), Fe(III) V(III) and Zn(II) complexes synthesized.
- The structures of metal complexes were characterized by different analysis.
- In addition, antioxidant, theoretical NMR and cyclic voltammetry studies done.

GRAPHICAL ABSTRACT



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ABSTRACT

A new Schiff base ligand was synthesized by reaction of 5-bromosalicylaldehyde with 1,2-bis(4-chloro-2-aminophenoxy)ethane. Then the Schiff base complexes were synthesized by the reaction of metal salts and the novel Schiff base. The molar conductivity properties of the complexes were studied and found out that the complexes are nonelectrolytes. The structures of the ligand and its metal complexes were characterized by elemental analysis, FT-IR, UV–VIS, magnetic susceptibility measurements, molar conductivity measurements, and thermal gravimetric analysis. In addition antioxidant, theoretical NMR studies and cyclic voltammetry of the complexes were done. Two methods namely metal chelating activity and diphenylpicrylhydrazyl (DPPH) radical scavenging method were used to determine the antioxidant activity, and antibacterial properties of the compounds were also studied.

Introduction

Schiff bases and their metal complexes play a key role in understanding the coordination chemistry of transition metals [1,2]. A large number of reports are available on the chemistry and the biological activities of transition metal complexes containing O, N and

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S, N donor atoms [3,4]. The transition metal Schiff base complexes have biological activities, antibacterial, antifungal, antioxidant and many industrial applications [5–9]. Transition metal complexes with tetradentate Schiff-base ligands have been extensively investigated as catalysts for a number of organic redox reactions and electrochemical reduction processes [10–12]. Cyclic voltammetry has been a useful technique to investigate the mechanisms of catalysis by Schiff-base metal complexes as well as to study the structure–reactivity relationship in the compounds [13–15]. The molecular parameters: Gaussian, theoretical NMR studies, total energy, heat of bonding energy, isolated energy, electronic energy, heat of formation, dipole moment, HOMO and LUMO of the ligand and complexes have been studied recently [16–21].

In the present work, we have synthesized a new Schiff base ligand by the reaction of 5-bromosalicylaldehyde and 1,2-bis (4-chloro-2-aminophenoxy)ethane. The corresponding Schiff base complexes were synthesized by the reactions of metal salts and the Schiff base. Spectral analyses, cyclic voltammetry, antioxidant studies and magnetic properties of the new compounds were studied in details. A theoretical NMR study was also successfully carried out as a supportive characterization study with linear regression analysis.

Experimental

The 1,2-bis(4-chloro-2-aminophenoxy)ethane used in the synthesis were prepared from 4-chloro-2-nitrophenol, 1,2-dibromoetane and K_2CO_3 as shown in Figs. 1 and 2 [22,23]. All the chemicals and solvents were of analytical grade and used as received. Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. IR spectra were recorded on a PERKIN ELMER SPECTRUM 100 FTIR spectrometer on a universal ATR accessory, with a wavenumber range of 4000–650 cm^{-1}. Electronic spectral studies were conducted on a PERKIN ELMER LAMBDA 750 model UV Visible spectrophotometer in the wavelength 200–900 nm. Molar conductivities were measured with a WTW LF model 330 conductivity meter using prepared solution (10^{-3} M) of the complexes in DMF solvent. ^1H and ^{13}C NMR spectra were recorded using a BRUKER AVANCE DPX-400 NMR spectrometer. Magnetic Susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20 °C) using $Hg[Co(SCN)_4]$ as a standard; diamagnetic corrections were calculated from Pascal's constants [24]. Thermal gravimetric analyses were determined on an EXSTAR S II TG/DTA 6300 Model. Electrochemical experiments were performed with an Autolab PGSTAT 128N potentiostat, (The Netherlands) using a three electrode system, glassy carbon working electrode (Φ: 3 mm, BAS), platinum wire as auxiliary electrode and Ag/AgCl (NaCl 3 M, Model RE-1, BAS, USA) as reference electrode. The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with the solvent/supporting electrolyte mixture. Before starting each experiment, the glassy carbon electrode was polished manually with alumina (Φ: 0.01 μm). Cyclic voltammetric (CV) experiments were recorded at room temperature in extra pure dimethyl formamide (DMF), and ionic strength was maintained at 0.1 mol L^{-1} with electrochemical grade tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. Solutions were deoxygenated by a stream of high purity nitrogen for 15 min prior to the experiments, and during the experiments nitrogen flow was maintained over the solution. Gaussian computations were carried out using a PC having 4G RAM.

Synthesis of Schiff base

5-Bromosalicylaldehyde (40 mmol) in ethanol (40 mL) was added dropwise to a stirred solution of 1,2-bis(4-chloro-2-aminophenoxy)ethane (20 mmol) in ethanol (60 mL). After the addition was completed, the stirring was continued for 2 h, and then precipitate was filtered, washed with ethanol and dried in the vacuum oven at 35 °C under the low pressure for 24 h (Fig. 3).

Synthesis of Schiff base complexes

A solution of metal salt in DMF (40 mL) was mixed with the Schiff base ligand (2 mmol) in DMF (60 mL) at a molar ratio 1:1. The contents were refluxed in 100 mL of DMF on an oil-bath for 3 h. The product was separated by filtration, washed with ethanol and dried in vacuum oven at room temperature for 24 h. All the complexes were almost insoluble in common organic solvents such as ethanol, methanol, benzene, acetone, nitrobenzene, dichloromethane and chloroform. However, they were fairly soluble in polar organic solvents such as dimethyl sulfoxide and dimethyl formamide. A representative reaction scheme for the reaction between metal salts and ligand can be seen on Fig. 4.

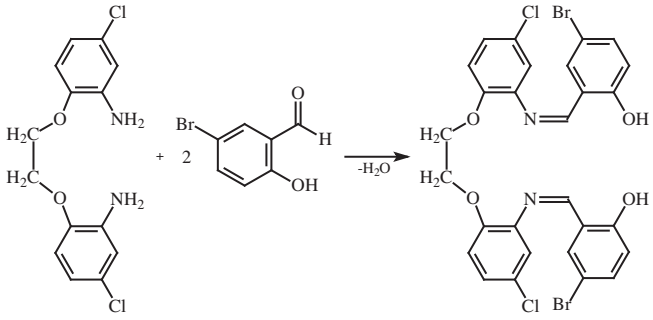

Fig. 3. Synthesis of the ligand (L).

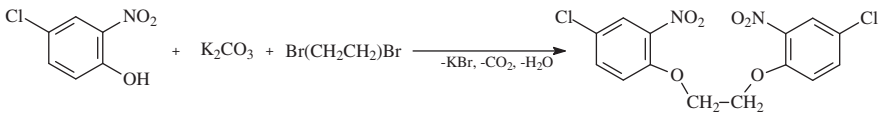

Fig. 1. Synthesis of the 1,2-bis(4-chloro-2-nitrophenoxy)ethane.

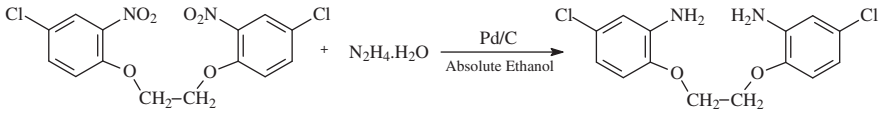

Fig. 2. Synthesis of the 1,2-bis(4-chloro-2-aminophenoxy)ethane (L).