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Synthesis, characterization, spectroscopic and theoretical studies of new zinc(II), copper(II) and nickel(II) complexes based on imine ligand containing 2-aminothiophenol moiety

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New dimer complexes of zinc(II), copper(II) and nickel(II) were synthesized using the Schiff base ligand which was formed by the condensation of 2-aminothiophenol and 2-hydroxy-5-methyl benzaldehyde. This tridentate Schiff base ligand was coordinated to the metal ions through the NSO donor atoms. In order to prevent the oxidation of the thiole group during the formation of Schiff base and its complexes, all of the reactions were carried out under an inert atmosphere of argon. The X-ray structure of the Schiff base ligand showed that in the crystalline form the SH groups were oxidized to produce a disulfide Schiff base as a new double Schiff base ligand. The molar conductivity values of the complexes in dichloromethane implied the presence of non-electrolyte species. The fluorescence properties of the Schiff base ligand and its complexes were also studied in dichloromethane. The products were characterized by FT-IR, ^{1}H NMR, UV/Vis spectroscopies, elemental analysis, and conductometry. The crystal structure of the double Schiff base was determined by single crystal X-ray diffraction. Furthermore, the density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d,p) level of theory for the determination of the optimized structures of Schiff base complexes.

1. Introduction

Schiff bases are an important class of organic compounds [1]. This kind of ligands have significant importance in chemistry, especially, in the development of Schiff base complexes, because Schiff base ligands are potentially capable of forming stable complexes with metal ions [2,3]. Schiff base ligands with sulfur and nitrogen donor atoms in their structures act as good chelating agents for metal ions [4,5]. Coordination of such compounds with metal ions, such as copper, nickel and iron, often enhance their biological activities [6]. Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest [7] because of their ability to possess unusual configurations, structural lability and their sensitivity to molecular environments [8]. Schiff base ligands have proven to be very effective in constructing supramolecular architectures such as coordination polymers, double helixes and triple helicates [9]. Schiff base metal complexes have been of interest in coordination chemistry for many years due to their facile synthesis and wide applications. These complexes have significant contribution in the development of catalysis and enzymatic reactions, magnetism, molecular architectures and materials chemistry [9–11].

Dinuclear transition metal complexes of Schiff base ligands have increased interest in the field of synthetic biological and magneto-chemistry due to their key roles in many applications [12] such as antibacterial, antiviral and antifungal agents [13]. Schiff bases are potential anticancer drugs [14] and the anticancer activity of their metal complexes can enhance in comparison to the free ligand [15]. The design of structural and functional model complexes of such dinuclear centers has been the subject of extensive investigations [16]. Furthermore, transition metal complexes with tridentate Schiff base ligands have been studied as catalysts for a number of organic oxidation and reduction reactions and also electrochemical reduction processes [17,18].

Among of different Schiff base complexes, nickel(II)-diimine complexes have been shown to possess second-order NLO properties [19] and also catalytic activity for the polymerization or copolymerization of olefins and vinylic monomers [20]. Moreover, Schiff base complexes of zinc have found numerous applications such as fluorescent emitters and active layers in organic light-

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emitting diodes (OLEDs) [21]. Furthermore, these complexes play structural and catalytic roles in enzymes and are one of the essential components for gene expression and signal transduction [22]. Although, a lot of Schiff bases with different structures have been synthesized and characterized, however, little attention has been given to Schiff bases which include disulfide bonds. We have recently reported the synthesis of a Schiff base ligand containing 2-mercaptoethylamine and its monomeric and dimeric metal complexes in 2:1 and 1:1 molar ratio, respectively [23,24]. In this paper, we reported synthesis and structural characterization of a new tridentate Schiff base ligand containing 2-aminothiophenol and its new dimeric complexes as a new class of inorganic compounds with sulfur atoms. The Schiff base and its complexes were characterized by FT-IR, ^{1}H NMR, UV–Vis spectroscopies, elemental analysis and molar conductance. The oxidized form of Schiff base was also characterized by X-ray crystallography. Emission behavior of the Schiff base and its metal complexes were studied by fluorescence spectroscopy. In addition to experimental studies, theoretical calculations were employed to complete and confirm the experimental observations. For this purpose, we described density functional theory (DFT) calculations for the three new zinc, copper and nickel complexes. Comparison of the experimental and theoretical parameters could be used as a useful tool for structural identification of the complexes.

2. Experimental

2.1. Materials and physical measurements

All reagents were commercially available and were used as received. Reagents used for the physical measurements were of spectroscopic grade. IR spectra were measured as KBr pellets on a Perkin-Elmer spectrum (RXI FT-IR spectrophotometer equipped with a *DTGS* detector) in the region of 400–4000 cm^{-1} using a resolution of 4 cm^{-1} and an average of 16 scans. Electronic spectra of DMSO solutions of compounds were measured in the region of 200–700 nm on an Analytik Jena Specord 205 spectrophotometer and fluorescence spectra were recorded on FP-6200 spectrofluorometer. The quantum yields were estimated with references to quinine sulfate with known ϕ_f of 0.546 [25]. Elemental analysis was performed using an elementar vario EL III. ^{1}H NMR spectra were obtained on a Bruker Avance DPX 500 MHz spectrophotometer in $CDCl_3$ as a solvent with tetramethylsilane as an internal reference. Melting points were determined on a Barnstead Electrothermal 9100. Conductivity was measured in DMSO solution (3×10^{-4} M) using a 712 conductometer (Metrohm).

2.2. Crystal structure determination and refinement

Single-crystal X-ray diffraction data for double Schiff base ligand were collected at 293 K. The X-ray diffraction measurements were made on a Single Crystal X-Ray Diffractometer STOE IPDS-2T with graphite monochromated Mo-Kα radiation. For the double Schiff base ligand, yellow needle shape crystal was chosen using a polarizing microscope and was mounted on a glass fiber which was used for data collection. Cell constants and orientation matrices for data collection were obtained by least-squares refinement of diffraction data from 4694 unique reflections. The structure was solved by direct methods using the SHELXS-97 program [26] and refined by full-matrix least-squares techniques SHELXL-97 [27] on F2. The subsequent difference Fourier maps were then refined on F2 by a full-matrix least squares procedure using anisotropic displacement parameters. The atomic factors were taken from the International Tables for X-ray Crystallography [28]. All refinements were performed using the X-STEP32 crystallographic software package [29].

2.3. Syntheses

2.3.1. Synthesis of tridentate Schiff base ligand, **H_2L**

A solution of 2-hydroxy-5-methyl benzaldehyde (0.649 g, 5.18 mmol) in 7 mL of absolute ethanol at 60 °C was slowly added to a solution of 2-aminothiophenol (0.706 g, 5.18 mmol) in 7 mL of absolute ethanol at 60 °C and the mixture stirred for 8 h in 80 °C under an inert atmosphere of argon. After removal of the solvent, the yellow precipitate was obtained and washed with n-hexane. Then, the product was dried in vacuo at room temperature. (yield: 72%), yellow, m.p: 175 °C, Anal. Calc. for [$C_{14}H_{13}NOS$] (**H_2L**): (M.W: 243.23), C, 69.13; H, 4.97; N, 5.76; S, 13.18%. Found: C, 68.94; H, 4.89; N, 6.06; S, 12.98%; IR (KBr, υ/cm^{-1}): 1613 υ(CN) (imine), 1156 υ(CO) (phenolic), 3436 υ(OH), 1441 υ(C=C) (aromatic), 753 υ(CS). ^{1}H NMR ($CHCl_3$-d$_1$): 12.66 (1H, s, –OH), 8.62 (1H, s, CH=N), 7.00–7.71(phenylic hydrogen group), 2.37 (3H, s, –CH_3).

2.3.2. Synthesis of zinc dimer complex, **Zn_2L_2**

A solution of $Zn(OAc)_2$ (0.045 g, 0.205 mmol) in ethanol was added dropwise to a solution (5 mL) of Schiff base **H_2L** (0.050 g, 0.205 mmol). The mixture was heated with stirring on a water bath at 80 °C for 8 h. The yellow solution of complex was left to stand for a night. A pale yellow precipitate was obtained and washed with cold ethanol and then dried in vacuo at room temperature. (yield: 45%), m. p: 343 °C, Anal. Calc. for: [$C_{28}H_{22}N_2Zn_2O_2S_2$] (**$Zn_2L_2$**): (M.W: 613.376), C, 54.82; H, 3.62; N, 4.57; S, 10.45%. Found: C, 54.10; H, 3.45; N, 4.79; S, 10.23%. IR (KBr, υ/cm^{-1}): 1625 υ(CN) (imine), 1162 υ(CO) (phenolic), 1464 υ(C=C) (aromatic), 751 υ(CS), 487 υ(Zn–O), 528 υ(Zn–N). ^{1}H NMR (DMSO-d_6): 8.59 (1H, s, CH=N), 6.59–7.43 (phenylic hydrogen group), 2.15 (3H, s, –CH_3).

2.3.3. Synthesis of copper dimer complex, **Cu_2L_2**

Copper acetate monohydrate (0.073 g, 0.360 mmol) in ethanol was added dropwise to a solution (5 mL) of Schiff base **H_2L** (0.090 g, 0.360 mmol). The mixture was heated with stirring on a water bath at 68 °C for 8 h. The resulting brown solution was evaporated and the brown precipitate product was collected and washed with cold ethanol. A brown solid was obtained. (yield: 51%), m. p:> 200 °C (decomp.), Anal. Calc. for: [$C_{28}H_{22}N_2Cu_2O_2S_2$]·$H_2O$ (**Cu_2L_2**): (M.W: 627.723), C, 53.58; H, 3.85; N, 4.46; S, 10.21%. Found: C, 53.27; H, 3.47; N, 5.01; S, 10.21%. IR (KBr, υ/cm^{-1}): 1622 υ(CN) (imine), 1139 υ(CO) (phenolic), 1460 υ(C=C) (aromatic), 751 υ(CS), 489 υ(Cu–O), 539 υ(Cu–N).

2.3.4. Synthesis of nickel dimer complex, **Ni_2L_2**

This complex was synthesized in the same manner as zinc or copper complex, except that an ethanolic solution of $Ni(OAc)_2.4H_2O$ (0.076 g, 0.307 mmol) was used and heated on a water bath at 57 °C for 6 h (yield: 51%), m. p: 234 °C, Anal. Calc. for [$C_{28}H_{22}N_2Ni_2O_2S_2$]·$4H_2O$ (**Ni_2L_2**): (M.W: 672.062), C, 50.04; H, 4.5; N, 4.17; S, 9.54%. Found: C, 50.89; H, 3.99; N, 4.77; S, 10.18%. IR (KBr, υ/cm^{-1}): 1621 υ(CN) (imine), 1327 υ(CO) (phenolic), 1461, υ(C=C) (aromatic), 750 υ(CS), 484 υ(Ni–O), 546 υ(Ni–N).

2.4. Computational method

All calculations were performed using DFT at the B3LYP/6-31G(d,p) level of theory as implemented in the GAMESS program suite [30] employing for metal Schiff base complexes. The structures of the Schiff base and complexes were optimized in the gas phase and the computational data for electronic absorptions were calculated in dichloromethane solvent. The vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and that there is only positive eigen values. The highest occupied molecular orbital (HOMO) and