Research Article

Synthesis, Spectroscopy, Theoretical, and Electrochemical Studies of Zn(II), Cd(II), and Hg(II) Azide and Thiocyanate Complexes of a New Symmetric Schiff-Base Ligand

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Synthesis of zinc(II)/cadmium(II)/mercury(II) thiocyanate and azide complexes of a new bidentate Schiff-base ligand (L) with general formula of MLX2 (M = Zn(II), Cd(II), and Hg(II)) in ethanol solution at room temperature is reported. The ligand and metal complexes were characterized by using ultraviolet-visible (UV-visible), Fourier transform infrared (FT-IR), 1H- and 13C-NMR spectroscopy and physical characterization, CHN analysis, and molar conductivity. 1H- and 13C-NMR spectra have been studied in DMSO-d6. The reasonable shifts of FT-IR and NMR spectral signals of the complexes with respect to the free ligand confirm well coordination of Schiff-base ligand and anions in an inner sphere coordination space. The conductivity measurements as well as spectral data indicated that the complexes are nonelectrolyte. Theoretical optimization on the structure of ligand and its complexes was performed at the Becke's three-parameter hybrid functional (B3) with the nonlocal correlation of Lee-Yang-Parr (LYP) level of theory with double-zeta valence (LANL2DZ) basis set using GAUSSIAN 03 suite of program, and then some theoretical structural parameters such as bond lengths, bond angles, and torsion angles were obtained. Finally, electrochemical behavior of ligand and its complexes was investigated. Cyclic voltammograms of metal complexes showed considerable changes with respect to free ligand.

1. Introduction

Schiff bases are very important class of ligands in coordination chemistry due to the wide applications of them in synthesis of a large variety of transition-metal complexes with various structural architectures [1–5]. These ligands are often prepared in suitable yields and purity during direct reaction between aldehyde or ketone and primary aromatic and/or aliphatic amines. In situ complexation reaction is another common method for synthesis of these compounds [6, 7]. Schiff-base transition metal complexes have been found to show attractive properties and applications. For example, some salen-type complexes have been found as interesting catalyst in organic synthesis [8–11]. Also some Schiff-base coordination compounds have shown interesting magnetic properties [12], a DNA-hydrolytic character [13], antibacterial behavior [14], nonlinear optical [15], and fluorescence properties [16]. In addition, in recent years, some transition metal complexes of Schiff bases have also been presented as building blocks in supramolecular assemblies [17]. Furthermore, a special literature survey on zinc, cadmium, and mercury complexes well confirm the wide utility of them in various fields of chemistry and biochemistry. Some complexes of above metal ion showed antibacterial activities [18–20]; antifungal activities [21]; antitumor and cytotoxic activities [22]. Several zinc enzymes have been found in which geometry around the zinc ion as active site is tetrahedral [23]. Some zinc(II) and cadmium Schiff-base complexes have been known as effective emitting layers, luminescent, fluorescent, and electroluminescent materials [24–27]. Zinc complexes can be used as Lewis-acid catalyst in organic synthesis [28]. A report has shown that cadmium and...
mercury Schiff-base complexes have an acceptable potential for inhibition of corrosion [29]. Recently in analytical chemistry point of view, we reported the utility of zinc, cadmium, and mercury Schiff-base complexes for construction of some ion selective electrodes [30, 31]. This variety of possible applications of IIB metal complexes especially with various Schiff-base ligands and geometries conducted us to develop the synthesis of new coordination compound of zinc group. As a part of our continuing studies on symmetric bidentate Schiff bases including N-atom donors and their IIB metal ions complexes [30–37] and due to the importance of Zn Cd and Hg complexes in chemistry and biochemistry as mentioned above, herein our aim is the synthesis and characterization of new zinc(II), cadmium(II), and mercury complexes of a novel N2-Schiff-base ligand; N,N′-bis((E)-3-(2-nitrophenyl)allylidene)propane-1,3-diamine. Then, theoretical modeling and electrochemical behavior of the ligand and its new complexes are described with respect to each other.

2. Experimental

2.1. Materials and Methods. All solvents and chemicals used in synthesis and analysis were provided from Aldrich, Merck, and/or BDH companies. Metal thiocyanate and azide salts were freshly prepared according to our previous report [32]. IR spectra were recorded on a JASCO FT/IR-680 spectrometer in the range of 4000–400 cm−1 as KBr pellets. 1H and 13C-NMR spectra were recorded on a Bruker DPX FT-NMR spectrometer at 500 MHz in DMSO-d6 solvent. Chemical shifts (δ) are reported in part per million (ppm) relative to an internal standard of TMS. Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a CHN elemental analyzer. Molar conductivities of the Schiff-base complexes were measured in DMSO (10−3 M) at room temperature by the use of Metrohm 712 conductometer with dip-type conductivity cell made of platinum black. Melting points (°C) were recorded on a BUCHI melting point B-545 instrument in open capillary tubes. Electronic spectra were recorded in DMF solution on a JASCO-V570 model spectrometer in the range of 200–800 nm. All cyclic voltammograms were obtained by a SAMAL500 CV instrument including a cell containing three electrodes: glassy carbon as working, platinum disk as supporting, and silver wire as reference electrodes. Scan rate was of 0.1 V/S. Cyclic voltammetry recording was performed on the solutions of ligand and its complexes in dry acetonitrile as well as tetrabutylammonium hexafluorophosphate as supporting electrolyte at room temperature.

2.2. Synthesis of the Schiff-Base Ligand (L). The ligand of N,N′-bis((E)-3-(2-nitrophenyl)allylidene)propane-1,3-diamine has been synthesized by the reaction between 2-nitrocinnamaldehyde (2 mmol, 0.354 g) and propane-1,3-diamine (1 mmol, 0.074 g) in ethanol under severe stirring for 4 h. The yellowish solution so obtained was subjected to evaporation for obtaining yellowish white precipitate. Then, the product was recrystallized from dichloromethane to afford the pure Schiff base in 76% yield. %C21H23N6O4S2: calc. C, 64.28%; H, 5.14%; N, 14.28%; found: C, 63.7%; H, 5.3%; N, 14.6%. Characteristic FT-IR and UV-visible spectral data have been summarized in Table 1. 1H NMR (DMSO-d6): 8.17 (d, 2H, J = 8.40 Hz), 8.02 (d, 2H, J = 8.40 Hz), 7.96 (d, 2H, J = 7.60 Hz), 7.45 (t, 2H, J = 7.20 Hz), 7.61 (t, 2H, J = 8.00 Hz, J = 7.60 Hz), 7.38 (d, 2H, J = 15.60 Hz), 6.98 (dd, 2H, J = 16.00 Hz, J = 8.80 Hz), 3.56 (t, 4H, J = 6.80 Hz), 1.90 (q, 2H, J = 6.80 Hz) ppm. 13C NMR (DMSO-d6): 162.85, 148.44, 135.70, 134.07, 133.00, 130.70, 130.32, 128.92, 125.00, 59.04, 32.24 ppm. m.p. = 163°C; ΛM (DMF) = 2.53 cm2 Ω−1 M−1.

2.3. Synthesis of Metal Complexes. All Schiff-base complexes were synthesized by gradual addition of ethanolic solution of ligand (0.5 mmol) to solution of metal (II) thiocyanate or azide salts in ethanol. The mixture was stirred for 2–3 hours severely at room temperature. The complexes as precipitate were filtered, washed with ethanol twice, dried under vacuum and finally recrystallized from dichloromethane/methanol or chloroform/ethanol. Characteristic FT-IR and UV-visible spectral data were summarized in Table 1 and other physical and spectral data are as follows.

(1) [ZnL(NCS)2]. Yield: 58%; yellowish white precipitate, %C21H23ZnN6O4S2: calc. C, 48.13%; H, 3.51%; N, 14.46%; found: C, 47.97%; H, 3.6%; N, 14.1%. 1H NMR (DMSO-d6): 8.24 (d, 2H, J = 8.40 Hz), 8.04 (d, 2H, J = 8.00 Hz), 7.96 (d, 2H, J = 7.60 Hz), 7.76 (t, 2H, J = 7.20 Hz, J = 6.80 Hz), 7.63 (2H, J = 6.80 Hz), 7.45 (dd, 2H, J = 16.00 Hz, J = 4.80 Hz), 7.03 (dd, 2H, J = 15.20 Hz, J = 8.40 Hz), 3.62 (4H, J = 5.60 Hz), 1.92 (q, 2H, J = 6.00 Hz) ppm; 13C NMR (DMSO-d6): 164.24, 148.46, 137.16, 135.79, 134.16, 132.16, 130.60, 128.90, 125.08, 59.25, 31.91 ppm. m.p. = 196°C (dec.). ΛM (DMF) = 36.22 cm2 Ω−1 M−1.

(2) [ZnL(N3)2]. Yield: 84%; white precipitate, %C21H23ZnN6O4: calc. C, 46.55%; H, 3.72%; N, 25.85%; found: C, 47.4%; H, 3.5%; N, 25.2%. 1H NMR (DMSO-d6): 8.29 (d, 2H, J = 8.80 Hz), 8.05 (d, 2H, J = 8.00 Hz), 7.94 (d, 2H, J = 7.60 Hz), 7.78 (t, 2H, J = 7.20 Hz, J = 6.70 Hz), 7.64 (4H, J = 8.00 Hz), 7.51 (d, 2H, J = 16.00 Hz), 7.03 (dd, 2H, J = 16.00 Hz, J = 8.80 Hz), 3.66 (4H, J = 6.00 Hz), 1.93 (q, 2H, J = 6.40 Hz) ppm; 13C NMR (DMSO-d6): 165.06, 148.50, 138.03, 134.22, 131.67, 130.67, 130.52, 128.94, 125.13, 59.38, 31.64 ppm. m.p. = 180°C (dec.). ΛM (DMF) = 25.47 cm2 Ω−1 M−1.

(3) [CdL(SCN)(NCS)]. Yield: 58%; yellowish white precipitate, %C21H21CdS2N6O4: calc. C, 44.49%; H, 3.25%; N, 13.53%; found: C, 44.9%; H, 3.4%; N, 13.7%. 1H NMR (DMSO-d6): 8.21 (d, 2H, J = 8.80 Hz), 8.03 (d, 2H, J = 8.00 Hz), 7.98 (d, 2H, J = 7.60 Hz), 7.77 (t, 2H, J = 7.60 Hz), 7.62 (2H, J = 7.60 Hz), 7.42 (d, 2H, J = 15.60 Hz), 7.08 (dd, 2H, J = 15.60 Hz, J = 8.40 Hz), 3.60 (4H, J = 5.60 Hz), 1.91 (q, 2H, J = 6.40 Hz) ppm; 13C NMR (DMSO-d6): 163.90, 148.45, 136.55, 134.15, 133.56, 132.67, 130.66, 130.50, 129.01, 125.05, 59.14, 32.25 ppm. m.p. = 179°C (dec.). ΛM (DMF) = 46.67 cm2 Ω−1 M−1.

(4) [CdL(N3)2]. Yield: 39%; white precipitate, %C21H21CdN6O4: calc. C, 42.83%; H, 3.42%; N, 23.79%; found: C,
The complexes were found to be decomposed in the range of 110–196°C. Solubility test showed that the titled complexes are soluble in organic solvents such as dichloromethane, chloroform, acetonitrile, and ethylacetate and insoluble in alcohols such as ethanol and methanol. The compounds were stable under ordinary laboratory conditions.

### 3.2. Molar Conductivity

The low molar conductivities of 10^{-3} M solutions of ligand and its complexes in DMF solvent were in the range of 2.53–46.67 cm^2 Ω^{-1} M^{-1} at room temperature indicate that all of them are nonelectrolytes [38, 39]. Molar conductance of mercury complexes was smoothly lower than zinc and cadmium analogues that state more stability of them toward dissociation in DMF solution.

### 3.3. FT-IR Spectra

Some important FT-IR absorption frequencies of the bidentate Schiff-base ligand and its zinc, cadmium, and mercury complexes have been collected in Table 1. In infrared spectrum of the ligand, lack of characteristic absorption frequencies of the starting aldehyde and amine at wave numbers of 1682 cm^{-1} and 3150–3300 cm^{-1} and then appearance of strong absorption frequencies at wave numbers of 1635 and 1615 cm^{-1}, assigned to asymmetric and symmetric stretching of C=O bonds, confirm the synthesis of ligand. The asymmetric and symmetric stretching vibrations of C=O bonds in the IR spectrum of the free ligand are enhanced in intensity while smoothly shift to lower wave numbers in the complexes spectra by 2–9 cm^{-1} and 1–5 cm^{-1}, respectively, and this is in consistency with coordination of the ligand to the metal ion centers via the azomethine nitrogen atoms [34, 35, 40]. Furthermore, in the case of mercury(II) complexes, the symmetric vibration of azomethine is vanished or probably unified with the asymmetric one. In the IR spectrum of Schiff-base ligand, several weak absorptions are observed at 3067, 2935, and 2843 cm^{-1} that are assignable to aromatic, aliphatic, and iminic C–H stretching vibrations, respectively, and also two strong absorption frequencies related to NO_2 groups are found at 1522 and 1345 cm^{-1}, that are nearly unchanged or shifted after coordination of ligand. In the IR spectrum of zinc thiocyanate complex, appearance of a very strong characteristic vibration at 2065 cm^{-1} may confirm coordination of N-bonded thiocyanate [41, 42].

### 3. Results and Discussion

#### 3.1. Physical Measurements and Microanalysis Data

Herein, the synthesis and spectral identification of a new symmetrical bidentate Schiff-base ligand of N,N'-bis(E)-3-(2-nitrophenyl)allylidene)propane-1,3-diamine and its complexes with zinc, cadmium, and mercury ions in general formula of MLX \( (X = SCN^-, N_3^-) \) are reported as shown in Figure 1. The elemental analysis data are in accordance to the calculated values confirming molar ratio of 1:1 between MX_2 and Schiff-base ligand at all complexes. The ligand is melted at 163°C and is soluble in common organic solvents.

#### 3.2. Table 1: FT-IR (cm^{-1}) and UV-visible (nm) spectral data of the Schiff base and their complexes.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>vCH_{1,4} (\text{cm}^{-1})</th>
<th>vCH_{2,6} (\text{cm}^{-1})</th>
<th>vCH_{3,6} (\text{cm}^{-1})</th>
<th>vNH (\text{cm}^{-1})</th>
<th>vNO (\text{cm}^{-1})</th>
<th>vNO (\text{cm}^{-1})</th>
<th>SCN/\text{N}_3</th>
<th>\lambda_{\text{max}} (nm)</th>
<th>\lambda_{\text{max}} (\text{cm}^{-1}, \text{M}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand</td>
<td>3067 (w)</td>
<td>2935 (w)</td>
<td>2843 (w)</td>
<td>1635 (m)</td>
<td>1615 (m)</td>
<td>1522 (vs)</td>
<td>1345 (s)</td>
<td>298 (6927)</td>
<td>326 (sh) (7582)</td>
</tr>
<tr>
<td>ZnL(NCS)_2</td>
<td>3062 (w)</td>
<td>2935 (w)</td>
<td>2863 (w)</td>
<td>1633 (s)</td>
<td>1610 (m)</td>
<td>1520 (vs)</td>
<td>1343 (s)</td>
<td>2065</td>
<td>323 (8737)</td>
</tr>
<tr>
<td>ZnL(N_3)_2</td>
<td>3057 (w)</td>
<td>2918 (w)</td>
<td>2850 (w)</td>
<td>1633 (vs)</td>
<td>1611 (s)</td>
<td>1518 (vs)</td>
<td>1347 (s)</td>
<td>2062</td>
<td>293 (3566)</td>
</tr>
<tr>
<td>CdL(SCN)(NCS)</td>
<td>3059 (w)</td>
<td>2917 (w)</td>
<td>2844 (w)</td>
<td>1632 (vs)</td>
<td>1612 (s)</td>
<td>1518 (vs)</td>
<td>1339 (s)</td>
<td>2058</td>
<td>2097</td>
</tr>
<tr>
<td>CdL(N_3)_2</td>
<td>3052 (w)</td>
<td>2924 (w)</td>
<td>2854 (w)</td>
<td>1626 (vs)</td>
<td>1520 (vs)</td>
<td>1346 (s)</td>
<td>3117</td>
<td>335 (10494)</td>
<td></td>
</tr>
<tr>
<td>HgL(SCN)_2</td>
<td>3057 (w)</td>
<td>2924 (w)</td>
<td>2854 (w)</td>
<td>1632 (vs)</td>
<td>1520 (vs)</td>
<td>1343 (s)</td>
<td>2034 (3075)</td>
<td>331 (10660)</td>
<td></td>
</tr>
</tbody>
</table>

#### 3.2. Table 1: FT-IR (cm^{-1}) and UV-visible (nm) spectral data of the Schiff base and their complexes.

- **Ligand**: v_{CH_{1,4}} = 3067 cm^{-1}, v_{CH_{2,6}} = 2935 cm^{-1}, v_{CH_{3,6}} = 2843 cm^{-1}, v_{NH} = 1635 cm^{-1}, v_{NO} = 1522 cm^{-1}, v_{NO} = 1345 cm^{-1}, SCN/\text{N}_3 = 298 cm^{-1}, \lambda_{\text{max}} = 6927 nm.
- **ZnL(NCS)_2**: v_{CH_{1,4}} = 3062 cm^{-1}, v_{CH_{2,6}} = 2935 cm^{-1}, v_{CH_{3,6}} = 2863 cm^{-1}, v_{NH} = 1633 cm^{-1}, v_{NO} = 1610 cm^{-1}, v_{NO} = 1520 cm^{-1}, v_{NO} = 1343 cm^{-1}, SCN/\text{N}_3 = 2065 cm^{-1}, \lambda_{\text{max}} = 8737 nm.
- **ZnL(N_3)_2**: v_{CH_{1,4}} = 3057 cm^{-1}, v_{CH_{2,6}} = 2918 cm^{-1}, v_{CH_{3,6}} = 2850 cm^{-1}, v_{NH} = 1633 cm^{-1}, v_{NO} = 1611 cm^{-1}, v_{NO} = 1518 cm^{-1}, v_{NO} = 1347 cm^{-1}, SCN/\text{N}_3 = 2062 cm^{-1}, \lambda_{\text{max}} = 3566 nm.
- **CdL(SCN)(NCS)**: v_{CH_{1,4}} = 3059 cm^{-1}, v_{CH_{2,6}} = 2917 cm^{-1}, v_{CH_{3,6}} = 2844 cm^{-1}, v_{NH} = 1632 cm^{-1}, v_{NO} = 1612 cm^{-1}, v_{NO} = 1518 cm^{-1}, v_{NO} = 1339 cm^{-1}, SCN/\text{N}_3 = 2058 cm^{-1}, \lambda_{\text{max}} = 330 cm^{-1}.
- **CdL(N_3)_2**: v_{CH_{1,4}} = 3052 cm^{-1}, v_{CH_{2,6}} = 2924 cm^{-1}, v_{CH_{3,6}} = 2854 cm^{-1}, v_{NH} = 1626 cm^{-1}, v_{NO} = 1520 cm^{-1}, v_{NO} = 1346 cm^{-1}, SCN/\text{N}_3 = 3117 cm^{-1}, \lambda_{\text{max}} = 10494 nm.
- **HgL(SCN)_2**: v_{CH_{1,4}} = 3057 cm^{-1}, v_{CH_{2,6}} = 2924 cm^{-1}, v_{CH_{3,6}} = 2854 cm^{-1}, v_{NH} = 1632 cm^{-1}, v_{NO} = 1520 cm^{-1}, v_{NO} = 1343 cm^{-1}, SCN/\text{N}_3 = 2034 cm^{-1}, \lambda_{\text{max}} = 10660 nm.

- **HgL(N_3)_2**: v_{CH_{1,4}} = 3057 cm^{-1}, v_{CH_{2,6}} = 2921 cm^{-1}, v_{CH_{3,6}} = 2854 cm^{-1}, v_{NH} = 1632 cm^{-1}, v_{NO} = 1520 cm^{-1}, v_{NO} = 1343 cm^{-1}, SCN/\text{N}_3 = 2034 cm^{-1}, \lambda_{\text{max}} = 10660 nm.
absorption frequencies at 2097 and 2058 cm\(^{-1}\) in cadmium complex IR spectrum maybe attributed to both \(S^-\) and \(N^-\) bonded mode of thiocyanates, respectively. This suggestion is in accordance to some previous reports on thiocyanate complexes [41]. Also mercury thiocyanate complex spectrum shows a strong sharp absorption at 2117 cm\(^{-1}\) that may be related to \(S^-\)coordination of thiocyanate ions [41–43]. The absorptions appeared at 2062, 2046, and 2034 cm\(^{-1}\) in azide complexes spectra are attributable to the \(\nu(N=N=N)\) of coordinated azides based on the literature reports [44–46].

### 3.4. Electronic Spectra

UV-visible spectra of the free ligand and complexes were recorded in DMF (Table 1). Two bands that appeared at 298 nm and 326 nm (as a shoulder) in the UV-visible spectrum of ligand maybe attributed to \(\pi \rightarrow \pi^*\) transitions within aromatic rings and azomethine groups, respectively (Table 1). In zinc thiocyanate and azide complexes, these two bands are observed at 303 nm (as shoulder), 323 nm, 293 nm, and 330 (as shoulder). In cadmium and mercury complexes, these bands are unified and appeared at red shifted wavelengths, 331–339 nm. Therefore, the coordination of the ligand and other anions to the metal ions is well confirmed by noticeable difference of the complexes spectral data with respect to the free ligand.

#### 3.5. \(^1\)H- and \(^{13}\)C-NMR Spectra

The \(^1\)H NMR spectroscopy has been used for confirmation of the binding of ligand to metal ions for all complexes. The \(^1\)H and \(^{13}\)C NMR spectral data have been summarized in Section 2. The \(^1\)H and \(^{13}\)C NMR spectra of ligand and zinc azide complex are illustrated in Figure 2. Regarding Figure 1, the \(^1\)H NMR spectrum of Schiff-base ligand in DMSO-\(d_6\) exhibits a doublet peak with coupling constant of 8.40 Hz, at 8.17 ppm assigned to imine (–N=C–) protons that is shifted to the downfield region at 8.21–8.48 ppm in the complexes, except for mercury azide complex (i.e., smoothly upfielded to 8.14 ppm), indicating coordination of ligand to metal ions. In the ligand spectrum, the aromatic hydrogens of \(H^\prime\) of ligand is seen at 7.96 ppm with coupling constant 8.40 Hz. This signal shifts to 8.03–8.14 ppm in the complexes. Hydrogens of \(H^\prime\) in ligand are observed as a doublet at 8.02 ppm with coupling constant 8.40 Hz. This signal shifts to 8.03–8.14 ppm in the complexes. Hydrogens of \(H^\prime\) in ligand are observed as a doublet at 7.96 ppm with coupling constant 8.40 Hz. This signal shifts to 8.03–8.14 ppm in the complexes. Hydrogens of \(H^\prime\) in ligand are observed as a doublet at 7.96 ppm with coupling constant 8.40 Hz. This signal shifts to 8.03–8.14 ppm in the complexes. Hydrogens of \(H^\prime\) in ligand are observed as a doublet at 7.96 ppm with coupling constant 8.40 Hz. This signal shifts to 8.03–8.14 ppm in the complexes. Hydrogens of \(H^\prime\) in ligand are observed as a doublet at 7.96 ppm with coupling constant 8.40 Hz. This signal shifts to 8.03–8.14 ppm in the complexes.

### 3.6. Theoretical Modeling of Ligand and Its Complexes

The initial structures of ligand and its complexes were sketched with HyperChem 8.0.8 software and PM3 semiempirical method. All geometries were optimized at the Becke’s three-parameter hybrid functional (B3) with the nonlocal correlation of Lee–Yang–Parr (LYP) level of theory with double-zeta valence (LANL2DZ) basis set using GAUSSIAN 03 suite of program, working on 2.3 GHz dual processors. Calculations were followed in the gas phase. Density functional theory (DFT) calculations were done in order to find the optimized geometry of the ligand and its complexes. For instance, the optimized structures of ligand, zinc thiocyanate, and azide complexes have been shown in Figure 3. Some selected structural parameters including bond lengths, bond angles, and torsion angles based on Figure 1 are summarized in Table 2. As seen in Table 2, \(M\)–N (imine) and \(M\)–X are increased from zinc to mercury complexes. \(N\)–M–N are increased from \(N^\prime\)–Hg–N > \(N^\prime\)–Cd–N > \(N^\prime\)–Zn–N whereas \(X\)–M–X are nearly increased with going from zinc to mercury complexes. \(N\)–\(C_0\)–\(C_0\)–\(C_7\) and \(N^\prime\)–\(C_0\)–\(C_0\)–\(C_7\) torsional angles are placed in the ranges of \(-176.6223\) to \(-179.7008(\circ)\) and \(178.3640\) to \(179.0566(\circ)\), respectively indicating nearly planar status around the \(C_0\)–\(C_0\) and \(C_7\)–\(C_7\). \(N\)–\(C_0\)–\(C_0\)–\(C_1\) torsional angles are found to be at the ranges: \(66.41\) to \(71.63(\circ)\) and \(66.39\) to \(73.23(\circ)\), respectively that suggest gauche conformation around the \(C_0\)–\(C_1\) and \(C_0\)–\(C_1\) bonds. Torsional angles around the bonds of \(C_7\)–\(C_7\) and \(C_7\)–\(C_7\) are in the range of \(-149.97\) to \(155.17(\circ)\) and \(149.98\) to \(-154.52(\circ)\), confirming out of plane torsion of aromatic rings with respect to suggestible molecular plane.

### 3.7. Electrochemical Behavior

The electrochemical properties of a substance in solution are investigated by cyclic voltammetry technique. In this paper, cyclic voltammograms of ligand and its zinc, cadmium, and mercury complexes were obtained in dry acetonitrile solutions on glassy carbon electrode with a scan rate of 0.1 V/S and are depicted in Figure 4. The redox potential data have been summarized in Table 3. The ligand is redox active in the potential window of \((-2)\)–\((+1.5)\) volt. Cyclic voltammogram of ligand shows its reduction in two negative potentials of \(-0.78\) and \(-1.54\) V. These reductive processes may be attributed to reduction of nitro groups [47]. In positive direction, the ligand is oxidized only at \(-0.63\) V. In zinc complexes, again two reduction and one oxidation waves are recorded but with an observable shift.
**Figure 1:** The structure of ligand and MLX₂ complexes (M = Zn(II), Cd(II), Hg(II); X = SCN⁻, N₃⁻).

**Figure 2:** ¹H-NMR and ¹³C-NMR of ligand ((a) and (b)) and ZnL(N₃)₂ ((c) and (d)), respectively.
Figure 3: Optimized structure of ligand (a), ZnL(N₃)₂ (b), and ZnL(NCS)₂ (c).

Table 2: Some selected structural data derived from theoretical optimization.

<table>
<thead>
<tr>
<th>Selected data</th>
<th>ZnL(NCS)₂</th>
<th>ZnL(N₃)₂</th>
<th>CdL(SCN)(NCS)</th>
<th>CdL(N₃)₂</th>
<th>HgL(SCN)₂</th>
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<tbody>
<tr>
<td>Bond length (Å)</td>
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<td></td>
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<td></td>
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<tr>
<td>M–N (imine)</td>
<td>2.1150</td>
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<td>2.3311</td>
<td>2.3599</td>
<td>2.4672</td>
<td>2.5162</td>
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<td>2.3453</td>
<td>2.3448</td>
<td>2.4498</td>
<td>2.4879</td>
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<td>M–X</td>
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<td>1.9735</td>
<td>2.5953</td>
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<td>2.1564</td>
<td>2.1662</td>
<td>2.6821</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>N’–M–N</td>
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<td>88.1673</td>
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<td>−178.3666</td>
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to more positive values in first waves in two complex and only second wave in zinc azide complex. Meanwhile, the second reduction wave of zinc thiocyanate shifts to less positive value. In contrast to zinc complexes, cadmium and mercury analogues are reduced and oxidized via reversible processes at the voltage range of (−0.77)–(−0.93) V and (−0.57)–(−0.72) V, respectively. As shown in Figure 4, thiocyanate complexes are nearly reduced harder than ligand except in the case of zinc complex so that the second reduction peak does not appear at (−2)–(+1.5) and furthermore the first reduction wave shifts to more negative values. Anodic oxidation of thiocyanate complexes also becomes harder than free ligand except about mercury complex so that they are oxidized in more positive values. A comparison between azide and thiocyanate complexes reveals that the former are reduced and/or oxidized easier than the latter. This can be due to more π-back bonding from metal to ligand in thiocyanate complex with respect to azide analogues because of softness character of thiocyanate that leads to more electron density on ligand structure in thiocyanate complex explaining the observed trend. On the other hand, the azide ion indirectly induces more positive character on the structure of coordinated ligand with respect to thiocyanate. Furthermore, it also reduces tendency of metal ion for π-back bonding to ligand. The ease of reduction in azide and thiocyanate complexes is ZnL(N\(_3\))$_2$ > CdL(N\(_3\))$_2$ > HgL(N\(_3\))$_2$ and ZnL(NCS)$_2$ > CdL(SCN)(NCS) > HgL(SCN)$_2$, respectively. Opposite order is deduced for oxidation peak in the azide and thiocyanate complexes. These trends can also be deduced based on π-back bonding phenomenon that is increased as mercury > cadmium > zinc in consistency with an increase in softness character of three ions.

3.8. Conclusion. In this work, we reported the synthesis, full spectroscopic characterization, electrochemical and theoretical investigation of a new symmetric bidentate Schiff-base ligand and its new zinc(II), cadmium(II), and mercury(II) azide and thiocyanate four coordinated compounds. The physical, spectral, and theoretical results predict pseudotetrahedral geometry for all coordination compounds. The ligand and its complexes structures were optimized at the nonlocal correlation of Lee-Yang-Parr (LYP) level of theory with double-zeta valence (LANL2DZ) basis set using Gaussian 03 suite of program, and finally some theoretical structural parameters such as bond lengths, bond angles, and torsional angles were extracted. Electrochemical behavior of ligand and its complexes was investigated by cyclic voltammetry technique. The cyclic voltammogram of ligand illustrated two reduction and one oxidation peaks. The zinc complexes exhibited a similar behavior with respect to ligand, but cadmium and mercury complexes showed a reversible electrochemical process.
Acknowledgments

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References


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