

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

Morteza Montazerzohori,¹ Kimia Nozarian,¹ and Hamid Reza Ebrahimi²

¹ Department of Chemistry, Yasouj University, Yasouj 7591874831, Iran

² Department of Chemistry, Majlesi Branch, Islamic Azad University, Isfahan, Iran

Correspondence should be addressed to Morteza Montazerzohori; mmzohori@mail.yu.ac.ir

Received 19 June 2012; Revised 18 September 2012; Accepted 19 September 2012

Academic Editor: Feride Severcan

Copyright © 2013 Morteza Montazerzohori et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Synthesis of zinc(II)/cadmium(II)/mercury(II) thiocyanate and azide complexes of a new bidentate Schiff-base ligand (L) with general formula of MLX_2 ($M = \text{Zn(II)}, \text{Cd(II)}, \text{and Hg(II)}$) 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 ^{13}C -NMR spectroscopy and physical characterization, CHN analysis, and molar conductivity. ^1H - and ^{13}C -NMR spectra have been studied in DMSO-d_6 . 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 confirms 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 SAMA500 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. %C₂₁H₂₀N₄O₄: 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 = 7.60, 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; Λ_M (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, %C₂₃H₂₀ZnS₂N₆O₄: calc. C, 48.13%; H, 3.51%; N, 14.46%; found: C, 47.9%; 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 = 7.6 Hz), 7.76 (t, 2H, J = 7.2 Hz, J = 6.80 Hz), 7.63 (t, 2H, J = 7.6 Hz, 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 (t, 4H, J = 5.6 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.). Λ_M (DMF) = 36.22 cm² Ω⁻¹ M⁻¹.

(2) [ZnL(N₃)₂]. Yield: 84%; white precipitate, %C₂₁H₂₀ZnN₁₀O₄: 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 = 7.6 Hz), 7.78 (t, 2H, J = 7.20 Hz, J = 7.60 Hz), 7.64 (t, 2H, J = 8.00 Hz, J = 7.2 Hz), 7.51 (d, 2H, J = 16.00 Hz), 7.03 (dd, 2H, J = 16.00 Hz, J = 8.80 Hz), 3.66 (t, 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.). Λ_M (DMF) = 25.47 cm² Ω⁻¹ M⁻¹.

(3) [CdL(SCN)(NCS)]. Yield: 58%; yellowish white precipitate, %C₂₃H₂₀Cd S₂N₆O₄: 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 (t, 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 (t, 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.). Λ_M (DMF) = 46.67 cm² Ω⁻¹ M⁻¹.

(4) [CdL(N₃)₂]. Yield: 39%; white precipitate, %C₂₁H₂₀CdN₁₀O₄: calc. C, 42.83%; H, 3.42%; N, 23.79%; found: C,

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

Compounds	$\nu\text{CH}_{\text{arom.}}$	$\nu\text{CH}_{\text{aliph.}}$	$\nu\text{CH}_{\text{imin}}$	$\nu\text{C}=\text{N}_{\text{asymm}}$	$\nu\text{C}=\text{N}_{\text{symm}}$	$\nu(\text{NO}_2)_{\text{asymm}}$	$\nu(\text{NO}_2)_{\text{symm}}$	$-\text{SCN}/-\text{N}_3$	$\lambda_{\text{max}}(\epsilon, \text{cm}^{-1}, \text{M}^{-1})$
Ligand	3067 (w)	2935 (w)	2843 (w)	1635 (s)	1615 (m)	1522 (vs)	1345 (s)	—	298 (6927) 326 (sh) (7582)
ZnL(NCS) ₂	3062 (w)	2935 (w)	2863 (w)	1633 (s)	1610 (m)	1520 (vs)	1343 (s)	2065	323 (8737) 303 (sh) (8179)
ZnL(N ₃) ₂	3057 (w)	2918 (w)	2850 (w)	1633 (vs)	1611 (s)	1518 (vs)	1347 (s)	2062	293 (3566) 330 (sh) (2625)
CdL(SCN)(NCS)	3059 (w)	2917 (w)	2844 (w)	1632 (vs)	1612 (s)	1518 (vs)	1339 (s)	2058 2097	339 (12697)
CdL(N ₃) ₂	3052 (w)	2924 (w)	2854 (w)	1636 (vs)	1616 (s)	1520 (vs)	1342 (s)	2046	333 (8840)
HgL(SCN) ₂	3057 (w)	2924 (w)	2854 (w)	1626 (vs)	—	1520 (vs)	1346 (s)	2117	335 (10494)
HgL(N ₃) ₂	3057 (w)	2921 (w)	2854 (w)	1632 (vs)	—	1520 (vs)	1343 (s)	2034	331 (10660)

42.4%; H, 3.6%; N, 24.2%. ¹H NMR (DMSO-*d*₆): 8.22 (d, 2H, *J* = 8.40 Hz), 8.04 (d, 2H, *J* = 8.00 Hz), 7.98 (d, 2H, *J* = 7.60 Hz), 7.71 (t, 2H, *J* = 7.60 Hz, *J* = 7.20 Hz), 7.63 (t, 2H, *J* = 7.60 Hz), 7.42 (d, 2H, *J* = 16.00 Hz), 7.14 (m, 2H), 3.62 (bs, 4H), 1.89 (q, 2H, *J* = 6.40 Hz) ppm. ¹³C NMR (DMSO-*d*₆): 164.08, 148.48, 136.54, 134.12, 132.71, 130.69, 130.50, 128.98, 125.05, 59.10, 32.25 ppm. m.p. = 179°C (dec.). Λ_{M} (DMF) = 17.72 $\text{cm}^2 \Omega^{-1} \text{M}^{-1}$.

(5) [HgL(SCN)₂]. Yield: 62%; yellowish white precipitate, %C₂₃H₂₀HgS₂N₆O₄: calc. C, 38.95%; H, 2.84%; N, 11.85%; found: C, 39.2%; H, 2.9%; N, 11.6%. ¹H NMR (DMSO-*d*₆): 8.48 (d, 2H, *J* = 8.00 Hz), 8.08 (d, 2H, *J* = 8.00 Hz), 7.96 (d, 2H, *J* = 7.60 Hz), 7.81 (t, 2H, *J* = 7.60 Hz), 7.67 (t, 2H, *J* = 8.00 Hz, *J* = 7.60 Hz), 7.60 (d, 2H, *J* = 15.60 Hz), 7.13 (dd, 2H, *J* = 15.20 Hz, *J* = 8.80 Hz), 3.80 (bs, 4H), 2.01 (m, 2H) ppm. ¹³C NMR (DMSO-*d*₆): 166.12, 148.56, 139.39, 134.27, 131.19, 131.06, 130.35, 129.08, 125.21, 117.80, 60.04, 31.65 ppm. m.p. = 123°C (dec.). Λ_{M} (DMF) = 19.90 $\text{cm}^2 \Omega^{-1} \text{M}^{-1}$.

(6) [HgL(N₃)₂]. Yield: 62%; yellowish white precipitate, %C₂₁H₂₀HgN₁₀O₄: calc. C, 37.25%; H, 2.98%; N, 20.69%; found: C, 37.6%; H, 3.2%; N, 20.3%. ¹H NMR (DMSO-*d*₆): 8.29 (d, 2H, *J* = 8.40 Hz), 8.14 (d, 2H, *J* = 8.40 Hz), 7.95 (d, 2H, *J* = 8.40 Hz), 7.86 (t, 2H, *J* = 7.60 Hz), 7.63 (t, 2H, *J* = 10.0 Hz, *J* = 7.20 Hz), 7.07 (dd, 2H, *J* = 15.6 Hz, *J* = 8.60 Hz), 6.62 (d, 2H, *J* = 16.40 Hz), 3.46 (bd, 4H), 2.07 (m, 2H) ppm. ¹³C NMR (DMSO-*d*₆): 167.5, 156.3, 136.33, 134.78, 134.16, 131.97, 129.46, 125.40, 125.07, 17.98 ppm. m.p. = 110°C (dec.). Λ_{M} (DMF) = 20.43 $\text{cm}^2 \Omega^{-1} \text{M}^{-1}$.

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 MLX₂ (X = SCN⁻, N₃⁻) 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 MX₂ and Schiff-base ligand at all complexes. The ligand is melted at 163°C and is soluble in common organic solvents.

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 $\text{cm}^2 \Omega^{-1} \text{M}^{-1}$ 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=N bonds, confirm the synthesis of ligand. The asymmetric and symmetric stretching vibrations of C=N 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 NO₂ 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]. Two

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 $\nu(\text{N}=\text{N}=\text{N})$ 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 band 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. ^1H - and ^{13}C -NMR Spectra. The ^1H NMR spectroscopy has been used for confirmation of the binding of ligand to metal ions for all complexes. The ^1H and ^{13}C NMR spectral data have been summarized in Section 2. The ^1H and ^{13}C NMR spectra of ligand and zinc azide complex are illustrated in Figure 2. Regarding Figure 1, the ^1H 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 ($-\text{HC}=\text{N}-$) 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 $\text{H}_{i,i'}$ split by $\text{H}_{h,h'}$ are seen 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 $\text{H}_{f,f'}$ in ligand are observed as a doublet at 7.96 ppm with coupling constant of 7.60 Hz due to coupling with $\text{H}_{g,g'}$. In complexes, this doublet appeared in the range of 7.94–7.98 ppm. Hydrogens of $\text{H}_{g,g'}$ that are split by $\text{H}_{f,f'}$ and $\text{H}_{h,h'}$ have been appeared as triplet at 7.45 ppm with coupling constants of 7.60 and 7.20 Hz. This ligand signal has been shifted to 7.71–7.86 ppm in the complexes. Hydrogens of $\text{H}_{h,h'}$ are exhibited as a triplet signal at 7.61 ppm with coupling constants of 8.00 and 7.60 Hz, that are seen at 7.62–7.67 ppm in titled coordination compounds. Olefin hydrogens of $\text{H}_{e,e'}$ split by $\text{H}_{d,d'}$ appeared as a doublet at 7.38 ppm with coupling constant of 15.60 Hz. In all complexes, the related signal is downfielded to 7.42–7.60 ppm except for mercury azide that is upfielded to 6.60 ppm. $\text{H}_{d,d'}$ hydrogens appeared as a doublet of doublet at 6.98 ppm with coupling constants of 16.00 and 8.80 Hz that shift to weaker fields at 7.03–7.14 ppm in coordinated ligand of complexes. The ^{13}C -NMR spectrum of the ligand shows azomethine carbons C (9, 9') resonances

at 162.85 ppm [32–35]. This peak is shifted to the downfield regions at 163.90–167.5 ppm in its complexes indicating well coordination of the imine nitrogens to metal ions. The other assigned signals are observed at 148.44 ($\text{C}_{5,5'}$), 135.70 ($\text{C}_{7,7'}$), 134.07 ($\text{C}_{2,2'}$), 133.00 ($\text{C}_{3,3'}$), 130.70 ($\text{C}_{1,1'}$), 130.32 ($\text{C}_{6,6'}$), 128.92 ($\text{C}_{4,4'}$), 125.00 ($\text{C}_{8,8'}$), 59.04 ($\text{C}_{10,10'}$), and 32.24 (C_{11}) ppm; these signals have been shifted to the up- or downfields in all of complexes indicating coordination of the ligand to metal ions. The additional signals at 135.79, 133.56, and 117.80 in thiocyanate complexes may be assigned to coordinated thiocyanate ions in zinc, cadmium, and mercury thiocyanate complexes, respectively.

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 angles are decreased as N'–Hg–N > N'–Cd–N > N'–Zn–N while X–M–X' are nearly increased with going from zinc to mercury complexes. N–C₉–C₈–C₇ and N'–C_{9'}–C_{8'}–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 C₉–C₈ and C_{9'}–C_{8'}. N–C₁₀–C₁₁–C_{10'} and N'–C_{10'}–C₁₁–C₁₀ 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 C₁₀–C₁₁ and C_{10'}–C₁₁ bonds. Torsional angles around the bonds of C₇–C₆ and C_{7'}–C_{6'} 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

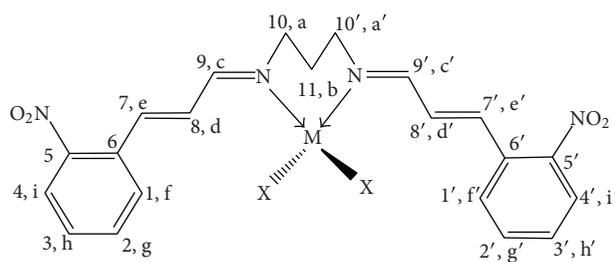


FIGURE 1: The structure of ligand and MLX_2 complexes ($M = Zn(II), Cd(II), Hg(II)$; $X = SCN^-, N_3^-$).

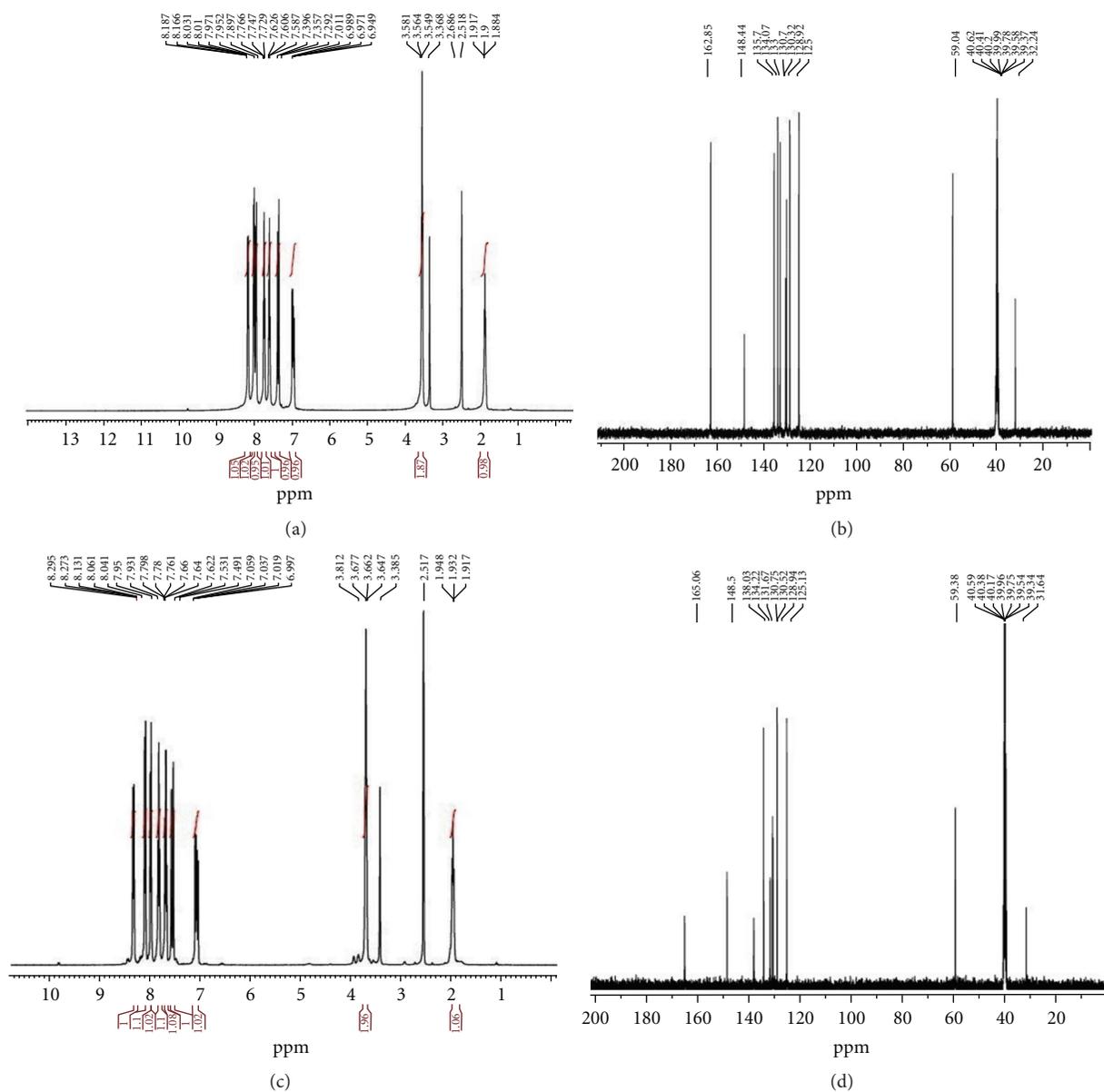


FIGURE 2: 1H -NMR and ^{13}C -NMR of ligand ((a) and (b)) and $ZnL(N_3)_2$ ((c) and (d)), respectively.

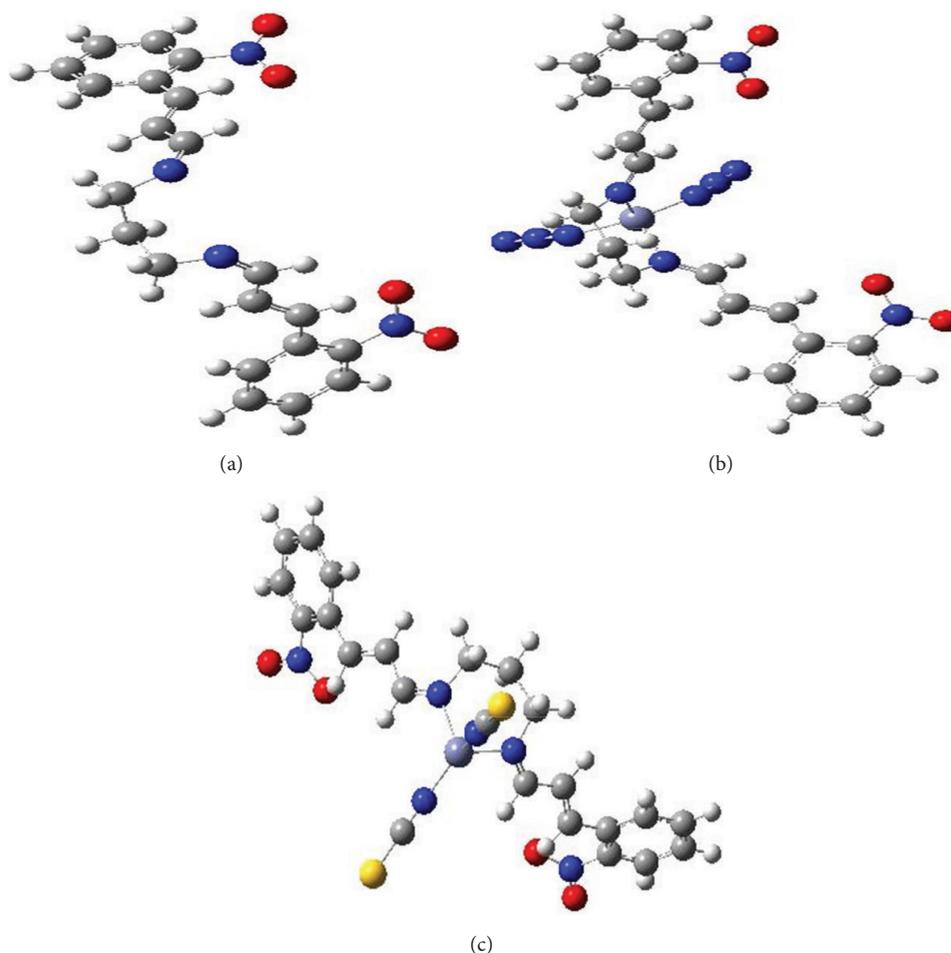


FIGURE 3: Optimized structure of ligand (a), $\text{ZnL}(\text{N}_3)_2$ (b), and $\text{ZnL}(\text{NCS})_2$ (c).

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

Selected data	$\text{ZnL}(\text{NCS})_2$	$\text{ZnL}(\text{N}_3)_2$	$\text{CdL}(\text{SCN})(\text{NCS})$	$\text{CdL}(\text{N}_3)_2$	$\text{HgL}(\text{SCN})_2$	$\text{HgL}(\text{N}_3)_2$
Bond length ($^{\circ}\text{A}$)						
M–N (imine)	2.1150	2.1226	2.3311	2.3599	2.4672	2.5162
M–N' (imine)	2.1150	2.1225	2.3453	2.3448	2.4498	2.4879
M–X	1.9700	1.9735	2.5953	2.1330	2.6680	2.2460
M–X'	1.9535	1.9507	2.1564	2.1662	2.6821	2.2246
Bond angle ($^{\circ}$)						
N'–M–N	89.8163	88.1673	83.2459	81.0377	80.0201	74.6799
N'–M–X	109.8485	101.4402	100.9224	102.1950	111.1427	94.1154
N'–M–X'	103.5345	107.7474	106.5551	97.1403	110.2779	94.8796
N–M–X	109.8436	101.4219	117.3905	110.3509	112.0082	90.5492
N–M–X'	103.5413	107.7841	100.9224	94.6580	101.5451	104.3265
X–M–X'	132.0564	138.8475	134.4819	150.3185	130.0291	164.2183
Torsion angle ($^{\circ}$)						
N–C ₉ –C ₈ –C ₇	-176.6223	-178.3666	-179.6795	-179.6153	-179.7008	-178.9212
N'–C ₉ '–C ₈ '–C ₇ '	176.6320	178.3640	178.5942	179.0566	176.8017	177.7678
N'–C ₁₀ '–C ₁₁ –C ₁₀	-67.07	-66.39	-68.49	-68.05	-73.23	-66.75
N–C ₁₀ –C ₁₁ –C ₁₀ '	67.07	66.41	71.63	70.41	70.29	69.43
C ₈ –C ₇ –C ₆ –C ₅	-149.97	-152.57	151.95	-153.48	155.17	-154.47
C ₈ '–C ₇ '–C ₆ '–C ₅ '	149.98	152.57	-154.52	153.12	-153.16	153.30

TABLE 3: Electrochemical data of ligand and complexes.

Compounds	E_{PC1} ($E_{PC/2}$), E_{PC2} ($E_{PC/2}$)	ΔE_{P1}^a	ΔE_{P2}^b	E_{Pa1} ($E_{Pa/2}$)
L	-0.78 (-0.70), -1.54 (-1.47)	-0.08	-0.07	-0.63 (-0.71)
ZnL(NCS) ₂	-0.76 (-0.67), -1.57 (-1.49)	-0.09	-0.13	-0.59 (-0.68)
ZnL(N ₃) ₂	-0.73 (-0.62), -1.50 (-1.44)	-0.09	-0.06	-0.57 (-0.66)
CdL(SCN)(NCS)	-0.86 (-0.75)	-0.09	—	-0.61 (-0.74)
CdL(N ₃) ₂	-0.77 (-0.67)	-0.1	—	-0.57 (-0.71)
HgL(SCN) ₂	-0.93 (-0.82)	-0.09	—	-0.72 (-0.83)
HgL(N ₃) ₂	-0.90 (-0.78)	-0.12	—	-0.70 (-0.82)

^a $\Delta E_{P1} = E_{PC1} - E_{PC/2}$; ^b $\Delta E_{P2} = E_{PC2} - E_{PC/2}$.

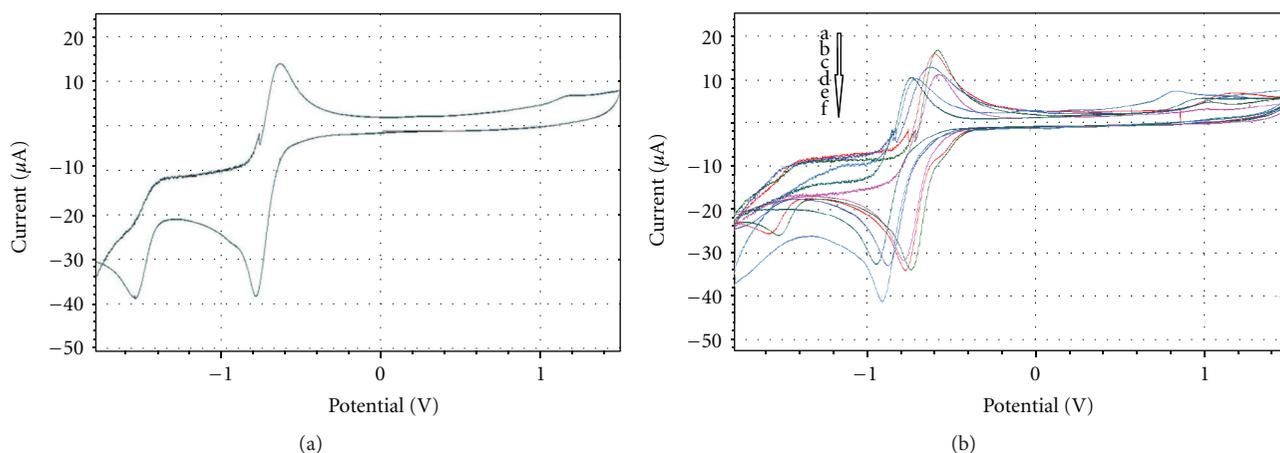


FIGURE 4: Cyclic voltammograms of ligand (a), ZnL(N₃)₂, ZnL(NCS)₂, CdL(SCN)(NCS), CdL(N₃)₂, HgL(N₃)₂, and HgL(SCN)₂ ((b): a, b, c, d, e, and f, resp.).

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 (-.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(N₃)₂ > CdL(N₃)₂ > HgL(N₃)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

Partial support of this research by Yasouj University is acknowledged. The authors do not have a direct financial relation with the commercial identity companies mentioned in this work.

References

- [1] S. Singh, N. Kaur, S. Varshney, and A. K. Varshney, "New coordination compounds of tin(IV) with schiff bases of dialdehyde/diketones and sulpha drugs," *Research on Chemical Intermediates*, vol. 30, no. 9, pp. 903–908, 2004.
- [2] S. Mohammed, A. Begum, S. Saha, M. Nethaji, and A. R. Chakravarty, "Iron(III) Schiff base complexes of arginine and lysine as netropsin mimics showing AT-selective DNA binding and photonuclease activity," *Journal of Inorganic Biochemistry*, vol. 104, no. 4, pp. 477–484, 2010.
- [3] S. Malik, S. Ghosh, and L. Mitu, "Complexes of some 3d-metals with a Schiff base derived from 5-acetamido-1,3,4-thiadiazole-2-sulphonamide and their biological activity," *Journal of Serbian Chemical Society*, vol. 76, no. 10, pp. 1387–1394, 2011.
- [4] K. Mounika, B. Anupama, J. Pragathi, and C. Gyanakumari, "Synthesis, characterization and biological activity of a Schiff base derived from 3-ethoxy salicylaldehyde and 2-amino benzoic acid and its transition metal complexes," *Journal of Scientific Research*, vol. 2, no. 3, pp. 513–524, 2010.
- [5] S. S. Konstantinov, B. C. Radovanovi, Z. B. Todrovi, and S. B. Ili, "Spectrophotometric study of Co(II), Ni(II), Cu(II), Zn(II), Pd(II) and Hg(II) complexes with isatin-thiosemicarbazone," *Journal of Serbian Chemical Society*, vol. 72, no. 10, pp. 975–981, 2007.
- [6] M. Sönmez and M. Şekerci, "The template synthesis, spectral characterization and thermal behaviour of new binuclear Schiff base complexes derived from N-aminopyrimidine with 2,3-butandion," *Journal of the Serbian Chemical Society*, vol. 72, no. 3, pp. 259–264, 2007.
- [7] M. M. Alam, "Template synthesis of new type of macrocyclic molecule derived from pyridine-2, 6-decarboxaldehyde and 1,2-bis(2-Aminoethoxy) ethane," *Journal of Bangladesh Academy of Science*, vol. 35, no. 1, pp. 61–65, 2011.
- [8] V. B. Sharma, S. L. Jain, and B. Sain, "Cobalt (II) Schiff base catalyzed aerobic oxidation of secondary alcohols to ketones," *Journal of Molecular Catalysis A*, vol. 212, no. 1-2, pp. 55–59, 2004.
- [9] K. C. Gupta and A. K. Sutar, "Catalytic activities of Schiff base transition metal complexes," *Coordination Chemistry Reviews*, vol. 252, no. 12-14, pp. 1420–1450, 2008.
- [10] M. Montazerzohori, M. Nasr-Esfahani, and P. Akhlaghi, "Catalytic oxidative decarboxylation of some benzylcarboxylic acid derivatives by a new iron(III) Schiff base complex," *Chinese Journal of Chemistry*, vol. 27, no. 5, pp. 1007–1011, 2009.
- [11] M. Nasr-Esfahani, M. Montazerzohori, and P. Akhlaghi, "Efficient biomimetic oxidative decarboxylation of some carboxylic acids catalyzed by a manganese (III) Schiff base complex," *Bulletin of the Korean Chemical Society*, vol. 30, no. 7, pp. 1583–1587, 2009.
- [12] G. X. Liu, X. M. Ren, H. Xu, C. Y. Tang, G. H. Wu, and Y. C. Chen, "Crystal structures and magnetic properties of two new schiff base complexes," *Chinese Chemical Letters*, vol. 15, no. 9, pp. 1105–1108, 2004.
- [13] N. Raman, J. Dhavethu Raja, and A. Sakthivel, "Synthesis, spectral characterization of Schiff base transition metal complexes: DNA cleavage and antimicrobial activity studies," *Journal of Chemical Sciences*, vol. 119, no. 4, pp. 303–310, 2007.
- [14] V. B. Badwaik, R. D. Deshmukh, and A. S. Aswar, "Transition metal complexes of a Schiff base: synthesis, characterization, and antibacterial studies," *Journal of Coordination Chemistry*, vol. 62, no. 12, pp. 2037–2047, 2009.
- [15] A. Trujillo, M. Fuentealba, D. Carrillo et al., "Synthesis, spectral, structural, second-order nonlinear optical properties and theoretical studies on new organometallic donor-acceptor substituted nickel(ii) and copper(ii) unsymmetrical schiff-base complexes," *Inorganic Chemistry*, vol. 49, no. 6, pp. 2750–2764, 2010.
- [16] S. Shit, J. Chakraborty, B. Samanta, G. M. Rosair, and S. Mitra, "Synthesis, structure and fluorescence properties of a trinuclear Zn(II) complex with N,N, O-donor schiff base ligands and bridging acetates," *Zeitschrift für Naturforschung Section B*, vol. 64, no. 4, pp. 403–408, 2009.
- [17] M. L. Wei, R. P. Sun, and P. F. Zhuang, "A new supramolecular compound based on Cd(II)-Schiff-base and keggin-type [PMo12O40]³⁻," *Jiegou Huaxue*, vol. 29, no. 11, pp. 1646–1651, 2010.
- [18] L. Shi, W. J. Mao, Y. Yang, and H. L. Zhu, "Synthesis, characterization, and biological activity of a Schiff-base Zn(II) complex," *Journal of Coordination Chemistry*, vol. 62, no. 21, pp. 3471–3477, 2009.
- [19] K. Shivakumar, Shashidhar, P. Vithal Reddy, and M. B. Halli, "Synthesis, spectral characterization and biological activity of benzofuran Schiff bases with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes," *Journal of Coordination Chemistry*, vol. 61, no. 14, pp. 2274–2287, 2008.
- [20] O. W. Salawu and A. O. Abdulsalam, "Synthesis, characterization and biological activities of Cd(II) complexes with hydrazide ligands," *Der Pharma Chemica*, vol. 3, no. 4, pp. 298–304, 2011.
- [21] P. H. Modh and D. R. Pandya, "Antimicrobial study of Novel salen type 2,2'-(ethane-1,2-diyldinitrilo)bis(phenylacetic acid) complexes of Zn and Cd," *Der Chemica Sinica*, vol. 3, no. 3, pp. 663–666, 2012.
- [22] M. T. H. Tarafder, M. A. Ali, D. J. Wee, K. Azahari, S. Silong, and K. A. Crouse, "Complexes of a tridentate ONS Schiff base. Synthesis and biological properties," *Transition Metal Chemistry*, vol. 25, no. 4, pp. 456–460, 2000.
- [23] F. Marchetti, C. Pettinari, R. Pettinari, A. Cingolani, D. Leonesi, and A. Lorenzotti, "Group 12 metal complexes of tetradentate N2O2-Schiff-base ligands incorporating pyrazole: synthesis, characterisation and reactivity toward S-donors, N-donors, copper and tin acceptors," *Polyhedron*, vol. 18, no. 23, pp. 3041–3050, 1999.
- [24] Y. Hamada, T. Sano, H. Fujii, Y. Nishio, H. Takahashi, and K. Shibata, "White-light-emitting material for organic electroluminescent devices," *Japanese Journal of Applied Physics Part 2*, vol. 35, no. 10, pp. L1339–L1341, 1996.
- [25] A. D. Garnovskii, A. S. Burlov, A. V. Metelitsa et al., "Electrochemical and chemical synthesis of new luminescent schiff base complexes," *Russian Journal of General Chemistry*, vol. 80, no. 2, pp. 292–300, 2010.
- [26] P. Roy, M. Manassero, K. Dhara, and P. Banerjee, "Synthesis, characterization and fluorescence properties of hexanuclear zinc(II) complexes," *Polyhedron*, vol. 28, no. 6, pp. 1133–1137, 2009.

- [27] Y. Yi, X. Q. Wei, M. G. Xie, and Z. Y. Lu, "Synthesis and color-tunable fluorescence properties of schiff base zinc (II) complexes used as electroluminescent materials," *Chinese Chemical Letters*, vol. 15, no. 5, pp. 525–528, 2004.
- [28] A. Erxleben and J. Hermann, "Di- and poly-nuclear zinc(ii) Schiff base complexes: synthesis, structural studies and reaction with an α -amino acid ester," *Journal of the Chemical Society, Dalton Transactions*, no. 4, pp. 569–575, 2000.
- [29] S. B. Ade1, M. N. Deshpande, and D. G. Kolhatkar, "Corrosion a universal environmental Problem: a role of Schiff base metal complexes as inhibitors," *Journal of Chemical and Pharmaceutical Research*, vol. 4, no. 2, pp. 1033–1035, 2012.
- [30] M. Ghaedi, M. Montazerzohori, A. Mousavi, S. Khodadoust, and M. Mansouri, "Construction of new iodide selective electrodes based on bis(trans-cinnamaldehyde)1,3-propanediimine (L) zinc(II) chloride [ZnLCl₂] and bis(trans-cinnamaldehyde) 1,3 propanediimine(L) cadmium(II) chloride [CdLCl₂]," *Material Science Engineering Data C*, vol. 32, no. 1, pp. 523–529, 2012.
- [31] M. Ghaedi, M. Montazerzohori, K. Mortazavi, M. Behfar, and F. Marahel, "Iodide-selective electrodes based on two new carriers: influence of various nanoparticle materials on the response performance of proposed electrodes," *International Journal of Electrochemical Science*, vol. 6, pp. 6682–6698, 2011.
- [32] M. Montazerzohori and S. A. Musavi, "Synthesis and spectral characterization of a new symmetric bidentate Schiff-base and its zinc complexes," *Journal of Coordination Chemistry*, vol. 61, no. 24, pp. 3934–3942, 2008.
- [33] M. Montazerzohori, S. Jooari, and S. A. Musavi, "Synthesis and spectroscopic studies of a new unsymmetrical ligand, N(E),N'(E)-bis[(E)-2-methyl-3-phenylallylidene] propane-1,2-diamine, and its zinc complexes," *Journal of Coordination Chemistry*, vol. 62, no. 8, pp. 1285–1292, 2009.
- [34] M. Montazerzohori, S. Jooari, and S. A. Musavi, "Synthesis and spectroscopic studies of some cadmium(II) and mercury(II) complexes of an asymmetrical bidentate Schiff base ligand," *Spectrochimica Acta Part A*, vol. 73, no. 2, pp. 231–237, 2009.
- [35] M. Montazerzohori, S. Khani, S. Jooari, and S. A. Musavi, "Synthesis, spectral and thermal behavior of some new four coordinated complexes," *Journal of Chemistry*, vol. 9, no. 4, pp. 2483–2492, 2012.
- [36] M. Montazerzohori and M. Sedighipoor, "Synthesis, spectral identification, electrochemical behavior and theoretical investigation of new zinc complexes of bis((E) 3-(2-nitrophenyl)-2-propenal)propane-1,2-diimine," *Spectrochimica Acta Part A*, vol. 96, pp. 70–76, 2012.
- [37] M. Montazerzohori, S. Khani, H. Tavakol, A. Hojjati, and M. Kazemi, "Synthesis, spectroscopic and thermal studies of some IIB group complexes with a new N2-Schiff base ligand," *Spectrochimica Acta Part A*, vol. 81, pp. 122–127, 2011.
- [38] G. G. Mohamed, M. M. Omar, and A. M. Hindy, "Metal complexes of Schiff bases: preparation, characterization, and biological activity," *Turkish Journal of Chemistry*, vol. 30, no. 3, pp. 361–382, 2006.
- [39] A. A. Osowole, "Syntheses and characterization of some tetradentate Schiff-base complexes and their heteroleptic analogues," *E-Journal of Chemistry*, vol. 5, no. 1, pp. 130–135, 2008.
- [40] P. S. Mane, S. M. Salunke, and B. S. More, "Synthesis and structural studies of transition metal complexes with bidentate Schiff base derived from 3-acetyl-6-methyl-(2H)-pyran-2,4(3H)-dione," *E-Journal of Chemistry*, vol. 8, no. 1, pp. S245–S252, 2011.
- [41] S. Satapathi, S. Das, K. Bhar, R. K. Kumar, T. K. Maji, and B. K. Ghosh, "Syntheses, structures and luminescence behaviors of mono- and dinuclear complexes of type [M(L)(NCS)₂]_n [M = Zn/Hg, n = 1; M = Cd, n = 2; L = (N,N-diethyl,N'-(pyridin-2-yl)benzylidene)ethane-1,2-diamine]: variation of coordination matrices and nuclearities with the change of congeneric metal ions," *Polyhedron*, vol. 30, no. 2, pp. 387–396, 2011.
- [42] M. Daković, Z. Popović, G. Giester, and M. Rajić-Linarić, "Thiocyanate complexes of the group 12 metals with pyridine-2-carboxamide: synthesis and structural characterization," *Polyhedron*, vol. 27, no. 1, pp. 210–222, 2008.
- [43] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B*, John Wiley & Sons, Hoboken, NJ, USA, 5th edition, 2009.
- [44] K. S. Singh, V. Svitlyk, and Y. Mozharivskyj, "Mono and dinuclear arene ruthenium(ii) triazoles by 1,3-dipolar cycloadditions to a coordinated azide in ruthenium(ii) compounds," *Dalton Transactions*, vol. 40, no. 5, pp. 1020–1023, 2011.
- [45] T. J. Mizoguchi and S. J. Lippard, "(μ -Oxo)bis(μ -carboxylato) bis(2,2'-bipyridyl)bis(X)diiron(III) complexes, X = NCS-, NCSe-, and Na-: synthetic models of pseudohalide derivatives of carboxylate-bridged diiron proteins," *Inorganic Chemistry*, vol. 36, no. 20, pp. 4526–4533, 1997.
- [46] N. Mondal, S. Mitra, V. Gramlich, S. O. Ghodsi, and K. M. A. Malik, "Synthesis, characterization and crystal structures of some four coordinated nickel(II) complexes with tridentate schiff base ligands," *Polyhedron*, vol. 20, no. 1-2, pp. 135–141, 2001.
- [47] I. Haque and M. Tariq, "Voltammetry of nitrobenzene at bare and DODAC coated Pt," *Journal of Chemical Society of Pakistan*, vol. 33, no. 4, pp. 529–534, 2011.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

