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Synthesis, spectral identification, electrochemical behavior and theoretical investigation of new zinc complexes of bis((E) 3-(2-nitrophenyl)-2-propenal) propane-1,2-diimine

Morteza Montazerozohori*, Maryam Sedighipoor

Department of Chemistry, Yasouj University, Yasouj 75918-74831, Iran

HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Synthesis of some new zinc complexes of a new asymmetric Schiff base is reported.
- The complexes were molecular and non-electrolyte.
- Electrochemical behavior of ligand showed quasi-reversible process.
- Complexes exhibited irreversible redox processes.
- Pseudo-tetrahedral was suggested for complexes based on the UB3LYP/ LANL2MB* level.

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ABSTRACT

Synthesis, spectroscopic, electrochemical behavior and theoretical investigation of some zinc complexes of a new Schiff base ligand of $bis((E) 3-(2-nitrophenyl)-2-propenal)propane-1,2-diimine (L) with a general formula of <math>ZnLX_2(X = Cl^-, Br^-, l^-, SCN^- \text{ and } N_3^-)$ are described. The ligand and its complexes were identified by elemental analysis, molar conductivity, UV–Visible spectra, FT-IR spectra, ¹H NMR and ¹³C NMR spectra. The complexes were found to be molecular and non-electrolyte based on conductivity measurement. The spectral data confirm coordination of ligand and anions(X⁻) to zinc ion center. Electrochemical behavior of ligand and complexes were investigated by cyclic voltammetry technique exhibiting different redox behavior of complexes with respect to free ligand so that the ligand and complexes showed quasi-reversible and irreversible electron transfer processes respectively. Molecular structures of the ligand and complexes have been optimized at the UB3LYP/LANL2MB* level of theory. Accordingly some theoretical thermodynamical and/or structural parameters such as HF-energy, Gibbs free energy, enthalpy, selected bond distances, bond angles and torsion angles of optimized structures are presented.

Introduction

A large number of Schiff bases as coordinating chelates have been studied due to easily formation of their complexes with various transition metal ions. Schiff bases and their complexes have been extensively introduced in a wide variety of applications including biological activities [1–4], clinical [5] and analytical fields [6–8]. In organic synthetic point of view, some Schiff base complexes catalyze a variety of organic reactions including oxidation [9], epoxidation [10], water photolysis [11] and decarboxylation [12]. Various types of Schiff base ligands have been widely used for the synthesis of coordination compounds [13–15]. Among many other coordination compounds, zinc Schiff base complexes have been found to show the luminescence properties [16–17]. In recent

^{*} Corresponding author. Tel./fax: +98 7412223048.

E-mail addresses: mmzohori@mail.yu.ac.ir, mmzohory@yahoo.com (M. Monta zerozohori).

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years, in addition to other properties, the electrochemical behavior of complexes is of interest for chemists because of its sensitivity and relatively short analysis time. Sometimes redox data give some crucial information on structural features, chemical and biochemical activity [18–23]. Accordingly the electrochemical studies of some Schiff base complexes are reported [24–26]. A literature survey shows that the reports on electrochemical behaviors of N₂-Schiff base ligands and their complexes are rare. Therefore in continuation of our program [27–29] on synthesis of zinc group complexes, in this work we wish to report synthesis, spectral identification, electro-

work we wish to report synthesis, spectral identification, electrochemical behaviors and theoretical investigation of bis((E) 3-(2nitrophenyl)-2-propenal)propane-1,2-diimine (L) as a N₂-donor Schiff base and its new zinc complexes.

Experimental

Materials and methods

2-Nitrocinnamaldehvde, 1.2-propanediamine, zinc halides and other chemicals were purchased from Aldrich. Merck or BDH Chemicals. Zinc thiocynate and azide were synthesized based on our previous report [27]. FT/IR spectra of compounds were recorded on JASCO-FT/IR680 sepectrophotometer in the range of the 4000–400 cm⁻¹as KBr pellets. Electronic spectra were obtained in DMF solutions by use of a JASCO-V570 sepectrophotometer. A Brucker DPX FT/NMR spectrometer at 500 MHz was used for recording of ¹H and ¹³C NMR spectra in DMSO-d₆. CHN analysis was performed using an elemental analyzer. BUCHI B-545 melting point instrument was applied for recording of melting points. Metrohm-712 conductometer with a dip-type conductivity cell made of platinum black was applied for measurement of molar conductivities of 10⁻³ M solutions of the ligand and its complexes in CHCl₃ at room temperature. Cyclic voltamograms of compounds have been recorded on a BHP 2063 Potentiostat Galvanostat instrument. Theoretical calculations were performed on the Schiff-base ligand and its complexes at the UB3LYP/LANL2MB* level of theory.

Cyclic voltammetry

All cyclic voltammograms were recorded in a cell containing three electrodes: glassy carbon as working, platinum disk as supporting and silver wire as reference electrodes at room temperature. Scan rate was of 0.1 V/S. For recording of cyclic voltammograms, 10^{-3} M of ligand and its zinc complexes in dry acetonitrile as well as tetrabutylammonium hexafluorophosphate as supporting electrolyte were used. All solutions were deoxygenated by passing a stream of pre-purified N₂ into the solution for at least 10 min prior to recording the voltammograms. All chemical potentials were modified using ferrocene/ferrocenium as internal standard electrode.

Synthesis of ligand (L)

Bis((E) 3-(2-nitrophenyl)-2-propenal)propane-1,2-diimine as a bidentate Schiff base ligand was prepared by condensation reaction of propane-1,2-diamine, (2 mmol) with 2-nitrocinnamalde-hyde (4 mmol) in absolute methanol (25 mL) under severe stirring for 1.5 h in an ice bath. After completion of the reaction, the reaction mixture was poured into cooled water (50 mL). Then the yellowish-white precipitate was filtered, washed and recrystal-lized from ethanol to obtain pure ligand in 75% [30]. Some important physical and spectral (IR and UV–Visible) data have been collected in Table 1 and 2. The ¹H and ¹³C NMR data of ligand based on scheme 1 are as following:

¹*HNMR* (*in* DMSO-d₆): 8.11(d, 1H_e J = 8.85 Hz), 8.09(d, 1H_{e'}, J = 8.85 Hz), 7.91(d, 2H_{kk'}, J = 8.15 Hz), 7.79(d, 2H_{hh'}, J = 7.85 Hz), 7.70(t(dd), 2H_{ii'}, J = 6.76 Hz), 7.56(t(dd), 2H_{jj'}, J = 7.75 Hz and J = 7.70 Hz), 7.34(d,2H_{gg'}, J = 15.90 Hz), 6.93(dd, 1H_f, J = 15.80 Hz and J = 8.75 Hz), 6.92(dd, 1H_f, J = 15.80 Hz and J = 8.62 Hz), 3.66(bd, 1H_b, J = 7.30 Hz), 3.53(m, 2H_{ac}), 1.19(d, 3H_d, J = 5.70 Hz) ppm. ¹³*CNMR*(*in* DMSO-d₆): 163.18(C₂), 161.14(C_{2'}), 147.92 (C_{10,10'}), 135.37(C₄), 135.21 (C_{4'}), 133.49(C_{9,9'}), 132.54(C₅), 132.40(C_{5'}), 130.17(C₃), 130.11(C_{3'}), 129.79(C₆), 129.17 (C_{6'}), 128.39(C_{7,7'}), 124.42(C_{8.8'}) 67.27(C_{1'}), 65.83(C₁), 20.37 (C₁₁).

Synthesis of zinc complexes

The zinc complexes were synthesized by gradually addition of ethanolic solution of ligand (0.5 mmol in 10 mL) to zinc halide, thiocynate or azide salts in absolute ethanol (0.5 mmol in 10 mL) under severe stirring for 2–3 h at room temperature. After this time, the ZnLX₂ complexes were obtained as precipitate that were filtered off and washed with ethanol several times. The complexes were purified via recrystallization from dichloromethane/ ethanol mixture (1:1) and dried at (80–100 °C) under vacuum and kept in a desiccator over silica-gel. Some important physical and spectral (IR and UV–Visible) data have been collected in Table 1 and 2. The ¹H and ¹³C NMR data of zinc complexes based on scheme 1 are suggested as in below:

[*ZnLCl*₂]: ¹HNMR(in DMSO-d₆): 8.32(t(2d), 2H_{e,e'}, *J* = 8.65 Hz and *J* = 8.30 Hz), 8.03(d, 2H_{k,k'}, *J* = 8.15 Hz), 7.83(d, 2H_{hh'}, *J* = 7.65 Hz), 7.77(t(dd), 2H_{ii'}, *J* = 7.45 Hz and *J* = 7.55 Hz), 7.63 (t(dd), 2H_{jj'}, *J* = 7.75 Hz and *J* = 7.70 Hz), 7.56(d, 1H_g, *J* = 15.95 Hz), 7.55 (d, 1H_{g'}, *J* = 15.75 Hz), 7.00(dd, 1H_f, *J* = 15.72 Hz and *J* = 8.97 Hz), 6.98(dd, 1H_f, *J* = 15.72 Hz and *J* = 8.97 Hz), 3.80 (m, 2H_{b,c}), 3.61(b dd, 1H_a, *J* = 16.78 Hz and *J* = 4.60 Hz), 1.22(d, 3H_d, *J* = 6.20 Hz) ppm. ¹³CNMR(in DMSO-d₆): 165.97(C₂), 163.83(C_{2'}), 147.96(C_{10,10'}), 138.48(C₄), 138.22(C_{4'}), 133.81(C_{9,9'}), 131.14(C₅), 130.86(C_{5'}), 130.40(C₃), 130.35(C_{3'}), 129.98(C₆), 129.93(C_{6'}), 128.40(C_{77'}), 124.64(C_{8.8'}),65.33(C_{1'}), 64.10 (C₁), 19.87(C₁₁) ppm.

[*ZnLBr*₂]: ¹HNMR(in DMSO-d6): 8.43(t(2d), 2H_{ee'}, *J* = 8.40 Hz and *J* = 7.50 Hz), 8.05(d, 2H_{kk'}, *J* = 8.10 Hz), 7.81(m, 4H_{hh'ii'}), 7.65(t, 4H_{jj'gg'}) detailed as [7.66 (t(dd), 2H_{jj'}, *J* = 7.05 Hz and *J* = 7.80 Hz), 7.65(d, 2H_{gg'}, *J* = 14.85 Hz], 7.06(sixtet, 2H_{ff}) detailed as [7.08 (dd,1H_f, *J* = 17.10 Hz and *J* = 9.05 Hz), 7.05(dd, 1H_f, *J* = 15.98 Hz and *J* = 9.00 Hz)], 3.89(m, 2H_{bc}), 3.64(dd, 1H_a, *J* = 20.10 Hz and *J* = 6.90 Hz), 1.26(d, 3H_d, *J* = 10.40 Hz) ppm. ¹³CNMR(in DMSO-d₆): 167.22(C₂), 165.16(C_{2'}), 147.95(C_{10,10'}), 139.98(C₄), 139.76(C_{4'}), 139.96(C_{9,9'}), 130.68(C₅), 130.64 (C_{5'}), 130.37 (C₃), 130.05(C_{3'}), 129.91(C₆), 129.86(C_{6'}), 128.34(C_{7.7'}), 124.76(C_{8.8'}), 64.34(C_{1'}), 63.30(C₁), 19.90(C₁₁) ppm.

[*ZnLl*₂]: ¹HNMR(in DMSO-d₆): 8.31(t(2d), 2H_{ee'}, *J* = 8.80 Hz and *J* = 8.75 Hz), 8.02(d, 2H_{kk'}, *J* = 8.05 Hz), 7.84(d, 2H_{hh'}, *J* = 8.05), 7.77(t(dd),2H_{ii'}, *J* = 7.45 Hz and *J* = 7.65 Hz), 7.62(t(dd), 2H_{ij'}, *J* = 8.05 Hz, *J* = 7.45 Hz), 7.53(d, 2H_{gg'}, *J* = 15.75 Hz), 7.06(sixtet, 2H_{ff'}) detailed as [7.06 (dd,1H_f, *J* = 15.62 Hz and *J* = 10.80), 7.04(dd, 1H_f, *J* = 15.65 Hz and *J* = 9.30 Hz)], 3.79(bd, 2H_{b,c}, *J* = 9.05), 3.06(dd, 1H_a, *J* = 13.87 Hz and *J* = 7.1 Hz), 1.22(d, 3H_d, *J* = 6.15 Hz) ppm. ¹³CNMR(in DMSO-d₆): 165.90(C₂), 163.96(C_{2'}), 147.95(C_{10,10'}), 138.72(C_{4+4'}), 133.81(C_{9.9'}), 131.08(C₅), 130.86(C_{5'}), 130.41(C₃), 130.38(C_{3'}), 130.00(C₆), 129.65(C_{6'}), 128.33(C_{7.7'}), 124.65(C_{8.8'}), 65.27(C_{1'}), 64.18(C₁), 20.04(C₁₁) ppm.

[*ZnL*(*NCS*)₂]: ¹HNMR(in DMSO-d₆): 8.20(d, 1H_e, *J* = 8.95 Hz), 8.18(d, 1H_{e'} *J* = 9.00 Hz), 8.00(d, 2H_{kk'}, *J* = 8.15 Hz),7.92(d, 2H_{hh'}, *J* = 7.80 Hz), 7.73(t(dd), 2H_{ii'}, *J* = 7.55 Hz and 7.70 Hz), 7.59(t(dd), 2H_{jj'}, *J* = 7.75 Hz and *J* = 7.70 Hz), 7.44 (d, 1H_g, *J* = 15.85 Hz), 7.43(d, 1H_{g'}, *J* = 15.80), 7.03 (septet, 2H_{fF}) detailed as [7.037 (dd, 1H_f, *J* = 15.25 Hz and *J* = 8.80 Hz), 7.04(dd, 1H_f, *J* = 15.55 Hz and *J* = 9.35 Hz)], 3.73(dd, 1H_b, *J* = 12.05 and *J* = 4.50 Hz), 3.65(sixtet, 1H_c, *J* = 6.10 Hz), 3.54(dd, 1H_a, *J* = 11.95 Hz and *J* = 6.40 Hz),

Table 1	
Analytical and physical data of the Schiff base ligand (L) and its Zn(II) complexe	S.

Compounds	Color	Decomposed point. (°C)	Yield (%)	Found (Calcd.) (%)			$\Lambda_{\rm M}({\rm cm}^2\Omega^{-1}{\rm M}^{-1})$
				С	Н	Ν	
L	Light yellow	74	75	64.42(64.28)	5.21(5.14)	14.18(14.28)	0.045
ZnLCl ₂	Cream	260	61	47.83(47.70)	3.73(3.81)	10.71(10.60)	0.030
ZnLBr ₂	Cream	282	60	41.1(40.84)	3.1(3.26)	9.2(9.07)	0.035
ZnLI ₂	Cream	265	80	35.10(35.44)	2.89(2.83)	7.80(7.87)	0.162
$ZnL(NCS)_2$	Cream	220	72	48.30(48.13)	3.42(3.51)	14.60(14.64)	0.055
$ZnL(N_3)_2$	Cream	195	55	46.7(46.55)	3.6(3.72)	26.1(25.85)	0.096

Table 2

Vibrational (cm⁻¹) and electronic (nm) spectral data of the Schiff base (L) and its zinc (II) complexes.

Compound	νCH_{imine}	vSCN	νN_3	vC=N	vC-N	vC=C	vM-N	vNO_2	$\lambda_{\max} (\varepsilon, \operatorname{cm}^{-1} \operatorname{M}^{-1})$
L	2828(w)	-	-	1635(m), 1616 (m)	1155(m)	1476(w), 1443(w)		1513(vs), 1350(vs)	216, 258, 326(sh)
ZnLCl2	2864(w)	-	-	1634(vs),1619(s)	1169(s)	1480(w),1440(m)	551(w), 512(w)	1527(vs), 1346(vs)	222, 258, 283(sh),326(sh)
ZnLBr2	2853(w)	-	-	1638(vs)	1171(s)	1476(w),1441(w)	517(w),486(w)	1518(vs), 1342(vs)	222, 267, 286, 326(sh)
ZnLI2	2854(w)	-	-	1636(vs)	1173(s)	1476(w),1442(m)	512(w),489(w)	1521(vs), 1343(vs)	227, 265, 285, 326(sh)
ZnL(NCS) ₂	2829(w)	2069(VS)	-	1635(vs)	1174(S)	1476(w),1442(w)	489(w)	1522(vs , 1342(w)	218, 264, 294, 322(sh)
ZnL(N ₃) ₂	2860(w)	-	2067(vs)	1636(vs)	1176(s)	1462(w),1442(w)	519(w),478(w), 458(w)	1516(vs), 1341(vs)	224, 267, 283, 326(sh)

1.19(d, $3H_d$, $J = 6.35 \text{ Hz}(\text{ppm.}^{13}\text{CNMR}(\text{in DMSO-d}_6): 164.72(C_2),$ 162.64(C_{2'}), 147.95(C_{10,10'}), 136.93(C_4), 136.69(C_4'), 135.20(C_{SCN}), 133.61(C_{9.9'}), 131.84(C_5), 131.62(C_{5'}), 130.09(C_3), 130.04(C_{3'}), 128.48(C_{6.6'}, C_{7.7'}), 124.52(C_{8.8'}), 66.31(C_{1'}), 64.93(C₁), 20.08(C₁₁) ppm.

[*ZnL*(*N*₃)₂]: ¹HNMR(in DMSO-d₆): 8.29(t(2d), 2H_{ee'}, *J* = 9.15 Hz and *J* = 11.20 Hz), 8.02(d, 2H_{kk'}, *J* = 8.15 Hz), 7.88(d, 2H_{hh'}, *J* = 7.85 Hz), 7.75(t(dd), 2H_{ii'}, *J* = 7.50 Hz and *J* = 7.65 Hz), 7.61(t(dd), 2H_{jj'}, *J* = 7.50 Hz and 7.80 Hz), 7.51(d, 1H_g, *J* = 16.05 Hz), 7.60(d, 1H_{g'}, *J* = 15.80 Hz), 7.04(dd, 2H_{ff'}, *J* = 15.75 Hz and *J* = 8.95 Hz), 3.75(m, 2H_{bc}), 3.57(dd, 1H_a, *J* = 18.55 Hz and *J* = 5.35), 1.19(d, 3H_d, *J* = 6.20 Hz(ppm. ¹³CNMR(in DMSO-d₆): 165.90(C₂), 163.76(C_{2'}), 147.96(C_{10,10'}), 138.07(C₄), 137.80(C_{4'}), 133.70(C_{9.9'}), 131.35(C₅), 131.06(C_{5'}), 130.29(C₃), 130.23(C_{3'}), 130.03(C₆), 129.97(C_{6'}), 128.45(C_{7.7'}), 124.59(C_{8.8'}), 65.56(C_{1'}), 64.11(C₁), 19.73(C₁₁) ppm.

Results and discussion

Physical and analytical data

All the analytical, physical and spectroscopic data of the Schiff base and its zinc complexes have been collected in Table 1 and 2. The analytical data are in agreement with the chemical formula of present ligand and its zinc coordination compounds (ZnLX₂; $X = Cr^-$, Br^- , I^- , SCN⁻ and N_3^-) (Scheme 1). All zinc complexes are soluble in most of common organic solvents such as chloroform, dichloromethane, dimethylformamide and dimethylsulfoxide but are non-soluble in alcohols such as ethanol and methanol. Melting point of Schiff base ligand is 74 °C but the zinc complexes are decomposed in the range of 195–282 °C. All complexes were found to have molecular structure based on their molar conductivities that were in the range of 0.03–0.162 cm² Ω^{-1} M⁻¹ in chloroform solvent at room temperature [24,29]. Conductivity values confirm coordination of Schiff base and X⁻ ions to zinc center collectively in the same coordination sphere.

Infra-red spectral data

Some important IR absorption frequencies of Schiff base ligand and its zinc complexes have been summarized in the Table 2. The IR spectrum of the Schiff base shows several weak peaks at 3079, 3022, 2988 and 2828 cm⁻¹ that are attributed to aromatic, olefinic, aliphatic and iminic C-H groups respectively. They have small changes on binding of ligand to zinc ion. In another region, the ligand IR spectrums exhibits two medium peaks at 1635 and 1616 cm⁻¹ confirming the formation of azomethine linkages that may be assigned to asymmetric and symmetric stretching vibrations, respectively [27-33]. After binding the ligand to zinc ion center, the intensity of azomethine asymmetric peak is increased and appeared as very strong peak in all IR spectra of zinc. The position of this peak is unchanged in the case of zinc thiocyanate complex; shifts to lower wave number by 2 cm⁻¹ in the case of zinc chloride complex and ultimately shifts to higher energy by $1-3 \text{ cm}^{-1}$ in the cases of zinc bromide, iodide and azide complexes. On the other hand, azomethine symmetric peak is shifted to higher wave numbers by 3–20 cm⁻¹ and merged with asymmetric peak in the case



Scheme 1. Structural formula of ligand and its zinc complexes.



Fig. 1. Cyclic voltammograms of ligand, (a) ZnLCl₂, ZnLBr₂, ZnLI₂, ZnL(NCS)₂ and ZnL(N₃)₂, (b) 1–5, respectively.

of zinc bromide, iodide, thiocyanate and azide complexes indicating coordination of the Schiff base to zinc ion through the iminic nitrogen(s) in all complexes.

In the ligand spectrum, asymmetric and symmetric stretching of NO₂ groups are present at 1513 and 1350 cm⁻¹ that are shifted by 3–14 and 4–9 cm⁻¹ to higher and lower wave numbers respectively after complexation [34]. Stretching vibrations of M– N in the complexes are seen as weak absorption frequencies at 450–550 cm⁻¹ [35] that confirm the coordination of two azomethine nitrogens of Schiff base ligand, -NCS and -N₃ ions. Also binding of azide and thiocyanate ions to zinc ion are certainly proved by appearance of very strong peaks assigned to stretching vibrations of coordinated azide and *N*-coordinated thiocyanate ions at 2067 and 2069 cm⁻¹, respectively [36–38].

UV-Visible Spectra

The electronic spectral data of ligand and its zinc complexes in chloroform have been presented in Table 2. In UV–visible spectrum of ligand, three bands including a band at 216 nm, a shoulder band at 326 nm and a very intensive band at 258 nm are observed that may be related to the π – π * transition of benzene rings, alkene and imine bounds respectively. After binding of ligand to zinc ion, the first band is red shifted at all complexes by 2–8 nm. The third band is also red shifted and smoothly converted to two intensive bands at the ranges of 258–267 and 283–294 nm after coordination. These changes in electronic spectra are due to coordination of ligand to zinc ion and then the π - back bounding from d-electrons of zinc to π * orbitals on ligand molecular in the complexes structures.

¹H and ¹³C NMR spectra

The ¹H and ¹³C NMR spectra of Schiff base ligand and all its zinc complexes (data brought in experimental section) provide required evidences for confirming of suggested structures in scheme 1. The ¹H NMR spectrum of the ligand shows the imine protons (H_e and $H_{e'}$ signals as two doublets(d) at 8.11 and 8.09 ppm with the same coupling constants of 8.85 Hz [39]. The signals assigned to aromatic hydrogens(kk' and hh') of the ligands are seen as two doublets(d) at 7.91 and 7.79 ppm with coupling constants of 7.85 and 6.76 Hz, respectively [40]. It is expected that two doublet of doublet signals(dd) be appeared for ii' and jj' but due to unification of two inside lines, two distinct triplets(t) observed at 7.70 and 7.56 ppm are attributed to ii' and jj' hydrogens respectively. Other hydrogen signals of ligand are appeared as: g and g' hydrogens due to coupling with f and f' as a doublet at 7.34 ppm; f and f' hydrogens as two separate doublet of doublets (dd) due to coupling with g and g' protons and then with e and e' at 6.93 and 6.92 ppm; ali-

phatic hydrogens of b, (a, c) and d as a broad doublet(bd), a multiplet(m) and a doublet(d) respectively at 3.66, 3.53 and 1.19 ppm. The ¹H NMR spectra of the zinc complexes of the ligand showed the proton signals of ligand as well as distinguishable changes. After coordination, two doublet signals of imine hydrogens are merged in the zinc chloride, bromide, iodide and azide complexes and observed as a downfielded triplets(t(2d)) at 8.29-8.43 ppm except for zinc thiocyanate complex that only downfielded of two separate doublet signals are seen at 8.20 and 8.18 ppm. Other spectral changes include downfielding of aromatic hydrogens of kk', ii' and jj' to 8.00-8.05, 7.73-7.77 and 7.59-7.63 ppm respectively and upfielding of hydrogens of hh' except for zinc thiocyanate complex. The g and g' hydrogens are separated and downfielded in zinc chloride, thiocyanate and azide complexes but only are downfieled in zinc bromide and iodie complexes with respect to free ligand. The hydrogen signals of f and f' shift to down field in zinc chloride. bromide iodide and thiocyanate complexes while they are merged and appeared at the same chemical shift in the zinc azide complex spectrum. All the aliphatic hydrogens signals of b, (a, c) and d are shifted to down field after coordination. Also in comparison with the free ligand, the signals of a and c hydrogens are observed separately. The ¹³C NMR spectrum of the ligand is suggested to show two different azomethine carbons signals at 163.18(C₂) and 161.14(C_{2'}) ppm, respectively [28,29]. These signals were found to be appeared at 165.64-168.55 and 162.54-165.70 ppm after binding of ligand to zinc ion center. The suggested carbon signals for C(10', 10), C(4',4), C(9',9), C(6',6) and C(8',8) in ligand spectrum are shifted to down field but the proposed signals for C(5',5), C(1',1)and C(11) smoothly are appeared at up field in the zinc complexes. The carbon signals that may be assigned to C(7',7) and C(3',3) are also changed after coordination but with different trends in zinc complexes.

Electrochemical behavior

Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution. Accordingly cyclic voltammograms of present ligand and its zinc complexes were recorded in dry acetonitrile solutions on glassy carbon electrode with scan rate of 0.1 V/S and are illustrated in Fig. 1. The redox potential data have been summarized in Table 3. The ligand is redox active within the experimental potential window of acetonitrile. It displays a semi-reversible cyclic voltammogram. With running toward negative voltages, Schiff base ligand is reduced in two negative potentials of -0.98 and -1.56 V. These reductive processes may be attributed to reduction of nitro groups to nitro radical anions [41]. In a reverse sweeping of voltage, the radical anions that appeared in reductive processes are oxidized at anodic potentials of -1.21, -0.81 and -0.57 V. Cyclic voltammograms of all zinc

Table	3
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Electrochemical data of ligand and complexes.

Compounds	$E_{PC1}(E_{PC/2}), E_{PC2}(E_{PC/2})$	$\Delta E_{\rm P1}^{\rm a}$	ΔE_{P2}^{b}	$E_{\text{Pa1}}(E_{\text{Pa}/2}), E_{\text{Pa2}}(E_{\text{Pa}/2}), E_{\text{Pa3}}(E_{\text{Pa}/2})$
L	-0.98(-0.88), $-1.56(-1.42)$	-0.10	-0.14	-1.21(-1.32), -0.81(-0.88), -0.57(-0.62)
ZnLCl ₂	-0.86(-0.73)	-	-0.13	-
ZnLBr ₂	-0.58(-0.49)	-	-0.09	-
ZnLI ₂	-0.46(-0.37)	-	-0.09	-
$ZnL(NCS)_2$	-0.76(-0.62)	-	-0.14	-
$ZnL(N_3)_2$	-0.64(-0.49)	-	-0.15	-

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

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

Table 4

Theoretical parameters of optimized structures including HF-energy, Gibbs free energy and enthalpy (in kJ/mol).

Thermodynamic parameters(theoretical)	L	ZnLCl ₂	ZnLBr ₂	ZnLI ₂	ZnL(NCS) ₂	ZnL(N ₃) ₂
HF energy	-1314.903	-1410.605	-1407.044	-1403.485	-1584.093	-1704.599
Zero temperature energy	0.399	0.404	0.403	0.403	0.421	0.424
Corrected zero temperature energy	0.383	0.388	0.387	0.387	0.406	0.408
Gibs free energy	-1314.569	-1410.271	-1406.714	-1403.157	-1583.746	-1704.252
Corrected Gibs free energy	-1314.585	-1410.288	-1406.730	-1403.172	-1583.762	-1704.2667
Total electron energy	-1314.477	-1410.169	-1406.609	-1403.050	-1583.635	-1704.139
Corrected total energy	-1314.520	-1410.216	-1406.657	-1403.098	-1583.688	-1704.191
Enthalpy	-1314.476	-1410.168	-1406.608	-1403.049	-1583.634	-1704.138
Corrected Enthalpy		-1410.184	-1406.624	-1403.065	-1583.651	-1704.154

Table 5

Selected bond distances, bond angles and torsion angles of optimized structures.

Selected data	L	ZnLCl ₂	ZnLBr ₂	ZnLI ₂	ZnL(SCN) ₂	$ZnL(N_3)_2$
Bond length(Å)						
M-N(1)	-	2.080	2.075	2.071	2.072	2.127
M-N(2)	-	2.091	2.086	2.072	2.062	2.131
M-X(1)	-	2.417	2.647	2.886	2.594	1.987
M-X(2)	-	2.440	2.619	2.852	2.610	1.955
C(2)=N(1)	1.325	1.328	1.328	1.330	1.333	1.326
C(2')=N(2)	1.324	1.330	1.331	1.333	1.332	1.327
Bond angle(°)						
N(2) - M - N(1)	-	83.67	84.02	84.30	84.57	80.90
N(2) - M - X(1)	-	112.20	114.46	112.99	115.34	115.50
N(2) - M - X(2)	-	113.39	111.65	112.78	114.35	101.37
N(1)-M-X(1)	-	110.78	104.56	109.41	113.81	102.64
N(1)-M-X(2)	-	106.28	111.88	107.97	104.02	106.10
X(1)-M-X(2)	-	123.14	122.99	122.48	118.89	136.10
Torsion angle(°)						
N(1)-C(1)-C(1')-N(2)	-67.13	-49.21	-48.82	-47.25	-45.26	-47.37
N(1)-C(2)-C(3)-C(4)	-179.64	179.06	179.72	179.27	-177.29	178.52
N(2)-C(2')-C(3')-C(4')	-0.48	-30.91	-30.24	28.32	33.33	36.25
C(3)-C(4) -C(5)-C(6)	0.21	-1.71	-1.46	-0.82	10.40	0.26
C(3')-C(4')-C(5')-C(6')	164.03	-164.60	-164.86	-171.62	-166.73	167.36



Fig. 2. Optimized structure of ligand (left) and zinc ZnLCl₂ (right).

complexes show only a reductive irreversible electrochemical wave. In the complexes voltammograms, one cathodic reduction

in the range of -0.46 to -0.86 V is seen that may be assigned to the first reduction of ligand at them. In comparison with free

ligand, the reduction potential is changed to more positive values due to the coordination of ligand to the zinc(II) ion center. As shown in Table 3, positive shift of reduction wave is increased in the order of $ZnLI_2 > ZnLBr_2 > ZnLCl_2$ for halide complexes and $ZnL(N_{3})_2 > ZnL(NCS)_2$ for two pseudo-halides complex.

Overall after binding of ligand to zinc center, the iminic nitrogens of ligand obtain positive formal charge. This positive charge is induced to the rest of ligand structure. Naturally more strength bonding to metal center leads to more induction of positive charge on the ligand surface. This causes easier reduction namely at less negative potential (or more positive). As it can be seen from theoretical calculation (Table 5), the bond length of Zn-N(iminic) of halide complexes is decreased as ZnLCl₂ > ZnLBr₂ > ZnLl₂ and/or in other phrase bond strength is ordered in contrary direction. It seems that the observed trend for ease of reduction in zinc halide complexes is in agreement with this explanation. But about two pseudo-halide zinc complexes namely zinc azide and thiocyanate. the observed trend for reduction viz. $ZnL(N_3)_2 > ZnL(NCS)_2$ is in contrast with before explanation. In this case it is suggested that another more effective agent may be responsible. We think more positive inductive property of azide with respect to thiocyanate on zinc indirectly reinforces positive charge on the ligand structure that leads to easier reduction of azide complex and observed trend.

Molecular modeling and analysis

Based on pseudo-tetrahedral geometry of zinc complexes, the molecular modeling and geometry optimization of Schiff base ligand (L) and all the complexes were performed at the UB3LYP/ LANL2MB* level of theory without considering any symmetry group. The similarity of some important structural parameters obtained for zinc chloride complex with X-ray structural ones in a similar complex suggests relative usefulness of the method for the complexes [42]. For instance, the optimized structures of ligand and its zinc chloride complex are depicted in fig. 2.

Some theoretical energetic parameters such as HF-energy, zero temperature energy, Gibbs free energy and enthalpy have been extracted and listed in Table 4. HF energy, the corrected Gibbs free energy, total electron energy and enthalpy of ligand are -1314.903, -1314.585, and -1314.492 kJ/mol respectively. After complex formation, these parameters shift to more negative values as in Table 4. Some selected bond distances, bond angles and torsion angles of optimized structures (based on numbering in scheme 1) are summarized in Table 5. Two different imine bond lengths of ligand including C(2)=N(1) and C(2')=N(2) are 1.324 and 1.325 Å that are increased to the range of 1.326-1.333 Å Confirming the coordination of azomethine groups through nitrogen atoms. Bond angles around the zinc ion are defined as N(2)-M-N(1), N(2)-M-X(1), N(2)-M-X(2), N(1)-M-X(1), N(1)-M-X(2) and X(1)-M-X(2) that are placed in the ranges of 80.90-84.57°, 112.20-115.50°, 111.65-114.35°, 102.64–110.78°, 104.02–111.88° and 118.89–136.10°, respectively. These values are in agreement with proposed pseudo-tetrahedral geometry for all zinc complexes. Torsion angle around of C(1)-C(1'), C(2)-C(3), C(2')-C(3'), C(4)-C(5) and C(4')-C(5') in ligand structure are -67.13°, -179.64°, -0.48°, 0.21° and 164.03° that are shifted to value ranges from -45.26° to -49.21° , -177.29° to 179.72°, -30.91° to 36.25°, -1.71° to 10.40° and -171.62° to 167.36° in zinc complexes, respectively.

Conclusion

In this research we reported the synthesis, full spectroscopic characterization, electrochemical and theoretical investigation of a new asymmetric bidentate Schiff base ligand and its zinc(II) halide, azide and thiocyanate complexes. The physical, spectral

and theoretical data suggest pseudo-tetrahedral geometry for all complexes. Electrochemical behavior of ligand and complexes were investigated by cyclic voltammetry technique. The cyclic voltammogram of ligand showed semi-reversible redox processes while the zinc complexes exhibited irreversible electrochemical behavior so that only a reductive wave is observed in their cyclic voltammograms. The ligand and its zinc complexes were subjected to molecular modeling at the UB3LYP/LANL2MB* level of theory. Optimization suggested pseudo-tetrahedral geometry for all zinc complexes. Accordingly some theoretical thermodynamic and structural parameters such as HF-energy, Gibbs free energy, enthalpy, selected bond distances, bond angles and torsion angles of optimized structures were presented.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.05.011.

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