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Synthesis, characterization and experimental, theoretical, electrochemical, antioxidant and antibacterial study of a new Schiff base and its complexes



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HIGHLIGHTS

- The 1,6-bis(2-(2-hydroxybenzilidenamino)-4-chlorophenoxy)hexane synthesized.
 New Cu(II), Ni(II), Co(II), Zn(II), Mn(II),
- New Cu(II), NI(II), Co(II), ZI(II), MI(II) Ti(III) and V(III) complexes synthesized.
- The structures of metal complexes were characterized by different analysis.
- In addition, antioxidant, theoretical NMR and cyclic voltammetry studies done.

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



ABSTRACT

A new Schiff base ligand was synthesized by reaction of salicylaldehyde with 1,6-bis(4-chloro-2-aminophenoxy)hexane. Then the Schiff base complexes were synthesized by metal salts and the Schiff base. The metal to ligand ratio of metal complexes was found to be 1:1. The Cu(II) complex is proposed to be square planar and the Co(II), Ni(II), Mn(II) and Zn(II) complexes are proposed to be tetrahedral geometry. The Ti(III) and V(III) complexes are proposed to be a capped octahedron in which a seventh ligand has been added to triangular face. The complexes are non-electrolytes as shown by their molar conductivities (Λ_M). The structure of metal complexes is proposed from elemental analysis, FT-IR, UV-vis, magnetic susceptibility measurements, molar conductivity measurements, Mass Spectra and thermal gravimetric analysis. In addition antimicrobial and antioxidant studies, cyclic voltammetry of the complexes, theoretical ¹H NMR and HOMO–LUMO energy calculations of the new di-functional ligand were done.

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Introduction

Metal complexes of Schiff bases are playing an important role in the development of coordination chemistry, which is evident in number of publications, including electrochemical studies,

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antioxidant and antimicrobial activities [1–8]. A large number of reports are available on the chemistry and the biological activities of transition metal complexes containing O,N and S,N donor atoms [9–11]. Through the years, Schiff bases played and developed a central role as chelating ligands in the main group and transition metal coordination chemistry [12–14]. Transition metal complexes with tetradentate Schiff-base ligands have been extensively investigated as catalysts for a number of organic redox reactions and electrochemical reduction processes [15–17]. The molecular parameters: total energy, heat of bonding energy, isolated energy, electronic energy, heat of formation, dipole moment, HOMO and LUMO of the ligand and complexes have been studied recently [18–22].

In the present work, we have synthesized a new Schiff base by reaction of salicylaldehyde and 1,6-bis(4-chloro-2-aminophenoxy)hexane. Then the Schiff base complexes were synthesized by the reactions of metal salts and the Schiff base. Spectral, cyclic voltammetry, antimicrobial studies, and magnetic properties of the new compounds were studied in detail.

Materials and methods

The 1,6-bis(4-chloro-2-aminophenoxy)hexane used in the synthesis were prepared from 4-chloro-2-nitrophenole, 1,6-dibromoropane and K₂CO₃ as shown in Fig. 1 [23,24]. All the chemicals and solvents were of analytical grade and used as received. Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. IR spectra were recorded on a PERKIN ELMER SPECTRUM 100 FTIR spectrophotometer on a universal ATR arm in the wave number range of 4000–650 cm⁻¹. Electronic spectral studies were conducted on a PERKIN ELMER LAMBDA 750 model UV Visible spectrophotometer in the wavelength 200-900 nm. Molar conductivities were measured with a WTW LF model 330 conductivity-meter using prepared solution of the complexes in DMF solvent. Electrochemical experiments were performed with an Autolab PGSTAT 128N potentiostat, (The Netherlands) using a three electrode system, glassy carbon working electrode (Φ : 3 mm, BAS), platinum wire as auxiliary electrode and Ag/AgCl (NaCl 3M, Model RE-1, BAS, USA) as reference electrode. The reference electrode was separated from the bulk solution by a frittedglass bridge filled with the solvent/supporting electrolyte mixture. Before starting each experiment, the glassy carbon electrode was polished manually with alumina (Φ : 0.01 µm). Cyclic voltammetric (CV) experiments were recorded at room temperature in extra pure dimethyl formamide (DMF), and ionic strength was maintained at 0.1 M with electrochemical grade tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. Solutions were deoxygenated by a stream of high purity nitrogen for 15 min prior to the experiments, and during the experiments nitrogen flow was maintained over the solution.

¹H and ¹³C NMR spectra were recorded using a BRUKER AVANCE DPX-400 NMR spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20 °C) using Hg[Co(SCN)₄] as a calibrant; diamagnetic corrections were calculated from Pascal's constants [25]. Mass spectral analyses were determined Agilent LC/MSD model. Thermal gravimetric analyses were determined on a EXSTAR S II TG/DTA 6300 Model. Gaussian computations were performed by using a standard personal computer having 4 GB RAM. Gaussian 09 and GaussView 5 software were used for the theoretical NMR calculations, Highest Occupied Molecular Orbital (HOMO)-Lowest Unoccupied Molecular Orbital (LUMO) energy calculation, and visualization processes [26,27]. 2,2-Diphenyl-1-picryl-hydrazyl (DPPH), ferrous chloride, 3-(2-pyridyl)-5,6-bis(4-phenyl-sulfonic acid)-1,2,4-triazine (ferrozine), ascorbic acid, trolox and dimethyl formamide (DMF) were obtained from Sigma (Sigma-Aldrich GmbH, Sternheim, Germany). The blank antimicrobial test discs purchased from Oxoid (7.0 mm, Oxoid Ltd, Wade Road, Basingstoke, Hants, RG24 8PW, UK).

Synthesis of Schiff base

To a stirred solution of 1,6-bis(4-chloro-2-aminophenoxy)hexane (20 mmol) in methanol (60 mL) was added dropwise salicylaldehyde (40 mmol) in methanol (40 mL). After the addition was completed, the stirring was continued for 2 h, and



Fig. 1. Synthesis of the 1,6-bis(4-chloro-2-aminophenoxy)hexane.

then precipitate was filtered and washed with methanol and dried in air (Fig. 2).

Synthesis of Schiff base complexes

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

Characterization of Schiff base (L)

Molecular Weight: 577. M.P: 168–170 °C. Color: Yellow. Yield: 9.3 g (80.9%). Anal Calcd. for $C_{32}H_{30}N_2O_4Cl_2$: C, 66.55, H, 5.19, N, 4.85. Found: C, 66.54, H, 5.37, N, 4.79. IR (cm⁻¹): 3049 v(Ar—CH), 2937, 2866 v(Alf.—CH), 1618 v(C=N), 1485, 1474 v(Ar—C=C), 1292, 1253 v(Ar—O), 1178, 1169 v(R—O). UV–vis: λ_1 = 262 nm (ε = 3200), λ_2 = 273 (ε = 3400) nm λ_3 = 384 nm (ε = 3600). ¹³C NMR (ppm, in DMSO-d₆): OCH₂CH₂CH₂: 65.26, OCH₂CH₂CH₂: 26.72, OCH₂CH₂CH₂: 22.12, OH—C: 162.08, HC=N: 160.76, (Ar—C): 109.06, 113.44, 119.52, 120.13, 121.41, 121.57, 129.35, 134.23, 136.03, 137.12. ¹H NMR (ppm, in DMSO-d₆): δ = 4.04 (t, OCH₂CH₂CH₂CH₂, J = 6.08), δ = 2.27 (OCH₂CH₂CH₂, dd, J = 6.86 Hz), δ = 1. 76 (OCH₂CH₂CH₂, d, J = 7.12 Hz), δ = 6.90–7.60 (Ar—H), δ = 8.99 (HC=N), δ = 13.60 (OH). Mass Spectra: m/z: 473 [L–(Cl)₂–(OH₂)⁺.

Characterization of CuL

Molecular Weight: 639. M.P: $152-154 \,^{\circ}$ C decompose. Color: Green. Yield: 0.97 g (76%). Anal Calcd. for CuC₃₂H₂₈N₂O₄Cl₂: C, 60.09, H, 4.38, N, 4.38. Found: C, 59.16, H, 4.53, N, 4.42. Selected IR data (KBr, $\nu \, \text{cm}^{-1}$): 3056 ν (Ar—CH), 2928, 2863 ν (Alf.—CH), 1605 ν (C=N), 1492, 1453,1446 ν (Ar—C=C), 1245, 1217 ν (Ar—O), 1147, 1129 ν (R—O). $\lambda_1 = 273 \, \text{nm}$ ($\varepsilon = 3800$), $\lambda_2 = 380 \, \text{nm}$ ($\varepsilon = 2000$) $\mu_{\text{eff}} = 1.81 \, \text{B.M. Mass Spectra: } m/z: 640 \, [CuL+H]^+.$

Characterization of NiL

Molecular Weight: 633. M.P: 136–138 °C. Color: Light Brown. Yield: 0.87 g (71%). Anal Calcd. for NiC₃₂H₂₈N₂O₄Cl₂: C, 60.66, H, 4.42, N, 4.42. Found: C, 60.47, H, 4.55, N, 5.04. Selected IR data (KBr, v cm⁻¹): 3065 v(Ar—CH), 2937, 2866 v(Alf.—CH), 1617, v(C=N), 1486, 1474 v(Ar—C=C), 1254, 1221 v(Ar—O), 1178, 1149



Fig. 2. Synthesis of the ligand (L).

v(R-O). UV-vis (λ_{max} , nm) in DMF: $\lambda_1 = 277$ nm ($\varepsilon = 3050$), $\lambda_2 = 353$ nm ($\varepsilon = 2900$), $\lambda_3 = 432$ nm ($\varepsilon = 180$). $\mu_{eff} = 2.73$ B.M. Mass Spectra: m/z: 635 [NiL+2H]⁺.

Characterization of CoL

Molecular Weight: 634. M.P: 137 °C decompose. Color: Red. Yield: 0.84 g (67%). Anal Calcd. for $CoC_{32}H_{28}N_2O_4Cl_2$: C, 60.56, H, 4.41, N, 4.41. Found: C, 60.81, H, 4.46, N, 4.73. Selected IR data (KBr, v cm⁻¹): 3054 v(Ar—CH), 2937, 2866 v(Alf.—CH), 1615, v(C=N), 1486, 1474 v(Ar—C=C), 1254, 1216 v(Ar—O), 1149, 1130 v(R—O). UV–vis (λ_{max} , nm) in DMF: $\lambda_1 = 271$ nm ($\varepsilon = 3300$), $\lambda_2 = 353$ nm ($\varepsilon = 3000$), $\lambda_3 = 436$ nm ($\varepsilon = 420$). $\mu_{eff} = 3.85$ B.M. Mass Spectra: m/z: 633 [CoL–H]⁺.

Characterization of ZnL

Molecular Weight: 640. M.P: 144–146 °C. Color: Orange. Yield: 0.77 g (60%). Anal Calcd. for ZnC₃₂H₂₈N₂O₄Cl₂: C, 60.00, H, 4.37, N, 4.37. Found: C, 60.71, H, 4.73, N, 5.06. Selected IR data (KBr, ν cm⁻¹): 3062 ν (Ar–CH), 2938, 2866 ν (Alf.–CH), 1615, ν (C=N), 1486, 1464 ν (Ar–C=C), 1250, 1217 ν (Ar–O), 1179, 1149 ν (R–O). ¹H NMR (ppm, in DMSO-d₆): δ = 4.02 (t, OCH₂CH₂CH₂, *J* = 6.12), δ = 2.26 (OCH₂CH₂CH₂, dd, *J* = 6.82 Hz), δ = 1.76 (OCH₂CH₂CH₂Cd, d, *J* = 7.08 Hz), δ = 6.93–7.62 (Ar–H), δ = 8.83 (HC=N). UV–vis (λ max, nm) in DMF: λ ₁ = 278 nm (ε = 3400), λ ₂ = 354 nm (ε = 3400). μ eff = Diamagnetic. Mass Spectra: *m*/*z*: 387 [ZnL–(O(CH₂)₆O)–(C₆H₃Cl)–(NCH)]⁺.

Characterization of MnL

Molecular Weight: 630. M.P: 138–142 °C. Color: Light Brown. Yield: 0.16 g (13%). Anal Calcd. for $MnC_{32}H_{28}N_2O_4Cl_2$: C, 60.95, H, 4.44, N, 4.44. Found: C, 58.53, H, 4.99, N, 5.07. Selected IR data (KBr, *v* cm⁻¹): 3065 *v*(Ar—CH), 2936, 2863 *v*(Alf.—CH), 1613, *v*(C=N), 1483, 1462 *v*(Ar—C=C), 1251, 1219 *v*(Ar—O), 1178, 1151 *v*(R—O). ¹H NMR (ppm): UV–vis (λ_{max} , nm) in DMF: λ_1 = 277 nm (ε = 2900), λ_2 = 354 nm (ε = 2800). μ_{eff} = 5.92. Mass Spectra: *m/z*: 631 [MnL+H]⁺.

Characterization of TiLCl

Molecular Weight: 657. M.P: 125–129 °C. Color: Light Brown. Yield: 0.60 g (46%). Anal Calcd. for TiC₃₂H₂₈N₂O₄Cl₃: C, 58.45, H, 4.26, N, 4.26. Found: C, 58.15, H, 4.60, N, 4.30. Selected IR data (KBr, v cm⁻¹): 3065 v(Ar—CH), 2940, 2867 v(Alf.—CH), 1613, v(C=N), 1504, 1475 v(Ar—C=C), 1249, 1217 v(Ar—O), 1150, 1130 v(R—O). UV–vis (λ_{max} , nm) in DMF: λ_1 = 284 nm (ε = 2100), λ_2 = 352 nm (ε = 1400). μ_{eff} = 1.67. Mass Spectra: m/z: 653 [TiLCl–4H]⁺.

Characterization of VLCl

Molecular Weight: 660. M.P: 126–130 °C. Color: Dark Brown. Yield: 0.67 g (51%). Anal Calcd. for VC₃₂H₂₈N₂O₄Cl₃: C, 58.09, H, 4.23, N, 4.23. Found: C, 63.74, H, 5.39, N, 5.09. Selected IR data (KBr, v cm⁻¹): 3064 v(Ar—CH), 2937, 2866 v(Alf.—CH), 1616, v(C=N), 1485, 1474 v(Ar—C=C), 1252, 1217 v(Ar—O), 1149, 1131 v(R—O). UV–vis (λ_{max} , nm) in DMF: λ_1 = 277 nm (ε = 3500), λ_2 = 354 nm (ε = 3500). μ_{eff} = 3.37 B.M. Mass Spectra: m/z: 570 [VLCl–(C₇H₅)–H]⁺.





Fig. 3. Synthesis the metal complexes of di-functional ligand (L).



Fig. 4. Suggested structures of the complexes.

Antioxidant analyses of complexes

DPPH scavenging activity

The free radical scavenging activities of synthesized compounds were measured by 2,2-diphenyl-1-picrylhydrazyl (DPPH) using the method of Agirtas et al. [28–30]. The diluted working solutions of the test metal complexes and the standards were prepared (5, 10, 25, 50 and 100 mg/L) in methanol. Ascorbic acid and trolox were used as standard. 0.002% of DPPH was prepared in methanol and 2 mL of this solution was mixed with 0.5 mL of sample solution and standard solution separately. The mixture was shaken vigorously and left standing at room temperature for 30 min. Then, the absorbance was measured at 517 nm in a spectrophotometer. Lower absorbance of the reaction mixture would indicate higher free radical scavenging activity. The capability to scavenge the DPPH radical was calculated using the following equation:

Scavengning activity $(\%_{\text{control}}) = (A_{\text{control}} - A_{\text{sample}})/A_{\text{control}} \times 100$

where A_{control} is the absorbance of the control reaction (containing all reagents except for the compounds and its complexes), and

 A_{sample} is the absorbance of the test compound. All tests were performed in triplicate [28].

Chelating effects on ferrous ions

Metal chelating activity (Fig 10) was determined according to the method of Agirtas et al. with some modifications. Briefly, 2 mL different concentration (5–100 mg/L) of compounds were mixed with 100 μ L of FeCI₂ (2 mM) solution. The reaction was then initiated by adding 400 μ L of ferrozine (5 mM) and was left standing for 10 min at room temperature. The chelating ability of synthesized compounds was determined by spectrophotometer at 562 nm against the blank. Blank was the solution with all reagents but without compounds. A lower absorbance indicates a higher chelating ability. EDTA was used as a positive control. The percentage inhibition of the ferrozine–Fe²⁺ complex formation was calculated as follows:

%Chelating activity = $(A_{\text{control}} - A_{\text{sample}})/A_{\text{control}} \times 100$

where A_{control} is the absorbance of the control reaction (containing only FeCl₂ and ferrozine), and A_{sample} is the absorbance of the compounds/standard [28–30].

Antimicrobial analyses

Antibacterial effects of synthesized compounds were studied by disc diffusion method *Escherichia coli* (ATCC 10536), *Staphylococcus aureus* (ATCC 6538), *Micrococcus luteus* (ATCC 9341), *Enterococcus hirae* (ATCC 10541), *Pseudomonas aeruginosa* (ATCC 9027), *Legionella pneumophila* subsp. *pneumophiia* (ATCC 33152) and *Bacillus subtilis* (6051) were experimented as test microorganisms. Amikacin (30 µg) and Tetracycline (30 µg) were used as standart antibacterial discs [30–32].

Results and discussion

Schiff base and complexes

In this work, we have found that in the reaction between 1,6bis(4-chloro-2-aminophenoxy)hexane and salicylaldehyde in ethanol, gave Schiff-base are formed as product and recrystallized from DMF. Then, the Schiff base was reacted with metal salts and the complexes were obtained. The product were washed with excess of ethanol, separated and dried in vacuum oven. The ligand and metal complexes were characterized by elemental analysis, IR, UV–vis, TGA–DTA, ¹H NMR and ¹³C NMR, conductivity measurements, cyclic voltammetry and magnetic susceptibility. In addition to experimental characterization techniques, a theoretical optimization, NMR and HOMO–LUMO studies were also done as a supportive characterization technique of new di-functional ligand. Furthermore, a linear regression analysis was also carried out to investigate the compatibility between experimental and theoretical ¹H NMR shifts. As the crystals were unsuitable for single-crystal X-ray structural determination and are insoluble in most common solvents, including water, methanol, ethanol, ethyl acetate and/or acetonitrile [33–36].

FTIR spectra

Characteristic IR bands of the ligand and complexes can be found in Table 1. Though O-H stretching bands must be observed around 3300 cm⁻¹ but it was not existed in the IR spectra of the ligand because of strong intramolecular hydrogen bonding. Similar observations were seen at the same frequency in IR spectra of salicylideneanilines [37–39]. The band at 1292 cm⁻¹ in the IR spectrum of the ligand is ascribed to the phenolic C-O stretching vibration. This band is found in the region 1215–1255 cm⁻¹ in the spectra of the complexes. These changes suggest that the o-OH group of this Schiff base moiety has taken part in complex formation. IR spectra of the ligands showed the absence of bands at 1735 and 3420 cm⁻¹ due to v(C=0) and $v(NH_2)$ stretching vibrations and instead, a new band appeared at ${\sim}1620\,\text{cm}^{-1}$ assigned to azomethine v(HC=N). This suggested that amino and aldehyde moieties of the starting reagents have been converted into the corresponding Schiff bases. The strong band within the range at *ca.* 1620 cm^{-1} in the spectra of all the complexes can be attributed to stretching vibrations of imine v (–C=N) [33–35]. The IR spectra of the complexes compared with those of the ligand indicate that the C=N band ca. 1620 cm^{-1} is shifted to lower values for complexes; these IR values are indicating coordination of the azomethine nitrogen to metal [36]. In the spectra of all the complexes are dominated by bands at 2965–2855 cm⁻¹ due to v(Alph.-CH)groups [37].

Electronic spectra

Electronic absorption spectral data of the complexes in dimethylformamide (DMF) at room temperature are presented in experimental section. The electronic spectra of the complexes in DMF show four bands in the visible–ultraviolet region. The absorption bands below at *ca*. 300 nm are practically identical and can be attributed to $\pi \rightarrow \pi^*$ transitions in the benzene ring and azomethine (-C=N) groups. The absorption bands observed within the *ca*. 300–400 nm range are most probably due to the transitions of $n \rightarrow \pi^*$ of imine groups [36]. The general character of these spectra is very similar to that of the corresponding complexes of phenoxy groups. This is probably due to the fact that metal-to-ligand charge transfer and ligand-to-metal charge transfer transitions have similar energy differences [38].

Magnetic measurements and molar conductivity

The magnetic moment measurements of compounds were carried out at 25 °C. Magnetic susceptibility measurements provide sufficient data to characterize the structure of the complexes. The magnetic moments of the complexes were given in the characterization of complexes. The complexes are non-electrolytes as shown by their molar conductivities ($\Lambda_{\rm M}$) in DMF (dimethyl formamide) at 10⁻³ M, which are in the range 5–10 Ω^{-1} cm² mol⁻¹. The molar conductivities of the compounds in DMF are in the range reported for non-electrolytes [34–36].

¹H NMR and ¹³C NMR

The ¹H NMR and ¹³C NMR spectra of free ligand and their diamagnetic complexes were recorded in DMSO-d₆ and reported along with possible assignments in the experimental section. Comparison of chemical shifts of the ligands with those of the complexes shows that the signals due to phenolic protons of the ligand were absent in the complexes, suggesting coordination after deprotonation. The azomethine proton (-CH=N-) undergoes a significant shift, indicating coordination of the azomethine nitrogen. More detailed information about the structure of the ligands was provided by ¹³C NMR spectra. All the carbon atoms due to heteroatomic and aromatic groups were found in their expected region [39]. The spectra of diamagnetic complexes, these signals shifted downfield due to the increased conjugation and coordination to the metal ions. The number of protons and carbons calculated from the integration curves agreed with those obtained from the values of the CHN analysis [40].

TGA studies

The thermal stabilities of the ligand and complexes were investigated using TGA. The thermogravimetric analysis (TGA) and curves were obtained at a heating rate of 10 °C/min in a nitrogen atmosphere over a temperature range of 50–900 °C.

The ligand and complexes' decomposition temperatures are as follows:

The ligand 316 °C, [CuL] 278 °C, [NiL] 301 °C, [CoL] 280 °C, [ZnL] 300 °C, [MnL] 225 °C, [TiLCl] 202 °C, [VLCl] 250 °C.

The decomposition of the molecules are consistent with the literature [34,39].

The weight losses for [CuL], [NiL], [CoL], [ZnL], [MnL], [TiLCl] and [VLCl] complexes were found to be approximately the same, when expressed as the percentages calculated stoichiometrically from their chemical formulas.

Table 1

Physical characterization, analytical, molar conductance and spectral data of the complexes.

Compound	Yield mass (%)	Color	Melting point (°C)	Formula weight	(calcd) Found		v(C=N) (cm ⁻¹)	$\mu_{\rm eff}$ (BM)	
					%C	%Н	%N		
Ligand (L)	9.3 (80.9)	Yellow	168-170	577	(66.55) 66.54	(5.19) 5.37	(4.85) 4.17	1618	-
[CuL]	0.97 (76)	Green	152-154 Decom.	639	(60.09) 59.16	(4.38) 4.53	(4.38) 4.42	1605	1.81
[NiL]	0.87 (71)	Light Brown	136-138	633	(60.66) 60.47	(4.42) 4.55	(4.42) 5.04	1617	2.73
[CoL]	0.84 (67)	Red	137 Decom.	634	(60.56) 60.81	(4.41) 4.46	(4.41) 4.73	1615	3.85
[ZnL]	0.77 (60)	Orange	144-146	640	(60.00) 60.71	(4.37) 4.73	(4.37) 5.06	1615	-
[MnL]	0.16 (13)	Light Brown	138-142	630	(60.95) 58.53	(4.44) 4.99	(4.44) 5.07	1613	5.92
[TiLCI]	0.77 (46)	Orange Light Brown	125-129	657	(58.45) 58.15	(4.26) 4.60	(4.26) 4.30	1613	1.67
[VLC1]	0.95 (58)	Dark Brown	126-130	660	(58.09) 63.74	(4.23) 4.39	(4.23) 5.09	1616	3.37

m: medium.



Fig. 5. Optimized (with B3LYP/6-311G) 3D view of di-functional ligand.

Single crystals of the complexes could not be isolated from any solvents. Due to that, definitive structure could not be done. However, the analytical, spectroscopic, and magnetic data enable us to propose the possible structures.

Mass Spectra

The Mass Spectra of the complexes peaks attributable to the molecular ions m/z: 473 $[L-(Cl)_2-(OH)_2]^+$, m/z: 640 $[CuL+H]^+$, m/z: 635 $[NiL+2H]^+$, m/z: 633 $[CoL-H]^+$, m/z: 387 $[ZnL-(O(CH_2)_6O)-(C_6H_3Cl)-(NCH)]^+$, m/z: 631 $[MnL+H]^+$, m/z: 653 $[TiLCl-4H]^+$, m/z: 570 $[VLCl-(C_7H_5)-H]^+$ [33-36].

Theoretical studies

1,6-Bis(2-(2-hydroxybenzilidenamino)-*p*-chlorophenoxy)hexane (L) was optimized (Fig. 5) by using restricted Becke-3-Lee-Yang-Parr (RB3LYP) level of Density Functional Theory (DFT) method, using the 6-311G basis set. Both Hatree-Fock (HF) and DFT methods were used for theoretical calculations. Gauge-Independent Atomic Orbital (GIAO) method was used to compute ¹H NMR shifts of the ligand in gas phase [41–44]. Tetramethylsilane (TMS) was used as reference in both HF and B3LYP NMR calculations of the ligand. Reference shielding of TMS for the protons were found as 32.5976 ppm and 31.8821 ppm in HF and B3LYP GIAO calculations, respectively. Theoretical 1H NMR shifts were displayed by GaussView program without any further computation or mathematical calculation. Additionally energy gap between Frontier orbitals (HOMO-LUMO) was also calculated by subtracting of energy value (eV) of LUMO from energy value of HOMO



Fig. 6. Frontier orbitals (HOMO-LUMO) views, corresponding energies, and energy gap between ground and excited states.

Table 2 Linear regression analysis results of the experimental and theoretical (HF and B3LYP/6-311G) 1H NMR values.						
Regression	Parameter	Value	Error	R	R^2	
Experimental vs. B3LYP/6-311+G(2d,p)	A B	1.1412 0.5447	0.6857 0.1021	0.70984	0.5	

Regression	Parameter	Value	Error	R	R^2	Adj. R ²	Ν
Experimental vs. B3LYP/6-311+G(2d,p)	A	1.1412	0.6857	0.70984	0.50387	0.48616	30
	В	0.5447	0.1021				
Experimental vs. HF/6-31G(d)	Α	1.1412	0.6857	0.70984	0.50387	0.48616	30
	В	0.5447	0.1021				
Experimental vs. B3LYP/6-311+G(2d,p) ^a	А	-0.7085	0.2659	0.97263	0.94601	0.94393	28
	В	0.9584	0.0449				
Experimental vs. HF/6-31G(d) ^a	А	0.00691	0.2659	0.97263	0.94601	0.94393	28
	В	0.95849	0.0449				

^a Without outlier.

Table 3

Voltammetric results at scan rate of 100 mV s⁻¹ vs. Ag/AgCl. Ec: cathodic potential, Ea: anodic potential.

L Ic: -0.71, Ilc: -1.89 Ia: -0.20, Ila: +0.63	Compound	Ec (V)	Ea (V)
CuL Ic: -1.25 Ia: -1.05, IIa: -0.30, IIIa: +0.48 NiL Ic: -1.95 Ia: +0.39 CoL Ic: -1.96 Ia: +0.60	L	Ic: -0.71, IIc: -1.89	la: -0.20, lla: +0.63
	CuL	Ic: -1.25	la: -1.05, lla: -0.30, llla: +0.48
	NiL	Ic: -1.95	la: +0.39
	CoL	Ic: -1.96	la: +0.60

orbitals at first excited and ground states respectively [45-50]. Frontier orbitals' view and the corresponding energy values can be seen in Fig. 6. Electron delocalization, π -bond forming by the interaction of p-orbitals (HOMO) electron donor and electron acceptor sides of the molecules can be seen in Fig. 6 as well. The energy gap between LUMO-HOMO 3.8762 eV is an energy level corresponding to $\pi \rightarrow \pi^*$ electron transition states and it is the data for the potential applications [45–50].

One of the most important part of this study; a regression analysis was also carried out to investigate the conformity between theoretical and experimental ¹H NMR shifts (Table 2).

The following universal equation was used so as to carry out linear regression analysis: [41-44].

$$y_{(Experimental_{^{1}H NMR)}} = A + B^{*} x_{(Theoretical_{^{1}H NMR)}}$$

The regression analysis between experimental and theoretical data shed light about which model fitted experimental data with or without outlier. First of all, the omission of outliers was the responsible for a meaningful increase in R-squared and Adj. R-squared, but a decrease in error. Although there were significant differences in



Fig. 7. Cyclic voltammograms of 1 mM compound solutions in DMF at glassy carbon electrode; A: L, B: CuL, C: NiL, D: CoL scan rate, v: 100 mV s⁻¹.

using the proposed models with or without outlier, there were much less significant differences between HF/6-31G and B3LYP/6-311G methods. In the light of the results, care must be taken in suggesting a model due to much similar coefficients of determination. As a result, HF/6-31G without outliers showed the closest value to zero and to one for A and B parameters respectively. In summary, the goodness of fitness therefore depends to some extent on which model of the theoretical calculations is adopted.

As can be seen in Table 2, experimental and theoretical ¹H NMR values are in a good conformity but there are small differences between experimental and theoretical NMR values. Those differences are due to acidic properties of the hydroxyl groups in ligand structure, and gas phase theoretical ¹H NMR calculations [41–44].

Electrochemical analysis

The electrochemical properties of the present compounds were investigated by CV and on a glassy carbon electrode in DMF containing 0.1 M TBAP, in the concentration of 1 mM vs. Ag/AgCl. The electrochemical data upon the peak potentials have been reported in Table 3. The oxidation potentials can be measured by cyclic voltammetry and then the HOMO and LUMO values are calculable [51]. The corresponding HOMO and LUMO levels were calculated using IIc and IIa waves for the L ligand. The estimations were done with the empirical relation $E_{\text{LUMO}} = [(E_{\text{IIC}} - E_{1/2}(\text{ferrocene})) + 4.8] \text{ eV}$ or $E_{\text{HOMO}} = [(E_{\text{IIC}} - E_{1/2}(\text{ferrocene})) + 4.8] \text{ eV}$. Ferrocene was used as external standard. It shows two peaks at 0.36 and 0.42 V hence the $E_{1/2}$ (ferrocence) is equal to 0.39 V which

can be used in equation to calculate the E_{HOMO} and E_{LUMO} . Based on cyclic voltammetry results, L shows E_{HOMO} = 5.04 eV, E_{gap} = 2.52 eV and E_{LUMO} = 2.52.

In the cathodic direction from ± 1.0 V to -2.3 V at scan rate of 100 mV s⁻¹, the CV of L is characterized by two cathodic waves (Ic and IIc at about -0.71 V and -0.189 respectively) and two waves were observed (Ia and IIa at about -0.20 V and ± 0.63 V respectively) as depicted by cyclic voltammograms given in Fig. 7A.

In Fig. 7B, the voltammogram taken at in the reduction direction of CuL complex, at the potential range of -2.3 V and +1.0 V, at 100 mV s⁻¹ scan rate is seen. The CV of CuL is characterized by one cathodic peak (Ic at about -1.25 V) and three anodic waves (Ia, IIa and IIIa t about -1.05 V, -0.30 V and +0.48 V). Δ Ep for Ia/ Ic from this redox couple was also found to be 200 mV. It indicates a quasi-reversible electron transfer in the electrode reaction. We should bear in mind that [52–54] after occurring the one-electron reduction process corresponding to [Cu^{II}L]/[Cu^IL], part of [Cu^IL₂] species are chemically decomposed to copper metal (reaction 1). Therefore, it may be assumed that the corresponding anodic waves (IIa and IIIa) are associated with the reoxidation of electrodeposited copper metal to free Cu⁺/Cu²⁺ according to the reaction 2:

$$[\text{CuIIL}] \leftrightarrow \text{Cu}^{2+} + \text{L} + \text{e}^{-} \leftrightarrow \text{Cu}^{+} + \text{L}$$
(1)

$$\mathbf{C}\mathbf{u}^+ \leftrightarrow \mathbf{C}\mathbf{u}^{2+} + \mathbf{e}^- \tag{2}$$

The effect of scan rates on CuL complex was investigated between the 50–1000 mV s⁻¹ (Fig. 8B). At high scan rate (400 mV s⁻¹>), The IIa peak was not observed (Fig. 8B).



Fig. 8. Cyclic voltammograms of 1×10^{-3} mol L⁻¹ compound solutions at different scan rates; A: L, B: CuL, C: NiL, D: CoL.

The voltammograms of NiL complex investigated in the same experimental conditions (from +1.0 V to -2.3 V at 100 mV s⁻¹ in Fig. 7C), one wave (Ic at about -1.95 V) and one anodic wave (Ia at about +0.39 V). The effect of scan rates on NiL complex was investigated between 50 and 1000 mV s⁻¹ (Fig. 8C). At high scan rate (200 mV s⁻¹>), the new reduction wave was observed at about 0.35 V.

In the potential range of -2.3 V to +1.0 V at scan rate of 100 mV s⁻¹, on the cathodic side, the CV of CoL complex (Fig. 7D) shows one cathodic peak (Ic at about -1.96) and one anodic peak (Ia at about +0.60 V). At high scan rate (200 mV s⁻¹>), the new reduction wave was observed at about 0.35 V.

From the CVs (Fig. 8), it was found that the initial oxidation peak current of L, CuL, NiL and CoL gradually increased and a negative shift in the peak potential existed with increasing scan rate. From the results obtained between 50 and 1000 mV s⁻¹, a plot of logarithm of peak current significantly correlated with the logarithm of scan rate for all L, CuL, NiL and CoL with slopes between 0.45, 0.46, 0.48 and 0.44, respectively (correlation coefficient



Fig. 9. Radical-scavenging activity on DPPH radicals (%) of the synthesized compounds.



Fig. 10. Chelating effect of synthesized compounds on ferrous ion.

Table 4

Inhibition diameter in millimeters. L = Ligand, AK = Amikacin (30 µg) and TE = Tetracycline (30 µg).

Ni(II) Mn(II) Ti(III) V(III) Bacteria L Co(II) Zn(II) AK TE Compounds and antibiotic discs 0 9 7 0 0 8 20 24 P. aeriginosa 0 8 9 S. aureus 0 0 7 9 14 23 34 L. pneumophila 0 0 0 0 0 8 9 16 18 9 7 7 B. subtilis 11 8 8 11 20 24 7 8 7 15 M. luteus 9 10 24 9 16 E. hirae 0 0 0 0 0 7 7 20 16 10 14 7 8 10 7 9 24 24 E. coli

between 0.991, 0.989, 0.978 and 0.961). These findings showed that the redox processes were predominantly diffusion controlled in the whole scan rate range studied [51].

Antimicrobial studies

DPPH radical scavenging activity

The model of scavenging the stable DPPH radical is a method that is widely used to evaluate antioxidant activities in a relatively short time compared with other methods. Scavenging abilities of synthesized compounds increased from 8.9% to 22.9%, from 8.6% to 26.9%, from 11.5% to 21.9%, from 14.0% to 27.5%, from 11.5% to 18.7%, from 5.4% to 21.9% and from 12.6% to 59.9% at 5.0 to 100 mg/mL for ligand, Ni(II), Co(II), Zn(II), Mn(II), Ti(III) and V(III), respectively (Fig. 9). Among the compounds the maximum DPPH radical-scavenging activities were obtained from V(III). Pawar et al. were studied macrocyclic Schiff bases with vanadium (V) complexes antioxidant activity and found scavenging abilities of synthesized compounds increased from 28.2% to 58.6% at 50.0 to 125 mg/mL. These results are similarly ours. Ascorbic acid and trolox exhibited higher radical scavenging activity than synthesized compounds at all the concentrations and their DPPH radical scavenging activities were found to be 99.0% and 98.5% at 100 mg/mL concentrations, respectively [55].

Chelating effects on ferrous ions

Transition metals have been proposed as the catalysts for the initial formation of radicals. Chelating agents may stabilize transition metals in living systems and inhibit a generation of free radicals, consequently reducing free radical-induced damage. To better estimate the antioxidant potential of the synthesized compounds, its chelating activity was evaluated against Fe^{2+} . The chelating effects of the compounds and EDTA on ferrous ions increased with increasing concentrations (Fig. 10). At all of the studied concentrations (5.0–100 mg/L) EDTA showed higher chelating activities than the synthesized compounds. The chelating effects of standard and our complexes on the ferrous ions decreased in the order of EDTA > ligand > V(III) > Zn(II) > Ni(II) > Ti(III) > Mn(II) > Co(II) and were 100.0, 77.3, 71.3, 67.2, 65.7, 58.3, 34.8 and 27.8 at the concentration of 100 mg/L, respectively [56,57].

Antimicrobial activity

All the compounds were evaluated for their antibacterial activity *in vitro* by using zone inhibition technique against *P. aeriginosa* (-), *S. aureus* (+), *L. pneumophila* (-), *B. subtilis* (+), *M. luteus* (+), *E. hirae* (+) and *E. coli* (-). Experiments were repeated three times and the results were expressed as values in Table 4. The results obtained were compared with the standard drugs amikacin and tetracycline. The results obtained were similar to the results from some previously published papers [56–58]. All the compounds showed antimicrobial activity against *B. Subtilis* and *M. luteus*. The table shows that compounds Ni(II), Ti(III) and V(III) exhibited significant activity against E. coli, M. luteus and S. aureus respectively [58].

Conclusions

The novel one Schiff base and its eight complexes were prepared and characterized by elemental analyses, FTIR and UV-vis spectra, ¹³C and ¹H NMR spectra, Conductivity measurements, magnetic susceptibilities and thermal gravimetric analyses. In addition cyclic voltammetry, theoretical and antimicrobial studies of the complexes were studied. General structures of the complexes are shown in Figs. 3 and 4. The Ni(II), Co(II), Mn(II) and Zn(II) complexes probability show tetrahedral geometry, Cu(II) complex probability show square planar geometry, Ti(III) and V(III) complex probability show a capped octahedron in which a seventh ligand has been added to triangular face around the central metal ions [59-68].

Di-functional ligand is the key compound of this study; entire experimental and theoretical calculations establish the successfully synthesizing of the ligand in the proposed structure.

From the results we can conclude that all compounds exhibited DPPH radical scavenging activity and chelating effects on ferrous ions. It was observed that, all compounds showed varying antimicrobial activity; in addition Ti(III) and V(III) possessed significant activity against all studied bacteria.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.03.094.

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