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Synthesis, Characterization and Antioxidant Studies of Triazine Schiff Bases and Their Nickel(II) and Zinc(II) Complexes

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The synthesis, characterization, thermogravimetric and antioxidant activity studies of Schiff bases derived from 4-phenyl-1,3,5-triazine-2,6-diamine and 3-hydroxy salicylaldehyde (H_2L1), 4-hydroxy salicylaldehyde (H_2L2) together with their nickel(II) and zinc(II) complexes are reported. The ligands were characterized by IR, ^{1}H and ^{13}C NMR, UV-Vis spectroscopy as well as elemental analysis. Spectral studies reveal that the ligands were acting as tetradentate chelating agents and coordinated to the metal center *via* deprotonated phenolate oxygen and azomethine nitrogen atoms in a 1:1 ligand to metal ratio. The antioxidant activities of the ligands and complexes were examined using the DPPH radical scavenging method. The results show that the ligands exhibit higher radical scavenging ability than the complexes.

Key Words: Schiff bases, Triazine, Metal complexes, Antioxidant activity.

INTRODUCTION

A great deal of information regarding the properties of synthetic Schiff bases of potential biological interest has arisen during the last few years[1,2], several of these compounds were synthesized, characterized and tested for various biological activities including antiulcer[3], antiinflammatory[4], antioxidants[5,6] and others. Such activities may be related to the structural arrangements of the ligands and to the nature of the substituent groups[7].

Different classes of organic compounds containing rich conjugated systems and hydroxyl groups were found to have potent antioxidant properties, among those flavonoides and their chromium and copper complexes[8]. However, those biological activities can be altered depending upon the types of substituents attached to the aromatic ring.

Free radicals are considered to responsible for the oxidative damage to biomolecules such as carbohydrates, proteins, lipids and DNA, thus accelerating various types of diseases[9].

In this work, we are encouraged to synthesize triazine Schiff bases containing hydroxyl groups attached to the aromatic ring (Fig. 1), along with their nickel(II) and zinc(II) complexes. The novel compounds were characterized on the bases of elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy, UV-Vis as well as thermogravimetric analysis (TGA) with a view to further investigating the radical scavenging abilities of these novel compounds using the DPPH method.

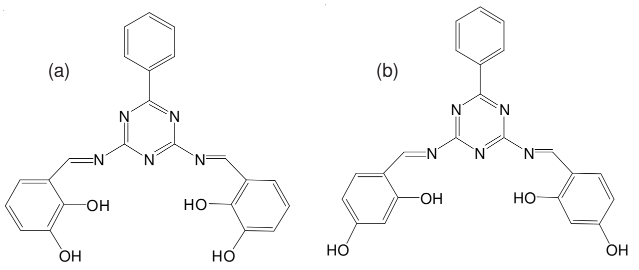

Fig. 1. Proposed structures of the ligands H_2L1 (a) and H_2L2 (b)

EXPERIMENTAL

4-Phenyl-1,3,5-triazine-2,6-diamine ($C_9H_9N_5$, FW 187.21), 3-hydroxysalicylaldehyde ($C_6H_3(OH)_2CHO$; FW 138.12), 4-hydroxysalicylaldehyde ($C_6H_3(OH)_2CHO$; FW 138.12) and DPPH were purchased from sigma-Aldrich and were used as received. Metal salts were of analytical grade. All other solvents are commercially available and used as received.

Physical measurements: IR spectra were recorded with a Perkin-Elmer FT-IR spectrophotometer model spectrum 2000 using KBr pellets as support in the range 4000-370 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a JEOL ECA-400 spectrometer, operating with a frequency of 400 MHz, using DMSO-d_6 as solvent. Electronic spectra, in DMSO solution, were obtained using a Varian 50 Conc UV-

TABLE-1
PHYSICAL PROPERTIES OF THE LIGANDS AND COMPLEXES

Compound	Formula	Yield (%)	Colour	Formula (wt)	Found (calcd.) (%)		
					C	H	N
H_2L1	$C_{23}H_{17}N_5O_4$	76	Grey	427.45	64.88 (64.56)	3.70 (3.97)	16.14 (16.37)
H_2L2	$C_{23}H_{17}N_5O_4$	78	Orange	427.45	64.21 (64.56)	3.79 (3.97)	16.42 (16.37)
$NiL1.2H_2O$	$C_{23}H_{15}N_5O_4.2H_2ONi$	77	Brown	520.14	53.25 (53.11)	3.38 (3.65)	13.54 (13.45)
$ZnL1.2H_2O$	$C_{23}H_{15}N_5O_4.2H_2OZn$	73	Yellow	526.81	52.38 (52.43)	3.42 (3.61)	13.08 (13.30)
$NiL2.2H_2O$	$C_{23}H_{15}N_5O_4.2H_2ONi$	76	Green	520.14	52.98 (53.11)	3.42 (3.65)	13.22 (13.45)
$ZnL2.2H_2O$	$C_{23}H_{15}N_5O_4.2H_2OZn$	79	Yellow	526.81	52.21 (52.43)	3.32 (3.61)	13.12 (13.30)

TABLE-2
IR SPECTRAL DATA OF LIGANDS AND COMPLEXES, WAVE NUMBERS EXPRESSED IN cm^{-1}

Compound	ν(O-H)	ν(C-H) Aliphatic	ν(C=N)	ν(C-O)	ν(M-O)	ν(M-N)
H_2L1	3446	2985	1627	1255	-	-
H_2L2	3401	2368	1628	1260	-	-
$NiL1.2H_2O$	3310 (H_2O)	2873	1622	1319	542	492
$ZnL1.2H_2O$		2795	1621	1257	545	
$NiL2.2H_2O$		2238	1622	1269	568	508
$ZnL2.2H_2O$	3301 (H_2O)	2358	1618	1258	511	

visible spectrophotometer over the wavelength range 200-800 nm. Thermogravimetric analysis was carried out on Perkin-Elmer Precisely TGA 4000 thermogravimetric analyzer. The instrument was adjusted at a heating rate of 20 ºC/min. The heating was performed from 50-900 ºC.

The DPPH free radical scavenging assay was performed in triplicate and the average value was obtained. All determinations were made using the infinite® 200 PRO plate reader (TECAN, Männedorf, Switzerland).

Synthesis of the ligands

H_2L1: A solution of 3-hydroxysalicylaldehyde (2 g, 14.48 mmol) and 4-phenyl-1,3,5-triazine-2,6-diamine (1.35 g, 7.21 mmol) was mixed and stirred under reflux for 2 h. The pale yellow powder formed was filtered and recrystallized from ethanol. It was dried in an oven at 80 ºC for 0.5 h.

Selected FT-IR data (KBr, ν_{max}, cm^{-1}): 3446 (O-H, m), 2985 (C-H, m), 1627 (C=N, s), 1255 (C-O, s).

H_2L2: The method is the same as for H_2L1, using 4-hydroxysalicylaldehyde (2 g, 14.48 mmol) and 4 phenyl-1,3,5-triazine-2,6-diamine (1.35 g, 7.21 mmol). Selected FT-IR data (KBr, ν_{max}, cm^{-1}): 3401 (O-H, m), 2368 (C-H, m), 1628 (C=N, s), 1260 (C-O, s).

General method for synthesis of the complexes: A solution of either H_2L1 or H_2L2 (0.60 g, 1.40 mmol) in ethanol (40 mL) was added to equimolar quantity of the metal acetate in ethanol. Few drops of triethylamine were then added. The mixture was magnetically stirred and refluxed for 3 h. The product formed was filtered and recrystallized from DMSO.

$NiL1.2H_2O$, selected FTIR data (KBr, ν_{max}, cm^{-1}): 2873 (C-H, m), 1622 (C=N, s), 1319 (C-O, s), 542 (Ni-O, w); $ZnL1.2H_2O$, selected FTIR data (KBr, ν_{max}, cm^{-1}): 2795 (C-H, s), 1621 (C=N, s), 1257 (C-O, s), 545 (Zn-O, w); $NiL2.2H_2O$, selected FTIR data (KBr, ν_{max}, cm^{-1}): 2238 (C-H, m), 1622 (C=N, s), 1269 (C-O, s), 568 (Ni-O, w); $ZnL2.2H_2O$, selected FTIR data (KBr, ν_{max}, cm^{-1}): 2358 (C-H, m), 1618 (C=N, s), 1258 (C-O, s), 511 (Zn-O, w).

Antioxidant activity of the ligands and complexes by DPPH method: Free radical scavenging activity of the test compounds were determined by the 1,1-diphenyl picrylhydrazyl (DPPH) assay method. Each of the Schiff bases and complexes were dissolved in DMSO to obtain concentration of 1 mg/mL. These stock solutions were then diluted to 5, 10, 25, 50 and 100 µg/mL. Then, 200 µL of each sample solution were combined with 50 µL of DPPH (0.3 mmol) in triplicate in a 96- well microtitre plate. Final concentrations of the Schiff bases were 4, 8, 20, 40 and 80 µg/mL. The microtitre plate was incubated for 0.5 h at room temperature. The plate was then read at 515 nm for 3 h with 20 min intervals to reach a steady state against DMSO as a blank. The percentage DPPH quenched was calculated according to the equation:

$$\text{DPPH quenched (\%)} = (\text{Abs. blank} - \text{Abs. sample})/\text{Abs. blank} \times 100$$

The percentage free radical scavenging activity (% inhibition) was plotted against concentration in µg/mL.

RESULTS AND DISCUSSION

The physical properties of the ligands and their complexes were listed in Table-1. Elemental analyses for the complexes confirm 1:1 metal to ligand stoichiometry. The compounds are stable at room temperature in the solid state. The ligands are soluble in ethanol, methanol, acetone and high boiling point solvents like DMSO and DMF, whereas the complexes dissolves only in DMSO and DMF and not soluble in either ethanol or methanol.

The main stretching frequencies of the IR spectra of the ligands and complexes were shown in Table-2. For the ligands, the spectra show the characteristics broad peaks at the range 3446-3307 cm^{-1} for intra-molecularly hydrogen bonded -OH groups[10], a strong peaks due to C=N stretching at 1628-1627 cm^{-1}, a medium intensity bands at 1260-1255 cm^{-1} assigned to C-O phenolic stretching and peaks in the region 1500-1000 cm^{-1} from benzene ring skeletal vibrations. The peak at 779 cm^{-1} is due to aromatic C-H out-of-plane stretching mode. The results strongly support the formation of the Schiff bases[11].

The IR spectra of the nickel complexes differ from that of the ligands. It is further noted that the -OH peaks, observed for the ligands at the range 3446-3307 cm^{-1}, is now observed at 3310-3301 cm^{-1} and are assigned to coordinated H_2O molecules in agreement with the results from elemental analyses. The peaks for C=N at *ca* 1627 cm^{-1} observed for the ligands is shifted towards lower frequency at 1622 cm^{-1} in both complexes. The new bands observed at the ranges 568-511 cm^{-1} and 508-492 cm^{-1} are assigned to Ni-O and Ni-N respectively. These suggest that the phenol oxygen's and imino nitrogen's are coordinated to Ni(II)[10].

The IR spectra for Zn(II) complexes shows the presence of all the expected functional groups. The wavenumbers of C=N (1621-1618 cm^{-1}) and C-O (1258-1257 cm^{-1}) groups are almost the same as for their nickel congeners and have not changed significantly.

The ^1H NMR spectra for H_2L1 is consistent with the expected structural formula in Fig. 1(a). The singlet at 10.16 ppm is due to phenolic hydrogen; a singlet at 8.21 ppm is due to imino hydrogen; and a multiplet in the range 6.70-7.61 ppm is due to the aromatic hydrogens. The integration ratio for these hydrogens is 2:1:6 respectively (expected ratio = 2:1:6) supports the molecular symmetry for the Schiff base[12].

The ^1H NMR spectra of H_2L2 is closely similar and can be explained in the same way. The replacement of the hydroxyl group in the 4th position of the salicyldehyde moiety doesn't impose significant impact in the chemical shift values.

Further evidence for the proposed structure in Fig. 1, can be drawn from ^{13}C NMR spectra. The spectra show 12 peaks assigned as follows: H_2L1 (DMSO-d_6) δ 170 ppm 3C-triazine ring, δ 111, 115, 124, 138, 138.4 ppm phenol, 160 ppm C-OH, δ 167 ppm C=N, δ 127, 129, 131, 134 ppm phenyl ring. There are no significant differences between ^{13}C NMR chemical shift values for the two ligands.

The UV-Vis spectral data of the ligands and their complexes in DMSO are listed in Table-3. The UV-Vis spectra for H_2L1 shows a high intensity broaden absorption band at about 286 nm ($\varepsilon = 1.4 \times 10^4$ $M^{-1}cm^{-1}$) assigned to π-π^* transition of the aromatic ring. The n-π^* transition of the azomethine chromophore is observed as a shoulder at about 344 nm ($\varepsilon = 1.2 \times 10^4$ $M^{-1}cm^{-1}$). Those values are in agreement with other Schiff bases reported in the literature[13].

TABLE-3
UV-Vis OF THE LIGANDS AND COMPLEXES

Compound	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	Tentative assignment
H_2L1	286	1.4×10^4	π-π^*
	344	1.2×10^4	n- π^*
H_2L2	282	1.4×10^4	π- π^*
	310	1.7×10^4	n-π^*
$NiL1.2H_2O$	902	405	$^3A_{2g} \rightarrow {}^3T_{2g}$
	736	189	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$
	343	0.31×10^4	CT
	260	0.38×10^4	π-π^*
	400	-	n-π^*
$ZnL1.2H_2O$	414	0.28×10^4	CT
	291	1.7×10^4	π-π^*
$NiL2.2H_2O$	260	2.1×10^4	π-π^*
$ZnL2.2H_2O$	296	1.9×10^4	π-π^*

For the ligand H_2L2, however, the spectra shows that the peak assigned to the π-π^* transition was found at 282 nm; ($\varepsilon = 1.4 \times 10^4$ $M^{-1}cm^{-1}$), while the peak for the n-π^* transition (310 nm; ε, 1.7×10^4 $M^{-1}cm^{-1}$) was shifted to higher energy compared to those of H_2L1 (286 nm, 344 nm respectively)[14].

For nickel complexes the UV-Vis spectra exhibits weak d-d bands at 902 nm (ε_{max} = 405 $M^{-1}cm^{-1}$) and 736 nm (ε_{max} = 189 $M^{-1}cm^{-1}$). These are consistent with an octahedral configuration at Ni(II), which can be assigned to the transitions: $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ respectively[15].

The peak at 343 nm ($\varepsilon = 0.31 \times 10^4$ $M^{-1}cm^{-1}$) is assigned to metal-ligand charge transfer (MLCT). The spectrum is also compared with that of H_2L1. It is noted that the π-π^* bands observed for the ligands at 282-286 nm were shifted in the complexes to *ca* 260 nm ($\varepsilon = 0.38 \times 10^4$ $M^{-1}cm^{-1}$). However, the n-π^* band may be hidden under the strong MLCT band at 343 nm. This band is significantly red-shifted to about 400 nm as a result of complexation to the Ni(II). These results are in agreement with literature result indicating the formation of the complexes[16].

The UV-Vis spectra of the zinc complexes shows that the MLCT and π-π^* peaks at 414 nm ($\varepsilon_{max} = 0.28 \times 10^4$ M^{-1} cm^{-1}) and 291 nm ($\varepsilon_{max} = 1.7 \times 10^4$ M^{-1} cm^{-1}) are lower in energy than the corresponding peaks for Ni(II) complexes. The MLCT peak is normally observed from 348 nm to 323 nm for Zn(II) complexes, involving electronic transitions from the full *d* orbitals of the metal ion ($3d^{10}$) to antibonding molecular orbitals of the ligands[17].

Thermal analysis: The thermal decomposition process for Ni(II) and Zn(II) complexes were examined and assessed in the temperature range 50-900 ºC. The obtained thermoanalytical data from the thermogravimetric curves were summarized in Table-4.

TABLE-4
THERMAL ANALYSIS DATA FOR THE COMPLEXES

Compound	Step	Decomposition T_{max} (°C)	Eliminated species
$NiL1.2H_2O$	First	140	$2H_2O$
	Second	330	Ligand
	Third	700	Residue (NiO)
$ZnL1.2H_2O$	First	200	$2H_2O$
	Second	700	Ligand
	Third	850	Residue (ZnO)
$NiL2.2H_2O$	First	142	$2H_2O$
	Second	750	Ligand
	Third	800	Residue (NiO)
$ZnL2.2H_2O$	First	185	$2H_2O$
	Second	450	Ligand
	Third	840	Residue (ZnO)

The data obtained indicate that nickel complexes are thermally stable until 80 ºC. Then they lost water molecules between 80-140 ºC. The decomposition proceeds approximately with three degradation steps. These steps occurred in between 80 and 720 ºC with net weight loss of 81.46 % for $NiL1.2H_2O$ and 80.93 % for $NiL2.2H_2O$.

Zinc complexes of both ligands are more thermally stable than their nickel counterparts. They start to lose their coordinated water molecules between 80-200 ºC and then the subsequent steps correspond to the slow decomposition of the ligand until about 700 ºC. The final decomposition products were metal oxides formed above 720 ºC for nickel complexes and 850 ºC for zinc complexes.

Antioxidant activity: The antioxidant activity of the ligands and their nickel and zinc complexes was measured in terms of their hydrogen donating or radical scavenging ability by UV-Vis spectrophotometer using the stable DPPH radical. The results were shown in Fig. 2(a) and (b).

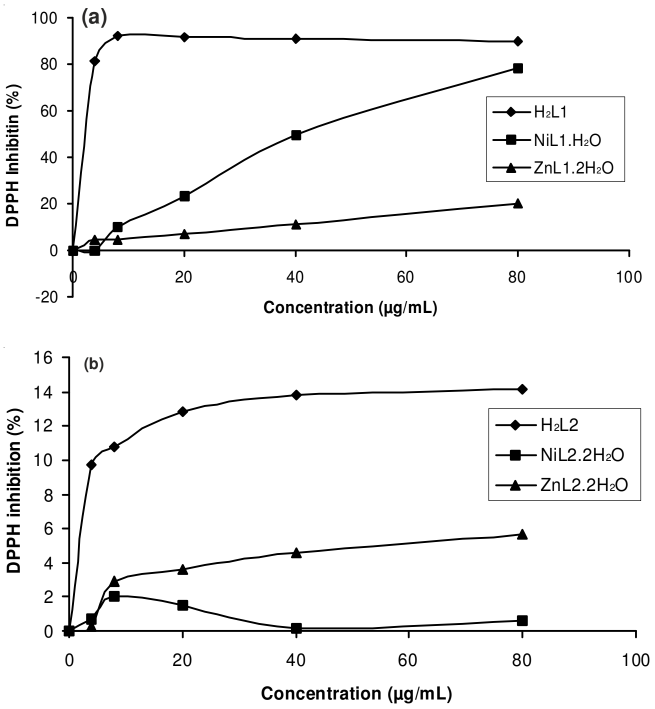

Fig. 2. (a) DPPH inhibition by H_2L1 and its Ni(II) and Zn(II) complexes; (b) DPPH inhibition by H_2L2 and its Ni(II) and Zn(II) complexes

It has been shown that the free radical scavenging ability of the novel Schiff bases is dependent on the chemical substituents attached to the aromatic rings and generally the antioxidant activity of all compounds was increased with increase of their concentration.

The prepared Schiff bases seem to have a very efficient conjugated system, which means that this type of compounds may play important role as antioxidant agents. In addition, the presence of hydroxyl groups, which are attached to aromatic rings can increase the conjugated systems and consequently increase the antioxidant activity of the corresponding Schiff bases. It is known that the antioxidant activity in phenolic compounds can take place through either of two mechanisms: hydrogen atom transfer and electron donating ability[8]. The mechanism, which occurs here could be similar to that mechanism, which occurs in hydroxy chalcones and hydroxy flavonoids derivatives[18,19]. When two hydroxyl groups are present in *o*- and *p*-positions in relation to each other, benzene ring systems are generally known to delocalize electrons. The phenoxyl radicals occurring at the *o*- or *p*-dihydroxylated benzene ring systems are much more readily converted to fairly stable semiquinone radicals, while *m*-dihydroxylated benzene ring systems are comparatively less efficient to delocalize electrons because the phenoxyl radicals are converted to quinone structure which is not much stable. Thus, the substitution patterns of the two hydroxyl groups in H_2L1 and H_2L2 are very important structural factors for their radical scavenging activity. However, the present study has shown that the *o*-substituted ligand H_2L1 exhibited better free radical scavenging activities than the *m*-substituted ligand H_2L2. It was noticed that all the formed complex compounds shows lower ability to scavenge free radicals. This phenomenon could be related to the involvement of hydroxyl groups in coordination to the metal ions.

Conclusion

Schiff base ligands derived from 4-phenyl-1,3,5-triazine-2,6-diamine and hydroxy salicylaldehydes along with their nickel and zinc complexes have been synthesized and characterized. The antioxidant studies of the compounds reveal that the ligands are more effective antioxidants than their metal complexes. They mainly act as a hydrogen atom transferring antioxidants in an oxidative process. However, chelating to the metal ions suppresses this property through coordination to the metal centre, thus hampers hydrogen atom abstraction through deprotonation. The *o*-substituted hydroxy ligands are much better effective antioxidants than their *m*-substituted counterparts.

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