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 flavonoids 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\(^8\).

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 \(^1\)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.
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 °C/min. The heating was performed from 50-900 °C.

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**

**H₃L₁:** 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 °C 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), 751 (C-H, m). Selected FTIR data (KBr, ν max, cm⁻¹): 3410 (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 H₃L₁ or H₃L₂ (0.60 g, 1.40 mmol) in ethanol (40 mL) was added to equimolar quantity of the metal acetate in ethanol or methanol. 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.

**NiL₁.2H₂O, selected FTIR data (KBr, ν max, cm⁻¹):** 2873 (C-H, m), 1622 (C-N, s), 1319 (C-O, s), 542 (Ni-O, w); ZnL₁.2H₂O, selected FTIR data (KBr, ν max, cm⁻¹): 2795 (C-H, s), 1621 (C-N, s), 1257 (C-O, s), 545 (Zn-O, w); NiL₂.2H₂O, selected FTIR data (KBr, ν max, cm⁻¹): 2238 (C-H, m), 1622 (C-N, s), 1269 (C-O, s), 568 (Ni-O, w); ZnL₂.2H₂O, 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-2-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:

\[
\% \text{DPPH quenched} = \frac{(Abs. \text{ blank} - Abs. \text{ sample})/Abs. \text{ blank}}{100}
\]

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 dissolve 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, 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.

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\(_2\)O 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=O, C-H, N-H and O-H are listed in Table-3. The UV-Vis spectra for the ligands and complexes in DMSO are listed in Table-3. The UV-Vis spectra of the zinc complexes shows that the absorption peaks at 282-286 nm were shifted in the complexes to ca. 260 nm (\(\epsilon = 0.38 \times 10^4\) M\(^{-1}\)cm\(^{-1}\)). However, the n-\(\pi^*\) band may be hidden under the strong MLCT band at 343 nm (\(\epsilon = 0.31 \times 10^4\) M\(^{-1}\)cm\(^{-1}\)) assigned to metal-ligand charge transfer (MLCT). The spectrum is compared with that of H\(_2\)L.1. It is noted that the n-\(\pi^*\) bands observed for the ligands at 282-286 nm were shifted in the complexes to ca. 260 nm (\(\epsilon = 0.38 \times 10^4\) M\(^{-1}\)cm\(^{-1}\)).

For nickel complexes the UV-Vis spectra exhibits weak d-d bands at 902 nm (\(\epsilon_{\text{max}} = 405\) M\(^{-1}\)cm\(^{-1}\)) and 736 nm (\(\epsilon_{\text{max}} = 189\) M\(^{-1}\)cm\(^{-1}\)). These are consistent with an octahedral configuration at Ni(II), which can be assigned to the transitions: \(\Delta g \rightarrow T_2g, \Delta g \rightarrow T_1g(F)\) respectively\(^{12}\).

The peak at 343 nm (\(\epsilon = 0.31 \times 10^4\) M\(^{-1}\)cm\(^{-1}\)) is assigned to \(\pi \rightarrow \pi^*\) transition (310 nm; \(\epsilon = 1.4 \times 10^4\) M\(^{-1}\)cm\(^{-1}\)). The peak for the n-\(\pi^*\) transition (310 nm; \(\epsilon = 1.7 \times 10^4\) M\(^{-1}\)cm\(^{-1}\)) was shifted to higher energy compared to those of H\(_2\)L.1 (286 nm, 344 nm respectively)\(^{14}\).

For the ligand H\(_2\)L.2, however, the spectra shows that the peak assigned to the \(\pi \rightarrow \pi^*\) transition was found at 282 nm; (\(\epsilon = 1.4 \times 10^4\) M\(^{-1}\)cm\(^{-1}\)). The data obtained indicate that nickel complexes are thermally stable until 80 °C. Then they lost water molecules between 80-140 °C. The decomposition proceeds approximately with three degradation steps. These steps occurred in between 80 and 720 °C with net weight loss of 81.46 % for Ni.1.2H\(_2\)O and 80.93 % for Ni.2.2H\(_2\)O.

Zinc complexes of both ligands are more thermally stable than their nickel counterparts. They start to lose their coordinated water molecules between 80-200 °C and then the subsequent steps correspond to the slow decomposition of the ligand until about 700 °C. The final decomposition products were

<table>
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<th>TABLE-4</th>
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<tr>
<td>THERMAL ANALYSIS DATA FOR THE COMPLEXES</td>
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<tr>
<td>Compound</td>
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<td>H(_2)L.1.H(_2)O</td>
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<td>ZnL.1.H(_2)O</td>
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The UV-Vis spectra of the zinc complexes shows that the MLCT and \(\pi \rightarrow \pi^*\) peaks at 414 nm (\(\epsilon_{\text{max}} = 0.28 \times 10^4\) M\(^{-1}\)cm\(^{-1}\)) and 291 nm (\(\epsilon_{\text{max}} = 1.7 \times 10^4\) 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\(^{17}\).

The \(\pi \rightarrow \pi^*\) transition (310 nm; \(\epsilon = 1.4 \times 10^4\) M\(^{-1}\)cm\(^{-1}\)) and the peak for the n-\(\pi^*\) transition (310 nm; \(\epsilon = 1.7 \times 10^4\) M\(^{-1}\)cm\(^{-1}\)) was shifted to higher energy compared to those of H\(_2\)L.1 (286 nm, 344 nm respectively)\(^{14}\).
metal oxides formed above 720 °C for nickel complexes and 850 °C 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).

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 and generally the antioxidant activity of all compounds increased with increase of their concentration.

When two hydroxyl groups are present in o- or 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$_2$L1 and H$_2$L2 are very important structural factors for their radical scavenging activity. However, the present study has shown that the o-substituted ligand H$_2$L1 exhibited better free radical scavenging activities than the m-substituted ligand H$_2$L2. 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 2-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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**REFERENCES**