Abstract

The Schiff-bases, I, II, III were prepared essentially by the condensation reaction between an amine, namely 2-amino-4-phenylthiazole, and an aldehyde: benzaldehyde (I), p-chlorobenzaldehyde (II) and p-nitrobenzaldehyde (III) in 1:1 molar ratio. The metal-complexes of Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ and La$^{3+}$ were also synthesized. The structure elucidation was based on: elemental analysis, IR, UV-Visible, $^1$H NMR and MS spectral analyses.

The impact of γ-radiation on the synthesized compounds was discussed via the post-radiation UV-Visible aftermaths. Some radiolysis products were postulated with the assistance of the obtained MS results. The thermal properties of the metal chelates were confirmed by the means of TGA results. The molar conductance of the derivatives supported the 1:1 and 1:2 electrolyte behaviors.

Metal-complex magnetic behavior in association with the UV-Visible data suggested the octahedral for all complexes except III$_b$ is tetrahedral arrangement, whereas, Cu-complexes demonstrated distorted geometry. Furthermore, the Cu-complex of the ligand III$_d$ proved to be very highly active against the Gram-positive Bacillus subtilis (NCTC-1040), whereas Co-complex of II$_b$ showed significant inhibition, similarly on Streptococcus pyogenes (ATCC-19615) and on the fungus Aspergillus fumigatus.

Keywords: Schiff-base, metal-complex, spectral analysis, γ-irradiation, antimicrobial activity

Introduction

The twentieth century has been characterized both by a drastic reduction in the mortality caused by infectious diseases and by a rise in the control of neoplastic pathologies. Nevertheless, microorganisms and viruses, on the one hand, and tumors, on the other, still represent a dreadful menace to men’s health and therefore, for a more efficient control, require the steady development of novel and more powerful drugs (1-6).

Chemists have reported on the chemical, structural and biological properties of Schiff-bases, which are characterized by the -N=CH-, azomethine group (7-12). Vicini et al. (13) synthesized different compounds bearing an azomethine linkage and evaluated in-
their antiviral, antimicrobial and antiproliferative activities with the aim of identifying lead compounds active against emergent and re-emergent human and cattle infectious diseases, e.g. AIDS, hepatitis B and C, tuberculosis, bovine viral diarrhea, or against drug-resistant cancers, e.g. leukaemia, carcinoma, melanoma, MDR tumors, for which no definitive cure or efficacious vaccine is available at present.

Metal complexes of Schiff-bases derived from substituted salicylaldehyde and heterocyclic compounds containing nitrogen, sulphur and/or oxygen atoms as ligands are of interest as simple structural models of more complicated biological systems (14-16). Chiral ligands were prepared by the condensation of salicylaldehyde or 5-t-butylsalicylaldehyde with 1, 2-diaminocyclo-hexane in ethanol (17, 18). Metal salen complexes were prepared by the treatment of the ligands with Cu$^{2+}$ or Ni$^{2+}$ salts. Mercury, as one of the most hazardous heavy metals in the environment, can be potentially removed by salen metal complexes for environmental remediation and the resultant bimetallic complexes may be used as chiral mercury reagents.

The interest in transition metal-complexes of Schiff-bases continues not only due to the interesting structural and bonding modes they possess but also due to synthetic flexibility, selectivity and sensitivity towards the central metal atom in addition to their varied industrial applications (19, 20).

In the present work three Schiff bases were prepared by the condensation reaction between the aromatic amine 2-amino-4-phenylthiazole and aldehydes, namely benzaldehyde, p-chlorobezaldehyde and p-nitro benzaldehyde. Some ligand metal-complexes were synthesized and characterized by physicochemical and spectral analyses. Some title compounds were subjected to γ-radiation and further spectral investigation was performed.

**Experimental**

**Materials**

All the employed chemicals were Merck-Germany, products. The Schiff-base implemented amine is 2-amino-4-phenylthiazole and the applied aldehydes are benzaldehyde, p-chlorobenzaldehyde and p-nitrobenzaldehyde. Metal-complexes were prepared by using the metal salts: Fe(NO$_3$)$_3$.9H$_2$O, Co(CH$_3$COO)$_2$.4H$_2$O,
Ni(CH₃COO)₂.4H₂O, Cu(CH₃COO)₂.2H₂O, Zn(CH₃COO)₂.2H₂O, and LaCl₃.7H₂O.

Solvents and other used chemicals were of highly pure grade.

**Instruments**

The IR spectra were recorded by Perkin Elmer 57928 RXIFT-IR system. Electronic absorption measurements were performed by Perkin Elmer lambda 35 UV-Visible spectrophotometer. The ¹H NMR spectra were carried out by Varian, Gemini 200 MHz spectrometer. Hewlett Packard MS 5988 spectrometer was used for mass spectrometry. Thermal analysis was applied by Shimadzu 50. Gamma-cell 220A was used for irradiation processes. Conductance Engineered System, U.S.A, was employed for the conductometric titration and molar conductance measurements.

**Conductometric measurements**

Further insight concerning the structure of these products was gleaned from a consideration of conductometric measurements. Thus, the conductometric titration is performed by titrating 25 ml of 1x10⁻³ M metal ion solution with increasing volume of 1x10⁻³ M complexing agent solution (Schiff-base derivatives) and the conductance is then recorded after stirring the solution for about 2 min.

By plotting the conductance value, after correction for dilution as a results of addition of chelating agent, VS milliliters of the reagent added applying the least square equation for Y values according to the following equation\(^{(21)}\)

\[
Y = m \times X + b
\]

where Y is one variable, X is the other, m is the slope of curve and b is the intercept on the ordinate (y axis) Y usually the measured variable plotted as a function of changing as shown in Figs (1). The titration curves are smooth straight lines for all the points, and the well defined breaks are coincident with the stoichiometric ratio of complexes formed in solution. The data are in good agreement with the (1:1) molar ratio suggested for these adducts.

The UV absorbance of the mixed solutions was recorded at 302, 300, 306, 276, 307 and 316 nm for Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and La³⁺, respectively.
Fig.(1) Conductometric titration curves for (Ia-IIIa)
The Schiff-bases (I-III) were prepared by condensation reaction in which the aldehyde, 0.1 mole, was dropwisely added to the amine, 0.1 mole, with continuous stirring. Thereafter, the reaction mixture was heated at 100°C for about 10 min in presence of 5 ml ethanol or acetic acid. The isolated yields were purified by recrystallization from a solvent, which gave analytical data see Table (1).

Table (1): Analytical and physical data of Schiff-bases (I-III):

<table>
<thead>
<tr>
<th>Compd. No.</th>
<th>Color</th>
<th>M.P. °C</th>
<th>Products</th>
<th>M. F.</th>
<th>M.Wt.</th>
<th>Elemental analysis</th>
<th>Calcd. / Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Yellowish brown 160-162</td>
<td>C_{6}H_{12}N_{2}S</td>
<td>264</td>
<td>72.7</td>
<td>4.58</td>
<td>10.6</td>
<td>12.1</td>
</tr>
<tr>
<td>II</td>
<td>Yellow</td>
<td>122-125</td>
<td>C_{6}H_{11}ClN_{2}S</td>
<td>298</td>
<td>64.3</td>
<td>3.71</td>
<td>9.38</td>
</tr>
<tr>
<td>III</td>
<td>Reddish yellow</td>
<td>190-192</td>
<td>C_{6}H_{11}N_{2}O_{2}S</td>
<td>309</td>
<td>62.1</td>
<td>3.58</td>
<td>13.5</td>
</tr>
</tbody>
</table>

Metal-complexes were prepared by the addition of the equimolar amounts of metal salt solution, 0.004 mole, to the Schiff-bases 0.004 moles in 25 ml ethanol. Thereafter, the reaction mixture was heated under reflux for 6 h. The solvent was then allowed to evaporate at room temperature and the obtained solid was filtered and washed with dry ethyl ether, Table (2).

A complementary study based on the electronic absorption spectra and the magnetic moment measurement of metal-complex, via Faraday method\(^{22}\), was employed to envisage the coordination geometry. The UV-Visible absorption within, \(\lambda_{\text{max}} = 200-1100 \text{ nm}\), was examined for DMF \(10^{-6} \text{ M}\) solutions in the UV- and \(10^{-3} \text{ M}\) in the Visible- sector at room temperature. Meanwhile the molar conductance of metal-complexes was detected in \(10^{-3} \text{ M}\) DMF solutions at room temperature.

Irradiation process were carried out for \(10^{-5} \text{ M}\) in the UV- sector and \(10^{-3} \text{ M}\) in the Visible-sector DMF of selected synthesized substances by an integral gamma dose of 30 kGy at a dose rate of 1.2 Gy s\(^{-1}\) under ambient conditions. The post- radiation aftermath was followed up by UV-Visible spectral analysis at the above mentioned concentrations. The synthesized compounds were also tested for the antimicrobial activity using ampicillin as a reference\(^{23}\).
Table 2: Analytical and physical data of Schiff-base complexes (I-III):

<table>
<thead>
<tr>
<th>Compd. No.</th>
<th>Color</th>
<th>M.P. °C</th>
<th>M. F.</th>
<th>Elemental analysis</th>
<th>Calcd. / Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N %</td>
<td>M %</td>
</tr>
<tr>
<td>Ia</td>
<td>Dark brown</td>
<td>223-225</td>
<td>C_{16}H_{14}FeN_{2}O_{6}S</td>
<td>13.36 / 12.85</td>
<td>10.65 / 11.63</td>
</tr>
<tr>
<td>Ib</td>
<td>Violet</td>
<td>325-327</td>
<td>C_{20}H_{22}CoN_{2}O_{6}S</td>
<td>5.87 / 5.21</td>
<td>12.34 / 11.78</td>
</tr>
<tr>
<td>Ic</td>
<td>Grey</td>
<td>&gt; 360</td>
<td>C_{20}H_{22}NiO_{6}S</td>
<td>5.87 / 5.03</td>
<td>12.30 / 11.63</td>
</tr>
<tr>
<td>Id</td>
<td>Brown</td>
<td>260-262</td>
<td>C_{20}H_{22}CuN_{2}O_{6}S</td>
<td>5.81 / 4.60</td>
<td>13.18 / 12.7</td>
</tr>
<tr>
<td>Ie</td>
<td>Dark yellow</td>
<td>197-200</td>
<td>C_{20}H_{22}NiO_{6}S</td>
<td>5.79 / 5.64</td>
<td>13.52 / 13.07</td>
</tr>
<tr>
<td>If</td>
<td>Pale white</td>
<td>232-235</td>
<td>C_{18}H_{17}Cl_{3}LaN_{2}O_{6}S</td>
<td>5.31 / 5.52</td>
<td>26.33 / 23.15</td>
</tr>
<tr>
<td>IIa</td>
<td>Dark brown</td>
<td>&gt; 360</td>
<td>C_{16}H_{15}ClFeN_{2}O_{6}S</td>
<td>12.54 / 11.34</td>
<td>10.00 / 9.28</td>
</tr>
<tr>
<td>IIb</td>
<td>Pale violet</td>
<td>257-260</td>
<td>C_{20}H_{21}ClCoN_{2}O_{6}S</td>
<td>5.47 / 4.61</td>
<td>11.51 / 10.31</td>
</tr>
<tr>
<td>IIc</td>
<td>Green</td>
<td>163-165</td>
<td>C_{20}H_{21}ClNiO_{6}S</td>
<td>5.48 / 5.32</td>
<td>11.47 / 10.27</td>
</tr>
<tr>
<td>IId</td>
<td>Greenish yellow</td>
<td>310-313</td>
<td>C_{20}H_{21}ClCuN_{2}O_{6}S</td>
<td>5.42 / 5.09</td>
<td>12.30 / 11.91</td>
</tr>
<tr>
<td>Ile</td>
<td>Pale white</td>
<td>210-212</td>
<td>C_{20}H_{21}ClNiO_{6}S</td>
<td>5.40 / 4.93</td>
<td>12.62 / 11.44</td>
</tr>
<tr>
<td>IIe</td>
<td>Pale white</td>
<td>320-322</td>
<td>C_{18}H_{17}ClLaN_{2}O_{6}S</td>
<td>4.98 / 4.59</td>
<td>24.71 / 23.61</td>
</tr>
<tr>
<td>IIIa</td>
<td>Dark brown</td>
<td>&gt; 360</td>
<td>C_{16}H_{15}FeN_{2}O_{6}S</td>
<td>14.76 / 13.86</td>
<td>9.81 / 8.97</td>
</tr>
<tr>
<td>IIIb</td>
<td>Greenish brown</td>
<td>225-228</td>
<td>C_{20}H_{21}CoN_{2}O_{6}S</td>
<td>8.08 / 7.25</td>
<td>11.28 / 10.64</td>
</tr>
<tr>
<td>IIIc</td>
<td>Dark yellow</td>
<td>220-222</td>
<td>C_{20}H_{21}NiO_{6}S</td>
<td>8.05 / 7.64</td>
<td>11.24 / 10.27</td>
</tr>
<tr>
<td>IIId</td>
<td>Brown</td>
<td>243-245</td>
<td>C_{20}H_{21}CuN_{2}O_{6}S</td>
<td>7.97 / 7.43</td>
<td>12.06 / 11.12</td>
</tr>
<tr>
<td>IIIe</td>
<td>Pale yellow</td>
<td>225-227</td>
<td>C_{20}H_{21}NiO_{6}S</td>
<td>7.95 / 7.79</td>
<td>12.37 / 11.44</td>
</tr>
<tr>
<td>IIIf</td>
<td>Greenish yellow</td>
<td>235-237</td>
<td>C_{18}H_{17}ClLaN_{2}O_{6}S</td>
<td>7.34 / 7.45</td>
<td>24.26 / 23.15</td>
</tr>
</tbody>
</table>
Results and Discussion

Schiff-base structural analysis

Elucidation of the chemical structures of the prepared Schiff-bases (I-III) were based on the elemental, Table 1, IR, UV, NMR and MS spectral analyses.

IR – spectra

The stretching vibration bands of the Schiff-bases I, II and III, respectively, are assigned as follows: 3060, 3086 and 3062 cm\(^{-1}\) for the stretching vibrations of the aromatic C-H bands; 1610, 1602 and 1602 cm\(^{-1}\) for vN=C; 1526, 1526 and 1520 cm\(^{-1}\) for vC=C; 1326, 1330 and 1336 cm\(^{-1}\) for vC-N; 766, 774 and 768 cm\(^{-1}\) for vC-S-C. The weak stretching bands at 2973 and 2865 cm\(^{-1}\) of II, and at 2944 and 2858 cm\(^{-1}\) of III are ascribed to the \(\delta\)C-H stretching vibration mode of the azomethine group. The deformation mode of the vibration bands at 1402 and 1488 cm\(^{-1}\) are accounted for the C-H bond and the band located at 824 cm\(^{-1}\) can be attributed to the vC-Cl in II. Meanwhile, the band at 768 cm\(^{-1}\) can be referred to the out-of-plane deformation of the C-H bond of the 1, 4-disubstituted benzene ring in III. The IR frequencies are listed in Table (3).

Table 3: Characteristic IR stretching vibration (cm\(^{-1}\)) of Schiff-bases (I-III)

<table>
<thead>
<tr>
<th>Compd. No.</th>
<th>Stretching vibration ((\nu)) in cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\nu)C-H(_{Ar})</td>
</tr>
<tr>
<td>I</td>
<td>3060</td>
</tr>
<tr>
<td>II</td>
<td>3086</td>
</tr>
<tr>
<td>III</td>
<td>3062</td>
</tr>
</tbody>
</table>

UV- Electronic absorption spectra

The electronic absorptions of the Schiff-bases I, II and III, respectively, revealed the following results: the regions of \(\lambda_{max} = 203-245\), 203-244 and 203-244 nm exhibit the structures of the phenyl ring transition (\(1L_a \leftarrow 1A\)); \(\lambda_{max} = 259, 255\) and 255 nm of the phenyl ring transition (\(1L_b \leftarrow 1A\)); \(\lambda_{max} = 270, 272\) and 272 nm of the \(\pi-\pi^*\) transition in the C=N group; and \(\lambda_{max} = 329, 330\) and 330 nm of the broad n-\(\pi^*\) transition of the N=C in I and II, in addition to N=O group in III. Signal absorptions are listed in Table (4).
Table 4: The electronic absorption spectra of Schiff-bases (I-III)

<table>
<thead>
<tr>
<th>Compd. No.</th>
<th>Electronic Absorption λ in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>¹Lₐ←¹A</td>
</tr>
<tr>
<td>I</td>
<td>203-245</td>
</tr>
<tr>
<td>II</td>
<td>203-244</td>
</tr>
<tr>
<td>III</td>
<td>203-244</td>
</tr>
</tbody>
</table>

¹H NMR – spectra

The ¹H NMR of the three Schiff-bases in DMSO-d₆ demonstrated multiplet signals within the range δ 7-8 attributed to the aromatic protons of two different phenyl rings. A common shift at δ 5.7 in I and II, and at δ 5.8 in III is ascribed to the thiazole ring proton. The azomethine proton is represented at δ 9 in I and II, and δ 8.4 in III. A singlet appeared at δ 7.3 exhibiting the absorption of the phenyl protons in the Cl- substituted aromatic ring in II.

The MS- spectra

The mass spectra of the three Schiff-bases I, II and III displayed the followings:

The molecular peak is respectively as follows for I, II and III: 264 (40.8%), 298 (42.4%) and 309 (24.6%). Two common ion peaks are m/e = 77 with 30.3%, 29.4% and 23.8% and m/e =89 with 43.7%, 78.8% and 47.8%, respectively, corresponding to M⁺ (C₆H₅) and M⁺ (C₇H₅), respectively. The base peaks are assigned respectively as follows: m/e =134 (100%), 133 (100%) and 175 (100%) representing in order the ions M⁺ (C₈H₆S), M⁺ (C₈H₆S) and M⁺ (C₉H₇N₂S). For I, the ion peaks m/e = 176 (83.8%) and 102 (24.8%) are accounted for M⁺ (C₈H₆N₄S) and M⁺ (C₉H₇). For II, the ion peaks m/e = 262 (32.9%), 221 (32.9%), 175 (87.1%) and 101 (52.9%) represent in order the ions M⁺ (C₁₀H₁₁N₂S), M⁺ (C₁₀H₁₁Cl N₂S), M⁺ (C₉H₇N₂S) and M⁺ (C₈H₆). For III, the ion peaks m/e = 263 (4.6%), 175 (100%), 133 (93.3%) and 101 (33.1%) are due in order to M⁺ (C₁₀H₁₁N₂S), M⁺ (C₈H₇N₂S), M⁺ (C₈H₆S) and M⁺ (C₈H₆).

The elemental and spectral analyses may corroborate the I, II and III structures as follows:
where, R is C₆H₅ in I : N-bezylidene-5-phenylthiazol-2-amine, p-Cl-C₆H₄ in II : N-(4-chlorobenzylidene)-5-phenylthiazol-2-amine and p-NO₂-C₆H₄ in III : N-(4-nitrobenzylidene)-5-phenylthiazol-2-amine.

**Metal-complex structural analysis**

Six metal-complexes were prepared for each synthesized Schiff-base: Iₐ₋ₖ, IIₐ₋ₖ and IIIₐ₋ₖ employing the metal ions Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and La³⁺, respectively. The structure recognition was based on the elemental, Table (2), and spectral analyses.

**IR- spectra**

Comparing the common bands, it is observed that the complex bands shift to lower or higher frequency. Furthermore, metal-nitrogen bonds were found common in the prepared coordination compounds.

For Iₐ₋ₖ, with respect to the order of metal ions, the weak broad bands at 3348, 3490, 3310, 3306 and 3280 cm⁻¹ were attributed to the associated water molecules. The weak bands observed at 2940, 2938, 2935, 2927 and 2957 cm⁻¹ were ascribed to the starching vibrations of the aliphatic C-H bond in the azomethine, and the acetate groups in Co, Ni, Cu and Zn metal-complexes. Also, the bands located at 1516, 1542, 1570, 1594, 1540 and 1534 cm⁻¹ were assigned for vC=N bond in the azomethine group which shift to lower frequency than that of the ligand asserting the nitrogen atom participation in the coordination sphere. The acetato complexes displayed also the asymmetric vCOO⁻ at 1605, 1590 and 1632 cm⁻¹ and the symmetric vCOO⁻ at 1342, 1330 and 1382 cm⁻¹ in Co, Cu and Zn metal-complexes, respectively. The weak bands appeared at 3086, 3098, 3028, 3065, 3098 and 3102 cm⁻¹ were ascribed to the starching vibrations of the aromatic C-H bond which demonstrated also in-plane bending deformation bands at 1392, 1408, 1410, 1480, 1440 and 1442 cm⁻¹. The vC-S-C bonds were represented by the bands at 690, 676, 684, 698, 694 and 700 cm⁻¹. The observed bands at 610, 616, 618, 624, 529 and 548 cm⁻¹, were accounted for M← N coordination bond.

Analogous elucidation was applied for IIₐ₋ₖ and IIIₐ₋ₖ metal-complexes. For IIₐ₋ₖ, with respect to the order of metal ions, the weak broad bands at 3364, 3496, 3358,
3374, 3316 and 3300 cm\(^{-1}\) were referred to the coordinated water molecules. The weak bands observed at 2955, 2975, 2968, 2948, 2937 and 2960 cm\(^{-1}\) were assigned for the starching vibrations of the aliphatic C-H bond of the azomethine, and the acetate groups in Fe, Co, Ni, Cu, Zn and La metal-complexes. The azomethine \(\nu C=N\) bond showed similar responses as that of I\(_{a-f}\) at 1518, 1528, 1526,1507, 1482, and 1536 cm\(^{-1}\). Co, Ni, Cu and Zn acetate groups gave \(\nu as\ COO^-\) and \(\nu sym\ COO^-\) bands at 1629, 1694, 1704 and 1642 cm\(^{-1}\), and 1344, 1330, 1332 and 1301 cm\(^{-1}\), respectively. The aromatic C-H bonds displayed the weak bands at 3020, 3068, 3062, 3100 and 3112 cm\(^{-1}\) beside the in-plane bending deformation mode of vibration at 1480, 1442, 1442, 1398 and 1442 cm\(^{-1}\) for Fe, Co, Ni, Zn and La metal-complexes, respectively. The \(\nu C-S-C\) band appeared the bands at 688, 678, 696, 698, 688 and 704 cm\(^{-1}\). The coordination bond M← N was noticed by the bands at 614, 616, 542, 490, 470 and 552 cm\(^{-1}\).

For I\(_{a-f}\), the coordinated water molecules associated with the complex exhibited the weak broad bands at 3346, 3456, 3354, 3370, 3368 and 3428 cm\(^{-1}\). The aliphatic C-H bond in the azomethine group, and the acetate groups in Fe, Co, Ni, Cu, Zn and La metal-complexes was assigned to the weak broad bands observed at 2975, 2940, 2936, 2926, 2932 and 2952 cm\(^{-1}\). Similar to the aforementioned, the \(\nu C=N\) bond in the azomethine group demonstrated the bands at 1518, 1532, 1528, 1518, 1522 and 1570 cm\(^{-1}\). The \(\nu as\ COO^-\) and \(\nu sym\ COO^-\) of Ni, Cu and Zn metal-complexes located at 1694, 1600 and 1602 cm\(^{-1}\), and 1336, 1338 and 1338 cm\(^{-1}\), respectively. The aromatic C-H bond exhibited the weak bands at 3034, 3065, 3044, 3064, 3058,1448 and 3180 cm\(^{-1}\), and the in-plane bending deformation mode of vibration at 1398, 1440 and 1468 cm\(^{-1}\) in the spectra of Fe, Co, Ni and La, respectively. The appearance of the bands located at 694, 682, 692, 698, 698 and 688 cm\(^{-1}\) was attributed to the \(\nu C-S-C\). Finally, the bands at 594, 614, 543, 538, 538 and 618 cm\(^{-1}\) were accounted for the coordination bond M← N.
The molar conductance of the complexes was measured in DMF solution of $10^{-3}$ M at room temperature. The metal-complexes of Fe, Co, Ni, Cu, Zn and La, I$_{a-f}$, respectively revealed 44.1, 8.5, 38.6, 14.7, 1.8 and 90.6 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Meanwhile, II$_{a-f}$ showed the molar conductance yields of 52.7, 12.6, 10.3, 38.6, 8.0 and 43.2 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ and the obtained results for III$_{a-f}$ in similar order were 78.5, 18.6, 16.7, 25.2, 10.2 and 396 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. The shown remarkable low values of I$_{a-e}$, II$_{b-f}$ and III$_{b-e}$ suggest the including of the associated anions in the coordination sphere of the metal-complex, indicating the non-electrolyte behavior. Further, the results of I$_{f}$, II$_{a}$ and III$_{a}$ showed 1:2 electrolyte behavior, suggesting the ionic nature.

**UV-Visible and magnetic behavior: coordination geometry**

The magnetic properties of the metal-complexes, as a result of the isolating effect of the ligand yield direct information on the electronic configuration of the central ions, oxidation state of metal ion and the number of the unpaired electrons of the d-shell.

The UV spectra of the metal-complexes exhibited absorption bands within $\lambda_{\text{max}} = 202$-247 nm and $\lambda_{\text{max}} = 250$-259 nm that correspond to ($^1L_a \leftarrow ^1A$) and ($^1L_b \leftarrow ^1A$) transitions of the ligand phenyl ring. Meanwhile, the bands at $\lambda_{\text{max}} = 268$-286 nm correspond to the $\pi$-$\pi^*$ transition while the bands at $\lambda_{\text{max}} = 302$-332 nm represent the n-$\pi^*$ transition of the C=N in the azomethine group. The d-d transitions appeared within $\lambda_{\text{max}} = 367$-797 nm.

The measured magnetic moment of Fe (III)-complexes I$_{a}$, II$_{a}$ and III$_{a}$, $\mu_{\text{eff}} = 5.03$-6.02 B.M., suggested the octahedral, high-spin, geometry. The coordination geometry was supported by three bands within $\lambda_{\text{max}} = 367$-606 nm that are assignable for $^6A_1 \rightarrow ^4T_1$ (G), $^6A_{1g} \rightarrow ^4E_g$, $^4A_{1g}$ (G) and $^6A_{1g} \rightarrow ^4E_g$ (D) transitions.

Both tetrahedral and high-spin octahedral Co (II)-complexes I$_{b}$, II$_{b}$ and III$_{b}$ possess three unpaired electrons, however, they may be distinguished by the magnitude of deviation of $\mu_{\text{eff}}$ from the spin-only value. The measured magnetic moment, $\mu_{\text{eff}} = 4.0$-4.41 B. M., shades light on the presence of three unpaired electrons indicating a high-spin octahedral configuration. This is supported by the band within the region $\lambda_{\text{max}} = 356$-441 nm representing the $^4T_{1g} \rightarrow ^4T_{1g}$ (P) transitions in I$_{b}$ and II$_{b}$ complexes. Meanwhile, III$_{b}$ exhibited a band within the region $\lambda_{\text{max}} = 375$-427 nm interpreted for $^4A_2$ (F) $\rightarrow ^4T_1$ (P) transition confirming a tetrahedral configuration.
The measured magnetic moment for Ni (II)-complexes I\(_c\), II\(_c\) and III\(_c\), \(\mu_{\text{eff}} = 2.84\)-3.18 B.M., is of high-spin at room temperature and consistent within the observed normal range for octahedral Ni (II)-complexes\(^{(26)}\). The suggested configuration is supported by the appearance of three bands within the region \(\lambda_{\text{max}} = 375-498\) nm in II\(_c\) and III\(_c\). As the ground state of Ni (II) in an octahedral coordination is \(^3\!A_{2g}\), the exhibited bands may be assigned to the \(^3\!A_{2g}(F) \rightarrow ^3\!A_{2g}(P)\) transition.

The measured magnetic moment for Cu (II)-complexes I\(_d\), II\(_d\) and III\(_d\), \(\mu_{\text{eff}} = 1.7\)-1.85 B. M., at room temperature is consistent within the range normally observed for distorted octahedral\(^{(27)}\). The \(^2\!E_g\) and \(^2\!T_{2g}\) states of the octahedral Cu\(^{+2}\) ion (d\(^9\), \(^2\!D\) term) split under the influence of the tetragonal distortion due to ligand field and Jan-teller distortion effect\(^{(28)}\). By distortion three spin allowed transitions are expected: \(^2\!B_{1g} \rightarrow ^2\!A_{1g}\), \(^2\!B_{1g} \rightarrow ^2\!B_{2g}\) and \(^2\!B_{1g} \rightarrow ^2\!E_g\). The Cu-complexes I\(_d\), II\(_d\) and III\(_d\) displayed bands in the region \(\lambda_{\text{max}} = 375-500\) nm referred to \(^2\!B_{1g} \rightarrow ^2\!B_{2g}\) and \(^2\!B_{1g} \rightarrow ^2\!E_g\) transitions. The Zn- and La-complexes are diamagnetic possessing the octahedral coordination. Measured magnetic moments are tabulated in Table (5).

**Table 5:** The magnetic properties of the metal Schiff-base complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Metal</th>
<th>(\mu_{\text{eff}}) (B. M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I(_a)</td>
<td>Fe</td>
<td>5.4</td>
</tr>
<tr>
<td>I(_b)</td>
<td>Co</td>
<td>4.41</td>
</tr>
<tr>
<td>I(_c)</td>
<td>Ni</td>
<td>2.84</td>
</tr>
<tr>
<td>I(_d)</td>
<td>Cu</td>
<td>1.78</td>
</tr>
<tr>
<td>I(_e)</td>
<td>Zn</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>I(_f)</td>
<td>La</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>II(_a)</td>
<td>Fe</td>
<td>5.67</td>
</tr>
<tr>
<td>II(_b)</td>
<td>Co</td>
<td>4.00</td>
</tr>
<tr>
<td>II(_c)</td>
<td>Ni</td>
<td>3.18</td>
</tr>
<tr>
<td>II(_d)</td>
<td>Cu</td>
<td>1.82</td>
</tr>
<tr>
<td>II(_e)</td>
<td>Zn</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>II(_f)</td>
<td>La</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>III(_a)</td>
<td>Fe</td>
<td>5.03</td>
</tr>
<tr>
<td>III(_b)</td>
<td>Co</td>
<td>4.31</td>
</tr>
<tr>
<td>III(_c)</td>
<td>Ni</td>
<td>2.93</td>
</tr>
<tr>
<td>III(_d)</td>
<td>Cu</td>
<td>1.83</td>
</tr>
<tr>
<td>III(_e)</td>
<td>Zn</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>III(_f)</td>
<td>La</td>
<td>Diamagnetic</td>
</tr>
</tbody>
</table>
\(^1\)H NMR spectra

\(^1\)H NMR spectra of Zn-complexes, I\(_e\), II\(_e\) and III\(_e\), were recorded in DMSO-d\(_6\). The signal appeared at \(\delta\) 9, 8.8 and 8.4, respectively, was of lesser intensity than seen for the azomethine proton in the ligands. The multiplet signals at \(\delta\) 7-7.6 in I\(_e\) and II\(_e\) spectra and at \(\delta\) 7.1-7.9 in III\(_e\) spectrum are attributed to the aromatic protons in the two different phenyl rings. The acetate methyl proton displayed a signal at \(\delta\) 1.83, 1.86 and 1.85, respectively.

In view of the spectral arguments the following conformations may be allowable for the metal-complexes I\(_a-f\), II\(_a-f\) and III\(_a-f\).

where,

\[\begin{align*}
I_a; & \quad M= Fe^{3+}, X=NO_3 \\
I_b; & \quad M= La^{3+}, X=Cl \\
I_c; & \quad M= Ni^{2+}, X=Aco \\
I_d; & \quad M= Cu^{2+}, X=Aco \\
I_e; & \quad M= Zn^{2+}, X=Aco
\end{align*}\]

and

\[\begin{align*}
II_a; & \quad M= Fe^{3+}, X=NO_3 \\
II_b; & \quad M= La^{3+}, X=Cl \\
II_c; & \quad M= Ni^{2+}, X= AcO \\
II_d; & \quad M= Cu^{2+}, X=Aco \\
II_e; & \quad M= Zn^{2+}, X=Aco
\end{align*}\]
where,

\[ \text{II}_a; \text{M}= \text{Fe}^{3+}, \text{X}=\text{NO}_3 \]
\[ \text{II}_b; \text{M}= \text{La}^{3+}, \text{X}=\text{Cl} \]

where,

\[ \text{II}_c; \text{M}= \text{Ni}^{2+}, \text{X}=\text{Aco} \]
\[ \text{II}_d; \text{M}= \text{Co}^{2+}, \text{X}=\text{Aco} \]
\[ \text{II}_e; \text{M}= \text{Cu}^{2+}, \text{X}=\text{Aco} \]
\[ \text{II}_f; \text{M}= \text{Zn}^{2+}, \text{X}=\text{Aco} \]

**Miscellaneous behaviors**

**γ- Irradiation stability**

γ- irradiated of ligand $10^{-5}$M in DMF solutions was conducted at conditions of: 30kGy total integratal dose, 1.2 Gy s$^{-1}$ dose rate, neutral medium, and ambient air and room temperature. The applied dose rate of relatively low linear energy transfer favors the non-interradical reactions (29). Further, the excitation energy received by the aromatic systems is channeled to relatively low-energy triplet excited states which have a low probability of dissociation (30). This is also confirmed for nitrobenzene as radiolysis yields which are low compared with nitromethane (31). Nevertheless, the presence of the aromatic ring does not stabilize the aromatic halide. This is mainly due to electron scavenging with formation of an aromatic radical and a stable halide ion that may be later converted to a halogen atom during
EFFECT OF γ-RADIATION AND CHARACTERIZATION...  

ion neutralization\(^{(32)}\). Analogues to the γ- radiolysis of acetone at a relatively low dose rate, 0.81 Gy s\(^{-1}\), DMF methyl radicals may produce similar products, e.g. H\(_2\), H\(_4\) and CO, and also attack the substrate giving various yields\(^{(33)}\).

Generally, the impact of irradiation was explicitly noticed in the resolution of the fingerprint of the ligands I, II, III. Contrarily, the phenylic transition region within \(\lambda_{\text{max}} = 200-260\) nm, revealed better and numerous resolved species, whereas, within \(\lambda_{\text{max}} = 260-320\) nm, less resolved and larger absorbance features were detected in association with the disappearance of the C=N \(\pi-\pi^*\) transition at 330 nm. This may shade light on the generation of various aromatic structures in addition to the formation of longer and diverse conjugated systems as a result of change in the azomethine bond and the likelihood of aromatic radical- radical recombinations. Simulating the MS yields, as a first approach, three potential radiolysis products may be suggested\(^{(34)}\):

**Postulated radiation- induced species**

The metal-complexes Ia-d and IIa-d displayed rather similar behaviors within the region \(\lambda_{\text{max}} = 200-340\) nm where the phenylic transitions exhibited much lesser absorbance with better resolution, whereas the \(\pi-\pi^*\) transition sector showed better resolution, whereas the \(\pi-\pi^*\) transition sector showed distortion in the structure with slight decrease in the general absorbance. On the other hand in the case of the metal-complexes IIIa-d, the region of the phenylic transitions demonstrated steadiness in absorbance with obvious decrease and distortion in the \(\pi-\pi^*\) transition sector. This may suggest that a fragmentation in the conjugated systems took place as a result of methyl radical attack aided by the withdrawing group NO\(_2\).

In the visible region at a concentration of 10\(^{-3}\) M, I\(_1\) gave two strong bands at \(\lambda_{\text{max}} = 367\) and 581 nm characterizing the presence of Fe (III) ion. By γ-irradiation the two bands completely disappeared suggesting the decomposition of the coordination structure. Similar observation was reported for I\(_b\) and I\(_c\) within the region \(\lambda_{\text{max}} = 350-450\) nm. Meanwhile, I\(_d\) showed some bands in the region \(\lambda_{\text{max}} = 350-500\) nm that turned out much less resolved by irradiation, probably by the generation of various species. Less resolved but persistent shapes were also noticed in the region \(\lambda_{\text{max}} = 350-500\) nm by irradiating II-and III-complexes.
It is evident that, distortion of the complex structure by irradiation definite at the applied conditions resulting in the formation of several structures \(^{(35)}\).

**Thermal stability**

The Fe-complex I\(_a\) exhibited a four-staged thermogram. A weight loss of 3.74% at 130 °C was accounted for one molecule of the coordination water. Two next steps showed weight loss of 11.41 and 11.8%, respectively, within the ranges 130-220 °C and 220-350 °C, referred to two NO\(_3\) groups. A last weight of 30.08% within the region 350-620 °C was assigned for [C\(_7\)H\(_6\)NO\(_3\)] adducts. The residue of 41.8% could withstand to 1000 °C.

Three decomposition stages were observed for II\(_d\) started by 6.01% weight loss within the range 100-160 °C ascribed to \(\sim\) two molecule of the coordination water. The second weight loss was 20.67 % within the range 160-390 °C attributed to two acetate groups. The last stage within the region 390-870 °C was of 56.63% accounted for [C\(_{16}\)H\(_{11}\)Cl NS] adduct. The residue of 15.5 % corresponds to the molecular weight 79.8 may be determined for a CuO molecule.

The metal-complex III\(_c\) demonstrated a four-staged thermal decomposition. A weight loss of 2.83% at 150 °C was attributed to one molecule of the coordination water. Within the range 170-320 °C a weight loss of 13.8% was referred to one acetate group and a nitrogen half-molecule. A weight loss of 15.32% followed within the region 320-420 °C ascribed to a separation of one benzene molecule. The last loss was 61.4% within the range 420-870 °C determined for [C\(_{16}\)H\(_{11}\)N\(_3\)O\(_2\)S] adduct. A residue of 6.23% proved thermal stability up to 1000 °C.

**Antimicrobial activity**

The synthesized metal-complexes were tested, using ampicillin as a reference, while dissolved by 1g/ml DMSO. Against the Gram-positive Bacillus *subtilis* (NCTC-1040), III\(_d\) showed very high activity, whereas II\(_b\) showed significant inhibition; II\(_d\) revealed moderate inhibition, and I\(_{a-c}\) and III\(_{b-c}\) exhibited weak inhibition. Further, against Streptococcus *pyogenes* (ATCC-19615), II\(_b\) showed significant inhibition, whereas II\(_d\) and III\(_{b-d}\) revealed weak inhibition.

The Gram-negative bacteria displayed the following: for *E. coli*, I\(_c\) showed significant inhibition, whereas II\(_b\) revealed moderate inhibition and III\(_{b-c}\) gave weak results. For Clostridium, I\(_c\) and III\(_d\) showed only weak inhibition.
The metal-complexes were also tested for the antifungal activity using Clofran as a reference. For Aspergillus *fungatus*, II₅ showed significant inhibition whereas III₄ revealed moderate activity.

**Conclusions**

The elemental and spectral analyses confirmed the proposed chemical structures of the synthesized Schiff-bases I, II and III and metal-complex derivatives I₃₋₆, II₃₋₆ and III₃₋₆. The broadness and shift to lower IR frequencies of the azomethine group evidenced the role of the group in the coordination process. The involvement of coordination water in the coordination sphere was also asserted by the TGA results. The UV-Visible spectra reported data in association with the magnetic behavior of metal-complexes suggested the dominance of the octahedral arrangement except Cu-complexes which displayed distorted octahedral geometry.

The γ-irradiation process revealed rather stronger influence on the metal-complexes than the parent ligands indicating lesser radiation stability behavior of the coordination arrangement. The radiolysis of the ligand and metal chelates substrates as well as the employed solvent was discussed and some presumably formed species were postulated.

The molar conductance values of the metal-complexes suggest the non-electrolytic behavior and the involvement of the acetate group, in the acetato complexes, in the coordination sphere. The molar conductance results indicated also the 1:1 electrolyte behavior in the case of I₆, II₃ and III₅ and the 1:2 electrolytes to III₆ suggesting the ionic nature. On the other hand, some metal-complexes demonstrated substantial antibacterial and antifungal activities. The Cu-complex III₄ has been proved to be very highly active against Bacillus *subtilis* in reference with ampicillin.

**References**


