Nickel(II)-oxaloyldihydrazone complexes: Characterization, indirect band gap energy and antimicrobial evaluation

Ayman H. Ahmed1*, A.M. Hassan1, Hosni A. Gumaa1, Bassem H. Mohamed1 and Ahmed M. Eraky1

Abstract: A series of oxaloyldihydrazones was prepared essentially by the usual condensation reaction between oxaloyldihydrazide and different aldehydes e.g. salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2-hydroxyacetophenone and 2-methoxy-benzaldehyde in 1:2 M ratio. The formed compounds were purified to give bis(salicylaldehyde)oxaloyldihydrazone (L1), bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (L2), bis(2-hydroxyacetophenone)oxaloyldihydrazone(L3) and bis(2-methoxy-benzaldehyde)oxaloyldihydrazone (L4). All the oxaloyldihydrazones (L1–L4) and their relevant solid nickel(II) complexes have been prepared and structurally characterized on the basis of the elemental analyses, spectral (UV–vis, IR, mass and 1H NMR), magnetism and thermal (TG) measurements. The dihydrazones coordinate to the metal center forming mononuclear complexes with L1, L3 and L4 in addition to binuclear complex with L2. The metal center prefers tetrahedral stereochemistry upon chelation. The optical indirect band gap energy for all compounds underlies the range of semiconductor materials. The prepared ligands and their metal complexes have been assayed for their antimicrobial activity against fungi as well as Gram-positive and Gram-negative bacteria. The resulting data indicate the ability of the investigated compounds to inhibit the growth of some micro-organisms, where L2 showed the highest activity among all the compounds. Minimum inhibitory concentration (MIC) of L2 against the growth of five micro-organisms was

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Ayman H. Ahmed was born in Benha, Egypt. He completed his undergraduate work in chemistry at Zagazig University (1991). He obtained his MSc degree (1998) and PhD (2002) at Al-Azhar University. Assistant professor in 2007, where he is now a full professor of inorganic chemistry. His work is relevant to coordination compounds and their biological studies in addition to synthesis of organic compounds as corrosion inhibitors. His current research is in the area of synthesis and characterization of solid complexes especially zeolite-encapsulated complexes. As a part of his ongoing studies, herein, he contributed in reporting the nickel(II)-oxaloyldihydrazone complexes: characterization, indirect band gap energy and antimicrobial evaluation

PUBLIC INTEREST STATEMENT
In view of the biological importance of oxaloyldihydrazones and their chelates, four types of dihydrazone ligands and their Ni(II) complexes have been synthesized and structurally characterized by elemental analyses, spectral (UV–vis., IR, mass and 1H NMR), magnetism and thermal (TG) measurements. The metal center prefers tetrahedral stereochemistry upon chelation. The optical indirect band gap energy for all compounds lays in the range of semiconductor materials. The prepared ligands and their metal complexes have been assayed for their antimicrobial activity against fungi as well as Gram-positive and Gram-negative bacteria. The resulting data indicate the ability of the investigated compounds to inhibit the growth of some micro-organisms, where L2 showed the highest activity among all the compounds. Minimum inhibitory concentration (MIC) of L2 against the growth of five micro-organisms was
determined which gives better response against *Aspergillus fumigatus* and *Bacillus subtilis* compared with some selected standard drugs.

**Subjects:** Human Biology; Inorganic Chemistry; Optoelectronics

**Keywords:** hydrazone complexes; synthesis; stereochemistry; biological activity

1. **Introduction**

Hydrazones and their derivatives constitute a versatile class of organic compounds that are important for drug design, organocatalysis and also for the syntheses of heterocyclic compounds (Barbazan et al., 2008). In addition, they find use as plasticizers, polymerization inhibitors and antioxidants. Despite hydrazones have been under study for a long time owing to their easy preparation, much of their basic chemistry remains unexplored. In fact, hydrazones played a central role in the development of coordination chemistry. Hydrazones obtained by the condensation of 2-hydroxy or methoxy aldehydes and ketones with hydrazides are considered potential polynucleating ligands because they have amide, azomethine and phenol/methoxy functions, thus offering a variety of bonding possibilities in metal complexes (Sherif & Ahmed, 2010). Extensive studies have revealed that the lone pair on trigonally hybridized nitrogen atom of the azomethine group is responsible for the chemical and biological activity (Ahmed & Ewais, 2012; Ghasemian et al., 2015; Hassan et al., 2015), compounds of this type have a great biological activity as antitumor and antiviral agents (Rollas & Küçükgüzel, 2007; Yuan, Lovejoy, & Richardson, 2004). Nevertheless, a lot of complexes derived from hydrazones \([M = \text{Cu(II)}, \text{Ni(II)}, \text{Pd(II)}, \text{Co(II)}, \text{V(IV)} \text{and Ru(II)}]\) have been studied (Hassan et al., 2015), little complexes of oxaloyldihydrazone ligands have been identified (Hassan et al., 2015; Lal, Adhikari, Kumar, Chokroborty, & Bhaumik, 2002; Lal, Basumatary, Adhikari, & Kumar, 2008; Salavati-Niasari & Sobhani, 2008). This is because oxaloyldihydrazones are soluble only in high polar solvents such as DMF and DMSO which requires much effort to isolate them or their complexes in pure form. Of worthy mention, some hydrazone complexes have been incorporated in zeolite-Y by analogous methods and the resulting materials were inferred by various physicochemical characterization techniques (Ahmed, 2014; Ahmed & Mostafa, 2009; Ahmed & Thabet, 2011, 2015).

Actually, investigation on new antimicrobial agents is important due to the resistance acquired by several pathogenic micro-organisms. The synthesized chemical compounds, which are used for the treatment of infectious diseases, are known as chemotherapeutic agents. Every year thousands of compounds are synthesized to find out potential chemotherapeutic agent to combat pathogenic micro-organisms. In this regard, mixed ligand metal complexes of ampicillin and chloramphenicol prepared using Ni(II), Co(II) and Fe(III) chlorides hexahydrate disclosed that the activity of the metal complexes had more potent antibacterial activity than the parent drugs (Ahmed & Ewais, 2012; Ajani, 2008). Indeed, hydrazones and their coordination compounds including nickel metal have wide applications as antitumour (Yuan, Lovejoy, & Richardson, 2004), antimicrobial activity (Al-Sha’alan, 2007), antimalarial (Walcovt, Loyevsky, Lovejoy, Gordeuk, & Richardson, 2004) and antiviral (Abdel-Aal, El-Sayed, & El-Ashry, 2006). The biological activity of hydrazone may be attributed to the formation of stable chelates with transition metals present in the cell, thus many vital enzymatic reaction cannot take place in the presence of hydrazone.

In view of the importance of oxaloyldihydrazones and their chelates, we have undertaken the synthesis and structural characterization studies on bivalent metal (Ni) complexes with some types of oxaloyldihydrazone ligands \(L_1-L_4\). The optical band gap of all isolated compounds has been determined to describe their optical and electronic properties. Moreover, the biological activity of the ligands and their complexes has been investigated to show the possibility for their uses in pharmaceutical industry as antibiotics to treat some diseases in medicine area.
2. Experimental

2.1. Materials and methods
The selected metal salts, diethyl oxalate, hydrazine monohydrate were purchased from Sigma–Aldrich. The employed aldehydes were of E-Merck grade. Oxalidihydrazide was prepared by the recipe described in Ref. (Hassan et al., 2015), (Exp/Lit. m.p = 240°C). Other chemicals and solvents were of highest purity and used without further purification. The 1H NMR spectra were recorded on a Jeol-FX-90Q Fourier NMR spectrometer at 25°C using DMSO solvent and TMS as an internal standard. Mass spectra of the ligands were performed by a Shimadzu-GC-MS-QP1000 EX using the direct inlet system. Metal contents (%wt) were estimated complexometrically by EDTA using xylenef orange as indicator and solid hexamine as buffer (pH 6). Elemental analyses (CHN), spectral (UV–vis., FTIR), \( \mu_{\text{eff}} \) and thermal (TG) measurements were carried out as reported (Salama, Ahmed, & El-Bahy, 2006). The optical band gap energy (\( E_g \)) of product compounds was calculated from Tauc’s equations (Rashad, Turky, & Kandil, 2013; Tauc, 1968).

2.2. Preparations

2.2.1. Preparation of oxaloyldihydrazone ligands
The dihydrazone ligands; bis(salicylaldehyde)oxaloyldihydrazone (L1), bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (L2), bis(2-hydroxyacetophenone) oxaloyldihydrazone (L3) and bis(2-methoxybenzaldehyde)oxaloyldihydrazone (L4); were prepared by general condensation procedure. Oxalicidihydrazide (0.01 mol) dissolved first in hot water (20 cm³) followed by adding methanol (40 cm³) was mixed with the appropriate aldehyde [salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2-hydroxyacetophenone and 2-methoxybenzaldehyde] (0.02 mol) in absolute methanol. The resulting mixture was refluxed for 3 h under constant stirring. The product separated out on concentrating the solution to half of its volume and cooling. The crystals of the desired ligand was collected by filtration through a Buchner funnel and dried in the oven at 50°C for 2 h. After that, the ligand was recrystallized from DMF–MeOH mixed solvent, collected, washed thoroughly on filter paper by acetone to remove any excess of DMF and then dried in an electric oven at 50°C for 2 h. The authenticity of the ligands was proved by elemental analyses, (IR, mass and 1H NMR) spectroscopy (Tables 1 and 2).

2.2.2. Preparation of solid complexes
The dihydrazone ligand (1 mmol) was dissolved in a minimum amount of DMF (20 ml) and then 50 ml methanol was added. The resulting solution was added slowly to a methanolic solution of Ni(II) acetate. The resulting mixture was heated under reflux for 3 h and then reduced to 15 cm³ by evaporation on hot plate. The resulting reaction mixture was cooled down to room temperature and the colored solid complexes were filtered off, washed several times with successive portions of hot solvents [DMF, 10–15 ml, methanol, 30–40 ml and acetone, 20–30 ml], respectively, to remove any excess of unreacted ligand and finally dried in an electric furnace at 80°C for 5 h.

2.3. Biological activity

2.3.1. Agar diffusion well method to determine antimicrobial activity
The synthesized compounds were screened for their antimicrobial activity against seven different test organisms having environmental and clinically importance. The micro-organism inoculums were uniformly spread using sterile cotton swab on a sterile Petri dish containing malt agar (for fungi) and nutrient agar (for bacteria). Ten mg/ml of each sample was added to each well (10 mm diameter holes cut in the agar gel, 20 mm apart from one another). The systems were incubated for 24–48 h at 37°C (for bacteria) and at 28°C (for fungi). After incubation, micro-organism growth was observed. Inhibition of the bacterial and fungal growth were measured in mm. Tests were performed in triplicate (Smânia, Monache, Smânia, & Cuneo, 1999). Minimal inhibitory concentration (MICs) of bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (L2) was determined by dissolving the
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specimen in DMSO and using different concentrations (0.001–0.078 mg/l). The minimal inhibitory concentration (MICs) was determined after incubation period.

3. Results and discussion
Oxaloyldihydrazones ligands (L₁–L₄) and their solid complexes with Ni(II) ion have been isolated in a pure form. Physical, analytical and spectroscopic data of the hydrazones and their related metal complexes are given in Tables 1 and 2. The complexes are air stable for long time, insoluble in MeOH/ EtOH, Et₂O, CHCl₃, acetone, CCl₄ as well as benzene. Complexes 1–3 are soluble in DMF and DMSO while complex 4 is partially soluble. Comparison of the elemental analysis for both the calculated

### Table 1. Analytical, physical and spectroscopic data of the oxaloyldihydrazones and their related metal complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Symbol</th>
<th>M.p (°C)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>M</th>
<th>¹H-NMR Chemical shift (δ ppm)</th>
<th>μₑffective M⁺</th>
<th>Found/calcd</th>
<th>Eₕ (eV)</th>
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<tr>
<td>C₁₆H₁₄N₄O₄</td>
<td>L₁</td>
<td>&gt;300</td>
<td>59.1</td>
<td>5.4</td>
<td>16.2</td>
<td>–</td>
<td>12.6 (NH, s), 10.98 (OH, s), 8.75 (CH=N, s), 6.6–8.40 (aromatic protons, m)</td>
<td>–</td>
<td>326.0/326.0</td>
<td>2.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yellow</td>
<td>58.9</td>
<td>4.3</td>
<td>17.2</td>
<td>–</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₆H₁₄N₄O₄</td>
<td>L₂</td>
<td>&gt;300</td>
<td>68.1</td>
<td>5.3</td>
<td>12.9</td>
<td>–</td>
<td>12.76 (NH, s), 12.57 (OH, s), 9.74 (CH=N, s), 7.0–8.8 (aromatic protons, m)</td>
<td>–</td>
<td>427.1/426.4</td>
<td>2.46</td>
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<tr>
<td></td>
<td></td>
<td>Yellow</td>
<td>67.7</td>
<td>4.3</td>
<td>13.2</td>
<td>–</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₆H₁₄N₄O₄</td>
<td>L₃</td>
<td>&gt;300</td>
<td>59.5</td>
<td>6.1</td>
<td>14.7</td>
<td>–</td>
<td>12.85 (NH, s), 11.85 (OH, s), 6.6–8.0 (aromatic protons, m), 2.48 (CH₃, s)</td>
<td>–</td>
<td>356.4/354.2</td>
<td>2.78</td>
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<tr>
<td></td>
<td></td>
<td>Pale yellow</td>
<td>61</td>
<td>5.1</td>
<td>15.8</td>
<td>–</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₈H₁₈N₄O₄</td>
<td>L₄</td>
<td>&gt;300</td>
<td>59.2</td>
<td>5.8</td>
<td>15.7</td>
<td>–</td>
<td>12.3 (NH, s), 11.9 (OH, s), 8.95 (CH=N, s), 6.8–8.5 (aromatic protons, m), 3.93 (OCH₃, s)</td>
<td>–</td>
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<td>White</td>
<td>61</td>
<td>5.1</td>
<td>15.8</td>
<td>–</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>[Ni(L₁)(OAc)₂].2H₂O</td>
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<td>44.0</td>
<td>4.2</td>
<td>10.1</td>
<td>11.9</td>
<td></td>
<td></td>
<td>3.8</td>
<td>2.28</td>
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<td>Orange</td>
<td>44.6</td>
<td>4.5</td>
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<td>10.9</td>
<td></td>
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<td>[Ni(L₂–2H).(H₂O)].3H₂O</td>
<td>2</td>
<td>&gt;300</td>
<td>44.9</td>
<td>3.4</td>
<td>8.2</td>
<td>17.9</td>
<td></td>
<td></td>
<td>3.9</td>
<td>1.87</td>
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<td></td>
<td></td>
<td>Break red</td>
<td>45.8</td>
<td>3.8</td>
<td>8.9</td>
<td>18.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(L₃–2H)].CH₃OH</td>
<td>3</td>
<td>&gt;300</td>
<td>51.0</td>
<td>4.3</td>
<td>12.2</td>
<td>12.4</td>
<td></td>
<td></td>
<td>3.6</td>
<td>2.08</td>
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<tr>
<td></td>
<td></td>
<td>Red</td>
<td>51.5</td>
<td>4.6</td>
<td>12.6</td>
<td>13.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(L₄–H)(OAc)].0.5H₂O</td>
<td>4</td>
<td>&gt;300</td>
<td>51.0</td>
<td>4.2</td>
<td>11.5</td>
<td>12.3</td>
<td></td>
<td></td>
<td>3.4</td>
<td>2.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Green</td>
<td>50.0</td>
<td>4.4</td>
<td>11.7</td>
<td>12.2</td>
<td></td>
<td></td>
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</table>
and found percentages indicates that the compositions of the synthesized complexes coincide well with the proposed formulae.

### 3.1. Chemical structures of dihydrazones and NiII-complexes

#### 3.1.1. IR spectra and bonding

The positions of the significant IR bands of dihydrazones and their nickel complexes are registered in Table 2.

**Ligands:** oxaloyldihydrazones (L₁-L₄) can exist either in the trans (staggered) configuration or cis-configuration, Figure 1, (Hassan et al., 2015; Lal, Adhikari, & Kumar, 1993). In cis-configuration, the dihydrazine can adopt either anti-cis-configuration or syn-cis-configuration. Infrared spectra showed strong bands at 1602–1617 cm⁻¹ assignable to the azomethine group (νC=N). The observation of these bands confirmed the interaction of dihydrazides with aldehydes forming azomethine linkages. The bands of ν(OH) phenolic/naphthoic, ν(NH) and ν(C=O) for L₁-L₃ were noticed at (3149, 3204 and 1666), (3476, 3166 and 1705(m)+1660(v.s)) and (3448, 3293 and 1689(m)+1651(v.s)) cm⁻¹, respectively. Meanwhile, L₄ which does not contain o-hydroxy group revealed ν(NH) at 3202 cm⁻¹ and ν(C=O) at 1653 cm⁻¹. The appearance of both ν(C=O) and ν(NH) simultaneously in the IR spectra of

<table>
<thead>
<tr>
<th>Symbol</th>
<th>ν(OH) phenolic (enolic)</th>
<th>ν(OH) H₂O/MeOH</th>
<th>ν(NH)</th>
<th>ν(C=H) aromatic (aliphatic)</th>
<th>ν(C=O) phenolic</th>
<th>δ(C–H) aromatic out of plane</th>
<th>ν(M–O) phenolic/enolic (carbonyl/methoxy)</th>
<th>λ max, nm (assignments)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₁</td>
<td>3149 (3278)</td>
<td>3204</td>
<td>3062 (2924)</td>
<td>1666</td>
<td>1620</td>
<td>1275</td>
<td>1403, 1458, 1486</td>
<td>756</td>
</tr>
<tr>
<td>L₂</td>
<td>3476 (-)</td>
<td>3166</td>
<td>3043 (2926)</td>
<td>1705</td>
<td>1621</td>
<td>1287</td>
<td>1465, 1541, 1574</td>
<td>741</td>
</tr>
<tr>
<td>L₃</td>
<td>3448 (-)</td>
<td>3293</td>
<td>3048 (2923)</td>
<td>1689</td>
<td>1607</td>
<td>1246</td>
<td>1449, 1486, 1512</td>
<td>746</td>
</tr>
<tr>
<td>L₄</td>
<td>3227 (-)</td>
<td>3202</td>
<td>3041 (2940)</td>
<td>1653</td>
<td>1600</td>
<td>964</td>
<td>1464, 1486, 1572</td>
<td>760</td>
</tr>
<tr>
<td>1</td>
<td>3362 (-)</td>
<td>3204</td>
<td>3063 (2924)</td>
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<td>1605</td>
<td>1276</td>
<td>1458, 1486</td>
<td>757</td>
</tr>
<tr>
<td>2</td>
<td>3377 (-)</td>
<td>3054 (2925)</td>
<td>1617</td>
<td>1302</td>
<td>1457</td>
<td>1538</td>
<td>747</td>
<td>547/458</td>
</tr>
<tr>
<td>3</td>
<td>3400 (-)</td>
<td>3283</td>
<td>3013 (2927)</td>
<td>1678</td>
<td>1611</td>
<td>1273</td>
<td>1445, 1489, 1536</td>
<td>748</td>
</tr>
<tr>
<td>4</td>
<td>3385 (-)</td>
<td>3202</td>
<td>3055 (2926)</td>
<td>1653</td>
<td>1602</td>
<td>1580</td>
<td>970</td>
<td>1464, 1488 756 /525</td>
</tr>
</tbody>
</table>

Table 2. Significant IR and electronic absorption data of oxaloyldihydrazones and their nickel complexes
L₁-L₄ indicates the presence of keto forms. The appearance of carbonyl groups (C=O) near 1660 cm⁻¹ as one band in case of L₁ and L₄ and pair of bands near (1660, 1700 cm⁻¹) for each L₂ and L₃ indicates the trans configuration (staggered, Figure 1) for (L₁ and L₄), while mixture of [cis(syn/anti-cis-structure) + trans (staggered structure), Figure 1] isomers for (L₂ and L₃). This suggestion results from the field effect phenomenon which can be elucidated as follows: when the two carbonyl (C=O::) groups are in the same direction (cis configuration), the non-bonding electrons present on oxygen atoms cause electrostatic repulsion. This causes a change in the state of hybridization of C=O group and also make it to go out of the plane of the double bond. Thus, the configuration diminished and absorption occurs at higher wave number. Subsequently, cis is absorbed (due to the field effect) at higher frequency compared to trans isomer. Thereby, L₂ and L₃ showed two bands for C=O, one of them (at high frequency) associated with syn/anti-cis-structure, while that at lower frequency is related to staggered configuration. The low intensity of high frequency bands (near 1700 cm⁻¹) compared with that at low frequency (near 1660 cm⁻¹) indicates the domination of staggered structure. Of worthy mention, NMR spectroscopy is in good agreement with this suggestion. The observation of OH (phenolic) group in L₁ at lower position (3149 cm⁻¹) is taken as evidence to the persistence of intermolecular H-bonding between the phenolic-OH and azomethine group (O–H…N) (Burger, Ruff, & Ruff, 1965). The proposition of intermolecular H-bond (O–H….O-H) between ligand molecules is excluded owing to the sharpness of this band. The remarkable downward frequency shift indicates the strength of this bond. In fact, ¹H NMR did not distinguish this H-bond in its spectra because execution of NMR analysis in high polar solvent (DMSO) led to break these bonds. The phenolic-OH group did not form H-bonding in case of ligands L₂ and L₃ where it is observed after 3400 cm⁻¹. Further, the existence of two bands at 3278 cm⁻¹ (L₂) and 3227 cm⁻¹ (L₃) may be attributed to ν(OH)enolic in H-bond bonding with azomethine group. The lower shift for these two bands than the normal value asserts the weakness of this bond. The obscure of enolic OH in NMR spectra of L₁ and L₄ may be attributed to factors: (1) its lower concentrations. Minute molecules may change one or two of its C=O groups into enolized configuration but the keto form is still dominated, (2) dilution by high polar DMSO disrupted these H-bonds returning the modified molecules into keto forms. The significant ν(C=O) groups

Figure 1. Proposed structures of oxaloyldihydrazone ligands, where L₁ (R = H, X = H, Y = H), L₂ (R = ph, X = H, Y = H), L₃ (R = H, X = H, Y = CH₃) and L₄ (R = H, X = CH₃, Y = H).
associated to the aromatic ring of the dihydrazones L₁-L₄ were observed at 1275, 1287, 1246 and 964 cm⁻¹, respectively (Burger et al., 1965; Chanu, Kumar, Ahmed, & Lal, 2012). All of the investigated hydrazones ligands showed 3–4 bands in the range 1400–1600 cm⁻¹ related to ν(C= C) of the aromatic ring. Also, each ligand exhibited strong band in the region 700–800 cm⁻¹ corresponding to the out-of-plane deformation of the aromatic ring. The positions of other bands assigned to ν(CH) aliphatic near 2900 cm⁻¹ and ν(CH) aromatic near 3050 cm⁻¹ are demonstrated in Table 2.

Ni(II) complexes: In these complexes, the dihydrazones (L₁-L₄) acts as bi-, tri-, tetra-dentate ligands towards the centered nickel(II) ion. Appearance of both ν(NH) and ν(C=O) after chelation (in case of 1) at the same position in addition to a negative shift of ν(C=N) indicated that its corresponding ligand coordinated in keto form via the azomethine group only. This negative shift of ν(C=N) arises from a decrease in the π-bond character of the azomethine (-C=N) group as a result of nitrogen to metal coordination (Ali, Ahmed, Mohamed, & Mohamed, 2007). The shift of ν(OH) phenolic of L₁ to higher frequency upon complexation (3149 → 3362 cm⁻¹) is due to the cleavage of H-bond of the type CH = N…..OH phenolic. Obscure of both ν(NH) and ν(C=O) after chelation (in case of 2) with splitting of ν(C=N) and positive shift of ν(C=O) naphthoic evidenced that C=O and NH groups are not contributed in coordination, whereas the corresponding ligand binds to the metal in enol form via the azomethine and deprotonated α-hydroxyl groups. The splitting of C=N occurred due to the enolization of two C=O groups in dihydrazone molecule assuming enol−enol skeleton. For 3 and in comparison to free L₃, the negative shift of ν(NH) (3293 → 3283 cm⁻¹), positive shift of ν(C=O) (1246→1273 cm⁻¹), obscure ν(OH)-phenolic as well as observation of ν(C=O) at its normal position (1678 cm⁻¹) ascertained the coordination of L₃ with Ni(II) ion through NH and deprotonated α-hydroxy groups. Despite the formation seven-membered ring around the nickel ion may be discouraged and rare, remaining of ν(CH = N) at nearly the same location ruled out its anticipation in construction of complex geometry. The observation of C=O as one band in 3 instead of two bands in L₃ with slight change in its location may be due to the presence of the two oxygen atom related to (O = C = N) part, Figure 2, in trans or cis symmetry. Perhaps the absorption of this group (C=O) at somewhat higher frequency (1678 cm⁻¹) supports the first suggestion i.e., cis structure. Unnoticeable ν(OH) of α-hydroxyl group in complexes 2 and 3 species supports the deprotonation of this group during the coordination of L₂ and L₃. In case of complex 4, half of the L₄ molecule was altered to enol form and coordination takes place by one side (one OMe, one C=N and one deprotonated enolized C=OH group). This proposition depends on the weakness in intensity of [ν(NH), ν(C=O) and ν(C=OMe)] and splitting of C=N. The splitting in the vibrational stretching C=O band observed in 4 at (1602, 1580 cm⁻¹) substantiated the presence of dissimilar azomethine groups (participated and unparticipated) (Salapathy & Sahoo, 1970). This result emphasizes the contribution of one azomethine group in bonding, Figure 2. The broadening of C=N band (at 1580 cm⁻¹) may be due to the absorption interference of C=N group generated by enolization.

Undoubtedly, the appearance of new M-O bands in all above complexes (Table 2) manifested the connection between the ligand and the central metal ion through the oxygen atom of ortho group

<table>
<thead>
<tr>
<th>Tested micro-organism</th>
<th>L₄/MICS (µg/ml)</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fungi</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aspergillus fumigatus</td>
<td>15.6</td>
<td>23.7</td>
</tr>
<tr>
<td>Synccephalastrum racemosum</td>
<td>31.25</td>
<td>19.7</td>
</tr>
<tr>
<td><strong>Gram-Positive Bacteria</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Streptococcus pneumoniae</td>
<td>125</td>
<td>23.8</td>
</tr>
<tr>
<td>Bacillus subtilis</td>
<td>15.6</td>
<td>32.4</td>
</tr>
<tr>
<td><strong>Gram-Negative Bacteria</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Escherichia coli</td>
<td>500</td>
<td>19.9</td>
</tr>
</tbody>
</table>

Table 3. The MIC of bis(2-hydroxy-naphthaldehyde)oxaloyldihydrazone (L₄)
Furthermore, crystalline and coordinated water molecules in nickel specimens were supposed to be based on the appearance of the broad bands within the range 3300–3500 cm\(^{-1}\). Other bands assignable to acetate ion (OAc) were detected in complex 1 at 1466 and 1359 cm\(^{-1}\), while in complex 4 at 1354 and 1437 cm\(^{-1}\) suggesting \(\nu_{as}\) and \(\nu_{s}\) carboxylic modes, respectively. The larger difference between the \(\nu_{as}\) and \(\nu_{s}\) frequencies confirmed the coordination of acetate as a unidentate anion through the C–O moiety of the carboxylic group (Nakamoto, 1970). The slight changes in the positions of \(\nu(C = C)\) upon chelation arise from metal–ligand interaction.

3.1.2. \(^1\)H NMR Spectra

The assignment of the main signals in \(^1\)H NMR spectra of all ligands (Hassan et al., 2015) is given in Table 2, where nickel complexes are not scanned owing to their paramagnetic nature. \(^1\)H NMR spectra of all ligands exhibited multiple signals of the aromatic protons in the 6.5–8.5 ppm region. The signals of equal integration observed in L\(_1\), L\(_2\), and L\(_3\), at \(\delta\) (12.6, 11), (12.8, 12.6) and (12.9, 11.8) ppm downfield of TMS have been assigned to NH and ortho-OH protons, respectively. On the other hand, L\(_4\) revealed a signal at 12.3 ppm attributed to secondary NH group. Upon the addition of D\(_2\)O, the OH and NH signals were obscured. Further, the existence of the \(\delta\)OH (phenolic/naphthoic) at its normal frequency excluded any intramolecular hydrogen bonding operating between ortho-OH and CH = N group (CH = N…H–O). The azomethine signals, \(\delta(CH = N)\), observed only in L\(_1\), L\(_2\), and L\(_3\) have been assigned at 8.75, 9.73 and 8.95 ppm, respectively. As reported in the literature (Kumar et al., 2011), if the dihydrazone exists in the syn-cis-configuration or staggered configuration, the \(\delta\)OH, \(\delta\)NH and \(\delta CH = N\), resonances, each should appear as a singlet. However, the appearance of these signals in the form of six signals (doublet of doublet) indicates anti-cis (chair) configuration. According to IR interpretation mentioned above, the staggered configuration is well-defined/dominated for all ligands (L\(_1\)–L\(_4\)). \(^1\)H NMR spectra of L\(_3\) and L\(_4\) differ from other ligands spectra where they showed signals at 2.55 and 3.9 ppm downfield of TMS due to the methyl (CH\(_3\)) and methoxy (OCH\(_3\)) protons, respectively (Abd El-Wahab, Abd El-Fattah, Ahmed, Elhenawy, & Alian, 2015; Hassan et al., 2015; Sherif & Ahmed, 2010).
3.1.3. Electronic spectra

The assignments of the observed electronic absorption bands of the oxaloylhydrazone and their metal complexes (Ali et al., 2007; Lever, 1984; Sutton, 1968) as well as the magnetic data of the formed chelates are shown in Table 1.

The electronic data of the studied ligands in paraffin oil exhibited five absorption bands at $\lambda_{\text{max}}$ (nm) equals 371–395 (n-π*, C=N), 345–390 (n-π*, C=O), 320–370 (π-π*, C=N), 290–348 (π-π*, C=O) and 270–320 (π-π*, aromatic ring). All of nickel complexes revealed a broad band within the range 595–666 nm assigned to $^3T_1 \rightarrow ^3T_1$ (P) transition. The observation of this band suggested a tetrahedral geometry around the Ni(II) ion. In spite of the complexes 2 and 3 having red color which is a characteristic for the square planar Ni(II) complexes, the paramagnetic nature of these complexes excluded this suggestion (square planner Ni(II) complexes are diamagnetic). Another band was observed for each complex in the range 445–470 nm characteristic to L-M charge transfer. This ligand–metal charge transfer (L→MCT) transition may be associated to, most probably, an electronic excitation from the HOMO of ortho-phenolate/naphtholate/methoxy oxygen to the LUMO of Ni(II) ion (McCollum et al., 1994).

3.1.4. Magnetic behavior

From the magnetic studies, the values of $\mu_{\text{eff}}$ in case of Ni(II)-complexes (1, 3 and 4) which contain one metal ion are close to spin only values and may be considered in good consistent with the proposed structures. For other consequential binuclear complexes (2), the magnetic moment values are less than that expected per molecular formula regarding the existence of two nickel ions in the proposed structure will enhance the magnetization. This can be explained on the basis of metal–metal interaction. It is suggested that these complexes have high spin but the presence of two metals near to each other in the same molecule may cause partial quenching of the spin moments of the metal ions (spin coupling) decreasing the magnetism (Sutton, 1968).

3.1.5. TG studies of Ni(II)-complexes

To examine the thermal stabilities of Ni(II)-complexes, thermogravimetric analysis (TG) for all complexes was carried out. The thermogram (TGA) data of complex 1 exhibited three stages of...
decomposition at different temperatures. The first stage in temperature range (50–160°C) corresponds to the loss of two crystalline water molecules (found/calculated = 6.5/6.7)% while the other two stages correspond to the gradual decomposition of the complex forming a mixture of NiO and NiCO₃ at the last stage (found/calculated = 17.9/18.0)%. The thermogram (TGA) data of complex (2) revealed five stages of decomposition. The first stage (50–155°C) corresponds to the loss of three crystalline water molecules (found/calculated = 17.9/18.0)%.

The second stage corresponds to the loss of (found/calculated = 6.7/5.7)% of the weight of complex at temperature range from (155–250°C) corresponding to the loss of two coordinated water molecules. The other three stages correspond to the gradual decomposition of the complex with the formation of 2NiCO₃ at the last stage (found/calculated = 37.4/37.7)%. TGA curve of complex (3) gave four stages of decomposition started at 50, 195, 250 and 400°C. The first stage (50–140°C) corresponds to the loss of one methanol molecule (found/calculated = 6.3/7.2)%.

The other three stages correspond to the gradual decomposition of the complex with the formation of NiO + NiCO₃ mixture at the last stage (found/calculated = 18.3/17.3)%. TG curve of complex (4) provided four stages of decomposition. The first one (50–250°C) is assigned to the loss of 0.5 crystalline water molecule beside one acetate group (found/calculated = 12.8/13.7)%. The other three stages are attributed to the gradual decomposition of the complex with the formation of NiO and NiCO₃ mixture at the last stage (found/calculated = 20.8/20.2)%.

In view of data presented and discussed above, structures of the nickel complexes can be represented by Figure 2.

3.1.6. Optical properties

To clarify the conductivity of the isolated complexes, the optical band gap energy (E₉) of oxaloyldihydrazones and their Ni(II) complexes have been calculated from the following equations:

The measured transmittance (T) was used to calculate approximately the absorption coefficient (α) using the relation

$$
\alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right)
$$

where d is the width of the cell and T is the measured transmittance. The optical band gap was estimated using Tauc’s equation (Rashad et al., 2013; Tauc, 1968):

![Antimicrobial activity for oxaloyldihydrazine ligands and their nickel(II) complexes.](image-url)
\[ a h \nu = A(h\nu - E_g)^m \]

where \( m \) is equal to 1/2 and 2 for direct and indirect transition, respectively, \( A \) is an energy-independent constant.

The values of \( \alpha \) calculated from the first equation were used to plot \((a h \nu)^2\) vs. \( h \nu \) (Figure 3) from which an indirect band gap was found by extrapolating the linear portion of the curve to \((a h \nu)^2 = 0\). The values of indirect optical band gap \( E_g \) were determined and given in Table 1. The \( E_g \) values of oxaloyldihydrazones (L1-L4) and Ni(II)-L complexes were found to be at 3.06–3.42 and 1.87–2.42 eV, respectively as indicated in Figure 3 and Table 1. Inspection of Table 1 revealed higher \( E_g \) values of ligands compared with their corresponding complexes. As reported in the literature (Karipcin et al., 2007), it is suggested that after complexation, metal leads to raise mobilization of the ligand electrons by accepting them in its shell. It can be evaluated that after formation of the complex, the chemical structure of the ligands is changed, the width of the localized levels is expanded and in turn, the band gap is smaller. This result is very significant in applications of electronic and optoelectronic devices because of the lower optical band gap of the materials (Mott & Davis, 1979). Of worthy mention, small band gap facilitates electronic transitions between the HOMO–LUMO energy levels and makes the molecule more electroconductive (Sengupta, Pandey, Srivastava, & Sharma, 1998). The obtained band gap values suggest that these complexes are semiconductors and lay in the same range of highly efficient photovoltaic materials. So, the present compounds could be considered potential materials for harvesting solar radiation in solar cell applications (Fu, Guo, Liu, Cai, & Huang, 2005; Karipcin et al., 2007; Mott & Davis, 1979; Sengupta et al., 1998).

3.1.7. Antimicrobial investigations

The results revealed a variable sensitivity of the 1–4 compounds towards the micro-organisms as shown in Figure 4. The data showed that all tested compounds have an appropriate activity against all the tested micro-organisms except for \( P. \) aeruginosa as Gram-negative bacteria and for \( C. \) albicans as fungi. The oxaloyldihydrazon ligand L2 exhibited the highest activity against all the tested micro-organisms, fungi, Gram-positive bacteria and Gram-negative bacteria. Complex 3 showed higher inhibition zones against \( B. \) subtilis and \( S. \) pneumoniae as Gram-positive bacteria as well as \( E. \) coli as Gram-negative bacteria, while the metal complex 2 exhibited the highest inhibition zone against \( S. \) racemosum and Aspergillus fumigatus. Complex 4 showed lower inhibition zones against all the tested micro-organisms except for \( S. \) pneumoniae as Gram-positive bacteria and \( S. \) racemosum as fungi. The dihydrazon ligand (L1) showed lower inhibition zones against \( S. \) pneumoniae as Gram-positive bacteria and \( S. \) racemosum as fungi.

In sum, the most active compound among all the tested compounds against the seven tested micro-organisms was L2 due to its wide spectrum of activity (Figure 4). The enhancement in antibacterial activity of the nickel(II) complexes (2, 3) can be explained based on the chelation theory (Mishra & Singh, 1997) where the activity of hydrazone increases upon coordination. This enhancement in activity may be rationalized on the basis that their structures mainly possess an additional \( \text{C} = \text{N} \) bond. Hydrazone ligands and their complexes act as antimicrobial agents against Gram-negative and Gram-positive bacteria, fungi and yeast (Loncle, Brunel, Vidal, Dherbomez, & Letourneux, 2004; Vicini, Zani, Cozzini, & Doytchinova, 2002). Chelation reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor groups and possibly the \( \pi \)-electron delocalization within the completely chelate ring system that is formed during coordination (Efthimiadou, Psomas, Sanakis, Katsaros, & Karaliota, 2007). These factors increase the lipophilic nature of the central metal atom and hence increase the hydrophobic character and liposolubility of the molecule favoring its permeation through the lipid layer of the bacterial membrane. Consequently, the metal complexes can easily penetrate into the lipid membranes and block the metal-binding sites of enzymes of the micro-organisms, thus destroying them more aggressively. These metal complexes also affect the respiration process of the cell and thus block the synthesis of proteins, which restrict further growth of the organism.
3.1.7.1. Minimum inhibitory concentration (MIC) of bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (L2): The antimicrobial screening concentrations of the compounds to be used were estimated from minimum inhibitory concentration (MIC) value, i.e. the lowest concentration of compounds which completely inhibits bacterial and fungal growth. The MIC of the synthesized L2 against the growth of micro-organisms was determined by standard serial dilution method (Cappucino & Sherman, 1999) and compared with that of standard drug (Amphotericin B for fungi, Ampicillin for Gram-positive bacteria and Gentamicin as Gram-negative bacteria), Table 3. The results showed that bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (L2) has higher activity against S. racemosum than A. fumigatus and no activity against C. albicans (as fungi), higher activity against S. pneumoniae than B. subtilis (as Gram-positive bacteria), lower activity against E. coli and finally no activity against P. aeruginosa (as Gram-negative bacteria). Some factors are responsible for the high activity of L2 towards several micro-organisms. (i) The high stability of L2 and this can be indicated from its high melting points (mp < 300°C), (ii) It has also been proposed that concentration plays a vital role in increasing the degree of inhibition, as the concentration increases the activity increases, (iii) the high ability of L2 to form hydrogen bond with the active centers of the cell constituents via the azomethine nitrogen atom, resulting in interference with the normal cell process and finally, (iv) it has been suggested that the hydrazones might inhibit enzyme production owing to the presence of nonbonding electron pairs on the N and O atoms. The existence of hydroxyl, carbonyl and imine (C=N) groups enhances antimicrobial activity.

4. Conclusion

A series of nickel(II)-hydrazone complexes derived from oxaloyldihydrazones (L1–L4) obtained by usual condensation of oxaloyldihydrazide and some selected aldehydes, namely salicylaldehyde (L1), 2-hydroxynaphthaldehyde (L2), 2-hydroxyacetophenone (L3) and 2-methoxybenzaldehyde (L4) have been isolated in pure form. All the ligands and their four solid nickel(II) complexes can be prepared by traditional reflux method. Comparison of the elemental analysis for both calculated and found percentages indicates that the compositions of the isolated solid complexes coincide well with the proposed formulae. Elemental analyses (C, H, N and M%), UV–Vis, FTIR spectroscopy and magnetism besides the change in ligand color upon complexation evidenced the formation of the desired nickel–hydrazone complexes. The dihydrazones give mononuclear complexes with L1, L3 and L4, but binuclear complex is formed with L2. The nickel in all complexes has tetrahedral geometry. The indirect band gap energy (Eg) of ligands and their related complexes lay in the range of semiconductor materials. The investigated compounds were assayed for their antimicrobial activities against seven test micro-organisms. The results suggested that the hydrazones and their complexes might retard enzyme production of some micro-organisms. The existence of the hydroxyl, carbonyl and azomethine (C=N) groups can enhance antimicrobial sensitivity.

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Citation information

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