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

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Abstract: A series of oxaloyldihydrazone ligands 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 (L_1), bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (L_2), bis(2-hydroxyacetophenone)oxaloyldihydrazone (L_3) and bis(2-methoxy-benzaldehyde)oxaloyldihydrazone (L_4). All the oxaloyldihydrzones (L_1 - L_4) 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 dihydrzones coordinate to the metal center forming mononuclear complexes with L_1 , L_3 and L_4 in addition to binuclear complex with L_2 . 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 L_2 showed the highest activity among all the compounds. Minimum inhibitory concentration (MIC) of L_2 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 oxaloyldihydrzones 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 metal complexes showed lower optical band gap energy than the original ligands indicating better conduction of complexes compared with the free ligands. All the investigated compounds have been assayed for their antimicrobial activity against fungi as well as Gram-positive and Gram-negative bacteria. The isolated solids may be considered as antimicrobial agents towards some micro-organisms.

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 & Küçükgül, 2007; Yuan, Lovejoy, & Richardson, 2004). Nevertheless, a lot of complexes derived from hydrazones [M = Cu(II), Ni(II), Pd(II), Co(II), V(IV) 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, Chakraborty, & 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 (Walcovrt, 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 oxaloyldihydrazones (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. Oxalaldihydrazide 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 xylenol orange as indicator and solid hexamine as buffer (pH 6). Elemental analyses (CHN), spectral (UV-vis., FTIR), μ_{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 oxalaldihydrazone ligands

The dihydrazone ligands; bis(salicylaldehyde)oxalaldihydrazone (L_1), bis(2-hydroxy-1-naphthaldehyde)oxalaldihydrazone (L_2), bis(2-hydroxyacetophenone) oxalaldihydrazone (L_3) and bis(2-methoxybenzaldehyde)oxalaldihydrazone (L_4); were prepared by general condensation procedure. Oxalaldihydrazide (0.01 mol) dissolved first in hot water (20 cm^3) followed by adding methanol (40 cm^3) 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_{aq} 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 cm^3 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)oxalaldihydrazone (L_2) was determined by dissolving the

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

Compound	Symbol	M.p (°C) Color	C	H	N	M	¹ H-NMR Chemical shift (δppm)	μ _{eff}	M ⁺ Found/ calcd	E _g (eV)
C ₁₆ H ₁₄ N ₄ O ₄	L ₁	>300	59.1	5.4	16.2	–	12.6(NH, s), 10.98(OH, s), 8.75(CH=N, s),	–	326.0/ 326.0	2.73
		Yellow	58.9	4.3	17.2	–	6.6–8.40 (aromatic protons, m)			
C ₂₄ H ₁₈ N ₄ O ₄	L ₂	>300	68.1	5.3	12.9	–	12.76(NH, s), 12.57(OH, s), 9.74(CH=N, s),	–	427.1/426.4	2.46
		Yellow	67.7	4.3	13.2	–	7.0–8.8 (aromatic protons, m)			
C ₁₈ H ₁₈ N ₄ O ₄	L ₃	>300	59.5	6.1	14.7	–	12.85(NH, s), 11.85(OH, s), 6.6–8.0(aro- matic	–	356.4/354.2	2.78
		Pale yellow	61	5.1	15.8	–	protons, m), 2.48(CH ₃ , s),			
C ₁₈ H ₁₈ N ₄ O ₄	L ₄	>300	59.2	5.8	15.7	–	12.3(NH, s), 11.9(OH, s), 8.95(CH=N, s)	–	355.0/354.4	3.05
		White	61	5.1	15.8	–	6.8–8.5(aro- matic protons, m), 3.93(OCH ₃ , s)			
[Ni(L ₁) (OAc) ₂].2H ₂ O	1	>300	44.0	4.2	10.1	11.9	–	3.8		2.28
		Orange	44.6	4.5	10.4	10.9	–			
[Ni ₂ (L ₂ -2H) (H ₂ O) ₂].3H ₂ O	2	>300	44.9	3.4	8.2	17.9	–	3.9		1.87
		Break red	45.8	3.8	8.9	18.6	–			
[Ni(L ₃ -2H)]. CH ₃ OH	3	>300	51.0	4.3	12.2	12.4	–	3.6		2.08
		Red	51.5	4.6	12.6	13.3	–			
[Ni(L ₄ -H) (OAc)].0.5H ₂ O	4	>300	51.0	4.2	11.5	12.3	–	3.4		2.42
		Green	50.0	4.4	11.7	12.2	–			

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 2. Significant IR and electronic absorption data of oxaloyldihydrazones and their nickel complexes

Symbol	$\nu(\text{OH})$ phenolic (enolic)	$\nu(\text{OH})$ $\text{H}_2\text{O}/$ MeOH	$\nu(\text{NH})$	$\nu(\text{C-H})$ aromatic (aliphatic)	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$ phenolic	$\nu(\text{C-O})$ OMe	$\nu(\text{C=C})$	$\delta(\text{C-H})$ aromatic out of plane	$\nu(\text{M-O})$ phenolic/ enolic (carbonyl/ methoxy)	$\lambda_{\text{max, nm}}$ (assignments)
L ₁	3149 (3278)	-/-	3204	3062 (2924)	1666	1620	1275		1403 1458 1486	756		387(n- π^* , C=N), 372(n- π^* , C=O), 340(π - π^* , C=N), 300 (π - π^* , C=O), 288(π - π^* , Phenyl)
L ₂	3476 (-)	-/-	3166	3043 (2926)	1705 1660	1621	1287		1465 1541 1574	741		395(n- π^* , C=N), 390(n- π^* , C=O) 370(π - π^* , C=N), 348(π - π^* , C=O), 320(π - π^* , Phenyl)
L ₃	3448 (-)	-/- -/-	3293	3048 (2923)	1689 1651	1607	1246		1449 1486 1512	746		378(n- π^* , C=N), 348(n- π^* , C=O), 322(π - π^* , C=N), 300 (π - π^* , C=O), 280(π - π^* , Phenyl)
L ₄	3227		3202	3041 (2940)	1653	1600		964	1464 1486 1572	760		371(n- π^* , C=N), 345(n- π^* , C=O), 320(π - π^* , C=N), 290 (π - π^* , C=O), 270(π - π^* , Phenyl)
1	3362 (-)	/3400	3204	3063 (2924)	1666	1605	1276		1458 1486	757		595 ($^3T_1 \rightarrow ^3T_1(P)$) 450(L \rightarrow MCT)
2		3377 (-)		3054 (2925)		1617 1602	1302		1457 1538	747	547/458	666 ($^3T_1 \rightarrow ^3T_1(P)$) 470(L \rightarrow MCT)
3		3400 (-)	3283	3013 (2927)	1678	1611	1273		1445 1489 1536	748	540/ /495	660 ($^3T_1 \rightarrow ^3T_1(P)$) 445(L \rightarrow MCT)
4		3385 (-)	3202	3055 (2926)	1653	1602 1580		970	1464 1488	756	/525	600 ($^3T_1 \rightarrow ^3T_1(P)$) 450(L \rightarrow MCT)

and found percentages indicates that the compositions of the synthesized complexes coincide well with the proposed formulae.

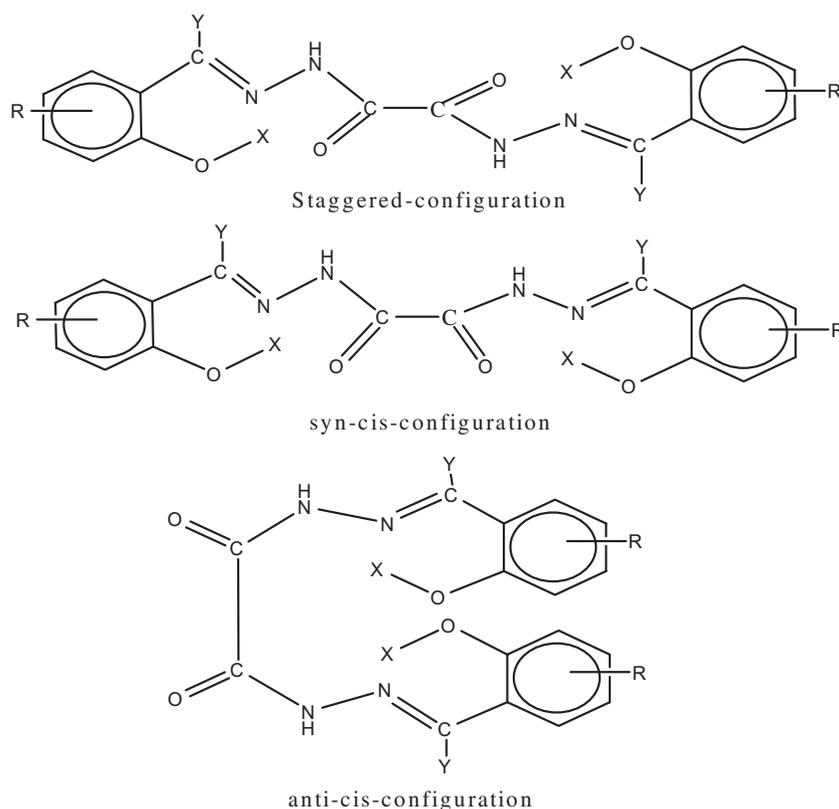
3.1. Chemical structures of dihydrazones and Ni_{II}-complexes

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 dihydrazone 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 ($\nu_{\text{C=N}}$). The observation of these bands confirmed the interaction of dihydrazides with aldehydes forming azomethine linkages. The bands of $\nu(\text{OH})_{\text{phenolic/naphthoic}}$, $\nu(\text{NH})$ and $\nu(\text{C=O})$ 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 $\nu(\text{NH})$ at 3202 cm⁻¹ and $\nu(\text{C=O})$ at 1653 cm⁻¹. The appearance of both $\nu(\text{C=O})$ and $\nu(\text{NH})$ simultaneously in the IR spectra of

Figure 1. Proposed structures of oxaloyldihydrazone ligands, where L_1 ($R = H, X = H, Y = H$), L_2 ($R = \text{ph}, X = H, Y = H$), L_3 ($R = H, X = H, Y = \text{CH}_3$) and L_4 ($R = H, X = \text{CH}_3, Y = H$).



L_1 - L_4 indicates the presence of keto forms. The appearance of carbonyl groups ($\text{C}=\text{O}$) near 1660 cm^{-1} as one band in case of L_1 and L_4 and pair of bands near ($1660, 1700 \text{ cm}^{-1}$) for each L_2 and L_3 indicates the trans configuration (staggered, Figure 1) for (L_1 and L_4), while mixture of [cis(syn/anti-cis-structure) + trans (staggered structure), Figure 1] isomers for (L_2 and L_3). This suggestion results from the field effect phenomenon which can be elucidated as follows: when the two carbonyl ($\text{C}=\text{O}::$) 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 $\text{C}=\text{O}$ 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, L_2 and L_3 showed two bands for $\text{C}=\text{O}$, 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 L_1 at lower position (3149 cm^{-1}) is taken as evidence to the persistence of intermolecular H-bonding between the phenolic-OH and azomethine group ($\text{O}-\text{H}\cdots\text{N}$) (Burger, Ruff, & Ruff, 1965). The proposition of intermolecular H-bond ($\text{O}-\text{H}\cdots\text{O}-\text{H}$) 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 L_2 and L_3 where it is observed after 3400 cm^{-1} . Further, the existence of two bands at 3278 cm^{-1} (L_1) and 3227 cm^{-1} (L_4) may be attributed to $\nu(\text{OH})_{\text{enolic}}$ 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 L_1 and L_4 may be attributed to factors: (1) its lower concentrations. Minute molecules may change one or two of its $\text{C}=\text{O}$ 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 $\nu(\text{C}-\text{O})$ groups

associated to the aromatic ring of the dihydrazones L_1 - L_4 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 $\nu(\text{C}=\text{C})$ 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 $\nu(\text{CH})_{\text{aliphatic}}$ near 2900 cm^{-1} and $\nu(\text{CH})_{\text{aromatic}}$ near 3050 cm^{-1} are demonstrated in Table 2.

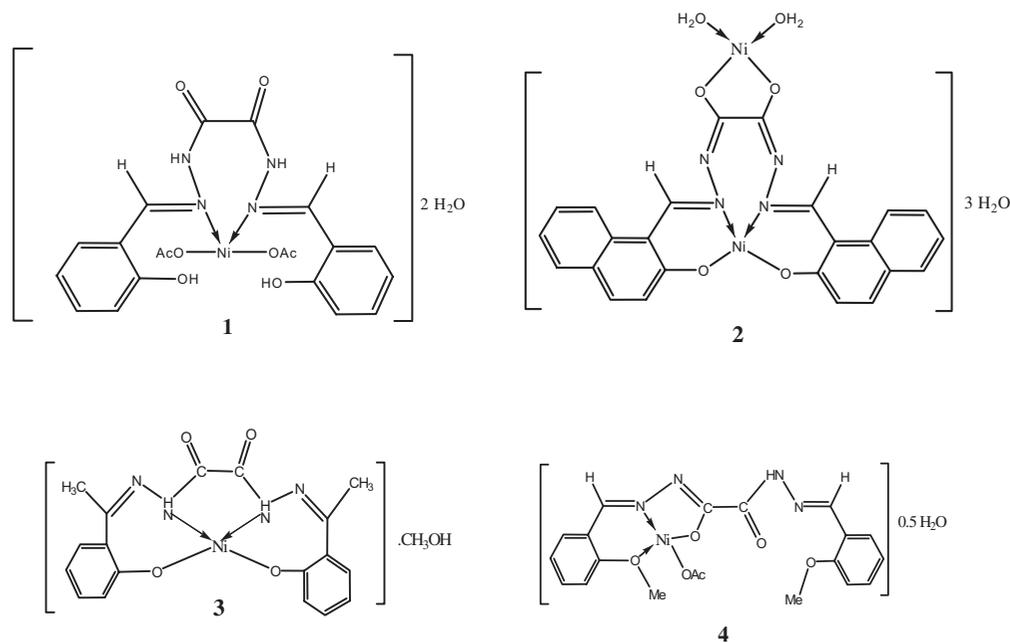
Ni(II) complexes: In these complexes, the dihydrazones (L_1 - L_4) acts as bi-, tri-, tetra-dentate ligands towards the centered nickel(II) ion. Appearance of both $\nu(\text{NH})$ and $\nu(\text{C}=\text{O})$ after chelation (in case of **1**) at the same position in addition to a negative shift of $\nu(\text{C}=\text{N})$ indicated that its corresponding ligand coordinated in keto form via the azomethine group only. This negative shift of $\nu(\text{C}=\text{N})$ arises from a decrease in the π -bond character of the azomethine ($-\text{C}=\text{N}$) group as a result of nitrogen to metal coordination (Ali, Ahmed, Mohamed, & Mohamed, 2007). The shift of $\nu(\text{OH})$ phenolic of L_1 to higher frequency upon complexation (3149 \rightarrow 3362 cm^{-1}) is due to the cleavage of H-bond of the type $\text{CH} = \text{N} \cdots \text{OH}_{\text{phenolic}}$. Obscure of both $\nu(\text{NH})$ and $\nu(\text{C}=\text{O})$ after chelation (in case of **2**) with splitting of $\nu(\text{C}=\text{N})$ and positive shift of $\nu(\text{C}=\text{O})_{\text{naphthoic}}$ evidenced that $\text{C}=\text{O}$ and NH groups are not contributed in coordination, whereas the corresponding ligand binds to the metal in enol form via the azomethine and deprotonated *o*-hydroxyl groups. The splitting of $\text{C}=\text{N}$ occurred due to the enolization of two $\text{C}=\text{O}$ groups in dihydrazone molecule assuming enol-enol skeleton. For **3** and in comparison to free L_3 , the negative shift of $\nu(\text{NH})$ (3293 \rightarrow 3283 cm^{-1}), positive shift of $\nu(\text{C}=\text{O})_{\text{phenolic}}$ (1246 \rightarrow 1273 cm^{-1}), obscure $\nu(\text{OH})$ -phenolic as well as observation of $\nu(\text{C}=\text{O})$ at its normal position (1678 cm^{-1}) ascertained the coordination of L_3 with Ni(II) ion through NH and deprotonated *o*-hydroxyl groups. Despite the formation seven-membered ring around the nickel ion may be discouraged and rare, remaining of $\nu(\text{CH} = \text{N})$ at nearly the same location ruled out its anticipation in construction of complex geometry. The observation of $\text{C}=\text{O}$ as one band in **3** instead of two bands in L_3 with slight change in its location may be due to the presence of the two oxygen atom related to ($\text{O} = \text{C}-\text{C}=\text{O}$) part, Figure 2, in trans or cis symmetry. Perhaps the absorption of this group ($\text{C}=\text{O}$) at somewhat higher frequency (1678 cm^{-1}) supports the first suggestion i.e., cis structure. Unnoticeable $\nu(\text{OH})$ of *o*-hydroxyl group in complexes **2** and **3** species supports the deprotonation of this group during the coordination of L_2 and L_3 . In case of complex **4**, half of the L_4 molecule was altered to enol form and coordination takes place by one side (one OMe , one $\text{C}=\text{N}$ and one deprotonated enolized $\text{C}-\text{OH}$ group). This proposition depends on the weakness in intensity of [$\nu(\text{NH})$, $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{OMe})$] and splitting of $\text{C}=\text{N}$. The splitting in the vibrational stretching $\text{C}=\text{N}$ 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 $\text{C}=\text{N}$ band (at 1580 cm^{-1}) may be due to the absorption interference of $\text{C}=\text{N}$ group generated by enolization.

Undoubtedly, the appearance of new $\text{M}-\text{O}$ 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 3. The MIC of bis(2-hydroxy-naphthaldehyde)oxaloyldihydrazone (L_2)

Tested micro-organism	L_2/MICS ($\mu\text{g}/\text{ml}$)	Standard
FUNGI		Amphotericin B
<i>Aspergillus fumigatus</i>	15.6	23.7
<i>Syncephalastrum racemosum</i>	31.25	19.7
GRAM-POSITIVE BACTERIA		Ampicillin
<i>Streptococcus pneumoniae</i>	125	23.8
<i>Bacillus subtilis</i>	15.6	32.4
GRAM-NEGATIVE BACTERIA		Gentamicin
<i>Escherichia coli</i>	500	19.9

Figure 2. Suggested structures of the Ni^{II}-oxaloyldihydrazone complexes.



(Kumar et al., 2011). 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 ν_{as} and ν_{s} carboxylic modes, respectively. The larger difference between the ν_{as} and ν_{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 $\nu(\text{C}=\text{C})_{\text{ph}}$ upon chelation arise from metal–ligand interaction.

3.1.2. ^1H NMR Spectra

The assignment of the main signals in ^1H 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. ^1H 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 δ (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_2O , the OH and NH signals were obscured. Further, the existence of the δOH (phenolic/naphthoic) at its normal frequency excluded any intramolecular hydrogen bonding operating between ortho-OH and $\text{CH}=\text{N}$ group ($\text{CH}=\text{N}\cdots\text{H}-\text{O}$). The azomethine signals, $\delta(\text{CH}=\text{N})$, observed only in L_1 , L_2 and L_4 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 δOH , δNH and $\delta\text{CH}=\text{N}$, 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. Actually, the features of the ^1H -NMR spectra of the dihydrazones are in consistent with the syn-cis- or staggered configuration. According to IR interpretation mentioned above, the staggered configuration is well-defined/dominated for all ligands (L_1 – L_4). ^1H 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 oxaloylhydrazones 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 λ_{\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 planar 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 \rightarrow 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).

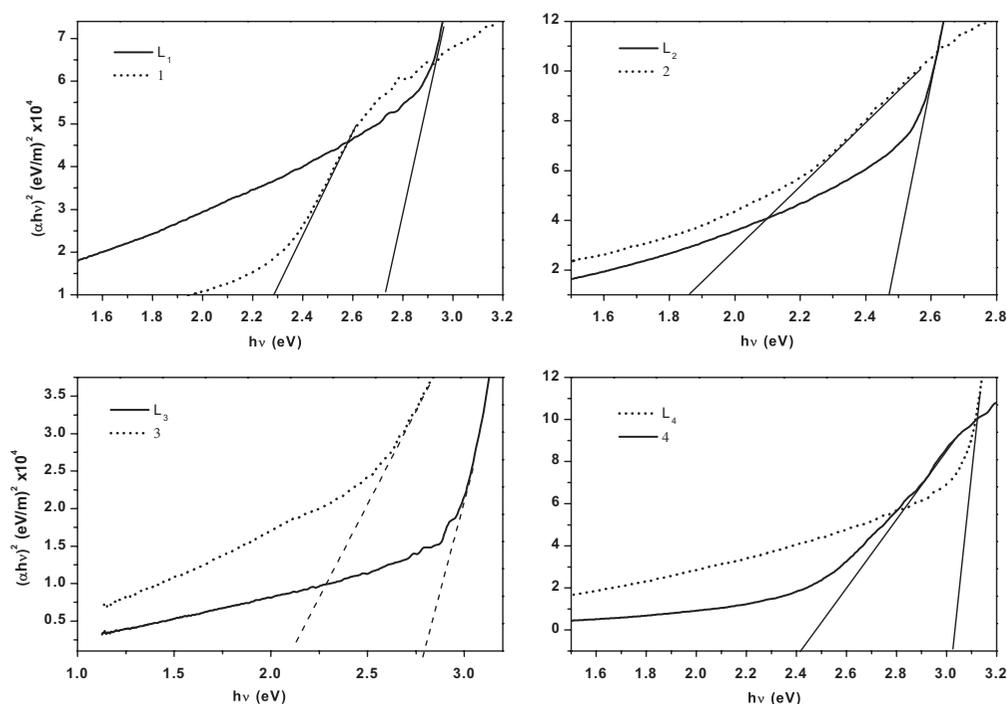
3.1.4. Magnetic behavior

From the magnetic studies, the values of μ_{eff} in case of Ni^{III}-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^{III}-complexes, thermogravimetric analysis (TG) for all complexes was carried out. The thermogram (TGA) data of complex (**1**) exhibited three stages of

Figure 3. Plots of $(\alpha h\nu)^2$ vs. $h\nu$ of oxaloyldihydrazones and their Ni^{II}-complexes.



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

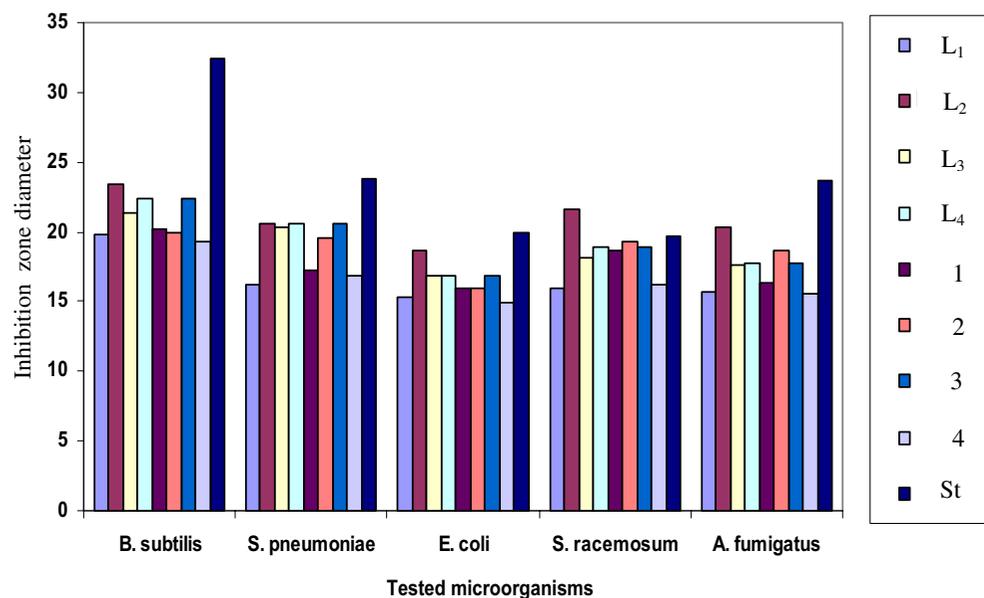
To clarify the conductivity of the isolated complexes, the optical band gap energy (E_g) of oxaloyldihydrazones and their Ni(II) complexes have been calculated from the following equations:

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

$$\alpha = 1/d \ln(1/T)$$

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):

Figure 4. Antimicrobial activity for oxaloyldihydrazone ligands and their nickel(II) complexes.



$$\alpha h\nu = A(h\nu - E_g)^m$$

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

The values of α calculated from the first equation were used to plot $(\alpha h\nu)^2$ vs. $h\nu$ (Figure 3) from which an indirect band gap was found by extrapolating the linear portion of the curve to $(\alpha h\nu)^2 = 0$. The values of indirect optical band gap E_g were determined and given in Table 1. The E_g values of oxaloyldihydrazones (L_1 - L_4) 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 oxaloyldihydrazone ligand L_2 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 dihydrazone ligand (L_1) 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 L_2 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 C=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 π -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 (L_2): 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 L_2 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 (L_2) 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 L_2 towards several micro-organisms. (i) The high stability of L_2 and this can be indicated from its high melting points ($mp < 300^\circ C$), (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 L_2 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 (L_1 - L_4) obtained by usual condensation of oxaloyldihydrazide and some selected aldehydes, namely salicylaldehyde (L_1), 2-hydroxynaphthaldehyde (L_2), 2-hydroxyacetophenone (L_3) and 2-methoxybenzaldehyde (L_4) 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 L_1 , L_3 and L_4 but binuclear complex is formed with L_2 . The nickel in all complexes has tetrahedral geometry. The indirect band gap energy (E_g) 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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References

- Abd El-Wahab, H., Abd El-Fattah, M., Ahmed, A. H., Elhenawy, A. A., & Alian, N. A. (2015). Synthesis and characterization of some arylhydrazone ligand and its metal complexes and their potential application as flame retardant and antimicrobial additives in polyurethane for surface coating. *Journal of Organometallic Chemistry*, 791, 99–106.
- Abdel-Aal, M. T., El-Sayed, W. A., & El-Ashry, E. H. (2006). Synthesis and antiviral evaluation of some sugar arylglycinoylhydrazones and their oxadiazoline derivatives. *Archiv der Pharmazie*, 339, 656–663. [http://dx.doi.org/10.1002/\(ISSN\)1521-4184](http://dx.doi.org/10.1002/(ISSN)1521-4184)
- Ahmed, A. H. (2014). Zeolite-encapsulated transition metal chelates: Synthesis and characterization. *Review Inorganic Chemistry*, 34, 153–175.
- Ahmed, A. H., & Ewais, E. (2012). Physicochemical and antimicrobial investigation on some selected arylhydrazone complexes. *Journal of Chemical*

- Pharmaceutical Research*, 4, 3349–3360.
- Ahmed, A. H., & Mostafa, A. G. (2009). Synthesis and identification of zeolite-encapsulated iron (II), iron (III)-hydrazone complexes. *Materials Science and Engineering: C*, 29, 877–883.
<http://dx.doi.org/10.1016/j.msec.2008.07.023>
- Ahmed, A. H., & Thabet, M. S. (2011). Metallo-hydrazone complexes immobilized in zeolite Y: Synthesis, identification and acid violet-1 degradation. *Journal of Molecular Structure*, 1006, 527–535.
<http://dx.doi.org/10.1016/j.molstruc.2011.09.061>
- Ahmed, A. H., & Thabet, M. S. (2015). Physicochemical studies and heterogeneous hydroxylation of benzene on Fe^{II}, Fe^{III}-semicarbazone/zeolite-Y clathrates. *Synthesis and Reactions in Inorganic and Metal-Organic Chemistry*, 45, 1632–1641
<http://dx.doi.org/10.1080/15533174.2015.1031038>
- Ajani, O. (2008). Synthesis, characterization, antimicrobial activity and toxicology study of some metal complexes of mixed antibiotics. *African Journal Pure Applied Chemistry*, 2, 69–74.
- Al-Sha'alan, N. H. (2007). Antimicrobial activity and spectral, magnetic and thermal studies of some transition metal complexes of a Schiff base hydrazone containing a quinoline moiety. *Molecules*, 12, 1080–1091.
- Ali, A. M., Ahmed, A. H., Mohamed, T. A., & Mohamed, B. H. (2007). Chelates and corrosion inhibition of newly synthesized Schiff bases derived from o-tolidine. *Transition Metal Chemistry*, 32, 461–467.
<http://dx.doi.org/10.1007/s11243-007-0184-8>
- Barbazan, P., Carballo, R., Covelo, B., Lodeiro, C., Lima, J. C., & Vazquez-Lopez, E. M. (2008). Synthesis, characterization, and photophysical properties of 2-hydroxybenzaldehyde [(1E)-1-pyridin-2-ylethylidene]hydrazone and its rhenium(I) complexes. *European Journal of Inorganic Chemistry*, 2008, 2713–2720.
[http://dx.doi.org/10.1002/\(ISSN\)1099-0682](http://dx.doi.org/10.1002/(ISSN)1099-0682)
- Burger, K., Ruff, I., & Ruff, F. (1965). Some theoretical and practical problems in the use of organic reagents in chemical analysis—IV. *Journal of Inorganic and Nuclear Chemistry*, 27, 179–190.
[http://dx.doi.org/10.1016/0022-1902\(65\)80208-1](http://dx.doi.org/10.1016/0022-1902(65)80208-1)
- Cappucino, J. G., & Sherman, N. (1999). *Microbiology a laboratory manual*. Addison: Wesley California.
- Chanu, O. B., Kumar, A., Ahmed, A., & Lal, R. A. (2012). Synthesis and characterisation of heterometallic trinuclear copper(II) and zinc(II) complexes derived from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone. *Journal of Molecular Structure*, 1007, 257–274.
<http://dx.doi.org/10.1016/j.molstruc.2011.11.001>
- Efthimiadou, E. K., Psomas, G., Sanakis, Y., Katsaros, N., & Karaliota, A. (2007). Metal complexes with the quinolone antibacterial agent N-propyl-norfloxacin: Synthesis, structure and bioactivity. *Journal of Inorganic Biochemistry*, 101, 525–535.
[http://dx.doi.org/10.1016/S0223-5234\(02\)01378-8](http://dx.doi.org/10.1016/S0223-5234(02)01378-8)
- Fu, M. L., Guo, G. C., Liu, X., Cai, L. Z., & Huang, J. S. (2005). Syntheses, structures and properties of three selenoarsenates templated by transition metal complexes. *Inorganic Chemistry Communications*, 8, 18–21.
<http://dx.doi.org/10.1016/j.inoche.2004.10.021>
- Ghasemian, M., Kakanejadifard, A., Azarbani, F., Zabardasti, A., Shiral, S., Saki, Z., & Kakanejadifard, S. (2015). The triazine-based azo-azomethine dyes; synthesis, characterization, spectroscopy, solvatochromism and biological properties of 2,2'-((6-methoxy-1,3,5-triazine-2,4-diyl)bis(sulfaneylidene))bis(2,1-phenylene) bis(azanylylidene)bis(methanylylidene)bis(4-(phenyldiazenyl)phenol). *Spectrochimica Acta*, 38, 643–647.
<http://dx.doi.org/10.1016/j.saa.2014.11.048>
- Hassan, A. M., Ahmed, A. H., Gumaa, H. A., Mohamed, B. H., Eraky, A. M., & Chem, J. (2015). Manganese(II) complexes of N,O-chelating dihydrazone: Synthesis, characterization, optical properties and corrosion inhibition on aluminum in HCl solution. *Journal of Chemical Pharmaceutical Research*, 7, 91–104.
- Karipcin, F., Dede, B., Caglar, Y., Hur, D., Ilcan, S., Caglar, M., & Sahin, Y. (2007). A new dioxime ligand and its trinuclear copper(II) complex: Synthesis, characterization and optical properties. *Optics Communications*, 272, 131–137.
<http://dx.doi.org/10.1016/j.optcom.2006.10.079>
- Kumar, A., Lal, R. A., Chanu, O. B., Borthakur, R., Koch, A., Lemtur, A., ... Choudhury, S. (2011). Synthesis and characterization of a binuclear copper(II) complex [Cu(H₂slox)], from polyfunctional disalicylaldehyde oxaloyldihydrazone and its heterobinuclear copper(II) and molybdenum(VI) complexes. *Journal of Coordination Chemistry*, 64, 1729–1742.
<http://dx.doi.org/10.1080/00958972.2011.580845>
- Lal, R. A., Adhikari, S., Kumar, A., Chakraborty, J., & Bhaumik, S. (2002). Synthesis and characterization of manganese(IV) complexes derived from the direct reaction of manganese(II) acetate tetrahydrate with oxaloyldihydrazone and 2-hydroxy-1-naphthaldehyde. *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, 32, 81–96.
<http://dx.doi.org/10.1081/SIM-120013148>
- Lal, R. A., Basumatary, D., Adhikari, S., & Kumar, A. (2008). Synthesis and properties of mononuclear and binuclear molybdenum complexes derived from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 69, 706–714.
<http://dx.doi.org/10.1016/j.saa.2007.05.023>
- Lal, R. A., Adhikari, S., & Kumar, A. (1993). Spectroscopic studies of isomerization of coordinated dihydrazone in tetranuclear dioxouranium(VI) complexes derived from bis(o-hydroxynaphthaldehyde) oxaloyldihydrazone. *Indian Journal of Chemical*, 36A, 1063–1067.
- Lever, A. B. P. (1984). *Inorganic electronic spectroscopy*. Amsterdam: Elsevier.
- Loncle, C., Brunel, J. M., Vidal, N., Dherbomez, M., & Letourneux, Y. (2004). Synthesis and antifungal activity of cholesterol-hydrazone derivatives. *European Journal of Medicinal Chemistry*, 39, 1067–1071.
<http://dx.doi.org/10.1016/j.ejmech.2004.07.005>
- McCollum, D. G., Hall, L., White, C., Ostrandor, R., Rheingold, A. L., Whelan, J., & Bosnich, B. (1994). Bimetallic reactivity. Preparation and characterization of symmetrical bimetallic complexes of a binucleating macrocyclic ligand, cytim, containing 6- and 4-coordinate sites. *Inorganic Chemistry*, 33, 924–933.
<http://dx.doi.org/10.1021/ic00083a016>
- Mishra, L., & Singh, V. K. (1997). Co(II), Ni(II) and Cu(II) and Zn(II) complexes with Schiff bases derived from 2-aminobenzimidazoles and pyrazolocarboxaldehyde. *Indian Journal of Chemical Technology*, 32A, 446.
- Mott, N. F., & Davis, E. A. (1979). *Electronic process in non-crystalline materials*. Oxford: Calendron Press.
- Nakamoto, K. (1970). *Inorganic spectra of inorganic and coordination compounds* (2nd ed.). New York, NY: Wiley.
- Rashad, M. M., Turkey, A. O., & Kandil, A. T. (2013). Optical and electrical properties of Ba_{1-x}Sr(x)TiO₃ nanopowders at different Sr₂₊ ion content. *Journal of Materials Science - Materials in Electronics*, 24, 3284–3291.
- Rollas, S., & Küçükgül, S. G. (2007). Biological activities of hydrazone derivatives. *Molecules*, 12, 1910–1039.
<http://dx.doi.org/10.3390/12081910>
- Salama, T. M., Ahmed, A. H., & El-Bahy, Z. M. (2006). Y-type zeolite-encapsulated copper(II) salicylidene-

- p-aminobenzoic Schiff base complex: Synthesis, characterization and carbon monoxide adsorption. *Microporous and Mesoporous Materials*, 89, 251–259. <http://dx.doi.org/10.1016/j.micromeso.2005.10.036>
- Salapathy, S., & Sahoo, B. (1970). Salicylaldazine metal chelates and their I.R. spectra. *Journal of Inorganic and Nuclear Chemistry*, 32, 2223–2227. [http://dx.doi.org/10.1016/0022-1902\(70\)80500-0](http://dx.doi.org/10.1016/0022-1902(70)80500-0)
- Salavati-Niasari, M., & Sobhani, A. (2008). Ship-in-a-bottle synthesis, characterization and catalytic oxidation of cyclohexane by host (nanopores of zeolite-Y)/ guest (Mn(II), Co(II), Ni(II) and Cu(II) complexes of bis(salicylaldehyde)oxaloyldihydrazone) nanocomposite materials. *Journal of Molecular Catalysis A: Chemical*, 285, 58–67. <http://dx.doi.org/10.1016/j.molcata.2008.01.030>
- Sengupta, S. K., Pandey, O. P., Srivastava, B. K., & Sharma, V. (1998). Synthesis, structural and biochemical aspects of titanocene and zirconocene chelates of acetylferrocenyl thiosemicarbazones. *Transition Metal Chemistry*, 23, 349–353. <http://dx.doi.org/10.1023/A:1006986131435>
- Sherif, E. M., & Ahmed, A. H. (2010). Synthesizing new hydrazone derivatives and studying their effects on the inhibition of copper corrosion in sodium chloride solution. *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, 40, 365–372.
- Smânia, A., Monache, F. D., Smânia, E. F. A., & Cuneo, R. S. (1999). Antibacterial activity of steroidal compounds isolated from *Ganoderma applanatum* (Pers.) Pat. (Aphyllphoromycetideae) fruit body. *International Journal of Medicinal Mushrooms*, 1, 325–330. <http://dx.doi.org/10.1615/IntJMedMushr.v1.i4>
- Sutton, D. (1968). *Electronic spectra of transition metal complexes*. London: McGraw Hill.
- Tauc, J. (1968). Optical properties and electronic structure of amorphous Ge and Si. *Materials Research Bulletin*, 3, 37–46. [http://dx.doi.org/10.1016/0025-5408\(68\)90023-8](http://dx.doi.org/10.1016/0025-5408(68)90023-8)
- Vicini, P., Zani, F., Cozzini, P., & Doytchinova, I. (2002). Hydrazones of 1,2-benzisothiazole hydrazides: Synthesis, antimicrobial activity and QSAR investigations. *European Journal of Medicinal Chemistry*, 37, 553–564. [http://dx.doi.org/10.1016/S0223-5234\(02\)01378-8](http://dx.doi.org/10.1016/S0223-5234(02)01378-8)
- Walcovrt, A., Loyevsky, M., Lovejoy, D. B., Gordeuk, V. R., & Richardson, D. R. (2004). Novel aroylhydrazone and thiosemicarbazone iron chelators with anti-malarial activity against chloroquine-resistant and -sensitive parasites. *International Journal of Biomedical Cell Biology*, 36, 401–407. [http://dx.doi.org/10.1016/S1357-2725\(03\)00248-6](http://dx.doi.org/10.1016/S1357-2725(03)00248-6)
- Yuan, J., Lovejoy, D. B., & Richardson, D. R. (2004). Novel di-2-pyridyl-derived iron chelators with marked and selective antitumor activity: In vitro and in vivo assessment. *Blood*, 104, 1450–1458. <http://dx.doi.org/10.1182/blood-2004-03-0868>



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