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Graphical abstract

New Nano-complexes of Zn(II), Cu(II), Ni(II) and Co(II) ions;

Spectroscopy, Thermal, Structural Analysis, DFT Calculations and

Antimicrobial Activity Application

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Novel thiophene-2-carbaldehyde nano-complexes of Zn(II) (1), Cu(II) (2), Ni(II)

(3), and Co(II) (4) were successfully prepared in nano-scale domain. The antimicrobial results and DFT calculations confirm that the prepared Zn(II) nano-complex (1) are a promising nano-material for antibacterial application.



New Nano-complexes of Zn(II), Cu(II), Ni(II), and Co(II) ions; Spectroscopy,

Thermal, Structural Analysis, DFT Calculations, and Antimicrobial Activity

Application

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Abstract

This work presents synthesis, characterization, and application of several metal (II) complexes with (E)-2-hydroxy-N'-((thiophen-2-yl)methylene)benzohydrazide (H₂L). Prepared complexes were identified by elemental, thermal, FT-IR, UV-Vis, ¹H-NMR, and XRD analysis, as well as molar conductivity and magnetic moment measurements. Changes in FT-IR and ¹H-NMR spectra of hydrazone ligand upon coordination indicated that the ligand behaves the same way as a monoanonic ligand with ONS donor sites. Kinetic parameters were determined for each thermal degradation stage of the ligand and its complexes using 'Coats–Redfern' method. All results confirm that all prepared compounds have 1:2 metal-to-ligand stoichiometry except Zn(II) complex,which has 1:1 metal-to-ligand stoichiometry. The antimicrobial activity for

complexes was investigated. The antimicrobial activity results revealed that Zn(II) complex (1) has a good potency against gram positive bacteria (*E. coli*) and gram negative bacteria (*P. vulgaris*) in comparision with doxymycin standard. AT B3LYP/6-311G (d,p) level, Density Functional Theory (DFT) calculations were carried out to investigate the optimized structure of both, the ligand and the complexes. Total energy, energy of HOMO, and LUMO as well as Mullikan atomic charges were calculated. Dipole moment, orientation, and structure activity relationship were performed and discussed.DFT calculations, moreover, confirmed practical antimicrobial results.

Keywards: inorganic compounds; Nano-complex; antimicrobial, DFT, Thermal analysis

1. Introduction

Sulphur containing heterocycles and their complexes are, nowadays, of the most promising classes of substances utilized in drug development. Benzothiophene derivatives, in combination with other ring systems and their metal complexes, have been used in pharmaceutical applications such as antiallergic, analgesic, anti-inflammatory, and ocular hypotensive activities [1-4]. Raloxifene, a drug based on benzo[b]-thiophene, has been approved by the U.S Food and Drug Administration for the prevention and treatment of osteoporosis associated with woman postmenopausal [5].

The preparation of metal complexes, based on benzothiophene derivatives in Nanodomain, creates new materials with unique physical, chemical, and biological properties. Most reports on transition metal complexes with benzothiophene derivatives-based ligand and their antimicrobial applications are in bulk scale [6]. Reports on Nano-scale transition metal complexes with benzothiophene derivatives-based ligand are still unexplored.

In this paper, we are, therefore, concerned with the synthesis and characterization of the new ligand, (E)-2-hydroxy-N/-((thiophen-2-yl)methylene)benzohydrazide, H_2L and its metal

Nano-complexes for antimicrobial application. The DFT calculations for model systems perfectly correlate with experimentally-determined metrical parameters. Besides, thermal stability of the reported metal complexes was studied.

2. Experimental

2.1. Materials

The starting materials used in these studies are analytical grade. They include methyl salicylate (Chemical Laboratory) and hydrazine hydrate (PanreacQuimica). Metal salts, Lithium hydroxide, and 2- thiophenecarbaldehyde from BDH, Analar or Merck chemicals were also used. All solvents used are of spectroscopic grade. Gram-negative bacteria: Klebsiella pneumoniae, Proteus vulgaris, and Escherichia coli (ATCC 28737); a Gram-positive bacterium: Staphylococcus aureus (AT 6538), and a pathogenic fungus: Candida albicans (ATCC10231) were used.

2.2. Characterization

Electronic spectra were carried out as DMF (10^{-3} M) solutions and recorded on a 'JASCO model V-550 UV-Vis' spectrophotometer. FT-IR spectra (4000-400 cm⁻¹) for metal complexes were recorded using 'FT-IR Nicolet IS10' spectrometer. Magnetic susceptibilities of complexes were measured by the 'Gouy' method at room temperature using shelwood scientific, Cambridge Science Park, magnetic susceptibility balance (England). Effective magnetic moments were calculated using the relation μ eff = $2.828(\chi_m.T)^{1/2}$ B.M., where χ_m is the molar susceptibility corrected using Pascal's constants for the diamagnetism of all atoms in compounds. ¹H-NMR spectra (DMSO-d₆) were recorded at room temperature on a 'Varian FT-290.90 MHZ' spectrometer. The XRD patterns were recorded using 'PHILIPS' diffractometer with CuKa1 radiation (k = 1.54056 Å). An accelerating voltage of 40 kV and an emission current of 30 mA were used. 'TGA-DTG' measurements were carried out on a 'Shimadzu' thermo gravimetric analyzer using 'TA-50 WSI' program. Microanalyses of carbon, hydrogen, nitrogen and sulfur were carried out at the Ministry of Defense, Chemical War Department. Melting or decomposition points were determined on a melting point apparatus (stuart), England. Molar

conductivities of 10⁻³ M solutions of solid complexes in DMF were measured using Corning conductivity meter NY 14831 model 441.

2.3. Synthesis of ligand, (E)-2-hydroxy-N'-((thiophen-2-yl)methylene)benzohydrazide, H_2L

The ligand H_2L was prepared on two steps (scheme 1).**First step**: Synthesis of salicylic acid hydrazide according to literature method [7,8]. **Second step**: preparation of hydrazone ligand through condensation of salicylic acid hydrazide stiochiometrically in molar ratio (1:1) with 2-thiophene carbaldehyde in absolute ethanol. The reaction mixture was refluxed for 2 hours. Drops of glacial acetic acid were added at the onset of reflux. After cooling, the obtained pale yellow crystals were filtered off, washed with ethanol, and recrystallized with 1:1 (v:v) DMF/H₂O to give pure crystals with m.p. of 260 °C.

2.4. Synthesis of transition metal complexes (1-4)

A 0.125 g (3 mmol) mixture of LiOH.H₂O and 0.738 g (3 mmol) of H₂L in 30 mL methanol were added to the metal salt (3 mmol); namely $Zn(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$, $Ni(NO_3)_2.6H_2O$, and $Co(NO_3)_2.6H_2O$ dissolved in the least amount of bi-distilled water. The reaction mixture was stirred for 12 hours to ensure complete formation of metal complexes. LiOH.H₂O was added as a deprotonating agent. The precipitate was filtered and washed several times with 50 % (v/v) methanol-water to remove any traces of unreacted starting materials. Finally, the precipitate was dried in vacuum desiccators over anhydrous CaCl₂.

Complexes obtained by this method are $[Zn(HL)(OH_2)_2(NO_3)] \cdot H_2O$ (1), $[Cu(HL)_2]$ (2), $[Ni(HL)_2]$ (3), and $[Co(HL)_2] \cdot H_2O$ (4). The chemical structure of transition metal Nano-complexes was collected in Scheme 2.

2.5. Antimicrobial study

Biological activities of synthesized hydrazone ligand, H₂L, and their metal complexes were studied for antibacterial and antifungal properties using agar diffusion method [9] in DMF solvent against different types of bacteria; Gram-positive- S. *aureus*, and *E. coli* (Escherichia coil) and Gram-negative- *K. pneumonia* and *P. vulgaris*, and *C. albicans* for fungus. S.aureus, C. albicans, E. coil, K. pneumonia, and P. vulgaris were originated from ATCC6538, ATCC10231, ATCC 28737, ATCC 547732 and ATCC 253674, respectively.

2.6. Computational method

Calculations were been performed using 'Khon-Sham's DFT' method subjected to the gradient-corrected hybrid density functional B3LYP [10]. This function is a combination of Becke's three parameters; non-local exchange potential with the non-local correlation functional of *Lee et al.* For each structure, a full geometry optimization was performed using this function [11] and the 6-311G (d,p) bases set [12] as implemented by Gaussian 09 package [13]. All geometries were visualized using either 'GaussView 5.0.9' [14] or 'chemcraft 1.6' 15] software packages. No symmetry constrains were applied during geometry optimization.

3. Results and discussion

3.1 Characterization of H₂L and its metal Nano-complexes

All complexes are stable under normal conditions. Upon heating, decomposition occurs. Complexes are soluble in both, DMF and DMSO, but insoluble in methanol and ethanol. Physical and analytical data of prepared compounds are listed in Table 1. Elemental analysis confirms the proposed chemical structure of H_2L and its metal Nano-complexes. All complexes of Cu(II), Ni(II), and Co(II) ions (**2**, **3** and **4**) have 1:2 metal-to-ligand stoichiometry, as shown from Scheme 2, whilst Zn(II) complex (**1**) has 1:1 metal-to-ligand stoichiometry. Molar conductance values of 10^{-3} M solution for all prepared Nano-complexes were measured at room temperature in DMF when in the range characteristic of non-electrolytic nature [16-19].

Supplement 1 shows the FT-IR spectra of H2L and its Cu complex. FT-IR data of H₂L and its metal Nano-complexes are listed in Table 2. The ligand (H₂L) can exhibit keto-enol tautomerism $-N(H)-C(=O)\leftrightarrow N=C(-OH)$ -, since it contains an azomethine–NH-C=O functional group. The presence of v(N-H) band at 3250 cm⁻¹ and v(C=O) band at 1654 cm⁻¹ [20-24] in FT-IR data of the ligand indicates that, in solid state, it remains as thione tautomer. Furthermore, the strong band due to v(C-S-C), stretching vibration of thiophene, appeared at 855 cm⁻¹ in the free ligand [24-28]. The disappearance of characteristic spectral bands of N-H and C=O of hydrazone ligand and the appearance of new bands of (C=N)_{enolic} in the region of 1510-1524 cm⁻¹[21,23,27] in all complexes suggest the coordination via enol form instead of keto form by deprotonation of

N-H proton during the tautomerisation process. Stretching vibrations of azomethine group C=N shifted to lower frequencies (10-13 cm⁻¹) due to coordination of nitrogen atom of azomethine group with the central metal atom[29]. The presence of a new band in the region of 417–479 cm⁻¹ due to v(M–N) is another indication of the involvement of nitrogen of azomethine group in the coordination [18]. FT-IR spectra of all Nano-complexes showed new band in the range of 515-580 cm⁻¹due to v(M–O) [18].v(C-S) stretching vibration of thiophene underwent a downward shift to 775, 783, 793, and 788 cm⁻¹ in Zn(II), Cu(II), Ni(II), and Co(II) Nano-complexes, respectively, indicating the participation of Sulphur of this entity in bonding with metals. FT-IR results of complex (1) showed new bands at 1290 and 1045 cm⁻¹ due to asymmetric and symmetric stretches v₁, and v₂, respectively, of coordinated nitrate group [18,30]. It is concluded that the ligand behaves as a monoanionic tridentate ligand coordinated to metal ions via azomethine N, carbonyl O, and thiophene S.

¹**H-NMR** data of H₂L and its diamagnetic Nano-complex (1) in DMSO-d₆, with and without D₂O, are listed in Table 3. The free ligand (H₂L) spectrum showed three signals at δ 12.44, δ 11.77, and δ 8.66 ppm due to –OH proton, -NH proton, and azomethine proton (-CH=N-), respectively [23,31]. The presence of –NH proton in ¹H-NMR spectrum of H₂L proved the thione nature (Supplement 2). Upon complexation, the signal for NH proton disappeared in diamagnetic complex (1) indicating that the ligand behaves as monoanionic. Signals due to azomethine proton shifted upon complexation (Supplement 2). This is due to the donation of the lone pair of electrons by nitrogen atom to the central metal ion, resulting in the formation of coordination linkage (M←N). The slightly down field shift of this signal is due to the existence of strong hydrogen bond in the free ligand. Moreover, the presence of the signal of –OH proton in the spectra of diamagnetic complex enhances the hypothesis which suggests that –OH protons are not participating in the coordination groups. ¹H-NMR spectra of H₂L and their complex (1) showed aromatic protons as a number of complex multiplets in the region of δ 6.84-7.93 ppm [22,23,25,31]. Signals due to protons of OH and NH groups completely disappeared on adding D₂O while other signals persisted at the same positions.

The electronic spectrum of H₂L is characterized by its absorption bands at 233 and 303 nm (Fig. 1a). The highest energy bands are assigned to π - π * transitions within C=O and C=N groups, whilst the lowest energy bands can be assigned to n- π *transitions within C=O and C=N

groups [25,32]. The electronic absorption spectrum of complex (2) shows a maximum broad band at 597 nm (Fig. 1b). This band is assigned to ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ transition in the octahedral Cu(II) Nano-complex [33]. The magnetic moment of Cu(II) Nano-complex is in agreement with the value of the octahedral geometry (1.8 B.M) [18,34]. Absorption spectrum of Ni(II) Nanocomplex (3) is characterized by broad structural bands at 522 and 702 nm (Fig. 1b). These bands are attributed to ${}^{3}A_{2g}$ (F) $\rightarrow {}^{3}T_{1g}(p)$, ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ transitions, respectively, in favor of the octahedral geometry [30,35]. Magnetic moment value of Ni(II) Nano-complex (2.9 B.M.) confirms the presence of two unpaired electrons in the octahedral geometry [36]. Co(II) Nanocomplex (4) shows a broad absorption spectrum with humps at 661 and 819 nm [30] (Fig. 1b). Magnetic moment value of Co(II) Nano-complex equals 4.3 B.M., which is in agreement with the values of Co(II) octahedral geometry [37]. The spectra of Zn(II) Nano-complex is dominated only by ligand bands.

TGA results of synthesized Nano-complexes are shown in Table 4. Fig. 2(a-b) represents TG-DTG curves for [Ni(HL₂] (**3**) and [Co(HL)₂]·H₂O (**4**) Nano-complexes as representative examples. Results show a good agreement with the theoretical formula as suggested by the analytical data (Table 1). Nano-complexes (**1**) and (**4**) become anhydrous at 70 and 76°C, respectively by losing lattice H₂O. Nano-complex (**1**) loses two coordinated water molecules in addition to one HNO₃ molecule in one step at 250 °C. The removal of C₄H₄S molecules in a separate step was observed for Nano-complexes (**3**) and (**4**) in the range of 350-379 °C. For Nano-complex (**2**), the removal of C₄H₄S molecules is accompanied by the elimination of one C₆H₆O molecule. The removal of HNO₃ molecule from Nano-complex (**1**) is accompanied by elimination of one HCN molecule.

In order to access the influence of structural properties of the ligand and the type of metal on thermal behavior of complexes, the order n, and the heat of activation E of various decomposition stages were determined through TG and DTG thermograms using Coats–Redfern equations in the following forms:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \frac{M}{T} + B \quad \text{for} \quad n \neq 1$$
$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \frac{M}{T} + B \quad \text{for} \quad n = 1$$

where M = -E/R and $B = \ln AR/\Phi E$; E, R, A, and Φ are the heat of activation, the universal gas constant, pre-exponential factor, and heating rate, respectively. The correlation coefficient, r, was computed using the least square method for different values of n by plotting the left-hand side of Eqs. versus 1000/T. The *n* value which gives the best fit $(r \approx 1)$ was chosen as the order parameter for the decomposition stage of interest. Fromboth, intercept and linear slope of such stage, A and E values were determined. Other kinetic parameters, ΔH , ΔS , and ΔG were computed using the relationships; $\Delta H = E - RT$, $\Delta S = R[\ln(Ah/kT) - 1]$, and $\Delta G = \Delta H - T\Delta S$, where k is Boltzmann's constant and h is Planck's constant. Kinetic parameters are listed in Table 5.The following remarks can be pointed out: (1) all Nano-complexes decomposition stages show the best fit for (n = 1), indicating a first order decomposition in all cases. Other *n* values (e.g. 0.00, 0.33 and 0.66) did not lead to better correlations. (2)The positive sign of ΔG for the investigated complexes reveals that the free energy of the final residue is higher than that of the initial compound, and all the decomposition stages are non-spontaneous processes [38].(3) Negative values of activation entropies ΔS indicate either a more orderly activated complex than reactants or slow reactions [39]. (4) Positive values of ΔH mean that decomposition processes are endothermic. In general, there are no obvious trends in values of ΔH and ΔS for the studied Nano-complexes. This is attributed to the fact that thermal decomposition of complexes is controlled, not only by structure of the ligand, but also by configuration of the coordination sphere [39].

Figs. 3 and 4 show XRD patterns of H_2L and its Nano-complexes. Patterns and results of XRD suggest that crystals of complexes are not perfect but lying between amorphous and crystalline character in comparison with free ligand. Due to this, complexes were not found suitable for single crystal XRD. From studying patterns, it can be noted that the diffraction angle and intensity of prepared complexes are different from those of the ligand. This result suggests that metal ions were bonded with the ligand to form new complexes. Broadening of peaks indicates that the particles were of Nano-meter scale [40].

The crystallite size of the complexes can be determined from the broadening of corresponding X-ray spectral peaks by Scherrer formula $L = K\lambda/\beta \cos \theta$ [41]. Where L is the crystallite size, λ is the wavelength of the X-ray radiation (Cu K α_1 = 1.54056Ű), K is usually taken as 0.9, and β is the line width at half-maximum height. Values obtained for H₂L, Zn(II), Cu(II), and Ni(II) complexes are 36,11, 22, and 22 nm, respectively. Crystal size of Co(II) complex couldn't be determined due to the highly amorphous pattern. Small crystal size was observed in case of Zn(II) complex (1). Obtained data confirm that sizes of prepared complexes are in the Nano-domain.

3.2 Antimicrobial activity

Antimicrobial activities of synthesized H₂L and its metal Nano-complexes were studied for antibacterial and antifungal properties by agar diffusion method [9] in DMF solvent against different types of bacteria; Gram-positive- S. aureus and E. coli and Gram-negative- K. pnemonia and P. vulgaris. Besides, C. albicans for fungus. Results were recorded by measuring the growth inhibition (zone of inhibition) surrounding the disc of material. Results of MIC are summarized in Table 6. Some antibiotics were evaluated for their antibacterial activities and their results were compared with free ligands and their binary metal Nano-complexes. Ligand (H₂L) is found ineffective to all bactria and fungus. Nano-complexes of H₂L show weak activity except for both, Zn(II) (1) and Co(II) complexes (4). Co(II) complex (4) is quite effective against E. coli, P. vulgaris, and C. albicans. Antimicrobial activity results revealed that Zn(II) complex (1) has a good potency against all Gram-positive bacteria specially E. coli and all Gram-negative bacteria specially *P. vulgaris* in comparisonwith doxymycin standard. A comparative study of H_2L and its Nano-complexes indicates that most complexes exhibited higher antimicrobial activity than the free ligand. Higher inhibition zone of metal Nano-complexes than those of ligands can be explained on basis of overton's concept and chelation theory. According to overton's concept of cell permeability, the lipid membrance surrounding the cell favours the passage of only lipid soluble materials due to which liposolubility is an important factor which controls the antifungal activity. On chelation, when metal ion chelates with ligand, its polarity will be reduced to a greater extent due to the overlap of the ligand orbital and the partail sharing of positive charge of the metal ion with donor groups. Futhermore, it increases the delocalization of π -electrons over the whole chelate ring, which results in an increase in the lipophilicity of metal complexes. This increased lipophilicity enhances the pentration of complexes into lipid membrance and restricts further multiplicity of microorganisms. These metal complexes also affect the respiration process of the cell, hence, they block the synthesis of protiens which restrict further growth of the organism [42].

One other important factor; they increase penetration of complexes into lipid membrane, and, consequently, increase antimicrobial activity in the complex crystal size [43]. As shown from XRD analysis, Zn(II) complex (1) is characterized with very low crystal size with respect to its parent molecule (H₂L) and other complexes. Those complexes give more explanation of the high antimicrobial activity against all tested bacteria and fungi in which the small size of Zn(II) complex (1) increases its absorption ability on the surface of the cell wall of microorganisms and the respiration process of the cell. Hence, it blocks the synthesis of protiens that restrictfurther growth of the organism[44]. Zn(II) complex (1), therefore, is essential for the growth-inhibitor effect.

3.3Ground state properties

The optimized structures of the ligand and the studied complexes are obtained using B3LYB/6-311G (p,d) level, numbering system, net charge, and the vector of dipole moment – all presented in Figs (5 and 6). The total energy (E_T), energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), energy gap (E_g), and dipole moment (μ) of the ligand and complexes are collected in Table 7. From calculations of energy gap, (Eg), which measures the chemical reactivity, Zn Nano-complex (1) was found to be more reactive than the ligand. Accordingly, one can put the order of decreasing the energy gap (E_g) asH₂L>Cu (2)>Co (4)>Zn (1)>Ni(3). The polarity or charge separation over the molecule, which is measured by the dipole moment (μ), shows that (μ) of Zn Nano-complex (1)> (μ)of other complexes and the ligand. Also, the vector of dipole moment of Zn Nano-complex (1) is in opposite direction of the vector (μ) of other complexes and the ligand. The general trend of dipole moment (μ) for studied complexes and the ligand, consequently, follows the order Zn (1)> H_2L >Co (4)>Cu (2)>Ni(3). Finally, the theoretically computed ionization energy (I.E.) of Zn Nano-complex (1), which measures the donating property (oxidation power), is 5.80 eV (Table 7). Accordingly, one can put the order of decreasing the donating power as Ni(3)>Co (4)>Cu (2)>Zn $(1)>H_2L$. However, the electron affinity (E.A) of Zn Nano-complex (1), which

measures the accepting property (reducing power), is 2.39 eV. The order of accepting properties of studied complexes and the ligand follows H_2L <Cu (2)<Co (4)<Ni(3)<Zn (1).

3.4Charge distribution analysis

Table 8 presents the net charge on active centers of studied metal complexes and the amount of charge transferred from ligands to central metal ions; i.e. $H_2L \rightarrow M$ (Zn), $H_2L \rightarrow M$ (Cu), $H_2L \rightarrow M$ (Ni) and $H_2L \rightarrow M$ (Co). The results of Table 8 show that Zn (1) metal ion received 1.077 e, Cu (2) metal ion received 0.855 e, Ni(3) metal ion received 1.020 e, and Co (4) metal ion received 0.968 e from its surrounding ligand. From the results of Table 8, there is a large electron back-donation from the metal ion to the donating sites O23, O24, N11, N12, S5, O26, O50, N27, N38, and S36 in Cu (2), Ni(3),and Co (4) complexes. While it is O23, O24, N11, N12, S5, O26, O50, N27, O34, O35, and O36 in Zn (1) complex. These results were further confirmed by comparing values of calculated charge on the liganding atoms in complexes and on the same atoms in the free ligand. In all studied complexes, the charge density increases on the donating atoms after complexation.

3.5Structure activity relationship

The biological activity of prepared complexes can be correlated to the calculated ground state properties. The higher reactivity of Zn (1) and Co (4) complexes over Cu (2) and Ni(3) can be explained in terms of energy gap which measure the reactivity; as the energy gap decreases the reactivity increases and the amount of electronic charge transferring from the ligand to the central metal ion increases (Table 7).

Theoretically, reactivity of prepared complexes follows the order: Ni(3) > Zn (1) > Co(4)>Cu (2) which is the same order of reactivity towards G-, G+, and fungus (Table 7).

Mullikan electronic charge from the ligand to the central metal ion of studied complexes follows the order: Zn (1) > Ni(3) > Co (4)>Cu (2) which is the same order of reactivity towards G-, G+, and fungus (Table 8).

4. Conclusion

Novel thiophene-2-carbaldehyde Nano-complexes of Zn(II) (1), Cu(II) (2), Ni(II) (3), and Co(II) (4) were successfully prepared and characterized with different techniques. Obtained

Nano-complexes were tested as antimicrobial agents. Experimental results indicate that Zn(II) complex (1) is a useful antimicrobial agent for different bacteria and fungus. Zn Nano-complex (1) was found to be more reactive and more polar than other complexes and the ligand. Theoretically, reactivity of the prepared complexes follows the order: Ni(3) > Zn (1) >Co (4)>Cu (2) which is the same order of reactivity towards G-, G+, and fungus.

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Table captions

Table 1: Physical data, elemental analysis and molar conductance values of H_2L and its metal Nano-complexes.

Table 2: Characteristic FT-IR bands (cm⁻¹) of H₂L and its metal Nano-complexes.

Table 3: ¹H-NMR chemical shift (ppm) at 25° C, internal reference TMS, of H₂L and its diamagnetic Zn(II) Nano-complex (1).

Table 4: Thermal analysis of the prepared Nano-complexes.

Table 5: Temperature of decomposition, and the kinetic parameters of H_2L and its Nanocomplexes Table 6: The antimicrobial activity of H₂L and its metal Nano-complexes.

Table 7: Total energy, "au", energy of HOMO, " eV ", of LUMO, " eV ", energy gap," eV ", and dipole moment," Debye", for the ligand and the studied complexes using B3LYP/6-311G(d,p).

 Table 8: Net charges on metals and active centers of the studied complexes using B3LYP/6-311G (d,p).

Figure Captions

Fig. 1: The electronic spectra of a) H_2L and b) its metal Nano-complexes ([Cu(HL)₂] (2), [Ni(HL)₂] (3) and [Co(HL)₂]·H₂O (4)).

Fig. 2: TGA-DTG curves of a) $[Ni(HL)_2]$ (3) and b) $[Co(HL)_2] \cdot H_2O$ (4)

Fig. 3: XRD pattern of free ligand, H₂L.

Fig. 4: XRD pattern of $[Zn(HL)(OH_2)_2(NO_3)] \cdot H_2O$ (1), $[Cu(HL)_2]$ (2), $[Ni(HL)_2]$ (3) and $[Co(HL)_2] \cdot H_2O$ (4) Nano-complexes.

Fig. 5: The optimized structure, numbering system, net charge and the vector of the dipole moment of the ligand using B3LYP/6-311G (d,p).

Fig. 6: The optimized structure, numbering system and the vector of the dipole moment of the studied complexes using B3LYP/6-311G (d,p).

Scheme captions

Scheme 1: Synthesis of the ligand, H₂L.

Scheme 2: Chemical structure of the prepared Nano-complexes.

Supplementary materials:

Supplement 1: FT-IR spectra of a) H_2L and b) [Cu(HL)₂] (2).

Supplement 2: ¹H-NMR of a) H_2L and b) $[Zn(HL)(OH_2)_2(NO_3)] \cdot H_2O(1)$.

Table 1

Compound	M.F (F.WT) Cole	Calar	M.P.	Yield		Elemental analysis, Found (Calc.)%				
Compound		Color	Co	%	С	Ĥ	N	S	Metal	Am Ohm ⁻¹ cm ² mol ⁻¹
H ₂ L	$\begin{array}{c} C_{12}H_{10}N_2O_2S\\ (246.28) \end{array}$	Pale yellow	246	90	58.80 (58.52)	4.18 (4.09)	11.60 (11.37)	12.99 (13.01)	- -	-
Prepared metal complexes										
(1) [Zn(HL)(OH ₂) ₂ (NO ₃)] ·H ₂ O	C ₁₂ H ₁₅ N ₃ O ₈ S Zn (426.700)	Yellow	>300	71	33.49 (33.71)	3.28 (3.54)	9.30 (9.84)	7.60 (7.51)	15.00 (15.31)	20
(2) [Cu(HL) ₂]	$\begin{array}{c} C_{24} H_{18} N_4 O_4 \\ S_2 Cu \\ (554.10) \end{array}$	Green	>300	83	51.61 (52.02)	3.29 (3.27)	9.88 (10.11)	10.78 (11.57)	11.00 (11.46)	15
(3) [Ni(HL) ₂]	$\begin{array}{c} C_{24}H_{18}N_4O_4S_2\\Ni\\(549.27)\end{array}$	Orange	>300	806	52.29 (52.48)	3.60 (3.30)	10.16 (10.19)	11.62 (11.67)	10.52 (10.68)	11
(4) [Co(HL) ₂]·H ₂ O	$\begin{array}{c} C_{24}H_{20}N_4O_5S_2\\ Co\\ (567.50)\end{array}$	brown	>300	78	50.41 (50.79)	3.93 (3.55)	9.65 (9.87)	10.75 (11.29)	10.00 (10.38)	19

Table 2.

		-			-	C			
Compound	v(OH) (phenolic/H ₂ O)	v (NH)	v (C=O)	v (C=N)	v (C=N) _{enolic}	v (C-S)	v (M-O)	v (M-N)	Additonal bands
H ₂ L	3450 br	3250 br	1654 s	1630 s	A	855	-	-	-
1	3442 br	-	-	1618s	1524 s	775	515m, 580 m	419 m, 441m	1290, 1045 (coordinate d nitrate)
2	3441 br	-	-	1619 s	1518 s	783	535m, 560 m	418 m, 478m	-
3	3441 br	-	-	¥ 1620 s	1510 s	793	536 m, 560 m	419 m, 479 w	-
4	3455 br	-	No.	1617 s	1510 s	788	533 m 558 w ,	417m, 473 m	-

S=(strong), br=(broad), m=(medium), w=(weak)

Table 3

Compound	δ(NH)	δ (OH)	δ (CH=N)	Additional bands
H_2L	11.77 (1H)	12.44(1H)	8.85(1H)	7.93 – 7.16 (4H) aromatic Protons , 6.92 – 6.82 (3H) aromatic Protons
1	_	12.45(1H)	8.95(1H)	7.36 – 7.15 (4H) aromatic Protons , 6.92- 6.84 (3H) aromatic Protons
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Table 4

Compound	Temp Range °C	% Loss in weight Found (Calc.)	Composition of the Residue	Probable Composition of the Expelled Groups
1	30.0-70.0 71.0-250	4.00 (4.22) 12.4 (12.6)	$[Zn(HL)(OH_2)_2(NO_3)]$ $[Zn(HL)(NO_3)]$	One molecule of Lattice water Two molecule of coordinated water
	251-330	27.0 (27.4)	[Zn(L)]	One molecule HNO ₃
	331-465	53.1 (53.4)	C ₇ H ₃ NZn	One molecule of HCN and C ₄ H ₄ S
2	30.0-363	62.9 (64.3)	$C_{10}H_4N_4O_3Cu$	One molecule of C_6H_6O and two molecule of C_4H_4S
	364-450	69.0 (69.2)	C ₉ H ₃ N ₃ O ₃ Cu	One molecule of HCN
3	30.0-379 380-438	30.1 (30.6) 47.1 (47.7)	$\begin{array}{c} C_{16}H_{10}N_4O_4Ni\\ C_{10}H_4N_4O_3Ni \end{array}$	Two molecule of C_4H_4S One molecule of C_6H_6O
4	30.076.0 77.0-350	3.00 (3.17) 32.4 (32.8)	$\begin{array}{l} [Co(HL)_{2}] \\ C_{16}H_{10}N_{4}O_{4}Co \end{array}$	One molecule of lattice water Two molecules of C_4H_4S

Table 5

Compound	Step	Т	A	Ε	Н	S	G
		(K)	(S^{-1})	(kJ	(kJ	(kJ mol ⁻¹	(kJmol ⁻¹)
				mol ⁻¹)	mol^{-1})	K^{-1})	
H_2L	first	451.00	38.19x 10 ⁸	141.32	137.57	-0.07	170.69
			_				
	sec	751.00	16.49x10 ⁻⁷	24.77	18.53	-0.25	211.28
$[\mathbf{Z}\mathbf{n}(\mathbf{H}\mathbf{I})(\mathbf{O}\mathbf{H}_{a})_{a}(\mathbf{N}\mathbf{O}_{a})]\cdot\mathbf{H}_{a}\mathbf{O}$	first	323.00	80.70 $\times 10^7$	75.09	72 41	-0.08	99.22
	mst	525.00	00.70 X10	15.07	/ 2,71	-0.00	JJ.44
	sec	434.00	37.20	21.94	18.33	-0.22	116.48
	third	564.00	34.94 x10 ⁷	100.98	96.29	-0.09	149.83
	fourth	671.00	28.34x10 ⁴	82.41	76.83	-0.15	181.00
Cu(HL) ₂]	first	470.00	12.54x10 ⁻⁷	13.86	9.96	-0.31	159.42
	sec	680.00	11.46x10 ⁻⁸	54.14	48.49	-0.29	250.52
[Ni(HL) ₂]	first	478.00	74.41x10 ⁻²	196.59	192.63	-0.02	206.92
	sec	682.00	10.92×10^5	122.27	116.61	-0.14	215.09
	first	326.00	12 82×10 ⁴	10.00	37 20	0.15	86.02
	11150	J20.00	40.00-10 ⁻⁷		J1.47 10.25	-0.13	00.74
	sec	487.00	40.99X10	14.40	10.35	-0.20	139.10

Table 6

	Diameter of inhibition zone (mm) at conc. of $(\mu g/ml)$								
Compound	Grame	e + Ve	Grame	fungus					
	S. aureus	E. Coil	K. Pneumoniae	P. Vulgaris	C. albicans				
H_2L	- (>50)	- (>50)	- (>50)	- (>50)	- (>50)				
(1)	15 (~10)	15(~1.5)	10 (~25)	7 (~1.5)	12 (~50)				
(2)	- (>50)	- (>50)	- (>50)	- (>50)	- (>50)				
(3)	- (>50)	- (>50)	- (>50)	- (>50)	- (>50)				
(4)	- (>50)	10 (~50)	- (>50)	10 (~50)	6 (~50)				
Doxymycin ^a	15 (~10)	10 (~10)	10 (~10)	15 (~10)	-				
Fluconazole ^b	-	E S	-	-	16 (~10)				
Antibacterial stan	dard		^b Antifungal sta	ndard.					

Table 7

Parameter	H_2L	1	2	3	4
E _T ,au	-1121.623	-3333.212	-3882.392	-3750.215	-3624.679
E _{HOMO} ,(eV)*	-6.126	-5.800	-5.792	-5.687	-5.781
E (- 1 /)++	2.042	2 202	2 222	2 204	2 2 7 7
E _{LUMO} ,(ev)**	-2.042	-2.393	-2.223	-2.304	-2.267
E _{gap} ,(eV)	4.083	3.406	3.569	3.382	3.513
μ, D	5.455	8.041	2.696	2.622	2.849

Y

* I.E = - E_{Hom}

** $E.A = -E_{Lumo}$

Table 8

Center	1	2	3	4
	Zn	Cu	Ni	Co
Μ	0.923	1.145	0.980	1.032
023	-0.523	-0.352	-0.348	-0.349
024	-0.692	-0.525	-0.498	-0.498
N11	-0.352	-0.216	-0.212	-0.213
N12	-0.407	-0.549	-0.497	-0.524
85	0.307	0.268	0.267	0.268
O26	-0.659	-0.612	-0.582	-0.609
O50	-0.657	-0.349	-0.348	-0.348
N27	-0.700	-0.155	-0.158	-0.153
N38		-0.597	-0.542	-0.545
S36	Q	0.462	0.462	0.464
034	-0.559			
035	-0.433			
V O36	-0.416			
$H_2L{ ightarrow}M$	1.077	0.855	1.020	0.968





Fig. 2











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Research highlights

New complexes of Zn(II), Cu(II), Ni(II), and Co(II) were prepared in nano scale.

scale.

- > Spectroscopic, thermal and crystal properties were studdied
- > The nano-complexes were tested as antimicrobial agents.
- > Zn(II) nano-complex is a promising material for antibacterial application.
- DFT calculations at the B3LYP/6-311G (d,p) level of theory for nanocomplexes

A ALA