Effect of gamma irradiation on spectral, XRD, SEM, DNA binding, molecular modeling and antibacterial property of some (Z)N-(furan-2-yl)methylene)-2-(phenylamino)acetoxyhydrazide metal(II) complexes

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ABSTRACT

A series of Ru(II), Pd(II), VO(II) and Hg(II) complexes with (Z)N-(furan-2-yl)methylene)-2-(phenylamino)acetoxyhydrazide (HL) has been synthesized. Investigation of synthesized metal complexes was achieved by using elemental analyses, magnetic moment, molar conductance, FT-IR, 1H-NMR, UV-Vis., spectroscopy and thermal techniques. The effect of gamma irradiation on powder samples of [Ru(L)Cl]2EtOH (B1), [Pd(L)Cl(H2O)]H2O (B2), [(VO)(HL)SO4]H2O (B3) and [Hg(HL)(H2O)2] (B4) complexes was also investigated (hereafter referred to as (A1), (A2), (A3) and (A4), respectively). Spectral, thermal, powder X-ray diffraction patterns (XRD) and surface morphological studies were performed before and after irradiation. Irradiation causes changes in spectral features. XRD studies revealed the decrease in the crystalline size of sample (B2) from 43.3 nm to 30.6 nm upon irradiation and irradiation induced the crystallinity of the complexes. Surface morphology of [Pd(L)Cl(H2O)]H2O (B2) before and after irradiation has been studied. Fluorescence studies revealed the possibility of the Pd(II) complex (B2) to form a binding mode with Heparin. In molecular modeling the possible structures of the ligand and its metal complexes were fully optimized with respect to the energy using the Hyper Chem. 8.03 molecular modeling program. Furthermore, the energies of highest occupied molecular orbital (EHOMO), energies of lowest unoccupied molecular orbital (ELUMO), energy gap (\(\Delta E = E_{LUMO} - E_{HOMO}\)), the absolute electronegativity, \(\chi\), the chemical potential, \(P\), the absolute hardness, \(\eta\) and the softness (\(\sigma\)) were obtained for the ligand and its complexes (B3), (B4). The antibacterial studies of the prepared compounds before and after gamma irradiation screened against both gram positive and gram negative bacteria proved that these compounds exhibit remarkable antibacterial activity and the irradiation improved the bioactivity for most complexes.

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1. Introduction

Pre-exposure of crystalline solids to ionizing radiation is one of the most novel and proficient ways of generating metastable phases of solid materials with advanced properties. Knowledge regarding the irradiation effect on the structural formula of complexes gives an insight about deformation in the complex crystal or reflecting its rigidity which in turn can be utilized in various fields of science and technology [1,2]. Irradiation of variable materials is known to increase the defect concentration leading to an increase in energy content and subsequent chemical damage. Hence, any subsequently measured properties such as the structural, textural, electrical, thermal, spectral or magnetic may be modified by irradiation [1–4]. Thermal studies showed that pre-exposure of materials to energetic radiation considerably affects the kinetics of thermal decomposition, it is well known that the activation energy and associated kinetic parameters reduced by irradiation [2–6]. The FT-IR studies indicated that the intensity of bands changed upon irradiation [5–8]. The impact of \(\gamma\)–irradiation on the UV–Vis spectra of some complexes was investigated [4,5]. The shapes of the spectral bands and the values of the absorbance showed a significant change after irradiation [4,5]. X-ray diffraction studies showed that pre-exposure of materials to energetic radiations may cause lattice distortion which
indicated by changes in lattice parameters, crystallinity, relative intensity of peaks and so on [1–7]. Changes in texture and surface morphology have been indicated by microscopic measurements of the irradiated materials [1,4]. The effect of irradiation on the catalytic activities of certain catalytic systems was reported [9]. The irradiation causes both an increase and a decrease in the specific surface areas and the catalytic properties depending on the nature of the irradiated solid, the dose of gamma rays and the nature of the catalyzed reactions [9]. Also, the effect of energetic radiation on the biological activities of materials was reported. The irradiation was found to cause changes in the antibacterial activity of different tested materials in some cases [6]. Modifying the semiconducting properties of materials by gamma irradiation was proposed. The modifications can be applied in semiconducting devices through their interrupted exposure to gamma irradiation doses within the selected investigated range [2,8]. Previously we have reported the effect of γ-irradiation on some copper(II)-complexes of N-Phenyl-2-(2-phenylamino)acetyl)hydrazine carbothioamide at a dose of 10 kGy and a dose rate of 1.2 Gys$^{-1}$ as well as the effect of γ-irradiation on physicochemical properties of Co(II), Cu(II) and Ru(III) complexes with tetrazola [N4] ligand. i.e. N,N'-naphthalene-1,8-diylbis(2-aminobenzamide). The FT-IR, UV–Vis. absorption spectra, TG/DTG and X-ray diffraction patterns were performed using the powdered samples before and after γ-irradiation, also the morphological properties of Cu(II) complex before and after γ-irradiation was performed by scanning electron microscopy [2,10]. In the present investigation we report the synthesis, spectroscopic characterization, molecular modeling and effect of gamma irradiation on powder samples of [Ru(L)Cl2·EtOH(B1), [Pd(L)(H2O)2]·H2O(B2), [VO(H2L)SO4]·H2O(R1) and [Hg(HL)(H2O)2] (B4) complexes. The antibacterial activity of both un-irradiated and irradiated complexes was tested.

2. Experimental

2.1. Materials and methods

All organic compounds and the solvents were purchased from Fluka or Merck (Nasr City, Egypt). The metal salts ruthenium(II) chloride trihydrate, palladium(II) chloride, VO(II) sulphate trihydrate and Hg(II) iodide were obtained from Fluka and used for complex preparation without further purification.

2.2. Preparation of the metal complexes

\[(Z)\rightarrow N-(furan-2-yl)methylene)-2-(phenylamino)acetohydrazide\] (HL) was prepared and characterized as previously reported [11]. Metal complexes were prepared by adding stoichiometric amount of the appropriate metal salt, RuCl3·3H2O, Na2PdCl4, VOSO4·3H2O or HgCl2 in EtOH (20 mL) to \((Z)\rightarrow N-(furan-2-yl)methylene)-2-(phenylamino)acetohydrazide\)(HL) (20 mL) in the same solvent in 1:1 M molar ratio. The reaction mixture was heated with stirring at ca. 60 °C for 6 h. The resulting solids were filtered off, washed several times with ETOH, and dried under vacuum over P4O10.

2.2.1. \([Ru(L)Cl2]EtOH, B1, A1 (M.F.: C23H30N6O4Cl2Ru and M.W.: 803)](322)

Elemental analyses of B1 gave: C = 41.84% (42.5), H = 4.2% (4.1), N = 10.46% (10.0), Cl = 8.84% (8.40) and Ru = 25.15% (25.6) (where the numbers in parenthesis represent the calculated value from the chemical formula). Electronic absorption spectra in mulls, $\lambda_{max}$/nm: 250, 310, 340, 380, 465 for B1, 250, 317, 345, 375, 380, 456 for A1. Selected IR frequencies (KBr disk, cm$^{-1}$): 3426, 3320 1620, 1600, 590, and 467 for B1 and 3490, 3325,1628, 1607, 600, 485 for A1.

2.2.2. \([Pd(L)(H2O)2]], H2O, B2, A2 (M.F.: C13H16N3O4ClPd and M.W.: 420)](323)

Elemental analyses of B2 gave: C = 37.1% (37.0), H = 3.8% (3.6), N = 9.1% (10.0), Cl = 8.45% (8.9) and Pd = 25.4% (25.2) (where the numbers in parenthesis represent the calculated value from the chemical formula). Electronic absorption spectra in mulls, $\lambda_{max}$/nm: 240, 340–375, 465 for B2: 250, 340–375, 468 for A2. Selected IR frequencies (KBr disk, cm$^{-1}$): 3450, 3200, 1625, 1598, 560, 480 for B2 and 3454, 3210, 1610, 1500, 550, 480 for A2.

2.2.3. \([VO(HL)SO4]H2O B3, A3 (M.F.: C13H18N2O3SgHg and M.W.: 623.5)](323)

Elemental analyses of B3 gave: C = 36.79% (36.7), H = 3.8% (3.9), N = 9.8% (9.7) and V = 12.0% (12.0) (where the numbers in parenthesis represent the calculated value from the chemical formula). Electronic absorption spectra in mulls, $\lambda_{max}$/nm: 260, 270–360, 760 for B3: 260, 270–360, 756 for A3. Selected IR frequencies (KBr disk, cm$^{-1}$): 3432, 3324, 1660, 1628, 1520, 971, 615, 500 and 3430, 3325, 1666, 1620, 972, 618, 502 for A3.

2.2.4. \([Hg(HL)(OH)(H2O)2]B4, A4 (M.F.: C13H18N2O3Hg and M.W.: 623.5)](323)

Elemental analyses of B4 gave: C = 25.0% (25.4), H = 2.88% (4.95), N = 6.7% (6.7), Cl = 10.0% (10.8) and Hg = 33.2% (33.0) (where the numbers in parenthesis represent the calculated value from the chemical formula). Selected IR frequencies (KBr disk, cm$^{-1}$): 3425, 3250, 1655, 1605, 1500, 600, 480 for B4 and 3430, 3390, 3225, 1650, 1605, 1505, 600, 503 for A4.

2.3. Physical measurement

Elemental analyses (C, H and N) were performed at Microanalytical unit, Cairo University. Metal and halide analyses were estimated using standard literature methods [12]. The Fourier Transform Infrared (FT-IR) measurements were performed (4000–400 cm$^{-1}$) in KBr discussing. Nenexeus-Nicolidite-640-MSAFT-IR, Thermo-ElectronicsCo. (Central Lab, Menoufia University, Shebin El-Kom, Egypt).$^{1}$H NMR spectra were recorded in DMSO- $d_6$ using 300 MHz Varian NMR spectrometer (Micro Analytical Center, The UV–visible absorption spectra were measured in Nujol mull using 4802 UV/vis double beam spectrophotometer. The molar conductivity measurements were made in DMF solution (10$^{-3}$ M) using a Tacussel conductometer type CD6N. The fluorescence spectra were carried out using LS 45 PerkinElmer Fluorescence Spectrometer. Magnetic susceptibilities of the complexes were measured by the modified Gouy method at room temperature using Magnetic Susceptibility Johnson Matthey Balance. The effective magnetic moments were calculated using the relation $\mu_{eff} = 2.828 \cdot (\gamma_m T)^{1/2}$ B M, where $\gamma_m$ is the molar magnetic susceptibility corrected for diamagnetism of all atoms in the compounds using Seilwood and Pascal’s constants. Thermal analysis (TG/DTG) was obtained by using a Shimadzu DTA/DTG-50 Thermal analyzer (Central Lab, Menoufia University, Shebin El-Kom, Egypt) with a heating rate of 10°C/min in nitrogen atmosphere with a flowing rate 20 mL/min in the temperature range 25–600°C using platinum crucibles. X-ray powder diffraction analyses of unirradiated (B1, B2, B3, B4) and irradiated (A1, A2, A3, A4) samples were carried out at the National Research center, Dokki, Cairo, Egypt by using Rigaku Model ROTA FLEX Ru-200. Radiation was provide by copper target (Cu anode 200 W) high intensity X-ray tube operated at 40 kV and 35 mA. Divergence and receiving slits were 1 and 0.1, respectively. Surface morphological study was recorded by taking scanning electron microscopy (SEM) images for unirradiated (B1) and irradiated (A1) samples of [Pd(L)(H2O)2]], H2O complex in JEOL model JSM–5500 equipment.

2.4. Theoretical calculation (molecular modeling)

Molecular modeling was applied to investigate the three dimensional arrangements of atoms in the complexes by employing semi-empirical molecular orbital calculations at the PM3 level provided by the HyperChem 8.03 program [13].

2.5. Antibacterial activity

The in vitro antibacterial activity studies were carried out at Genetic Engineering and Biotechnology Research Institute, Department of Microbial Biotechnology at Sadat City University, Egypt, by using Broth Dilution Method [14] with some alterations, to investigate the inhibitory effect of some synthesized complexes (B1-B4) and (A1-A4) on the sensitive organisms Streptococcus pyogenes as Gram-positive bacteria and Escherichia coli as Gram-negative bacteria. Nutrient broth medium was prepared by using Brain Heart Infusion (BHI) broth and distilled water. The test compounds in measured quantities were dissolved in DMSO which has no inhibition activity to get two different concentrations (1 µg/mL, 5 µg/mL) of compounds. The strains selected for the study were prepared in (BHI) broth medium with shaking and autoclaved for 20 min 15 pounds of pressure and at 121 °C before inoculation. The bacteria were then cultured for 24 h at 37 °C in an incubator. One ml of the standard bacterial culture was used as inoculation in a nutrient broth. For growth studies, culture of microbial cells were inoculated and grown aerobically in BHI broth for control and along with various concentrations of the test compounds in individual flasks. Growth was calculated turbidometrically at 650 nm using conventional Spectrophotometer, in which turbidity produced is proportional to the number of viable organisms per milliliter of sample and were used to the calculated % inhibition.

2.6. Irradiation studies

For irradiation studies the samples of complexes B1,B2,B3 and B4 were subjected to gamma irradiation to a dose of 60 kGy using Indian 60Co γ-ray cell type GE-4000 A (at room temperature at the Egyptian Atomic Energy Authority Nasr City, Egypt) at a dose rate of 2.2 kGy h⁻¹. After removing the samples from the radiation field the FT-IR, UV–Vis and 1H-NMR spectra were recorded. The FT-IR spectra were recorded at room temperature.

2.7. Spectroscopic analysis

Electronic spectral analysis of the complexes in DMF (10⁻³ M) solution shows that the complexes are essentially non-electrolytes indicating coordination of the anions [15].

3. Results and discussion

3.1. Elemental analysis and molar conductance

The new compounds have been characterized by elemental analyses, spectral (IR, UV–Vis, ¹H NMR, magnetic, molar conductivity measurements and thermal analysis (TG/DTG) technique. The elemental analyses data are consistent with the proposed molecular formulas that show the molar ratio is 1 M:1 L or 2 M:2 L. All complexes are insoluble in most common solvents, including ethanol, methanol, ethyl acetate and acetonitrile but soluble in DMF. The values of molar conductivities in DMF (10⁻³ M) solution (Table 1) showed that the complexes are essentially nonelectrolytes indicating coordination of the anions [15].

3.2. ¹H-NMR and FT-IR spectra

The ¹H NMR spectrum of [Pd(L)(CH₂O)]·H₂O (B₂) has been recorded in DMSO-d₆ at room temperature. The disappearance of the signal due to the proton of the amide (−CONH) group in the ¹H NMR spectrum indicates its involvement in enolisation with adjacent carbonyl group and subsequent coordination of oxygen atom via deprotonation, while the signal due to the proton of imine −N=CH group was appeared at δ = 7.84 ppm and shows some changes due to coordination with the Pd(II) ion [16]. A multiplet signals of aromatic and furan protons appeared at δ = 7.00–7.29 ppm. The strong band observed at 1671 cm⁻¹ in the IR spectrum of the ligand (HL) was referred to (>C=O), this band has shifted to lower wave number in [(VO)(HL)SO₄]·H₂O (B₃) and [Hg(HL)(H₂O)₂]·(B₄) complexes indicating its coordinating behavior towards these metal ions. In case of [Ru(L)Cl₂·EtOH] (B₁) and [Pd(L)(CH₂O)]·H₂O (B₂) complexes, the ν(C=O) was disappeared and two additional bands in the 1620–1598 cm⁻¹ range, assigning to ν(N−N=N−C⁺) are appeared, this indicates that (ν(C=O)) group was undergone enolisation with adjacent NH group and deprotonated and finally coordinated to metal ion. Which is further supported by the absence of the signal corresponding to −NH−OH in the ¹H NMR spectrum of Pd(II) complex. The band at 936 cm⁻¹ is assigned to ν(N−N) stretching vibration of hydrazine residue. This band in the complexes shifts slightly to a higher wave number side conforming the involvement of one of nitrogens of –N=N−N− in bonding with the metal ions. However, The new weak non-ligand bands in the region 600–550, 503–480 cm⁻¹ in the spectra of complexes are tentatively assigned to ν(M-O), ν(M-N) [17,18]. The appearance of the broad strong absorption band in complexes at about 3435–3350 cm⁻¹ can be reasonably attributed to the presence of coordinated/lattice held water or ethanol molecule this is further confirmed by elemental and thermogravimetric analyses. The IR spectrum of the free Schiff’s base ligand shows a broad medium band at 3324 cm⁻¹ due to ν(NH) stretch of the −CONH group. This band shifts slightly to a higher wavenumber side in (B₁), (B₂) complexes indicating the non-involvement of N’ of the amide group in bonding. Furthermore, the ν(N−N−C) stretching vibrations of the furan ring observed at 1021 cm⁻¹, remains unaltered in the metal complexes, indicating non-participation of the furan ring oxygen atom in the bonding with metal ions [19].

The ν(V=O) in the FT-IR spectrum of the vanadyl complex was also seen at 971 cm⁻¹. The IR spectra of the irradiated complexes (A₁–A₄) showed that the position, shape as well as intensity of IR bands especially ν(NH), ν(C=O), ν(C=N), ν(M-O) and ν(M-N) are found to be slightly changed upon irradiation and production of few side bands were observed in irradiated complexes, which are probably due to general distortion of the lattice planes by irradiation.

3.3. Electronic spectra and magnetic moments

The electronic spectra of the current complexes (before and after irradiation) have been recorded in Nujol mulls in the 200–800 nm range. Ru(II) complex displays band in region 465 nm in the electronic spectrum, is reasonably assignable to a combination of ligand to metal charge transfer and metal d-d band transitions [20,21]. The other high intensity bands appearing around 250–380 nm were due to ligand–ligand centered transition. Magnetic moment measurements show that the binuclear complex is diamagnetic as expected for the bivalent state (low spin, d⁶, S = 0) of each ruthenium center. The electronic absorption spectrum of Pd(II) complex (B₂) displayed a very intense band at ca. 465 nm is reasonably assignable to a combination of ligand to metal charge transfer and metal d-d band transitions, the diamagnetic behavior
The electronic absorption spectra of VO(II) complex displayed a chromic or hypochromatic shift in ($\epsilon_{\text{max}}$). The magnetic moment value ($\mu_{\text{eff}} = 1.87$ B M$\cdot$) is consistent with the presence of one unpaired electron. The diamagnetic Hg(II) complex B4 has a d10 system, so it does not show d-d transitions.

After irradiation all the above mentioned peaks are present and exhibited hypsochromic or bathochromic shift, besides, hyperchromic or hypochromic shift in ($\epsilon_{\text{max}}$). The difference between the absorption bands can be dedicated to irradiation deformation of the compound. This result is good agreement with reported studies [25]. Irradiation can induce perturbation of energy levels as well as deformity in the molecule. In addition, the magnetic moment value recorded for complexes don’t altered indicating no change in the complexes geometry.

### 3.4. Thermal analysis before and after $\gamma$ irradiation

The thermal behavior of both irradiated and un-irradiated complexes was investigated by thermogravimetric analysis (TG/DTG) under nitrogen atmosphere in the temperature range (20–800 °C).

#### 3.4.1. Ru(II) complex

The DTG curve of ruthenium(II) complex (B1) shows endothermic DTG peak at 50 °C, which is assigned to remove of one ethanol molecule as indicated by TG weight loss (calcld. 5.8, found 5.8%) in the temperature range 28–100 °C, the TG curve also shows several decomposition stages started at 150 °C ended with the formation of 2Ru as final residue (calcld. 25.17, found 25.8%). After $\gamma$ irradiation the TG curve of the complex (A1) shows endothermic DTG peak at 54 °C, which is assigned to remove of one ethanol molecule as indicated by TG mass loss (calcld. 5.8, found 5.8%) the desolvated complex is stable up 143 °C and above this temperature the thermal decomposition occurs in a several successive steps, between 143 and 430 °C with the formation of 2RuO (calcld. 29.14, found 28.50%). Thus the enhanced decomposition of irradiated complex A1 may be attributed to lattice defect that is a fundamental step in a solid decomposition [6]. The thermal decomposition of both desolvated un-irradiated and irradiated complexes were of the same profile.

#### 3.4.2. Pd(II) complex

The DTA curve of the un-irradiated palladium(II) complex (B2) shows mass loss from room temperature up to 100 °C, due to dehydration with loss of one half water molecule (calcld. 2.14, found 2.2%). The complex is stable up to 246 °C, and above this temperature the thermal decomposition occurs in several steps, between 247 and 492 °C, correlated with exothermic DTG peaks at 261,386 and 483 °C that are attributed to degradation of the organic matter with the formation of PbO as final residue (calcld. 30.04%, found 31.00%). The TG curve of the irradiated complex (A2) shows mass loss from room temperature up to 100 °C, is due to dehydration with loss of one half water molecule (calcld. 2.14, found 2.2%). The complex is stable up to 300 °C, and above this temperature the thermal decomposition occurs in single step, between 300 and 430 °C, ended with the formation of PbO2 (calcld 34.39%, found 35.26%) as final residue. It is worth to mention that the remaining lattice water half molecule together with the one coordinated water molecule is lost during complex decomposition. The un-irradiated complex (B2) is thermally less stable (d.t = 246 °C) than the irradiated (A2) (d.t = 300 °C).

#### 3.4.3. VO(II) complex

The DTG curve of the un-irradiated VO(II) complex (B3) shows broad endothermic DTG peak at 57 °C, which is assigned to loss of one water molecule as indicated by TG weight loss (calcld. 4.24, found 4.24%) in the temperature range 30–118 °C, the TG also shows several decomposition stages started at 150 °C, was assigned to the loss of organic part ended with the formation of vanadyl oxide above 554 °C(calcld. 23.38, found 24.00%) [26]. The DTG curve of irradiated VO(II) complex (A3) shows broad endothermic DTG peak at 63 °C, which is assigned to loss of one water molecule as indicated by TG weight loss (calcld. 4.24, found 4.24%) in the temperature range 30–110 °C. Several decomposition stages started at 180 °C, was assigned to the loss of organic part, the TG thermogram for the irradiated VO(II) displayed a high residual part revealing its high thermal stability.

#### 3.4.4. Hg(II) complex

Figs. 1 and 2 show the recorded TG and DTG curves of [Hg(HL)(OH)(H2O)]2 complex before and after irradiation. The TG curves show no mass loss up to 110 and 120 °C, respectively, indicating the absence of outside solvent molecules. Both (B4), (A4)

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Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Compounds</th>
<th>Color</th>
<th>Yield(%)</th>
<th>Mol. Wt.</th>
<th>Calc. (Found)%</th>
<th>$\lambda$nm $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>[Ru(L)Cl]2·EtOH</td>
<td>Black (65)</td>
<td>803</td>
<td>41.84(42.5)</td>
<td>4.20(4.10)</td>
<td>10.46(10.0)</td>
</tr>
<tr>
<td>B2</td>
<td>[Pd(L)Cl(H2O)]·H2O</td>
<td>Yellow (65)</td>
<td>420</td>
<td>37.1(37.0)</td>
<td>3.8(3.6)</td>
<td>9.10(8.60)</td>
</tr>
<tr>
<td>B3</td>
<td>[VO(HL)SO4·H2O]</td>
<td>Brownish green (65)</td>
<td>423</td>
<td>36.79(36.7)</td>
<td>3.8(3.9)</td>
<td>9.8(9.7)</td>
</tr>
<tr>
<td>B4</td>
<td>[Hg(HL)(OH)(H2O)]2</td>
<td>Red (75)</td>
<td>623.5</td>
<td>25.01(26.4)</td>
<td>2.88(4.95)</td>
<td>6.7(6.7)</td>
</tr>
</tbody>
</table>

$^a$ Molar conductivity ohm$^{-1}$ cm$^2$ mol$^{-1}$ in 10$^{-3}$ M DMF.
complexes start to decompose above these temperatures, leaving no residue [27].

3.5. Molecular modeling and quantum chemical parameters

Several attempts to grow appropriate single crystals of the synthesized metal chelates for X-ray crystallography were unsuccessful. Thus, to confirm the geometries of the complexes, molecular modeling studies were performed by applying the HyperChem program package [13]. Molecular orbital geometry optimization allows a quantitative discussion not only of the geometry but also the ground electronic properties of the investigated complexes. Geometric and electronic structures of the ligand and some metal complexes were calculated by the optimization of their bond lengths and bond angles. The calculated bond lengths and bond angles for the ligand and B3 and B4 complexes are listed in Tables (S1-S3). The optimized structures of the ligand and its complexes are shown in Figs. (3–5). The theoretical data showed the following observations:

The obtained bond lengths of the C9–O10 and N11–N12 groups for the ligand are 1.2001 and 1.3517 Å, respectively. The bond lengths of these groups suffer an obvious change than the original free ligand. Upon complexation with VO(II) ion, both C9–O10 and N11–N12 bond showed decrease in their length than the free ligand, while upon complexation with Hg(II) ion the bond length of C9–O10 become longer while N11–N12 become shorter than free ligand, The change in this bond length confirms the coordination of oxygen of carbonyl and nitrogen atom (Table 2). The M–O bond length is shorter than M–N bond length i.e. the bond length obeyed the order M–N > M–O. The VO(II) metal center is five coordinated within the range 73.33°–176.27°. The Hg(II) metal center is six coordinated suggesting octahedral geometry. The minimum and maximum angles around the metal centers are found to be 88.54° O(30)-Hg(23)-O(29), 174.95° O(30)-Hg(23)-I(25), 82.57° O(30)-Hg(23)-O(24), 87.90° O(30)-Hg(23)-N(12), 93.64° O(30)-Hg(23)-O(10), 85.53° O(29)-Hg(23)-I(25), 95.48° O(29)-Hg(23)-O(24), 156.47° O(29)-Hg(23)-N(12), 92.68° I(25)-Hg(23)-O(24), 91.86° I(25)-Hg(23)-N(12), 107.09° O(24)-Hg(23)-O(10), and 73.70° N(12)-Hg(23)-O(10). These data show a distortion around the metal centers. The quantum chemical parameters (the energy of the highest occupied molecular orbital $E_{\text{HOMO}}$ energy of the
The lowest unoccupied molecular orbital (ELUMO), energy gap (ΔE), electronegativity (χ), chemical potentials (\(\mu\)), dipole moment (\(\mu\)), hardness (\(\eta\)), softness (\(\sigma\)), additional electronic charge (\(\Delta N_{\text{max}}\)) were also calculated [28–31], and are presented in Table (3). The calculated dipole moments for the ligand and its complexes indicated that the VO(II) complex has a higher dipole moment (6.852 D), i.e. it is more polarizable, than the other compounds. The dipole moment values of the complexes are larger compared with the value of the ligand (Table 4).

The negative values of \(E_{\text{HOMO}}\) and \(E_{\text{LUMO}}\) indicated that the investigated compounds are stable.

The high HOMO energy of Hg(II) complex implies that the ligand is a better electron donor towards Hg(II) ion than the VO(II) ion. The calculated energy gap (ΔE) of the Hg(II) and V(II) complexes showed that Hg(II) complex has a lower energy gap (6.878 eV). This indicates that Hg(II) ion is more reactive towards the ligand and has more probable complex formation ability.

### Table 2
The selected bond length (Å) of the ligand (HL) and its complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>C3-N7</th>
<th>N7-C8</th>
<th>C8-C9</th>
<th>C9-O10</th>
<th>C9-N11</th>
<th>N11-N12</th>
<th>N12–C13</th>
<th>C13-C14</th>
</tr>
</thead>
<tbody>
<tr>
<td>HLB</td>
<td></td>
<td>1.3499</td>
<td>1.4540</td>
<td>1.4596</td>
<td>1.2001</td>
<td>1.4159</td>
<td>1.3517</td>
<td>1.3370</td>
<td>1.3519</td>
</tr>
<tr>
<td>[Hg(HL)(OH)(H2O)]</td>
<td></td>
<td>1.3512</td>
<td>1.4452</td>
<td>1.5205</td>
<td>1.2117</td>
<td>1.3784</td>
<td>1.3480</td>
<td>1.3454</td>
<td>1.3403</td>
</tr>
</tbody>
</table>

### Table 3
The calculated quantum chemical parameters of the ligand and VO(II),Hg(II) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(E_{\text{HOMO}})</th>
<th>(E_{\text{LUMO}})</th>
<th>ΔE</th>
<th>χ</th>
<th>η</th>
<th>σ</th>
<th>P_\text{I}</th>
<th>(\Delta N_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Hg(HL)(OH)(H2O)]</td>
<td>−8.845</td>
<td>−1.967</td>
<td>6.878</td>
<td>5.406</td>
<td>3.439</td>
<td>0.291</td>
<td>−5.406</td>
<td>1.572</td>
</tr>
</tbody>
</table>

### Table 4
The energetic properties of the ligand and VO(II),Hg(II) complexes.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ligand</th>
<th>VO(II)</th>
<th>Hg(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total energy (kcal/mol)</td>
<td>44.8818</td>
<td>70.5425</td>
<td>55.4392</td>
</tr>
<tr>
<td>Potential energy (kcal/mol)</td>
<td>27.6502</td>
<td>48.3231</td>
<td>29.6222</td>
</tr>
<tr>
<td>Kinetic energy (kcal/mol)</td>
<td>17.2316</td>
<td>22.2193</td>
<td>25.8172</td>
</tr>
<tr>
<td>Dipole moment (Debye)</td>
<td>4.662</td>
<td>6.852</td>
<td>4.738</td>
</tr>
<tr>
<td>HOMO (eV)</td>
<td>−7.477</td>
<td>−8.978</td>
<td>−8.845</td>
</tr>
<tr>
<td>LUMO (eV)</td>
<td>−1.265</td>
<td>−1.549</td>
<td>−1.967</td>
</tr>
</tbody>
</table>

### 3.6. X-ray diffraction

The X-ray diffractograms of both unirradiated and irradiated...
samples of Pd(II) and VO(II) complexes (B2, B3 and A2, A3) are given in Fig. 6a and b, respectively. Lattice constants are listed in Table (5).

It is noted that, irradiation influence the x-ray diffraction pattern for both samples where the crystallization increased. The intensities of the powder lines and the corresponding 2θ values are found to be more different for the irradiated samples. The un-irradiated samples (B2 and B3) were found to have very few reflections and hence could not to be indexed especially (B3), indicating the amorphous nature of the complexes whereas upon irradiation both samples changed to crystalline materials with high intensity and sharp line of diffraction [35]. The average crystallite size D is given by Scherer’s equation: 

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]

where, \( \lambda \) is the X-ray wavelength (in nm), \( \beta \) is the peak width of the diffraction peak profile at half maximum height resulting from small size in radians. The value of \( \beta \) in the 2θ axis of diffraction profile must be in radians. The 0 is Bragg angle and can be in degrees or radians since Cos0 corresponds to the same number [36]. It was found that the calculated crystallite size is in the nano range. For sample (B2) the crystallite size is 3.0 nm for both un-irradiated and irradiated sample whereas, the crystallite size of sample (B2) is 43.3 nm and 30.6 nm for both un-irradiated and irradiated sample, respectively. The change in the crystallite size may be due to the stress caused by irradiation.

3.7. Surface morphology

SEM micrographs at different resolutions of complex [Pd(L) Cl(H2O)](H2O) were taken before (Fig. 7 a-c) and after (Fig. 7 d-f) γ-irradiation. The SEM images show that there is a homogeneous matrix with an ideal shape of uniform phase material. An ice rock like shape is observed. By comparing, the figures show significant changes in the surface morphology upon irradiation. Based on analyses and spectral, theoretical studies data we suppose that the structures of the complexes are best formulated as shown in Scheme 1.

3.8. The fluorescence studies

The fluorescence spectra for ligand (HLB), Ru(II) and Pd(II) complexes (B1 and B2) were recorded at room temperature (298 K)
with concentration of 100 μg/mL in the absence and in the presence of Heparin (5 μg/mL) in DMSO solution (Fig. 8a and b). The excitation wavelength was 300 nm and emission wavelengths were ranging from 320 to 450 nm.

In the absence of Heparin, the fluorescence intensity of the free ligand HLB increases (hyperchromism) as compared to its complexes B1 and B2. The Fluorescence intensity of the Ru(II) complex (B1) and the ligand (HLB) increased with Heparin and the position of the maximum emission wavelength remained unchanged [37]. The Fluorescence intensity of Pd(II) complex (B2) in presence or in absence of Heparin was similar and the position of the maximum wavelength remained unchanged [38]. Fluorescence studies revealed the possibility of the Pd(II) complex (B2) to form a binding mode with Heparin. Ru(II) complex (B1) and ligand (HLB) showed no fluorescence quenching capability when compared with complex (B2) as a quencher [39].

3.9. Antibacterial activity

The synthesized ligand and its unirradiated (B1-B4) and irradiated (A1-A4) metal complexes were tested as anti-bacterial agents against gram positive bacteria as *S. pyogenes* and gram negative bacteria as *E. coli*. Results recorded in Table S3 and depicted in Fig. 9 showed that the ligand and the tested compounds before (B1-B4) and after (A1-A4) irradiation have remarkable biological activity for both concentrations (1.5 μg/mL) and that the antibacterial activity of these compounds was proportionally increased with increasing concentration for both two bacterial strains [40–42]. Exposure to gamma irradiation increased the antibacterial property for most complexes towards both *E. coli* and *S. pyogenes* in both concentrations [43]. The antibacterial studies of the prepared compounds proved that these compounds exhibit remarkable antibacterial activity and can be used in the future as therapeutic drugs for pathogenic bacterial diseases.

4. Conclusions

In this work the effect of γ irradiation on Ru(II),Pd(II), VO(II) and Hg(II) complexes of (Z)-N-(furan-2-yl)methylene)-2-(phenylamino)acetohydrazide (HL) at applied dose of 60 kGy have been studied. The analytical, experimental and theoretical measurements confirmed the chemical structure of the current compounds. The unirradiated and irradiated compounds were screened for their antibacterial activity. The results obtained can be summarized as follows:

1. The ligand ligates as neutral or monobasic bidentate.
2. IR spectra exhibit high intensity bands upon irradiation.
Fig. 8a. Fluorescence intensity of 100 μg/mL of Ru(II) complex (B1) at zero time (pink); 100 μg/mL of ligand (HLB) (blue); ligand with 5 μg/mL Heparin (red); Ru(II) complex (B1) with 5 μg/mL Heparin (black). (b) Fluorescence intensity of Pd(II) complex (B2) with 5 μg/mL Heparin (black); 100 μg/mL of Pd(II) complex at zero time (pink); 100 μg/mL of ligand (HLB) (blue); ligand with 5 μg/mL Heparin (red).

Fig. 9. Graphical representation of bacterial activities of ligand and its metal(II) complexes before (B1-B4) and after (A1-A4) gamma irradiation at concentrations (1 and 5 μg/mL).
3. The proposed structure of complexes was geometrically optimized and the structural parameters were calculated.
4. The computational calculations also proved that the Hg(II) complex has six coordination and VO(II) complex has five coordination geometries, this is also in a good agreement with the experimental results.
5. X-ray diffraction patterns and SEM showed improving of the crystallite size upon gamma-irradiation.
6. Ru(II) complex (B1) and ligand (HLa) showed no fluorescence quenching capability when compared with complex (B2) as a quencher.
7. In vitro antibacterial activity of all synthesized compounds indicated that they are potent antibacterial agents. Besides, the antibacterial activity increases upon irradiation for some complexes.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2019.02.069.

References