# Impact of gamma-ray irradiation on some aryl-amide-bridged Schiff-base complexes: spectral, TGA, XRD, and antioxidant properties

H. A. El-Boraey<sup>1</sup> · O. A. El-Gammal<sup>2</sup> · N. G. Abdel Sattar<sup>1</sup>

Received: 7 August 2019 © Akadémiai Kiadó, Budapest, Hungary 2019

#### Abstract



Some aryl amide Schiff base Co(II), Ni(II) and Cu(II) distance between Cu(II) and complexes (1–7) have been obtained and identified by various analytical and spectroscopic tools. To through a light on the probability of structure changes with  $\gamma$ -irradiation, powder samples of complexes 1, 3, 5 and 6 were irradiated with <sup>60</sup>Co  $\gamma$ -rays at dose of 100 kGy (hereafter referred to as 1F, 3F, 5F and 6F). Spectral, molar conductance, magnetic susceptibility, thermal, X-ray diffraction and antioxidant activity for the irradiated complexes were gained using similar methods used for the non-irradiated complexes. The data revealed that the irradiated complexes were not seriously affected by the utilized  $\gamma$ -irradiation dose.

Keywords  $\gamma$ -Irradiation · Metal complexes · Spectral · Modeling · IC<sub>50</sub>

# Introduction

Studies on the effects produced in solids materials by the interaction of ionizing radiation have received considerable attention [1–5]. Energetic  $\gamma$ -radiation can affect on the color, chemical composition, spectral, catalytic properties, magnetic, structural, optical, electrical, thermal and biological behavior of variety of solids [6–8].  $\gamma$ -irradiation can enhance thermal decomposition process of the solids, owing to lattice defects and chemical damage [8–10].  $\gamma$ -irradiation also affects on crystallinity leading to changes in lattice parameters according to X-ray studies [11–14]. The specific surface areas, the particle size and the catalytic activities of certain  $\gamma$ -irradiated catalytic systems can be altered upon irradiation [15]. FT-IR and electronic spectral studies showed that the position and intensity of the characteristic bands changed upon irradiation [16, 17] and irradiation can encourage

**Electronic supplementary material** The online version of this article (https://doi.org/10.1007/s10967-019-06946-3) contains supplementary material, which is available to authorized users.

disturbance of energy levels as well as distortion of electronic spectrum [18–21]. These changes provide essential information about the physicochemical consequences of radiation effects in solids materials [4, 22].

The chemistry of aryl amide Schiff base ligands is a fascinating area of research and has attracted a lot of attention owing to their versatile bioactivities and their extensive applications in many scientific fields [23–29]. So, the ligation of Schiff base with transition metal ions is with great significance in the range of bioinorganic chemistry and medicine. However, over generation of free radicals may encourage some oxidative damages to bio-molecules like carbohydrates, proteins, lipids, DNA and so on. Antioxidants interact with the free radicals, acting as electron donors and prevent the damage by reactive oxygen species (ROS) [30]. A lot of Schiff base complexes have been examined as potential scavengers of ROS [31–34]. In addition, synthetic antioxidants are vastly used due to their effective and are cheaper than natural antioxidants [35].

Recently, we have reported the impact of  $\gamma$ -irradiation on spectral, X-ray diffraction, SEM, DNA binding, molecular modeling and antibacterial activity of some acetohydrazide dervative metal(II) complexes [36]. The physicochemical effect of  $\gamma$ -irradiation at 30 kGy dose on some transition metal complexes with the tetraaza [N<sub>4</sub>] ligand (L) had been reported by us [37]. Previously, we studied the impact of high energetic ionizing radiation on hydrazine carbothioamide derivative (H<sub>2</sub>L) and its Cu(II) complexes [10].

H. A. El-Boraey helboraey@yahoomail.com

<sup>&</sup>lt;sup>1</sup> Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-Kom 32511, Egypt

<sup>&</sup>lt;sup>2</sup> Department of Pathology, University Hospital, Menoufia University, Shebin El-Kom 32511, Egypt

With this regard and in continuation of our previous studies on the impact of ionizing  $\gamma$ -irradiation on powder solid samples of metal complexes, the present work aims to study the impact of  $\gamma$ -irradiation on some aryl amide bridged Schiff base metal complexes. Spectral, molar conductivity, magnetic susceptibility measurements, thermal and XRD of both non-irradiated and irradiated samples were studied. Moreover, the antioxidant activity of both non-irradiated and irradiated relative to ascorbic acid.

# Experimental

### Materials

All the reagents used were procured from Sigma-Aldrich Company. Metal salts (E. Merck) were used without additional purification. All solvents were used as received.

# Synthesis of H<sub>2</sub>L ligand

N,N'-(1,2-phenylene)bis(2-aminobenzamide) (S) has been prepared according to previous reported method [38]. The current H<sub>2</sub>L ligand: N,N'(1,2-phenylene)bis(2-(((Z)-(2-hydroxynaphthalen-1-yl)methylene)amino)benzamide) (Fig. 1) has been prepared by adding ethanolic solution (20 mL) of (S) (0.5 g, 0.144 mmol) to a solution of 2-hydroxy-1-naphthaldehyde in the same solvent (0.4976 g, 0.289 mmol) in 1:2 molar ratio, respectively. The reaction mixture was allowed to reflux with stirring about 12 h at 70–80 °C. The yellow solid product formed was isolated and washed many times with cold ethanol and dried over P<sub>4</sub>O<sub>10</sub>/CaCl<sub>2</sub>.



*N*,*N*'-(1,2-phenylene)bis(2-(((*Z*)-(2-hydroxynaphthalen-1-yl)methylene)amino)benzamide)

Fig. 1 Proposed structure of the ligand  $H_2L$ 

#### Synthesis of the metal complexes

0.5 g of (H<sub>2</sub>L) in 30 mL ethanol was magnetically stirred in a bottom flask to which a dropwise addition of ethanolic solution of CoCl<sub>2</sub>·6H<sub>2</sub>O, Co(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, Ni(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O, CuBr<sub>2</sub> and CuN<sub>2</sub>O<sub>6</sub>·3H<sub>2</sub>O for complexes (**1**–7), respectively in 1:1 molar ratio. The reaction mixture was heated under reflux near 12 h. The reaction progress was confirmed by thin-layer chromatography (TLC). The formed solid precipitate was removed by filtration, washed with ethanol several times, dried and stored in a desiccator at 25 °C under P<sub>4</sub>O<sub>10</sub>/CaCl<sub>2</sub> for further characterization.

#### **Physical measurements**

Microanalyses (carbon, hydrogen and nitrogen), metals and halide analyses, molar conductivity, magnetic measurements, FT-IR, electronic, proton magnetic resonance, EPR spectra and TG were all performed as described in the literature [36, 37, 39].

## **Irradiation studies**

For irradiation studies, powder samples of complexes 1, 3, 5 and 6 (hereafter referred to as 1F, 3F, 5F and 6F) were irradiated at dose of 100 kGy with the <sup>60</sup>Co  $\gamma$ -ray Indian at a dose rate of 2.2 kGy h<sup>-1</sup> cell type GE-4000 A. The samples were irradiated at 25 °C in the absence of air, at the Atomic Energy Authority of Egypt, Nasr City. For the irradiated samples the FT-IR, electronic, EPR, XRD spectra, molar conductance, magnetic measurements and TG were performed by the same methods used for the non-irradiated complexes [36, 37].

### **Antioxidant study**

The antioxidant property of the ligand, non-irradiated complexes (1, 3, 5 and 6) and their corresponding irradiated samples (1F, 3F, 5F and 6F) was evaluated by 1,1'-diphenyl-2-picrylhydrazyl (DPPH) method [40] and compared with standard (Ascorbic acid). To a different concentrations (100, 150 and 200 µg mL<sup>-1</sup>) in dimethylsulphoxide (DMSO) of each sample solutions (2 mL), a solution of 400 µM DPPH (2 mL) in methanol was added. The mixture was allowed to stand in the dark 25 °C for 30 min. The absorbance values of the mixture were then recorded at 517 nm. The percentage of inhibition of the DPPH radical (%) was calculated using equation reported elsewhere [40].

# **Results and discussion**

#### **Microanalyses and molar conductance**

The ligand H<sub>2</sub>L i.e.: N, N' (1,2-phenylene)bis(2-(((Z)-(2-hydroxynaphthalen-1-yl)methylene)amino)benzamide) was allowed to react with some transition metal(II) salts, in 1:1 molar ratio to yield the current complexes (1-7). All isolated complexes are colored and air stable. They are partially soluble in most popular organic solvents by heating but readily soluble in DMSO and dimethylformamide (DMF). The elemental and physical data of the ligand and its complexes were tabulated in Table 1. Microanalyses data showed that all complexes are formed in 1M:1L molar ratio and agree well with the suggested formula.

Conductivity measurements of  $10^{-3}$  M solutions of the complexes in DMF at 25 °C were recorded and the data are given in Table 1. All complexes have molar conductance values in the range of 1–34  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> and are non-electrolytic in nature [41].

## Color and molar conductivity of irradiated complexes

Upon irradiation, color change was observed only for cobalt(II) complex (1). Its color changed from red to brown after  $\gamma$ -irradiation (1F). This change in color may be owing to surface changes generated by  $\gamma$ -irradiation [4]. The metal complexes exposed to  $\gamma$ -irradiation showed slight change in values of  $\Lambda_m$  and there is no alteration in their non-electrolytic behavior (Table 1) [41].

#### **Spectroscopic studies**

#### Proton nuclear magnetic resonance spectrum of the ligand

The spectrum (<sup>1</sup>H-NMR) of the ligand was measured in DMSO- $d_6$  solution. <sup>1</sup>H-NMR spectrum showed singlet at  $\delta = 15.41$  ppm corresponding to –OH protons which corresponds to two protons. Singlet at  $\delta = 10.42$  ppm is corresponded to the amide (-CO-NH-) protons, with integration intensity equivalent to two hydrogens and the appearance of a singlet at  $\delta = 8.97$  ppm is owing to imine proton (-CH=N-) which integrated to two protons [23–25]. Additionally, the <sup>1</sup>H-NMR spectrum exhibits a multiplets at  $\delta = 6.7 - 8.21$  ppm corresponding to aromatic protons. Thus, the <sup>1</sup>H-NMR data confirm the proposed structure (Fig. 1).

 $(A_{\rm m})^{\rm a}$  irradiated  $(A_{\rm m})^{\rm a}$  nonirradiated Cl/Br 7.86/7.70 7.70/7.81 Σ 7.48/7.60 6.97/6.58 8.56/9.00 z 4.587/4.60 Microanalysis calcd./F% 4.27/4.35 4.73/4.60 Η 67.29/67.26 62.77/61.96 77.06/77.60 temp./°C Decomp. 210 150 170 150 170 170 170 Empirical formula yield (%)  $C_{42}H_{32}N_4O_6Co(74)$  $C_{42}H_{38}N_4O_9Co(91)$ C<sub>42</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub> (90) Bright yellow Dark red Color Red  $[Co(L)(H_2O)_2] \cdot 3H_2O$ [Co(L)]·2H,O Compound . No

Table 1 Physical and microanalyses data for the investigated compound

24 34

24 34

8.61/8.30

7.70/7.20 5.93/6.88

5.79/7.38 5.01/6.13 7.09/7.37

7.71/7.82

7.30/7.40

17.15/17.5

8.04/8.69

4.56/4.70 3.86/3.78

63.84/64.29

 $C_{42}H_{36}N_4O_9Br_2Cu(85)$  $C_{42}H_{34}N_4O_6CI_2Cu(64)$ 

> Dark brown Dark yellow

 $Cu(H_2L)Br_2(H_2O)_2] \cdot H_2O$ 

6

[Cu(H,L)Cl,(H,O),]  $Ni(L)(H_2O)_2] \cdot H_2O$ Ni(H<sub>2</sub>L)Cl<sub>2</sub>]·H<sub>2</sub>O

[Cu(L))H,O),J·2H,O

Dark brown

Orange

Red

C<sub>42</sub>H<sub>36</sub>N<sub>4</sub>O<sub>8</sub>Cu(78)

17 L

3

8.68/8.50

7.523/7.81

7.32/7.32

4.18/3.90 4.43/3.85 4.12/3.58

65.91/65.41 65.73/65.49 61.12/60.94 54.12/53.93

 $C_{42}H_{32}N_4O_6Cl_2Ni(83)$ 

 $C_{42}H_{34}N_4O_7Ni(95)$ 

cm<sup>2</sup> mol<sup>-1</sup> DMF solution in 10<sup>-3</sup> M solution  $^{a}\Omega^{-1}$ 

No.	Compound	ν(OH/NH)	ν(C=N)	ν(C–O)	ν(M–O)	ν(M–N)	$\lambda_{\max}$ (nm)	(B.M.)
	H <sub>2</sub> L	3412, 3241(b)	1623(s)	1284(m)	_	_	461, 444, 366, 321	_
1	[Co(L)]·2H <sub>2</sub> O	3429(b)	1613(s)	1209 (w)	563(w)	472(w)	460, 435, 320	3.15
1F	$[Co(L)] \cdot 2H_2O$	3433(b)	1615(s)	1210(s)	542(s)	495(s)	458, 432, 319	3.15
2	$[Co(L)(H_2O)_2]\cdot 3H_2O$	3419(b)	1603(s)	1260(m)	566(m)	495(m)	486, 454, 430, 328	2.59
3	[Ni(H <sub>2</sub> L)Cl <sub>2</sub> ]·H <sub>2</sub> O	3425(b)	1613(s)	1270(m)	562(w)	433(w)	466, 441, 321	dia
3F	[Ni(H <sub>2</sub> L)Cl <sub>2</sub> ]·H <sub>2</sub> O	3433(b)	1615(s)	1284(s)	539(s)	496(s)	462, 440, 360, 320	dia
4	$[Ni(L)(H_2O)_2] \cdot H_2O$	3425(m)	1605(s)	1210(m)	572(m)	424(m)	458, 445, 323	3.60
5	$[Cu(H_2L)Cl_2(H_2O)_2]$	3416(b)	1608(s)	1286(m)	563(w)	437(w)	465, 442, 365, 319	2.12
5F	$[Cu(H_2L)Cl_2(H_2O)_2]$	3431(b)	1616(s)	1284(s)	539(s)	471(s)	462, 440, 365, 320	2.12
6	$[Cu(H_2L)Br_2(H_2O)_2] \cdot H_2O$	3431(b)	1611(s)	1284(m)	586(w)	450(w)	475, 446, 325	2.10
6F	$[Cu(H_2L)Br_2(H_2O)_2] \cdot H_2O$	3431(b)	1614(s)	1285(s)	539(s)	498(s)	471, 445, 365, 335	2.10
7	$[Cu(L)(H_2O)_2] \cdot 2H_2O$	3415(b)	1607(s)	1274(m)	550(w)	467(w)	457, 445, 350, 323	2.10

**Table 2** FT-IR (cm<sup>-1</sup>), UV/vis ( $\lambda_{max}$ , nm) and magnetic susceptibility data ( $\mu_{eff}$ , B.M.) of the compounds

s strong, m medium, w weak, b broad

## FT-IR

The characteristic FT-IR spectral data of the obtained compounds are summarized and given in Table 2. In the infrared spectrum of H<sub>2</sub>L the occurrence of peaks at 3412 and 3241 cm<sup>-1</sup> is attributable to  $\nu$ (OH) and  $\nu$ (NH) vibration modes, respectively. The strong band appeared at 1623 cm<sup>-1</sup> in the spectrum of the ligand is owing to imine group vibration. The lowering of imine frequency value in all complexes 1603–1613 cm<sup>-1</sup> indicates the involvement of imine nitrogen in the coordination [24]. The naphthalic  $\nu$ (C–O) vibration band in the free ligand appeared at 1284 cm<sup>-1</sup>. The shift of this band to lower frequency 1209–1274  $\text{cm}^{-1}$  in metal complexes (1, 2, 4 and 7) emphasis the coordination through deprotonated oxygen atom [12]. New observed band at about  $586-550 \text{ cm}^{-1}$ is consistent with  $\nu$ (M–O) vibrations. Another new band at about 495–433 cm<sup>-1</sup> was attributed to  $\nu$ (M–N) vibrations [30]. The presence of water of crystallization and/or coordination in the compounds structure, as indicated by microanalysis data, render it difficult to get information from  $\nu(OH)$  of the H<sub>2</sub>L ligand which will be interfered by those of water molecules. Therefore, the above arguments confirmed that the ligand coordinates as a dibasic tertradentate one in complexes (1, 2, 4, 7) ligates through the imine nitrogen atoms and the oxygen atoms of the deprotonated hydroxyl groups or as a neutral bidentate one in complexes (3, 5, 6) with imine nitrogen atoms.

#### FT-IR of irradiated complexes

By comparing the FT-IR spectra of non-irradiated and irradiated complexes (Fig. 2a, b; Table 2), it is noted that, medium intensity band centered around 1670 cm<sup>-1</sup> was appeared in the FT-IR spectra of all irradiated complexes

except for complex (1F). This peak may be due to the existence of ketoamine-enolimine toutomerism in these complexes due to transformation of the ligand molecule induced by  $\gamma$ -irradiation [23, 42]. The absence of this peak in the infrared spectrum of complex (1F) obviously confirms the deprotonation of naphtholic hydroxyl groups. In addition, pronounced changes in the intensities as well as position of some characteristic peaks are observed. The broad bands of  $\nu$ (OH/NH) in the irradiated complexes (1F, 3F, 5F) are observed at higher energy (Table 2). The imine stretching vibration was shifted to higher energy to the extent of 8 cm<sup>-1</sup> in some irradiated complexes. For bands corresponding to the  $\nu$ (M–O), these bands were shifted to lower energy upon  $\gamma$ -irradiation whereas the bands due to the  $\nu$ (M–N) were shifted to higher energy. The shift observed in the FT-IR bands may be owing to the deformity of lattice planes induced by  $\gamma$ -irradiation [4].

# UV-visible spectral studies and magnetic susceptibility measurements

The UV/vis spectra of the ligand and its complexes were done in DMF solution. The absorption bands showed by the compounds alongside with their magnetic susceptibility data at 25 °C ( $\mu_{\text{eff}}$  B.M.) are collected in Table 2. The electronic absorption spectrum of the free ligand shows strong absorption bands with maxima at 321, 366, 444–461 nm, respectively. The first absorption with maxima at 321 nm is assigned to the  $\pi \rightarrow \pi^*$ , transition through the aromatic rings, imine and carbonyl groups. The other bands 366, 444–461 nm are attributed to the  $n \rightarrow \pi^*$  transition between the lone pair of electrons of the imine and carbonyl groups and the conjugated  $\pi$  bond of the aromatic rings and charge transfer (CT) band [26].



Fig. 2 a FT-IR spectra of complexes (1, 1F) and b FT-IR spectra of complexes (5, 5F)

The UV/vis spectrum of Co(II) complex (1) displays bands with maxima at 460–435 nm which may be due to ligand–metal charge transfer (LMCT) transition. The value of magnetic moment is 3.15 B.M., so square planar geometry was suggested for this complex [43]. Complex (2) has electronic transition bands at 486–454 nm which may be correlated to  ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(P)$  transition, its magnetic moment value is 2.59 B.M., confirming the low spin octahedral configuration [26, 44].

The UV/vis spectrum of nickel(II) complex (3) displays bands with maxima at 466–441 nm which correspond to LMCT transition that hides the d–d transition. The diamagnetic behavior of this complex confirms its square planar geometry [43]. Nickel(II) complex (4) exhibits band at 458–445 nm which corresponds to LMCT transition. The  $\mu_{eff}$  of this complex recorded at room temperature is 3.6 B.M., confirming the octahedral configuration [26].

The copper(II) complexes (5, 6, 7) showed UV/vis broad spectral bands within 475–457 nm range due to LMCT transition in a distorted octahedral configuration.

The  $\mu_{\text{eff}}$  of all copper complexes is 2.10 B.M., that is correlated to the existence of one unpaired electrons [45].

#### UV-visible spectral studies of irradiated complexes

Comparing the electronic spectra of irradiated complexes with that of non-irradiated complexes we observed that, for irradiated [Co(L)].2H<sub>2</sub>O (**1F**) the broad peaks corresponded to LMCT transitions at 458, 432 nm were recorded with a small shift in  $\lambda_{max}$  to higher energy side to the extent of 1–3 nm with no change in the measured magnetic moment value of the irradiated sample (3.15 B.M), indicating that there is no change in the geometry upon  $\gamma$ -irradiation and the observed color change (brown) is due to surface changes and deformation of the complex structure as a result of  $\gamma$ -irradiation [43]. When the LMCT band of irradiated [Ni(H<sub>2</sub>L)Cl<sub>2</sub>]·H<sub>2</sub>O complex (**3F**) is compared with that of non-irradiated [Ni(H<sub>2</sub>L)Cl<sub>2</sub>]·H<sub>2</sub>O (**3**), the LMCT band, slightly shifted to higher energy side at 462, 440 nm was observed in complex (**3F**). Also the diamagnetic behavior of the irradiated complex confirms its square planar geometry so, there is no change in the configuration after  $\gamma$ -irradiation [43]. The electronic spectra of the irradiated (**5F**) and (**6F**) complexes also exhibited hypsochromic shift in electronic absorption peaks. Also there is no change in the magnetic moment values (2.10, 2.10 B.M.) for these complexes indicating that there is no configuration change after  $\gamma$ -irradiation.

# EPR spectra of non-irradiated and irradiated copper(II) complexes

The room temperature (300 K) EPR spectra of the non-irradiated Cu(II) complex (6) and its irradiated (6F) were performed on the X-band frequency 9.719 GHz. By comparing, the EPR spectra of both non-irradiated and irradiated sample were seen to be quite similar except slight decrease in the intensity of the perpendicular component of the irradiated sample (Fig. 1S). Both spectra displayed the parallel and the perpendicular features indicating axially symmetric anisotropy spectra. The g-tensor parameters with  $g_{//}=2.197$  and  $g_{\perp} = 2.026$  for complex (6) and  $g_{//} = 2.190$ ,  $g_{\perp} = 2.036$  for complex (6F) i.e.  $g_{1/2} > g_{1/2} > 2.0023$ , indicated that the Cu(II) center has a tetragonal distorted geometry with  $d_{x2-y2}$  ground state for both samples [46]. The  $g_{//}$  is less than 2.3 suggesting covalent bond character around the Cu(II) ion. The exchange interaction parameter  $G = g_{1/2} - 2.0023/g_{\perp} - 2.0023$ for complexes (6, 6F) is higher than 4 (7.579) for complex (6) and (6.333) for complex (6F)) suggesting no exchange coupling in the solid state. The bonding coefficients  $\alpha^2$ (covalent in-plane  $\sigma$ -bonding),  $\beta^2$  and  $\gamma^2$  (covalent in-plane and out-of-plane  $\pi$ -bonding) have been computed for both non-irradiated and irradiated samples, using Eqs. (2) and (3) [47, 48].

$$\alpha^2 = \frac{A_{//}}{0.036} + (g_{//} - 2.0023) + \frac{3}{7}(g_\perp - 2.0023) + 0.04 \quad (2)$$

$$\beta^2 = (g_{//} - 2.0023)E/8\lambda\alpha^2 \tag{3}$$

where  $(\lambda = -828 \text{ cm}^{-1})$  and *E* is the electronic transition energy. The smaller value of  $\alpha^2$  (0.558, 0.5249) compared to  $\beta^2$  (1.107, 1.146) showed that the in-plane  $\sigma$ -bonding has greater covalent bond character than the in-plane  $\pi$ -bonding. The values of  $\gamma^2$  are 0.992 for complex (**6**), 1.021 for complex (**6F**). For complex (**6F**)  $\gamma^2 > 1$  shows considerable ionic character of the out-of-plane  $\pi$ -bonding.

The parallel  $K_{//}$  and perpendicular  $K_{\perp}$  components of orbital reduction factors were calculated by the expressions notified elsewhere [49]. The complexes (**6**, **6F**) showed  $K_{//}$ ,  $K_{\perp}$  in the order  $K_{//} > K_{\perp}$  due to considerable out-of-plane  $\pi$ -bonding [49]. The small values of K (0.641, 0.613) suggest

the covalent character of the complexes [50]. The quotient  $f = g_{//} A_{//}$  gives value of 194, 193 cm which correlated to a marked distortion around the copper(II) site.

#### **Thermal studies**

Thermal properties have been carried out using TGA, at heating rate 10 °C min<sup>-1</sup> in N<sub>2</sub> atmosphere from RT-800 °C using platinum crucible. The results of the thermal analysis for both non-irradiated and  $\gamma$ -irradiated metal complexes are shown in Table 3. The TG thermograms of non-irradiated and irradiated complexes have nearly the similar profile, it is seen that the desolvated non-irradiated and irradiated complexes decomposed in two or three steps.

The TG curve of Co(II) complex (1) (Fig. 3a) shows mass loss of 4.8 (Calc. 4.8%) within the region 25–150 °C, which agrees well with elimination of two water molecules. The TG thermogram also reveals that complex (1) decomposed at 150 °C giving Co metal as a final residue. The TG curve of Co(II) complex (2) shows weight loss of 6.72 (Calc. 6.72%) due to the removal of three water molecules in RT-170 °C range. The coordinated water molecules were removed with decomposition steps, where a gradual weight loss appeared in 170–600 °C range, and CoO as is remain as a final residue.

The TG thermograms of Ni(II) complexes (3, 4) (Fig. 3a) displays weight loss of 2.3 (Calc. 2.3%) and 2.3 (Calc. 2.3%), respectively within RT-150 °C range, corresponding to removal of one hydrated water molecule for both complexes, after that the TG curves show that complex (3) starts degradation at 150 °C, whereas complex (4) decomposed at 270 °C, followed by the oxidation to nickel oxide for both complexes.

The TG thermogram of Cu(II) complex (5) (Fig. 3b) shows no weight loss till 170 °C, confirming the absence of  $H_2O$  or solvent molecules outside coordination sphere. However, The TG thermograms of Cu(II) complexes (6, 7) (Fig. 3b) show weight loss of 1.93 (Calc. 1.93%) in the 25–110 °C range; 4.5 (Calc. 4.5%) in the 25–170 °C range, respectively correlated with release of one hydrated water molecule (complex 6), two water molecules (complex 7). The complexes (5, 7) start the decomposition process at 170 °C, while complex (6) decomposed at 160 °C. The decomposition process ended with the air stable CuO as end product for all Cu(II) complexes.

#### Thermal properties of irradiated complexes

To highlight the impact of  $\gamma$ -rays on the thermal behavior of irradiated complexes, their TG thermograms were also recorded (Table 3). The TG curve of irradiated Co(II) complex (**1F**) (Fig. 3a) shows mass loss of 4.8 (Calc. 4.8%) in the 25–150 °C range which corresponds to the elimination

Table 3TGA data of thecompounds

No	Compound	Temp. range/°C	Mass loss%		Reaction
			Calc.	F.	
1	[Co(L)]·2H <sub>2</sub> O	25-150	4.807	4.807	-2H <sub>2</sub> O
		150-700	86.37	86.37	-decomp.
		at 700	8.823	8.901 <sup>a</sup>	≡Co
1F	$[Co(L)] \cdot 2H_2O$	25-150	4.807	4.807	$-2H_2O$
		170-800	88.70	88.70	-decomp.
		at 800	6.493	6.810 <sup>a</sup>	≡Co
2	$[Co(L)(H_2O)_2]\cdot 3H_2O$	25-170	6.725	6.725	$-3H_2O$
		170-270	4.475	4.48	$-2H_2O$
		270-600	76.50	76.50	-decomp.
		at 600	12.30	12.50 <sup>a</sup>	≡CoO
3	$[Ni(H_2L)Cl_2]\cdot H_2O$	25-150	2.353	2.353	$-H_2O$
		150-700	89.90	89.90	-decomp.
		at 700	7.747	7.810 <sup>a</sup>	≡NiO
3F	$[Ni(H_2L)Cl_2]\cdot H_2O$	25–90	2.353	2.353	$-H_2O$
		190–550	91.20	91.20	-decomp.
		at 550	6.447	6.515 <sup>a</sup>	≡Ni
4	$[Ni(L)(H_2O)_2] \cdot H_2O$	25-150	2.347	2.347	$-H_2O$
		270-600	87.64	87.64	-decomp.
		at 600	10.01	10.01 <sup>a</sup>	≡NiO
5	$[Cu(H_2L)Cl_2(H_2O)_2]$	170-800	91.00	91.50	-decomp.
		at 800	9.000	$8.500^{a}$	$\equiv$ CuO
5F	$[Cu(H_2L)Cl_2(H_2O)_2]$	180-620	92.29	92.68	-decomp.
		at 620	7.701	7.311 <sup>a</sup>	$\equiv Cu$
6	$[Cu(H_2L)Br_2(H_2O)_2] \cdot H_2O$	25-110	1.932	1.932	$-H_2O$
		160-800	89.30	90.00	-decomp.
		at 800	8.768	8.068 <sup>a</sup>	≡CuO
6F	$[Cu(H_2L)Br_2(H_2O)_2] \cdot H_2O$	25-110	1.932	1.932	$-H_2O$
		190–650	91.25	91.17	-decomp.
		at 650	6.818	6.901 <sup>a</sup>	≡Cu
7	$[Cu(L)(H_2O)_2] \cdot 2H_2O$	25-170	4.559	4.559	$-2H_2O$
		170-570	85.37	85.37	decomp.
		at 570	10.07	10.07 <sup>a</sup>	≡CuO

<sup>a</sup>Final percent

of two hydrated water molecules. The complex starts decomposition at 170 °C and the residual part was Co metal. The complete sublimation of the organic ligand finished at 800 °C whereas for non-irradiated complex the sublimation process finished at 700 °C.

The TG curve of irradiated Ni(II) complex (**3F**) (Fig. 3a) displays mass loss of 2.3 (Calc. 2.3%) in the 25–90 °C range, which agrees well with the elimination of one hydrated water molecule. By comparison, complex (**3F**) lost its water molecule at lower temperature than complex (**3**). The complex progressively decomposed at 190 °C, leaving Ni as a final end residue. The decomposition process of irradiated (**3F**) finished at 550 °C, while for non-irradiated sample it completely finished at 700 °C.

The TG thermogram of Cu(II) complex (**5F**) (Fig. 3b) also shows no weight loss till 180 °C, confirming the absence of  $H_2O$  or solvent of crystallization. However, The TG thermogram of Cu(II) complex (**6F**) (Fig. 3b) shows mass loss of 1.93 (Calc. 1.93%) in the 25–110 °C range related to release of one hydrated water molecule. The complexes (**5F**, **6F**) start the decomposition process at 180, 190 °C, the sublimation of the organic ligand ended at 620 and 650 °C, respectively leaving Cu as final decomposition product. This indicates that irradiation enhances the thermal stability for the irradiated complexes (**3F**, **5F**, **6F**), this may be related to the intramolecular and/or intermolecular hydrogen bonds present in ketoamine –enolimine forms of these complexes [**35**].



Fig. 3 a TG curves of non-irradiated complexes (1 and 3) and their irradiated (1F and 3F) and b TG curves of non-irradiated complexes (5 and 6) and their irradiated (5F and 6F)



Fig. 4 XRD patterns of non-irradiated complexes (5 and 6) and their irradiated (5F and 6F)

## X-ray diffraction studies of non-irradiated and irradiated complexes

The X-ray diffractograms for copper(II) complexes (5, **5F**) and (6, **6F**) before and after irradiation are given in Fig. 4. It is noted that all samples are found to have very

few reflections indicating their amorphous nature [37]. The intensity of powder lines of irradiated Cu(II) complex (**6F**) is found to be slightly different from non-irradiated sample (**6**). While for (**5**, **5F**) the intensities of powder lines are almost the same.



Fig. 5 3D structure of  $[\rm Ni(\rm H_2L)Cl_2]\cdot\rm H_2O$  (3) (protons are omitted for simplicity)

# Molecular modeling studies of ligand and its Ni(II) complex (3)

The model geometric structure of the ligand (Fig. 2S) and its [Ni(H<sub>2</sub>L)Cl<sub>2</sub>]·H<sub>2</sub>O complex (3) (Fig. 5) was achieved utilizing Hyper Chem Sketch 15.0 version [51]. The selected bond lengths and bond angles of significant importance were computed and the data are reported in Tables 1S, 2S. The bond lengths of the azomethine (C=N): N(32)–C(34), and N(31)-C(33) for the ligand are 1.262 and 1.267 Å, respectively. Upon chelation, the bond length of these groups altered to 1.267 and 1.289 Å. The bond lengths become somewhat longer confirming the chelation with Ni(II) ion which occurs via N atoms of the two imine (>C=N)groups. Other changes have been noted in other bond lengths. The actual bond angles of the azomethine (C=N): C(34)-N(32)-C(30) and C(33)-N(31)-C(21) for the ligand are 119.04° and 133.24°, respectively. These bond angles in the complex changed to 123.23 and 120.11°. The values of bond angles (Tables 1S, 2S) confirmed that Ni(II) ion has square planar configuration [36, 48].

Based on the above discussions, the possible structures for the metal complexes are shown in Fig. 6a, b.

# Antioxidant activity of non-irradiated and irradiated samples

The antioxidant property of the synthesized ligand (H<sub>2</sub>L) and its non-irradiated (1, 3, 5, 6) and irradiated (1F, **3F**, **5F**, **6F**) complexes were determined by their scavenging ability on the stable 1,1'-diphenyl-2-picrylhydrazyl (DPPH) free radical [40]. As depicted in Fig. 7, the calculated IC<sub>50</sub> values = 253.15, 292.32, 75.13, 20.00, 41.28  $\mu$ g mL<sup>-1</sup> for H<sub>2</sub>L, 1, 3, 5, 6, respectively



Fig. 6 a Structure of the complexes  $(1,\,2,\,4$  and 7) and b structure of the complexes  $(3,\,5$  and 6)

these values demonstrated that the non-irradiated complexes have greater antioxidant activities than their free ligand except for complex (1). Among the series studied, Cu(II) complex (5) possesses excellent antioxidant activity ( $IC_{50} = 20.00 \ \mu g \ mL^{-1}$ ) better than ascorbic acid ( $IC_{50} = 28.21 \ \mu g \ mL^{-1}$ ). This confirmed the potential value of metal ion in improving the antioxidant activity of the ligand [52, 53]. The scavenging activity of the non-irradiated compounds is in the order:



Fig. 7  $IC_{50}$  plot of the ligand, non-irradiated, irradiated compounds and ascorbic acid as standard

 $\label{eq:cu(II)(5)} \mbox{Cu(II)(5)} > \mbox{Ascorbic acid} > \mbox{Cu(II)(6)} > \mbox{Ni(II)(3)} > \mbox{H}_2\mbox{L} > \mbox{Co(II)(1)}$ 

It is worth to notify that  $\gamma$ -irradiation leaded to noteworthy change in the values of the antioxidant activity. The irradiated samples (**1F**, **3F**, **5F**, **6F**), with IC<sub>50</sub> values 22.08, 153.03, 73.57, 196.57 µg mL<sup>-1</sup>, respectively and based on data on Fig. 7, it was seen that the IC<sub>50</sub> of complex (**1F**) was enhanced upon  $\gamma$ -irradiation it presents an excellent antioxidant activity better than ascorbic acid (IC<sub>50</sub> = 28.21 µg mL<sup>-1</sup>). Other exposed metal complexes showed decrease in their antioxidant activity but still better than their non-irradiated free ligand. The antioxidant scavenging activity after irradiation is in the order

$$\begin{split} & \text{Cu(II)}(\mathbf{1F}) > \text{Ascorbic acid} > \text{Cu(II)}(\mathbf{5F}) > \\ & \text{Ni(II)}(\mathbf{3F}) > \text{Co(II)}(\mathbf{6F}) > \text{H}_2\text{L} \end{split}$$

This pronounced property of the complexes may be due to the chelating function of the organic ligand to the metal ions [33]. The higher antioxidant activity of complexes (3, 5, 6)than complex (1) may be due to the significant contribution of the hydroxyl groups [35]. The increased free radical scavenging action of the irradiated complex (1F) can be assigned to the surface changes generated by  $\gamma$ -irradiation which may facilitate the release of hydrogen atom or an electron to reduce the DPPH radical [35]. However, the decreased free radical scavenging action of the irradiated complexes (3F, 5F, 6F) may be related to the intramolecular and/or intermolecular hydrogen bonds present in ketoamineenolimine toutomeric forms of these complexes that dislikes the DPPH scavenging activity, due to the enhanced binding of the hydrogen atoms. It was known that the H-bond increases the structure stability, thus, the energy required to

☑ Springer

remove the hydrogen atom from it is higher than in the non H-bonded one [35].

### Conclusion

In our study, the impact of  $\gamma$ -ray irradiation on the physicochemical properties of some aryl amide Schiff base Co(II), Ni(II) and Cu(II) complexes was investigated by different analytical, spectral, thermal and XRD tools. The results showed the rigidity of the complexes to the applied dose and can be summarized as follows:

- 1. Change in color was observed in the irradiated Co(II) complex (1F).
- 2. New FT-IR side peaks, slight change in position, shape and intensity of some FT-IR peaks were appeared after irradiation in some irradiated complexes.
- 3. No change in geometry was observed.
- 4. XRD patterns of both non-irradiated and irradiated complexes indicated their amorphous nature.
- 5. TGA results suggested that  $\gamma$ -irradiation enhanced the dehydration process for Co(II) complex (1F) and increases the thermal stability for complexes (3F, 5F, 6F).
- Antioxidant activity was enhanced by γ-irradiation for Co(II) complex(1F).

#### **Compliance with ethical standards**

**Conflict of interest** Authors have declared that no conflicts of interest exist.

# References

- Abd El-Wahab MMM, Mahfouz RM (1996) Gamma irradiation effects on the electrical conductivity behaviour and thermal decomposition induction period in nickel oxalate. Thermochim Acta 274:281–287
- El-Sayed SM, Amer MA, Meaz TM, El-Shershaby HA (2014) Radiation effect on optical, morphological and magnetic properties of aluminum-substituted M phase barium hexaferrite. Radiat Eff Defects Solids 169:1045–1055
- Krishnan G, Jayashri TA, Geetha Devi K (2009) Effect of gamma radiation on thermal decomposition, X-ray diffraction and electronic spectra of nickel(II) complexes of diethylenetriamine, pyridine and 2-amino pyridine. Radiat Phys Chem 78:184–190
- Jayashri TA, Krishnan G, Viji K (2014) Effect of γ-irradiation on non-isothermal decomposition kinetics, X-ray diffraction pattern, infrared spectrum and antibacterial property of tris(1,2 diaminoethane) nickel(II) oxalate. J Radioanal Nucl Chem 302:1021–1026

- 5. Krishnan G, Jayashri TA, Sudha P (2009) Thermal, X-ray diffraction and electronic spectral studies of gamma irradiated nickel(II) complexes of ethylenediamine, triethylenetetramine and *o*-toluidine. Radiat Phys Chem 78:933–938
- Jayashri TA, Viji K (2018) Spectral, X-ray diffraction, surface morphological and thermal studies of gamma-irradiated potassium bis(oxalato)zincate(II) dehydrate. Radiat Eff Defect Solids 173:986–995
- Angadi VJ, Anupama AV, Kumar R, Choudhary HK, Matteppanavar S, Somashekarappa HM, Rudraswamy B, Sahoo B (2017) Composition dependent structural and morphological modifications in nanocrystalline Mn-Zn ferrites induced by high energy γ-irradiation. Mater Chem Phys 199:313–321
- 8. Jayashri TA, Krishnan G, Viji K (2017) Spectral, thermal and antimicrobial studies of gamma irradiated potassium diaquabis (oxalato) cobaltate(II). Orient J Chem 33:371–377
- Sumithra IS, Jayashri TA, Krishnan G (2015) X-ray diffraction, spectral, thermal and surface morphological studies of gammairradiated diaquamalonatomanganese(II) (DMM). J Radioanal Nucl Chem 307:835–842
- Abou Sekkina MM, El-Boraey HA, Aly SA (2014) Further studies on the properties and effect of high energetic ionizing radiation on copper(II) complexes: <sup>1</sup>H NMR, electronic absorption, ESR spectra and solid electrical conductivity. J Radioanal Nucl Chem 300:867–872
- 11. Abou-Sekkina MM, Elsheikh MY (1986) Effects of gamma radiation doses on the infrared absorption spectra of solid transition metal complexes. Isot Environ Health Stud 22:17–20
- Yakalı G, Çakıcı A, Eke C, Cin GT, Aygün M (2017) Synthesis, spectroscopic and X-ray structural characterization, quantum chemical studies and investigation of gama-irradiated effects of the novel hydrazone compound: [(E)-3-(2-nitrophenyl)-(E)-1-(2-phenylhydrazono)]-1- phenylallylidene. J Mol Struct 1134:244–252
- 13. Refat MS, Sharshar T, Elsabawy KM, Heiba ZK (2013) Physicochemical impact studies of gamma rays on "aspirin" analgesics drug and its metal complexes in solid form: synthesis, spectroscopic and biological assessment of Ca(II), Mg(II), Sr(II) and Ba(II) aspirinate complexes. J Mol Struct 1047:37–47
- Samuel J, Surendran A, Culas S (2013) Kinetic analysis for non-isothermal decomposition of un-irradiated and gamma-irradiated potassium bromate. J Radioanal Nucl Chem 295:53–61
- El-Shobaky HG, El-Mohsen A, Turky M (2002) Effect of gamma-irradiation on surface and catalytic properties of Co<sub>3</sub>O<sub>4</sub> and NiO catalysts. J Radioanal Nucl Chem 254(1):151–158
- 16. Marzouka MA, ElBatala FH, Abdelghanyb AM (2013) Ultraviolet and infrared absorption spectra of Cr<sub>2</sub>O<sub>3</sub> doped—sodium metaphosphate, lead metaphosphate and zinc metaphosphate glasses and effects of gamma irradiation: a comparative study. Spectrochim Acta 114:658–667
- Neacsu A, Gheorghe D, Marinescu C, Stancu E, Tecuceanu V, Ciuculescu C (2019) The effect of gamma rays upon L-proline and 4-hydroxy-L-proline. A thermochemical study. Radiat Phys Chem 156:115–127
- Yakalia G, Biçerb A, Ekec C, Cin GT (2018) Solid state structural investigations of the bis(chalcone) compound with single crystal X-ray crystallography, DFT, gamma-ray spectroscopy and chemical spectroscopy methods. Radiat Phys Chem 145:89–96
- Assar ST, Abosheiasha HF, El Sayed AR (2017) Effect of γ-rays irradiation on the structural, magnetic, and electrical properties of Mg–Cu–Zn and Ni–Cu–Zn ferrites. J Magn Magn Mater 421:355–367
- Barakat MF, El-Banna M (2013) Effects of gamma radiation on iron (III) complex with sodium salicylate in aqueous solutions. Arab J Nucl Sci Appl 46(5):100–105

- Aly SA, Elembaby D (2019) Synthesis, spectroscopic characterization and Study the effect of gamma irradiation on VO<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Ru<sup>3+</sup>, Pd<sup>2+</sup>, Ag<sup>+</sup> and Hg<sup>2+</sup> complexes and antibacterial activities. Arab J Chem. https://doi.org/10.1016/j.arabj c.2019.08.007
- 22. Angadi VJ, Anupama AV, Choudhary HK, Kumar R, Somashekarappa HM, Mallappa M, Rudraswamy B, Sahoo B (2016) Mechanism of  $\gamma$ -irradiation induced phase transformations in nanocrystalline Mn<sub>0.5</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> ceramics. J Solid State Chem 246:119–124
- Ajlouni AM, Taha ZA, Al-Hassan KA, Abu Anzeh AM (2012) Synthesis, characterization, luminescence properties and antioxidant activity of Ln(III) complexes with a new aryl amide bridging ligand. J Lumin 132:1357–1363
- Aljahdali MS, Abdou El-Sherif A, Hilal RH, Abdel-Karim AT (2013) Mixed bivalent transition metal complexes of 1,10-phenanthroline and 2-aminomethylthiophenyl-4-bromosalicylaldehyde Schiff base: spectroscopic, molecular modeling and biological activities. Eur J Chem 4(4):370–378
- Creaven BS, Duff B, Egan DA, Kavanagh K, Rosair G, Thangella VR, Walsh M (2010) Anticancer and antifungal activity of copper(II) complexes of quinolin-2(1H)-one-derived Schiff bases. Inorg Chim Acta 363:4048–4058
- Shebl M, Khalil SME, Al-Gohani FS (2010) Preparation, spectral characterization and antimicrobial activity of binary and ternary Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ce(III) and UO<sub>2</sub>(VI) complexes of a thiocarbohydrazone ligand. J Mol Struct 980:78–87
- 27. Tolia C, Papadopoulos AN, Raptopoulou CP, Psycharis V, Garino C, Salassa L, Psomas G (2013) Copper(II) interacting with the non-steroidal antiinflammatory drug flufenamic acid: structure, antioxidant activity and binding to DNA and albumins. J Inorg Biochem 123:53–65
- Shakir M, Hanif S, Alam MF, Younus H (2016) Molecular hybridization approach of bio-potent CuII/ZnII complexes derived from N, O donor bidentate imine scaffolds: synthesis, spectral, human serum albumin binding, antioxidant and antibacterial studies. J Photochem Photobiol B Biol 165:96–114
- El-Boraey HA, Abdel-Rahman RM, Atia EM, Hilmy KH (2010) Spectroscopic, thermal and toxicity studies of some 2-amino-3-cyano-1,5-diphenylpyrrole containing Schiff bases copper (II) complexes. Cent Eur J Chem 8(4):820–833
- Ejidike IP, Ajibade PA (2015) Synthesis, characterization, antioxidant, and antibacterial studies of some metal(II) complexes of tetradentate Schiff base ligand: (4E)-4-[(2-{(E)-[1-(2,4-dihydroxyphenyl)ethylidene]amino}ethyl)imino]pentan-2-one. Bioinorg Chem Appl 2015:890734
- Aboafia SA, Elsayed ShA, El-Sayed AKA, El-Hendawy AM (2018) New transition metal complexes of 2,4-dihydroxybenzaldehyde benzoylhydrazone Schiff base (H<sub>2</sub>dhbh): synthesis, spectroscopic characterization, DNA binding/cleavage and antioxidant activity. J Mol Struct 1158:39–50
- 32. El-Boraey HA, El-Salamony MA (2019) Transition metal complexes with polydentate ligand: synthesis, characterization, 3D molecular modelling, anticancer, antioxidant and antibacterial evaluation. J Inorg Organomet Polym Mater 29:684–700
- Zhang Y, Fang Y, Liang H, Wang H, Hu K, Liu X, Yi X, Peng Y (2013) Synthesis and antioxidant activities of 2-oxo-quinoline-3-carbaldehyde Schiff-base derivatives. Bioorg Med Chem Lett 23:107–111
- Ibrahim MM, Mersal GAM, Ramadan AM, Shaban SY, Mohamed MA, Al-Juaid S (2017) Synthesis, characterization and antioxidant/cytotoxic activity of oxovanadium(IV) complexes of methyliminodiacetic acid and ethylenediaminetetracetic acid. J Mol Struct 1137:742–755
- 35. Tadele KT (2017) Antioxidant activity of Schiff bases and their metal complexes: a recent review. J Pharm Med Res 3(1):73–77

- 36. Aly S, El-Boraey HA (2019) 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)acetohydrazide metal(II) complexes. J Mol Struct 1185:323–332
- El-Boraey HA, Mansour AI (2018) Synthesis, spectral and gamma ray irradiation studies on metal complexes of N,N'-naphthalene-1,8-diylbis(2-aminobenzamide). Inorg Nano-Met Chem 48:8–15
- Swamy SJ, Veerapratap B, Nagaraju D, Suresh K, Someshwar P (2003) Non-template synthesis of 'N4' di- and tetraamide macrocylic ligands with variable ring sizes. Tetrahedron 59:10093–10096
- West TS (1969) Complexometry with EDTA and related reagents, 3rd edn. DBH Ltd. Pools, London
- 40. Khan I, Ali S, Hameed S, Rama NH, Hussain MT, Wadood A, Uddin R, Ul-Haq Z, Khan A, Ali S, Choudhary MI (2010) Synthesis, antioxidant activities and urease inhibition of some new 1,2,4-triazole and 1,3,4-thiadiazole derivatives. Eur J Med Chem 45:5200–5207
- 41. Geary WG (1971) The use of conductivity measurements in organic solvents for the characterization of coordination compounds. Coord Chem Rev 7:81–122
- 42. Gutierrez K, Corchado J, Lin S, Chen Z, Piñero Cruz DM (2018) A non-innocent salen naphthalene ligand and its Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> metal complexes: structural, electrochemical, and spectroscopic characterization and computational studies. Inorg Chim Acta 474:118–127
- 43. Sherif OE, Abdel-Kader NS (2013) Spectroscopic and biological activities studies of bivalent transition metal complexes of Schiff bases derived from condensation of 1,4-phenylenediamine and benzopyrone derivatives. Spectrochim Acta A 117:517–526
- 44. Abdel-Rahman LH, Ismail NM, Ismael M, Abu-Dief AM, Ahmed EA (2017) Synthesis, characterization, DFT calculations and biological studies of Mn(II), Fe(II), Co(II) and Cd(II) complexes based on a tetradentate ONNO. J Mol Struct 1134:851–862

- 45. Franco E, Lopez-Torres E, Mendiola MA, Sevilla MT (2000) Synthesis, spectroscopic and cyclic voltammetry studies of copper(II) complexes with open chain, cyclic and a new macrocyclic thiosemicarbazones. Polyhedron 19:441–451
- 46. El-Boraey HA, El-Gammal OA (2015) New15-membered tetraaza (N<sub>4</sub>) macrocyclic ligand and its transition metal complexes: spectral, magnetic, thermal and anticancer activity. Spectrochim Acta A 138:553–562
- West DX, Yang Y, Klein TL, Goldberg KI (1995) Binuclear copper(II) complexes of 2-hydroxyacetophenone <sup>4</sup>N-substitutedthiosemicarbazones. Polyhedron 14:1681–1693
- El-Ghamry HA, Fathalla ShK, Gaber M (2017) Synthesis, structural characterization and molecular modelling of bidentate azo dye metal complexes: DNA interaction to antimicrobial and anticancer activities. Appl Organomet Chem 32:e4136
- El-Boraey HA, El-Din SA, El Sayed I (2017) New complexes with 19-membered pyridine-based macrocycle ligand. J Therm Anal Calorim 129:1243–1253
- El-Boraey HA, Emam SM, Tolan DA, El-Nahas AM (2011) Structural studies and anticancer activity of a novel (N<sub>6</sub>O<sub>4</sub>) macrocyclic ligand and its Cu(II) complexes. Spectrochim Acta A 78:360–370
- 51. Hyperchem sketch (2008) Release v15.0.0 for windows Molecular modeling system, Hypercube, Inc
- 52. Dharmaraja J, Balamurugan J, Shobana S (2017) Synthesis, structural elucidation, microbial, antioxidant and nuclease activities of some novel divalent M(II) complexes derived from 5-fluorouracil and L-tyrosine. J Saudi Chem Soc 21:S67–S76
- El-Gammal OA, Alshater H, El-Boraey HA (2019) Schiff base metal complexes of 4-methyl-1H-indol-3-carbaldehydederivative as a series of potential antioxidants and antimicrobial: synthesis, spectroscopic characterization and 3D molecular modeling. J Mol Struct 1195:220–230

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.