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Molecular modeling, spectral investigation and thermal studies of the new asymmetric Schiff base ligand; (E)-N'-(1-(4-((E)-2-hydroxybenzylideneamino)phenyl)ethylidene)morpholine-4-carbothiohydrazide and its metal complexes: Evaluation of their antibacterial and anti-molluscicidal activity

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Esam M. Emara, Plants Protection Researches Institute, Agricultural Researches Center, Giza, Egypt. Email: esamemara@ymail.com A new tetradentate asymmetric Schiff base ligand; (E)-N'-(1-(4-((E)-2hydroxybenzylideneamino)phenyl)ethylidene)morpholine-4-carbothiohydrazide (H<sub>2</sub>L) was prepared by consecutive condensation reactions between *p*-aminoacetophenone, salicylaldehyde and 4-morpholinethiosemicarbazide. The structures of the obtained ligand along with its Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Cr(III), Fe(III) and Ru(III) complexes were authenticated by different analytical and spectral techniques. The ligand behaves as a monobasic tetradentate one and chelates with metal ions through the deprotonated phenolic oxygen, imine nitrogen, thione sulfur and azomethine nitrogen atoms (ONNS chromophore). All nonelectrolyte metal complexes possess octahedral geometry, except Ni(II) and Cu(II) complexes (2, 3) which have tetra-coordinate structures. The thermal stability of metal complexes is higher than that of the free ligand and the general thermal degradation pathways were discussed based on thermogravimetric technique. The activation thermodynamic parameters as well as the order of reaction (n) were estimated from DTG curves by using Piloyan method. Thermogravimetric analyses and mass spectra of metal complexes confirm the number of solvents in their inner and outer spheres. Molecular modeling data were used to demonstrate the thermal decomposition pathways of the ligand and its metal complexes, confirming their chemical structures. The ESR spectra of Cu(II) complexes indicate that the unpaired electron is localized mainly in the  $d_{(x-y)}^{2}$  orbital with axial symmetry. Powder X-ray diffraction analyses for Co(II), Cu(II) and Ru(III) complexes (1, 3, 7) show that copper complex has a crystalline nature, whereas, cobalt and ruthenium complexes are amorphous. The ligand and its metal complexes were tested in vitro for their anti-molluscicidal activity against Eobania vermiculata. The results reveal that the investigated compounds have remarkable antimolluscicidal activities against the tested land snail with various sensitivity levels. The synthesized compounds were also screened in vitro for their antibacterial activity against Gram-positive bacteria; *Staphylococcus aureus* and Gram-negative bacteria; *Escherichia coli* and the results were compared with the activity of ceftriaxone. The data show that all investigated compounds display a high antibacterial activity against the tested bacterial strains with different inhibition degrees and the activity is significantly higher against *Staphylococcus aureus* than *Escherichia coli*.

#### **KEYWORDS**

antibacterial activity, anti-molluscicidal activity, molecular modeling, spectral investigation, thermal studies

## **1** | INTRODUCTION

Transition metal complexes derived from Schiff base ligands are one of the most exhaustively studied topic in coordination chemistry, due to their enhanced activities compared to other complexes.<sup>[1-5]</sup> Schiff base complexes show important physiological and pharmacological activities due to their favorable cell membrane permeability.<sup>[6-10]</sup> Metal complexes of Schiff bases have a wide variety of applications including biological, clinical, analytical applications, catalysis and organic synthesis.<sup>[11-13]</sup> Schiff bases of metal complexes have been designed and synthesized to explore their pharmacological activity, for instance finding applications as model analogs of certain metallo-enzymes. Thiosemicarbazones are of a considerable pharmacological interest since a number of their derivatives have shown a broad spectrum of chemotherapeutic properties.<sup>[14]</sup> The wide range of biological activities possessed by substituted thiosemicarbazones includes cytotoxic, antitumor, antibacterial, anti-molluscicidal and antiviral properties.<sup>[14-16]</sup> The linkage with metal ions enhances the biological properties of these ligands.<sup>[14]</sup> Eobania vermiculata is a harmful animal to a wide variety of plants such as; flowers, ornamental, fruits, vegetables and shrubs. This species may be controlled by using chemical pesticides. However, the usage of agrochemicals with high concentrations may cause mortality to non-target species. So, the snail combat with lower concentrations is required to avoid such risks.<sup>[15,16]</sup> In our continuing studies of the relationship between the biological activity and the structures of metal complexes derived from 4morpholinethiosemicarbazide moiety,<sup>[15,16]</sup> we have prepared and characterized nine metal complexes obtained from the new asymmetric Schiff base ligand; (E)-N-(1-(4-((*E*)-2-hydroxybenzylideneamino)phenyl)ethylidene) morpholine-4-carbothiohydrazide  $(H_2L)$ . The prepared compounds were investigated by elemental, spectral (mass, <sup>1</sup>H NMR, UV-Vis., ESR) studies, thermal analyses,

magnetic susceptibility, molecular modeling, X-ray diffraction and molar conductivity measurements.

## 2 | EXPERIMENTAL

## 2.1 | Materials and methods

The chemicals and solvents employed in this study were of analytical grade (Merck, Sigma Aldrich and BDH) and were used without purification.

A Perkin Elmer-2400 elemental analyzer was used to execute the elemental analyses (C, H, N and S) at Main Defense Chemical Laboratory. Metal ion contents of synthesized complexes were determined complexometrically and gravimetrically.<sup>[17]</sup> Mohr's method was carried out to assess the chloride content.<sup>[17]</sup> Shimadzu Op-2010 Plus spectrometer was employed to record Fast Atom Bombardment Mass Spectra (FAB-MS). Nicolet FT-IR spectrophotometer was utilized to perform infrared spectra within range (4000-400 cm<sup>-1</sup>). The <sup>1</sup>H NMR spectra were achieved by using DMSO- $d_6$  on a Varian Gemini 200 NMR spectrometer at 300 MHz. Perkin Elmer Lambda 4B spectrophotometer was used to do the electronic absorption spectra in Nujol mulls. Molar conductivity measurements were conducted in DMF solution (10<sup>-3</sup> M) by using CD6N Tacussel conductimeter. Bruker BioSpin GmbH had been used for recording the electron spin resonance (ESR) spectra in the X-band frequency 9.714 GHz on a microcrystalline powder with microwave power around 2.012 mW at room temperature. The thermal analyses (TG/DTG) were registered on a Shimadzu DAT/TG-50 thermal analyzer under nitrogen atmosphere with a flowing rate of 20 ml/min within range (25–900 °C) using platinum crucibles with a heating rate of 10°C/min. Johnson Matthey magnetic susceptibility balance was employed to carry out the magnetic susceptibility by utilizing a modified Gouy method at room temperature and diamagnetic corrections were estimated by using Pascal's constants.<sup>[18]</sup> Powder X-ray diffraction investigations were measured at room temperature by using a Bruker MeasSrv diffractometer equipped with graphite monochromator by Co K<sub> $\alpha$ </sub> radiation ( $\lambda = 1.78897$  Å). The melting points were obtained by using Stuart melting point apparatus. Biological measurements were carried out at Plants Protection Researches Institute, Giza, Egypt.

## 2.2 | Synthesis of the asymmetric Schiff base ligand $(H_2L)$

The starting moiety (4-morpholinethiosemicarbazide) synthesized according the was to published literature.<sup>[16,19]</sup> The entitled ligand; (E)-N'-(1-(4-((E)-2hydroxybenzylideneamino)phenyl)ethylidene)morpholine-4-carbothiohydrazide was prepared via two steps. Firstly, 0.1 mol of salicylaldehyde (10.66 ml) was condensed with 0.1 mol of p-aminoacetophenone (13.52 g) dissolved in 35 ml of ethanol with stirring under reflux for 3 h at 50 °C. The reaction mixture was then cooled overnight after which a vellow precipitate was formed, filtered off and dried under vacuum over anhydrous CaCl<sub>2</sub>. Secondly, 0.1 mol of 4-morpholinethiosemicarbazide (16.12 g) was added gradually to an ethanolic solution of 0.1 mol (23.93 g) of the formed yellow precipitate with stirring under reflux for 2 h at 70 °C. After that, the reaction mixture was cooled for about one hour followed by stirring and warming at 40 °C for 3 h. The obtained ligand was filtered off, washed with ethanol and dried under vacuum over anhydrous CaCl<sub>2</sub>. The melting point of the ligand is 167 °C. Based on elemental analyses and spectral studies, the chemical structure of the prepared asymmetric Schiff base ligand is represented in Figure 1.

## 2.3 | Synthesis of the asymmetric Schiff base metal complexes

The complexes originated from the reactions of the ligand with chloride salts of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Cr(III), Fe(III), Ru(III) and Cu(II) perchlorate were prepared by the addition of 0.01 mol of an ethanolic solution (20 ml) of the appropriate metal salt to 0.01 mol of the ligand dissolved in 20 ml of hot ethanol (1 M:1 L). The reactants were stirred with reflux for 4 h at 80°C. The formed complexes were filtered off, washed with ethanol and dried under vacuum over anhydrous CaCl<sub>2</sub>.



FIGURE 1Structure of (E)-N-(1-(4-((E)-2-hydroxybenzylideneamino)phenyl)ethylidene)morpholine4-carbothiohydrazide ( $H_2L$ )

Analytical and physical data of the asymmetric Schiff base ligand and its obtained metal complexes are listed in Table 1.

#### 2.4 | Biological studies

## 2.4.1 | Anti-molluscicidal activity

The anti-molluscicidal activity of the asymmetric Schiff base ligand ( $H_2L$ ) and its metal complexes against *Eobania vermiculata* was reported. The investigated snails were collected from untreated ornamental plants fields at Sadat city, Menoufia governorate, Egypt. The collected land snails were transferred directly to the laboratory into muslin sacks. The animals were kept in small plastic boxes provided with moist optimal soil and feeding on fresh green lettuce leaves for two weeks for adaptation. Adult healthy animals with almost the same shell diameter were used and starved for 24 h before treatments. The treatments were carried out by using contact technique.<sup>[16]</sup> Five concentrations (100, 200, 300, 400, 500 ppm) of the tested compounds were prepared by using DMF. A parallel control test was carried out.

## 2.4.2 | Antibacterial activity

Microorganism and inoculums preparation

The ligand and its metal complexes were tested *in vitro* against representative Gram- positive bacteria species; *Staphylococcus aureus* and Gram-negative species; *Escherichia coli*. The tested microorganisms were provided from The Department of Parasitology and Animal Diseases, National Research Center, Dokki, Egypt. The bacterial strains were maintained on agar slant at 4°C and cultured on a fresh agar plates. For disc diffusion assay, bacterial liquid cultures were initiated by placing a loop of bacteria from the slant into 10 ml of LB media.

#### Agar diffusion test

Agar diffusion method was conducted to detect the bacterial susceptibility to the prepared compounds.<sup>[8]</sup> A volume of 100  $\mu$ L of cell culture suspension matching with 0.5 McFarland of each tested organism was spread onto the surface of solid agar medium (Muller Hinton agar). The prepared compounds were adjusted to a concentration of 50 mg/ml using DMSO as solvent. The concentration of DMSO in the medium had no effects on the growth of the tested microorganisms. Filter paper discs with a diameter of 7 mm each were impregnated with 15  $\mu$ L of each of the different compounds. Then the agar plates containing microorganisms, soaked with paper discs were incubated at 37 ± 0.1°C for 24 h. The inhibition of the bacterial growth was evaluated by measuring the diameter (cm)

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TABLE 1 Analytical and physical data of the asymmetric Schiff base ligand (H<sub>2</sub>L) and its metal complexes

No.	Compound	F.W.	Elemen	ntal an	alyses F	ound/(	Calcd.)	%	M.P.	Δ
	Empirical formula	Color	С	Н	Ν	S	Cl	М	(°C)	$(\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1})$
	H <sub>2</sub> L.0.25H <sub>2</sub> O	386.99	62.34	5.68	14.10	8.49	—	—	167	—
	$C_{20}H_{22.5}N_4SO_{2.25}$	Pale yellow	(62.07)	(5.86)	(14.48)	(8.29)	—	—		
1	$[Co_{2}(HL)_{2}Cl_{2}(H_{2}O)_{2}].7H_{2}O \\ C_{40}H_{60}N_{8}S_{2}O_{13}Co_{2}Cl_{2}$	1113.97 Brown	43.02 (43.13)	5.21 (5.43)	10.31 (10.06)	5.96 (5.76)	6.52 (6.37)	10.32 (10.58)	224	27
2	$\label{eq:constraint} \begin{split} &[Ni_2(HL)Cl_3(H_2O)].5EtOH.1.25H_2O\\ &C_{30}H_{55.5}N_4SO_{9.25}Ni_2Cl_3 \end{split}$	876.25 Brown	41.39 (41.12)	6.12 (6.38)	5.97 (6.39)	3.93 (3.66)	11.89 (12.15)	13.23 (13.40)	174	39
3	$\label{eq:cu2} \begin{split} & [Cu_2(HL)Cl_3(H_2O)].2.5EtOH \\ & C_{25}H_{38}N_4SO_{5.5}Cu_2Cl_3 \end{split}$	748.27 Green	40.47 (40.13)	5.19 (5.12)	7.71 (7.49)	4.07 (4.29)	14.61 (14.23)	16.89 16.99)	197	37
4	$\label{eq:cu2} \begin{split} & [Cu_2(HL)_2(H_2O)_2(ClO_4)_2].8H_2O\\ & C_{40}H_{62}N_8S_2O_{22}Cu_2Cl_2 \end{split}$	1269.22 Dark green	38.06 (37.85)	4.69 (4.92)	9.12 (8.83)	5.41 (5.05)	_	10.22 (10.01)	214	32
5	$[Cr_2(HL)Cl_2(OH)_3(H_2O)_3].6.75EtOH.0.5H_2O\\ C_{33.5}H_{71.5}N_4SO_{15.25}Cr_2Cl_2$	981.53 Light brown	40.79 (40.99)	6.97 (7.34)	5.47 (5.71)	3.53 (3.27)	7.54 (7.23)	10.14 (10.59)	169	26
6	$[Fe_{2}(HL)Cl_{5}(H_{2}O)_{3}].2EtOH.4.5H_{2}O\\C_{24}H_{48}N_{4}SO_{11.5}Fe_{2}Cl_{5}$	897.94 Dark brown	31.71 (32.10)	5.36 (5.39)	6.48 (6.24)	3.71 (3.57)	20.01 (19.77)	12.48 (12.44)	212	39
7	$[Ru_{2}(HL)Cl_{5}(H_{2}O)_{3}].2EtOH.4.5H_{2}O\\C_{24}H_{48}N_{4}SO_{11.5}Ru_{2}Cl_{5}$	988.38 Dark brown	29.53 (29.17)	5.09 (4.90)	5.61 (5.67)	3.47 (3.24)	17.67 (17.96)	20.63 (20.45)	187	13
8	$\label{eq:2.1} \begin{split} &[Zn_2(HL)_2Cl_2(H_2O)_2].8.5H_2O\\ &C_{40}H_{63}N_8S_2O_{14.5}Zn_2Cl_2 \end{split}$	1153.89 Off white	41.58 (41.64)	5.54 (5.50)	10.05 (9.71)	5.86 (5.56)	6.49 (6.15)	11.69 (11.33)	172	6
9	$\label{eq:cd2} \begin{split} & [Cd_2(HL)_2Cl_2(H_2O)_2].13H_2O\\ & C_{40}H_{72}N_8S_2O_{19}Cd_2Cl_2 \end{split}$	1329.02 Yellow	36.28 (36.15)	5.79 (5.46)	8.72 (8.43)	4.58 (4.83)	5.13 (5.34)	16.73 (16.92)	173	14

of the clear zone around each disc. All experiments were made in duplicate and the results were confirmed in three independent experiments. Ceftriaxone discs were used as positive control.

#### 3 | RESULTS AND DISCUSSION

The molar conductance values of metal complexes (Table 1) in DMF ( $10^{-3}$  M) conclude that all complexes are non-electrolytes and anions exist in the inner sphere of these complexes.<sup>[20,21]</sup> Moreover, all metal complexes are stable and freely soluble in DMF and DMSO. Analytical data establish that complexes were formed with chemical formulae;  $[M_2(HL)_2Cl_2(H_2O)_2].nH_2O$  (where; M = Co(II), Zn(II) and Cd(II), n = (7, 8.5, 13), respectively),  $[M_2(HL)Cl_3(H_2O)].nEtOH.mH_2O$  (where; M = Ni(II) and Cu(II), n = (5, 2.5) and m = (1.25, 0), respectively) and  $[Cu_2(HL)_2(H_2O)_2(ClO_4)_2].8H_2O$ . Also, the separated binuclear complexes have chemical formulae;  $[M_2(HL)Cl_5(H_2O)_3].2EtOH.4.5H_2O$  (where; M = Fe(III) and Ru(III)) and  $[Cr_2(HL)Cl_2(OH)_3(H_2O)_3].6.75EtOH.0.5H_2O$ .

#### 3.1 | Mass spectra

The mass spectrum of the ligand  $(H_2L)$  was performed and the observed molecular ion peaks establish its proposed geometry and chemical formula. The ligand spectrum displays a molecular ion peak at m/z = 388 amu, matches with its theoretical molecular weight (Figure S1). The spectrum reveals that the ligand possesses a monomeric structure. Moreover, it shows a series of molecular ion peaks corresponding to several fragment ions. The mass spectra of metal complexes emphasize the number of solvents in their inner and outer spheres (Figure S1). The mass spectra of metal complexes (1-9) exhibit molecular ion peaks at m/z = 1113, 877, 748, 1269, 982, 897, 989, 1153, 1330 amu, respectively, compatible with their suggested molecular weights (Table 1).

## 3.2 | <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectrum of the asymmetric Schiff base ligand (Figure S2) displays two medium singlet signals at  $\delta$  10.98 and 9.88 ppm, assignable to –OH and –NH protons, respectively.<sup>[22,23]</sup> Also, the proton signal of the imine group (HC=N) presents at  $\delta$  8.90 ppm.<sup>[22,24]</sup> The resonance signals observed within ranges;  $\delta$  (6.60–7.99), (3.07–3.83) and (2.19–2.48 ppm), ascribed to aromatic, morpholine ring and –CH<sub>3</sub> protons, respectively.<sup>[25–28]</sup> The –OH signal of the ligand disappeared upon chelation with Zn(II) and Cd(II) ions (Figure S3), indicating that the ligand chelates in a monobasic fashion with the

participation of the deprotonated phenolic oxygen atom in complexation. Also, the -NH and (HC=N) signals undergo changes in their position upon chelation, pointing to the involvement of the imine and azomethine nitrogen atoms in complexation.

#### 3.3 | IR spectra

The most distinct spectral bands of the ligand and its metal complexes are represented in Table 2 and shown in Figure 2. The spectrum of the asymmetric Schiff base ligand displays absorption bands at 3446, (3279, 3132), 1617 and 1542 cm<sup>-1</sup>, assignable to v(OH), v(NH), v(C=N) and v(CH=N), respectively.<sup>[15,22-24,29]</sup> Also, the  $\delta(NH)$ ,  $\delta(OH)$ , v(C-O) and  $\gamma(NH)$  assigned by bands at 1466, 1415, 1182 and 792 cm<sup>-1</sup> (Table 2), respectively.<sup>[15,30-32]</sup> The absence of v(SH) band near 2500 cm<sup>-1</sup> with the appearance of thioamide bands (I–IV) and  $\gamma(C=S)$  at 1482, 1300, 1244, 935 and 510 cm<sup>-1</sup>,



FIGURE 2 IR spectra of the ligand and its Co(II) complex (1)

respectively,<sup>[15,29,31]</sup> confirming the existence of the ligand in the thione form.

The spectra of all metal complexes display bands in strong and broad natures within range ( $3418-3468 \text{ cm}^{-1}$ ), ascribed to  $\nu(OH)$  of lattice solvents.<sup>[16,25]</sup> The

TABLE 2	Infrared spectral bands	(cm <sup>-1</sup> ) of the as	ymmetric Schiff base	ligand and its meta	l complexes
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		ν(OH)	ν(C=N)	ν(CH=N)	ν(C=S)	γ(NH)	ν(M-N)
No.	Compound	ν(NH)	δ(NH)	ν(C-O)	γ(C=S)	ν(M-O)	
	H <sub>2</sub> L.0.25H <sub>2</sub> O	3446(m,b) 3279(s) 3132(w)	1617(s) 1466(m)	1542(s) 1182(m)	935(w) 510(s)	792(s)	
1	[Co <sub>2</sub> (HL) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].7H <sub>2</sub> O	3430(s,b) 3189(w)	1601(s) 1440(s)	1517(w) 1205(m)	909(w) 491(m)	812(m) 465(w)	437(w)
2	[Ni <sub>2</sub> (HL)Cl <sub>3</sub> (H <sub>2</sub> O)].5EtOH.1.25H <sub>2</sub> O	3426(s,b) 3189(w) 3142(m)	1605(s) 1446(s)	1564(s) 1213(m)	917(w) 502(m)	797(m) 454(w)	432(w)
3	[Cu <sub>2</sub> (HL)Cl <sub>3</sub> (H <sub>2</sub> O)].2.5EtOH	3442(s,b) 3183(m) 3119(m)	1606(s,sp) 1444(s)	1535(m) 1203(m)	913(w) 520(m)	816(m) 489(w)	459(vw)
4	[Cu <sub>2</sub> (HL) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ].8H <sub>2</sub> O	3422(s,b) 3229(m) 3123(m)	1605(s,sp) 1439(s)	1534(m) 1205(s)	920(w) 545(m)	812(m) 461(vw)	426(vw)
5	[Cr <sub>2</sub> (HL)Cl <sub>2</sub> (OH) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ].6.75EtOH.0.5H <sub>2</sub> O	3418(s,b) 3279(s)	1604(s) 1465(s)	1539(m) 1209(m)	921(w) 510(w)	819(w) 484(w)	462(w)
6	[Fe <sub>2</sub> (HL)Cl <sub>5</sub> (H <sub>2</sub> O) <sub>3</sub> ].2EtOH.4.5H <sub>2</sub> O	3420(s,b) 3223(s) 3147(m)	1594(s) 1460(w)	1535(m) 1172(m)	914(m) 523(w)	817(w) 456(w)	433(w)
7	[Ru <sub>2</sub> (HL)Cl <sub>5</sub> (H <sub>2</sub> O) <sub>3</sub> ].2EtOH.4.5H <sub>2</sub> O	3444(s,b) 3212(w)	1597(s) 1438(s)	1552(m) 1200(s)	912(w) 550(w)	812(m) 459(vw)	443(vw)
8	$[Zn_2(HL)_2Cl_2(H_2O)_2].8.5H_2O$	3468(s,b) 3278(m,sp) 3223(m,sp)	1608(s) 1451(s)	1562(s) 1179(m)	940(w) 542(m)	795(s) 486(w)	456(w)
9	[Cd <sub>2</sub> (HL) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].13H <sub>2</sub> O	3444(s,b) 3239(w) 3152(w)	1607(s) 1437(s)	1564(s) 1153(w)	940(w) 544(m)	800(m) 486(w)	450(w)

vw: very weak, w: weak, m: medium, s: strong, b: broad, sp: splitted

disappearance the  $\delta$ (OH) ligand band (1415 cm<sup>-1</sup>) in all complexes along with the (blue/red) shifts of  $\nu$ (C–O) by (3-29) and (18-31 cm<sup>-1</sup>), respectively, confirming the involvement of the deprotonated phenolic oxygen atom in complexation (Table 2). The  $\nu$ (CH=N) band (1542 cm<sup>-1</sup>) shifts to (higher/lower) frequency by (10–22) and (3–25 cm<sup>-1</sup>), respectively. However, the  $\nu$ (C=N) ligand band (1617 cm<sup>-1</sup>) undergoes blue shift by (9–23 cm<sup>-1</sup>) upon chelation. The different modes of vibrations of NH group are strongly affected upon complexation (Table 2). The observed shifts in the above mentioned bands on comparison with those of the free ligand emphasize the involvement of the azomethine and imine nitrogen atoms in chelation. Moreover, the v(C=S)and  $\gamma$ (C=S) ligand bands undergo changes in their shape and position upon chelation (Table 2), asserting the participation of thione sulfur atom in complexation. The spectra of all metal complexes exhibit new bands within ranges; (426-462) and  $(454-489 \text{ cm}^{-1})$ , attributed to v(M-N) and v(M–O), respectively.<sup>[33,34]</sup> The spectrum of Cu(II) perchlorate complex displays two splitted bands at (1112, 1036) and a medium absorption band at 628 cm<sup>-1</sup>, due to  $(v_3)$ and  $(v_4)$ , respectively, indicating to a monodentate coordinated perchlorate group.<sup>[25]</sup>

Based on elemental analyses, IR and <sup>1</sup>H NMR spectra; the asymmetric Schiff base ligand chelates with all metal complexes in a monobasic tetradentate manner through the deprotonated phenolic oxygen, imine nitrogen, thione sulfur and azomethine nitrogen atoms (ONNS chromophore).

## 3.4 | Molecular modeling studies

The molecular modeling calculations are widely increasing for expecting of the reaction pathways and elucidating the products structure.<sup>[35]</sup> The multidentate ligands containing nitrogen and oxygen atoms are versatile and useful for assembly new molecules, because they can coordinate many transition metal ions. Thus, the synthesis of new complexes is significant for understanding the biological phenomena and exploiting artificial models.<sup>[35]</sup> Moreover, a theoretical support for the experimental findings regarding the donor atoms could be achieved by comparing the molecular models of the complexes with those of the free ligands. Molecular modeling data are useful in investigating thermal degradation mechanisms, electronic structures as well as the stereochemistry of compounds.<sup>[16,36]</sup> Molecular modeling studies for the ligand along with the representative examples; Co(II) and Cu(II) complexes (1, 3) were carried out by using (MM<sup>+</sup>) calculations.<sup>[36]</sup> The fundamental bond lengths of the investigated compounds are represented in Table 3 and shown in (Figures 3-5). The bond lengths of the ligand (Figure 3) are in the order; C(11)-C(16) >C(7) = S(33) > C(7) - N(8) > C(23) - C(25) > N(22) = C(23)

**TABLE 3** Molecular modeling data of the ligand and its Co(II), Cu(II) complexes (1, 3)

Ligand (H <sub>2</sub> L)		$[Co_2(HL)_2Cl_2(H_2O)_2].7H_2O$ co	mplex (1)	$[Cu_2(HL)Cl_3(H_2O)].2.5EtOH \text{ complex } (3)$		
Bond	Bond length (Å)	Bond	Bond length (Å)	Bond	Bond length (Å)	
N(1)-C(7)	1.320	$N(1)-C(7) \approx N(33)-C(39)$	1.462	N(1)-C(7)	1.462	
C(7)–N(8)	1.485	$C(7)-N(8) \approx C(39)-N(40)$	1.671	C(7)-N(8)	1.562	
C(7)=S(33)	1.492	$C(7)=S(32) \approx C(39)=S(64)$	1.592	C(7)=S(32)	1.539	
N(8)-N(10)	1.352	$N(8)-N(10) \approx N(40)-N(42)$	1.952	N(8)-N(10)	1.752	
N(10)=C(11)	1.260	$N(10)=C(11) \approx N(42)=C(43)$	1.507	N(10) = C(11)	1.577	
C(11)-C(16)	1.503	$C(11)-C(16) \approx C(43)-C(48)$	1.420	C(11)-C(16)	1.420	
C(19)-N(22)	1.358	$C(19)-N(22) \approx C(51)-N(54)$	1.462	N(22)=C(23)	1.462	
N(22)=C(23)	1.358	$N(22)=C(23) \approx N(54)=C(55)$	1.462	C(23)-C(25)	1.420	
C(23)-C(25)	1.420	$C(23)-C(25) \approx C(55)-C(57)$	1.420	C(26)-O(31)	1.404	
C(26)-O(31)	1.355	$C(26)-O(31) \approx C(58)-O(63)$	1.405	$N(10)-Cu(33) \approx N(22)-Cu(34)$	1.646	
		$N(10)-Co(66) \approx N(42)-Co(65)$	1.678	O(31)-Cu(34)	1.684	
		$N(22)-Co(65) \approx N(54)-Co(66)$	1.637	S(32)–Cu(33)	1.752	
		$O(31)-Co(65) \approx O(63)-Co(66)$	1.736	$Cu(33)-Cl(38) \approx Cu(33)-Cl(40) \approx Cu(34)-Cl(39)$	2.160	
		$S(32)-Co(66) \approx S(64)-Co(65)$	2.150	Cu(34)-O(35)	1.810	
		$Co(65)-Cl(67) \approx Co(66)-Cl(71)$	2.180			
		$Co(65)-O(68) \approx Co(66)-O(72)$	1.801			



**FIGURE 3** Molecular modeling for the ligand **(H<sub>2</sub>L)** 



**FIGURE 4** Molecular modeling of Co(II) complex **(1)** (Hydrogen atoms were omitted for simplicity)

FIGURE 5 Molecular modeling of Cu(II) complex (3)

> N(8)–N(10) > N(10)=C(11). The modeling data of Co(II) complex (1) reveal that Co atom is 1.637, 1.736, 1.678 and 2.150 Å away from the imine nitrogen, deprotonated phenolic oxygen, azomethine nitrogen and thione sulfur atoms, respectively (Figure 4). The N–NH bond length is (N(8)–N(10)  $\approx$  N(40)–N(42) = 1.952 Å (Table 3). The two chloride ions are equidistant from cobalt atoms (2.180 Å) and complete the octahedral

coordination sphere around Co(II) ions. In Cu(II) complex (3) (Figure 5), the stability order of bonds is; Cu(33)–Cl(38)  $\approx$  Cu(33)–Cl(40)  $\approx$  Cu(34)–Cl(39) < Cu(34)–O(35). The electron density on the coordinating atoms of the free ligand decreases after electron pair donation to metal ions, resulting in a relative increase in the bond length. So, it is noteworthy to mention that the active coordinating groups in complexes are more

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lengthen than those of the free ligand.<sup>[37]</sup> This is exactly the case in Co(II) and Cu(II) complexes (1, 3) in which the (C–O), (CH=N), (C=N) and (C=S) bonds are longer than those of the free ligand (Table 3), confirming the coordination behavior of the ligand (ONNS chromophore) and convenient with the IR and <sup>1</sup>H NMR spectral studies.

# 3.5 | Electronic spectra and magnetic moment

The electronic spectral data of the ligand  $(H_2L)$  and its metal complexes in addition to the magnetic moment values (B.M.) for metal complexes are tabulated in

Table The 4. electronic spectrum the of thiosemicarbazone ligand exhibits an absorption band at 269 nm, due to  $\pi$ - $\pi$ \* transition of phenyl rings.<sup>[16,36]</sup> Also. the spectrum shows two medium bands at 365 and 422 nm, attributed to  $n-\pi^*$  transitions of the thiosemicarbazone moiety, involving mainly the ligand chromophores; (C=N) and (C=S), respectively.<sup>[16,38,39]</sup> The first n- $\pi^*$  transition band (365 nm) undergoes blue shift by (6-29 nm) upon complexation. While, the second one (422 nm) exhibits (hypthochromic/bathochromic) shifts by (6-31) and (5-8 nm), respectively (Table 4), pointing to ligand to metal charge transfer (LMCT).<sup>[25]</sup> This indicates that the imine nitrogen, thione sulfur and azomethine nitrogen atoms participate in chelation.

TABLE 4 Electronic spectral data and magnetic moment values of the ligand and its metal complexes

No.	Compound	Electronic spectral bands (nm)	Assignment	$\mu_{eff.}$ (B.M.) <sup>a</sup>
	H <sub>2</sub> L.0.25H <sub>2</sub> O	365, 422 269	n-π* π-π*	
1	[Co <sub>2</sub> (HL) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].7H <sub>2</sub> O	662 553 430 238, 348	$\label{eq:target} \begin{array}{l} {}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(P) \\ {}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(P) \\ LMCT \\ Intraligand transition \end{array}$	4.97
2	[Ni <sub>2</sub> (HL)Cl <sub>3</sub> (H <sub>2</sub> O)].5EtOH.1.25H <sub>2</sub> O	678 427 233, 341	${}^{3}T_{1}(F) \rightarrow {}^{3}T_{1}(P)$ LMCT Intraligand transition	3.36
3	[Cu <sub>2</sub> (HL)Cl <sub>3</sub> (H <sub>2</sub> O)].2.5EtOH	688 561 429 261, 336	$\label{eq:B1g} \begin{array}{c} ^2B_{1g} \rightarrow {}^2E_g \\ ^2B_{1g} \rightarrow {}^2A_{1g} \\ LMCT \\ Intraligand \ transition \end{array}$	1.27
4	[Cu <sub>2</sub> (HL) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ].8H <sub>2</sub> O	681 576 416 253, 344	$\label{eq:B1g} \begin{array}{c} ^2B_{1g} \rightarrow ^2B_{2g} \\ ^2B_{1g} \rightarrow \ ^2E_g \\ LMCT \\ Intraligand \ transition \end{array}$	1.61
5	[Cr <sub>2</sub> (HL)Cl <sub>2</sub> (OH) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ].6.75EtOH.0.5H <sub>2</sub> O	622 534 466 402 235,351	$\label{eq:A2g} \begin{array}{l} {}^{4}A_{2g} \rightarrow {}^{4}T_{1g} \left( P \right) \\ {}^{4}A_{2g} \rightarrow {}^{4}T_{1g} \left( F \right) \\ {}^{4}A_{2g} \rightarrow {}^{4}T_{2g} \left( F \right) \\ LMCT \\ Intraligand transition \end{array}$	3.79
6	[Fe <sub>2</sub> (HL)Cl <sub>5</sub> (H <sub>2</sub> O) <sub>3</sub> ].2EtOH.4.5H <sub>2</sub> O	783, 592 466 411 239, 348	$\label{eq:A1g} \begin{array}{c} {}^{6}A_{1g} \rightarrow {}^{5}T_{1g} \\ {}^{6}A_{1g} \rightarrow T_{2g}\left(G\right) \\ LMCT \\ Intraligand transition \end{array}$	5.43
7	[Ru <sub>2</sub> (HL)Cl <sub>5</sub> (H <sub>2</sub> O) <sub>3</sub> ].2EtOH.4.5H <sub>2</sub> O	727 586 433 391 236, 351	$\label{eq:target} \begin{array}{c} ^{2}T_{2g} \rightarrow \ ^{4}T_{1g} \\ ^{2}T_{2g} \rightarrow \ \ ^{4}T_{2g} \\ ^{2}T_{2g} \rightarrow \ \ ^{2}A_{2g} \\ LMCT \\ \\ Intraligand \ transition \end{array}$	1.53
8	$[Zn_2(HL)_2Cl_2(H_2O)_2].8.5H_2O$	409 252, 359	LMCT Intraligand transition	Diamagnetic
9	$[Cd_2(HL)_2Cl_2(H_2O)_2].13H_2O$	413 257, 354	LMCT Intraligand transition	Diamagnetic

<sup>a</sup>: (per metal ion).

The (d–d) electronic transitions of  $[Co_2(HL)_2Cl_2(H_2O)_2]$ .7H<sub>2</sub>O complex locate at 662 and 553 nm, ascribed to  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(P)$  ( $\upsilon_2$ ) and  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$  ( $\upsilon_3$ ) transitions, respectively.<sup>[25,40]</sup> The magnetic moment value (4.97 B.M.) is compatible with the (d–d) electronic transitions to establish a high spin octahedral environment around Co(II) ions.<sup>[25]</sup>

The electronic spectrum of [Cu<sub>2</sub>(HL)Cl<sub>3</sub>(H<sub>2</sub>O)].2.5EtOH complex (3) shows two intense bands at 688 and 561 nm, characteristic to  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  and  ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$  transitions, respectively. The electronic transitions as well as magnetic moment value (1.27 B.M.) typified with a square planar geometry around Cu(II) ions.<sup>[36,40-42]</sup> In the contrary, the electronic spectrum of [Cu<sub>2</sub>(HL)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>].8H<sub>2</sub>O complex (4) displays two medium absorption bands at 681 and 576 nm, due to  ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$  and  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  transitions, respectively, attributed to a distorted octahedral geometry around Cu(II) ions.<sup>[16,41,42]</sup> The magnetic moment value of Cu(II) complex (4) (1.61 B.M.) provides another evidence for the distorted octahedral geometry.<sup>[16,25]</sup>

[Cr<sub>2</sub>(HL)Cl<sub>2</sub>(OH)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>].6.75EtOH.0.5H<sub>2</sub>O complex displays magnetic moment value (3.79 B.M.), which mainly follows the estimated value for three unpaired electrons and corresponding to a high spin octahedral Cr(III) complex.<sup>[43]</sup> Moreover, the electronic spectrum of the Cr(III) complex displays three intense absorption bands at 622, 534 and 466 nm, assignable to <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1g</sub> (P), <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1g</sub> (F) and <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub> (F), transitions respectively, pointing to an octahedral environment around Cr(III) ions.<sup>[44]</sup>

The spectrum of  $[Fe_2(HL)Cl_5(H_2O)_3].2EtOH.4.5H_2O$  complex exhibits absorption band at 466 nm, due to  $^6A_{1g} \rightarrow T_{2g}$  (G) transition and two splitted bands at 783 and 592 nm, attributed to  $^6A_{1g} \rightarrow {}^5T_{1g}$  transition. These transition bands are identical with  $d^2sp^3$  hybridized octahedral Fe(III) ions.<sup>[45-47]</sup> This is also supported by the observed magnetic moment value (5.43 B.M.).<sup>[47]</sup>

The octahedral geometry of [Ru<sub>2</sub>(HL)Cl<sub>5</sub>(H<sub>2</sub>O)<sub>3</sub>].2EtOH.4.5H<sub>2</sub>O complex is confirmed with the appearance of three electronic absorption bands at 727, 586 and 433 nm, characteristic to  ${}^{2}T_{2g} \rightarrow {}^{4}T_{1g}$ ,  ${}^{2}T_{2g} \rightarrow {}^{4}T_{2g}$  and  ${}^{2}T_{2g} \rightarrow {}^{2}A_{2g}$  transitions, respectively.<sup>[48]</sup> Also, the magnetic moment value (1.53 B.M.) establish an octahedral geometry for Ru(III) complex.<sup>[48,49]</sup>

The mononuclear Co(II), Cu(II), Zn(II) and Cd(II) complexes **(1, 4, 8, 9)** adopt a sandwich structure to confirm the octahedral geometry.<sup>[25]</sup> The relatively low

magnetic moment value of some investigated complexes may be attributed to the effect of ligand field, metal–metal interaction or considerable electron delocalization.<sup>[36,48]</sup>

The aforementioned data gathered with the IR and <sup>1</sup>H NMR spectral studies to confirm the chemical structure for metal complexes shown in Figure 6.

#### 3.6 | Thermal studies

The thermogravimetric data of the ligand  $(H_2L)$  and its metal complexes are listed in Table 5 and represented in Figure 7. The DTG curves of the ligand and its metal complexes were analyzed by using the rate equation:

$$d\alpha/dt = k(1-\alpha)^n$$

Where;  $\alpha$  is the decomposed fraction, n is the order of reaction and k is the rate constant obtained by Arrhenius equation:  $K = Ae^{-E^*/(RT)}$  where; E\* is the activation energy, A is the frequency factor, R is the gas constant and T is the temperature in kelvin. These parameters were calculated by using the initial rate method, where *lnI* (intensity of the DTG or DTA curve) is plotted against



FIGURE 6 Proposed structure for metal complexes

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 TABLE 5
 Thermal decomposition of the asymmetric Schiff base ligand and its metal complexes

No.	Compound	TG range (°C)	DTG peak (°C)	Mass Loss % Found	Calcd.	Assignment	T <sub>S</sub> (°C)
	H <sub>2</sub> L.0.25H <sub>2</sub> O	19-171 171-229 229-500 500-678	200 <sup>c</sup> 259 <sup>c</sup> 619 <sup>h</sup>	1.07 33.21 51.35 14.37	1.16 33.64 50.97 14.23	$\begin{array}{c} Loss \ of \ 0.25 \ mol \ of \ H_2O^a \\ Loss \ of \ C_5H_8NSO^d \\ Loss \ of \ C_{13}H_{11}NO^d \\ Loss \ of \ C_2H_3N_2^d \end{array}$	171
1	[Co <sub>2</sub> (HL) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].7H <sub>2</sub> O	25-233 233-455 455-899	43 <sup>e</sup> 284 <sup>c</sup> 532 <sup>c</sup> At 899	7.88 46.79 30.11 15.22	8.09 46.55 30.20 15.16	Loss of 5 mol of $H_2O^a$ Loss of 4 mol of $H_2O$ , $Cl_2$ and $C_{17}H_{21}N_5S_2O^d$ Ligand pyrolysis <sup>d</sup> $Co_2O_2 + 0.25C^r$	233
2	[Ni <sub>2</sub> (HL)Cl <sub>3</sub> (H <sub>2</sub> O)].5EtOH.1.25H <sub>2</sub> O	25-187 187-479	- 227 <sup>e</sup> 297 <sup>e</sup>	- 44.74	45.24	Stable Loss of 2 mol of EtOH, 1.25 mol of $H_2O$ , 1.5 $Cl_2$ and $C_{11}H_{13}NO^d$	187
		479-899	517 <sup>c</sup> 683 <sup>e</sup>	37.60	37.37	Ligand pyrolysis <sup>d</sup> 2NiO + 0.25 $C^{r}$	
3	[Cu <sub>2</sub> (HL)Cl <sub>3</sub> (H <sub>2</sub> O)].2.5EtOH	23-203 203-477	- 250°	2.13 51.53	1.54 51.50	Loss of 0.25 mol of EtOH <sup>b</sup> Loss of 2.25 mol of EtOH, $1.5Cl_2$ and $C_{11}H_{13}NO^d$	203
		477-899	371 <sup>4</sup> 554 <sup>f</sup> 718 <sup>f</sup> 877 <sup>f</sup> At 899	21.21	21.68	Ligand pyrolysis <sup>d</sup> $2CuO + 2.5C^{r}$	
5	[Cr <sub>2</sub> (HL)Cl <sub>2</sub> (OH) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ].6.75EtOH.0.5H <sub>2</sub> O	26-179 179-395	49 <sup>e</sup> 210 <sup>I</sup> 267 <sup>e</sup>	4.58 40.91	4.69 41.25	Loss of one mol of $EtOH^b$ Loss of 1.75 mol of $EtOH$ , 1.5 H <sub>2</sub> O, Cl <sub>2</sub> , (OH) <sub>3</sub> and C <sub>11</sub> H <sub>13</sub> NO <sup>d</sup>	179
		395-626	466 <sup>c</sup> At 626	43.73 10.78	43.47 10.59	Ligand pyrolysis <sup>d</sup> 2Cr <sup>r</sup>	
6	[Fe <sub>2</sub> (HL)Cl <sub>5</sub> (H <sub>2</sub> O) <sub>3</sub> ].2EtOH.4.5H <sub>2</sub> O	29-213 213- 450 450-899	- 334 <sup>e</sup> 504 <sup>I</sup> At 899	0.80 41.08 40.24 17.88	1.28 41.29 39.64 17.79	Loss of 0.25 mol of $EtOH^{b}$ Loss of one mol of $H_{2}O$ , 2.5 $Cl_{2}$ and $C_{11}H_{13}NO^{d}$ Ligand pyrolysis <sup>d</sup> $Fe_{2}O_{3}^{r}$	213
7	[Ru <sub>2</sub> (HL)Cl <sub>5</sub> (H <sub>2</sub> O) <sub>3</sub> ].2EtOH.4.5H <sub>2</sub> O	27-194 194-498	49 <sup>e</sup> 345 <sup>c</sup> At 498	9.72 64.50 25.78	9.32 65.37 25.31	Loss of 2 mol of $EtOH^b$ Ligand pyrolysis <sup>d</sup> $Ru_2O_3^r$	194
8	[Zn <sub>2</sub> (HL) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].8.5H <sub>2</sub> O	32-175 175-498 498-899	- 244 <sup>c</sup> 608 <sup>h</sup> At 899	3.26 52.08 32.96 11.70	3.12 51.97 33.58 11.33	Loss of 2 mol of $H_2O^a$ Loss of 8.5 mol of $H_2O$ , $Cl_2$ and $C_{17}H_{21}N_5S_2O^d$ Ligand pyrolysis <sup>d</sup> $2Zn^r$	175
9	[Cd <sub>2</sub> (HL) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].13H <sub>2</sub> O	34-178 178-637 637-899	- 233 <sup>c</sup> 643 <sup>e</sup> At 899	1.78 63.60 17.90 16.72	2.03 63.57 17.48 16.92	Loss of 1.5 mol of $H_2O^a$ Loss of 13.5 mol of $H_2O$ , $Cl_2$ and $C_{24}H_{30}N_6S_2O_4^{\ d}$ Ligand pyrolysis <sup>d</sup> $2Cd^r$	178

<sup>a</sup>: Dehydration, <sup>b</sup>: Desolvation, <sup>d</sup>: Decomposition, <sup>c</sup>: strong, <sup>e</sup>: medium, <sup>f</sup>: weak, <sup>h</sup>: broad, <sup>I</sup>: broad strong, <sup>r</sup>: final residue.



\*: Weight of sample

FIGURE 7 (TG/DTG) curves of the ligand and its complexes

(1/T) for the low temperature peak, <sup>[15,25]</sup> giving a straight line with a slope (-E\*/R). The intensity (I) represented  $d\alpha/dt$  in DTG curve and  $\Delta T$  in DTA curve.<sup>[14,24]</sup> The thermodynamic and kinetic parameters of the ligand and its metal complexes are collected in Table 6.

The thermogram of the ligand reveals that the dehydration process takes place within (19–171 °C) range

and associated with 1.07% TG weight loss, ascribed to the removal of 0.25 mol of  $H_2O$ . The thermal degradation of the dehydrated ligand starts at 171 °C, compatible with its measured melting point (Table 1). Thermal decomposition process occurs through three continuation steps. It begins with the elimination of (C<sub>5</sub>H<sub>8</sub>NSO) fragment at temperature range (171–229 °C), associated with a strong

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TABLE 6	Kinetic parameters of the therm	al decomposition of the as	ymmetric Schiff base ligand and	its metal complexes
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No.	Compound	Stage No.	Temperature range (°C)	DTG peak (°C)	n	ΔE*/ KJ/mol	ΔH*/ KJ/mol	A/s <sup>-1</sup>	-ΔS*/ KJ/mol.K	ΔG*/ KJ/mol
	H <sub>2</sub> L.0.25H <sub>2</sub> O	I II III	171-229 229-500 500-678	200 <sup>c</sup> 259 <sup>c</sup> 619 <sup>h</sup>	0.89 0.78 0.66	200.09 175.58 155.47	196.52 171.15 148.05	70.43 37.98 6.32	0.2217 0.2278 0.2470	263.74 240.17 245.12
1	[Co <sub>2</sub> (HL) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].7H <sub>2</sub> O	I II III	25-233 233-455 455-899	43 <sup>e</sup> 284 <sup>c</sup> 532 <sup>a</sup>	1.43 1.14 1.08	95.54 610.41 403.24	92.92 605.78 396.54	53.66 399.93 57.82	0.2206 0.2086 0.2277	157.11 673.37 472.84
2	[Ni <sub>2</sub> (HL)Cl <sub>3</sub> (H <sub>2</sub> O)].5EtOH.1.25H <sub>2</sub> O	I II	187-479 479-899	227 <sup>e</sup> 297 <sup>e</sup> 517 <sup>c</sup> 683 <sup>e</sup>	1.13 1.35 1.24 0.96	142.84 253.70 480.02 609.83	138.68 248.96 473.45 601.88	30.28 64.46 86.68 78.95	0.2292 0.2240 0.2242 0.2266	210.64 318.62 543.41 670.08
3	[Cu <sub>2</sub> (HL)Cl <sub>3</sub> (H <sub>2</sub> O)].2.5EtOH	I II	203-477 477-899	250 <sup>a</sup> 371 <sup>f</sup> 554 <sup>f</sup> 718 <sup>f</sup> 877 <sup>f</sup>	1.43 0.59 1.42 0.89 0.66	285.67 437.32 225.36 603.13 578.12	281.25 431.96 218.11 594.90 568.56	105.90 132.81 16.65 69.54 40.76	0.2191 0.0384 0.2382 0.2279 0.2336	351.58 443.79 299.62 663.51 676.25
5	[Cr <sub>2</sub> (HL)Cl <sub>2</sub> (OH) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ].6.75EtOH.0.5H <sub>2</sub> O	I II III	26-179 179-395 395-626	49 <sup>e</sup> 210 <sup>I</sup> 267 <sup>e</sup> 466 <sup>a</sup>	1.28 1.26 1.29 1.38	116.61 126.75 707.67 302.33	113.93 122.74 703.18 296.19	75.55 26.45 589.91 42.01	0.2179 0.2300 0.2051 0.2297	178.43 197.49 763.90 368.54
6	[Fe <sub>2</sub> (HL)Cl <sub>5</sub> (H <sub>2</sub> O) <sub>3</sub> ].2EtOH.4.5H <sub>2</sub> O	I II	213- 450 450-899	334 <sup>e</sup> 504 <sup>I</sup>	0.76 1.17	593.75 301.18	588.61 293.32	277.04 19.94	0.2125 0.2379	678.72 399.68
7	[Ru <sub>2</sub> (HL)Cl <sub>5</sub> (H <sub>2</sub> O) <sub>3</sub> ].2EtOH.4.5H <sub>2</sub> O	I II	27-194 194-498	49 <sup>e</sup> 345 <sup>a</sup>	1.22 0.97	92.86 252.17	90.19 247.12	47.91 52.74	0.2217 0.2262	156.92 336.23
8	$[Zn_2(HL)_2Cl_2(H_2O)_2].8.5H_2O$	I II	175-498 498-899	244 <sup>c</sup> 608 <sup>h</sup>	1.12 1.42	429.28 374.32	424.98 367.00	247.35 38.01	0.2119 0.2319	497.47 481.60
9	[Cd <sub>2</sub> (HL) <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].13H <sub>2</sub> O	I II	178-637 637-899	233 <sup>a</sup> 643 <sup>e</sup>	1.41 0.75	148.20 399.79	143.99 392.17	31.44 38.51	0.2290 0.2322	219.10 502.93

<sup>a</sup>: strong, <sup>e</sup>: medium, <sup>f</sup>: weak, <sup>h</sup>: broad, <sup>I</sup>: broad strong.

DTG peak at ( $T_{\text{max}}$ = 200 °C). This step is convenient with the degradation process initiated with breaking up the (C(7)–N(8)) bond to liberate (C<sub>5</sub>H<sub>8</sub>NSO) moiety (Scheme S1). The rest steps associated by the removal of the remaining organic part of the ligand at (229–500) and (500–678 °C) regions, with a strong and broad DTG peaks at ( $T_{\text{max}}$ = 259, 619 °C), respectively (Table 5). The three thermal decomposition steps of the ligand proceed via first order reaction with activation energy; 200.09, 175.58 and 155.47 KJ/mol, respectively (Table 6).

The TG curves of octahedral Co(II) and Zn(II) complexes indicate that these complexes undergo the same thermal decomposition pathway (isothermal). The two complexes are partially dehydrated at (25–233 °C) region (Table 5). After that, the Co(II) and Zn(II) complexes are thermally decomposed via two distinguishable steps. The first one takes place within ranges; (233–455) and (175–498 °C), associated with 46.79 and 52.08% TG weight loss, respectively, equivalent to liberation of lattice water molecules overlapped with coordinated ones, dechlorination and partial ligand pyrolysis. This degradation step proceed via first order reaction with activation energy; 610.41 and 429.28 KJ/mol for Co(II) and Zn(II) complexes, respectively (Table 6). This is in agreement with the pyrolytic process started with the rupture of (N–NH), (M $\leftarrow$ S), (M–O), (M $\leftarrow$ N) bonds to liberate (C<sub>17</sub>H<sub>21</sub>N<sub>5</sub>S<sub>2</sub>O) moiety. Thermal decomposition pathway of Co(II) complex as a representative example is compatible with the following bond lengths order; Co(65)-Cl(67) $\approx$  Co(66)-Cl(71) > S(64)-Co(65)  $\approx$  S(32)-Co(66) > N(8)- $N(10) \approx N(40) - N(42) > Co(65) - O(68) \approx Co(66) - O(72) >$ O(31)-Co(65)  $\approx O(63)$ -Co(66). The molecular modeling data gathered with TG weight loss to ensure the proposed thermal degradation mechanism of Co(II) complex (Scheme S2). The last step starts at 455 up to 899 °C, involved in complete ligand pyrolysis, leading to the formation of  $(Co_2O_3 + 0.25 C)$  and zinc metal as final products (Table 5).<sup>[15,50]</sup> The last decomposition step of Co(II) and Zn(II) complexes is distinguished by DTG peaks with various intensities at  $(T_{\text{max}} = 532 \text{ and } 608 \text{ }^{\circ}\text{C})$  with activation energy and order of reaction; (403.24 KJ/mol, 1.08) and (374.32 KJ/mol, 1.42), respectively.

The thermogram of the tetrahedral Ni(II), square planar Cu(II) (3) and octahedral Cr(III), Fe(III) complexes establish that they are isothermal. The desolvation process of these complexes occurs within range (23-213 °C). The thermal decomposition stage comprises of two well-defined steps. The first step associated with 44.74, 51.53, 40.91 and 41.08% TG weight loss at (187-479), (203-477), (179-395) and (213-450 °C) regions for Ni(II), Cu(II) (3), Cr(III) and Fe(III) complexes, respectively. These TG weight losses are compatible with the removal of (C11H13NO) fragment, lattice solvent molecules interfered with coordinated ones along with elimination of anions. Modeling structure of Cu(II) complex (3) as a model for this set of complexes reveals that the coordinated water molecule and chloride ions are 1.810 and 2.160 Å away from copper atoms, respectively (Figure 5), convenient with the suggested thermal degradation pathway of Cu(II) complex (3) (Scheme S3). The last step accompanied by TG weight loss, identical with complete ligand pyrolysis (Table 5) within range (395-899 °C). The thermal decomposition processes run out with the formation of metal, metal oxide or (metal oxide + C) as final residues.<sup>[25,47,51,52]</sup>

The desolvation step of  $[Ru_2(HL)Cl_5(H_2O)_3].2EtOH.4.5H_2O$ takes place at (27-194 °C) region. The thermal degradation begins at 194 °C via one progressive stage (Table 5), accompanied by 64.50% TG weight loss. This step is characterized by a strong DTG peak at ( $T_{max}$  = 345 °C) with activation energy and order of reaction (252.17 KJ/mol, 0.97). The achievement of the thermal decomposition in one step reveals that the degradation reaction proceeds hurriedly.<sup>[16]</sup> On the other hand, the octahedral [Cd<sub>2</sub>(HL)<sub>2</sub>Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].13H<sub>2</sub>O undergoes partial dehydration up to 178 °C. The decomposition process occurs through two distinct steps. The first step is characterized by 63.60% TG weight loss in (178-637 °C) range, corresponding to removal of (rest hydrated water and coordinated water molecules), dechlorination and partial ligand pyrolysis. The ligand pyrolysis was completed at 899 °C. This process associated with a medium DTG peak at  $(T_{max} = 643 \text{ °C})$  with activation energy 399.79 KJ/mol (Table 6), leading to the formation of cadmium metal as a final residue.<sup>[16]</sup> The high temperature range of the removal of lattice solvents in some investigated complexes may be attributed to hydrogen bonding.<sup>[16]</sup>

The thermogravimetric data along with the calculated kinetic and thermodynamic parameters concluded the following:

- 1. The degradation steps of all metal complexes proceed through first order reaction (Table 6).
- 2. The higher thermal stability of the binuclear octahedral Fe(III) complex than that of the binuclear

octahedral Ru(III) complex is attributed to the smaller ionic radius of Fe(III) ion than Ru(III) ion.<sup>[25,36]</sup> The calculated activation energy of the decomposition steps of Fe(III) complex is higher than that of Ru(III) complex, convenient with the thermal stability order of these complexes.

3. The change of entropy values ( $\Delta S^*$ ) of all metal complexes, for the thermal decomposition steps reveals that the transition states are more ordered, i.e. in a less random molecular configuration than the reacting complexes. Moreover, the fraction appeared in the calculated order of the thermal reactions (n), confirmed that the reactions proceeded in complicated mechanisms.<sup>[53,54]</sup>

#### 3.7 | ESR spectral studies

Typical ESR spectra of [Cu<sub>2</sub>(HL)Cl<sub>3</sub>(H<sub>2</sub>O)].2.5EtOH and  $[Cu_2(HL)_2(H_2O)_2(ClO_4)_2]$ .8H<sub>2</sub>O complexes are shown in Figure 8. The spectra reveal;  $g_{\parallel} = (2.25, 2.21), g_{\perp} =$ (2.08, 2.04) and G = (3.19, 5.51), respectively (Table 7). The estimated g<sub>ll</sub> value for the two complexes is less than 2.3, pointing to a significant covalent character of the metal ligand bond.<sup>[15,16]</sup> The observed trend;  $g_{\parallel} > g_{\perp} >$ 2.0023 for the complexes concludes that the unpaired electron is localized mainly in the  $d_{(x -y)}^{2}$  orbital of the Cu(II) ion with axial symmetry.<sup>[16,25,36]</sup> These spectral features are characteristic for tetragonal geometry for the aforesaid complexes.<sup>[55]</sup> The axial symmetry parameter (G) was calculated from the relation;  $G = (g_{\parallel} - 2.0023) / (g_{\parallel} - 2.0023)$  $(g_{\perp} - 2.0023)$ , in order to measure the exchange interaction between Cu(II) centers in a polycrystalline solid. According to Hathaway, if G > 4, the exchange interaction is negligible, but if G < 4, exchange interaction in the solid complexes is considered.<sup>[25]</sup> Cu(II) chloride complex (3) has (G) value less than 4, indicating to exchange interaction between Cu(II) centers and consistent with the magnetic moment value for this complex (Table 4). While, the (G) value for Cu(II) perchlorate complex (4) is 5.51 (Table 7), ruling out the exchange interaction between Cu(II) ions and compatible with the magnetic moment value of this complex (1.61 B.M.).

#### 3.8 | Powder X-ray diffraction analysis

The purity of Co(II), Cu(II) and Ru(III) complexes **(1, 3, 7)** were checked by performing powder X-ray diffraction analysis at room temperature. The X-ray diffraction patterns (Figure 9) indicate that copper complex has a crystalline nature, whereas, cobalt and ruthenium complexes are amorphous. The liability of cobalt(II) ion may lead to the amorphous nature of its complex.<sup>[56]</sup>



FIGURE 8 ESR spectra of Cu(II) complexes (3, 4)

TABLE 7 ESR parameters of copper(II) complexes

	Con	Complexes					
Parameters	[Cu <sub>2</sub> (HL)Cl <sub>3</sub> (H <sub>2</sub> O)].2.5EtOH (3)	[Cu <sub>2</sub> (HL) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ].8H <sub>2</sub> O (4)					
g//	2.25	2.21					
g⊥	2.08	2.04					
gav.*	2.14	2.10					
G**	3.19	5.51					

\*:  $g_{av} = (2 g_{\perp} + g_{||})/3.$ 

\*\*: G =  $(g_{||} - 2.0023) / (g_{\perp} - 2.0023)$ .



FIGURE 9 X-ray diffraction curves for Co(II), Cu(II) and Ru(III) complexes (1, 3, 7)

## 3.9 | Biological studies

## 3.9.1 | Anti-molluscicidal activity

The  $LC_{50}$  values of the asymmetric Schiff base ligand as well as its metal complexes are given in Table 8. The results reveal that the uncoordinated nitrogen and sulfur

atoms of the free ligand are responsible for its toxicity.<sup>[16]</sup> The enhanced toxicity of the tested metal complexes is ascribed to the reactions of metal ions with enzymes.<sup>[16]</sup> The data (Table 8) show that the high toxic effect of copper(II) complexes **(3, 4)** is due to the high toxicity of copper ions.<sup>[15,16]</sup> Copper is known to have a very high

**TABLE 8** Anti-molluscicidal activity of the asymmetric Schiffbase ligand and its metal complexes

No.	Compounds	LC <sub>50</sub> (ppm)
	$H_{2}L.0.25H_{2}O$	229.07
1	$[Co_2(HL)_2Cl_2(H_2O)_2].7H_2O$	223.88
2	$[Ni_2(HL)Cl_3(H_2O)].5EtOH.1.25H_2O$	267.86
3	[Cu <sub>2</sub> (HL)Cl <sub>3</sub> (H <sub>2</sub> O)].2.5EtOH	196.86
4	$[Cu_2(HL)_2(H_2O)_2(ClO_4)_2].8H_2O$	131.27
5	$[Cr_2(HL)Cl_2(OH)_3(H_2O)_3].6.75EtOH.0.5H_2O$	427.39
6	[Fe <sub>2</sub> (HL)Cl <sub>5</sub> (H <sub>2</sub> O) <sub>3</sub> ].2EtOH.4.5H <sub>2</sub> O	251.34
7	[Ru <sub>2</sub> (HL)Cl <sub>5</sub> (H <sub>2</sub> O) <sub>3</sub> ].2EtOH.4.5H <sub>2</sub> O	168.54
8	$[Zn_2(HL)_2Cl_2(H_2O)_2].8.5H_2O$	242.05
9	$[Cd_2(HL)_2Cl_2(H_2O)_2].13H_2O$	237.59

affinity for free thiol groups (cysteine) of protein. It is likely that Cu(II) ions are binding to free thiol group of ALP enzyme, causing enzyme inactivation. Alternatively, Cu(II) ions can bind and distort the active site of enzymes, or even compete for Zn(II) and Mg(II) binding sites in these enzymes; however, due to the redox cycling nature of Cu(II), it is possible that some redox reactions involving the enzyme may be involved as well.<sup>[16,57]</sup> The increased sensitivity of Eobania vermiculata toward Ru(III) complex may be attributed to the cytotoxicity of ruthenium ions. Also, the toxicity of Co(II) complex is ascribed to the activity of cobalt ions on ALP and ACP enzymes, causing immobilization of these enzymes, locking them in a nonideal conformation and may be an artefact of their system.<sup>[57]</sup> The cytotoxicity of nickel complex may be due to the interference with the metabolism of essential metals, such as Fe(II), Mn(II), Ca(II), Zn(II), Cu(II) or Mg(II), which can suppress or modify the toxic effects of nickel. The toxic functions of nickel probably result primarily from its ability to replace other metal ions in enzymes and proteins or binding to cellular compounds containing oxygen, sulfur and nitrogen atoms, such as enzymes and nucleic acids, which are then inhibited.<sup>[58]</sup> Nickel has been shown to be immunotoxic, altering the activity of all specific types involved in the immunological response.<sup>[58]</sup> The susceptibility of Eobania vermiculata toward Cd(II) complex is assigned to its binding with the metal-ion binding site of enzymes.<sup>[57]</sup> Cadmium concentration increases 3,000 fold when it binds to cystein-rich protein such as metallothionein. In the liver, the cystein-metallothionein complex causes hepatotoxicity and then it circulates to the kidney and gets accumulated in the renal tissue causing nephrotoxicity. Cadmium has the capability to bind with cystein, glutamate, histidine and aspartate ligands and can lead to the deficiency of iron. Cadmium and zinc have the same

oxidation states and hence cadmium can replace zinc present in metallothionein, thereby inhibiting it from acting as a free radical scavenger within the cell.<sup>[59]</sup> The toxic effect of Fe(III) complex is related to the wide range of harmful free radicals that produced when the absorbed iron fails to bind to the protein, which in turn affects on the concentration of iron in cells and biological fluids. This circulating unbound iron results in corrosive effect of the gastrointestinal tract and biological fluids.<sup>[59]</sup> An extremely higher level of iron enters into the body crossing the rate-limiting absorption step and becomes saturated. Due to the disruption of oxidative phosphorylation by free iron, the ferrous iron is converted to ferric iron that releases hydrogen ions, thus increasing metabolic acidity. The free iron can also lead to lipid peroxidation, which results in severe damage to mitochondria, microsomes and other cellular organelles. The toxicity of iron on cells has led to iron mediated tissue damage involving cellular oxidizing and reducing mechanisms and their toxicity towards intracellular organelles such as mitochondria and lysosomes. A wide range of free radicals that are believed to cause potential cellular damage are produced by excess intake of iron.<sup>[59]</sup> The relatively lower toxicity of Cr(III) complex compared to other tested compounds is attributed to the weak membrane permeability of Cr(III) ions.<sup>[59]</sup>

## 3.9.2 | Antibacterial activity

Transition metal complexes with nitrogen containing ligands have gained an increasing importance due to their potential application in bacteriostasis.<sup>[60]</sup> The inhibition zones (cm) of the asymmetric Schiff base ligand and its metal complexes against the growth of the representative Gram-positive bacteria; S. aureus and Gram-negative bacteria; E. coli are listed in Table 9 and shown in Figure 10. The results reveal that all investigated compounds display antibacterial activity against S. aureus, while 7 out of the 10 tested compounds show antibacterial activity against E. coli with different inhibition degrees. Based on the size of the inhibition zones, the antibacterial activity was significantly higher against S. aureus than E. coli. The susceptibility of the tested bacterial strains toward the asymmetric Schiff base ligand is lower than ceftriaxone and is generally enhanced by chelation with metal ions.<sup>[60]</sup> Zn(II) complex exhibits a comparable antibacterial activity against S. aureus and E. coli with inhibition zones; 2.00 and 2.20 cm, respectively, compared to 1.90 and 2.10 cm for ceftriaxone. This is attributed to the strong binding energy of Zn(II) complexes.<sup>[8]</sup> The antibacterial activity of Cu(II), Zn(II), Cd(II) and Fe(III) complexes against S. aureus is higher than that of ceftriaxone. While, ceftriaxone shows higher antibacterial 16 of 18 WILEY Organometallic Chemistry

 TABLE 9
 Antibacterial activity of the asymmetric Schiff base ligand and its metal complexes

		Inhibition Zo	ne (cm)
No.	Compound	Staphylococcus aureus	Escherichia coli
	$H_{2}L.0.25H_{2}O$	1.30	1.10
	Ceftriaxone	1.90	2.10
1	$[Co_2(HL)_2Cl_2(H_2O)_2].7H_2O$	1.90	0.70
2	[Ni <sub>2</sub> (HL)Cl <sub>3</sub> (H <sub>2</sub> O)].5EtOH.1.25H <sub>2</sub> O	1.50	1.80
3	[Cu <sub>2</sub> (HL)Cl <sub>3</sub> (H <sub>2</sub> O)].2.5EtOH	2.70	0.95
4	$[Cu_2(HL)_2(H_2O)_2(ClO_4)_2].8H_2O$	2.10	0.90
5	[Cr <sub>2</sub> (HL)Cl <sub>2</sub> (OH) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ].6.75EtOH.0.5H <sub>2</sub> O	1.50	-
6	[Fe <sub>2</sub> (HL)Cl <sub>5</sub> (H <sub>2</sub> O) <sub>3</sub> ].2EtOH.4.5H <sub>2</sub> O	2.10	1.00
7	[Ru <sub>2</sub> (HL)Cl <sub>5</sub> (H <sub>2</sub> O) <sub>3</sub> ].2EtOH.4.5H <sub>2</sub> O	1.80	-
8	$[Zn_2(HL)_2Cl_2(H_2O)_2].8.5H_2O$	2.00	2.20
9	$[Cd_2(HL)_2Cl_2(H_2O)_2].13H_2O$	2.20	-



FIGURE 10 Inhibition zones of the tested compounds against S. aureus and E. coli

activity against *E. coli* than all tested compounds, except Zn(II) complex (Table 9). This increased activity of metal complexes can be discussed based on the basis of Overtone's concept.<sup>[61]</sup> According to this concept of cell permeability, the lipid membrane that surrounds the cell favors passage of only lipid soluble materials due to very less liposolubility, which is an important factor that

control antimicrobial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases delocalization of  $\pi$ -electrons over the whole chelate ring and enhances lipophilicity of the compound, increasing the penetration of the compounds into lipid membranes and blocking of the metal binding sites in the enzymes of the microorganism. These compounds also disturb the respiration process of the cell and thus block the synthesis of proteins that restricts further growth of the organisms. Furthermore, the mode of action of the compound may involve formation of a hydrogen bond through the azomethine group with active center of cell constituents, resulting interference with the normal cell process.<sup>[62]</sup>

#### 4 | CONCLUSION

A new series of some transition metal complexes was prepared from the novel asymmetric tetradentate thiosemicarbazone Schiff base ligand; (E)-N'-(1-(4-((E)-2hydroxybenzylideneamino)phenyl)ethylidene)morpholine-4-carbothiohydrazide  $(H_2L)$ . The ligand and its metal complexes were investigated by elemental analyses, spectral (mass, <sup>1</sup>H NMR, UV-Vis., ESR) studies, thermal analyses, magnetic susceptibility, molecular modeling, X-ray diffraction and molar conductivity measurements. Spectral data prove that the asymmetric Schiff base ligand chelates with all metal complexes as a monobasic tetradentate one. Analytical and spectral studies emphasize the formation of sandwich octahedral and binuclear tetra-coordinate complexes (Co(II), Cu(II) (4), Zn(II), Cd(II) and Ni(II), Cu(II) (3), respectively. Whereas, Fe(III), Cr(III) and Ru(III) ions formed octahedral binuclear complexes. The thermal decomposition behaviors of the prepared compounds as well as the estimated kinetic and activation thermodynamic parameters were obtained by using thermogravimetric technique. Molecular modeling data asserted the thermal decomposition pathways of the investigated compounds. The ESR spectra of Cu(II) complexes reveal that the unpaired electron is localized mainly in the  $d_{(x - y)}^{2}$  orbital with axial symmetry. The prepared compounds show a considerable anti-molluscicidal activity against Eobania vermiculata. The enhanced toxicity of the tested metal complexes may be due to the reactions of metals with enzymes. Therefore, these compounds may be used as anti-molluscicidal agents to control the propagation of Eobania vermiculata. The in vitro antibacterial activity of the prepared compounds against the Gram-positive bacteria; Staphylococcus aureus and Gramnegative bacteria; Escherichia coli show that the zones of inhibition is much larger for the tested complexes than that of the free ligand, due to the effect of metal ions.

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#### SUPPORTING INFORMATION

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