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Synthesis, Characterization and DNA Binding Studies of Zn(II)/Cu(II) Complexes with 2,2`-Diphenyl Acetic Acid/2-(4-Hydroxyphenyl)Acetic Acid Ligand Precursors and Nitrogen Bases

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Abstract

The hydrated complexes 1, 3, 7 and 8 with the general formula $(RCOO)_2M.xH_2O$ (where M = Zn & x = 6; M = Cu & x = 5,6) were synthesized by the reaction of sodium salt of 2,2`-diphenyl acetic acid or 2-(4-hydroxyphenyl)acetic acid (RCOONa) with $Zn(NO_3)_2.6H_2O$ or $CuSO_4.5H_2O$ in an aqueous medium. The addition of methanolic solution of either bipyridine (bpy) or 1,10-phenanthroline (phen) to an aqueous suspension of 1, 3, 7 and 8 (produced *in situ*) result in the formation of mixed ligand products with the general formulae $(RCOO)_2M(bpy).xH_2O$ (2, 4, 9 and 10) and $(RCOO)_2M(phen).xH_2O$ (5 and 6). The complexes were characterized by microanalysis, FTIR and NMR (^1H and ^{13}C) spectroscopic techniques. The FTIR data suggested a bidentate coordination mode of the carboxylate ligand and complexes exhibited four/six-coordinated geometry in the solid state. The spectroscopic data also revealed the presence of coordinated water molecules in all complexes. ^1H and ^{13}C NMR data demonstrated the coordination between ligand and the metal in complex 1. The complexes were tested for their binding with salmon sperm DNA (SS-DNA). The DNA binding potential of the complexes owed to the presence of zinc metal and the nature of the incorporated ligand. The complexes showed a significant hypochromic effect and an intercalating mode of binding with SS-DNA. The complexes were screened against various bacterial and fungal strains to check their biological activity. All the complexes showed significant antibacterial activity but none of complex exhibit antifungal activity.

Keywords: Transition metal complexes; Zinc; Copper; IR; NMR; SS-DNA; Biological activity; Thermal analysis.

1. Introduction

The synthesis and design of novel coordination products based on transition or non-transition metals and multifunctional bridging ligands are of great research interest, due to the interesting topologies and potential applications of the complexes as functional materials. The bridging ligands such as carboxylates are very effective due to their versatile bridging modes [1, 2]. Metal complexes with bridging carboxylates as well as stable organic radical ligands are of considerable interest to the field of molecular magnetism [3]. There are reports that heterocyclic compounds play a significant role in a large number of biological systems e.g., N-donor compounds with six membered rings being a component of several enzymes and drugs. Therefore many complexes have been synthesized from the heterocyclic ligands and their antimicrobial activities were reported [4].

The carboxylate ligands are common ligand in many zinc as well as iron and calcium proteins. For example, all mono-, binuclear non-heme iron proteins and all polynuclear zinc proteins have at least one carboxylate group per metal ion [5, 6]. Moreover, it is well known that these carboxylate groups often shift between mono- and bidentate coordination and between binding to one or two metal ions. This flexible motion is believed to be of catalytic significance and has been termed carboxylate shift [7].

Zinc(II) cations, due to their d^{10} electronic configuration, form complexes with a flexible coordination environment, and the geometries of these complexes can vary from tetrahedral to octahedral, and severe distortions of the ideal polyhedral occur easily. Zinc(II) chemistry plays an important role in biological systems. Zinc-containing carboxylato-bridged complexes form a variety of structural motifs in hydrolytic metalloenzymes, such as phosphatases and aminopeptidases [8, 9]. The catalytic role of zinc comprises Lewis acid activation of the substrate, generation of a reactive nucleophile (Zn–OH) and stabilization of leaving groups. The synthesis of Zn(II) complexes require ligands to react with Zn(II) reagents in the presence or absence of alkali in a large quantity of organic solvents or aqueous solution by heating or at room temperature [10]. Zinc(II), dehydrated zinc, is used in medicine to treat the Zn(II) deficiency in organisms [11]. There is great interest to synthesize model complexes of zinc containing enzymes. Consequently, complexes containing other N-donor ligands have been prepared, and complexes with nitrogen from monomeric and polymeric ligands with functional groups containing nitrogen have been studied [12-14].

Copper is one of essential elements required for normal human metabolism [15]. Copper(II) is known to play a significant role in biological systems and also as a pharmaceutical agent. Its antibacterial properties have been known for thousands of years. Synthetic copper(II) complexes have been reported to act as a potential anticancer and cancer inhibiting agents and a number of copper complexes have been found to be active both *in vitro* and *in vivo* [16, 17].

Nitrogen-containing ligands have found wide applications in chemotherapy and asymmetric catalysis. Among them, bipyridine and 1,10-phenanthroline have been the most attractive due to their various functions. The 1,10-phenanthroline (phen) and its derivatives exhibit antiviral, antifungal and antimycoplasmal activities [18]. DNA damage in the presence of Cu-phenanthroline is attributed to the highly reactive hydroxyl radicals, OH· generated through the site-specific Fenton reaction [19].

Keeping in view the applications of metal (Zn(II)/Cu(II)) coordination chemistry, the carboxylate ligand precursors and bipyridine/1,10-phenanthroline bases, we have synthesized various mixed ligand metal complexes using the carboxylate ligand, metal salts and bipyridine/1,10-phenanthrolineas starting materials. The synthesized complexes were characterized by elemental analyses (CHN), FTIR and ^{1}H &^{13}C NMR spectroscopy. After structural verification, the products were subjected to DNA binding studies with salmon sperm DNA (SS-DNA). Their biological activity was also checked against various bacterial and fungal strains.

2. Experimental

2.1. Materials and Methods

2,2`-Diphenylacetic acid, 2-(4-hydroxyphenyl)acetic acid, bipyridine, 1,10-phenanthroline, $Zn(NO_3)_2.6H_2O$ and $CuSO_4.5H_2O$ were purchased from Aldrich (USA). Solvents were dried before use by a standard procedure [20].

Melting points were found in capillary tubes by an electrochemical melting point apparatus, MP-D Mitamura Rieken Kogyo (Japan). Elemental analyses (CHN) were performed by CHNS-932 analyzer Leco (USA). Infrared spectra were recorded by Perkin Elmer FT-IR-1000 spectrophotometer in the range of 4000-400 cm^{-1}. The ^{1}H and ^{13}C NMR spectral measurements were made at 300 Hz and 75 Hz, respectively using the DMSO-d_6 solvent by a Bruker FT-NMR spectrometer.

2.2. Syntheses

2.2.1. Procedure for the Synthesis of Sodium salt of 2,2`-Diphenylacetic Acid and 2-(4-Hydroxyphenyl) Acetic Acid

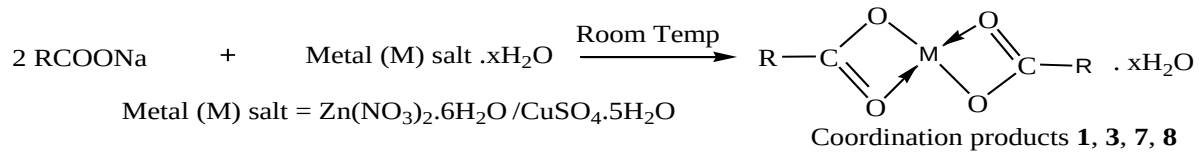
2,2`-Diphenylacetic acid/2-(4-hydroxyphenyl)acetic acid (1 mmol) was dissolved in distilled water (50 ml) in a round bottom two necked flask with stirring. Then an aqueous solution (10 ml) of sodium bicarbonate (1 mmol) was added drop wise to the above solution. The reaction mixture was continuously stirred for 2 h at room temperature. The solid product obtained was dried in open air.

$$RCOOH \xrightarrow{NaHCO_3} RCOONa + H_2O + CO_2$$

2.2.2. General Procedure for the Synthesis of Transition Metal Complexes

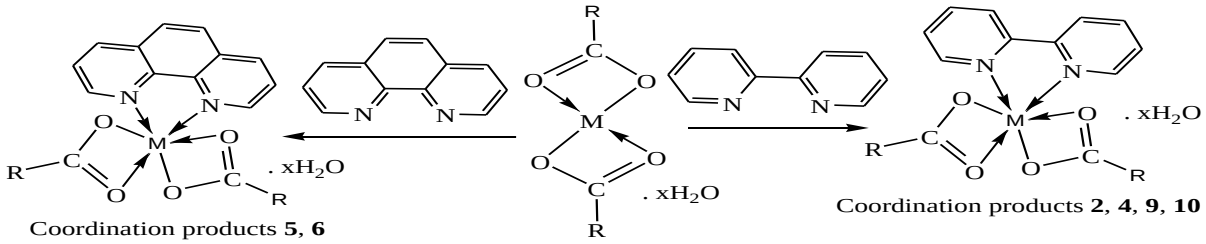
Sodium salt of 2,2`-diphenylacetic acid/2-(4-hydroxyphenyl)acetic acid (1 mmol) was dissolved in water in a round bottom two necked (100 ml) flask at room temperature with continuous stirring. Solution of $Zn(NO_3)_2.6H_2O$/$CuSO_4.5H_2O$ (1 mmol) in water was added dropwise to the above solution and reaction mixture was stirred at room temperature for 2 h to yield the products **1**, **3**, **7** and **8** (Scheme 1) which can be isolated by evaporation of the solvent by a rotary evaporator.

For the synthesis of remaining complexes (**2**, **4**, **5**, **6**, **9** and **10**), the reaction mixture containing **1**, **3**, **7** and **8** were not isolated from the reaction vessel but it was further stirred for 2 h after addition of methanolic solution of 2,2`-bipyridine/1,10-phenanthroline. Solvent was evaporated by using rotary evaporator under reduced pressure. The solid product obtained was dried in open air and recrystallized in methanol:petroleum ether (1:1) mixture (Scheme 2).



Coordination products **1**, **3**, **7**, **8**

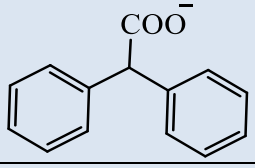
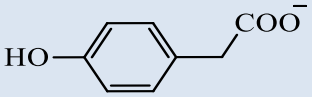
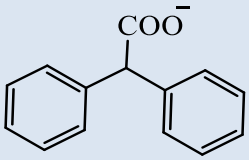
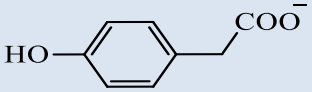
Scheme 1



Coordination products **5**, **6**

Coordination products **2**, **4**, **9**, **10**

Scheme 2

Compound No.	M	R-COO$^-$	x
1, 2	Zn		6
3, 4, 5, 6	Zn		6
7, 9	Cu		5
8, 10	Cu		5

3. Results and Discussion

The zinc/copper coordination products **1**, **3**, **7** and **8** were synthesized by the reaction of 2,2`-diphenylacetic acid/2-(4-hydroxyphenyl)acetic acid with a metal salt ($Zn(NO_3)_2.6H_2O/CuSO_4.5H_2O$) in water. The addition of bipyridine/1,10-phenanthroline to the reaction mixture of **1**, **3**, **7** and **8** has resulted in the formation of products **2**, **4**, **5**, **6**, **9** and **10**. The complexes have sharp melting points and are stable in air. The elemental analysis (CHN) data agreed well with the proposed molecular composition of the products. The physical data of the complexes are summarized in Table 1.

Table-1. Physical data of the complexes **1-10**

Comp. No.	Molecular formula	Mol. wt	Yield (%)	m.p (^{0}C)	Elemental analysis (calculated/found)		
					%C	%N	%H
1	$C_{28}H_{22}O_4Zn.6H_2O$	595.4	76	194	56.4/56.8	-	5.7/5.3
2	$C_{38}H_{30}N_2O_4Zn.6H_2O$	751.6	59	198	60.7/60.3	3.7/3.3	5.6/5.2
3	$C_{16}H_{14}O_6Zn.6H_2O$	475.4	80	270	40.3/40.7	-	5.5/5.1
4	$C_{26}H_{22}N_2O_6Zn.6H_2O$	631.6	73	-	5.4/5.8	4.4/4.8	5.4/5.8
5	$C_{28}H_{22}N_2O_6Zn.6H_2O$	655.6	88	199	51.2/51.6	4.3/4.7	5.2/5.6
6	$C_{40}H_{30}N_2O_4Zn.6H_2O$	775.6	82	234	61.9/61.5	3.6/3.2	5.5/5.1
7	$C_{28}H_{22}O_4Cu.5H_2O$	575.5	84	222	58.4/58.0	-	5.6/5.2
8	$C_{16}H_{14}O_6Cu.5H_2O$	455.5	79	216	42.2/42.6	-	5.3/5.7
9	$C_{38}H_{30}N_2O_4Cu.5H_2O$	731.7	85	290	62.3/62.7	3.8/3.4	5.5/5.9
10	$C_{26}H_{22}N_2O_6Cu.5H_2O$	611.7	81	244	51.0/50.4	4.6/4.2	5.3/5.7

3.1. IR Spectroscopy

Infrared spectra were recorded in the range 4000–400 cm^{-1} for the coordinated products **1-10** and the data is given in the Table 2.

The carbonyl stretching frequency was substantially lowered in the metallic complexes as compared to their free carboxylic acid precursors (2,2`-diphenylacetic acid or 2-(4-hydroxyphenyl)acetic acid). The lowering down of

υ(C=O) value verifies the coordination of the carboxylic donor site with a metal i.e., Zn(II) in complexes **1-6** and Cu(II) in the remaining products **7-10** [21]. The mode of metal carboxylate interaction can be predicted from Δυ = $\upsilon COO_{(asym)}$-$\upsilon COO_{(sym)}$ value; a smaller Δυ value indicates that carboxylate groups are coordinated more symmetrically. The Δυ value of the coordinated products **1-10** was observed in a range of 211–239 cm^{-1} suggesting a chelating coordination mode of the carboxylate group [22, 23]. Thus four and six-coordinated geometries were assigned to the metal centers in the solid state depending upon whether an additional stabilizing ligand (i.e., base such as bipyridine or 1,10-phenanthroline) is a part of the complex structure or not, respectively. The coordination with either zinc or copper metal was further convinced by the occurrence of weak to medium strength bands in the range of 470-476 cm^{-1} and 418-429 cm^{-1} for metal-oxygen and metal-nitrogen bonds, respectively.

There was occurrences of broad band at 3417-3429 cm^{-1} due to asymmetric and symmetric vibrations of O-H moieties and medium strength bands at 828-856 cm^{-1} for $\rho_r(H_2O)$ due to stretching and bending (rocking) vibrations in the water molecules. The existence of these two bands (OH and $\rho_r(H_2O)$) evidently depicted the presence of water molecules in the investigated zinc/copper complexes [24]. The evidence for the presence of incorporated water in the complexes was verified by ^{1}H NMR spectroscopy and thermal analysis.

Table-2. FTIR data[a] of the complexes 1-10

Comp. No.	υCOO			υM-O	υM-N	υOH	$\rho_r(H_2O)$
	υ_{asym}	υ_{Sym}	Δυ				
1	1625s	1414s	211	476m	-	3417b	854m
2	1624s	1413s	211	470m	418w	3419b	853m
3	1621s	1382s	239	473m	-	3426b	852m
4	1625s	1410s	215	471m	420w	3420b	856m
5	1622s	1382s	240	472m	420w	3429b	846m
6	1624s	1413s	211	476m	419w	3419b	853m
7	1612s	1398s	214	474w	-	3417b	843m
8	1626s	1410s	216	471m	-	3421b	828m
9	1612s	1398s	214	474w	429m	3418b	843m
10	1612s	1398s	214	474w	428m	3418b	843m

[a]Abbreviations: s = strong; m = medium; w = weak; b = broad

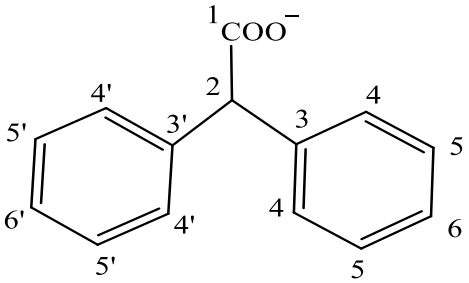
3.2. ^{1}H and ^{13}C NMR Spectroscopy

The ^{1}H and ^{13}C NMR spectra of the complex **1** were recorded in DMSO-d_6 at room temperature. The number of protons found by integration of peaks in the spectra agreed very well with those calculated from the expected composition. The data is reported in Table 3. ^{1}H NMR results showed that the coordinated product **1** had no –COOH signal indicating deprotonated carboxylic precursor for coordination with the metal. The methyne proton exhibited a singlet at 3.38 ppm. Chemical shift at 4.91 ppm appeared as a singlet for the incorporated water. The ^{13}C NMR spectrum displayed the carboxylate and methyne signals at 177.5 ppm and 58.9 ppm, respectively. The aromatic carbon atoms were appeared at 142.4 ppm, 128.4 ppm, 129.2 ppm and 129.5 ppm, respectively.

Table-3. ^{1}H and ^{13}C NMR data[a] (in ppm) of the complex **1**

Proton/carbon No.	1	2	3,3′	4,4′	5,5′	6,6′	H_2O
^{1}H NMR shifts	-	3.38s	-	7.36d (1.5)	7.22-7.28m	7.14-7.20m	4.91s
^{13}C NMR shifts	177.5	58.9	142.4	128.4	129.2	129.5	-

[a]The numerical values within the parenthesis correspond to $^3J(^1H, ^1H)$; Multiplicity is given as: s = singlet, d = doublet, m = multiplet; The numbering scheme used in ^{1}H and ^{13}C NMR spectroscopic data has been given below:



3.3. DNA Interaction Studies

DNA is generally accepted as a target for most of the anticancer agents. So, the synthesized complexes were evaluated for their potential of binding with DNA by electronic absorption spectroscopy. The mode of interaction of zinc/copper complexes with salmon sperm DNA (SS-DNA) was determined by the comparison of the absorbance and the shifts in a wavelength range of 200-400 cm^{-1} with and without DNA. The spectra were recorded at different DNA concentrations by keeping the concentration of the complexes (solvent, DMSO) constant [25]. The DNA binding activities owed to the nature of coordinated metal and aromatic ligand precursor. The presence of a phenyl group facilitates the interaction with double stranded DNA [26, 27].

Thus only the zinc complexes **1-4** exhibited their binding with DNA (Figures 1, 2, 3, 4) out of all the coordination products (**1-10**). None of the copper complex showed any tendency to bind with DNA. The UV spectra showed a significant hypochromic effect and an intercalating mode of binding. Generally hypsochromism and red shift are associated with intercalative binding of the complex to the double helix of DNA due to strong intercalation between the complex and the base pairs of DNA. The extent of hypsochromism is commonly consistent with the strength of the intercalative interaction [25].

After 24 h, spectra of the investigated products were recorded again, which produced the identical results which verified the stability of drug-DNA complex. The intrinsic binding constants (K) were calculated for the DNA active products by using the following Benesi-Hildebrand equation [18]:

$$\frac{A_0}{A - A_0} = \frac{\varepsilon_G}{\varepsilon_{H\text{-}G} - \varepsilon_0} + \frac{\varepsilon_G}{\varepsilon_{H\text{-}G} - \varepsilon_G} \times \frac{1}{K[DNA]}$$

Where K = binding constant; A_0 = absorbance of the drug; A = absorbance of the drug and its complex with DNA; ε_G = absorption coefficient of drug; ε_{H-G} = absorption coefficient of drug–DNA complex.

The association constants were obtained from the intercept-to-slope ratios of $A_0/(A\text{-}A_0)$ *vs.* 1/[DNA] plots. The binding constants were found to be 3.0×10^3 M^{-1}, 1.2×10^3 M^{-1}, 3.6×10^3 M^{-1} and 9.4×10^3 M^{-1} for the complexes **1**, **2**, **3** and **4**, respectively. The highest binding potential of the complex **4** was rendered to the coordination of 2-(4-hydroxyphenyl) acetic acid as well as bipyridine with the zinc metal center. The complex **3** possesses the same structural composition like **4** with the exception that it has not incorporated bipyridine, so it exhibits the second highest value of binding constant. The complexes **1** and **2** having different ligand precursor (2,2`-diphenylacetic acid with or without bipyridine) showed comparatively lower affinity for DNA.

The Gibb's free energies (ΔG) were determined by using equation:

$\Delta G = -RT \ln K$

where T is the temperature (298 K) and R is general gas constant (8.314 $JK^{-1}mol^{-1}$). The Gibb's free energies were found −20 $KJmol^{-1}$ (complex **1**), −18 $KJmol^{-1}$ (complex **2**), −20 $KJmol^{-1}$ (complex **3**) and -22 $KJmol^{-1}$ (complex **4**). The negative values of ΔG suggest that the interaction of compound with the target DNA is a spontaneous process.

Fig-1. Absorption spectra of 35 µM (λ_{max}= 260 nm) solution of complex **1** in the absence and presence of 7 to 42 µM DNA solution, The arrow direction indicates increasing concentration of DNA with hypochromic effect and 2 nm of blue shift. The graph represents the plot of $A_o/A\text{-}A_o$ *vs.* $1/[DNA]\ (\mu M)^{-1}$ for the calculation of binding constant (K) and Gibb's free energy(ΔG)

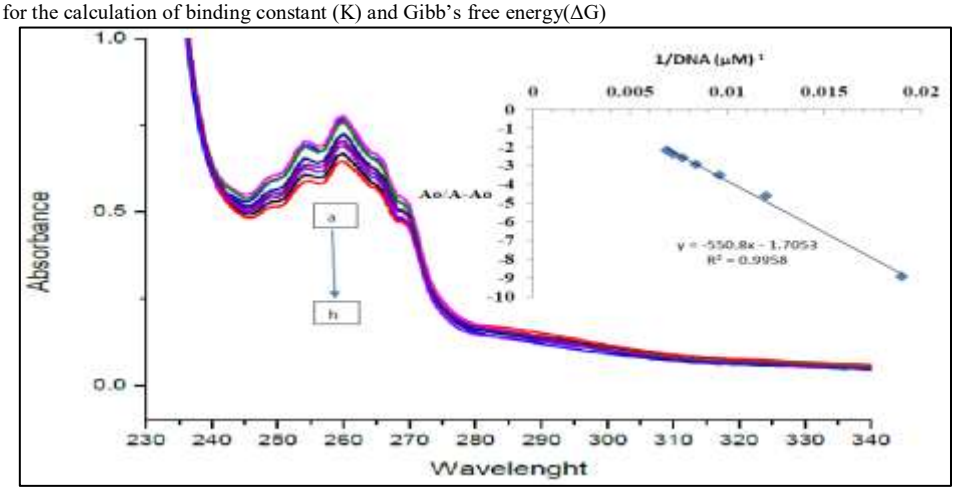


Fig-2. Absorption spectra of 42 µM (λ_{max}= 293 nm) of complex **2** in the absence and presence of 5 to 40 µM DNA solution, The arrow direction indicates increasing concentrations of DNA with hypochromic effect and 2 nm of blue shift. The graph represents the plot of $A_o/A\text{-}A_o$ *vs.* $1/[DNA]\ (\mu M)^{-1}$ for the calculation of binding constant (K) and Gibb's free energy(ΔG)

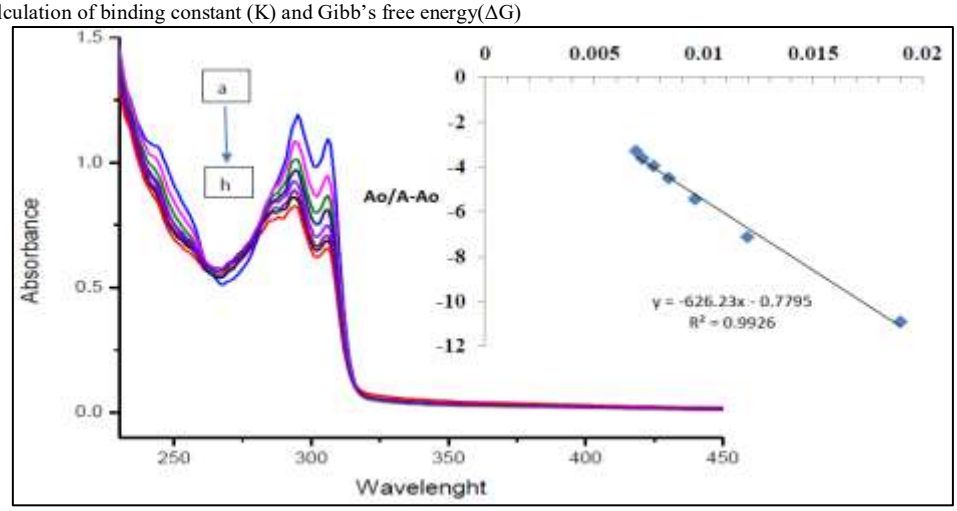


Fig-3. Absorption spectra of 45 µM (λ_{max}= 278 nm) of complex **3** in the absence and presence of 5 to 40 µM DNA solution, The arrow direction indicates increasing concentrations of DNA with hypochromic effect and 1-2 nm of blue shift. The graph represents the plot of $A_o/A\text{-}A_o$ *vs*. $1/[DNA]\ (\mu M)^{-1}$ for the calculation of binding constant (K) and Gibb's free energy(ΔG)

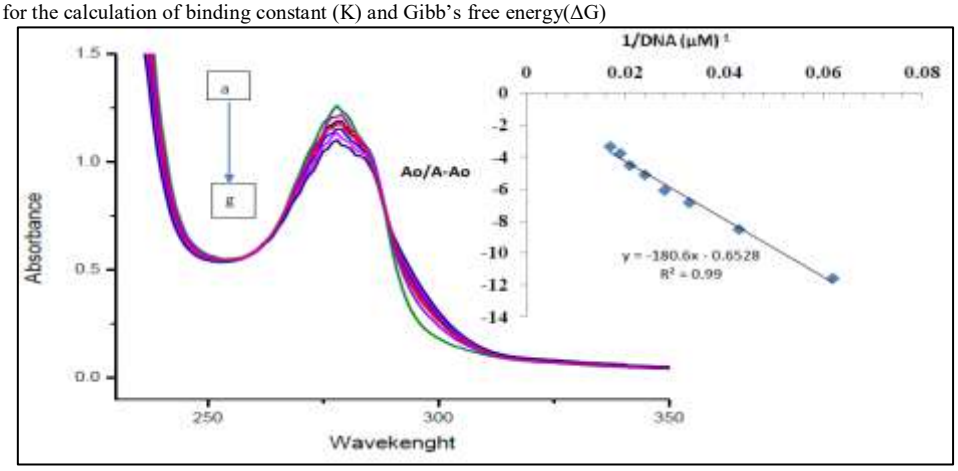
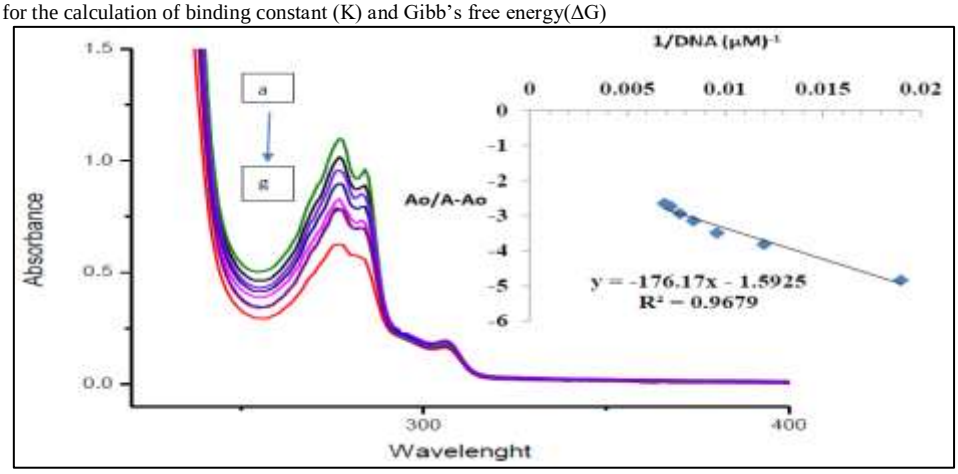


Fig-4. Absorption spectra of 40 µM (λ_{max}= 282 nm) of complex **4** in the absence and presence of 7 to 42 µM DNA solution, The arrow direction indicates increasing concentrations of DNA with hypochromic effect and 1-2 nm of blue shift. The graph represents the plot of $A_o/A\text{-}A_o$*vs*. $1/[DNA]\ (\mu M)^{-1}$ for the calculation of binding constant (K) and Gibb's free energy(ΔG)



3.4. Antibacterial Activity

The antibacterial activity against *E. coli* (gram positive) and *B. subtilis* (gram negative) was evaluated by using of agar disc diffusion method [28]. The standard antibacterial drug used was ciprofloxacine. Zinc(II) complexes of carboxylates appeared to have good antibacterial activity; e.g., a strong inhibitive effect was noticed towards *E. coli.* The antibacterial activity of the complexes against the selected types of bacterial strains is presented in Table 4.

Table-4. Antibacterial activity data of complexes **1-10**

Comp. No.	Zone of inhibition (mm)		Standard drug
	***E. coli* (-)**	***B. subtilis* (+)**	**Ciprofloxacine**
1	8.8±0.02	8.2±0.04	13
2	8.3±0.2	8.4±0.4	13
3	8.6±0.02	8.4±0.05	13
4	8.2±0.4	8.2±0.6	13
5	8.8±0.4	9±0.8	13
6	8.9±0.7	8.9±0.9	13
7	8.9±0.1	8.2±0.2	13
8	8.3±0.4	8.5±0.6	13
9	8.3±0.5	8.2±0.6	13
10	8.7±0.2	8.3±0.1	13

The free ligand was totally inactive against all the tested bacterial strains but the coordination with transition elements has induced the biological potential in consequent complexes. The complex **7** showed maximum antibacterial activity against *E. coli* whereas complex **5** showed maximum inhibition against *B. subtilis*.

3.5. Antifungal Activity

The synthesized compounds were examined for their antifungal activity against *A. niger* by using disc diffusion method [29]. The results indicated that all complexes were found inactive against the tested fungal strain which is in accordance with literature [30]. The standard drug used was pencillium.

3.6. Thermogravimetric Analysis

The thermal decomposition pattern and kinetic patterns of complexes **1-10** are given in Tables 5 and 6, respectively.

Table-5. Thermal Decomposition Pattern of complexes **1-10**

Comp. No.	Temp. °C	Evolved Components	Residual Component	% wt. loss	
				Calcd.	Obs.
1	280-620	$C_{28}H_{34}O_9$	ZnO	86.35 13.65	84.9 15.1
2	200-500	$C_{38}H_{42}O_9N_2$	ZnO	89.19 10.81	88.10 11.9
3	260-700	$C_{16}H_{26}O_{11}$	ZnO	82.9 17.10	81.8 18.2
4	100-800	$C_{26}H_{34}O_{11}N_2$	ZnO	87.13 12.87	86.0 14.0
5	240-500	$C_{28}H_{32}O_8$	ZnO	85.88 14.12	85.5 14.5
9	260-800	$C_{28}H_{34}O_{11}N_2$	ZnO	87.60 12.4	86.9 13.1
10	260-800	$C_{40}H_{42}O_9N_2$	ZnO	89.52 10.48	88.8 11.2

Table-6. Kinetic Parameters of complexes **1-10**

Comp. No.	Temp. °C	Order (n)	Act. Energy (KJ/mol)	Enthalpy (KJ/mol)	Entropy (J/molK)
1	280-620	1.16	47.38	43.81	-29.36
2	200-500	1.01	31.83	28.75	-89.57
3	260-700	1.11	23.31	19.92	-164.05
4	100-800	1.08	15.32	11.71	-223.75
5	240-500	1.03	28.20	25.65	-74.91
9	260-800	1.23	30.65	26.33	-159.41
10	260-800	0.99	7.55	4.39	-269.97

Compound **1** showed one step decomposition in the temperature range 280–620 °C, evolving $C_{28}H_{34}O_9$ (84.9%) leaving only ZnO. The decomposition was order of 1.16 and calculated activation energy is 47.38 kJ/mol. The reaction's enthalpy is 43.81kJ/mol and entropy is -29.36 J/molK.

Compound **2** is stable upto 200 °C, evolving $C_{38}H_{42}O_9N_2$, leaving only 11.9 % ZnO as residue. The decomposition was order of 1.01 with the activation energy as 31.83 kJ/mol. The enthalpy of reaction is 28.75 kJ/mol and entropy is -89.57 J/molK.

Complex **3** is stable upto 260 °C, showing one step decomposition. The step proved the loss of $C_{16}H_{26}O_{11}$group with 81.8 % weight loss. The mandatory activation energy is 23.31 kJ/mol with the order 1.11 and leaving ZnO as a residue. The enthalpy for decomposition is 19.92 kJ/mol, whereas entropy is -164.05 J/molK.

In complex **4**, thermogravimetric trace showed a mass loss over a temperature range of 100-800 °C leaving 14.0 % residues (ZnO) with the elimination of $C_{26}H_{34}O_{11}N_2$. The reaction was the order of 1.08 with the activation energy of 15.32 kJ/mol.

The enthalpy of the system is 11.71 kJ/mol and entropy is -223.75 J/molK. Complex **5** is stable upto 500 °C, showing one step decomposition. The step showed the loss of $C_{28}H_{32}O_8$ group with 85.5% weight loss.

The required activation energy is 28.20 kJ/mol with the order 1.03 and gives ZnO as residue. The enthalpy for decomposition is 25.65 kJ/mol, whereas entropy is -74.91 J/molK.

In complex **9**, thermogravimetric trace shows a mass loss over a temperature range of 260-800 °C leaving 13.1 % residues (Zn O) with the elimination of $C_{28}H_{34}O_{11}N_2$. The reaction was the order of 1.23 with the activation energy of 30.65 kJ/mol. The enthalpy of the system is 26.33 kJ/mol and entropy is -159.41 J/molK.

Compound **10** is stable upto 260 °C, showing single stage decomposition with the utmost weight loss upto800 °C with 0.99 reaction order and 7.55 kJ/mol activation energy. The lasting component till 800 °C is ZnO. The enthalpy of reaction is 4.39kJ/mol and entropy is -269.97 J/molK.

4. Conclusion

The hydrated zinc and copper coordination compounds have been synthesized by reacting 2,2`-diphenylacetic acid/2-(4-hydroxyphenyl)acetic acid with a corresponding metal salt ($Zn(NO_3)_2.6H_2O$ or $CuSO_4.5H_2O$) in methanolic/aqueous medium in the presence or absence of bipyridine/1,10-phenanthroline. The complexes demonstrate a bidentate coordination mode of the ligand for binding with zinc or copper and exhibited four/six-coordinated geometry in the solid state. ^1H and ^{13}C NMR data verified the metal ligand coordination. The DNA binding potential of the complexes owed to the presence of zinc metal and the nature of the incorporated ligand. The UV data showed a significant hypochromic effect and an intercalating mode of binding of complexes with SS-DNA.

All complexes showed significant antibacterial activity but none of complex exhibit antifungal activity. The thermal decomposition and different kinetic parameters (e.g., order of reaction, activation energy and enthalpy of reaction) were calculated.

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