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Spectroscopic characterizations and biological studies on newly synthesized Cu²⁺ and Zn²⁺ complexes of first and second generation dendrimers

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ABSTRACT

The novel Cu(II) and Zn(II) complexes of first and second generation poly(propylene amine) dendrimers (PPA), comprising 1,8-naphthalimde units on periphery have been synthesized. These new complexes were characterized by elemental analysis, molar conductivity, spectral methods (IR, ¹H NMR and UV-vis spectra) and thermal analysis (TG and DTG) techniques. From elemental analysis as well as thermal studies it has found that the first generation dendrimer behaves as bidentate ligand and forming chelates with 1:2 (ligand:metal) and 1:4 (ligand:metal) stoichiometry for second generation dendrimer. Different kinetic parameters namely activation energy (ΔE^*), enthalpy of activation (ΔH^*), entropy of activation (ΔS^*) and free energy change of activation (ΔG^*) are calculated using Coats–Redfern equation. The antibacterial activity of dendrimers and their complexes was evaluated against some Gram positive and negative bacteria.

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1. Introduction

Dendrimer chemistry expanded rapidly because it is significance both in basic research and application [1]. Dendrimers represent a unique class of molecules with a regular branched structure [2,3]. They are well-defined three-dimensional macromolecules [4]. In recent years they have been receiving increased attention mainly because of their symmetry, high degree of branching and high density of the terminal functional groups which can participate in different reaction [5–7].

Dendrimers with electroactive groups have found applications as components in different sensors and electroluminescent devices. On the other hand the introduction of different types of chromophores in dendrimers macromolecules makes these macromolecules photoactive with potential applications in photochemical molecular devices [8–12]. Some of these compounds have also been investigated for use as biosensors [13,14]. Dendrimers are a class of three dimension polymers suitable for a wide rang of biomedical applications; drug delivery, RNA, DNA and detoxication, microarray system, catalysis [15,16]. They are a class of nanoscopic polymers with highly branched spherical structure and a unique surface of primary amines as well as tertiary

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amines at branch point. Dendrimers can transport DNA into a large variety of cell types and have emerged as a promising non-viral gene carrier for genetic medicines due to their safety and efficiency [17–21].

On the other hand, the applications of 1,8-naphthalimide possessing bright color, good photostability and physiological activities have also been widely studied. They are used in solar energy collectors [22], as laser active media [23,24], as potential photosensitive biological activity units [25], and in medicine [26]. Recently, they have been examined in liquid crystal systems for utilization in electro-optical devices [27-31]. Some 1,8-naphthalimide derivatives which exhibit good fluorescence 'off-on' switching in the presence of protons or transition metal cations can perform as fluorescent sensors of photoinduced electron transfer (PET) [32-36]. The results from the spectral characterization of dendrimers zero and second generation performed in the presence of metal ions reveal that the newly synthesized materials are highly sensitive to Cu^{2+} and Co^{2+} this makes them reliable detectors of Cu^{2+} and Co²⁺ ions pollution in the environment especially at industrial sites [37].

In addition 1,8-naphthalimide was chosen as the fluorophore component in the dendrimer molecules in view of earlier investigation into it is possible use in nanomeric PET for protons and transition metal ions [38–40]. Obviously, the fluorescence intensity is affected by the formation of complexes between the rare earth metal ion and internal amido groups of PAMAM from dendrimer. Moreover, the formation of these complexes cause a change in the polarization of the chromophoric system that evoked by complex

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Fig. 1. Structure of first generation dendrimer PPA (PPA1).

formation in the central part of the dendrimer. The internal amido groups of PAMAM can become in the reactions with the rare earth ions (receptor) [41]. So the fluorescence properties of the novel compounds in the presence of different metal cations show that these dendrimer could act as fluorescent properties of this fluorescing dendrimer are based on the complexing ability of the PAMAM core [40,42–45].

Poly(propylene amine) (PPA) dendrimers are interesting class, as they exhibit stronger basicity and hydrophobicity in the interior of the macromolecule due to the presence of tertiary amino groups. Each generation comprises 2^{n+1} tertiary amino groups in the interior and $2^{n+1} - 2$ peripheral functional groups, where n is the number of generation. The photophysical properties of poly(propylene amine) dendrimers functionalized with dansyl or azobenzene units at the periphery have been investigated [46–52].

In this work, the study is focused on syntheses and spectroscopic studies, thermal investigation, kinetic parameters as well as the antibacterial screening of dendrimer from first (Fig. 1) and second (Fig. 2) generation with their Cu²⁺ and Zn²⁺ complexes.



Fig. 2. Structure of second generation dendrimer PPA (PPA2).

2. Experimental

DAB-dendr-4Am, DAB-dendr-8Am dendrimers and 1,8-naphthalic anhydride, CuCl₂·4H₂O, ZnCl₂·6H₂O and other chemicals were purchased from Fluka, Aldrich and Merck companies, and were used without further purification as received.

2.1. Synthesis of ligands PPA1, PPA2 and their metal complexes

2.1.1. Synthesis of PPA from first generation (PPA1)

0.65 ml (0.002 M) of DAB-dendr-4Am was reacted with excess of 1,8-naphthalic anhydride in 50 ml ethanol. The reaction mixture was refluxed and heated for 2 h at 80 °C. Afterwards the solution was poured into 200 ml water and the resulting precipitate was filtered off, washed with water and dried to a constant weight. In order to remove the unreacted 1,8-naphthalic anhydride, the precipitate was treated with 20 ml 5 wt.% NaOH solution. Thus the unreacted 1,8-naphthalic anhydride was dissolved and removed after filtration while the modified poly(propylene amine) remained as the precipitate. Yield: 53.8%.

2.1.2. Synthesis of PPA from second generation (PPA2)

0.78 ml (0.001 M) of DAB-dendr-8Am was reacted with excess of 1,8-naphthalic anhydride in 50 ml ethanol. The reaction mixture was refluxed and heated for 1 h at 80 °C. Then the solution was poured into 200 ml water and the resulting precipitate was filtered off, washed with water and dried to a constant weight. The unreacted 1,8-naphthalic anhydride was dissolved in 20 ml 5 wt.% NaOH solution and removed after filtration while the modified poly(propylene amine) remained as the precipitate. Yield: 65.4%.

2.1.3. Synthesis of metal complexes

All resulted complexes were synthesized by adding of the appropriate metal salts (1.0 mmol; in 25 ml methyl alcohol) to hot solution of the ligands (1.0 mmol; in 25 ml chloroform). The reaction performed molar ratio (1:4) ligand:metal with PPA1 and (1:8) with PPA2. The resulting solution were stirred and heated on a hot plate at 80 °C for 3 h. The volume of the obtained solution was reduced to one-half by evaporation 1 day later, the color solid washed with ethanol and diethyl ether (50:50 v/v), finally dried under vacuum, the synthesized complexes were recrystallized from ethanol. The complexes were isolated as powdered material. Elemental analysis CHN, IR, UV–vis, ¹H NMR and TGA as well as atomic absorption spectra confirmed the composition of metal complexes.

2.2. Analysis

Elemental analyses were performed using a PerkinElmer CHN 2400 elemental analyzer. Molar conductance measurements of the PPA1 and PPA2 ligands and their complexes with 1.0×10^{-3} mol/l in DMSO were carried out using Jenway 4010 conductivity meter. ¹H NMR spectra recorded using Varian 200 MHz spectrometer with DMSO as solvent, chemical shift are given in ppm relative to tetramethylsilane. The UV/vis, spectra were obtained in DMSO solution $(1.0 \times 10^{-3} \text{ M})$ for the ligands PPA1 and PPA2 and their four complexes with a Jenway 6405 Spectrophotometer using 1 cm quartz cell, in the range 200-600 nm. Magnetic measurements were carried out on a Sherwood Scientific magnetic balance in the micro analytical laboratory using Gouy method. Calibration: tow very good solid calibrants are $Hg[Co(CNS)_4]$ and $[Ni(en)_3](S_2O_3)$. They are easily prepared pure, do not decompose or absorb moisture and pack well. Their susceptibilities at 20 °C are 16.44×10^{-6} and 11.03×10^{-6} c.g.s. units, decreasing by 0.05×10^{-6} and 0.04×10^{-6} per degree temperature raise, respectively, near room temperature. The cobalt compound, besides having the higher susceptibility, also packs rather densely and is suitable for calibrating low fields, while

the nickel compound with lower susceptibility and density is suitable for higher field [53], here we are used $Hg[Co(CNS)_4]$ only as calibrant.

IR spectra (4000–400 cm⁻¹) were recorded as KBr pellets on Bruker FT-IR Spectrophotometer. Thermogravimetric analyses (TG/DTG) were carried out in the temperature range from 25 to 800 °C in a steam of nitrogen atmosphere using Shimadzu TGA 50H thermal analysis. The experimental conditions were: platinum crucible, nitrogen atmosphere with a 30 ml/min flow rate and a heating rate 10 °C/min.

2.3. Microbiological investigations

For these investigations the filter paper disc method was applied. The investigated isolates of bacteria were seeded in tubes with nutrient broth (NB). The seeded NB (1 cm^3) was homogenized in the tubes with 9 cm³ of melted (45 °C) nutrient agar (NA). The homogeneous suspensions were poured into Petri dishes. The discs of filter paper (diameter 4 mm) were ranged on the cool medium. After cooling on the formed solid medium, $2 \times 10^{-5} \text{ dm}^3$ of the investigated compounds were applied using a micropipette. After incubation for 24 h in a thermostat at 25-27 °C, the inhibition (sterile) zone diameters (including disc) were measured and expressed mm. An inhibition zone diameter over 7 mm indicates that the tested compound is active against the bacteria under investigation. The antibacterial activities of the investigated compounds were tested against Escherichia coli, Pseudomonas aeruginosa as Gram negative, Bacillus subtilis and Staphylococcus aureus as Gram positive. The concentration of each solution was 1.0×10^{-3} mol dm³. Commercial DMSO was employed to dissolve the tested samples.

3. Result and discussion

PPA refluxed with 1,8-naphthalic anhydride readily gives rise to the corresponding PPA1 and PPA2 which was easily identified by its IR, ¹H NMR and elemental analysis. Complexes were obtained upon reaction between metal(II) ions and ligands at 1:4 and 1:8 molar ratio ligand: metal for PPA1 and PPA2, respectively. The ligands PPA1 and PPA2 with reaction with CuCl₂·6H₂O and ZnCl₂·6H₂O salts, yield complexes corresponding to the general formula: $[Cu_2(PPA1)(H_2O)_4]$ ·2Cl₂·4H₂O, $[Zn_2(PPA1)(H_2O)_4]$ ·2Cl₂·8H₂O, $[Cu_4(PPA2)(H_2O)_8]$ ·4Cl₂·4H₂O and $[Zn_4(PPA2)(H_2O)_8]$ ·4Cl₂·6H₂O, the dendrimers PPA1 and PPA2 containing more than one metal cation per ligand.

The newly synthesized ligands and their complexes are very stable at room temperature in the solid state. The ligands and their metal complexes are generally soluble in DMF and DMSO. The color, yield, melting point, decomposition points, elemental analyses and molar conductance of ligands and their complexes are presented in Table 1. The analytical data are in a good agreement with the proposed stoichiometry of the complexes.

3.1. Infrared spectra

The most important bands in the infrared spectra of the PPA1 and PPA2 ligands and its complexes are presented in Table 2. The position of these bands provide significant indication regarding the bonding sites of the ligand molecules when interacted to Cu(II) and Zn(II) ions. The functional groups of the ligands and the metal complexes have been appeared by infrared spectra, as given in Figs. 3 and 4. The infrared spectra of ligands showed bands around 1383 cm⁻¹ which was assigned to the stretching vibration of the ν (C–N) tertiary amine, this band not shifted in the complexes. Infrared spectra of ligands show intensive absorption bands at 1773–1769 and 1734–1729 cm⁻¹ which can be assigned to the

demental analysis and physical	data of ligands PPA1, PPA2 aı	nd their complexes									
Compounds	Empirical formula	M.wt (g/mol)	Color	M.P.	Yield (%)	μ_{eff}	$\Lambda_{ m m}~(\Omega { m cm}^2~{ m mol}^{-1})$	Content (calcula	ited) found		
								%C	Н%	%N	%M
PA1	C ₆₄ H ₅₆ N ₆ O ₈	1037.16	White yellowish	192	93	1	9	(74.11)74.65	(5.44)5.21	(8.10)7.98	1
Cu ₂ (PPA1)(H ₂ O) ₄].2Cl ₂ .4H ₂ O	C ₆₄ H ₇₂ N ₆ O ₁₆ Cl ₄ Cu ₂	1450.19	Green	215	62	1.90	122	(53.03)54.00	(5.00)5.11	(5.80)5.42	(8.76)8.13
$Zn_2(PPA1)(H_2O)_4].2Cl_2.8H_2O$	C ₆₄ H ₈₀ N ₆ O ₂₀ Cl ₄ Zn ₂	1525.94	Brown	>300	61.5	I	118	(50.37)50.01	(5.28)5.17	(5.51)5.31	(8.57)9.71
PA2	$C_{136}H_{128}N_{14}O_{16}$	2214.56	White yellowish green	135	95	I	8	(73.76)73.10	(5.83)5.53	(8.85)8.66	1
$Cu_4(PPA2)(H_2O)_8].4Cl_2.4H_2O$	$C_{136}H_{152}N_{14}O_{28}Cl_8Cu_4$	2968.55	Brown	198	65.4	1.92	224	(55.03)54.72	(5.16)5.31	(6.61)6.32	(8.56)7.13
$Zn_4(PPA2)(H_2O)_8].4Cl_2.6H_2O$	C ₁₃₆ H ₁₆₀ N ₁₄ O ₃₂ Cl ₈ Zn ₄	3047.98		>300	62.6	I	216	(53.59)54.01	(5.29)5.67	(6.43)6.17	(8.58)9.90

Table 2

Infrared spectral data for dendrimer ligands and their complexes (cm⁻¹).

Compounds	v (OH) hydrated H ₂ O	v (C–H) aromatic	<i>v</i> _s (C=0)	<i>v</i> _{as} (C=0)	v (C–N) tertiary	v (OH) coordinated H ₂ O	v (M–O)
PPA1	3397(br)	3065(m)	1729(s)	1655(s)	1383(m)	-	-
$[Cu_2(PPA1)(H_2O)_4] \cdot 2Cl_2 \cdot 4H_2O$	3543(br)	3055(m)	1696(vs)	1587(s)	1383(m)	824(w)	428(w)
$[Zn_2(PPA1)(H_2O)_4] \cdot 2Cl_2 \cdot 8H_2O$	3482(br)	3070(m)	1697(vs)	1587(s)	1387(m)	825(w)	415(w)
PPA2	3379(br)	3067(m)	1734(vs)	1655(s)	1383(m)	-	-
$[Cu_4(PPA2)(H_2O)_8] \cdot 4Cl_2 \cdot 4H_2O$	3446(br)	3060(m)	1697(vs)	1587(s)	1384(m)	825(w)	427(w)
$[Zn_4(PPA2)(H_2O)_8] \cdot 4Cl_2 \cdot 6H_2O$	3449(br)	3062(m)	1697(vs)	1587(s)	1384(m)	824(w)	420(w)



Fig. 3. IR spectra of A = PPA1; B = Cu(II)/PPA1 and C = Zn(II)/PPA1 compounds.



Fig. 4. IR spectra of A = PPA2; B = Cu(II)/PPA2 and C = Zn(II)/PPA2 compounds.



Fig. 7. ¹H NMR spectra of ligand PPA2.

asymmetrical and symmetrical carbonyl groups vibrations respectively, of the 1,8-naphthalmide [54], this peak is affected after complexation. This means that the carbonyl groups are participated in the complexation. While the bands observed at approximately 824 cm⁻¹ is assigned to coordinated water molecule [55]. The coordination is confirmed by the presence of a new band at 409–428 cm⁻¹ that can be assigned to ν (M–O) [56]. Infrared spectra indicates that the coordination take place through oxygen atom of carbonyl group of 1,8-naphthalamide as bidentate.

3.2. ¹H NMR spectra

¹H NMR spectra of ligand PPA1 and Cu(II) complex (Figs. 5 and 6). ¹H NMR (DMSO-d₆) δ (ppm) = 1.24(m, 12H, N-CH₂-CH₂), 2.18(t, 12H, CH₂-N(CH₂)-CH₂), 4.13(t, 8H, CH₂-N of naphthalamide), 7.74(m, 8H, Ar-H), 8.31(m, 16H, Ar-H).

¹H NMR spectra of ligand PPA2 and Cu(II) complex (Figs. 7 and 8). ¹H NMR (DMSO-d₆) δ (ppm) = 1.3(m, 26H, N-CH₂CH₂-CH₂-N),



Fig. 8. ¹H NMR spectra of Cu(II) complex of PPA2 ligand.

2.15(t, 36H, N-CH₂), 4.14(t, 16H, CH₂-N of naphthalamide), 7.70(m, 16H, Ar-H-3,8), 8.59(m, 32H, Ar-H-4,5,6,7).

Given the way the former (Figs. 5–8) believe that there is no difference in places of the signals of ¹H NMR spectra in comparison between PPA1 and PPA2 and their Cu(II) complexes except for the decreasing in the intensities according to electronic configuration of the new complexes.

3.3. Molar conductivities of metal chelates

Conductivity measurements in non-aqueous solution have frequently been used in structural studies of metal chelates within the limits of their solubility. The molar conductivity values for two ligands and all Cu(II) and Zn(II) complexes in (10^{-3} M) were in range of $6-224 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ suggesting them to be electrolytes (Table 1). This result was confirmed from the chemical analysis where Cl⁻ ions precipitate by addition AgNO₂ solution. This fact elucidated that the Cl⁻ ions are present, and that two water molecules completes the coordination sphere of the studied complexes.

3.4. Electronic absorption spectra

The spectra of PPA from first and second generation in DMSO are shown in Fig. 9. There are two detected absorption bands at around 360 and 385 nm (Table 3). Assigned to π - π * and n- π * interaligand transition, respectively. These transition also found in the spectra of the complexes. The position of the absorption maximum of dendrimer appears at the same position regardless of the presence of metal cations.

3.5. Magnetic measurements

Magnetic measurements were carried out on a Sherwood Scientific magnetic balance according to the Gouy method. The magnetic



Fig. 9. Electronic spectra of the poly(propylene amine) dendrimers ligands and their metal complexes.

Table 3
Electronic spectra of PPA1, PPA2 ligands and their complexes.

Compounds	$\lambda_{max (nm)}$	$\varepsilon (\mathrm{mol^{-1}cm^{-1}})$	Assignment
PPA1	360	1997	$\pi - \pi^*$
	385	1764	n- π^*
Cu(II) complex	350	2824	$\pi - \pi^*$
	385	1665	n- π^*
Zn(II) complex	355	2989	$\pi - \pi^*$
	385	1687	n- π^*
PPA2	360	2017	$\pi - \pi^*$
	385	1707	n- π^*
Cu(II) complex	360	2249	$\pi - \pi^*$
	385	1699	n- π^*
Zn(II) complex	360	2507	π−π*
	385	1684	n−π*

moments of Cu(II) complexes at T = 293 K are given in Table 1. From the data given in Table 1, the observed values of the effective magnetic moments $\mu_{\rm eff}$ measured for Cu(II) complexes lie between 1.90 and 1.92 B.M. is an indicative of square planner geometry.

3.6. Thermal studies

The poly(propylene amine) dendrimers of Cu(II) and Zn(II) complexes are stable at room temperature and can be stored for several months without any change. Cu(II) and Zn(II) complexes of PPA-dendrimers were studied by thermogravimetric analysis from ambient temperature to 800 °C N₂ atmosphere. The TG curves



M=Cu or Zn, L=PPA1 or PPA2, n, m=1,2,...,8; X=Cl

Scheme 1. Thermal degradation steps of Cu(II) and Zn(II) complexes of PPA1 and PPA2 ligands.

were drawn as percentage mass loss versus temperature (TG) curves. Typical TG and DTG curves are presented in Fig. 10, and the temperature range and percentage mass losses of decomposition reaction are given in Table 4, together with evolved moiety and theoretical percentage mass losses. The overall loss of mass from TG curves is 94.22%, 83.52%, 89.39%, 89.20, 91.51% and 91.47% for PPA1, $[Cu_{2}(PPA1)(H_{2}O)_{4}]\cdot 2Cl_{2}\cdot 4H_{2}O_{4}$ $[Zn_2(PPA1)(H_2O)_4] \cdot 2Cl_2 \cdot 8H_2O$, PPA2, $[Cu_4(PPA2)(H_2O)_8] \cdot 4Cl_2 \cdot 4H_2O$ and $[Zn_4(PPA2)(H_2O)_8]$ ·4Cl₂·6H₂O, respectively. All the complexes show three stages of mass loss in their TG/DTG curves (Scheme 1). The analysis of thermal curves of complexes clearly indicates that the weight loss of first stage between 25 and 200 $^\circ$ C (DTG_{max}: \sim 75 $^\circ$ C) corresponding to loss of hydrated water molecules. Because of the low temperature the water molecules may be considered as crystal water. The second stage between 150 and 300 °C (DTG_{max}: \sim 200 °C) corresponding to loss of coordinated water molecules and chloride ions. The decomposition was completely at >700 °C for all complexes.



Fig. 10. The TG and DTG of the poly(propylene amine) dendrimers ligands and their metal complexes.

Table 4

Thermal decomposition of the poly(propylene amine) dendrimers ligands and their metal complexes.

Compounds	Steps	Temperature range	DTG peaks	Weight loss (calc.)found %	Assignment
PPA1	1st 2nd	25-400 400-610 610-	350 547	(75.60)75.21 (18.51)18.71 (5.78)6.08	$\begin{array}{c} C_{48}H_{24}O_8N_4 \\ C_{11}H_{32}N_2 \\ 5C \end{array}$
$[Cu_2(PPA1)(H_2O)_4] \cdot 2Cl_2 \cdot 4H_2O$	1st 2nd 3rd	25–150 150–250 250–380	75 200 310	(4.96)5.05 (4.96)5.25 (23.03)23.56	$\begin{array}{l} 4H_{2}O\\ 4H_{2}O\\ 4Cl + C_{11}H_{32}N_{2} \end{array}$
[Zn ₂ (PPA1)(H ₂ O) ₄]·2Cl ₂ ·8H ₂ O	1st 2nd 3rd	380-600 600- 25-200 200-500 500-665 665-	497 80 324 621	(50.20)50.74 (16.48)15.40 (9.43)8.97 (26.54)26.68 (53.47)52.61 (10.61)11.71	$\begin{array}{c} C_{46}H_{24}O_6N_4\\ 2CuO+7C\\ 8H_2O\\ 4H_2O+4Cl+C_{11}H_{32}N_2\\ C_{53}H_{28}O_6N_4\\ 2ZnO\\ \end{array}$
PPA2	1st	25–600 600–	290	(88.93)89.17 (10.83)10.80	$\begin{array}{c} C_{116}H_{128}O_{16}N_{18}\\ \textbf{20C} \end{array}$
[Cu ₄ (PPA2)(H ₂ O) ₈]-4Cl ₂ -4H ₂ O	1st 2nd 3rd 4th	25–140 140–250 250–700 700–	75 200 300	(2.42)2.20 (14.37)14.66 (74.59)75.95 (7.49)7.19	4H ₂ O 8H ₂ O + 8Cl C ₁₃₆ H ₁₂₈ O ₁₆ N ₁₈ 4Cu
$[Zn_4(PPA2)(H_2O)_8]\cdot 4Cl_2\cdot 6H_2O$	1st 2nd 3rd 4th	25-140 140-280 280-600 600-	75 270 310	(4.72)4.47 (14.03)14.50 (72.57)73.62 (8.53)7.41	8H ₂ O 8H ₂ O + 8Cl C ₁₃₆ H ₁₂₈ O ₁₆ N ₁₈ 4Zn

3.6.1. Poly(propylene amine) dendrimers ligand (PPA1) and (PPA2)

The poly(propylene amine) dendrimers ligands from first and second generation PPA1 and PPA2 melts at 192 and 135 °C, respectively, with simultaneous decomposition. The main peak was observed at 350 and 290 °C for PPA1 and PPA2, respectively, from the TG profile, it appears that the sample decomposes in one sharp stage over the wide temperature range 25–800 °C. The decomposition occurs with a mass loss (calcd.: 75.60%, found: 75.21%) for PPA1 ligand and (calcd.: 75.60%, found: 75.21%) for PPA2 ligand.

The final products are carbon atoms as residue, interpretive for no sufficiently of oxygen atoms encouraged the liberated carbon as carbon monoxide or dioxide.

3.6.2. $[Cu_2(PPA1)(H_20)_4] \cdot 2Cl_2 \cdot 4H_20$

The TG of the $[Cu_2(PPA1)(H_2O)_4]\cdot 2Cl_2\cdot 4H_2O$ complex reveals a mass loss in the temperature range 25–150 °C (DTG_{max}; 75) corresponding to loss of four hydrated water molecules, weight loss (calcd.: 4.96%, found: 5.05%) for the first stage. The activation energy of the thermal dehydration of this complex is 29.8 kJ mol⁻¹.

The second stage, within temperature range 150–250 °C (DTG_{max}; 200) corresponding to loss of four coordinated water molecules (calcd.: 4.96%, found: 5.25%). The energy of activation of this step is 11.5 kJ mol⁻¹. Reported data on thermal analysis studies were collected in nitrogen atmosphere media which, indicate that the Cu(II) complex decompose to give Cu(II) oxide and few carbon atoms as residue above 700 °C, weight loss (calcd.: 16.48%, found: 15.40%).

3.6.3. [Zn₂(PPA1)(H₂O)₄]·2Cl₂·8H₂O

The thermal decomposition of Zn(II) complex with the general formula $[Zn_2(PPA1)(H_2O)_4]$ ·2Cl₂·8H₂O is thermally decomposed in a successive three decomposition steps. The first stage within the temperature range 25–200 °C (DTG_{max}; 80 °C) may be attributed to the loss of eight hydrated water molecules, weight loss (calcd.: 9.43%, found: 8.97%). The activation energy of the thermal dehydration of this complex is 11.8 kJ mol⁻¹ The second step occurs within the temperature range 200–500 °C (DTG_{max}; 324 °C) with an estimated mass loss (calcd.: 26.54%, found: 26.68%) is reasonably accounted for the decomposition of four coordinated water molecules, four chloride ions and organic moieties ($C_{11}H_{32}N_2$).

Table 5

Thermodynamic data of the thermal decomposition poly(propylene amine) dendrimers ligands and their metal complexes.

Complex	Stage	Method	Parameter					r
			$E(J \operatorname{mol}^{-1})$	A (s ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔH (J mol ⁻¹)	ΔG (J mol ⁻¹)	
PPA1	1st	CR HM	$\begin{array}{c} 1.86\times10^5\\ 1.77\times10^5\end{array}$	$\begin{array}{c} 1.56 \times 10^{12} \\ 9.48 \times 10^{12} \end{array}$	-17.6 -2.61	$\begin{array}{c} 1.63 \times 10^{5} \\ 1.72 \times 10^{5} \end{array}$	$\begin{array}{c} 1.74 \times 10^{5} \\ 1.73 \times 10^{5} \end{array}$	0.99164 0.99487
Cu(II) complex	3rd	CR HM	$\begin{array}{c} 1.38\times10^5\\ 1.57\times10^5\end{array}$	$\begin{array}{c} 1.50\times10^{7}\\ 3.33\times10^{8} \end{array}$	-115 -89.7	$\begin{array}{c} 1.31\times10^5\\ 1.50\times10^5\end{array}$	$\begin{array}{c} 2.20\times10^5\\ 2.19\times10^5\end{array}$	0.99409 0.99880
Zn(II) complex	3rd	CR HM	$\begin{array}{c} 1.38\times10^5\\ 1.38\times10^5\end{array}$	$\begin{array}{c} 9.16\times10^9\\ 1.47\times10\end{array}$	-60 -56	$\begin{array}{c} 1.33\times10^5\\ 1.33\times10^5\end{array}$	$\begin{array}{c} 1.69\times10^5\\ 1.67\times10^5\end{array}$	0.99458 0.99547
PPA2	1st	CR HM	$\begin{array}{c} 7.18\times10^{4}\\ 8.05\times10^{4} \end{array}$	$\begin{array}{c} 2.53\times10^{4}\\ 2.11\times10^{5} \end{array}$	-166 -148	$\begin{array}{c} 6.71\times10^{4} \\ 7.58\times10^{4} \end{array}$	$\begin{array}{c} 1.61\times10^5\\ 1.60\times10^5\end{array}$	0.99905 0.99999
Cu(II) complex	3rd	CR HM	$\begin{array}{c} 8.79\times10^{4}\\ 1.04\times10^{5}\end{array}$	$\begin{array}{c} 6.31\times10^5\\ 3.10\times10^7\end{array}$	-139 -107	$\begin{array}{c} 8.31\times10^{4}\\ 9.94\times10^{4}\end{array}$	$\begin{array}{c} 1.63 \times 10^{5} \\ 1.61 \times 10^{5} \end{array}$	0.98935 0.98907
Zn(II) complex	3rd	CR HM	$\begin{array}{c} 7.20\times10^4 \\ 7.85\times10^4 \end{array}$	$\begin{array}{c} 7.05\times10^3\\ 7.73\times10^4\end{array}$	177 157	$\begin{array}{c} 6.72\times10^4 \\ 7.73\times10^4 \end{array}$	$\begin{array}{c} 1.70\times10^5\\ 1.65\times10^5\end{array}$	0.96216 0.99430

Two zinc oxide molecules were left as residue, weight loss (calcd.: 10.61%, found: 11.74%).

3.6.4. [Cu₄(PPA2)(H₂O)₈]·4Cl₂·4H₂O

The Cu(II) complex of poly(propylene amine) dendrimers from second generation gives three stages of decomposition pattern. The first stage, within the temperature range of $25-140 \circ C$ (DTG_{max};

75 °C), represents the loss of four hydrated water molecules, weight loss (calcd.: 2.42%, found: 2.20%). The activation energy of the thermal dehydration of this complex is 71.9 kJ mol⁻¹. The second stage, within the temperature range of 140–250 °C (DTG_{max}; 200 °C) represents the loss of eight coordinated water molecules and eight chloride ions with an estimated mass loss (calcd.: 14.37%, found: 14.66%). The energy of activation of this step is 93.1 kJ mol⁻¹. The



Fig. 11. Coats-Redfern (CR) of the degradation steps of the dendrimer and their complexes.



Fig. 11. (Continued).

third stage was hardly to detect the exact degradation of organic moieties because of, this step is widely extending from 250 to 700 °C, weight loss (calcd.: 74.59%, found: 75.95%). the final decomposition products is four atoms of copper metal, weight loss (calcd.: 8.49%, found: 7.19%).

3.6.5. [Zn₄(PPA2)(H₂O)₈]·4Cl₂·6H₂O

Thermal decomposition of d¹⁰ transition metal complex $[Zn_4(PPA2)(H_2O)_8]$ $4Cl_2 \cdot 4H_2O$ proceeds in three stages. These stages are related to the decomposition of eight hydrated water molecules in the first stage, weight loss (calcd.: 4.72%, found: 4.47%) within temperature range 25–140 °C (DTG_{max}; 75 °C). The activation energy of the thermal dehydration of this complex is $34.9 \text{ kJ} \text{ mol}^{-1}$. The second stage within temperature range $140-280 \circ \text{C}$ (DTG_{max}; 270 °C) corresponding to loss of eight coordinated water molecules and eight chloride ions, weight loss (calcd.: 14.03%, found: 14.50%). The energy of activation of this step is $105 \text{ kJ} \text{ mol}^{-1}$. The third stage hardly to detect the exact degradation of organic moieties because of this step is widely extending from 280 to 700 °C. The final decomposition products is four atoms of zinc metal, weight loss (calcd.: 8.53%, found: 7.41%).

3.7. Kinetic studies

Coats–Redfern [57] and Horowitz–Metzger [58] are the two methods mentioned in the literature related to decomposition kinetics studies; these two methods are applied in this study. From the TG curves, the activation energy, *E*, pre-exponential factor, *A*, entropies, ΔS , enthalpy, ΔH , and Gibbs free energy, ΔG , were calculated by well-known methods; where

$$\Delta H = E - RT$$
 and $\Delta G = \Delta H - T\Delta S$.

The linearization curves of Coats–Redfern and Horowitz– Metzger methods are shown in Fig. 11. Kinetic parameters for the first stages, calculated by employing the Coats–Redfern and Horowitz–Metzger equations, are summarized in Table 5. The calculated values of ΔE^* , ΔS^* , ΔH^* and ΔG^* for the decomposition steps are given in Table 5. According to the kinetic data obtained from DTG curves, the high values of the activation energies reflect the thermal stability of the complexes. The entropy of the activation was found to have negative values in all of the complexes. Negative values indicate that the decomposition reactions proceed with changes in order which may be more ordered due to the decomposition of the complexes.

3.8. Microbiological investigation

The biological activity of the poly(propylene amine) dendrimers ligands (PPA1) and (PPA2) and their metal complexes were tested against bacteria because bacteriums can achieve resistance to antibiotics through biochemical and morphological modifications. In testing the antibacterial activity of these compounds, we used more than one test organism to increase the chance of detecting antibiotic principles in tested materials. The organisms used in the present investigations included two Gram positive bacteria (*B. subtillis* and *S. aureus*) and two Gram negative bacteria (*E. coli and P. aereuguinosa*). The results of the bactericidal screening of the synthesized compounds are recorded in Fig. 12 and Table 6. The data obtained reflect the following results:

3.8.1. Bacillus subtillis (G^+)

Antibacterial activity of all ligands and their metal complexes towards *B. subtillis* are detected and show moderate activity, except



Fig. 12. The inhabitation zone of the poly(propylene amine) dendrimers ligands and their Cu(II) and Zn(II) complexes on some kinds of bacterial.



Fig. 13. Structure of PPA1 complex.



Fig. 14. Structure of PPA2 complex.

Table 6

Antibacterial activity data of the poly(propylene amine) dendrimers ligands and their metal complexes, inhibition zone (mm).

Compound	Bacillus subtili G ⁺	Staphylococcus aureus G ⁺	Escherichia coli G-	Pseudomonas aeruginosa G-
PPA1	8	-	7	_
Cu(II) complex	12	-	7	7
Zn(II) complex	10	-	8	7
PPA2	8	7	12	10
Cu(II) complex	14	13	13	12
Zn(II) complex	16	11	14	12

Cu/PPA2 and Zn/PPA2 show marked activity. *B. subtillis* was inhibited by the complexes according to this order.

Zn/PPA2 > Cu/PPA2 > Cu/PPA1 > Zn/PPA1 > PPA1 = PPA2

3.8.2. Staphylococcus aureus (G^+)

All ligands and their Cu(II) and Zn(II) complexes are detected and show that, PPA1 ligand and their metal complexes have no effect towards *S. aureus.* PPA2 and their metal complexes have moderate activity.

3.8.3. Escherichia coli (G⁻)

The activity of the poly(propylene amine) dendrimers ligands and their metal complexes are detected towards *E. coli*, all tested compounds have activity (Table 6). PPA1 and their metal complexes show weak activity but PPA2 and their metal complexes exhibit moderate activity.

3.8.4. Pseudomonas aereuguinosa (G^-)

Range of activities for all ligand and their metal complexes have weak activity or moderate activity except PPA1 have no effect towards *P. aereuguinosa*.

The structures of Cu(II) and Zn(II) complexes with PPA1 and PPA2 under the above interpretation can be designed as shown in Figs. 13 and 14.

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