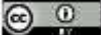# Exploring the Multifunctional PVC-DPG Polymer Complexes: Synthesis, Characterization and Evaluation of the Antibacterial Activity

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Article's Information	Abstract
	Polyvinyl chloride (PVC) has attracted great attention because of its applications in different fields such as industrial and medical fields. In this work PVC has been reacted with diphenylglyoxime (DPG) in Tetrahydrofuran (THF) to form PVC–DPG polymer, then the synthesized polymer reacted with alcoholic solutions of different metal ions (Fe(II), Co(II), Ni(II), Pd(II), Pt(IV) and Cu(II) to form colored metal ion complexes. All compounds are characterized by Fourier-transform infrared (FTIR), Ultraviolet (UV-Vis) spectroscopies, magnetic susceptibility and conductivity measurements. All complexes were examined with staphylococcus aureus (Gram-positive) and Escherichia coli (Gram-negative), confirming the biological activity against these bacteria.

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1. Introduction

One of the most important applications of modified PVC is anti-bacterial and anti-fungal [1], in addition to the different applications such as in solar system and enhancing photophysical features of compounds [2, 3] and in specific biomedical fields such as probes, catheters and as material for tubing in hemodialysis [4]. Most PVC is used as rigid and it becomes flexible when plasticizers such as Di(2-ethylhexyl)phthalate (DEHP) are added to the PVC. Tubing and bags that were used in hospitals contain DEHP which can transfer into the bloodstream and cause many diseases increasing the risk of cancer, affecting the development of children in pregnant women and affecting the male reproductive system [5]. DEHP has been detected in the blood kept in blood banks. Dialysis patients who receive long-term and regular blood transfusions and whose blood comes into contact with the PVC tubing system of dialysis receive high levels of DEHP per treatment. [6, 7]. In the last few years, the synthesis of polymer-bound to chelating ligands which coordinate with specific metal ions has attracted considerable attention [8]. Different polydentate ligands bounded to polymers have been synthesized and shown many applications in different fields. Some examples of these complexes are, polydentate amines, crown-ethers, bipyridines, porphyrine, phosphines and naphthyridines have been bounded to polystyrene and polystyrene-divinylbenzene copolymers [9]. The lack of information appears to exist as to whether, and to what extent, such metal ion complexation can influence the properties of the macromolecule. In recent studies, PVC was modified by replacing halogen groups with heterocyclic moieties [10], these modifications improve the dielectric property, thermal stability and some other properties which are important in many applications, especially industrial and medical fields. The displacement of chlorine atoms from the PVC chain gives the possibility of anchoring of chelating ligand to the PVC chain and the subsequent synthesis of transition metal complexes. In this study, we bound poly(vinyl chloride) (PVC) to dimethylglyoxime (DPG) then later coordinated with selected transition metal ions to form different complexes which considered anti-bacterial agents.

2. Materials and Methods
2.1. Synthesis of PVC-DPG

1 g of PVC (Petkin) in 25 ml of THF (A.Ainc) was refluxed with 4gm of DPG (BDH) for 20 hrs at 60 ˚C in the presence of 0.5 g of KOH (Fluka). Keep the reaction until the solution turns yellow. After that, methanol was added to the reaction mixture to form a precipitate. The precipitate was filtered under vacuum and the remaining solution reacted with Ni(II) solution (in absolute ethanol) to confirm the complete removal of unreacted DPG, Figure 1 shows the reaction scheme for the synthesis of PVC-DPG polymer [11].

2.2. Synthesis of PVC-DPG-M ion complexes

Transition metal chlorides of Fe(II), Co(II), Ni(II), Pd(II), Pt(IV) and Cu(II) 1% (w/v) (BDH) in absolute ethanol (Hyman Limited) were added dropwise to the PVC-DPG 0.25% (w/v) in THF . The precipitates were filtered, washed with excess absolute ethanol, then added THF to remove any unreacted PVC-DPG, and dried at 40˚C under vacuum for 4hr [11].
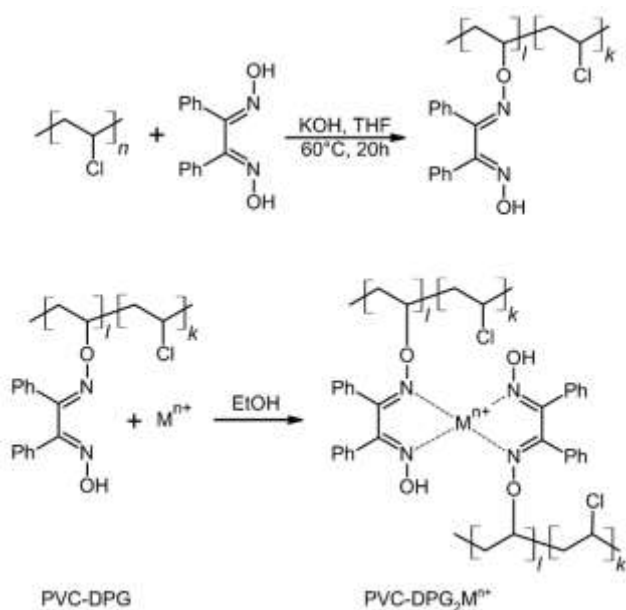

Figure 1.Schem synthesis of PVC-DPG polymer and its complexes. M= of Fe(II), Co(II), Ni(II), Pd(II), Pt(IV) and Cu(II)

Bacterial culture media

The antimicrobial activity was carried out by the agar diffusion method. In a 1L conical flask, 20gm of nutrient agar (Maknus Lab. Co.) was added, then stirred with heating until it dissolved. The flask was kept in an autoclave for 20 minutes at 120 °C. Next, the medium was left to cool down to about 55 °C and the solution was transferred to the dishes. Now, the medium was ready for bacteria growth and it was tested with two bacteria that were chosen in this study by streaking method. The medium was saturated with tested synthesized compound solutions in dimethylformamide (DMF) and incubated for one day at 37 °C.

3. Characterization:

The infrared spectra were taken for the complexes on a Shimadz 8300 Fourier transform infrared spectrophotometer (FTIR) and compared with synthesized polymer ligand as a (CsI) disc. The measurements were carried out in the range of 4000 - 200 cm-1. Shimadzu UV-Vis 160A Ultraviolet spectrophotometer was utilized to analyze the absorbance bands produced from synthesized compounds at room temperature using silica cells of 1.0 cm length. The spectra were recorded in the range of 200-1100 nm in DMF. Bruker Magnet B.M.6 was used to obtain the magnetic properties of the synthesized complexes. The measurements were carried out at room temperature using the Faraday method. Conductmeter LF 521(WTW) was employed to obtain the molar conductivity of the prepared complexes. The concentrations of all samples were 10^{-3} M at room temperature. Gallencamp M.F.B 600.010F was used to measure the melting point of all the prepared compounds.

4. Results and discussion:

Table 1 shows the physical properties of the prepared complexes. Identification and study have been done using FTIR and UV-Vis. spectrophotometry, magnetic susceptibility, solubility and conductivity measurements. The FTIR spectrum of PVC gives the following information, the medium to weak peak at (2870) cm1- may be attributed to C-H symmetric stretching of the -CH2- group. A strong peak at 605 cm-1 was observed which may be attributed to the υ(C-Cl) band. Another peak at 1435 cm-1 was observed which could be attributed to (C-H) bending of the -CH2- group, Another weak band at 1630 cm-1 corresponds to C=C stretching [12]. The FTIR spectrum of DPG shows the following common features. A strong broad peak at 3210 cm-1 was observed which could be attributed to (OH) stretching vibration. Weak band at 1650 cm-1 which attributed to υ(C=N) stretching vibration. Another strong sharp peak at 980 cm-1 was

observed which could be attributed to N-O stretching vibration table 2 [12, 13].

Table 1. Physical data of PVC, PVC-DPG and PVC-DPG complexes

Compounds	Color	M.P,°C	Solubility
PVC PVC-DPG	White Yellow	212-215 110-113	Soluble in THF,C_6H_6, DMF,$CHCl_3$ and insoluble in C_2H_5OH
PVC-DPG-Fe(II)	Brown	140-142	
PVC-DPG-Co(II)	Brown	151-154	
PVC-DPG-Ni(II)	Pink	142-146	Slightly soluble in DMF, THF and insoluble in C_2H_5OH ,C_6H_6 and $CHCl_3$.
PVC-DPG-Pd(II)	Brown	143-146	
PVC-DPG-Pt(IV)	Brown	142-146	
PVC-DPG-Cu(II)	Green	147-150	

The FTIR of PVC-DPG polymer shows the following bands. The first weak broadband that appeared at 3400 cm⁻ may correspond to υ(O-H) group, and the second strong sharp band that appeared at (965) cm⁻¹ could be attributed to the υ(N-O) bond. The strong sharp band at 1260 cm⁻¹ could be attributed to the (C-O) stretching vibration group, this new bond formed between the oxygen (HO-N) of DPG and the carbon of the (C-Cl) group of PVC after the elimination of the HCl molecule [12]. The strong-sharp band that appeared at 618 cm⁻¹ could be attributed to υ(C-Cl) of the remaining (C-Cl) groups, while the weak band at 1645 cm⁻¹ could be attributed to (C=N) stretching vibration of the DPG moiety, this band appeared at 1650 cm⁻¹ in the free DPG. The FTIR spectrum of the Fe (II) complex shows a weak band appeared at 1620 cm⁻¹ which is attributed to υ(C=N) of the DPG moiety which is lower by 25 cm⁻¹ than that of the free PVC-DPG ligand, this indicates the bonding of Fe(II) ion with the polymer through the nitrogen of (C=N) group. Furthermore, the formation of a (Fe-N)

coordinated bond appears as a weak band at 475 cm⁻¹. The band corresponding to υ(N-O) at 970 cm⁻¹ this value is higher than that of the free ligand by 5 cm⁻¹ [9,10]. While The FTIR spectrum of Co(II) complex shows the following diagnostic bands, the medium band correspond to υ(C=N) appeared at 1632 cm⁻¹, this value appeared at (13) cm⁻¹ lower than the band in the free PVC-DPG graft polymer, this indicate the bending of cobalt ion with the polymer through the nitrogen of υ(C=N) group, this υ(N-O) appeared at 973 cm⁻¹, which is higher than the value of the free ligand by 8 cm⁻¹. Further evidence for the formed of (Co-N) band came from the appearance of weak sharp band at 482 cm⁻¹ as a shoulder which attributed to the υ(Co-N) table 2 [12,13].

The FTIR spectrum of Ni(II) complex shows the weak band appeared at 1625 cm⁻¹ which is attributed to υ(C=N)of the DPG moiety was shifted by 20 cm⁻¹ compared to that of the uncomplexed (free) PVC-DPG polymer, indicating the bonding of nickel ion with the polymer through the nitrogen of (C=N) group, the band attributed to υ(N-O) came at 974 cm⁻¹, this value is higher than[11,12]. that of the free ligand by 9 cm⁻¹, another weak band appears at 475 cm⁻¹ which gives further information for the formation of (Ni-N) coordinated bond [9]. The FTIR spectrum of Pd(II) complex shows the following bands:- the band due to the υ(C=N) was traced in the spectrum and assigned to the medium shoulder at 1625 cm⁻¹, which can be regarded as a shift of the original band (of the free PVC-DPG graft polymer)to a lower frequency by 20 cm⁻¹ this also indicates the bonding of Pd(II) ion with the polymer through the nitrogen of (C=N) group. In addition, the formation of a Pd-N coordinated bond was confirmed by the presence of a weak band at 435 cm⁻¹ and the band corresponding to υ(N-O) was confirmed by a band at 962 cm⁻¹ [12, 13].

The FTIR spectrum of Pt(IV) complex shows the following diagnostic band, a strong sharp band appeared at 1670 cm⁻¹ which corresponds to υ(C=N) of the DPG moiety showing blue shift by 25 cm⁻¹ compared to free PVC-DPG polymer, indicating the bonding of Pt ion with the polymer through the nitrogen of (C=N) group, another band appeared at 470 cm⁻¹ which give additional information about the formation of (Pt-N) coordinated bond, [11] the band corresponding to υ(N-O) came at 975 cm⁻¹, this value is higher than that of the free ligand by 10 cm⁻¹. It has been

found that, in general, the υ (N-O) appeared at either lower or higher frequencies on the complexation of the polymer with the metal ion. This depends on the type of the metal ion, where the electron-rich ions, i.e., Cu(II), can donate electrons to the orbital of (N=C) making the N=C bond longer and consequently absorbing at a lower frequency [13]. Concerning the FTIR of the Cu(II) complex, it shows the following absorption bands. The moderate band appears at 1620 cm-1 which is attributed to υ(C=N) of the DPG moiety which was shifted by 25 cm-1 compared to free PVC-DPG polymer, this indicates the coordination of copper (II) ion with the polymer through the nitrogen of C=N group. Moreover, the presence of a weak broad band at 480 cm-1 as a shoulder which attributed to (Cu-N) [12]. The weak broad band that appeared at 920 cm-1 can be attributed to υ(N-O) of the DPG moiety, which undergoes a red shift by 45 cm-1 compared to that of the uncomplexed (free) PVC-DPG polymer Table 2.

Table 2. FTIR of PVC, PVC-DPG and its complexes

Compound	υ (C-H) Stretching cm⁻¹	υ (C-H) Bending cm⁻¹	υ (OH) cm⁻¹	υ (N-O) cm⁻¹	υ (C-O) cm⁻¹	υ (C=N) cm⁻¹	υ(C-Cl) cm⁻¹	M-N cm⁻¹
PVC	2870	1430					605s	
DPG			3210	980s		1650		
PVC-DPG	2900	1430	3400	965	1260s	1645w	618s	
PVC-DPG-Fe(II)	3100	1435		970	1260	1620w	700	475w
PVC-DPG-Co(II)	2950	1431		973	1250	1632m	705	482ws
PVC-DPG-Ni(II)	3150b	1433		974	1260	1625w	705	475w
PVC-DPG-Pd(II)	3000	1410		962	1255	1625m	680	435w
PVC-DPG-Pt(IV)	3050	1435		975	1260	1670s	690	470
PVC-DPG-Cu(II)	3125	1433		920w	1260	1620m	700	480w

Magnetic moment and suggested structure for all complexes are presented in Table 4 the structures were suggested according to the bands of FTIR, UV-Vis spectra, and magnetic and conductivity measurements. The (UV-Vis) spectrum of Fe(II) complex shows two adsorption bands were assigned, the first at 300 nm. (33,333 cm⁻¹) which is assigned to intraligand transition and at 585 nm (17,100 cm⁻¹) which is attributed to $^5E_2 \rightarrow \, ^5T_2$ [12]. The magnetic susceptibility and molar conductivity in Table 3 indicate the complex to be paramagnetic 5.0 B.M. octahedral complex and non-conducting. The electronic spectrum of the brown cobalt complex table 3 showed two absorption bands at 670 nm (14933 cm-1) and 577 nm. (17320 cm⁻¹) which can be assigned as $T_{1g} \rightarrow \, A_{2g}(F)$ v₂ and $T_{1g} \rightarrow \, ^4T_{1g}(P)$ υ3 transition respectively in octahedral filed. Using (Tanabo –Sugano) diagram for d⁷ configuration, to calculate the first d-d transition (v1 = 7600 cm⁻¹) which correspond to $T_{1g} \rightarrow \, T_{2g}$. The calculated value of nephelauxetic factor β (0.78), indicates that the complex has considerable covalent character. The relatively high value of 10 Dq and the low value of magnetic moment (1.00 B.M) indicate the coordination of nitrogen with cobalt ions through a band of high covalent character. The magnetic susceptibility and molar conductivity in Table 4 indicate that the complex is paramagnetic and non-electrolyte. From these results, an octahedral geometry around Co(II) can be suggested [14]: Square-planer Ni(II) complexes are usually orange or red. The rose color yield indicated a square-planer geometry. The spectrum of the present complex showed a weak shoulder at 435 nm. (23,000 cm⁻¹) which is characteristic of a square-planer geometry [14].

Another stronger shoulder was observed at 385 nm. (25,974 cm⁻¹) which can be attributed to charge transfer band, this band usually makes a simple crystal field treatment in appropriates, and unambiguous assignments are difficult. The separation of the two orbitals, i.e. dxy and dx²-y², for square planer splitting evidently always being sufficient to force spine-pairing and consequent diamagnetism. This was the case in our complex, where the measured magnetic moment was 0.25 B.M. and the complex was electrolytic. The electronic spectrum of the brown Pd(II) complex , table(2) showed two absorption bands. The first weak band appeared at 651 nm (15,360 cm⁻¹) which attributed to the transition $^3T_{2g} \rightarrow {}^3T_{1g}(F)$ as $v2$ for octahedral geometry around Pd(II) ion. A second d-d band expected to appear at 517 nm. (19320 cm⁻¹) for the transition $^3T_{2g} \rightarrow {}^3T_{1g}(P)$ could not be observed due to presence of higher intensity charge transfer band at 320 nm (31,250 cm⁻¹) which mask the expected weaker band the complex did not show any bands which refer to the square planer geometry The magnetic susceptibility and molar conductivity measurements showed that the complex is paramagnetic 2.5 B.M. and nonconductive. From these results and the others obtained in this study the expected geometry around Pd(II) complex is octahedral [14,15].

The electronic spectrum of the brown Pt complex, showed weak absorption band at 566 nm. (17,655 cm⁻¹) which refer to $^1A_{1g} \rightarrow {}^1T_{1g}$ transition for d⁶ system of ³D term and assigned as $v1$, and a second band was observed as a shoulder at 338 nm.

(29,586 cm⁻¹) which was considered to be L → M charge transfer band .the second band expected to appear at about 450 nm. For octahedral complexes was not observed in our case due to the appearance of charge transfer band at 340 nm as broad shoulder which extend to the 500 nm. The magnetic susceptibility and molar conductivity measurements table 4 indicate that the complex is diamagnetic and electrolyte [15].

The Cu(II) complexes are usually blue or green and that come from single broad between 11000 and 16000 cm⁻¹. The d⁹ ion is characterized by large distortion from octahedral symmetry and the band is unsymmetrical. In this study, the green Cu complex shows a broad band at 698 nm. (14320) cm⁻¹ which can be assigned to the $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transition, [11]. The magnetic value of 1.43 B.M. table 3 may be attributed to the space coupling of two copper atoms (locating in two adjacent polymer layer). This square planar geometry is changed to a distorted octahedral in the solution due to the coordination of solvent molecules of the empty positions of oxide this was achieved by DMF solvent addition to the complex and the green color turned to yellow.

The magnetic moment and conductivity measurements confirm that the complex is paramagnetic and conductive. According to these data and those obtained from FTIR spectra and molar conductivity measurement, a square planer geometry around Cu(II) [16,17].

Table 3. Electronic transition of prepared complexes

Compounds	Absorption bands cm⁻¹	Transition	10 Dq (cm⁻¹)
PVC-DPG-Fe(II)	17,100	$^5E_2 \rightarrow {}^5T_2$	17100
PVC-DPPG-Co(II)	7,600 14,933 17,320	$^4T_{1g} \rightarrow {}T_{2g}$ $^4T_{1g} \rightarrow {}^4A_{2g}(F)$ $^4T_{1g} \rightarrow {}^4T_{1g}(P)$	7600
PVC-DPG-Ni(II)	23,000	$^1A_{1g} \rightarrow {}^1T_{1g}$	23000
PVC-DPG-Pd(II)	19,320 15,360	$^3T_{2g} \rightarrow {}^3T_{1g}(P)$ $^3T_{2g} \rightarrow {}^3T_{1g}(F)$	-
PVC-DPG-Pt(IV)	17,655	$^1A_{1g} \rightarrow {}^1T_{1g}$	17655
PVC-DPG-Cu(II)	14,320	$^2B_{1g} \rightarrow {}^2B_{2g}$ $^2B_{1g} \rightarrow {}^2E_g$	14320

Table 4. Magnetic moment, conductivity and suggested structure for complexes

Complex	Magnetic moment μ_{eff} (B.M.)	Conductivity $\mu s.\ cm^{-1}$	Suggested Structure
Fe(II)	5.00	31	Octahedral
Co(II)	1.00	26	Octahedral
Ni(II)	0.25	88	Square planer
Pd(II)	2.5	28	Octahedral
Pt(IV)	Diamagnetic	72	Octahedral
Cu(II)	1.43	90	Square planer

4.1. Determination of the Molecular weight for PVC and PVC-DPG by dilute solution viscometry

The molecular weight of the prepared polymer was determined using Mark-Houwink equation:

$$[\eta] = KM^a \quad \dots (1)$$

where, $[\eta]$ = Intrinsic viscosity, M= Molecular weight, K and a = Mark-Houwink constants [18]. Different concentrations were made by dissolving the polymer in solvent [g/100ml] and the flow time of pure solvent is $[t_0]$ while the flow time of polymer solvent is [t]. The relative viscosity was calculated according to the following equation:

$$\eta\ re = \frac{t}{t_0} \quad \dots (2)$$

The specific viscosity: $\eta(sp) = \eta(re) - 1,$ the intrinsic viscosity $(\eta_{int.}) = \eta(sp)/c$, and it was calculated via extrapolation of the reduced viscosity of four polymer solutions to zero concentration by plotting the relation between the concentration (C) and viscosity $/\eta/$ of PVC and PVC-DPG polymer. Table 5 The molecular weight of PVC was calculated using the Mark-Heuwink equation, and it was found to be 146275.75 gm/mol. The unit number of the polymer has been also calculated by diving the molecular weight of the polymer to the MW of the monomer MW(PVC)/MW (VC) = 146275.75/62.5 = 2340 monomer. Following the same calculation, the MW of PVC-DPG was calculated, and it was found to be 195,747 g/mol. The MW of bonded DPG was obtained by subtracting the MW of PVC from that of the mixed PVC-DPG polymer. The number of bonded DPG was calculated by dividing MW of bonded DPG to the free DPG, and it has been found to be 876. The ratio of bonded DPG to the unit number of PVC is equal to 1:5.

Table 5. Viscosity of PVC and PVC-DPG at different concentrations

C (g/100ml) ×10^{-1}	$/\eta/$ (ml/g) PVC	$/\eta/$ (ml/g) PVC-DPG
1.0	1.75	2.0
2.0	2.25	2.5
3.0	2.75	3.5
4.0	3.25	4.0

The biological activity of prepared complexes was evaluated against the growth of Gram-positive (Staphylococcus aureus) and Gram-negative (Escherichia coli). Table 6. All complexes showed high activity against both types of bacteria. In addition, these complexes exhibited higher biological activity toward Staphylococcus aureus than Escherichia coli. The variation in the activity of the different compounds against these bacteria might be attributed to the difference in the composition of the cell wall structure of bacteria. The bacterial cell wall consists of polysaccharide chains, and the gram-positive bacteria, consist of a glycan of N-acetylglucosamine and N-acetylmuramic acid and cross-linking peptide chains.

In comparison, gram-negative bacteria are composed of one layer of peptidoglycan surrounded by an outer membrane [19]. The inactivity of some compounds can be related to the ability of bacteria to resist some chemical compounds. It may be due to the presence of a thick membrane surrounding the cell wall, which has a highly fatty character. [20]. Also, chemical compounds may cross the cell wall very slowly, this enables the bacteria to have enough time to destroy and eliminate these compounds. Furthermore, the lack of activity may be related to the low concentration of the tested compounds, which are lower or higher than the active concentration.

Table 6. Biological activity of PVC-DPG complexes

Comp.	Conc. mg/ml	Staphylococcus aureus	Escherichia coli
		Inhibition zone (mm.)	
PVC-DPG-Fe(II)	Conc.1	13.0	9.0
	Conc.2	11.0	6.0
PVC-DPG-Co(II)	Conc.1	25.0	18.0
	Conc.2	18.0	15.0
PVC-DPG-Ni(II)	Conc.1	16.0	15.0
	Conc.2	10.0	9.0
PVC-DPG-Pd(II)	Conc.1	22.0	15.0
	Conc.2	18.0	8.0
PVC-DPG-Pt(IV)	Conc.1	22.0	12.0
	Conc.2	18.0	6.0
PVC-DPG-Cu(II)	Conc.1	14.0	18.0
	Conc.2	10.0	11.0

*Conc.1 =20mg/ml; conc.2 =10mg/ml

5. Conclusions

In conclusion, the reaction between Polyvinyl chloride (PVC) and diphenylglyoxime (DPG) takes place by replacing the chloride molecules of the PVC chain with DPG through the hydroxyl group, and the final polymer compound coordinates with transition metal ions by nitrogen atoms of the DPG molecules. With respect to the biological study, all prepared complexes show biological activity against Staphylococcus aureus (Gram-positive) and Escherichia coli (Gram-negative) compared to the PVC and PVC-DPG. Therefore we conclude that the presence of transition metal ions is important to improve the biological activity and that will lead to enhancing the therapeutic efficiency of drugs.

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