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Porous palladium aminophosphates: synthesis, characterization, antimicrobial and cytotoxicity studies†

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Novel palladium aminophosphates have been synthesized at room temperature employing palladium acetate, orthophosphoric acid and aliphatic amines. The PNPAP, PNOAP and PNDDAP obtained were characterized by various spectral and physico-chemical techniques. Small angle powder X-ray diffraction patterns show that PNDDAP is probably mesoporous. The SEM images of PNPAP, PNOAP and PNDDAP show typical layered, flake and tubular like morphologies. The presence of –Pd–O, Pd–N–, –P–O, P–N vibrations in the framework of palladium aminophosphates was confirmed by infrared and Raman spectral studies. Palladium in tetrahedral coordination was confirmed from UV-Vis DRS studies in the frameworks of PNPAP, PNOAP and PNDDAP. The PNPAP and PNDDAP show two ^{31}P MAS NMR peaks which indicate the existence of two crystallographically non equivalent tetrahedrally co-ordinated phosphorous atoms. The PNPAP, PNOAP and PNDDAP were evaluated for biological applications. Only PNDDAP exhibits potent antimicrobial and nematicidal activity on *M. incognita*. All the palladium containing aminophosphates show DNA cleavage activity on λDNA. The *in vitro* anticancer studies reveal that PNPAP and PNDDAP show activity only on the HL60 cell line. PNOAP shows good anticancer activity on HL60 and MCF7 cell lines and moderate activity on the HeLa cell line.

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1. Introduction

Phosphate based materials are important in several industrial acid catalysed reactions.[1] In recent years inorganic phosphorous containing materials have received much attention on account of their ability to selectively uptake specific ions, resistance to oxidation, high thermal and chemical stability. In addition, the presence of phosphate in materials seems to enhance catalytic properties, stabilize surface area, crystal phase, improve surface acidity and make the material porous.[2] Research on phosphate based materials with open frameworks is currently in progress due to their applications in catalysis and gas separation.[3] The study of phosphates of transition metals has received great attention in recent years. Phosphate frameworks stabilize reduced oxidation states, due to their high charge (PO_4^{3-}) and hence favour the formation of anionic frameworks with a high degree of chemical, mechanical and thermal stability.

During recent years, there has been considerable progress in the anticancer chemistry of palladium based metal compounds. Palladium(II) compounds are isostructural and isoelectronic with platinum(II) and are potentially attractive as anticancer agents,[4,5] and in some cases they have been more active than *cis*-platin.[6] The compounds of palladium are also important due to their anti-amoebic activity[7] and can act as effective antitumor drugs and exhibit relatively few side effects compared to other heavy metal compounds.[8] The cytotoxic and antiproliferative studies show that the compounds of Pd(II) exhibit good cytotoxic activity against different cell lines.[9–11] Recently, *trans*-palladium(II) complexes with ligand containing pyridine or phosphoric residue have been described to be cytotoxically active.[12–14] Palladium compounds serve as alternative metal-based drugs and are non-toxic.[15–21] Palladium ions are capable of interacting with DNA thereby cross bindings and inhibiting its synthesis as well as inducing apoptosis.[22,23]

Aminophosphates are amine and phosphorous based materials. The organic functionality in aminophosphate framework enhances hydrophobicity and shows high activity in base catalysed reactions. Incorporation of transition metals such as titanium or vanadium or palladium in aminophosphates leads to novel materials with redox properties. In particular, titanium cation Ti^{4+} in framework positions is found to exhibit good activity in shape selective redox reactions.[24]

This manuscript deals with the synthesis of palladium aminophosphates at room temperature and their characterization by various physico-chemical techniques palladium aminophosphates are also evaluated for their biological applications namely antimicrobial, nematicidal, DNA cleavage and anticancer activities.

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2. Experimental

The synthesis of palladium aminophosphates was carried out at room temperature. In a typical synthesis, a pre-determined quantity of aliphatic amines (*n*-propyl amine (5.5 mL) or *n*-octyl amine (11.0 mL) or *n*-dodecyl amine (15.4 mL)) was added to 0.0037 g of palladium acetate and stirred. To this mixture, 0.94 mL orthophosphoric acid was added at once and stirred vigorously to get solid products (0.02 $PdO : P_2O_5 : 8 RNH_2$). The products thus obtained were thoroughly washed with diethyl ether, dried at 40 °C for about 30 min and ground to fine powder.

Qualitative phase analysis of palladium aminophosphate has been studied using a Bruker AXS D8 advance diffractometer at room temperature with Cu-Kα X-ray source of wavelength 1.5406 Å using Si (Li) PSD detector. The morphology of the material was investigated using scanning electron microscopy (SEM) on a JEOL Model JSM-6390LV. Fourier transform infrared spectroscopy (FT-IR) was recorded on Thermo Nicolet, Avatar 370 spectrophotometer equipped with a pyroelectric detector (DTGS type); a resolution of 4 cm^{-1} was adopted and provided with KBr beam splitter. Dispersive Raman spectroscopy was performed on Bruker senterra at a wavelength of 532 nm using laser radiation as source. The coordination and oxidation state of palladium in palladium aminophosphate was examined by diffuse reflectance UV-Visible spectrophotometer (UV-Vis DRS) on Varian, Cary 5000 in the wavelength range of 175–800 nm. X-ray photoelectron spectroscopic analysis carried out using ESCA-3000 (VG Scientific, UK) instrument. The ^{31}P magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy was performed at room temperature on a Bruker DRX-500 AV-III 500(S) spectrometer, with a spinning rate of 10–12 KHz operating at 121.49 MHz using a 5 mm dual probe. The ^{13}C cross polarization magic-angle spinning (CP-MAS) nuclear magnetic resonance (NMR) spectroscopy was performed at room temperature on a DSX-300 Avance-III 400(L) NMR spectrometer with a spinning rate of 10–12 KHz operating at 75.47 MHz using a 5 mm dual probe.

Palladium aminophosphates *viz.* PNPAP, PNOAP and PNDDAP were evaluated for their biological activity such as antimicrobial, nematicidal, DNA cleavage and anticancer activities using the procedures given in the ESI.†

3. Results and discussion

Powder X-ray diffraction patterns of PNPAP, PNOAP and PNDDAP are shown in Fig. 1. The XRD pattern in PNDDAP show the presence of mesoporosity due to the presence of first peak at 4.2°. Sharp peaks indicate the presence of crystalline nature in PNDDAP. The characteristic peak of Pd (111) at $2\theta = 40.1°$ was indistinguishable, probably due to low amount of palladium or relatively small well-dispersed palladium species.[25,26]

The scanning electron microscopy images of PNPAP, PNOAP and PNDDAP are shown in Fig. 2. The SEM image of PNPAP

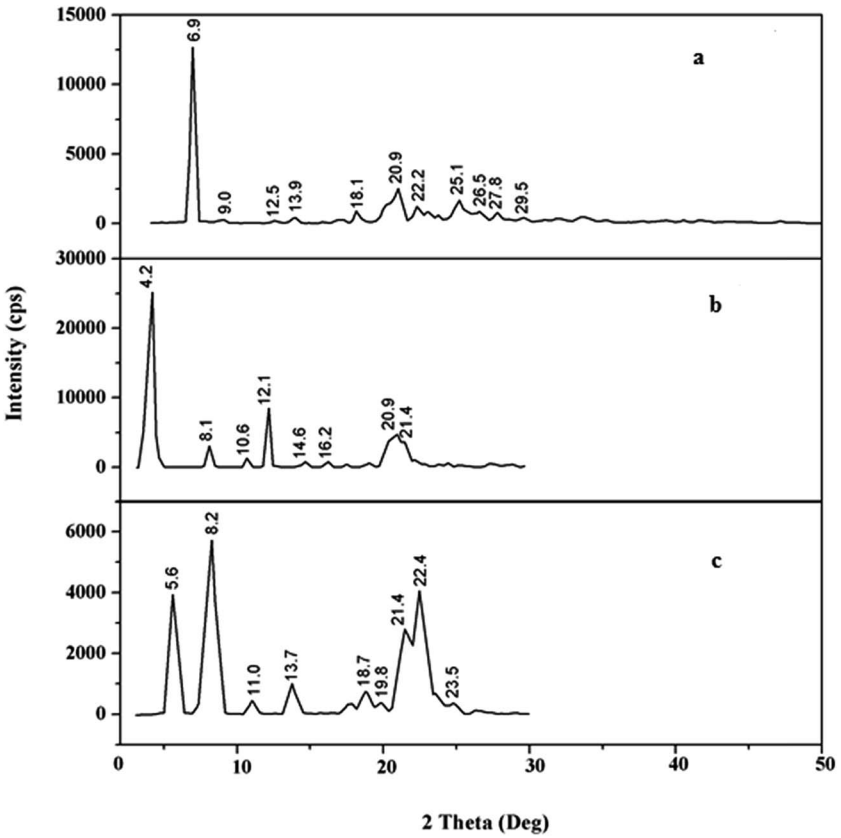

Fig. 1 Small angle powder X-ray diffraction patterns of (a) PNPAP, (c) PNOAP and (b) PNDDAP.

shows layered material, while PNOAP shows homogeneous distribution of the material with large spherical and irregular flake like structures. The SEM image of PNDDAP shows small tubular like morphology.

The BET surface area of palladium aminophosphates are 70, 90 and 130 $m^2 g^{-1}$ for PNPAP, PNOAP and PNDDAP respectively. The samples follows type II adsorption/desorption isotherm. The reduction in surface area compared to reported for zeolites[26] is due to the obstruction of pores by linear alkyl groups present in amines.

FT-IR spectra of PNPAP, PNOAP and PNDDAP are shown in Fig. 3. The broad bands observed at 3446, 3400 and 3334 cm^{-1} in PNPAP, PNOAP and PNDDAP are due to O–H or N–H stretching vibrations.[27] The bands in the range of 2970–2850 cm^{-1} corresponds to asymmetric and symmetric stretching vibrations of $-CH_2$ group of alkyl chain. Peaks in the range of from 1640–1630 cm^{-1} are attributed to H–O–H bending vibrations of adsorbed water. The bending vibrations of $-CH_2$ group of alkyl chain were observed around 1478–1468 cm^{-1}.[28] Peaks in the range 390–340 cm^{-1} corresponds to the presence of Pd–O vibrations.[29] Sharp bands in the range 550–450 cm^{-1} are characteristic of Pd–N vibrations.[30] The bands at 986, 1070, 1064, 1090, 977 and 1067 cm^{-1} are due to P–O stretching vibrations in palladium aminophosphates.[31,32] The peaks at 1234 and 1238 cm^{-1} in PNOAP and PNDDAP are assigned to C–N stretching vibrations.

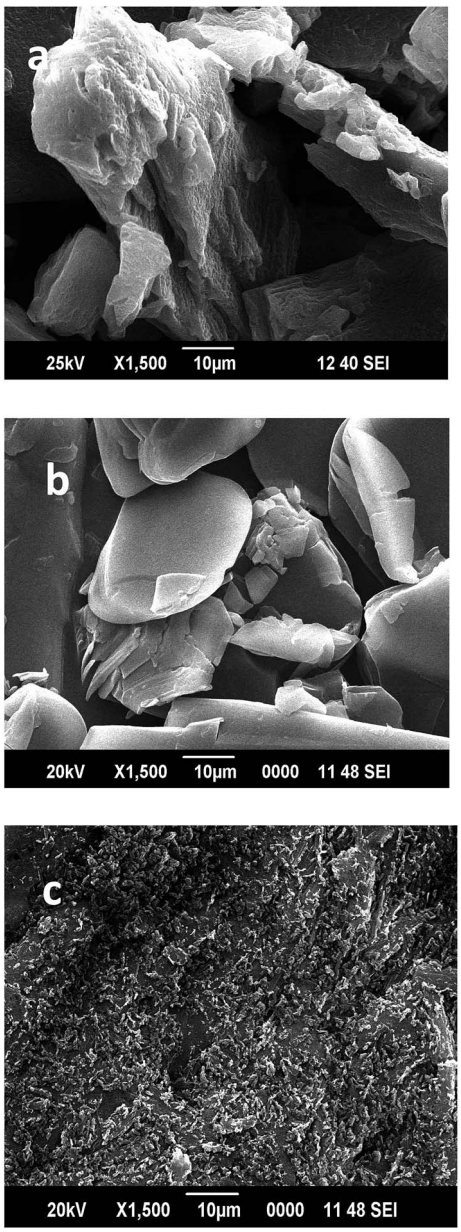

Fig. 2 Scanning electron micrograph images of (a) PNPAP, (b) PNOAP and (c) PNDDAP.

The dispersive Raman spectra of PNPAP, PNOAP, PNDDAP are shown in Fig. 4. The bands observed in the range 2990–2880 cm^{-1} in PNPAP and PNOAP corresponds to $-CH_2-$ stretching vibrations of alkyl chain.[33] The peak at 414 cm^{-1} in PNPAP corresponds to Pd–O stretching vibration.[34]

The UV-Vis diffuse reflectance spectra of PNPAP, PNOAP and PNDDAP are shown in Fig. 5. The PNOAP and PNDDAP show bands at 250, 270, 375 and 475 nm are corresponds to the presence of Pd–O(N_3) (Fig. 8). The bands around 250 and 270 nm corresponds to $(N)O^{2-} \rightarrow Pd^{2+}$ charge transfer transitions. The bands around 375 nm is attributed to $\nu_3(^1A_{1g} \rightarrow {}^1B_{1g})$ transitions. The broad band around 475 nm is due to d–d transitions of tetrahedrally co-ordinated palladium with nitrogen and oxygen environment.[35]

The ^{31}P MASNMR spectra of PNPAP, PNOAP and PNDDAP are shown in Fig. 6. PNPAP shows two peaks, one at 5.304 ppm and the other at 2.308 ppm. The peaks are almost in 1 : 1 intensity ratios. Similarly ^{31}P MASNMR spectrum of PNOAP shows two peaks one at 5.558 ppm and the other at 3.262 ppm. Two peaks in PNPAP and PNOAP suggest the existence of two crystallographically non equivalent phosphorous atoms. The PNDDAP spectrum shows a single peak at 1.875 ppm. Only one peak in PNDDAP indicates that there is a unique chemical environment of phosphorous atoms.

The ^{13}C MASNMR spectra of PNPAP, PNOAP and PNDDAP are shown in Fig. 7. Both the spectra show peaks at 41.02 and 39.45 ppm, which corresponds to the C_1, carbon bonded to nitrogen atom of amino groups, respectively. The peaks at 33.42 ppm in PNDDAP can be assigned to the C_2 carbon linked to C_1 carbon which is directly attached to nitrogen of amino group. Peaks at 21.37 and 25.17 ppm in both the spectra can be assigned to the carbon of methylene ($-CH_2$) group. Peaks at 12.17 and 15.12 ppm in PNPAP and PNDDAP can be attributed to the carbon of terminal $-CH_3$ group of amine molecules.

Based on the above characterization, we have proposed the following plausible mechanism for palladium aminophosphate synthesis and basic structure of the catalysts (Fig. 8). This is a trifunctional catalyst due to the presence of palladium ion (redox), amine (Lewis base) and exchangeable proton (acid) sites. As the reaction is carried out in solvent free condition, there is no effluent from the synthesis of catalyst. It mean 100% yield. So the input palladium and amine are present in the basic structure. The presence of solid acid sites are deduced from the proposed structure, which is confirmed by the NaCl ion exchange experiment.

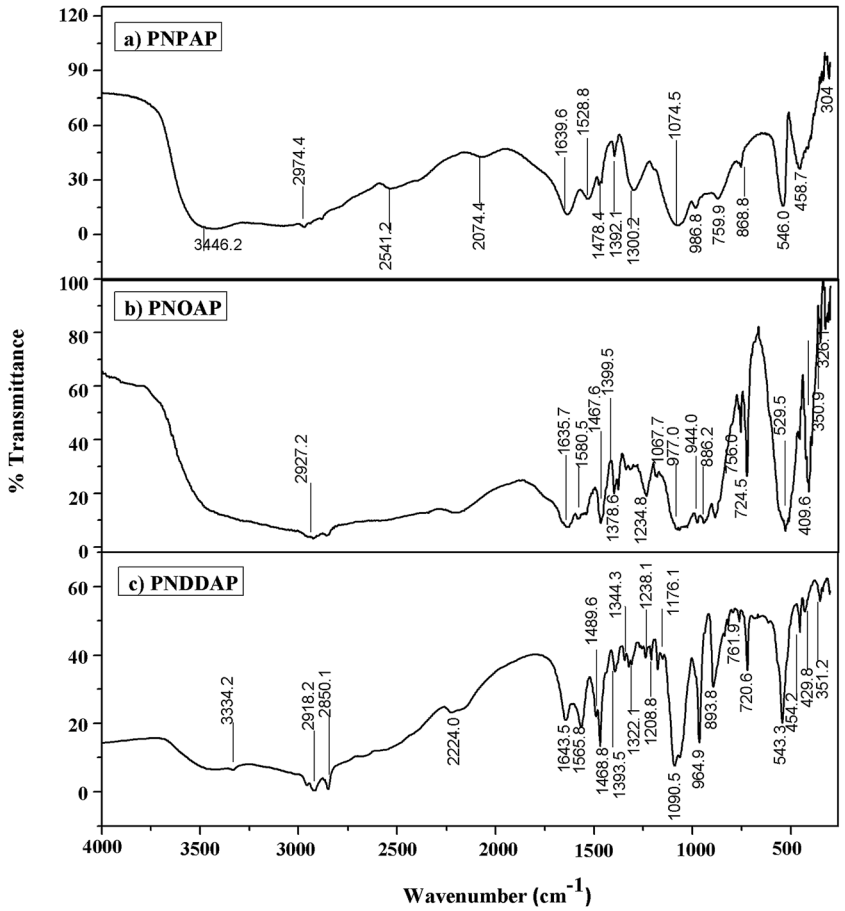

Fig. 3 Fourier transform infra red spectra of (a) PNPAP, (b) PNOAP and (c) PNDDAP.

The palladium containing aminophosphates were evaluated for their antimicrobial activity. The minimum inhibitory concentration (MIC) values of the antimicrobial activity of palladium aminophosphates are presented in Table 1. The results reveal that the PNPAP does not show any antimicrobial activity. The PNOAP shows moderate activity against bacterial strains *Staphylococcus aureus*, *Pseudomonas fluorescens* and *Proteus vulgaris*.

PNDDAP is found to inhibit the growth of bacteria and the MIC values were found in the range of 18 to 28 μg mL^{-1}. The PNDDAP exhibits the maximum anti-bacterial activity against *S. aureus* with a MIC value of 18 μg mL^{-1} and moderate against *P. fluorescens* with a MIC value of 28 μg mL^{-1}. The MIC value against *E. coli* was found to be 22 μg mL^{-1}. The anti-fungal activity of PNDDAP against *C. albicans* shows a MIC value of 18 μg mL^{-1}. The PNDDAP exhibits less to moderate activity when compared with the standard antibiotics ampicillin and clotrimazole. Among the palladium aminophosphates, PNDDAP was found to be most efficient against bacteria. The difference in activity of palladium aminophosphates against microbial strains depends on their impermeability of the microbial cells.[37,38]

Variation in the alkyl chain length of amine is thought to influence the extent of antimicrobial activity.[36] The longer alkyl chain shows higher antimicrobial activity than shorter chains. The higher alkyl chain integrates easily with the lipid bilayer of the cell membrane and causes membrane disruption and inevitably causes leakage of the cell contents.[39,40] These studies lead to the conclusion that the antimicrobial activity depends on the properties of amine side chains of palladium aminophosphates.[41]

The longer alkyl chain amine in PNDDAP reduces the polarity of the palladium ion by partial sharing of its charge with the positive charge of the palladium ion.[42,43] Further, it increases the electron delocalization over the whole framework of PNDDAP and enhances its lipophilicity. The lipophilicity of the palladium aminophosphates increases with increase in bulkiness of alkyl chain amine.[44,45] The enhanced lipophilicity of PNOAP and PNDDAP favors the materials to penetrate into lipid membranes of the bacterial cell more efficiently and facilitates the blockage of metal binding sites in the enzymes of microorganisms.[46,47]

Further the activity of PNOAP and PNDDAP can also be explained on the basis of overtones concept and chelation theory or due to the effect of the palladium ion on the normal cell process.[48] According to overtones concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid soluble materials. Liposolubility is an

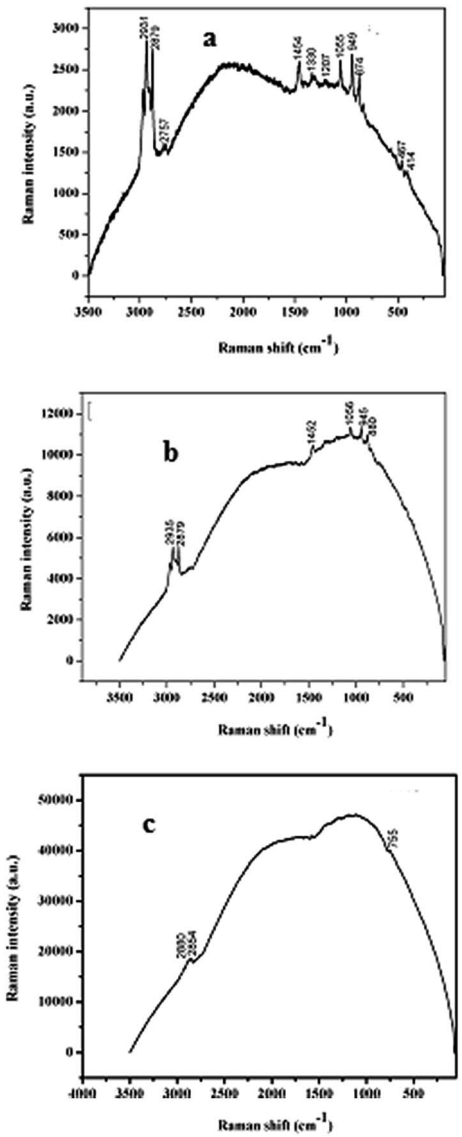

Fig. 4 Dispersive Raman spectra of (a) PNPAP and (b) PNOAP and (c) PNDDAP.

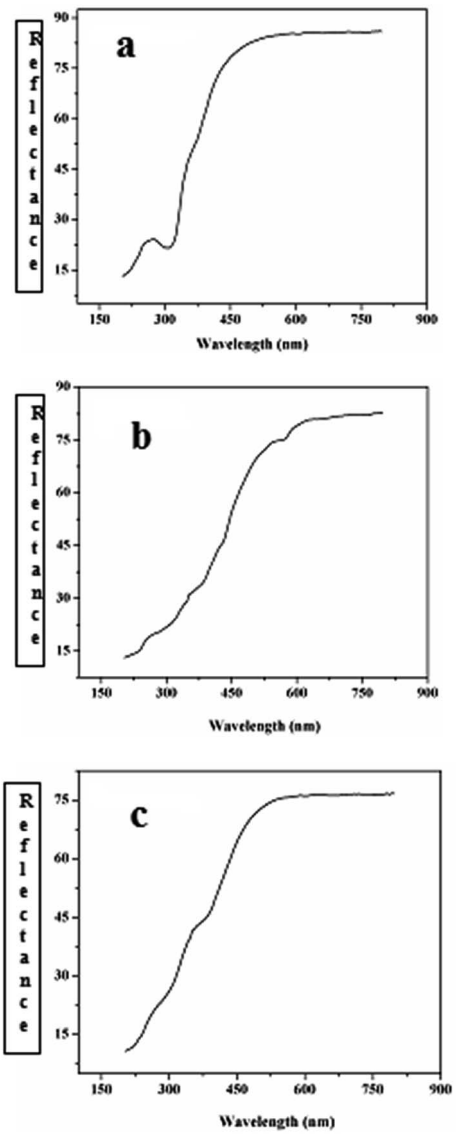

Fig. 5 Ultra violet-visible diffused reflectance spectra of (a) PNPAP (b) PNOAP and (c) PNDDAP.

important factor which controls the antimicrobial activity. The activity of PNOAP and PNDDAP is due to the increased lipophilic nature of the material araising from chelation.[49] The inactivity of PNPAP in antimicrobial activity is due to its low lipophilicity which makes the material not to penetrate through the lipid membrane.

The nematicidal activity of palladium containing aminophosphates was evaluated against *Meloidogyne incognita* with different concentrations after 24 and 48 h and the results are presented in Table 2. The results reveal that, PNPAP and PNOAP do not show any activity. PNDDAP exhibits good activity indicating 68% mortality in 250 μg mL^{-1} concentration after 48 h exposure. Aliphatic amines having the carbon chain length from 9 to 35 carbon atoms are found to be highly lethal to nematodes and parasites.[50] However the activity of PNDDAP depends on concentration and time *i.e.*, the activity was found to be more at high concentrations and increased with incubation time. The percentage mortality of PNDDAP increased from 11 to 68% with increase in the concentration from 50 to 250 μg mL^{-1} and incubation time from 24 to 48 h.

The DNA cleavage activity was studied for palladium aminophosphates using agarose gel electrophoresis on λDNA. The gel electrophoresis image of palladium aminophosphates is shown in Fig. 9. DNA control in Fig. 9 "Lane C" does not show any cleavage in its lane. $FeSO_4$ in Fig. 9 "Lane +ve" was used as standard, shows disappearance of control bands was observed in its lane, indicating DNA cleavage. Lanes of PNOAP and PNDDAP compounds clearly show complete disappearance of control bands. The results indicate that these palladium aminophosphates exhibit significant DNA cleavage activity without using any external reagents like H_2O_2. The DNA cleavage activity of palladium aminophosphates may be due to electrostatic interactions of palladium ions with the base pairs of amino acids present in λDNA molecule.[50]

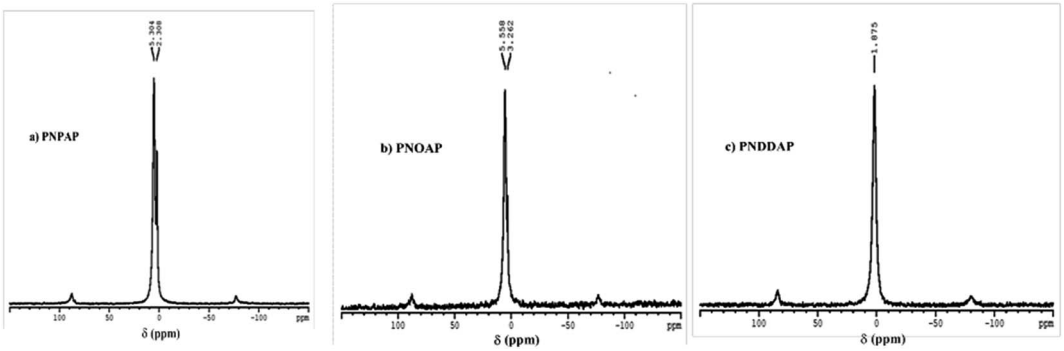

Fig. 6 ^{31}P magic angle spinning nuclear magnetic resonance spectra of (a) PNPAP, (b) PNOAP and (c) PNDDAP.

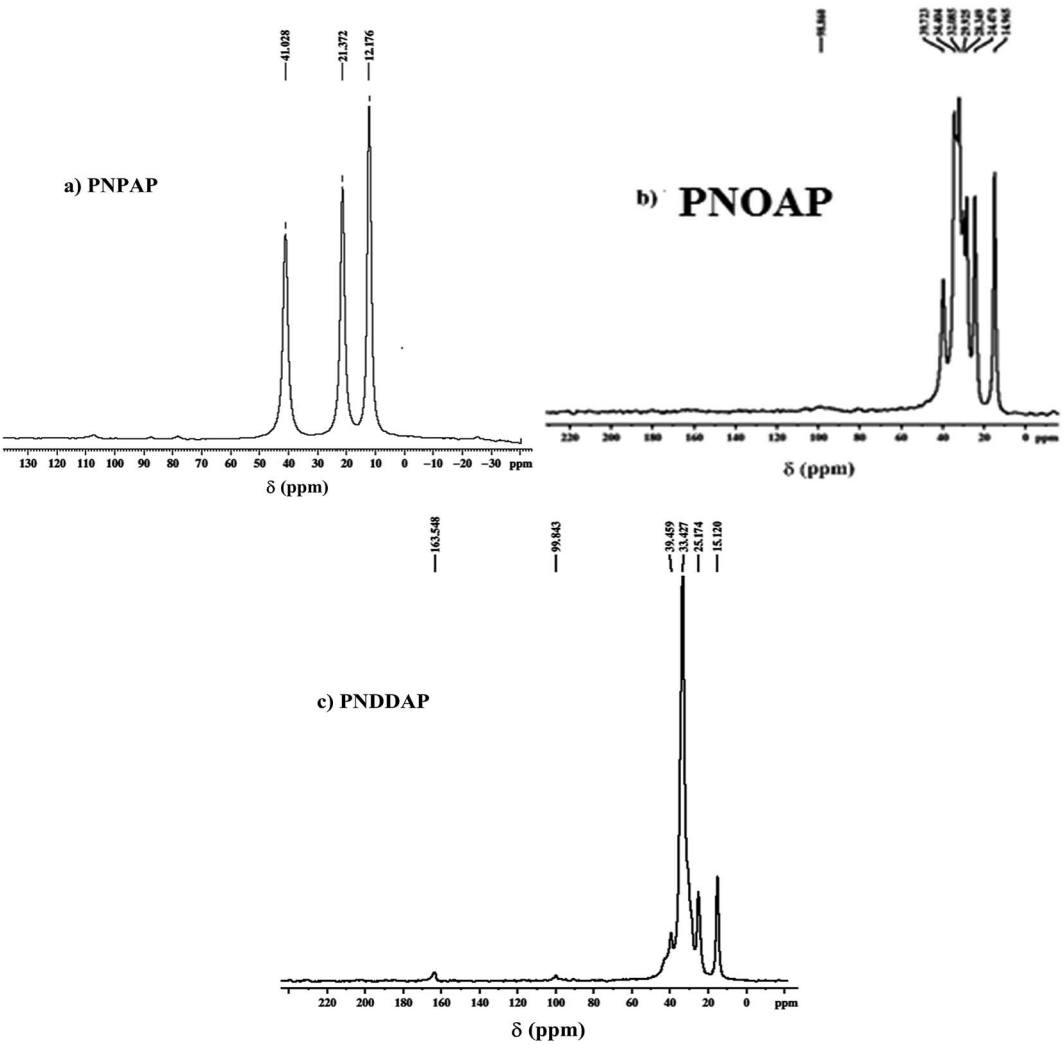

Fig. 7 ^{13}C magic angle spinning nuclear magnetic resonance spectra of (a) PNPAP (b) PNOAP and (c) PNDDAP.

The palladium containing aminophosphates PNPAP, PNOAP and PNDDAP were evaluated for *in vitro* anticancer activity against human cancer cell lines such as MCF7, HeLa and HL60 cell lines by sulforhodamine B assay. The growth inhibition of 50% (GI50) values of palladium aminophosphates and standard drug doxorubicin obtained against selected cancer cell lines are shown in Table 3.

Estimation based on GI50 values shows that all the palladium aminophosphates exhibit anticancer activity. PNPAP and PNDDAP show activity exclusively on HL60 cell line with GI50 values of 34.2 and 42.3 μg mL^{-1}. PNOAP exhibits good activity

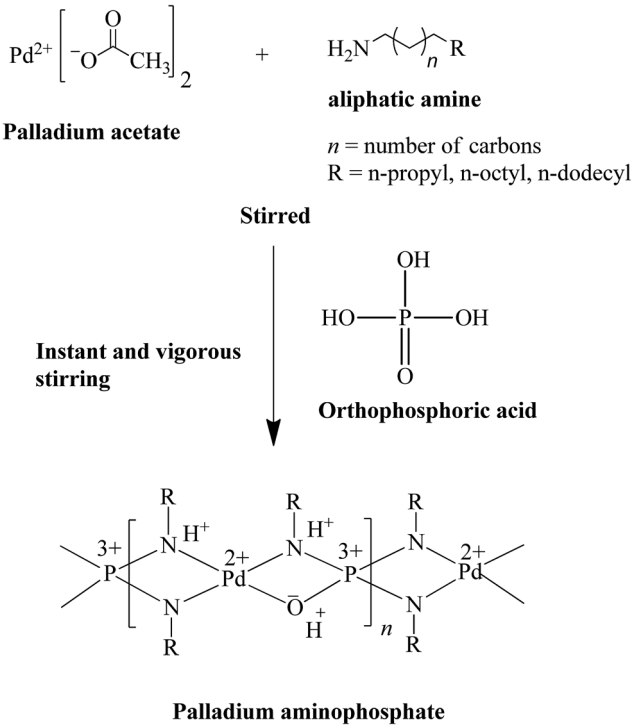

Fig. 8 Synthesis mechanism and proposed basic structure of palladium aminophosphate.

Table 1 Minimum inhibitory concentration values (μg mL^{-1}) of antimicrobial activity of palladium aminophosphates

Compound	*B. subtilis*	*S. aureus*	*P. vulgaris*	*P. fluorescens*	*E. coli*	*C. albicans*
PNPAP	—	—	—	—	—	—
PNOAP	—	40	40	40	—	—
PNDDAP	20	18	22	28	22	18
Ampicillin	14	12	16	16	16	—
Clotrimazole	—	—	—	—	—	10

Table 2 Nematicidal activity (% mortality) observed against different concentrations of palladium aminophosphates on *Meloidogyne incognita*. Effect of incubation time on % mortality

	24 h			48 h		
	Concentration (μg mL^{-1})					
	250	150	50	250	150	50
Compound	% mortality					
PNPAP	—	—	—	—	—	—
PNOAP	—	—	—	—	—	—
PNDDAP	36	23	11	68	55	35

on MCF7 (Fig. 10b) and HL60 cell lines (Fig. 10c) with GI50 values of 36.9 and 37.2 μg mL^{-1} and moderate activity on HeLa cell line with a GI50 value of 63.1 μg mL^{-1} (Fig. 10a).

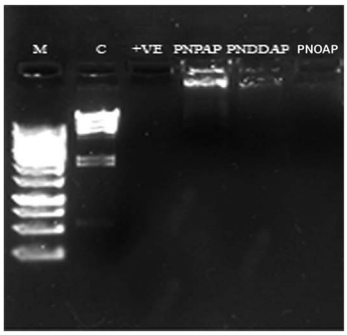

Fig. 9 Gel electrophoresis image of palladium aminophosphates: DNA cleavage activity of palladium aminophosphates against λDNA: lane M. DNA + marker, lane C. DNA alone, lane +ve. DNA + $FeSO_4$, lane PNPAP. DNA + PNPAP, lane PNDDAP. DNA + PNDDAP, lane PNOAP. DNA + PNOAP.

The low anticancer activity of palladium compounds is due to their rapid hydrolysis (10^5 times faster than corresponding platinum analogues) and higher lability in biological fluids. This may lead to easy dissociation, formation of very reactive palladium species and decompose before entering the cell, make the palladium species inaccessible to the target cancer cells.[51,52]

The polarity of the amine allows the material to be soluble in the cancer cell line solution medium and also be able to interact with the cell membrane.[53,54] Once the material is on the membrane, it should pass through the cell or it must interact with the membrane and induce other physiological pathways. In the case of palladium aminophosphates the polar group amino interacts with the aqueous medium and non-polar group alkyl chain interacts with the hydrophobic portion of the cell membrane.[54]

It is reported in the literature[54] that the dual hydrophilic–lipophilic character of the material, allows the material to interact with DNA through a nonconventional way, both covalently (through direct binding of the metal centre to the purine bases) and non-covalently (*via* hydrophobic and hydrogen bonding close contacts). It is also indicated that in the literature the hydrophobic group interacts with the DNA minor groove prior to covalent bond formation, and this pre-association affects the crosslink formation as well as local structure of the resulting adducts.

The biological activity of a material strongly depends on the nature of the amine, metal coordination, hydrophilicity and lipophilicity. In the case of palladium aminophosphates the palladium and amine tuning will change the cytostatic activity. The amine stabilizes the material so that the material can reach the cancerous cell. The combination of both metallic and organic group may reveal new modes of biological action.

4. Conclusions

Novel palladium aminophosphates have been synthesized at room temperature in solvent free condition. The synthesized PNPAP, PNOAP and PNDDAP were characterized in detail. A plausible structure of the synthesized materials are proposed.

Table 3 Anticancer activity of palladium aminophosphates on human cancer cell lines HeLa, MCF7 and HL60 using sulforhodamine B assay[a]

	GI50		GI50		GI50	
Cell lines	PNPAP	Doxorubicin	PNOAP	Doxorubicin	PNDDAP	Doxorubicin
HeLa	>80	<10	63.1	<10	>80	<10
MCF7	>80	<10	36.9	<10	>80	<10
HL60	34.2	<10	37.2	<10	42.3	<10

[a] Note: GI50 (μ molar) = growth inhibition of 50% (GI50) drug concentration resulting in a 50% reduction in the net protein increase, doxorubicin = positive control compound, HeLa = cervix, MCF7 = breast and HL60 = leukemia cancer cell lines.

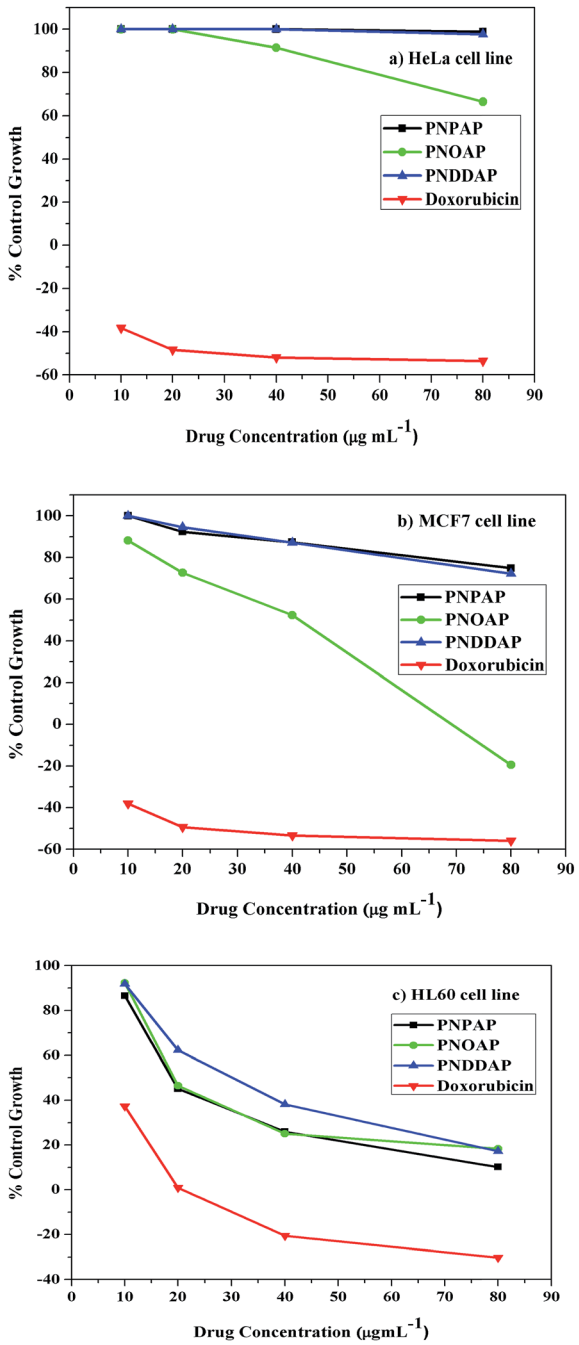

Fig. 10 Anticancer activity of palladium aminophosphates on human cancer cell lines (a) HeLa, (b) MCF7 and (c) HL60 using sulforhodamine B assay.

The PNPAP, PNOAP and PNDDAP were evaluated for biological applications. Only PNDDAP exhibits potent antimicrobial and nematicidal activity on *M. incognita*. All the palladium aminophosphates shows DNA cleavage activity on λDNA. The *in vitro* anticancer studies reveal that PNPAP and PNDDAP show activity only on HL60 cell line. PNOAP shows good anticancer activity on HL60 and MCF7 cell lines and moderate on HeLa cell line.

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