IJASRM

International Journal of Advanced Scientific Research and Management, Special Issue 5, April 2019

www.ijasrm.com

ISSN 2455-6378

Antiradical And Electrochemical Behaviour Of Some Palladium(II) Complexes

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Abstract

The diseases like atherosclerosis, cancer, inflammatory joint disease, asthma, diabetes, senile dementia and degenerative eye disease have a common symptom of free radical generation. Palladium(II) and ligands like nuclebases, allyal alcohol, indole, crotonaldehyde and cinnamaldehyde are used to treat the various diseases. The aim of this study was to screen the free radical inhibitory activity of palladium (II) complexes and their electrochemical activity.

The palladium(II) complexes were synthesized in the molar ratio of 1:2 (metal to ligands). The synthesized palladium(II) complexes were examined for their electrochemical behaviour in suitable electrolyte solution. Further, the palladium(II) complexes were screened for their DPPH and ABTS inhibitory activity using spectrophotometric assay system. The synthesized complexes and respective ligands were dissolved in suitable electrolyte. Entire complexes and ligands show simple irreversible wave for Pd(II)complexes and ligands redox couples in −2.5 to 50 mV potential range and scan rate was 300 mV/S except indole. All the complexes were screened for their DPPH and ABTS inhibitory activity. PdCl2 shows the DPPH scavenging activity having 634.84 µg/ml IC50 amoung all complexes while for palladium(II) complexes of allay alcohol, crotonaldehyde and indole shows the ABTS inhibitory activity. The data obtained from our experiment reveals that the all palladium(II) complexes are an irreversible wave for palladium(II) redox system except indole ligand. The PdCl2 is potent inhibitor for DPPH free radical while palladium(II) complex of indole scavenge potentially ABTS free radicals among all synthesized palladium(II) complex .

Keywords: *Palladium(II), DPPH, ABTS, Free radicals, Electrochemical behaviour.*

1. Introduction

Oxidative stress is defined as a disturbance in the equilibrium between free radicals (FR), reactive oxygen species (ROS) and the endogenous defense mechanisms[1]. It is the disturbance in the balance between oxidant-antioxidant states which favours the production of oxidant species[2]. Human body requires both oxidant and antioxidant species for normal metabolism, signal transduction and regulation of cellular functions. Therefore, each cell maintains a condition of homeostasis between the oxidant and antioxidant species[3,4]. Oxidative stress may lead to injury to all the important cellular components like proteins, DNA and membrane lipids, which can cause cell death. Oxidative stress has also implicated in various physiological and pathological processes, including DNA damage, proliferation, cell adhesion, and survival which has been validated by several experimental and clinical data in large number of pathological states as well as aging [2,3].

Metals have been used in medicines for centuries [5-7]. After the success of cis-platin as an anticancer

agent, an interest in the study of the palladium(II) based chemotherapies has been advocated due to significantly similar coordination properties of Pt(II) and Pd(II)[5]. Numerous palladium complexes with comparable antitumor activity and enhanced antiviral, antibacterial and antifungal activity have been synthesized[8]. These promising results encourage further research in this field, for further applications. The coordination chemistry of N or O donor ligands is an interesting area of research [6-9].

In the present work we are intended to synthesize and investigate the palladium(II) complexes with different types of ligand, electrochemical behaviour of palladium(II) complexes and free radical scavenging activity.

2. Materials and Methods

2.1 Synthesis of Palladium(II) complexes with different ligands

The Palladium(II) complexes of allyal alcohol, crtonaldehyde, cinnamaldehyde, adenine, guanine, cytosine, thymine and indole were prepared by the method reported by Stephen J. Lippard et.al. the 1:2 molar ratio of alcoholic solution of ligand's was added to a filtered acidic solution of palladium chloride ($PdCl_2$) in (0.1 N HCl), with shaking. The resulting solution was heated for 4 hours with shaking continuously at 80 ^{0}C over a water bath. A coloured precipitated was obtained. The precipitate was filtered in centrifuge machine and wash several times distilled water and finally with ethanol. Synthesized complexes were dried in vacuum desiccator over silica gel at room temperature.

2.2 Electrochemical behaviour by cyclic voltammeter of Ligands and Palladium(II) complexes

The cyclic voltammetric measurements were carried out with a Metrohm, Netherlands Instrument having san electrochemical cell with a three – electrode system. The auxiliary electrode was an Ag /$AgCl_2$. Platinum disk was used as a working electrode, while a platinum wire electrode used as a reference electrode. The concentration of all compounds were same i.e. 0.003 mg. Palladium chloride, adenine, guanine, cytosine, indole,thiamine and complexes (Pd+adenine, Pd+ guanine, Pd+cytosine) were analyzed in 25 ml solution 0.5 M KCl. While, cinnamaldehyde, crotonaldehyde, allyl alcohol and complexes (Pd+cinnamaldehyde ,Pd+crotonaldehyde,Pd+ allyl alcohol) were taken in 20 mM solution of TBAP in DMF and Complexes Pd+indole, Pd+thiamine were recorded in 20 mM of TBAP in acetonitrile.

2.3 DPPH Scavenging Activity

The assay for free radical DPPH method adopted as it is described by Tripathi et al. (2013). In brief, 30 µl of various dilutions (100-1000 µg/ml) of test of samples, 125 µl of tris-HCl buffer (0.05M, pH 7.4) and 125 µl of DPPH solution (0.004% W/V in methanol) were added. After incubation in dark for 30 min at 36 ºC the decolonsization of DPPH was recorded spectrophotometrically at 517 nm (Synergy H_4 multimode micro plate reader, Biotek instrument). Ascorbic acid was used as positive control and assay were performed in triplicate. Results were expressed as milligram of ascorbic acid equivalent per ml of extract. The percentage of inhibition of DPPH was calculated using the following equation:

% Inhibition = (1-(Abs of Sample/Abs of Control)×100

2.4 ABTS Scavenging Activity

The assay for free radical ABTS method adopted modified as it is described by Formagio et al. (2014) suitable for microplate. In brief, 30 µl of various dilutions (100-1000 µg/ml) of methanolic extracts of samples, 180 µl of ABTS (Phosphate Buffer Saline,7 mM ABTS, 2.45 Ammonium persulfate, pH 7.4) was added. After incubation in dark for 30 min at 36 ºC the decolonization of ABTS was recorded spectrophotometrically at 734 nm (Synergy H_4 multimode micro plate reader, Biotek instrument). Ascorbic acid was used as positive control and assay were performed in triplicate. Results were expressed as milligram of ascorbic acid equivalent per ml of extract. The percentage of inhibition of DPPH was calculated using the following equation:

% Inhibition= (1-(Abs of Sample/Abs of Control)×100

3. Results and Discussion

3.1 Cyclic voltammetry

Cyclic voltammetry is the most flexible electro analytical technique for the study of electro active species. The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak current (ipa), cathodic peak current (ipc), anodic peak potential (Epa) and cathodic peak potential (Epc). The cyclic voltammogram (CV) of Allyl Alcohol,Crotonaldehyde, Cinnamadehyde and complexes (Pd+cinnamaldehyde ,Pd+crotonaldehyde,Pd+ allyl alcohol) in 20 Mm TBAP(DMF), Complexes Pd+indole, Pd+thiamine

in 20 mM TBAP (acetonitrile) while Palladium chloride, adenine, guanine, cytosine, indole, thiamine and complexes (Pd+adenine, Pd+ guanine, Pd+cytosine) in 0.1 M KCl (water) in electrolyte is shown . The complexes of palladium (II) (Allyl Alcohol, Cinnamaldehyde, Crotonaldehyde, Guanine, Adenine, Thiamine, Indole) exhibits a completely irreversible reduction at $E_{1/2}$ = -528, -154.5 and -303.5, -252.5, -274.5, -210, -353 and -805 mV respectively . Palladium (II) complex of cytocine doesn't show $E_{1/2}$ value. No return wave was decimated at 300 mV/s in palladium cytosine complexes. The electrochemical data of ligand and their respective palladium(II) complexes are summarised in **Table 1** and the voltamogram of ligand and its palladium(II)complex is given in **Fig 1**.

Table 1: The Cyclic Voltameter Parameters of ligands and their palladium (II) complexes.

S.No	Metal,Ligand, Complexes	Epc (mV)	Epa (mV)	Δ Ep(mV)	$E_{1/2}$ (mV)
1	Palladium Chloride	227 -990	- 427 -903	-654 87	-100 -946.5
2	Allyl Alcohol	-390	-114	276	-252
3	Cinnamaldehyde	-787	-120	667	-453.5
4	Crotonaldehyde	-761	-119	642	-440
5	Cytosine	-418	-100	318	-259
6	Guanine	-121 34.7	-109	12	-115
7	Thiamine	-845			
8	Indole	140 -432	-104	-244	18
9	Pd+Allyl Alcohol	-921	-135	786	-528
10	Pd+Cinnamaldehyde	-150 -503	-159 -104	-9 399	-154.5 -303.5
11	Pd+Crotonaldehyde	-394	-111	283	-252.5
12	Pd+Cytosine	-106			
13	Pd+Guanine	-412	-137	275	-274.5
14	Pd+ Adenine	-219	-201	-18	-210
15	Pd+Thiamine	-602	-104	-498	-353
16	Pd+Indole	-733			

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www.ijasrm.com

ISSN 2455-6378

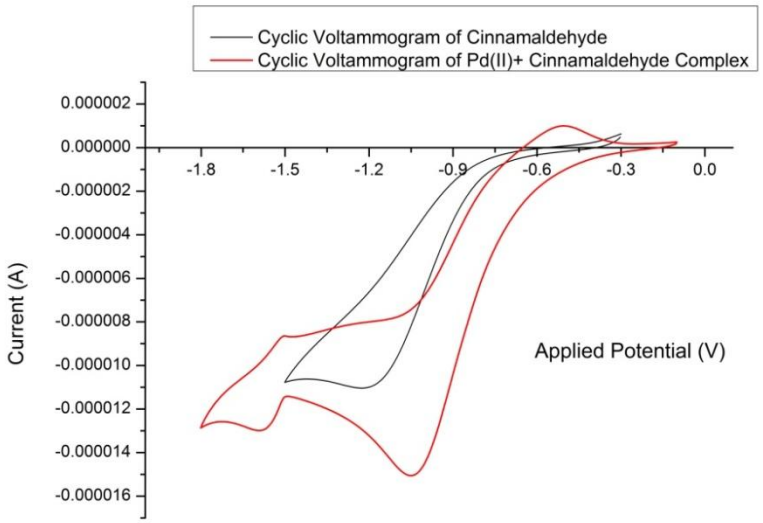

Fig1: The cyclic volttamogram of Cinnamaldehyde and palladium(II) complex

3.2 DPPH Scavenging Activity

Sharma Nitin Kumar *et al.* (2016) reported the palladium(II) complexes of methyl substituted benzylamine ligands (BLs) shows the DPPH Scavenging activity. They concluded that Pd_2MBA shows the higher scavenging activity among all the complexes. MaškoviÃ„Â *et al.* (2018) synthesized the complexwith palladium and reported that these complexes have the good ABTS and DPPH scavenging activity while comparing to Ascorbic acid. Raković Ivana R *et al.* (2018) synthesized the palladium (II) complexes different chelate ligands containing nitrogen donor atoms and studied the Antimicrobial, antioxidant and DNA-binding activity and reported that $[Pd(dach)Cl_2]$ have the 83.36±1.19 µg/ml EC_{50} value. V Asha Kumar et al. (2018) synthesised and characterized the complex using 2,4-dihydroxybenzaldehyde-4-phenyl-3-thiosemicarbazone and reported that the Pd(II) complex shown better activity than the standard Vitamin-C. The **Table 2** and **Fig 2** represents the IC_{50} values of palladium(II) complexes and and curve pattern of inhibition. The DPPH curve reveals that $PdCl_2$ have the DPPH scavenging activity on complexsation with ligands $PdCl_2$ lost its DPPH quenching activity.

Table 2 IC_{50} values of complexes for DPPH

S.N.	Complex	IC_{50} in µg/ml
1	Pd+Allyal Alcohol	ND
2	Pd+Corotonaldehyde	ND
3	Pd+Cinnamaldehyde	ND
4	Pd+Indole	ND
5	Pd+Thymine	ND
6	Pd+Cytosine	ND
7	Pd+Adnine	ND
8	Pd+Gauanine	ND
9	$PdCl_2$	634.84

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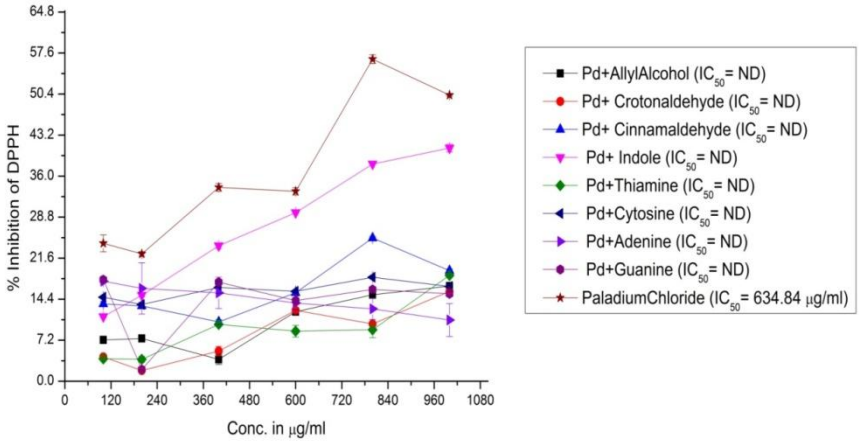

Fig 2 DPPH Scavenging Activity of Palladium Chloride and Complexes

3.2 ABTS Scavenging Activity

Jelena M Mašković *et al.* (2018) reported the DPPH and ABTS scavenging activity of palladium(II) complexes. Elangovan Sindhuja et al. (2014) reported the interaction of palladium (II) with DNA/protein, toxicity ABTS scavenging activity. Icsel C et al. (2015) prepared palladium(II) and platinum(II) complexes with 5,5-diethylbarbiturate (barb), 2-phenylpyridine (Hppy), 2,2'-bipyridine (bpy) and 2,2'-dipyridylamine (dpya) and reported that the palladium(II) complex of thiocarboxamide have the lowest IC50 value.

The **Table 3** and **Fig 3** represents the values of IC_{50} and curve pattern of inhibition. In our study we have found that the Palladium(II) complexe of indole have the highest ABTS scavenging activity i.e. 145.20 µg/ml.

Table 3: IC_{50} value of complexes for ABTS

S.N.	Complex	IC_{50} in µg/ml
1	Pd+Allayal Alcohol	303.06
2	Pd+Corotonaldehyde	302.47
3	Pd+Cinnamaldehyde	ND
4	Pd+Indole	145.20
5	Pd+Thymine	ND
6	Pd+Cytosine	ND
7	Pd+Adnine	ND
8	Pd+Guanine	ND
9	$PdCl_2$	ND

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ISSN 2455-6378

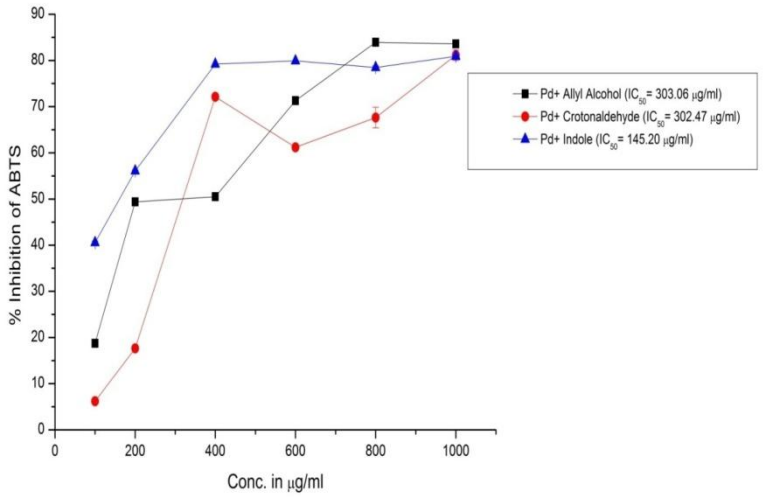

Fig 3: ABTS Scavenging Activity of Palladium Complexes

4. Conclusion

The data obtained from cyclic voltammeter its appears all the Palladium(II) complexes of Allayal Alcohol, Corotonaldehyde, Cinnamaldehyde, Indole, Thymine, Cytosine, Adnine and Guanine are irreversible waves. The ligands and their palladium (II) interact with DPPH and ABTS to inhibit its free radicals. $PdCl_2$ and Pd+Indole are most promising agents for inhibiting DPPH and ABTS free radicals respectively.

References

[1] McCord JM, The evolution of free radicals and oxidative stress. Am J Med 108, 652-659 (2000).

[2] Harman D, Aging: a theory based on free radical and radiation chemistry. J Gerontol, 11, 298-300 (1956).

[3] Halliwell B, Free radicals, proteins and DNA: oxidative damage versus redox regulation. Biochem Soc Trans, 24, 1023-1027(1996).

[4] Halliwell B, How to characterize a biological antioxidant. Free Radic Res Commun, 9, 1-32 (1990) .

[5] Mahendra Kumar Mishra, Ruchita Tripathi, Pandeya K B, Tripathi I P, α-Amylase Inhibition And Electrochemical Behavior Of Some Oxovanadium (Iv) Complexes Of L-Amino Acids, Asian J Pharm Clin Res, 11, 218-224 (2018).

[6] Pandeya K B, Tripathi I P, Mishra Mahendra Kumar and Jaiswal N. Antiradical and Antioxidant properties of some oxovanadium(IV) complexes of l-amino acids. Journal of Biological Sciences and Medicine. 2, 38-47 (2016).

[7] Rau T, Eldik R van in: Sigel H, Sigel A (Eds.), Metal Ions in Biological Systems, Dekker M, New York, 1996, pp. 339–378.

[8] Graham R D, Williams D R, The Synthesis And Screening For Anti-Bacterial, Cancer, Fungicidal And Viral Activities Of Some Complexes Of Palladium And Nickel. J. Inorg. Nucl. Chem. 41, 1245–1249 (1979).

[9] Filipović N R, Bacchi A, Lazić M, Pelizzi G, Radulović S, Sladić D M, Todorović T R, Anđelković K K. Synthesis, structure and cytotoxic activity evaluation of a dinuclear complex of Cd(II) with N',N'2 -bis[(1E)-1-(2-pyridyl)ethylidene]propanedihydrazide. Inorg. Chem. Commun. 11, 47–50 (2008).

[10] Garoufis A, Hadjikakou S K, Hadjiliadis N, Palladium coordination compounds as antiviral, antifungal, antimicrobial and antitumor agents. Coord. Chem. Rev. 253: 1384–1397 (2009).

[11] Lippard Stephen J, Timothy Johnstone C Reinterpretation of the Vibrational

Spectroscopy of the Medicinal Bioinorganic Synthon C,c,t-[Pt(NH[subscript3]) [subscript 2] Cl [subscript 2] (OH) [subscript 2]]. Journal of Biological Inorganic Chemistry. 19, 667–674 (2014).

[12] Tripathi I P, Mishra Mahendra Kumar, Mishra Chinmayi, Tripathi Ruchita, Kamal Arti, Tripathi Pranav, Shukla Ved Prakash, Gangele Richa and Pandeya K B Assessment of Antioxidant and Total Polyphenolic Content of Some Plants of Euphorbiaceae Family. Indian Journal Of Applied Research. 3, 1-4 (2013).

[13] Formagio A S N, Robeerta C, Volobuff F, Evaluation of antioxidant activity, total Flavonoids, tannins and phenolic compounds in Psychotria leaf extracts. Antioxidants. 3, 745-757 (2014).