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Evaluation of Electrochemical and Biological Characteristics of Schiff Base *N*,*N*'-Benzene-1,2-Diylbis[1-(Pyrazin-2-yl)Methanimine] Complex of Palladium(II)

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ABSTRACT

A palladium(II) complex of Schiff base *N*,*N*'-benzene-1,2-diylbis[1-(pyrazin-2-yl)methanimine] was synthesized and used for the selective determination of fluoride ion in various water, fruit juice and toothpaste samples. The selectivity calculated by mixed potential method indicates the high selectivity of the complex towards fluoride ion over other tested anions. The electrode based on DBP as plasticizer has a liner concentration range of 1.6 x 10^{-7} M – 1.0x 10^{-2} M with lower detection limit of 5.2 x 10^{-7} M and has fast response time of about 10 s.

1. Introduction

Palladium is one of the most versatile metals in the modern organic synthesis. Palladium complexes are particularly useful as a catalyst for various organic syntheses of natural products, polymers and pharmaceuticals. It has been reported that palladium complexes exhibit remarkable selectivities and have been successfully used as ionophore in membrane sensors for selective determination of particular anions and gases [1-3].

Fluoride is one of the most toxic substances to humans when ingested in the large amount. The high conception of fluoride may cause nutritional deficiencies, kidney disease and diabetes. Drinking water is the main source of fluoride content; it is also available in many types of toothpaste, mouthwashes and fruits juices used daily at home. Thus the determination of fluoride ion is a subject of concern particularly in pharmaceutical and food industry [4-6].

In the present study a new palladium complex of Schiff base have been synthesized and used for the selective determination of fluoride ion in various samples. The selectivity coefficient calculated by match potential method indicates the high selectivity of the electrode towards fluoride ion over other tested anions.

2. Experimental Methods

2.1 Reagents and Instruments Used

The chemicals pyrazine-2-carbaldehyde, benzene-1,2-diamine, oleic acid (OA), Dibutylphthalate (DBP), 1-chloro naphthalene (CN) and sodium tetraphenyl borate (NaTPB) were purchased from Sigma-Aldrich. The high molecular weight Polyvinyl chloride (PVC), acetone, absolute ethanol, and metal salts were bought from Fluka. All reagents were used without further purification. Double distilled water was used for preparing all aqueous solution.

The FTIR spectra of the ligand and complex were recorded on Labtronics FTIR spectrometer in the range of 4000 – 350 cm^{-1}. The ^{1}HNMR and^{13}CNMR spectra were recorded in $CDCl_3$ on a Bruker Avance 300 MHz spectrometer. The pH and potential measurements were recorded with a digital pH meter and potentiometer (Equiptronics EQ-602).

2.2 Synthesis of N,N'-Benzene-1,2-Diylbis[1-(Pyrazin-2-yl)Methanimine] (L)

The Schiff base ligand, N,N'-benzene-1,2-diylbis[1-(pyrazin-2-yl)methanimine] was synthesized by stirring pyrazine-2-carbaldehyde (1 mmol in 5 mL absolute ethanol) and benzene-1,2-diamine (1 mmol in 5 mL absolute ethanol) in reflux for 70 min under nitrogen atmosphere, resulting in a pale yellow solution of ligand. The solution was allowed to evaporate in vacuum till the micro crystals of the ligand form (Scheme 1). The micro crystals were washed with ethanol and then recrystallized from ethanol-/chloroform (2:1, v/v). The analytical and physical data of the ligand are given below.
Empirical formula: $C_{16}H_{12}N_6$, formula weight: 288.306 $gmol^{-1}$, yield: 76%.
^{1}H NMR (ppm): 8.52 (s, 2H, pyridinic), 8.28 (s, 2H, iminic), 7.67 (d, 4H, pyridinic), 7.39-7.21 (d, 2H, aromatic), 6.85 (t, 2H, aromatic).
^{13}C NMR (ppm): (16 C aromatic); 176.4, 173.4, 173.23, 172.46, 164.43, 161.16, 159.36, 149.32, 136.24, 134.76, 133.46, 123.75, 121.92, 119.37, 109.92, 109.45.

2.3 Synthesis of Complex

The palladium(II) complex of ligand *N*,*N*'-benzene-1,2-diylbis[1-(pyrazin-2-yl)methanimine] was synthesized by the method available in the literature [7]. A solution of Palladium chloride (3 mmol in acetone) was added drop wise into the flask containing solution of Schiff base ligand (3 mmole in 10 mL acetone). The mixture was stirred for 20 min and refluxed (85 °C) under nitrogen atmosphere after which the solid product had formed. The product was then separated by vacuum filtration, washed with cold acetone solution and dried in a vacuum desiccator at room temperature.

The FTIR analysis of the free ligand and its complex with Pd(II) shows significant changes in IR stretching frequencies. The change of C=N stretching frequencies from 1633 – 1640 cm^{-1} in the free ligands to lower values of 1603 - 1608 cm^{-1} in the Pd(II) complexe of the ligand indicating the co-ordination of azomethine nitrogens to the palladium metal ion. The C=N stretching frequencies of pyrazine decreases from 1456 – 1462 cm^{-1} to 1424 – 1440 cm^{-1} due to the coordination of lone pair of nitrogen with Pd(II) ion. A broad band at 1424 – 1440 cm^{-1} indicates the C=N stretching of un-coordinated pyrazine nitrogen.
Schiff base free ligand: 1633 – 1640 (C = N), 1424 – 1440 (C = N), 1542, 1454 (C = C ar.) cm^{-1}.
Schiff base Complex: 1603 - 1608 (C = N), 1456 - 1462 (C = N), 1532, 1472 (C = C ar.) cm^{-1}.

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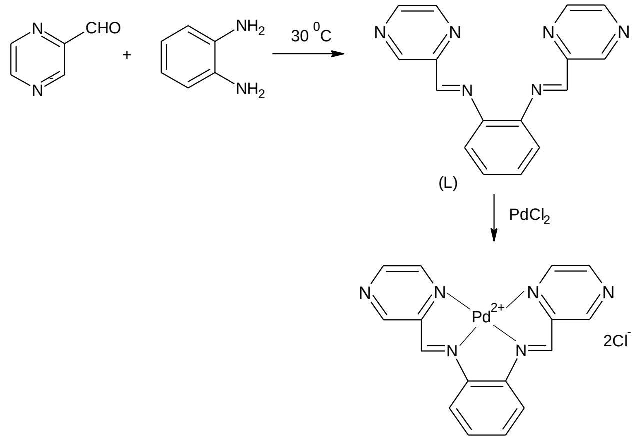
The magnetic moment study shows that the Pd(II) complex with the Schiff base ligand is diamagnetic which is consistence with the square planer stereochemistry of the complex.



Scheme 1 Synthesis of ionophore

2.4 Calculation of Formation Constant

The formation constant (K_f) of complexation kinetics dictates the stability of complex, since the stability of complex increases with increasing the K_f. To investigate the stability of complexes of newly synthesized Schiff base with different metal ions the formation constants were calculated by molar conductance ratio using equation 1 and 2. All the measurements were studded at constant ionic strength of solution [8].

$$K_f = \frac{[ML^+]}{[M^+][L]} \times \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \qquad (1)$$

where

$$[L] = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})} \qquad (2)$$

Here, Λ_M, Λ_{ML}, and Λ_{obs} are the molar conductance of the cation before addition of ligand, complex and solution during titration, C_L and C_M are the analytical concentration of the ionophore added, and the analytical concentration of the cation respectively. The solutions of various metal ions were prepared by dilution the standard solution. The complex formation constants, K_f, and the molar conductance of complex, Λ_{obs}, were obtained by using a nonlinear least squares program KINFIT [9], and the results are summarized in Table 1.

Table 1 Formation complex values of complexation reaction of ligand and metal ions

Metal ions	Formation constants ($\log K_f$)	Metal ions	Formation constants ($\log K_f$)
Pd(II)	4.12 ± 0.10	Cd(II)	3.08 ± 0.10
Pt(II)	3.64 ± 0.12	Ag(I)	2.74 ± 0.11
Ni(II)	3.42 ± 0.10	Au(I)	2.62 ± 0.14
Co(II)	3.14 ± 0.11	Ca(II)	2.53 ± 0.15
Zn(II)	3.11 ± 0.13	Na(I)	0.15

2.5 Preparation of Polymeric Membrane Electrode

The Pd(II) complex of *N,N'*-benzene-1,2-diylbis[1-(pyrazin-2-yl)methanimine] was used as electroactive material for the selective determination of fluoride ion in various samples by PVC based ion selective electrode. To prepare membrane electrode the components i.e. high molecular weight PVC, plasticizer, anionic additive and Ionophore (Schiff base complex) were dissolved in 20 mL THF and shaken to remove the air. The solution so obtained was transfer into a glass ring of ~20 mm diameter. The THF was allowed to evaporate for about 24 hrs. The membrane of about ~0.3 mm of thickness and 5 mm of diameter were removed from glass plate and fixed at one end of a glass tube [10]. A saturated silver electrode than inserted in the tube to make electrical contact, another standard silver electrode was used as external reference electrode. The potential measurements were calculated by following cell assembly.

External Saturated Silver Electrode	Internal Solution (0.01M)	Fluoride selective membrane	Test solution	Internal Saturated Silver Electrode

3. Results and Discussion

The tetradentate Schiff base ligand *N,N'*-benzene-1,2-diylbis[1-(pyrazin-2-yl)methanimine] was synthesized for the complexation reaction of Pd(II) ion. The Pd(II) complex of the ligand was characterized by FTIR, and ^1H and ^{13}C NMR and conductivity measurements. The complex is soluble in methanol, ethanol, acetonitrile, acetone, dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) at room temperature.

The PVC based membrane of the complex shows a good selectivity towards fluoride ion. The membrane electrode with composition of PVC: plasticizer (OA, CN, and DBP): additive: ionophore in the ratio of 33%: 64%: 1%: 2% (w/w) was found to be best over other tested membrane electrodes (Table 1).

Table 1 optimization of membrane components

Electrode No.	Membrane Composition (%)				Linear working range (M)[a]	Slope (mV/dec. of activity)[a]	Response Time (sec)
	PVC	Additive	Plasticizer	Ionophore			
1	33	1, NaTPB	64, DBP	2	1.6×10^{-7}- 1×10^{-2}	-29.60 ± 1	5
2	32	1, NaTPB	65, DBP	2	1.6×10^{-7}- 1×10^{-2}	-29.80 ± 1	5
3	34	1, NaTPB	63, DBP	2	1.8×10^{-7}- 1×10^{-2}	-29.40 ± 1	6
4	33	1, NaTPB	64, OA	2	4.2×10^{-6}- 1×10^{-2}	-24.60 ± 1	14
5	33	1, NaTPB	64, CN	2	5.0×10^{-6}- 1×10^{-2}	-24.70 ± 1	16

The polarity of the plasticizer plays a significant role in the complexation kinetics of metal ion with ligand because they provide the suitable medium for the complexation reaction. Due to this reason membranes of varying composition were prepared and their response characters were investigated. The data presented in table 1 indicates that the membranes based on DBP as plasticizer (electrode no. 1, 2 and 3) have lower detection limit of 5.2×10^{-7} M in the linear concentration range of 1.6×10^{-7} M – 1.0×10^{-2} M, with slope of calibration curve -29.60 ± 1 (mV/decay). The data also indicates that 64% DBP as plasticizer has the best possible response.

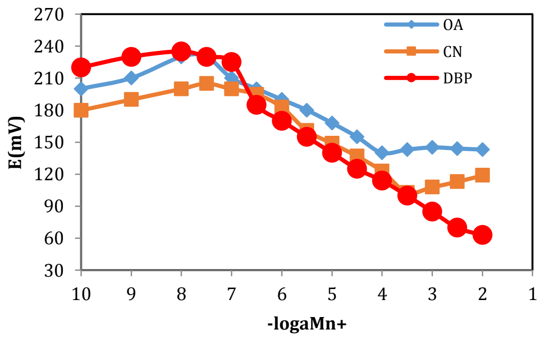


Fig. 1 Calibration curve of fluoride selective electrode with different plasticizers

Thus electrode no. 1 is considered as most optimized electrode and was used for further studies. The potentiometric response of electrodes of different plasticizers is shown in Fig. 1. The additive NaTPB was used to diminish the ohmic resistance. The high amount of additive (>1%) significantly decreases the linear working range and detection limit due to competition kinetics between ionophore and additive.

The potential response of ion-selective electrode is significantly depends on the pH of test solution. In the present study the effect of pH on response mechanism of electrode no. 1 was investigated in the range of 1.0 – 8.0. It was observed that the potential of the electrode remains almost constant within the pH range of 2.8 – 6.3. However significant potential drift was observed beyond this pH which may be due to completion kinetic of H^+ ion and ionophore at lower pH and precipitation of ionophore at higher pH.

The response time of the electrode no. 1 was investigated by change in potential with time. It was observed that the electrode reached a static potential within the variation of ±1 mV in a very short time of about 10 s. To investigate the reversibility and reproducibility the response time was calculated by changing the concentration of test solution from lower to higher and that higher to lower for whole concentration range. The average response time for the sequences remains almost same.

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Table 2 Life time of electrode no. 1

Time (weeks)	Detection limit (M)	Slope (mV/decay)
1	5.2×10^{-7}	-29.60 ± 1
2	5.2×10^{-7}	-29.60 ± 1
3	5.4×10^{-7}	-29.20 ± 1
4	5.6×10^{-7}	-29.00 ± 1
5	1.0×10^{-5}	-25.60 ± 1
6	8.8×10^{-6}	-21.60 ± 1

The life time of the electrode no. 1 was calculated as a function of lower detection limit. It was observed that the lower detection limit and slope of calibration curve remains almost same for a period of 4 weeks. Thus the electrode no. 1 could be used for a period of 4 weeks without any change in response characters however after 4 weeks considerable variation in the working range and detection limit was observed. This is probably due to the leaching of membrane components to the solution with the time. After 6 weeks the response of the membrane becomes non-linear (Table 2).

The ionophore of the ion-selective electrode may shows the response to various anions in the solution therefore the selectivity of the ionophore towards a particular ion is a subject of great importance for the analytical utility of the ion-selective electrodes. In the present study the selectivity of electrode no. 1 over other anion was investigated by match potential method (MPM). The potential of the electrode was measured with a fixed activity of fluoride ion. In another experiment, an interfering ion (A^-) is successively added to an identical reference solution (containing fluoride), until the measured potential matches the one obtained with the primary ions. The selectivity coefficient, K^{MPM}, is then calculated by the resulting fluoride ion to the interfering ion activity ratio, $K^{MPM} = a_{F^-}/a_{A^-}$. The selectivity coefficients for various anions are summarized in Table 3 [11 - 14].

Table 3 Selectivity coefficients of various interfering ions (A^-)

Interfering ion B	Selectivity coefficient ($K^{MPM}_{Ho,B}$)
Cl^-	1.2×10^{-4}
Br^-	1.4×10^{-4}
I^-	1.8×10^{-4}
S^{2-}	1.1×10^{-4}
CO_3^{2-}	1.3×10^{-4}
SCN^-	1.1×10^{-4}
CH_3COO^-	1.5×10^{-4}

3.1 Analytical Application

The electrode no. 1 was used for the selective determination of fluoride ion in drinking water and fruit juice samples. The test solution of samples was prepared by dilution of the sample solution with an ionic buffer solution. The ionic buffer solution was prepared by sodium chloride (1 mol) glacial acetic acid (60 mL) 1,2-cyclohexanediamineN,N,N',N'-tetraacetic acid (1 mmol) and 5 mole of NaOH in 1 L of water. All the measurements were conducted at constant pH of 5.3 (Table 4).

Table 4 Fluoride ion concentration in water and fruit juice samples

Water samples	Mean concentration (mg/L)	Fruit juice	Mean concentration (mg/L)
Tap water	0.07 ± 0.005	Orange	0.42 ± 0.10
River water	0.12 ± 0.10	Apricot	0.39 ± 0.12
Industrial waste water	0.32 ± 0.12	Peach	0.08 ± 0.005

The electrode no. 1 was also applied for the determination of fluoride ion in various toothpaste samples. The test sample was prepared by adding 0.5 g of the toothpaste sample in 20 mL of ionic buffer; the mixture was boiled for 3 min. The solution was diluted to 50 mL with double distilled water. The determinations of fluoride for each sample were repeated in triplicate analyses (Table 5).

Table 5 Fluoride ion concentration in various toothpaste samples

Toothpaste sample	Mean concentration (μg/g)
Dauber red	1245 ± 35
Glister	1347 ± 29
Colgate	1329 ± 38

4. Conclusion

A palladium(II) complex of Schiff base ligand *N,N'*-benzene-1,2-diylbis[1-(pyrazin-2-yl)methanimine] was synthesized and used for the selective determination of fluoride in various water samples, fruit juice and toothpaste samples. The electrode with the composition of PVC: DBP: NaTPB: ionophore in the ratio of 33%: 64%: 1%: 2% (w/w) has a wide concentration range of 1.6×10^{-7} M – 1.0×10^{-2} M with lower detection limit of 5.2×10^{-7} M. The electrode no. 1 could be uses in a pH range of 2.8 – 6.3 for a period of 4 weeks without any divergence in response characters.

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