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2, 4-Dihydroxy-5-Bromo-α-Phenylacetophenone thiosemicarbazone (DHB-α-PAT) as Analytical Reagent: Studies on Pd(II) Chelate

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ABSTRACT

Pd(II) was determined spectrophotometrically after complexing with 2, 4 Dihydroxy-5-bromo-α-phenyl acetophenone thiosemicarbazone(DHB-α-PAT) at room temperature at pH 2.0 in 50%(V/V) aqueous ethanol at 430nm. Beer's law was obeyed upto 17.02 ppm of Pd(II). Molar absorptivity and Sandell's sensitivity were found to be 3.869×10^3 *lit* mol^{-1} cm^{-1} *and 0.02750 µg/*cm^2 *respectively. Composition of chelate was determined using Job's method of continuous variation and Yoe and Jones mole ratio method which was found to be 1:2 (M:L). The stability constant determined spectrophotometrically was found to be* 1.36×10^9*. Gibb's free energy change for complex formation reaction was also calculated and found to be -12.536 k cal/mol. From TGA, the energy of activation was calculated using Broido method and found to be 14.23 k cal/mol for decomposition. Study of Antibacterial activity of reagent and Pd(II)-DHB-α-PAT complex were also done using Broth Dilution Method. The reagent has been satisfactorily applied for the determination of Palladium in palladiased carbon sample.*

Keywords: Spectroscopic determination, phenyl acetophenone thiosemicarbazone, DHB-α-PAT.

INTRODUCTION

The thiosemicarbazone of aldehydes and ketones in which the carbonyl groups are found to be better chelating agents and they have been exploited to the maximum extent by many workers[1-6]. Many organic reagents like o-hydroxy oximes, oximes, thiosemicarbazones, chalcone oxime, anilides, various heterocyclic compounds have been used for gravimetric and spectrophotometric reagent for Pd(II). Spectrophotometric methods have been used to confirm the stoichiometry of the complex and to determine the stability constant of the complex. The stoichiometry was also confirmed by thermo gravimetric analysis. Here we have synthesized a reagent [DHB-α-PAT] for spectroscopic determination of Pd(II).

MATERIALS AND METHODS

Reagents and solutions: 2, 4-dihydroxy-α-phenylacetophenone was prepared from resorcinol, phenyl acetic acid and anhydrous zinc chloride according to the method of H. Nogemi[7]. The bromination of 2, 4-dihydroxy-α-phenyl acetophenone using Br_2 in glacial acetic acid gives 2, 4-dihydroxy-5-bromo-α-phenylacetophenone.The reagent was prepared by the reaction of 2, 4-dihydroxy-5-bromo-α-phenyl acetophenone with alcoholic solution of thiosemicarbazide[8]. It was crystallized from absolute alcohol. (m. p. 95 ºc)

Pd(II)-metal solution: A stock solution of Pd(II) (0.01M) was prepared by dissolving an accurately weighed amount of palladium chloride using little concentrated hydrochloric acid in deionized water. Solution of other diverse ions were prepared by dissolving their salts (A.R.Grade) in deionized water.

RESULTS AND DISCUSSION

Characterization of reagent

Elemental analysis: Elemental analysis of the reagent was done using "Carlo-Erba Elemental Analyzer Model 1106". The percentage elements, found are in agreement with its molecular formula. The results are given in the following table 1.

Table 1: Elemental analysis of Reagent

Reagent	**%Carbon [Calc.]**	**%Hydrogen [Calc.]**	**%Nitrogen [Calc.]**	**%Sulphur [Calc.]**
DHB-α-PAT	47.32% [47.38%]	3.66% [3.71%]	10.96% [11.05%]	8.37% [8.43%]

UV-Visible spectral studies: The UV-Visible spectrum of reagent in ethanol was recorded on Shimadzu UV–1700 Perkin-Elmer Lambada-35 UV-Visible spectrophotometer. Wavelength of maximum absorption was found to be 280 nm that falls in UV region.

FT-IR Spectral studies: FTIR spectrum of the reagent was recorded on a Simadzu 8400-S spectro photo meter in KBr pallet. The bands which are observed are given in table 2.

Table 2: IR Spectra

Reagent	$\nu^{(O-H)}$ **Phenolic**	$\nu^{(C-H)}$ **aliphatic**	$\nu^{(C-H)}$ **aromatic**	$\nu^{(C=N)}$	$\nu^{(C=S)}$	$\nu^{(-N-N)}$	$\nu^{(-C-Br)}$
DHB-α-PAT	3394 cm^{-1}	2908 cm^{-1}	3061 cm^{-1}	1618cm^{-1}	1298cm^{-1}	1143cm^{-1}	541 cm^{-1}

^{1}H-NMR Spectral studies: The NMR spectrum of the reagent was taken in DMSO. The NMR spectrum was recorded on Brucker Avance-II 400 NMR spectrophotometer using TMS as reference. Assignment of signals to different protons is given in table 3.

Table 3. NMR Spectra

Reagent	-CH$_2$ (singlet)	-NH$_2$ (singlet)	Aromatic Proton (multiplet)	-CSNH (singlet)	Phenolic -OH (singlet)
DHB-α-PAT	**δ= 3.48**	**δ= 4.25**	**δ= 6.5-8.0**	**δ= 11.13**	**δ=12.62**

Spectrophotometric study of Pd(II)- DHB-α-PAT: 5 mg of chelate was dissolved in 25mL of 50%(v/v) ethanol and absorption of the solution was measured between 340nm-800nm.Spectra of complex shows shoulder band at 430 nm, and this wave length was selected for further spectrophotometric work. pH study of chelate from pH=1.0-4.0 was done using buffer and maximum absorbance was observed at pH=2.0.So, pH=2.0 was selected for further spectrophotometer work. Different aliquots of Pd(II) solution were taken and buffer solution was added to maintain the pH 2.0. The excess reagent was added for complete complex formation. These solutions were diluted to 25ml with aqueous ethanol so as to keep 50% concentration of aqueous ethanol in final diluted solution. The absorbance was measured at 430nm and plotted against the concentration of Pd(II). It was found that Beer's law was obeyed up to 17.02 ppm of Pd(II). Molar absorptivity and Sandell's sensitivity(14) were calculated form graph and it was found to be 3.869 x 10^3 lit mol^{-1} cm^{-1} and 0.02750 µg/cm^2 respectively. Job's method of continuous variation(15) and Yoe and Jones mole ratio method(16) were used to determine the stoichiometry of the complex. It was found to be 1:2[M:L]. This is in agreement with stoichiometry determined from thermogravimetric analysis. The stability constant was calculated using the formula,

$$K = \frac{1-\propto}{4 \propto^3 C^2} \ , where \ \propto = \frac{Em - Es}{Em}$$

where, α = degree of dissociation, Em = maximum absorbance found from graph. Es = absorbance at the stoichiometric molar ratio of the metal to reagent in complex. C = concentration of complex.
The average stability constant from the above two methods was found to be 1.36 x 10^9 and ΔG° for complex formation reaction at 27°C was found to be -12.536 k cal mol^{-1}.

Effect of diverse ion: Interference due to associated ions was examined in the determination of 17.02 ppm of Pd(II) at pH-2.0 using the reagent DHB-α-PAT. The tolerance limit was taken as the amount of foreign ion required to cause ± 2% error in the absorbance. Many anions like F^-, Cl^-, Br^-, NO_3^-, and SO_4^{-2} do not interfere even they are 100-fold excess in the determination of palladium at pH-2.0. Sr(II), Ca(II), Mg(II), Cd(II), Na(I), K(I), Ba(II) and Zr(IV), do not interfere when they present up to 10-fold excess.

Thermogravimetric analysis: From TG analysis of the Pd(II) chelate, it was found that there is no weight loss up to 200°C indicating that the chelate can be dried safely without decomposition at 110°C. Loss in weight from 200°C to 830°C is due to removal of organic ligand molecules. Observed loss and weight of metal residue agrees well with the formula of the chelate in which M:L ratio is 1:2. Activation energy Ea was calculated using Broido method and found to be 14.23 k cal mol^{-1} for the single step decomposition.

IR Spectra: Interpretation of IR spectra of the chelate shows that weak band around 3394 cm^{-1} in comparison of ligand molecule , which shows that during chelate formation, the hydrogen of 2- hydroxy group is lost and oxygen forms covalent bond with metal whereas 4- hydroxy group does not take part in complex formation . The bands of aliphatic C-H stretching and aromatic C-H stretching are observed at nearly same positions in reagent as well as in palladium complex. The band due to C=N stretching which is observed at 1618 cm^{-1}in ligand is shifted to around 1593 cm^{-1} in complex. This may be due to coordination of palladium metal through nitrogen. -C=S stretching, -C-Br stretching and -N-N stretching are observed at 1298cm^{-1}, 541cm^{-1} , and 1143cm^{-1} respectively. Thus, in the chelates, metal is covalently bonded with oxygen and coordinately bonded with nitrogen.

Table 4. Reported percentage of Pd(II) in palladiased carbon sample = 5.01%

Absorbance	ppm Pd(II)taken	ppm Pd(II)found	% of Pd(II)obtained	%Error
0.182	**5.025**	**5.00**	**4.99**	**-0.40%**
0.544	**15.075**	**14.95**	**4.97**	**-0.80%**

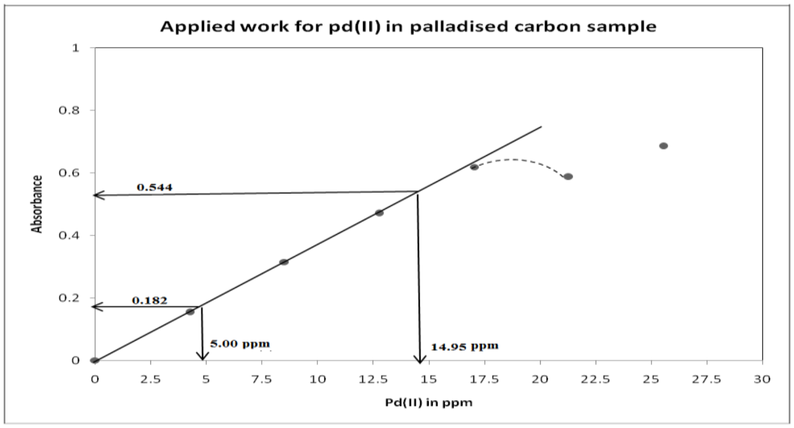

Fig 1. Beer's law plot

Antibacterial activity of reagent and chelate: Thiosemicarbazones being chelating agent's shows good antibacterial activity [9-11] by hinder the growth of bacteria by chelating the metal ions which are present in trace in biological fluids. The antibacterial properties of the reagent and Pd(II) complex were studied by using "Broth Dilution Method" [12, 13] to evaluate the antibacterial activity.

From results we can conclude that, DHB-α-PAT reagent shows poor activity against E.coli (Gram-ve) bacteria while shows same activity for S.Aureus (Gram+ve) bacteria like "Ampicilline Drug ". Similarly, Pd(II)-DHB-α-PAT chelate shows poor activity against E.coli (Gram -ve) bacteria than S. aureus (Gram+ve) bacteria which is more than "Ampicilline Drug".The results are given in tables 5 and 6.

Table 5 . Antibacterial activity

STANDARD DRUGS	E.Colli [gram –ve] [microgram /ml]	S.Aures [gram +ve] [microgram /ml]
GENTAMYCINE	0.05	0.25
AMPICILINE	100	250
CHLORAMPHENICOL	50	50
CIPROFLOXACIN	25	50
NORFLOXACIN	10	10

Table 6

SAMPLE	E.Colli [gram –ve] [microgram /ml]	S.Aures [gram +ve] [microgram /ml]
DHB-α-PAT	200	250
Pd(II)- DHB-α-PAT	200	125

APPLICATION

Spectrophotometric determination of Palladium in palladiased carbon: The sample of palladiased carbon which was contained 0.5025gm of palladium was dissolved in concentrated nitric acid by heating on a sand bath. It was heated till little amount of acid was left. Similar treatment was given 2-3 times. The solution was heated on a sand bath to remove excess of acid and the solution was diluted to 1000 ml with doubly distilled water in a volumetric flask. From this 1000 ml solution, 25.0 mL solution was taken and again diluted with doubly distilled water to 100 ml stock solution (1ml =125.625µg). The stock solution was used after standardization with standard method[17] . An aliquot of the above diluted solution 1.0 ml and 3.0 ml was pipette out in a 50 mL beaker. To this solution excess of reagent DHB-α-PAT was added and the pH was adjusted to 2.0 with buffer. The solution was diluted to the 25mL mark with aqueous ethanol as to keep 50% concentration of ethanol in final diluted soln. Absorbance was measured at 430 nm using ligand blank. The results obtained are given in table 4 and the graph is given in fig.1.

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