Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2018, 7 (2): 443-448

(International Peer Reviewed Journal)

Analytical Application of 3-hydroxy-3-propyl-1-(4-carbamimidoylsulfamoyl)phenyltriazene (CSPT) in the Spectrophotometric Determination of Palladium(II)

Pushplata Salvi, Poonam Sharma, Jaishri Chopra, Meena K. Rathore, Rekha Dashora and Ajay K. Goswami*

Coordination Chemistry Lab, Department of Chemistry, M. L. Sukhadia University, Udaipur (Raj.)-313001, INDIA

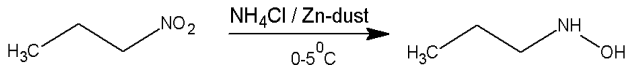
E mail: pushplataudr@gmail.com, akumargoswami56@gmail.com

Accepted on 11th February, 2018

ABSTRACT

The spectrophotometric behavior of complex of Pd(II) with 3-hydroxy-3-propyl-1-(4-carbamimidoylsulfamoyl)phenyltriazenehas been studies in ppm level. The reagent forms light violet coloured complex with Pd(II) in alcoholic medium at pH range 1.8-2.2. The mean value of molar absorbtivity and sandell's sensitivity was calculated and was found to be 8372 L mol^{-1} and 12.71 mg cm^{-1}for the complex. It was observed that 3-hydroxy-3-propyl-1-(4-carbamimidoylsulfamoyl) phenyltriazene forms 1:2 complex with Pd(II).

Graphical Abstract



1 2

Reduction of Nitro Compound

Keywords: 3-hydroxy-3-propyl-1-(4-carbamimidoylsulfamoyl)phenyltriazene, Spectrophotometric determination of Pd(II), PASS, CADD.

INTRODUCTION

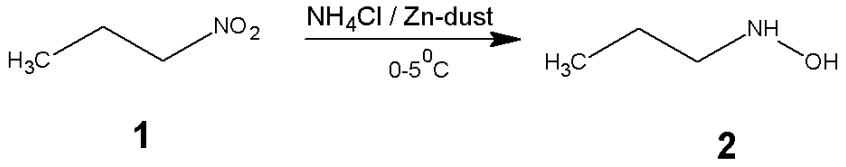
Hydroxytriazene possess the functional group [-N(OH)-N=N-]. The complexing ability [1-2] of this class of compounds have been explored exhaustively in our laboratory during last many years. Their application as analytical reagents [3-6] is quite established as shown by various reviews. Hydroxytriazenes and their metal complexes have been found to possess a number of biological activities like anti-inflammatory [7], antimicrobial [8], analgesic [9], antifungal [10], antibacterial [10], wound healing [11], insecticidal [12]. In the present paper 3-hydroxy-3-propyl-1-(4-carbamimidoylsulfamoyl)phenyltriazene has been synthesized using standard method, duly

characterized by elemental analysis(CHN), melting point determination, IR and ^{1}HNMR. Biological activity of 3-hydroxy-3-propyl-1-(4-carbamimidoylsulfamoyl)phenyltriazene has been screened using computer aided program PASS. PASS (Prediction of Activity Spectra for Substances) [13-14] is a very simple tool for prediction of probable activity theoretically on the basis of molecular structure which would pave a way to CADD.

MATERIALS AND METHODS

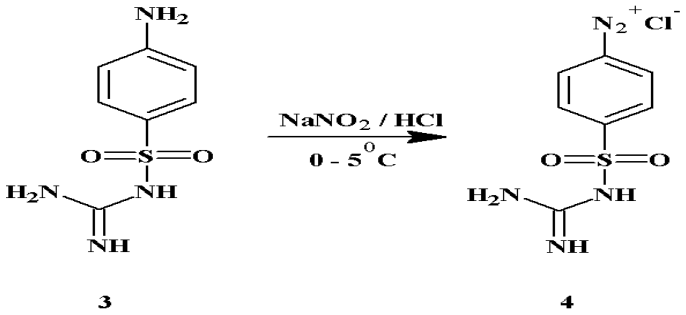
Reagents were synthesized as per standard method using AR grade chemicals. The synthesis is completed in three steps.

Step-1: Preparation of hydroxylamine: In the preparation of hydroxylamine, 0.1 mole of nitropropane, 0.1 mole of NH_4Cl and 75 (50 mL water+25 mL spirit) mL solvent were mixed and stirred mechanically at 0-5^{o}C and then 20 gm of Zn dust was added in the small lots to maintain temperature of the reaction between 0-5^{o}C. After one hour the reaction mixture was filtered and the solution obtained was kept in refrigerator at about 0^{o}C which was further used for coupling.



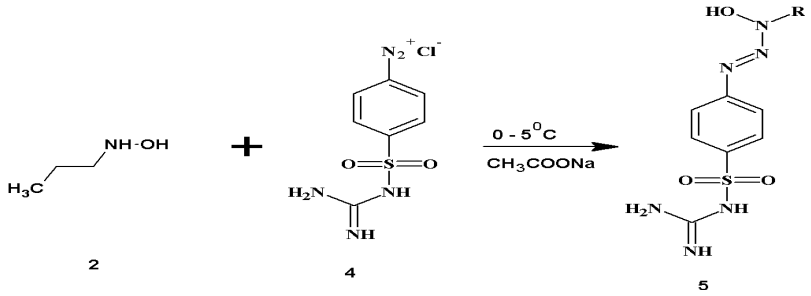
Scheme 1. Reduction of Nitro Compound

Step-2: Preparation of diazonium salts: 4-Amino-N-(aminoiminomethyl)benzenesulfonamide (0.1 mole) was dissolved in mixture containing 25 mL of HCl and 25 mL of water. In other beaker 0.1 moles sodium nitrite was dissolved in minimum quantity of water. The temperature of the reaction mixture was maintained between 0-5^{o}C. To this solution, sodium nitrite solution was added drop by drop with stirring. The diazotized product so obtained was directly used for coupling.



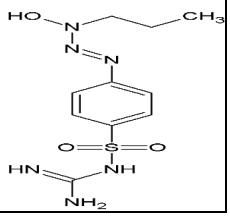
Scheme 2. Diazotization of 4-Amino-N-(aminoiminomethyl)benzenesulfonamide

Step-3: Coupling: The temperature of hydroxylamine prepared in step-1 and diazotized product obtained from step-2 (4) were maintain between 0-5^{o}C. Step-2 solution was added to solution obtained in step-1 with continuous stirring and pH of the solution was maintained 5-7 by adding sodium acetate solution. The resultant product was filtered, washed with cold water and dried. The crude compounds were purified and recrystallized. The purity of hydroxytriazenes was checked by I.R, ^{1}H NMR and melting point determination. Their compositions were verified by elemental analysis. The synthetic scheme 3 can be represented as



Scheme 3. Synthetic Hydroxytriazene

Table 1. Physical Characteristics of the reagents

Reagent	Molecular Formula	Color and Shape of the reagent	M.P.^{0}C	Analysis		
				Calculated	Experimental	Structure
3-hydroxy-3-propyl-1-(4-carbamimidoylsulfamoyl) phenyltriazene	$C_{10}H_{15}N_6O_3S$	Light violet crystal	172	C- 39.99% H- 5.37% N- 27.98%	C- 38.92% H- 5.17% N- 27.78%	

Characterization data of synthesized hydroxytriazenes

3-hydroxy-3-propyl-1-(4-carbamimidoylsulfamoyl)phenyltriazene 5d: IR 3426($_{O-H}$), 3346($_{N-H}$), 1609 ($_{C=N}$), 1335($_{N=N}$), 1126($_{S=O}$)cm^{-1}; ^{1}HNMR (DMSO): δ: 12.36(1H,s,OH), 7.2-7.8(H, m, ArH), 6.64(1H,s,SO_2NH), 3.25(4H,s,NH_2), 2.49-2.48(2H,t,CH_2), 4.19-4.13(4H,m,CH_2), 1.42-1.39 (2H,t,CH_3).

Spectrophotometric Studies of Pd (II) complexes

Standard solution of Pd (II): A 10^{-2} M stock solution of AR grade palladium chloride was prepared by dissolving the required quantity of palladium chloride in the minimum volume of hot concentrate HCl and diluting with double distilled water. The solution was then standardized complexometrically using sulfosalicylic acid as an indicator with EDTA, ammonium acetate and standard ferric ammonium sulphate solutions. Dilute solution is prepared using stock solution when required.

Reagent solution: A stock solution of 10^{-3} M is prepared by dissolving the required amount of hydroxytriazene in alcohol. Solutions of desired concentrations were prepared by appropriate dilution of the stock solution with alcohol.

Solutions for pH adjustment:

(a) Tris buffer solution- A 1% solution of tris (hydroxymethyl) amino methane was prepared by dissolving 1.0 gm of the tris buffer in minimum quantity of distilled water and then making it up to 100 mL with distilled water.

(b) Perchloric acid solution- A 1 % Perchloric acid solution was prepared by dissolving 1.0 mL of the Perchloric acid in minimum quantity of distilled water and then making up to 100 mL with distilled water.

Instrument: ELICO double beam SL 210 UV-VIS spectrophotometer was used for study.

Selection of suitable working wavelength: Solution of Pd: R in 1:10 ratio was taken in 10 mL volumetric flask and was made up to the mark with alcohol. Absorbance of solution against its reagent blank was measured in the wavelength region 300-500nm. The working wavelength is selected in a region where the absorption of Pd (II) complex was maximum and absorption due to reagent was minimum.

Effect of pH on absorbance: Absorbance of each solution at various pH values containing Pd (II) and reagent solution in 1:10 ratio was carried out at working wavelength against reagent blank. The optimum pH range for constant maximum absorbance was selected.

Composition of the Pd (II) complex: The composition of the Pd (II) complex was determined using Job's method and mole ratio method of Yoe and Jones. The composition as determined by both the method agreed well.

Job's method: In this method set of solution was prepared by varying the volume of equimolar Pd (II) and reagent solution from 0 to 3 mL. After pH adjustment the solution were made up with alcohol. The absorbance of solution was measured at working wavelength against reagent blank. The composition of complex was found to be 1:2 [Pd: R].Complex composition with Pd (II) has been tabulated in table-2.

Mole ratio method: In this method the concentration of Pd (II) was kept constant and reagent concentration was varied. A series of solution having Pd (II):R ratio 1:1 to 1:10 were prepared with maintaining the pH of constant absorbance. Absorbance of each solution of a set was measured at working wavelength against reagent blank. The composition was found to be 1:2 [Pd:R] by this method. It agree with the ratio determination by Job's method, thus proving Pd (II)-hydroxytriazenes for 1:2 Pd (II):R complex.

Beer's validity law: A set of solution having M:L ratio 1:10 was prepared. The studies were performed under optimum condition of pH, concentration and solvent at corresponding working wavelength. The absorbance was measured for the complex against the reagent blank.

Sandell's sensitivity: The molar absorptivity of the Pd (II) complexes was calculated from the Beer's law graph and the value thus obtained was used for determining Sandell's sensitivity of the complex. The values show that the method used is quite sensitive and satisfactory for the determination of Pd (II).

Table 2. Spectrophotometric Determination of Pd (II) with Reagents

S. No.	Pd (II) complex with reagent	Job's/ Mole ratio Composition of the complex [Pd(II) : R]	Working wavelength or λ max (nm)	Optimum pH range	Molar absorbtivity [$L.mol^{-1}.cm^{-1}$]	Sandell's sensitivity [$mg.cm^{-2}$]
1	3-hydroxy-3-propyl-1-(4-carbamimidoylsulfamoyl)phenyltriazene	1 : 2	367	1.8 – 2.4	8372	12.71

RESULTS AND DISCUSSION

3-hydroxy-3-propyl-1-(4-carbamimidoylsulfamoyl)phenyltriazene forms 1:2 complex with Pd(II). 3-hydroxy-3-propyl-1-(4-carbamimidoylsulfamoyl)phenyltriazene act as bidentate ligand which indicates a tetra-coordinated Pd (II) complex with probable square planner geometry. The result of

PASS prediction for 3-hydroxy-3-propyl-1-(4-carbamimidoylsulfamoyl)phenyltriazene is given in table-3.

Table 3. Prediction of percent activity(Pa) and inactivity(Pi) of3-hydroxy-3-propyl-1-(4-carbamimidoylsulfamoyl)phenyltriazene

Pa	Pi	Activity
0,870	0,005	Antiinflammatory
0,818	0,006	Omptin inhibitor
0,645	0,024	Venombin AB inhibitor
0,608	0,013	Cathepsin T inhibitor
0,619	0,062	Polyporopepsin inhibitor
0,620	0,076	CDP-glycerol glycerophosphotransferase inhibitor
0,544	0,011	Gingipain K inhibitor
0,531	0,023	Methylumbelliferyl-acetate deacetylase inhibitor
0,486	0,018	Carboxypeptidase D inhibitor
0,471	0,012	Clostripain inhibitor
0,469	0,025	Neuropeptide Y4 antagonist
0,431	0,019	Para amino benzoic acid antagonist
0,452	0,053	Endopeptidase So inhibitor
0,429	0,040	Renal tissue kallikrein inhibitor
0,484	0,101	Glutamyl endopeptidase II inhibitor
0,398	0,022	Acrosin inhibitor
0,368	0,014	Peptidyl-Lys metalloendopeptidase inhibitor
0,365	0,026	Antineoplastic (pancreatic cancer)

APPLICATION

3-hydroxy-3-propyl-1-(4-carbamimidoylsulfamoyl)phenyltriazene (CSPT) regent is used to for the determination of Pd(II) and is a probable activity reagent as anti-inflammatory and biological active compound.

CONCLUSIONS

As described above ligand has been developed as an analytical reagent for the determination of Pd (II). It can be seen from the results of PASS prediction that most probable activity of reagent is anti-inflammatory and is biologically active compound. Thus, it will be useful drug candidate if explored further.

REFERENCES

[1]. K. Paliwal, D. Gorji, S. Kumar, N. Naulakha, A.K. Goswami, D.N. Purohit, Complexometric determination ofChromium(III) from binary and tarnary mixture using 3-Hydroxy-3-phenyl-1-(m-nitro phenyl)triazenes, *Asian J.Chem*., **2001**, 13, 299-304.
[2]. R. Khanam, J.C. Sharma, S. Khan, R. Dashora, R.S. Chauhan, A.K. Goswami, Complexometric Determination of Zinc (II) in Pharmaceutical Samples using Hydroxytriazenes, *Int. J. Pharm. Sci. and Drug Research*, **2010**, 2, 43.
[3]. D.N. Purohit, Nizamuddin, A.M. Golwalkar, Hydroxytriazenes as chelating agents in analytical chemistry, *Revs. Anal. Chem*., **1985**, 8, 13-123.
[4]. D.N. Purohit, Hydroxytriazenes- a review of a new class of chelating agents, *Talanta*, **1967**, 14, 3, 353-359.

[5]. D. N. Purohit, M. P. Tyagi, S. Banu, Spectrophotometric determination of uranium (VI) – A Review, *Prol. Soc. Quim (Peru)*, **1985**, 51, 117.
[6]. A. K. Goswami, S. Khan, R. Dashora, D.N. Purohit, Review of spectrophotometric methods for determination of iron, *Revs. Anal. Chem*., **2004**, 25, 1-74.
[7]. S. Agrawal, P. K. Baroliya, A. Bhargava, I. P. Tripathi, A. K. Goswami, Synthesis, characterization, theoretical prediction of activities and evaluation of biological activities of some sulfacetamide based hydroxytriazenes, *Bioorg. Med. Chem. Lett*., **2016,** 26, 12, 2870-2873.
[8]. A. K. Goswami, D.N. Purohit, Synthesis and Antimicrobial Activities of Some Hydroxytriazenes- A New Class of Biologically Active Compounds, Anal. *Sci*., **2001**, 17, 789.
[9]. L.S. Chauhan, C.P. Jain, R.S. Chauhan, A.K. Goswami, Synthesis and analgesic activity of hydroxytriazenes, *Asian J. chem*., **2007**, 19, 4684-4688.
[10]. A. O. Ombaka, A.T. Muguna, J.M. Gichumbi, Antibacterial and Antifungal activities of noval hydroxytriazenes, *J. Environ. Chem. Ecotoxicol*., **2012**, 4, 7, 133-136.
[11]. L. S. Chauhan, C.P. Jain, R.S. Chauhan, A.K. Goswami, Wound Healing Activity of some Substituted Hydroxytriazenes, *Adv. Pharmacol. Toxicol*., **2006**, 7, 73.
[12]. O. Ombaca, S. Ressalan, R.S. Chauhan, A.K. Goswami, D.N. Purohit, Insecticidal activity of some substitutedhydroxytriazenes, *Pesticide Research J*., **199**8, 10, 235-236.
[13]. A.V. Stepanchikova, A.A. Lagunin, D.A. Filimonov, V.V. Poroikov, Prediction of biological activity spectra for substances: Evaluation on the diverse sets of drug-like structures, *Curr. Med. Chem*., **2003**, 10, 225-233.
[14]. Anzali, G. Barnickel, B. Cezanne, M. Krug, D. Filimonov, V. Poroikov, Discriminating between drugs and nondrugs by prediction of activity spectra for substances (PASS), *J. Med. Chem*., **2001**, 44, 2432-37.