

SYNTHESIS, SPECTRAL AND ANTIFUNGAL STUDIES ON OXIDATIVE ADDITION PRODUCTS OF PALLADIUM (0) COMPLEXES LIGATED BY TRIAZOLES

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ABSTRACT

The oxidative addition products of Palladium (0) complexes ligated by methyl, ethyl, propyl and phenyl derivatives of 4-amino-5-mercapto-3-substituted-1,2,4-Triazole were isolated in the composition $[Pd(P\phi_3)_2(\text{ligand})_2]X_2$ ($X = Cl/NO_3$) using precursor compound $[Pd(P\phi_3)_4]$. All compounds were characterised by elemental analysis, conductivity, magnetic, UV-vis, IR and 1H NMR data. The triazole molecule behaves as monodentate ligand bonding through the thione sulphur atom. Oxidative addition products of ethyl and phenyl substitution of ligand were screened for their antifungal activity against *Aspergillus favus* species.

Keywords : Oxidative addition products, Pd(0), Antifungal activities, Thioamides.

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INTRODUCTION

The derivatives of 1,2,4-triazole exhibit a variety of interesting biological action including antibacterial¹⁻², antifungal³⁻⁵, anti-HIV-1⁶ and other pharmacological activities⁷⁻⁹. Triazoles having thioamide group (HNCS) have versatile coordination behavior¹⁰⁻¹² and survey of literature reveals that very less amount of work have been done on oxidative addition products of low-valent Palladium (0). The present investigation aims at synthesis, spectral characterization and antifungal studies of some oxidative addition products of Palladium (0) complexes ligated by 4-amino-5-mercapto-3-substituted-1,2,4- triazoles.

EXPERIMENTAL

All chemicals used were either of Anal R or CP-grade. The ligands, 4-amino-3-substituted-5-mercapto-1,2,4-triazoles were prepared by some modified method reported in literature¹³. All derivatives, Methyl (AMtTH), Ethyl (AEtTH), Propyl (APrtTH) and Phenyl (APtTH) were crystallized from water : ethanol (1 : 1) solution (yield 60 – 65%).

The complexes were prepared using a general method. A freshly prepared zerovalent Palladium complexes¹⁴ were suspended in 50 mL ethanol and Stoichiometric quantity of 15-20% ethanolic HCl or HNO₃ was slowly added with stirring on magnetic stirrer at 60-65°C for two hours in a covered beaker. On cooling the mixture, yellow solid crystals were obtained. The crystals were filtered, washed with ice-cool ethanol and dried in a Vacuo desiccator.

Analysis

1 : $[Pd(P\phi_3)_2(AMtTH)_2]Cl_2$

Calculated (%) for $PdC_{42}H_{42}N_8S_2P_2Cl_2$: C, 52.42; H, 4.36; N, 11.64; Pd, 11.06;

Found (%) : C, 52.55; H, 4.37; N, 11.80; Pd, 11.0

2 : $[Pd(P\phi_3)_2(AEtTH)_2]Cl_2$

Calculated (%) for $PdC_{44}H_{46}N_8P_2S_2Cl_2$: C, 53.36; H, 4.64; N, 11.32; Pd, 10.75;

Found (%) : C, 53.82; H, 4.60; N, 11.21; Pd, 10.78

3 : [Pd(Pφ₃)(H₂O)(A_{Et}TH)₂]Cl₂Calculated (%) for PdC₂₆H₃₃N₈OPS₂Cl₂ : C, 41.85; H, 4.42; N, 15.02; Pd, 14.27;

Found (%) : C, 41.52; H, 4.45; N, 15.21; Pd, 14.30

4 : [Pd(Pφ₃)(H₂O)(A_{Et}TH)₂](NO₃)₂

Calculated (%) : C, 39.07; H, 4.13; N, 17.53; Pd, 13.22

Found (%) : C, 39.11; H, 4.14; N, 17.66; Pd, 13.50

5 : [Pd(Pφ₃)₂(A_{Prt}TH)₂]Cl₂Calculated (%) for PdC₄₆H₅₀N₈P₂S₂Cl₂ : C, 54.25; H, 4.91; N, 11.00; Pd, 10.50;

Found (%) : C, 54.26; H, 5.01; N, 11.21; Pd, 10.45

6 : [Pd(Pφ₃)₂(A_{Pt}TH)₂]Cl₂Calculated (%) for PdC₅₂H₄₆N₈P₂S₂Cl₂ : C, 57.49; H, 4.42; N, 10.31; Pd, 9.80;

Found (%) : C, 57.71; H, 4.45; N, 10.22; Pd, 9.82

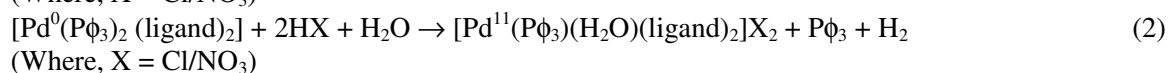
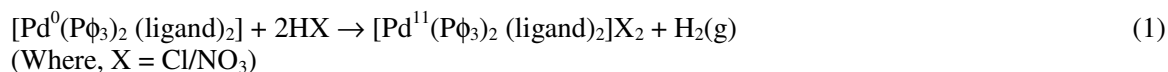
7 : [Pd(Pφ₃)(H₂O)(A_{Pt}TH)₂](NO₃)₂Calculated (%) for PdC₃₄H₃₃N₁₀O₇PS₂ : C, 45.61; H, 3.68; N, 15.65; Pd, 11.89;

Found (%) : C, 45.68; H, 3.66; N, 15.60; Pd, 11.92

Elemental analysis was carried out at CDRI, Lucknow, Metal and Sulphur were determined gravimetrically. Conductance measurements were carried out on digital control Dynamics (APX 185) conductivity meter, The magnetic susceptibility measurements were made using Gouy balance at RT using Hg[Co(CNS)₄] as calibrant. The electronic spectra were recorded in DMF and the IR Spectra of the ligands and complexes were taken on Jasco FT/IR-5300 Spectrophotometer using KBr discs. The antifungal activities were measured on cup plate methods reported in literature¹⁴.

RESULTS AND DISCUSSION

The structure of all the oxidative addition products were established on the basis of their spectroscopic and analytical data. Oxidative addition of zerovalent palladium complexes yielded stable yellow solids when treated with ethanolic 15% inorganic acids.



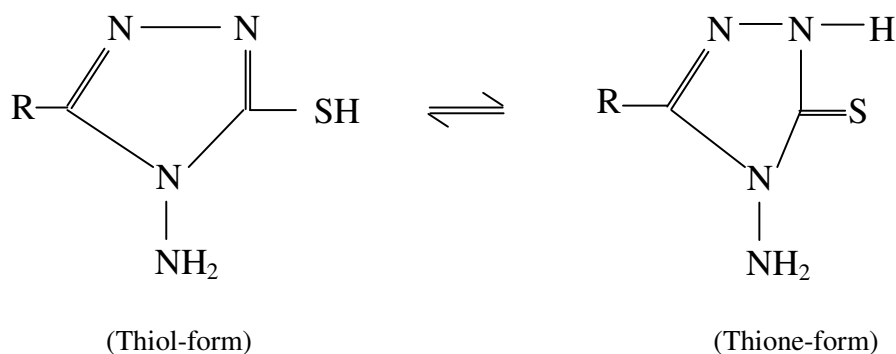
One mol of H₂ per mol of Pd was evolved when aqueous acids were used. The coordinated water molecule could not be replaced when refluxed in CH₃OH using excess of triphenyl phosphine. The molar conductance value 160-170 Λ⁻¹cm²mol⁻¹ in DMF (10⁻³ M) was in agreement with uni-bivalent electrolyte¹⁶. The low value of molar conductance of complexes probably due to solvation.

Magnetic measurements and electronic spectra

All isolated products were found to be diamagnetic which suggest square planar configuration¹⁷. The ligand field bands in the spectra of complexes (table 2) at 27670-27700 cm⁻¹ (¹A_{1g}→¹E_{1g}), 23760-23770 cm⁻¹ (¹A_{1g}→¹B_{1g}) and at 21610-21740 cm⁻¹ (¹A_{1g}→¹A_{2g}) are in agreement with the transition suggested by Shaikh et. al.¹⁸ and others¹⁹ for four coordinated square planar complexes. Hence, all oxidative addition products are four co-ordinated square planar.

IR Spectra

The ligands contain thioamide group (HNCS) apart from an amino group and exhibit thiol-thione tautomerism²⁰.



(R = CH₃-; CH₃CH₂-; n - CH₃CH₂CH₂-); and C₆H₅-

All ligands display four split bands between 3260-3040 cm⁻¹ due to interaction between NH and NH₂ groups which remain almost unperturbed in position and higher in intensity on complexation indicating the absence of bonding neither through imino nitrogen (-NH) nor through amino nitrogen (-NH₂). The thioamide band I of ligands also remain unchanged in position on coordination to all Pd (II) complexes suggesting the absence of bonding through nitrogen atom considering our previous observations²¹⁻²³.

Thioamide band III and IV of ligands have major contributions from $\nu_{C=S}$ ²⁴. On complexation, thioamide band III is shifted lower frequency about 50-60 cm⁻¹ and band IV is also shifted by 65-70 cm⁻¹. This indicates the formation of strong Pd - S bond in all complexes²⁵. New single bands at 375-480 cm⁻¹ and at 325-320 cm⁻¹ in far infrared spectra of complexes suggest two P ϕ ₃ groups and two thione ligands are at trans-disposition in planar complexes and assigned to Pd - P and Pd - S stretching modes respectively. The non-ligand bands at 3420 \pm 10, 1605 \pm 5 and 810 cm⁻¹ are assigned to ν_{H_2O} , δ_{H_2O} and π_{H_2O} modes of coordinated water molecule²⁶. Such bands are not present in other complexes (Sl. No. 1, 2, 5 & 6). The coordinated water molecule is further supported by non-ligand band at 485 \pm 5 cm⁻¹ due to Pd - O stretching mode²⁷.

¹H NMR Spectra

The ¹H NMR Spectra of methyl (AMtTH) and Phenyl (APtTH) derivatives of 4-amino-5-mercapto-3-substituted-1,2,4-triazoles and some of their complexes (Sl. No. 1 & 6) were recorded in CDCl₃/TMS to substantiate further mode of metal-ligand bonding. The ligands 4-amino-5-mercapto-3-methyl-1,2,4-triazole (AMtTH) display strong multiplet in the region δ 2.12 PPM, δ 4.32-4.34 PPM, δ 7.7-7.72 PPM and δ 3.08 PPM due to methyl, amino, imino and thiol protons respectively of the ligand. Thiol proton is not observed in the spectrum of its complex (Sl. No. 1) indicating thione tautomeric form and coordination of ligand through thione sulphur. The ligand APtTH display strong signals at δ 7.8-7.9 PPM, δ 7.7-7.72 PPM and δ 4.32-4.34 PPM due to phenyl, imino and amino protons respectively are observed at the same position indicating that they are intact on complexation. The broad signals in the range δ 8.33-8.86 PPM range due to protons of coordinated P ϕ ₃²⁸ in the complexes. Such signals are not observed in the spectra of both AMtTH and APtTH. The broad nature of protons signals may be due to close proximity of P ϕ ₃ molecules with triazoline ring nitrogen in the crystal lattice of complexes.

Antifungal Activity

All complexes of AEtTH and APtTH were screened for their antifungal activities against *Aspergillus flavus* species using DMSO as solvent and results are given in table 2. The standard fungicide used for comparison was carbendazim²⁹. The inhibition zone formed around each filter paper after inoculation for 96 hours at room temperature were measured. All oxidative addition products of Pd (0) complexes exhibit

significant antifungal activities. The antifungal activity of complexes increases with increase in concentration. The complexes (S. No. 4 & 6) having nitrate group exhibit maximum activity. The other complexes display moderate activities and may be classified as mixed fungicides.

Table-1: Major IR Spectral data of ligands and complexes (cm^{-1})

Compounds	Thioamide Bands*				vPd-O/ (vPd-S)	vPd-P
	Band I	Band II	Band III	Band IV		
AMtTH ($\text{C}_3\text{H}_6\text{N}_4\text{S}$)	1580 (s)	1315 (s)	990 (m)	925 (s)	— (—)	(—)
$[\text{Pd}(\text{P}\Phi_3)(\text{AMtTH})_2]\text{Cl}_2$	1590 (s)	1330 (m) 1315 (m)	970 (m) 950 (m)	850 (m)	480 (m) (320 m)	430 (m)
AEtTH ($\text{C}_4\text{H}_8\text{N}_4\text{S}$)	1570 (s)	1340 (m)	1050 (s)	770 (s)	— (—)	—
$[\text{Pd}(\text{P}\Phi_3)_2(\text{AEtTH})_2]\text{Cl}_2$	1580 (s)	1330 (m) 1320 (m)	930 (m)	730 (m)	485 (m) (330 m)	435 (m)
$[\text{Pd}(\text{P}\Phi_3)(\text{H}_2\text{O})(\text{AEtTH})_2]\text{Cl}_2$	1585 (s)	1330 (m) (1325 m)	925 (m)	725 (m)	480 (m) (335 m)	440 (m)
$[\text{Pd}(\text{P}\Phi_3)_2(\text{AEtTH})_2](\text{NO}_3)_2$	1590 (s)	1335 (m) 1325 (m)	925 (m)	720 (m)	480 (m) (320 m)	430 (m)
APrtTH ($\text{C}_5\text{H}_{10}\text{N}_4\text{S}$)	1565 (s)	1370 (m)	1045 (s)	760 (m)	— (—)	—
$[\text{Pd}(\text{P}\Phi_3)_2(\text{APrtTH})_2]\text{Cl}_2$	1570 (m)	1325 (m)	1000 (m)	710 (m)	480 (m) (310 m)	420 (m)
APtTH ($\text{C}_8\text{H}_8\text{N}_4\text{S}$)	1525 (s)	1245 (s)	1140 (s)	760 (m)	— (—)	—
$[\text{Pd}(\text{P}\Phi_3)_2(\text{APtTH})_2]\text{Cl}_2$	1530 (s)	1250 (s)	1100 (m)	750 (m)	480 (m) (315 m)	425 (m)
$[\text{Pd}(\text{P}\Phi_3)(\text{H}_2\text{O})(\text{APrtTH})_2]\text{Cl}_2$	1530 (s)	1255 (s)	1105 (m)	755 (m)	485 (m) (320 m)	410 (m)

Table – 2 : Electronic Spectral Data and Antifungal Data of Complexes

Complexes	Electronic Spectra d-d Transition (λ_{max})/ Assignment	Fungicidal activity Average % inhibition A. flavus (PPM)		
		1000	100	10
$[\text{Pd}(\text{P}\Phi_3)_2(\text{AEtTH})_2]\text{Cl}_2$ (S. No. 2)	22600 ($^1\text{A}_{1g} \rightarrow ^1\text{E}_{1g}$) 27700 ($^1\text{A}_{1g} \rightarrow ^1\text{E}_{1g}$) 29400 ($^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$)	60.0	52.1	44.3
$[\text{Pd}(\text{P}\Phi_3)(\text{H}_2\text{O})(\text{AEtTH})_2]\text{Cl}_2$	23420 ($^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$) 28440 ($^1\text{A}_{1g} \rightarrow ^1\text{E}_{1g}$) 30300 ($^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$)	65.3	45.3	39.1
$[\text{Pd}(\text{P}\Phi_3)(\text{H}_2\text{O})(\text{AEtTH})_2](\text{NO}_3)_2$	22885 ($^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$) 28560 ($^1\text{A}_{1g} \rightarrow ^1\text{E}_{1g}$) 31100 ($^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$)	88.8	74.3	65.5
$[\text{Pd}(\text{P}\Phi_3)_2(\text{APrtTH})_2]\text{Cl}_2$	24200 ($^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$) 31150 ($^1\text{A}_{1g} \rightarrow ^1\text{E}_{1g}$)	61.3	51.2	44.3
$[\text{Pd}(\text{P}\Phi_3)(\text{H}_2\text{O})(\text{APrtTH})_2](\text{NO}_3)_2$	24290 ($^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$) 30770 ($^1\text{A}_{1g} \rightarrow ^1\text{E}_{1g}$)	89.6	78.5	68.3
Carbendazim	—	97.8	88.6	82.0

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[RJC-1007/2013]

*International Journal of***Chemical, Environmental and Pharmaceutical Research**

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ISSN: 2229-3892(Print); ISSN: 2229-5283(Online)

[Abstracted in : Chemical Abstracts Service , American Chemical Society, USA and CAB(I) , UK]

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