



SYNTHESIS, CHARACTERISATION AND OXIDATIVE ADDITION PRODUCTS OF PALLADIUM (0) COMPLEXES LIGATED BY HETEROCYCLIC THIOAMIDE

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ABSTRACT

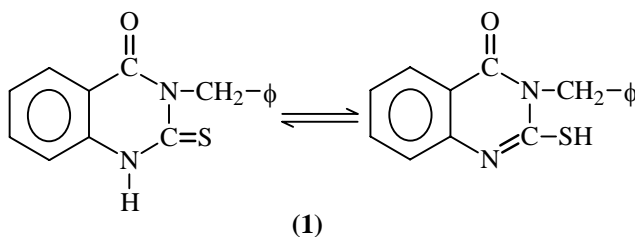
The phosphine complexes of palladium (0) with heterocyclic thioamide, 2-mercapto-3-benzyl-quinazoline-4-one have been isolated and characterised on the basis of elemental analyses, molar conductance, magnetic moment and spectral studies. Oxidative addition products with inorganic acids have also been reported. The coordination of thioamide ligand occurs through sulphur and square planar configuration to Pd (II) and tetrahedral geometry to Pd (0) complexes are assigned.

Key words: Pd (0), Oxidative addition, Thioamide.

INTRODUCTION

Palladium (0) complexes are among the most versatile transition metal catalyst used for organic synthesis¹, cross-coupling reactions²⁻⁴, isomerisation of alkenes⁵, borylation of aryl halides⁶, hydrogenation and hydroformylation reaction⁷. They have unique and interesting insights into structure, bonding and reactivity of the molecules, which display either coordinative dissociation or coordinative addition⁸⁻¹⁰. The present paper is devoted to the synthesis and characterisation of some novel palladium (0) complexes with heterocyclic thioamide 2-mercapto-3-benzyl-quinazoline-4-one (I). Oxidative addition products with inorganic acids and a thorough investigations of structure, nature of bonding and various physico-chemical properties of new compounds isolated during reactions are reported here in.

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EXPERIMENTAL

All the chemicals used were of either Anal R or CP-grade. 2-mercapto-3-benzylquinazolin-4-one (BZQTH) was prepared by the method of Dave et al.¹¹ The precursor complex Pd(Pφ₃)₄ was prepared by the method reported in previous literature¹². All new Pd(0) complexes were prepared by ligand substitution in benzene reported in our earlier method¹³. Oxidative addition to freshly prepared palladium(0) complexes were carried out using 30% ethanolic solution of inorganic acid as reported in our previous communication¹⁴. The carbon, hydrogen and nitrogen analyses and IR, UV-vis, ¹H NMR, molar conductance and magnetic moment data were obtained as reported earlier¹⁵. The molecular weight of palladium(0) complexes were measured cryoscopically using highly purified benzene as solvent.

Analysis

Sl. No. 1 : Calculated (%) for [Pd(Pφ₃)₂(BZQTH)₂] (yellow) :

PdC₆₆H₅₄N₄O₂P₂S₂ : C = 67.90; H = 4.62; N = 4.80, Pd = 9.12

Found (%) : C = 68.11; H = 4.71; N = 4.72; Pd = 9.11

Sl. No. 2 : Calculated (%) for [Pd(Pφ₃)₂(BZQTH)₂]Cl₂ (yellow) :

PdC₆₆H₅₄N₄O₂P₂S₂Cl₂ : C = 64.00; H = 4.36; N = 4.52, Pd = 8.59

Found (%) : C = 64.01; H = 4.33; N = 4.88; Pd = 8.40

Sl. No. 3 : Calculated (%) for [Pd(Pφ₃)H₂O(BZQTH)₂]Cl₂ (light yellow) :

PdC₄₈H₄₁N₄O₃S₂PCl₂ : C = 57.98; H = 4.12; N = 5.63, Pd = 10.71

Found (%) : C = 58.11; H = 4.32; N = 5.66; Pd = 10.80

Sl. No. 4 : Calculated (%) for [Pd(Pφ₃)(H₂O)(BZQTH)₂](BF₄)₂ (yellow) :

PdC₄₈H₄₁N₄O₃S₂PB₂F₈ : C = 52.55; H = 3.74; N = 5.10, Pd = 9.70

Found (%) : C = 52.32; H = 3.75; N = 5.23; Pd = 10.01

Sl. No. 5 : Calculated (%) for [Pd(Pφ₃) (H₂O) (BZQTH)₂](ClO₄)₂ (Faint yellow)PdC₄₈H₄₁N₄O₁₁S₂PCl₂ : C = 51.36; H = 3.65; N = 4.99, Pd = 9.48

Found (%) : C = 51.38; H = 3.66; N = 5.01; Pd = 9.55

RESULTS AND DISCUSSION

The analytical data are consistent with proposed stoichiometries. The precursor complex, [Pd (Pφ₃)₄] extensively dissociate in benzene solution and ligand substitution yielded [Pd (Pφ₃)₂ (ligand)₂] easily. The ethanolic solution of HCl formed [Pd(Pφ₃)₂ (ligand)₂]Cl₂ but aqueous solution of inorganic acids yielded the complexes [Pd (Pφ₃)₂ (H₂O) (ligand)₂]X₂ (X = Cl, BF₄ and ClO₄). The coordinated water molecule could not be replaced even by refluxing in methanol using excess of triphenyl phosphine. The molar conductance value in DMF (10⁻³ M) is in agreement with required by uni-bivalent electrolyte. The low value of molar conductance was observed for bulky anions due to their bigger size and solvation.

Electronic spectra of [Pd⁰(Pφ₃)₂ (ligand)₂] display a very broad and strong band at 28500 cm⁻¹ of considerable high intensity due to charge transfer. The other ligand field bands are obscured by CT band and high degree of d-p mixing in zero valent complex appears. The known preferential tetrahedral structure to Pd (0) complex may be tentatively assigned following previous literature¹⁵ and zero valent palladium complex is iso-structural with precursor complex of Pd(Pφ₃)₄.

All oxidative reaction products of [Pd⁰(Pφ₃)₂ (ligand)₂] display a band around at 24200-24400 cm⁻¹ assigned to ¹A_{1g} → ¹B_{1g} transition indicate square planar geometry of Pd (II) complexes¹⁶. The band at 30760-31700 cm⁻¹ was a shoulder on CT band at 32800-33210 cm⁻¹ is of a ligand field origin assigned to ¹A_{1g} → ¹E_g transition. Thus, electronic spectra and magnetic moment data is in fairly good agreement for square planar environment of ligands¹⁶⁻¹⁸.

IR Spectra

The characteristics bands due to νNH (3240 cm⁻¹), thioamide band I (1520 cm⁻¹) and ν_{C=O} (1710 cm⁻¹) of 2-mercapto-3-benzyl-quinazoline-4-one (ligand) remain almost unchanged in position and intensity indicating the absence of bonding through imino nitrogen atom and carbonyl oxygen of the ligand¹⁹. However, thioamide band IV (ν_{C=S}) observed at 805 cm⁻¹ in free ligand red shift to lower frequency 35-40 cm⁻¹ on complexation indicating bonding through thiocarbonyl sulphur²⁰ and formation Pd-S bond. New band in

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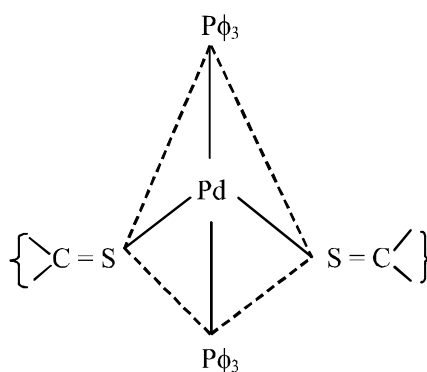
far IR Spectra of complexes at 330-320 cm^{-1} assigned to Pd-S stretching mode. Moreover, the presence of single Pd-S stretching mode is due to trans-disposition of two thioamide ligands in complexes.

The absorption associated with counter anions in complexes are identified at 1085 (sb), 620 (m) cm^{-1} for ionic perchlorate²¹ and at 1060 (m) cm^{-1} for ionic tetrafluoroborate²². The presence of coordinated water molecule is indicated by the non-ligand bands at 3420-3440 cm^{-1} , 1600 (m) cm^{-1} and 840 (m) cm^{-1} are assigned to $\nu\text{H}_2\text{O}$, $\delta\text{H}_2\text{O}$ and $\pi\text{H}_2\text{O}$ modes respectively²³. The non-ligand band at 480-485 cm^{-1} in complexes assigned to $\nu_{\text{Pd-O}}$ mode. The characteristic bands due to $\text{P}\phi_3$ group are also present in the expected region²⁴.

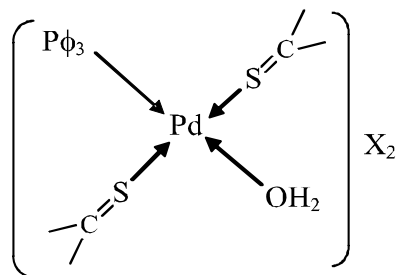
¹H NMR Spectra

The ¹H NMR spectra of ligand and Pd (II) complex (Sl. No. 2 and 3) were recorded in CDCl_3/TMS to substantiate further metal-ligand bonding. The broad signals in the range δ 8.23-8.92 PPM range are due to aromatic protons of $\text{P}\phi_3$ ²⁵. The signals due to the aromatic protons of ligand are observed at δ 7.62-7.72 PPM. The aromatic proton at position-5 is deshielded by the carbonyl oxygen and the extreme signal at δ 8.12 PPM is considered due to this proton. The signal due to N-H are observed at δ 3.2 PPM in the ligand remain almost unchanged on complexation indicating no deprotonation during complexation and imino proton is intact. The CH_2 group attached to the nitrogen atom of the quinazoline ring is deshielded giving signal at δ 4.85 PPM. These observations are consistent with the conclusion drawn from IR spectra.

Thus, on the basis of aforesaid discussion, the tetrahedral structure of Pd (0) and square planar structure of Pd (II) complexes may be assigned :



Tetrahedral Structure of Pd (0) complex



Square planar Structure of Pd (II) complexes
(X = Cl, BF₄ and ClO₄)

Table 1: IR characterization bands (cm⁻¹) and electronic spectral bands of ligand and complexes

Compound	IR Spectra			Electronic spectra d-d Transition cm ⁻¹ / (assignments)
	ν_{NH}	Thioamide band IV ($\nu_{\text{C-S}}$)	$\nu_{\text{Pd-O/}}$ ($\nu_{\text{Pd-S}}$)	
BZQTH (ligand)	3240 (m)	805 (m)	=	(-)
[Pd(Pφ ₃) (BZQTH) ₂]	3245 (m)	785 (m)	490 (m) [330 (w) 320 w]	(-)
[Pd(Pφ ₃) (BZQTH) ₂ Cl ₂]	3255 (m)	780 (m)	480 (m) (330 w)	24200 (¹ A _{1g} → ¹ B _{1g}) 31680 (¹ A _{1g} → ¹ E _g)
[Pd(Pφ ₃)(H ₂ O) (BZQTH) ₂ Cl ₂]	3240 (m)	760 (m)	480 (m) (320 w)	24400 (¹ A _{1g} → ¹ B _{1g}) 31690 (¹ A _{1g} → ¹ E _g)
[Pd(Pφ ₃)(H ₂ O) (BZQTH) ₂](BF ₄) ₂	3250 (m)	772 (m)	485 (m) (330 w)	24340 (¹ A _{1g} → ¹ B _{1g}) 31700 (¹ A _{1g} → ¹ E _g)
[Pd(Pφ ₃)(H ₂ O) (BZQTH) ₂](ClO ₄) ₂	3240 (m)	775 (m)	480 (m) (340 w)	24360 (¹ A _{1g} → ¹ B _{1g}) 30760 (¹ A _{1g} → ¹ E _g)

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