



SPECTRAL STUDIES ON HYDRIDOPHOSPHINE COMPLEXES OF Pt-GROUP METALS : PART VI : OXIDATIVE-ADDITION TO Pt (0) COMPOUNDS

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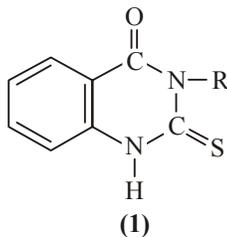
ABSTRACT

Oxidative addition products of mixed-ligand phosphine complexes of platinum (0) with 3-substituted phenyl and propyl derivatives of 2-mercapto-quinazoline-4-one using some inorganic acids have been investigated. The reaction products are characterized by elemental analyses, IR, ¹H NMR and electronic spectra. The square planar configuration have been tentatively assigned to all isolated products.

Key words: Platinum (0), Oxidative-addition, Thioamide ligands.

INTRODUCTION

The literature survey reveals a resurgence of interest to investigate platinum compounds due to a new class of potent antitumour agent^{1,2} and for development of Pt-based anticancer drugs³⁻⁵. These compounds have very interesting insight into structure, bonding and reactivity of molecules in solution. We have reported ligand displacement⁶⁻⁸ as well as oxidative-addition⁹⁻¹¹ with various ligands in our earlier communications. The present study reports oxidative-addition products on platinum (0) compounds of substituted quinazoles (I) using inorganic acids. The tentative structure of isolated solid products are assigned on the basis of elemental analysis, IR, UV-Vis, ¹H NMR and other physico-chemical measurements.



(R = CH₃CH₂CH₂- and C₆H₅-)

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EXPERIMENTAL

All chemicals used were of CP grade or AR grade. The n-propyl and phenyl derivatives of 2-mercapto-3-substituted-quinazoline-4-one were prepared by the method of Dave et al.¹² The zero valent precursor complex was prepared using our earlier method¹³. The calculated amount of 30% ethanolic solution of HNO₃/H₂SO₄/HClO₄ to precursor complex [Pt⁰(Pφ₃)₂(ligand)₂] yielded solid complexes. These are given in Table 1.

Table 1: Analytical, physical and electronic spectral data of complexes

Complex (Colour)/Molecular formula	Molar conductance ($\Lambda^{-1}\text{cm}^2\text{mol}^{-1}$)	Analysis % Found/(Calc.)				λ_{max} / Assignment (cm^{-1})
		C	H	N	Pt	
[PtH(Pφ ₃)(Pr QTH) ₂]ClO ₄ (White) PtC ₄₀ H ₄₀ N ₄ O ₆ S ₂ PCl	19.80	48.31	4.11	5.62	19.55	24390 (¹ A _{1g} → ¹ B _{1g})
		(48.12)	(4.02)	(5.61)	(19.54)	30300 (¹ A _{1g} → ¹ E _g) 35090 (CT Band)
[PtH(Pφ ₃)(Pr QTH) ₂]HSO ₄ (White) PtC ₄₀ H ₄₁ N ₄ O ₆ S ₃ P	20.20	48.28	4.32	6.66	19.78	24000 (¹ A _{1g} → ¹ B _{1g})
		(48.24)	(4.12)	(6.62)	(19.59)	29400 (¹ A _{1g} → ¹ E _{1g}) 34482 (CT Band)
[PtH(Pφ ₃)(Pr QTH) ₂]ClO ₄ (White) PtC ₄₆ H ₃₆ N ₄ O ₆ S ₂ P	21.60	53.64	3.50	5.50	18.98	24000 (¹ A _{1g} → ¹ B _{1g})
		(53.59)	(3.49)	(5.43)	(18.93)	30350 (¹ A _{1g} → ¹ E _{1g}) 36090 (CT Band)
[PtH(Pφ ₃)(P QTH) ₂]HSO ₄ (White) PtC ₄₆ H ₃₇ N ₄ O ₆ S ₃ P	24.80	52.10	3.55	5.32	18.35	24380 (¹ A _{1g} → ¹ B _{1g})
		(52.92)	(3.48)	(5.26)	(18.34)	30310 (¹ A _{1g} → ¹ E _{1g}) 34500 (CT Band)

Cont...

Complex (Colour)/Molecular formula	Molar conductance ($\Lambda^{-1}\text{cm}^2\text{mol}^{-1}$)	Analysis % Found/(Calc.)				λ_{max} / Assignment (cm^{-1})
		C	H	N	Pt	
[PtH($P\phi_3$)(PQTH) $_2$]NO $_3$ (Faint yellow) PtC $_{46}$ H $_{36}$ N $_5$ O $_5$ S $_2$ P	19.70	53.72	3.51	6.96	19.00	24400 ($^1A_{1g} \rightarrow ^1B_{1g}$)
		(53.69)	(3.50)	(6.80)	(18.96)	30360 ($^1A_{1g} \rightarrow ^1E_{1g}$) 34560 (CT Band)

Elemental analysis, magnetic moment, conductometric, IR, UV-Vis and ^1H NMR spectral measurements were obtained as reported in previous report¹⁴.

RESULTS AND DISCUSSION

Oxidative-addition results in high melting ($> 250^\circ\text{C}$), colourless and diamagnetic hydrides of Pt (II).



The molar conductance value in DMF (10^{-3}M) is in agreement with required by univalent electrolyte and the low value may be due to large ions. The electronic spectral bands at $24000\text{-}24390\text{ cm}^{-1}$ ($^1A_{1g} \rightarrow ^1B_{1g}$), $29400\text{-}30300\text{ cm}^{-1}$ ($^1A_{1g} \rightarrow ^1E_{1g}$) and $34480\text{-}35090\text{ cm}^{-1}$ (CT band) are consistent with square planar geometry¹⁵. The ($^1A_{1g} \rightarrow ^1E_{1g}$), transition band is a shoulder on charge transfer band and it indicates extensive d-p mixing in the complexes.

IR Spectra

The characteristic νNH (3220 cm^{-1}), $\nu\text{C}=\text{O}$ (1680 cm^{-1}) and thioamide band I¹⁶ (1520 cm^{-1}) in the ligands remained unaltered on complexation indicating the absence of bonding through imino nitrogen and carbonyl oxygen atom. However, thioamide band IV ($\nu\text{C}=\text{S}$) and band III ($\nu\text{C}=\text{S} + \nu\text{C}=\text{N}$) red shift by $34\text{-}40\text{ cm}^{-1}$ and $20\text{-}30\text{ cm}^{-1}$, respectively indicates bonding through thiocarbonyl sulphur atom.¹⁶⁻¹⁸ The formation of Pt-S bond in complexes was further confirmed by the presence of a doublet below 300 cm^{-1}

separated by 10-15 cm^{-1} in far IR spectra and two thione ligands at trans position in square planar structure.

The IR absorption band of medium intensity between 2100-2120 cm^{-1} is assigned to $\delta\text{Pt-H}$ and another less intense one between 800-790 cm^{-1} , is due to $\delta\text{Pt-H}$ mode and these are in agreement with the criteria suggested by Chatt et al.¹⁹ considering trans-effect of $P\phi_3$ group. It appears that the $\nu\text{Pt-H}$ in these complexes is sensitive to electron releasing effect of alkyl group. The more electron donating alkyl group induce greater electron density on the hydride ligand and Pt-H stretching band shifted towards higher wave number as one moves from phenyl substitution to propyl substitution in the ligand.

The presence of anions in the complexes was confirmed by bands at 3420 (OH), 1252-1230 ($\nu_{\text{as}} \text{SO}_3$), 1057 ($\nu_{\text{s}} \text{SO}_3$), 1017 (νSO) for bisulphate²⁰, at 1337 ($\nu_{\text{as}} \text{NO}_3^-$), 822 (δNO_3^-) for nitrate²¹ and 1094 cm^{-1} ($\nu_{\text{as}} \text{ClO}_4^-$) for perchlorate²² indicating their uncoordinated nature. The characteristics bands due to $P\phi_3$ ²³ were also present in the expected region.

¹H NMR Spectra

The ¹H NMR spectra of ligands and some complexes (1, 3, 7) were recorded in CDCl_3/TMS to substantiate metal-ligand bonding, further. The spectra of complexes display multiplets in the region $\delta 6.8-7.2$ ppm due to aromatic protons of coordinated $P\phi_3$ molecule.²⁴ However, the aromatic phenyl proton signals are observed at $\delta 7.8-8.5$ ppm. The aromatic proton at position-5 is deshielded by carbonyl oxygen and hence, the extreme signal at $\delta 8.3$ ppm is considered to be due to this proton. The signal due to NH is always difficult to identify because of the quadrupole moment of nitrogen and the exchange of this proton. However, a peak observed at $\delta 3.2$ ppm in the ligands remain almost at the same position on complexation indicating absence of deprotonation of imino group proton. The n-propyl derivative shows signals at $\delta 1.75$ (t, CH_3), $\delta 2.2$ (CH_2) and $\delta 4.7$ (t, CH_2) attached the nitrogen atom of the quinazoline ring. Thus, N-H group is in tact on coordination and coordination occurs through thiocarbonyl sulphur. These observations are consistent with the conclusion drawn from IR spectral studies.

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