

Synthesis, Spectral and Antibacterial Screening of Mixed-Ligand Phosphine Complexes of Pd(0) and Pt(0) Ligated with Ammonium Salt of Anthranilic Acid



Chemistry

KEYWORDS : Pd(0) and Pt(0) species, Phosphine, Tetrahedral, Anthranilic acid bio-activities

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ABSTRACT

Four coordinated tetrahedral complexes of Palladium (0) and Platinum (0) with ammonium salt of anthranilic acid are prepared and their structure are deduced and elucidated using elemental analysis, conductometric, iodometric and acidimetric titrations, IR, UV-vis and ¹H NMR spectral data. The antimicrobial screening of few complexes are examined. The antibacterial activity of ligand is increased on complexation.

INTRODUCTION

The literature survey revealed that anthranilic acid occurs either as positively or a negatively charged ion¹ or as neutral molecule² depending on the environment and pH of the solution.³⁻⁴ Bergman et al⁵ have reported anthranilic acid as an amphoteric compound like other amino acids having both acidic and basic behaviour. Borowski and Cole-Hamilton⁶ have examined structure and properties of Anthranilato and N-phenyl anthranilato-rhodium (I) complexes containing triphenyl phosphine. The present study aims at synthesis and spectral properties of low-valent Pd(0) and Pt(0) complexes incorporating phosphine and ammonium salt of anthranilic acid in continuation of our previous report.⁷⁻⁹

EXPERIMENTAL

All chemical used were of AR grade or CP grade. Anthranilic acid and triphenyl phosphine were obtained from E. Merck. Solvents were dried before use. The precursor complexes (M⁰(Pφ₃)₄) (M = Pd/Pt) were prepared by the method reported in literature.¹⁰⁻¹¹ The new Palladium (0) and Platinum (0) complexes were prepared by ligand substitution in benzene following our previous method¹² and their micro-analytical data is given in Table 1.

IR Spectra of ligand and complexes were recorded with the help of Perkin Elmer Model E21 using KBr pellets technique. The magnetic measurements were made on gouy balance using Hg[Co(SCN)₄] as calibrant. Electronic spectra of ligand and complexes were recorded using Hilger Watt UV/vis spectrophotometer in DMF (10⁻³ M). The ¹H NMR spectra were recorded on a high resolution Varian HR-100 (cross coil type) NMR spectrophotometer.

The C, H, N analyses were done at the micro-analytical section of CDRI Lucknow. The estimation of metal was done by standard method.

RESULTS AND DISCUSSION

The precursor complexes M⁰(Pφ₃)₄ (M = Pd/Pt) display ligand substitution in benzene and ethanol (1:1) as :



The analytical data of complexes are in good agreement with the molecular formula proposed. All compounds were stable solid and fair soluble in DMF and DMSO and molar conductance values in DMF (10⁻³ M) were found in the range of 18.62 – 20.36 $\Lambda^{-1}cm^2mol^{-1}$ indicating their non-electrolytic nature.¹³ The diamagnetic nature of complexes indicated d¹⁰ – configuration for zero valent metal which was further supported and confirmed by iodometric and acidimetric titrations.¹⁴

Spectral Characterization

The free ligand exhibits two bands of 29850 cm⁻¹ ($\pi \rightarrow \pi^*$) and at 27625 cm⁻¹ ($n \rightarrow \pi^*$) in electronic spectra.¹⁵ However, a very strong and broad band between 37745 – 35840 cm⁻¹ due to charge transfer was observed in complexes indicating high degree of d-p mixing.

Infrared Spectra

Some selected IR bands of interest are given in Table 2. A comparison of the IR bands of Pφ₃ and anthranilic acid and corresponding Pd⁰ and Pt⁰ complexes indicate the following :

- The νNH of anthranilic acid observed at 3305 – 3295 cm⁻¹ and 3135-3125 cm⁻¹ shifted to lower frequency by 20-15 cm⁻¹ and 95-90 cm⁻¹ indicate the bonding through –NH₂ group of ligand.
- New bands at 480 cm⁻¹ and 485 cm⁻¹ in complexes are assigned to Pd-N and Pt-N stretching modes respectively confirmed the bonding through amino nitrogen.
- The band at 1300 cm⁻¹ in the spectrum of ligand may be due to νC-N of primary amino group. This band shifts to lower frequency of 1270 cm⁻¹ due to coordination of nitrogen to metal on complexation.
- The energy difference between ν_{asym} (COO) and ν_{sym} (COO) in complexes is 255 cm⁻¹ and close to the value of free ligand ruled out coordination through carboxylate group.¹⁶
- New bands in complexes at 1570 cm⁻¹, 1390 cm⁻¹, 740 cm⁻¹ and 530 cm⁻¹ are observed due to coordinated Pφ₃ molecule.¹⁷ The non-ligand band at 327-335 cm⁻¹ are assigned due to metal-P stretching mode in complexes also supports the coordinated triphenyl phosphine.
- Bands around 3150, 3040, 1680 and 1400 cm⁻¹ in the spectra of ligand and complexes are due to ammonium ion.¹⁸

¹H NMR Spectra

The free ligand exhibited signals at δ7.72-6.52 (multiplet) PPM and δ8.45 PPM due to phenyl proton and amino protons. The amino proton signals are low field shifted on complexation and the integrated intensities of the signals agree with the assigned structure of complexes. (Str. I to II) The phenyl protons of triphenyl phosphine are observed as multiplet δ7.71-6.76 PPM indicating coordinated Pφ₃ molecules.

Thus, on the basis of analytical data, valence requirements, IR spectral data and ¹H NMR spectral data, the tetrahedral structure isostructural with precursors may be proposed.

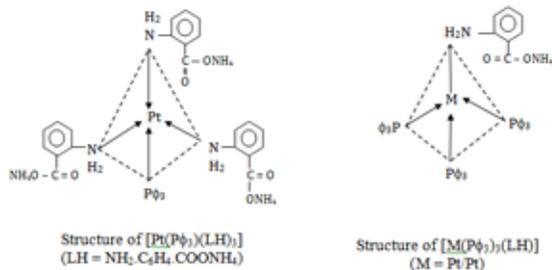


Table-3 : Inhibition circle diameter in millimeter for the bacteria after 24 hrs. incubation paid and 37°C for compounds

Compounds	Bacillus	Klebsiella spp	Staphylococcus
Control DMSO	11.1	10.0	13.5
Anthranilic acid	18.3	14.0	20.8
$[Pt(P\phi_3)(LH)_3]$	19.6	14.6	21.5
$[Pd(P\phi_3)_3](LH)_3$	20.2	15.1	21.7

Antimicrobial activities

The synthetic complexes (Sl. No. 1 & 4) were further evaluated for their antibacterial properties against three types of bacteria using nutrient agar medium by disc diffusion method.¹⁹ The test solution were prepared in DMSO and soaked in filter paper of 5 mm diameter and 1 mm thickness. These discs were placed on the already seeded plates and incubated at 37°C for 24 hours.²⁰ The zone of inhibition of bacterial growth is given in table 3. The antibacterial activity revealed that the activity of ligand increases on complexation.

Table – 1 : Analytical and Physical data of complexes

Sl. No.	Complex/ Colour, (MF)	Analysis (%) : Found/(Calcd)				Molar conduct ($\Lambda m^{-1} cm^{-2} mol$)
		C	H	N	Metal	
1.	$[Pt(P\phi_3)(LH)_3]$ Golden Brown (PtC ₃₀ H ₄₅ N ₆ O ₆ P ₃)	57.10 (50.92)	4.91 (4.89)	9.10 (9.14)	21.28 (21.21)	18.62
2.	$[Pt(P\phi_3)_3(LH)_3]$ Nut Brown (PtC ₃₀ H ₅₅ N ₂ O ₂ P ₃)	64.44 (64.49)	4.86 (4.84)	2.42 (2.46)	17.10 (17.21)	20.36
3.	$[Pt(P\phi_3)_2(CS_2)(LH)]$ Mid Cream (PtC ₄₀ H ₄₂ N ₂ O ₂ P ₂ S ₂)	55.66 (55.63)	4.22 (4.21)	3.00 (2.95)	20.34 (20.54)	18.30
4.	$[Pd(P\phi_3)_3(LH)_3]$ Leaf Brown (PdC ₃₀ H ₅₇ N ₂ O ₂ P ₃)	71.32 (71.45)	5.21 (5.14)	2.50 (2.52)	9.60 (9.59)	22.32

(LH = $NH_2C_6H_4COONH_4$; AH = $NH_2C_6H_4COOH$)

Table 2 : Major IR and ¹H NMR Spectral data of ligand and complexes

Complex	IR cm ⁻¹			¹ H NMR (δPPM)	
	vasym NH ₂ / (vsym NH ₂)	vasym COO/ (vsym COO)	vM-N	NH ₂ Protons	Aromatic protons
$[Pt(P\phi_3)(LH)_3]$	3400 (s) (3315 m)	1670 (m) (1430 m)	485 m	8.42	7.71-6.56 (multiplet)
$[Pt(P\phi_3)_3(LH)_3]$	3410 (s) (3305 m)	1560 (m) (1415 m)	480 m	8.38	7.75-6.66 (multiplet)
$[Pt(P\phi_3)_2(CS_2)(LH)]$	3415 (s) (3310 m)	1685 (m) (1430 m)	485 m	8.40	7.70-6.60 (multiplet)
$[Pd(P\phi_3)_3(LH)_3]$	3420 (s) (3315 m)	1680 (m) (1435 m)	486 (m)	8.42	7.78-6.68 (multiplet)

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