Synthesis and Characterization of Mixed - Ligand Phosphine and Arsine Complexes of PT-Groups Metals With 2-Aminothiophenol

Chemistry Abstract

KEYWORDS : Low-valent, Pt-metals, Chelates, Spectra

R.N. Pandey P.G. Centre of Chemistry (M.U.), College of Commerce, Patna – 800020, India

Kalpana Shahi P.G. Centre of Chemistry (M.U.), College of Commerce, Patna – 800020, India

Sheo Shankar Kumar P.G. Centre of Chemistry (M.U.), College of Commerce, Patna – 800020, India

ABSTRACT

Convenient synthesis and characterization of some new phosphine and arsine complexes of Pt-metals ligated with 2-aminothiophenol (ATP) with composition $[Rh(E\phi3)2(ATP)]$, (E = P/As), $[M(CO)(E\phi3)(ATP)]$ (M = Rh(I)/ Ir(I); E = P/As), $[MX(E\phi3)(ATP)]$ (M = Pd(II)/Pt(II); X = Cl, Br, I; E = P/As) has been described. The square planar structure of complexes were deduced using elemental analysis, magnetic susceptibility measurement, IR, UV-vis, 1H NMR spectral data. 2-aminothiophenol acts as mononegative bidentate ligand in all complexes.

INTRODUCTION

Metal chelates of 2-aminothiophenol are investigated by several workers.[1-3] Some bis-chelates of transition metals (III)[4], di-oxo-Transition metals[5] and high-valent Niobium (V) and Tantalum (V)[6] of this ligand are reported in our previous report. The present study reports some mixed-ligand phosphine and arsine complexes of Rhodium (I), iridium (I), Platinum (II) and Palladium (II) with 2-aminothiophjenol. The metal-ligand vibrations in far-IR spectra are thoroughly analysed and structure of complexes are deduced using different physic-chemical data.

EXPERIMENTAL

All chemical used for the preparation of precursor complexes were analytical quality and used without further purification. 2-amino-thiophenol (Schuchardt, Munchen) was a commercial product. The starting complexes, $[Rh(E\phi_3)_3Cl]$[7] (E=P/As), $[RhCl(CO)(P\phi_3)_2]$[7], $[IrCl(CO)(P\phi_3)_2]$[8], $[PtX_2(E\phi_3)_2]$[9] (E = P/As; Cl/Br) and $[Pd(E\phi_3)_2Cl_2]$[10] (E = P/As) were prepared by the methods reported in literature.

PREPARATION OF NEW COMPLEXES

Preparation of rhodium (I) complexes

All the complexes were prepared by using a general method. Benzene solution of $[Rh(E\phi_3)_3Cl]$ (E = P/As) or $[RhCl(CO)(P\phi_3)_2]$ and 2-aminothiophenol in ethanol and monoethyl ether of ethylene glycol (1:1) were mixed in equimolar ratio and solid products were isolated following our previous method.[11]

Analysis:

Sl. No. 1 : $[Rh(P\varphi3)2(ATP)]$ (Orange brown) : Calculated (%) for RhC42H36NSP2 (750.91) : C = 67.11; H = 4.79; N = 1.86; Rh = 13.70; Found (%) : C = 67.00; H = 4.81; N = 1.88; Rh = 13.69;

Sl. No. 2 : $[Rh(As\varphi3)2(ATP)]$ (Light yellow-brown) : Calculated (%) for RhC42H36NSAs2 (838.91) : C = 60.07; H = 4.29; N = 1.66; Rh = 12.26; Found (%) : C = 60.11; H = 4.30; N = 1.65; Rh = 12.28;

Sl. No. 3 : $[Rh(CO)(P\varphi3)(ATP)]$ (Yellow-brown) : Calculated (%) for RhC25H21NSOP (516.91) : C = 58.03; H = 4.06; N = 2.71; Rh = 19.90; Found (%) : C = 58.11; H = 4.16; N = 2.78; Rh = 20.01;

Preparation of iridium (I) complexes

Benzene solution of Vaska compound $[IrCl(CO)(P\phi_3)_2]$ or $[Ir(CO)(As\phi_3)_2Cl]$ and ethanolic solution of 2-amino thiophenol were mixed in equimolar ratio and solid products were isolated following our published procedure.[12]

Sl. No. 4 : $[Ir(CO)(P\varphi3)(ATP)]$ (Yellow-brown) : Calculated (%) for IrC25H21NOSP (606.2) : C = 49.48; H = 3.46; N = 2.30; Ir = 31.70; Found (%) : C = 49.49; H = 3.51; N = 2.21; Ir = 31.80;

Sl. No. 5 : $[Ir(CO)(As\varphi3)(ATP)]$ (Faint yellow) : Calculated (%) for IrC25H21OSAs (650.2) : C = 46.13; H = 3.22; N = 2.15; Ir = 29.56; Found (%) : C = 46.21; H = 3.30; N = 2.01; Ir = 29.62;

Preparation of Pt (II) Complexes

Benzene solution of $[PtX_2(E\phi_3)_2]$ (E = P/As; X = Cl, Br, I) and ethanolic solution of 2-aminothiophenol in molar ratio 1:1 were stirred on magnetic stirrer at 85°C for 1h. The solid products were obtained on concentration and cooling the reaction mixture.[13]

Sl. No. 6 : $[PtCl(P\varphi3)(ATP)]$ (Yellow) : Calculated (%) for PtC24H21NSPCl (616.5) : C = 46.71; H = 3.40 ; N = 2.27; Pt = 31.63; Found (%) : C = 46.72; H = 3.50; N = 2.30; Pt = 31.68;

Sl. No. 7 : $[PtCl(As\varphi3)(ATP)]$ (Faint yellow) : Calculated (%) for PtC24H21NSAsCl (660.5) : C = 43.60; H = 3.17; N = 2.11; Pt = 29.52; Found (%) : C = 43.72; H = 3.20; N = 2.20; Pt = 29.56;

Sl. No. 8 : $[PtBr(P\varphi3)(ATP)]$ (Orange) : Calculated (%) for PtC24H21NSPBr (661) : C = 43.57; H = 3.17; N = 2.11; Pt = 29.50; Found (%) : C = 43.67; H = 3.20; N = 2.20; Pt = 29.55;

Sl. No. 9 : $[PtBr(As\varphi3)(ATP)]$ (Light orange) : Calculated (%) for PtC24H21NSAsBr (705) : C = 40.85; H = 2.97; N = 1.98; Pt = 27.25; Found (%) : C = 40.86; H = 3.01; N = 2.01; Pt = 27.30;

Sl. No. 10 : $[PtI(P\varphi3)(ATP)]$ (Brown) : Calculated (%) for PtC24H21NSPI (708) : C = 40.67; H = 2.96; N = 1.97; Pt = 27.54; Found (%) : C = 40.68; H = 3.01; N = 1.69; Pt = 27.62;

Sl. No. 11 : $[PtI(As\varphi3)(ATP)]$ (Pale yellow) : Calculated (%) for PtC24H21NSAsI (749) : C = 38.45; H = 2.80; N = 1.86; Pt = 26.03; Found (%) : C = 38.50; H = 2.82; N = 1.99; Pt = 26.01;

Preparation of Pd(II) Complexes

Benzene solution of $[PdCl_2(E\phi_3)_2]$ (E = P/As) and methanolic solution of 2-aminothiophenol were mixed in equimolar ratio and solid products were isolated following our previous method reported in literature.[11]

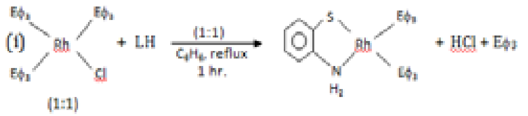
Sl. No. 12 : $[PdCl(P\varphi3)(ATP)]$ (Yellow) : Calculated (%) for PdC24H21NSPCl (528) : C = 54.54; H = 3.97; N = 2.65; Pd = 20.15; Found (%) : C = 54.50; H = 4.01; N = 2.60; Pd = 20.01;

Sl. No. 13 : $[PdCl(As\varphi3)(ATP)]$ (Faint yellow) : Calculated (%) for PdC24H21NSAsCl (572) : C = 50.34; H = 3.67; N = 2.44; Pd = 18.60; Found (%) : C = 50.30; H = 3.66; N = 2.11; Pd = 18.75;

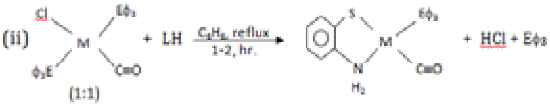
Elemental analyses, spectral, conductance and magnetic data were obtained as reported in our previous paper.[5]

RESULTS AND DISCUSSION

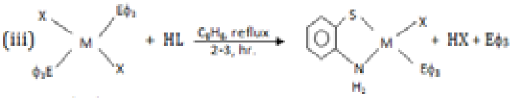
All precursors complexes display ligand substitution reaction in benzene without change in oxidation state of metal and analytical results were satisfactory and consistent with proposed stoichiometry (Str. I to Str. III). All isolated solid products were non-hygroscopic stable solid and soluble in DMF, DMSO and other coordinating solvents. The oxidation state of univalent rhodium in complexes were verified by titrating the complexes with ceric ammonium sulphate using ferroin as indicator.[14] The complexes were titrated for two electron charge. All complexes were diamagnetic indicating, Rh^+ (d^8), Ir^+ (d^8), Pt^{++} (d^8) and Pd^{++} (d^8) species in square planar configuration. The molar conductance in DMF (10^{-3} M) was found to be less than 15 $\wedge^{-1}cm^2mol^{-1}$ suggesting their non-electrolyte nature.[15]



(E = P/As; LH = ATP)
(Str. I)



(M = Rh/Ir; E = P/As; LH = ATP)
(Str. II)



(M = Pt, E = P/As, X = Cl, Br, I; LH = ATP
and M = Pd, E = P/As, X = Cl, LH = ATP)
(Str. III)

Electronic Spectra

The electronic spectrum of 2-aminothiophenol showed two high intensity bands lying at 32260 cm^{-1} and 30485 cm^{-1} assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition. Electronic spectra of Pd(II) complexes display bands at 18550 cm^{-1} ($^1A_{1g} \rightarrow {}^1B_{1g}$), 27800 cm^{-1} ($^1A_{1g} \rightarrow {}^1E_g$) and high intensity band at 37800 cm^{-1} (CT band) consistent with square planar geometry.[16-18] The d-d transition bands from the spectra of Pt(II) complexes having low intensity around 23250 cm^{-1} assignable to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition similar to planar complexes reported by Gray et al[19]. Electronic spectra of rhodium (I) complexes exhibits three bands at 13850, 18350 and 23750 cm^{-1}. The first band (13850 cm^{-1}) is broad and weak while at 18350 cm^{-1} and 23750 cm^{-1} are of medium intensity bands. The first band may be due to spin-forbidden $^1A_{1g} \rightarrow {}^3A_{2g}$ transition. The other band at 18350 cm^{-1} may be due to spin allowed $^1A_{1g} \rightarrow {}^1B_{1g}$ transition. The third band (23750 cm^{-1}) could not be assigned. Dutta et al[20] and Vaska et al[21] have characterized square planar rhodium (I) complexes by its band in the region 25000 – 28000 cm^{-1} due to T_{2g} (Metal) → π^* (ligand). Martin et al[14] have assigned a band in the region 20000 cm^{-1} for square planar Rh(I) complexes. The square planar geometry may be reasonably assigned considering previous literature.[22-24] Electronic spectra of iridium (I) complexes display a single band of very strong broad high intensity band at 27850 cm^{-1} and other ligand field bands are obscured. Ir^+ is strong reducing and high degree of d-p mixing may be assumed.[11-13]

IR Spectra

The IR spectrum of 2-aminothiophenol shows ν_{asy} NH_2 (3460 cm^{-1}) and ν_{sym} NH_2 (3340 cm^{-1}) red shift to lower frequency and observed at 3310 – 3315 cm^{-1} and 3410 – 3415 cm^{-1} respectively on complexation indicating Metal – N bond. New bands between 510 – 500 cm-1 support formation of of Metal-N bond and assigned to M-N stretch mode. The ν_{SH} (2560 cm^{-1}) is not found in spectra of complexes indicating coordination through deprotonated sulphur.[3] 2-aminothiophenol acts amononegative bidentate anion in all complexes (Str. I, II & III). The metal sensitive characteristic bands at 1450, 1090, 1000 and 750 cm^{-1} ($As\phi_3$) and at 1085, 505, 430, 395, 247 and 210 cm^{-1} ($P\phi_3$) were also present in the expected region.[25-27] The non-ligand new band at 2020 cm^{-1} in $[Rh(CO)(P\phi_3)(ATP)]$[28] and at 1905 cm-1 in $[Ir(CO)(P\phi_3)(ATP)]$[29] agreement with previous literature due to terminal carbonyl group.

^{1}H NMR Spectra

The free 2-aminothiophenol exhibits signals at δ 3.68 PPM due to intramolecularly hydrogen bonded thiol proton. This proton signal disappeared on complexation indicating the formation of Metal-S bond.[30] The aromatic protons signals of ligand (ATP) are observed in the range of δ 6.64–7.30 complex multiplet are slightly low field shifted and the integrated intensities of these signals agree well with the formation of complexes. The amino proton signals of ligand (ATP) observed at δ 3.68 PPM are low field shifted on complexation and the integrated intensities of the signals agree. All the complexes showed signals in the δ 8.2 – 8.88 PPM range due to aromatic protons of $P\phi_3/As\phi_3$.[31]

Table-1 : Characteristic and diagnostic IR Spectral bands of ligand (ATP) and complexes (cm^{-1})

Compounds	ν_{asym} NH_2	ν_{sym} NH_2	ν_{SH}	$\nu_{C\equiv O}$	$\nu_{M\text{-}Cl}$	$\nu_{M\text{-}S}$
ATP (ligand)	3460 (m)	3340 (m)	2560 (m)	-	-	-
$[Rh(P\varphi_3)_2(ATP)]$	3420 (m)	3310 (m)	-	-	-	310 w
$[Rh(As\varphi_3)_2(ATP)]$	3410 (m)	3315 (m)	-	-	-	315 w
$[Rh(CO)(P\varphi_3)(ATP)]$	3415 (m)	3310 (m)	-	2010 (m)	-	310 w
$[Ir(CO)(P\varphi_3)(ATP)]$	3420 (m)	3312 (m)	-	1915 (m)	-	303 w
$[Ir(CO)(As\varphi_3)(ATP)]$	3415 (m)	3315 (m)	-	1905 (m)	-	305 w
$[PtCl(P\varphi_3)(ATP)]$	3425 (m)	3310 (m)	-	-	335 m 295 m	310 w
$[PtCl(As\varphi_3)(ATP)]$	3418 (m)	3320 (m)	-	-	346 m	320 w
$[PtBr(P\varphi_3)(ATP)]$	3415 (m)	3315 (m)	-	-	315 m 285 m	320 w
$[PtBr(As\varphi_3)(ATP)]$	3420 (m)	3310 (m)	-	-	320 m 285 m	325 w
$[PtI(P\varphi_3)(ATP)]$	3405 (m)	3315 (m)	-	-	295 m 280 w	330 w
$[PtI(As\varphi_3)(ATP)]$	3415 (m)	3315 (m)	-	-	300 w 295 w	325 w
$[PdCl(P\varphi_3)(ATP)]$	3410 (m)	3315 (m)	-	-	325 w 315 w	360 w
$[PdCl(As\varphi_3)(ATP)]$	3420 (m)	3315 (m)	-	-	360 w 340 w	365 w

Table-2 : ^{1}H NMR and Electronic spectra of selected complexes and ligand

Compound	Electronic spectra (cm^{-1})	1H NMR Spectra (δPPM)		
	λ_{max} (Assignments)	Amino Proton	Phenyl Proton	Thiol Proton
ATP (ligand)	32260 ($\pi \rightarrow \pi^*$) 30485 ($n \rightarrow \pi^*$)	3.68	6.64-7.22 (multiplet)	3.66
[Rh($P\varphi_3$)$_2$(ATP)]	23750 ($T_{2g} \rightarrow \pi^*$)/CT Band 18350 ($^1A_{1g} \rightarrow {}^1B_{1g}$) 13850 ($^1A_{1g} \rightarrow {}^3T_{1g}$)	3.55	6.62-7.10 (multiplet)	-
[Rh($As\varphi_3$)$_2$(ATP)]	23830 ($T_{2g} \rightarrow \pi^*$)/CT Band 18360 ($^1A_{1g} \rightarrow {}^1B_{1g}$) 13960 ($^1A_{1g} \rightarrow {}^3T_{1g}$)	3.56	6,40-6.92 (multiplet)	-
[Ir(CO)($P\varphi_3$)(ATP)]	37040-3720 (CT Band) 26620 ($T_{2g} \rightarrow \pi^*$)	3.11-4.41	6.61-6.68 (multiplet)	-
[PtCl($P\varphi_3$)(ATP)]	38460 CT Band 27710 ($^1A_{1g} \rightarrow {}^1B_{1g}$) 31238 ($^1A_{1g} \rightarrow {}^1E_g$)/CT Band	3.40	6,45-6.68 (multiplet)	-
[PtCl($As\varphi_3$)(ATP)]	37730 CT Band 24390 ($^1A_{1g} \rightarrow {}^1B_{1g}$) 32330 ($^1A_{1g} \rightarrow {}^1E_g$)/CT Band	3.52	6.52-7.11 (multiplet)	-
[PdCl($P\varphi_3$)(ATP)]	37800 CT Band 27800 ($^1A_{1g} \rightarrow {}^1E_g$) 18550 ($^1A_{1g} \rightarrow {}^1B_{1g}$)	3.67	6.60-7.10 (multiplet)	-
[PdCl($As\varphi_3$)(ATP)]	37810 CT Band 27770 ($^1A_{1g} \rightarrow {}^1E_g$) 18970 ($^1A_{1g} \rightarrow {}^1B_{1g}$)	3.66	6.56-6.68 (multiplet)	-

REFERENCE

1. L.F. Larkworthy, J.M. Murphy and D.J. Phillips, Inorg. Chem. 7, 1436 (1968). | 2. R. John Wasson, J. Shirley Wasson and M. Gerald, Wattermann. Inorg. Chem. 9, 1576, (19670). | 3. B. Singh and R.V. Choudhary, Indian J. Chem. Vol. 13, 926 (1975). | 4. R.N. Pandey and A.K. Nag, J. Ultra Chem. Vol. 8(3), 329 (2012). | 5. R.N. Pandey and Pramila Sharma, J. Ultra Scientist, Vol. 25(I) B, 157 (2013). | 6. R.N. Pandey and Pramila Sharma, Oriental J. Chem. Vol 29(2), 673 (2013). | 7. J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A, 1711 (1966). | 8. L. Vaska and J.W. DI Luzio, J. Am. Chem. Soc. 83, 2784 (1961). | 9. L. Malatesta and C. Cariello, J. Chem. Soc. 2323 (1958). | 10. N. Miyaura and A. Suzuki, Org. Synth, Coll. Vol. 8, 532 (1993). | 11. R.N. Pandey, Arun Kumar, R.S.P. Singh, A.N. Sahay and Shashi Kant Kumar, J. Indian Chem. Soc. Vol. 69, 804 (1992). | 12. R.N. Pandey and Shashikant Kumar, J. Indian Chem. Soc. 70, 563 (1993). | 13. R.N. Pandey, Sunil Kumar, Shashikant Kumar, (Miss) Rita Roy Choudhary, and A.N. Sahay, Indian J. Chem. Vol. 32A, 987 (1993). | 14. B. Martin, W.R. Mc Whinnie and G.H. Waind, J. Inorg. Nucl. Chem. 23, 207 (1961). | 15. W.J. Geary, Coord. Chem. Rev. 7, 8 (1971). | 16. S. Chandra and R. Singh, Indian J. Chem. Sect A, 27, 417 (1988). | 17. R.N. Pandey and Renu Bala, J. Ultra Chem. Vol 7(1), 1 (2011). | 18. S. Das and S. Pal, J. Organomet. Chem. 689, 352 (2004). | 19. W.R. Mason and H.B. Gray, J. Am. Chem. Soc. 90, 5721 (1968). | 20. D.K. Dutta and M.M. Singh, Transition Met. Chem. 5, 244 (1980). | 21. R. Bondy, B.R. Flynn, G.L. Geoffary, H.B. Gray, J. Peonl (Jr) and L. Vaske, Inorg. Chem. 15, 1485 (1975). | 22. T. Ramasami and J.E. Espenson, Inorg. Chem. 19, 1523 (1980). | 23. R.N. Pandey and R.N. Sharma, J. Ind. Council Chem. Vol. 27(2), 223 (2010). | 24. R.N. Pandey and A.K. Nag, Rasayan J. Chem. Vol. 4(1), 142 (2011). | 25. D.H. Brown, A. Mohammad and D.W.A. Sharp, Spectrochim. Acta, 21, 663 (1965). | 26. K. Shobalake, C. Postmus, J.R. Ferraro and K. Nakamoto, Appl. Spectrosc. 23, 12 (1969). | 27. M.S. El-Shahawi and A.F. Shoair, Spectrochim. Acta, Part A, 60, 121 (2004). | 28. R.N. Pandey, D.P. Singh, Priya and R.K. Singh, Oriental J. Chem. Vol. 26(4), 1513 (2010). | 29. R. Uson, L.A. Oro and M. Fernanadez, J. Organomet. Chem. 193, 127 (1980). | 30. J.L. Burmrister, Coord. Chem. Rev. 1, 205 (1966), 3, 255 (1968). | 31. S. Kanchanadevi, K.P. Balasubramanian, V. Chinnusamy, R. Karvembu and K. Natarajan, Trans. Met. Chem. 30, 330 (2005). |