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Spectral and Biological Evaluation of some Organoiridium (1) derivatives ligated by heterocyclic thioamides

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Abstract

Some organoiridium(1) complexes with Para Substituted phenyl derivatives of 1- Substituted tetrazoline-5-thione have been prepared and characterized using elemental analysis, IR, Uv-vis. 'HMR and other physico-chemical data. All complexes are Square Pyramidal and the basal position is occupied by bulky $P\phi_3$, $SnCl_3^-$ and tetrazole ligands considering steric preferences. The antifungal activity of organoiridium (1) complexes against A. niger, A. Flavus and C. Albicans and antimicrobial activity against E. coli, S. enteritidis, S. aurens and S. epidermitis are examined.

Key words : Organoiridium(1), antimicrobial, antifungal, Heterocyclic Thicamides.

Introduction

Thioamides exhibit versatile coordination behaviour[1-4]. Cowper *et.al.*[5] have reported antimicrobial activity of some 1,2,4-tetrazoles having thiamide group. These compounds are claimed to possess anti-convulsant[6], radioprotective[7], spermatostatic[8] and many other potential biological activity[9-11]. The present investigation describes, preparation, spectral characterization and biological screening of some organo-iridium (I) complexes of 1-para substituted phenyl-tetrazoline-5-thiones. The antifungal activities against A. niger, A. Flavus and C. Albicans and antimicrobial activities against E. coli, S. enteritidis, S. aurens and S. epidermitis of isolated products organoiridium (1) compounds have been reported herein.

Experimental

All the chemicals used were of CP grade or AR grade. 1-substituted tetrazoline-5-thiones were prepared by the method of Lieber *et. al.*[12] and organoiridium(I) compounds were prepared by our previous method reported in literature[13]. Elemental analysis, magnetic measurements conductivity, IR, UV-Vis, 'H NMR Spectral data were obtained as we have reported earlier[14].

Analysis :

S.L. No.1: [Ir H(CO)($P\phi_3$)(P-CH_3-L)$_2$]: Yellowish Brown (M.Pt.=173°C): Calculated (%) for **$IrC_{35}H_{32}ON_8PS_2$** : C=48.40; H= 3.68; N= 12.9; Ir = 22.10; Found (%) : C = 48.34; H = 3.65; N = 12.32; Ir = 22.20

S.L. No.2: [Ir H(CO)($P\phi_3$)(P-CH_3O-L)$_2$]: Yellowish Brown (M.Pt.=187°C) Calculated (%) for **$IrC_{35}H_{32}O_3N_8PS_2$** : C=46.70; H=3.55; N= 12.45; Ir = 21.37; Found (%) : C = 46.68; H = 3.56; N = 12.50; Ir = 21.32

S.L. No.3: [IrH(CO)($P\phi_3$)(P-CH_3CH_2O-L)$_2$]: Yellowish Brown (M.Pt.= 172°C) : Calculated (%) for **$IrC_{37}H_{36}N_8O_2S_2P$** : C = 47.88; H= 3.88; N= 12.07; Ir = 20.72;

S.L. No.4:[$IrSnCl_3$)(CO)($P\phi_3$)(P-CH_3CH_2O-L)$_2$]: Yellow (M.Pt.= 172°C) Calculated (%) for $IrC_{37}H_{35}N_8O_3S_2PCl_3Sn$: C=38.56; H=3.03; N= 9.72; Ir = 16.69; Found (%) : C = 38.55; H = 3.31; N = 9.58; Ir = 16.70

S.L. No.5: [Ir H(CO)($P\phi_3$)(P-Cl-L)$_2$]: Brownish Grey (M.Pt.= 168°C) : Calculated (%) for **$IrC_{33}H_{26}N_8O_3S_2Cl_2P$** : C = 42.11; H= 2.76; N= 11.91; Ir = 20.44; Found (%) : C = 42.32; H = 2.70; N = 11.96; Ir = 20.50

Results and Discussion

Elemental analysis correspond to [IrH(CO)($P\phi_3$)(ligand)$_2$] stoichiometry. Molar conductance of complexes were found to be less than $10\Omega^{-1}$ cm^2 mol^{-1} in DMF suggesting their non-electrolytic nature. The molecular weight of complexes were determined cryoscopically in highly purified C_6H_6 and indicated them to be monomeric. All the freshly prepared complexes were appreciably soluble in non polar solvents but less solubility was observed in non-polar solvents after long standing in air. The diamagnetic value of magnetic moment indicated univalent iridium (d^8) and basic Square- Pyramidal configuration was assumed considering previous literature[15]. The violet colour of iodine solution in CCl_4 was discharged by all complexes supporting $Ir^+(d^8)$ species. However, oxidation state of iridium was verified iodometrically following the method reported in literature[16].

Electronic spectra of complexes display only a one very strong broad band between 42560-34040 cm^{-1} assigned to charge transfer. The other ligand field bands are obscured by CT band. However, two strong bands at 44240 cm^{-1} and 38160 cm^{-1} in [Ir H(CO)($P\phi_3$)(P-Cl-L)$_2$] are observed. The first band may be entirely of charge transfer origin and the second band presumably because to $1A_{1g} \rightarrow 1B_{1g}$ transition considering M.O. diagramme of Square-Pyramidal (C_4V) configuration.

Infra red Spectra :

A comparision of the IR Spectral bands of the ligands and complexes indicate the following :

(i) Thioamide band IV mainly due to $\upsilon C = S$ mode undergoes considerable red shift of 25-50 cm^{-1} on complexation suggesting bonding through thiocarbonyl sulphur of ligand[17-18].

(ii) The systematic shift (Table 1) of other thioamide bands of ligand also support bonding through thiocarbonyl sulphur which results increase in multiplicity of CN bond and decrease in bond multiplicity of CS bond having bonding through thione tautomeric form of ligand and the degeneracy of thioamide bands is disturbed[19].

(iii) The non-ligand bands around 1990 cm^{-1} and 690 cm^{-1} assigned to υIr-H and δIr-H modes[20]. New band of medium intensity around 1890cm^{-1} assigned to $C \overleftarrow{=} O$ modes of coordinated carbonyl group[21]. The $\upsilon C \overleftarrow{=} O$ mode is observed at higher frequency (2020 cm^{-1}) in [Ir H(CO)($P\phi_3$)(CH_3CH_2O-L)$_2$($SnCl_3$)] and Ir-C bond (540 & 520 cm^{-1}) in [Ir H(CO)($P\phi_3$)(P-CH_3CH_2O-L)$_2$($SnCl_3$)] is stronger than Ir-C bond (500 & 460 cm^{-1}) in [Ir H(CO)($P\phi_3$)(P-CH_3CH_2O-L)$_2$]. Hence, the Carbonyl group is probably of shorter distance at apical position in Square Pyramidal configuration of former complexes and bulky tetrazoles, $P\phi_3$ and may occupy basal position considering steric preference. Since π-bonding is more favourable along Z-axis, the apical position of π-ligand like CO seems to be reasonable and trans-arrangement for bulky heterocyclic thioamide ligands considering straight- jacket effect.

(iv) Two week bands at 455 and 435 cm^{-1} in far infrared Spectrum of [Ir (CO)($P\phi_3$)(CH_3CH_2O-L)$_2$($SnCl_3$)] are assigned to υSnCl. The υSnCl of free are generally observed at 289 and 255 cm^{-1} and shifted to higher frequencies upon coordination to metal ion[22]. Boschi *et. al.*[23] have observed similar observations for coordinated ion.

(v) The presence of one Ir-S stretching mode at 285 indicates two tetrazole ligands at trans in Square Pyramidal configuration.

'H NMR Spectra :

The 'H NMR Spectra of ligands and corresponding complexes (Sl. no. 1 & 2) were recorded in $CDCl_3$/ TMS to substantiate further mode of metal- ligand bonding. All complexes display broad multiplet in the region δ7.42 to δ7.72 PPM due to phenyl protons of ligands. The broad nature of peak may be probably due to large quadrupole resonance broadening effect of tetrazole nitrogen atoms or ligand exchange reaction occuring in solution[24]. The methyl protons, methoxy protons and imino proton observed at δ2.4 PPM, 3.74 PPM and at δ1.25 PPM respectively in the Spectrum of ligands are almost at the same position indicating that they are intact on coordination to Ir(I)ion. Thus, imino proton is intact and deprotonation has not occured on complexation. These observations are consistent with conclusions drawn from IR Spectral data.

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

Compd. P-CH_3-L (ligand)	υIr-H/ (δIr-H)	υC=O/ (υIr-C)	Thioamide Bands			
			Band I 1505(S)	Band II 1290 m	Band III 1060 m	Band IV 800 m
[IrH(CO)(Pϕ_3)(P-CH_3-L)$_2$]	2000(m) (690 m)	1895(m) 485(m)	1510(s)	1270(m)	1035m	750 m
P-CH_3O-L(ligand)	- (-)	- (-)	1512(s)	1305(m)	1065(m)	805(m)
[IrH(CO)(Pϕ_3)(P-CH_3O-L)$_2$]	2010 m (710 m)	1905 (m) (485 m)	1515 (s)	1270 (m)	1035 (m)	785 (m)
P-Cl-L (ligand)	-	-	1498(s)	1310(m)	1050 m	770 (m)
[IrH(CO)(Pϕ_3)(P-Cl-L)$_2$]	2015(m) (715 m)	1910 m (490 m)	1505 (s)	1265 (m)	1030 (m)	790 (m)
P-CH_3CH_2O-L(ligand)	- (-)	- (-)	1515(s)	1315(m)	1060 (m)	790 (m)
[IrH(CO)(Pϕ_3)(P-CH_3CH_2O-L)$_2$]	2010 (m) (720 m)		1520 (s)	1270 (m)	1040 (m)	740 (m)
[Ir(CO)(Pϕ_3)(P-CH_3CH_2O-L)$_2$ $SnCl_3$]	- (-)		1505 (s)	1275	1035 (m)	735 (m)

L = 1-Phenyl tetrazoline-5-thione

Microbiological Studies :

All ligands and complexes were examined for their antimicrobial activity against bacteria viz. E. coli, S. aureus S. enteritis and S. epidermitis using disc diffusion method[25]. Standard antibiotic amikacin, ctrioxone, Erythromycin and tetracycline were used under similar conditions at 37°C for 48 hours. The antifungal activity of complexes were done by serial dilution method[26] in DMF solvent between 50-200 μgml^{-1} against Fungi, Viz A. niger, A. Flavus and C. Albicans. The results of antibacterial and antifungal activity are given in table 2 and 3 respectively.

Complexes exhibit slightly higher antimicrobial activity than free ligands (Table 2). Such increased activity of complexes can be explained on the basis of overtones concept[27] and Tweedys chelation theory[28]. The antibacterial activity on complexation reduces the polarity of the central metal ion by partial sharing of its positive charge with the donor groups increasing lipophilic nature of the central atom which increase permeability across the lipid membrane[29-30]

All the organoiridium(I) complexes screened showed moderate toxicity to fungal samples but their activity decreases considerably upon dilution. The presence of chlorine atom in ligand increases fungitoxicity.

Table 2. Antimicrobial activities of ligands and organoiridium compounds :- (20 μgml^{-1})

Compounds	E. Coli	S. enteritidis	S. aurens	S. epidermitis
P-CH_3-L (Ligand)	-	+	++	+
Complex (Sl. No. 1)	+	++	+++	++
P-Cl-L (ligand)	+	++	++	+
Complex (Sl. No. 5)	++	+++	++++	++
P-CH_3O-L (Ligand)	-	NT	++	NT
Complex (Sl. No. 2)	+	NT	+++	NT
P-CH_3CH_2O-L (Ligand)	-	+	++	NT
Complex (Sl. No. 3)	+	++	+++	NT
Complex (Sl. No. 4)	++	+	+++	NT
Amikacin (stand)	+++	++	++	++
Ctrioxone (stand)	++	+++	+++	++
Erythromycine (stand)	++	+++	+++	++
Tetracycline (stand)	+	+	++	+

Inhibition diameter in mm; (+) 10-15 mm; (++) 15-20 mm; (+++) 20-30 mm; (-) inactive (inhibitionzone < 10 mm); NT = not Tested.

Table 3. Antimicrobial % inhibition of complexes :- (μgml^{-1})

Complex	A. niger			A. Flavus			B. Albicans		
	50	100	200	50	100	200	50	100	200
P-CH_3-L (Sl. No. 1)	+	+	++	+	+	++	+	++	++
P-Cl-L (Sl. No. 5)	++	++	++++	++	++	+++	++	++	+++
P-CH_3O-L (Sl. No. 2)	+	++	++	+	++	++	+	++	+++
P-CH_3CH_2O-L (Sl. No. 4)	+	++	+++	NT	NT	NT	NT	NT	NT
Griscofulvin (stand)	++	+++	++++	++	++	+++	++	+++	++++

Inhibition diameter in mm; (-) not effective, (NT), not tested (+) 10-15 mm; (++) 15-20 mm; (+++) 20-25 mm; (++++) (25-29) mm.

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