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Structural and Antifungal Evaluation of Palladium(II) Complexes Ligated by Triphenyl Phosphine and Isomeric 1-substituted phenyl tetrazoline-5-thione

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ABSTRACT

A series of phosphine complexes of palladium (II) ligated with 1-substituted phenyl tetrazoline-5-thione have been prepared and identification of complexes are established on the basis of elemental analysis, magnetic susceptibility, conductivity, IR, UV-vis and ^{1}H NMR spectral data. The phenyl ring was substituted to correlate the electronic effect of such substituents on the magnitude of the anti-fungal activity against Aspergillus favus species.

Key words: Palladium (II), Thioamides, antifungal activity, structure and Bonding

INTRODUCTION

The relationship between structural and biological properties of metal complexes with thioamide ligands has been reviewed by West et.al.[1] Several Palladium (II) complexes having thioamide ligands are reported to be potential anti-tumor activity[2-3] and significant antifungal activity[4]. Cowper and Co-workers[5] have examined the antimicrobial activity of some 1,2,3,4-Tetrazole having thioamide group. The present paper aims at structural and biological evaluation of some Palladium (II) complexes ligated by 1-substituted phenyl- tetrazoline-5-thione. The phenyl ring was substituted at various locations with methyl and chloro groups to correlate the electronic effect of such substituents on the magnitude of the bio-activities.

The identification of all Palladium (II) complexes have been established on the basis of elemental analysis, Magnetic, conductivity, IR, UV-vis and ^{1}H NMR spectral data.

EXPERIMENTAL

All the chemicals used were of AR grade or CP grade. The ligand, 1-substituted tetrazoline-5-thione[6] and complexes[7] were prepared by the method reported in literature. Elemental analysis, magnetic measurements, IR, UV-vis and ^{1}H NMR spectral data were obtained as reported in our previous paper.[8]

Analysis

Sl. No. 1 : $[Pd(P\phi_3)_2(P\text{-}CH_3\text{-}L)_2]Cl_2$ (Yellow) :
Calculated (%) for $C_{52}H_{46}N_8P_2S_2Cl_2Pd$: C, 57.51; H, 4.23; N, 10.32; Pd, 9.76;
Found (%) : C, 57.46; H, 4.33; N, 10.52; Pd, 10.02;

Sl. No. 2 : $[Pd(P\phi_3)(H_2O)(P\text{-}CH_3\text{-}L)_2](NO_3)_2$ (Yellow) :
Calculated (%) for $C_{34}H_{33}N_{10}O_7S_2P.Pd$: C, 45.63; H, 3.69; N, 15.65; Pd, 11.85; Found (%) : C, 45.83; H, 3.70; N, 15.50; Pd, 12.01;

Sl. No. 3 : $[Pd(P\phi_3)_2(P\text{-}Cl\text{-}L)_2]Cl_2$ (Yellow) :
Calculated (%) for $C_{50}H_{40}N_8P_2S_2Cl_4Pd$: C, 53.28; H, 3.55; N, 9.94; Pd, 9.41;
Found (%) : C, 53.25; H, 3,56; N, 10.10; Pd, 9.45;

Sl. No. 4 : $[Pd(P\phi_3)_2(O\text{-}Cl\text{-}L)_2](NO_3)_2$ (Yellow) :
Calculated (%) for $C_{50}H_{40}N_{10}O_6P_2S_2Pd$: C, 50.89; H, 3.39; N, 11.87; Pd, 8.99;
Found (%) : C, 50.91; H, 3.41; N, 11.88; Pd, 8.88;

Sl. No. 5 : $[Pd(P\phi_3)(H_2O)(P\text{-}Cl\text{-}L)_2](NO_3)_2$ (Yellow) :
Calculated (%) for $C_{32}H_{27}N_{10}O_7S_2Cl_2P.Pd$: C, 41.06; H, 2.88; N, 14.97; Pd, 11.33; Found (%) : C, 41.26; H, 2.98; N, 14.63; Pd, 11.35;

Sl. No. 6 : $[Pd(P\phi_3)_2(P\text{-}Cl\text{-}L)_2]Cl_2$ (Yellow) :
Calculated (%) for $C_{50}H_{40}N_8P_2S_2Cl_4Pd$: C, 53.28; H, 3.55; N, 9.94; Pd, 9.41;
Found (%) : C, 53.33; H, 3.58; N, 10.20; Pd, 9.48;

Sl. No. 7 : $[Pd(P\phi_3)_2(M\text{-}CH_3\text{-}L)_2]Cl_2$ (Yellow) :
Calculated (%) for $C_{52}H_{46}N_8P_2S_2Cl_2Pd$: C, 57.51; H, 4.23; N, 10.32; Pd, 9.76;
Found (%) : C, 57.66; H, 4.42; N, 10.35; Pd, 10.02;

Sl. No. 8 : $[Pd(P\phi_3)_2(O\text{-}CH_3\text{-}L)_2]Cl_2$ (Yellow) :
Calculated (%) for $C_{52}H_{46}N_8P_2S_2Cl_2Pd$: C, 57.52; H, 4.23; N, 10.32; Pd, 9.76;
Found (%) : C, 57.62; H, 4.40; N, 10.52; Pd, 10.02;

Sl. No. 9 : $[Pd(P\phi_3)(H_2O)(O\text{-}Cl\text{-}L)_2](NO_3)_2$ (Yellow) :
Calculated (%) for $C_{32}H_{27}N_{10}O_7S_2Cl_2PPd$: C, 41.06; H, 2.88; N, 14.97; Pd, 11.33; Found (%) : C, 41.22; H, 2.80; N, 14.96; Pd, 11.50;

RESULTS AND DISCUSSION

The analytical data of complexes are consistent with proposed stiochiometries. The molar conductance of complexes was measured in DMF (10^{-3} M) which indicate them uni-bivalent electrolyte and value was found between 170-181.5 $\Lambda^{-1}cm^2mol^{-1}$. This indicates the presence of ionic chloride and ionic nitrate in complexes. The chemical analysis of sodium extract solution of complexes and infrared spectra further confirmed the presence of anions in the outer sphere of all complexes.

The d – d transition bands in the electronic spectra of complexes at 26980 – 27770 cm^{-1} ($^1A_{1g} \rightarrow {}^1E_g$), 22600 – 23820 cm^{-1} ($^1A_{1g} \rightarrow {}^1B_{1g}$) and at 21670 – 21690 ($^1A_{1g} \rightarrow {}^1A_{2g}$) are in agreement with the transition suggested for four coordinated Palladium (II) complexes having square planar structure[9-10]. The diamagnetic behavior of complexes also supports the square planar structure of complexes. The other bands in ultra-violet region are assigned to intra-ligand charge transfer.

IR Spectra

Considering thioamide function of ligands and complexes (table 1) and nature of shift of thioamide bands indicates thioamide-sulphur coordination[11-13]. Thioamide band IV with high ν_{CS} character red shift to lower frequency on complexation[13-15]. Further evidence in support of the coordination of thione sulphur of thioamide moiety is provided by presence of new Pd – S stretching vibration in the low-frequency IR spectra. The single ν_{Pd-S} bands at 320 – 325 cm^{-1} confirms two thioamide ligands at their trans disposition in square planar geometry[16-17]. The presence single Pd – P stretching mode also supports two $P\phi_3$ ligands are at Trans in square planar structure.

The presence of ionic nature of nitrate anion in complexes (Sl. No. 2, 4, 5 & 9) is indicated by non-ligand bands at 1360 cm^{-1} and 795 cm^{-1} and presence of coordinated water molecule in complexes (Sl. No. 2, 5 & 9) at 3440 cm-1 (νH_2O), 1605 cm-1 (δH_2O), 790 cm^{-1} (πH_2O) and 480 cm^{-1} (ν_{Pd-O}). These assignments are consistent with our previous report[10].

^{1}H NMR spectra

The ^{1}H NMR spectra of ligands and complexes were recorded in $CDCl_3$/TMS to substantiate further mode of metal-ligand bonding. All the complexes showed broad signals in the range

Table 1: Major IR and ^{1}H NMR Spectral data of ligands and Palladium (II) complexes

Compounds	IR (cm^{-1}) Thioamide Bands						^{1}H NMR (PPM)		
	Band I	Band II	Band III	Band IV	ν_{Pd-S}/ (ν_{Pd-P})	ν_{Pd-O}	Imino proton	Methyl proton	Phenyl proton
O-CH_3-L (ligand)	1500 (m)	1290 (m)	1025 (m)	810 (m)	- (-)	-	1.25	2.40	7.30 – 7.85
Complex (Sl. No. 8)	1510 (m)	1285 (m)	1005 (m)	780 (m)	320 w (430 m)	480 (m)	1.23 1.52	2.94	7.45
M-CH_3-L (ligand)	1500 (s)	1280 (ms)	1060 (m)	790 (m)	- (-)	-	1.20	2.26	7.50
Complex (Sl. No. 7)	1515 (m)	1270 (s)	1035	780 (m)	310 w (425 m)	485 (m)	1.21 2.53	2.94	7.46
P-CH_3-L (ligand)	1500 (ms)	1280 (s)	1044 (m)	810 (m)	- (-)	-	1.25	2.40	7.31 – 7.82
Complex (Sl. No. 9)	1510 (m)	1290 (m)	1030 (m)	750 (m)	325 w (430 m)	480 (m)	1.42 1.72	2.85	7.65
Complex (Sl. No. 2)	1515 (m)	1295 (m)	1020 (m)	765 (m)	330 w (435 m)	485 (m)	1.50 2.20	2.88	7.65
P-Cl-L (ligand)	1498 (m)	1280 (s)	1055 (m)	780 (m)	- (-)	-	1.28	-	7.40 – 8.30
Complex (Sl. No. 3)	1500 (m)	1295 (m)	1030 (m)	750 (m)	335 w (430 m)	480 (m)	1.45	-	7.28 – 7.85
Complex (Sl. No. 4)	1510 (m)	1280 (s)	1020 (m)	755 (m)	330 w (435 m)	482 (m)	1.42	-	7.45 – 7.82
Complex (Sl. No. 5)	1515 (m)	1285 (m)	1025 (m)	760 (m)	335 w (440 m)	480 (m)	1.45	-	7.45 – 7.84
O-Cl-L (ligand)	1500 (m)	1290 (m)	1025 (m)	810 (m)	- (-)	-	1.25	-	7.50 – 9.68
Complex (Sl. No. 6)	1510 (m)	1295 (m)	1015 (m)	780 (m)	332 w (425 m)	485 (m)	1.22 2.53	-	7.52 – 8.95

δ8.22 – 8.85 PPM range due to aromatic protons of $P\phi_3$ molecule[18]. The broad multiplet in the region 7.30 – 7.84 PPM due to phenyl protons of both ligands and complexes. The broad nature of peak may be due to the presence of four nitrogen atoms which display large quadrupole resonance broadening effect[19]. The methyl protons and imino protons of ligands are observed almost at the same positions at δ 2.40 – 2.94 PPM and δ1.25 – 1.42 PPM respectively. This indicates that imino proton is intact and deprotonation has not occurred on complexation and coordination occurs only through thione sulphur. This is consistent with IR spectral results.

Antifungal activity

All Palladium (II) complexes were screened for their antifungal activity against Aspergllus flavus, a common fungicide using cup-plate method reported in literature[20]. The solvent used was DMSO. The inhibition zone formed around each filter paper at room temperature for about 96 hrs. inhibition[21] was measured. The standard fungicide carbendazim was used for comparison. The results are shown in table 2.

The antifungal activity of complexes increases with increase in concentration. The complex $[Pd(P\phi_3)_2(P\text{-}Cl\text{-}L)_2](NO_3)_2$ proved to be the most active antifungal agent in the study. A close examination of the structures of the active compounds reveal that antifungal activity was more confined to ligands substituted at para-position of 1-phenyl-tetrazoline-5-thione rather than other substitution position, ortho and meta. The structure activity correlation of these complexes showed that

Table 2: Fungicidal activity and electronic spectral data of complexes

Complex	AV % inhibition *A. flavus* (PPM)			Electronic Spectral Bands (d – d Transition) (cm^{-1})
	1000	100	10	
$[Pd(P\phi_3)_2(P\text{-}CH_3\text{-}L)_2]Cl_2$	47.4	26.3	20.5	22600 ($^1A_{1g} \rightarrow {}^1B_{1g}$) 27770 ($^1A_{1g} \rightarrow {}^1E_g$) 30030 ($^1A_{1g} \rightarrow {}^1A_{2g}$)
$[Pd(P\phi_3)(P\text{-}CH_3\text{-}L)_2](NO_3)_2$	60.0	50.7	43.2	19450 ($^1A_{1g} \rightarrow {}^1B_{1g}$) 27770 ($^1A_{1g} \rightarrow {}^1E_g$) 37740 (CT Band)
$[Pd(P\phi_3)_2(P\text{-}Cl\text{-}L)_2]Cl_2$	80.8	70.5	65.6	27700 ($^1A_{1g} \rightarrow {}^1E_g$) 23820 ($^1A_{1g} \rightarrow {}^1B_{1g}$) 21770 ($^1A_{1g} \rightarrow {}^1A_{2g}$)
$[Pd(P\phi_3)_2(P\text{-}Cl\text{-}L)_2](NO_3)_2$	89.3	76.6	65.3	27780 ($^1A_{1g} \rightarrow {}^1E_g$) 23850 ($^1A_{1g} \rightarrow {}^1B_{1g}$) 21670 ($^1A_{1g} \rightarrow {}^1A_{2g}$)
$[Pd(P\phi_3)_2(O\text{-}Cl\text{-}L)_2]Cl_2$	55.9	39.2	20.5	27760 ($^1A_{1g} \rightarrow {}^1E_g$) 23890 ($^1A_{1g} \rightarrow {}^1E_g$) 21770 ($^1A_{1g} \rightarrow {}^1A_{2g}$)
$[Pd(P\phi_3)_2(O\text{-}CH_3\text{-}L)_2]Cl_2$	35.6	28.5	19.5	27680 ($^1A_{1g} \rightarrow {}^1E_g$) 23810 ($^1A_{1g} \rightarrow {}^1B_{1g}$) 21690 ($^1A_{1g} \rightarrow {}^1A_{2g}$)
$[Pd(P\phi_3)_2(m\text{-}CH_3\text{-}L)_2]Cl_2$	37.2	28.2	20.5	26980 ($^1A_{1g} \rightarrow {}^1E_g$) 23690 ($^1A_{1g} \rightarrow {}^1B_{1g}$) 21660 ($^1A_{1g} \rightarrow {}^1A_{2g}$)
$[Pd(P\phi_3)(H_2O)(P\text{-}Cl\text{-}L)_2]Cl_2$	88.2	73.6	55.6	18450 ($^1A_{1g} \rightarrow {}^1B_{1g}$) 27725 ($^1A_{1g} \rightarrow {}^1E_g$) 37690 (CT Band)
Carbendazim (stand)	98.7	88.2	80.5	-

para substituted phenyl ring with either electron donating or electron withdrawing functions exhibit maximum activity and in general the presence of nitrate group increased the magnitude of the activity

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