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Physico-chemical and Bio-chemical Studies of Some Organoruthenium(II) Complexes with Mixed Ligand Physiologically Active Substituted Quinazole-4-one

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Mixed ligand complexes of ruthenium chelate of oxygen, nitrogen and sulphur containing ligand 2-mercapto-3-phenyl quinazole-4-one having general formula (RuH(Z)($P\Phi_3$)n $(QPMTH)_m$ Cl] (where Z = CO/CS, if n =1 or 2 and then m = 2 or 1, QPMTH = 2-mercapto-3-phenyl quinazole-4-one) have been prepared and characterized by IR, UV spectral data, magnetic and conductance measurements. IR spectra of complexes suggest the coordination of ligand through sulphur atom and $P\Phi_3$, CS and CO are present as secondary ligands in complextion. UV spectral data and magnetic moment values of the complexes suggest octahedral geometry and molar conductance values of the complexes support their non-electrolytic nature.

Key Words: Organoruthenium(II) complexes, Substituted quinazole-4-one.

INTRODUCTION

Synthesis, characterization and biological studies of ruthenium complexes have received considerable attention owing to their interesting physical and photo chemical properties related to many biological system[1-4]. They provide interesting insights into bonding, structure and reactivity of molecules[5,6]. So, we report here the synthesis and characterization of products of reaction 2-mercapto-3-phenyl quinazole-4-one (QPMTH) (Fig. 1) with Ru(II) ions.

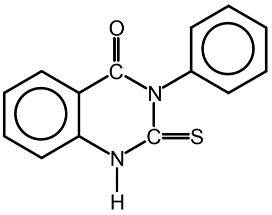

Fig. 1. (QPMTH)

EXPERIMENTAL

All chemicals used were of AR or CP grade. Solvents were distilled and dried before use. The complex $[RuH(CO)(P\Phi_3)_3Cl]$ was prepared by the method of Agarwala *et al.*[7] in different isomeric forms. $[Ru(P\Phi_3)_4Cl_2]$ was prepared by the method of Stephenson and Wilkinson[8]. The ligand QPMTH was prepared by the method described in literature[9]. All complexes were prepared under nitrogen atmosphere using general methods.

A solution of the ligand in dry benzene was added slowly and continuously to stirred solution of black isomer of $[RuH(CO)(P\Phi_3)_3Cl]$ or $[RuH(CS)(P\Phi_3)_3Cl_2]$ in benzene in an appropriate ratio. The mixture was refluxed for 1 h and allowed to cool in ice bath. The compound obtained with different metal ligands ratio were washed with ice-cold benzene and dried under reduced pressure.

Carbon, hydrogen and nitrogen analysis, infrared and electronic spectra were recorded at Central Drug Research Institute, Lucknow and anaytical laboratory Magadh University, Bodh Gaya. Magnetic measurements were made by Gouy method at room temperature (300 K). Calibration was done using $Hg[Co(NCS)_4]$ as standard. The conductivity measurements were measured in DMF (10^{-3} M) solution with the help of sistronic conductometer. Analytical and physical data of complexes are given in Table-1.

Antifungal activities have been studied on *Aspergillus flavus* using cup-plate technique[10].

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF COMPLEXES

Compd. (colour)	m.p. (°C)	Elemental analysis %: Found (Calcd.)				Ω_m (ohm^{-1} cm^2 mol^{-1})
		C	H	Cl	Ru	
$[RuH(CO)(P\Phi_3)_2(QPMTH)Cl]$ (Light yellow)	92	65.35 (66.28)	(4.12 (4.35)	3.51 (3.77)	10.21 (10.73)	7.12
$[RuH(CO)(P\Phi_3)(QPMTH)_2Cl]$ (Yellow)	151	63.03 (63.12)	3.18 (3.86)	3.75 (3.81)	10.23 (10.84)	6.14
$[RuH(CO)(P\Phi_3)_3Cl]$ (Black)	142	53.12 (53.32)	3.81 (3.74)	7.58 (8.30)	23.23 (23.64)	5.92
$[RuH(CS)(P\Phi_3)_3Cl]$ (Brown)	95	68.02 (68.22)	4.29 (4.75)	3.19 (3.67)	10.21 (10.44)	9.61
$[RuH(CS)(P\Phi_3)_2(QPMTH)Cl)]$ (Brown)	78	89.14 (89.72)	5.21 (5.90)	4.98 (5.10)	14.19 (14.52)	7.91
$[RuH(CS)(P\Phi_3)(QPMTH)_2Cl)]$ (Yellow)	86	61.72 (62.06)	3.21 (3.80)	3.39 (3.75)	10.31 (10.66)	7.72

RESULTS AND DISCUSSION

The mononuclear complex with the general formula $[RuH(Z)(P\Phi_3)_2(QPMTH)Cl]$ (where Z = CO/CS could easily be prepared in qualitative yield by replacement reaction of black isomer of $[RuH(CO)(P\Phi_3)_3Cl]$ and $[RuH(CS)(P\Phi_3)_3Cl]$ with QPMTH in benzene in 1:1 molar ratio. Additional replacement occured by increasing the time of refluxing to 3 h. The general formula of its disubsituted product is $[RuH(Z)(P\Phi_3)Cl(QPMTH)_2]$ (where Z = CO/CS). The bonded hydride ion, chlorine carbonyl and thiocarbonyl groups are not replaced. The carbonyl and triphenyl phosphine groups show large *trans* effect and the two replaced $P\Phi_3$ molecules must have been present in the *trans*-position to C=O group and one of the three $P\Phi_3$ in the $[RuH(CO)(P\Phi_3)_3Cl]$.

All reported complexes show non-conductive and dimagnetic nature indicating spin pairing in d^6 system for Ru(II) ions having $^1A_{1g}$ as ground state. Electronic spectra of all Ru(II) complexes show two medium broad bands at 375-380 and 570-575 nm which are assigned as $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively having octahedral configuration[11]. All other transition in UV region is assigned to intra ligand $n\rightarrow\pi^*$ transition.

QPMTH contains thioamide moiety (H-N-C=S) which gives four well charactrized thioamide bands at 1530(s), (1270 and 1230), 990m and 800 (ws) cm^{-1} in their IR spectra[12-14]. The blue shifting of thioamide band I, considerable red shifting of rest of thioamide band and splitting of thioamide I and II bands suggest the participation of ligand through thione sulphur atom on complexation with Ru(II) ion. The appearance of non-ligand bands at 1635(s), 1390(m), 1060(m), 970(w), 915(w) and 720(w), 540(m) and 510(w) cm^{-1} in all Ru(II) complexes are assigned as $\nu(P\Phi_3)$ mode of vibrations[15,16] and are involved in bonding with ruthenium ions in complex formation.

The new non-ligand bands at 2130-1990(m) 1870(m) and 1540(m), are assigned as ν(Ru-H), ν(Ru-CO) and ν(Ru-CS), respectively[17-19]. The ν(SH) band[20] at 2360 cm^{-1} of ligand is disappeared in all complexes after complexation may be due to involvement of sulphur atom in bonding with ruthenium ion.

New bands obtained at 480(m) and 470(m) are assigned as ν(Ru-P) and ν(Ru-Cl) in far IR spectra in all the present complexes[21]. Thus, on the basis of normal coordinate analysis octahedral configuration have been tentatively assigned for Ru(II) complexes.

Antifungal activities: QPMTH and all Ru(II) complexes were screened for their antifungal activities against *Aspergillus flavus* species at 10, 100 and 1000 ppm concentrations for about 96 h inhibition. The solvent used was DMF. The inhibition zone formed around each filter paper after inoculation for 96 h at room temperature were measured and results are shown in Table-2. The standard fungicide used for comparison was carbendazim[22]. $[RuH(CS)(P\Phi_3)_2(QPMTH)Cl]$, $[RuH(CS)(P\Phi_3)_3Cl]$ and $[RuH(CS)(P\Phi_3)_2(QPMTH)Cl]$ may be considered as good fungicides and all other may be considered as moderate fungicides.

TABLE-2
FUNGICIDAL ACTIVITIES OF COMPLEXES

Compd.	Average inhibition of *A. flavus* (ppm)		
	10	100	1000
$[RuH(CO)(P\Phi_3)_3Cl]$	61.4	66.1	69.2
$[RuH(CO)(P\Phi_3)_2(QPMTH)Cl]$	55.1	59.2	71.6
$[RuH(CO)(P\Phi_3)(QPMTH)_2Cl]$	66.1	69.2	74.4
$[RuH(CS)(P\Phi_3)_3Cl]$	71.2	79.4	85.3
$[RuH(CS)(P\Phi_3)_2(QPMTH)Cl]$	60.1	70.3	82.4
$[RuH(CS)(P\Phi_3)(QPMTH)_2Cl]$	64.1	79.2	89.9
Carbendazim	90.1	94.3	98.8

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