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Synthesis and Characterization of Some Organometallic Compounds of Iridium(I) with 2-Mercapto-3-Substituted Quinazoline-4-ones

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Few organo-iridium complexes with 2-mercapto-3-substituted quinazoline-4-ones have been prepared and characterized by various physico-chemical methods. These are found to be non-hygroscopic, air-stable, non-conducting and diamagnetic in nature. The nature of shifting and change in intensity of all four thioamide bands of ligands are used to diagnose the bonding mode between the ligand and metal. Metal-ligand vibrations in the far infrared spectra of complexes have been thoroughly examined.

Key Words: Synthesis, Organometallic compounds, Iridium(I), 2-Mercapto-3-substituted quinazoline-4-ones.

INTRODUCTION

Synthesis and characterization of organo-iridium(I) compounds have drawn special attention owing to their versatile catalytic potential[1–3]. They have unique and interesting insights into structure, bonding and reactivity of molecules which generally undergo oxidative addition reactions[4, 5]. In this paper, we describe the synthesis and characterization of some mixed ligand carbonyl hydrido phosphine compounds of iridium(I) with 2-mercapto-3-substituted-quinazoline-4-ones (Fig. 1) in view of their catalytic interest.

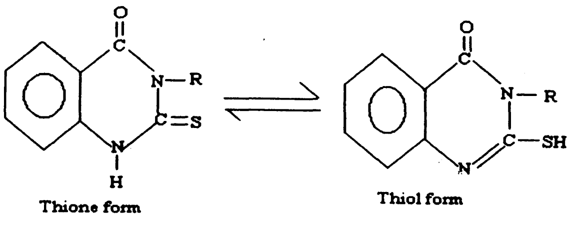

Fig. 1

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EXPERIMENTAL

All chemicals used were of CP grade. The ligand 2-mercapto-3-substituted quinazoline-4-one was prepared by the method reported in literature[6]. All the complexes were prepared by stirring a suspension of $IrCl_3$ (0.05 mol), triphenyl phosphine ($\rho\phi_3$) (0.6 mol) and KCl (0.05 mol) in ethanol (100 mL) at 85°C for 2 h. The mixture was then allowed to evaporate on a water-bath and the residue was suspended in a mixture of 2-mercapto-3-substituted-quinazoline-4-one (0.1 mol) in benzene and monoethyl ether of ethylene glycol (1 : 1). The mixture was again stirred and kept at room temperature overnight. The resulting solid complexes were filtered, washed with methanol and dried over anhydrous $CaCl_2$ in a vacuum desiccator.

(1) Carbonyl hydrido 2-mercapto-3-substituted-quinazoline-4-one bis-(triphenyl phosphine) iridium(I) [$IrH(CO)(P\phi_3)_2(PQTH)$]: Found : C, 61.3; H, 4.1; N, 2.7; Ir, 19.3%; Calcd.: C, 61.2; H, 4.1; N, 2.8; Ir, 19.3%. Properties: Silver grey coloured solid, non-hygroscopic, diamagnetic; soluble in EtOH, C_6H_6, EMK, DMF, TMF and insoluble in H_2O and CCl_4 and partially soluble in, $CHCl_3$, diethyl ether; m.p., 98°C.

(2) Carbonyl hydrido bis(2-mercapto-3-phenyl quinazoline-4-one) triphenyl phosphine iridium(I) [$IrH(CO)(P\phi_3)(PQTH)_2$]: Found: C, 56.8, H, 3.6 N, 5.7, Ir, 19.3%; Calcd.: C, 56.9, H, 3.6, N, 5.6, Ir, 19.4%. Properties: Vellum coloured crystalline solid, non-hygroscopic, soluble in DMF, THF and insoluble in C_6H_6, $CHCl_3$, CCl_4, m.p. = 130°C; diamagnetic.

(3) Carbonyl hydrido bis(2-mercapto-3-*m*-tolyl-quinazoline-4-one) triphenyl phosphine iridium(I) [$IrH(CO)(P\phi_3)(m\text{-}QTH)_2$]: Found: C, 54.1, H, 3.8, N, 5.4, Ir, 18.7%; Calcd.: C, 54.2, H, 3.9, N, 5.5, Ir, 18.8%. Properties: Portland stone colour crystalline solid, non-hygroscopic, soluble in DMF, THF; insoluble in EtOH, $CHCl_3$, CCl_4; diamagnetic, m:p. = 128°C.

(4) Carbonyl hydrido 2-mercapto-3-substituted-quinazoline-4-one bis(triphenyl phosphine) iridium(I) [$IrH(CO)(P\phi_3)(SnCl_3)(m\text{-}QTH)$]: Found: C, 38.1, H, 2.8, N, 2.8, Ir, 19.6%; Calcd.: C, 38.0, H, 2.8, Ir, 19.7%. Properties: Light straw coloured crystalline solid; soluble in DMF, THF; insoluble in diethyl ether, EtOH, C_6H_6, $CHCl_3$, CCl_4, EMK; diamagnetic, m.p. = 165°C.

Carbon, hydrogen and nitrogen analyses were done at CDRI Lucknow. Analysis of metal was carried out using standard method. Magnetic measurements were made by means of Gouy method at room temperature. The conductivity of the complexes (10^{-3} M in DMF) was measured with the help of Systronics conductometer. Infrared spectra (KBr) were recorded on a Perkin-Elmer 621 spectrophotometer and electronic spectra (dioxane) on a Carl-Zeiss (Jena) spectrophotometer.

RESULTS AND DISCUSSION

All compounds were prepared by the reaction of triphenyl phosphine ($P\phi_3$) and $IrCl_3$ in solvent monoethyl ether of ethylene glycol which acts both as reducing agent and supplier of CO. The abstraction of hydride ligand occurs from ethanol.

Analytical data indicate that the complexes have the stoichiometry [$IrH(CO)(P\phi_3)(Ligand)_2$]. All are diamagnetic and decolorize violet solution of iodine in CCl_4 indicating d^8-configuration (Ir^+). Their electronic spectra display a single very strong broad band at 42550–34602 cm^{-1} assigned to charge transfer band[7]. The other ligand field bands are obscured due to high intensity of CT band. However, two strong bands at 44264 and 38162 cm^{-1} in $[IrH(CO)(P\phi_3)_2(SnCl_3)(mQTH)]$ are observed. The first band may be of charge transfer origin and the second band presumably because of $^1a_{1g} \rightarrow {}^1b_{1g}$ transition considering MO diagram[8] of square pyramidal C_{4v} group symmetry.

A comparison of the IR spectra of the complexes with those of the corresponding ligands indicates the formation of iridium-sulphur bond. This is expected because the "softer" sulphur atom tends to combine with soft Ir(I)-ion[9]. The formation of (Ir—S) bond results in a decrease in frequency of thioamide band[10, 11] by 40–50 cm^{-1}. Moreover, the systematic change in position and intensity of other thioamide bands (Table-1) also supports the formation of iridium-sulphur bond[12–14]. Coordination through carbonyl group is ruled out because in all cases ν(C=O) band is shifted to higher wave number. All compounds display characteristic bands due to coordinated $P\phi_3$, CO and hydride group in the respective complexes. Interestingly, the position of ν(CO) and ν(Ru—H) in the IR spectra of complexes shifted toward higher and lower frequencies. It indicates a decrease in the metal to carbonyl carbon interaction and an increase in the (Ir—H) bond order. It appears that Ir—C bond is stronger in shorter distance at apical position in square-pyramidal structure. The fact is substantiated by the position of ν(CO) and ν(Ir—C) bands observed at higher frequencies in comparison to other complexes. However, the position of bulky ligands $P\phi_3$, $SnCl_3$, PQTH or mQTH may be reasonable considering steric preferences. The *trans*-arrangement for bulky heterocyclic ligands like PQTH or mQTH may also be assumed considering a straight-jacket effect.

TABLE-1

KEY IR SPECTRAL BANDS (cm^{-1}) OF LIGANDS AND THEIR METAL COMPLEXES

Compound	ν(N—H)	ν(C=O)	ν(C=O)	ν(Ir—H)/ δ(Ir—H)	Thioamide bands*			
					I	II	III	IV
PQTH	3240 mb	1648 sb	—	—	1525 s	1270 s	1030 m	800 w
$[IrH(CO)(P\phi_3)_2(PQTH)$	3360 sb	1680 sb	1885 wb (1880 wb)	2128 m (720 m)	1525 m	1260 m (1230 m)	970 w	750 w
$[IrH(CO)(P\phi_3)_2(PQTH)_2]$	3400 sb	1700 sb	1890 m	2180 m (620 m)	1525 s	1260 m (1225 m)	980 w	770 w
mQTH	3210 m	1710 m	—	—	1525 s	1265 m (1230 m)	1020 m	800 w
$IrH(CO)(P\phi_3)(mQTH)_2]$	3300 mb	1715 m	1880 m (1810 m)	1950 m (625 m)	1520 m	1230 m	990 m	785 w
$[IrH(CO)(P\phi_3)(SnCl_3)(mQTH)]$	3400 sb	1710 m	1940 m	1980 m (730 m)	1530 m	1280 w	990 w	780 w

*Band I [δ(NH) + ν(C—N)]; Band II [ν(C—N) + δ(NH) + δ(CH) + ν(C—S)];

Band III (ν(C—N) + ν(C—S)]; Band IV [ν(C$\overset{\cdot\cdot}{-}$S)]

Two weak bands at 465 and 440 cm^{-1} in the far IR spectrum of [IrH(CO)(Pϕ_3)($SnCl_3$)(mQTH)] are assigned to ν(Sn—Cl) of coordinated $SnCl_3$ group[15]. The other non-ligand bands at 420 and 310 cm^{-1} ν(Ir—P) and at 240, 222 cm^{-1} ν(Ir—S) and at 515, 500 cm^{-1} ν(Ir—C) have been tentatively assigned.

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