



Synthesis and Spectroscopic Properties of Mixed-Ligand Phosphine Complexes of Ruthenium(II) with Heterocyclic Thioamides

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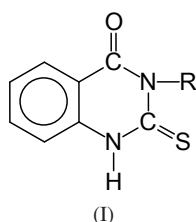
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Mixed-ligand organometallic complexes of ruthenium(II) have been prepared and characterized using various physico-chemical techniques. The possible octahedral structures and metal-ligand vibrations in far IR spectra are discussed. ¹H NMR spectral data are consistent with the conclusion drawn from IR spectra.

Key Words: Mixed-ligand, Organoruthenium(II)-complexes.

INTRODUCTION

The literature survey reveals that substituted quinazoles are important class of organic compounds of immense biological significance¹⁻⁴ and very interesting coordination behavior⁵⁻⁸. The present study describes synthesis, spectroscopic properties and physico-chemical investigations of some new organometallic complexes of ruthenium(II) with mixed-ligand triphenyl phosphine and 2-mercapto-3-alkyl-quinazole-4-one(I) owing to their use as catalytic activities⁹ and medicinal properties¹⁰⁻¹³.



(R = *n*-Propyl and *n*-butyl)

EXPERIMENTAL

All chemicals used were either chemically pure or AR grade. Solvents were distilled and dried before use. The ligands¹⁴, precursor complex [Ru(Pφ₃)₄Cl₂]¹⁵ and [RuH(CO)(Pφ₃)₃Cl]¹⁶ were prepared by the methods reported in literature.

Preparation of the complexes

Preparation of [Ru(Pφ₃)₂(LH)₂Cl₂] (S. No. 1 and 2): A solution of ligand (2 mmol) in dry benzene was added slowly

to a continuously stirred solution of [Ru(Pφ₃)₄Cl₂] (1 mmol). The mixture was refluxed for 0.5 h and then concentrated to ca. 15 mL and addition of dry ether (15 mL), solid products were obtained and dried *in vacuo*.

Preparation of [RuH(CO)(Pφ₃)₂(LH)₂Cl] (S. No. 3 and 4): The yellow isomer of [RuH(CO)(Pφ₃)₃Cl] (950 mg, 1 mmol) and ligand (2 mmol) were dissolved in minimum amount of dry benzene separately and mixed and stirred on magnetic stirrer about 0.5 h. The yellow solution was evaporated to half volume and ether added to a cooled solution of the reaction mixture. The yellow solid obtained was filtered off, washed with benzene and ether and dried *in vacuo*. Analytical data are given in Table-1.

Preparation of [RuH(CO)(Pφ₃)₂(Py)(LH)]BF₄ (S. No. 5 and 6): A suspension of [RuH(CO)(Pφ₃)₃Cl] (955 mg, 1 mmol) in methanol (50 mL) was stirred until the solid dissolved completely and it was then treated with an excess of pyridine (7.58 mmol) in methanol (10 mL). The ligand (1 mmol) solution in methanol was mixed with previous solution and was stirred for 0.5 h on magnetic stirrer. A solution of NH₄BF₄ in methanol (10 mL) was added. On concentration under vacuum separated bright yellow to orange solid which after filtration was washed with methanol before being dried under vacuum yield 78 %.

IR spectra of ligands and complexes were recorded on a Perkin-Elmer 577 spectrophotometer in the range of 4000-200 cm⁻¹ as KBr pellets and electronic spectra on a Beckmann DU-6, spectrophotometer. The ¹H NMR spectra were recorded with 90 MHz NMR spectrometer in CDCl₃ solution using TMS as the internal indicator in the range of 0-10 ppm. The

TABLE-1
 ANALYTICAL, PHYSICAL DATA OF COMPLEXES

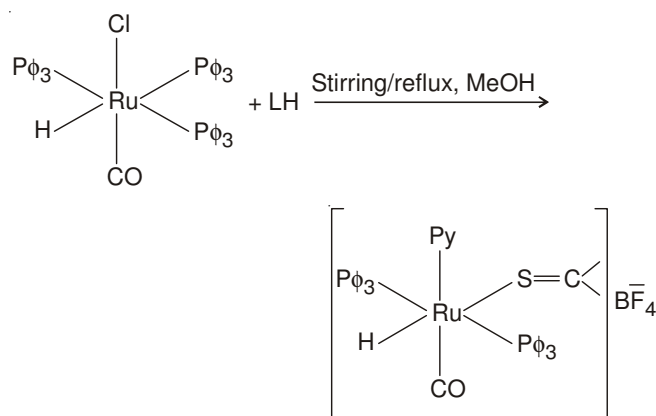
S. No.	Complex (colour)/m.f.	Analysis (%) found/(calcd.)				Molar conductance ($\Lambda^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
		C	H	N	Pt	
1	[Ru(P ϕ_3) ₂ (PrQTH) ₂ Cl ₂] (Black)	61.36	4.82	5.11	8.92	5.8
	C ₅₈ H ₅₄ N ₄ O ₂ P ₂ S ₂ Cl ₂ ·Ru	(61.26)	(4.75)	(4.92)	(8.89)	
2	[Ru(P ϕ_3) ₂ (BuQTH) ₂ Cl ₂] (Black)	61.89	4.99	4.85	8.85	6.2
	C ₆₀ H ₅₈ N ₄ O ₂ P ₂ S ₂ Cl ₂ ·Ru	(61.85)	(4.98)	(4.81)	(8.67)	
3	[RuH(CO)(P ϕ_3) ₂ (PrQTH) ₂ Cl] (Yellow)	56.85	4.72	6.55	11.82	7.2
	C ₄₁ H ₄₀ N ₄ O ₃ PS ₂ Cl·Ru	(56.71)	(4.61)	(6.45)	(11.64)	
4	[RuH(CO)(P ϕ_3) ₂ (BuQTH) ₂ Cl] (Yellow)	57.82	5.01	6.35	11.35	6.12
	C ₄₃ H ₄₄ N ₄ O ₃ PS ₂ Cl·Ru	(57.62)	(4.91)	(6.25)	(11.27)	
5	[RuH(CO)(P ϕ_3) ₂ (Py)(PrQTH)BF ₄] (Bright yellow)	61.21	5.11	4.32	9.89	25.36
	C ₅₃ H ₄₈ N ₃ O ₂ P ₂ SBF ₄ ·Ru	(61.16)	(5.02)	(4.04)	(9.71)	
6	[RuH(CO)(P ϕ_3) ₂ (Py)(BuQTH)BF ₄] (Orange)	61.56	4.86	4.02	9.88	26.32
	C ₅₄ H ₅₀ N ₃ O ₂ P ₂ SBF ₄ ·Ru	(61.49)	(4.74)	(3.98)	(9.58)	

magnetic measurements were made on a Gouy balance using Hg[CO(SCN)₄] as calibrant. The molar conductance of complexes (10⁻³ M) were measured in DMF using Wiss-Wekstatter Weithem Obb type LBR conductivity meter.

RESULTS AND DISCUSSION

The *n*-propyl (PrQTH) and *n*-butyl (BuQTH) derivatives of 2-mercapto-3-substituted quinazole-4-one display ligand substitution in benzene without change in oxidation state of ruthenium with [Ru(P ϕ_3)₄Cl₂] and [RuH(CO)(P ϕ_3)₃Cl] and the isolated solid products are given in Table-1.

The cationic mononuclear complexes with the general formulation [RuH(CO)(P ϕ_3)₂(Py)(LH)]⁺ (LH = PrQTH and BuQTH) could easily be prepared in quantitative yield by reaction of [RuH(CO)(P ϕ_3)₃Cl] with heterocyclic thioamide ligands in presence of pyridine in methanol in 1:1 molar ratio.



The mononuclear complexes (S. No. 5 and 6) are bright yellow to orange, air stable, non-hygroscopic shiny crystalline solids. These are sparingly soluble in chloroform, methanol and ethanol, highly soluble in acetone, acetonitrile, dimethyl formamide and insoluble in benzene, petroleum ether, and diethyl ether. These exhibit 1:1 conductance behaviour in DMF. Analytical data of the complexes are consistent with our formulations (Table-1).

The characteristic IR bands observed in the spectra of ligands at 3225-3200 v(NH), 1680 cm⁻¹ v(C=O) and 1530-1525 cm⁻¹ (thioamide band 1)¹⁷ remained practically unaltered on complexation indicating non-coordination of imino nitrogen

and carbonyl oxygen atom. However, thioamide band III (1030-995 cm⁻¹) and band IV (800 cm⁻¹) red shift to lower frequency by 30-40 and 40-50 cm⁻¹, respectively indicating bonding through thiocarbonyl sulphur atom^{18,19}. A single new band due to Ru-Cl (460-450 cm⁻¹) and Ru-S (310-300 cm⁻¹) stretching mode indicate two chlorine (S. No. 1 and 2) and two thione ligands (S. No. 1-4) are at *trans*-position in octahedral structure.

The non-ligand bands at 2040-2020 and 720-710 cm⁻¹ assigned to v(Ru-H) and δ(Ru-H) modes and medium bands at 1900-1950 and 510 cm⁻¹ indicate v(C≡O) and v(Ru-C) modes of coordinated carbonyl group in the complexes²⁰. It is observed that the position of v(Ru-H) in these complexes is sensitive to the electron donating ability of alkyl groups. This band shifted towards higher wave number as one move from *n*-propyl complex to *n*-butyl complex. It suggests that more electron donating alkyl group induce greater electron density on the hydride ligand²¹. Characteristic band due to counter anion were observed at 1070 cm⁻¹ (S. No. 5 and 6) and were also present in the expected region²².

The diamagnetic nature of all the complexes indicate divalent ruthenium (*d*⁶) having ground term ¹A_{1g} in octahedral environment. The electronic spectra of complexes display three to four bands in the region 640-250 nm. The band around 540 nm, (¹A_{1g} → ¹T_{2g}), 460 nm, (¹A_{1g} → ¹T_{2g}), 320 nm (A_{2g} → π*) and 250 nm (π-π*) similar to those octahedral ruthenium(II) complexes.

¹H NMR spectra: ¹H NMR spectra of ligands and some complexes (S. No. 1 and 2) were recorded in CDCl₃/TMS to substantiate further metal ligand bonding. The aromatic protons signals are observed at δ 7.8-8.5 ppm and the aromatic proton at position-5 is deshielded by carbonyl oxygen so the extreme signal at δ 8.3 ppm is considered to be due to this proton. The methyl proton of butyl group are observed as triplet at δ 1.73 and the two middle CH₂ signal are complex and are centred at δ 2.1 and δ 2.3 ppm. The CH₂ group attached to nitrogen atom of the quinazole ring is deshielded giving a triplet at δ 4.8 ppm. In addition to the aromatic proton signals, the *n*-propyl derivatives shows signals at δ 1.76 (t, CH₃), signal complicated due to-CH₂-at δ 2.2 and δ 4.7 ppm for CH₂ attached to nitrogen atom. The imino proton of ligand remain almost unchanged and observed at δ 3.2 ppm on complexation. Aromatic protons of P ϕ_3 ligand resonated as broad multiplet

in the region δ 7.52-7.18 ppm in complexes^{23,24}. Thus, thione tautomeric form of the ligand is coordinated and imino proton is intact on complexation.

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