

Synthesis and Spectral Characterization of Organometallic Complexes of Ruthenium (II and III) with Mixed Ligands

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ABSTRACT

The synthesis and characterization of some hexa-coordinated organometallic complexes of ruthenium (II and III) with mixed ligands triphenyl phosphine, triphenyl arsine and 2-aminothiophenol are reported. The tentative structure of complexes are deduced by analytical, conductance, magnetic susceptibility, IR, electronic spectra and NMR data. Two P ϕ_3 or As ϕ_3 are at trans in proposed octahedral structure.

Keywords : Bis-chelates, Ru (II and III), Phosphine, Arsine.

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INTRODUCTION

Organometallic derivatives of ruthenium have drawn special attention owing to their use as efficient photocatalyst for solar energy conversion Schemes[1], strong role in bio-inorganic chemistry[2], redox enzyme system[3], development of new drugs[4-5] and potential in vitro and in vivo trypanocidal activities[6]. These organic derivatives continue to attract interest from academic as well as industrial need due to unique structural insights, reactivity and great catalytic applications[7]. The present paper aims at synthesis, spectral and structural studies of some new phosphine and arsine complexes of ruthenium (II and III) ligated by 2-aminothiophenol using various physico-chemical data.

MATERIALS AND METHODS

All the reagent used were of anal R or CP grade. Solvents were dried before use. The ligand, 2-aminothiophenol (Schuchardt, Munchen) was used after redistillation under reduced pressure. The precursor complexes, [RuCl₂(P ϕ_3)₄][8], [RuH(CO)(E ϕ_3)₃Cl][9-10], (E = P/As) and [RuX₃(E ϕ_3)₃][11-13] (X = Cl, Br; E = P, As) were prepared by the method reported in literature.

Preparation of Ruthenium (II) complexes

[RuCl(CO)(E ϕ_3)₂(-S-C₆H₄NH₂)] (E = P/As)

Equimolar solution of precursor and 2-aminothiophenol in benzene were refluxed for 4-5 hrs and solid products were isolated following our previous method[14].

Analysis

1 : [RuCl(CO)(P ϕ_3)₂(-S-C₆H₄NH₂)] : Brown (dia. Mag.)

Calculated (%) for RuC₄₃H₃₆ONSP₂Cl : C, 63.50; H, 4.3; N, 1.72; Ru, 12.43; Found(%) : C, 63.63; H, 4.40; N, 1.66; Ru, 12.42

2 : [RuCl(CO)(As ϕ_3)₂(-S-C₆H₄-NH₂)] : Light Brown (dia. Mag.)

Calculated (%) : RuC₄₃H₃₆ONS As₂Cl : C, 57.31; H, 3.99; N, 1.55; Ru, 11.21; Found(%) : C, 57.30; H, 4.01; N, 1.65; Ru, 11.30

Preparation of [Ru(P ϕ_3)₂(-S-C₆H₄-NH₂)₂] and [Ru(P ϕ_3)(H₂O) (S-C₆H₄-NH₂)₂].5H₂O

These complexes were prepared by ligand substitution in benzene using [Ru(P ϕ_3)₄Cl₂] following our previous method reported in literature[15].

Analysis

3 : [Ru(P ϕ_3)₂(-S-C₆H₄-NH₂)₂] Black (dia-mag.)

Calculated (%) for RuC₄₈H₄₂N₂S₂P₂ : C, 65.98; H, 4.81; N, 3.20; Ru, 11.56; Found(%) : C, 65.65; H, 4.82; N, 3.30; Ru, 11.65

4 : [Ru(P ϕ_3)(H₂O) (S-C₆H₄-NH₂)₂]. 5H₂O Green (dia. Mag.)

Calculated (%) for **RuC₃₀H₃₉O₆N₂S₂P** : C, 50.06; H, 5.42; N, 3.89; Ru, 14.04; Found(%) : C, 50.12; H, 5.50; N, 3.91; Ru, 14.14

Preparation of Ruthenium (III) complexes

The complexes [RuX(Eφ₃)(S-C₆H₄-NH₂)₂] (X = Cl, Br, NO₃, NCS; E = P/As) were prepared by our previous method reported in literature[16].

Analysis

5 : [RuCl(Pφ₃)(S-C₆H₄-NH₂)₂]: Brown (Para. Mag. 1.98 BM)

Calculated (%) for **RuC₃₀H₂₇N₂S₂PCl** : C, 55.68; H, 4.17; N, 4.33; Ru, 15.62 ; Found(%) : C, 55.72; H, 4.22; N, 4.36; Ru, 15.70

6 : [RuBr(Pφ₃)(S-C₆H₄-NH₂)₂]: Dark Brown (Para. Mag. 1.98 BM)

Calculated (%) for **RuC₃₀H₂₇N₂S₂PBr** : C, 52.10; H, 3.90; N, 4.05; Ru, 14.61 ; Found(%) : C, 52.23; H, 4.01; N, 4.11; Ru, 14.72

7 : [RuBr(Asφ₃)(S-C₆H₄-NH₂)₂]: Yellow Brown (Para. Mag. 1.98 BM)

Calculated (%) for **RuC₃₀H₂₇N₂S₂AsBr** : C, 48.98; H, 3.67; N, 3.81; Ru, 13.74 ; Found(%) : C, 49.02; H, 3.68; N, 3.92; Ru, 13.75

8 : [Ru(NO₃)(Pφ₃)(S-C₆H₄-NH₂)₂]: Brown (Para. Mag. 1.98 BM)

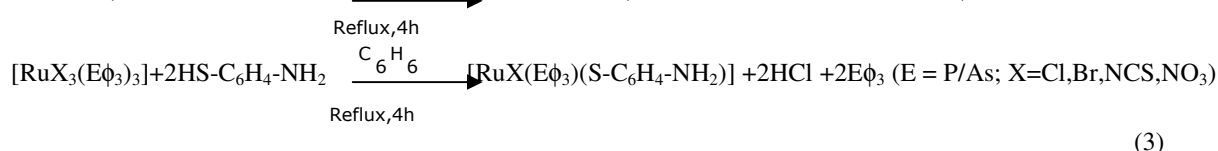
Calculated (%) for **RuC₃₀H₂₇N₃O₃PS₂** : C, 53.49; H, 4.01; N, 4.16; Ru, 15.00; Found(%) : C, 53.54; H, 4.11; N, 4.25; Ru, 15.15

9 : [Ru(NCS)(Pφ₃)(S-C₆H₄-NH₂)₂]: Brown (Para. Mag. 2.0 BM)

Calculated (%) for **RuC₃₁H₂₇N₃S₃P** : C, 55.60; H, 4.03; N, 4.18; Ru, 15.09; Found(%) : C, 55.72; H, 4.13; N, 4.28; Ru, 15.16

RESULTS AND DISCUSSION

The analytical data consistent with the proposed stoichiometries of the complexes. All isolated products were air stable and soluble in DMF, DMSO and other coordinating organic solvents. Ligand substitution reaction with precursors complexes yielded all solid products:



The molar conductance in DMF (10⁻³M) of complexes was found to be less than 10-15 Ohm⁻¹ cm² mol⁻¹ indicating their non-electrolytic nature and anions are present in the inner sphere of complexes.

Magnetic moment and UV-vis Spectra

The substitution products of [RuH(CO)(Eφ₃)₃Cl] (E = P/As) and [Ru(Pφ₃)₄Cl₂] are diamagnetic indicating Ru⁺⁺ (d⁶) and ¹A_{1g} ground state. Three to four bands in 13335-40000 cm⁻¹ range. The d-d transition bands at 13070 (E_{max} = 1680) cm⁻¹ (¹A_{1g} → ³T_{1g}), 15385 (E_{max} = 3520) cm⁻¹ (¹A_{1g} → ¹T_{1g}), 18520 (E_{max} = 3280) cm⁻¹ and 30480 (E = 5360) (T_{2g} → π*) are consistent with octahedral structure[17-18].

The magnetic moment value of [RuX(Eφ₃)(S-C₆H₄NH₂)₂] (X = Cl, Br, NCS, NO₃; E = P/As) are in the range of 1.98-2.01 BM corresponding to a single unpaired electron in a low spin 4d⁵ configuration[19] and oxidation state of ruthenium is +3. So, the ground state of ruthenium (III) is ²T_{2g} and the first excited doublet level in order of increasing energy are ²A_{2g} and ²T_{1g} which arises from ⁴T_{2g} → ¹E_g configuration. The electronic Spectra of complexes show three bands in 17390-29400 cm⁻¹ region. However, some complexes (No. 6 and 7) display a single band of very strong intensity at 27500 cm⁻¹ due to charge transfer. The electronic spectral bands at 23790 cm⁻¹ is assigned due to ²T_{1g} → ²A_{2g} transition and other bands at 18310 cm⁻¹ and 14010 cm⁻¹ are due to spin forbidden transitions. The ligand field parameters were calculated by standard method [20] and are observed to be 10Dq = 26795 cm⁻¹, B = 535

cm^{-1} , $B = 0.85$, $C = 2530$ and $\nu_2/\nu_1 = 1.30$. The B value is 65-70% of the free ion value. The octahedral structure of all ruthenium (III) complexes may be assigned considering previous report[16].

ESR Spectra

The X- band ESR Spectrum of $[\text{RuCl}(\text{P}\phi_3)(-\text{S}-\text{C}_6\text{H}_4\text{NH}_2)_2]$ recorded in the Polycrystalline form exhibited only one signal with g value 2.38 indicating high symmetry around ruthenium (III) ion[21]. The value of 'g' is also in agreement with a low spin symmetry of ligand field reported for octahedral Ruthenium (III) complexes[22].

IR Spectra

The $\nu_{\text{sym}} \text{NH}_2$ and $\nu_{\text{asym}} \text{NH}_2$ of free ligand (ATP) are observed at 3340 cm^{-1} and 3460 cm^{-1} red shift to lower frequency at $3300\text{-}3315 \text{ cm}^{-1}$ and $3400\text{-}3410 \text{ cm}^{-1}$ respectively on complexation indicating the formation of Ru-N bond. The presence of new band of medium intensity in the far- IR spectra of complexes at $480\text{-}520 \text{ cm}^{-1}$ supports these observations and assigned to $\nu_{\text{Ru-N}}$ stretching mode. The $\nu \text{ S-H}$ band is present at 2560 cm^{-1} in the spectrum of free ligand, does not appear in the spectra of complexes indicating coordination of metal through deprotonated thiol sulphur[16]. A weak non-ligand band at $340\text{-}365 \text{ cm}^{-1}$ supports the formation of metal- sulphur bond and is assigned due to Ru-S stretching mode. Thus, the presence of simultaneous Ru-N and Ru-S bond was assumed and the ligand 2-aminothiophenol acts as bidentate anion.

The presence of anion in the complexes was indicated by non-ligand bands at 2080 cm^{-1} , 760 cm^{-1} and 480 cm^{-1} (No.9) for terminal coordinated isothiocyanate anion[23], at 1510 cm^{-1} , 1350 cm^{-1} and 1000 cm^{-1} correspond to ν_4 , ν_1 and ν_2 vibrations of monodentate nitro group[24] (No.8) in ruthenium (III) complexes. Separation between the two bands ν_4 and ν_1 vibrations (Ca. 160 cm^{-1}) indicates the monodentate nature of nitrate group. The combination bands for nitrate group Ca. 1800 cm^{-1} are not located in the Spectrum of complex (No.8). The non-ligand band at $1968\text{-}1960 \text{ cm}^{-1}$ in carbonyl complexes (No.1 and 2) supports terminal $\text{C} \equiv \text{O}$ group. The characteristic bands due to $\text{P}\phi_3$ or $\text{As}\phi_3$ were also present in the expected region [25].

^1H NMR and ^{31}P NMR Spectra

The metal-ligand bonding is further substantiated by ^1H NMR spectra of free ligand (ATP) and complexes. The free ligand (ATP) display signals at δ 6.64-7.30 PPM (multiplet), δ 3.68 PPM and δ 3.69 PPM due to aryl protons, amino protons and intramolecularly hydrogen bonded thiol protons. The thiol proton disappeared from the spectra of complexes indicating their replacement by metal ion during complexation[26]. The phenyl protons are slightly low field shifted and the integrated intensities of these signals agree well with the formulation of the complexes. The amino protons are also low field shifted on complexation and the integrated intensities of the signals agree well with assigned structure of complexes. The signals found at δ 8.65 – 8.18 PPM range as broad multiplet in complexes are due to aromatic protons of coordinated $\text{P}\phi_3$ / $\text{As}\phi_3$.

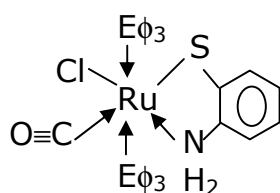
The ^{31}P NMR Spectra of two complexes (No.1 and 2) was recorded in order to confirm the presence of $\text{P}\phi_3$ group and $\text{As}\phi_3$ group and to determine the geometry of complexes. The appearance of signal around 23.70– 28.68 in the spectra of complexes confirmed the presence of magnetically equivalent phosphorus atoms and suggesting that the two $\text{P}\phi_3$ or $\text{As}\phi_3$ groups are trans to each other [27] in octahedral structure.

Thus on the basis of above physico-chemical and spectral data the following octahedral structure may be suggested to all isolated products.

Table-1: Major IR and ^1H NMR Spectral data of ligands and complexes.

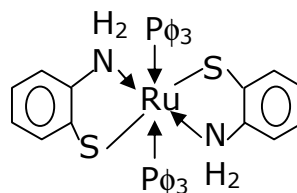
Compds.	IR (cm^{-1})				^1H NMR (δ PPM)		
	$\nu_{\text{a}} \text{NH}_2/$ ($\nu_{\text{s}} \text{NH}_2$)	$\nu \text{ Ru-N}$	$\nu \text{ Ru-S}$	$\nu \text{ Ru-P}$	Amino Proton	Phenyl Proton	Thiol Proton
ATP (ligand)	3460 m (3340 m)	-	-	-	3.68	6.64-7.30 (multiplet)	3.66
No.1: Ru(II)-complex	3420 m (3310 m)	490 m	340 w	370 m	3.54	6.62-7.12 (multiplet)	-
No.2: Ru(II)-complex	3415 m (3305 m)	485 m	350 w	-	3.52	6.66-7.02 (multiplet)	-
No.3: Ru(II)-complex	3420 m (3320 m)	500 m	355 w	445 m	3.55	6.66-7.2 (multiplet)	-

No.4: Ru(II)-complex	3410 m (3320 m)	480 m	345 w	440 m 435 m	3.60	6.68-7.2 (multiplet)	-
No.5: Ru(III)-complex	3400 m (3300 m)	510 m	360 w	490 m 485 m	3.65	6.66-7.3 (multiplet)	-
No.6: Ru(III)-complex	3405 m (3310 m)	510 m	365 w	480 m 485 m	3.55	6.69-7.2 (multiplet)	-
No.7: Ru(III)-complex	3400 m (3300 m)	510 m	360 w	-	3.66	6.68-7.32 (multiplet)	-
No.8: Ru(III)-complex	3410 m (3300 m)	490 m	355 w	480 m 490 m	3.65	6.66-6.98 (multiplet)	-
No.9: Ru(III)-complex	3415 m (3310 m)	520 m	365 w	490 m 485 m	3.62	6.68-7.2 (multiplet)	-

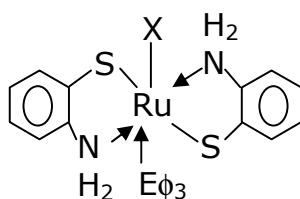


(E = P/As)

Oh-Str.-Ru(II)- Complex
(No. 1 & 2)



Oh-Str.-Ru(II)- Complex
(No. 3)



(X = Cl, Br, NO₃, NCS; E = P/As)

Oh-Str.-Ru(II)- Complex
(No. 5 to S. No. 9)

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