Mixed- Ligand Phosphine and Arsine Complexes of Ruthenium (III) Ligated by Heterocyclic Thioamide

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ABSTRACT

Mixed ligands bis-chelates of general formula [RuX(EΦ)(IPT5T)2] (X= Cl, Br, NCS or NO3; E= P/As) have been prepared and investigated. The ligand 1-phenyl tetrazoline-5-thione acts as bidentate (N,S) supported by IR, and 1HNMRspectral data. The distorted octahedral structure of all Ru(III) compounds are assigned on the basis of elemental, magnetic and other physico-chemical data.

Key words: Ru(III), bis-chelates, Mixed- ligands.

INTRODUCTION

Organometallic complexes of ruthenium are important class of compounds having great catalytic and biological properties and biological properties. The present paper is devoted to the synthesis and characterization of new ruthenium(III) complexes with 1-phenyl tetrazoline-5-thione (I).

Experimental

All the chemicals used were of Analar or Cp grade. Solvents were dried prior to use. 1-phenyl tetrazoline-5-thione was prepared by the method of Liber et al. The starting complexes [RuX(EΦ)3](X= Cl, Br; E= P/As) were prepared according to the literature procedures.

Preparation of [RuX(EΦ)(IPT5T)2] (X= Cl, Br, NCS or NO3; E= P/As)

All reactions were carried out under anhydrous conditions and complexes were prepared using a general method.

Ethanolic solution of ligand and benzene solution of precursor’s complexes were mixed in molar ratio 2:1(L:M) and refluxed for 5 hours. The
resulting dark coloured solution was concentrated to ~ 5 cm³ and some small quantity of ether was added to it. The precipitated brown coloured solids were filtered, washed with ether and dried in vacuo.

For the preparation of thiocyanate and nitrate complexes, ethanolic solution of NH₄SCN/LiNO₃ was added to benzene solution of [RuX(EO₃)₃] and refluxed with solution of ligand using desired molar ratio. The complexes were obtained by the concentration of refluxed solution to ~5 cm³ and addition of small quantity of ether.

**RESULTS AND DISCUSSION**

The analysis of carbon, hydrogen and nitrogen were performed at CDRI Lucknow, India. The IR spectra of ligand and complexes were recorded on a Perkin-Elmer Model-577 spectrophotometer in the range of 4000-200 cm⁻¹ as KBr pellets. The magnetic measurements were made on a Gouy balance and the diamagnetic corrections for the ligand molecule were applied. The UV and Visible spectra of the ligand and complexes were recorded on a Beckmann and Carl Zeiss (Jenna) spectrophotometer. The molar conductance values indicate their non-electrolytic nature and magnetic moment value of the complexes (table-1) fall in the range of 1.90-2.01 BM corresponding to a single unpaired electron.

- **[Ru(PΦΦΦΦΦ)(1PT5T)₂Cl]**
  - S.No. 1: calculated (%) for RuC₃₂H₂₅N₈S₂PCl: C, 51.02; H, 3.32; N, 14.88; Ru, 13.42; Found (%): C, 51.15; H, 3.38; N, 14.90; Ru, 13.42;

- **[Ru(PΦΦΦΦΦ)(1PT5T)₂Br]**
  - S.No. 2: calculated (%) for RuC₃₂H₂₅N₈S₂PBr: C, 48.18; H, 3.13; N, 14.05; Ru, 12.67; Found (%): C, 48.35; H, 3.10; N, 14.12; Ru, 12.87;

- **[Ru(AsΦΦΦΦΦ)(1PT5T)₂Cl]**
  - S.No. 3: calculated (%) for RuC₃₂H₂₅N₈S₂AsCl: C, 48.21; H, 3.13; N, 14.06; Ru, 12.68; Found (%): C, 48.11; H, 3.25; N, 14.21; Ru, 12.72;

- **[Ru(AsΦΦΦΦΦ)(1PT5T)₂Br]**
  - S.No. 4: calculated (%) for RuC₃₂H₂₅N₈S₂AsBr: C, 45.66; H, 2.97; N, 13.32; Ru, 12.01; Found (%): C, 45.69; H, 3.01; N, 13.42; Ru, 12.32;

- **[Ru(PΦΦΦΦΦ)(1PT5T)₂NCS]**
  - S.No. 5: calculated (%) for RuC₃₃H₂₅N₉S₃P: C, 51.09; H, 3.22; N, 16.25; Ru, 13.03; Found (%): C, 51.13; H, 3.01; N, 16.22; Ru, 13.13;

- **[Ru(PΦΦΦΦΦ)(1PT5T)₂(NO₃)]**
  - S.No. 6: calculated (%) for RuC₃₂H₂₅N₉S₂O₃P: C, 49.29; H, 3.29; N, 16.17; Ru, 12.96; Found (%): C, 49.39; H, 3.30; N, 16.27; Ru, 13.01;

- **[Ru(X(EO₃)₃)]** (X=Cl, Br, NCS, NO₃; E=P/As; 1PT5T= deprotonated 1-phenyl tetrazoline-5-thione of tautomeric form. The molar conductance values indicate their non-electrolytic nature and magnetic moment value of the complexes (table-1) fall in the range of 1.90-2.01 BM corresponding to a single unpaired electron.
in low spin $4d^6$ configuration consistent with reported value reported in previous literature\textsuperscript{15}.

The room temperature EPR spectra of powered sample were recorded at X-band frequencies. All the complexes showed a single isotropic resonance with a "$g$" value in the range 2.10-2.30 ranges indicating high symmetry around ruthenium(II) ion\textsuperscript{16}. Such isotropic lines are probably due to the results of either intermolecular spin exchange which can broaden the lines or due to occupancy of unpaired electron in degenerate orbital\textsuperscript{17}. The values of "$g$" is also in agreement with low spin symmetry of the ligand field similar to "$g$" value reported for octahedral \textsuperscript{18-20}Ru (III) complexes. Electronic spectra of complexes showed two to three bands in the 250-670 nm region. The band in the 535-485 nm region have been assigned to the $^{2}T_{2g} ightarrow ^{2}A_{2g}$ transitions is in conformity with assignments made for similar ruthenium (II) complexes\textsuperscript{21-23}. Other bands in the 345-355 nm region have been assigned to charge transfer transition and the other two bands at 675 and 470 nm are spin-forbidden transitions\textsuperscript{24}. In general the electronic spectra of all complexes are characteristic of an octahedral environment around Ru (III) ions.

**IR Spectra**

A close observation of infra red spectrum of ligand and ruthenium (III) complexes indicate simultaneous Ru-S and Ru-N bonding in all complexes. The $v_{\text{N-H}}$ at 3145 cm$^{-1}$ of ligand 1-phenyltetrazoline-5-thione disappears from the spectra of complexes indicating deprotonation of N-H proton. Further evidence in support of this comes from systematic shift\textsuperscript{25-28} of thiomide bands of the ligand on complexation. The formation of simultaneous Ru-S and Ru-N bond blue shift thiomide band I (20-35 cm$^{-1}$), band III (25-30 cm$^{-1}$) and band IV(30-40 cm$^{-1}$) of ligand due to increase in CN bond order and decrease in CS bond order\textsuperscript{29-30}. These observations are further supported by the presence of new non-ligand bond at 420 cm$^{-1}$ and 350 cm$^{-1}$ assigned to $v_{\text{Ru-N}}$ and $v_{\text{Ru-S}}$ modes respectively.

The non-ligand bands at Ca. 1505,1350 and 1000 cm$^{-1}$ correspond to $v_{\text{4}}$, $v_{\text{1}}$, and $v_{\text{2}}$ vibration of coordinated nitrate group in $[\text{Ru(NO}_3\text{)}_2(\text{P}_3\text{E}_3)(\text{1PT5T})_2]$ are in agreement with previous literature\textsuperscript{31}. Separation between the two bands $v_{\text{u}}$ and $v_{\text{i}}$(ca. 155 cm$^{-1}$) indicate the monodentate

| Compound | $\mu eH$ (BM) | $\lambda$ max. (nm) | Thiomide Bands |
|----------|--------------|---------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Ligand (1PT5TH) | - | 305,265 | 1520 | 1290 | 980 | 740 |
| 1. $[\text{Ru}(\text{P}_3\text{E}_3)(\text{1PT5T})_2\text{Cl}]$ | 2.01 | 675, 485, 345 | 1500 | 1300 | 1000 | 800 |
| 2. $[\text{Ru}(\text{P}_3\text{E}_3)(\text{1PT5T})_2\text{Br}]$ | 1.90 | 670, 470, 350 | 1515 | 1295 | 970 | 795 |
| 3. $[\text{Ru}(\text{As}_3\text{E}_3)(\text{1PT5T})_2\text{Cl}]$ | 2.00 | 660, 355 | 1520 | 1310 | 965 | 760 |
| 4. $[\text{Ru}(\text{As}_3\text{E}_3)(\text{1PT5T})_2\text{Br}]$ | 2.01 | 665, 350 | 1510 | 1310 | 975 | 745 |
| 5. $[\text{Ru}(\text{P}_3\text{E}_3)(\text{1PT5T})_2\text{(NCS)}]$ | 1.90 | 675, 470, 355 | 1515 | 1315 | 980 | 740 |
| 6. $[\text{Ru}(\text{P}_3\text{E}_3)(\text{1PT5T})_2\text{NO}_3]$ | 1.90 | 605,535,345 | 1525 | 1315 | 985 | 745 |

**Table 1: Physico-chemical data of Ru(III) complexes**

The Tentative Octahedral structure of $[\text{RuX(E}_3\text{P}_3)(\text{1PT5T})_2]$ (X= Cl, Br, NCS or NO$_3$; E= P/As)
nature of nitrate group. Ca. 1800 cm\(^{-1}\) are not observed in the spectrum of the present complex. A very strong band of medium intensity at 2085 cm\(^{-1}\), 760 cm\(^{-1}\) and 480 cm\(^{-1}\) confirms the presence of N-bonded isothiocyanato group and assigned to \(\nu_{\text{NCS}}, \nu_{\text{C=S}}\) and \(\delta_{\text{CNS}}\) modes\(^{32}\).

1\(^{1}\)H NMR Spectra

All complexes display broad multiplet in the region \(\delta_{7.45-7.75}\) ppm due to phenyl protons in complexes. The broad nature of peak may be due to large quadruple resonance broadening effect of tetrazoline nitrogen atom\(^{33}\). The resonances due to imino proton in the ligand observed at \(\delta_{4.25}\) ppm is absent in the spectra of the complexes suggesting formation of Ru-N bond and deprotonation of N-H group on complexation. The aromatic protons of P\(\Phi_3\) ligand resonated as a broad multiplet in the region \(\delta_{7.32-7.15}\) ppm in complexes.

REFERENCES

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