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

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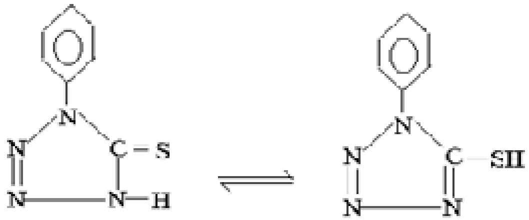
ABSTRACT

Mixed ligands bis-chelates of general formula $[RuX(E\Phi_3)(IPT5T)_2]$ (X= Cl, Br, NCS or NO_3; E= P/As) have been prepared and investigated. The ligand 1-phenyl tetrazoline -5-thione acts as bidentate (N,S) supported by IR, and ^{1}HNMRspectral 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 [1-4], medicinal[5-7] and biological properties[8-10]. 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.*[11]. The starting complexes $[RuX_3(E\Phi_3)_3]$[12-14] (X= Cl, Br; E= P/As) were prepared according to the literature procedures.

Preparation of $[RuX(E\Phi_3)(IPT5T)_2]$ (X= Cl, Br, NCS or NO_3; 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 ~ 5cm^3 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 NH_4SCN/$LiNO_3$ was added to benzene solution of [RuX(EÖ$_3$)$_3$] and refluxed with solution of ligand using desired molar ratio. The complexes were obtained by the concentration of refluxed solution to ~5cm^3 and addition of small quantity of ether.

[Ru($P\Phi_3$)(1PT5T)$_2$Cl]
S.No. 1: calculated (%) for $RuC_{32}H_{25}N_8S_2PCl$: 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($P\Phi_3$)(1PT5T)$_2$Br]
S.No. 2: calculated (%) for $RuC_{32}H_{25}N_8S_2PBr$: 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($As\Phi_3$)(1PT5T)$_2$Cl]
S.No. 3: calculated (%) for $RuC_{32}H_{25}N_8S_2AsCl$: 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($As\Phi_3$)(1PT5T)$_2$Br]
S.No. 4: calculated (%) for $RuC_{32}H_{25}N_8S_2AsBr$: 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($P\Phi_3$)(1PT5T)$_2$NCS]
S.No. 5: calculated (%) for $RuC_{33}H_{25}N_9S_3P$: 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($P\Phi_3$)(1PT5T)$_2$(NO_3)]
Sl.No. 6: calculated (%) for $RuC_{32}H_{25}N_9S_2O_3P$: 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;

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-1as KBr pillets. 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 of complexes(10^{-3}M) were measured in DMF (10^{-3}M) using Wiss-Werkstatter Weitheim obb type LBR conductivity meter. ^{1}H NMR spectra of ligand and Ru(III) complexes were recorded with 90 MHZ NMR spectrophotometer using TMS as internal indicator. The complexes were dissolved in $CDCl_3$ for recording their ^{1}HNMR spectra in the range of 0-10 ppm. The number of protons were obtained with the help of internal calibrator. EPR spectra of the powdered samples were recorded on a Bruker E-112 Varian model instrument in X-band frequencies at room temperature.

RESULTS AND DISCUSSION

The analytical data of the complexes correspond to the composition [RuX($E\Phi_3$)(1PT5T)$_2$] (X=Cl, Br, NCS, NO_3; 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 i9n the range of 1.90-2.01 BM corresponding to a single unpaired electron

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

Compound	μeH(BM)	λ max.(nm)	Thiomide Bands			
			I	II	III	IV
Ligand (1PT5TH)	-	305,265	1520	1290	980	740
1.[Ru(PΦ_3)(1PT5T)$_2$Cl]	2.01	675, 485, 345	1500	1300	1000	800
2. [Ru(PΦ_3)(1PT5T)$_2$Br]	1.90	670, 470, 350	1515	1295	970	795
3. [Ru(AsΦ_3)(1PT5T)$_2$Cl]	2.00	660, 355	1520	1310	965	760
4. [Ru(AsΦ_3)(1PT5T)$_2$Br]	2.01	665, 350	1510	1310	975	745
5. [Ru(PΦ_3)(1PTST)$_2$(NCS)]	1.90	675, 470, 355	1515	1315	980	740
6. [Ru(PΦ_3)(1PT5T)$_2$NO$_3$]	1.90	605,535,345	1525	1315	985	745

in low spin 4d^5 configuration consistent with reported value reported in previous literature[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[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[17]. The values of "g" is also in agreement with low spin symmetry of the ligand field similar to "g" value reported for octahedral

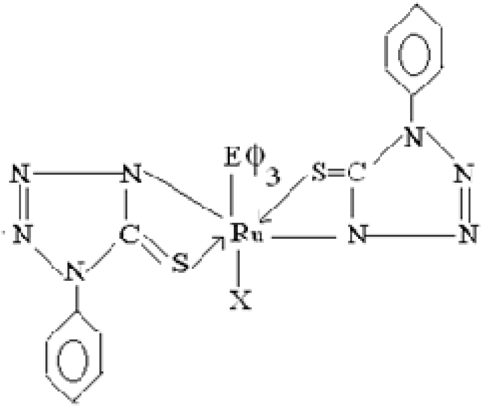
Ru (III) complexes[18-20]

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 $2T_{2g} \rightarrow 2A_{2g}$ transitions is in conformity with assignments made for similar ruthenium (III) complexes[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[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 υ_{N-H} at 3145cm^{-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[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 (20-35cm^{-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[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 υ_{Ru-N} and υ_{Ru-S} modes respectively.

The non-ligand bands at Ca. 1505,1350 and 1000 cm^{-1} correspond to υ_4, υ_1 and υ_2 vibration of coordinated nitrate group in [Ru(NO$_3$)(PΦ_3)(1PT5T)$_2$] are in agreement with previous literature[31]. Separation between the two bands υ_4 and υ_1(ca. 155 cm^{-1}) indicate the monodentate



Tentative Octahedral structure
of [RuX(EΦ_3) (IPT5T)$_2$]
(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 2085cm^{-1}, 760 cm^{-1} and 480 cm^{-1} confirms the presence of N-bonded isothiocynato group and assigned to υ_{NCS} , $\upsilon_{C=S}$ and δ_{CNS} modes[32].

^{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 $\delta_{1.25}$ 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.

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