A Study of Ru(II) Complexes of some Selected N–S Donors

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Abstract

A number of Ru(II) complexes of six monoacid bidentate N–S donors in the form of ring substituted 4-phenylthiosemicarbazides have been synthesized and characterized by elemental analysis, conductance and magnetic susceptibility measurements as well as by various spectroscopic techniques such as UV–Vis, IR and NMR spectroscopy. All the complexes have the general formula $[Ru(LH)_2X_2]\cdot nH_2O$ where LH = a substituted thiosemicarbazide and X = Cl and I. From IR study the *trans* disposition of these two coordinated X^- ions has been established. In all the complexes the ligand binds itself to the Ru(II) ion in its keto form through its thiocarbonyl sulphur atom and the nitrogen atom of the terminal $-NH_2$ group of the thiosemicarbazide moiety. Reactivity of these $[Ru(LH)_2X_2]\cdot nH_2O$ complexes towards various types of reagents like pyridine, DMF, NH_4SCN, $NaHSO_3$, C_6H_5CN and PPh_3 has been examined and the products have been characterized. In all these reactions ruthenium is found to retain its +2 oxidation state. Antibacterial activity of some of the $Ru(LH)_2X_2\cdot nH_2O$ complexes have been examined against *E. coli* and the corresponding minimum inhibitory concentration (MIC) values are reported.

Introduction

At present coordination chemistry of ruthenium(II) bound to nitrogen donors is an active area of research for various reasons. Many such compounds exhibit important catalytic and photochemical activity [1]. Some of these compounds are also implicated as model systems for studies on nitrogen fixation [2] and at least one such compound (the pentammine aquo ruthenium(II) complex) has been found to possess DNA binding characteristic [3]. However, a survey of relevant literature has revealed that the chemistry of Ru(II) ligated to chelating ligands containing mixed hard–soft donor atoms like nitrogen and sulfur has not been adequately explored. In this context we have undertaken a programme of systematically studying ruthenium complexes of some N–S donors such as thiosemicarbazides and thiosemicarbazones and this paper reports the first part of our investigation in this area. Our interest in this programme is two-fold. Firstly to examine the reactivity of ruthenium(II) ligated to NS donor centres towards various types of Lewis bases of both hard and soft type. Secondly, to examine the biological activity of these complexes. It has been proposed [4] that complexes in which the metal atom is of class (b) and is bound with ligands which contain sulfur donor centres are likely to be biologically most active, mainly because these two factors usually confer lipid solubility on metal complexes. As the ligands of our choice are known to possess antibacterial, antiviral, antimaterial, antileprotic and antitumor activities [5] it is quite possible that due to ligation to ruthenium this activity may be significantly modified.

Results and Discussion

The ligands used in this work are 4-substituted thiosemicarbazides e.g. 4-phenyl, 4-(*p*-methyl phenyl), 4-(*p*-chloro phenyl), 4-(*p*-ethoxy phenyl), 4-(*p*-methoxy phenyl), 4-(*o*-methoxy phenyl) thiosemicarbazides all of which can exist in keto and enol form. Though there are one or two cases in which the thiosemicarbazides act as monodentate ligands binding to the metal centre through the sulfur atom, in almost all other cases thiosemicarbazides react as chelating ligands towards transition metal ions utilising the sulfur atom and the terminal hydrazinic nitrogen atom of the thiosemicarbazide chain [6]. The only known solid complexes of thiosemicarbazide coordinating through the sulfur atom only are the polymeric Ag(I) complexes [7]. We have prepared several dichlorobis thiosemicarbazide complexes of ruthenium(II) by reacting $RuCl_3$ with the corresponding donor molecules taken in slight excess of the stoichiometric requirement, all the reactions being carried out in ice cold conditions. The corresponding iodo complexes were prepared in methanol under reflux. In all cases deep red–violet air stable com-

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TABLE I. Analytical Data for Ru(II) Complexes

Complex	Colour	C[a] (%)	H[a] (%)	N[a] (%)	X
$Ru(4PhTSCH)_2Cl_2 \cdot 2H_2O$	red–violet	30.8(30.9)	4.1(4.0)	15.6(15.5)	12.8(13.1)
$Ru(4PhTSCH)_2I_2$	rose–red	23.3(23.2)	3.9(3.0)	11.9(12.2)	36.1(36.8)
$Ru(4p\text{-}CH_3PhTSCH)_2Cl_2 \cdot 2H_2O$	red–violet	33.4(33.7)	4.8(4.5)	14.5(14.7)	12.2(12.4)
$Ru(4p\text{-}CH_3PhTSCH)_2I_2$	rose–red	24.8(25.0)	3.6(3.4)	10.9(11.7)	35.2(35.4)
$Ru(4p\text{-}ClPhTSCH)_2Cl_2$	red–violet	29.0(29.2)	2.9(2.8)	14.4(14.6)	24.9(24.7)
$Ru(4p\text{-}ClPhTSCH)_2I_2$	rose–red	22.7(22.1)	2.9(2.1)	11.5(11.7)	33.1(33.5)
$Ru(4o\text{-}OCH_3PhTSCH)_2Cl_2$	red–violet	33.8(33.9)	4.0(3.8)	14.6(14.8)	12.8(12.5)
$Ru(4p\text{-}OCH_3PhTSCH)_2Cl_2$	red–violet	33.6(33.9)	4.0(3.8)	14.5(14.8)	12.9(12.5)
$Ru(4p\text{-}OC_2H_5PhTSCH)_2Cl_2$	red–violet	36.0(36.3)	4.6(4.3)	13.9(14.1)	11.9(11.9)
$Ru(4PhTSC)_2py_2$	green	50.6(50.7)	4.5(4.2)	18.1(18.2)	
$Ru(4PhTSCH)_2(SCN)_2$	brown	34.6(34.8)	3.5(3.2)	20.5(20.3)	
$Ru(4PhTSC)_2(PPh_3)_2$	yellow	62.3(62.7)	4.9(4.6)	8.6 (8.8)	
$Ru(4PhTSCH)_2(HSO_3)_2$	red	28.1(28.1)	3.3(3.3)	14.0(14.0)	
$[Ru(4PhTSCH)_2(C_6H_5CN)_2]Cl_2$	red	47.0(47.1)	3.8(3.9)	15.7(15.7)	

[a]Calculated values in parenthesis.

pounds were obtained. These complexes are of general formula *trans*-$Ru(LH)_2X_2 \cdot nH_2O$ (LH = thiosemicarbazide ligand, X = Cl, I) and contained thiosemicarbazides exclusively in their keto form. The relevant analytical data for the complexes are given in Table I.

It is well known that thiosemicarbazides in the free state exist in *trans* configuration with respect to the thiocarbonyl sulfur and the terminal nitrogen atom of the thiosemicarbazide moiety [6] but during complex formation they became *cis* to each other [8]. In the IR spectra of the ligands there are two strong bands in the 3000–3300 cm^{-1} region corresponding to $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ beside one or two ν(NH) bands in the same region, a strong band near 1600–1640 cm^{-1} corresponding to $\delta(NH_2)$ and the ν(CS) band near 720–750 cm^{-1} [9]. On complexation both the $\delta(NH_2)$ band and the ν(CS) band are lowered by 10–20 cm^{-1}, except in 4PhTSCH where the latter band shifts to a higher frequency. These observations clearly indicate the participation of the NH_2 group and thiocarbonyl sulfur in coordination to the metal ion. The IR spectra of the complexes in the $\nu(NH_2)$ region are generally obscured by a strong absorption due to the presence of lattice water. All the dichloro complexes exhibit one strong band at 310 cm^{-1} which is assigned to the ν(Ru–Cl) vibration [10]. This band is absent in the corresponding iodo complexes. The presence of only one ν(Ru–Cl) band indicates a *trans* dihalo structure for the complexes. Since the iodo complexes possess all the characteristic properties of the chloro complexes we have concluded that the iodo complexes also possess the *trans* dihalo configuration. However, we could not detect the ν(Ru–I) signal because it is outside the range of our instrument which could record up to 250 cm^{-1} only. A weak shoulder near 320 cm^{-1} observed in the IR spectra of all the halo complexes, may be assigned to the ν(Ru–N) vibration [11]. This shoulder is found to become more prominent in the iodo complexes where the ν(Ru–Cl) band at 310 cm^{-1} is absent. All the chloro complexes are diamagnetic and therefore ruthenium is present in the +2 oxidation state. The nonconducting nature of the complexes confirms that the halogens are coordinated and only one strong band near 310 cm^{-1} indicates that the halogens are situated *trans* to each other. Based on these observations we propose the following two structures for these dihalo complexes (Fig. 1): (a) possessing NN and SS *cis* but XX *trans* configuration; (b) possessing NN, SS and XX *trans* (all *trans*) configuration. Of these two possibilities, the existence of an all *trans* structure is indicated by the fact that the NMR spectra of the $Ru(p\text{-}CH_3PhTSCH)_2I_2$ complex in $CDCl_3$ exhibits only one signal due to CH_3 protons at δ 1.93 ppm. [*p*-CH_3TSCH = (4-(*p*-methyl phenyl) thiosemicarbazide]. The nature of the electronic spectra (see below) of all the complexes also supports this conclusion.

The electronic spectra of most of the complexes exhibit a band near 750 nm which may be assigned

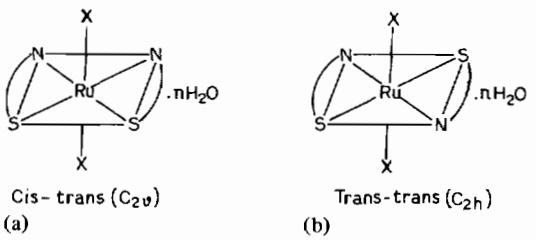

Fig. 1. Possible structures of Ru(II) *trans*-dihalobis (ring-Complexes

TABLE II. Electronic Spectral Data for the Important Metal Complexes

Complexes	Bands (ϵ (dm^3 mol^{-1} cm^{-1})) λ_{max} (nm)
$Ru(4PhTSCH)_2Cl_2 \cdot 2H_2O$	510(3, 459.93), 290(sh)(10, 869.56), 270(16, 521.73)
$Ru(4PhTSCH)_2I_2$	715(317.86), 520(2, 942.72), 310(4, 832.14), 270(9, 282.80)
$Ru(4p\text{-}CH_3PhTSCH)_2Cl_2 \cdot 2H_2O$	720(802.42), 518(2, 856.46), 290(7, 985.31)
$Ru(4p\text{-}CH_3PhTSCH)_2I_2$	700(748.43), 525(4, 942.52), 310(11, 609.19), 280(15, 057)
$Ru(4p\text{-}ClPhTSCH)_2Cl_2$	730(888.76), 515(5, 117.15), 278(15, 486.13)
$Ru(4p\text{-}ClPhTSCH)_2I_2$	720(267.99), 525(5, 551.44), 310(20, 000), 280(23, 501.11)
$Ru(o\text{-}OCH_3PhTSCH)_2Cl_2$	720(218.90), 520(6, 521.73), 280(17, 391), 210(37, 037)
$Ru(4p\text{-}OCH_3PhTSCH)_2Cl_2$	720(421.55), 525(2, 137.91), 290(2, 469.13)
$Ru(4p\text{-}OC_2H_5PhTSCH)_2Cl_2$*	720, 520, 290
$[Ru(4PhTSCH)_2(C_6H_5CN)_2]Cl_2$	650(1, 698.24), 510(5, 370.31), 300(13, 777.77), 250(23, 555.56), 215(30, 666.66)

*Quantitative spectra were not obtained because of its low solubility.

to the d–d transition $^1A_{1g} \rightarrow {}^1T_{1g}$ as is suggested by their ϵ values (Table II). However the most important feature of the electronic spectra is that all the complexes exhibit an intense absorption near 510 nm ($\epsilon > 2000$ mol^{-1} dm^3 cm^{-1}) which could be assigned to a MLCT band. This band probably corresponds to an electronic excitation from a metal d_π level to the π^* level of the ligand. This assignment is supported by the fact that a CNDO calculation [12] of two of the ligands, 4-phenyl thiosemicarbazide and 4-(*p*-chlorophenyl) thiosemicarbazide, indicate that the LUMO of these ligands are indeed a π^* orbital. The single MLCT band of this type supports the proposed all *trans* structure, because, if the ligands were in the *cis* disposition then we should have observed two MLCT bands of this type [13]. In fact in the corresponding *trans* dihalobis thiosemicarbazone Ru(II) complexes of α,α diketones, where the two sulfur atoms must be *cis* to each other, we get two MLCT bands as expected [14]. In the iodo compounds this MLCT band shifts to a higher wavelength because I^- increases the electron density on Ru(II) much more than Cl^-, resulting in a more facile MLCT transition. The last observation also supports the fact that the transition near 510 nm is indeed a MLCT instead of LMCT in which case the reverse trend is expected when Cl^- is replaced by I^-. This MLCT also supports the assignment of a +2 oxidation state of ruthenium since for Ru(III) the MLCT is expected at a much higher energy.

Another interesting feature of the charge transfer band is that as the *p*-substituents on the phenyl ring of the thiosemicarbazide are varied the position of the CT band is not much affected but the ϵ value of this band varies in a systematic way with the substitutent. In fact if we plot log ϵ *versus* Hammett σ_p value for the *p*-substituents we get a linear plot (Fig. 2). A tentative explanation of this behaviour may be presented as follows. Zwickel and Creutz, from a naive MO consideration, showed [13] that

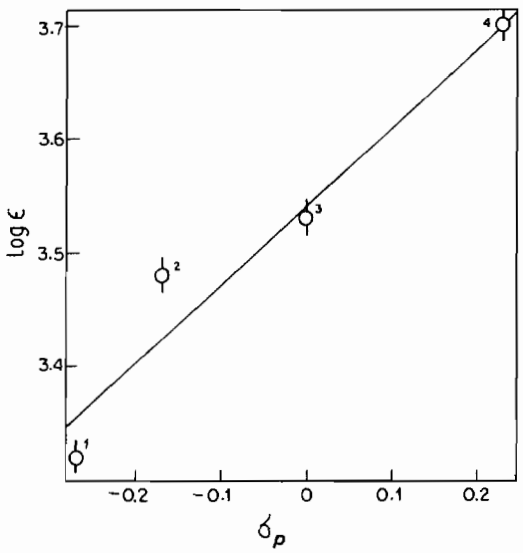

Fig. 2. Least-squares plot of log ϵ against Hammett σ_p values. (1) $Ru(4p\text{-}OCH_3PhTSCH)_2Cl_2$, (2) $Ru(4p\text{-}CH_3PhTSCH)_2Cl_2 \cdot 2H_2O$, (3) $Ru(4PhTSCH)_2Cl_2 \cdot 2H_2O$, (4) $Ru(4p\text{-}ClPhTSCH)_2Cl_2$.

for *trans* Ru(II) complexes the energy of the allowed MLCT band may be expressed as

$$\Delta E = \frac{\delta}{2} + \frac{1}{2}\sqrt{\delta^2 + 8\beta^2}$$

where $\beta = \alpha_L - \alpha_{Ru}$, $\beta = (\pi^* | H | t_{2g})$, $\alpha_L = (\pi^* | H | \pi^*)$, $\alpha_{Ru} = (t_{2g} | H | t_{2g})$. Now as the *p*-substituent becomes more and more electron donating it icreases electron density on the C(3) atom and thus pushes the π^* level (LUMO) to a higher energy, *i.e.* α_L increases. In fact CNDO calculation shows that LUMO for the 4-*p*-chloro substituent has an energy of +3.35 eV and that of unsubstituted 4-phenyl thiosemicarbazide is +3.60 eV. But the increase in the electron donating capacity of the substituents also increases the elec-

tron density at the donor atoms (N and S) thus making them stronger σ donors and hence, enhancing the energy of the d-orbitals [15]. Thus δ remains more or less constant and so does ΔE. However if there is an increase in electron density at the donor atoms, metal to ligand charge transfer becomes less facile as the *p*-substituent becomes more and more electron donating. This is manifested in terms of decreased intensity of the MLCT band.

Beside the band at 510 nm there is also an intense band at 310 nm which also is probably of charge transfer origin. The intense band near 260 nm is probably of ligand origin.

Reactivity

In order to study the reactivity of these compounds we have chosen $Ru(4PhTSCH)_2Cl_2 \cdot 2H_2O$ as the representative complex (4PhTSCH = keto form of 4-phenyl thiosemicarbazide). All the reactions of this complex are also expected to take place with other complexes as well, as they do not differ significantly from each other either electronically or stereochemically.

Conductance values of these complexes in MeOH are found to be well below the value expected for a 1:1 electrolyte [16]. At the same time they are not absolutely non-conducting ($\lambda_M \sim 60$ ohm^{-1} cm^2 mol^{-1} in MeOH). This suggests that the halo groups are somewhat labile and the observed conductance is due to partial replacement of the halo groups by the solvent molecules. This observation is also supported by the fact that during the study of reactivity of these compounds the two halogens are readily replaced by various monodentate donors. The various reactions of the complex $Ru(4PhTSCH)_2Cl_2$ are schematically represented in Fig. 3.

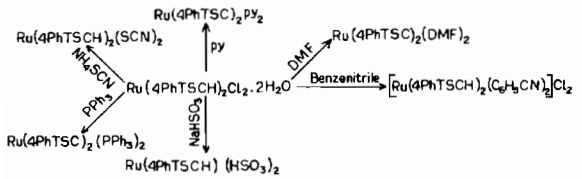

Fig. 3. Reactions of $Ru(4PhTSCH)_2Cl_2 \cdot 2H_2O$ with various Lewis bases.

It was found that the bright red–violet colour of the methanolic solution of the parent compounds discharged slowly on keeping for 24 h (the band at 510 nm disappears) with the deposition of a black compound which is insoluble in many of the common solvents like methanol, ethanol, benzene, dichloromethane, chloroform etc. However it is completely soluble in DMF and partly so in acetone yielding light yellow solutions. The black residue is probably polymeric in nature and no definite composition could be assigned to it. On addition of pyridine to the freshly prepared methanolic solution of the parent compound the red colour gradually changed to yellow and finally became green. The green compound isolated from that solution was found to be a bis pyridine complex with ligands in the enol form. The compound is diamagnetic and non-conducting in MeOH indicating that the ligand is in the enol form. When cytidene or cytosin was added to a bright red–violet methanolic solution of $Ru(4PhTSCH)_2Cl_2$ and the reaction monitored spectrophotometrically at 40 °C, the intensity of the 510 nm band was found to diminish gradually and vanish after ~15 min. The final colour of the solution was yellow. This reaction indicated that $Ru(4PhTSCH)_2Cl_2$ binds readily with a nucleotide and a nucleic acid base. The DMF solution of $Ru(4PhTSCH)_2Cl_2$ shows a gradual increase in conductance until it becomes constant. The colour of the solution changes from red–violet to yellowish-brown and the band at 510 nm gradually disappears. The final value of conductance corresponds exactly to the value expected if the following reaction takes place

$$[Ru(4PhTSCH)_2Cl_2] + 2DMF \rightarrow$$

$$[Ru(4PhTSC)_2(DMF)_2] + 2HCl$$

The thiocyanato complex obtained by refluxing a methanolic solution of freshly prepared $Ru(4PhTSCH)_2Cl_2$ with a saturated solution of NH_4SCN in MeOH, shows only one strong IR band near 2100 cm^{-1} indicating that the two SCN^- groups are *trans* to each other and they are probably bonded through the sulfur atom [17]. When 1 mole of the parent complex is reacted with 2.5 mole of PPh_3 in MeOH medium again we have replacement of the two halogens by two PPh_3 molecules with simultaneous enolisation of the ligand. The halides have also been replaced by bisulfite and benzonitrile. The IR spectrum of the bisulfite complex exhibits the presence of new bands at 1225 and 1155 cm^{-1} (ν_{as} and ν_s of HSO_3^-) as well as at 990, 600 and 500 cm^{-1}, which may be attributed to a coordinated bisulfite group. In the bis benzonitrile complex a single sharp band ν(CN) appears at 2210 cm^{-1} indicating a $\Delta\nu$(CN) value of -21 cm^{-1} [$\Delta\nu(CN) = \nu(C_6H_5CN\text{-(free)}) - \nu(C_6H_5CN\text{(complexed)})$]. If we compare this with $\Delta\nu$(CN) of the corresponding *trans*-$[Ru(NH_3)_4(C_6H_5CN)_2]^{2+}$ complex moiety where it is ~ -18 cm^{-1} [18], we may draw the following conclusions from it: the π back-bonding capability of the *trans*-$[Ru(4PhTSCH)_2]^{2+}$ moiety is comparable, in fact slightly better, than that of the *trans*-$[Ru(NH_3)_4]^{2+}$ moiety as indicated in their corresponding $\Delta\nu$(CN) values. This conclusion is corroborated by the fact that in the *trans*-$[Ru(4PhTSCH)_2(C_6H_5CN)_2]Cl_2$ complex we get two charge transfer bands at 510 and 650 nm which may be assigned to the $d_{\pi \rightarrow \pi^*}$ of 4PhTSCH and $d_{\pi \rightarrow \pi^*}$ of C_6H_5CN respectively.

The latter band is at a considerably lower energy than that of the corresponding band of the *trans* tetrammine complex (362 nm). This is probably due to the fact that the appreciable back bonding between d_π(Ru) and the thiosemicarbazide keeps the effective nuclear charge on ruthenium quite high, which, in its turn, lowers the energy of the π^* orbital of the benzonitrile group by electrostatic and charge interaction as predicted by Mayer [19]. This results in a good $d_{\pi\rightarrow\pi^*}$ back bonding between ruthenium and benzonitrile and thus lowers the energy of the MLCT transition and increases the $\Delta\nu$(CN) value compared to that of the analogous tetrammine complex where the above mechanism is inoperative.

Biological Activity

A preliminary study on the biological activity of some of the complexes reported in this study in the form of their *in vitro* antibacterial activity was made in the following manner.

A culture was grown from a single coloney of *E. coli* in a nutrient broth kept in an Erlenmeyer flask and incubated at 37 °C in a BOD incubator shaker. Standard solutions of $[Ru(4PhTSCH)_2Cl_2]\cdot 2H_2O$, $[Ru(4pClPhTSCH)_2Cl_2]$, $[Ru(4PhTSCH)_2I_2]$ and $[Ru(4pClPhTSCH)_2I_2]$ complexes were prepared in 1:1 DMSO:ethanol mixture and requisite volumes of these solutions were added to 10 ml of the medium kept in 20 ml sterilised test tubes. 0.1 ml of the *E. coli* culture was added to each test tube and the tubes were incubated for 24 h at 37 °C. The result of this bacterial growth inhibition study is presented below in terms of minimum inhibitory concentration (MIC).

Compound	MIC	
	(μg/ml)	(μM/ml)
$Ru(4PHTSCH)_2Cl_2\cdot 2H_2O$	200	0.37
$Ru(4PhTSCH)_2I_2$	150	0.21
$Ru(4pClPhTSCH)_2Cl_2$	175	0.30
$Ru(4pClPhTSCH)_2I_2$	60	0.08

These results indicate that all the four complexes exhibit significant antibacterial activity. Such activity is found to depend on (i) the nature of the ligand and (ii) the nature of the coordinated halide ions, the latter factor being more dominant. Antibacterial activity of all the reported complexes is being examined in detail under various experimental conditions. The results, along with the possible mode of action of the antibacterial action, will be reported in the future.

Experimental

$RuCl_3$ obtained commercially (Aurora Mathey) was thrice evaporated to dryness with concentrated HCl and then kept in a vacuum desiccator over solid NaOH. RuI_3 was prepared by adding an excess of KI to an aqueous solution of $RuCl_3$ which was stirred for ½ h, and then warmed on a water bath for another ½ h. RuI_3 separated out as a black insoluble solid. It was filtered, washed several times with distilled water and finally dried over fused $CaCl_2$. The ligands were prepared from the corresponding amines by a slight modification of the standard procedure [20]. Elemental analyses were obtained from the microanalytical laboratory of this Department. Halides were estimated in the usual way. The IR spectra were recorded on a Perkin-Elmer 783 instrument as KBr and CsBR discs. Electronic spectra of the compounds were recorded on a Pye-Unicam model SP8-150 UV–Vis spectrophotometer. Electrical conductance data in solution were obtained on a Philips PR-9500 conductivity bridge fitted with a dip type cell. Magnetic susceptibilities were measured at room temperature by a Princeton Applied Research Vibrating Sample Magnetometer using $Hg[Co(SCN)_4]$ as the calibrant.

Preparation of $Ru(LH)_2Cl_2$

The $Ru(LH)_2Cl_2\cdot 2H_2O$ type complexes were prepared by reacting a methanolic solution of the ligand (2.2 mmol) in ice cold condition to which a previously cooled solution of $RuCl_3$ (1 mmol) in MeOH was added drop by drop with constant stirring. The stirring was continued for a further hour after the addition was completed. The solution was then concentrated at room temperature in a rotary evaporator when a deep red–violet compound separated out. It was filtered, washed several times first with distilled water followed by hot benzene in which the ligand is soluble. The compounds were dried over fused $CaCl_2$.

Preparation of $Ru(LH)_2I_2$

To prepare the iodo complexes, 1 mmol of RuI_3 was refluxed with 2.5 mmol of the ligand for 1 h in MeOH, the whole thing was then filtered hot and the residue was rejected. The filtrate was evaporated to dryness, redissolved in chloroform, petroleum ether (80–100° fraction) was added to the chloroform solution and a deep violet compound separated out. It was filtered, washed successively with water and hot benzene and then dried over fused $CaCl_2$.

Preparation of $Ru(4PhTSC)_2(PPh_3)_2$

1 mmol of $Ru(4PhTSCH)_2Cl_2$ in MeOH was refluxed with 2.5 mmol of PPh_3 for 2 h. The solution was then filtered hot. The filtrate was concentrated to a small volume in a rotary evaporator, n-hexane was added to the concentrate with stirring and a bright yellow compound separated out. It was filtered, washed several times with petroleum-ether and dried over fused $CaCl_2$.

Preparation of $Ru(4PhTSC)_2py_2$

1 mmol of $Ru(4PhTSCH)_2Cl_2$ in MeOH was treated with 3 ml of pyridine, stirred for ½ h and then kept on a water bath for 15 min. Concentration of the solution in a rotary evaporator yield a green compound, which was filtered, washed with ether and dried in a desiccator.

Preparation of $Ru(4PhTSCH)_2(HSO_3)_2$

1 mmol of $Ru(4PhTSCH)_2Cl_2$ in MeOH was treated with 2.5 mmol of $NaHSO_3$ dissolved in 10 ml of water and stirred for 2 h. The resultant solution was then evaporated to dryness on a water bath, washed with water and dried over conc. sulfuric acid.

Preparation of $[Ru(4PhTSCH)_2(C_6H_5CN)_2]Cl_2$

To an ice cold solution of 1 mmol of $RuCl_3$ in MeOH, a methanolic solution of 2.2 mmol of 4-phenyl thiosemicarbazide was added drop by drop and the mixture was stirred in ice cold conditions for 1 h. To the resultant red solution 0.5 ml of benzonitrile was added and the mixture was stirred at room temperature for 3.5 h. The solution was evaporated to dryness and the residue redissolved in 1:2 chloroform:methanol mixture. When this solution was slowly evaporated the desired compound separated out. It was filtered, washed with water and benzene and then dried over fused $CaCl_2$.

Preparation of $Ru(4PhTSCH)_2(SCN)_2$

To a freshly prepared methanolic solution of $Ru(4PhTSCH)_2Cl_2$ (1 mmol) about 2.5 mmol of NH_4SCN was added. The mixture was refluxed for 45 min, cooled to room temperature and then concentrated on a rotary evaporator when a yellowish-brown compound separated out. It was filtered, washed several times with water and dried over fused $CaCl_2$.

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