



# Synthesis and characterization of bis(2,2'-bipyridine) ruthenium complexes containing thiosemicarbazide ligands: unique redox series

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(Received 10 September 1996; accepted 22 May 1997)

**Abstract**—Two series of heterochelates of ruthenium(II) containing two bipyridyl molecules and a bidentate chelating sulfur–nitrogen donor ligand in the form of 4-aryl substituted thiosemicarbazides have been synthesized and characterized. The first series of complexes are dicationic in which the ring substituted 4-aryl thiosemicarbazides (N–S) are chelated in the keto form through the hydrazinic nitrogen and the thione sulfur atom. They are of the  $[\text{Ru}(\text{bpy})_2\text{NS}]^{+2}$  type. The second series have the general formula  $[\text{Ru}(\text{bpy})_2\text{NS}]^{+1}$  in which the thiosemicarbazide moiety remains chelated to the  $\text{Ru}^{\text{II}}$  centre through the hydrazinic nitrogen and the deprotonated thiolato S-atom. All the complexes have been characterized by elemental analysis, UV–vis, IR and EPR spectroscopy. The complexes were found to constitute a three membered redox series which were investigated by cyclic voltammetry. © 1997 Elsevier Science Ltd

**Keywords:** ruthenium complexes; bis(2,2'-bipyridine) $\text{Ru}^{\text{II}}$  core; NS donors; thiosemicarbazide ligands; mixed ligand complexes; Redox series.

The study of redox series or electron transfer series has been a fascinating area of research for more than two decades [1–5]. Such studies are of great help in the understanding the general theory of redox reactions, providing useful insight into metal–ligand bonding, intramolecular electron transfer and concept of oxidation state in coordination chemistry. They are also useful for tailoring of redox reagents, elucidation of mechanisms of redox catalysis and biological electron transfer processes. Moreover, as several redox orbitals are involved in a redox series, they can be utilised to probe the extent to which different substituents affect the various redox orbital involved.

Though most of the transition metals are found to form redox series involving a wide variety of ligands [1] acting as series stabilizers or carriers, the series in which the  $\text{Ru}^{\text{II}}$  centre is bound to one or more bipyridine ligands have attracted researchers to the greatest

extent [3–13]. The motivations of such studies are extremely diverse and ranges from their practical applicability [14,15] such as in solar energy conversion, in catalytic water splitting etc. to their importance in investigating fundamental chemical phenomena such as localization versus delocalization of redox orbitals [12,16–19], photochemically induced isomerization [20,21], ligand substitution [22–24], relative stability of redox orbitals [8,9,13,25] as well as structural reorganisation on electron transfer [4]. In particular, a number of complexes containing a  $\text{Ru}(\text{bpy})_2^{+2}$  core with a variety of coligands like 1,2-di-iminolenes [8], 1,2-dioxolenes [4,8,10], 1,2-dithiolenes [7] and their mixed derivatives have been studied extensively. As these complexes are richly endowed with redox orbitals, they undergo extremely interesting electronic and electrochemical changes creating diverse structure and bonding situations. Moreover, such complexes also exhibit interesting spectro-electrochemical correlations [6,7,26].

In 1970 Holm and coworkers [27] demonstrated

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that  $\text{Pt}^{\text{II}}$  complexes of 1,4-di substituted thiosemicarbazides form an electron transfer series. We have demonstrated [28] that 4-aryl substituted thiosemicarbazone of salicylaldehyde acts as a stabilizer of a redox series involving molybdenum, where molybdenum shuttles between +4, +5 and +6 oxidation states. These are the only reports in which the thiosemicarbazide group of ligands are utilised as a potential stabilizer or carrier of redox series. In this paper we report synthesis and characterization of a series of aryl substituted thiosemicarbazide complexes of the  $\text{Ru}(\text{bpy})_2^{+2}$  moiety, with the ligand present in both keto and enolate forms. The redox series formed by these complexes are investigated by cyclic voltammetry, EPR and UV-vis spectroscopy. EPR and electrochemical data are discussed in terms of orbital mixing.

## EXPERIMENTAL

### Physical measurements

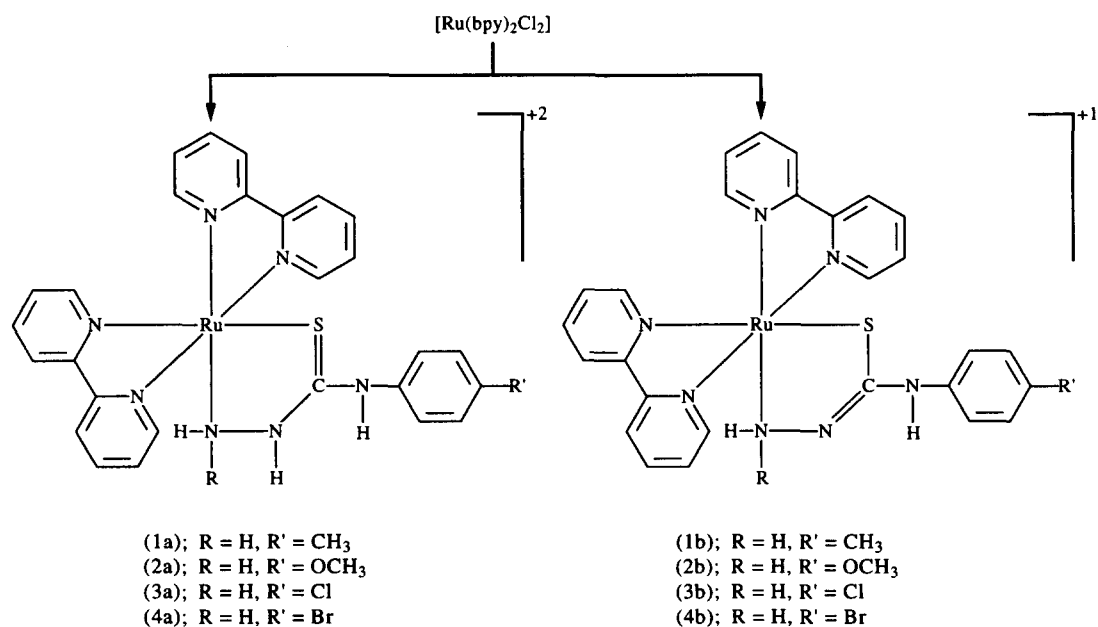
Elemental analyses were done by a Perkin-Elmer 240 C,H,N analyser. Electrical conductivity in solution was measured at 298 K by using a Philips PR 9500 conductivity bridge with a dip type cell, calibrated with 0.02 M KCl solution. IR spectra were recorded at 298 K on a Perkin-Elmer 783 spectrophotometer as KBr pellets. Electronic spectra were recorded in acetonitrile solutions with Shimadzu Model UV-2100 and Hitachi Model 330 spectrophotometers. Magnetic moments of solid complexes were determined using a PAR model 155 vibrating sample magnetometer with  $\text{Hg}[\text{Co}(\text{SCN})_4]$

as calibrant. EPR spectra were recorded on a Varian E4 X-band spectrometer. Cyclic voltammetric experiments were performed under dry nitrogen atmosphere using a Bioanalytical system CV-27 Electrochemical analyser and a BAS Model X-Y recorder at 298 K. A standard three electrode electrochemical cell consisting of a platinum working electrode (BAS), a platinum wire auxiliary electrode and a Ag/AgCl reference electrode separated from the test solution by a home made salt bridge containing the solvent mixture (50% water/acetonitrile) and the supporting electrolyte (TEAP) was used. Ferrocene was used as internal standard for the measurement of  $\Delta E_p$  values. With the above electrode configuration ferrocene is oxidised at 0.46 V Ag/AgCl.

### Materials

$\text{Cis}[\text{Ru}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  was prepared by a previously reported procedure [29]. The ligands 4-(*p*-methylphenyl)thiosemicarbazide [4-(*p*- $\text{CH}_3$ ) $\text{C}_6\text{H}_4$ TSCH], 4-(*p*-methoxyphenyl)thiosemicarbazide [4-(*p*- $\text{OCH}_3$ ) $\text{C}_6\text{H}_4$ TSCH], 4-(*p*-chlorophenyl)thiosemicarbazide [4-(*p*-Cl) $\text{C}_6\text{H}_4$ TSCH] and 4-(*p*-bromophenyl)thiosemicarbazide [4-(*p*-Br) $\text{C}_6\text{H}_4$ TSCH] were prepared from the corresponding amines by a slight modification of the standard procedure [30].

All other chemicals were A.R. grade and used without further purification. All reactions were performed under dry nitrogen. For the cyclic voltammetric experiments, the solvent and supporting electrolyte (TEAP) were prepared and purified by standard methods [31], 0.1 M concentrations of supporting electrolyte were employed for all voltammetric studies.



**Preparation of [Ru(bpy)<sub>2</sub>(4-(*p*-CH<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>TSCH)](ClO<sub>4</sub>)<sub>2</sub> (1a), [Ru(bpy)<sub>2</sub>(4-(*p*-OCH<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>TSCH)](ClO<sub>4</sub>)<sub>2</sub> (2a), [Ru(bpy)<sub>2</sub>(4-(*p*-Cl)C<sub>6</sub>H<sub>4</sub>TSCH)](ClO<sub>4</sub>)<sub>2</sub> (3a), [Ru(bpy)<sub>2</sub>(4-(*p*-Br)C<sub>6</sub>H<sub>4</sub>TSCH)](ClO<sub>4</sub>)<sub>2</sub> (4a).** **Warning:** Perchlorate salts of metal complexes are potentially explosive [32].

Solution of a thiosemicarbazide (0.5 mmol) in methanol (15 cm<sup>3</sup>) was added to a methanol (25 cm<sup>3</sup>) solution of [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>]·2H<sub>2</sub>O (260 mg, 0.5 mmol) and the resultant solution was refluxed for 4 h under dry nitrogen. It was then filtered and the residue, if any, was rejected. Volume of the filtrate (pH = 4) was then reduced in a rota-evaporator, excess of aqueous LiClO<sub>4</sub> was added and it was kept in a refrigerator. The precipitate that settled down was filtered under nitrogen. It was washed thoroughly with water and recrystallised from dichloromethane. Yields ranged from 50 to 60% based on [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>]·2H<sub>2</sub>O.

**Preparation of [Ru(bpy)<sub>2</sub>(4-(*p*-CH<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>TSC)](ClO<sub>4</sub>) (1b), [Ru(bpy)<sub>2</sub>(4-(*p*-OCH<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>TSC)](ClO<sub>4</sub>) (2b), [Ru(bpy)<sub>2</sub>(4-(*p*-Cl)C<sub>6</sub>H<sub>4</sub>TSC)](ClO<sub>4</sub>) (3b), [Ru(bpy)<sub>2</sub>(4-(*p*-Br)C<sub>6</sub>H<sub>4</sub>TSC)](ClO<sub>4</sub>) (4b).** A methanol (25 cm<sup>3</sup>) solution of [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>]·2H<sub>2</sub>O (260 mg, 0.5 mmol) was added to the thiosemicarbazide (0.05 mmol) solutions in methanol (20 cm<sup>3</sup>) and refluxed under dry nitrogen. The refluxed solution was then filtered and the pH of the filtrate was adjusted to 8–9 with conc. NH<sub>4</sub>OH. It was then stirred for 2 h under dry nitrogen. The volume of the solution was reduced to half and excess of aqueous LiClO<sub>4</sub> solution was added. The precipitated solid was filtered, washed with water and finally recrystallised from dichloromethane. Yield ~ 50%.

The ruthenium(II) complexes reported in this study were characterised by (1) the methods of preparation; (2) satisfactory elemental analysis (Table 1); (3) room temperature magnetic moment and solution conductance measurements; (4) IR spectra (Table 2); (5) cyclic voltammetric results (Table 3); (6) UV–vis spectra (Table 4) and (7) EPR spectra.

All the complexes are diamagnetic which indicates that the formal oxidation state of ruthenium in them is +2. The dicationic complexes (1a–4a) and monocationic complexes (1b–4b) behave as 1:2 and 1:1 (Table 1) [33] electrolytes respectively in acetonitrile, indicating that ClO<sub>4</sub><sup>-</sup> is not coordinated to the Ru<sup>II</sup> centre, which is corroborated by the presence of the band of ionic perchlorate in their IR spectra.

The electron transfer behaviour of the ruthenium(II) complexes have been examined in MeCN solution (0.1 M TEAP) at a platinum working electrode with the help of cyclic voltammetric technique. Relevant data are summarised in Table 3. The electrochemical reversibility of the different redox processes (except where it is mentioned as irreversible) were indicated by  $i_{pc}/i_{pa} \sim 0.9-1$ , where  $i_{pc}$  and  $i_{pa}$  could be measured accurately. Peak potential separations ( $\Delta E_p$ ) between anodic and cathodic waves vary between 60–80 mV at 200 mV s<sup>-1</sup> scan rate. Though the  $\Delta E_p$  values for a few couples are slightly higher than ideal Nernstian value of 59 mV, such deviations are known to occur in similar systems for a number of reasons [6,7]. Coulometric experiments or comparison of  $\Delta E_p$  and peak current values of the couples with those of equimolar *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O solutions were used for confirmation of the one

Table 1. Analytical and physical data for the ruthenium complexes

Complex	Analysis			Molar Conductance <sup>a</sup> $\Lambda_M$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )
	C	N	H	
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSCH)](ClO <sub>4</sub> ) <sub>2</sub> (1a)	42.4 (42.4)	12.4 (12.2)	3.4 (3.4)	215
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -OCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSCH)](ClO <sub>4</sub> ) <sub>2</sub> (2a)	41.5 (41.6)	12.1 (12.0)	3.3 (3.2)	245
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Cl)PhTSCH)](ClO <sub>4</sub> ) <sub>2</sub> (3a)	39.8 (39.9)	12.0 (12.0)	3.0 (3.0)	261
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Br)C <sub>6</sub> H <sub>4</sub> TSCH)](ClO <sub>4</sub> ) <sub>2</sub> (4a)	37.7 (37.3)	11.3 (10.9)	2.8 (2.8)	225
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) (1b)	48.5 (48.2)	14.2 (13.9)	3.8 (3.7)	147
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -OCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) (2b)	47.4 (47.3)	13.8 (13.4)	3.7 (3.5)	134
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Cl)C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) (3b)	45.4 (45.5)	13.7 (13.4)	3.2 (3.3)	137
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Br)C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) (4b)	42.8 (42.4)	12.9 (13.0)	3.0 (3.0)	136

<sup>a</sup> Acetonitrile.

Table 2. Important IR bands ( $\text{cm}^{-1}$ ) for the compounds

Complex	$\delta(\text{NH}_2)/\nu(\text{CN})$ or $\delta(\text{NH}) + \nu(\text{CN})$	$\delta(\text{NH}) + \nu(\text{CN} + \text{CC}) + \nu(\text{CN})$	$\nu(\text{CS})$	Pyridine ring vibration (out of plane) <sup>a</sup>	Other characteristic bands <sup>c</sup>
4-( <i>p</i> -CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSCH	1605	1580, 1545	805	—	—
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSCH)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>1a</b> )	1635, 1600	1550(w), 1510	770	635	1100(b) <sup>d</sup> , 505, 430
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) ( <b>1b</b> )	1600	1550(w), 1510	770	630	1100(b) <sup>d</sup> , 535, 515, 430
4-( <i>p</i> -OCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSCH	1630	1520, 1503	794	—	—
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -OCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSCH)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>2a</b> )	1625, 1595	1550(w), 1500	770	630	1100(b) <sup>d</sup> , 565, 520, 425
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -OCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) ( <b>2b</b> )	1596	1550(w), 1502	765	625	1090(b) <sup>d</sup> , 570, 530, 425
4-( <i>p</i> -Cl)C <sub>6</sub> H <sub>4</sub> TSCH	1630	1580, 1530, 1486	760	—	—
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Cl)C <sub>6</sub> H <sub>4</sub> TSCH)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>3a</b> )	1630, 1600	1555, 1490	775	635	1100(b) <sup>d</sup> , 580, 525, 500, 430
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Cl)C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) ( <b>3b</b> )	1600	1550(w), 1490	770	635	1100(b) <sup>d</sup> , 545, 520, 470, 430
4-( <i>p</i> -Br)C <sub>6</sub> H <sub>4</sub> TSCH	1615	1580, 1545	760	—	—
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Br)C <sub>6</sub> H <sub>4</sub> TSCH)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>4a</b> )	1627, 1600	1584, 1546, 1485	770	630	1100(b) <sup>d</sup> , 575, 510, 425
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Br)C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) ( <b>4b</b> )	1607	1500	770	630	1100(b) <sup>d</sup> , 542, 510, 430

<sup>a</sup> Ref.: S. K. Chattopadhyay and S. Ghosh, *Inorg. Chim. Acta*, 1989, **163**, 245.

<sup>b</sup> = Broad.

<sup>c</sup> New bands of weak to medium intensity of lower wave number may be assign to the vibrations  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{S})$ ; Ref.: G. K. Gupta and S. K. Dikshit, *Polyhedron*, 1987, **6**, 1009.

<sup>d</sup> Band of ionic ClO<sub>4</sub><sup>-</sup>; sh = shoulder; w = weak.

Table 3. Cyclic voltammetric results<sup>a,b</sup> at 298 K

Complex	Oxidation $E_{1/2}$ , V ( $\Delta E_p$ , mV)	Reduction $E_{1/2}$ , V
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSCH)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>1a</b> )	0.28(60), 0.83(60)	-1.41, -1.65, -1.82
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -OCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSCH)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>2a</b> )	0.28(60), 0.82(55)	-1.44, -1.67
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Cl)C <sub>6</sub> H <sub>4</sub> TSCH)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>3a</b> )	0.29(60), 0.81(60)	-0.95 <sup>d,e</sup> , -1.56
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Br)C <sub>6</sub> H <sub>4</sub> TSCH)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>4a</b> )	0.29(60), 0.79(75)	-1.07 <sup>d,e</sup> , -1.40 <sup>d</sup>
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) ( <b>1b</b> )	0.41(60), 0.60(80)	-1.04 <sup>d,e</sup> , -1.53
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -OCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) ( <b>2b</b> )	0.39(60), 0.60(80)	-0.91 <sup>d</sup> , -1.58, -1.69, -1.82 <sup>d</sup>
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Cl)C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) ( <b>3b</b> )	0.49 <sup>c</sup> , 0.71(70)	-1.58 <sup>d</sup> , -1.80
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Br)C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) ( <b>4b</b> )	0.45 <sup>c</sup> , 0.66(80)	-1.56, -1.82

<sup>a</sup> Conditions: 0.1 M TEAP in CH<sub>3</sub>CN vs Ag/AgCl; Solute concentration:  $\sim 10^{-3}$  M; Working electrode: Platinum.

<sup>b</sup>  $E_{1/2} = 0.5(E_{pa} + E_{pc})$ ,  $\Delta E_p = E_{pc} - E_{pa}$ , where  $E_{pa}$  and  $E_{pc}$  are anodic and cathodic peak potentials, respectively.

<sup>c</sup> Oxidative response only,  $E_{1/2}$  value was calculated taking  $\Delta E_p = 60$  mV.

<sup>d</sup> Reductive response only,  $E_{1/2}$  value was calculated taking  $\Delta E_p = 60$  mV.

<sup>e</sup> Corresponding oxidative response at  $E_{pa} = -0.75$  V.

electron and reversible nature of the electron transfer reactions. Plots of peak currents vs the square root of scan rate are linear, indicating that diffusion-controlled redox processes are taking place at the electrode.

All the complexes exhibit highly rich (Fig. 1) optical spectra. It is noted that the dicationic complexes **1a-4a** (ligand in the thione form) are similar to each other (Table 4) but differ from those of the monocationic complexes **1b-4b** (thiolato form). This points to the

Table 4. UV–vis spectral data for Ru(bpy)<sub>2</sub>(L–L) complexes

Complex	Band I	Band II	Abs max, nm (10 <sup>-3</sup> ε, M <sup>-1</sup> cm <sup>-1</sup> ) <sup>a</sup>	Band III	Band IV	Band V
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>1a</b> ) <sup>b</sup>	625(0.94)	530(1.89), 485(sh)(3.90)	408(7.16), 309(sh)(19.41)	290(39.17), 258(sh), (23.36), 242(27.34)	218(32.12)	
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -OCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>2a</b> )	708(sh)(1.65)	562(5.15) 458(6.58)	382(sh)(7.79), 309(sh)(21.11)	290(48.00), 258(sh), (27.24), 242(32.00)	219(35.40)	
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Cl)C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>3a</b> )	678(sh)(1.39)	555(sh)(3.98) 473(5.63)	365(sh)(7.28), 312(sh)(17.15)	291(50.31), 258(sh), (29.19), 244(33.04)	218(36.16)	
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Br)C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) <sub>2</sub> ( <b>4a</b> )	671(sh)(1.40)	570(sh)(2.54), 467(4.28)	387(sh)(5.23), 310(sh)(17.16)	290(38.38), 258(sh), (24.61), 244(27.62)	218(30.36)	
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) ( <b>1b</b> )	—	507(11.07), 457(sh)(8.69)	351(14.50)	293(72.73), 287(sh), (61.07), 245(36.08)	218(38.03)	
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -OCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) ( <b>2b</b> )	—	505(8.37), 457(8.70)	351(12.60)	292(63.31), 287(sh), (58.82), 243(36.72)	219(42.60)	
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Cl)C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) ( <b>3b</b> )	—	507(sh)(5.40), 453(6.76)	352(sh)(8.10)	291(48.83), 255(sh), (24.47), 244(29.37)	218(29.56)	
[Ru(bpy) <sub>2</sub> (4-( <i>p</i> -Br)C <sub>6</sub> H <sub>4</sub> TSC)](ClO <sub>4</sub> ) ( <b>4b</b> )	—	499(9.62), 455(9.34)	361(sh)(12.92)	293(73.06), 257(sh), (34.60), 244(42.36)	218(47.21)	

<sup>a</sup> In acetonitrile.<sup>b</sup> Electronic spectra (200–2500 nm) of **1a** in acetonitrile (oxidised electro-chemically at 0.5 V) 1911, 1411, 685(sh), 542, 481(sh), 362, 290, 244, 212; sh = Shoulder.

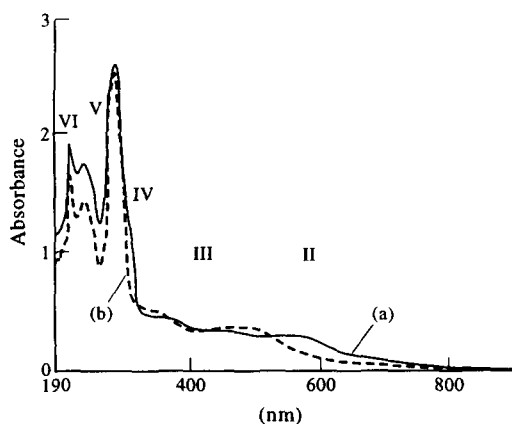


Fig. 1. Electronic spectra of complexes in acetonitrile: (a) for complex  $\text{Ru}(\text{bpy})_2(4-(p\text{-OCH}_3)\text{C}_6\text{H}_4\text{TSC})(\text{ClO}_4)_2$  (**2a**), (concentration =  $0.544 \times 10^{-4}$  moles/litre); (b) for complex  $[\text{Ru}(\text{bpy})_2(4-(p\text{-OCH}_3)\text{C}_6\text{H}_4\text{TSC})](\text{ClO}_4)$  (**2b**), (concentration =  $0.392 \times 10^{-4}$  moles/litre).

significance of the particular form of the donor atoms of the ligand through which it coordinates to the metal ion. The visible and UV spectra of the complexes exhibit a maximum of nine peaks, which have been labelled as band I–V for convenience of discussion, with two closely spaced wavelength bands being grouped together.

The infrared spectra of the complexes exhibit a number of bands, which often result from the overlapping of bipyridine and 4-(*p*-substituted phenyl) thiosemicarbazide vibrations, and thus precise assignment of individual bands are quite difficult. Table 2 contains the more important IR bands of the ligands and their complexes along with their tentative assignments. The presence of uncoordinated (ionic) perchlorate was clearly evidenced by the strong and broad band around  $1100 \text{ cm}^{-1}$ .

### Synthesis

The different *bis*-(bipyridyl) complexes were prepared from  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  by reacting it with different thiosemicarbazides under dry nitrogen atmosphere. When pH of the solution is raised to 8.5–9 by ammonia the ligands undergo enolisation followed by complex formation. All the complexes were isolated as their perchlorate salts.

### Electrochemistry

A close look at the electrochemical data in Table 3 reveals that each of the four complexes (**1a**, **2a**, **3a**, and **4a**) forms a three membered (A, B and C) electron transfer series, [eq. (1) and Fig. 2] each successive member of a series differing by one electron.

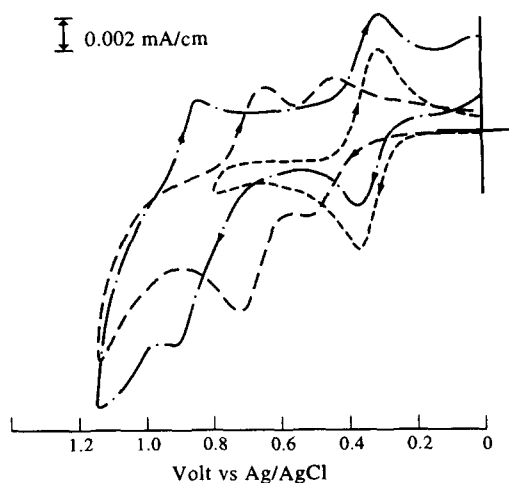
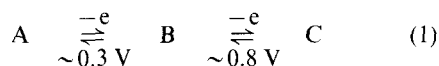
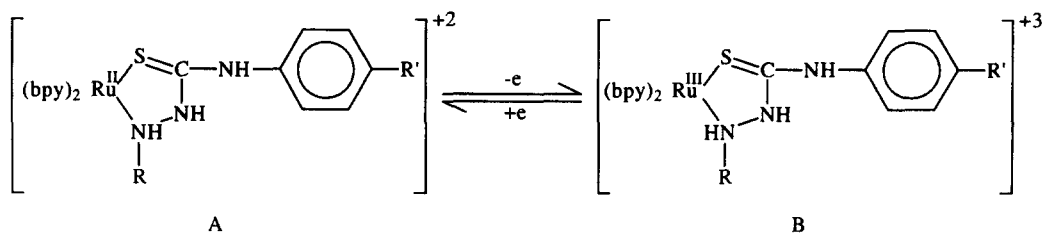


Fig. 2. Cyclic voltammograms of  $10^{-3}$  M solution (scan rate  $200 \text{ mV s}^{-1}$ ) of (a) *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2$  (---), (b)  $\text{Ru}(\text{bpy})_2(4-(p\text{-OCH}_3)\text{C}_6\text{H}_4\text{TSC})(\text{ClO}_4)_2$  (**2a**) (-·-·-·-), (c)  $[\text{Ru}(\text{bpy})_2(4-(p\text{-OCH}_3)\text{C}_6\text{H}_4\text{TSC})](\text{ClO}_4)$  (**2b**) (---) in  $\text{CH}_3\text{CN}$  (0.1 M TEAP) at a platinum electrode (298 K).



The general member of a series can be designated as  $[(\text{bpy})_2\text{Ru}(\text{H}_x\text{NS})]^{z+}$ , where  $x = 1$  or 2 and  $z = 2-3$ . The first members ( $x = 2, z = 2$ ) of the two series were isolated as perchlorate salts  $[(\text{bpy})_2\text{Ru}^{\text{II}}(\text{H}_2\text{NS})](\text{ClO}_4)_2$  (A). The species A undergoes a one electron oxidation near 0.28–0.30 V (couple I). The  $i_{\text{pa}}/i_{\text{pc}}$  value ( $\sim 1$ ),  $\Delta E_p$  value (60 mV) (which is not much dependent on scan rate) and the current heights at peak potentials were comparable with those in an equimolar *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  solution (Fig. 2). This confirmed that the above process is a one electron transfer reaction. When the compounds **1a** and **3a** were oxidised electrochemically at 0.50 V in acetonitrile solution, their frozen glass EPR spectra recorded at 77 K was found to be highly anisotropic; exhibiting nearly identical spectra for **1a** and **3a**. The  $g$  values found for **1a** are  $g_1 = 2.30, g_2 = 2.44$  and  $g_3 = 2.66$ . For **3a** these are  $g_1 = 2.34, g_2 = 2.43$  and  $g_3 = 2.46$ . These values suggest that the unpaired electron is predominantly metal centred. Thus the first step (couple I) of the above mentioned electron transfer series involve a  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$  oxidation process, which may be represented by eq (2). This is further confirmed by the presence of two *d-d* bands at 1411 nm and 1911 nm in the acetonitrile solution of **1a** oxidised at 0.50 V which is characteristic of  $\text{Ru}^{\text{III}}$  complexes [34]. Hence the second member (B) of the above electron transfer series may be represented as  $[(\text{bpy})_2\text{Ru}^{\text{III}}(\text{H}_2\text{NS})]^{3+}$  i.e.,  $x = 1$  and  $z = 2$ .

The species B also undergoes a one electron reversible oxidation at 0.79–0.83 V (couple II) producing the species C. When the compound **1a** is subjected to constant potential electrolysis at 0.9 V in acetonitrile,

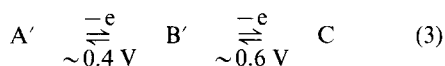


R = H, R' = CH<sub>3</sub>, OCH<sub>3</sub>, Cl and Br

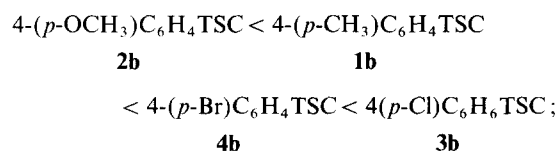
.....(2)

the resultant solution is EPR silent both at 77 K and room temperature. Two possible explanations can be offered: (i) species C is a Ru<sup>IV</sup> complex, as Ru<sup>IV</sup> is known to be EPR silent [34], (ii) species C is a Ru<sup>III</sup> complex containing a stabilized ligand radical, and the spin exchange between the unpaired electrons of ruthenium and the ligand radical [35] is responsible for the disappearance of the EPR signal. Again, the potential difference between couple I and couple II is 0.5 V, whereas the difference between Ru<sup>II</sup>/Ru<sup>III</sup> and Ru<sup>III</sup>/Ru<sup>IV</sup>, potentials are normally observed round 1.0 V. It is also known that oxidation of Ru<sup>II</sup> to Ru<sup>IV</sup> in a diimine ligand environment is normally extremely difficult [36]. Moreover, it has also been observed that when primary amines are bonded to the Ru(bpy)<sub>2</sub> moiety, oxidation of amine precedes the formation of a Ru<sup>IV</sup> species [6,37–38]. Root *et al.* [6] observed that for Ru(bpy)<sub>2</sub><sup>2+</sup> complexes with amine thioether as coligands, no Ru<sup>IV</sup> species was formed even at as high a potential as 1.30 V (vs SSCE in MeCN). Thus the species C, produced by one electron oxidation of B followed (or precede) by a proton release can be considered as a Ru<sup>III</sup> complex containing a metal stabilized ligand radical with the formula [(bpy)<sub>2</sub>Ru<sup>III</sup>(HNS)]<sup>+3</sup> (i.e.  $x = 1, z = 3$ , *vide supra*).

The thiolate complexes **1b**, **2b**, **3b** and **4b** also form a similar three-membered electron transfer series (eq. 3 and Fig. 2), where A' represents **1b**, **2b**, **3b** and **4b** with the general formula [(bpy)<sub>2</sub>Ru(HNS)]<sup>+z</sup> with  $z = 1-3$ .



At a potential of 0.4 to 0.5 V A' is oxidised to B', the couple being reversible for **1b** and **2b** and irreversible for **3b** and **4b**. The observed potential increases in the order:



this is also the order of decrease in electron donating ability of the ligands. When compound **1b** is oxidised chemically by iodine in dichloromethane solution and

then the frozen glass EPR spectrum recorded at 77 K, isotropic signal at  $g = 2.20$  was observed [39]. A genuine Ru<sup>III</sup> complex is expected to exhibit highly anisotropic EPR signal [25] as we have noted before for the species B. The isotropic nature of the EPR signal, as well as the observed dependance of the potential on the electron donating ability of the ligand suggests that the unpaired electron in B' [(bpy)<sub>2</sub>Ru<sup>III</sup>(HNS)]<sup>+2</sup> is predominantly ligand centred [13]. However, the high  $g$  value indicates an appreciable contribution from the metal orbital to the M.O. containing the unpaired electron [17,39,40]. B' is further oxidised to C at a potential around 0.60 V. When the compound **1b** is oxidised electrochemically at 0.7 V, the resultant solution is EPR silent even at 77 K. As argued earlier, such a situation may arise in C because of the spin exchange between the unpaired electron on the ligand and that on Ru<sup>III</sup>. Thus the couple at 0.60 V representing the oxidation of B' to C involves a Ru<sup>II</sup>/Ru<sup>III</sup> oxidation.

#### Electrochemical reduction of complexes

In the negative potential region we encounter reversible (or sometimes irreversible) reduction processes for the dicationic as well as monocationic complexes. The first reduction potential in each of the complexes are attributed to coordinated thiosemicarbazide, where the electron probably enters a  $\pi^*$  orbital of the ligand. The data in Table 3 show that reduction of the dicationic complexes shifts to more and more negative potential in the order  $4-(p\text{-Cl})\text{C}_6\text{H}_4\text{TSCH} < 4-(p\text{-Br})\text{C}_6\text{H}_4\text{TSCH} < 4-(p\text{-CH}_3)\text{C}_6\text{H}_4\text{TSCH} < 4-(p\text{-OCH}_3)\text{C}_6\text{H}_4\text{TSCH}$  which parallels the increase in electron donating ability of the ligands and reflects the  $p$ -substituent effect in the phenyl ring. The second and third reductions are bipyridine based, and correspond to the addition of electron to the  $\pi^*$  orbitals of the two bipyridyl ligands, very well documented in the literatures [3–12].

#### Electronic spectra

All the dicationic complexes exhibit a band around 600–800 nm (band I) which may be assigned to a MLCT transition involving  $t_{2g}$  orbitals of Ru<sup>II</sup> and

a  $\pi^*$  orbital of the thiosemicarbazide ligand. In the monocationic complexes, the thiosemicarbazide moiety is present in thiolate form, and the  $\pi^*$  orbital is expected to be filled. Hence, the above MLCT transition is expected to be absent in the monocationic complexes which indeed is the case.

The most important feature of the spectral transitions is that all the complexes exhibit three to four strong bands in the 570–300 nm region. For Ru<sup>II</sup> complexes metal to ligand charge transfer transitions are expected in this region [4–10]. In the ideal  $C_{2v}$  symmetry of the Ru(bpy)<sub>2</sub><sup>2+</sup> moiety there are two degenerate  $\pi^*$  orbitals of bpy, designated as  $\pi^*(1)$ ; at somewhat higher energy there is another set of a doubly degenerate  $\pi^*$  orbitals, designated as  $\pi^*(2)$  [6–8, 41–44]. So, under this condition normally two Ru(4d)  $\rightarrow \pi^*(\text{bpy})$  transitions are expected. However, due to the asymmetric nature of the thiosemicarbazide ligand in these complexes and their weaker back-bonding ability compared to bipyridyl, the  $t_{2g}$ <sup>6</sup> manifold of the Ru<sup>II</sup> will undergo a splitting. As a result upto four MLCT transitions are expected [7] involving Ru(4d) and  $\pi^*(\text{bpy})$  orbitals. These transitions can be readily identified by comparison of their position and intensity with those of the other *bis*(bipyridyl) complexes reported in the literature containing coligands with N,O [34]; N,S [6,45]; O,O [4,8,46] and S,S [7] donor systems. Based on these observations we assign these transitions (band II) around 570 nm and 470 nm for the dicationic complexes and around 500 nm and 450 nm for the monocationic complexes as Ru(4d) $\pi \rightarrow \pi^*(1)$  transitions [4,6,7,45]. The band around 310 nm (band III) and 400 nm for the dicationic complexes and around 350 nm for the monocationic complexes can be ascribed [4,8] to Ru(4d) $\pi \rightarrow \pi^*(2)$  transition.

A band at 290 nm (band IV) can be assigned to a  $\pi \rightarrow \pi^*$  transition of the bipyridyl ligand [8,47–51]. Similar transitions of comparable intensity have been observed for other *bis*(bipyridyl)Ru(II) complexes [8,47–51]. Other peaks at higher energy (~245 nm) are also likely to be due to a second bipyridyl intraligand  $\pi \rightarrow \pi^*$  transition [50–52] or phenyl  $\pi \rightarrow \pi^*$  transition [53] and the highest energy band due to  $n \rightarrow \pi^*$  transition [6].

## CONCLUSIONS

The present study demonstrates that like the 1,2 diiminolones, 1,2 dioxolones and 1,2 dithiolones, the thiosemicarbazides can also form an interesting three membered redox series. Electrochemical, EPR and UV–vis spectroscopy indicates that ruthenium shuttles between +2 and +3 oxidation states, whereas the ligand shuttles between the thiosemicarbazide and thiosemicarbazide radical forms. Along with the electron transfer process, proton transfer is also involved in one of the steps. Spectroscopic and electrochemical data also indicate that unlike most ruthenium bis-

bipyridyl complexes, where the  $\pi^*$  orbital is the LUMO based on bpy, in the complexes containing thiosemicarbazide, the LUMO is a  $\pi^*$  orbital located on the thiosemicarbazide ligand.

*Acknowledgement*—The authors are grateful to the Department of Science and Technology (Government of India), New Delhi, for financial support.

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