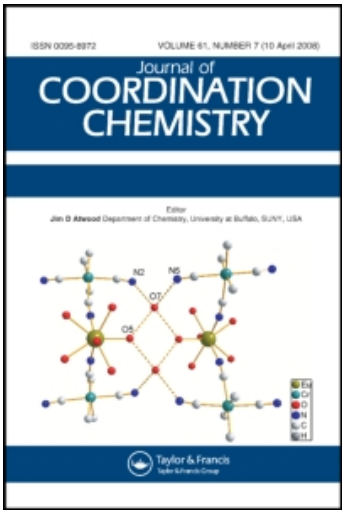

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Synthesis and spectroscopic studies of novel mononuclear and binuclear ruthenium(III) complexes with bidentate and tridentate acyclic hydrazones

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Synthesis and spectroscopic studies of novel mononuclear and binuclear ruthenium(III) complexes with bidentate and tridentate acyclic hydrazones

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Nine novel acyclic hydrazone ligands, FINH = N-(furylidene)-N′-iso nicotinoylhydrazine, FNH = N-(furylidene)-N′-nicotinoylhydrazine, PINH = N-(pyrienylidene)-N′-isonicotinoylhydrazine, PNH = N-(pyrienylidene)-N′-nicotinoylhydrazine, TINH = N-(thienylidene)-N′-isonicotinoylhydrazine, TNH = N-(thienylidene)-N′-nicotinoylhydrazine, FSH = N-(furylidene)-N′-salicyloylhydrazine, PSH = N-(pyrienylidene)-N′-salicyloylhydrazine and TSH = N-(thienylidene)-N′-salicyloylhydrazine, have been synthesized. Their corresponding mononuclear and binuclear ruthenium(III) complexes have been prepared by the reaction of the ligand with $RuCl_3 \cdot 3H_2O$ in 1 : 2 and 2 : 2 molar ratio and are characterized by elemental analyses, thermogravimetric analyses (TGA and DTG), IR, electronic, magnetic susceptibility and electrical conductance measurements. Electronic spectra and magnetic susceptibility measurements of the solid complexes (both mono- and binuclear) indicate an octahedral geometry around ruthenium(III). Particular emphasis is given to the binuclear complexes in which FSH, PSH and TSH behave as tridentate ligands and chloride bridges the Ru(III) ions. Conductance measurements show the mononuclear complexes are electrolytic and binuclear complexes are of non-electrolytic. The fungicidal activities of the ligands and metal complexes against *Fusarium oxysporium* and *Aspergillus niger* are described.

Keywords: Hydrazones; Mononuclear and binuclear complexes; Thermogravimetry; Catalytic activity

1. Introduction

Ruthenium(III) complexes continue to receive attention [1–5]; complexes with nitrogen and oxygen donor ligands show good activity in screening, and preferentially concentrate in tumor tissues. There are significant structural differences between ruthenium and platinum-based antitumor drugs; yet ruthenium based drugs could be suitable alternatives to cis-platin and carbo-platin [6, 7]. Antitumor ruthenium chelates are octahedral in contrast to the square planar cis-platin or carbo-platin. Acid hydrazides

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and their corresponding products, heteroaroylhydrazones, have attracted much attention in synthetic chemistry and inorganic chemistry due to their use in biological systems and analytical chemistry [8–13]. The catalytic activity depends upon the structure of the Schiff-base ligands. Furthermore, binuclear complexes are found to be better catalysts than mononuclear complexes [14]. Mixed ligand ruthenium complexes, by virtue of their wide range of reversible and accessible oxidation states, have proved to be useful catalysts [15–18] in reactions such as hydrogenation, oxidation, carbonylation, hydroformylation, etc. Their use as catalysts for aryl–aryl coupling has not been discussed widely, although mild and efficient aromatic cross-couplings have been described recently [19–21]. Bioactivity has been attributed to their complexation ability with the metal ions, which of course, increase the lipophilicity of the complexes, facilitating transport of metal ions through the cell membrane [22]. Hydrazone complexes with transition metals possess a diverse spectrum of pharmaceutical activities, such as antitumor and antioxidative activities as well as the inhibition of lipid peroxidation [23–25]. Further, hydrazones can coordinate to transition metals either in the enolic form or in the keto form. We are interested in the reactivity properties of mononuclear ligand bridged and binuclear complexes where cooperative features may enhance reactivity of the individual sites. To this end we are developing synthetic methodologies and investigating the properties of a series of complexes containing ruthenium bridged derivatives.

2. Experimental

2.1. *Materials used*

The metal salt $RuCl_3 \cdot 3H_2O$ (Merck), furfural, pyridene-2-carboxaldehyde, thiophene-2-carboxaldehyde (Acros) and hydrazine hydrate (Qualigens), were used as received. Ethanol (Qualigens) was distilled before use.

2.2. *Synthesis of hydrazones*

Isonicotinic hydrazide, nicotinic hydrazide and salicylic hydrazide were prepared by the method of Tang [13]. Hydrazones FINH, FNH, PINH, PNH, TINH, TNH, FSH, PSH and TSH (figure 1) were prepared according to an improved method [26]. A mixture of isonicotinic, nicotinic or salicylic hydrazide (0.1 mol) in 20 mL EtOH and furfural, pyridene-2-carboxaldehyde or thiophene-2-carboxaldehyde (0.1 mol) (1 : 1 molar ratio) in 25 mL EtOH was heated at reflux for 4 h. The resulting solution was concentrated to half its original volume, cooled to ambient temperature for 2 h, filtered to collect the crystals, which were washed with 95% EtOH and recrystallized with the same solvent then dried *in vacuo* over $CaCl_2$, yield 80–90%.

2.3. *Preparation of mononuclear complexes* $[Ru(FINH)_2Cl_2]Cl$, $[Ru(FNH)_2Cl_2]Cl$, $[Ru(PINH)_2Cl_2]Cl$, $[Ru(PNH)_2Cl_2]Cl$, $[Ru(TINH)_2Cl_2]Cl$, $[Ru(TNH)_2Cl_2]Cl$

A solution of 2 mmol each of FINH (0.398 g), FNH (0.398 g), PINH (0.454 g), PNH (0.454 g), TINH (0.465 g) or TNH (0.465 g) in EtOH (20 cm^3) was added dropwise

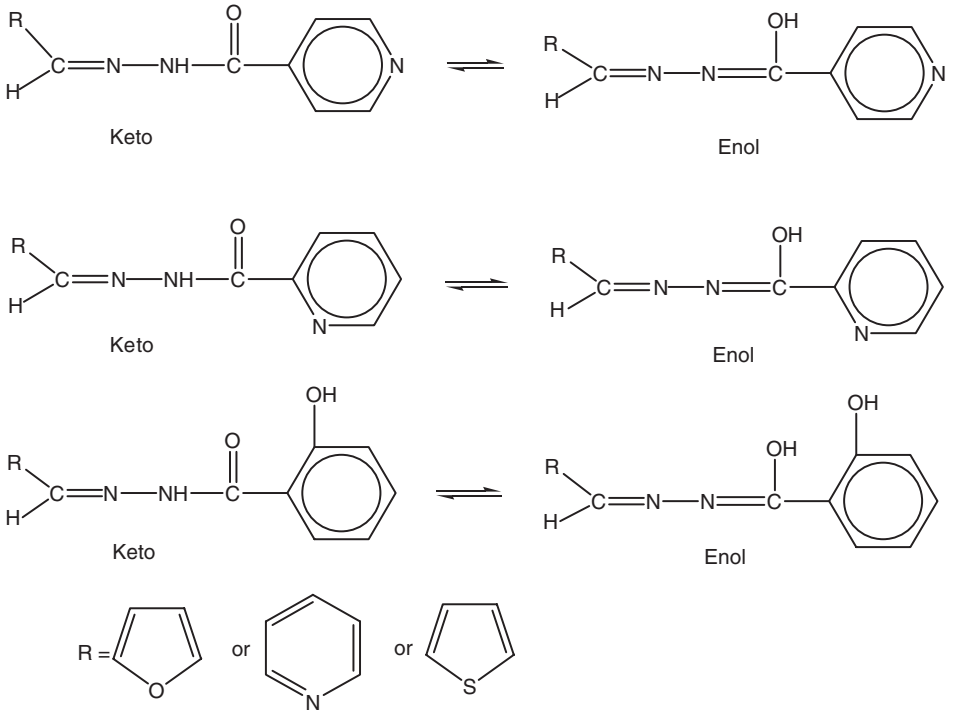


Figure 1. Keto-enol tautomeric forms of hydrazones.

into a solution of $RuCl_3 \cdot 3H_2O$ (1 mmol, 0.261 g) in EtOH (30 cm^3) with stirring. The reaction mixture was continuously heated for 12 h under reflux, concentrated to half its volume, cooled at room temperature for 4 h and filtered. The solid was washed twice with ethanol and diethyl ether, and dried *in vacuo*. Brown solid powders were obtained, which were confirmed by elemental analyses (table 1).

2.4. *Preparation of binuclear [Ru(FS)Cl_2]$_2$, [Ru(PS)Cl_2]$_2$, [Ru(TS)Cl_2]$_2$ complexes*

FSH (0.462 g, 2 mmol), PSH (0.450 g, 2 mmol) or TSH (0.468 g, 2 mmol) in EtOH (50 cm^3), was added to 0.522 g of $RuCl_3 \cdot 3H_2O$ in EtOH (50 cm^3), and the mixture was refluxed with stirring at 25°C. The progress of the reaction was monitored by silica gel TLC. After 30 min of stirring, the color of the reaction mixture turned reddish brown from light brown and TLC showed the disappearance of the starting complex. The solvent was evaporated and the residue was chromatographed on a silica gel column. The dark brown fraction eluted using benzene–acetonitrile (4 : 1 v/v) was collected, and again chromatographed under similar conditions. The residue was recrystallized from hexane, and the complexes obtained were dried under vacuum.

2.5. *Physical measurements*

Elemental analyses were obtained from the Microanalytical Laboratory of CDRI, Lucknow, India. Metals and chlorides were determined volumetrically and

Table 1. Elemental analyses and some physical properties of the solid complexes.

Compound	Color	Yield %	Melting point (°C)	Formula Weight	Analyses found % (Calculated %) C	H	N	S	Cl	M	Λ ($\Omega^{-1}cm^2mol^{-1}$)	*m/e*
FINH	Brown	90	178	199.2	66.1 (66.3)	4.3 (4.5)	21.1 (21.0)	–	–	–	–	198
FNH	Dark brown	88	167	199.2	66.4 (66.3)	4.4 (4.5)	21.0 (21.0)	–	–	–	–	198
PINH	Yellow	85	120	227.2	63.2 (63.4)	4.9 (4.8)	24.3 (24.6)	–	–	–	–	228
PNH	White	80	132	227.2	63.3 (63.4)	4.5 (4.8)	24.4 (24.6)	–	–	–	–	226
TINH	White	86	226	232.2	56.6 (56.8)	4.2 (4.3)	18.2 (18.0)	13.4 (13.8)	–	–	–	234
TNH	White	90	220	232.2	56.9 (56.8)	4.0 (4.3)	18.1 (18.0)	13.5 (13.8)	–	–	–	232
FSH	Brown	90	198	230.2	62.3 (62.6)	4.0 (4.3)	12.3 (12.1)	–	–	–	–	230
PSH	White	90	190	225.2	69.0 (69.3)	4.7 (4.9)	18.3 (18.6)	–	–	–	–	226
TSH	White	85	228	235.2	56.5 (56.1)	4.5 (4.7)	12.1 (11.9)	13.8 (13.6)	–	–	–	234
$[Ru(FINH)_2Cl_2]Cl$	Brown	65	>360	605.8	43.5 (43.6)	2.6 (2.9)	13.4 (13.8)	–	17.2 (17.5)	16.8 (16.6)	113	570
$[Ru(FNH)_2Cl_2]Cl$	Brown	61	>360	605.8	43.2 (43.6)	2.7 (2.9)	13.9 (13.8)	–	17.4 (17.5)	16.6 (16.6)	120	570
$[Ru(PINH)_2Cl_2]Cl$	Brown	65	>360	659.9	43.5 (43.6)	3.3 (3.0)	16.6 (16.9)	–	16.5 (16.1)	15.0 (15.3)	99	624
$[Ru(PNH)_2Cl_2]Cl$	Brown	51	>360	659.9	43.8 (43.6)	3.2 (3.0)	16.8 (16.9)	–	16.4 (16.1)	15.6 (15.3)	110	624
$[Ru(TINH)_2Cl_2]Cl$	Brown	54	>360	669.9	39.6 (39.4)	2.8 (2.7)	12.3 (12.5)	9.2 (9.5)	15.4 (15.8)	14.8 (15.0)	104	634
$[Ru(TNH)_2Cl_2]Cl$	Brown	52	>360	669.9	39.4 (39.4)	2.4 (2.7)	12.2 (12.5)	9.4 (9.5)	15.9 (15.8)	15.2 (15.0)	98	634
$[Ru(FS)Cl_2]_2$	Brown	53	>360	802.3	38.8 (35.9)	2.4 (2.2)	6.3 (6.9)	–	17.4 (17.6)	25.0 (25.1)	38	804
$[Ru(PS)Cl_2]_2$	Brown	56	>360	792.4	39.0 (39.4)	2.3 (2.5)	10.4 (10.6)	–	17.5 (17.9)	25.3 (25.5)	26	790
$[Ru(TS)Cl_2]_2$	Brown	51	>360	810.4	32.3 (32.6)	2.0 (2.2)	6.6 (6.9)	7.6 (7.9)	17.8 (17.5)	24.7 (24.9)	20	810

gravimetrically [27]. Electronic spectra were recorded using dimethyl formamide solutions in 1 cm cells with a Perkin-Elmer Lambda 15 UV/Vis spectrophotometer. IR spectra were scanned as KBr pellets on a Perkin-Elmer PC-16F FTIR spectrometer in the 4000–350 cm^{-1} regions. Magnetic susceptibility measurements were carried out at room temperature by Gouy's balance using $Co[Hg(SCN)_4]$ as a calibrant. The conductivity measurements were made using a systronic conductivity meter with a dip type cell, using approximately 10^{-3} M solutions of the complexes in DMF. Molecular FAB mass spectra were obtained on a JEOL SX 102/DA-6000 mass spectrometer using m-nitrobenzyl alcohol (NBA) as a matrix. Thermogravimetric data were obtained in air at 10°C min^{-1} in the 25–750°C range using a Shimadzu TGA-50 H analyzer. Electrochemical results were collected with a BAS CV-27 electrochemical analyzer and a BAS Model X-Y recorder at 298 K. Cyclic voltammetry experiments were carried out using a Pt working electrode, Pt auxiliary electrode and Ag–AgCl reference electrode.

3. Results and discussion

3.1. *Synthesis and thermal stability*

Condensation of isonicotinic, nicotinic or salicylic hydrazide with furfural, pyridene-2-carboxaldehyde or thiophene-2-carboxaldehyde in ethanol using a 1 : 1 molar ratio, gave the corresponding heteroaroylhydrazones. The purity of the prepared hydrazones was checked by TLC, elemental analyses (table 1), IR and FAB mass spectra. The isolated hydrazones were soluble in alcohol, DMF and DMSO but insoluble in water. All nine hydrazones were thermally stable, beginning decomposition at ca 200–250°C.

The reaction of FINH, FNH, PINH, PNH, TINH and TNH with ruthenium(III) chloride, using 2 : 1 molar ratio, afforded monoruthenium(III) complexes $[Ru(FINH)_2Cl_2]Cl$, $[Ru(FNH)_2Cl_2]Cl$, $[Ru(PINH)_2Cl_2]Cl$, $[Ru(PNH)_2Cl_2]Cl$, $[Ru(TINH)_2Cl_2]Cl$, $[Ru(TNH)_2Cl_2]Cl$. Complexes were stable up to 200°C, indicating the absence of water. The presence of chloride ion outside and inside the coordination sphere was confirmed by dynamic TGA studies. Complexes register a weight loss of 3.3% at 261°C, which correspond to loss of half of a molecule of chlorine. A small exothermic peak at 355°C in the DTA corroborated the formation of the transient intermediate which immediately transformed to product. After 400°C the complex starts to decompose and a mass loss of 35–37% at 442–446°C corresponds to loss of one ligand. The total mass loss up to 560–571°C is found to be 90.1% which shows the formation of ruthenium oxide. The high mass of the residue may be attributed to carbonaceous matter. Thus the decomposition pattern obtained from TGA curve confirms the proposed formulation of the complexes.

Reaction of ruthenium(III) chloride with FSH, PSH and TSH using 2 : 2 molar ratio, gave the expected chloro complexes $[Ru(FS)Cl_2]_2$, $[Ru(PS)Cl_2]_2$ and $[Ru(TS)Cl_2]_2$. TGA of these solid complexes indicate common behavior. The thermograms can be subdivided into three main regions: The first region extends up to 310°C and includes elimination of coordinated Cl^-. The second region indicates thermal stability and extends up to 532°C. The third region extends up to 750°C and represents

decomposition of the complex to ruthenium oxide. The metal content in the residue was calculated and found to be consistent with the elemental analyses of the complexes.

3.2. *Infrared spectra*

A comparison of the IR spectra of the free ligands with metal complexes may be concluded as follows:

(1) The IR spectra of the ligands FINH, FNH, PINH, PNH, TINH and TNH are similar with bands at 3300–3280, 1665–1645, 1615–1595 and 1010–890 cm^{-1} attributed to ν(NH), ν(C=O), ν(C=N) and ν(N–N), respectively. Thus the ligands remained in the keto form in the solid state. Bonding of these hydrazones to ruthenium(III) has been suggested by a careful comparison of the infrared spectra of the complexes with those of the free ligands for a few bands. The shift to low frequency of the ν(C=O) (30 cm^{-1}) mode that appears at 1665–1645 cm^{-1} in the spectrum of hydrazones suggest carbonyl oxygen coordination. This is supported by the negative shift of 25 cm^{-1} for the amide II and positive shift of 20 cm^{-1} for the amide III band upon complexation [28, 29]. The ν(C=N) and ν(N–N) bands show downward and upward shifts of 25 and 20 cm^{-1}, respectively in the complexes due to coordination of the imine nitrogen [28]. Thus the ligands are neutral and bidentate.

(2) A comparison of IR spectra of FSH, PSH and TSH and their binuclear ruthenium(III) complexes shows the following:
Bands in the spectra of the ligands at 3430 and 910 cm^{-1} were attributed to ν(OH) and δ(OH), respectively. In the spectra of the complexes $[Ru(FS)Cl_2]_2$, $[Ru(PS)Cl_2]_2$ and $[Ru(TS)Cl_2]_2$, δ(OH) is absent; it is difficult to confirm disappearance of ν(OH) because it occurs at the same range where ν(NH) is located. This indicates deprotonation of the hydroxyl group and coordination of the ligand as a mononegative anion. The band due to ν(NH) remains unaltered ligand indicating non-participation of –NH in coordination and that the ligand coordinates in the keto form. The shifts of ν(C=O) and ν(C=N) to lower frequency by 40–60 and 25–45 cm^{-1}, respectively suggest bonding through the carbonyl oxygen and azomethine nitrogen [30, 31]. Coordination of the nitrogen to the metal atom reduces the electron density in the azomethine causing a shift in the ν(C=N) band [32]. The small shift to higher frequency of the ν(N–N) band at $\sim$1010 cm^{-1} and its splitting may be taken as additional evidence for the participation of the nitrogen in bonding [33]. The FSH, PSH and TSH ligands are mononegative tridentate with ruthenium ions, coordinating via the oxygen of the hydroxyl group in the keto form. Further support for the coordination of the ligands to the metal ions was provided by the appearance of bands at 440–500, 360–390 and 350–380 cm^{-1}, which are assigned to ν(Ru–O), ν(Ru–N) and ν(Ru–Cl), respectively [31].

3.3. *Electronic absorption spectra*

Due to the limited solubility, the solution absorption spectra of the ruthenium(III) complexes were recorded in DMF solution. The monomeric and dimeric complexes showed three bands in the region 28 000–13 000 cm^{-1}. However the band around 23 400–22 600 cm^{-1} for the mononuclear complex is weak, and it is observed only as a shoulder. Most of the complexes have O_h microsymmetry. The electronic spectra

of the ruthenium(III) compounds are dominated by intense ligand to metal charge transfer transitions, as confirmed by the gradual red shift of the lowest energy λ_{max} from chloro complexes. The data [34, 35] concerning interpretation of the absorption spectra of ruthenium(III) coordination compounds revealed low spin states in $[Ru(FS)Cl_2]_2$, $[Ru(PS)Cl_2]_2$ and $[Ru(TS)Cl_2]_2$. Spectra of such compounds also reveal three absorption bands generated by charge transfer, in good agreement with other data [36, 37] and confirming a low spin state. All the observed bands lie in the typical range of ligand to metal charge transfer transitions of octahedral ruthenium(III) complexes with heterocyclic ligands [35–37]. The observed high values of 10 Dq are usually associated with considerable electron delocalization as an overall effect of covalent bonding. The calculated values of the B, C, and 10 Dq parameters confirm the octahedral structure of the complexes.

3.4. *Magnetic susceptibility measurements*

Magnetic susceptibility measurements were carried out at room temperature. All the complexes are paramagnetic with μ_{eff} values of 1.7–1.9 BM indicating one unpaired d electron confirming a low spin d^5 ruthenium(III) [38].

The magnetic moment of all three ligand-bridged binuclear complexes $[Ru(FS)Cl_2]_2$, $[Ru(PS)Cl_2]_2$ and $[Ru(TS)Cl_2]_2$ were measured at room temperature. The μ_{eff} values per ruthenium atom for these complexes are 0.70, 0.82 and 1.0 BM, respectively i.e. less than expected for the low spin d^5 configuration. This may be due to the magnetic exchange interaction between ruthenium ions [39, 40] of a binuclear compound.

3.5. *Electrical conductance*

The conductance values of the ruthenium complexes (10^{-3} M in DMF) are found to be 113, 120, 99, 110, 104, 98 for mononuclear complexes and 38, 26 and 20 $\Omega^{-1}\,cm^2\,mol^{-1}$ for binuclear complexes. These results indicate that the mononuclear complexes are 1 : 1 electrolytes and the binuclear complexes are not electrolytic in DMF at 27°C [32].

3.6. *Electrochemistry*

Cyclic voltagrams exhibit mostly reversible ruthenium(III)/ruthenium(II) reduction peaks in the −0.4 to −0.18 range (table 2). These values, in most cases, are more negative than is usually observed for the ruthenium(III)/ruthenium(II) reduction in complexes of N, O donor ligands. This indicates significant stabilization of the ruthenium(III) state in these complexes for reasons already discussed.

3.7. *Mass spectrometry*

The mass spectral behavior of the ligands and complexes was studied. The *m*/*e* values are reported in table 1. The ligands FINH, FNH, PINH, PNH, TINH, TNH, FSH, PSH and TSH are identified by their FAB mass spectrum, which shows many peaks due to various fragments. All the fragments of the ligand FINH are shown in figure 2.

Table 2. Electronic spectra and cyclic voltammetry of the ruthenium(III) complexes.

Complex	Localization of the absorption bands (low spin) in cm^{-1}			ν_2/ν_1	10 Dq	B	C	β	μ_{eff} (BM)	Cyclic voltametric data (298 K) $E_{1/2}$, V; (ΔE_P, mV)[a] Reduction
	$^2T_{2g} \rightarrow {}^4T_{1g}$	$^2T_{2g} \rightarrow {}^4T_{2g}$	$^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$							
$[Ru(FINH)_2Cl_2]Cl$	13600	17400	22800	1.27	26341.6	475	2591	0.76	1.8	−0.22(50)
$[Ru(FNH)_2Cl_2]Cl$	13700	17640	22680	1.28	26165.8	492	2500	0.78	1.7	−0.29(40)
$[Ru(PINH)_2Cl_2]Cl$	13260	17310	22820	1.30	26512.9	506	2680	0.81	1.8	−0.18(30)
$[Ru(PNH)_2Cl_2]Cl$	13800	17600	22700	1.27	26141.6	475	2491	0.76	1.9	−0.26(50)
$[Ru(TINH)_2Cl_2]Cl$	14100	18100	23200	1.28	26733.3	500	2533	0.80	1.8	−0.19(60)
$[Ru(TNH)_2Cl_2]Cl$	14150	18200	23400	1.28	26989.5	506	2577	0.81	1.7	−0.25(80)
$[Ru(FS)Cl_2]_2$	12560	17200	27200	1.36	32660	580	4300	0.93	0.7	−0.33(60)
$[Ru(PS)Cl_2]_2$	12600	17400	27300	1.38	32800	600	4300	0.96	0.8	−0.15(150)
$[Ru(TS)Cl_2]_2$	12500	17100	27200	1.37	32675	575	4325	0.92	1.0	−0.17(80)

[a] Conditions: supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, Ag/AgCl; solute concentration, 10^{-3} M. Scan rate, 0.4 V s^{-1}; and temperature 298 K, $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potential, $\Delta E_P = E_{Pa} - E_{Pc}$.

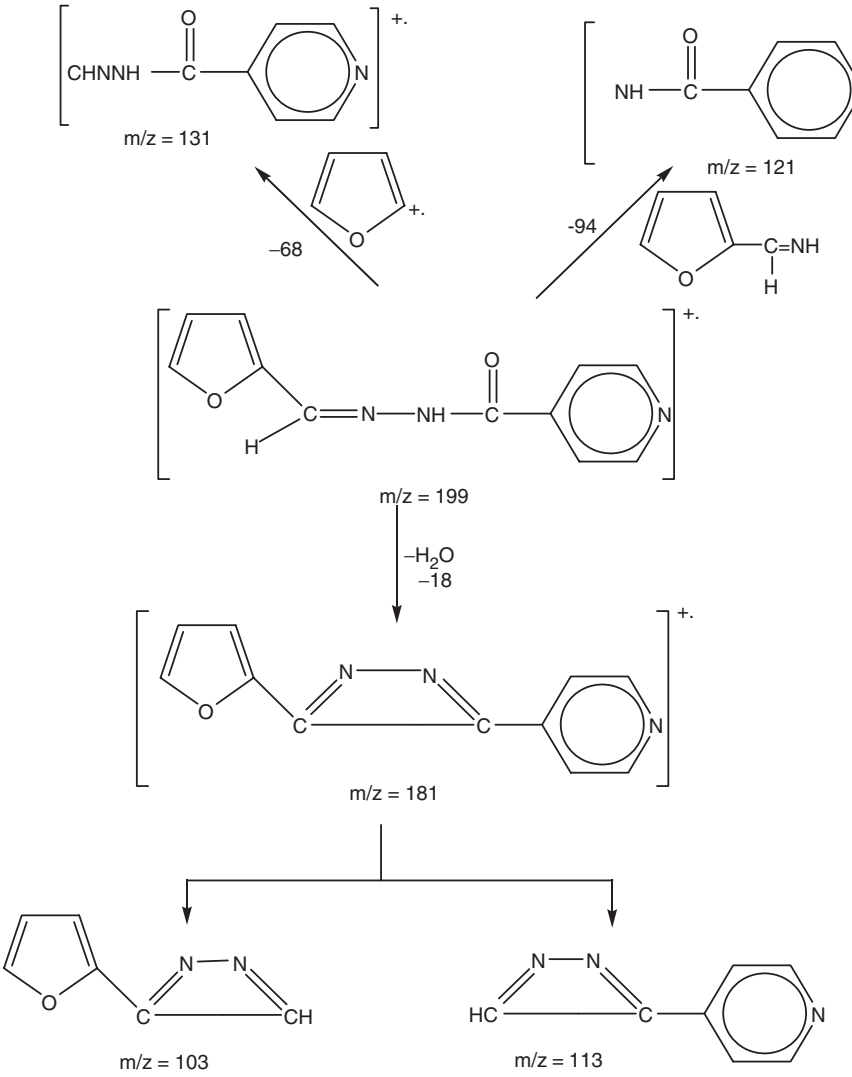
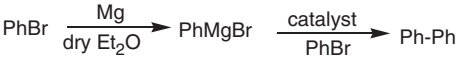


Figure 2. Fragmentation pattern for FINH.

4. Applications of novel ruthenium(III) complexes

4.1. *Catalytic studies*

All ruthenium complexes have been used as catalysts in aryl–aryl coupling. The system chosen for our study is the coupling of phenylmagnesium bromide with bromobenzene to yield biphenyl as the product (scheme 1). Bromobenzene was first converted into the corresponding Grignard reagent. Then bromobenzene, followed by the complex chosen for the investigation, was added to the above reagent and the mixture was heated under reflux for 6 h. After work up, the mixture, yielded biphenyl. Only a small amount of Ph_2 is formed when the reaction is carried out without the catalyst, insignificant compared to the yields of Ph_2 obtained from the catalysed reactions.



Scheme 1. Formation of biphenyl.

Table 3. Yields of biphenyl with Ru^{III} complexes as catalyst.

Sl No.	Catalyst	Yield of Ph–Ph (ln *g*)	%
1	$[Ru(FINH)_2Cl_2]Cl$	0.385	24.4
2	$[Ru(FNH)_2Cl_2]Cl$	0.540	34.4
3	$[Ru(PINH)_2Cl_2]Cl$	0.310	19.7
4	$[Ru(PNH)_2Cl_2]Cl$	0.345	22.0
5	$[Ru(TINH)_2Cl_2]Cl$	0.285	18.2
6	$[Ru(TNH)_2Cl_2]Cl$	0.400	25.5
7	$[Ru(FS)Cl_2]_2$	0.625	39.8
8	$[Ru(PS)Cl_2]_2$	0.645	41.1
9	$[Ru(TS)Cl_2]_2$	0.620	39.5

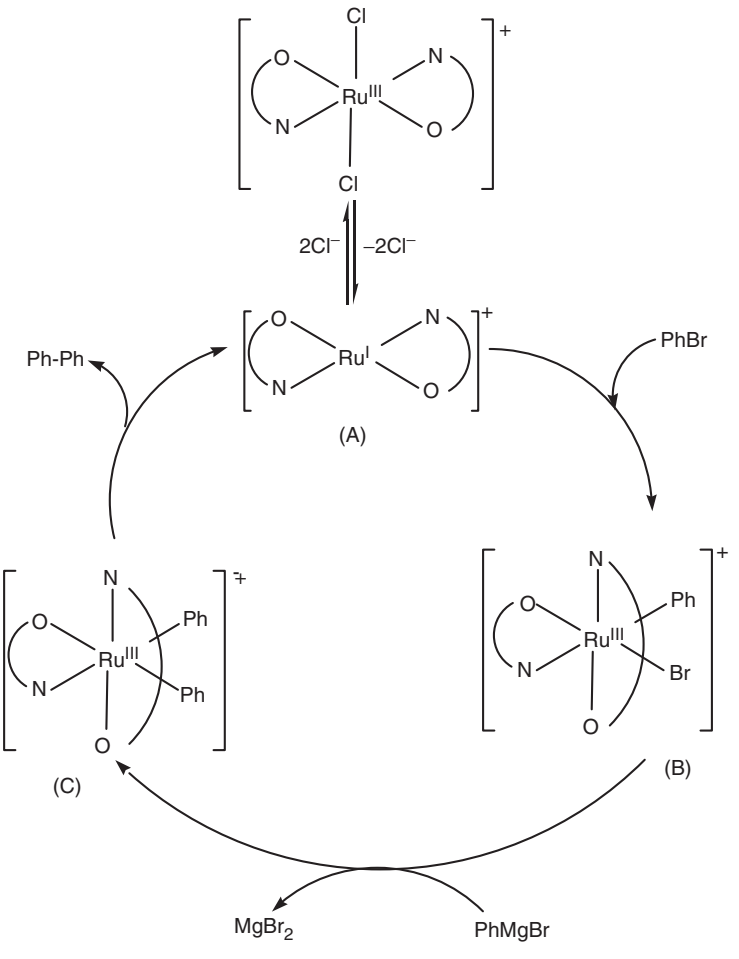
Table 4. Antifungal activity of hydrazones and their complexes.

	Antifungal activity % inhibition zone ($\mu g\,mL^{-1}$)					
	Fusarium oxysporium			*Aspergillus niger*		
Compounds	100 ppm	500 ppm	1000 ppm	100 ppm	500 ppm	1000 ppm
Redomil[a]	56.8	70.0	89.0	55.4	71.0	89.1
FINH	12.0	13.6	20.3	12.3	14.1	20.2
FNH	11.8	13.5	21.1	11.2	13.8	20.9
PINH	12.6	14.5	22.2	12.5	13.9	22.0
PNH	9.2	9.8	10.5	9.0	9.9	10.1
TINH	10.0	10.7	11.3	10.3	10.7	11.2
TNH	9.2	9.9	10.2	9.0	9.7	10.0
FSH	12.3	14.1	20.8	12.0	14.0	21.2
PSH	10.2	10.9	11.1	10.0	10.6	11.2
TSH	13.6	14.5	25.2	14.5	15.9	26.0
$[Ru(FINH)_2Cl_2]Cl$	39.2	58.9	71.1	39.6	58.1	70.0
$[Ru(FNH)_2Cl_2]Cl$	37.1	55.6	71.5	37.2	55.9	72.0
$[Ru(PINH)_2Cl_2]Cl$	37.9	56.2	72.5	38.1	56.6	75.2
$[Ru(PNH)_2Cl_2]Cl$	38.2	57.3	74.9	38.5	57.6	74.8
$[Ru(TINH)_2Cl_2]Cl$	38.1	57.6	70.9	38.4	57.2	70.2
$[Ru(TNH)_2Cl_2]Cl$	36.6	54.1	71.2	36.2	54.6	71.1
$[Ru(FS)Cl_2]_2$	37.5	55.3	79.3	37.3	55.5	80.9
$[Ru(PS)Cl_2]_2$	37.9	56.5	78.5	37.8	56.2	78.1
$[Ru(TS)Cl_2]_2$	38.8	60.0	80.3	39.5	59.9	79.1

[a] Commercial fungicide.

The optimum quantity of catalyst $[Ru(FNH)_2Cl_2]^+$ required for the coupling of the phenylmagnesium bromide with bromobenzene has been investigated by performing a series of experiments using different mole ratios of phenylmagnesium bromide and $[Ru(FNH)_2Cl_2]^+$. The results are presented in table 3. This study revealed the optimum mole ratio of the Grignard reagent to ruthenium complex to be 100 : 1 in agreement with a recent observation [41].

The catalytic properties of the new binuclear complexes have also been compared with that of similar mononuclear complexes showing that ruthenium(III) binuclear complexes are better catalysts than the respective mononuclear complexes. This could



Scheme 2. Possible mechanism for the coupling of PhMgBr with PhBr catalyzed by Ru^{III} complexes.

be because of bicentered catalysis in binuclear complexes [42]. The yields of biphenyl obtained from the reactions catalyzed by the new ruthenium(III) complexes are low when compared to the yield obtained from the reaction catalyzed by $NiCl_2(PPh_3)_2$ [41]. This may be due to the fact that the active species (A, d^7 configuration) derived from ruthenium complexes are less stable compared to the active species (d^{10} configuration) obtained from $NiCl_2(PPh)_2$; the effectiveness of catalysts is directly related to their ability to generate the corresponding active species [43].

Based on the above observations, the possible mechanism for the coupling of PhMgBr with PhBr catalyzed by ruthenium complexes is shown in scheme 2. A similar mechanism is expected for binuclear complexes. The existence of ruthenium–aryl intermediates (B and C) is evident from the literature [44].

4.2. *Antifungal activity studies*

The ruthenium(III) complexes together with their parent ligands FINH, FNH, PINH, PNH, TINH, TNH, FSH, PSH and TSH were tested for *in vitro* growth inhibitory

activity against various pathogenic fungi. Proper temperature, necessary nutrients and growth medium free from other microorganisms were employed for the preparation of the cultures of fungi using aseptic technique. Three replicates were used for each test.

The antifungal activities were evaluated against *Fusarium oxysporium* and *Aspergillus niger* by the agar plate diffusion technique [8]. Cultures of the fungi were prepared in potato dextrose agar (PDA) medium and were purified by single spore isolation technique. The results of biological screening have been compared with the conventional fungicide Ridomil as a standard. Although the heterocyclic hydrazones alone were quite toxic, their activity increased upon complexation (table 4). Concentration plays a vital role in increasing the degree of inhibition. In general metal complexes are more potent than their ligands, hence may serve as vehicles for activation as principal cytotoxic species. The effect of resonating rings on toxicity may be assessed from electronic theory [45] and chelation theory [46]. Resonating structures, such as pyridine, furan, thiophene and benzene rings activate potentially reactive [47].

5. Conclusion

Here we have described the synthesis and characterization of ruthenium(III) monomers and bis-μ-chloro Ru(III)–Ru(III) dimers having bidentate and tridentate heterocyclic hydrazones. All isolated compounds are ruthenium(III) complexes. In no case did we obtain ruthenium(II) complexes, although it is known that pyridine can reduce ruthenium(III) to ruthenium(II). The σ-donor capacity of these heterocyclic hydrazones overshadows their π-acceptor properties and, together with the N, O donor character of these ligands, has led to stabilization of ruthenium(III).

All of the new coordination compounds were brown and gave well-formed micro-polycrystals that appear to be indefinitely stable in the dry solid state. The catalytic and antifungal activities were checked for the prepared complexes.

The following structures are (figures 3 and 4) proposed for the complexes:

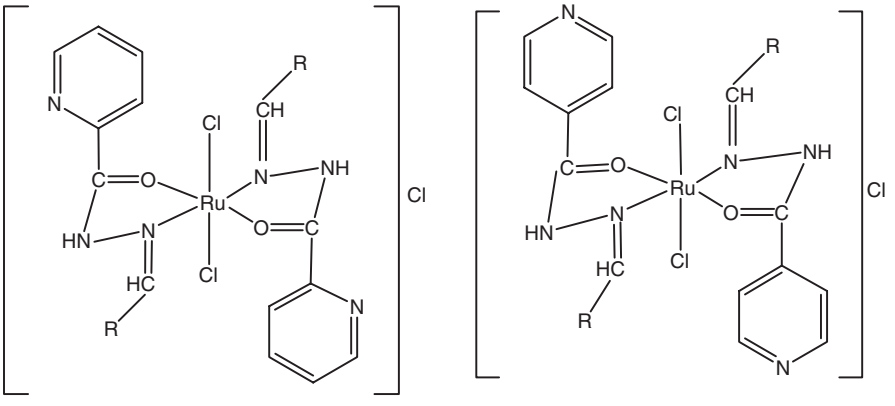


Figure 3. The suggested structure of mononuclear complexes.

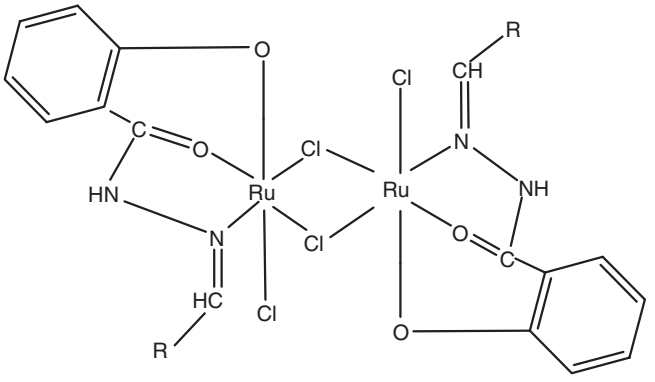


Figure 4. The suggested structure of binuclear complexes.

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