A Study of Ruthenium Complexes of some Selected N–S Donors Part II*. Ligational Behaviour of 2-Formylpyridine(4-phenyl) Thiosemicarbazone towards Ruthenium

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Abstract

Ru(II) and Ru(III) complexes of the biologically active tridentate NNS donors 2-formylpyridine(4-phenyl) thiosemicarbazone (L_1H) and 2-formylpyridine thiosemicarbazone (LH) have been synthesized and characterized by elemental analysis, conductance and magnetic susceptibility measurements, as well as by spectroscopic techniques such as UV–Vis, IR and NMR. A series of mononuclear bis chelates of the formulae $[Ru(L_1H)_2](SCN)_2$, $[Ru(L_1H)(L_1)]Cl$, $[Ru(L_1)_2]$, $[Ru(L)(LH)]ClO_4 \cdot 2H_2O$ and mononuclear mixed ligand complexes such as $[Ru(L_1H)Cl_2(CH_3OH)]$, $[Ru(L_1H)(imz)Cl_2]$, $[Ru(L_1H)(2\text{-pico})(imz)]ClO_4$, $[Ru(L_1H)(TTSC)]Cl \cdot \frac{1}{2}(C_2H_5)_2O$, $[Ru(L_1H)(imz)(thiosal)]Cl \cdot CH_3OH$, $[Ru(L_1H)(bipy)Cl]Cl_2 \cdot CH_2Cl_2$ have been isolated and characterized. Binuclear complexes $[Ru_2(L_1)_2(OH)_2]$, $[Ru_2(L_1)_2Cl_4] \cdot 4H_2O$, $[Ru_2(L_1)_2(SCN)_4] \cdot H_2O$, $[Ru_2(L_1)(imz)Cl_4] \cdot 3CH_3OH$, $[Ru_2(L_1)(H_2O)Cl_4]$ have also been synthesized and characterized. From the analysis of spectroscopic and magnetic data the donor sites of the ligands have been located and the geometries of the donor environment around the Ru(II)/Ru(III) acceptor centre have been proposed.

Introduction

As a part of our continued programme of exploring the chemistry of ruthenium ligated to different types of N–S chelating ligands, so as to fulfil certain objectives mentioned in a recent publication [1], we report here synthesis, characterization and evaluation of the antibacterial activity of the complexes of Ru(II) and Ru(III) with two biologically active ligands 2-formylpyridine(4-phenyl) thiosemicarbazone (L_1H) and 2-formylpyridine thiosemicarbazone (LH). Though an extensive investigation of the chemistry of coordination complexes of α-(*N*)formyl heteroaromatic thiosemicarbazones with iron and to a lesser extent that of cobalt and copper has been reported previously [2–6], such studies with ruthenium are yet to be reported. Ruthenium being the congener of iron its behaviour with these ligands *vis-à-vis* that of iron should be chemically interesting. Again, chemistry of the α-(*N*)formyl heteroaromatic thiosemicarbazones has assumed considerable importance because of the manifestation of a variety of biological activities such as antileukamic, antitumor and antimalarial properties in these ligands and their iron complexes [7–13]. Moreover, a few papers have reported considerable enhancement of a particular biological activity of an active organic ligand on its chelation to some selected metal ions [1, 14–19]. In addition, substitution reactions of such complexes, in which, the ligand occupies three coordination sites while one or two of the remaining sites are occupied by weak monodentate donors, with a variety of monodentate or polydentate substrates are likely to have special importance in correlating the biological activity of these compounds with their chemical reactivity. In the light of the above discussion a systematic investigation of the coordination chemistry of this group of ligands ligated to the ruthenium acceptor centre and examination of the antibacterial activity of the ligands and their ruthenium complexes seems worth pursuing.

Results and Discussion

Ruthenium(III) chloride (or thiocyanate) reacts with 2-formylpyridine(4-phenyl) thiosemicarbazone (L_1H) or 2-formylpyridine thiosemicarbazone (LH) to give a pair of complexes – a mononuclear ruthenium(II) complex and a binuclear ruthenium(III) complex, in each case. The different synthetic reactions for the preparation of various ruthenium complexes are illustrated in Scheme 1 and Scheme 2. Analytical data for the complexes is given in Table 1. For convenience of discussion we shall discuss the mononuclear complexes first and deal with the binuclear ones later.

*Ref. 1 should be considered as Part 1.

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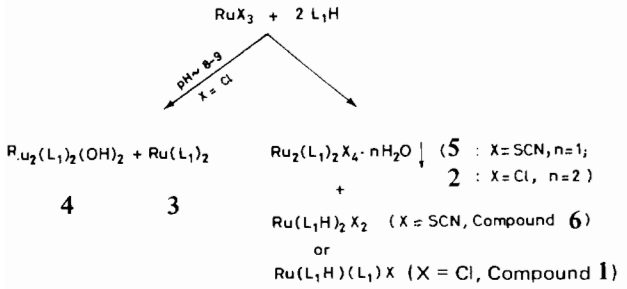
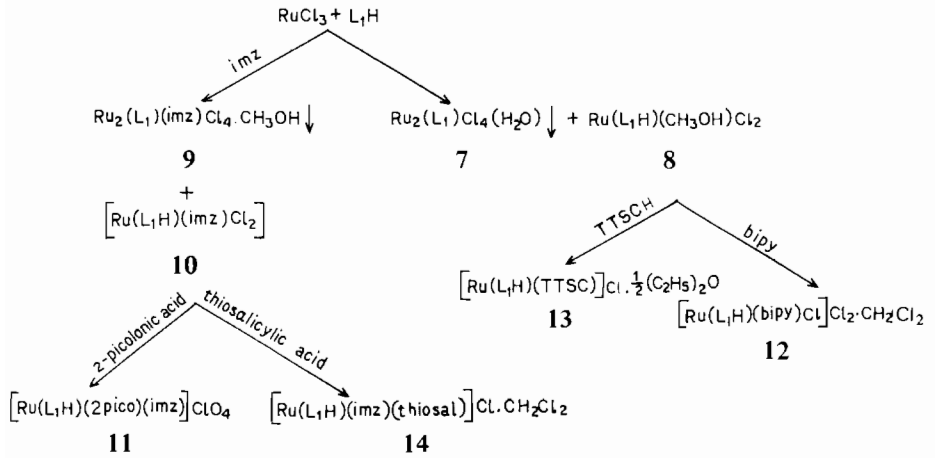


Scheme 1.

The ligand L_1H on reacting with ruthenium chloride in a 2:1 molar ratio in methanolic solution produces the compounds $[Ru(L_1H)(L_1)]Cl$ (**1**) and $Ru_2(L_1)_2Cl_4 \cdot 4H_2O$ (**2**). In the mononuclear complex $[Ru(L_1H)(L_1)]Cl$ (**1**) one of the ligands is present in the non-deprotonated form while the other one is present in the deprotonated thiolate form. When the pH of the reaction medium is raised to 8–9 using alcoholic NaOH, compounds $Ru(L_1)_2$ (**3**) and $Ru_2(L_1)_2(OH)_2$ (**4**) are obtained. Compound **3** ($Ru(L_1)_2$) is a mononuclear complex in which both



Scheme 2.

TABLE 1. Analytical data for complexes

Complex	C [a]	H [a]	N [a]	Cl^- [a]
1 $[Ru(L_1H)(L_1)]Cl$	47.9 (48.1)	3.6 (3.5)	17.3 (17.3)	5.4 (5.5)
2 $Ru_2(L_1)_2Cl_4 \cdot 4H_2O$	33.4 (33.6)	3.1 (3.2)	11.9 (12.1)	15.0 (15.3)
3 $[Ru(L_1)_2]$	50.8 (51.0)	3.8 (3.6)	18.1 (18.3)	
4 $Ru_2(L_1)_2(OH)_2$	41.6 (41.8)	3.1 (3.2)	14.7 (15.0)	
5 $Ru_2(L_1)_2(SCN)_4 \cdot H_2O$	37.3 (37.4)	2.6 (2.5)	17.5 (17.4)	
6 $[Ru(L_1H)_2](SCN)_2$	46.0 (46.1)	3.1 (3.3)	19.4 (19.2)	
7 $Ru_2(L_1)(H_2O)Cl_4$	25.4 (25.2)	2.3 (2.1)	8.8 (9.0)	23.1 (23.0)
8 $Ru(L_1H)(CH_3OH)Cl_2$	36.6 (36.5)	3.3 (3.5)	12.3 (12.2)	15.1 (15.4)
9 $Ru_2(L_1)(imz)Cl_4 \cdot CH_3OH$	29.3 (29.2)	2.5 (2.7)	11.8 (12.0)	20.5 (20.3)
10 $Ru(L_1H)(imz)Cl_2$	38.5 (38.7)	3.2 (3.0)	16.8 (16.9)	14.0 (14.3)

(continued)

TABLE 1. *(continued)*

Complex	C [a]	H [a]	N [a]	Cl^- [a]
11 $[Ru(L_1H)(2\text{-pico})(imz)]ClO_4$	41.0 (40.8)	3.2 (3.1)	15.2 (15.1)	
12 $[Ru(L_1H)(bipy)Cl]Cl_2 \cdot CH_2Cl_2$	43.0 (42.8)	3.1 (3.0)	11.8 (11.5)	14.3 (14.6)
13 $[Ru(L_1H)(TTSC)]Cl \cdot \frac{1}{2}O(C_2H_5)_2$	45.1 (45.3)	4.0 (4.1)	16.2 (16.0)	5.5 (5.8)
14 $[Ru(L_1H)(imz)(thiosal)]Cl \cdot CH_3OH$	44.3 (44.6)	3.7 (3.9)	13.1 (13.0)	5.7 (5.5)
15 $Ru_2(LH)_2Cl_6 \cdot 3H_2O$	20.4 (20.2)	2.5 (2.6)	13.6 (13.5)	25.6 (25.7)
16 $[Ru(LH)(L)]ClO_4 \cdot 2H_2O$	28.2 (28.2)	3.0 (3.2)	18.6 (18.8)	

[a]Calculated values in parentheses.

TABLE 2. Some important IR bands for the compounds

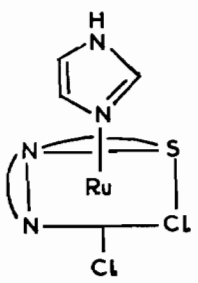
Compound	ν(C=N) + ν(C=C)	ν(CS)	Other characteristic vibrations
L_1H	1605, 1592	780(s)	620, 400
LH	1610	780(s)	620, 420
1 $[Ru(L_1H)(L_1)]Cl$	1625, 1615	780(sh)	630(w), 500(w)
2 $Ru_2(L_1)_2Cl_4 \cdot 4H_2O$	1620(sh), 1605	770(sh)	630(w), 500(w)
3 $[Ru(L_1)_2]$	1620, 1610(sh)	765(sh)	630(w), 495(w)
4 $Ru_2(L_1)_2(OH)_2$	1630, 1615	770(sh)	625(w), 510(w,sh)
5 $Ru_2(L_1)_2(SCN)_4 \cdot H_2O$	1620, 1605	780(sh)	630(w), 480(w), 2120(s)
6 $[Ru(L_1H)_2](SCN)_2$	1630, 1620	770(sh)	630(w), 480(w), 2100(s)
7 $Ru_2(L_1)(H_2O)Cl_4$	1615(sh), 1600	760(sh)	630(w), 490(w), 312
8 $Ru(L_1H)(CH_3OH)Cl_2$	1610(sh), 1600	770(sh)	620(w), 500(w), 330, 315
9 $Ru_2(L_1)(imz)Cl_4 \cdot CH_3OH$	1610, 1590	760(sh)	630, 480(w), 315
10 $Ru(L_1H)(imz)Cl_2$	1600, 1580	780(sh)	660(w), 630, 500(sh), 330, 310
11 $[Ru(L_1H)(2\text{-pico})(imz)]ClO_4$	1620, 1600	770(sh)	660, 640(sh), 630(s), 500, 460, 1635(s), 1100(s, br)
12 $[Ru(L_1H)(bipy)Cl]Cl_2 \cdot CH_2Cl_2$	1610, 1596	770(sh)	660, 650, 630, 610, 600, 320, 310(sh)
13 $[Ru(L_1H)(TTSC)]Cl \cdot \frac{1}{2}(C_2H_5)_2O$	1605–1610, 1600	780(sh)	620(vw), 500
14 $[Ru(L_1H)(imz)(thiosal)]Cl \cdot CH_3OH$	1610(sh), 1600	765(sh)	670, 660, 640, 625, 470, 2660, 1680
15 $Ru_2(LH)_2Cl_6 \cdot 3H_2O$	1620(sh), 1612	770(sh)	630(sh), 440(sh)
16 $[Ru(LH)(L)]ClO_4 \cdot 2H_2O$	1610(sh), 1600	770(sh)	640(sh), 630, 440, 1100–1140(s,br)

the ligands are present in the enolate form. Compound **1** ($[Ru(L_1H)(L_1)]Cl$) has low solubility in dichloromethane and chloroform but is highly soluble in methanol and DMF in which it behaves as a 1:1 electrolyte. Compound **3** ($Ru(L_1)_2$) on the other hand has high solubility in dichloromethane, chloroform and DMF where it behaves as a non-electrolyte.

The important IR bands of the ligands L_1H and LH and their metal complexes are listed in Table 2. It can be easily seen from the Table that in all cases the overlapping ν(C=N) and ν(C=C) vibrations around 1600 cm^{-1} and the pyridine ring deformation vibrations around 620 and 480 cm^{-1} suffer a positive shift of 10–15 cm^{-1} on coordination. The sharp band at 780 cm^{-1} in the ligand, assigned to the ν(CS) vibration, suffers a hypsochromic shift of 10–15 cm^{-1} on coordination and its intensity is greatly reduced in the metal complexes. The IR spectra thus indicate that in all the complexes the ligand behaves in a tridentate chelating manner coordinating through the imino nitrogen, the pyridine nitrogen and the sulfur atom in thioketo or thiolato form. The NMR spectrum of the ligand L_1H exhibits signals at δ 12.0 ppm (1H,S), δ 10.24 ppm (1H,S) and δ 7.2–8.8 ppm (10H, multiplets), which are assigned to the aldimine proton, the NH ptoron of the Ph–NH group, and an overlapping band of pyridine ring protons, phenyl

ring protons and NH proton respectively. In compound **1** ($[Ru(L_1H)(L_1)]Cl$) the aldimine proton is located at δ 8.89 ppm. X-ray crystallographic studies [3, 20] have upheld the contention of some earlier workers [21, 22] that in the bis chelate complexes of 2-formylpyridine thiosemicarbazone the two ligands occupy mutually perpendicular coordination planes. We believe that in both the complexes **1** and **3** the ligands assume the same sort of spatial disposition. The mononuclear thiocyanato complex $Ru(L_1H)_2(SCN)_2 \cdot H_2O$ (**6**) contains an additional strong band at 2110 cm^{-1} corresponding to the ν(CN) vibration of the thiocyanate moiety. The aldimine proton gives rise to a signal at δ 12.48 ppm in the NMR spectrum of the complex. This compound is partly soluble in MeOH and completely so in DMF in which it behaves as a 1:1 electrolyte. This observation along with a rather high value of ν(CN) in this complex compared to that of ionic thiocyanates indicates there is a fairly strong interaction of the thiocyanate group with the complex moiety both in the solid state and in solution. This is also supported by the nature of the electronic spectrum of this complex which is quite different from **1** and **2** (see later).

It can be seen from Scheme 2 and Sections (e) and (f) of 'Experimental' that by slight modification of the reaction procedure the monochelate complexes $[Ru(L_1H)(CH_3OH)Cl_2]$ (**8**) and $[Ru(L_1H)(imz)Cl_2]$ (**10**) can also be prepared along with the corresponding dimeric compounds $Ru_2L_1(H_2O)Cl_4$ (7) and $Ru_2L_1(imz)Cl_4 \cdot CH_3OH$ (**9**). However the compound **8** ($[Ru(L_1H)(CH_3OH)Cl_2]$) is found to undergo slow polymerization on storing even in the solid state. IR spectra of compound **8** exhibit two strong bands at 330 and 315 cm^{-1} whereas that of **10** ($[Ru(L_1H)(imz)Cl_2]$) contains bands at 330 and 310 cm^{-1} which are assigned to the ν(Ru–Cl) vibrations of a *cis* dichloro moiety [1]. The NMR spectra of compound **10** ($[Ru(L_1H)(imz)Cl_2]$) exhibits signals at δ 9.12 and δ 14.56 ppm assigned to the resonances of aldimine proton and NH proton of the imidazole respectively. Besides, the IR spectra of compound **10** $[Ru(L_1H)(imz)Cl_2]$ also contain some additional bands in the 620–660 cm^{-1} region characteristic of the imidazole ring. On the basis of the above facts compound **10** is proposed to have the structure shown. Compound **10** ($[Ru(L_1H)(imz)Cl_2]$) is found to react with ligands like picolinic acid and thiosalicylic acid leading to the isolation of the complexes $[Ru(L_1)(2\text{-pico})(imz)]ClO_4$ (**11**) and $[Ru(L_1H)(thiosal)(imz)]Cl \cdot CH_3OH$ (**14**) respectively. In the picolinic acid complex ν_{as}(CO) is observed at 1630 cm^{-1} compared to that at 1700 cm^{-1} for the free picolinic acid. This along with the appearance of some new bands ascribable to the pyridine ring vibration around 400–500 cm^{-1} in the above complex leads to the conclusion that picolinic acid has coordinated through the pyridine ring nitrogen and carboxylate oxygen. The complex is diamagnetic and hence ruthenium is present in the +2 oxidation state. The NMR spectrum of the complex exhibits signals due to the aldimine proton at δ 9.12 ppm and imidazole NH at δ 14.52 ppm, but no resonance is observed due to carboxylic proton, thus confirming that picolinic acid has acted in a monoacidic bidentate manner. The probable structure of the complex is as shown. As expected compound **11** ($[Ru(L_1H)(2\text{-pico})(imz)]ClO_4$) behaves as a 1:1 electrolyte. Compound **14** ($[Ru(L_1H)(imz)(thiosal)]Cl \cdot CH_3OH$) also behaves as a 1:1 electrolyte in methanol. Moreover, it is diamagnetic and hence is a Ru(II) complex. Thiosalicylic acid exhibits a weak band around 2660 cm^{-1} which is due to the ν(S–H) mode. The presence of a weak band around 2660 cm^{-1} in the spectrum of **14** indicates the nonparticipation of the –SH group of thiosalicylic acid in coordination. On the other hand, ν_{as}(CO) of the carboxylate group of thiosalicylic acid located at 1670 cm^{-1} in complex **14** is 50 cm^{-1} higher than the corresponding vibration found in the spectrum of the sodium salt of the acid. These two observations suggest that thiosalicylic acid is ligated in a monodentate manner in compound **14** ($[Ru(L_1H)(imz)(thiosal)]Cl \cdot CH_3OH$) through the deprotonated carboxyl group, while the SH group remains uncoordinated. This suggestion is also supported by the analysis of the NMR spectral data of the complex. The NMR spectrum of the complex contains two signals at δ 9.12 and δ 14.56 ppm assigned to the aldimine proton and NH proton of the imidazole



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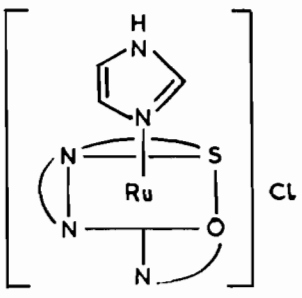

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moiety. As there are no other signals in the δ 9–20 ppm region except the above two, we may conclude that the carboxylic group of the thiosalicylic acid moiety is coordinated in the deprotonated form. The aromatic proton signals of the thiosalicylic acid overlap with those of the ligand L_1H and they occur together as multiplets in the δ 6.8 to δ 8.4 ppm region. The signal due to the S–H proton of the thiosalicylic acid overlaps with the signals of the methanol moiety and could not be identified separately. Thus complex **14** ($[Ru(L_1H)(imz)(thiosal)]Cl\cdot CH_3OH$) is apparently penta coordinated though a pseudo octahedral geometry cannot be ruled out. Compound **14** on stirring with excess of KSCN in methanol undergoes exchange of Cl^- by SCN^-. However, the thiocyanate analog thus produced is non-electrolytic in nature and exhibits a strong band at 2120 cm^{-1} corresponding to the ν(CN) vibration of the thiocyanate moiety probably coordinating through its S atom. Thus the thiocyanate analog of compound **14** seems to be octahedral. Bidentate ligands like bipyridyl (bipy) or 4-(*p*-tolyl)thiosemicarbazide (TTSCH) are found to react with compound **8** ($Ru(L_1H)(CH_3OH)Cl_2$) leading to the isolation of complexes $[Ru(L_1H)(bipy)Cl]Cl_2\cdot CH_2Cl_2$ (**12**) and $[Ru(L_1H)(TTSC)]Cl\cdot\frac{1}{2}(C_2H_5)_2O$ (**13**). Compound **12** has one electron magnetic moment (1.9 BM) and hence it is a Ru(III) complex, whereas **13** is diamagnetic and hence it is a Ru(II) complex. The NMR spectrum of compound **13** ($[Ru(L_1H)(TTSC)]Cl\cdot\frac{1}{2}(C_2H_5)_2O$) contains signals at δ 8.28 ppm due to the aldimine proton and an unresolved triplet at δ 2.32 ppm due to the CH_3 proton of the *p*-tolyl group. The CH_3 and CH_2 protons of ether (present as solvent of crystallization) occur at δ 2.52 and δ 3.04 ppm respectively. Both compounds **12** ($[Ru(L_1H)(bipy)Cl]Cl_2\cdot CH_2Cl_2$) and **13** ($[Ru(L_1H)(TTSC)]Cl\cdot\frac{1}{2}(C_2H_5)_2O$) are soluble in methanol in which compound **12** behaves as a 1:2 electrolyte, while compound **13** is found to behave as a 1:1 electrolyte.

When ruthenium chloride is reacted with 2-formylpyridine thiosemicarbazone (LH), two compounds **15** ($Ru_2(LH)_2Cl_6\cdot 3H_2O$) and **16** ($[Ru(LH)(L)]ClO_4\cdot 2H_2O$) are obtained. Compound **16** ($[Ru(LH)(L)]ClO_4\cdot 2H_2O$) is similar to compound **1** ($[Ru(L_1H)(L_1)]Cl$) behaving as a 1:1 electrolyte in methanol. Addition of excess of imidazole or 2-methyl imidazole to a methanolic solution of **1** or **16** at room temperature resulted in a gradual increase in conductance which attains a steady value after 3 to 4 h. However, with benzimidazole the above reaction is extremely slow at room temperature and proceeds to an appreciable extent on raising the temperature to ~50 °C. In all the above cases the involvement of imidazole (or its substituted derivatives) in coordination is indicated by the appearance of a new band at 500 nm in the electronic spectra of the reaction mixture. Spectrophotometric experiments also indicate that though compound **1** possesses a weak shoulder at 480 nm and compound **16** exhibits a shoulder at 500 nm, on addition of imidazole the molar absorbance values of both the complexes at 500 nm gradually decrease to a constant value when the shoulders take the shape of a distinct band. However, attempts to isolate the imidazole complex from this reaction mixture invariably leads to a mixture of products. The gradual increase in conductance can be rationalized by considering the Ru(II) complex as substitutionally labile in which one of the two coordinated ligands is replaced by imidazole present in large excess. The above process may be represented by the following equilibria which is driven towards the right hand direction due to the presence of a large excess of imidazole which finally results in the observed increase in conductance.

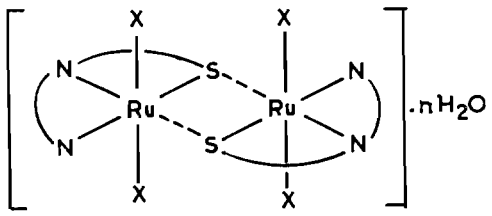
$$[Ru(L_1H)(L_1)]ClO_4 \rightleftharpoons [Ru(L_1H)(L_1)]^+ + ClO_4^-$$

$$\Big\downarrow\Big\uparrow \text{imz, } H_2O$$

$$[Ru(L_1H)(imz)_3]^{2+} + L_1H + OH^- + ClO_4^-$$

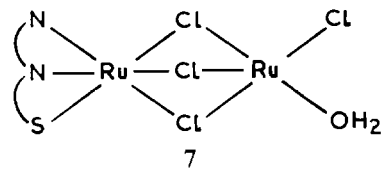
Formation of the monochelate complex containing imidazole as proposed above is substantiated by the isolation of the complex of the type $[Ru(L_1H)(imz)Cl_2]$ in the solid state and also corroborated by the fact that the bulkier ligand benzimidazole, reacts very slowly as all three incoming bulky ligands have to enter *cis* to each other.

The binuclear complexes **2** ($Ru_2(L_1)_2Cl_4\cdot 4H_2O$), **4** ($Ru_2(L_1)_2(OH)_2$) and **5** ($Ru_2(L_1)_2(SCN)_4\cdot H_2O$) mentioned earlier separate out of solution during the reaction of a methanolic solution of ruthenium chloride or ruthenium thiocyanate with the ligand (L_1H). They are of the general formula $Ru_2L_2X_m\cdot nH_2O$, X = Cl, $n = 4$, $m = 4$; X = SCN, $n = 1$, $m = 4$; and X = OH, $n = 0$, $m = 2$. These compounds are sparingly soluble in methanol, but readily soluble in DMF in which they are non-conducting. Room temperature magnetic moment values of these complexes lie in the range of 0.86–1.2 BM per ruthenium. The IR spectrum of **2** exhibits a strong band at 310 cm^{-1}, assignable to the ν(Ru–Cl) vibration of a terminal Ru–Cl bond. This band is absent in the IR spectra of **4** and **5**. The IR spectrum of **5** shows an additional band at 2120 cm^{-1} assignable to the ν(CN) vibration of the thiocyanate moiety. Such high values of ν(SCN) are generally indicative of S-bonded thiocyanate. On the basis of the above facts the following structure is proposed for complexes **2** and **5**. The very low magnetic moment arises probably from spin–spin coupling between the adjacent Ru(III) centres via the thiolato bridge of the deprotonated ligands.



2 (X = Cl); 5 (X = SCN)

Complex **4** ($Ru_2(L_1)_2(OH)_2$) contains only two hydroxy groups and in this complex each metal ion is probably penta coordinated. The binuclear complexes **7** ($Ru_2(L_1)(H_2O)Cl_4$) and **9** ($Ru_2(L_1)(imz)Cl_4 \cdot CH_3OH$) obtained during the preparation of monochelate complexes **6** and **10** are slightly different from **2**, **4** and **6** discussed above. These are again sparingly soluble in MeOH, readily soluble in DMF and DMSO, behaving as non-electrolytes in the latter two solvents. Magnetic moment values of **7** and **9** are 1.00 and 1.20 BM per ruthenium atom respectively. Both the compounds exhibit a strong band at 315 cm^{-1} assignable to a terminal ν(Ru–Cl) vibration. Based on the above facts the following structures are proposed for **7** and **9**. Some lowering of the magnetic moment probably occurs due to interaction between t_{2g} orbitals of the face sharing coordination polyhedra of the two adjacent ruthenium centres.



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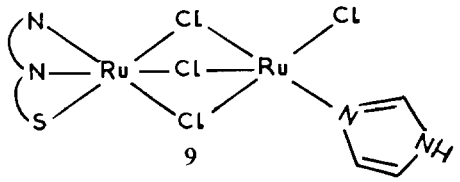

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We have prepared a few Co(III), Fe(III) and Rh(III) compounds of the ligands L_1H and LH in order to check whether there is any difference in ligational behaviour of the ligands towards Co(III), Rh(III) and Fe(III) ions, which have similar d electron configuration with Ru(II) and Ru(III) respectively. While the details of our observations regarding Co(III), Fe(III) and Rh(III) will be reported in a separate communication we would like to mention here a significant difference in behaviour between Co(III) and Fe(III) on the one hand and Ru(III) on the other. Thus the reaction of LH or L_1H with Ru(III) results in the simultaneous formation of a mononuclear Ru(II) complex and binuclear Ru(III) complex, whereas both Co(III) and Fe(III) yield only monomeric ones under identical conditions. This difference could be traced to the nature of the starting material. In alcoholic solution ruthenium chloride exists as a mixture of chloro and oxo chloro dimer and polymer. When it reacts with the ligand it results in the formation of both mono and binuclear complexes and because of the lower solubility of the dimer it separates out of the reaction mixture as a major reaction product. But for $CoCl_2 \cdot 6H_2O$ and $FeCl_3$ (anhydrous) as the starting material, no such complexity arises. This argument is further supported by the fact that if we use a well-characterized mononuclear complex $Ru(acac)_3$ as the starting material and allow it to react with L_1H in the presence of a small amount of perchloric acid we get only a mononuclear complex $[Ru(L_1)(L_1H)](ClO_4)_2$ in the solid state.

Electronic Spectra

The electronic spectra of the complexes in the visible region are dominated by charge transfer transitions. (Data is given in Table 3.) In the mononuclear Ru(II) bis chelates of ligand L_1H, the ligand band at 325 nm corresponding probably to a $\pi \rightarrow \pi^*$ transition of the pyridine ring, is split into two. In compound **1** this split band occurs at 330 and 250 nm whereas in compound **3** it is located at 330 and 235 nm. Compound **1** contains two MLCT bands in the visible region, one at 480 nm and another at 380 nm. Compound **3** on the other hand contains

TABLE 3. Electronic spectral data for metal complexes

Complex	Bands λ_{max} (nm) (log ϵ)
1[b]	480(sh,w)(3.84), 380(sh)(4.43), 330(4.65), 250(4.69)
2[a]	370(sh)(4.12), 335(4.17)
3[c]	480(sh)(3.67), 330(4.27), 235(4.54)
4[a]	460(3.31), 350(3.74)
5[a]	750(2.9), 650(3.38), 540(3.61), 380(3.98), 320(4.49)
6[a]	700(3.23), 540(3.60), 400(4.00), 325(4.46), 240[b]
7[a]	480(3.62), 330(4.15)
8[a]	470(3.69), 360(4.0), 250[b]
9[a]	700(3.30), 460(3.83), 350(4.20), 580(3.56)
10[a]	650(2.83), 500(3.32), 350(3.85)
11[a]	700(3.00), 470(4.00), 350(4.38)
12[b]	440(3.73), 420(3.78), 350(3.92), 280(4.39), 250(4.22), 235(4.25)
13[b]	490(3.76), 350(4.33), 250(4.54)
14[a]	700(2.79), 500(3.62), 350(4.17)
15[a, d]	470(sh), 300
16	700(2.24), 500(3.77), 315(4.61), 205

[a]Spectra in DMF. [b]Spectra in MeOH. [c]Spectra in CH_2Cl_2. [d]Quantitative spectra were not obtained because of low solubility of the compound.

only one such band at 480 nm. The greater number of bands of compound **1** compared to **3** is probably due to the lower symmetry of **1** as the two ligands are non-equivalent, one existing in thiolato form and another in thioketo form. In the case of the thiocyanato complex **6** we get three bands located at 700, 540 and 400 nm. The appreciable difference in band positions for the thiocyanato complexes is consistent with our assumption that one of the thiocyanates is quite strongly associated with the complex moiety making it somewhat different from **1** and **3**. In all the mononuclear monochelate complexes of ruthenium a characteristic band is located at 470–500 nm which is again assignable to a MLCT transition. Some additional bands are present in the different mixed chelate complexes whose nature and position are dependent on the nature of coligands in these complexes. The electronic spectra of the binuclear complexes are all dominated by intense CT bands and it has not been possible to assign the bands because of the complex electronic structure and appreciable metal–metal interaction existing in these complexes. Correct assignments can only be made if detailed structure and MO calculation of these molecules are worked out.

Biological Activity

As mentioned in 'Introduction' antibacterial activity of the ligands and some of their ruthenium complexes reported in this paper have been evaluated so as to examine whether the activities of the ligands are, in any way, modified due to their chelation to the ruthenium acceptor centre. As many of the compounds described in this paper are not soluble in the culture medium their activity cannot be evaluated. The detailed method followed in this work has already been discussed elsewhere [1]. The data is given in Table 4. The minimum inhibitory concentration (*MIC*) data presented in Table 4 clearly indicates that in some cases there is considerable increase of antibacterial activity of the ligands due to their chelation to the ruthenium acceptor centre. In fact for the binuclear complex $Ru_2(L_1)(imz)Cl_4 \cdot CH_3OH$ there is 85% enhancement of activity compared to the free ligand value, whereas for $Ru(L_1H)(imz)Cl_2$ the enhancement is 60%. Of the numerous possible factors responsible for such an activation [14] the presence of one or more labile sites is probably of prime importance. Preliminary spectrophotometric experiments indicate that the active ruthenium compounds readily react with histidine and nucleic acid bases like adenine, guanine and cytosine. The metal complexes exhibiting antibacterial activity can thus bind themselves to the nitrogen/oxygen donor points of the bacterial DNA [23, 24] utilizing the labile sites and thereby interfere with a vitally important biochemical process like DNA replication or RNA to DNA conversion leading to termination of the life process of the bacteria.

TABLE 4. *In vitro* antibacterial activity data against *E. coli* expressed as minimum inhibitory concentration (*MIC*) in micromoles/ml (μm/ml)

Compound	*MIC* (μm/ml)
L_1H	0.20
LH	0.34
$[Ru(L_1H)(L_1)]Cl$	0.19
$[Ru(L_1H)_2](SCN)_2$	0.17
$Ru_2(L_1)_2Cl_4 \cdot 2H_2O$	0.07
$Ru_2(L_1)_2(SCN)_4 \cdot H_2O$	0.06
$Ru_2(L_1H)_2Cl_6 \cdot 4H_2O$	0.05
$Ru(L_1H)(imz)Cl_2$	0.08
$Ru_2(L_1)(imz)Cl_4 \cdot CH_3OH$	0.03
$[Ru(LH)(L)]ClO_4 \cdot 2H_2O$	0.08

Experimental

$RuCl_3 \cdot XH_2O$ was obtained from Aurora Matthey (India). Thiosemicarbazide obtained from Loba Chemie Industry was recrystallized from ethanol. 4-Phenyl thiosemicarbazide was prepared according to the published procedure [1]. Elemental analyses were obtained using a Perkin-Elmer 240 C,H,N analyser. Halides were estimated argentometrically, in the usual way. The IR spectra were recorded on a Perkin-Elmer 783 spectrophotometer as KBr or 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 susceptibility was measured at room temperature by a Princeton Applied Research vibrating sample magnetometer using $Hg[Co(SCN)_4]$ as the calibrant. The NMR spectra were recorded on a Jeol FX 100 NMR spectrometer using TMS as an internal standard. Pyridine-2-aldehyde thiosemicarbazone was prepared by the standard method [25]. The ligand pyridine-2-aldehyde(4-phenyl) thiosemicarbazone and the different metal complexes were prepared according to the procedures given below.

(a) Preparation of 4-Phenyl Thiosemicarbazone of Pyridine-2-aldehyde (L_1H)

4-Phenyl thiosemicarbazide (1 mmol) was dissolved in hot dehydrated alcohol and to it 1 mmol of pyridine-2-aldehyde was added and the mixture was stirred for 4 h, when a yellowish white compound separated out. The solution was then filtered and the residue was washed several times with cold alcohol. The yellowish residue was stirred with 100

ml alcohol for a few minutes, filtered and dried over fused $CaCl_2$. It was recrystallized from hot alcohol. Melting point 195 °C.

(b) Preparation of $[Ru(L_1H)(L_1)]Cl$ (1) and $Ru_2(L_1)_2Cl_4 \cdot 4H_2O$ (2)

About 260 mg (1 mmol) of the ligand 2-formylpyridine(4-phenyl) thiosemicarbazone (L_1H) were dissolved in 30 ml of hot methanol and to it 150 mg of $RuCl_3$ dissolved in 20 ml of methanol were added drop by drop with continuous stirring. A brown precipitate began to appear at this stage. After the addition was complete the mixture was stirred for 4 h and filtered. The residue was washed several times with methanol and then dried in a desiccator. Analytical data for this compound corresponds to the formula $Ru_2(L_1)_2Cl_4 \cdot 2H_2O$ (**2**).

The filtrate was evaporated to dryness, the dried mass was washed several times with water and then kept overnight in a sulfuric acid desiccator. The compound was then recrystallized from 4:1 dichloromethane–methanol mixture. The compound analyzed for $[Ru(L_1H)(L_1)]Cl$ (**1**).

(c) Preparation of $Ru(L_1)_2$ (3) and $Ru_2(L_1)_2(OH)_2$ (4)

The preparative procedure is similar to that outlined in (b) except that in this case pH of the reaction medium was adjusted to 8–9 by the addition of alcoholic NaOH. The residue was thoroughly washed with methanol and dried over $CaCl_2$ in a desiccator. The resultant compound analyzed for $Ru_2(L_1)_2(OH)_2$ (**4**).

The compound $Ru(L_1)_2$ (**3**) was isolated from the filtrate following a procedure similar to that used for the preparation of **1**. The compound was recrystallized from dichloromethane.

(d) Preparation of $Ru_2(L_1)_2(SCN)_4 \cdot H_2O$ (5) and $[Ru(L_1H)_2](SCN)_2$ (6)

A total of 150 mg of $RuCl_3$ was refluxed with 20 ml saturated solution of ammonium thiocyanate in methanol for 45 min. The solution was first cooled to room temperature and then added drop by drop to a solution of 1 mmol of ligand (L_1H) in 30 ml methanol. The mixture was stirred for 4 h and then filtered. The residue was washed several times with methanol and dried over fused $CaCl_2$. The compound analyzed for $Ru_2(L_1)_2(SCN)_4 \cdot H_2O$ (**5**).

On concentration the filtrate deposited a microcrystalline compound which was filtered, washed several times with distilled water and finally dried over fused $CaCl_2$. The compound analyzed for $[Ru(L_1H)_2](SCN)_2$ (**6**).

(e) Preparation of $Ru_2(L_1)(H_2O)Cl_4$ (7) and $Ru(L_1)(CH_3OH)Cl_2$ (8)

A total of 150 mg of $RuCl_3$ was dissolved in 20 ml of methanol and to it 0.5 mmol of ligand (L_1H) dissolved in 30 ml of methanol was added drop by drop (addition time 3–4 h) with continuous stirring. After complete addition the stirring was continued for 3 h. The mixture was then filtered, the residue was washed several times with methanol and finally dried over fused $CaCl_2$. The compound analyzed for $Ru_2(L_1)(H_2O)Cl_4$ (**7**).

The filtrate was evaporated to dryness, the dried mass was washed several times with water and the residue was finally recrystallized from MeOH. It analyzed for $Ru_2(L_1)(CH_3OH)Cl_2$ (**8**).

(f) Preparation of $Ru_2(L_1)(imz)Cl_4 \cdot CH_3OH$ (9) and $Ru(L_1H)(imz)Cl_2$ (10)

To a methanolic solution of 150 mg $RuCl_3$ a methanolic solution of 0.5 mmol of ligand L_1H dissolved in 30 ml of methanol was added drop by drop (total addition time ~4 h) with continuous stirring. After complete addition, 70 mg (1 mmol) of imidazole was added to the reaction mixture and then stirring was continued for further 5 h. The mixture was then filtered, residue washed several times with MeOH and finally dried over fused $CaCl_2$. The compound analyzed for $Ru_2(L_1)(imz)Cl_4 \cdot CH_3OH$ (**9**) (imz = imidazole).

The mother liquor (pH 6–7) was evaporated almost to dryness on a hot plate and kept overnight in a sulfuric acid desiccator. The solid mass thus obtained was then triturated twice with hot acetone and the supernatant liquid was decanted off. The residue was again triturated twice with ether and the granular compound obtained thereby was dried over fused $CaCl_2$. It analyzed for $[Ru(L_1H)(imz)Cl_2]$ (**10**).

(g) Preparation of $[Ru(L_1H)(2\text{-pico})(imz)]ClO_4$ (11)

Compound **10** (1 mmol) was dissolved in 30 ml of methanol and to it 1 mmol of 2-picolinic acid was added; the mixture was stirred for 18 h at room temperature and then filtered. The reddish brown filtrate was concentrated to half its volume and 10 ml of saturated solution of $NaClO_4$ was added to it. The mixture was again stirred vigorously when a brown compound gradually separated out. It was washed several times with water and finally dried over fused $CaCl_2$.

(h) Preparation of $Ru(L_1H)(bipy)Cl_3 \cdot CH_2Cl_2$ (12)

Compound **8** (1 mmol) was dissolved in 30 ml of MeOH and 1 mmol of bipyridyl was added to it. The solution was stirred for 36 h, filtered and the filtrate was evaporated to dryness on a hot plate and then kept in a sulfuric acid desiccator for 2 days. The dried mass was triturated several times with acetone and the supernatant liquid decanted off. Finally it was recrystallized from dichloromethane to which a small volume of methanol was added.

(i) Preparation of $[Ru(L_1H)(TTSC)]Cl \cdot \frac{1}{2}(C_2H_5)_2O$ (13)

To 1 mmol of compound **8** dissolved in MeOH (20 ml) 1 mmol of 4(4′-tolyl)thiosemicarbazide (TTSCH)

in 30 ml MeOH was slowly added and the solution was stirred for 72 h. The mixture was then filtered and the reddish brown filtrate was evaporated to dryness in a rotary evaporator. The dried mass was stirred twice with 20 ml portions of boiling ether and the supernatant was decanted off. The compound was then dried over fused $CaCl_2$.

(j) Preparation of [Ru(L$_1$H)(imz)(thiosal)]Cl·CH$_3$OH (14)

Compound **10** (1 mmol) was dissolved in 30 ml MeOH and 1 mmol of thiosalicylic acid was added to it. The mixture was stirred for 18 h, filtered, the filtrate evaporated to dryness and the residue was kept in a calcium chloride desiccator for 24 h. The dried residue was dissolved in a 10:1 dichloromethane–methanol mixture, filtered and the filtrate was allowed to evaporate at room temperature. The resultant solid was purified by washing twice with 10 ml portions of diethyl ether and dried oyer fused $CaCl_2$.

(k) Preparation of Ru$_2$(LH)$_2$Cl$_6$·3H$_2$O (15) and [Ru(LH)(L)]ClO$_4$·2H$_2$O (16)

2-Formylpyridine thiosemicarbazone (LH) (1 mmol) was dissolved in 30 ml MeOH and to it a solution of 150 mg of $RuCl_3$ in 20–30 ml MeOH was added drop by drop with stirring. After complete addition stirring was continued for a further 5 h. The solution was then filtered, the residue was washed several times with MeOH and dried in a $CaCl_2$ desiccator. The solid compound obtained was **15**.

The filtrate was concentrated to half of its volume and 10 ml saturated aqueous solution of sodium perchlorate was added to it. On cooling a brown solid separated out. It was filtered, washed several times with cold water and finally dried over fused $CaCl_2$ to give compound **16**.

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