

Complexes of ruthenium(III), rhodium(III) and iridium(III) with ligands bearing 2,6-diacetylpyridine bis(S-alkylisothiosemicarbazones): Synthesis, spectral studies and structural elucidation

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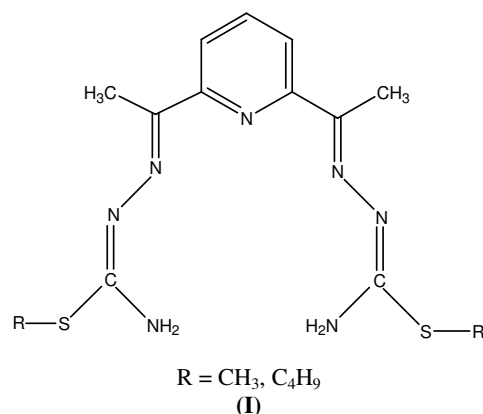
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Reactions of the ligands, 2,6-diacetylpyridine bis(S-methylisothiosemicarbazone) and 2,6-diacetylpyridine bis(S-butylisothiosemicarbazone) with ruthenium(III), rhodium(III) and iridium(III) have been studied and their structures have been proposed based on elemental analyses, molar conductance, magnetic moment, spectral data (IR, ^1H NMR, FAB mass) and thermal investigations. The ligands behave as pentacoordinated and give acyclic complexes of the general formula $[\text{M}(\text{H}_2\text{L})\text{Cl}_2]\text{Cl}$ and macrocyclic complexes, $[\text{M}(\text{L}')\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$, which are formed by template condensation by using β -diketones. Pentagonal bipyramidal geometries are observed for acyclic and macrocyclic complexes. In both types of complexes, the ligands coordinate in their amino form. The thermal stability and mode of decomposition of the various complexes have been studied by TGA techniques. Conductance measurements reveal 1:1 electrolytic nature of the complexes.

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Isouthiosemicarbazones are potentially tautomeric systems and have long been known to exist in either the amino form, $>\text{C}=\text{N}-\text{N}=\text{C}(\text{SR})\text{NH}_2$, or the imino form, $>\text{C}=\text{N}-\text{NH}-\text{C}(\text{SR})=\text{NH}$. Thus, S-alkylated derivatives of thiosemicarbazide act exclusively as bidentate ligands involving the coordination of two terminal nitrogen atoms instead of sulphur¹⁻³. Due to their very interesting and effective physicochemical properties, structural and pharmacological characteristics including biological activity and analytical applications, thiosemicarbazones/isouthiosemicarbazones as well as their metal complexes have been a subject of many studies⁴⁻⁸. The chelating properties of 2,6-diacetylpyridine bis(S-alkylisouthiosemicarbazones) have been investigated towards several metal ions. From the view point of different denticity, 2,6-diacetylpyridine has been found to be a

versatile tridentate chelating agent having two reactive carbonyl groups capable of undergoing Schiff base condensation with various di- and polyamines⁹⁻¹³. Thus, isouthiosemicarbazones of 2,6-diacetylpyridine, (which are potentially very active pentadentate ligands) involving N_5 donor set of atoms occupy a special place^{14, 15} and play an important role in the development of macrocyclic complexes¹⁶. Such complexes show relevance to biological systems, stabilities and unusual structures. S-alkylatedisouthio-semicarbazides have proved to be efficient building blocks in template design and synthesis of various complexes of mononuclear macrocyclic nature, with symmetrical and nonsymmetrical architectures¹⁷. The condensation can easily be achieved by template as well as nontemplate methods. Template synthesis leading to macrocyclic products has been used increasingly to construct complex molecules which either cannot be prepared by traditional methods or give poor yield. We report herein the use of the ligand, 2,6-diacetylpyridine bis(S-alkylisouthiosemicarbazones) in preparing acyclic ruthenium(III), rhodium(III) and iridium(III) derivatives and their macrocyclic products with β -diketones via cyclization. The structure of the ligand used in the present study is shown below (**I**):



Experimental

High purity 2,6-diacetylpyridine (Fluka), methyl iodide/butyl iodide (Lancaster), acetylacetone, benzoylacetone (Acros), $\text{RuCl}_3\cdot 3\text{H}_2\text{O}$, $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ and $\text{IrCl}_3\cdot 3\text{H}_2\text{O}$ (Loba Chemie, Bombay) were used as received. The S-alkylisouthiosemicarbazides were prepared using the reported procedure¹⁸. All other

solvents used were AR grade and used as received. Microanalytical (C, H & N) data were obtained with an Elementar Vario EL 1108 at SAIF, Central Drug Research Institute, Lucknow, India. IR spectra were recorded using Perkin Elmer PC-16F FTIR spectrophotometer by using KBr pellets. ^1H NMR spectra were recorded in Bruker DRX-300 spectrometer in deuterated dimethylsulphoxide ($\text{DMSO-}d_6$). FAB mass spectra were recorded in a Jeol SX 102/DA-600 mass spectrometer using *m*-nitrobenzyl alcohol as matrix. Magnetic susceptibility measurements were carried out at room temperature by Gouy's balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant. The conductivity measurements were made using a Systronics conductivity meter with a dip type cell, using 10^{-3} M solutions of the complexes in DMF. Thermogravimetric data were obtained in air at $10^\circ\text{C min}^{-1}$ in the $25\text{-}750^\circ\text{C}$ range using Shimadzu TGA-50 H analyzer.

Preparation of the ligands

2,6-Diacetylpyridine (0.1 mol) was dissolved in ethanol (10 cm^3) in a round bottom flask. To this solution, freshly prepared ethanolic solution (10 cm^3) of S-alkylisothiosemicarbazide (0.1 mol) was added. The reaction mixture was allowed to reflux at 35°C with stirring for 3 h. The creamish white to pinkish cream coloured precipitate appeared on cooling in crushed ice for 1-2 h. The complex which separated out by filtration, washed carefully with cold methanol, recrystallized in ethanol and dried *in vacuo* over fused calcium chloride in desiccator.

Preparation of the complexes

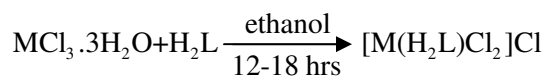
The $[\text{M}(\text{H}_2\text{L})\text{Cl}_2]\text{Cl}$ complexes were prepared by adding freshly prepared ethanolic solution (15 cm^3) of the 2,6-diacetylpyridine bis(S-alkylisothiosemicarbazones) (0.01 mol) to a warm ethanolic solution of $\text{RuCl}_3\cdot 3\text{H}_2\text{O}$ or $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ or $\text{IrCl}_3\cdot 3\text{H}_2\text{O}$ (0.01 mol) in 1:1 ratio. The reaction mixture was refluxed for about 12-18 h with constant stirring. The product formed was filtered off and washed with cold ethanol followed by diethyl ether and finally dried *in vacuo* over fused calcium chloride.

The $[\text{M}(\text{L}')\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ complexes were prepared by adding an ethanolic solution (20 cm^3) of the ligand, 2,6-diacetylpyridine bis(S-alkylisothiosemicarbazone) (0.01 mol), to an ethanolic solution (20 cm^3) of $\text{RuCl}_3\cdot 3\text{H}_2\text{O}$ or $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ or $\text{IrCl}_3\cdot 3\text{H}_2\text{O}$ (0.01 mol) with rapid stirring under mild heating for 5-10 minutes, followed by addition of acetylacetone or

benzoylacetone (0.01 mol) from a dropping funnel. The precipitate separated out and the reaction mixture was again refluxed at ambient temperature with constant stirring for about 15-16 h. The resulting mixture was then cooled overnight in order to get clear precipitation. The complexes were filtered, washed with ethanol and diethyl ether and dried *in vacuo* over fused calcium chloride.

Results and discussion

Condensation of S-methyl/butylisothiosemicarbazide in ethanolic medium with 2,6-diacetylpyridine resulted in isothiosemicarbazones. Complexes are formed by both nontemplate and template methods, and exhibit cyclization through acetylacetone and benzoylacetone with Ru(III), Rh(III) or Ir(III) trichloride and isothiosemi-carbazones. Although isothiosemicarbazones are potentially active and exhibit tautomeric system, in the present case only the amino form $>\text{C}=\text{N}-\text{N}=\text{C}(\text{SR})\text{NH}_2$ has been reported. However, macrocyclic complexes formed by cyclization have shown the neutral form of the ligand where both the NH_2 groups condense with carbonyl group of diketone moiety. The obtained microcrystalline complexes were found to be stable in air and moisture with colour variation from brown to black. All the complexes were found soluble in dimethylformamide and dimethylsulphoxide, but were insoluble in ethanol, methanol, ether, acetone, tetrahydrofuran, chloroform and water. The reactions can be represented by the following equations:



H_2L = DPMI, DPBI; M = Ru(III), Rh(III), Ir(III)

R' = CH_3 , C_6H_5 ; R'' = CH_3 , C_6H_5

L' = $\text{L}_1\text{-L}_4$ [macrocyclic ligands derived by condensation of 2,6-diacetylpyridine bis(S-alkylisothiosemicarbazones) with β -diketones]

The molar conductivity (λ_M) of freshly prepared DMF solution (10^{-3} M) is $85\text{-}120\text{ S cm}^2\text{ mol}^{-1}$ for the complexes which corresponds to the 1:1 electrolytic

nature for acyclic and macrocyclic complexes. The analytical results of compounds support the formulations represented in Table 1.

The magnetic moment for all Ru(III) complexes are in the range 1.60-1.75 B.M. at room temperature; lower than the predicted normal values. These low values may be indicative of the presence of lower symmetry ligand fields and the formation of molecular orbital by the extended overlap of the metal and ligand orbitals¹⁹. Progressive quenching of the orbital angular momentum by spin orbit coupling that removes the degeneracy of the triplet ground term

causes lowering of the magnetic moment²⁰. Thus, extensive spin orbit coupling can reduce the magnetic moment below that of the spin only value. Rh(III) and Ir(III) complexes show zero magnetic moment at room temperature and suggest diamagnetic structure with d^6 paired electrons^{21,22}.

The infrared spectra of 2,6-diacetylpyridine bis(S-alkylisothiosemicarbazones) were compared with their complexes of Ru(III), Rh(III) and Ir(III). The pyridine ring vibrations, most affected by nitrogen of pyridine in coordination with a metal atom, are pyridine ring deformation, inplane ring

Table 1—Analytical and physical data of the ligands and their ruthenium(III), rhodium(III) and iridium(III) complexes

Comp. (Emp. formula)	Colour	Yield (%)	Stirring/ refluxing time (h)	Found (Calc.) (%)					
				C	H	N	Cl	S	M
DPMI (C ₁₃ H ₁₅ N ₇ S ₂)	Cream White	80	3	46.0 (46.2)	5.4 (5.6)	28.9 (29.0)	-	18.6 (18.9)	-
DPBI (C ₁₉ H ₃₁ N ₇ S ₂)	Pinkish Cream	70	3	54.0 (54.1)	7.1 (7.3)	23.2 (23.2)	-	15.0 (15.2)	-
[Ru(DPMI)Cl ₂]Cl (C ₁₃ H ₁₉ N ₇ S ₂ Cl ₃ Ru)	Black	68	12	28.4 (28.6)	3.2 (3.4)	18.0 (18.0)	19.0 (19.5)	11.6 (11.7)	18.3 (18.5)
[Rh(DPMI)Cl ₂]Cl (C ₁₃ H ₁₉ N ₇ S ₂ Cl ₃ Rh)	Brown	76	10	28.4 (28.5)	3.1 (3.4)	17.6 (17.9)	19.4 (19.4)	11.4 (11.7)	18.4 (18.6)
[Ir(DPMI)Cl ₂]Cl (C ₁₃ H ₁₉ N ₇ S ₂ Cl ₃ Ir)	Brown	64	15	24.3 (24.5)	2.6 (2.9)	15.3 (15.4)	16.4 (16.7)	10.0 (10.0)	30.2 (30.2)
[Ru(DPBI)Cl ₂]Cl (C ₁₉ H ₃₁ N ₇ S ₂ Cl ₃ Ru)	Black	62	14	36.2 (36.3)	4.3 (4.9)	15.3 (15.6)	16.6 (16.9)	10.0 (10.1)	16.0 (16.0)
[Rh(DPBI)Cl ₂]Cl (C ₁₉ H ₃₁ N ₇ S ₂ Cl ₃ Rh)	Brown	60	12	36.0 (36.1)	4.2 (4.9)	15.5 (15.5)	16.5 (16.6)	10.0 (10.1)	15.9 (16.1)
[Ir(DPBI)Cl ₂]Cl (C ₁₉ H ₃₁ N ₇ S ₂ Cl ₃ Ir)	Brown	60	12	31.6 (31.7)	4.2 (4.3)	13.5 (13.6)	14.5 (14.7)	8.6 (8.9)	26.5 (26.7)
[Ru(L ₁)Cl ₂]Cl·H ₂ O (C ₁₈ H ₂₅ N ₇ S ₂ OCl ₃ Ru)	Black	70	9	34.3 (34.5)	4.4 (3.9)	15.3 (15.6)	16.6 (16.9)	10.0 (10.2)	16.0 (16.1)
[Rh(L ₁)Cl ₂]Cl·H ₂ O (C ₁₈ H ₂₅ N ₇ S ₂ OCl ₃ Rh)	Black	72	10	34.0 (34.3)	3.6 (3.9)	15.4 (15.6)	16.7 (16.9)	10.0 (10.1)	16.0 (16.2)
[Ir(L ₁)Cl ₂]Cl·H ₂ O (C ₁₈ H ₂₅ N ₇ S ₂ OCl ₃ Ir)	Blackish Brown	60	18	30.1 (30.1)	3.4 (3.4)	13.4 (13.6)	14.6 (14.8)	8.8 (8.9)	26.7 (26.8)
[Ru(L ₂)Cl ₂]Cl·H ₂ O (C ₂₃ H ₂₇ N ₇ S ₂ OCl ₃ Ru)	Brown	78	12	40.0 (40.1)	3.6 (3.9)	14.1 (14.2)	15.2 (15.4)	9.2 (9.3)	14.4 (14.6)
[Rh(L ₂)Cl ₂]Cl·H ₂ O (C ₂₃ H ₂₇ N ₇ S ₂ OCl ₃ Rh)	Brownish Black	76	10	40.0 (40.0)	3.8 (3.9)	14.0 (14.2)	15.1 (15.3)	9.1 (9.2)	14.5 (14.7)
[Ir(L ₂)Cl ₂]Cl·H ₂ O (C ₂₃ H ₂₇ N ₇ S ₂ OCl ₃ Ir)	Brown	60	18	35.2 (35.3)	3.2 (3.4)	12.3 (12.5)	13.4 (13.6)	8.1 (8.2)	24.3 (24.6)
[Ru(L ₃)Cl ₂]Cl·H ₂ O (C ₂₄ H ₃₇ N ₇ S ₂ OCl ₃ Ru)	Black	60	14	40.3 (40.5)	5.1 (5.2)	13.6 (13.8)	14.7 (14.9)	9.0 (9.0)	14.0 (14.2)
[Rh(L ₃)Cl ₂]Cl·H ₂ O (C ₂₄ H ₃₇ N ₇ S ₂ OCl ₃ Rh)	Brown	60	12	40.2 (40.4)	5.1 (5.1)	13.5 (13.7)	14.3 (14.7)	8.6 (8.9)	14.2 (14.3)
[Ir(L ₃)Cl ₂]Cl·H ₂ O (C ₂₄ H ₃₇ N ₇ S ₂ OCl ₃ Ir)	Brown	63	12	35.7 (35.9)	4.3 (4.6)	12.1 (12.2)	13.1 (13.2)	7.8 (7.9)	23.6 (23.9)
[Ru(L ₄)Cl ₂]Cl·H ₂ O (C ₂₉ H ₃₉ N ₇ S ₂ OCl ₃ Ru)	Black	62	15	45.0 (45.0)	4.8 (5.0)	12.4 (12.6)	13.6 (13.7)	8.0 (8.2)	12.8 (13.0)
[Rh(L ₄)Cl ₂]Cl·H ₂ O (C ₂₉ H ₃₉ N ₇ S ₂ OCl ₃ Rh)	Black	60	12	44.2 (44.9)	4.6 (5.0)	12.2 (12.6)	13.2 (13.5)	8.2 (8.2)	13.0 (13.1)
[Ir(L ₄)Cl ₂]Cl·H ₂ O (C ₂₉ H ₃₉ N ₇ S ₂ OCl ₃ Ir)	Brownish Black	62	12	40.0 (40.2)	4.4 (4.5)	11.2 (11.3)	12.0 (12.2)	7.2 (7.4)	22.1 (22.2)

deformation and out-of-plane deformation²³. These vibrations appear at *ca.* 1580-1585, 620-640 and 410-420 cm^{-1} , respectively, in the free ligands. Inplane deformation and out-of-plane deformation bands show an upward shift of *ca.* 25-40 cm^{-1} , respectively upon coordination to metal atom²⁴. Although pyridine ring deformation band is less sensitive to coordination, in the spectra of some complexes this band is probably superimposed or masked out. The $\nu(\text{M-N}_{\text{py}})$ vibration²⁵ located at *ca.* 260-285 cm^{-1} verified the coordination of pyridine nitrogen with metal atom. Medium band at *ca.* 1610 cm^{-1} was assigned to $\delta(\text{NH}_2)$ groups of isothiosemicarbazide moieties and showed downward shift (8-15 cm^{-1}) due to the involvement of NH_2 (isothioamide group) with metal atom in coordination. The ligands showed two weak bands at *ca.* 1640 cm^{-1} and 1620 cm^{-1} , assigned to respectively the azomethine linkage of the isothiosemicarbazide^{26,27}, $-\text{N}=\text{C}(\text{SR})\text{NH}_2$, and the isothiosemicarbazide linkage, $\text{C}_5\text{H}_3\text{N}-(\text{CH}_3)\text{C}=\text{N}-$, formed by the condensation of isothiosemicarbazide with 2,6-diacetylpyridine. Band due to isothiosemicarbazide ($-\text{N}=\text{C}(\text{SR})\text{NH}_2$) fragment remained at the same position but the $\text{C}_5\text{H}_3\text{N}-(\text{CH}_3)\text{C}=\text{N}-$ linkage shifted to lower frequency by *ca.* 15-20 cm^{-1} in the complexes. The appearance of a weak band $\nu(\text{C}=\text{N})$ is in accord with other observations⁶. This was again confirmed by the presence of $\nu(\text{M-N})$ vibrations at 365-380 cm^{-1} . This indicates involvement of only one of the azomethine linkage in coordination. The new bands appearing in the complexes in the range 320-340 cm^{-1} may be assigned to $\nu(\text{M-Cl})$. The infrared spectra of the macrocyclic complexes formed by template synthesis have shown only a few of the

significant changes in comparison to the parent acyclic complexes. Most characteristic aspect that has been observed is the absence of $\nu(\text{N-H})$ and $\delta(\text{NH}_2)$ bands due to the isothioamide group observed in acyclic complexes²⁸. This confirms the condensation of the NH_2 groups with β -diketones carbonyl group oxygen, which shows the new azomethine linkage as weak band²⁹ at *ca.* 1630 cm^{-1} and 1620 cm^{-1} , attributed to the $>\text{C}=\text{N}$ stretching mode of newly formed azomethine linkages. These observations clearly indicate that the two terminal groups of the isothiosemicarbazone complexes condense with the carbonyl oxygen atoms of the β -diketones giving rise to the cyclic product. On the basis of above spectral features, a seven coordinated structure is proposed for the acyclic and macrocyclic complexes. Infrared spectra showed that the 2,6-diacetylpyridine bis(S-alkylisothiosemicarbazone) ligands acts as neutral quinque dentate ligands coordinating through pyridine nitrogen, two azomethine nitrogen atoms and two isothioamide nitrogen atoms. In the acyclic and macrocyclic complexes, N_5 type coordination was observed with pentacoordinated ligand with the two axial positions occupied by chloride ions.

In the proton magnetic resonance spectra of the complexes recorded in $\text{DMSO-}d_6$ (Table 2), the resonance line intensities were determined by planimetric integration. Azomethine protons of the ligands are observed as sharp singlets in a different integral ratio in range δ 8.20-8.35 ppm. This undergoes downfield shift in their corresponding complexes. Effective signal as a singlet at about δ 4.35-4.40 ppm due to the NH_2 protons of isothiosemicarbazide is observed in the ligands. This

Table 2—¹H NMR (δ , ppm) spectra of the ligands and their rhodium(III) and iridium(III) Complexes

Comp.	$\delta(\text{CH}=\text{N})$	$\delta(\text{NH}_2)$	$\delta(\text{py-N})$	$\delta(\text{S-methyl/butyl})$	δCH_2
DPMI	8.20 (s)	4.35 (s)	7.30 (s)	1.90 (s)	-
DPBI	8.35 (s)	4.40 (s)	7.45 (s)	2.00 (t)	-
[Rh(DPMI)Cl ₂]Cl	9.10 (s)	4.36 (s)	7.50 (s)	1.90 (s)	-
[Ir(DPMI)Cl ₂]Cl	9.15 (s)	4.35 (s)	7.55 (s)	1.91 (s)	-
[Rh(DPBI)Cl ₂]Cl	9.18 (s)	4.40 (s)	7.66 (s)	2.01 (t)	-
[Ir(DPBI)Cl ₂]Cl	9.10 (s)	4.39 (s)	7.65 (s)	2.02 (t)	-
[Rh(L ₁)Cl ₂]Cl·H ₂ O	9.10 (s)	-	7.50 (s)	1.93 (s)	2.20 (s)
[Ir(L ₁)Cl ₂]Cl·H ₂ O	9.16 (s)	-	7.50 (s)	1.90 (s)	2.20 (s)
[Rh(L ₂)Cl ₂]Cl·H ₂ O	9.18 (s)	-	7.52 (s)	1.90 (s)	2.20 (s)
[Ir(L ₂)Cl ₂]Cl·H ₂ O	9.15 (s)	-	7.55 (s)	1.91 (s)	2.20 (s)
[Rh(L ₃)Cl ₂]Cl·H ₂ O	9.20 (s)	-	7.68 (s)	2.00 (t)	2.25 (s)
[Ir(L ₃)Cl ₂]Cl·H ₂ O	9.20 (s)	-	7.66 (s)	1.93 (t)	2.25 (s)
[Rh(L ₄)Cl ₂]Cl·H ₂ O	9.22 (s)	-	7.70 (s)	2.00 (t)	2.25 (s)
[Ir(L ₄)Cl ₂]Cl·H ₂ O	9.21 (s)	-	7.68 (s)	1.91 (t)	2.25 (s)

s = singlet, t = triplet

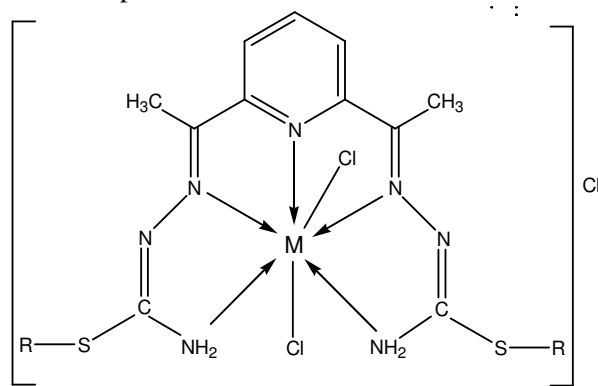
is observed at the same position in the spectra of acyclic complexes. Due to cyclization by β -diketones, this NH_2 group disappears and gives no signal in NMR region in the macrocyclic complexes. The spectra of the ligands show pyridine ring protons signal at δ 7.30-7.45 ppm as singlet and exhibit downfield shift in the complexes to show the involvement of pyridine nitrogen in coordination with metal ions. Signals due to S-alkyl (methyl/butyl) group occurred as singlet and triplets in range δ 1.90–2.02 ppm in ligands as well as in complexes without any significant chemical shift.

The mass spectrum of the ligand, DPML, shows the molecular ion peak at $m/z = 337$: M^+ . The other important peaks that were obtained after fragmentation are as follows: 290 $[\text{M-SCH}_3]^+$, 234 $[\text{M-SCH}_3\text{-NH}_2\text{-CN-N}]^+$, 178 $[\text{M-SCH}_3(\text{NH}_2\text{-CN-N})_2]^+$ and 131 $[\text{M-SCH}_3\text{-(NH}_2\text{-CN-N)}_2\text{-SCH}_3]^+$. The other ligands show a similar mode of fragmentation with molecular ion peak $m/z = 421$. Complexes of ruthenium(III), rhodium(III) and iridium(III) with macrocyclic ligands with composition $[\text{M}(\text{L}_1)\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ show peaks because of fragmentation of water molecule. In $[\text{Ru}(\text{L}_1)\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$, the molecular ion peak is observed at $m/z = 624$ and it shown other peaks at 606, 500 and 485, respectively. Other important peaks included fragments of the ligands could not be identified. Although these data obtained due to FAB mass serve to substantiate the formation of compound, they do not allow us to elucidate the exact structure of the compounds.

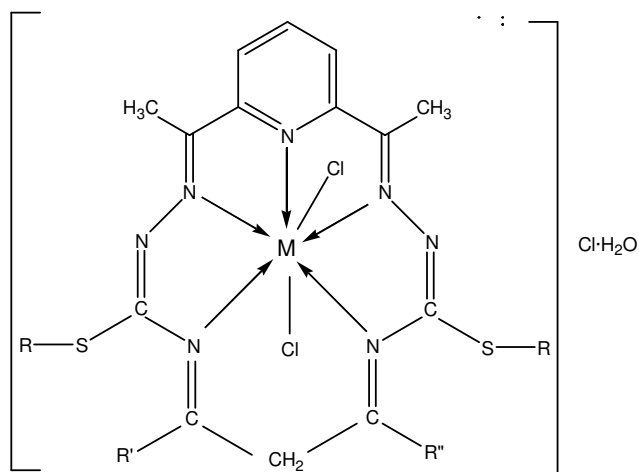
Thermal analyses give information about the stability of metal chelates and decide to some extent whether the water molecules are inside or outside the coordination sphere. In all the acyclic complexes, decomposition involved two steps: the first step indicated loss of two chloride ions in the temperature range 280–300°C, while the second loss was observed at 350–450°C range giving M_2O_3 ($\text{M} = \text{Ru(III), Rh(III), Ir(III)}$). In macrocyclic complexes, the first loss occurs in the 105-115°C range corresponding to one water molecule. The organic moieties such as the ligand decompose in a gradual manner with increase in temperature. Although thermal degradation of organic moiety could not be approximated, the complete decomposition of ligand occurred at 580-600°C in all the complexes. At the final step as the end product stable metal oxides such as Ru_2O_3 ,

Rh_2O_3 or Ir_2O_3 and sometimes even RuO_2 were found at 680-720°C as carbonaceous matter.

On the basis of the above analytical and spectral data the structures (II) and (III) have been suggested for the complexes.



$\text{M} = \text{Ru(III), Rh(III), Ir(III)}$; $\text{R} = \text{CH}_3, \text{C}_4\text{H}_9$
(II)



$\text{M} = \text{Ru(III), Rh(III), Ir(III)}$; $\text{R} = \text{CH}_3, \text{C}_4\text{H}_9$;
 $\text{R}' = \text{CH}_3, \text{CH}_3$; $\text{R}'' = \text{CH}_3, \text{C}_6\text{H}_5$
(III)

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