



Synthesis, Characterization and Thermal Studies of Rh(III) Complexes Derived from Bidentate Schiff Bases

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The Schiff base ligands were derived from 2-hydroxy-3-methoxybenzaldehyde (HL₁), 4-hydroxy-3-methoxybenzaldehyde (HL₂), with *p*-toluidine and 3-hydroxybenzaldehyde with 4-hydroxybenzhydrazide (HL₃) and 3-hydroxy-2-naphthoic hydrazide (HL₄). The Rh(III) metal complexes of these Schiff base ligands have been synthesized and characterized by IR, electronic, ¹H NMR spectra as well as by elemental analysis, thermogravimetry, molar conductance and magnetic susceptibility measurements. IR and ¹H NMR data shows that all the Schiff bases behave as bidentate and coordinated to Rh(III) *via* nitrogen and oxygen.

Key Words: Schiff base, Rh(III) complexes, ¹H NMR.

INTRODUCTION

The Schiff base ligands lend themselves readily to structural modification that offers considerable control over complex stability and reactivity¹. Bidentate ligands with two donor centers play an important role in modern coordination chemistry^{2,3}. Schiff bases themselves are fungicides, their activity being enhanced by the presence of hydroxyl group in the ligand molecule⁴. Schiff base complexes present a great variety of biological activity ranging from antitumor, fungicide, bacteriocide, antiinflammatory and antiviral activity as well as their physicochemical effects⁵⁻¹¹. Schiff base complexes of the most transition metals have been well documented whereas information on platinum-metal complexes with these ligands is scarce and virtually not much information is available on Rh(III) complexes¹²⁻¹⁴. The chemistry of rhodium has been receiving considerable current attention, largely because of the interesting chemical properties exhibited by the complexes of these metal¹⁵.

In the present work, we report some Rh(III) complexes with the Schiff bases derived from 2-hydroxy-3-methoxybenzaldehyde (HL₁), 4-hydroxy-3-methoxybenzaldehyde (HL₂), with *p*-toluidine and 3-hydroxybenzaldehyde with 4-hydroxybenzhydrazide (HL₃) and 3-hydroxy-2-naphthoic hydrazide (HL₄).

EXPERIMENTAL

All the chemicals used were of A.R. grade 2-hydroxy-3-methoxybenzaldehyde was obtained from Spectrochem Pvt. Ltd., Mumbai and 4-hydroxy-3-methoxybenzaldehyde,

3-hydroxybenzaldehyde, 4-hydroxybenzhydrazide, 3-hydroxy-2-naphthoic hydrazide and hydrated rhodium trichloride obtained from S.D.F. Chemical Limited, Mumbai, *p*-toluidine from S.R.L. Pvt. Limited Mumbai and were used without further purification. Distilled solvents were used throughout the experiments.

Synthesis of Schiff bases: The Schiff bases were prepared by the general procedure¹⁶. The Schiff base was prepared by condensing equimolar quantities of 25 mL hot ethanolic solution of 2-hydroxy-3-methoxybenzaldehyde (0.152 g, 0.001 mol) and 25 mL hot ethanolic solution of *p*-toluidine (0.107 g, 0.001 mol). The reaction mixture was refluxed for 5-6 h on water bath. The solution was reduced to 1/4th of its original volume and poured in ice cold water. The orange precipitate was obtained. It was filtered, washed several times with cold methanol, recrystallized from ethanol. The purity of ligands was checked by thin layer chromatography and elemental analysis. Structure of Schiff base (HL₁) is shown in Fig. 1. The other Schiff bases were prepared using the similar procedure.

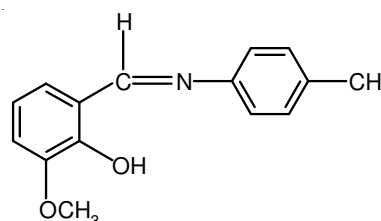


Fig. 1. Structure of Schiff base (HL₁)

Synthesis of metal complexes: The metal complexes were synthesized by refluxation-precipitation method. The hot ethanolic solution of respective Schiff base ligands (0.003 mol or 0.002 mol) was mixed with ethanolic solution of rhodium trichloride (0.209 g, 0.001 mol) and with constant stirring on hot plate at 100 °C. The solution was stirred for 6 h till the colour of reaction mixture was changed from light orange to dark brown (pH was adjusted to optimum level). The reaction mixture was refluxed on water bath for 8 h then the volume of the reaction mixture was reduced to 1/4th of its original volume and poured on ice cold water to yield brown colour precipitate. The precipitate was allowed to stand for 24 h, then filtered off, washed with hot water, ethanol and dried in oven at 105 °C.

Physical measurements: Elemental analysis was carried out on Euro Vector, CHNS-O Analyzer, EA 3000, Italy. The metal content of all the metal complexes were determined at the Department of Earth Science, IIT Powai, Mumbai on ICP-AES Jobinyvon Horiba ultima 2. The solubility of all the complexes was examined by different polar and non polar solvents. The molar conductivity of ligands and complexes were recorded using 1×10^{-3} M solution in DMSO on Equip-tronics conductivity meter EQ-660A. The electronic absorption spectra of ligand and complexes were recorded in the UV-visible region using DMSO as solvent on UV-2401PC UV-vis spectrophotometer supplied by Shimadzu. IR spectra were recorded using KBr pellet on FTIR-4200 supplied by M/S Shimadzu

Corporation. ^1H NMR spectra were obtained from Bruker Advance 2, 300 MHz NMR spectrometer. TGA and DTA measurements were obtained from Pyris Diamond TG/DT Analyzer supplied by Perkin-Elmer.

RESULTS AND DISCUSSION

The Schiff bases was synthesized by using equimolar quantities of 2-hydroxy-3-methoxybenzaldehyde (HL_1), 4-hydroxy-3-methoxybenzaldehyde (HL_2) with *p*-toluidine and 3-hydroxybenzaldehyde with 4-hydroxybenzhydrazide (HL_3) and 3-hydroxy-2-naphthoic hydrazide (HL_4). The metal complexes of Rh(III) were synthesized using 1:3 or 1:2 (metal:ligand) stoichiometric proportions. All the complexes are stable in air, non hygroscopic and brown colour solids. The metal complexes are insoluble in water but soluble in DMSO. All the complexes show very low molar conductance values in the range of 4-14 $\text{Scm}^2 \text{mol}^{-1}$ which indicate that the complexes are non electrolytic in nature¹⁷. The physical and analytical data of Schiff bases and metal complexes are shown in Table-1.

Infrared spectra: The important bands in IR spectra of the Schiff bases and their Rh(III) complexes are assigned in Table-2. Schiff base showed a strong absorption band in the range of 1646-1618 cm^{-1} characteristic of $\nu(\text{C}=\text{N})$, whereas the broad band at 3500-3300 cm^{-1} characteristics of hydrogen bonded $\nu(\text{O}-\text{H})$ stretching vibration¹⁸. The azomethine $\nu(\text{C}=\text{N})$

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF LIGANDS AND METAL COMPLEXES

Ligands/complexes	Colour	m.p. (°C)	m.w.	Elemental analysis (%) found (calcd.)				
				C	H	N	Cl	Rh
HL_1 [C ₁₅ H ₁₅ O ₂ N]	Orange	100	241.31	74.45 (74.66)	6.19 (6.27)	5.86 (5.80)	–	–
HL_2 [C ₁₅ H ₁₅ O ₂ N]	Yellow	118	241.31	74.74 (74.66)	6.23 (6.27)	5.79 (5.80)	–	–
HL_3 [C ₁₄ H ₁₂ O ₃ N ₂]	White	260	256.00	64.94 (65.62)	4.63 (4.68)	11.09 (10.93)	–	–
HL_4 [C ₁₈ H ₁₄ O ₃ N ₂]	White	260	306.00	70.39 (70.58)	5.12 (4.57)	9.64 (9.18)	–	–
[Rh(L ₁) ₃] [Rh C ₄₅ H ₄₂ O ₆ N ₃]	Dark brown	>300	823.78	65.10 (65.55)	4.98 (5.10)	5.25 (5.10)	–	12.19 (12.42)
[Rh(L ₂) ₂ Cl·H ₂ O] [Rh C ₃₀ H ₂₈ O ₄ N ₂ Cl·H ₂ O]	Dark brown	>300	636.47	56.50 (56.57)	4.23 (4.75)	4.09 (4.40)	5.87 (5.57)	16.84 (16.16)
[Rh(L ₃) ₂ Cl·H ₂ O] [Rh C ₂₈ H ₂₂ O ₆ N ₄ Cl·H ₂ O]	Brown	>300	666.90	50.89 (50.43)	3.78 (3.32)	7.98 (8.40)	5.54 (5.32)	15.63 (15.43)
[Rh(L ₄) ₂ ·(H ₂ O) ₂] [Rh C ₃₆ H ₂₆ O ₆ N ₄ ·(H ₂ O) ₂]	Brown	295	748.90	57.03 (57.68)	4.03 (4.01)	7.37 (7.48)	–	13.63 (13.74)

TABLE-2
INFRARED SPECTRAL, MOLAR CONDUCTIVITY AND MAGNETIC SUSCEPTIBILITY
DATA OF SCHIFF BASES AND METAL COMPLEXES

Ligands/complexes	IR spectral data (cm^{-1})					Molar cond. ($\text{Scm}^2 \text{mol}^{-1}$)	μ_{eff} (BM)
	$\nu(\text{C}-\text{O})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{Rh}-\text{N})$	$\nu(\text{Rh}-\text{O})$		
HL_1	1363	–	1618	–	–	3.6	–
HL_2	1384	–	1624	–	–	3.9	–
HL_3	1337	1685	1646	–	–	2.8	–
HL_4	1349	1634	1622	–	–	10.1	–
[Rh(L ₁) ₃]	1321	–	1614	500	457	4.6	Diamag.
[Rh(L ₂) ₂ Cl·H ₂ O]	1342	–	1594	634	485	4.4	Diamag.
[Rh(L ₃) ₂ Cl·H ₂ O]	1292	1681	1634	521	455	13.5	Diamag.
[Rh(L ₄) ₂ ·(H ₂ O) ₂]	1307	1636	1611	623	479	12.7	Diamag.

bands showed a lower shift in Rh(III) complexes indicating the coordination of azomethine nitrogen atom of Schiff base to metal¹⁹. The phenolic oxygen of Schiff base is coordinated with the metal by loss of proton which is confirmed by the lower shift of $\nu(\text{C-O})$ by 50-30 cm^{-1} in complexes from its position in the free ligand¹⁶. In addition, all complexes shows additional weak to medium intensity bands in the region 634-500 and 485-455 cm^{-1} which were absent in the IR spectra of ligands, these can be attributed to $\nu(\text{Rh-N})$ and $\nu(\text{Rh-O})$, respectively^{20,21}.

Thus IR spectra give evidence that bonding of ligand to metal ion occurs through nitrogen and oxygen indicating bidentate nature of ligand. As is known, magnetic susceptibility measurements provide information to characterize the geometry of the complexes. All the complexes are diamagnetic in nature having octahedral geometry. The magnetic moments of the complexes were measured at room temperature by Gouy's method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ ($\chi_g = 16.44 \times 10^{-6} \text{ g cm}^{-3}$) as a standard^{22, 23}. The data is represented in Table-2.

Electronic spectral data: Electronic spectral data for ligands and its Rh(III) complexes are summarized in Table-3. Ligand (HL_1) showed three high intensity bands at 31055, 35460 and 39761 cm^{-1} indicates $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$ transitions, respectively. The electronic absorption spectrum of $[\text{Rh}(\text{L}_1)_3]$ complex exhibit bands at 23584 and 32258 cm^{-1} which can be assigned as $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ transitions whereas band at 37878 cm^{-1} is due to ligand to metal charge transfer transitions. These transitions are in increasing order of energy, arising in octahedral Rh(III) complexes²⁴⁻²⁷. The UV-vis spectral data for all ligands and their metal complexes is given in Table-3.

¹H NMR spectroscopy: The ¹H NMR spectra of Schiff bases and its metal complexes were recorded in $\text{CDCl}_3/\text{DMSO}-d_6$. The $-\text{CH}_3$ and $-\text{OCH}_3$ appeared at 2.37-2.39 and 3.94-3.98 ppm²⁶. The significant azomethine proton signal due to $\text{CH}=\text{N}$ was observed in the range of 8.32-8.63 ppm in free ligands and in rhodium complexes it showed a downfield shift, indicating the involvement of azomethine nitrogen (Table-4) in coordination²⁷. The $-\text{OH}$ protons that appeared at 9.93-11.93 ppm in ligands, disappeared in Rh(III) complexes, indicating the loss of $-\text{OH}$ proton due to complexation²⁸.

Thermal analysis: The thermal behaviour of the metal complexes was studied by recording thermogravimetric curves (Figs. 2 and 3). The thermal analysis gives information about the stability and decomposition pattern for metal chelates. It also helps to decide water molecule present in complex is coordinated water molecule or is of crystallization.

TABLE-3
UV-VIS SPECTRAL DATA OF
LIGANDS AND METAL COMPLEXES

Ligands/complexes	Electronic spectral data (cm^{-1}) ($\epsilon = \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \times 10^5$)		
	Assignments for d-d transition		
HL_1	31055 (1.2)	35460 (1.1)	39761 (0.7)
HL_2	30075 (0.8)	34904 (0.5)	39920 (0.3)
HL_3	30211 (0.2)	32573 (0.2)	36101 (0.1)
HL_4	31364 (0.2)	31948 (0.2)	38314 (0.2)
$[\text{Rh}(\text{L}_1)_3]$	23584 (0.6)	32258 (2.0)	37878 (3.9)
$[\text{Rh}(\text{L}_2)_2\text{Cl}\cdot\text{H}_2\text{O}]$	27739 (2.7)	35523 (2.8)	38535 (3.3)
$[\text{Rh}(\text{L}_3)_2\text{Cl}\cdot\text{H}_2\text{O}]$	23894 (0.1)	34013 (2.8)	38684 (2.3)
$[\text{Rh}(\text{L}_4)_2\cdot(\text{H}_2\text{O})_2]$	23446 (1.1)	32520 (3.9)	38461 (4.7)

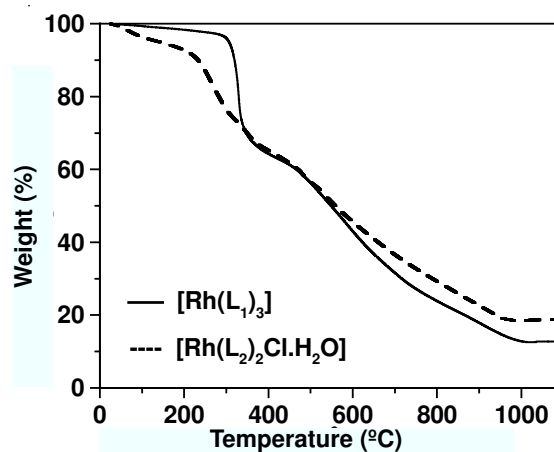


Fig. 2. Thermogravimetric curve of Rh(III) complexes of HL_1 and HL_2

Thermal stability of $[\text{Rh}(\text{L}_1)_3]$ complex was up to 300 $^{\circ}\text{C}$ after that rate of decomposition increases. The organic matter is first decomposed and finally at around 980 $^{\circ}\text{C}$ metal oxide *i.e.*, Rh_2O_3 remains as residue. The complexes $[\text{Rh}(\text{L}_2)_2\text{Cl}\cdot\text{H}_2\text{O}]$, $[\text{Rh}(\text{L}_3)_2\text{Cl}\cdot\text{H}_2\text{O}]$ and $[\text{Rh}(\text{L}_4)_2\cdot(\text{H}_2\text{O})_2]$ shows endothermic peaks which confirms the presence of coordinated water molecule. $[\text{Rh}(\text{L}_2)_2\text{Cl}\cdot\text{H}_2\text{O}]$ shows mass loss up to 224 $^{\circ}\text{C}$ was found 8.66 % which corresponding loss of one coordinated water and chlorine molecule (8.46 % cal.). $[\text{Rh}(\text{L}_3)_2\text{Cl}\cdot\text{H}_2\text{O}]$ and $[\text{Rh}(\text{L}_4)_2\cdot(\text{H}_2\text{O})_2]$ both complexes shows endothermic peaks

TABLE-4
¹H NMR SPECTRAL DATA OF LIGAND AND METAL COMPLEXES

Ligand/complexes	¹ H NMR chemical shift (ppm)					
	Aromatic	CH=N	OCH ₃	OH (aldehyde)	OH (amine)	CH ₃
HL_1	6.85-7.26	8.63	3.94	9.92	–	2.39
HL_2	6.09-7.67	8.36	3.98	9.93	–	2.37
HL_3	6.78-7.80	8.32	–	11.57	10.12	–
HL_4	6.81-7.95	8.35	–	11.93	11.30	–
$[\text{Rh}(\text{L}_1)_3]$	6.39-7.00	8.90	3.64	–	–	2.11
$[\text{Rh}(\text{L}_2)_2\text{Cl}\cdot\text{H}_2\text{O}]$	6.40-7.00	8.95	3.64	–	–	2.12
$[\text{Rh}(\text{L}_3)_2\text{Cl}\cdot\text{H}_2\text{O}]$	6.79-7.81	8.55	–	–	10.17	–
$[\text{Rh}(\text{L}_4)_2\cdot(\text{H}_2\text{O})_2]$	6.83-7.91	8.53	–	–	10.15	–

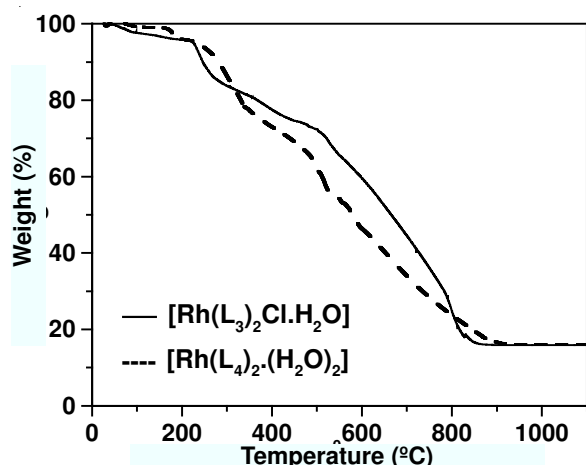


Fig. 3. Thermogravimetric curve of Rh(III) complexes with HL₃ and HL₄

of coordinated water. The TGA data reveal the good agreement with the molecular formula suggested from the elemental analysis.

Conclusion

The Schiff bases and its Rh(III) complexes were characterized by elemental analysis, spectral studies (IR, ¹H NMR, UV-vis), molar conductance and thermal analysis. On the basis of above spectral data Rh(III) complexes shows octahedral geometry. Schiff base behave as bidentate ligand. The proposed structures of the metal complexes have shown in Fig. 4-7.

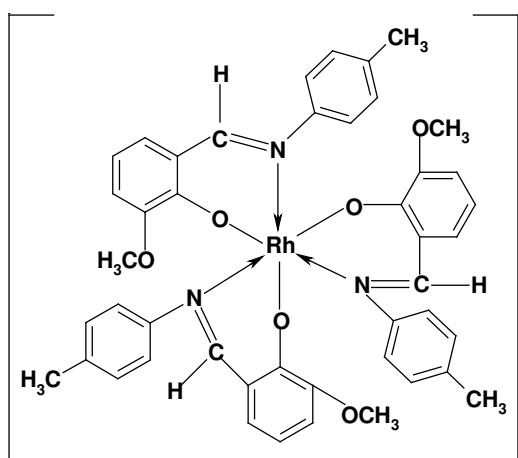


Fig. 4. Structure of Rh complex of HL₁

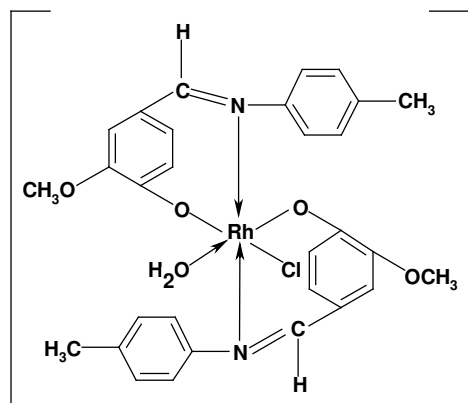


Fig. 5. Structure of Rh complex of HL₂

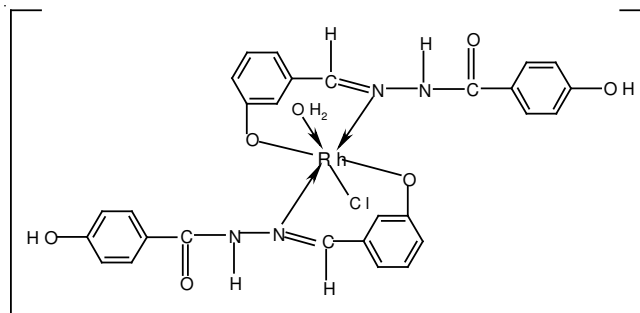


Fig. 6. Structure of Rh complex of HL₃

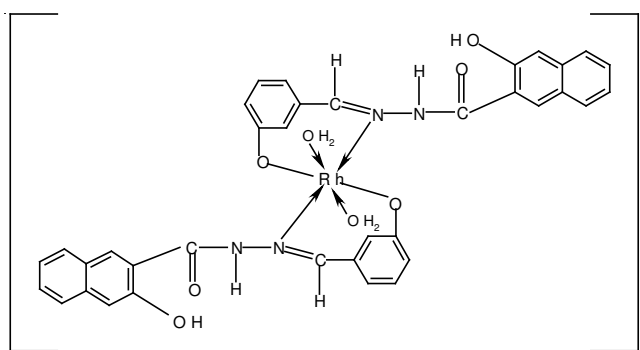


Fig. 7. Structure of Rh complex of HL₄

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