Asian Journal of Chemistry Vol. 22, No. 8 (2010), 5976-5980

Synthesis, Characterization and Thermal Studies of Ru(III), Rh(III) and Pd(II) Complexes Derived from 2-Hydroxy-1-Naphthaldehyde and 3-Amino Phenol

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The Schiff base derived from 2-hydroxy-1-naphthaldehyde and 3-amino phenol and its metal complexes have been synthesized and characterized by IR, ^{1}H NMR, UV, elemental analysis, molar conductivity and thermal analysis. From the analytical and spectral data, the stoichiometries have been found to be 1:2 for all the complexes. The Ru(III) and Rh(III) complexes exhibit octahedral structures, whereas Pd(II) complex show square planar structure.

Key Words: Ru(III), Rh(III), Pd(II) Complexes, 3-Amino phenol, 2-Hydroxy-1-naphthaldehyde.

INTRODUCTION

A large number of study have been reported on Schiff bases and their metal complexes. In general Schiff bases show very good coordinating ability with the transition metal ions[1-3]. The variety of studies on transition metal complexes of Schiff bases show interesting properties such as chemical, biological (*viz.*, antibacterial, antifungal, antimalarial, antiviral, antitumour activities), analytical as well as physiochemical effects[4-8]. As platinum group metals are of high importance[9,10]. In present studies Ru(III), Rh(III) and Pd(II) complexes of Schiff base derived from 2-hydroxy-1-naphthaldehyde and 3-amino phenol are reported.

EXPERIMENTAL

All the chemical used were of AR grade 2-hydroxy-1-naphthaldehyde was obtained from Fluka-Chemica, 3-amino phenol and metal salts were obtained from SD Fine-Chem. Ltd., distilled solvents were used throughout the experiments.

Synthesis of ligand: The Schiff base was prepared by condensing equimolar quantities of 2-hydroxy-1-naphthaldehyde (1.72 g) and 3-amino phenol (1.09 g). 25 mL hot ethanolic solution of 2-hydroxy-1-naphthaldehyde was slowly added to 25 mL hot ethanolic solution of 3-amino phenol. The reaction mixture was then refluxed for 4 h on water bath then hot reaction mixture was poured in ice-cold water. The precipitate obtained was filtered, washed with cold water, recrystallized from ethanol and air dried. Structure of Schiff base is shown in Fig. 1.

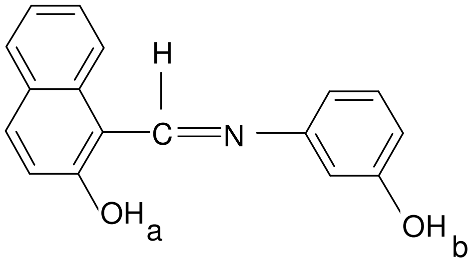

Fig. 1. Structure of Schiff base

Synthesis of metal complexes: The metal complexes were synthesized by refluxation-precipitation method. The hot ethanolic solution of Schiff base (0.002 mol) was mixed with ethanolic solution of palladium chloride (0.177 g, 0.001 mol), rhodium trichloride (0.207 g, 0.001 mol) and ruthenium trichloride (0.261 g, 0.001 mol) with constant stirring. The pH of reaction mixture was adjusted to 3.26 for Pd(II) complex. Ru(III) complex was precipitated at pH 9.4 and Rh(III) complex was precipitated at pH 8.5. The reaction mixture was refluxed on water bath for *ca.* 8 h. The respective metal complexes separated were filtered, washed with hot water and then with 5 % hot ethanol and dried in oven at 80 ºC.

The melting point of the Schiff base and all metal complexes were determined by open capillary method. Elemental analysis was carried out in the micro-analytical laboratory, IIT Powai, Mumbai. The metal content for 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 ligand 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-2401 PC UV-vis spectrophotometer supplied by Shimadzu. IR Spectra were recorded using KBr pellet on FTIR-4200 supplied by M/S Shimadzu Corporation. ^{1}H NMR spectra were obtained from Bruker Advance 2, 300 MHz NMR spectrometer.

RESULTS AND DISCUSSION

The Schiff base is synthesized by using equimolar quantities of 2-hydroxy-1-naphthaldehyde and 3-amino phenol. The metal complexes of Ru(III), Rh(III) and Pd(II) were synthesized using 1:2 stoichiometric proportions. The metal complexes derived vary in their colour. All the complexes are air stable, non hygroscopic, coloured solids. The metal complexes are insoluble in water but soluble in DMSO and DMF. All the complexes show very low molar conductance values *i.e.*, 6-18 × 10^{-3} S cm^2 mol^{-1} which indicate that the complexes are non electrolytic in nature. The physical, analytical and conductivity data of Schiff base and metal complexes are shown in Table-1.

TABLE-1
PHYSICAL, ANALYTICAL AND CONDUCTIVITY DATA OF SCHIFF BASE AND ITS METAL COMPLEXES

Ligand/complexes	Colour	m.p. (°C)	m.w. (g)	Elemental analysis (%) Found/(calcd.)					Molar cond. (S cm^2 mol^{-1})
				C	H	N	Cl	Metal	
HL$_1$	Yellow	255	263.00	78.45 (77.57)	4.77 (4.94)	5.38 (5.32)	–	–	0.005
[RuL$_2$H$_2$OCl]·2H$_2$O	Brown	290	714.57	53.62 (54.32)	3.65 (4.53)	3.07 (3.73)	3.96 (4.51)	12.03 (12.84)	0.006
[RhL$_2$H$_2$OCl]·3H$_2$O	Brown	>300	734.40	56.03 (55.56)	4.03 (4.36)	3.19 (3.81)	3.89 (4.83)	13.63 (14.01)	0.012
[PdL$_2$]·H$_2$O	Brown	160	648.42	62.52 (62.92)	4.57 (4.01)	4.44 (4.32)	–	15.23 (16.41)	0.018

The infrared spectra of the Schiff base and its metal complexes are recorded in Table-2. Schiff base showed a strong absorption band at 1632 cm^{-1} characteristic of ν(C=N), whereas the broad band at 3250 cm^{-1} characteristics of hydrogen bonded ν(O-H) stretching vibration[11]. The azomethine ν(C=N) band at 1632 cm^{-1} in Schiff base is shifted to lower frequency in Ru(III), Rh(III) and Pd(II) complexes by 33, 18 and 31 cm^{-1}, respectively which indicates the coordination of azomethine nitrogen in complexation[12]. The phenolic oxygen of Schiff base is coordinated with the metal by loss of proton which is continued by the lower shift of ν(C-O) by 15-30 cm^{-1} in complexes from its position in ligand[13]. The lower shift of ν(C-O) band occurring in free ligand from 1480-1349 to 1340-1250 cm^{-1} in metal complexes indicates another co-ordination site is phenolic oxygen of Schiff base[14].

TABLE-2
IR AND ELECTRONIC SPECTRAL DATA

Ligand/complexes	IR Spectral data cm^{-1}				Electronic spectral data cm^{-1}
	ν(O-H)	ν(C=N)	ν(M-N)	ν(M-O)	
C$_{17}$H$_{13}$O$_2$N	3350	1632	–	–	29586, 38095, 45662
Ru[C$_{34}$H$_{26}$O$_5$N$_2$Cl]·2H$_2$O	3310	1599	577	486	27360, 38461
Rh[C$_{34}$H$_{26}$O$_6$N$_2$Cl]·3H$_2$O	3400	1614	566	462	22320, 27360, 38461
Pd[C$_{34}$H$_{24}$O$_4$N$_2$]·H$_2$O	3377	1616	568	477	23068, 26667, 31446

Electronic spectrum of ligand showed three high intensity bands at 29586, 38095 and 45662 cm^{-1} indicates $n \rightarrow n^*$ and $\sigma \rightarrow \sigma^*$ transitions. The electronic spectra of Pd(II) complex showed bands at 23068, 26667 and 31446 cm^{-1} which may be assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$, $^1A_{1g} \rightarrow {}^1E_{1g}$ and $^1A_{1g} \rightarrow {}^1A_{2g}$, respectively. The band at 31446 cm^{-1} is considered as charge transfer transition. Hence, a square planar geometry may be assigned for Pd(II) complex[15]. The electronic absorption spectrum of Rh(III) complex exhibit bands at 27360 and 38461 cm^{-1} have been assigned to the $^2T_{2g} \rightarrow {}^2A_{2g}$ transition. The Ru(III) complex may be assigned octahedral geometry. The electronic spectrum of Rh(III) complex showed bands at 22320 and 27360 cm^{-1} which have been assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively[16] whereas the band appearing at 38461 cm^{-1} is a charge transfer transition. The Rh(III) complex may be assigned octahedral geometry[17]. The IR and electronic spectral data have shown in Table-2.

^{1}H NMR: The ^{1}H NMR spectra of Schiff base and its metal complexes were recorded in DMSO. The aromatic protons in Schiff base were appeared in the range 6.70-8.50 ppm and metal complexes were appeared in the range 6.20-8.60 ppm. The azomethine proton in Schiff base appeared (δ = 8.40 ppm) have showed downfield shifting in metal complexes (δ = 9.00-9.80 ppm) this indicates the coordination of azomethine nitrogen atom in metal complexation. The appearance of peaks (δ = 14.34 and 10.50 ppm) indicates the presence of two different hydroxyl protons but the disappearance of peak (δ = 14.34 ppm) indicates the deprotonation of hydroxyl proton due to co-ordination of oxygen to the metal whereas the existence of (δ = 10.50-11.00 ppm) signal indicates the presence of one phenolic hydroxyl group in the metal complexes.

Thermal analysis: The TGA/DTA analysis of the metal complexes was carried out to get information about the stability of the metal complexes and amount of organic content present in complexes. TGA/DTA analysis was carried out in the range 0-1000 ºC at 10 ºC/min. The Ru(III), Rh(III) and Pd(II) complexes have shown the initial weight loss of 4.44, 6.04 and 3.09 %, respectively in the temperature range 0-130 ºC which indicates the presence of 2, 2 and 1 molecule of lattice water in all the complexes, respectively[18]. Ru(III) and Rh(III) complexes have shown weight loss by 3.01 and 1.86 % in the temperature range 130-240 ºC indicating the presence of one molecule of coordinated water in both the complexes. Ru(III), Rh(III) and Pd(II) complexes have shown weight loss by 75.37, 70.69, 78.13 % indicating the loss of organic content resulting in the formation of corresponding oxides with further increase in the temperature.

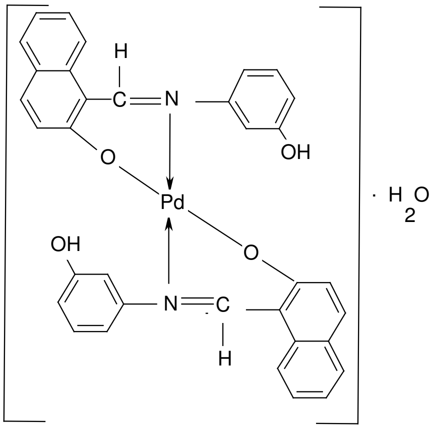

Fig. 2. Structure of Pd(II) complex

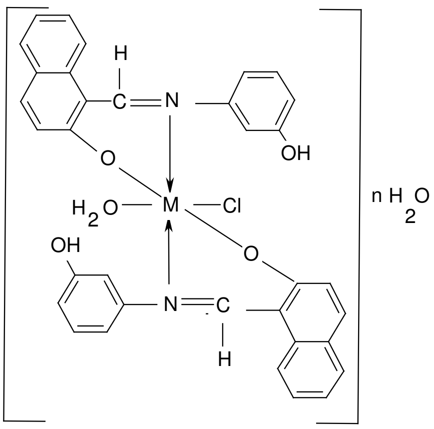

Fig. 3. Structure of Ru(III) and Rh(III) complexes where M = Ru and Rh, n = 2 for Ru and n = 3 for Rh

Conclusion

The Schiff base of 2-hydroxy-1-napthaldehyde and 3-amino phenol and its Ru(III), Rh(III) and Pd(II) complexes were characterized by elemental analysis, spectral studies (^{1}H NMR, IR, UV-vis), molar conductance and thermal analysis. On the basis of above data Pd(II) complex show square planar structure whereas Ru(III) and Rh(III) complexes show octahedral structures. Schiff base behave as bidentate ligand. The proposed structures of the metal complexes have shown in Figs. 2 and 3.

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(*Received*: 16 September 2009; *Accepted*: 30 April 2010) AJC-8649