

Structural Studies of Transition Metal Complexes of 2-Furoin Oxime

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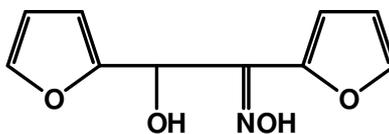
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The synthesized palladium, ruthenium and rhodium complexes of 2-furoin oxime contained the metal:ligand stoichiometry 1:2 for palladium complex and 1:3 for ruthenium and rhodium complexes. The ligand and its metal complexes were characterized for various analytical parameters and spectral features. The structures of these complexes are also proposed.

Key Words: Synthesis, Pd(II), Ru(III), Rh(III) complexes, 2-Furoin oxime.

INTRODUCTION

Palladium complexes play a unique role among biologically active ions. It has been investigated for its antitumor, anti-HIV and antifungal activities¹. Oxime derived palladium complexes is very efficient catalyst for the Heck-Mizoroki reaction². Chiral ruthenium(II) complexes, RuCl₂(PPh₃) (oxazalin ferrocenyl phosphine) were found to be effective catalyst for asymmetric hydrosilylation of ketoximes to give the corresponding primary amines³. It was thought worth while to investigate the structural features of these elements with the oxime of 2-furoin (**I**). In this communication, synthesis and the characterization of the palladium, ruthenium and rhodium complexes of the 2-furoin oxime are reported.



Structure of 2-furoin oxime (**I**)

EXPERIMENTAL

Synthesis of ligand: The chemicals used were of synthetic grade supplied by Sisco-Chem, India. The ligand was synthesized by refluxing 5 g (0.01 mol) of 2-furoin in 100 mL ethanol with (1.808 g, 0.01 mol) hydroxylamine

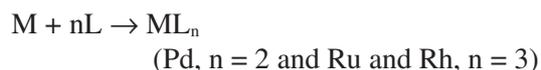
hydrochloride and sodium acetate (2.13 g, 0.01 mol) dissolve in minimum quantity of water. The ligand was separated by pouring the reaction mixture on ice. The isolated product (4.52 g) was filtered, dried and recrystallized from methanol (yield ~ 84 %).

Preparation of metal complexes: The palladium complex of the oxime ligand was prepared by mixing an aqueous solutions of palladium chloride (0.085 g, 0.01 mol) with 250 mL of methanolic solution of the ligand (0.2 g, 0.02 mol) at pH 2. The ruthenium complex was prepared using ruthenium trichloride hydrate (0.072 g, 0.01 mol) and the oxime (0.2g, 0.03 mol) at pH 10. The rhodium complex was prepared using rhodium trichloride hydrate (0.073 g, 0.01 mol) and the oxime (0.2 g, 0.03 mol) at pH 7. The precipitates of these complexes were digested on a water bath, filtered washed with distilled water, dried at 80 °C.

Analytical methods: Elemental analysis (C, H, N) and the metal content in each of the complexes were determined using standard procedures reported in literature⁴. magnetic susceptibility measurements were carried out at room temperature by the Gouy balance method using CO[Hg(SCN)]₄ as the standard⁵. Infrared spectra of the ligand and complexes were taken on a FTIR-4200 spectrometer supplied by the M/s Shimadzu corporation. Electronic absorption spectra in the UV-Vis region and reflectance spectra of all compounds were recorded on a UV-Vis spectrophotometer supplied by the M/s Shimadzu corporation.

RESULTS AND DISCUSSION

The general equations for the preparation of 2-furoin oxime complex are illustrated to the following equations,



The chemical composition, colour and molar conductance of the complexes are summarized in Table-1. The percentage yields for these complexes are satisfactory, ranging between 60-70 %. The elemental analysis indicate that the palladium complex have a 1:2 metal:ligand stoichiometry while ruthenium and rhodium complexes have 1:3 metal:ligand stoichiometry. All the complexes are sparingly soluble in various polar and non-polar solvents however, are soluble in DMSO and DMF. The molar conductance measurement values are in the range $4.0-9.6 \times 10^{-3} \text{ S cm}^2 \text{ mol}^{-1}$. The low molar conductance suggest that the compound are non-electrolytic in nature.

Various electronic absorption bands exhibited by H(L) and its metal complexes in the solution and/or reflectance spectra and their tentative assignment are summarized in Table-2. The shifting of the ligand bands in the spectra of the metal complexes indicate that the energy states of the electron system of the H(L) under go considerable alterations on complex

TABLE-1
PHYSICAL AND ANALYTICAL DATA

Ligand/ (m.f.)	m.w./ (colour)	Yield (%)/ m.p. (°C)	Molar cond. $\times 10^{-3}$ S cm ² mol ⁻¹	Elemental analysis (%):			
				Found (Calcd.)			
				C	H	N	M
H(L) (C ₁₀ H ₉ NO ₄)	207.00 (Yellow)	84 (160)	4.3	58.10 (57.97)	4.30 (4.35)	6.71 (6.76)	–
Pd(L)₂ (PdC ₂₀ H ₁₆ O ₈ N ₂)	532.42 (Brown)	62 (212)	9.6	44.99 (45.07)	3.01 (3.01)	5.13 (5.26)	19.60 (19.98)
Ru(L)₃ (RuC ₃₀ H ₂₄ O ₁₂ N ₃)	719.00 (Brown)	59 (230)	8.5	49.81 (50.06)	2.98 (3.33)	5.31 (5.84)	13.90 (14.05)
Rh(L)₃ (RhC ₃₀ H ₂₄ O ₁₂ N ₃)	720.90 (Brown)	60 (218)	7.8	49.12 (49.93)	3.15 (3.32)	5.83 (5.82)	14.00 (14.27)

TABLE-2
MAGNETIC AND ELECTRONIC SPECTRAL DATA OF
LIGAND AND METAL COMPLEXES

H(L)	Diamag.	39062 (1.161)	38167	Intra ligand transition
		32,573 (0.511)	31,446	
Pd(L)₂	Diamag.	38167 (1.601)	31347	Intra ligand transition
		25974 (0.715)	24330	Charge transfer
Ru(L)₃	1.90	37735 (1.803)	30769	Charge transition
		33557 (1.315)	24096	d-d transition
Rh(L)₃	Diamag.	38461 (1.120)	36164	Intra ligand transition
		22172 (1.480)	27855	Charge transition

formation. The spectral features indicate square planar geometry for the Pd(II) complex and octahedral geometry for the Ru(III) and Rh(III) complexes. The electronic spectra of the Pd(II) complex show bands in the range of 38167-25974 cm⁻¹ which are assigned $\pi \rightarrow \pi^*$ and ${}^1A_{1g} \rightarrow {}^1E_u$ transition and characteristic of square planar symmetry⁶. The electronic absorption spectrum of Ru(III) complex exhibit bands in the range of 37735-33557 cm⁻¹. The strong absorption bands observed around 37735 cm⁻¹ can be assigned to intra ligand $\pi \rightarrow \pi^*$ transitions. The absorption band observed at 27397 and 37735 cm⁻¹ are assigned to ${}^2T_{2g} \rightarrow {}^2A_{2g}$ and ${}^2T_{2g} \rightarrow {}^2T_{1g}$ transition. The band due to the second spin forbidden transition ${}^2T_{2g} \rightarrow {}^4T_{2g}$ is usually hidden under the tail of the spin allowed band. The spectral features indicate octahedral symmetry for Ru(III) complex^{7,8}. The electronic spectrum of Rh(III) complex exhibit bands in the range of 38461-22172 cm⁻¹ which are assignable to $\pi \rightarrow \pi^*$ transition in the ligand and charge transfer transition in the complex. The *d-d* bands are obscured by the high intensity charge

transfer bands. The electronic spectra suggest that the energy state of the π electron system of ligand suffer substantial alteration on complexation. This often obscures the two $d-d$ bands found towards the blue end of the visible region corresponding to the transition from ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1T_{2g}$ upper state. The Rh(III) complex may be assigned to octahedral geometry⁹.

The magnetic susceptibility measurements of the complexes were performed under ambient conditions. The room temperature magnetic moments of Ru(III) is found to be 1.9 BM. This is in agreement with the fact that Ru(III) complexes (d^5) are of low spin type with one unpaired electron and are octahedral¹⁰⁻¹². It is well known that all Rh(III) compound are diamagnetic. This is due to the combination of three factors *viz.*, (i) inherent tendency of the octahedral d^6 configuration to assume the low spin t_{2g}^6 arrangement, (ii) relatively high ligand field strength in the complexes of tripositive ions in the second and the third transition series, and (iii) greater tendency toward spin paring among $4d^n$ and $5d^n$ configuration than their analogues¹³. The Pd(II) complex is diamagnetic and suggest that it may have square planar configuration¹⁴⁻¹⁶.

The infrared spectra of 2-furoin oxime and its Pd(II), Ru(III) and Rh(III) complexes have been examined in the region 4000-650 cm^{-1} . The broad band at 3300-3040 cm^{-1} in H(L) is assigned to hydrogen bonded OH stretching frequency. In the spectrum of the Pd(II) complex the OH stretching band is found to be at 3400 cm^{-1} and that of Ru(III) and Rh(III) complexes is found to be at 3415 and 3420 cm^{-1} . IR spectrum of ligand shows a very strong band at 1638 cm^{-1} which is assigned to $\nu(\text{C}=\text{N})$ azomethine group. In the complexes the $\nu(\text{C}=\text{N})$ band is blue-shifted to the region 1616-1590 cm^{-1} indicating the coordination of azomethine nitrogen with the metal¹⁷. It is possible that both oximino and alcoholic OH may be involved in coordination with metal ion. The pK_a value of alcoholic OH is lower than oximino OH group. Thus alcoholic oxygen binds with the metal ion after deprotonation. The appearance of OH stretching vibration in the metal complexes indicate that oximino OH of the ligand is not involve in coordination with the metal ion¹⁸. The characteristic C-O-C bands of furan (1250 and 1080 cm^{-1}) in the ligand, remain unchanged in the complex, ruling out the possibility of coordination through the oxygen atom of furan ring¹⁹. The additional bands around 560 and 450 cm^{-1} are assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ stretching vibration, respectively. It may therefore be inferred that the complex formation takes place through the oximic nitrogen and oxygen of the CH(OH) group²⁰⁻²².

The thermal analysis of the complexes shows that they are thermally stable to a varying degree in the range 250-280 °C The complexes do not show lattice water or water of crystallization. With further increase in temperature in the range investigated, the complexes show decomposition by fragmentation and thermal degradation of the organic part of the metal complexes,

finally resulting in the corresponding metal oxides PdO, RuO and RhO in Pd(II), Ru(III) and Rh(III) complexes, respectively.

The ^1H NMR spectra of Ru(III) complex show broad signals due to its paramagnetic nature. The ^1H NMR spectrum of metal complexes shows multiplet in the range of 6.60-8.40 ppm. The signal due to oximic proton appears as a singlet in the range of 9.30-9.80 ppm (Table-3). However, absence of signal in the vicinity of down field at 5.40 ppm in the metal complexes corresponding to the ligand suggest that alcoholic oxygen coordinate with the metal ion after deprotonation.

TABLE-3
 ^1H NMR DATA OF LIGAND AND ITS METAL COMPLEXES IN δ ppm

Compound	δ (aromatic)	δ (alcoholic)	NOH
H(L)	6.2-8.6	5.4	10.03
Pd(L)₂	6.4-8.5	-	9.63
Ru(L)₃	6.6-8.1	-	9.57
Rh(L)₃	6.4-8.1	-	9.80

X-Ray powder diffractogram: The X-ray diffractogram of complexes were recorded in the range 5° to 60° 2θ value. The major reflexes were measured and the corresponding d-value were calculated. An independent indexing for each of these reflexes were carried out by least square method. The Miller indices (hkl) were calculated and refined using Back-cal program by computational method and data has been summarized in Table-4. The data indicates the monoclinic crystal system for all the complexes.

TABLE-4
CRYSTAL LATTICE PARAMETERS OF METAL COMPLEXES

Complex	a (\AA)	b (\AA)	c (\AA)	D_{obs}	D_{cal}	Vol. (\AA^3)	SD (%)	Porosity (%)
Pd(L)₂	21.6319 ± 0.0331	20.5460 ± 0.1070	36.1623 ± 0.2845	1.786	1.780	15882.09	0.737	0.7372
Ru(L)₃	21.8251 ± 0.0507	19.9396 ± 0.1082	36.3355 ± 0.3390	2.481	2.480	15612.50	0.163	0.8772
Rh(L)₃	21.8412 ± 0.0371	20.3213 ± 0.1162	35.1390 ± 0.2764	2.452	2.448	15392.91	0.646	0.6464

Based on spectroscopic investigations, the proposed structures of the metal complexes have been illustrated in Figs. 1 and 2.

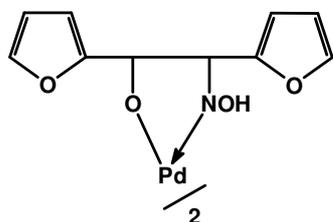
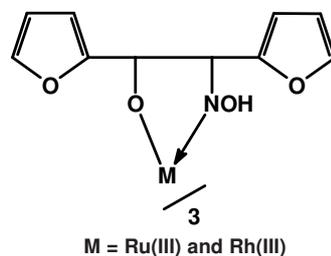


Fig. 1



M = Ru(III) and Rh(III)

Fig. 2

Biological activity: The ligand and its metal complexes were screened for antibiographical and antifungal activities by agar plate method using Echinocandian as control. The antibacterial activity for the compounds was tested against *E. coli* and *Staphylococcus aureus*. The antifungal activity of the compound was tested against *Candida albicans*, *Candida krusei*, *Candida glabrata* and *Aspergillus fumigatus*. Table-5 revealed that the ligand is inactive toward all strains but the metal complexes are fungi toxic in nature and hence serve as vehicles for activation of the ligand as principle cytotoxic species^{23,24}.

TABLE-5
ANTIFUNGAL AND ANTIBACTERIAL STUDIES

Compd.	Conc. (mg/mL)	Zone size (mm)					
		CA	CK	CG	AF	SA	EC
H(L)	1.0	–	–	–	–	–	–
Pd(L)₂	1.0	21	18	10	12	–	–
Ru(L)₃	1.0	17	–	11	14	–	–
Rh(L)₃	1.0	16	15	12	9	–	14

CA = *Candida albicans*; CK = *Candida krusei*; CG = *Candida glabrata*; AF = *Aspergillus fumigatus*; SA = *Staphylococcus aureus*; EC = *Escherichia coli*.

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(Received: 20 August 2007;

Accepted: 26 April 2008)

AJC-6545

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