

Synthesis characterisation and X-ray diffraction studies of some Pd(II), Ru(III) and Rh(III) complexes of furfuraldoxime

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ABSTRACT

Metal(II) complexes of the type ML_2 [Where M-Pd (II),] oxime derived from furfural and hydroxylamine hydrochloride and $ML_3 \cdot nH_2O$ [where M-Ru(III), Rh(III), n=2] have been prepared and characterised by elemental analysis, molar conductivity, IR, electronic spectra, magnetic susceptibility studies and X-ray diffraction spectra. Molar conductivity measurements indicate that the complexes are non-electrolytic in nature. From the analytical and spectral data, the stoichiometry of complexes have been found to be 1:3 (metal:ligand) for Ru (III) and Rh (III) whereas 1:2 for Pd (II) complex. Magnetic susceptibility measurements indicate diamagnetic behaviour of complexes except Ru (III) complex, which is paramagnetic in nature. The X-ray diffraction studies suggest monoclinic crystal system for these complexes.

Key words: X-ray diffraction studies, metal complexes, furfuraldoxime.

INTRODUCTION

Oxime derivatives of aldehydes and ketones are mainly used in analytical chemistry¹. Furfuraldehyde and their oxime have aroused considerable interest with regard to their chelating ability with the transition metal ions^{2,3,4}. The chemistry of metal oxime complexes is of interest because these species display a variety of reactivity mode and also because they possess catalytic and biological activity^{5,6} oximes derived Pd (II) complex is very efficient catalyst for the Heck-Mizoroki reaction⁷. Ru (III) complexes were found to be effective catalyst for asymmetric hydrosilylation of ketoxime to give corresponding primary amines⁸ Rh NHC complex is used as radio pharmaceutical based on ¹⁰⁵Rh. The structures of the synthesized metal chelates were established by physico-chemical techniques, which includes spectral and magnetic measurements. The structure of the ligand have illustrated in Fig. 1.

EXPERIMENTAL

All chemicals used for the synthesis were of AR grade. Furfuraldehyde was obtained from S.D. fine chemicals. Metal salt from S.D. fine chemicals. Distilled solvents were used throughout the experiments. The furfuraldoxime was prepared by the method described by Brady and Goldstein¹⁰

Synthesis of furfuraldoxime

The furfuraldoxime was prepared by method described by Bardy and Goldstein¹⁰. Furfuraldehyde (13.5g) was slowly added to a cold

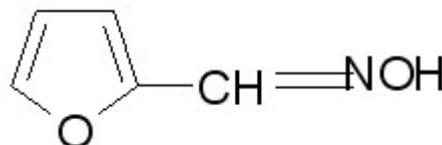


Fig. 1

mixture of sodium hydroxide (14g in 15 mL water) and hydroxylamine hydrochloride (12g in 20 mL water). After 1hrs the solution was filtered and cooled in a freezing mixture and a slightly excess of ice-cold saturated aqueous solution of ammonium chloride was slowly added with constant stirring. The crystalline precipitate was washed with little cold water and air dried. The yield of the crude oxime was 11.5g. After crystallizing thrice from petrol ether, 4g of pure furfuraldoxime was obtained. (m.p 75^o-76^oC)

Synthesis of Metal-Complexes

The metal complexes were synthesised by mixing the ethanolic solution of ligand (1%w/v) with the metal solution (1mg/cm³). The pH of the reaction mixture was adjusted to 2 for Pd (II) complex where as Rh (III) complex was precipitated at pH 8 and Ru (III) complex was precipitated at pH 10. The solid complexes obtained were filtered, washed with hot water and then with hot methanol and dried in vacuum dessicator.

Physical measurement

The melting point of all the complexes were determined by open capillary method. Elemental analysis was carried out in the micro analytical laboratory University of Mumbai. The metal content for all the metal complexes were determined as reported in the literature^{11,12}. The complexes were examined for solubility using various polar and non-polar solvents. Molar conductivity of ligand and metal complexes were recorded using 1x10⁻³M solutions

in DMF on Toshiniwal TSM-15 Conductivity meter. The electronic absorption spectra of ligand and complexes were recorded in the UV-visible region using DMF as solvent on UV-visible 2100 spectrophotometer supplied by M/S Perkin Elmer-lambda 25. IR spectra were recorded using KBr pellet on FTIR-4200 supplied by M/s Shimadzu Corporation. Magnetic susceptibility measurements were made at room temperature on Gouy's balance using Hg[Co(SCN)₄] as calibrant. X-ray diffraction spectra on X-ray diffractometer supplied by M/s. Philips, Holland. The experimental results are summarised in Table 1 and 2.

RESULTS AND DISCUSSION

The oxime of furfuraldehyde is a white crystalline substance having melting point 75^oC. The metal complexes derived from this oxime vary in their colour. The elemental analysis suggests metal: ligand stoichiometry as 1:2 for Pd complex and 1:3 for Ru and Rh complex indicated by close agreement with the analytical data and theoretical molecular formula. The metal complexes are soluble in DMF and DMSO. The molar conductance value suggests that these complexes are non-electrolyte in nature.

IR spectra

The IR spectra of the ligand and the metal complexes were recorded in Table-2. The prominent features in the spectrum of the ligand furfuraldoxime

Table 1: Analytical data of ligand and metal complexes

Compounds	M.W	M.P (°C)	Stoichio- metry	Molar- Conduct x10 ⁻³ S cm ² mol ⁻¹	Elemental analysis (%)				μ eff (B.M)
					found (calc)			Metal	
					C	H	N		
C ₅ H ₅ O ₂ N (white)	111.00	75	—	4.60	53.70 (54.05)	4.33 (4.50)	12.50 (12.61)	—	—
PdC ₁₀ H ₁₀ N ₂ O ₄ Cl ₂ (yellow)	399.42	276	1: 2	7.10	30.18 (30.04)	2.65 (2.50)	6.50 (7.01)	26.05 (26.64)	—
RhC ₁₅ H ₁₂ O ₆ N ₃ ·2H ₂ O (yellow)	469.90	247	1: 3	7.16	38.08 (38.30)	2.36 (2.55)	8.35 (8.93)	20.96 (21.89)	—
RuC ₁₅ H ₁₂ O ₆ N ₃ ·2H ₂ O (brown)	467.07	214	1: 3	8.12	37.90 (38.54)	2.57 (2.56)	8.75 (8.99)	21.64 (20.63)	1.8

are sharp and strong absorption band at 3200-1640 cm^{-1} characteristic of ν (-OH) and ν (C=N) respectively. The IR spectra of metal complexes exhibit a broad absorption band in the region of 3200-3400 cm^{-1} with weak intensity attributed to the ν (-OH) group¹³. The peak at C.a 830 cm^{-1} does not appear hence confirms the absence of coordinated water as reported in literature¹⁴ It can be further confirmed by TGA analysis. IR spectrum of ligand shows a very strong band at 1632 cm^{-1} which is assigned to ν (C=N) azomethine. The lowering of ν (C=N) azomethine group to the extent of 20-40 cm^{-1} in all the complexes indicates the participation of azomethine nitrogen. The ligand atom during chelation exhibit the additional bands around 593 and 520 cm^{-1} assigned to ν (M-N) and ν (M-O) stretching vibration respectively¹⁵, similar assignments to ν (M-N) and ν (M-O) are reported in the literature^{16,17,18,19}.

Electronic absorption spectra

Electronic spectrum of ligand showed three high intensity band lying at 29411, 40816, 45454 cm^{-1} assigned to $n \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions respectively in ligand. Pd(II) complex is diamagnetic in nature. The electronic spectrum of Pd (II) complex shows a band at 35855 cm^{-1} due to $^1A_{1g} \rightarrow B_{1g}$ transition. The Pd(II) assigned square planar geometry²⁰. The electronic spectrum of Rh(III) complex show $\pi \rightarrow \pi^*$ transition in the ligand and charge transfer transition. The d-d bands are obscured by the high intensity charged transfer bands. The U.V spectra suggest that the energy states of the π electron system of the ligand suffer substantial alternation on complexation. This often obscures the two d-d bands found towards the blue end of the visible region corresponding to the transition from $A_{1g} \rightarrow T_{1g}$ and $^1T_{2g}$ upper state. The Rh(III) complex may be assigned octahedral

Table 2: Uv-visible, density and ir spectral data of ligand and metal complexes

Ligand/complexes	IR Spectral data (cm^{-1})				Electronic spectral data (cm^{-1}) ($E = \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \times 10^4$)		
	ν (O-H)	ν [C=N]	ν (M-N)	ν (M-O)	Assignment for d-d transition		
$\text{C}_5\text{H}_5\text{O}_2\text{N}$			-		29411	40816	45454
	3221	1632		-	(1.24)	(0.80)	(1.82)
$\text{PdC}_{10}\text{H}_{10}\text{N}_2\text{O}_4\text{Cl}_2$	3205	1562	566	512	25068	31605	39745
					(0.58)	(1.17)	(1.18)
$\text{RhC}_{15}\text{H}_{12}\text{O}_6\text{N}_3 \cdot 2\text{H}_2\text{O}$	3414	1593	593	520	25706	29325	37313
					(0.71)	(1.09)	(0.79)
$\text{RuC}_{15}\text{H}_{12}\text{O}_6\text{N}_3 \cdot 2\text{H}_2\text{O}$	3351	1594	592	430	29498	-	38759
					(1.79)		(1.29)

Table 3: Crystal lattice parameters of metal complexes

Complex	a \AA	b \AA	c \AA	Vol \AA^3	D_{obs} g/cm^3	D_{cal} g/cm^3	Porosity %
$\text{PdC}_{10}\text{H}_{10}\text{N}_2\text{O}_4\text{Cl}_2$	20.7968 ± 0.0551	21.2004 ± 0.1882	33.6274 ± 0.5634	14762.97	1.5968	1.4335	10.22
$\text{RhC}_{15}\text{H}_{12}\text{O}_6\text{N}_3 \cdot 2\text{H}_2\text{O}$	21.3481 ± 0.0522	20.9451 ± 0.0666	41.0895 ± 0.6000	18798.26	1.5527	1.3252	14.60
$\text{RuC}_{15}\text{H}_{12}\text{O}_6\text{N}_3 \cdot 2\text{H}_2\text{O}$	21.4682 ± 0.0915	20.7668 ± 0.3985	41.4682 ± 0.9064	18470.11	1.5460	1.5238	13.11

geometry²¹. The electronic absorption spectrum of Ru(III) complex exhibit bands at 29498, 38759cm⁻¹ which are assigned to ${}^2T_{2g} \rightarrow {}^2A_{2g}$ and ${}^2T_{2g} \rightarrow {}^2T_{1g}$. The band due to the second spectrum forbidden transition ${}^2T_{2g} \rightarrow {}^4T_{2g}$ is usually hidden under the tail of the spectrum allowed band. The magnetic moment value of Ru (III) complex is 1.80 B.M which support Ru (III) complex is octahedral in nature^{22,23}. It is well known that all Rhodium (III) compound are diamagnetic. This is due to the combination of 3 factors viz; 1) Inherent tendency of the octahedral

d^6 configuration to assume the low spin t_{2g}^6 arrangement. 2) The relatively high ligand field strength in the complexes of tripositive ions in the second and the third transition series. 3) The greater tendency toward spin pairing among $4d^n$ and $5d^n$ configuration than their $3d^n$ analogs. The Pd (II) complex obtain by the present method is found to be identical with that obtain by Coakley and Casey by their method. It is diamagnetic and posses weakly covalent or ionic bond Pd-Cl bond.

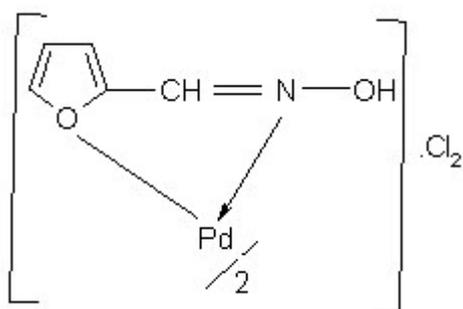


Fig. 2

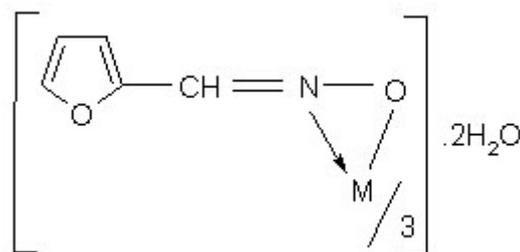


Fig. 3: M = Ru(III) and Rh(III)

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 obtained 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 programme by computational method and data has been summarized in Table 3. The data indicates the monoclinic crystal system for all the complexes²⁴.

Thermal analysis

The thermal analysis of the Pd (II) complex show that it is thermally stable up to 250°C . The complexes of Rh(III) and Ru(III) show a significant loss in weight at the temperature range 60° - 170°C . This observation suggests the presence of water of crystallization. The complex of Pd (II) do not show such significant loss indicating absence of any 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.

¹H NMR spectra

The ¹H NMR spectra of the Ru (III) complex show broad signals due to its paramagnetic nature. However an important and easily discernible feature of the spectrum of the Rh (III) and Ru (III) complexes is the absence of the proton signal due to the =NOH group of ligand which indicate coordination through the oximino nitrogen after deprotonation. A sharp signals due to aryl proton appears in the range 6.3 – 8.3 ppm in all complexes.

Biological activity

The ligand and its metal complexes were screened for antibiological and antifungal activities by agar plate method using Echinocandin as control. The anti bacterial 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*. The result, Table no 4 reveal 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 cyto toxic species ²⁵.

CONCLUSION

On the basis of magnetic susceptibility measurements, crystal lattice parameters, analytical and spectral data Pd(II) complex of furfuraldoxime exhibit square planar structure where as Rh (III) and Ru (III) complexes of furfuraldoxime exhibit octahedral structure. The proposed structure of the metal complexes have illustrated in fig. 2 and 3.

REFERENCES

1. Singh R.B., Garg B.S. and Singh R.P., *Talanta*, 26, 425 (1978).
2. Singh J., Malik O.P. and Gupta S.P., *J. Indian Chem. Soc.*, 52, 656 (1975).
3. Jetley U.K., Singh J. and Rastogi S.N., *Chem. Era*, 15, 23(1979).
4. Lal K., Singh J. and Gupta S.P., *J. Inorg. Nucl. Chem*, 40, 356 (1978).
5. Kim S.J. and Takizawa T., *Bull. of Jpn*, 48, 2197 (1975).
6. P.S. Patel, R.M. Ray and M.M Patel, *Indian J. Chem*, 32A, 597 (1993)
7. Alonso D., *Advanced Synthesis and Catalysis* 344 (2), 172-183 (2002)
8. Takei and Nishibayashi Y., *Chemical Communication*, (22), 2360-2361 (2001).
9. Youngs W., *Medicinal Inorganic Chem.*, 903, 414 – 427 (2005).
10. Brady D.L. and Goldstein R.T., *J. Chem. Soc.*, 9-27 (1959).
11. Vogel, A.I., *Textbook of Quantitative Chemical Analysis* 5th Ed. ELBS (1989).
12. Sherikar A. and Dhadke. P.M., *Ph.D Thesis* (TKS5262) University of Mumbai (1996).
13. Nakamoto K., *Infrared Spectra of Inorganic and Coordination Compounds*, New York, 159, 214 (1969).
14. Rao C.N. and Ferraro J.R., *Spectroscopy in Inorganic Chemistry*, Vol.10, Academic press, New York, P 149 (1970).
15. Rao N.R., Rao P.V., Reddy G.V. and Ganorkar M.C., *Indian J. Chem.*, 26 A, 887 (1987).
16. Srivastava T.N. and Chauhan A.K.S., *Indian J. Chem.*, 19A, 269 (1980).
17. Chatt J., Duncanson L.A. and Benanzi, *Nature*, 17, 1042 (1956).
18. Parris E. and Long G., *Inorg. Nucl. Chem.*, 32, 1585 (1956).
19. N.B. Colthup, L.H. Daly and B.E. Wiberly, *Introduction to Infrared and Raman Spectroscopy*, Academic press New York, 340 (1964).
20. Acouta A.Y., Maki A.K.T. and Mostafa M.M., *Spectrochim. Acta*, 44A, 1291 (1988).
21. Ozcan E. and Mizaoglu R. *Synth. React. Inorganic. Met. Org. Chem.*, 18(6), 559 (1988).
22. Haldar B.C, *Indian J. Chem*, L1, 224- 230 (1974).
23. Dhadke P.M. and Haldar B.C., *J. Indian Chem. Soc.*, 55, 18 (1978).
24. Swar Y.A. and Mehta B.H., *Asian J. of Chem.*, 13, 928 -932 (2001).
25. Makode T. and Aswar A.S., *Indian J. Chem.*, 43A, 2120 (2004).