

## PHYSICOCHEMICAL CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF ORTHO HYDROXY ACETOPENONE OXIME WITH Cr(III), Mn(II) and Fe(III)

\*P. R. Shirole

Department of Chemistry, Pratap College, Amalner (India) Affiliated to North Maharashtra University, Jalgaon.

Article Received on  
27 May 2018,

Revised on 17 June 2018,  
Accepted on 07 July 2018

DOI: 10.20959/wjpr201814-12896

\*Corresponding Author

P. R. Shirole

Department of Chemistry,  
Pratap College, Amalner  
(India) Affiliated to North  
Maharashtra University,  
Jalgaon.

### ABSTRACT

The mixed ligand complexes of the type  $[ML_1L_2]Cl$  have been synthesized, by the reactions of metal chlorides with two different ligands in 1:1:1 molar ratios. [Where  $L_1$ =Ortho hydroxy acetophenone oxime(OHACPHOX)  $L_2$ = Anthranilic acid(ANT). The resulting products have been characterized on the basis of elemental analysis, magnetic measurement, IR and Electronic spectra, conductivity measurement, thermal analysis, antimicrobial activities. Ligands are bonded to metals through oxygen and nitrogen donor atoms. The metal complexes shows octahedral nature.

**KEYWORDS:** Mixed ligand complexes, oxime, salicylaldehyde and anthranilic acid.

### INTRODUCTION

Transition metal complexes of oxime, anthranilic acid shows remarkable antitumor, antiviral, anticancer, anti-malarial, anti-fungal, anti-bacterial and catalytic activities. By considering these applications, we have carried out synthesis and characterization and biochemical study of mixed ligand complexes of Cr(III),Mn(II) and Fe(III) with Ortho hydroxy acetophenone oxime ( $L_1$ ) and Anthranilic acid( $L_2$ ). In this complexation reaction ortho-hydroxyacetophenone oxime and anthranilic acid are acting as a bidentet ligand with oxygen and nitrogen as the donor species.

In the present study oxime constitute one of the most important classes of Oxygen and nitrogen donor ligands. The formation of a verity of metal complexes from these ligands indicates the spectacular progress in co-ordination and bioinorganic chemistry to the real

impetus towards developing. In view of the above applications, synthesis and characterization and biochemical studies of Cr(III), Mn(II) and Fe(III) complexes obtained from ortho hydroxy acetophenone oxime and anthranilic acid carried out. The synthesized complexes are characterized by elemental analysis, study of IR and electronic spectra, biological activities, magnetic properties, conductivity measurement. The compositions of these complexes were determined by the CHN and S analyses. For the characterization of these compounds we have used IR and UV spectral studies.

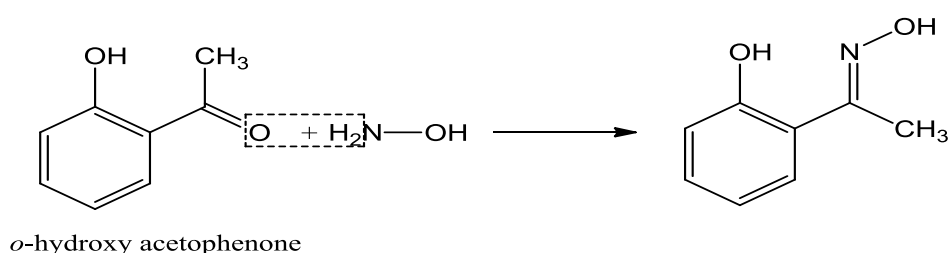
## MATERIALS AND METHODS

The compounds ortho-hydroxyacetophenone, anthranilic acid, hydroxylamine hydrochloride and chromium(III)chloride, manganese(II)chloride and iron(III) chloride used were of analytical grade. The amount of metal is determined complexometrically by EDTA using suitable indicator. Carbon, hydrogen and nitrogen analysis were carried out on Perkin Elmer CHNS analyzer, Specific conductance were measured at room temperature in DMF by a Systronics direct reading 304 conductivity meter using a glass conductivity cell having a cell constant 1.0. IR spectra were taken on JASCO 6600 FTIR SPECTROPHOTOMETER and JASCO - 670 -UV SPECTROPHOTOMETER, from Central Research Laboratory, Pratap College, Amalner. Thermo gravimetric analysis was performed on STA 6000 Central Research Laboratory, Pratap College, Amalner. Microbial activities were carried out from PG Department of Microbiology, Pratap College, and Amalner.

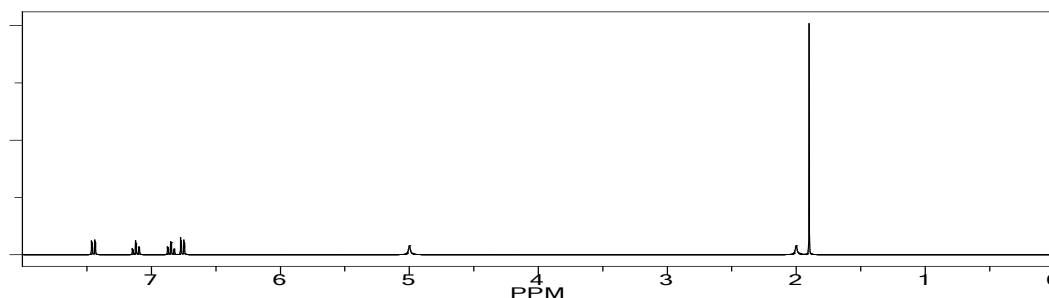
### Synthesis of Ligands

#### Ligands L<sub>1</sub>: Ortho-hydroxyacetophenone oxime.

It is synthesized by mixing equal quantities of 0.1 molar ethanolic solutions of ortho-hydroxyacetophenone and hydroxyl amine hydrochloride in a round bottom flask to this reaction mixture 3-4 drops of glacial acetic acid is added to acidify the reaction mixture. This reaction mixture was then refluxed in water bath for two hours. Faint yellow product separates out from solution on cooling. Filter and recrystallized it from ethyl alcohol and record the melting point.

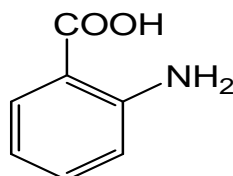


### NMR Spectrum of Ortho-hydroxyacetophenone oxime



### Ligands L<sub>2</sub>: Anthranilic acid

As anthranilic acid is easily available in market, SD fine make of analytical reagent grade anthranilic acid is used by recrystallizing it from aqueous ethanol.



Anthranilic acid

### NMR Spectrum of Anthranilic acid

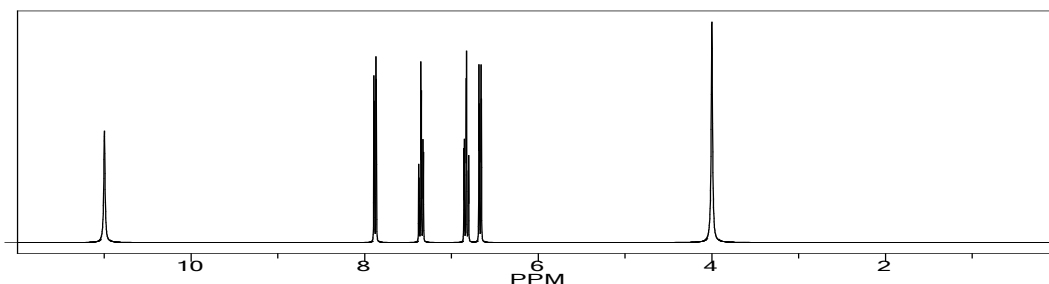


Table 1: The physical properties of ligands.

Name of ligand	Nature	Method of Purification	Meltingpoint	
			°C(observed)	°C( reported)
Ortho hydroxyacetophanone oxime	Yellowish Shining Crystals	Recrystallized from aq. Ethanol	114	114
Anthranilic acid	White Shining Crystals	Recrystallized from aq. Ethanol	60	60

### Synthesis of complexes

**1. Preparation of M(OHACPHOX)<sub>2</sub>:** To methanolic solution of metal chloride, alcoholic solution of O-hydroxy acetophenone oxime was added with continuous stirring at room temp, a clear solution was obtained. Then the solution was refluxed on a heating mental at about

60-70°C for 4 h. The colored solid complex separates out from solution. The solid product is filtered on cooling, washed with methanol, dried.

**2. Preparation of M(ANT)<sub>2</sub>:** For preparation of this complex equal volumes ethanolic solution of anthranilic acid and ethanolic solution of metal chloride was mixed together in 1:2 molar proportions in a round bottom flasks with continuous stirring at room temperature. The clear shown was refluxed in a water bath for three hours. The colored solid complex separates out from solution. The solid product is filtered on cooling, washed with methanol, dried in inert atmosphere.

### 3. Preparation of M(OHACPHOX)(ANT) mixed complexes

To methanolic solution of metal chloride a mixture of O-hydroxy acetophenone oxime and anthranilic acid ligands dissolved in hot methanol were added in molar ratio 1:1:1 with continuous stirring at room temp to get clear solution. Then the solution was refluxed on a water bath for four hours. The colored solid complex separates out from solution. The solid product is filtered on cooling, washed with methanol, dried and weight of the complex obtained is taken to determine practical yield.

## RESULTS AND DISCUSSION

### Analytical Properties

The mixed ligand complexes obtained having different colors, their physical properties are listed in table 2. These complexes were insoluble in chloroform, carbon tetrachloride, methanol, ethanol but soluble in DMF and DMSO. For the conformation of the formation of the mixed ligand complexes ML<sub>1</sub> L<sub>2</sub>, the TLC of the mixed ligand complexes with M(L<sub>1</sub>)<sub>2</sub> and M(L<sub>2</sub>)<sub>2</sub> was taken. It shows that the R<sub>f</sub> value of mixed ligand complexes is being intermediate of the two corresponding symmetrical bis-complexes.

**Table 2: Physical properties of Mixed ligand complexes.**

Complex	Colour	Mole. Wt	% Yield Of the comp.	% of metal (Calculated)	% of C	% of H	% of N
[Cr(OHACPHOX)(ANT)(H <sub>2</sub> O) <sub>2</sub> ] Cl	Gray	413.93	71.04	(11.36) 11.40	(54.73) 54.61	(5.85) 5.74	(5.40) 5.29
[Mn(OHACPHOX)(ANT)(H <sub>2</sub> O) <sub>2</sub> ]	Purple	378.93	72.31	(12.72) 12.41	(53.85) 54.65	(5.27) 5.39	(7.38) 7.33
[Fe(OHACPHOX)(ANT)(H <sub>2</sub> O) <sub>2</sub> ] Cl	Redish brown	523.04	67.29	(12.14) 12.06	(54.41) 54.27	(5.82) 5.71	(5.35) 5.31

## Spectral Properties

### 1. Electronic Spectra

Electronic absorption spectra are generally supporting the results obtained for the structural investigation by other methods. The electronic spectral measurement was used for determining the stereochemistry of metal ions in the complex based on the positions and number of d-d transitions peaks. The electron absorption spectra of the Schiff bases and its Cr (III), Mn (II) and Fe (III) complexes were recorded at room temperature.

**Table 3: The electronic spectra of mixed ligand complexes in  $\text{cm}^{-1}$ .**

Sr.no	Name of the complex	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_2/\nu_1$
1	OHACPHOX	8314	25906		
2	ANT	8771	20790	26315	
3	[Cr(OHACPHOX)(ANT)(H <sub>2</sub> O) <sub>2</sub> ] Cl	9387	16724	27151	1.421
4	[Mn(OHACPHOX)(ANT)(H <sub>2</sub> O) <sub>2</sub> ]	8102	19292	31347	1.865
5	[Fe(OHACPHOX)(ANT)(H <sub>2</sub> O) <sub>2</sub> ] Cl	11241	18671	32362	2.270

The electronic spectra of Cr(III) complexes exhibits bands in the range 9387,16724 and 27151  $\text{cm}^{-1}$  with  $\nu_2/\nu_1$  ratio 1.421 corresponding to  ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$ ,  ${}^6A_{1g} \rightarrow {}^4E_{2g}({}^4G)$ ,  ${}^6A_{1g} \rightarrow ({}^4G) {}^4E_{2g}({}^4D)$  transitions, respectively suggesting octahedral environment around Cr(III) ion. The electronic spectra of Mn(II) shows three bands at 8102,19292 and 31347  $\text{cm}^{-1}$ . For the transitions  ${}^6A_{1g} \rightarrow {}^4T_{1g}$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  and  ${}^6A_{1g} \rightarrow {}^4A_{1g}$  with  $\nu_2/\nu_1$  ratio of 1.485 indicating octahedral geometry around Mn(II) ion in the complex. The spectrum of Fe(III) consists of three bands 11241,18671 and 32362  $\text{cm}^{-1}$  with  $\nu_2/\nu_1$  ratio 2.270. The first transition corresponds to  ${}^6A_{1g} \rightarrow {}^4T_{1g}$ , while two transitions  ${}^6A_{1g} \rightarrow {}^4E_g$  and  ${}^6A_{1g} \rightarrow {}^4E_{2g}$  are degenerate, indicating octahedral symmetry around Fe(III) ion.

### IR spectra

IR spectra of the mixed ligand complexes the shows bands at 1555-1589 $\text{cm}^{-1}$  may be assigned to the symmetric and asymmetric  $\nu(\text{C}=\text{N})$  vibrations. A strong band in the region 1621-1657 $\text{cm}^{-1}$  are due to  $\nu(\text{C}=\text{O})$  groups. On complex formation, the position of these bands is shifted toward lower side as compared to the metal free ligand. This indicates that the coordination takes place through the nitrogen and oxygen atom of the(C=N) and (C=O) groups. Band appearing in the region at 3524--3602 $\text{cm}^{-1}$  is due to presence of -OH from water molecule. The band at 574-587  $\text{cm}^{-1}$  indicates presence of metal nitrogen bonding while bands in the region 724-731  $\text{cm}^{-1}$  shows presence of metal oxygen bonding.

**Table 4: IR spectra of mixed ligand complexes.**

Ligand/ Complex	$\nu_{\text{OH}}$ (H <sub>2</sub> O)	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$
OHACPHOX		1699	1511			
ANT		1707	1578	1379		
[Cr(OHACPHOX) (ANT)(H <sub>2</sub> O) <sub>2</sub> ] Cl	3524	1647	1546	1347	574	731
[Mn(OHACPHOX) (ANT)(H <sub>2</sub> O) <sub>2</sub> ]	3564	1621	1539	1358	579	724
[Fe(OHACPHOX) (ANT)(H <sub>2</sub> O) <sub>2</sub> ] Cl	3602	1657	1557	1361	577	730

**Electrical conductivity, Magnetic Properties and thermogravimetric analysis**

Molar conductivity of the complexes is ranging from 66-92  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ , indicating electrolytic nature of the complexes. Thermo gravimetric analysis shows loss in wt in the range 8.412-8.620 within the temp. range 50-250<sup>0</sup>C, indicating loss of two water molecules. Magnetic susceptibility values of the complexes shows octahedral geometry of the complexes.

Complex	TGA		Molar Conductance( $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ )	$\mu_{\text{eff}}$ (B.M.)
	Decomposition temp( $\pm 5^\circ\text{C}$ )	% loss		
[Cr(OHACPHOX) (ANT)(H <sub>2</sub> O) <sub>2</sub> ] Cl	50-200	8.521	89.12	4.879
[Mn(OHACPHOX) (ANT)(H <sub>2</sub> O) <sub>2</sub> ]	50-200	8.412	66.43	4.34
[Fe(OHACPHOX) (ANT)(H <sub>2</sub> O) <sub>2</sub> ] Cl	100-250	8.620	92.48	5.36

**Microbiological Activities**

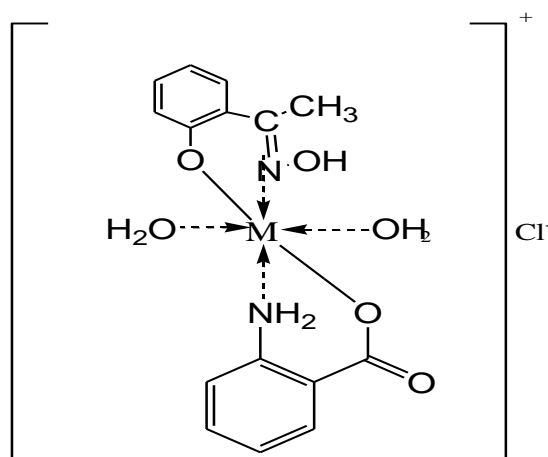
The compound synthesized in the present investigation has been subjected to antimicrobial screening programs based on their structural features so as to ascertain their activity against five different microorganisms *E.coli.*, *Baciillus Sp* *Staphylococcus sp.*, *Pseudomonas Sp.* and *Proteus Sp.*

The solvent used was DMSO, and the sample concentrations were, 100ppm. The results of preliminary study on antimicrobial activity indicated that most of the complexes show moderate activity against these organisms.

Table 5: Microbiological activities (zone inhibition in mm).

Ligand/Complex	<i>E.coli.</i>	<i>Baciullus Sp.</i>	<i>Staphylococcus sp.</i>
OHACPHOX	10	08	09
ANT	10	12	13
[Cr(OHACPHOX)(ANT)(H <sub>2</sub> O) <sub>2</sub> ] Cl	14	13	16
[Mn(OHACPHOX)(ANT)(H <sub>2</sub> O) <sub>2</sub> ]	13	16	-
[Fe(OHACPHOX)(ANT)(H <sub>2</sub> O) <sub>2</sub> ] Cl	12	14	17

By considering all the above properties of the mixed ligand complexes the structure of the metal complexes should be as given below,



Where M=Cr(III),Mni(II) or Fe(III)

## ACKNOWLEDGEMENT

The author is thankful to Principal, Pratap college, Amalner; Head, Department of Chemistry for providing necessary facility.

## REFERENCES

1. A.I.Vogel, "A Text Book of Quantitative Inorganic Analysis", 3<sup>rd</sup> edn.
2. Abdul Salam A.K. Abdul Rahman Diala, Jour, Volume, 39, 2009.
3. R.N.Prasad, Jindal, R.P. Sharma. Curr. Sci., 1984; 53: 1128.
4. G. Mukherjee And Ansuman, Das., Proc. Indian Acad. Sci. (Chem. Sci.), June 2002; 114(3): 163-174.
5. S. Chandra, K.B.Pandeya and R.P.Singh, J.Inorg. Nucl. Chem., 1977; 39: 2079.
6. Chitra S., Nagajothi A., Parameswari K., Research Journal of Chemical Sciences., Feb. 2013; 3(2): 35-43.

7. Pandeya S N and Dimmock, J R, Pharmazie, 1993; 48(9): 659-666.
8. S.A.Patil, A.D.Kulkarni, P.S.Badmi., Int. J. Electrochem. Sci., 2009; 4: 717-729.
9. Sarika Anand, Transition Metal Chemistry, 2007; 32: 816-821.
10. Abbas Noor Al-Shareefi, W.Abbas Jawed, J. App. Chem., 2013; 2(3): 438-446.
11. R.N.Prasad, Jindal, R.P.Sharma., Curr. Sci, 1984; 53: 1127.
12. Brajesh Kumar, Arun Kumar, International J. Scientific Engineering and Applied Science (IJSEAS) - Volume-1, Issue-5, ISSN: 2395-3470, August 2015.
13. Lever A.B.P., "Electronic Spectra of dn ions. in Inorganic Electronic Spectroscopy", 2<sup>nd</sup> Ed. Elsevier.
14. S. Chandra, L. K. Gupta., Spectrochimica Acta Part A, 2005; 61: 269-275.
15. R.N.Prasad, M.Jindal, M.Jain., J. Ind. Chem. Soc., 1990; 67: 874.
16. G N mukherjee and Ansuman Das., Proc. Indian Acad. Sci.(Chem. Sci.), June 2002; 114(3): 163-174.
17. S. Chandra, K.B.Pandeya and R.P.Singh, J. Inorg. Nucl. Chem., 1977; 39: 2079.
18. P.R.Shirode, P.M.Yeole, Chem. Sci. Trans., 2014; 3(3): 1186-1192.
19. R.N. Prasad, M.Sharma, Anjali Agrawal, J. Ind. Chem. Soc., 2008; 85: 36-41.
20. K.N.Thimmaiah, W.D.Lloyd, G.T.Chandrappa, Inorg. Chim. Acta., 1985; 106: 81.
21. Md.Belayet Hossain, M.Saidul Islam, Journal of Bangladesh Chemical Society, 2012; 25(2): 139-145.
22. Majed M. Hania, E-Journal of Chemistry <http://www.e-journals.net> 2009; 6(S1): S508-S514.
23. Lutfullah Ahmad Umar, Mohammed Muzibur Rahman, Mohammad Mansoob Khan, Yoon Bong Hahn, Turk J Chem., 2007; 31: 179 – 189.