

## RESEARCH ARTICLE

## Synthesis and structural aspects of coordination polymers of p-phenylene-di-acrylyl- bis-N-phenyl and fumaryl -bis- N-phenyl hydroxamic acids with Cd(II) and Hg(II)

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Manuscript Details	ABSTRACT
<p>Received : 10.02.2016 Revised : 08.03.2016 Accepted: 18.03.2016 Published: 10.05.2016</p> <p><b>ISSN: 2322-0015</b></p> <p><b>Editor: Dr. Arvind Chavhan</b></p>	<p>The present article describes the synthesis, structural features and thermal studies of some coordination polymers. The coordination polymers have been synthesized by heating p-phenylene di-acrylyl -bis-N-Phenyl (PAPHA), Fumaryl - bis-N- phenyl (FPHA) hydroxamic acids with metal acetate in ethanol and dimethyl formamide mixture in water bath for about two hours. Coordination polymers of Cd(II) and Hg(II) have been characterized by elemental analysis and IR spectroscopy. Thermogravimetric analysis has been used to determine the thermal stability of coordination polymers.</p>
<p><b>Cite this article as:</b> Kulkarni Nirupama K. Synthesis and structural aspects of coordination polymers of p-phenylene-di-acrylyl- bis-N-phenyl and fumaryl -bis- N-phenyl hydroxamic acids with Cd(II) and Hg(II), <i>Int. Res. Journal of Science &amp; Engineering</i>, 4(1): 27-30.</p> <p><b>Copyright:</b> © Author(s), This is an open access article under the terms of the Creative Commons Attribution Non-Commercial No Derivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.</p>	<p><b>Keywords:</b> Coordination polymers, p-phenylene-di-acrylyl- bis-N-phenyl and fumaryl -bis- N-phenyl hydroxamic acids, infrared spectra, thermogravimetric analysis.</p> <p><b>INTRODUCTION</b></p> <p>Coordination polymers span specific fields such as organic, inorganic, electrochemistry, biology, material science, pharmacology etc. having many potential applications (Fromm, 2008). Their interdisciplinary nature make them particularly fascinating with varied applications (Kitagawa, 2006). Luminescence arises from electronic transitions from an excited state caused by photoexcitation to the ground state resulting in emission of light. Coordination polymers are potentially most versatile luminescent species due to their emission properties coupled with guest exchange. Luminescent supra molecules have recently attracted much interest because of their potential applications in optoelectronic devices as sensors and probes (Batton, 2008).</p> <p>Coordination polymers have short organic and inorganic bridges which provide pathways for electrical conduction. In some cases they show semi conductivity (Batton, 2008). They also show variety of applications because of their porous structure (Kitagawa, 2004). Polymers constructed from metal ion and connector ligands with a potential to be</p>

engineered for a wide range of applications in heterogeneous catalysis (Jang, 2006), imaging (Rieter, 2006) and sensing (Rieter, 2007) are reported.

Biodegradable polymers can be used in various applications of biomedicines and plastic technology (Duncan, 2003).

The possibility for wide choice of both metal and ligands makes the area of coordination polymers particularly fascinating. Considerable work has therefore been reported in this field.

Polymers have replaced a number of conventional materials in various applications during past number of years and remarkable progress has been made in the area of coordination polymers

Coordination polymers containing chelating groups can be used as thermally stable materials for surface coating (Arpagaus, 2005). Efforts have been made to prepare coordination polymers of some ligands in the present study.

## MATERIALS AND METHODS

All the chemicals used were of A R grade. Solvents were double distilled before use.

### Instruments

Microanalysis for C, H, and N was carried out at micro-analytical unit CDRI, Lucknow India. Infrared spectra in the region 4000-400  $\text{cm}^{-1}$  were recorded using a specord-75-infrared spectrophotometer by nujol mull technique at Department of Chemistry, RTM Nagpur University Nagpur. Metal content in the polymers was determined by classical oxide method.

Thermal stability has been studied by recording differential thermograms maintaining the heating rate at 8 $^{\circ}$ /min.

### Synthesis of p-phenylene - di-acrylyl - bis-N-phenyl and Fumaryl - bis - N-phenyl hydroxamic acids

The ligands were prepared by modified method of Priyadarshini and Tandon (Priyadarshini, 1967) based on Scotten Baumann reaction. In this method freshly prepared N-hydroxylamine and vacuum distilled acid chloride in stoichiometric proportion are reacted at low temperature (0 $^{\circ}$  C or lower) in diethylether medium containing aqueous suspension of sodium bicarbonate. A freshly prepared, crystallized N-phenyl-hydroxylamine (0.25M), diethylether (100 ml), sodium

bicarbonate (0.3M) and distilled water (30ml) were taken in a 500 ml beaker and the mixture was cooled to 0 $^{\circ}$  C or lower. To the above mixture a solution of acid dichloride (0.1M) in diethylether (150 ml) was added drop wise with constant stirring for about an hour. The product separated was filtered and washed thoroughly with saturated solution of sodium bicarbonate to remove any acidic impurities present. The products were crystallized from DMF-ethanol mixture. Both PAPHA and FPFA were yellow in colour (m. pts. 225 $^{\circ}$  and 194 $^{\circ}$  C) respectively.

The elemental analysis data of these ligands is as follows:

PAPHA (%Found: C,71.4, H,5.11,N,6.84) (%Calc: C,72, H,5.00, N, 7.00)

FPFA (%Found: C,64.7, H,5.07, N,8.89) (%Calc: C: 64.4,H,4.69, N, 9.39)

### Synthesis of coordination polymers

The ligand and metal acetate in equimolar proportion (0.01M) with ethanol (75ml) and dimethyl formamide (25ml) were heated in a water bath for two hours. The insoluble product formed was filtered and washed thoroughly several times with DMF and ethanol till free from unused reactants and dried.

The products obtained as amorphous powders were found to be insoluble in almost all common organic solvents such as chloroform, benzene, acetone, ethanol, DMF, cyclohexane, nitrobenzene etc. This indicates their polymeric nature.

## RESULTS AND DISCUSSION

The composition of these polymers is proposed on the basis of their elemental analysis, the result of which is given in table 1 and 2.

Thermal studies have been used to ascertain water of crystallization as well as coordination and thermal stability of these polymers.

### Infrared spectral studies

The O-H stretching band is observed at 3095  $\text{cm}^{-1}$  in PAPHA and 3100  $\text{cm}^{-1}$  in FPFA. Sharp band at 1595  $\text{cm}^{-1}$  in PAPHA and at 1600  $\text{cm}^{-1}$  in FPFA is assigned to carbonyl stretching vibration. The N-O stretching vibration is observed at 970 and 965  $\text{cm}^{-1}$  in PAPHA and FPFA respectively.

**Table 1:** Elemental Analysis of PAPHA Polymers

Proposed composition of the polymer	% Found (Calculated)	% Found (Calculated)	% Found (Calculated)	% Found (Calculated)
	C	H	N	M
(CdL) <sub>n</sub>	55.40 (56.43)	3.85 (3.53)	5.19 (5.48)	21.39 (22.02)
(HgL) <sub>n</sub>	47.90 (48.11)	2.92 (3.01)	4.00 (4.68)	32.90 (33.51)

L=PAPHA

**Table 2:** Elemental Analysis of FPHA Polymers

Proposed composition of the polymer	% Found (Calculated)	% Found (Calculated)	% Found (Calculated)	% Found (Calculated)
	C	H	N	M
(CdL) <sub>n</sub>	45.60 (47.01)	3.42 (2.94)	6.85 (6.86)	27.19 (27.52)
(HgL) <sub>n</sub>	38.00 (38.66)	2.36 (2.42)	4.25 (5.64)	40.29 (40.39)

L=FPHA

**Table 3:** Assignments of infra-red spectra (cm<sup>-1</sup>) of PAPHA and its Polymers

PAPHA	Cd (II) Polymer	Hg (II) Polymer	Assignment
3095 b	-----	-----	O-H
1595s	1555s	1590s	C=O
970s	960s	960s	N-O
-----	520w	455w	M-O

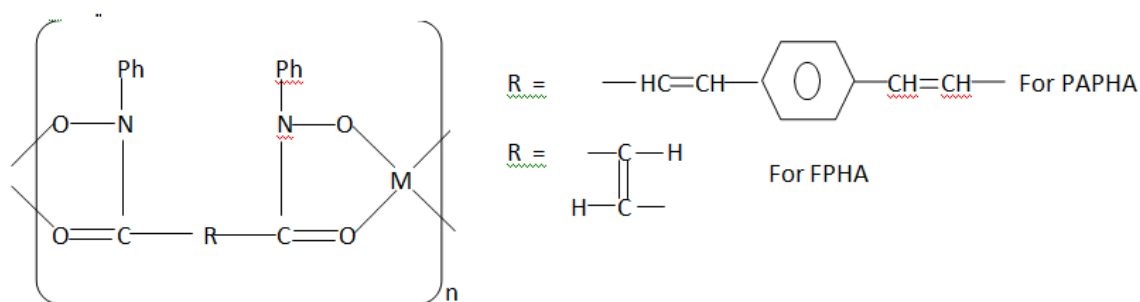
b-broad, s-strong, w-weak

**Table 4:** Assignments of infra-red spectra (cm<sup>-1</sup>) of FPHA and its Polymers

FPHA	Cd(II) Polymer	Hg(II) Polymer	Assignment
3100b	-----	-----	O-H
1600s	1560s	1590s	C=O
965s	940s	950s	N-O
-----	445w	570w	M-O

b-broad, s-strong, w-weak

### Proposed Structure of the Polymer:



As anticipated O-H band disappears in the polymers. The carbonyl band is found to have been displaced towards lower frequency side in polymers which is indicative of the formation of C-O—M coordinate bond. The N-O band is slightly shifted towards lower frequency side with considerable increase in intensity. In both cases the evidence of metal to oxygen (of the ligand) bonding is observed at a frequency between  $570\text{ cm}^{-1}$  and  $445\text{ cm}^{-1}$ .

The assignments of frequencies for the ligands and their respective polymers are shown in table 3 and 4.

#### Thermal studies of coordination polymers

The decomposition temperatures were determined by the half decomposition curve technique.

In DTA and TGA curve of Cd (II)-PAPHA polymer no weight loss is observed upto  $280^{\circ}\text{C}$  which may be due to absence of water of hydration and water of coordination. A sharp exotherm in TGA is not associated with major weight loss. Temperature ( $280^{\circ}\text{C}$ ) corresponding to the larger exotherm is taken as the decomposition temperature. Weight loss continues up to  $610^{\circ}\text{C}$ . Total weight loss is 77.9% , practical is 73%.

In Hg(II)-PAPHA polymer also no weight loss is observed upto  $300^{\circ}\text{C}$  which may due to absence of water of hydration and water of coordination. The sharp exotherm ( $300^{\circ}\text{C}$ ) in DTA is not associated with major weight loss. Temperature ( $345^{\circ}\text{C}$ ) corresponding to the larger exotherm is taken as the decomposition temperature. Weight loss continues upto  $820^{\circ}\text{C}$ . Theoretical weight loss is 85.9%. Practical is 83.00%.

In Cd(II) -FPHA polymer also no weight loss up to  $300^{\circ}\text{C}$  is observed indicating absence of water of hydration and water of coordination. Weight loss corresponding to the first exotherm ( $300^{\circ}\text{C}$ ) is taken as the decomposition temperature. Weight loss continues upto  $500^{\circ}\text{C}$ . Theoretical weight loss is 81.9% .Practical is 80.6%.

In Hg(II)-FPHA polymer also weight loss starts at  $260^{\circ}\text{C}$  indicating absence of water of hydration and water of coordination. Weight loss starts at  $260^{\circ}\text{C}$  which corresponds to the sharp exotherm. Weight loss continues up to  $510^{\circ}\text{C}$ . Temperature corresponding to the broader exotherm ( $300^{\circ}\text{C}$ ) is taken as the decomposition temperature. Theoretical weight loss is 82.3%. Practical is 81.0%.

## CONCLUSIONS

All the polymers are suggested to be tetrahedral in the nature on the basis of elemental analysis.

All the coordination polymers are found to be highly thermally stable and insoluble in almost all organic solvents and hence can be used as highly thermally stable powder coating materials.

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