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Synthesis and characterization of some polychelates derived from cardanol based resin copolymers and different metal ions like, Cu(II), Zn(II), Ni(II) & Co(II).

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Abstract
At first a number of resin copolymers were synthesised by reacting cardanol-furfural & O-Substituted aromatic acids, alcohols & ketones in presence of acid/base catalyst. Then poly chelats were prepared by reacting resin copolymers with metal salt solutions like, Cu(II), Zn(II), Ni(II) & Co(II) under suitable conditions. They are characterised by FTIR analysis, T.G analysis of some poly chelates have been carried out to understand thermal stable compared with their corresponding resin copolymers. The Physico-Chemical properties of polychelates also been studied.

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I. Introduction

Present investigation reveals that the copolymers act as ligands due to presence of lone pairs of electrons on the group like –COOH, -OH, $-NH_2$, -X etc. in side the copolymers. The copolymers prepared from cardanol – furfural- substituted aromatic acids, phenols, ketones, as well as aliphatic compounds like urea, thiourea are able to form metallic chelates. In this paper, the preparation, physico-chemical properties, FTIR and TG analysis of some metallic chelates have been explained. Some of chelates have been prepared by using the metal ions like Cu^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2}, Mn^{+2}, etc.

According to Morgan and Drew, chelate is a ring compound (complex), the central metal ion is bonded by the polydentate ligands.

The polydentate ligands whose structures permit the attachment of their two or more donor atoms (or sites) to the same metal ion simultaneously and thus produce one or more rings are also called chelates.

The chelates are highly applied in the field of analytical chemistry, i.e. quantitative analysis of metal ion viz. Al^{+3}, Ni^{+2}, and Mg^{+2} which forms highly stable and coloured complex and chelating agents are also used as indicators in the estimation of certain metal ions. In addition with metallic chelates are used for softening of water, in food preservation, in solvent extraction and in the elimination of harmful radioactive metals from human body.

EXPERIMENTAL
Step-I: Synthesis of Copolymers.
Step-II: Synthesis of Polychelates

STEP-I: SYNTHESIS OF COPOLYMERS

A number of copolymers have been synthesised from cardanol by condensing with furfural and various aromatic substrates viz.substituted aromatic acids, alcohols, amines and ketons etc. as well as some aliphatic compounds like urea and thiourea in presence of acid and base catalyst.

Copolymers prepared from substituted aromatic acids

METHOD-I

Condensation of cardanol-furfural and o-hydroxy benzoic acid in presence of basic catalyst.

Reagents taken:

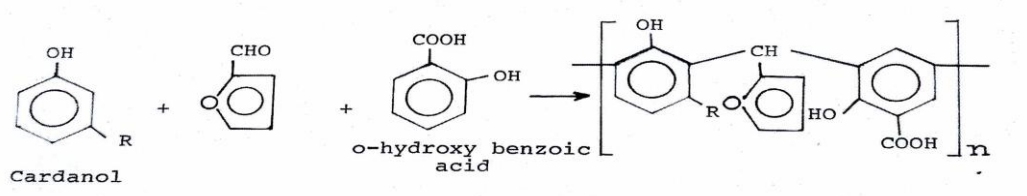
i) Cardanol- 1.192 gm
ii) Furfural- 3.84 gm
iii) O-hydroxy benzoic acid-0.552 gm.

Catalyst used :- NaOH (4N) 2 ml

Procedure: A mixture of 1.192 gm (4 m.mole) of cardanol, 3.84 gm (40 m.mole) of furfural and 0.552 gm (4 m.mole) of o-hydroxy benzoic acid were refluxed for 6-7 hrs at 80-100^0C in presence of 2 ml of (4N) NaOH

catalyst with periodical shaking. After completion of reaction, the product was washed with 10 % HCl then hot water in order to remove the basic and unreacted impurities, filtered and the residue was dried in vacuum at 60^0C, collected.

Polycondensation reaction for above method may be represented as follows:



Similarly by using method-I, number of resins have been prepared, by taking different comonomers viz. P-hydroxy benzoic acid, o-amino benzoic acid, p-amino benzoic acid, o-chloro benzoic acid, p-chloro benzoic acid, o-methyl benzoic acid & p-methyl benzoic acid in presence of acid or base catalyst.

STEP-II: SYNTHESIS OF POLYCHELATES:

Preparation of metallic chelates from the cardanol –furfural-o-hydroxy benzoic acid-copolymer have been explained below.

Preparation of Cu(II) chelates: A mixture of 0.2gm of copper (II) acetate in 50ml DMF and 0.4 gm copolymer in 50ml of DMF was taken in a conical flask, 0.5 gm of sodium acetate was added to it to maintain P^H of 3.5. After constant stirring for some time at room temperature a greenish coloured metal chelate was precipitated out, filtered and the residue was washed with ethanol, then collected the dried product.

Preparation of Zn(II) chelates: A mixture of 0.5gm of copolymer in 1:1 DMF-methanol and 0.4 gm of zinc sulphate in 1:1 DMF-methanol were refluxed for 4 hrs in presence of few ml concentrated solution of sodium acetate in DMF-methanol and kept overnight. The separated chelate was filtered, then washed with DMF-methanol solution and hot water, chelate was dried in side vacuum at 60^0C and collected.

Preparation of Co(II) chelate: A mixture of 0.2 gm of copolymer and 0.2 gm of $Co(NO_3)_2$ were dissolved in 25 ml of ethanol, the contents were refluxed for 2 hrs in presence of few ml of clear solution of 1.5 gm of sodium acetate with a periodical strring. A coloured precipitate was obtained, filtered then washed with 4 to 5 time by hot water and finally with hot ethanol and dried inside over at 50^0C, collected.

Preparation of Ni(II) chelate: 0.5 gram of the copolymer was dissolved in a mixture of DMF-methanol (1:1). The pH of the solution was just adjusted by addition of dilute NH_4OH solution and 0.4 gm of Nickel sulphate solution in DMF-methanol (1:1) was added dropwise to the copolymer solution with constant stirring. A pale yellow coloured chelate was separated out, then filtered, the residue was washed with DMF-methanol, hot water then dried in oven at 60^0C and collected.

By using above methods several metallic polychelates have been prepared by using different copolymers. In which o-NH_2-benzoic acid, o-chloro benzoic acid, m-cresol, o-hydroxy acetophenone, p-amino benzoic acid and urea/ thiourea were acts as comonomers.

The physico-chemical properties of the several metallic chelates are given in table-1

TABLE-1
"PHYSICO-CHEMICAL PROPERTIES OF THE CHELATES"

Sl.No	Name of the resins	Metal ion	Yield (%)	Colour	Structure	Decomposition Temperture
(1)	Cardanol-furfural-o-hydroxy benzoic acid	Cu^{+2}	40	Greenish	Amorphous	>360
		Ni^{+2}	50	Yellow	Crystalline	>360
		Zn^{+2}	40	Bluish	Amorphous	>360
		Co^{+2}	45	Pink	Crystalline	>360
		Mn^{+2}	40	Brown	Crystalline	>360
(2)	Cardanol-furfural-o-amino benzoic acid	Cu^{+2}	45	Green	Crystalline	>360
		Ni^{+2}	50	Yellow	Crystalline	>360
		Zn^{+2}	30	Bluish	Crystalline	>360
		Co^{+2}	35	Light Pink	Crystalline	>360
		Mn^{+2}	40	Brown	Crystalline	>360
(3)	Cardanol-furfural-o-chloro benzoic acid	Cu^{+2}	40	Bluish	Crystalline	>360
		Ni^{+2}	30	Pale Yellow	Crystalline	>360
		Zn^{+2}	50	Brown	Amorphous	>360
		Co^{+2}	35	Pink	Amorphous	>360
		Mn^{+2}	45	Brown	Amorphous	>360

TABLE-1 (CONTD...)
"PHYSICO-CHEMICAL PROPERTIES OF THE CHELATES"

Sl.No	Name of the resins	Metal ion	Yield (%)	Colour	Structure	Decomposition Temperture
(4)	Cardanol-furfural-p-NH_2-benzoic acid	Cu^{+2}	40	Green	Crystalline	>360
		Ni^{+2}	50	Yellow	Crystalline	>360
		Zn^{+2}	35	Brown	Crystalline	>360
		Co^{+2}	40	Pink	Crystalline	>360
		Mn^{+2}	40	Brown	Crystalline	>360
(5)	Cardanol-furfural-urea	Cu^{+2}	35	Green	Amorphous	>360
		Ni^{+2}	40	Yellow	Amorphous	>360
		Zn^{+2}	50	Brown	Amorphous	>360
		Co^{+2}	40	Light Pink	Amorphous	>360
		Mn^{+2}	38	Brown	Amorphous	>360
(6)	Cardanol-furfural-o-hydroxy acetophenone	Cu^{+2}	50	Light green	Crystalline	>360
		Ni^{+2}	36	Pale Yellow	Crystalline	>360
		Zn^{+2}	48	Brown	Crystalline	>360
		Co^{+2}	40	Pink	Crystalline	>360
		Mn^{+2}	25	Brown	Crystalline	>360

TABLE-2
"PHYSICO-CHEMICAL PROPERTIES OF THE CHELATES"

Copolymer (Cardanol-Fu-O-OH-benzoic acid)	Cu (II) chelate	Ni(II) chelate	Co(II) chelate	Zn(II) chelate	Probable assignments
3650	3500	3500	3500	3500	O-H-stretching chelated
3450					Hydrogen bonded O-H stretching in chelate
1700	1600	1600	1600	1600	C=o stretching chelated
2980	2980	2980	2980	2980	Aromatic C-H stretching
920	920	920	920	920	Trans double bond bending vibration in side chain of cardanol moiety.
1589	1500	1500	1500	1500	-C(=O)-O⁻ carboxylate Ion stretching.
1240	1230	1230	1230	1230	-O-H bending

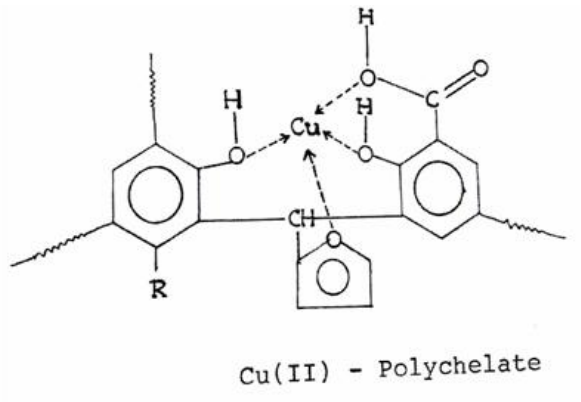
CHARACTERISATION OF THE CHELATES

i) FTIR analysis of metallic polychelates:

The FTIR data (cm^{-1}) of the different metallic polychelates prepared from the copolymer cardanol-furfural-substituted aromatic compounds are furnished in the table-2 and the FTIR spectral pictures of metallicpolychelates are shown in Fig (1)

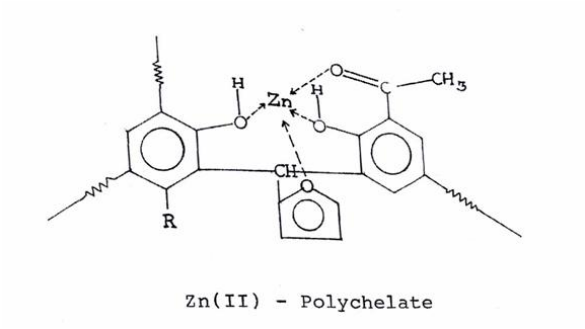
From the FTIR spectrum of Cu(II) polychelate prepared from the copolymer cardanol-furfural-o-hydroxy benzoic acid was observed that the value of stretching vibration in the chelate are 3400 cm^{-1}, 1600cm^{-1}, 1290cm^{-1} respectively, but in case of copolymer, the stretching frequencies of above groups are 3450 cm^{-1}, 1700cm^{-1}, 1320cm^{-1} etc. This change in frequency values confirms the formation of metallic polychelate. In addition with, we may also conclude that there is no intramolecular hydrogen bonded frequency in case metallic polychelate and broad band at 1330 cm^{-1} indicate the Cu(II) polychelate have planar structure and Cu(II)polychelate has magnetic moment 1.72 B.M which also indicates the square planar structure.

From this we may conclude that the decrease in the values of stretching vibration frequencies of the characteristic group (-OH, C=O, $-NH_2$, C=C, etc) in case of metallic polychelates than corresponding copolymers, confirms formation of metallic chelates. Structure for polychelate of Cu(II) prepared from Cardanol-furfural-o-hydroxy benzoic acid copolymer may be represented as



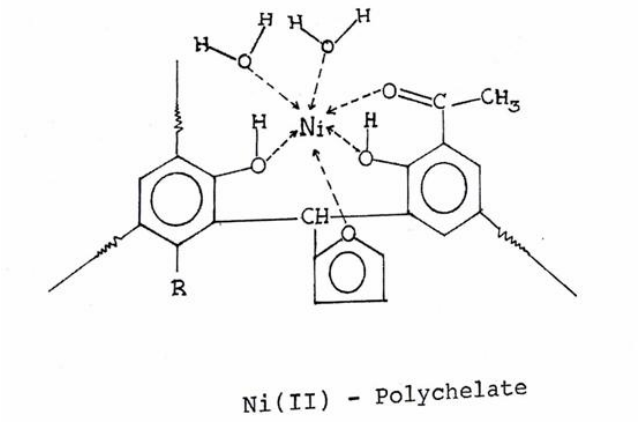
Cu(II) - Polychelate

Similar, the structure of polychelate of Zn(II) prepared from the resin copolymer [cardanol-furfural-o-hydroxy acetophenone] may be represented as follows.



Zn(II) - Polychelate

Structure for the Ni (II) polychelate prepared from the resin copolymer 2-OH-acetophenone-cardanol-furfural may be represented as follows.



Ni(II) - Polychelate

The magnetic moment of 3.14 BM and paramagnetic behaviour of Ni(II) complex suggested distorted octahedral geometry for Ni(II) polychelate.

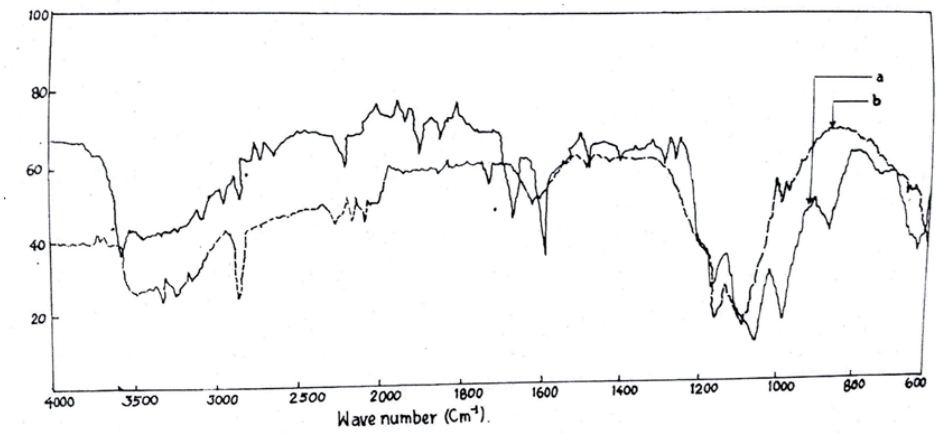


Fig.1 (a) FTIR-spectrum of the Cu^{+2} polychelate prepared from the copolymer Cardanol-furfural-o-hydroxy benzoic acid.
(b) FTIR-spectrum of the Zn^{+2} polychelate prepared from the copolymer Cardanol-furfural-o-hydroxy benzoic acid.

II) **TG** Analysis of Cu^{+2} polychelate

The TG curve for the Cu^{+2} polychelate derived from the copolymer cardanol-furfural-o-hydroxy benzoic acid is shown in fig.(2) from this thermogram it was observed that metallic polychelates are also more thermally stable because there is only 25-30% of weight loss appears around 1000^0C. In the temperature range 30-200^0C there is a sharp decrease in weight takes place, it may be due to loss of moisture contents and in the temperature 200-500^0C about 8% of weight is lost. This may be due to fragmentation side chain of cardanol, and no weight loss appears around 500-1000^0C.

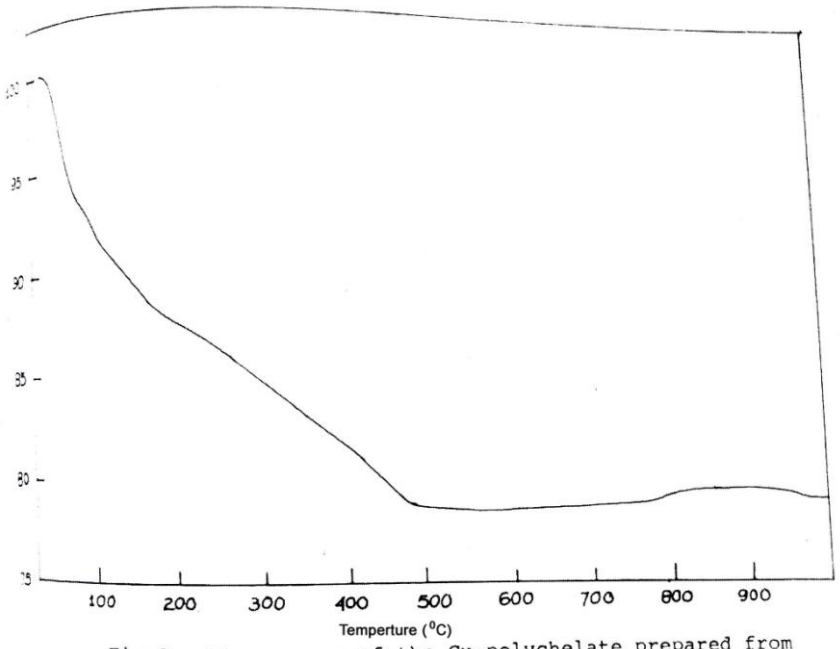


Fig.2 : Thermogram of the Cu-polychelate prepared from the copolymer (Cardanol-furfural-o-hydroxy benzoic

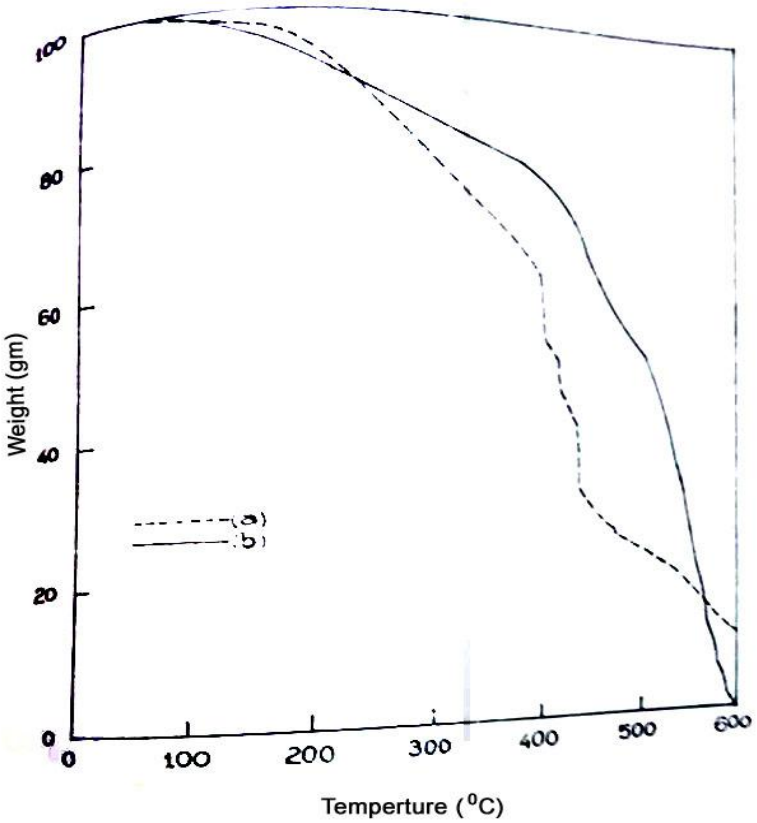


Fig:3 : Thermogram of the copolymers
(a) Cardanol-Fu-OHBA
(b) Cardanol-Fu-p-hydroxy acetophenone

II. RESULTS & DISCUSSION

1) FTIR data analysis of different metal (Cu^{+2-}, Co^{+2}, Ni^{+2} & Zn^{+2}) polychelates explain the formation of stable chelates under suitable conditions.
2) Copolymers derived from cardanol-furfural & o-hydroxy benzoic acid/ O-NH_2/O-X-benzoic acid for metal chelates due to presence of lone pair of electrons on hetero atoms like-O,-N-,-X etc.
3) Synthesis of metal polychelates is very complicated and the yield is more than 50%
4) Metal polychelates are coloured, crystaline & melting point is $>360^0$C
5) From the T.G analysis it was found that polychelates are quite stable up to 300^0C, but these are less stable than resin copolymers, it may be due to steric effect in the co polymers.
6) Polychelates are widely used in analytical field like softening of hard water and removal of radio active molecules from living organisms.
7) Polychelates are also used in solvent extraction and food preservation.

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