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Synthesize and characterization of p-hydroxybenzoic acid urea formaldehyde Copolymer chelats with($Ca^{(II)}$,$Sr^{(II)}$ and $Ba^{(II)}$)ions

Asst.Dr.Basima Abdulhusin Zaidan
Department of chemistry, College, Ibn Al-Haitham,
University of Baghdad,
P.O. 4150, Adhamiyah, Baghdad, Iraq.

ABSTRACT

Copoymer (PUF) were synthesized by the condensation of p-hydroxybenzoic acid (P) –urea (U) –formaldehyde (F) in the presence of HCl catalysts.

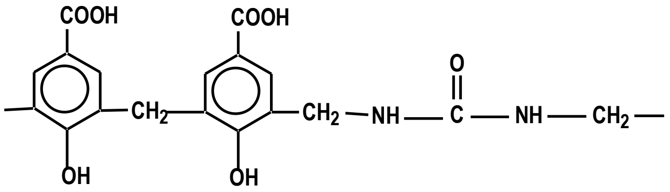
Chelates of $Ca^{(II)}$, $Sr^{(II)}$, and $Ba^{(II)}$ have been prepared from copolymer (PUF). The probable structures were elucidated on IR and A.A spectroscopy. Thermogravimetric analysis and derivative of the thermogravimetric (DTG). has been carried out to ascertain the relative thermal stability of ligand and chelates from the above data we suggested octahedral geometry for $Ca^{(II)}$, $Sr^{(II)}$, and $Ba^{(II)}$ chelates.

INTRODUCTION

The coordination polymers with metal ions have received constantly growing interest the last years (1 , 2). These compounds have been known and used for many years, though they have not been recognized such until fairly recent times (3) . The tanning of leather ,which an ancient art, depends upon the coordination of metal ions with the polypeptides of hide. The complexes which are thus formed are much more resistant to bacterial attack, weather and wear than is original hide (4). So this papere reports the prepare of p-hydroxybenzoic acid-urea-formaldehyde(PUF) copolymer(5) .

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material’s thermal stability and its fraction of volatile components the weight change that occurs as a specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. Sometimes, the measurement is performed in a lean oxygen atmosphere to slow down oxidation

The suggested structure of copolymer are show in figre [1] (6).



figre [1]
p-hydroxybenzoic acid-urea-formaldehyde copolymer

PRACTICAL APPLICATION

a.Uses in nuclear chemistry.
b.Separation possibilities.
c. Recovery of traces of metal ions.
d. Miscellaneous analytica(7)

The chelating polymers containing varios ligands and have reported that they are more practical than gel-type resins for the removal and recovery of heavy metal ion from industrial waste(8), and recovery of uranium from sea water ect.(9,10)

EXPERIMENTAL

1 – Reagents and physical measurement

The reagents used in this work were purchased from Fluka − Dehenge Chemical Co. These reagents were of high purity and used without further purification.

IR spectra were recorded as KBr discs in which the studied compound amounts at 5 mg per 500 mg KBr using a Shimadzu 8400 FTIR Spectrophotometer in range (4000 − 400)cm $^{-1}$. Thermogravimetric analysis and derivative of the thermogravimetric (DTG) behavior of chelates polymers and ligand polymer was evaluated by means of the Stanton Redcroft TG-760 series on samples weighting about 65 mg at 20 °C / min heating reat in the oxygen atmosphere, up to 1000 °C.

2 – Preparation

a - PREPARATION OF COPOLYMER

The p-hydroxybenzoic acid-urea-formaldehyde(PUF) copolymer was preparted by mixing of the monomers corresponding their reaction ratio as reported of p-hydroxybenzoic acid (0.2 mol, 27.624 gm), urea (0.2 mol, 12 gm), 37 %aq formaldehyde (0.4 mol, 12 gm), and (2 M) HCl (200 ml) was heated at 100 °C on an oil bath for 5 hours with stirring. The solid product obtained was immediately removed from the flasks soon as the reaction period was over. It was washed with cold water, dried, and powdered. The powder was repeatedly washed with hot water to remove unreacted monomers. The air dried copolymer was Soxhlet extracted with ether to remove the excess of p-hydroxybenzoic acid and p-hydroxybenzoic acid formaldehyde copolymer which might be present along with (PUF) copolymer. For further purification it was dissolved in 8% NaOH and filtered. The yellowish product was precipitated by gradual addition of 1:1 (v/v) concentrated HCl /water with constant stirring. The copolymer was filtered, washed with hot water, dried in air, and kept in vacuum over silica gel .

b -PREPARATION OF CHELATES

A solution of (1.86 gm, 0.01 mol) (PUF) copolymer in DMF (100 ml) and filtered through a G_2 grade sintered funnel was added to corresponding nitrate Strontium nitrate(1.058 gm 0.005 mol) , Barium nitrate(1.058 gm 0.005 mol) and calcium nitrate (1.180 gm 0.005 mol) were dissolved in (100 ml) DMF with a slight amount of water. A solid products precipitated at 5.5 pH when the saturated solution of sodium acetate in water was added in an adequate quantity. The product were digested for some time on water bath. They were filtered and washed with DMF, large amount of hot water, and acetone. The air –dried chelate was finely powdered kept in a vacuum desiccator over silica gel.

3. RESULTS AND DISCOSSION

3 .1 The comparison of the IR spectra of the chelates polymers { p-hydroxybenzoic acid-urea-formaldehyde chelat with Ca^{II} or Sr^{II} or Ba^{II} }and ligand polymer (PUF) copolymer Figs [7, 8, 9, and 10] revealed that the spectra of polymeric chelates do not significantly differ from each other, but they differ from that of the ligand in some characteristic frequencies . A broad band obtained in the(3367 cm^{-} ,3383 cm^{-} ,3394 cm^{-} and 3376 cm^{-}) in the spectrum of polymeric chelates is much less broad than in the ligand , indicating the absence of hydrogen bonding in the chelates and the participation of phenolic −OH in the coordination , The bands exhibited in the free copolymer at 1572 cm^{-} and 1448 cm^{-} are due to ν_s C−O in (COO^{-}) and ν_{as} C−O in (COO^{-}) respectively. The shifted for the chelates to lower frequencies (1550 cm^{-}, 1545 cm^{-} and 1560 cm^{-}) and (1390 cm^{-} , 1385 cm^{-} and 1410 cm^{-}) respectively indicating the ionization of — COOH and the (COO^{-}) involvement in coordination. A band at 1687 cm^{-} due toν C=O in the (-COOH group)of ligand (11) . Abroad band containing several inflecations appearing in the region (2400 cm^{-} −3600 cm^{-}) may be assigned to theν −OH of polymeric associated phenolic group (12). The bands appeared at (922 cm^{-} ,925 cm^{-} and 915 cm^{-}) which may be attributed to νO–H deformation (out of plan) and the shifting of δ O–H band in all chelates towards higher frequns are afurther indication to involvement in the coordination (table 1). 1, 2, 3, 5 tetrasubstitution (12) of the aromatic acid ring is recognized from bands appearing at (773 cm^{-} , 775 cm^{-} , 775 cm^{-} and 772 cm^{-}) due to δ −CH (out of-plane) and (1122 cm^{-} , 1120 cm^{-}, 1122 cm^{-} and 1130 cm^{-}) due to δ −CH (in-plane) and bands appearing at (630 cm^{-} , 640 cm^{-}, and 636 cm^{-}) due to δ −NH (out of plane) of amide of ligand and all chelates suggesting the absence of coordination through the amide group.

3 .2 Dynamic methods associated with weight change:

(a) THERMOGRAVMETRY (TG) is a technique which records the weight of a substance in an environment heated or cooled at a controlled rate as a function of time or temperature

(b) DERIVATIVE THERMOGRAVIMETRY (DTG) is a technique which yields the first derivative of the thermogravimetric curve with respect to either time or temperature .The possibility of coordinated water molecules as suggested from IR spectra is confirmed by TG data.

The TG and DTG curves for the chelates polymers and ligand polymer are given in the Figs [3, 4, 5, and 6] . The analysis of TG data (table 2) indictes that the polymeric chelates decompose in the two stage. In all the chelates the rate of decomposition in the first stage is slow as compared with the second stage. Decomposition is complete at about (600 °C) in all chelates . The possibility of coordinate water molecules as suggested from IR spectra is confirmed by TG. Weight loss in $Sr^{(II)}$, $Ba^{(II)}$, and $Ca^{(II)}$ chelates in the range 150-250 °C may be due to the two water molecules(6,13). Since the lossof water molecule is abserved at higher temperature,it may be attributed to coordinated water molecules and not the water of crystallization.' The observed weight loss is a little higher than required in this region and this may be due to some other chain degradation reactions involved in pyrolysis of the chelates. The $Sr^{(II)}$ chelate in the above temperature range seems to be more stable.

The following structure fig. [2] may be proposed for the chelates polymers(6) .

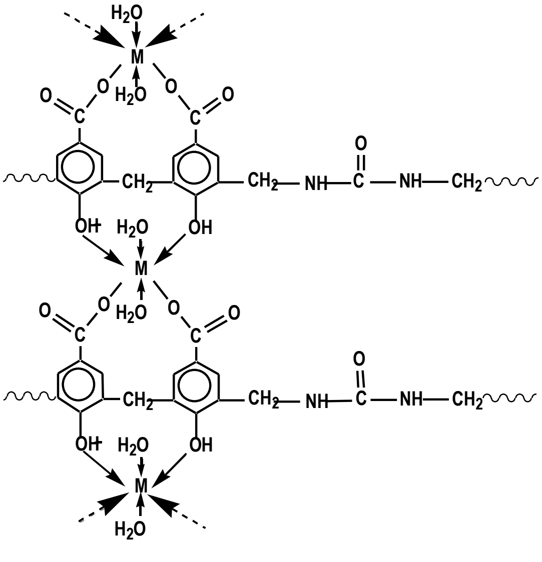


fig. [2] p-hydroxybenzoic acid-urea-formaldehyde copolymer chelate with (M)

M = Ca^{II} or Sr^{II} or Ba^{II}

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Groups	*Ligand*	*Chelate with Sr(II)*	*Chelate with Ba(II)*	*Chelate with Ca(II)*

Table (1)

IR spectral data of ligand and chelats polymers

ν O-H polymeric	3367 Cm^{-}	3383Cm^{-}	3394Cm^{-}	3376Cm^{-}
ν C =O of COOH	1687 Cm^{-}			
ν-CH aromatic	1615 Cm^{-}	1610 Cm^{-}	1610Cm^{-}	1615 Cm^{-}
ν_s C-O in CO_2^{-}	1572 Cm^{-}	1550Cm^{-}	1545Cm^{-}	1560Cm^{-}
ν_{as} C-O in CO_2^{-}		1390Cm^{-}	1385Cm^{-}	1410Cm^{-}
δ -CH(in plan) aromatic	1122 Cm^{-}	1120Cm^{-}	1122Cm^{-}	1130 Cm^{-}
ν O - H deformatin (out of plan)		922 Cm^{-}	925 Cm^{-}	915 Cm^{-}
δ -CH (out of plan) aromatic	773 Cm^{-}	775 Cm^{-}	775 Cm^{-}	772 Cm^{-}
δ N-H (out of plan) of Amid	630 Cm^{-}	640 Cm^{-}	636 Cm^{-}	636Cm^{-}

Polymer	T_1°C	%Wt at T_1	T_2°C	%Wt at T_2	T_3°C	%Wt at T_3

Table (2)

Thermal dataof the ligand and chelates with

Ca^{II} , $Sr^{II}$and Ba^{II}

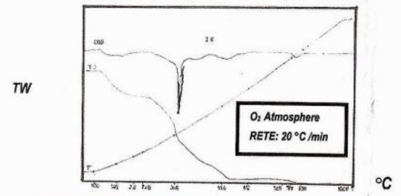
		remain	lose		remain	lose		remain	lose
1	120	83.72	16.28	269	59.42	40.58	562	18.03	81.97
2	154	92.11	17.89	346	49.71	50.29	516	6.81	93.19
3	139	94.22	5.78	340	62.47	37.53	642	16.82	83.82
4	143	96.11	3.89	316	77.95	22.95	499	17.85	92.15

1 = Ligand *p-hydroxybenzoic acid-urea-formaldehyde copolymer*

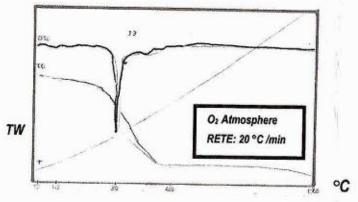
p-hydroxybenzoic acid-urea-formaldehyde chelat with Ca^{II}
2 =

3 = ***p-hydroxybenzoic acid-urea-formaldehyde chelat with Sr^{II}***

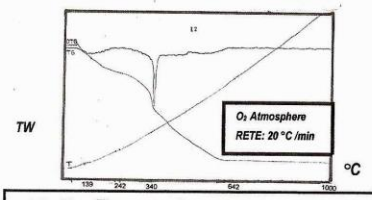
4 = ***p-hydroxybenzoic acid-urea-formaldehyde chelat with Ba^{II}***



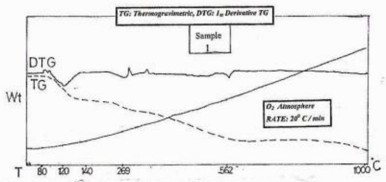
Fig(3) **Thermogravimetric analtsis of polymer Chelate p- hydroxybenzoic acid ureaformaldehyde with Ca^{II}**



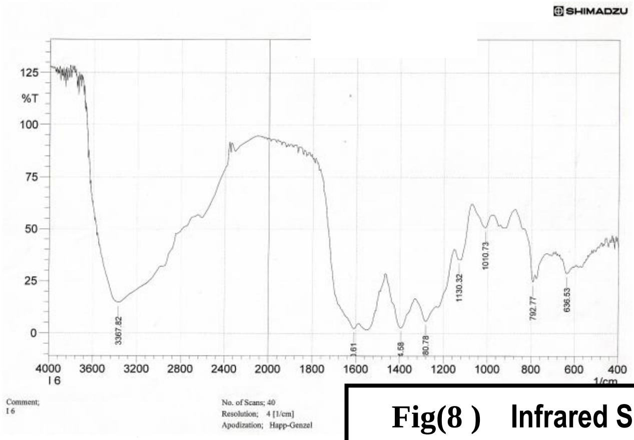
Fig(4) **Thermogravimetric analtsis of polymer Chelate p- hydroxybenzoic acid ureaformaldehyde with Ba^{II}**



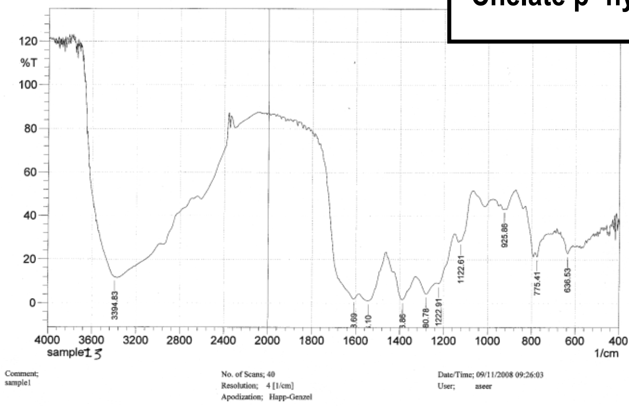
Fig(5) **Thermogravimetric analtsis of polymer Chelate p- hydroxybenzoic acid ureaformaldehyde with Sr^{II}**

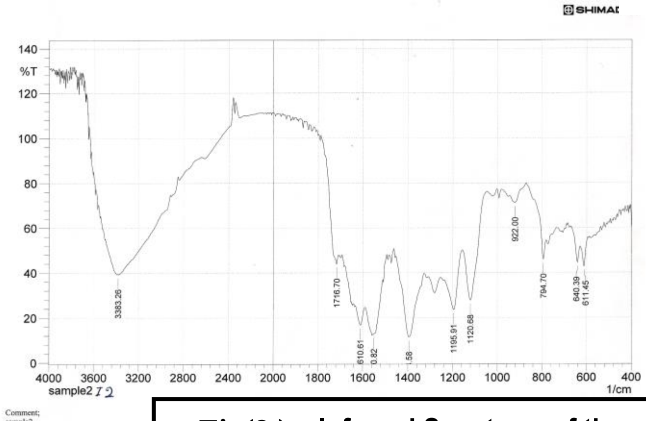


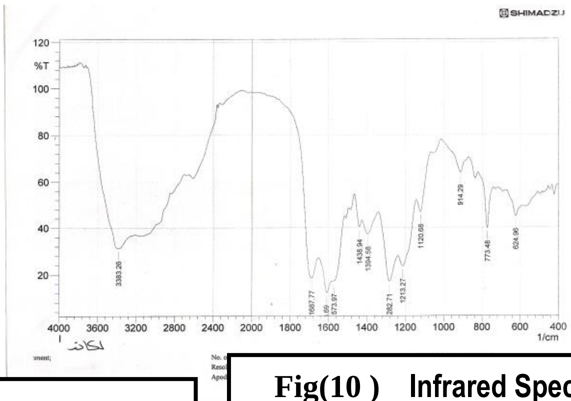
Fig(6) **Thermogravimetric analtsis of polymer Ligand p- hydroxybenzoic acid ureaformaldehyde**



Fig(8) Infrared Spectrum of the polymer:
Chelate p- hydroxybenzoic acid ureaformaldehyde with Ba







Fig(9) Infrared Spectrum of the polymer :
Chelate p- hydroxybenzoic acid ureaformaldehyde with Sr^{II}

Fig(10) Infrared Spec
Ligand p- hydroxybenzoic

Fig(7) Infrared Spectrum ofthe polymer :
Chelate p- hydroxybenzoic acid ureaformaldehyde with Ca^{II}

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تحضير وتشخيص كو بوليمرات يوريا –فورمالدهايد باراهايدروكسي حامض البنزوك المخلبية مع الأيونات الفلزية

($Ca^{(II)}$,$Sr^{(II)}$,$Ba^{(II)}$)

م.د.باسمه عبد الحسين زيدان
جامعة بغداد
كلية التربية أبن الهيثم قسم الكيمياء
العراق – بغداد – الأعظمية P. O.4150

الخلاصة

تم تحضير كوبوليمر يوريا – فورمالدهايد بارا – هيدروكسي حامض البنزويك (PUF) بطريقة التكثيف وبوجود حامض HCl ، كذلك حضرت كوبوليمراته مع الايونات الفلزيه Ba^{+2}, Sr^{+2} ,Ca^{+2} بطرائق تلائم العمل في الأستخدامات الصناعية المقاومة للحراره . شخص الكوبوليمر المحضر (PUF) ومعقداته مع الأيونات الفلزيه المذكورة بأستخدام مطيافيه تحت الحمراء IR والتحليل الحراري TGA والتحليل الحراري التفاضلي DTG التي تؤشر الثبات الحراري العالي للمركبات المحضرة . ومن معطيات هذه التقنيات تم افتراض الشكل ثماني السطوح للكوبوليمرات المحضره