



Thermo Gravimetric, Antimicrobial and Ir-Spectroscopic Studies of Alkali Metal Complexes With the Schiff Base Isonitroso P-Chloroacetophenone

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Abstract- Complexes of Alkali metals using the Schiff base Isonitroso-p-chloroacetophenone (p-CIHNAP) have been synthesized. These complexes were studied on the basis of elemental analysis, TGA and DTA properties, IR spectral studies and antimicrobial activity. They were assigned by the general formula $M(p-CIINAP)_2$ (where M=alkali metals such as K, Rb and Cs)

Keywords- Schiff's bases, IR spectroscopy, TGA, DTA techniques and antimicrobial properties.

Introduction:

Many coordination compounds are useful in chemical, biological and thermochemical sciences ^{1,2}. The Schiff base Isonitroso phenyl-2-propanone have been used in the synthesis of transition metal complexes. ^{3,4} Some transition metal complexes were also been synthesized using novel Schiff base tetra dentate thiazole and their antimicrobial study have been performed ⁵. The Ligand p-methyl Isonitrosoacetophenone (HIMP) have also been used for few analytical applications ⁶. The ligand p-Chloroisonitrosoacetophenone was also been studied for few transition metals. ⁷ However, Infra Red spectroscopic studies of the complexes of Potassium, Rubidium and Cesium with p-Chloroisonitrosoacetophenone have not been reported so far. Present paper describes synthesis and characterization of complexes of Potassium, Rubidium and Cesium on the basis of Thermo gravimetric, antimicrobial and Infra Red spectroscopic techniques.

Experimental

All the chemicals were purified by using the methods given by Vogel ⁸. The ligand p-Chloroisonitrosoacetophenone has been synthesized by the procedure described by Muller and Pechmann ⁹. The crude product has been recrystallized from benzene. Its melting point was determined by using the Rast method. It was found to be equal to 158^o C.

Synthesis of K (CIINAP)₂Complex-A solution of Potassium Chloride was prepared by dissolving 0.755 g solid KCl in a minimum amount of distilled water. Similarly a solution of p-Chloroisonitrosoacetophenone was also prepared by dissolving 3.670 g p-HCIINAP in a minimum quantity of alcohol. Both these saturated solutions were mixed together. A pH of above mixture was maintained at 6.5 by adding few drops of conc. HCl. This mixture was refluxed on a water bath for 10 hours by applying a water condenser. The resultant mixture was kept in vacuum desiccators





for 10-11 hours. A pale yellow colored Potassium salt of p-ChloroIsonitrosoacetophenone was precipitated out. It was filtered, washed with alcohol, recrystallized from ether and dried in air. Then it was subjected to melting point determination and percentage compositions of the elements Potassium, Carbon, Hydrogen, Nitrogen and Chlorine present in it.

Synthesis of Rb (ClINAP)₂ Complex-Rubidium Chloride solution was prepared by dissolving 1.209 g solid RbCl in a minimum amount of distilled water. Similarly 3.670 g of p-HClINAP was also dissolved in a minimum quantity of alcohol. Both these saturated solutions were mixed together. A pH of above mixture was maintained at 6.5 by adding few drops of conc. HCl. This mixture was refluxed on a water bath for 10 hours by applying a water condenser. The resultant mixture was kept in vacuum desiccators throughout the night. A brown colored Rubidium salt of p-ChloroIsonitrosoacetophenone was precipitated out. It was filtered, washed with alcohol, recrystallized from ether and dried in air. Then it was subjected to melting point determination and percentage compositions of the elements Rubidium, Carbon, Hydrogen, Nitrogen and Chlorine present in it.

Synthesis of Cs(p-ClINAP)₂ Complex-A saturated solution Cesium Chloride was prepared by dissolving 1.950 g solid CsCl in a minimum quantity of distilled water. Similarly 3.670 g of p-ChloroIsonitrosoacetophenone was dissolved in a minimum quantity of alcohol. Both these solutions were mixed together. A pH of above mixture was maintained at 6.5 by adding few drops of conc. HCl. The above mixture was heated on a water bath for 9 hours by applying a water condenser. After heating, the resultant mixture was kept in vacuum desiccators for 14-15 hours. A dark brown colored complex Cesium salt of p-ChloroIsonitrosoacetophenone was precipitated out. It was filtered, washed with alcohol and recrystallized from ether and dried in air. The melting point of the complex was determined using electrically heated melting point apparatus and then analyzed for the elements Cesium, Carbon, Hydrogen and Nitrogen and Chlorine. (Table no.1)

Result and Discussion:

Molecular weight determination and Chemical analysis data (Table no.1) indicated that the complexes of alkali metal ions with p-ChloroIsonitrosoacetophenone (p-HClINAP) may be represented by the molecular formula $M(p\text{-ClINAP})_2$, where M = alkali metal ions such as K, Rb and Cs. From the molar conductance values (1-80 mho) of these complexes in Nitrobenzene it was observed that all the complexes were non-electrolytic in nature but their electrolytic character have been gradually increased from Potassium to Cesium.¹⁰

IR spectra of the Ligand p-HClINAP and its complexes with K Rb and Cs metals

A small amount pure and dry complex of potassium, rubidium and cesium was sandwiched in KBr pallets. The IR spectra of above complexes and the ligand were examined in the region 4000-400 cm^{-1} . The spectra of these complexes were practically identical. Frequencies of some significant bands of free ligand and its





alkali metal complexes are given in Table 2. In the IR spectra of the Ligand, a spectra due to $\nu(\text{O-H})$ of oxime group was observed at 3220 cm^{-1} but in the IR spectra of complexes of K, Rb and Cs, the spectra due to $\nu(\text{O-H})$ of oxime group was absent. This may be due to the replacement of oxime proton by metal ion during the formation of complexes¹⁰. It was observed that, in the IR spectra of free ligand a band was observed at around 3220 cm^{-1} is known to be lowered due to the hydrogen bonded OH stretching^{12,13} (Figure.1). The IR spectra of $\text{K}(\text{p-ClINAP})_2$, $\text{Rb}(\text{p-ClINAP})_2$ and $\text{Cs}(\text{p-ClINAP})_2$ complexes (Figure.2-4) have shown the bands at 1650 and 1630 cm^{-1} respectively are assigned to the perturbed $\nu\text{C=N}$ stretching vibration involving bonding through Nitrogen donor atoms. In the above metals complexes, the bands due to $\text{N}\rightarrow\text{O}$ stretching frequencies were appeared at around 1350 and 1350 cm^{-1} respectively. Sharp peaks which were appeared in the range $1400\text{-}1300\text{ cm}^{-1}$ are characteristics of N-O stretching mode in aromatic ring¹⁴

The IR spectra which were observed in between $900\text{-}960\text{ cm}^{-1}$ due to N-O vibrations at lower range than $\text{N}\rightarrow\text{O}$ is generally observed in simple Oximes synthesized by Palm and Werbin¹⁵. A band due to $\nu\text{C=O}$ seen at 1670 cm^{-1} in p-HClINAP was absent in all the complexes indicating a successful attachment of the carbonyl oxygen to metal ion. In above alkali metal complexes, the $\nu\text{C=N}$ band appeared in the region of $1670\text{-}1630\text{ cm}^{-1}$ while in ligand $\nu\text{C=N}$ frequency appeared at 1610 cm^{-1} . Shift of bands towards the higher field side indicated wider delocalization of electronic charge in the newly formed chelate ring.

The IR spectra of free ligand p-HClINAP have shown a broad band in the region $3250\text{-}3200\text{ cm}^{-1}$ due to hydrogen bonded OH of $=\text{NOH}$. This band was due to OH stretching frequency. This is an important feature of infrared spectra of alkali metal complexes.

In these complexes, some new peaks were also observed in the range $1370\text{-}1270\text{ cm}^{-1}$. These new peaks appeared in these complexes were due to $\text{N}\rightarrow\text{O}$ stretching frequencies. The appearance of these $\text{N}\rightarrow\text{O}$ frequencies at higher side may be due to the presence of intermolecular or intra molecular hydrogen bonding in the ligand. The shift of N-O bands in the region $1370\text{-}1270\text{ cm}^{-1}$ indicated increase in double bond character of the N-O linkage which was suggested six member ring structures. It is significant to note that, metal complexes of p-HClINAP are in coordination only through the oxime Oxygen or Nitrogen atom.

Hence it was concluded that, in the IR spectrum of above ligand, a broad band appeared in the range $3300\text{-}3200\text{ cm}^{-1}$ was due to the hydrogen bonded OH of $=\text{NOH}$. Weak broad band appeared in the range $3550\text{-}3500\text{ cm}^{-1}$ were due to hydrogen bonded OH of $=\text{NOH}$ of one of the ligand molecules. The order of these bands represented that, the hydrogen bonding have been increased from Potassium to Cesium. This is a structure forming feature of alkali metal complexes of the type ML.HL ¹⁵. From the observations of decomposition temperatures of these complexes, it was also confirmed that the strength of hydrogen bond increases with increase in the decomposition temperatures of complexes.

In the K, Rb and Cs metal complexes of p-Chloro Isonitrosoacetophenone, vibrational frequency of C=N band appeared in the region $1670\text{-}1630\text{ cm}^{-1}$ while the





ligand frequency for C=N band appeared at 1610 cm^{-1} . The shift of band towards higher field side indicated the wider delocalization of electronic charge in the newly formed chelate ring¹⁶. The intensity and the shift observed in band positions are in good agreement with the intensity and the shift observed in the band position observed by Percy and Thortan¹⁷.

Antimicrobial properties of the ligand and its complexes with K, Rb and Cs metals

The ligand p-Chloro Isonitrosoacetophenone and its alkali metal complexes with K, Rb and Cs have been tested against antibacterial activity *S. Aureus*, *E. Coli*, *B. Subtilis*, *P. Aeruginosa*, *K. Pneumoniae* and *B. Cereus* and against antifungal activities *F. Oxysporium*, *A. Niger* and *C. Albicans*.

From the results, the complexes of K, Rb and Cs have shown maximum zone of inhibition (table 3 and 4) and hence they were found to inhibit the growth to all tested strains of bacteria and fungi. It may be due to more penetrating power of these complexes to the cell wall of bacteria, which prevent biosynthesis of peptidoglycan or may find better fit at the receptor site as compared to other complexes. Though the ligand p-Chloro Isonitrosoacetophenone has exhibited satisfactory antibacterial and antifungal activity against all the tested strains, its activity was less when compared with these alkali metal complexes and hence it was suggested that, the above ligand cannot be suitable against all the strains. When the synthesized complexes were compared for their antibacterial and antifungal activities against the standard drugs Gentamycin and Miconazole, then it was observed that, none of the synthesized complexes have shown more antibacterial and antifungal activities than these standard drugs.

TGA and DTA properties of the ligand and its complexes with K, Rb and Cs metals

The ligand and complexes were studied on the basis of TGA and DTA techniques. All the complexes were found to be stable at room temperature and they are not associated with water molecules. It was observed that they started losing their weights due to loss of ligand by fragmentation. After heating, they formed corresponding metal oxide.

The thermal stabilities and decomposition temperatures of ligand p-HCIINAP and its alkali metal complexes have been reported using TGA and DTA techniques. All these complexes were found to be very stable at room temperature and water molecules were not associated with them. When these complexes were heated, they started losing their weights by loss in the weight of ligand by fragmentation. After further heating they produced corresponding metal oxides.

All the complexes have shown sharp exothermic peaks in the DTA curves in temperature range 400°C to 700°C . The TGA curves have shown sudden loss in the weights of samples. This shows that, these complexes have been decomposed slowly after the initial decomposition in number of steps till the formation of metal oxide has been completed. (Figure. 5- 6)





When the complex of Potassium with p-ClHINAP was heated, then nearly 80 percent loss in the weight of sample was observed due to its decomposition at higher temp. The endothermic peak in DTA curve was observed at 225°C which indicates the formation of stable compound. The resultant decomposed compound was not stable to heat. The TGA curve has been indicated the gradual decrease in the weight of complex up to 740°C. The complex has produced an oxide of Potassium above 740°C. Some amount of heat was liberated during the decomposition of complex. This was confirmed from the peak area of exotherms of DTA curve. (Figure.5)

Rubidium complex of p-Chloro Isonitrosoacetophenone has shown continuous loss in the weight of sample in between 450-500°C. This is due to the decomposition of complex in this region. A loss in the weight of sample in this temperature range has confirmed the loss of moisture or solvent from the complex. TGA curve of above complex have shown an inflection at 475°C. When the decomposition of the complex was completed, formation of oxide of Rubidium has been observed in the temperature range 500 to 600°C. Strong exotherms in the DTA curve at 480°C have indicated the liberation of some amount of heat. This was confirmed from the peak area of DTA curve. (Figure.6)

The TGA curve of the complex of Cs (p-ClINAP)₂ have indicated continuous loss in the weight of sample up to 500°C due to loss of water molecules from its coordinate sphere. The DTA curve of above complex has shown sharp exotherms at 495°C which indicates that some amount of heat was liberated during the heating of complex. When this complex was further heated, then it decomposed completely at 550°C by forming the oxide of Cesium. (Figure.7)

Table. 1- Analytical data of the alkali metal complexes of p-Chloro Isonitrosoacetophenone

Ligand/Complex	Color	M.P. °C	% C	% H	% N	% M	% Cl
p-ClHINAP	Pale yellow	158	52.01 (52.32)	3.05 (3.29)	7.25 (7.63)	-----	18.95 (19.05)
K(p-ClINAP) ₂	Yellowish Brown	226	47.45 (47.52)	2.40 (2.48)	6.80 (6.93)	9.50 (9.65)	17.42 (17.57)
Rb(p-ClINAP) ₂	Brown	231	42.40 (42.62)	2.10 (2.22)	6.12 (6.22)	18.70 (18.97)	15.65 (15.76)
Cs(p-ClINAP) ₂	Dark Brown	249	38.80 (38.95)	1.90 (2.01)	5.40 (5.63)	26.55 (26.69)	14.20 (14.26)

(Theoretically calculated values are given in parenthesis)

Table. 2-IR spectra of p-HClINAP and its complexes of alkali metals

Assignment	p-ClHINAP	K(ClINAP) ₂	Rb(ClINAP) ₂	Cs(ClINAP) ₂
OH	-----	3509	3509	3510
OH of NOH	3230	-----	-----	-----
C=O	1680	-----	-----	-----
C=N	1616	1642	1642	1644
C-H	-----	1455	1500	1460





N---O	-----	1297	1298	1300
M-N	-----	661	661	660

Table. 3- Antibacterial activity data of p-ClHINAP and its K, Rb and Cs metal complexes(Bacteria along with zone of inhibition in mm)

Ligand/Complex	<i>S.Aureus</i>	<i>E. Coli</i>	<i>B. Subtilis</i>	<i>P. Aeruginosa</i>	<i>K. Pneumoniae</i>	<i>B. Cereus</i>
Ligand	14	12	13	13	12	14
K(ClINAP) ₂	18	16	18	17	18	20
Rb(ClINAP) ₂	19	17	19	18	19	20
Cs(ClINAP) ₂	19	17	19	19	19	20
Gentamycin	22	19	20	20	21	22

Table. 4- Antifungal activity data of p-ClHINAP and K, Rb and Cs metal complexes(Fungi along with zone of inhibition in mm)

Ligand/ Complex	<i>F. Oxysporium</i>	<i>A. Niger</i>	<i>C. Albicans</i>
Ligand	14	13	13
K(ClINAP) ₂	21	20	22
Rb(ClINAP) ₂	22	21	23
Cs(ClINAP) ₂	23	20	22
Miconazole	24	23	24

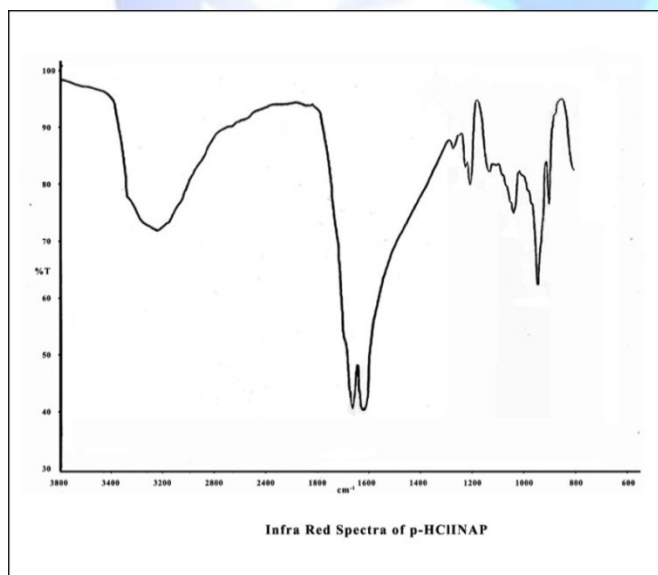


Figure.1

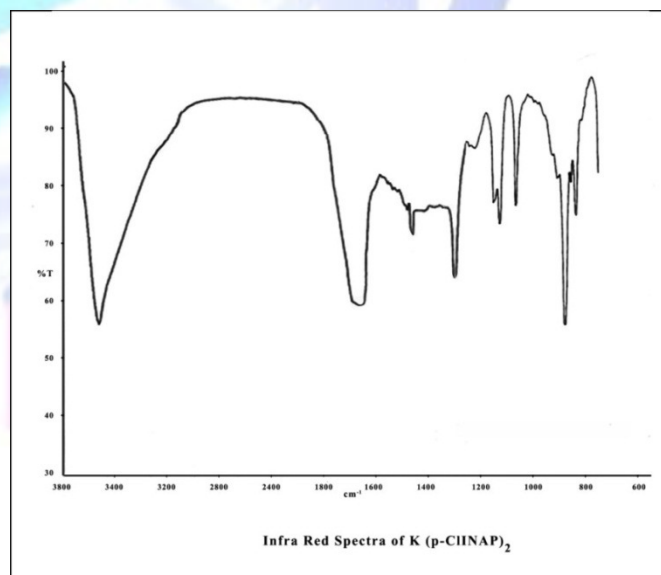


Figure.2



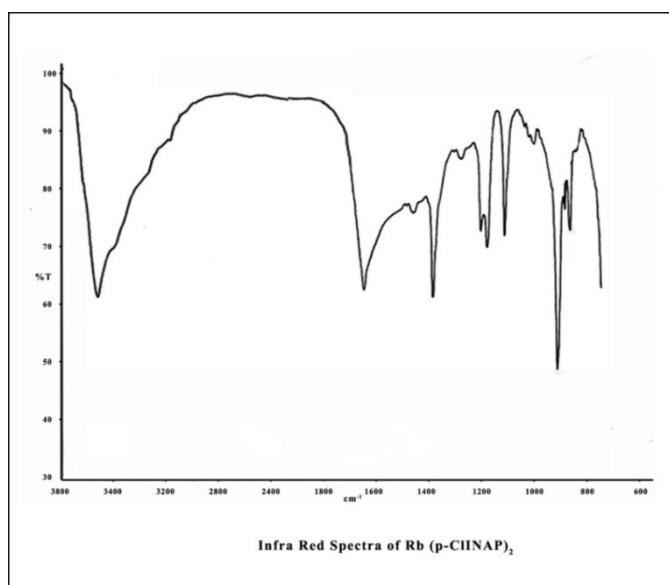


Figure.3

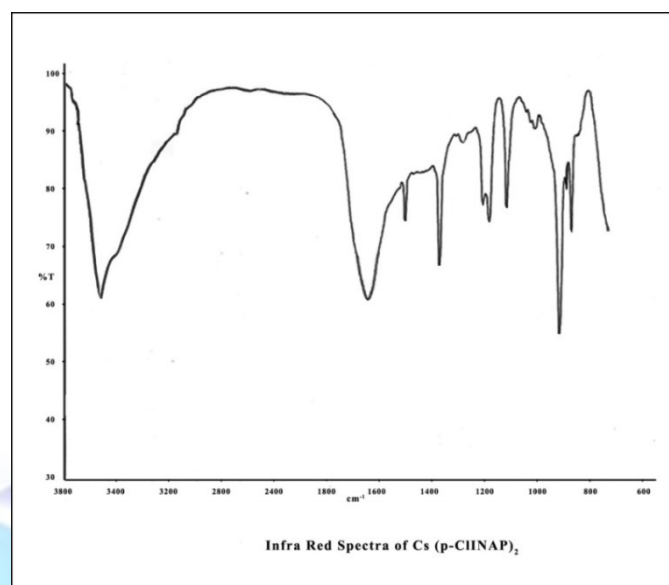


Figure.4

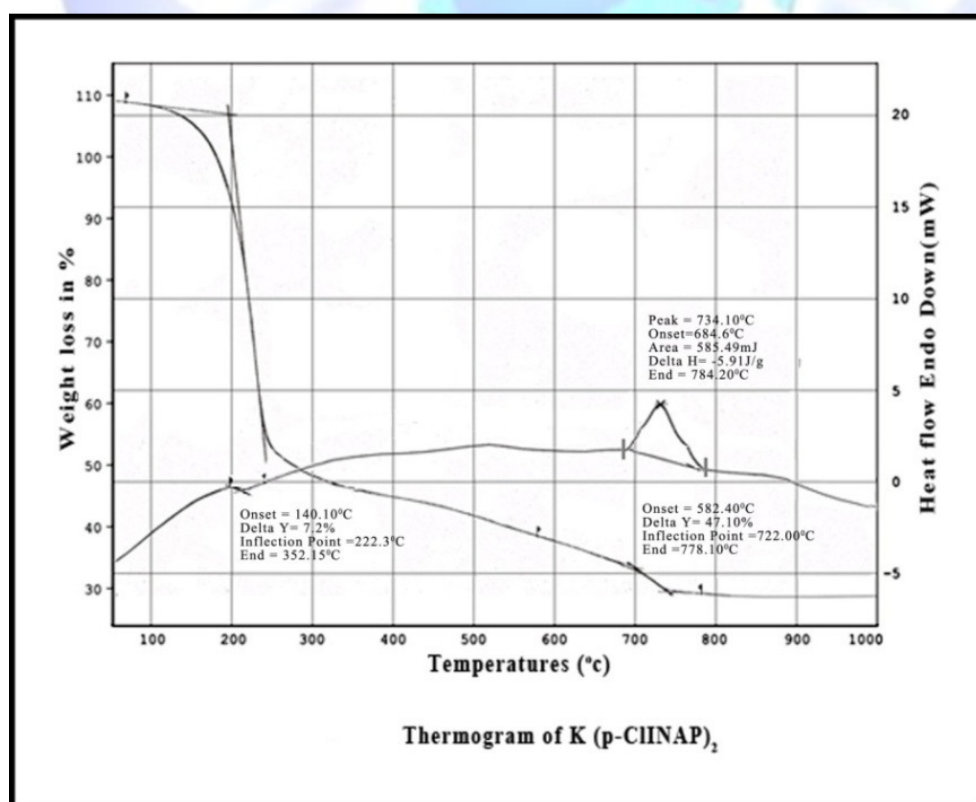


Figure.5



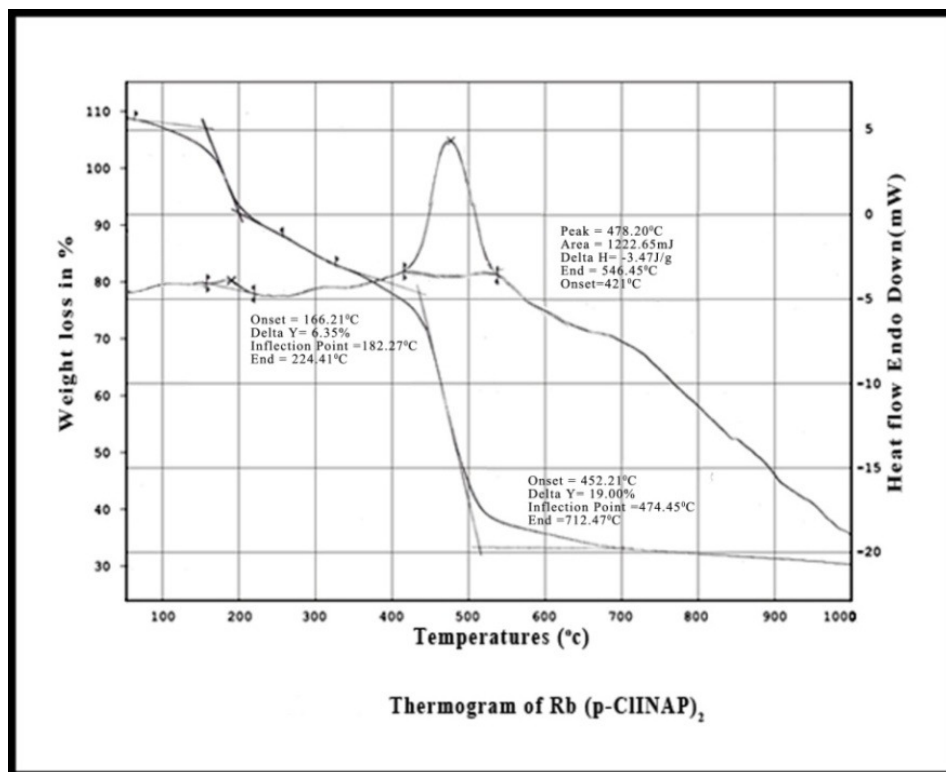


Figure.6

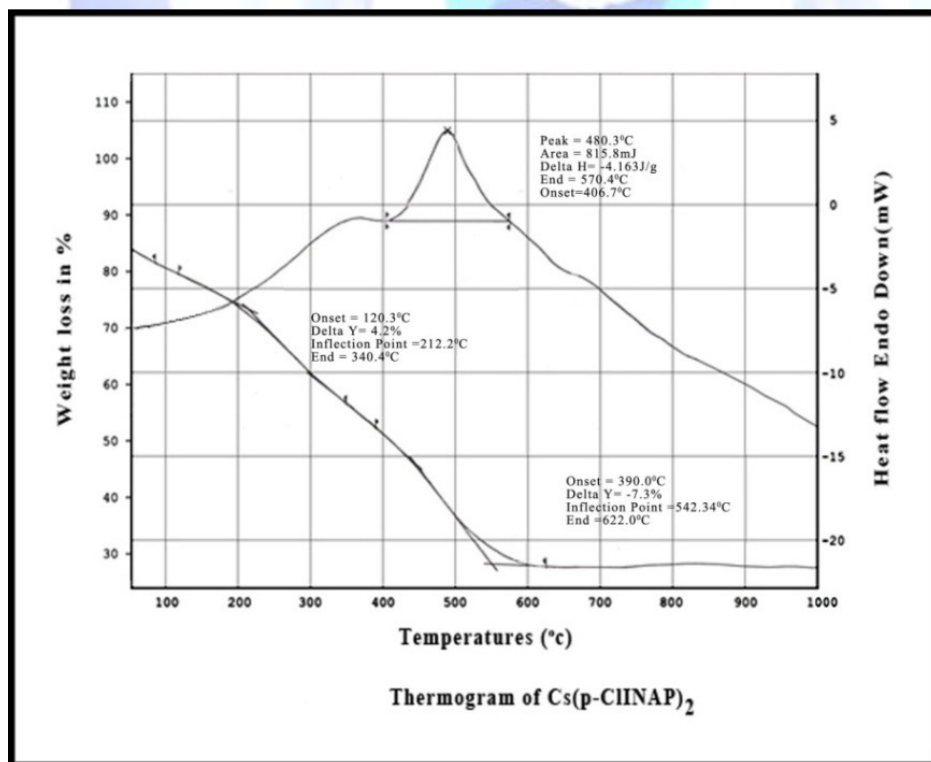


Figure.7



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