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SYNTHESIS, CHARACTERIZATION, X-RAY DETERMINATION AND ELECTROCHEMICAL STUDIES OF NEW NICKEL (II) COBALT (II) AND CHROMIUM (III) COMPLEXES CONTAINING N-PHENYL P-CARBOXYLMALEIMIDE LIGANDS

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ABSTRACT: *Synthesis of n-phenyl p-carboxymaleimide bidentate ligand from acetic anhydride and maleanilic acid was complex with Co(II),Ni(II) and tridentate complex with Cr(III),the complexes have been characterized in the light of element analyses ,spectral(FTIR,Uv-Vis)and electrochemical method using conductmetric ,the resulting nanoparticles were characterized by X-ray diffraction (XRD).*

KEYWORDS: Synthesis, X-Ray, Electrochemical, Nickel (ii), Cobalt (ii), Chromium (iii) N-Phenyl, P-Carboxylmaleimide Ligands

INTRODUCTION

Maleimide is a chemical compound with the formula $H_2C_2(CO)_2NH$. This unsaturated imide is an important building block in organic synthesis. The name is a contraction of maleic acid and imide, the -C(O)NHC(O)- functional group[1]. Maleimides also describes a *class* of derivatives of the parent maleimide where the N*H* group is replaced with alkyl or aryl groups such as a methyl or phenyl, respectively[2-4]. The substituent can also be a polymer such as polyethylene glycol. Human hemoglobin chemically modified with maleimide-polyethylene glycol is a blood substitute called MP4[5].

Maleimide and its derivatives are prepared from maleic anhydride by treatment with amines followed by dehydration.[4] A special feature of the reactivity of maleimides is their susceptibility to additions across the double bond either by Michael additions or via Diels-Alder reactions.

Martials

Dry ethyl ether and acetic anhydride manufacture by BDH, maleic anhydride and nickel chloride manufacture by Aldrich , cobalt chloride manufacture by Alpha, p-aminobenzoic manufacture by Fluka acid and petroleum ether manufacture by Merck ,cyclohexane chromium chloride and sodium acetate manufacture by RDH.

METHOD

Synthesis of p-carboxy n-phenylmaleimide ligand

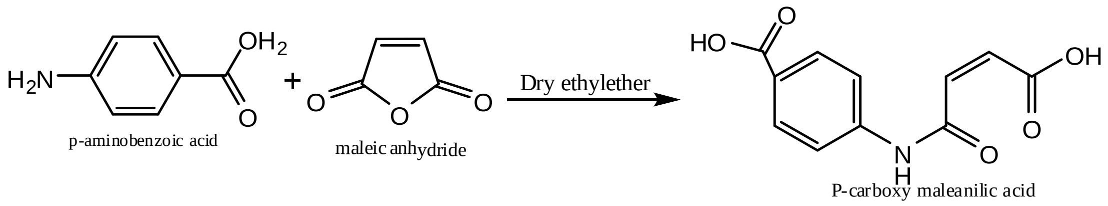
In first step a 5-l. three-necked flask provided with a paddle-type stirrer, a reflux condenser, and a dropping funnel are placed 196 g. (2 moles) of maleic anhydride , and 2.5 l. of ethyl ether[6-11] . The stirrer is started and, when all the maleic anhydride has dissolved, a solution of

182 ml. (186 g., 2 moles) of p-aminobenzoic acid in 200 ml. of ether is run in through the dropping funnel . The resulting thick suspension is stirred at room temperature for 1 hour and is then cooled to 15–20° in an ice bath. The product is obtained by suction filtration. It is a fine, cream-colored powder of p-carboxy maleanilic acid, m.p. 200–201°, suitable for use in the next step without purification. The yield is 371–374 g. (97–98%).

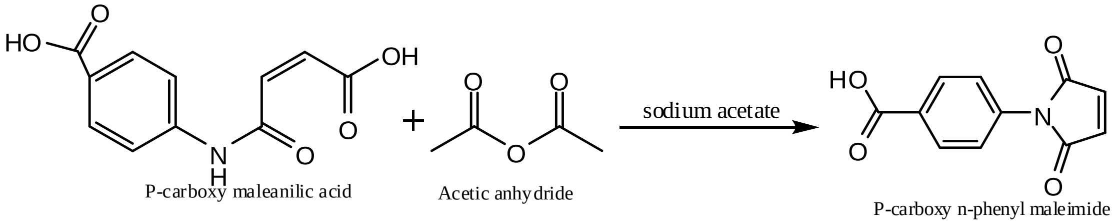
In second step a 2-l. Erlenmeyer flask are placed 670 ml. of acetic anhydride and 65 g. of anhydrous sodium acetate. The p-carboxy maleanilic acid (316 g.), obtained as described above, is added, and the resulting suspension is dissolved by swirling and heating on a steam bath for 30 minutes

The reaction mixture is cooled almost to room temperature in a cold water bath and is then poured into 1.3 l. of ice water. The precipitated product is removed by suction filtration, washed three times with 500-ml. portions of ice-cold water and once with 500 ml. of petroleum ether (b.p. 30–60°), and dried. The yield of crude P-carboxy n-phenylmaleimide is 214–238 g. (75–80%), m.p. 88–89°. Recrystallization from cyclohexane gives canary-yellow needles, m.p. 89–89.8° .

In first step

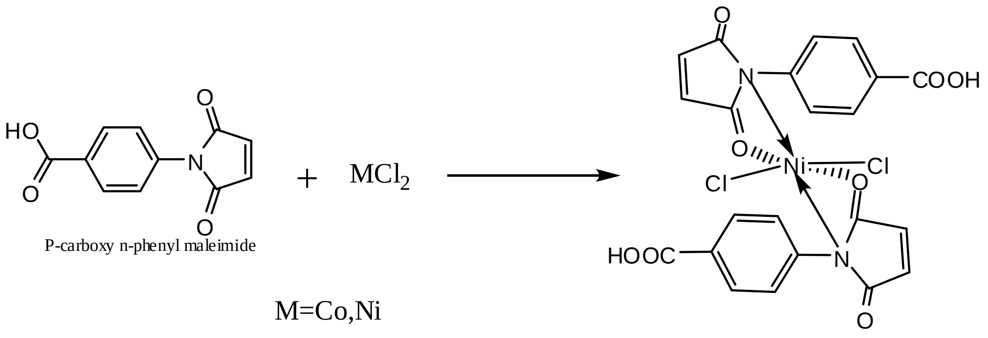


In second step



Synthesis of complex

The aqueous solution of 0.005 mol of metal salts of($CoCl_2$,$CrCl_3$ and $NiCl_2$) was added with constant stirring to an ethanol solution of 0.01mol of p-carboxy n-phenylmaleimide . Reaction mixture was stirred at room temperature for 8 hours. The colored precipitate was obtained .The precipitate was filtered and washed with water and then with methanol and dried over calcium chloride in a desiccator .All the complexes were prepared in 1:2 ratio metal to ligand .



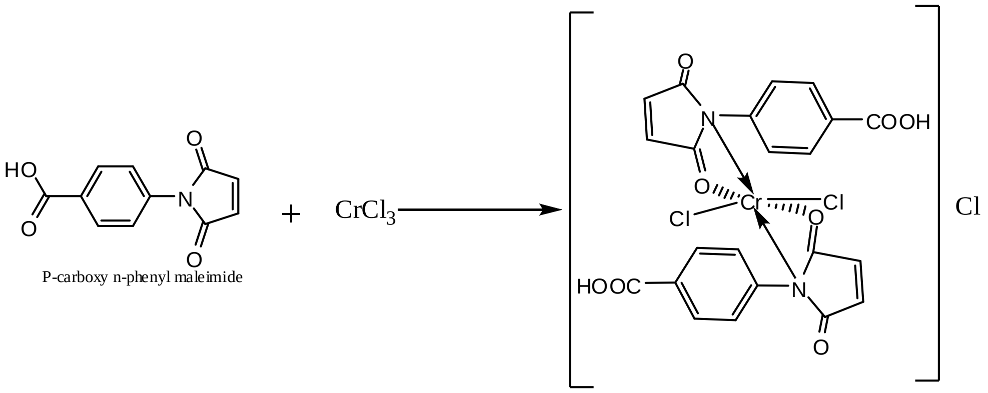
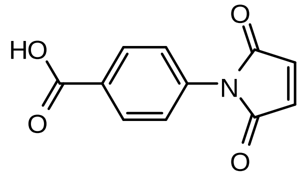
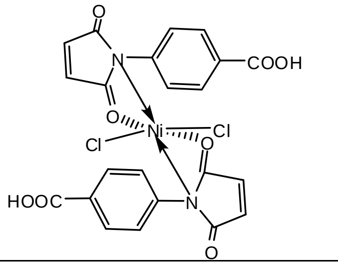
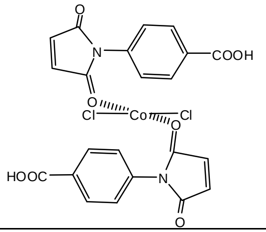
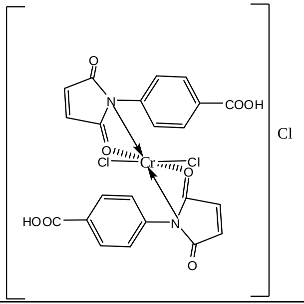


Table (1) show physical properties of complexes

Group	Empirical formula	Color	m.p. °C	Λ $\Omega^{-1}\ cm^{2}\ eq^{-1}$	Suggestion Structure
L	$C_{11}H_7O_3N$	Yellow	88-89.8	0.000452	 P-carboxy n-phenyl maleimide
1	$Ni\ (C_{11}H_7O_3N)_{2}.2Cl$	Pall Green	170-172	0.0133	
2	$Co(C_{11}H_7O_3N)_{2}..2Cl$	Pink	160-162	0.009100	

3	Cr($C_{11}H_7O_3N.2Cl$] Cl	Dark green	250- 252	0.00768	

CHARACTERIZATION AND DISCUSSION

Infrared spectra

From FTIR analysis for p-carboxy n-phenylmaleimide show in the Figure(1)the starching of hydroxyl group of carboxyl in 3101.54cm^{-1},straching band of carbonyl group of carboxyl in 1724.36cm^{-1},starching band of carbonyl group of cycloimide 1680.07cm^{-1} ,when starching of imide group show in 1516.05cm^{-1}.This bands shifted in complex with metal we show hydroxyl group in 3373.50cm^{-1} ,the carbonyl of cycloimide shifted to1681.93cm^{-1}, when starching of imide group show in 1604.77 cm^{-1} Ni complex show in Figure (1a),` but the in Co complex the hydroxyl group shifted to 3408cm^{-1}, the carbonyl of cycloimide shifted to 1680cm^{-1} , when starching of imide group show in1604.77cm^{-1} show in Figure (1b) and in Cr complex the hydroxyl group shifted to 3099.61cm^{-1} ,the carbonyl of cycloimide shifted to1680.63cm^{-1}, when starching of imide group show in 1595.93cm $^{-1}$ show in Figure (1c) .

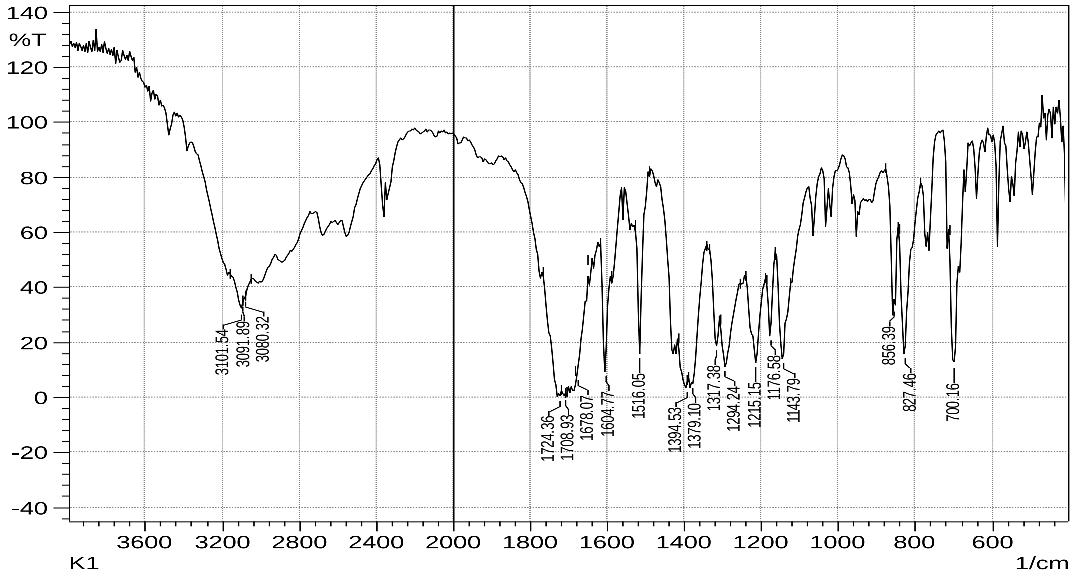


Figure (1) FT-IR of p-carboxy n-phenylmaleimide

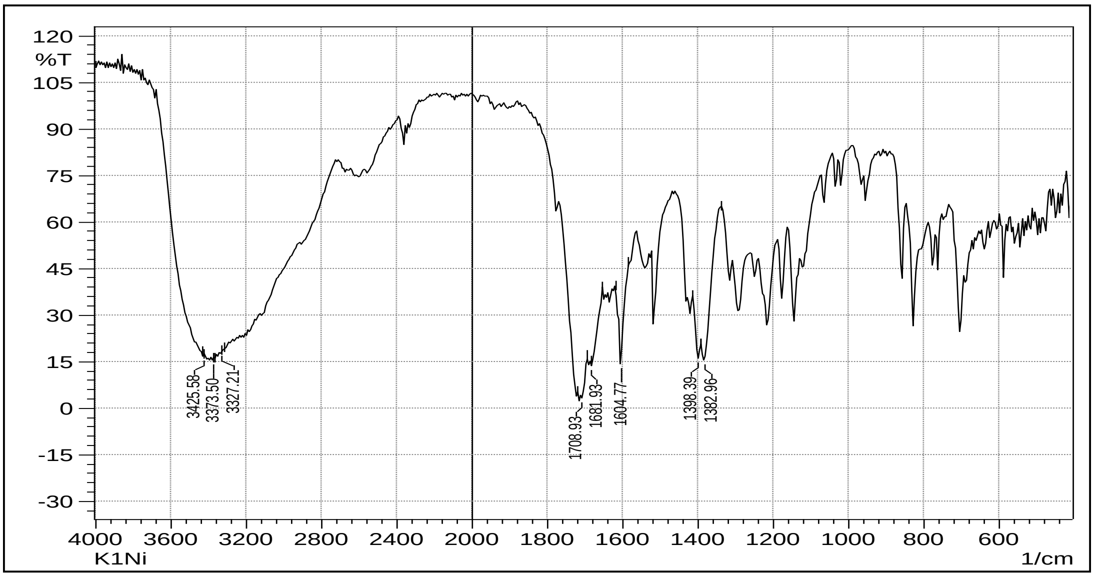


Figure (1a) FT-IR of p-carboxy n-phenylmaleimide complex with Ni

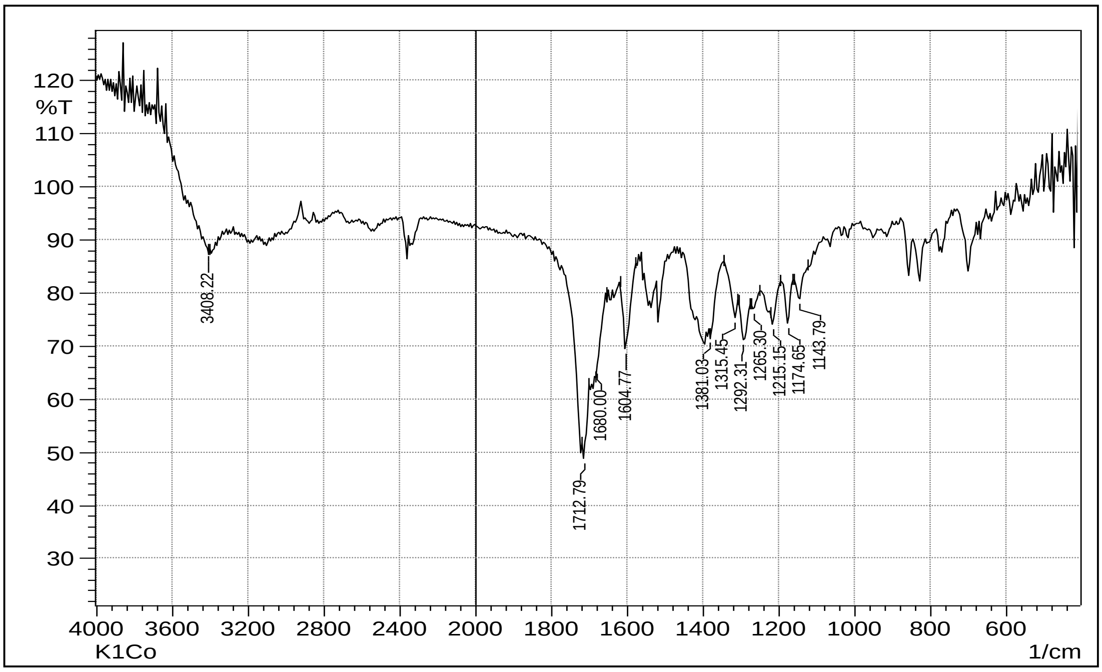


Figure (1b) FT-IR of p-carboxy n-phenylmaleimide complex with Co

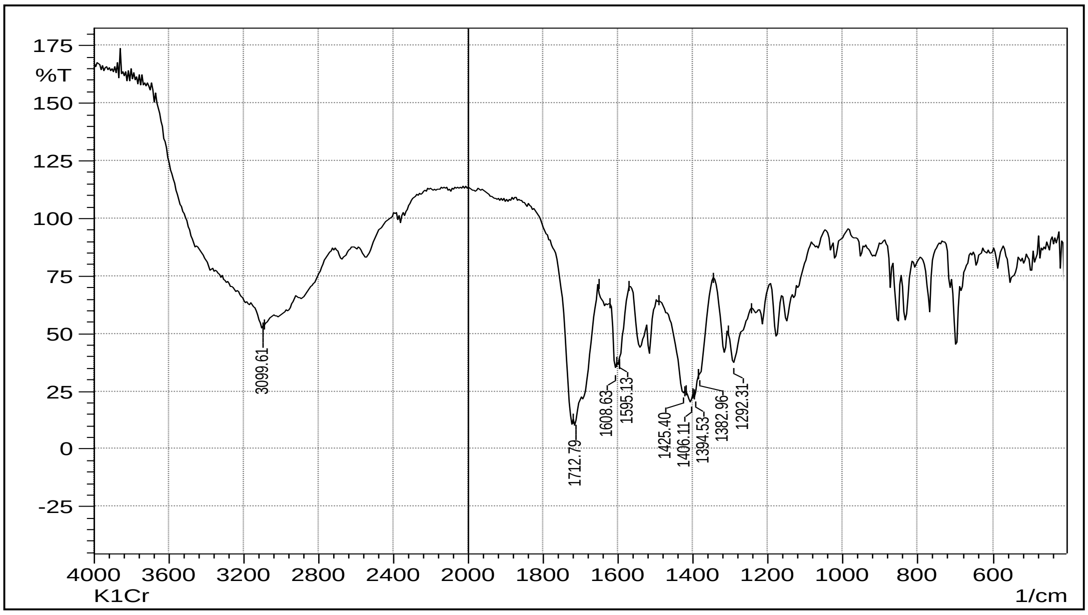


Figure (1c) FT-IR of p-carboxy n-phenylmaleimide complex with Cr

Electronic Spectra

The solution electronic spectra of the ligand and the complexes were recorded in ethanol as solvent in the UV-Visible region in Figure (2) shows the electronic spectra of the p-carboxy n-phenyl maleimide it shows two strong absorption bands at 218 and 226 nm .These bands may be due to $n \longrightarrow \pi^*$ electronic transition involving lone pair of electrons located on the nitrogen atom of maleimide group, and $\pi \longrightarrow \pi^*$ transitions of double bond of hetero ring group.

On complexation these bands were shifted to lower wave length in the complexes bands below300nm are attributed to the intra ligand transition .The electronic spectrum of the Ni-p-carboxy n-phenyl maleimide complex was shown in the Figure (2a) .It exhibits an intense band at 216 nm with a shoulder at 244 nm were assigned to the intermolecular charge transfer of the ligand ($\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$) in the N-C=O. The electronic spectrum of the Co-p-carboxy n-phenyl maleimide complex waxs shown in the Figure(2b) .It shows two intense bands and one less intense shoulder band .The intense bands at 220nm with shoulder at 248nm and another moderate band at 284nm were ascribed to the intermolecular charge transfer of the ligand ($\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$)in the N-C=O group . The electronic spectrum of the Cr-p-carboxy n-phenyl maleimide complex was shown in the Figure(2c) .It shows one intense band at 218nm and another band at 252 nm and at 286 nmwere ascribed to the intermolecular charge transfer of the ligand ($\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$)in the N-C=O group.

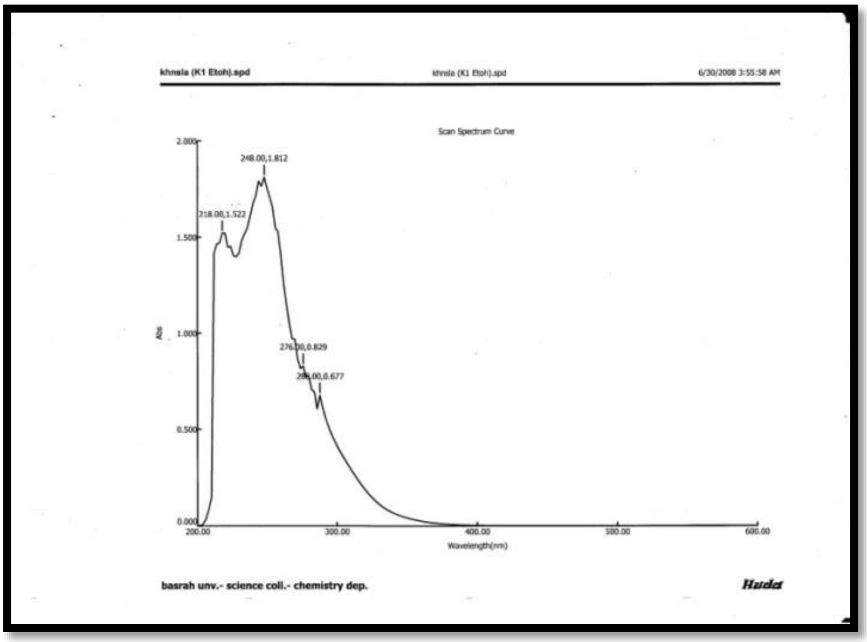


Figure (2) Ultra violet of ligand

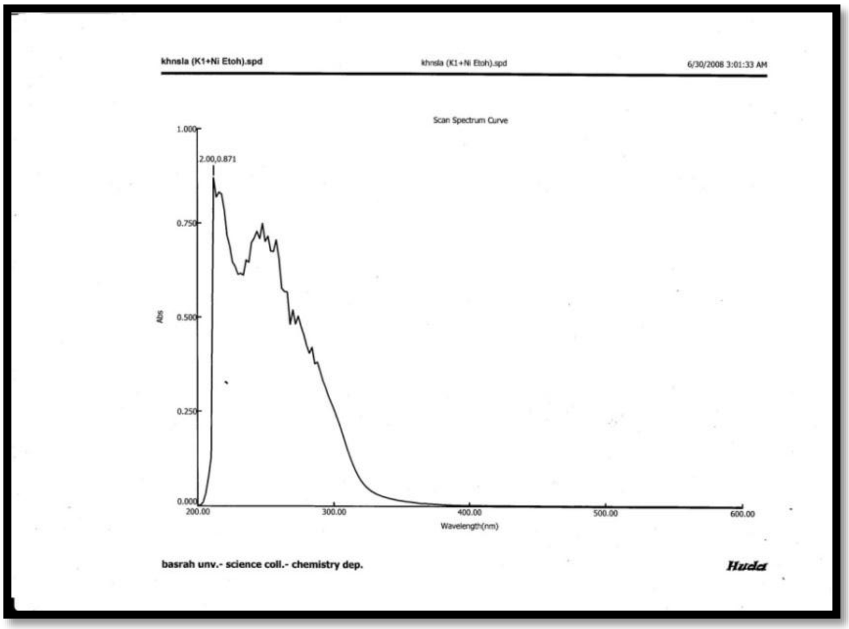


Figure (2a) Ultra violet of ligand with Ni

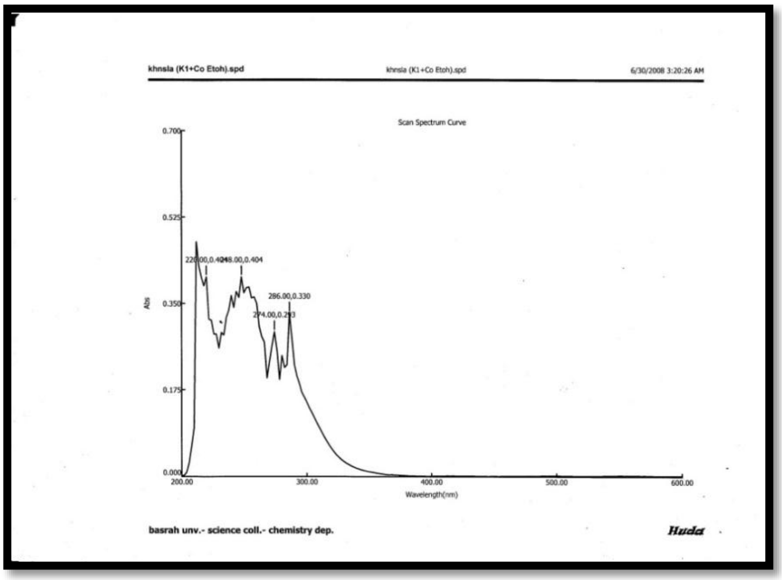


Figure (2b) Ultra violet of ligand with Co

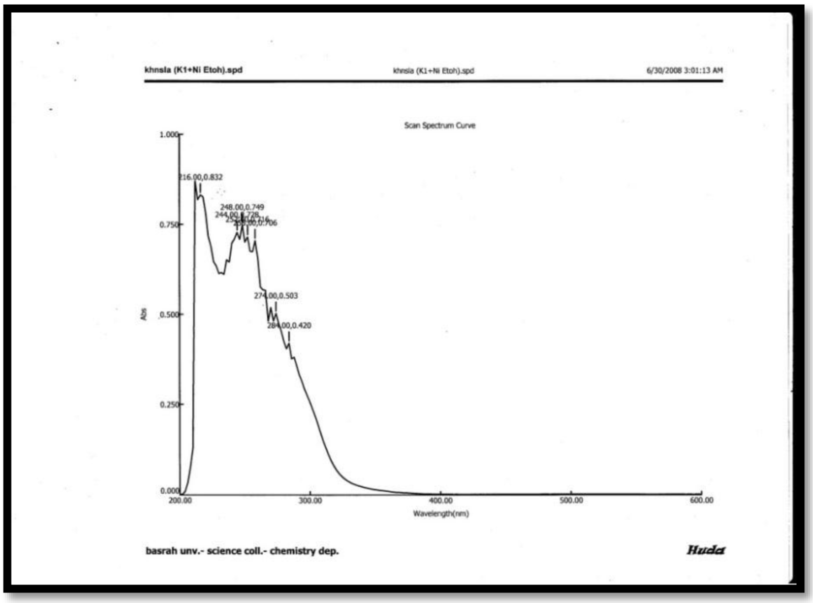


Figure (2c) Ultra violet of ligand with Cr

X-ray Diffraction (XRD)

The energetic x-rays can penetrate deep into the materials and provide information about the bulk structure. Powder XRD (X-ray Diffraction) is perhaps the most widely used x-ray diffraction technique for characterizing materials. As the name suggests, the sample is usually in a powdery form, consisting of fine grains of single crystalline material to be studied. The technique is used also widely for studying particles in liquid suspensions or polycrystalline solids (bulk or thin film materials)[12].

The powder X-ray diffraction data showed identical features with very poor crystallinity .The patterns were qualitative and dispersive in intensity for ligand and complex with Co and Cr metal complexes .The patterns of the complex had been indexed by standard methods.

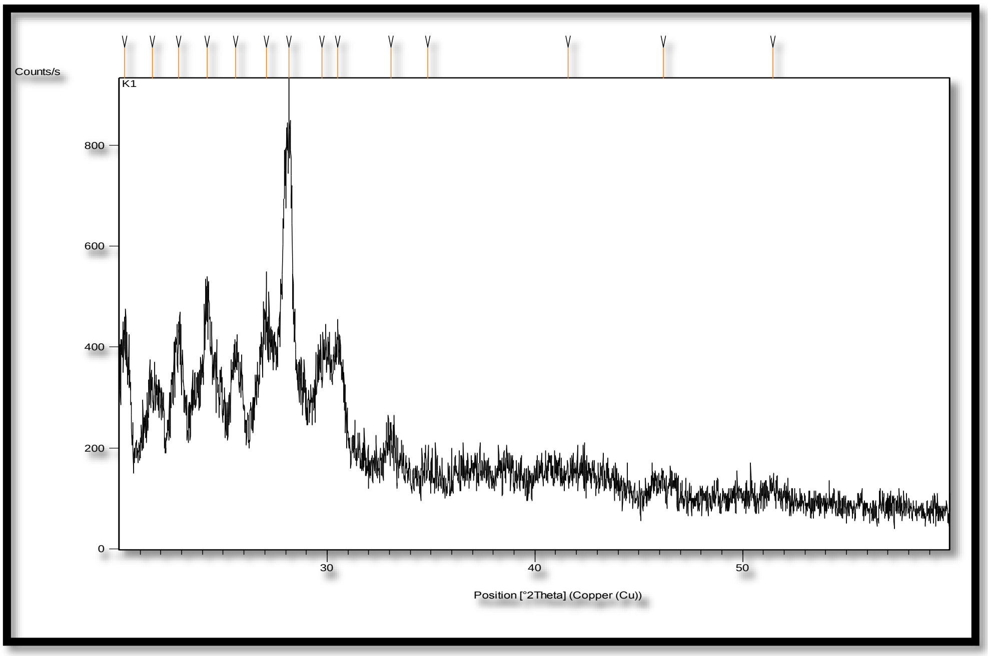


Figure (3) X-ray diffraction data of the Co-p-carboxy n-phenyl malimied complex

Table(2) powder X-ray diffraction data of the p-carboxy n-phenyl malimied

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
20.2513	68.06	0.3936	4.38512	44.12
21.5806	47.33	0.3149	4.11792	30.68
22.8426	66.88	0.4723	3.89319	43.35
24.2382	79.98	0.2362	3.67210	51.84
25.5938	60.75	0.2362	3.48060	39.37
27.0863	75.61	0.3149	3.29210	49.01
28.1597	154.28	0.1968	3.16901	100.00
29.7650	60.09	0.3149	3.00165	38.95
30.5062	66.83	0.4723	2.93039	43.32
33.0746	27.11	0.3936	2.70847	17.57
34.8424	16.87	0.7872	2.57500	10.93
41.6139	15.31	1.8893	2.17031	9.93
46.1781	9.94	0.9446	1.96587	6.44
51.4443	8.41	1.1520	1.77485	5.45

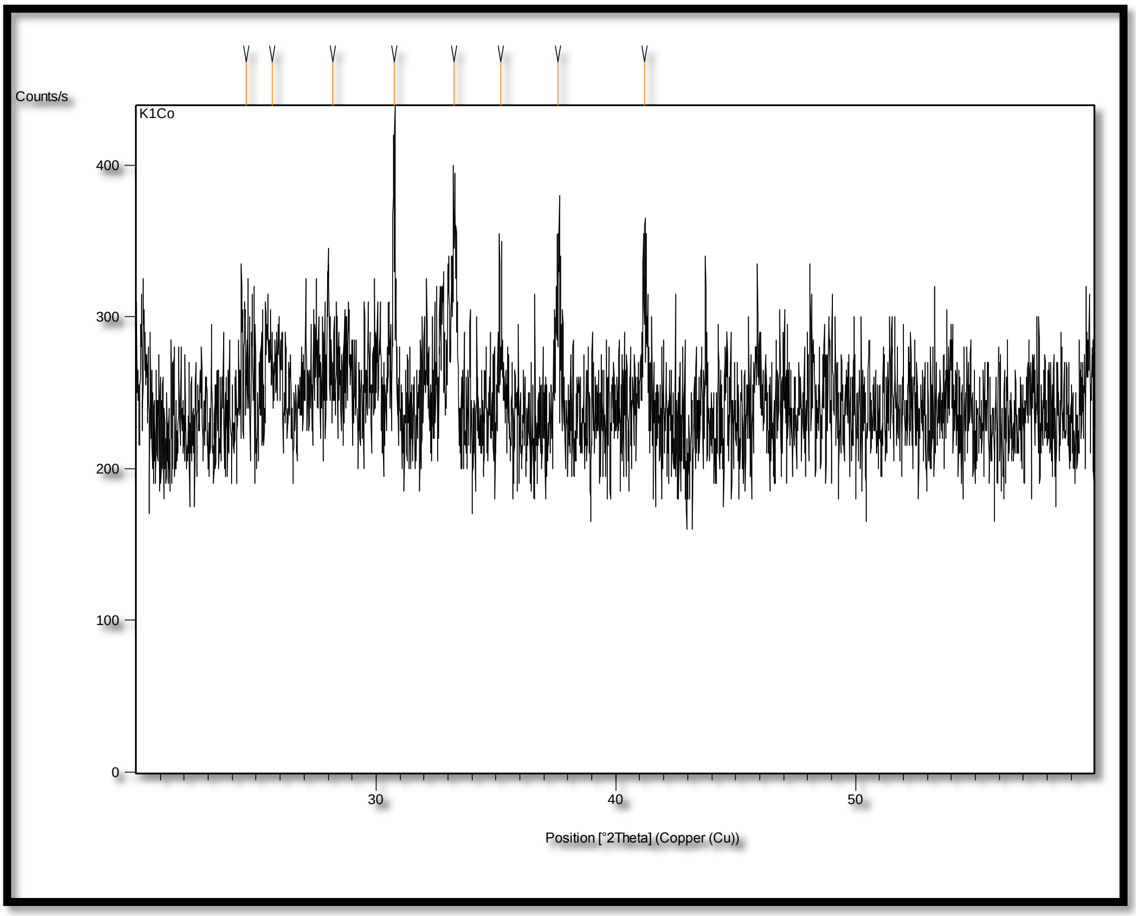


Figure (2a) X-ray diffraction data of the Co-p-carboxy n-phenyl malimied complex

Table(2a) powder X-ray diffraction data of the Co-p-carboxy n-phenyl malimied complex

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
24.5861	6.57	0.4723	3.62092	24.00
25.6844	8.29	0.6298	3.46852	30.27
28.1905	6.52	1.2595	3.16561	23.82
30.7551	27.37	0.1181	2.90724	100.00
33.2700	27.07	0.1574	2.69301	98.88
35.1997	8.87	0.2362	2.54967	32.39
37.5966	21.14	0.1968	2.39245	77.25
41.2126	17.32	0.2400	2.18869	63.29

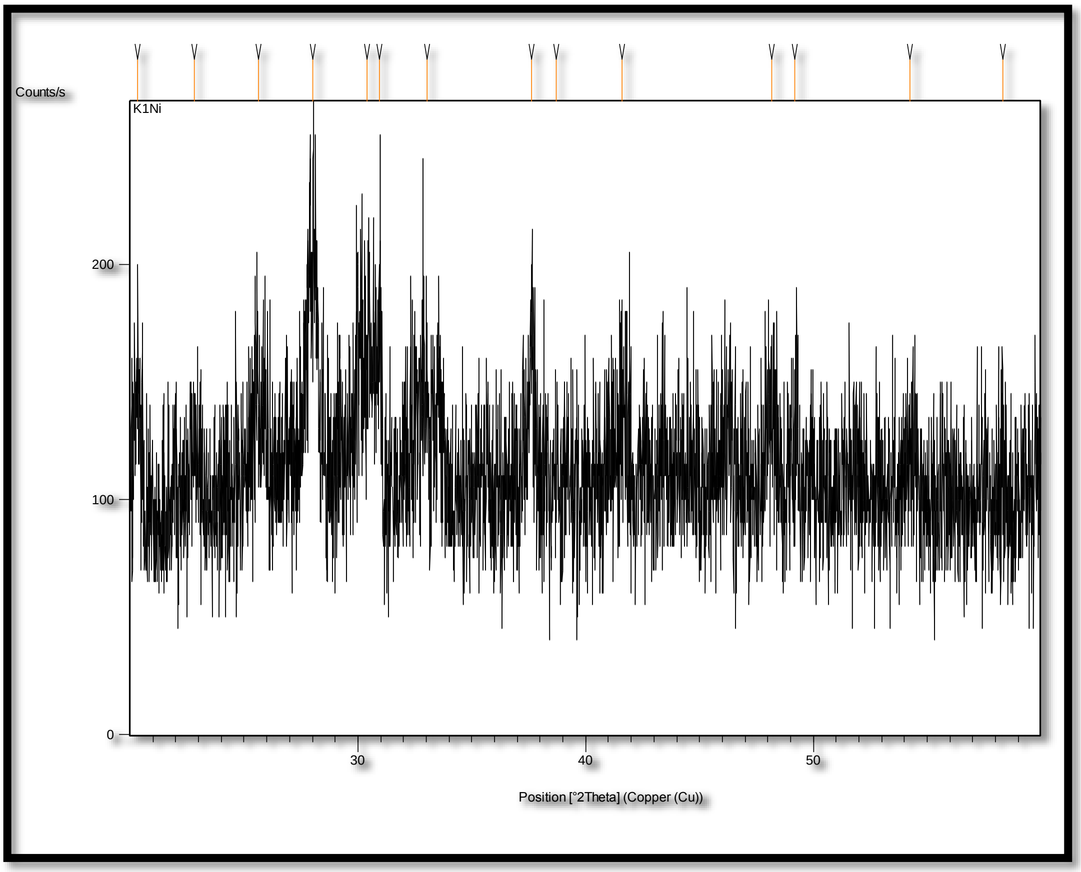


Figure (2b) X-ray diffraction data of the Cr-p-carboxy n-phenyl malimied complex

Table(2b) powder X-ray diffraction data of the Cr-p-carboxy n-phenyl malimied complex

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
20.3356	8.04	0.2362	4.36713	42.90
22.8269	3.61	0.4723	3.89584	19.25
25.6361	8.68	0.6298	3.47494	46.33
28.0068	18.74	0.3936	3.18596	100.00
30.4185	12.14	0.9446	2.93864	64.75
30.9598	17.77	0.1181	2.88848	94.81
33.0468	6.72	0.9446	2.71068	35.83
37.6290	14.59	0.2362	2.39046	77.82
38.7226	2.48	0.2755	2.32543	13.25
41.5896	7.24	0.6298	2.17152	38.62
48.1556	6.61	0.4723	1.88966	35.27
49.1874	5.49	0.4723	1.85241	29.31
54.2315	3.73	0.6298	1.69143	19.91
58.3062	1.63	0.6720	1.58125	8.72

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