Synthesis and Characterization of Imine-Azo Polymer Ligands Derive a from Azo compounds , Acetylacetone and Amines and Their Metal Complexes with (Mn^{+2},Ni^{+2},Zn^{+2})

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Abstract :

In this work, series of compounds (ligands and polymers) were synthesized from reaction of azo compound with acetylacetone to produce compound diimine azo [NAP], which reacts with (4-aminoethoxy aniline, 2-amino thiophene ,2-amino thiazole , 4-amino benzamide) to produce four ligands [MAP , TAP, PAP, BAP] respectively . The ligand (TAP) was reacted with (Mn^{2+},Ni^{2+},Zn^{2+})to form metal complexes the optimal conditions of complexes (stoichiometric study , mole ratio, job method ,pH ,concentration of metals and ligand ,molar conductance), were also studied All ligands and complexes and were tested for antibacterial and antifungi activity.All ligands with complexes were characterized by (^{1}H.NMR–spectra ,FTIR–spectra (CHN)-analysis) , Sehiff base .

Keyword: polymer-of-polyester ,schiff-ligand, complexes

الخلاصة :

تضمنت الدراسة تحضير سلسلة مركبات (ليكاندات وبوليمرات) من تفاعل مركب آزو مع الأسيتايل أسيتون ليُنتج مركب ثنائي إيمين–أزو [NAP]والدي بدوره يتفاعل مع (4–ميثوكسي أنيلين , 2–أمينوثايوفين ,2–أمينو ثيازول , 4–أمينو بنزمايد) لينتج ليكاندات [BAP, PAP, TAP ,MAP] على التوالي .المركب (TAP) أُستخدم كليكاند مع أيونات (Mn^{2+},Ni^{2+},Zn^{2+}) لتكوين معقدات ودراسةالظروف المثلى لتعقيدها (تكافؤية المعقدات, النسب المولية, طريقة جوب , الدالة الحامضية ,تركيز الليكاند وألأيونات ,التوصيلية المولارية), مع تحضير بوليمرين . جميع الليكاندات المحضرة مع المعقدات والبوليمرات دُرست فعاليتها البكتيرية والفطرية وكذلك ,شُخصت بتقنيات (طيف الاشعة تحت الحمراء, طيف بروتون الرنين النووي المغناطيسي ,التحليل الدقيق للعناصر) ودرجات الانصهار.

كلمات مفتاحية :بوليمربولي أستر ,ليكاند شيف ,معقدات.

Introduction:

The synthesized imine-azo in the present study are containing two imine groups which linked with azo-group and the hetero cyclic compounds bearing (imine-azo) in their structure have many applications in Biological science. These compounds were clinically known and have a wide range of bio activities such as antibacterial drugs [1,2],in synthesis of polymers[3,4], heterocyclic compounds [5,6] have applicatioons in several fields [7-10] which due to several methods for preparing imine compounds in literature , but the method which is carried out through condensation reaction of carbonyl compounds with primary aromatic amine is most used are chelating ligands in coordination chemistry ,they are also useful in catalysis and in medicine , the utility of schiff bases lay in their usefullness as synthons in the synthesis of bioactive molecules, schiff bases belongs to a widely used group of organic intermediates important for production compounds as a ligand with transition metals to form complexes [11-13] and in synthesis of several polymers

Polyesters represent a class of polymers which contains the ester functional group in their main chain. Although polyesters do exist in nature (natural polyesters have been known since around 1830), the term polyester generally refers to the large family of synthetic polyesters (resins), which includes polycarbonates and polyethylene terephthalates (PET) [14-16].Polyesters are widely used materials with diverse applications (fibers, plastics and coatings). They are strong, colorfast, and resistant to corrosion and chemical attack. In general they have extremely good mechanical properties and are heat resistant .

Measurements :

-All chemical used were supplied from Fluka and Merck-chemical company.

-All measurements were carried out by :

*Melting points :Electro thermal 9300 ,melting point Engineering LTD ,U.K .

*FTIR-spectra: fourrier transform infrared shimadzu (8300) ,(FTIR), KBr-disc was used .

*^{1}H.NMR-Spectra in DMSO-solvent ,in ppm unit, and (CHN)-Analysis.

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Preparation of ligands [(NAP),(MAP) , (TAP), (PAP), (BAP)]:

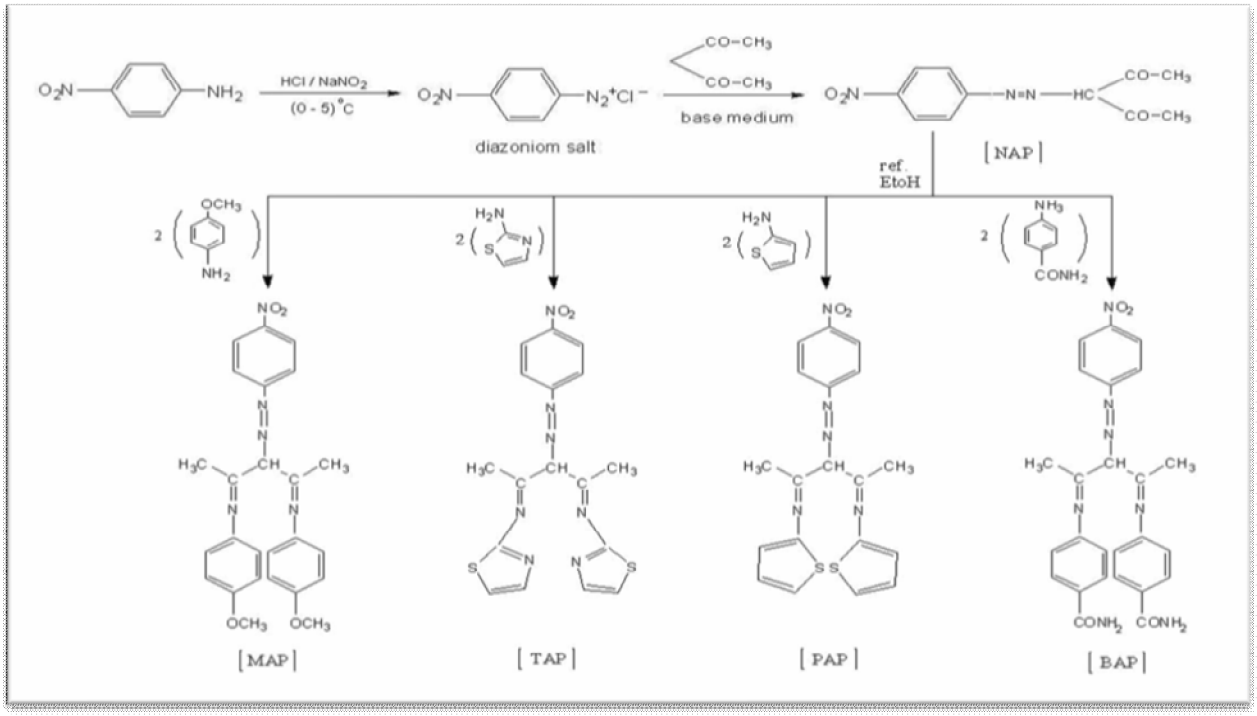
The ligand [(NAP) , (MAP), (PAP), (BAP)] prepared accordinds to procedure [5,17] , (13.8 g) of 4-nitro aniline disolved in (3ml) hydrochloric acid at (0-5)C ,(0.7 g) of sodium nitrite solution added to give diazonium salt, then (5 ml) acetylacetone added to the mixture yiled (4.5g , 0.01 mole) of [NAP]. The product was mixed individually with [(0.02mole ,2.4g of 4-methoxy aniline) , (0.02mole ,1.8g of 2-amino thiophene),(0.02mole , 2g of 2-amino thiazole),(0.02mole ,2.6g of 4-amino benzamide)] respectively in presence of absolute ethanol refluxing for (6-9)hrs .The precipitate was filtered and recrystallized to yield (87, 82,89 ,85)% of [(MAP), (PAP) ,(TAP) ,(BAP)] respectively .

[MAP] : 3-(4-nito benzene azo)-2,4-bis (4-methoxy phenyl imine)-pentane .

[PAP] : 3-(4-nito benzene azo)-2,4-bis (2-thiophene imine)-pentane .

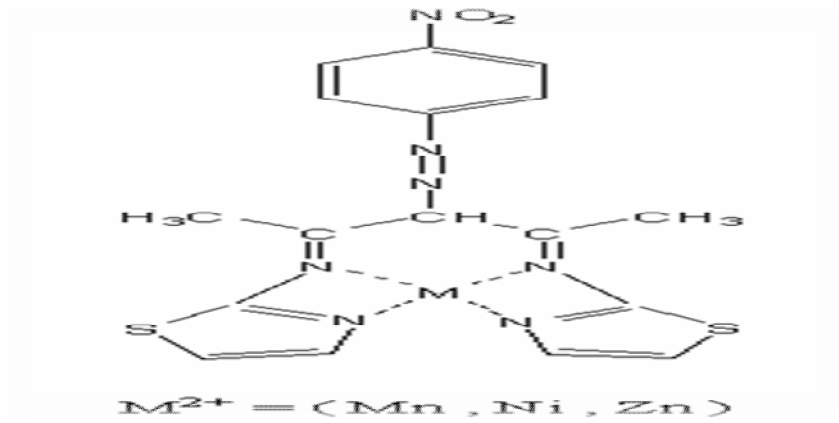
[BAP] : 3-(4-nito benzene azo)-2,4-bis (4-benzamide imine)-pentane .

[TAP] : 3-(4-nito benzene azo)-2,4-bis (2-thiazole imine)-pentane .



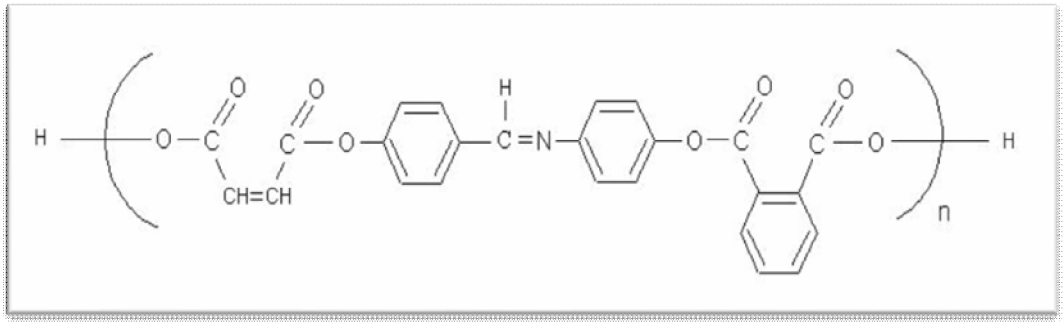
Preparation of complexes of ligands (TAP)with (Mn^{2+},Ni^{2+}, Zn^{2+}):

The complexes prepared according to procedure [5]: hot ethanolic solution(5ml) of the metal halide (Mn^{2+},Ni^{2+}, Zn^{2+})respectively with ethanolic solution of ligand (TAP) in (1:1) (ligand: metal) molar ratios were mixed ,respectively. After stirring for (2hrs) , precipitates formed , the solids were filtered ,dried , recrystallized from absolute ethanol to give complexes (Mn^{2+},Ni^{2+}, Zn^{2+}) respectively .

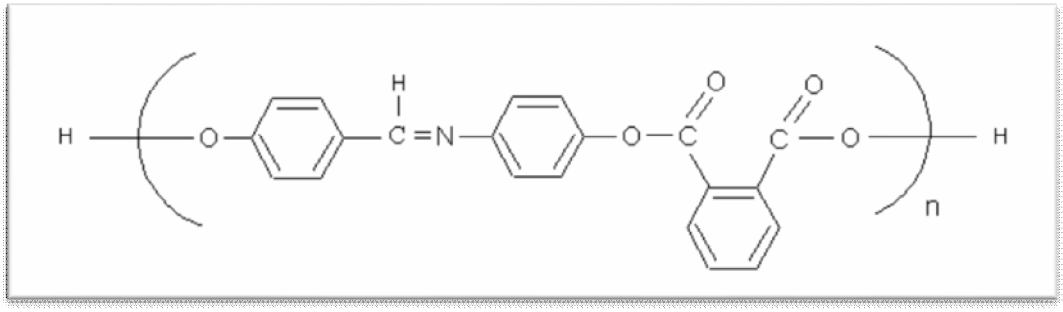


Preparation of Polymers [A] and [B] :

The reaction was carried out in a 100 ml round bottom flask and fitted with a reflux condenser and thermometer. phthalic anhydride (0.1805 g, 0.0244 mole), maleic anhydride (0.073 g,0.015mole), 4(4-hydroxy phenyl)-imine phenol (0.023 mole) were dissolved in 10 ml of acetone followed by addition zinc chloride (0.1662g , 0.0244 mol) of as catalyst . The mixture was heated to 60˚C with a continuous stirring for 6 h . The solution allowed cool to room temperature and the polymer dried after evaporation of solvent



Polymer [A]



Polymer [B]

Results and discussion :

This study involved ,synthesis ,characterization ,bio- chemical studies of structure of four ligands and two complexes with ligand (TAP) and study of optimal conditions for formation of complexes .all compounds were characterized by different methods :

Study of optimal condition :

The optimal conditions for formation of complexes were studied in this work . The optimal concentrations were found to be ; TAP-ligand: ($1x10^{-3}$M) , Mn^{2+}: $0.9x10^{-4}$, Ni^{2+}: $0.7x10^{-4}$, Zn^{2+}: $0.9x10^{-4}$ M . while the optimal pH was 7 .Figures(1-3) ,show that stochiometric of the prepared complexes (M:L) are (1:1) which measured by the molar conductance measurements .Table (1) shows melting points, molar conductance , λ max and the elemental analysis of the prepared ligands and complexes.

The I.R -spectra of the prepared ligands, shows bands: at (1482-1492)cm^{-1} due to azo group (-N=N-) (1610-1620)cm^{-1} assigned to imine[14] group (-CH=N) in ligands .The later showed ashift towards longer wave number (1635-1676) cm^{-1} due to complexation of ligand TAP with (Mn^{2+} ,Ni^{2+} and Zn^{2+}) ions via N-atom of azomethine group (CH=N). Appearance of bands at (439-472) cm^{-1} and (518-522) cm^{-1} are conform the coordination[15] to nitrogen and oxygen atoms.Bands at (1667 and 1676) cm^{-1} in are attributed to imine group[17,18] of polymers [A] and [B]. These data are summarized in Table (1) and showing in Figures (4-12).

The ^{1}H.NMR-spectra shown in polymers [A] and [B] show signals at δ (8.65 -8.81) due to the proton of azomethine[5,17] group ,doublet signals at δ (2.34 -2.44) due to protons of (-CH_2=CH_2-COO-) in polymer [A], and signals at δ (6.93 -6.62) assigned to phenyl group in the two polymers ,figs (13and 14).

The suggestion Figures of complexes:

Structurally ,the above data indicate that NAP, MAP ,TAP, PAP and BAP are bi dentate ligands and TAP is coordinated to (Mn^{2+} ,Ni^{2+} and Zn^{2+}) ions via N-atom of azomethine and thiazole group to form a tetrahedral complexes[2,6] .

Antimicrobial tests :

The antimicrobial activity of the prepared ligands and complexes against bacteria (*staphyllococcus .aureus*) and fungi (Aspergillus *niger*) were studied using holes methods[17-20] ,the TAP -Mn^{2+} ,Ni^{2+}, Zn^{2+} complexes exhibited at ($1x10^{-3}$)M concentration higher activity towards bacteria than fungi , as shows in Table (3). Data in Table (3) shows that those complexes are more active compared to the ligands .This attributed to the presence of metal while may be increase the breakage and penetration of bacterial cell wall.

Table(1): Melting point, Molecule Formla and Element analyses

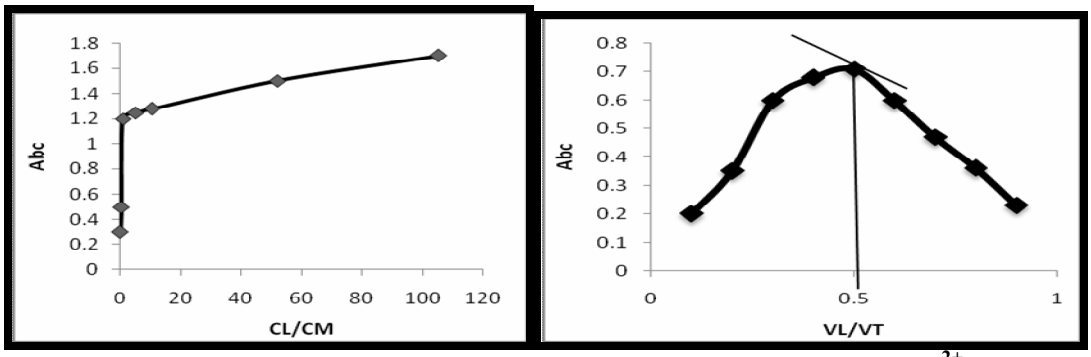
Compounds	M.p(c°)	$Ω^{-1}.cm^{-1}.mol^{-1}$ Molar conductance (DMSO - Solvent)	$λ_{max}$	Calc ./ found			
				C%	H%	N%	M%
$C_{11}H_{11}O_4N_3$ (NAP)	190	--	356	53.01 52.91	4.41 4.34	16.86 16.66	/
$C_{25}H_{25}O_4N_5$ (MAP)	202	--	365	65.35 65.26	5.44 5.30	15.25 15.17	/
$C_{19}H_{17}O_2N_5S_2$ (PAP)	210	--	360	55.47 55.35	4.13 4.06	17.03 16.97	/
$C_{25}H_{23}O_4N_7$ (BAP)	207	--	380	61.85 61.67	4.74 4.62	20.20 20.11	/
$C_{17}H_{19}O_2N_7S_2$ (TAP)	220	--	388	48.92 48.88	4.55 4.40	23.50 23.37	/
$C_{17}H_{19}O_2N_7S_2$ [Mn(TAP)]	245	7.52	440	43.31 43.19	4.03 4.06	20.80 20.64	11.64 11.67
$C_{17}H_{19}O_2N_7S_2$ [Ni(TAP)]	250	8.13	455	42.88 42.76	3.99 3.83	20.63 20.51	12.34 12.36
$C_{17}H_{19}O_2N_7S_2$ [Zn(TAP)]	240	7.34	450	42.29 42.20	4.43 4.32	20.31 20.17	15.67 15.61

Table (2):FT.IR data (cm^{-1}) of the prepared ligands, complexes and polymers.

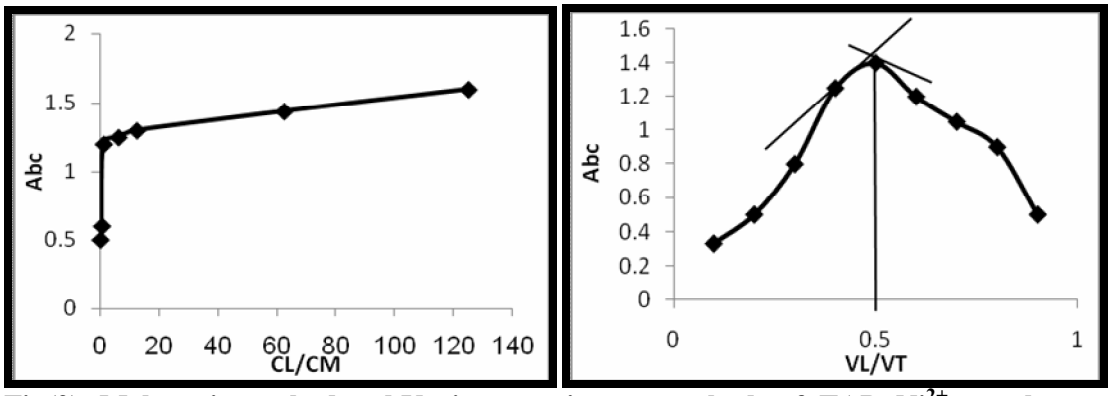
Compounds	Name of compounds	Only (Importance groups)		
		(CH=N) Imine	(-N=N-)	(M-N), (M-O)
(NAP)	3-(4-nitro phenyl azo)-2,4-dione-pentane	---	1492	---
(MAP)	2,4-(bis(4-methoxy phenyl imine))-3-(4-nitro phenyl) azo pentyl	1618	1490	--- ---
(PAP)	2,4-(bis(2-thiophene imine))-3-(4-nitro phenyl) azo pentyl.	1620	1482	---
(BAP)	2,4-(bis(4-benzamide imine))-3-(4-nitro phenyl) azo pentyl	1620	1490	---
(TAP)	2,4-(bis(2-thiazole imine))-3-(4-nitro phenyl) azo pentyl	1610	1489	---
[Mn(TAP)]	Complex	1644	1510	439 518
[Ni(TAP)]	Complex	1635	1489	472 518
[Zn(TAP)]	Complex	1647	1515	465 522
Polymer[A]	Polymer	1676	----	---
Polymer[B]	Polymer	1667	----	---

Table (3): biological activity of ($1x10^{-3}$)M of ligands and complexes

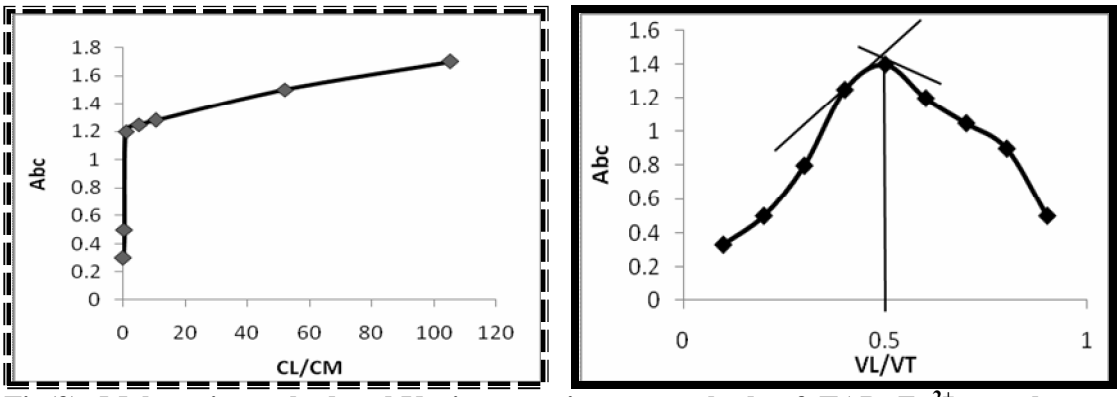
Compounds	Zone of Inhibition	
	Bacteria staphyllococus. Aureus	Fungi Aspergillus
(NAP)	10	6
(MAP)	12	8
(PAP)	16	12
(BAP)	14	11
(TAP)	18	14
[Mn(TAP)]	27	21
[Ni(TAP)]	27	22
[Zn(TAP)]	29	26



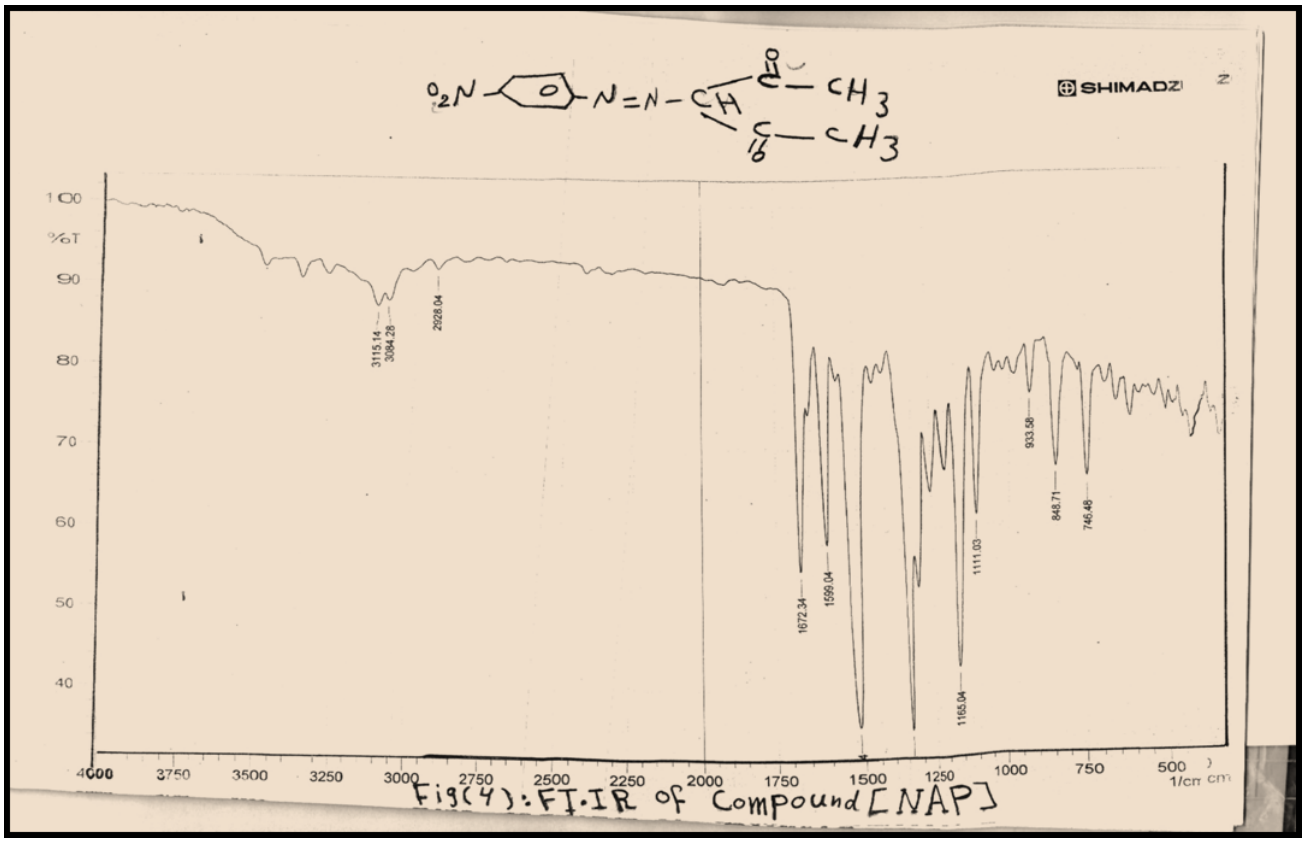
Fig(1) :Mole ratio method and Various continuous method of ATP- Mn^{2+} complex



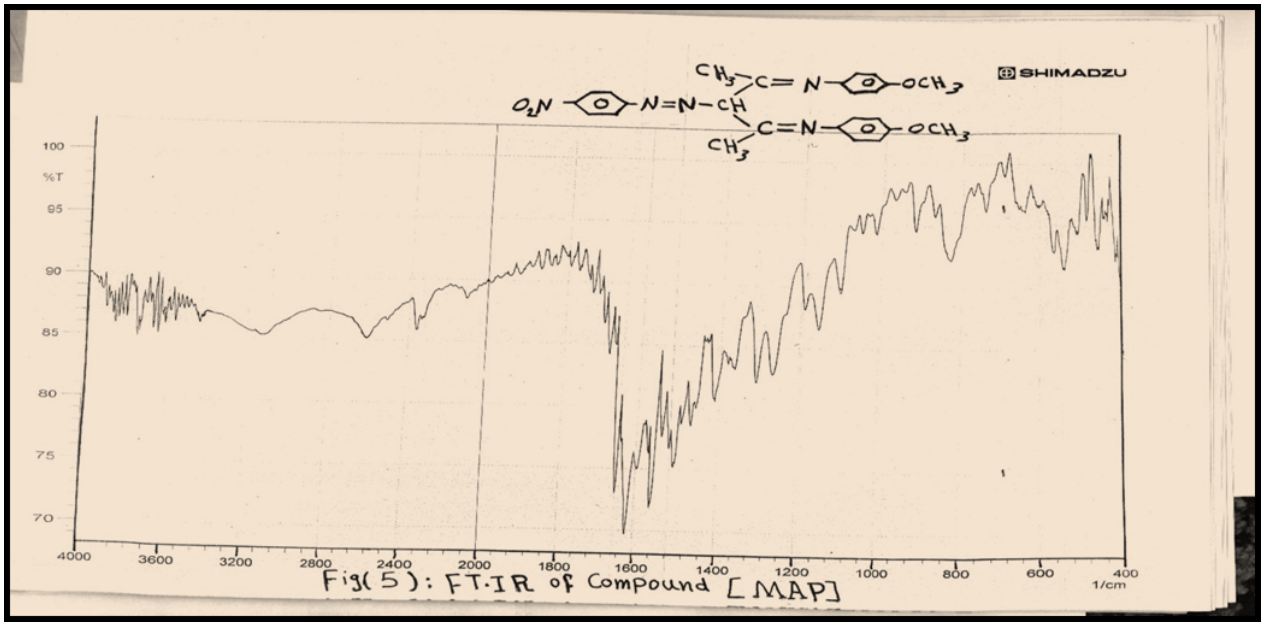
Fig(2) :Mole ratio method and Various continuous method of TAP- Ni^{2+} complex



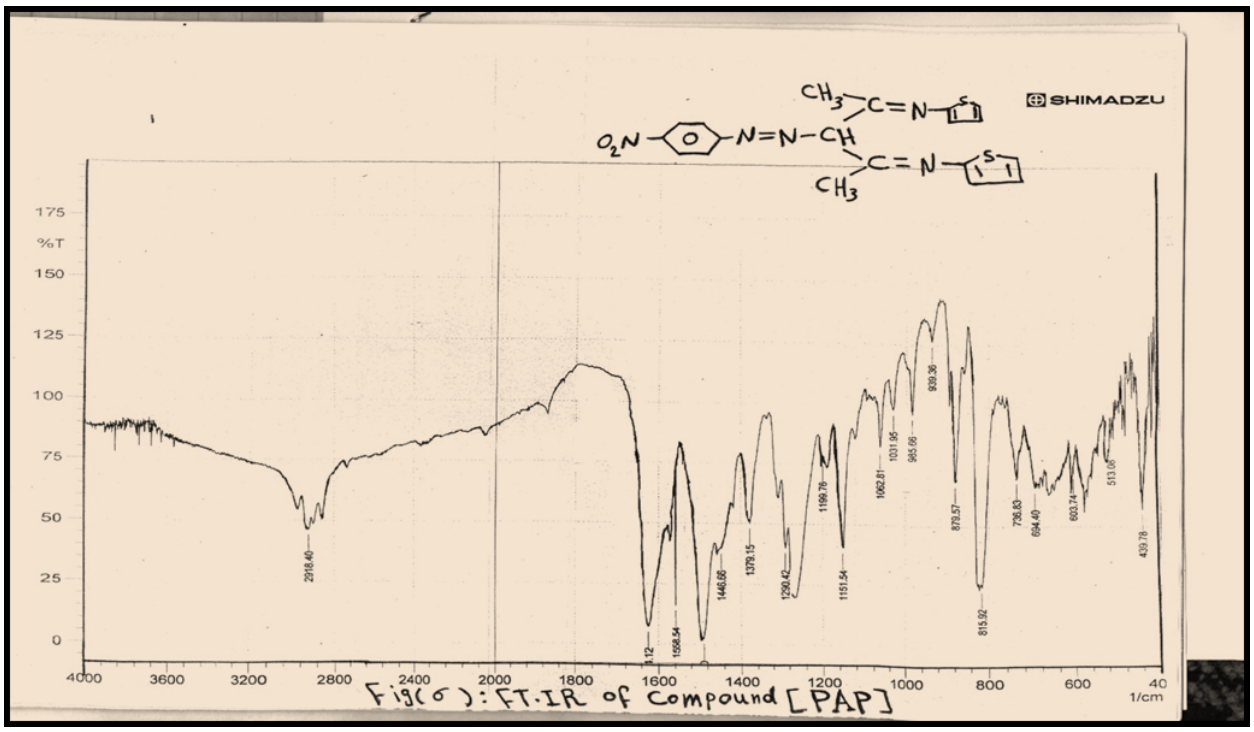
Fig(3) :Mole ratio method and Various continuous method of TAP- Zn^{2+} complex



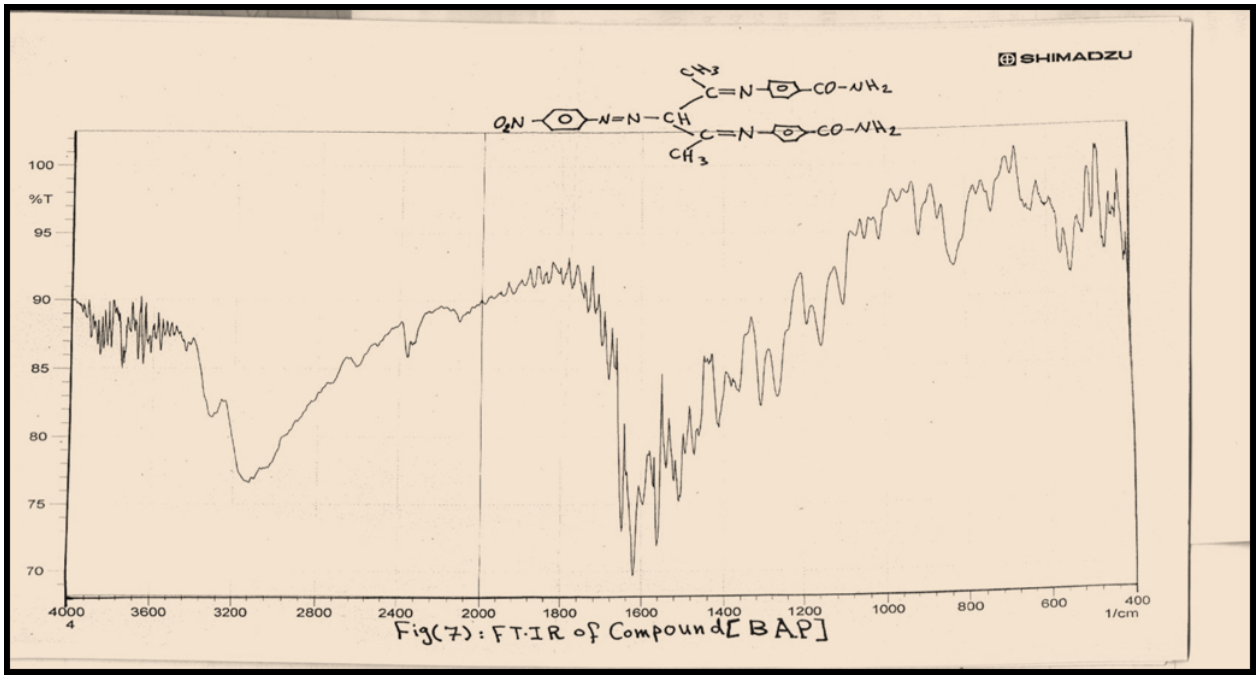
Fig(4):FTIR- of compound [NAP]



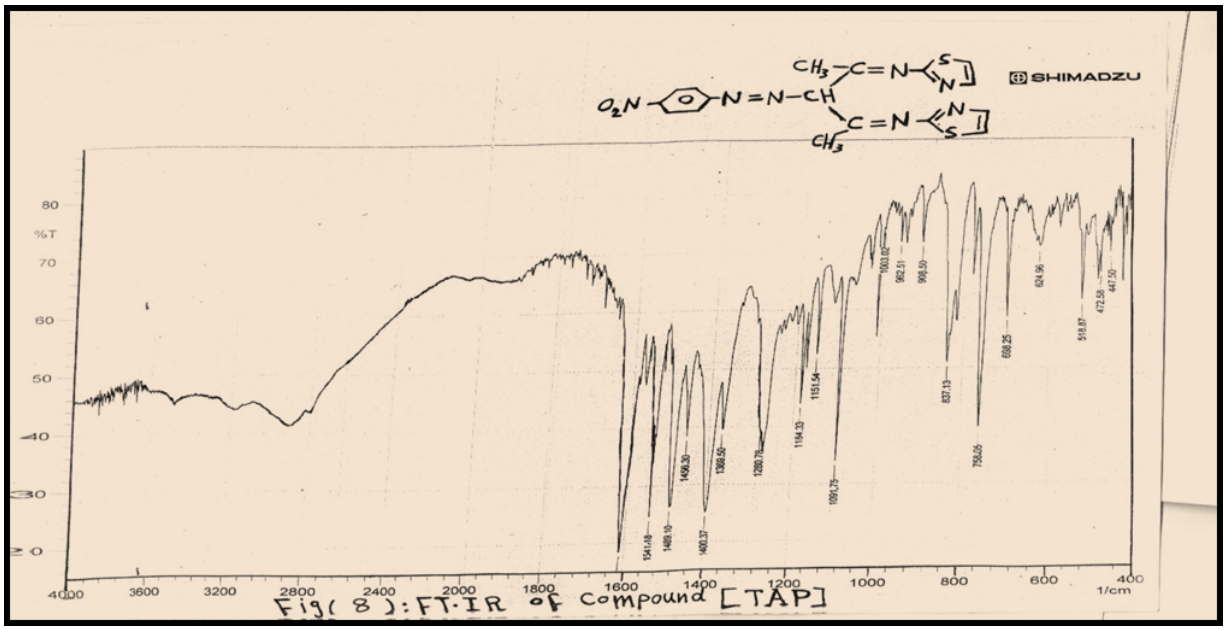
Fig(5):FTIR- of compound [MAP]



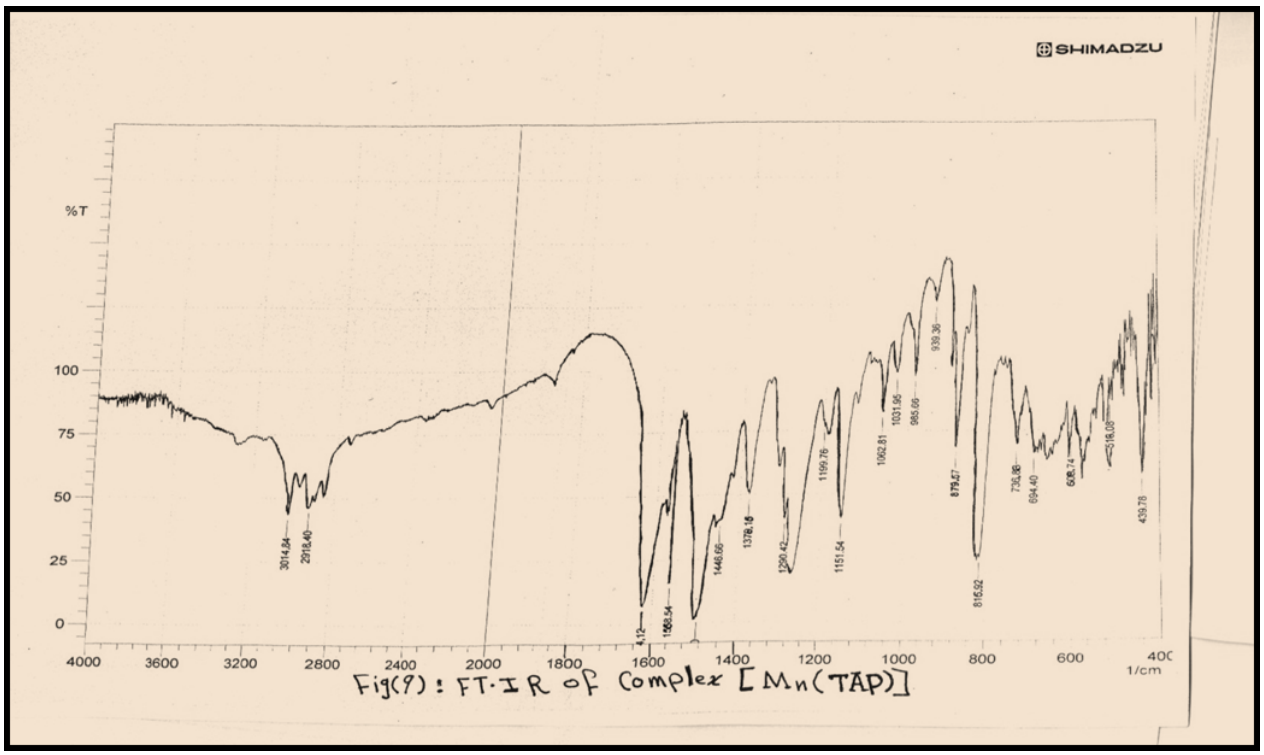
Fig(6):FTIR- of compound [PAP]



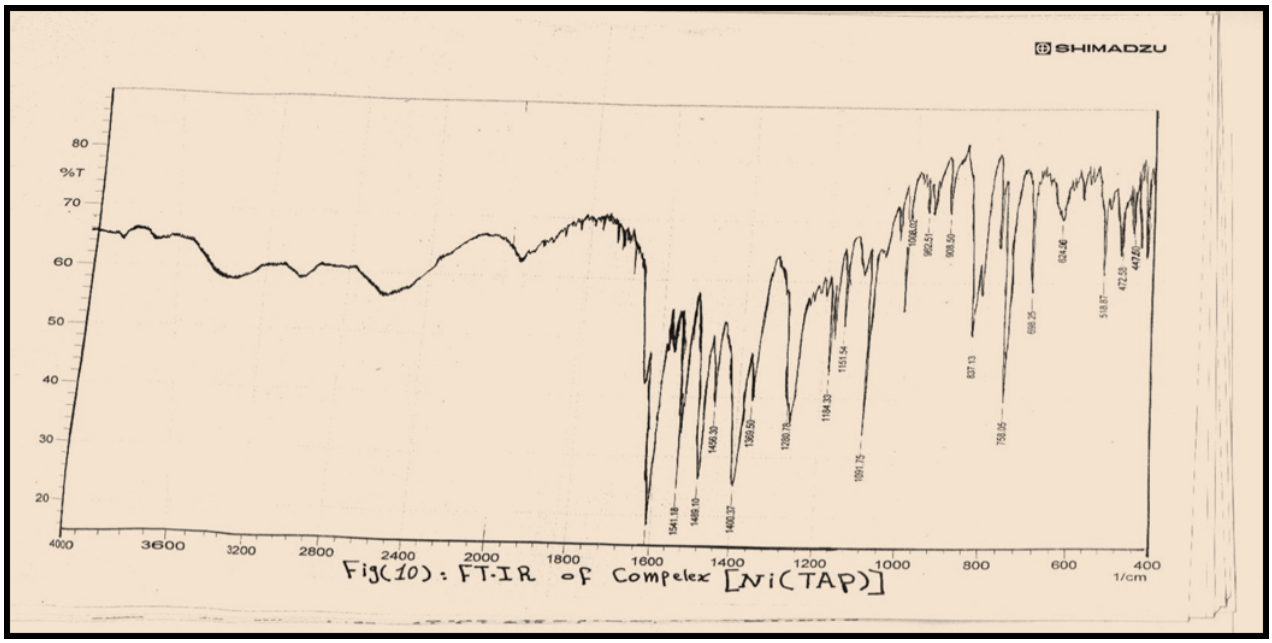
Fig(7):FTIR- of compound [BAP]



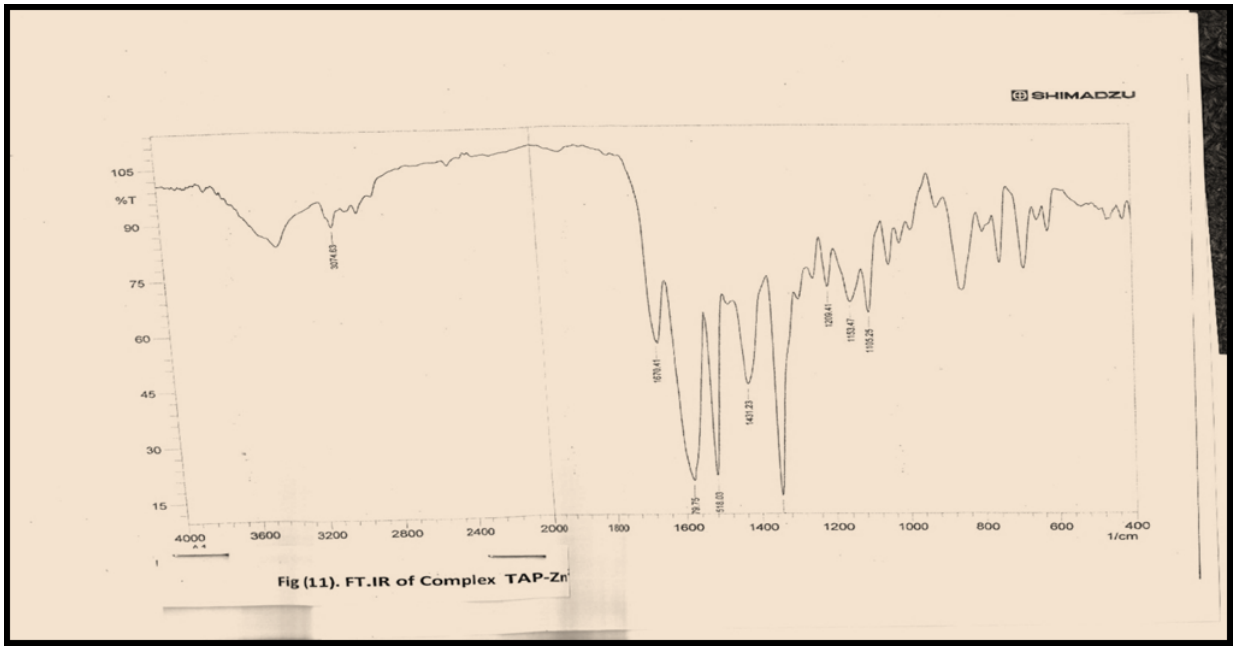
Fig(8):FTIR- of compound [TAP]



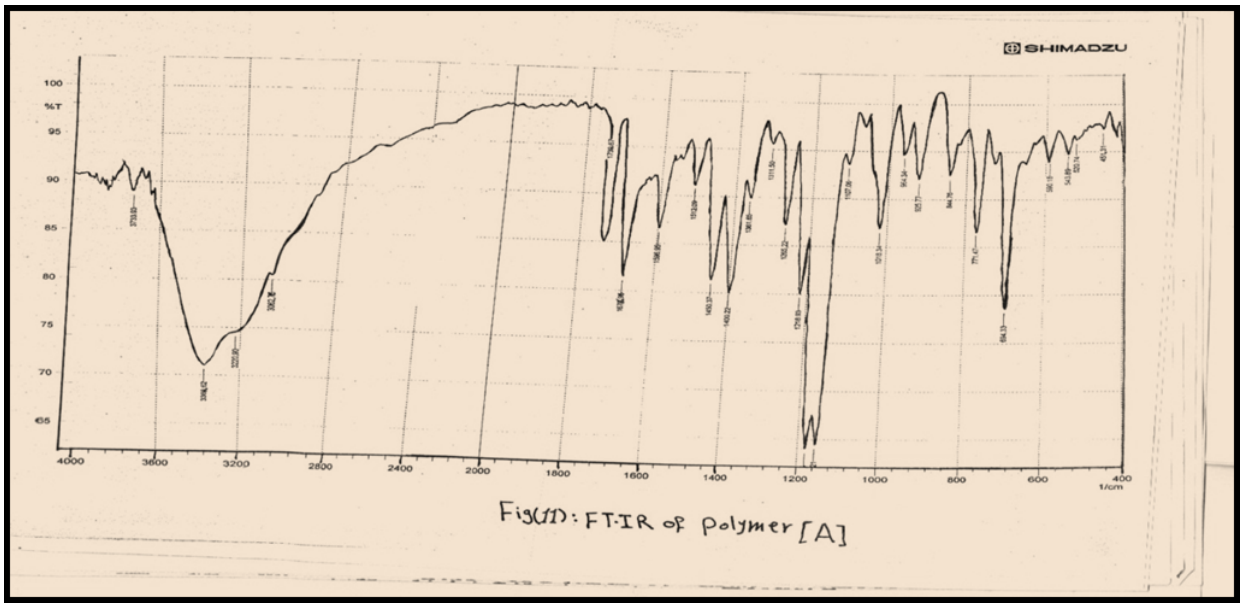
Fig(9):FTIR- of complex [Mn (TAP)]



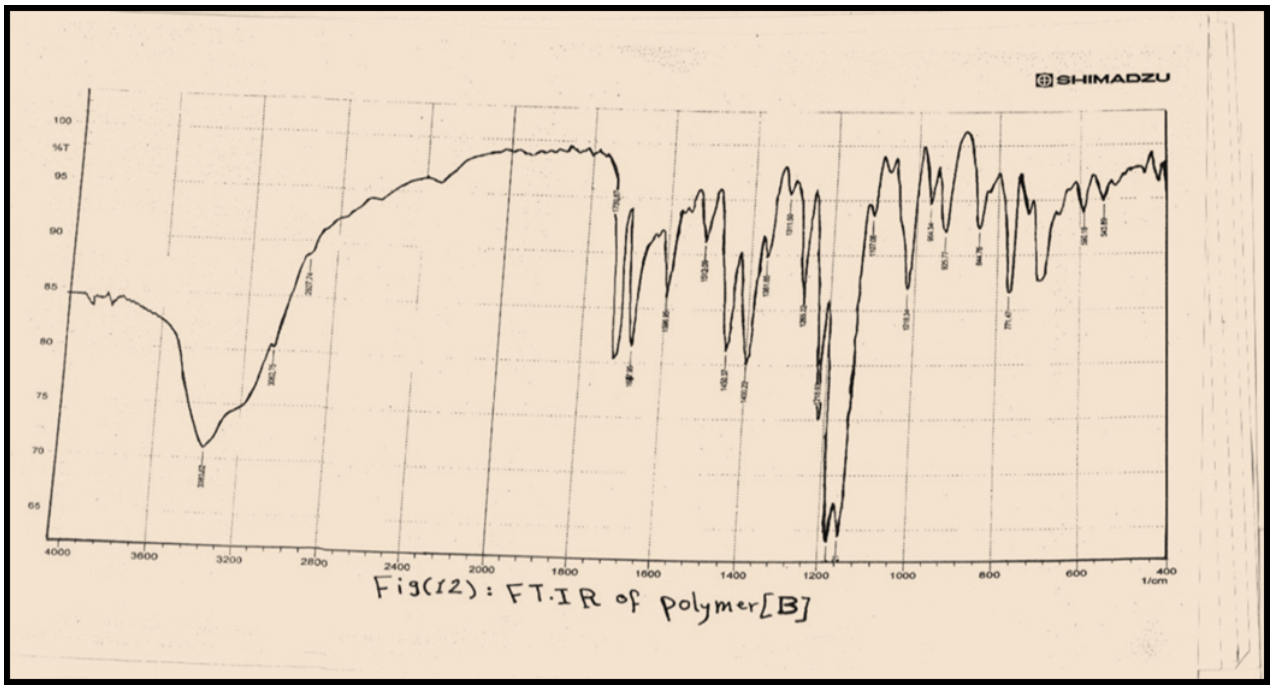
Fig(10):FTIR- of complex [Ni (TAP)]



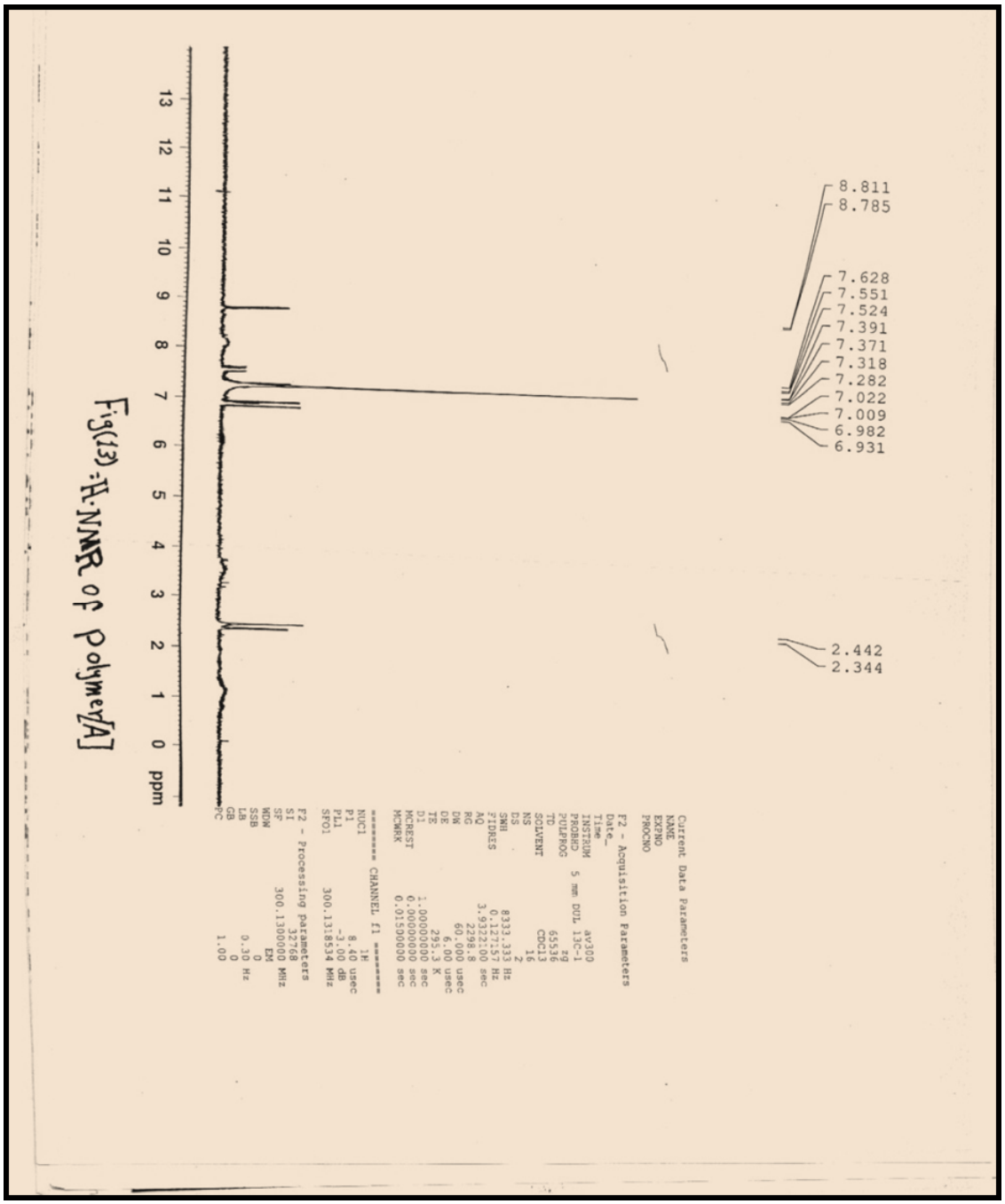
Fig(11):FTIR- of complex [Zn (TAP)]



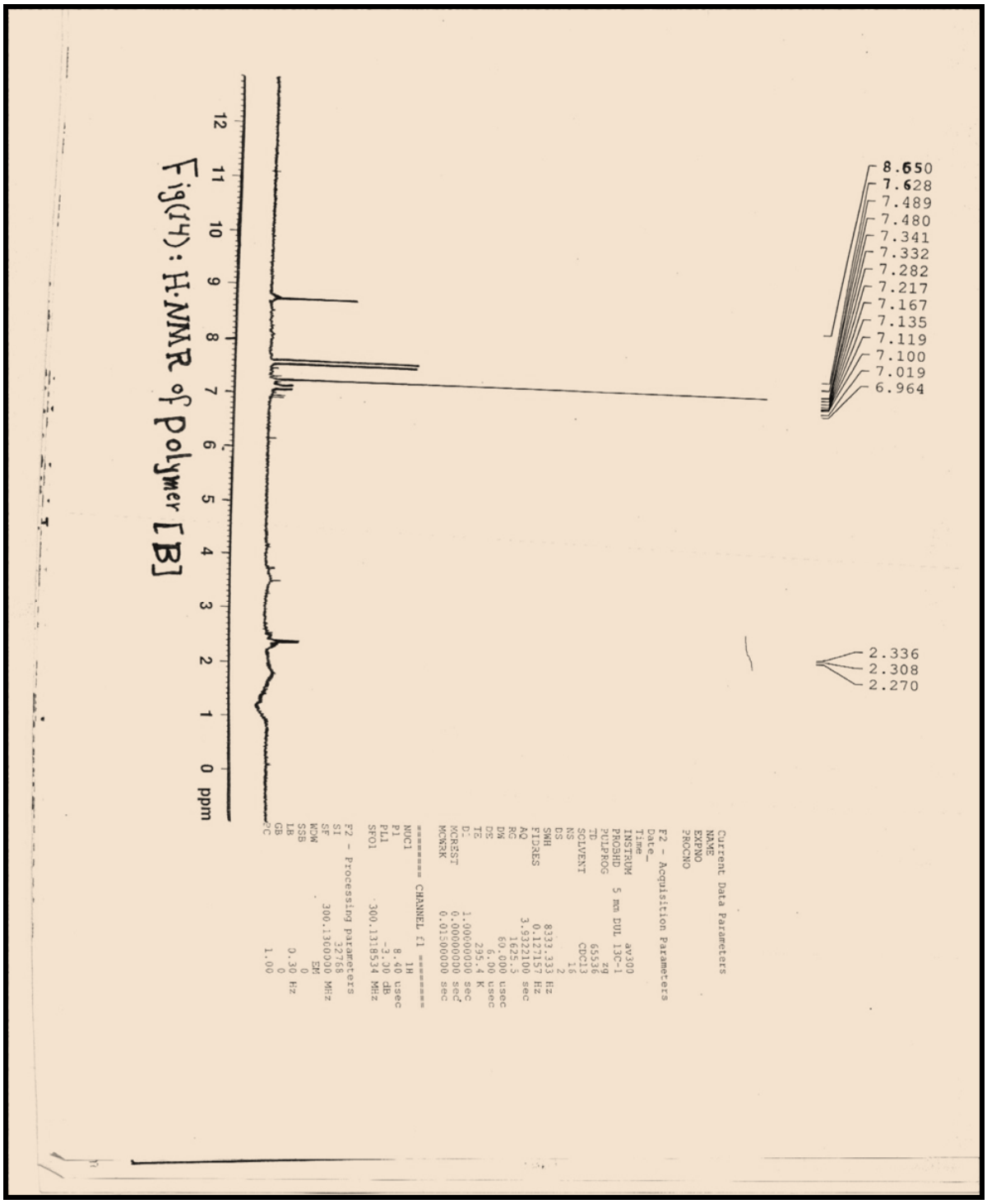
Fig(12):FTIR- of polymer [A]



Fig(13):FTIR- of polymer [B]



Fig(14): ^{1}HNMR- of polymer [A]



Fig(15): ^{1}HNMR- of polymer [B]

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