STUDYING OF BEHAVIOR (SPECTRAL, THERMAL ,CHROMATOGRAPHY) OF AZO-- THIAZOL LIGANDS

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(**Received on Date: 2nd June 2016** **Date of Acceptance : 13th July 2016**)

ABSTRACT

Series derivatives of azo – thiazole ligands were synthesized in this paper through reaction of amine thiazole derivatives in azotation reaction by coupling with other compounds bearing of imine group , then cyclization of double bonds in (-CH=N-) with other compounds such as (azide , anhydride , alkyl halide , alkyl amine) ,to give cyclic compounds as a ligands. The structure of the newly formatted ligands (five ligands) were characterized by using (TLC) and some techniques((FT.IR ,^{1}H.NMR ,Chromatography Analysis,DSC-Measurement)),melting points then studying((chromatography behavior , thermal measurements for stability of ligands , studying of physical characterization)) .

Keyword :many , melt , monite .

No:of Figures: 17 **No: of Tables: 4** **No:of References:23**

Introduction

The first preparation of dyes compounds, Mauveine, was discovered by Perkin in 1856. The early dyes industry saw the discovery of the principal dye chromogens (the basic arrangement of atoms responsible for the color of a dye , azo dyes may be classified according to their chemical structure (groups which included in compounds) or by their usage or application method as a (polymers , antibacterial , ligands in coordination chemistry , medical, electronics , photocopying and laser printing , and other applications in other fields). The former approach is adopted by practicing dye chemists, who use terms such as azo dyes, thiazole dyes, and imidazole dyes[1-5] .

The azo compounds are one of the most important class, accounting for commercial dyes, and having been studied more than any other class. Azo dyes contain at least one azo group (-N=N-) but can contain two groups (dis azo), or more. The azo group is attached to two groups, of which at least one, but more usually both, are aromatic[6-11]. Diazonium compounds are generally stable only in aqueous solution at (0-5)C temperatures. When heated, they decompose by eliminating nitrogen to form the corresponding phenol compounds [12-16].

The chromatography technique[13,14, 21] is method to studying of behavior for some of compounds and from this method we can separate of organic compounds ,the mechanism of separation in this technique depends on stationary phase in thi technique , rate of carrier gas, temperature , polarity of compounds ,weight of compounds

,important functional groups in compounds .

Experimental :

All measurement were carried out by : **melting** points in electro thermal 9300 ,LTD, U.K., **FT.IR** ,KBr –disc ,shimadzu 8300 ., **^{1}H.NMR** –spectra in DMSO –solvent .,in Kashan university in Iran ., **chromatography** Technique ,Thermal analysis in Iraq.

Preparation of Ligand [1] :

A mixture of P–methoxy–aniline (0.02 mole) and (0.02 mole) of ammonium thiocyanate was reacted with glacial acetic and bromine, the precipitate was filtered and dried , which (0.02 mole) dissolved in (4ml) of conc (HCl) in (0-5)C^0 , solution of sodium nitrite (0.3 gm) added and ethanolic solution of 4 –chloro formal phenol was added to solution mixture ,after (48 hrs) ,the precipitate dried , which (0.02 mole) heated with (0.01 mole) of 2–amino thiazole in presence of absolut ethanol with glacial acetic acid (drops) for (3hrs) to produce (80%) of Ligand [1] according to procedure [6, 13] .

Preparation of Ligand [2] :

(0.02 mole) of ligand [1] was reacted with (0.02 mole) chloro ethoyl chloride in (50ml) of 1,4-dioxane in presence of tri ethyl at (<10)C° , the solution mixture was stirred for (4 hrs) according to

procedure[13]., after that filtered and dried to produce (81%) of Ligand [2].

Preparation of Ligand [3] :

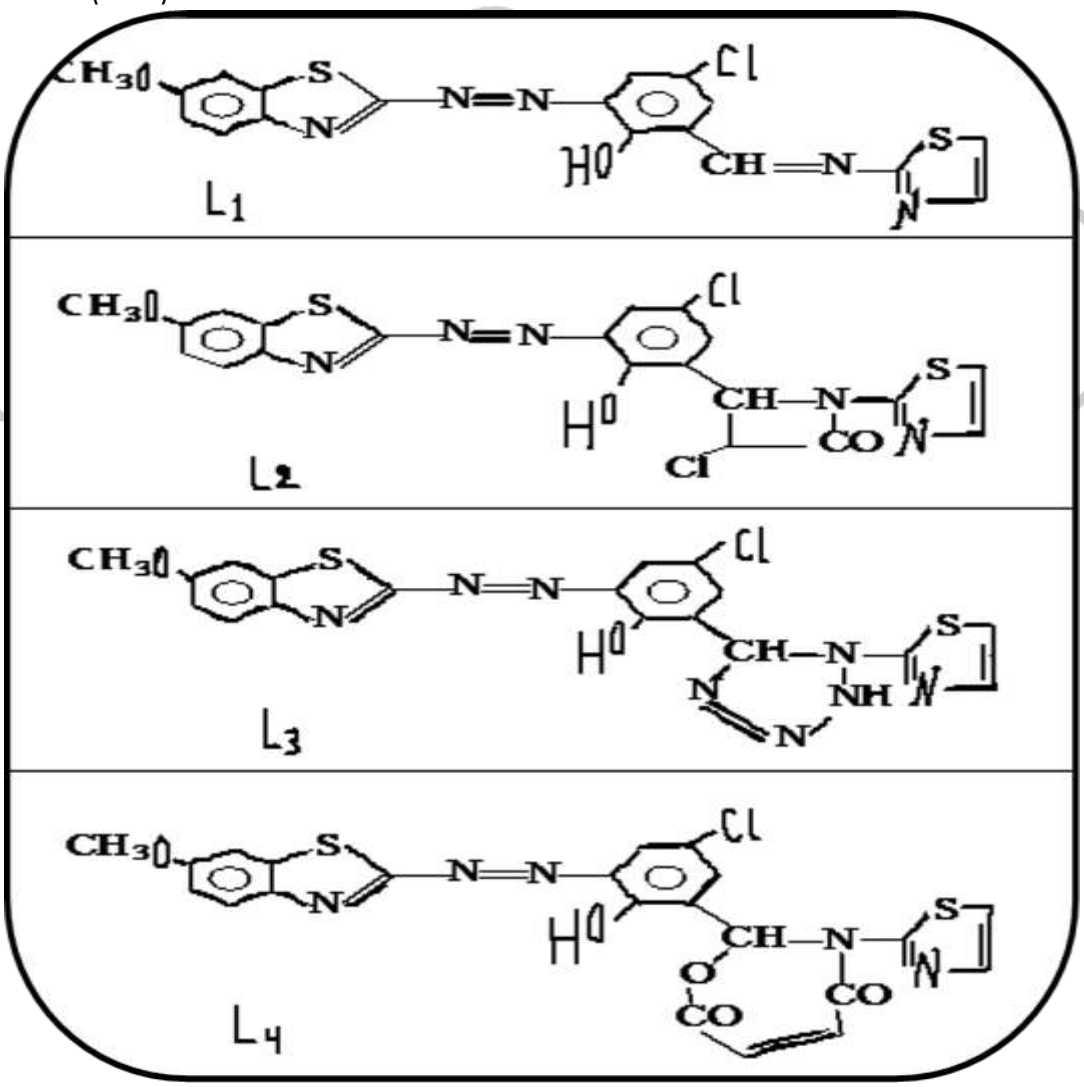
According to paper[13]., A mixture of (0.02mole) of ligand [1] and metal azide (0.02mole) was heated in presence of (50ml) of tetrahydrofuran ,the solution and precipitate were filtered and dried ,re crystallized from 1,4-dioxane to obtain (78%) of Ligand [3].

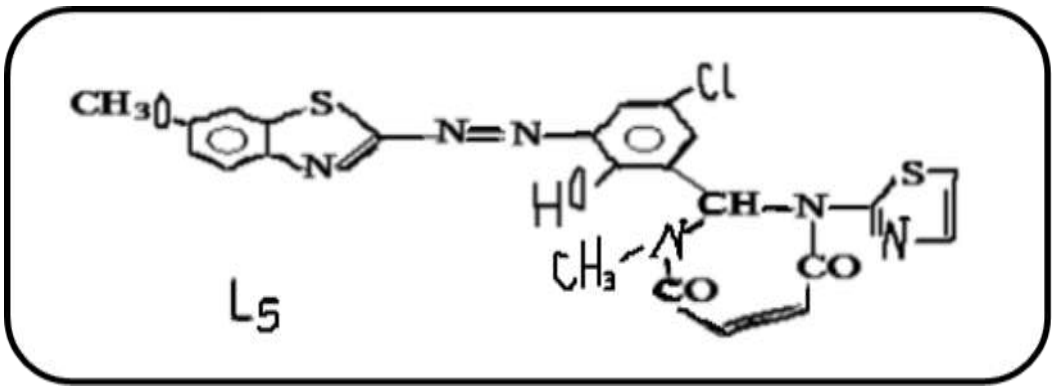
Preparation of Ligand [4] :

A mixture (0.02mole) of Ligand [1] and (0.02mole) of maleic anhydride heateded for (6hrs) in benzene as a solvent ,the precipitate was filtered and dried , after re crystallized from 1,4-dioxane , gave (%81) of Ligand [4] according to paper[13].

Preparation of Ligand [5] :

According to paper[13]., ligand [4] (0.001mole) refluxed with (0.001mole) of methyl amine for (5hrs) in presence of benzene as a solvent .,the precipitate was filtered and dried , re crystallized to give (%80) of Ligand [5].





Results and Discussion :

Thiazole – Azo ligands synthesized in this work from amino benzo thiazole derivatives which linked after that with imine compound to using it as initial material in preparation other ligands .Many studying carried out in many methods and technique (thermal , Analytical , physical measurements) :

UV-Visible – Spectra and Physical properties :

All synthesized ligands in this work was scanned to determination of maximum wave length by electronic spectroscopy methods by using absolute ethanol as a solvent for salvation of ligands ., all results of analysis ,products % ,melting points are listed in Table (1) and some figures (1, 2).

Table (1) : λmax and physical measurements of Ligands .

Ligands	M.P (C°)	λmax	Product %
Ligand1	168	372	80
Ligand2	192	386	81
Ligand3	212	398	78
Ligand4	226	405	81
Ligand5	232	400	80

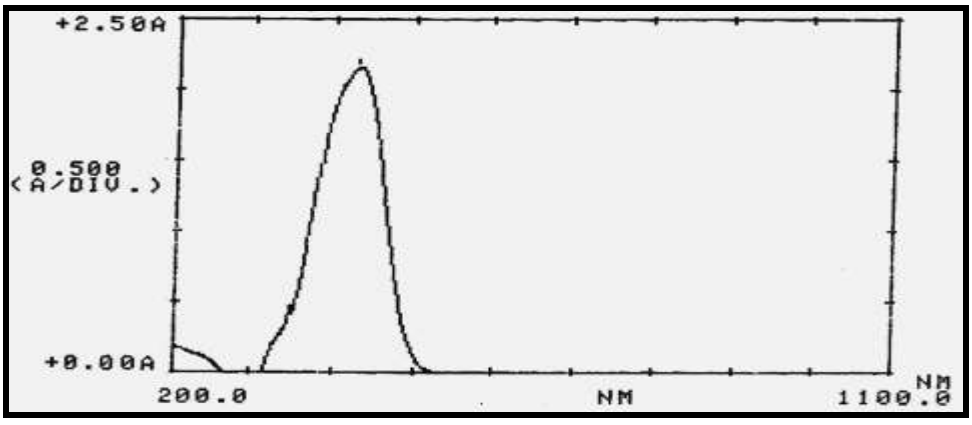


Fig (1) : UV-Visible of Ligand [4]

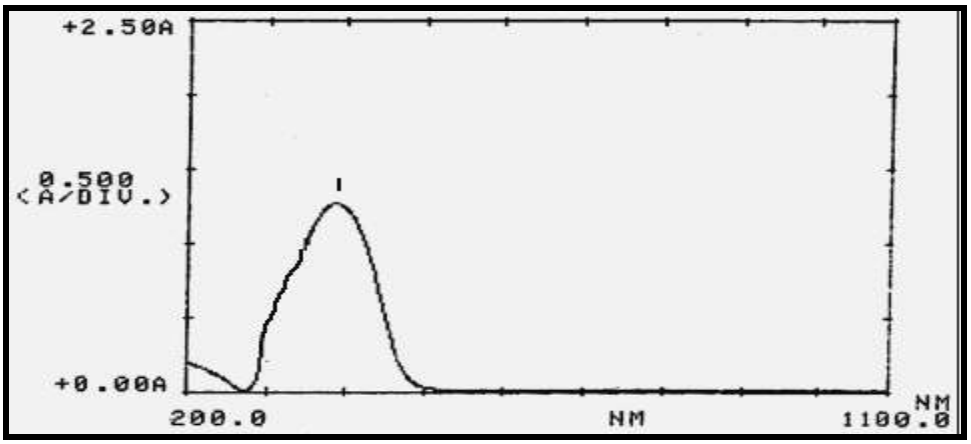


Fig (2) : UV-Visible of Ligand [5]

The FT.IR–spectra showed frequency at (1625)cm^{-1} due to (CH=N) imine group[16,17] in ligand [1] ,which disappeared and other frequencies appeared in production ligands represent [(1692)cm^{-1} due to (-CO-N-) amide[6] ., (730)cm^{-1} to (C-Cl)] in ligand [2]., frequency at [(3200)cm^{-1} due to (-NH)endocycle of tetrazole cycle] in ligand [3]., frequencies at [(1687)cm^{-1} to lactam (-CO-N-) ., (1728)cm^{-1} to lactone[13,19] (-CO-O) and (3081)cm^{-1} due to (=CH) alkene] in ligand [4]., frequencies at [(1677)cm^{-1} to (-CO-N-) amide ., (3290)cm^{-1} due to hydroxyl group (OH) and (3076)cm^{-1} due to (=CH) alkene] in ligand [5] ., and other results of functional groups[13] in Table (2) and some of figures (3-6).

Table (2): I.R Spctra (cm^{-1}) of Ligands .

Ligands	(-N=N-) azo	Only Important Groups
Ligand1	1470	(CH=N)imine group:1625 , (OH): 3420
Ligand2	1476	(C-Cl):730 , (OH): 3432 , (-CO-N-)amide: 1692
Ligand3	1456	(NH) endo cycle of tetrazole:3200 , (OH): 3400
Ligand4	1489	(-CO-O-)lactone of oxazepine:1728 .,(=CH) alkene:3081 , (OH): 3441, (-CO-N-)lactam of oxazepine: 1687
Ligand5	1498	(OH) hydroxyl group:3453 ,(=CH)alkene :3076, (CO-N) : 1677

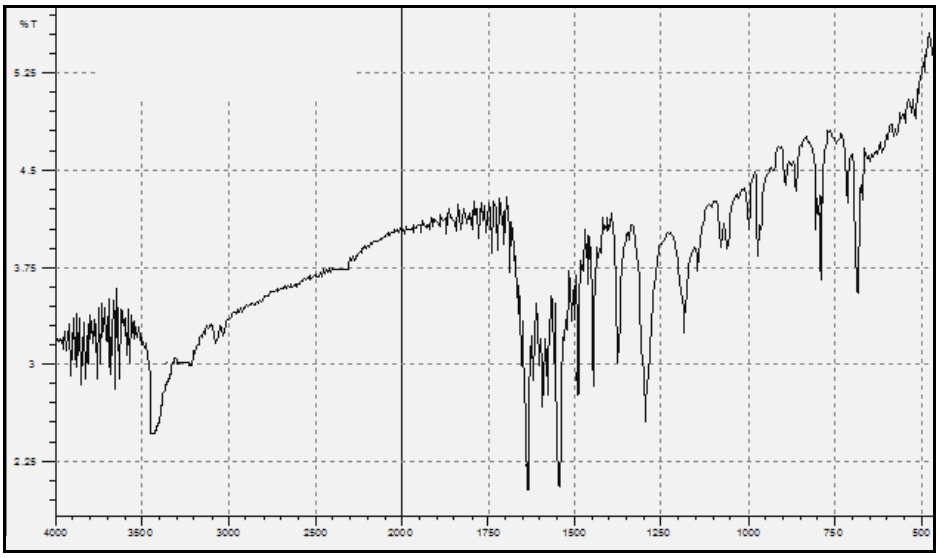


Fig (3): I.R spectra of Ligand [1]

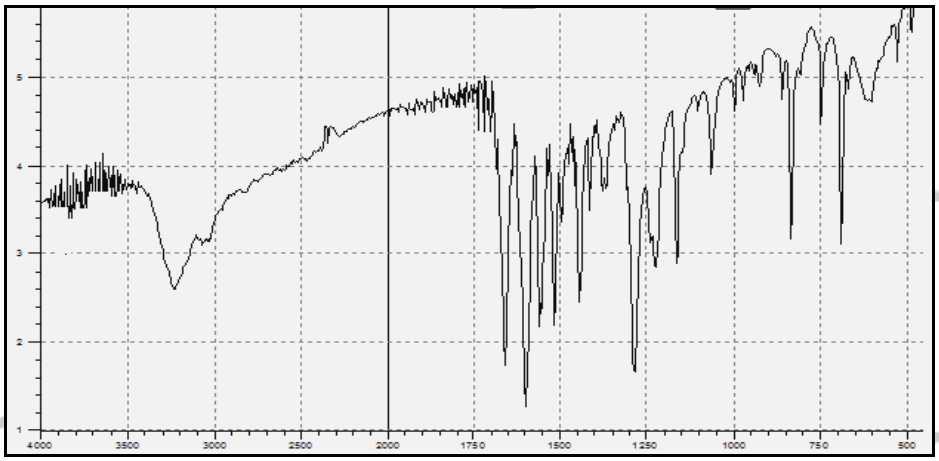


Fig (4): I.R spectra of Ligand [2]

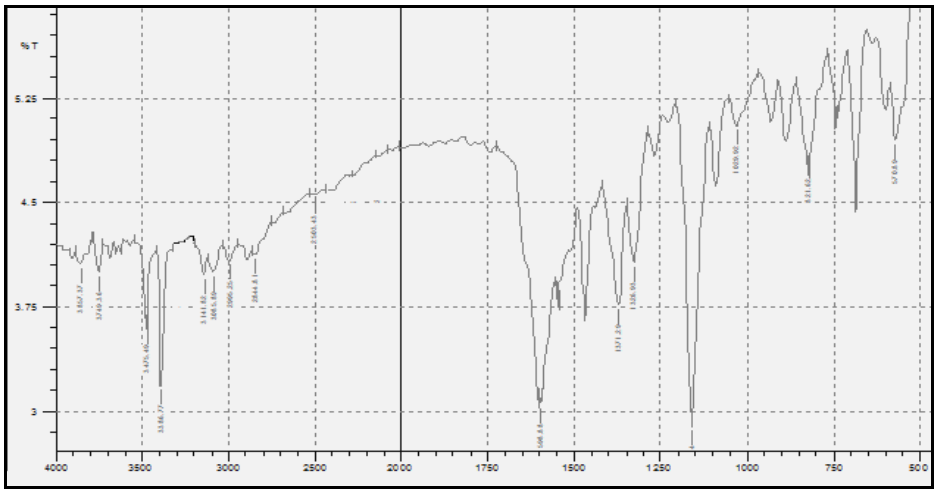


Fig (5): I.R spectra of Ligand [3]

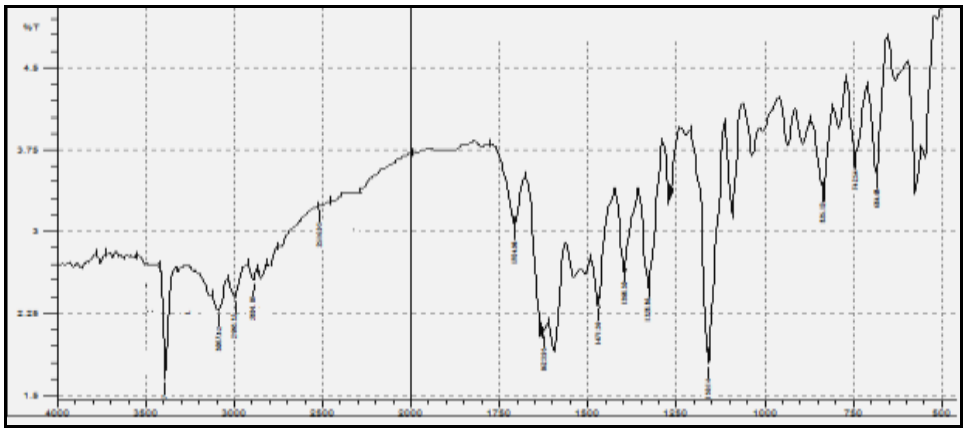


Fig (6): I.R spectra of Ligand [4]

^{1}H.NMR - spectra for some of synthesized compounds ., shown signals at ƃ (8.40) due to proton[13] of schiff base (-CH=N-) and δ 11.30 due to proton of hydroxyl group (OH)] of phenol in ligand [1] ., which disappeared and other peaks appeared in production ligands such as : peaks at [ƃ 3.22 due to (N-CH-N) ., ƃ 4.84 due to (NH) of tetrazole] in ligand [3]., other peaks at [ƃ 4.45 due to (O-CH-N) of oxazepine and ƃ (4.88, 4.91) due to protons of (CH=CH) alkene] in ligand [4]., other data in Table (4) and figures (7-9) .

Table (4):^{1}H.NMR Spectra in (δ PPM) of Ligands .

Ligands	Important peaks
Ligand1	8.40(CH=N) imine group, 11.3 (OH) phenol.
Ligand3	3.22 (N-CH-N) endo cycle ., 4.84(NH) of tetrazole ring , 11.15 (OH) phenol.
Ligand4	4.45 (O-CH-N)endo cycle .,(4.88, 4.91)(CH=CH) endo cycle , 11.24 (OH) phenol

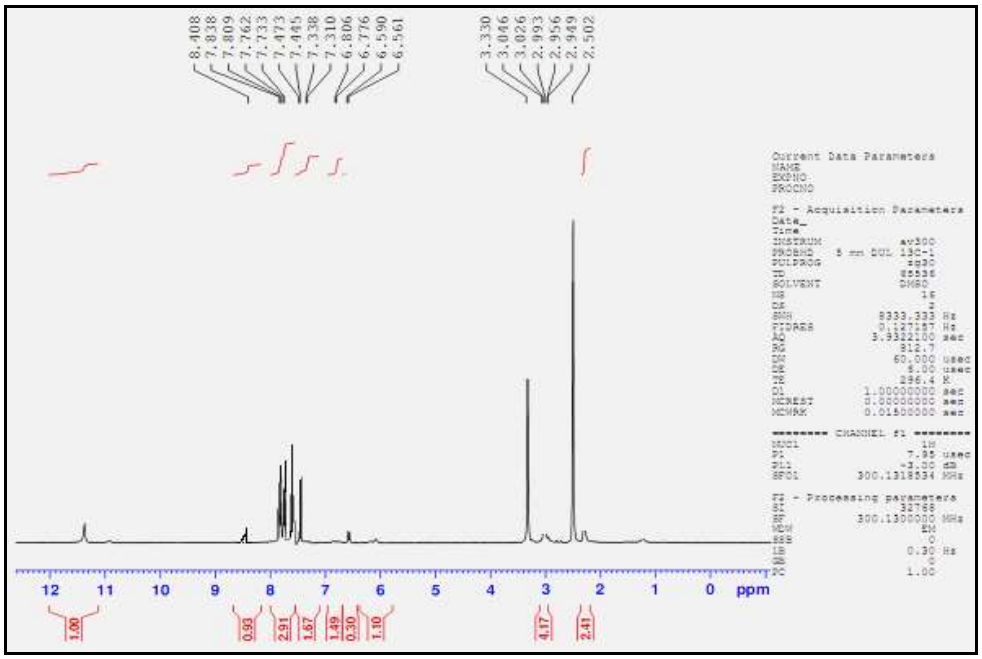


Fig (7): ^{1}H.NMR spectra of Ligand [1]

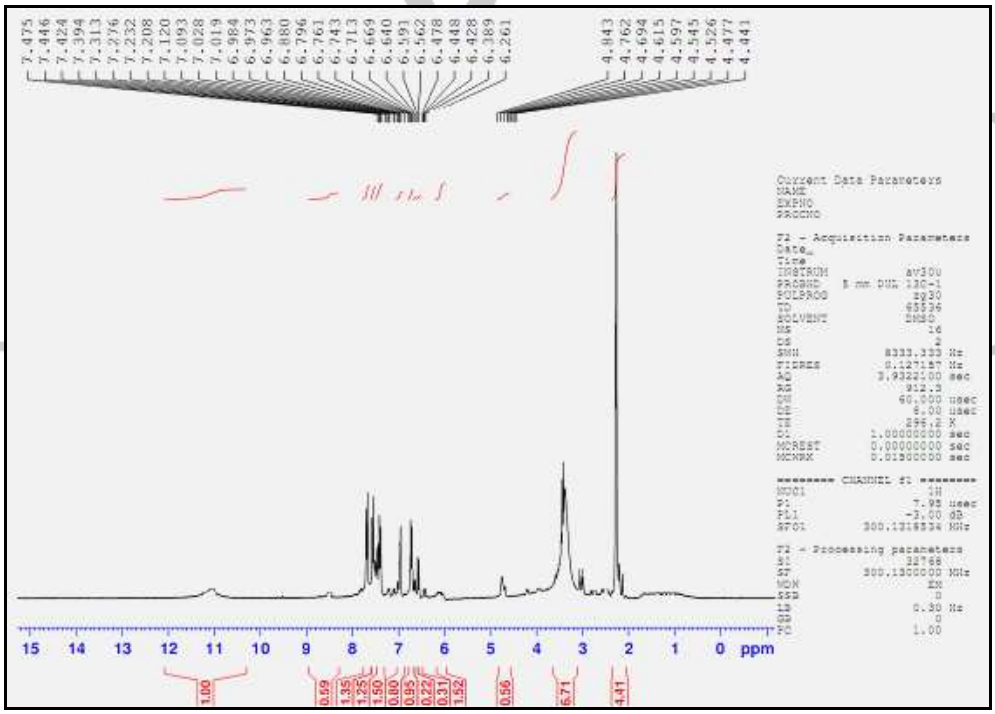


Fig (8): ^{1}H.NMR spectra of Ligand [3]

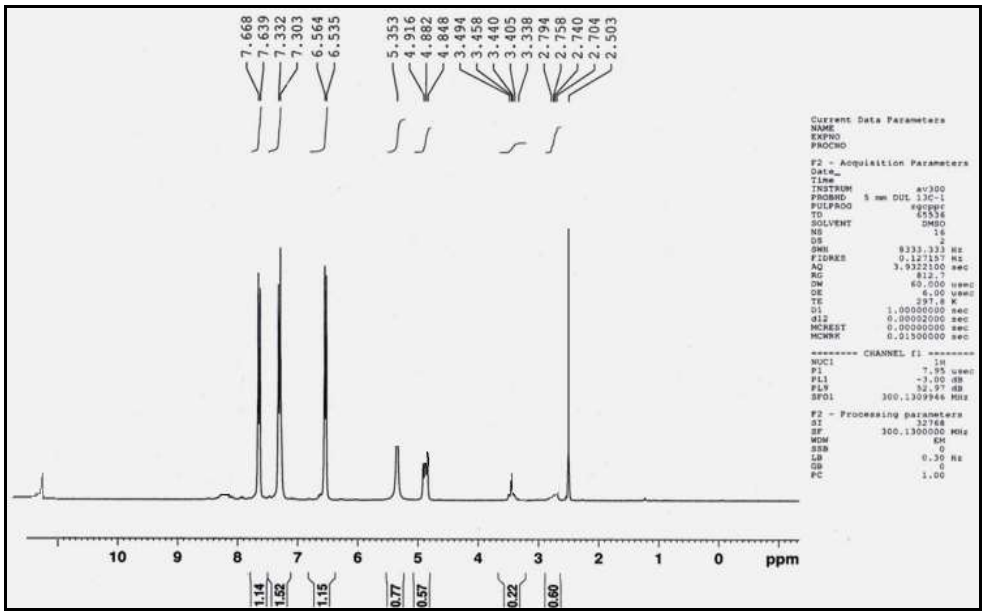


Fig (9): ^{1}H.NMR spectra of Ligand [4]

Chromatography Behavior of Ligands : Solutions of Ligands were prepared in concentration (1 ppm), and injected by using a syringe (Hamilton) in capacity (10ml) through nitrogen (gas flow 25 ml/min) . The Ligands separated according to polarity and molecular weight ., for this reason , ligand [3] separated in the first time due to[21] its polarity (presence of OH group in structure and NH group), then ligands [1] and [2] , then ligand [4] , after that ligands [5] because of their high molecular weight more than other ligands , figures (10-14).

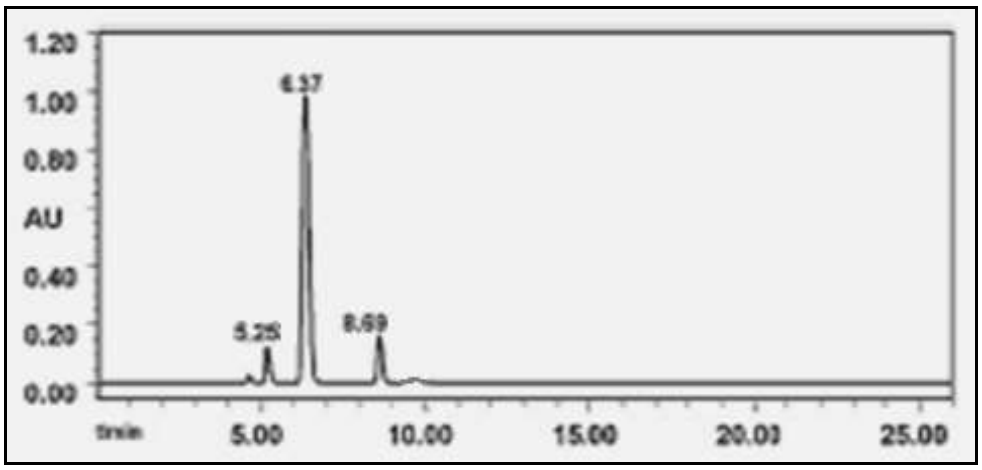


Fig (10): Chromotogram of Ligand [1]

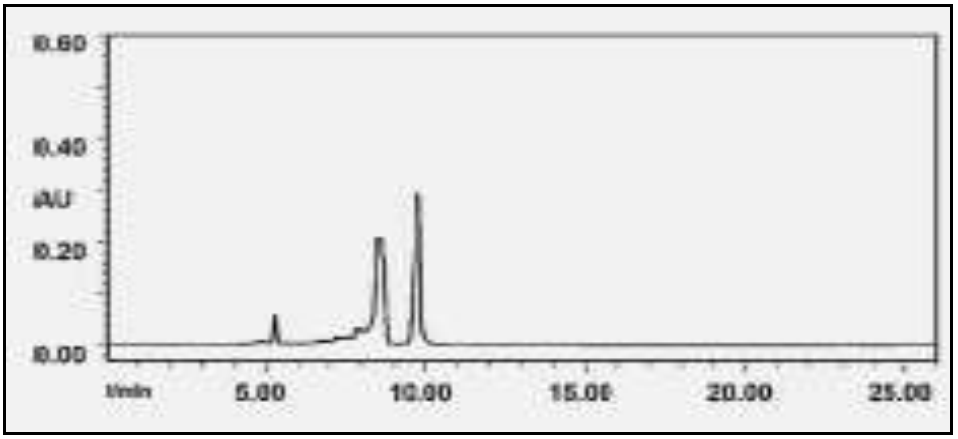


Fig (11): Chromotogram of Ligand [2]

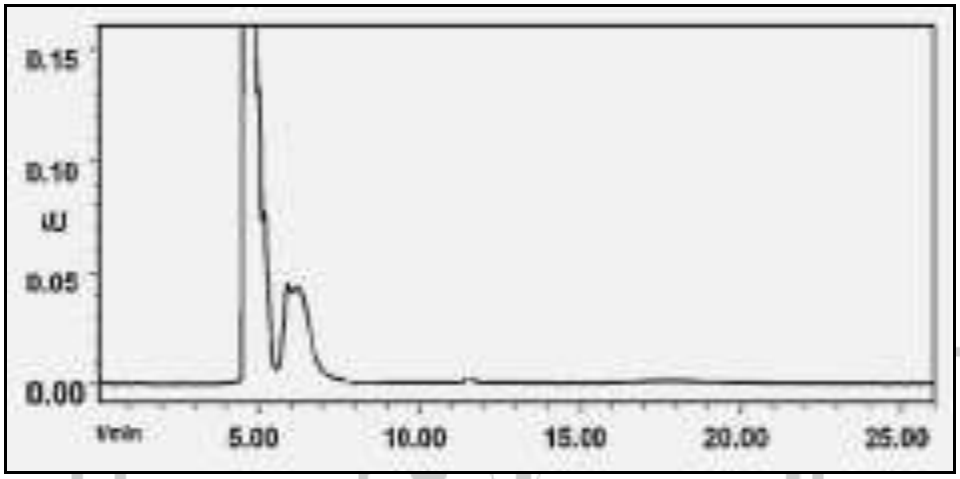


Fig (12): Chromotogram of Ligand [3]

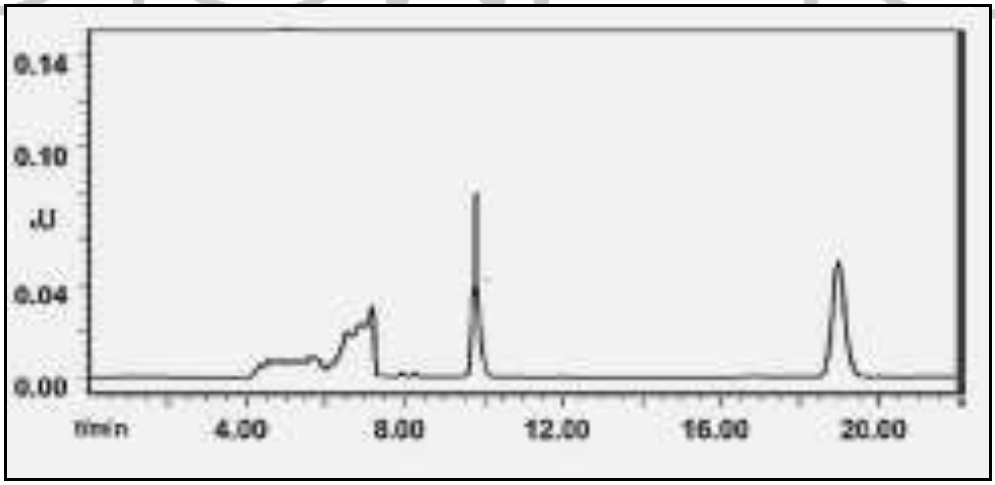


Fig (13): Chromotogram of Ligand [4]

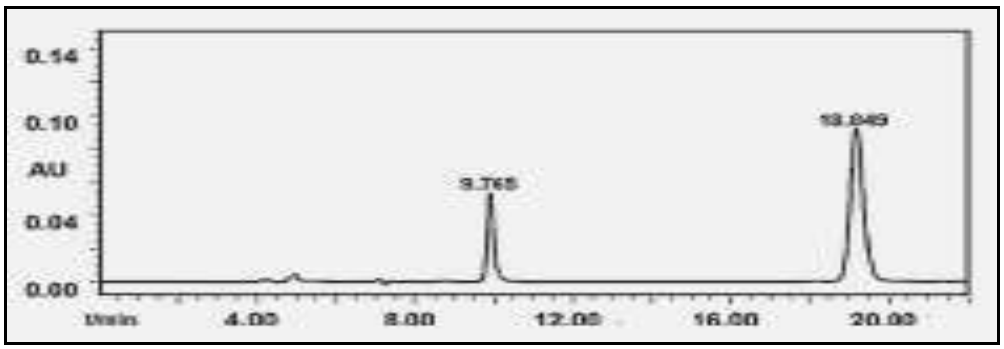


Fig (14): Chromotogram of Ligand [5]

DSC – Thermal Analysis :

DSC–Thermal analysis carried out for some ligands in some figures (15-17) , DSC- Curves appear high stability toward high temperature :

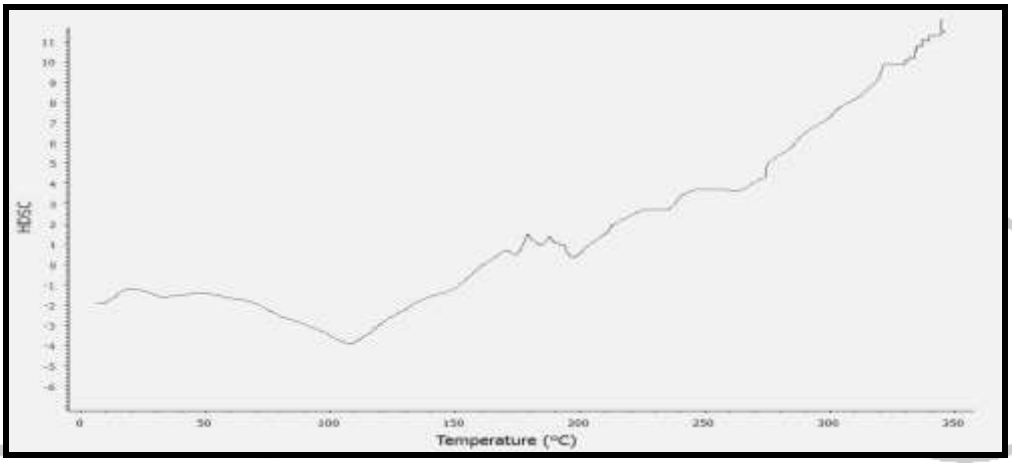


Fig (15) : DSC of Ligand [1]

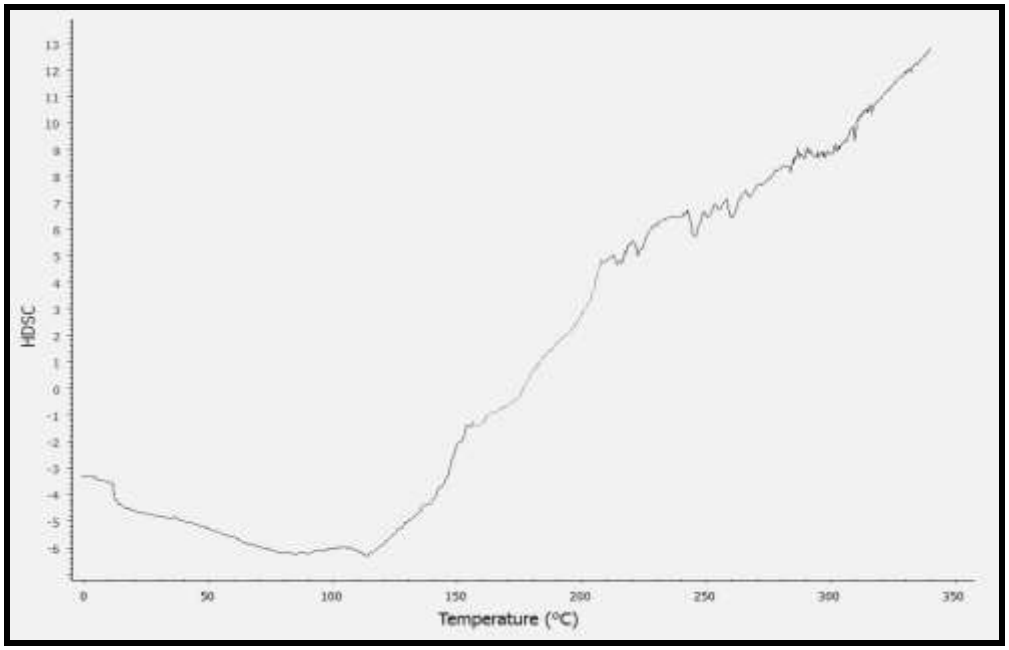


Fig (16) : DSC of Ligand [2]

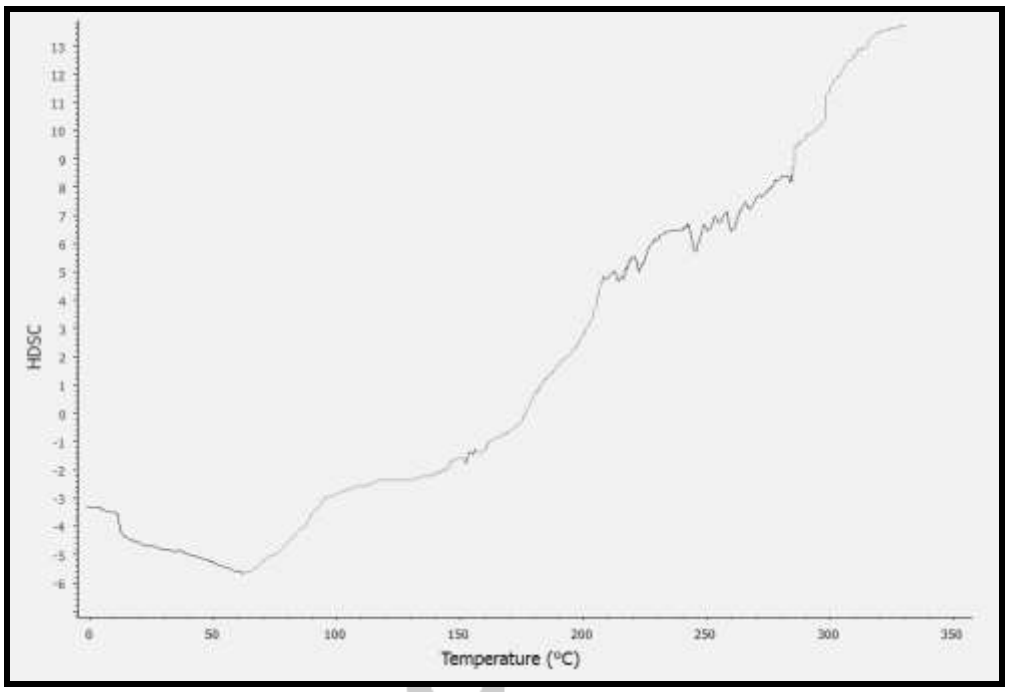


Fig (17) : DSC of Ligand [3]

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