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Synthesis and Characterization of New Coordination Complexes and Its Effect on poly (vinyl chloride) Thermal Stabilization

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ABSTRACT:

A Schiff base, N, N'-(4H-1,2,4-Triazole-3,5-Diyl) bis(4-Methoxy-2-Methylbenzamide) (L) , was synthesized via the condensation of (3,5-Diamino-1,2,4-Triazole) with (methyl 4-methoxy-2-methylbenzoate), along with three complexes: $[Ni(L)Cl_2]$, $[Fe(L)Cl_2]Cl$, and $[Co(L) Cl_2]Cl$. The compounds were characterized by using NMR, MASS, FTIR, Elemental analyses, Magnetic susceptibility, and Molar electrical conductivity. Results showed that (L) acts as a polydentate ligand through its carbonyl and amine groups. FTIR spectra confirmed coordination of Fe, Ni, and Co with (O, N), while magnetic susceptibility indicated octahedral geometries with paramagnetic and diamagnetic properties (μeff =2.4, 0.36) for Fe and Co, respectively, while a square planar for Ni (μeff = 0.2). The stabilization effect of the polymer was investigated using the synthesized complexes by UV–Vis spectroscopy at wavelengths of 275 and 385 nm. The results showed that these complexes significantly enhanced the thermal stability of the polymer by increasing its decomposition temperature.

Keywords:1, 2, 4-Triazole, Coordination complexes, Magnetic Susceptibility. Thermal stabilization, poly (vinyl chloride)

1-INTRODUCTION:

The study of the structure, synthesis, and reactivity of compounds having ring structures that contain atoms other than carbon is known as heterocyclic chemistry, a branch of organic chemistry. The purine and pyrimidine bases that make up DNA and RNA, respectively, demonstrate that life is fundamentally a heterocyclic phenomena. Heterocyclic chemistry offers special reagents and synthetic techniques needed for the synthesis of drugs [1], pesticides [2], and surfactants [3]. Its significance in related chemistries, such as biochemistry [4], polymer science [5, 6], dye chemistry [7-8], and materials science, cannot be overlooked in the current era of scientific research. Triazoles are a significant chemotype of organic compounds that are five-membered heterocyclic aromatic systems containing three nitrogen atoms, including 1,2,4-Triazole and its derivatives. for their numerous uses in industry, agriculture, and medicine. [9–11]Poly (vinyl chloride) (PVC), one of the most used thermoplastic materials, is renowned for its exceptional mechanical qualities, chemical resistance, and adaptability. However, both processing and long-term use are significantly hampered by its poor thermal stability. When heated, PVC dehydrochlorinates, forming conjugated polyenes, discolouration, and resistance to physical and mechanical properties.PVC becomes coloured by mixing with overlapping amounts of regrind. In addition, the evolution of hydrogen chloride (HCl) will accelerate degradation by an autocatalytic reaction [12, 13]. To solve this problem, a number of thermal stabilizers have been developed. Conventional stabilizers, for example, lead salts and organotin compounds, are effective however, their environmental compatibility and toxicity are becoming issues of concern. Therefore, developing environmentally friendly and efficient stabilizers is one of the major research targets [14]. It is reasoned that candidate alternates may be transition metal coordination complexes having the ability to neutralize HCl, scavenge free radicals as well coordinate with reactive chlorine sites along the polymer chain [15]. Polydentate or chelating coordination complexes of transition metals, e.g., with Fe, Co, and Ni, additionally show more than one stabilization. They are capable of acting as antioxidants and of inhibiting radical-mediated degradation, and interacting with labile chlorine atoms or ionized centers at the polymer backbone and hinder chain scission as well as delaying the dehydrochlorination process [16–18]. These complexes offer a more environmentally friendly and safe non-Pb-containing stabilizer systems and do not sacrifice the thermal attributes of PVC. In this study, the cyclic coordination complexes of iron (Fe^{+3}), cobalt (Co^{+3}), and nickel (Ni^{+2}) have been synthesized and tested as thermal stabilizers for PVC. the mean aim of this study was to evaluted their effectiveness as thermal stabilizer in order to understanding how these complexes effect on polymer stabilization .

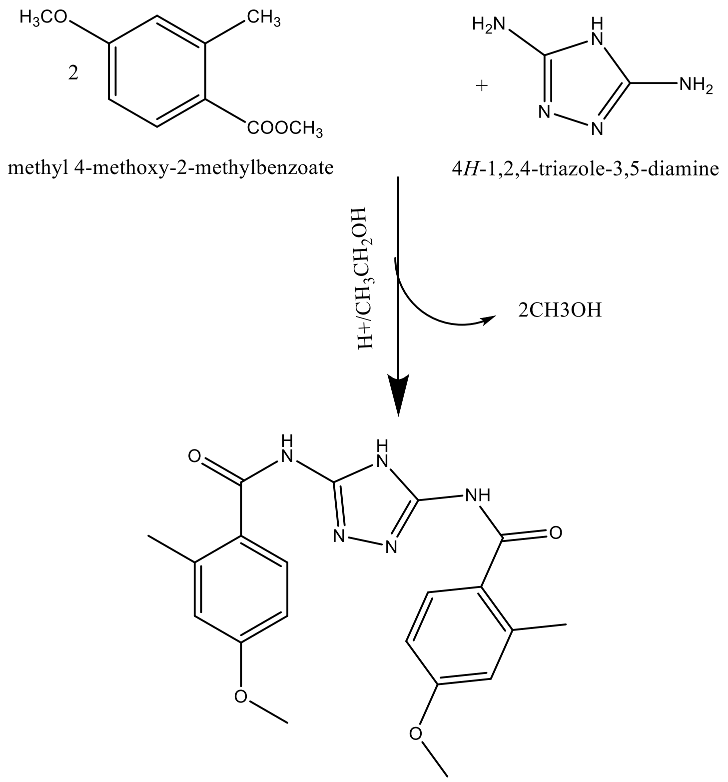
2-Experimental

A Stuart melting point (digital) SMP30 apparatus was used to record the Melting point. FTIR spectra were measured by a Shimadzu (FTIR) model 4800 s Spectrophotometer between the ranges (4000–400) cm−1 using KBr and CsI discs. A Shimadzu UV-Vis 16 ultraviolet spectrophotometer is used to measure the UV-visible spectra at room temperature (R.T.) using a 1 cm quartz cell and examined between 200–1100 nm at a concentration of 10−3 M in DMSO. All the above measurements were taken at the University of Thi Qar, College of Science, Department of Chemistry. Elemental analysis is used to determine (C ,H, N) for the new ligand [L] by a device of the type (Thermofinigan flash) at the University of Tehran / Iran. The Mass Spectra of the ligands and their complexes were recorded by a type of device (HP/MS Model 5973 Network Mass Selective Detector) at the University of Tehran / Iran, , energy of 70 eV. The 1H- NMR spectrum of the ligand was recorded by a device (Bruker DRX System

AL (500 MHz) Using a solvent DMSO – d6, HDO, in Iran, University of Tehran, using .Measurement of Conductivity was carried out at room temperature in DMSO using an Inolab multi-740, WTW 82362, Germany. Magnetic susceptibility of novel synthesized complexes was recorded at room temperature by the (Balance Magnetic Susceptibility Model – M.S.B. Auto), in Al-Nahrain University, College of Science. And all chemical were used of the highest purity, the employed Chemicals and there supplier companies were Fluca and B.D.H .

2. 1. Preparation of the Ligand (L)

Schiff base was synthesized by refluxing a methanolic solution of (0.02 mol, 3.6 g) methyl 4-methoxy-2-methylbenzoate incorporated with (0.01 mol,0.991 g) of 3,5-diamino-1,2,4-triazole for 4 h. After concentration, the mixture was left overnight at room temperature to yield a yellow precipitate, which was recrystallized from methanol and dried in a vacuum desiccator yield: 1.95 g (76.68%). The reaction progress was monitored by TLC (n-hexane/ethyl acetate 7:3). The product was obtained as a yellow powder, $C_{20}H_{21}N_5O_4$ (molecular weight = 395.42 g/mol), m.p. 123-125 °C.

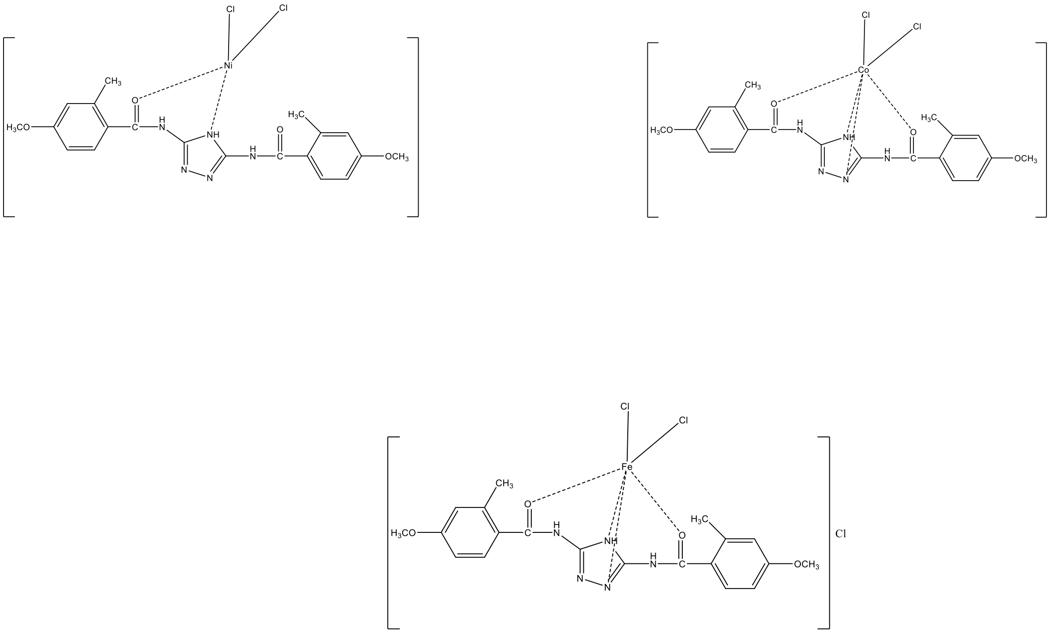


N,*N'*-(4*H*-1,2,4-Triazole-3,5-diyl)bis(4-Methoxy-2-Methylbenzamide)

scheme (1) Chemical equations for synthesis of the ligand

2-2- Preparation of the complexes of ligand

A methanolic solution of (CoCl3·6H2O, FeCl3, and NiCl2·6H2O) (1 mmol) was added dropwise to a refluxing solution of the ligand (L: 1 mmol) in methanol (5 mL). The mixture was cooled to room temperature and left to stand for 3 days. The resulting solids were filtered off, washed with cold methanol, and dried in a vacuum desiccator.[11]. The molecular formula and physical characteristics of the resultant complexes are documented in Table 1, schem 2.



Scheme: chemical structures of preparation complexes

2-3. The thermal stabilization of poly (vinyl chloride) by the complexes

2-3-1- PVC Films Preparation

PVC with Fe, Co, and Ni complexes were mixed using a solid-state blending method. The pre-synthesized compounds were incorporated at a concentration of 3 wt% (w/w), corresponding to 0.03 g of additive per 1 g of PVC. The blending process was carried out using a ceramic mortar to ensure effective mechanical homogenization, with continuous manual grinding for 30 minutes. This treatment aimed to enhance the dispersion of the additive within the polymer matrix and to minimize agglomeration, thereby improving interfacial interaction and compatibility between the components of the polymer composite.

2-3-2- Study of stabilization sample by UV.Visible light

Visible and ultraviolet spectroscopy was used to monitor the changes occurring in pure PVC and treated PVC the stabilizer during the thermal stress exposure process for time periods of 15, 30, 45, and 60 minutes at wavelengths of 275 and 385 nm. The samples were prepared for measuring visible and ultraviolet spectra by weighing 0.3

grams of the mixture (polymer + stabilizer) and placing it in a porcelain crucible, which was then placed in an oven at a temperature of 195°C in the presence of air for the aforementioned time periods. Afterward, the mixture was cooled, and the PVC was purified through reprecipitation by dissolving it in THF at room temperature, followed by precipitation by adding methanol with continuous mechanical stirring. The solution was then filtered and dried under vacuum at 45°C for 48 hours. Then, 0.0083 g of PVC and the purified PVC from the stabilizer were dissolved in 5 mL THF to prepare a solution. UV- Visible absorption of pure & stabilized PVC samples were recorded.

3. Results and Discussion

The newly prepared ligand and its corresponding complexes are found to be thermally stable in the solid state at room temperature with the free ligand being fairly soluble in most of polar organic solvents, and the metal complexes are highly soluble in polar aprotic solvents like DMF and DMSO.

3-1- Molar Conductance

The molar conductance of the 10^{-3} M DMSO solutions of the metal complexes were judiciously calculated. Values of Molar Conductance are organized systematically in Table 1, the data associated with the Co (III) and Fe (III) complexes imply that these compounds behave as 1:1 electrolytes; thus, it can be deduced that a single chloride ion exists outside the Coordination Sphere. The above statement is further supported by results obtained for Ni (II) complex, where the molar conductance values (Λm), are not enough to justify an ionic species; therefore, this complex is assumed to be neutral.

3-2- Magnetic Moments

Magnetic moment (μeff) data for the complexes with novel ligands are listed in Table 1. The magnetic moment for the Fe(III) complex 1 is reported at 2.4 BM, indicating one unpaired electron [12], and which may assume a spin free octahedra geometry, thus suggesting the low-spin state for Fe(III). Conventionally, the μeff value of 0.2BM for Ni (II) complex suggests the low-spin square planar geometry. The magnetic moment of Co (III) derivative, which is 0.36 BM, reveals not found the absence of unpaired electrons and suggested octahedral geometry.

Table 1: Some physical properties, molecular formula, and of the resulting complexes

no.	**Compound**	**m.wt**	**color**	**m.p**	**yield %**	(Λm) a	**μ_{eff}**
1	Ligand	395.42	Yellow	123-125	75.2	…	…..
2	[Ni(L)Cl$_2$]	524.9	**yellowish-green**	188-189	65.1	32	0.2
3	[Fe(L) Cl$_2$] Cl	557.6	Dark Brown	161-163	85.7	77	2.4
4	[Co(L) Cl$_2$] Cl	560.7	Orange	185-186	63.0	81	0.36

a = (S cm^2 mol^{-1}). (In DMSO Solvent).

3.3. IR spectra

The IR spectral data provide clear evidence of the ligand's coordination behavior toward the metal ions. The free ligand displayed characteristic bands at 3261 cm^{-1} (amide N–H), 1671 cm^{-1} (νC=O amide), and 1563 cm^{-1} (νC=N), along with bands attributed to (N–Hendocyclic) and aromatic(C–H) vibrations. Upon complex formation, the (νC=N),(νC=O)(amide), and endocyclic (νN–H) stretching frequencies shifted to lower wavenumbers by approximately 8–25 cm^{-1}, indicating the involvement of nitrogen and oxygen atoms in coordination due to electron density donation to the metal center. In contrast, the aromatic (νC–H) vibrations showed only reduced intensity without significant shifts, suggesting that these groups do not participate in bonding. Additional confirmation of coordination was provided by the appearance of new bands in the low-frequency region, assigned to (νM–N) (514–532 cm^{-1}), (νM–O) (568–577 cm^{-1}), and (νM–C)l (210–308 cm^{-1}) vibrations. These findings support the conclusion that the ligand behaves as a bidentate chelator in the Ni complexes and a quadridentate chelator in the Fe and Co complexes, coordinating through the azomethine nitrogen and carbonyl oxygen atoms.Table 2).

Table (2)

compound	νNH amide	νC=Oamide	νC=N endocyclic	νNH endocyclic	νC-H aromatic	νM-N	νM-O	νM-Cl
ligand	3261	1671	1563	3221	3165	-----	-----	----
Co-L	3232	1623	1545	3278	3134	514	568	201
Fe-L	3211	1654	1521	3189	3123	529	577	277
Ni-L	3234	1621	1543	3162	3167	532	562	338

3-4- 1H NMR spectra

The 1H NMR spectrum of the ligand reveals characteristic signals attributed to the (–NHendocyclic) proton, which is observed at 10.77 ppm. Additionally, the signal at 6.84 ppm can be ascribed to the two protons associated with the (–NH) groups of the ligand. The signal identified at 3.38 ppm is likely corresponding to the (-OCH3) protons. and the band between (7.19-8.29) ppm may be assigned to aromatic ring protons [20-22], and the band at 2.5 ppm refers to -CH3 groups, (Figure 1).

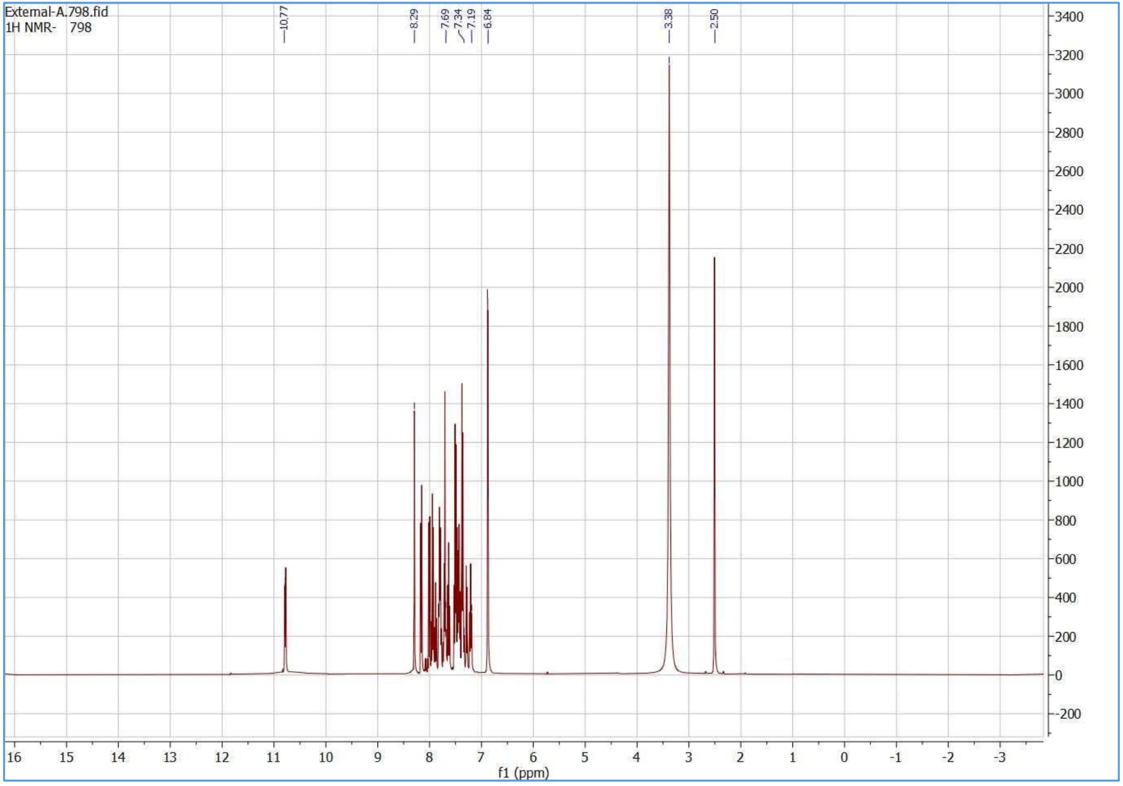
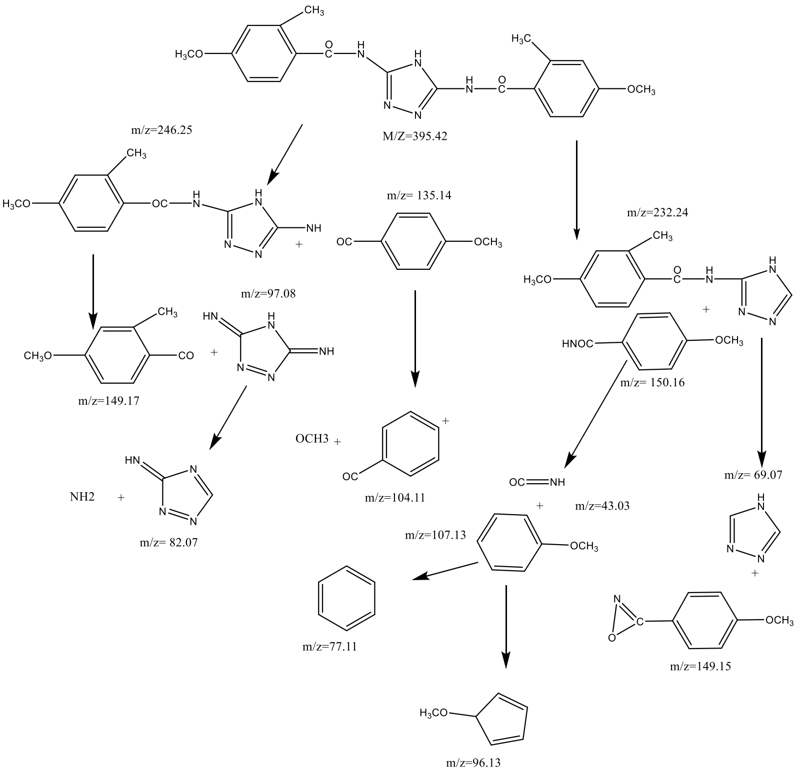


Figure (1) The 1H NMR spectrum of the ligand

3-5-Mass spectra

3-5-1 Mass spectra of ligand

The ligand spectrum appearance of the molecular ion peak (M^+), series of peaks and base peak, the mechanism of breakup embedded in the scheme (2), (table 4. Figure 1).



Scheme (2)The mechanism of ligand breakup

Table 4 : Significant peaks observed in the Ligand

Number	Fragmentation Observed	M/Z
1	$C_{20}H_{21}N_5O_4$ (Molecular ion)	395
2	$C_{11}H_{12}O_2$	135
3	$C_{11}H_{12}N_4O_2$	232
4	$C_9H_9O_2$	149
5	$C_2H_3N_5$	97
6	$C_8H_8NO_2$	150
7	$C_2H_2N_4$	82
8	C_6H_5 (base peak)	77
9	C_7H_4O	104
10	$C_2H_3N_3$	69

3-5-2 Mass Spectra Observed of Iron-L

Mass Spectrum for the Iron complex was dominated by a molecular ion (M^+) , base peak and a series of prominent fragment peaks attributed to the stepwise loss of chloride atoms, the fragmentation pattern of which is outlined in Table 5 figure 2.

Table (5) Significant peaks of mass spectrum for Fe--L

no.	Fragmentation	M/Z

1	$[Fe(L)\,Cl_2]^{+\cdot}Cl$	557
2	$[Fe(L)\,Cl_2]^{+\cdot}$	521
3	$[Fe(L)\,Cl]^{+\cdot}$	486
4	$[Fe(L)]^{+\cdot}$	450

3-5-3 Mass spectra observed for the Nickel complex

The Nickle-complex spectrum reveals the presence of the Molecular ion (M+), base peak, and a series of significant peaks associated with the loss of chloride atoms, with the breakdown illustrated in (table 7, Figure 3).

Table (6) Significant peaks observed of mass spectrum for Ni-complex

Number	Fragmentation	m/z
1	$[Ni(L)\,Cl_2]^{+\cdot}$	524
2	$[Ni(L)\,Cl]^{+\cdot}$	488
3	$[Ni(L)]^{+\cdot}$	453

3-5-4 Mass spectra observed of Co-complex

The Co-complex spectrum reveals the presence of the molecular ion peak (M+), base peak, and a series of significant peaks associated with the loss of chloride atoms, with the breakdown illustrated in (Table 5, Figure 4).

Table 7 : Significant peaks observed of mass spectrum for Co-complex

Number	Fragmentation	M/Z
1	$[Co(\,L\,)\,Cl_2]^{+\cdot}\,Cl$	560
2	$[Co(L)\,Cl_2]^{+\cdot}$	524
3	$[Co(L)\,Cl]^{+\cdot}$	486
4	$[Co(L)]^{+\cdot}$	453

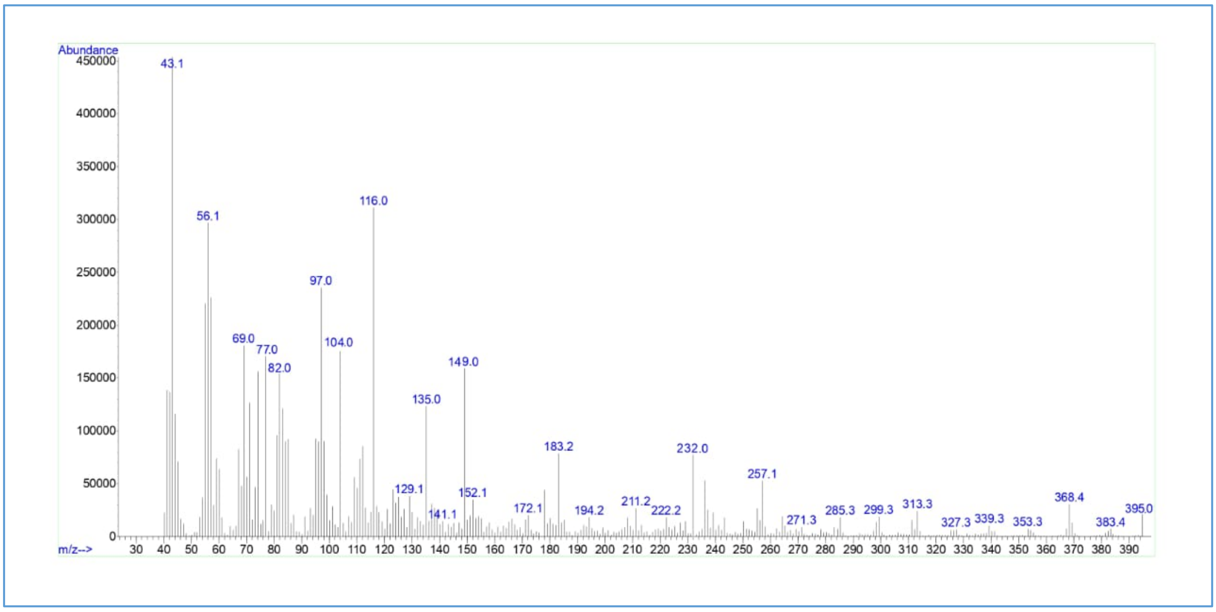


Figure (1)mass spectrum for Ligand

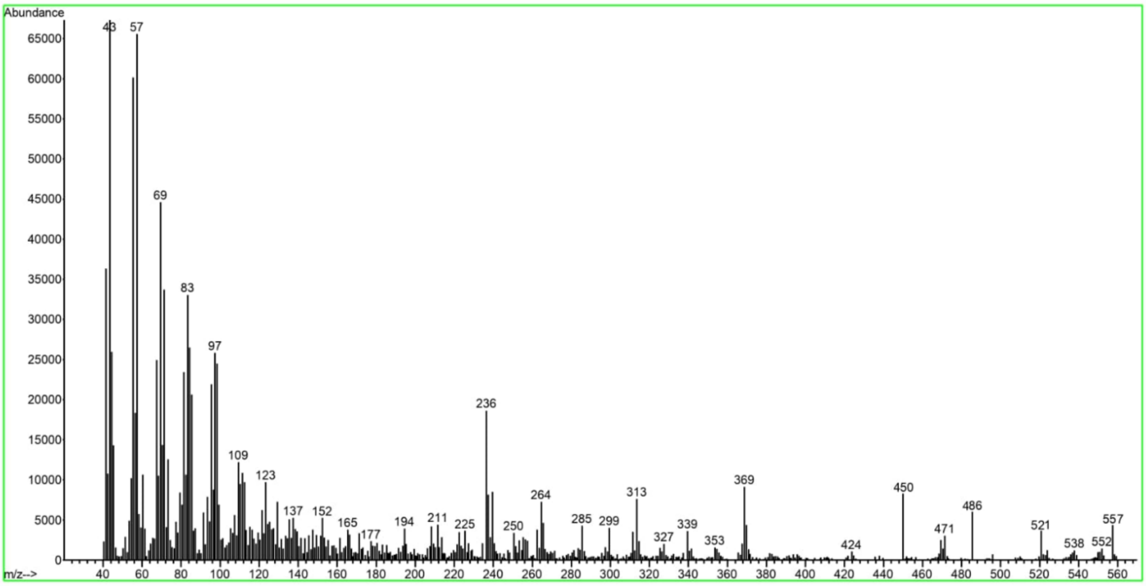


Figure (2)mass spectrum for Fe--L

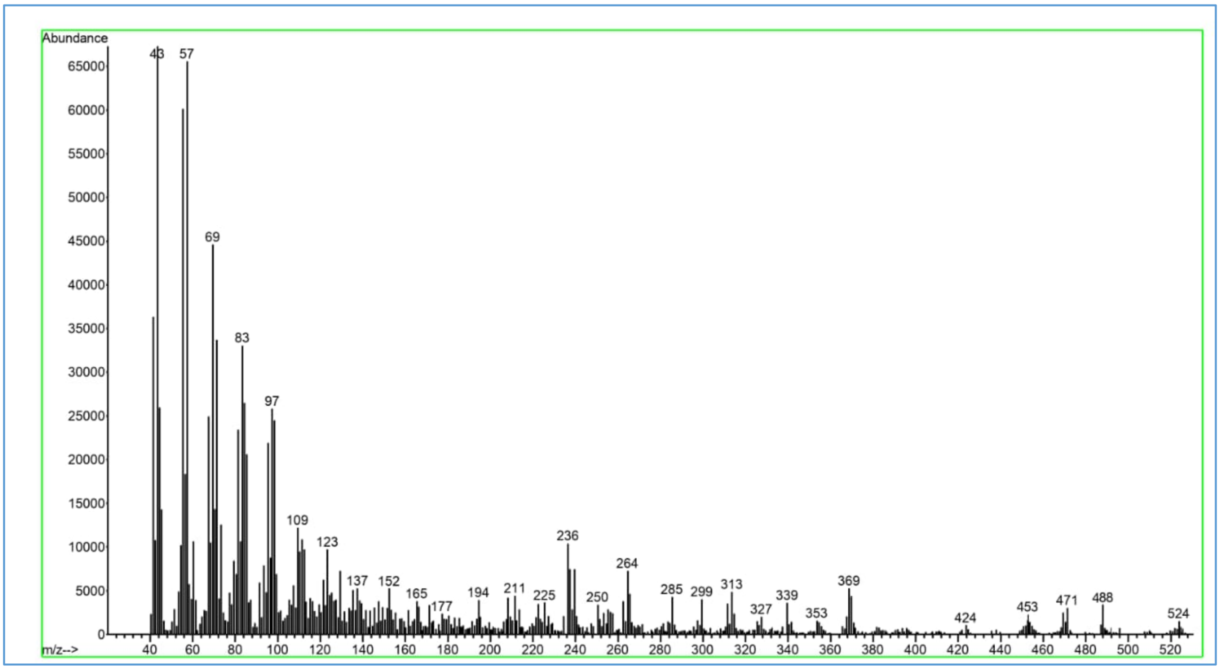


Figure (3)mass spectrum for Ni--L

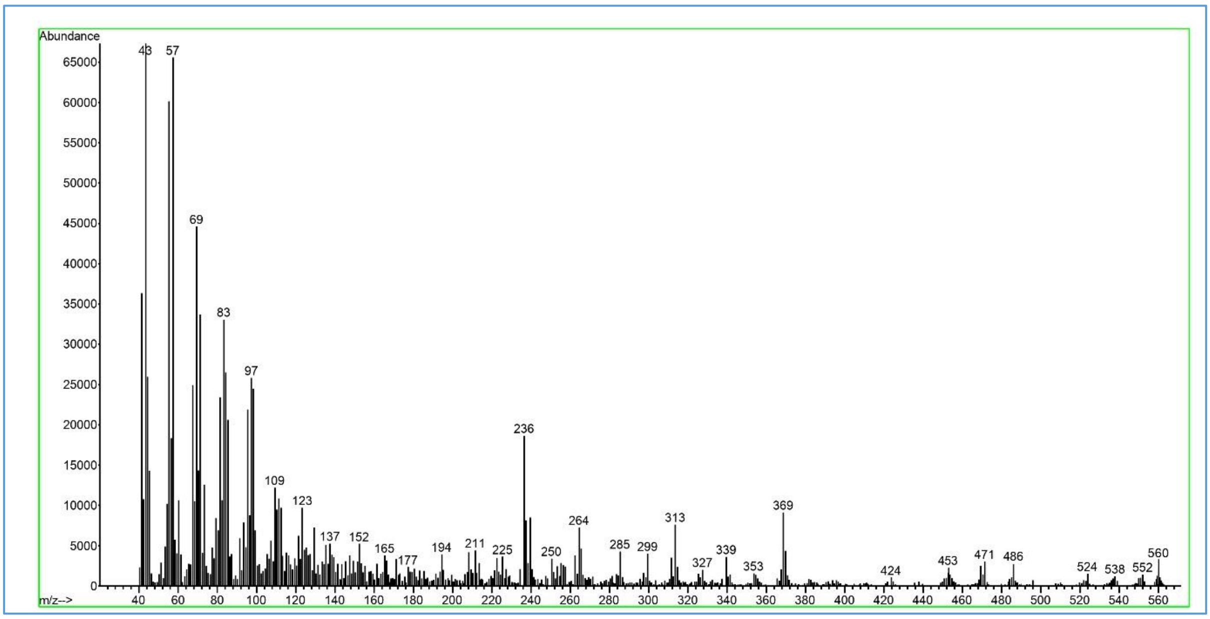


Figure (4)mass spectrum for Co--L

3-6- CHN analysis

All CHN analysis data has been summarized in table (8).

Table (8) CHN Analysis For The Prepared Compound

Compound	**Founded %**			**Calculated %**		
$C_{18}H_{17}N_5O_4$	H%	C %	N %	H%	C%	N%
	5.35	60.75	17.71	5.43	61.05	17.46

4- The thermal stabilization of PVC – Complexes

Polyvinyl chloride (PVC) decomposes when exposed to high temperatures, releasing hydrogen chloride gas, either during its manufacturing or during its use. This decomposition leads to the formation of consecutive double bonds (polyenes) of different lengths, in addition to the formation of isolated bonds. Some studies have indicated that short-chain polyenes (2-4 consecutive double bonds) are more likely to form, while other studies have suggested that polyenes are active in secondary reactions, leading to cross-linking and consequently causing undesirable changes in the polymer’s properties. From all this, the role of thermal stabilizers added to PVC becomes clear. To monitor the changes occurring in unstabilized and stabilized PVC chains with various complexes under study when exposed to thermal stress at 194°C for time periods of 15, 30, 45, and 60 minutes, this research employed visible and ultraviolet spectroscopy for this purpose, based on previous studies involving reprecipitated PVC from the complexes. The study was conducted at two wavelengths, 275 and 385, which correspond to the absorption of three and seven double bonds, respectively. The absorption intensity at 275 nm is greater compared to the absorption intensity at 385 nm, which indicates the concentration of the triple polyenes in the polymeric chain is higher than the concentration of heptakis polyenes, which is to be expected since the triple double bonds in the polymer will form at the beginning of thermal stress exposure. We also find that the absorption intensity increases with the duration of thermal stress exposure, indicating an increase in the polymer chain content in successive double bonds. On the other hand, the study showed a clear decrease in absorption intensity at the wavelengths 275 and 385 for the polymer stabilized with the prepared complexes compared to the unstabilized polymer. The study also showed that the polymer stabilized with the cobalt complex is more efficient than the other complexes under study based on the absorption values at the wavelengths, as shown in Table 9, Figures 1and 2.

Table (9) Absorption values for unmodified PVC and PVC reprecipitated from metal complexes

No.	Com.	Absorption at 275 nm				Absorption at 385 nm			
		Heat stress time (min)				Heat stress time (min)			
		15	30	45	60	15	30	45	60

1	PVC unstabil.	0.253	0.398	0.643	0.895	0.136	0.185	0.232	0.343
2	PVC+Fe comp.	0.083	0.265	0.581	0.794	0.109	0.123	0.184	0.265
3	PVC+Co.comp.	0.061	0.234	0.514	0.731	0.072	0.106	0.167	0.240
4	PVC+Ni.comp.	0.072	0.250	0.561	0.751	0.086	0.114	0.177	0.256

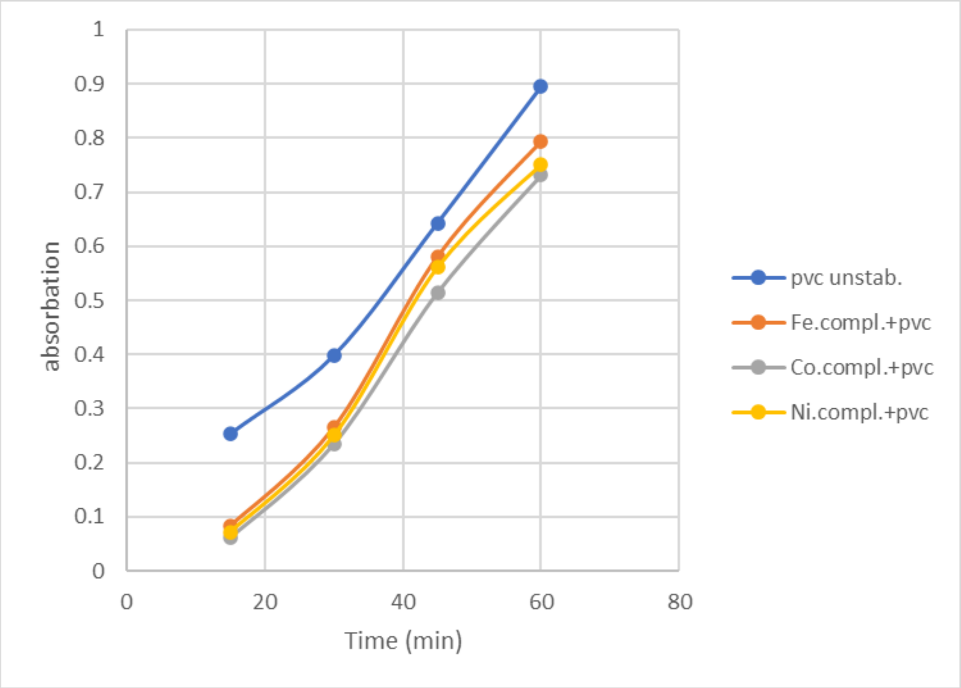


Figure: (1) Absorption band relationship at 275 nm for unstabilized PVC and for PVC reprecipitated from prepared metal complexes.

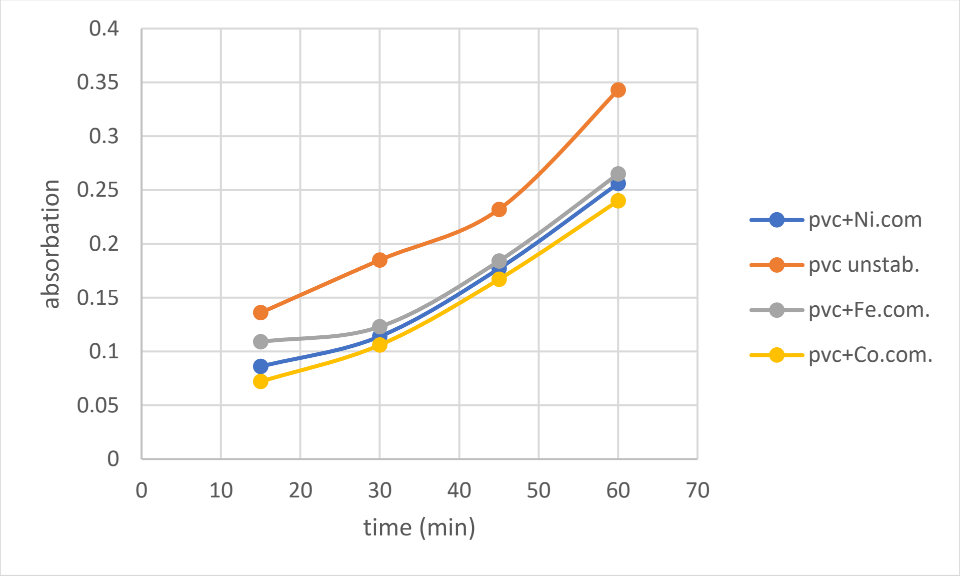


Figure: (2) Absorption band relationship at 385 nm for unstabilized PVC and for PVC reprecipitated from prepared metal complexes.

5-Conclusions

The findings from infrared spectroscopy, elemental analysis, ^{1}H NMR spectroscopy, mass spectrometry, magnetic moments, and molar conductivity. Help determine the structure of the ligand and its compounds. The chromium and iron compounds take the octahedral configuration, and the nickel complex takes the square planar configuration. Spectroscopic studies showed that the prepared metal complexes are considered good thermal stabilizers for PVC, as they capture active chlorine atoms in the polymer chain and prevent the formation of free radicals. The complexes are also ranked according to their effectiveness as follows: Co > Ni > Fe.

6- Acknowledgement

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