

Synthesis and Characterization of Ni(II), Cu(II), Co(II), Cr(II) and Fe(II) Metal Complexes of New 1,3,4-Triazole Derivative

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Abstract

A Schiff base of 1,3,4-triazole derivative have been synthesized by the reaction between 5-(4-methylphenyl)-1,3,4-oxadiazole-2-thiol and hydrazine in the presence pyridine as catalyst to yield the 4-amino-5-(4-methylphenyl)-4H-1,2,4-triazole-3-thiol which was treated with aromatic aldehyde to gave five member heterocyclic ring schiff base called 5-(4-methylphenyl)-4-[(pyridin-2-ylmethylidene)amino]-4H-1,2,4-triazole-3-thiol as didentate ligand. The last compound reacted with hydrated metal chlorides NiCl_2 , CuCl_2 , CoCl_3 , CrCl_3 and FeCl_3 in presence of ethanol as solvent to yield 1,3,4-triazole complexes. The structures of synthesized ligand and their complexes have been established on the basis of their spectral FTIR, Mass, $^1\text{H-NMR}$, elemental analysis C,H,N as well as Molar conductance .The purity of the compounds was confirmed by TLC.

Key words :Characterization , Complexes , Triazole ,Schiff bases.

1.Introduction :-

1,3,4-Triazole (1) is planar five member heterocyclic system with two carbon and three nitrogen atoms , one pyrrole type and two

pyridine type in the 1-,3- and 4- positions . There are three other known isomers : 1,2,4-triazole (2) 1,2,3-triazole (3) and 1,2,5-triazole (4) (1) .

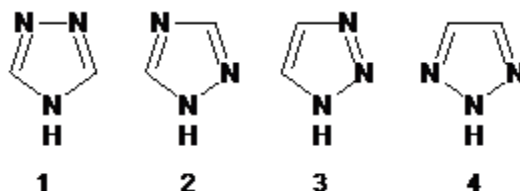


Fig.1.Isomeric forms of triazole

In recent years derivatives of 1,3,4-triazole have attracted considerable interesting recently because of their unique structure and their wide range of applications in pharmaceutical chemistry remarkable as anesthetic, antibiotic activity , antiviral antibacterial,antifungal,antineoplastic,antimicrobial,anti-inflammatory,antiproliferative and antifungal . (2-4) .

The triazole antifungal drugs included fluconazole(5), isavuconazole , itraconazole , voriconazole (6), pramiconazole, and posaconazole (5) .

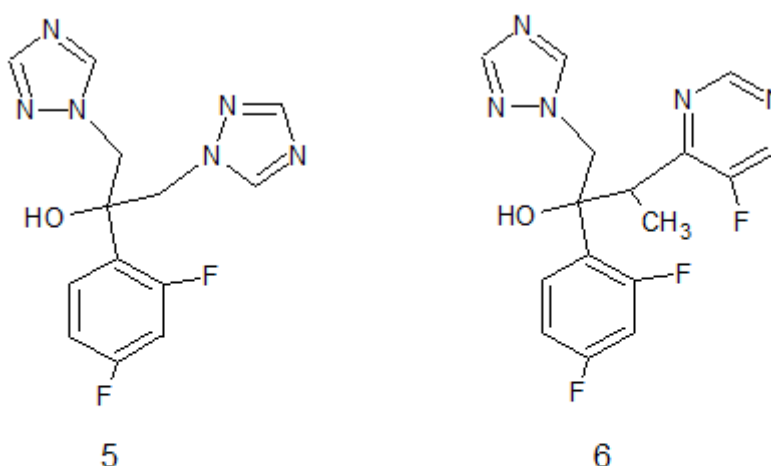


Fig.2. Structure formula of some triazole derivative drugs

1,3,4-triazole played vital roles in the coordination chemistry (inorganic chemistry) as nitrogen-containing heterocyclic ligands .

Therefore , the present article study aimed to synthesis of some new 1,3,4-triazole derivatives as didentate ligand with some transition metal ion such as, Cu (II),Ni (II) Fe(III), Cr(III), Co(III) .to form tetrahedral geometry complexes $[Cu(L)Cl_2]$, $[Ni(L)Cl_2]$ and octahedral geometry complexes respectively $[Fe(L)Cl_2]Cl$, $[Cr(L)Cl_2]Cl$, $[Co(L)Cl_2]Cl$, which have higher biological activity and low toxicity of 1,3,4-triazole makes it possible to regard their metal complexes as substances of versatile biochemical and pharmaceutical destination for instance among all other ligand.

Generally , metal complexes of ligands such as ,N-heterocycles exhibit enhanced biological activities compared to the uncomplexed ligand (6).

2.Experimental work :-

2.1.Synthesis of ligand

A mixture of 0.1 mole of the ester ethyl 4-methylbenzoate and 0.2 mole of hydrazine hydrate were was stirred at room temperature in 100ml of absolute ethanol for 4hr.The resultant mixture **[A]** was concentrated, cooled ,The purity of the compound was followed by TLC. Color : Wight crystal, Yield: 95 % , M.P 141-143 °C. [7]

A mixture of compound (A) (0.1 mole) with (5.6 gm, 0.1mole) KOH and (12 ml, 0.2 mole) of CS_2 in 100 ml of ethanol .The resulting mixture was refluxed for (10 hrs). The solution was concentrated and cooled and acidified to pH 5-6 with hydrochloric acid solution and recrystallized from ethanol .The light yellow precipitate which separated was filtered and recrystallized from ethanol to give 5-(4-methylphenyl)-1,3,4-oxadiazole-2-thiol **[B]** ,The purity of the compound was followed by TLC .Yield: 85%, M.P 201-203 °C [8].

A mixture of the of compound (B) (0.05 mol) in pyridine (25 ml), and hydrazine hydrate (0.1 mole) was refluxed for 8 hours. The reaction mixture was cooled to room temperature, dissolved in

water, then after acidification with concentrated HCl the solid was separated, washed with water, filtered off, dried and finally crystallized from pyridine to give 4-amino-5-(4-methylphenyl)-4H-1,2,4-triazole-3-thiol **[C]** . M.P 193-195°C, yield 82 % [9].

To a solution of triazoles [C] (0.05mole) in absolute ethanol (50 ml) was added an equimolar amount of the aromatic aldehyde pyridine-2-carbaldehyde

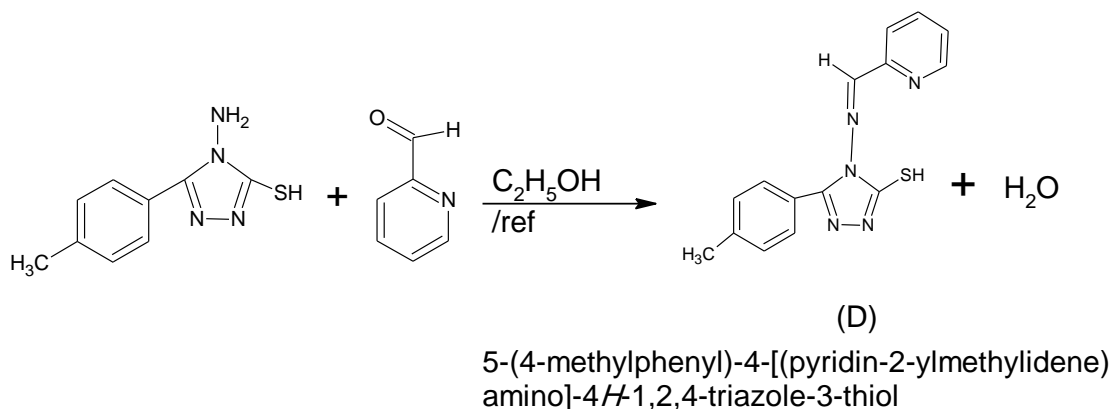
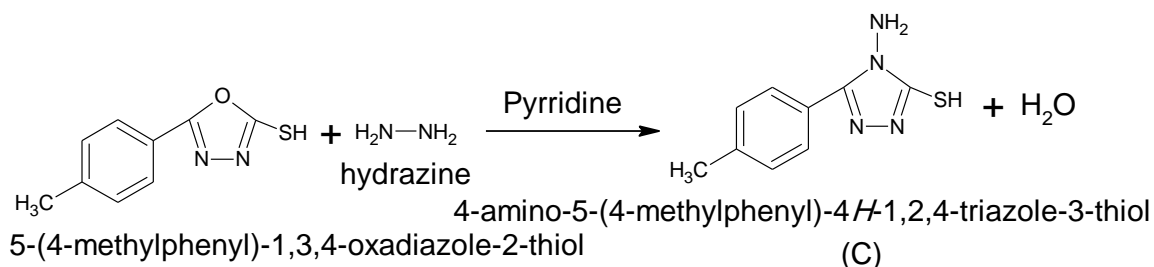
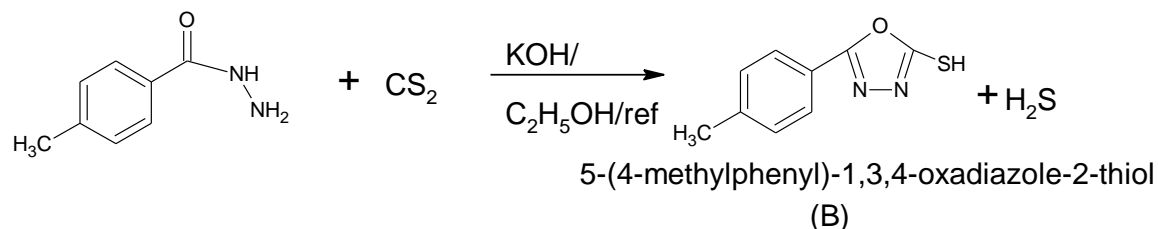
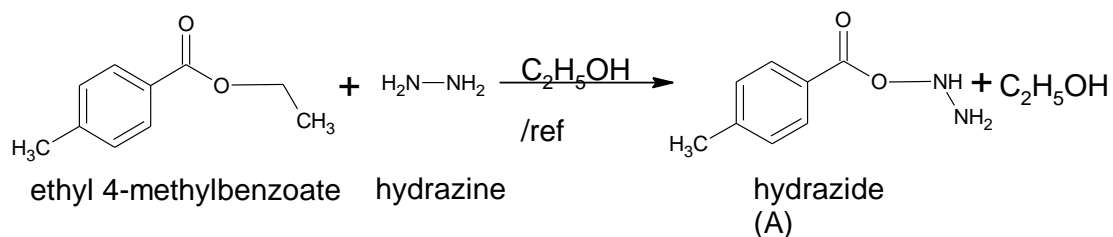
0.05mole and the mixture was refluxed at 100°C for 8 hr. After completion of reaction, the mixture was cooled and poured into the ice cold water. The solid obtained was filtered, washed with ice cold water, dried and recrystallized from ethanol, to give 5-(4-methylphenyl)-4-[(pyridin-2-ylmethylidene) amino]-4H-1,2,4-triazole-3-thiol **[D]** (schiff base). M.P 203-205°C, yield 78 % [10].

2.2. Synthesis of metal complexes

A solution of (0.2 mole) of $\text{CoCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$ dissolved in 10 ml of absolute ethanol was added drop by drop to (0.2 mole) of ligand dissolved in 30 ml of absolute ethanol. The mixture was heated with stirring for 45 min; the resulting precipitate was filtered off, washed with distilled water then dried [11], the physical properties of the prepared complexes listed in Table(1)

3. Present work:-

Preparation of Ligand:-



Scheme 1: Synthesis of **1,3,4-triazole derivatives ligand**

4 . RESULTS AND DISCUSSION

The 1,3,4-triazole ligand and their metal complexes were subjected to elemental analyses. The results of elemental analyses (C, H, N) with molecular formula and melting points are presented in Table 1 and 2. The results obtained are in good agreement with those calculated for the suggested formula. The structures of the

synthesized 1,3,4-triazole ligand and their metal complexes are also confirmed by IR, ¹H NMR , MASS , spectra and molar electrical conductivity which are discussed below.

Table 1: The experimental result and physical data of 1,3,4-triazole ligand and its complexes

No	Formula	M.wt	Color	m.p. °c	Yield%
L	C ₁₅ H ₁₃ N ₅ S	295	Pink	203-205	78
1	[Fe(L)2Cl2]Cl	753	Pale brown	212-214	72
2	[Co(L)2Cl2]Cl	756	Deep Yellow	221-223	68
3	[Cr(L)2Cl2]Cl	749	Yellow	209-211	75
4	[Cu(L)Cl2]	429	Greenish blue	215-217	77
5	[Ni(L)Cl2]	425	Deep green	208-210	72

Table 2: The elemental analysis of Ligand data of 1,3,4-triazole ligand

Theoretical Data		
C	H	N
61.00%	4.44 %	23.71%
practical Data		
C	H	N
59.91%	4.47%	23.82%

4.1. Infra-Red Spectroscopy :-

FTIR (KBr, cm⁻¹) of 1,3,4-triazole derivative ligand band showed ; 3053V(C-H)Aro and 2959 V(C-H)Ali, 2708 V(S-H) , 1619 V(C=N). FTIR band of the complexes was shifted to a higher frequency as showed in table 3. indicating its involvement in coordination with metal ion . These findings are further supported by the appearance of new bands at 354–365 cm⁻¹ of v(S-M) and 567-570

cm⁻¹ of $\nu(\text{N-M})$.all data tabulated in Table3 as shown in (Fig. 1,2,3) [12].

Table 3: IR spectral data (cm-1) of the ligand and their metal complex in KBr pellets

Vibration mode	Ligand	Ligand+Fe	Ligand+Ni	Ligand+Co
$\nu(\text{C-H})_{\text{Aro}}$	3053	3087	3098	3095
$\nu(\text{C-H})_{\text{Ali}}$	2959	2950	2962	2960
$\nu(\text{S-H})$	2708	2780	2744	2792
$\nu(\text{C=N})_{\text{out ring}}$	1619	1627	1626	1635
$\nu(\text{S-M})$	----	354	365	362
$\nu(\text{N-M})$	----	570	570	567

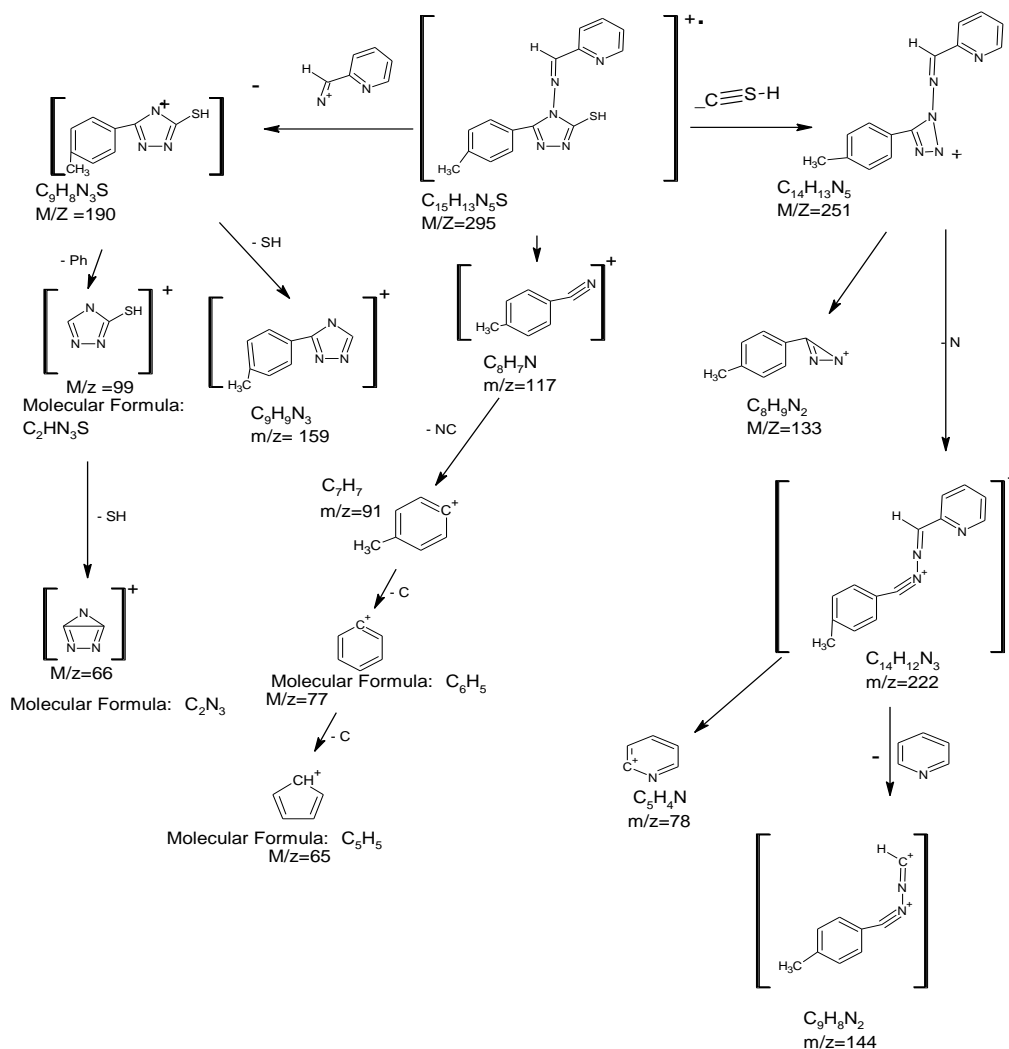
4.2. ¹H NMR spectra data of ligand : -

The ¹H NMR spectra of the 1,3,4-triazole derivative ligand in DMSO solutions with assignments are collected in Table (4). The ¹H NMR spectra of the free ligand (Fig. 3) showed the aromatic proton signals appearing at (7-8) ppm and (6.6-7.2) ppm, also showed C-H proton at 8.9 ppm correspond to the azomethene group, and also showed proton at 3.4 and 4.1 ppm correspond to the CH₃ and SH of thiol group respectively. .all data tabulated in Table3 as shown in (Fig. 4) .[13]

Table 4: ¹H NMR spectra data of ligand Mass spectra :-

Signal No.	Signal Position (ppm)	Relative No of Protons	Inference
1	7-8	4H	Ar-H
2	6.6-7.2	4H	Ar-H
3	8.9	1H	-CH
5	4.1	1H	-SH
6	3.4	3H	-CH

Mass spectral data confirm the structure of the prepared 1,3,4-triazole derivative ligand as show in the following scheme and their Ni(II) ,Cu(II) ,Fe (III),CO(III) and Cr(III), complexes as indicated by the molecular ion peaks corresponding to their molecular weight all data $[\text{Ni}(\text{L})\text{Cl}_2]^+$ (425), $[\text{Ni}(\text{L})\text{Cl}]^+$ (390), $[\text{Ni}(\text{L})]^+$ (354), $[\text{Cu}(\text{L})\text{Cl}_2]^+$ (429), $[\text{Cu}(\text{L})\text{Cl}]^+$ (394), $[\text{Cu}(\text{L})]^+$ (359), $[\text{Cr}(\text{L}_2)\text{Cl}_2]^+\cdot\text{Cl}$ (749), $[\text{Cr}(\text{L}_2)\text{Cl}_2]^+$ (714), $[\text{Cr}(\text{L}_2)\text{Cl}]^+$ (678), $[\text{Cr}(\text{L}_2)]^+$ (642), $[\text{Fe}(\text{L}_2)\text{Cl}_2]^+\cdot\text{Cl}$ (753), $[\text{Fe}(\text{L}_2)\text{Cl}]^+$ (717), $[\text{Fe}(\text{L}_2)\text{Cl}]^+$ (682), $[\text{Fe}(\text{L}_2)]^+$ (646), $[\text{Co}(\text{L}_2)\text{Cl}_2]^+\cdot\text{Cl}$ (756), $[\text{Co}(\text{L}_2)\text{Cl}_2]^+$ (720), $[\text{Co}(\text{L}_2)\text{Cl}]^+$ (685), $[\text{Co}(\text{L}_2)]^+$ 649. as shown in the schema No 2,(Fig.5, 6,7,8,9&10)_[14].



Scheme 2: Fragmentaion mass spectral of the ligand

4.3. Molar conductance measurements:

The molar conductance data of the synthesized complexes solution tabulated in the table number 6. were measured at room temperature in ($10^{-3}M$) DMSO solvent. Two exhibited low value of molar conductivity (0-20) which indicates that complexes $[Cu(L)Cl_2]$ and $[Ni(L)Cl_2]$ under study is non-electrolyte. The obtained value suggests that no anions ((Counter Ions)) present outside the coordination sphere and showed good agreement with that reported in the literature , The other complexes $[Fe(L)Cl_2]Cl$, $[Co(L)Cl_2]Cl$ and $[Cr(L)Cl_2]Cl$ exhibited (31-34 $\Lambda_M(S \cdot cm^2 \cdot mole^{-1})$) value of molar conductivity which indicates that complexes under study is 1:1 electrolyte. The obtained value suggests that an anions ((Counter Ions)) present outside the coordination sphere and showed good agreement with that reported in the literature [10].

Table 6 : standard value of molar conductance data

Solvent	Electrolyte Type $\Lambda_M(S \cdot cm^2 \cdot mole^{-1})$		
	Non Electrolyte	1:1	1:2
Dimethyl sulfoxide	0-20	30-40	70-80

Table 7. Molar conductance data of all complexes measurements were made in anhydrous DMSO at 25oC ,Concentration 10^{-3} at 298K .

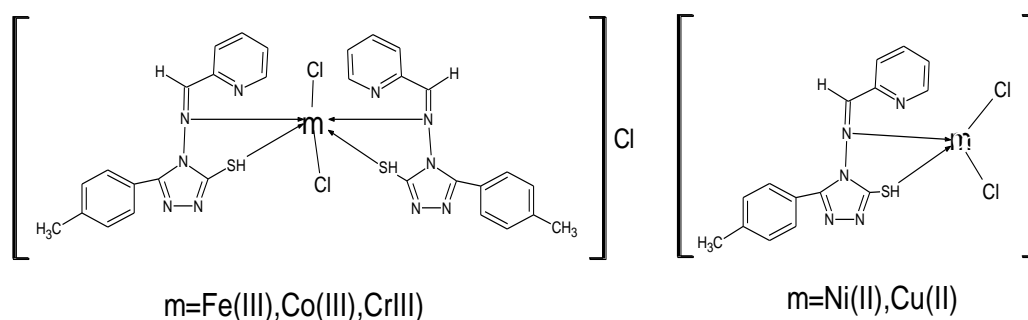
NO	Formula	solvent	Standar rd Λ M	Practical Λ M(S.cm ² .mol ⁻¹)	Electrolyte Type
1	[Cu(L)Cl ₂]	Dimethyl sulfoxide	0-20	13.3	Non Electrolyte
2	[Ni(L)Cl ₂]	Dimethyl sulfoxide	0-20	12.6	Non Electrolyte
3	[Fe(L)Cl ₂]Cl	Dimethyl sulfoxide	30-40	32	1:1
4	[Co(L)Cl ₂]Cl	Dimethyl sulfoxide	30-40	31	1:1
5	[Cr(L)Cl ₂]Cl	Dimethyl sulfoxide	30-40	34	1:1

5. Conclusion :

In the present study, Ni(II), Cu(II), Fe(III) Co(III) and Cr(III) complexes with 1,3,4-triazole derivative ligand have been synthesized and confirmed by ¹HNMR ,IR, Mass spectra, elemental analyses C,H,N and Molar conductance .

Appearance the band between (354-365 cm⁻¹) of ν (S-M) and (567-570 cm⁻¹) of ν (N-M) in the prepared complexes while disappeared in the prepared ligand further support the coordinate was appeared through the sulphur of thiol group and the other done through the nitrogen of the azomethen group .

According to all and the physical and chemical measurements, we can suggested the chemical configuration of the prepared complexes as octahedral and tetrahedral geometry complexes as shown in the scheme (3).



Scheme 3: tetrahedral and octahedral complexes.

References

- 1- R.R Gupta, M.kumat, V.Gupta ; Heterocyclic Chemistry five Membred Heterocyclic ;Volume II ;pp No 501 ;2009 .
- 2-SABIR HUSSAIN[§]*, JYOTI SHARMA[#] and MOHD.AMIR[§]:Synthesis and Antimicrobial Activities of 1,2,4-Triazole and 1,3,4-Thiadiazole Derivatives of
- 3-Yanwei Wang ^{1,3,†}, Kehan Xu ^{1,†}, Guojing Bai ¹, Lei Huang ¹, Qiuye Wu ¹, Weihua Pan ^{2,*} and Shichong Yu ^{1,*} : Synthesis and Antifungal Activity of Novel Triazole Compounds Containing Piperazine Moiety : Molecules 2014, 19, 11333-11340; doi:10.3390/molecules190811333 .
- 4-Rajeev Kharb, Mohammad Shahar Yar : Pharmacological significance of triazole scaffold: Journal of Enzyme Inhibition and Medicinal Chemistry, 2011; 26(1): 1–21
- 5-Nickie D. Greer, PharmD, BCPS Posaconazole (Noxafil): a new triazole antifungal agent ; Proc (Bayl Univ Med Cent). 2007 Apr; 20(2): 188–196.
- 6- A. M. Hammam , M. A. EL-Gahami, Z. A. Khafagi, M. S. AL-Salimi and S. A. Ibrahim*;Synthesis and Characterization of Some New Antimicrobial Transition Metal Complexes with 1, 2, 4-Triazole-3-thione Schiff Bases; J. Mater. Environ. Sci. 6 (6) (2015) 1596-1605 Hammam et al.

- 7 - Zafer Asim Kaplancikli ; Synthesis of Som; Oxadiazole Derivatives as New Anticandidal Agents ; molecules ; Molecules 2011, 16,pp 7662-7671
- 8- Ali Omairi Mohammad; Synthesis and Characterization of some Oxadiazoles and Thiadiazoles derivatives ; J. of university of anbar for pure science : Vol.4:NO.1 : 2010;pp
- 9- Fathy A. Yassin and Amal F. Seleim; Synthesis and reactions of oxadiazolo, thiadiazolo and triazolo phthalazin-1(2H)-one derivatives ; Der Pharma Chemica, 2012, 4 (3):860-866 .
- 10- Atheer A. Ali, Basim I. Al-Abdali ; Synthesis and characterization of 4-(((3-mercapto-5-phenyl-4H-1,2,4-triazole-4-yl)imino)methyl)-2-methoxyphenol and its complexes with Zr(IV), Cd(II) and Sn(II) ions ; .Iraqi Journal of Science, 2015, Vol 56, No.2B, pp: 1274-1288.
- 11- Mahasin Alias*, Ameena N. Seewan*, Sura Khalil* and Carolin Shakir*;
Synthesis, Spectral Study and Theoretical Treatment of Some Transition Metal Complexes of 5-(4-Nitro Phenyl)-4-Amino-3-Mercapto Propenyl-1,2,4-Triazole Ligand; Journal of Al-Nahrain University Vol.17 (3), September, 2014, pp.69-80
- 12- Marinela M. Dîrtu 1, Yves Boland 1, Damien Gillard 1, Bernard Tinant 1, Koen Robeyns 1, Damir A. Safin 1, Eamonn Devlin 2, Yiannis Sanakis 2 and Yann Garcia 1,*;New Mononuclear Cu(II) Complexes and 1D Chains with 4-Amino-4H-1,2,4-triazole; Int. J. Mol. Sci. 2013, 14 ;PP23598- 23613 .
- 13- SABIR HUSSAIN§*, JYOTI SHARMA# and MOHD.AMIR; Synthesis and Antimicrobial Activities of 1,2,4-Triazole and 1,3,4-Thiadiazole Derivatives of 5-Amino-2-Hydroxybenzoic Acid ; E-Journal of Chemistry ; Vol. 5, No.4, pp. 963-968, October 2008 .
- 14- Khosrow ZAMANI, Khalil FAGHIHI ,M. Reza SANGI and Javad ZOLGHARNEIN ; Synthesis of Some New Substituted 1,2,4-Triazole and 1,3,4-Thiadiazole and Their Derivatives; Turk J Chem; 27 (2003) ,PP 119- 125.
- 15- M. A. El-Gahami*, 1,2 , A. H. Abdel Salam1,3 , H. M. Albishri1; Synthesis, magnetic, spectral and antimicrobial activity of new

Schiff bases complexes derived from 1,2,4-triazole-5-thione ; J. Mater. Environ. Sci. 6 (10) (2015) ;pp2886-2894 .

7.Appendices :-

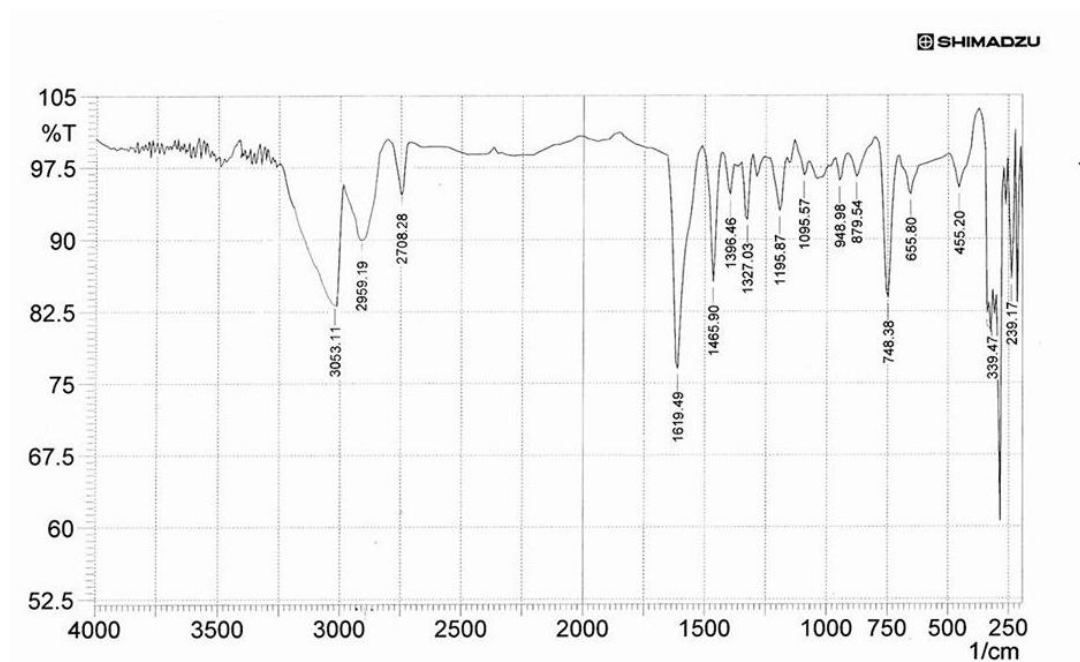


Figure 1 : IR spectra of ligand

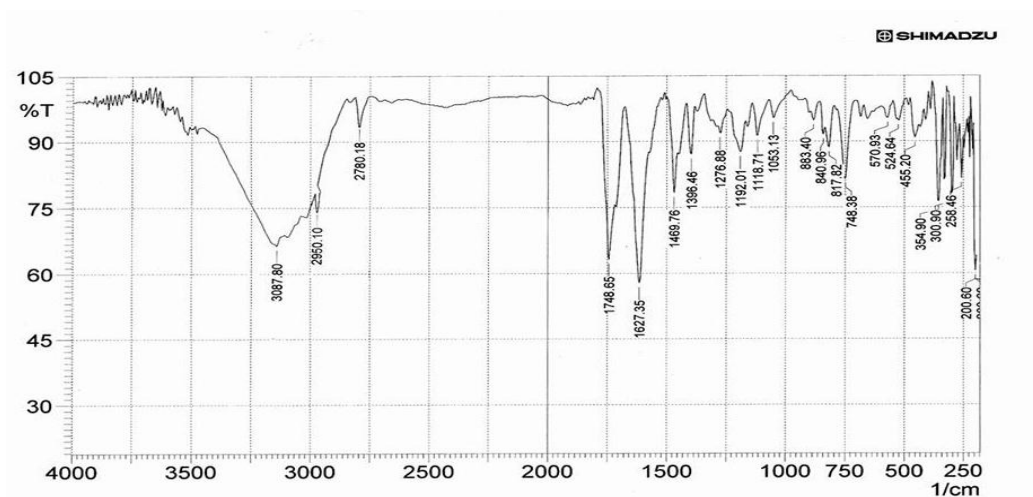


Figure 2: IR spectra of Fe(III) complexes

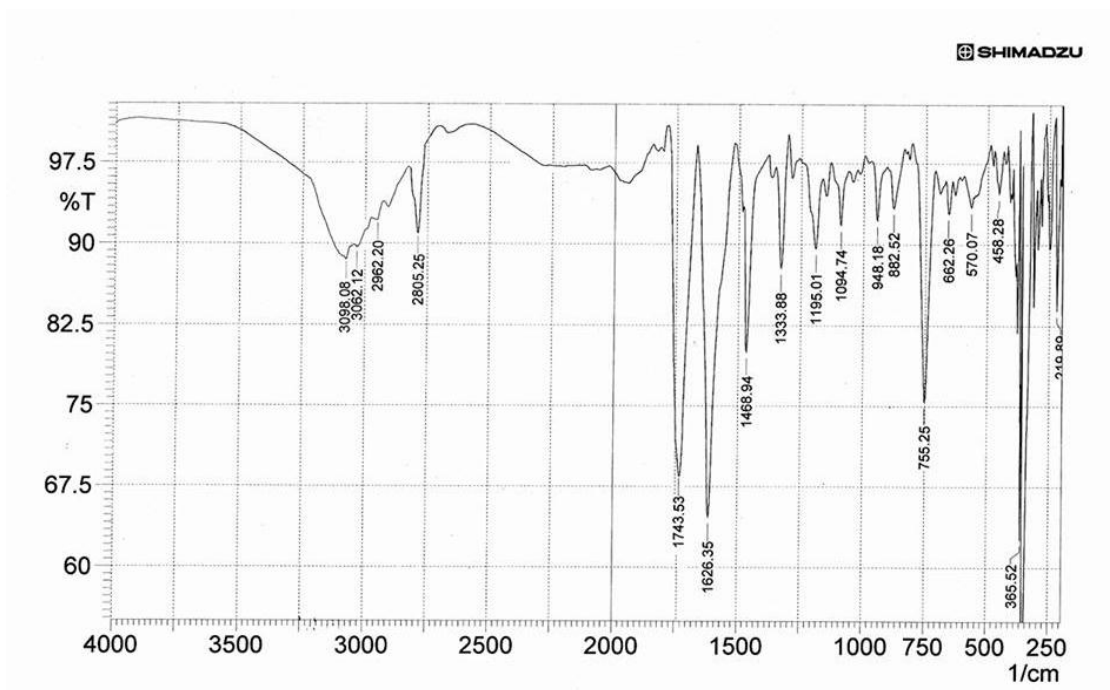


Figure 3: IR spectra of Ni(II) complexes

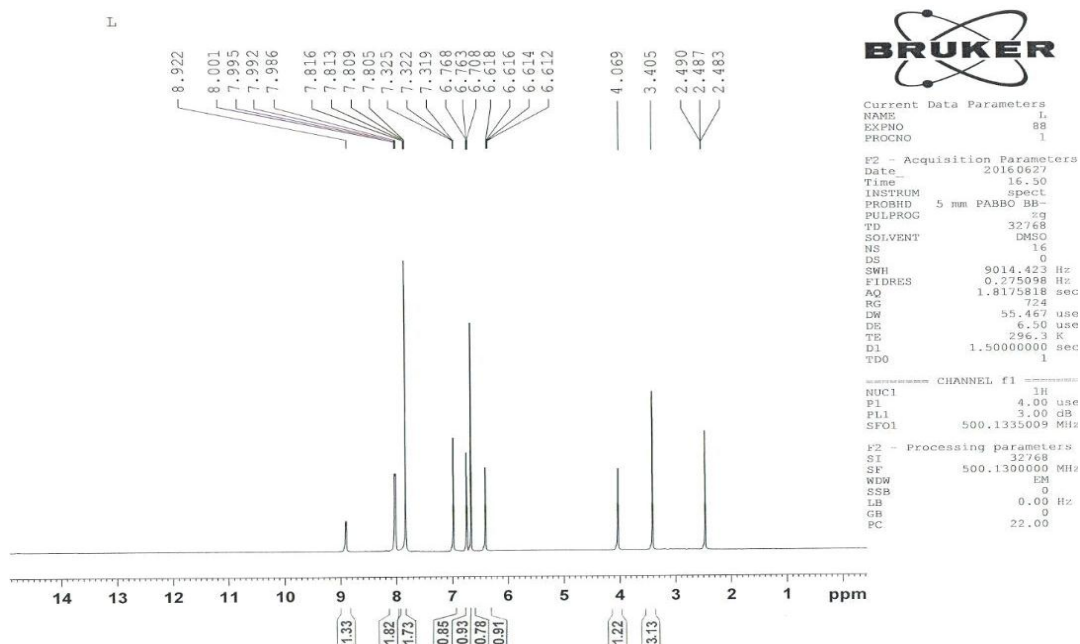


Figure 4: ¹H NMR spectra of ligand

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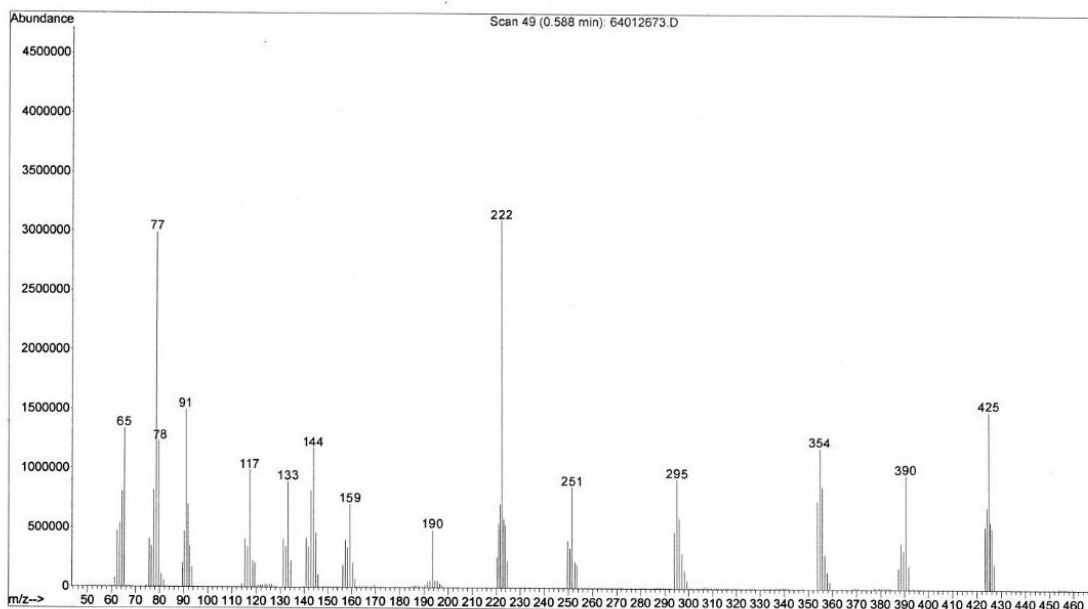


Figure 5: Mass spectral data of the ligand

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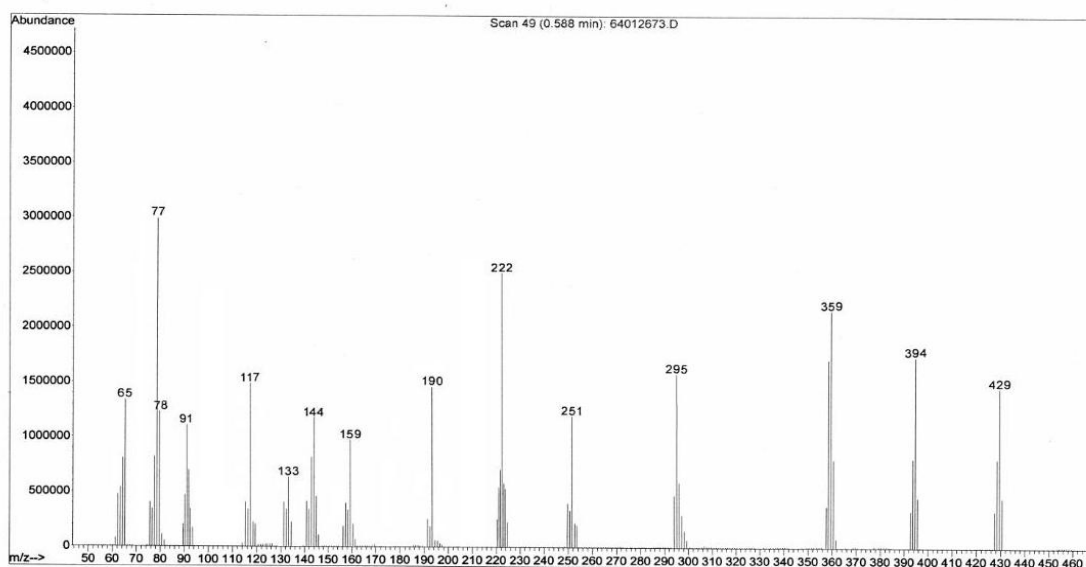


Figure 6: Mass spectral data of the Ni(II) complexes

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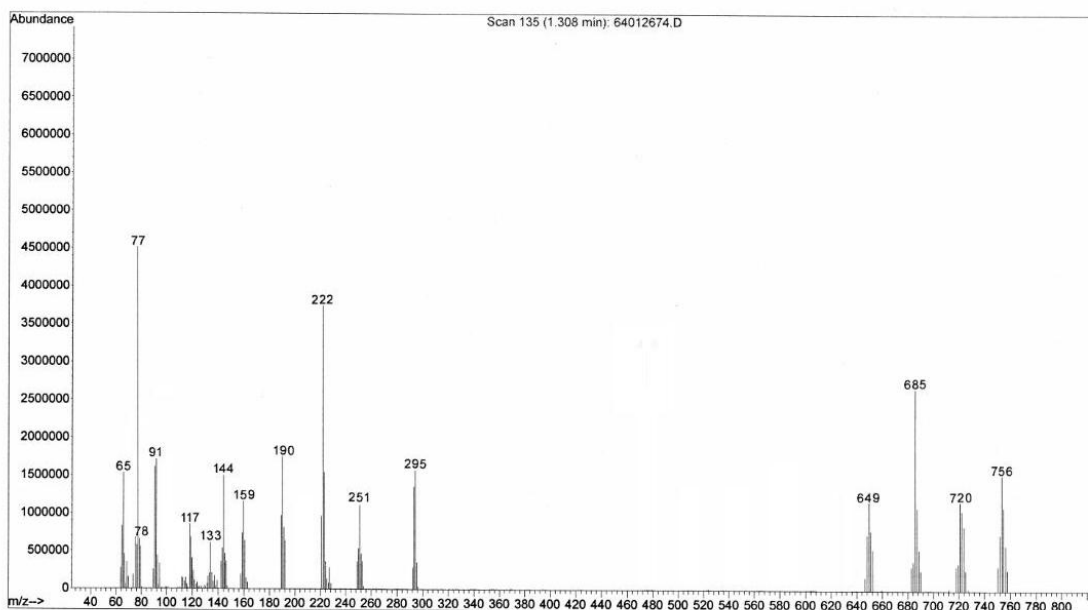


Figure 7: Mass spectral data of the Cu(II) complexes

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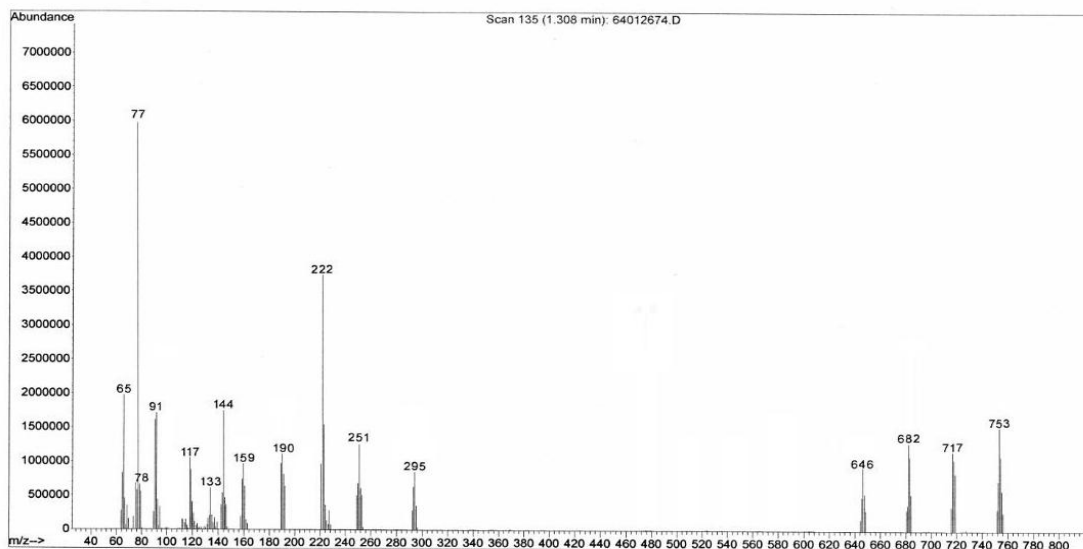


Figure 8: Mass spectral data of the Co(III) complexes

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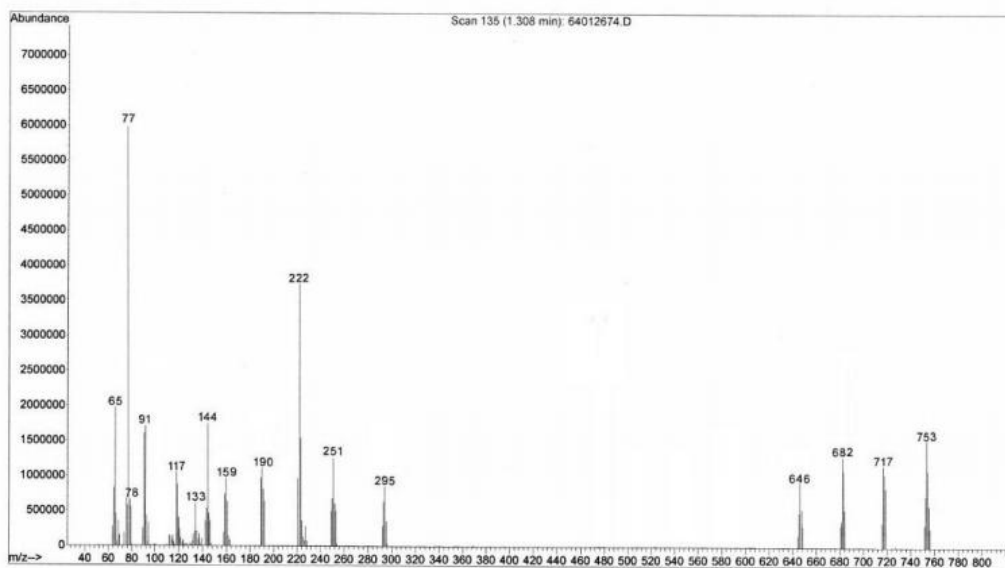


Figure 9: Mass spectral data of the Fe(III) complexes

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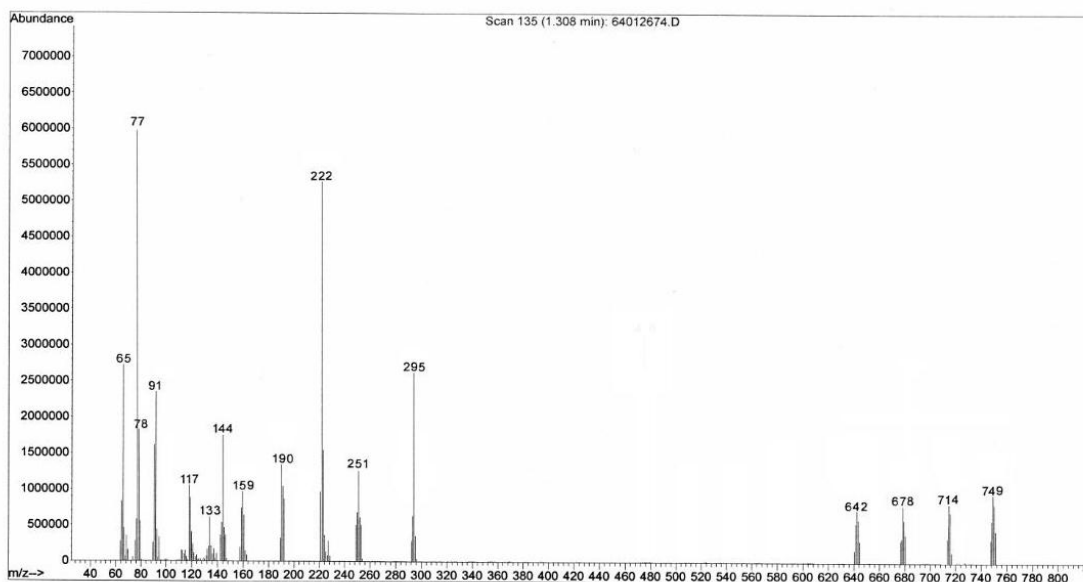


Figure 10: Mass spectral data of the Cr(III) complexes