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Synthesis & Spectroscopic Study of Ni (II), Cu (II), Co (III), Cr (III) &Fe (III) Complexes with 1, 3, 4-thiadiazol

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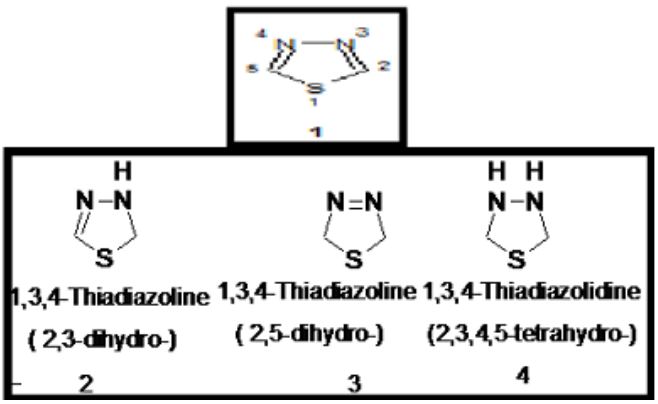
Abstract: ***The solid complexes of Fe (III), Cr (III), Co (II), Ni (II), andCu (II)) with Synthesis of N-[5- (4-methylphenyl)-1, 3, 4-thiadiazol-2-yl] acetamide have been synthesized and characterized by using the spectroscopic IR, 1HNMR, Mass as well as by elemental analyses C, H, N and Molar conductance the were studied. It may be concluded that the ligand coordinate through Nitrogen atoms and oxygen atoms shown in Scheme (2). For all the complexes. It may be concluded that the ligand coordinate through C=N thiadiazol and C=O as the ligand. For all the complexes. This view is further supported by the appearance of a band corresponding to the metal–nitrogen stretching vibration at (597 442-) cm–1 and the metal–oxygen stretching vibration at (341-372) cm–1 in the complexes . The physicochemical data suggest the octahedral geometry for all complexes except for Ni and Cu complexes which were tetrahedral respectively***

Keywords: synthesis. Characterization, Complexes, thiadiazole, heterocyclic complexes, properties of complexes octahedral, the properties of tetrahedral complexes

1. Introduction

The progress achieved in the synthesis of heterocyclic compounds with biological potential is due to improvement of the methodological study of tested substances too. It is known that many 1, 3, 4-thiadiazole derivatives have biological activity, with their antibacterial [1-3] , antimycobacterial [4, 5] , antimycotic [6] , antifungal [7, 8] , antidepressive [9] , and cardiotonic [10] action being notable. Recent research has also established for these heterocycles an analgesic [11] and anti-inflammatory [12, 13] activity. 1, 3, 4-Thiadiazole is a sulfur-containing aromatic heterocyclic with nitrogen atoms at the 3-and 4-positions and is numbered as shown in its structure. 1, 3, 4-Thiadiazole exists in two partially reduced (dihydro-) forms, 2 and 3 and named as 1, 3, 4-Thiadiazolines depending on the position of the double bond. the completely reduced (tetrahydro-)1, 3, 4-Thiadiazole is known as 1, 3, 4-Thiadiazolidine 4. 1, 3, 4-Thiadiazole exhibit varying biological activity and are, therefore find their uses in the fields of pharmaceuticals



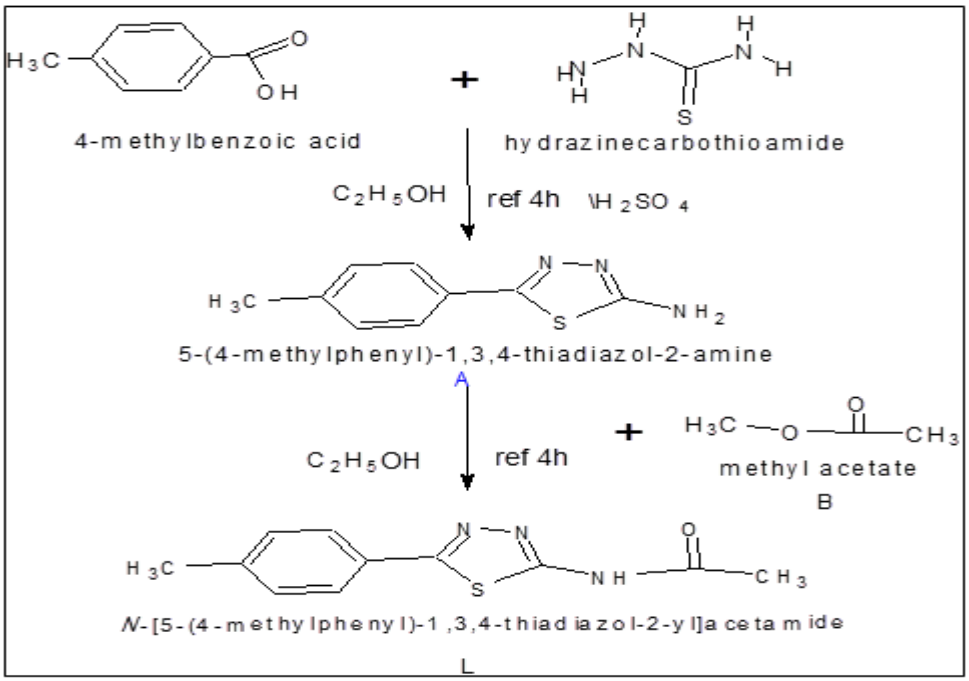
Scheme 1

2. Experimental Work

2. 1 Preparation of Ligand

[N - [5- (4-Methylphenyl) - 1, 3, 4 – Thiadiazol – 2 - Yl] Acetamide] (Scheme 2) Was Prepared As Follows

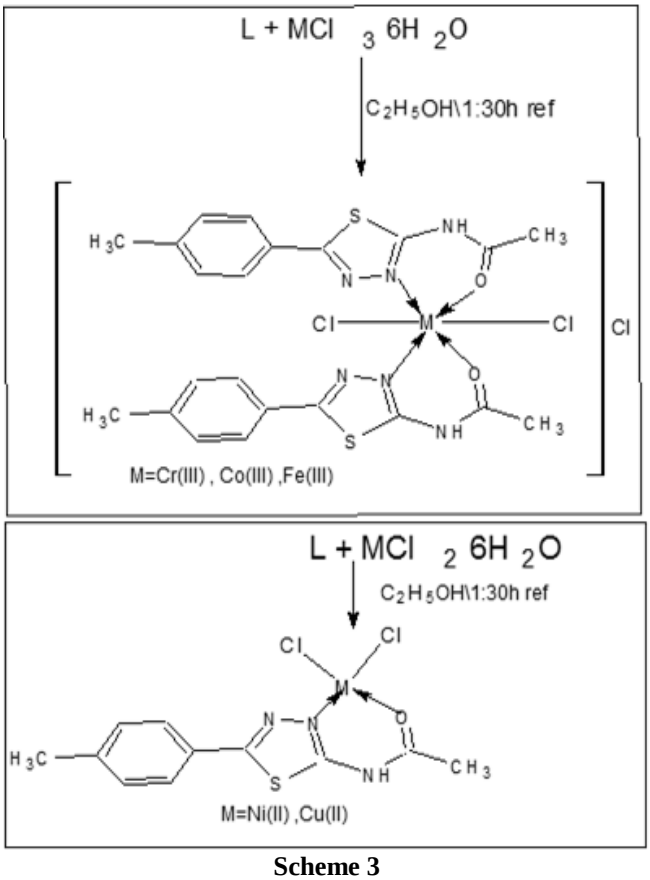
- A mixture of thiosemicarbazide (9. 11 g, 0. 1mol), 4-methylbenzoic acid (13.6g, 0. 1 mol), and conc. Sulphuric acid (5 ml) in 100 ml of ethanol was refluxed for 4 hour and poured onto crushed ice. The solid separated out was filtered, washed with cold water and recrystallized from ethanol to separate product [A] . The purity of the compound was followed by TLC. Yield (70%), m. p. 208 – 210C. [14]
- A mixture of [A] (19. 1 g, 0. 1 mol) and methyl acetate (7. 4 g, 0. 1mol)was refluxed in absolute ethanol (35 mL) for (9) hours The brown N-[5- (4-methylphenyl)-1, 3, 4-thiadiazol-2-yl] acetamide [L] was filtered, dried and recrystallized from ethanol. The purity of the compound was followed by TLC. Yield (70 %), m. p. 248 – 250 C. [15] Scheme 2.



Scheme 2

2. 2 Preparation of Complexes

The hydrated metal chloride salts of The Fe (III), Cr (III), Co (III), Ni (II) and Cu (II) (0. 01 mol) was added to solution of the ligand (0. 01mol) in hot absolute ethanol (50 mL) and the mixture was refluxed on a water bath for 1:30 hours and the solvent was evaporated in vacuum to half of the original volume and then cooled. The isolated complexes were filtered off, washed several times with ethanol and finally dried in air. [16] Scheme 3



Scheme 3

3. Results & Discussion

4-1 The purity of the ligand and its complexes were checked by TLC using silica gel-G as adsorbent. , elemental analysis tabulated in Table (1), Melting point, magnetic susceptibility, physical properties and molar conductance of all the compounds studied are tabulated in Table (2). . The calculated values were in a good agreement with the experimental values.

3.1 Mass Spectra

The mass spectrum of the ligand ([N-[5- (4-methylphenyl)-1, 3, 4-thiadiazol-2-yl] acetamide] and its complexes [17] . all the compounds studied are tabulated in Table (3) and figure (1-3)

3.2 Infra-Red Spectroscopy

The FTIR spectrum for L shows a characteristic stretching absorption bands 3025 cm-1 , 1614 cm-1, 1330 cm-1, 1434 cm-1, 1595 cm-1 and 1717cm-1, , assigned to, υC-H, C=N of the 1, 3, 4-thiadiazol ring, asymmetrical C-S-C, symmetrical C-S-C stretching, C=N and C=O respectively. The C=N stretching vibrations are important to predict the bonding mode of the ligand These bands shift lower wavelength in the spectra of complexes compare with ligand, observed changes are the evidences of complexion had happened [15] . The IR data of the complexes are shown in Table (4) and figure (4-5). The Table lists the stretching frequency (υ) for some of the characteristics groups exhibited by the ligand and complexes.

3.3nuclear Magnetic Resonance

The data of proton NMR of the ligand displayed good solubility in DMSO. The proton nuclear magnetic resonance spectral data gave additional support for the composition of

the ligand. The spectra also exhibit singlet 3 H–CH3 peaks at (2. 54-2. 50)ppm due to methyl group in The spectra also exhibit a singlet peaks at 3.34 ppm due to NH group[16] , the aromatic ring [17] exhibit peaks at (7. 66 -7. 20)ppm. the proton NMR of the ligand shown in figure (6)

3.4 Figures and Tables

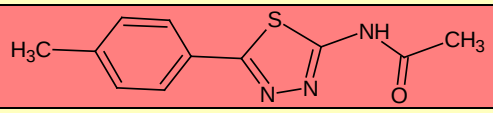
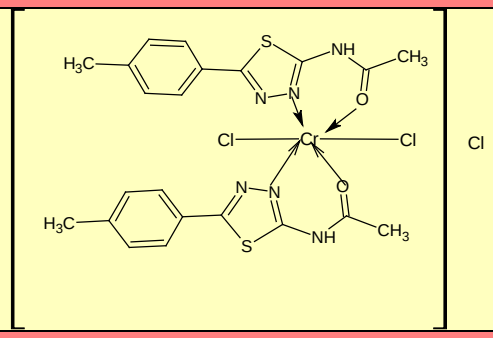
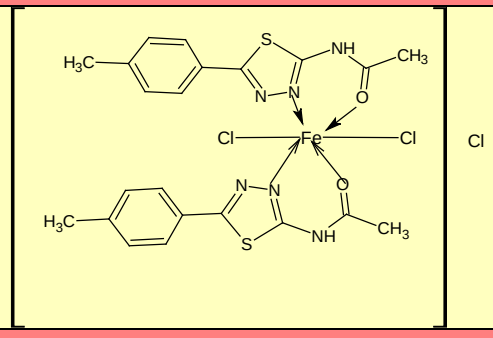
Table 1: Analitical data for the ligand

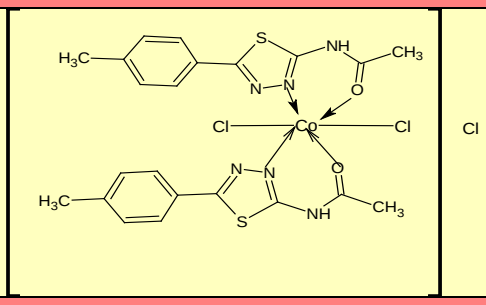
Theoretical			Experimental		
C%	H%	N%	C%	H%	N%
56. 63	4. 75	18. 01	56. 61	4. 78	18.

Table 2: conductance, physical properties and magnetic data of the ligand and its complexes

No	Compound	Molecular formula	color	Λ $Scm^2 mol^{-1}$	Melting Point	M. Wt	**Yield%**
1	Ligand	$[C_{11}H_{11}N_3OS]$	brown	-------	248-250	233.2	**70**
2	$[Cr (L)_2Cl_2] Cl$	$[Cr (C_{11}H_{11}N_3OS)_2Cl_2] Cl$	Yellow	32	238-240	9 .642	**87**
3	$[Fe (L)_2Cl_2] Cl$	$[Fe (C_{11}H_{11}N_3OS)_2Cl_2] Cl$	Pink	30	270-272	7 .628	**76**
4	$[Co (L)_2Cl_2] Cl$	$[Co (C_{11}H_{11}N_3OS)_2Cl_2] Cl$	Dark brown	29	190-192	8 .631	**92**
5	$[Ni LCl_2]$	$[Ni (C_{11}H_{11}N_3OS) Cl_2]$	Purple	16	260-258	8 .362	**90**
6	$[Cu LCl_2]$	$[Cu (C_{11}H_{11}N_3OS) Cl_2]$	Orange	20	222-220	7 .367	**81**

Table 3: The mass spectrum of the ligand and complexes

Complexes		**Molcular Ion**
L		**233**
$[C_9H_7N_2S]^{+\cdot}$		**175**
$[C_8H_8NS]^{+\cdot}$		**150**
$[C_7H_7]^{+\cdot}$		**91**
$[C_6H_6]^{+\cdot}$		**77**
$[Cr (L)_2 Cl_2] Cl^{+\cdot}$		**625**
$[Cr (L)_2 Cl_2]^{+\cdot}$		**590**
$[Cr (L)_2 Cl]^{+\cdot}$		**554**
$[Cr (L)_2]^{+\cdot}$		**519**
$[C_7H_7]^{+\cdot}$		**91**
$[C_6H_6]^{+\cdot}$		**77**
$[Fe (L)_2 Cl_2] Cl$		**628**
$[Fe (L)_2 Cl_2]^{+\cdot}$		**593**
$[Fe (L)_2 Cl]^{+\cdot}$		**558**
$[Fe (L)_2]^{+\cdot}$		**522**
$[C_{20}H_{16}N_6 Fe O_2 S_2]^{+\cdot}$		**492**
$[C_9H_7 FeN_2 S]^{+\cdot}$		**231**
$[C_7H_7]^{+\cdot}$		**91**

$[C_6H_6]^{+\cdot}$		77
$[Co\ (L)_2\ Cl_2]\ Cl$		632
$[Co\ (L)_2\ Cl_2]$		596
$[Co\ (L)_2\ Cl]^{+\cdot}$		561
$[Co\ (L)_2]^{+\cdot}$		526
$[C_9H_7N_2S]^{+\cdot}$		175
$[C_8H_8NS]^{+\cdot}$		150

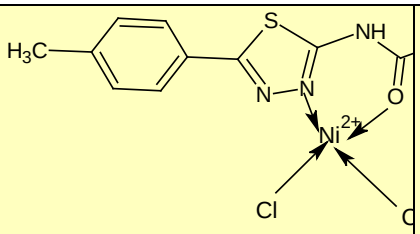
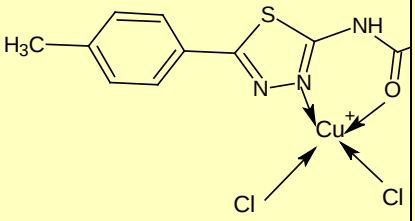
$[Ni\ (L)\ Cl_2]^{+\cdot}$		363
$[Ni\ (L)\ Cl]^{+\cdot}$		328
$[Ni\ (L)]^{+\cdot}$		291
$[C_8H_7N_5S]^{+\cdot}$		149
$[NiC_4H_4N_3SO]^{+\cdot}$		200
$[C_9H_7SN_2]^{+\cdot}$		175
$[C_7H_7]^{+\cdot}$		91
$[C_6H_6]^{+\cdot}$		77
[Cu (L) Cl2] $^{+\cdot}$		367
$[Cu\ (L)\ Cl]^{+\cdot}$		332
$[Cu\ (L)]^{+\cdot}$		397
$[CuC_9H_7N_2S]^{+\cdot}$		238
$[C_6H_6]^{+\cdot}$		77

Table 4: Infra-Red Spectroscopy absorption bands of ligand and its complexes

NO	Compound	υC-H	C=Nυ out ring	C=N υ of ring	υ C-S-C Sy, Asy	υC=O	υM-N	υM-O	**υM-Cl**
L	$[C_{11}H_{11}N_3OS]$	3229	1539	1685	1361 Sy 1404Asy	1715		-----	
1	$[Cr (L)_2 Cl_2] Cl$	3261	1583	1632	1349 1425	1731	521	354	**256**
2	$[Fe (L)_2 Cl_2] Cl$	3287	1531	1641	1363 1427	1744	597	372	**250**
3	$[Co (L)_2 Cl_2] Cl$	3220	1591	1622	1365 1397	1732	442	341	**278**
4	$[Ni L Cl_2]$	3237	1519	1673	1328 1425	1773	532	356	**262**
5	$[Cu L Cl_2]$	3216	1577	1634	1369 1435	1710	458	361	**248**

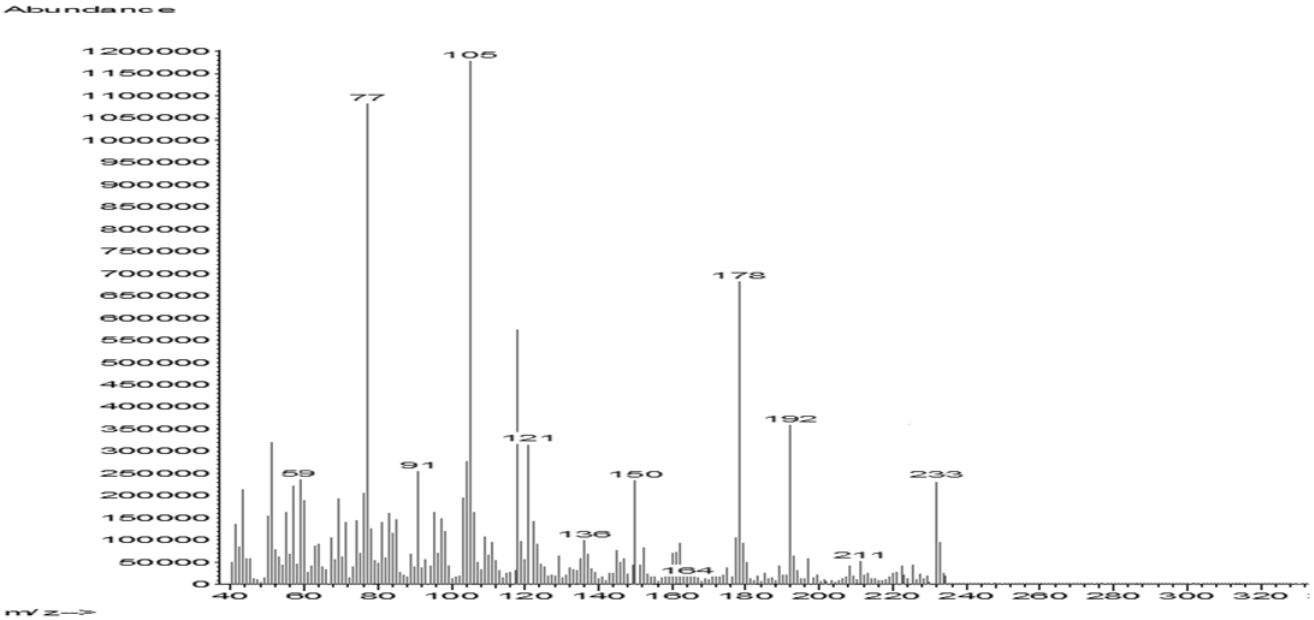


Figure 1: Mas spectrum of the ligand cm^{-1}

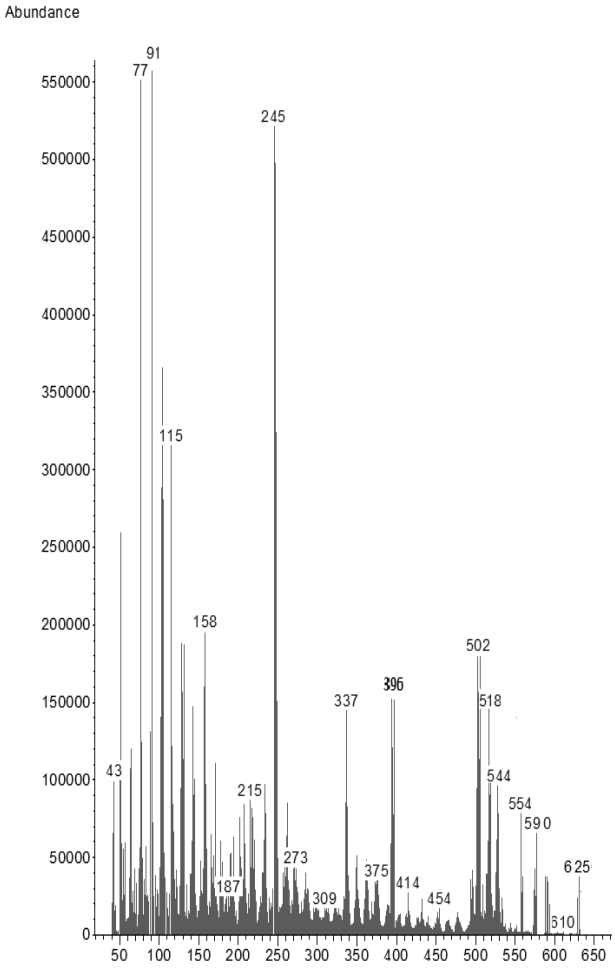


Figure 2: Mas spectrum of [Cr $(L)_2$ Cl_2] Cl cm^{-1}

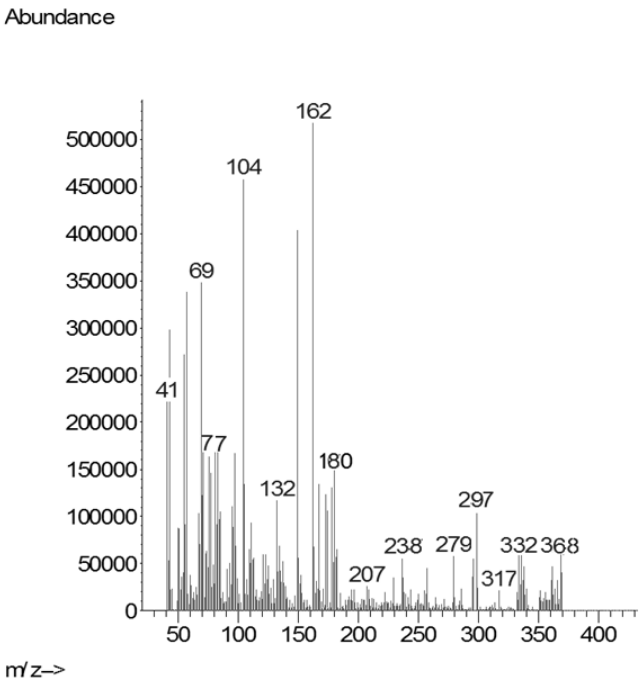


Figure 3: Mass spectrum of [Cu (L) Cl_2] cm^{-1}

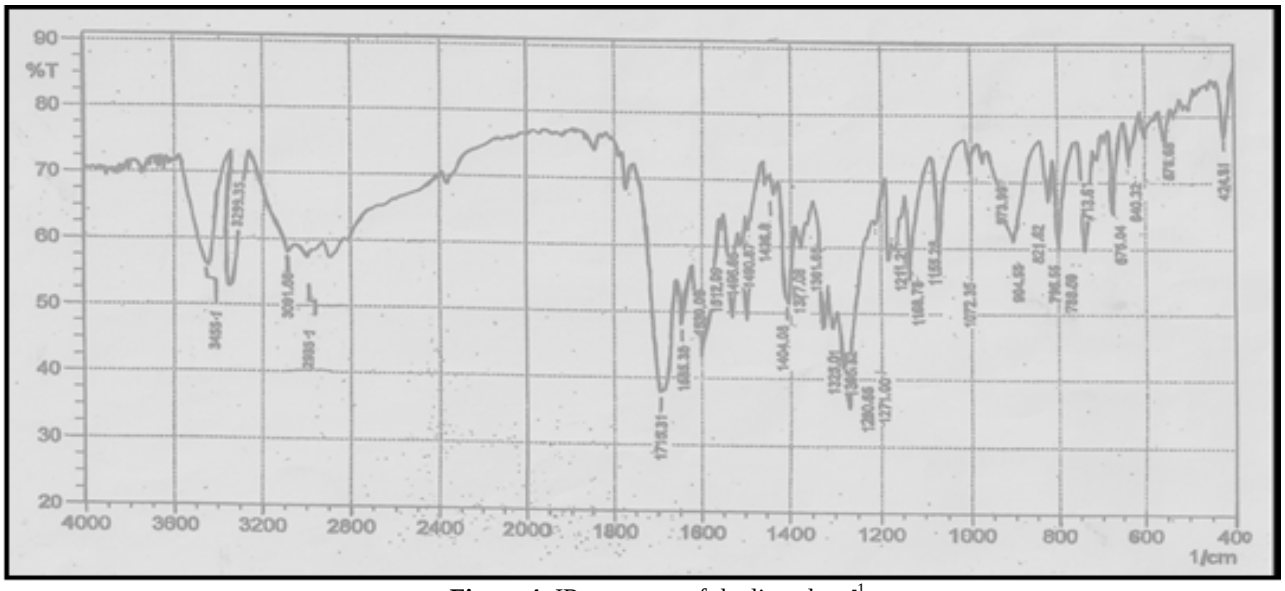


Figure 4: IR spectrum of the ligand cm^{-1}

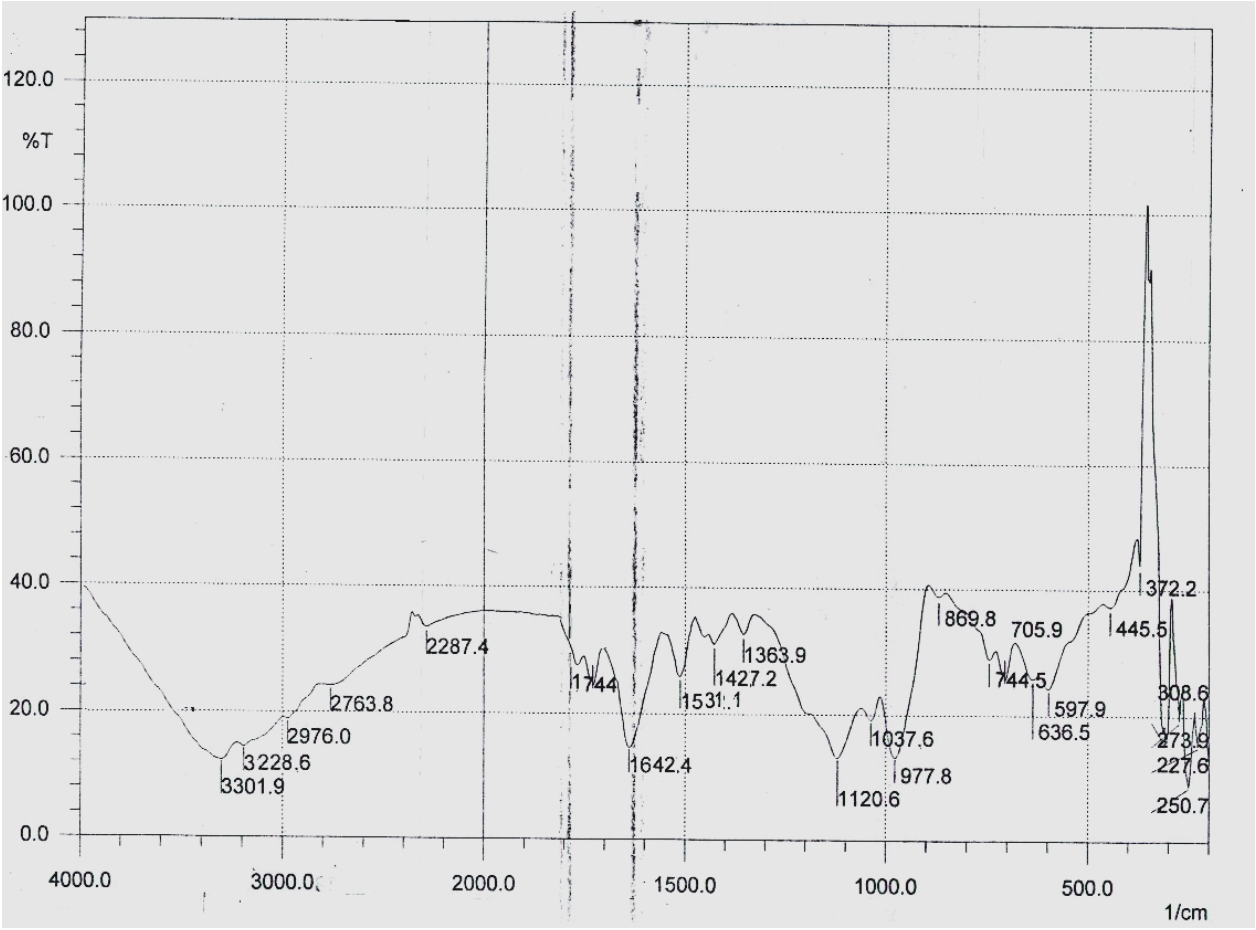


Figure 5: IR spectrum of [Fe $(L)_2$ Cl_2] Cl cm^{-1}

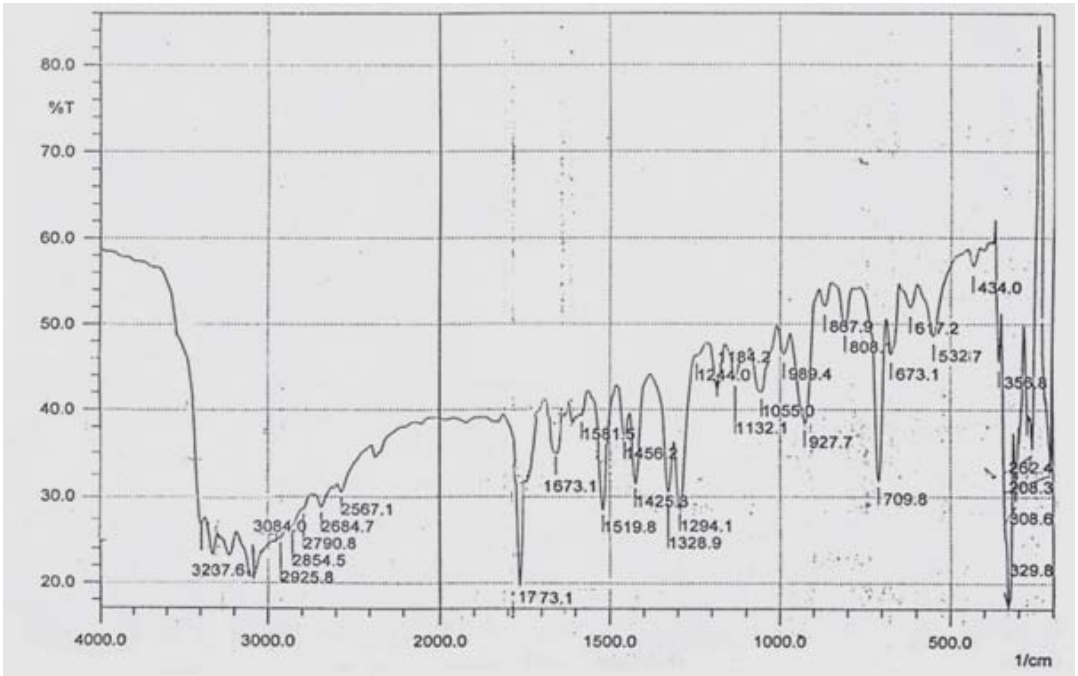


Figure 6: IR spectrum of [Ni L Cl_2] cm^{-1}

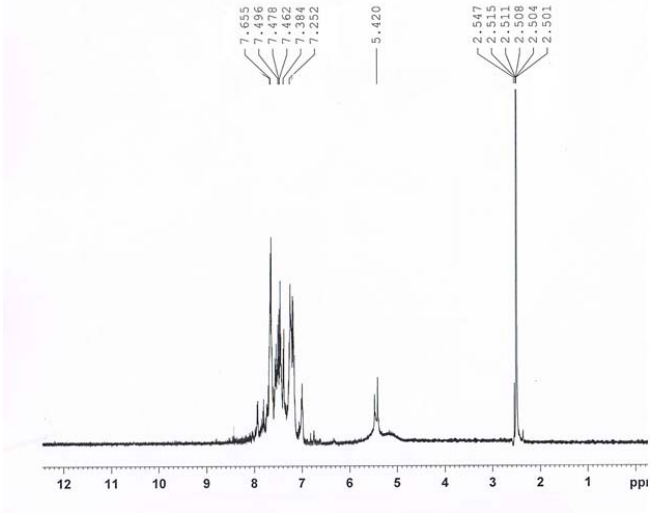


Figure 7: NMR spectrum of the ligand cm^{-1}

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Author Profile

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