

# Syntheses new legend [a4-methyl benzaldehyde[5-(3-furyl)-1,3,4-oxadiazol-2-yl]hydrazine]with some transition metal complexes

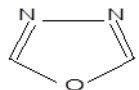
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**Abstract:** A new ligand [a4-methylbenzaldehyde[5-(3-furyl)-1,3,4-oxadiazol-2-yl]hydrazine] (L) and its Cr(III),Fe(III) Co(II), Ni(II)and Cu(II) complexes were synthesized. The authenticity of the ligand and its transition metal complexes were established by elemental analyses and conductance measurements, as well as spectroscopic (IR, <sup>1</sup>HNMR, mass). . It may be concluded that the ligand coordinate through Nitrogen atoms. for all the complexes. This view is further supported by the appearance of a band corresponding to the metal–nitrogen stretching vibration at  $\text{cm}^{-1}$  in the complexes. The molar conductance studies suggest an tetrahedral and octahedral geometry of the complexes .the Ni and Cu atoms leading to the formation tetrahedral geometry .Octahedral geometry was proposed for the Cr(III),Fe(III)andCo(III)prepared complexes

**Keywords:** - 1,3,4-oxadiazol , heterocyclic complexes , properties of complexes octahedral , the properties of tetrahedral complexes.

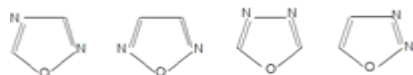
## 1 INTRODUCTION

In heterocyclic compounds the rings are not entirely composed of carbon atoms. There may be present one or more hetero atoms in rings. Heterocyclic system in drugs generally have certain substitutions & functionalisation.[1] Heterocyclic compounds are those compounds whose ring contain beside carbon, one or more atoms of other element. The non-carbon atoms in such ring are referred to as hetero atoms. The common hetero atoms are nitrogen, oxygen & sulphur. The important of heterocyclic compounds are present in most of the members of vit- Bcomplex, antibiotics , alkaloids, amino acid, drugs, dyes, enzyme & genetic material DNA and havingtherapeutics use.[2] Heterocyclic compounds having five membered rings containing two carbon atom, one oxygen, two nitrogen & two double bond such as oxadiazole



### 1.2 1,3,4-Oxadiazole

The oxadiazole drug were the first effective chemotherapeutics agents to be employed systemically for the prevention and cure of bacterial infection in human beings. the sequence of these atoms may be different as 1,2,4-oxadiazole (a), 1,2,5-oxadiazole (b), 1,3,4-oxadiazole (c) and 1,2,3-oxadiazole(d) [3]



A large no. of drugs used clinically have oxadiazole ring as a structural

building block. Literature survey reveals that the derivatives of the 1,3,4-oxadiazoles played an vital role in the medicinal chemistry. the derivative of 1,3,4-oxadiazole with suitable substitution at 2,5-position are becoming an important member in the heterocyclic family not only because of their wide range usages as photosensitive & electrical materials but also because of their broad spectrum in biological activities like as\_ Antibacterial, anti-inflammatory . anticonvulsant, anticancer, anti-tubercular, anthelmintic, analgesic, CNS depressant & other activities[4] .1,3,4-Oxadiazole derivatives are well known to have a wide range of biological activities. Examples of such activities are anti-inflammatory [5], antifungal [6], antiparasitic [7] and antimicrobial[8-9] effects

## 2 Procedure for Paper Submission

### 2.1 :- Preparation of the ligand

The new ligand [a4-methylbenzaldehyde[5-(3-furyl)-1,3,4-oxadiazol-2-yl]hydrazine] (Scheme 1) was prepared as follows:

- A mixture of propanate methyl 3-furoate (12g, 0.1mole) and hydrazine hydrate (0.2mole, 10ml) dissolved in ethanol (50mL)[12] was refluxed on a water bath for 3 hr, The resultant mixture[A] was concentrated and the white solid which separated was filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on pre-coated silica gel.

- A mixture of [A] (12g, 0.1mol), KOH (5.6g, 0.1mol) in 150ml ethanol and CS<sub>2</sub> (7.6mL, 0.1mol) was refluxed on a water bath for 10 hr, until the evolution of H<sub>2</sub>S gas ceased [13,14].

The excess CS<sub>2</sub> was removed under reduced pressure. The resultant mixture[B] was acidified with acetic acid and the white solid which separated was filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on precoated silica gel.

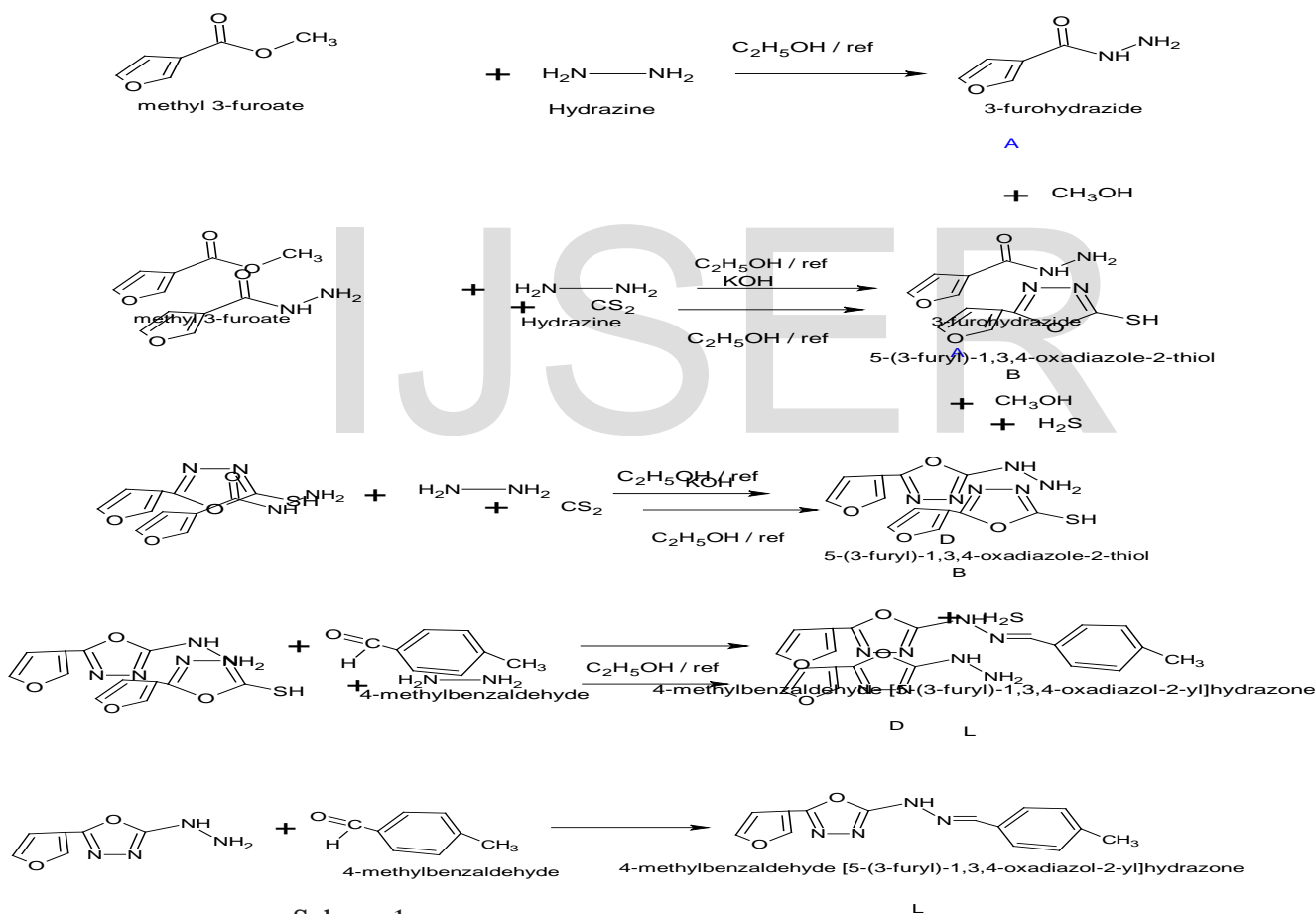
- A mixture[B] (16.8g,0.1mol) and hydrazine hydrate (0.2mole, 10ml) dissolved in ethanol (50 mL) was refluxed on a water bath for 3 hr ,until the evolution of H<sub>2</sub>S gas ceased. The excess CS<sub>2</sub> was removed under reduced pressure. The resultant mixture[C] was concentrated and the light pink solid which separated was filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on precoated silica gel.

- A mixture[D] (16.6g,0.1mol) and (4-methyl bezaldehyde) (12mL,0.1mol) dissolved in ethanol (150mL) was refluxed on a water bath for 4 hr, . The resultant mixture[ligand] was concentrated and the yellow solid which separated was filtered and recrystallised from ethanol.

(1 mmol) in 15 mL ethanol with 50 ml of an ethanolic solution of the ligand (1mmol, 0.3 g) for 4 hr. The resultant solids which separated were filtered, washed with ethanol and dried in air.

### 2.3 :- Measurements

Elemental C, H and N analysis were carried out on a Thermofinigan flash analyzer, the FTIR spectra in the range (4000-200) cm<sup>-1</sup> were recorded as CsI discs using a Shimadzu FTIR spectrophotometer, molar conductance measurements were made in anhydrous DMSO at 25 °C using Inolabcond 720,.The 1H nuclear magnetic resonance spectra were recorded on a Mercury-300BB NMR 300 spectrometer, DOSO-d<sub>6</sub> used as solvent. Melting points were determined in open capillary tubes using an electro thermal melting point /SMP31 apparatus. Mass spectra were recorded in the range (0-900) m/e on a 5973 network mass selective detector



Scheme 1

### 2.2 Preparation of complexes

The Cr(III), Co(III), Fe(III), Ni(II) and Cu(II) complexes were prepared by refluxing the respective hydrated metal chloride

### 3 :- RESULTS & DISCUSSION

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[10,11].

Table 1. Analytical data for the ligand

Experimental			Theoretical		
C%	H%	N%	C%	H%	N%
62.34	4.21	20.96	62.68	4.51	20.88

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

No	Compound	color	$\Delta S \text{ cm}^2 \text{ mol}^{-1}$	Melting Point	M.Wt	Yield%
1	[C <sub>14</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> ]	Dark brown	-----	182-180	286	84
2	[Cr (L) <sub>2</sub> Cl <sub>2</sub> ]Cl	Green	31	189-191	695	90
3	[Fe (L) <sub>2</sub> Cl <sub>2</sub> ]Cl	Brown	38	168-170	699	88
4	[Co (L) <sub>2</sub> Cl <sub>2</sub> ]Cl	Yellow	30	177-179	702	93
5	[Ni LCl <sub>2</sub> ]	Nutty	27	184-186	397	90
6	[Cu LCl <sub>2</sub> ]	Pink	12	175-153	402	89

### 3.1 :- Infra-Red Spectroscopy

The FTIR spectrum for L shows a characteristic stretching absorption bands at 3340 cm<sup>-1</sup> and 1663 cm<sup>-1</sup> assigned to  $\nu(\text{N-H})$  group, C=N of 1,3,4-oxadiazol. The C=N and N-H 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 complexation had happened. The IR data of the complexes are shown in Table (3) and figure(1-3). The Table lists the stretching frequency ( $\nu$ ) for some of the characteristics groups exhibited by the ligand and complexes [12, 10].

Table 3: Characteristic absorption bands of ligand and its complexes

NO	Compound	$\nu \text{ N-H}$	$\nu \text{ C=N}$	$\nu \text{ C-O-C}$	$\nu \text{ M-Cl}$
L	[C <sub>14</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> ]	3340	1663	1361(asy) 1425(sy)	-----
1	[Cr (L) <sub>2</sub> Cl <sub>2</sub> ]Cl	3360	1541	1361(asy) 1423(sy)	372
2	[Fe (L) <sub>2</sub> Cl <sub>2</sub> ]Cl	3340	1645	1343(asy) 1419(sy)	467
3	[Co (L) <sub>2</sub> Cl <sub>2</sub> ]Cl	3285	1648	1335(asy) 1403(sy)	380
4	[Ni LCl <sub>2</sub> ]	3334	1655	1330 (asy) 1420(sy)	391
5	[Cu LCl <sub>2</sub> ]	3332	1641	1344 (asy) 1417(sy)	437

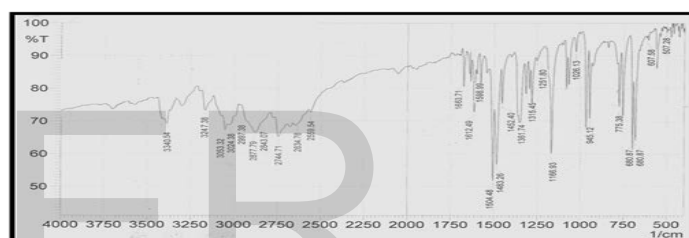
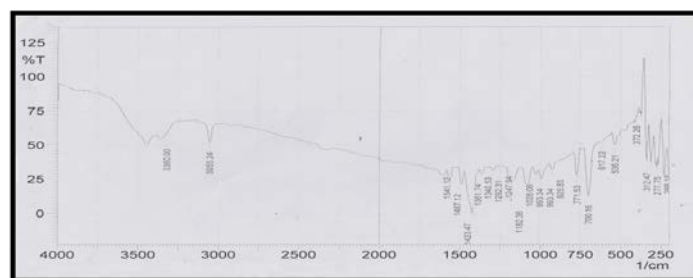
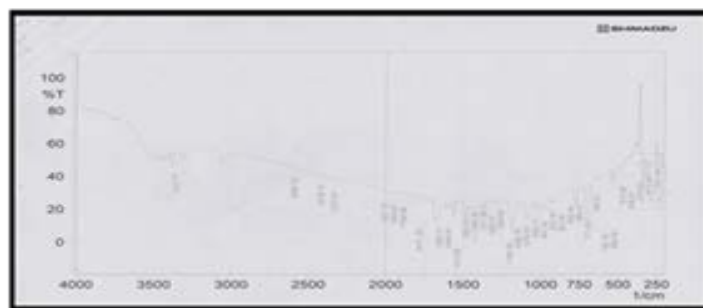
Figure (1) IR spectrum of the ligand cm<sup>-1</sup>Figure (2) IR spectrum of [Cr (L)<sub>2</sub>Cl<sub>2</sub>] Cl cm<sup>-1</sup>

Figure (3) IR spectrum of  $[Ni L Cl_2]$   $cm^{-1}$

Table (4):- The mass spectrum of the ligand and complexes

### 3.2 :- Nuclear 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 a singlet 3H-CH<sub>3</sub> peaks at (2.51-2.50)ppm due to methyl group[7] The spectra also exhibit a singlet peaks at 5.799 ppm due to NH group[10], exhibit a singlet 1H(CH=N)peaks at 4.93 ppm .the aromatic ring exhibit peaks at 7.5 8.1-7.630 ppm [12]. 3H (furyl) exhibit peaks at 8.964 -8.04  $\delta$ ppm [13] the proton NMR of the ligand shown in figure(4)

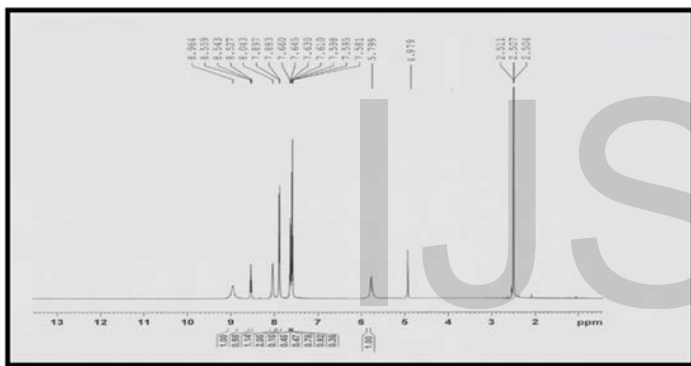


Figure (4) NMR spectrum of the ligand  $cm^{-1}$

### 3.3 :- Mass spectra

The mass spectrum of the ligand(a4-methylbenzaldehyde[5-(3-furyl)-1,3,4-oxadiazol-2-yl]hydrazine and its complexes[14]. all the compounds studied are tabulated in Table (4) and figure(5-7)

Ion	the structure	Molecular Ion
L		268
$[C_5H_3NO_2]^+$		109
$[C_9H_9N_3O]^+$		175
$[C_8H_9N_2]^+$		133
$[C_6H_4N_4O_2]^+$		164
$[C_7H_7]^+$		91
$[Cr(L)_2 Cl_2] Cl$		695
$[Cr(L)_2 Cl_2]^+$		660
$[Cr(L)_2 Cl]^+$		624
$[Cr(L)_2]^+$		589
$[H_6 C_{10}N_2O_4]^+$		218
$[C_{18}H_{18}N_6O_2]^+$		402
$[C_{14}H_{14}]^+$		182
$[C_{12}H_8N_8O_4Cr]^+$		380
$[Fe(L)_2 Cl_2] Cl$		699
$[Fe(L)_2 Cl_2]^+$		663
$[Fe(L)_2 Cl]^+$		628
$[Fe(L)_2]^+$		592
$[FeC_{18}H_{18}N_6O_2]^+$		406
$[FeC_{10}H_6N_8O_4]^+$		358
$[FeC_{12}H_6N_4O_4]^+$		326
$[Co(L)_2 Cl_2] Cl$		702
$[Co(L)_2 Cl_2]^+$		666
$[Co(L)_2 Cl]^+$		630
$[Co(L)_2]^+$		596
$[C_{12}H_8N_8O_4 Co]^+$		387
$[C_{18}H_{18}N_6O_2 Co]^+$		409
$[Ni(L) Cl_2]^+$		397
$[Ni(L) Cl]^+$		362
$[Ni(L)]^+$		326
$[C_9H_9N_3NiO]^+$		233
$[C_6H_4N_4NiO_2]^+$		222
$[C_7H_7]^+$		91
$[C_5H_3NO_2]^+$		109
$[Cu(L) Cl_2]^+$		402
$[Cu(L) Cl]^+$		367
$[Cu(L)]^+$		331
$[C_9H_9CuN_3O_2]^+$		238
$[C_6H_4CuN_3O]^+$		213
$[C_6H_3CuN_2O_2]^+$		198
$[C_8H_8 N]^+$		118

all synthesized compounds were in full agreement with the proposed structure

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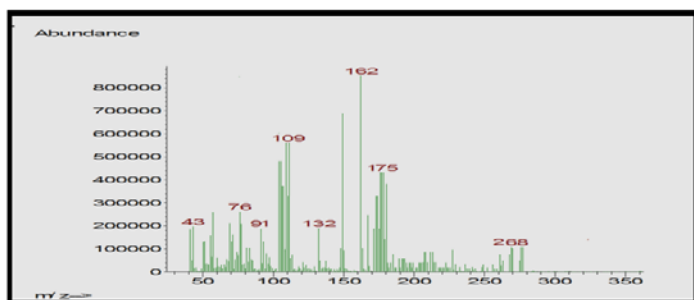


Figure (5) Mas spectrum of the ligand  $\text{cm}^{-1}$

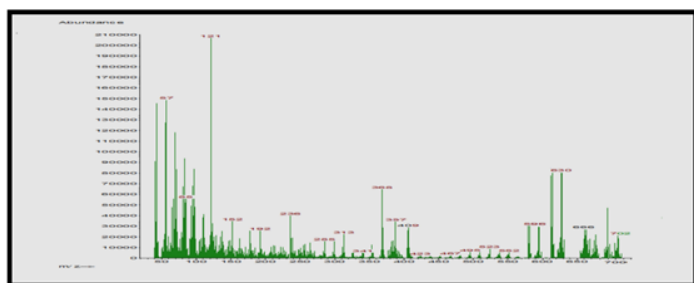


Figure (6) Mas spectrum of  $[\text{Co}(\text{L})_2\text{Cl}_2]\text{Cl}$   $\text{cm}^{-1}$

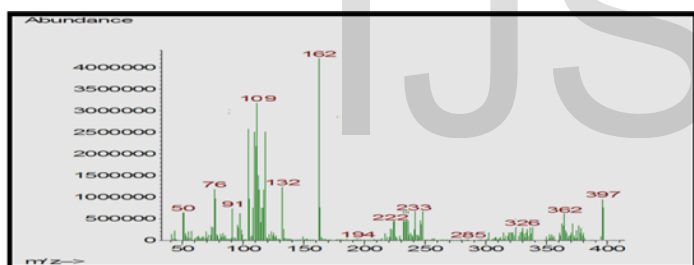


Figure (7) Mas spectrum of  $[\text{Ni}(\text{L})_2\text{Cl}_2]$   $\text{cm}^{-1}$