

## Some Transition Metal Complexes with 2-thioacetic acid-5-pyridyl-1,3,4-oxadiazol

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### Abstract

New metal complexes of the ligand 2-thioacetic acid-5-Pyridyl-1,3,4-oxadiazole (HL) with the metal ions Ni (II) Cu(II) Co (II) and Fe (III) were prepared in alcoholic medium, the prepared complexes were characterized by FTIR spectroscopy, electronic spectroscopy, elemental analysis, magnetic susceptibility, conductivity measurements and CHNO and S analysis. From the Spectral measurements, monomer and octahedral structures for the complexes were proposed.

### Introduction

The oxadiazole ring systems have a long history of application in pharmaceutical industries due to their activity. A large number of 1,3,4-oxadiazoles have been discussed in the literature because of application as hypotensives [1], anti-fungals [2-3], anti-inflammatory [4], anti-microbials [5-7], antimitotics [8] and muscle relaxants [9]. They also possess tranquilizing, antitubercular, hypoglycaemic, herbicidal, antiviral, amoebicidal, insecticide, hypnotic and sedative activities. Some material applications of 1,3,4-Oxadiazole derivatives lie in the field of liquid crystals [10]. Transition metal complexes of 1,3,4-Oxadiazoles have also been an active area of research [11-13]. 1,3,4-oxadiazole derivatives are also among the most widely employed electron conducting and hole blocking (ECHB) materials in organic light-emitting diodes (LEDS) [14]. 1,3,4-Oxadiazole considered as an important five-membered compound among the huge heterocyclic families, has been studied as an excellent candidate for material applications during the past years [15-18]. The wide range of applications of the ligand and its metal complexes are used our interest to prepare a new series of some of those metal complexes.

### Experiment:

#### 1- Preparation of Ethyle Isonicotinate (2):

In a round bottom flask a mixture of Isonicotinic acid (0.1 mol) with 200 ml absolute ethanol and 5 ml H<sub>2</sub>SO<sub>4</sub> was refluxed overnight. 10% Sodium bicarbonate was added to the solution until litmus paper turned blue. The ester layer was separated and extracted by using 20 ml ether. The ether

layer was separated, dried using anhydrous MgSO<sub>4</sub>, filtered and evaporated on water bath.

#### 2- Preparation of Isonicotinic acid hydrazide(3):

A suspension of ethyle isonicotinate (2) (0.12 mol) with hydrazine hydrate (0.12 mol) was refluxed for 1 hr after that (40 ml) of absolute ethanol was added and the reflux continued for further 3 hrs. Cooling the solution produced white crystals.

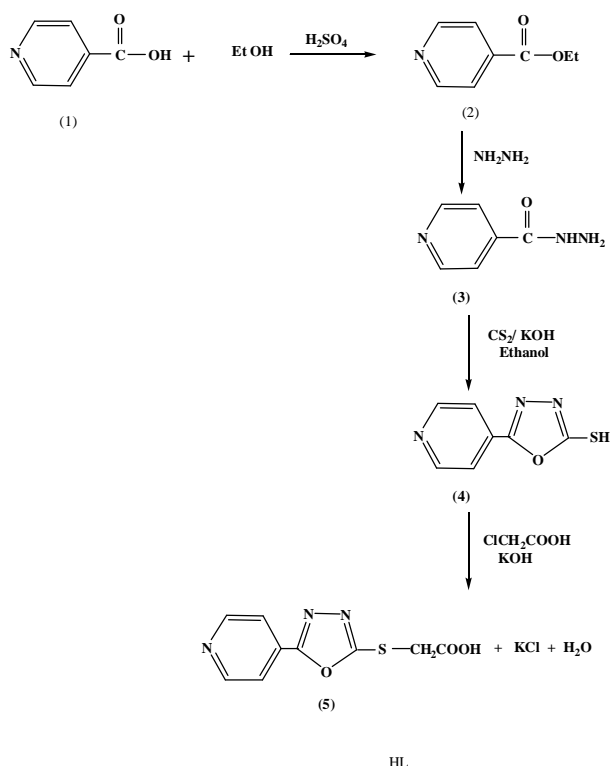
#### 3- Preparation of [2- mercapto-1,3,4-oxadiazole-5-yl] pyridine(4):

To a mixture of isonicotinic acid hydrazide (3) (0.01 mol) in ethanol (20 ml) was added a solution of KOH (0.02 mol) in ethanol (5 ml) followed by CS<sub>2</sub> (20 ml). The reaction mixture was heated under reflux for 8 hrs. Then it was concentrated, acidified with dilute hydrochloric acid and the resulting solid was collected, washed with water and recrystallized to give compound (4).

#### 4-Preparation of 2- thioacetic acid-5-pyridyl-1,3,4-oxadiazol(5 ([HL]):

A mixture of [2-mercapto-1,3,4-oxadiazole-5-yl] pyridine (0.1 mol) and chloroacetic acid (0.1 mol) in presence of KOH (0.02 mol) as a basic media was refluxed for 3 hrs., to give the white precipitate. The reaction mixture was added to 20 ml of water, extracted with ethyle acetate. The white precipitate produced by evaporation of ethyle acetate, was filtered and crystallized from ethanol to give the final product.

The steps of the synthesis HL can be shown below:



### Preparation of complexes

Ethanol solutions of the suitable metal salt ( $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) was added to an alkaline solution of 2-thioacetic acid -5-pyridyl-1,3,4-oxadiazole in 1:2 (metal: ligand) molar ratios and refluxed for 3 hrs., crystalline colored precipitates was formed at room temperature the resulting solids were filtered off, wash with distilled water, dried and recrystallized from

ethanal and dried at  $50\text{ }^\circ\text{C}$  for half hour. The Table (1) show the physical data of the prepared ligand and complexes.

### Instrumentation:

All chemical used were of reagent grade (supplied by either Merck or fluka) and used as supplied. Elemental C,H,N,O and S analysis were carried out on a Fison E A 1108 analyzer, the FTIR spectra in the range ( $4000\text{--}200$ )  $\text{cm}^{-1}$  were recorded as CsI discs on FTIR 8300 Shimadzu spectrophotometer, UV-visible spectra were measured using Shimadzu UV-Vis. 160A-ultra-violet spectrophotometer in the rang ( $200\text{--}1000$ ) nm. The magnetic susceptibility values of the prepared complexes were obtained at room temperature using magnetic susceptibility balance Bruke magnet B.M.6. Atomic absorption measurements of the prepared complexes were obtained using Shimadzu 680 cc- flame.

### Results and Discussion

Physical and analytical data of all the compounds studied are shown in Table (1). The data of CHNOS and metal analysis were obtained using flame atomic absorption technique. The calculated values were in a good agreement with the experimental.

**Table (1)**  
**Physical data for preparation Ligand and its complexe.**

Symbol	Melting point $^\circ\text{C}$	Color	(Calculated) Found %					M	Suggest formula
			C	H	O	N	S		
HL	179-182	white	(45.56) 46	(2.95) 2.78	(20.25) 20.21	(17.72) 16.10	(13.50) (13.44)	—	$\text{C}_9\text{H}_7\text{O}_3\text{N}_3\text{S}$
CoL	200d	Brown	(37.96) 36.88	(3.16) 3.12	(14.05) 14.19	(14.76) 14.45	(11.24) 10.89	(10.36) 10.23	$\text{CoL}_2(\text{H}_2\text{O})_2$
CuL	198	Green	(25.50) 25.43	(2.12) 2.10	(15.11) 14.89	(9.91) 9.86	(7.55) 7.45	(7.55) 7.54	$\text{CuL}_2(\text{H}_2\text{O})_2$
NiL	212d	Grey	(25.65) 25.55	(2.13) 2.10	(15.20) 15.18	(9.97) 9.88	(7.60) 7.25	(7.00) 7.10	$\text{NiL}_2(\text{H}_2\text{O})_2$
FeL	192-195	Brownish red	(25.23) 25.20	(2.10) 2.00	(14.95) 14.88	(9.81) 9.79	(7.46) 7.43	(6.54) 6.49	$\text{FeL}_2\text{Cl}(\text{H}_2\text{O})$

### Infra – Red Spectroscopy

The FTIR spectrum of the ligand, show a characteristic stretching absorption bands at 3430, 1635 and 1350 assigned to hydroxyl, carbonyl  $\nu(\text{COO})$  asym. and  $\nu(\text{COO})$  sym.

group respectively. The (COO) stretching vibrations are important to predicate the bonding mode of the ligand. The values of  $\Delta\nu$  ( $\Delta\nu = \nu$  asym. (COO) -  $\nu$  sym. (COO)) can be divided into three groups [19]:

- a. In compounds where  $\Delta\nu(\text{COO}) > 350 \text{ cm}^{-1}$  the carboxylate group binds in a monodentate fashion. However, other very weak intra- and inter molecular interactions can not be excluded.
- b. When  $\Delta\nu(\text{COO}) < 200 \text{ cm}^{-1}$ , the carboxylate groups of these compounds can be considered to be bidentate.
- c. In compounds where  $\Delta\nu(\text{COO}) > 200 \text{ cm}^{-1}$  and  $< 350 \text{ cm}^{-1}$  an intermediate state between monodentate and bidentate (aniso bidentate) occurs. It has also been suggested that the  $\Delta\nu(\text{COO})$  value in the

chelating mode is less than the  $\Delta\nu(\text{COO})$  in a bridging mode the disappearance of the hydrogen from hydroxyl group on complexation indicate that the complexation is through the oxygen atom. stretching of metal – oxygen bands of complexes appeared in low frequency (450-410)  $\text{cm}^{-1}$  [20]. All the complexes exhibit a broad band at 3500-3400  $\text{cm}^{-1}$  followed by another band at 723-790  $\text{cm}^{-1}$  assignable to coordinated water molecules [21]. The IR data of the ligand and complexes are shown in Table (2).

**Table (2)**  
**Characteristic absorption bands of 2- thioacetic acid-5-pyridyl-1,3,4 oxadiazole and its complexes( $\text{cm}^{-1}$ ).**

Compound	$\nu(\text{O-H})$	$\nu(\text{COO})$ asym.	$\nu(\text{COO})$ sym.	$\nu(\text{M-O})$	$\nu(\text{M-Cl})$
HL	3430	1635	1350	–	–
CoL	–	1587	1354	446	–
CuL	–	1570	1342	440	–
NiL	–	1590	1356	410	–
FeL	–	1580	1351	428	380

#### Ultra Violet – Visible Spectroscopy:

The electronic spectrum of the Co(II) complex exhibited absorption bands at 11574 and 15360  $\text{cm}^{-1}$ , which may be assigned to transition  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}$  and  ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_2$  respectively [22]. The Ni(II) complex displayed an electronic spectrum with transitions at 13106, 20790 and 26881  $\text{cm}^{-1}$ . These bands may be assigned to the transition  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$  respectively [23]. The Cu(II) complex displayed bands 11682  $\text{cm}^{-1}$  which may be assigned to the transition  ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$  the second band at around 29800  $\text{cm}^{-1}$  may be due to charge transfer [24]. The Fe(III) complex displayed an electronic spectrum with transition at 12750, 18000, 28555  $\text{cm}^{-1}$ . These bands may be assigned to the transition  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G}^4)$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G}^4)$  and  $(\text{L}) \rightarrow \text{Fe}(\text{C.T})$  respectively [25]. The high value of 10 Dq and the low value of nephelauxetic factor indicate the covalent

character between metal ions and the ligand, Table (3).

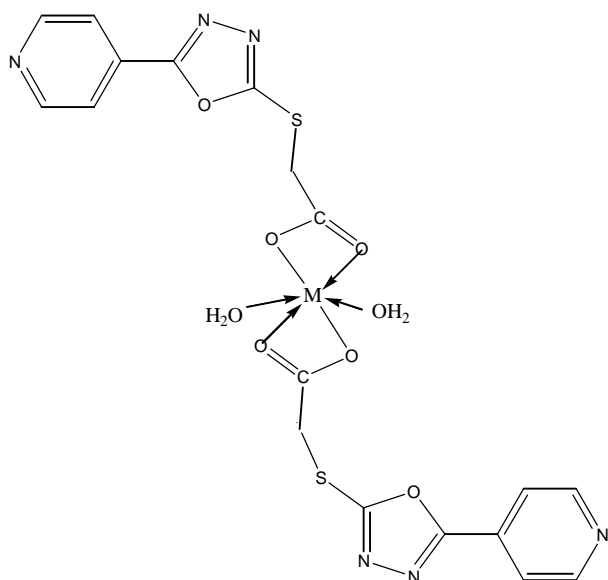
#### Magnetic Susceptibility and Conductivity Measurements:

The experimental magnetic moment for each metal complexes is listed in Table (3). These magnetic measurements give an idea about the electronic state of the metal ion in the complex. The magnetic moment for Co(II) complex has a magnetic moment of 3.44 BM which is typical of Co(II) ion in an octahedral environment [26]. A magnetic moment value of 2.90 BM is observed for Ni(II) complex, expected for octahedral geometry. The Cu(II) complex exhibits a value of 1.78 BM, expected for  $S = 1/2$  system having an octahedral geometry. The magnetic moment for Fe(III) is 5.58 BM with five unpaired electrons. The molar conductivity data obtained in DMSO suggest that all the complexes are non-electrolyte in nature.

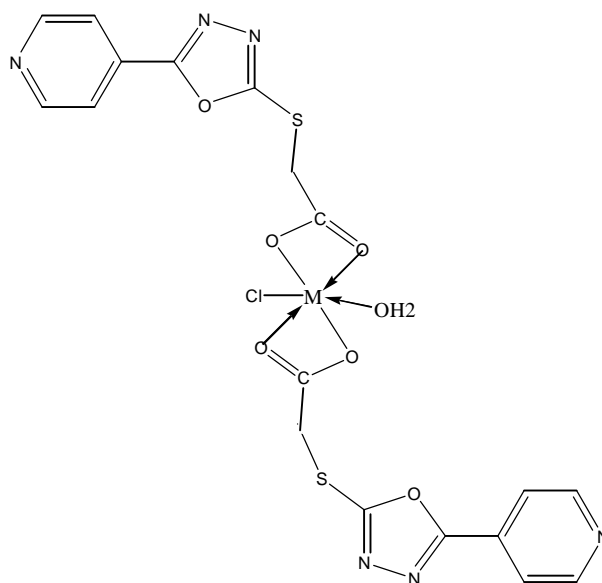
**Table (3)**  
**Electronic spectra, conductance (in DMF) and magnetic moment for metal complexes.**

Symbol	Band $cm^{-1}$	Assignment	$\bar{\nu}$	$10Dq/E$	$10Dq$	$\beta$	Conductivity $mscm^{-1}$	$m_{eff}$ . B.M	Suggested structure
Co	11574	$^4T_{1g} \rightarrow ^4T_{2g}$	771.6	1.5	11574	0.684	18	3.44	Octahedral
	15360	$^4T_{1g}(F) \rightarrow ^4T_{2g}$							
Ni	13106	$^3A_{2g} \rightarrow ^3T_{2g}$	744.6	1.7	13106	0.71	9	2.90	octahedral
	21790	$^3A_{2g} \rightarrow ^3T_{1g}(F)$							
	26881	$^3A_{2g} \rightarrow ^3T_{1g}(p)$							
Cu	11682	$^2E_g \rightarrow ^2T_{2g}$					7	1.78	Octahedral
	29800	$L \rightarrow Cu(C.T)$							
Fe	12750	$^6A_{1g} \rightarrow ^4T_{1g}$	566.6	2.2	12750	0.534	10	5.58	Octahedral
	18000	$^6A_{1g} \rightarrow ^4T_{2g}$							
	28555	$(L) \rightarrow Fe(C.T)$							

On the basis of the preceding discussion, the structure of the complexes may be suggested as follows:



Where M=Ni(II), Cu(II) and Co(II)



And this for M=Fe(III)

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### الخلاصة

حضرت معقدات الليكاند [2] ثايو حامض اسيتك -5- بيريدايلز -4,3,1-او كسادايوزول [HL] مع الايونات الفلزية التالية: نيكيل (II) والنحاس (II) والكوبلت (II) والحديد (III) في وسط كحولي. شخضت المعقدات عن طريق تحليل العناصر الدقيقة (CHN) والتحليل الطيفي تحت الحمراء والمرئي فوق البنفسجية وتقنيات اخرى كالتوصيلية والحساسية المغناطيسية. اقترحت الصيغ الكيميائية والاشكال الهندسية للمعقدات على ضوء النتائج التي تم الحصول عليها.