

# Preparation, characterization and X-Ray powder diffraction (XRD) study of some complexes containing oxadiazole moiety

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## ABSTRACT

A ligand; 2-(methylethylato) thio-5- (m-nitrophenyl)-1,3,4-oxadiazole was prepared from reaction of chloromethylethylester with 2-thio-5-(m-nitro-phenyl) -1,3,4-Oxadiazole. The ligand forms complexes with Fe(II), Co(II), Ni(II), Cu(II), Cd(II), Hg(II), Zn(II) and Ca(II) in good yield. The synthesized complexes have been characterized on the basis of physicochemical investigations including infrared and electronic spectroscopy, magnetic moment measurements, molar conductance and elemental analysis. The structures of the synthesized compounds have been investigated by X-ray powder diffraction and  $^1\text{H NMR}$ . They have been found to have the formula;  $[\text{M}(\text{A}_3)(\text{H}_2\text{O})_n]\text{X}_2$ , where:  $\text{M}=\text{Fe}(\text{II}), \text{Co}(\text{II})$ ;  $n=3$  and  $\text{Cd}(\text{II})$ ;  $n=1$ ,  $\text{X}=\text{Cl}^-$  or  $\text{NO}_3^-$ ,  $[\text{M}(\text{A}_3)(\text{H}_2\text{O})(\text{CH}_3\text{CO}_2)]\text{Ac}$ ,  $\text{M}=\text{Co}(\text{II}), \text{Ni}(\text{II}),$  and  $\text{Cu}(\text{II})$ ,  $\text{Ac}=\text{acetate}$  and  $[\text{M}(\text{A}_3)(\text{H}_2\text{O})\text{Cl}_2]$ ,  $\text{M}=\text{Hg}(\text{II}), \text{Zn}(\text{II})$   $\text{Ca}(\text{II})$ ;. Infrared spectral data suggest that the ligand  $\text{A}_3$ : behaves as a, tridentate ligand with N,S,O donor sequence towards the metal ions. On the basis of the above physicochemical data, octahedral and tetrahedral geometries were assigned for the complexes.

**Keyword:** 2-(methylethylato) thio-5- (m-nitrophenyl)-1,3,4-oxadiazole complexes, X-ray powder diffraction, Transition and non transition Complexes.

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## INTRODUCTION

Heterocyclic thiones are known in the field of coordination chemistry because of their potential multifunctional donor sites, viz either exocyclic sulfur or endocyclic nitrogen. <sup>(1,2)</sup> As background, we note that aromatic oxadiazole based compounds have attracted particular attention in the context of research on organic light-emitting diodes (LED). The oxadiazoles feature high electron affinities, which in turn, facilitate both electron injection and transport processes of importance in molecular and polymeric LED devices <sup>(3-5)</sup>. Indeed, polymers containing oxadiazole units have been widely used in experimental devices as both electron-transporting and hole-blocking materials <sup>(6)</sup>. The Oxadiazole ring is electron deficient, resulting in poor hole transport but good transport properties. Although some types of metal complexes have found to be good emitters and/or excellent electron transport with excellent thermal properties <sup>(7)</sup>. Some material application of 1,3,4-Oxadiazole derivatives lie in the field of liquid crystals <sup>(8)</sup>. Also, 1,3,4- oxadiazoles and their derivatives are known to exhibit diverse pharmacological activities such as antimicrobial, antihistaminic, anticancerous <sup>(9)</sup>. In the continuing our work on oxadiazole derivatives, we synthesized and characterized a new 1,3,4-oxadiazole ligand characterized physicochemically.

## EXPERIMENTAL

### 1-Chemicals

All chemicals and solvents used were of analytical grade. The metal salts were commercially available pure samples and all chemicals used throughout this investigation available from Merck, B.D.H Aldrich or Fluka.

### 2- Analytical and physical measurements

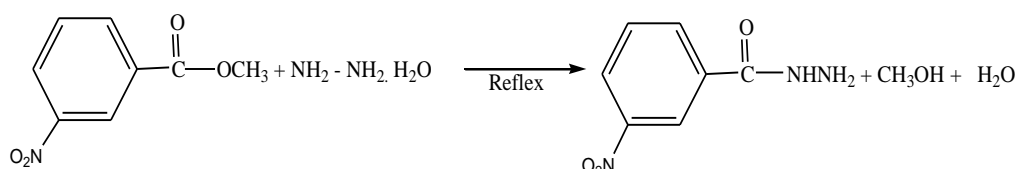
Melting point and decomposition temperature were determined using SMP30 melting point apparatus. IR spectra measurements were recorded using FTIR-Tensor 27-Burker Co. Germany 2003 as KBr pellets in the range (400-4000  $\text{cm}^{-1}$ ). UV-visible spectral measurements were done on Shimaduz 1800 spectrophotometer for  $10^{-3}$  M complexes in DMF solvent at room temp. using 1cm quartz cell in range (190-1100) nm. The (CHN) and  $^1\text{H NMR}$  analysis were

determined at the center of Dicle University Science and Technology Research (DUBTAM )- Turkey, and the NMR of the ligand was recorded on Bruker Ultra Shield 300 MHz using deuterated DMSO  $-d_6$  as solvent and  $Me_4Si$  as internal reference. Elemental analysis were carried out on a CHN analyzer type 4010 model 2011 Costech Elemental Combustion. Molar conductance of complexes were measured at room temp. for  $10^{-3}M$  in DMF using Multiline F-SET-2WTW Wissenschaft Technische Werkstattem 82362 Weicheim. Magnetic susceptibility of the complexes was measured by Bruker -BM6 using Faraday method.. Metal contents were estimated spectrophotometrically using atomic absorption SonsAAGB Scientific Equipment. X-ray powder diffraction data for complexes (5 &7) were measured at General Company for Geological Survey and Mining-Bagdad by using Shimadzu X-ray Diffraction 7000 model 2009 and the crystal data for complexes were analyzed by using Match Program Version 1.6c.

### 3-PREPARATION OF THE STARTING MATERIALS

#### Preparation of meta-nitrobenzoylhydrazine

On the first step Hydrazine hydrate (5g, 0.1mole) was added drop-wise to m-nitromethylbenzoate (18.1g, 0.1 mole) in absolute ethanol, after adding, the mixture was refluxed for 2 hours and then cooled and the creamy solid product formed was collected by filtration, washed with cold ethanol and purified by crystallization from ethanol and, dried at  $50^{\circ}C$ , yield (67%), m.p  $152-154^{\circ}C$  empirical formula.  $C_7H_7N_3O_3$



	%C	%H	%N
Calc.	46.40	3.86	23.20
Found	46.87	3.92	23.84

#### Preparation of 2-thio-5-(m-nitrophenyl) -1,3,4-Oxadiazole (A1)

In the second step, this compound was prepared according to the modified procedure (young wood 1955)<sup>(10)</sup>. The hydrazide of the step1(m-nitrobenzoyl hydrazine) (18.1 g, 0.1M). was allowed to react with carbon disulphide (120 ml, 0.2 M of  $CS_2$ ) in the presence of ethanolic potassium hydroxide (5.6 g, 0.1M of KOH in 70 ml absolute ethanol) under reflux conditions until the liberation of  $H_2S$  gas has been stopped and is detected with lead (II) acetate paper it turns grey in the presence of  $H_2S$  gas followed by acidification with dilute HCl to give yellowish precipitate, which was filtered, wash with cold water, and dried under vacuum( Fig.1). The yield (85%), mp  $250-252^{\circ}C$ , empirical formula  $C_8H_5N_3O_3S$ .

The yield product was characterized by CHN analysis, IR and  $H^1NMR$ .

	%C	%H	%N
Calc.	43.04	2.42	18.84
Found	43.31	2.61	18.93

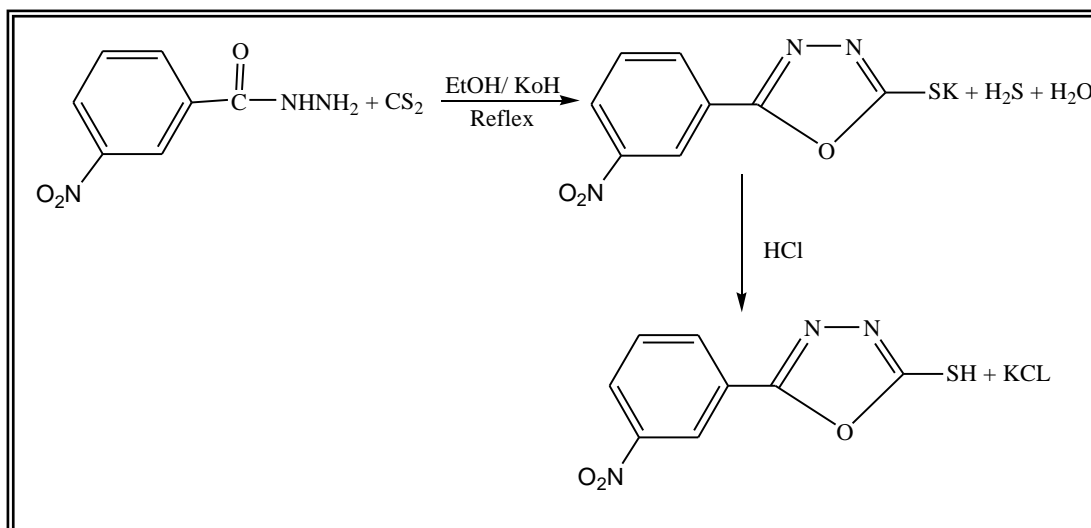


Fig.1

### Preparation of 2-(methylethylate)thio-5-(m-nitrophenyl)-1,3,4-Oxadiazole(A3)

A2-thio-5-(m-nitro-phenyl) -1,3,4-Oxadiazole (A1) (22.3g , 0.1 M ) was dissolve dinethanolic potassium hydroxide (5.6 g ,0.1M of KOH in 100 ml absolute ethanol) followed by slow addition of dropwise of chloromethylethylester (10.9, 0.1M).The mixture has been refluxed for 3 hours with stirring, followed by cooling, then evaporated to half its volume, cooled, filtered, the yellowish precipitate recrystallized from ethanol, and dried under vacuum (Fig.2) . The yield (70%), mp 218--220°C empirical formula  $C_{11}H_9N_3O_5S$ .

The yield product was characterized by IR and  $H^1$ NMR.

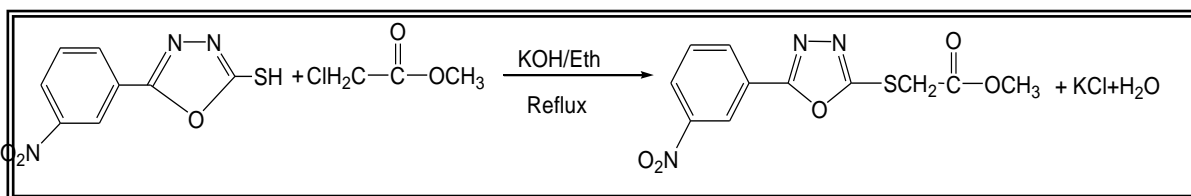
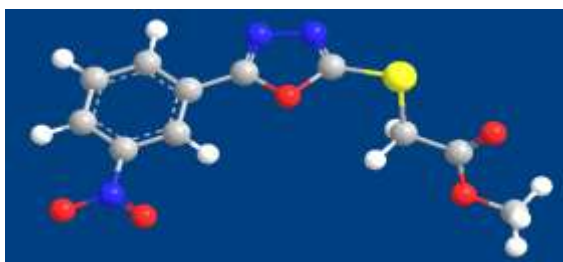
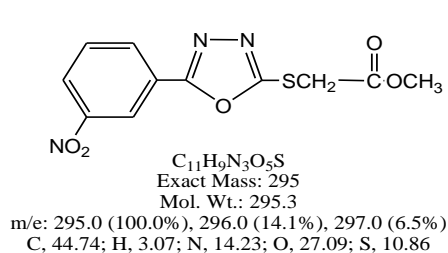
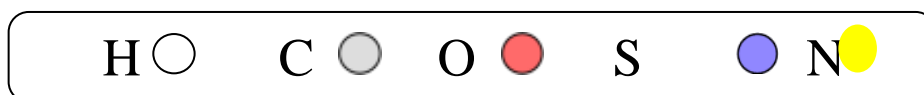


Figure 2: The structure of the prepared ligand A3



(Chemi Office.version. Ultra 8.0.2D & 3D)



	%C	%H	%N
Calc.	44.74	3.05	14.23
Found	44.90	2.89	14.56

### Preparation of the Complexes in Mole Ratio (1:1) Ligand: Metal

An ethanolic solution of the ligand A3 (2.95 g, 0.01M in 25 ml ethanol) has been added to a solution of 0.01mol of each of metal salts 0.01M (Table 1) in 20 ml of distilled water or ethanol).

The mixture has been refluxed for 1/2- 2 hours with stirring, followed by cooling and .The product has been filtered off, recrystallized from ethanol then evaporated to half its volume, cooled, filtered , washed and dried examination of elemental analyses data, given in Table 1 & 2.

### RESULTS AND DISCUSSION

Table 1 revealed conductivity data obtained in DMF at  $10^{-3}M$ . The molar conductance values of the complexes (1,2,5,7 and 8) are in the range ( 139-172)  $ohm^{-1} cm^2 mol^{-1}$  indicating a ( 1:2) electrolytic nature of these complexes<sup>(11)</sup>. While the molar conductance values of the complexes(3,4 and 6) are in the range (67-85)  $ohm^{-1} cm^2 mol^{-1}$  indicating (1:1) electrolytic nature of these complexes<sup>(11,12)</sup>. On other hand, complexes (8-11) are non-electrolytic indicating neutral complexes<sup>(13)</sup> in nature. The molar conductance values are in a good agreement with given formulations.

**Table1: Analytical data and some physical properties of the complexes**

Comp. No.	Metal Salt	Wt(g) Metal Salt	Wt(g) A3	$\Omega$ $ohm^{-1} cm^2 mol^{-1}$	Complexes	m.p or d* °C	Color
1	CoCl <sub>2</sub> .6H <sub>2</sub> O	2.38	2.95	139	[Co(A3)(H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>2</sub>	>300	brown
2	Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	2.91	2.95	150	[Co(A3)(H <sub>2</sub> O) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	260-263	brown
3	Co(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> .4H <sub>2</sub> O	2.49	2.95	76	[Co(A3)(H <sub>2</sub> O)(CH <sub>3</sub> CO <sub>2</sub> )]Ac	218-221	yellow
4	Ni(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> .4H <sub>2</sub> O	2.49	2.95	85	[Ni(A3)(H <sub>2</sub> O)(CH <sub>3</sub> CO <sub>2</sub> )]Ac	>300	light green
5	FeCl <sub>2</sub> .6H <sub>2</sub> O	2.35	2.95	172	[Fe(A3)(H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>2</sub>	>300	Light green
6	Cu(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> .H <sub>2</sub> O	1.99	2.95	67	[Cu(A3)(H <sub>2</sub> O)(CH <sub>3</sub> CO <sub>2</sub> )]Ac	>300	yellow
7	Cd(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O	3.08	2.95	145	[Cd(A3)(H <sub>2</sub> O)](NO <sub>3</sub> ) <sub>2</sub>	285d	white
8	CdCl <sub>2</sub>	1.83	2.95	140	[Cd(A3)(H <sub>2</sub> O)]Cl <sub>2</sub>	214-116	white
9	HgCl <sub>2</sub>	2.72	2.95	22	[Hg(A3)(H <sub>2</sub> O)]Cl <sub>2</sub>	188-191	white
10	ZnCl <sub>2</sub>	1.36	2.95	19	[Zn(A3)(H <sub>2</sub> O)]Cl <sub>2</sub>	271d	white
11	CaCl <sub>2</sub>	1.11	2.95	13	[Ca(A3)(H <sub>2</sub> O)]Cl <sub>2</sub>	280-283	white

**Table 2 : Elemental analysis of the complexes**

Comp. No.	Complexes	Found%(Calc.)CHN, M			
		C	H	N	M
1	[Co(A3)(H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>2</sub>	27.55	3.13	8.76	12.31
		27.79	3.21	8.99	12.53
2	[Co(A3)(H <sub>2</sub> O) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	24.81	2.81	13.15	11.09
		25.02	3.00	13.23	11.25
3	[Co(A3)(H <sub>2</sub> O)(CH <sub>3</sub> CO <sub>2</sub> )]Ac	36.73	3.46	8.57	12.04
		37.95	3.52	8.77	12.22
4	[Ni(A3)(H <sub>2</sub> O)(CH <sub>3</sub> CO <sub>2</sub> )]Ac	36.73	3.46	8.57	12.00
		37.02	3.50	8.66	12.31
5	[Fe(A3)(H <sub>2</sub> O) <sub>3</sub> ]Cl <sub>2</sub>	27.73	3.15	8.82	11.76
		27.98	3.00	9.02	12.00
6	[Cu(A3)(H <sub>2</sub> O)(CH <sub>3</sub> CO <sub>2</sub> )]Ac	36.36	3.43	8.48	12.92

		36.50	3.61	8.53	13.01
7	[Cd(A3)(H <sub>2</sub> O)](NO <sub>3</sub> ) <sub>2</sub>	24.40	2.36	12.75	20,40
		24.52	2.44	12.97	20.50
8	[Cd(A3)(H <sub>2</sub> O)]Cl <sub>2</sub>	26.61	2.62	8.46	22.58
		27.02	2.81	8.59	22.71
9	[Hg(A3)(H <sub>2</sub> O) Cl <sub>2</sub> ]	22.60	2.22	7.19	34.41
		22.83	2.54	7.00	34.50
10	[Zn(A3)(H <sub>2</sub> O)Cl <sub>2</sub> ]	29.39	2.89	9.35	14.47
		30.12	3.03	10.04	14.67
11	[Ca(A3)(H <sub>2</sub> O)Cl <sub>2</sub> ]	31.13	2.59	9.90	9.43
		31.27	2.70	10.00	9.65

### Infrared spectra:

A compound A1 shows two bands a weak band at 2730cm<sup>-1</sup> which is characteristic of stretching vibration of the SH group and sharp band at 3225cm<sup>-1</sup> due to NH stretching vibration<sup>(14)</sup>. These bands which subsequently disappeared in the ligand A3, indicating a group substitution occurred on position 2, and a new absorption bands appeared at 1430cm<sup>-1</sup>, which has been attributed to bending frequency of -SCH<sub>2</sub> group. This is further supported by the appearance of the band at 705 cm<sup>-1</sup> due to stretching vibration of C-S bond<sup>(15)</sup>. In the spectra of the ligand A3 showed, a weak band at 2997 cm<sup>-1</sup> due to sym. & asym. C-H aliphatic of CH<sub>2</sub> group, and this band remains unaltered on complexation<sup>(16)</sup>. The IR spectra of the A3 ligand shows a strong band in the region 1605 cm<sup>-1</sup>, which is characteristic of the azomethane (stretching vibration of C=N) group. In all complexes, this band is slightly shifted to lower frequency<sup>(17)</sup> indicating coordination of the A3 through azomethine nitrogen atoms to the metal center (through the nitrogen atom, of the oxadiazole ring). This view is further supported by the appearance of a band corresponding to the metal-nitrogen<sup>(18)</sup> stretching vibration at 435-442 cm<sup>-1</sup> in the complexes. The spectra of A3 shows a broad band at 975 cm<sup>-1</sup> due to N-N group (A3) shifts towards higher frequency (980-990) on complexation<sup>(19)</sup>. A comparison of the IR spectra of the free ligand A3 and metal complexes reveal that the band due to carbonyl ester appeared at 1730cm<sup>-1</sup> and medium absorption band at 1014 cm<sup>-1</sup> has been attributed to C-O stretching vibration of the ester. This observation was further indicated by the strong appearance of a band between the ranges of (545-560) and (700-709) cm<sup>-1</sup>. In the IR spectra of the complexes which, could not be traced to free A3 have been tentatively assigned to [M-OH] and [M-O=C] stretch bands of the metal complexes<sup>(20)</sup>. In the ligand spectra of A3 shows a characteristic band at 1035cm<sup>-1</sup> which was assigned to the stretching of C-O-C group of the oxadiazole ring and this band remains unaltered on complexation indicating the absence of coordination through oxygen of this group<sup>(21)</sup>. On the other hand, the spectra of (2&7) complexes showed the presence of additional band at (1382,742) cm<sup>-1</sup> due to ionic nature of nitrate group<sup>(22)</sup>. The aqua complexes contain weak to medium a broad band at (3320-3410) cm<sup>-1</sup> due to stretching vibration OH of water<sup>(23)</sup> and a sharp shoulder at (1500) cm<sup>-1</sup> may be assigned to bending vibration of water. Water molecules are coordinated, confirmed by occurrence of additional strong and sharp band at 700-707cm<sup>-1</sup> due to OH rocking vibrations. The IR spectra of all the acetato complexes showed two types of stretching vibrations at 1520,1320cm<sup>-1</sup> due to ionic nature of one group and bidentate nature of the other group<sup>(24)</sup>. Whereas, the spectra of complexes (3,4 and 6) showed two stretching vibrations of symmetric and asymmetric acetato group at (1350-1381)cm<sup>-1</sup> and (1525-1560)cm<sup>-1</sup> indicating the bidentate nature of this group<sup>(21)</sup>. The difference between (vas-vs) less than 200 cm<sup>-1</sup>, which indicates the bidentate coordination of the acetate group with the central metal ion<sup>(24)</sup>. In addition the coordination of chloride could not be inferred from infrared spectra of the complexes because the band due to these group occurred beyond the range of our infrared spectrophotometer, whereas for Cl- ligand has been checked by AgNO<sub>3</sub>. The chloride complexes (1,5 & 8) showed a band at (570, 600) cm<sup>-1</sup> has been attributed to ionic<sup>(24)</sup>, (Table 3).

### <sup>1</sup>H NMR spectra

The proton nuclear magnetic resonance spectrum for the compounds A1 & A3 was carried out using DMSO-d<sub>6</sub> as solvent and the following peaks were detected: A1 exhibits a sharp singlet at 10.7 ppm due to SH and this peak expected for 1,3,4-oxadiazole-thiol. Signals were observed in region 8.18-8.28 ppm due to aromatic protons. While the ligand A3 exhibits a single t signals at (δ = 4.16 ppm) referring to CH<sub>2</sub>-S group proton. On the other hand, the signal at (δ = 3.72 ppm) is assigned to O-CH<sub>2</sub> group also, the aromatic protons were observed in the region 8.66-7.86 ppm<sup>(25)</sup>.

Table 3: Selected I.R. bands of the ligand and its complexes ( in cm

Comp No.	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu\text{C}-\text{S}$	$\nu_{\text{s}}\text{CO}$	$\nu(\text{M}-\text{N})$	$\nu(\text{S}-\text{CH}_2)$	$\nu(\text{M}-\text{S})$	Others
A3	1605	975	705	1730	-	1430	-	$\nu\text{C}-\text{H}$ 2997, $\nu\text{C}-\text{O}-\text{C}$ 1035, 1353,1522( $\text{NO}_2$ sy,asy.)
1	1585	989	690	1637	435	1410	419	$\nu\text{-OH}_2$ 3400,701 $\nu\text{M}-\text{O}$ 550, $\nu_{\text{ionic}}\text{Cl}$ 600
2	1590	985	702	1637	435	1412	423	$\nu\text{-OH}_2$ 3400,705 $\nu\text{M}-\text{O}$ 560, $\nu_{\text{ionic}}\text{NO}_3$ 1382,738
3	1592	980	745	1660	439	1410	427	$\nu\text{-OH}_2$ 3369,702 $\nu\text{M}-\text{O}$ 550, $\nu\text{CH}_3\text{CO}_2$ ,1525,1381,1320
4	1575	973	740	1648	442	1397	419	$\nu\text{-OH}_2$ 3346,708 $\nu\text{M}-\text{O}$ 532 $\text{CH}_3\text{CO}_2$ ,1560,1350,1320
5	1576	980	699	1632	442	1366	419	$\nu\text{-OH}_2$ 3320,707 $\nu\text{M}-\text{O}$ 545, $\nu_{\text{ionic}}\text{Cl}$ 570 ,
6	1592	990	685	1640	440	1373	414	$\nu\text{-OH}_2$ 3410,700 $\nu\text{M}-\text{O}$ 545, $\nu\text{CH}_3\text{CO}_2$ ,1525,1353,1320
7	1575	980	665	1635	433	1365	422	$\nu\text{-OH}_2$ 3410,700 $\nu\text{M}-\text{O}$ 520, $\nu_{\text{ionic}}\text{NO}_3$ 1386,740
8	1580	980	690	1690	435	1360	420	$\nu\text{-OH}_2$ 3400, 700 $\nu\text{M}-\text{O}$ 520, $\nu_{\text{ionic}}\text{Cl}$ 570
9	1579	989	700	1682	440	1360	422	$\nu\text{-OH}_2$ 3379, 700 $\nu\text{M}-\text{O}$ 560
10	1575	977	668	1660	440	1350	400	$\nu\text{-OH}_2$ 3400,701 $\nu\text{M}-\text{O}$ 550
11	1570	980	700	1665	435	1362	412	$\nu\text{-OH}_2$ 3365,700 $\nu\text{M}-\text{O}$ 550

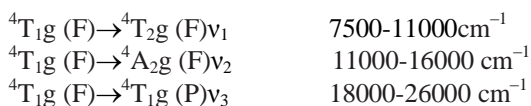
### Electronic Spectra and magnetic moment

The electronic spectra of the ligand and the complexes in DMF solution have been recorded giving ultraviolet spectra, d-d spectra and charge transfer spectra (Table 4). The ultraviolet spectra for A3 exhibited two bands in the UV intervals at  $31746\text{cm}^{-1}$  and  $363636\text{cm}^{-1}$ , assigned to  $n \rightarrow \pi^*$  ( $\text{C}=\text{S}$ ), and  $\pi \rightarrow \pi^*$  ( $\text{C}=\text{N}$ ) transitions respectively. All these transitions were also found in the spectra of the complexes but they were shifted to lower frequencies confirming the coordination of the ligand to the metal ions<sup>(26)</sup>.



The electronic spectra of Fe(II) complex (5) is characteristic of an octahedral geometry having high spin electronic configuration. According to this electronic distribution only one well defined  ${}^5T_{2g} \rightarrow {}^5E_g$  transition. However, due to the Jahn Teller effect, the  ${}^5E_g$  term is split in two terms which are responsible for the occurrence of a band and a shoulder in the spectrum. Hence Fe(II) complex showed a pair of low intensity bands at 10638, 10857 and the band at  $38610\text{ cm}^{-1}$  may be due to (C.T) (Table 6). The complex 5 shows magnetic moments at room temperature calculated from the corrected magnetic susceptibilities is 5.15 B.M revealing the presence of five unpaired electrons are present in the complex molecule and indicating high spin octahedral iron (II) complex<sup>(27)</sup>. The experimental electronic spectrum of Co(II) complexes

(1,2,&3) exhibit bands at (9478,9460 and 9415)  $\text{cm}^{-1}$  due to  $\nu_1$ , (12615, 11384 and 10881)  $\text{cm}^{-1}$  due to  $\nu_2$ , and 17006, 20190 and  $21841\text{ cm}^{-1}$  due to  $\nu_3$ , which are assigned to following transitions:



and these values agree with high spin octahedral configuration. The magnetic moment obtained for complexes 1,2 and 3 are 4.10,3.95 and 4.05 B.M. respectively and this values greater than theoretical value (3.87) B.M. due to orbital contribution<sup>(27)</sup>. While Ni(II) complex 4 exhibits electronic spectrum<sup>(24)</sup> bands at 10946,16247 and  $30120\text{ cm}^{-1}$  respectively, and assigned to transitions :

${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F) \nu_1$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) \nu_2$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P) \nu_3$  respectively. The octahedral geometry of Ni(II) ion in the complex is confirmed by the measured magnetic moment value, 2.70 B.M<sup>(28)</sup>. The Cu(II) complex 6 shows one broad band peaking at  $16112\text{ cm}^{-1}$ . This band may arise from the  ${}^2E_g \rightarrow {}^2T_{2g}$  transition of  ${}^2D$  state. This band has been comparable both in position and width with the earlier reported octahedral complexes. Because the eg state has been highly affected by Jahn taller effect, therefore, copper complex had distorted octahedral geometry is confirmed by the measured magnetic moment value<sup>(29)</sup>, 1.72 B.M

**Table 4: Electronic spectra data of the complexes**

Comp. No.	Electronic transitions of d-d $\text{cm}^{-1}$			
	$\nu_1$	$\nu_2$	$\nu_3$	CT
1	9478	12615	17006	38469
2	9460	11384	20190	38610
3	9415	10881	21841	33112
4	10946	16247	30120	35668
5	10638	10857	-	38610
6	16112	31056	29762	27778

CT = charge transfer band

### X-ray Powder Diffraction Analysis

The XRD patterns indicate a crystalline nature for Fe(II) and Cd(II) complexes. Indexing of the diffraction patterns was performed using High Score Plus software (Match<sup>(30)</sup> program, and their Miller indices (hkl) along with observed and calculated  $2\theta$  angle, d values, and relative intensities, From the indexed data the unit cell parameters were also calculated and. The Powder XRD patterns of the compounds are completely different from those of the starting materials, demonstrating the formation of coordination compounds. It is found that Fe(II) and Cd(II) complexes have orthorhombic and tetragonal structure As shown in Tables (5&6). Moreover, using diffraction data, the mean crystallite sizes of the complexes, D, were determined according Scherrer equation ( $D = 0.9 \lambda / (\beta \cos \theta)$ ), where  $\lambda$  X-ray wavelength ( $1.5406\text{ \AA}$ ),  $\theta$  is Bragg diffraction angle, and  $\beta$  is the full width at half maximum of the diffraction peak<sup>(31)</sup>.

**Table 5: Crystal data and structure refinement for complex**

No	Complex	5
1	Molecular Formula	$\text{FeC}_{11}\text{H}_{15}\text{N}_3\text{O}_8\text{SCL}_2$
2	Molecular weight	476
3	Crystal system	Orthorhombic
4	Space group	Pca (61)
5	Unit cell parameters ( $\text{\AA}$ )	a= 14.166 , b= 14.549 , c= 150187

6	Cell Volume (A <sup>03</sup> )	3130.06.93
7	Z	8
8	θ range , deg	1.93– 46.58
9	Index ranges	0 ≤ h ≤6, 0 ≤ k ≤8, 0 ≤ L ≤ 6

Table 6: Crystal data and structure refinement for complex

No	Complex	7
1	Molecular Formula	CdC <sub>11</sub> H <sub>15</sub> N <sub>3</sub> O <sub>8</sub> SCl <sub>2</sub>
2	Molecular weight	532
3	Crystal system	Pi Tetragonal
4	Space group	P-4(81)
5	Unit cell parameters (A <sup>0</sup> )	a= 20.1 A <sup>0</sup> , c= 5.33 A <sup>0</sup>
6	Cell Volume (A <sup>03</sup> )	2153.37 A <sup>03</sup>
7	Z	4
8	θ range , deg	10.55 – 50.06
9	Index ranges	29 ≤ h ≤ 30 12 ≤ k ≤ 6 15 ≤ L ≤ 3

### CONCLUSION

according to various physicochemical, spectral and the measurements of XRD analysis the crystal geometries of some complexes has been established, and we concluded that the metal ions are hexacoordinate with most probable octahedral structure has been suggested for most complexes. Whereas, cadmium complexes have tetrahedral geometries. The analytical and spectroscopic ir data showed that ligand (A3) acts as tridentate coordinated to the metal ions through oxygen carbonyl ester, sulfur thioether and azomethine nitrogen atoms.

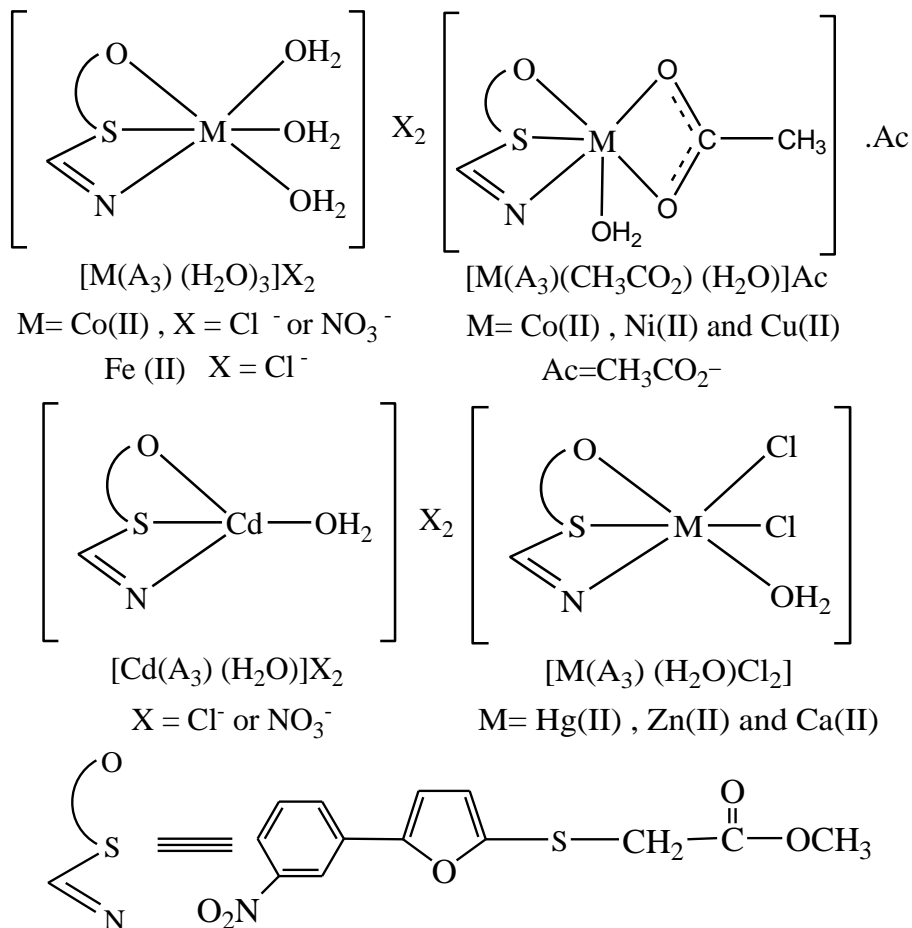
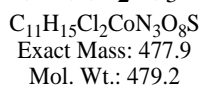
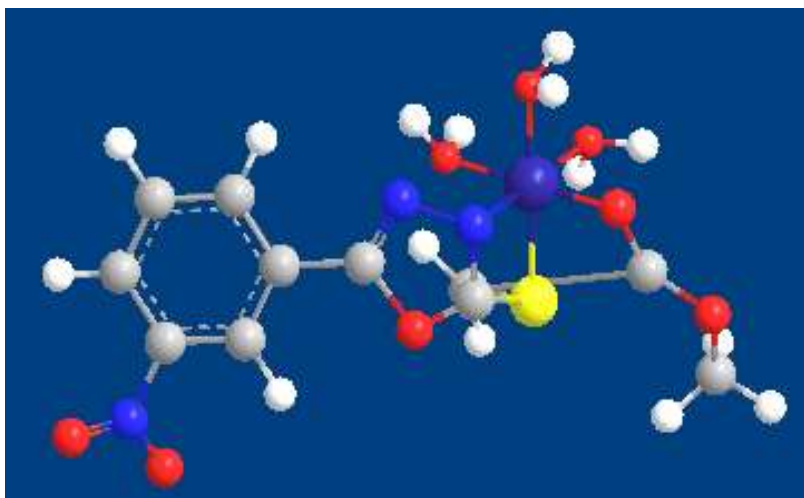
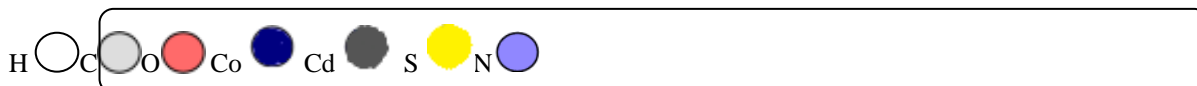
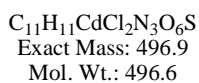
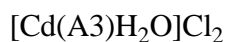
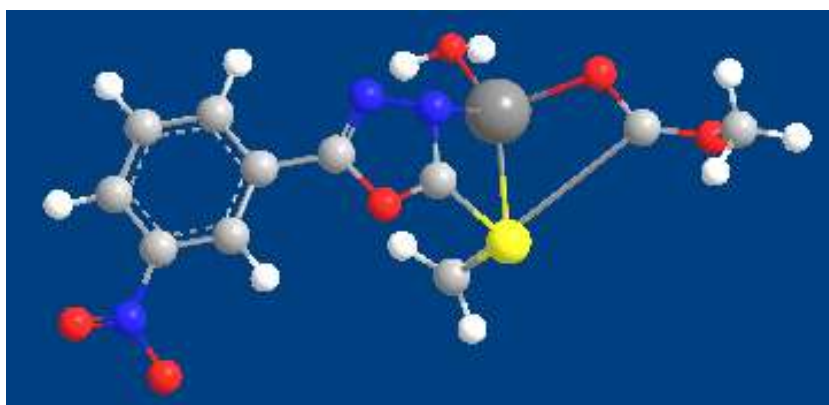


Fig. (3): The structure of the prepared complexes





m/e: 477.9 (100.0%), 479.9 (71.0%), 481.9 (14.9%), 478.9 (14.3%), 480.9 (10.0%), 482.9 (2.0%)  
 C, 27.57; H, 3.16; Cl, 14.80; Co, 12.30; N, 8.77; O, 26.71; S, 6.69



m/e: 496.9 (100.0%), 494.9 (69.0%), 498.9 (64.9%), 495.9 (51.2%), 497.9 (34.0%), 493.9 (29.0%), 492.9 (26.3%), 500.9 (19.6%), 499.9 (12.4%), 490.9 (3.5%), 501.9 (2.8%), 502.9 (2.6%), 488.9 (2.5%)  
 C, 26.60; H, 2.23; Cd, 22.64; Cl, 14.28; N, 8.46; O, 19.33; S, 6.46

**Fig. (4): The structures of complexes 1 & 8 Chemi Office. version. Ultra 8.0.2D & 3D**

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