

Synthesis, spectroscopic and X-ray powder diffraction (XRD) of some oxdiazole complexes

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ABSTRACT

Complexes of the ligand; 2-(ethylacetato) thio-5- (m-nitrophenyl)-1,3,4-oxadiazole with Co(II), Fe(II), Ni(II), Cu(II), Cd(II), Hg(II), Zn(II) and Ca(II) have been synthesized and characterized on the basis of physicochemical investigations including infrared and electronic spectroscopy, magnetic moment measurements, molar conductance and elemental analysis. The structures of the ligand and its complexes have been investigated by X-ray powder diffraction (for complexes) and ¹H NMR (for ligand). They have been found to have the formula; $[M(A_2)(H_2O)_n]X_2$; M=Co(II), Fe(II); n=3 and Cd(II); n=1, X= Cl⁻ or NO₃⁻, $[M(A_2)(H_2O)(CH_3CO_2)]Ac$. M=Co(II), Ni(II), and Cu(II), Ac=acetate and $[M(A_2)(H_2O)Cl_2]$, M= Hg(II), Zn(II), Ca(II);. Infrared spectral data suggest that the ligand A₂: 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: Ox diazole Complexes, X-ray powder diffraction, Metal complexes

INTRODUCTION

1,3,4-oxadiazoles and their derivatives are known to exhibit diverse pharmacological activities such as antimicrobial, antihistaminic, anticancerous, anti-inflammatory, antihypertensive and anticonvulsant activities^(1,2). 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)⁽³⁾. The oxadiazole ring is electron deficient, resulting in poor hole transport but good transport properties. Although some types of metal complexes have been found to be good emitters and/or excellent electron transport with excellent thermal properties⁽⁴⁾. Some material application of 1,3,4-oxadiazole derivatives lie in the field of liquid crystals⁽⁵⁾. The heterocyclic thiones represent an important type of compound in the field of coordination chemistry because of their potential multifunctional donor sites, viz either exocyclic sulfur or endocyclic nitrogen⁽⁶⁾. For this reason our aim was to synthesize various 1,3,4-oxadiazole derivatives to make notable contributions to this class of heterocyclic compounds. There are a few reports on the metal complexes of 5-m-nitrophenyl-1,3,4-oxadiazole-2-substituted thione.

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 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 ¹H 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 -d₆ as solvent and Me₄ Si as internal reference. Elemental analysis was 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 Werkstatte 82362 Weicheim. Magnetic susceptibility of the complexes was measured by Bruker -BM6 using Faraday method. Metal contents were estimated spectrophotometrically using atomic absorption Spectrophotometric 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

3.1- 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 °c , yield (67%), m.p 152-154 °c empirical formula. C₇H₇N₃O₃



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

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

In thesecond step , this ligand was prepared according to the modified procedure (young wood 1955⁽⁷⁾).The hydrazide of the step 1(m-nitrobenzoyl hydrazine) (18.1 g , 0.1M). was allowed to react with carbon disulphide (120 ml, 0.2 M of CS₂) in the presence of ethanolic potassium hydroxide (5.6 g ,0.1M of KOH in 70 ml absolute ethanol) under reflux conditions until the libration of H₂S gas has been stopped and is detected with lead(II)acetate paper it turns grey in the presence of H₂S 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 °c,empirical formula C₈H₅N₃O₃S.

The yield product was characterized by CHN analysis, IR and H¹NMR.

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

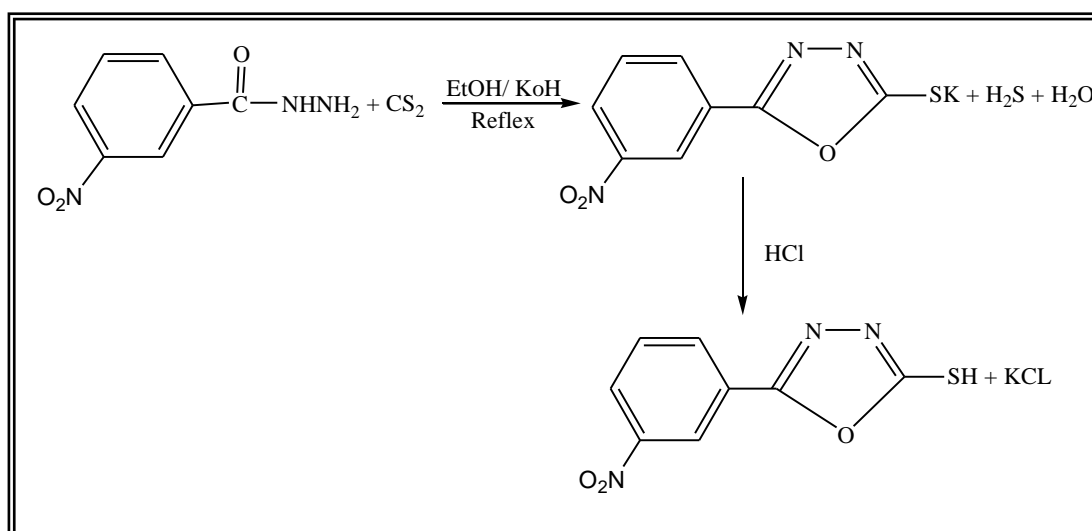


Fig.1

3.3-Preparation of 2-(ethylacetato) thio-5-(m-nitrophenyl)-1,3,4-Oxadiazole(A2)

A2-thio-5-(m-nitro-phenyl) -1,3,4-Oxadiazole (A1) (22.3g , 0.1 M) was dissolve edinetanolic potassium hydroxide (5.6 g ,0.1M of KOH in 100 ml absolute ethanol) followed by slow addition of drop wise of chloromethylethylester (12.25, 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%) ,mp218--220° cempirical formula $C_{12}H_{11}N_3O_5S$.

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

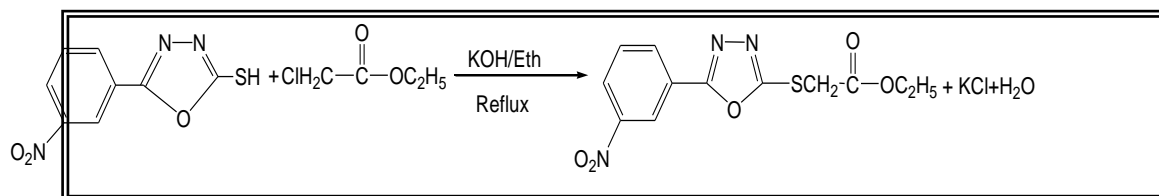
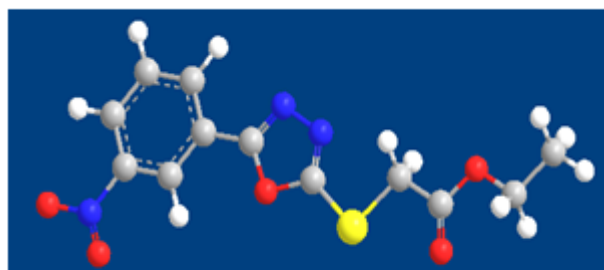
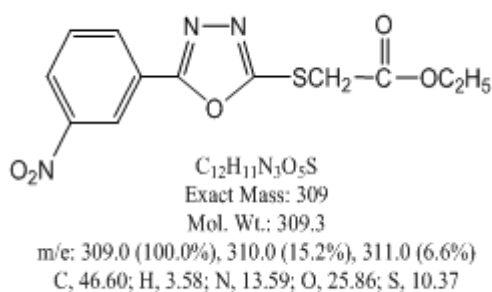
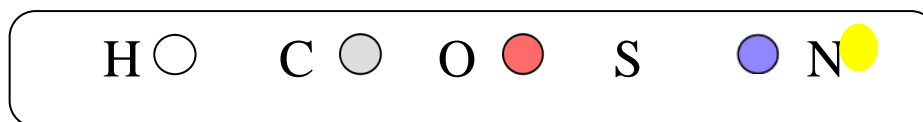


Figure 2: The structure of the prepared ligand A2



(A2)

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



	%C	%H	%N
Calc.	46.60	3.55	13.59
Found	46.29	3.61	13.73

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

An ethanolic solution of the ligand A2 (3.09 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

The prepared ligand and its complexes are solid and coloured, insoluble in water, but soluble in DMF. 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 (130-173) $ohm^{-1} cm^2 mol^{-1}$ indicating a (1:2) electrolytic nature of these complexes⁽⁸⁾. While the molar conductance values of the complexes(3,4 and 6) are in the range (70-82) $ohm^{-1} cm^2 mol^{-1}$ indicating (1:1) electrolytic nature of these complexes^(8,9). On other hand, complexes (9-11) are non electrolytic indicating neutral complexes⁽¹⁰⁾ 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) Salt	Metal	Wt(g) A2	Ω $\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	Complexes	m.p or d* $^{\circ}\text{C}$	Color
1	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$		2.38	3.09	130	$[\text{Co}(\text{A}_2)(\text{H}_2\text{O})_3]\text{Cl}_2$	242d	Dark brown
2	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$		2.91	3.09	163	$[\text{Co}(\text{A}_2)(\text{H}_2\text{O})_3](\text{NO}_3)_2$	226d	Pale brown
3	$\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 6\text{H}_2\text{O}$		2.49	3.09	75	$[\text{Co}(\text{A}_2(\text{H}_2\text{O}))(\text{CH}_3\text{CO}_2)]\text{Ac}$	270d	Brown
4	$\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$		2.49	3.09	70	$[\text{Ni}(\text{A}_2(\text{H}_2\text{O}))(\text{CH}_3\text{CO}_2)]\text{Ac}$	>300	Green
5	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$		1.99	3.09	173	$[\text{Fe}(\text{A}_2)(\text{H}_2\text{O})_3]\text{Cl}_2$	176	Brown redish
6	$\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$		1.99	3.09	82	$\text{Cu}(\text{A}_2)(\text{H}_2\text{O})(\text{CH}_3\text{CO}_2)]\text{Ac}$	<300	Pale green
7	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$		3.08	3.09	140	$[\text{Cd}(\text{A}_2)(\text{H}_2\text{O})](\text{NO}_3)_2$	241d	Pale yellow
8	CdCl_2		1.83	3.09	132	$[\text{Cd}(\text{A}_2)(\text{H}_2\text{O})]\text{Cl}_2$	260d	Pale yellow
9	HgCl_2		2.71	3.09	13	$[\text{Hg}(\text{A}_2)(\text{H}_2\text{O})]\text{Cl}_2$	183	White
10	ZnCl_2		1.36	3.09	18	$[\text{Zn}(\text{A}_2)(\text{H}_2\text{O})]\text{Cl}_2$	210	White
11	CaCl_2		1.10	3.09	21	$[\text{Ca}(\text{A}_2)(\text{H}_2\text{O})]\text{Cl}_2$	238d	Pale yellow

Table 2 : Elemental analysis of the complexes

Comp.No.	Complexes	Found%(Calc.)CHN, M			
		C	H	N	M
1	$[\text{Co}(\text{A}_2)(\text{H}_2\text{O})_3]\text{Cl}_2$	29.20	3.44	8.52	11.96
		(29.72)	(3.69)	(8.89)	(12.00)
2	$[\text{Co}(\text{A}_2)(\text{H}_2\text{O})_3](\text{NO}_3)_2$	26.56	3.11	12.82	10.80
		(26.61)	(3.51)	(12.95)	(11.00)
3	$[\text{Co}(\text{A}_2)(\text{H}_2\text{O})(\text{CH}_3\text{CO}_2)] \cdot \text{Ac}$	38.09	3.76	8.33	11.70
		(38.40)	(3.95)	(8.92)	(11.92)
4	$[\text{Ni}(\text{A}_2)(\text{H}_2\text{O})(\text{CH}_3\text{CO}_2)] \cdot \text{Ac}$	38.11	3.77	8.33	11.65
		(38.53)	(3.61)	(9.00)	(11.80)
5	$[\text{Fe}(\text{A}_2)(\text{H}_2\text{O})_3]\text{Cl}_2$	29.38	3.46	8.57	11.42
		(30.00)	(3.80)	(8.91)	(11.65)
6	$[\text{Cu}(\text{A}_2)(\text{H}_2\text{O})(\text{CH}_3\text{CO}_2)] \cdot \text{Ac}$	37.75	3.73	8.50	12.48
		(37.99)	(3.91)	(8.94)	(12.60)
7	$[\text{Cd}(\text{A}_2)(\text{H}_2\text{O})](\text{NO}_3)_2$	25.57	2.31	12.43	19.89
		(25.65)	(2.50)	(12.93)	(20.07)
8	$[\text{Cd}(\text{A}_2)(\text{H}_2\text{O})]\text{Cl}_2$	28.23	2.55	8.23	19.89
		(28.43)	(2.83)	(8.71)	(20.10)
9	$[\text{Hg}(\text{A}_2)(\text{H}_2\text{O})]\text{Cl}_2$	24.04	2.17	7.01	33.51
		(24.38)	(2.47)	(7.30)	(33.93)
10	$[\text{Zn}(\text{A}_2)(\text{H}_2\text{O})]\text{Cl}_2$	31.07	2.80	9.06	14.11
		(31.28)	(3.01)	(9.34)	(14.51)
11	$[\text{Ca}(\text{A}_2)(\text{H}_2\text{O})]\text{Cl}_2$	32.87	2.96	9.58	9.13
		(33.04)	(3.04)	(9.70)	(9.41)

Infrared spectra:

The coordination sites of the ligand involved in the bonding with metal ions had been determined by careful comparison of the infrared spectra of those compounds with that of the parent ligand. The ligand basically composed of different groups of potent ability to coordinate with the metal ions. The IR spectra of the A1 shows two bands a weak band at 2350cm^{-1} which is characteristic of stretching vibration of the SH group and sharp band at 3434cm^{-1} due to NH stretching vibration⁽¹¹⁾. These bands which subsequently disappeared in the ligand A2, indicating a vibration substitution occurred on position 2, and a new absorption bands appeared at 1428cm^{-1} , which has been attributed to bending frequency of $-\text{SCH}_2$ group. This is further supported by the appearance of the band at 708cm^{-1} due to stretching vibration of C-S bond⁽¹²⁾. In the spectra of the ligand A2 showed, a weak band at 2984cm^{-1} due to sym. & asym. C-H aliphatic of CH_2 group, and this band remains unaltered on complexation⁽¹³⁾.

The IR spectra of the A2 ligand shows a strong band in the region 1607cm^{-1} , which is characteristic of the azo group (stretching vibration of C=N) group. In all complexes, this band is slightly shifted to lower frequency⁽¹⁴⁾ indicating coordination of the A2 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⁽¹⁵⁾ stretching vibration at $471-490\text{cm}^{-1}$ in the complexes. The spectra of A2 shows a broad band at 970cm^{-1} due to N-N group (A2) shifts towards higher frequency ($982-1109$) on complexation⁽¹⁶⁾. A comparison of the IR spectra of the free ligand A2 and metal complexes reveal that the band due to carbonyl ester appeared at 1729cm^{-1} and medium absorption band at 1014cm^{-1} 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^{-1} . In the IR spectra of the complexes which could not be traced to free A2 have been tentatively assigned to [M-OH] and [M-O=C] stretch bands of the metal complexes⁽¹⁷⁾.

In the ligand spectra of A2 shows a characteristic band at 1064cm^{-1} which was assigned to the stretching was assigned to 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⁽¹⁸⁾. On the other hand, the spectra of (2&7) complexes showed the presence of additional band at ($1382, 742$) cm^{-1} due to ionic nature of nitrate group⁽¹⁹⁾. The aqua complexes contain weak to medium a broad band at ($3362-3422$) cm^{-1} due to stretching vibration OH of water⁽²⁰⁾ and a sharp shoulder at (1500) cm^{-1} may be assigned to bending vibration of water. Water molecules are coordinated, confirmed by occurrence of additional strong and sharp band at $700-709\text{cm}^{-1}$ due to OH rocking vibrations. The IR spectra of all the acetate complexes showed two types of stretching vibrations of acetate at $1520, 1320\text{cm}^{-1}$ due to ionic nature of one group and bidentate nature of the other group⁽¹⁸⁾ an absorption band in the region ($1373-1350$) cm^{-1} that is assigned to the $\nu(\text{COO}^-)$ asymmetric stretching vibrations of the acetate ion and another in the region ($1458-1478$) cm^{-1} that can be assigned to the $\nu(\text{COO}^-)$ symmetric stretching vibration of the acetate ion. The difference between (ν_{as} - ν_{s}) less than 120cm^{-1} , which indicates the bidentate coordination of the acetate group with the central metal ion⁽¹⁸⁾. 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_3 . The chloride complexes (1&8) show a band at 600cm^{-1} has been attributed to ionic⁽²¹⁾ (Table 3).

¹H NMR spectra

The proton nuclear magnetic resonance spectrum for the ligands A1 & A2 was carried out using DMSO-d_6 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 observed in region 8.18–8.28 ppm due to aromatic protons. While the ligand A2 exhibits a singlet signals at ($\delta = 4.16$ ppm) referring to $\text{CH}_2\text{-S}$ group proton). On the other hand, the signal at ($\delta = 4.3$ ppm) is assigned to O- CH_2 group and multiplet signals at ($\delta = 1.2$ ppm) due to CH_3 group also, a multiplet signal due to COOC_2H_5 group. The aromatic protons were observed in the region 7.86–8.62 ppm⁽²²⁾.

Table 3: Selected I.R. bands of the ligand and its complexes (in cm^{-1})

Comp No.	$\nu(\text{C=N})$	$\nu(\text{N-N})$	$\nu\text{C-S}$	$\nu_{\text{s}}\text{CO}$	$\nu(\text{M-N})$	$\nu(\text{S-CH}_2)$	$\nu(\text{M-S})$	Others
A2	1607	970	708	1729	-	1428	-	$\nu\text{C-H } 2984,$ $\nu\text{C-O-C } 1064, \nu\text{NO}_2, 1388,$ 741

1	1524	990	689	1586	490	1392	418	v-OH ₂ 3406,704 vM-O 550, V _{ionic} Cl 600
2	1526	982	691	1591	484	1464	421	v-OH ₂ 3373,705,vM-O 502, V _{ionic} NO ₃ 1382,742
3	1591	1064	742	1591	482	1463	425	v-OH ₂ 3362,705,vM-O, 547, vsCOO ⁻ 1478, vasCOO ⁻ 1373 ,
4	1529	989	654	1587	473	1350	423	v-OH ₂ 3422,705vM-O 546, , vsCOO ⁻ 1458, vasCOO ⁻ 1350
5	1522	989	708	1583	480	1372	413	v-OH ₂ 3410,700, vM-O 545, V _{ionic} Cl 600,
6	1532	1109	689	1581	472	1370	419	v-OH ₂ 3422,709,vM-O 546, vsCOO ⁻ 1458, vasCOO ⁻ 1350
7	1526	1060	667	1578	471	1348	423	v-OH ₂ 3417,706,vM-O 521, vionicNO ₃ ,1382,742
8	1528	985	690	1580	490	1385	419	v-OH ₂ 3400,705,vM-O 550, V _{ionic} Cl 600
9	1524	989	700	1579	485	1389	422	v-OH ₂ 3379,700,vM-O 560
10	1532	1025	656	1585	478	1356	411	v-OH ₂ 3410,703, vM-O 555
11	1530	988	710	1581	480	1371	413	vM-OH ₂ ,3362,707 vM-O 560

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 A2 exhibited two bands in the UV intervals at 30487 cm⁻¹ and 38461 cm⁻¹, assigned to n → π* (C=S), and π → π* (C=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⁽²³⁾.

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} → 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 9398, 10857 and 11682 cm⁻¹ (Table 6) and The band at 38610 cm⁻¹ may be due to (C.T). The complex 5 shows magnetic moments at room temperature calculated from the corrected magnetic susceptibilities is 5.38 B.M revealing the presence of five unpaired electrons are present in the complex molecule and indicating high spin octahedral iron (II) complex⁽²³⁾. The experimental electronic spectrum of Co(II) complexes (1,2&3) exhibit

bands at (9407, 9460 and 9460) cm^{-1} due to ν_1 , (10857, 10929 and 12224) cm^{-1} due to ν_2 , and 150150, 150384 and 16241 cm^{-1} due to ν_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 4.61,4.83 and 4.75 B.M.respectively and this values greater than theoretical value (3.87)B.M.due to orbital contribution ⁽²⁴⁾.WhileNi(II) complex 4 exhibitselectronic spectrum⁽²⁴⁾. bands at 10893,18461 and 28322 cm^{-1} respectively, and assignedto 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 octahedralgeometry of Ni(II) ion in the complex isconfirmedby the measured magnetic

moment value, 2.70 B.M.⁽²⁵⁾. The Cu(II) complex 6showsone broad band peaking at15152 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⁽²⁶⁾ .

Table 4: Electronic spectra data of the complexes

Comp. No.	Electronic transitions of d-d cm^{-1}			
	ν_1	ν_2	ν_3	CT
1	9460	12224	150150	38469
2	9460	10929	15384	38610
3	9407	10857	16247	33112
4	10893	18461	28322	35668
5	9398	10857	11682	38610
6	15152	28430	30211	-

CT = charge transfer band

X-ray Powder Diffraction Analysis

Growth of single crystal of oxadiazole compounds from various solvents including DMF, ethanol, chloroform etc. failed and so they were characterized by XRD . X-ray powder diffraction analysis of the parent metal salts from which they were prepared metal complexes was carried out to determined the type of crystal system, lattice parameters, and the cell volume. As shown in Table 5 the XRD patterns indicate a crystalline nature for metal complexes. Indexing of the diffraction patterns was performed using High Score Plus software (Match program). For Fe(II) and Cd(II) complexes, for example ,their Miller indices (hkl) along with observed and calculated 2θ 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. 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 λ X-ray wavelength (1.5406 Å°), θ is Bragg diffraction angle, and β is the full width at half maximum of the diffraction peak⁽²⁷⁾ .

Table 5: Crystal data and structure refinement for complexes 5&7

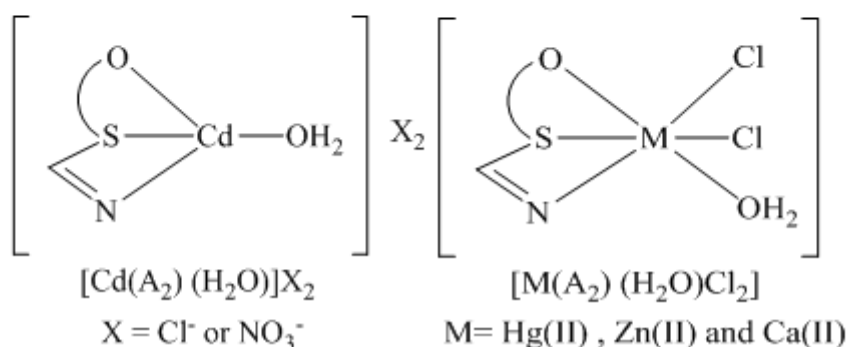
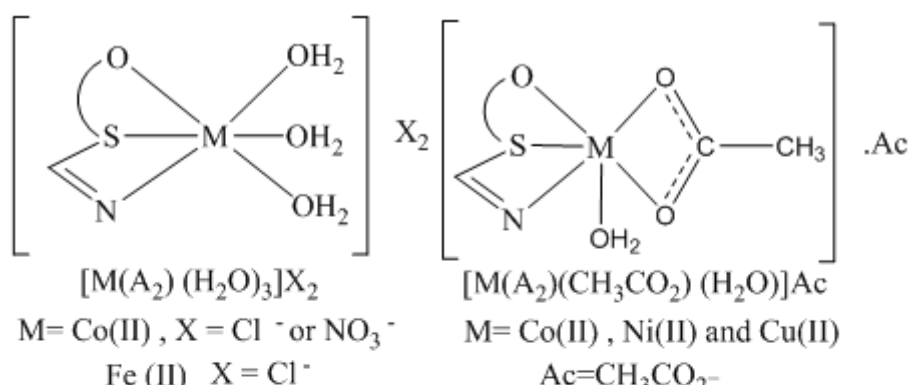
No	Complex	5
1	Molecular Formula	$C_{12}H_{17}N_3O_8SFe$
2	Molecular weight	490
3	Crystal system	Pi Orthorhombic
4	Space group	Pbca(61)
5	Unit cell parameters (Å°)	a= 14.166 , b= 14.549 , c= 15.187
6	Cell Volume (Å°)	3130.06
7	Z 8	α ($^\circ$) 113.14(3) β ($^\circ$) 92.05(3)

		γ ($^\circ$) 102.75(3)
8	θ range , deg 26.97	1.93 – 46.58
9	Index ranges R indices (all data)[$I > 2 \sigma(I)$]	$17 \leq h \leq 6$ $11 \leq k \leq 8$ $15 \leq L \leq 8$

No	Complex	7
1	Molecular Formula	$C_{12}H_{13}N_5O_{11}SCd$
2	Molecular weight	563
3	Crystal system	Pi Tetragonal
4	Space group	P-4(81)
5	Unit cell parameters (A°)	$a = 20.1 \text{ A}^\circ$, $c = 5.33 \text{ A}^\circ$
6	Cell Volume (A^{03})	2153.37 A^{03}
7	Z 4	α ($^\circ$) 73.11(3) β ($^\circ$) 61.25(3) γ ($^\circ$) 25.34(3)
8	θ range , deg	10.55 – 50.06
9	Index ranges	$0 \leq h \leq 11$ $0 \leq k \leq 6$ $0 \leq L \leq 3$

CONCLUSION

From the above discussion of various physicochemical, spectral and according to the measurements of XRD analysis, the crystal geometries of some complexes has been established, and we concluded that the metal ions are hex coordinate with most probable octahedral structure has been suggested for most complexes. Whereascadium complexes have tetrahedral geometries. The analytical and spectroscopic ir data showed that ligand (A2) acts as tridentate coordinated to the metal ions through oxygen carbonyl ester , sulfur thioether and azomethine nitrogen atoms.



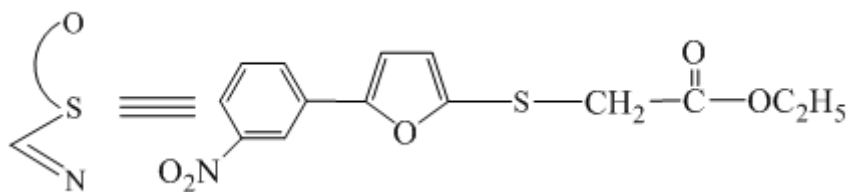
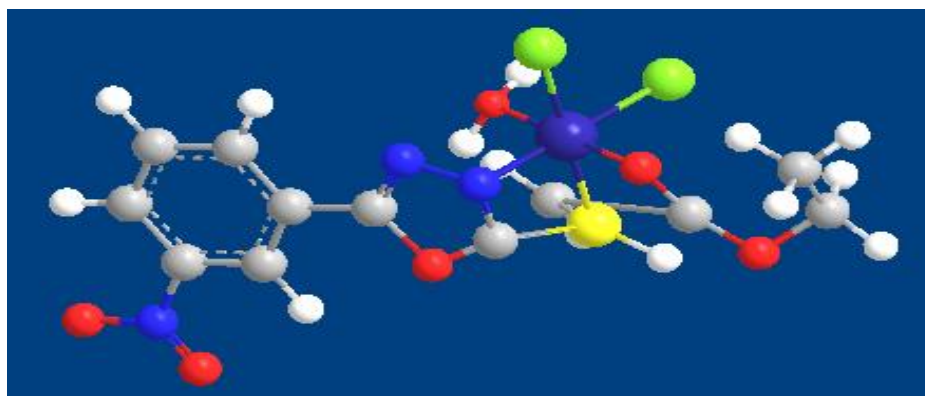
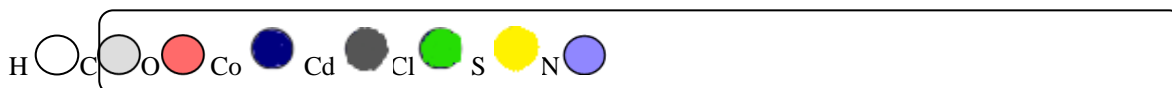
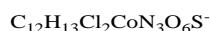


Fig.3: The structure of the prepared complexes



[Co(A2)(H₂O)Cl₂]

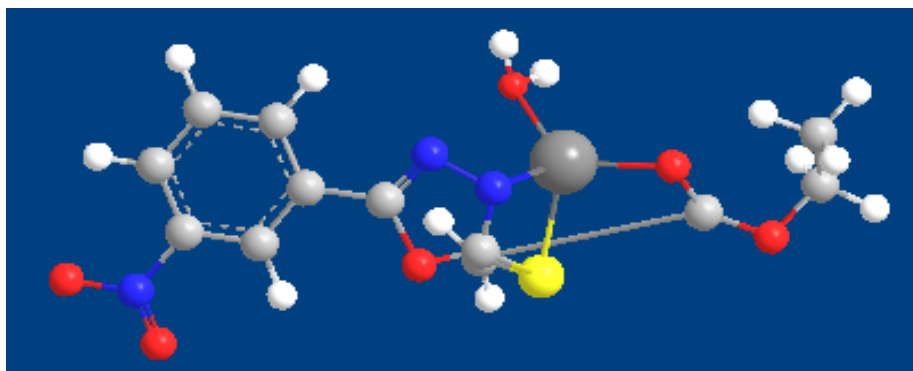


Exact Mass: 456

Mol. Wt.: 457

m/e: 456 (100.0%), 458 (70.8%), 457 (15.3%), 460 (14.7%), 459 (10.6%), 461 (2.1%)

C, 31.53; H, 2.87; Cl, 15.51; Co, 12.89; N, 9.19; O, 21.00; S, 7.01



[Cd(A2)(H₂O)]Cl₂



Exact Mass: 511

Mol. Wt.: 511

m/e: 511 (100.0%), 509 (68.9%), 513 (65.0%), 510 (51.7%), 512 (34.9%), 508 (29.1%), 507 (26.1%), 515 (19.7%), 514 (13.0%), 505 (3.5%), 516 (3.0%), 517 (2.6%), 503 (2.5%)

C, 28.23; H, 2.57; Cd, 22.01; Cl, 13.89; N, 8.23; O, 18.80; S, 6.28

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

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