

Synthesis and Studies of $\bar{1}, \bar{2}$ -bis ($\bar{5} - \bar{2}$ Thiolethylsulfide-1, 3, 4-Oxadiazole-2yl) Ethane and it's Complexes with (M (II): Cu, Ni, Co, Hg)

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ABSTRACT

The new ligand $\bar{1}, \bar{2}$ -bis ($\bar{5} - \bar{2}$ -thiolethylsulfide) -1, 3, 4- oxadiazole-2yl) ethane (BTESOE) was prepared from the reaction of $\bar{1}, \bar{2}$ - bis-($\bar{5} - \bar{2}$ - chloro ethylsulfide)-1,3,4-oxadiazol-2yl) ethane with sodium sulphide in aqueous ethanol solution. The ligand was characterized using IR, UV/Vis, ^1H -n.m.r, ^{13}C -n.m.r, mass spectroscopies and molar conductivity. BTESOE was employed to synthesize four complexes with metals (M (II): Cu, Ni, Co and Hg), the complexes were studied using IR, UV/Vis, atomic spectroscopies, molar conductivity and magnetic susceptibilities techniques. The results showed that each of these complexes has an octahedral geometry structures.

Keywords: Synthesis, Thiolethylsulfide, complexes.

($\bar{2}$ - $\bar{4}$ $\bar{3}$ $\bar{1}$ - $\bar{2}$ - $\bar{5}$) $\bar{2}, \bar{1}$

M(II): (Hg, Co, Ni, Cu)

- $\bar{1}, \bar{3}, \bar{4}$ - ($\bar{2}$ - $\bar{5}$) $\bar{2}, \bar{1}$
 2- $\bar{4}, \bar{3}, \bar{1}$ - ($\bar{2}$ - $\bar{5}$) $\bar{2}, \bar{1}$ (BTESOE) - ($\bar{2}$
 - ($\bar{2}$ - $\bar{5}$) $\bar{2}, \bar{1}$ (BTESOE) . (^1H , ^{13}C .n.m.r)
 (M(II): Hg, Co, Ni, Cu)

INTRODUCTION

The study of compounds which contains (S, N) have taken a wide area in an organic and inorganic fields (Hoggarte, 1952). An important type are those containing thioamide group-NCS. This group is also found in many basic structure of drug either as a part of an open chain e.g. thiocarbonate R-NH-(S)NR₂ or involved in a heterocyclic ring e.g. thio derivatives of oxadiazoles (Mehdi *et al.*, 2002).

The synthesis and characterization of new 5-alkyl substituted 1,3,4-oxadiazole-2thiones) and 5-alkyl substituted -3 (2, 4 dimethyl phenyl) 1,3,4-oxadiazole -2-thiones using the synthesis procedure based on the ring closes reaction of appropriate acid hydrazides with carbon disulphide. Mannich bases for some of these compounds were synthesized with benzaldehyde and primary amines. They were characterized by spectral data and most of them were tested for their antibacterial and antituberculestatic activity (Aydogan *et al.*, 2002).

The synthesis of the new ligands of disulphide ligands containing oxadiazole triazole and thiazole rings with some of their complexes was performed corresponding of their importance as a multi-basic donor sites and they showed a relation with pharmaceutical characters and biological activities (Mehdi and Musa, 2004).

Musa synthesized a new macroligands contains (S, O, N) and their complexes (Musa, 2002). The interactions of metal ions with N, S donor atoms have been recognized for their anticancer properties with the potential to develop metal based drug (Al-Jibori *et al.*, 2002; Othman *et al.*, 2004; Mehdi and Musa, 2004).

In recent years numerous compounds of thio-oxadiazole were synthesized such of those reported by Demirbas (Demirbas, 2005), in which the compounds containing- SH group were converted to their substituted derivatives.

In the present work the efforts have been made to synthesize a cyclic macro thioxadiazole compounds which contain more than one sulphur atom and study of their reaction with some metal ions.

EXPERIMENTAL

Chemical and Instruments:

All chemicals are of analytical grade. The characterizing measurements were obtained using the following instruments:

- 1- Melting points and decomposed degrees were determined using Electrothermal 9100(U-k). (College of science, University of Salahaddin/Erbil).
- 2- IR spectra were obtained using Maston spectrophotometer was in the (400-4000) cm⁻¹ range, using KBr discs. (College of science, University of Salahaddin/Erbil).
- 3- ¹H, ¹³C-n.m.r were recorded on a 400 Bruker spectrophotometer for solution in DMSO. (Cardiff University, England).
- 4- Mass spectra were recorded using Micromass ZQ "Water" in methanol solution. (Cardiff University, England).
- 5- UV - Visible spectra on a DataStream CE 3000 series, using nugal, mull paper technique. (College of science education, University of Salahaddin/Erbil).
- 6- Magnetic susceptibilities of the complexes were determined at 25 °C using Bruker magnetic BM6. (College of science, University of Mousil)

- 7- Conductivity measurements were made (DMSO as solvent) by using Jenway conductivity meter 4200 (0.93 cell constant U.K). (College of science education, University of Salahaddin/Erbil)
- 8- Atomic absorptions were measured using PYE UNICAM SP9 atomic absorption spectrophotometer. (College of science education, University of Salahaddin/Erbil)

1. Synthesis of the (BTESOE) ligand (IV):-

a. Preparation of succinic dihydrazide (I):

A hydrazine hydrate (6.38 gm, 127.447 m.mole) was added to a solution of diethyl succinate (20.96 gm, 62.91 m.mole) in 50 ml of ethanol, and then 50 ml of ethanol was added to the mixture. It was refluxed for three hours, then left to cool at room temperature to give white precipitate crystals which filtered off, washed with cold ethanol and recrystallized with ethanol, yield 85.67%, m.p (169-170 C^o) (Al-Hete, 1999).

b. Preparation of $\bar{1}, \bar{2}$ -bis($\bar{5}$ -thio-1, 3, 4- oxadiazole -2yl)ethane (II):

A 10 ml of an ethanolic solution of (1.12gm, 20 m.mole) of potassium hydroxide was poured to a solution of (1.46 gm, 9.98 m.mole of (I) in (ethanol: water) (10:5) ml the mixture was refluxed for 30 minutes, then (1.52 gm, 1.20 ml, 20 m.mole of carbon disulphide (CS₂) was added gradually. The mixture was concentrated with rotary evaporator to 10 ml, then poured to beaker contained (5 ml of concentrated hydrochloric acid with ice) to give white precipitate which was filtered off, dried and recrystallized with ethanol, m.p (149-152 C^o), yield 75.78 % (Al-Hete, 1999), soluble in acetonitrile and ethanol.

c. Synthesis of $\bar{1}, \bar{2}$ -bis($\bar{5} - \bar{2}$ -chloroethylsulphide)-1,3,4-oxadiazole -2yl]ethane (III):

According to (Musa *et al.*, 2002) solution of (1.2 gm, 5.217m.mole of (II) in (15:10) ml (ethanol: water) was added to a solution [0.53gm, 9.46 m.mole) of potassium hydroxide in 10 ml of ethanol. The mixture was refluxed for 30 minutes, and was left for five minutes followed by addition of (0.92 gm, 9.29 m.mole, 0.73 ml) of 1,2 dichloroethane. The mixture was refluxed for 24 hours at laboratory temperature. The mixture was evaporated and the white precipitate was filtered off, recrystallized with ethanol, dried under a vacuum, m.p (162-164 C^o) (yield 78.75 %) soluble in ethanol, methanol, DMSO, DMF, Chloroform and acetonitrile.

d. Synthesis of $\bar{1}, \bar{2}$ -bis($\bar{5} - \bar{2}$ -chloroethylsulphide)-1,3,4-oxadiazole -2yl]ethane (IV):

A solution of an excess of sodium sulphide in (5:3) ml (ethanol: water) was added to a solution of (1.23 gm, 3.46 m.mole) of (III) in 25 ml of ethanol. The mixture was refluxed for eight hours, it was evaporated to give white precipitate which filtered, recrystallized from ethanol and dried under vacuum (d.p=223^o) (Yield= 81.37 %). It is soluble in ethanol, methanol, DMSO and DMF.

2. Synthesis of the solid complexes:

A. Synthesis of dichlorohexaaque $\bar{1}, \bar{2}$ -bis [($\bar{5} - \bar{2}$ -thiolthylsulphide)-1,3,4-oxadiazole-2yl] ethane dicopper (II):

To a solution of (0.1 gm, 0.290 m.mole) of (IV) in 10 ml of ethanol, a 5 ml of cupric chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (0.09 gm, 0.527 m.mole) was added, a gray mixture was appeared which returned to green mixture after addition of (0.0325 gm, 0.583 m.mole) of potassium hydroxide. The mixture was heated to reflux for two hours to give green precipitate, which filtered off, washed with warm water and ethanol (d.p = 203-205 °) and (Yield 53-84%), slightly soluble in DMSO.

B. Synthesis of dichlorohexaaque $\bar{1}, \bar{2}$ -bis [($\bar{5} - \bar{2}$ -thiolthylsulphide)-1,3,4-oxadiazole-2yl] ethane dicnickel (II):

The complex was synthesized in a yield (38.04%) by means of the procedure described as follow:-

To 10 ml of ethanol solution (0.1 gm, 0.29 m.mole) of (IV), a 5 ml of ethanolic solution of (0.126 gm, 0.530 m.mole) of nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) was added, a gray mixture was prepared , a solution of (0.032 gm, 0.581 m.mole) of potassium hydroxide in 5 ml of ethanol was dropwised. The mixture was refluxed for two hours to give a pale green precipitate which filtered off, washed with warm water and ethanol, (d.p=210 °) soluble in DMSO.

C. Synthesis of dichlorohexaaque $\bar{1}, \bar{2}$ -bis [($\bar{5} - \bar{2}$ -thiolthylsulphide)-1,3,4-oxadiazole-2yl] ethane dicobalt (II):

A (0.12 gm, 0.504 m.mole) of $\text{CoCl}_2 \cdot \text{H}_2\text{O}$ was dissolved in 5 ml of absolute ethanol and added dropwise to a 10 ml of ethanolic solution of (0.1 gm, 0.29 m.mole) of (IV) to give gray mixture which followed by addition of (0.03 gm, 0.581 m.mole) of potassium hydroxide in 5 ml of ethanol. The mixture was refluxed for two hours to give a dark brown product, which filtered off, washed with warm water and ethanol and dried in a vaccum (d.p = 210°) (Yield= 51.72%), slightly soluble in DMSO and DMF.

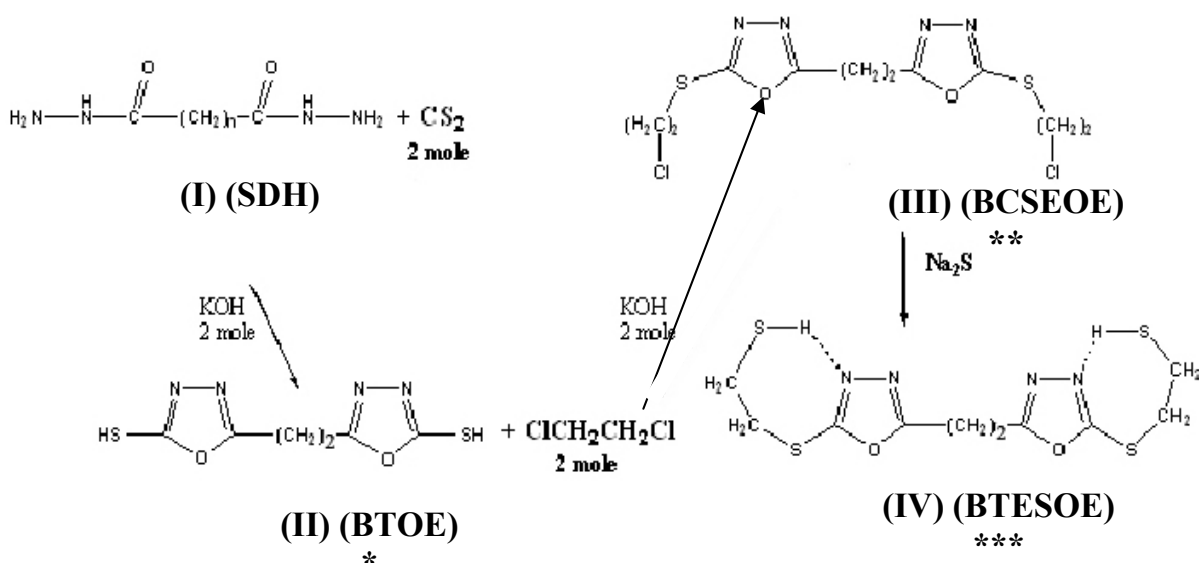
D. Synthesis of dichlorohexaaque $\bar{1}, \bar{2}$ -bis [($\bar{5} - \bar{2}$ -thiolthylsulphide)-1,3,4-oxadiazole-2yl] ethane dimercury (II):

A 5 ml of ethanolic solution of mercuric chloride hexahydrate ($\text{HgCl}_2 \cdot 6\text{H}_2\text{O}$) (0.087 gm , 0.320 m.mole) was poured to a 10 ml of ethanolic solution of (0.1 gm, 0.29 m.mole) of (IV), followed by addition of a solution of (0.032 gm 0.581m.mole) of potassium hydroxide in 5 ml of ethanol. The mixture was refluxed for two hours to give a white precipitate, which filtered off, washed with warm water and ethanol, dried under a vaccum (d.p =201 °) (Yield = 42.85 %) slightly soluble in DMSO and DMF.

RESULTS AND DISCUSSION

1. Synthesis and characterization of $\bar{1}, \bar{2}$ -bis[$\bar{5}(\bar{2}$ thiolethylsulphide-1, 3, 4-oxadiazol-2yl] ethane (BTESOE)

The ligand was synthesized according to the following scheme:-



Were **I**: succinic dihydrazide (SDH).

II: $\bar{1}, \bar{2}$ -bis [5- thiol-1, 3, 4 - oxadiazole- 2yl] ethane (BTOE).

III: $\bar{1}, \bar{2}$ -bis [$\bar{5}, \bar{2}$ - Chloroethylphidel] - 1, 3, 4- oxadiazole- 2yl) ethane (BCSEOE).

IV: $\bar{1}, \bar{2}$ -bis [$\bar{5}, \bar{2}$ - thioethylsulphide-1, 3, 4- oxadiazol-2yl] ethane (BTESOE)

* and **: New ligand under the publishing.

***: The Present ligands

The infrared study of the ligand (IV) (BTESOE):-

The i.r spectra of (BTESOE) showed two bands at (2920 and 2570) cm^{-1} which due to the $\nu(\text{N-H})$ and $\nu(\text{S-H})$ stretching respectively indicated of the binding of $-\text{CH}_2\text{CH}_2\text{Cl}$ group with H-thiol group Fig. (1). Also the IR spectra of (II) showed disappearance bands at 2537 cm^{-1} in the compound due to displacement $\text{ClCH}_2\text{CH}_2-$ group (AMT) (Dubey and Kausshik, 1985). In the spectrum of (IV) the band of $\nu(\text{C}=\text{S}, \text{C}=\text{N})$ was appeared at 1477 cm^{-1} (Ram, 1963), the shifting of this band in (III) to 1483 cm^{-1} suggests the effect of withdrawing group ($-\text{CH}_2\text{CH}-\text{Cl}$) on $(\text{N}=\text{C}=\text{S})$ band (Al-Hete, 1999). The shifting of $\nu(\text{C}=\text{N})$ band in spectra of (III) at 713 cm^{-1} to two splitted bands at (677-747) cm^{-1} in spectrum of ligand (IV) and compared it with deprotonated thiozolidine (Preti and Tosi, 1974).

The other bands are listed in Table (1).

The $^1\text{H-n.m.r}$ study of the ligand (IV) (BTESOE):

The $^1\text{H-n.m.r}$ spectrum showed a signal at (2-6) ppm which due to $-(\text{CH}_2)_2-$ with a ratio 36-613 while the $[-\text{S}-(\text{CH}_2)_4-\text{S}-]_2$ 3.4 ppm with ratio 62.58 (de Melo *et al.*, 1998; Field and kalman, 1997) Fig. (2), and Table (2).

The $^{13}\text{C-n.m.r}$ study of the ligand

The $^{13}\text{C-n.m.r}$ in MeOD according to system in Fig. (3), showed a signal at $[\delta = 171-48, 173-023]$ ppm may due to $(\text{C}_1-\bar{1})$ and $(\text{C}_2-\bar{2})$ for ligand (II) and (III) Table (3) (Al-Hete, 1999; Slothers, 1972).

The peaks at $[\delta = 46.85, 46.93]$ ppm were due CH_2 and CH_2SH (Demirbas, 2005; Hammad and Hashem, 2000). The results were compared with those obtained with ChemOffice program Fig. (3).

The mass spectra of the ligand (IV) (BTESOE)

The parent ion of m/z 230 with abundance (17.17) which is due to molecular weight ion $(\text{S}_2\text{N}_4\text{O}_2\text{C}_2\text{H}_6)^*$ / another peak at 546 is found might due to combination two radical of $\dot{\text{S}}\text{C}_6\text{N}_4\text{v}_2\text{H}_4\dot{\text{S}}$. The rest of fragmentations are illustrated in Table (4).

The characterization study of (BTESOE)complex.

The complexes with binary metal ions (Cu, Ni, Co, Hg) were prepared in the ratio 1:2 L: M.

The infrared study of (BTESOE) complexes

The IR spectra of the ligand complexes showed a broad band at $(3417-3477)\text{ cm}^{-1}$ and at $(725.763)\text{ cm}^{-1}$ which due to $\nu(\text{OH}_2)$ of coordinated water molecules. The $\nu(\text{S-H})$ band which observed in the ligand spectrum at $(2920)\text{ cm}^{-1}$ was disappeared in the spectra of the complexes, indicated the replacement of amino proton by means of metal ion. The Observation of splitted bands between $(1608-1625)\text{ cm}^{-1}$ are due to $\nu(\text{C=N})$ for (BTESOE) complexes. The frequency bands were lowered from those in free ligands which was observed at 1599 cm^{-1} this included involvement of the (C=N) coordinated group in the complex and the increasing of the (C=N) bond character upon complexation as a result of removal of the proton in the free ligand. This suggestion is supported with the study of a green Ni(II) complex with 4,5-diphenyl- 1,2,4-triazole-3-thione and with the infrared of 1,3,N,N-bis (Salcydine) propylene diamine (salt MH2) with Sb as Ph_2SbBr (saltm), which exhibited a strong band at 1620 cm^{-1} . This band was shifted a 25 cm^{-1} from a spectrum of a free ligand, including sensitiveness of $\nu(\text{C=N})$ band chleation (Abdullah, 2003; Catpathy *et al.*, 1983). The explanation also agreed with those observed in the study of Musa *et al.*, on Cu(II) complexes with [2, 2-1, 3, 4- oxadiazole]-1, 4-butane, which exhibited a medium intensity band at 1580 cm^{-1} which deviated from free ligand spectrum. The band due to coordinated $\nu(\text{C=N})$ in the metal complexes (Mehdi, 1999).

The appearance of $\nu(\text{M-S})$ and (M-N) at a 420 cm^{-1} and 470 cm^{-1} respectively supported disappearance of $\nu(\text{S-H})$ and $\nu(\text{N-H})$ the complexation (Demirbas, 2008; Hamad and Hashem, 2000). The $\nu(\text{C-S})$ band of free ligand was displayed at 677 cm^{-1} this band was shifted upon complexation Table (5) and Fig. (4).

The electronic transition study of (BTESOE) complexes:

The UV/Vis Spectra of green Cu complex using nugol mull paper technique showed a band at $17,182\text{ cm}^{-1}$ were assigned to ${}^2B_{1g} \xrightarrow{\nu_2} {}^2E_g$, a transition which in assign to distorted octahedral geometry (Jassim, 1993). The green Ni (II) complexes exhibited two bands 17, 241 (ν_2), 22, 727 (ν_3) cm^{-1} which assigned to ${}^3A_{2g} \xrightarrow{\nu_2} {}^3T_{1g(F)}$ and ${}^3A_{2g} \xrightarrow{\nu_3} {}^3T_{1g(P)}$ in Oh configuration.

The ν_1 value was measured to be equal to $(10,060)\text{ cm}^{-1}$. The results concluded to be octahedral (Sutton, 1968). The dark brown Co complexes exhibited two bands at

(17.673 and 27.760) which due to ${}^4T_{1g} \xrightarrow{\nu_2} {}^4T_{1g(p)}$ and ${}^4T_{1g} \xrightarrow{\nu_3} {}^4A_{2g}$ transitions (Bimanesh *et al.*, 1985).

The Hg (II) colorless complex showed a real shifting from the spectra of a free ligand at 29.328 cm^{-1} might be explained to effect of complexation (Bimanesh *et al.*, 1985). The molar conductivity measurement expressed no ionic complexes Table (5) were estimated and fit octahedral from of another similar complexes (Radhakrishan and Joseph, 1976).

The Molar conductivities, Magnetic susceptibility and atomic absorption analysis for (BTESOE) complexes with M (II): (Cu, Ni, Co and Hg).

The molar conductivity measurements of the complex in 10^{-3} M concentration in DMSO at laboratory temperature were expressed of nonionic complexes Table (6).

The magnetic susceptibilities measurements were carried out at 25 C° Table(5). The results expressed of an octahedral from each complex as in $[\text{Ni}(\text{bmp})\text{Br}_2]$; $[\text{bmp} = \{1,3\text{-bis}(\text{o-methylthiophenylthiopropene})\}]$ which has a magnetic moment ($M_{\text{eff}} = (2.9\text{-}3.0) \text{ B.M}$ (William *et al.*, 1975) and $[\text{Co}(3,5\text{-diphiso})_2(\text{NCS})_2] \cdot 2\text{H}_2\text{O}$ has a magnetic moment ($M_{\text{eff}} = 4.6 \text{ B.M}$) (Deveto *et al.*, 1977) $\text{Cu}(\text{SAAP})\text{Cl}[\text{SAAP-Salicyli-4-aminoantipyridine}]$ contains one unpaired electron with ($M_{\text{eff}} = 1.97 \text{ B.M}$) (Radhakrishan and Joseph, 1976), and a white complex of $[\text{Hg}(\text{HL})_2 \cdot 2\text{H}_2\text{O}]$ is a diamagnetic complex (where HL = (2-hydroxyimino-3(2-imino-pyridyl-butane (Bimanesh *et al.*, 1985).

The nephelauxetic parameter:

The ratio of β (Racah parameter) for complex and that for free ion is given the symbol β is called the nephelauxetic parameter:

$$\beta = \frac{\bar{B}(\text{Complex})}{B(\text{Complex})} \quad \text{Where } \bar{B} : \text{Electronic repulsion value for the complex}$$

B: Electronic repulsion value for free ion

A small β value implies that there have been some delocalizations of the electron from the metal into the ligand. Generally the smaller nephelauxetic parameter is the more covalent character of the bonding between the metal and ligand which is to be expected for softer ligand (Bridson, 2003).

The β value of each complex where been determined as the following example:-

To determine β for $[\text{Ni}(\text{BTESOE})\text{CH}_2(\text{H}_2\text{O})_6]$ using the equation

$$15\bar{B} = \nu_3 + \nu_2 - 3\nu_1$$

$$15\bar{B} = 22727 + 17670 - 3(10063)$$

$$\therefore \bar{B} = 608.533$$

$$\therefore \beta = \frac{\bar{B}}{B} = \frac{608.533}{1030} = 0.66$$

Where B value = 1030 (Bridson, 2003).

The atomic absorption analysis were used to determine a ration of M:L for the complexes Table(6), using curve fitting least square equation. For example the weight of

Table 4: The (BTESOE) (47) mass spectral data

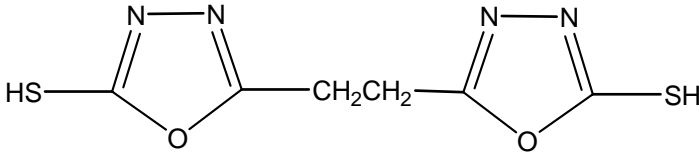
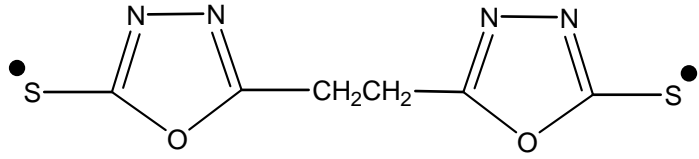
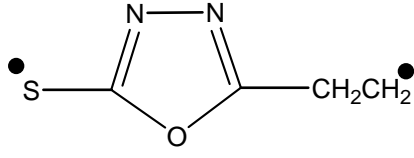
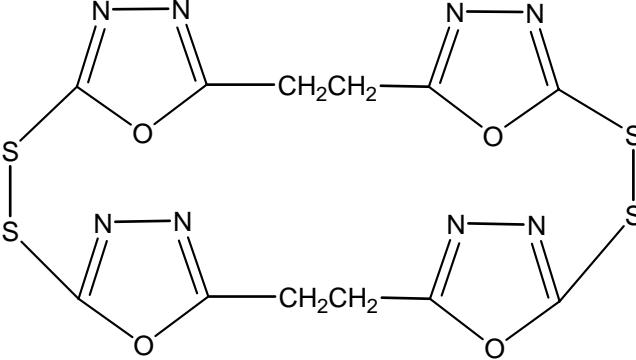
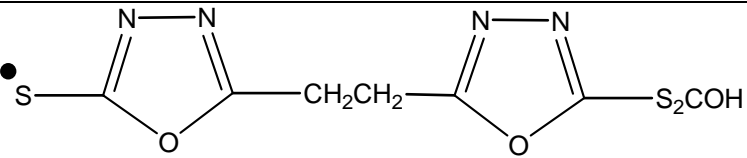
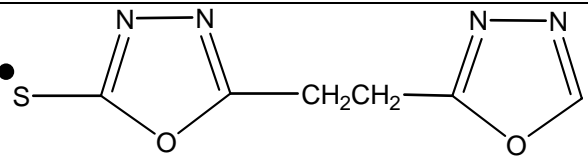
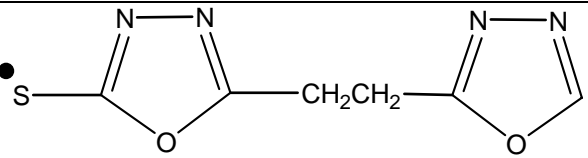
S.N	Fragment ion	M/Z	Relative Abundance (%)
1		230	17.17
2		228	14.77
3		128	67.04
4		456	44.34
5		289	63.33
6		260	100.0
7		196	8.88

Table 5: The electronic spectra, magnetic susceptibility and molar conductivity of the (BTESOE) complexes

Synthesized compounds	Absorption band cm^{-1} (nm)	Transition Assignment	$\epsilon \times 10^3$ $\text{l.mol}^{-1} \cdot \text{cm}^{-1}$	Magnetic susceptibility (B.M)	Molar conductivity $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$
$[\text{Cu}_2(\text{BTESOE})\text{Cl}_2 \cdot (\text{OH}_2)_6]$	17.663(565)	${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$	1.22	-	2.05
$[\text{Ni}_2(\text{BTESOE})\text{Cl}_2 \cdot (\text{OH}_2)_6]$	10.0634(ν_1)	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$	1.110	3.36	2.04
	17.6704(ν_2)	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1gF}$	1.52		
	22.7273(ν_3)(440)	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g(P)}$	--		
$[\text{Co}_2(\text{BTESOE})\text{Cl}_2 \cdot (\text{OH}_2)_6]$	10.000(ν_1)	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$	0.686	4.71	2.05
	17.6704(ν_2)(565)	${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$	0.858		
	21.413(ν_3)(467)	${}^4\text{T}_{1g(P)} \rightarrow {}^3\text{T}_{1g}$	--		
$[\text{Hg}_2(\text{BTESOE})\text{Cl}_2 \cdot (\text{OH}_2)_6]$	29.32551(341)	$\pi \rightarrow \pi^*$	0.950	-	2.08
BTESOE(IV)	27777	$\pi \rightarrow \pi^*$	0.966	-	2.04

Table 6: The atomic absorption data for (BTESOE) complexes

Standard curve Cu(II) ion		Standard curve Ni(II) ion		Standard curve Co(II) ion	
Conc.(ppm)	Abs.	Conc.(ppm)	Abs.	Conc.(ppm)	Abs.
2	41	5	10	5	9
4	97	10	22	10	18
6	160	15	34	15	28
8	122	20	43	20	37
** $[\text{Cu}_2(\text{BTESOE})_2(\text{H}_2\text{O})_6]$	163	** $[\text{Ni}_2(\text{BTESOE})_2\text{Cl}_2(\text{H}_2\text{O})_6]$	166	** $[\text{Co}_2(\text{BTESOE})\text{Cl}_2(\text{H}_2\text{O})_6]$	123

a=2.15

b= 30.3

r= 0.999

**Conc. =66.18ppm

a= -0.5

b= 2.22

r= 0.998

**Conc. =66.18ppm

a= -0.5

b= 1.88

r= 0.9997

**Conc. =66.18ppm

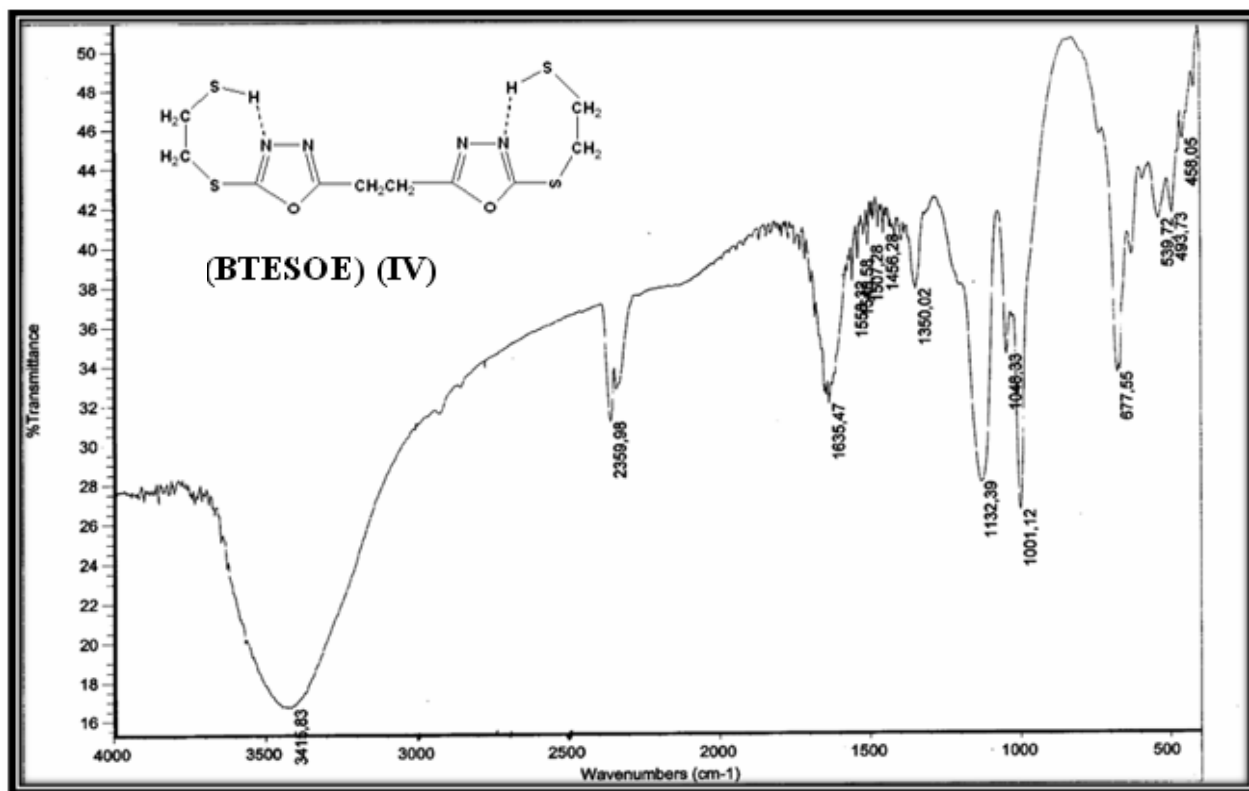


Fig. (1): Infrared spectrum of (BTESOE) (IV)

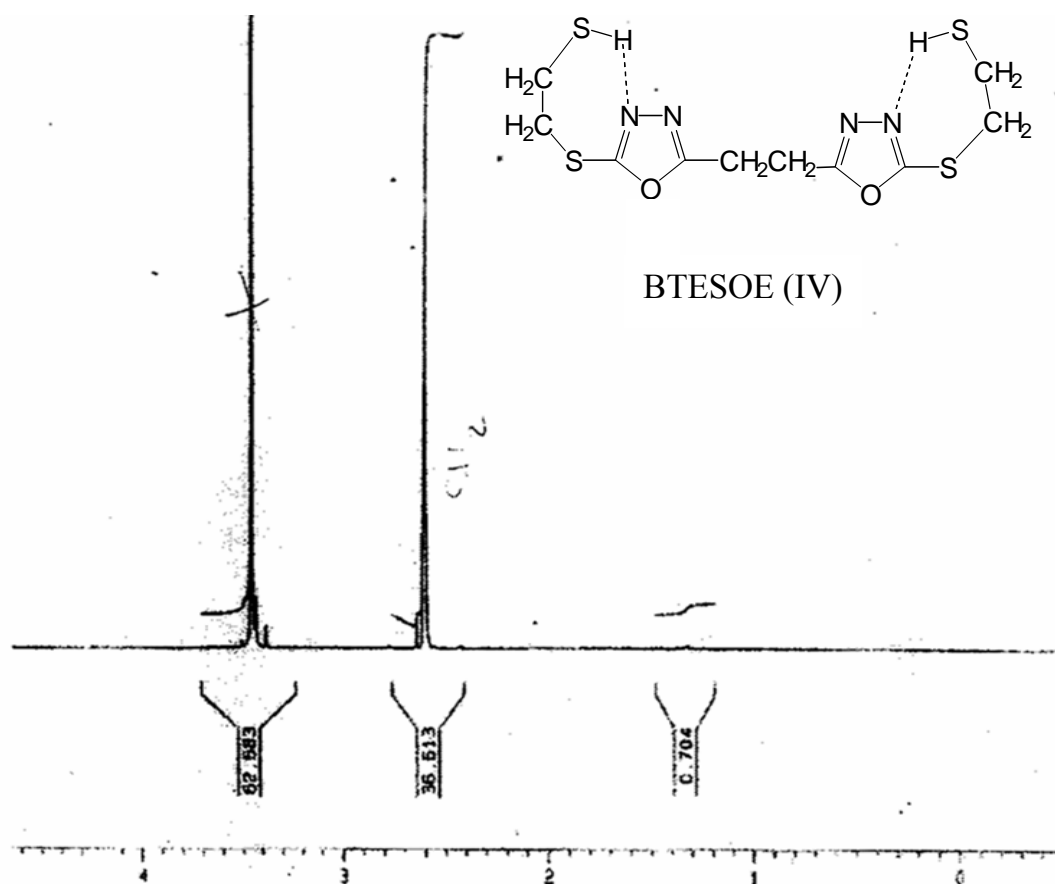


Fig. 2: The ^1H -NMR of (BTESOE) (IV)

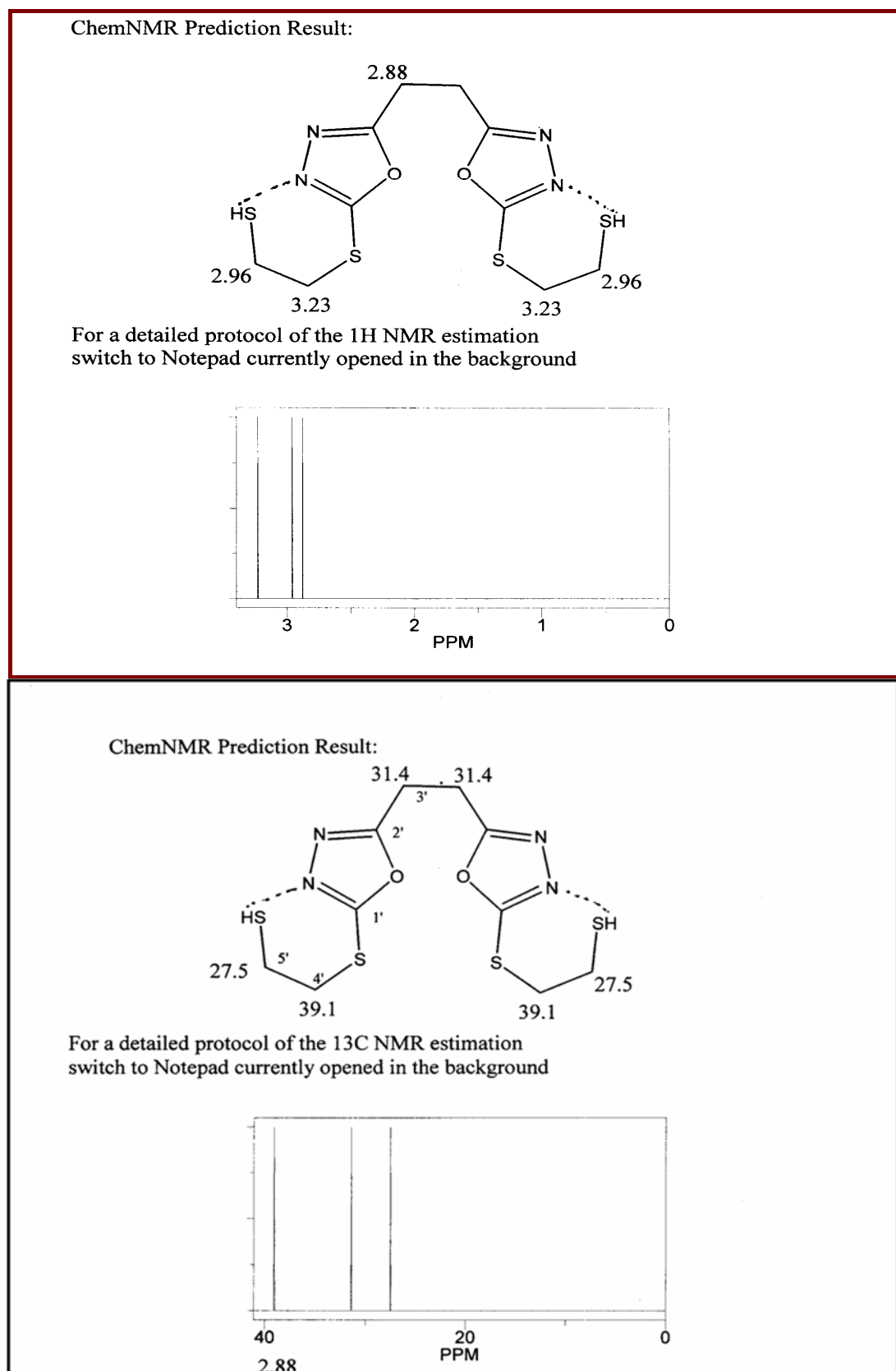
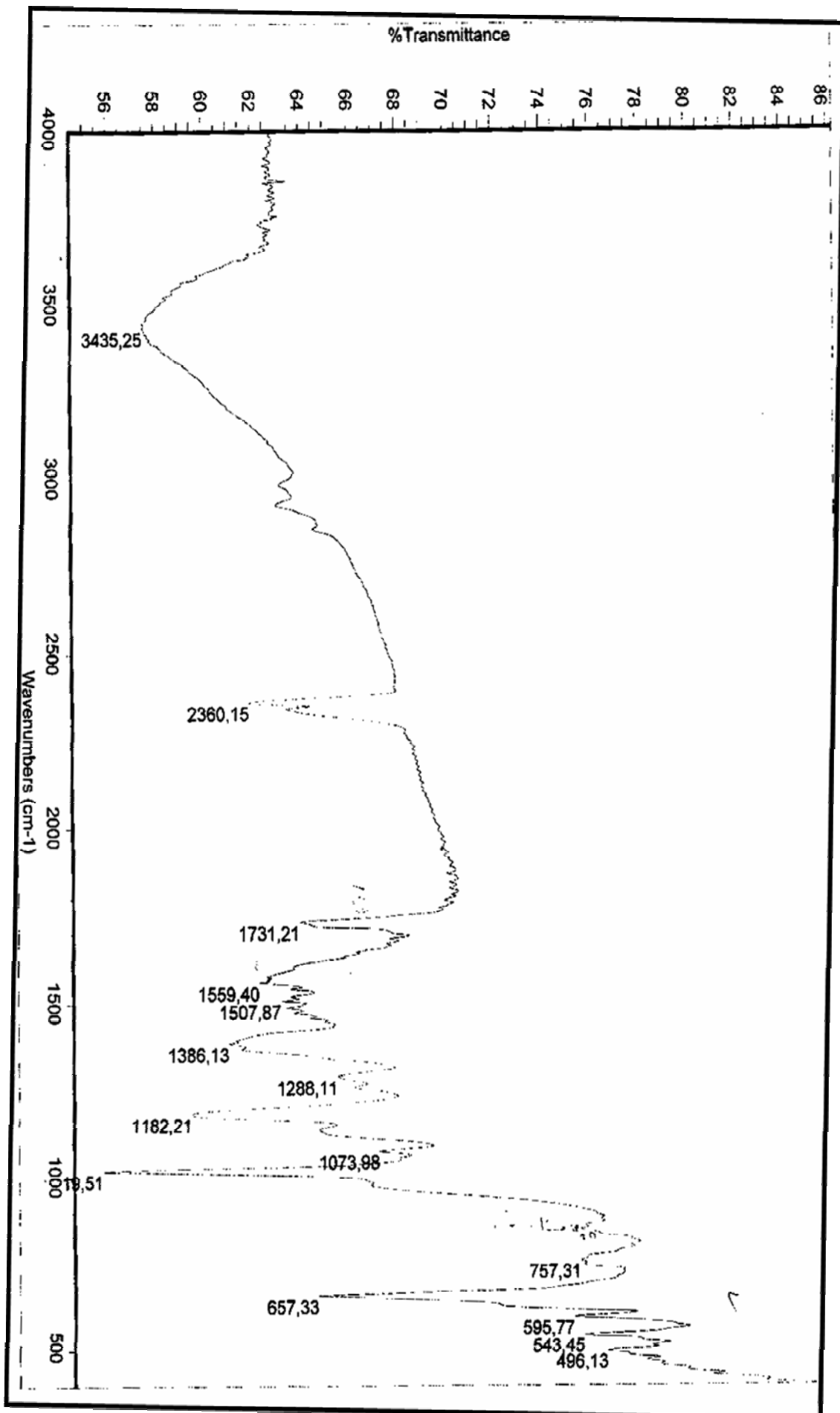


Fig. 3: The ^1H -NMR and ^{13}C -NMR of (BTESOE) (IV) obtained by Chem Office program

Fig. 4: The infrared spectrum of $[\text{Cu}_2(\text{BTESOE})_2\text{Cl}_2(\text{OH}_2)_6]$ complex



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