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Preparation and Characterization of complexes VO(IV) and Cu(II) with the new ligand (1,2-diphenylethane-1,2-diylidene-bis(hydrazine-2,1-iylidene))bis (methan-1-yl-1-ylidene)diphenol (DEDHIMD) and study biological activaty

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Abstract

The new ligand of (**1,2-diphenylethane-1,2-diylidene-bis(hydrazine-2,1-iylidene))bis (methan-1-yl-1-ylidene)diphenol (DEDHIMD)**، has been prepared by reacting Salicyladehyde with Benzil dihydrazone (prepared from benzil with hydrazine in ethanol) in ethanol. This Ligand has been Identified by Using ^{1}HNMR، UV-Vis.& FTIR Spectra. We have also prepared chelate complex by reacting this ligand with metal ions VO(IV) and Cu(II).The preparation has been conducted after fixing the optimum conditions of concentration. U.V-Vis. spectra of the complexes solution of the above metal ions with the ligand (**DEDHIMD**) have been studied for a range of concentrations which obey Lampert-Beers Law. The structure of complex are deduced according to mole ratio method which was obtained from the spectroscopic studies of the complex solution. The ratio of metal: ligand obtained is (1:1) to the complexes ions. The (UV -Vis) absorption spectrum of complex in ethanol solution showed chromic shift، as compared with that of free ligand. The infrared spectra of the chelating complex have been studied، they were also compared with the ligand spectrum، they showed obvious changes in the band positions، some of them has been disappeared while others are shifted، this may indicate that a coordination between the metal ions and our ligand takes place. The conductivity measurements of our complexes have not shown that ionic character. Depending on these results، in addition to the measurements of magnetic susceptibility of our complexes it seems of these complexes are paramagnetic. We can conclude that the proposed geometrical structures of the complexes of VO(IV) and Cu(II) ions are octahedral. The determination of the biological activity of complexes were carried out on ***Pseudomonas averuginose, Serratia fonticola and Staphylococcus aureus*** bacteria.

Introduction

In acid hydrazides ,the presence of two nitrogen atoms addition to the carbonyl group makes it possible for such compounds to act as ligands[1,2,3]. The coordination chemistry of acid hydrazides and their Schiff bases with aldehydes and ketones are special interest in a variety of a ways in which theses species could be bonded with the metal ions. This reaction in neutral and basic media gives different types of metal complexes[4,5,6]. Also, they can coordinate with more than one donor atom , act as multidentate ligands and formation of oxygen bridged bi-and tri nuclear complexes have been reported. In addition to their ability to act as complexing agents, these ligands play an important role in biological systems and they have proved to be antitumour and numerous activities[7,8].

The present work describes the preparation and characterization of homo binuclear complexes of VO(IV), Fe(III), Co(III), Ni(II) and Cu(II) formed with benzilidenedi (benzoylhydrazine) in neutral and basic media[9,10].

ISSN: 2073-8854
Magazin of Al-Kufa University for Biology / VOL.5 / NO.2 / year : 2013

Experimental

Apparatus and materials

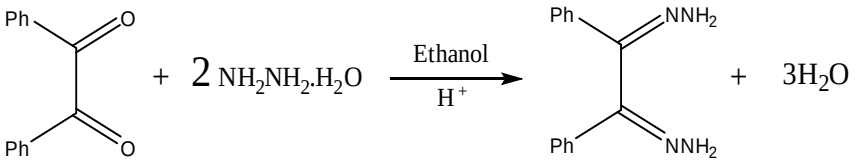
All the reagents and solvents were of reagent-grade quality and purchased from commercial suppliers .The Melting points were determined on a Electro thermal melting point, (GOWLLANDS, England).[1]HMNR spectrum (JEOL, U.M.) solvent (DMSO) (400 MHz), IR spectra were recorded using KBr discs 4000-400 cm^{-1} on FTIR Test scan (Shimadzu model 8400S).while the UV-Vis. Spectra were recorded in ethanol on (Shimadzu model 1800) . Molar conductance measurements were determined in ethanol by using a Alpha Digital conductivity meter (model 800) .

Preparation of Ligand :-

The ligand Prepared by two steep:-

1- Benzil di hydrazone:-

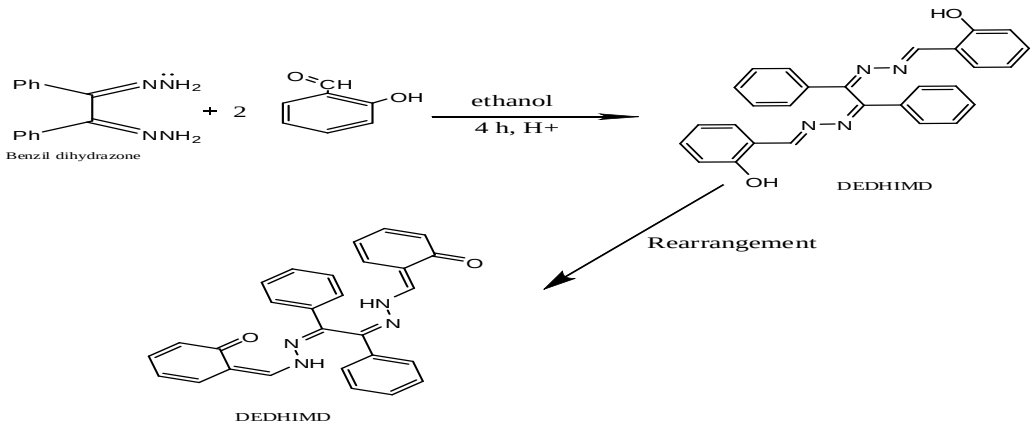
(0.21 g, 0.001 mole) of benzil was dissolved in 15ml of ethanol absolute[(11)] and added (0.1 ml, 0.002mol) from hydrazine and two drops from acetic aced. The mixture is boiled under refluxed for 2.5 hours in (70-75 C^0), using Rotary evaporator to separation ligand from solvent, the presenting 80% of yield, using TLC to determent end reaction by mobile solvent ((1:1) of Ethyl acetate and Toluene) Scheme(1).



Scheme(1) prepation of Benzil di hydrazone from Benzil and hydrazine

2- (DEDHIMD) :-

(0.238 g, 0.001 mole) of Benzil di hydrazone was dissolved in 20ml of absolute ethanol [(12,13)] and added (0.244 ml, 0.002mol) from Salicyladehyde and two drops from acetic aced. The mixture is boiled under refluxed for 4 hours in (70-75 C^0), using Rotary evaporator to separation ligand from solvent, the presenting 70% of yield and using TLC to determent end reaction by mobile solvent ((1:1) of Ethyl acetate and Toluene), The ligand rearrangement [(14)] showed in Scheme(2).



Scheme(2) preparation of (DEDHIMD)

ISSN: 2073-8854
Magazin of Al-Kufa University for Biology / VOL.5 / NO.2 / year : 2013

Preparation of the solid complexes

Take (0.001mol in 10 ml ethanol) from of ligand solution (0.001 mole) of $VOSO_4$ and $CuSO_4.4H_2O$ dissolved in (15 ml) water was added drop wise with stirring. The pH of the reaction mixture was adjusted to ≈ (8.5). A solid complex was obtained, collected by filtration ,washed by ethanol and water several times and dried .

Characterization of ligand and its complexes

The complexes were insoluble in water but soluble in ethanol, DMF and DMSO solvents. The ligand was (yellow) crystals, but the complexes of this ligand from deep yellow to (yellow- brown) color. Table (1) appears some physical properties of the prepared complexes.

Table (1) Physical properties of the ligand and it's complexes

Comp.	Formula	Color	Yield(%)	M.P(ºC)
DEDHIMD	C26H22N4O4	yellow	70	150
VO(IV)-DEDHIMD	[VO L (H2O)]	yellow- brown	85	240 dec.>
Cu(II)- DEDHIMD	[Cu L (H2O)2]	yellow	83	>250 dec.

Molar Conductivity and molar ratio of the complexes

we study molar conductivity of the complexes (10^{-3}M) in ethanol and moler ratio method to determine percentage metal to ligand.

Study of biological activity

The determination of the biological activity of ligand and complexes were studied on *Pseudomonas averuginose, Serratia fonticola and Staphylococcus aureus* bacteria. Using Toda's Method in agar from Molar Hilton, in the concentration (10^{-4} M) from ligand ,metal and complexes (5×10^{-4})M from complexes only .

Results and discussion

^{1}H NMR spectra

The ^{1}HNMR spectrum of the ligand (DEDHIMD) in (DMSO) displayed the presence of the broad singlet signal due to the hydrogen,(2 , 2.85 ppm, to solvent (DMSO))[15] ,(6.35 ppm, d, H-N)[16],(6.85-7.370 ppm, d, H-Ar)[7,17],(8.49ppm, d, H-C aldehyde)[18] as shown in Fig(1).

ISSN: 2073-8854
Magazin of Al-Kufa University for Biology / VOL.5 / NO.2 / year : 2013

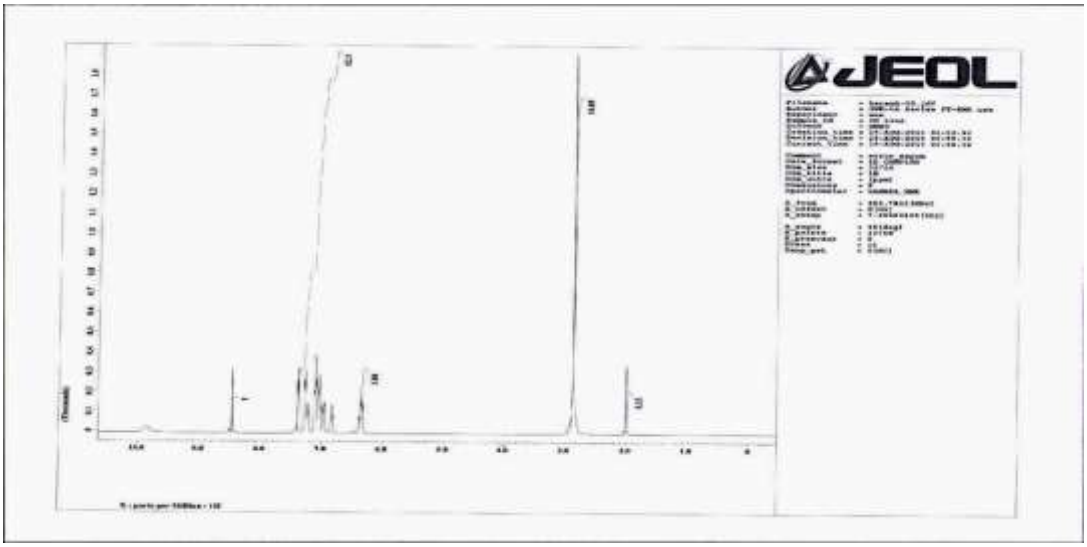


Fig (1) : HNMR spectrum to the ligand(DEDHIMD)

Electronic spectra

The electronic spectral data of the ligand and its complexes were recorded in ethanol and their assignments are listed in(table 2). The UV-Visible spectrum of the ligand as show in Fig.(2) appear the absorption peak at (412 nm) and (306 nm) assigned to (n→π*) and (π→π*) transitions respectively [28,29]. While the electronic spectra of the complexes show in Figs.(3,4) to exhibited that The electronic transitions red shift to (420nm) and (325nm) for VO(IV) complex and (447nm) and (333nm) for Cu(II) complex because the coordination to these groups in table (2).

Table (2) Electronic spectra of the ligand and it's complexes

Compound	λ nm	Assignment	eff.μ
DEDHIMD	412 305	n→π* π→π*	----------
VO(IV)-DEDHIMD	420, 325 558, 515, 800	Ligand field d-d transition	B.M2.1
Cu(II)- DEDHIMD	447, 333 594, 499	Ligand field d-d transition	B.M1.8

ISSN: 2073-8854
Magazin of Al-Kufa University for Biology / VOL.5 / NO.2 / year : 2013

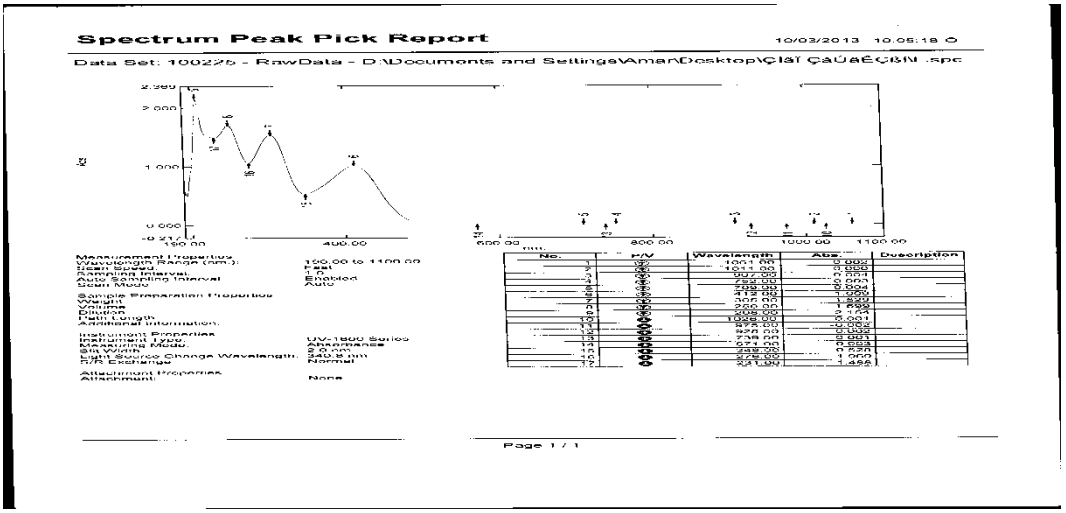


Fig.(2) UV-Vis. spectrum DEDHIMD

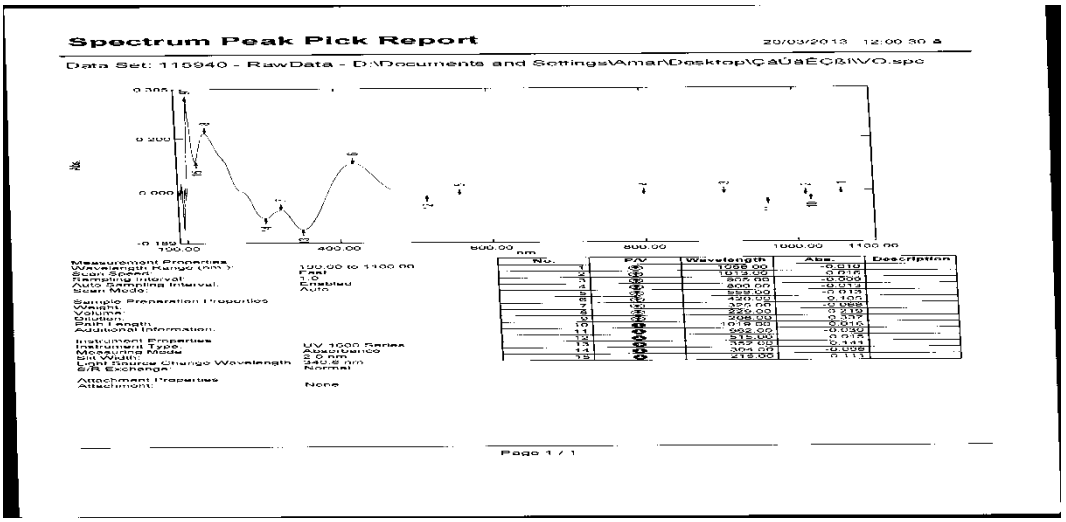


Fig.(3) UV-Vis. spectrum VO(IV)- DEDHIMD

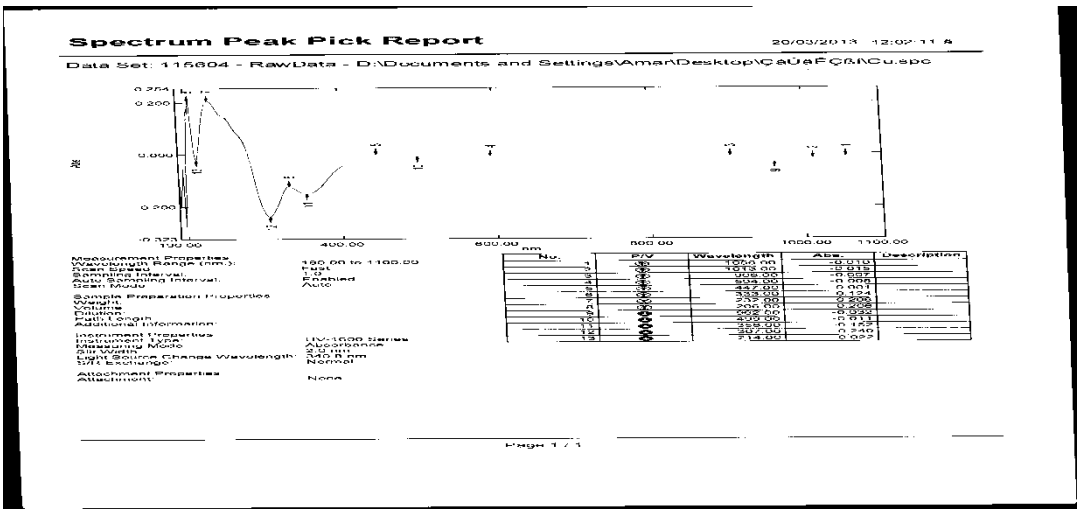


Fig.(4) UV-Vis. spectrum Cu(II)- DEDHIMD

ISSN: 2073-8854
Magazin of Al-Kufa University for Biology / VOL.5 / NO.2 / year : 2013

Molar Conductivity and molar ratio of the complexes

The molar conductance of the complexes[20] are shown in Table (3) were carried out in ethanol at room temperature , the values indicate that the complexes are non-electrolytes nature ,where the values suggest that no anions present outside the coordination spheres**,** and the Composition of the complexes were determined by molar ratio method[21] at fixed concentration for pH =8.5 at maximum wavelengths of absorption. method indicated that the ratio of metal ion to ligand molecules was (1:1). The results also shown in Table (3).

Table (3) Metal : Ligand ratios and Molar Conductivity of the complexes.

Comp.	pH	λ max (nm)	Metal :Ligand	Conductivity S.mol^{-1}.cm^2
VO(IV)-DEDHIMD	8.5	420	1:1	3.4
Cu(II)- DEDHIMD	8.5	447	1:1	3.3

IR spectra

The wave numbers of some characteristic bands in the IR spectra of ligand, The ν(N-H) stretching vibration appears at (3085 cm^{-1}) and other vibration at(1571 cm^{-1} ,1155cm^{-1})[22,23], The ν(C=O) stretching vibration appears at (1676 cm^{-1})[8] and (C=N) vibration(1622cm^{-1}) [24] and (C=C) vibration at (1600cm^{-1}) band usually overlaps with the bands of the aromatic rings in the free ligand spectra Fig(7).

The infrared band assignments of the ligand complexes of VO(IV) and Cu(II) ions shown in (Table 4). This band to vanish and splitting in the spectra of complexes , The broad band at (3417, 3275cm^{-1}) in of the ligand complexes of VO(IV) and Cu(II) ions which assigned to υ(-OH water coordination (stretching)) and other vibration to water coordination at (1087, 1116 cm^{-1})[25,26] Fig.(8,9). about involvement of (N-H) group in coordination with metal ions via nitrogen group vanish (1571 cm^{-1} ,1155cm^{-1}) and (C=O) via shifting about (10-23 cm^{-1}) and splitting . New bands in the region (11120 cm^{-1}) to (V=O)[27] Fig.(8), These were assigned in the spectra of metal complexes. These bands were not present in the spectrum of ligand, and they due to ν(M─N)and υ(M-O) vibrations respectively . via nitrogen and oxygen atoms in complexation table (4).

Table(4): FTIR to ligand and complexes

Comp.	(N-H)	C-H arom.	.C=O	(C=N)	(C=C)	(V=O)	(O-H) at water
Benzil di hydrazine	**3450,3384,3211**	**3053**	**------**	**1622**	**1596**	**-----**	**-----**
DEDHIMD	**3085,1571,1155**	**3064**	**1676**	**1622**	**1600**	**-----**	**------**
VO(IV)-DEDHIMD	**vanish**	**3062**	**1663**	**1622**	**1600**	**1112**	**3417,1087**
Cu(II)-DEDHIMD	**vanish**	**3061**	**1665,1653**	**1622**	**1600**	**------**	**3275,1116**

ISSN: 2073-8854
Magazin of Al-Kufa University for Biology / VOL.5 / NO.2 / year : 2013

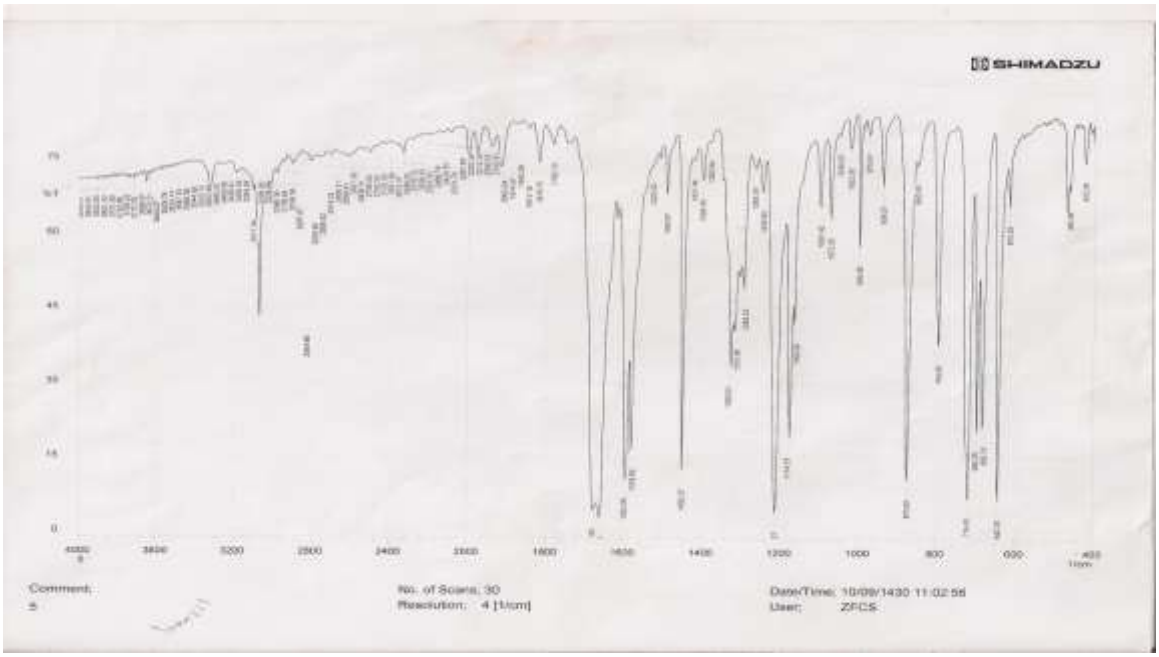


Fig.(5) FTIR spectrum benzil

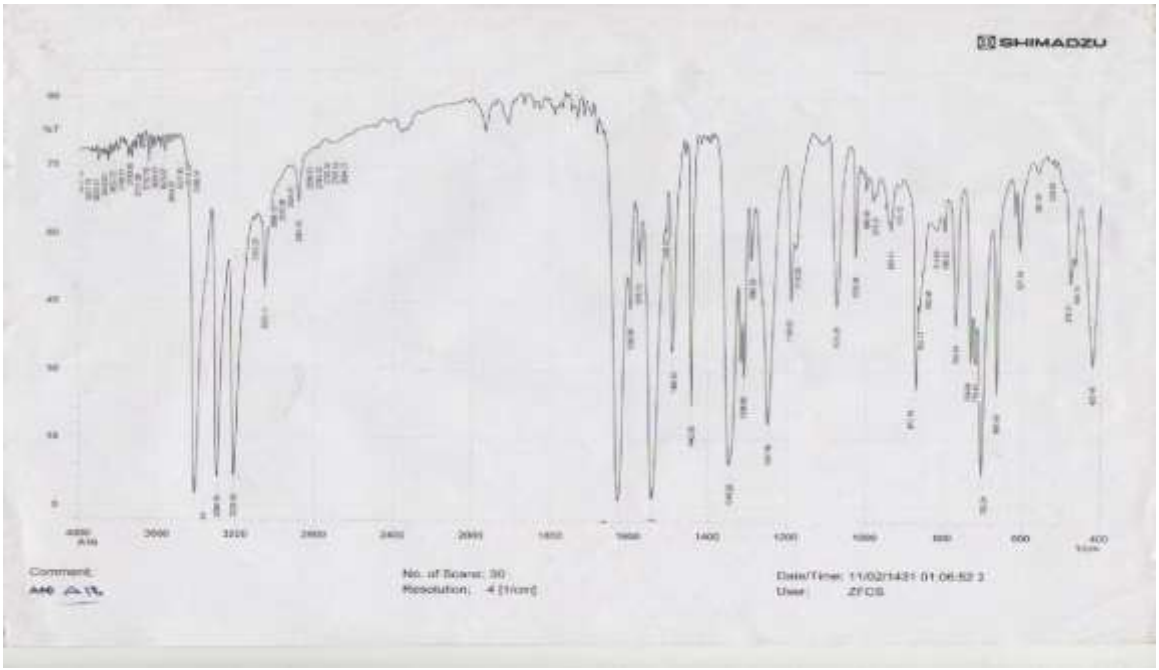


Fig.(6) FTIR spectrum Benzil di hydrazone

ISSN: 2073-8854
Magazin of Al-Kufa University for Biology / VOL.5 / NO.2 / year : 2013

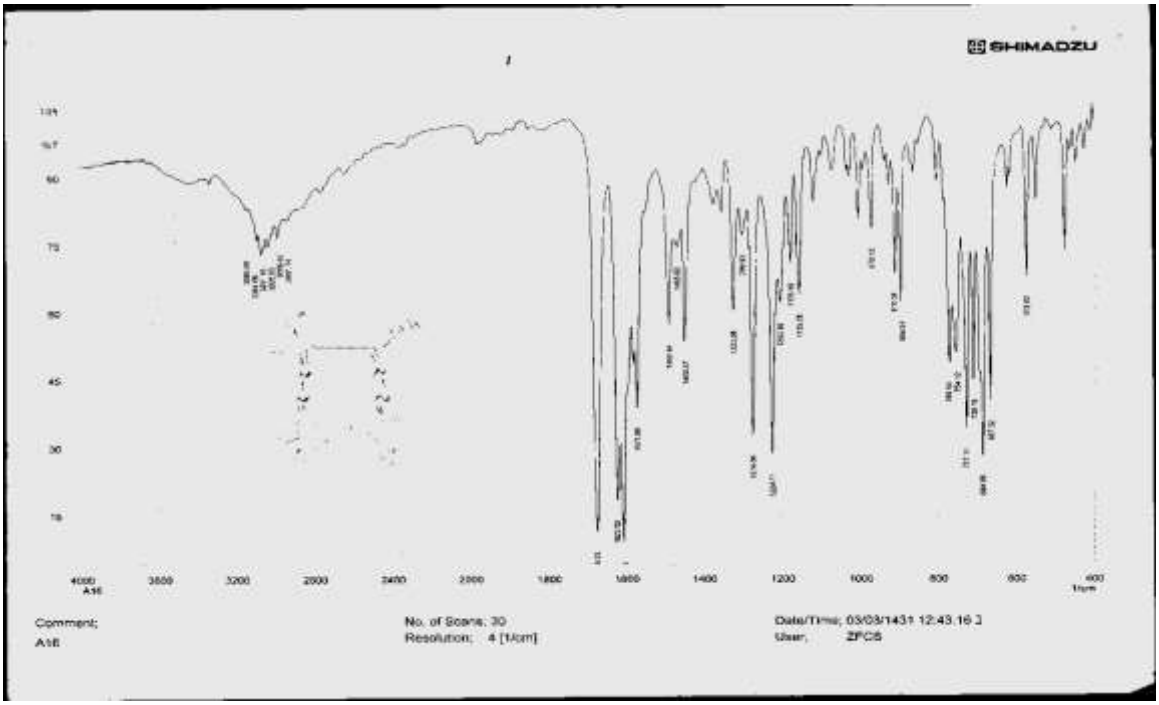


Fig.(7) FTIR spectrum DEDHIMD

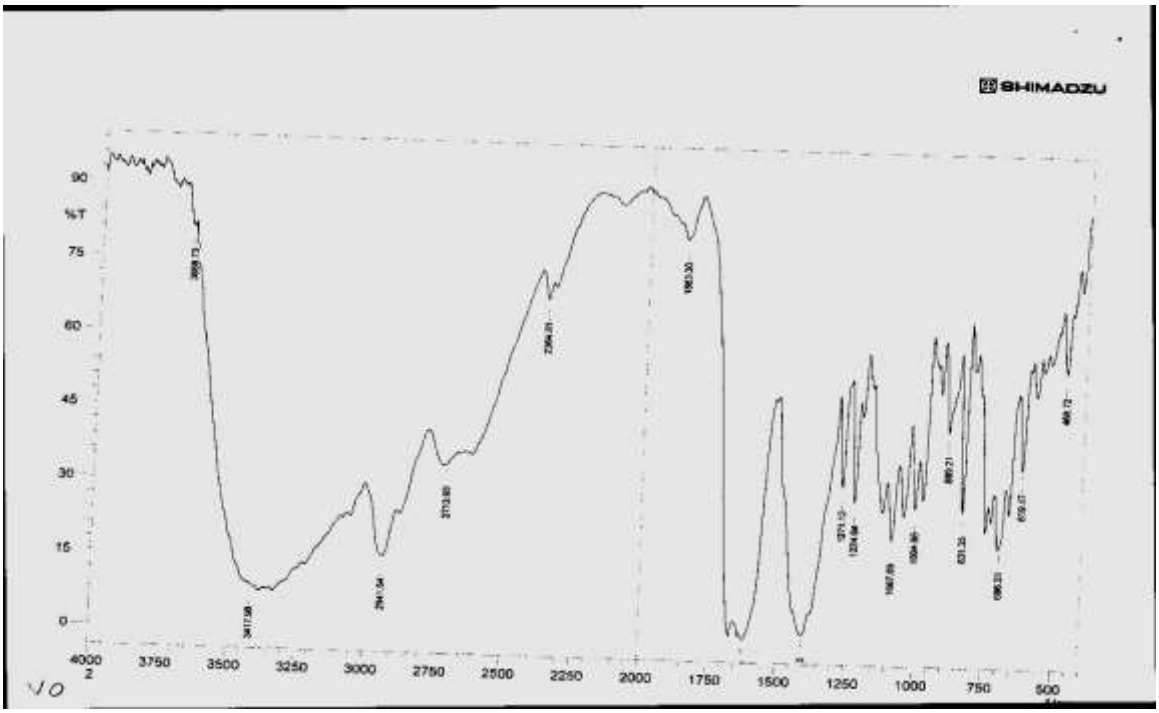


Fig.(8) FTIR spectrum VO(IV)- DEDHIMD

ISSN: 2073-8854
Magazin of Al-Kufa University for Biology / VOL.5 / NO.2 / year : 2013

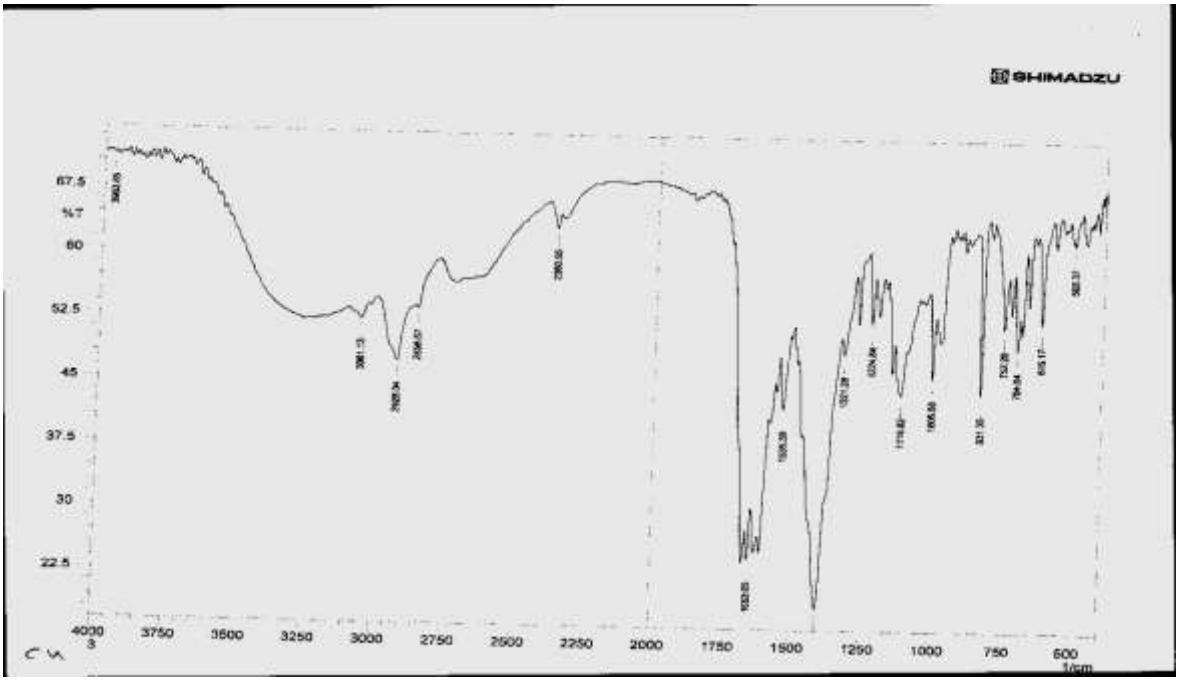


Fig.(9) FTIR spectrum Cu(II)- DEDHIMD

Study of biological activity:-

The results gave an indication for inhibition of bacteria under investigation during the testing the prepared ligand and complexes. In case of increasing the concentration the ligand and complexes [30,31] as shown in table(5) and Fig.(10-15). From the results we can using in industry.

Table (5) : Inhibition Zone of ligand and complexes using Toda's Method

Pseudomonas averuginose			
Ligand ***(A)***	*Complex* Cu^{+2}	*(*MSO_4*) (C)*	*Complex* VO^{+2}
1/2 cm (10^{-4} M)	1/4 cm (10^{-4}M) ***(B)***	Zero (Cu^{+2} 10^{-4} M)	1/3 cm (10^{-4}M) ***(B)***
		Zero (VO^{+2} 10^{-4} M)	
	1/2 cm(5×10^{-4}M) ***(D)***		1/2 cm(5×10^{-4}M) ***(D)***
Serratia fonticola			
1/2 cm (10^{-4} M)	Zero (10^{-4}M) ***(B)***	Zero (Cu^{+2} 10^{-4} M)	1/2 cm (10^{-4}M) ***(B)***
		Zero (VO^{+2} 10^{-4} M)	
	1 cm (5×10^{-4}M) ***(D)***		1 cm(5×10^{-4}M) ***(D)***
Staphylococcus aureus			
1/4 cm (10^{-4} M)	1/4 cm (10^{-4}M) ***(B)***	Zero (Cu^{+2} 10^{-4} M)	Zero (10^{-4}M) ***(B)***
		1/4 cm (VO^{+2} 10^{-4} M)	
	1/2 cm(5×10^{-4}M) ***(D)***		1/2 cm(5×10^{-4}M) ***(D)***

ISSN: 2073-8854
Magazin of Al-Kufa University for Biology / VOL.5 / NO.2 / year : 2013

Fig.(10): ***Pseudomonas averuginose***

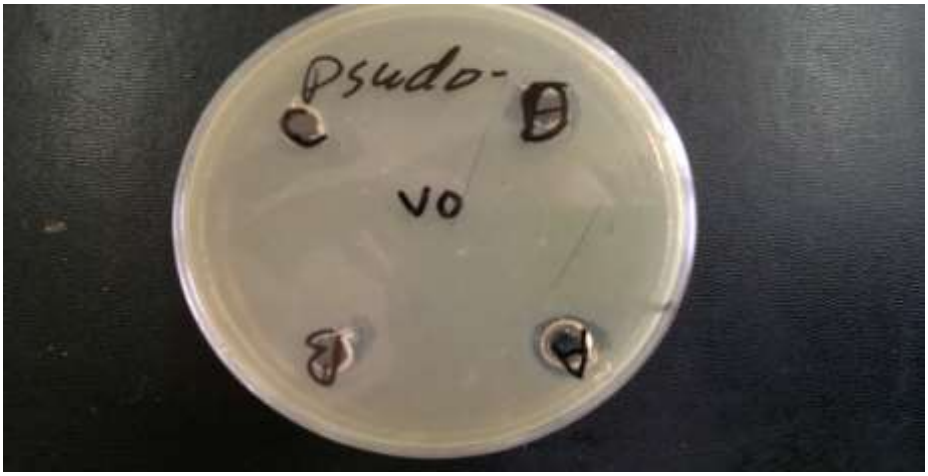


Fig.(11): ***Pseudomonas averuginose***

Fig.(12): ***Serratia fonticola***

ISSN: 2073-8854
Magazin of Al-Kufa University for Biology / VOL.5 / NO.2 / year : 2013

Fig.(13): ***Serratia fonticola***

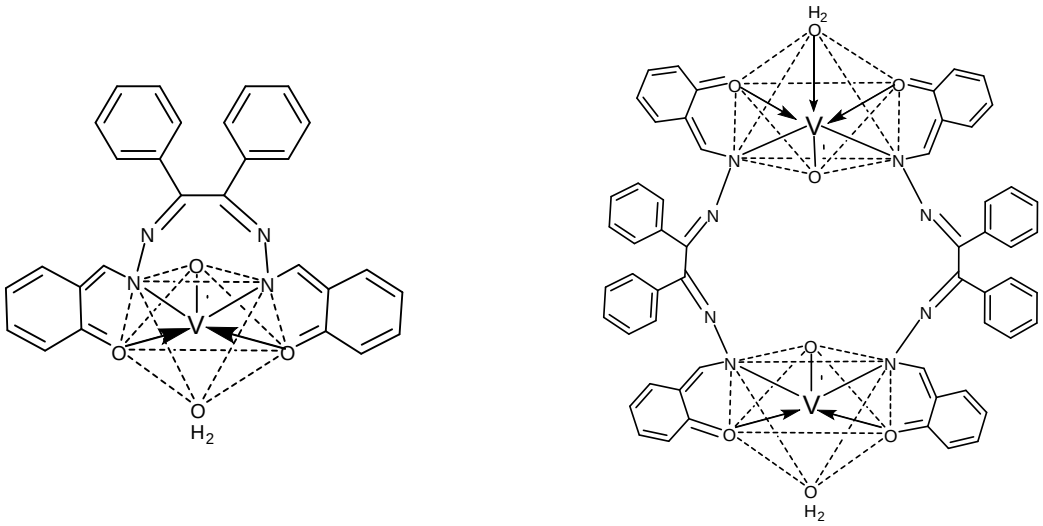
Fig.(14): ***Staphylococcus aureus***

Fig.(15): ***Staphylococcus aureus***

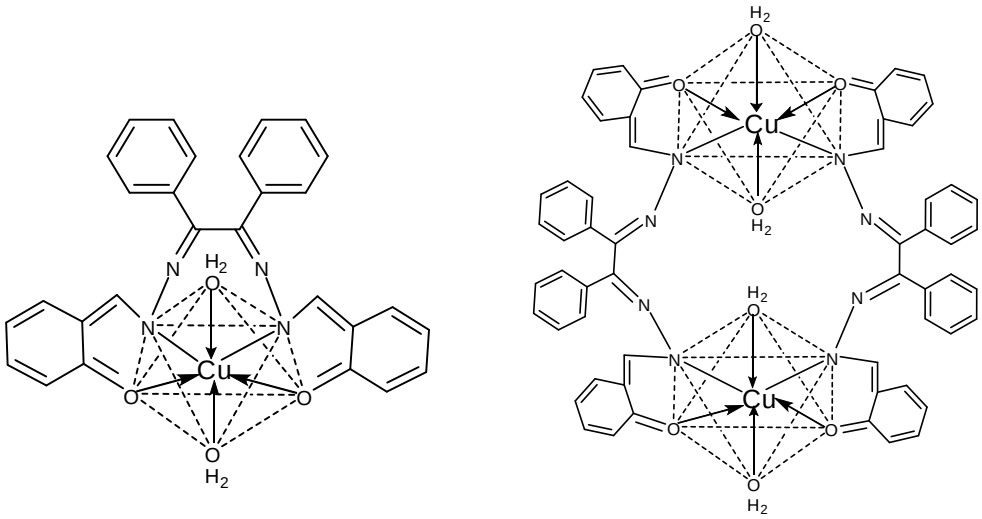
Suggested chemical Structure formula for the complexes

ISSN: 2073-8854
Magazin of Al-Kufa University for Biology / VOL.5 / NO.2 / year : 2013

According to these results (FTIR, U.V.-Vis., molar conductivity and mole ratio) the structural formula of prepared complexes may be proposed in Fig. (16)and Fig.(17)



Fig(16) Suggested VO(IV) complex



Fig(17) Suggested Cu(II) complex

Conclusion

1- prepared ligand coordinate with VO(IV) and Cu(II) from type (tetradentate).
2- Preparation the complexes were (1:1) (ligand :metal) from results (UV.-Vis, FTIR, molar conductivity and mole ratio).
3- Biological activity of bacteria (gram positive and gram negative) be no effect, From the results we can using in industry

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الخلاصة:-

الليكاند الجديد (1,2- ثنائي فنيل ايثان-1,2- دايلدين –ثنائي (هايدرازين 2,1-يلدين) ثنائي مثيل 1-يل-1- يلدين)ثنائي فينول(DEDHIMD) ،يمكن تحضيره من خلال تفاعل سلسلديهايد مع بنزل داي هايدرازون (حضر من بنزل مع الهايدرازين في الايثانول) في الايثانول، شخص الليكاند من خلال اطياف HNMR, FTIR وUV-Vis. وتم تحضير معقدين من خلال مفاعلة الليكاند مع VO(IV) وCu(II) بعد توفير الظروف المناسبة وضمن تراكيز خاضعة الى قانون بير –لامبيرت، وكانت النسبة المولية هي (1:1) (لكياند:ايون فلزي)، واستخدم الايثانول كمذيب لليكاند والمعقدات عند قياس طيف UV-Vis. وقد حصلت ازاحة للقمم. طيف FTIR للمعقدات الكليتية تم مقارنتها مع طيف الليكاند لمعرف حدوث التناسق بين الايون الفلزي والليكاند ، وتم قياس التوصيلية المولارية للمعقدات وكانت عديمة التوصيلية مما يعني انها متعادلة ، وكانت الخصائص المغناطيسية لها بارا مغناطيسية للمعقدين VO(IV) وCu(II) ، وتم اقتراح الشكل الهندسي بالاستناد لهذة النتائج وكان الشكل هو ثماني السطوح. كما تم تحديد الفعالية البايولوجية مع ثلاث انواع من البكتريا.