

**Synthesis and Theoretical Study of Cu (II) and V (IV)
with 2-(2,3-dimethyl phenyl) amino benzoic
acid ligands and 2-(2,5-dichloro phenyl)
amino phenyl acetic acid**

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Abstract

New complexes of the ligands 2-(2,3-dimethyl phenyl) amino benzoic acid and 2-(2,5-dichloro phenyl) amino phenyl acetic acid with copper(II) and vanadyl (IV) ions have been prepared. These complexes were characterized by infrared, U.V-visible spectral data, molar conductivity and thermogravimetric analysis. It was shown that the stoichiometry to be 1:2(metal to ligand), in which the ligands are acting as a bidentate ligands through the amino and carboxylate groups. The molecular modeling of all complexes was performed using MM+ molecular mechanics and ZINDO/1, ZINDO/s semi-empirical methods. The calculated IR, U.V-visible data of the complexes have been compared with recorded spectrum. The assignments of the most important vibrational modes are aided by the animation option of the HyperChem program. The method used to simulate the geometry, ZINDO/1, provide the best geometric copper Complex [I] and [III] described as distorted square planer, while oxovanadium complexes [II] and [IV] founded in the distorted square pyramidal. The proposed mechanism of the interaction between the ligands and the Cu (II), VO (IV) cations was investigated.

-2

(-2,5)-2 (2,3)

ZANDO/s, ZANDO/1

(hyper chem. Program)MM+

INTRODUCTION

During the last few years considerable interest has been focused on the use of transition metal ions complexes as drug (Sorenson, 1982; Cini et al., 1995) due to the successful of cis – platines as anti – cancer drug (Natil et al., 1999; Boulikas, 2003). The special important of copper(II) and VO(IV) complexes, because of copper(II) ion is biological essential transition metal required for a variety of metalloproteinase in different organisms (Planka et al, 1989; Antholine, 1988). Also vanadium has an important role in many biological processes. Particularly it has been proposed that delivery of vanadium in higher organisms is performed by transferring (Nevesa et al, 1998). Transferring is glycoprotein's whose primary function is to bind and transport iron (Turel et al, 2003).

The most famous method of obtaining information about the structures of many of these complexes is X-ray for the structural studies (Qian et al, 2004). Owing to the difficulties in obtaining single crystal form of some compounds, the minimized conformation of the compounds may be calculated using the semi-empirical methods and then supported experimentally (Bayaria et al, 1999).

In present work we performed initially molecular modeling of Cu (II) and VO (IV) complexes using both molecular mechanics and semi-empirical methods parameterized for first-row transition metals using HyperChem demo (Hyper, 2002). The geometric parameters obtained without any constrains by the MM+ molecular mechanics, semi-empirical ZINDO/1 methods, as well as the Model Builder tool. Following geometrical optimization, calculations of IR and U.V spectra of complexes have also been carried out.

The aim of the present work is prepare ,characterization and compare the calculated infrared ,U.V visible data with recorded IR and U.V visible spectra to the four new complexes of copper(II) , vanadyl (IV) with biological active ligand 2-(2,3-dimethyl phenyl) amino benzoic acid and 2-(2,5-dichloro phenyl) amino phenyl acetic acid.

EXPERIMENTAL

a) Physical Measurements:

The melting point of all synthesized complexes were measured with electro thermal Gallen Kamp melting apparatus. The I.R. spectra as KBr disks were recorded on a Pye – Unicam SP3 – 300 Spectrophotometer ($200 - 4000 \text{ cm}^{-2}$). The U.V. spectra were measured on a JASCO – UV – visible Spectrophotometer using 1.0 cm quartz cell. Conductivity measurement were carried out for 10^{-3}M in CH_3Cl_2 using HANNA conductivity meter ERC214R, using standard conductivity cell constant equal to 0.785 cm^{-1}

b) Preparation:

All materials used in this paper were obtained from Aldrich and Fluka chemical company.

2 – (3,3-Dimethyl phenyl)amino benzoic acid and 2- (2,5- dichloro phenyl) amino phenyl acetic acid ligands

2 – (3,3-dimethyl phenyl)amino benzoic acid and 2- (2,5- dichloro phenyl) amino phenyl acetic acid were prepared and purified using the procedures described in the literature (Vogal ,1977; Clarke , 1986). The two ligand were converted to their sodium salts by treatment with 1:1 equivalent of NaOH in ethanol to obtain corresponding sodium salts.

Bis [2 – (3,3-Dimethyl phenyl)amino benzoic acid] Copper(II), complexes [I]

Complex [I] was prepared by mixing a the solutions of [2 – (3,3-dimethyl phenyl)amino benzoic acid sodium salt(0.4825 gm , 0.002 mol) and $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ (0.16843 gm , 0.001mol) in 25ml water at room temperature . The past green crystalline product was obtained on standing

for a 3 hour .The precipitate was collected by filtration and washed t with cold ethanol. Table [1] showed the physical properties of the compound [I]. Bis [2 – (3,3-Dimethyl phenyl)amino benzoic acid] vanadyl(IV), Complex [II]

Complex [II] was prepared by reflux of solutions of (0.25305gm , 0.002mol) vanadyl sulfate $VOSO_4.H_2O$ in 25ml water and (0.4825 gm, 0.002 mol) from 2 – (3,3-dimethyl phenyl) amino benzoic acid Sodium salt with stirred for 2hours.After cooled down the violate product was filtered off and recrystallization by chloroform. Table [1] showed the physical properties of the compound [II].

Bis[2- (2,5- Dichloro phenyl) amino phenyl acetic acid]Copper(II) complex [III] .

This complex was prepared by slow addition of hot (0.5942gm , 0.002 mol) 2- (2,5- dichloro phenyl) amino phenyl acetic acid sodium salt in 25 ml to the $CuCl_2.H_2O$ (0.16843 gm , 0.001mol) in 25ml water with stirring . The mixture was refluxed for 30 min. . After cooled down the solvent was evaporated and recrystallization Table [1] explains the physical properties of the compound [III].

Bis[2- (2,5- Dichloro phenyl) amino phenyl acetic acid Vanadyl (IV)complex [IV]

complex [IV] were prepared by reaction (0.25305gm , 0.002mol) vanadyl sulfate $VOSO_4.H_2O$ in 25ml water with (0.5942gm , 0.002 mol) from 2- (2,5- dichloro phenyl) amino phenyl acetic acid sodium salt in 25 ml water. After 2 h. reflux the mixture was allowed to reach room temperature .An small portion of triethyl amine was added to the solution to give colored precipitation which collected was recrystallization by diethyl ether. Table [1] showed the physical properties of the prepared compound.

Method of Calculation:

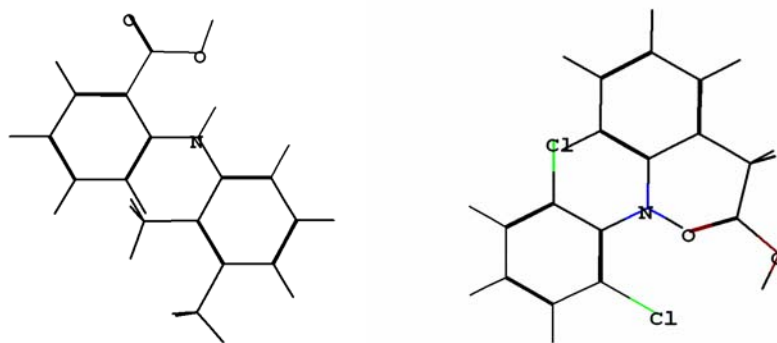
The molecular modeling studies were carried out on a Pentium IV computer with a 1.7 GHZ processor performed using quantum mechanical

methods as implemented with Hyper chem. 6.5demo program (by Hyper Cube In, USA).

The geometry optimization of all prepared complexes were obtained by using quantum mechanic and semi-empirical calculation (MM+, ZINDO/1, ZINDO/s) at the RHF level for the singlet lowest energy state with on configuration interaction and Polak – Ribiere algorithm until the RMS gradient less than 0.01 Kcal/mol /A°

Result and Discussion

The reaction of Cu(II) and VO(IV) ions with 2-(3,3-dimethyl phenyl)amino benzoic acid and 2- (2,5- dichloro phenyl) amino phenyl acetic acid were carried out in water . The metal to ligand ratio in all cases as 1:2. Figure (1) illustrates the two ligands used in this study:



2 – (2,3-dimethyl phenyl)
amino benzoic acid

2-(2,5-dichloro phenyl)amino
Phenyl acetic acid

Figure (1): Shown the optimization geometry (MM+ method) of ligandes which used in the study.

All the complexes are stable at room temperature but they decompose without melting. Most compound of high melting point may due to high stability, and insoluble in most polar and non-polar solvents . However, except the high solubility in dichloromethane and chloroform. Table (1) shown all the complexes can be easily obtained in a good yield.

Table (1) : physiochemical properties of the ligand and synthesis complexes.

list	Name of compound	Melting point / °C	Coulor	Yield %
1	2-(3,3-Dimethyl phenyl)amino benzoic acid	230	Whit crystal	70
2	2- (2,5- Dichloro phenyl) amino phenyl acetic acid	283	Off white	80
3	Bis [2 - (3,3-Dimethyl phenyl)amino benzoic acid] Copper(II)	>146 dec.	Paste green	82
4	Bis [2 - (3,3-Dimethyl phenyl)amino benzoic acid] vanadyl(IV)	>285 dec.	violate	85
5	Bis[2- (2,5- Dichloro phenyl) amino phenyl acetic acid]Copper(II)	>115 dec.	Green	78
6	Bis[2- (2,5- Dichloro phenyl) amino phenyl acetic acid] vanadyl(IV)	>178 dec.	Steel blue	80

The complexes were studied by thermogravimetric techniques (Niema,2003), the method involve heating the metal complexes at constant heating rate to reach suitable temperature, in order to get the most stable compound CuO the complex [I] , [III]and V₂O₅ to the [II] ,[IV] respectively . The behind data are listed in table (2) which confirm that the complexes posses the 1:2 ratio metal to ligand.

Table (2): the weight percent of copper and vanadium, and molar conductivity of the new preparation complexes .

Compound	% Cu		%V		Conductivity Λ_m ohm ⁻¹ cm ² mol ⁻¹
	% calculation	% Founded*	% calculation	% Founded*	
[I]	10.32	9.92			12.88
[II]			7.91	7.935	5.36
[III]	9.83	9.18			14.82
[IV]			6.57	6.65	5.74

*obtained from the thermogravimetric analysis techniques.

The electrical conductance in dichloromethane table (2) ranging between 12.8-14.8 to the copper complexes and 5.36 – 5.74 ohm⁻¹cm²mol⁻¹ for vanadyl complexes indicate the metal to ligand ratio equal to 1:2 according to the previous study (Mohammed,2005;Sharma et al,2004).

The sites of coordination in the complexes were characterized by comparison between the infrared absorption spectra of the free ligand with these complexes. Table (3) includes experimental and calculated infrared data. Also from table (2) complex [I] and complex [II] show N—H stretching between (3280- 3275 cm⁻¹) and (3310 – 3300 cm⁻¹) respectively while the position of N—H stretching to the free ligand 2-(2,3-dimethyl phenyl) amino benzoic acid are between (3360 – 3350 cm⁻¹). Also complex [III] and complex [IV] appear N—H stretching between (3275 - 3270 cm⁻¹) and (3260 - 3255 cm⁻¹) respectively while N—H stretching of the free ligand 2-(2, 5-dichloro phenyl) amino phenyl acetic acid are at (3395 - 3390 cm⁻¹).

The C=O stretching of complexes [I], [II], [III] and [IV] are in the (1500,1630,1550 and 1560 cm⁻¹ respectively while the vibrations frequency

to the C=O stretching are located in the (1645 , 1675 cm^{-1}) for the two free ligands.

These bands are displaced by (20 - 45 cm^{-1}) for N—H and C=O stretching

to the complexes - compared with the bands of ligands, indicate that the two ligands are attached with Cu(II) and VO(IV) through the nitrogen and oxygen atoms . also the coordination between metal ions Cu(II) and VO(IV) and ligand are not strong due to the nitrogen atoms in the ligand connected with two phenyl group , which reflect the low basicity and less availability of the nitrogen lone pairs electrons for coordination .

In IR spectra *figure (2-7)* of the complexes , bands appearing at about 1145 cm^{-1} and 1175 cm^{-1} have been assigned to C—O stretching bonds in the ligands (Clarke , 1986) , are shifted to lower frequency in the complexes with some reduction in intensity.

Further support for such type of coordination was obtained from the bands at 420 – 490 cm^{-1} which attributed to M—O stretching vibrations where M are Cu(II) or VO(IV). the second group of bands appearing at 530 – 585 cm^{-1} are assigned to M—N stretching (Nakamoto ,1977).

The most relevant band of the complex [II] and [IV] in the infrared spectra are present in table (3). The spectrum of complex [II] exhibited a weak band at 980 cm^{-1} and medium band at 950 cm^{-1} to the complex [IV], which it attributed to the stretching of the terminal V=O bond. If we compare the two above complexes with VOSO₄ compound spectra, we observed that V=O band displaced to lower frequencies (950 – 980 cm^{-1}). Similar results are obtained in other complexes of oxovanadium (IV) with 8 – quinolate Li et al,2004), enoylacetonate (Sharma et al,2004) as ligands. This displacement can be attributed to the electronic donation of the base to vanadium ions (V—N), which increase the electronic density on the

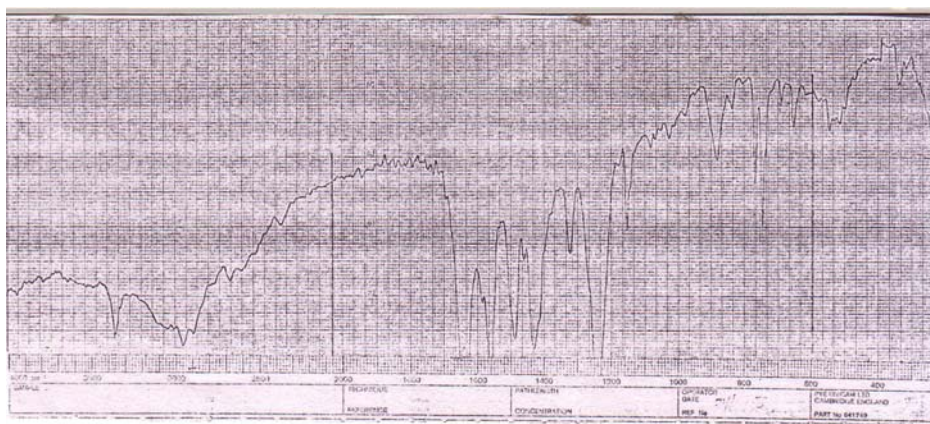


Figure (2): IR spectrum for ligand (1)

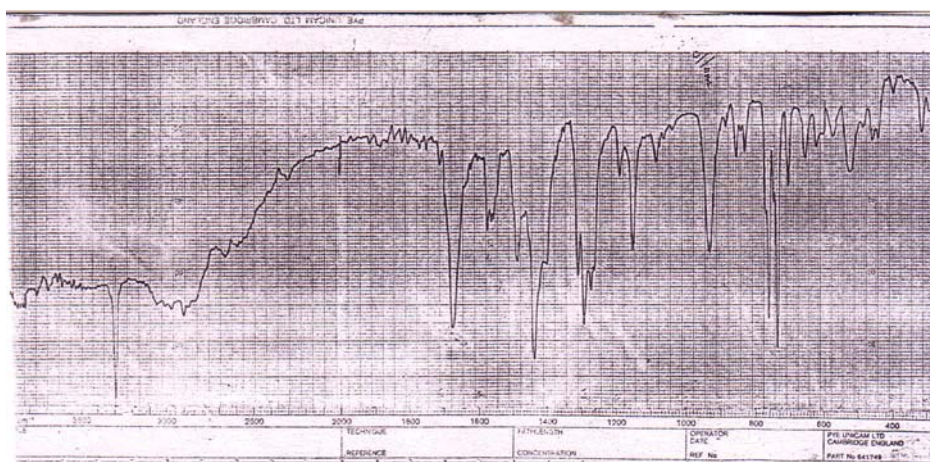


Figure (3): IR spectrum for ligand (2)

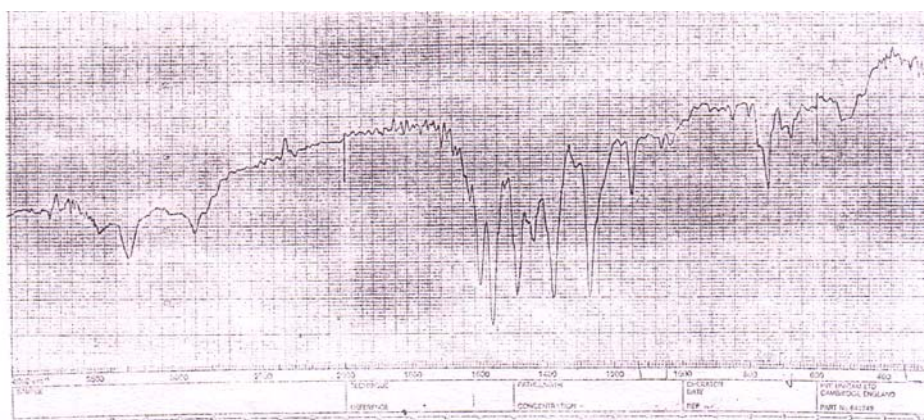


Figure (4): IR spectrum for complex [I]

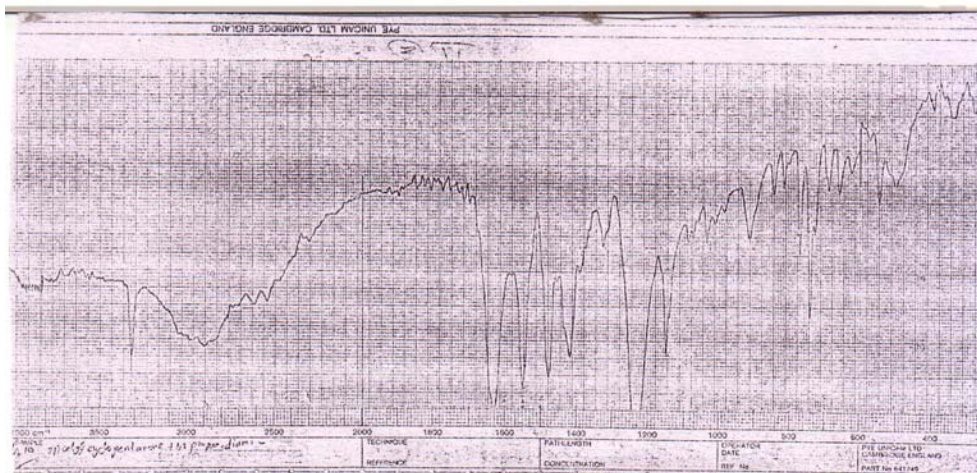


Figure (5): IR spectrum for complex[II]

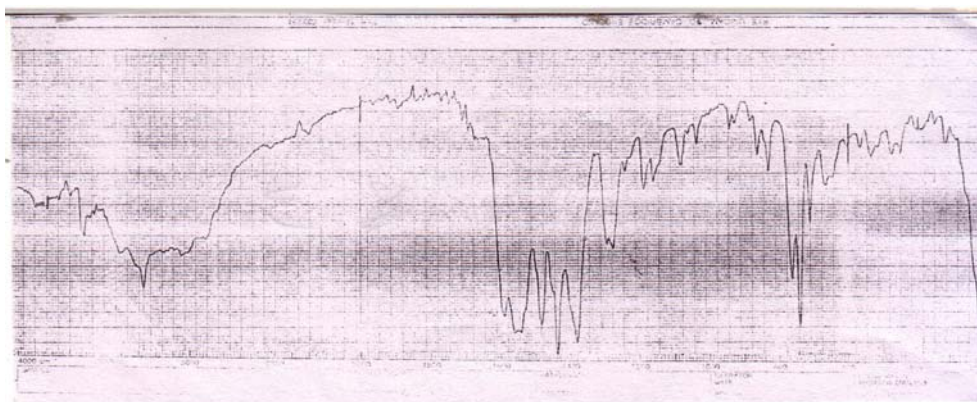


Figure (6): IR spectrum for complex[III]



Figure (7): IR spectrum for complex[IV]

metal d- orbitals ,and consequently the $P_{\pi} \rightarrow d_{\pi}$ donation from the oxygen atom to vanadium is expected to be reduced(Dytta et al,199).

The electronic spectra figure (8) were measured in CH_2Cl_2 in the uv-visible region reveals the following transitions at $\lambda_{max}/nm / (\epsilon / cm^2 mol^{-1} cm^{-1})$, experimental and calculated data are listed in Table (3). The intensities absorption at $\lambda_{max} < 340 nm$ are assigned to intraligand $\pi - \pi^*$ transitions of ligands, based on similarities with the absorption of the free ligands ⁽¹³⁾.

The absorption of copper(II)complexes are analyzed assuming D_{4h} symmetry(Doadrio et al ,2002). The e_g and t_{2g} level of the 2D free ion term are farther split into B_{1g} , A_{1g} , B_2 , and E_g levels respectively. Thus, three spin allowed transitions are expected in the visible and near IR region of copper (II) and such band are assigned to the $^2B_{1g} \rightarrow ^2A_{1g}$, $^2B_{1g} \rightarrow ^2B_g$. The level sequences will depend on the Jahn-Teller effect (Bindery et al ,200).

The electronic spectrum of the present copper (II) complexes table (4) displays a broad band at 1562.5 and 15150.5 cm^{-1} for the complex [I] and [III] attributed to the transition $^2B_{1g} \rightarrow ^2E_g$ and $^2B_{1g} \rightarrow ^2A_{1g}$. The second band below 460 nm with high intensity could be assigned to MLCT for copper complexes [I] and [II] according to results published aerial (Doadrio et al ,2002).

Table (3)

Cu—N Starch.	Calc.			510(w)		490.3(w)	
	Abs.			550(w)		520(w)	
Cu—O Starch.	Calc.			382.4 (w)		430(w)	
	Abs.			420(w)		480(w)	
V—N Starch.	Calc.				570.1 (w)		590.8 (w)
	Abs.				545(w)		560(w)
V—O Starch.	Calc.				490.6 (w)		465.2 (w)
	Abs.				495(w)		490(w)
O==V Starch.	Calc.				947.7 (m)		945.1 (s)
	Abs.				920(m)		930 (m)
C—O Starch.	Calc.	1193.8 (m)	1165 (m)	1109.3 (m)	1113.6 (m)	1138.1 (m)	1170 (m)
	Abs.	1163 (m)	1145 (m)	1145 (m)	1440 (m)	1175 (m)	1140 (m)
C—N Starc.	Calc.	1342.7 (m)	1295 (m)	1248.5 (m)	1288 (m)	1264.3 (m)	1210.5 (m)
	Abs.	1245 (m)	1295 (m)	1275 (m)	1230 (m)	1285(m)	1275 (m)
C==O starch.	Calc.	1902.8 (s)	1743.3 (s)	1636.4 (m)	1623.5 (m)	1634.7(s)	164 8(s)
	Abs.	1645 (s)	1675 (s)	1595 (s)	1630 (s)	1550(s)	1560 (s)
N—H Starch.	Calc.	3565 (w)	3412.2 (w)	3420 (w)	3200 (w)	3300(w)	3450(w)
	Abs.	3360 (w)	3295 (w)	3275 (w)	3310 (w)	3275 (w)	3260 (w)
compound		Ligand 1	Ligand 2	Complex [I]	Complex [II]	Complex [III]	Complex [IV]

Table (4) : Electronic data of all preparation complexes.

Compound	Transition	Recorded λ_{max}/nm	Calculated ^(a) λ_{max}/nm
Complex [I]	d—d MLCT	640(1562.5cm ⁻¹) 430(23201.8 cm ⁻¹)	730.17(13696.7 cm ⁻¹) 471.21(21231.4 cm ⁻¹)
Complex [II]	d—d d—d	660(1515.5 cm ⁻¹) 380(26315.7 cm ⁻¹)	610(16393. 4cm ⁻¹) 468.32(21359. 2cm ⁻¹)
Complex [III]	d—d MLCT	630(15873.0 cm ⁻¹) 450 (22222.2 cm ⁻¹)	690.2(14488.55cm ⁻¹) 510.42(19592.0 cm ⁻¹)
Complex [IV]	d—d d—d	640(15635 cm ⁻¹) 360(27777.7 cm ⁻¹)	670.12(15873.0 cm ⁻¹) 490.32(20394.8 cm ⁻¹)

a) The calculation methods are ZINDO/s

In general , oxovanadium (IV) display three band in the 10.000 – 30.000 cm⁻¹(Bindery et al ,2000). In this work table(4)the oxovanadium complexes [II] and[IV] exhibited two band .According Balhausen and Gray (BG)(Ballhusen et al,1962) , the first broad band attributed to overlap two transition ${}^2B \rightarrow {}^2E$ ($d_{xy} \rightarrow d_{zx} \rightarrow d_{yz}$) and ($d_{xy} \rightarrow d_{x^2-y^2}$) (${}^2B_2 \rightarrow {}^2B_1$) transition. The band at 2135.92 and 20394.8 cm⁻¹ for

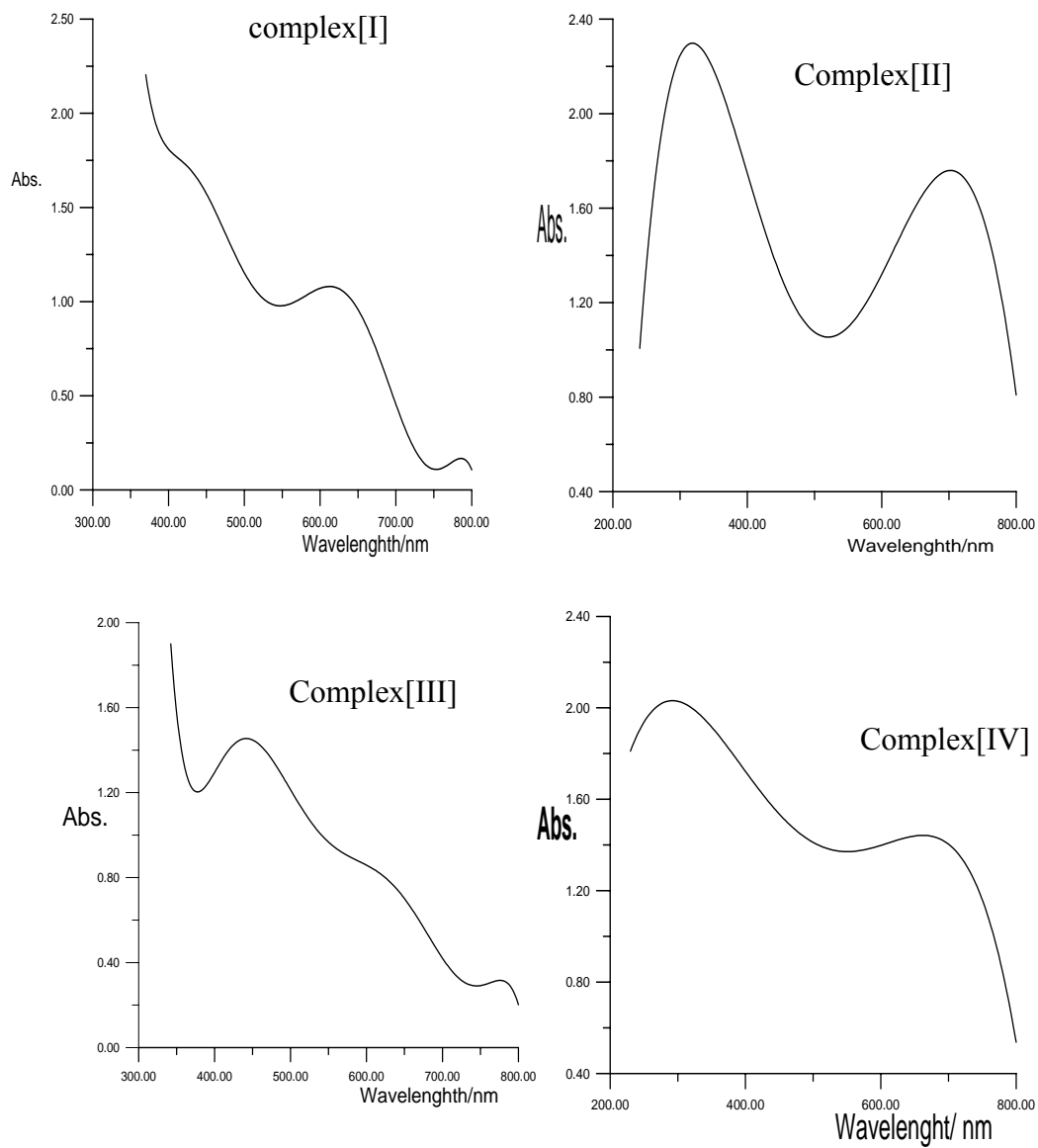


Figure (8): Recorded uv. Spectrum for all preparation complexes[I] to [IV].

complex [II] and [IV] respectively may either be assigned to the $d_{xy} \rightarrow d_z^2$ (${}^2B_2 \rightarrow {}^2A_1$) transition or through to be low energy charge transfer band. In conclusion, due to steric interaction of the large size of ligands, VO^{+2} complexes have the distorted square pyramidal structure.

On the other hand, there are several ways to describe the energy of a molecule. The classic method and it is still very useful also for large molecules- is to describe the energy as a sum of contributions from bond distances, bond angles, torsion angles and non-bonded interactions.

The total energy of the molecule should in this framework be written as

$$E_{\text{total}} = \sum E_b + \sum E_{\text{ang}} + \sum E_{\text{torsion}} + \sum E_{\text{nb}}$$

where the sums are over all interactions of each type. Hyperchem has several procedures for minimizing the total energy of a molecule as a function of the geometry(Hyper,2002).

All obtained Cu (II) complexes exhibit similar electronic absorption spectra , also , VO(IV) exhibit similar electronic absorption spectra which indicate that the central ions and ligands are coordinated in a similar mode.

According to the geometry optimization, proposed molecular structure of all preparation complexes using ZINDO/1 method is shown in Fig(9). Table (5) explains the energy.

Table (5): some calculated energy factor of preparation complexes figure (9) in their ground state.

Quantity	Comple xes	[I]	[II]	[III]	[IV]
ZNDO/1					
Total		-	-	-	-
Energy(Kcal/ mol)		221649.75	202770.166	247987.60	229070.19
Binding		65	6	50	35
Energy(Kcal/ mol)		-	20034.9128	-	-
Isolated		20079.305	-	18467.630	18385.418
Atomic		0	182735.253	5	7
Energy(Kcal/ mol)		-	7	-	-
Electronic		201570.71	-	229519.97	210684.77
Energy		49	1577502.30	45	48
Kcal/mol)		-	41	-	-
Core-Core		1652134.7	1374732.13	1846324.3	178846.33
Interaction		14	755	63	00
(Kcal/mol)		1430484.9	-	1598336.7	1558979.1
HE Energy		564	-32.17123	585	364
Correction		-71.05122	-	-52.2853	-37.2369
(Kcal/mol)			12906.8658		
Heat of					
Formation					
(Kcal/mol)					

	13053.017 0		12083.978 5	11900.007 7
mm+total energy(kcal/m ol)	3235.9060	3036.4877	6930.676	2537.7331

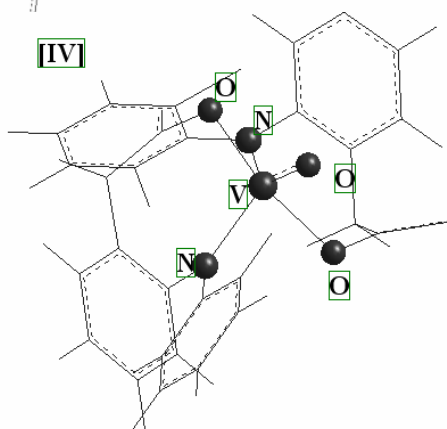
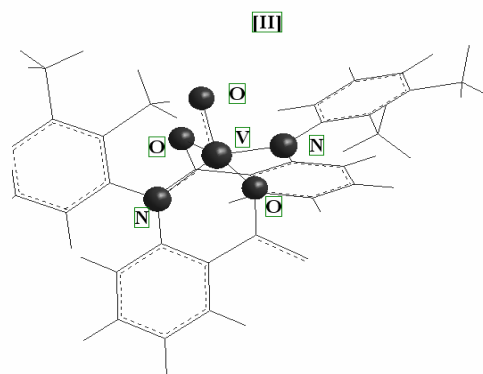
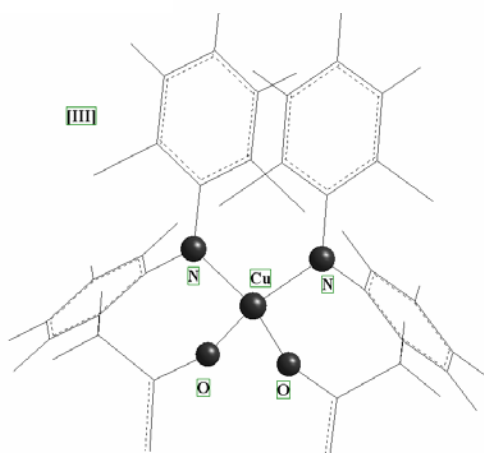
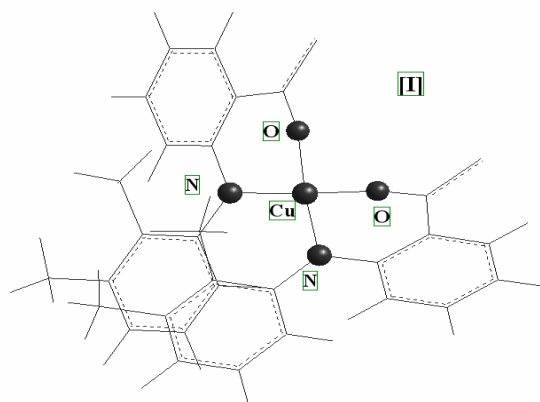


Figure (9): Shown the optimization geometry (ZANDO/1 method) of new complexes [I],[II],[III]and [IV] respectively.

To elucidate the molecular structures of the all-new preparation complexes ZINDO/I methods were carried out which Emphasis that The molecular structure of copper Complex [I] and [III] can best be described as distorted square planer , while oxovanadium complexes [II] and [IV] founded in the distorted square pyramidal.

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