# IR, Electronic Properties and Conductivity Studies of 2,2`-[1,2-ethylene is(azyliden)bis(1,2-diphenylethanol) and N1,N4-bis (diphme) benzene-1,4-diamine vanadium(IV) oxide and their Biologically Application

Salem Et. Ashoor*, Eman B. Ben-said and Hager S. Aljabu

***Abstract*—** Schiff bases complexes can be possess biological activities. The Schiff bases were prepared from ethylene diamine $\{H_2NC_2H_2NH_2\}$ with the benzoine {(Ph)COCOH(Ph)} in ration (1:2) respectively (**L2**) and 1,4-diaminebenzene $\{H_2NC_6H_5NH_2\}$ and benzophenone $\{(C_6H_5)_2CO$**} (L2)**,these were reacted with vanadium -aminophenol and its complexes were synthesized. They were characterized using elemental study IR and UV spectroscopy. The complexes were obtained with the general formula **VOL1** and **VOL2** were the synthesised via the reaction between **L1**, **VO(acac)$_2$** and also the reaction between **L2** and **VO(acac)$_2$**. Here ligand is functioning as a tetra and pi-dentate ligand coordinating through the oxygen phenol, di-nitrogen from **L1** also di-nitrogen from **L2** respectively. Electric conductivity also did prove to be useful use for conductively of these complexes via using Ohm`s equation also optimisation of these complexes were tested by using HyperChem release 7.5 for simulation the complexes were shown the total energy of them. These complexes were tested in antibacterial studies, were shown equal effected.

***Keywords*—**About Schiff bases compounds; VO(acac)$_2$, VOL1, VOL2; electronic Properties, optimization; conductively, Ohm`s equation; antibacterial studies.

## I. Introduction

SCHIFF bases are typically formed by the condensation of a primary amine and an aldehyde/ketone, it`s a functional group that contains a carbon-nitrogen double bond and nitrogen connected to alkyl or phenyl group and become wildly using in many applications such antibacterial, antifungal activity.[1] increase the activity of Schiff bases are normally using for application after camping with inorganic compounds. Z. Chohan and his group have reported the sanitized of Schiff base derived from the salicylaldehydes and then reacted with some transition metal and then forwarded to there application for antifungal, antibacterial and antitumor activities.[2] Anticancer activity via Schiff base complexes derived from 4-hydroxysalicylaldehyde and amines have been reported by W. Zishen and his group.[3] The demonstration of amine-carbonyl condensation constitutes the number of enzyme-mediated and understanding mechanism of amine-carbonyl condensation have received great attention by D. Barton *et al*.[4] A family of new Schiff base types such pyridoxal-5-phoshate as co-factor in enzyme-mediated transformations of α–amino acids (e.g. racemization, α- and β– decarboxylation, retroaldolization, α,β-elimination and transmination.[5,6] Anther thiourea compound has been used for anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity in experimental animals.[7] El-ajaily *et al.*[8] have Sanitized and investigated some complexes derived from salicylaldhyde and histidine and they found to have antibacterial activation on some pathogenic bacteria. Schiff base of types 3-enehydrazono-2-salicylidindolinone and there Complexes incorporating Co(II), Ni(II), Cu(II) and Zn(II) and they have activated for some antibacterial such *Staphylococus aureus, Enteroccus, Proteus mirabilis, Escherichia coli, Bacillus anthracis, Pseudomonas aeruginosa* and *Candida albicans*.[9]

More recently, a series of oximes, semicarbazones and phenylhydrazones and their antibacterial activities and then were comparing against *E. Coli*., which gave different results of activity.[10] Again thermal behaviour and antimicrobial activity were investigated for a series of thiourea derivatives on (*Enterococcus faecalis, Staphylococcus aureus and Staphylococcus epidermidis*) and other species of fungi (Candida albicans, Candida krusei, Candida glabrata and Candida paraposilosis).[11] However, a synthesis of two potentially heptadentate ($N_4O_3$) Schiff-base ligands derived from condensation of Tris(3-aminopropyl)-amine and Salicylaldehyde or 4-Hydroxysalicylaldehyde, Nickel(II) and Copper(II) Complexes of the former ligand have been reported by H. Keypourl and his group.[12] *The design and synthesis of monosubstituted and disubstituted azanaphthoquinone annelated pyrroles with anticancer activity are described by nipawan pongprom and his group.[13] subsequent the synthesis, spectral analysis and biological activities of some 4-phenyl-2-hydroxy-chlorosubstituted-2-*

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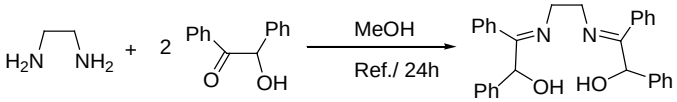
*imino-1, 3-thiazene with phenyl thiourea and diphenyl thiourea have been carried out in two series. In series I they got 4-(2-hydroxy-3,5-dichlorophenyl-6-(ethyl)-2-iminophenyl-1,3-thiazene and 4-(2-hydroxy-3,5-dichlorophenyl-6-(ethyl)-2-iminophenyl-3-phenyl-1,3-thiazene(3a-6a) from 2-hydroxy-3,5-dichloroacetophenone from phenyl thiourea were achieved by S. P. Rathod.* [14] In early this year R. Shyam *et al.* described the series of novel methylene-bis-8-substituted [1,5]-benzothiazepines and also other compound was prepared by the reaction of methylene-bis-chalcones-3 with 2-amino-5-methyl-thiophenol.The structures of the synthesized compounds were confirmed by their IR, 1H, 13C NMR and Mass spectral analyses. All the synthesized compounds were tested for their antimicrobial activity against Gram-positive, Gram-negative bacteria and fungi. Among the synthesized compounds, the compounds 4f, and 4g, were found to be the most active against *Bacillus subtilis*, *Bacillussphaericus*, *Staphylococcus aureus*, *Klebsiella aerogenes* and *Chromobacterium violaceum*. Similarly thesecompounds showed potent antifungal effect against *Candida albicans*, *Aspergillus fumigatus*, *Trichophytonrubrum*, and *Trichophyton mentagrophytes*. It is interesting to note that the compounds with heterocyclic ring substituents at the 4th position of benzothiazepine system displayed notable antibacterial activity, almost equal to that of streptomycin and penicillin.[15]

## II. EXPERIMENTAL

*A. Synthesis of 2,2`-[1,2-ethylene bis(azyliden)bis1,2-diphenylethanol){(HOPhHCCPh)NC$_2$H$_4$N(CPhCHPhHO)}(Ph= C$_6$H$_5$) L1*

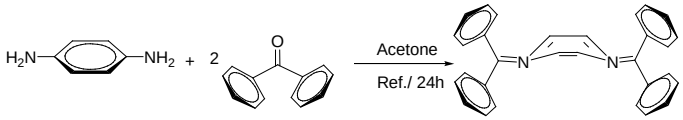
A solution of ethylene diamine {$H_2NC_2H_2NH_2$}( 1.42 g, 0.024 mol) in ethanol (100 ml) and slowly adding (10 g, 0.047 mol) of benzoine {(Ph)COCOH(Ph)} in (100 ml) of the ethanol at room temperature and then the temperature was increased to reflex overnight with stirring. During that time the colure was changed from callas to brown and finally to orange. After that was filtrated, work-up yielded **L1** as yellow compound material in (71%) yield after slow cooling of the methanol solution to 0 $^oC$. **L1** is air and thermally stable (Scheme 1).




Scheme 1

*B. Synthesis of N1,N4-bis(diphme)benzene-1,4-diamine {(Ar) $_2$NC$_6$H$_5$N(Ar)$_2$}(Ar = C$_6$H$_5$):*[16]

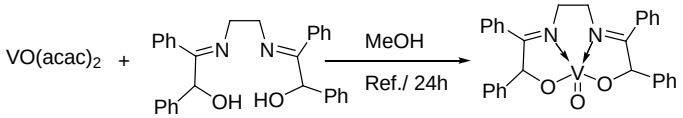
This was achieved by slowly adding a solution of 1,4-diaminebenzene {$H_2NC_6H_5NH_2$}( 2.9 g, 0.029 mol) in acetone (70 ml) and followed by benzophenone {$(C_6H_5)_2CO$} ( 10 g, 0.054 mol ) in (100 ml) of acetone at room temperature and after 20 minutes in room temperature stirring the temperature was arise to reflux overnight stirring. During that time the colure was changed from light brown to darkness brown. work-up yielded **L2** as brown crystalline material in 87% yield after slow cooling of the $Et_2O$ solution to -4 $^oC$. **L2** is air and thermally stable (Scheme 2).




Scheme 2

*C. [2,2`-[1,2-ethylene bis(azyliden)bis1,2-diphenylethanol) vanadium(IV) oxide [{(OArCCAr)$_2$NC$_2$H$_2$N}VO](Ar= C$_6$H$_5$) (1)*

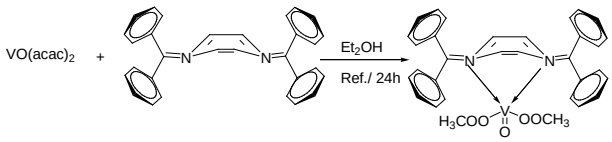
The changing the steric environment around the vanadium center was examined by addition a bulky of **L1** and the synthesis of **1** was achieved by slow addition a solution of **L1** (1.68g, 3.7 × $10^{-3}$ mol) in $Et_2O$ to a stoichiometric amount of $VO(acac)_2$ (1.0g, 3.7×$10^{-3}$ mol) in $Et_2O$ at room temperature, then temperature was arise to reflex over night. Work-up yielded [VO{$NC_2H_4N(CPhCHPhHO_2)$}(Ph= $C_6H_5$) (**1**) as a brown powder material in 65% yield after slow cooling of an $Et_2O$ solution to -4 °C, and also **2** is air and thermally stable (Scheme 3).




Scheme 3

E *Bis(diphenylmethyene) benene- 1, 4- diamine diacetylacetonato oxo vanadium(IV)] [{(Ph2C)NC6H4N(Ph2C)}VO(OOCH3)2] (Ph= C6H5) (2):*

A solution of **L2** (1.7g, 3.89 ×$10^{-3}$ mol) in 100 ml ethanol was add to solution of $VO(acac)_2$ were ac = $CH_3OO$ (1g, 3.75 × $10^{-3}$ mol) in 60 ml in same solvent and mixture were stir in room temperature, then the temperature was arising up to the reflex for 24 hours. Work up after removing the solvent, the light green of the product was obtained in yield 51%. (Scheme 4).




Scheme 4

## III. SPECTROSCOPIC TECHNIQUES

Electronic spectra were recorded at room temperature on UV-Vis spectrophotometer mini 1240- Shimadzu in the range 200 – 900 nm. Conductivity measurement was carryout in glass device and photometer using power supply EA-PS 2016-050 and then applied power was measurements employing Metr max 12 IEC61010-1 with internal resistance of 5KOhm and the current was measured using AVOMETER CEM-DT

3900. IR Spectrophotometer JASCO-FT-IR-460 plus using (KBr) disk in the range 400 – 4000 $cm^{-1}$.

The antibacterial studies were conducted with bacterial stains of Escherichia Coli and Bacillus Subtills in cultural medium of nutrient Agar. This Agar medium was prepared in distilled water and inoculation was done in Petri dishes using platinum wire. The compounds were dissolved in (EtOH and $H_2O$) in ration (1:4) and 2mm diameter blotting paper disc are dipped in this solution and then dried in an incubator. This was applied on the bacteria and plates were kept in incubator at 37°C for 24 hours. The zone of inhibition was measured in mm and its percentage is calculated. Method of calculation the semi-empirical method was done on Hyperchem program version 7.5 running on a Windows XP workstation with a Pentium IV PC.

## IV. Results and Discussions

### A. UV spectra study

The electronic spectra of the complexes were recorded in ethanol medium. The ligands **L1** and **L2** were showed absorption of $\lambda_{max}$ 248 nm and 246 nm respectively on 4.03 $x10^3$ $cm^{-1}$ and 4.07 $x10^3$ $cm^{-1}$ respectively, these were characterized as bands which is assigned due to $\pi \rightarrow \pi^*$[17, 18]. The spectrum of **VOL1**and **$(acac)_2$VOL2** complex **1** showed d-d transition with absorption at 242 nm and 330 nm at 41322 $cm^{-1}$, 30303 $cm^{-1}$ and complex **2** was found $\lambda_{max}$ at 230 nm, 275 nm and 410 nm on 43478 $cm^{-1}$, 36363 $cm^{-1}$ and 24390 $cm^{-1}$ respectively, which is assigned respectively, which suggested due to $^2A_{1g} \rightarrow {}^2B_{1g}$ ($dz^2 \rightarrow dx^2\text{-}y^2$)$\nu_1$, $^2B_{2g} \rightarrow {}^2B_1g$ (dxy → $dx^2\text{-}y^2$) $\nu_2$ and $^2Eg \rightarrow {}^2B_1g$ (dxz, dyz → $dx^2\text{-}y^2$) $\nu_3$ transition respectively, and these typically of the complexes in type elongated tetragonal. [19]

### B. IR spectra Study

On comparison of the IR spectra of the ligand **L1** showed observe a strong and intense peak observed in *ν*(3452 $Cm^{-1}$) which indicates the presence of O–H stretching frequency and peaks at *ν*(3084, 1649, 1594 $Cm^{-1}$) and (1178 $Cm^{-1}$) stretching especially for CH aromatic, C=N, C=C aromatic and C-N respectively.

The peaks of the complex **1** showed peaks at *ν*(1600 $Cm^{-1}$, 1205 $Cm^{-1}$ and 570 $Cm^{-1}$) corresponds to C=N, C-O and V-O stretching respectively. Again, the peaks of the complex **2** showed peaks at *ν*(1627 $Cm^{-1}$ and 1134 $Cm^{-1}$) stretching, those especially for corresponds to C=N, C-N. Peaks appear at *ν*(986 $Cm^{-1}$ and 547 $Cm^{-1}$) stretching with corresponds to C-O and V-O [20-24]

### C. Electronic and structural properties

Geometry optimization of complexes **1** and **2**, the studied of the molecules were done by performing the semi-empirical molecular mechanics theory at the level PM3 and MM+ using the restricted Hartree–Fock (RHF) procedure. The Polak–Ribier algorithm was used for the optimization. The electronic properties of $[\{(OArCCAr)_2NC_2H_2N\}VO]$(Ar= $C_6H_5$) (**1**) and $[\{(Ph_2C)NC_6H_4N(Ph_2C)\}VO(OOCH_3)_2]$ (Ph= $C_6H_5$) (**2**) were shown in table 1 and 2.

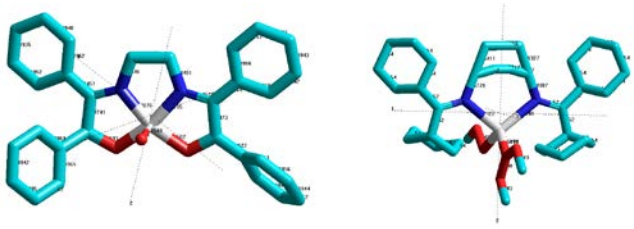
TABLE 1 ELECTRONIC PROPERTIES OF 1.

| | |
|---|---|
| Total energy | 171.920135 (kcal/mol) |
| Geometry optimization | E = 23.320744 Grad = 0.691205 Converged = YES (540 Cycles 540 Points) |
| Molecular dynamic | Energy 206.095 (kcal/mol) T = 884.08K |
| Single point | Energy = 111.226143 Gradient = 40.798996 |
| Monte Carlo | Time= 100 steps Potential = 53.655 (kcal/mol) T = 300 K. |
| Gradient | 30.9866570 (kcal/mol/Ang) |

TABLE 2 ELECTRONIC PROPERTIES OF 2.

| | |
|---|---|
| Total energy | 448.715637 (kcal/mol) |
| Geometry optimization | E = 34.091759 Gradient = 0.087978 Converged = YES (334 Cycles 737 Points) |
| Molecular dynamic | Energy 75.8532 (kcal/mol) T = 165.994 |
| Single point | Energy = 448.715637 Gradient = 74.208641 |
| Monte Carlo | Time= 100 steps Potential = 63.2135 (kcal/mol) T = 300 K. |

The optimized structure of complexes **1** and **2** were shown in figure 1 (A and B).



**A** **B**

Fig.1 Optimized structure of complexes **1** and **2** via Hyper-hem 7.5 program (A = **1** and B = **2**)

### D. Antibacterial study

The antibacterial studies were conducted with bacterial stains of *Escherichia Coli* and *Bacillus Subtills* in cultural medium of nutrient Agar. This Agar medium was prepared in distilled water and inoculation of media in Petri dishes is referred to as plating out or looping out. The compounds were dissolved in (EtOH and $H_2O$) in ration (1:4) and 2mm diameter blotting paper disc are dipped in this solution and then dried in an incubator. This was applied on the bacteria and plates were kept in an incubator. This was applied on the bacteria and plates were kept in incubator at 37°C for 24 hours. The zone of inhibition by complexes **1** and **2** were measured in 5-10 mm. these classify as active complexes. [25-27

### E. Conductivity study

Conductivity behaviours of the **1** and **2** were followed the Arrhenius behaviour and the activation energy can be

calculated using different temperatures. The conductivity of these compounds **1** and **2** have been explained in term of the following Eq.

$\sigma = 1/\rho$ = Ω. $cm^{-1}$ were $\rho = R\ A/L$ and $A = \pi r^2$ $A = 3.14 \times (0.25)^2$ = zz → R = V/I = 0.99462**V**/ $2.18956\times10^{7}$ = dd => p = dd zz/0.1 = $7.13167005\times10^{-7}$ **(**Ω.cm).

Where: P = specific resistance (Resistively) & A = surface area & R = resistance & V = voltage & I = current intensity

The final equation to calculate the conductivity of **1** and **2** will be $\boldsymbol{\sigma = 1/\rho}$=> $\boldsymbol{\sigma = 1}/7.13167005\times10^{-7} = 1.4021961\times10^{6}$ $(\Omega.\ cm)^{-1}$

The value of conductivity was shown to be within the range of semiconductors values ($1.4021961\times10^{6}$ $(\Omega.\ cm)^{-1}$) and this value within the range of others complexes were in publication.[28-30]

The following graph explains the relation between voltage, current after applied and measured current values at room temperature (Table 1). The slope equal to resistance, from the obtained the resistance the resistively was calculated according to the above mentioned equations (Figure 2).

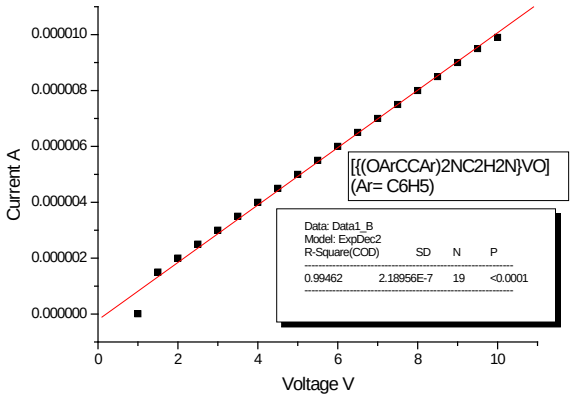
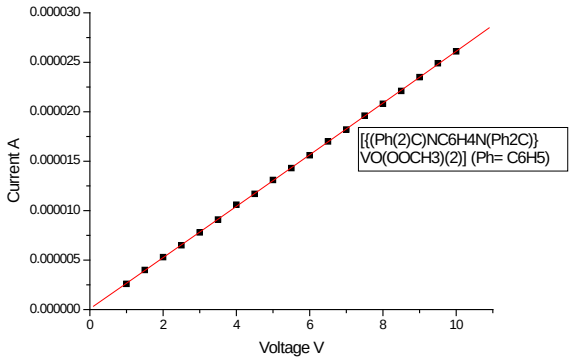



Fig. 2 of complex **1**




Fig, 3 of complex 2

TABLE 1: THE RELATION BETWEEN VOLTAGES, CURRENT AFTER APPLIED AND MEASURED CURRENT VALUES AT ROOM TEMPERATURE FOR THE COMPLEX 1.

| Voltage (V) | Current ($\times10^{-6}$) | Voltage (V) | Current ($\times10^{-6}$) |
|---|---|---|---|
| 1 | 1 | 6 | 6 |
| 1.5 | 1.5 | 6.5 | 6.5 |
| 2 | 2 | 7 | 7 |
| 2.5 | 2.5 | 7.5 | 7.5 |
| 3 | 3 | 8 | 8 |
| 3.5 | 3.5 | 8.5 | 8.5 |
| 4 | 4 | 9 | 9 |
| 4.5 | 4.5 | 9.5 | 9.5 |
| 5 | 5 | 10 | 9.9 |
| 5.5 | 5.5 | | |

TABLE 2: THE RELATION BETWEEN VOLTAGES, CURRENT AFTER APPLIED AND MEASURED CURRENT VALUES AT ROOM TEMPERATURE FOR THE COMPLEX 2.

| Voltage (V) | Current ($\times10^{-6}$)- | Voltage (V) | Current ($\times10^{-6}$)- |
|---|---|---|---|
| 1 | 2.7 | 6 | 1.69 |
| 1.5 | 4.3 | 6.5 | 1.84 |
| 2 | 5.6 | 7 | 1.97 |
| 2.5 | 7 | 7.5 | 2.12 |
| 3 | 8.6 | 8 | 2.26 |
| 3.5 | 9.8 | 8.5 | 2.41 |
| 4 | 1.12 | 9 | 2.53 |
| 4.5 | 1.28 | 9.5 | 2.68 |
| 5 | 1.4 | 10 | 2.83 |
| 5.5 | 1.55 | | |

Conductivity arises mainly while the activation energy increase, the conductivity is due the electronic transfer between the aromatic system and nitrogen attaced the aromatic (delocalization electron). The conductivity of **2** has been measured in the voltage range 1 to 10 V. It is found to follow the Jonscher`s power law.

## V. CONCLUSIONS

The chemistry presented in this paper shows that the chelating di-imdes of V(IV) are accessible, the coordination sphere around the metal centre in case of penta-membered ring has been examined the geometry optimization of the studied molecules were done by performing the semi-empirical molecular orbital theory at the level PM3 using the restricted Hartree–Fock (RHF) procedure. Coordination around the V(IV) centre is best described as bi-permedal geometry, therefore research was initiated to examine the Conductivity behever of compound **3** was followed the activation energy. The inclusion of we found the value of conductivity was showen to be withen the range of semiconductors values ($2.69 \times 10^{7}$ ) Ω cm.

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