# COMPLEXES OF Zn(II) AND VO (IV) SULPHATES WITH KETO AND ENOL FORMS OF ISOBUTRYL ACETIC ACID, 4-AMINO BENZOIC ACID AND 4-CYANO BENZOIC ACID HYDRAZIDES.

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Abstract: Metal complexes formed by the reactions of isobutryl acetic acid hydrazide [IBAH], 4-amino benzoic acid hydrazide[4-ABAH] and 4-cyano benzoic acid hydrazide[4-CBAH] with manganese(II) and cobalt(II) ions were prepared and characterized by elemental analysis, conductance measurements, i.r., and electronic absorption spectra studies. The results showed that the hydrazides reacted with the metal salts in 1:2 molar ratio in all the complexes and acts as neutral bidentate ligands. The solubility test on the ligands and its metal(II) complexes revealed their solubility in ethanol and dimethylsulphoxide (DMSO). The molar conductance of the ligands and metal(II) complexes measured are indicative of their non-electrolytic nature. The infrared spectra of the hydrazide showed that  $\Box$  (C=O), the carbonyl stretching mode called "amide1" band, the coupling between the in-plane bending  $\Box$  (N-H) and  $\Box$  (C-N) called the "amide II" band and the stretching frequency for the amino group  $\Box(NH_2)$  all experienced shifts to lower wave numbers in the complexes suggesting the coordination of the moieties to the metal ions. The electronic spectra of the Zn(II) complexes exhibited only a high-intensity bands and are assigned to a charge transfer, while the absorption spectra of Vo(IV) complexes showed three absorption bands characterized of  ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$  transitions at 22,727-12,048 cm<sup>-1</sup> which is consistent with square pyramidal geometry. The synthesized ligands, along with their metal(II) complexes, were screened for their in vitro antibacterial activity against three Gram-negative (Escherichia coli, Klebsiella Pneumonia and Pseudomonas aeruginosa,) and two Gram-positive (Streptococcus lactis and Staphylococcus aureus) bacterial strains. The results of these studies show the that the free ligand and its metal complexes show positive effect towards Staphylococcus aureus. The metal(II) complexes show more biological activity than their ligands in all the micro organisms tested.

**Keywords:** ligands, oxovanadium (IV)complexes; 4-aminobenzoicacid antimicrobial; electronic spectra; square pyramidial geometry.

### Introduction

Keto and enol forms of compounds containing amides and amino group have not only found extensive application in organic synthesis, but several of these molecules display significant biological activity<sup>[1]</sup>. In the last decade keto and enol forms of hydrazides have received more attention mainly because of their wide application in the field of catalysis and due to their antimicrobial<sup>[2]</sup>, antituberculosis<sup>[3]</sup>, and antitumour activity<sup>[4]</sup>. They easily form stable complexes with most transition metal ions.

Keto and enol forms of hydrazides have also increased the interest in the development of the field of bioinorganic chemistry<sup>[5]</sup>. Keto form of N'-acetyl- 4-(4-X phenylsulfonyl) benzohydrazide, X=H, Cl, Br as ligand and related molecules are good ligands due to the presence of at least one carbon to oxgen atom with a localized pair of electrons. The successful application has led to the

formation of series of novel compounds with a wide range of physical, chemical and biological properties <sup>[6]</sup>, spanning a broad spectrum of reactivity and stability.

A search of literature reveals that much work has been done on complexation of keto forms hydrazides but not much on the deprotonated form . Hydrazides show keto-enol tautomerism and can acts as mononegative bidentate or mononegative tridentate<sup>[7]</sup>.

Keeping in view of the pronounced spectroscopic and biological activity of copper (II) and nickel (II) complexes, cobalt(II) and Mn (II) complexes of keto and enol form derived from isobutryl acetic acid hydrazide[IBAH], 4-amino benzoic acid hydrazide[4-ABAH] and 4-cyano benzoic acid hydrazide[4-CBAH], it was thought of worthwhile to synthesize and characterize some new metalligand complexes of Zinc (II) and Oxovanadium (IV) with this hydrazides.

The aim of this work is to: Prepare the ligands: Isobutyryl acetic acid hydrazide [IBAH], 4-Cyanobenzoyl acid hydrazide [4-CBAH], and 4-Aminobenzoyl acid hydrazide [4-ABAH] , from the following esters; Ethylisobutyrylacetate, Methyl- 4-cyanobenzoate and Ethyl-4-aminobenzoate .

To complex this ligands with the following metalloelements in solutions: Zinc(II)sulphate pentahydrate and Oxovanadium(IV) sulphate monohydrate.

To deprotonate some part of the complexes prepared from the complexation of the ligands.

To characterised these complexes by the following: I.R and UV-VIS spectral studies, conductivity measurement, melting point/decomposition, and elemental analysis.

To study possible geometry and coordination of these metallo-elements to the ligands.

To study the position / coordination point of the sulphate ions to the metal.

To study the antimicrobial screening for both the ligands and the complexes with some known bacteria.

### Material

Zinc(II)sulphate pentahydrate and Oxovanadium(IV) sulphate monohydrate, ethyl isobutryl acetate, methyl-4cyanobenzoate, ethyl-4-aminobenzoate, were of reagent grade and obtained from commercial sources (Sigma-Aldrich Chemical Ltd. and BDH) and used without further purification. All solvents used were of analytical grade.

### Experimental

### **Preparation of the hydrazides**

The hydrazides were prepared using the method describe in the literature.<sup>[8]</sup>

16.55ml [17.04gm,0.34mol] of hydrazine hydrate was added to 30ml [60.20gm, 0.38mol] of ethylisobutrylacetate in [80ml] of absolute ethanol. The mixture was refluxed for eight hours, in a 250ml round-bottomed flask. The mixture was poured into a beaker and left over night to crystallize. The crude product was recrystallised from absolute ethanol. The final crystals obtained were dried over CaCl<sub>2</sub> in a desiccator and weighed . Yield = 65%, Color = Milky. The other ligands were similarly prepared using the same procedure and equimolar quantities of hydrazine hydrate and the appropriate esters .

### **Preparation of the complexes**

## Preparation of Zn<sup>2+</sup> - [IBAH]<sub>2</sub> SO<sub>4</sub>. H<sub>2</sub>O Complex

2.20 gm [0.014mol] of Isobutric acetic acid hydrazide [IBAH] was dissolved in [50ml] of ethanol . 2.50gm [0.014mol] of Zinc sulphate heptaahydrate was also dissolved in 50ml of water, and the [IBAH] was then poured gently into the zinc solution on a magnetic stirer with constant stiring for about 8 min and left for 20 min to cool . The crystals formed were yellowish in colour , they were filtered and dried over CaCl<sub>2</sub> in the desiccator for about 5 days and weighed . Yield = 56% . The remaining complexes were similarly prepared using the same procedure and equimolar quantities of the metal salt and the respective ligands.

### **Preparation of deprotonated complex**

The preparation of deprotonated complexes can be represented by the general equation below:



## Preparation of Zn<sup>2+</sup> - [IBA]<sub>2</sub> . 2H<sub>2</sub>O Complex

4.20gm [0.014mol] of Isobutric acetic acid hydrazide [IBAH] was dissolved in [50ml] of ethanol . 4.50gm [0.025mol] of Zinc sulphate heptahydrate was also dissolved in 50ml of water. 4.0gm [0.074mol] of sodium methoxide was also dissolved in 50ml of water . The three solutions were mixed together on a magnetic stirer with constant stiring for about 5 min and left for 20 min to cool . The crystals formed was yellowish in colour , which was filtered out and washed with water, then ethanol and dried over CaCl<sub>2</sub> in the desiccator for about 5 days and weighed. Yield = 68% . The remaining complexes were similarly prepared using the same procedure and equimolar quantities of the metal salt and the respective ligands.

# Solubilities determination for ligands and their complexes

The solubilities of both ligands and the metal complexes were carried out in different solvents such as follows: Water, Methanol, Ethanol, Petroleum ether, Ethyl acetate, Chloroform, Benzene, and Dimethylsulfoxide by shaking a small amount of the ligands and the complex in a test tube and their result is shown in table 3.

### **Antimicrobial Screening**

Antimicrobial screening of ligands and the complexes in ethanol was carried out using Nutrient Agar. Petri dishes

containining alredy jelled nutrient agar were inoculated with some micro-organisms: *Escherichia Coli*, *Pseudomonas aeroginosa*, *Staphylococcus aureus*, *Streptococcus lactis* and *Klebsiella pneumonia*. The petridishes were then impregnated with disks containing the solutions of the ligand and the complexes . This was done in duplicate and incubated for 24 hrs in an oven at  $37^{0}C^{[9]}$ .

### **Results and Discussion**

All the hydrazides obtained were milky crystals which gave a moderate yield above 50 %. The ligands are quite stable in air and light . They could be stored for months without any appreciable change. The results of the melting points of the ligands are presented in Table 1. The results obtained shows that the melting points are high above 115  $^{\circ}$ C , and sharp, indicating the purity of the prepared ligands<sup>[10]</sup>. Table 1

The ligand used in this work are prepared by the general equation below :

# $RCOOR'' + N_2H_4 \xrightarrow{C_2H_5OH} R - CO - NH - NH_2 + ROH + H_2O$

[
$$R_1 = (CH_3)_2 CHCOCH_2$$
,  $C_6H_4CN$  and  $C_6H_4NH_2$ ,  $R_2 = CH_3$  or  $C_2H_5$ ]

The complexes of the hydrazides were synthesized , using M (II) sulphates , where ( $M = Zn^{2+}$ ,  $VO^{2+}$ ). The reaction of equimolar quantities of the metal (II) sulphate salts and the appropriate hydrazide yielded complexes having 1:2 metal to ligand stoichiometry , according to the general equation .

$$MSO_4.nH_2O_+ R_1COCH_2CONHNH_2 \xrightarrow{H_2O} M(R)$$

[
$$R_1 = (CH_3)_2CH$$
,  $C_6H_4CN$  and  $C_6H_4NH_2$ ,  $R_2 = CH_3$  or  $C_2H_5$ ,  $M = Zn^{2+}$ ,  $VO^{2+}$ ,  $n = 1-2$ ]

while the deprotonated complexes was prepared by the reaction of equimolar quantities of the metal (II) sulphate salts with the appropriate hydrazide and sodium methoxide yielded complexes having 1:2 metal to ligand stoichiometry , according to the general equation .

$$MSO_4 .nH_2O_+ {}^2R_1COCH_2CONHNH_2 + RO^{-}Na^{+} \xrightarrow{H_2O} M(RCOCH_2C = N - NH_2)_2$$

$$[R_1 = (CH_2)_2CH_1, C_6H_4CN_1, and C_6H_4NH_2, R_2 = CH_2, C_2H_5, M = Co_1, Mn, n = 1-5_1]$$

The complexes obtained were fine crystals with good yield (45 -80%), high melting points above 180°C, with decomposition observed in some of the complexes . The result in Table 1, shows that the complexes have 1:2 stoichometry with the ligands. All the complexes are colour solids and crystalline substances, They are quite stable in air and light, and could be stored for months without any appreciable change. The results of elemental analyses are presented in Tables 1. The results obtained are in good agreement with those calculated for the suggested formulae and the melting points are sharp, indicating the purity of the prepared complexes. The analytical data Table 1 shows that the complexes have the general empirical formulae  $[ML_2]SO_4.nH_2O$  and  $[ML_2].nH_2O$  (where L = IBAH, 4-CBAH, 4 -ABAH, IBA, 4-CBA, 4-ABA, n = 1-2 and M = Zn , VO.<sup>[11]</sup>

#### **Solubility**

The solubility of ligands and their complexes in table 2 shows that both the complexes and the ligands were carried out in different solvents and they are not soluble in most organic solvents except ethanol and dimethyl sulphoxide and sparingly soluble in methanol. There is no clearly different between the solubility of deprotonated and protonated complexes except in the time taken for them to

 $\begin{array}{c} O \\ | \\ mol \\ nol \end{array} N M(RCOCH_2C = N - NH_2)_2 \cdot nH_2O + NaHSO_4 + R_2OH \\ _2H_5 M = Co , Mn, n = 1-5 ]$ 

actually dissolve in all the solvents used. This suggests a polymeric nature / structure for this compounds.  $^{[12]}$ 

### **Infrared** spectra

The IR data of hydrazides [IBAH,4-CBAH,4-ABAH] and their complexes are presented in **Table 2**. The IR spectra of the complexes were compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation. There were some guide peaks in the spectra of the ligands, which were helpful in achieving this goal. The position and/or the intensities of these peaks are expected to change upon chelation. The most interesting features of this spectra are listed in **Table 2**. There is a general displacement due to the coordination process<sup>[13]</sup>.

There are three major vibrations that have been used successfully to infer coordination of ligands to the metal in the spectra of complexes of hydrazides.<sup>[233]</sup> These are the  $\Box$  (C=O), the carbonyl stretching mode called "amide1" band, the coupling between the in-plane bending  $\delta$ (N-H) and  $\Box$  (C-N) called the "amide II" band and the stretching frequency for the amino group  $\Box$  (NH<sub>2</sub>).

Assignment of bands above  $3000 \text{cm}^{-1}$  are only tentative since bands due to  $\Box(OH)$ ,  $\Box(NH)$ , and  $\Box(NH_2)$  appear in this region as unresolved bands,<sup>[13-14]</sup> also band complexity does not allow a distinction between stretching frequencies of the -NH group and those of the -NH<sub>2</sub> group.<sup>[13-14]</sup>

In all the ligands the amino group band  $\Box(NH_2)$  was observed as a medium strong band centred at 3855, 3281 and 3420cm<sup>-1</sup>. This band was shifted to lower wave number in all the complexes i.e between 3000 cm<sup>-1</sup> – 3410cm<sup>-1</sup> including the deprotonated complexes. This indicates coordination of the metal ions to the amino group.<sup>[13]</sup>

Similarly, the "amide I" band (i.e. ( $\Box C=O$ ) was observed at 1666cm<sup>-1</sup>, 1631cm<sup>-1</sup> and 1608cm<sup>-1</sup> for the ligands was shifted to 1650-1620 cm<sup>-1</sup> in the complexes, indicating that the ligands also coordinate through the carbonyl oxygen.<sup>[65,72,78]</sup> Since molecular association in the solid state of hydrazides have been reported to lower the  $\Box(NH_2)$  and  $\Box(C = O)$  bands.<sup>[13,14,15]</sup> The "amide II" band was observed at 1528 cm<sup>-1</sup>, 1561 cm<sup>-1</sup> and 1506 cm<sup>-1</sup> in all the ligands, It was also shifted in all the complexes.

A significant change observed in the infrared spectra of the oxovanadium complexes compared to their respective ligands is the appearance of strong absorption band due to V=O stretching frequency in the complexes. All the complexes exhibited a strong V=O stretching band at 920 - 981 cm<sup>-1</sup>, which suggests monomeric square pyramidal structures . The  $\Box$ (V=O) stretching frequency of the hydrazide derivative occurs at 955 cm<sup>-1</sup>, which is also consistent with polymeric system involving ....O=V....V=O.... bridge.<sup>[15]</sup> These bands were absent in the spectra of the ligands.

Further conclusive evidence of the coordination of the hydrazides with the metal ions was shown by the appearance of new bands at 300 - 400 and 300 - 550  $\text{cm}^{-1}$ assigned to the metal - nitrogen (M-N) and metal-oxygen (M-O) vibrations, respectively. Although this bands were too weak to be observed in some of the complexes. These bands were absent in the spectra of the uncomplexed hydrazide thus confirming participation of the O and N atoms in the coordination. It has been established that the metal-ligand vibrational modes are very sensitive to substituent effects.<sup>[14,15]</sup> This was proposed on the basis of isotopic labeling studies  $({}^{15}N - and {}^{18}O - labelling)$ . The substituent effects were based on the position of substitution rather than on the nature of the substituents. The v(M-O) bands are observed to exhibit higher vibrational frequencies than the v(M-N) bands for the meta - substituents while the order is reversed for the parasubstituents regardless of the nature of the substituents . It was suggested that the transmission of the substituent effects in the hydrazide complexes are propagated largerly by a mesomeric mechanism.

The ligands are likely bidentate forming five-membered chelate rings with the metal ions through the primary amino nitrogen and the carbonyl oxygen. The spectral features observed are consistent with the structural patterns of the compound and those of the hydrazides already reported in the literature.<sup>[15]</sup>

### **Electronic spectra**

The electronic spectral measurements were used for assigning the stereochemistries of metal complexes based on the positions and number of d-d transition peaks. The

electronic absorption spectra of metal(II) complexes were recorded in  $10^{-3}$  M solutions of each complex in ethanol in the range 200 –1000 nm at room temperature.

For d<sup>10</sup> ions, the UV spectrum provides no information about the environment.<sup>[16]</sup> The Zn (II) complexes are diamagnetic, as expected for the d<sup>10</sup> configuration.<sup>[17]</sup> The diamagnetic Zn(II) d<sup>10</sup> complexes do not exhibit any characteristic *d-d* transitions. The electronic spectra of the Zn(II) complexes exhibited only a high-intensity band at 28,350–29, 145 cm<sup>-1</sup> and are assigned to a charge transfer. However, in analogy with those described for Zn(II) complexes containing N-O donor hydrazides from literature and according to the empirical formulae, couple with the infrared spectrum of this complexes an octahedral geometry can be proposed for the complexes<sup>[17]</sup>

Oxovanadium(IV) complexes have extremely short V=O bond compared to the other equatorial vanadium-ligand (V-L) bonds. Such complexes are therefore under tetragonal compression such that of the five 3d orbitals the dz<sup>2</sup> orbital is the most destabilized. The relative ordering of the d orbitals is then:  $d_{xy} < d_{yz} < d_{x2-y2} < d_{z2}$ . Such complexes should exhibit three d-d transitions:  $d_{xy} \rightarrow d_{xz}$ ,  $d_{yz}$ ;  $d_{xy} \rightarrow d_{z2}$ .<sup>[16,17]</sup> The assignments of electronic spectral bands of VO<sup>2+</sup> complexes have been a matter of controversy. Ballhausen and Gray (BG) have provided a convenient energy level scheme for these complexes. In general, oxovanadium (IV) complexes display 3 low intensity bands in the 10,000-30,000 cm<sup>-1</sup> range<sup>[18]</sup>.

According to the BG scheme, the first and subsequent charge transfer transitions are predicted to occur at higher energies (beyond 30,000 cm<sup>-1</sup>) and often band III is not observed, but is thought to be buried beneath the low energy tail of the much more intense charge transfer band. Following the ordering of energy levels (BG scheme), the first band, which is centered at ca 13,000 cm<sup>-1</sup>, is assigned to an unresolved band resulting from the  $d_{xy} \rightarrow d_{xz}$ ,  $d_{yz}$  ( $^2B_2 \rightarrow ^2E$ ) transition. The second band (in region 15,000-16,000 cm<sup>-1</sup>) is attributed to  $d_{xy} \rightarrow d_{x2-y2}$  ( $^2B_2 \rightarrow ^2B_1$ ) transitions. The band at about 23,000 cm<sup>-1</sup> may either be assigned to the  $d_{xy} \rightarrow d_{z2}$  ( $^2B_2 \rightarrow ^2A_1$ ) transition or thought to be a low energy charge transfer band.

The expected d-d transitions for the five coordinate square pyramidal VO(IV) complex which consist of three bands as explained above was found in this work. The electronic spectra of all oxovanadium(IV) complex recorded in ethanol as a solvent exhibited three bands between 300 nm , and 800 nm characteristics of the transition  ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$  and  ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$ . Therefore, it is possible to propose the geometry of the oxovanadium complexes to be a five coordinated square pyramidal with a formula based on the physical, conductance, i.r. and u-v data.<sup>[18,19]</sup>

### **Biological activity**

In the light of interesting antimicrobial activities of the coordination complexes, the ligands and their corresponding complexes were screened for antibacterial activity against *Staphylococcus Aureus*, *Streptococcus lactis*, *Klebsiella pneumonia*, *Pseudomonas aeruginosa*, and *Escherichia*  *coli*, by nutrient agar method. The radial growth of the colony was recorded on completion of the incubation and the mean diameter for each complex at a single concentration was recorded.<sup>[9]</sup> The screening data of the inhibition of the bacteria are given in (Table 4). From the data, it is clear that the metal complexes of the hydrazides have greater inhibiting power than the free ligands .

The comparison of the biological activities of the synthesized compounds and the free ligands shows that

the free ligand and its metal complexes show positive effect towards *Staphylococcus aureus*. Such increased activity of the metal chelates can be explained based on chelation theory.<sup>[20]</sup> On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups.<sup>[21]</sup>

S/n	Compounds	Emperical Formulae	Formular Weight	Colour	M.P/Dec Temp °C	% yield	Molar Cond. Ohm <sup>-1</sup> $cm^2$	Eleme Fou	ental Analysis Ind (Calc)	
%S0	$O_4$									%N 1.
H]	C <sub>6</sub> H <sub>12</sub> N	<sub>2</sub> O <sub>2</sub> 1	44.1718 Milky	190	65	1.3	-		-	[IB
2.	[4-CBAH]	C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> O	161.1426	Milky	118	62	1.1	-	-	
3.	[4-ABAH]	$C_7H_9N_3O$	151.1660	Milky	212	68	1.5	-	-	
4.	Zn[IBAH] <sub>2</sub> SO <sub>4</sub>	.2H <sub>2</sub> O C <sub>12</sub> H <sub>28</sub> N <sub>4</sub> O	<sub>10</sub> SZn 485.82774	Yellowish	210	56	1.5	13.39 (13.45)	19.87 (19.77)	
5.	Zn[4-CBAH] <sub>2</sub> S	O <sub>4</sub> .H <sub>2</sub> O C <sub>16</sub> H <sub>16</sub> N <sub>6</sub>	O <sub>7</sub> SZn 501.7905	Brownish	260	52	1.9	13.81 (13.03)	19.25 (19.14)	
6.	Zn[4-ABAH] <sub>2</sub> S	$SO_4.H_2O$ $C_{14}H_{20}N_0$	<sub>5</sub> O <sub>7</sub> SZn 481.8008	Pale-brown	267	62	1.7	14.10 (13.57)	18.92 (19.94)	
7.	Zn[IBA] <sub>2</sub> . 2H <sub>2</sub>	O C <sub>12</sub> H <sub>26</sub> N	<sub>4</sub> O <sub>6</sub> Zn 387.7482	Yellowish	245	68	3.1	16.61 (16.89)	-	
8.	Zn[4-CBA] <sub>2</sub> . H	$_{2}O$ $C_{16}H_{14}N_{6}O$	O <sub>3</sub> Zn 403.711	Brownish	234	52	2.7	16.21	(15.13)	
9.	Zn[4-ABA] <sub>2</sub> . 2	$2H_2O$ $C_{14}H_{20}N_6$	O <sub>4</sub> Zn 401.7366	Dirty-brown	191	67	3.0	16.01	(16.28)	
10.	VO[IBAH] <sub>2</sub> SO	$D_4.H_2O$ $C_{12}H_{26}N_4$	O <sub>9</sub> SV 453.3639	Reddish-purpl	e 292	56	1.7	11.28 (11.24)	21.32 (21.19)	
11.	VO[4-CBAH]	$_{2}SO_{4}.H_{2}O$ $C_{16}H_{16}$	N <sub>6</sub> O <sub>7</sub> SV 487.3420	Bluish-green	212	72	1.5	10.32 (10.45)	19.55 (19.71)	
12.	VO[4-ABAH]	$_{2}$ SO <sub>4</sub> .H <sub>2</sub> O C <sub>14</sub> H <sub>2</sub>	20N <sub>6</sub> O <sub>7</sub> SV 467.3523	Reddish-pur	ple 289	63	1.9	11.26 (10.90)	20.33	

# Table 1: Analytical data of ligand and complexes

13.	VO[IBA] <sub>2</sub> . H <sub>2</sub> O	$C_{12}H_{24}N_4O_5V$	355. 2844	Maroon	199	71	3.1	14.32 (14.34)	-
14.	VO[4-CBA] <sub>2</sub> . H <sub>2</sub> O	$C_{16}H_{14}N_6O_3V$	389.2625	Dark-brown	189	76	2.5	13.51 (13.09)	-
15.	VO[4-ABA]2 .2H2O	$C_{14}H_{20}N_6O_4Ni$	395.0400	Yellowish	245	72	3.0	15.01	- (14.86)

# Note : Figure in bracket are calculated values

S/n	Compounds	□(OH)	Amide I □(C-O/C=O)	A □(NH/NH2)	Amide II		-N) 🗆 (	(M-O)	$\Box$ (SO <sub>4</sub> <sup>2-</sup> ) $\Box$	(V=O)
1.	IBAH	-	1666	3855, 3460	1528	-	-	-	-	
2.	4-CBAH	-	1631	3281	1561	-	-	-	-	
3.	4-ABAH	-	1608	3420, 3466	1506	-	-	-	-	
4.	Zn[IBAH] <sub>2</sub> SO <sub>4</sub> .2H <sub>2</sub> O	3500	1625	3250	1456	400	488	730	-	
5.	Zn[4-CBAH] <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O	3450	1630	3430	1566	420	468	740	-	
6.	Zn[4-ABAH] <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O	3452	1640	3100,3450	1550	400	490	770	-	
7.	Zn[IBA] <sub>2</sub> . 2H <sub>2</sub> O	-	1640	3280	1556	320	500	-	-	
8.	Zn[4-CBA] <sub>2</sub> . H <sub>2</sub> O	3400	1635	3430	1479	378	505	-	-	
9.	Zn[4-ABA] <sub>2</sub> . 2H <sub>2</sub> O	3450	1640	3100, 3400	1470	399	478	-	-	
10.	VO[IBAH] <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O	3550	1630	3220	1450	310	496	710	959	
11.	VO[4-CBAH] <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O	3400	1630	3380, 3400	1465	400	483	700	966	
12.	VO[4-ABAH] <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O	3400	1640	3090, 3400	1450	410	490	740	985	
13.	VO[IBA] <sub>2</sub> . H <sub>2</sub> O	3500	1650	3250	1466	400	500	-	979	

# Table II. Diagnostic IR bands for the ligands and complexes (cm<sup>-1</sup>)

14.	VO[4-CBA] <sub>2</sub> .H <sub>2</sub> O	3450	1650	3410	1570	400	467 -	-	974
15.	VO[4-ABA]2 . 2H2O	3550	1640	3095,3400	1556	400	488 -	-	971

# Table III. Electronic spectral data for the complexes

S/n	Compounds	$\lambda \max (nm)$	$\lambda \text{ cm}^{-1}$	Assignments	Probable Geometry
1. Z	Zn[IBAH] <sub>2</sub> SO <sub>4</sub> .2H <sub>2</sub> O	349	28,680	СТ	Octahedral
2. Zr	n[4-CBAH] <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O	353	28,350	СТ	Octahedral
3. Z	n[4-ABAH]2SO4.H2O	352	28,445	СТ	Octahedral
4. Z	n[IBA] <sub>2</sub> . 2H <sub>2</sub> O	343	29,145	СТ	Octahedral
5. Z	$Zn[4-CBA]_2$ . $H_2O$	350	28,610	СТ	Octahedral
6. Z	$Zn[4-ABA]_2$ . $H_2O$	354	28,225	CT	Octahedral
7. V	/O[IBAH] <sub>2</sub> SO <sub>4</sub> . H <sub>2</sub> O	830 665 440	12,048 15,037 22,727	${}^{2}B_{2} \rightarrow {}^{2}E$ ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$ ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$	Square pyramidal
8. V	/O[4-CBAH] <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O	647 573 377	15,456 17,452 26,525	${}^{2}B_{2} \rightarrow {}^{2}E$ ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$ ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$	Square pyramidal
9.	VO[4-ABAH] <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O	647 573 377	15,456 17,452 26,525	${}^{2}B_{2} \rightarrow {}^{2}E$ ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$ ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$	Square pyramidal
10.	VO[IBA] <sub>2</sub> . H <sub>2</sub> O	830 665 440	12,048 15,037 22,727	${}^{2}B_{2} \rightarrow {}^{2}E$ ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$ ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$	Square pyramidal
11. V	O[4-CBA] <sub>2</sub> .H <sub>2</sub> O	830 665 440	12,048 15,037 22,727	${}^{2}B_{2} \rightarrow {}^{2}E$ ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$ ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$	Square pyramidal
12.	VO[4-ABA]2 . 2H2O	830	12,048	${}^{2}B_{2} \rightarrow {}^{2}E$	

665	15,037	$^{2}B_{2} \rightarrow ^{2}B_{1}$	Square pyramidal
440	22,727	$^{2}B_{2} \rightarrow ^{2}B_{1}$	

### Table IV : Antimicrobial activity result of Ligands and Complexes

S/n	Compounds	Staphy.A	Strep.L	Kleb.P	E. Coli	Pseudo.A
1.	IBAH	+				
2.	4-CBAH	+ +				
3.	4-ABAH	+				
4. Zr	[IBAH]SO4.2H <sub>2</sub> O	+	+++	++		+++
5. Zi	n[4-CBAH] <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O	+	+++	+++	+++	++
6. Zr	1[4-ABAH]2SO4.H2O	+	++	++	++	+++
7. Zn	[IBA] <sub>2</sub> . 2H <sub>2</sub> O	+ +	+	+++	+++	++
8. Zr	[4-CBA] <sub>2</sub> . H <sub>2</sub> O	+ +	++	+++	+ +	+++
9. Zr	[4-ABA] <sub>2</sub> . 2H <sub>2</sub> O	+ +	+	+++		·
10. V	O[IBAH] <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O	+	++	+ +	+ +	+ +
11. V	/O[4-CBAH] <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O	+ +	+++		+ +	+ +++
12. V	/O[4-ABAH] <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O	++	+	+ +	+ +	+ +
13. V	O[IBA] <sub>2</sub> . H <sub>2</sub> O	+	+++	+	+++	+
14. V	O[4-CBA] <sub>2</sub> . H <sub>2</sub> O	+ +	+ +	+ +	+++	++
15. V	O[4-ABA]2 .2H2O	+ +	+++	+ + +	+	+ +

**Key** : High active = +++ (inhibition zone >12mm); Moderately active = ++ (inhibition zone >9-12mm)

Slightly active = + (inhibition zone > 6 - 9mm); Inactive = - - (inhibition zone < 6mm),  $E \cdot coli$  - Escherichia coli;  $Pseudo \cdot A - Pseudomonas aeruginosa$ ;  $Staphy \cdot A - Staphylococcus aureus$ ; Strep.L - Streptococcus lactis; Kleb.P - Klebsiella Pneumonia

### Conclusion

On the basis of their physic chemical properties, the following structures are suggested



Scheme 1: For 1:2 octahedral geometry, where  $M = Zn^{2+}$  and  $R = (CH_3)_2 CHC = OCH_2$ ,  $C_6H_4CN$  and  $C_6H_4NH_2$ 



Scheme 2 : For 1:2 square pyramidal geometry, where  $M = VO^{2+}$ , and  $R = (CH_3)_2CHC = OCH_2$ ,  $C_6H_4CN$  and

 $C_6H_4NH_2$ 

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