

COMPLEXES OF Ni (II) AND Cu (II) SULPHATES WITH KETO AND ENOL FORMS OF ISOBUTRYL ACETIC ACID, 4-AMINO BENZOIC ACID AND 4-CYANO BENZOIC ACID HYDRAZIDES .

J.N.Nwabueze¹, O.W.Salawu²

¹Department of Chemistry, Faculty of natural science, University of Abuja, PMB 117, Gwagwalada, Abuja, Nigeria

² Department of Chemistry, Faculty of Natural Sciences, Kogi State University, PMB 1008, Anyigba, Kogi State, Nigeria.

* correspondence author

*E-mail: olalekansalawu.1974@gmail.com

Abstract: Metal complexes formed by the reactions keto and enol forms of isobutryl acetic acid hydrazide [IBAH], 4-amino benzoic acid hydrazide [4-ABAH] and 4-cyano benzoic acid hydrazide [4-CBAH] with nickel(II) and copper(II) sulphate 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 $\nu(\text{C}=\text{O})$, the carbonyl stretching mode called “amide I” band, the coupling between the in-plane bending $\nu(\text{N}-\text{H})$ and $\nu(\text{C}-\text{N})$ called the “amide II” band and the stretching frequency for the amino group $\nu(\text{NH}_2)$ 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 copper(II) complexes show a single broad band between 13,004 -15,168 cm^{-1} assigned to a $d \rightarrow d$ transition for a square planar geometry. The electronic absorption spectra of Ni(II) complexes of showed two bands respectively around 20,000 – 14,006 cm^{-1} and assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ respectively which are consistent with a six coordinate octahedral 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 that the free ligands and their 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: Hydrazide; 4-cyanobenzoic acid; 4-aminobenzoic acid antimicrobial; infra-red; Metal-complexes

Introduction

The coordination chemistry of nitrogen-oxygen donor ligands is an interesting area of research^[1]. Complexes of substituted hydrazine such as hydrazides, thiosemicarbazides, hydrazones and diacylhydrazines are of general interest as models for bioinorganic processes^[2].

In fact the rapidly developing field of bioinorganic chemistry is centered on the presence of metal complexes in the biological systems.^[3] Moreover, the study of coordination compounds has enabled the inorganic chemist to make significant progress in refining the concept of chemical bonding and to explain the influence

that bonding has on the various properties of the compounds .

Most of the transition metal complexes are colored and their colors are different from the transition metal salts and the ligands, then this is an important indication to the occurrence of coordination^[1]. Therefore the colored complexes show different characteristic absorption bands in their position, intensity

or both when compared with the bands of the ligands and the metal salts and this is another indication for occurrence of coordination^[4].

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^[6].

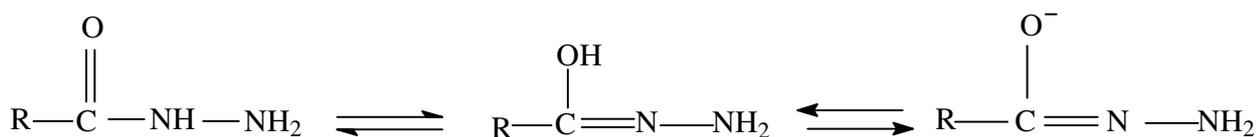


fig 1 : keto - enol tautomerism of hydrazide

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 metallo-elements in solutions: Copper(II)sulphate pentahydrate Nickel(II) sulphate hexahydrate.

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.

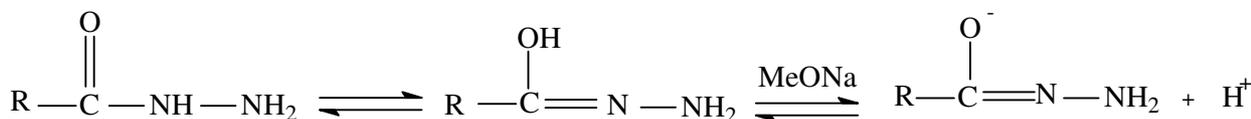
To study the antimicrobial screening for both the ligands and the complexes with some known bacteria.

Material

CuSO₄.5H₂O, NiSO₄.6H₂O, ethyl isobutyryl acetate, methyl-4-cyanobenzoate, 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.^[7] 16.55ml [17.04gm,0.34mol] of



Preparation of Cu²⁺ - [IBA]₂ . 2H₂O Complex

3.50gm [0.022mol] of Isobutyric acetic acid hydrazide [IBAH] was dissolved in [50ml] of ethanol 4.50gm [0.018mol] of Copper(II) sulphate pentahydrate was also dissolved in 50ml of water. 4.0gm [0.074mol] of sodium methoxide (CH₃ONa) was dissolved in 50ml of water. In all the cases the sodium methoxide concentration was slightly in excess. The three solutions were mixed together on a magnetic stirrer with constant stirring for about 12 min and left for 40 min to cool. The crystals formed was green in colour, which was filtered out and

hydrazine hydrate was added to 30ml [60.20gm, 0.38mol] of ethylisobutyrylacetate 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 CaCl₂ 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 Cu²⁺ - [IBAH]₂ SO₄. H₂O Complex

2.5 gm [0.02 mol] of isobutyric acetic acid hydrazide [IBAH] was dissolved in [50ml] of ethanol. 2.50gm [0.01mol] of Copper(II) sulphate pentahydrate was also dissolved in 50ml of water, and the [IBAH] was then poured gently into the copper(II) solution on a magnetic stirrer with constant stirring for about 10 min and left for 30 min to cool. The crystals formed were dark-green in colour, they were filtered and dried over CaCl₂ in the desiccator for about 3 days and weighed. Yield = 72%. 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 deprotonation of the ligands can be represented by the general equation below

washed with water, then ethanol and dried over CaCl₂ 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.

Antimicrobial Screening

Antimicrobial screening of the ligands and the complexes in ethanol was carried out using Nutrient Agar. Petri dishes containing already jelled nutrient agar were inoculated with some micro-organisms: *Escherichia Coli*,

Pseudomonas aeruginosa, *Staphylococcus aureus*, *Streptococcus lactis* and *Klebsiella pneumonia*. The petri-dishes 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°C.

Instrumental Measurements

The conductivity measurement were made using Equiptronics model numbered Eq-660A Conductivity Meter. Melting points are taken in open capillaries and are uncorrected. IR spectra were recorded on a FTIR-8400S Fourier Transform Infrared Spectrophotometer using KBR pellets technique. The UV-Visible spectra

were recorded on a 21D Milton Roy UV-VIS spectrophotometer in absolute ethanol.

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. 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 °C, and sharp, indicating the purity of the prepared ligands^[7]. Table 1

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



[R₁ = (CH₃)₂CHCOCH₂, C₆H₄CN and C₆H₄NH₂, R₂ = CH₃ or C₂H₅],

The complexes of the hydrazides were synthesized, using M (II) sulphates, where (M = Cu, Ni). The reaction of equimolar quantities of the metal (II) sulphate salts and

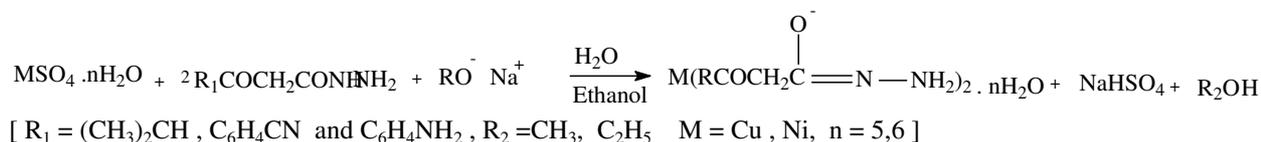
the appropriate hydrazide yielded complexes having 1:2 metal to ligand stoichiometry, according to the general equation.



[R₁ = (CH₃)₂CH, C₆H₄CN and C₆H₄NH₂, R₂ = CH₃ or C₂H₅, M = Cu, Ni, n = 5,6],

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.



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 stoichiometry. All the complexes are coloured solids and crystalline substances, the colours of the copper complexes range from green to greyish green which is normal for copper (II) complexes except Cu[H₂L₂]₂.2H₂O and Cu[H₃L₂]₂SO₄.H₂O which is brown and dirty brown respectively. 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 [ML₂]₂SO₄.nH₂O and [ML₂]₂.nH₂O (where L = IBAH, 4-CBAH, 4-ABAH, IBA, 4-CBA,4-ABA, n = 5,6 and M = Ni(II), Cu(II)).^[8,9]

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 actually dissolve in all the solvents used. This suggests a polymeric nature / structure for this compounds.^[10]

Infrared spectra

Solid state infrared spectra of the ligands and the complexes are analyzed and the most interesting features are listed in Table 2. There is a general displacement due to the coordination process.

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.^[11] These are the ν(C=O), the carbonyl stretching mode called "amide I" band, the coupling between the in-plane bending δ(N-H) and ν(C-N) called the "amide II" band

and the stretching frequency for the amino group $\nu(\text{NH}_2)$.

Assignment of bands above 3000cm^{-1} are only tentative since bands due to $\nu(\text{OH})$, $\nu(\text{NH})$, and $\nu(\text{NH}_2)$ appear in this region as unresolved bands,^[12] also band complexity does not allow a distinction between stretching frequencies of the $-\text{NH}$ group and those of the $-\text{NH}_2$ group.^[1]

In all the ligands the amino group band $\nu(\text{NH}_2)$ was observed as a medium strong band centred at 3855, 3281 and 3420cm^{-1} . This band was shifted to lower wave number in all the complexes i.e between 3000cm^{-1} – 3410cm^{-1} including the deprotonated complexes. This indicates coordination of the metal ions to the amino group.^[11]

Similarly, the “amide I” band (i.e. $\nu(\text{C}=\text{O})$) was observed at 1666cm^{-1} , 1631cm^{-1} and 1608cm^{-1} for the ligands was shifted to $1650\text{--}1620\text{cm}^{-1}$ in the complexes, indicating that the ligands also coordinate through the carbonyl oxygen.^[11] Since molecular association in the solid state of hydrazides have been reported to lower the $\nu(\text{NH}_2)$ and $\nu(\text{C}=\text{O})$ bands.^[1] The “amide II” band was observed at 1528cm^{-1} , 1561cm^{-1} and 1506cm^{-1} in all the ligands, It was also shifted in all the complexes between $1486\text{--}1456\text{cm}^{-1}$ in the cobalt(II) complexes.

The broad band in the region $3034\text{--}3740\text{cm}^{-1}$ is accorded to $\nu(\text{O-H})$ stretching vibrations, a feature indicating the presence of water. Bands around this region may however be assigned to $\nu_s(\text{OH})$ of water molecules or hydrogen bonding. This band is supported by an additional band appearing in the range $890\text{--}750\text{cm}^{-1}$ attributed to the distortion vibration of the $\nu(\text{O-H})$ bond, indicates the presence of water molecules, or confirms the presence of lattice held water molecules in the complexes. The water molecules could be lattice or coordinated water.^[11,12]

The spectra of some of the complexes show a very sharp non-ligand band around 770cm^{-1} which are due to the ν_3 and ν_2 vibrational modes of uncoordinated sulphate group, since the stretching vibrations of the sulphate ion are usually observed as a sharp singlet around 1100cm^{-1} and a medium band around 680cm^{-1} .^[13] The sulphate ions are therefore probably in the outer coordination sphere for this complexes, since it fall in the range at which sulphate absorbs $1120\text{--}1080\text{cm}^{-1}$.^[11-13] In the spectra of deprotonated complexes, the ν_4 band expected around 1100cm^{-1} was not found in all the complexes, probably lost in these complexes, this is an indication that sulphate group was not present in these complexes.^[13]

The nature of the metal-ligand bonding is confirmed by the newly formed bands at $\sim 500\text{cm}^{-1}$ and 400cm^{-1} in the spectra of complexes, which is tentatively assigned to M-O and M-N vibrations^[1].

The spectral features observed are consistent with the structural patterns of the compound and those of the hydrazides already reported in the literature.^[14]

Electronic spectra

The Cu(II) ion with d^9 -configuration in a complex can be either distorted octahedral or tetrahedral or square planar geometry.^[14] The electronic spectra of all the copper (II)

complexes show a single broad $d\rightarrow d$ bands between $600\text{nm} - 900\text{nm}$. The bands are located at $15,168\text{cm}^{-1}$ (659nm), $15,384\text{cm}^{-1}$ (650nm), $13,000\text{cm}^{-1}$ (769nm) for the isobutylic acetic acid hydrazide, 4-cyanobenzoic acid hydrazide complexes and all the deprotonated complexes of isobutylic acid hydrazide and 4-aminobenzoic acid hydrazide, which are consistent with an octahedral geometry for these complexes^[15,16] Thus, an octahedral geometry is proposed for all the copper(II) complexes, since octahedral copper(II) chelates usually show a $d\rightarrow d$ band in the range $11,000\text{--}17,000\text{cm}^{-1}$.^[20,206,209] These results are consistent with octahedral structures, since the four lower orbitals are often so close together in energy, that individual transitions therefrom to the upper d level cannot be distinguished - hence the single absorption band.^[14-16]

The electronic spectrum of the nickel (II) complexes show two $d\rightarrow d$ bands located around $20,000\text{cm}^{-1}$ (500nm) and $14,000\text{cm}^{-1}$ (714nm). This bands have been assigned to the spin - allowed transitions, ${}^3A_{2g}\rightarrow{}^3T_{1g}(\text{P})$ and ${}^3A_{2g}\rightarrow{}^3T_{1g}(\text{F})$ which is usually observed for octahedral nickel (II) complexes.^[17] The third spin - allowed transition to the ${}^3T_{2g}$ level, usually expected in the near infrared region below $10,000\text{cm}^{-1}$ could not be observed as the region is outside the spectral range of the instrument.

The single band in the spectrum of deprotonated complexes of 4-cyanobenzoic acid hydrazide and 4 - aminobenzoic acid hydrazide is split giving rise to two maxima at $15,384\text{cm}^{-1}$ (650nm) and $13,793\text{cm}^{-1}$ (725nm). This band has been assigned to the ${}^3T_1(\text{F})\rightarrow{}^3T_1(\text{P})$ transition in tetrahedrally coordinated nickel(II) ion. Thus, these transitions and the values of the field parameters correspond to those characteristic for a distorted octahedral and tetrahedral geometry for all the nickel (II) complexes.^[17,18]

Biological activity

1. The free ligand and its metal complexes show positive effect towards *Staphylococcus aureus*.
2. The Ni(II) complexes show higher antibacterial effect towards *Staphylococcus .A* and *Escherichia .C* than any of the complexes.
3. The copper(II), and Nickel (II) complexes have more biological activity than their ligands, in all the micro organisms tested with .

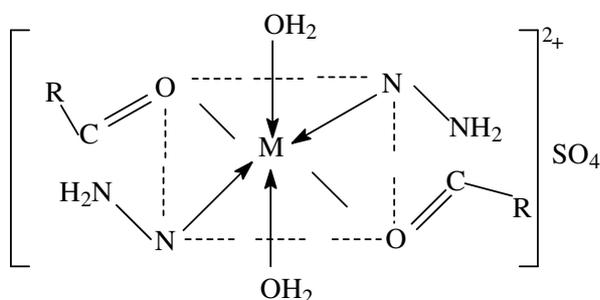
Such increased activity of the metal chelates can be explained based on chelation theory.^[19] On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups.^[20] Further, it increases the delocalization of π electrons over the whole chelate ring and enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms.^[21] These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organisms.^[21] Although it is difficult to make out an exact structure reactivity relationship between the microbial activity and the structure of these complexes, it can possibly be concluded that the complexation as well as

addition of a substrate enhances the activity of the complexes. The variation in the toxicity of different antimicrobial agents against different organisms as suggested by Garrod et al^[22] depends either on the impermeability of the cell or differences in ribosome to the antimicrobial agents. Though the results suggested that the metal complexes have remarkable toxic property, than their hydrazides, this shows that complexes of

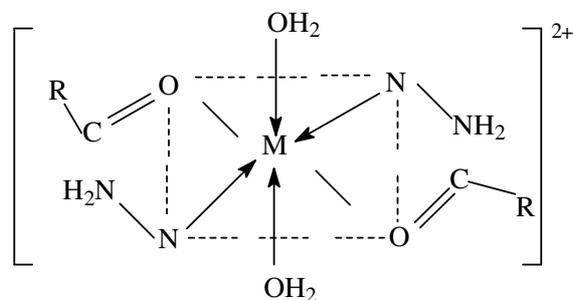
hydrazides inhibit the growth of organisms to a greater extent.

Conclusion

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



A



B

Scheme A. for 1:2 octahedral geometry, where M = Cu^{II} and Ni^{II} and R= (CH₃)₂CHC=OCH₂, C₆H₄CN and C₆H₄NH

REFERENCES

- Orgel.L.E., (1966) , "An Introduction to Transition Metal Chemistry Ligand Field Theory", Methuen, p.55 .
- Sone K., Fukuda Y., (1987), Inorganic Thermochemistry, Inorganic Chemistry Concept, Springer-Verlag: Heidelberg, vol. 10.
- Bhyrappa.P.; Young.J.K.; Moore.J.S.; Suslick.K.S., (1996), Hydrazide – Hydrazones and metal ions: Synthesis and Catalysis.
- Furst A.(1963), *The Chemistry of Chelation in Cancer*. 3rd ed. Springfield, Ill: Thomas.
- Williams DR. (1972) . *Journal of the Chemical Society. Dalton Transactions*. (7): 790–797.
- Jones AD, Williams DR. (1971) . *Journal of the Chemical Society A*: 3159–3162.
- Sinn E, Harris CM. (1969) ; Schiff base metal complexes as ligands. *Coordination Chemistry Reviews*. 4(4):391–422.
- Bjerrum.J., (1941) , "Metal ions Formation in Aqueous Solution", Haase, Copenhagen .
- Castillo-Blum.S.E.; Barba-Behrens.N., (2000). *Coord. Chem. Rev.* 196, 3-10 .
- Bjerrum.L., (1999) , "Metal (II) ions with hydrazine – hydrazide: Formation in Aqueous Solution", *Chem. Rev.* 10, 1875-1914 .
- Nakamoto K., (1992), *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn., John Wiley and Sons, New York,
- Bellamy L.J., (1973), *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London.
- Percy.G.C., Thornton.D.A., (1972) . *J. Inorg. Nucl. Chem.* 34, 3357 .
- Mabbs.F.E., (1993) , Some Aspects of spectroscopy of hydrazine, hydrazide , and hydrazones , *Chem. Soc.Rev.* 313.
- Chohan.J.U., Hussain.Z., Humayun.O.L., (1993) . *Synth.react.Inorg , Met Org. Chem*, 23, 1061 – 1071 .
- Sonmez.M., Sekerel.M., (2002) . *Pub. J. of chem.* 76, 907-914 .
- Prabhu.P.S., Dodwad.S.S., (1986) , Studies on some Schiff base complexes . *J. Indian of chem.* 58, 478-482 .
- Yamada.S., (1999) , Advancement in stereochemical aspects of Schiff base metal complexes, *Coord. Chem. Rev.* 5, 190–192 .
- National Committee for Clinical Laboratory Standard, NCCLS: (1999) . Document M45-A, 26(19), Willanova, PA., USA.
- Chohan ZH, Arif M, Shafiq Z, Yaqub M, Supuran CT., (2006) . *Journal of Enzyme Inhibition and Medicinal Chemistry*. 21(1):95–103.
- Chohan ZH, Scozzafava A, Supuran CT., (2003) . *Synthesis and Reactivity in Inorganic and Metal- Organic Chemistry*. 33(2):241–257.
- Chohan Z., (2002) . *Applied Organometallic Chemistry*. 16(1):17–20

Table 1: Analytical data of ligand and complexes

s/n	Compounds	Empirical Formulae	Formular Weight	Colour	M.P/Dec Temp °C	% yield	Molar Cond. Ohm ⁻¹ cm ²	Elemental Analysis Found	(Calc)
								%M	%SO ₄
1.	[IBAH]	C ₆ H ₁₂ N ₂ O ₂	144.1718	Milky	190	65	13	-	-
2.	[4-CBAH]	C ₈ H ₇ N ₃ O	161.1426	Milky	118	62	11	-	-
3.	[4-ABAH]	C ₇ H ₉ N ₃ O	151.1660	Milky	212	68	15	-	-
4.	Cu[IBAH]SO ₄ .H ₂ O	C ₁₂ H ₂₆ N ₄ O ₉ SCu	465.9684	Dark-green	218	72	2.1	14.19 (13.64)	21.25 (20.62)
5.	Cu[4-CBAH] ₂ SO ₄ .H ₂ O	C ₁₆ H ₁₆ N ₆ O ₇ SCu	499.4648	Dirty-brown	205	69	1.3	12.04 (12.27)	19.21 (19.23)
6.	Cu[4-ABAH] ₂ SO ₄ .H ₂ O	C ₁₄ H ₂₀ N ₆ O ₇ SCu	479.9568	Dark-green	210	70	2.1	14.11 (13.24)	20.10 (20.02)
7.	Cu[IBA] ₂ . 2H ₂ O	C ₁₂ H ₂₆ N ₄ O ₆ Cu	385.9042	Green	220	56	3.1	16.20 (16.47)	-
8.	Cu[4-CBA] ₂ . 2H ₂ O	C ₁₆ H ₁₆ N ₆ O ₄ Cu	419.8822	Brown	190	74	3.6	15.72 (15.13)	-
9.	Cu[4-ABA] ₂ . H ₂ O	C ₁₄ H ₁₈ N ₆ O ₃ Cu	381.1877	Greyish-green	196	70	2.6	16.49 (16.67)	-
10.	Ni[IBAH] ₂ SO ₄ .2H ₂ O	C ₁₂ H ₂₈ N ₄ O ₁₀ SNi	479.1311	Light-green	290	74	1.9	12.26 (12.25)	20.26 (20.05)
11.	Ni[4-CBAH] ₂ SO ₄	C ₁₆ H ₁₄ N ₆ O ₆ SNi	477.0786	Pale-brown	310	72	1.7	12.35 (12.30)	20.14 (20.14)
12.	Ni[4-ABAH] ₂ SO ₄	C ₁₄ H ₁₈ N ₆ O ₆ SNi	457.0889	Light-green	218	48	1.6	13.25 (12.84)	21.27 (21.02)

13.	Ni[IBA] ₂ .H ₂ O	C ₁₂ H ₂₄ N ₄ O ₅ Ni	363.0363	Yellowish-orange	240	69	2.9	16.20	- (16.17)	
14.	Ni[4-CBA] ₂ .H ₂ O	C ₁₆ H ₁₆ N ₆ O ₄ Ni	415.0296	Pale-brown	201		62	3.6	14.70 (14.14)	-
15.	Ni[4-ABA] ₂ .2H ₂ O	C ₁₄ H ₂₀ N ₆ O ₄ Ni	395.0400	Yellowish	245		72	3.0	15.01 (14.86)	-

Note : Figure in bracket are calculated values

Table II. Diagnostic IR bands for the ligands and complexes (cm⁻¹)

S/n	Compounds	□(OH)	Amide I		Amide II		□(M-N)	□(M-O)	□(SO ₄ ²⁻)
			□(C-O/C=O)	□(NH/NH ₂)	□(C-N)				
1.	IBAH	-	1666	3855, 3460	1528	-	-	-	
2.	4-CBAH	-	1631	3281	1561	-	-	-	
3.	4-ABAH	-	1608	3420, 3466	1506	-	-	-	
4.	Cu[IBAH] ₂ SO ₄ .H ₂ O	3350	1620	3220, 3440	1470	395	480	710	
5.	Cu[4-CBAH] ₂ SO ₄ .H ₂ O	3350	1620	3400, 3300	1573	305	490	770	
6.	Cu[4-ABAH] ₂ SO ₄ .H ₂ O	3450	1625	3050	1450	310	450	720	
7.	Cu[IBA] ₂ .2H ₂ O	3550	1622	3250, 3410	1477	410	510	-	
8.	Cu[4-CBA] ₂ .2H ₂ O	3452	1640	3440	1565	400	470	-	
9.	Cu[4-ABA] ₂ .H ₂ O	3400	1635	3100, 3450	1570	420	488	-	
10.	Ni[IBAH] ₂ SO ₄ .2H ₂ O	3450	1630	3250	1565	350	478	700	
11.	Ni[4-CBAH] ₂ SO ₄	-	1630	3350, 3450	1555	310	499	730	
12.	Ni[4-ABAH] ₂ SO ₄	-	1630	3120, 3410	1450	-	495	710	

13.	Ni[IBA] ₂ . H ₂ O	3400	1640	3280, 3410	1500	400	500	-
14.	Ni[4-CBA] ₂ .H ₂ O	3350	1633	3410	1475	410	500	-
15.	Ni[4-ABA] ₂ . 2H ₂ O	3550	1630	3120	1550	320	505	-

Table III. Electronic spectral data for the complexes

S/n	Compounds	λ max (nm)	λ cm ⁻¹	Assignments	Probable Geometry
1.	Cu[IBAH] ₂ SO ₄ .H ₂ O	659	15,168	d→d	Octahedral
2.	Cu[4-CBAH] ₂ SO ₄ .H ₂ O	650	15,385	d→d	Octahedral
3.	Cu[4-ABAH] ₂ SO ₄ .H ₂ O	769	13,004	d→d	Octahedral
4.	Cu[IBA] ₂ . 2H ₂ O	600	14,107	d→d	Octahedral
5.	Cu[4-CBA] ₂ . 2H ₂ O	705	14,184	d→d	Octahedral
6.	Cu[4-ABA] ₂ . H ₂ O	689	14,514	d→d	Octahedral
7.	Ni[IBAH] ₂ SO ₄ .2H ₂ O	500 716	20,000 13,966	³ A _{2g} (F) → ³ T _{1g} (P) ³ A _{2g} (F) → ³ T _{1g} (F)	Octahedral
8.	Ni[4-CBAH] ₂ SO ₄	500 714	20,000 14,000	³ A _{2g} (F) → ³ T _{1g} (P) ³ A _{2g} (F) → ³ T _{1g} (F)	Octahedral
9.	Ni[4-ABAH] ₂ SO ₄	500 699	20,000 14,006	³ A _{2g} (F) → ³ T _{1g} (P) ³ A _{2g} (F) → ³ T _{1g} (F)	Octahedral
10.	Ni[IBA] ₂ . H ₂ O	500 714	20,000 14,006	³ A _{2g} (F) → ³ T _{1g} (P) ³ A _{2g} (F) → ³ T _{1g} (F)	Octahedral
11.	Ni[4-CBA] ₂ .H ₂ O	650 725	15,385 13,793	³ T ₁ (F) → ³ T ₁ (P)	Tetrahedral
12.	Ni[4-ABA] ₂ . 2H ₂ O	650 725	15,385 13,793	³ T ₁ (F) → ³ T ₁ (P)	Tetrahedral

Table IV : Antimicrobial activity result of Ligands and Complexes

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

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

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