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GREEN SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF MIXED LIGAND COMPLEXES OF Co (II), Ni (II) and V(III) METALS USING SOME AMINO ACIDS AS LIGANDS

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ABSTRACT
Co (II), Ni (II) and V (III) metal complexes were synthesized mechanochemically using L-Leucine, L-Tyrosine and Creatinine as mixed ligands. The metals and the ligands were grounded using an agate mortar with a pestle. The compounds formed were characterized using their melting/decomposition temperature, solubility, magnetic susceptibility, conductivity measurement, Infrared analysis and scanning electron microscope (SEM). The Metal – ligand ratios were investigated via Job's method of continuous variation. The shifts of bands (for instance 1693-1677 cm^{-1} to 1674-1607 cm^{-1}) in C=O and the appearance of new bands in the complexes (683-669 and 713-750 cm^{-1} indicates the complexation. The lower conductivity measurement values (15.00 to 32.40) $\mu S.cm^{-1}$ suggested the non-electrolytic nature of the complexes. The magnetic effective value of the metal complexes showed that all the three complexes are paramagnetic and octahedral. It was concluded that the amino acids (ligands) coordinated in a bidentate way through the nitrogen from the amino group and oxygen from carboxylate. The complexes were screened for their antimicrobial activities against two bacterial isolates (*Streptococcus pneumoniae* and *Klebsiella pneumoniae*). All the complexes exhibited good activity against the organisms.

Keywords: antibacterial, metal complexes, amino acids, mixed ligands, Grinding

INTRODUCTION

The studies under the area of mechanochemistry, which cover the grinding chemistry, ball milling, sonication etc., are certain of interest to the researchers working on the development of green methodologies (Achar et al., 2017). Mechanochemical synthesis emerged as the most advantageous, environmentally sound alternative to traditional routes for nanomaterial preparation with outstanding properties for advanced applications. (Xu *et al.,* 2015). Mechanochemical synthesis involves a reaction between dry reactants i.e. with no added liquid that might act as a solvent. However, some reactions in this type can result in the generation of liquid during the reaction. For example, when any of the reactants is a hydrate producing liquid water during the reaction or when liquid by-product such as water or acetic acid are produced as condensates during the reaction (Friščić, 2012).

Sani and Lawal (2017) have investigated the solvent-assisted mechanochemical synthesis of a widely-used class of organic imine-based ligand. Specifically, a diamine-type ligand is formed from 2-hydroxy-1-naphthaldehyde and 1, 2 - phenylenediamine under solvent assisted mechanochemical conditions. Similarly, two Co (II) complexes containing malonic and isonicotinic acids have been prepared by manual grinding of stoichiometric amounts of the starting materials. Elemental analysis (CHN), IR, UV-vis spectroscopic techniques, TGA-DTG investigation and X-ray powder diffraction analysis were used to characterize the two compounds. Isonicotinic acid coordinated to the metal via the pyridine ring nitrogen and one oxygen atom of the carboxylic group while malonic acid coordinated via both oxygen atoms of the carboxylate groups indicating bidentate coordination mode in the two compounds. The compounds were exposed to some volatile organic compounds (VOCs) containing nitrogen or oxygen donor atoms in the solid-state and their vapochromic behaviors studied using color changes, FT-IR and solid-state UV-vis spectroscopies. Heating the samples exposed to the VOCs for a few minutes at 100 °C regenerates the original material without degradation, even after several heating cycles (Tella et al. 2016).

Also, Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of mixed ligands, Riboflavin (HL) and 4-aminobenzoic acid (HL1) were synthesized and characterized by percentage metal, infrared and electronic (solid reflectance) spectroscopies**,** room temperature magnetic moments, melting points and conductance measurements. The conductance measurements in DMSO and percentage metal analysis indicated that all the metal (II) complexes were covalent and analyzed as [M (HL) (HL1) X], where X = Cl /SO. Infrared spectra data confirmed that coordination was via the 2 4oxygen atoms of two hydroxyl groups in Riboflavin, and the carboxylate oxygen atoms in

4-aminobenzoic acid respectively. Furthermore, electronic spectra data indicated that all the metal (II) complexes adopted octahedral geometry; while room-temperature magnetic moment measurements indicated spin-crossover, that is high spin low spinoctahedral equilibrium for all the complexes with the exceptions of the Cu (II) and Zn (II) complexes. *In-vitro* antimicrobial activities of the metal (II) complexes**,** riboflavin and *p*-aminobenzoic acid against *Escherichia spp, Proteus mirabilis, Streptococcus pyogenes, Candida albicans, Salmonella sp, Streptococcus sp, Bacillus spp, Staphylococcus sp* and *Pseudomonas* spp revealed that all the metal (II) complexes and ligands were active against *Pseudomonas* sp with inhibitory zones range of 7.0-11.0 mm. The antioxidant studies on the metal complexes showed that the Zn (II) complex had the best antioxidant activity of about 62 percentage inhibitions, which was about twice the percentage inhibition of the standards, ascorbic acid and D-tocopherol **(**Agbaje et al.**,** 2015**)**.

This paper aims to synthesize, characterize and study the antimicrobial activities of Co (II), Ni (II) and V (III) metal complexes via green synthesis method.

MATERIALS AND METHODS

MATERIALS

All the chemicals were used as obtained without further purification. Most of the chemicals are of analytical grade. All the glass wares used in this work were washed with detergent and rinsed with distilled water and dried in an oven at 110^0c.

All weighing was carried out using an electronic balance. The infrared spectral analysis was recorded using FTIR model vertex 70/70v. Conductivity measurement was done using a conductivity meter (DDS-11) using DMSO as a solvent. Melting point and decomposition temperatures were determined using Bamstead Electrothermal melting point apparatus IA9100. The proposed molecular structure of the complex was drawn by using chemsketch program ACD (2016). The antimicrobial screening was carried out in the microbiology laboratory, department of microbiology, Umaru Musa Yar'adua University Katsina. Nigeria.

METHODS

MECHANOCHEMICAL SYNTHESIS OF METAL COMPLEXES

The metal complexes of Ni (II), Co (II) and V (III) were synthesized by grinding 5 mmol of each of the metal salts with 5 mmol of L-leucine, L-tyrosine and Creatinine in an agate mortar with a pestle for 10-20 minutes which gave a crystalline powdered and was dried at 50^0C (Muhammad and Kurawa, 2019).

Mechanochemical synthesis of metal (II) complexes:

$$\mathbf{Lcn+Tyr+Crn+MCl_2} \xrightarrow[\text{Grinding}]{} \mathbf{[M(Lcn)(Tyr)(Crn)]}$$

Where: M = Metal (Co^{2+} and $Ni2^{+}$), Lcn = L-Leucine ($C_6H_{13}NO_2$), Tyr = L-Tyrosine ($C_9H_{11}NO_3$) and Crn = Creatinine ($C_4H_7N_3O$).

Mechanochemical synthesis of metal (III) complex:

$$\mathbf{Lcn.+Crn+VCl_3} \xrightarrow[\text{Grinding}]{} \mathbf{[V(Lcn)(Crn)Cl_2]}$$

Determination of Antibacterial Activity

The antimicrobial Activities of the metal complexes and the ligands against two bacterial isolates (*streptococcus pneumoniae* and *Klebsiella pneumoniae*) were determined by the paper disc diffusion method (cheesbrough, 2008).

RESULT AND DISCUSSION

The results obtained from Tables 1 and 2 show some physicochemical properties of the ligands and their complexes.

Three metal complexes were synthesized mechanochemically.

The complexes were prepared by grinding the respective metal salts with the ligands using 5:5 mole ratios, which means 5 mmole of the metal salt: 5 mmole of each of the ligands. The metal salts reacted with the ligands by mechanochemical synthesis and produced solid complexes. The colour of the ligands and the metal (II) and (III) complexes are white powder, white and off white crystals for L-tyrosine, L-leucine and Creatinine respectively while, that of metal complexes are blue, light green and light green for the complexes of Co(II), Ni(II) and V(III) respectively. The melting point of the ligands are 343,331and 300 ^{0}c for L-Tyrosine, L-Leucine and Creatinine respectively. The melting/decomposition temperatures are 247, >400 and 267 ^{0}c also for V (III), Co (II) and Ni (II) metal complexes respectively. The high melting/decomposition temperatures of the complexes revealed their stability (Muhammad and Kurawa, 2019). However, the melting/decomposition temperatures of Ni (II) and V (III) complexes are lower than that of the others. This is due to some amount of uncoordinated water content in the Ni (II) complex. The V (III) complex [V (Lcn)(Crn)Cl_2] has 1:2 M:L ratio which is different from the other complexes with a 1:3 Metal: Ligand ratio. The complex has the lowest melting/decomposition temperature as compared to others. This is probably because of its lower thermal stability that may be related to its structure (Gurbuz et al., 2015).

The molar conductance of the complexes in DMSO was found to be in a low range (15.00 to 32.4) $\mu S.cm^{-1}$ supporting the non-electrolytic behaviour of the complexes (Al-noor and Abdulkarim, 2015). The sequence of the conductivity was found to be in the following order:

Ni > V > Co.

The ligands and their complexes are insoluble in most common organic solvents such as chloroform, ethanol, methanol and n-hexane but they are relatively soluble in Dimethyl sulfoxide and Dimethylformamide except a few of them which are either insoluble or slightly soluble. They are all slightly soluble in water as shown in Table 2.

All the complexes are paramagnetic. Co (II) complex is 4.81 BM, Ni (II) is 3.0 BM and V (III) is 3.83 BM. These values are in the range of octahedral geometry of complexes (Aurora et al 2009)

Table 1: Some Physical properties of the ligands and their complexes

Compound	**Color**	**Yield %**	**M.Wt Calc.**	**Melting point ^{0}C**	**Decomposition Temperature ^{0}C**	$\mu_{eff\ (BM)}$	**Molar conductivity *$\mu S.cm^{-1}$***
($C_6H_{13}NO_2$)	White	-	131.18	331	-	-	-
($C_9H_{11}NO_3$)	White	-	181.19	343	-	-	-
($C_4H_7N_3O$)	White	-	113.12	300	-	-	-
[Co (Lcn)(tyr)(crn)]	Blue	82	482.42	-	> 400	4.81	15.00
[Ni (Lnc)(tyr)(crn)].$6H_2O$	Light Green	79	590.18	-	267	3.0	32.40
[V(Lcn)(crn)Cl_2]	Light Green	78	365.24	-	247	3.83	32.30

Table 2: Solubility of the ligands and metal complexes in some common solvents

Compound	$CHCl_3$	C_2H_5OH	H_2O	CH_3OH	DMF	DMSO	n-hexane
L-leucine	IS	IS	SS	IS	IS	IS	IS
L-tyrosine	IS	IS	SS	IS	SS	SS	IS
Creatinine	IS	IS	SS	IS	**S**	SS	IS
Co (II) Complex	IS	IS	SS	IS	SS	**S**	IS
Ni (II) Complex	IS	IS	SS	IS	IS	**S**	IS
V (III) Complex	IS	IS	SS	IS	SS	**S**	IS

(S = soluble, SS = slightly soluble, IS = insoluble)

Fourier Transform Infrared Spectroscopy (FTIR)

The IR spectra of the ligands and their complexes were listed in Table 3. The IR spectra of the complexes were compared with those of the free ligands to determine the coordination sites that may involve/participate in the coordination. In the process of the comparison, it was found that the *v(N-H)* stretching vibration in the three ligands was 2959 – 3242. However, these bands were shifted to higher wavenumbers in the complexes (3469 - 3304) indicating the participation of the nitrogen atom from the amino substituents in the coordination of the metal ions with the ligands (Aiyelabola et *al*, 2017). Supporting this further is the observed shift to lower wavenumber for the *v* (C – N) stretching frequency from 1421 – 1365 to 1346 – 1331 cm^{-1} upon complexation.

There were significant shifts in the *v*(C=O) stretching frequency of the ligands (1693 – 1677),

which lowered upon complexation (1674 – 1607). This is because of the involvement of carbonyl oxygen in the coordination.

The C – O stretching band of the ligands was seen at 1365 – 1313 cm^{-1}. These were got shifted to a lower frequency (1246 – 1216) cm^{-1} in the complexes, indicating deprotonation and coordination of the hydroxyl oxygen to the metal ion (Sani and Lawal, 2017).

The new bands at 750 – 713 and 683 – 669 cm^{-1} in the spectra of the complexes were assigned to *v* M – O and *v* M – N stretching vibration respectively (Abdul Qadir et al, 2014).

Hence, it is concluded that all the three ligands behave as bidentate free ligands in all the complexes and that the coordination takes place in the oxygen and nitrogen atoms.

TABLE 3: showing some selected Vibrational Frequencies of ligands and the complexes.

Compound	***v*(N-H)** cm^{-1}	***v*(C=O)** cm^{-1}	***v*(C-O)** cm^{-1}	***v*(C-N)** cm^{-1}	***v*(M-N)** cm^{-1}	***v*(M-O)** cm^{-1}
L-Leucine	2959	1677	1316	1365	-	-
L-Tyrosine	3204	1677	1365	1421	-	-
Creatinine	3242	1693	-	1399	-	-
Co (II) Complex	3339	1644	1242	1335	680	713
Ni (II) Complex	3324	1607	1240	1334	683	743
V(III) Complex	3327	1629	1246	1346	671	750

SCANNING ELECTRON MICROSCOPE (SEM)

The results of scanning electron micrograph (SEM) were presented in figures 1 to 6. Figure 1 to 3 shows the SEM images of the metal salts plus the three ligands (L-Leucine, L-Tyrosine and Creatinine) before grinding (mechanochemical reaction). Figures 4 to 6 indicate the SEM images of the metal complexes produced after grinding. Looking at the images, the morphologies of figures 4 to 6 are entirely different from that of 1 to 3. This indicates the possible conversion of the reactants (the metal salts plus the ligands) into the products the (complexes).

SEM IMAGES BEFORE GRINDING

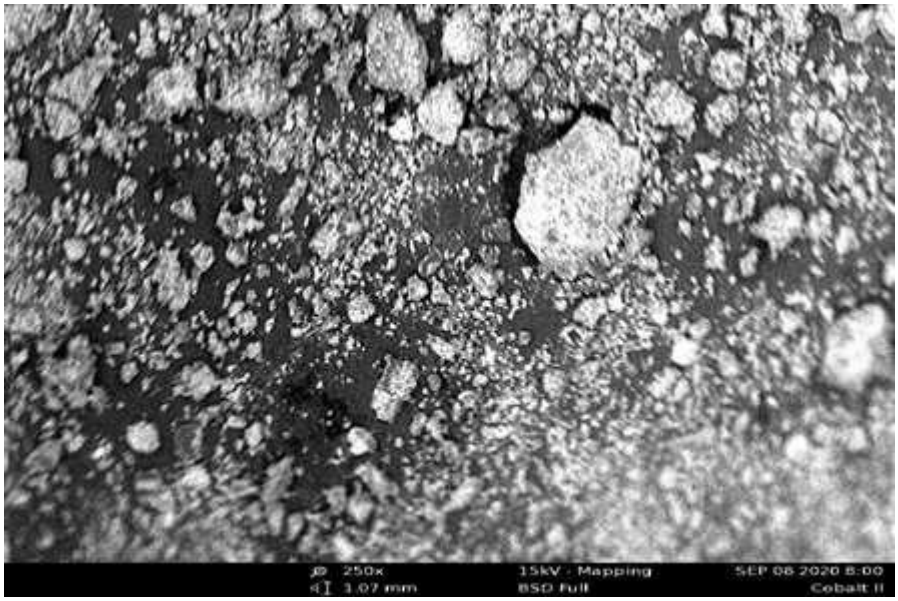


Figure 1: SEM image of Cobalt (II) salt plus ligands

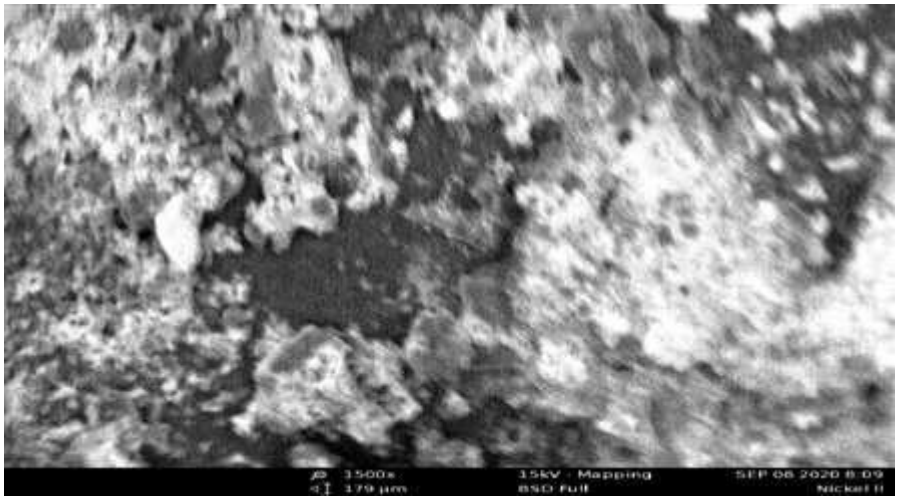


Figure 2: SEM image of Nickel (II) salt plus ligands

Figure 3: SEM image of Vanadium (III) salts plus ligands

SEM IMAGES AFTER GRINDING

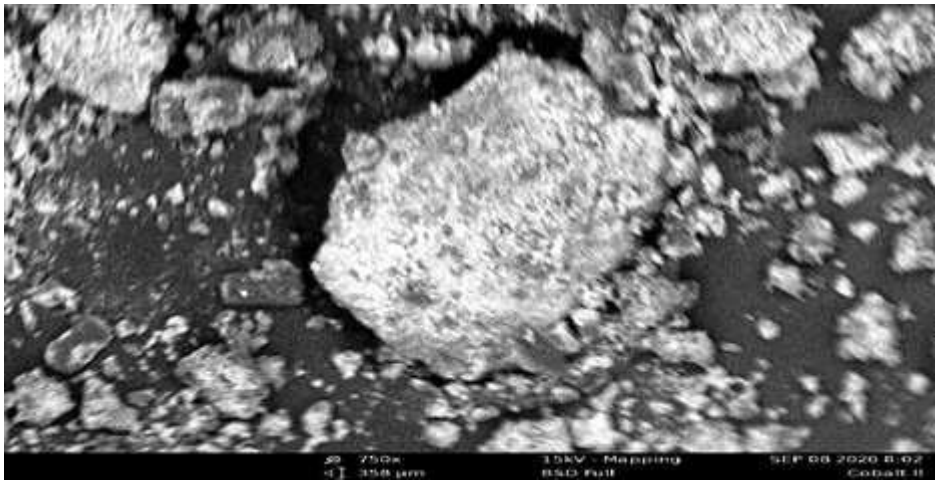


Figure 4: SEM image of Cobalt (II) Complex

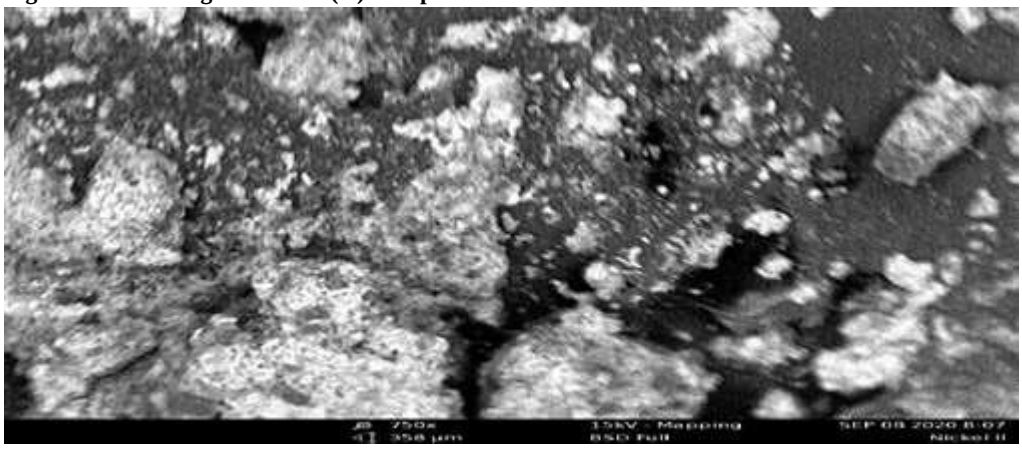


Figure 5: SEM image of Nickel (II) Complex

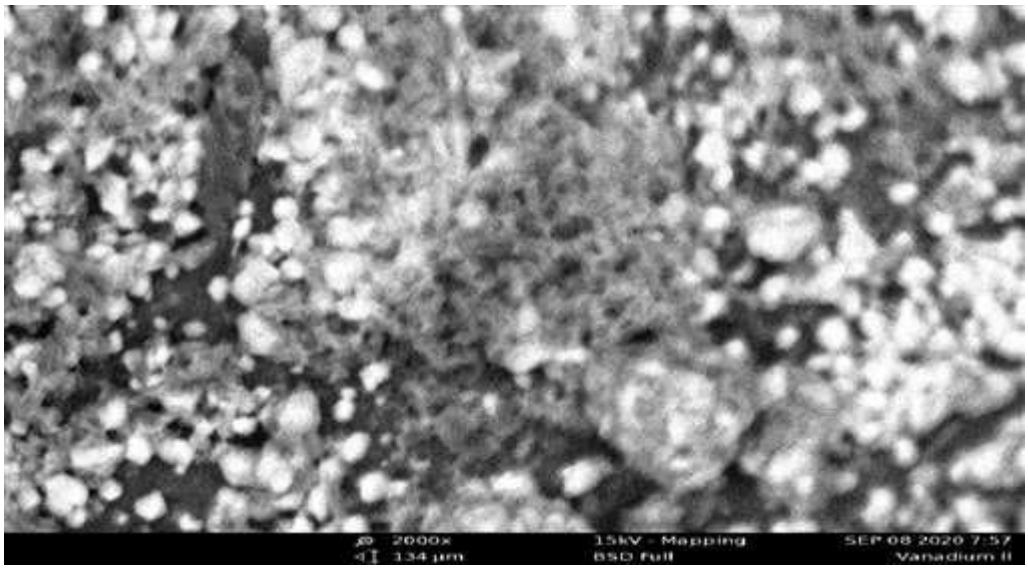


Figure 6: SEM image of Vanadium (III) Complex

Antibacterial activity

The antimicrobial activities of free ligand and their complexes were evaluated using the micro broth paper disc diffusion method towards two bacteria (*Streptococcus pneumoniae* and *Klebsiella pneumoniae*). The results were compared with that of Augmentin (control) against the two organisms and were presented in Tables 4 and 5. The study shows high activities at higher concentrations in each case and vice-versa. It also revealed that the activities of the free ligands are more pronounced after complexation (Mannir et al., 2020).

Table 4: Showing the Antibacterial Activity of ligands/complexes against *Streptococcus pneumoniae* (zone of inhibition in **mm**).

Complexes/Ligands	**100 mg/ml**	**50 mg/ml**	**25 mg/ml**	**12.5 mg/ml**
V (III) Complex	20	15	14	9
Ni (II) Complex	17	15	10	NA
Creatinine(ligand)	12	10	10	NA
L-Tyrosine(ligand)	14.5	12	9.8	NA
L-Leucine(ligand)	14	10	8.5	NA
Co (II) Complex	38	19	14	9
Control	27			

Key

NA = NO activity

Control = Augmentin

Table 5: showing the Antibacterial Activity of ligands/complexes against *Klebsiella pneumoniae* (zone of inhibition in **mm**).

Complexes/Ligands	**100 mg/ml**	**50 mg/ml**	**25 mg/ml**	**12.5 mg/ml**
V (III) Complex	19	14	10	NA
Ni (II) Complex	15	9	NA	NA
Creatinine(ligand)	8	NA	NA	NA
L-Tyrosine(ligand)	NA	NA	NA	NA
L-Leucine(ligand)	NA	NA	NA	NA
Co (II) Complex	36	21	15	12
Control	24			

Key

NA = NO activity

Control = Augmentin

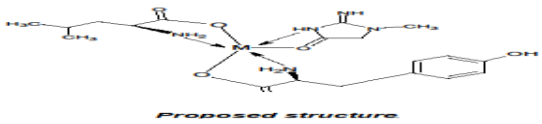
CONCLUSION

Co (II), Ni (II) and V (III) complexes of mixed ligands of L-Leucine, L-Tyrosine and Creatinine were synthesized and characterized; the study shows that:

All the synthesized complexes are non-electrolyte in nature.

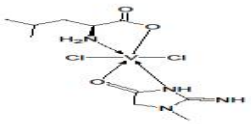
The three ligands behave as neutral bidentate that coordinate through O and N.

The complexes have a high decomposition temperature, which indicates complexation.
Both the ligands and the complexes exhibited antibacterial activity at varying degrees.
The values showed that the ligands become more pronounced when coordinated to metal ions.
The antibacterial activity of the complexes follow the order, Co (II) > V (III) > Ni (II)
In conclusion, these complexes could effectively be utilized for the treatment of some common diseases caused by *streptococcus pneumoniae* and *Klebsiella pneumoniae*.



Proposed structure

Where M = Ni (II) and Co (II) Metals



Proposed structure of V (III) Complex

PROPOSED MOLECULAR STRUCTURES OF THE COMPLEXES FOR METALS (II) AND (III)

REFERENCES

A. C Tella, S. O Owalude, L. O Alimi, A. C Oladipo S.J Olatunji, O. G Adeyemi (2016): *Facile Synthesis and Vapochromic Studies of Co (ii) complexes bearing 'NO' and 'OO' donor ligands*: Egyptian Journal of basic and applied Sci 3: (2): 125 – 133.

Abdul Qadir M, Ahmad M, Ahmad A, Naz S, Azhar S, Khan R, Hussain R and Waseem R (2014**).** *Synthesis of metal complexes with amino acids for Animal Nutrition*. Research gate 12(6): 858-861.

Achar Kumar Tapas, Anima Bose and Prasenjit Mal (2017): *Mechanochemical Synthesis of Small Organic Molecules:* Bilstein journal, org. chat 1(3):1907-1931.

Agbaje O. Osowole A.A, Malumi; E.O and Wakil SM (2015), *Synthesis, spectroscopic characterization, antimicrobial and antioxidant properties of some metal (ii) complexes of mixed ligands – riboflavin and 4 – Aminobenzoic acid*, research and review journal of chemistry. 14(2):1905 – 1933.

Aiyelabola T., Akinkunmi E., Obuotor E, Olawuni I, Isabirye D and Jordaan J (2017), *Synthesis, characterization and Biological activities of coordination compounds of 4-Hydroxy-3-nitro-2H-chromen-2-one and its aminoethanoic acid and pyrrolidine-2-carboxilic acid mixed ligand complexes*, Bioinorganic chemistry and Application. 10(1155):1-16.

Al-noor T.H and Abdul Karim L.K (2015). *Synthesis, characterization and Anti-Bacterial Activities of Co (II), Ni (II), Cu (II), Cd (II) and Hg (II) mixed ligand complexes of L-leucine and trimethoprim antibiotic:* chemistry and material research: 7(3):32-39

Aurora Reiss, Stelian Florea, Theodor Caprouio, Nicolae Stanica (2009), *synthesis characterization and antibacterial activity of some transition metals with the Schiff base N-(2-furanyimethylene)-3-aminodibenzofuran*, Turk J Chem. 33 (2009), 775 – 783.

Cheesbrough M. (2008) *District laboratory practice in tropical countries. Press syndicate publishers,* University of Cambridge, Edinburgh Cambridge United Kingdom. 194 – 204.

Friščić T. (2012): *Supramolecular concept and new techniques Mechanochemistry: cocrystals, cages, rotaxanes, open, metal -organic frame work"* chemical society reviews. 41: 3493-3510.

Gurbuz D, Cinarli A, Tavman A and Tan B.S (2015), *Synthesis characterization and antimicrobial activity of some transition metal complexes of N-(5-Chloro-2-hydroxyphenyl)-3-methoxy-salicyladimine;* Chemical society of Ethiopia. 29(1): 63 – 74.

Mannir M, Nura S.G and Jabiru M (2020), *Solvent – Free synthesis and evaluation of antimicrobial activity of Vanadium (III) metal complex using two amino acids as mixed ligands*, International journal of innovative research and Development. 9(9):173 – 178.

Muhammad M and Kurawa M.A (2019): "*solid state synthesize characterization and antimicrobial studies of Ni (11), Co (11), and Cu (11) complexes 1-(4-nitropheny1) imino] methy1) naphthalen-2-ol*" Chemsearch journal. 10 (1):38 -45

Sani S and Lawal AM (2017): *Liquid – assisted mechanochemical synthesis: green Approach to synthesis of Co (11) Schiff base complex and of antimicrobial activities*" international journal of innovative research and development. 6(12)79-86

Xu, C., De, S., Alina M., B., Ojeda and lugues R (2015): *"mechanochemical synthesis of advanced nanomaterials for catalytic application*" royal society of chemistry. 51, 6698-6713.