

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Synthesis, Characterization and Antimicrobial Evaluation Of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) Complexes of Pyridine -2- Carboxylic Acid.

MO Agwara ^{1*}, NB Ndosiri ¹, A Mohamadou ², and AM Condé ³

¹Laboratory of Coordination Chemistry, Department of Inorganic Chemistry, Faculty of Science, University of Yaoundé I, P.O. Box 812, Yaoundé, Cameroun

²Institute de Chimie Moléculaire de Reims, Groupe de Chimie de coordination, Faculté des Sciences, Université de Reims Champagne-ardenne, France.

³Département de Chimie, Faculté des Sciences, Université de Douala, Cameroun.

ABSTRACT

Metal (II) complexes of pyridine -2- carboxylic acid, $[M (C_6H_4NO_2)_2 (H_2O)]$ (M=Mn, Co, Ni, Cu, Zn; x=1 or 2) have been synthesized. The complexes with are air stable and molecular have been characterized by elemental analyses, conductance, IR and visible spectroscopy and room temperature magnetic susceptibility measurements. The results suggest octahedral coordination (Mn, Co, Ni, Cu, Zn) and square pyramidal structures (Cu) in which the picolinate ion is a bidentate N-and O-donor ligand. These structures have been confirmed by single X-ray crystallography for Co(II), Ni(II),and Cu(II) complexes. Thermal studies showed significant mass loss corresponding to the lost of uncoordinated and coordinated water molecules as well picolinate ions. Antimicrobial studies on nine bacterial and four fungal species reveal that the ligand and metal salts have selective activity on the bacterial species and no activity on the fungal species. The manganese and copper zinc complexes exhibited activity on *S.aureus* while the cobalt complex showed activity against *K.pneumonia*.

Keywords: pyridine -2- carboxylic acid; antimicrobial; complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II)

**Corresponding author*

INTRODUCTION

It is known that life processes in plants and animals involve about 25 essential elements [1]. Some of these metal ions are known to be involved in biological phenomena such as kidney functioning, muscle contraction, transportation in cells, cell division and they are generally coordinated to organic functions in the body [2,3]. Many transition metal complexes with N- and O- donor atoms have been known to have antibacterial as well as anti-mycotic properties [4-9].

A good number of metal complexes of pyridine-2-carboxylic acid (picolinic acid) have been synthesized and characterized [10-13]. The picolinate ion structure has two carboxylate oxygen atoms and one pyridyl nitrogen atom as potential donor sites leading to a variety of ligation modes [14]. The different ligation modes could lead to many applications of these coordination compounds. For example much attention has been paid on pyridine-2-carboxylic acid and its complexes for the design of new pharmaceuticals [10-13], blood sugar reduction due to the insulin properties [15-16], intermediate in the production of local anaesthesia [17] and nutritional supplements [13]. The ruthenium(II)-arene complexes with pyridine-2-carboxylic acid, $[n^6\text{-p-cymene})\text{RuCl(pic)}]\text{H}_2\text{O}$ was tested in two human cancer cell lines Hela (cervix) and Fem X (melanoma) and found to exhibit cytotoxicity activity [18].

In our previous papers [19,20] we reported on the antifungal and antibacterial activities of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) complexes containing hexamethylenetetramine, 1,10-phenanthroline and 2,2'-bipyridine as ligands. In this paper we continue our fundamental research work on the antimicrobial and antifungal resistance problem in our country, Cameroon. This time using pyridine-2-carboxylic acid (picolinic acid) as ligand. In this paper, we report on the synthesis, characterization and antimicrobial evaluation of divalent metal complexes of pyridine-2-carboxylic acid (M=Mn, Co, Ni, Cu, Zn) using resistant bacterial and fungal species from the Central Hospital of Yaoundé, Cameroon and "Centre Pasteur du Cameroun", Yaoundé.

EXPERIMENTAL

Commercial reagents were used as obtained without further purification. The solvents, ethanol and diethylether were dried and distilled according to standard methods. The fungi species were clinical isolates from the Yaounde central hospital (Cameroon), while the bacterial strains were provided by "Centre Pasteur du Cameroun", Yaoundé.

Physical measurements

Elemental analysis for carbon, nitrogen and hydrogen were carried out on a Fisons instrument 1108 CHNS-O (France), while Mn(II), Co(II), Cu(II) and Zn(II) were quantitatively estimated by compleximetric titrations [21]. The melting point/decomposition temperatures of the complexes were determined using the LEICA VmHB melting point apparatus (Koffler's system) in the temperature range 50-260 °C. Conductance measurements were carried out in

water using the Tacussel conductimeter, model CD810 at room temperature. Infrared spectra were recorded on a Perkin- Elmer model IR-457 spectrometer and a spectrum 100 FT-IR Perkin-Elmer spectrometer while electronic absorption spectra of the complexes dissolved in ethanol were recorded on a Hitachi U-2000 Spectrophotometer at room temperature. Measurement of room temperature magnetic susceptibility of the powdered complexes was done using the Gouy balance [22] using $\text{Hg}[\text{Co}(\text{SCN})_4]$, as calibrant, while thermogravimetric analysis of the complexes was carried out using a TGA Perkin-Elmer STA 6000 simultaneous thermal analyser under a nitrogen atmosphere. X-ray diffraction was carried out with a CCD bidimensional diffractometer using monochromic radiation, $\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$, operating at 50kV and 40mA.

Synthesis

The divalent metal complexes of pyridine -2- carboxylic acid were generally synthesized using 1:2 molar reactant ratio of metal salt to pyridine -2- carboxylic acid in alkaline medium [10].

Typically, the compound $[\text{Co}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ was prepared by adding dropwise, pyridine -2- carboxylic acid (4.0 mmol, 0.49 g) in 15 mL of water, 5 mL of ethanol and NaOH (0.16 g, 4.0 mmol) to a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.48 g, 2.0 mmol) while stirring at room temperature. Stirring was continued for two hours during which an orange precipitate was obtained. The precipitate was filtered, washed with ethanol and dried in a desiccator. The filtrate was preserved for one week during which orange crystals were obtained. These crystals were filtered, washed with ethanol and dried in a desiccator.

The manganese, nickel, copper and zinc picolinates were similarly synthesized.

Antimicrobial tests

The antifungal tests were carried out in the Applied Microbiology and Molecular Pharmacology Laboratory of the University of Yaoundé I. Four candida fungi species, *Candida albicans*, *Candida parapsilosis*, *Candida krusei* and *Cryptococcus néoformans*, used for the screening were clinical isolates from the Central Hospital, Yaounde Cameroon. pyridine -2- carboxylic acid, metal salts and the metal complexes were tested.

Disc diffusion test

The antimicrobial agent incorporated in a disc diffuses at the surface of the inoculated medium and creates an inhibition zone diameter that is proportional to the efficacy of the compound being tested. The method described by Carvallert et al. was used [23].

Culture media (Mueller Hinton and Sabouraud Dextrose Agar) were prepared according to the manufacturer's guideline. Briefly, a mass of the culture medium was weighed and

dissolved in distilled water. After boiling, the culture medium was autoclaved at 121°C for 15 minutes, then it was spread at the surface of Petri dishes and left to solidify.

The compounds were weighed (40mg) and dissolved in 1mL of tween 80 (10%) making a concentration of 40mg/mL. Positive control, (4mg/mL) nystatin and gentamycine, was also prepared.

The yeasts and the bacterial strains were clinical isolates from pathological samples. A colony from a 24 hours fresh culture was dissolved in 1 mL of sterile distilled water, adjusted at 0.5 Mc Farland scale ($1-5.10^8$ cfu/mL) and diluted at $1/10^{\text{th}}$ for *Staphylococcus aureus*, $1/100^{\text{th}}$ for other bacteria, and $1/1000$ for yeasts.

After labeling, prepared inocula were spread at the surface of the solidified culture medium using a sterile cotton swab and kept for pre-diffusion at room temperature for 15 minutes.

Filter paper discs (6 mm) were deposited at the surface of the inoculated Petri dishes, and 5 μ L of products were added on discs, using a micropipette.

Petri dishes were then incubated at 37°C for 24 hours and 48 hours respectively for bacteria and yeasts. and the inhibition zone diameters measured.

Each test was performed three times and the mean calculated and expressed in the form of diameters \pm SD (Standard deviation). A compound was considered active when the IZ was greater than 6 mm.

RESULTS AND DISCUSSION

The physical and analytical data of the complexes are presented in Table 1. All the complexes are crystalline with yields that range from 61% to 87%. All the complexes are very stable in air whereas the starting metal salts are generally hygroscopic. All the complexes decomposed within the temperature range of (100-240) °C of Koffler`s apparatus that was used. However, the melting point of pyridine -2- carboxylic acid, which was confirmed using the same apparatus is 137°C, as that reported in the literature [24]. There was however a colour variation with temperature for the complexes of Mn(II), Co(II), Ni(II) and Cu(II) which could be attributed to change in crystal structure from octahedral to tetrahedral as water molecules were removed. The elemental analytical results for carbon, hydrogen and nitrogen as well as the estimated metal contents are very close to the calculated values (Table 1).

Table 1: Physical and analytical data of the complexes complexes.

Complex	Color	%Yield	Melting Point (°C)	Elemental Analysis %Found (%calculated)			
				%C	%N.	%H	%M
[Mn(C ₆ H ₄ NO ₂) ₂ (H ₂ O) ₂].H ₂ O	Greenish-Yellow	77	150	38.73 (38.83)	7.85 (7.55)	4.20 (4.34)	15.00 (14.80)
[Co(C ₆ H ₄ NO ₂) ₂ (H ₂ O) ₂].H ₂ O	Orange	87	100	38.44 (38.41)	7.46 (7.47)	4.25 (4.30)	15.69 (15.71)
[Ni(C ₆ H ₄ NO ₂) ₂ (H ₂ O) ₂].H ₂ O	Blue	65	118	38.54 (38.44)	7.69 (7.47)	4.22 (4.30)	15.67 (15.66)
[Cu(C ₆ H ₄ NO ₂) ₂ (H ₂ O)]	Deep-blue	75	240	44.10 (44.24)	8.70 (8.60)	3.23 (3.09)	19.41 (19.51)
[Zn(C ₆ H ₄ NO ₂) ₂ (H ₂ O) ₂].2.H ₂ O	White	61	160	37.75 (37.77)	7.31 (7.34)	4.20 (4.23)	16.98 (17.13)

The molar conductance values of the metal (II) complexes are summarized in Table 2. These molar conductance values are very low, i.e. 0.13 to 2.2 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, indication that they are non-electrolytes [25] as they are molecular in nature [26].

Table 2: Molar Conductivity, Electronic Spectral data and Magnetic moments for the complexes

Complex	Molar Conductivity ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	Electrolytic Type	Band Maxima (cm^{-1})	Assignment	Magnetic Moment μ_{eff} (B.M)
[Mn(C ₆ H ₄ NO ₂) ₂ (H ₂ O) ₂].2.H ₂ O	2.17	Non-electrolyte			
[Co(C ₆ H ₄ NO ₂) ₂ (H ₂ O) ₂].2.H ₂ O	1.01	Non-electrolyte	20000 cm^{-1} 17241 cm^{-1}	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}$	4.76
[Ni(C ₆ H ₄ NO ₂) ₂ (H ₂ O) ₂].2.H ₂ O	2.20	Non-electrolyte	15873 cm^{-1} 10526 cm^{-1}	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g} \rightarrow {}^3T_{2g}$	2.86
[Cu(C ₆ H ₄ NO ₂) ₂ (H ₂ O)]	0.13	Non-electrolyte	15625 cm^{-1}	${}^2E_g \rightarrow {}^2T_g$	1.63
[Zn(C ₆ H ₄ NO ₂) ₂ (H ₂ O) ₂].2.H ₂ O	0.97	Non-electrolyte			

The relevant IR band frequencies of the ligand and the metal complexes are presented in Table 3. Strong and sharp peaks characteristic of pyridine -2- carboxylic acid are observed in the spectra of the complexes, with significant shifts, an indication that the ligand is coordinated to the metal ions [27]. The IR spectra of all the complexes show similar features, for example, the characteristic absorption bands of C=O and C-O of the ligand at (1715 cm^{-1}) and (1347 cm^{-1}) regions have disappeared, while the absorption bands of the asymmetric [$\nu_{\text{as}}(\text{COO}^-)$] and symmetric [$\nu_{\text{s}}(\text{COO}^-)$] stretching vibrations of the carboxylate anion, around 1642-1628 cm^{-1} and 1388-1352 cm^{-1} regions appear (Table 3) with $\Delta\nu(\text{COO}^-)$ in the range 231-290 cm^{-1} . This clearly indicates a unidentate bonding mode of O⁻ in these complexes [27, 28]. The coordination of water molecules to the metal ions in the picolinate results in the appearance of vibrational bands at 659-640 cm^{-1} . The absorption bands in the range 3000-3500 cm^{-1} in the spectra of these complexes is due to ν (OH) vibrations originating from both lattice water molecules and

coordinated water molecules. The broadness of the bands could be an indication of the presence of strong hydrogen bonding in the complexes. The stretching vibrations of the $\nu(\text{M-O})$ mode around $579\text{-}459\text{ cm}^{-1}$ is at slightly higher energy than the corresponding $\nu(\text{M-N})$ mode around $446\text{-}427\text{ cm}^{-1}$ [29] which are similar to values of other complexes of the ligand [27].

Table 3: Selected IR Absorption bands of pyridine -2- carboxylic acid and the derived complexes (cm^{-1})

Compound	$\nu(\text{OH})$	$\nu_{\text{as}}(\text{COO}^-)$	$\nu(\text{C=O})$	$\nu(\text{ring})$	$\nu_{\text{s}}(\text{COO}^-)$	$\nu(\text{C-H})$	$\nu(\text{M-OH}_2)$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
pyridine -2- carboxylic acid	3436 br	-	1715m	1598vs	-	799s	-	-	
$[\text{Mn}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	3437br	1619s	-	1589vs	1388vs	769vs	655w	540w	427w
$[\text{Co}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	3353br	1628vs	-	1593vs	1373vs	765vs	640m	579w	444w
$[\text{Ni}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	3376br	1628vs	-	1594s	1377vs	769	645w	582w	446w
$[\text{Cu}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})]$	3436br	1642vs	-	1569s	1352vs	774s	659m	567w	455w
$[\text{Zn}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	3310br	1616s	-	1596	1355s	765vs	649m	459w	433

The visible absorption spectrum of the cobalt complexes revealed two bands at $20,000\text{ cm}^{-1}$ and $17,241\text{ cm}^{-1}$ that have been assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ respectively [30]. All the three allowed octahedral bands were not observed due to limitation of the spectroscopic instrument.

In the visible region of the electronic spectrum of nickel complexes, the bands at $15,873, 10526\text{ cm}^{-1}$ are typical of d-d transitions and these have been assigned to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow \text{are } {}^3\text{T}_{2g}$ respectively [31]. According to Sutton [32], the ratio of the first to second band for octahedral nickel (II) is less than 1.8 while for tetrahedral complex it is approximately 2.2. The value of 1.51 for this complex is indicative of octahedral nickel (II). In the visible spectrum of the copper complexes, the band 15625 cm^{-1} has been assigned to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_g$ transition [33].

The room temperature magnetic moment of the cobalt complex, $[\text{Co}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ was found to be 4.76 BM. Although this value is higher than the spin only value of 3.87 BM. it is within the range for octahedral high spin d^7 configuration for cobalt (II) [12, 29, 34] as pyridine -2- carboxylic acid is a weak field ligand.

The room temperature magnetic moment of $[\text{Ni}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ is 2.86 BM. This value is similar to other values of nickel (II) in octahedral geometry [1, 29, 35].

The magnetic moments of simple Cu^{2+} complexes are generally lower than 2.2 BM. regardless of the stereochemistry [36]. The room temperature magnetic moment for the copper (II) complex is 1.63 BM. This value is close to 1.40 BM. [35] for which octahedral geometry has been assigned.

The structures of these complexes have been confirmed by single X-ray crystallography as, represented in figures 1-3 [17, 37]

Thermogravimetric analysis of the complexes show that the complexes undergo decomposition involving more than one step, to give metal oxide as residue and various gases resulting from the (Table 4).

Table 4: Thermo-analytical Results (TGA) of the Complexes

Complex	Temperature Range(°C)	Probable Volatile products	Weight loss (%)	
			Calculated	Found
[Mn(C ₆ H ₄ NO ₂) ₂ (H ₂ O) ₂].2.H ₂ O	140-180	2H ₂ O	9.63	9.36
	180-300	2H ₂ O	9.63	9.63
	300-500	2C ₅ H ₅ N	42.09	48.75
	500-670	2CO ₂	23.71	15.25
			Total:85.06	0.84
				Total:83.83
[Co(C ₆ H ₄ NO ₂) ₂ (H ₂ O) ₂].2.H ₂ O	100-140	4H ₂ O	19.19	18.80
	150-420	2CO ₂	23.45	20.56
	420-610	2C ₅ H ₅ N	42.11	40.65
			Total:84.75	Total:80.01
[Ni(C ₆ H ₄ NO ₂) ₂ (H ₂ O) ₂].2.H ₂ O	50-200	4H ₂ O	19.20	17.05
	200-400	2C ₅ H ₅ N	42.14	53.88
	400-800	2CO ₂	23.45	18.97
			Total:84.79	Total:89.90
[Cu(C ₆ H ₄ NO ₂) ₂ (H ₂ O)]	50-75	H ₂ O	5.53	7.65
	75-140	1CO ₂	13.51	13.96
	140-180	1C ₅ H ₅ N	24.25	24.18
	240-380	1C ₆ H ₄ NO ₂ ⁻	37.45	33.60
			Total:80.74	Total:79.39

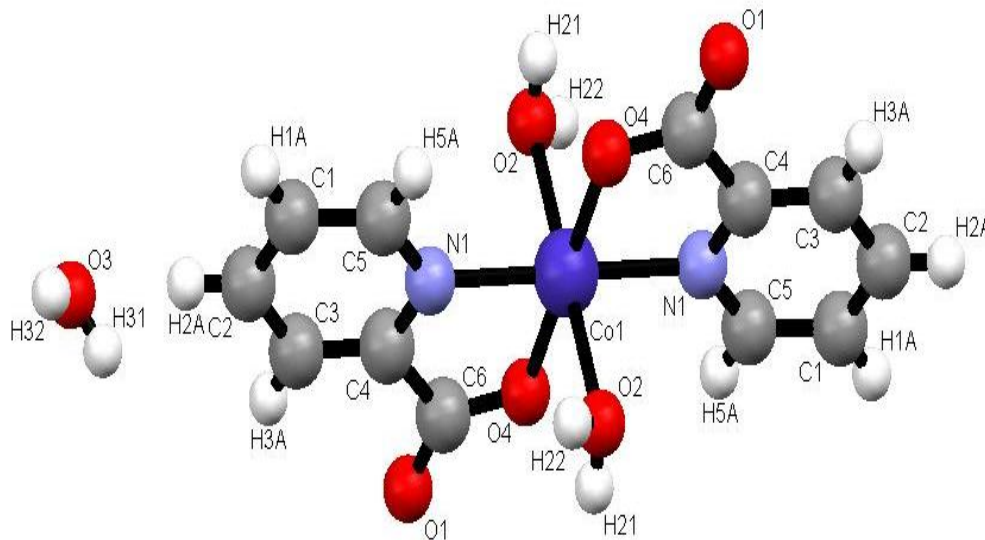


Figure 1: X-ray crystal structure of [Co (C₆H₄NO₂)₂ (H₂O)₂]. 2H₂O

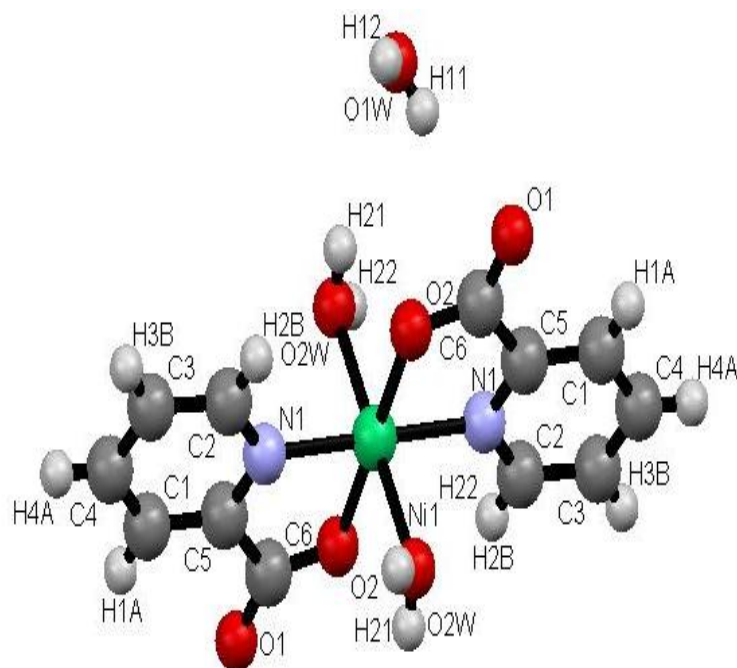


Figure 2: X-ray crystal structure of $[\text{Ni}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

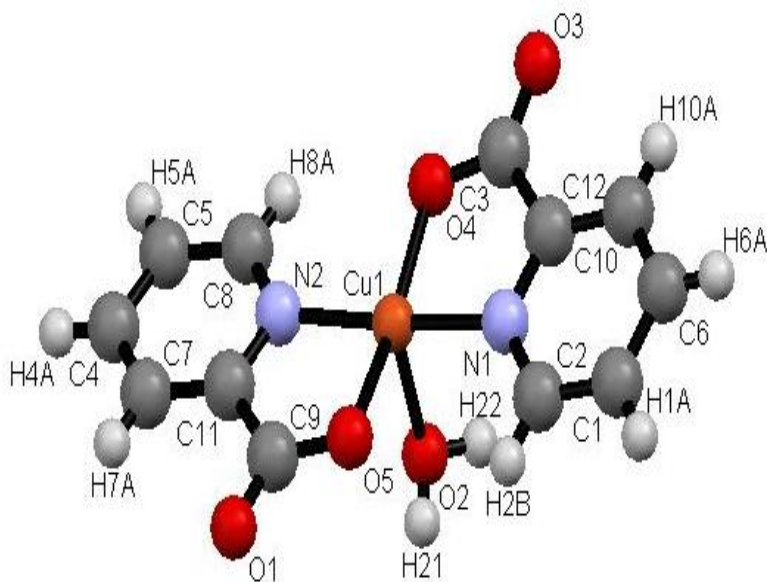


Figure 3: X-ray crystal structure of $[\text{Cu}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})]$

Antimicrobial tests

The ligand, metal salts and metal picolinates were tested for antimicrobial activity against four yeasts and nine bacteria obtained from the Central hospital, Yaoundé, Cameroun and “Centre Pasteur”, Yaoundé Cameroun. The results of susceptibility of these microbes

towards the compounds, judged by the inhibition zone growth diameter (IZ), are presented in Table 5.

Table 5: Antimicrobial Activity of the Picolimates (IZ diameters in mm)

Micro-organisms	1	2	3	4	5	6	7	8	9	10	11	GENT	NYST
	<i>C. Krusie</i>	0±0	0±0	0±0	0±0	0±0	0±0	14±1.2	13±1.2	0±0	8±1.3	12±1.4	--
<i>C. albicans</i>	0±0	0±0	0±0	0±0	0±0	0±0	13±0.6	12±0	5±0.1	0±0	11±1.3	--	20 ± 1.1
<i>C. néoformans</i>	0±0	0±0	0±0	0±0	0±0	0±0	0±0	13±0	0±0	7±1.1	16±0.7	--	20 ± 0.7
<i>C. parapsilosis</i>	0±0	0±0	0±0	0±0	0±0	0±0	17±0.1	12±0	0±0	0±0	14±0	--	14 ± 0.4
<i>P. aeruginosa</i>	9±0.3	0±0	0±0	0±0	0±0	0±0	9	10	9	-	-	25 ± 0.2	--
<i>c. freundii</i>	10± 1	0±0	0±0	0±0	0±0	0±0	-	-	-	-	-	28 ± 0.9	--
<i>E. coli</i>	0±0	0±0	0±0	0±0	0±0	0±0	13	7	9	8	8	29 ± 0	--
<i>K. pneumoniae</i>	12 ± 0.7	7±0	0±0	0±0	0±0	0±0	11	10	10	8	7	24 ± 0.6	--
<i>S. auréus</i>	12 ± 0	0±0	0±0	9±0	7±0.1	8± 1.1	10	7	8	7	7	38 ± 0.4	--
<i>S. thyphi</i>	9±0	0±0	0±0	0±0	0±0	0±0	12	9	9	-	-	26 ± 0.4	--
<i>M. morgani</i>	0±0	0±0	0±0	0±0	0±0	0±0	11	8	-	7	-	25 ± 0.1	--
<i>E. cloacae</i>	6±0	0±0	0±0	0±0	0±0	0±0	11	9	9	-	-	30 ± 0.9	--
<i>S. flexineri</i>	0±0	0±0	0±0	0±0	0±0	0±0	13	10	9	7	8	32 ± 1.6	--

1=pyridine-2-carboxylic acid 2=[Co(C₆H₄NO₂)₂(H₂O)₂].2H₂O,
 3=[Ni(C₆H₄NO₂)₂(H₂O)₂].2H₂O, 4=[Cu(C₆H₄NO₂)₂(H₂O)], 5=[Zn(C₆H₄NO₂)₂(H₂O)₂].2H₂O, 6= [Mn(C₆H₄NO₂)₂(H₂O)₂].2H₂O, 7= Co(NO₃)₂.6H₂O, 8 = Ni(NO₃)₂.6H₂O,
 9 = ZnCl₂, 10 = MnCl₂.4H₂O, 11= CuCl₂.2H₂O, GENT= Gentamycin, NYST= Nystatin

The results presented in Table 5 show that the ligand and a few of the metal complexes have selective activity on the bacterial strains. Pyridine -2- carboxylic acid also shows selective mild antibacterial susceptibility on some of the tested bacterial pathogens (5/9) and no activity on the candida species. None of the complexes exhibited any activity on the four candida species. Zinc, manganese and copper complexes exhibited some activity on the bacterial strain, *S. auréus*, with inhibition zones in the range 7-9 mm. The cobalt complex showed activity against *K. pneumoniae* with an inhibition zone of 7 mm. The activities exhibited by the complexes of zinc, manganese and copper on *the staphylococcus aureus* can be further studied as a potential therapy against this pathogen.

CONCLUSION

Complexes of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) with pyridine -2- carboxylic acid as ligand have been synthesized and characterized using elemental analyses, conductance measurements, magnetic and spectroscopic studies and single crystal X-ray structure. The results suggest that the metal complexes assume distorted octahedral geometry in which Mn(II), Co(II), Ni(II) and Zn(II) have two molecules of the ligand and two aqua ligands each in the coordination sphere, whereas the copper complexes has a distorted square- pyramidal geometry in with two molecules of the ligand and one aqua ligand are in the coordination sphere. Conductance values indicate that the complexes are non electrolytes. Thermogravimetric analyses show that the complexes undergo more than one step decomposition of both the coordinated and uncoordinated water molecules and picolinate ions to metal oxide and various gases.

The X-ray crystal structure of three of the complexes; $[\text{Co}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, $[\text{Ni}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})]$ have been confirmed as reported [17,37]. $[\text{Co}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, belongs to the monoclinic crystal system with space group $P2_1/c$, with coordinates, $a = 9.7852(2) \text{ \AA}$, $b = 5.11800(10) \text{ \AA}$, $c = 14.5069(2) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 90.4270(10)^\circ$, $\gamma = 90.00^\circ$, $V = 726.49(2) \text{ \AA}^3$, $Z = 4$. The complexes $[\text{Ni}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ also belongs to monoclinic crystal system, with space group $P2_1/c$, with coordinates, $a = 9.67068(3) \text{ \AA}$, $b = 5.14990(10) \text{ \AA}$, $c = 14.3957(4) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 90.024^\circ$, $\gamma = 90.00^\circ$, $V = 716.94(3) \text{ \AA}^3$, $Z = 4$. $[\text{Cu}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})]$ crystallizes in the orthorhombic crystal system, space group $Pbca$, with coordinates $a = 12.7042(2) \text{ \AA}$, $b = 12.6859(2) \text{ \AA}$, $c = 14.7894(2) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, $\gamma = 90.00^\circ$, $V = 2383.52 \text{ \AA}^3$, $Z = 8$.

Antimicrobial studies on nine bacterial strains and four candida species reveal that the ligand and some of the the metal picolinate have selective activity on a few bacterial strains and no activity on the candida species. The zinc manganese and copper complexes exhibited some activity on the bacterial strain, *Staphylococcus aureus*, while the cobalt complex showed activity against *K. pneumonia*. These could be studied further as a potential therapy against this pathogen.

ACKNOWLEDGMENTS

We thank Dr. Harold Brice Tahn Jeazet of Institut Für Anorganische Chemie, University of Düsseldorf, Germany for thermogravimetric analysis of the compounds and Mr Thiery Ngouna Kammalac of the Laboratory of Applied Microbiology and Molecular Pharmacology, Faculty of Sciences, University of Yaounde I Cameroon, for the antimicrobial tests.

REFERENCES

- [1] Satya Prakash GD, Tuli SK, Basu RD, Madan. Advanced Inorganic Chemistry. S Chand and Company LTD India 2009; II: 534-5894.

- [2] C Xiao- Ming, Y Bao-Hui, H Xiao-Chun, X Zhi-Tao. J Chem Soc Dalton Trans 1996; 3465-3468.
- [3] DGA Harshani, D Beoku-Belts, K Panayotis, K Govindaraju, R Powls, NP Tomkinson, AG Sykes. J Chem Soc Dalton Trans 1992; 2145-2149.
- [4] R Natarajan, S Sivasangu. J Serb Chem Soc 2010; 75(6): 773-788.
- [5] C Barry, K Kwanagh, M Mcxcann, M Devereux and M Geraghty. Biometals 2003; 16(2): 1572-1773.
- [6] HD Revanasiddappa, L Shivakumar, KS Prasad, B Vijay, B Jayalakshmi. Chemical Sciences 2012: CSJ-64.
- [7] Pragnesh K, Panchal MN, Patel. Nano-Metal Chemistry 2005; 34(7): 1277-1289.
- [8] MO Agwara, PT Ndifon, NB Ndosiri, AG Paboudam, DM Yufanyi, A Mohamadou. Bull Chem Soc Ethiop 2010; 24(3): 393-389.
- [9] MO Agwara, JN Foba-Tendo, C Amah, DM Yufanyi, NB Ndosiri. RJPBCS 2012; 3(3): 95-102.
- [10] D Daipayan, JD Atish, R Ambarish, JM Arek, M Ali. Indian Journal of Chemistry 2008; 47A: 1656-1660.
- [11] AMA Morsy, FA Mautner. Polyheron 1993; 12(14): 1751-1756.
- [12] VM Ellis, RS Vagg, EC Watton. J Inorg nucl Chem 1974; 36: 1031-1038.
- [13] GW Evans, EC Johnson. J Nutr 1981; 111(1): 68-70.
- [14] C Papatiantafyllopoulou, CP Raptopoulou, A Terzis, JF Janssens, E Manessi- Zoupa, PP Spyros, JC Plakatouras. Polyhedron 2007 ; 26:4053-4063.
- [15] Y Yoshikawa, E Ueda, K Kawabe. J Biol Inorg Chem 2002; 7: 68-73.
- [16] Y Yoshikawa, E Ueda, Y Kojima, H Sakurai. Journal of the American College of Nutrition 1998; 17(2): 109-115.
- [17] S Soralova, M Breza. Polyhedron 2010; 29: 2440-2444.
- [18] I Ivanka, GS Sanja, G Nevenka, R Sinisa, R Alexander, TI Ziveslav, BK Keppler. J Serb Chem Soc 2011; 76(1): 53-61.
- [19] MO Agwara, DM Yufanyi, JN Foba-Tendo, MA Afamba, DT Ndinteh. J Chem Pharm Res 2011; 3(3): 196-204.
- [20] NB Ndosiri, MO Agwara, Ag Paboudam, PT Ndifon, DM Yufanyi, C Amah. Res J Pharm Bio Chem Sci 2013; 386-397.
- [21] DC Haris. Quantitative Chemical Analysis. WH Freeman : New York 1991; 3: 279-299.
- [22] WW Poterfield. Inorganic Chemistry: A United Approach. Academic Press Inc 1984; 2: 579-587.
- [23] JS Carvallert et al. American Society for microbiology 2005; 1-231.
- [24] RC Weast, MJ Astle, WH Beyer. Handbook of Chemistry and Physics 1985-1986, 66th Edn. CRC Press, C157- C400.
- [25] WJ Geary. Coordination Chemical Review 1971; 7: 81-82.
- [26] SH Wheeler, C Steven, Zingheim LC, Nathan. J Inorg Nucl Chem 1978; 40: 779-783.
- [27] BS Parajon- Costa, CC Wagner, EJ Baran. Journal of the Argentine Chemical Society 2004; 92(1/3): 109-117.
- [28] S Parbati, D Rupam, G Sakiprasad, WS Sheldrick. Polyhedron 2001; 20: 3349-3354.
- [29] A Kleinstein. Spectroscopic J Inorg Nucl Chem 1971; 33: 405 - 412.
- [30] PT Ndifon, MO Agwara, NJ Njapba, GA Paboudam, MD Yufanyi, J Ngoune, A Galindo, E Alvarez, A Mohamadou. Transition Met Chem 2009; 34: 745.



- [31] B Yan, QY Xie. Journal of the Chinese Chem Soc 2004; 51: 697-702.
- [32] D Sutton. Electronic Spectra of transition metal complexes, Mc Graw-Hill, London, 1968; 129.
- [33] PAN Reddy, M Nethaji, AR Chakravarty. Inorg Chim Acta 2002; 337: 450-458.
- [34] Pradyot Patnaik. Handbook of Inorganic Chemicals. MCGraw-Hill 2002; 1: 233-991.
- [35] FA Cotton, G Wilkinson, CA Murillo, M Bochmann. Advanced Inorganic Chemistry. John Wiley and Sons, Inc: New York 1999; 6: 619-821.
- [36] JD Lee. Concise Inorganic Chemistry. Chapman and Hall 1991; 4: 209-851.
- [37] Z Heren, CE Cüneyt, C Keser, NO Iskeleli. Acta Cryst 2006; E62: m796-m798.