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Synthesis, Characterization and Antimicrobial Activities of Some Nicotinamide – metal Complexes

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KEYWORDS: Synthesis, Metal complexes, Nicotinamide, Antibacterial, Antifungal.

ABSTRACT: Some transition metal complexes of nicotinamide have been prepared and characterized using melting point, conductivity measurement, infrared, electronic, HNMR and atomic absorption spectroscopic methods. . The antibacterial and antifungal studies of the metal complexes and the ligand have been evaluated against *Escherichia coli, Staphylococcus and Bacillus subtilis , Aspergillus flavus, Aspergillus niger and penicillum species.* It was found that nicotinamide formed stable metal complexes with these metal ions. The analysis of the spectroscopic data shows that nicotinamide act as monodentate, coordinating through the nitrogen atom of the pyridine ring. All the complexes exhibit 4- coordinate geometry. The results of the antimicrobial studies showed that the metal complexes have higher inhibitory activity than the original nicotinamide against the tested bacteria and fungi species. © JASEM

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Introduction:

In the search for novel vitamins-metal complexes, the modification of existing vitamin by coordination to a metal ion has attracted considerable attention in recent years. This has led to lots of study on vitamin-metal complexes, with the hope of improving and enriching the quality of existing vitamins, thereby serving as better substitute as chemotherapeutic agents (Obaleye and Orjiekwe (1993). Despite the fact that some metal complexes of vitamins: ascorbic acid, thiamine hydrochloride, pyridoxine have been reported in literature (Franklin and Richrdson (1989), Thompson(1980), Adeyemo (1981), Cramer *et al* (1984) , Hadjiliadis and Yannopoulous (1983) . Very few reports on the synthesis and characterization of nicotinamide have appeared in literature. Thus, this article reports the synthesis, characterization and antimicrobial studies of some metal complexes of nicotinamide.

MATERIALS AND METHODS

The metal salts used for the synthesis were obtained from British Drug House Chemical Limited, England and were used as supplied. Nicotinamide was obtained from Swiss Chemical Limited Lagos. Cultures of the micro-organisms used were obtained from Department of Microbiology, University of Ilorin.

Synthesis of Metal complexes: The synthetic procedure described by Obaleye *et al* (1994) was employed in the synthesis of the complexes. 1.231g (10 mmol) of Nicotinamide was dissolved in 20 ml methanol. 10ml of aqueous solution of 5 mmol of metal salts (M=$CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $MnCl_2.4H_2O$, $CuCl.6H_2O$, $ZnCl_2$ and $CuCl_2$) were added to the Nicotinamide solution. The colour change and pH were recorded. The mixture was stirred with a magnetic stirrer for 2 hours. Precipitated products were obtained after few days. The precipitate formed was collected by filtration, washed with methanol and dried over $CaCl_2$ in a dessicator.

The proposed equation for the reaction is: $MX_2.nH_2O + 2Nic \rightarrow M(Nic)_2X_2+nH_2O$. M = metal ion, X = Halide, Nic = Nicotinamide ligand

Characterization of the complexes: Infrared spectra of the ligand and the complexes were recorded in KBr pellets in the range (4000-400cm^{-1}) on Buck Scientific M500 IR spectrometer. Electronic spectra

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were on Aquamate Scientific Spectrophotometer model V4.60. The metal content was done using an alpha 4 Atomic Absorption Spectrophotometer with PM 8251 simple-pen recorder. Conductivity measurements were carried out using WTW conductometer Bridge.

Antimicrobial studies: The antimicrobial activity of the ligand and its metal complexes were determined according to the procedure previously reported by Obaleye *et al* (1994) . The bacteria species used for this study include *Escherichia coli, Staphylococcus and Bacillus subtilis* while the fungi species used include *Aspergillus flavus, Aspergillus niger and penicillum species.*

RESULT AND DISCUSSION

The results of the physical properties and spectroscopic data are presented in table(1-4)

Table 1: Some physical properties of Nicotinamide and its complexes**.**

Ligand/complex	Colour	Mpt(°C)	R_f	%yield	%metal calcd (found)	Wavelength (nm)
Nicotinamide	White	130-132	0.50	-	-	218,280
$Ni(Nic)_2Cl_2$	Green	150(decomp.)	0.58	65.0	15.7(15.2)	290,395,410,590
$Mn(Nic)_2Cl_2$	Whitish	176-178	0.65	63.2	12.4(12.8)	380
$Co(Nic)_2Cl_2$	Pink	180-182	0.62	56.0	14.8(14.1)	204,390,410,445
$Zn(Nic)_2Cl_2$	White	154-156	0.67	60.0	16.5(16.0)	385
$Cu(Nic)_2Cl_2$	Blue	192-194	0.71	68.0	15.4(15.3)	204,292,580

Table 2; Selected Infrared data (cm-1) for Nicotinamide and its complexes

Ligand/complex	v NH_2	v C=O	v C=N	N-Hdef	v M-N
Nicotinamide	3351(m)	1685(s)	1381(s)	1162(m)	-
$Ni(Nic)_2Cl_2$	3332(m)	1655(s)	1387(s)	1150(m)	694(m)
$Mn(Nic)_2Cl_2$	3302(w)	1612(s)	1381(s)	1150(w)	688(s)
$Co(Nic)_2Cl_2$	3333(w)	1612(s)	1387(s)	1150(w)	694(s)
$Zn(Nic)_2Cl_2$	3381(s)	1697(s)	1375(s)	1150(w)	639(s)
$Cu(Nic)_2Cl_2$	3387(m)	1697(s)	1375(s)	1156(s)	639(s)

w=weak, s=strong,m=medium.

All the complexes were slightly soluble in distilled water, ethanol and methanol. Most of the complexes were crystalline formed exceptions are $Ni(Nic)_2Cl_2$ and $Cu(Nic)_2Cl_2$ which exist in powder form. All the complexes melt above 154 °C, except $Ni(Nic)_2Cl_2$ which decomposed at 150 °C (Lawal,2010).

The Infrared spectrum of nicotinamide was compared with those of its complexes. The medium absorption bands at 3351 cm^{-1} due to NH_2 vibration in the spectrum of free nicotinamide was not significantly shifted in the spectra of the complexes showing that NH_2 groups are not involved in coordination . The band at 1150cm^{-1} due to N-H deformation vibration position in the metal complexes, also support that no coordination has occurred through this point.

The v (C=N) vibrations which occurs at 1395cm^{-1} in the free nicotinamide was shifted in the metal complexes due to coordination via the nitrogen of the pyridine ring (David,2000) .

The bands between 610cm^{-1} and 630cm^{-1} in the infrared spectra of the metal complexes which could not be traced in the spectrum of the free nicotinamide have been tentatively assigned to v M-N stretching band (Nakamato *et al* (1970), Gohzalez- vergara *et al* (1982)

Proton –NMR Spectra of Nicotinamide and its Complex: The ^{1}H-nmr spectra and the assignment for Nicotinamide and its complex in DMSO are presented in table 3.

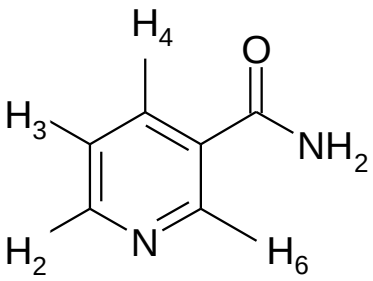
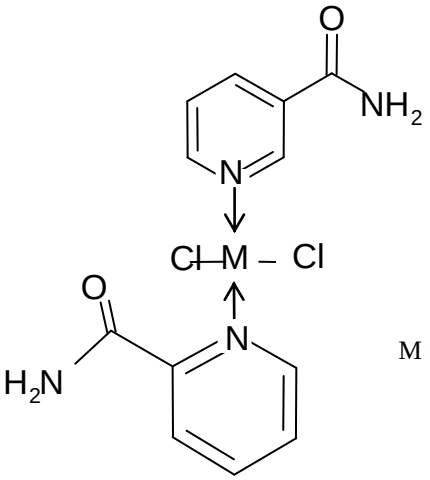


Table 3: ^{1}H–nmr Signal Assignment of Nicotinamide and its Complex

Assignment	∂ ppm (Nicotinamide)	∂ ppm $Co(Nic)_2Cl_2$,
H (2)	8.70	7.80
H (6)	8.23	7.51
- $CONH_2$	9.05	9.00



M = Ni(II), Mn(II), Co(II), Zn(II),Cu(II)

Proposed structure for Nicotinamide metal complexes

e proton NMR spectra assignments of the free nicotinamide were compared with that of its complex. The peak at 8.70 ppm due to H(2) shifted to 7.80 ppm while ∂ H (6) shifted from 8.23 ppm to 7.51 ppm in the complex, due to coordination through the nitrogen of the pyridine ring. The $Ni(Nic)_2Cl_2$ was insoluble in DMSO, the ^{1}H-NMR and ^{B}C-NMR signal obtained contains mainly the solvent peaks (David,2000).

Based on the spectroscopic data obtained and in the absence of X-ray crystallographic data, the proposed structure tentatively proposed for nicotinamide-metal complex is shown in figure below:

*Antimicrobial activity Study***:** The result of the antibacterial and antifungal activities are presented in table 4 and table 5 respectively.

Table 4: Antibacterial activities of Nicotinamide and its metal complexes showing the zone of inhibition against the organisms.

Ligand/complex	E.coli		Staphylococcus		Bacillus subtilis	
	50ppm	100ppm	50ppm	100ppm	5oppm	100ppm
Nicotinamide	14±1.2	20±1.1	15±1.6	17±1.3	19±1.2	21±1.1
$Zn(Nic)_2Cl_2$	16±1.2	21±1.2	18±1.2	20±1.4	21±1.3	24±1.6
$Cu(Nic)_2Cl_2$	19±1.2	23±1.1	21±1.4	23±1.5	22±1.5	26±1.1

Table 5: Antifungal activities test of Nicotinamide and its metal complexes showing the zone of inhibition against the organisms.

Ligand/complex	Aspergillus flavus		Aspergillus Niger		Penicillum sp	
	50ppm	100ppm	50ppm	100ppm	5oppm	100ppm
Nicotinamide	15±1.1	19±1.2	10±0.8	17±1.4	12±1.2	20±1.6
$Zn(Nic)_2Cl_2$	14±1.2	21±1.9	14±0.8	20±1.9	17±1.1	22±1.5
$Cu(Nic)_2Cl_2$	20±1.3	24±1.9	18±0.9	22±1.9	24±1.6	28±1.8

The antibacterial activities test of nicotinamide and its metal complexes were tested against three bacteria species, which include *Eschericia coli, Staphylococcus aureus and Bacillus subtilis*. Zn(II) and Cu(II) complexes of nicotinamide showed the highest inhibition against the Bacillus subtilis. The antifungal activities test of free nicotinamide and its metal complexes are tested against three fungi species: *Aspergillus flavus, Aspergillus niger and penicillum species.* The result showed that Cu(II) complex of nicotinamide has the highest activity against all the three fungi species (Mishra and Soni, 2008)

Conclusion: The results of both the physical and spectroscopic data confirm that nicotinamide is a chelating ligand. In all the complexes, Nicotinamide coordinate to the metal ions through the nitrogen of pyridine ring. The result of the antibacterial and antifungal activities shows that nicotinamide-metal complexes have higher antibacterial and antifungal activities compared to the free nicotinamide.

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