International Journal of Scientific Research in Engineering and Management (IJSREM)
Volume: 08 Issue: 11 | Nov - 2024 SJIF Rating: 8.448 ISSN: 2582-3930

Comprehensive Analysis of Metal Complexes Derived from 2-Picolinic Acid: Structural, Chemical, and Functional Insights

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Abstract:

Non-aqueous method was used for synthesis of metal (II) complexes of picolinic acid and characterization was done using different techniques including infrared (FT-IR), Ultraviolet-visible, ^{1}H-NMR and Electron Spin Resonance (ESR) spectroscopy. Other studies including conductance, magnetic susceptibility and thermal analysis were also carried out. The thermal analysis indicated that these complexes are thermally stable and start to decompose at temperatures above 260°C. The FT-IR spectroscopy also established the presence of important functional groups found in the metals and the respective ligands groups such as C=O, C=N, O- H, C= C and M-O. The thermogravimetric analysis showed that these complexes are not hydrated. Electronic spectra revealed additional information about the complexes' geometry: cobalt and nickel complexes were octahedral, while the copper complex displayed distorted octahedral geometry. Additional investigations on these metal complexes were electrochemical studies. Lastly, the activity of the complexes against an array of microorganisms was evaluated. The nickel (II) complex exhibited the greatest inhibition against four chosen strains of bacteria tested, which were superior among other tested complexes.

KEYWORDS:

Antimicrobial Activity; Cyclic Voltammetry; Metal (II) complexes; Picolinic acid.

Introduction

Picolinic acid is a chelator that also occurs naturally in humans and aids in the absorption of certain metals. Zinc dipicolinate is a common health supplement because it satisfies the body's need for zinc which is required for several biological activities. Similarly, manganese, a trace metal that is essential for man and plants, is also required for the process of photosynthesis most especially in specific redox reactions of photosystem I and II. Inadequate manganese levels in a human being may result to diseases such as osteoarthritis and osteoporosis. Considered a ferromagnetic element, cobalt is associated with the element of vitamin B12. This is a vitamin that is important for the production of blood cells and is also used in the management of people with anemia. Another important micro nutrient, Nickel affects the hormonal activity and the metabolism of lipid. Copper is an essential micronutrient for humans and is involved in many physiological processes, which include healing of wounds and fighting off infections. It is largely found in the bones and muscles and is controlled by the liver. The antibiotics have been the center of investigations because of their use in acne treatment, management of Alzheimer's disease, and controlling dental plaques. Zinc is an important trace element that is used in numerous physiological processes including DNA synthesis, immunity, cell division, protein synthesis, wound healing and tissue regeneration but too much intake of zinc can inhibit the absorption of copper and iron. Much attention has been given to the coordination chemistry of picolinic acid as regards its coordination to metal ions through nitrogen and carboxylate oxygen[1-4]. Trustworthy results are available

on the antibacterial effect of metal complex of mixed ligands[5,6], the electrochemical behavior of Cu(II) complexes with picolinic acid and the biological effects of Co(II) complexes with imide groups[7–15]. Moreover, cobalt and picolinic acid complexes have also shown the activity of homogeneous hydrogen evolution from.

Materials and Methods

Materials

The chemicals needed to prepare the five picolinic acid complexes were of high purity and included ethanol, diethyl ether, picolinic acid (as the ligand), five different metal carbonates, and perchloric acid.


(Ligand picolinic acid)

Synthesis of five metal(II) perchlorate

By use of simple precipitation technique, five different metal perchlorate complexes-Co, Mn, Ni, Cu and Zn respectively were formulated. To begin with, 10g of each carbonate of the metals (Cobalt(II) carbonate, Manganese(II) carbonate, Nickel(II) carbonate, Copper(II) carbonate and Zinc carbonate) was treated with 14 ml of 70% aqueous perchloric acid. Water was then used to recrystallize the obtained compounds. In preparation of the complexes, one mole of each metal(II) perchlorate was mixed with three moles of a ligand in ethanol. The solution was refluxed for six hours followed by concentration and cooling of the mixture. Excess ligand was removed from the reaction mixture by washing with diethyl ether. After, the five complexes synthesized were crystallized.

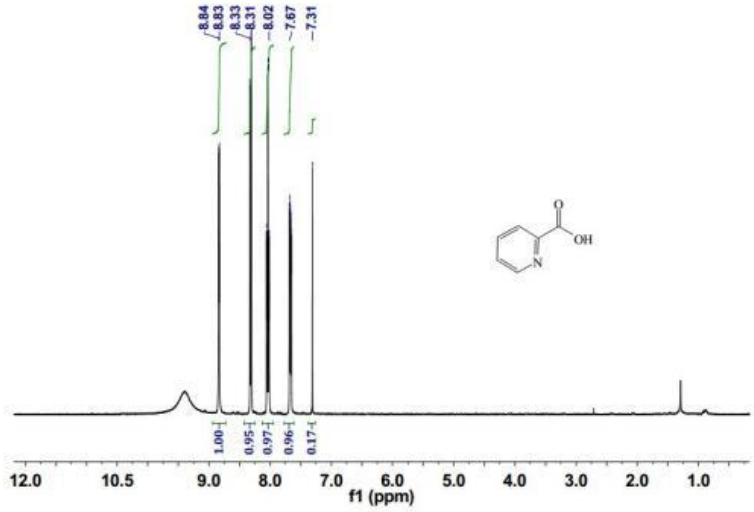
Characterization of Complexes and their Anti-microbial activity

The FT-IR spectra of five synthesized perchlorate complexes were recorded using a Shimadzu FT-IR 8400S spectrometer after mixing the complexes with KBr. The UV-Vis spectra of three of these complexes were recorded in ethyl alcohol and methanol on a Hitachi U-3400 spectrophotometer. The NMR spectra of the zinc complex and its ligand were also recorded in DMSO-d6 and CDCl3, respectively. The TGA measurements were performed within the temperature ranges of 50-800°C in nitrogen atmosphere to determine the thermal stability of the five complexes with α-Al2O3 as a reference. Magnetic measurements on the susceptibility of perchlorate complexes were done using Gouy's apparatus[16-20]. The electrochemical experiments were performed using a VSP (SNO147) instrument with tetrabutylammonium perchlorate as a supporting electrolyte and by cyclic voltammetry. Antimicrobial activity of the ligand and its five complexes was determined against three fungi and four bacteria by using the agar diffusion method.

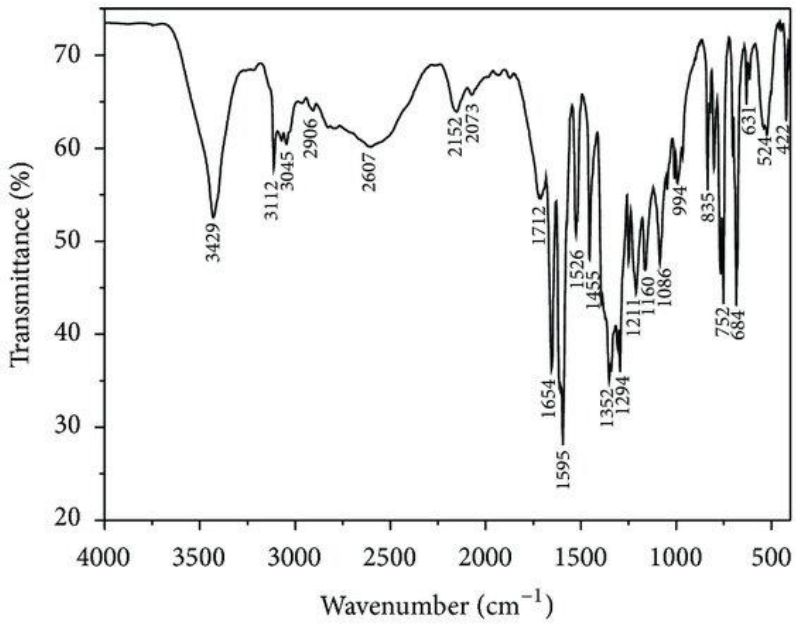
Results and Discusion

In accordance with their formulation, the molar conductance of the synthesized complexes was evaluated. Conductance measurements showed that the complexes act as 1:2 electrolytes with the anions situated outside the coordination sphere[21-22]. The magnetic moments and melting points of the synthesized metal complexes are shown

in Table . The corresponding values for the metal ions ± the predicted ones, fit well. Upon heating, the complexes stand stable and start decomposing at temperatures higher than 260°C[23-27].



1H-NMR of 2-PICOLINIC ACID (Ligand)



FTIR of 2-PICOLINIC ACID (Ligand)

Physicochemical properties of metal complexes.

Complex	Conductance values $Ohm^{-1}cm^2mol^{-1}$	Type of Electrolyte		Melting Point	Colour
$[FeL_3])^{2+}(ClO_4)_2$	171.89	1:2	6.02	260	White
$[NiL_3]^{2+}(ClO_4)_2$	186.6	1:2	4.9	260	Brown
$[CrL_3]^{2+}(ClO_4)_2$	202.23	1:2	2.9	290	Light Blue
$[CoL_3]^{2+}(ClO_4)_2$	193.07	1:2	1.9	310	Dark Blue
$[ZnL_3]^{2+}(ClO_4)_2$	172.19	1:2	–	280	White

L=Picolinic acid

FT-IR of five metal complexes.

Compound	stretching cm^{-1}	acid cm^{-1}	cm^{-1}	cm^{-1}	stretching cm^{-1}	cm^{-1}	cm^{-1}
Ligand	3396	1742	1675	1599	3099	–	–
$[FeL_3]^{2+}(ClO_4)_2$	3400	1705	1655	1598	3181	551	430
$[NiL_3]^{2+}(ClO_4)_2$	3408	1724	1653	1602	3153	524	420
$[CrL_3]^{2+}(ClO_4)_2$	3404	1726	1653	1602	3153	524	418
$[CoL_3]^{2}(ClO_4)_2$	3427	1707	1654	1600	3157	551	449
$[ZnL_3]^{2+}(ClO_4)_2$	3497	1707	1643	1592	3242	530	441

Electronic spectra of metal complexes.

Complex	Medium	Assignment	Stereochemistry
$[CoL_3]^{2+}(ClO_4)_2$	Ethanol	19,607cm^{-1} $^4T_{1g} \longrightarrow {}^4T_{1g}(P)$	Octahedral
$[NiL_3]^{2+}(ClO_4)_2$	Ethanol	28,089cm^{-} $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$	Octahedral
$[CrL_3]^{2+}(ClO_4)_2$	Ethanol	15,290 cm^{-1} $^2Eg \longrightarrow {}^2T_2g$	Distorted octahedral

^{1}H – NMR of Ligand and Nickel(II)perchlorate complexes.

Compound	Aromatic ring proton (ppm)	Carboxylic acid proton (ppm)
$Ligand^{2+}$	7.6-8.8	9.76
$[NiL_3]\ (ClO_4)_2$	7.5-9.07	13.48

L = Picolinic acid

Conclusion

Metal(II) Perchlorate complexes were studied the spectral characteristics showing that the ligand coordinates via the nitrogen atom of the pyridine and the oxygen atom of the carbonyl group. The classical bipyramidal structure of the complex is corroborated by these studies. The thermal analysis revealed the lack of moisture content in all the complexes[28]. Cyclic voltammetry (CV) studies proved that cobalt–nac complex has two oxidation states reachable via a quasi-reversible one electron transfer reduction process. The manganese(II) and zinc(II) complexes displayed a reversible one-electron reduction process; whereas, the copper(II) and cobalt(II) complexes exhibited reduction and oxidation process that were not reversible. Both the ligand and the complexes showed pronounced antifungal and antibacterial activity.

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