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Synthesis and Antibacterial Activities of Bimetallic Complexes of Cobalt (II) and Nickel (II) Acetophenolate

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Abstract - Bimetallic complexes of cobalt (II) and nickel (II) acetophenone with tin chloride were synthesized and characterized by elemental analyses, conductivity measurement, magnetic and spectral data. The complexes are 1:2 adducts and non-electrolytes in solution. The ligands and their complexes were screened for antibacterial activities against Staphyloccus aureus and Escherichia coli. Cobalt (II) bimetallic complexes were found active against the tested microorganisms.

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Synthesis and Antibacterial Activities of Bimetallic Complexes of Cobalt (II) and Nickel (II) Acetophenolate

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Abstract - Bimetallic complexes of cobalt (II) and nickel (II) acetophenone with tin chloride were synthesized and characterized by elemental analyses, conductivity measurement, magnetic and spectral data. The complexes are 1:2 adducts and non-electrolytes in solution. The ligands and their complexes were screened for antibacterial activities against *Staphyloccus aureus* and *Escherichia coli*. Cobalt (II) bimetallic complexes were found active against the tested microorganisms.

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I. INTRODUCTION

Acetophenone is a viscous colourless aromatic ketone. It is used as a precursor in resins and fragrances (Hardo and Manfred, 2002). It has a melting and a boiling point of 19-20°C and 220°C respectively. In industry, acetophenone is used in the production of propylene oxide [1].

Acetophenone occurs naturally in many foods such as apple, cheese, apricot, banana, beef and cauliflower [2]. It is a polymerization catalyst for the manufacture of olefin and an intermediate for pharmaceutical, agrochemical and other organic compounds. It has been used as a drug to induce sleep and as teargas in warfare [3].

Schiff bases and it's metal chelates have played an important role in the development of chemical industries through catalysis, substrate carrier and dyes[4].Tucareso, a schiff base forming immunomodulator is currently undergoing pilot phase 1\11 clinical trials as an immunopotentiator in chronic hepatitis B virus infection, HIV infection and malignant melanoma [5].

These ligands are widely studied because of their coordinating properties and abilities [6,7]..The ligands are important compounds in medicinal and pharmaceutical field. They show biological activities including antibacterial, antifungal, anticancer, and herbicidal activities[8].Schiff base are utilized as starting materials in the synthesis of industrial and biological compounds[9].

The work is aimed at carrying out syntheses, conductivity measurement and electronic spectral of biologically active bimetallic complexes of cobalt (II) and nickel (II) of acetophenone and their antibacterial activities.

II. MATERIALS AND METHODS

The reagents used are of analytical grade and were used without further purifications. Metal complexes of cobalt (II) and nickel (II) acetophenolate were prepared according to well established methods in literature [10].

a) Preparation of cobalt (II) acetophenolate

1.25g of cobalt (II) chloride was weighed into a 100cm^3 beaker and 10cm^3 of acetophenone was added. The mixture was heated to 90°C on a hot water bath and was stirred continuously. Temperature was maintained for 15 minutes with stirring. The mixture was cooled in an ice bath and on cooling the dark pink product formed was vaccum-filtered and air dried for 15 minutes. The product was later dried in a descicator over a silica gel, weighed and its percentage yield determined (56%).

$$CoCl_2.6H_2O + 2C_6H_5C\,(O)CH_3 \rightarrow$$
$$[Co(C_6H_5OC(O)CH_3)_2Cl_2]^{2+} + 6H_2O$$

Similar method was used for the preparation of nickel (II) acetophenolate.

$$NiCl_26H_2O + 2C_6H_5C(O)CH_3 \longrightarrow$$
$$[Ni(C_6H_5C(O)CH_3)_2CI_2]^{2+} + 6H_2O$$

b) Preparation of the bi metallic complexes [4]

A general method has been used for the preparation of the binuclear complexes by the reaction of the metal salts and the Schiff base ligand at a metal to ligand molar ratio of 2:1.The mixture was heated on water bath to ensure complete dissolution of the metal salt. To this solution the ligand (2.2g, 5mmol dissolved in 10cm^3 ethanol) was added gradually. The reaction mixture was were filtered, washed with ethanol and dried in over an hydrous calcium chloride (62%). The procedure was used to prepare and isolate the ML^1.

$$L + SnCl_4 \longrightarrow LSn + 4Cl$$

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c) Evaluation of antimicrobial activities[12]

The antimicrobial activities of the test compounds were assayed against two micro organisms *Staphylococus aureus and Escberichia coli* regarded as pathogen to man and animal. All media and bacteria suspension were prepared using a suitable method. The *in-vitro* evaluation of antimicrobial activities was performed according to the diffusion technique .The bacterial including *staphylococcus aureus and Escherichia coli* were grown in nutrient broth at 37°C for 24 hours. The ligands and their complexes were tested using diffusion on solid media . Sterile (5mm) diameter sensitivity paper disc were impregnated with concentration of dimethyl formamide (DMF), ligands and their bimetallic complexes at concentration of 50μg/cm^3 and placed in the nutrient agar. The plates were then incubated for 24 hours. Additionally antibiotics disc for cephalosporin were tested as positive control. The results were recorded by measuring the growth inhibition surrounding the disc.

d) Physical measurement

The infrared spectra of the complexes were measured as KBr disc on Perkin Elmer FTIR Paragon 1000 spectrometer in the range 4000-400cm^{-1}while the electronic spectra in chloroform were recorded on Perkin Elmer λ20.The elemental analyses (C and H) were determined. Nickel and Cobalt were determined titrimetrically [13]. .Magnetic susceptibilities were measured on Johnson Matthey magnetic susceptibility balance and diamagnetic corrections were calculated using Pascal's constants [14].Melting point were determined using a Stuart scientific melting point SMPI machine. Molar conductivity at room temperature was measured in water using ELCOM-CM-82 conductivity machine using 10^{-3}mol dm^{-3} stock solution of the complexes.

III. RESULTS AND DISCUSSION

All complexes are coloured and amorphous in nature. Acetophenone complexes of nickel (II) $[Ni(Acet)_2]$ is greenish yellow while its cobalt (II) complexes $\{Co(Acet)_2\}$ are pinkish and are all soluble in polar solvents such as dimethlyformanide (DMF), dimethylsulfoxide (DMSO), methanol, ethanol and water, but insoluble in chloroform, diethyl ether and petroleum ether. The elemental analyses showed the complexes as 1:2 adducts and the conductivity data suggest non-electrolytic behavior (Table 1).

a) Molar conductance

The molar conductance of the metal complexes in DMSO were observed below 14.0 ohm^{-1} cm^2 mol^{-1} showing that they were non-electrolyte. A value of 60-115 ohm^{-1} cm^{2}mol^{-1} is expected for 1:1 electrolyte.

b) Electronic Spectra

Nickel (II) complexes are known to have a range of coordination numbers from six (octahedral) to four(square planar/tetrahedral).Their electronic spectra are typically characterized by the existence complexes of complicated equilibra involving this structural type [15].The electronic spectra of the complexes of $[Ni(Acet)_2CI_2].H_2O$ has three characteristic absorption at 14,000, 25,000 and 33,000cm^{-1} bands while its bimettalic counterpart has characteristic band at around 24,000 cm^{-1} indicative of octahedral stereochemistry (Table I). These signals are assigned to ^3A_2g to Tig (F),v_1 ,v_2, v_4 and ^3A_2g to $^3T_I g(P)$, V_3 respectively. Octahedral nickel (II) complexes exhibit another transition from ^3A_2g to $^3T_{2g}$ at approximate 900cm^{-1} but this may not be determined when the splitting constant is nearly unity and the v_2 transition appears as a well-defined doublet due to the spin forbidden level ^1E_g spinning intensity through configuration interaction with the $^3T_{1g}(E)$ level [16,17]. Therefore the presence of the two characteristic band v_2 and v_3 confirmed that the stereochemistry of the complexes as octahedral and has not changed from its bimetallic complex.

The electronic data of $[Co(Acet)_2CI_2].H_2O$ and its bimetallic complexes(Table 2).The metal complex exhibit a multiple band at 15,748cm^{-1} The band is assigned to the $^4T_{1g}(F)$ to$^4T_{2g}(P)$ transition and its bimetallic complex exhibits a band at 19,230cm^{-1} and band was assigned $^4T_{1g}(F)$ to$^4T_{2g}(P)$ The electronic spectra indicate that cobalt in bimetallic complexes remains in an octahedral environment [16,18].

c) Magnetic moment

The magnetic moment of nickel (II) in a cubic field falls between 2.8 - 4.2B.M,tetrahedral complexes have moment in the range 3.20 -4.10 B.M while in octahedral field falls between 4.2- 5.1 B.M. The nickel complexes reported in this work are diamagnetic and consequently octahedral geometry. $[Co(acet)_2CI_2].H_2O$ and its bimetallic complex has magnetic moments between (4.37 – 4.75)BM. These together with the electronic spectra data are suggestive of an octahedral geometry. [16,18].

d) Infrared spectra

A comparison of the infrared spectra of the complexes with the parent ligand in DMSO solution shows the conformity with what was reported in literature on similar system[16,18,19].Table 3.The broad band at(3350-3490)cm^{-1} in the metal and bimetallic complexes was observed and assigned to υ (O-H) stretching frequencies. The strong band, which are very prominent at (957-729)cm^{-1} are attributed to υ (C-H) bands of phenyl ring. The $\upsilon(C=O)$in the parent ligand is shifted to lower region in the complexes by (60-44) cm^1, thus indicating coordination through the carbonyl oxygen of the ketone. The weak bands around 530-540 cm^{-1} has been assigned to $\upsilon(M-O)$ stretching frequencies in metal carbonyl complexes. Also, the bands observed at around 680-575 cm^{-1} was assigned to $\upsilon(M-M)$ in the complexes. The strong band observed in the ligand at around 2850 cm^{-1} is shifted to a lower region in the complexes by (50-40)cm^{-1},thus showing coordination through the cabanion (methyl hydrogen) in the acetophenone [20].

e) Antibacterial Activity

Acetophenone and its metal and bimetallic complexes were screened for their antibacterial activity and the results have been presented in Tables 4 and 5. The bimetallic complexes of cobalt (II) showed good activity against gram positive *Staphylococcus aureus* and least activity against gram negative *Escherichia coli*. While on the other hand the bimetallic complexes of nickel (II) showed least activity against the gram positive and gram negative bacteria. The enhance activity of the complexes over ligands can be explained in terms of chelation theory [21]. Although chelation is not the only criteria for antibacterial activity, some important factor such as nature of the metal ion, metal ion coordinating site, hydrophilicity, hypophilicity and presence of co-ligands have considerable influence on the antibacterial activity. The chelate complexes deactivated various cellular enzymes which play vital role in various metabolic pathways of these microorganisms. Other factors such as solubility, conductivity and dipole moment affected by the presence of metal ions, may be the reasons for increasing the biological activities of the metal complexes compared to the corresponding ligands. Therefore the antibacterial activity of the metal complexes cannot be ascribed to chelation alone but it's an intricate blend of all of the above contributions.

IV. CONCLUSION

The ligand acts as bidentate with carbonyl oxygen atom and carbon as donors. The antibacterial activity of the acetophenone is enhanced upon complexation with metal ions particularly for cobalt (II).

Table 1: Analytical data and physical properties of the complexes

COMPOUND	FW(gmol^{1})	COLOUR	%YIELD	% M		M.P	Ohm^{-1}cm^{-1}mol^{-1}
				Found	Calculated		
$[Ni(C_6H_5COCH_3)_2CI_2].H_2O$	389.99	Greenish	64.00	15.07	15.05	256	20
$Ni(C_6H_5COCH_3)_2Sn].H_2O$	579.68	Light green	71.60	10.14	10.13	226	36
$C_6H_5COCH_3)_2CI_2].H_2O$	390.21	Pink	76.00	15.12	15.10	245	32
$[Co(C_6H_5COCH_3)_2CI_2].H_2O$	579.90	Light pink	81.00	10.18	10.16	234	40

Table 2: Magnetic moments and electronic spectra (cm^{-1}) of the complexes.

Compound	μ_{eff}B.M	Elecronic spectra (cm^{-1})
$[Ni(L_2CI_2].H_2O$	0	14,000;25,000;30,000
$[Ni(L_2Sn].H_2O$	0	24,000
$[Co(L_2CI_2].H_2O$	4.75	15,748
$[Co(L_2Sn].H_2O$	4.37	19,230

Table 3 : Diagnostic infrared spectra for the complexes (cm^{-1})

Compounds	υ(O-H)	υ(C- H)	υ(C=O)	Δ(C=O)	υ(C-H)	ΔH(C-H)	υ(M-M)	υ(M-O)
L	-	870m,747s	1689	-	2850		-	-
$[Ni(L_2CI_2].H_2O$	3490	870m,749s	1639	50	2803	47	-	530
$[Ni(L_2Sn].H_2O$	3350	890m,750s	1630	59	2802	48	575	535
$[Co(L_2CI_2].H_2O$	3517	950m,729s	1645	44	2804	46	-	540
$[Co(L_2Sn].H_2O$	3428	957m,766s	1640	49	2802	48	680	532

Table 4a. Diameter of zones of inhibition (Aliyu & Nwabueze, 2009)

Diameter of inhibition (mn)	Symbol	Comments
12-15	+	Insignificant activity
16-20	++	Minimum activity
21-25	+++	Moderate activity
26-35	++++	Maximum activity

Key: + = activity

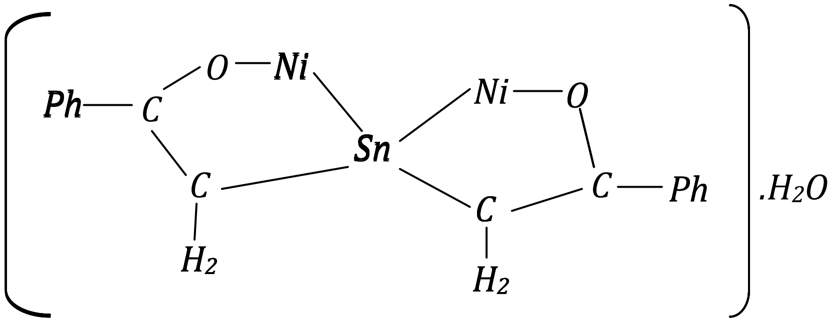
Table 4b. Biological test on *Escherichia coli* (gram negative) $50\mu g/cm^3$.

Complexes/Ligands	Diameter of zone of inhibition(mm)	Symbol	Comments
Acetophenone	13	+	Insignificant activity
$[Ni(acet)_2CI_2].H_2O$	12	+	Insignificant activity
$[Ni(acet)_2.Sn]].H_2O$	14	+	Insignificant activity
$[Co(acet)_2CI_2].H_2O$	17	++	Minimum activity
$[Co(acet)_2.Sn].H_2O$	16	++	Minimum activity
DMF(Solvent control)	-	-	No activity
Cephalosporin(positive control)	23	+++	Moderate activity

Table 5: Microbial Tests on *Staphylococcus aureus* (gram positive) $50\mu g/cm^3$

Complexes/Ligands	Diameter of zone of inhibition(mm)	Symbol	Comments
Acetophenone	17	++	Minimum activity
$[Ni(acet)_2CI_2].H_2O$	12	+	Insignificant activity
$[Ni(acet)_2.Sn_4].H_2O$	13	+	Insignificant activity
$[Co(acet)_2CI_2].H_2O$	23	+++	Moderate activity
$[Co(acet)_2.Sn].H_2O$	21	+++	Moderate activity
DMF(Solvent control)	-	-	No activity
Cephalosporin (positive control)	28	++++	Maximum activity

Proposed structure for the Bimetallic complexes of acetophenone.



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