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SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL STUDIES OF Co(II), Ni(II) AND Zn(II) COMPLEXES OF SCHIFF BASE DERIVED FROM 4-METHOXY ANILINE

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ABSTRACT

Three new transition metal complexes have been prepared using the Schiff base furan-2-ylmethylene-(4-methoxy-phenyl)-amine. These complexes were characterized by various physico- chemical analyses such as elemental analyses, metal estimation, anion estimation, conductivity measurements and magnetic moment measurements. They were also confirmed by spectral analyses like FTIR, UV-Visible, NMR and Mass. The result shows that the ligand is acting in a bidentate manner through its 'N' and 'O' donor atoms .The ligand and the complexes were screened for antibacterial study against Escherichia coli in different concentrations.

KEY WORDS: 4-methoxy aniline, NMR, Antibacterial activity, Furfuraldehyde

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INTRODUCTION

Schiff bases containing 'N', 'O' donor ligands play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions[1]. The interaction of these donor ligands and metal ions give complexes of different geometries and these complexes are potentially biologically active. Schiff bases have many applications. Schiff bases of chromium and copper ions give fast colours to leather and food packages. Schiff bases and their complexes are used in solvent extraction, precipitation reaction, complexometric titrations and fluorometry. These are used for dyeing synthetic fibres[2] and also used in colour photography to reduce photosensitivity of photographic emulsions[3]. Schiff bases found many biological applications also. 'Rhodopsin' the visual pigment contains an azomethine linkage. Schiff bases of benzophenone derivatives are reported to show biological activities such as cytotoxic activities against human oral squamous carcinoma cells.In the present work we have prepared a Schiff base by condensing 4-methoxy aniline and Furan-2-carbaldehyde. Using this Schiff base three new complexes of Co(II), Ni(II) and Zn(II) were prepared and characterized by various physic chemical methods.

MATERIAL AND METHODS

High purity grade reagents were used for the synthesis of ligand and the complexes. 4-methoxy aniline and Furan-2-carbaldehyde were purchased from their manufactures (BDH-AR, Merck-GR). The solvent used for the preparation of ligand and complexes was methanol. The commercial sample of this was purified by standard methods[4]. Other reagents employed include ethanol, chloroform, perchloric acid, ammonium hydroxide, ammonium thiocyanate, pyridine, potassium iodide, EDTA and thiosulphate. All of the metal salts used for the preparation of the complexes were AR grade samples.The complexes were analyzed for metal and halide content by standard methods[5]. The electrical conductance of the complexes in methanol and DMF (10^{-3} m solution) were measured at room temperature using a Systronics direct reading conductivity meter Model No.306. The Infrared spectra of the ligands and complexes were recorded in the range of 4000-400 cm^{-1} on a Schimadzu IR Prestige-21 Spectrometer. Electronic spectra of the ligands and the complexes in methanol were measured in the range 200-900 nm on Perkin Elmer Lamda 25 UV-Visible spectrophotometer. The Elemental analyses (C, H, N) were carried out on a Vario EL-III CHN Elemental analyzer at the SAIF, Cochin University of Science and Technology. The magnetic moments were measured at room temperature on a Sherwood Scientific magnetic susceptibility meter. ^{1}H NMR spectrum of ligand was recorded in JEOL GSX 400 NBFT NMR spectrometer using TMS as reference. Mass spectrum of the complex was recorded in JEOL JMS 600H instrument.

SYNTHESIS OF THE SCHIFF BASE FURAN-2-YLMETHYLENE-(4-METHOXY-PHENYL)-AMINE (FAMP)

A methanolic solution of 4-methoxy aniline (0.05 mol) and Furan-2-carbaldehyde (0 .05 mol) was boiled under reflux on a water bath for 5 hrs. The resulting solution was concentrated and cooled to get the solid ligand. It was filtered and repeatedly washed with cold water and recrystallized from methanol.

SYNTHESIS OF THE COMPLEXES

The metal complexes have been prepared by mixing methanolic solution of respective metal salts with methanolic solution of the Schiff base FAMP in 1:1 ratio. The reaction mixture was refluxed on water bath for 4-5 hours. The solid products appeared on standing the solution were filtered washed with methanol-water mixture and recrystallised from methanol and dried over anhydrous $CaCl_2$.

RESULTS AND DISCUSSION

All the complexes were amorphous solids and were soluble in methanol, acetone, DMSO and DMF. . The purity of the Schiff base was confirmed by elemental analysis as well as by IR spectral studies. For FAMP the emperical formula was $C_{12}H_{11}NO_2$, and the microanlytical values are found to be: C 71.73%, H 5.38%, N 6.88%, against the calculated values: C 71.69%, H 5.37%, N 6.93%. The molar conductance value of 10^{-3} molar concentration of the complexes carried out in methanol as solvent indicated that Co(II) and Ni(II) complexes are non electrolytes while Zn(II) complex is 1:2 electrolyte. The magnetic moment values calculated supports octahedral geometry for Ni(II) and Co(II) complexes. Analytical data of the complexes are presented in Table-1, along with their molar conductance and magnetic moment values.

Table 1
Analytical data of FAMP complexes

Complex	Metal%	C%	N%	H%	μeff	Conductivity Methanol
$[Co[FAMP]_2Cl_2]$.	11.0 (11.1)	54.1 (54.7)	5.2 (5.2)	3.2 (3.2)	4.68	11.9
$[Ni[FAMP]_2Cl_2]$	11.0 (11.2)	54.1 (54.8)	9.3 (9.2)	5.2 (5.3)	3.23	13.5
$[Zn(FAMP)_2]Cl_2$	13.9 (13.8)	61.6 (61.9)	12.2 (12.0)	5.9 (5.8)	--	152

IR SPECTRAL DATA

Azomethine group (C=N) has a characteristic stretching frequency. In general, upon coordination to metal ions this band is shifted to lower frequencies with respect to the free ligand. A strong band at 1610 cm^{-1}shown by the ligand FAMP is attributable to the C=N stretching[6] is shifted in the complexes between 1580-1590 cm^{-1} indicating the coordination of azomethine nitrogen to the metal ions. This is supported by the appearance of new band in the region 459-468 cm-^{1} in the complexes due

to v_{M-N}[7]. The band at 1673 cm^{-1} in the FABP spectrum is shifted in the range 1630-1636 cm^{-1} in the complexes indicating the coordination of C=O group which is further supported by the formation of new bands in the regions 528-541cm^{-1} attributed to v_{M-O} bands respectively[8]. The IR spectral data of the ligand and the complexes are given in Table 2.

Table 2
Important IR spectral data of FAMP and its complexes

FAMP	$[Co[FAMP]_2Cl_2]$.	$[Ni[FAMP]_2Cl_2]$	$[Zn(FAMP)_2]Cl_2$	Assignment
2999	2895	2902	2925	$\bar{\upsilon}_{C-H\ Stch}$
1610	1588	1594	1590	$\bar{\upsilon}_{C=N\ Stch}$
------	541	536	528	$\bar{\upsilon}_{M-O}$
------	468	463	459	$\bar{\upsilon}_{M-N}$

ELECTRONIC SPECTRA

The electronic spectra of FAMP consists of two bands around 339 and 252 nm corresponds to n→π* and π→π* transitions[9]. The absorption bands of the complexes are shifted to longer wavelengths compared to that of the ligand. Also new bands are appeared in the region due to d-d transition. The important electronic spectral bands of the ligand and the complexes are given in Table 3.

Table 3
Electronic spectral bands of FAMP and its complexes

Compound	λ_{max}(nm)	Assignment
FAMP	339	n→π*
	252	π→π*
$[Ni(FAMP)_2Cl_2]$	338	n→π*
	255	π→π*
	480	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
	550	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
$[Co(FAMP)_2Cl_2]$	336	n→π*
	257	π→π*
	510	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	570	$T_{1g}(F) \rightarrow {}^4A_{2g}(F)$

^{1}H NMR SPECTRUM

The ^{1}H NMR spectrum of FAMP showed a multiplet between 6.6-7.6 ppm δ may be due to the aromatic protons and the peak at δ= 8.4 ppm for the azomethine proton and protons of OCH_3 group at δ 3.8 ppm. The NMR spectrum is shown in Fig 1.

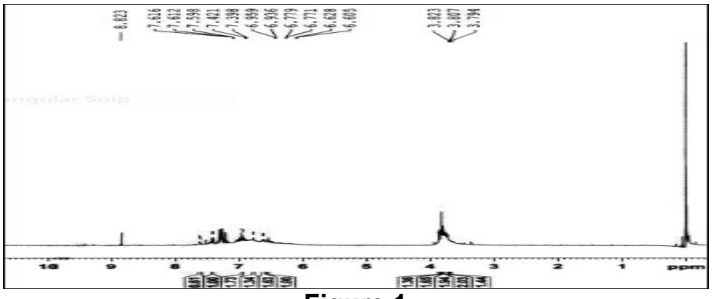

Figure 1
NMR spectrum of FAMP

MASS SPECTRUM

The mass spectrum of nickel (II) complex of FAMP shows a base peak at m/z = 532. A peak at 202 is due to $[C_{12}H_{11}N\ O_2]$+ ion. The other peaks are due to further fragmentation of the ligand moiety. The mass spectrum of the complex is shown in Fig 2.

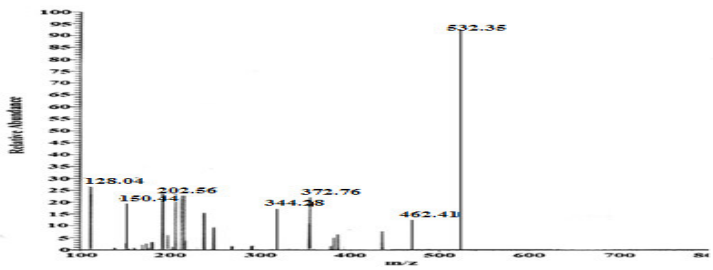

Figure 2
Mass spectrum of $[Ni[FAMP]_2Cl_2]$

Based on the analytical data and various physico-chemical analyses the complexes can be formulated as $[Co(FAMP)_2Cl_2]$, $[Ni(FAMP)_2Cl_2]$, $[Zn(FAMP)_2]Cl_2$. The proposed structures of the ligand and the complexes are shown in Fig 3-6.

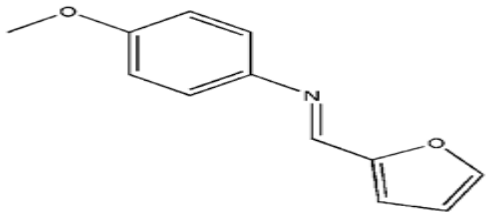

Figure *3*
Structure of FAMP

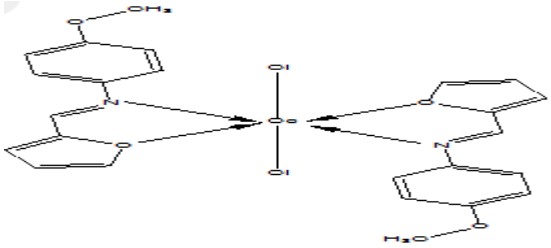

Figure 4
structure of $[Co(FAMP)_2Cl_2]$

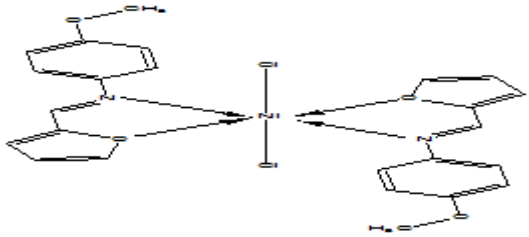

Figure 5
structure of $[Ni(FAMP)_2Cl_2]$

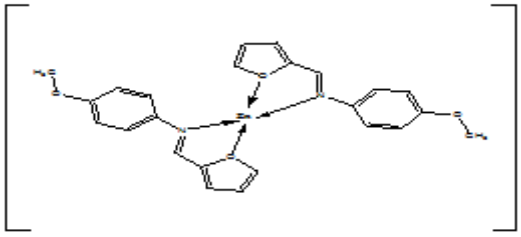

Figure 6
Structure of $[Zn(FAMP)_2]Cl_2$

ANTI BACTERIAL ACTIVITY

The in vitro biological screening effects of the investigated compounds were tested against the bacteria Escherichia coli by using disc diffusion method by taking DMSO as solvent. Gentamycin was used as a positive control. The result indicates that the ligand and zinc complex shows the highest antibacterial activity against E.coli. The study of the growth inhibition zone of the Schiff base indicated that the lipid membrane that surround the cell favours the passage of only lipid soluble materials due to which liposolubility is considered to be an important factor that controls the anti microbial activity. The inhibition zone of antibacterial activity of FAMP and its complex are shown in Table 4.

The anti bacterial activity of FAMP and its complexes are shown in figs 7-10.

Table 4
Antibacterial activity of FAMP and its complexes

Compound	Bacterial inhibition zone(mm)
FAMP	1
$[Ni(FAMP)_2Cl_2]$	Nil
$[Co(FAMP)_2Cl_2]$	Nil
$[Zn(FAMP)_2]Cl_2$	1.5

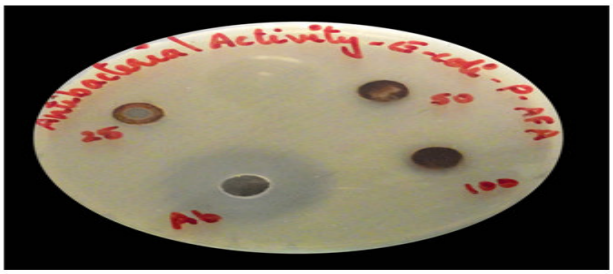

Figure 7
The antibacterial activity of FAMP and its Complexes FAMP

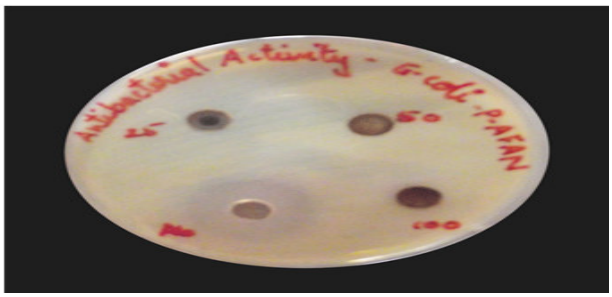

Figure 8
[Ni(FAMP)$_2$Cl$_2$]

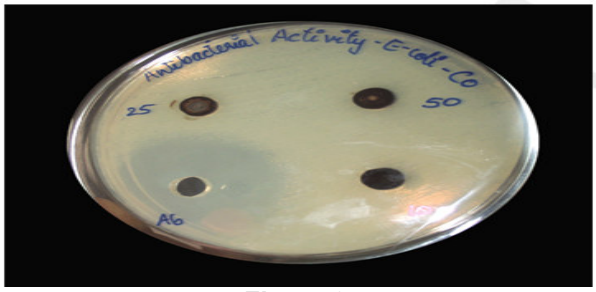

Figure 9
[Co(FAMP)$_2$Cl$_2$]

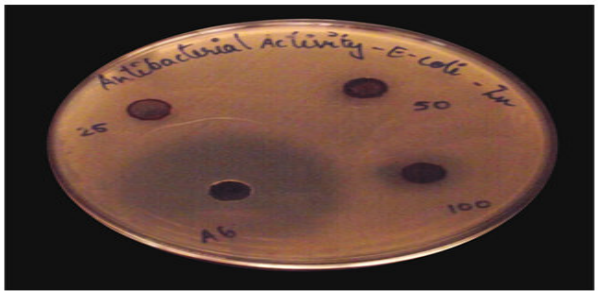

Figure 10
[Zn(FAMP)$_2$]Cl$_2$

CONCLUSION

Three new complexes of Co(II), Mn(II), and Ni(II) were prepared using the Schiff base FAMP. Characterization of the ligand and complexes has been done on the basis of analytical and physical measurements. . From their spectral and magnetic data it is confirmed that the nickel and cobalt complexes possess octahedral geometry having the formula [Ni[FAMP]$_2$Cl$_2$] and [Co[FAMP]$_2$Cl$_2$]. On the basis of analytical data, metal estimation and conductance measurements tetrahedral geometry is assigned for the zinc complex. The ligand and metal complexes were screened for their physiological activities against E.coli. The result shows Zn(FAMP)$_2$]Cl$_2$ complex has more activity than the ligand.

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CONFLICT OF INTEREST

Conflict of interest declared none.

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