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Research Article

SYNTHESIS AND CHARACTERIZATION OF METAL COMPLEXES OF A *N*-(FURAN-2-YLMETHYLIDENE)- PYRAZINE-2-CARBOXAMIDE SCHIFF BASE

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ABSTRACT

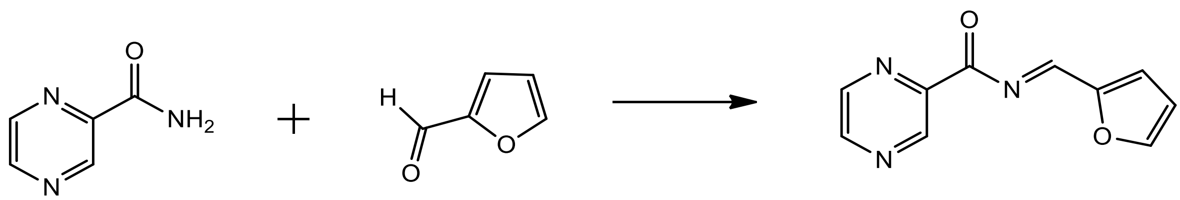
The Fe(III), Ru(III), Co(II), Ni(II), Cu(II), Pd(II), Zn(II), Cd(II) and Hg(II) complexes of a Schiff base derived from pyrazine-2-carboxamide and furan-2-carbaldehyde (FMPCA: 1) have been synthesized and structurally characterized by various physico-chemical data. The ligand acts as a neutral, bidentate one towards the metal ions coordinating through azomethine nitrogen and furan oxygen. The geometry and the bonding characteristics associated with the complexes have been deduced from relevant spectral data. Consolidating all the data obtained Fe, Ru, Co, Ni and Cu Complexes have been assigned to octahedral geometry, Pd complex, a square planar geometry and the Zn, Cd and Hg complexes tetrahedral in geometry. Further, the ligand and the metal complexes have been screened for their antimicrobial activity, the Hg complex exerting the highest activity.

Keywords: Pyrazine-2-carboxamide, furan-2-carbaldehyde, Schiff base, Synthesis, Characterization.

INTRODUCTION

Schiff bases are the compounds having azomethine linkage (-C=N) and are very significant due to their stability, chelating properties and biological applications. In the last few decades, extensive work has been done on synthesis and biological studies of Schiff bases and their metal-based derivatives Schiff base ligands are excellent coordinating molecules and can exhibit variety in the structure of their metal complexes. Literature survey reveals that Schiff bases have assumed importance in various fields such as coordination chemistry [1], analytical chemistry [2] and pigments, dyes [3] and polymer [4,5] industries; in biochemical researches, especially as model compounds of several vitamins and enzymes [6,7] and in agriculture as fungicides, pesticides and bactericides [8,9]. It has been reported that certain Schiff bases exhibit antitubercular activities [10]. We have undertaken the synthesis and characterization of a Schiff base of antitubercular drug, pyrazine-2-carboxamide and its metal complexes.

FMPCA



Pyrazine-2-carboxamide furan-2-carbaldehyde *N*-(furan-2-ylmethylidene)-pyrazine-2-carboxamide

MATERIAL AND METHODS

All the chemicals used were of AR or BDH grade. The ligand FMPCA was prepared by refluxing an equimolar mixture of furan-2-carbaldehyde with pyrazine-2-carboxamide in methanol in presence of a few drops of acetic acid for about 3 hrs. The solid that separated was filtered, washed with water and recrystallized from methanol. The colour, yield (%), M.P. and elemental analysis (%) of FMPCA are respectively. yellow, 72, 152-172ºc [found C,54.20; H,3.00; N,18.50]

The Fe(III), Ru(III), Co(II), Cu(II), Pd(II) and Hg(II) complexes of ligands were prepared taking metal chlorides and Ni(II), Zn(II) and Cd(II) complexes taking metal acetates. In the preparation of metal complexes, the metal and the ligand were combined in 1:2 mole ratio using required quantities of methanol so as to effect the solubility of the metal salts and the ligand. The contents were refluxed on a hot water bath for 2-3 hrs and the solid that separated was filtered, washed with water, hot methanol and ether and was vacuum dried over fused $CaCl_2$.

The elemental analyses(C,H,N) of the ligand and the complexes were carried out at C.S.M.C.R.I., Bhavanagar. Conductance measurements were made in DMF at 10^{-3} M concentration on a Digisun digital conductivity meter. Gouy balance calibrated with $Hg[Co(NCS)_4]$ was used to measure the magnetic susceptibility of metal complexes at room temperature. The IR spectra of ligand and their metal complexes in KBr were recorded in the range 4000-450 cm^{-1} using Perkin Elmer 100 FT-IR spectrophotometer. The electronic spectra of metal complexes were recorded on

Perkin Elmer UV-VIS spectrophotometer. WIN-EPR (BRUKER) spectrophotometer operating in the frequency range 8.8-9.6 GHz was employed in recording the ESR spectrum of Cu(II) complex in DMF at LNT.

Considering the biological importance pyrazinamide derivatives and the possible synergistic effect of metal ion association with these compounds on their biological activity, the ligand : FMPCA and their Fe, Ru, Cu, Pd, Zn and Hg complexes have been studied Agar cup plate method for their activity against the two gram positive bacterial strains: *Staphylococcus Aurus, Basillus Subtillus* and two gram negative bacterial strains: *Salmonella typhi*, *Escherichia coli* and two fungal strains: *Aspergillus niger and Penicillium rubrum.*

RESULTS AND DISCUSSION

The Fe(III), Ru(III), Co(II), Ni(II), Cu(II), Pd(II), Zn(II), Cd(II) and Hg(II) complexes of FMPCA are stable at room temperature and are non-hygroscopic. Upon heating, the complexes decompose without melting. The complexes are insoluble in water, slightly soluble in hot methanol and fairly soluble in dimethylformamide and dimethylsulphoxide.

The elemental analyses (Table 1) show that Fe(III), Ru(III), Co(II), Ni(II), and Cu(II) complexes have 1:2 and the Pd(II), Zn(II), Cd(II) and Hg(II) complexes 1:1 metal-ligand stoichiometry.

Fe(III), and Ru(III) complexes conform to 1:1 electrolytic and the rest to non electrolytic type. The magnetic moment data suggest that the Fe(III), Ru(III), Co(II), Ni(II) and Cu(II) complexes are paramagnetic corresponding respectively to five, one, three, two and one unpaired electrons while others are diamagnetic.

IR SPECTRAL DATA

The IR spectral data of FMPCA and its complexes are presented in Table 2. A low intensity band that appears at 1669 cm^{-1} in the ligand and at higher frequencies in the complexes has been assigned to νC=O [11,12]. A band that shows up at 1600 cm^{-1} in the ligand due to azomethine group has been lower shifted by 15-32 cm^{-1} in the complexes indicating that the nitrogen of this group is coordinated to the metals [13]. A large intensity band due to pyrazine ring appears at 1174 cm^{-1} in the ligand and it remains unshifted in the complexes indicating that the ring is not involved in coordination [14]. Further, the ligand reveals a sharp band at 802 at cm^{-1} due to νC-O (furan cyclic) which undergoes downward shift by 20-40 cm^{-1} in the complexes suggesting the participation of the oxygen of this entity in bonding with the metals [15]. Thus, it may be concluded that the ligand acts towards the metals studied in a neutral, bidentate manner, coordinating through the nitrogen of azomethine group and the oxygen of furan entity.

ELECTRONIC SPECTRAL DATA

The electronic spectral data of the Ru(III), Co(II), Ni(II), Cu(II) and Pd(II) complexes along with the assignment are furnished in Table 3. These transitions are characteristic of octahedral geometry for Ru (III) (low spin), Co(II), Ni(II) and Cu(II) complexes, and a square planar geometry for the pd(II) complex [16-19].

The Fe(III) complex, owing to transitions in it being spin-forbidden and the Zn(II), Cd(II) and Hg(II) complexes due to filled configurations do not show d-d bands .Based on the other data obtained, Fe(III) complex has been assigned octahedral (high spin) geometry and the other three complexes, tetrahedral geometry.

ESR SPECTRAL STUDY

The ESR spectrum of the Cu(II)- FMPCA complex is of anisotropic nature from which $g_{\|}$ and $g_{\perp}$ have been respectively calculated from the lower and higher field peaks as 2.10 and 2.00, the g_{av} ($g_{\|} + g_{\perp}/3$) being 2.76 [20,21]. Since $g_{\|}$ is greater than $g_{\perp}$ for the complex, the unpaired electron is present in the metal $d_{x^2-y^2}$ orbital giving $^2B_{1g}$ as the ground state-a characteristic of elongated octahedral case.

ANTI MICROBIAL ACTIVITY

The antimicrobial activity of FMPCA and its complexes has been studied against bacteria *Bacillus megaterium* (Gram +ve), and *Klebsiella pneumonia* (Gram –ve) and fungi: *Pencilium rubrum* and *Aspergillus niger* wherein the zone of inhibition measured in the mm (Table 4).

The results indicate that the complexes are in general more active than the free ligand. Further, Hg complex, of all the compounds, exerts highest activity on the bacteria as well as fungi studied. [22]

Table 1: Analytical and physical data of metal complexes

Metal complex	Colour	Percent			Molar Conductance $\Omega^{-1}cm^2mol^{-1}$	μ_{eff} B.M.
		C	H	N		
$[Fe(C_{10}H_7N_3O_2)_2Cl_2]Cl$	Black	40.18(40.26)	2.08(2.36)	13.72(14.08)	62	5.60
$[Ru(C_{10}H_7N_3O_2)_2Cl_2]Cl$	Dark black	36.26(37.42)	2.08(2.20)	12.94(13.09)	55	1.88
$[Co(C_{10}H_7N_3O_2)_2Cl_2]$	Rose red	42.21(42.57)	2.24(2.50)	14.68(14.89)	12	4.84
$[Ni(C_{10}H_7N_3O_2)_2(OAc)_2]$	Dark green	46.00(47.16)	3.15(3.30)	13.50(13.75)	14	2.88
$[Cu(C_{10}H_7N_3O_2)_2Cl_2]$	green	41.28(42.28)	2.36(2.48)	14.51(14.77)	10	1.81
$[Pd(C_{10}H_7N_3O_2)Cl_2]$	Grey	29.72(30.44)	1.68(1.79)	9.98(10.65)	18	-
$[Zn(C_{10}H_7N_3O_2)(OAc)_2]$	Black	41.06(41.96)	3.02(3.27)	9.68(10.49)	12	-
$[Cd(C_{10}H_7N_3O_2)(OAc)_2]$	Black	37.22(37.55)	2.80(2.93)	8.56(9.38)	11	-
$[Hg(C_{10}H_7N_3O_2)Cl_2]$	Black	24.10(24.57)	1.38(1.44)	8.08(8.60)	10	-

Values in parentheses are the calculated ones

Table 2: IR Spectral data of FMPCA and its complexes

S.No.	Compound	ν C=O	ν C=N	ν C-O (furan ring)
1	FMPCA	1669	1600	802
2	Fe- FMPCA	1682	1577	768
3	Ru- FMPCA	1688	1576	772
4	Co- FMPCA	1690	1575	792
5	Ni- FMPCA	1700	1582	786
6	Cu- FMPCA	1702	1580	794
7	Pd- FMPCA	1708	1585	781
8	Zn- FMPCA	1732	1588	774
9	Cd- FMPCA	1690	1581	792
10	Hg- FMPCA	1688	1568	766

Table 3: Electronic Spectral Data

Complex	Frequency (cm^{-1})	Assignment
Ru- FMPCA	12230 19480 22250	$^2T_{2g} \rightarrow {}^4T_{1g}$ $^2T_{2g} \rightarrow {}^4T_{2g}$ $^2T_{2g} \rightarrow {}^2A_{2g}$
Co- FMPCA	12180 15560 19450	$^4T_1g \rightarrow {}^4T_{2g}$ $^4T_1g \rightarrow {}^4A_{2g}$ $^4T_1g \rightarrow {}^4T_1g(P)$
Ni- FMPCA	9985 11210 19720	$^3A_{2g} \rightarrow {}^3T_{2g}$ $^3A_{2g} \rightarrow {}^3T_{1g}$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$
Cu- FMPCA	11855 22440	$^2B_{1g} \rightarrow {}^2B_{2g}$ $^2B_{1g} \rightarrow {}^2E_g$
Pd- FMPCA	12620 19650 28550	$^1A_{1g} \rightarrow {}^1A_{2g}$ $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1E_g$

Table 4: Antimicrobial activity of FMPCA and its complexes

S.NO	Compound	Zone of inhibition (mm)			
		Bacteria		Fungi	
		B.Megaterium	*K.Pneumonia*	*Pencilium rubrum*	*Aspergillus niger*
1	FMPCA	20	22	-	-
2	Fe- FMPCA	-	35	12	18
3	Ru- FMPCA	26	29	22	20
4	Co- FMPCA	19	21	10	12
5	Ni- FMPCA	11	14	24	32
6	Pd- FMPCA	16	21	22	24
7	Cu- FMPCA	22	22	23	22
8	Zn- FMPCA	24	15	18	26
9	Cd- FMPCA	22	25	24	20
10	Hg- FMPCA	30	32	38	41

CONCLUSION

Based on the foregoing discussion, it may be concluded that the ligand acts in a neutral, bidentate manner coordinating to the metals through nitrogen of azomethine group and oxygen of furan. Fe(III), Ru(III), Co(II), Ni(II) and Cu(II) complexes are octahedral, Pd(II) complex square planar and the Zn(II), Cd(II) and Hg(II) complexes tetrahedral in geometry. The metal complexes are more active in inhibiting the microbial growth than the ligand, the Hg complex exerting the highest activity.

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