



Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis and characterization of metal complexes of a novel Schiff base

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ABSTRACT

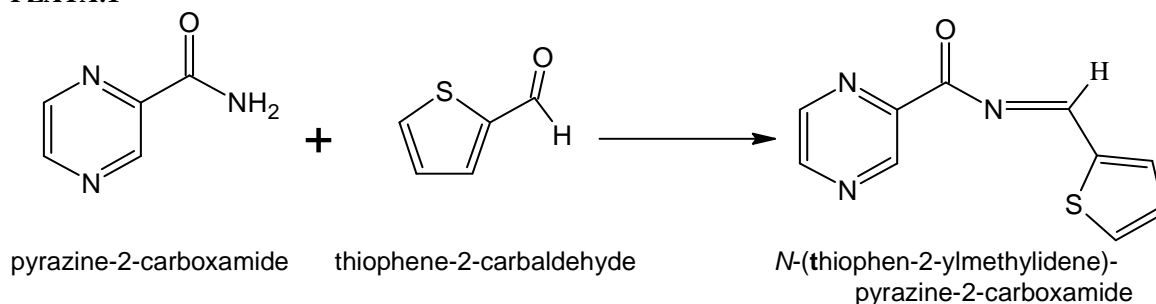
The Fe(III), Ru(III), Co(II), Ni(II), Cu(II), Pd(II), Zn(II), Cd(II) and Hg(II) complexes of a Schiff base derived from pyrazine-2-carboxamide and thiophene-2-carbaldehyde (PZATA: 1) have been synthesized and structurally characterized by various physico-chemical data. The ligand acts as a neutral, bidentate one towards the metal ions coordinating through azomethine nitrogen and thiophene sulphur. The geometry and the bonding characteristics associated with the complexes have been deduced from relevant spectral data. Further, the ligand and the metal complexes have been screened for their antimicrobial activity and the results are presented.

Keywords: pyrazine-2-carboxamide, thiophene-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 [1]. Literature survey reveals that Schiff bases have assumed importance in various fields such as coordination chemistry [2], analytical chemistry [3] and pigments, dyes [4] and polymer [5,6] industries; in biochemical researches, especially as model compounds of several vitamins and enzymes [7,8] and in agriculture as fungicides, pesticides and bactericides [9,10]. It has been reported that certain Schiff bases exhibit antitubercular activities [11]. We have undertaken the synthesis and characterization of a Schiff base of antitubercular drug, pyrazine-2-carboxamide and its metal complexes.

PZATA:1



EXPERIMENTAL SECTION

All the chemicals used were of AR or BDH grade. The ligand PZATA was prepared by refluxing an equimolar mixture of thiophene-2-carbaldehyde with pyrazine-2-carboxamide in methanol in presence of a few drops of concentrated H₂SO₄ for about 3 hrs. The solid that separated was filtered, washed with water and recrystallised from methanol. The colour, yield (%), m.p. and elemental analysis(%) of PZATA are respectively. yellow, 68, 178-180°C [found C,55.20; H,3.18; N,19.30]

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 CaCl₂.

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. The thermograms of Ru(III), Co(II), Cu(II), and Pd(II) complexes were recorded on SDT Q 600 instrument in the temperature range 0-700°C.

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 PZATA 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.

Table-1: Analytical and physical data of metal complexes

Metal complex	Colour	Percent			Molar Conductance Ω ⁻¹ cm ² mol ⁻¹	μ _{eff} B.M.
		C	H	N		
[Fe (C ₁₀ H ₇ N ₃ OS) ₂ Cl ₂]Cl	Brown	39.68(40.26)	2.08(2.36)	13.72(14.08)	70	5.67
[Ru (C ₁₀ H ₇ N ₃ OS) ₂ Cl ₂]Cl	Dark brown	37.06(37.42)	2.08(2.20)	12.94(13.09)	68	1.85
[Co (C ₁₀ H ₇ N ₃ OS) ₂ Cl ₂]	Rose red	42.01(42.57)	2.24(2.50)	14.68(14.89)	10	4.89
[Ni (C ₁₀ H ₇ N ₃ OS) ₂ (OAc) ₂]	Red	46.80(47.16)	3.15(3.30)	13.50(13.75)	10	2.86
[Cu (C ₁₀ H ₇ N ₃ OS) ₂ Cl ₂]	Light green	41.78(42.28)	2.36(2.48)	14.51(14.77)	12	1.81
[Pd (C ₁₀ H ₇ N ₃ OS)Cl ₂]	Grey	30.02(30.44)	1.68(1.79)	9.98(10.65)	11	-
[Zn (C ₁₀ H ₇ N ₃ OS)(OAc) ₂]	Light Yellow	41.16(41.96)	3.02(3.27)	9.68(10.49)	12	-
[Cd (C ₁₀ H ₇ N ₃ OS)(OAc) ₂]	Yellow	37.01(37.55)	2.80(2.93)	8.56(9.38)	11	-
[Hg (C ₁₀ H ₇ N ₃ OS)Cl ₂]	Yellow	23.90(24.57)	1.38(1.44)	8.08(8.60)	10	-

Values in parentheses are the calculated ones.

IR SPECTRAL DATA

The IR spectral data of PZATA and its complexes are presented in Table 2. A low intensity band that appears at 1674 cm⁻¹ in the ligand and at higher frequencies in the complexes has been assigned to ν C=O [12]. A band that shows up at 1607 cm⁻¹ in the ligand due to azomethine group has been lower shifted by 15-30 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 810 cm^{-1} due to $\nu\text{ C-S}$ (thiophene cyclic) which undergoes downward shift by $20\text{-}40\text{ cm}^{-1}$ in the complexes suggesting the participation of the sulphur of this entity in bonding with the metals [15]. A non-ligand band that appears in the complexes around 490 cm^{-1} has been assigned to $\nu\text{ (M-N)}$ [16]. 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 sulphur of thiophene entity.

Table-2 IR Spectral data of PZATA and its complexes :

S. No.	Compound	$\nu\text{ C=O}$	$\nu\text{ C=N}$	$\nu\text{ C-S}$ (thiophene ring)	$\nu\text{ M-N}$
1	PZATA	1674	1607	810	--
2	Fe- PZATA	1680	1580	770	490
3	Ru- PZATA	1675	1584	775	495
4	Co- PZATA	1693	1589	780	485
5	Ni- PZATA	1700	1582	783	492
6	Cu- PZATA	1704	1593	792	471
7	Pd- PZATA	1680	1585	784	488
8	Zn- PZATA	1732	1588	793	495
9	Cd- PZATA	1690	1581	790	498
10	Hg- PZATA	1699	1576	774	500

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 below.

Complex	Frequency (cm^{-1})	Assignment
Ru-PZATA	12340	${}^2\text{T}_{2g} \longrightarrow {}^4\text{T}_{1g}$
	19320	${}^2\text{T}_{2g} \longrightarrow {}^4\text{T}_{2g}$
	22520	${}^2\text{T}_{2g} \longrightarrow {}^2\text{A}_{2g}$
Co-PZATA	12080	${}^4\text{T}_{1g} \longrightarrow {}^4\text{T}_{2g}$
	15680	${}^4\text{T}_{1g} \longrightarrow {}^4\text{A}_{2g}$
	19650	${}^4\text{T}_{1g} \longrightarrow {}^4\text{T}_{1g}(\text{P})$
Ni-PZATA	9615	${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{2g}$
	11110	${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}$
	19610	${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}(\text{P})$
Cu-PZATA	11765	${}^2\text{B}_{1g} \longrightarrow {}^2\text{B}_{2g}$
	22220	${}^2\text{B}_{1g} \longrightarrow {}^2\text{E}_g$
Pd-PZATA	12460	${}^1\text{A}_{1g} \longrightarrow {}^1\text{A}_{2g}$
	19650	${}^1\text{A}_{1g} \longrightarrow {}^1\text{B}_{1g}$
	25500	${}^1\text{A}_{1g} \longrightarrow {}^1\text{E}_g$

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 [17-21].

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)-PZATA complex is of slight anisotropic nature from which g_{\parallel} and g_{\perp} have been respectively calculated from the lower and higher field peaks as 2.19 and 2.06, the g_{av} ($(g_{\parallel} + g_{\perp})/3$) being 2.10 [22]. Since g_{\parallel} is greater than g_{\perp} for the complex, the unpaired electron is present in the metal $d_{x^2-y^2}$ orbital giving ${}^2\text{B}_{1g}$ as the ground state—a characteristic of elongated octahedral case [23].

THERMAL STUDIES

A look at the thermograms of Ru(III), Co(II), Cu(II) and Pd(II) complexes indicates that they are stable to different temperatures. For example Ru(III) complex starts losing weight at 200, Co(II) complex at 198, Cu(II) complex at 240 and Pd(II) complex at 300°C . All the four complexes lose weight on heating almost in a continuous manner.

While the decomposition of the Ru(III), Cu(II), and Pd(II) complexes is incomplete at the temperature studied (700°C), that of the Co(II) complex is complete, it attaining the constancy in weight at 540°C. The per cent weight loss computed from its thermogram suggests that the final product of decomposition corresponds to CoO.

ANTI MICROBIAL ACTIVITY

The antimicrobial activity of PZATA and its Fe, Ru, Pd, Zn and Hg 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 (Table 3) [24,25].

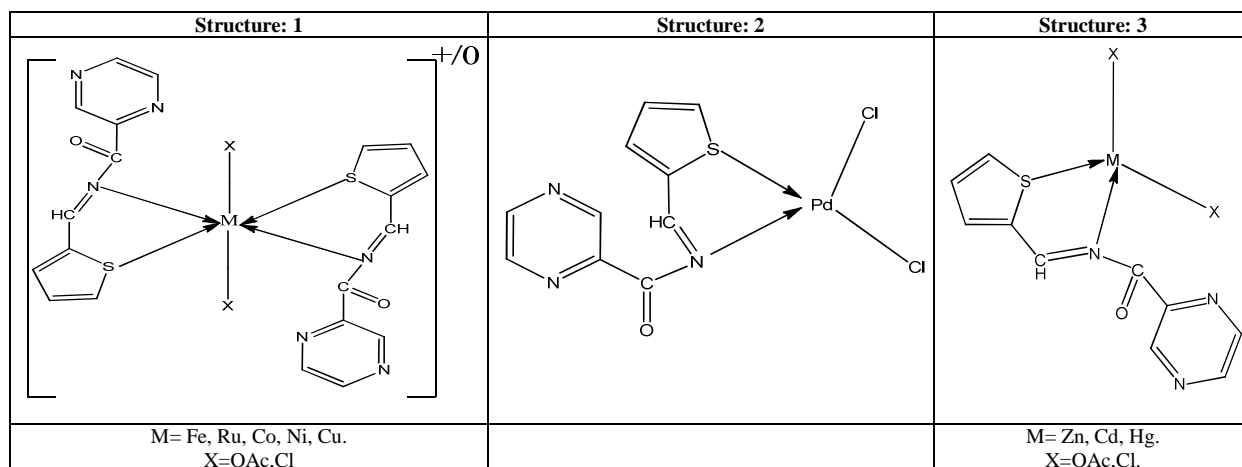
The results indicate that the complexes are in general more active than the free ligand. Further, Hg complex, of all the compounds, exerts highest activity on the bacteria as well as fungi studied.

Table-3: Antimicrobial activity of PZATA and its complexes

S.NO	Compound	Zone of inhibition (mm)			
		Bacteria		Fungi	
		<i>B.Megaterium</i>	<i>K.Pneumonia</i>	<i>Pencilium rubrum</i>	<i>Aspergillus niger</i>
1	PZATA	10	25	-	-
2	Fe- PZATA	-	40	12	14
3	Ru- PZATA	20	23	22	20
4	Pd- PZATA	19	21	10	12
5	Zn- PZATA	11	14	36	33
6	Hg- PZATA	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 sulphur of thiophene. Fe(III), Ru(III), Co(II), Ni(II) and Cu(II) complexes are octahedral (Structure: 1), Pd(II) complex square planar (Structure: 2), and the Zn(II), Cd(II) and Hg(II) complexes tetrahedral in geometry (Structure: 3). 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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