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Synthesis and characterization of Schiff base complexes of Zr(IV) and Th(IV) complexes of Schiff base derived from furan 3- carboxaldehyde and 3- amino pyridine

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Abstract

The Schiff base complexes Zr(IV) and Th(IV) of furan 3- carboxaldehyde and 3- amino pyridine were synthesized and characterized by elemental analysis, conductivity measurements, infrared spectral measurements, XRD and antibacterial studies. The conductance measurements indicate that all the complexes are non-electrolytes. The results indicate that the metal complexes of Zr(IV) and Th(IV) are octacoordinated and have moderate antibacterial activity.

Keywords- *Antibacterial studies, Molar conductivity, Elemental analysis, IR, Schiff base.*

1. Introduction

Schiff bases are widely used for synthetic purposes both by organic and inorganic chemists. In addition, Schiff bases show numerous biological activities including antibacterial, antifungal, and antitumor and antiherbicidal activities. Such bases are also used as ligands for complex formation with some transition and non-transition metal ions [1]. Compounds containing imines bases have not only found extensive application in organic synthesis, but several of these molecules display significant biological activity [2,3]. In the last decade Schiff base ligands have received more attention mainly because of their wide application in the field of catalysis and due to their antimicrobial5, anti-tuberculosis, and anti-tumour activity [4-6]. They easily form stable complexes with most transition metal ions. Schiff base complexes (derived from heterocyclic compounds) have increased the interest in the development of the field of bioinorganic chemistry [7]. Heterocyclic compounds such as pyridine, amino pyridine and related molecules are good ligands due to the presence of at least one ring nitrogen atom with a localized pair of electrons. The successful application has led to the formation of series of novel compounds with a wide range of physical, chemical and biological properties [8], spanning a broad spectrum of reactivity and stability. Keeping in view of the pronounced biological activity of the metal complexes of Schiff bases derived from heterocyclic compounds, it was thought of worthwhile to synthesize and characterize some new metal ligand complexes of Zr(IV) and Th(IV) from Schiff base derived from furan 3 - carboxaldehyde and 3- amino pyridine.

2. Materials And Methods

2.1 Chemicals

All the chemicals used were of GR/AR grade quality obtained from Merck chemicals. All the solvent used were purified by standard methods [9]. The micro analytical data (C, H, N) were collected using Perkin Elmer 2400 instrument.IR spectra were obtained using Schimadzu FTIR 470 IR spectrophotometer.1H NMR spectrum was obtained using Brucker Advance 111,400 MHz spectrometer. Conductance measurements were obtained using systronics-305conductivity meter. Electronic spectra of the ligands and its complexes were obtained using Schimadzu 1601, UV-Visible spectrometer. Powder XRD of complexes were recorded using Brucker AXS DS advance instrument.

2.2 Preparation of Schiff base ligand(L).

The ligand is prepared by taking equimolar ratio of furan-3-carboxaldehyde and 3-amino pyridine, which are dissolved in ethanol. It is then refluxed for one hour and reaction product is poured into ice. Yellow precipitate formed is filtered and washed with water.

2.2 Synthesis of Schiff base metal complexes.

The metal complexes were prepared by adding aqueous solution of Zr(IV) nitrate and Th(IV) nitrate to the ligand in ethanol in 1:1 molar ratio and refluxed for about twelve hours at 80^0C. [10,11]. The precipitated solids were washed with ethanol, diethyl ether and hot water and finally dried under vacuum at 90^0C.

3. Results And Discussion

All the metal complexes are coloured solids, stable towards air and have high melting points (above 230^oC). The complexes are insoluble in water and common organic solvents, but are soluble in DMF, $CDCl_3$ and DMSO.

3. 1 Elemental Analysis

The analytical data suggested that all the complexes are mononuclear with the ligand coordinated to the central metal atom. The metal to ligand ratio in all complexes was 1:2[12,13]. The details are given in Table 1.

Table: 1 Physical characteristics and analytical data of the complexes.

Compound	Yield %	Colour	Mol. Formula	Mol. Wt.	Elemental Analysis Found (Calcd) %		
					C	H	N
Ligand(L)	60	Brown	$C_{10}H_8ON_2$	172	69.76 (69.81)	4.65 (4.45)	16.27 (16.20)
$[Zr L_2(NO_3)_2] 2H_2O$	58	Light brown	$C_{20}H_{16}O_8 N_6Zr$	719.24	33.36 (33.0)	2.22 (2.19)	7.78 (7.53)
$[Th L_2(NO_3)_2]2H_2O$	57	Grey	$C_{20}H_{16}O$	860.5	27.89 (27.33)	1.85 (1.77)	6.5 (6.46)

3. 2 Molar Conductivity

The observed molar conductance data in 10^{-3} M DMF indicate non-electrolytic nature of complexes because their conductivity values were in the range 20-24 ohm^{-1} cm^{2}mol^{-1} (Table 2), thus all the complexes are non electrolytes. But the conductivity values were slightly higher than for non-electrolytes. This may be due to the partial solvolysis of the complexes in DMF medium [14].

Table 2. Molar Conductance data of the complexes

Compound	Molar conductance Ohm^{-1} cm^2 mol^{-1}
Ligand(L) $C_{10}H_8ON_2$	22
$[Zr L_2(NO_3)_2]2H_2O$	20
$[Th L_2(NO_3)_2]2H_2O$	24

3. 3 IR Spectra

The IR Spectrum provides the valuable information regarding the nature of functional groups coordinated to the metal atom. The selected IR spectral data of the ligand and complexes given in the Table 3. The IR spectra of the ligand showed a broad band in the region 3347 cm^{-1} - 3213 cm^{-1} due to N-H stretching of amine. The absorption band at 1623 cm^{-1} [15] can be assigned to C=N stretching. In all the complexes this bond is shifted to lower frequencies in the range 1638 cm^{-1} – 1622 cm^{-1} up on complexation with metal, which can be attributed to coordination to imine nitrogen to metal centre. The bands in the region 745 cm^{-1} - 707 cm^{-1} is due to M-O stretching frequency. Absorption peaks in the region 1567 cm^{-1} -1549 cm^{-1}of complexes is due to C-NO_2 stretching frequency.

Table 3. Selected FT IR frequencies (cm^{-1}) of the ligand and complexes

Ligand/ Complex	ν_{N-H}	$\nu_{C=N}$	ν_{C-N}	ν_{C-H}	ν_{M-N}	ν_{C-NO2}	ν_{H2O}
Ligand(L) $C_{10}H_8ON_2$	3347	1344	1623	2114	-		

[Zr $L_2(NO_3)_2$]2H_2O	3150	1326	1622	3100	706	1566	3100
[Th $L_2(NO_3)_2$]2 H_2O	3347	1471	1638	3101	745	1560	3101

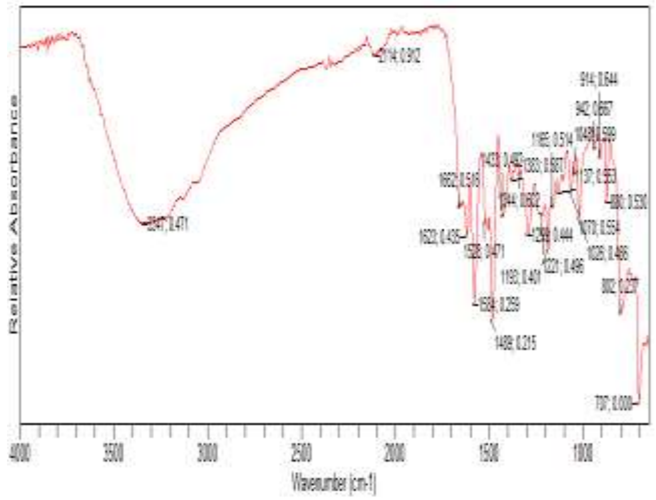

Fig:1- FTIR Spectrum of Schiff base ligand (L)

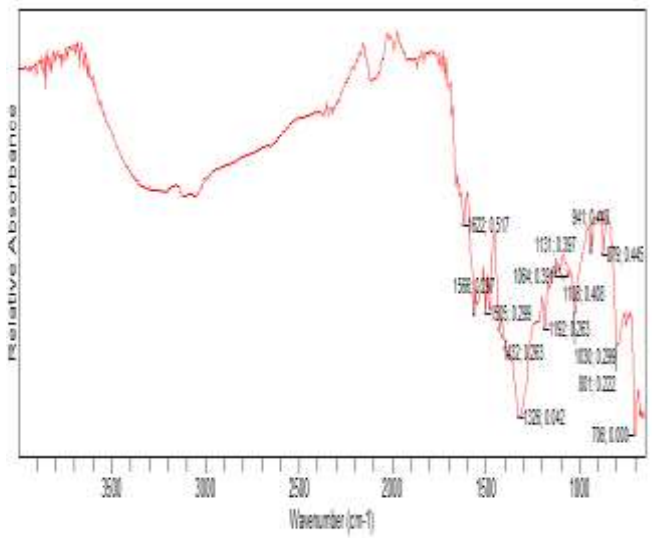

Fig. 2 FTIR spectrum of Zr(IV) complex

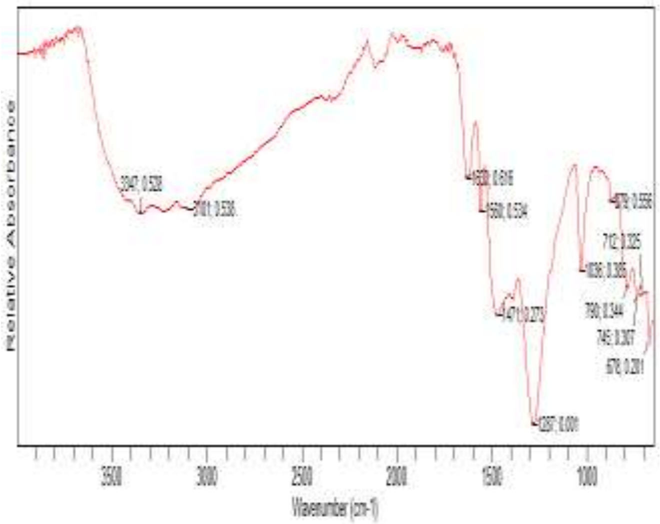

Fig. 3 FTIR spectrum of Th(IV) complex

3. 4 ^{1}H NMR Spectra

The ^{1}H NMR Spectra of the ligand shows a peak at δ= 9.81ppm is accommodate to the azomethine proton of the CH=N group. Peaks around δ= 6.7 – 7.59 ppm shows the presence aromatic ring proton. The peak at δ= 1.9 -1.06ppm is due to the proton at the furan ring. ^{1}H NMR Spectra of the ligand is shown in Fig.4

On complexation a signal appears due to the proton attached to azomethine group at δ= 9.89 ppm. This field shift indicates the deshielding of azomethine proton coordination through the nitrogen atom of the azomethine group. The multi signals at the range of δ= 6.92 – 7.58 are assigned to the aromatic protons of the ring in the metal(IV) complex [16,17]. Slight downfield shift is observed in all other signals of Zr(IV) complex.

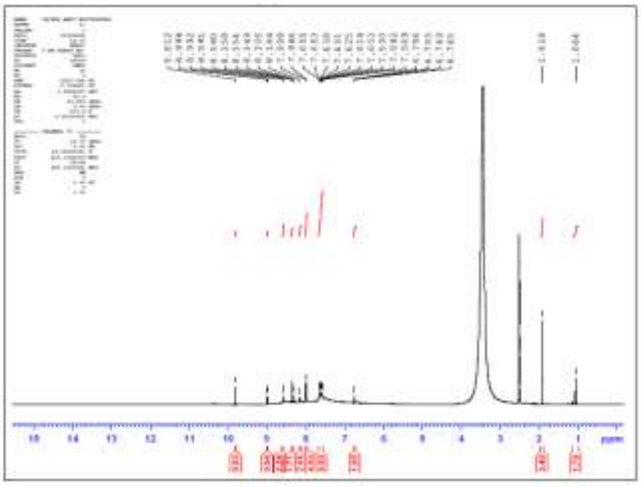

Fig. 4 ^{1}H NMR Spectra of ligand

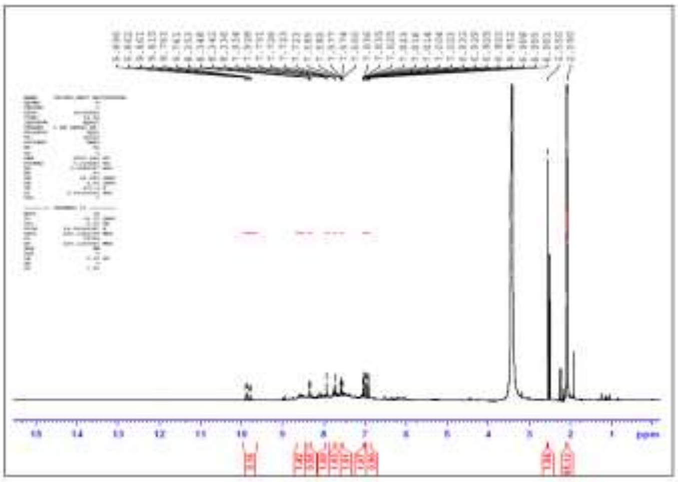

Fig. 5 ^{1}H NMR Spectra of Zr(IV) complex

Based on the above results the proposed structure of Ligand and its metal complexes is given below,

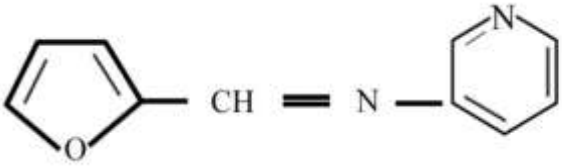

Fig.6 Structure of Ligand

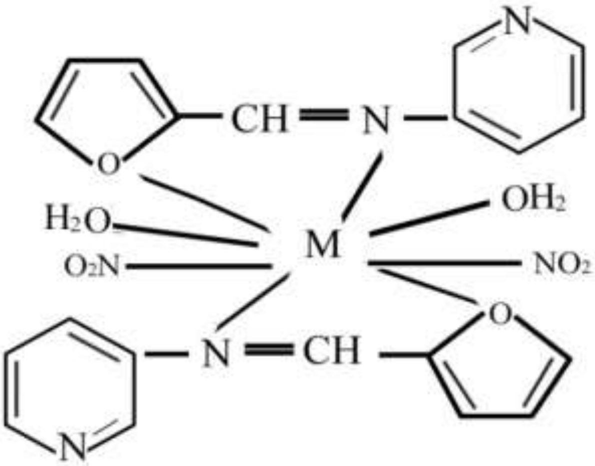

Fig.7 Structure of metal complexes with Ligand (M= Zr, Th)

3. 5 X-ray Diffraction Analysis

The powder XRD for the complexes was performed. The data are given in Table: 4. The respective diffractogram were given in Fig: 8. The grainsize of the complexes were calculated using Scherre's formula are given in table. The calculated grain size for Zr(IV) complex is in the range of 21-24 nm and for Th(IV) complex is in the range 20-19nm. This values suggested the crystals of the Zr(IV) and Th(IV) complexes are in nano size [18].

Table:4 XRD data of complexes

Ligand/ Complex	Crystal size(nm)
[Zr L_2 $(NO_3)_2$]$2H_2O$	21-24
[Th L_2 $(NO_3)_2$]$2H_2O$	19-20

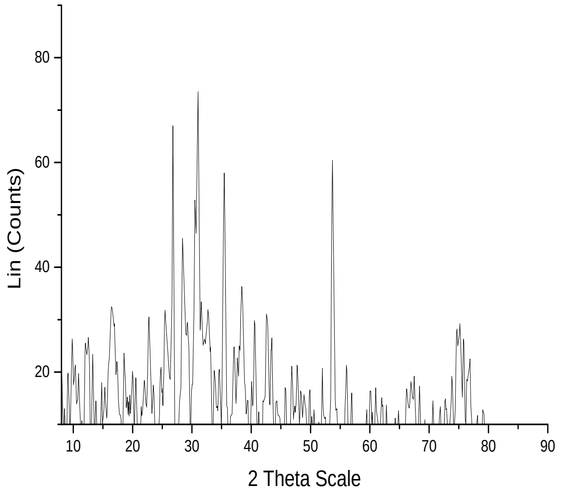

Fig. 8 XRD Spectrum of Zr (IV) Complex of Ligand

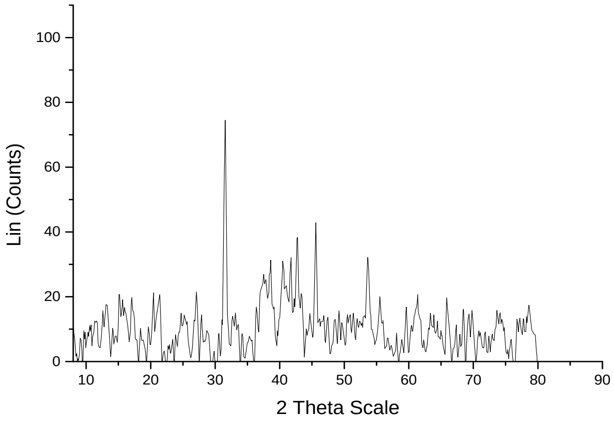

Fig.9 XRD Spectrum of Th (IV) Complex of Ligand

3. 6 Antibacterial activity

The results of antibacterial activity substantiate the findings of earlier researchers [19], that biologically in active compounds become active and less biologically active compounds become more active upon coordination. Such enhancement in biological activity of metal complexes can be explained on the basis of Overtone's concept and chelation theory. According to Overtone' concept of cell permeability, the lipid membrane that surrounds the cell favours the passage as only lipid soluble materials due to which lipo solubility is an important factor that controls antimicrobial activity. On chelation, the polarity of the metal ion is reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π – electron over the whole chelate ring and enhanced lipophilicity of the complex. This enhanced the lipophilicity in turn enhances the penetration of the complexes into lipid membranes and blocking of metal binding sites on the enzymes of the micro-organisms.

The present investigation suggests that all the metal complexes of the ligand bearing metal ion, phenolic moiety, benzene ring – N= CH- group have comparatively more biological activity [20]. This study serves as a basis for the chemical modifications directed towards the development of new class of antibacterial agents.

Antibacterial activities of the ligand, complexes and standard drugs were screened by disc diffusion method in DMSO as solvent. The results of antibacterial study are given in Table-5. The antibacterial activity was estimated based on the size of inhibition zone in the discs. Under identical conditions the Schiff base complexes of Th(IV) are found to be more active, others exhibit moderate activity

Table. 5 Antibacterial activity data of ligand and its complexes.

Ligand/Complex	**S. aureus**	**Styphi**	**Vcholera**
Ligand(L) $C_{10}H_8ON_2$	6mm	-	-
$[Zr\ L_2(NO_3)_2]$ $2H_2O$	13mm	11mm	8mm
$[Th\ L_2(NO3)_2]$ $2H_2O$	16mm	12mm	14mm
Positive	30mm	25mm	26mm

4. Conclusion

Schiff base transition metal complexes Zr(IV) and Th(IV) were synthesised from furan-3- carboxaldehyde using 3-amino pyridine, and characterized on the basis of analytical and spectral data. Elemental analysis shows the metal to ligand ratio is 1:2. Conductivity measurements show all complexes are non-electrolytes. From XRD and crystalline nature of complexes is confirmed. Anti-bacterial study shows that all complexes are more active than ligand.

5. References

1. M. Gielen, E.R.T. Tiekink, "*Mettallotherapeutic drugs and metal based diagnostic agents. The use of metals in medicine*", John wiley & sons, England, (2005).
2. M.N Hughes; "*The inorganic chemistry of biological process*", 2nd edn, Wiley, (1984).

3. M. H. Tarafder, N. Saravanan, K.A. Crouse, A. M. Ali, Coordination chemistry and biological activity of nickel(II) and copper(II) ion complexes with nitrogen–Sulphur donor ligands derived from S-benzyl dithio carbazate (SBDTC),"*Transition Metal Chemistry*", 26, 2001,613-618
4. R. Sahu, D. S. Thakur and P. Kasharp, “Schiff Base; and over view office medicinal chemical potential for new drug molecules”, *International Journal of Pharmaceutical Sciences and Nano technology, vol.5(3)*, (2012).
5. Battacharya. P. K. *Indian Chemical Society*, *52,1982*, 505.
6. Ahmed M. El- Hendawy, Abd El- Ghany El-Kourashy, Mai M. Shanab, Schiff base complexes of ruthenium(III), molybdenum(VI) and uranium(VI), and use of the former as catalytic organic oxidants, *Polyhedron, 11(5)*, 1992, 523- 530
7. P. G. Cozzi, “Metal- Salen Schiff Base Complexes in Catalysis: Practical Aspects,” *Chemical Society Reviews, 33(7)*, 2004, 410-421.

8. FSS.A. Carey, *Organic chemistry*,5th edn,2003, 724.
9. A. A. Soliman, G. G. Mohamad, Study of the ternary complexes of copper with salicylidene-2-aminothiophenol and some amino acids in the solid state, *Thermochem. Acta, 421(1),* 2004,151- 159
10. D. P. Singh, R. Kumar, R. Mehani, S. K. Verma, Synthesis and characterization of divalent metal complexes with ligand derived from the reaction of 4-aminopyridine and biacetyl, *Journal of Serbian Chemical Society, 71*,2006, 939.
11. Isac Sobana Raj. C, Allen Gnana Raj G, Synthesis, Characterization, Metal ion intake and Antibacterial Activity of Schiff base Complexes of Zr(IV) and Th(IV) derived from Di-α-formyl methoxy bis (3-pentadecenylphenyl) methane [DFMPM] and Aniline, *Int. J. Res. Chem. Environ, 4 (2)* ,2014, (36-42)
12. C. Isac Sobana Raj, G. Allen Gnana Raj and M. Antilin Princela, Synthesis and Characterization of Bioactive Transition Metal Complexes of Zr(IV) and Th(IV) using di-α-formylmethoxy bis (3-penta decenyl phenyl) methane (DFMPM) derived from Cardanol, *AJCPR, 3(1),*2015, 208–214
13. Hermansen Ralph D. and Lau Steren E., Adhesive of epoxy resin, amine-terminated ban and conductive filler, *US. Patent 5929141 A, 8/9011*, 2004, 153
14. Bismi S. Prakash, Isac Sobana Raj. C, M. Stalin Joseph, Synthesis and Characterization of Bioactive Transition Metal Complexes of Zr(IV) and Th(IV) using natural sources, *Int. J. Res. Chem. Environ. Vol. 6(3),2016,* (30-39)
15. Bismi S Prakash, Isac Sobana Raj. C, Allen Gnana Raj. G, Synthesis, Characterisation and Anti Cancerous Studies of Schiff Base Complexes of Co(II), Cu(II) And Ni(II) Using DFMPM and L-Histidine, *Int. Journal of Engineering Research and Application, 7(7, [Part -9])* 2017,38-49
16. D. K. Mishra and A. P. Mishra, *International Journal PRD, 3(5)*,2011, 24-31.

17. Tuncel M., Ozbulbul A. and Serin S., Synthesis and Characterization of the thermally stable Schiff base polymers and their Copper(II), Cobalt(II) and Nickel(II) complexes, *Reactive and functional Polymers, 68*,2008, 292

18. Destri S., Pasini M., Pelizzi C., Porzio W., Predieri G., Vignali C., Synthesis and Characterization of Conjugated Polyazines and Polyazomethines Containing the Thienylene Moiety and Flexible Hydrocarbon Side Chains, *Macro Molecules, 32*,1999, 353

19. British Pharmacopoeia-II, *Biological assay and Tests, the Stationary Office Ltd*., London, A-205, 1998

20. K. L. P. Sheeja Lovely 1, and M. Christudhas, The DNA cleavage and antimicrobial studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes of 4- pyridine carboxaldehyde with 4-aminopyridine, *IOSR Journal of Applied Chemistry (IOSR-JAC), 4(3)* ,2013,14-19