Synthesis, Analytical and Spectral Studies of Novel Schiff Base Complexes of Th(IV) and UO₂(VI) Along with their X-Ray Diffraction Data and Toxic Effects

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Abstract: Schiff base was obtained using furfuraldehyde and 2-amino pyridine to prepare new complexes of thorium(IV) and dioxouranium(VI) metals by various anions. The synthesized ligands and complexes were analytically studied through spectral data, elemental analysis and conductance measurements along with x-ray diffraction pattern. The complexes showed various coordination number and their toxic effects to bacterial and fungal genus was studied by two different methods of measurement.

Keywords: Synthesis, Analytical studies, Thorium(IV) and dioxouranium complexes, Schiff base, Toxicity.

Introduction

Thorium(IV) and dioxouranium(VI) metal ions have atomic radii 1.17 Å and 1.90 Å respectively and have high positive charge, so that these metals can easily achieve high coordination number¹.

According to the definition of Pearson² these metals are hard acids and possess vacant inner *d*-orbitals, hence can expand their co-valency with increase in their coordination number. Their enormous complex forming tendency is attributed to the vacant inner *5f* sub shell which can expand greatly to accommodate a number of ligands. The greater spatial extension of *5f* orbitals of actinides along with the fact that these orbitals are diffused at the periphery of atom make them suitable to form number of complexes because in such situation the orbitals are disturbed by ligands³. Coordination number greater than four can be achieved by them through donations of electrons from ligands into the *d*-orbitals of these metal atoms. The hybridization may be predicted by assuming the contribution of atomic orbitals towards the combination of hybridization orbitals. In this present work the Schiff base was derived from furfuraldehyde and 2- amino pyridine to obtain 2*N*-(Furfuraldiene)amino pyridine {2-FAPy}.

Experimental

All the chemicals used were of AR grade and were used without further purification. Elemental analysis was carried on Elemental Vario EL III Carlo Erba 1108 CDRI Lucknow. Conductivity measurements for the complexes have been carried out on Elico 01/01 cell type conductivity bridge. Molecular weights were determined in freezing PhNO_2 using Beckmann Thermometer method cryoscopically in the laboratory. IR spectra were taken through Shimadzu 8201 PC ($4000\text{--}400\text{ cm}^{-1}$). Mass spectra were obtained through JEOL SX- 102 (FAB) PMR spectra of selected samples were recorded on τ scale through Bruker Avance IT 400 NMR spectrometer. Electronic spectral studies were done through Perkin Elmer Lambda 15 x-ray diffraction studies were conducted through powder pattern method at wavelength λ $1.54\text{ \AA}$. Biocidal studies of representative complexes were conducted on fungal and bacterial species by paper disc method on PDA medium in our laboratory in DMF solvent.

Preparation of complexes

Th^{4+} and UO_2^{2+} complexes of Schiff base 2-FAPy were prepared by refluxing the nitrate, iodide, isothiocyanate, perchlorate salts of Th^{4+} and UO_2^{2+} in proper M:L ratio using ethanol solvent. Uranyl acetate was also complexed with 2-FAPy in proper M:L ratio. The complexes were left in petri dish to obtain crystalline product and were recrystallised with solvent and washed with solvent and ether.

Synthesis of ligand

Solution of furfuraldehyde (1 mmole) in approx. 30 mL ethanol was mixed with solution of 2-amino pyridine (1 mmole) in approx. 30 mL ethanol. The resultant solution was refluxed in RB flask fitted with water condenser for six hours. On cooling Schiff base crystallized out which was filtered and re-crystallized with proper solvent. The structure of ligand is given in Figure 1.

Figure 1. Structure of ligand.

Results and Discussion

The analytical data for the ligand metal complexes are listed in Table 1. It is observed that most of the complexes are non- hygroscopic and anhydrous as is evident from molecular weight and percentage of H values; which are nearly same for theoretical and experimentally calculated data. It is evident from the results that ratio of molecular weights for $\text{ThX}_4.2\text{L}$ ($\text{X} = \text{NO}_3^-$), $\text{ThX}_4.4\text{L}$ ($\text{X} = \text{NCS}^-$), for observed and calculated approaches unity (0.98); suggestive of the fact that no change corresponding to ionization occurs in solution for these complexes. This fact is found valid for $\text{UO}_2\text{X}_2.2\text{L}$ ($\text{X} = \text{NO}_3^-$, NCS^- , CH_3COO^-) also⁴.

For $\text{ThI}_4.4\text{L}$, this ratio is approximately one-third *ie.*, 0.53; 0.36 for $\text{UO}_2(\text{ClO}_4)_2.4\text{L}$ and approximately one -fifth for $\text{Th}(\text{ClO}_4)_4.6\text{L}$. This is suggestive of the fact that anions of the complexes are ionisable, primary valencies of complex and that they ionize furnishing more than one ion in solution^{5,6}.

Mass spectral studies

Mass spectra of Schiff base was recorded. For 2-FAPy the parent ion peak is obtained at 173 m/z ($\text{M}+1$) peak. Base peak at 154 m/z is formed from parent ion through loss of H_3O^+ . Other significant peaks are recorded at 136 and 289 m/z values.

Table 1. Analytical results of 2-FAPy and its complexes.

Base/Complex	Elemental Analysis Data			Mol. Wt. obs (calcd)	M.P. °C	Cond. $\Omega \text{ cm}^{-1}$
	% C	% H	% N			
	Obs (calcd)	Obs (calcd)	Obs (calcd)			
2-FAPy	60.07(57.8)	4.82(5.2)	17.90(16.18)	173(172)	168-175	-
[Th(2-FAPy) ₂ (NO ₃) ₄]	25.2(28.36)	1.16(1.89)	10.08(13.23)	809(826)	236	1.6
[Th(2-FAPy) ₄ I ₂]	50.70(48.9)	3.16(3.1)	9.85(9.1)	374(1136)	184	111.1
[Th(2-FAPy) ₄ (NCS) ₄]	44.6(48.5)	2.46(2.7)	13.15(14.3)	1132(1156)	200	1.4
[Th(2-FAPy) ₆ (ClO ₄) ₄]	38.98(39.2)	2.34(2.6)	8.84(9.16)	244(1222)	212	200.9
[UO ₂ (2-FAPy) ₂ (NO ₃) ₂]	30.02(32.6)	2.54(2.17)	13.09(15.2)	721(736)	179	1.9
[UO ₂ (2-FAPy) ₂ (NCS) ₂]	65.9(63.1)	2.19(2.11)	15.3(13.4)	713(728)	201	1.1
[UO ₂ (2-FAPy) ₄](ClO ₄) ₂	19.74(20.7)	1.27(1.38)	4.71(4.8)	416.5(1157)	203	196.4
[UO ₂ (2-FAPy) ₂ (CH ₃ COO) ₂]	65.1(66.20)	12.96(13.24)	6.81(7.72)	710.5(725)	164	2.8
[UO ₂ (2-FAPy) ₂ I ₂]	31.86(33.42)	1.88(2.22)	6.54(7.79)	704(718)	224	1.64

IR spectral studies

IR spectra of Schiff base were recorded. For 2-FAPy the prominent peak at 1603 cm^{-1} shows variation in its complexes. This peak is of aromatic aldehydic system involved in azomethine linkage. When the IR spectra of ligands are compared with those of complexes then shift in the azomethine ($-\text{C}=\text{N}-$) peaks are observed through which the metal atom is believed to be bonded thus the azomethine bond is considered to be a part of coordination^{7,8}. The important peaks of Th(IV) and UO_2^{2+} (VI) are listed in Tables 2 & 3.

Table 2. Infra red absorpton frequencies (cm^{-1}) for thorium(IV) complexes of 2-FAPy.

Assignment	2-FAPy	Th(NO ₃) ₄ . (2-FAPy) ₂	ThI ₄ (2-FAPy) ₄	Th(NCS) ₄ (2-FAPy) ₄	Th(ClO ₄) ₄ (2-FAPy) ₆
C=N stretching azomethine	1603 1528	1668 1626	1599	1593	1667 1624
Ring stretching N phenyl	1382	1383	1384	1383	1380
stretching	1312			1352	1326
Ring bending of benzene	1151	1166	1152	1151	1087
Ring bending and deformation	1492	1479	1479	1490	1546
C-N-C bending	985 943	996	994	996	998
Out of plane ring deformation	775 735	768	769	768	768
Out of plane for mono substituted benzene	669	669	669	670	628
ν M-N metal ligand vibration	-	551	515	510	514

Table 3. Infra red absorption frequencies (cm^{-1}) for dioxouranium(VI) complexes of 2-FAPy.

Assignment	2-FAPy	$\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot (2\text{-FAPy})_2$	$\text{UO}_2(\text{NO}_3)_2 (2\text{-FAPy})_2$	$\text{UO}_2\text{I}_2(2\text{-FAPy})_2$	$\text{UO}_2(\text{NCS})_2 (2\text{-FAPy})_2$	$\text{UO}_2(\text{ClO}_4)_4 (2\text{-FAPy})_4$
C=N stretching	1603	1605	1665			
azomethine	1528	1540	1626	1601	1596	1651
Ring stretching <i>N</i> -phenyl	1382					
stretching	1312	1325	1383	1384	1384 1352	1376
Ring bending of benzene	1151	1152	1163	1151	1152	1111
Ring bending and deformation	1492	1473	1478	1478	1476	1428
C-N-C bending	985 943	930	996	994	901	970
Out of plane ring deformation	775 735	770	768	768	765	760
Out of plane (mono substituted benzene)	669	677	624	670 623	699	671
$\nu(\text{M-N})$ metal ligand vibration	-	519	515	514	510	509

PMR spectral studies

In the PMR spectra of 2-FAPy and its iodide complex with dioxouranium(VI) the furan protons imparted their characteristic peaks between 7.38 ppm values⁹ on δ scale. Interaction of $\alpha\alpha'$ and $\beta\beta'$ as well as $\alpha\beta$ protons of the heterocycle produced peak between 7.3 to 7.8 ppm values on δ scale. The azomethine proton also produce its significant peak in the same scale proton of the pyridine ring produces multiplet in 4.9-5.7 cps range because of α - β interactions. Significant peaks of iodide complexes are in form of multiplet in the range 7.69-7.83 and a pentet in 6.72-6.75 ppm range.

X ray diffraction studies

In this present investigation two representatives samples were chosen for x-ray diffraction studies through powder method *viz* $[\text{Th}(2\text{-FAPy})_2(\text{NO}_3)_4]$, $[\text{Th}(2\text{-FAPy})_4\text{I}_2]$ (Figure 2 & 3). The analysis was based on Bragg's equation and a , b , c ; angles and constants hkl along with inter planar distance ' d ' were obtained¹⁰⁻¹⁴.

The results were analyzed to obtain crystal system along with other parameters. The results are tabulated in Tables 4 & 5. $[\text{Th}(2\text{-FAPy})_2(\text{NO}_3)_4]$ belongs to orthorhombic system with $a = 15.393\{8\}\text{\AA}$, $b = 76.94\{4\}\text{\AA}$, $c = 7.479\{9\}\text{\AA}$ (Table 4). $[\text{Th}(2\text{-FAPy})_4\text{I}_2]$, belongs to orthorhombic system with $a = 16.757\{2\}\text{\AA}$, $b = 9.937\{3\}\text{\AA}$, $c = 4.068\{2\}\text{\AA}$ (Table 5).

Figure 2. X-Ray diffraction for $[\text{Th}(\text{2-FAPy})_2(\text{NO}_3)_4]$.

Figure 3. X-Ray diffraction for $[\text{Th}(\text{2-FAPy})_4\text{I}_2]$

Table 4. Crystallographic data for [Th(2-FAPy)₂(NO₃)₄].

2θ obs.	I	hkl	d _{obs}	d _{calcd.}
11.509	30	200	7.682	7.7
11.866	26	001	7.452	7.47
19.298	37	301	4.595	4.610
21.870	45	101	4.060	4.074
23.762	82	022	3.820	3.756
23.786	100	113	3.452	3.452
27.757	49	113	3.211	3.221
28.050	39	420	3.178	3.181

Table 5. Crystallographic data for [Th(2-FAPy)₄I₂]

2θ obs.	I	hkl	d _{obs}	d _{calcd.}
10.625	53	200	8.369	8.319
11.755	37	200	7.549	7.522
12.814	38	001	6.936	6.902
14.079	48	101	6.311	6.285
18.983	39	020	4.695	4.671
19.398	65	301	4.583	4.572
21.819	64	220	4.074	4.070
22.529	83	101	3.948	3.648
27.538	100	-	3.235	3.236

Toxic effects on microorganisms

Three complexes of this series were chosen [UO₂(2-FAPy)₂(NCS)₂] [UO₂(2-FAPy)₄(ClO₄)₂], [Th(2-FAPy)₄(ClO₄)₆] for toxic effects study. Thorium perchlorate complex of this ligand was found to be least effective for *E.coli* and uranium perchlorate was found to be most effective for bacterial toxicity. It was interesting to note that moderate concentration of complex of uranium salt is found to be maximum toxic for bacterial growth. For *Aspergillus* species maximum concentration of thorium and dioxouranium complexes is 60%; it was found to be most potent fungal inhibitor. The uranyl complexes showed maximum toxicity as the development of fungal colony was farthest from this complex sample disc. The significant results are shown in Table 6. Cause of toxicity might be accumulation of heavy metals in microbes affecting its mobility and confirming its toxicity in further exposure of intracellular metal binding site and increasing passive. Intracellular accumulation of these heavy metals occur through ion pump and ion channel *etc.* Permeability of cell membrane to toxic metals can result accumulations¹⁵⁻¹⁹.

Table 6. Colony diameter/ radial distance of colony around sample disc (cm).

Study	Complex ↓	Pure DMF	Complex conc. in DMF		
			20%	40%	60%
Antibacterial <i>E.coli</i>	[UO ₂ (2-FAPy) ₂ (NCS) ₂]	0.2/0.0	0.1/0.0	0.1/0.3	0.1/0.3
Antifungal <i>Aspergillus</i>	[UO ₂ (2-FAPy) ₂ (ClO ₄) ₂]	0.5/0.1	0.4/0.2	0.3/0.3	0.2/0.4
Antifungal <i>Mucor</i>	[UO ₂ (2-FAPy) ₂ (ClO ₄) ₂]	4.0/0.2	2.5/0.1	1.0/0.1	1.0/0.1

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