

Synthesis, Characterization & Bioactivity Investigation of New Uranium & Thorium Complexes with Bidentate Schiff Bases as Ligands

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The UO₂(VI) and Th(IV) complexes with 4-N-(metaphenoxybenzylidene) aminoantipyrine and 2-N-(metaphenoxybenzylidene)furfurylamine have been synthesized and characterized by physicochemical data. Ligands behave as bidentate towards the metal ions. The integrated ligands and their metal complexes were subjected to antifungal studies. These studies demonstrated the enhanced activity of metal complexes with respect to Schiff bases.

Keywords: Schiff base, Metal Complexes, metaphenoxybenzaldehyde, Furfurylamine Aminoantipyrine, Antifungal studies.

1. INTRODUCTION

The interest in the Schiff bases as ligands for the coordination compounds formation with different actinide ions has been demonstrated by numerous studies [1-3]. Even 15 decades after the first synthesis, Schiff bases continue to surprise chemists. Schiff bases have played a major role in the development of modern coordination chemistry because of their relevance to many interdisciplinary research fields. The chelated complexes of Schiff bases have potential and important applications in different scientific fields. Many results concerning their antimicrobial studies [4], analytical and material applications in addition to their important role in catalysis and organic synthesis [5-7].

To continue the investigation in this area [8-10], new coordination complexes with uranyl(VI) and thorium(IV) ions with 4-aminoantipyrine and furfurylamine derived Schiff bases were synthesized and their properties were discussed.

2. EXPERIMENTAL

The metal salts used in complexation were AR grade. FTIR spectra in KBr pellets were recorded using the Perkin-Elmer-577 spectrophotometer. CHN analysis were done on a Perkin-Elmer CHN microanalyzer. Magnetic susceptibility measurements were made at room temperature on a Gouy balance using copper sulphate pentahydrate as the calibrant. The metal contents in the complexes were determined gravimetrically following standard procedures [11]. The molar conductance measurements were carried out at room temperature with Toshniwal conductivity Bridge (cell constant 0.5 cm⁻¹) using the 1×10⁻³ M solution of the complexes in DMSO.

The ligand 4-N-(metaphenoxybenzylidene)aminoantipyrine (MPBAAP) was prepared by mixing equimolar quantities of ethanolic 4-aminoantipyrine and ethanolic metaphenoxybenzaldehyde with constant stirring. The light yellow coloured precipitate formed immediately at room temperature. It was washed with ethanol, ether and dried under vacuum. Schiff base 2-N-(metaphenoxybenzylidene)furfurylamine (MPBFA) was prepared by refluxing ethanolic solution of furfurylamine and ethanolic solution of metaphenoxybenzaldehyde for 2.5 hours and then passed over anhydrous sodium sulphate. The solvent was removed under vacuum 35-40°C. A dark red coloured liquid was obtained.

The $\text{UO}_2(\text{VI})$ and $\text{Th}(\text{IV})$ complexes were prepared by adding slowly with continuous stirring an ethanolic solution of respective metal salts to a solution of the MPBAAP ligand in benzene-ethanol (3:1) and the MPBFA ligand in the ethanol maintaining the stoichiometric metal-ligand ratio (1: 2). Whereupon $\text{UO}_2(\text{MPBAAP})_2(\text{NO}_3)_2$ and $\text{Th}(\text{MPBAAP})_2(\text{NO}_3)_4$ complexes were appeared during stirring, filtered, washed with benzene-ethanol/ethanol solution and dried under vacuum over fused calcium chloride. In the case of $\text{UO}_2(\text{MPBAAP})_2(\text{CH}_3\text{COO})_2$ and $\text{UO}_2(\text{MPBFA})_2(\text{NO}_3)_2$ complexes, the resulting reaction mixtures were refluxed for 2.5 to 5 hours. The volume of the reaction mixture of $\text{UO}_2(\text{MPBAAP})_2(\text{CH}_3\text{COO})_2$ was reduced to 1/4th of its original volume, cooled and 10-15 ml ether was added. coloured complex precipitated out immediately, filtered, washed and dried under vacuum over fused CaCl_2 . Complex $\text{UO}_2(\text{MPBFA})_2(\text{NO}_3)_2$ was precipitated out after refluxing.

3. RESULTS AND DISCUSSION

The physical, analytical and molar conductance data of the ligand and their complexes are given in Table 1. This is in agreement with the proposed structures of the ligands and their complexes. All the uranyl and thorium complexes were soluble in coordinating solvents like DMF and DMSO. They are stable in air and moisture. The molar conductance data in DMSO for the complexes indicate them to be non-electrolyte in nature. However, the conductivity values are higher than expected for non-electrolytes probably due to partial Salvolysis of the complexes in DMSO medium [12]. The magnetic moment values of uranyl and thorium complexes were found in the range 0.44 to 0.60. These lower values indicated that complexes are diamagnetic in nature.

TABLE 1: Colour, analytical, magnetic moment and molar conductance data for Schiff bases and their complexes.

Compounds	Colour	M.P. (°C)	% Analysis found (calculated)				μ_{eff} (B.M)	Molar Conductance
			M	C	H	N		
MPBAAP	Light Yellow	139-140	-	75.10 (75.16)	5.60 (5.52)	10.82 (10.92)	-	-
UO ₂ (MPBAAP) ₂ (NO ₃) ₂	Yellow	234-235	20.45 (20.51)	49.55 (49.65)	3.60 (3.62)	9.60 (9.65)	0.48	17.60
UO ₂ (MPBAAP) ₂ (CH ₃ COO) ₂	Light Yellow	152-153	20.75 (21.06)	53.25 (53.09)	4.37 (4.24)	7.39 (7.43)	0.55	16.80
Th(MPBAAP) ₂ (NO ₃) ₄	Brick Red	155-157	16.25 (16.77)	47.58 (47.27)	3.54 (3.44)	11.67 (11.49)	0.32	19.67
MPBFA	Dark red liquid	205-209 (B.P)	-	77.84 (77.94)	5.35 (5.45)	5.10 (5.05)	-	-
UO ₂ (MPBFA) ₂ (NO ₃) ₂	Yellow	>250	24.82 (25.09)	45.50 (45.58)	3.05 (3.19)	5.78 (5.90)	0.50	18.20

The important IR spectral bands (4000-200cm⁻¹) of the free ligand MPBAAP/MPBFA when compared with complexes provided meaningful information regarding the bonding sites of the ligands (Table 2).

The IR spectrum of ligands exhibited bands at 1660 cm⁻¹, 1590-1645 cm⁻¹ and 1245cm⁻¹ which were assigned to $\nu\text{C}=\text{O}$ (pyrazolone ring), $\nu\text{C}=\text{N}$ (azomethine) and $\nu\text{C}-\text{O}-\text{C}$ (furyl oxygen) respectively. In the IR spectra of the complexes, these bands were either shifted

towards the lower frequency side or disappeared after complexation. This shift/disappearance is suggestive of coordination of metal through the nitrogen of $>C=N$ [13], oxygen of pyrazolone ring and furyl oxygen.

TABLE 2: Important IR spectral bands (cm^{-1}) of Schiff bases and their metal complexes.

Compounds	$\nu_{C=O}$ (ring)	$\nu_{C=N}$	ν_{C-O-C}	ν_{M-O}	ν_{M-N}
MPBAAP	1660 s	1590 m	-	-	-
$\text{UO}_2(\text{MPBAAP})_2(\text{NO}_3)_2$	1600 m	1560 s	-	450 m	540 w
$\text{UO}_2(\text{MPBAAP})_2(\text{CH}_3\text{COO})_2$	1650 s	1580 m	-	425 w	555 m
$\text{Th}(\text{MPBAAP})_2(\text{NO}_3)_4$	1640 w	1565 s	-	445 m	550 w
MPBFA	-	1645 m	1245m	-	-
$\text{UO}_2(\text{MPBFA})_2(\text{NO}_3)_2$	-	1620 v,b	absent	420 m	515 m

Abbreviations: s=strong, m=medium, w=weak, v=very, b=broad

In the spectra of $\text{UO}_2(\text{MPBAAP})_2(\text{NO}_3)_2$ complex, three bands were observed at 1300, 1035, and 1525cm^{-1} . These three bands were assigned to ν_1 , ν_2 and ν_4 mode respectively due to coordinated nitrate ion [14]. Since the magnitude of the separation of ν_4 and ν_1 was found to be 225cm^{-1} which suggest that nitrate ions are coordinated bidentately [15]. In the spectra of $\text{UO}_2(\text{MPBAAP})_2(\text{CH}_3\text{COO})_2$ complex, two bands observed at 1530 and 1310cm^{-1} which were assigned to ν_{as} and ν_{sym} respectively. This indicated that acetate ions are coordinated in bidentate fashion [16]. In the spectra of the $\text{UO}_2(\text{MPBFA})_2(\text{NO}_3)_2$ complex, three additional bands observed at 1500, 1300 and 1030cm^{-1} corresponding to ν_4 , ν_1 and ν_2 frequencies. Since the magnitude of splitting of ν_4 and ν_1 was of the order of about 200cm^{-1} in the complex, the nitrate ions are coordinated bidentately [15]. The fourth and fifth additional relative bands appeared in the spectra of all uranyl complexes at $\sim 915-930$ and $\sim 815-830\text{cm}^{-1}$ were due to the $\nu_{\text{as}}\text{O}=\text{U}=\text{O}$ and $\nu_{\text{sym}}\text{O}=\text{U}=\text{O}$ stretching vibrations respectively [17]. In the spectra of thorium complex, three additional bands were observed at 1355, 1090 and 1230cm^{-1} which are assigned to ν_4 , ν_2 and ν_1 vibrations respectively of the nitrate group. The ν_4 and ν_1 bands are the splitted bands of the free nitrate group and the difference $\nu_4 - \nu_1$ is 125cm^{-1} indicating that nitrate groups are coordinated to the metal ion monodentately [18]. The coordination through Oxygen and nitrogen have been further confirmed by the appearance of ν_{M-O} and ν_{M-N} new bands at about 420-450 and $540-575\text{cm}^{-1}$ respectively [17].

On the basis of above observation the ligands MPBAAP and MPBFA act as bidentate ligand. The coordination number of eight is suggested to uranyl(VI) and thorium(IV) complexes.

3.1 Antifungal Activity

Antifungal activity of ligands and their metal complexes is given in Table 3. All the synthesized ligands and complexes were screened for their antifungal activities against fungus species viz. *A. flavour*, *A. niger*, *C. tetrasperma* and *A. Sydowi* by poisoned food

technique [19]. From the screening results it was observed that the complexes were found to be more active than the Schiff bases.

TABLE 3: Antifungal activity of ligands and their metal complexes.

Compounds	Zone of inhibition (in mm)											
	<i>A. flavour</i>			<i>A. niger</i>			<i>C. tetrasperma</i>			<i>A. sydowi</i>		
Conc. of compounds (in ppm)	50	100	150	50	100	150	50	100	150	50	100	150
MPBAAP	10	18	27	09	15	25	21	22	30	10	20	30
UO ₂ (MPBAAP) ₂ (NO ₃) ₂	22	40	55	18	31	62	25	45	65	18	35	58
UO ₂ (MPBAAP) ₂ (CH ₃ COO) ₂	15	25	40	13	24	38	20	40	60	12	33	55
Th(MPBAAP) ₂ (NO ₃) ₄	20	35	58	20	35	50	22	34	52	15	30	50
MPBFA	8	14	20	10	12	14	10	13	18	8	15	20
UO ₂ (MPBFA) ₂ (NO ₃) ₂	13	25	35	12	22	30	13	26	36	14	28	45

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