

# Uranium (VI) and Thorium (IV) Complexes with bis-benzimidazoles

Nalini R<sup>1</sup>, Madhusudhan Reddy K<sup>2</sup>, Basavarajaiah S M<sup>3</sup>, Venkatesh Babu K R<sup>4</sup>,  
Ramakrishna Reddy K<sup>5</sup>

<sup>1,5</sup>Department of Chemistry, Nrupathunga University, Bengaluru

<sup>2</sup>Department of Chemistry, Maharani Science College for women, Mysore

<sup>3</sup>P.G. Department of Chemistry, Vijaya College, R.V. Road, Bengaluru

<sup>4</sup>Department of Physics, Nrupathunga University, Bengaluru

**Abstract:** Uranyl nitrate and thorium nitrate react with different bis-benzimidazoles in suitable solvents to yield products of the type  $[\text{UO}_2(\text{L}^1)_2\text{NO}_3]\text{NO}_3 \cdot \text{H}_2\text{O}$ ,  $[\text{Th}(\text{L}^1)_2(\text{NO}_3)_4]4\text{H}_2\text{O}$ ,  $[\text{UO}_2(\text{L}^2)_2\text{NO}_3]\text{NO}_3 \cdot \text{H}_2\text{O}$ ,  $[\text{Th}(\text{L}^2)_2(\text{NO}_3)_4]4\text{H}_2\text{O}$ ,  $[\text{UO}_2(\text{L}^3)_2\text{NO}_3]\text{NO}_3 \cdot \text{H}_2\text{O}$  and  $[\text{Th}(\text{L}^3)_2(\text{NO}_3)_4]4\text{H}_2\text{O}$  where  $\text{L}^1=1,3\text{-bis}(\text{benzimidazol-2-yl})\text{benzene}$ ,  $\text{L}^2=1,3\text{-bis}(1\text{-methylbenzimidazol-2-yl})\text{benzene}$  and  $\text{L}^3=2,6\text{-bis}(1\text{-methylbenzimidazol-2-yl})\text{pyridine}$ . All these complexes are insoluble in common organic solvents and are soluble in DMF and DMSO. All the complexes were characterized by elemental analysis, infrared spectra, <sup>1</sup>H NMR spectra, TGA and conductivity studies in addition to magnetic susceptibility measurements. All the ligands act as bidentate with tertiary nitrogen as donor site. A coordination number of eight for dioxouranium ion,  $\text{UO}_2^{2+}$  and twelve for Th(IV) complexes were proposed.

**Key words:** Bis-benzimidazoles, Elemental analysis, Thermal gravimetric studies, FT-IR.

## 1. INTRODUCTION

Benzimidazole molecule is known to play a fundamental role in many biological systems; it is moreover, extensively used in industrial processes as a corrosion inhibitor for metal and alloy surfaces[1]. Several biological metalloproteins and metalloenzymes involve an imidazole moiety bonded to metal ions. In the process of synthesizing model compounds which mimic both the structure and reactivity of the metal ion sites in these biomolecules, benzimidazoles and their derivatives have assumed significant importance[1]. Benzimidazole derivatives have been used as potential ligands for preparing models of copper proteins. Bulky benzimidazoles can induce structural distortions leading to some unusual geometry around the metal ion. Investigations have shown that the benzimidazole derivatives and their complexes exhibit antitumor, antibacterial, anticarcinogenic, anthelmintic, fungicidal and polio virus inhibitor activities[2]. Benzimidazole derivatives are receiving considerable attention as ligands since various substituents could significantly modify the physical and chemical properties of their metal complexes relative to those of the complexes with the parent ligand. Steric and electronic factors would cause large variations in the  $\sigma$ -donor as well as  $\pi$ -donor/acceptor abilities of the N-atoms in such systems. It is suggested that the five and six membered N-heterocycles, both being  $\pi$ -electron deficient, differ in their  $\pi$ -acceptor capacity. While the latter are excellent  $\pi$ -acceptors, the former are much poorer  $\pi$ -acceptors but better  $\pi$ -donors[2]. This perhaps, is responsible for the interesting ligating behaviour of the planar multidentate N-heterocycles with coupled five and six-membered rings, viz., 1, 3-bis(benzimidazol-2-yl)benzene( $\text{L}^1$ ), 1, 3-bis(1-methylbenzimidazol-2-yl) benzene( $\text{L}^2$ ), 2, 6-bis(1-methyl benzimidazol-2-yl) pyridine( $\text{L}^3$ ). Benzimidazole derivatives and their transition metal complexes have been extensively investigated. Substituents of the benzimidazolyl derivatives could significantly modify their reactivity towards metal ions. Further several of their metal complexes may serve as models to mimic the active centers of metallobio-molecules.

The dioxouranium (VI) ion,  $\text{UO}_2^{2+}$ , is rather unusual in its structure and coordination behaviour. It has a linear shape and depending on the chemical and stereo chemical nature of the ligand, can coordinate through two to six such groups in the equatorial plane with a strong tendency to make these ligating atoms co-planar[2-4]. A wide variety of organic and inorganic ligands form complexes with dioxouranium (VI)[5-7].

The high charge on thorium (IV) makes it highly susceptible to complex formation with a wide variety of ligands[5-7], often forming unusual complexes with a relatively higher coordination number. Therefore it is considered worthwhile to synthesize and characterize a few complexes of dioxouranium (VI) and thorium (IV) with bidentate donor ligands such as 1,3-Bis(benzimidazol-2-yl) benzene ( $\text{L}^1$ ), 1,3-Bis(1-methyl benzimidazol-2-yl)benzene( $\text{L}^2$ ) and 2, 6-Bis(1-methyl benzimidazol-2-yl) pyridine( $\text{L}^3$ ).

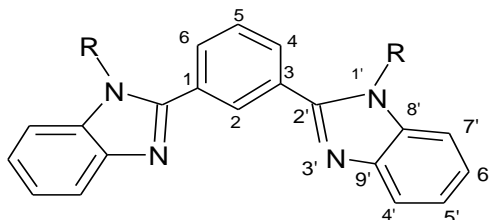
2. MATERIALS AND MEASUREMENTS

Uranyl nitrate  $[UO_2(NO_3)_2 \cdot 6H_2O]$  and Thorium nitrate  $[Th(NO_3)_4 \cdot 5H_2O]$  of BDH and Merck were used as such. Tetrahydrofuran, butanol, ethanol, methanol, isopropanol and acetone were purified by standard methods and used. Elemental analysis (C, H and N) was carried out by employing a CHNS analyzer, (Vario EL III). Uranium and thorium content of the complexes were determined gravimetrically by oxalate-oxide method [7,8]. The nitrate content of the complexes was determined gravimetrically using nitron reagent<sup>9</sup>. IR spectra were recorded in the range  $4000-400\text{ cm}^{-1}$  using Perkin-Elmer 580 infrared spectrometer and Nicolet impact 400 D FTIR spectrometer. Spectra were recorded in KBr pellets. The magnetic susceptibility measurements were carried out by Gouy method at the laboratory temperature. Conductivity measurements were made using Toshniwal conductivity bridge (CLO1/O2A) having a specially fabricated conductivity cell of cell constant  $1.0\text{ cm}^{-1}$ . The proton NMR data was recorded using Bruker Advance DPX spectrometer at 400 MHz. TGA studies of the complexes were carried out up to  $1500^\circ\text{C}$  with simultaneous Differential Thermal analysis (DTA) using TGA-DTA Perkin Elmer STA6000, Perkin Elmer Diamond.

3. SYNTHESIS OF LIGANDS

**3.1. Preparation of 1, 3-bis (benzimidazol-2-yl) benzene [10]:** Isophthalic acid (8.3g; 0.05mol) was added to a mixture of o-phenylenediamine (10.8g; 0.1mol) in phosphoric acid (50ml). The contents were stirred at a temperature of  $250^\circ\text{C}$  on a sand bath for 4h. The greenish-blue melt obtained was poured into 1000ml of cold water and neutralized with 10% solution of sodium carbonate. The resulting pink coloured solid on recrystallisation from ethanol gave white needles (6.95g; 84%).

**3.2. Preparation of 1,3-bis(1-methylbenzimidazol-2-yl)-benzene [10]:** 1-Methyl-o-phenylenediamine dihydrochloride (39g; 0.1mol) was added in small quantities to hot phosphoric acid (100ml) to get a brown solution. The hot mixture was treated with isophthalic acid (8g; 0.05mol) and stirred at  $200^\circ\text{C}$  on a sand bath for 4h. The resultant mixture was poured into 1000ml cold water. It was neutralized with 10% sodium carbonate so as to obtain a brown solid. The later on crystallization from methanol gave a light pink solid (20g; 60%)



	<u>R</u>	
L <sup>1</sup>	H	1, 3-bis(benzimidazol-2-yl)benzene
L <sup>2</sup>	CH <sub>3</sub>	1, 3-bis(1- methylbenzimidazol-2-yl)benzene

**3.3. Preparation of 1, 3-bis (1-methyl benzimidazol-2-yl) pyridine:** It was prepared by taking dipicolinic acid (pyridine-2, 6-dicarboxylic acid) and 1-methyl o-phenylene diamine by the procedure mentioned above.



L<sup>3</sup> 2,6-bis(1-methyl benzimidazol-2yl)pyridine

**3.4. Synthesis of Complexes of UO<sub>2</sub> (VI) and Th (IV):** The complexes  $[UO_2(L^1)_2NO_3]NO_3 \cdot H_2O$  and  $[Th(L^1)_2(NO_3)_4]4H_2O$ ;  $[UO_2(L^2)_2NO_3]NO_3 \cdot H_2O$  and  $[Th(L^2)_2(NO_3)_4]4H_2O$  and  $[UO_2(L^3)_2NO_3]NO_3 \cdot H_2O$  and  $[Th(L^3)_2(NO_3)_4] 4H_2O$  were synthesized by general procedure. The metal salt solution in ethanol was mixed with a stoichiometric amount of ligand solution in the same solvent. The solution was refluxed for about 6-8 h, and concentrated. On cooling the desired metal complexes obtained were collected by filtration, followed by repeated washing with small aliquots of ethanol and finally dried in vacuo.

**4.RESULTS AND DISCUSSION**

Uranyl nitrate  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and Thorium nitrate  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  react with different bis-benzimidazoles (L) in 1:2 molar ratio in ethanol to yield either white or coloured solids. These are insoluble in common organic solvents and soluble in DMF and DMSO. The elemental analysis and other physical properties of these complexes are summarized in Table 1. The complexes have fairly high melting point and not soluble in suitable solvents for determination of molecular weight by cryoscopic method or Rast - camphor method.

**4.1.Molar Conductance and Magnetic Susceptibility Measurements:** The molar conductance values of the complexes in DMSO ( $10^{-3}$ - $10^{-4}$ M) are shown in Table1. The uranyl complexes showed conductance values attributable to a uni-univalent electrolyte[11]. It is observed that covalently bonded  $\text{NO}_3$  (bidentate) groups are present in the thorium complexes in the solid state. Therefore, based on IR data, non-electrolytic structures have been proposed for all the thorium complexes. But the slightly higher conductivity values observed in DMSO for the thorium complexes may be attributed to the replacement of coordinated anions by DMSO molecules due to solvolysis[12,13]. The magnetic susceptibility measurements reveal that all the complexes are diamagnetic as generally expected for U(VI) and Th(IV).

Sl. No	Complexes	Colour	Yield %	M.P(°C)	$\lambda_{\text{MS}} \text{ cm}^2 \text{ mol}^{-1}$	Nitrate Content % Found (%Calc)	Elemental Analysis (%Calculated)			
							M	C	H	N
1	$[\text{UO}_2(\text{L}^1)_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$	Buff	85	220	100.0	12.21 (12.00)	23.02 (23.06)	46.54 (46.51)	2.94 (2.90)	13.40 (13.56)
2	$[\text{UO}_2(\text{L}^2)_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$	Pale yellow		260	88.8	12.01 (11.39)	21.93 (21.87)	48.31 (48.52)	3.52 (3.49)	13.02 (12.86)
3	$[\text{UO}_2(\text{L}^3)_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$	White	90	250(d)	82.0	11.20 (11.37)	21.80 (21.83)	46.02 (46.23)	3.40 (3.30)	15.40 (15.44)
4	$[\text{Th}(\text{L}^1)_2(\text{NO}_3)_4] \cdot 4\text{H}_2\text{O}$	White	85	216	45.2	21.00 (21.16)	19.82 (19.79)	40.70 (40.95)	3.09 (3.07)	14.39 (14.33)
5	$[\text{Th}(\text{L}^2)_2(\text{NO}_3)_4] \cdot 4\text{H}_2\text{O}$	Pale yellow	75	260(d)	38.0	20.15 (20.19)	18.93 (18.89)	43.02 (42.99)	3.54 (3.58)	13.62 (13.68)
6	$[\text{Th}(\text{L}^3)_2(\text{NO}_3)_4] \cdot 4\text{H}_2\text{O}$	White	90	222	35.1	20.18 (20.16)	18.84 (18.86)	41.01 (40.97)	3.43 (3.41)	15.83 (15.92)

Table 1. Analytical and Physical data of U(VI) and Th(IV) complexes

**4.2.Electronic spectra:** The electronic spectra of the complexes in DMF solution gave no bands in the 330-750nm region. The absorption bands obtained below 330nm correspond to the ligand  $\pi - \pi^*$  transitions and are not of much help in deciding the geometry around the central uranium (VI) and Th(IV) complexes[14].

**4.3.IR Spectral Studies:** The IR spectra of the complexes are comparable with those of the uncoordinated N-heterocycle ligands except for minor shifts in the position of some bands and the data are depicted in Table.2. The spectra of U(VI) and Th(IV) complexes containing  $\text{L}^1$  display  $\gamma(\text{NH})$  around  $3200\text{cm}^{-1}$  which, has shifted by  $40\text{cm}^{-1}$  to lower frequency as compared to that of the uncoordinated ligand  $\text{L}^1$ . A close similarity in the spectra of complexes with other ligands  $\text{L}^2$  and  $\text{L}^3$  suggests the same coordination environment around the metal ion. The positions of  $\gamma(\text{NH})$  and  $\gamma(\text{CN})$  in the spectra of the complexes are suggestive of coordination of heterocycle via the tertiary nitrogen of the imidazole moiety[15]. The broad absorption bands in the region  $3500$  to  $3400\text{ cm}^{-1}$  are attributable to coordinated or lattice held water molecules in the complexes[12,16].

In general, the IR spectra of the benzimidazole ligands (KBr) show the peaks around the following frequencies[20] 3500-3200  $\text{cm}^{-1}$  ( $\gamma_{\text{N-H}}$ );  $\sim 1590\text{cm}^{-1}$ (N-H in plane bending); 1540  $\text{cm}^{-1}$ , ( $\delta_{\text{C-H}}$  and  $\gamma_{\text{C=C}}$  vibration); 1320 $\text{cm}^{-1}$  ( $\gamma_{\text{C-N}}$  and  $\delta_{\text{N-H}}$ ); 1620 $\text{cm}^{-1}$ ( $\gamma_{\text{C=N}}$  and  $\delta_{\text{C=C}}$ ); 1410  $\text{cm}^{-1}$ , 1275  $\text{cm}^{-1}$ , 1000  $\text{cm}^{-1}$ , 740  $\text{cm}^{-1}$ , 615  $\text{cm}^{-1}$ , 430  $\text{cm}^{-1}$  are assigned to ring vibrations. All the complexes show a shift in these frequencies indicating the co-ordination of the ligand to the metal.

The uncoordinated nitrate ( $D_{3h}$ ) is expected to exhibit[12] three IR active fundamentals:  $\gamma_2(A_2)$  831  $\text{cm}^{-1}$ ;  $\gamma_3(E)$  1390  $\text{cm}^{-1}$ ; and  $\gamma_4(E)$  790 $\text{cm}^{-1}$ ; whereas a coordinated nitrate ( $C_{2v}$ ) exhibits six such fundamentals[11,12]  $\gamma_4(B_1)$ , 1530-1480 $\text{cm}^{-1}$ ,  $\gamma_1(A_1)$ , 1290  $\text{cm}^{-1}$ ;  $\gamma_2(A_1)$ , 1030 $\text{cm}^{-1}$ ;  $\gamma_5(B_2)$ , 810 $\text{cm}^{-1}$ ,  $\gamma_3(A_1)$ , 740  $\text{cm}^{-1}$  and  $\gamma_6(B_1)$ , 731  $\text{cm}^{-1}$ . The magnitude  $\gamma_4-\gamma_1 = (140-185 \text{ cm}^{-1})$  in these complexes[11,16] might be considered to be in favour of the bidentate character of the  $C_{2v}$  nitrate. The IR spectra of the nitrate complexes of both uranium and thorium in KBr pellets showed bands  $\approx 1500, 1290, 1030, 820, 745$  and 720  $\text{cm}^{-1}$  corresponding to the presence of bidentate nitrate groups[11,16]. The uranyl complexes of Table 2 also showed intense signals around 1380-1390 $\text{cm}^{-1}$ , which can be assigned to the presence of free  $\text{NO}_3(D_{3h})$ . However, the disappearance of a signal  $\sim 1380-1390\text{cm}^{-1}$  in all the complexes of thorium indicate the absence of free  $\text{NO}_3(D_{3h})$  group[16,17].

The uranyl ion exhibits[12] three vibrational frequencies: symmetric ( $\gamma_1$ ), asymmetric ( $\gamma_2$ ) and stretching and bending ( $\gamma_3$ ) frequencies. With the linear uranyl ions, only asymmetric stretching is easily observed. However, IR forbidden-symmetric stretching mode often appears in the complexes. The IR bands observed around 920 and 810  $\text{cm}^{-1}$  as sharp bands correspond to the asymmetric ( $\gamma_3$ ) and symmetric ( $\gamma_1$ ) stretching vibrations respectively in all uranyl complexes. These are in conformity with the reported work [18]. From the IR spectra it can be concluded that the ligands  $L_1$ ,  $L_2$  and  $L_3$  act as bidentate. The bidentate nature of  $L_3$  ligand may be due to the possibility of rotation of the C-C bond between one of the molecules of benzimidazole and pyridine moiety.

Table 2: Significant IR absorptions of  $L^1$ ,  $L^2$  and  $L^3$  and their U(VI) and Th(IV) complexes in  $\text{cm}^{-1}$ .

Sl. No	Ligand/Complex	$\gamma_{\text{O-H}}(\text{H}_2\text{O})$	$\gamma_{\text{NH}}$	$\gamma_{\text{CH}}$ of N-CH <sub>3</sub>	$\gamma_{\text{C=C}}$ / $\gamma_{\text{C=N}}$	o-Sub PyRi ng vib	Uranyl Vibrato n $\gamma_3$ $\gamma_1$	Nitrate vibrations
	$L^1$	----	3240	----- -	1626,158 0	-----		-----
1	$[\text{UO}_2(L^1)_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$	3400	3110	-----	1595	-----	940 800	1490(1393), 295, 1020, 820(830), 741, 720(725)
2	$[\text{Th}(L^1)_2(\text{NO}_3)_4]4\text{H}_2\text{O}$	3416	3167	-----	1569	-----		1497, 1290, 1036, 809, 741, 716
	$L^2$	-----	--	3350	1616,158 0	-----		-----
3	$[\text{UO}_2(L^2)_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$	3450	---	3178	1590	-----	915 765	1500(1388), 1300, 1025, 820(835), 747, 716(720)
4	$[\text{Th}(L^2)_2(\text{NO}_3)_4]4\text{H}_2\text{O}$	3416	----	3200	1512	-----		1512, 1290, 1036, 814, 747, 720
	$L^3$	-----	----	3441	1595,157 4	1124		-----
5	$[\text{UO}_2(L^3)_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$	3426	----	3300	1590	1120	925 819	1512(1383), 1284, 1020, 820(830), 740, 730(720)
6	$[\text{Th}(L^3)_2(\text{NO}_3)_4]4\text{H}_2\text{O}$	3426	----	3250	1517	1118		1522, 1290, 1031, 809, 747, 716

(Free nitrate modes are in paranthesis)

**4.4.  $^1\text{H}$  NMR Spectra:**  $^1\text{H}$  NMR spectral data of the free ligands and their complexes are presented in Table 3. The spectra of the free ligands display a doublet at  $\delta 8.26$  ( $L^1$ ),  $\delta 8.04$  ( $L^2$ ) and  $\delta 8.26$  ( $L^3$ ) for H-4 and H-6. Further the spectra are illustrative of the two-benzimidazole groups being equivalent. The peaks due to the H-4' and H-7' are observed as a singlet at  $\delta 7.70$  and  $\delta 7.64$  for  $L^1$ , while the peaks corresponding to H-4' and H-7' of  $L^2$  are located as doublet at  $\delta 7.71$  and  $\delta 7.65$ . For the ligand  $L^3$  the respective peaks were observed as doublets at  $\delta 7.76$  and  $\delta 7.69$ . A broad singlet displayed at  $\delta 13.1$  arises due to the imine proton. The N-CH<sub>3</sub> peak of ligand  $L^2$  is located at  $\delta 3.96$  and for  $L^3$  at  $\delta 4.26$  as singlet. In complexes, the spectral pattern results in downfield chemical shifts of the ring protons, which is in accordance with a lowering of electron density in the ring system[19]. The coordination in case of ligand  $L^1$  also results in an upfield shift

of the imine proton signal from  $\delta$ 13.11 to  $\delta$ 3.36 in the complexes[10]. Similar observations were made by earlier authors[15].

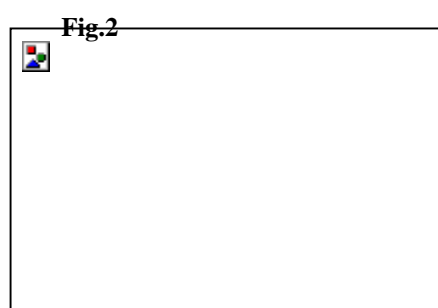
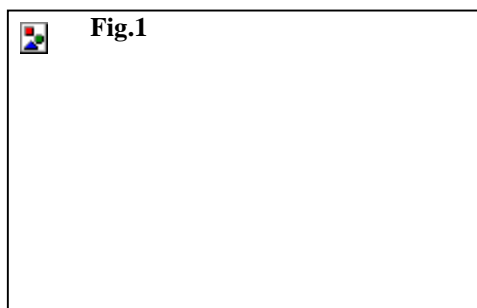
Table.3  $^1\text{H}$  NMR Chemical Shifts (ppm) for  $\text{L}^1$ ,  $\text{L}^2$  and  $\text{L}^3$  and their U(VI) and Th(IV) Complexes in ppm

Sl. No.	Ligand/Complex	Benzene ring			Benzimidazole ring				N-H/N-CH <sub>3</sub>
		H-2	H-4,6	H-5	H-4'	H-5'	H-6'	H-7'	
	$\text{L}^1$	9.05s	8.26dd	7.73t	7.70d	7.23m	7.23m	7.64d	13.11bs
1	$[\text{UO}_2(\text{L}^1)_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$	9.12s	8.29d	7.82t	7.77m	7.31m	7.31m	7.68m	3.36s
2	$[\text{Th}(\text{L}^1)_2(\text{NO}_3)_4]4\text{H}_2\text{O}$	9.1s	8.36dd	7.97t	7.79m	7.45m	7.45m	7.78	3.92s
	$\text{L}^2$	8.30s	8.04dd	7.78t	7.71d	7.29m	7.29m	7.65d	3.96s
3	$[\text{UO}_2(\text{L}^2)_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$	8.35s	8.07d	8.86t	7.78d	7.35m	7.35m	7.70d	4.0s
4	$[\text{Th}(\text{L}^2)_2(\text{NO}_3)_4]4\text{H}_2\text{O}$	8.40s	8.16d	8.98t	7.83m	7.41m	7.41m	7.77m	4.01s
		H-3,5	H-4	--	H-4'	H-5'	H-6'	H-7'	
	$\text{L}^3$	8.39d	8.20t	--	7.76d	7.3t	7.3t	7.69d	4.26bs
5	$[\text{UO}_2(\text{L}^3)_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$	8.47d	8.25t	--	7.86d	7.36t	7.36t	7.78t	4.26s
6	$[\text{Th}(\text{L}^3)_2(\text{NO}_3)_4]4\text{H}_2\text{O}$	8.49d	8.43t	--	7.93d	7.56t	7.51t	7.85d	4.86bs

**4.5. Thermal Gravimetric Studies (TGA):** TGA studies of the complexes were carried out in nitrogen atmosphere at the rate of  $10^\circ\text{C}$  per minute up to  $700^\circ\text{C}$ . In the thermal decomposition studies of the U(VI) and Th(IV) complexes, a general pattern is observed where the water of hydration is lost followed by the loss of uncoordinated nitrate, coordinated nitrate, ligand molecules and the decomposition of the complex to finally give the oxides,  $\text{U}_3\text{O}_8$  or  $\text{ThO}_2$ , at higher temperatures. Considering the initial decomposition temperature of the complexes as a rough guide, the stability of complexes follows the order  $[\text{UO}_2(\text{L}^3)_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O} > [\text{UO}_2(\text{L}^2)_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O} > [\text{UO}_2(\text{L}^1)_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$  and  $[\text{Th}(\text{L}^3)_2(\text{NO}_3)_4] \cdot 4\text{H}_2\text{O} > [\text{Th}(\text{L}^1)_2(\text{NO}_3)_4] \cdot 4\text{H}_2\text{O} > [\text{Th}(\text{L}^2)_2(\text{NO}_3)_4] \cdot 4\text{H}_2\text{O}$ . Similar observations were made by earlier authors[21].

### CONCLUSION

Six new complexes of U(VI) and Th(IV) with bis-benzimidazole ligands are synthesised and characterised by elemental analysis, FT-IR,  $^1\text{H}$  NMR, Electronic spectroscopy, TGA studies as well as by conductivity measurements. All the ligands act as bidentate with tertiary nitrogen as donor site. A coordination number of eight for dioxouranium ion,  $\text{UO}_2^{2+}$  and twelve for Th (IV) complexes are proposed. The proposed structures are presented in Fig.1 and 2.



Where X=CH or N and R= H or  $\text{CH}_3$ .



**REFERENCES**

- [1] Maria Marinescu. "Recent advances in the use of benzimidazoles as corrosion inhibitors." *BMC Chemistry* (2019): 13.136, DOI: <https://doi.org/10.1186/s13065-019-0655-y>
- [2] Aravazhi Amalan Thiruvalluvar, Gopalsamy Vasuki, Jayaraman Jayabharathi and Sivaraman Rosepriya. "Chemistry and Applications of Benzimidazole and its Derivatives." (2019): DOI:10.5772/intechopen.85291
- [3] Jonathan L Sessler, Patricia J Melfi and Dan Pantos. "Coordination Chemistry Reviews." 250(7-8), April (2006): 816-843. DOI:10.1016/j.ccr.2005.10.007
- [4] Silvia Berto, Francesco Crea, Pier Giuseppe Daniele Antonio Gianguzza, Alberto Pettignano and Silvio Sammartano. "Coordination Chemistry Reviews." Volume 256, Issues 1-2, Jan (2012): Page 63-81. DOI:10.1016/j.ccr.2011.08.015
- [5] Clément Camp, Nicholas Settineri, Julia Lefèvre, Andrew R. Jupp, José M. Goicoechea, Laurent Maron and John Arnold, *Chem. Sci.*, (2015):6, 6379-6384. DOI: <https://doi.org/10.1039/C5SC02150B>
- [6] Ashleigh L. Ward, Heather L. Buckley, Wayne W. Lukens, and John Arnold, *J. Am. Chem. Soc.* (2013): 135, 37, 13965-13971. DOI: <https://doi.org/10.1021/ja407203s>
- [7] Doina Humelnicu, A.Pui, Corina Malutan, Th. Malutan, I. Humelnicu, *Journal of Saudi Chemical Society*, Volume 24, Issue 6, June (2020): Pages 451-460. DOI: <https://doi.org/10.1016/j.jscs.2020.04.001>
- [8] I. M. Kolthoff and P. J. Elving (Eds), *Treaties on analytical Chemistry*, Vol. VIII, Part II, Interscience, New York, (1963).
- [9] A. I. Vogel, *A text book of quantitative Inorganic Analysis*. 4th Edition, Longman, London, 1978
- [10] Xianjin Xu, Zhenxing Xi, Wanzhi Chen and Daqi Wang. "Synthesis and structural characterization of copper(II) complexes of pincer ligands derived from benzimidazole." *Journal of Coordination Chemistry*, Volume 60, (2007): Issue 21. DOI: <https://doi.org/10.1080/00958970701261352>
- [11] Samina Khan, Ch. Jamil Anwar and M. Arshad, *Radiochimica Acta*, September 25, (2009): DOI: <https://doi.org/10.1524/ract.92.8.501.39280>
- [12] Didarul A. Chowdhury, Mohammad N. Uddin and Md. Akter H. Sarker, Chiang Mai "Synthesis and Characterization of Dioxo-uranium(VI) Complexes of Some Aroylhydrazines and Their Schiff Bases With Acetone." *J. Sci.* (2008): 35(3), 483-494. DOI: [www.science.cmu.ac.th/journal-science/josci.html](http://www.science.cmu.ac.th/journal-science/josci.html)
- [13] Ram K. Agarwal and Surendra Prasad. "Synthesis and Studies of Spectral and Thermal Properties of Some Mixed Ligand Complexes of Thorium(IV) and Dioxouranium(VI) With Semicarbazones as Primary Ligand and Sulfoxide as Secondary Ligand." *Iran. J. Chem. & Chem. Eng.* Vol. 23, No.2, 2004
- [14] Shivakumaraiah and N. M. Nanje Gowda. "Reactions of Zinc Salts with bis(Benzimidazolyl) Derivatives." *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry* 33(7) January (2003):1207-1220 DOI:10.1081/SIM-120023488
- [15] A. K. Srivastava, A. S. Chauhan and Kishor Arora, *Oriental Journal of Chemistry*, Volume 31, Number Special Issue, DOI : <http://dx.doi.org/10.13005/ojc/31.Special-Issue1.18>
- [16] V. K. Revankar, V. B. Mahale. "Studies on biologically active complexes of Co(II), Ni(II) and Cu(II) with Benzimidazole oximes." *Indian J. Chem.* 1989, 28A, 683
- [17] P. C. Vyas, C. K. Ojha. (Mrs), S Mittal, G. K Joshi, *J. Indian chem.Soc.* 1988, XV, 611.
- [18] R.A. Lal, J Chakraborty, A. Kumar; S. Haumik, R.K Nath, Ghosh. D. "A study on heterobimetallic chemistry of polyfunctional bis(2-hydroxy-1-naphthaldehyde) maloloyldihydrazone: Dioxouranium(VI), dioxomolybdenum(VI), zinc(II), copper(II), nickel(II) and cobalt(II) complexes." *Indian. J. Chem.* 2004, 43A, 516-526.
- [19] K. C. Rout, R. R. Mohanty, S. Jena and K. C. Dash. "Dioxouranium(VI) and thorium(IV) complexes with 2-(2'-pyridyl)1-methylbenzimidazole and reaction of dioxouranium(VI) complex with mercury(II), cobalt(II) and nickel(II)". *Polyhedron*, 1996, 15, 5, 1023. [https://doi.org/10.1016/0277-5387\(95\)00173-2](https://doi.org/10.1016/0277-5387(95)00173-2)
- [20] N. Shashikala, *Transition metal complexes with substituted benzimidazoles*, Ph.D Thesis, 1990, Bangalore University.
- [21] R. R. Mohanty, K. C. Rout, S. Jena and K. C. Dash. "Mononuclear dioxouranium(VI) and thorium(IV) complexes with potential tetradentate bridging chelators." *Polyhedron*, Vol.13, No.4, pp.559-565(1994): [https://doi.org/10.1016/S0277-5387\(00\)84732-4](https://doi.org/10.1016/S0277-5387(00)84732-4)