

## 3-Benzylidene/Furfurylidene/(Pyridyl/Thienyl-2'-methylene) imino-5-p-sulphonamido phenyl azo-2-thiohydantoin과 UO<sub>2</sub>(VI), ZrO(IV) 및 Th(IV) 이온의 동종이핵 착물에 대한 합성 및 특성

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## Synthesis and Characterization of Homobinuclear Complexes of UO<sub>2</sub>(VI), ZrO(IV) and Th(IV) ions with 3-Benzylidene/Furfurylidene/(Pyridyl/Thienyl-2'-methylene) imino-5-p-sulphonamido phenyl azo-2-thiohydantoin

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**요약.** [M<sub>2</sub>L(NO<sub>3</sub>)<sub>n</sub>(H<sub>2</sub>O)<sub>m</sub>]의 일반식을 갖는 일련의 동종이핵 착물을 합성하여 원소분석, 열분석, 몰 전기전도도, 자기모멘트 및 분광학적 방법(IR, UV-vis 및 <sup>1</sup>H-NMR)을 통해 특성을 조사하였다. 이 경우, 일반식에 있어서 M=UO<sub>2</sub>(VI), ZrO(IV), Th(IV); L=3-benzylidene-imino-5-p-sulphonamido phenyl azo-2-thiohydantoin(bispt), 3-furfurylidene-imino-5-p-sulphonamido phenyl azo-2-thiohydantoin(fispt), 3-pyridyl-2'-methylene-imino-5-p-sulphonamido phenyl azo-2-thiohydantoin(pmispt) 및 3-thienyl-2'-methylene-imino-5-p-sulphoanamido phenyl azo-2-thiohydantoin(tmispt); Th(IV)에 대해서 n=8 그 외의 것에 대해서는 n=4, bispt에 대해서는 m=4 그 외의 것에 대해서는 m=3을 의미한다. 이러한 결과에서 얻은 정보를 통해 리간드들은 4배위를 하는 것으로 확인되었는데, 즉 한 중심금속은 azomethine 질소 및 카르보닐 산소에 배위되는 반면, 또 다른 중심금속은 아조 질소 및 thioimido 질소에 배위되어 위의 조성을 갖는 동종이핵 착물을 이룬다. 몇 가지 병원균에 대한 리간드와 그들의 지르코닐 착물의 독성 연구도 수행하였다.

**주제어:** 3-치환된 thiohydantoin, 구조 및 열적 성질, IR 및 <sup>1</sup>H NMR 스펙트럼

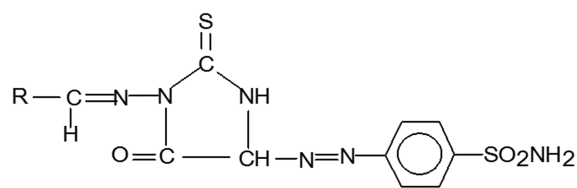
**ABSTRACT.** A series of homobinuclear complexes of the type [M<sub>2</sub>L(NO<sub>3</sub>)<sub>n</sub>(H<sub>2</sub>O)<sub>m</sub>] where M=UO<sub>2</sub>(VI), ZrO(IV), Th(IV); L=3-benzylidene-imino-5-p-sulphonamido phenyl azo-2-thiohydantoin(bispt), 3-furfurylidene-imino-5-p-sulphonamido phenyl azo-2-thiohydantoin(fispt), 3-pyridyl-2'-methylene-imino-5-p-sulphonamido phenyl azo-2-thiohydantoin(pmispt) and 3-thienyl-2'-methylene-imino-5-p-sulphoanamido phenyl azo-2-thiohydantoin(tmispt); n=8 for Th(IV) and 4 for others, m=4 for bispt and 3 for others have been synthesized and characterized on the basis of elemental analysis, thermal analysis, molar conductance, magnetic moment and spectroscopic data (IR, electronic and <sup>1</sup>H-NMR). In the light of this information, the ligands can be visualized as tetradentate co-ordinating through azomethine nitrogen, carbonyl oxygen to one metal centre where as azo nitrogen and thioimido nitrogen to the other metal centre yielding homo binuclear complexes of the above composition. The fungi toxicity of the ligands & their zirconyl complexes against some fungal pathogen has been studied.

**Keywords:** 3-substituted thiohydantoin, Structure and Thermal Properties, IR and <sup>1</sup>H NMR spectra

### INTRODUCTION

Multimetallic complexes have received much attention in connection with their potential relevance to bioinorganic chemistry.<sup>1</sup> The polydentate and compartmental ligands can form such multimetallic clusters by binding two or more metal centres in close proximity. The homo-multimetallic molecular complexes are of interest in areas

like multimetallic enzymes, homogeneous catalysis and heterogeneous catalysis. Many enzymes in biological system are homo-metallic that perform their biological function by redox co-operativity.<sup>2</sup> The toxicological importance of the ligands containing -N-C=S moiety and their metal complexes has been well established as potential antifungal and antibacterial agent.<sup>3</sup> Therefore, the studies of such bioactive ligands and their complexation behaviour have



R=Phenyl, Furyl, Pyridyl, Thienyl.

Fig. 1.

received much importance now-a-days. In continuation of our consistent effort towards synthesis and characterization of such type of complex,<sup>4,5</sup> we report here the synthesis and characterization of hitherto unknown homobinuclear complexes with the title ligands, bispt, fispt, pmispt and tmispt obtained by replacing one H-atom of methylene group at the 5<sup>th</sup> position of the thiohydantoin moiety in 3-benzylidene/furfurylidene (pyridyl/thienyl-2'-methylene) imino-2-thiohydantoin by p-sulphonamido phenyl azo group as given in Fig. 1 with UO<sub>2</sub>(VI), ZrO(IV) and Th(IV) ions. This is our continuing investigation on the coordination chemistry of multidentate ligands containing NOS donors.<sup>6-9</sup>

## EXPERIMENTAL

### Material and Method

Reagent grade chemicals were used in the present study. The solvents were purified before use by standard process. The starting materials such as 3-benzylidene/furfurylidene/(pyridyl/thienyl-2'-methylene) imino-2-thiohydantoin by the method reported earlier.<sup>10</sup>

**Preparation of Ligands (L), L=bispt/fispt/pmispt/tmispt:** Sulphanilamide (0.1 mol) dissolved in glacial acetic acid and water (25 mL) was diazotized with NaNO<sub>3</sub> in an ice bath. The resulting dilute solution was added gradually with stirring to previously cooled solution of 3-benzylidene imino-2-thiohydantoin (0.1 mol) in NaOH kept in ice bath. After addition, the mixture was mechanically stirred for half an hour during which the yellow colour azo dye separated out. It was filtered and recrystallized from ethanol. The ligands fispt, pmispt and tmispt were prepared by adopting the similar procedure as adopted for bispt from 3-furylidene(pyridyl/thienyl-2'-methylene) imino-2-thiohydantoin respectively.

**Preparation of the complexes of the type [M<sub>2</sub>L(NO<sub>3</sub>)<sub>n</sub>(H<sub>2</sub>O)<sub>m</sub>] where M=UO<sub>2</sub>(VI), ZrO(IV), Th(IV):** A hot ethanolic solution of ligand(L) was mixed with corresponding hydrated UO<sub>2</sub>(VI)/ZrO(IV)/Th(IV) nitrates dis-

solved in minimum volume of ethanol in 1:2 molar proportion and the p<sup>H</sup> of the resulting solution was adjusted to ~6.5-7 by drop wise addition of dilute ammonia. UO<sub>2</sub>(VI) complexes separated out immediately while complexes of ZrO(IV) and Th(IV) were obtained only after refluxing for 7 to 8 hours on a water bath. In each case microcrystalline coloured complex was obtained which was filtered off washed several times with ethanol followed by ether and finally dried in vacuo over fused CaCl<sub>2</sub>.

**Analysis and Physical measurements:** The metal contents in the complexes were determined gravimetrically following standard procedure.<sup>11</sup> A weighed quantity of compound (0.2-0.3 g) was treated with a few drops of conc. H<sub>2</sub>SO<sub>4</sub> and 1mL of conc. HNO<sub>3</sub>. It was heated till the organic matter decomposed and sulphur trioxide fumes came out. The same process was repeated two to three times to decompose the substance completely. Then it was dissolved in water and the resulting solution was used for analysis of metal ions. Uranium, zirconium and thorium were precipitated as ammonium diuranate, zirconium mandelate and thorium oxalate followed by sufficient ignition to their respective oxide as U<sub>3</sub>O<sub>8</sub>, ZrO<sub>2</sub> and ThO<sub>2</sub>. Sulphur was determined as BaSO<sub>4</sub>. The molar conductance measurements were carried out at room temperature with a Toshniwal conductivity Bridge (model CL-01-06, cell constant 0.5 cm<sup>-1</sup>) using 1×10<sup>-3</sup>M solution of the complexes in DMSO. Carbon, hydrogen and nitrogen contents of the complexes were determined by using a MLW-CHN micro analyser. FTIR spectra in KBr pallets were recorded on a Varian FTIR spectrophotometer, Australia. The electronic spectra of the complexes in DMSO were recorded on a Perkin-Elmer spectrophotometer. Thermogravimetric analyses were done by Netzsch-429 thermoanalyzer. The <sup>1</sup>H-NMR spectra of the complexes were recorded in DMSO-d<sub>6</sub> medium on JEOL, GSX-400 model equipment.

## RESULTS AND DISCUSSION

The complexes were formulated from the analytical data and molar conductance data support the suggested formulae (Table 1). The complexes are highly coloured and insoluble in water and common organic solvent such as ethanol, methanol, acetone, CCl<sub>4</sub>, CHCl<sub>3</sub>, benzene and ether but moderately soluble in highly coordinating solvents such as DMF and DMSO. They are diamagnetic, non hygroscopic, highly stable under normal conditions and all of them decompose above 250 °C. The molar con-

**Table 1.** Analytical and physical data of the complexes

Sl no	Compounds	Colours	$\Lambda_m^a$	C Found (Calcd)	H Found (Calcd)	N Found (Calcd)	S Found (Calcd)	M Found (Calcd)
1	bispt	Yellow	-	47.71 (47.76)	3.42 (3.48)	20.81 (20.89)	15.87 (15.92)	-
2	fispt	Light brown	-	42.81 (42.85)	3.04 (3.06)	21.37 (21.42)	16.29 (16.32)	-
3	pmispt	grey	-	44.62 (44.66)	3.19 (3.22)	24.27 (24.31)	15.83 (15.88)	-
4	tmsipt	Light yellow	-	41.13 (41.17)	2.87 (2.94)	20.54 (20.58)	23.47 (23.52)	-
5	(UO <sub>2</sub> ) <sub>2</sub> bispt(NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub>	Brown	24.56	15.17 (15.21)	1.71 (1.74)	11.06 (11.09)	5.05 (5.07)	37.69 (37.71)
6	(ZrO <sub>2</sub> ) <sub>2</sub> bispt(NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub>	Silver grey	23.87	20.46 (20.50)	2.31 (2.34)	14.92 (14.95)	6.81 (6.83)	19.43 (19.47)
7	(Th) <sub>2</sub> bispt(NO <sub>3</sub> ) <sub>8</sub> (H <sub>2</sub> O) <sub>4</sub>	Pale yellow	33.65	13.35 (13.38)	1.51 (1.53)	13.63 (13.66)	4.43 (4.46)	32.33 (32.35)
8	(UO <sub>2</sub> ) <sub>2</sub> fispt(NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3</sub>	Canary yellow	25.66	13.59 (13.61)	1.41 (1.45)	11.31 (11.34)	5.14 (5.18)	38.55 (38.57)
9	(ZrO <sub>2</sub> ) <sub>2</sub> fispt(NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3</sub>	Cabinet grey	22.27	18.41 (18.49)	1.96 (1.98)	15.39 (15.41)	7.01 (7.04)	20.03 (20.07)
10	(Th) <sub>2</sub> fispt(NO <sub>3</sub> ) <sub>8</sub> (H <sub>2</sub> O) <sub>3</sub>	Straw yellow	34.49	11.91 (11.94)	1.26 (1.28)	13.91 (13.94)	4.51 (4.55)	32.7 (33.0)
11	(UO <sub>2</sub> ) <sub>2</sub> pmispt(NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3</sub>	Dark yellow	18.95	14.42 (14.45)	1.49 (1.52)	12.34 (12.36)	5.12 (5.14)	38.20 (38.23)
12	(ZrO <sub>2</sub> ) <sub>2</sub> pmispt(NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3</sub>	Straw yellow	23.15	19.49 (19.50)	2.04 (2.06)	16.72 (16.75)	6.94 (6.96)	19.80 (19.83)
13	(Th) <sub>2</sub> pmispt(NO <sub>3</sub> ) <sub>8</sub> (H <sub>2</sub> O) <sub>3</sub>	Dirty white	35.54	12.64 (12.70)	1.32 (1.34)	14.79 (14.82)	4.52 (4.56)	32.71 (32.74)
14	(UO <sub>2</sub> ) <sub>2</sub> tmsipt(NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3</sub>	Dark brown	24.19	13.41 (13.44)	1.40 (1.44)	11.17 (11.20)	7.64 (7.68)	38.04 (38.08)
15	(ZrO <sub>2</sub> ) <sub>2</sub> tmsipt(NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3</sub>	Steel grey	22.85	18.09 (18.13)	1.91 (1.94)	15.07 (15.11)	10.33 (10.36)	19.60 (19.64)
16	(Th) <sub>2</sub> tmsipt(NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3</sub>	Greyish white	21.95	10.08 (10.12)	1.22 (1.26)	13.75 (13.78)	6.71 (6.75)	32.59 (32.63)

<sup>a</sup>Ohm<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup>

ductance data values in DMSO for the complexes indicate them to be non-electrolyte in nature. However the conductivity values are higher than those expected for non-electrolytes probably due to partial solvolysis of the complexes in DMSO medium.<sup>12</sup>

### IR Spectra

The introduction of p-sulphonamido azophenyl group at 5<sup>th</sup> position of 2-thiohydantoin moiety of 3-benzylidene/furfurylidine/(pyridyl/thienyl-2' methylene)-2-thiohydantoin did not cause any shift of the band position due to  $\nu$ N-H (~3400 cm<sup>-1</sup>) and thioimido-I (~1450 cm<sup>-1</sup>), II (~1320 cm<sup>-1</sup>), III (~1080 cm<sup>-1</sup>), IV (~840 cm<sup>-1</sup>),  $\nu$ C=O (~1710 cm<sup>-1</sup>) and azomethine  $\nu$ C=N (~1640 cm<sup>-1</sup>) of thiohydantoin moiety. Only additional band system of three strong bands

at ~3300, ~1360 and ~1175 cm<sup>-1</sup> due to sulphonamido group<sup>13</sup> and a band of medium intensity at ~1600 cm<sup>-1</sup> due to stretching vibration of azo(-N=N-) group were observed in the IR spectrum of the ligands. On comparing IR spectra of the ligands with complexes, stretching bands corresponding to azomethine,  $\nu$ C=O group, azo group and thioimido (NH) groups were found to be invariable shifted by 20-30 cm<sup>-1</sup> towards lower frequency region indicating the co-ordination of azomethine nitrogen, carbonyl oxygen, azonitrogen and thioimidic nitrogen to the metal ions consequently the band occurring at ~1050 cm<sup>-1</sup> due to  $\nu$ N-N of the ligand is blue shifted to ~1070 cm<sup>-1</sup> in all the complexes. The presence of furan ring in fispt is also indicated by the appearance of band at 1500 cm<sup>-1</sup> due to  $\nu$ C-O-C group of furan ring.<sup>14</sup> The position of this band is shifted

to lower frequency region in the metal complexes suggesting participation of oxygen atom of furan ring in complexation.

In addition to thioimide bands and a band due to azomethine  $\nu(\text{C}=\text{N})$ , a system of bands at  $\sim 1580$ ,  $\sim 1430$ ,  $\sim 1000$  and  $\sim 600 \text{ cm}^{-1}$  corresponding to antisymmetric ring stretching, symmetric ring stretching, ring breathing and in plane deformation mode of pyridine nucleus were observed in IR spectrum of the ligand pmispt.<sup>14</sup> It became difficult to arrive at any conclusion from the bands occurring at finger print region due to overlapping nature, regarding the co-ordination behaviour of ring nitrogen atom of pyridine moiety, however the shifting of band at  $600 \text{ cm}^{-1}$  to high frequency region by  $20\text{-}30 \text{ cm}^{-1}$  in the present complexes suggested the involvement of pyridine ring nitrogen atom to the metal ion.<sup>15</sup> The ligand tmispt contains both the thiophene ring and thioimide groups. All the bands due to above groups were not observed in the IR spectrum of tmispt. Instead IR spectrum of this ligand only exhibits bands at  $\sim 1440$ ,  $\sim 1310$ ,  $\sim 1070 \text{ cm}^{-1}$  assignable to thioimide I, II and III bands respectively being overlap with ring stretching vibration of thiophene ring, where as the bands observed at  $\sim 840 \text{ cm}^{-1}$  and  $800 \text{ cm}^{-1}$  may be assigned due to thioimide IV band and  $\nu\text{C-S-C}$  vibration respectively.<sup>13</sup> The characteristics IR bands due to  $\nu\text{C-S-C}$  (thiophene ring) shifted their position to lower frequency region thereby indicating the coordination of ring sulphur atom to the metal ion.<sup>14</sup> The IR spectra of all the complexes show additional bands at  $\sim 1390$  and  $\sim 1020 \text{ cm}^{-1}$  which unambiguously suggest the presence of coordinated nitrate anions in unidentate manner corresponding to  $\nu_2$  and  $\nu_4$  mode of vibration of coordinated nitrate ion under  $\text{C}_{2v}$  symmetry.<sup>16</sup> The presence of nitrate ion in the coordination sphere of all the complexes has also been supported

by non-electrolytic nature of complex in DMSO. Besides the bands observed at  $\sim 3500(\text{s})$ ,  $\sim 880(\text{m}) \text{ cm}^{-1}$  may assigned to  $\nu(\text{OH})$ , and  $\rho(\text{r})$  of co-ordinated water, which is further confirmed by thermal analysis.

The occurrence of new bands at  $\sim 530\text{-}515$  and  $\sim 460\text{-}450 \text{ cm}^{-1}$  in the spectra of the complexes further suggest the coordination of metal ions through oxygen and nitrogen respectively. The uranyl complexes exhibit a strong band at  $\sim 940\text{-}900 \text{ cm}^{-1}$  and the medium intensity band at  $\sim 835\text{-}820 \text{ cm}^{-1}$  assignable to  $\nu_{\text{as}}(\text{O}=\text{U}=\text{O})$  and  $\nu_{\text{s}}(\text{O}=\text{U}=\text{O})$  mode respectively.<sup>17</sup> The zirconyl complexes exhibit one strong band in the region  $\sim 900\text{-}870 \text{ cm}^{-1}$  which can be attributed to the  $\nu(\text{Zr}=\text{O})$  indicating the presence of  $(\text{Zr}=\text{O})^{2+}$  moiety in these complexes.<sup>18</sup>

### Thermal analysis

All these complexes follow the same pattern of thermal decomposition. The thermogram of the complexes exhibited the characteristics of co-ordinate water. The complexes remain almost unaffected up to  $\sim 140^\circ\text{C}$ . There after a slight depression up to  $\sim 200^\circ\text{C}$  is observed. The weight loss at this temperature is equivalent to four water molecule for bispt complexes and three water molecules for other complexes indicating them to be coordinated water<sup>19</sup> in conformity with our earlier observations from analytical and IR spectral investigation. Simultaneous elimination of coordinated water suggests them to be in the same chemical environment. The anhydrous complexes remain stable up to  $400^\circ\text{C}$  and there after the complexes shows rapid degradation presumably due to decomposition of organic constituents of the complexes molecules as indicated by the steep fall in the percentage of weight loss. The decomposition temperature varies for different complexes as shown in *Table 2*.

**Table 2.** Important features of thermo gravimetric analysis (TGA)

Complex	Total wt for Tg (mg)	Temp. Range of water loss ( $^\circ\text{C}$ )	% of water loss		Decomposition temp. ( $^\circ\text{C}$ )	% wt of residue		Composition of the residue
			Found	Calc.		Found	Calc.	
5	95	140-190	5.67	5.70	380-730	44.45	44.47	$\text{U}_3\text{O}_8$
6	110	135-180	7.65	7.68	370-690	26.29	26.31	$\text{ZrO}_2$
7	105	140-180	5.01	5.02	390-740	36.79	36.82	$\text{ThO}_2$
8	108	150-200	4.34	4.37	390-735	45.46	45.48	$\text{U}_3\text{O}_8$
9	93	130-185	5.91	5.94	365-690	27.09	27.12	$\text{ZrO}_2$
10	94	145-190	3.81	3.84	395-735	37.52	37.55	$\text{ThO}_2$
11	102	145-195	4.31	4.33	385-740	45.05	45.08	$\text{U}_3\text{O}_8$
12	105	130-190	5.84	5.87	375-700	26.74	26.80	$\text{ZrO}_2$
13	98	140-190	3.79	3.81	400-745	37.23	37.26	$\text{ThO}_2$
14	103	148-200	4.29	4.32	395-720	44.87	44.90	$\text{U}_3\text{O}_8$
15	107	135-190	5.81	5.84	360-685	26.62	26.65	$\text{ZrO}_2$
16	96	140-190	3.75	3.79	400-740	37.10	37.13	$\text{ThO}_2$

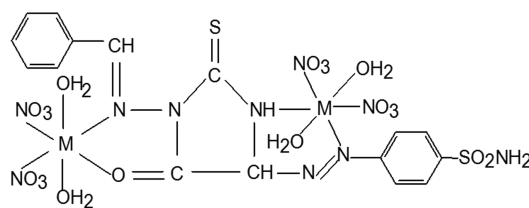
### Electronic spectra

The electronic spectra of complexes in DMSO are quite similar. The present system of ligands where 2-thiohydantoin is coupled at 3-position with benzylidene/furfurylidene/(pyridyl/thienyl-2'-methylene) imino group and at 5 position with *p*-sulphonamido-phenyl azo group display only two bands corresponding to  $\lambda_{\max}$ , 280-300 nm and 350-400 nm assignable to  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transition respectively indicating extensive conjugation. The  $\text{UO}_2(\text{VI})$  complexes display mainly one weak band at 440 nm and a highly intense band in the range  $\sim 300$  nm which may be due to  $^1\Sigma_g^+ \rightarrow ^3\Pi_u$  transitions and charge transfer being overlapped with  $\pi$ - $\pi^*$  transition respectively.<sup>20</sup> It may be noted that the band occurring at 370 nm is due to uranyl moiety because of apical oxygen  $\rightarrow f^0(\text{U})$  transition is being merged with the ligand band due to  $n \rightarrow \pi^*$  transition as evident from broadness and intensity. The electronic spectra of  $\text{ZrO}(\text{IV})$  and  $\text{Th}(\text{IV})$  complexes exhibit only highly intensive additional band in the region 370-400 nm which may be due to charge transfer besides the ligand bands.

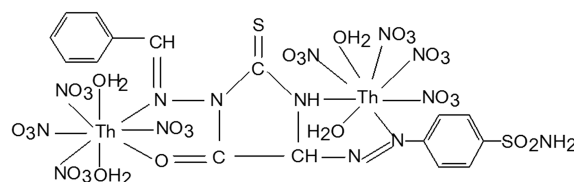
### $^1\text{H}$ NMR spectra

The  $^1\text{H}$  NMR spectra of the ligands as well as the complexes are recorded in  $\text{DMSO-d}_6$  medium. The  $^1\text{H}$  NMR spectra of the ligands show a complex broad multiplet at  $\delta$  8.4-7.3 ppm corresponding to nine aromatic protons for bispt, While the ligands like fispt, pmispt and tmispt show additional multiplets at  $\delta$  7.5-6.20 ppm corresponding to three protons of furan moiety of fispt, at  $\delta$  8.0-8.7 ppm corresponding to four aromatic protons for pyridine moiety of pmispt and at  $\delta$  7.78-7.22 ppm corresponding to three protons of thiophene moiety of tmispt, besides the multiplet at  $\delta$  8.7-8.5 ppm due to four phenyl ring protons.<sup>21</sup> The former multiplets undergo downfield shift to some extent probably due to involvement of ring O-atom, ring N-atom, ring S-atom in complexation, because of lowering of electron density in the ring system as evidenced from IR investigation while the latter multiplet remains practically unaltered.

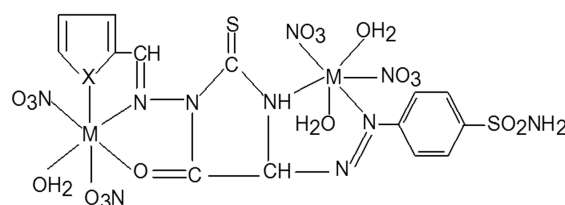
Another set of three distinct  $^1\text{H}$  NMR peaks were observed at  $\delta \sim 9.5$  ppm (1H),  $\delta \sim 9.1$  ppm (1H) and at  $\delta \sim 3.42$  ppm in the present system of ligands corresponding to  $\text{N}=\text{C}-\text{H}$  proton,  $-\text{NH}$  proton and  $-\text{CH}$  protons (thiohydantoin moiety). The signals due to  $\text{H}-\text{C}=\text{N}$  proton and  $\text{N}-\text{H}$  proton show a downfield shift by  $\delta$  0.3-0.4 ppm indicating the coordination of azomethine nitrogen and amidic nitrogen to the metal ions. However, the position of peaks due to  $-\text{CH}$  proton does not change appreciably because



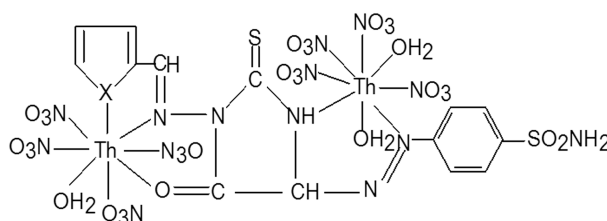
**Fig. 2.**  $(\text{M}=\text{UO}_2^{2+}, \text{ZrO}^{2+}) (\text{UO}_2)_2(\text{bispt})(\text{NO}_3)_4(\text{H}_2\text{O})_4$   $(\text{ZrO})_2(\text{bispt})(\text{NO}_3)_4(\text{H}_2\text{O})_4$ .



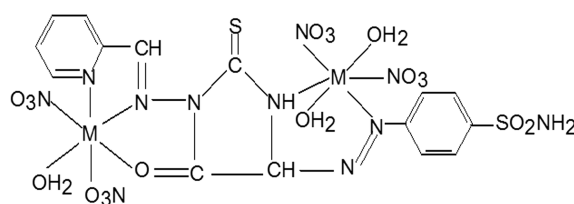
**Fig. 3.**  $(\text{Th})_2(\text{bispt})(\text{NO}_3)_8(\text{H}_2\text{O})_4$ .



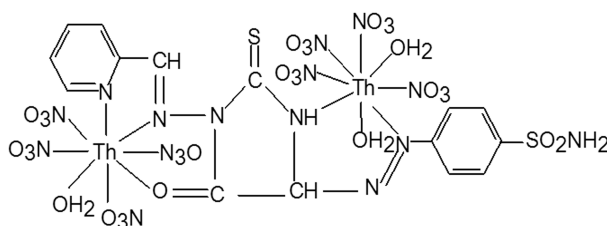
**Fig. 4.**  $(\text{M}=\text{UO}_2^{2+}, \text{ZrO}^{2+})(\text{X}=\text{O},\text{S})$ .



**Fig. 5.**  $(\text{Th})_2(\text{fispt})(\text{NO}_3)_8(\text{H}_2\text{O})_3$   $(\text{Th})_2(\text{tmispt})(\text{NO}_3)_4(\text{H}_2\text{O})_3$   $(\text{X}=\text{O},\text{S})$ .



**Fig. 6.**  $(\text{UO}_2)_2(\text{pmispt})(\text{NO}_3)_4(\text{H}_2\text{O})_3$   $(\text{ZrO})_2(\text{pmispt})(\text{NO}_3)_4(\text{H}_2\text{O})_3$   $(\text{M}=\text{UO}_2^{2+}, \text{ZrO}^{2+})$ .



**Fig. 7.**  $(\text{Th})_2(\text{pmispt})(\text{NO}_3)_4(\text{H}_2\text{O})_3$ .

**Table 3.** Fungi toxicity of the ligands and Zr(IV) complexes

Ligand/complexes	Aspergillus niger % of inhibition control					Aspergillus flavus % of inhibition over control				
	100	200	400	800	1000	100	200	400	800	1000
Bispt	8.4	12.1	14.2	28.2	52.5	6.5	11.6	14.7	26.3	48.1
Fispt	10.6	15.3	22.8	39.1	50.3	11.4	17.5	25.3	32.5	54.7
Pmispt	15.2	20.3	25.4	42.6	60.1	15.6	19.1	23.3	41.2	62.3
tmispt	18.7	25.7	32.1	64.8	77.0	17.3	25.3	32.4	64.3	75.2
(ZrO) <sub>2</sub> bispt(NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub>	11.7	17.4	16.3	31.2	55.1	10.2	15.5	15.1	29.2	52.1
(ZrO) <sub>2</sub> fmispt(NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3</sub>	13.4	16.6	23.5	52.1	54.6	13.1	18.7	26.2	35.6	57.8
(ZrO) <sub>2</sub> pmispt(NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3</sub>	16.1	21.7	26.3	48.3	63.2	16.3	21.3	28.3	45.2	65.3
(ZrO) <sub>2</sub> tmispt(NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>3</sub>	19.4	26.2	34.3	66.3	78.5	18.5	26.6	36.1	68.5	76.7

of the coordination of the ligand with metal ion. Besides an additional peak at  $\delta \sim 3.5$  ppm is observed in all the complexes indicating the presence of coordinated water molecules.<sup>22</sup>

### Fungicidal Screening

The antifungal activity of ligand bispt, fispt, pmispt, tmispt and zirconium complexes were tested against the organism *Aspergillus niger*, *Aspergillus flavus* by a typical procedure,<sup>23</sup> well diffusion method<sup>24</sup> method. A well was made on NCCLS approved standard potato dextrose agar medium inoculated with micro organism. The well was filled with the test solutions prepared by dissolving the complex in DMSO using a micropipette and the plates were incubated at 35 °C for five days. During this period the test solution diffused affected the growth of the inoculated bacteria. The % of inhibition was calculated as

$$\% \text{ of inhibition} = 100(P-Q)/P$$

Where Q=Area of colony growth with test sample

P=Area of colony growth without test sample

The results obtained have been presented in the Table 3 as given below.

The results of antifungal screening indicate that the complexes are more active than the free ligand. Increased activity of the complexes can be explained on the basis of chelation theory, there by increasing delocalization of  $\pi$  electron in the chelating ring.<sup>25</sup>

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