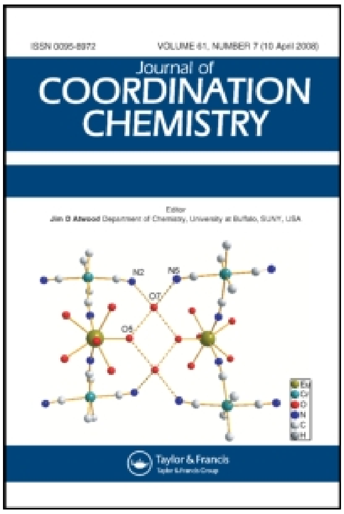

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and fluorescence studies of Th(IV) complexes of Schiff bases derived from 2,6-diformyl-4-methyl phenol and 3-substituted-4-amino-5-mercapto-1,2,4-triazoles

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To cite this Article Reddy, B. Nagaraja , Avaji, Prakash Gouda , Badami, Prema S. and Patil, Sangamesh A.(2008) 'Synthesis, characterization and fluorescence studies of Th(IV) complexes of Schiff bases derived from 2,6-diformyl-4-methyl phenol and 3-substituted-4-amino-5-mercapto-1,2,4-triazoles', Journal of Coordination Chemistry, 61: 11, 1827 — 1838

To link to this Article: DOI: 10.1080/00958970701618221

URL: http://dx.doi.org/10.1080/00958970701618221

Journal of Coordination Chemistry
Vol. 61, No. 11, 10 June 2008, 1827–1838

Synthesis, characterization and fluorescence studies of Th(IV) complexes of Schiff bases derived from 2,6-diformyl-4-methyl phenol and 3-substituted-4-amino-5-mercapto-1,2,4-triazoles

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(*Received 29 December 2006; in final form 6 June 2007*)

Thorium(IV) complexes have been synthesized by reacting Th(IV) nitrate with Schiff bases derived from 2,6-diformyl-4-methyl phenol and 3-substituted-4-amino-5-mercapto-1,2,4-triazoles in ethanol. These complexes have been characterized on the basis of elemental analyses, molar conductance and spectral studies. Analytical and spectral data suggest structures in which Th(IV) is six-coordinate, which is supported by coordination of seven nitrate ions with one bidentate, hydroxyl group of 2,6-diformyl-4-methyl phenol in a bidentate fashion and two azomethine groups through nitrogen atoms. The fluorescence and solid state electrical conductivity properties have been studied.

Keywords: Synthesis; Characterization; 1,2,4-Triazoles; Th(IV) complex

1. Introduction

In continuation of our earlier work on metal complexes with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole [1, 2], we report Th(IV) complexes of Schiff bases derived from 3-substituted-4-amino-5-hydrazino-1,2,4-triazole and substituted salicylaldehydes [3]. Several reports have highlighted the complexing ability of Schiff bases derived from triazoles [4–12], however, no attempts have been made to study Th(IV) complexes with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazoles and 2,6-diformyl-4-methyl phenol. Fluorimetric methods have proven useful for assay of metal ions in solution [13]. Reports are available on the effect of metal ions on fluorescence emission of aromatic heterocyclic ligands [14]. Therefore, it was thought worthwhile to study the synthesis, characterization and fluorescence properties of Th(IV) complexes with the following Schiff bases (figure 1).

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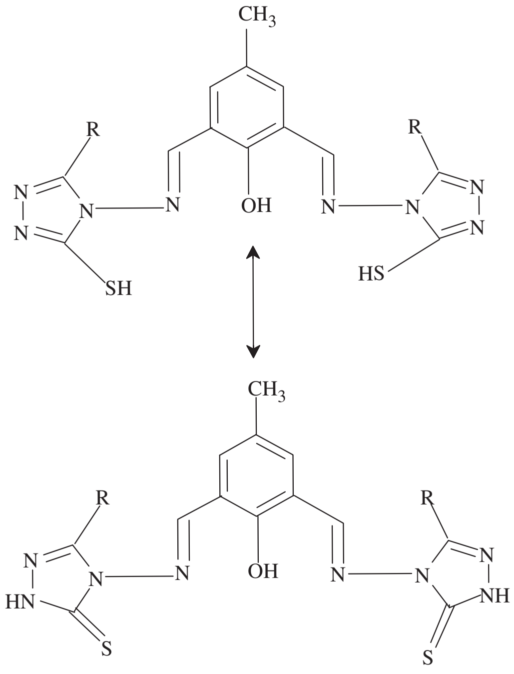
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970701618221



	R
I	H
II	CH_3
III	C_2H_5
IV	C_3H_7

Figure 1. Tautomeric forms of Schiff bases (I–IV).

2. Experimental

2.1. *Physical measurements*

IR spectra of the ligands and their Th(IV) complexes were recorded on a HITACHI model 270 IR spectrophotometer in the region 4000–250 cm^{-1} using KBr disks. Electronic spectra of the complexes were recorded in DMF on a VARIAN CARY Bio-50 model UV-spectrophotometer in the region 200–1100 nm. Proton NMR spectra of a representative ligand and complex were recorded in DMSO on BRUKER-300 MHz spectrometer using TMS as internal reference. Perkin-Elmer Diamond instrument was used for recording TGA data. Fluorescence was carried out on a model HITACHI F-2000. The FAB-mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon (6 KV, 10 mA) as the FAB gas. The accelerating voltage was 10 KV and the spectra were recorded at room temperature; *m*-nitrobenzyl alcohol was used as the matrix. The mass spectrometer was operated in the positive ion mode and electrical conductivity of solid complexes was measured using digital micro voltmeter model DMV-001.

2.2. *Synthesis*

All chemicals used for preparing triazoles and their Schiff bases were reagent grade. The 3-substituted-4-amino-5-mercapto-1,2,4-triazoles were prepared as reported [15, 16]. The 2,6-diformyl-4-methyl phenol was prepared according to the reported method [17].

2.3. *Synthesis of Schiff bases*

The mixture of 3-substituted-4-amino-5-mercapto-1,2,4-triazole (0.02 mol) and 2,6-diformyl-4-methyl phenol (0.01 mol) in ethanol containing a few drops of concentrated HCl was heated under reflux for 3–4 h. The product which separated on cooling was filtered, washed with ethanol and crystallized from ethanol.

2.4. *Synthesis of Th(IV) complexes*

Th(IV) nitrate (0.02 mol) was treated with Schiff base (0.01 mol) in ethanol and the reaction mixture was heated under reflux on a water bath for 2 h. Then, the reaction mixture was cooled and precipitation initiated by adding aqueous ammonia. The precipitated complex was filtered and washed thoroughly with distilled water, absolute alcohol, then with distilled ether. The complex was dried under reduced pressure over dried calcium chloride.

2.5. *Analysis*

Thorium and sulphur in the complexes were analyzed gravimetrically as thorium dioxide and $BaSO_4$, respectively [18]. The nitrogen was determined by Dumas' method [18]. The carbon and hydrogen were determined by CHN analyzer and the data agree with calculated values.

3. Results and discussion

The complexes are light yellow and not soluble in common organic solvents, but soluble to a limited extent in DMF and DMSO. The insolubility of these complexes in nitrobenzene thwarted determination of their molecular weights by cryoscopic method. The analytical data (table 1) indicate that these complexes conform to 2 : 1 stoichiometry of the type $M_2L(NO_3)_7$. The molar conductivity measurements at 10^{-3} M in DMF indicate that these complexes are non-electrolytes in DMF.

3.1. *Infrared spectra*

The important IR frequencies which characterize the Schiff bases are discussed in the following text (table 2):

(1) These Schiff bases exist in thiol and thione form (figure 1) as they exhibit a broad medium band in the region 3160–3130 cm^{-1} and a broad band of weak intensity around 2400 cm^{-1} due to ν(NH) and ν(SH) vibrations, respectively.

Table 1. Elemental analysis and molar conductance (in DMF) of Th(IV) complexes of Schiff bases derived from 2,6-diformyl-4-methyl phenol and 3-substituted-4-amino-5-mercapto-1,2,4-triazole.

Ligand no.	Complex no.	Empirical formula	Found (Calcd) M%	N%	S%	Molar conductance ($Ohm^{-1} cm^2 mol^{-1}$)
I	**1**	$Th_2(C_{13}H_{11}N_8S_2O)(NO_3)_7$	36.82 (36.91)	16.61 (16.70)	5.12 (5.09)	31.4
II	**2**	$Th_2(C_{15}H_{15}N_8S_2O)(NO_3)_7$	36.15 (36.10)	16.38 (16.34)	4.91 (4.98)	33.5
III	**3**	$Th_2(C_{17}H_{19}N_8S_2O)(NO_3)_7$	35.28 (35.33)	15.89 (15.99)	4.79 (4.87)	37.6
IV	**4**	$Th_2(C_{19}H_{23}N_8S_2O)(NO_3)_7$	34.53 (34.60)	15.71 (15.65)	4.68 (4.77)	39.2

Table 2. Important infrared frequencies (in cm^{-1}) of Schiff bases derived from 2,6-diformyl-4-methyl phenol and 3-substituted-4-amino-5-mercapto-1,2,4-triazole along with their assignments.

Ligand no.	ν(NH)	ν(S)	ν(C=N)	ν(OH)	Thiamide +ν(C=C) I	Thiamide II	Thiamide III	Thiamide IV
I	3130brm	2401w	1782s	3389brm	1610s	1340s	1040s	720m
II	3157brm	2400w	1780s	3390brm	1605s	1341s	1040s	721m
III	3145brm	2399w	1779s	3392brm	1608s	1345s	1035s	723m
IV	3160brm	2389w	1781s	3391brm	1585s	1340s	1045s	720m

Table 3. Important infrared frequencies (in cm^{-1}) of Th(IV) complexes along with their assignments.

Complex no.	ν(C=N)	ν(C=S)	Th–O	Th–N
1	1646s	720w	450m	540m
2	1652s	721w	452m	535m
3	1648s	723w	455m	538m
4	1650s	720w	453m	542m

(2) A group of bands of varying intensity in the region 1605–1585 cm^{-1}, 1340 cm^{-1}, 1040 cm^{-1} and 721 cm^{-1} are assigned to thiamide – I, II, III and IV vibrations in free ligands as the ligands contain NCSH or NHCS groups.

(3) All these ligands exhibit bands around 1780 cm^{-1}, 3390 cm^{-1} and 1610–1585 cm^{-1} due to ν(C=N), ν(OH), C=N and C=C of the heterocyclic ring and aromatic vibrations, proof for the presence of 2,6-diformyl-4-methyl phenol moiety.

The important IR frequencies (table 3) which characterize the Th(IV) complexes are discussed in the following text:

(1) All complexes show a broad medium band in the region 3160–3130 cm^{-1} and weak medium intensity band at 2400 cm^{-1} due to ν(NH) and ν(SH) vibrations, indicating non involvement of SH in coordination.

(2) The band due to phenolic-OH at 3390 cm^{-1} in free ligand disappears in the spectra of the Th(IV) complexes, suggesting coordination of phenolic oxygen to the Th(IV) via deprotonation.

Table 4. ^{1}H NMR spectral data of Schiff bases I–IV.

Ligand no.	NH–C=S	SH	CH=N	Phenolic-OH	Aromatic protons	Alkyl protons
I	13.52	2.48	11.45	10.55	7.48–7.65	2.12
II	13.77	2.54	11.50	10.50	7.50–7.80	2.15
III	13.65	2.5	11.48	10.46	7.52–7.70	2.18
IV	13.74	2.52	11.46	10.52	7.54–7.75	2.20

(3) The strong band due to (C=N) around 1785 cm^{-1} in the free Schiff bases appears at 1650 cm^{-1} for the Th(IV) complexes, indicating coordination of azomethine to thorium through the nitrogen.

(4) The Th(IV) complexes exhibit a strong band in the region 1260–1240 cm^{-1}, attributed to coordinated nitrate [19].

(5) The band due to phenolic C–O at 1505 cm^{-1} in the Schiff bases can be used as a sensitive probe to estimate the monodentate and bridging bidentate nature of oxygens. In case of mononuclear complexes where oxygen is monodentate, the phenolic ν(C–O) band shifts to higher frequency about 10–15 cm^{-1}, whereas in bridging cases the shift is of the order of 35 cm^{-1}. In the present complexes the phenolic ν(C–O) band is at 1550 cm^{-1}, a shift of 45 cm^{-1}, suggesting that phenolic oxygen atoms are bidentate.

(6) In these Th(IV) complexes the ν(M–N) bands are assigned in the region 540–450 cm^{-1} [20].

3.2. *Magnetic data*

All these complexes are diamagnetic as expected.

3.3. *NMR spectra*

The NMR spectral data of all the Schiff bases is presented in table 4 and one representative ligand(II) and its Th(IV) complex are explained below:

(1) The ^{1}H NMR spectra of Schiff base(II) exhibited signals at 13.77 ppm due to NH–C=S protons. The characteristic resonance due to SH protons at 2.54 ppm indicates thiol-thione tautomerism. Another characteristic resonance due to the azomethine protons is at 11.5 ppm.

(2) We also observed a multiplet at 7.5–7.8 ppm due to aromatic protons. The ligand exhibits a signal at 10.50 ppm and 2.15 ppm due to phenolic OH proton and methyl protons, respectively. All these observations support the IR interpretation.

(3) The corresponding Th(IV) complex **2** exhibits resonance due to –SH proton at 2.49 ppm, unchanged for Th(IV) complexes, suggesting that the SH group has not taken part in coordination. There is a remarkable change in the position of resonance due to azomethine proton (CH=N) which appeared at 10.88 ppm in the Th(IV) complex relative to the corresponding ligand (10.18 ppm). This downfield shift indicates coordination of azomethine to the metal through nitrogen.

Table 5. Thermogravimetric data for Th(IV) complex of Schiff base derived from 2,6-diformyl-4-methyl phenol and 3-methyl-4-amino-5-mercapto-1,2,4-triazole.

Complex no.	Empirical formula	Decomposition temperature (°C)	% Weight loss		Inference
			Calcd	Obtd.	
2	$Th_2(C_{15}H_{15}N_8S_2O)(NO_3)_7$	215	19.92	19.72	Decomposition of triazole moieties
		215–475	10.19	10.98	Decomposition of 2,6-diformyl-4-methyl phenol moiety
		475–1000	30.11	29.21	Decomposition of ligand molecule

(4) The resonance due to aromatic protons is at 7.88 ppm. The signal due to –OH of the ligand (10.93 ppm) disappears, indicating complexation occurs via deprotonation. This supports IR inferences.

(5) The signal due to methyl proton at 3.32 ppm is unaffected in the Th(IV) complex. All these observations provide support for the IR data.

3.4. *FAB-mass spectra of Th(IV) complex*

The FAB-mass spectrum of ligand contains peak at *m*/*z* 389 corresponding to the molecular ion species $[LII+H]^+$. The FAB-mass spectrum of the complex shows the peak at *m*/*z* 1285 is corresponding to the molecular ion $[Th_2(LII)(NO_3)7]^+$. The intense peak at *m*/*z* 851 corresponding to the $[Th_2(LII)]^+$ due to removal of seven nitrate ions from the molecular ion of the complex. In the FAB-mass spectrum of complex **2** there is an intense peak at *m*/*z* 389 corresponding to the species $[LII+H]^+$. This indicates that the species $[Th_2(LII)]^+$ undergoes demetallation to give the diimine Schiff base ligand(II) under FAB conditions.

3.5. *Thermogravimetric analysis*

Thermal decomposition of **2** (table 5) has been studied as a function of temperature. In the TG curve, Th(IV) complex decomposes significantly up to 215°C and then gradually between 215–475°C and significant decomposition from 475–1000°C. Finally it shows no change with further increase in temperature. Decomposition of Th(IV) complex occurs with the triazole moieties, 2,6-diformyl-4-methyl phenol and ligand molecule. The final weight of metal oxide residue is almost equal to the calculated weight residue.

3.6. *Kinetic study*

The Freeman and Corrol procedure and equation [21] have been used to evaluate order of reaction and energy of activation from a single experimental curve (figure 2) from the plot of $(\Delta \log dw/dt)/(\Delta \log Wr)$ *vs.* $(\Delta T^{-1})/(\Delta \log Wr) \times 10^3\,K^{-1}$. The values of order of reaction and energy of activation are listed in table 6. The fraction values of order of reaction obtained may be due to the determination in nitrogen rather than in vacuum.

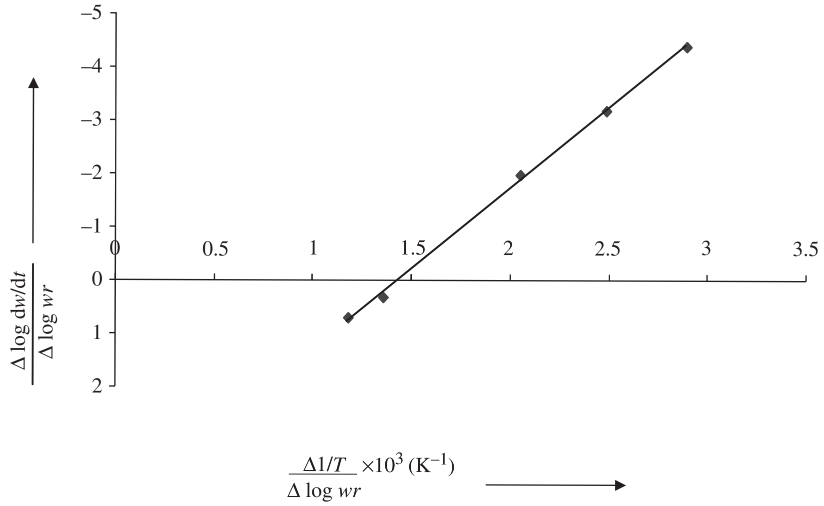


Figure 2. Kinetics of thermal decomposition studies of **2**.

Table 6. Kinetics of thermal decomposition studies of **2**.

Empirical formula	$\frac{\Delta \log dw/dt}{\Delta \log wr}$	$\frac{\Delta 1/T}{\Delta \log wr} \times 10^3\ K^{-1}$	Order of reaction	Energy of activation E_a (kcal mol^{-1})
$Th_2(C_{15}H_{15}N_8S_2O)(NO_3)_7$	−4.3949	2.891	1.35	13.97
	−3.1646	2.488		
	−1.9733	2.055		
	+0.7201	1.182		
	+0.3294	1.361		

3.7. *Study of solid state electrical conductivity*

The d.c. solid state electrical conductivity of **2** was measured in pellet form in the temperature range 32 to 245°C. Pellets were prepared as circular discs with the help of a hydraulic press by subjecting a small quantity of powder to a pressure of about $8\times10^6\,kg\,m^{-2}$. A thin layer of silver coating is made on the surface of the pellet with silver paste. The resistivity behavior of the complex was studied as a function of temperature using the standard probe method. The d.c. resistance of the sample was measured at different temperatures. The $10^3/T$ (K) and corresponding $\log\sigma$ values are listed in table 7. The plot of electrical conductivity *versus* temperature for $Th_2(C_{15}H_{15}N_8S_2O)(NO_3)_7$ is shown in figure 3. As the temperature increases there is a gradual decrease in d.c. resistivity. In the present complex, conductivity increases with increasing temperature indicating a semiconductor. Complex **2** shows semiconducting behavior in the temperature range 70 to 245°C.

The calculated activation energy may be attributed to interaction between electrons of the d-orbitals of the cation and π-orbitals of the ligand. This interaction localizes the π-electronic charge on the ligand [22].

Table 7. The $10^3/T$ (K) and corresponding $\log\sigma$ values (complex **2**).

$10^3/T$ (K)	$\log\sigma$	Activation energy E_a (eV)
1.930	−10.5301	
1.968	−10.7055	0.1024
2.008	−10.7851	
2.049	−10.8829	
2.092	−11.0151	
2.136	−11.1451	
2.183	−11.1870	
2.232	−11.2460	
2.283	−11.2800	
2.336	−11.2946	
2.392	−11.3020	
2.450	−11.3076	
2.512	−11.3241	
2.577	−11.3602	
2.645	−11.3842	
2.717	−11.4200	
2.793	−11.4402	
2.873	−11.4823	
2.915	−11.4856	

Diameter of the sample 1 cm. Thickness of the sample 0.129 cm.

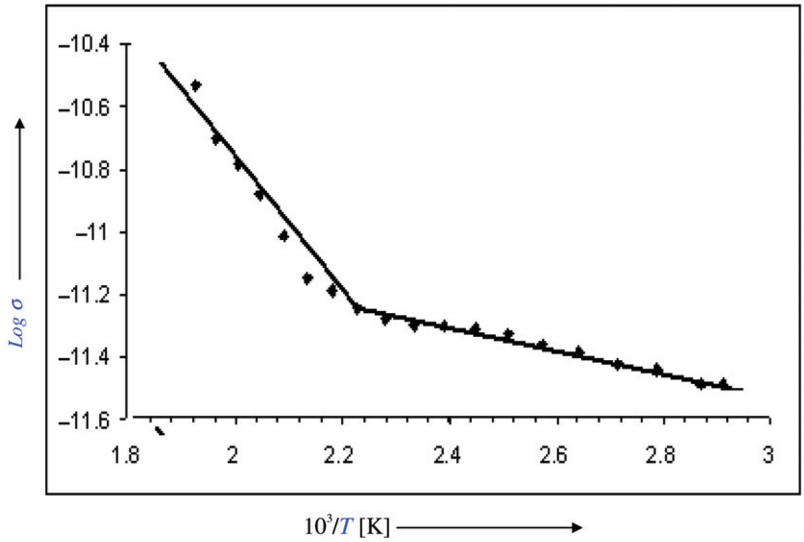


Figure 3. Electrical conductivity *vs.* temperature of **2**.

3.8. *Fluorescence studies*

3.8.1. Uv-visible absorption spectra of the Schiff base and its Th(IV) complex

3.8.1.1. Absorption spectrum of the Schiff base. The absorption spectrum of Schiff base(II) was measured in DMF, THF, MeCN and toluene (10^{-3} M) at room temperature as a function of time. The UV-vis spectral data are listed in table 8.

Table 8. UV-vis spectra of Schiff base and its Th(IV) complex in different solvents.

Compound no.	Solvents	Absorption (nm)
Ligand (II)	DMF	367, 508, 914, 1004
	DMF with NaOH	367, 508, 915, 1004
	THF	367, 909
	THF with NaOH	367, 463, 909
	MeCN	370, 894
	MeCN with NaOH	362, 457, 894
Complex **2**	DMF	254, 349, 805, 1010
	THF	348, 904
	MeCN	255, 350, 805, 1010
	Toluene	350, 877, 1010

UV-vis spectra show four bands in DMF at 367, 508, 914 and 1004 nm. The band at 508 nm is associated with the phenoxide ion in 2,6-diformyl-4-methyl phenol with 3-substituted-4-amino-5-mercapto-1,2,4-triazole. UV-vis spectra in DMF and THF show no changes as a function of time, indicating stability of the Schiff base in DMF and THF, whereas in MeCN and toluene there is a small change as a function of time suggesting less stability. The absence of the 508 nm band THF and MeCN shows the absence of phenoxide ion. However, addition of 0.2% NaOH to the Schiff base in THF and MeCN gives a band around 463 nm, due to phenoxide.

3.8.1.2. Absorption spectra of Th(IV) complex. Absorption spectral data of **2** is reported in table 8. The complex is relatively stable in DMF and THF as a function of time. The absorption band of phenoxide around 508 nm completely disappears due to metal ligand interaction.

3.8.2. Fluorescence emission spectra. In previous studies, transition metal ions decrease the fluorescence quite effectively [23–25]; several distinct processes viz., the magnetic perturbations, redox activity, electronic energy transfer, etc., have been invoked [24] to rationalize fluorescence quenching by transition metal ions. Fluorescence spectral studies of Schiff base and its Th(IV) complex were done in DMF, THF, MeCN and toluene as a function of time, and the emission spectral data are listed in table 9.

3.8.3. Fluorescence spectra of the Schiff base. The Schiff base is characterized by an emission band around 565 nm with intensity of 213 in DMF due to phenoxide anion. This is supported by formation of a 524 nm emission band in 2,6-diformyl-4-methyl phenol in DMF attributed to formation of the phenoxide anion. The emission band around 565 nm is absent in other solvents (THF, MeCN and toluene), but this band was observed around 535 nm in these solvents on addition of 0.2% NaOH solution.

The emission spectra of Schiff base in THF, MeCN and toluene display two bands after three days at 337 and 434, 348 and 415 and 337 and 437 nm, respectively. The addition of 0.2% NaOH solution decreases the intensity of the emission bands at 434 nm band in THF, 415 nm in MeCN and 437 nm in toluene, and simultaneously a new band is formed around 537, 530 and 538 nm, respectively. The changes in these

Table 9. Emission spectra of Schiff base and its Th(IV) complex in different solvents.

Compound no.	Solvents	Excitation (nm)	Emission bands (nm)
Ligand (II)	DMF	505	565
	DMF with NaOH	505	546
	THF	312	337, 434
	THF with NaOH	312	357, 537
	MeCN	296	348, 415
	MeCN with NaOH	296	345, 530
	Toluene	300	337, 437
	Toluene with NaOH	300	341, 538
Complex **2**	DMF	368	401, 462
	DMF with NaOH	360	488
	THF	360	402, 467
	THF with NaOH	360	347, 413
	MeCN	360	404, 467
	MeCN with NaOH	360	404, 497
	Toluene	360	464
	Toluene with NaOH	360	527

spectra are due to changes in the dielectric properties of the solvent in the excited state. In the excited state ($n\pi^*$), a localized positive charge is created on the oxygen [26] making the proton easily available. Thus, the bands at 537, 530 and 538 nm may be attributed to this partially ionized species or phenolate ion of Schiff base.

3.8.4. Fluorescence spectra of Th(IV) complex.

The emission spectrum of the Th(IV) complex was measured in DMF, THF, MeCN and toluene as a function of time. There is a small change in emission due to the dielectric constant of the different solvents. The emission was quenched in the complex due to strong bonding interaction between the metal and the ligand. The emission band at 460 nm was observed in all solvents, indicating metal to ligand charge transfer (LMCT) in the Th(IV) complex. The strong emission band around 535 nm in all the solvents for the ligand is absent in the Th(IV) complex due to metal binding to oxygen of phenoxide. The interaction of Schiff base with alkali leads to the formation of various types of complexes in the excited state, depending upon the nature of solvents.

4. Conclusion

Analytical, IR, ^{1}H NMR, FAB-mass spectra and TG/DTA data taken together show that complexes have stoichiometry M_2 L $(NO_3)_7$, in which Th(IV) exhibits coordination number of six [27–36]. Schiff base(II) and its Th(IV) complex **2** show fluorescence properties. The disappearance of the emission band due to Schiff base in **2** confirms coordination of the phenolic oxygen to the Th(IV). The thermal conductivity measurement studies made on the Th(IV) complex indicate semiconducting behavior in the temperature range 70 to 245°C. All these observations put together lead us to propose the structure (figure 4).

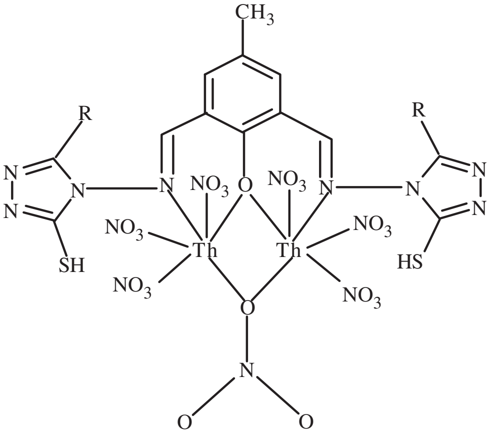


Figure 4. Six-coordinated Th(IV) complexes.

Acknowledgement

One of the authors (B. Nagaraja Reddy) is grateful to the University Grants Commission, southwestern regional office, Bangalore for the award of teacher fellowship under F.I.P Xth plan.

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