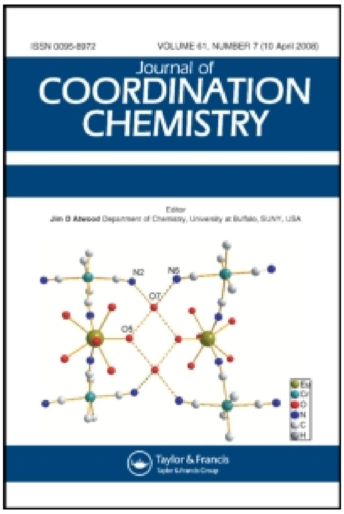

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, spectral, thermal, solid state d.c. electrical conductivity, fluorescence and biological studies of lanthanum(III) and thorium(IV) complexes of 24-membered macrocyclic triazoles

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To cite this Article Avaji, Prakash Gouda and Patil, Sangamesh Amarappa(2008) 'Synthesis, spectral, thermal, solid state d.c. electrical conductivity, fluorescence and biological studies of lanthanum(III) and thorium(IV) complexes of 24-membered macrocyclic triazoles', Journal of Coordination Chemistry, 61: 16, 2570 — 2583

To link to this Article: DOI: 10.1080/00958970801948064

URL: http://dx.doi.org/10.1080/00958970801948064

Journal of Coordination Chemistry
Vol. 61, No. 16, 20 August 2008, 2570–2583

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Synthesis, spectral, thermal, solid state d.c. electrical conductivity, fluorescence and biological studies of lanthanum(III) and thorium(IV) complexes of 24-membered macrocyclic triazoles

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(*Received 15 July 2007; in final form 18 October 2007*)

A series of La(III) and Th(IV) complexes have been synthesized by template condensation of 2,6-diformyl-4-methylphenol, *bis*-(4-amino-5-mercapto-1,2,4-triazol-3-yl)alkanes and $La(NO_3)_3 \cdot 6H_2O/Th(NO_3)_4 \cdot 5H_2O$ in 2 : 2 : 1 molar ratio in ethanol. These complexes were characterized by elemental analyses, magnetic susceptibility, molar conductance, spectral (IR, UV–Vis, ^{1}H-NMR, FAB-mass), thermal, fluorescence and solid state d.c. electrical conductivity studies. The complexes are insoluble in water but soluble in DMF and DMSO. The observed molar conductance values indicate non electrolytes. Elemental analyses suggest 1 : 1 stoichiometry, $[La(L^{I-IV})(NO_3)(H_2O)_2] \cdot 3H_2O$ and $[Th(L^{I-IV})(NO_3)_2(H_2O)_2] \cdot 3H_2O$. Spectroscopic studies indicate that coordination occurs through phenolic oxygen after deprotonation, nitrogen of azomethine group and bridging bidentate nitrates. The solid state d.c. electrical conductivity indicates semiconducting nature. All the Schiff bases and their La(III) and Th(IV) complexes were evaluated for biological properties; some compounds show promising results.

Keywords: Synthesis; Biological; Complex; Macrocyclic; *Bis* triazole

1. Introduction

Macrocyclic ligands with lanthanides have applications as contrast agents for magnetic resonance imaging [1], catalysts for specific cleavage of RNA [2], stains for fluorescence imaging [3] and cancer radiotherapy [4]. Thus, there has been continued interest in design of new macrocyclic ligands having various industrial applications [5, 6].

Attempts have been made to obtain La(III) complexes with chiral 3 + 3 macrocycles derived from (1R, 2R)-1,2-diaminocyclohexane and 2,6-diformyl-4-methylphenol [7], tetraiminodiphenol macrocycle in the solid state and in solution [8], 20-membered hexaaza macrocyclic Schiff bases [9] and very recently Th(IV) complexes with Schiff bases derived from semicarbazones and diphenyl sulfoxide [10]. These La(III) and

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970801948064

Th(IV) complexes are characterized by elemental, spectral, thermal and X-ray crystallographic studies.

No one has reported synthesis of La(III) and Th(IV) complexes with Schiff bases derived from 2 + 2 condensation of 2,6-iformyl-4-methylphenol and *bis*-(4-amino-5-mercapto-1,2,4-triazol-3-yl)alkanes which have NON NON donor sites and varied coordinating abilities. Such ligands aroused our interest in elucidating the structure of La(III) and Th(IV) complexes.

Solid state d.c. electrical conductivities of La(III) and Th(IV) complexes of the Schiff bases have been investigated from room temperature to 250°C and indicate that the complexes are semiconductors. The fluorescence properties of the Schiff bases and their La(III) and Th(IV) complexes have been investigated in DMF, DMSO, THF and MeCN.

In this article, we report the synthesis, spectral, thermal, solid state d.c. electrical conductivities, fluorescence and biological studies of La(III) and Th(IV) complexes with the Schiff bases shown in figure 1.

2. Experimental

All chemicals used were of reagent grade. Solvents were distilled and dried before use according to the standard procedure [11]. 2,6-Diformyl-4-methylphenol was prepared by known method [12, 13]. The lanthanum of the complexes was analyzed by volumetric method using EDTA solution [14]. The thorium was determined by a gravimetrically as ThO_2 [14]. Carbon, hydrogen, nitrogen and sulphur were estimated by using C, H, N and S analyzer. The results of elemental analyses and molar conductance values are listed in tables 1 and 2.

2.1. *Physical measurements*

The IR spectra of the ligands and their La(III) and Th(IV) complexes were recorded on a HITACHI-270 IR spectrophotometer in the 4000–350 cm^{-1} region in KBr disks. The electronic spectra of the complexes were recorded in DMF on a VARIAN CARY 50-BIO UV-spectrophotometer in the region of 200–1100 nm. The proton NMR spectra of ligands and complexes were recorded in DMSO-d_6 on a BRUKER 300 MHz spectrometer at room temperature using TMS (Me_4Si) as an internal reference. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon (6 KV, 10Am) 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. Thermogravimetric analysis data were measured from room temperature to 1000°C at a heating rate of 10°C min^{-1}. The data were obtained by using a PERKIN–ELMER DIAMOND TG/DTG instrument. Solid state DC electrical conductivity of solid complexes was measured using a digital micro voltmeter model DMV-001. Molar conductivity measurements were recorded on an ELICO-CM-82 T conductivity bridge with a cell having cell constant 0.51; magnetic moments were determined on a Faraday balance.

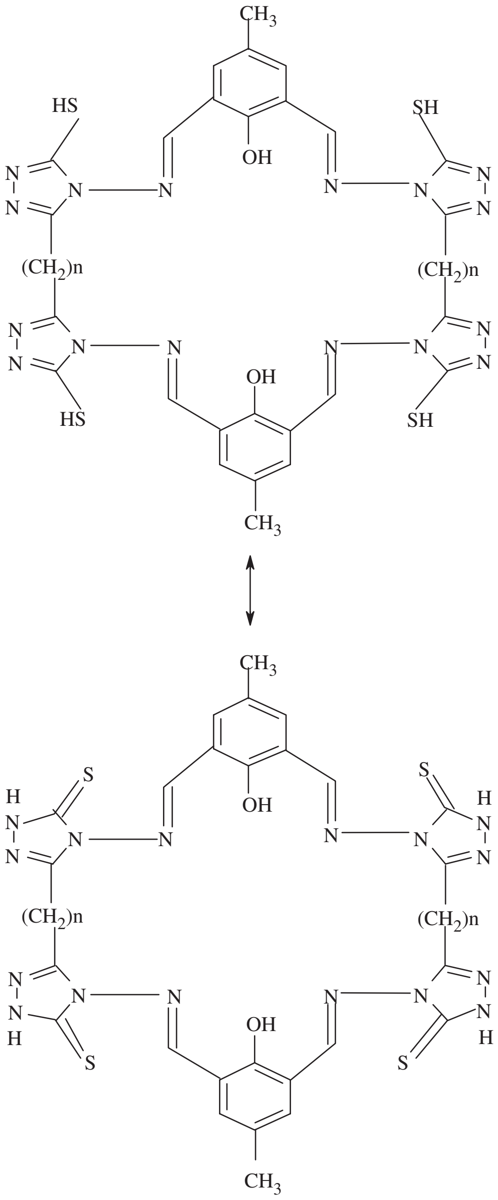


Figure 1. Structure of Schiff bases in thiol-thione tautomeric forms.

2.2. *Synthesis of bis-(4-amino-5-mercapto-1,2,4-triazol-3-yl)alkanes*

Thiocarbohydrazide (0.02 mol) was treated with 0.01 mol of dicarboxylic acid (malonic, succinic, adipic and glutaric acids) in 4N HCl. The reaction mixture was refluxed for 6 h and set aside overnight to cool. The bistriazole was precipitated by treatment of the reaction mixture with ammonia. The solid was filtered, washed with water and recrystallized from ethanol. Purities of the samples were verified by elemental analyses (scheme 1).

2.3. *Synthesis of macrocyclic ligands (H_2L^I–H_2L^{IV})*

2,6-diformyl-4-methylphenol (2 mmol) in ethanol (20 mL) was added to an ethanol solution of *bis*-(4-amino-5-mercapto-1,2,4-triazol-3-yl)alkanes (2 mmol, 30 mL) containing a few drops of concentrated HCl. The reaction mixture was refluxed for 3 h. The mixture was cooled to room temperature and the solvent removed under reduced pressure until a solid formed that was washed with cold ethanol and dried under vacuum. m.p. 235–230°C, yield (70–75%), analytical data listed in table 1.

2.4. *Synthesis of La(III) (1–4) and Th(IV) (5–8) complexes*

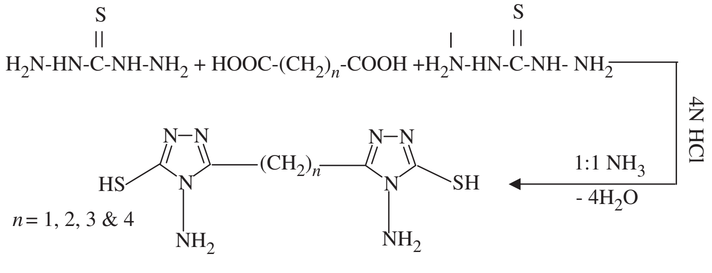
La(III) (**1**–**4**) and Th(IV) (**5**–**8**) complexes of H_2L^I–H_2L^{IV} were prepared adapting the template method to the insolubility of the ligands in common organic solvents.

Table 1. Analytical data of H_2L^I–H_2L^{IV}.

Comp. No.	Empirical formula	C% Obsd.	C% Calcd	H% Obsd.	H% Calcd	N% Obsd.	N% Calcd	S% Obsd.	S% Calcd	%Yield	m.p. (°C)
H_2L^I	($C_{28}H_{24}N_{16}S_4O_2$)	44.32	44.37	3.12	3.16	29.48	29.55	16.79	16.88	60	240
H_2L^{II}	($C_{30}H_{28}N_{16}S_4O_2$)	46.56	46.63	3.58	3.60	29.10	29.01	16.52	16.58	60	245
H_2L^{III}	($C_{32}H_{32}N_{16}S_4O_2$)	48.78	48.85	4.10	4.07	28.44	28.49	16.22	16.28	65	233
H_2L^{IV}	($C_{34}H_{36}N_{16}S_4O_2$)	51.06	51.00	4.46	4.50	28.04	28.00	16.06	16.00	65	235

Table 2. Elemental analyses of La(III) and Th(IV) complexes and their molar conductance data.

Comp. No.	Empirical formula	M% Obsd.	M% Calcd	N% Obsd.	N% Calcd	S% Obsd.	S% Calcd	Molar conductance λ_m ($cm^2\ \Omega^{-1} mol^{-1}$)
1	$[La(L^I)(NO_3)(H_2O)_2] \cdot 3H_2O$	13.25	13.27	25.35	25.12	12.25	12.22	21.22
2	$[La(L^{II})\ (NO_3)(H_2O)_2] \cdot 3H_2O$	13.05	13.10	23.15	23.24	12.01	12.06	23.24
3	$[La(L^{III})\ (NO_3)(H_2O)_2] \cdot 3H_2O$	12.89	12.93	24.45	24.32	11.86	11.90	21.32
4	$[La(L^{IV})\ (NO_3)(H_2O)_2] \cdot 3H_2O$	12.72	12.76	25.11	25.01	11.71	11.75	25.01
5	$[Th(L^I)(NO_3)_2(H_2O)_2] \cdot 3H_2O$	19.24	19.30	28.58	28.46	10.58	10.64	20.46
6	$[Th(L^{II})(NO_3)_2(H_2O)_2] \cdot 3H_2O$	19.10	19.07	26.21	26.13	10.46	10.52	20.12
7	$[Th(L^{III})(NO_3)_2(H_2O)_2] \cdot 3H_2O$	18.83	18.86	25.42	25.32	10.38	10.40	22.42
8	$[Th(L^{IV})(NO_3)_2(H_2O)_2] \cdot 3H_2O$	18.61	18.64	24.38	24.45	10.21	10.28	24.45



Scheme 1. Synthesis of *bis*-(4-amino-5-mercapto-1,2,4-triazol-3-yl)alkanes.

2,6-Diformyl-4-methylphenol (2 mmol), *bis*-(4-amino-5-mercapto-1,2,4-triazol-3-yl)alkanes (2 mmol) and the respective metal nitrates (2 mmol) in super dry alcohol were refluxed for 2–3 h. The separated complexes were collected by filtration, washed with hot ethanol and dried in vacuum desiccators over P_2O_5 (yield 60–70%).

3. Results and discussion

All the La(III) and Th(IV) complexes are colored, non-hygroscopic solids and stable in air. The complexes are soluble in DMF and DMSO. Elemental analyses show 1 : 1 stoichiometry; molar conductance values at 10^{-3} M in DMF are too low for any dissociation and the La(III) and Th(IV) complexes are non-electrolytes. In order to establish whether water molecules present in the complexes coordinate to the metal, weighed complexes were dried over P_2O_5 in a vacuum for 1 h and then weighed again with no loss in weight, suggesting the water molecules are coordinated to the metal. All the complexes are diamagnetic.

3.1. *IR spectra*

Important IR frequencies of the Schiff bases and their La(III) and Th(IV) complexes are presented in tables 3 and 4.

The Schiff bases have tautomeric thiol and thione forms. A medium band at 3150 cm^{-1} due to ν(NH) indicates the thione form, while a weak broad band centered at 2400 cm^{-1} due to ν(SH) is suggestive of the thiol form. These observations confirm the thiol-thione tautomerism.

Table 3. The important infrared frequencies (in cm^{-1}) of H_2L^I–H_2L^{IV}.

Ligand No.	ν(NH)	ν(SH)	ν(C=N)	H-bonded-OH	ν_{CH3}	Phenolic C–O	Thiamide I	Thiamide II	Thiamide III	Thiamide IV
H_2L^I	3150	2395	1625	2750	2935	1290	1605	1320	1040	746
H_2L^{II}	3156	2400	1622	2745	2930	1285	1610	1315	1045	750
H_2L^{III}	3142	2385	1630	2720	2938	1295	1595	1317	1038	740
H_2L^{IV}	3145	2390	1628	2736	2928	1288	1592	1318	1036	747

Table 4. Important infrared frequencies (in cm^{-1}) of La(III) and Th(IV) complexes.

Complex No.	ν(OH)	ν(C=N)	ν(NH)	ν(SH)	ν_{CH3}	Phenolic C–O	ν(M–N)	ν(M–O)	ν(N=O) ν_1	$\nu_{asym}(NO_2)$ ν_5	$\nu_{sym}(NO_2)$ ν_2
1	3240	1605	3144	2362	2927	1370	550	490	1450	1320	1028
2	3250	1608	3146	2351	2926	1380	545	485	1460	1336	1030
3	3246	1605	3142	2364	2932	1375	546	488	1465	1335	1024
4	3248	1603	3143	2350	2922	1378	548	485	1455	1340	1030
5	3242	1600	3142	2348	2918	1376	550	490	1462	1334	1026
6	3250	1604	3150	2355	2920	1380	544	490	1470	1340	1030
7	3244	1607	3144	2362	2925	1374	550	486	1468	1338	1024
8	3250	1609	3150	2353	2924	1380	546	490	1470	1340	1030

A medium to high intensity band around 1620 cm^{-1} was assigned to ν(C=N) confirming the presence of 2,6-diformyl-4-methyl phenol. The NCSH and NHCS groups have thiamide vibrations around 1320 cm^{-1} due to the thiamide-II vibrations, thiamide-III vibrations at 1045–1040 cm^{-1} and triamide-IV bands (mainly from ν(C=S)) located at 750 cm^{-1}.

In addition to the above IR absorptions, a broad weak band with fine structure in the region 2750–2720 cm^{-1} can be attributed to intramolecular H-bonded-OH. Medium intensity bands in the 1600–1575 cm^{-1} region are regarded as a combination of C=N of triazole ring and aromatic C=C stretching vibrations. A high intensity band at 1295–1285 cm^{-1} with an additional band around 1500 cm^{-1} was assigned to the phenolic ν(C=O) vibrations.

In the complexes we observed the following changes: (1) The characteristic band due to ν(C=N) appears around 1600 cm^{-1}, suggesting that the C=N group is coordinated to the metal through nitrogen. The bands due to ν(C=N) of the heterocyclic ring for the complexes appears almost in the same region as observed in the ligands [15]. (2) The high intensity band due to phenolic C–O in the region 1295–1285 cm^{-1} in the Schiff bases is a medium to high intensity band in the 1370–1380 cm^{-1} region in the complexes, supporting formation of M–O bands via deprotonation [16]. (3) A broad band of medium intensity at 3400–3300 cm^{-1} is due to the symmetric and antisymmetric O–H stretching vibrations of lattice water [17]. Those at 3250 and 840 cm^{-1} are characteristic of coordinated water [18]. The medium intensity band in the region around 490 cm^{-1} is characteristic of ν(M–O) vibration of the phenolic oxygen and the coordinated water molecules [19] and a band at 550 cm^{-1} is due to ν(M–N) [20]. (4) The infrared spectra of the nitrato complexes contain bands characteristic of both coordinated and ionic nitrates. The bands at 1470 cm^{-1} and around 1340 cm^{-1} are due to the ν(N=O)(ν_1) and ν_{asym} (NO$_2$) (ν_5), respectively, of coordinated nitrate. The ν_{sym} (NO$_2$) vibration (ν_2) at 1030 cm^{-1} is characteristic of bidentate chelating nitrate. The separation ($\Delta\nu$) of the nitrate stretching fundamentals (ν_1–ν_5) has been used as a criterion to distinguish between mono- and bidentate chelating nitrates [21], increasing as the coordination changes from mono- to bidentate and bridging. The magnitude of this separation ($\Delta\nu = 130$) indicates bidentate coordination. (5) All La(III) and Th(IV) complexes exhibited broad medium intensity bands around 3140 cm^{-1} and a weak band around 2350 cm^{-1} due to ν(NH) and ν(SH) vibrations. The band due to ν(C=S) at 750 cm^{-1} for ligands is unperturbed in the complexes indicating that sulphur does not coordinate.

3.2. ^{1}H-NMR spectra

The ^{1}H-NMR spectra of all Schiff bases exhibited signals at 13.6 and 13.5 ppm due to –NH protons. The resonance due to SH of all the compounds appeared at 3.5 ppm indicating thiol-thione tautomerism. The azomethine protons in all the compounds appear at 8.92 ppm. Multiplets at 7.5–7.8 ppm are due to aromatic protons. The Schiff bases exhibit a signal at 10.50 ppm due to phenolic OH proton and a signal at 2.5 ppm due to methyl protons.

The following changes are observed for La(III) and Th(IV) complexes: (1) The signal due to azomethine (8.92 ppm) shows a downfield shift to 9.28 ppm indicating coordination of azomethine to the metal. (2) The resonance due to phenolic –OH at

10.50 ppm disappears in the spectrum of complexes confirming deprotonation and coordination. (3) The signal due to coordinated water protons in the complexes appears at 5.5 ppm.

The signals at 3.5 ppm due to SH proton are unaffected in the metal complexes, indicating the sulfur is not coordinated. The signal due to NH proton around 13.60 ppm, the aromatic protons at 7.5–7.8 ppm and the methyl protons at 2.5 ppm are unaffected in the metal complexes.

3.3. *Electronic absorption spectra*

The electronic absorption spectra of the complexes for freshly prepared solutions in DMF, DMSO, THF and MeCN at room temperature show a broad band around 31000 cm^{-1} assigned to $\mathrm{L} \rightarrow \mathrm{M}$ charge transfer transition.

3.4. *FAB mass spectral studies of Schiff base (H_2L^{II}) and its La(III) (2) and Th(IV) (6) complexes*

The FAB spectrum of H_2L^{II} (Supplementary Data) shows a molecular ion peak at *m*/*z* 773 equivalent to its molecular weight. Fragmentation leads to $[C_{30}H_{28}N_{16}O_2S_4]^+$. The FAB mass spectrum of **2** (Supplementary data) contains the molecular ion peak M^+ at *m*/*z* 1048 equivalent to its molecular weight. This molecular ion undergoes fragmentation with loss of five water molecules, giving $[La(L^{II})(NO_3)_2]^+$ at *m*/*z* 972. Further fragmentation by loss of one nitrate gave a fragment at *m*/*z* 910. Finally dematallation forms $[L^{II}+H]^+$ at *m*/*z* 772.

The Th(IV) (**6**) complex shows a molecular ion at *m*/*z* 1217 from $[Th(L^{II})(NO_3)_2(H_2O)_2] \cdot 3H_2O$. Loss of five water molecules gives $[Th(L^{II})(NO_3)_2]^+$ at *m*/*z* 1127; further loss of two nitrates gives $[Th(L^{II})]^+$ at *m*/*z* 1003. Finally, it undergoes dematallation to form the species $[L^{II}+H]^+$ giving a fragment ion at *m*/*z* 772. In **2** and **6** the metal ion is bonded to two phenoxides which endogenously coordinated to the metal ion; the other coordinating sites in the ligand are the azomethine nitrogens.

3.5. *Thermogravimetric analyses*

TGA and DTG studies for **2** and **6** show gradual decomposition with formation of respective metal oxide above 600°C (Supplementary Data). The proposed chemical changes with temperature are presented in table 5.

3.6. *Kinetic study*

The Freeman and Corroll procedure [22] was used to evaluate order of reaction and energy of activation (Supplementary Data) from the plot of $((\Delta \log \mathrm{d}w/\mathrm{d}t)/(\Delta \log Wr))$ *versus* $(\Delta T^{-1}/\Delta \log Wr) \times 10^3\ \mathrm{K}^{-1}$. In order to determine the thermal stabilities, the parameters T_o (temperature of onset of decomposition), T_{10} (temperature for 10% weight loss), $T_{\max}$ (temperature of maximum weight loss), activation energy and order of reaction, were evaluated; the determined order of reaction and energy of activation are listed in table 5.

Table 5. Thermogravimetric data of **2** and **6**.

		% Weight loss				
Empirical formula	Decomposition temperature (°C)	Obsd.	Calcd	Inference	Order of reaction	Energy of activation
$[La(L^{II})(NO_3)(H_2O)_2] \cdot 3H_2O$	225–230	3.38	3.38	Loss of coordinated water molecules	0.98	13.46
	260–300	47.82	47.83	Loss of *bis* triazole moieties		
	410–500	24.66	24.67	Loss of aldehyde moieties		
$[Th(L^{II})(NO_3)_2(H_2O)_2] \cdot 3H_2O$	225–230	2.95	2.96	Loss of coordinated water molecules	0.78	20.47
	260–300	41.76	41.77	Loss of one *bis* triazole moieties		
	410–500	21.55	21.54	Loss of one aldehyde moieties		

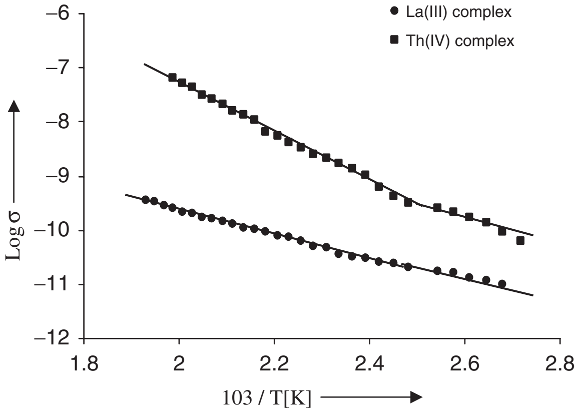


Figure 2. Electrical conductivity *vs* temperature of **2** and **6**.

In **6** the activation energy (E_a) was higher than for **2**, indicating that **6** is more thermally stable.

3.7. *Solid state d.c. electrical conductivity studies of La(III) (2) and Th(IV) (6) complexes*

The d.c. electrical conductivity of **2** and **6** were measured in pellets coated with silver paste from 30 to 230°C. The pellet was dried at 100°C for 24 h in air, and then the sample was allowed to cool slowly to room temperature. Resistive behavior of these samples was studied as a function of temperature using the standard probe method.

Typical plot of electrical conductivity ($\log \sigma$) *versus* temperature (T^{-1}) for the above said complexes are shown in figure 2. As the temperature increases there is a gradual decrease in d.c. resistivity. The value of electrical conductivity and activation energy (E_a) is listed in table 6. In these two complexes, the conductivity increases with increase in temperature, indicating that these complexes are semiconductors.

Table 6. Electrical conductivity measurements of **2** and **6**.

Comp. No.	Empirical formula	Electrical conductivity σ (*T*) $\Omega\,cm^{-1} \times 10^{-8}$ (at 100°C)	Activation energy E_a (eV) (at 100°C)
2	$[La(L^{II})(NO_3)(H_2O)_2] \cdot 3H_2O$	0.58	15.246
6	$Th(L^{II})(NO_3)_2(H_2O)_2] \cdot 3H_2O$	0.36	19.820

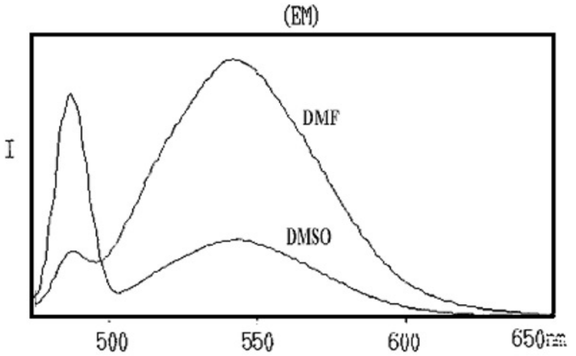


Figure 3. Emission spectrum of Schiff base (H_2L^{II}) in DMF and DMSO. Compounds/Antibiotics.

The increase in conductivity can be explained on the basis of clustering of ions, which effectively lower the concentration of stable bands and conduction will be due to the hopping process. The calculated activation energy may be attributed to interaction between the electrons of d-orbitals of a cation and the π-orbitals of the ligand. Thus, interaction localizes the π-electronic charge on the ligand. The observed conductivity data clearly show that the unpaired electron(s) present in the complexes are not participating in the conduction pathways and also rule out the possibility of partial oxidation of these complexes.

3.8. *Fluorescence studies*

The emission spectra of Schiff base (H_2L^{II}) and its La(III) (**2**) and Th(IV) (**6**) complexes were investigated in various solvents *viz*., DMF, DMSO, THF and MeCN.

3.8.1. Absorption and emission spectra of Schiff base (H_2L^{II}). The Schiff base (H_2L^{II}) has a weak absorption band at 440 nm (Supplementary Data) due to 2,6-diformyl-4-methyl-phenolate [23]. The emission of the Schiff base was observed around 545 nm (figure 3) in DMF and DMSO, due to formation of phenoxide anion and cleavage of the imine bond [24]. Upon addition of aqueous alkali (2% NaOH) to the above solutions we observed the λ_{max} of the Schiff base undergoes a blue shift in DMF/DMSO solutions (Supplementary Data) due to hydrogen bond formation.

3.8.2. Absorption and emission spectra of 2 and 6. The complexes exhibit an intense broad absorption in the near UV about 370 nm and a weak absorption in the blue

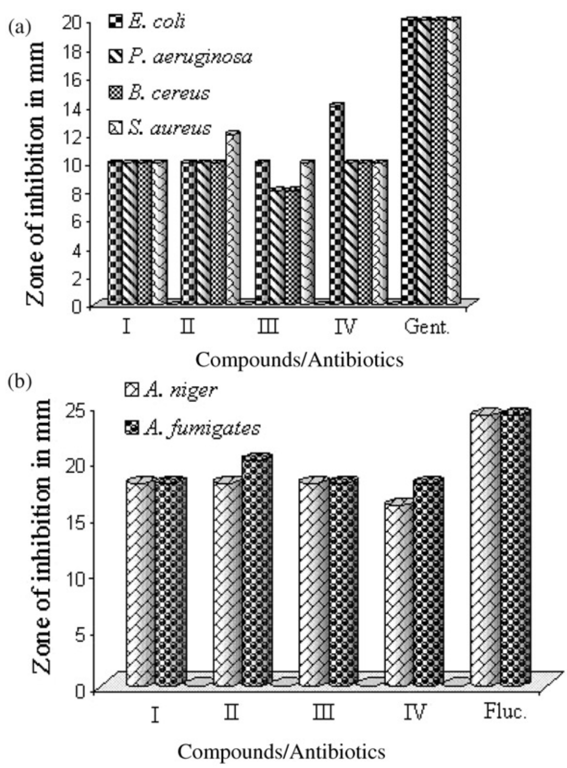


Figure 4. (a) *In vitro* antibacterial spectrum of compounds (H_2L^I–H_2L^{IV} and Gentamycine). (b) *In vitro* antifungal spectrum of compounds (H_2L^I–H_2L^{IV} and Fluconazole).

region about 450 nm. The absorptions are almost certainly associated with the Schiff base portion of the macrocyclic ligand and are also observed for macrocyclic chromophores [25] in metal complexes. A strong absorption at 370 nm is typical of imine-phenolates [26].

Complexes **2** and **6** have an emission band around 530 and 540 nm in DMF and DMSO, respectively, (Supplementary Data) red shifted due to interaction of phenolic oxygen with the metal ion. Fluorescence enhancement is unusual [27] since in previous studies transition metal ions decrease the fluorescence quite effectively [28, 29]. Magnetic perturbations, redox activity, *etc.* have been invoked [29] to rationalize fluorescence quenching by transition metal ions. In the present case, obviously none of these processes are operational.

3.9. *Biological study*

Antibacterial and antifungal activities of H_2L^I–H_2L^{IV} and their metal complexes have been studied by agar diffusion [30, 31]. The antibacterial activities were done by using two Gram-positive organisms (*Staphylococcus aureus* and *Bacillus cerius*) and two Gram-negative organisms (*Pseudomonas aeruginosa* and *Escherichia coli*). *Aspergillus niger* and *Aspergillus fumigates* were used for antifungal activities

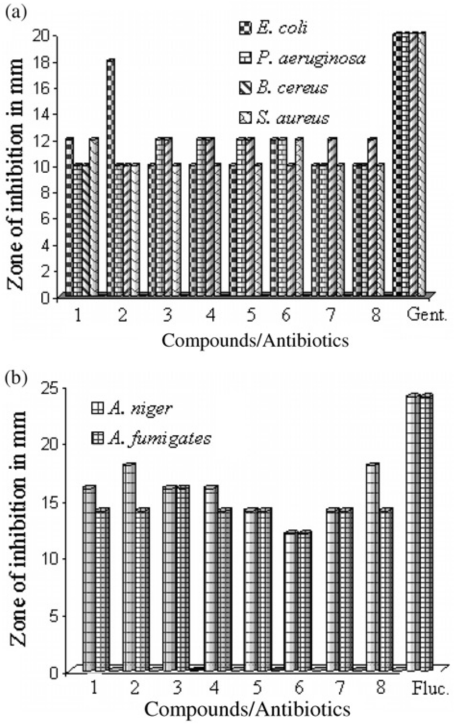


Figure 5. (a) *In vitro* antibacterial spectrum of La(III) and Th(IV) complexes (**1**–**8** and Gentamycine); (b) *In vitro* antifungal spectrum of La(III) and Th(IV) complexes (**1**–**8** and Fluconazole).

at 10 µg mL^{-1} concentrations in DMF used as control. The bacteria were subcultured in agar medium. The petri dishes were incubated for 24 h at 37°C. Standard antibacterial drug (Gentamycine) was also screened under similar conditions for comparison. The fungi were subcultured in potato dextrose agar. Standard antifungal drug (Fluconazole) was used for comparison. The petri dishes were incubated for 48 h at 37°C.

3.10. *In vitro antibacterial and antifungal assay of H_2L^I–H_2L^{IV} and their La(III) and Th(IV) complexes*

The microbial results of antibacterial and antifungal activities obtained are systematized in figures 4(a)–(b) and 5(a)–(b) and table 7. In bacteriological studies H_2L^{II} and H_2L^{IV} show moderate activity towards *E. coli*; the remaining Schiff bases were inactive towards *E. coli*, *P. aeruginosa*, *B. cereus* and *S. aureus*; **2** is highly active towards *B. cereus*.

In antifungal activity H_2L^I–H_2L^{IV} show high activity against *A. niger* and *A. fumigates*. Complexes **2**, **4** and **8** are highly active against *A. niger*; the remaining complexes have moderative or weak activity against *A. niger* and *A. fumigates*.

Table 7. Bacteriological results of Schiff bases and their La(III) and Th(IV) complexes.

Comp.	Empirical	Activity against bacteria (mm)				Activity against fungi (mm)	
No.	formula	*E. coli*	*P. aeruginosa*	*B. cereus*	*S. aureus*	*A. niger*	*A. fumigates*
H_2L^I	$(C_{28}H_{24}N_{16}S_4O_2)$	10	10	10	10	18	18
H_2L^{II}	$(C_{30}H_{28}N_{16}S_4O_2)$	14	10	10	12	18	20
H_2L^{III}	$(C_{32}H_{32}N_{16}S_4O_2)$	10	08	08	10	18	18
H_2L^{IV}	$(C_{34}H_{36}N_{16}S_4O_2)$	14	10	10	10	16	18
1	$[La(L^I)(NO_3)(H_2O)_2]\cdot 3H_2O$	12	10	10	12	16	14
2	$[La(L^{II})(NO_3)(H_2O)_2]\cdot 3H_2O$	18	10	10	10	18	14
3	$[La(L^{III})(NO_3)(H_2O)_2]\cdot 3H_2O$	10	12	12	10	16	16
4	$[La(L^{IV})(NO_3)(H_2O)_2]\cdot 3H_2O$	10	12	12	10	16	14
5	$[Th(L^I)(NO_3)_2(H_2O)_2]\cdot 3H_2O$	10	12	12	10	14	14
6	$[Th(L^{II})(NO_3)_2(H_2O)_2]\cdot 3H_2O$	12	12	10	12	12	12
7	$[Th(L^{III})(NO_3)_2(H_2O)_2]\cdot 3H_2O$	10	10	12	10	14	14
8	$[Th(L^{IV})(NO_3)_2(H_2O)_2]\cdot 3H_2O$	10	10	12	10	18	14
	Gentamycine	20	20	20	20	–	–
	Flucanazole	–	–	–	–	24	24

Less than 12 mm – inactive; 12–14 mm – weakly active; 14–16 mm – moderately active; above 16 mm – highly active.

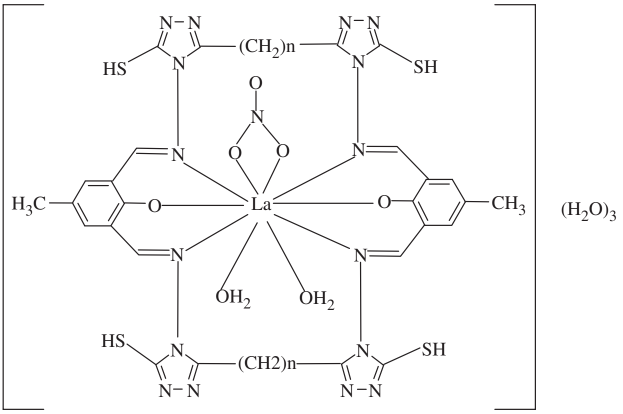


Figure 6. Proposed structures of La(III) complexes, $n = 1, 2, 3$ & 4.

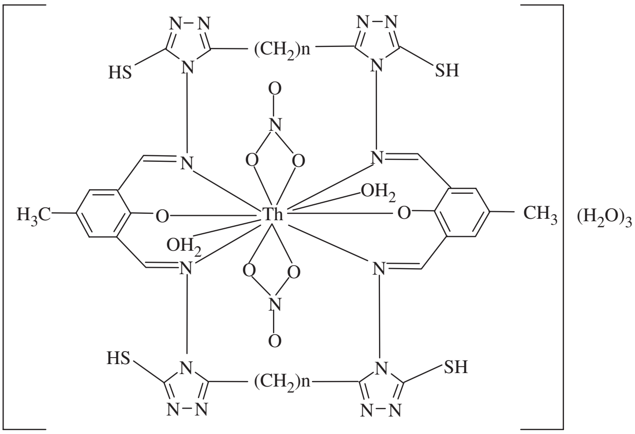


Figure 7. Proposed structures of Th(IV) complexes, $n = 1, 2, 3$ & 4.

4. Conclusion

The synthesized Schiff bases (H_2L^I–H_2L^{IV}) are hexadentate ligands through azomethine nitrogens and phenolic oxygens. Bonding of ligands to metal was confirmed by analytical, IR, ^{1}H NMR, electronic, magnetic, FAB mass, fluorescence and thermal studies. Semiconductor behavior has been inferred from solid state d.c. electrical conductivity studies.

In biological studies some compounds show promising results. The structures shown in figures 6 and 7 are proposed.

Acknowledgements

The authors are grateful to Prof S.T Nandibewoor, Head, Department of Chemistry, Karnatak University, Dharwad, for the facilities. Thanks are also due to Prof A. Venkataramana, Department of Material Science, Gulbarga University, Gulbarga, for the facilities to obtain solid state d.c. electrical conductivity data. Thanks are also due to Mr. Gururaj Rao, Department of Biotechnology, Gulbarga University, Gulbarga, for the facilities to obtain the biological results of synthesized compounds.

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