

## Synthesis and characterization of $\text{UO}_2^{\text{VI}}$ , $\text{ZrO}^{\text{IV}}$ and $\text{VO}^{\text{IV}}$ complexes with a 14-membered macrocyclic tetradentate $[\text{N}_4]$ ligand

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**Abstract :** A series of macrocyclic complexes of the type  $[\text{M}(\text{L}/\text{L}')(\text{NO}_3)_2].n\text{H}_2\text{O}$  and  $[\text{VO}(\text{L}/\text{L}')(\text{SO}_4)].2\text{H}_2\text{O}$ , where L is a Schiff base "2,5,9,12-tetraaza-1,6,8,13-tetramethyl-cyclotetradec-1,5,8,9,12-tetraene (TTCTT)" and L' is another Schiff base "3,8,14,19-dibenzo-2,5,9,12-tetraaza-1,6,8,13-tetramethyl-cyclotetradec-1,5,8,9,12-tetraene (DTTDT)",  $\text{M} = \text{UO}_2^{\text{VI}}$  and  $\text{ZrO}^{\text{IV}}$ ,  $n = 1$  or  $2$  respectively is obtained by *in situ* reaction of ethylene diamine/orthophenylene diamine and acetylacetone with the above oxocations. The coordination template effect governs the steric course of the reaction. The complexes are characterized on the basis of elemental analysis, thermal analysis, molar conductivity, magnetic moment, electronic, infrared and  $^1\text{H}$  NMR spectral studies. The results indicate that the  $\text{VO}^{\text{IV}}$  ion is penta coordinated yielding paramagnetic complexes where as  $\text{UO}_2^{\text{VI}}$  and  $\text{ZrO}^{\text{IV}}$  ions are hexa coordinated yielding diamagnetic complexes of above composition.

**Keywords :** Macrocyclic Schiff base,  $\text{UO}_2^{\text{VI}}$ ,  $\text{ZrO}^{\text{IV}}$ ,  $\text{VO}^{\text{IV}}$ , electronic, IR and  $^1\text{H}$  NMR spectra.

### Introduction

Schiff base polyazamacrocyclic complexes have undergone a phenomenal growth during the recent years because of the versatility offered by these complexes in the field of modeling of some bio system and transport processes in biosphere, stabilizing of high oxidation states and selective ion recognition, biological and catalytic system<sup>1</sup>. However, studies on the complexes involving macrocyclic ligands synthesized from ethylene diamine/orthophenylene diamine and acetylacetone especially with  $\text{UO}_2^{\text{VI}}$ ,  $\text{ZrO}^{\text{IV}}$  and  $\text{VO}^{\text{IV}}$  ions having unusual coordination behavior has not been studied as yet, which prompted us to carry out such type of investigation keeping in view of interesting stereo chemical possibilities, enhanced stabilities and their wide applications in the above mentioned fields. The present paper reports template synthesis and characterization of 14-membered tetraaza macrocyclic complexes involving the titled macrocyclic Schiff bases with the correspondmg oxo/dioxo cations.

### Results and discussion

The analytical and physical data of the complexes are presented in Table 1. The complexes are highly coloured

and insoluble in water and common organic solvents such as ethanol, methanol, acetone,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , benzene and ether but moderately soluble in highly coordinating solvents such as DMF and DMSO. They are non-hygroscopic, highly stable under normal conditions and all of them decompose above  $250^\circ\text{C}$ . The molar conductance data in DMSO for the complexes indicate the complexes to be non-electrolyte in nature. However, the conductivity value is higher than as expected for non-electrolytes probably due to partial solvolysis of the complexes in DMSO medium<sup>2</sup>. The elemental analytical data are in quite agreement with the suggested formulae of the complexes.

#### IR spectra :

As the Schiff base ligand could not be isolated, the spectra of the complexes were compared with spectra of the starting materials and other related compounds. Ethylene diamine/orthophenylene diamine exhibit a pair of strong bands precisely located at  $\sim 3310$ ,  $\sim 3275$  and  $\sim 1600\text{ cm}^{-1}$  which may be assigned to asymmetric, symmetric and deformation mode of vibration of  $\text{NH}_2$  group respectively. Acetylacetone is known to exhibit a strong

Table 1. Analytical and physical data of the complexes

Sl. no.	Compds.	Colour	Yield (%)	M.p. (°C)	$\mu_{\text{eff}}$	$\Lambda_m^a$	Found (Calcd.)%				
							C	H	N	S	M
1.	[UO <sub>2</sub> (TTCTT)(NO <sub>3</sub> ) <sub>2</sub> ].2H <sub>2</sub> O	Yellow	79.2	>250	Dia	20.11	25.42 (25.45)	3.89 (3.93)	12.70 (12.72)	-	36.03 (36.06)
2.	[UO <sub>2</sub> (DTTDT)(NO <sub>3</sub> ) <sub>2</sub> ].2H <sub>2</sub> O	Brownish yellow	70.8	>250	Dia	18.96	34.71 (34.73)	3.92 (3.94)	11.01 (11.05)	-	31.28 (31.31)
3.	[ZrO(TTCTT)(NO <sub>3</sub> ) <sub>2</sub> ].H <sub>2</sub> O	Daffodil	73	>250	Dia	32.95	32.59 (32.62)	5.40 (5.43)	16.29 (16.31)	-	17.65 (17.66)
4.	[UO <sub>2</sub> (DTTDT)(NO <sub>3</sub> ) <sub>2</sub> ].2H <sub>2</sub> O	Daffodil	71	>250	Dia	33.32	42.89 (42.92)	5.18 (5.20)	13.62 (13.65)	-	14.77 (14.79)
5.	[VO(TTCTT)(SO <sub>4</sub> )].2H <sub>2</sub> O	Black	72.6	>250	1.81	17.41	37.55 (37.58)	6.23 (6.26)	12.48 (12.52)	7.13 (7.15)	11.37 (11.40)
6.	[VO(DTTDT)(SO <sub>4</sub> )].2H <sub>2</sub> O	Chocolate	76	>250	1.78	15.60	46.87 (46.89)	5.66 (5.68)	9.91 (9.94)	5.64 (5.68)	9.02 (9.05)

<sup>a</sup> $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .

band  $\sim 1720 \text{ cm}^{-1}$  assignable to carbonyl  $\nu\text{C}=\text{O}^3$ . The IR spectra of the complexes show the following remarkable features :

The most notable features of the spectra is disappearance of  $\nu\text{NH}_2$ ,  $\delta\text{NH}_2$  and  $\nu\text{C}=\text{O}$  bands but appearance of a new band at  $1580 \text{ cm}^{-1}$ . The last band is due to azomethine  $\nu\text{C}=\text{N}$  stretching vibration of azomethain group resulting from condensation of ethylene diamine/ orthophenylene diamine with acetylacetone. The position of the band is in comparatively lower frequency region than usual  $\nu\text{C}=\text{N}$  value which leads us to suggest that azomethine nitrogen atom has taken part in the complexation as evidenced from the appearance of bands in the region  $430\text{--}480 \text{ cm}^{-1}$  assignable to  $\nu(\text{M}\text{--}\text{N})^4$ . The IR bands due to  $\nu(\text{M}\text{--}\text{O})$  appears at  $400\text{--}450 \text{ cm}^{-1}$ . Consequently the band occurring at  $\sim 1250\text{--}1300 \text{ cm}^{-1}$  due to  $\nu\text{C}\text{--}\text{N}$ , in case of ligand containing orthophenylene diamine is blue shifted to  $1490 \text{ cm}^{-1}$  while that in case of ethylene diamine, it practically remains unaltered. This is because C-N assumes a partial double bond character upon coordination to the metal ion through resonance in the former case. The uranyl complexes exhibit a strong band at  $\sim 880\text{--}910 \text{ cm}^{-1}$  and a weak band in the region  $760\text{--}790 \text{ cm}^{-1}$  corresponding, to  $\nu_{\text{as}}(\text{U}\text{--}\text{O})^5$  and  $\nu_{\text{s}}(\text{U}\text{--}\text{O})^6$  respectively in good agreement with the linear nature of  $\text{UO}_2^{2+}$  group<sup>7</sup>. On careful observation of the spectra of the nitrate com-

plexes, an additional band at about  $1410 \text{ cm}^{-1}$  was observed. This band is probably  $\nu_5$  band. The other two bands have been assigned as  $\nu_1$  and  $\nu_2$  bands appearing at  $\sim 1291$  and  $\sim 1105 \text{ cm}^{-1}$  respectively. These data are in consistent with coordination of nitrate group in unidentate manner through oxygen atom<sup>8</sup>. The zirconyl complexes exhibit one strong band in the region  $900\text{--}855 \text{ cm}^{-1}$  which can be attributed to the  $\nu(\text{Zr}=\text{O})$  as reported earlier<sup>9</sup> indicating the presence of  $(\text{Zr}=\text{O})^{2+}$  moiety in these complexes. In the oxovanadium polychelates strong bands at  $\sim 965 \text{ cm}^{-1}$  are assigned to  $\nu(\text{V}=\text{O})$  modes<sup>10</sup>. However in vanadyl complexes, an additional series of four bands appeared at  $\sim 1080$ ,  $\sim 1015$ ,  $\sim 968$  and  $\sim 645 \text{ cm}^{-1}$  indicating the coordination of sulphate group in unidentate manner through oxygen atom<sup>11</sup> and the symmetry being lowered from  $T_d$  to  $C_{3v}$  upon coordination. Besides, the bands observed at  $\sim 3500 \text{ cm}^{-1}$  may be assigned to  $\nu(\text{O}\text{--}\text{H})$  of coordinated or lattice water. However, all the complexes loss water when heated to  $\sim 100 \text{ }^\circ\text{C}$  indicating the presence of lattice water molecules which has been confirmed by thermal analysis.

#### <sup>1</sup>H NMR spectra :

The <sup>1</sup>H NMR spectra of all the complexes in DMSO-*d*<sub>6</sub> show a sharp signal at 2.40–2.48 ppm corresponding to imine methyl ( $\text{CH}_3\text{--C}=\text{N}$ ; 12H)<sup>12</sup> protons. A singlet is observed in the region 3.95 ppm assignable to (N-CH<sub>2</sub>-

$\text{CH}_2\text{-N}$ ; 8H) protons of ethylene diamine moiety for I, III and V complexes whereas the II, IV and VI complexes show a multiplet in the region 7.16–7.32 ppm which may be assigned to aromatic protons. A singlet is also observed in the region  $\delta$  2.51–2.98 ppm which may be assigned to methylene ( $=\text{C-CH}_2\text{-C}=\text{}$ ; 4H) protons<sup>13</sup>.

**Electronic spectra :**

The electronic spectra of the  $\text{UO}_2^{\text{VI}}$  complexes are quite similar. The complexes display mainly one weak band at  $\sim 460$  nm and a highly intense band at  $\sim 385$  nm, which may be due to  $^1\Sigma_g^+ \rightarrow ^3\Pi_4$  transitions and charge transfer transitions respectively. It may be noted that the band occurring at 365 nm is due to uranyl moiety because of apical oxygen  $\rightarrow f^0(\text{U})$  transition<sup>14</sup> is being merged with the ligand band due to  $n \rightarrow \Pi^*$  transition as evident from broadness and intensity. The electronic spectra of  $\text{Th}^{\text{IV}}$  and  $\text{ZrO}^{\text{IV}}$  exhibit only one extra highly intensive band in the region 345–380 nm which may be due to charge transfer band besides the ligand bands. However, the electronic spectra could not provide structural details of these complexes. The electronic spectra of  $\text{VO}^{\text{IV}}$  complexes show three bands at  $\sim 12300$ ,  $\sim 18500$  and  $\sim 25800$   $\text{cm}^{-1}$  corresponds to transitions,  $d_{xy}(b_2) \rightarrow d_{xz}d_{yz}(e)$ ,  $d_{xy}(b_2) \rightarrow d_{x^2-y^2}(b_1)$  and  $d_{xy}(b_2) \rightarrow d_{z^2}(a_1)$  respectively, indicating the complexes to be in distorted octahedral environment under  $C_{4v}$  symmetry<sup>15</sup>.

**Thermal analysis :**

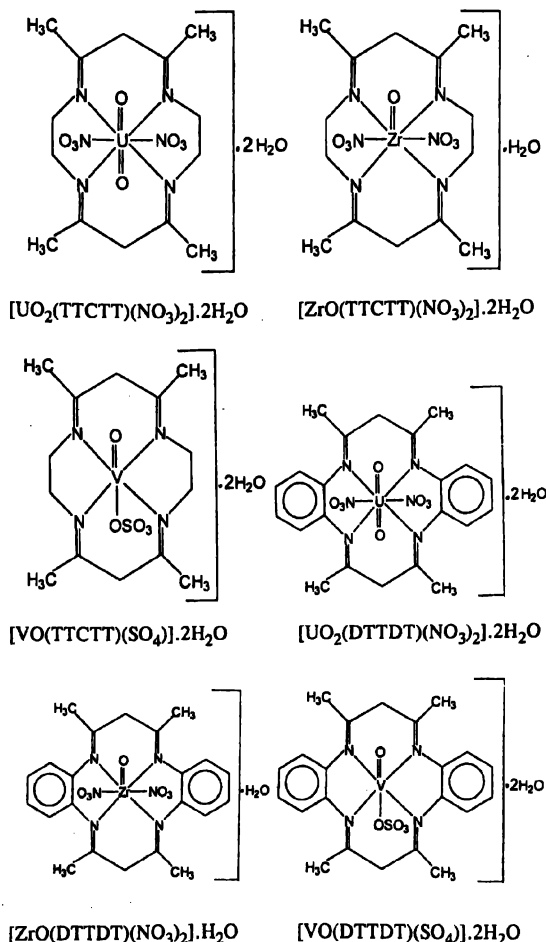
All the complexes follow the same pattern of thermal decomposition. The complexes remain almost unaffected upto  $\sim 60$  °C. After this a slight depression upto  $\sim 120$  °C is observed. The weight loss at this temperature range is equivalent to one and two water molecules for uranyl and zirconyl complexes respectively indicating them to be lattice water in conformity with our earlier observations from analytical and IR spectral investigations. Once the lattice water was eliminated, the anhydrous complexes remain stable upto  $\sim 365$  °C and thereafter the complexes show rapid degradation presumably due to decomposition of organic constituents of the complex molecules as indicated by the steep fall in the percentage weight loss. The decomposition continues upto  $\sim 800$  °C and reaches

to a stable product in each complex as indicated by the consistency in weight in the plateau of the thermogram. The decomposition temperature varies for different complexes as shown in Table 2. The thermal stability of such complexes is found to be in the following order :

(TTCTT) complexes :  $\text{ZrO}^{\text{IV}} > \text{UO}_2^{\text{VI}} > \text{VO}^{\text{IV}}$

(DTTDT) complexes :  $\text{UO}_2^{\text{VI}} > \text{ZrO}^{\text{IV}} > \text{VO}^{\text{IV}}$

Based on the foregoing observation the following tentative structures have been proposed for the present complexes.



**Materials and methods :**

All the chemicals used of AR grade. The solvents were purified before use by standard procedures. As the Schiff base ligand isolation was futile, all the metal com-

Table 2. Thermal characteristics of the complexes

Complex	Total wt.	Temp. range of	% of water loss	Decomposition temp. (°C)
	for $T_g$ (mg)	water loss	Found (Calcd.)	
[UO <sub>2</sub> (TTCTT)(NO <sub>3</sub> ) <sub>2</sub> ].2H <sub>2</sub> O	103	70–110	2.70 (2.72)	360–800
[UO <sub>2</sub> (DTTDT)(NO <sub>3</sub> ) <sub>2</sub> ].2H <sub>2</sub> O	109	75–110	2.33 (2.36)	375–780
[ZrO(TTCTT)(NO <sub>3</sub> ) <sub>2</sub> ].H <sub>2</sub> O	104	70–120	6.97 (6.99)	395–780
[ZrO(DTTDT)(NO <sub>3</sub> ) <sub>2</sub> ].H <sub>2</sub> O	92	65–120	5.83 (5.85)	390–800
[VO(TTCTT)(SO <sub>4</sub> )].2H <sub>2</sub> O	87	60–115	8.02 (8.05)	355–770
[VO(DTTDT)(SO <sub>4</sub> )].2H <sub>2</sub> O	95	60–115	6.74 (6.77)	365–760

plexes were synthesized *in situ* by taking different amount of metal salts, ethylene diamine/*o*-phenylene diamine and acetylacetone.

*Preparation of the complexes of the type [M(TTCTT)(NO<sub>3</sub>)<sub>2</sub>].nH<sub>2</sub>O, M = UO<sub>2</sub><sup>VI</sup>, ZrO<sup>IV</sup> and [VO(L)(SO<sub>4</sub>)].2H<sub>2</sub>O :*

An ethanolic solution of hydrated metal nitrates/vanadyl sulphate (1 mmol) was added to a hot ethanolic solution of the mixture of ethylene diamine (2 mmol) and acetylacetone (2 mmol). The resulting mixture was refluxed on a water bath for 5–6 h during which a coloured complex was precipitated out in each case. It was filtered off, washed several times with ethanol followed by ether and finally dried *in vacuo* over anhydrous CaCl<sub>2</sub>.

*Preparation of the complexes of the type [M(DTTDT)(NO<sub>3</sub>)<sub>2</sub>].nH<sub>2</sub>O, M = UO<sub>2</sub><sup>VI</sup>, ZrO<sup>IV</sup> and [VO(L)(DTTDT)(SO<sub>4</sub>)].2H<sub>2</sub>O :*

Same procedure was adopted to prepare [M(DTTDT)(NO<sub>3</sub>)<sub>n</sub>].nH<sub>2</sub>O and [VO(DTTDT)(SO<sub>4</sub>)].H<sub>2</sub>O by taking orthophenylene diamine instead of ethylene diamine.

Estimation of uranium, zirconium and vanadium was done by standard methods. Sulphur was estimated as BaSO<sub>4</sub> and nitrogen was estimated by Kjeldal method.

Room temperature magnetic susceptibilities were measured by Gouy method<sup>16</sup>. 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 estimated by using a MLW-CHN microanalyser. FTIR spectra in KBr pellets were recorded on a Varian FTIR spectrophotometer, Australia.

The electronic spectra of the complexes were recorded on a Perkin-Elmer\* spectrophotometer. Thermo gravimetric analysis was done by Netzch-429 thermoanalyser at a rate of 10 °C min<sup>-1</sup> in air. Around 50–100 mg of the sample was used in each case. The <sup>1</sup>H NMR spectra of the diamagnetic complexes were recorded in DMSO-*d*<sub>6</sub> medium on JEOL GSX-400 model equipment. The ESR spectrum of the vanadyl complexes has only been recorded in solid state on Varian Associate spectrophotometer using 100 KHz, X-band (RT), scan range 2.0 × 1 KG and field set 3200. Purity of these complexes were established by TLC on silica gel using DMSO as solvent.

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