

## CHAPTER II

### *Synthesis and spectroscopic studies of 2,2'-dipyridylamine La(III), Ce(III), Pr(III), Th(IV), UO<sub>2</sub>(VI) and peroxo derivative of UO<sub>2</sub>(VI)*

Nitrato (1 - 6) and isothiocyanato (8 - 12) 2,2'-dipyridylamine (HPDA) complexes of La(III), Ce(III), Pr(III), Th(IV) and UO<sub>2</sub>(VI) have been synthesised. Acetato complex of UO<sub>2</sub>(VI) (7) has also been reported. One peroxo complex(13) of UO<sub>2</sub>(VI) is also synthesized and characterized. The complexes have been characterized by elemental analyses, molar conductances, magnetic measurements, UV-VIS, IR and thermogravimetric methods. The lanthanide nitrato complexes (1 - 3) are 1:1 electrolyte; both chelated nitrato and ionic nitrate are established by IR measurements. The ambidentate thiocyanate binds through hard donor N-site. The values of both the bond stretching force constant ( $F_{U=O}$ ) and bond length ( $R_{U=O}$ ) of uranyl complexes (5 - 7, 12, 13) have been calculated. The peroxo content in (13) is determined by redox titration and is found to be thermally stable.

## 1. Introduction :

The coordination chemistry of 2,2'-dipyridylamine (HPDA) has been described for a range of transition metals<sup>1-6</sup>. The ligand is nonplanar<sup>7</sup>, *trans* conformation<sup>8</sup>, differ from  $\alpha$ -diimine ligands viz. bipyridine o-phenanthroline and forms six-membered chelate ring when coordinated as bidentate mode. The removal of N-H proton presses ligand configurations toward planar<sup>5</sup> and can act as bidentate<sup>1-5</sup> and tridentate<sup>6</sup> chelating agent. The coordination complexes exhibit luminescence behaviour<sup>9</sup> and some of them are used in photocatalytic water splitting reactions<sup>10</sup>, hydrolysis of amides esters and enzyme model compounds<sup>11</sup>.

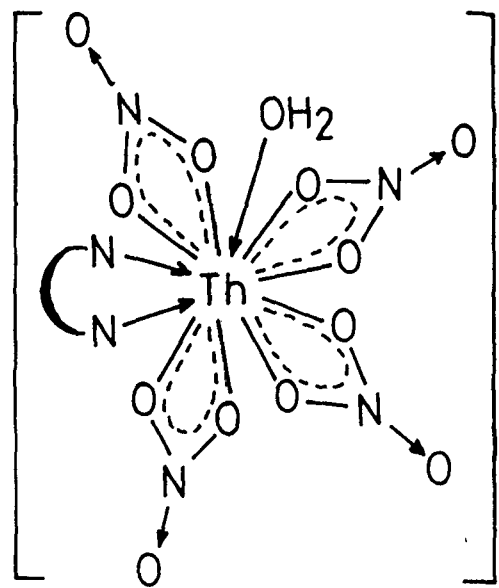
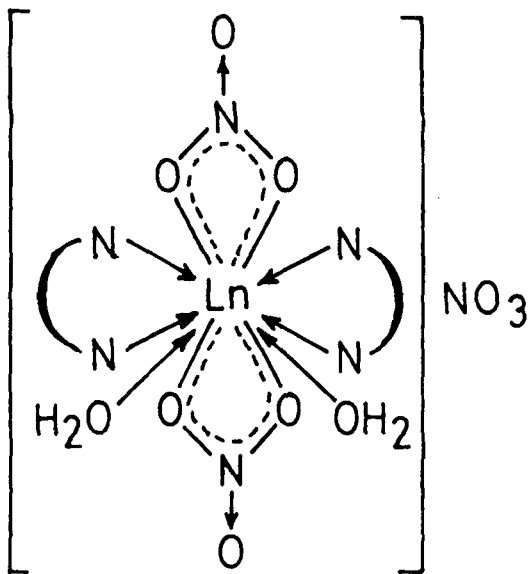
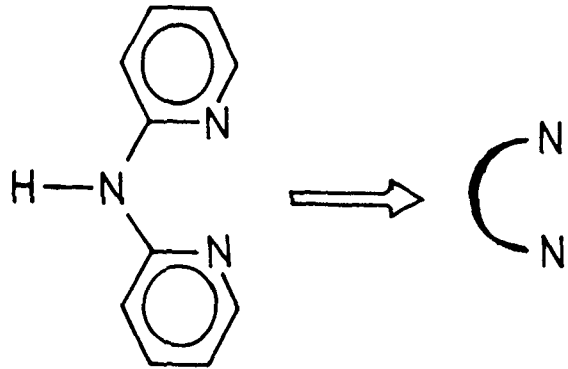
The coordination chemistry of f-block elements is an active area of current research<sup>12,13</sup> because they exhibit high coordination number and coordination geometries unknown or unusual for d-transition metals. On this background we report in this chapter synthesis and spectroscopic characterisation of 2,2'-dipyridylamine complexes of La(III), Ce(III), Pr(III), Th(IV) and UO<sub>2</sub>(VI) complexes and peroxo derivative of UO<sub>2</sub>(VI).

## 2. Results and Discussion :

### A. *Ligands and Complexes :*

2,2'-dipyridylamine act as (N,N)diimine type ligand forming six membered chelate ring and also  $\text{NO}_3^-$  or  $\text{CH}_3\text{COO}^-$  acts as bidentate chelating agent. The ambidentate thiocyanate binds through hard donor N-site.

Nitrato 2,2'-dipyridylamine complexes of La(III) (1), Ce(III) (2) and Pr(III) (3) have been synthesised by the reaction of hydrated nitrate salts of corresponding lanthanide ions with HDPA in 1:2 mole ratio in warm absolute ethanol mixture. Nitrato 2,2'-dipyridylamine Th(IV) (4) and  $\text{UO}_2(\text{VI})$  (5) complexes are prepared by the reaction of  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with HDPA in 1:1 mole ratio in stirred methanolic solution and to synthesise the complex of  $\text{UO}_2(\text{VI})$ , (6), the reaction should be carried out in ethanol. Isothiocyanato complexes of the above metal ions (8-12) have been synthesised by allowing the reaction of the nitrate salts with KCNS 1:3 mole ratio for lanthanides, 1:2 for  $\text{UO}_2(\text{VI})$  and for Th(IV), and then with HDPA in warm ethanol solvent for 2-3 hrs. In similar process the acetato 2,2'-dipyridylamine complex of  $\text{UO}_2(\text{VI})$  (7) have been prepared by using  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  instead of uranyl nitrate salt in 1:1 mole

Table-II.1

Ln =	La(III)	Ce(III)	Pr(III)
	(1)	(2)	(3)

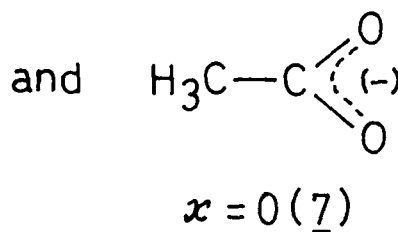
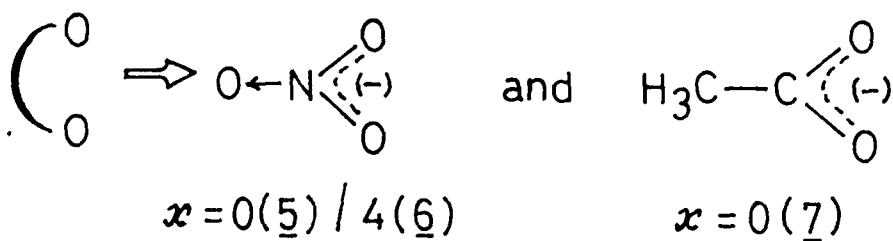
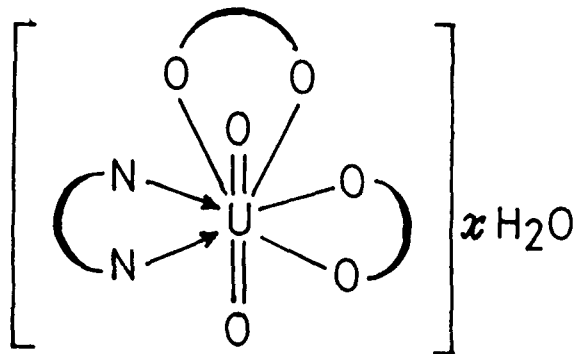
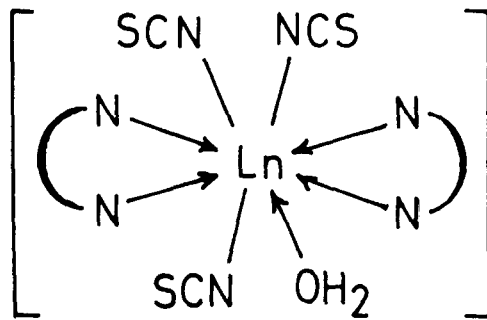
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Table-II.1 (contd.)

Ln =	La(III)	Ce(III)	Pr(III)
	<u>8</u>	<u>9</u>	<u>10</u>

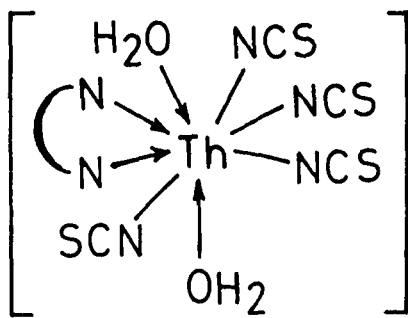
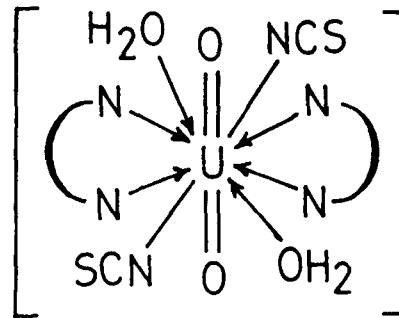
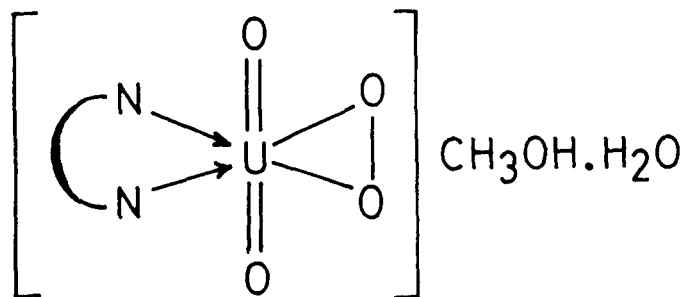
111213CH<sub>3</sub>OH.H<sub>2</sub>O

Table II.2

## Analytical Data and Physical Properties of Complexes

Complexes	Found	(Calcd.)	%	M	Yield %	Decomposition Temp <sup>o</sup> C	$\Lambda_M^{-1}$ ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	$\mu$	BM
	C	H	N						
[La(C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> ) <sub>2</sub> (ONO <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) (1)	33.81 {34.14}	2.88 {3.13}	16.92 {17.13}	a	50	>350	48.4	dia	
[Ce(C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> ) <sub>2</sub> (ONO <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) (2)	34.24 {34.09}	2.94 {3.12}	17.64 {17.90}	22.34 {19.90}	54	>400	50.8	2.32	
[Pr(C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> ) <sub>2</sub> (ONO <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) (3)	33.64 {34.05}	3.44 {3.12}	18.54 {17.87}	a	58	>400	42.6	3.51	
[Th(C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O)] (4)	18.21 {17.94}	1.42 {1.64}	15.01 {14.65}	36.11 {34.68}	72	>450	4.2	dia	
[UO <sub>2</sub> (C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> ) <sub>2</sub> (ONO <sub>2</sub> ) <sub>2</sub> ] (5)	21.52 {21.24}	1.41 {1.59}	11.64 {12.39}	40.04 {42.12}	76	>450	1.4	dia	
[UO <sub>2</sub> (C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> ) <sub>2</sub> (ONO <sub>2</sub> ) <sub>2</sub> ]·4H <sub>2</sub> O (6)	18.52 {18.84}	2.54 {2.67}	11.24 {10.99}	39.24 {37.36}	80	>450	1.8	dia	
[UO <sub>2</sub> (C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> ) <sub>2</sub> (OOCCH <sub>3</sub> ) <sub>2</sub> ] (7)	29.62 {30.05}	2.76 {2.68}	7.34 {7.51}	40.80 {42.58}	68	>450	0.7	dia	
[La(C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> ) <sub>2</sub> (NCS) <sub>3</sub> (H <sub>2</sub> O)] (8)	40.88 {41.02}	3.14 {2.97}	19.04 {18.72}	a	52	>400	2.8	dia	
[Ce(C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> ) <sub>2</sub> (NCS) <sub>3</sub> (H <sub>2</sub> O)] (9)	39.89 {40.94}	2.64 {2.97}	18.55 {18.69}	22.04 {20.78}	55	>400	3.1	2.26	
[Pr(C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> ) <sub>2</sub> (NCS) <sub>3</sub> (H <sub>2</sub> O)] (10)	41.31 {40.89}	3.08 {2.96}	19.04 {18.67}	a	60	>400	2.6	3.44	
[Th(C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] (11)	25.28 {25.04}	2.21 {1.94}	15.08 {14.61}	36.24 {34.58}	68	>450	2.1	dia	
[UO <sub>2</sub> (C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> ) <sub>2</sub> (NCS) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] (12)	35.11 {34.55}	3.06 {2.88}	14.18 {14.66}	29.84 {31.15}	74	>450	0.8	dia	
[UO <sub>2</sub> (C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> ) <sub>2</sub> (O <sub>2</sub> )](CH <sub>3</sub> OH)(H <sub>2</sub> O) <sup>b</sup> (13)	25.52 {25.24}	3.16 {2.87}	8.24 {8.03}	44.18 {45.51}	85	>450	0.9	dia	

<sup>a</sup> Not determined. <sup>b</sup> Peroxo content: 5.8% (found), 6.1% (calcd).

ratio in methanol. Peroxide complex of  $\text{UO}_2(\text{VI})$  (13) are prepared by adding the methanolic solution of HDPA to an aqueous solution of uranyl nitrate in stirring condition and then to this mixture till precipitate become appear  $\text{H}_2\text{O}_2$  in excess is added maintaining the pH 3.5-4 with glacial acetic acid. The mixture is allowed to stirr another 1 hr. The precipitated yellow product was filtered, washed with methanol and dried in vacuo. The compounds synthesised are listed in **Table II.1**.

#### ***B. Physical Characteristics :***

Lanthanum(III) (1 and 8) and thorium(IV) (4 and 11) are white crystalline solids. Cerium(III) (2 and 9) and uranium(VI) (5, 6, 7, 12 and 13) complexes are pale yellow, yellow orange or brown. Praseodymium(III) (3 and 10) complexes are pale green. The complexes are stable at room temperature. The nitrato complexes except uranium(VI) derivatives are fairly soluble in coordinating solvents like acetonitrile, pyridine, DMSO, DMF. The isothiocyanato complexes are less soluble.

The molar conductances of (1)-( 3) in DMF showed 1:1 electrolytic nature shown in **Table II.2**. The room temperature magnetic moments of the complexes which are corrected showed diamagnetism for

lanthanum(1 and 8), thorium(4 and 11) and uranium(5, 6, 7, 12 and 13) and paramagnetism for cerium(2 and 9) and praseodymium(3 and 10) complexes. The magnetic moments have shown very little deviation from the Van Vleck values<sup>14</sup>. The peroxy compound(13) is brown, diamagnetic and ESR silent. In the presence of dilute  $H_2SO_4$ , it is dissolved in water and the liberated  $H_2O_2$  is estimated by redox titration<sup>15(d)</sup>. The analytical results showed the  $UO_2(VI):O_2:H_2DPA$  ratio as 1:1:1 in agreement with the formula (Table II.2).

### C. Spectral Characterisation :

#### (i) UV-VIS Spectra :

The electronic spectra of (1) - (4) and (8) - (11) are recorded in acetonitrile due to their fair solubility in common organic solvents. The spectra are dominated by absorption band. The free ligand absorbs at  $\sim 310nm^2$ . The complexes exhibit band around  $\sim 315nm$  and (3) and (10) exhibit more narrow bands at 445, 480 and 585nm characteristic of  $3H_4 \rightarrow 3P_2$ ,  $3P_0$  and  $3D_2$  transitions respectively<sup>16</sup>. Uranyl complexes (5), (6), (7), (12) and (13)



exhibit bands in DMSO due to intraligand charge transfer at ~312nm and a band 380-400nm which is absent in free ligand may be due to apical oxygen  $\rightarrow f^0(U)$  transition<sup>17</sup>. A representative spectra is given as **Fig.II.A**.

(ii) *IR Spectra* :

The infrared spectra provide information regarding the nature of bonding between the central metal ion, HPDA and other anions ( $\text{NO}_3^-$ ,  $\text{OAC}^-$ ,  $\text{NCS}^-$ ) and the important frequencies are set out in **Table II.3**. The free ligand shows the sharp band  $\sim 3260 \text{ cm}^{-1}$  due to the stretching of secondary amine and in complexes is slightly shifted in either directions,  $3220\text{-}3265 \text{ cm}^{-1}$ . This band in (6) is submerged in the stretch of water of crystallisation. The intense bands around  $3420\text{-}3480 \text{ cm}^{-1}$  (1)-(4) and (8)-(11) are assigned as coordinated water<sup>18</sup>, while in (6) a broad and intense band centred at  $3300 \text{ cm}^{-1}$  may be due to water of crystallisation. In (13) observable stretches at  $\sim 3650$  and  $\sim 3400 \text{ cm}^{-1}$  are assigned to coordinated water<sup>10</sup> and methanol<sup>19</sup> respectively. The N-H bending mode of free ligand appears at  $\sim 1603 \text{ cm}^{-1}$  and blue shifted in complexes to  $1620\text{-}1630 \text{ cm}^{-1}$ . In the complexes strong

bands in the region  $1640-1670\text{ cm}^{-1}$  are assigned to C=N which is observed in the ligand at  $1610\text{ cm}^{-1}$ . This blue shift may suggest that the ligand coordinates through both  $\sigma$ - and  $\Pi$ -donation. The  $\Pi$ -donation will decrease the  $\Pi^*$  electron density of the C=N group and hence increases both its bond order and vibrational frequency<sup>20</sup>.

In the spectra of (1) - (6) the frequencies of the bands assigned as vibrational modes of the nitrate groups suggest the presence of the coordinated nitrates. The vibrational fundamentals around  $\nu_4$ ,  $1510-1550$ ;  $\nu_1$ ,  $1305-1325$ ;  $\nu_2$ ,  $1040-1055$ ;  $\nu_6$ ,  $820-860$ ;  $\nu_3/\nu_5$ ,  $720-740$ ; and combination band  $\nu_2 + \nu_6$ ,  $1780-1795\text{ cm}^{-1}$  suggest chelating ( $C_{2v}$ ) bidentate nitrate groups<sup>21-23</sup>. The appearance of a strong and broad band around  $1380\text{ cm}^{-1}$  also ( $\nu_3(E')$ ) confirms the presence of ionic nitrates<sup>23</sup> ( $D_{3h}$ ) in (1) - (3) ( $\Lambda_M$  values also support) and the absence of same in the spectra of (4 - 6) is suggestive of coordinated nitrates. The acetato complex (7) shows  $\nu_{as}(\text{COO})$  and  $\nu_s(\text{COO})$  at  $1580$  and  $1435\text{ cm}^{-1}$  respectively. This defines bidentate chelating acetato groups ( $\Delta\nu = \nu_{as} - \nu_s = 145\text{ cm}^{-1}$ )<sup>24,25</sup>. The spectra of (8) - (12) exhibit the  $\nu(\text{CN})$ ,  $\nu(\text{CS})$  and

$\delta(\text{NCS})$  mode in regions 2080-2100, 790-805 and 475-480  $\text{cm}^{-1}$  respectively, suggesting N-coordination of this ambidentate anion<sup>21,26,27</sup>. The infrared spectra due to coordinated HDPA in the complexes show close resemblance to the uncoordinated ligand with the exception of shift and splitting of some bands and the fundamental frequencies. The bands of interest are the ring breathing mode near 1000  $\text{cm}^{-1}$ , an out-of-plane C-H deformation near 770  $\text{cm}^{-1}$  and the two in-plane and out-of-plane ring deformation bands at ~600, ~640 and 400, 420  $\text{cm}^{-1}$  respectively<sup>21</sup>. The peroxoderivative (13) is characterized by three bands due to metal peroxo groupings<sup>28,29,30</sup> ( $C_{2v}$  symmetry) :

$\nu_1(\text{O-O})$ , 810  $\text{cm}^{-1}$ ; the symmetric stretch  $\nu_2(\text{U} \begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{O} \end{array} )$  580  $\text{cm}^{-1}$  and antisymmetric  $\nu_3(\text{U} \begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{O} \end{array} )$ , 630  $\text{cm}^{-1}$ . In the far infrared region some new medium and weak bands are observed in the range 280-410  $\text{cm}^{-1}$  assign and  $\nu(\text{M-N})$  modes<sup>26,31,32</sup>.

The uranium(VI) complexes exhibit a strong absorption in the range 920-940  $\text{cm}^{-1}$  corresponding to  $\nu(\text{O=U=O})$ <sup>20,33</sup> in (5) - (7), (12) and  $\nu(\text{U=O})$  modes<sup>28</sup> in (13). The bond stretching force constant ( $F_{\text{U=O}}$ ) for the U=O bond has been calculated according to the Jones formulae<sup>34</sup> ( $F_{\text{U=O}}$ , 6.85-7.18 m dyne/A<sup>0</sup>) and also the bond

Table II.3

Some selected IR spectral data of the complexes\*

Complex	$\nu, \text{cm}^{-1}$										
	$\nu_{\text{O-H}}$	$\nu_{\text{N-H}}$	$\nu_{\text{C-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{NO}_3}$	$\nu_{\text{ONO}_2}$	$\nu_{\text{M-N/}}$ $\text{M-O}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-S}}$	$\nu_{\text{NCS}}$	$\nu_{\text{O=U=O}}$
1	3,450	3,235	30,50	1,650	1,385	1560,1350,1030 815,770	385 305	-	-	-	-
2	3,445	3,225	30,30	1,655	1,382	1560,1355,1028 815,770	380 300	-	-	-	-
3	3,445	3,220	3,020	1,650	1,380	1555,1365,1025 810,770	385 290	-	-	-	-
4	3,430	3,265	3,040	1,660	-	1560,1370,1030 815,770	380 295	-	-	-	-
5	-	3,260	3,020	1,660	-	1520,1250,825 720	360 280	-	-	-	925
6	a	a	3,020	1,655	-	1525,1240,820 720	355 265	-	-	-	930
7 <sup>b</sup>	-	3,265	3,010	1,655	-	-	340 260	-	-	-	920

\* in KBr disk

Table II.3 (Contd.)

Some selected IR spectral data of the complexes\*

Complex	$\nu, \text{cm}^{-1}$										
	$\nu_{\text{O-H}}$	$\nu_{\text{N-H}}$	$\nu_{\text{C-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{NO}_2}$	$\nu_{\text{ONO}_2}$	$\nu_{\text{M-N/M-O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-S}}$	$\nu_{\text{NCS}}$	$\nu_{\text{O=U=O}}$
8	3,480	3,240	3,040	1,655	-	-	390	2,080	790	475	-
9	3,460	3,230	3,045	1,660	-	-	385	2,075	800	480	-
10	3,450	3,215	3,030	1,655	-	-	380	2,072	795	475	-
11	3,460	3,260	3,220	1,660	-	-	375	2,090	800	475	-
12	3,480	3,250	3,010	1,660	-	-	355	2,100	805	480	922
13	3,550	3,250	3,020	1,665	-	-	350 290	-	-	-	910

<sup>a</sup>  $\nu_{\text{O=U=O}}$  and  $\nu_{\text{N-H}}$  are overlapped, 3100-3400 br, s  $\text{cm}^{-1}$ .<sup>b</sup>  $\nu_{\text{as(COO)}}$ , 1580;  $\nu_{\text{s(COO)}}$ , 1445  $\text{cm}^{-1}$ .

\* in KBr disk

length ( $R_{U=O}$  , 1.70-1.74 Å) those are in the expected range (1.60-1.92Å)<sup>33</sup>.

$$\text{Jones Formula : } R_{UO} = \beta \cdot F_{UO}^{-1/3} + d_{UO}$$

F in mdynes,  $\beta = 1.08$ ,  $d_{UO} = 1.17$ ,  $R_{UO} = 1.76$  Å

#### D. *Thermal Analysis* :

Nine of the thirteen complexes were subjected to thermal analyses and the results are found out in **Table II.4**.

The complexes (1), (2), (11) and (12) lose weight in the temperature range 120-180°C corresponding to two moles coordinated water while (4) and (8) loose weight for one mole of coordinatd water. The complex (6) suffers endothermic loss of H<sub>2</sub>O in one step in the temperature range 90°- 120° C , suggesting four moles water of crystallisation. The thermal decomposition of (13) starts at 75°C with minimum at 130°C in the endothermic DTA curve corresponding to the mass loss of coordinated methanol and water in overlapping step. The active oxygen is released from the complex in the second step of decomposition manifested in the DTA curve by the exothermic effect with maximum at 190°C. All the complexes undergo complete decomposition at 400-650°C and the final temperature depends on nature of the complex. The

Table II.4

*TGA data of the complexes*

Complex	Mass loss Starts at °C	Final phase is reached °C	Final residue	
			Theo.	Expt.
<u>1</u>	120	400	23.18	24.28
<u>2</u>	120	440	24.44	23.31
<u>4</u>	110	510	39.46	38.54
<u>5</u>	330	560	49.68	50.22
<u>6</u>	90	580	44.06	44.86
<u>7</u>	120	450	24.21	23.64
<u>11</u>	120	540	39.34	40.26
<u>12</u>	130	600	36.74	35.24
<u>13</u>	75	600	53.66	54.58

decomposition starts first gradually and then rapidly into the final residue  $\text{Ln}_2\text{O}_3$  ((1), (2) and (8)),  $\text{ThO}_2$  ((4) and (11)) and  $\text{U}_3\text{O}_8$  ((2), (6), (11), and (13))<sup>35</sup>.

### ***E. Epilogue :***

On the basis of these results, the formulae of the complexes are suggested in **Table II.2**. The coordination number varies from 6 to 12 and in most cases it is 8. Usually the coordination number is increased in the case of nitrate complexes due to the small bite of the bidentate nitrate group<sup>23</sup>.

## **3. Experimental :**

### ***A. Materials :***

Lanthanide nitrates were obtained from M/S Indian Rare Earths Ltd., Kerala (India) and were used as such Hydrated dioxouranium and thorium salts were BDH reagents and used as supplied 2,2'-Dipyridylamine (HDPA) was an Alderich reagent. Hydrogen peroxide was purchased from Merck and methanol and glacial acetic acid were SRL reagents. Other solvents, acetonitrile, ether, pyridine, DMSO and DMF were of reagent grade purchased from Qualigence. The solvents, methanol and ethanol, were distilled and dried by standard methods.



### B. *Physical Measurements :*

The elemental analyses, IR electronic spectroscopy, thermal study conductance and magnetic moments measurements were recorded as in Chapter I. Uranium was estimated gravimetrically by oxine<sup>15(a)</sup> weighing as  $UO_2(\text{oxin})_2$ , oxinH or ignited  $U_3O_8$ . Thorium of the complex was digested and then estimated gravimetrically by sebacic acid<sup>15(b)</sup> weighing as ignited  $ThO_2$ . Cerium was also estimated gravimetrically as oxide via iodate<sup>15(c)</sup>. All other metals were estimated as oxide from the residue of thermogravimetric analyses. Peroxo content of (13) was determined by dissolving the complex(13) in  $H_2SO_4$  and titrating the liberated  $H_2O_2$  iodometrically<sup>15(d)</sup>.

### C. *Preparation :*

#### *Complexes :*

i)  $[Ln(HDPA)_2(ONO)_2(H_2O)_2](NO_3)_3(1)-(3)(Ln=La,Ce,Pr) :$

The complexes were prepared by a common procedure<sup>36</sup>. To lanthanum(III) nitrate(0.32g, 1mmol) in 20ml of warm absolute ethanol was added to 10ml of ethanolic HDPA (0.34g, 2.0mmol). The resulting solution was refluxed over steam bath for 2 hr. the solid products were filtered and washed with ethanol, ether and dried in vacuo over  $CaCl_2$ .

**ii) Actinide Nitrate Complexes, (4)-(7) :**

In a typical preparation<sup>37</sup>, HDPA (0.17g, 1 mmol) in methanol (10ml) was added to the methanolic solution (10 ml) of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.5g, 1 mmol) with continuous stirring for 2hr. The colour of the solution turned to deep yellow. The solution was slowly evaporated in air and the yellow precipitate was removed by filtration, washed with methanol and dried in vacuo. The same reaction in ethanolic solution resulted hydrated complex (6).

**iii) Isothiocyanato Complexes (8)-(12) :**

The preparation follows a common process<sup>21,26</sup>. To an ethanolic solution (15 ml) of KCNS (0.29g, 3.0 mmol), warmed to 50°C, was slowly added to an ethanolic solution (10ml) of the appropriate lanthanum nitrate (1.0 mmol) or actinide nitrate (0.75g, 1.5 mmol for  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.44g, 0.75 mmol for  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ ). The resulting mixture was stirred and cooled whereupon the precipitated  $\text{KNO}_3$  was removed by filtration. The filtrate was mixed with a warm solution of HDPA (0.34g, 2.0 mmol) for Ln(III), 0.5g, 3 mmol for  $\text{UO}_2(\text{VI})$  and 0.13g, 0.75 mmol for Th(IV) in absolute ethanol (25ml) and stirred for 3 hr. The precipitate was filtered and washed with ethanol, ether and dried in vacuo.

iv)  $[UO_2(HDPA)(O_2)] \cdot CH_3OH \cdot H_2O$ , (13):

To a methanolic solution (10ml) of HDPA (0.17g, 1 mmol) was slowly added an aqueous solution (10ml) of  $UO_2(NO_3)_2 \cdot 6H_2O$  (0.5g, 1mmol). It was stirred for 30 min whereupon a precipitate began to appear. Hydrogen peroxide (30%, 10ml) was added and the mixture was stirred for additional 1 hr. The pH of the solution was adjusted at 3.5-4 by adding glacial acetic acid. The compound was filtered, washed with methanol and dried in vacuo.

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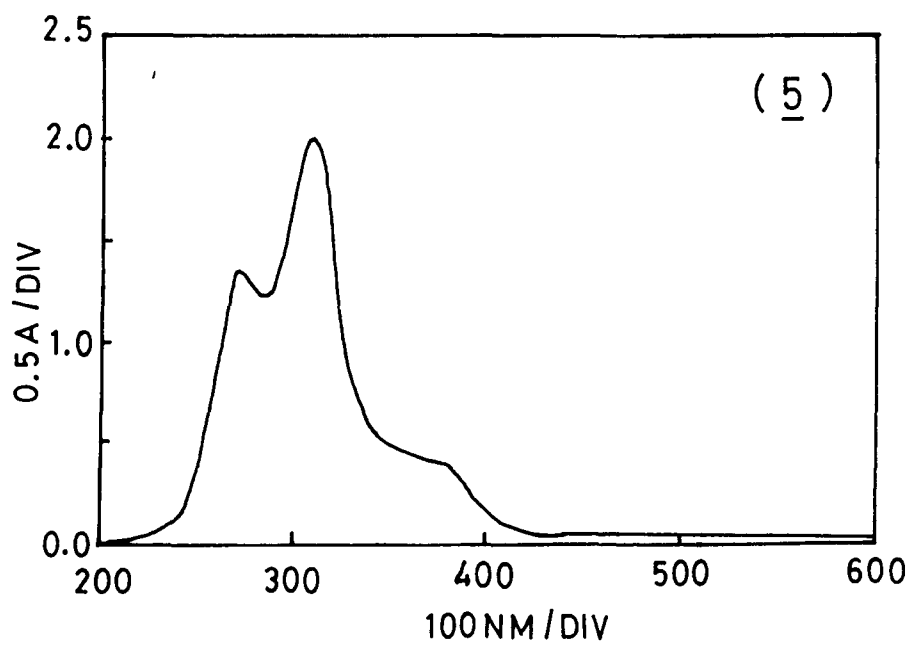
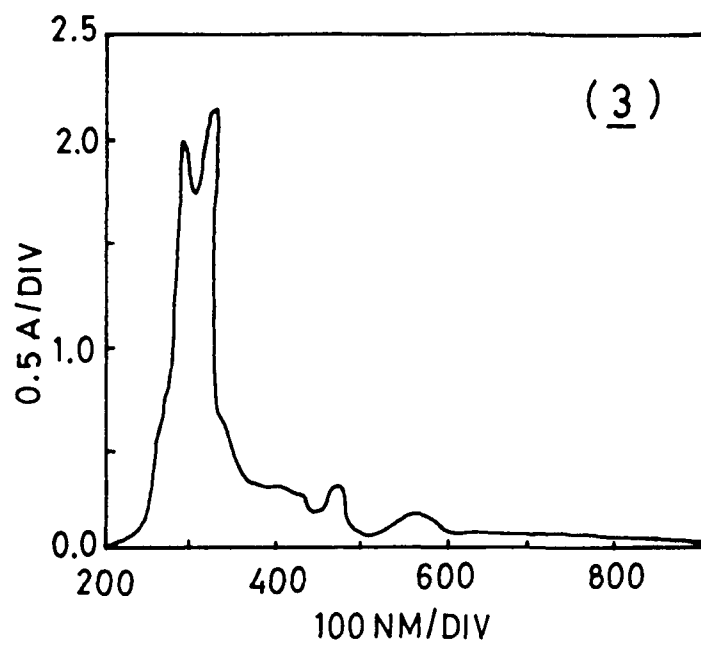


Fig.II.A. UV-VIS spectra



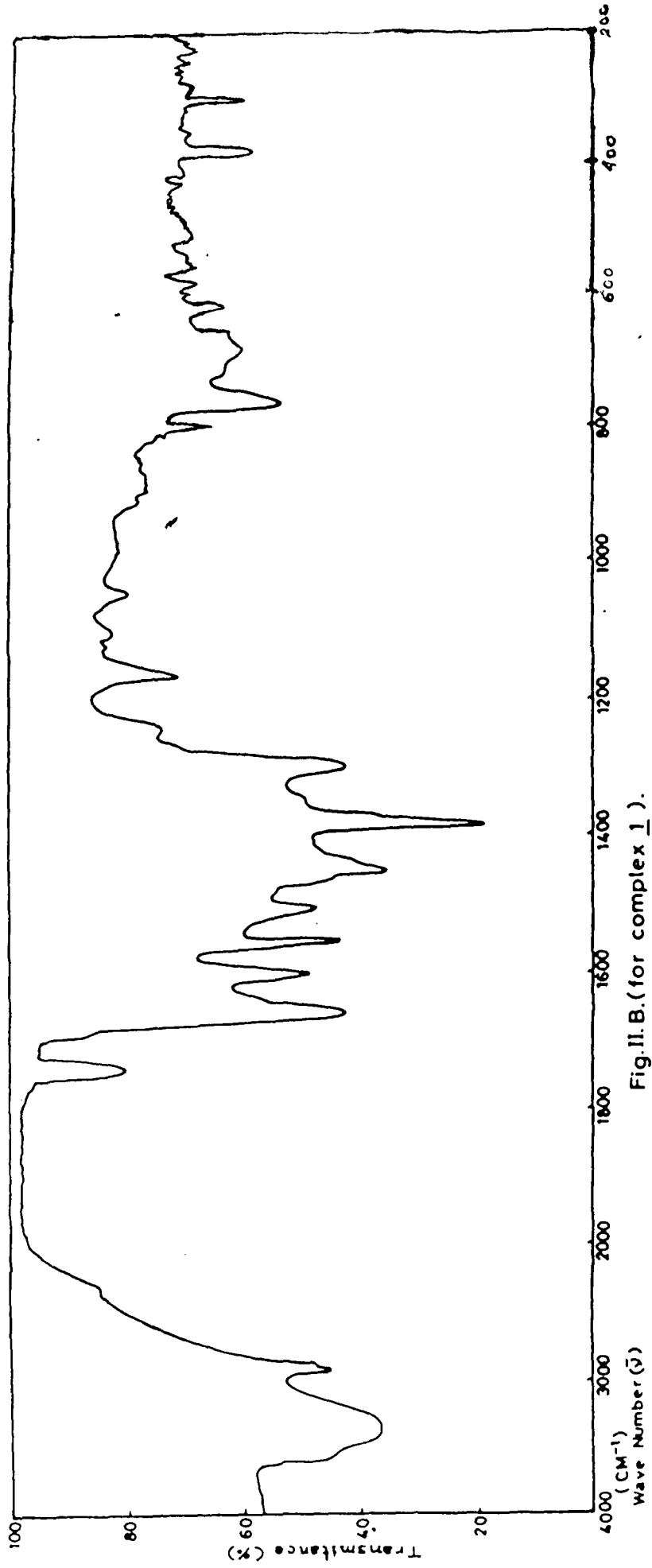
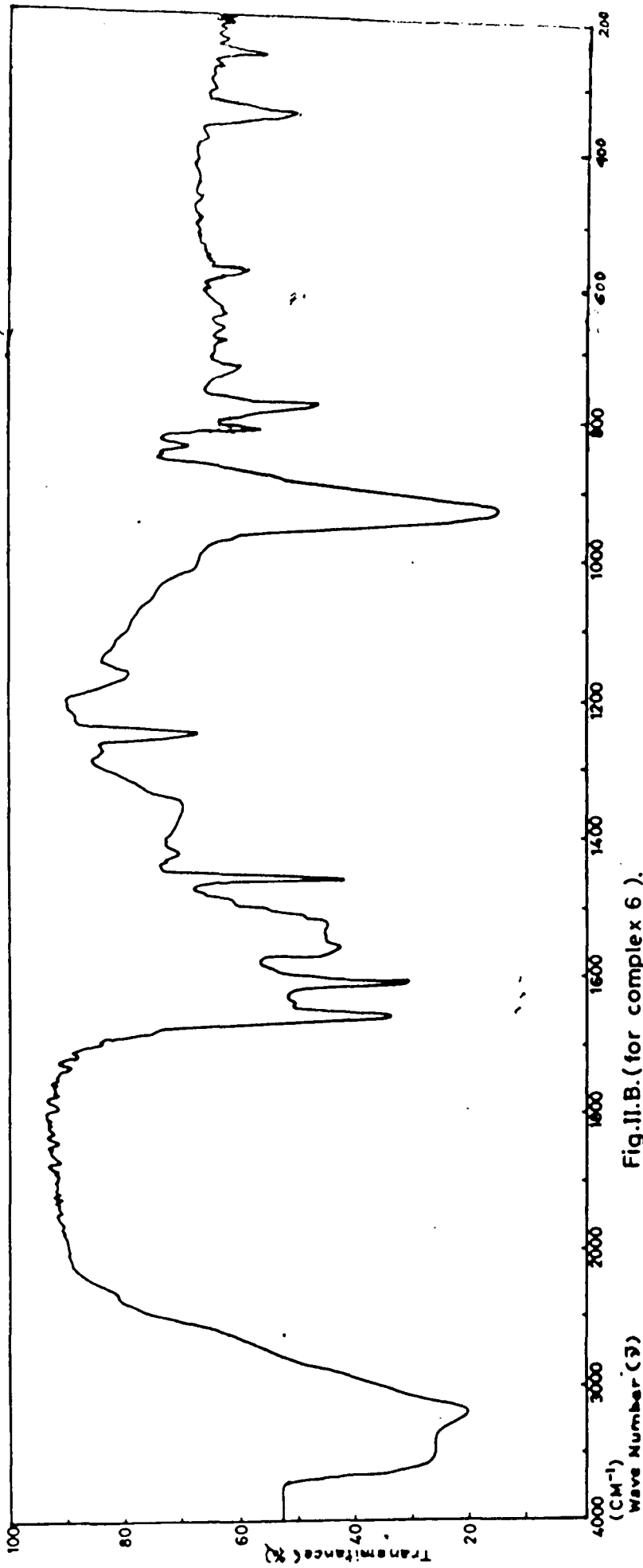


Fig. II. B. (for complex 1).



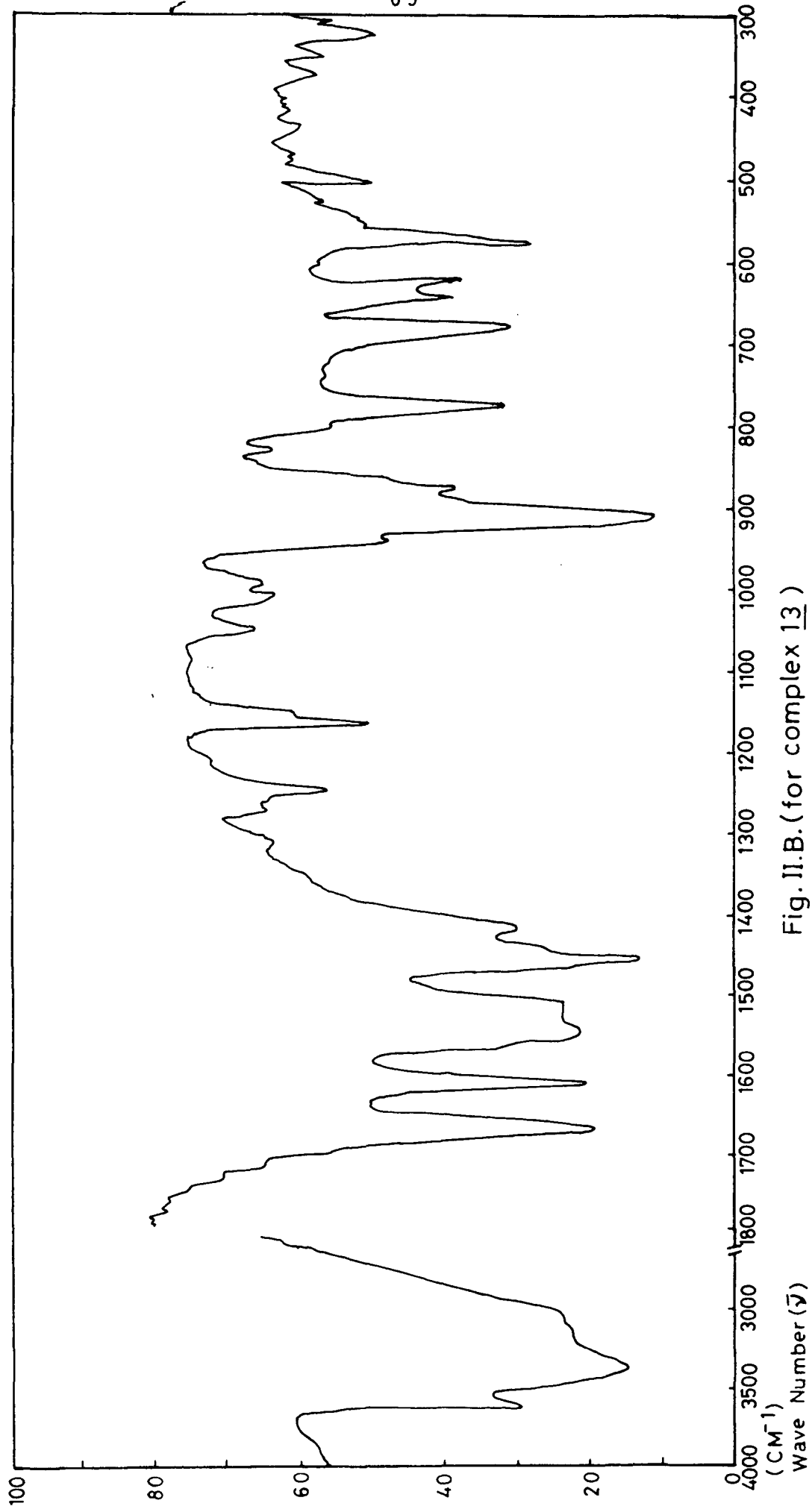


Fig. II.B. (for complex 13)

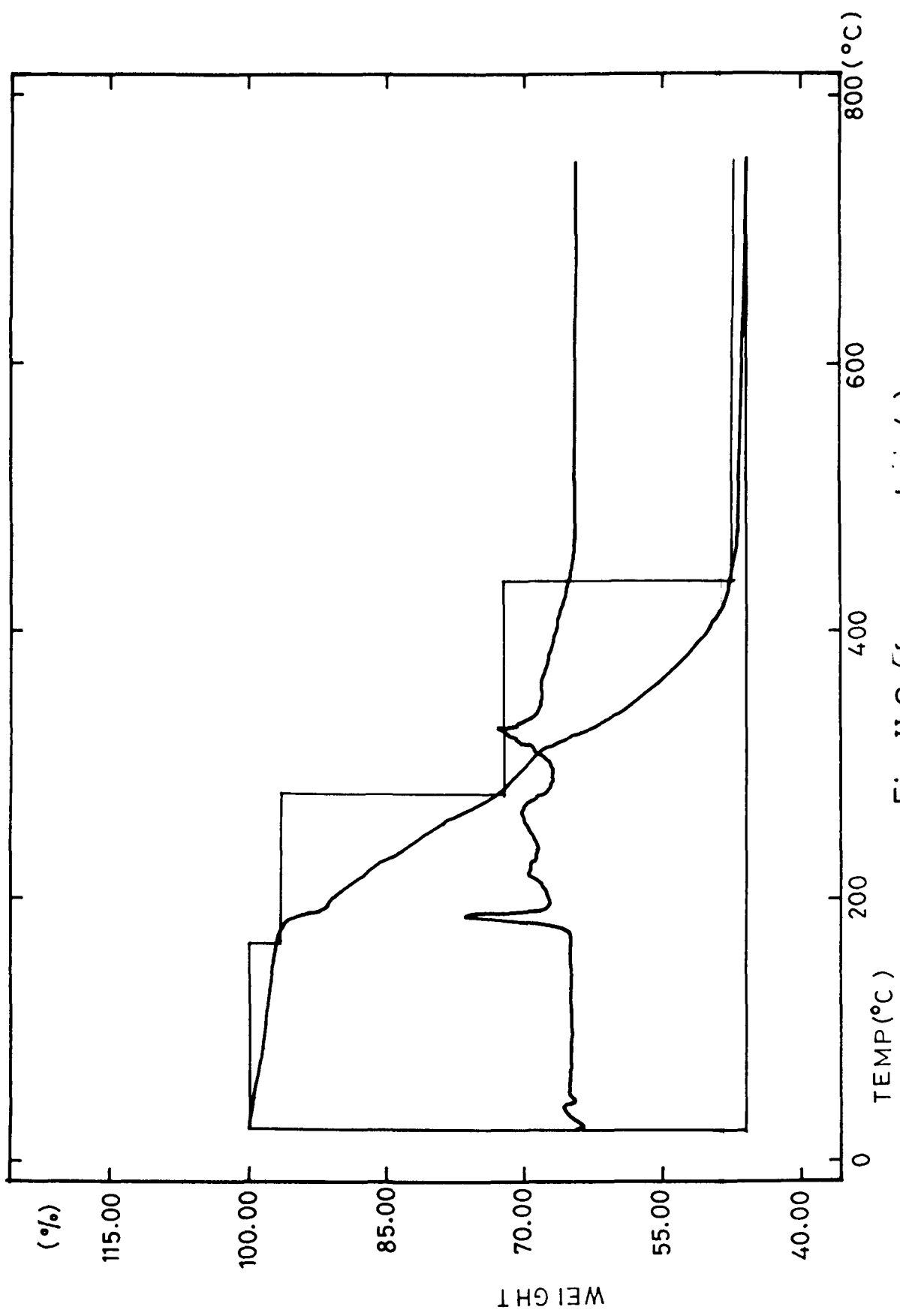


Fig.II.C.(for complex 4).

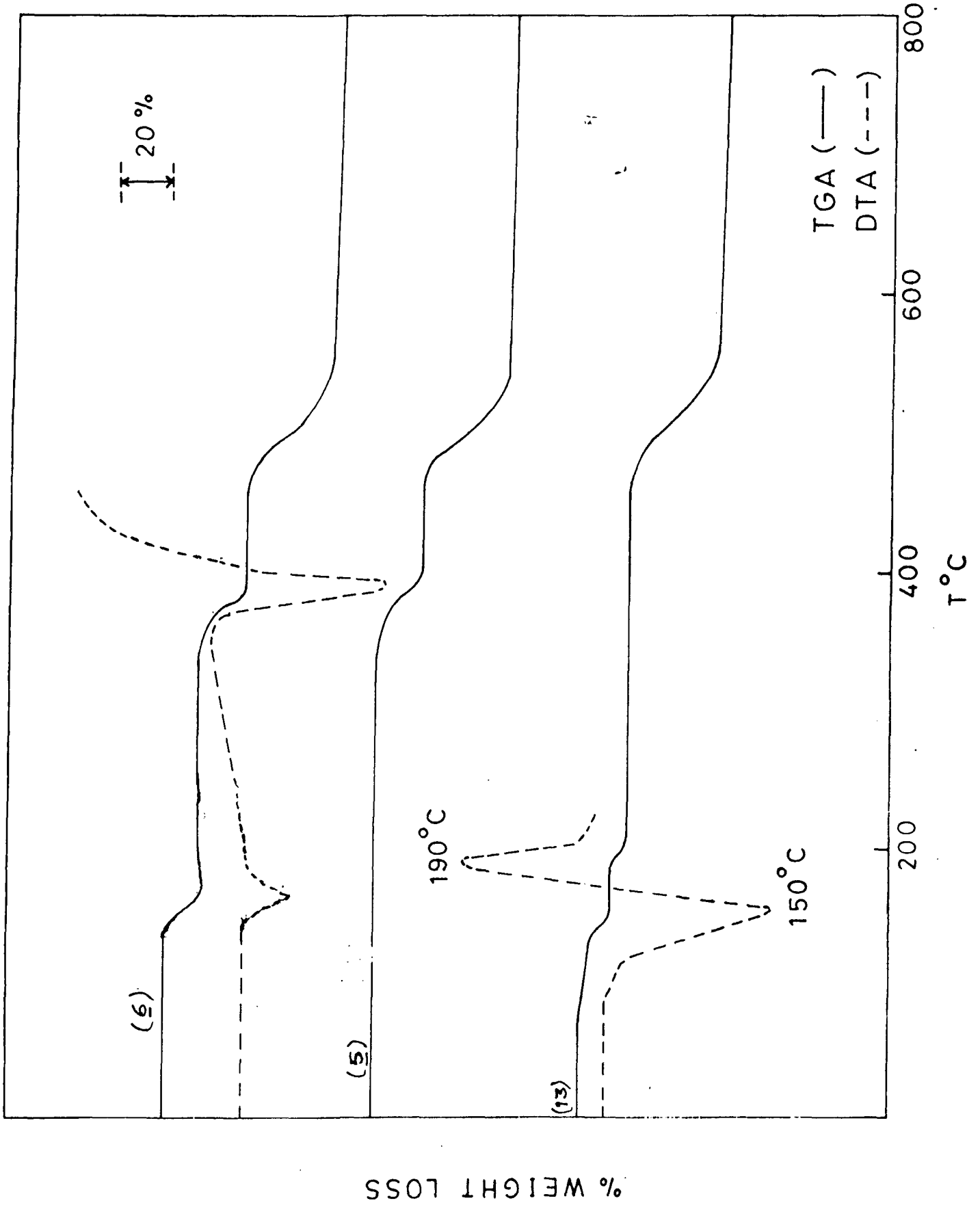


Fig - II.C