

## CHAPTER : VII

### *Chemistry of azoimidazoles : synthesis and spectral characterisation of Pb(II), Ag(I), Pd(II) and UO<sub>2</sub>(VI)-azoimidazoles complexes*

Arylazoimidazoles (1) are  $\alpha$ -diimine type N,N-chelating agent. Due to the presence of two different heterocyclic-N donor centres, N(1) and N(3) the ligand may either act as soft base on binding through pyrrolic-N(1) or as hard base when it binds via pyridinic-N(3) centre. The metal ions Pb(II), Ag(I), Pd(II) preferentially bind N(1) centre while UO<sub>2</sub>(VI) prefers N(3) centre. The uranyl complexes (5) are monomeric and ionic of formula [UO<sub>2</sub>(1)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>(5). Thermal dehydration significantly moves one of the ionic nitrate to the coordination zone and gives [UO<sub>2</sub>(1)<sub>2</sub>(NO<sub>3</sub>)](NO<sub>3</sub>). Pb(II), Ag(I) and Pd(II) complexes are polymeric in nature. They are characterised by elemental analyses, IR, UV-VIS, <sup>1</sup>H NMR (partly) and conductance measurements.

## 1. Introduction

The heterocyclic molecules are increasingly used in the field of coordination chemistry<sup>1</sup>. Especially the use of imidazole type ligands or molecules having this group are rapidly expanding due to the realisation that the interaction between such ligands and metal ions plays an important role in a variety of biological systems<sup>2</sup>. Molecules having imidazole system with pendant arm containing donor centres at suitable positions to maintain chelate structure are of current interest<sup>3,4</sup>. Imidazoles having two different N-donor centres : N(3) as hard donor and N(1) as soft donor seek class a and class b metal ions respectively. This accounts the use of benzimidazole for the gravimetric estimation of Ag(I)<sup>5</sup>. Incorporation of azo group at C-2 position of the imidazole group synthesises arylazoimidazole that may either act as N(3), N(a) or N(1), N(a) chelating molecule (N(a), azo-N to maintain five membered chelate structure (1)). Besides, N(1) may coordinate singly to soft acids and may give polymeric backbone through N(3) coordination as usual in imidazole family<sup>5,6</sup>. Azoimidazoles are  $\alpha$ -diimine type N,N chelating ligand and may tune the redox and spectroscopic properties of a metal centre<sup>7</sup>. This property coupled with the biomimetic properties of imidazole

lead us to investigate the coordination behaviour with heavy metal ions. Reports on the complexes of arylazoimidazoles are scarce<sup>8</sup>. In this chapter we describe synthesis and spectral characterisation of Pb(II), Ag(I), Pd(II) and UO<sub>2</sub>(VI) complexes.

## 2. Results and Discussions :

### A. Ligands and Complexes :

2-Arylazoimidazoles (1) are  $\alpha$ -diimine type N,N chelating ligand and are synthesized by coupling imidazole with diazonium ions at pH 7. The purification is made *via* extraction by 2(N)HCl and reprecipitated with Na<sub>2</sub>CO<sub>3</sub><sup>8,9</sup>. There are two heterocyclic N-centres; pyrrolic N(1) is a soft donor centre while pyridinic N(3) is hard donor centre<sup>10</sup>. Five membered chelate structure is developed *via* coordination through heterocyclic-N and azo-N. Imidazole itself and its derivatives in bioactive systems bind through N(3) to transition metals<sup>2</sup>. Soft acids like Ag(I), Cu(I) generally coordinate through pyrrolic centre N(1)<sup>6</sup>.

The complexes are synthesized on stirring methanolic solution of ligand and metal salts in methanol or aqueous solution. Pb(II) (2), Ag(I) (3) and Pd(II) (4) complexes are precipitated immediately after addition of salt solution while UO<sub>2</sub>(VI) (5)

complexes are obtained on refluxing the methanolic solution for a period of 3 hr. The complexes so obtained are filtered, washed with water or MeOH-water and dried in vacuo. The complexes are in **Table VII.1** and analytical data are given in **Table VII.2**.

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

The molar conductance measurements suggest uranyl complexes are 1:2 conductor in DMF. Ag(I) (3) and Pd(II) (4) complexes are almost insoluble even in DMSO, DMF while Pb(II) (2) and UO<sub>2</sub>(VI) (5) complexes are soluble in these solvents. Due to their insolubility in common organic solvents the molecular weight measurements could not be performed.

The complexes (2-4) are thermally stable even at higher temperature than 300°C. Uranyl complexes (5) lose weight at 120-140°C correspond to two equivalent of water molecules and ligands are released at 350° -400°C. These complexes undergo complete decomposition above 600°C first gradually and then rapidly to the final residue without giving any intermediate.

### **C. Spectral Characterisation :**

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

The electronic spectra of (2) - (5) are recorded in DMSO while

Table-VII.1

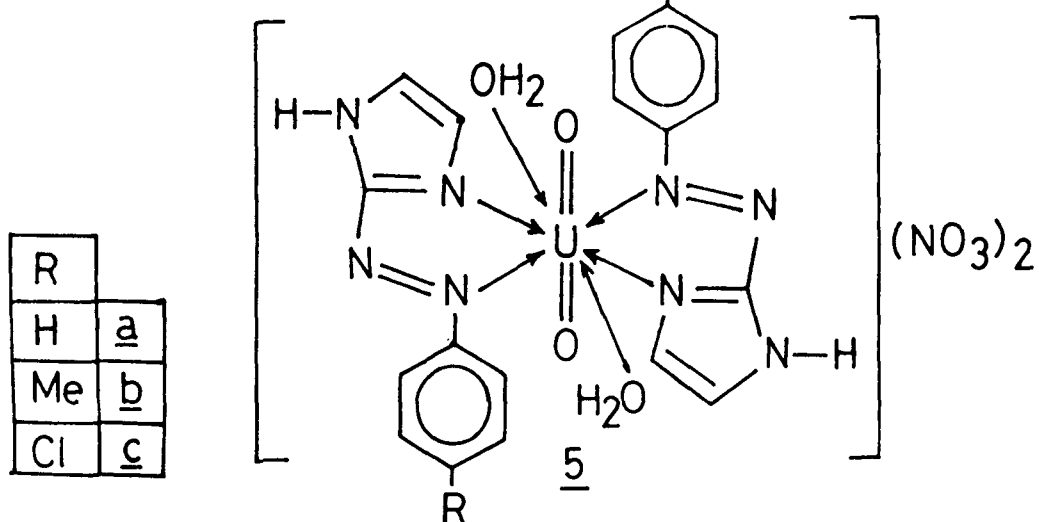
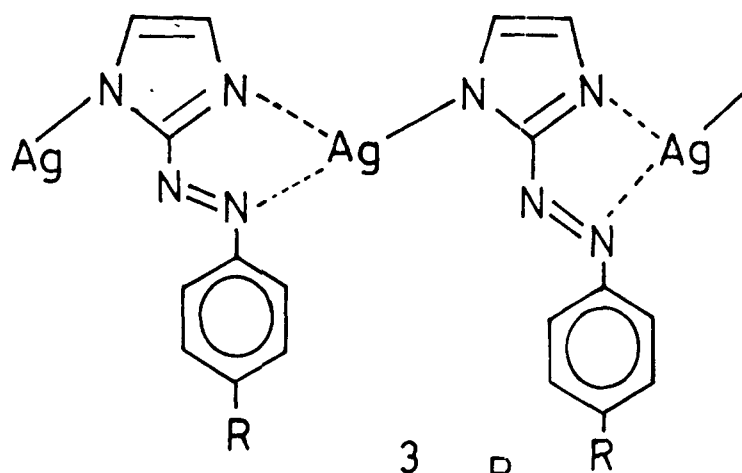
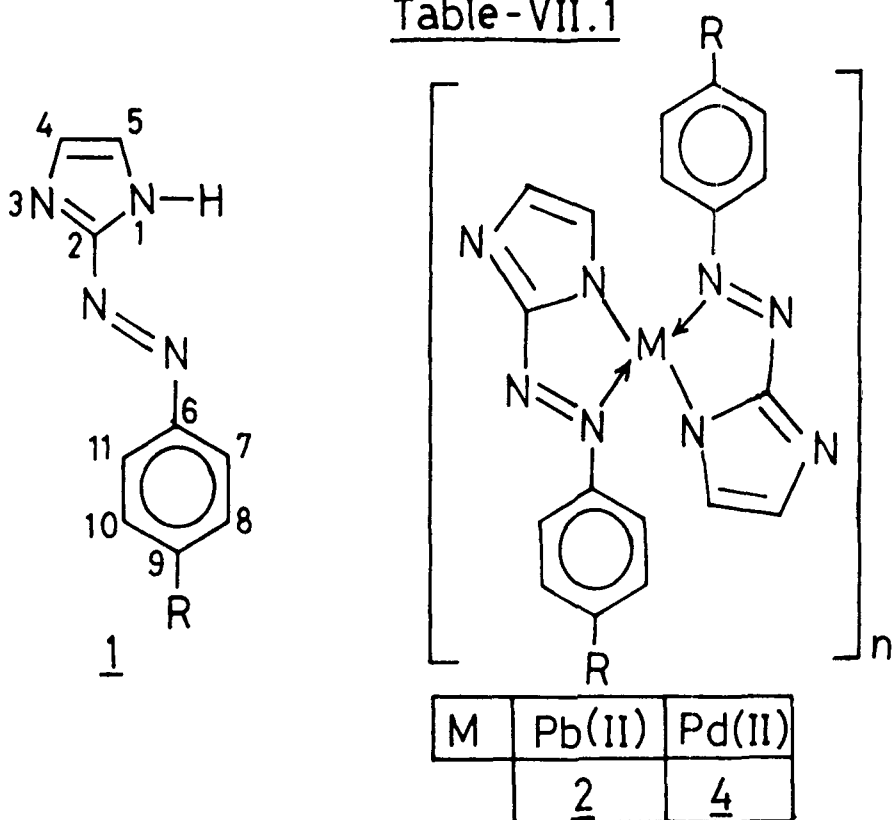


Table VII.2

*Microanalytical data of complexes (2) - (5)*

Complex	Found (calcd)%			
	C	H	N	M
[Pb( <u>1a</u> ) <sub>2</sub> ] ( <u>2a</u> )	38.94 (39.20)	2.66 (2.54)	20.08 (20.33)	39.24 (37.56)
[Pb( <u>1b</u> ) <sub>2</sub> ] ( <u>2b</u> )	41.28 (41.59)	3.30 (3.11)	19.59 (19.41)	34.04 (35.88)
[Pb( <u>1c</u> ) <sub>2</sub> ] ( <u>2c</u> )	34.64 (34.95)	1.67 (1.94)	18.39 (18.12)	35.27 (33.49)
[Ag( <u>1a</u> ) ] ( <u>3a</u> )	38.55 (38.70)	2.64 (2.51)	19.77 (20.07)	36.26 (38.71)
[Ag( <u>1b</u> ) ] ( <u>3b</u> )	41.12 (40.96)	2.91 (3.07)	19.32 (19.11)	35.09 (36.86)
[Ag( <u>1c</u> ) ] ( <u>3c</u> )	34.61 (34.45)	2.08 (1.91)	17.68 (14.86)	33.79 (34.45)
[Pd( <u>1a</u> ) <sub>2</sub> ] ( <u>4a</u> )	47.88 (48.17)	3.26 (3.12)	25.11 (24.98)	-
[Pd( <u>1b</u> ) <sub>2</sub> ] ( <u>4b</u> )	51.24 (50.38)	3.52 (3.78)	23.88 (23.51)	-
[Pd( <u>1c</u> ) <sub>2</sub> ] ( <u>4c</u> )	41.47 (41.75)	2.42 (2.32)	21.47 (21.65)	-
[UO <sub>2</sub> ( <u>1a</u> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] (NO <sub>3</sub> ) <sub>2</sub> ( <u>5a</u> )	28.12 (27.98)	2.71 (2.58)	17.69 (18.08)	28.94 (30.75)
[UO <sub>2</sub> ( <u>1b</u> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] (NO <sub>3</sub> ) <sub>2</sub> ( <u>5b</u> )	30.12 (29.93)	3.10 (2.99)	17.29 (17.46)	30.93 (29.68)
[UO <sub>2</sub> ( <u>1c</u> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] (NO <sub>3</sub> ) <sub>2</sub> ( <u>5c</u> )	25.84 (25.62)	2.26 (2.14)	16.49 (16.61)	26.82 (28.23)

the same of (1) are recorded in  $\text{CHCl}_3$ . The saturated solution of Ag(I) and Pb(II) complexes are taken due to insolubility of these two complexes. The free ligands absorb at 285 and 375nm. The complexes exhibit around ~290 and 380nm due to intraligand charge transfer and for the complexes (5) a new band around 402nm which is absent in free ligand may be due to apical oxygen  $\rightarrow f^0 (U)$  transition<sup>11</sup>.

ii) *IR Spectra:*

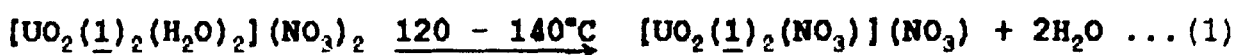
In the IR spectra of the ligands  $\nu(\text{N-H})$  2600  $\text{cm}^{-1}$ ,  $\nu(\text{N=N})$  1400-1410  $\text{cm}^{-1}$ ,  $\nu(\text{C=N})$  1580-1600  $\text{cm}^{-1}$  and other bands 1500-1300, 790, 775, 700-660  $\text{cm}^{-1}$ , correspond to imidazole moiety are observed. The complexes (2 - 4) do not exhibit any absorption due to N-H stretching that suggests deprotonation of this functional and pyrrolic N(1)-coordination. In uranyl complexes (5)  $\nu(\text{N-H})$  is red shifted to 2525  $\text{cm}^{-1}$  and defines quite different coordination mode. A broad medium intense band centered at 3550  $\text{cm}^{-1}$  is designated as coordinated water<sup>12</sup> and confirmed from thermal studies. The N=N stretching mode varies peculiarly in complexes. It is red shifted by 50-60  $\text{cm}^{-1}$  in palladium(II) complexes (4) and in uranyl complexes (5) by 20-30  $\text{cm}^{-1}$ . While

this band almost remain insensitive (shifted by  $\sim 5 \text{ cm}^{-1}$ ) in Pb(II) (2) and Ag(I) (3) complexes. This suggests azo-N coordinates in former complexes (4 and 5) and maintains five membered chelate structure. In Pb(II) and Ag(I) complexes this remains free. The structural studies of Ag-imidazole system suggests a complex packing of polymeric chain containing linearly coordinated silver atoms bridged by imidazolate ligands<sup>6</sup> The similar argument may be extended in our cases to explain the polymeric behaviour of Pb(II), Ag(I) and Pd(II) complexes. Class b character of these metal ions satisfy their ionic charges in the complexes via N(1)-H dissociation and coordination number may be fulfilled by imidazolate bridging from neighbouring molecule and/or azo-N coordination giving five membered chelate structure. Selected IR data are collected in **Table VII.3.**

The uranyl complexes (5) exhibit a sharp single high intense peak at  $1360 \text{ cm}^{-1}$  for ionic nitrate. The complexes obtained from thermal dehydration are analysed by IR spectra. A sharp stretch at  $1360\text{-}1370 \text{ cm}^{-1}$  corresponds to  $\text{NO}_3^-$  and other stretches at



1540-1550, 1350-1355, 1020-1025, 810-815 and 750-755  $\text{cm}^{-1}$  are assigned to chelated  $\text{ONO}_2$  group<sup>13</sup>. Thus two coordinated water molecules are eliminated and the stereochemistry is satisfied by shifting the counter ion from the outside of the coordination sphere as shown in equation (1). The dehydrated complex does not absorb water



molecules reversely when exposed to air for several days and is 1:1 electrolyte.

Dioxouranium complexes of 2,2-bipyridyl (N,N-chelating ligand) are structurally characterised<sup>14</sup>. They are of  $[\text{UO}_2(\text{bpy})(\text{NO}_3)_2]$ . Both nitrate groups act as bidentate chelator. Other complexes of N,N-chelating ligand from five membered heterocycle imidazole type frame viz. 2, (2-pyridyl)-benzimidazole (PBH), 2,2-biimidazole ( $\text{H}_2$  Biim) of dioxouranium are all bis complexes of the formulae  $\text{UO}_2\text{L}_2(\text{NO}_3)_2$  (L= PBH,  $\text{H}_2$  Biim)<sup>4</sup>. Herein the uranyl complexes are all ionic bis complexes  $[\text{UO}_2(\underline{1})_2(\text{H}_2\text{O})](\text{NO}_3)_2$  (5). The presence of five membered ring may provide less steric hindrance and may allow the ligand association to increase coordination number. In addition the IR spectra show characteristic absorption bands at 920-900  $\text{cm}^{-1}$  assigned to  $\nu$  as( $\text{UO}_2$ ) of the  $\text{UO}_2^{2+}$  moiety<sup>15,16</sup>. A weak

Table VII.3

*Some selected IR stretching data and conductance measurement*

	IR data <sup>a</sup> , cm <sup>-1</sup>						$\Lambda_M^b$ Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
	$\nu(N-H)$	$\nu(N=N)$	$\nu(C=N)$	Imidazole stretchings			
(2a)	-	1396	1600	1380	795	750	5
(2b)	-	1390	1588	1372	800	755	4
(2c)	-	1405	1605	1395	810	760	8
(3a)	-	1400	1600	1390	800	755	-
(3b)	-	1400	1605	1395	790	760	-
(3c)	-	1410	1600	1380	785	765	-
(4a)	-	1355	1580	1400	800	775	-
(4b)	-	1340	1572	1390	810	765	-
(4c)	-	1360	1585	1405	800	770	-
(5a) <sup>c</sup>	2525	1380	1605	1390	800	780	140
(5b) <sup>c</sup>	2520	1375	1600	1380	815	770	160
(5c) <sup>c</sup>	2528	1390	1610	1400	810	775	145

<sup>a</sup>In KBr disk; <sup>b</sup>In DMF; <sup>c</sup> $\nu(UO_2)$ : (5a), 915; (5b), 920; (5c), 900 cm<sup>-1</sup>  
and  $\nu(NO_2)$ : (5a), 1365; (5b), 1370; (5c), 1360 cm<sup>-1</sup>.

stretching around  $300-320\text{ cm}^{-1}$  may be assigned to  $\nu(\text{U-N})$ .

iii)  $^1\text{H NMR}$ :

$^1\text{H}$  NMR spectra of uranium(VI), and lead(II) complexes are collected in  $\text{DMSO-d}_6$ . Due to sparing solubility of palladium(II) and silver(I) complexes do not provide good spectra to analyse. There are three well-defined resonances in the aromatic region and spectral data are collected in **Table VII.4**. Representative spectrum shown in **Fig. VII.C**. Imidazolic 4- and 5-H protons resonate at the same positions at upper field may be due to interconversion of protonic positions<sup>4,10</sup>. Downfield signals are subdivided into two parts of which most downfield resonance may be due to 7- and 11-H supported from integration data and another signal is highly sensitive to substituent at 9-th position; Me-substitution shifts it to upfield due to electron releasing effect of methyl group through +I effect while Cl- substitution shifts it to lower field certainly due to electron withdrawing effect<sup>17</sup>. These signals correspond to symmetrical AA'BB' multiplet. Thus the aryl ring protons are established on complexation the protons are downfield shifted compared to free ligand suggesting metal coordination. N(1)-H proton signal does not appear even at appreciably high concentration in  $\text{DMSO-d}_6$ ,

Table VII.4

*<sup>1</sup>H NMR spectral data in DMSO-d<sub>6</sub>*

Complex	$\delta$ , ppm			
	4,5-H	7,11-H	9-H	Me
(1a) <sup>a</sup>	7.37	7.98	7.40	-
(1b) <sup>b</sup>	7.34	7.96	7.16	2.37
(1c) <sup>c</sup>	7.38	8.05	7.58	-
(2a)	7.55	7.98	7.41	-
(2b)	7.54	7.92	7.18	2.35
(2c)	7.56	8.02	7.55	-
(5a)	7.48	7.95	7.59	-
(5b)	7.46	7.94	7.32	2.36
(5c)	7.52	8.08	7.64	-

<sup>a</sup> $\delta$ (N-H), 10.4;  $\delta$ (9-H), 7.40; <sup>b</sup> $\delta$ (N-H), 10.3; <sup>c</sup> $\delta$ (N-H), 10.4 ppm.

this may be due to rapid exchange of N(1)-H in the solvent<sup>4</sup>. In Pb(II) complexes (2) imidazolic protons 4-H and 5-H suffer sufficient downfield shifting while aryl protons remain almost unperturbed. This supports our previous proposition of imidazole coordination while arylazo group remains free.

#### D. *Epilogue* :

Thus a comparison has made between the binding of metal ions to N(1) vs. N(3) centre. The physical and spectroscopic investigation suggest that Pb(II), Ag(I) and Pd(II) preferentially bind pyrrolic N(1) centre and chelate structure maintained in palladium(II) complexes (4) *via* coordination through N(a) (azo) centre. The polymerisation is continued through N(3) coordination of imidazolate fragment to the neighbouring metal centre. The hard acid  $UO_2(VI)$  binds N(3) and chelation is achieved through azo-N coordination.

### 3. Experimental :

#### A. *Materials* :

Aromatic amines, imidazole,  $AgNO_3$  were obtained from E. Merck.  $UO_2(NO_3)_2 \cdot 6H_2O$ ;  $Pb(OAc)_2 \cdot 3H_2O$  were SD's Lab Chem Chemicals.  $PdCl_2$  was obtained from Arrora Mathey and from it  $Na_2PdCl_4$  was prepared

by usual procedure<sup>18</sup>.  $\text{Na}_2\text{CO}_3$ ,  $\text{HCl}$ ,  $\text{CaCl}_2$  and the solvents  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CN}$ ,  $\text{DMF}$ ,  $\text{DMSO}$  etc. were of reagent grade purchased from Qualigence.

### **B. Physical Measurements :**

The elemental analyses, IR, UV-VIS spectra conductance measurement and  $^1\text{H}$  NMR spectra were recorded as in chapter I. Uranium, Silver and Lead were determined gravimetrically<sup>19</sup>.

### **C. Preparation :**

#### **1. Ligands :**

The ligands 2-(arylo) imidazoles (1) were prepared by reported procedure<sup>12</sup>. The details are given as follows for (1a). To an aqueous solution (25ml) of imidazole (3.0 g, 0.044 mol) and  $\text{Na}_2\text{CO}_3$  (7.0 g, 0.066 mol) at  $5^\circ\text{C}$  diazotized solution of aniline (4 g, 0.043 mol) was added dropwise with continuous stirring, The temperature was controlled at ice cold condition. The orange compound so precipitated was filtered, washed with cold water and extracted with 2(N)HCl (15 ml x 2). The solution was neutralized by powder  $\text{Na}_2\text{CO}_3$  and pH of the solution was checked at 7. The precipitate was filtered, washed and dried. The yield was 55%;

m.p.  $190 \pm 1^\circ\text{C}$ . The yield of other ligands vary 50-60%. Their melting points are  $235 \pm 2^\circ\text{C}$  (1b);  $240 \pm 1^\circ\text{C}$  (1c).

## 2. Complexes :

### 2.a. Lead(II)(2), silver(I)(3) and palladium(II)(4) complexes :

The preparation follows common procedure. To methanolic solution (15 ml) of (1a) (0.35g, 2.03 mmol) aqueous solution of  $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$  (0.38 g, 1 mmol) /  $\text{AgNO}_3$  (0.35 g, 2.06 mmol) /  $\text{Na}_2\text{PdCl}_4$  (0.3 g, 1.02 mmol) was added in dropwise precipitate appeared. The solution was stirred for about 1 h and the precipitate was filtered, washed and dried over  $\text{CaCl}_2$ . The yield was 80-90%. Other complexes were prepared similarly and the yield was as above.

### 2.b. Uranyl complexes (5a) :

To methanolic solution (20 ml) of 1a (0.35 g, 2.03 mmol)  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.5 g, 1.0 mmol) in the same solvent was added in dropwise and the solution was refluxed over steam bath for a period of 3 h. The solution volume was reduced and the precipitate was filtered, washed with  $\text{MeOH-H}_2\text{O}$  (1:1 v/v) and dried in vacuo, the yield was 55%. Other complexes were prepared similarly and yield varied 50-65%.

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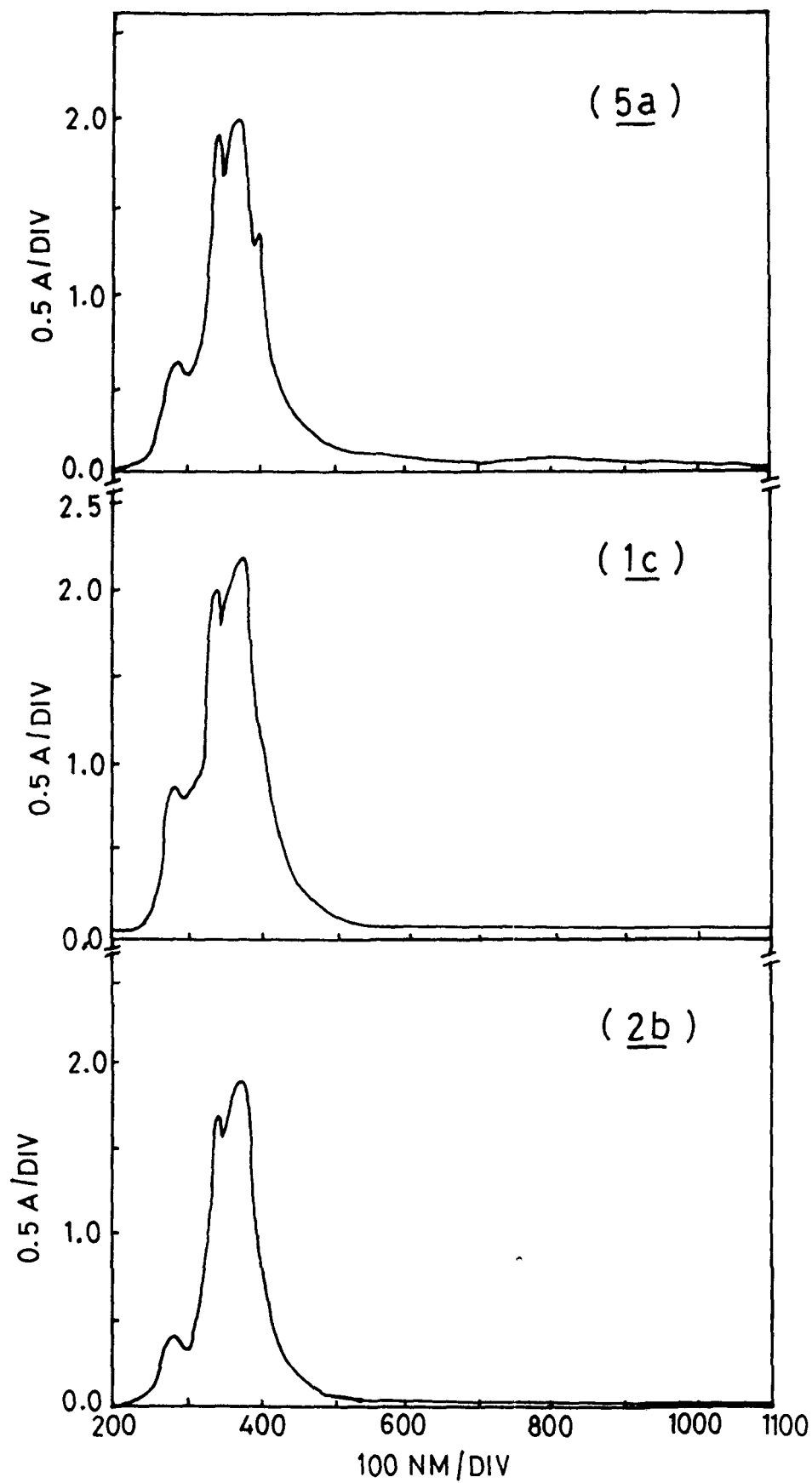
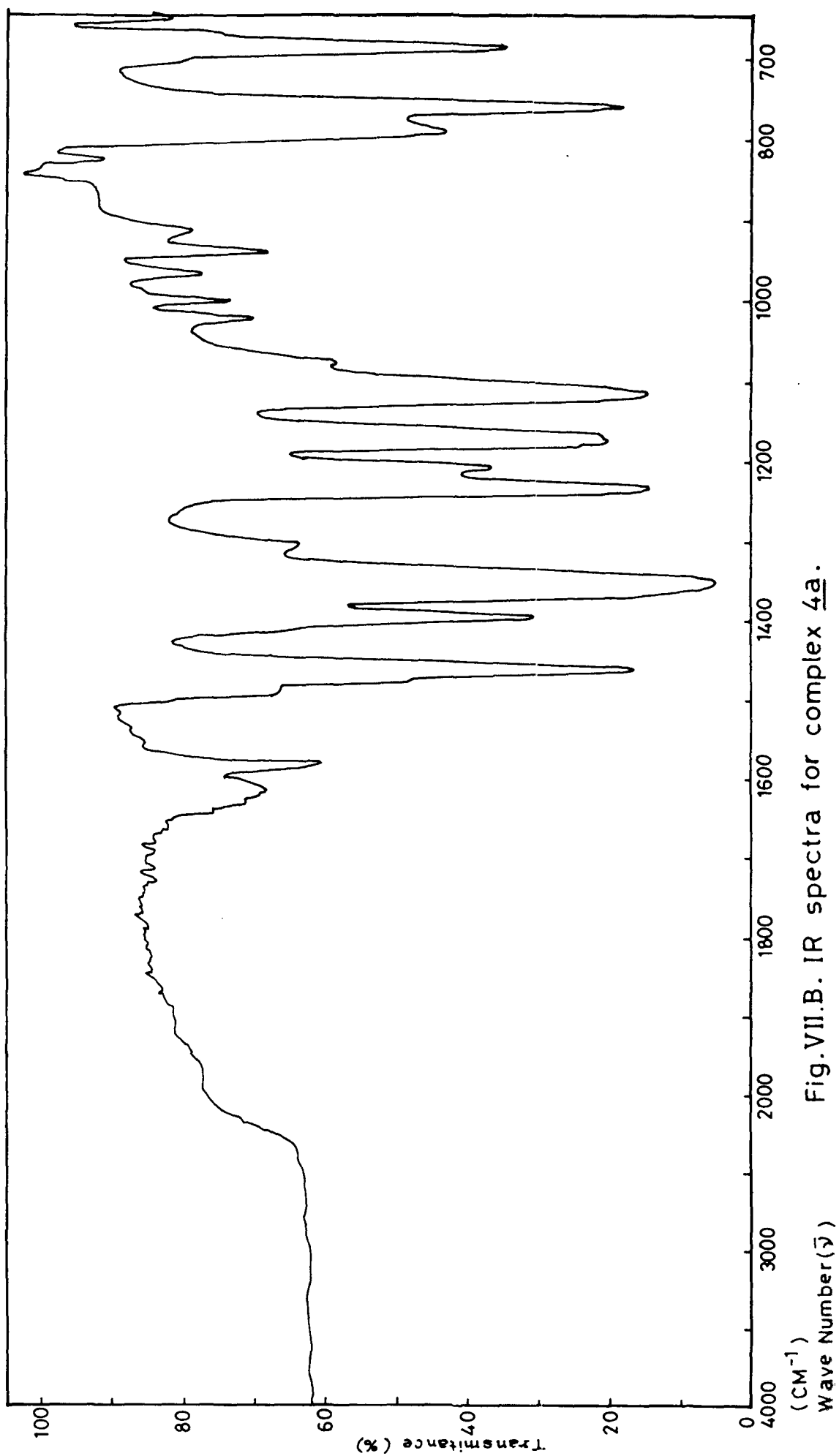


Fig.VII.A. UV-VIS spectra.



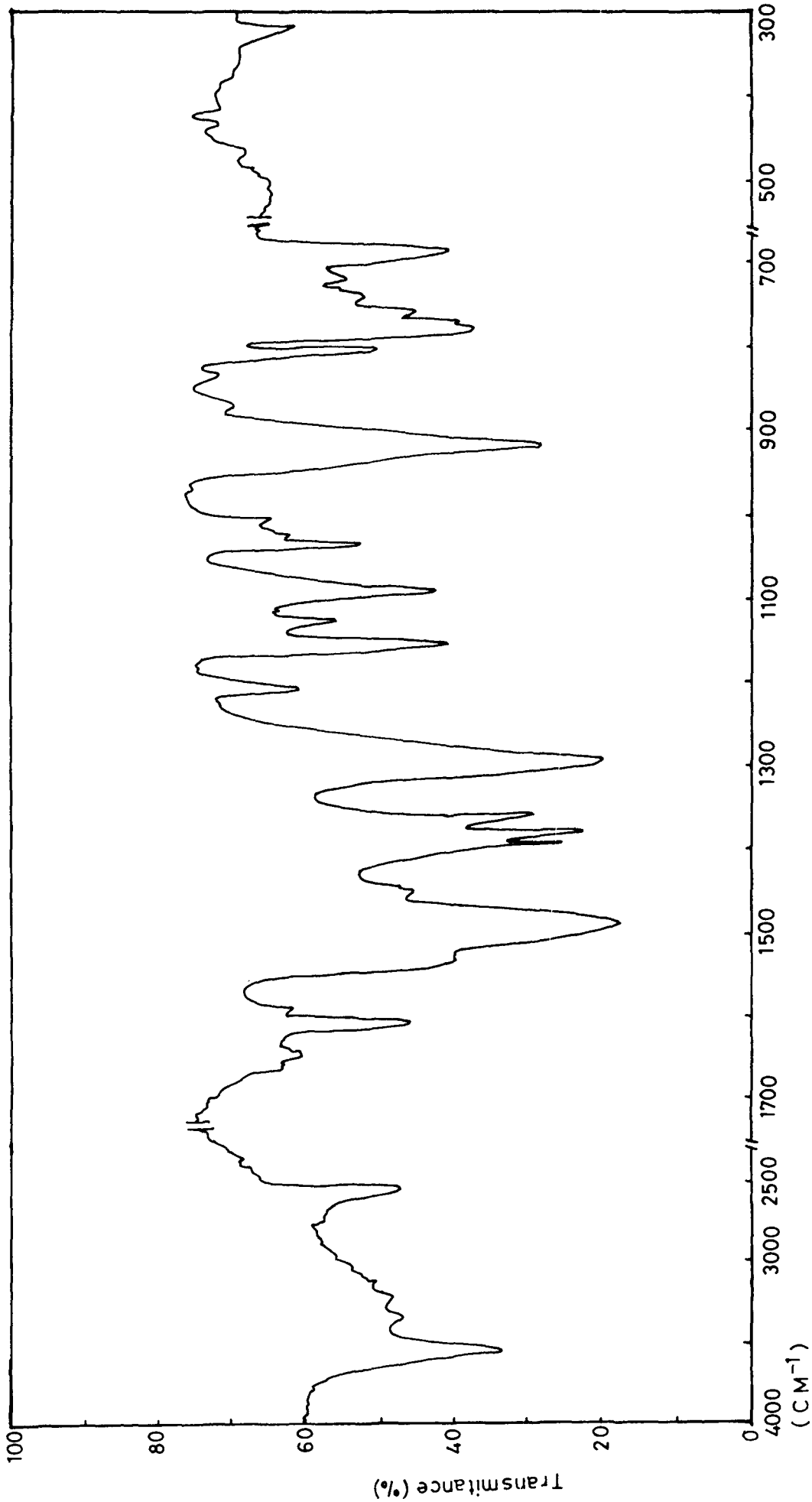
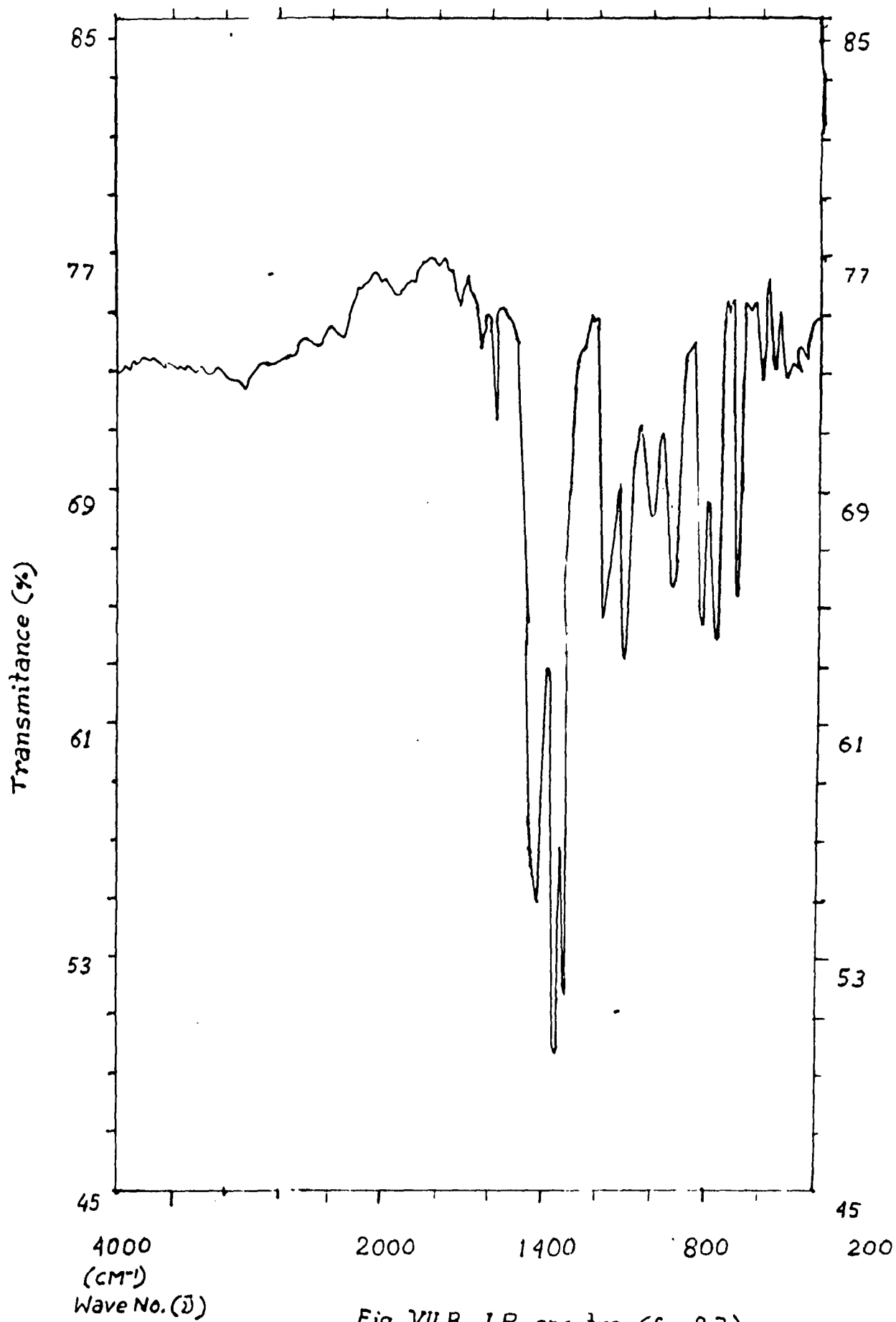


Fig. VII.B. IR spectra for 5a.

Wave Number ( $\bar{\nu}$ )



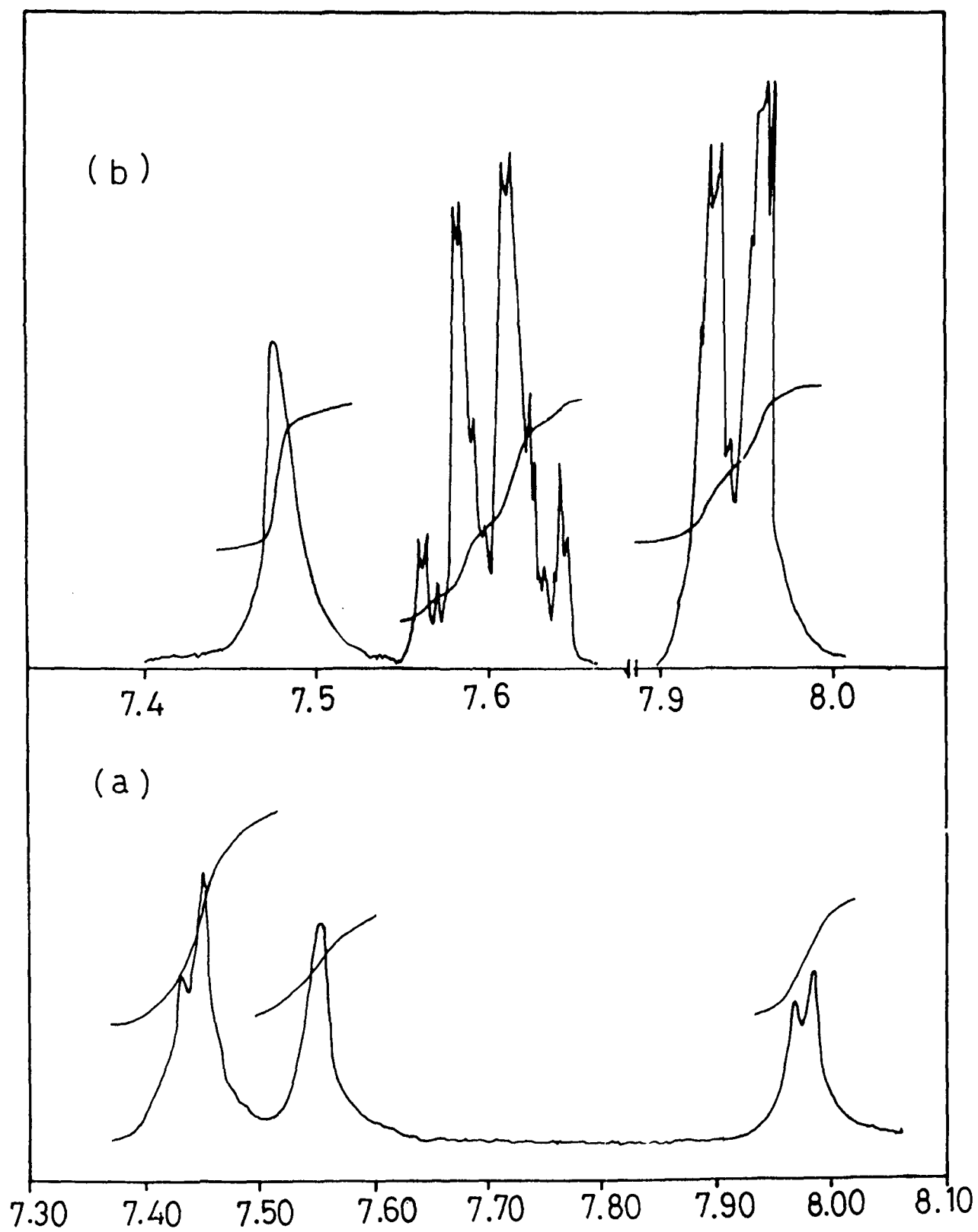


Fig.1.  $^1\text{H}$  NMR spectra of (a) (2a) and (b) (5a) in  $\text{DMSO-d}_6$ .