

# CHAPTER V

## *Synthesis and characterisation of mixed ligand complexes of $UO_2(L-L)_2$ ( $L-L = acac, bzac, ox$ ) and heterocyclic bases*

Three series of mixed ligand uranyl complexes  $UO_2(L-L)_2B$  :  $L-L =$  acetylacetonato(acac) (1), benzoylacetonato(bzac) (2) and 8-hydroxyquinolinato(ox) (3) and  $B =$  imidazole(a), 2-aminopyridine(b), pyrimidine(c) and 2-aminopyrimidine(d) have been synthesised. The complexes are characterised by elemental analysis, IR, electronic spectroscopy and thermal study.  $\nu(O=U=O)$  is highly sensitive to electron releasing behaviour of coordinated heterocyclic bases.

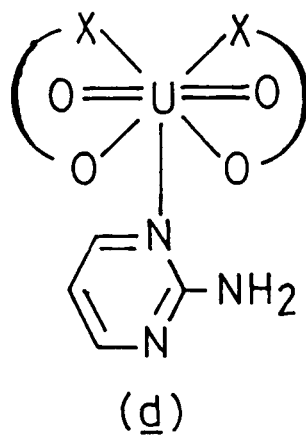
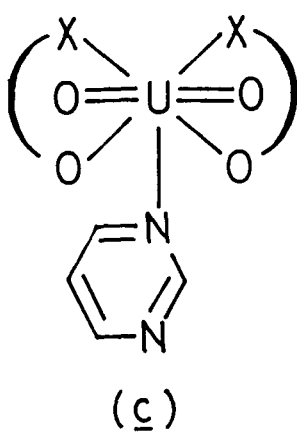
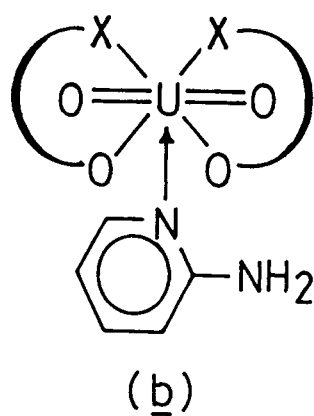
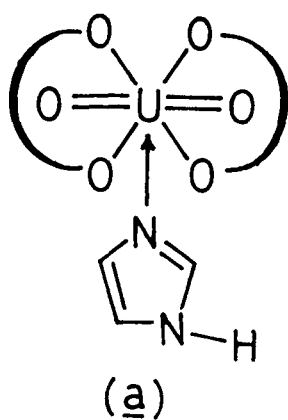
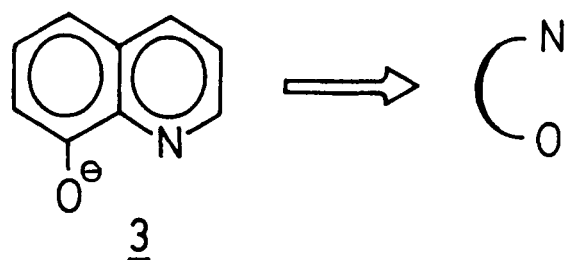
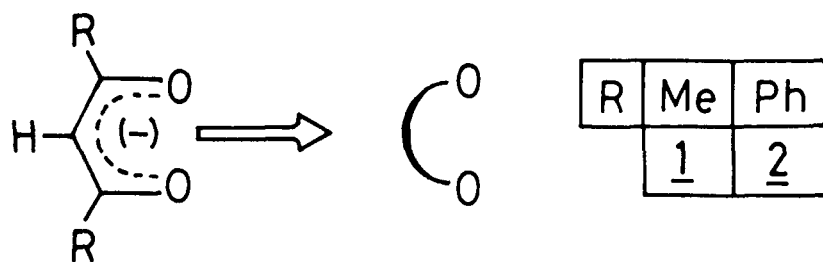
## 1. Introduction :

The versatility of  $\beta$ -diketones<sup>1,2</sup> and 8-hydroxyquinoline<sup>2,3</sup> as chelating ligands have already been established. They are O-O and N-O chelators respectively. The coordination chemistry of nontransition and transition metals of these ligands are well known in literature<sup>1-3</sup>. Many of the divalent metal ions form square planar complexes<sup>1j</sup> are readily adducted with neutral ligands containing nitrogen or oxygen as donor atoms. Of the various donor ligands heterocyclic nitrogen bases are of specially used due to their biological importance. In this chapter we describe the hitherto unknown mixed ligand complexes of  $UO_2(L-L)_2$  (L-L=acetylacetonato(acac), benzoylacetonato(bzac) and 8-hydroxyquinolinato(ox)) and heterocyclic bases.

## 2. Results and Discussions :

### *2.1. Ligands and Complexes :*

Two series of ligands :  $\beta$ -diketones(1 ,2) and 8-hydroxyquinoline(3) are used in this work. The ligands and complexes described in this chapter are listed in **Table V.1** The  $\beta$ -diketones (1,2) are mono negative bidentate O,O chelators and 8-hydroxyquinoline(3) is monobasic bidentate N,O chelators. The

Table - V.1

X = O / N

complexes were synthesised by refluxing either the mixture of stoichiometric amount of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and bidentate chelating ligand or previously synthesised  $\text{UO}_2(\text{LL})_2$  followed by one equivalent of heterocyclic base. Heterocyclic bases are imidazole(imz), 2-aminopyridine(2-apy), pyrimidine(pym) and 2-aminopyrimidine(2-apym).

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

The complexes do not have a sharp melting point and decomposed at high temperature. The complexes are, in general, sparingly soluble in organic solvents like methanol, chloroform, acetonitrile, benzene etc. The molecular weights of the complexes could not be determined by cryoscopic method or by any other method due to lack of specific arrangements. The molecular conductances in DMSO ( $\Lambda_m$  3-10  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) show that complexes are non-electrolytes indicating that the chelate anions are covalently bonded in all the cases.

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

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

The electronic spectra of saturated solution of the complexes have been recorded in DMSO. Imidazole (1a - 3a) and

Table - V.2

*Analytical data of dioxuranium(VI) complexes*

Complex	Found (Calcd.)%			
	C	H	N	U
$(C_5H_7O_2)_2(C_3H_4N_2)UO_2$ ( <u>1a</u> )	28.89 (29.10)	3.21 (3.36)	5.34 (5.22)	46.10 (44.40)
$(C_5H_7O_2)_2(C_5H_6N_2)UO_2$ ( <u>1b</u> )	31.91 (32.03)	3.71 (3.56)	5.11 (4.98)	40.18 (42.35)
$(C_5H_7O_2)_2(C_4H_4N_2)UO_2$ ( <u>1c</u> )	29.72 (30.66)	3.41 (3.28)	5.24 (5.11)	44.44 (43.43)
$(C_5H_7O_2)_2(C_4H_5N_3)UO_2$ ( <u>1d</u> )	29.61 (29.84)	3.26 (3.38)	7.64 (7.46)	40.18 (42.27)
$(C_{10}H_9O_2)_2(C_3H_4N_2)UO_2$ ( <u>2a</u> )	40.48 (41.82)	3.46 (3.33)	4.48 (4.24)	38.14 (36.06)
$(C_{10}H_9O_2)_2(C_5H_6N_2)UO_2$ ( <u>2b</u> )	42.69 (43.73)	3.64 (3.50)	4.24 (4.08)	35.27 (34.69)
$(C_{10}H_9O_2)_2(C_4H_4N_2)UO_2$ ( <u>2c</u> )	42.62 (42.86)	3.18 (3.27)	4.01 (4.17)	36.28 (35.42)
$(C_{10}H_9O_2)_2(C_4H_5N_3)UO_2$ ( <u>2d</u> )	41.24 (41.92)	3.15 (3.35)	6.28 (6.11)	36.07 (34.64)
$(C_9H_6NO)_2(C_3H_4N_2)UO_2$ ( <u>3a</u> )	41.19 (40.26)	2.74 (2.56)	4.64 (4.47)	36.11 (38.03)
$(C_9H_6NO)_2(C_5H_6N_2)UO_2$ ( <u>3b</u> )	41.24 (42.33)	2.58 (2.76)	4.40 (4.29)	38.40 (36.50)
$(C_9H_6NO)_2(C_4H_4N_2)UO_2$ ( <u>3c</u> )	41.64 (41.38)	2.34 (2.51)	4.58 (4.39)	39.08 (37.30)
$(C_9H_6NO)_2(C_4H_5N_3)UO_2$ ( <u>3d</u> )	41.12 (40.43)	2.79 (2.60)	6.32 (6.43)	38.12 (36.45)

2-aminopyridine(1b - 3b) adducts are comparatively more soluble than the rest. Pyrimidine bases have the potential ability of meta related ring nitrogen to form a zigzag polymer chain structure<sup>4</sup>. Here the complexes (1c - 3c) and (1d - 3d) are sparingly soluble. The absorption spectra provide three well defined bands in the regions 245-285, 320-360 and 400-460nm and a shoulder in the high energy region 210-230nm (Table V.3). The shoulder and the first band may be ascribed  $\Pi \rightarrow \Pi^*$  intraligand charge transfer transitions, to those of the complexing agents<sup>2</sup> and heterocyclic bases<sup>5</sup>. The third band which is absent in the spectra of ligands, is due to apical oxygen  $\rightarrow f^0(U)$  transition<sup>6</sup> within the uranyl entity.

(ii) *IR spectra :*

The selected IR spectral data of the complexes are presented in Table V.3. Imidazole adducts (1a - 3a) exhibit strong band  $\sim 3500 \text{ cm}^{-1}$  corresponds to  $\nu(\text{N-H})$  which is slightly red shifted ( $\Delta\nu = 10 \text{ cm}^{-1}$ )<sup>5a</sup> suggesting N-H group remains almost unaffected and other nitrogen coordinates. 2-aminopyridine adducts (1b - 3b) exhibit N-H stretching<sup>11</sup>  $\nu_{\text{as}}$  3420-3430;  $\nu_{\text{s}}$  3335-3345  $\text{cm}^{-1}$  and 2-aminopyrimidine adducts (1d - 3d) show the N-H bands  $\nu_{\text{as}}$  3535 - 3545;

$\nu_{3450-3460} \text{ cm}^{-1}$  those are either slightly red shifted or remain unchanged upon coordination. These suggest that  $-\text{NH}_2$  group remains free and pyridine or pyrimidine nitrogen coordinates. The  $\nu(\text{C-O})$  ( $\beta$ -diketone) band in complexes (1-2) appears at 1570-1590  $\text{cm}^{-1}$  while  $\nu(\text{C-O})$  (phenolic) (3) 1580-1595  $\text{cm}^{-1}$  is blue shifted upon coordination with uranium<sup>7</sup>. Four characteristic ring stretching modes of heterocyclic groups appear at :

<u>Imidazol</u> (in $\text{cm}^{-1}$ ) ( <u>1a</u> - <u>3a</u> )	<u>2-aminopyridine</u> <sup>5b</sup> (in $\text{cm}^{-1}$ ) ( <u>1b</u> - <u>3b</u> )	<u>pyrimidindine</u> <sup>5b</sup> (in $\text{cm}^{-1}$ ) ( <u>1c</u> - <u>3c</u> )	<u>2-aminopyrimidine</u> <sup>3b</sup> (in $\text{cm}^{-1}$ ) ( <u>1d</u> - <u>3d</u> )
1565 - 1560	1610 - 1590	1580 - 1565	1570 - 1555
1510 - 1500	1570 - 1560	1490 - 1460	1500 - 1485
1468 - 1454	1520 - 1500	1420 - 1400	1460 - 1445
1340 - 1330	1460 - 1440	1375 - 1360	1340 - 1330

These are slightly blue shifted on coordination to metal ion. All the complexes display very strong bands 890-930  $\text{cm}^{-1}$  assignable to  $\nu_3(\text{O=U=O})$  modes<sup>8</sup>. Imidazole adducts (1a - 3a) exhibit a marked decrease in  $\nu(\text{O=U=O})$ . Compare to pyrimidine derivatives (1c - 3c). This may be due to electron releasing behaviour of the respective hetrocycle<sup>9</sup>. The force constant ( $F_{\text{U=O}}$ ) for the U=O band has been calculated according to the published method<sup>11</sup> and the

values are 6.58-7.15 mdyne/A<sup>0</sup> <sup>8</sup>. The  $F_{U=O}$  in each case was used to calculate the U=O band length using Jone's formula<sup>10</sup> and the present values (1.71 - 1.74 A<sup>0</sup>) are in the expected range (1.60 - 1.92 A<sup>0</sup>)<sup>8a,12</sup>. The stretching at 410-480 and 515-545 cm<sup>-1</sup> are assignable to  $\sqrt{(U-O)^2}$ . The position of  $\sqrt{(U-N)}$  bond is difficult to assign.

**Table - V.3**  
*Selective infrared and UV-VIS spectral data of complexes*

Complex	$\nu, \text{cm}^{-1}$				UV-VIS (in nm)
	$\nu(N-H)$	$\nu(UO_2)$	$\nu(C-O)$	$\nu(U-O)$	
<u>1a</u>	3490	892	1585	420, 525	218, 245, 322, 402
<u>1b</u>	3420, 3335	900	1580	415, 535	215, 260, 325, 420
<u>1c</u>	-	920	1570	412, 515	220, 250, 340, 450
<u>1d</u>	3540, 3453	910	1575	412, 520	230, 260, 360, 410
<u>2a</u>	3495	895	1592	422, 540	220, 280, 330, 405
<u>2b</u>	3425, 3340	905	1585	415, 552	222, 262, 340, 440
<u>2c</u>	-	925	1580	410, 535	225, 260, 320, 460
<u>2d</u>	3545, 3460	915	1585	415, 540	220, 250, 330, 415
<u>3a</u>	3500	900	1595	475, 525	223, 245, 338, 418
<u>3b</u>	3430, 3345	905	1585	470, 520	225, 240, 340, 430
<u>3c</u>	-	928	1580	485, 535	225, 248, 340, 430
<u>3d</u>	3535, 3450	915	1585	480, 530	223, 250, 335, 435

#### D. Thermal Analysis :

The complexes were subjected to thermal analysis (**Table V.4**) and



**Table - V.4**  
*TGA data of dioxouranium(VI) complexes*

Complex	Mass loss	First phase	% Final residue	
	starts at (°C)	is reached (°C)	Theo.	Expt.
<u>1a</u>	275	600	52.36	50.82
<u>1b</u>	230	600	49.94	46.77
<u>1c</u>	300	620	49.85	45.91
<u>1d</u>	145	590	49.24	48.98
<u>2a</u>	280	610	42.52	40.59
<u>2b</u>	240	600	40.91	40.01
<u>2c</u>	290	620	41.76	39.78
<u>2d</u>	150	595	40.85	38.52
<u>3a</u>	275	600	44.83	41.24
<u>3b</u>	245	630	43.04	42.32
<u>3c</u>	310	600	43.99	42.23
<u>3d</u>	140	580	42.98	41.18

the monodentate ligand is evolved by a one step process in the 140-300°C temperature range followed by the decomposition of the complex in the range 400-650°C to the final residue  $U_3O_8$  without giving any intermediate<sup>12</sup>. Isolation of the first step thermally pyrolysed complex is characterised by spectroscopic and elemental analyses and is established as unadducted  $UO_2(LL)_2$ .

### ***x. Epilogue :***

The foregoing discussion suggests in the adducts the linear  $O=U=O$  is perpendicular to planar pentagon formed by two bidentate ligands and heterocyclic base (**Table V.1**). The coordinated base is thermally susceptible and the pyrimidine adducts are found to be highest stability.

## **Experimental :**

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

Uranyl acetate and Uranyl nitrate were purchased from BDH, acetylacetone was obtained from Ubichem Ltd., Oxine was taken from Loba-Chemie Industrial Co., Imidazole from Glaxo, benzoylacetone, pyrimidine, 2-aminopyrimidine and 2-aminopyridine were Aldrich reagents. Methanol, chloroform, acetonitrile, benzene, DMSO etc. were SD chemical grade.

**B. Physical Methods :**

The elemental analysis, IR, thermal study, UV-VIS and conductance measurement were carried out as in chapter I. Uranium was determined by standard procedure<sup>13</sup>.

**C. Preparation :**

The complexes were synthesised by two different procedures.

Method A : In a typical process, to a methanolic solution of acetylacetone (0.2g; 2.0 mmol) was added with stirring  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.5g; 1.0 mmol) and refluxed for 1 hr. on steam bath. This resulting solution was filtered at hot condition immediately. To this filtrate imidazole (0.07g; 1 mmol) was added and further refluxed for 1 hr. The orange red precipitate was filtered, washed with methanol and dried in vacuo. Yield 70%. The yield of other complexes vary 70-80%.

Method B :  $\text{UO}_2(\text{L-L})_2 \cdot \text{H}_2\text{O}$  (LL=acac,bzac) or  $\text{UO}_2(\text{OX})_2 \cdot \text{HOX}$  were synthesised by reported procedure<sup>2</sup>. To methanolic suspension of  $\text{UO}_2(\text{acac})_2 \cdot \text{H}_2\text{O}$  (0.5g; 1.03 mmol), imidazole (0.07g; 1.0 mmol) was added and refluxed for 1 hr. The orange red product so obtained was filtered, washed with methanol and dried in vacuo; yield 85%. Other complexes were also prepared similarly using 2-aminopyridine, pyrimidine and 2-aminopyrimidine separately in place of imidazole and the yield vary 80-90%.

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