



## URANYL COMPLEXES WITH SOME POLYPHENOLIC LIGANDS

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Solid distorted octahedral complexes of  $\text{UO}_2^{+2}$  ion with resacetophenone (RP); Phloroacetophenone (PA);  $\beta$ -resocyaldehyde (RA), 5-C-prenylgallacetophenone (PG); 2',4'-Dihydroxy-4-methoxychalcone (DMC) and 2,5,7-Trihydroxy-4-methoxy isoflavone (TMI) have been prepared. The information regarding structure and composition is supported by elemental analysis, infra-red, electronic absorption and magnetic studies.

**KEYWORDS:**  $\text{UO}_2^{+2}$  complexes, Polyphenolic ligands, Characterization.

**INTRODUCTION**

The uranyl ( $\text{UO}_2^{+2}$ ) ion is the most common functional unit in the chemistry of U (VI) [1]. In the advent of nuclear energy and the use of Uranium Oxide as reactor fuel, the chemistry of the uranyl ion has played an essential role in the processing of uranium ore, nuclear fuel and nuclear waste [2]. The linear arrangement of  $\text{UO}_2^{+2}$  ion, with extremely short U-O bond lengths, and high thermal and chemical stability reflect some of the unusual properties of this functional group [3]. It is generally agreed that uranium-oxygen bonds in uranyl ion involve six types of U-O interactions. All the uranium compounds are radioactive. However, uranium is usually in deplet form, except in the content of nuclear industry. Deplet uranium consists mainly of  $^{238}\text{U}$  which is a weak alpha emitter, its radioactivity is only hazardous with direct contact or ingestion.  $\text{UO}_2^{+2}$  ion behaves as a hard acceptor. Complexes of uranyl ion are important in the extraction of uranium from its ores and in nuclear fuel processing.  $\text{UO}_2^{+2}$  ion complexes having eight coordination number have been reported [4-5]. The coloured reactions of polyphenols on chromatograms have been reported [6-7]. Keeping in view the importance of uranyl complexes, solid uranyl complexes:

$[\text{UO}_2(\text{C}_8\text{H}_7\text{O}_3)_2(\text{C}_2\text{H}_5\text{OH})_2]$ ,  $[\text{UO}_2(\text{C}_8\text{H}_7\text{O}_4)_2(\text{C}_2\text{H}_5\text{OH})_2]$ ,  $[\text{UO}_2(\text{C}_7\text{H}_5\text{O}_3)_2(\text{C}_2\text{H}_5\text{OH})_2]$ ,

$[\text{UO}_2(\text{C}_{13}\text{H}_{15}\text{O}_4)(\text{C}_2\text{H}_5\text{OH})_4]\text{NO}_3$ ,  $[\text{UO}_2(\text{C}_{16}\text{H}_{13}\text{O}_4)(\text{C}_2\text{H}_5\text{O}_4\text{H})_4]\text{NO}_3$  and  $[\text{UO}_2(\text{C}_{16}\text{H}_{11}\text{O}_4)(\text{C}_2\text{H}_5\text{OH})_4]\text{NO}_3$  of RP, PA, RA, PG, DMC and TMI respectively are reported in present communication. All the six polyphenolic ligands can also be used as potential analytical reagent for the estimation of Uranium.

**MATERIALS AND METHODS**

All the polyphenolic ligands were prepared by reported methods [8-12]. Their purity was checked by single spot on T.L.C. and also supported by their infra red and electronic absorption spectroscopy. All the coloured solid complexes were prepared by mixing the ethanolic solution of  $\text{UO}_2(\text{NO}_3)_2$  and the respective ligand in molar ratio of 1:2. The solid complexes precipitated were separated by

filtration, recrystallised from ethanolic solution and dried in vacuum over anhydrous Calcium Chloride. The solid complexes obtained were found to be stable at room temperature and were not affected by atmospheric moisture. They suffered decomposition above  $225^\circ\text{C}$  without melting. The complexes were found to be insoluble in water. Elemental analysis of the complexes was done by using micro analytical combustion method. The experimental values are in close agreement with the theoretical values (table-I). The uranium content was estimated gravimetrically by getting stable  $\text{U}_3\text{O}_8$  oxide as the end product. IR of the ligands and complexes was done by using KBr pellets recorded on Perkin Elmer 377 grating I R spectrophotometer over the region 4000-200  $\text{cm}^{-1}$ . The electronic absorption spectra of the complexes were recorded as diffuse reflectance spectra on VSU2P (Carl Ziess) spectrophotometer from 50,000 to 12,500  $\text{cm}^{-1}$ . Magnetic study of the complexes was done by using the Guoy method.

**RESULTS AND DISCUSSION**

Elemental analysis (Table-I) is in close agreement with the reported composition of the complexes. Principal bands ( $\text{cm}^{-1}$ ) in the IR spectra of the ligands and complexes are recorded in table II. The comparison of the ligand spectra and the spectra of the complexes shows shifts in the principal bands corresponding to  $\nu(\text{O-H})$ ,  $\nu(\text{C=O})$ ,  $\nu(\text{O-C})$  of the ligands because of complexation with Uranyl ion. In the ligand spectra, the  $\nu(\text{O-H})$  bands due to intramolecular hydrogen bonded hydroxyls appears at 3200, 3500, 3200, 3400, 3300, and 3100  $\text{cm}^{-1}$ ; the  $\nu(\text{C=O})$  bands appears at 1630, 1630, 1670, 1630, 1600, 1630  $\text{cm}^{-1}$  and the  $\nu(\text{O-C})$  bands at 1060, 1060, 1080, 1075, 1040, 1020  $\text{cm}^{-1}$  for resacetophenone; phloroacetophenone; 4,5,7-trihydroxy-3-(p-methoxy)-phenyl-coumarin; 5-C-Prenyl-gallacetophenone; 2',4'-dihydroxy-4-methoxychalcone and  $\beta$ -resocyaldehyde respectively. The shifts in  $\nu(\text{O-H})$ ,  $\nu(\text{C=O})$  and  $\nu(\text{O-C})$  bands in each case indicate complex formation (table II). In addition to these changes new bands appear in the spectra of the complexes corresponding to  $\nu(\text{M-O})$  or  $\nu(\text{M-}$

0+C-C). The bands at  $950,570\text{cm}^{-1}$  for resacetophenone;  $940,580\text{ cm}^{-1}$  for phloracetophenone;  $950,610\text{cm}^{-1}$  for prenylated gallacetophenone;  $940,580\text{ cm}^{-1}$  for 2/4-dihydroxy methoxyphenone and  $930,600\text{cm}^{-1}$  for  $\beta$ -resorcyoldehyde complexes[13-14]. In these complexes the bands around  $1530, 1520, 1510$  and  $1500\text{ cm}^{-1}$  appear as a result of the coordinated ethanol molecules. The  $\text{UO}_2^{+2}$  ion has characteristic  $\nu(\text{U-O})$  stretching at  $950\text{ cm}^{-1}$ . This frequency depends upon the ligands present in equatorial position. The electronic spectra of the complexes arise no f-f or f-d transition [15] as no electron is present in 5f or 4d- orbitals of the U(VI) ion. This is also supported by zero values of Bohr magneton of the complexes. The bands appearing in the spectra can only be assigned as charge transfer bands on account of electronic

transitions (16-17) within the ligand, ligand to metal and metal to ligand.

From the above discussion of results, it is concluded that the solid complexes have distorted octahedral [18-19]. It is also concluded from the composition of the complexes that when the size of the chelating ligand is increased, the number of coordinated chelating ligands decreases from two to one due to steric hindrance. All the ligands in solution exist as mononegative anion by the abstraction of proton of the hydroxyl group. All the ligands behave as bidentate chelating ligands coordinating through oxygens of the carbonyl group and the oxygens of the adjacent hydroxyl groups present in the vicinal positions. The coordinated ethanol molecules making up the required coordination number. The structure of the complexes being tentatively represented as;

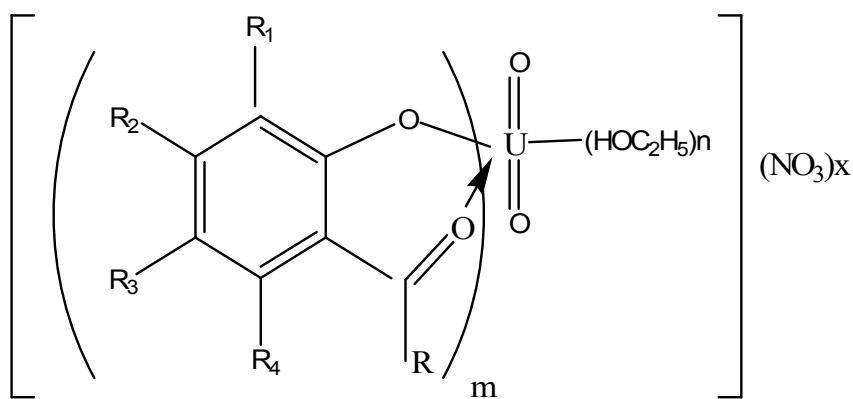


Fig:- 1

For Complex No.1:  $\text{R}=\text{CH}_3$ ;  $\text{R}_2=\text{OH}$ ;  $\text{R}_1, \text{R}_3, \text{R}_4=\text{H}$ ;  $m=2$ ;  $n=2$ ;  $x=0$

For Complex No.2:  $\text{R}=\text{CH}_3$ ;  $\text{R}_2, \text{R}_4=\text{OH}$ ;  $\text{R}_1, \text{R}_3=\text{H}$ ;  $m=2$ ;  $n=2$ ;  $x=0$

For Complex No.3:  $\text{R}=\text{H}$ ;  $\text{R}_3=\text{OH}$ ;  $\text{R}_1, \text{R}_2, \text{R}_4=\text{H}$ ;  $m=2$ ;  $n=2$ ;  $x=0$

For Complex No.4:  $\text{R}=\text{CH}_3$ ;  $\text{R}_1, \text{R}_2=\text{OH}$ ;  $\text{R}_3=\text{prenyl group}$ ;  $\text{R}_4=\text{H}$ ;  $m=1$ ;  $n=4$ ;  $x=1$

For Complex No.5:  $\text{R}=\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{OCH}_3$ ;  $\text{R}_2=\text{OH}$ ;  $\text{R}_1, \text{R}_3, \text{R}_4=\text{H}$ ;  $m=1$ ;  $n=4$ ;  $x=1$

Tentative structure for complex No.6 is shown in Fig.2

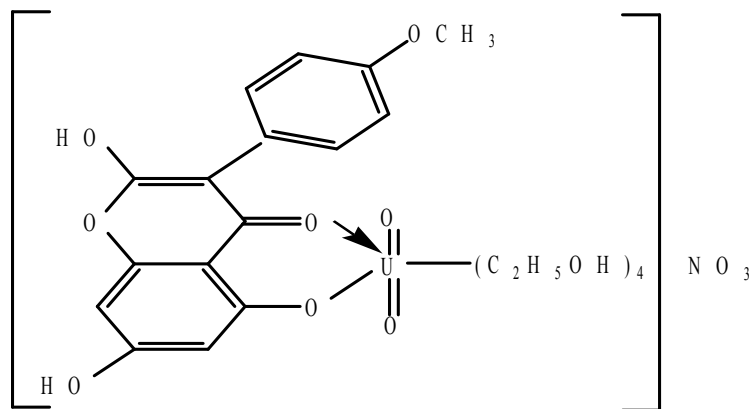


Fig : 2

**TABLE -1:** Elemental analysis of the Complexes of U(VI) with some ligands

S.No	Complex	Found			Calculated		
		C	H	M	C	H	M
1	[UO <sub>2</sub> (C <sub>8</sub> H <sub>7</sub> O <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> ]	36.60	3.90	35.62	36.14	3.91	35.85
2	[UO <sub>2</sub> (C <sub>8</sub> H <sub>7</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> ]	35.01	4.20	34.07	34.47	3.73	34.20
3	[UO <sub>2</sub> (C <sub>7</sub> H <sub>5</sub> O <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> ]	33.57	4.21	37.29	33.95	3.45	37.42
4	[UO <sub>2</sub> (C <sub>13</sub> H <sub>15</sub> O <sub>4</sub> ) (C <sub>2</sub> H <sub>5</sub> OH) <sub>4</sub> ]NO <sub>3</sub>	33.73	5.06	31.61	33.55	5.19	31.69
5	[UO <sub>2</sub> (C <sub>16</sub> H <sub>13</sub> O <sub>4</sub> ) (C <sub>2</sub> H <sub>5</sub> OH) <sub>4</sub> ]NO <sub>3</sub>	36.49	4.78	30.38	36.68	4.71	30.32
6	[UO <sub>2</sub> (C <sub>16</sub> H <sub>11</sub> O <sub>6</sub> ) (C <sub>2</sub> H <sub>5</sub> OH) <sub>4</sub> ]NO <sub>3</sub>	35.72	4.27	29.09	35.33	4.29	29.20

**TABLE II: Principal bands (cm<sup>-1</sup>)** in the I R spectra of ligands and complexes

S. No	Complexes	$\nu(\text{O-H})$	$\nu(\text{C=O})$	$\nu(\text{O-C})$	$\nu(\text{M-O})$ or $\nu(\text{M-O+C-C})$
1	RP Ligand (C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> )	3200	1630	1060	--
	[UO <sub>2</sub> (C <sub>8</sub> H <sub>7</sub> O <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> ]	3300	1610	1020	1520,950,570
2	PA Ligand (C <sub>8</sub> H <sub>8</sub> O <sub>4</sub> )	3500	1630	1060	--
	[UO <sub>2</sub> (C <sub>8</sub> H <sub>7</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> ]	3460	1625	1020	1530,940,580
3	RA Ligand (C <sub>7</sub> H <sub>6</sub> O <sub>3</sub> )	3100	1630	1120	--
	[UO <sub>2</sub> (C <sub>7</sub> H <sub>5</sub> O <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> ]	3300	1640	1130	1500,930,600
4	PG Ligand(C <sub>13</sub> H <sub>16</sub> O <sub>4</sub> )	3500	1630	1075	--
	[UO <sub>2</sub> (C <sub>13</sub> H <sub>15</sub> O <sub>4</sub> )(C <sub>2</sub> H <sub>5</sub> OH) <sub>4</sub> ]NO <sub>3</sub>	3400	1625	1030	1520,930,610
5	DMC Ligand (C <sub>16</sub> H <sub>14</sub> O <sub>4</sub> )	3300	1600	1040	--
	[UO <sub>2</sub> (C <sub>16</sub> H <sub>13</sub> O <sub>4</sub> )(C <sub>2</sub> H <sub>5</sub> OH) <sub>4</sub> ]NO <sub>3</sub>	3300	1610	1020	1510,940,580
6	TMI Ligand (C <sub>16</sub> H <sub>12</sub> O <sub>6</sub> )	3200	1670	1080	--
	[UO <sub>2</sub> (C <sub>16</sub> H <sub>11</sub> O <sub>6</sub> )(C <sub>2</sub> H <sub>5</sub> OH) <sub>4</sub> ]NO <sub>3</sub>	3300	1610	1020	1530,950,610

**TABLE III: Diffuse- Reflectance Spectrum**

S. No	Complexes	$\mu_{\text{eff}}(\text{B.M.})$	Bands (cm <sup>-1</sup> )
1	[UO <sub>2</sub> (C <sub>8</sub> H <sub>7</sub> O <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> ]	0.00	40616,25500,20600
2	[UO <sub>2</sub> (C <sub>8</sub> H <sub>7</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> ]	0.00	40800,25000,20500,38461,33898
3	[UO <sub>2</sub> (C <sub>7</sub> H <sub>5</sub> O <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> OH) <sub>2</sub> ]	0.00	25740,23155,20800
4	[UO <sub>2</sub> (C <sub>13</sub> H <sub>15</sub> O <sub>4</sub> ) (C <sub>2</sub> H <sub>5</sub> OH) <sub>4</sub> ]NO <sub>3</sub>	0.00	40950,24000,21000
5	[UO <sub>2</sub> (C <sub>16</sub> H <sub>13</sub> O <sub>4</sub> ) (C <sub>2</sub> H <sub>5</sub> OH) <sub>4</sub> ]NO <sub>3</sub>	0.00	41500,25000,20000
6	[UO <sub>2</sub> (C <sub>16</sub> H <sub>11</sub> O <sub>6</sub> ) (C <sub>2</sub> H <sub>5</sub> OH) <sub>4</sub> ]NO <sub>3</sub>	0.00	40750,33100,20900

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