



## Synthesis, Spectral and Thermal Properties of Hydrazinium, Aminoguanidinium and Pyridinium Uranyl Pyridine-2,6-Dicarboxylates

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Anionic complexes, pyridine-2,6-dicarboxylato uranyl complex containing protonated weak bases such as hydrazine, guanyl hydrazine and pyridine as charge neutralizing entities have been isolated from aqueous solution containing respective bases, dipicolinic acid and uranyl nitrate hexahydrate. The molecular compositions and structural geometries have been assigned by analyzing their elemental analyses, spectral data and thermal patterns and the molecular formulae,  $A_2[UO_2(PDC)_2]$  where  $A = N_2H_5^+/AGH^+$  (aminoguanidinium) or  $PYH^+$  (pyridinium) cation and PDC = pyridine-2,6-dicarboxylate dianion has been proposed for the newly synthesized coordination compounds. Oxidative degradation in air yielded  $U_3O_8$  as the residue, which has been proposed on the basis of thermogravimetric weight loss and powder XRD pattern. Based on the spectral results and careful analyses, a hexagonal bipyramidal geometry has been assigned for all the three uranyl(II) complexes.

**Keywords:** Hydrazinium, Guanyl hydrazinium, Pyridinium, Pyridine-2,6-dicarboxylate, Uranyl(II) cation.

### INTRODUCTION

Uranium and uranyl complexes received much attention during last few decades among the actinide elements due to the structural diversity [1-4] and their applications in various areas like optical, magnetic and catalytic activities [5-8]. A large number of aliphatic and aromatic carboxylic acids such as monodentate, bidentate, polydentate acids form variety of complexes in which polydentate ligands are effective in the formation of chelates with interesting geometries [9].

Since uranium is frequently accessible in various oxidation states and has versatile coordination chemistry. The hexavalent state is stable under ambient conditions for uranyl dioxo cation  $UO_2^{2+}$  in aqueous solution. It is reported in most of the coordination network solids with carboxylate ligands in which the uranyl adopts predominantly 6-, 7- or 8-coordination surroundings with bipyramidal geometries such as hexagonal bipyramidal, pentagonal bipyramidal and tetragonal bipyramidal structures respectively.

The interaction of several metal ions with pyridine-2,6-dicarboxylic acid ( $H_2PDC$ ) has been investigated by several researchers [10-13] and crystal structures of some of the comp-

ounds were reported [14-17]. Furthermore, in the structures of all those complexes referred in the literature, PDC anion coordinated to metal ions as tridentate ligand with coordination of nitrogen atom and two carboxylate oxygen atoms, (O, N, O coordination) resulting in the formation of stable five membered rings. In spite of many of uranyl carboxylate complexes including pyridine dicarboxylate complexes reported in the literature [18] corresponding hydrazine complexes of metal pyridine dicarboxylate are very less [19]. Indeed hydrazine based uranyl PDC complexes have not been reported so far. Our continued efforts on hydrazine complexes recently we were succeeded in isolating several new hydrazine based uranyl-PDC complexes and their spectral and thermal properties have been investigated in the present article.

### EXPERIMENTAL

All the chemicals and solvents were purchased from S.D. Fine Chemicals, Mumbai, India. The solvents were distilled before use and double distilled water was used for the synthesis of complexes.

The hydrazine content was determined by volumetric analysis using a 0.025 M  $KIO_3$  solution under Andrew's condition

and the uranium(VI) content was determined gravimetrically using oxine [20,21]. Elemental analyses (C, H and N) were analyzed using Perkin-Elmer 2400 CHN elemental analyzer. IR spectra of the complexes were recorded (KBr disc) in the range 4000-400  $\text{cm}^{-1}$  on a Bruker alpha spectrophotometer. The simultaneous TG-DTA traces of the samples in air were recorded on a SWITG/DTA 6200 thermal analyzer using about 5 mg of the samples with the heating rate of 10  $^{\circ}\text{C}/\text{min}$  and platinum cups as sample holder.

**Synthesis of the complexes:** The complexes were synthesized by adding an aqueous solution (30 mL) containing a mixture of bases hydrazine hydrate (2 mL, 0.04 mol) (**1**), aminoguanidine bicarbonate (5.49 g, 0.04 mol) (**2**) or pyridine (3.2 mL, 0.04 mol) (**3**) and pyridine-2,6-dicarboxylic acid (3.34 g, 0.02 mol) to an aqueous solution (30 mL) of uranyl nitrate hexahydrate (5.02 g, 0.01 mol). The pale yellow solutions obtained was filtered and the clear solutions was allowed to stay at room temperature. The crystalline complexes formed and settled at the bottom were removed, washed with ice cold distilled water and dried in air. All the three isolated complexes are water soluble and stable in air at room temperature.

## RESULTS AND DISCUSSION

Uranyl ion in aqueous medium reacts with pyridine-2,6-dicarboxylic acid in the presence of weak bases like hydrazine, aminoguanidine or pyridine to form ionic complexes **1**, **2** and **3**, respectively. The complexes precipitated from the aqueous solution were filtered and washed with alcohol. The analytical data of the synthesized complexes are summarized in Table-1. The molar conductances of the complexes are in the range 160-170  $\text{mho cm}^{-1}$ , which are in accordance with the 2:1 electrolytic nature.

**IR analysis:** Infrared spectral studies provide valuable informations especially in the case of hydrazine based metal complexes. The N-N stretching bands in these systems are very much useful in assigning the coordination of nitrogen from

hydrazinium moiety. In the present series of complexes in complex **1** N-N stretching observed at 970  $\text{cm}^{-1}$  for hydrazine complex (Fig. 1a) and at 1100  $\text{cm}^{-1}$  for aminoguanidinium complex **2** (Fig. 1b) were in accordance with the ionic nature of these cations. It is quite expected that the strong bidentate chelating ability of pyridine dicarboxylate ion around the uranyl moiety may not provide any space for inclusion of their cation in the primary coordination sphere. These ions probably present outside the sphere as charge neutralizing species. The monodentate coordination behaviour of carboxylate groups of PDC was assigned on the basis of the bands observed in the regions 1620-1600  $\text{cm}^{-1}$   $\nu_{\text{asy}}$  and 1390-1370  $\text{cm}^{-1}$   $\nu_{\text{sym}}$ . Beside these both the complexes show asymmetric and symmetric O=U=O stretching in the regions 940-920 and 840-830  $\text{cm}^{-1}$ , respectively. Broad bands with splitting observed between 3400-3200  $\text{cm}^{-1}$  are attributed to N-H stretching of hydrazinium and aminoguanidinium cations. Furthermore, the absence of any sharp and strong bands between 1750-1700  $\text{cm}^{-1}$  clearly reveals the deprotonation of the acid to yield dicarboxylate dianion during complexation. Hence it is expected that the complexes when dissolved in water to yield three ions (two cation and one dianion) as shown below:



IR spectrum of complex **3** (Fig. 1c) shows asymmetric and symmetric stretchings of O=U=O of uranyl cation in the region 930 and 830  $\text{cm}^{-1}$ , respectively. The carboxylate groups of PDC show bands in the region 1610-1590 and 1380-1360  $\text{cm}^{-1}$  for asymmetric and symmetric stretchings, respectively which reveal the monodentate coordination behaviour. The band around 3400  $\text{cm}^{-1}$  is attributed to N-H stretching of pyridinium cation. This clearly indicates the protonation of pyridine during the formation of complex. The N-H stretching observed in the pyridinium complex is the clear evidence for the ionic nature of the cations present in all the three complexes though in complexes **1** and **2**, there is a possibility of coordination of nitrogen atom which were not protonated.

TABLE-1  
ANALYTICAL DATA OF SYNTHESIZED URANYL(II) COMPLEXES

Complex	m.w.	Colour	Elemental analyses (%): Found (calcd.)				
			Hydrazine	Metal	C	H	N
( $\text{N}_2\text{H}_5$ ) <sub>2</sub> [ $\text{UO}_2(\text{PDC})_2$ ] ( <b>1</b> )	666.06	Yellow	9.53 (9.60)	35.50 (35.73)	25.10 (25.25)	0.97 (0.90)	4.10 (4.20)
(AGH) <sub>2</sub> [ $\text{UO}_2(\text{PDC})_2$ ] ( <b>2</b> )	750.08	Yellow	8.41 (8.52)	31.63 (31.73)	23.50 (23.98)	1.68 (1.73)	11.15 (11.20)
(PYH) <sub>2</sub> [ $\text{UO}_2(\text{PDC})_2$ ] ( <b>3</b> )	760.11	Green	–	31.31 (32.00)	37.89 (38.52)	2.36 (2.16)	7.36 (7.17)

AGH = Aminoguanidinium; PYH = Pyridinium; PDC = Pyridine dicarboxylate.

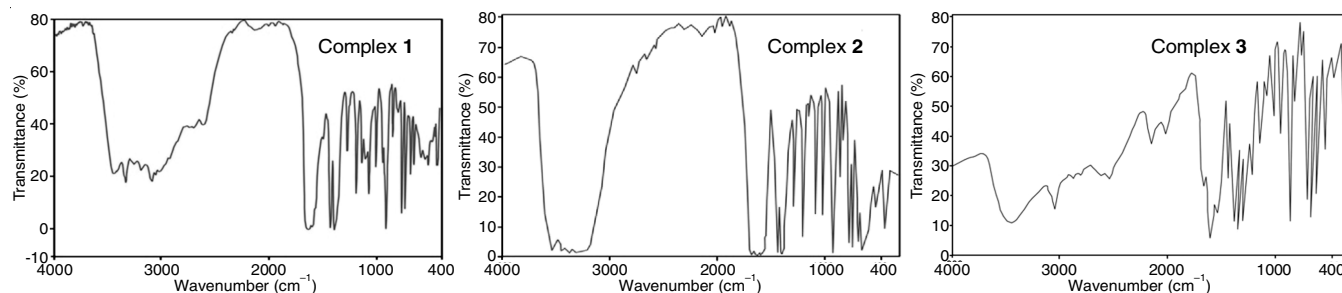


Fig. 1. IR spectra of uranyl(II) complexes **1**, **2** and **3**

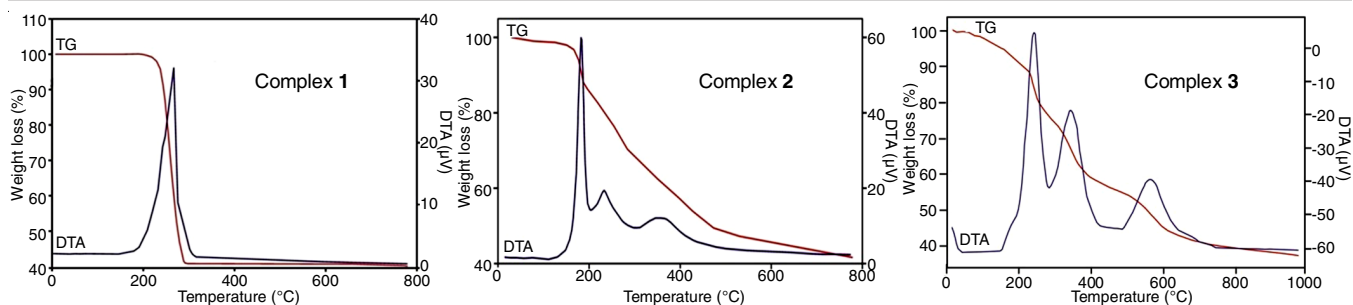
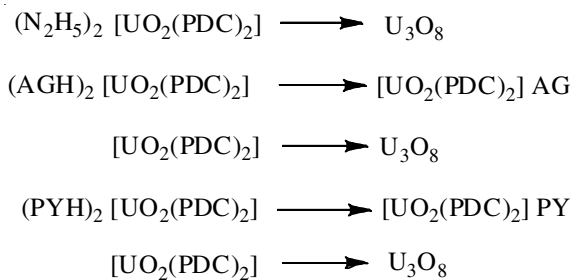


Fig. 2. Simultaneous TG-DTA thermograms of uranyl(II) complexes **1**, **2** and **3**

**Thermal studies:** Hydrazine based systems gain interest due to the presence of endothermic N-N bond. Further the end product (uranyl oxides) formed are expected to be pure and possess better surface properties. In the present study, complex **1** undergoes single step decomposition (Fig. 2a) to yield  $U_3O_8$  as the final residue in the temperature range 200-300 °C with a strong exotherm at 270 °C in DTA. The weight loss observed (59%) is in good agreement with the theoretical value (57.97%). Three steps decomposition was observed for aminoguanidinium complex during controlled heating. Between 180-220 °C, TG weight loss shows the elimination of one aminoguanidine molecule and DTA shows an exotherm which is sharp at 200 °C. Further exothermic decomposition with a DTA peak at 250 °C resulted in the formation of uranyl pyridine-2,6-dicarboxylate as an intermediate. The total weight loss for the above two stages is 21% reveals the elimination of second aminoguanidine molecule. The intermediate at about 500 °C yield  $U_3O_8$  as a final residue. The total weight loss was 63% which is well in accordance with the theoretical value (62.68%) for the formation of the proposed product. The third stage was also exothermic and the DTA was observed at 350 °C (Fig. 2b).

Complex **3** undergoes three step decomposition upon heating (Fig. 2c). In the first step, a loss of one pyridine molecule is observed in the temperature range 200-230 °C with a weight loss of 12.00%, which is in good agreement with the theoretical value (11.75%). In the second step, the complex decomposes exothermally between 250-400 °C with an exotherm at 360 °C to give uranyl pyridine-2,6-dicarboxylate as an intermediate, which further decomposes exothermally in the range 500-650 °C to yield  $U_3O_8$  as the final residue. The weight losses observed for second and third steps were 25.00 and 64.00% respectively, which are in good agreement with the theoretical values (24.45 and 63.16%).

The thermal degradation of the complexes undergoes the following steps, which is represented as follows:



The final thermal degradation temperature is lower for hydrazine complex than aminoguanidine complex which is in turn lower than pyridine complex. This is attributed to the presence of endothermic N-N bond in hydrazinium cation, which undergoes violent exothermic degradation during pyrolysis. In case of aminoguanidinium complex the substitution in the N-N bond makes its degradation less violent than previous one. Due to the absence of N-N bond the pyridine complex undergoes degradation at higher temperature than the other two.

**Powder XRD analysis:** The X-ray powder diffraction patterns of all the three complexes **1**, **2** and **3** shows the sharp and intense signals (Fig. 3). The patterns are almost superimposable which reveals their structural similarity. This could be due to the same structure of coordination sphere. The precursor complexes on thermal degradation yielded uranium oxide,  $U_3O_8$  as the final residue. Formation of  $U_3O_8$  is also confirmed by powder X-ray diffraction technique. The X-ray powder diffraction pattern of the oxide prepared from the complex is shown in Fig. 4. The obtained peaks are well matched with the standard  $U_3O_8$  pattern (JCPDS file no. 08-0244).

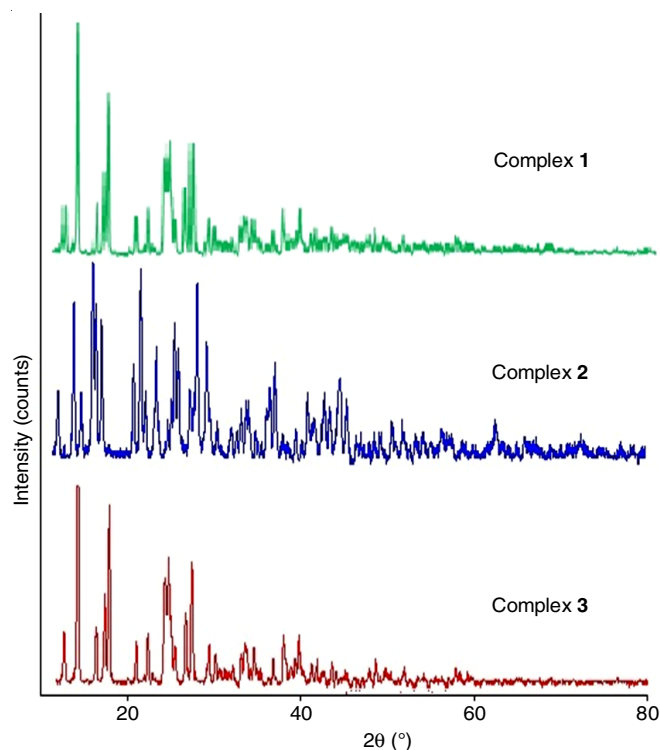


Fig. 3. Powder X-ray diffraction of uranyl(II) complexes **1**, **2** and **3**

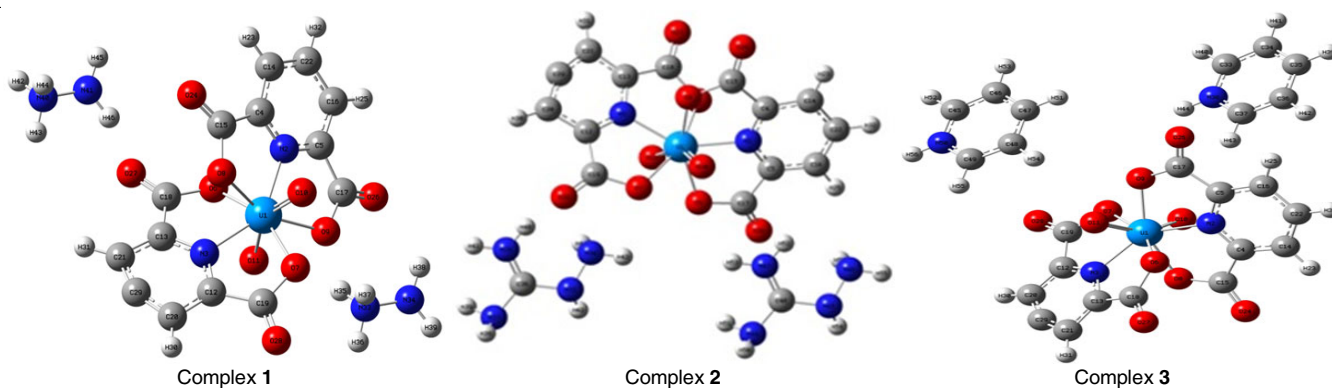
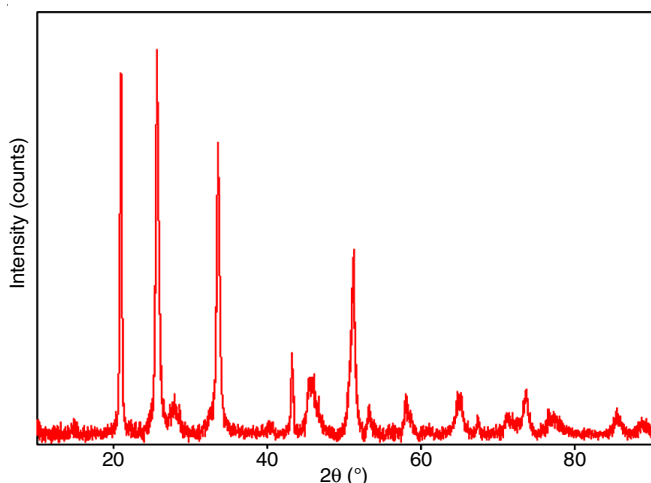


Fig. 5. Proposed structure of uranyl(II) complexes 1, 2 and 3

Fig. 4. Powder X-ray diffraction of  $U_3O_8$ 

On the basis of analytical, spectral, thermal and X-ray powder diffraction studies the following structures have been tentatively assigned for the hydrazinium, aminoguanidinium and pyridinium complexes, respectively (Fig. 5).

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#### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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