

Preparation and thermal reactivity of hydrazinium uranyl carboxylates

K. Kuppusamy, B.N. Sivasankar, S. Govindarajan*

Department of Chemistry, Bharathiar University, Coimbatore-641 046, India

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Abstract

Hydrazinium uranyl carboxylates with the formula $N_2H_5[UO_2L_3] \cdot nH_2O$, where for L = salicylate, $n = 4$; for L = benzoate and *p*-hydroxybenzoate, $n = 2$; for L = hydrazinecarboxylate, $n = 1$; for L = acetate, propionate and thioglycolate, $n = 0$, and dihydrazinium uranyl phthalate ($N_2H_5)_2[UO_2(o-C_6H_4(COO)_2)_2]$ have been prepared in aqueous media. The electronic spectra of the complexes confirm the presence of the uranyl cation in the molecules. The infrared spectra of the complexes show the N–N stretching frequency of $N_2H_5^+$ in the range of 970–980 cm^{-1} confirming its ionic nature. The small separation ($\Delta\nu < 150 cm^{-1}$) between the asymmetric and symmetric stretching vibrations of the carboxylate groups in all the complexes except hydrazinecarboxylate and phthalate compounds, reveals the bidentate chelate coordination of the carboxylate groups. The hydrazinecarboxylate group is coordinated through O and N atoms as a bidentate chelate. IR frequencies also show that one of the carboxylates in the phthalate complex is a monodentate and the other is bidentate chelate. Thus the phthalate ligand bridges in both uni- and bidentate fashion. Simultaneous TG–DTA shows that the aromatic carboxylate complexes, including hydrazinium uranyl hydrazinecarboxylate monohydrate, decompose exothermically whereas the aliphatic counterparts decompose both endo- and exothermically. Except for $N_2H_5[UO_2(N_2H_3COO)_3] \cdot H_2O$ all other complexes decompose via uranyl carboxylate intermediate to give U_3O_8 as the final product. The water molecules are lost endothermically at low temperature (around 100°C) indicating the presence of water molecules as water of crystallisation.

Keywords: Aliphatic and aromatic carboxylates; Hydrazinecarboxylate; Hydrazinium uranyl carboxylates; IR spectra; Thermal decomposition

* Corresponding author.

1. Introduction

The most important of the actinide elements is uranium and much information is available about its chemistry, particularly its coordination chemistry. Though it exhibits variable valency, its hexavalent uranyl cation (UO_2^{2+}) is unique in the sense that it forms a number of stable complexes like d-block elements. It is a well established fact that both in crystalline compounds and in solution UO_2^{2+} is linear and forms a great variety of complexes with negative ions and neutral molecules. In these complexes coordination generally occurs on or near the equatorial plane, the coordination polyhedron being either a pentagonal or a hexagonal bipyramidal.

A great variety of compounds is formed between monocarboxylic acids and the uranyl cation. The most characteristic type being the tricarboxylate, viz., $\text{MUO}_2(\text{RCOO})_3 \cdot n\text{H}_2\text{O}$ [1] where $\text{M} = \text{Na}, \text{K}$ or NH_4 , $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ or $\text{C}_6\text{H}_4(\text{OH})$ and $n = 0-9$. The dicarboxylic acid, oxalic acid, forms compounds [1–3] of the type $\text{M}_2[(\text{UO}_2(\text{C}_2\text{O}_4)_2) \cdot n\text{H}_2\text{O}]$, where $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ or NH_4 . These compounds have been prepared [1–3] from aqueous solutions of uranyl ion on addition of excess alkali or ammonium carboxylates. Some have been characterised by spectral, crystallographic and thermal studies. A survey of the literature reveals that only few hydrazinium ($\text{M} = \text{N}_2\text{H}_5^+$) analogues viz., $\text{N}_2\text{H}_5\text{UO}_2(\text{CH}_3\text{COO})_3$ [4], $\text{N}_2\text{H}_5\text{H}(\text{UO}_2)_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ [5], $(\text{N}_2\text{H}_5)_2\text{UO}_2(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, $(\text{N}_2\text{H}_5)_4\text{UO}_2(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2\text{O}$ [6], $(\text{N}_2\text{H}_5)_6(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5 \cdot n\text{H}_2\text{O}$ [7], and $(\text{N}_2\text{H}_5)_2\text{UO}_2(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ [8] have been reported. No thermal studies have been reported for $\text{N}_2\text{H}_5\text{UO}_2(\text{CH}_3\text{COO})_3$ whereas for oxalate complexes thermal studies [5–8] and single crystal X-ray crystallographic studies [7, 8] have both been reported. In these compounds N_2H_5^+ is not coordinated. No reports are available on hydrazinium uranyl carboxylates with aromatic carboxylic acids, hydrazinecarboxylic, propionic or thioglycolic acids. This prompted us to make a systematic study of the preparation and thermal reactivity of these complexes; the results of these and of electronic and IR spectral studies of the above complexes are reported.

2. Experimental

2.1. Preparation

Hydrazinium hydrazidocarboxylate, was prepared by the dissolution of 0.25 mol of ammonium carbonate in 0.05 L hydrazine hydrate as reported elsewhere [9]. Hydrazinium benzoate, salicylate and *p*-hydroxybenzoate and dihydrazinium phthalate were prepared by the methods standardized in our laboratory and reported previously [10].

Benzoate, hydroxylbenzoate, hydrazinecarboxylate and phthalate complexes

Uranyl nitrate hexahydrate (5.02 g, 0.01 mol) was dissolved in 0.1 L distilled water. To the clear solution 0.1 L of an aqueous solution of the ligand (e.g., hydrazinium benzoate, 6.17 g, 0.04 mol) was added with stirring. The complexes were formed slowly.

After an hour at room temperature the mixture was digested at 60°C for 1 h, then cooled and the solid product filtered off, washed with alcohol and ether and dried over P₂O₅. Hydroxybenzoate complexes are moderately soluble whereas the benzoate and phthalate complexes are insoluble.

In the case of hydrazinecarboxylate system the light yellow precipitate formed initially dissolved, on continuous stirring, to give a clear solution. The clear solution formed yellow crystals in 2–3 days. They were removed, and processed as before. The final product has low solubility.

The salicylate complex is orange in colour indicating the presence of phenolic OH [1]. The other complexes are yellow in colour.

Acetate, propionate and thioglycolate complexes

Method I

These complexes were prepared by adopting a procedure similar to that followed to prepare hydrazinium metal thiocyanates [11]. The freshly prepared solid N₂H₅[UO₂(N₂H₃COO)₃]·H₂O was added to dilute aqueous solutions (0.2 L) of acetic, propionic and thioglycolic acids (0.03 mol dm⁻³) in small portions while maintaining the reaction temperature around 20°C. The solid decomposed with the evolution of carbon dioxide to give a yellow solution. The addition of the solid was continued until the solution became neutral. The resulting solution was left to stand open to the atmosphere at room temperature. Yellow crystals separated in 2–3 days. They were removed from the solution washed twice with alcohol and dried in air. The acetate and propionate complexes are stable in air whereas the thioglycolate complex decomposes on standing in air for long periods. All are soluble in water.

Method II

The complexes were also prepared by adding an aqueous solution (0.1 L) containing a mixture of hydrazine hydrate 99–100% (1.5 ml, 0.03 mol) and the corresponding acid (acetic acid, 1.80 ml; propionic acid 2.22 ml or thioglycolic acid, 2.17 ml; 0.03 mol) to an aqueous solution (0.1 L) of uranyl nitrate hexahydrate (5.02 g, 0.01 mol). The resultant solution was kept at room temperature for crystallization. The crystals formed after 2–3 days were separated and handled as before.

2.2. *Physico-chemical techniques*

The hydrazine content of the complexes was determined by titration with 0.025 M KIO₃ under Andrews conditions [12]. The uranium(VI) in the complexes was determined gravimetrically using oxine [12].

Electronic spectra of the complexes were recorded on a Hitachi Perkin Elmer 20/200 recording spectrophotometer using water as solvent. For water-insoluble complexes the solid state absorption spectra were recorded in Nujol mull. Infrared spectra were recorded by the KBr disc technique using a Perkin Elmer 597 spectrophotometer.

An STA 1500 thermal analyser and Shimadzu DT40 were used to record the simultaneous TG–DTA of all the complexes. The experiments were performed in air

with a heating rate of $10^{\circ}\text{C min}^{-1}$ in the temperature range ambient to 600°C , using platinum cups as sample holders.

3. Results and discussion

The results of chemical analyses are given in Table 1. The data are in agreement with the formulae proposed.

3.1. Electronic spectra

The visible absorption spectra of the complexes show λ_{max} around 430 nm ($23,260\text{ cm}^{-1}$) which is assigned to the ${}^1\Sigma_g^+ \rightarrow {}^3\Pi_u$ transition of the uranyl ion [13]. The results are given in Table 1.

3.2. Infrared spectra

The important IR data of the complexes are given in Table 1. Characteristic IR absorption of the uranyl ion [1, 6], both asymmetric and symmetric stretchings of $\text{O}=\text{U}=\text{O}$, are observed in the regions $910\text{--}930$ and $830\text{--}870\text{ cm}^{-1}$, respectively. The absorption bands in the region $970\text{--}980\text{ cm}^{-1}$ are assigned [14, 15] to N–N stretching of ionic N_2H_5^+ in the complexes, as observed in previous studies [4–8]. The bidentate chelate coordination of $\text{N}_2\text{H}_3\text{COO}^-$ in its complex is confirmed by the N–N stretching at 1000 cm^{-1} [14]. In the monocarboxylate complexes under study, the difference between the asymmetric and symmetric stretching frequencies of the carboxylates is seen in the range $80\text{--}150\text{ cm}^{-1}$ confirming [16] the bidentate chelate coordination of the COO^- groups.

The same type of coordination for acetate, propionate, butyrate and salicylate complexes of similar composition has been reported [1] on the basis of crystallographic studies. However, in the phthalate complex, the two carboxylate groups have different modes of coordination as revealed by the splitting of the asymmetric, symmetric and bending absorption bands of the COO^- groups. Two different $\Delta\nu$ values viz., 220 cm^{-1} and 120 cm^{-1} corresponding to monodentate and bidentate chelate coordination of the carboxylate groups are observed. Thus the phthalate ligand bridges in both uni- and bidentate fashion. This kind of coordination has been reported on the basis of a crystal structure determination of μ -phthalato binuclear $\text{Co}(\text{II})$ complexes [17]. The absorptions at $3450\text{--}3550\text{ cm}^{-1}$ and $1610\text{--}1630\text{ cm}^{-1}$ have been attributed to O–H stretching and H–O–H bending vibrations of lattice water molecules [16] in aromatic carboxylate and hydrazinecarboxylate complexes.

3.3. Thermal studies

The simultaneous TG–DTA data of the complexes are summarised in Table 2.



Table I
Analytical and Spectral data

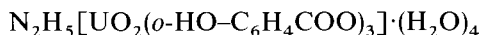
Compound	Hydrazine in %Uranium in %				IR absorption bands in cm^{-1}							Electronic spectra ${}^{15}\Sigma_g^+ \rightarrow {}^3\Pi$ in cm^{-1}
	Found		Calcd.		O-H str. of H_2O	H-O-H bending	COO ⁻¹ Asy. Str.	COO ⁻¹ Sym. Str.	N-N Str.	UO ₂ Asym. Str.	UO ₂ Sym. Str.	
	Found	Calcd.	Found	Calcd.								
$\text{N}_2\text{H}_5[\text{UO}_2(\text{C}_6\text{H}_5\text{COO})_3] \cdot (\text{H}_2\text{O})_2$	4.60	4.56	34.00	33.89	3500	1610	1590	1440	980	920	860	22950
$\text{N}_2\text{H}_5[\text{UO}_2(o\text{-HO-C}_6\text{H}_4\text{COO})_3] \cdot (\text{H}_2\text{O})_4$	3.90	4.07	30.00	30.26	3450	1620	1600	1460	970	930	870	23200
$\text{N}_2\text{H}_5[\text{UO}_2(p\text{-HO-C}_6\text{H}_4\text{COO})_3] \cdot (\text{H}_2\text{O})_2$	4.20	4.27	31.50	31.72	3450	1610	1590	1440	980	910	850	23200
$(\text{N}_2\text{H}_5)_2[\text{UO}_2(o\text{-C}_6\text{H}_4(\text{COO})_2)_2]$	9.70	9.65	36.00	35.83	-	-	1620	1400	980	930	870	23300
$\text{N}_2\text{H}_5[\text{UO}_2(\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$	23.20	23.47	43.00	43.58	3550	1630	1580	1460	1000 970	910	-	23300
$\text{N}_2\text{H}_5[\text{UO}_2(\text{CH}_3\text{COO})_3]$	6.70	6.67	49.10	49.57	-	-	1540	1460	980	930	-	23420
$\text{N}_2\text{H}_5[\text{UO}_2(\text{CH}_3\text{CH}_2\text{COO})_3]$	6.20	6.14	45.00	45.57	-	-	1540	1460	970	930	830	23310
$\text{N}_2\text{H}_5[\text{UO}_2(\text{HSCCH}_2\text{COO})_3]$	5.40	5.56	40.90	41.30	-	-	1540	1460	970	930	-	23260

Table 2
Thermal data

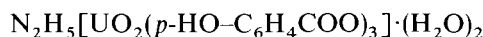
Compound	DTA peak temperature in °C ^a	Thermogravimetry		Decomposition product	
		Temp. range in °C	Weight loss in %		
			Found		Calcd.
$N_2H_5[VO_2(C_6H_5COO)_3] \cdot (H_2O)_2$	100(+)	50–125	4.80	5.13	$N_2H_5[VO_2(C_6H_5COO)_3]$ $VO_2(C_6H_5COO)_2 \cdot C_6H_5COOH$ $VO_2(C_6H_5COO)_2$ U_3O_8
	160(-)	125–175	10.00	9.69	
	240(-)	175–300	26.70	27.08	
	420(-)	300–440	59.00	60.04	
$N_2H_5[VO_2(o-HO-C_6H_4COO)_3] \cdot (H_2O)_4$	75(+)	50–150	9.30	9.16	$N_2H_5[VO_2(o-HO-C_6H_4COO)_3]$ $VO_2(o-HO-C_6H_4COO)_2$ $VO_2(o-O-C_6H_4COO)$ U_3O_8
	200(-)	150–210	31.00	30.67	
	325(-)	210–380	48.00	48.36	
	425(-)	380–500	63.60	64.31	
$N_2H_5[VO_2(p-HO-C_6H_4COO)_3] \cdot (H_2O)_2$	100(+)	70–130	5.00	4.80	$N_2H_5[VO_2(p-HO-C_6H_4COO)_3]$ $VO_2(p-HO-C_6H_4COO)_2 \cdot C_6H_4OHCOOH$ U_3O_8
	210(-)	130–225	9.80	9.07	
	310(-)	225–380	62.00	62.60	
	335(-)] ^d				
$(N_2H_5)_2[VO_2(o-C_6H_4(COO)_2)_2]$	265(+)	230–300	10.00	9.65	$VO_2[o-C_6H_4COOHCOO]_2$ $VO_2[o-C_6H_4(COO)_2]$ U_3O_8 UO_3 U_3O_8 Melting $VO_2(CH_3COO)_2$ U_3O_8
	425(-)	300–430	34.00	34.65	
	445(-)	430–460	57.00	57.75	
	140(-)	120–150	47.00	47.64	
$N_2H_5[VO_2(N_2H_3COO)_3] \cdot H_2O$	440(-)	150–460	49.00	48.61	Melting $VO_2(CH_3COO)_2$ U_3O_8
	220(+)	–	–	–	
	235(-)	225–250	20.00	19.18	
	275(+)]	250–380	42.00	41.55	
$N_2H_5[VO_2(CH_3COO)_3]$	350(+)]	–	–	–	Melting $VO_2(CH_3CH_2COO)_2$ U_3O_8
	220(+)	–	–	–	
	230(-)	210–240	20.50	20.32	
	250(+)]	240–350	46.00	46.26	
$N_2H_5[VO_2(HSCH_2COO)_3]$	320(+)]	–	–	–	$VO_2(HSCH_2COO)_2 \cdot N_2H_4$ Melting $VO_2(HSCH_2COO)_2$ U_3O_8
	190(-)	160–220	16.20	15.98	
	290(+)	–	–	–	
	335(+)	300–360	22.40	21.54	
450(+)	410–460	52.00	51.30		

^a d: doublet; (+): endotherm; (-): exotherm

The complex shows four steps of decomposition in TG and four peaks in DTA (Fig. 1). The first endothermic peak at 100°C in the temperature range 50–125°C (TG) corresponds to loss of two lattice water molecules. The same mode of dehydration was reported [18] for the similar type of complexes, $\text{LaUO}_2(\text{CH}_3\text{COO})_5 \cdot 3\text{H}_2\text{O}$ and $\text{LaUO}_2(\text{C}_2\text{H}_5\text{COO})_5 \cdot 3\text{H}_2\text{O}$. The second step is exothermic at 160°C showing the loss of an N_2H_4 molecule. The third step is also exothermic at 240°C to produce the uranyl benzoate intermediate which undergoes exothermic decomposition at 420°C to form U_3O_8 as the final solid product. These results are in accordance with the TG.



The first step in the decomposition sequence corresponds to the dehydration of the complex. The endotherm at 75°C, corresponds to dehydration, indicating that water molecules are not coordinated and remain only as water of hydration. In the second step the anhydrous complex decomposes in the exothermic mode at 200°C with the weight loss corresponding to the removal of a molecule each of hydrazine and salicylic acid to form uranyl disalicylate. This undergoes exothermic decomposition at 325°C to give uranyl salicylate as evidenced by the weight loss. This intermediate again undergoes exothermic decomposition at 425°C to form U_3O_8 and it is supported by the weight loss indicated by TG (Fig. 2).



This complex decomposes in three steps. The first step involves endothermic decomposition at 100°C corresponding to loss of the water of hydration as indicated by TG weight loss. The anhydrous compound further decomposes with the loss of hydrazine. This is observed as an exotherm at 210°C. The final step corresponds to the decomposition of the intermediate to U_3O_8 . This is found as an exotherm (doublet) at 310 and 335°C. Thermogravimetric data are in accordance with the DTA results.

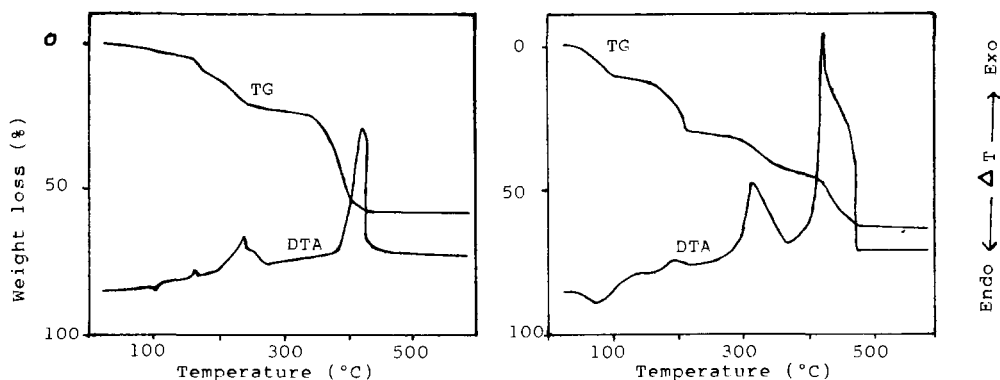
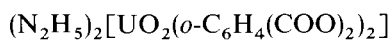
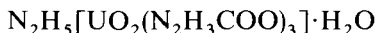


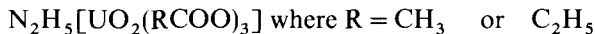
Fig. 1. TG-DTA of $\text{N}_2\text{H}_5[\text{UO}_2(\text{C}_6\text{H}_5\text{COO})_3] \cdot (\text{H}_2\text{O})_2$.

Fig. 2. TG-DTA of $\text{N}_2\text{H}_5[\text{UO}_2(o\text{-HO-C}_6\text{H}_4\text{COO})_3] \cdot (\text{H}_2\text{O})_4$.

The TG curve of this complex shows (Fig. 3) three distinct steps of decomposition, corresponding to the formation of uranyl bis(hydrogenphthalate), uranyl phthalate and U_3O_8 . The decomposition is complete below 460°C , which is probably due to highly exothermic fracture of N–N bonds. The DTA of the complex confirms the steps observed in TG. The first endotherm is followed by two exotherms. The complex loses two molecules of hydrazine in the temperature range $230\text{--}300^\circ\text{C}$. A similar observation has been made for the hydrazinium uranyl oxalate system [7]. In the second and third steps the phthalates undergo exothermic decomposition to give finally U_3O_8 as the end product.



The single-step exothermic decomposition of this complex is similar to that observed in the thermal decomposition of its Co and Ni analogues [9]. The first exotherm at 140°C is associated with almost complete decomposition to form UO_3 . This is probably due to high heats of combustion of simultaneous decomposition of four hydrazine moieties in this complex. The second exotherm at 440°C is a simple conversion of UO_3 to U_3O_8 . This mode of decomposition is supported by the thermal reactivity of $UO_2(N_2H_3COO)_2\cdot N_2H_4\cdot H_2O$ [19] also in two steps but with a slightly higher temperature of decomposition.



The acetate and propionate analogues follow the same pattern of decomposition. Just before decomposition both these complexes melt, as indicated by the endotherms at 220°C . This has not been observed in other complexes. The first step exothermic decomposition, at 235 and 230°C , respectively, leads to the formation of the uranyl carboxylate intermediates. The final step involves the endothermic decomposition of the intermediates to form U_3O_8 . This is in accordance with broad endotherms in DTA at 275 and 350°C and at 250 and 320°C , respectively. The decomposition of the

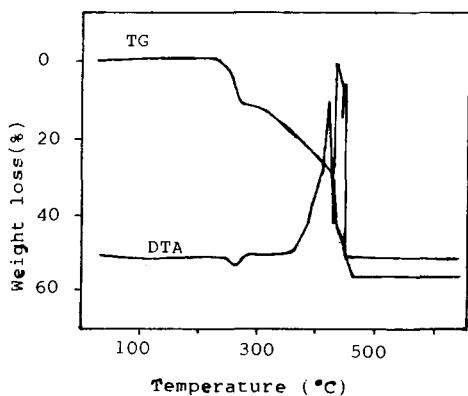
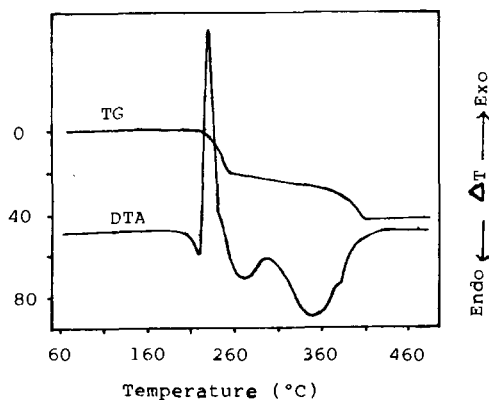


Fig. 3. TG-DTA of $(N_2H_5)_2[UO_2(o-C_6H_4(COO)_2)_2]$.

Fig. 4. TG-DTA of $N_2H_5[UO_2(CH_3COO)_3]$.



propionate complex takes place at a comparatively low temperature and this may be associated with a greater entropy change for CH_3CH_2 than for CH_3 . Interestingly the same mode of decomposition was observed [1] with their ammonium and sodium analogues. The simultaneous TG–DTA of the acetate complex is shown in Fig. 4 as a representative example.



Thermal decomposition of this complex begins at about 160°C and proceeds in three stages. The first step is an exothermic (190°C) loss of thioglycolic acid to form uranyl thioglycolate hydrazinate. This undergoes melting at 290°C followed by an endothermic decomposition at 335°C to form the intermediate uranyl thioglycolate. In the final stage the intermediate shows endothermic decomposition at 450°C to form the solid U_3O_8 as the final product. Similar thermal reactivity has been already reported [1] for ammonium uranyl thiophene-2-carboxylate system.

4. Conclusion

Aliphatic and aromatic carboxylic acids containing carboxyl as the only coordinating group generally form the same types of complexes with uranyl ion as does acetic acid. Thus, in all the complexes the coordination geometry around U(VI) is hexagonal bipyramid. The thermal reactivity of the complexes reveals that they decompose at lower temperatures than their ammonium or sodium analogues to form U_3O_8 as the final product. This may be due to the “fueling” nature of hydrazine. In the complexes reported here and previously, N_2H_5^+ is not coordinated.

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