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HEXAVALENT URANIUM DICARBOXYLATES WITH HYDRAZINE

Preparation, characterization and thermal studies

S. Yasodhai and S. Govindarajan[*]

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

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Abstract

The uranium complexes of composition, $UO_2X{\cdot}N_2H_4{\cdot}H_2O$, *X*=succinate or glutarate, $UO_2X_2{\cdot}N_2H_4{\cdot}H_2O$, *X*=Hadipate, Hpimelate, Hsuberate, Hazelate and Hsebacate and $UO_2X{\cdot}N_2H_4$, where *X*=malate and oxydiacetate have been prepared and characterized by analytical, spectral (IR and electronic), thermal and X-ray powder diffraction studies. Hydrazine acts as a monodentate ligand in uranyl succinate, glutarate, malate and oxydiacetate hydrazinates and bidentate in uranyl adipate, pimelate, suberate, azelate and sebacate hydrazinate hydrate complexes. The dicarboxylate anions bind the uranium through uni- and bidentate fashion depending upon the coordination polyhedra. All the dicarboxylate hydrazinate complexes in this series decompose to give U_3O_8 as the end product through their respective uranyl dicarboxylate intermediates. Malate and oxydiacetate compounds decompose exothermically in a single step. The coordinated water is confirmed from thermal data. The complexes of succinate to sebacate seem to possess hexagonal bipyramidal geometry around uranium, whereas pentagonal bipyramidal geometry has been proposed for both malate and oxydiacetate complexes.

Keywords: dicarboxylates, hydrazinates, spectral studies, thermal decomposition

Introduction

Like *d*-block divalent cations, the hexavalent uranyl cation (UO_2^{2+}) forms a number of complexes with a variety of anions and neutral molecules. Among the anions, a large amount of carboxylate complexes of uranium have been prepared and characterized [1–10]. A great variety of carboxylate complexes of uranium with sodium, potassium and ammonium has been reported [6–8]. The corresponding $N_2H_5^+$ complexes of carboxylates, especially dicarboxylates are limited [1, 14]. But, oxalate complexes of uranium with hydrazinium cations have been well characterized by thermal and X-ray crystallographic studies [1, 4]. In these compounds, $N_2H_5^+$ ion is not coordinated to uranium. As a whole, in the uranium complexes, the $(O–U–O)^{2+}$ group has

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[*] Author to whom all correspondence should be addressed.

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been found to be linear and the coordination generally occurs on or near the equatorial plane forming a pentagonal or hexagonal bipyramidal geometry.

The thermal studies of uranium complexes are very scanty. In hydrazine complexes [10], it is more important due to the fueling nature of hydrazine. Therefore, in continuation to our work on divalent transition metal dicarboxylate hydrazine complexes [11–16], we herein report the results of the preparation, characterization and thermal studies of hexavalent uranium complexes of hydrazine with dicarboxylic acids such as succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, malic and oxydiacetic acids.

Experimental section

Uranyl nitrate hexahydrate, dicarboxylic acids and hydrazine hydrate (99–100%) used were of analytical grade and the solvents were distilled before use.

Preparation of $UO_2X\cdot N_2H_4\cdot H_2O$ (X=succinate or glutarate), $UO_2X\cdot N_2H_4$ (X=malate or oxydiacetate) and $UO_2(Hadi)_2\cdot N_2H_4\cdot H_2O$

An aqueous solution (20 mL) of dicarboxylic acid (for e.g., succinic acid, 0.59 g, 0.005 mol) and hydrazine hydrate (0.25 mL, 0.005 mol) was added to an aqueous solution (20 mL) of uranyl nitrate hexahydrate (0.63 g, 0.00125 mol). Except adipate, all the other compounds were precipitated from the reaction solutions after a day, whereas adipate compound has been separated by the reverse addition of the reactants. These compounds were repeatedly washed with water, alcohol and ether, and air dried.

Preparation of $UO_2X_2\cdot N_2H_4\cdot H_2O$ (X=Hpimelate, Hsuberate, Hazelate or Hsebacate)

An aqueous solution (20 mL) containing 0.63 g (0.00125 mol) of $UO_2(NO_3)_2\cdot 6H_2O$ was mixed with a ligand solution of dicarboxylic acid (for e. g., pimelic acid, 0.8 g, 0.005 mol) and hydrazine hydrate (0.25 mL, 0.005 mol for pimelate, suberate and azelate; 0.4 mL, 0.008 mol for sebacate). The complexes of pimelate and suberate separated from the solution after a day, but the azelate and sebacate within an hour. The complexes obtained were separated and washed as above.

These compounds are insoluble in water and alcohol and the other organic solvents like acetone, chloroform, etc.

The uranium(VI) content in these compounds was estimated gravimetrically using oxine reagent. The amount of hydrazine in the complexes was determined by titration with 0.025 M KIO_3 under Andrews' conditions. The reflectance spectra of the powdered complexes were recorded on a Shimadzu 240A UV visible spectrophotometer in the 200–800 nm range. The infrared spectra were recorded on KBr pellets with a Shimadzu FTIR-8201PC spectrophotometer in the range of 4000–400 cm^{-1}. The simultaneous TG-DTA measurements were carried out on a STA 1500 thermal analyzer. The experiments were done in air using platinum cups as sample holders with 5–10 mg of the samples at the heating rate of 10°C min^{-1}. The X-ray powder dif-

Table 1 Analytical and electronic spectral data

Compound	Hydrazine/% observed (calculated)	Uranium/% observed (calculated)	Carbon/% observed (calculated)	Hydrogen/% observed (calculated)	Nitrogen/% observed (calculated)	Yield/%	Electronic spectral data Band positions/cm^{-1}
$UO_2(suc)\cdot N_2H_4\cdot H_2O$	07.25(07.34)	53.80(54.59)	14.11(11.01)	02.82(02.29)	06.79(06.42)	75	23529, 22831, 21834, 21142
$UO_2(glu)\cdot N_2H_4\cdot H_2O$	05.61(07.11)	53.91(52.89)	14.07(13.33)	02.97(02.67)	05.93(06.22)	72	22840, 21732, 21140
$UO_2(Hadi)_2\cdot N_2H_4\cdot H_2O$	06.15(06.90)	50.51(51.29)	15.37(15.52)	02.88(03.02)	05.61(06.03)	65	23529, 22831, 21930, 21277
$UO_2(Hpim)_2\cdot N_2H_4\cdot H_2O$	04.97(05.02)	38.74(37.30)	25.30(26.33)	03.83(04.39)	04.69(04.27)	68	23810, 23202, 22321, 21413, 20576
$UO_2(Hsub)_2\cdot N_2H_4\cdot H_2O$	04.65(04.80)	37.10(35.74)	27.29(28.83)	05.31(04.80)	03.93(04.20)	72	23620, 22980, 21572, 20461
$UO_2(Haze)_2\cdot N_2H_4\cdot H_2O$	05.97(04.61)	35.32(34.29)	31.76(31.12)	04.77(05.18)	04.36(04.03)	70	23866, 23419, 22624, 22075, 21368, 20790
$UO_2(Hseb)_2\cdot N_2H_4\cdot H_2O$	03.77(04.40)	32.50(32.96)	32.98(33.24)	04.72(05.26)	03.28(03.88)	67	23641, 23041, 22321, 21739 20877
$UO_2(mal)\cdot N_2H_4$	07.20(07.37)	53.49(54.84)	10.88(11.06)	01.85(01.84)	06.51(06.45)	62	22124, 22277, 20576, 19802
$UO_2(oda)\cdot N_2H_4$	07.11(07.37)	55.32(54.84)	11.65(11.06)	02.29(01.84)	06.08(06.45)	70	23474, 21552, 20877, 20450, 19802

suc – succinate dianion; glu – glutarate dianion; Hadi – hydrogenadipate; Hpim – hydrogenpimelate; Hsub – hydrogensuberate; Haze – hydrogenazelate; Hseb – hydrogensebacate monoanion; mal – malate dianion; oda – oxydiacetate dianion fraction patterns were obtained on a JEOL JDX 8030 X-ray diffractometer using CuK_α radiation.

Results and discussion

The chemical analyses of the complexes are given in Table 1 and are best fit with the proposed composition for the complexes.

The reflectance spectra of the hydrazinates exhibit bands in the range 23866–19802 cm^{-1}, which is assigned to the transition, $^1\sum_{g+}\rightarrow{}^3\Pi_u$ of the uranyl ion [17]. The band positions are listed in Table 1.

The infrared spectral band positions of the complexes are given in Table 2. In these complexes, the absorption frequencies in the range 3600–3320 cm^{-1} has been attributed to O–H stretching frequency of water, free carboxyl group or hydroxyl group of the malic acid. The N–H stretching frequencies of the hydrazine complexes appear in the range 3440–3070 cm^{-1}. The C=O stretching of the free carboxyl group in the adipate, pimelate, suberate, azelate and sebacate complexes register a band around 1700 cm^{-1}, augmenting monoanionic nature of the dicarboxylic acids in these complexes.

The deprotonated carboxyl groups in the monoanionic complexes show an asymmetric and symmetric stretching frequencies near 1525 and 1460 cm^{-1}, respectively, with an average separation of 65 cm^{-1}, illustrating bidentate coordination of the deprotonated carboxyl group [18]. The dianionic succinate and glutarate also register asymmetric and symmetric average separations below 170 cm^{-1}, showing bidentate coordination of both the deprotonated carboxyl groups of the dianion. The malate and oxydiacetate hydrazinates show an asymmetric and symmetric stretches at 1660; 1640 and 1364; 1406 cm^{-1}, respectively, with a separation of above 170 cm^{-1}, indicating the monodentate coordination of both the carboxylate groups in the dianion.

N–N stretching frequencies in the range 988–951 cm^{-1} show the bidentate bridging behaviour of hydrazine in the complexes of succinate, glutarate, malate and oxydiacetate. The rest of the complexes register a band near 920 cm^{-1} which overlaps with a O–U–O asymmetric stretching of the uranyl ion, showing the monodentate coordination of the neutral hydrazine. The O–U–O asymmetric stretching frequency of the complexes appears around 920 cm^{-1}.

Simultaneous TG an DTA data of the prepared complexes are given in Table 3. In the series, the hydrated dicarboxylate hydrazinates decompose through their respective dicarboxylate intermediates to give U_3O_8 as the end residue, whereas the anhydrous malate and oxydiacetate hydrazinates decopose exothermically in a single step to give U_3O_8.

Table 2 Infrared spectral data/cm^{-1}

Succinate	Glutarate	Adipate	Pimelate	Suberate	Azelate	Sebacate	Malate	Oxydiacetate	Assignments
3560– 3320 b	3570	3471	3600– 3520 b	3600– 3440 b	3500– 3450 b	3480– 3400 b	3440	–	ν(O–H) of water/ acid/O–H group
3300 3219 –	3440 3360 3270	3360 3230 3110	3360 3230 3070	3360 3220 3080	3358 3230 3120	3354 3220 3100	3338 3250 3120	3352 3300 –	ν(N–H)
–	–	–	1701	1710	1700	1700	–	–	ν(C=O) of free COOH
1533	1526	1528	1526	1529	1520	1526	1660	1640	$\nu_{asy}(COO^{-})$
1456 1396	1458 1408	1458 1406	1458 –	1460 –	1460 –	1460 –	1364 –	1406 –	$\nu_{sym}(COO^{-})$
962	988	–	–	–	–	–	970	951	ν(N–N)
908	916	922	926	924	926	920	914	922	ν_{asy}(O–U–O)
889	827	845	802	883	882	880	806	837	ν_{sym}(O–U–O)

Table 3 Thermal data

Compound	DTA peak temp/°C	Thermogravimetry (TG)		Decomposition product
		Temp. range/°C	Mass loss/% found (calcd.)	
$UO_2(suc)\cdot N_2H_4\cdot H_2O$	86(+) 216(+) 482(–)	70–130 198–220 220–550	04.00(04.13) 10.00(11.47) 38.00(35.63)	$UO_2(suc)\cdot N_2H_4$ $UO_2(suc)$ U_3O_8
$UO_2(glu)\cdot N_2H_4\cdot H_2O$	68(+) 215(+) 378(–)	57–70 206–225 225–250	04.50(04.00) 11.00(11.00) 40.00(37.63)	$UO_2(glu)\cdot N_2H_4$ $UO_2(glu)$ U_3O_8
$UO_2(Hadi)_2\cdot N_2H_4\cdot H_2O$	241(+) 288(–) 380(–) 436(–)	226–245 245–460	10.00(10.78) 42.00(39.51)	$UO_2(Hadi)_2$ U_3O_8
$UO_2(Hpim)_2\cdot N_2H_4\cdot H_2O$	201(+) 305(+) 390(–) 464(–)	187–205 205–490	07.00(07.84) 52.00(56.00)	$UO_2(Hpim)_2$ U_3O_8
$UO_2(Hsub)_2\cdot N_2H_4\cdot H_2O$	170(+) 281(–) 390(–)	161–185 185–450	06.00(07.51) 60.00(57.86)	$UO_2(Hsub)_2$ U_3O_8
$UO_2(Haze)_2\cdot N_2H_4\cdot H_2O$	212(–) 265(–) (s) 337(–) (s) 377(–) 476(–)	200–215 215–480	07.00(07.20) 60.00(59.56)	$UO_2(Haze)_2$ U_3O_8
$UO_2(Hseb)_2\cdot N_2H_4\cdot H_2O$	192(+) 263(–) 383(–) 471(–)	165–205 205–480	07.00(06.93) 60.00(61.13)	$UO_2(Hseb)_2$ U_3O_8
$UO_2(mal)\cdot N_2H_4$	303(–) 334(–) 425(–) 499(–)	293–510	34.00(35.33)	U_3O_8
$UO_2(oda)\cdot N_2H_4$	332(–) 365(–) 444(–)	328–550	36.00(35.33)	U_3O_8

s – shoulder

$UO_2(OOC(CH_2)_nCOO)\cdot N_2H_4\cdot H_2O$, (n=2 or 3)

These two compounds exhibit a similar decomposition pattern. The dehydration below 100°C shows the presence of hydrated water molecule in these compounds. Then the endothermic decomposition of both the anhydrous hydrazinate complexes yield their respective dicarboxylate intermediate above 200°C (TG temperature range 200–225°C for both the complexes). The exothermic decomposition of the intermediates completes within 550°C resulting in U_3O_8 as the final product. A representative example of simultaneous TG-DTA of $UO_2(glu)\cdot N_2H_4\cdot H_2O$ is given in Fig. 1.

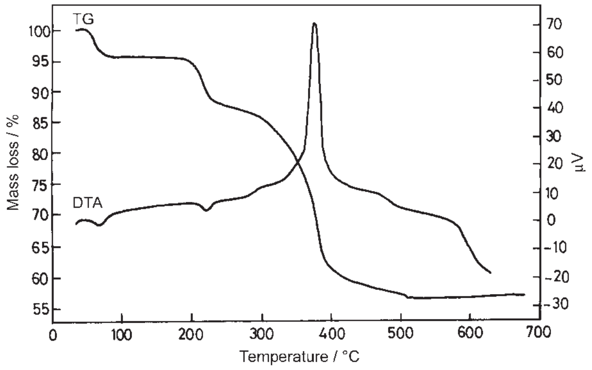

Fig. 1 Simultaneous TG-DTA of $UO_2(glu)\cdot N_2H_4\cdot H_2O$

$UO_2(HOOC)(CH_2)_nCOO)_2\cdot N_2H_4\cdot H_2O$, (n=4, 5, 6 or 8)

In these complexes, dehydration and dehydrazination take place continuously. An endothermic transformation allows a respective dicarboxylate intermediate which on further exothermic decomposition gives U_3O_8 as the solid end residue. TG temperature ranges are in accordance with DTA results. Simultaneous TG-DTA curves of the pimelate compound are given in Fig. 2 as a reference.

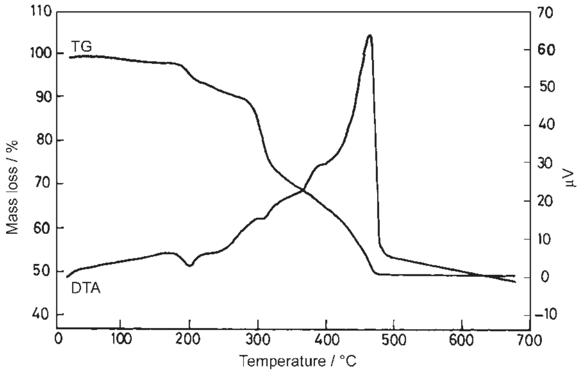

Fig. 2 Simultaneous TG-DTA of $UO_2(Hpim)_2\cdot N_2H_4\cdot H_2O$

$UO_2(Haze)_2\cdot N_2H_4\cdot H_2O$

The complete two-step exothermic decomposition of this complex gives U_3O_8 as the end residue. In contrast to other complexes, the dehydration and dehydrazination occur exothermically (Fig. 3). Similar mode of decomposition has also been observed in the cases of Zn and Cd azelate hydrazinates [15]. This may be due to the effect of an-ion on decomposition. Exothermic multiplets are observed for the decomposition of monoanionic intermediates, which are given in Table 3.

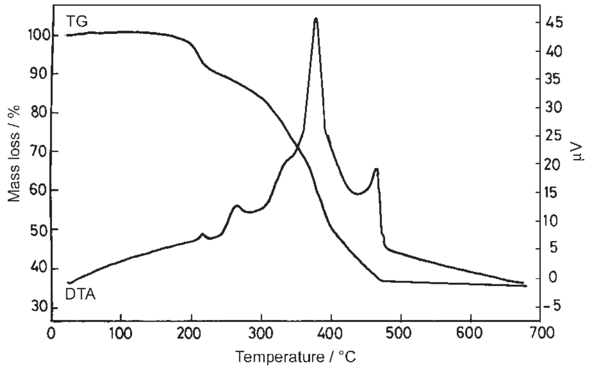

Fig. 3 Simultaneous TG-DTA of $UO_2(Haze)_2 \cdot N_2H_4 \cdot H_2O$

$UO_2X \cdot N_2H_4$, (X=malate or oxydiacetate)

Simultaneous TG-DTA of both the titled compounds (Figs 4 and 5) show a single step exothermic decomposition to yield U_3O_8 as the end product. From the curves, it is observed that these two complexes are stable up to 300°C. The decomposition starts at around 300 and completes within 550°C. Though TG shows a continuous single step decomposition, the DTA exhibits an exothermic multiplets for both the compounds.

The close examination of the X-ray powder patterns of the similar type of complexes seems to reveal isomorphism (Table 4) among them. However, it is not very clear due to the poor resolution of the diffractograms owing to the powdery nature of the compounds.

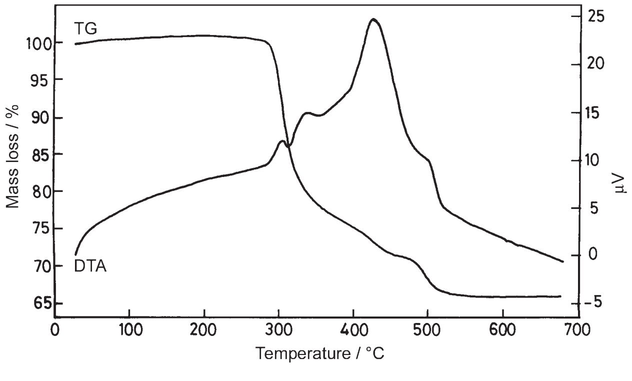

Fig. 4 Simultaneous TG-DTA of $UO_2(mal) \cdot N_2H_4$

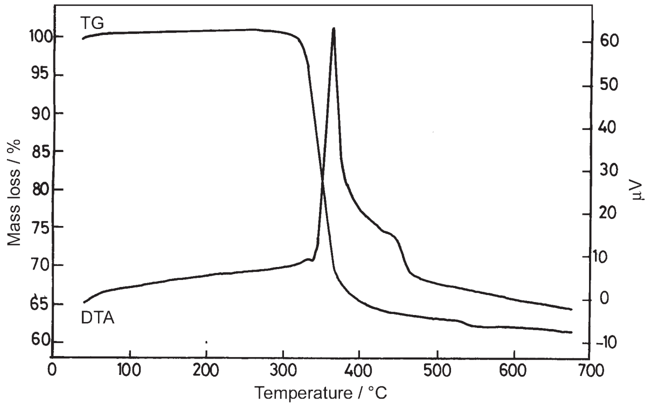

Fig. 5 Simultaneous TG-DTA of $UO_2(oda)\cdot N_2H_4$

Table 4 XRD data (*d* spacings in Å)

Suc.	Glu.	Adip.	Pim.	Sub.	Aze.	Seb.	Mal.	Oda.
12.44	12.42	12.45	12.98	11.47	11.47	12.53	12.48	12.44
6.96	7.21	7.02	10.16	9.63	9.02	7.37	7.43	6.23
4.92	4.00	6.10	7.89	6.84	6.96	6.51	6.55	5.21
4.00	3.52	4.98	6.60	6.00	6.37	5.57	4.69	4.64
3.46	2.95	3.83	5.82	4.10	5.82	4.48	4.15	4.13
3.10	2.34	3.36	4.77	3.30	5.15	2.89	3.78	3.86
2.83	1.83	2.23	4.09	2.85	3.83	–	3.46	3.10
2.45	–	–	3.78	–	3.22	–	3.00	2.06
2.31	–	–	–	–	–	–	2.29	1.55
2.18	–	–	–	–	–	–	2.20	–
2.08	–	–	–	–	–	–	1.75	–
2.00	–	–	–	–	–	–	–	–
1.91	–	–	–	–	–	–	–	–
1.85	–	–	–	–	–	–	–	–

From the physico-chemical studies, it is found that in the adipate, pimelate, suberate, azelate, sebacate, succinate and glutarate complexes, the dicarboxylate anions are present as a bi- or tetradentate chelating ligand and in the rest as a bidentate through two carboxylate anions. The monodentate and bridging bidentate coordination are observed for the neutral hydrazine molecule. The water coordination in hydrated compounds is confirmed by thermal analyses. Based on them, the hexagonal bipyramidal geometry around uranium is proposed for the complexes of succinate to sebacate whereas pentagonal bipyramidal coordination for the anhydrous malate and oxydiacetate compounds.

Conclusions

Though many hydrazinium uranyl carboxylates are known [1–4], the complexes of uranyl carboxylates with neutral hydrazines are not known, except uranyl hydrazidocarboxylate hydrazinate hydrate of composition, $UO_2(N_2H_3COO)_2{\cdot}N_2H_4{\cdot}H_2O$ [5]. Among the regular dicarboxylates, our attempt to isolate the uranyl malonate hydrazinate was unsuccessful due to the formation of insoluble uranyl malonate. Mono- and bidentate bridging coordination of hydrazine and the bidentate and tetradentate chelation of the dicarboxylate anions are observed in the reported complexes. The lower and the substituted dicarboxylic acids are dianionic in their complexes, whereas the higher dicarboxylates are monoanionic with a free carboxyl group. The malate and oxydiacetate hydrazinates decompose in a single step, whereas the regular dicarboxylate hydrazinates decompose through carboxylate intermediates. However, all of them leave U_3O_8 as the solid end residue.

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