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SYNTHESIS AND THERMAL BEHAVIOUR OF STRONTIUM URANYL MALONATE AND BARIUM URANYL MALONATE TRIHYDRATES

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ABSTRACT

The synthesis and thermal behaviour of strontium uranyl malonate and barium uranyl malonate trihydrates are described. Their thermal behaviour has been investigated by DTA, TG and X-ray diffraction techniques. In the thermal dehydration of these compounds, the monohydrate and anhydrous intermediates have been isolated and the anhydrous complexes yield on decomposition the orthorhombic monouranates β-$SrUO_4$ or $BaUO_4$ as final products.

INTRODUCTION

In previous papers, the synthesis, characterization and thermal behaviour of some neutral and anionic uranyl malonate derivatives with the monovalent cations Li, Na, K and NH_4 have been described [1,2]. In these anionic complexes, the formation of the monouranates M_2UO_4 occurs by reaction between the intermediates alkaline carbonate and diuranate.

In order to extend this study to the formation processes of the alkaline-earth monouranates, uranyl malonate complexes with strontium and barium were prepared, and their decomposition reactions were investigated by DTA, TG and X-ray diffraction techniques. The intermediate compounds isolated during the heating process were characterized.

EXPERIMENTAL

Apparatus

Differential thermal analysis (DTA) and thermogravimetric (TG) experiments were carried out in a still air atmosphere (Deltatherm D-2000), with a

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heating rate of 10°C min^{-1}. In the DTA studies, precalcined alumina was used as reference material.

The X-ray diffraction diagrams were obtained with a Philips 1310/00 unit, using both Debye–Scherrer camera and diffractometric (LiF curved crystal monochromator) techniques. Cu K_α radiation was used.

A Coleman model 33 microanalyzer was used for the carbon and hydrogen determinations.

Synthesis

The strontium and barium compounds were obtained as well-formed yellow crystals from an aqueous solution of malonic acid, uranyl nitrate and the corresponding metal hydroxide, in the molar ratio 2 : 1 : 2.

To an aqueous solution of malonic acid and uranyl nitrate (2 : 1), a hot solution of strontium or barium hydroxide is added with continuous stirring. When one mole of metal hydroxide has been added, uranyl malonate trihydrate, $UO_2(C_3H_2O_4) \cdot 3\ H_2O$, precipitates [2]. If up to two moles of the metal hydroxide are added, the former compound re-dissolves and a clear solution (pH 5.5) is obtained. After standing for about 1 week, the respective uranyl malonate trihydrate crystallizes.

Analysis

The carbon and hydrogen content was determined by the conventional microcombustion method. Uranium, strontium and barium were determined gravimetrically. From samples dissolved in dilute nitric acid, strontium and barium were precipitated with H_2SO_4. The strontium or barium sulphates were filtered off, and uranium was precipitated from the filtered liquid as $(NH_4)_2U_2O_7$; the ammonium diuranate was calcined to U_3O_8 at about 850°C. The metal contents were calculated from the products obtained after ignition of the samples at 800°C, to yield the monouranates MUO_4 (M = Sr, Ba) identified by their X-ray diffraction patterns, as shown below. The water content was deduced from the weight loss observed in the TG curves which agrees with that obtained from the chemical analysis.

Calcd. for $Sr[UO_2(C_3H_2O_4)_2] \cdot 3\ H_2O$ (%): C, 11.69; H, 1.62; U, 38.66; Sr, 14.23. Found (%): C, 12.16; H, 1.71; U, 38.62; Sr, 14.21.

Calcd. for $Ba[UO_2(C_3H_2O_4)_2] \cdot 3\ H_2O$ (%): C, 10.82; H, 1.50; U, 35.77; Ba, 20.64. Found (%): C, 11.28; H, 1.58; U, 35.75; Ba, 20.55.

RESULTS AND DISCUSSION

The compounds crystallize in the orthorhombic system; Tables 1 and 2 show the lattice parameters, $\sin^2\theta$, d-spacings, intensities of the reflections

TABLE 1

X-ray crystallographic data of the strontium uranyl malonate trihydrate (orthorhombic: $a = 16.729$ Å, $b = 23.247$ Å, $c = 6.848$ Å)

$\sin^2\theta_{cal}$	$\sin^2\theta_{exp}$	d_{cal} (Å)	d_{exp} (Å)	I/I_0	hkl
0.00440	0.00439	11.62	11.63	10	020
0.00849	0.00848	8.36	8.37	30	200
0.00959	0.00959	7.87	7.87	22	210
0.01289	0.01281	6.79	6.80	68	220
0.01590	0.01587	6.11	6.12	44	111
0.01707	0.01719	5.90	5.90	50	021
0.01759	0.01761	5.81	5.81	100	040
0.01839	0.01835	5.68	5.69	75	230
0.01919	0.01922	5.56	5.56	70	121
0.02227	0.02221	5.17	5.17	20	211
0.02469	0.02466	4.91	4.91	30	131
0.02557	0.02558	4.82	4.82	46	221
0.02609	0.02612	4.77	4.77	20	240
0.03027	0.03028	4.43	4.43	10	041
0.03106	0.03111	4.37	4.37	12	231
0.03239	0.03244	4.28	4.28	100	141
0.03288	0.03278	4.25	4.26	52	311
0.03508	0.03501	4.12	4.12	70	410
0.03599	0.03611	4.06	4.06	27	250
0.03837	0.03852	3.94	3.93	20	420
0.03959	0.03964	3.87	3.87	25	060
0.04387	0.04365	3.68	3.69	55	430
0.04808	0.04796	3.52	3.52	40	260
0.05281	0.05289	3.35	3.35	20	102
0.05438	0.05424	3.31	3.31	10	161
0.05721	0.05739	3.22	3.22	18	122
0.05928	0.05936	3.17	3.16	65	351
0.06271	0.06261	3.08	3.08	17	132
0.06686	0.06692	2.98	2.98	20	511
0.07038	0.07023	2.91	2.91	35	080
0.07090	0.07066	2.90	2.90	27	312
0.07429	0.07426	2.83	2.83	50	322
0.08518	0.08520	2.64	2.64	22	181
0.08668	0.08658	2.62	2.62	22	252
0.09155	0.09158	2.55	2.55	13	281
0.09240	0.09233	2.54	2.54	19	162

and Miller indices. Figure 1 shows the DTA and TG curves and their thermal behaviours are summarized in Table 3. The dehydration reaction occurs in two consecutive steps, and the monohydrated and anhydrous compounds are formed. Table 4 shows the interplanar spacings and relative intensities of X-ray reflections of the monohydrated and anhydrous strontium uranyl malonate, and barium uranyl malonate monohydrate. The anhydrous barium salt is amorphous as shown in the X-ray diffraction diagrams.

TABLE 2

X-ray crystallographic data of the barium uranyl malonate trihydrate (orthorhombic: a = 17.063 Å, b = 23.604 Å, c = 6.855 Å)

$\sin^2\theta_{cal}$	$\sin^2\theta_{exp}$	d_{cal} (Å)	d_{exp} (Å)	I/I_0	hkl
0.00816	0.00823	8.53	8.50	13	200
0.00923	0.00929	8.02	8.00	18	210
0.01243	0.01250	6.91	6.90	80	220
0.01575	0.01577	6.14	6.14	52	111
0.01707	0.01706	5.90	5.90	83	040
0.01776	0.01786	5.78	5.77	70	230
0.01895	0.01896	5.60	5.60	48	121
0.02429	0.02423	4.95	4.95	38	131
0.02523	0.02515	4.85	4.86	44	240
0.03041	0.03033	4.42	4.43	10	231
0.03175	0.03160	4.33	4.34	100	141
0.03373	0.03390	4.20	4.19	75	410
0.03483	0.03466	4.13	4.14	35	250
0.03528	0.03530	4.10	4.10	20	321
0.03788	0.03786	3.96	3.96	23	241
0.04226	0.04238	3.75	3.74	45	430
0.04637	0.04633	3.58	3.58	65	411
0.05370	0.05388	3.33	3.32	13	112
0.05768	0.05751	3.21	3.21	40	351
0.05982	0.06001	3.15	3.15	15	212
0.06474	0.06474	3.03	3.03	25	511
0.06765	0.06791	2.96	2.96	37	042
0.06942	0.06923	2.93	2.93	25	361
0.07106	0.07125	2.89	2.89	38	460
0.07328	0.07354	2.85	2.84	15	531
0.07775	0.07788	2.76	2.76	20	620
0.08295	0.08296	2.68	2.68	40	181
0.09034	0.09017	2.56	2.57	30	551
0.10015	0.09995	2.44	2.44	20	650
0.10991	0.10975	2.33	2.33	58	452
0.11102	0.11099	2.31	2.31	28	272
0.12514	0.12529	2.18	2.18	45	612
0.13159	0.13154	2.13	2.13	65	233
0.14515	0.14497	2.02	2.02	40	292

The product isolated after the decomposition of the anhydrous complexes does not show a well-defined X-ray powder diagram. Three broad bands have been observed in the X-ray diagrams of the strontium and barium compounds ignited at 400 and 550°C at about 27, 31.5 and 45 2θ angles; they could be assigned approximately to the most intense reflections of the poorly crystallized β-strontium and barium monouranates. On the other hand, the diagrams of the residues after the last exothermic transformation (660–695°C and 625–655°C, respectively) correspond to well crystallized

TABLE 3

Thermal behaviour of the compounds

Compound	Thermal effects temperature (°C)	Transformation	Weight loss (%)	
			Calcd.	Found
$Sr[UO_2(C_3H_2O_4)_2]\cdot 3\,H_2O$	120–185	Removal of two water molecules and formation of $Sr[UO_2(C_3H_2O_4)_2]\cdot H_2O$	5.85	5.9
	230–300	Removal of one water molecule and formation of $Sr[UO_2(C_3H_2O_4)_2]$	2.92	3.0
	300–660	Decomposition of the anhydrous product	27.94	27.6
	660–695	Crystallization of strontium monouranate, β-$SrUO_4$	–	–
$Ba[UO_2(C_3H_2O_4)_2]\cdot 3\,H_2O$	120–190	Removal of two water molecules and formation of $Ba[UO_2(C_3H_2O_4)_2]\cdot H_2O$	5.41	5.4
	215–285	Removal of one water molecule and formation of $Ba[UO_2(C_3H_2O_4)_2]$	2.71	2.7
	285–625	Decomposition of the anhydrous product	25.85	25.7
	625–655	Crystallization of barium monouranate, $BaUO_4$	–	–

TABLE 4

X-ray powder diffraction data for the monohydrated and anhydrous strontium uranyl malonate, and the monohydrated barium uranyl malonate

$Sr[UO_2(C_3H_2O_4)_2]\cdot H_2O$				$Sr[UO_2(C_3H_2O_4)_2]$		$Ba[UO_2(C_3H_2O_4)_2]\cdot H_2O$	
d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
7.26	53	3.49	24	7.42	100	7.56	70
6.91	22	3.24	100	5.98	90	6.17	40
5.96	61	3.15	17	5.75	90	6.07	60
5.90	100	3.09	25	4.67	60	5.34	15
5.21	30	2.94	20	3.84	30	5.18	45
5.04	57	2.59	20	3.71	70	3.73	100
4.82	16	2.56	20	3.64	30	3.33	75
4.60	30	2.47	15	3.48	40	2.45	23
4.23	13	2.38	20	3.31	35	2.38	15
4.06	13	2.32	20	3.16	25	2.17	25
3.67	61	2.21	20	2.35	15	1.89	30
3.62	70	2.13	22	2.30	20	1.80	15

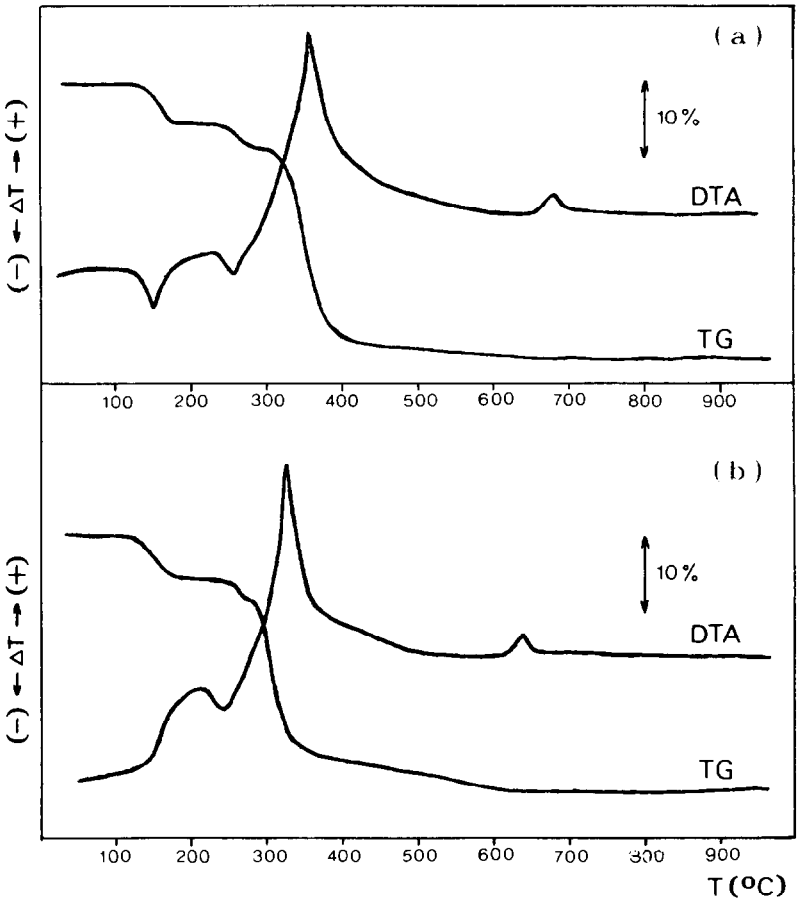

Fig. 1. DTA and TG curves of: (a) strontium uranyl malonate trihydrate; (b) barium uranyl malonate trihydrate.

β-$SrUO_4$ [3] or $BaUO_4$ [4,5]. These two exothermic effects can be attributed to the crystallization reaction of the alkaline-earth monouranates.

It can be concluded that by the thermal decomposition of the title compounds, β-$SrUO_4$ or $BaUO_4$ are directly obtained, and no intermediate carbonates or uranium oxides are formed.

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