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THERMAL DECOMPOSITION OF YTTRIUM, LANTHANUM AND LANTHANIDE COMPLEXES OF SQUARE ACID IN AIR ATMOSPHERE

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The conditions of thermal decomposition of the Y, La and lanthanide complexes of square acid in air atmosphere have been studied. On heating, the complexes of Y, La, Ce(III), Pr(III), Nd, Sm, Eu(III), Gd, Tb(III) and Ho decompose in two steps. First, the hydrated complexes lose crystallization water to form anhydrous salts. The complexes of Dy and Er decompose in three steps; they are dehydrated in two steps to form anhydrous salts. The complexes of Tm, Yb and Lu are dehydrated in three steps; in two steps they lose water molecules to form octahydrates, which in the third step are dehydrated during decomposition. On heating, the anhydrous complexes of Y, Ce(III), Pr(III), Eu(III), Gd, Tb(III), Dy, Ho and Er and the octahydrated salts of Tm, Yb and Lu decompose directly to the oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7. The anhydrous complexes of La, Nd and Sm decompose to Ln_2O_3 with intermediate formation of $Ln_2O_2CO_3$.

1,2-Diketocyclobutenediol, known as square acid, is a crystalline solid soluble in water. As a pseudoacid of lamination, it is ferroelectric [1, 2]. The salts of square acid are little known. The thermal decomposition of Ni(II) squarate has been studied in air and nitrogen atmospheres [3]. The salt was found to be stable up to 560 K. The X-ray spectrum of Ni(II) squarate has been recorded, and its structure has been determined [4]. Complexes of Ac(III) with formulae $Ac(C_4O_4)^+$ and $Ac(C_4O_4)_2^-$ have been identified in solution by an ion-exchange method, and their stability constants have been determined [5].

The aim of the present work was to obtain solid-state Y, La and lanthanide complexes of square acid and to examine the conditions and products of their thermal decomposition.

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Experimental

Complexes of Y, La and lanthanides from Ce(III) to Lu were prepared by adding equivalent amounts of a 0.087 *M* solution of square acid to a hot solution of rare earth chloride. The precipitate of rare earth squarate was heated in the mother liquor for 0.5 h, then filtered off, washed with water to remove Cl^- ions and dried at 303 K to constant weight.

The complexes of Y, La and lanthanides were prepared in crystalline form. The squarates of Y, La, Ce(III), Sm, Gd, Dy and Lu were white, those of Nd and Er pink, those of Pr(III) and Eu(III) green-yellow, those of Tb(III), Tm and Yb beige, and that of Ho cream-coloured.

The carbon and hydrogen contents of the rare earth squarates were determined by elemental analysis. The rare earth element contents were determined by thermogravimetry and by ignition of the complexes to the oxides at 1173 K. The water contents were determined by thermogravimetry and by isothermal heating at definite temperatures.

On the basis of the elemental analyses (Table 1), it was found that the complexes of the rare earths with square acid were prepared as hydrated compounds with a metal to ligand mole ratio of 2 : 3. The salts exhibited various degrees of hydration. The salts of La, Ce(III), Pr(III) and Sm crystallize with 13 water molecules, those of Nd, Gd, Tb(III) and Ho with 10 water molecules, that of Eu(III) with 8, that of Y

Table 1 Analytical data

Complex	Ln, %		C, %		H, %	
	calcd.	found	calcd	found	calcd.	found
$Y_2(C_4O_4)_3 \cdot 9H_2O$	26.6	26.5	21.5	21.7	2.7	2.7
$La_2(C_4O_4)_3 \cdot 13H_2O$	32.8	32.7	19.8	19.1	3.0	2.9
$Ce_2(C_4O_4)_3 \cdot 13H_2O$	32.9	32.8	16.9	16.9	3.1	3.3
$Pr_2(C_4O_4)_3 \cdot 13H_2O$	33.1	32.9	16.9	17.1	3.1	2.9
$Nd_2(C_4O_4)_3 \cdot 10H_2O$	35.8	35.8	20.9	21.0	2.5	2.7
$Sm_2(C_4O_4)_3 \cdot 13H_2O$	34.5	34.5	16.5	16.4	2.9	2.7
$Eu_2(C_4O_4)_3 \cdot 8H_2O$	38.8	38.8	18.4	18.6	2.0	2.0
$Gd_2(C_4O_4)_3 \cdot 10H_2O$	37.8	37.8	17.3	17.7	2.4	2.4
$Tb_2(C_4O_4)_3 \cdot 10H_2O$	38.1	38.0	17.3	17.8	2.4	2.5
$Dy_2(C_4O_4)_3 \cdot 26H_2O$	28.7	28.5	12.7	13.5	4.6	4.0
$Ho_2(C_4O_4)_3 \cdot 10H_2O$	38.9	39.0	17.0	17.5	2.6	2.4
$Er_2(C_4O_4)_3 \cdot 14H_2O$	36.6	36.8	15.8	16.0	3.1	2.9
$Tm_2(C_4O_4)_3 \cdot 26H_2O$	29.8	30.0	12.6	13.2	4.6	4.0
$Yb_2(C_4O_4)_3 \cdot 22H_2O$	32.1	32.0	13.3	13.3	4.0	3.9
$Lu_2(C_4O_4)_3 \cdot 22H_2O$	32.3	32.5	13.3	13.3	4.0	3.8

with 9, that of Er with 14, those of Yb and Lu with 22, and those of Dy and Tm with 26 water molecules.

The IR spectra of the studied complexes were recorded in the range 4000–400 cm^{-1}. They are similar to one another. Analysis of the IR spectra confirms the compositions of the complexes.

X-ray studies confirmed that the complexes are crystalline compounds of low symmetry, with large unit cells. They are characterized by different structures and different degrees of crystallinity.

The thermal stabilities of Y, La and lanthanide squarates were studied. The measurements were made on a Q–1500 D derivatograph at a heating rate of 10 $\mathrm{deg \cdot min^{-1}}$. The samples were heated in air atmosphere. The results are presented in Figs 1–7. The solid decomposition products were calculated from the weight loss in the TG curve and were confirmed by recording the IR spectra.

Results and discussion

On the basis of the thermal curves recorded for all the prepared complexes, the temperatures and products of decomposition were established. The results are given in Figs 1–7.

When heated in air atmosphere, the square acid complexes of Y, La and lanthanides from Ce(III) to Lu decompose in different ways.

The hydrates of Y, La, Ce(III), Pr(III), Nd, Sm, Eu(III), Gd, Tb(III) and Ho lose crystallization water in one step in the interval 313–573 K, which is associated with a strong endothermic effect. The anhydrous salts formed are quite strong, except for

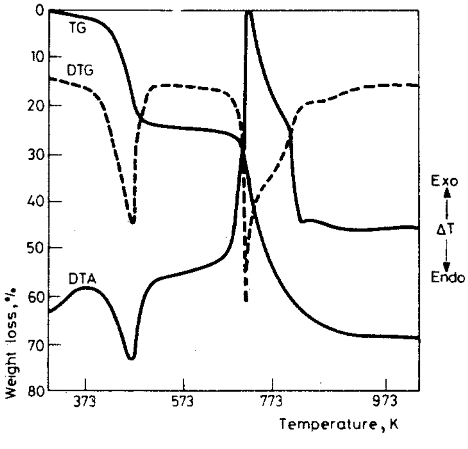

Fig. 1 TG, DTG and DTA curves of $Y_2(C_4O_4)_3 \cdot 9H_2O$

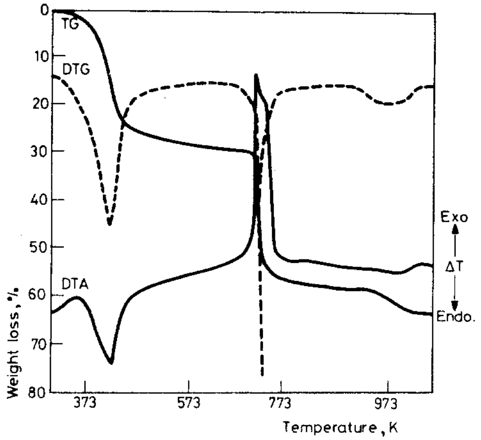

Fig. 2 TG, DTG and DTA curves of $La_2(C_4O_4)_3 \cdot 13H_2O$

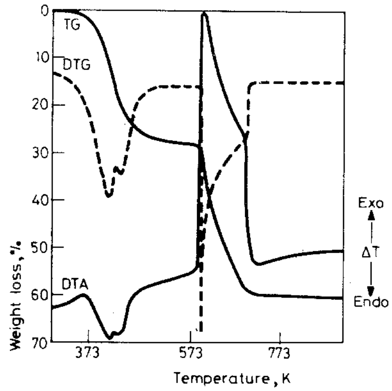

Fig. 3 TG, DTG and DTA curves of $Ce_2(C_4O_4)_3 \cdot 13H_2O$

Ce(III) squarate. The squarate of dysprosium is dehydrated in two steps on heating. It loses 8 water molecules at 413–513 K, and the next 18 water molecules at 513–633 K, forming the anhydrous salt, which immediately decomposes directly to Dy_2O_3. The hydrate of erbium squarate, crystallizing with 14 water molecules, is also dehydrated in two steps. The complex loses 12 water molecules in the interval 313–503 K, and the next 2 molecules at 553–673 K, to yield the anhydrous salt, which decomposes directly to Er_2O_3. The most hydrated thulium, ytterbium and lutetium squarates are dehydrated in three steps. Thulium squarate hydrate loses 12 water molecules at 363–433 K, and then a further 6 water molecules at 433–493 K. The octahydrate formed decomposes directly to Tm_2O_3.

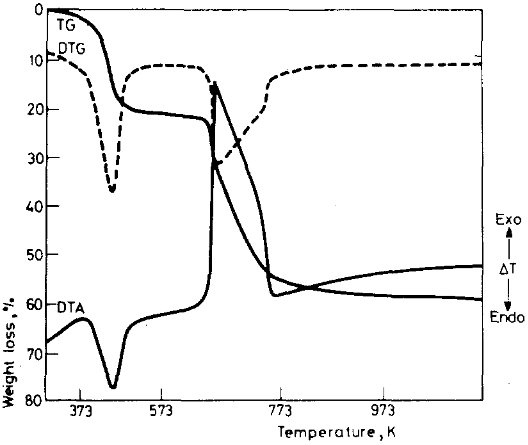

Fig. 4 TG, DTG and DTA curves of $Tb_2(C_4O_4)_3 \cdot 10H_2O$

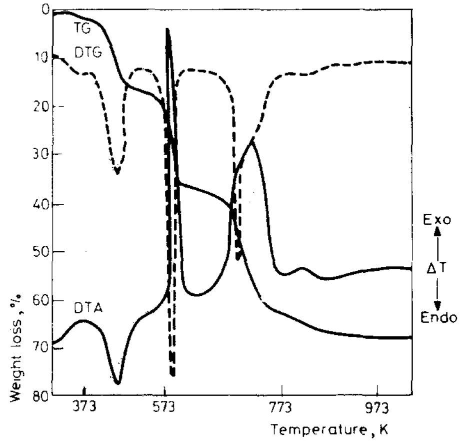

Fig. 5 TG, DTG and DTA curves of $Dy_2(C_4O_4)_3 \cdot 26H_2O$

The squarates of ytterbium and lutetium lose 14 of the 22 water molecules in two steps to form unstable octahydrates, which decompose to Yb_2O_3 and Lu_2O_3.

The ranges of dehydration temperatures of the rare earth squarates are presented in Fig. 8. These were found to vary periodically with increasing atomic number; erbium has the highest value.

The results indicate that the anhydrous rare earth squarates, except those of Ce(III) and Dy, are stable, whereas the octahydrates of Tm, Yb and Lu squarates are very unstable. When heated in air, the anhydrous complexes of Y, Ce(III), Pr(III), Eu(III), Gd, Tb(III), Dy, Ho and Er, and the octahydrates of Tm, Yb and Lu,

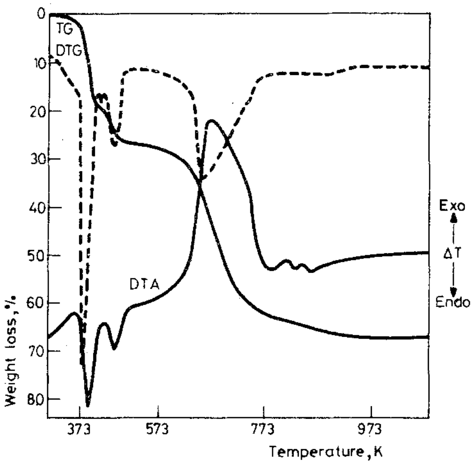

Fig. 6 TG, DTG and DTA curves of $Tm_2(C_4O_4)_3 \cdot 26H_2O$

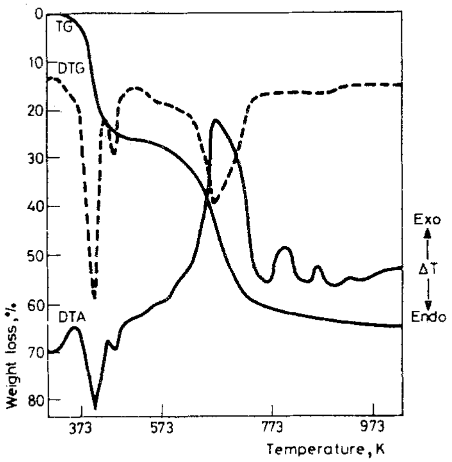

Fig. 7 TG, DTG and DTA curves of $Lu_2(C_4O_4)_3 \cdot 22H_2O$

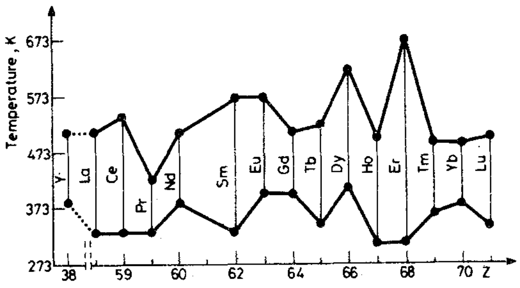

Fig. 8 Relationship between range of dehydration temperatures and Z

decompose directly to the oxides, whereas the anhydrous complexes of La, Nd and Sm decompose to Ln_2O_3 with the intermediate formation-of $Ln_2O_2CO_3$. The rare earth oxides are formed at 863–963 K, except for those of La, Nd, Tb and Tm, which are formed at 1053–1123 K (Fig. 9). The temperatures of oxide formation vary periodically with increasing atomic number Z and decreasing ionic radius in the lanthanide series. The double–double effect has been observed.

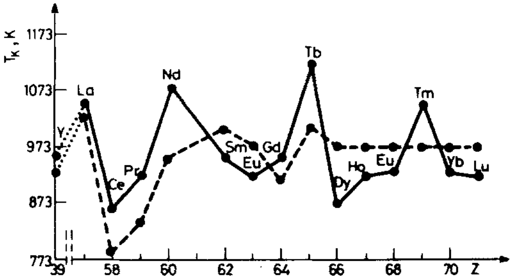

Fig. 9 Relationship between T_k and Z for rare earth squarates. ——— and oxylates – – – –

The crystallization water in the prepared complexes is bonded in different ways. It is outer sphere water connected by hydrogen-bond to the ligand oxygen atoms and lattice water, and in Tm, Yb and Lu squarates it is inner sphere water too.

Square acid is known to be a compound similar to oxalic acid. The rare earth complexes of square acid are more strongly hydrated (except for the Y complex) than those of oxalic acid, which are usually prepared as decahydrates. On heating, the hydrated oxalates of the light lanthanides [6–8] lose crystallization water to form anhydrous salts, which are very unstable. The hydrated oxalates of the heavy lanthanides lose some water molecules on heating, to form hydrates containing less water molecules, which then decompose to the oxides. Only the anhydrous oxalates of La, Pr(III) and Nd decompose to the oxides with the intermediate formation of $Ln_2O_2CO_3$. The temperatures of oxide formation (T_k) are presented in Fig. 9. These vary periodically with increase of the atomic number and decrease of the ionic radius from La to Tb, while they have the sâme value (973 K) for the compounds from Dy to Lu.

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Zusammenfassung — Die thermische Zersetzung von Komplexen von Y, La und Lanthaniden mit Squaresäure in Luft wurde untersucht. Beim Erhitzen zerfallen die Komplexe von Y, La, Ce(III), Pr(III), Nd, Sm, Eu(III), Gd, Tb(III) und Ho in zwei Schritten. Die hydrierten Komplexe geben zuerst Wasser ab und bilden wasserfreie Salze. Die Komplexe von Dy und Er zerfallen in drei Schritten, wobei sie in zwei Schritten zu wasserfreien Salzen dehydriert werden. Die Komplexe von Tm, Yb und Lu werden in drei Schritten dehydriert. Sie geben in zwei Schritten einige Wassermoleküle ab, um Octahydrate zu bilden, die dann während des Zerfalles dehydriert werden. Die wasserfreien Komplexe von Y, Ce(III), Pr(III), Eu(III), Gd, Tb(III), Dy, Ho und Er sowie die Octahydratsalze von Tm, Yb, und Lu zerfallen beim Erhitzen direkt zu den Oxiden Ln_2O_3, CeO_2, Pr_6O_{11} und Tb_4O_7. Die wasserfreien Komplexe von La, Nd und Sm zerfallen über das Zwischenprodukt $Ln_2O_2CO_3$ zu Ln_2O_3.

Резюме — В атмосфере воздуха изучены условия термического разложения комплексов иттрия, лантана и лантаноидов со скваровой кислотой. При нагревании комплексы иттрия, лантана, неодима, самария, гадолиния, гольмия м трехвалентных церия, празеодима, европия и тербия разлагаются в две стадии. Гидратные комплексы сначала теряют кристаллизационную воду, давая безводные соли. Комплексы диспрозия и эрбия разлагаются в три стадии. Дегидратация их протекает в две стадии с образованием безводных солей. Комплексы тулия, иттербия и лютеция дегидратируются в три стадии. На первых двух стадиях они теряют несколько молекул воды, образуя октагидраты, которые на третьей стадии дегидратируются с разложением. При нагревании безводные комплексы иттрия, гадолиния, диспрозия, гольмия, эрбия, трехвалентных церия, празеодима, европия, тербия, а также октагидраты тулия, иттербия и лютеция разлагаются прямо до окислов Ln_2O_3, CeO_2, Pr_6O_{11} и Tb_4O_7. Безводные комплексы лантана, неодима и самария разлагаются до Ln_2O_3 с образованием промежуточного продукта $Ln_2O_2CO_3$.