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THERMAL DECOMPOSITIONS OF Y, La AND LIGHT LANTHANIDE THIODIGLYCOLATES

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The conditions of thermal decomposition of the thiodiglycolates of Y, La and light lanthanides from Ce to Gd have been studied. On heating, these complexes decompose in various ways. Hydrated thiodiglycolates of La, Ce(III), Pr(III) and Gd lose crystallization water in one step, while those of Y, Nd, Sm and Eu(III) do so in two steps. The anhydrous complexes subsequently decompose in several steps to the oxysulfates $Ln_2O_{3-x}(SO_4)_x$.

The salts of thiodiglycolic acid are little known. In recent years the stability constants of thiodiglycolic acid complexes of Ca(II), Pb(II), Zn(II), Cd [1, 4], Cu(II), Ni(II), Co(II) [1, 3–5] and rare earth ions [2] have been determined. The thiodiglycolic acid complexes of Cu(II), Ni(II) and Co(II) [1, 3–5] are stronger than those of diglycolic acid. Substitution of an oxygen atom in diglycolic acid by a sulfur atom changes the complexing properties of the ligand.

Thiodiglycolates of rare earth elements in the solid state have not been studied so far. As a continuation of our work on the thermal decompositions of rare earth carboxylates [6–8], we now report the thermal decompositions of Y, La and light lanthanide thiodiglycolates.

Experimental

The thiodiglycolates of Y, La, Ce(III), Pr(III), Nd, Sm, Eu(III) and Gd were prepared by dissolving freshly precipitated rare earth hydroxides in an equivalent amount of hot thiodiglycolic acid and crystallizing. The solids formed were filtered off, washed with water and dried at 30° to constant weight.

The contents of carbon and hydrogen were determined by elemental analysis. The contents of rare earth elements were determined by dissolving the obtained

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Table 1 Analytical data of Ln complexes with thiodiglycolic acid

Complex	Ln, %		Carbon, %		Hydrogen, %	
	Calcd.	Found.	Calcd.	Found.	Calcd.	Found
$Y_2(C_4H_4O_4S)_3 \cdot 7H_2O$	23.76	23.83	19.26	18.96	3.50	3.46
$La_2(C_4H_4O_4S)_3 \cdot 2H_2O$	36.64	36.48	19.00	18.87	2.13	2.69
$Ce_2(C_4H_4O_4S)_3 \cdot 3H_2O$	36.01	41.48	18.52	18.61	2.33	2.39
$Pr_2(C_4H_4O_4S)_3 \cdot 3H_2O$	36.12	40.29	18.47	18.74	2.33	2.22
$Nd_2(C_4H_4O_4S)_3 \cdot 3H_2O$	36.62	36.35	18.29	18.69	2.30	2.49
$Sm_2(C_4H_4O_4S)_3 \cdot 5H_2O$	36.02	36.41	17.25	16.70	2.65	2.76
$Eu_2(C_4H_4O_4S)_3 \cdot 5H_2O$	36.25	35.75	17.18	17.08	2.64	2.61
$Gd_2(C_4H_4O_4S)_3 \cdot 5H_2O$	37.04	36.76	16.98	16.60	2.61	3.28

complexes in HCl solution, precipitating the oxalates and igniting these to oxides at 960°. The elemental analysis data are given in Table 1.

From the results, the thioglycolates of Y, La, Ce(III), Pr(III), Nd, Sm, Eu(III) and Gd were found to be hydrated complexes with the general formula $Ln_2(C_4H_4O_4S)_3 \cdot nH_2O$. The thiodiglycolate of La was obtained as the dihydrate, those of Ce(III), Pr(III) and Nd as the trihydrates, those of Sm, Eu(III) and Gd as the pentahydrates, and that of Y as the heptahydrate. The complexes are soluble in water.

The IR spectra of thiodiglycolic acid and the prepared thiodiglycolates were recorded over the range 4000–400 cm^{-1}. Analysis of the IR spectra confirms the elemental data.

The thermal stabilities of the complexes were studied by means of TG, DTG and DTA techniques. The measurements on the Pr(III), Nd and Sm complexes (Figs

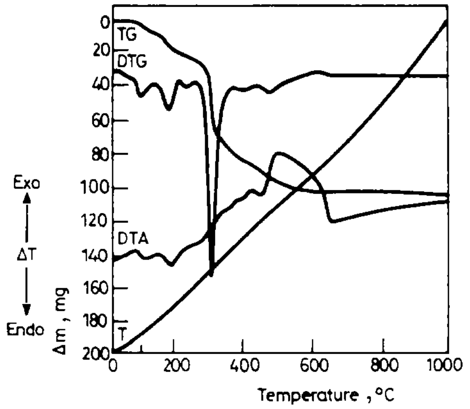

Fig. 1 TG, DTG and DTA curves of $Y_2(C_4H_4O_4S)_3 \cdot 7H_2O$

4–6) were made with an OD–102 derivatograph with a sensitivity TG 200 mg, and those on the Y, La, Ce(III), Eu(III) and Gd complexes Figs 1–3, 7, 8 with a Q 1500 D derivatograph with a sensitivity TG 200 mg. The samples were heated in ceramic crucibles in air atmosphere at a heating rate of 10 deg min^{-1}, and that of La in a nitrogen atmosphere (Fig. 9) and at a heating rate of 5 deg min^{-1} (Fig. 10) additionally.

The analysis and identification of the solid products of decomposition were performed on the basis of elemental analysis and IR and X-ray spectra.

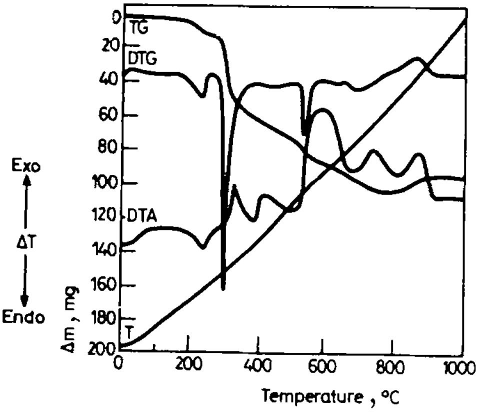

Fig. 2 TG, DTG and DTA curves of $La_2(C_4H_4O_4S)_3 \cdot 2H_2O$

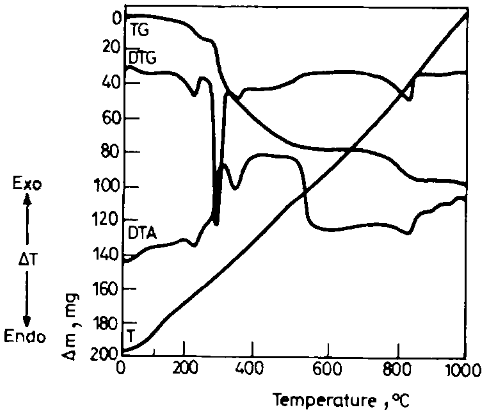

Fig. 3 TG, DTG and DTA curves of $Ce_2(C_4H_4O_4S)_3 \cdot 3H_2O$

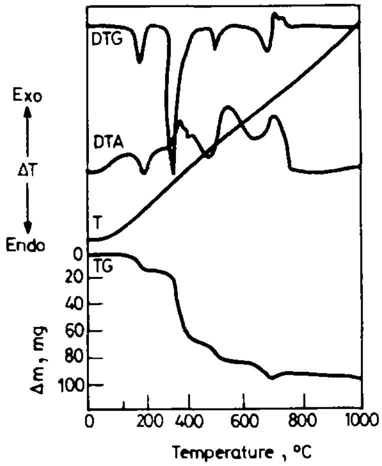

Fig. 4 TG, DTG and DTA curves of $Pr_2(C_4H_4O_4S)_3 \cdot 3H_2O$

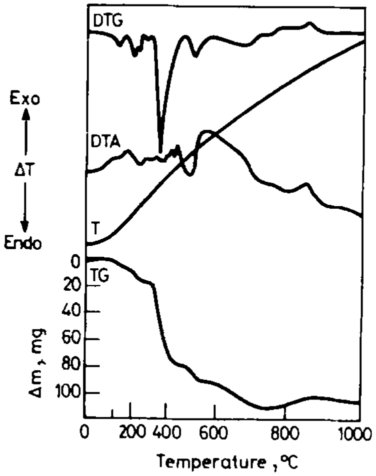

Fig. 5 TG, DTG and DTA curves of $Nd_2(C_4H_4O_4S)_3 \cdot 3H_2O$

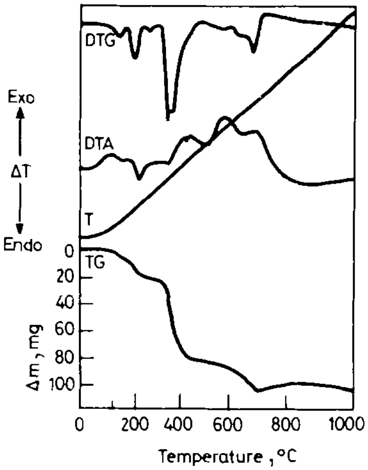

Fig. 6 TG, DTG and DTA curves of $Sm_2(C_4H_4O_4S)_3 \cdot 5H_2O$

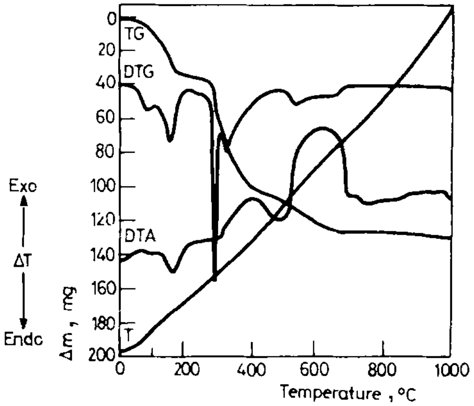

Fig. 7 TG, DTG and DTA curves of $Eu_2(C_4H_4O_4S)_3 \cdot 5H_2O$

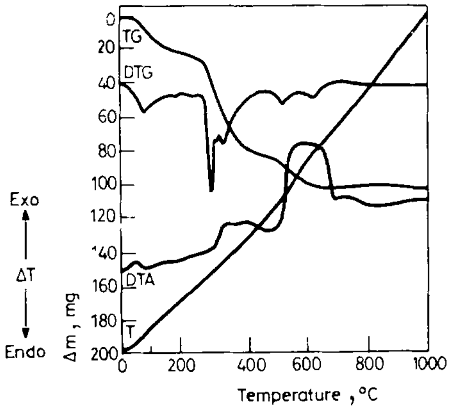

Fig. 8 TG, DTG and DTA curves of $Gd_2(C_4H_4O_4S)_3 \cdot 5H_2O$

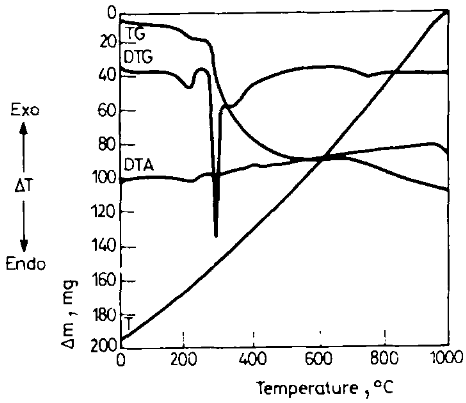

Fig. 9 TG, DTG and DTA curves of $La_2(C_4H_4O_4S)_3 \cdot 2H_2O$ in nitrogen atmosphere

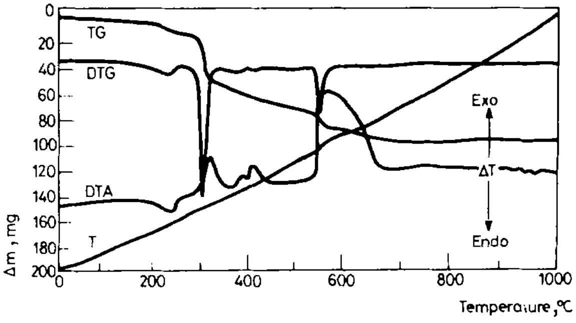

Fig. 10 TG, DTG and DTA curves of $La_2(C_4H_4O_4S)_3 \cdot 2H_2O$ at a heating rate 5 deg·min^{-1}

Results

From the thermal curves of the thiodiglycolates, the temperatures of dehydration and thermal decomposition were evaluated and are presented in Tables 2 and 3, respectively, where:

ΔT_1 = temperature range corresponding to the endothermic loss of a given number of crystallization water molecules (°C),
T = peak temperature of DTG (°C),
T_{min} = temperature corresponding to minimum in the DTA curve (°C),
$n\mathrm{H_2O}$ = loss of n $\mathrm{H_2O}$,
ΔT_2 = temperature range corresponding to decomposition of the anhydrous complex until the formation of oxysulfates (°C), and
T_2 = temperature of oxysulfate formation (°C).

Table 2 Temperature data of dehydration of Y, La and light lanthanide thiodiglycolates

Complex	ΔT_1, °C	T, °C	T_{min}, °C	H_2O	Loss of weight, %	
					Calcd.	Found.
$Y_2(C_4H_4O_4S)_3 \cdot 7H_2O$	55–115	85	96	2 } 7	16.85	16.8
	125–212	165	172	5		
$La_2(C_4H_4O_4S)_3 \cdot 2H_2O$	180–260	240	245	2	4.75	4.8
$Ce_2(C_4H_4O_4S)_3 \cdot 3H_2O$	185–250	220	235	3	6.95	6.8
$Pr_2(C_4H_4O_4S)_3 \cdot 3H_2O$	145–250	180	192	3	6.93	7.0
$Nd_2(C_4H_4O_4S)_3 \cdot 3H_2O$	80–130	102	118	1 } 3	6.86	8.0
	180–275	200	235	2		
$Sm_2(C_4H_4O_4S)_3 \cdot 5H_2O$	90–160	125	150	2 } 5	10.78	11.0
	170–240	200	218	3		
$Eu_2(C_4H_4O_4S)_3 \cdot 5H_2O$	62–130	100	108	2 } 5	10.74	10.8
	148–200	180	190	3		
$Gd_2(C_4H_4O_4S)_3 \cdot 5H_2O$	55–140	90	110	5	10.61	10.8

The results demonstrated that the thiodiglycolates of Y, La and light lanthanides decompose in various ways (Figs 1–9). The hydrated thiodiglycolates of La, Ce(III), Pr(III) and Gd lose crystallization water in one step, to the accompainment of an endothermic effect. These hydrated complexes are very stable. Dehydration begins at 145–160°. The hydrated complexes of Y, Nd, Sm and Eu(III) undergo dehydration in two stages, accompanied by two endothermic effects. The thiodiglycolate of Gd is very unstable and begins to lose crystallization water at 55°.

When heated to 1000°, the anhydrous complexes decompose exothermically to the oxysulfates $Ln_2O_{3-x}(SO_4)_x (0 < x < 3)$. These complexes, of variable com-

Table 3 Temperature data of decomposition of Y, La and light lanthanide anhydrous thiodiglycolates

Complex	ΔT_2	Loss of weight, %		T_2	Decomposition product
		Calcd.	Found.		
$Y_2(C_4H_4O_4S)_3\cdot 7H_2O$	280–700	64.05	64.0	700	$Y_2O_{2.46}(SO_4)_{0.54}$
$La_2(C_4H_4O_4S)_3\cdot 2H_2O$	260–900	46.48	47.2	900	$La_2O_2(SO_4)$
$Ce_2(C_4H_4O_4S)_3\cdot 3H_2O$	285–850	48.20	48.0	850	$Ce_2O_{2.05}(SO_4)_{0.95}$
$Pr_2(C_4H_4O_4S)_3\cdot 3H_2O$	320–780	46.96	47.0	780	$Pr_2O_{1.95}(SO_4)_{1.05}$
$Nd_2(C_4H_4O_4S)_3\cdot 3H_2O$	320–900	51.60	52.0	900	$Nd_2O_{2.44}(SO_4)_{0.56}$
$Sm_2(C_4H_4O_4S)_3\cdot 5H_2O$	320–850	52.48	52.0	850	$Sm_2O_{2.40}(SO_4)_{0.60}$
$Eu_2(C_4H_4O_4S)_3\cdot 5H_2O$	300–645	50.30	51.2	645	$Eu_2O_{2.21}(SO_4)_{0.79}$
$Gd_2(C_4H_4O_4S)_3\cdot 5H_2O$	290–715	50.88	51.2	715	$Gd_2O_{2.32}(SO_4)_{0.68}$

position, are known in the literature. They are obtained by the thermal decomposition of sulfates or hydroxysulphates at 700–1000° [9].

The anhydrous thiodiglycolates of Y, La and light lanthanides decompose in several stages. On heating they are carbonized, and are next reduced by carbon to sulfides. At the same time they are partially oxidized to sulfates (in the solid product there are both sulfide and sulfate ions). During heating in air atmosphere, the sulfides are oxidized to sulfates. The oxysulfates $Ln_2O_{3-x}(SO_4)_x$ (Table 3) are the final products of decomposition. They do not contain sulfide ions. In the TG curves of the La, Pr(III), Nd and Sm complexes it is possible to observe an increase in weight (small for Gd) in the temperature range 710–900°, which is connected with the oxidation of sulfide ions to sulfate. The increase in weight is lower during heating at 5 deg min^{-1} (Fig. 10). This process is not observed in nitrogen atmosphere (Fig. 9).

References

1 R. M. Tichane and W. E. Bennet, J. Am. Chem. Soc., 79 (1957) 1293.
2 I. Grenthe and W. C. Fernelius, "Formation Constants and Magnetic Behaviour of Some Rare Earth Chelates" in Rare Earth Research, E. V. Kleber, The Macmilian Company, New York, 1961.
3 H. M. Djatlowa, Kompleksony izd. Chimija, Moskwa, 1970.
4 M. Yasada, K. Yamasaki and H. Ohtaki, Bull. Chem. Soc. Japan, 33 (1960) 1067.
5 A. Sandell, Acta. Chem. Scand., (1960).
6 W. Brzyska and W. Ferenc, J. Thermal Anal. 22 (1981) 53.
7 W. Brzyska and A. Kula, J. Thermal Anal., 25 (1982) 531.
8 W. Brzyska, R. Kurpiel-Gorgol and M. Dąbkowska, J. Thermal Anal., 28 (1983) 333.
9 Gmelin Handbuch der Anorganischen Chemie, System Number 39, Supplement volume C8, Springer Verlag, Berlin–Heidelberg–New York, 1981.

Zusammenfassung — Bedingungen der thermischen Zersetzung der Thiodiglycolate von Y, La und den leichten Lanthaniden von Ce bis Gd wurden untersucht. Beim Erhitzen zersetzen sich diese Komplexe auf verschiedene Weise. Hydratisierte Thiodiglycolate von La, Ce(III), Pr(III) und Gd verlieren das Kristallwasser in einem Schritt, die von Y, Nd, Sm, und Eu(III) dagegen in zwei Schritten. Die wasserfreien Komplexe zersetzen sich in mehreren Schritten zu den Oxysulfaten $Ln_2O_{3-x}(SO_4)_x$.

Резюме — Изучены условия термического разложения тиодигликолятов иттрия, лантана и легких лантанидов от церия до гадолиния. Эти комплексы различным образом разлагаются при нагревании. Гидраты тиодигликолятов лантана, трехвалентных церия, празеодима и гадолиния теряют кристаллизационную воду в одну стадию, а комплексы иттрия, неодима, самария и европия — в две стадии. Безводные комплексы последовательно разлагаются в несколько стадий образуя оксисульфаты $Ln_2O_{3-x}(SO_4)_x$.