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# PREPARATION AND CHARACTERIZATION OF HEAVY LANTHANIDE THIODIGLYCOLATES

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Thiodiglycolates of heavy lanthanides, prepared in the reactions of the hydroxides of the rare earths with thiodiglycolic acid, have the general formula $Ln_2(C_4H_4O_4S)_3 \cdot nH_2O$, where $n = 5$ for Ln = Tb and Dy, $n = 6$ for Ln = Ho, Er and Tm, and $n = 7$ for Ln = Yb and Lu. On heating, the hydrated complexes lose the crystallization water in two steps, and the resulting anhydrous complexes decompose to the oxides $Ln_2O_3$ and $Tb_4O_7$ via the intermediate formation of $Ln_2O_{3-x}(SO_4)_x$.

The temperatures of oxide formation decrease with increasing atomic number of the lanthanides. The solubilities of the heavy lanthanide thiodiglycolates are of the order of $10^{-2}$ mol·dm$^{-3}$.

In previous works, thiodiglycolic acid was applied for the ion-exchange separation of rare earths [1], and the physico-chemical properties of the solid complexes $Ln_2(C_4H_4O_4S)_3 \cdot nH_2O$ for Y, La and the light lanthanides were determined [2]. As a continuation of our work, we now report on an investigation of the physico-chemical properties and thermal decomposition of heavy lanthanide complexes with thiodiglycolic acid.

## Experimental

The thiodiglycolates of Tb(III), Dy, Ho, Er, Tm, Yb and Lu were prepared by dissolving freshly precipitated lanthanide hydroxides in an equivalent amount of thiodiglycolic acid, followed by crystallization at room temperature. The solids formed were filtered off, washed with hot water and dried at 30° to constant weight.

The contents of carbon and hydrogen were determined by elemental analysis. The lanthanide contents were determined by dissolving samples of the prepared complexes in dilute HCl, precipitating the oxalates and igniting these to the oxides

**Table 1** Analytical data on Ln complexes with thiodiglycolic acid

| Complex* | Ln, % | | Carbon, % | | Hydrogen, % | |
|---|---|---|---|---|---|---|
| | calcd. | found | calcd. | found | calcd. | found |
| $Tb_2(C_4H_4O_4S)_3 \cdot 5H_2O$ | 37.29 | 37.45 | 16.91 | 16.86 | 2.60 | 2.54 |
| $Dy_2(C_4H_4O_4S)_3 \cdot 5H_2O$ | 37.81 | 38.00 | 16.76 | 17.08 | 2.58 | 2.58 |
| $Ho_2(C_4H_4O_4S)_3 \cdot 6H_2O$ | 37.38 | 37.56 | 16.33 | 16.51 | 2.74 | 2.81 |
| $Er_2(C_4H_4O_4S)_3 \cdot 6H_2O$ | 37.70 | 38.12 | 16.25 | 16.34 | 2.73 | 2.52 |
| $Tm_2(C_4H_4O_4S)_3 \cdot 6H_2O$ | 38.00 | 38.30 | 16.17 | 16.35 | 2.71 | 2.82 |
| $Yb_2(C_4H_4O_4S)_3 \cdot 7H_2O$ | 37.75 | 38.08 | 15.72 | 15.59 | 2.86 | 2.90 |
| $Lu_2(C_4H_4O_4S)_3 \cdot 7H_2O$ | 38.02 | 38.45 | 15.66 | 15.63 | 2.84 | 2.87 |

at 900–950°; the TG curves were also used. The crystallization water contents were determined from the TG curves. The results obtained are given in Table 1.

The IR spectra of thiodiglycolic acid, the studied thiodiglycolates of the heavy lanthanides, and sodium thiodiglycolate were recorded on a UR–20 spec-

**Table 2** Frequency of maximum of absorption bands in IR spectra of heavy lanthanide thiodiglycolates, $cm^{-1}$

| Tb | Dy | Ho | Er | Tm | Yb | Lu | Assignment |
|---|---|---|---|---|---|---|---|
| 3640–3000 | 3640–3000 | 3660–3000 | 3700–3000 | 3700–3000 | 3700–3000 | 3700–3000 | stretching vibration of OH group of $H_2O$ |
| — | — | 1655 | 1655 | 1655 | 1655 | 1655 | vibration of crystallization water |
| 2970 | 2970 | 2960 | 2960 | 2960 | 2960 | 2960 | asym. stretching vibration of $CH_2$ |
| 2920 | 2920 | 2920 | 2915 | 2915 | 2915 | 2915 | sym. stretching vibration of $CH_2$ |
| 1570 | 1570 | 1545, 1580 | 1545, 1580 | 1545, 1580 | 1545, 1580 | 1545, 1580 | asym. valency vibration of $COO^-$ |
| 1400 | 1400 | 1440 | 1440 | 1440 | 1440 | 1440 | sym. valency vibration of $COO^-$ |
| 1225 | 1225 | 1225 | 1225 | 1225 | 1225 | 1225 | vibration of —S—$CH_2$— |
| 945 | 945 | 955 | 960 | 960 | 960 | 960 | valency vibration of CO |
| 725 | 725 | 720 | 720 | 725 | 725 | 725 | vibration of —C—S—C |
| 675 | 675 | — | — | — | — | — | vibration of —C—S—C |
| 620 | 620 | 620 | 620 | 620 | 615 | 620 | metal-oxygen bond |

trophotometer over the range 4000–400 cm$^{-1}$. The samples were prepared as KBr discs (Table 2).

The thermal stabilities of the prepared complexes were studied by means of TG, DTA and DTG techniques. The measurements were made with a Q–1500D derivatograph with sensitivity TG – 100 mg, DTG – 500 µV, DTA – 500 µV, using $Al_2O_3$ as reference material. Samples of 100 mg were heated to 1500° at a heating rate of 7.5 deg·min$^{-1}$ in ceramic crucibles in air atmosphere (Figs 1–7).

The solid products of thermal decomposition were identified on the basis of the TG curves and were verified via chemical analysis and the IR spectra.

The solubilities of the prepared complexes in water were determined at 22°. The salts were put into flasks filled with distilled water, and mixing was continued for 24 hrs to obtain saturated solutions. The contents of lanthanides in the saturated solutions were determined by the oxalate method. The solubilities of the complexes were calculated on the basis of the mass of lanthanide oxide.

## Results

The thiodiglycolates of Tb(III), Dy, Ho, Er, Tm, Yb and Lu were prepared as crystalline solids with general formula $Ln_2(C_4H_4O_4S)_3 \cdot nH_2O$, those of Tb and Dy

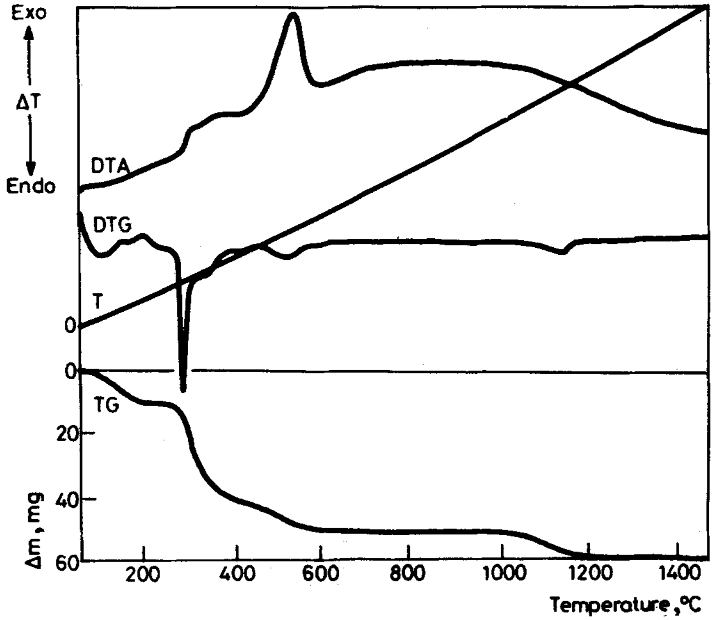

**Fig. 1** TG, DTG and DTA curves of $Tb_2(C_4H_4O_4S)_3 \cdot 5H_2O$

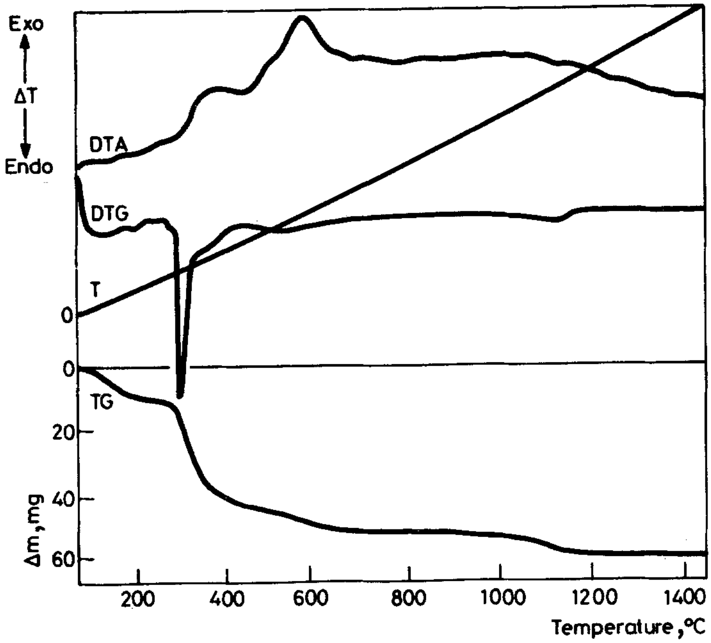

Fig. 2 TG, DTG and DTA curves of $Dy_2(C_4H_4O_4S)_3 \cdot 5H_2O$

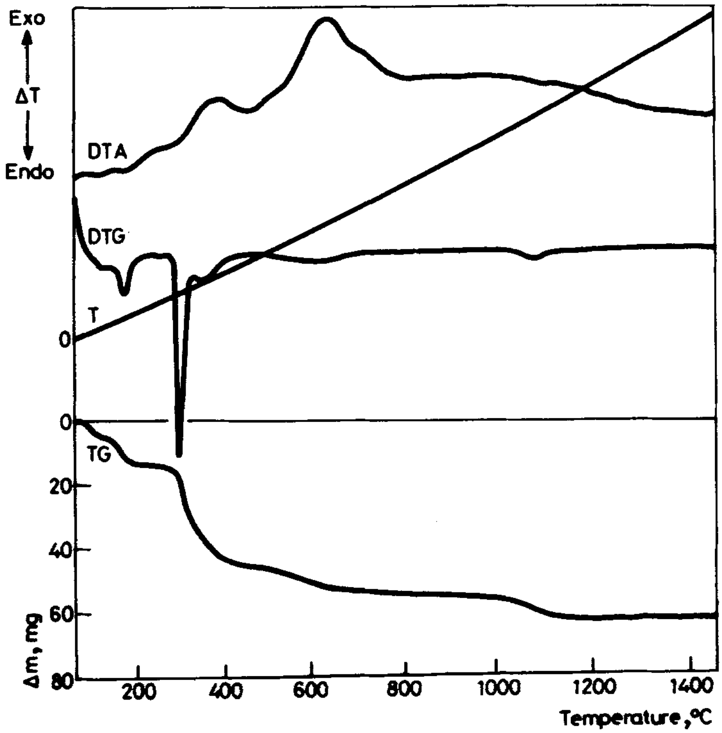

Fig. 3 TG, DTG and DTA curves of $Ho_2(C_4H_4O_4S)_3 \cdot 6H_2O$

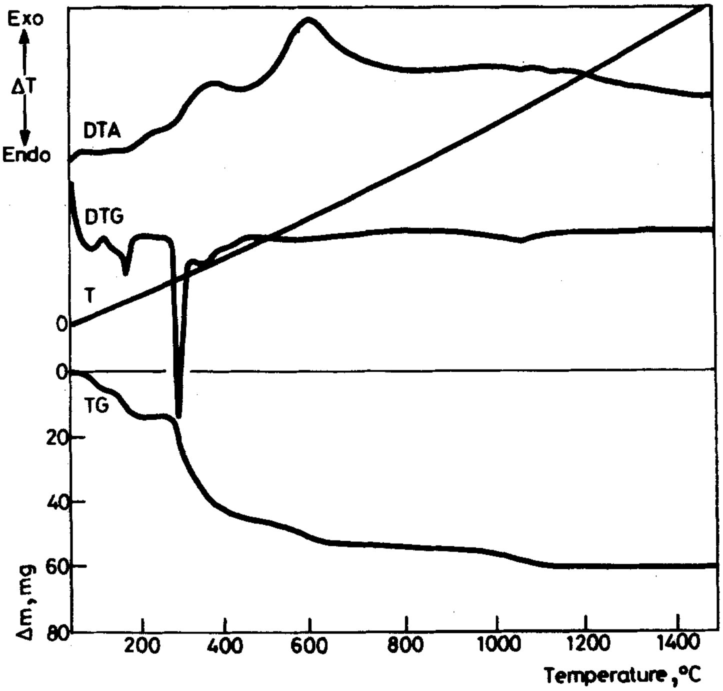

Fig. 4 TG, DTG and DTA curves of $Er_2(C_4H_4O_4S)_3 \cdot 6H_2O$

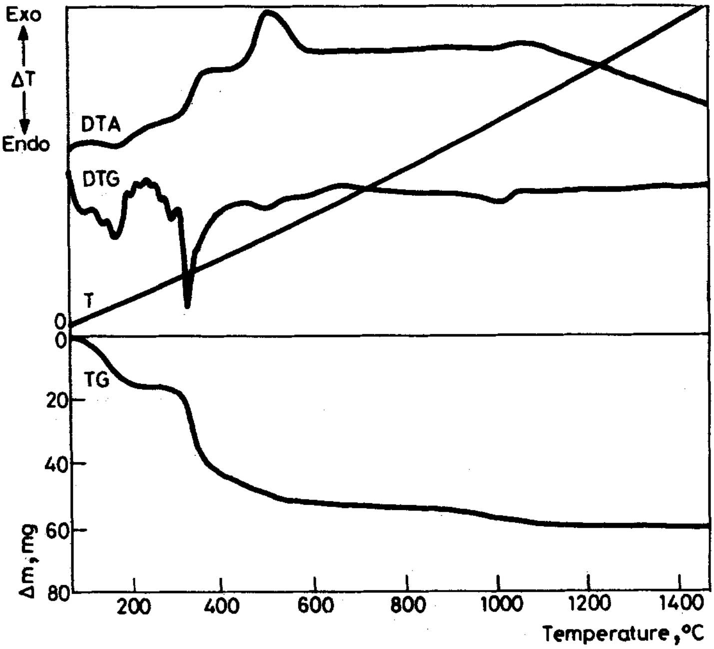

Fig. 5 TG, DTG and DTA curves of $Tm_2(C_4H_4O_4S)_3 \cdot 6H_2O$

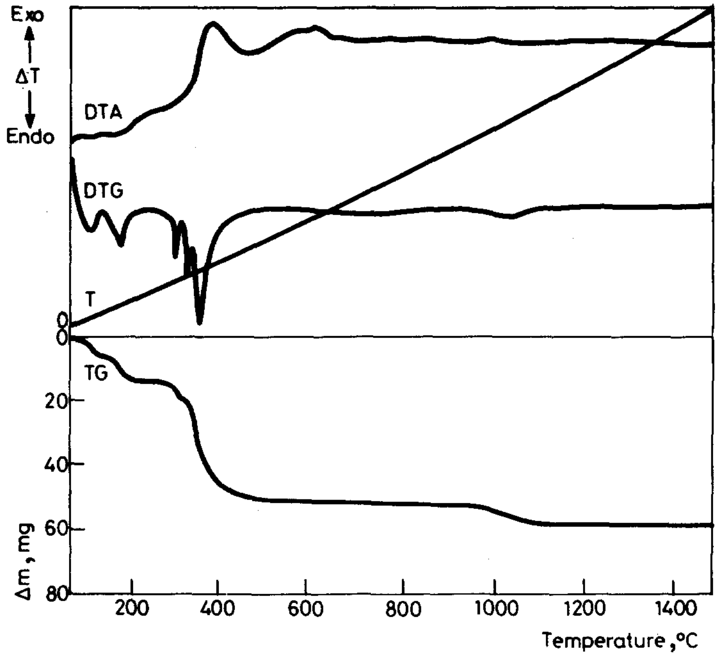

**Fig. 6** TG, DTG and DTA curves of $Yb_2(C_4H_4O_4S)_3 \cdot 7H_2O$

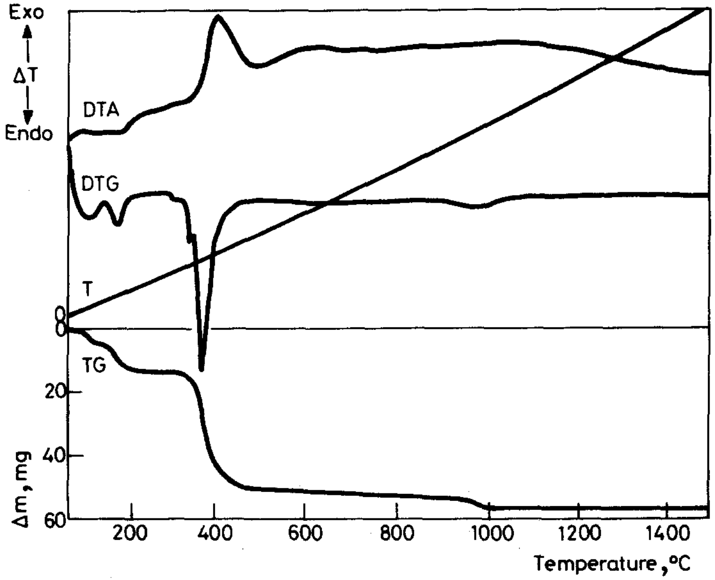

**Fig. 7** TG, DTG and DTA curves of $Lu_2(C_4H_4O_4S)_3 \cdot 7H_2O$

as pentahydrates, those of Ho, Er and Tm as hexahydrates, and those of Yb and Lu as heptahydrates.

Analysis of the IR spectra confirmed the results obtained from elemental analysis (Table 2). The IR spectrum of thiodiglycolic acid exhibits a strong absorption band of the valency vibration of the OH groups at 3400–2750 cm$^{-1}$, bands of asymmetrical and symmetrical vibrations of $CH_2$ at 2730 and 2600 cm$^{-1}$, respectively, a strong band of valency vibration of the COOH group at 1690 cm$^{-1}$, a band of —S—$CH_2$— at 1425 cm$^{-1}$ lying in the range of the C—OH band, sharp bands at 1305, 1225, 1195 and 920 cm$^{-1}$ (the band at 1225 cm$^{-1}$ due to —S—$CH_2$—), bands of deformation vibrations of C—H at 870, 830 and 790 cm$^{-1}$, and a band of —C—S—C— at 660 cm$^{-1}$.

The spectra of the prepared lanthanide thiodiglycolates display a broad absorption band at 3700–3000 cm$^{-1}$ and a sharp band at 1655 cm$^{-1}$, which indicate the presence of crystallization water in the complexes. The band at 1655 cm$^{-1}$ has a sharp maximum only for the complexes of Ho, Er, Tm, Y and Lu. The band characteristic of the free acid at 1690 cm$^{-1}$ is not present in the spectra of the prepared complexes, and the bands of the asymmetrical and symmetrical vibrations of the —$OCO^-$ group appear at 1570–1545 cm$^{-1}$ and 1440–1400 cm$^{-1}$, respectively. The absorption band of the $OCO^-$ group is broad; it is known in the literature as background [3]. This band is split in the spectra of Ho, Er, Tm, Yb and Lu and has two maxima. This character of the absorption band is probably caused

**Table 3** Temperature data on dehydration of heavy lanthanide thiodiglycolates

| Complex | $\Delta T_1$, °C | $T$, °C | $T_{min}$, °C | $H_2O$ | | Loss in weight, % | |
|---|---|---|---|---|---|---|---|
| | | | | | | calcd. | found |
| $Tb_2(C_4H_4O_4S)_3 \cdot 5H_2O$ | 55–155 | 108 | 120 | 3 | 5 | 10.57 | 10.40 |
| | 155–220 | 170 | 175 | 2 | | | |
| $Dy_2(C_4H_4O_4S)_3 \cdot 5H_2O$ | 55–160 | 110 | 120 | 3 | 5 | 10.48 | 10.40 |
| | 160–220 | 190 | 195 | 2 | | | |
| $Ho_2(C_4H_4O_4S)_3 \cdot 6H_2O$ | 60–140 | 110 | 110 | 3 | 6 | 12.25 | 13.60 |
| | 140–195 | 160 | 165 | 3 | | | |
| $Er_2(C_4H_4O_4S)_3 \cdot 6H_2O$ | 55–130 | 90 | 100 | 3 | 6 | 12.18 | 12.80 |
| | 130–195 | 165 | 170 | 3 | | | |
| $Tm_2(C_4H_4O_4S)_3 \cdot 6H_2O$ | 50–145 | 140 | 145 | 3 | 6 | 12.14 | 13.60 |
| | 145–190 | 170 | 195 | 3 | | | |
| $Yb_2(C_4H_4O_4S)_3 \cdot 7H_2O$ | 50–130 | 85 | 100 | 3 | 7 | 13.75 | 13.60 |
| | 130–190 | 165 | 170 | 4 | | | |
| $Lu_2(C_4H_4O_4S)_3 \cdot 7H_2O$ | 50–130 | 85 | 105 | 3 | 7 | 13.70 | 13.60 |
| | 130–190 | 160 | 165 | 4 | | | |

by the influence of the deformation vibration of HOH through the hydrogen-bond. The absorption band of —S—$CH_2$— and 1425 $cm^{-1}$ appears in the range of symmetrical vibration of the —$OCO^-$ group. The absorption band of the metal-oxygen bonds appears at 620–615 $cm^{-1}$.

The separation of the absorption bands $\Delta\nu$ of the asymmetrical and symmetrical vibrations of the $OCO^-$ group has a value of *ca* 170 $cm^{-1}$, which shows the participation of ionic Ln-ligand bonding in the studied complexes. On the basis of the shifts of the absorption bands $\nu_{as}$ to lower frequencies and of $\nu_{sym}$ to higher ones, it is possible to confirm that the $OCO^-$ group is involved in symmetrical bidentate chelating. It is impossible to define clearly the mode of sulphur-lanthanide ion coordination. The absorption bands of the M–S bonds are weak and appear at frequencies less than 400 $cm^{-1}$ [4].

From the thermal curves recorded for the studied lanthanide thiodiglycolates, the analytical data on the dehydration are presented in Table 3, and those on the decomposition of the anhydrous complexes are given in Table 4; where:

$\Delta T_1$ = temperature range corresponding to endothermic loss of the given number of crystallization water moles (°C)
$T$ = DTG peak temperature (°C)
$T_{min}$ = temperature corresponding to minimum in DTA curve
$H_2O$ = number of $H_2O$ moles lost
$\Delta T_2$ = temperature range corresponding to decomposition of anhydrous complex to oxysulfate (°C)
$T_{max}$ = temperature corresponding to maximum in DTA curve of oxysulfate formation (°C)
$T_2$ = temperature of oxide formation (°C)

**Table 4** Temperature data on decomposition of heavy lanthanide thiodiglycolates

| Complex | $\Delta T_2$ | $T_{max}$ | $Ln_2O_{3-x}(SO_4)_x$ | $T_2$ | End-product of decom-position | Loss in weight, % | |
|---|---|---|---|---|---|---|---|
| | | | | | | calcd. | found |
| $Tb_2(C_4H_4O_4S)_3 \cdot 5H_2O$ | 270–590 | 835 | $Tb_2O_{2.40}(SO_4)_{0.60}$ | 1170 | $Tb_4O_7$ | 56.1 | 55.9 |
| $Dy_2(C_4H_4O_4)S_3 \cdot 5H_2O$ | 280–655 | 975 | $Dy_2O_{2.72}(SO_4)_{0.28}$ | 1145 | $Dy_2O_3$ | 56.6 | 56.2 |
| $Ho_2(C_4H_4O_4S)_3 \cdot 6H_2O$ | 280–690 | 930 | $Ho_2O_{2.54}(SO_4)_{0.46}$ | 1130 | $Ho_2O_3$ | 57.2 | 56.6 |
| $Er_2(C_4H_4O_4S)_3 \cdot 6H_2O$ | 270–670 | 960 | $Er_2O_{2.78}(SO_4)_{0.22}$ | 1085 | $Er_2O_3$ | 56.9 | 56.4 |
| $Tm_2(C_4H_4O_4S)_3 \cdot 6H_2O$ | 250–610 | 860 | $Tm_2O_{2.74}(SO_4)_{0.26}$ | 1045 | $Tm_2O_3$ | 56.7 | 56.1 |
| $Yb_2(C_4H_4O_4S)_3 \cdot 7H_2O$ | 280–510 | 590 | $Yb_2O_{2.29}(SO_4)_{0.71}$ | 1065 | $Yb_2O_3$ | 57.0 | 56.6 |
| $Lu_2(C_4H_4O_4S)_3 \cdot 7H_2O$ | 315–510 | 615 | $Lu_2O_{2.51}(SO_4)_{0.49}$ | 1020 | $Lu_2O_3$ | 56.8 | 56.3 |

The hydrated thiodiglycolates of the heavy lanthanides are very unstable and begin to lose crystallization water at 50°. They undergo dehydration in two stages, accompanied by two endothermic effects. The anhydrous complexes are stable up to 270–315°. When heated to 1500°, they decompose and oxidize exothermically to yield the oxides $Ln_2O_3$ and $Tb_4O_7$ via the oxysulfates $Ln_2O_{3-x}(SO_4)_x$. These compounds are also obtained on the thermal decomposition of sulfates or hydroxysulfates [5].

The anhydrous thiodiglycolates of the heavy lanthanides decompose to oxides in several stages. On heating, they are carbonized at ca 280° (the products are black; $S^{2-}$ and $SO_4^{2-}$ ions are not detected). In the next step, during heating, they are reduced by carbon to sulfides and at the same time are partially oxidized to sulfates (at 500°, both sulfide and sulfate ions are present in the solid black product). At 900°, all solid products contain sulfate ions, but not sulfide ions.

The oxides obtained by decomposition of the heavy lanthanide thiodiglycolates are formed in the temperature range 1000–1200°. The temperatures of oxide formation decrease with increase of the atomic number of the lanthanide, and differ slightly from those described in the literature for oxide formation via decomposition of the anhydrous sulfates [6].

The thiodiglycolates of the heavy lanthanides are less stable than those of La and the light lanthanides. The temperatures of oxide formation decrease with increase of the atomic number of the cation, from 1425° for La to 1020° for Lu; this is connected with the increasing ionic potential and counterpolarization effect. Only the cerium(III) complex is very unstable: $CeO_2$ is formed at 810° [2].

The thiodiglycolates of the heavy lanthanides are soluble in water. Their solubilities at 22° are of the order of $10^{-2}$–$10^{-3}$ mol·dm$^{-3}$ (Table 5) and decrease from Tb to Lu.

**Table 5** Solubilities of heavy lanthanide thiodiglycolates in water at 22 °C

| Complex | Solubility mol·dm$^{-3}$·10$^{2}$ |
|---|---|
| $Tb_2(C_4O_4O_4S)_3 \cdot 5H_2O$ | 1.52 |
| $Dy_2(C_3H_4O_4S)_3 \cdot 5H_2O$ | 1.65 |
| $Ho_2(C_4H_4O_4S)_3 \cdot 6H_2O$ | 1.12 |
| $Er_2(C_4H_4O_4S)_3 \cdot 6H_2O$ | 0.93 |
| $Tm_2(C_4H_4O_4S)_3 \cdot 6H_2O$ | 0.79 |
| $Yb_2(C_4H_4O_4S)_3 \cdot 7H_2O$ | 0.68 |
| $Lu_2(C_4H_4O_4S)_3 \cdot 7H_2O$ | 0.65 |

In recent years, many papers have been published on the complexes of lanthanides with organic ligands containing sulfur, which indicates the great interest in this group of compounds.

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**Zusammenfassung** — In der Reaktion von Seltenerdenhydroxiden und Thiodiglykolsäure wurden die Thiodiglykolate von Lanthaniden mit der allgemeinen Formel $Ln_2(C_4H_4O_4S)_3 \cdot nH_2O$ hergestellt (mit $n = 5$ für Ln = Tb und Dy, mit $n = 6$ für Ln = Ho, Er und Tm und mit $n = 7$ für Ln = Yb und Lu). Die Hydratkomplexe verlieren ihr Kristallwasser beim Erhitzen in zwei Stufen, die entstehenden wasserfreien Komplexe zerfallen über die intermediäre Form $Ln_2O_{3-x}(SO_4)_x$ in die Oxide $Ln_2O_3$ und $Tb_4O_7$. Die Temperatur der Oxidbildung nimmt mit steigender Ordnungszahl der Lanthaniden ab. Die Löslichkeit der untersuchten Lanthanidenthiodiglykolate liegt in der Größenordnung $10^{-2}$ mol/dm$^{-3}$.

**Резюме** — Реакцией гидроокисей редкоземельных элементов с тиодигликолевой кислотой получены тиодигликоляты общей формулы $Ln_2(C_4H_4O_4S)_3 \cdot nH_2O$, где $n = 5$ для Ln = Tb и Dy, $n = 6$ для Ln = Ho, Er и Tm, и $n = 7$ для Ln = Yb и Lu. Гидратные комплексы при нагревании теряют кристаллизационную воду в две стадии, а образующиеся безводные комплексы разлагаются до оксидов $Ln_2O_3$ и $Tb_4O_7$ через стадию образования промежуточного продукта $Ln_2O_{3-x}(SO_4)_x$. Температуры образования оксидов уменьшаются с увеличением атомного веса лантаноидов. Растворимость тиодигликолятов редкоземельных металлов составляла порядка $10^{-2}$ моль·дм$^{-3}$.