

SOME PROPERTIES AND THERMAL DECOMPOSITION OF YTTRIUM AND LANTHANIDE BENZOHYDROXAMATES

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Abstract

The conditions of formation and some properties of yttrium and lanthanide benzohydroxamates were studied.

Simultaneous TG-DTG-DTA studies under non-isothermal conditions were carried out in air atmosphere in the temperature range 20–1000°C. The IR spectra and X-ray patterns of some thermal decomposition products were recorded.

Keywords: benzohydroxamates, lanthanides(III)

Introduction

The hydroxamic acids, $RC(O)NHOH$, behave as chelating agents, coordinating to metal ions via the two oxygen atoms. The hydroxamates of iron(III) are the best-known such compounds [1–5]. They are usually red, which facilitates quantitative determination of the content of hydroxamic acid or iron(III) in solution. Iron(III) benzohydroxamate is likewise the best-known complex of benzohydroxamic acid with metal ions [6–8]. Molybdenum(VI) benzohydroxamate has been widely described [9–15]. The benzohydroxamates of chromium(III) [16–18], gallium(III) [5, 19], cobalt(III) [18, 20] and indium(III) [21] are also known. We have not found any reference to benzohydroxamates of yttrium(III) or the lanthanides(III).

The aim of this paper is to report on the preparation of rare earth benzohydroxamates in the solid state, their properties and their thermal decompositions in an atmosphere of air.

Experimental

Materials

Benzohydroxamic acid (>98%; Merck, Germany), HCl (p.a. 36% solution), $NH_3 \cdot H_2O$ (p.a. 25% solution), Lu_2O_3 (99.9%; POCh Gliwice, Poland), Y_2O_3

(99.9%), La₂O₃ (99.5%), Ce(NO₃)₃·6H₂O (99%), Pr₆O₁₁ (99.5%), Nd₂O₃ (99.9%), Sm₂O₃ (99%), Gd₂O₃ (99.5%; prepared in our laboratory), Eu₂O₃ (99.9%), Tb₄O₇ (99.9%), Dy₂O₃ (99.9%; Koch Light Laboratories Ltd., England), Ho₂O₃ (99%), Tm₂O₃ (99%; Riedel-de Haën, Germany), Er₂O₃ (99.9%) and Yb₂O₃ (99.9%; Fluka AG, Buchs GS, Switzerland) were used.

Benzohydroxamates of Y(III) and lanthanides(III) (without Pm) were prepared by adding a 0.03 M solution of the metal chloride (Ce(III) was used as nitrate) to a hot 0.1 M solution of benzohydroxamic acid. The resulting mixture was adjusted to pH 5.5 with NH₃·H₂O solution. The precipitate formed was heated in the mother liquor for 1 h, filtered off, washed with hot water to remove Cl⁻ and NH₄⁺, and dried at 35°C to constant weight. The compounds obtained were characterized via methods of elemental analysis. The analysis are presented in Table 1.

Methods

IR spectra of benzohydroxamic acid and of its complexes with yttrium and the lanthanides were recorded with a Specord M80 spectrophotometer within the range 4000–400 cm⁻¹, with a sensitivity of ±2 cm⁻¹. Samples were prepared as KBr discs.

Table 1 The results of the elemental analysis of Y(III) and lanthanide benzohydroxamates and their solubility at water at 25°C ($L = C_7H_6NO_2$)

| Complex | %Ln | | %C | | %H | | %N | | Solubility/ mol dm ⁻³ |
|------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------------------------------------|
| | found | calc. | found | calc. | found | calc. | found | calc. | |
| YL ₃ ·H ₂ O | 17.21 | 17.44 | 49.49 | 48.84 | 3.92 | 3.88 | 8.25 | 8.14 | 5.3·10 ⁻⁵ |
| LaL ₃ ·H ₂ O | 24.99 | 24.60 | 43.90 | 44.60 | 3.48 | 3.54 | 7.32 | 7.43 | 1.4·10 ⁻⁵ |
| Ce ₆ OL ₁₇ | 26.86 | 26.52 | 45.00 | 45.08 | 3.34 | 3.22 | 7.28 | 7.51 | 1.1·10 ⁻⁵ |
| PrL ₃ ·H ₂ O | 24.21 | 24.87 | 44.65 | 44.44 | 3.62 | 3.53 | 7.61 | 7.41 | 1.7·10 ⁻⁵ |
| NdL ₃ ·H ₂ O | 24.60 | 25.26 | 44.40 | 44.21 | 3.60 | 3.51 | 7.56 | 7.37 | 2.5·10 ⁻⁵ |
| SmL ₃ ·H ₂ O | 26.29 | 26.04 | 43.33 | 43.75 | 3.44 | 3.47 | 7.22 | 7.29 | 5.3·10 ⁻⁵ |
| EuL ₃ ·H ₂ O | 26.08 | 26.30 | 43.96 | 43.60 | 3.49 | 3.46 | 7.33 | 7.27 | 7.3·10 ⁻⁵ |
| GdL ₃ ·H ₂ O | 26.63 | 26.93 | 43.71 | 43.22 | 3.47 | 3.43 | 7.28 | 7.20 | 10.2·10 ⁻⁵ |
| TbL ₃ ·H ₂ O | 27.10 | 27.18 | 43.20 | 43.08 | 3.43 | 3.42 | 7.20 | 7.18 | 6.0·10 ⁻⁵ |
| DyL ₃ ·H ₂ O | 27.27 | 27.61 | 43.35 | 42.82 | 3.44 | 3.40 | 7.23 | 7.14 | 4.9·10 ⁻⁵ |
| HoL ₃ ·H ₂ O | 27.85 | 27.92 | 42.75 | 42.64 | 3.39 | 3.38 | 7.12 | 7.11 | 4.8·10 ⁻⁵ |
| ErL ₃ ·H ₂ O | 28.41 | 28.16 | 42.12 | 42.50 | 3.34 | 3.37 | 7.00 | 7.08 | 3.3·10 ⁻⁵ |
| TmL ₃ ·H ₂ O | 28.55 | 28.40 | 42.13 | 42.35 | 3.34 | 3.36 | 7.00 | 7.06 | 2.6·10 ⁻⁵ |
| YbL ₃ ·H ₂ O | 29.07 | 28.88 | 41.79 | 42.07 | 3.30 | 3.34 | 6.96 | 7.01 | 2.5·10 ⁻⁵ |
| LuL ₃ ·H ₂ O | 28.62 | 29.12 | 42.66 | 41.93 | 3.39 | 3.33 | 7.12 | 6.99 | 1.6·10 ⁻⁵ |

Simultaneous TG-DTG-DTA curves under non-isothermal conditions were obtained with a Paulik-Paulik-Erdey Derivatograph Q-1500D. Samples (100 mg) were heated in platinum crucibles (ϕ 9 mm) at 20–1000°C in air atmosphere at a heating rate of 10°C min⁻¹. The reference material was α -Al₂O₃ in a platinum crucible.

X-ray diffraction patterns of the intermediates of thermal decomposition were recorded by the Debye-Scherrer method, using a DRON-2 diffractometer with Ni-filtered CuK α radiation.

The solubilities of the complexes in water at 25°C were examined spectrophotometrically with the use of arsenazo III.

Results and discussion

The complexes of benzohydroxamic acid with yttrium(III) and the lanthanides were prepared as solid, roentgenographically amorphous compounds, with colours characteristic of yttrium(III) and the lanthanide(III) ions (except for the europium complex, which is cream-coloured, and the cerium compound, which is brown). The general formula of the prepared compounds is Ln(C₇H₆NO₂)₃·H₂O, where Ln= Y(III), La(III), Pr(III), Nd(III), Sm(III)-Lu(III). Under the applied preparation conditions, cerium forms a complex of undetermined composition. Polarographic analysis shows that about 15% of the cerium ions present are tetravalent. We suggest the formula Ce(III)₅Ce(IV)O(C₇H₆NO₂)₁₇. Its composition is confirmed by elemental analysis. All of the complexes are slightly soluble in water (Table 1).

The IR spectra of the yttrium and lanthanide benzohydroxamates were recorded and compared with those of benzohydroxamic acid. Table 2 lists the most important bands and their assignments (in this Table, the following notation of the vibrations modes is used: ν – stretching vibration, δ – deformation vibration, β – in-plane deformation vibration, γ – out-of-plane deformation vibration, C_{Ar} – aromatic carbon atom).

During heating, the benzohydroxamates of yttrium and the lanthanides decompose in several steps. The thermal data on the particular decomposition stages are listed in Tables 3–5. Some typical TG, DTG and DTA curves are given in Figs 1 and 2.

The cerium complex decomposes violently above 150°C and an undefined product is formed at 210°C. The next stage of thermal decomposition begins at 300°C and probably yields unstable Ce(CO₃)₂ (mass loss: observed 49.0%, theoretical 50.76%). The compound decomposes above 370°C, and CeO₂ is formed at 530°C.

The hydrated complexes of yttrium and the lanthanides (La, Pr–Lu) lose their water molecules in continuous mode at 50–150°C, without sharp endothermic effects in the DTA curves. This indicates that the water present in the compounds is loosely bound. The stability of the anhydrous complexes increases insignificantly along the lanthanide series.

Table 2 Frequencies of the maxima of the IR spectra of benzohydroxamic acid and of Y and lanthanide benzohydroxamates (cm^{-1})

| Acid | Y | La | Ce | Pr | Nd | Sm | Eu | Assignment |
|-------|-------|-------|-------|-------|-------|-------|-------|---|
| 3296s | 3288m | 3248m | | 3256m | 3256m | 3264m | 3256m | $\nu\text{C}=\text{O}^*$, νOH from H_2O^{**} |
| 3056m | 3080m | 3050m | 3060m | 3056m | 3056m | 3054m | 3066m | νNH , $\nu\text{C}_{\text{Ar}}-\text{H}$ |
| 2768s | | | | | | | | νOH |
| 1648s | | | | | | | | $\nu\text{C}=\text{O}$ (amide I band) |
| | 1620s | 1620s | | 1620s | 1620s | 1620s | 1620s | δHOH |
| 1612s | 1604s | 1604s | 1604s | 1604s | 1604s | 1604s | 1604s | $\nu\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}$, $\beta\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}$ |
| 1572s | | | | | | | | |
| 1564s | 1568s | 1568s | 1568s | 1568s | 1568s | 1568s | 1568s | $\beta\text{NH}+\nu\text{CN}$ (am. II band) |
| 1556s | 1532m | 1538m | 1536m | 1534m | 1535m | 1533m | 1532m | νNO |
| 1488m | 1484m | 1484m | 1484m | 1484m | 1484m | 1488m | 1484m | $\nu\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}$, $\beta\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}$ |
| 1432m | | | | | | | | δOH |
| 1402m | | | | | | | | |
| | 1342 | 1343m | 1345m | 1340m | 1340m | 1340m | 1343m | νCO |
| 1328m | | | | | | | | βOH |
| 1313m | 1312m | 1308m | 1308m | 1308m | 1308m | 1308m | 1308m | $\nu\text{CN}+\beta\text{NH}$ (am. III band) |
| 1160m | 1156s | 1156s | 1156s | 1156s | 1156s | 1156s | 1156s | $\beta\text{C}_{\text{Ar}}\text{H}$ |
| | 1056m | 1052m | 1052m | 1052m | 1052m | 1056m | 1056m | νCO |
| 1040m | | | | | | | | |
| 1024m | 1024m | 1024m | 1024m | 1024m | 1024m | 1024m | 1024m | $\nu\text{C}-\text{N}(\text{H})$ |
| | 916m | 912m | 912m | 912s | 912s | 912m | 912s | νNO |
| 896m | | | | | | | | $\nu\text{N}-\text{O}(\text{H})$ |
| 825w | | | | | | | | |
| 800m | | | | | | | | γOH |
| 785m | 784m | 784m | 784m | 784m | 784m | 784m | 784m | γNH |
| 703m | | | | | | | | $\beta\text{O}=\text{CN}$ (amide IV band) |
| 688s | 692s | 696s | 692s | 692s | 692s | 692s | 692s | γNH (amide V band), $\gamma\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}$ |
| 528m | | | | | | | | $\gamma\text{C}=\text{O}$ (amide VI band) |
| | 470w | 450w | 448w | 448w | 448w | 448w | 453w | $\nu\text{Ln}-\text{O}$ |

Table 2 Continued

| Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | Assignment |
|-------|-------|-------|-------|-------|-------|-------|-------|---|
| 3248m | 3264m | 3288m | 3264m | 3248m | 3272m | 3312m | 3320m | $\nu\text{C}=\text{O}^*$, νOH from H_2O^{**} |
| 3060m | 3060m | 3055m | 3070m | 3060m | 3060m | 3065m | 3080m | νNH , $\nu\text{C}_{\text{Ar}}-\text{H}$ νOH $\nu\text{C}=\text{O}$ (amide I band) |
| 1620s | 1620s | 1620s | 1620s | 1620s | 1620s | 1620s | 1620s | δHOH |
| 1604s | 1604s | 1604s | 1604s | 1604s | 1604s | 1604s | 1606s | $\nu\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}$, $\beta\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}$ |
| 1568s | 1568s | 1568s | 1568s | 1568s | 1568s | 1568s | 1568s | $\beta\text{NH}+\nu\text{CN}$ (am. II band) |
| 1530m | 1528m | 1533m | 1532m | 1532m | 1524m | 1532m | 1532m | νNO |
| 1484m | 1484m | 1484m | 1484m | 1480m | 1484m | 1484m | 1484m | $\nu\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}$, $\beta\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}$ δOH |
| 1335m | 1344m | 1346m | 1343m | 1347m | 1333m | 1347m | 1350m | νCO βOH |
| 1308m | 1312m | 1312m | 1308m | 1308m | 1308m | 1312m | 1308m | $\nu\text{CN}+\beta\text{NH}$ (am. III band) |
| 1156s | 1156s | 1156s | 1156s | 1156s | 1156s | 1156s | 1156s | $\beta\text{C}_{\text{Ar}}-\text{H}$ |
| 1056m | 1056m | 1056m | 1056m | 1060m | 1060m | 1060m | 1060m | νCO |
| 1024m | 1024m | 1024m | 1024m | 1024m | 1024m | 1024m | 1024m | $\nu\text{C}-\text{N}(\text{H})$ |
| 916s | 916s | 916s | 916s | 916s | 916s | 920s | 920s | νNO $\nu\text{N}-\text{O}(\text{H})$ |
| 784m | 784m | 784m | 784m | 784m | 784m | 784m | 784m | γOH γNH $\beta\text{O}=\text{CN}$ (amide IV band) |
| 692s | 692s | 692s | 692s | 692s | 692s | 692s | 692s | γNH (amide V band), $\gamma\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}$ $\gamma\text{C}=\text{O}$ (amide VI band) |
| 456w | 472w | 470w | 480w | 480w | 476w | 476w | 486w | $\nu\text{Ln}-\text{O}$ |

(s – strong, m – medium, w – weak; * – for acid, ** – for complexes)

Decomposition of the complexes begins at 160–180°C. In the first step of decomposition, unstable solid products are formed. The IR spectra of these com-

pounds were recorded (Table 6). The crystallization water vibrations and the CO group vibrations disappear too. The range of metal-oxygen vibrations ($500\text{--}400\text{ cm}^{-1}$) is distinctly changed. The aromatic structures in the compounds are retained: we observed the stretching and deformation vibrations of the aro-

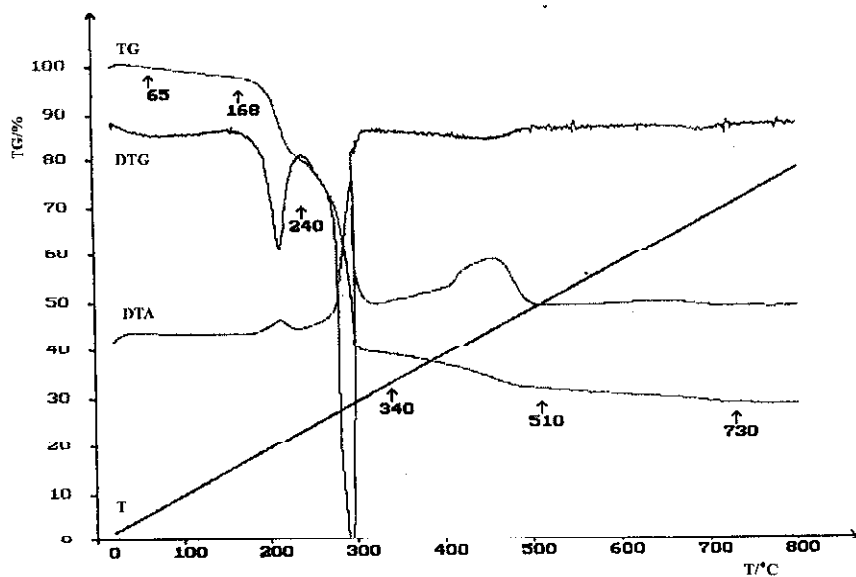


Fig. 1 TG, DTG and DTA curves of samarium(III) benzohydroxamate. Heating rate $10^{\circ}\text{C min}^{-1}$

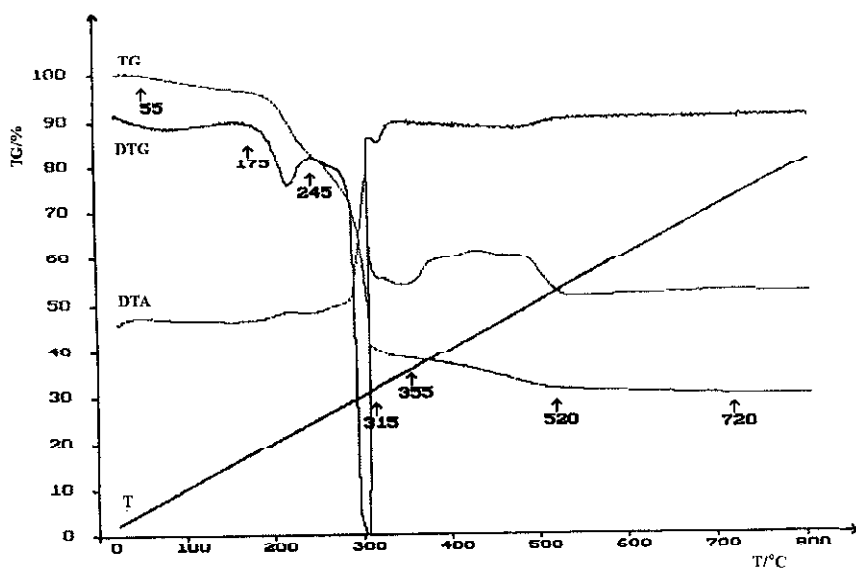


Fig. 2 TG, DTG and DTA curves of erbium(III) benzohydroxamate. Heating rate $10^{\circ}\text{C min}^{-1}$

Table 3 Thermal data of the dehydration and decomposition process at 20–300°C of Y and lanthanide benzo-hydroxamates in air atmosphere, (L = Ce, F, NO₂)

| Complex | $T_{\text{range}}/^{\circ}\text{C}$ | Mass loss/% | | Product* | $T_{\text{range}}/^{\circ}\text{C}$ | Mass loss/% | $T_{\text{range}}/^{\circ}\text{C}$ | Mass loss/% |
|------------------------------------|-------------------------------------|-------------|-------|------------------|-------------------------------------|-------------|-------------------------------------|-------------|
| | | calc. | found | | | | | |
| YL ₃ ·H ₂ O | 55–155 | 3.49 | 3.2 | YL ₃ | 175–250 | 23.4 | 255–320 | 61.0 |
| LaL ₃ ·H ₂ O | 60–150 | 3.19 | 2.9 | LaL ₃ | 160–235 | 22.7 | 238–320 | 51.5 |
| Ce ₆ OL ₁₇ | | | | | 145–210 | 39.3 | | |
| PrL ₃ ·H ₂ O | 60–150 | 3.17 | 2.9 | PrL ₃ | 165–240 | 22.2 | 245–315 | 53.7 |
| NdL ₃ ·H ₂ O | 50–147 | 3.16 | 3.2 | NdL ₃ | 160–240 | 21.1 | 243–315 | 55.8 |
| SmL ₃ ·H ₂ O | 65–150 | 3.13 | 3.0 | SmL ₃ | 168–240 | 20.7 | 243–310 | 55.2 |
| EuL ₃ ·H ₂ O | 50–145 | 3.11 | 3.2 | EuL ₃ | 170–245 | 20.2 | 248–310 | 53.3 |
| GdL ₃ ·H ₂ O | 50–145 | 3.08 | 3.0 | GdL ₃ | 170–245 | 20.0 | 248–325 | 53.5 |
| TbL ₃ ·H ₂ O | 50–140 | 3.08 | 3.2 | TbL ₃ | 170–247 | 20.3 | 250–325 | 55.1 |
| DyL ₃ ·H ₂ O | 50–140 | 3.06 | 3.2 | DyL ₃ | 175–245 | 19.7 | 248–310 | 55.5 |
| HoL ₃ ·H ₂ O | 55–145 | 3.05 | 3.2 | HoL ₃ | 177–247 | 19.3 | 250–315 | 53.7 |
| ErL ₃ ·H ₂ O | 55–145 | 3.04 | 3.0 | ErL ₃ | 175–245 | 18.6 | 248–310 | 53.6 |
| TmL ₃ ·H ₂ O | 60–150 | 3.03 | 3.1 | TmL ₃ | 180–250 | 18.5 | 255–315 | 53.5 |
| YbL ₃ ·H ₂ O | 55–150 | 3.00 | 3.0 | YbL ₃ | 170–245 | 17.9 | 250–315 | 52.7 |
| LuL ₃ ·H ₂ O | 50–140 | 3.00 | 3.1 | LuL ₃ | 175–240 | 17.9 | 245–310 | 52.0 |

T_{range} – temperature range of dehydration

$T_{\text{range I}}$ – temperature range of I stage of decomposition

$T_{\text{range II}}$ – temperature range of II stage of decomposition

* Product of dehydration

Table 4 Thermal data of the decomposition process above 300°C of Y and lanthanide benzo hydroxamates in air atmosphere

| Compound of lanthanide | $T_{\text{range I}}/^\circ\text{C}$ | Mass loss ^a / % | $T_{\text{range V}}/^\circ\text{C}$ | Mass loss ^b /% | | Product | $T_{\text{final}}/^\circ\text{C}$ | Mass loss ^c /% | | Final product |
|------------------------|-------------------------------------|--------------------------------------|-------------------------------------|---------------------------|-------|--|-----------------------------------|---------------------------|-------|----------------------------|
| | | | | calcd. | found | | | calcd. | found | |
| Y | 325-345 | 65.8 | 385-555 | 75.58 | 75.7 | $\text{Y}_2\text{O}_3 \cdot 2\text{C}$ | -780 | 77.91 | 78.2 | Y_2O_3 |
| La | | | 345-545 | 65.84 | 65.8 | $\text{La}_2\text{O}_3 \cdot 5\text{C}$ | -880 | 71.15 | 70.7 | La_2O_3 |
| Ce | 300-360 | 49.0 | 368-530 | 67.37 | 67.0 | CeO_2 | 530 | 67.37 | 67.0 | CeO_2 |
| | | [Ce(CO ₃) ₂] | | | | | | | | |
| Pr | | | 355-590 | 66.78 | 66.7 | $\text{Pr}_6\text{O}_{11} \cdot 9\text{C}$ | -850 | 70.00 | 69.8 | Pr_6O_{11} |
| Nd | | | 345-525 | 67.37 | 67.3 | $\text{Nd}_2\text{O}_3 \cdot 3\text{C}$ | -760 | 70.53 | 70.3 | Nd_2O_3 |
| Sm | | | 340-510 | 66.67 | 66.4 | $\text{Sm}_2\text{O}_3 \cdot 3\text{C}$ | -730 | 69.79 | 69.5 | Sm_2O_3 |
| Eu | | | 335-490 | 66.44 | 66.4 | $\text{Eu}_2\text{O}_3 \cdot 3\text{C}$ | -730 | 69.55 | 69.3 | Eu_2O_3 |
| Gd | | | 345-520 | 66.89 | 66.9 | $\text{Gd}_2\text{O}_3 \cdot 2\text{C}$ | -720 | 68.95 | 69.3 | Gd_2O_3 |
| Tb | | | 355-505 | 67.52 | 67.4 | $\text{Tb}_4\text{O}_7 \cdot \text{C}$ | -780 | 68.03 | 68.3 | Tb_4O_7 |
| Dy | 312-330 | 57.8 | 355-520 | 66.27 | 66.2 | $\text{Dy}_2\text{O}_3 \cdot 2\text{C}$ | -720 | 68.31 | 68.7 | Dy_2O_3 |
| Ho | 320-335 | 56.2 | 365-520 | 66.50 | 66.4 | $2\text{Ho}_2\text{O}_3 \cdot 3\text{C}$ | -720 | 68.02 | 68.1 | Ho_2O_3 |
| Er | 315-337 | 56.3 | 355-520 | 65.77 | 65.9 | $\text{Er}_2\text{O}_3 \cdot 2\text{C}$ | -720 | 67.79 | 67.5 | Er_2O_3 |
| Tm | 318-350 | 57.5 | 380-535 | 66.05 | 66.2 | $2\text{Tm}_2\text{O}_3 \cdot 3\text{C}$ | -700 | 67.56 | 67.4 | Tm_2O_3 |
| Yb | 318-355 | 57.7 | 385-550 | 66.11 | 66.5 | $\text{Yb}_2\text{O}_3 \cdot \text{C}$ | -650 | 67.11 | 66.9 | Yb_2O_3 |
| Lu | 315-345 | 55.2 | 370-570 | 66.89 | 67.5 | Lu_2O_3 | 570 | 66.89 | 67.5 | Lu_2O_3 |

 $T_{\text{range IV}}$ - temperature range of I stage of decomposition $T_{\text{range II}}$ - temperature range of II stage of decomposition T_{final} - temperature of product formation

* Found mass loss

matic ring. Additionally, the distinct bands at $1408\text{--}1408\text{ cm}^{-1}$ (strong), $857\text{--}850\text{ cm}^{-1}$ (medium) and 720 cm^{-1} (medium), ascribed to vibration of the carbonate ion appear in the IR spectra.

Table 5 DTG and exothermic DTA peaks on decomposition of Y and lanthanide benzo hydroxamates in air atmosphere ($L = \text{C}_7\text{H}_6\text{NO}_2^-$)

| Complex | DTG _{max} / | | | | DTA _{max} / | | | DTA _{range} /°C | |
|------------------------------------|----------------------|-----|-----|---------|----------------------|-----|-----|--------------------------|---------|
| | °C | | | | °C | | | | |
| YL ₃ ·H ₂ O | 95 | 225 | 310 | 330 | 490 | 228 | 315 | 340 | 405–550 |
| LaL ₃ ·H ₂ O | 100 | 203 | 300 | | 485 | 203 | 302 | | 380–540 |
| Ce ₆ OL ₁₇ | | 205 | | 353 390 | | 207 | | | 340–530 |
| PrL ₃ ·H ₂ O | 75 | 210 | 290 | | 485 | 212 | 295 | | 375–580 |
| NdL ₃ ·H ₂ O | 75 | 210 | 300 | | 480 | 211 | 301 | | 370–515 |
| SmL ₃ ·H ₂ O | 80 | 213 | 295 | | 455 | 213 | 297 | | 360–500 |
| EuL ₃ ·H ₂ O | 80 | 218 | 301 | | 450 | 220 | 303 | | 350–485 |
| GdL ₃ ·H ₂ O | 75 | 215 | 300 | | 470 | 215 | 301 | | 360 510 |
| TbL ₃ ·H ₂ O | 85 | 220 | 304 | | 465 | 220 | 306 | | 365–500 |
| DyL ₃ ·H ₂ O | 82 | 222 | 305 | 316 | ~450 | 222 | 307 | 320 | 370–510 |
| HoL ₃ ·H ₂ O | 85 | 222 | 307 | 320 | ~450 | 222 | 310 | 325 | 370–520 |
| ErL ₃ ·H ₂ O | 85 | 220 | 307 | 320 | ~460 | 220 | 309 | 325 | 365–520 |
| TmL ₃ ·H ₂ O | 90 | 225 | 304 | 330 | ~470 | 225 | 309 | 340 | 400–540 |
| YbL ₃ ·H ₂ O | 90 | 222 | 304 | 330 | ~480 | 222 | 308 | 340 | 385–540 |
| LuL ₃ ·H ₂ O | 85 | 222 | 304 | 327 | ~480 | 222 | 307 | 330 | 375–535 |

This stage of decomposition is accompanied by the combustion of some products of degradation and a slight exothermic effect is exhibited in the DTA curve (Table 5).

When heated above $240\text{--}250^\circ\text{C}$, the compounds decompose very violently and the organic moiety undergoes combustion. The DTA curve reveals a very sharp and strong exothermic effect (Table 5). This stage of decomposition is completed above 310°C and the solid products formed are stable up to $335\text{--}350^\circ\text{C}$ in the cases of La and the light lanthanide compounds (from Pr to Tb). In the cases of Y and the heavy lanthanide salts (from Dy to Lu), the solid products of degradation formed at $310\text{--}315^\circ\text{C}$ immediately decompose and the compounds then obtained are stable up to $355\text{--}385^\circ\text{C}$.

All solid intermediates obtained above 310°C have undefined composition. Their IR spectra exhibit intense vibrations of CO_3^{2-} ($1408\text{--}1400$, $850\text{--}840$ and $720\text{--}718\text{ cm}^{-1}$), and several medium and weak bands (at $1548\text{--}1520$, $1510\text{--}1500$,

Table 6 The comparison of the frequencies [cm^{-1}] of IR spectra of Ce, Gd, Dy, Tm benzoxyhydroxamates (BENZ) and their thermal decomposition products (TDP) formed at 210–250°C

| Ce | Pr | | Gd | | Dy | | Tm | | Assignment |
|---------------|--------------|---------------|--------------|---------------|--------------|---------------|--------------|---------------|--|
| | TDP 210°C | BENZ 240°C | TDP 240°C | BENZ 240°C | TDP 250°C | BENZ 250°C | TDP 250°C | BENZ 250°C | |
| BENZ 3060m | 3256m | 3060w | 3248m | 3060m | 3288m | 3055m | 3060w | 3060m | 40°C VOH |
| 3080m | 3056m | 3060w | 3060m | 3060w | 3055m | 3055w | 3060w | 3060m | 40°C vNH+vC _{Ar} -H |
| 1604s | 1620s | 1620s | 1620s | 1620s | 1620s | 1620s | 1620s | 1620s | 40°C δHOH |
| 1596s | 1604s | 1596s | 1604s | 1604s | 1604s | 1604s | 1604s | 1604s | 40°C v+βC _{Ar} -C _{Ar} |
| 1568s | 1568s | 1568s | 1568s | 1572s | 1568s | 1556s | 1560s | 1568s | 40°C βNH+vCN |
| 1536m | 1534m | 1532s | 1530m | 1540s | 1533m | 1534s | 1530s | 1524m | 40°C vNO, vC=N |
| 1484m | 1484m | 1512s | 1484m | 1480m | 1484m | 1480m | 1480m | 1484m | 40°C v+βC _{Ar} -C _{Ar} |
| 1416s | 1404s | 1404s | 1404s | 1404s | 1408s | 1408s | 1404s | 1404s | 40°C CO ₂ |
| 1345m | 1340m | 1340m | 1335m | 1335m | 1346m | 1346m | 1333m | 1333m | 40°C vCO |
| 1308m | 1308m | 1304m | 1308m | 1304m | 1312m | 1304m | 1308m | 1304m | 40°C vCN+βNH |
| 1156s | 1156s | 1156w | 1156s | 1156m | 1156s | 1160m | 1160m | 1156s | 40°C βC _{Ar} -H |
| 1072v | 1072v | 1072w | 1056m | 1056m | 1068w | 1068w | 1065w | 1065w | 40°C vCO |
| 1052m | 1052m | 1024m | 1056m | 1024m | 1056m | 1056m | 1060m | 1060m | 40°C vC-N(H) |
| 1024m | 1024m | 1024m | 1024m | 1024m | 1024m | 1024m | 1024m | 1024m | 40°C vNO |
| 912m | 912s | 910w | 916s | 912m | 916s | 912m | 912m | 916s | 40°C CO ₂ |
| 848w | 848w | 850w | 848w | 848w | 857w | 857w | 850w | 850w | 40°C γNH |
| 784m | 784m | 785w | 784m | 784m | 784m | 784w | 784m | 784m | 40°C CO ₂ |
| 716m | 716m | 720m | 720m | 720m | 720m | 720m | 720m | 720m | 40°C γNH, γC _{Ar} -C _{Ar} |
| 692s | 684m | 690m | 692s | 688m | 692s | 588s | 690m | 692s | 40°C vNH, γC _{Ar} -C _{Ar} |
| 560w | 560w | 540w | 540w | 540w | 540w | 540w | 540w | 540w | 40°C vL _N -O |
| 448w | 448w | 448w | 448w | 448w | 448w | 448w | 448w | 448w | 40°C vL _N -O |

(s - strong, m - medium, w - weak, se - several weak bands)

1080–1070 and 980 cm^{-1}), probably due to an organic residue. Roentgenographic analysis shows that all mentioned intermediates of the thermal decomposition are amorphous.

When heating is continued the formation of new intermediates is observed. The X-ray patterns contain very distinct peaks. We identify these products as mixtures of lanthanide oxides with a residue of organic carbon. The contents of carbon in the light lanthanide oxides are greater than those in the heavy lanthanide oxides. The carbon burns out continuously and the pure lanthanide oxides are formed. It is impossible to determine exactly the temperature of the end of decomposition. The temperature of oxide formation generally decreases along the lanthanides series, from 880°C for La to 570°C for Lu (except for CeO_2 , which is formed at the lowest temperature, 530°C). The thermal decomposition of yttrium benzohydroxamate approximates to that of a heavy lanthanide complex, but the temperature of Y_2O_3 formation fits into the range for the light lanthanide group.

Conclusions

The benzohydroxamates of yttrium and the lanthanides obtained under the conditions described above are solid, roentgenographically amorphous compounds that are slightly soluble in water. Their general formula is $\text{Ln}(\text{C}_7\text{H}_6\text{NO}_2)_3 \cdot \text{H}_2\text{O}$, where $\text{Ln} = \text{Y(III)}, \text{La(III)}, \text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}\text{--}\text{Lu(III)}$. On being heated in air atmosphere, the complexes decompose in several steps. In the first stage of degradation, the anhydrous compounds are formed. It was impossible to determine the compositions of the other intermediates formed above 200°C. The oxides of yttrium and the lanthanides are the final products of thermal dissociation.

Cerium benzohydroxamate is an anhydrous compound. Its composition is difficult to determine. When heated, it decomposes in three steps, forming CeO_2 as final product.

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