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2,2'-Bipyridyl Complexes with Heavy Rare-Earth Bromides and YBr_3

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Compounds of the formula $LnBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$, $LnBr_2OH(2\text{-}bipy)_2 \cdot 4\,H_2O$ (Ln = Tb, Dy, Ho, Er, Yb, Lu), $YBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ and $YBr_3(4\text{-}bipy)_2 \cdot 6\,H_2O$ (*2-bipy* = 2,2'-bipyridyl; *4-bipy* = 4,4'-bipyridyl) were prepared and their infrared spectra investigated between 4 000–400 cm^{-1}. They have been characterized by their thermal properties.

(Keywords: 2,2'-Bipyridyl complexes; 4,4'-Bipyridyl complexes; Infrared spectra; Rare-earth complexes; Thermal decomposition)

2,2'-Bipyridylkomplexe der Seltenerdmetallbromide und YBr_3

Es wurden 2,2'-Bipyridylkomplexe des Typs $LnBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$, $LnBr_2OH(2\text{-}bipy) \cdot 4\,H_2O$ (Ln = Tb, Dy, Ho, Er, Yb, Lu), $YBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ und $YBr_3(4\text{-}bipy)_2 \cdot 6\,H_2O$(*2-bipy* = 2,2'-Bipyridyl, *4-bipy* = 4,4'-Bipyridyl) dargestellt. Die IR-Spektren (4 000–400 cm^{-1}) und die thermischen Eigenschaften dieser Verbindungen wurden untersucht.

Introduction

In the previous work [1] the formation conditions of $LnBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ and $LnBr_2OH(2\text{-}bipy)_2 \cdot 4\,H_2O$ (where La ÷ Gd, except Ce, Pm) and their physico-chemical properties have been studied.

The aim of present work has been to examine the compounds of 2,2'-bipyridyl with heavy lanthanide bromides. This paper also reports the preparation of *2-bipy* and *4-bipy* complexes with YBr_3. IR spectra and the thermal decomposition of these compounds is described.

Experimental

2,2'-Bipyridyl obtained from POCh-Gliwice, was recrystallised from 50% solution of ethanol/water and then from absolute ethanol. Platelike crystals were

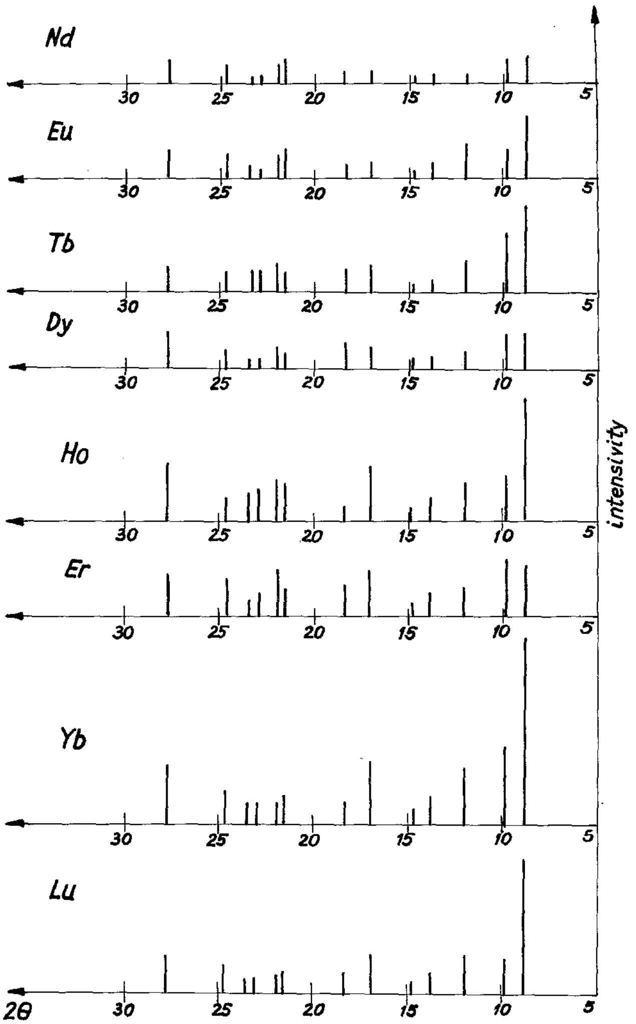

Fig. 1. X-ray diffraction patterns of $LnBr_2OH(2\text{-}bipy)_2 \cdot 4\,H_2O$

obtained with a melting point of 69.5 °C. Analytical reagent grade 4,4′-bipyridyl was a Schuchard (München) product. The source of the lanthanide and Y materials were lanthanide oxides and Y_2O_3 99.9 percent pure. They were purchased either from Koch-Light Lab. or Fluka A. G. Hydrated rare earth bromide was prepared by dissolving rare earth oxide in concentrated HBr and carefully evaporating. The products were purified by recrystallization from 2 *M* HBr solution and crystallized under vacuum [2]. The products were analysed for rare earth ion

Table 1. *Analytical data of the compounds* $Ln\mathrm{Br}_3$(*2-bipy*)$_2 \cdot 6\,\mathrm{H_2O}$, YBr_3 (*2-bipy*)$_2 \cdot 6\,\mathrm{H_2O}^{a}$ *and* YBr_3(*4-bipy*)$_2 \cdot 6\,\mathrm{H_2O}^{b}$

Ln	%Metal calcd. found	%Br calcd. found	%C calcd. found	%N calcd. found	%H calcd. found
Tb	19.40	29.27	29.33	6.84	3.45
	19.74	28.80	29.44	7.10	3.60
Dy	19.75	29.14	29.20	6.81	3.43
	20.05	28.95	29.73	6.52	3.45
Ho	19.99	29.05	29.11	6.79	3.42
	19.74	28.90	29.20	6.57	3.47
Er	20.21	28.97	29.03	6.77	3.41
	20.65	28.99	29.29	6.70	3.57
Yb	20.77	28.77	28.83	6.72	3.39
	20.65	28.92	29.12	6.63	3.45
Lu	20.95	28.70	28.76	6.71	3.38
	21.18	28.98	28.79	6.93	3.39
Y^{a}	11.87	32.00	32.07	7.48	3.77
	11.72	32.49	32.00	7.05	3.97
Y^{b}	11.87	32.00	32.07	7.48	3.77
	11.56	31.87	32.47	7.53	3.60

by standard titration methods using *EDTA*. Hydrated yttrium bromide was obtained in analogy.

Preparation of Compounds. All the compounds $Ln\mathrm{Br}_3$(*2-bipy*)$_2 \cdot 6\,\mathrm{H_2O}$ (Tb ÷ Lu, Y, except Tm) and $Ln\mathrm{Br_2OH}$(*2-bipy*)$_2 \cdot 4\,\mathrm{H_2O}$ (Tb ÷ Lu, except Tm) were prepared by the method published in a previous paper [1]. YBr_3(*4-bipy*)$_2 \cdot 6\,\mathrm{H_2O}$ was prepared by exactly the same procedure used for the *2-bipy* compounds.

The composition of these compounds was verified by analysis for Ln^{3+} and Y^{3+} ions, C, N, H (by standard microanalytical techniques) and bromides (by *Volhard* method). The data for the analyses are given in Tables 1 and 2.

The infrared spectra were recorded on a Carl Zeiss UR 10 spectrophotometer in the 4 000–400 cm^{-1} region. The KBr disc method was employed.

The X-ray diffraction analysis was carried out with a DRON-1 X-ray analyser using copper radiation and nickel filter. Diffractograms were recorded with an automatic recorder for $2\,\theta$ angles from 2 to 50°.

The thermal decomposition studies were carried out using a derivatograph OD-102/1 500 °C with α-$\mathrm{Al_2O_3}$ as inert substance in air atmosphere. The measurements were performed within a temperature range 20—800 °C, the heating rate of the samples 5 $°\mathrm{C\,min}^{-1}$, the sensitivity of the galvanometers $^{1}/_{5}$ for the DTA curve, $^{1}/_{5}$ for the DTG curve, and 50 mg for the TG curve. The size of the sample was 50 mg.

Results and Discussion

The compounds which were prepared for this study are listed in Tables 1 and 2. The isolated 2,2′-bipyridyl complexes with heavy rare earth bromides have analogous composition as with the bromide salts in series

Table 2. *Analytical data of the compounds* $LnBr_2OH(2\text{-}bipy)_2 \cdot 4\,H_2O$

Ln	%Metal calcd. found	%Br calcd. found	%C calcd. found	%N calcd. found	%H calcd. found
Tb	22.07	22.19	33.36	7.78	3.50
	22.44	22.18	33.06	8.00	3.63
Dy	22.45	22.08	33.19	7.74	3.48
	22.11	22.50	33.55	7.99	3.52
Ho	22.71	22.05	33.08	7.69	3.47
	22.52	22.01	33.00	7.72	3.40
Er	22.96	21.94	32.97	7.69	3.46
	23.00	22.04	33.05	7.70	3.50
Yb	23.57	21.51	32.71	7.63	3.43
	23.20	21.90	32.80	7.71	3.40
Lu	23.77	21.71	32.63	7.61	3.42
	24.00	22.04	32.40	7.90	3.50

La ÷ Gd (except Ce and Pm) [1]. The yttrium compounds were only isolated as $YBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ and $YBr_3(4\text{-}bipy)_2 \cdot 6\,H_2O$. They are a new example of complexes with ligand isomerism.

All compounds are air stable and present similar colours that those of the rare earth ions. The compounds $TbBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ and $TbBr_2OH(2\text{-}bipy)_2 \cdot 4\,H_2O$ showed green fluorescence at room temperature. The fluorescence was observed in the light from LS/58 quartz lamp. All compounds dissolve fairly in methanol and ethanol.

IR spectra

Principal IR Bands of Bipyridyl in the Complexes

The IR spectrum of free 2,2′-bipyridyl [3] undergoes a change when coordinated with a lanthanide or yttrium. Table 3 shows the effect of complex formation on the principal modes of 2,2′-bipyridyl. The IR spectra for the 2,2′-bipyridyl compounds with heavy rare earth bromides and YBr_3 are similar to those of the group La ÷ Gd [1]. IR data of all isolated compounds show that these are *cis*-bis 2,2′-bipyridyl chelates [4, 5].

IR spectra of free 4,4′-bipyridyl also undergo a change when coordinated with yttrium. New bands are observed for the $YBr_3(4\text{-}bipy)_2 \cdot 6\,H_2O$ at 1 500, 1 530, 1 390 and 1 330 cm^{-1}. The characteristic ring breathing mode (982 cm^{-1}) in substituted pyridines is shifted in this complex at 1 008 cm^{-1}. These changes are due to the coordinated nature of the pyridine nitrogen atom [6, 7]. The ring vibration $>C=C<$ and $>C=N—$ appearing at 1 530 cm^{-1} and 1 590 cm^{-1} in the free ligand are observed at 1 570 cm^{-1} and at 1 605 cm^{-1}, respectively. Such an effect has been observed previously for compounds of *4-bipy* with $LnBr_3$ [8].

Water Vibrations

For the complexes $LnBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$, $YBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ and $YBr_3(4\text{-}bipy)_2 \cdot 6\,H_2O$, in the OH stretching region a very large broad absorption band extending from 3 150–3 590 cm^{-1} was observed. In the OH bending region a single band (or shoulder) was generally observed at about 1 640 cm^{-1}.

In the 820–440 cm^{-1} region, absorption due to librational modes of coordinated water could be assigned (tabulated in Table 3; results for $YBr_3(4\text{-}bipy)_2 \cdot 6\,H_2O$: H_2O_{roc}—814 cm^{-1}; H_2O_{wag}—540 cm^{-1}; LnO_{str}—445, 485 cm^{-1}).

Similar results are observed for the compounds $LnBr_2OH(2\text{-}bipy)_2 \cdot 4\,H_2O$.

Coordination Hydroxyl Vibrations

In the hydroxo complexes vibration frequencies for coordinated hydroxyl (stretching *Ln*—O vibrations) are observed as strong bands between 447–463 cm^{-1}. This band shifts to higher frequencies with an increasing of atomic number. The deformation vibration *Ln*—OH in these compounds shows up as a weak band at about 970–975 cm^{-1}.

The obtained diffractograms (Fig. 1) show that compounds of formula $LnBr_2OH(2\text{-}bipy)_2 \cdot 4\,H_2O$ (where *Ln* = Nd, Eu [1], Tb, Dy, Ho, Er, Yb, Lu) are isostructural.

Thermal Investigations

Thermal decomposition data obtained for the compounds $LnBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$, $YBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ and $YBr_3(4\text{-}bipy)_2 \cdot 6\,H_2O$ are summarized in Table 4.

The complexes $LnBr_3(2\text{-}bipy)_3 \cdot 6\,H_2O$ (*Ln* = Tb, Dy, Ho, Er, Yb and Y) dehydrate progressively. In the first stage for Tb, Dy and Ho complexes 1 mol water, for Er 2 mol water, is split off; in the second stage they lose all water. $YbBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ loses the water in 3 steps, at first it eliminates 1 mol water (65–100 °C), at 100–110 °C the next 1 mol water, at 110–140 °C it loses all water. $YBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ begins its decomposition at 60 °C to produce $YBr_3(2\text{-}bipy)_2 \cdot 2\,H_2O$ at 100 °C and is anhydrous at 155 °C.

$LuBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ loses all water between 80–200 °C, and 0.25 mol *2-bipy* with endothermic DTA peaks at 90 °C and 140 °C.

Table 3. *Principal IR bands of* $Ln\mathrm{Br}_3$(*2-bipy*)$_2 \cdot 6\ \mathrm{H_2O}$, YBr_3(*2-bipy*)$_2 \cdot 6\ \mathrm{H_2O}$ *and* $Ln\mathrm{Br}_2\mathrm{OH}$(*2-bipy*)$_2 \cdot 4\ \mathrm{H_2O}$ [cm^{-1}]

Assignment	Tb	Dy	Ho	Er	Yb	Lu	Y
			$Ln\mathrm{Br}_3$(*2-bipy*)$_2 \cdot 6\ \mathrm{H_2O}$				
ring str. $>C=N—$ and	1 605 vs	1 596 vs	1 605 vs	1 595 vs	1 598 vs	1 595 s	1 596 vs
ring str. $>C=C<$	1 580 m	1 570 w	1 580 m	1 570 m	1 585 s	1 570 w	1 570 w
	1 575 m	1 565 sh	1 575 m	1 563 sh	1 562 sh		1 556 w
new bands resulting	1 500 m	1 490 m	1 500 m	1 494 s	1 495 w		
from complexation	1 480 s		1 482 s	1 472 s	1 475 w		1 470 s
	1 390 s	1 380 m	1 396 m	1 380 m	1 396 m	1 380 m	1 390 m
	1 325 s	1 315 m	1 324 s	1 315 m	1 314 m	1 310 m	1 350 w
	1 164 s	1 170 m	1 165 s	1 165 m	1 160 m	1 162 s	1 336 w
ring breathing mode	1 015 vs	1 010 vs	1 015 vs	1 010 vs	1 010 vs	1 010 vs	1 008 s
H out of pl. bend		780 sh	778 sh	770 vs	775 sh	772 m	770 vs
	764 vs	770 m	765 vs	750 s	760 s	760 s	
	740 s	736 s	740 s		735 s	740 m	735 m
ring torsion	408 m	408 w	410 m	410 m	410 m	412 m	415 m
coordinated water vibrations							
$\mathrm{H_2O}$ rock.	820 m	815 w	820 m	815 m	815 vw	815 w	814 vs
$\mathrm{H_2O}$ wag.	545 vw	548 w	545 w	547 w	548 w	548 w	548 w
$Ln\mathrm{O}$ str.	475 sh	475 sh	475 sh	475 w	465 vw	460 s	465 vw
	445 m	448 m	450 s	453 s	450 s	440 w	450 s

Assignment	Tb	Dy	Ho	Er	Yb	Lu
			*Ln*Br$_2$OH(*2-bipy*)$_2$ · 4 H$_2$O			
ring str. >C=N— and	1 598 vs	1 603 vs	1 602 vs	1 602 vs	1 598 vs	1 603 vs
ring str. >C=C<	1 570 s	1 585 s	1 580 m	1 580 m	1 580 m	1 585 m
	1 565 m	1 575 sh	1 575 m	1 575 m	1 575 sh	1 580 sh
new bands resulting	1 520 w	1 498 s	1 500 s	1 498 s	1 490 s	1 492 s
from complexation	1 485 s	1 482 vs	1 485 vs	1 485 vs	1 472 vs	1 485 vs
	1 315 s	1 322 s	1 320 s	1 323 s	1 320 s	1 318 s
	1 180 s	1 185 s	1 185 s	1 185 m	1 175 m	1 185 m
		1 175 vs	1 175 vs	1 175 m	1 160 s	1 172 s
ring breathing mode	1 002 vs	1 012 vs	1 015 vs	1 016 vs	1 016 vs	1 016 vs
H out of pl. bend	780 vs	780 vs	770 vs	778 vs	770 vs	780 vs
	765 vs	770 vs	762 vs	763 vs	760 vs	765 vs
	740 vs	742 vs	740 vs	742 s	735 vs	742 vs
ring torsion	410 s	409 s	409 s	410 s	415 s	415 s
coordinated water vibrations						
H$_2$O rock.	810 m	823 m	823 m	820 m	817 m	818 m
H$_2$O wag.	550 w	548 w	545 s	546 w	549 w	549 w
*Ln*O str.	475 sh	478 sh	475 sh	474 sh		480 sh
coordinated OH$^-$ jon						
Ln-OH def.	970 w	975 w	975 w	976 w	975 w	973 w
*Ln*O str.	447 vs	450 vs	452 vs	454 s	462 vs	463 vs

w, m, s, v, sh weak, medium, strong, very, shoulder

Table 4. *Thermal decomposition data of the compounds* $LnBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$, $YBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ *and* $YBr_3(4\text{-}bipy)_2 \cdot 6\,H_2O$ *in air*

Compound	Step of decomposition	% loss mass		Temp. range [°C]	Temp. of endothermic peak [°C]
		Calculated	Determined from TG		
1	2	3	4	5	6
$TbBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$					
↓	I	2.20	2.0	65–100	80
$TbBr_3(2\text{-}bipy)_2 \cdot 5\,H_2O$					
↓	II	11.00	11.0	100–135	120
$TbBr_3(2\text{-}bipy)_2$					
↓	III	14.30	14.0	135–265	142
$TbBr_3(2\text{-}bipy)_{1.25}$					
↓	IV	14.30	14.2	265–320	316
$TbBr_3(2\text{-}bipy)_{0.5}$					
↓	V	27.09	27.2	320–400	383
$TbOBr$					
↓	VI	8.29	9.0	440–560	
Tb_4O_7					
$DyBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$					
↓	I	2.19	2.0	70–100	80
$DyBr_3(2\text{-}bipy)_2 \cdot 5\,H_2O$					
↓	II	10.95	11.0	100–135	108
$DyBr_3(2\text{-}bipy)_2$					
↓	III	14.24	13.8	135–280	140
$DyBr_3(2\text{-}bipy)_{1.25}$					
↓	IV	14.24	14.5	280–340	300
$DyBr_3(2\text{-}bipy)_{0.5}$					
↓	V	26.97	27.0	340–400	392
$DyOBr$					
↓	VI	8.74	8.2	440–640	
Dy_2O_3					
$HoBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$					
↓	I	2.18	2.0	65–90	80
$HoBr_3(2\text{-}bipy)_2 \cdot 5\,H_2O$					
↓	II	10.92	11.0	90–138	108
$HoBr_3(2\text{-}bipy)_2$					
↓	III	14.20	13.5	138–265	140
$HoBr_3(2\text{-}bipy)_{1.25}$					
↓	IV	14.20	14.0	265–320	295
$HoBr_3(2\text{-}bipy)_{0.5}$					
↓	V	15.27	16.0	320–380	372
$2\,HoBr_3 \cdot HoOBr$					
↓	VI	11.62	11.5	380–570	420
$HoOBr$					
↓	VII			>570	
Ho_2O_3					

Table 4 *(continued)*

Compound	Step of decomposition	% loss mass		Temp. range [°C]	Temp. of endothermic peak [°C]
		Calculated	Determined from TG		
1	2	3	4	5	6
$ErBr_3(\mathit{2\text{-}bipy})_2 \cdot 6\,H_2O$					
↓	I	4.35	4.0	60–90	80
$ErBr_3(\mathit{2\text{-}bipy})_2 \cdot 4\,H_2O$					
↓	II	8.71	8.2	100–136	100
$ErBr_3(\mathit{2\text{-}bipy})_2$					
↓	III	4.72	4.5	136–155	138
$ErBr_3(\mathit{2\text{-}bipy})_{1.75}$					
↓	IV	9.44	10.0	155–260	160
$ErBr_3(\mathit{2\text{-}bipy})_{1.25}$					
↓	V	40.98	41.0	260–400	298, 360
$ErOBr$					
↓	VI	8.69	9.0	420–600	420
Er_2O_3					
$YbBr_3(\mathit{2\text{-}bipy})_2 \cdot 6\,H_2O$					
↓	I	2.16	2.0	65–100	80
$YbBr_3(\mathit{2\text{-}bipy})_2 \cdot 5\,H_2O$					
↓	II	2.16	2.2	100–110	105
$YbBr_3(\mathit{2\text{-}bipy})_2 \cdot 4\,H_2O$					
↓	III	8.64	8.5	110–140	120
$YbBr_3(\mathit{2\text{-}bipy})_2$					
↓	IV	14.06	14.0	140–288	142
$YbBr_3(\mathit{2\text{-}bipy})_{1.25}$					
↓	V	14.06	13.7	288–320	298
$YbBr_3(\mathit{2\text{-}bipy})_{0.5}$					
↓	VI	18.01	19.0	320–370	360
$YbBr_3 \cdot YbOBr$					
↓	VII	8.64	9.0	370–535	438
$YbOBr$					
↓	VIII	8.62	8.6	535–600	
Yb_2O_3					
$LuBr_3(\mathit{2\text{-}bipy})_2 \cdot 6\,H_2O$					
↓	I	17.62	17.5	80–200	90, 140
$LuBr_3(\mathit{2\text{-}bipy})_{1.75}$					
↓	II	9.35	8.5	200–262	230
$LuBr_3(\mathit{2\text{-}bipy})_{1.25}$					
↓	III	14.03	14.0	262–360	298
$LuBr_3(\mathit{2\text{-}bipy})_{0.5}$					
↓	IV	26.57	27.0	360–450	385, 430
$LuOBr$					
↓	V	8.65	8.8	490–660	
Lu_2O_3					

Table 4 *(continued)*

Compound	Step of decomposition	% loss mass Calculated	% loss mass Determined from TG	Temp. range [°C]	Temp. of endothermic peak [°C]
1	2	3	4	5	6
$YBr_3(\textit{2-bipy})_2 \cdot 6\,H_2O$					
↓	I	4.81	5.0	60–100	90
$YBr_3(\textit{2-bipy})_2 \cdot 2\,H_2O$					
↓	II	9.62	9.5	100–155	120, 124
$Ybr_3(\textit{2-bipy})_2$					
↓	III	5.21	5.2	155–195	162
$YBr_3(\textit{2-bipy})_{1.75}$					
↓	IV	5.21	5.0	195–220	215
$YBr_3(\textit{2-bipy})_{1.5}$					
↓	V	50.48	50.2	220–420	280, 300, 380
$YOBr$					
↓	VI	9.60	9.5	480–620	455
Y_2O_3					
$YBr_3(\textit{4-bipy})_2 \cdot 6\,H_2O$					
↓	I	14.23	14.0	60–100	95
$YBr_3(\textit{4-bipy})_2$					
↓	II	15.64	15.2	100–200	145, 150
$YBr_3(\textit{4-bipy})_{1.25}$					
↓	III	10.43	10.5	200–237	220
$YBr_3(\textit{4-bipy})_{0.75}$					
↓	IV	5.21	5.0	240–270	252
$YBr_3(\textit{4-bipy})_{0.5}$					
↓	V	29.82	33.0	270–400	375
$YOBr$[a]					
↓	VI	9.60	7.0	480–620	
Y_2O_3					

[a] Some contamination by Y_2O_3

$YBr_3(\textit{4-bipy})_2 \cdot 6\,H_2O$ loses water within the temperature range 60–100 °C, with an endothermic peak at 95 °C.

With increasing temperature 2,2′-bipyridyl is released in three stages. The intermediates postulated are $\textit{Ln}Br_3(\textit{2-bipy})_{1.25}$ and $\textit{Ln}Br_3(\textit{2-bipy})_{0.5}$ ($\textit{Ln}$ = Tb, Dy, Ho, Yb, Lu). Above 320 °C $HoBr_3(\textit{2-bipy})_{0.5}$ decomposes to $2\,HoBr_3 \cdot HoOBr$. Within the temperature range 370–535 °C $HoOBr$ was formed and formation of Ho_2O_3 begins at 570 °C. The transition compounds $\textit{Ln}Br_3(\textit{2-bipy})_{0.5}$ ($\textit{Ln}$ = Tb, Dy and Lu) are decomposed to

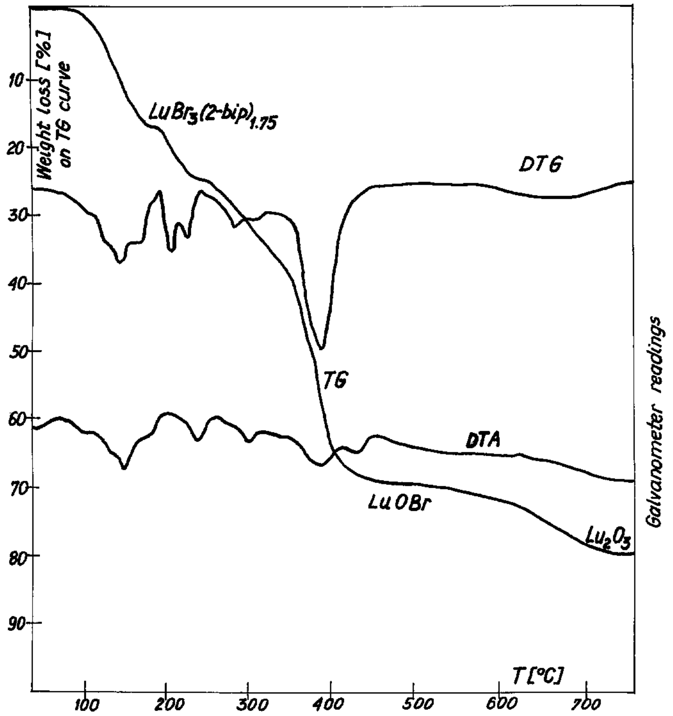

Fig. 2. Derivatogram of $LuBr_3$(*2-bipy*)$_2 \cdot 6\, H_2O$ in air

*Ln*OBr within the temperature range between 320–400 °C for Tb; 340–400 °C for Dy and 360–450 °C for Lu. Formation of Tb_4O_7 begins at 440 °C; Dy_2O_3 at 440 °C; Lu_2O_3 at 490 °C. During thermal decomposition of the intermediate product $YbBr_3$(*2-bipy*)$_{0.5}$ a compound of the formula $YbBr_3 \cdot YbOBr$ is formed which is converted to YbOBr. On an increase of temperature YbOBr decomposes to Yb_2O_3.

The yttrium complexes also loses *2-bipy* in 3 steps. At first 0.25 mol of *2-bipy* (155–195 °C) was eliminated and formed the transition compound YBr_3(*2-bipy*)$_{1.75}$. It lost 0.25 mol *2-bipy* and decomposed to YBr_3(*2-bipy*)$_{1.5}$. Within the range above 220–420 °C the decomposition of YBr_3(*2-bipy*)$_{1.5}$ takes place and forms YOBr. Over the temperature 480 °C the compound YOBr converts to the oxide.

Similar interpretations were made for YBr_3(*4-bipy*)$_2 \cdot 6\, H_2O$ but it loses *4-bipy* in 4 steps.

The derivatogram of $LuBr_3$(*2-bipy*)$_2 \cdot 6\, H_2O$ is shown—as an example—in the Fig. 2.

Thermal curves for *Ln*Br_2OH(*2-bipy*)$_2 \cdot 4\, H_2O$ (*Ln* = Tb, Dy, Ho,

Table 5. *Thermal decomposition data of the compounds* $Ln\mathrm{Br_2OH}(2\text{-}bipy)_2 \cdot 4\,\mathrm{H_2O}$ *in air*

Compound	Step of decomposition	% loss mass		Temp. range [°C]	Temp. of endothermic peak [°C]
		Calculated	Determined from TG		
1	2	3	4	5	6
$\mathrm{TbBr_2OH}(2\text{-}bipy)_2 \cdot 4\,\mathrm{H_2O}$					
↓	I	10.01	10.0	70–140	125
$\mathrm{TbBr_2OH}(2\text{-}bipy)_2$					
↓	II	16.27	16.0	140–200	145
$\mathrm{TbBr_2OH}(2\text{-}bipy)_{1.25}$					
↓	III	10.84	10.5	200–300	300
$\mathrm{TbBr_2OH}(2\text{-}bipy)_{0.75}$					
↓	IV	33.78	33.0	300–420	370
$2\,\mathrm{TbOBr} \cdot \mathrm{Tb_4O_7}$					
↓	V	3.14	4.0	460–560	
$\mathrm{Tb_4O_7}$					
$\mathrm{DyBr_2OH}(2\text{-}bipy)_2 \cdot 4\,\mathrm{H_2O}$					
↓	I	9.96	10.5	80–130	120
$\mathrm{DyBr_2OH}(2\text{-}bipy)_2$					
↓	II	16.19	15.5	130–180	140
$\mathrm{DyBr_2OH}(2\text{-}bipy)_{1.25}$					
↓	III	10.79	11.0	180–300	300
$\mathrm{DyBr_2OH}(2\text{-}bipy)_{0.75}$					
↓	IV	27.36	27.0	300–400	384
DyOBr					
↓	V	9.94	9.0	440–640	
$\mathrm{Dy_2O_3}$					
$\mathrm{HoBr_2OH}(2\text{-}bipy)_2 \cdot 4\,\mathrm{H_2O}$					
↓	I	9.92	9.5	80–140	128
$\mathrm{HoBr_2OH}(2\text{-}bipy)_2$					
↓	II	16.13	16.5	160–218	145
$\mathrm{HoBr_2OH}(2\text{-}bipy)_{1.25}$					
↓	III	10.75	10.0	220–310	306
$\mathrm{HoBr_2OH}(2\text{-}bipy)_{0.75}$					
↓	IV	32.33	32.0	310–500	400
$2\,\mathrm{HoOBr} \cdot \mathrm{Ho_2O_3}$					
↓	V	4.95	5.0	500–640	
$\mathrm{Ho_2O_3}$					
$\mathrm{ErBr_2OH}(2\text{-}bipy)_2 \cdot 4\,\mathrm{H_2O}$					
↓	I	25.97	26.2	80–190	100, 400
$\mathrm{ErBr_2OH}(2\text{-}bipy)_{1.25}$					
↓	II	10.72	9.8	190–290	
$\mathrm{ErBr_2OH}(2\text{-}bipy)_{0.75}$					
↓	III	32.12	33.0	290–413	300, 360

Table 5 *(continued)*

Compound	Step of decomposition	% loss mass		Temp. range [°C]	Temp. of endothermic peak [°C]
		Calculated	Determined from TG		
1	2	3	4	5	6
$2\,\text{ErOBr} \cdot \text{Er}_2\text{O}_3$					
↓	IV	4.94	5.0	415–600	
Er_2O_3					
$\text{YbBr}_2\text{OH}(\textit{2-bipy})_2 \cdot 4\,\text{H}_2\text{O}$					
↓	I	9.81	9.5	70–130	124
$\text{YbBr}_2\text{OH}(\textit{2-bipy})_2$					
↓	II	10.64	10.2	130–200	150
$\text{YbBr}_2\text{OH}(\textit{2-bipy})_{1.25}$					
↓	III	10.64	11.0	200–285	285
$\text{YbBr}_2\text{OH}(\textit{2-bipy})$					
↓	IV	37.18	37.4	285–445	367
$2\,\text{YbOBr} \cdot \text{Yb}_2\text{O}_3$					
↓	V	4.90	5.0	460–600	
Yb_2O_3					
$\text{LuBr}_2\text{OH}(\textit{2-bipy})_2 \cdot 4\,\text{H}_2\text{O}$					
↓	I	9.79	9.6	70–135	124
$\text{LuBr}_2\text{OH}(\textit{2-bipy})_2$					
↓	II	10.61	10.0	135–218	145
$\text{LuBr}_2\text{OH}(\textit{2-bipy})_{1.5}$					
↓	III	10.61	10.5	220–260	240
$\text{LuBr}_2\text{OH}(\textit{2-bipy})$					
↓	IV	37.10	38.0	260–420	402
$2\,\text{LuOBr} \cdot \text{Lu}_2\text{O}_3$					
↓	V	4.90	5.0	520–660	
Lu_2O_3					

Er) compounds have similar patterns. In the first step 4 mol of water is split off. The complexes began to lose water above 70–80 °C. The compounds become anhydrous at 140 °C for Tb, Ho, 130 °C for Dy and 190 °C for Er. 2,2′-Bipyridyl is split off in three steps. The intermediates postulated are $Ln\text{Br}_2\text{OH}(\textit{2-bipy})_{1.25}$ and $Ln\text{Br}_2\text{OH}(\textit{2-bipy})_{0.75}$. With increasing temperature the intermediate compounds $Ln\text{Br}_2\text{OH}(\textit{2-bipy})_{0.75}$ decompose to $2\,Ln\text{OBr} \cdot Ln_2\text{O}_3$ (or DyOBr) and finally to oxides.

A similar interpretation was made for $\text{YbBr}_2\text{OH}(\textit{2-bipy})_2 \cdot 4\,\text{H}_2\text{O}$ and $\text{LuBr}_2\text{OH}(\textit{2-bipy})_2 \cdot 4\,\text{H}_2\text{O}$ but Yb formed in the III stage a transition compound $\text{YbBr}_2\text{OH}(\textit{2-bipy})$, when Lu formed in the II stage

$LuBr_2OH$(*2-bipy*)$_{1.5}$ and in the III stage it was converted to $LuBr_2OH$(*2-bipy*).

In the temperature range 460–560 °C for Tb, 500–640 °C for Ho, 415–600 °C for Er, 460–600 °C for Yb, and 520–660 °C for Lu the basic bromides 2 *Ln*OBr · Ln_2O_3 convert to oxides.

The thermal properties of two types of compounds with *2-bipy* differ in their deamination products. The compounds of formula *Ln*Br_2OH(*2-bipy*)$_2$ · 4 H_2O give as a result of full deamination the intermediate compounds 2 *Ln*OBr · Ln_2O_3 (except Dy). Similar basic salts (2 *Ln*ONO_3 · Ln_2O_3) have been observed by *Dutt* [9] during thermal decomposition of the rare-earth nitrate hydrates. The complexes *Ln*Br_3(*2-bipy*)$_2$ · 6 H_2O form in principle *Ln*OBr, only for Ho and Yb the intermediates postulated are 2 $HoOBr_3$ · HoOBr and YBr_3 · YbOBr. *Wendland* [10] has also reported a compound 2 $HoCl_3$ · HoOCl during thermal decomposition of $HoCl_3$ · 6 H_2O.

The composition of intermediate compounds formed at various stages of thermal decomposition were evaluated by calculation from weight loss measurements (TG curves), only the compounds 2 *Ln*OBr · Ln_2O_3, *Ln*OBr, (YOBr) and the final product are isolated using the method described in literature [11, 12]. The chemical composition of these products was established on the basis of the determination of *Ln* (Y) and bromides. The error in the results was determined thermogravimetrically and using chemical analysis in comparison with theoretical values (equal to ca. 1%).

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