Monatshefte für Chemie 117, 783–792 (1986)

Monatshefte für Chemie
Chemical Monthly

Complex Compounds of 2,2′-Bipyridyl with Some Rare-Earth Bromides

Danuta M. Czakis-Sulikowska* and **Joanna Radwańska-Doczekalska**

Institute of General Chemistry, Politechnical University, PL-90924 Łódź, Poland

(Received 18 February 1985. Accepted 27 February 1985)

The preparation of a series of new compounds $Ln\mathrm{Br}_3(2\text{-}bipy)_2 \cdot 6\,\mathrm{H_2O}$ (Ln = La, Pr, Nd, Eu, Gd) and $Ln\mathrm{Br}_2\mathrm{OH}(2\text{-}bipy)_2 \cdot 4\,\mathrm{H_2O}$ (Ln = Pr, Nd, Sm, Eu, Gd) is described. The IR spectra of these compounds are discussed. The thermal decomposition of compounds $Ln\mathrm{Br}_3(2\text{-}bipy)_2 \cdot 6\,\mathrm{H_2O}$ has been investigated.

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

2,2′-Bipyridylkomplexe einiger Seltenerdmetallbromide

Es wurden 2,2′-Bipyridylkomplexe des Typs $Ln\mathrm{Br}_3(2\text{-}bipy)_2 \cdot 6\,\mathrm{H_2O}$ (Ln = La, Pr, Nd, Sm, Eu, Gd) und $Ln\mathrm{Br}_2\mathrm{OH}(2\text{-}bipy)_2 \cdot 4\,\mathrm{H_2O}$ (Ln = Pr, Nd, Sm, Eu, Gd) dargestellt. Die IR-Spektren werden diskutiert. Die thermische Zersetzung von Verbindungen $Ln\mathrm{Br}_3(2\text{-}bipy)_2 \cdot 6\,\mathrm{H_2O}$ wird untersucht.

Introduction

Only fragmentary informations are available in the literature concerning the weakly basic nitrogen donors complexes with lanthanide bromides[1,2]. *Basile* et al.[3] have prepared several mono and bis terpyridyl-rare earth(III) bromide complexes and the results obtained from the infrared studies on these compounds are reported. The complexes $Ln\mathrm{Br}_3(phen)_n \cdot m\mathrm{H_2O}$ (Ln = La–Lu, $n = 2$–4; $m = 2$–12, $phen$ = 1,10-phenanthroline) also have been isolated[4,5]. In our previous paper[6,7] we described a series of compounds $Ln\mathrm{Br}_3(4\text{-}bipy)_2 \cdot 6\,\mathrm{H_2O}$ (Ln = La, Pr, Nd) and $Ln\mathrm{Br}_3(4\text{-}bipy)_3 \cdot 4\,\mathrm{H_2O}$ (Ln = Sm, Eu, Gd, Ho, Tb, Dy, Er, Yb, $4\text{-}bipy$ = 4,4′-bipyridyl). 2,2′-Bipyridyl complexes of rare-earths are obtained when the anion is chloride, nitrate, salicylate, thio- and selenocyanate and perchlorate[8–20]. In this paper compounds of 2,2′-bipyridyl with some rare-earth bromides have been prepared and studied.

Experimental

2,2′-Bipyridyl obtained from Schuchardt München, was recrystallized from absolute ethanol. The rare earth(III) salts as hydrated products were prepared by dissolving the appropriate oxide (99.9% purity, obtained from Koch-Ligh Lab. and Fluka A. G.) in concentrated HBr solution. The product was crystallized under vacuum[21]. Other chemicals were of analytical reagent grade from POCh—Gliwice.

C, N and H were analyzed by standard microanalytical techniques. Ln^{3+} was determined by titration with *EDTA*, and bromide by gravimetric precipitation with silver ion.

The IR spectra were obtained in the 4 000–400 cm^{-1} region with a Carl Zeiss UR 10 instrument using KBr disks. The thermal decomposition studies were made with derivatograph OD-102/1 500 °C with α-Al_2O_3 as the inert substance. Other operating conditions: T_{max} 800 °C; heating rate 5 °C/min; the mass of sample—50 mg; sensitivity: TG—50 mg; DTA—1/5; DTG—1/5; air atmosphere. The X-ray diffractograms were recorded on a diffractometer DRON-1, using CuK_α radiation and nickel filter. Diffractograms were recorded with an automatic recorder for 2θ angles.

Preparation of the Compounds LnBr$_3$(2-*bipy*)$_2 \cdot 6\,H_2O$

The hydrated lanthanide bromides were dissolved in 75% ethanol. The *pH* of the solutions is adjusted to above 1.5 with 2 *M* HBr. 2,2′-Bipyridyl was dissolved separately in a minimum volume of absolute alcohol. The rare-earth bromide solution is added to the 2,2′-bipyridyl solution in a mole ration of 1 : 2. The mixture was heated up to 80 °C for about 15 min and then allowed to cool. During several days the compounds crystallized with an empirical formula LnBr$_3$(2-*bipy*)$_2 \cdot 6\,H_2O$. They were washed with ethyl alcohol and ethyl ether and dried in open air. The results of analyses for these complexes are collected in Table 1.

Preparation of the Compounds LnBr$_2$OH(2-*bipy*)$_2 \cdot 4\,H_2O$

These complexes were prepared by dissolving approximately 0.01 moles of the hydrated lanthanide bromides in 50 ml of 75% ethanol at *pH* ~ 5–6. 2,2′-Bipyridyl (0.02 *M*) was dissolved separately in a minimum volume of 75% ethanol and added to the warm solution of rare-earth bromide. The mixture was heated up to 80 °C for about 15 min and allowed to cool. This solution was evaporated for crystallization at room temperature. The precipitate obtained was filtered, washed with small portion of cold absolute ethanol, then ethyl ether, and dried in open air. This procedure gives very small-crystalline compounds of the formula LnBr$_2$OH(2-*bipy*)$_2 \cdot 4\,H_2O$. The analytical results are tabulated in Table 2.

Results and Discussion

The complexes LnBr$_3$(2-*bipy*)$_2 \cdot 6\,H_2O$ and the hydroxo complexes LnBr$_2$OH(2-*bipy*)$_2 \cdot 4\,H_2O$ have been prepared. From weakly acid solutions the hydroxo complexes are isolated. In the case of more acidic solutions, *pH* ~ 1.5, the complexes LnBr$_3$(2-*bipy*)$_2 \cdot 6\,H_2O$ were obtained. All compounds are air stable and present similar colours than those of the rare earth ions. The compounds EuBr$_3$(2-*bipy*)$_2 \cdot 6\,H_2O$ and EuBr$_2$OH(2-

bipy)$_2 \cdot 4\, H_2O$ showed pink fluorescence. The fluorescence was observed in the light from a LS/58 quartz lamp at room temperature. All compounds dissolve fairly well in ethanol.

The X-ray diffraction analysis revealed isostructurality between Pr and Nd as well as between Sm and Eu in the compounds of type *Ln*Br$_3$(2-*bipy*)$_2 \cdot 6\, H_2O$.

Infrared Spectra

The principal absorption frequencies and assignments[22] for all compounds are collected in Table 3. All the complexes exhibit a very strong band between 1 590–1 600 cm^{-1} and a medium band at 1 560–1 580 cm^{-1}. These absorptions are principally ring stretching vibrations similar to the bands at 1 578 cm^{-1} and 1 552 cm^{-1} in the free ligand[20]. The ring breathing motion at 991 cm^{-1} is shifted 10–25 cm^{-1} to higher frequencies in the metal complexes. The characteristic aromatic out-of-plane hydrogen deformation modes in unbonded 2-*bipy* are observed at 750 and 738 cm^{-1}. All the compounds possess very intense absorptions at 758–767 cm^{-1} and medium or strong intensity absorptions at $\sim$ 742 cm^{-1}. Similar to the free ligand, a torsional ring motion appears at 406–409 cm^{-1} for the hydroxo complexes and at 415 cm^{-1} for the *Ln*Br$_3$(2-*bipy*)$_2 \cdot 6\, H_2O$ compounds. This is about 10–17 cm^{-1} higher than in the free ligand (398 cm^{-1})[22]. New bands are observed for the complexes at about 1 495, 1 315 and 1 152–1 170 cm^{-1} for *Ln*Br$_3$(2-*bipy*)$_2 \cdot 6\, H_2O$, also in the regions: 1 500–1 490, 1 315–1 320 and 1 177–1 185 cm^{-1} for the hydroxo complexes.

Table 1. *Analytical data of the compounds* *Ln*Br$_3$(2-*bipy*)$_2 \cdot 6\, H_2O$

Ln	%Metal calcd. found	%Br calcd. found	%C calcd. found	%N calcd. found	%H calcd. found
La	17.38	30.00	30.06	7.01	3.53
	17.36	29.11	31.00	6.62	3.72
Pr	17.59	29.92	29.99	6.99	3.52
	18.08	30.09	30.02	6.45	3.55
Nd	17.93	29.80	29.86	6.97	3.51
	18.18	29.91	29.92	6.50	3.48
Sm	18.55	29.58	29.64	6.91	3.48
	18.25	29.51	29.85	6.88	3.48
Eu	18.71	29.52	29.58	6.90	3.48
	18.77	29.78	29.00	6.73	3.51
Gd	19.24	29.33	29.39	6.85	3.45
	19.58	28.86	28.89	6.91	3.52

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

Ln	%Metal calcd. found	%Br calcd. found	%C calcd. found	%N calcd. found	%H calcd. found
Pr	20.07	22.76	34.21	7.98	3.59
	19.59	23.09	35.02	7.95	3.80
Nd	20.44	22.65	34.05	7.94	3.57
	20.52	22.46	33.75	7.73	3.64
Sm	21.13	22.46	33.76	7.87	3.54
	21.19	22.58	33.42	8.24	3.61
Eu	21.31	22.41	33.68	7.86	3.53
	21.46	23.00	32.95	8.00	3.60
Gd	21.89	22.24	33.43	7.80	3.51
	22.04	22.87	33.00	7.88	3.60

The results tend to indicate that both 2-*bipy* molecules are chelated to the metals[22]. A similar interpretation made *Sinha*[13] for the bis-2,2′-bipyridyl complexes with lanthanide(III) when the anion is nitrate or chloride and we for the compounds $Ln(2\text{-}bipy)_3(\mathrm{ClO_4})_3 \cdot 6\,H_2O$[20].

The spectra of all 2,2′-bipyridyl complexes show strong and broad absorption bands in the water stretching region (3 125–3 598 $\mathrm{cm^{-1}}$) and a strong (or medium) band in the water bending region (1 630 $\mathrm{cm^{-1}}$). These frequencies are not included in Table 3.

In addition, the following coordination water frequencies have been observed[25, 26]. The bands of weak intensity in the range 812–840 $\mathrm{cm^{-1}}$ and in the range 545–574 $\mathrm{cm^{-1}}$ have been assigned to the H_2O rocking and wagging modes, respectively. The band observed in the range 446–460 $\mathrm{cm^{-1}}$ has been assigned to the metal—oxygen (for co-ordinated water) stretching vibration in $Ln\mathrm{Br_3}(2\text{-}bipy)_2 \cdot 6\,H_2O$ and at 475 $\mathrm{cm^{-1}}$ for hydroxo complexes.

Vibration frequencies of metal—ligand bands for coordinated hydroxyl and water molecules lie roughly in the region from 300 $\mathrm{cm^{-1}}$ to 500 $\mathrm{cm^{-1}}$ (Ref.[27]). In the hydroxo complexes $Ln\mathrm{Br_2OH}(2\text{-}bipy)_2 \cdot 4\,H_2O$, these vibration frequencies for coordinated hydroxyl (stretching *Ln*—O vibrations) are observed as strong band between 420–445 $\mathrm{cm^{-1}}$. These frequencies were metal dependent: Gd > Eu > Sm > Nd > Pr. The deformation vibrations Ln—OH in these compounds exhibit a weak band at about 970 $\mathrm{cm^{-1}}$.

Thermal Investigation

The thermal properties for $Ln\mathrm{Br_3}(2\text{-}bipy)_2 \cdot 6\,H_2O$ complexes were investigated.

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

Assignment	La	Pr	Nd	Sm	Eu	Gd
			$Ln\mathrm{Br}_3(2\text{-}bipy)_2 \cdot 6\,\mathrm{H_2O}$			
ring str. C=N	1 590 vs	1 600 vs	1 600 vs	1 596 s	1 592 s	1 596 s
ring str. C=C	1 565 m	1 570 m	1 578 m	1 572 m	1 570 m	1 570 m
new bands re-	1 490 m	1 495 m	1 496 m	1 492 m	1 495 m	
sulting from	1 480 m					
complexation	1 310 s	1 312 s	1 315 s	1 316 m	1 310 s	1 315 vs
		1 170 m	1 162 s	1 152 m	1 154 m	1 170 w
ring breathing mode	1 000 s	1 010 vs	1 010 vs	1 010 vs	1 006 s	1 009 vs
H out of pl.	760 s	762 vs	760 vs	763 s	763 s	760 vs
bend	740 m	740 s	738 s	736 m	740 m	740 s
ring torsion coordinated	415 m	415 m	416 s	415 m	415 s	415 m
water vibrations						
H_2O rock.	820 vw	812 w	818 m	840 m	840 w	816 w
H_2O wag.	560 w	545 w	566 w	574 w	574 w	573 w
LnO str.	460 w	457 w	460 w	458 w	460 w	446 s
			$Ln\mathrm{Br}_2\mathrm{OH}(2\text{-}bipy)_2 \cdot 4\,\mathrm{H_2O}$			
ring str. C=N		1 600 vs	1 598 vs	1 600 vs	1 596 vs	1 600 vs
ring str. C=C		1 570 w	1 580 w	1 572 w	1 560 w	1 566 w
new bands re-		1 500 m	1 494 m	1 495 m	1 490 m	1 495 s
sulting from		1 320 s	1 320 m	1 322 m	1 315 s	1 322 s
complexation		1 185 w	1 185 w	1 185 w	1 177 m	1 185 w
ring breathing mode		1 015 vs	1 014 vs	1 015 vs	1 015 vs	1 016 vs
H out of pl.		767 vs	765 vs	766 vs	758 vs	765 vs
bend		740 s	740 s	740 s	742 s	742 s
ring torsion		406 m	407 m	408 m	409 m	409 m
coordinated water vibrations						
H_2O rock.		820 w	818 w	828 w	815 w	820 w
H_2O wag.		545 w	574 w	547 w	547 w	545 w
LnO str.		475 w	474 w	475 w	475 w	475 w
coordinated OH^- ion						
Ln—OH def.		975 w	975 vw	975 vw	968 w	972 w
LnO str.		420 m	426 s	437 vs	442 s	445 s

The $Ln\mathrm{Br}_3(2\text{-}bipy)_2 \cdot 6\,\mathrm{H_2O}$ (*Ln* = Pr, Nd, Sm, Eu) complexes decompose according to the following scheme:

$$Ln\mathrm{Br}_3(2\text{-}bipy)_2 \cdot 6\,\mathrm{H_2O} \xrightarrow{\mathrm{I}} Ln\mathrm{Br}_3(2\text{-}bipy)_2 \cdot 3\,\mathrm{H_2O} \xrightarrow{\mathrm{II}}$$

$$\xrightarrow{} Ln\mathrm{Br}_3(2\text{-}bipy)_2 \xrightarrow{\mathrm{III}} Ln\mathrm{Br}_3(2\text{-}bipy)\ (\text{or } \mathrm{EuBr}_3) \xrightarrow{\mathrm{IV}}$$

$$\xrightarrow{} Ln\mathrm{OBr} \xrightarrow{\mathrm{V}} Ln_2\mathrm{O}_3\ (\mathrm{Pr}_6\mathrm{O}_{11})$$

$\mathit{Ln}Br_3(2\text{-}\mathit{bipy})_2 \cdot 6\,H_2O$ began to lose water above 90 °C (Pr), 100 °C (Nd), 60 °C (Sm) and 95 °C (Eu), at first 3 mole H_2O were eliminated. The compounds became anhydrous at 200 °C for Pr, Nd, at 165 °C for Sm and 180 °C for Eu. 2,2′-Bipyridyl was split off in two stages for Pr, Nd and Sm. At first 1 mole of 2-*bipy* was eliminated to form $\mathit{Ln}Br_3(2\text{-}\mathit{bipy})$, (temperature range 210–300 °C for Pr, 235–300 °C for Nd, 260–330 °C for Sm).

In step IV they lost the remaining 2-*bipy* and were converted to *Ln*OBr. On increasing the temperature the *Ln*OBr molecules are decomposed to oxides. The DTA curves show the presence of 4 endothermic peaks.

Table 4. *Thermal decomposition data*

Compound	Step of decomposition	% loss mass		Temp. range [°C]	Peak temp. in DTA [°C]
		Calculated	Determined from TG		
$LaBr_3(2\text{-}\mathit{bipy})_2 \cdot 6\,H_2O$					
↓	I	6.76	6.5	50–100	75 endo
$LaBr_3(2\text{-}\mathit{bipy})_2 \cdot 3\,H_2O$					
↓	II	6.76	6.8	100–150	115 endo
$LaBr_3(2\text{-}\mathit{bipy})_2$					
↓	III	9.77	9.5	150–215	160 endo
$LaBr_3(2\text{-}\mathit{bipy})_{1.5}$					
↓	IV	9.77	10.8	215–250	240 endo
$LaBr_3(2\text{-}\mathit{bipy})$					
↓	V	37.54	35.7	290–460	460 exo
LaOBr[a]					
$PrBr_3(2\text{-}\mathit{bipy})_2 \cdot 6\,H_2O$					
↓	I	6.75	6.5	90–130	100 endo
$PrBr_3(2\text{-}\mathit{bipy})_2 \cdot 3\,H_2O$					
↓	II	6.75	7.0	130–200	155 endo
$PrBr_3(2\text{-}\mathit{bipy})_2$					
↓	III	19.50	20.3	210–300	280 endo
$PrBr_3(2\text{-}\mathit{bipy})$					
↓	IV	37.45	38.0	300–475	390 endo
PrOBr					
↓	V			> 500	
Pr_6O_{11}					
$NdBr_3(2\text{-}\mathit{bipy})_2 \cdot 6\,H_2O$					
↓	I	6.72	6.5	100–140	110 endo
$NdBr_3(2\text{-}\mathit{bipy})_2 \cdot 3\,H_2O$					
↓	II	6.72	7.0	140–200	160 endo
$NdBr_3(2\text{-}\mathit{bipy})_2$					
↓	III	19.42	20.4	235–300	295 endo
$NdBr_3(2\text{-}\mathit{bipy})$					

Table 4 continued

Compound	Step of decomposition	% loss mass		Temp. range [°C]	Peak temp. in DTA [°C]
		Calculated	Determined from TG		
↓	IV	37.29	36.5	300–415	395 endo
NdOBr					440 endo
↓	V			> 490	
Nd_2O_3					
$SmBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$					
↓	I	6.67	7.5	60–118	110 endo
$SmBr_3(2\text{-}bipy)_2 \cdot 3\,H_2O$					
↓	II	6.67	6.5	118–165	140 endo
$SmBr_3(2\text{-}bipy)_2$					
↓	III	19.27	19.5	260–330	300 endo
$SmBr_3(2\text{-}bipy)$					
↓	IV	37.01	36.5	330–510	390 endo
SmOBr					
↓	V			> 660	
Sm_2O_3					
$EuBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$					
↓	I	6.65	7.0	95–130	120 endo
$EuBr_3(2\text{-}bipy)_2 \cdot 3\,H_2O$					
↓	II	6.65	7.0	130–180	160 endo
$EuBr_3(2\text{-}bipy)_2$					
↓	III	38.46	37.7	260–360	320 endo
$EuBr_3$					340 exo
↓	IV	17.71	18.4	360–620	588 exo
EuOBr					
↓	V			> 650	
Eu_2O_3					
$GdBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$					
↓	I	8.82	8.4	80–126	108 endo
$GdBr_3(2\text{-}bipy)_2 \cdot 2\,H_2O$					
↓	II	4.41	4.5	126–150	142 endo
$GdBr_3(2\text{-}bipy)_2$					
↓	III	9.55	9.0	150–280	200 endo
$GdBr_3(2\text{-}bipy)_{1.5}$					
↓	IV	19.11	18.5	280–325	308 endo
$GdBr_3(2\text{-}bipy)_{0.5}$					
↓	V	27.15	25.5	325–400	382 endo
GdOBr[b]					
↓	VI			> 510	
Gd_2O_3					

[a] Some contamination by $LaBr_3$.

[b] Some contamination by $GdBr_3$.

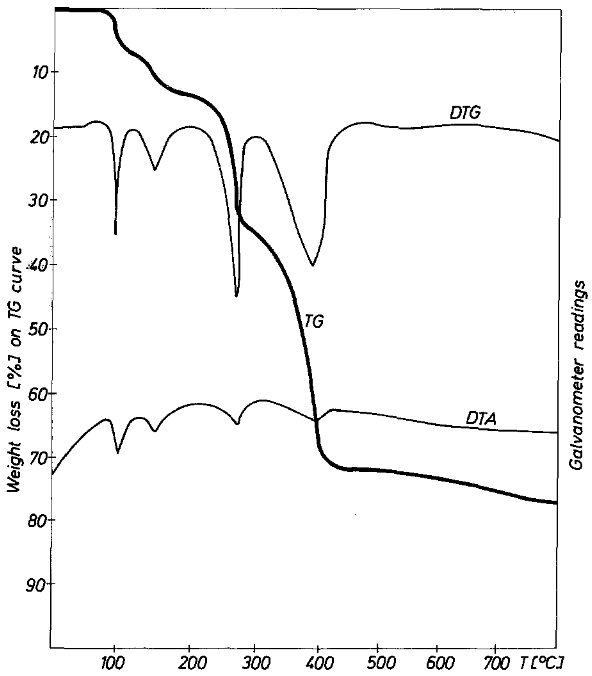

Fig. 1. Derivatogram of $PrBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ in air

The transition compound $EuBr_3(2\text{-}bipy)_2$ loses all 2-*bipy* in one stage and is converted to $EuBr_3$. Within the temperature range 360–620 °C it forms *Eu*OBr. Formation of Eu_2O_3 begins at 650 °C.

$LaBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ loses water above 50 °C and at 100 °C $LaBr_3(2\text{-}bipy)_2 \cdot 3\,H_2O$ is formed. On further heating the trishydrate decomposes and at 150 °C it forms $LaBr_3(2\text{-}bipy)_2$. 2,2′-Bipyridyl is lost in 3 steps. At first 0.5 mol of 2-*bipy* was elimined and formed the transition compound $LaBr_3(2\text{-}bipy)_{1.5}$. It lost 0.5 mol 2-*bipy* and decomposed to $LaBr_3(2\text{-}bipy)$. The DTA curves show the presence of 4 endothermic processes. From 290–460 °C LaOBr is formed, with some contamination by $LaBr_3$; LaOBr is stable in the temperature range 480–700 °C.

$GdBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ dehydrates progressively above 80 °C, to give $GdBr_3(2\text{-}bipy)_2 \cdot 4\,H_2O$ at 126 °C. 2,2′-Bipyridyl is lost in 3 steps and forms $GdBr_3(2\text{-}bipy)_{1.5}$ and $GdBr_3(2\text{-}bipy)_{0.5}$. Over a temperature of 325 °C it lost the remaining 2-*bipy* and was converted to GdOBr. Formation of Gd_2O_3 begins at 510 °C.

The compositions of intermediate compounds formed at various stages of the thermal decomposition were evaluated by calculation from weight loss measurements, only LnOBr was isolated and confirmed by analysis of the metal content.

Data supporting the mode of decomposition are recorded in Table 4. One sees that agreement between the experimental results and the calculated values is quite good.

The thermal decomposition curve of $PrBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ is shown, as example, in the Fig. 1.

Conclusions

The complexes of the type $LnBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ (*Ln* = La, Pr, Nd, Sm, Eu, Gd) and $LnBr_2OH(2\text{-}bipy)_2 \cdot 4\,H_2O$ (*Ln* = Pr, Nd, Sm, Eu, Gd) have been isolated as crystalline or small-crystalline compounds. The compounds $LnBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ and $LnBr_3(4\text{-}bipy)_2 \cdot 6\,H_2O$ (*Ln* = La, Pr, Nd) are new example of complexes with ligand isomerism.

All the compounds of the type $LnBr_3(2\text{-}bipy)_2 \cdot 6\,H_2O$ lose water in 2 steps. The first step in their decomposition is attributed to the loss of the water of crystallization, while the second step of dehydration corresponds probably to the elimination of coordinated water. The IR spectra of all isolated compounds suggest that the water in these complexes is both coordinated and crystalline water. The IR data shows also, that these compounds are *cis*-bis 2,2′-bipyridyl chelates[19,22].

During the thermal decomposition of these compounds partial deamination takes place. The thermal decomposition of 2,2′-bipyridyl complexes with lanthanide bromides runs similar as in the case $LnBr_3(4\text{-}bipy)_n \cdot mH_2O$[6,7] and other 2,2′-bipyridyl complexes with rare earths[15].

This work was partly supported by the Nuclear Problems Institute, Warsaw, Poland, Problem No. 04.3.13. We thank Mgr. *R. Janiszweski* for some preparations.

References

[1] *Forsberg J. H.*, Coord. Chem. Rev. **10**, 195 (1973).

[2] *Garnovskii D. A., Paniuskin V. T., Gricenko T. V.*, Koord. Chim. **7**, 483 (1981).

[3] *Basile L. J., Gronet D. L., Ferraro J. R.*, Spectrochim. Acta **24 A**, 707 (1968).

[4] *Labanov N. I.*, Zh. Neorgan. Chim. **17**, 2844 (1972).

[5] *Eremin Ju. G., Bondorienko G. I.*, ibid. **18**, 1715 (1973).

[6] *Czakis-Sulikowska D. M., Radwańska-Doczekalska J.*, Theory—Structure—Properties of Complex Compounds. IXth Summer School an Coordination Chemistry, p. 39, Karpacz-Bierutowice, 1975.

[7] *Czakis-Sulikowska D. M., Radwańska-Doczekalska J.*, J. Inorg. Nucl. Chem. **41**, 1299 (1979).

[8] *Labanov N. I., Smirnova V. A.*, Zh. Neorg. Khim. **8**, 2208 (1963); ibid. **12**, 1825 (1965).

[9] *Tsintsadze G. V., Golub A. M., Kopa M. V.*, ibid. **14**, 2743 (1969).

[10] *Golub M. A., Kopa M. V., Skopenko V. W., Tsintsadze G. V.*, Z. anorg. allg. Chem. **375**, 302 (1970).

[11] *Golub A. M., Kopa M. V., Andreichenko O. E.*, Zh. Obshch. Khim. **39**, 1382 (1969).

[12] *Hart F. A., Laming F. P.*, J. Inorg. Nucl. Chem. **26**, 579 (1964); ibid. **27**, 1825 (1965).

[13] *Sinha S. P.*, Spectrochim. Acta **20**, 879 (1964); J. Inorg. Nucl. Chem. **27**, 115 (1965); ibid. **28**, 189 (1966).

[14] *Carassiti V., Seminara A., Seminara-Musumeci A.*, Ann. Chim. (Rome) **54**, 1025 (1964).

[15] *Kokunov J. V., Segal E. J.*, Rev. Roumaine Chim. **16**, 1647 (1971).

[16] *Brezina F.*, Monatsh. Chem. **100**, 1684 (1969).

[17] *Jeriemin Ju. G., Bondarienko T. I.*, Zh. Neorg. Khim. **21**, 387 (1976).

[18] *Kopa M. V.*, ibid. **18**, 2072 (1973).

[19] *McWhinnie W. R., Miller J. D.*, Advances in Inorg. Chem. Radiochem. **12**, 137 (1965).

[20] *Czakis-Sulikowska D., Radawńska-Doczekalska J.*, Monatsh. Chem. **113**, 827 (1982).

[21] *Bukietyńska K., Jeżowska-Trzebiatowska B.*, Theory—Structure—Properties of Complex Compounds, IX^th^ Summer School on Coordination Chemistry, p. 39, Karpacz—Bierutowice 1975.

[22] *Strukl J. S., Walter J. L.*, Spectrochim. Acta **27 A**, 209 (1971); ibid. **27 A**, 223 (1971).

[23] *Hanni A., Morlot G., Brehat F.*, ibid. **24 A**, 1167 (1968).

[24] *Nakamoto K.*, Infrared Spectra of Inorganic and Coordination Compounds. New York: J. Wiley. 1963.

[25] *Nakagawa I., Shimanouchi T.*, Spectrochim. Acta **20 A**, 420 (1964).

[26] *Juchnievic G. V.*, Uspiechi Khim. **32**, 1397 (1963).

[27] *Baran V.*, Coord. Chem. Rev. **6**, 65 (1971).