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4,4′-Dipyridyl Complexes of Rare-Earth Thiocyanates

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4,4′-Dipyridyl complexes of rare-earth thiocyanates of the formula *Ln*(4-*dipy*)$_2$(NCS)$_3$ · 5 H_2O (*Ln* = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Y, 4-*dipy* = 4,4′-dipyridyl) have been synthesized. The IR spectra of these compounds and other physical properties are discussed. The thermal decomposition of some compounds (in the order Gd ÷ Lu) has been investigated.

(Keywords: 4,4′-Dipyridyl complexes; Rare-earth complexes; Infrared spectra; Thermal decomposition)

4,4′-Dipyridylkomplexe von Seltenerdmetallthiocyanaten

Es wurden 4,4′-Dipyridylkomplexe des Typs *Ln*(4-*dipy*)$_2$(NCS)$_3$ · 5 H_2O mit *Ln* = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu und Y dargestellt. Die IR-Spektren und andere physikalische Eigenschaften werden diskutiert und die thermische Zersetzung von einigen Verbindungen (in der Reihe Gd ÷ Lu) untersucht.

Introduction

In our previous papers[1—4] we described compounds of the type *Ln*(4-*dipy*)$_2$(NO$_3$)$_3$ · nH$_2$O (*Ln* = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb, Lu, Y), *Ln*(4-*dipy*)Cl$_3$ · nH$_2$O (*Ln* = La, Ce, Pr, Nd, Sm), *Ln*(4-*dipy*)$_2$Cl$_3$ · 6 H_2O (*Ln* = Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Y), Pr(4-*dipy*)$_3$Cl$_3$ · 6 H_2O, *Ln*(4-*dipy*)$_2$Br$_3$ · 6 H_2O (*Ln* = La, Pr, Nd), *Ln*(4-*dipy*)$_3$Br$_3$ · 4 H_2O (*Ln* = Sm, Eu, Gd, Dy, Ho, Er, Yb) and *Ln*(4-*dipy*)$_8$(ClO$_4$)$_3$ · HClO$_4$ · 4 H_2O (*Ln* = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Y). We have found that the number of 4,4′-dipyridyl groups coordinated to the lanthanide ion depends on the coordinating ability of the anion present. Maximum coordination by 4,4′-dipyridyl in the case of presence of the weakly coordinating perchlorate is observed. It should be very interesting to perform a comparative study of the complexes of lanthanide pseudohalogens with 4,4′-dipyridyl.

Only fragmentary informations[5—11] are available in the literature concerning the dipyridyl complexes with rare-earths. There are few papers describing compounds of 2,2′-dipyridyl (2-*dipy*) with lanthanide thiocyanates and selenocyanates. *Hart* and *Laming*[7] obtained compounds of the type $Ln(2\text{-}dipy)_3(NCS)_3$ (Ln = La, Ce, Dy). The complexes $Ln(2\text{-}dipy)_2(NCSe)_3$, $Ln(2\text{-}dipy)_2(NCSe)_3 \cdot (CH_3OH$ or $C_2H_5OH)_2$ and $Ln(2\text{-}dipy)_3(NCSe)_3$ have been described too[8—10]. In this paper compounds of 4,4′-dipyridyl with rare earth thiocyanates have been prepared and studied.

Experimental

The lanthanide oxides and Y_2O_3, all of 99,9% purity, were obtained from Koch-Light Lab. and Fluka A.G. The lanthanide and yttrium perchlorates as the hydrated products were synthesized as described in the literature[12]. The composition of these salts has been controlled by determining the metal percentage. Analytical reagent grade 4,4′-dipyridyl was a Schuchard München product, perchloric acid 60% "proanalyse grade" was obtained from Hopkin Williams. Other chemicals were of analytical reagent grade from POCh-Gliwice.

The lanthanide content was determined complexometrically with standard *EDTA* solution against xylenol orange as indicator. Nitrogen, carbon and hydrogen were determined microanalytically and thiocyanates by the *Volhard* method.

IR spectra (4000–400 cm^{-1}) were measured with a Carl Zeiss UR 10 spectrophotometer. The samples were prepared by using KBr pellets. The X-ray diffractograms of the compounds were obtained using a DRON-1 diffractometer with nickel filtered CuK_α radiation. The diffraction curves were recorded over the range of 2θ. Thermal investigations were made with a derivatograph type OD-102/1500 °C over a temperature range of 20–800 °C at a heating rate of 7 °C per minute; the sensitivity of the galvanometer for DTA curves was 1/5 and for DTG curves 1/5 as well; the TG sensitivity was 50 mg; for the mass sample 50 mg; α-Al_2O_3 served as reference material. The fluorescence was observed in the light from a LS/58 quartz lamp at 21 °C.

Preparation of 4,4′-Dipyridyl Complexes

The solvated lanthanide and yttrium thiocyanates were prepared according to the following general reaction $Ln(ClO_4)_3 + 3\,KNCS \leftrightarrows Ln(NCS)_3 + 3\,KClO_4\downarrow$.

Procedure: a sample of lanthanide or yttrium perchlorate containing about 0.02 mol Ln was placed in a 100 cm^3 flask, dissolved in 50 cm^3 of 96 percent ethanol and then a small excess of solid KNCS was added. The mixture was stirred for 1 hour and cooled for 12 hours at a temperature of 4 °C. The precipitate of $KClO_4$ was separed and the clear solution was concentrated. The product was filtered and dried at room temperature. Finally, in this product the lanthanide content was determined.

The solid 4,4′-dipyridyl (0.02 mol) was added to a warm solution of lanthanide and yttrium thiocyanates in 75 percent ethanol (0.01 mol in 50 cm^3). The mixture was heated up to 80 °C for about 10 min and then allowed to cool. Using the method of slow crystallization from these solutions were obtained

Table 1. *Analytical data of the compounds* $Ln(4\text{-}dipy)_2(NCS)_3 \cdot 5\,H_2O$

Ln	% Metal calcd. found	% C calcd. found	% N calcd. found	% H calcd. found	% NCS calcd. found
Y	13.36	41.50	14.73	3.94	26.18
	14.00	41.93	14.69	3.99	26.20
La	19.41	38.60	13.70	3.66	24.35
	19.76	39.02	13.38	3.95	24.35
Pr	19.64	38.50	13.66	3.65	24.28
	19.47	38.73	13.27	3.86	24.38
Nd	20.01	38.32	13.60	3.64	24.17
	19.55	39.00	13.39	3.91	24.34
Sm	20.68	38.00	13.49	3.60	23.97
	20.75	38.42	13.75	3.44	24.01
Eu	20.85	37.91	13.46	3.60	23.91
	21.00	38.00	12.99	3.81	24.03
Gd	21.43	37.64	13.36	3.57	23.74
	21.81	38.02	12.98	3.50	23.91
Tb	21.60	37.55	13.33	3.56	23.69
	22.00	37.67	13.09	3.70	24.00
Dy	21.98	37.37	13.26	3.55	23.57
	21.68	37.70	13.20	3.40	23.26
Ho	22.24	37.25	13.22	3.53	23.49
	21.87	37.00	13.15	3.43	23.30
Er	22.48	37.13	13.18	3.52	23.42
	21.95	37.00	12.90	3.90	23.52
Yb	23.08	36.85	13.08	3.50	23.24
	23.04	36.95	12.80	3.79	23.33
Lu	23.28	36.75	13.04	3.49	23.18
	22.97	36.90	12.70	3.35	23.07

crystalline complexes. The crystalline precipitates were filtered, washed repeatedly with small portions of cold absolute ethanol and ether-ethanol (1 : 1) mixture. After that they were dried in open air. The results of analyses for all lanthanide compounds prepared are presented in Table 1.

Results and Discussion

The analytical data show that all 4,4′-dipyridyl complexes have the formula $Ln(4\text{-}dipy)_2(NCS)_3 \cdot 5\,H_2O$, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu and Y. All compounds are air stable. Some complexes showed fluorescence at room temperature: $Sm(4\text{-}dipy)_2(NCS)_3 \cdot 5\,H_2O$ and $Eu(4\text{-}dipy)_2(NCS)_3 \cdot 5\,H_2O$—pink, $Tb(4\text{-}dipy)_2(NCS)_3 \cdot 5\,H_2O$—green and $Dy(4\text{-}dipy)_2(NCS)_3 \cdot 5\,H_2O$—light yellow. All complexes are fairly soluble in methanol, acetone, acetonitryle, slightly soluble in ethanol and water, practically insoluble in benzene and carbon tetrachloride.

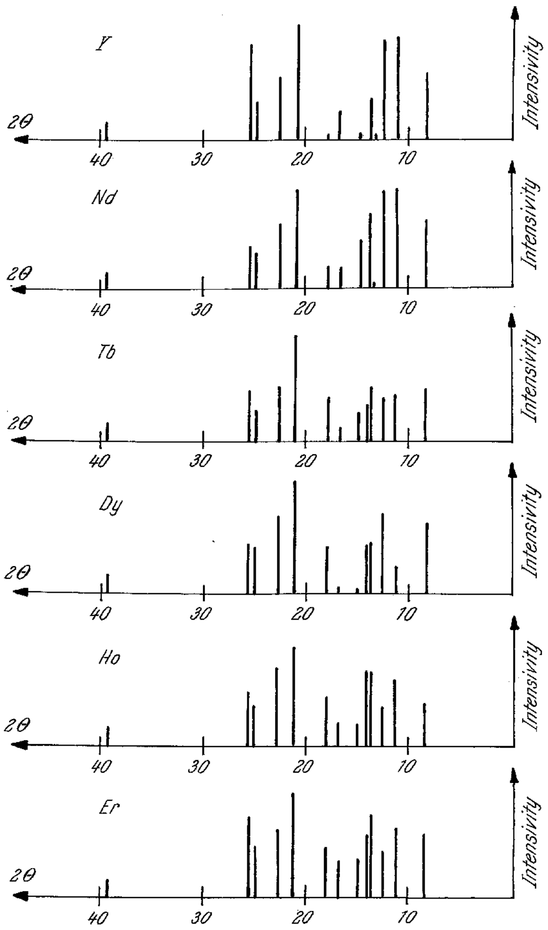

Fig. 1. X-ray diffraction patterns of *Ln*(4-*dipy*)$_2$(NCS)$_3$·5H_2O

X-Ray Powder Patterns

Preliminary diffractometric studies show that these compounds are crystalline or very slight crystalline (La, Gd). The X-ray diffraction analysis revealed isostructurality in the group of the compounds *Ln*(4-*dipy*)$_2$(NCS)$_3$ · 5H_2O, where *Ln* = Y, Nd, Tb, Dy, Ho and Er (Fig. 1).

Infrared Spectra

Table 2 shows the principal IR bands of the 4,4′-dipyridyl complexes. IR spectra of free 4,4′-dipyridyl undergoes a modification when

Table 2. *Principal IR bands of the Ln(4-dipy)*$_2$(NCS)$_3 \cdot 5\,H_2O$ *compounds* [cm^{-1}]

	Pyridine frequencies			Pyridine	New bands
	νCN	νCC	δCH	breathing	resulting from complexation
4-dipy	1 590 vs	1 530 s	802 vs	982 vs	
Y	1 600 s	1 532 m	800 m	992 w	1 310 w
La	1 600 vs	1 540 m	800 m	1 000 m	1 320 w
Pr	1 595 s	1 526 m	800 s	990 m	1 315 w
Nd	1 600 s	1 525 m	800 vs	1 000 m	1 310 w
Sm	1 600 s	1 525 m	800 s	1 005 s	1 306 m
Eu	1 600 s	1 536 m	800 s	998 m	1 320 w
Gd	1 600 s	1 540 m	805 vs	1 000 m	1 320 m
Tb	1 600 vs	1 538 m	800 vs	1 000 s	1 325 m
Dy	1 600 s	1 536 w	800 s	1 000 m	1 315 m
Ho	1 600 s	1 535 m	800 s	1 000 m	1 322 m
Er	1 600 s	1 536 w	800 vs	1 000 s	1 316 w
Yb	1 600 vs	1 532 m	800 m	992 s	1 315 w
Lu	1 600 vs	1 532 m	800 m	990 w	1 315 w

Table 3. *Infrared bands of thiocyanate groups for*
Ln(4-dipy)$_2$(NCS)$_3 \cdot 5\,H_2O$ [cm^{-1}]

Ln	νCN	δNCS	*Ln*	νCN	δNCS
Y	2 080, 2 105 s, pd	470 m	Gd	2 085, 2 100 s, pd	472 m
La	2 080, 2 105 s, pd	475 m	Tb	2 060, 2 075 s, pd	475 m
Pr	2 058, 2 080 sd	475 m		2 090 s	
	2 095 sh		Dy	2 085, 2 100 s, pd	475 m
Nd	2 085, 2 095 s, pd	470 m	Ho	2 090, 2 105 s, pd	472 m
Sm	2 060, 2 070 s, pd	474 m	Er	2 080, 2 105 s, pd	470 m
	2 095 sh		Yb	2 075, 2 098 sd	475 m
Eu	2 055, 2 075 sd	470 m	Lu	2 075, 2 098 sd	474 m
	2 090 sh				

s—strong, pd—poorly resolved doublet, sd—strong doublet, m—medium, sh—shoulder, w—weak.

coordinated with a lanthanide and yttrium. New bands are observed for the complexes within the region 1 322–1 306 cm^{-1}. The characteristic ring breathing mode (982 cm^{-1}) in substituted pyridines is shifted in complexes (1 005–990 cm^{-1}). These changes are assigned for the coordinated nature of the pyridine nitrogen atom[12,13]. The ring vibration $>C{=}C<$ appearing at 1 530 cm^{-1} in the free ligand are observed in the region 1 540–1 525 cm^{-1}. The bands corresponding to ring vibration > C=N— at unbonded 4-*dipy* are shifted about 10 cm^{-1} towards higher wave numbers. Within the region 1 210–740 cm^{-1} the spectrum of the free ligand is richer in lines. For all complexes a very strong and broad band in the water stretching region (3 400–3 350 cm^{-1}) and a medium band or shoulder in the water bending region (1 640–1 630 cm^{-1}) is observed.

Table 3 presents a list of the ν_{CN} and δ_{NCS} bands for these complexes. The mode ν_{CN} of the IR spectra of Ln(4-*dipy*)$_2$(NCS)$_3 \cdot 5\,H_2O$ (Ln = Y, La, Nd, Gd, Dy, Ho, Er, Yb, Lu) is observed at 2 105–2 075 cm^{-1} as a very strong dublet or poorly resolved dublet. These bands can be attributed to the coordinated isothiocyanate group. The infrared spectra of Pr, Sm, Eu and Tb complexes probably correspond to both ionic and N-bonding coordinate thiocyanate groups[14,15]. The ν_{CS} frequencies could not be identified in the spectra of the investigated complexes due to the proximity of these bands to 4-*dipy*; δ_{NCS} bands are identified at ~ 470 cm^{-1}.

Thermal Investigations

Thermal studies have been carried out on Ln(4-*dipy*)$_2$(NCS)$_3 \cdot 5\,H_2O$ where Ln = Gd, Tb, Dy, Ho, Er, Yb and Lu.

Thermal curves for Gd, Tb, Dy, Ho and Er compounds have similar patterns. After three stages of weight loss, the mass of the samples becomes stable above 520–600 °C. The DTA curves exhibit several endothermic peaks. Among them, peaks I (130–145 °C) and II (250–290 °C) and also III (405–415 °C) are connected with the immediate weight loss of the sample. The DTA curves show also two exotermic peaks, from which the one is very strong and broad. The maximal temperatures of the first exothermic peak are observed about 350–370 °C. The second exothermic process appears in the DTA curves at 435–480 °C. The characteristic temperatures of endo- and exothermic peaks, as well as loss of mass on particular stages of thermal decomposition of these compounds are collected in Table 4. The general pyrolysis pattern consisted of the following sequence:

$$Ln\,(4\text{-}dipy)_2(NCS)_3 \cdot 5\,H_2O \xrightarrow{\text{I}} Ln(4\text{-}dipy)_2(NCS)_3 \xrightarrow{\text{II}}$$

$$\longrightarrow Ln_2S_3 \xrightarrow{\text{III}} Ln_2O_3\ (Tb_4O_7)$$

The complexes began to lose water above 60–95 °C. The compounds become anhydrous at 160 °C for Gd, Dy, Er, at 190 °C for Ho and 140 °C for Tb. With increasing temperature the intermediate compounds Ln(4-*dipy*)$_2$(NCS)$_3$ decompose to Ln_2S_3 and finally to oxides. The minimum

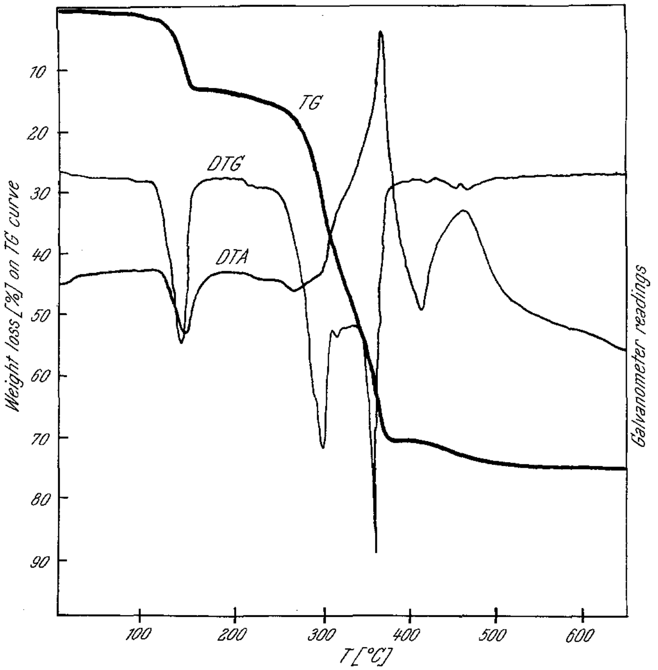

Fig. 2. Derivatogram of Dy(4-*dipy*)$_2$(NCS)$_3$ · 5 H$_2$O

decomposition temperature range for step III was 380–410 °C. The exothermic process which was observed for step II corresponds to partial oxidation of thiocyanates during decomposition of *Ln*(4-*dipy*)$_2$(NCS)$_3$. The second exothermic effect results from the oxidation of *Ln*$_2$S$_3$ to oxides. The possible intermediate products of decomposition of *Ln*$_2$S$_3$ did appear in the TG curves. The derivatogram of Dy(4-*dipy*)$_2$(NCS)$_3$ · 5 H$_2$O is shown—as an example—in the Fig. 2.

The compositions of the intermediate compounds formed at various stages of the thermal decomposition were evaluated by calculation from weight loss measurements (TG curves), only the compound. *Ln*$_2$S$_3$ and the final product are isolated using the method described in literature[16, 17]. The chemical composition of these products was established on the basis of the determination of *Ln* and sulphide[18]. The error in the results, determined thermogravimetrically and using chemical analysis in comparison with theoretical values, was equal to ca. 1%.

For *Ln*(4-*dipy*)$_2$(NCS)$_3$ · 5 H$_2$O (*Ln* = Yb, Lu) the pyrolysis has nearly identical patterns as for compounds Gd ÷ Er, with the exception

Table 4. *Thermal decomposition data*

Compound	Step of decomposition	% loss of mass		Temp. range [°C]	Peak temp. in DTA [°C]
		Calculated	Determined from TG		
1	2	3	4	5	6
$Gd(4\text{-}\mathit{dipy})_2(NCS)_3\cdot 5\,H_2O$					
↓	I	12.27	12.0	60–160	145 endo
$Gd(4\text{-}\mathit{dipy})_2(NCS)_3$					
↓	II	59.88	59.0	200–395	250 endo 355 exo
Gd_2S_3					
↓	III	3.28	3.7	400–570	405 endo 450 exo
Gd_2O_3					
$Tb(4\text{-}\mathit{dipy})_2(NCS)_3\cdot 5\,H_2O$					
↓	I	12.24	12.0	60–140	130 endo
$Tb(4\text{-}\mathit{dipy})_2(NCS)_3$					
↓	II	59.61	59.0	170–360	260 endo 360 exo
Tb_2S_3					
↓	III	2.73	3.0	380–550	410 endo 435 exo
Tb_4O_7					
$Dy(4\text{-}\mathit{dipy})_2(NCS)_3\cdot 5\,H_2O$					
↓	I	12.19	12.5	60–160	140 endo
$Dy(4\text{-}\mathit{dipy})_2(NCS)_3$					
↓	II	59.32	59.0	210–380	260 endo 365 exo
Dy_2S_3					
↓	III	3.26	4.0	400–520	410 endo 460 exo
Dy_2O_3					
$Ho(4\text{-}\mathit{dipy})_2(NCS)_3\cdot 5\,H_2O$					
↓	I	12.15	11.8	95–190	140 endo
$Ho(4\text{-}\mathit{dipy})_2(NCS)_3$					
↓	II	59.13	59.0	210–405	290 endo 370 exo
Ho_2S_3					
↓	III	3.27	3.6	410–600	410 endo 440 exo
Ho_2O_3					

Table 4 (continued)

Compound	Step of decomposition	% loss of mass		Temp. range [°C]	Peak temp. inDTA [°C]
		Calculated	Determined from TG		
1	2	3	4	5	6
$\mathrm{Er}(4\text{-}\mathit{dipy})_2(\mathrm{NCS})_3 \cdot 5\,\mathrm{H_2O}$					
↓	I	12.11	12.0	90–160	140 endo
$\mathrm{Er}(4\text{-}\mathit{dipy})_2(\mathrm{NCS})_3$					
↓	II	58.94	58.5	190–400	280 endo 380 exo
$\mathrm{Er_2S_3}$					
↓	III	3.24	3.0	410–580	415 endo 480 exo
$\mathrm{Er_2O_3}$					
$\mathrm{Yb}(4\text{-}\mathit{dipy})_2(\mathrm{NCS})_3 \cdot 5\,\mathrm{H_2O}$					
↓	I	12.01	11.2	100–180	130 endo
$\mathrm{Yb}(4\text{-}\mathit{dipy})_2(\mathrm{NCS})_3$					
↓	II	5.21	5.0	180–220	200 endo
$\mathrm{Yb}(4\text{-}\mathit{dipy})_{1.75}(\mathrm{NCS})_3$					
↓	III	10.42	10.5	220–265	240 endo
$\mathrm{Yb}(4\text{-}\mathit{dipy})_{1.25}(\mathrm{NCS})_3$					
↓	IV	42.87	43.0	265–395	360 exo
$\mathrm{Yb_2S_3}$					
↓	V	3.21	3.5	400–680	405 endo 420 exo
$\mathrm{Yb_2O_3}$					
$\mathrm{Lu}(4\text{-}\mathit{dipy})_2(\mathrm{NCS})_3 \cdot 5\,\mathrm{H_2O}$					
↓	I	11.98	11.5	50–140	120 endo
$\mathrm{Lu}(4\text{-}\mathit{dipy})_2(\mathrm{NCS})_3$					
↓	II	5.19	5.00	160–220	185 endo
$\mathrm{Lu}(4\text{-}\mathit{dipy})_{1.75}(\mathrm{NCS})_3$					
↓	III	10.39	10.50	220–260	225 endo
$\mathrm{Lu}(4\text{-}\mathit{dipy})_{1.25}(\mathrm{NCS})_3$					
↓	IV	42.76	43.0	260–390	380 exo
$\mathrm{Lu_2S_3}$					
↓	V	3.21	3.0	440–660	410 endo 460 exo
$\mathrm{Lu_2O_3}$					

that the 4-*dipy* moiety was split off in three stages (Table 4). At first 0.25 mol of 4-*dipy* (180–220 °C for Yb, 160–220 °C for Lu) was eliminated and formed the transition compound $Ln(4\text{-}dipy)_{1.75} \cdot (NCS)_3$. It losed 0.5 mol 4-*dipy* and decomposed to $Ln(4\text{-}dipy)_{1.25}(NCS)_3$. Elimination of all water, 0.25 mol and 0.5 mol 4-*dipy* is an endothermic process. The DTA curves show the presence of three endothermic peaks. Within the range above 260–395 °C the decomposition of $Ln(4\text{-}dipy)_{1.25}(NCS)_3$ takes place and forms Ln_2S_3. Over the temperature 400 °C for Yb and 440 °C for *Ln* the compound Ln_2S_3 converts to oxides. The exothermic process attains a maximum at a temperature 360–380 °C for step IV, while for step V it takes place from 420 °C (Yb) to 460 °C (Lu). The exothermic effect results from oxidation processes.

The values of energy of activation (E_a) for dehydration of the compounds $Ln(4\text{-}dipy)_2(NCS)_3 \cdot 5\,H_2O$ (*Ln* = Gd, Tb, Dy, Ho, Er, Yb, Lu) were determined from TG and DTA curves, using the method of *Pilojan* and *Novikova*[19,20]. The authors determined the value of E_a from the equation

$$\ln m - 2 \ln T_{max} = C - E_a/RT \quad \text{for} \quad \alpha \leqslant 0.4 \div 0.6$$

where: $\alpha = m/\mu$ is the degree of dehydration;
m = the weight loss (from the TG curve) at temperature T;
μ = total weight loss;
T_{max} = the maximal temperature of the endoeffect in the dehydration process;
C = constant coefficient.

The activation energy is determined by a graphical method; $\lg m - 2 \lg T_{max}$ is plotted against $1/T$. The plot is a straight line with a slope of $E_a/R \cdot 2.303$ (Fig. 3 as an example). The values of the energy of the dehydration reaction (the first stage of decomposition) are

Ln	Gd	Tb	Dy	Ho	Er	Yb	Lu
E_a [kcal/mol]	19.2	19.2	24.0	24.7	22.8	21.9	21.0

Fig. 4 shows the values of energy of activation for the dehydration of the compounds $Ln(4\text{-}dipy)_2(NCS)_3 \cdot 5\,H_2O$ as a function of the atomic number.

Conclusions

Complexes of the general formula $Ln(4\text{-}dipy)_2(NCS)_3 \cdot 5\,H_2O$ (*Ln* = La, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Yb, Lu and Y) have been isolated as crystalline compounds.

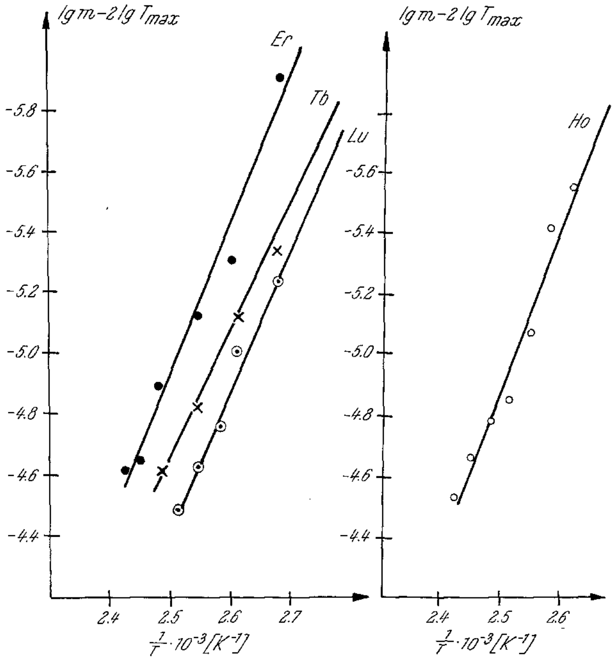

Fig. 3. Typical $\lg m - 2\lg T_{max}$ v.s. $1/T$ plots for $Ln(4\text{-}dipy)_2(NCS)_3 \cdot 5\,H_2O$

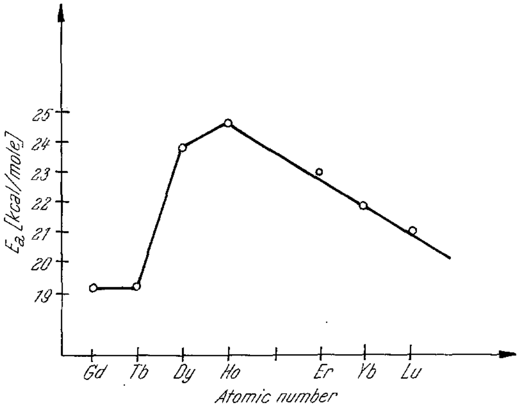

Fig. 4. The values of energy of activation (E_a) for the dehydration of compounds $Ln(4\text{-}dipy)_2(NCS)_3 \cdot 5\,H_2O$ as a function of the atomic number

The IR spectra of these compounds suggest that 4,4′-dipyridyl is coordinated to a metal ion. The IR spectra of the compounds of Y, La, Nd, Gd, Dy, Ho, Er, Yb and Lu suggest that the thiocyanate groups in these compounds are N-coordinated. N-bonding thiocyanate groups are also indicated in the compounds $(Et_4N)_3Ln(NCS)_6$ (Ln = La, Ce, Nd) and $(Bu_4N)_3[Ln(NCS)_6]$ (Ln = Gd, Eu, Ho, Dy)[21]. The ionic and nitrogen bonded thiocyanate groups exist probably in the complexes of Pr, Sm, Eu and Tb. Similar *Hart* and *Laming*[22] interpreted the IR spectra of the compound $[Yb(NCS)_2(C_{12}H_8N_2)_2]NCS$. The nature of the bonding of the SCN groups is not full clear in many complexes of lanthanides and other metals[14, 21—29]. For an explaination concerning these compounds further studies of the crystal and molecular structure are necessary.

The thermolysis of complexes in the series Gd ÷ Er has similar patterns. During the thermal decomposition of Yb and Lu complexes partial deamination takes place. Similar observations have been made in the case of $Ln(4\text{-}dipy)_2X_3 \cdot n\mathrm{H_2O}$ ($X = \mathrm{Cl^-}, \mathrm{Br^-}, \mathrm{NO_3{}^-}$)[1—3] and in the case of 2,2′-dipyridyl complexes[30, 31]. The intermediate compounds $Ln(4\text{-}dipy)_2(NCS)_3$ and $Ln(4\text{-}dipy)_{1.25}(NCS)_3$ decompose to Ln_2S_3. The thermal decomposition of thiocyanate complexes to metal sulphides as intermediate products is noted in the literature[16]. The final products of the compounds investigated are the oxides.

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