

THERMAL DECOMPOSITION OF 2,2'-DIPYRIDYL AND 4,4'-DIPYRIDYL COMPLEXES WITH RARE-EARTH ELEMENTS IN AIR ATMOSPHERE

D. Czakis-Sulikowska and J. Radwańska-Doczekalska

Institute of General and Ecological Chemistry, Polytechnical University, 90-924 Łódź, Poland

Abstract

The present work provides data concerning thermal decomposition of 2,2'-dipyridyl(2-dipy) and 4,4'-dipyridyl(4-dipy) with rare-earth elements (*Ln*) based on literature and our own sustained studies which comprised about 100 complexes.

Keywords: complexes, 2,2'-dipyridyl, 4,4'-dipyridyl, rare-earth elements, thermal decomposition

Thermal decomposition of 2,2'-dipyridyl complexes with rare-earth elements

The first data concerning thermal stability of 2,2'-dipyridyl complexes with *Ln* come from 1965. Hart and Laming [1] determined the temperature of decomposition of several 2-dipy complexes with LnX_3 salts ($X=Cl^-$, NCS^- , CH_3COO^-). The thermal stability of hydrated complexes is considerably lower than that of anhydrous complexes. For instance the temperature of decomposition of $CeCl_3(2-dipy)_2 \cdot H_2O$ 115–120°C, whereas for $YbCl_3(2-dipy)$ it is 220–230°C. A few years later Golub *et al.* [2] published data concerning $Ln(SeCN)_3(2-dipy)_2 \cdot EtOH$ (*EtOH* = ethanol, *Ln* = La, Ce, Pr, Nd). According to these authors, the relatively high decomposition temperatures of these compounds (about 125–155°C) indicate that EtOH is a component of the inner coordination sphere of the complex. Gradual deamination of 2-dipy complexes with *Ln* was first reported in 1966 [6]. The authors studied thermal decomposition of $Ln(NO_3)_3(2-dipy)_2$ complexes (*Ln* = Pr, Nd, Tm) and found out that endothermic changes related to elimination of 1 mole of 2-dipy occur the range 200–375°C. At temperatures exceeding 375°C, an endothermic process begins, in which the second 2-dipy mole is released. Over the range 400–900°C nitrates are decomposed to form rare-earth oxides. Gradual deamination processes were also observed in the course of thermal decomposition of $Ln(CH_2BrCOO)_3(2-$

dipy) ($Ln = Nd, Er$) [4]. Spacu and Antonescu [5] described thermal decomposition of $LnX_3(2\text{-dipy})\cdot H_2O$ ($Ln = La \rightarrow Eu, Dy, Er$; $X = CCl_3COO^-, CHCl_2COO^-, CH_2ClCOO^-$). At temperatures over $80^\circ C$ water is released. Anhydrous compounds liberate 2-dipy at about $150^\circ C$. At $210\text{--}240^\circ C$ the formation of rare-earth oxychlorides begins. In 1976, Eremin and Bondarenko [6] investigated thermal analysis of $[Ln(NCS)_4(2\text{-dipy})_2]\cdot 2\text{-dipy}\cdot H$ complexes ($Ln = Y, La, Sm, Eu$). They found out that at $148\text{--}265^\circ C$ 2 moles of 2-dipy and 1 mole of HSCN are released and the remaining 2-dipy and 3 moles of HSCN are eliminated as the temperature increases to about $480\text{--}515^\circ C$. Recent publications concern thermal properties of the free 2-dipy and 2-dipy-HCl [7]. The temperature of the endothermic effects connected with the release of 2-dipy and dissociation and release of 2-dipy-HCl is $201^\circ C$ and $208^\circ C$, respectively. Our study concerned the processes of thermal decomposition in air of 2-dipy complexes with LnX_3 salts and $Tm(NO_3)_3$, (where $X = ClO_4^-, Br^-, NCS^-$; $Ln = La \rightarrow Lu$, except Pm [8–10]). On heating, the complexes of 2-dipy with $Ln(ClO_4)_3$ decomposed with an explosion [8, 10]. Thermal stability of $LnBr_3(2\text{-dipy})_2\cdot 6H_2O$ and $LnBr_2OH\cdot(2\text{-dipy})\cdot 4H_2O$ is similar [9]. A number of endothermic effects accompany the processes of dehydration and deamination. Dehydration begins below $100^\circ C$ and is a single-stage process in the case of $LnBr_2OH(2\text{-dipy})_2\cdot 4H_2O$, and two-stage process in the case of $LnBr_3(2\text{-dipy})_2\cdot 6H_2O$ (only the Yb complex takes 3 stages to dehydrate, while the Lu complex loses all water and 0.25 mole of 2-dipy simultaneously). Anhydrous compounds undergo deamination in different ways, with the formation of $LnOBr$, which then transforms into rare-earth oxides. Thermal decomposition of $Ln(NCS)_3(2\text{-dipy})_2\cdot 5H_2O$ compounds is complex and difficult to interpret [10]. Dehydration begins at about $60\text{--}70^\circ C$ and proceeds gradually [10]. Gradual deamination of all anhydrous $Ln(NCS)_3(2\text{-dipy})_2$ complexes (and partly also of dehydrated Yb and Lu complexes) is their common property. In the case of Gd, Tb, Dy, Yb and Lu complexes $Ln(NCS)_3$ are the final products of deamination. In the case of the remaining complexes, the final stage of deamination overlaps the process of full or partial decomposition of thiocyanates. These processes are accompanied by high and rapid loss in mass and strong exothermic effects. The products of this stage of decomposition are difficult to identify. They probably include oxysulfides and lanthanide thiocyanatosulfates (the presence of S^{2-} , SCN^- , SO_4^{2-} ions was observed in the sinters). As the temperature increases, these decomposition products change into oxosulfates, which yield corresponding oxides, via $Ln_2O_{3-x}(SO_4)_x$. Pyrolysis of $Ln(NCS)_3(2\text{-dipy})_3$ ($Ln = Ce, Pr, Nd$) and $Ln(NCS)_3(2\text{-dipy})_3\cdot H_2O$ complexes proceeds in a similar way. The decomposition of Ce complex begins at $210^\circ C$ and is in accordance with literature [1].

Thermal decomposition of 4,4'-dipyridyl complexes with rare-earth elements

Our studies concerning synthesis and thermal properties of 4-dipy complexes with LnX_3 salts, where $\text{Ln} = \text{Y, La} \rightarrow \text{Lu}$ (except Pm), $\text{X} = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-, \text{NCS}^-$ and ClO_4^- began in 1975 [8, 10–15]. Thermal decomposition of 4-dipy complexes is similar to that of 2-dipy compounds. $\text{Ln}(\text{ClO}_4)_3(4\text{-dipy})_8 \cdot \text{HClO}_4 \cdot 4\text{H}_2\text{O}$ complexes and $\text{Ce}(\text{ClO}_4)_3(4\text{-dipy})_7 \cdot 6\text{H}_2\text{O}$ [8, 10] decompose with an explosion. Thermal decomposition of other complexes begins with dehydration which proceeds in one or more stages and with clear endothermic effects. Deamination is usually gradual, intermediate compounds of low stability (e. g. $\text{YCl}_3(4\text{-dipy})_{1.5}$ [12]) being formed. The final stage of deamination results in the formation of LnX_3 or LnOX complexes ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-$). Like in the case of 2-dipy complexes with $\text{Ln}(\text{NCS})_3$ the final stage of deamination of $\text{Ln}(\text{NCS})_3 \cdot (4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$ overlaps thermal decomposition of thiocyanates and results in the formation of stable $\text{Ln}_2\text{O}_2\text{SO}_4$ complexes. A very strong exothermic peak is visible in the DTA curves. The final products of decomposition of the complexes under discussion are lanthanide oxides. Figures 1 and 2 present the thermoanalytical curves of $\text{Ce}(\text{NCS})_3(4\text{-dipy})_3$ and $\text{TmCl}_3(2\text{-dipy})_2 \cdot \text{H}_2\text{O}$ in air atmosphere. Activation energy E_a of the dehydration reaction (first stage of dehydration) was determined for $\text{Ln}(\text{NCS})_3 \cdot (4\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$ complexes [16, 17]. It occurred that there is no regular relationship between E_a and the atomic number Z of the lanthanides (Fig. 3). The Pr complex exhibits the lowest E_a value in the process involving the loss of 5 water molecules, whereas the highest E_a value is observed in the case of Eu complex (elimination of 4 water molecules). The relatively low E_a values indicate that the water eliminated in the first stage of dehydration is bonded in the outer sphere.

Discussion and conclusions

The analysis of literature data and results of our study leads to a number of general conclusions about thermal decomposition of 2-dipy and 4-dipy complexes with rare-earth elements.

In spite of their different structures, thermal decomposition of 2-dipy and 4-dipy complexes proceeds in similar way. 2,2'-Dipyridyl in these compounds is a didentate ligand with a cis-conformation and forms chelate complexes, whereas bridging molecules are more typical for 4,4'-dipyridyl.

Thermal stability of different types of hydrated complexes is similar. The process of their dehydration usually begins below 100°C and proceeds in one or more stages. The final stage of dehydration is sometimes connected with the onset of deamination. Several stages of dehydration indicate different modes of

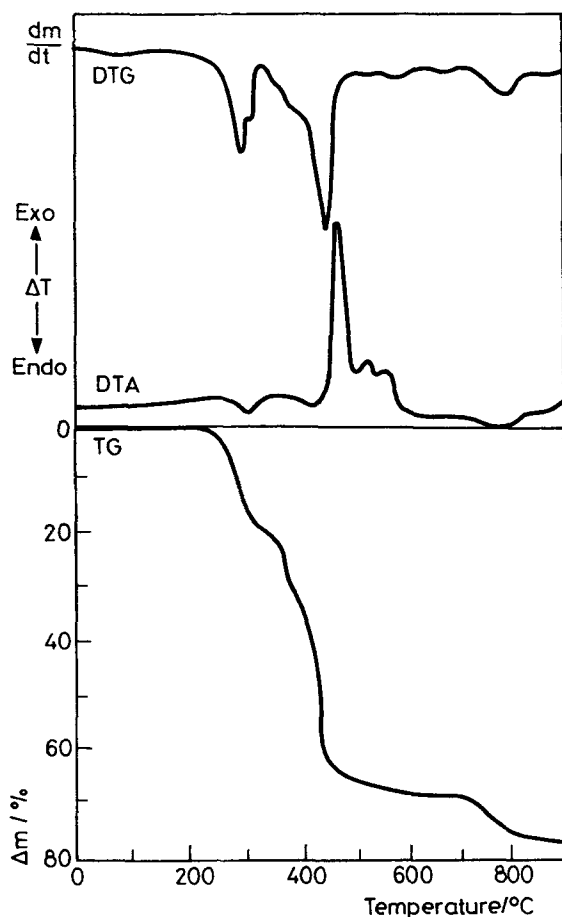


Fig. 1 Thermoanalytical curves of $\text{Ce}(\text{NCS})_3(2\text{-dipy})_3$ in air

water bonding in given compound (outer and inner sphere water). If the dehydration is a one-stage process at low temperature ranges, the conclusion may be that the water is bonded only in the outer sphere. A several-stage dehydration at both low and high temperature ranges (e. g. $\text{Y}(\text{NCS})_3(2\text{-dipy})_2 \cdot 5\text{H}_2\text{O}$ loses 1 mole of water at $60\text{--}80^\circ\text{C}$, and another at $102\text{--}130^\circ\text{C}$; and at $130\text{--}168^\circ\text{C}$ and $178\text{--}200^\circ\text{C}$ one and two moles H_2O , respectively) may indicate different location of water molecules within the same coordination sphere (inner and outer). Similar conclusions about the mode of water bonding have been made for many other lanthanide complexes [18, 19].

The process of deamination is usually gradual, transient complexes of $\text{LnX}_3(\text{dipy})_n$ being formed. Only several complexes undergo one-stage deamination. Final products of deamination are complexes of LnX_3 or $\text{LnOX}(\text{Ln}_2\text{OSO}_4)$

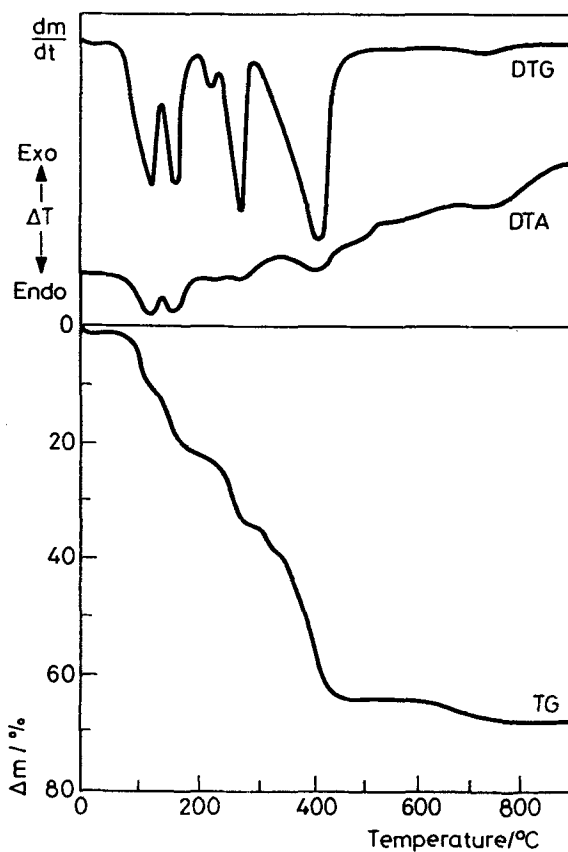


Fig. 2 Thermoanalytical curves of $TmCl_3(2-dipy)_2 \cdot H_2O$ in air

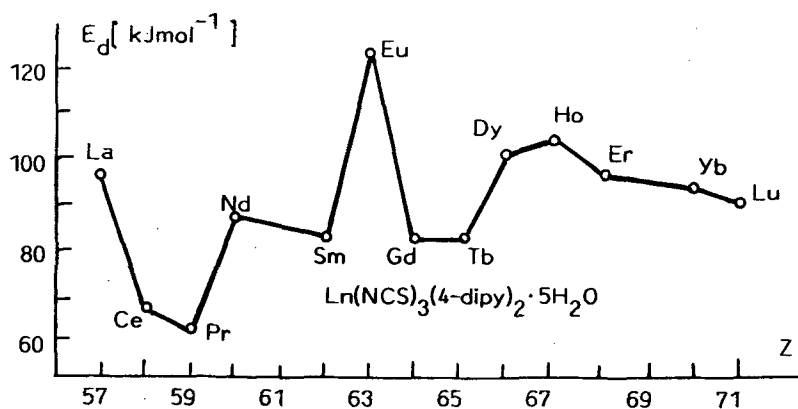


Fig. 3 Relationship between E_d and Z

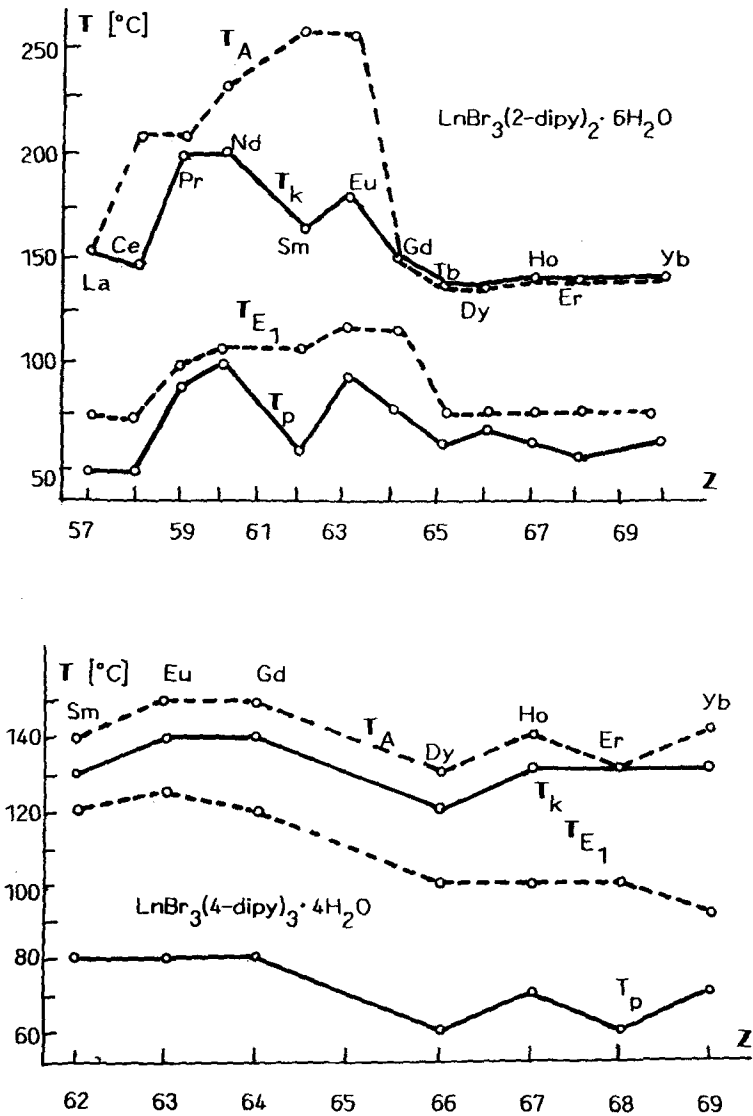


Fig. 4 Relationship between temperature and Z

type, or other intermediate complexes, e. g. $\text{CeOBr} \cdot \text{CeO}_2$, $\text{EuOCl} \cdot 2\text{EuCl}_3$, $\text{TbOCl} \cdot 2\text{TbCl}_3$ [12] (identified also by Wendlandt [20] in pyrolysis of simple lanthanide salts). Further increase of temperature causes transformation of these complexes into corresponding lanthanide oxides.

Table 1 Thermal decomposition of 2,2'-dipyridyl (L) complexes with thulium salts in air

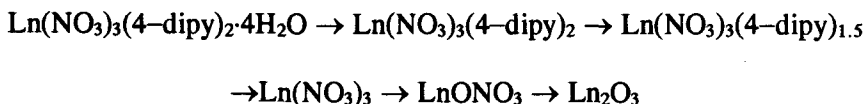
Compound	Step of decomposition	Mass loss/ %		Temp. range/ °C	Peak temp. in DTA/ °C
		Calculated	Determined from TG		
1	2	3	4	5	6
TmCl ₃ L ₂ ·H ₂ O					
↓	I	9.42	10.0	80–120	116 endo
TmCl ₃ L _{1.75}					
↓	II	12.89	11.9	120–180	135 endo
TmCl ₃ L _{1.25}					220 endo
↓	III	12.89	13.0	200–275	270 endo
TmCl ₃ L _{0.75}					
↓	IV	28.41	29.0	288–405	405 endo
TmOCl					500 endo
↓	V	4.54	4.2	540–742	560 endo
Tm ₂ O ₃					
TmBr ₃ L ₂ ·6H ₂ O					
↓	I	2.17	2.5	70–100	75 endo
TmBr ₃ L ₂ ·5H ₂ O					120 endo
↓	II	15.58	15.5	110–155	145 endo
TmBr ₃ L _{1.75}					240 endo
	III	50.32	50.5	155–605	270 endo
↓ */					310 endo
TmOBr					460 endo
↓	IV	8.67	9.2	605–750	682 endo
Tm ₂ O ₃					
Tm(NO ₃) ₃ L ₂					220 endo
	I	63.00	63.5	200–420	310 endo
↓					340 exo
					380 endo
TmONO ₃					440 endo
↓	II	8.09	8.8	440–640	500 endo
					565 exo
Tm ₂ O ₃					620 exo

Table 1 Continued

Compound	Step of decomposition	Mass loss/ %		Temp. range/ °C	Peak temp. in DTA/ °C
		Calculated	Determined from TG		
1	2	3	4	5	6
Tm(NCS) ₃ L ₂ ·5H ₂ O					
↓	I	2.42	2.2	40–65	50 endo
Tm(NCS) ₃ L ₂ ·4H ₂ O					
↓	II	9.66	10.0	108–175	130 endo
Tm(NCS) ₃ L ₂					300 endo
↓	III	56.68	56.0	218–405	340 exo
					375 exo
					405 endo
Tm ₂ O ₂ SO ₄					430 endo
↓	IV	5.36	5.5	400–700	480 endo
Tm ₂ O ₃					

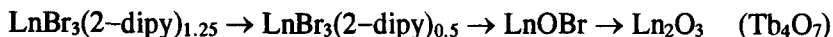
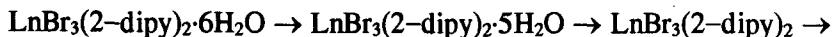
*/ probably via TmOBr·TmBr₃

It was observed that a given of complexes thermal decomposition often proceeds in different ways. A common mechanism of pyrolysis was found for only very few groups of complexes, e. g.:



where $Ln = Y, Nd, Eu, Gd, Tb, Dy, Ho, Er$ [12]

or



where $Ln = Tb, Dy, Ho$, [9].

Detailed thermal decomposition data obtained for the complexes TmCl₃(2-dipy)₂·H₂O, TmBr₃(2-dipy)₂·6H₂O, Tm(NO₃)₃(2-dipy)₂, and Tm(NCS)₃(2-dipy)₂·5H₂O are summarized, as example, in Table 1 [10].

The initial (T_p) and final (T_k) temperature of dehydration, initial temperature of deamination (T_A) and temperatures of endothermic dehydration effects (T_E) do not exhibit a regular dependence on the atomic number of the lanthanide in

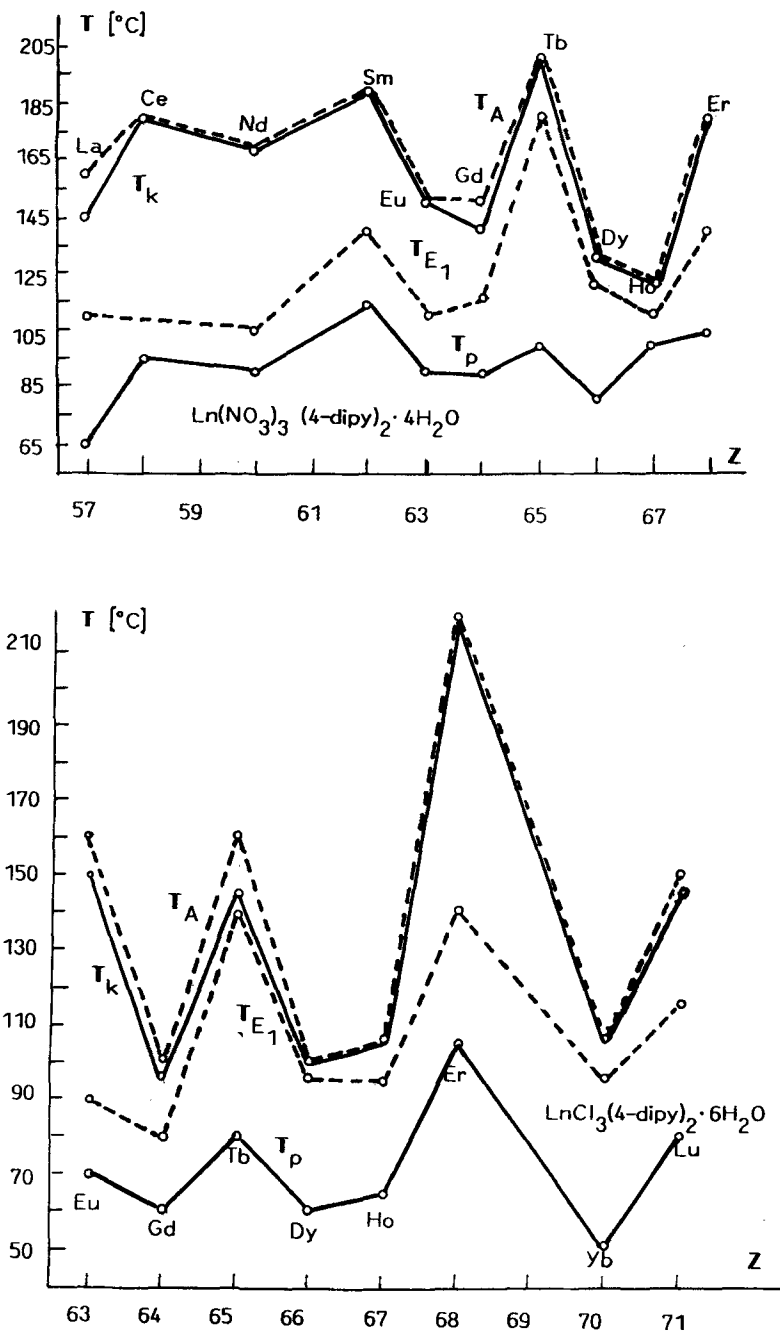


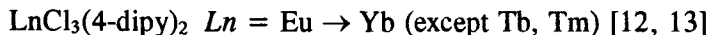
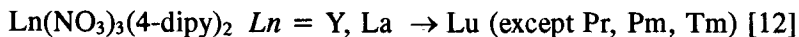
Fig. 5 Relationship between temperature and Z

the same type of complexes. Figures 4 and 5 illustrate the above mentioned relationship.

Thermal stability of 2-dipy and 4-dipy complexes with yttrium salts is most similar to that of corresponding Eu, Gd or Tb complexes. Thus thermal properties of yttrium complexes are similar to those of rare-earth elements of the middle part of the series.

Our studies on 2-dipy and 4-dipy complexes with $\text{Ln}(\text{NCS})_3$, as well as other data [21, 22] show that the main intermediate products of pyrolysis of thiocyanate metal complexes are sulfides and sulfates. Hence the interpretation of thermal decomposition of $[\text{Ln}(\text{NCS})_4(2\text{-dipy})_2] \cdot 2\text{-dipyH}$ presented in [6] does not seem very probable.

Thermal examination of 2-dipy and 4-dipy complexes with lanthanides resulted in identification of many intermediate compounds which are new examples or complexes with ligand isomerism. Some of them are listed below:



Analogous 2-dipy complexes were obtained by direct synthesis from solutions [1, 23]. Formation of other intermediate compounds, which are new examples of complexes with ligand isomerism e. g.: $\text{Yb}(\text{NCS})_3\text{L}_2 \cdot 4\text{H}_2\text{O}$, $\text{Gd}(\text{NCS})_3\text{L}_2$, $\text{Dy}(\text{NCS})_3\text{L}_2$, $\text{Y}(\text{NCS})_3\text{L}_2$, $\text{TmBr}_3\text{L}_{1.75}$, $\text{TmCl}_3\text{L}_{0.75}$ (where $L = 2\text{-dipy}$ or 4-dipy , respectively) [10, 14, 15] was also identified by thermal analysis. Thus there are possibilities of obtaining many new lanthanide complexes which cannot be synthesized from solutions by thermochemical methods. There is a significant way to obtain new materials with specific properties.

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References

- 1 F. A. Hart and F. P. Laming, *J. Inorg. Nucl. Chem.*, 27 (1965) 1825.
- 2 A. M. Golub, M. V. Kopa and O. E. Andriejcienko, *Zh. Obshch. Khim.*, 39 (1969) 1382.
- 3 V. A. Smirnova, N. I. Lobanov and A. I. Vlasov, *ibid.*, 12 (1966) 2419.
- 4 I. V. Kokunov and E. J. Segal, *Rev. Roumoine Chim.*, 16 (1971) 1.
- 5 P. Spacu and E. Antonescu, *ibid.*, 14 (1969) 201.
- 6 G. Eremin and G. I. Bondarenko, *Zh. Neorg. Khim.*, 21 (1976) 376.
- 7 J. Lubkowski, A. Bujewski, J. Szychliński, M. Walewski and J. Blazejowski, *J. Thermal Anal.*, 38 (1992) 2221.

- 8 D. Czakis-Sulikowska, J. Radwańska-Doczekalska and T. Miazek, *Monatsh. Chem.*, 113 (1982) 827.
- 9 D. Czakis-Sulikowska, J. Radwańska-Doczekalska, *ibid.*, 117 (1986) 783; *ibid.*, 118 (1987) 1243.
- 10 D. Czakis-Sulikowska, J. Radwańska-Doczekalska and M. Markiewicz, *Polish J. Chem.*, 63 (1989) 417; *ibid.*, 66 (1992) 751; *ibid.*, 67 (1993) 1; *Monatsh. Chem.*, in press.
- 11 D. Czakis-Sulikowska and J. Radwańska-Doczekalska, *J. Inorg. Nucl. Chem.*, 41 (1979) 1299.
- 12 D. Czakis-Sulikowska and J. Radwańska-Doczekalska, *Roczniki Chem. (Ann. Soc. Chim. Polonorum)* 50 (1976) 218; *ibid.*, 49 (1975) 197; *Polish J. Chem.*, 53 (1979) 2439.
- 13 D. Czakis-Sulikowska and J. Radwańska-Doczekalska, *Theory-Structure Properties of Complexes Compounds*, 2nd Summer School on Coordination Chemistry, Karpacz-Bierutowice 1979, p. 39.
- 14 D. Czakis-Sulikowska, J. Radwańska-Doczekalska and M. Markiewicz, *J. Thermal Anal.*, 41 (1994) 81.
- 15 D. Czakis-Sulikowska, J. Radwańska-Doczekalska and G. Sójka, *Monatsh. Chem.*, 115 (1984) 961.
- 16 G. O. Pilojan and O. S. Novikova, *Zh. Neorg. Khim.*, 12 (1967) 602.
- 17 Ch. A. Cherchas and T. P. Jezierskaya, *Izv. Acad. Nauk SSSR*, 1 (1977) 45.
- 18 W. Ferenc, *Monatsh. Chem.*, 120 (1989) 1075; *ibid.*, 119 (1988) 1345.
- 19 W. Ferenc and W. Brzyska, *ibid.*, 118 (1987) 1087; *ibid.*, 119 (1988) 407.
- 20 W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 9 (1959) 136.
- 21 A. Cygański and T. Majewski, *Analyst.*, 104 (1979) 167.
- 22 H. Ladzińska-Kulińska, *Thermochim. Acta*, 33 (1979) 293.
- 23 N. I. Labanov and V. A. Smirnova, *Zh. Neorg. Khim.*, 8 (1963) 2208.

Zusammenfassung — Ausgehend von Literaturangaben und unseren eigenen Untersuchungen von mehr als 100 Komplexen liefert vorliegende Arbeit Angaben zur thermischen Zersetzung von 2,2'-Dipyridyl(2-dipy) und 4,4'-Dipyridyl(4-dipy) mit Seltenerdenelementen (*L_n*).