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Synthesis and Properties of 2,2′-Dipyridyl and 4,4′-Dipyridyl Complexes with Thulium Salts

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Summary. New complexes of 2,2′-dipyridyl and 4,4′-dipyridyl with thulium salts TmX_3 (where $X = Cl^-$, Br^-, NO_3^-, NCS^-, and ClO_4^-) have been prepared and their solubilities in water at 21 °C were determined. The IR spectra of these compounds are discussed. The conditions of thermal decomposition of the complexes were also studied.

Keywords. 2,2′-Dipyridyl complexes; 4,4′-Dipyridyl complexes; Thulium complexes; Infrared spectra; Thermal decomposition.

Synthese und Eigenschaften von 2,2′-Dipyridyl- und 4,4′-Dipyridylkomplexen mit Thuliumsalzen

Zusammenfassung. Es wurden neue 2,2′-Dipyridyl- und 4,4′-Dipyridyl-Komplexe mit Thuliumsalzen TmX_3 ($X = Cl^-$, Br^-, NO_3^-, NCS^-, ClO_4^-) dargestellt und ihre Wasserlöslichkeit bei 21 °C bestimmt. Die IR-Spektren werden diskutiert. Das thermische Verhalten der erhaltenen Komplexe wurde untersucht.

Introduction

The compounds of 2,2′-dipyridyl (2-*dipy* or *L*) and 4,4′-dipyridyl (4-*dipy* or *Y*) with thulium are comparatively little known. *Hart* and *Laming* [1] obtained the complex $TmCl_3(2\text{-}dipy)_2$. The thermal decomposition point for this complex is 230–240 °C. *Labanov* and *Smirnova* [2] have prepared the compound $Tm(NO_3)_3(2\text{-}dipy)_2$ from 95% ethanol solution. Its physico-chemical properties were not investigated.

The present paper shows the results of the synthesis of complexes of 2-*dipy* and 4-*dipy* with TmX_3, where $X = Cl^-$, Br^-, NO_3^-, NCS^-, and ClO_4^-. The thermal decomposition, IR spectra and other properties of these compounds have been investigated.

Results and Discussion

The compounds prepared for this study are listed in Table 1. The isolated 2-*dipy* complexes with $Tm(NCS)_3$ and $TmBr_3$ have analogous composition as the complexes with thiocyanate salts in the series Sm–Lu [14] and bromide salts in the series La–Lu (except Ce and Pm) [13]. The compound $Tm(NO_3)_3(2\text{-}dipy)_2$ has a similar composition as that obtained by *Labanov* and *Smirnova* [2]. The 2-*dipy*

Table 1. Analytical data of 2,2′-dipyridyl (*L*) and 4,4′-dipyridyl (*Y*) complexes with thulium and their solubility (*S*) in water at 21 °C

Compound	% Tm calcd. found	% N calcd. found	% C calcd. found	% H calcd. found	% *X* calcd. found	$S\cdot 10^2$ ($mol\cdot l^{-1}$)
$TmCl_3L_2\cdot H_2O$	27.89	9.25	39.66	3.00	17.56	
	27.4	9.1	34.0	3.0	17.4	2.93
$TmBr_3L_2\cdot 6H_2O$	20.38	6.76	28.97	3.40	28.91	
	21.0	6.7	29.0	3.2	28.9	4.75
$Tm(NO_3)_3L_2$	25.32	14.69	36.00	3.32		
	26.0	14.2	36.1	3.2		3.38
$Tm(NCS)_3L_2\cdot 5H_2O$	22.66	13.15	37.05	3.51	23.37	
	22.7	13.2	37.2	3.5	23.0	1.50
$Tm(ClO_4)_3L_2\cdot 6H_2O$	19.03	6.31	27.06	3.18	33.61	
	18.5	6.4	27.4	3.2	34.0	1.70
$TmCl_3Y_3\cdot 6H_2O$	19.83	9.86	42.30	4.26	12.48	
	20.0	9.9	42.7	4.0	12.8	0.53
$TmBr_3Y_2\cdot 6H_2O$	20.38	6.76	28.97	3.40	28.91	
	21.0	6.5	29.1	3.3	28.9	1.70
$Tm(NO_3)_3Y_2\cdot 3H_2O$	23.42	13.59	33.30	3.07		
	23.2	14.0	33.5	3.1		2.40
$Tm(NCS)_3Y_4\cdot 8H_2O$	15.19	13.86	46.44	4.35	15.67	
	15.5	13.5	46.0	4.3	15.0	0.90
$Tm(ClO_4)_3Y_8\cdot HClO_4\cdot 4H_2O$	8.94	11.86	50.86	3.89	21.06	
	9.0	11.6	50.9	3.9	21.7	0.38

$X = Cl^-$, Br^-, NCS^-, or ClO_4^-

complex with $TmCl_3$ obtained in the present work is hydrated, in comparison with the compound described by *Hart* and *Laming* [1]. The composition of the 2-*dipy* compound with $Tm(ClO_4)_3$ is different from other complexes of rare earths [4].

The reaction between 4-*dipy* and thulium perchlorate affords a complex of analog chemical composition as all rare earth ions (except Pm and Ce) with the general formula $Ln(ClO_4)_3$(4-*dipy*)$_8\cdot HClO_4\cdot 4H_2O$ [4]. Thulium chloride and nitrate also give compounds with 4-*dipy*: $TmCl_3$(4-*dipy*)$_3\cdot 6H_2O$ and $Tm(NO_3)_3$(4-*dipy*)$_2\cdot 3H_2O$, similar as Pr and Yb, respectively [13]. The complex of 4-*dipy* with $Tm(NCS)_3$ was obtained with a metal to 4-*dipy* ratio of 1:4 (formula: $Tm(NCS)_3$(4-*dipy*)$_4\cdot 8H_2O$). It has a composition different from other compounds of 4-*dipy* with $Ln(NCS)_3$ [14] and crystallizes very slow. The isolated compound $TmBr_3$(2-*dipy*)$_2\cdot 6H_2O$ has a similar composition as the complexes of Y, La, Pr, Nd, and Tb [13, 15, 16].

All isolated compounds are air stable at room temperature. They are practically insoluble in benzene, $CHCl_3$, and CCl_4. The solubility of the complexes in water is in the range of 10^{-2}–10^{-3} $mol\cdot l^{-1}$ (Table 1).

From diffractogram analysis it appears that the obtained complexes are crystalline compounds. The $Tm(NCS)_3$(2-*dipy*)$_2\cdot 5H_2O$ complex (Fig. 1a) has the

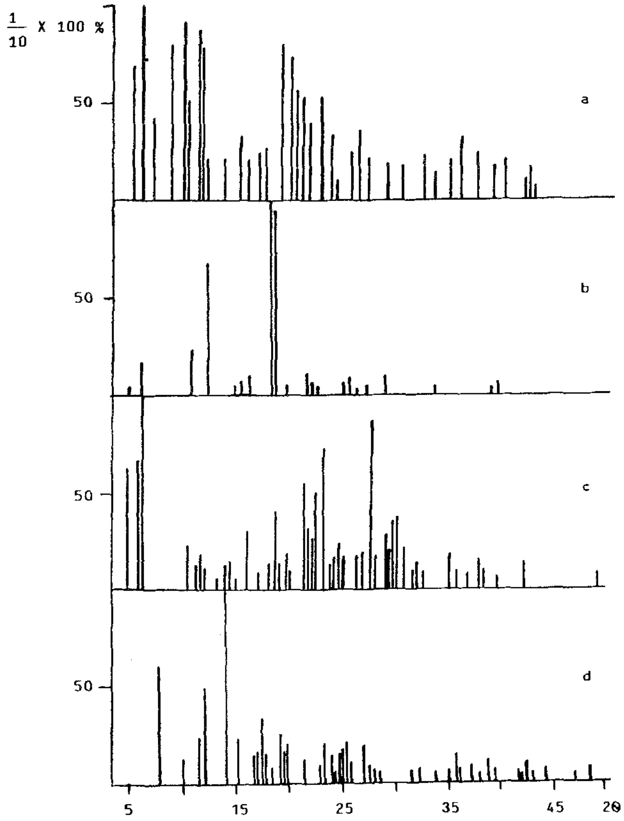

Fig. 1. X-ray diffraction patterns of complexes $Tm(NCS)_3(2\text{-}dipy)_2 \cdot 5H_2O$ (a), $Tm(ClO_4)_3(4\text{-}dipy)_8 \cdot HClO_4 \cdot 4H_2O$ (b), $TmBr_3(4\text{-}dipy)_2 \cdot 6H_2O$ (c), and $Tm(NO_3)_3(4\text{-}dipy)_2 \cdot 3H_2O$ (d)

same structure as other lanthanide (Y, Sm–Yb) complexes of this type [14]. The $Tm(ClO_4)_3(4\text{-}dipy)_8 \cdot HClO_4 \cdot 4H_2O$ compound is characterized by high symmetry (Fig. 1b) and is isostructural with other 4-*dipy* complexes with $Ln(ClO_4)_3$ [4]. The remaining compounds are characterized by low symmetry (as an example, see Figs. 1c and 1d).

Infrared Spectra

Water Vibrations. In the O–H stretching region a very broad-absorption for hydrates, extending from about 3750 to 3080 cm^{-1}, occured. In the O–H bending region, a weak band was observed at about 1640 cm^{-1}.

Perchlorate Vibrations. The presence of a very strong band at 1110–1100 cm^{-1} (asymmetric stretch ν_3) and a medium band (asymmetric band ν_4) at 656 cm^{-1} for the 2-*dipy* complex is observed. The spectra of the 4-*dipy* complex show the ν_3 band at 1090 cm^{-1} and the ν_4 band at 650 cm^{-1}. A weak band (ν_1) is observed at 928 and 935 cm^{-1} for 2-*dipy* and 4-*dipy* complexes, respectively. This indicates that in the investigated compounds the perchlorate ion (T_d) remains uncoordinated [17, 18]. If the perchlorate group would be coordinated and the symmetry lowered from T_d to C_{3v}, the broad ν_3 band should be split into two strong peaks at approximately 1030 and 1140 cm^{-1}, and the ν_1 mode should exhibit a much stronger intensity and be shifted to a slightly lower frequency [19]. Although the ν_1 mode for ionic perchlorates is theoretically forbidden in the IR, it is invariable present in solid spectra due to the activation by site symmetry [17]. This weak band has been observed in IR spectra of several other lanthanide complexes containing tetrahedral perchlorate [4, 20].

Thiocyanate Vibrations. ν_{CN} of the NCS^- group appears as a strong doublet at about 2110–2070 cm^{-1} in the case of the 2-*dipy* complex. The position of ν_{CS} is observed as a weak band at 814 cm^{-1}. The δ_{NCS} band can be identified at 480 cm^{-1}.

The ν_{CN} mode of the IR spectra of 4-*dipy* complex is observed at 2098–2084 cm^{-1} as a very strong doublet. The ν_{CS} frequencies could not be identified in the spectra of $Tm(NCS)_3$(4-*dipy*)$_5 \cdot H_2O$ due to the proximity of the 4-*dipy* band. The δ_{NCS} band is identified at 470 cm^{-1}. Analysis of the region characteristic for thiocyanate absorption for 2-*dipy* and 4-*dipy* complexes suggests that the thiocyanate groups in these compounds are N-coordinated [1, 21, 22]. The coordinated isothiocyanate groups exist also in other 2-*dipy* complexes with rare earth thiocyanates (except $Dy(NCS)_3$ (2-*dipy*)$_2 \cdot 5H_2O$ and *Ln*$(NCS)_3$(4-*dipy*)$_2 \cdot 5H_2O$, where Ln = Pr, Sm, Eu, and Tb [3]; in these compounds both the ionic and N-bonded thiocyanate groups exist [14]).

Nitrate Vibrations. The vibration modes of the nitrate group for the complexes studied are assigned for unidentate nitrate group with c_{2v} symmetry and for nitrate ions of D_{3h} symmetry [23, 24]. The observed bands [cm^{-1}] for the nitrate group are as follows: 1518 (ν_4), 1258 (ν_1), 1025 (ν_2), and 807–802 (ν_6) for the 2-*dipy* complex and 1547 (ν_4), 1300 (ν_1), 1018 (ν_1), and 810 (ν_6) for the 4-*dipy* complex). The asymmetrical stretching frequency for the nitrate ion, ν_3, occurs as a strong absorption in the region of 1385–1380 cm^{-1}. The weak band at 830 cm^{-1} (2-*dipy* complex) and at 835 cm^{-1} (4-*dipy* complex) may be assigned to ν_2 of the nitrate ion. This suggests that these complexes contain both coordinated unidentate nitrate groups and nitrate ions. *We* [13] and *Sinha* [25] also observed frequencies due to both ionic and coordinated groups in other 2-*dipy* and 4-*dipy* complexes with some rare earth nitrates.

2,2′-Dipyridyl and 4,4′-Dipyridyl Vibrations in the region 1600–400 cm^{-1}. The IR spectrum of free 2-*dipy* [25, 26] and 4-*dipy* [27] undergoes a change when coordinated with thulium. For consistency, only the fundamental vibration modes of 2-*dipy* and 4-*dipy* are reported in Table 2. Such an effect has been observed previously for compounds of 2-*dipy* and 4-*dipy* with other rare earth salts [13–16]. IR spectra of these compounds suggest that 2-*dipy* and 4-*dipy* are coordinated to a thulium ion. In the case of 2-*dipy* compounds, the IR data indicated the presence of *cis*-2,2′-dipyridyl chelates [16].

Thermal Investigations. The 2-*dipy* and 4-*dipy* compounds with thulium perchlorate heated in air atmosphere are explosive.

$TmCl_3$(2-*dipy*)$_2 \cdot H_2O$ loses water and 0.25 mole of 2-*dipy* within the temperature range of 80–120 °C with an endothermic peak at 116 °C. The remaining 2-*dipy* is split off in three stages. In the temperature ranges 120–180 °C and 200–275 °C, intermediate compounds containing 1.25 mole and 0.75 mole of 2-*dipy* were formed, respectively. Above 288 °C, the intermediate compound $TmCl_3$(2-*dipy*)$_{0.75}$ is

Table 2. Basic IR bands of complexed 2-*dipy* and 4-*dipy* ligands (cm^{-1})

Compound	Pyridine frequencies			Pyridine breathing	New bands resulting from complexation
	ν_{CN}	ν_{CC}	γ_{CH}		
1	2	3	4	5	6
2-*dipy* = *L* [26]	1579 vs	1553 s	753 vs	995 m	
			738 m		
$TmCl_3L_2 \cdot H_2O$	1602 s	1580 s	760 s	1015 s	1490 w
	1598 vs	1558 m	750 s		1470 s
			740 s		1462 s
					1172 m
					1115 w
$TmBr_3L_2 \cdot 6H_2O$	1598 vs	1575 m	770 s	1010 vs	1525 w
		1565 m	760 vs		1485 s
			735 s		1470 s
					1175 w
					1115 w
$Tm(NO_3)_3L_2$	1598 vs	1570 m	765 vs	1012 vs	1490 vs
		1560 m	740 s		1470 vs
					1160 s
					1112 w
$Tm(NCS)_3L_2 \cdot 5H_2O$	1598 vs	1575 s	762 vs	1012 vs	1493 m
		1563 s	742 s		1472 m
					1178 m
					1108 w
$Tm(ClO_4)_3L_2 \cdot 6H_2O$	1602 vs	1575 m	770 vs	1017 vs	1496 m
	1587 s	1562 w	740 s		1472 vs
					1160 s
					1114 w
4-*dipy* = *Y* [27]	1590 vs	1530 s	802 vs	982 vs	
			730 s		
$TmCl_3Y_3 \cdot 6H_2O$	1595 vs	1555 w	800 vs	1003 s	1455 w
		1535 m	725 vw		1315 m
					1045 w
$TmBr_3Y_2 \cdot 6H_2O$	1593 vs	1535 w	805 sh	1005 s	1468 w
			790 s		1355 s
			745 vw		1285 m
					1050 m
$Tm(NO_3)_3Y_2 \cdot 3H_2O$	1605 vs		810 vs	1008 s	1460 vs
	1575 s	1536 vw	750 s		1432 m
			725 vw		1042 m
$Tm(NCS)_3Y_4 \cdot 8H_2O$	1595 vs	1534 m	808 vs	998 vs	1486 w
					1320 w
	1570 w		730 m		1038 m
$Tm(ClO_4)_3Y_8 \cdot HClO_4 \cdot 4H_2O$	1600 s	1535 s	805 vs	1000 s	1488 w
	1570 w		730 vw		1322 m

v, s, m, w, sh: very, strong, medium, weak, shoulder decomposed to TmOCl. The decomposition to the oxide, Tm_2O_3, began at 540 °C (the temperature observed by *Wendlandt* was 535 °C [29]).

$TmCl_3$(4-*dipy*)$_3$·$6H_2O$ losses all water between 78 and 118 °C with an endothermic DTA peak at 110 °C. During the thermal decomposition of $TmCl_3$(4-*dipy*)$_3$, a partial deamination takes place. The following intermediate compounds were detected in the thermolysis curves: $TmCl_3$(4-*dipy*)$_{2.75}$ (118–140 °C), $TmCl_3$(4-*dipy*)$_2$ (140–240 °C), $TmCl_3$(4-*dipy*)$_{1.5}$ (240–272 °C), and $TmCl_3$(4-*dipy*)$_{0.75}$ (272–338 °C). At 405 °C a complete loss of 4-*dipy* takes place and TmOCl is formed. On temperature elevation TmOCl decomposes to Tm_2O_3.

$TmBr_3$(2-*dipy*)$_2$·$6H_2O$ loses water above 70 °C, and at 100 °C $TmBr_3$(2-*dipy*)$_2$·$5H_2O$ is formed. On further heating the pentahydrate decomposes and forms $TmBr_3$(2-*dipy*)$_{1.75}$ at 155 °C. From 155–605 °C, TmOBr is formed (probably *via* TmOBr·$TmBr_3$). Formation of Tm_2O_3 begins at 605 °C.

$TmBr_3$(4-*dipy*)$_2$·$6H_2O$ loses all water within the temperature range of 40–180 °C with endothermic peaks at 80, 115, and 140 °C. 4,4′-Dipyridyl is split off in three stages and $TmBr_3$(4-*dipy*)$_{1.75}$ and $TmBr_3$(4-*dipy*)$_{0.5}$ are formed. From 305–400 °C, TmOBr·$TmBr_3$ is formed. Formation of TmOBr begins at about 427 °C. These processes are accompanied by a few endothermic effects and one exothermic effect.

The most thermally stable compound is $Tm(NO_3)_3$(2-*dipy*)$_2$, which starts losing 2-*dipy* at a temperature of 200 °C and is converted to $TmONO_3$. On increasing the temperature, $TmONO_3$ decomposed to the oxide. The DTA curve shows several endo- and exothermic peaks.

$Tm(NO_3)_3$(4-*dipy*)$_2$·$3H_2O$: at first 2 moles of water are eliminated (125–150 °C), while at 170–250 °C it loses all water and 0.5 mole of 4-*dipy*. The decomposition of $Tm(NO_3)_3$(4-*dipy*)$_{1.5}$ begins at above 250 °C to produce $TmONO_3$ (probably *via* $Tm(NO_3)_3$·$2TmONO_3$) and finally to the oxide.

$Tm(NCS)_3$(2-*dipy*)$_2$·$5H_2O$ loses water in two steps in the temperature ranges 40–65 °C and 108–175 °C with two endothermic effects, respectively. At the third stage, the complex loses 2-*dipy* and the main process of thiocyanate decomposition takes place. The intermediate products of the thermal decomposition of $Tm(NCS)_3$ are difficult to identify (the solid products contain sulfide and sulfate ions). We obtained similar results for 2-*dipy* complexes with *Ln*$(NCS)_3$ [14]. During heating in air the intermediate products form $Tm_2O_2SO_4$ at 400 °C. The DTA curve shows several exothermic peaks, the first of which is very strong (340 °C). On temperature elevation, $Tm_2O_2SO_4$ decomposes stepwise to the oxide.

$Tm(NCS)_3$(4-*dipy*)$_4$·$8H_2O$ also loses water in two steps. At the first stage, 1 mole of water is split off (80–138 °C), and at 138–160 °C it loses all water. Endothermic effects are observed at 108 °C and 138 °C. The anhydrous complex eliminates 2.25 moles of 4-*dipy* (160–280°), and $Tm(NCS)_3$(4-*dipy*)$_{1.75}$ is formed. Upon further heating, intermediate compounds decompose to $Tm_2O_2SO_4$. Exothermic processes appear on the DTA curve at 328 °C. Decomposition of $Tm_2O_2SO_4$ to the oxide takes place within the temperature range of 400–700 °C.

The obtained crystalline compounds $TmBr_3$(2-*dipy*)$_2$·$6H_2O$ and $TmBr_3$·(4-*dipy*)$_2$·$6H_2O$ and the intermediate compounds formed during the thermal decomposition process are new examples of complexes with ligand isomerism.

Experimental

The hydrated thulium salts were prepared from 99.9% pure oxides (obtained from Koch-Light Lab.) according to the procedure described in the literature [3–6] for other lanthanide salts. The composition of these salts was controlled by determining the thulium content. The ligands 2-*dipy* and 4-*dipy* p.a. were obtained from Schuchard München, perchloric acid 60% p.a. was a Hopkin-Williams product. Other chemicals were analytical reagent grade from POCh-Gliwice.

The thulium content was determined complexometrically with a standard *EDTA* solution against xylenol orange as indicator. The chloride, bromide, and thiocyanate content was established by *Volhard*'s method and the perchlorate content by solvent extraction with ferroin [7]. Nitrogen, carbon and hydrogen were determined by elemental analysis, using V_2O_5 as oxidized agent. Analysis and identification of the solid decomposition products were performed by elemental and chemical analysis [8, 9], IR spectra and derivatographic curves. Some intermediate and final products were isolated [10, 11].

The IR spectra were recorded within the 4000–400 cm^{-1} region with a M-80 Specord instrument. Samples were prepared as KBr discs.

Thermal investigations were carried out with a derivatograph type Q-1500 in the temperature range 20–1000 °C at a heating rate of 4 $°C\,min^{-1}$ in air atmosphere in ceramic crucibles. A sample of 50 mg α-Al_2O_3 served as reference. The sensitivity of the galvanometer for DTA curves was 1/5; DTG-1/5.

The X-ray diffractograms were recorded using a D-5000 diffractometer and CuK_α (Ni-filtered) radiation. The measurements were made within the range $2\theta = 3$–$50°$ by means of the *Debye–Scherrer* method.

The solubilities of the complexes in water at 21 ± 1 °C were determined by measuring the concentration of Tm(III) ions in saturated solutions by the Arsenazo(III) method [12].

All complexes were prepared by methods published in previous papers [3, 4, 13].

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