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4,4'-Dipyridyl and 2,2'-Dipyridyl Complexes of Rare-Earth Perchlorates

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4,4'-Dipyridyl and 2,2'-dipyridyl complexes of rare-earth perchlorates of the formula $Ln(4\text{-}dipy)_8(ClO_4)_3HClO_4 \cdot 4\,H_2O$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Y, 4-*dipy* = 4,4'-dipyridyl) and $Ln(2\text{-}dipy)_3(ClO_4)_3 \cdot 6\,H_2O$ (Ln = Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Y, 2-*dipy* = 2,2'-dipyridyl) have been synthesized. The IR spectra of these compounds and other physical properties are discussed.

(Keywords: 4,4'-Dipyridyl complexes; 2,2'-Dipyridyl complexes; Infrared spectra; Rare-earth complexes)

4,4'-Dipyridyl- und 2,2'-Dipyridylkomplexe von Seltenerdmetallperchloraten

Es wurden 4,4'-Dipyridylkomplexe des Typs $Ln(4\text{-}dipy)_8(ClO_4)_3HClO_4 \cdot 4\,H_2O$ mit Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Y und 2,2'-Dipyridylkomplexe des Typs $Ln(2\text{-}dipy)_3(ClO_4)_3 \cdot 6\,H_2O$ mit Ln = Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu und Y dargestellt. Die IR-Spektren und andere physikalische Eigenschaften werden diskutiert.

Introduction

The studies on lanthanide compounds with weakly basic nitrogen donors are concerned with the synthesis of these complexes, with primary emphasis upon the characterization of their species with respect to coordination number and molecular structures. Also their spectral and other physical properties were investigated[1–5].

The number of weakly basic N-donors coordinated to the lanthanide ion depends primarily upon the coordinating ability of the anion present. When the anion is a strongly chelating 1,3-diketone or acetate,

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only mono-substituted complexes are obtained[6,7]. Bis-2,2′-dipyridyl[7,8] and bis-4,4′-dipyridyl[9,10] complexes are obtained when the anion is nitrate or chloride. Also the complexes of the type $Ln(2\text{-}dipy)_2X_3 \cdot (H_2O$ or $CH_3OH)_n$ ($X = SeCN^-$, SCN^-, $n = 0$, 1, 2) are isolated[4]. Tris-2,2′-dipyridyl complexes are obtained when the anion is thiocyanate[7] or selenocyanate[11] and tris-4,4′-dipyridyl compounds when the anion is bromide[5].

Maximum coordination by the chelating neutral N-donor is obtained when the anion is the weakly coordinating perchlorate. Thus both the eight-coordinate $Ln(phen)_4(ClO_4)_3$[12] (*phen* = 1,10-phenanthroline) and nine-coordinate $Ln(terpy)_3(ClO_4)_3$[13] (*terpy* = terpyridyl) species have been isolated.

We report here the synthesis of 4,4′-dipyridyl and 2,2′-dipyridyl complexes with lanthanide perchlorates and yttrium perchlorate. Investigation of lanthanide perchlorates compounds with 4,4′-dipyridyl seemed particularly interesting because its structure should preclude chelation. Consequently the maximum number of weakly basic N-donors coordinated to the lanthanide ion can be expected.

The complexes prepared have been characterized in the solid state by infrared spectroscopy and other physical properties.

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[14]. 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.

Lanthanides and yttrium were determined by titration with *EDTA* using xylenol orange as indicator. N, C, and H were determined microanalytically, perchlorate by solvent extraction with ferroin[15].

The IR spectra in KBr pellets were recorded with Carl Zeiss UR 10 spectrophotometer. IR spectra were measured in the region 4 000–700 cm^{-1}. The X-ray diffractograms were recorded on a diffractometer DRON-1, using CuK_α radiation and nickel filter. The intensity of the reflections was measured with a scintillation counter. Powder patterns were recorded with on automatic recorder for 2θ angles from 2° to 60°. The fluorescence of compounds were observed in the light from LS/58 quartz lamp at room temperature.

Solubility determinations were made by adding an excess of 4,4′-dipyridyl or 2,2′-dipyridyl complex to 25 cm^3 of water in 50 cm^3 flasks. The flasks were immersed in a constant temperature bath (21 °C) and stirred with magnetic strirrers. The solubility equilibria were established during 48 h. After this time, aliquots of 5 or 10 cm^3 were drawn througt cotton filters with pipettes. Data on the solubility of investigated compounds were obtained by complexometrically determination of total Ln(III) in saturated solution.

Table 1. *Analytical data of the compounds* $Ln(4\text{-}dipy)_8(ClO_4)_3HClO_4 \cdot 4\,H_2O$ *and their solubilities in water* (S/mmol dm^{-3}) *at* 21 °C

Ln	% Metal calcd. found	% H calcd. found	% C calcd. found	% N calcd. found	% ClO_4 calcd. found	S mmol dm^{-3}
La	7.47	3.96	51.68	12.05	21.39	4.1
	7.51	4.00	50.75	11.90	22.00	
Pr	7.57	3.95	51.62	12.04	21.37	5.0
	8.00	3.90	50.90	12.00	21.37	
Nd	7.74	3.95	51.53	12.02	21.33	5.8
	8.10	4.10	51.00	11.80	22.00	
Sm	8.04	3.93	51.36	11.98	21.26	3.1
	8.04	4.00	51.00	11.36	22.05	
Eu	8.12	3.93	51.32	11.97	21.25	4.1
	8.20	3.80	50.80	11.28	21.40	
Gd	8.37	3.92	51.18	11.94	21.19	3.8
	8.34	3.90	50.50	11.20	21.00	
Tb	8.46	3.92	51.13	11.93	21.17	3.6
	8.50	4.05	51.00	10.98	22.00	
Dy	8.63	3.91	51.03	11.90	21.13	3.3
	9.05	4.20	50.80	11.01	21.80	
Ho	8.75	3.90	50.97	11.89	21.10	4.3
	8.90	3.79	50.10	11.46	22.00	
Er	8.86	3.90	50.90	11.87	21.07	2.7
	8.80	4.15	49.80	11.10	21.80	
Yb	9.14	3.90	50.75	11.84	21.01	4.0
	8.90	3.50	50.35	11.53	21.40	
Lu	9.23	3.88	50.70	11.82	20.99	4.6
	9.30	4.15	50.00	11.74	21.00	
Y	4.91	4.07	53.11	12.39	21.99	4.0
	4.57	3.90	53.00	12.40	21.17	

Preparation of 4,4′-Dipyridyl Complexes

The hydrated lathanide and yttrium perchlorates were dissolved in 75% ethanol containing a few drops of 2 *M*-$HClO_4$. To a warm solution of metal salt (2 mmol in 50 cm^3) was added 8 mmol 4,4′-dipyridyl in 100 cm^3 75% ethanol. Precipitation of the product occured immediately. The isolated precipitate was filtered off, washed with small quantities of cold ethanol, then ethanol-ether (50:50) mixture and dried at room temperature for six days. A complete list of complexes and their analyses are given in Table 1.

Preparation of 2,2′-Dipyridyl Complexes

The hydrated lanthanide and yttrium perchlorates were dissolved in 75% ethanol containing a few drops of 2 *M*-$HClO_4$ and treated with a solution of 2,2′-

Table 2. *Analytical data of the compounds* $Ln(2\text{-}dipy)_3(ClO_4)_3 \cdot 6\,H_2O$ *and their solubilities in water* (S/mmol dm^{-3}) *at* 21 °C

Ln	% Metal calcd. found	% H calcd. found	% C calcd. found	% N calcd. found	% ClO_4 calcd. found	S mmol dm^{-3}
Pr	13.87	3.57	35.47	8.27	29.37	14.7
	13.58	3.56	35.00	8.50	28.90	
Sm	14.66	3.54	35.14	8.20	29.10	37.2
	14.50	3.42	35.50	8.20	29.70	
Eu	14.80	3.53	35.08	8.18	29.05	14.4
	14.16	3.40	35.18	8.20	28.87	
Gd	15.23	3.52	34.90	8.14	28.90	15.2
	15.00	3.56	34.70	8.00	30.00	
Tb	15.37	3.51	34.85	8.13	28.86	16.0
	14.90	3.40	34.10	7.78	28.10	
Dy	15.66	3.50	34.73	8.10	28.76	43.0
	15.16	3.30	34.10	8.00	29.05	
Ho	15.86	3.49	34.64	8.08	28.69	13.8
	16.25	3.45	35.10	8.52	29.00	
Er	16.05	3.48	34.57	8.06	28.62	15.8
	16.52	3.18	35.20	8.40	27.90	
Yb	16.51	3.46	34.38	8.02	28.47	18.4
	17.00	4.00	34.05	7.92	29.20	
Lu	16.66	3.46	34.31	8.00	28.42	—
	15.85	3.30	34.00	7.80	29.15	
Y	9.12	3.76	37.38	8.72	30.95	—
	8.90	3.60	37.00	8.80	31.05	

dipyridyl in 75% ethanol (molar ratio Ln:2-$dipy$ = 1:4). The mixtures were heated up to 80 °C for about 30 min and then allowed to cool. Using the method of slow crystallization (about 10 days), from these solutions were obtained small crystalline compounds. The products were filtered, washed with small portions of cold ethanol, then ethyl ether, pressed almost dry and dried in open air. Results of analysis are summarized in Table 2.

Results and Discussion

The analytical data show that all 4,4′-dipyridyl complexes have the formula $Ln(4\text{-}dipy)_8(ClO_4)_3HClO_4 \cdot 4\,H_2O$, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu and Y. The complexes are nonhygroscopic contrary to the free perchlorate. The colour of the compounds is similar in shade to that of free ion. The solid 4,4′-dipyridyl complexes of

Eu and Tb showed fluorescence at room temperature, intense pink and light-green, respectively.

The 2,2-dipyridyl complexes of Pr, Sm, Eu, Tb, Ho, Dy, Er, Yb, Lu and Y have been isolated as perchlorates containing three moles of 2-*dipy*. Analytical results suggest that the compounds prepared contain 6 water molecules per one metal atom. All complexes are white except those of Pr (light-green) and Er (pink). Some 2,2′-dipyridyl complexes in the solid state show fluorescence at room temperature: Eu (intense pink), Tb (ligh green), Sm (light blue), Gd, Dy, Ho, Er and Yb (blue-violett).

Table 3. *Principal IR bands of the Ln(4-dipy)*$_8$(ClO$_4$)$_3$HClO$_4$·4 H$_2$O *compounds* [cm^{-1}]

n	Pyridine frequencies ν_{CX}	ν_{CC}	δ_{CH}	Pyridine breathing	New bands resulting from complexation	ν_3 ionic	ν_1 ClO$_4$
a	1 595 vs	1 520 m	800 vs	1 000 m	1 315 w	1 115 sh	920 vw
r	1 600 vs	1 534 m	800 vs	1 000 m	1 324 w	1 120 sh	925 vw
d	1 596 vs	1 535 m	798 vs	1 000 m	1 322 w	1 120 sh	924 vw
m	1 600 vs	1 532 m	800 vs	1 000 m	1 330 w	1 118 sh	930 vw
u	1 600 vs	1 530 m	800 vs	1 002 m	1 322 w	1 120 sh	926 w
d	1 596 s	1 534 m	798 s	1 000 m	1 318 w	1 116 w	920 vw
b	1 598 vs	1 530 m	800 vs	1 000 m	1 320 w	1 115 sh	924 vw
y	1 600 vs	1 535 m	800 vs	1 000 m	1 325 w	1 120 sh	926 vw
o	1 600 s	1 533 m	800 s	1 000 m	1 316 w	1 115 vw	926 vw
r	1 602 vs	1 530 m	798 vs	1 000 m	1 320 w	1 118 vw	925 vw
b	1 600 vs	1 532 m	800 vs	1 000 m	1 318 w	1 120 sh	930 w
u	1 600 vs	1 530 m	800 vs	1 000 m	1 320 w	1 116 sh	930 w
	1 597 s	1 532 m	800 vs	1 000 m	1 320 w	1 120 w	922 vw

The 4,4′-dipyridyl and 2,2′-dipyridyl compounds are air stable, and heated in air atmosphere are explosive. All compounds dissolve fairly in ethanol and water (Table 1 and 2).

Infrared Spectra

Some characteristic and diagnostically valuable IR frequencies (cm^{-1}) of 4,4′-dipyridyl complexes are given in Table 3. The IR spectra of all these complexes are similar, with the free 4,4′-dipyridyl bands undergoing shifts owing to complex formation. The ring vibrations (C=N) appearing at 1 590 cm^{-1} in a free ligand are observed in complex at 1 595-1 600 cm^{-1}. In spectra of complexes there occur new absorption bands within the region 1 315-1 330 cm^{-1}. The characteristic pyridine mode (982 cm^{-1}) is shifted to higher frequency (1 000 cm^{-1}) upon coordination. Thus the disappearance of the free ligand band at 982 cm^{-1}, together with the appearance of a band in the 1 000 cm^{-1} region, is indicative of *Ln*—N bond formation in the 4,4′-dipyridyl complexes[16,17].

Table 4 presents the principal IR bands of the 2,2′-dipyridyl complexes. These spectra are similar. The bands observed in unbonded ligand at 1 578 cm^{-1} (attributed to the C=N ring vibration) and 1 552 cm^{-1} (C=C ring vibration) are somewhat shifted in the complexes (1 600-1 605 cm^{-1} and 1 585-1 570 cm^{-1}, respectively). Slight perturbation of C—H in-plane deformation modes β-CH are also seen. In the spectra of the complexes new bands appear within the regions 1 530-1 470 cm^{-1} and 1 320-1 305 cm^{-1}. Within the region 1 240-1 100 cm^{-1} the complex compounds have richer spectra. The strong band at 750 cm^{-1} shifts 10-20 cm^{-1} to higher frequency, also a satellite of this band at 734 cm^{-1} gains intensity and is strongly split away from the parent peak. Thus, the obtained compounds are cis-2,2′-dipyridyl chelate compounds[1,8,18,19].

The spectra of all 4,4′-dipyridyl and 2,2′-dipyridyl complexes show strong and broad absorption band in the water stretching region and shoulder in the water bending region (1 630 cm^{-1}).

In investigated region of IR spectra of $Ln(2\text{-}dipy)_3(ClO_4)_3 \cdot 6\,H_2O$ complexes, bands attributed to perchlorate group, show only one peak ν_3 at about 1 120-1 100 cm^{-1} and a weak peak ν_1 at 940-920 cm^{-1}. The spectra of all 4,4′-dipyridyl complexes show the ν_3 band of perchlorate appearing at 1 115-1 120 cm^{-1} and the weak ν_1 band at 926-930 cm^{-1}. The weak band at 925-930 cm^{-1} is to be attributed to the forbidden ν_1 frequency of the ClO_4^- which appears even in the case of ionic perchlorates like $KClO_4$ and NH_4ClO_4[20]. This shows that in the compounds investigated the perchlorate ion remains uncoordinated. Coordination of the perchlorate ion (T_d symmetry) lowers the site symmetry of this ion to C_{3v}, resulting in splitting of the band 1 111 cm^{-1} and intensification of a band around 927 cm^{-1}[20-24]. The perchlorate groups are also not coordinated in the lanthanide complexes with other weakly basic N-donors[12,25].

X-ray Powder Patterns

The X-ray powder patterns of all 4,4′-dipyridyl complexes are similar; consequently, these compounds are isostructural. Preliminary diffractometric measurements suggest that the crystals formed are of

Table 4. *Partial IR bands assignments of* $Ln(2\text{-}dipy)_3(ClO_4)_3 \cdot 6\,H_2O$ *compounds* [cm^{-1}]

	Pyridine frequencies			Pyridine breathing	New bands resulting from complexation	ν_3 ionic	ν_1 ClO_4
	ν_{CN}	ν_{CC}	γ—CH				
r	1 600 s	1 580 s	760 s 730 m	1 000 s	1 530 m 1 495 m 1 470 m 1 310 m	1 115 vs	920 w
m	1 600 s	1 570 s	760 vs 730 m	1 010 vs	1 530 m 1 496 m 1 478 m 1 320 m	1 120 vs	930 m
u	1 602 s	1 585 s	768 vs 730 m	1 008 vs	1 530 m 1 490 w 1 480 m 1 316 m	1 106 vs	926 m
d	1 600 s	1 584 s	755 s 730 m	1 010 s	1 530 m 1 494 m 1 480 w 1 310 m	1 110 vs	940 m
b	1 600 s	1 580 s	765 vs 738 m	1 008 s	1 530 m 1 492 w 1 478 w 1 315 m	1 112 vs	940 w
y	1 600 s	1 585 s	760 vs 740 m	1 010 s	1 530 m 1 490 w 1 475 w 1 317 m	1 110 vs	922 w
o	1 600 s	1 582 s	770 vs 730 m	1 015 s	1 530 m 1 488 w 1 470 m 1 316 m	1 120 vs	925 w
r	1 602 s	1 584 m	770 vs 734 m	1 014 s	1 535 m 1 492 w 1 470 m 1 314 m	1 105 vs	924 w
b	1 602 s	1 585 m	765 vs 735 m	1 020 m	1 534 m 1 492 w 1 478 m 1 320 m	1 105 vs	935 w
u	1 604 s	1 582 s	764 vs 735 m	1 012 vs	1 530 m 1 496 w 1 470 w 1 320 m	1 100 vs	920 w
	1 600 s	1 580 s	762 vs 730 m	1 010 s	1 532 m 1 490 w 1 470 w 1 312 m	1 102 vs	920 w

$\gamma_{\text{—CH}}$ out-of-plane deformation high symmetry. In the case of 2,2′-dipyridyl compounds, diffractometric measurements show, that these complexes are very slight crystalline.

Conclusion

For the complexes studied the IR spectra of 4,4′-dipyridyl and 2,2′-dipyridyl are modified by co-ordination with lanthanide ions. The perchlorate groups are not coordinated. The X-ray diffraction analysis revealed iostructurality in the group of compounds of formula $Ln(4\text{-}dipy)_8(ClO_4)_3HClO_4 \cdot 4\,H_2O$.

The compounds isolated in this work as perchlorate salts, provide additional examples of high-coordinated lanthanide complexes utilizing weakly basic N-donors. In the 2,2′-dipyridyl complexes a coordination number greater than six is probably achieved by bonding of water molecules. In the 4,4′-dipyridyl complexes inclusion of water in the coordination sphere gives twelve-coordinated complexes.

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