

# Synthesis and characterization of cationic pyridine-2-thiolate complexes of lanthanoid(III): crystal structures of pentagonal bipyramidal $[\text{Ln}(\text{SC}_5\text{H}_4\text{N})_2(\text{hmpa})_3]\text{I}$ ( $\text{Ln} = \text{Sm}, \text{Yb}$ ; hmpa = hexamethylphosphoric triamide) <sup>☆</sup>

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## Abstract

The cationic thiolate complexes of general formula  $[\text{Ln}(\text{SC}_5\text{H}_4\text{N})_2(\text{hmpa})_3]\text{I}$  ( $\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Er}, \text{Yb}$ ; hmpa = hexamethylphosphoric triamide) were prepared in modest yields by the reaction of metallic lanthanoids with 2,2'-dipyridyl disulfide and iodine in the presence of HMPA. The structure of **1** is a pentagonal bipyramidal seven-coordinated geometry consisting of two apical HMPA together with two chelating pyridine-2-thiolate ligands and one HMPA ligand in the pentagonal plane, which was confirmed by X-ray analysis for the samarium complex **1c** (monoclinic, space group  $P2_1/c$  with  $a = 16.614(3)$ ,  $b = 13.350(4)$ ,  $c = 21.302(3)$  Å,  $\beta = 100.14(1)^\circ$ ,  $V = 4650(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $R = 0.039$  for 4247 reflections with  $I > 3\sigma(I)$  and 442 parameters) and the ytterbium complex **1f** (monoclinic, space group  $C2$  with  $a = 19.909(4)$ ,  $b = 11.140(3)$ ,  $c = 21.273(3)$  Å,  $\beta = 105.20(1)^\circ$ ,  $V = 4553(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $R = 0.038$  for 4746 reflections with  $I > 3\sigma(I)$  and 442 parameters).

**Keywords:** Lanthanoids; Cationic complexes; Crystal structure; Iodide; Pyridine-2-thiolate; Hexamethylphosphoric triamide

## 1. Introduction

Interest in chalcogenolate complexes of lanthanoid elements stems largely from their capability as precursors for catalysts and new materials and for understanding the bonding between the lanthanoid and chalcogen atoms [1–22]. Preparative routes to such complexes have mostly involved metathetical reactions of lanthanoid halides with chalcogenolate anions with some exceptions, i.e. the reaction of amide and alkyl complexes with bulky thiols [23] and the oxidative reaction of low-valent organolanthanoid complexes with organic disulfides [5,6,10,11]. In these reactions, the purification of chalcogenolate complexes is in most cases hampered by the strong interaction of the products with salts.

Recently, we have reported a practical and high-yield synthetic method starting from metallic lanthanoids.

Thus, thiolate complexes of samarium and ytterbium in oxidation states of two and three were obtained in good yield by simple thermal reactions between metals and diaryl disulfides on controlling the stoichiometry of the reagents [19–22]. Considering the advantage of an electron-pair donor site neighboring the thiolate coordination, we carried out the reaction of 2,2'-dipyridyl disulfide with lanthanoid metals and iodine in the presence of HMPA (hexamethylphosphoric triamide). Here we report the synthesis and crystallographic characterization of cationic pentagonal-bipyramidal complexes of general formula  $[\text{Ln}(\text{SC}_5\text{H}_4\text{N})_2(\text{hmpa})_3]\text{I}$  ( $\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Er}, \text{Yb}$ ).

## 2. Results and discussion

### 2.1. Preparation of pyridine-2-thiolate of lanthanoid

Cationic pyridine-2-thiolate complexes (**1**) of lanthanoid elements were obtained by the direct reaction of

<sup>☆</sup> Dedicated to Professor H. Schumann on the occasion of his 60th birthday.

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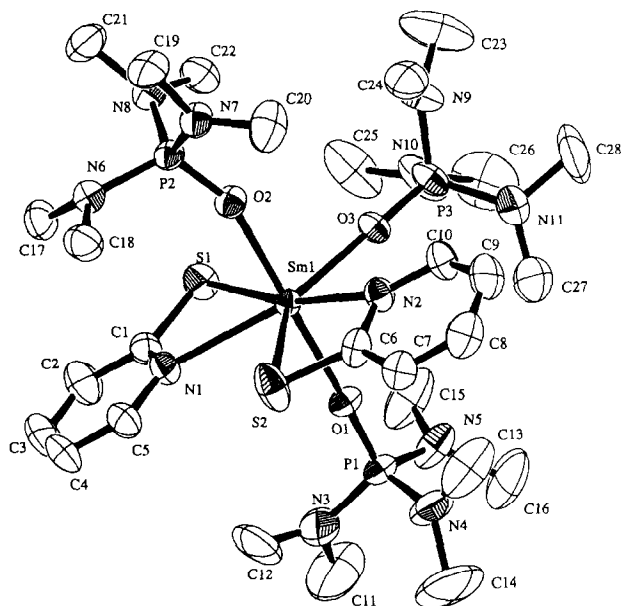


Fig. 1. ORTEP drawing of the cationic part of **1c** with the numbering scheme. Hydrogen atoms are omitted for clarity.

metallic lanthanoids with 2,2'-dipyridyl disulfide in the presence of iodine and HMPA. Treatment of metallic samarium with 2,2'-dipyridyl disulfide in THF at 50°C for 24 h in the presence of iodine and HMPA afforded a brown solution, from which brown prisms of  $[\text{Sm}(\text{SPy})_2(\text{hmpa})_3]\text{I}$  (**1c**) were obtained in 61% yield. Complex **1c** is more stable to air oxidation and to moisture than other thiolate complexes prepared so far. This stability is attributed to the chelating coordination of pyridine-2-thiolate ligands combined with strong  $\pi$ -donation from the HMPA ligands.

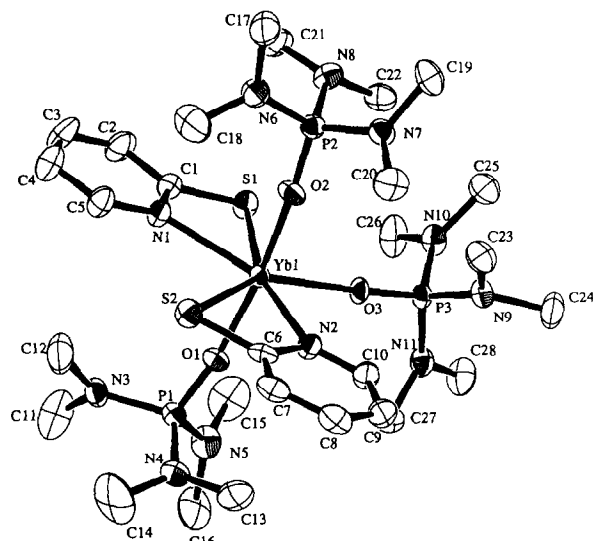


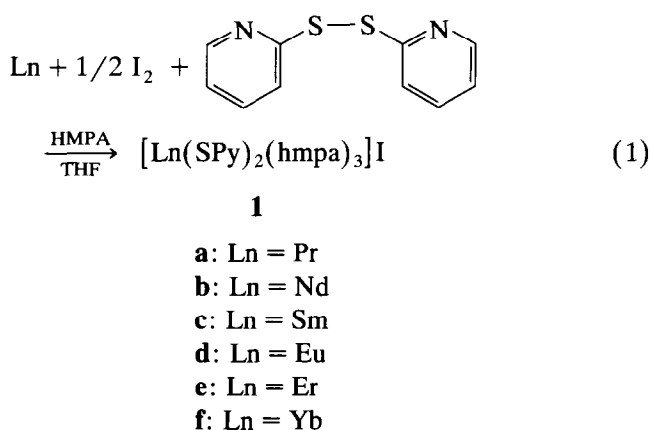
Fig. 2. ORTEP drawing of the cationic part of **1f** with the numbering scheme. Hydrogen atoms are omitted for clarity.

This synthetic method can be applied for the preparation of similar complexes from Pr, Nd, Eu and Yb. The formulas of the newly prepared complexes were elucidated by elemental analysis and crystallographic studies for **1c** and **1f** (see below). We have already reported the synthesis of neutral arenethiolate complexes from the reaction of metals such as samarium, europium and ytterbium with diaryl disulfide in the presence of a catalytic amount of iodine [21,22]. When we carried out the reaction of Sm with 2,2'-dipyridyl disulfide in the presence of a catalytic amount of iodine, the reaction proceeded readily and all the metal was consumed. We obtained an oily compound which is assumed to be  $\text{Sm}(\text{SPy})_3(\text{hmpa})_x$ . As shown in Eq. (1), Pr, Nd and Er afforded complexes **1a**, **1b** and **1e**, respectively. This is in sharp contrast to the fact that diaryl disulfides such as diphenyl disulfide and di(2,4,6-triisopropylphenyl) disulfide did not react with these metals.

Table 1  
Selected bond distances and angles in **1c** and **1f**

	<b>1c</b>	<b>1f</b>
<i>Selected bond distances (Å)</i>		
Ln–S(1)	2.894(2)	2.773(3)
Ln–S(2)	2.846(3)	2.828(3)
Ln–N(1)	2.542(7)	2.428(9)
Ln–N(2)	2.566(7)	2.439(10)
Ln–O(1)	2.259(5)	2.181(8)
Ln–O(2)	2.300(5)	2.212(8)
Ln–O(3)	2.319(5)	2.227(6)
P(1)–O(1)	1.492(5)	1.496(9)
P(2)–O(2)	1.492(5)	1.478(8)
P(3)–O(3)	1.483(5)	1.492(6)
<i>Selected bond angles (°)</i>		
S(1)–Ln–S(2)	135.43(7)	141.34(10)
S(1)–Ln–O(1)	90.9(2)	90.3(2)
S(1)–Ln–O(2)	88.5(1)	96.1(2)
S(1)–Ln–O(3)	86.8(1)	80.3(2)
S(1)–Ln–N(1)	57.1(2)	59.8(2)
S(1)–Ln–N(2)	166.6(2)	159.2(2)
S(2)–Ln–O(1)	88.7(2)	86.3(2)
S(2)–Ln–O(2)	93.0(1)	84.3(2)
S(2)–Ln–O(3)	137.8(1)	138.3(2)
S(2)–Ln–N(1)	78.4(2)	81.7(2)
S(2)–Ln–N(2)	57.5(2)	59.4(2)
O(1)–Ln–O(2)	178.1(2)	170.4(3)
O(1)–Ln–O(3)	88.4(2)	95.3(3)
O(2)–Ln–O(3)	89.7(2)	92.9(3)
O(1)–Ln–N(1)	88.9(2)	90.3(3)
O(1)–Ln–N(2)	92.9(2)	89.7(3)
O(2)–Ln–N(1)	92.3(2)	86.7(3)
O(2)–Ln–N(2)	87.3(2)	86.9(4)
O(3)–Ln–N(1)	143.7(2)	139.8(3)
O(3)–Ln–N(2)	80.6(2)	78.9(3)
N(1)–Ln–N(2)	135.7(2)	141.1(3)
Ln–S(1)–C(1)	81.4(3)	81.2(4)
Ln–S(2)–C(6)	82.7(3)	81.6(4)
Ln–O(1)–P(1)	175.9(4)	167.6(5)
Ln–O(2)–P(2)	157.7(3)	159.7(6)
Ln–O(3)–P(3)	179.4(4)	171.8(5)

An oxidation state of two has been generally observed for arenethiolate complexes of Sm, Eu and Yb. These Ln(II) complexes were now found to react further with similar organic disulfides to afford the corresponding Ln(III) complexes. This stepwise formation of Ln(III) thiolate complexes must be the cause of the ready formation of complexes of Sm, Eu and Yb in an oxidation state of two. Since pyridine-2-thiolate is a chelating ligand and HMPA is fairly strong donor ligand, we could isolate cationic complexes **1** through the reaction shown in Eq. (1). Recently the preferred coordination of HMPA to  $\text{YbI}_2$  affording a similar dicationic complex,  $[\text{Yb}(\text{thf})_2(\text{hmpa})_4]\text{I}_2$ , has been reported [24].



## 2.2. Crystal structures of pyridine-2-thiolate complexes of samarium and ytterbium

The cationic parts of the molecular structures of compounds **1c** and **1f** are shown in Figs. 1 and 2, respectively. Selected bond distances and angles in these two complexes are given in Table 1. Both cationic complexes **1c** and **1f** have essentially the same structure of pentagonal bipyramidal geometry with two HMPA ligands occupying two apical positions. In the pentagonal plane, two chelating pyridine-2-thiolate ligands and one HMPA ligand are coordinating. Thus, three HMPA ligands are arranged in meridional fashion. A similar pentagonal bipyramidal structure has been reported for some lanthanide and Group 3 metal complexes, e.g.,  $\text{Yb}(\text{TePh})_2(\text{py})_5$  [25],  $[\text{SmI}_2(\text{thf})_5][\text{Co}(\text{CO})_4]$  [26],  $[\text{Yb}(\text{H}_2\text{O})_5(\text{hmpa})_2]\text{Cl}_3$  [27],  $[\text{Y}(\text{OCMe}_3)\text{Cl}(\text{H}_2\text{O})_5][\text{BPh}_4]$  [28] and  $\text{La}[\text{TeSi}(\text{SiMe}_3)_3]_3(\text{dmpc})_2$  [17].

Comparative structural data for some of the thiolate complexes of samarium and ytterbium are shown in Table 2. Among those thiolate complexes of samarium, the Sm–S distances (2.894(2) and 2.846(3) Å, av. 2.870(3) Å) found for **1c** are the longest among the trivalent complexes,  $\text{Sm}(\text{SC}_6\text{H}_2^1\text{Pr}_{3-2,4,6})_3(\text{py})_2(\text{thf})$  (av. 2.740(3) Å) [21],  $[\text{Li}(\text{tmeda})_3][\text{Sm}(\text{S}^t\text{Bu})_6]$  (av. 2.827(3) Å) [29],  $\text{Sm}(\text{SC}_6\text{H}_2^1\text{Bu}_{3-2,4,6})_3$  (av. 2.644(8) Å) [23] and  $\text{Sm}(\text{SPh})_3(\text{hmpa})_3$  (2.811(2)–2.837(2) Å, av. 2.821(2) Å) [22], but is comparable to terminal

Table 2  
Comparative structural data for lanthanoid thiolate complexes

Complex	Ln–S <sup>a</sup> (Å)	Ln–S–C <sup>a</sup> (°)	Mode of Ln–S	CN <sup>b</sup>	Ref.
<b>1c</b>	2.870(3)	82.1(3)	Terminal	7	This work
$[\text{Sm}(\text{SAr})(\mu\text{-SAr})(\text{thf})_3]_2^c$	2.908(6)	124.0(8)	Terminal	6	[21]
	3.017(6)	123.7(7)	Bridging		
$\text{Sm}(\text{SAr})_3(\text{py})_2(\text{thf})^c$	2.740(3)	121.8(3)	Terminal	6	[21]
$\text{Sm}(\text{SPh})_3(\text{hmpa})_3$	2.821(2)	114.6(2)	Terminal	6	[22]
$\text{Sm}[\text{SC}_6\text{H}_2^1\text{Bu}_{3-2,4,6}]_3$	2.645(9)	82.9(8)	Terminal	3	[23]
$[\text{Sm}(\mu\text{-SPh})(\eta\text{-C}_8\text{H}_8)(\text{thf})_2]_2$	2.924(8)	121.4(7)	Bridging	8	[19]
$[\text{Sm}((\mu\text{-SAr})(\eta\text{-C}_8\text{H}_8)(\text{thf})_2)_2]^c$	2.883(6)	127.0(8)	Bridging	7	[19]
$[\text{Li}(\text{tmeda})_3][\text{Sm}(\text{S}^t\text{Bu})_6]$	2.821(2)	–	Terminal	6	[29]
$[\text{Eu}(\text{SAr})(\mu\text{-SAr})(\text{thf})_3]_2^c$	2.898(4)	124.6(5)	Terminal	6	[21]
	3.016(3)	123.8(5)	Bridging		
<b>1f</b>	2.801(3)	81.4(4)	Terminal	7	This work
$\text{Yb}(\text{SAr})_3(\text{py})_3^c$	2.648(7)	116.8(8)	Terminal	6	[21]
$\text{Yb}(\text{SPh})_3(\text{hmpa})_3$	2.728(3)	116.0(1)	Terminal	6	[22]
$\text{YbCp}^*_2(\text{SPh})(\text{NH}_3)$	2.675(3)	118.5(3)	Terminal	8	[5]
$\text{Yb}[\text{SC}_6\text{H}_2^1\text{Bu}_{3-2,4,6}]_2(\text{dme})_3^d$	2.756(8)	125.0(8)	Terminal	6	[23]
$\text{Yb}(\text{SPh})_2(\text{py})_4$	2.827(3)	101.6(3)	Terminal	6	[25]
$[\text{Li}(\text{tmeda})_3][\text{Yb}(\text{S}^t\text{Bu})_6]$	2.737(2)	–	Terminal	6	[29]

<sup>a</sup> Averaged value.

<sup>b</sup> CN = coordination number.  $\eta$ -Pentamethylcyclopentadienyl and  $\eta$ -cyclooctatetraene may be taken as occupying three and four coordination sites around the metal, respectively.

<sup>c</sup> Ar = 2,4,6-triisopropylphenyl.

<sup>d</sup> dme = Dimethoxyethane.

Sm–S bonds found for the divalent complex,  $[\text{Sm}(\text{SC}_6\text{H}_2^i\text{Pr}_{3-2,4,6})(\mu\text{-SC}_6\text{H}_2^i\text{Pr}_{3-2,4,6})(\text{thf})_3]_2$  (2.908(6) Å) [21]. The Sm–N bond distances (2.542(7) and 2.566(7) Å) are comparable to those (2.533(7) and 2.543(9) Å) found for  $\text{Sm}(\text{SC}_6\text{H}_2^i\text{Pr}_{3-2,4,6})_3(\text{py})_2(\text{thf})$  [21]. Since the pyridine-2-thiolate acts as a four-membered chelating ligand, the bond angles Sm–S–C in **1c** are acute (81.4(3) and 82.7(3)°).

For complex **1f**, the Yb–S distances (2.773(3) and 2.828(3) Å, av. 2.801(3) Å) are the longest among the Yb(III) complex having terminal thiolate ligands,  $\text{Yb}(\text{SPh})_3(\text{hmpa})_3$  (av. 2.728(3) Å),  $\text{Yb}(\text{SC}_6\text{H}_2^i\text{Pr}_{3-2,4,6})_3(\text{py})_3$  (av. 2.648(6) Å) [21] and  $(\text{C}_5\text{Me}_5)_2\text{Yb}(\text{SPh})(\text{NH}_3)$  (av. 2.675(3) Å; two molecules in an asymmetric unit) [5], and the divalent complex,  $[\text{Yb}(\text{SC}_6\text{H}_2^i\text{Bu}_{3-2,4,6})_2(\text{dme})_2]$  (2.756(8) Å) [23]. The bond angles Yb–S–C in **1f** are also acute for the same reason as in **1c**.

The average Sm–O distances (av. 2.305(5) Å) in **1c** and Yb–O distances (av. 2.207(8) Å) in **1f** are comparable to those in  $\text{Sm}(\text{SPh})_3(\text{hmpa})_3$  (av. 2.299(4) Å) and  $\text{Yb}(\text{SPh})_3(\text{hmpa})_3$  (av. 2.208(3) Å), respectively. These distances in **1c** and **1f** are much shorter than for other O-donor ligands such as THF. Such short Ln–O distances and larger bond angles Ln–O–P indicate the strong interaction between samarium and oxygen atoms of HMPA. Thus, the  $p\pi$ -donation from the oxygen atom of HMPA compensates the electron deficiency of the samarium center.

In both complexes, pentagonal planes consisting of five coordinating atoms are exactly planar since the angle sums for the samarium atom in **1c** and the ytterbium atom in **1f** are 360.4° and 360.1°, respectively. In the pentagonal plane, two pyridine-2-thiolate ligands coordinate in an array of S–N and S–N (head-to-tail). Two oxygen atoms of HMPA ligands deviate slightly from the ideal apical positions and the bond angle O(1)–Sm–O(2) (178.1(2)°) in **1c** and O(1)–Yb–O(2) (170.4°) are nearly linear.

### 3. Conclusion

We have demonstrated that the direct reaction of various lanthanoid elements such as Pr, Nd, Sm, Eu, Er and Yb with 2,2'-dipyridyl disulfide and iodine in the presence of HMPA affords cationic complexes,  $[\text{Ln}(\text{SPy})_3(\text{hmpa})_3]\text{I}$  (**1**). The chelating 2-pyridinethiolate ligand stabilized lanthanoid thiolate complexes against moisture and air oxidation compared with other thiolate complexes prepared so far [19–22]. Crystallographic studies of **1c** and **1f** confirmed that complexes **1** have a cationic pentagonal bipyramidal seven-coordinated geometry.

## 4. Experimental section

### 4.1. General

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by the use of the standard Schlenk technique under an argon atmosphere. THF and diethyl ether were dried over sodium benzophenone ketyl and then distilled before use.

$^1\text{H}$  (270 MHz) NMR spectra were measured on a JEOL GSX-270 spectrometer. Elemental analyses were performed at the Elemental Analysis Center of Osaka University. All melting points were measured in sealed tubes and were not corrected.

### 4.2. Synthesis of complexes **1a–f**

#### 4.2.1. Synthesis of $[\text{Pr}(\text{SPy})_2(\text{hmpa})_3]\text{I}$ (**1a**)

To a mixture of Pr metal (238 mg, 1.69 mmol) and 2,2'-dipyridyl disulfide (373 mg, 1.69 mmol) in THF (25 ml) were added HMPA (0.9 ml) and iodine (214 mg, 0.84 mmol) and the reaction mixture was stirred at 50°C. A brownish red solution resulted after 24 h, then the unreacted metal was filtered off. The supernatant solution was concentrated and then cooled to –20°C, affording brownish green crystals of **1a** in 14% yield (235 mg), m.p. 143–145°C. Anal. Calc. for  $\text{C}_{28}\text{H}_{62}\text{N}_{11}\text{O}_3\text{P}_3\text{S}_2\text{IPr}$ : C, 32.79; H, 6.09; N, 15.02. Found: C, 32.68; H, 6.06; N, 14.96%.

#### 4.2.2. Synthesis of $[\text{Nd}(\text{SPy})_2(\text{hmpa})_3]\text{I}$ (**1b**)

To finely divided Nd metal (169 mg, 1.17 mmol) and 2,2'-dipyridyl disulfide (259 mg, 1.17 mmol) in THF (20 ml) was added HMPA (1.0 ml). To this reaction mixture cooled at 0°C was added iodine (149 mg, 0.59 mmol), then the reaction mixture was stirred at 50°C for 24 h. The resulting deep-red solution was separated from the unreacted metal. Concentration and cooling to –20°C afforded brown prisms of **1b** in 35% yield (418 mg), m.p. 170–172°C. Anal. Calc. for  $\text{C}_{28}\text{H}_{62}\text{N}_{11}\text{O}_3\text{P}_3\text{S}_2\text{INd}$ : C, 32.68; H, 6.07; N, 14.97. Found: C, 32.77; H, 6.09; N, 14.94%.

#### 4.2.3. Synthesis of $[\text{Sm}(\text{SPy})_2(\text{hmpa})_3]\text{I}$ (**1c**)

To a mixture of Sm metal powder (204 mg, 1.36 mmol) and 2,2'-dipyridyl disulfide (299 mg, 1.36 mmol) in THF (20 ml) cooled at 0°C were added HMPA (1.0 ml) and iodine (173 mg, 0.68 mmol) and the reaction mixture was stirred at 50°C. A brown solution resulted after 24 h, and then the unreacted metal was filtered off. Concentration and cooling to –20°C afforded brown prisms of **1c** in 61% yield (857 mg), m.p. 120–122°C.  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta$  = 2.70 (d, 54H,  $^3J_{\text{H,P}} = 7.26$  Hz, HMPA), 7.03 (br, 2H, 3- $\text{C}_5\text{H}_4\text{N}$ ), 6.70 (t, 2H, 5- $\text{C}_5\text{H}_4\text{N}$ ), 7.41 (t, 2H, 4- $\text{C}_5\text{H}_4\text{N}$ ), 8.19 (br, 2H, 6-

C<sub>5</sub>H<sub>4</sub>N). Anal. Calc. for C<sub>28</sub>H<sub>62</sub>N<sub>11</sub>O<sub>3</sub>P<sub>3</sub>S<sub>2</sub>ISm: C, 32.49; H, 6.04; N, 14.88. Found: C, 32.69; H, 6.09; N, 14.86%.

#### 4.2.4. Synthesis of [Eu(SP<sub>y</sub>)<sub>2</sub>(hmpa)<sub>3</sub>]I (**1d**)

Iodine (181 mg, 0.71 mmol) was added to a mixture of Eu metal powder (217 mg, 1.43 mmol) and 2,2'-dipyridyl disulfide (315 mg, 1.43 mmol) in THF (20 ml) containing HMPA (0.8 ml) and the reaction mixture was stirred at 50°C. A brown-red solution resulted after 24 h, then the unreacted metal was filtered off. Concentration and cooling to -20°C afforded yellowish green needles of **1d** in 33% yield (495 mg), m.p. 174–182°C. Anal. Calc. for C<sub>28</sub>H<sub>62</sub>N<sub>11</sub>O<sub>3</sub>P<sub>3</sub>S<sub>2</sub>IEu: C, 32.44; H, 6.03; N, 14.86. Found: C, 32.50; H, 6.05; N, 14.82%.

#### 4.2.5. Synthesis of [Er(SP<sub>y</sub>)<sub>2</sub>(hmpa)<sub>3</sub>]I (**1e**)

A mixture of finely divided Er metal (169 mg, 1.01 mmol) and 2,2'-dipyridyl disulfide (223 mg, 1.01 mmol) in THF (15 ml) was placed in a Schlenk tube, then HMPA (0.6 ml) and iodine (128 mg, 0.50 mmol) were added successively. After the reaction mixture had been stirred at 50°C for 24 h, a deep brown solution resulted and then the unreacted metal was filtered off. On cooling to -20°C, pink needles of **1e** were obtained in 24%

Table 3  
Crystal data and data collection parameters for **1c** and **1f**

Parameter	<b>1c</b>	<b>1f</b>
Formula	C <sub>28</sub> H <sub>62</sub> N <sub>11</sub> O <sub>3</sub> P <sub>3</sub> S <sub>2</sub> ISm	C <sub>28</sub> H <sub>62</sub> N <sub>11</sub> O <sub>3</sub> P <sub>3</sub> S <sub>2</sub> IYb
Formula weight	1035.22	1057.86
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>C</i> 2 (No. 5)
<i>a</i> (Å)	16.614(3)	19.909(4)
<i>b</i> (Å)	13.350(4)	11.140(3)
<i>c</i> (Å)	21.302(3)	21.273(3)
β (°)	100.14(1)	105.20(1)
<i>Z</i>	4	4
<i>V</i> (Å <sup>3</sup> )	4650(1)	4553(1)
<i>D</i> <sub>calc.</sub>	1.478	1.543
Radiation	Mo Kα	Mo Kα
Crystal size (mm)	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.20
Abs. coeff. (cm <sup>-1</sup> )	21.62	29.69
Scan mode	2θ - ω	2θ - ω
temp. (°C)	23	23
Scan speed (° min <sup>-1</sup> )	16	16
Scan width (°)	1.00 + 0.30 tan θ	1.73 + 0.30 tan θ
2θ <sub>max</sub> (°)	55	55
Unique data ( <i>I</i> > 3σ( <i>I</i> ))	4247	4746
No. of variables	442	442
<i>R</i>	0.039	0.038
<i>R</i> <sub>w</sub>	0.037	0.053
GOF	1.25	2.87
Largest peak (e Å <sup>-3</sup> )	0.43	0.58

Table 4  
Atomic coordinates of complex **1c**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Sm(1)	0.73912(3)	0.20142(3)	0.79671(2)	3.392(8)
I	0.27988(5)	0.22755(6)	0.97140(4)	8.42(3)
S(1)	0.8662(2)	0.2513(2)	0.7250(1)	5.37(7)
S(2)	0.6037(2)	0.3042(2)	0.8319(2)	7.31(8)
P(1)	0.5975(2)	0.1219(2)	0.6482(1)	5.64(7)
P(2)	0.8790(1)	0.3174(2)	0.9332(1)	4.14(6)
P(3)	0.8299(2)	-0.0607(2)	0.8135(1)	5.24(7)
O(1)	0.6561(3)	0.1498(4)	0.7069(3)	5.3(2)
O(2)	0.8263(3)	0.2492(4)	0.8880(2)	4.4(1)
O(3)	0.7949(3)	0.0417(4)	0.8068(3)	4.6(1)
N(1)	0.7490(4)	0.3715(5)	0.7449(3)	4.6(2)
N(2)	0.6485(4)	0.1229(5)	0.8694(3)	4.7(2)
N(3)	0.5906(7)	0.2102(9)	0.5960(5)	12.4(4)
N(4)	0.5084(5)	0.0973(7)	0.6661(5)	8.2(3)
N(5)	0.6292(5)	0.0199(7)	0.6193(4)	7.7(3)
N(6)	0.8686(4)	0.4386(5)	0.9200(3)	4.4(2)
N(7)	0.8556(4)	0.2999(6)	1.0042(3)	5.2(2)
N(8)	0.9751(4)	0.2944(6)	0.9296(3)	5.0(2)
N(9)	0.8927(5)	-0.0690(7)	0.8812(4)	7.2(3)
N(10)	0.8814(6)	-0.0854(7)	0.7580(4)	8.1(3)
N(11)	0.7590(6)	-0.1434(6)	0.8121(4)	7.1(3)
C(1)	0.8100(6)	0.3620(6)	0.7130(4)	4.6(2)
C(2)	0.8264(7)	0.4387(8)	0.6715(5)	7.3(3)
C(3)	0.7783(8)	0.5220(8)	0.6652(5)	7.7(4)
C(4)	0.7168(8)	0.5312(8)	0.6984(6)	7.7(4)
C(5)	0.7036(6)	0.4551(7)	0.7369(5)	6.5(3)
C(6)	0.5888(5)	0.1907(6)	0.8672(4)	4.6(2)
C(7)	0.5185(6)	0.1682(7)	0.8922(5)	5.6(3)
C(8)	0.5129(7)	0.0787(9)	0.9216(5)	6.8(3)
C(9)	0.5771(7)	0.0110(8)	0.9272(5)	7.4(4)
C(10)	0.6419(6)	0.0365(7)	0.8990(5)	5.7(3)
C(11)	0.581(1)	0.182(2)	0.5264(8)	24.3(9)
C(12)	0.582(1)	0.310(1)	0.6102(10)	23.9(8)
C(13)	0.4976(9)	0.057(1)	0.7242(7)	12.3(6)
C(14)	0.4322(8)	0.107(1)	0.6197(9)	17.9(7)
C(15)	0.7119(7)	0.012(1)	0.6104(7)	11.1(5)
C(16)	0.5747(9)	-0.0612(10)	0.5924(7)	12.5(5)
C(17)	0.9010(7)	0.4842(7)	0.8679(5)	6.5(3)
C(18)	0.7958(6)	0.4884(7)	0.9345(5)	6.7(3)
C(19)	0.8994(6)	0.3536(8)	1.0598(4)	6.7(3)
C(20)	0.8040(7)	0.2233(9)	1.0177(5)	8.6(4)
C(21)	1.0442(6)	0.3531(8)	0.9624(5)	7.5(3)
C(22)	0.9992(6)	0.2025(8)	0.9034(5)	6.7(3)
C(23)	0.9645(9)	-0.133(1)	0.8926(7)	14.5(6)
C(24)	0.8714(7)	-0.0303(9)	0.9390(5)	7.9(4)
C(25)	0.9393(9)	-0.014(1)	0.7405(7)	12.1(5)
C(26)	0.878(1)	-0.179(1)	0.7247(7)	14.2(6)
C(27)	0.6853(8)	-0.1376(8)	0.7680(7)	11.0(5)
C(28)	0.771(1)	-0.2356(9)	0.8490(7)	13.9(6)

yield (253 mg), m.p. 204–206°C. Anal. Calc. for C<sub>28</sub>H<sub>62</sub>N<sub>11</sub>O<sub>3</sub>P<sub>3</sub>S<sub>2</sub>IEr: C, 31.97; H, 5.94; N, 14.64. Found: C, 32.16; H, 5.93; N, 14.77%.

#### 4.2.6. Synthesis of [Yb(SP<sub>y</sub>)<sub>2</sub>(hmpa)<sub>3</sub>]I (**1f**)

To a mixture of finely divided Yb metal (380 mg, 2.20 mmol) and 2,2'-dipyridyl disulfide (486 mg, 2.20 mmol) in THF (20 ml) cooled at 0°C were added HMPA (1.2 ml) and iodine (280 mg, 1.10 mmol) and

the reaction mixture was stirred at 50°C for 24 h. A brown solution with precipitated solids was obtained. The product was extracted with THF (100 ml) and then the solution was concentrated to ca. 80 ml. Addition of diethyl ether (10 ml) gave brown crystals of **1f** in 45% yield (1.05 g), m.p. 200–202°C. Anal. Calc. for

C<sub>28</sub>H<sub>62</sub>N<sub>11</sub>O<sub>3</sub>P<sub>3</sub>S<sub>2</sub>IYb: C, 31.79; H, 5.91; N, 14.56. Found: C, 31.77; H, 5.86; N, 14.65%.

#### 4.3. Crystallographic data collections and structure determination of **1c** and **1f**

Crystals of **1c** suitable for X-ray diffraction sealed in glass capillaries under an argon atmosphere were mounted on a Rigaku AFC-5R four-circle diffractometer for data collection using Mo K $\alpha$  radiation. Three standard reflections were chosen and monitored every 150 reflections. Measured non-equivalent reflections with  $I > 3.0\sigma(I)$  were used for the structure determination. Empirical absorption correction was carried out based on an azimuthal scan.

The systematic absences of  $h0l$  ( $l$  odd) and  $0k0$  ( $k$  odd) indicate the space group to be  $P2_1/c$ . The structure was solved by the direct method (SAPI91) [30] and expanded using standard Fourier maps. In the final refinement cycle (full-matrix), hydrogen atom coordinates were included at idealized positions, and the hydrogen atoms were not refined but were given the same temperature factor as that of the carbon atom to which they were bonded. All calculations were performed using the TEXSAN crystallographic software package. For 442 variable parameters and 4247 observed reflections with  $I > 3.0\sigma(I)$ ,  $R$  and  $R_w$  values of 0.039 and 0.037, respectively, were obtained. The data obtained are given in Tables 3 and 4.

The crystal structure of **1f** was also solved by X-ray analysis. Sampling of crystals suitable for X-ray analysis was the same for **1c**. Three standard reflections were chosen and monitored every 150 reflections, indicating some increase in intensity (+3.9%), and thus this phenomenon was accounted for by applying a linear correction factor. Empirical absorption correction was carried out based on an azimuthal scan.

The systematic absences of  $hkl$  ( $h+k$  odd) indicate the space group to be  $C2$ . The structure was solved by the direct method (SHELXS86) [31] and expanded using standard Fourier maps. In the final refinement cycle (full-matrix), hydrogen atom coordinates were included at idealized positions, and the hydrogen atoms were not refined but were given the same temperature factor as that of the carbon atom to which they were bonded. All calculations were performed using the TEXSAN crystallographic software package. For 442 variable parameters and 4746 observed reflections with  $I > 3.0\sigma(I)$ ,  $R$  and  $R_w$  values of 0.038 and 0.053, respectively, were obtained. The data obtained are given in Tables 3 and 5.

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Table 5  
Atomic coordinates of complex **1f**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Yb(1)	0.25211(2)	0.0000	0.24476(2)	2.582(8)
I(1)	0.0000	0.4965(2)	0.0000	4.50(2)
I(2)	0.5000	0.4451(2)	0.5000	5.42(4)
S(1)	0.2362(2)	0.1971(3)	0.1626(2)	3.86(7)
S(2)	0.1742(2)	-0.1832(3)	0.2849(2)	4.50(8)
P(1)	0.2439(2)	-0.2098(3)	0.1108(2)	3.33(7)
P(2)	0.2244(2)	0.1998(3)	0.3706(2)	3.41(7)
P(3)	0.4334(1)	0.1089(3)	0.2698(1)	2.87(6)
O(1)	0.2558(4)	-0.1184(7)	0.1641(4)	3.6(2)
O(2)	0.2356(4)	0.0984(8)	0.3298(4)	4.0(2)
O(3)	0.3627(3)	0.0586(7)	0.2647(4)	3.3(2)
N(1)	0.1366(4)	0.0671(9)	0.1863(5)	3.6(2)
N(2)	0.3101(5)	-0.1538(9)	0.3216(5)	3.6(2)
N(3)	0.1651(5)	-0.200(1)	0.0631(6)	4.7(3)
N(4)	0.2566(6)	-0.345(1)	0.1406(7)	5.1(3)
N(5)	0.3003(6)	-0.185(1)	0.0704(6)	5.1(3)
N(6)	0.1457(5)	0.189(1)	0.3808(6)	5.1(3)
N(7)	0.2838(5)	0.1929(10)	0.4393(5)	4.1(3)
N(8)	0.2329(6)	0.334(1)	0.3422(6)	4.5(3)
N(9)	0.4777(5)	0.101(1)	0.3442(5)	3.9(2)
N(10)	0.4352(5)	0.2470(10)	0.2458(6)	4.1(3)
N(11)	0.4697(5)	0.034(1)	0.2241(5)	4.1(3)
C(1)	0.1489(6)	0.162(1)	0.1522(6)	3.4(3)
C(2)	0.0935(8)	0.226(1)	0.1104(9)	5.4(4)
C(3)	0.0277(7)	0.192(2)	0.1069(9)	6.4(5)
C(4)	0.0133(7)	0.094(2)	0.1397(9)	6.1(4)
C(5)	0.0703(6)	0.034(1)	0.1812(7)	4.9(3)
C(6)	0.2574(7)	-0.226(1)	0.3313(6)	3.6(3)
C(7)	0.2698(8)	-0.320(1)	0.3710(8)	4.7(4)
C(8)	0.3393(9)	-0.346(1)	0.4059(7)	5.3(4)
C(9)	0.3927(8)	-0.276(1)	0.3966(7)	5.0(4)
C(10)	0.3745(7)	-0.180(1)	0.3539(7)	4.3(3)
C(11)	0.1481(9)	-0.214(3)	-0.005(1)	9.8(8)
C(12)	0.1051(9)	-0.191(2)	0.089(1)	9.5(7)
C(13)	0.3167(9)	-0.373(2)	0.1909(10)	7.2(5)
C(14)	0.203(1)	-0.440(2)	0.127(1)	12.5(8)
C(15)	0.316(1)	-0.065(2)	0.054(1)	8.3(6)
C(16)	0.3222(9)	-0.278(2)	0.0300(9)	8.4(6)
C(17)	0.1222(8)	0.269(2)	0.4238(10)	8.2(6)
C(18)	0.0955(9)	0.100(2)	0.350(1)	8.9(6)
C(19)	0.3051(8)	0.293(2)	0.4867(7)	5.6(4)
C(20)	0.3025(9)	0.076(2)	0.4714(8)	6.0(4)
C(21)	0.1756(8)	0.387(1)	0.2937(9)	6.3(5)
C(22)	0.3018(7)	0.362(1)	0.3323(8)	4.8(4)
C(23)	0.4476(8)	0.108(1)	0.4012(7)	5.2(4)
C(24)	0.5541(7)	0.119(2)	0.3666(9)	6.5(5)
C(25)	0.4610(8)	0.347(1)	0.2905(8)	5.4(4)
C(26)	0.4081(8)	0.280(2)	0.1779(8)	6.4(4)
C(27)	0.4558(8)	-0.095(2)	0.213(1)	7.5(6)
C(28)	0.5267(7)	0.076(2)	0.1961(7)	6.1(4)

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