ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2014, Vol. 40, No. 3, pp. 184–188. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © Yu.A. Bryleva, L.A. Glinskaya, O.V. Antonova, T.E. Kokina, S.V. Larionov, 2014, published in Koordinatsionnaya Khimiya, 2014, Vol. 40, No. 3, pp. 184–187.

Coordination Polymer [Sm(Biq)(*iso*-$Bu_2PS_2)_3]_n$: Synthesis, Structure, and Photoluminescence

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Received July 23, 2013

Abstract—A heteroligand complex [Sm(Biq)(*iso*-$Bu_2PS_2)_3]_n$ (Biq = 6,6'-biquinoline) is synthesized. According to the X-ray diffraction data, the complex is one-dimensional coordination polymer. The crystal structure is built of chains consisting of fragments Sm(*iso*-$Bu_2PS_2)_3$ and molecules of the bidentate-bridging ligand Biq. The coordination polyhedron N_2S_6 of the Sm atom is a distorted tetragonal antiprism. The complex exhibits red photoluminescence (λ_{max} = 562, 598, 642, and 703 nm).

DOI: 10.1134/S1070328414030026

INTRODUCTION

Investigations on the synthesis of lanthanide (Ln) complexes with N- and O-donor organic ligands possessing photo- and electroluminescence properties are being successfully developed [1–5]. This is due to both aspiration for obtaining novel substances and establishing relationships between the structure of complexes and the luminescence properties and prospects of using compounds for the production of luminescent devices and sensors. The data on the luminescence properties of the Ln complexes with S-donor organic ligands appeared only recently. The luminescent Ln compounds with the monothiolate reagent mercaptobenzthiazole were synthesized [6]. The synthesis of the Ln complexes including 1,1-dithiolate ligands $R_2NCS_2^-$ was described, and their luminescence properties were studied [7–12]. We synthesized the luminescent Ln complexes with other types of 1,1-ditholate ligands: *iso*-$Bu_2PS_2^-$ and (*iso*-PrO)$_2PS_2^-$ ions [13–18].

The study of the structures of the synthesized luminescent Ln complexes with 1,1-dithiolate ligands showed that they can be classified as mononuclear compounds [8, 9, 11, 13–18]. It is interesting to obtain coordination polymers of Ln with 1,1-dithiolate ligands. 6,6'-Biquinoline (Biq) containing two fragments of the fluorophore (quinoline) is promising as an additional bridging ligand for the solution of the above problem.

The purpose of this work is to synthesize the coordination polymer of Sm(III) containing *iso*-$Bu_2PS_2^-$ ions and Biq and to study its structure and luminescence properties.

EXPERIMENTAL

The following reagents were used for the synthesis of the complex: $Sm(NO_3)_3 \cdot 6H_2O$ (analytical grade), 6,6'-biquinoline (high-purity grade), and *iso*-$Bu_2PS_2Na \cdot 3H_2O$ obtained by the evaporation of a 50% aqueous solution of *iso*-Bu_2PS_2Na (Fluka). The solvents were *iso*-PrOH (special purity grade) and MeCN (analytical grade).

Synthesis of *catena*-tris(diisobutyldithiophosphinato)(μ-6,6'-biquinoline)samarium(III) [Sm(Biq)(*iso*-$Bu_2PS_2)_3]_n$ (I). A solution of *iso*-$Sm(NO_3)_3 \cdot 6H_2O$ (0.29 g, 1.0 mmol) in *iso*-PrOH (5 mL) was added with stirring to a solution of *iso*-$Bu_2PS_2Na \cdot 3H_2O$ (0.11 g, 0.25 mmol) in *iso*-PrOH (2 mL). The formed precipitate of $NaNO_3$ was filtered off on a paper filter, and a hot solution of Biq (0.06 g, 0.25 mmol) in *iso*-PrOH (7 mL) was added to the filtrate. The obtained solution was stirred for 1 h and evaporated to a minimum volume. A cream-colored precipitate was filtered off with suction, washed with *iso*-PrOH (3 mL), and dried in a drying box above anhydrone. The product was recrystallized from MeCN (10 mL). The yield was 0.1 g (50%).

For $C_{42}H_{66}N_2P_3S_6Sm$			
anal. calcd., %:	C, 48.8;	H, 6.4;	N, 2.7.
Found, %:	C, 49.3;	H, 6.0;	N, 3.2.

IR (KBr, ν, cm^{-1}): 523, 613 $\nu(PS_2)$, 1589, 1644 ν(C=C, C=N).

Analyses to C, H, and N were carried out on a Euro EA 3000 analyzer. IR spectra in the range from 400 to 3800 cm^{-1} were recorded in KBr pellets on a Scimitar FTS2000 spectrophotometer. The luminescence and photoluminescence excitation spectra of the solid

Table 1. Cryatallographic characteristics and experimental and structure refinement details for complex **I**

Parameter	Value
Empirical formula	$C_{42}H_{66}N_2P_3S_6Sm$
FW	1034.59
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	13.6678(6)
b, Å	25.6255(10)
c, Å	14.3613(6)
β, deg	93.533(1)
V, Å^3	5020.4(4)
Z; ρ_{calcd}, g/cm^3	4; 1.369
μ, mm^{-1}	1.545
Crystal sizes, mm	0.35 × 0.25 × 0.10
Scan range, θ, deg	1.63–27.55
Number of measured reflections	32318
Number of independent reflections	11552
R_{int}	0.0367
Number of reflections with $I > 2\sigma(I)$	8756
Number of refined parameters	535
Goodness-of-fit for F^2	1.004
R factor, $I > 2\sigma(I)$	$R_1 = 0.0457$
	$wR_2 = 0.1241$
R factor (for all I_{hkl})	$R_1 = 0.0665$
	$wR_2 = 0.1410$
Residual electron density (max/min), e/Å^3	2.024/–1.075

Table 2. Selected interatomic distances (Å) and bond angles (deg) in the structure of complex **I**

Bond	d, Å	Angle	ω, deg
Sm(1)–N(2)	2.699(4)	N(2)Sm(1)N(1)	147.5(1)
		N(2)Sm(1)S(6)	109.2(1)
Sm(1)–N(1)	2.731(4)	N(1)Sm(1)S(6)	82.18(9)
Sm(1)–S(6)	2.884(1)	N(2)Sm(1)S(3)	82.42(8)
Sm(1)–S(3)	2.894(1)	N(1)Sm(1)S(3)	107.87(8)
Sm(1)–S(1)	2.917(1)	S(6)Sm(1)S(3)	141.63(4)
Sm(1)–S(2)	2.924(1)	N(2)Sm(1)S(1)	76.94(9)
Sm(1)–S(4)	2.942(1)	N(1)Sm(1)S(1)	76.71(9)
Sm(1)–S(5)	2.965(1)	S(6)Sm(1)S(1)	75.81(4)
P(1)–C(51)	1.822(7)	S(3)Sm(1)S(1)	142.12(4)
P(1)–C(11)	1.833(6)	N(2)Sm(1)S(2)	77.51(9)
S(1)–P(1)	2.010(2)	N(1)Sm(1)S(2)	75.6(1)
S(2)–P(1)	2.007(2)	S(6)Sm(1)S(2)	141.93(4)
S(3)–P(2)	2.022(2)	S(3)Sm(1)S(2)	75.51(4)
S(4)–P(2)	2.005(2)	S(1)Sm(1)S(2)	69.25(4)
S(5)–P(3)	2.000(2)	N(2)Sm(1)S(4)	139.76(9)
S(6)–P(3)	2.023(2)	N(1)Sm(1)S(4)	70.86(9)
P(2)–C(52)	1.821(6)	S(6)Sm(1)S(4)	80.49(4)
P(2)–C(12)	1.834(5)	S(3)Sm(1)S(4)	69.02(3)
P(3)–C(53)	1.827(5)	S(1)Sm(1)S(4)	141.94(4)
P(3)–C(13)	1.832(6)	S(2)Sm(1)S(4)	119.32(4)
S(1)–P(1)	2.010(2)	N(2)Sm(1)S(5)	69.73(9)
S(2)–P(1)	2.007(2)	N(1)Sm(1)S(5)	140.9(1)
S(3)–P(2)	2.022(2)	S(6)Sm(1)S(5)	68.98(3)
S(4)–P(2)	2.005(2)	S(3)Sm(1)S(5)	82.26(4)
S(5)–P(3)	2.000(2)	S(1)Sm(1)S(5)	118.52(4)
		S(2)Sm(1)S(5)	142.42(4)
		S(4)Sm(1)S(5)	78.60(4)

sample of complex **I** were measured on a Cary Eclipse Varian fluorescence photometer at 300 K ($V = 700$ V, slit 5 nm). The photoluminescence spectrum was recorded at $\lambda_{ex} = 350$ nm.

Single crystals useful for X-ray diffraction analysis were grown by the slow evaporation of a solution of complex **I** in MeCN.

X-ray diffraction analysis. An experimental array was obtained at room temperature on a Bruker X8 APEX CCD automated diffractometer using a standard procedure. The structure was solved by a direct method and refined by full-matrix least squares in the anisotropic (for non-hydrogen atoms) approximation (SHELXL-97) [19]. The crystallographic characteristics of complex **I** are given in Table 1. Selected interatomic distances and bond angles are listed in Table 2. The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (no. 943091; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif) or can be obtained from the authors.

RESULTS AND DISCUSSION

It was shown that heteroligand complex **I** was formed in a medium of *iso*-PrOH at the used concentrations and molar ratios of the reactants. According to the elemental analysis data, the composition of complex **I** is Sm(Biq)(*iso*-$Bu_2PS_2)_3$. The complex was obtained in a small excess of the sulfur-containing ligand (molar ratio Sm^{3+} : *iso*-$Bu_2PS_2^-$ = 1 : 4).

According to the X-ray diffraction data, compound **I** is a coordination 1D polymer. The chains consist of Sm(*iso*-$Bu_2PS_2)_3$ fragments and molecules

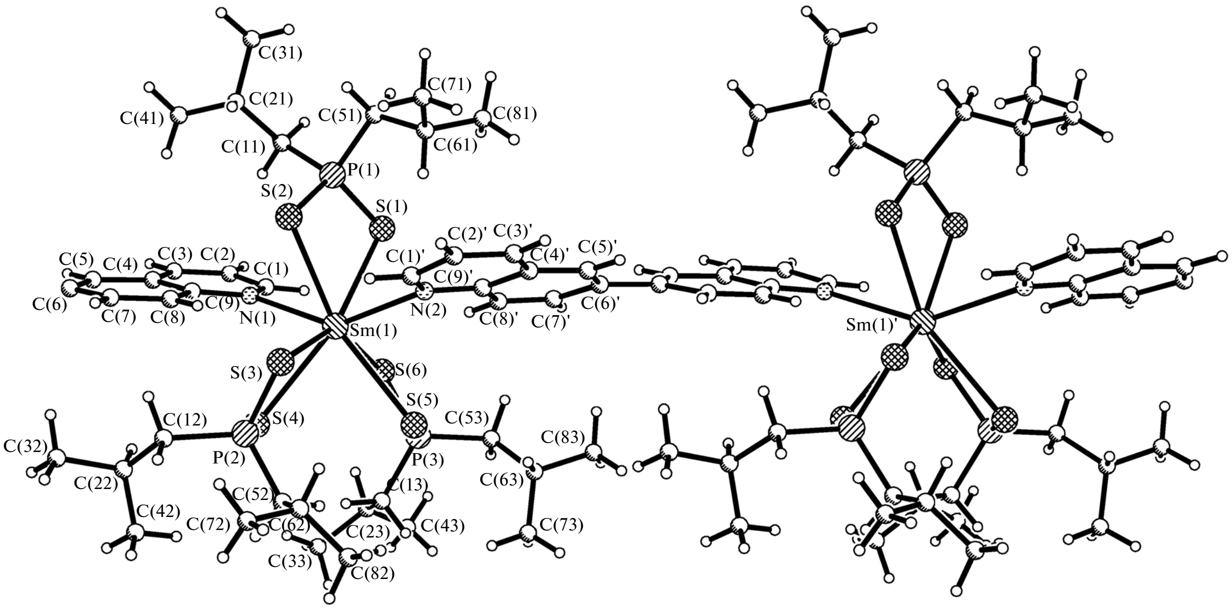

Fig. 1. Fragment of the polymer chain with enumerated non-hydrogen atoms.

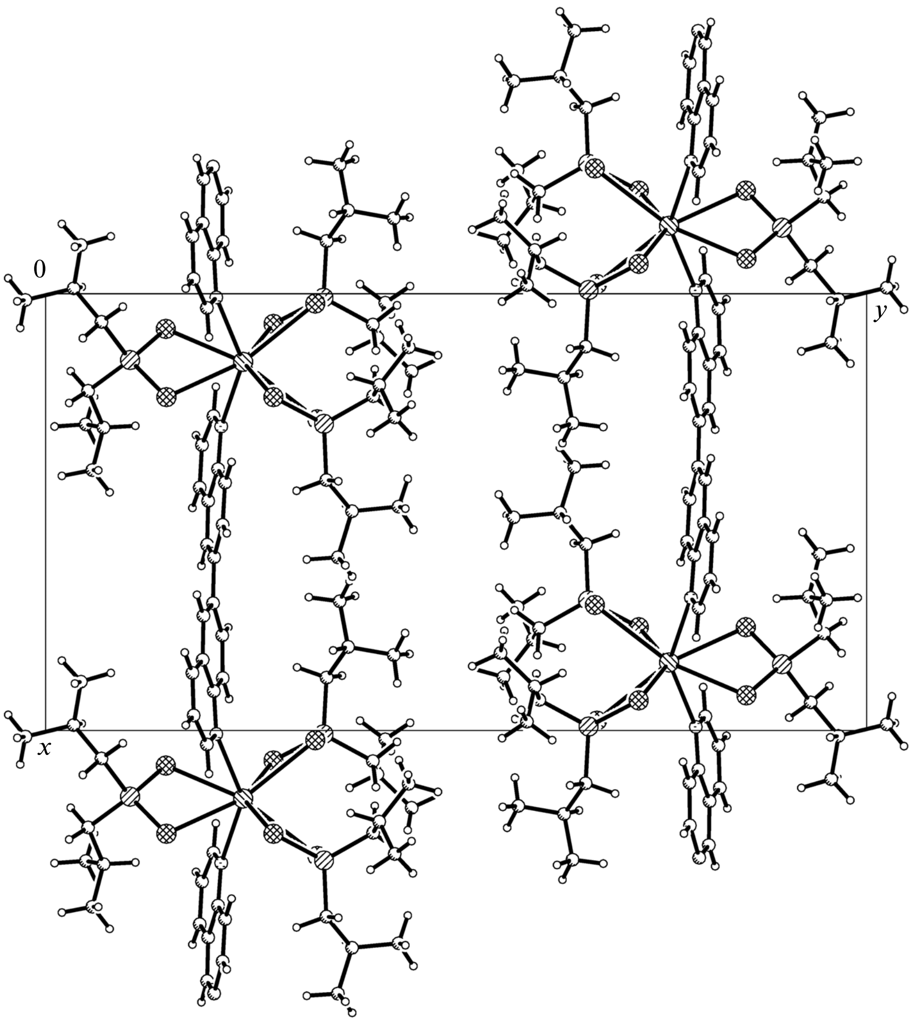

Fig. 2. Packing of the polymer chains in the projection onto the (001) plane.

of the bidentate-bridging ligand (6,6'-biquinoline). The structure of the chain fragment with designations of all atoms is depicted in Fig. 1. The coordination sphere of the Sm atom includes six S atoms of three bidentate-chelating ligands *iso*-$Bu_2PS_2^-$ (Sm–S 2.884(1)–2.965(1) Å) and two N atoms of the bidentate-bridging ligands Biq (Sm–N 2.699(4) and 2.731(4) Å). The coordination polyhedron of the Sm atom is a distorted tetragonal antiprism. The average deviation of the atoms in the quadrangular faces of the antiprism formed by the N(1)S(2)S(3)S(4) and N(2)S(1)S(5)S(6) atoms is 0.083(1) and 0.051(1) Å, respectively. Both faces are almost planar and parallel to each other, and the dihedral angle between their planes is only 7.87(6)°. Three chelate cycles SmS_2P are also nearly planar: the average deviations of the atoms from the planes of each cycle are 0.048(1), 0.086(1), and 0.076(1) Å. The pyridine and benzene rings of the bicyclic Biq fragments are almost planar, and the deviations of the atoms from their average statistical planes are 0.029(4) and 0.022(4) Å. The rotation angle of two bicyclic Biq fragments is 28.9(1)°. The Sm–S and Sm–N distances in structure **I** are consistent with similar distances in the mononuclear [Sm(Phen)(*iso*-$Bu_2PS_2)_3$] complex, whose N_2S_6 polyhedron is also a tetragonal antiprism [16].

The crystal structure of complex **I** in the projection onto the (001) plane is shown in Fig. 2. The one-dimensional polymer chains containing translationally identical Sm atoms are extended along the *x* axis. The distance between the Sm atoms in the chain is 13.668(2) Å. The closest distance between the Sm atoms in the adjacent chains multiplied by the sliding plane *n* is 9.615(2) Å, and the closest S(4)···C(3)(Biq) contact is 3.653(5) Å.

In the IR spectra of complex **I**, the bands at 623 and 523 cm^{-1} characteristic of stretching vibrations of the PS_2^--group [20–22] are shifted by 14 and 5 cm^{-1}, respectively, to high frequencies compared to the positions of these bands in the spectrum of salt *iso*-$Bu_2PS_2Na \cdot 3H_2O$. This indicates the coordination of the PS_2 fragment and agrees with the X-ray diffraction data.

The ultraviolet irradiation of the samples of complex **I** results in red luminescence. The photoluminescence spectrum of the complex contains four bands at 562, 598, 642, and 703 nm corresponding to the transitions $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $\rightarrow {}^6H_{7/2}$, $\rightarrow {}^6H_{9/2}$, $\rightarrow {}^6H_{11/2}$, respectively (Fig. 3). The bands at 598 and 642 nm are most intense.

It is most likely that complex **I** is the first example for the luminescent coordination Ln polymer containing dithiolate ligands.

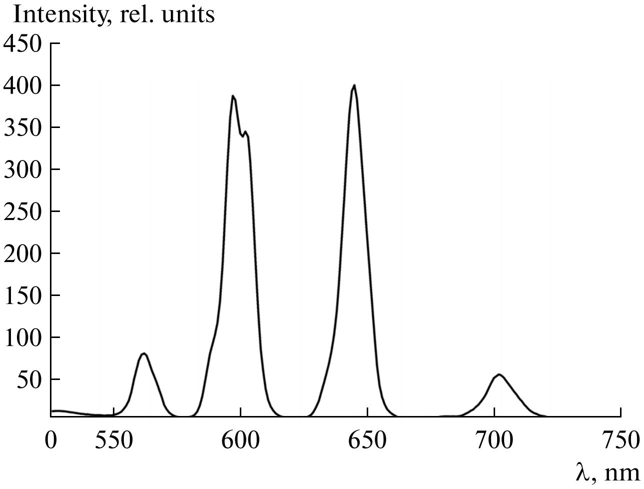

Fig. 3. Photoluminescence spectrum of complex $[Sm(Biq)(iso\text{-}Bu_2PS_2)_3]_n$.

ACKNOWLEDGMENTS

The authors are grateful to N.V. Kurat'eva for X-ray diffraction analysis, N.E. Alferova for recording IR spectra, and A.P. Zubareva and O.S. Koshcheeva for elemental analysis data.

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Translated by E. Yablonskaya