ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 1, pp. 41–48. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © Yu.A. Bryleva, T.E. Kokina, E.M. Uskov, L.A. Glinskaya, O.V. Antonova, S.V. Larionov, 2013, published in Koordinatsionnaya Khimiya, 2013, Vol. 39, No. 1, pp. 45–52.

Synthesis and Photoluminescence of the Heteroligand Sm(III) Complexes Containing Nitrogen Heterocycles (Phen, 2,2'-Bipy) and Anions $C_4H_8NCS_2^-$, *iso*-$Bu_2PS_2^-$, (*iso*-PrO)$_2PS_2^-$, and NO_3^-. Crystal Structure of Sm(2,2'-Bipy)$_2(NO_3)_3$

Yu. A. Bryleva[a, *], **T. E. Kokina**[a, b], **E. M. Uskov**[a], **L. A. Glinskaya**[a], **O. V. Antonova**[a], **and S. V. Larionov**[a]
[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences,*
pr. akademika Lavrent'eva 3, Novosibirsk, 630090 Russia
[b] *Novosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090 Russia*
**e-mail: tapzu_bryleva@mail.ru*

Received March 23, 2012

Abstract—The photoluminescence spectra of the known complexes, Sm(L)$_2$(NO$_3$)$_3$ (**I**, **II**), Sm(L)(*iso*-Bu$_2$PS$_2$)$_3$ (**III**, **IV**), Sm(L)(*iso*-Bu$_2$PS$_2$)$_2$(NO$_3$) (**V**, **VI**) (L = Phen, 2,2'-Bipy), and Sm(Phen)(C$_4$H$_8$NCS$_2$)$_3$ (**VIII**), and new compounds, Sm(Phen)((*iso*-PrO)$_2$PS$_2$)$_3$ (**VII**) , Sm(2,2'-Bipy)(C$_4$H$_8$NCS$_2$)$_3$ · 0.5CH$_2$Cl$_2$ (**IX**), are obtained and interpreted. Using the X-ray structure analysis data, the crystal structure of the [Sm(2,2'-Bipy)$_2$(NO$_3$)$_3$] complex (**II**) is determined. Structure **II** consists of discrete mononuclear molecules having a ten-vertex coordination polyhedron N$_4$O$_6$. The ligands 2,2'-Bipy and NO_3^- are bidentate-cyclic. The influence of the composition of the complexes on the photoluminescence (PL) intensity in the series **I**–**VI** is considered. The dependence of the intensity of the band with λ_{max} = 647 nm in the PL spectra of complexes **III**, **VII**, and **VIII** on the type of the sulfur-containing ligand in their composition is established. The band intensity changes in the series **VIII** > **III** > **VII**.

DOI: 10.1134/S107032841301003X

Coordination compounds of lanthanides (Ln) with organic ligands serve as materials for the production of luminescence devices [1–4]. The luminescent complexes of lanthanide ions ("hard" acids according to Pearson) with ligands (containing donor atoms N and O) ("hard" bases) are studied in most detail [5, 6]. A promising way for the preparation of a new group of compounds with photoluminescence (PL) is the synthesis of heteroligand lanthanide complexes containing molecules of nitrogen heterocycles L (L = Phen, 2,2'-Bipy) and organic anions (bearing the CS_2^- and PS_2^- groups) ("soft" bases). A considerable number of heteroligand coordination compounds Ln(L)(R$_2$NCS$_2$)$_3$ have been synthesized during recent years [7–12]. The La, Pr, Sm, Eu, Gd, Tb, and Dy complexes of similar composition (R = Et, *iso*-Bu, Bz) are shown to possess PL [13]. The heteroligand complexes Ln(L)(*iso*-Bu$_2$PS$_2$)$_3$ (Ln = Pr, Nd, Sm, Eu) were synthesized [14, 15]. In addition, the compounds Ln(L)(*iso*-Bu$_2$PS$_2$)$_2$(NO$_3$) (Ln = Nd, Sm, Eu, Tb, Dy) containing ligands of three types were prepared [15–17]. It was found that Ln(Phen)(*iso*-Bu$_2$PS$_2$)$_3$ (Ln = Nd, Sm), Sm(2,2'-Bipy)(*iso*-Bu$_2$PS$_2$)$_3$ [14, 15, 18], and Ln(L)(*iso*-Bu$_2$PS$_2$)$_2$(NO$_3$) (Ln = Nd, Sm, Eu, Tb, Dy) [15–17] are photoluminescent. The influence of the composition of the compound on the PL intensity was considered using the Nd(III) complexes as an example [15].

It seemed interesting to consider in more detail a similar influence of the Sm(III) complexes. To solve this problem, we studied the PL of both new and earlier known heteroligand Sm(III) complexes containing nitrogen heterocycles L and various 1,1-dithiolate ligands (pyrrolidinedithiocarbamate ($C_4H_8NCS_2^-$), diisopropyldithiophosphate ((*iso*-PrO)$_2PS_2^-$), and diisobutyldithiophosphinate (*iso*-$Bu_2PS_2^-$) ions, as well as NO_3^- ions.

EXPERIMENTAL

For the synthesis of the complexes we used Sm(NO$_3$)$_3$ · 6H$_2$O (analytical grade), Phen · H$_2$O (analytical grade), 2,2'-Bipy (Merck), *iso*-Bu$_2$PS$_2$Na · 3H$_2$O obtained by the evaporation of a 50% aqueous solution of *iso*-Bu$_2$PS$_2$Na (Fluka), (*iso*-PrO)$_2$PS$_2$K obtained from Zn[(*iso*-PrO)$_2$PS$_2$]$_2$ (Reakhim) using a procedure [19] proposed for the synthesis of (EtO)$_2$PS$_2$K from Ni[(EtO)$_2$PS$_2$]$_2$, and C$_4$H$_8$NCS$_2$NH$_4$ (Aldrich). The solvents were *iso*-

PrOH (special purity grade), EtOH (rectificate), and CH_2Cl_2 (reagent grade).

The complexes were synthesized using described procedures: $Sm(Phen)_2(NO_3)_3$ (**I**) and $Sm(2,2'\text{-}Bipy)_2(NO_3)_3$ (**II**) [20], Sm(Phen)(*iso*-$Bu_2PS_2)_3$ (**III**) and Sm(2,2'-Bipy)(*iso*-$Bu_2PS_2)_3$ (**IV**) [14], and Sm(Phen)(*iso*-$Bu_2PS_2)_2(NO_3)$ (**V**) and Sm(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$ (**VI**) [17].

Synthesis of tris(diisopropyldithiophosphato)(1,10-phenanthroline)samarium(III) Sm(Phen)((*iso*-PrO)$_2$PS$_2$)$_3$ (VII). A solution of (*iso*-PrO)$_2$PS$_2$K (0.26 g, 1.03 mmol) in *iso*-PrOH (7 mL) was added with stirring to a solution of $Sm(NO_3)_3 \cdot 6H_2O$ (0.09 g, 0.21 mmol) in *iso*-PrOH (2 mL). A precipitate of $NaNO_3$ that formed was filtered off on a paper filter, and a solution of Phen · H_2O (0.04 g, 0.21 mmol) in *iso*-PrOH (2 mL) was added to the filtrate. The mixture was stirred for 10 min, and a cream-colored precipitate that formed was filtered off with suction, washed with *iso*-PrOH (4 mL), and dried in a desiccator over anhydrone. The yield was 0.13 g (65%).

For $C_{30}H_{50}N_2O_6P_3S_6Sm$			
anal. calcd. (%):	C, 37.1;	H, 5.2;	N, 2.9.
Found (%):	C, 36.3;	H, 5.2;	N, 3.2.

Synthesis of tris(pyrrolidinedithiocarbamato)(1,10-phenanthroline)samarium(III) Sm(Phen)(C$_4$H$_8$NCS$_2$)$_3$ (VIII). A solution of $C_4H_8NCS_2NH_4$ (0.16 g, 1 mmol) in an *iso*-PrOH–CH_2Cl_2 (2 : 3 vol/vol) (25 mL) was added with stirring to a solution of $Sm(NO_3)_3 \cdot 6H_2O$ (0.11 g, 0.25 mmol) in *iso*-PrOH (2 mL). A precipitate of NH_4NO_3 that formed was filtered off on a paper filter, and a solution of Phen · H_2O (0.04 g, 0.25 mmol) in *iso*-PrOH (2 mL) was added to the filtrate. The mixture was stirred for 30 min, and a light yellow precipitate was treated as in the synthesis of complex **VII**. The product was recrystallized from CH_2Cl_2 (8 mL). The yield was 0.09 g (50%).

For $C_{27}H_{32}N_5S_6Sm$			
anal. calcd. (%):	C, 42.2;	H, 4.2;	N, 9.1.
Found (%):	C, 42.0;	H, 4.1;	N, 9.0.

Synthesis of tris(pyrrolidinedithiocarbamato)(2,2'-bipyridine)samarium(III)–methylene chloride (1 : 0.5) solvate Sm(2,2'-Bipy)(C$_4$H$_8$NCS$_2$)$_3$ · 0.5CH$_2$Cl$_2$ (IX). A solution of $C_4H_8NCS_2NH_4$ (0.32 g, 2 mmol) in an *iso*-PrOH–CH_2Cl_2 (1 : 1 vol/vol) (30 mL) was added with stirring to a solution of $Sm(NO_3)_3 \cdot 6H_2O$ (0.22 g, 0.5 mmol) in *iso*-PrOH (8 mL). A precipitate of $C_4H_8NCS_2NH_4$ that formed was filtered off on a paper filter, and a solution of 2,2'-Bipy (0.08 g, 0.5 mmol) in *iso*-PrOH (4 mL) was added to the filtrate. The mixture was stirred for 30 min and then treated as in the synthesis of complex **VII**. The light yellow product was recrystallized from CH_2Cl_2 (15 mL). The yield was 0.12 g (30%).

For $C_{25.5}H_{33}N_5S_6ClSm$			
anal. calcd. (%):	C, 38.9;	H, 4.2;	N, 8.9.
Found (%):	C, 38.3;	H, 4.0;	N, 8.7.

Microanalyses 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 magnetic susceptibility was measured by Faraday's method at ambient temperature. The luminescence excitation and PL spectra of solid samples **I**–**IX** were recorded on a Cary Eclipse fluorescence spectrophotometer (Varian) at $T = 300$ K, $V = 650$ V, and a gap of 5 nm. The PL spectra of complexes **I**, **III**, **V**, **VIII**, and **IX** were recorded at $\lambda_{exc} = 340$ nm; those of complexes **II**, **IV**, and **VI** were measured at $\lambda_{exc} = 320$ nm, and the spectrum of complex **VII** was obtained at $\lambda_{exc} = 330$ nm.

X-ray structure analysis. Single crystals useful for X-ray structure analysis were grown by the slow evaporation of a solution of complex **II** in MeCN. The experimental set of X-ray reflections was obtained on an X8 APEX automated diffractometer at ambient temperature 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 using the SHELXL-97 program package [21]. The main crystallographic characteristics for complex **II** are given in Table 1. Selected interatomic distances and bond angles for the structure of complex **II** are listed in Table 2. The full tables of atomic coordinates, bond lengths, and bond angles for structure **II** were deposited with the Cambridge Crystallographic Data Centre (no. 869331; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif) and can be available from the authors.

RESULTS AND DISCUSSION

Compounds **I**–**VI** were synthesized according to known procedures. New complex **VII** is formed due to the reaction of the Sm^{3+} ions with the (*iso*-PrO)$_2$PS$_2^-$ ions and Phen at a molar ratio of 1 : 5 : 1, respectively. An excess of the sulfur-containing ligand was required for the synthesis of compound **VII**. This compound is the first example for the heteroligand lanthanide complexes containing the nitrogen heterocycle and dialkyldithiophosphate ions. The known complex **VIII** [10] was synthesized by a procedure different from the described one [10] by the choice of the starting Sm(III) salt and solvent used in the synthesis. Earlier undescribed complex **IX** containing pyrro-

Table 1. Crystallographic characteristics, experimental details, and refinement parameters for the structure of complex **II**

Parameter	Value
Empirical formula	$C_{20}H_{16}N_7O_9Sm$
FW	648.75
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a, Å	16.8226(4)
b, Å	9.0461(3)
c, Å	14.9599(4)
V, Å^3	2276.6(1)
Z; ρ_{calcd}, mg/cm^3	4; 1.893
μ, mm^{-1}	2.648
Crystal sizes, mm	0.15 × 0.12 × 0.1
Scan range, θ, deg	2.90–27.00
Number of measured reflections	15328
Number of independent reflections	2475
R_{int}	0.0168
Number of reflections with $I > 2\sigma(I)$	2475
Number of refined parameters	177
Goodness-of-fit for F^2	1.062
R factor, $I > 2\sigma(I)$	$R_1 = 0.0140$, $wR_2 = 0.0368$
R factor (for all I_{hkl})	$R_1 = 0.0167$, $wR_2 = 0.0379$
Residual electron density (max/min), e/Å^3	0.631/–0.344

Table 2. Selected interatomic distances (d, Å) in the structure of complex **II**

Bond	d, Å	Bond	D, Å
Sm(1)–O(4)	2.509(2)x2	C(1)–C(6)	1.489(2)
Sm(1)–O(1)	2.510(1)x2	C(2)–C(3)	1.375(3)
Sm(1)–N(1)	2.561(1)x2	C(3)–C(4)	1.385(3)
Sm(1)–O(2)	2.567(1)x2	C(4)–C(5)	1.391(2)
Sm(1)–N(2)	2.572 (1)x2	C(5)–C(6)	1.490(2)
N(1)–C(1)	1.341(2)	C(6)–C(7)	1.389(2)
N(1)–C(5)	1.348(2)	C(7)–C(8)	1.387(2)
N(2)–C(10)	1.339(2)	C(8)–C(9)	1.378(2)
N(2)–C(6)	1.356(2)	C(9)–C(10)	1.389(2)
N(3)–O(3)	1.219(2)	N(4)–O(5)	1.214(3)
N(3)–O(2)	1.266(2)	N(4)–O(4)	1.272(2)
C(1)–C(2)	1.392(2)	N(3)–O(1)	1.276(2)

lidinedithiocarbamate ions and 2,2'-Bipy was synthesized similarly.

The experimental values of μ_{eff} for complexes **I**–**IX** (Table 3) lie in the usual range of magnetic moments for Sm(III) ($\mu_{eff} = 1.4–1.7\ \mu_B$) [22].

The structures of almost all compounds with the composition $Ln(Phen)_2(NO_3)_3$ have been studied to presently [23]. The crystals of complex **I**, as well as other compounds of this isostructural series, crystallize in the monoclinic crystal system (space group $C2/c$) and are built of the molecular mononuclear complexes [24]. Ligands NO_3^- and Phen are bidentate-chelating. The coordination polyhedron of the Sm atom is the ten-vertex polyhedron N_4O_6. The structures of compounds $Ln(2,2'\text{-}Bipy)_2(NO_3)_3$ were studied to a lower extent. We determined the crystal structure of complex **II** by X-ray structure analysis. Compound **II** is isostructural to the compounds of La(III) and Lu(III) with a similar composition [25–27]. Crystal structure **II** consists of mononuclear molecules (Fig. 1a). The coordination sphere of the Sm^{3+} ion includes four N atoms of two bidentate chelating ligands (2,2'-Bipy) and six O atoms of three bidentate-cyclic NO_3^- groups. The Sm–O and Sm–N distances

Table 3. Effective magnetic moments of complexes **I–IX**

Compound	μ_{eff}, μB
Sm(Phen)$_2$(NO$_3$)$_3$ (**I**)	1.52
Sm(2,2'-Bipy)$_2$(NO$_3$)$_3$ (**II**)	1.59
Sm(Phen)(*iso*-Bu$_2$PS$_2$)$_3$ (**III**)	1.53
Sm(2,2'-Bipy)(*iso*-Bu$_2$PS$_2$)$_3$ (**IV**)	1.51
Sm(Phen)(*iso*-Bu$_2$PS$_2$)$_2$(NO$_3$) (**V**)	1.52
Sm(2,2'-Bipy)(*iso*-Bu$_2$PS$_2$)$_2$(NO$_3$) (**VI**)	1.52
Sm(Phen)((*iso*-PrO)$_2$PS$_2$)$_3$ (**VII**)	1.52
Sm(Phen)(C$_4$H$_8$NCS$_2$)$_3$ (**VIII**)	1.52
Sm(2,2'-Bipy)(C$_4$H$_8$NCS$_2$)$_3$ · 0.5CH$_2$Cl$_2$ (**IX**)	1.52

range from 2.509(1) to 2.567(1) Å and from 2.561(1) to 2.572(1) Å, respectively (Table 2).

The molecular crystal packing of complex **II** is presented in the projection onto the plane (001) (Fig. 1b). The chains along the z axis are formed due to the participation of the O atoms of the nitrate groups in intermolecular interactions (Fig. 1c). The O(3) atoms form hydrogen bonds with the CH cycles of 2,2'-Bipy of the adjacent molecules of the complex: the distances are O(3)···C(1) 3.373(2), O(3)···C(9) 3.227(2) Å.

The structures of complexes **III** and **IV** were considered earlier [17]. According to the X-ray structure analysis data, mononuclear complex **III** and molecules of MeCN compose the crystal structure of solvate Sm(Phen)(*iso*-Bu$_2$PS$_2$)$_3$ · MeCN [17]. In compounds **III** and **IV** the coordination polyhedron of the Sm atom is the tetragonal antiprism N_2S_6. The experimental diffraction pattern of complex **V** is consistent with the theoretical one calculated on the basis of the X-ray structure analysis data for a single crystal of compound [Dy(Phen)(*iso*-Bu$_2$PS$_2$)$_2$(NO$_3$)] [17], which indicates their isostructural character. The coordination sphere of the Dy^{3+} ion includes bidentate-cyclic Phen, the NO_3^- ion, and two *iso*-$Bu_2PS_2^-$. The coordination polyhedron $N_2O_2S_4$ is a distorted dodecahedron. Probably, in compounds **V** and **VI** the Sm atoms form a similar coordination polyhedron.

The IR spectra of complexes **VII–IX** contain bands corresponding to vibrations of the main functional groups and fragments (Table 4). The IR spectrum of complex **VII** exhibits the change in the position of the ν(PS$_2$) and ν(P–O–R) bands compared to the spectrum of (*iso*-PrO)$_2$PS$_2$K, indicating the coordination of the (*iso*-PrO)$_2$$PS_2^-$ ions [28, 29]. The ν(CS$_2$) band in the IR spectra of complexes **VIII** and **IX** is shifted by 18 cm^{-1} towards high frequencies compared to the position of this band in the spectrum of $C_4H_8NCS_2NH_4$, indicating the coordination of the CS$_2$ fragment [30]. It is most likely that in complexes **VII–IX** the sulfur-containing ligands $C_4H_8NCS_2^-$, and (*iso*-PrO)$_2$$PS_2^-$ perform the bidentate-cyclic function and the structures of compounds **VII** and **VIII** and complex Sm(2,2'-Bipy)(C$_4$H$_8$NCS$_2$)$_3$ in the composition of solvate **IX** are similar to that described above for mononuclear complex **III** [17].

Red luminescence is observed upon the UV irradiation of solid samples of complexes **I–IX**. It has earlier been shown that at 300 K and λ_{exc} = 365 nm complexes **III** and **IV** have the PL characteristic of the Sm^{3+} ion [18]. The PL excitation spectra of compounds **I–IX** were recorded to obtain the optimum photoexcitation conditions (Figs. 2–5). Complexes **I**, **III**, and **V** containing Phen are efficiently excited with the UV light at 230–380 nm with λ_{max} = 340 nm (Fig. 2). Complexes **II**, **IV**, and **VI** containing 2,2'-Bipy are excited in the range from 230 to 360 nm with λ_{max} = 320 nm (Fig. 3). Therefore, the absorption edges of these complexes are shifted to the blue spectral range compared to the absorption edges of complexes **I**, **III**, and **V**. Complex **VIII** containing the pyrrolidinedithiocarbamate ion is excited with the UV light at 230–390 nm with λ_{max} = 340 nm, and

Table 4. Selected vibrational frequencies (cm^{-1}) in the IR spectra of (*iso*-PrO)$_2$PS$_2$K, C$_4$H$_8$NCS$_2$NH$_4$, and complexes **VII–IX**

Assignment	(*iso*-PrO)$_2$PS$_2$K	**VII**	Assignment	C$_4$H$_8$NCS$_2$NH$_4$	**VIII**	**IX**
ν(PS$_2$)	678, 587, 560	675, 556	ν(N–C=S)	1416, 1377	1463, 1423	1427
ν(P–O–R)	983, 938	989, 969	ν(CS$_2$)	990	1008	1008

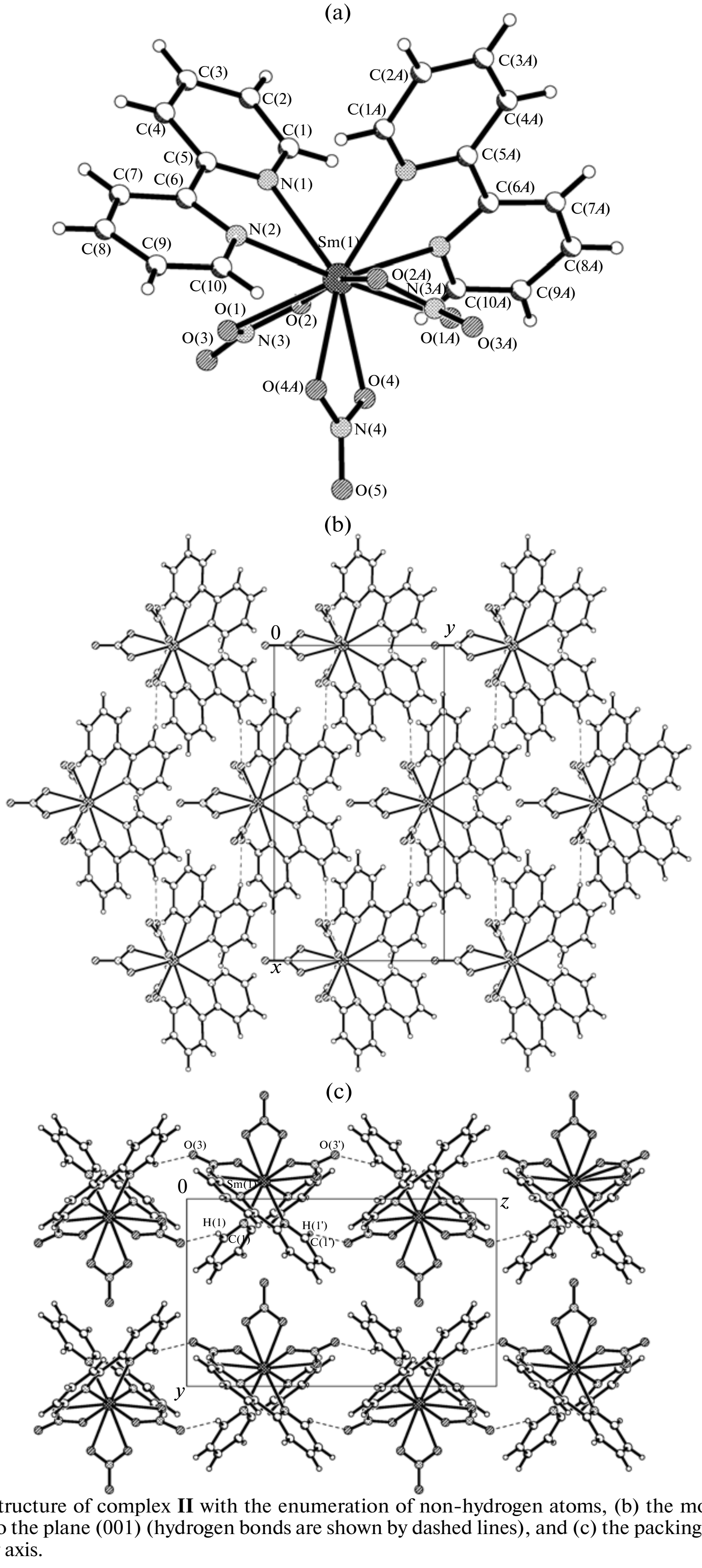

Fig. 1. (a) Molecular structure of complex **II** with the enumeration of non-hydrogen atoms, (b) the molecular packing in the structure projected onto the plane (001) (hydrogen bonds are shown by dashed lines), and (c) the packing fragment of the chains in the direction of the *z* axis.

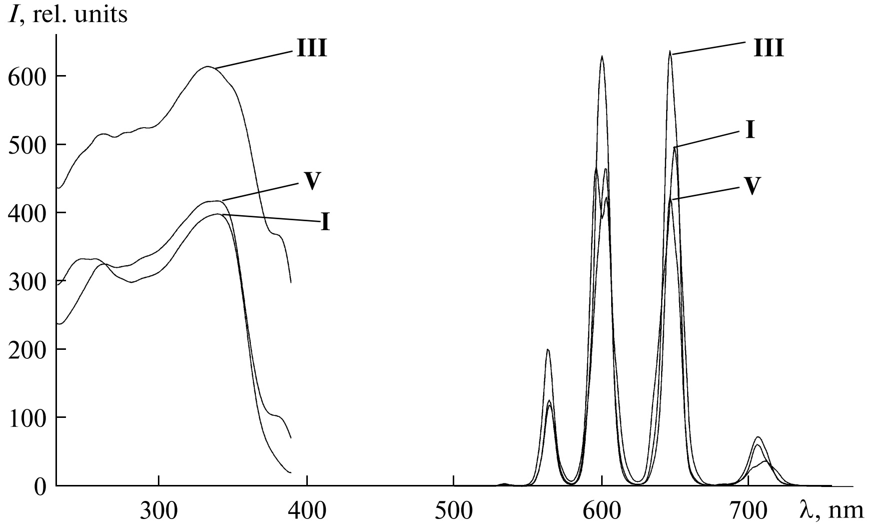

Fig. 2. Luminescence excitation and PL spectra ($V = 500$ V, gap 5 nm, $\lambda_{exc} = 340$ nm) of complexes **I**, **III**, and **V** containing 1,10-Phen.

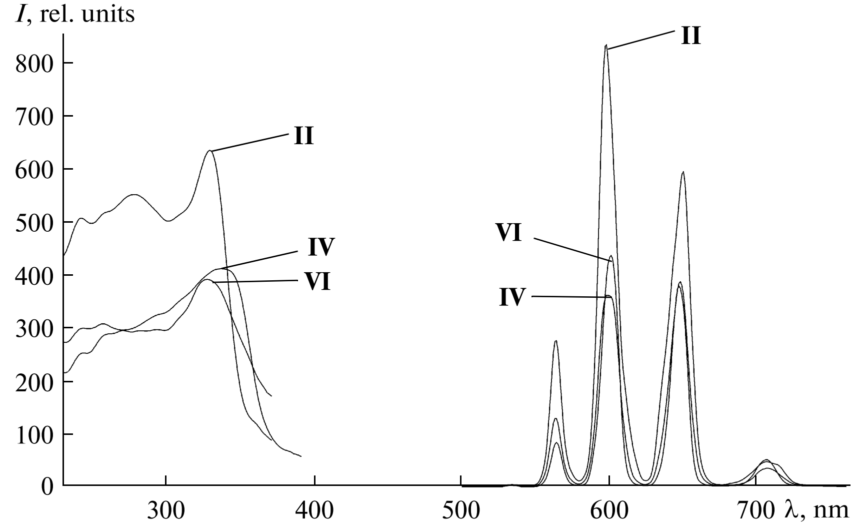

Fig. 3. Luminescence excitation and PL spectra ($V = 500$ V, gap 5 nm, $\lambda_{exc} = 320$ nm) of complexes **II**, **IV**, and **VI** containing 2,2'-Bipy.

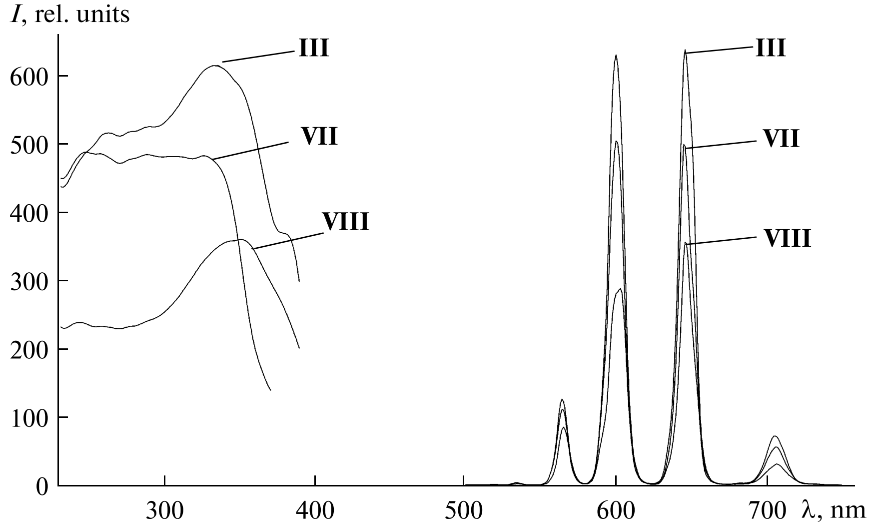

Fig. 4. Luminescence excitation and PL spectra ($V = 500$ V, gap 5 nm) of complexes **III**, **VIII** ($\lambda_{exc} = 340$ nm), and **VII** ($\lambda_{exc} = 330$ nm) with three types of sulfur-containing ligands.

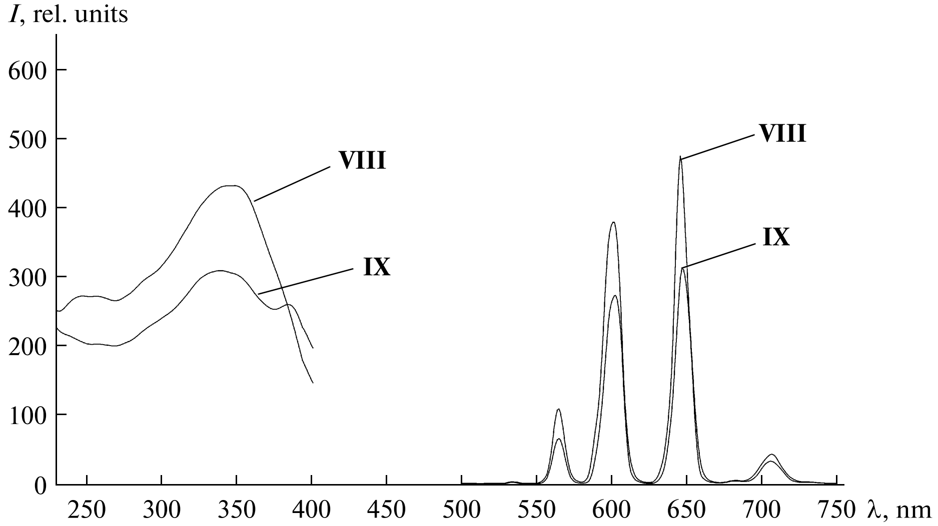

Fig. 5. Luminescence excitation and PL spectra ($V = 500$ V, gap 5 nm, $\lambda_{exc} = 340$ nm) of complexes **VIII** and **IX**.

complex **VII** containing the diisopropyldithiophosphate ion is excited at 230–350 nm with $\lambda_{max} = 330$ nm. Therefore, the shift of the absorption edge to the red spectral range is observed for complex **VIII**, whereas the absorption edge of complex **VII** exhibits a blue shift compared to the absorption edge of complex **III** (380 nm) containing the diisobutyldithiophosphinate ion (Fig. 5).

The PL spectra of complexes **I**–**IX** contain four bands with λ_{max} about 564, 600, 647, and 707 nm corresponding to the transitions $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, $^4G_{5/2} \rightarrow {}^6H_{9/2}$, and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ in the Sm^{3+} ion (Table 5). The bands with λ_{max} about 600 and 647 nm have the most intensity (I) in the spectra. The spectra of compounds **I**–**VI** were compared in order to consider the influence of the composition of the complexes on the PL at a qualitative level. Figure 2 shows the PL spectra of Phen-containing complexes **I**, **III**, and **V**. It is seen that the highest I belongs to the band in the spectrum of complex **III**, whose composition includes no NO_3^- group (coordination node SmN_2S_6). The second place in I belongs to complexes **I** (node SmN_4O_6, contains no dithiolate ligand) and **V** including three types of ligands: Phen, NO_3^-, and *iso*-$Bu_2PS_2^-$ (node $SmN_2O_2S_4$). The intensities of the bands for these complexes are approximately similar. Another

Table 5. Positions of the bands (nm) in the PL spectra of complexes **I**–**IX** (band intensities (rel. units) are given in parentheses)

Complex	Assignment			
	$^4G_{5/2} \rightarrow {}^6H_{5/2}$	$^4G_{5/2} \rightarrow {}^6H_{7/2}$	$^4G_{5/2} \rightarrow {}^6H_{9/2}$	$^4G_{5/2} \rightarrow {}^6H_{11/2}$
$Sm(Phen)_2(NO_3)_3$ (**I**)	563 (201)	596 (468)	649 (497)	710 (37)
$Sm(2,2'\text{-}Bipy)_2(NO_3)_3$ (**II**)	563 (275)	598 (832)	650 (690)	705 (52)
Sm(Phen)(*iso*-$Bu_2PS_2)_3$ (**III**)	564 (127)	600 (631)	646 (639)	706 (74)
Sm(2,2'-Bipy)(*iso*-$Bu_2PS_2)_3$ (**IV**)	563 (129)	600 (362)	648 (388)	707 (36)
Sm(Phen)(*iso*-$Bu_2PS_2)_2(NO_3)$ (**V**)	563 (119)	602 (467)	646 (424)	705 (61)
Sm(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$ (**VI**)	564 (83)	601 (436)	647 (377)	707 (47)
Sm(Phen)((*iso*-$PrO)_2PS_2)_3$ (**VII**)	564 (112)	600 (505)	645 (500)	707 (58)
$Sm(Phen)(C_4H_8NCS_2)_3$ (**VIII**)	565 (85)	603 (289)	646 (356)	707 (32)
$Sm(2,2'\text{-}Bipy)(C_4H_8NCS_2)_3 \cdot 0.5CH_2Cl_2$ (**IX**)	565 (66)	602 (275)	648 (308)	706 (33)

situation is observed when considering the PL spectra of complexes **II**, **IV**, and **VI** containing 2,2'-Bipy (Fig. 3). Compound **II** (node SmN_4O_6) occupies the first place in the value of *I*. The second place belongs to complexes **IV** (node SmN_2S_6) and **VI** (node $SmN_2O_2S_4$) having almost the same *I* of the bands.

The PL spectra of the Sm(III) complexes with Phen and various sulfur-containing ligands, viz., *iso*-$Bu_2PS_2^-$- (**III**), $(PrO)_2PS_2^-$- (**VII**), and $C_4H_8NCS_2^-$-ions (**VIII**), are shown in Fig. 4. The intensities of the bands in the spectra of these compounds change in the following order: **III > VII > VIII**. Evidently, the transition from the functional group CS_2^- to the PS_2^- group favors the PL intensity.

The intensity of the bands in the PL spectrum of complex **VIII** containing Phen is almost 1.5 times higher than *I* of the corresponding bands of compound **IX** containing 2,2'-Bipy (Fig. 5). A similar pattern is observed for complexes **III** and **IV**. The bands in the PL spectrum of compound **III** are 2.5 times more intense than the bands of complex **IV**, most likely, due to the sensitizing effect of Phen on the Sm^{3+} ion [17].

Thus, the study of the PL spectra of complexes **I–VI** and **VIII** and newly synthesized complexes **VII** and **IX** showed that these compounds luminesce in the visible spectral range. The dependence of *I* of the bands in the PL spectra on the type of the sulfur-containing ligand in the composition of the Phen-containing complexes was established. The data obtained indicate that the further syntheses and studies of the structures and PL of the lanthanide complexes with the sulfur-containing ligands bearing the donor group $ЭS_2^-$ (E = P, C) and nitrogen heterocycles are promising.

ACKNOWLEDGMENTS

The authors are grateful to D.Yu. Naumov for X-ray structure analysis, V.A. Daletskii for magnetochemical data, N.E. Alferova for recording IR spectra, A.P. Zubareva and O.S. Koshcheeva for elemental analysis data, A.V. Alekseev for X-ray diffraction analysis data, and M.I. Pakhmanov for help in PL spectra recording.

REFERENCES

1. Katkova, M.A., Vitukhnovskii, A.G., and Bochkarev, M.N., *Usp. Khim.*, 2005, vol. 74, no. 12, p. 1193.
2. Bünzli, J.-C.G., *Acc. Chem. Res.*, 2006, vol. 39, p. 53.
3. Metelitsa, A.V., Burlov, A.S., Bezuglyi, S.O., et al., *Russ. J. Coord. Chem.*, 2006, vol. 32, no. 12, p. 858.
4. Katkova, M.A. and Bochkarev, M.N., *Dalton Trans.*, 2010, vol. 39, p. 6599.
5. De Sa, G.F., Malta, O.L., de Mello Donega, C., et al., *Coord. Chem. Rev.*, 2000, vol. 196, p. 165.
6. Kido, J. and Okamoto, Y., *Chem. Rev.*, 2002, vol. 102, p. 2357.
7. Gorshkov, N.N., Sidorenko, G.V., and Suglobov, D.I., *Radiokhimiya*, 1994, vol. 36, no. 2, p. 154.
8. Fan, X.-Z., Chen, S.-P., Xie, G., et al., *Acta Chim. Sinica*, 2006, vol. 64, no. 10, p. 1022.
9. Domrachev, G.A., Zav'yalova, L.V., Svechnikov, G.S., et al., *Russ. J. Gen. Chem.,* 2003, vol. 73, no. 4, p. 560.
10. Meng, X.-X., Gao, S.-L., Chen, S.-P., et al., *Acta Chim. Sinica*, 2004, vol. 62, no. 22, p. 2233.
11. Varand, V.L., Glinskaya, L.A., Klevtsova, R.F., and Larionov, S.V., *Zh. Strukt. Khim.*, 1998, vol. 39, no. 2, p. 300.
12. Varand, V.L., Glinskaya, L.A., Klevtsova, R.F., and Larionov, S.V., *Zh. Strukt. Khim.*, 2000, vol. 41, no. 3, p. 663.
13. Regulacio, M.D., Publico, M.H., Vasquez, J.A., et al., *Inorg. Chem.*, 2008, vol. 47, no. 5, p. 1512.
14. Varand, V.L., Klevtsova, R.F., Glinskaya, L.A., and Larionov, S.V., *Russ. J. Coord. Chem.*, 2000, vol. 26, no. 11, p. 817.
15. Larionov, S.V., Varand, V.L., Klevtsova, R.F., et al., *Russ. J. Coord. Chem.*, 2008, vol. 34, no. 12, p. 931.
16. Varand, V.L, Uskov, E.M., Korol'kov, I.V., and Larionov, S.V., *Russ. J. Gen. Chem.*, 2009, vol. 79, no. 2, p. 228.
17. Bryleva, Yu.A., Kokina, T.E., Glinskaya, L.A., et al., *Russ. J. Coord. Chem.*, 2012, vol. 38, no. 11, p. 687.
18. Kokina, T.E., Klevtsova, R.F., Uskov, E.M., et al., *Zh. Strukt. Khim.*, 2010, vol. 51, no. 5, p. 976.
19. Larionov, S.V., Kirichenko, V.N., Sadovskii, A.P., and Shklyaev, A.A., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.*, 1979, no. 3, p. 87.
20. Lobanov, N.I. and Smirnova, V.A., *Zh. Neorg. Khim.*, 1963, vol. 8, no. 9, p. 2206.
21. Sheldrick G.M., *SHELXL-97. Programs for the Refinement of Crystal Structures*, Göttingen (Germany): Univ. of Göttingen, 1997.
22. Greenwood, N. and Earnshaw, A., *Chemistry of the Elements*, Oxford: Butterworth Heinemann, 2002, vol. 2.
23. Sadikov, G.G., Antsyshkina, A.S., Rodnikova, M.N., and Solonina, I.A., *Kristallografiya*, 2009, vol. 54, no. 1, p. 54.
24. Zheng, Y.-Q., Zhou, L.-X., Lin, J.-L., and Zhang, S.-W., *Z. Anorg. Allg. Chem.*, 2001, vol. 627, p. 1643.
25. Al-Karaghouli, A.R. and Wood, J.S., *Inorg. Chem.*, 1972, vol. 11, no. 10, p. 2293.
26. Kravchenko, V.B., *Zh. Strukt. Khim.*, 1962, vol. 13, no. 2, p. 345.
27. Kepert, D.L., Semenova, L.I., Sobolev, A.N., and White, A.H., *Aust. J. Chem.*, 1996, vol. 49, p. 1005.
28. Wasson, J.R., Wolterman, G.M., and Stoklosa, H.J., *Top. Curr. Chem.*, 1973, no. 35, p. 65.
29. Shopov, D., Ivanov, S., Kateva, I., and Karshalykov, K., *Izv. Otd. Khim. Nauki Blg. AN*, 1970, vol. 3, no. 1, p. 33.
30. Halls, D.J., *Microchim. Acta*, 1969, vol. 1, p. 68.