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Synthesis and Photoluminescence of Complexes $Tm(L)(iso\text{-}Bu_2PS_2)_2(NO_3)$ (L = Phen, 2,2'-Bipy). Crystal Structures of Compounds $[Ln(2,2'\text{-}Bipy)(iso\text{-}Bu_2PS_2)_2(NO_3)] \cdot C_6H_6$ (Ln = Tm, Tb)

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Abstract—Heteroligand complexes $Tm(L)(iso\text{-}Bu_2PS_2)_2(NO_3)$ (L = 2,2'-Bipy (**II**), Phen (**III**)) are synthesized. According to the X-ray phase analysis data, complex **III** is isostructural to mononuclear compound $[Dy(Phen)(iso\text{-}Bu_2PS_2)_2(NO_3)]$ including, according to the X-ray diffraction data, a coordination polyhedron $DyN_2O_2S_4$ (distorted dodecahedron). Single crystals of compounds $[Ln(2,2'\text{-}Bipy)(iso\text{-}Bu_2PS_2)_2(NO_3)] \cdot C_6H_6$ (Ln = Tm (**IV**), Tb (**V**)) are obtained. An X-ray diffraction analysis shows that the crystal structures of these isostructural compounds are formed by molecules of mononuclear complexes $[Ln(2,2'\text{-}Bipy)(iso\text{-}Bu_2PS_2)_2(NO_3)$ and uncoordinated C_6H_6 molecules. In complexes **IV** and **V**, the ligands $[Ln(2,2'\text{-}Bipy)(iso\text{-}Bu_2PS_2^-$, and NO_3^- are bidentate-cyclic. The coordination polyhedron $LnN_2O_2S_4$ is a distorted dodecahedron. Complexes **II** and **III** possess photoluminescence in the visible spectral range (λ_{max} = 478 and 477 nm, respectively).

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INTRODUCTION

Lanthanide (Ln) complexes play an important role among luminescent coordination compounds of metals with organic ligands, being interesting for the development of light-emitting diodes and biochemical sensors [1–5]. The most part of publications is devoted to the Ln complexes (hard Pearson's acids), whose ligands are hard bases and bear donor atoms N and O.

Researchers only recently began to study the luminescence of the Ln complexes with S-containing ligands (soft bases). The luminescent Ln compounds with 2-mercaptobenzthiazole, whose bidentate anions are coordinated through the S and N atoms, were thus obtained [6]. Other studied compounds contain bidentate 1,1-dithiolate ligands. Salt $Na[Eu(S_2CNMe_2)_4] \cdot 3.5H_2O$ was found to have photoluminescence (PL) at temperatures <100 K [7]. It has been found later [8] that heteroligand complexes $[Eu(L)(Et_2NCS_2)_3]$ (L = Phen, 2,2'-Bipy) [9–11] and $Eu(Phen)(Ph_2NCS_2)_3$ exhibit PL at 300 K. The studies of the PL of the heteroligand Ln complexes containing dithiocarbamate ligands were extended [12] due to using other ligands ($iso\text{-}Bu_2NCS_2^-$- and $Bz_2NCS_2^-$ ions) and a greater number of Ln (La, Pr, Sm, Eu, Gd, Tb, and Dy). Interestingly, the complexes of Sm^{3+} and Pr^{3+} ions have a more intense emission than the compounds of Eu^{3+}, Tb^{3+}, and Dy^{3+} ions [12]. The PL spectra of compounds $Sm(Phen)(C_4H_8NCS_2)_3$ and $Sm(2,2'\text{-}Bipy)(C_4H_8NCS_2)_3 \cdot 0.5CH_2Cl_2$ ($C_4H_8NCS_2^-$ is the pyrrolidinedithiocarbamate ion) were recorded [13].

We started to synthesize luminescent complexes bearing dialkyl dithiophosphinate and dialkyl dithiophosphate ligands. Compounds $Ln(L)(iso\text{-}Bu_2PS_2)_3$ (Ln = Nd, Sm) luminescing at 300 K [13–15] and complex $Sm(Phen)\{(iso\text{-}PrO)_2PS_2\}_3$ [13] were obtained. The PL intensity of complexes $Sm(Phen)(A)_3$ (A = $iso\text{-}Bu_2PS_2^-$, $iso\text{-}(PrO)_2PS_2^-$, $C_4H_8NCS_2^-$) was found to be higher than that of the compounds, whose S-containing ligands include the PS_2^- group [13]. Complexes $Ln(L)(iso\text{-}Bu_2PS_2)_2(NO_3)$ (Ln = Nd, Sm, Eu, Tb, Dy) bearing three types of ligands possess luminescence [13, 14, 16, 17]. According to the X-ray diffraction data, mononuclear complex $[Dy(Phen)(iso\text{-}Bu_2PS_2)_2(NO_3)]$ includes a coordination polyhedron $DyN_2O_2S_4$ (distorted dodecahedron) [17].

The purpose of this study is the synthesis of the heteroligand complexes of the Tm^{3+} ion containing three types of ligands (L, NO_3^- and *iso*-$Bu_2PS_2^-$ ions), the study of their PL and structures, and the determination of the structure of complex Tb(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$. X-ray diffraction data on the Ln(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$ complexes were lacking.

EXPERIMENTAL

The following reagents were used for the synthesis of the complexes: $Tm(NO_3)_3 \cdot 4H_2O$, 2,2'-Bipy, and 1,10-Phen · H_2O (analytical grade), $Tb(NO_3)_3 \cdot 5H_2O$ (high-purity grade), *iso*-$Bu_2PS_2Na \cdot 3H_2O$ obtained by the evaporation of a 50% aqueous solution of *iso*-Bu_2PS_2Na (Fluka), and *iso*-PrOH (special purity grade). Complex Tb(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$ (**I**) was synthesized using a known procedure [17].

Synthesis of (nitrato)bis(diisobutyldithiophosphinato)(2,2'-bipyridyl)thulium(III), Tm(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$ (II). A solution of *iso*-Bu_2PS_2Na · $3H_2O$ (0.29 g, 1.0 mmol) in *iso*-PrOH (5 mL) was added with stirring to a solution of $Tm(NO_3)_3 \cdot 4H_2O$ (0.11 g, 0.25 mmol) in *iso*-PrOH (2 mL). A formed precipitate of $NaNO_3$ was filtered off on a paper filter, and a solution of 2,2'-Bipy (0.04 g, 0.25 mmol) in *iso*-PrOH (2 mL) was added to the filtrate. The obtained solution was stirred for 1 h. A white precipitate formed was filtered off with suction, washed with *iso*-PrOH (3 mL), and dried in a desiccator over anhydrone. The yield was 0.15 g (75%).

For $C_{26}H_{44}N_3O_3P_2S_4Tb$

anal. calcd., %:	C, 38.8;	H, 5.5;	N, 5.2.
Found, %:	C, 38.4;	H, 5.5;	N, 5.2.

IR (KBr; ν, cm^{-1}): 528, 606 ν(PS_2), 1296, 1438, 1488, ν(NO_3), 1570, 1601 ν(C=C, C=N). $\mu_{eff} = 7.30\ \mu_B$.

Synthesis of (nitrato)bis(diisobutyldithiophosphinato)(1,10-phenanthrolinethulium(III), Tm(Phen) (*iso*-$Bu_2PS_2)_2(NO_3)$ (III). A solution of *iso*-Bu_2PS_2Na · $3H_2O$ (0.29 g, 1.0 mmol) in *iso*-PrOH (4 mL) was added with stirring to a solution of $Tm(NO_3)_3 \cdot 4H_2O$ (0.11 g, 0.25 mmol) in *iso*-PrOH (2 mL). A precipitate of $NaNO_3$ was filtered off on a paper filter, and a solution of Phen · H_2O (0.05 g, 0.25 mmol) in *iso*-PrOH (2 mL) was added to the filtrate. The obtained solution was stirred for 1 h. A white precipitate formed was filtered off with suction, washed with *iso*-PrOH (3 mL), and dried in a desiccator over anhydrone. The yield was 0.12 g (60%).

For $C_{28}H_{44}N_3O_3P_2S_4Tm$

anal. calcd., %:	C, 40.5;	H, 5.3;	N, 5.1.
Found, %:	C, 40.2;	H, 5.5;	N, 4.9.

IR (KBr; ν, cm^{-1}): 531, 608 ν(PS_2), 1288, 1426, 1506 ν(NO_3), 1589, 1627 ν(C=C, C=N). $\mu_{eff} = 7.33\ \mu_B$.

Analyses to C, H, and N were carried out on a Euro EA 3000 analyzer. IR spectra in a range of 400–3800 cm^{-1} were recorded on a Scimitar FTS2000 spectrophotometer (KBr pellets). Magnetic susceptibility was measured by the Faraday method at ambient temperature. The PL spectra of solid samples of complexes **II** and **III** were measured at 300 K on a DFS-24 fluorescence spectrophotometer, using excitation with a mercury lamp with $\lambda_{exc} = 313$ nm.

Single crystals of compounds [Tm(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$] · C_6H_6 (**IV**) and [Tb(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$] · C_6H_6 (**V**) suitable for X-ray diffraction analysis were grown by the slow evaporation of solutions of complexes **I** and **II** in benzene.

X-ray diffraction analysis. For single crystals of compounds **IV** and **V**, the unit cell parameters and reflection intensities were measured at a low temperature (150 K) on a Bruker X8 Apex CCD automated diffractometer equipped with a two-coordinate detector using a standard procedure (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). The crystallographic characteristics and details of X-ray diffraction experiments and refinement of structures **IV** and **V** are given in Table 1. The structures were solved by a direct method and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms using the SHELXL-97 program package [18]. Positions of all hydrogen atoms were determined from the difference Fourier syntheses and included into refinement in the riding model. Selected interatomic distances and bond angles for compounds **IV** and **V** are listed in Table 2. The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (nos. 920398 (**V**) and 920399 (**IV**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam. ac.uk) and are available from the authors.

X-ray phase analysis of polycrystals was carried out on a DRON-3M diffractometer (CuK_α radiation, Ni filter, 2θ range 3°–45°, increment 0.03° 2θ, scan time 3 s). Samples for the study were prepared as follows. Polycrystals were triturated in an agate mortar in the presence of heptane, and the obtained suspension was deposited on the polished side of a standard quartz cell. After heptane was dried, the sample became a thin regular layer (thickness ~100 μm). The diffraction pattern of complex **III** was indexed using the data of the theoretical diffraction pattern calculated from the X-ray diffraction data for a single crystal of the [Dy(Phen)(*iso*-$Bu_2PS_2)_2(NO_3)$] complex [17].

RESULTS AND DISCUSSION

The reactions of Tm^{3+} ions with ions *iso*-$Bu_2PS_2^-$, NO_3^- and L in *iso*-PrOH at the used concentrations in

Table 1. Crystallographic characteristics and details of X-ray experiment and structure refinement for the structures of compounds [Tm(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)] \cdot C_6H_6$ (**IV**) and [Tb(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)] \cdot C_6H_6$ (**V**)

Parameter	Value	
	IV	**V**
Empirical formula	$C_{32}H_{50}N_3O_3P_2S_4Tm$	$C_{32}H_{50}N_3O_3P_2S_4Tb$
FW	883.86	873.85
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, Å	12.9545(2)	12.9744(4)
b, Å	16.5934(3)	16.5805(5)
c, Å	19.1195(3)	19.2148(6)
β, deg	105.92(1)	105.88(1)
V, Å^3	3952.3(1)	3975.8(2)
Z; ρ_{calcd}, g/cm^3	4, 1.485	4, 1.460
μ, mm^{-1}	2.571	2.103
Crystal sizes, mm	0.34 × 0.13 × 0.08	0.4 × 0.12 × 0.08
Scan range, θ, deg	1.63–30.57	1.63–28.34
Number of measured reflections	36083	29082
Number of independent reflections (R_{int})	12092 (0.0143)	9883 (0.0157)
Number of reflections with $I > 2\sigma(I)$	10180	8373
Number of refined parameters	606	606
Goodness-of-fit for F^2	1.023	1.004
R factor, $I > 2\sigma(I)$	$R_1 = 0.0166$ $wR_2 = 0.0334$	$R_1 = 0.0172$ $wR_2 = 0.0359$
R factor (for all I_{hkl})	$R_1 = 0.0240$ $wR_2 = 0.0359$	$R_1 = 0.0245$ $wR_2 = 0.0389$
Residual electron density (max/min), e/Å^3	0.580/–0.379	0.630/–0.322

a small excess of the dithiolate ligand (molar ratio Tm^{3+} : *iso*-$Bu_2PS_2^-$ is 1 : 4) afford heteroligand complexes **II** and **III** stable in air. In addition, single crystals of compounds **IV** and **V** were obtained.

The values of μ_{eff} for complexes **II** and **III** are similar to those given for the Tm(III) complexes [19]. Therefore, the reaction of the Tm^{3+} ion with the *iso*-$Bu_2PS_2^-$ ions possessing reduction properties [20] is not accompanied by a change in the oxidation state of this ion.

According to the X-ray diffraction data, the crystals of compounds **IV** and **V** are isostructural (Table 1). Their crystal structures consist of molecules of mononuclear complexes Ln(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$ and uncoordinated benzene molecules localized between the molecules of the complexes. The molecular packing in compound IV (projection along the z axis) is shown in Fig. 1. The H···H contacts (~3.1 Å) between the hydrogen atom of the C(4)H fragment of the benzene molecule and one of the H atoms of the isobutyl group are the shortest distances between the molecules of benzene and complex Tm(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$. In structure **IV** one can distinguish layers of molecules of the complexes parallel to the yz plane. One layer falls onto one unit cell. The projection of the layer of molecules of the complex in structure **IV** is shown in Fig. 2. The shortest Ln···Ln distance is 8.873(2) Å in **IV** and 8.864(2) Å in **V**.

Table 2. Selected interatomic distances *d* (Å) and bond angles in the structures of the complexes in the composition of compounds **IV** and **V***

Bond	*d*, Å		Angle	ω, deg	
	IV	**V**		**IV**	**V**
Ln(1)–O(2)	2.436(1)	2.386(1)	O(2)Ln(1)O(1)	52.37(4)	53.35(3)
Ln(1)–O(1)	2.445(1)	2.399(1)	O(2)Ln(1)N(1)	139.14(4)	140.31(4)
Ln(1)–N(1)	2.483(1)	2.429(1)	O(1)Ln(1)N(1)	167.11(4)	165.23(4)
Ln(1)–N(2)	2.551(1)	2.506(1)	O(2)Ln(1)N(2)	74.01(4)	73.76(4)
Ln(1)–S(2)	2.8246(4)	2.7837(4)	O(1)Ln(1)N(2)	126.34(4)	127.00(4)
Ln(1)–S(4)	2.8300(4)	2.7980(3)	N(1)Ln(1)N(2)	65.33(4)	66.66(4)
Ln(1)–S(1)	2.8327(4)	2.8042(4)	O(2)Ln(1)S(2)	76.60(3)	77.18(3)
Ln(1)–S(3)	2.8572(4)	2.8207(4)	O(1)Ln(1)S(2)	85.40(3)	85.72(3)
Ln(1)–N(3)	2.875(1)	2.825(1)	N(1)Ln(1)S(2)	92.08(3)	92.33(3)
S(1)–P(1)	2.006(1)	2.003(1)	N(2)Ln(1)S(2)	80.03(3)	79.11(3)
S(2)–P(1)	2.011(1)	2.012(1)	O(2)Ln(1)S(4)	121.81(3)	121.10(3)
S(3)–P(2)	2.013(1)	2.012(1)	O(1)Ln(1)S(4)	81.84(3)	81.09(3)
S(4)–P(2)	2.011(1)	2.009(1)	N(1)Ln(1)S(4)	92.14(3)	91.31(3)
P(1)–C(11)	1.824(2)	1.825(2)	N(2)Ln(1)S(4)	136.90(3)	137.33(3)
P(1)–C(51)	1.826(2)	1.825(2)	S(2)Ln(1)S(4)	139.86(1)	140.45(1)
P(2)–C(12)	1.827(2)	1.827(2)	O(2)Ln(1)S(1)	126.05(3)	126.02(3)
P(2)–C(52)	1.827(2)	1.827(2)	O(1)Ln(1)S(1)	82.55(3)	80.93(3)
O(1)–N(3)	1.279(2)	1.277(2)	N(1)Ln(1)S(1)	84.67(3)	84.55(3)
O(2)–N(3)	1.274(2)	1.274(2)	N(2)Ln(1)S(1)	137.42(3)	137.93(3)
O(3)–N(3)	1.213(2)	1.213(2)	S(2)Ln(1)S(1)	71.21(1)	71.82(1)

* The C–C bond lengths in the benzene ring are 1.351(4)–1.379(5) Å in **IV** and 1.355(4)–1.381(5) Å in **V**. In 2,2'-Bipy the C–C bond lengths are 1.380(2)–1.389(2) Å in **IV** and 1.381(2)–1.394(2) Å in **V**. The C–C bond lengths in the *iso*-$Bu_2PS_2^-$ ligand are 1.515(3)–1.539(3) Å in **IV** and **V**.

The molecular structures of complexes Ln(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$ (Ln = Tm, Tb) are nearly the same: the structure of a molecule of complex Tm(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$ only is shown in Fig. 3. The Ln atoms coordinate pairs of the N atoms of the bidentate-cyclic 2,2'-Bipy ligand (Tm–N 2.483(1) and 2.5551(1) Å, Tb–N 2.429(1) and 2.506(1) Å), the S atoms of two bidentate-cyclic *iso*-$Bu_2PS_2^-$ ligands (Tm–S 2.8246(4)–2.8572(2) Å, Tb–S 2.7837(4)–2.825(1) Å), and the O atoms of the bidentate NO_3^- group (Tm–O 2.436(1) and 2.445(1) Å, Tb–O 2.386(1) and 2.399(1) Å). The coordination of the above ligands results in the closure of three four-membered chelates (two LnS_2P and LnO_2N cycles) and the five-membered metallocycle LnN_2C_2. The coordination polyhedron $LnN_2O_2S_4$ is a distorted dodecahedron. The calculation of the planes passing through the atoms of the chelates LnS_2P, LnN_2C_2, and LnO_2N shows that in molecules of the complexes the maximum deviation of the atoms from the root-mean-square planes of the cycles does not exceed 0.020(1) Å.

Table 3. Positions of five strongest diffraction lines (2θ) for complexes **I**, **II** and **VI**, **VII**

Complex	2θ				
I	8.34	10.11	10.50	12.31	20.35
II	8.42	10.13	10.57	12.42	20.38
VI	8.30	10.06	10.55	12.32	20.33
VII	8.29	10.13	10.42	12.18	20.32

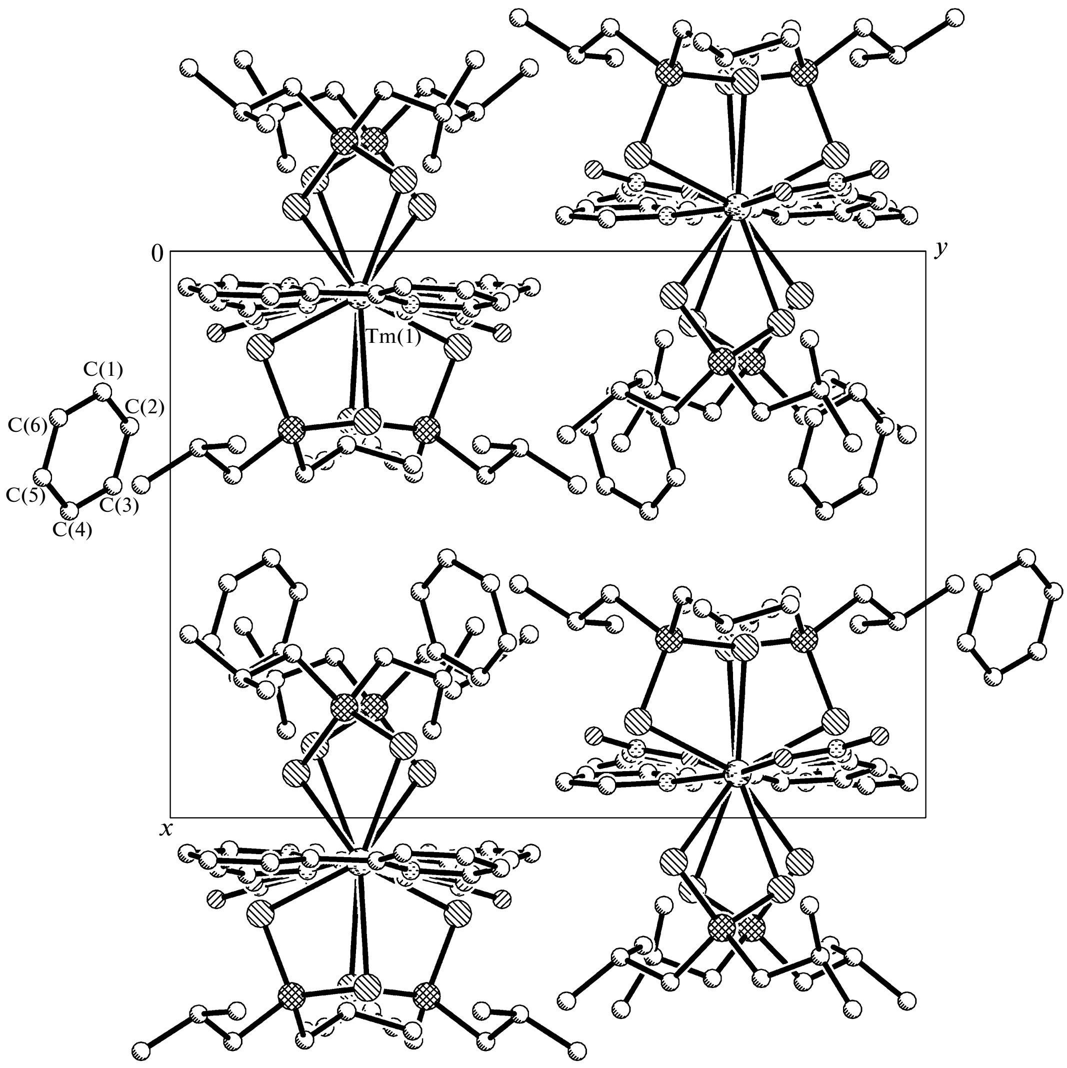

Fig. 1. Projection of the crystal structure of compound **IV** on the (001) plane (hydrogen atoms are omitted).

The dihedral angles between the SLnS and SPS planes are 2.98(3)°, 0.15(3)° for **IV**, 2.68(3)° and 0.15(3)° for **V**. The angles of unfolding of the planar pyridine cycles of the 2,2'-Bipy molecule around the C(5*p*)–C(6*p*) bonds in the both complexes are nearly equal (15.0(1)° and 15.3(1)°).

We assume that the structures of complexes **I** and **II** are similar to their structures in compounds **IV** and **V**.

Table 4. Positions of five strongest diffraction lines (2θ) for complexes **III** and **VIII**

Complex	Indices *h k l*				
	2 0 0	0 2 1	0 4 0	1 2 1	2 2 1
VIII	8.85	9.72	10.11	10.69	13.17
III	8.89	9.75	10.03	10.72	13.18

According to the X-ray phase analysis of the polycrystals (Table 3), complexes **I** and **II** and earlier obtained compounds Ln(2,2'-Bipy)(*iso*-Bu_2PS_2)$_2$(NO_3) (Ln = Sm (**VI**), Dy (**VII**)) [17] are isostructural (Table 3). This indicates a similar structure of the group of complexes Ln(2,2'-Bipy)(*iso*-Bu_2PS_2)$_2$(NO_3) (Ln = Sm, Tb, Dy, Tm), and the coordination polyhedron is $LnN_2O_2S_4$ (dodecahedron).

The X-ray phase analysis shows that complex **III** is isostructural to mononuclear complex [Dy(Phen)(*iso*-Bu_2PS_2)$_2$(NO_3)] (**VIII**) [17] containing, according to the X-ray diffraction data, the $DyN_2O_2S_4$ polyhedron (distorted dodecahedron) (Table 4). Evidently, two groups of complexes Ln(L)(*iso*-Bu_2PS_2)$_2$(NO_3) (L = 2,2'-Bipy, Phen) have the same structures.

The IR spectra of complexes **II** and **III** exhibit bands near 607 and 530 cm^{-1} characteristic of stretching vibrations of the coordinated PS_2^- group and very

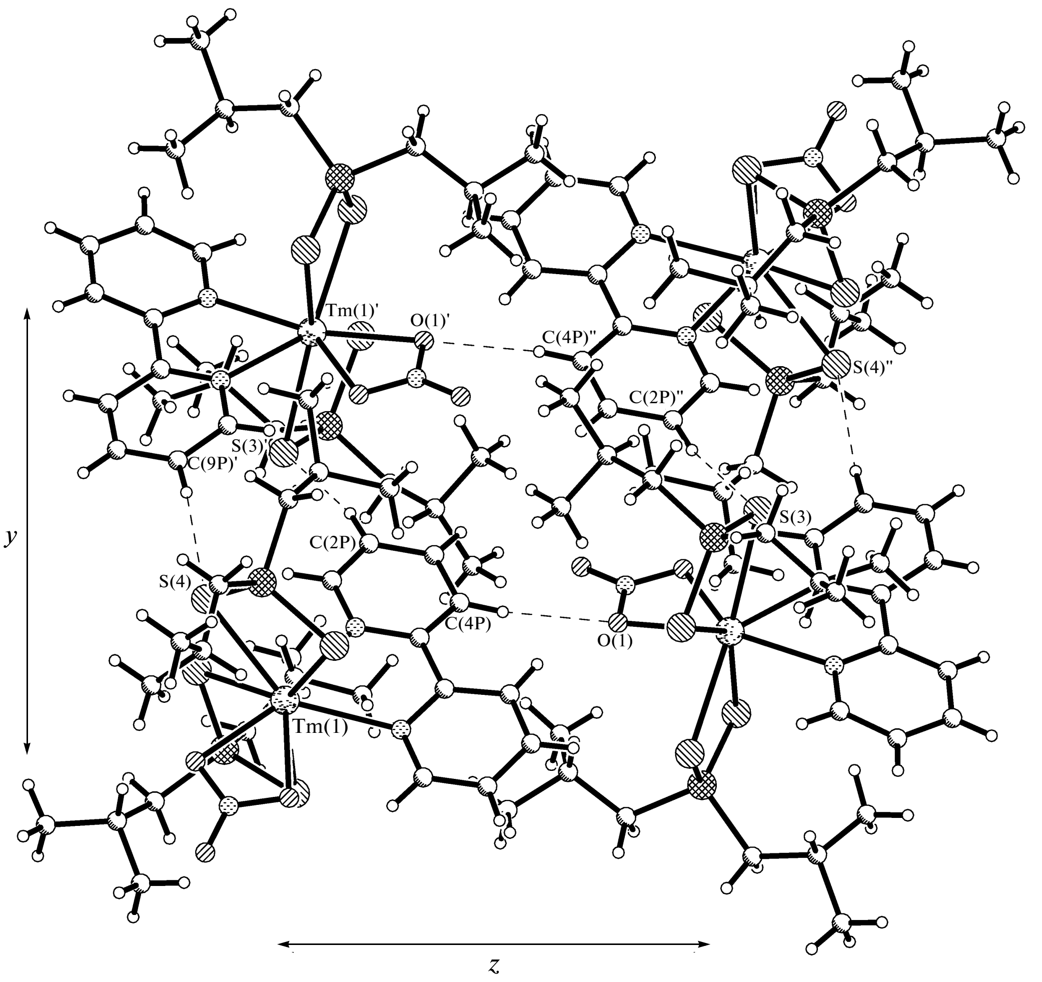

Fig. 2. Fragment of one molecular layer of complex Tm(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$ in structure **IV** (dashed lines show the shortest contacts H···O and H···S).

strong bands at 1500 and 1290 cm^{-1} that should be assigned to the split ν_3 band of the bidentate-coordinated NO_3^- group [18, 21–23].

Upon UV irradiation, complexes **II** and **III** manifest PL in the visible spectral range. The PL spectrum of complex **III** contains a band at 477 nm corresponding to the $^1G_4 \rightarrow {}^3H_6$ transition in the Tm^{3+} ion (Fig. 4). In the PL spectrum of complex **II**, a similar band with a lower intensity is observed at 478 nm. The PL spectrum of complex **III** exhibits a low-intensity band at 649 nm corresponding to the $^1G_4 \rightarrow {}^3F_4$ transition in the Tm^{3+} ion.

As a result of our work, the groups of luminescent compounds Ln(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$ and Ln(Phen)(*iso*-$Bu_2PS_2)_2(NO_3)$ containing three types of ligands were extended due to the complexes of the Tm^{3+} ion. The molecular structures of lanthanide complexes Ln(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$ were determined for the first time using X-ray diffraction analysis.

The results on the syntheses of the heteroligand lanthanide complexes containing coordinated *iso*-$Bu_2PS_2^-$ and NO_3^- ions and the data on the structures of these complexes are interesting for the chemistry of extraction processes of separation of actinides and Ln. Dithiophosphinic acids containing both alkyl (Cyanex-301) [24] and aryl [25] radicals are successfully applied in these processes. For instance, the extraction separation of Am^{3+} ions and lanthanides (La^{3+}, Eu^{3+}, Lu^{3+}) using Cyanex-301 (the aqueous phase contained $NaNO_3$) was studied [26]. In addition, the authors performed theoretical calculations for a large group of these metals, including the heteroligand complexes containing $Me_2PS_2^-$ and NO_3^- ions. Our experimental data on the Ln–S and Ln–O bond

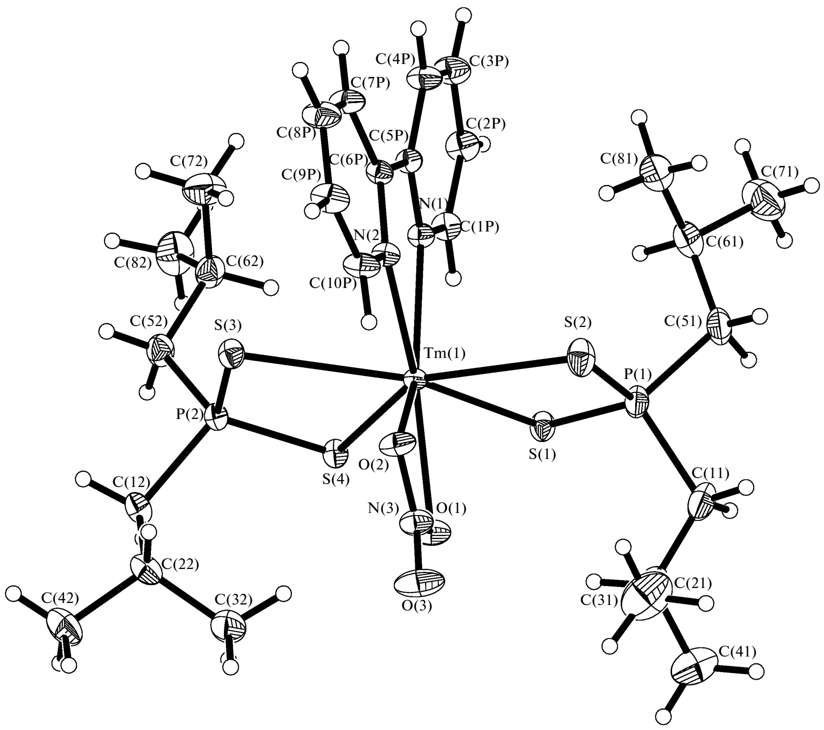

Fig. 3. Molecular structure of complex Tm(2,2'-Bipy)(*iso*-$Bu_2PS_2)_2(NO_3)$ with 50% thermal ellipsoids of non-hydrogen atoms.

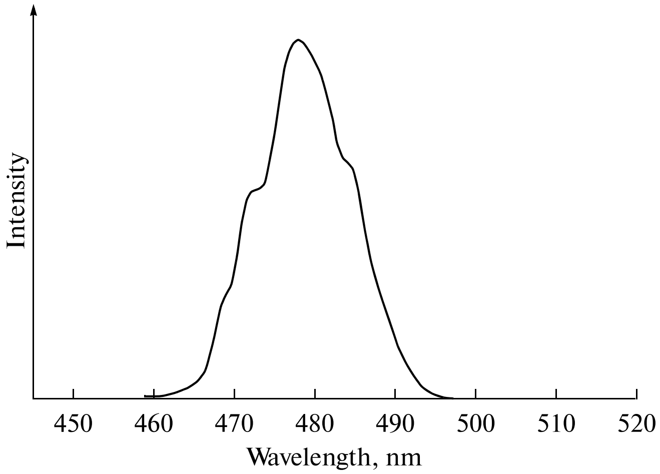

Fig. 4. PL spectrum of complex Tm(Phen)(*iso*-$Bu_2PS_2)_2(NO_3)$.

lengths in the heteroligand Ln complexes can be used in these calculations.

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