Synthesis and Photoluminescence of Complexes

**Tm(L)(iso-Bu$_2$PS$_2$)$_2$(NO$_3$) (L = Phen, 2,2'-Bipy).**

Crystal Structures of Compounds

\[ [\text{Ln}(2,2'-\text{Bipy})(iso-Bu$_2$PS$_2$)$_2$(NO$_3$)] \cdot C_6H_6 \ (\text{Ln} = \text{Tm}, \text{Tb}) \]

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**Abstract**—Heteroligand complexes Tm(L)(iso-Bu$_2$PS$_2$)$_2$(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-Bu$_2$PS$_2$)$_2$(NO$_3$)] including, according to the X-ray diffraction data, a coordination polyhedron DyN$_2$O$_2$S$_4$ (distored dodecahedron). Single crystals of compounds [Ln(2,2'-Bipy)(iso-Bu$_2$PS$_2$)$_2$(NO$_3$)] \cdot C$_6$H$_6$ (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'-Bipy)(iso-Bu$_2$PS$_2$)$_2$(NO$_3$)] and uncoordinated C$_6$H$_6$ molecules. In complexes IV and V, the ligands [Ln(2,2'-Bipy)(iso-Bu$_2$PS$_2$)$_2$(NO$_3$)] are bidentate-cyclic. The coordination polyhedron LnN$_2$O$_2$S$_4$ is a distorted dodecahedron. Complexes II and III possess photoluminescence in the visible spectral range ($\lambda_{\text{max}}$ = 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-mercaptopenthiazole, 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$_2$CNMe$_2$)$_2$] \cdot 3.5H$_2$O was found to have photoluminescence (PL) at temperatures <100 K [7]. It has been found later [8] that heteroligand complexes [Eu(L)(Et$_2$NCS$_2$)$_2$] (L = Phen, 2,2'-Bipy) [9–11] and Eu(Phen)(Ph$_2$NCS$_2$)$_3$ 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-Bu$_2$NCS$_2$- and B$_2$NCS$_2$ 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$_4$H$_8$NCS)$_3$ and Sm(2,2'-Bipy)(C$_4$H$_8$NCS)$_3$ \cdot 0.5CH$_2$Cl$_2$ (C$_4$H$_8$NCS$_2$ is the pyrrolidinedithiocarbamate ion) were recorded [13].

We started to synthesize luminescent complexes bearing dialkyl dithiophosphinate and dialkyl dithiophosphate ligands. Compounds Ln(L)(iso-Bu$_2$PS$_2$)$_2$ (Ln = Nd, Sm) luminescing at 300 K [13–15] and complex Sm(Phen)((iso-PrO)$_2$PS)$_2$ [13] were obtained. The PL intensity of complexes Sm(Phen)(A)$_3$ (A = iso-Bu$_2$PS$_2^-$, iso-(PrO)$_2$PS$_2^-$, C$_4$H$_8$NCS$_2^-$) was found to be higher than that of the compounds, whose S-containing ligands include the PS$_2$ group [13]. Complexes Ln(L)(iso-Bu$_2$PS$_2$)$_2$(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-Bu$_2$PS$_2$)$_2$(NO$_3$)] includes a coor-
and dried in a desiccator over anhydride. The yield of
analytical grade). Complex Tb(2,2’-Bipy)(iso-
Bu2PS2)(NO3) (II) was synthesized using a known procedure [17].

The following reagents were used for the synthesis of the complexes: Tb(NO3)3 · 4H2O, 2,2’-Bipy, and 1,10-Phen · H2O (analytical grade), Tb(NO3)3 · 5H2O (high-purity grade), iso-Bu2PS2Na · 3H2O obtained by the evaporation of a 50% aqueous solution of iso-Bu2PS2Na (Fluka), and iso-PrOH (special purity grade). Complex Tb(2,2’-Bipy)(iso-Bu2PS2)2(NO3) (I) was synthesized using a known procedure [17].

Synthesis of (nitrato)bis(diisobutyldithiophosphati-
no)(2,2'-bipyridyl)thulium(III), Tm(2,2’-Bipy)(iso-
Bu2PS2)2(NO3) (II). A solution of iso-Bu2PS2Na · 3H2O (0.29 g, 1.0 mmol) in iso-PrOH (5 mL) was added with stirring to a solution of Tb(NO3)3 · 4H2O (0.11 g, 0.25 mmol) in iso-PrOH (2 mL). A formed precipitate of NaNO3 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 anhydride. The yield was 0.15 g (75%).

For C26H44N3O3P2S4Tb
anal. calc., %: C, 38.8; H, 5.5; N, 5.2.
Found, %: C, 38.4; H, 5.5; N, 5.2.

IR (KBr; v, cm⁻¹): 531, 608 ν(PS2), 1288, 1426, 1506 ν(NO3), 1589, 1627 ν(C=C, C=N). μeff = 7.33 μB.

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 λexc = 313 nm.

Single crystals of compounds [Tm(2,2’-Bipy)(iso-
Bu2PS2)2(NO3) · C7H6 (IV) and [Tb(2,2’-Bipy)(iso-
Bu2PS2)2(NO3) · C7H6 (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 (MoKα radiation, λ = 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 (CuKα radiation, Ni filter, 20 range 3°–45°, increment 0.03°, 20, 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-Bu2PS2)2(NO3)] complex [17].

RESULTS AND DISCUSSION

The reactions of Tb3+ ions with ions iso-Bu2PS2,
NO3 and L in iso-PrOH at the used concentrations in