Synthesis, Structures, and Photoluminescence of Heteroligand Complexes Ln(L)(iso-Bu2PS2)2(NO3) (Ln = Sm, Tb, Dy; L = Phen, 2,2'-Bipy)


Abstract—Heteroligand complexes Ln(L)(iso-Bu2PS2)2(NO3) (Ln = Sm, Tb, Dy; L = Phen, 2,2'-Bipy) (I–VI) are synthesized. The structure of Dy(Phen)(iso-Bu2PS2)2(NO3) (III) is determined from the data of X-ray structure analysis. The crystal structure of complex III is based on discrete mononuclear molecules in which the Dy atom has distorted dodecahedral coordination (polyhedron N2O2S4). The ligands Phen, iso-Bu2PS2 and NO3 are bidentate-cyclic. According to the X-ray diffraction analysis data, complexes I and II are isostructural to compound III. Complexes I–VI have photoluminescence in the visible spectral range. The photoluminescence spectra of solid samples of compounds I–VI exhibit bands corresponding to the radiative electron transitions of the Sm3+, Tb3+, and Dy3+ ions. Among the studied compounds I–VI, the Tb(III) complexes are characterized by the most intense photoluminescence.

DOI: 10.1134/S1070328412100016

The direction related to the synthesis and study of the luminescence properties of complexes is being intensely developed in the coordination chemistry of lanthanides [1–7]. This interest is evoked by prospects of using lanthanide complexes for the preparation of luminescent devices and markers. According to Pearson’s principle, lanthanide ions are “hard” acids. Correspondingly, the known lanthanide complexes possessing luminescence usually contain “hard” bases with donor N and O atoms as ligands. It is of doubtless interest to obtain luminescent lanthanide complexes with sulfur-containing ligands, which are “soft” bases. For example, the luminescent lanthanide compounds containing the monodentate ligands coordinated through the S atom were synthesized [8]. Organic anions bearing the CS2 and PS2 groups (dithiocarbamates, xanthogenates, dithiophosphinates, and dithiophosphates) should be assigned to sulfur-containing ligands promising for the synthesis of luminescent lanthanide complexes. The lanthanide complexes containing only the indicated anions as ligands, for instance, Eu(ET2NCS2)3 and (ET4N)[Eu(ET2NCS2)4], were synthesized [9]. It seems that heteroligand complexes containing nitrous heterocycles, which are fluorophores (1,10-phenanthroline (Phen), 2,2'-bipyridine (2,2'-Bipy), and others) along with sulfur-containing ligands are more promising for the preparation of luminescent compounds. For example, compounds Eu(Phen)(ET2NCS2)3 and Eu(2,2'-Bipy)(ET2NCS2)3 have earlier been obtained [10–12]. However, it has been shown only recently [13] that the heteroligand complexes Eu(Phen)(R2NCS2)3 (R = Et, Ph) and Eu(2,2'-Bipy)(ET2NCS2)3 have luminescence at 300 K. The synthesis and photoluminescence (300 K) of the heteroligand Sm(III) and Pr(III) complexes containing R2NCS2 ions (R = Et, iso-Bu, Bz) and Phen, 2,2'-Bipy, and 5-Cl-Phen ligands were described [14]. Heteroligand compounds Nd(Phen)(iso-Bu2PS2)3(NO3), Nd(Phen)(iso-Bu2PS2)3 [15], Eu(L)(iso-Bu2PS2)3(NO3) [16], and Sm(L)(iso-Bu2PS2)3 (L = Phen, 2,2'-Bipy) [17, 18] were synthesized. All these compounds have photoluminescence. Therefore, the possibility to synthesize compounds containing three types of ligands, namely, iso-Bu2PS2, and NO3 ions and L molecules, was accomplished only in the case of the heteroligand Nd(III) and Eu(III) complexes bearing the iso-Bu2PS2 ions. It should be demonstrated that similar complexes can be synthesized for other ligands as well. In addition, it was necessary to obtain data on the crystal structures of compounds Ln(L)(iso-Bu2PS2)3(NO3), since the X-ray structure analysis data are available only for complex Y(Phen)(iso-Bu2PS2)3(NO3) [19].
The purpose of this work is the synthesis of the heteroligand Sm(III), Tb(III), and Dy(III) complexes containing the \( \text{iso-Bu}_2\text{PS}_2 \), and \( \text{NO}_3^- \) ions and the Phen or 2,2'-Bipy molecule and the study of their structures and photoluminescence.

**EXPERIMENTAL**

The following reagents were used in the synthesis of the complexes: Sm\((\text{NO}_3)_3\) · 6H\(_2\)O and Phen · H\(_2\)O (analytical grade), Tb\((\text{NO}_3)_3\) · 5H\(_2\)O and Dy\((\text{NO}_3)_3\) · 5H\(_2\)O (high-purity grade), and \( \text{iso-Bu}_2\text{PS}_2\text{Na} \cdot 3\text{H}_2\text{O} \) obtained by the evaporation of a 50% aqueous solution of \( \text{iso-Bu}_2\text{PS}_2\text{Na} \) (Fluka). The solvents used were \( \text{iso-Bu}_2\text{PS}_2\text{Na} \) · PrOH (special purity grade) and MeCN (analytical grade).

**Synthesis of (nitrato)bis(diisobutyldithiophosphinato)(1,10-phenanthroline)samarium(III) Sm(Phen)\((\text{iso-Bu}_2\text{PS}_2\text{Na})_2(\text{NO}_3)\) (I).** A solution of \( \text{iso-Bu}_2\text{PS}_2\text{Na} \) · 3H\(_2\)O (0.22 g, 0.75 mmol) in \( \text{PrOH} \) (2 mL) was added to the filtrate. The resulting solution was stirred for 20 min, and the precipitate formed was filtered off on a paper filter, and a solution of Phen (0.04 g, 0.25 mmol) in \( \text{PrOH} \) (3 mL) was added to the filtrate. The precipitate was treated in the same way as in the synthesis of compound I. The yield was 0.15 g (75%).

**Synthesis of (nitrato)bis(diisobutyldithiophosphinato)(1,10-phenanthroline)terbium(III) Tb(Phen)\((\text{iso-Bu}_2\text{PS}_2\text{Na})_2(\text{NO}_3)\) (II).** A solution of \( \text{iso-Bu}_2\text{PS}_2\text{Na} \) · 3H\(_2\)O (0.29 g, 1 mmol) in \( \text{iso-PrOH} \) (5 mL) was added with stirring to a solution of Sm\((\text{NO}_3)_3\) · 6H\(_2\)O (0.11 g, 0.25 mmol) in \( \text{iso-PrOH} \) (3 mL). A precipitate of NaNO\(_3\) that formed was filtered off on a paper filter, and a solution of Phen · H\(_2\)O (0.05 g, 0.25 mmol) in \( \text{iso-PrOH} \) (2 mL) was added to the filtrate. The resulting solution was stirred for 40 min, and a cream-colored precipitate formed was filtered off with suction, washed with \( \text{iso-PrOH} \) (4 mL), and dried in a desiccator above anhydrone. The yield was 0.10 g (50%).

**Synthesis of (nitrato)bis(diisobutyldithiophosphinato)(1,10-phenanthroline)dysprosium(III) Dy(Phen)\((\text{iso-Bu}_2\text{PS}_2\text{Na})_2(\text{NO}_3)\) (III).** A solution of \( \text{iso-Bu}_2\text{PS}_2\text{Na} \cdot 3\text{H}_2\text{O} \) (0.29 g, 1 mmol) in MeCN (6 mL) was added with stirring to a solution of Dy\((\text{NO}_3)_3\) · 3H\(_2\)O (0.11 g, 0.25 mmol) in MeCN (2 mL). A precipitate of NaNO\(_3\) that formed was filtered off on a paper filter, and a solution of Phen · H\(_2\)O (0.05 g, 0.25 mmol) in MeCN (2 mL) was added to the filtrate. The resulting solution was stirred for 20 min, and the formed white precipitate was filtered off with suction, washed with MeCN (5 mL), and dried in a desiccator above anhydrone. The yield was 0.09 g (40%).

**Synthesis of (nitrato)bis(diisobutyldithiophosphinato)(2,2'-bipyridine)samarium(III) Sm(2,2'-Bipy)(\text{iso-Bu}_2\text{PS}_2\text{Na})_2(\text{NO}_3)\) (IV).** A solution of \( \text{iso-Bu}_2\text{PS}_2\text{Na} \) · 3H\(_2\)O (0.29 g, 1 mmol) in \( \text{iso-PrOH} \) (4 mL) was added with stirring to a solution of Sm\((\text{NO}_3)_3\) · 6H\(_2\)O (0.11 g, 0.25 mmol) in \( \text{iso-PrOH} \) (2 mL). A precipitate of NaNO\(_3\) that formed was filtered off on a paper filter, and a solution of 2,2'-Bipy (0.08 g, 0.50 mmol) in \( \text{iso-PrOH} \) (2 mL) was added to the filtrate. The resulting solution was stirred for 40 min. The cream-colored precipitate formed was treated in the same way as in the synthesis of compound I. The yield was 0.15 g (75%).

**Synthesis of (nitrato)bis(diisobutyldithiophosphinato)(2,2'-bipyridine)terbium(III) Tb(2,2'-Bipy)(\text{iso-Bu}_2\text{PS}_2\text{Na})_2(\text{NO}_3)\) (V).** A solution of \( \text{iso-Bu}_2\text{PS}_2\text{Na} \) · 3H\(_2\)O (0.29 g, 1 mmol) in \( \text{iso-PrOH} \) (2 mL) was added to the filtrate. The precipitate was treated similarly to that in the synthesis of compound I. The yield was 0.12 g (65%).

**Synthesis of (nitrato)bis(diisobutyldithiophosphinato)(1,10-phenanthroline)dysprosium(III) Dy(Phen)\((\text{iso-Bu}_2\text{PS}_2\text{Na})_2(\text{NO}_3)\) (VI).** A solution of \( \text{iso-Bu}_2\text{PS}_2\text{Na} \) · 3H\(_2\)O (0.29 g, 1 mmol) in \( \text{iso-PrOH} \) (2 mL) was added to the filtrate. The precipitate was treated similarly to that in the synthesis of compound I. The yield was 0.17 g (85%).

**IR ((KBr), \( \nu \), cm\(^{-1}\)):** 528, 603 \( \nu(\text{PS}_2) \), 1281, 1426, 1503 \( \nu(\text{NO}_3) \), 1590, 1620 \( \nu(\text{C}=\text{C}, \text{C}=\text{N}) \). \( \mu_{\text{eff}} = 10.27 \mu\text{B} \).

**IR ((KBr), \( \nu \), cm\(^{-1}\)):** 528, 603 \( \nu(\text{PS}_2) \), 1281, 1426, 1503 \( \nu(\text{NO}_3) \), 1590, 1620 \( \nu(\text{C}=\text{C}, \text{C}=\text{N}) \). \( \mu_{\text{eff}} = 1.52 \mu\text{B} \).