Synthesis and Molecular and Crystal Structures of Binuclear Complexes of Sm(III), Eu(III), Gd(III), Tb(III), and Dy(III) Nitrates with 4,4,10,10-Tetramethyl-1,3,7,9-Tetraazospiro[5.5]undecane-2,8-Dione

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Abstract—Binuclear complexes of Sm(III), Eu(III), Gd(III), Tb(III), and Dy(III) nitrates with 4,4,10,10-tetramethyl-1,3,7,9-tetraazospiro[5.5]undecane-2,8-dione (C11H20N4O2, SC)—[Sm(NO3)3(SC)(H2O)]2 (I), [Eu(NO3)3(SC)(H2O)]2 (II), [Gd(NO3)3(SC)(H2O)]2(NO3)2 (III), [Tb(NO3)3(SC)(H2O)]2 (IV), and [Dy(NO3)3(SC)(H2O)]2 (V) are synthesized, and their X-ray diffraction analyses are carried out. The crystals of complexes I–V are monoclinic: space group P21/n for I and P21/c for II, IV, and V. In centrosymmetric coordination complexes II, IV, and V, the Ln atoms are coordinated by two O(1) and O(2) atoms of two molecules of the SC ligands bound by a symmetry procedure (1 – x, –y, 1 – z), three bidentate nitrate anions, and a water molecule. The coordination numbers of the metal atoms are equal to 9, and the coordination polyhedra are considerably distorted three-capped trigonal prisms, whose bases include the O(1), O(2), O(12), and O(3), O(7), O(9) atoms. The dihedral angle between the bases of the prism is 18°, and that between the mean planes of the side faces is 55°–71° for I, 17° and 55°–71° for II, 16° and 55°–70° for IV, and 16° and 55°–70° for V. The Sm...Sm distance in complex I is 9.44 Å, Eu...Eu in II is 9.42 Å, Tb...Tb in IV is 9.36 Å, and Dy...Dy in V is 9.36 Å. The gadolinium atom in complex III is coordinated by two oxygen atoms of two ligand molecules bound by a symmetry procedure (–x, –y + 1, –z + 1), two bidentate nitrate anions, and three water molecules. One of the nitro groups in compound III is localized in the external coordination sphere of the metal. The coordination number of gadolinium is 9, and the coordination polyhedron is a significantly distorted three-capped trigonal prism, whose base includes the O(1), O(2), O(7) and O(4), O(5), O(9) atoms. The dihedral angle between the bases of the prism is 22.8°, and that between the mean planes of the side faces is 53°–72°. The Gd...Gd distance in complex III is 9.17 Å.

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INTRODUCTION

Coordination compounds of rare-earth metals with ligands of the class of cyclic spirobisuresae remains almost unstudied to date. One of these ligands is 4,4,10,10-tetramethyl-1,3,7,9-tetraazospiro[5.5]undecane-2,8-dione, or spirocarbon (C11H20N4O2, SC).

This ligand as a urea precursor has a series of valuable biological properties: a low toxicity level, LD50 = 3000 mg/kg of the weight of white mice [1], membrane tropism [2], and the ability to penetrate through and to be accumulated in mice and human cytoplasm of leukemia L1210 and CEM-T4 cell lines, respectively [3]. This ligand also favors an increase in the amount of protein and a decrease in starchiness in oats grains [4]. The efficiency of application of spirocarbon as a stimulator of callus formation in Forsythia europaea and root formation in Philadelphus coronaries [5] was proved, and the efficiency of using spirocarbon as a stimulator of growth and development in sheep breeding was shown [6]. Therefore, the synthesis and study of coordination compounds of this ligand as a hard Lewis base will clarify the chemistry of the interaction of Sk with rare-earth metal atoms in more detail.

The purpose of this work is to synthesize coordination compounds of Sm(III), Eu(III), Gd(III), Tb(III), and Dy(III) nitrates, being hard Lewis acids, with spirocarbon and water molecules, namely, [Sm(NO3)3(SC)(H2O)]2 (I), [Eu(NO3)3(SC)(H2O)]2 (II), [Gd(NO3)3(SC)(H2O)]2(NO3)2 (III), [Tb(NO3)3(SC)(H2O)]2 (IV), and...
and to determine their structures.

**EXPERIMENTAL**

**Synthesis of I.** The reagents were Sm(NO$_3$)$_3$·6H$_2$O (reagent grade), SC obtained according to a described procedure [7], and acetone (special purity grade). A weighed sample of samarium nitrate (1.72 g, 3.8 mmol) was dissolved in acetone (20 mL), spirocarbon (0.82 g, 3.1 mmol) was introduced, and the mixture was magnetically stirred for 5–10 min. The obtained solution was filtered and left to stand in a closed vessel for several days to form crystals. Isolated pale orange crystals were filtered off, washed with acetone, and dried in air. The yield was ~62% (based on the ligand).

**Synthesis of II.** The reagents were Eu(NO$_3$)$_3$·6H$_2$O (reagent grade), SC obtained using a described procedure [7], and acetone (special purity grade). A weighed sample of europium nitrate (3.17 g, 7.1 mmol) was dissolved in acetone (20 mL), and spirocarbon (1.8 g, 7 mmol) was added. The reaction mixture was magnetically stirred for 5–10 min. The obtained solution was filtered and left to stand in an open vessel for several days to form crystals. Isolated pale yellow crystals were filtered off, washed with acetone, and dried in air. The yield was ~87% (based on the ligand).

**Synthesis of III.** The reagents were Gd(NO$_3$)$_3$·6H$_2$O (reagent grade), SC obtained according to a described procedure [7], and acetone (special purity grade). A weighed sample of gadolinium nitrate (2.21 g, 4.9 mmol) was dissolved in acetone (20 mL), and then spirocarbon (1.10 g, 4.3 mmol) was added. The reaction mixture was magnetically stirred for 5–10 min. The obtained solution was filtered and left to stand in an open vessel for several days to form crystals. Isolated white crystals were filtered off, washed with acetone, and dried in air. The yield was ~79% (based on the ligand).

**Synthesis of IV.** The reagents were Tb(NO$_3$)$_3$·5H$_2$O (reagent grade), SC obtained according to a described procedure [7], and acetone (special purity grade). A weighed sample of terbium nitrate (3.04 g, 6.9 mmol) was dissolved in acetone (20 mL), and then spirocarbon (1.45 g, 5.6 mmol) was added. The reaction mixture was magnetically stirred for 5–10 min. The obtained solution was filtered and left to stand in an open vessel for several days to form crystals. Isolated pale pinkish crystals were filtered off, washed with acetone, and dried in air. The yield was ~98% (based on the ligand).

**Synthesis of V.** The reagents were Dy(NO$_3$)$_3$·5H$_2$O (reagent grade), SC obtained according to a described procedure [7], and acetone (special purity grade). A weighed sample of dysprosium nitrate (2.37 g, 5.4 mmol) was dissolved in acetone (20 mL), and then spirocarbon (1.06 g, 4.1 mmol) was added. The reaction mixture was magnetically stirred for 5–10 min. The obtained solution was filtered and left to stand in an open vessel for several days to form crystals. Isolated pale greenish crystals were filtered off, washed with acetone, and dried in air. The yield was ~64% (based on the ligand).

The reaction mixture was magnetically stirred for 5–10 min. The obtained solution was filtered and left to stand in an open vessel for several days to form crystals. Isolated white crystals were filtered off, washed with acetone, and dried in air. The yield was ~79% (based on the ligand).

The element analysis results for complexes I–V are presented in Table 1. Analyses to C, H, and N in complexes I–V were performed on an EA-3000 elemental analyzer (EuroVctor, Italy).

<table>
<thead>
<tr>
<th>Compound (empirical formula)</th>
<th>Content (found/calculated), %</th>
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<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>I (C$<em>{22}$H$</em>{44}$N$<em>{14}$O$</em>{24}$Sm$_2$)</td>
<td>22.19/22.22</td>
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<tr>
<td>II (C$<em>{22}$H$</em>{44}$N$<em>{14}$O$</em>{24}$Eu$_2$)</td>
<td>22.11/22.16</td>
</tr>
<tr>
<td>III (C$<em>{22}$H$</em>{52}$N$<em>{14}$O$</em>{28}$Gd$_2$)</td>
<td>20.52/20.72</td>
</tr>
<tr>
<td>IV (C$<em>{22}$H$</em>{44}$N$<em>{14}$O$</em>{24}$Tb$_2$)</td>
<td>21.89/21.90</td>
</tr>
<tr>
<td>V (C$<em>{22}$H$</em>{44}$N$<em>{14}$O$</em>{24}$Dy$_2$)</td>
<td>21.59/21.77</td>
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