STRUCTURE OF [Dy(Phen)(C$_4$H$_8$NCS)$_2$]$_3$·3CH$_2$Cl$_2$ SOLVATE.

MAGNETIC PROPERTIES AND PHOTOLUMINESCENCE OF [Ln(Phen)(C$_4$H$_8$NCS)$_2$]$_3$ (Ln = Sm, Eu, Tb, Dy, Tm) COMPLEXES


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It is found that diffraction patterns of complexes I-V of the composition [Ln(Phen)(C$_4$H$_8$NCS)$_2$]$_3$ (Ln = Sm, Eu, Tb, Dy, and Tm respectively) are similar. Single crystals of [Dy(Phen)(C$_4$H$_8$NCS)$_2$]$_3$·3CH$_2$Cl$_2$ (VI) obtained are. According to the X-ray crystallographic data, in the structure of VI the unit cell contains two crystallographically independent molecules of the [Dy(Phen)(C$_4$H$_8$NCS)$_2$]$_3$ complex and six CH$_2$Cl$_2$ molecules. The N$_2$S$_6$ coordination polyhedron of the Dy atom is a distorted square antiprism. In the range of 2-300 K the magnetic properties of complexes I-V are studied. It is found that complex III passes to the magnetically ordered state; the spontaneous magnetization at 2 K is 24 600 G·cm$^3$/mol. At 300 K compounds I-IV exhibit photoluminescence in the visible spectral range. It is found that the photoluminescence intensity of complex I is several times higher than the photoluminescence intensity of complexes II-IV.

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An important role in the development of luminescent devices is played by lanthanide (Ln) complexes with organic ligands [1-5]. The works published are usually devoted to the investigation of luminescence of Ln complexes with O and N donor ligands. The study of the structure and luminescence of Ln complexes with S-containing ligands has been started only recently. Luminescent Ln compounds with a monothiolate ligand 2-mercaptobenzothiazole, whose anions are coordinated through S and N atoms, according to the X-ray crystallographic data [6], are obtained. The Ln complexes with 1,1-dithiolate ligands (dithiocarbamates, dithiophosphinates, dithiophosphates) have drawn the attention. It is shown that the Na[Eu(S$_2$CNMe$_2$)$_4$]·3.5H$_2$O complex exhibits photoluminescence (PL) at a temperature <100 K [7]. The introduction of Ln fluorophores into the composition of complexes (nitrogen heterocycles such as 1,10-phenanthroline (Phen) and 2,2′-bipyridyl (2,2′-Bipy)) increases the luminescence intensity of the compounds. The works [8, 9] describe the synthesis and structure of [Eu(L)(Et$_2$NCS)$_2$]$_3$ (L = Phen, 2,2′-Bipy) complexes having a EuN$_2$S$_6$ coordination core. It is found that the [Eu(L)(Et$_2$NCS)$_2$]$_3$ and [Eu(Phen)(Ph$_2$NCS)$_2$]$_3$ complexes exhibit PL at 300 K [10]. The authors of [11] investigated at 300 K

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PL of mixed-ligand Ln complexes (La, Pr, Sm, Eu, Gd, Tb, and Dy), containing different dithiocarbamate $R_2NCS_2$ ligands ($R = Et, i$-Bu, and Bz) and nitrogen heterocycles L and 5-$Cl$-Phen. The PL intensity depends on the type of substituents in the $R_2NCS_2$ ligand and changes in the order Bz $>$ Et $>$ i-Bu. Moreover, these authors determined the crystal structures of $[Sm(Phen)(i-Bu_2NCS_2)]_3$, $[Pr(Phen)(Et_2NCS_2)]_3$, and $[Pr(Phen) (i$-$Bu_2NCS_2)]_3$ complexes [11]. It seemed interesting to study the structure and properties of mixed-ligand Ln complexes with the dithiocarbamate ligand having a fragment of the nitrogen heterocycle. The pyrrolidinedithiocarbamate ($C_4H_8NCS_2$) ion is available as such a ligand. The synthesis of mixed-ligand $[Ln(Phen)(C_4H_8NCS_2)]_3$ (Ln = Sm, Eu, Tb, Dy, Tm) complexes is described in [12-14].

The aim of this work is to study the structure, magnetic properties, and PL of these complexes.

**EXPERIMENTAL**

For the synthesis of the complexes Sm(NO$_3$)$_3$·6H$_2$O (analytical grade), Eu(NO$_3$)$_3$·6H$_2$O, Tm(NO$_3$)$_3$·4H$_2$O (chemically pure), Tb(NO$_3$)$_3$·5H$_2$O, Dy(NO$_3$)$_3$·5H$_2$O (reagent grade), Phen·H$_2$O (analytical grade), $C_4H_8NCS_2$·NH$_4$ (Aldrich) were used. Solvents were i-PrOH (high purity grade) and CH$_2$Cl$_2$ (chemically pure).

**Synthesis of tris(pyrrolidinedithiocarbamate)(1,10-phenanthroline)samarium(III) $[Sm(Phen)(C_4H_8NCS_2)]_3$** (I). To a solution of 0.11 g (0.25 mmol) of Sm(NO$_3$)$_3$·6H$_2$O in 2 ml of i-PrOH a solution of 0.16 g (1.0 mmol) of $C_4H_8NCS_2$·NH$_4$ in 25 ml of the i-PrOH–CH$_2$Cl$_2$ mixture (2:3 in volume) was added under stirring. The NH$_3$NO$_3$ precipitate formed was filtered out on a paper filter, then to the filtrate a solution of 0.05 g (0.25 mmol) of Phen was added. The precipitate was filtered and dried in a desiccator over anhydron. The yield was 0.13 g (70%). Found, %: C 42.1, H 4.2, N 9.1. Calculated for $C_{32}H_{27}N_{10}Sm$: C 42.0, H 4.1, N 8.9.

**Synthesis of tris(pyrrolidinedithiocarbamate)(1,10-phenanthroline)europium(III) $[Eu(Phen)(C_4H_8NCS_2)]_3$** (II), tris(pyrrolidine thiocarbamate)(1,10-phenanthroline) terbium (III) $[Tb(Phen)(C_4H_8NCS_2)]_3$ (III), tris(pyrrolidinedithiocarbamate)(1,10-phenanthroline)dysprosium (III) $[Dy(Phen)(C_4H_8NCS_2)]_3$ (IV), tris(pyrrolidinedithiocarbamate)(1,10-phenanthroline)thulium(III) $[Tm(Phen)(C_4H_8NCS_2)]_3$ (V) was performed by the above procedure. The yield was 70%, 70%, 80%, and 40% respectively. For II found, %: C 42.3, H 4.7, N 9.1. Calculated for $C_{32}H_{27}N_{10}Eu$: C 42.1, H 4.2, N 9.1. For III found, %: C 42.0, H 4.1, N 8.9. Calculated for $C_{32}H_{27}N_{10}Tb$: C 41.7, H 4.1, N 9.0. For IV found, %: C 40.8, H 4.1, N 8.8. Calculated for $C_{32}H_{27}N_{10}Dy$: C 41.1, H 4.1, N 9.0. For V found, %: C 41.1, H 4.4, N 8.8. Calculated for $C_{32}H_{27}N_{10}Tm$: C 41.2, H 4.1, N 8.9.

The C, H, N microanalyses were carried out on a Euro EA 3000 analyzer. The molecular weight of complex I in the (CHCl$_3$) solution was found by vapor-phase osmometry on a Knauer apparatus. The powder X-ray diffraction (XRD) analysis of polycrystals of complexes I-V was performed on a Shimadzu XRD-7000 diffractometer (CuK$_\alpha$ radiation, Ni filter, 20 range 5-60°, step 0.03° 20, point acquisition time 1 s). In order to perform powder XRD the precipitates of complexes I-V were obtained by slow evaporation of the solvent (without a ventilator). Samples for the study were prepared as follows: polycrystals were ground in an agate mortar in the presence of heptane; the suspension obtained was deposited on a polished side of the standard quartz cuvette. After heptanes evaporation the sample represented a thin uniform layer (thickness of ~100 μm).

On slow evaporation of the solution of complex IV in CH$_2$Cl$_2$ single crystals of $[Dy(Phen)(C_4H_8NCS_2)]_3$·3CH$_2$Cl$_2$ compound (VI) suitable for the X-ray crystallographic analysis were grown. For the single crystal of compound VI the unit cell parameters and reflection intensities were measured at a low temperature (150 K) on an automated Bruker X8 Apex CCD diffractometer equipped with a two-dimensional detector using the standard procedure (MoK$_\alpha$ radiation, $\lambda = 0.71073$ Å, graphite monochromator). Crystallographic characteristics, details of the XRD experiments and refinement of structure VI are summarized in Table 1. The structure was solved by a direct method and refined by the full-matrix least squares technique.