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Syntheses, Structures, and Phosphorescence of Complexes (A)[Gd(L)$_4$] and [Gd(Phen)(L)$_3$] (L = *iso*-$Bu_2PS_2^-$, $C_4H_8NCS_2^-$; A = NH_4^+, Et_4N^+)

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Abstract—Complexes (A)[Gd(L)$_4$] and [Gd(Phen)(L)$_3$] (L = *iso*-$Bu_2PS_2^-$, $C_4H_8NCS_2^-$; A = NH_4^+, Et_4N^+) are synthesized. The crystal structure of compound [Gd(Phen)(*iso*-Bu_2PS_2)$_3$] · MeCN is determined by X-ray diffraction analysis (CIF file CCDC no. 1455418). The structure consists of molecules of the mononuclear complex [Gd(Phen)(*iso*-Bu_2PS_2)$_3$] and MeCN. The coordination polyhedron N_2S_6 of the Gd atom is a distorted antiprism. The complexes exhibit phosphorescence in a range of 400–600 nm. The energies of the triplet levels of the ligands $C_4H_8NCS_2^-$ (23336 cm^{-1}) and *iso*-$Bu_2PS_2^-$ (23506 cm^{-1}) are determined from the phosphorescence spectra of complexes (A)[Gd(L)$_4$] in frozen ethanol (77 K).

Keywords: complex, gadolinium, 1,1-dithiolate ligands, structure, phosphorescence

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INTRODUCTION

The complexes of lanthanides (Ln) with organic ligands are widely used for the production of luminescent devices [1–4]. The most part of published works deal with the luminescence of Ln complexes with O- and N-donor ligands. The studies on the luminescence of the Ln complexes with S-containing ligands have been started quite recently. The luminescent Ln compounds containing monothiolate ligands were described [5–9]. The complexes with 1,1-dithiolate ligands were found to exhibit luminescence. Complex Na[Eu(S_2CNMe_2)$_4$] · 3.5H_2O possesses photoluminescence (PL) only at low temperatures (<100 K) [10]. The PL of the heteroligand dithiocarbamate complexes [Eu(L')(Et_2NCS_2)$_3$] (L' = Phen, 2,2'-Bipy) and Eu(Phen)(Ph_2NCS_2)$_3$ at 300 K was described [11]. The PL of the Ln complexes (Ln = La, Pr, Sm, Eu, Gd, Tb, Dy) containing ligands $R_2NCS_2^-$ (R = Et, *iso*-Bu, Bz) and 2,2'-Bipy, Phen, and 5-Cl-Phen [12], as well as that of compounds [Ln(Phen)($C_4H_8NCS_2$)$_3$] and [Ln(2,2'-Bipy)($C_4H_8NCS_2$)$_3$] · 0.5CH_2Cl_2 (Ln = Sm, Eu, Tb, Dy, Tm) [13, 14] and [Ln(Phen)($C_5H_{10}NCS_2$)$_3$] (Ln = Sm, Pr, Eu, Tb, Dy) [15] at 300 K, was studied. In addition, the PL at 300 K was observed for the dithiophosphinate complexes [Ln(L')(*iso*-Bu_2PS_2)$_2$(NO_3)] (Ln = Sm, Tb, Dy, Tm; L' = Phen, 2,2'-Bipy) [16, 17] and [Sm(L')(*iso*-Bu_2PS_2)$_3$] (L' = Phen, 2,2'-Bipy) [18], as well as for dithiophosphate complex Sm(Phen)((*iso*-PrO)$_2PS_2$)$_3$ [19].

The molar absorption coefficients of the forbidden *f*–*f* transitions for Ln^{3+} ions are low ($\varepsilon \approx 1–10$ mol^{-1} L cm^{-1}) and, hence, the narrow absorption bands corresponding to these transitions are superimposed, as a rule, on the "tails" of more intense absorption bands ($\varepsilon \approx 10^4–10^5$ mol^{-1} L cm^{-1}) corresponding to the transitions inside the organic ligands. For these reasons, the *f*–*f* luminescence is excited due to the absorption of photons by the ligands, the energy of the excited states of which is transferred to the *f* terms of the electron shell of the Ln^{3+} ions. The efficiency of the energy transfer is governed by the rate constants of each step in this multistep process. Owing to the fast intersystem crossing, the ligand gets, as a rule, to the excited singlet state S_1 from which the energy transfer to the Ln^{3+} ion is also possible. However, the presence of the

heavy Ln^{3+} ion with a high spin-orbital coupling constant results in the situation where the intersystem crossing becomes predominant for the ligand, and the ligand transits to the excited triplet state T_1 (transition $S_1 \rightarrow T_1$).

Thus, in the most part of cases, the energy transfer to the Ln^{3+} ion occurs from the T_1 state of the ligand with the energy E_T. It is shown for Eu(III) and Tb(III) β-diketonates that the highest efficiency of the energy transfer and, correspondingly, a higher quantum yield of *f–f* luminescence are achieved in the case where E_T is by 1000–2000 cm^{-1} higher than the energy of the level of the Ln^{3+} ion to which the energy transfers [1]. These are the levels $^5D_1$ (19000 cm^{-1}) and $^5D_0$ (17300 cm^{-1}) for the Eu(III) complexes, whereas this is the $^5D_4$ level (20500 cm^{-1}) for the Tb(III) complexes. The use of a set of organic molecules with different energies of the triplet state made it possible to show that for the ligands with $E_T > 19000$ cm^{-1} in the Eu(III) complexes the $^5D_1$ level was populated first and the $^5D_0$ level began to luminesce only in 1 μs [1]. Only the $^5D_0$ level is emitting if $E_T < 19000$ cm^{-1}.

Thus, the E_T energy of the T_1 level of the ligand is the main factor governing the luminescence intensity of the Ln(III) complexes. The coordination of the ligand to the Ln^{3+} ion can change the value of E_T and, therefore, the phosphorescence spectra of the complexes of the Gd^{3+} ion measured in frozen solutions (liquid nitrogen temperature) are used for the determination of E_T. The Gd^{3+} ion was chosen because of the high energy of the resonance level $^6P_{7/2}$ (32000 cm^{-1}) compared to that of the T_1 state of many organic ligands, which makes the energy transfer to this ion impossible. Therefore, the emission spectra of the complexes of the Gd^{3+} ion contain only the phosphorescence bands corresponding to the energy transitions $T_1 \rightarrow S_0$. It is assumed that E_T of the ligand for the Gd(III) complexes and complexes of other Ln(III) are close.

The values of E_T of ligands $Et_2NCS_2^-$, 2,2'-Bipy, and 5-Cl-Phen were found to be 23095, 22727, and 21142 cm^{-1}, respectively [12]. The energies of the T_1 level of Phen lie in a range of 21882–22222 cm^{-1} depending on the type of dithiocarbamate ligand [12]. Published data on the energies of the T_1 levels of dithiophosphinate and dithiophosphate ligands for the Ln(III) complexes are lacking.

This work is devoted to the syntheses and study of the structures of the Gd(III) complexes with pyrrolidinedithiocarbamate and diisobutyldithiophosphinate ions ($C_4H_8NCS_2^-$ and *iso*-$Bu_2PS_2^-$, respectively). To determine the T_1 levels of the coordinated ligands, the phosphorescence spectra of these compounds at 77 K in frozen ethanol and in the solid state were used.

EXPERIMENTAL

The following reagents were used for the syntheses of the complexes: $GdCl_3 \cdot 6H_2O$ and Phen · H_2O (analytical grade), *iso*-$Bu_2PS_2Na \cdot 3H_2O$ obtained by the evaporation of a 50% aqueous solution of *iso*-Bu_2PS_2Na (Fluka), Et_4NCl (high-purity grade), and $C_4H_8NCS_2NH_4$ (Aldrich, 97%). The solvents used were *iso*-PrOH (special purity grade), MeCN (analytical grade), CH_2Cl_2 (reagent grade), and EtOH (rectified).

Synthesis of ammonium tetrakis(pyrrolidinedithiocarbamato)gadolinate $(NH_4)[Gd(C_4H_8NCS_2)_4]$ (I). A solution of $C_4H_8NCS_2NH_4$ (0.33 g, 2.0 mmol) in an EtOH–CH_2Cl_2 (1 : 1 vol/vol) mixture (20 mL) was added with stirring to a solution of $GdCl_3 \cdot 6H_2O$ (0.19 g, 0.5 mmol) in EtOH (2 mL), and the obtained mixture was evaporated by 2/3 of the volume. A precipitate that formed was filtered off on a glass filter with suction. The filtrate was evaporated to a minimum volume, and a white precipitate was filtered off with suction, washed with EtOH (2 times by 3 mL), and dried in a drying box over anhydrone. The yield was 0.08 g (25%).

For $C_{20}H_{36}N_5S_8Gd$

anal. calcd., %:	C, 31.6;	H, 4.8;	N, 9.2.
Found, %:	C, 32.8;	H, 5.1;	N, 8.9.

IR (KBr), ν, cm^{-1}: 1009 ν(CS_2), 1425 ν(C⎓N).

Synthesis of tetraethylammonium tetrakis(diisobutyldithiophosphinato)gadolinate $(Et_4N)[Gd(iso\text{-}Bu_2PS_2)_4]$ (II). A solution of *iso*-$Bu_2PS_2Na \cdot 3H_2O$ (0.57 g, 2.0 mmol) in EtOH (4 mL) was added with stirring to a solution of $GdCl_3 \cdot 6H_2O$ (0.19 g, 0.5 mmol) in EtOH (2 mL). A precipitate of NaCl was filtered off, and a solution of Et_4NCl (0.08 g, 0.5 mmol) in *iso*-PrOH (4 mL) was added to the filtrate. The mixture was stirred for 1 h, a precipitate of NaCl was filtered off, and the filtrate was evaporated to dryness. Dichloromethane (8 mL) was added to the dry product, an undissolved residue was filtered off, and the filtrate was evaporated to dryness. A white substance was dried in a drying box over anhydrone. The yield was 0.28 g (50%).

For $C_{40}H_{92}NP_4S_8Gd$

anal. calcd., %:	C, 42.2;	H, 8.2;	N, 1.2.
Found, %:	C, 42.7;	H, 8.1;	N, 1.2.

IR (KBr), ν, cm^{-1}: 528 $\nu_s(PS_2)$, 621 $\nu_{as}(PS_2)$.

Synthesis of tris(pyrrolidinedithiocarbamato)(1,10-phenanthroline)gadolinium(III) $[Gd(Phen)(C_4H_8NCS_2)_3]$ (III). A solution of $C_4H_8NCS_2NH_4$ (0.16 g, 1.0 mmol) in an *iso*-PrOH–CH_2Cl_2 (2 : 3 vol/vol) mixture (25 mL) was added with stirring to a

solution of $GdCl_3 \cdot 6H_2O$ (0.09 g, 0.25 mmol) in *iso*-PrOH (2 mL). A precipitate of NH_4NO_3 was filtered off, and a solution of Phen · H_2O (0.05 g, 0.25 mmol) in *iso*-PrOH (2 mL) was added to the filtrate. The mixture was stirred for 1 h. A precipitate was filtered off and dried in a drying box over anhydrone. The product was recrystallized from CH_2Cl_2 (8 mL), and the solvent was evaporated to a minimum volume. A white precipitate was filtered off and dried in a drying box over anhydrone. The yield was 0.12 g (60%).

For $C_{27}H_{32}N_5S_6Gd$

anal. calcd., %:	C, 41.8;	H, 4.2;	N, 9.0.
Found, %:	C, 41.8;	H, 4.0;	N, 9.0.

IR (KBr), ν, cm^{-1}: 1010 $\nu_{as}(CS_2)$, 1428 ν(C=N), 1585, 1620 ν(C=C), ν(C=N).

Synthesis of tris(diisobutyldithiophosphinato)(1,10-phenanthroline)gadolinium(III) [Gd(Phen)(*iso*-$Bu_2PS_2)_3$] (IV). A solution of *iso*-$Bu_2PS_2Na \cdot 3H_2O$ (0.57 g, 2.0 mmol) in MeCN (7 mL) was added with stirring to a solution of $GdCl_3 \cdot 6H_2O$ (0.19 g, 0.5 mmol) in EtOH (2 mL). A precipitate of NaCl was filtered off, and a solution of Phen · H_2O (0.10 g, 0.5 mmol) in MeCN (2 mL) was added to the filtrate. The solution was evaporated to dryness to form oil. A solid phase was formed after recrystallization from hot MeCN. A white substance was filtered off and dried in a drying box over anhydrone. The yield was 0.28 g (65%).

For $C_{36}H_{62}N_2P_3S_6Gd$

anal. calcd., %:	C, 44.8;	H, 6.5;	N, 2.9.
Found, %:	C, 43.8;	H, 6.5;	N, 2.7.

IR (KBr), ν, cm^{-1}: 535 $\nu_s(PS_2)$, 615 $\nu_{as}(PS_2)$, 1591 ν(C=C), ν(C=N).

Single crystals of compound [Gd(Phen)(*iso*-$Bu_2PS_2)_3$] · MeCN (**IVa**) suitable for X-ray diffraction analysis were grown by the evaporation of a solution of complex **IV** in warm MeCN.

Microanalyses 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 in KBr pellets on a Scimitar FTS2000 spectrophotometer.

X-ray diffraction analysis. The unit cell parameters and reflection intensities of compound **IVa** 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, λ = 0.71073 Å, graphite monochromator). The crystallographic characteristics and details of the X-ray diffraction experiment and structure refinement for compound **IVa** are presented in Table 1. The structure was solved by a direct method and refined by full-matrix least squares on F^2 in the anisotropic approximation for non-hydrogen atoms using the SHELXL-97 program package [20]. The positions of hydrogen atoms were calculated geometrically and refined in the riding model (the parameters of the hydrogen atoms were calculated in each refinement cycle by the coordinates of the corresponding C atoms). The positions of the hydrogen atoms of the MeCN molecule were localized from the difference electron density synthesis and included into the refinement in the isotropic approximation together with non-hydrogen atoms. Selected interatomic distances and bond angles are given in Table 2. The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1455418; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) and are available from the authors.

X-ray phase analysis was carried out on a DRON-3M diffractometer (CuK_α radiation, Ni filter, Bragg–Brentano focusing). Polycrystals of complex **III** were triturated in an agathic mortar in the presence of heptane, and the obtained suspension was deposited on the polished side of a standard quartz cell. After heptane was evaporated, the sample represented a thin regular layer (thickness ~100 μm). The detection was carried out with a rate of 1 deg/min at room temperature in the range of 2θ angles from 5° to 60°.

A setup in which samples were excited with the fourth harmonic of a neodymium laser (266 nm, 5 ns) was used for recording the kinetics and phosphorescence spectra of complexes **I–IV**. The complexes were dissolved in ethanol, and the solutions were frozen in quartz cells with a thickness of 2–5 mm. The solid samples were triturated and squeezed between two quartz glasses. In both cases, the samples were placed in a quartz optical cryostat where they were kept in liquid nitrogen. Luminescence was focused to the inlet gap of an MDR-23 monochromator and detected with a PMT-84 photomultiplier. The signal from the PMT was delivered to a Lecroy Wave Suffer 64 digital oscillograph, which made it possible to digitize the luminescence kinetics in the range from nanoseconds to hundreds of milliseconds. The kinetics detected in a wide spectral range was transformed into the scan of luminescence spectra in time.

RESULTS AND DISCUSSION

Complex **I** is formed as a result of the reaction of $GdCl_3 \cdot 6H_2O$ and $C_4H_8NCS_2NH_4$ (molar ratio 1 : 4) in an EtOH–CH_2Cl_2 mixture at room temperature in air via the reaction

Table 1. Crystallographic characteristics and experimental and structure refinement details for compound **IVa**

Parameter	Value
Empirical formula	$C_{38}H_{65}N_3P_3S_6Gd$
FW	1006.45
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	11.0574(4)
b, Å	15.0710(5)
c, Å	15.4560(5)
α, deg	89.161(1)
β, deg	75.479(1)
γ, deg	73.382(1)
V, Å^3	2384.7(1)
Z; ρ_{calcd}, g/cm^3	2; 1.402
μ, mm^{-1}	1.783
Crystal sizes, mm	0.16 × 0.13 × 0.08
Scan θ, range, deg	1.90–30.98
Number of measured/independent reflections (R_{int})	32346/13202 (0.0274)
Number of reflections with $I > 2\sigma(I)$	11512
Number of refined parameters	473
GOOF on F^2	1.027
R factor, $I > 2\sigma(I)$	$R_1 = 0.0266$, $wR_2 = 0.0538$
R factor (for all I_{hkl}) wR_2	$R_1 = 0.0345$, $wR_2 = 0.0563$
Residual electron density (max/min), *e*/Å^3	0.748/–0.395

Table 2. Selected interatomic distances (*d*) and bond angles (ω) in complex **IV** in the composition of compound **IVa***

Bond	*d*, Å	Bond	*d*, Å
Gd(1)–N(1F)	2.585(2)	S(1)–P(1)	2.0102(7)
Gd(1)–N(2F)	2.619(2)	S(2)–P(1)	2.0111(7)
Gd(1)–S(1)	2.8960(5)	S(3)–P(2)	2.0143(7)
Gd(1)–S(2)	2.8697(5)	S(4)–P(2)	2.0105(7)
Gd(1)–S(3)	2.8424(5)	S(5)–P(3)	2.0005(7)
Gd(1)–S(4)	2.9313(5)	S(6)–P(3)	2.0127(7)
Gd(1)–S(5)	2.8963(5)	P(2)–C(21)	1.822(2)
Gd(1)–S(6)	2.8698(5)	P(2)–C(25)	1.822(2)
P(1)–C(11)	1.819(2)	P(3)–C(31)	1.824(2)
P(1)–C(15)	1.829(2)	P(3)–C(35)	1.811(2)
C(1S)–C(2S)	1.441(4)	C(2S)–N(1S)	1.135(4)
Angle	ω, deg	Angle	ω, deg
N(1F)Gd(1)N(2F)	63.45(5)	S(2)Gd(1)S(5)	83.34(1)
S(1)Gd(1)S(2)	70.07(1)	S(3)Gd(1)S(5)	84.42(2)
S(3)Gd(1)S(4)	70.50(1)	S(3)Gd(1)S(6)	87.20(2)
S(5)Gd(1)S(6)	69.68(1)	S(5)Gd(1)S(4)	72.69(1)
S(2)Gd(1)S(4)	75.05(1)	S(6)Gd(1)S(1)	77.26(1)

* F designates atoms of Phen; the C–C bond lengths in the rings of the Phen molecule vary in the range 1.348(3)–1.446(3) Å, where as those in the *iso*-$Bu_2PS_2^-$ ions lie in a range of 1.507(3)–1.550(3) Å.

$$GdCl_3 \cdot 6H_2O + 4C_4H_8NCS_2NH_4 \xrightarrow{EtOH\text{-}CH_2Cl_2} (NH_4)[Gd(C_4H_8NCS_2)_4] + 3NH_4Cl\downarrow + 6H_2O.$$

(I)

Complex **II** was synthesized in two stages. At the first stage, the reaction of $GdCl_3 \cdot 6H_2O$ and *iso*-$Bu_2PS_2Na \cdot 3H_2O$ (molar ratio 1 : 4) in EtOH at room temperature in an air atmosphere in a solution probably afforded the tetrakis-complex Na[Gd(*iso*-$Bu_2PS_2)_4$](Solv). A precipitate of NaCl was filtered off.

$$GdCl_3 \cdot 6H_2O + 4iso\text{-}Bu_2PS_2Na \cdot 3H_2O \xrightarrow{EtOH} Na[Gd(iso\text{-}Bu_2PS_2)_4](Solv) + 3NaCl\downarrow + 18H_2O.$$

We failed to isolate this complex from the solution as a solid phase and, hence, a solution of Et_4NCl in *iso*-PrOH was added to the obtained solution. The exchange reaction gave complex **II**, which was isolated in the solid state by the evaporation of the mother liquor after a precipitate of NaCl was filtered off.

$$Na[Gd(iso\text{-}Bu_2PS_2)_4]_{(solv)} + Et_4NCl \xrightarrow{EtOH} (Et_4N)[Gd(iso\text{-}Bu_2PS_2)_4] + NaCl\downarrow .$$

(II)

In the earlier published articles, the Ln tetrakis-complexes were synthesized using an inert atmosphere, absolute ethanol, and anhydrous reagents [21, 22]. The procedures developed by us made it possible to synthesize complexes **I** and **II** in an air atmosphere without the dehydration of the reagents and solvents. The synthesized complexes are stable in air for a prolong time.

The bands corresponding to stretching vibrations of CS_2 and PS_2 groups, respectively, were identified in the IR spectra of complexes **I** and **II** [23]. The $\nu_{as}(CS_2)$ (complex **I**) and $\nu_{as}(PS_2)$ (complex **II**) bands are shifted to the range of high frequencies compared to the positions of these bands in the spectra of salts $C_4H_8NCS_2NH_4$ and *iso*-$Bu_2PS_2Na \cdot 3H_2O$, respectively, indicating the coordination of the S atoms of ligands $C_4H_8NCS_2^-$ and *iso*-$Bu_2PS_2^-$ in these compounds. It is most likely that the molecular structures of complexes **I** and **II** resemble those of complexes Na[La($Et_2NCS_2)_4$] [24] and (Ph_4P)[Pr($Me_2PS_2)_4$] [25], the structures of which were determined by X-ray diffraction analysis. In these compounds, the Ln^{3+} ions coordinate four 1,1-dithiolate ligands to form a coordination polyhedron S_8. In addition, the structure contains the outer-sphere cation.

A procedure somewhat different from the described one [26] was used for the synthesis of heteroligand complex **III**. A mixture of *iso*-PrOH–CH_2Cl_2 and rectified EtOH were used instead of absolute EtOH. The formed precipitate of NH_4NO_3 was filtered off. Unlike [26], the yield of the complex was estimated in our work. The dithiocarbamate salt was taken in a minor excess to increase the yield of the complex (the molar ratio $Gd^{3+} : C_4H_8NCS_2^-$ is 1 : 4). In an EtOH–MeCN medium at the used concentrations of the reagents, heteroligand complex **IV** is formed, which was also obtained at a minor excess of the sulfur-containing ligand (the molar ratio Gd^{3+} : *iso*-$Bu_2PS_2^-$ is 1 : 4).

The diffraction patterns of complex **III** and earlier synthesized complex [Dy(Phen)($C_4H_8NCS_2)_3$] [13] with a similar composition are similar (they are available from the authors), indicating the same phase compositions of the samples of these complexes. It can be assumed that the crystals of the complexes are isostructural. The crystal structure of compound [Dy(Phen)($C_4H_8NCS_2)_3$] $\cdot$ $3CH_2Cl_2$ has previously been determined by X-ray diffraction analysis [13]. It is found that the coordination sphere of the Dy atom in the mononuclear [Dy(Phen)($C_4H_8NCS_2)_3$] complex contains two N atoms of the bidentate chelating ligand Phen and six S atoms of three bidentate chelating ligands $C_4H_8NCS_2^-$. The coordination polyhedron N_2S_6 is a distorted dodecahedron. It is most likely that complex **III** has a similar molecular structure.

According to the X-ray diffraction data, the crystal structure of compound **IVa** consists of molecules of mononuclear complex **IV** (Fig. 1a) and MeCN molecules located in the general positions. The coordination sphere of the Gd atom contains two N atoms of the bidentate chelating ligand Phen and six S atoms of three bidentate chelating ligands *iso*-$Bu_2PS_2^-$. The coordination polyhedron N_2S_6 of the Gd atom is a distorted antiprism. Three four-membered chelates GdS_2P and the five-membered metallocycle GdN_2C_2 are formed by the coordination of the ligands. The Gd–N distances are 2.585(2) and 2.619(2) Å. In three four-membered chelates GdS_2P, the Gd–S bond lengths differ (2.8424(5)–2.9313(5) Å), indicating their nonequivalence (Table 2). The GdS_2P chelates are nearly planar, and the maximum deviation of the atoms from their planes is 0.093(1) Å. The dihedral angles between the SGdS and SPS planes are 6.4(1)°, 3.4(1)°, and 14.3(1)°; i.e., the cycles are deformed. The GdN_2C_2 chelate has an envelope conformation with the deviation of the of Gd atom from the N_2C_2 plane by 0.375(4) Å. The Phen molecule is almost planar: the mean deviation of the atoms from their root-mean-square plane is 0.014(2) Å. The bond lengths and bond angles in the studied structure of molecule **IV** are comparable with similar values in the

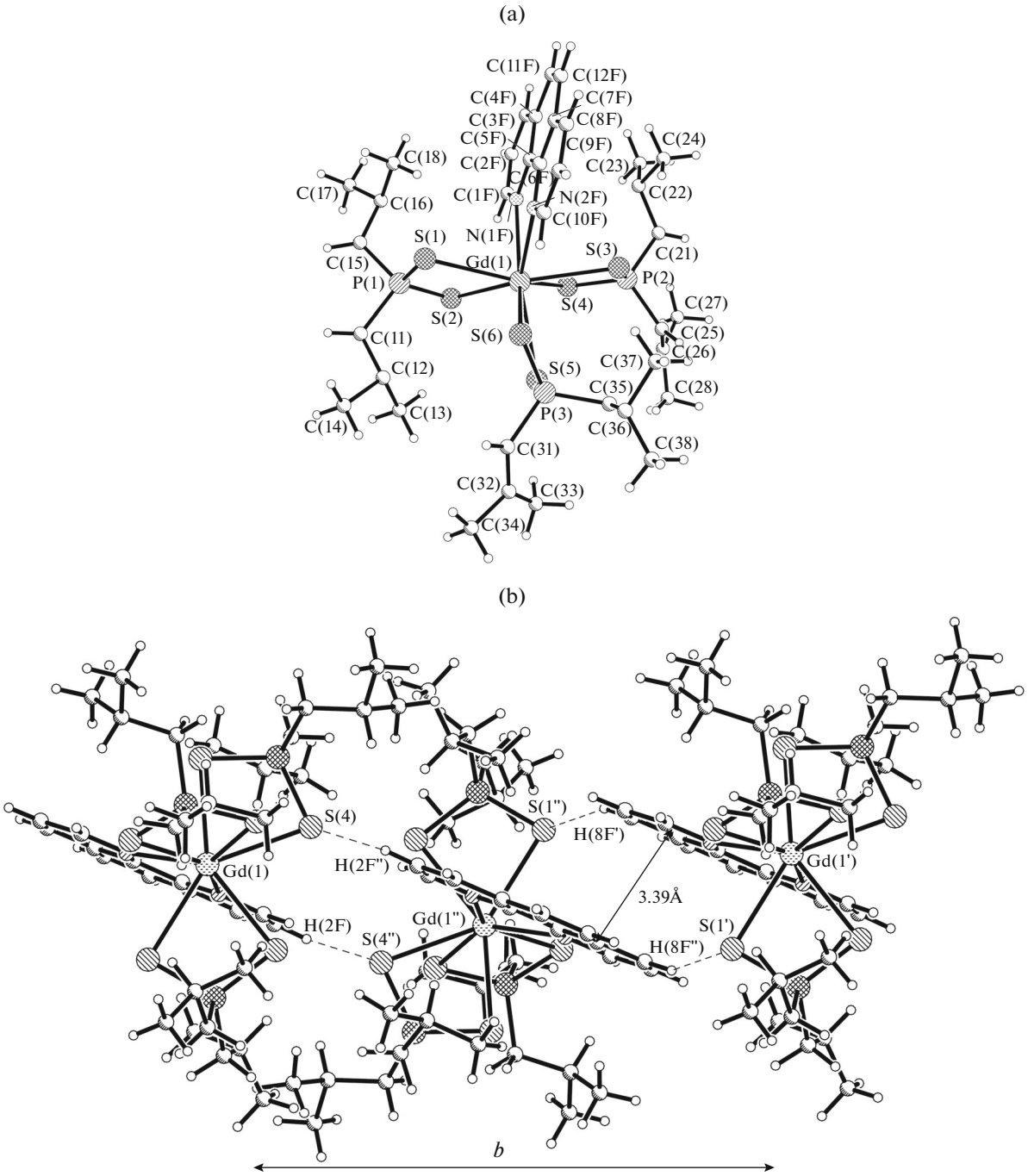

Fig. 1. (a) Structure of the [Gd(Phen)(*iso*-$Bu_2PS_2)_3$] molecule in compound **IVa** with designations of non-hydrogen atoms and (b) the chain fragment in the crystal structure of compound **IVa**.

structure of compound [Sm(Phen)(*iso*-$Bu_2PS_2)_3$] · MeCN [18].

The fragment of the mutual arrangement of the adjacent [Gd(Phen)(*iso*-$Bu_2PS_2)_3$] molecules in a crystal of compound **IVa** is presented in Fig. 1b. The distances between two parallel planes of the Phen molecules shifted relative to each other are 3.39 Å, and those between the centers of the Phen rings are 5.75 Å. The found values correspond to π–π interactions between the Phen cycles [27]. The nearest weak contacts of the S(4) and S(1") atoms with the H(2F") and H(8F') atoms of the adjacent Phen molecules are 2.858(4) and 2.870(2) Å, respectively. These weak contacts provide the formation of supramolecular ensembles in the structure in the form of zigzag chains with a Gd(1)···Gd(1') distance of 10.182(2) Å. There are no contacts shortened compared to the sum of the

van der Waals radii between the molecules of complex **IV** and MeCN: the shortest S(4)···C(1S) distance is 3.956(5) Å. It is most likely that this packing effect affects the elongation of the Gd(1)–S(4) bond. The presence of weak contacts and hydrogen bonds makes it possible to assign compound **IVa** to solvates. A comparison of the mutual spatial arrangement of the molecules of the complexes in the structures of the Gd(III) and Sm(III) compounds [18] showed no strong hydrogen bonds between the molecules, which favors the inclusion of the solvate MeCN molecules into the crystal structure.

The IR spectra of complexes **III** and **IV** contain bands corresponding to the vibrations of the CS_2 and PS_2 groups, respectively, and shifted to high frequencies compared to the positions of these bands in the spectra of $C_4H_8NCS_2NH_4$ and *iso*-$Bu_2PS_2Na \cdot 3H_2O$, indicating the coordination of the 1,1-dithiolate ions in these compounds. In addition, the bands corresponding to ν(C=C) and ν(C=N) in the Phen aromatic rings were found in a range of 1585–1620 cm^{-1} in the IR spectra of complexes **III** and **IV** [23].

The phosphorescence spectra of complexes **I–IV** in frozen ethanol (77 K) and the phosphorescence spectrum of free Phen in CH_2Cl_2 (77 K) presented earlier [28] are shown in Fig. 2. The decomposition of these spectra to the Gaussian components made it possible to determine the position of the 0–0 transition in the vibrational structure of the spectrum and the energies E_T of the ligands in these complexes. The respective results along with some published data on the values of E_T of the ligands in the Gd(III) complexes are listed in Table 3. The values of E_T are presented with an accuracy governed by the width of the vibrational components in the phosphorescence spectrum and equal to ~50 cm^{-1}.

The data in Table 3 show that the phosphorescence spectra of the complexes containing Phen are governed by this molecule. The averaging over all complexes containing the Phen molecule (Table 3) gives $E_T = 22000 \pm 170$ cm^{-1}, which almost coincides with $E_T = 21834$ cm^{-1} for the free ligand Phen [28, 30]. For the $(Et_4N)[Gd(iso\text{-}Bu_2PS_2)_4]$ and $(NH_4)[Gd(C_4H_8NCS_2)_4]$ complexes, the energies of the triplet levels of the 1,1-dithiolate ligands *iso*-$Bu_2PS_2^-$ (23506 cm^{-1}) and $C_4H_8NCS_2^-$ (23336 cm^{-1}) are by ~1500 cm^{-1} higher than the energy of the T_1 level of the Phen ligand. A similar value of E_T (23095 cm^{-1}) of the $Et_2NCS_2^-$ ligand is presented for complex $(Et_2NH_2)[Gd(Et_2NCS_2)_4]$ in [12].

The vibrational structure in the phosphorescence spectra of the complexes containing Phen is characterized by frequencies of 1350 ± 100 cm^{-1}. The decay times of the triplet state and phosphorescence (transition $T_1 \rightarrow S_0$) vary fairly strongly: from unities to hundreds of ms (Table 3). The relative phosphorescence intensities for the four complexes studied are also given in Table 3. The highest phosphorescence intensity is observed for compound **IV**, and the phosphorescence of other three complexes **I–III** turned out to be considerably weaker.

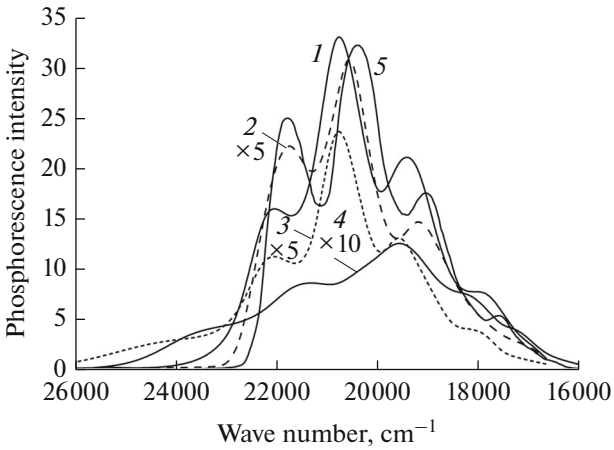

Fig. 2. Phosphorescence spectra of complexes (*1*) $[Gd(Phen)(iso\text{-}Bu_2PS_2)_3]$, (*2*) $[Gd(Phen)(C_4H_8NCS_2)_3]$, (*3*) $(Et_4N)[Gd(iso\text{-}Bu_2PS_2)_4]$, and (*4*) $(NH_4)[Gd(C_4H_8NCS_2)_4]$ in frozen ethanol (77 K, $\lambda_{exc} = 266$ nm) and (*5*) the phosphorescence spectrum of Phen in CH_2Cl_2 at 77 K [28].

The phosphorescence spectra and kinetics in the solid phase at 77 K were determined for complexes **II** and **IV** (Fig. 3). In this case, the kinetics of the phosphorescence decay (Fig. 3b) is not described by one exponential and is satisfactorily processed only in the three-exponential approximation

$$I(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + A_3 e^{-\frac{t}{\tau_3}}.$$

The lifetimes of the excited states for the solid samples of complexes **II** and **IV** are presented in Table 3, where the percent of emitted quanta is indicated in parentheses ($100A_i\tau_i/\Sigma A_i\tau_i$, %). A complicated kinetics is characteristic of the fluorescence and phosphorescence of solid samples of many compounds. The distribution over luminescence times is related to the nonuniform local environment of molecules in microcrystals. Some molecules are located near defects of the crystalline lattice, whereas others are arranged on the surface of the crystals. In addition, the high concentration of molecules in crystals can result in excitation migration and luminescence on the centers with a lower arrangement of the levels. The values of E_T of the ligands for complexes **II** and **IV** in the solid phase do not differ strongly from these parameters for the complexes in frozen ethanol.

Thus, the study of the phosphorescence spectra of the synthesized compounds $(A)[Gd(L)_4]$ and $[Gd(Phen)(L)_3]$ (L = *iso*-$Bu_2PS_2^-$, $C_4H_8NCS_2^-$; A =

Table 3. Energies and lifetimes of the triplet states of the ligands of the Gd(III) complexes in frozen solutions or in the solid phase at 77 K

Compound	State	Energy of triplet level E_T, cm^{-1}	Lifetimes of triplet state	Relative phosphorescence intensity
$(NH_4)[Gd(C_4H_8NCS_2)_4]$ (**I**)	Solution in ethanol	23336	3.3 ± 0.8 ms	0.06
$(Et_4N)[Gd(iso\text{-}Bu_2PS_2)_4]$ (**II**)	″	23506	290 ± 20 ms	0.13
$[Gd(Phen)(C_4H_8NCS_2)_3]$ (**III**)	″	21740	750 ± 20 ms	0.2
$[Gd(Phen)(iso\text{-}Bu_2PS_2)_3]$ (**IV**)	″	22088	5.6 ± 0.2 ms	1
$(Et_4N)[Gd(iso\text{-}Bu_2PS_2)_4]$ (**II**)	Solid phase	22650	0.3 (4%), 1.5 (32%), 13 (64%) ms	0.1
$[Gd(Phen)(iso\text{-}Bu_2PS_2)_3]$ (**IV**)	″	21400	1.3 (3%), 6.7 (40%), 17.3 (57%) ms	1
$(Et_2NH_2)[Gd(Et_2NCS_2)_4]$	″	23095 [12]		
$[Gd(Phen)(Et_2NCS_2)_3]$	″	22222 [12]		
$[Gd(Phen)(iso\text{-}Bu_2NCS_2)_3]$	″	22026 [12]		
$[Gd(Phen)(Bz_2NCS_2)_3]$	″	21882 [12]		
$[Gd(Phen)_2Cl_3] \cdot 2H_2O$	Solution in ethanol–DMF mixture	22075 [29]		
$Phen \cdot H_2O$	Solution in CH_2Cl_2	21834 [28, 30]	1.1 s	

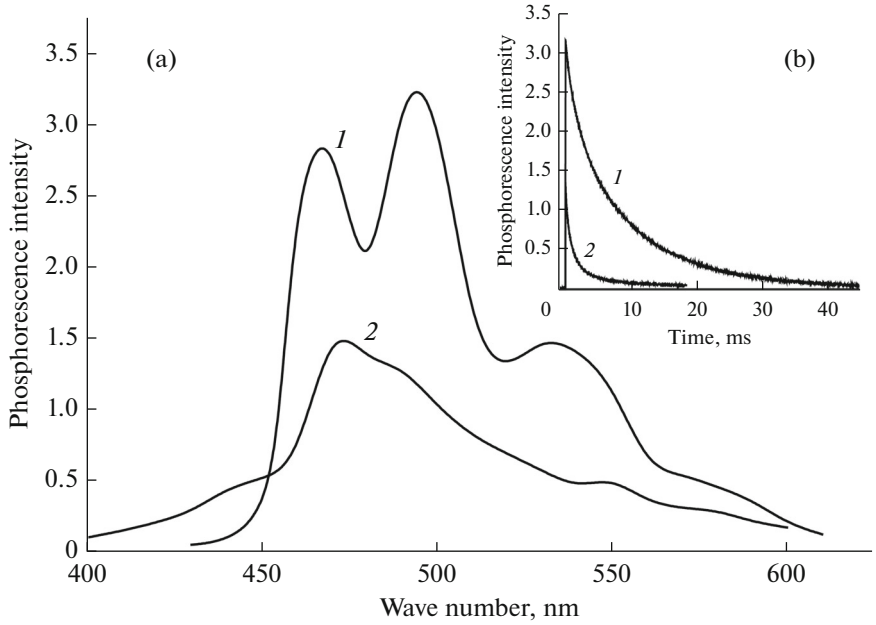

Fig. 3. Phosphorescence (a) spectra and (b) kinetics for complexes (*1*) $[Gd(Phen)(iso\text{-}Bu_2PS_2)_3]$ and (*2*) $(Et_4N)[Gd(iso\text{-}Bu_2PS_2)_4]$ in the solid state at 77 K.

NH_4^+, Et_4N^+) allowed us to determine the energies of the triplet levels of the ligands $C_4H_8NCS_2^-$ and *iso*-$Bu_2PS_2^-$.

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