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Peculiarities of the Interaction of Rare-Earth Metal Thiocyanates with *s*-Triazine

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Abstract—The reactions of thiocyanates $Ln(NCS)_3 \cdot 6H_2O$ (Ln = Y, Eu, and Tb) with 2,4,6-tris(2-pyridyl)-*s*-triazine (Tptz) in MeOH, MeCN, and H_2O afford neutral or ionic thiocyanate complexes with one coordinated Tptz molecule. The uniqueness of the complexes is the presence of the second Tptz molecule in the *exo* coordination. The transformation of Tptz into the *endo* coordination occurs upon recrystallization from an aprotic solvent. The structural peculiarities of the synthesized compounds are determined by powder X-ray diffraction, IR spectroscopy, and single-crystal X-ray diffraction (CIF files CCDC nos. 1827916–1827921).

Keywords: rare-earth metal thiocyanates, *s*-triazine, single-crystal X-ray diffraction

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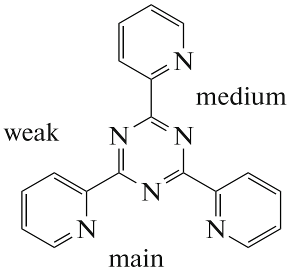
INTRODUCTION

The chemistry of lanthanide compounds with organic N-donor ligands, which enhance the efficiency of the intrinsic luminescence of lanthanides in the visible range due to the transfer of the intramolecular energy from the excited triplet state of the ligand to the metal ion (antenna effect), is being intensively developed in the recent decades. Aromatic N-donor ligands are used as efficient sensitizers of lanthanide ions. Various classes of N-heterocyclic chelating ligands as sensitizers of the emission of Ln^{3+} ions for the preparation of complexes with promising properties were discussed in the review [1].

We showed that the emission characteristics increased considerably upon the intrasphere coordination of the classical ligands, Bipy and Phen, and, in addition, the luminescence intensity increased for solid solutions formed by isostructural crystals of the europium and yttrium compounds [2].

N-Donor *s*-triazine, 2,4,6-tris(2-pyridyl)-*s*-triazine (Tptz), has become customary as an analytical reagent since the 1950s and is used in the extraction and separation of metals. The polydentate character of Tptz (the main, medium, and weak positions of N-donors, Scheme 1) [3] and large π-system favoring the stabilization of the complexes are of special interest for coordination chemistry [4, 5].



Scheme 1.

The possibility of simultaneous functioning of Tptz as a tri- and bidentate ligand for the use as a linker in the development of supramolecular architectures attracts attention in the recent time [6–9]. The data on the coordination chemistry of Tptz mainly concern the transition metal compounds, and lanthanides are chosen as objects of the study in the recent works. It is established [10] that Tptz is the tridentate ligand in the $[Eu(DBM)_3(Tptz)]$ complex (DBM is dibenzoylmethane) and the main position of the N-donors participates in the coordination. In this complex, the red emission of the Eu^{3+} ion is promoted by the ligand (antenna effect). In the mononuclear compounds $[Ln(Tptz)(NCS)_3(H_2O)(CH_3OH)_2]$ (Ln = Gd and Eu) and $[Tb(Tptz)(NCS)_3(H_2O)_3]$, the heterocyclic ligand is also tridentate via the main position. The study of the photophysical characteristics revealed the influence of Tptz on the emission of the Eu^{3+} and Tb^{3+} ions in the complexes [11].

In this work, the influence of the medium (solvent nature and reactant ratio) on peculiarities of the reactions of hydrated thiocyanates $Ln(NCS)_3 \cdot 6H_2O$ (Ln = Y, Eu, Tb) with the polydentate (polyvariant) ligand Tptz was studied. This implied the synthesis of the mononuclear neutral (ionic) compounds with coordinated anions NCS^- and molecular ligands Tptz, H_2O, MeOH, and MeCN.

EXPERIMENTAL

Thiocyanates $Ln(NCS)_3 \cdot 6H_2O$ [2], Tptz (Aldrich), and solvents (methanol, ethanol, and acetonitrile), which were not additionally purified or dried, were used in the study. All procedures were carried out in air.

Synthesis of $[Y(H_2O)_2(Tptz)(NCS)_3]_2 \cdot$ Tptz $\cdot$ $3.5H_2O$ (I). Thiocyanate $Y(NCS)_3 \cdot 6H_2O$ (0.1800 g, 0.495 mmol) was dissolved in methanol (15 mL), and the solution was added to a solution of Tptz (0.1510 g, 0.483 mmol) in methanol (10 mL). The mixture was refluxed for ~90 min with stirring. An almost homogeneous solution was obtained. Greenish crystals precipitated on cooling to room temperature. The yield of compound **I** was 0.126 g (17%) based on Y.

For $C_{60}H_{51}N_{24}O_{7.5}S_6Y_2$ (*FW* = 1534.41)

Anal. calcd., %	C, 46.96	H, 3.35	N, 21.91	S, 12.54
Found, %	C, 46.06	H, 2.76	N, 21.74	S, 12.91

IR (ATR), ν, cm^{-1}: 416 m, 490 m, 610 w, 633 m, 666 s, 674 m, 768 vs, 809 w, 862 w, 1008 m, 1052 w, 1097 w, 1151 w, 1256 m, 1300 w, 1376 s, 1434 w, 1474 m, 1491 m, 1515 vs, 1548 s, 1576 w, 1597 w, 1644 vw, 2045 m, 2075 m, 3060 w, 3079 w, 3350 w.

Synthesis of $[Ln(H_2O)(MeOH)(Tptz)(NCS)_3] \cdot$ Tptz (II). Ligand Tptz (~1 mmol) was dissolved in MeOH (10 mL), and a solution of $Ln(NCS)_3 \cdot 6H_2O$ (~0.5 mmol) in MeOH (15 mL) was added dropwise on stirring. The solid phase was immediately formed. The heterogeneous mixture was refluxed on stirring for ~30 min, cooled to room temperature, transferred onto the filter, washed with methanol, and dried at room temperature over silica gel in a vacuum desiccator.

The yield of $[Y(H_2O)(MeOH)(Tptz)(NCS)_3] \cdot$ Tptz (**IIa**) was 0.37 g (79%) based on Y.

For $C_{40}H_{30}N_{15}O_2S_3Y$ (*FW* = 937.87)

Anal. calcd., %	C, 51.22	H, 3.22	N, 22.40	S, 10.25
Found, %	C, 50.55	H, 3.95	N, 22.80	S, 10.80

IR (ATR), ν, cm^{-1}: 415 m, 493 m, 632 m, 666 s, 675 m, 768 vs, 809 w, 862 w, 981 w, 1008 m, 1052 w, 1097 w, 1255 m, 1300 w, 1378 s, 1434 m, 1473 m, 1491 m, 1515 vs, 1549 s, 1576 w, 1647 w, 2043 m, 2058 m, 2073 m, 3057 w, 3079 w, 3241 w, 3322 w, 3505 w, 3564 w.

The yield of $[Eu(H_2O)(MeOH)(Tptz)(NCS)_3] \cdot$ Tptz (**IIb**) was 0.40 g (82%) based on Eu.

For $C_{40}H_{30}N_{15}O_2S_3Eu$ (*FW* = 1000.93)

Anal. calcd., %	C, 47.99	H, 3.02	N, 20.99	S, 9.61
Found, %	C, 47.50	H, 3.42	N, 21.63	S, 10.01

IR (ATR), ν, cm^{-1}: 414 m, 490 m, 632 m, 666 s, 675 s, 768 vs, 809 w, 852 w, 862 m, 980 w, 1008 m, 1051 w, 1097 w, 11506 w, 1255 m, 1300 w, 1376 s, 1434 m, 1473 m, 1491 m, 1514 vs, 1548 s, 1576 w, 1648 w, 2036 m, 2052 m, 2069 m, 3057 w, 3079 w, 3241 w, 3314 w, 3501 w, 3581 w.

The yield of $[Tb(H_2O)(MeOH)(Tptz)(NCS)_3] \cdot$ Tptz (**IIc**) was 0.40 g (81%) based on Tb.

For $C_{40}H_{30}N_{15}O_2S_3Tb$ (*FW* = 1007.89)

Anal. calcd., %	C, 47.67	H, 3.00	N, 20.85	S, 9.54
Found, %	C, 47.18	H, 3.14	N, 21.60	S, 10.02

IR (ATR), ν, cm^{-1}: 415 m, 491 m, 632 m, 666 s, 675 m, 768 vs, 809 w, 854 w, 862 m, 1008 m, 1052 w, 1097 w, 1255 m, 1300 w, 1376 s, 1405 w, 1434 m, 1473 m, 1491 m, 1514 vs, 1548 s, 1576 w, 1593 w, 1648 w, 2041 m, 2055 m, 2072 m, 3057 w, 3079 w, 3240 w, 3315 w, 3498 w, 3581 w.

Synthesis of $[Y(H_2O)(MeCN)(Tptz)(NCS)_3] \cdot$ Tptz (III). Thiocyanate $Y(NCS)_3 \cdot 6H_2O$ (0.0950 g, 0.256 mmol) in MeCN (15 mL) was introduced into a solution of Tptz (0.1646 g, 0.527 mmol) in MeCN (25 mL). The mixture was refluxed and stirred for 60 min. The yield of compound **III** was 0.17 g (70%) based on Y.

For $C_{41}H_{29}N_{16}OS_3Y$ (*FW* = 946.88)

Anal. calcd., %	C, 52.00	H, 3.08	N, 23.67	S, 10.16
Found, %	C, 51.00	H, 2.89	N, 22.84	S, 11.11

IR (ATR), ν, cm^{-1}: 414 m, 610 w, 622 w, 633 m, 666 s, 673 m, 741 w, 766 vs, 810 w, 861 w, 909 vw, 979 w, 993 w, 1008 m, 1049 w, 1253 m, 1300 w, 1374 s, 1385 s, 1402 w, 1434 m, 1473 m, 1491 m, 1514 vs, 1546 s, 1575 w, 2055 s, 2076 m, 3062 w, 3435 w.

Synthesis of $[Y(H_2O)_3(Tptz)(NCS)_2] \cdot NCS \cdot$ Tptz $\cdot$ $1.5H_2O \cdot 1.25MeOH$ (IV). Ligand Tptz (0.6013 g, 1.925 mmol) was dissolved in MeOH (10 mL), and a solution of $Y(NCS)_3 \cdot 6H_2O$ (0.3581 g, 0.965 mmol) in H_2O (5 mL) was introduced into the obtained yellow solution. On the next day, polyhedra were formed in a bright yellow solution on the bottom and walls of the crystallizer, filtered off, and washed with methanol. The yield of compound **IV** was 0.82 g (84%) based on Y. The X-ray diffraction analysis showed the single-phase character of compound **IV**.

For $C_{40.25}H_{38}N_{15}O_{5.75}S_3Y$ (*FW* = 1011.93)

Anal. calcd., %:	C, 48.07	H, 3.78	N, 20.76	S, 9.51
Found, %:	C, 48.36	H, 4.41	N, 20.04	S, 9.57

IR (ATR), ν, cm^{-1}: 419 m, 489 m, 632 s, 666 s, 674 m, 739 m, 770 vs, 814 w, 852 m, 1007 m, 1052 w, 1095 w, 1151 w, 1259 m, 1304 w, 1372 s, 1386 m, 1434 m, 1471 m, 1492 m, 1519 o.c, 1549 m, 1573 w, 2002 w, 2063 m, 3063 w, 3360 w, 3503 w.

Synthesis of $[Y(H_2O)_3(Tptz)(NCS)_2]_5$-$[Y(H_2O)_2(Tptz)(NCS)_3]_5[Y(H_2O)(Tptz)(NCS)_4]_2$ · $(NCS)_3$ · $37H_2O$ (V). A mixture of solutions of $Y(NCS)_3 \cdot 6H_2O$ (0.3657 g, 0.985 mmol) in MeOH (15 mL) and Tptz (0.1507 g, 0.482 mmol) in MeOH (10 mL) was refluxed for 90 min. A bright yellow solution and a crystalline precipitate were formed after reflux. The precipitate was filtered off and washed with EtOH. The crystals of compound **V** were obtained from the mother liquor. The yield of compound **V** was 0.22 g (33.2%) based on Y.

For $C_{252}H_{272}N_{108}O_{64}S_{36}Y_{12}$ (*FW* = 8058.79)

Anal. calcd., %	C, 37.56	H, 3.40	N, 18.77	S, 14.32
Found, %	C, 38.02	H, 2.86	N, 19.32	S, 15.05

IR (ATR), ν, cm^{-1}: 414 s, 633 s, 666 s, 674 s, 768 vs, 854 m, 861 m, 981 m, 1010 s, 1052 m, 1082 m, 1096 m, 1148 m, 1301 m, 1374 s, 1384 s, 1434 m, 1473 m, 1491 s, 1515 vs, 1544 s, 1597 w, 1606 w, 2046 m, 3062 m, 3110 m, 3273 m.

Concentrating of saturated solutions (the solubility is very low) of compound **IIa** in MeCN at room temperature gave several transparent crystals of the "cabochon" shape, the X-ray structure analysis of which showed the formation of $[Y(Tptz)_2(NCS)_3] \cdot MeCN$ (**VI**).

Elemental analysis was performed using standard procedures on a EUROEA 3000 CHN-analyzer at the JRC PMR IGIC RAS. Attenuated total reflection IR spectra (ATR-IR) were recorded in a range of 400–4000 cm^{-1} on a Bruker ALPHA instrument.

Powder X-ray diffraction analysis was carried out on a Bruker D8 Advance diffractometer (CuK_α, Ni filter, LYNXEYE detector) at the JRC PMR IGIC RAS.

Single-crystal X-ray diffraction analysis. The experimental data for compounds **I**, **IV–VI**, and Tptz · xH_2O (x = 4, 4.85) were collected on a Bruker SMART APEX2 diffractometer (MoK_α radiation, λ = 0.71073 Å). [12]. An absorption correction was applied using the semiempirical method by equivalents (SADABS) [13]. The structures were determined by a combination of a direct method and Fourier syntheses. The populations of the disordered positions of two coordinated NCS groups and solvate MeOH and H_2O molecules in the structure of compound **IV** were obtained by the isotropic refinement with fixed thermal parameters of the disordered atoms (U_{iso} = 0.06 $Å^2$) and were not refined in the subsequent calculations. All the five checked single crystals of compound **V** were of poor quality. The single crystals of Tptz · $4H_2O$ were found in the syntheses of compound **V**. One crystal of Tptz · $4.85H_2O$ has grown on the Petri dish at the surface of the mother liquor while sampling the crystals. In all the structures, the hydrogen atoms of the Tptz molecules were calculated from the geometric concepts (as well as those of the solvate MeOH and MeCN molecules). The hydrogen atoms of the H_2O molecules were partially localized from the difference Fourier syntheses, were calculated in part from the geometric concepts, or were not localized.

The structures of compounds **I** and **VI** were refined by anisotropic full-matrix least squares. The structure of compound **IV** was refined in the anisotropic—isotropic (some disordered atoms) approximation. In the structure of compound **V**, only the Y and S atoms were anisotropically refined, and all 227 crystallographically independent O, N, and C atoms were isotropically refined. The crystallographic data and refinement parameters for the structures are presented in Table 1. All calculations were performed using the SHELXS and SHELXL programs [14].

The experimental data for the structures of compounds **I**, **IV**, **V**, **VI**, and Tptz · xH_2O (x = 4, 4.85) were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1827916–1827921, deposit@ccdc.cacp.ac.uk or http:// www.ccdc.cacp.ac.uk).

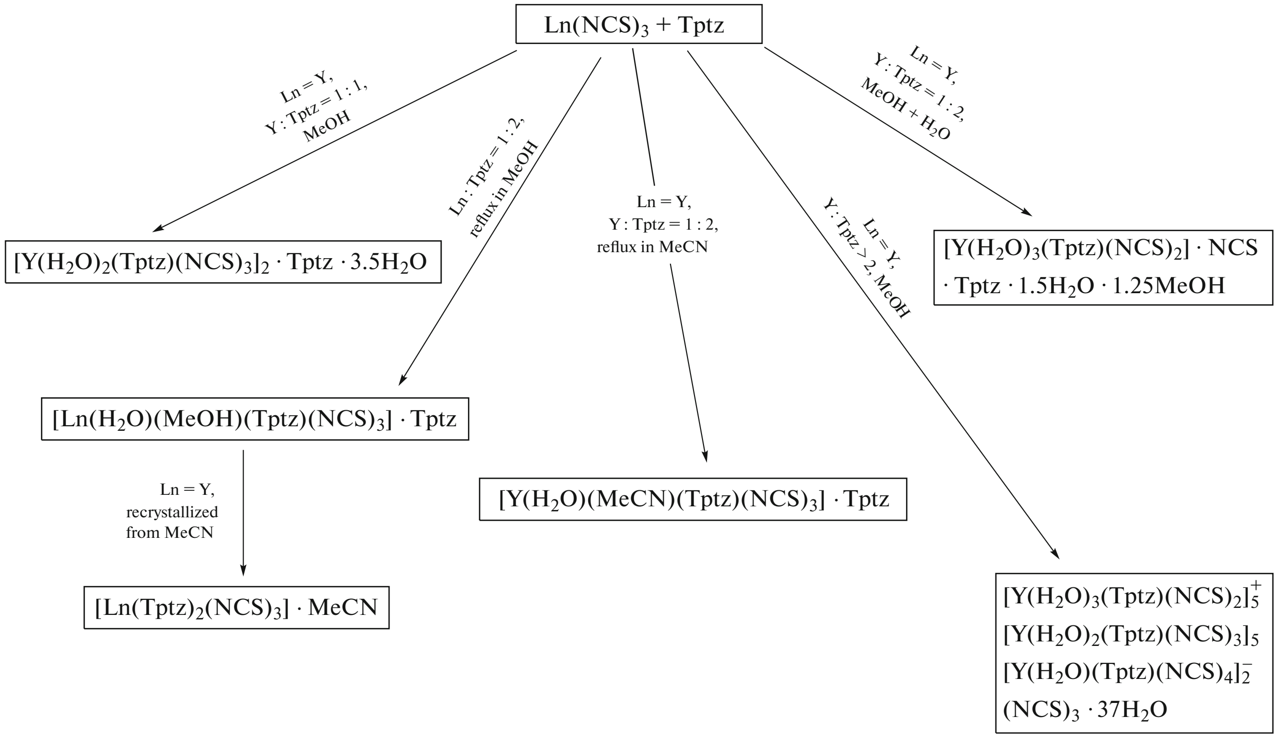
RESULTS AND DISCUSSION

The reaction of yttrium thiocyanate with Tptz at the ligand to metal ratio of 1 : 1 (reflux in methanol) was accompanied by the formation of compound **I** in which one ligand molecule is coordinated. Another Tptz molecule is in the outer sphere for two neutral complexes $[Y(H_2O)_2(Tptz)(NCS)_3]$ (Scheme 2) in which the coordination node YO_2N_6 (coordination number of Y is 8) is formed by the Tptz molecule, three NCS^- anions, and two water molecules. A low yield of compound **I** and the presence of the solvate Tptz molecule allowed the second Tptz molecule to incorporate into the coordination sphere of yttrium with an increase in the ligand to metal ratio. Compounds $[Ln(H_2O)(MeOH)(Tptz)(NCS)_3] \cdot Tptz$ (**IIa**, **IIb**, and **IIc** for Y, Eu, and Tb, respectively) were obtained from the solutions with the ratio Tptz : Ln = 2 by reflux for ~30 min. Interestingly, the

Table 1. Selected crystallographic data and refinement results for the structures of compounds **I**, **IV**, **V**, **VI**, and Tptz · xH$_2$O (x = 4, 4.85)

Parameter	Value					
	I	**IV**	**V**	**VI**	4.85H$_2$O	Tptz · 4H$_2$O
Empirical formula	$C_{60}H_{51}N_{24}O_{7.5}S_6Y_2$	$C_{40.25}H_{38}N_{15}O_{5.75}S_3Y$	$C_{252}H_{272}N_{18}O_{64}S_{36}Y_{12}$	$C_{41}H_{27}N_{16}S_3Y$	$C_{18}H_{20}N_6O_4$	$C_{18}H_{21.70}N_6O_{4.85}$
FW	1598.43	1008.94	8058.84	928.87	384.40	399.71
T, K	150(2)	173(2)	150(2)	150(2)	150(2)	120(2)
Radiation, λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$P2_1$
a, Å	10.3107(7)	10.6403(6)	14.4452(8)	14.7135(6)	4.4465(13)	15.112(3)
b, Å	28.2542(19)	19.8893(13)	22.3159(12)	15.1194(7)	16.998(5)	3.7812(7)
c, Å	23.8112(16)	21.0695(13)	27.9678(15)	20.1361(9)	24.544(7)	17.457(3)
α, deg	90	90	89.806(2)	69.5370(10)	90	90
β, deg	93.278(2)	94.346(2)	80.0080(10)	83.964(2)	90	102.503(6)
γ, deg	90	90	86.306(2)	81.896(2)	90	90
V, Å^3	6925.3(8)	4446.1(5)	8860.2(8)	4147.3(3)	1855.1(9)	973.9(3)
Z	4	4	1	4	4	2
ρ_{calcd}, g/cm^3	1.533	1.507	1.510	1.488	1.376	1.363
μ,mm^{-1}	1.919	1.517	2.235	1.610	0.101	0.102
F(000)	3252	2070	4096	1888	808	421
Sample size, mm	0.16 × 0.02 ×0.02	0.28 × 0.2 × 0.18	0.2 × 0.08 × 0.06	0.34 × 0.2 × 0.16	0.3 × 0.04 × 0.04	0.24 × 0.02 × 0.02
Range of θ, deg	2.106–26.061	2.048–26.050	2.048–20.816	2.080–28.300	2.047–28.129	2.390–26.014
Ranges of *h, k, l*	$-12 \le h \le 12$	$-13 \le h \le 12$	$-14 \le h \le 14$	$-19 \le h \le 19$	$-5 \le h \le 5$	$-18 \le h \le 18$
	$-34 \le k \le 34$	$-24 \le k \le 24$	$-22 \le k \le 22$	$-19 \le k \le 19$	$-22 \le k \le 22$	$-4 \le k \le 4$
	$-29 \le l \le 29$	$-26 \le l \le 25$	$-27 \le l \le 27$	$-26 \le l \le 26$	$-32 \le l \le 32$	$-21 \le l \le 21$
Number of measured reflections	105163	39706	85605	52090	22942	10532
Number of independent reflections (R_{int})	13677 (0.1800)	8770 (0.0866)	18553 (0.2090)	20211 (0.0559)	4448 (0.0804)	3841 (0.1017)
S	1.009	0.896	1.092	0.997	1.063	0.915
R_1, wR_2 ($I > 2\sigma(I)$)	0.0607, 0.1258	0.0467, 0.1160	0.0882, 0.2183	0.0511, 0.1173	0.0681, 0.1571	0.0672, 0.1684
R_1, wR_2 (all data)	0.1453, 0.1573	0.0905, 0.1265	0.1785, 0.2490	0.1162, 0.1404	0.1246, 0.1880	0.1566, 0.2019
Flack parameter					–0.1(10)	0.5
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	1.696/–1.254	0.639/–0.710	1.076/–0.906	0.975/–0.702	0.276/–0.313	0.359/–0.310

increase in the duration of reflux up to 2 h at Tptz : Ln = 2 did not affect the compositions and yields of compounds **IIa–IIc**. Taking into account the data of elemental analysis and IR spectroscopy, as well as the results of single-crystal X-ray diffraction for complex **I**, one can assume that the coordination node LnO_2N_6 (the coordination number of Ln is 8) in compounds **IIa–IIc** is formed by the Tptz molecule, three NCS^- anions, and water and MeOH molecules; and the external sphere contains one Tptz molecule. Thus, under the conditions studied, the coordinated water molecules are not substituted by the second Tptz ligand, and only one coordinated water molecule in compound **I** is replaced by the MeOH molecule in compound **II**. According to the powder X-ray diffraction data, the crystals of compounds **IIa–IIc** are isostructural and were obtained in a yield of ~80%. All attempts to obtain single crystals for structural investigations were unsuccessful. No coordination of the second Tptz molecule was revealed when methanol was replaced by acetonitrile (Scheme 2). Complex **III** $[Y(H_2O)(MeCN)(Tptz)(NCS)_3] \cdot Tptz$ was obtained in which the coordination number is 8 and the coordination node is YON_7 due to the replacement of the water molecule by MeCN. As in the case of compounds **IIa–IIc**, the coordination sphere of compound **III** contains two monodentate ligands H_2O and MeCN, and the second Tptz molecule is still in the external sphere.



Scheme 2.

The reaction of yttrium thiocyanate with Tptz in a mixed methanol–water solvent at the ratio Tptz : Y = 2 results in the formation and isolation (in an almost quantitative yield of 84%) of compound **IV** with the coordination number 8 and two Tptz molecules, but only one of them is coordinated by yttrium. Compound **IV** is also formed at the ratio Tptz : Y = 1 but with a lower yield. The coordination sphere is aquated in the presence of water with the displacement of the acido ligand NCS^- to the external sphere to form cationic complex **IV**. A similar situation was observed in alcoholic solutions in the reactions of yttrium thiocyanate with 4,7-phenanthroline. Thiocyanate goes from the *endo* to *exo* coordination mode under the effect of ditopic 4,7-Phen, and an associate with the cationic complex $[Y(H_2O)_7(NCS)](NCS)_7 \cdot 5(4,7\text{-Phen}) \cdot 5H_2O$ is formed [15].

Thus, compounds **I–IV** obtained in various solvents and under different synthesis conditions have two main peculiarities: the coordination number of the complexing atom is 8 and the *exo*-coordinated molecule of the polydentate Tptz ligand is present. A simple method was used for the transformation of Tptz into the *endo* coordination (see the synthesis of $[Y(Tptz)_2(NCS)_3] \cdot MeCN$ (**VI**) in Experimental). In neutral complex **VI**, the coordination number of Y is 9 and the coordination node is YN_9. The reason for this transformation is possibly caused by peculiarities of the formation of hydrogen bonds OH···N of the Tptz ligand and π interactions of the heterocycles.

A similar situation of changing the composition of the complex, coordination number of the complexing atom, and desolvation affected by the aprotic solvent (CH_2Cl_2) was observed for the Pr, Eu, Dy, and Yb complexes with 2,6-di(pyrazolyl)pyridines [16]. To accomplish the variation of the coordination of Tptz, we carried out experiments in MeOH for the ratios Y : Tptz ≥ 2 (Scheme 2). Surprisingly, the isolated solid phase contains the supramolecular ensemble $[Y(H_2O)_3(Tptz)(NCS)_2]_5[Y(H_2O)_2(Tptz)(NCS)_3]_5[Y(H_2O)(Tptz)(NCS)_4]_2 \cdot (NCS)_3 \cdot 37H_2O$ (**V**) in all complexes of which Tptz is coordinated only through the main position. Although the synthesis was carried out in a methanolic solution, ensemble **V** contains no alcohol molecules neither in the first coordination sphere of the complexes, nor in the solvate shell, which either contains no Tptz molecule. It is most likely that the water molecules are first substituted by Tptz to form $[Y(H_2O)_2(Tptz)(NCS)_3]$ in an excess of the starting aqua complex $[Y(H_2O)_5(NCS)_3]$ in the solution. The formed complex undergoes disproportionation to the cationic $[Y(H_2O)_3(Tptz)(NCS)_2]^+$ and anionic $[Y(H_2O)(Tptz)(NCS)_4]^-$ complexes, as we observed in the case of formation of $Eu_3(H_2O)_{12}(EtOH)_3(NCS)_9$ [17] and $Dy_3(H_2O)_{12}(EtOH)_3(NCS)_9$ [18]. The disproportionation of the halide (thiocyanate) complexes $2MX_3 \rightarrow MX_2^+ + MX_4^-$ to the cationic and anionic forms has been known long ago and was confirmed in our work [19]. The formation of complex products consisting of cationic and anionic forms was also revealed for the complexes of three-charged Ln of the composition LnX_3L_n [20–23].

The IR spectra of complexes **I–VI** contain an intense absorption band as an asymmetric doublet at 1549–1514 cm^{-1} caused by the ν(C=C) and ν(C=N) vibrations of the Tptz ligand (a strong singlet at 1515 cm^{-1} for free Tptz), which is consistent with the data [11] for similar compounds. The ν(CN) band of the NCS group is most informative in the IR spectra of the thiocyanate compounds. For example, the spectrum of the starting compound $[Y(H_2O)_5(NCS)_3] \cdot H_2O$ exhibits a split band at 2103 and 2085 cm^{-1} (intensity ratio ~1 : 2), indicating the nonequivalent position of the acido ligands in the structure [24]. The replacement of the coordinated water molecules by tridentate Tptz is manifested as a shift of the band caused by the ν(CN) vibrations to low frequencies and appreciable changes in the structure of this band: 2075 and 2045 cm^{-1} for compound **I**; 2073, 2058, and 2043 cm^{-1} for **IIa**; 2077 and 2053 cm^{-1} for **III**; 2063 cm^{-1} (shoulder) for compound **IV**; and a multicomponent band with a maximum at 2046 cm^{-1} for **V**, which coincides with the structural variations in these yttrium compounds. The band corresponding to the ν(CN) vibrations is also shifted in compounds **IIb** and **IIc**: 2069, 2052, and 2036 cm^{-1} (2095, 2077 cm^{-1} in the starting Eu thiocyanate) and 2071, 2055, and 2041 cm^{-1} (2108, 2085 cm^{-1} in the starting Tb thiocyanate). It is noteworthy that the IR spectra of compounds **IIa–IIc** are similar, and their crystals are isostructural according to the single-crystal X-ray diffraction.

The structure of compound **I** is formed by molecular complexes $[Y(H_2O)_2(Tptz)(NCS)_3]$ (Fig. 1a), Tptz molecules, and solvate H_2O molecules. Two crystallographically independent complexes $[Y(H_2O)_2(Tptz)(NCS)_3]$ have the same structures, the coordination number of Y is equal to 8, and the coordination polyhedron of Y is dodecahedron. The first trapezohedron contains three N(Tptz) atoms and one N atom of one of the NCS^- ligands, and the second trapezohedron contains two $N(NCS^-)$ atoms and the O atoms of the coordinated H_2O molecules. Different degrees of distortion of the polyhedra should be mentioned: in the Y(1) complex the coordinated atoms of the trapezohedra lie in one plane with accuracies of 0.092 and 0.132 Å, while the accuracies are 0.018 and 0.034 Å for the Y(2) complex. All hydrogen atoms of both coordinated and solvate H_2O molecules participate in hydrogen bonds, the cooperative effect of which results in the formation of a 2D layered structure (the layers are perpendicular to the *z* axis). The coordinated and solvate Tptz molecules are involved in stacking interactions to form piles parallel to the *a* axis (Fig. 1b). The average distance between the aromatic rings is $a/3 = 3.40$ Å.

The crystals of compound **IV** contain cationic complexes $[Y(H_2O)_3(Tptz)(NCS)_2]^+$ (Fig. 2a), NCS^- anions, uncoordinated Tptz molecules, and solvate H_2O and MeOH molecules. Each of two coordinated NCS^- anions is disordered over two positions in ratios of 45 : 55 and 15 : 85 in such a way that each nitrogen atoms of each pair occupy one position. The coordination number of Y is 8, and the polyhedron is an average between a square antiprism (bases O(1,2)N(2,7), O(3)N(1,3,6)) and a two-capped trigonal prism (bases N(1,2,7) and O(1,2)N(3), caps O(3), N(6)). An extensive network of hydrogen bonds unites structural units into a 3D framework. The coordinated and solvate Tptz molecules are involved in stacking interactions to form piles parallel to the *a* axis (Fig. 2b).

The structure of compound **V** is formed by the cationic ($[Y(H_2O)_3(Tptz)(NCS)_2]^+$), molecular ($[Y(H_2O)_2(Tptz)(NCS)_3]$), and anionic ($[Y(H_2O)(Tptz)(NCS)_4]^-$) complexes (Fig. 3), NCS^- anions, and crystallization H_2O molecules. The coordination

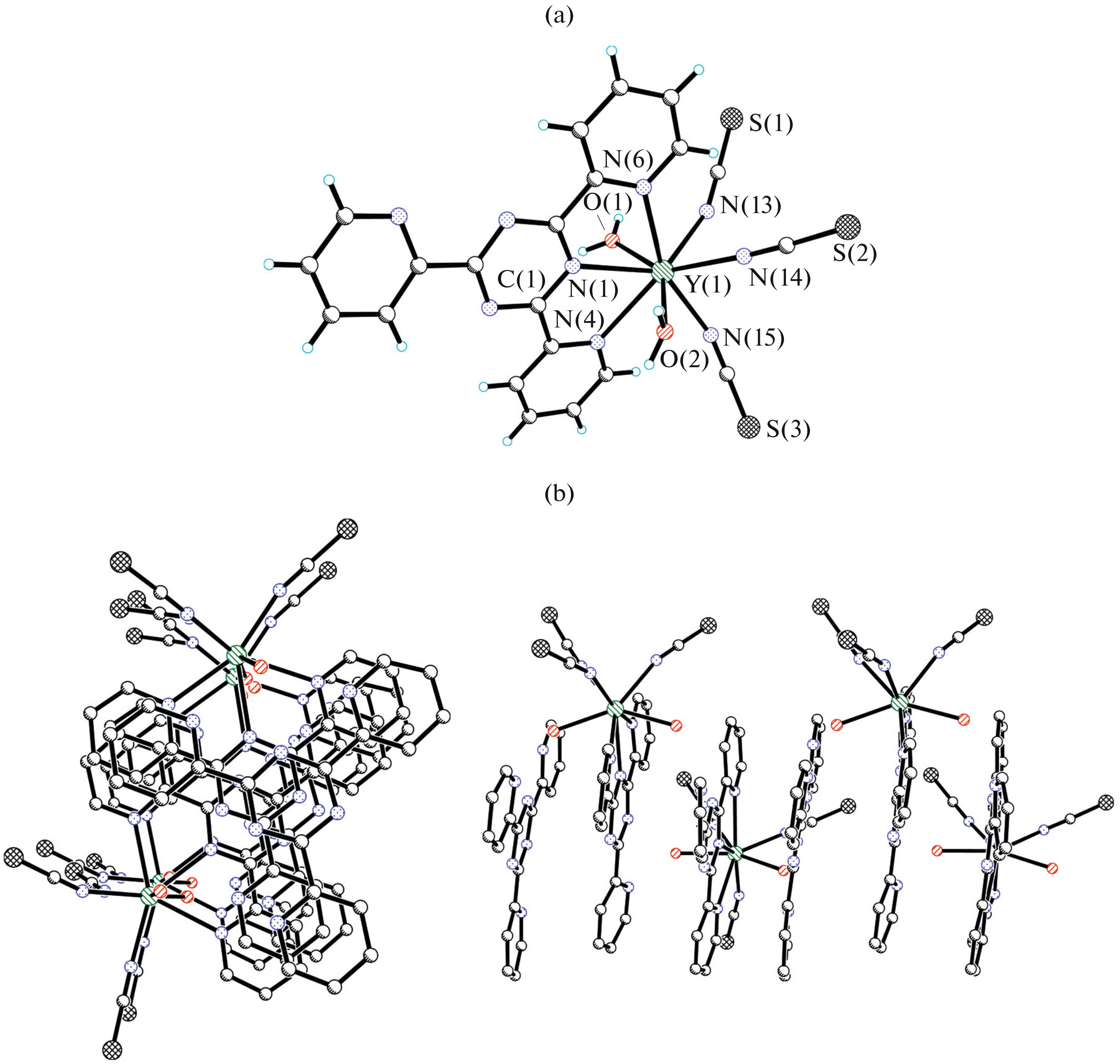


Fig. 1. (a) Structure of complex $[Y(H_2O)_2(Tptz)(NCS)_3]$ and (b) two projections of the Tptz piles in the structure of compound **I**.

number of Y is 8 in all the six independent complexes. In three Y(1,5,6) complexes, one position in the coordination environment of Y is occupied by the O atom of the H_2O molecule and the N atom of the NCS^- anion in a ratio of 1 : 1 according to the statistics. In the case of Y(1,5), one position is occupied by the molecular and anionic complexes. In the case of Y(6), one position is occupied by the cationic and molecular complexes. The layers of the complexes linked by stacking interactions can be distinguished in the structure of compound **V**, and the disordered solvate H_2O molecules are located between the layers (Fig. 4).

The structure of compound **VI** is formed by complexes $[Y(Tptz)_2(NCS)_3]$ (Fig. 5) and solvate MeCN molecules. In two crystallographically independent complexes, the coordination number of Y is 9 and the polyhedron is a strongly distorted three-capped trigonal prism (each cap contains two N atoms of the central Tptz fragment and one N atom of the NCS^- anion). The mean planes of the Tptz ligands in each complex are nearly perpendicular to each other, whereas the mean planes of the Tptz ligands of two different complexes are parallel in pairs. Thus, taking into account the crystal symmetry (space group $P\bar{1}$), we can assert that the structure contains two sets of approximately parallel Tptz ligands. Stacking interactions take place in each set (Fig. 6).

The single crystals of $Tptz \cdot xH_2O$ ($x = 4, 4.85$) were selected as impurity phases. The first structure is ordered, whereas in the second structure one of the aromatic rings is disordered over two positions with a ratio of 1 : 1.

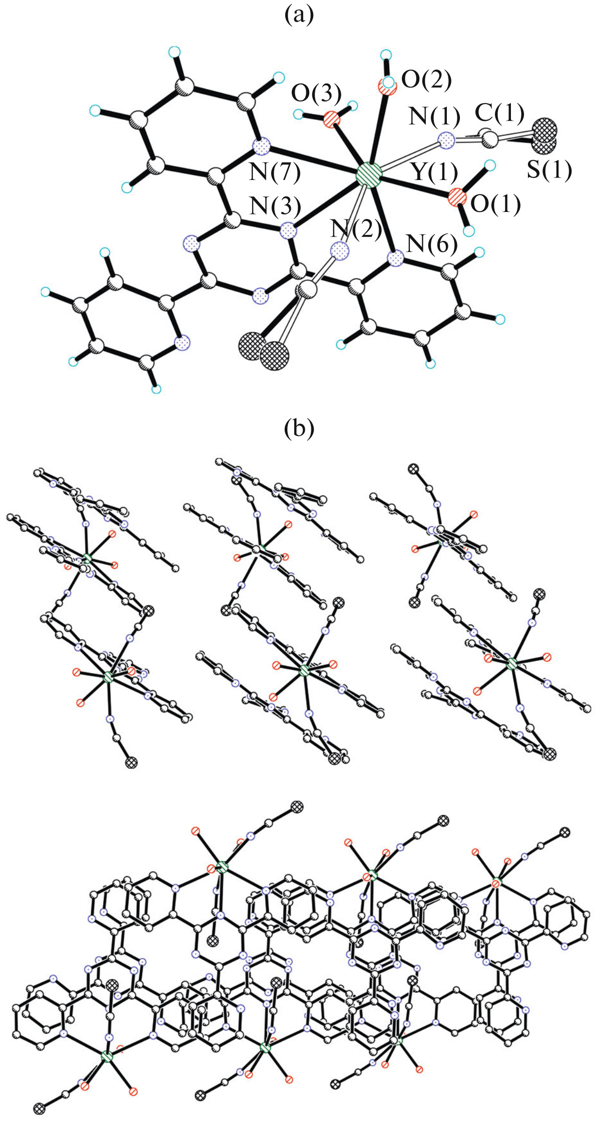


Fig. 2. (a) Structure of complex $[Y(H_2O)_3(Tptz)(NCS)_2]^+$ and (b) two projections of the Tptz piles in the structure of compound **IV**.

It follows from the consideration of the obtained data that the thiocyanate precursor and the Tptz : Ln molar ratio are decisive for the formation of various thiocyanate complexes with Ln with Tptz in such solvents as MeOH, MeCN, and H_2O. The use of the neutral complexes $Ln(NCS)_3 \cdot 6H_2O$ (Ln = Y, Eu, Tb) instead of the known procedure (according to which the metal thiocyanate complexes are formed in alcoholic solutions due to the metathesis reaction between lanthanide chlorides (nitrates) and potassium thiocyanate) afforded the complexes with the coordination number of Ln equal to 8 and the Tptz molecule in the *exo* coordination, which was not observed in [11]. The anhydrous complexes $[Ln(Tptz)_2(NCS)_3] \cdot MeCN$ can be promising objects with high photophysical characteristics.

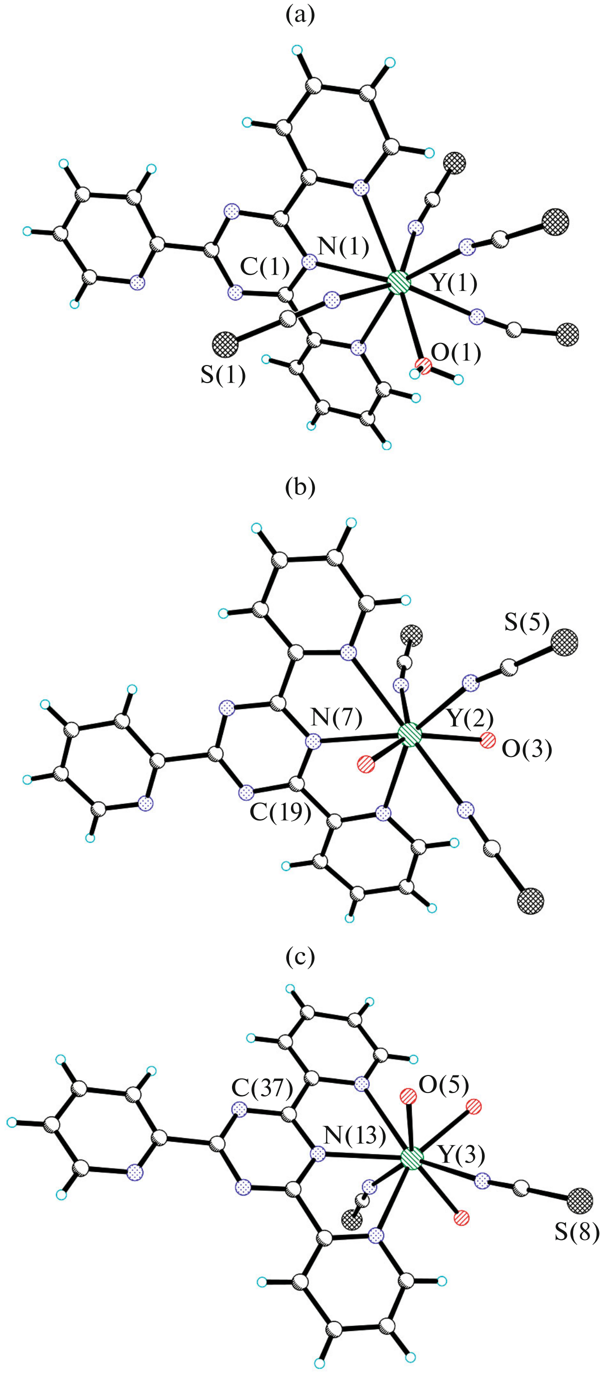


Fig. 3. Structures of complexes (a) $[Y(H_2O)(Tptz)(NCS)_4]^-$, (b) $[Y(H_2O)_2(Tptz)(NCS)_3])$, and (c) $[Y(H_2O)_3(Tptz)(NCS)_2]^+$ in compound **V**.

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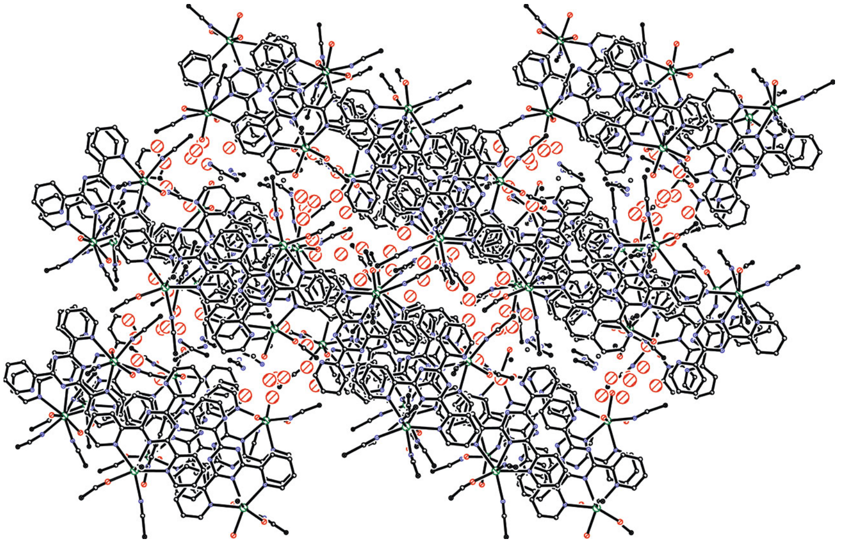

Fig. 4. Projection of the structure of compound **V** along the *a* axis (solvate H_2O molecules are shown by large circles).

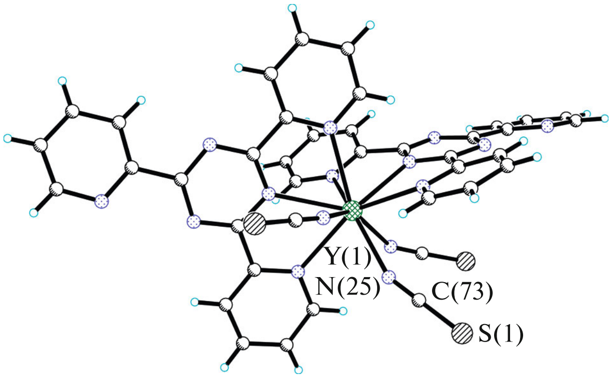

Fig. 5. Structure of complex $[Y(Tptz)_2(NCS)_3]$ in compound **VI**.

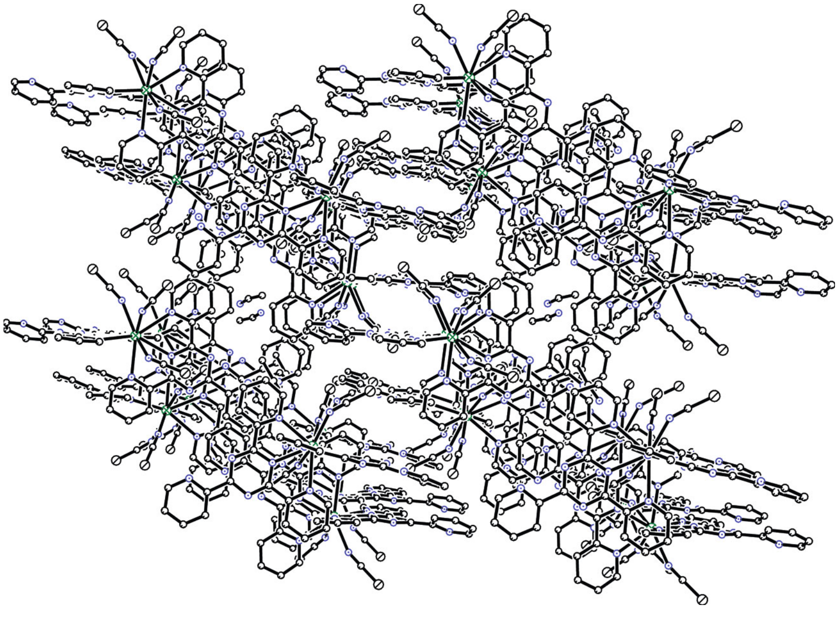

Fig. 6. Projection of the structure of compound **VI** along the *b* axis.

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