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Thiocyanates of Rare-Earth Elements with Tetramethylphenanthroline

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Abstract—Molecular $[M(NCS)_3(H_2O)(Me_4Phen)_2] \cdot (Me_4Phen) \cdot 0.75EtOH$ and anionic $[H(Me_4Phen)][M(NCS)_4(Me_4Phen)_2]$ complexes are synthesized using thiocyanates $M(NCS)_3 \cdot 6H_2O$ (M = Y, Eu, Tb) and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4Phen). The complexes are characterized by IR spectroscopy and elemental, X-ray phase, and X-ray diffraction analyses (CIF files CCDC no. 1498178–1498184). The thermoanalytical study shows that the solvate molecules Me_4Phen are localized in the internal coordination sphere of the molecular complexes at 195–250°C. The magnetic behavior of the Eu and Tb complexes is governed by the nature of the Ln ion.

Keywords: thiocyanates of rare-earth elements, tetramethylphenanthroline, X-ray diffraction analysis, thermal transformations, magnetic characteristics

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INTRODUCTION

Unlike transition metal compounds, thiocyanate compounds of rare-earth elements have no wide bibliography. The literature analysis of this field is given rather completely in the article [1] and review [2]. A low toxicity of the thiocyanate anion predetermines its use in pharmacology, and variability and easiness of binding with metal ions find use in biochemical assays. Researchers are presently interested in rare-earth element thiocyanates due to real and perspective applications in extraction, sensor devices, and diagnostics and therapy of oncological problems. Impressive results were obtained for the molecular complex of lanthanum thiocyanate with phenanthroline, $La(NCS)_3(Phen)_3$ (coordination mode LaN_9), showing cytotoxicity toward a series of cancerous cells [3]. The classical bidentate neutral ligand, 1,10-phenanthroline (Phen), forms coordination compounds of diverse composition with rare-earth element salts in which the coordination number of the rare-earth element is equal to 8–10. We have previously synthesized the ionic complex $[HPhen][Y(NCS)_4(Phen)_2]$ in which the coordination polyhedron of yttrium is formed by eight nitrogen atoms (YN_8), four of which belong to the NCS^- anions and four atoms belong to the molecular ligands [4]. The reactions of Y and Eu thiocyanates with Bipy and Phen in neutral and acidic solutions were described [5].

In this work, we studied specific features of the reactions of the tetramethyl derivative of Phen, 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4Phen), with Y, Eu, and Tb thiocyanates in neutral solutions and in the presence of acid HNCS, which made it possible to isolate and structurally characterize the heteroleptic complexes of rare-earth elements with the coordination modes MN_7O and MN_8 for the molecular and anionic forms, respectively.

EXPERIMENTAL

The following reagents were used: $[Y(H_2O)_5(NCS)_3] \cdot H_2O$ (high-purity grade) [6] and $[M(H_2O)_5(NCS)_3] \cdot H_2O$ (M = Eu, Tb) synthesized earlier [7], as well as Me_4Phen (Aldrich). All procedures were carried out in air.

Synthesis of molecular complexes $[M(NCS)_3(H_2O)(Me_4Phen)_2] \cdot (Me_4Phen) \cdot 0.75EtOH$ (M = Y (I), Eu (II), and Tb (III)) was carried out using the following procedure. A solution of $M(NCS)_3 \cdot 6H_2O$ (0.1 mmol) in ethanol (10 mL) was introduced into a solution of Me_4Phen (0.3 mmol) in ethanol (10 mL), and the mixture was stirred for ~20 min. On the next day, the solid phase was separated on a dense paper filter, washed with ethanol, and dried at room temperature.

The yield of compound **I** was 0.045 g (57% based on Y).

For $C_{52.5}H_{54.5}N_9O_{1.75}S_3Y$ (*FW* = 1024.66)
anal. calcd., %: C, 61.54; H, 5.36; N, 12.30; S, 9.39.
Found, %: C, 61.17; H, 5.22; N, 12.28; S, 9.65.

The yield of compound **II** was 0.070 g (70% based on Eu).

For $C_{52.5}H_{54.5}N_9O_{1.75}S_3Eu$ (*FW* = 1087.72)
anal. calcd., %: C, 57.97; H, 5.05; N, 11.59; S, 8.84.
Found, %: C, 57.78; H, 5.12; N, 11.55; S, 9.48.

The yield of compound **III** was 0.080 g (93% based on Tb).

For $C_{52.5}H_{54.5}N_9O_{1.75}S_3Tb$ (*FW* = 1094.68)
anal. calcd., %: C, 57.60; H, 5.02; N, 11.52; S, 8.79.
Found, %: C, 56.50; H, 5.07; N, 11.17; S, 10.14.

Synthesis of anionic complexes $[H(Me_4Phen)][M(NCS)_4(Me_4Phen)_2]$ (M = Y (IV), Eu (V), and Tb (VI)) was carried out using the following procedure. An aqueous solution of HNCS (~0.1 mmol) was introduced into a solution of Me_4Phen (~0.3 mmol) in EtOH (10 mL), and then a solution of $M(NCS)_3 \cdot 6H_2O$ (~0.1 mmol) in EtOH (10 mL) was added. The mixture was stirred for 20 min. The heterogeneous mixture was left to stay overnight. The isolated solid phase was washed with EtOH and dried at room temperature.

The yield of compound **IV** was 0.058 g (53.8% based on Y).

For $C_{52}H_{49}N_{10}S_4Y$ (*FW* = 1031.18)
anal. calcd., %: C, 60.57; H, 4.79; N, 13.58; S, 12.44.
Found, %: C, 60.40; H, 4.75; N, 12.76; S, 12.75.

The yield of compound **V** was 0.062 g (56.6% based on Eu).

For $C_{52}H_{49}N_{10}S_4Eu$ (*FW* = 1094.24)
anal. calcd., %: C, 57.07; H, 4.51; N, 12.80; S, 11.72.
Found, %: C, 57.00; H, 4.32; N, 11.78; S, 12.15.

The yield of compound **VI** was 0.066 g (65.2% based on Tb).

For $C_{52}H_{49}N_{10}S_4Tb$ (*FW* = 1101.20)
anal. calcd., %: C, 56.71; H, 4.48; N, 12.72; S, 11.64.
Found, %: C, 56.51; H, 4.20; N, 11.55; S, 12.26.

Elemental analysis was conducted using standard procedures on an EA1108 Carlo Erba CHN-analyzer at the Center for Collective Use of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences). IR spectra of attenuated total reflection (ATR) were recorded in a range of 400–4000 cm^{-1} on a Bruker ALPHA instrument.

X-ray phase analysis was carried out on a Bruker D8 Advance diffractometer (CuK_{α}, Ni filter, LYNX-EYE detector) at the Center for Collective Use of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences).

The thermochemical behavior of the synthesized compounds was studied using differential scanning calorimetry (DSC) and thermogravimetry (TG) on NETZSCH DSC 204 F1 and NETZSCH TG 209 F1 instruments, respectively [6].

The magnetochemical studies of the complexes were conducted on a Quantum Desing PPMS-9 magnetometer in a range of 2–300 K and in a magnetic field of 5 kOe [7].

X-ray diffraction analysis. Experimental data for compounds **I** and **VII–XII** were collected on a Bruker SMART APEX2 diffractometer (λ (MoK_{α}), graphite monochromator) [8] (table). Absorption corrections for compounds **VIII–XII** were applied by the semiempirical method for equivalents using the SADABS program [9]. The structures were determined by a combination of a direct method and Fourier syntheses. The populations of the disordered fragments were obtained by the isotropic refinement of the structures with the fixed thermal parameters of disordered atoms and were ignored in subsequent calculations. The structures were refined by full-matrix anisotropic–isotropic (some disordered atoms) least squares. The hydrogen atoms were partially localized from the difference Fourier syntheses and were partially calculated from geometric concepts. All calculations were performed using the SHELXS-2014 and SHELXL-2014 programs [10].

The experimental data for the structures of compounds **I** and **VII–XII** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC no. 1498178–1498184); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Compounds **I–III** were isolated from solutions of $M(NCS)_3 \cdot 6H_2O$–$3Me_4Phen$–EtOH. The X-ray phase analysis showed the phase purity of the isolated polycrystalline powders of compounds **I–III** and that they were isostructural to the yttrium analog $[Y(NCS)_3(H_2O)(Me_4Phen)_2] \cdot (Me_4Phen) \cdot$

Selected structural data and refinement results for compounds **I** and **VII–XII**

Parameter	Value						
Compound	**I**	**VII**	**VIII**	**IX**	**X**	**XI**	**XII**
T, K	173(2)	120(2)	150(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$Pca2_1$	$C2/c$	$P\overline{1}$	$P2_1/c$	$P2_1/c$	$P\overline{1}$
a, Å	13.013(2)	21.370(5)	7.2633(9)	12.7763(10)	13.3591(5)	15.1937(6)	14.2771(12)
b, Å	16.460(3)	12.850(3)	22.346(2)	18.4850(14)	37.0510(16)	22.3522(9)	20.3287(17)
c, Å	23.929(4)	20.409(5)	18.147(2)	21.9837(17)	13.8105(6)	14.2875(6)	21.6458(18)
α, deg	90	90	90	89.167(2)	90	90	94.519(2)
β, deg	100.172(3)	90	91.151(4)	76.699(2)	109.2840(10)	95.4260(10)	98.871(2)
γ, deg	90	90	90	80.980(2)	90	90	99.823(2)
V, Å^3	5044.9(15)	5604(2)	2944.8(6)	4988.9(7)	6452.2(5)	4830.5(3)	6080.5(9)
Z	4	4	8	4	4	4	4
ρ_{calcd}, g/cm^3	1.349	1.276	1.333	1.481	1.449	1.456	1.448
μ, mm^{-1}	1.329	0.116	0.216	1.474	1.189	1.477	1.192
F(000)	2134	2296	1248	2272	2896	2164	2736
Crystal size, mm	0.18 × 0.16 × 0.1	0.08 × 0.08 × 0.02	0.32 × 0.04 × 0.04	0.2 × 0.1 × 0.01	0.16 × 0.03 × 0.02	0.2 × 0.12 × 0.1	0.24 × 0.2 × 0.1
Range of θ, deg	2.079–25.682	2.101–23.256	2.141–25.666	2.094–26.440	2.143–28.314	2.249–28.333	2.045–26.401
Range of indices	$-15 \le h \le 15$, $-20 \le k \le 20$, $-29 \le l \le 29$	$-23 \le h \le 23$, $-14 \le k \le 14$, $-22 \le l \le 22$	$-8 \le h \le 8$, $-27 \le k \le 27$, $-22 \le l \le 22$	$-15 \le h \le 15$, $-23 \le k \le 23$, $-27 \le l \le 27$	$-17 \le h \le 17$, $-49 \le k \le 48$, $-18 \le l \le 18$	$-15 \le h \le 20$, $-28 \le k \le 29$, $-19 \le l \le 15$	$-17 \le h \le 17$, $-25 \le k \le 25$, $-27 \le l \le 27$
Collected reflections	41507	39829	29902	55433	58483	36155	56053
Independent reflections (R_{int})	9576 (0.1593)	8053 (0.2826)	2795 (0.1191)	20392 (0.1142)	15840 (0.1021)	11849 (0.0390)	24579 (0.0780)
Completeness to $\theta = 25.242°$, %	99.9	99.9	100.0	99.9	99.9	99.9	99.6
Max, min transmission			0.7455, 0.5415	0.7454, 0.5935	0.7457, 0.5672	0.7452, 0.492	0.7454, 0.6494
Restraints/parameters	6/610	43/729	0/236	0/1225	0/818	0/606	0/1531
GOOF	0.809	0.751	1.032	0.927	0.914	1.050	0.882
R_1, wR_2 ($I > 2\sigma(I)$)	0.0493, 0.0872	0.0670, 0.1174	0.0501, 0.1220	0.0548, 0.0954	0.0530, 0.1105	0.0371, 0.0836	0.0490, 0.0865
R_1, wR_2 (all data)	0.1491, 0.1056	0.2475, 0.1658	0.1105, 0.1532	0.1533, 0.1240	0.1416, 0.1318	0.0536, 0.0900	0.0872, 0.0945
Flack parameter		0.2(4)					
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.520/–0.504	0.247/–0.257	0.206/–0.311	1.210/–1.673	3.182/–1.278	1.232/–0.679	1.896/–1.032

0.75EtOH (vide infra). Interestingly, the X-ray diffraction analysis of the crystals obtained in the synthesis of compound **I** after the solid phase was isolated from the mother liquor showed the formation of $[HMe_4Phen] \cdot NCS \cdot 3Me_4Phen \cdot 4H_2O$ (**VII**). The formation of the similar agglomerate can be related to an enhanced accepting ability of Me_4Phen increasing due to the introduction of four methyl groups into the condensed N-heterocycles. It is most likely that the ligand is protonated in a solution due to the coordination water molecules of the aquathiocyanate complex: $M(NCS)_3(H_2O)_5 \cdots Me_4Phen \rightarrow [HMe_4Phen]^+$. To compensate a charge of the protonated ligand, NCS^- should be extracted from the coordination sphere, so that the formed $[HMe_4Phen] \cdot NCS$ is isolated in the form of ensemble **VII**. This process occurs predominantly from the mother liquid of compound **I** and decreases noticeably in the syntheses of compounds **II** and **III**. The yield of the molecular complexes increases in parallel in the series Y–Eu–Tb, being 57, 70, and 93%, respectively. This tendency corresponds to a decrease in the acidity of the coordinated H_2O molecules with an increase in the number of the rare-earth element.

The IR spectra of samples **I–III** exhibit two ν(CN) bands with 2073.4 and 2047.9, 2066.3 and 2039.4, and 2070.6 and 2045.1 cm^{-1} and an intensity ratio of ~1 : 2. The stretching vibrations of the hydroxyl groups of the coordinated water molecule and solvate ethanol molecule are observed at 3272.94 and 3200.7, 3271.5 and 3180.9, and 3281.4 and 3195.0 cm^{-1} for compounds **I**, **II**, and **III**, respectively.

Powdered compounds **IV–VI** were obtained from solutions of $M(NCS)_3 \cdot 6H_2O$–$3Me_4Phen$–HNCS–EtOH in the syntheses of the anionic complexes. The X-ray phase analyses of these powders demonstrated their similarity. The absence of stretching vibration bands of hydroxyl groups in the IR spectra of compounds **IV–VI** indicates that the anionic complexes were obtained without coordinated (solvate) water or alcohol molecules. It should be mentioned that many "needles" of the protonated ligand, $HMe_4PhenNCS$ (**VIII**), were observed in the mother liquor from the synthesis of compound **V**. The crystals of the hydrated anionic complex $[H(Me_4Phen)][Eu(NCS)_4(Me_4 Phen)_2] \cdot H_2O$ (**IX**) were found in the mother liquor after the solid phase was separated in the synthesis of compound **V** in methanol. No impurity phase is observed on the X-ray pattern of the polycrystalline powders of compound **V**. We have earlier established the formation of the non-solvated anionic yttrium complex with Phen, $[HPhen][Y(NCS)_4(Phen)_2]$, obtained from an aqueous solution [4]. Therefore, we attempted to synthesize an anionic europium complex in an $EtOH–H_2O$ (~2 : 1) mixed solvent. The crystals of the anionic complex $[H(Me_4Phen)]_2[Eu(NCS)_4(Me_4Phen)_2](NCS) \cdot H_2O$ (**X**) and molecular solvated compound $[Eu(NCS)_3(Me_4Phen)_2(H_2O)] \cdot (Me_4Phen) \cdot 0.3H_2O$ (**XI**) were isolated from this solution. The crystals of $[Eu(NCS)_2(H_2O)_3(Me_4Phen)_2] \cdot (NCS) \cdot 2(Me_4Phen)$ (**XII**) were identified in the obtained heterogeneous mixture upon the recrystallization of a powder of compound **V** from a mixture of ethanol (15 mL) and water (5 mL). The array of experimental data (the absence of absorption bands of hydroxyl groups in the IR spectra of compounds **IV–VI** and the absence of traces of the solvated anionic forms of compounds **IX** and **X** in the X-ray powder patterns) makes it possible to attribute compounds **IV–VI** to the non-solvated complexes $[H(Me_4Phen)][M(NCS)_4(Me_4Phen)_2]$ by analogy to the yttrium and europium compounds with phenanthroline [5].

Compound **I** is formed by the molecular complexes $[Y(NCS)_3(H_2O)(Me_4Phen)_2]$ and solvate molecules Me_4Phen and EtOH (Fig. 1a). The coordination number of the Y atom is 8, and the coordination polyhedron is a square antiprism with the O(1)/N(1, 3, 4) and N(2, 3, 6, 7) atoms in the bases. The O–H···O(N) hydrogen bonds join the structural units. The S and C atoms of the N(1)C(1)S(1) ligand are disordered over two positions in a ratio of 3 : 1, and the site occupancy of the EtOH solvate molecule is 0.75. The Me_4Phen solvate molecule participates in the stacking interaction with the coordinated Me_4Phen molecule (Fig. 1b). The angle between the root-mean-square planes of the Me_4Phen aromatic rings is 2.4°, and the shortest contacts are as follows: C(4)···N(9) 3.218, C(4)···C(46) 3.450, and C(15)···C(47) 3.444 Å.

The structure of compound **IX** contains the anionic complexes $[Eu(NCS)_4(Me_4Phen)_2]^-$ (Fig. 2), protonated ligands $[H(Me_4Phen)]^+$, and solvate H_2O molecules (two crystallographically independent structural units in each molecule). The structures of the complexes in compound **IX** are the same, the coordination number of Y is 8, and the coordination polyhedron is a square antiprism, each base of which is formed by the N atoms of one Me_4Phen ligand and two N atoms of the NCS ligands. The aromatic Phen fragments of the coordinated ligands and cations are involved in stacking interactions to form piles (Fig. 3a). Two crystallographically independent water molecules form the centrosymmetric associate $(H_2O)_4$ (Fig. 3b) with O···O distances of 2.853(7) and 2.825(7) Å. The H atoms forming hydrogen bonds inside the associate are disordered over two positions in such a way that tetramers twisted clockwise and

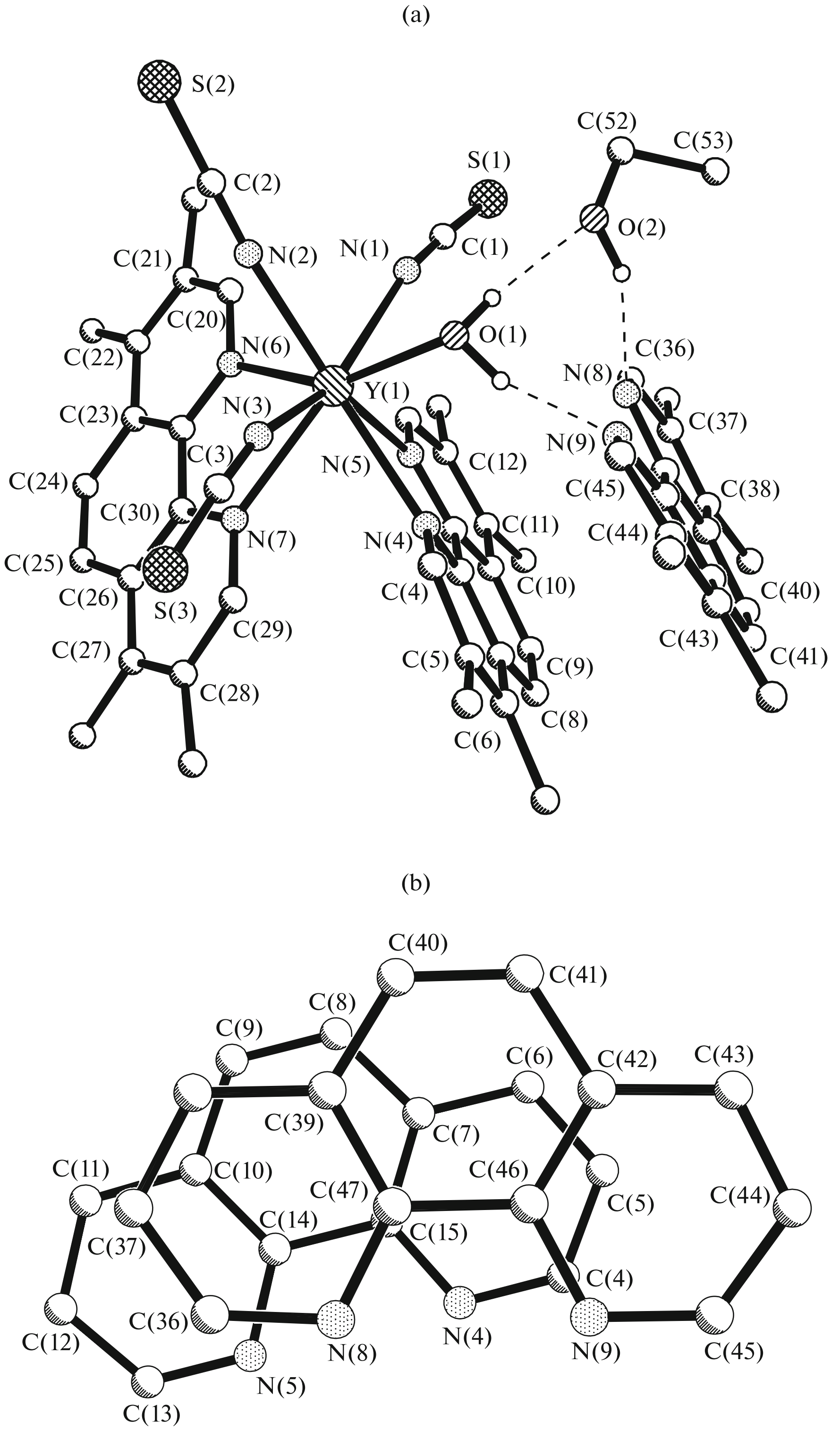

Fig. 1. Fragment of the structure for compound **I** (the (a) H atoms bound to the C atoms and (b) H atoms and Me groups are omitted).

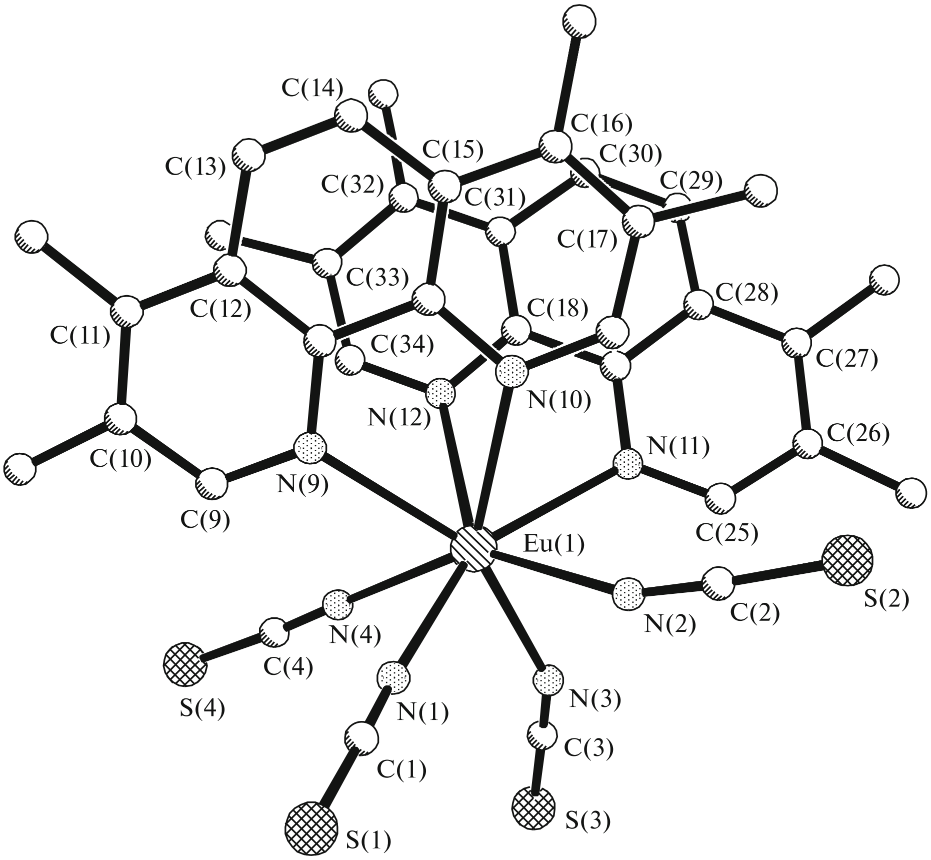

Fig. 2. Structure of the complex in compound **IX** (H atoms are omitted).

anticlockwise can conventionally be distinguished. The ordered H atoms are involved in hydrogen bonds O–H···S.

The composition of compound **X** differs from that of compound **IX** by [H(Me_4Phen)](NCS). The structure of the complexes in compounds **IX** and **X** is the same (Figs. 2 and 4a). The addition cation $[H(Me_4Phen)]^+$ displaces the anionic complexes from the piles in the structure of compound **IX** (Fig. 3a), resulting in the formation of purely cationic piles in compound **X** (Fig. 4b).

The structure of the complex in compound **XI** (Fig. 5a) is similar to that found in compound **I** with allowance for the replacement of the complexing agent. Two hydrogen bonds O–H···N join the molecular complex and solvate Me_4Phen molecule (in the structure of compound **I**, the associate also contains the solvate EtOH molecule, Fig. 1a). Stacking interactions join the solvate Me_4Phen molecules into centrosymmetric dimers (Fig. 5b). The structure contains centrosymmetric cavities partially occupied by disordered H_2O molecules.

The structure of compound **XII** is formed by the cationic complexes $[Eu(NCS)_2(H_2O)_3(Me_4Phen)_2]^+$, NCS^- anions, and solvate Me_4Phen molecules. The structures of two crystallographically independent complexes are the same (Fig. 6a), the coordination number of Eu is 9, and the coordination polyhedron is a three-capped trigonal prism. The structural functions of four independent Me_4Phen molecules differ. Two of them form associates (similar to those observed in the structure of compound **IX**) with the complexes via the O–H···N hydrogen bonds, and two other molecules form piles with the complexes via the stacking interaction with the coordinated Me_4Phen molecules (Fig. 6b).

The structures of compounds **I–III** formed by the molecular complexes $[M(NCS)_3(H_2O)(Me_4Phen)_2]$ and solvate molecules Me_4Phen and EtOH are most interesting from the viewpoint of the behavior at elevated temperatures. The thermal behavior of compounds **I–III** was studied in a range of 30–400°C. These isostructural compounds are stable at room temperature and decompose similarly (Fig. 7).

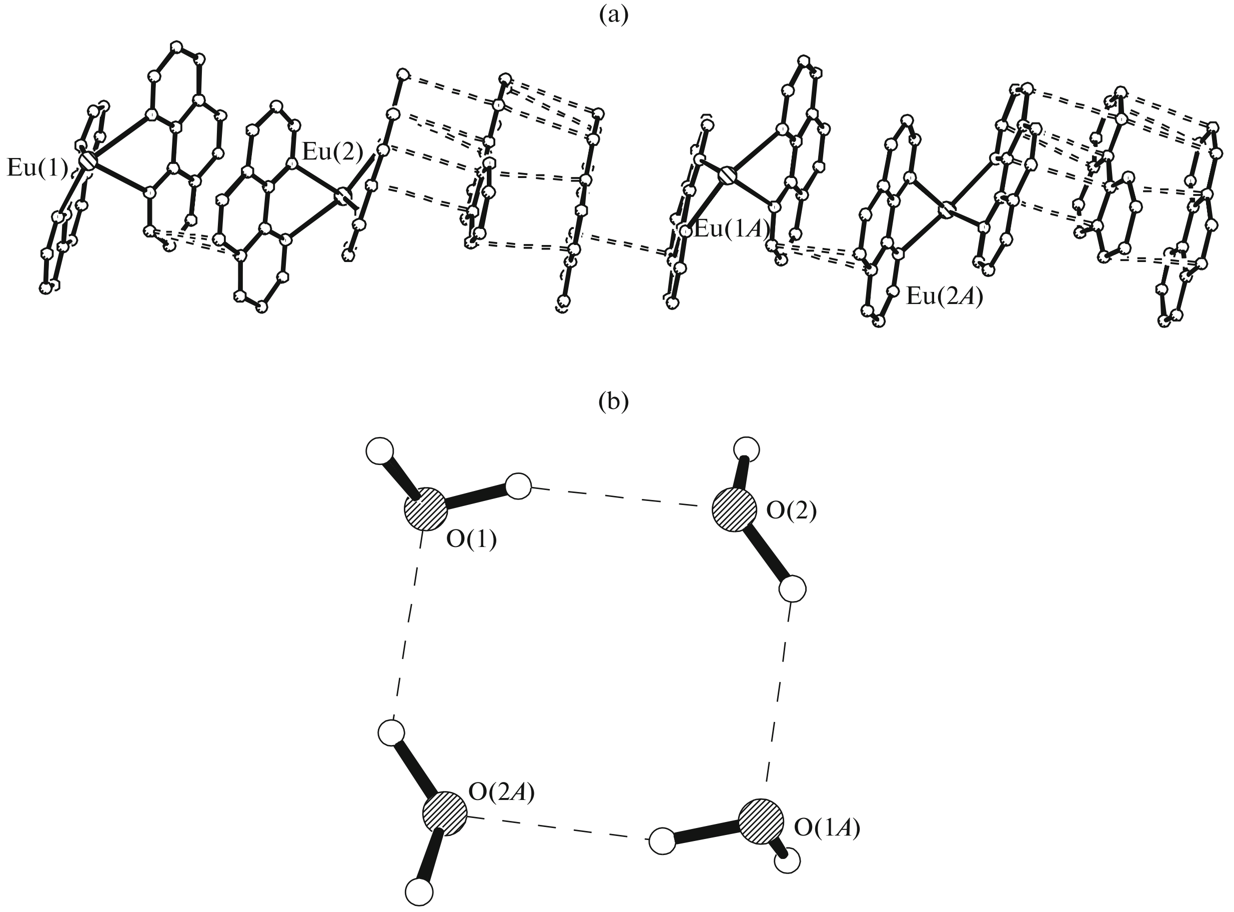

Fig. 3. Fragments of the structure of compound **IX**: (a) with the contacts N···C and C···C < 3.50 Å and (b) centrosymmetric $\{H_2O\}_4$ (one set of disordered H atoms is shown).

The first stage is the removal of the solvate EtOH molecules (80–120°C, $\Delta m = 3.7 \pm 1.0\%$ (for **I**), $\Delta m = 3.3 \pm 1.0\%$ (for **II**), and $\Delta m = 3.1 \pm 1.0\%$ (for **III**)). A double endothermic effect is observed in the DSC curve in a temperature range of 40–120°C (Fig. 7). Probably, the first endothermic effect corresponds to energy expenses to the cleavage of the hydrogen bonds joining the structural units between each other. The loss of the coordinated water molecules in the compounds starts at 145 (**II**), 150 (**III**), and 155°C (**I**). The further heating leads to a considerable exothermic effect ($T_{\max}$ = 195 (**II**), 240 (**III**), and 250°C (**I**)) (Fig. 8a), which is not accompanied by a change in the sample weight. The weights of the obtained intermediates remain almost unchanged to 288, 292, and 300°C for compounds **II**, **III**, and **I**, respectively. The obtained results suggest that the removal of coordinated water results in the incorporation of solvate Me_4Phen into the internal sphere of the metal. A similar fact was observed for compounds $[M(NCS)_3(H_2O)(Phen)_2] \cdot Phen \cdot 0.5H_2O$ (M = Eu, Y) [5]. Interestingly, the dependence of the temperature of the incorporation of solvate Me_4Phen ($T_{\max}$) into the internal sphere of the metal on the ionic radius of M^{3+} is rather distinct (Fig. 8b). The data for similar complexes with Phen are also presented and make it possible to reveal a noticeable role of the steric factor that governs the dynamics of insertion of condensed heterocyclic ligands into the coordination sphere of the rare-earth element. For more bulky Me_4Phen, $T_{\max}$ increases by 30–60°C depending on the complexing agent (Fig. 8b). The intermediates obtained from compounds **I–III** undergo melting with decomposition above 300°C (Fig. 7).

The temperature dependences of the dc magnetic susceptibility were studied in a range of 300–2 K for compounds **I–III** and **V**. The value of $\chi_m T$ at 300 K for compound **III** is close to the theoretical value [11]. As the temperature decreases, the values of $\chi_m T$ do not change noticeably down to 100 K but decrease smoothly with the further temperature decrease and achieve a minimum at $T = 2$ K (Fig. 9). The temperature dependence of the inverse magnetic susceptibility

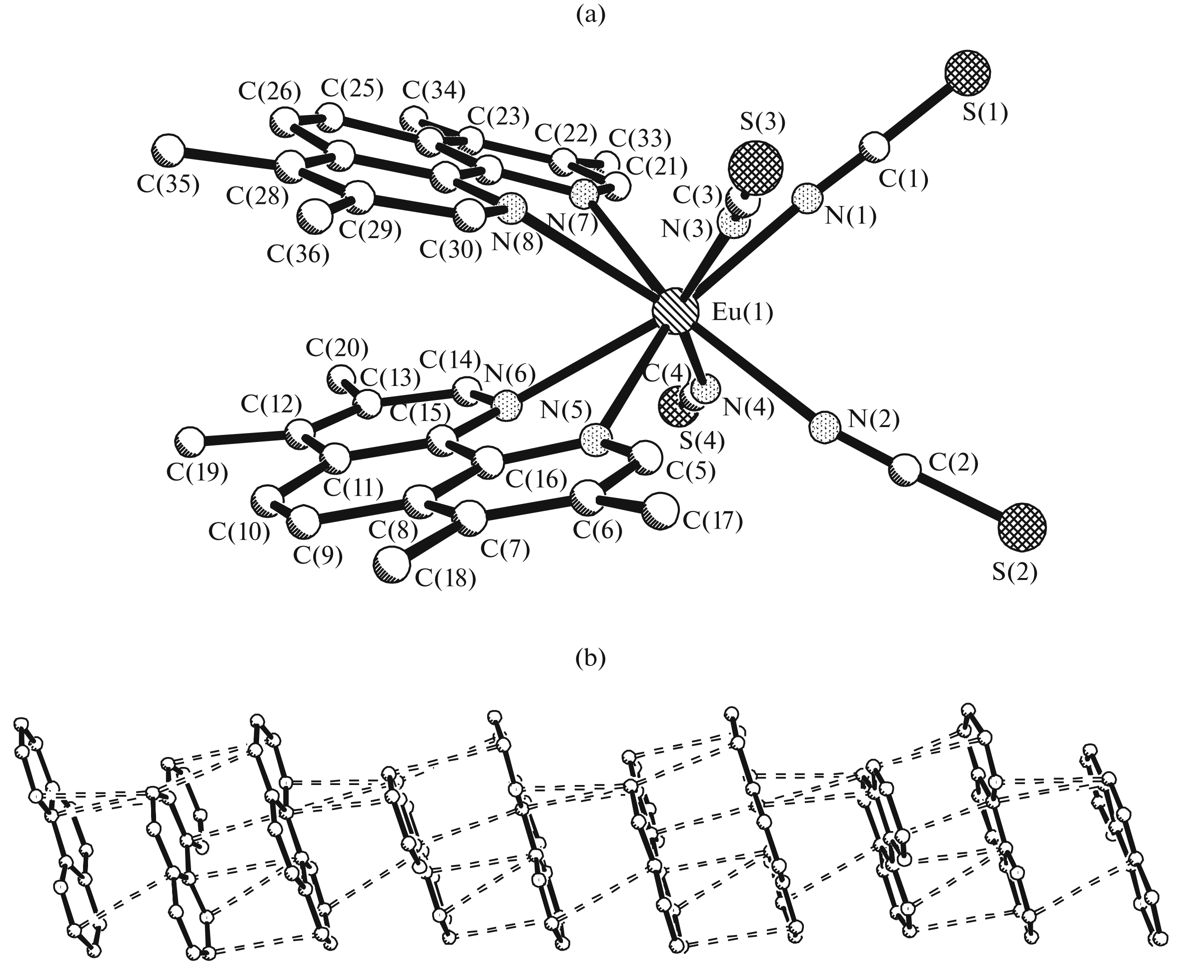

Fig. 4. Complex in the structure of compound **X**: (a) H atoms are omitted and (b) the fragment of the structure of compound **X** with the contacts N···C and C···C < 3.50 Å.

$1/\chi_m$ in a range of 100–300 K obeys the Curie–Weiss law with the constants $C = 12.390 \pm 0.012$ cm^3 mol^{-1} K and $\theta = -2.06 \pm 0.21$ K. This behavior can be due to the splitting of the m_J levels in the zero field as a result of the ligand field effect, Zeeman effect upon external field application, and/or weak antiferromagnetic interactions between the terbium ions.

Compounds **II** and **V** demonstrate the magnetic behavior typical of the known mononuclear, polynuclear, or polymer systems of Eu^{3+} ions [12]. Unlike other Ln^{3+} ions, the energy spectrum of Eu^{3+} ($4f^6$) is characterized by a low splitting between the nonmagnetic ground state $^7F_0$ and the first excited multiplet. Taking into account the spin-orbital Hamiltonian, $H_{SO} = \lambda\mathbf{L}\cdot\mathbf{S}$, the first excited state $^7F_1$ is only by λ cm^{-1} higher by energy than that of the $^7F_0$ level. At 200–300 K, the energy of thermal fluctuations is sufficient for the population of only three first energy levels at 0, λ ($^7F_1$), and 3λ ($^7F_2$) (the population of $^7F_2$ is usually insignificant: ~1% [13]), which is accompanied by the appearance of a significant magnetic moment at room temperature (Fig. 10). The temperature increase is accompanied by a monotonic decrease in χ_mT to 0.034 (**II**) and 0.029 (**V**) cm^3 mol^{-1} K at $T = 2$ K. As for the most part of other Eu^{3+} complexes, this decrease in χ_mT is due to a decrease in the population of the excited levels. As the temperature decreases, the values of χ_m increase rather rapidly to ~130 K and almost reach a plateau in a range of 120–30 K. A sufficiently sharp increase in χ_m in the range of helium temperatures is probably caused by the presence in the samples of paramagnetic impurities at a level of several ppm.

Only one parameter of the spin-orbital interaction, λ, is sufficient for the description of the experimental data $\chi_mT(T)$ [14]. The estimation of the energy distance between the $^7F_0$ and $^7F_1$ levels, λ_{C-P}, from the magnetochemical data $\chi_m(T)$ is also possible using the

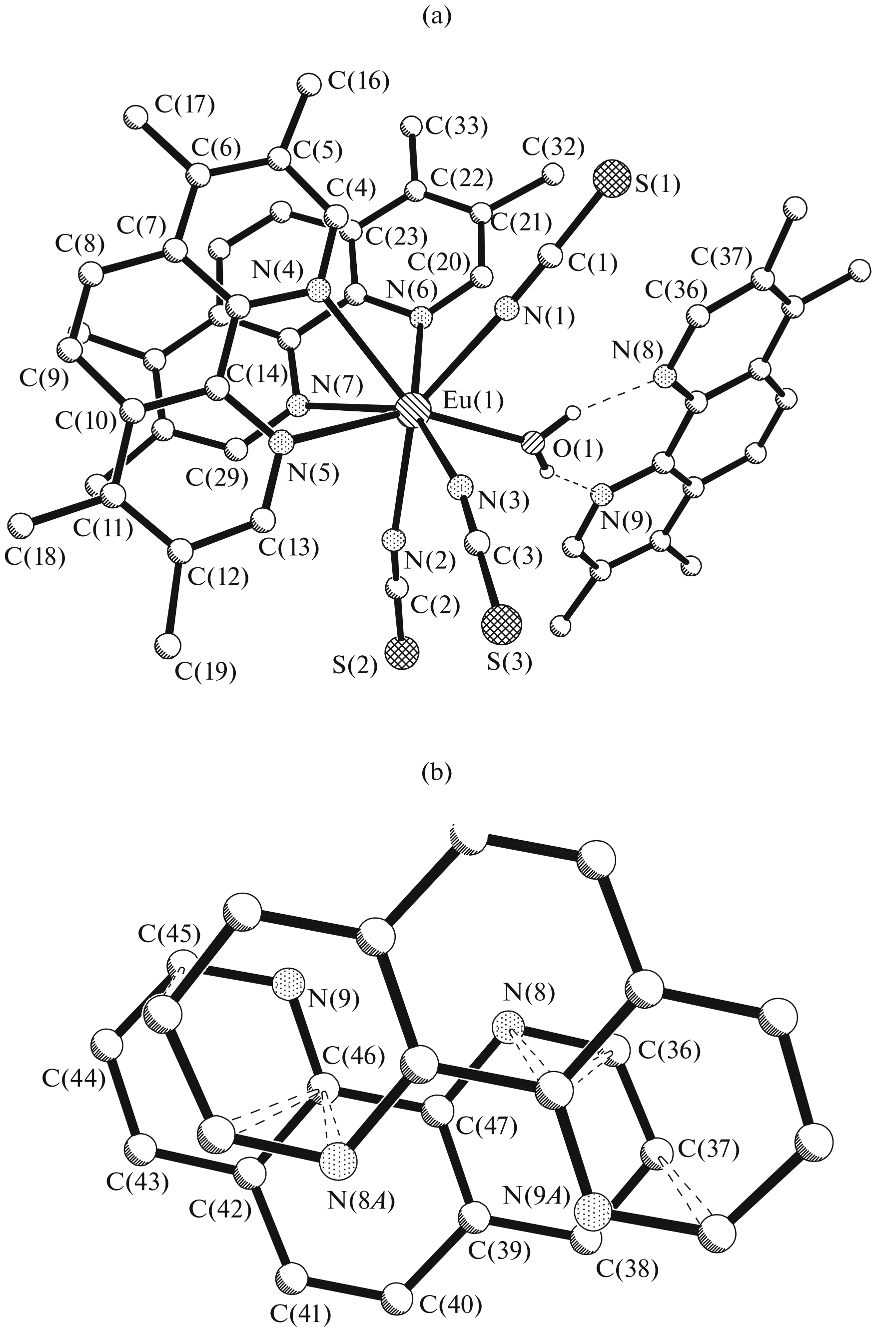

Fig. 5. Fragments of the structure of compound **XI** (the (a) H atoms bound to the C atoms and (b) H atoms of the Me group are omitted).

Caro–Porcher equation [15]. For the compounds considered, the estimated values of λ and λ_{C-P} are 252 and 254 cm^{-1} for compound **II** and 270 and 293 cm^{-1} for compound **V**. It is seen that the values of λ_{C-P} are satisfactorily consistent. The values obtained are fairly low, and also the low value ($\lambda = 253$ cm^{-1}) was obtained for polymer $\{[Eu_2(Dpa)_2(C_2O_4)_2(H_2O)_2] \cdot H_2O\}_n$ (Dpa is 2,2'-(2-methylbenzimidazolium-1,3-diyl) diacetate, and $C_2O_4^{2-}$ is oxalate) [16]. Such low values are caused, probably, by a noticeable crystalline field effect in the structures considered.

The obtained results compared to the known data [5] allow one to make the following generalizations. The reactions of rare-earth element thiocyanates with

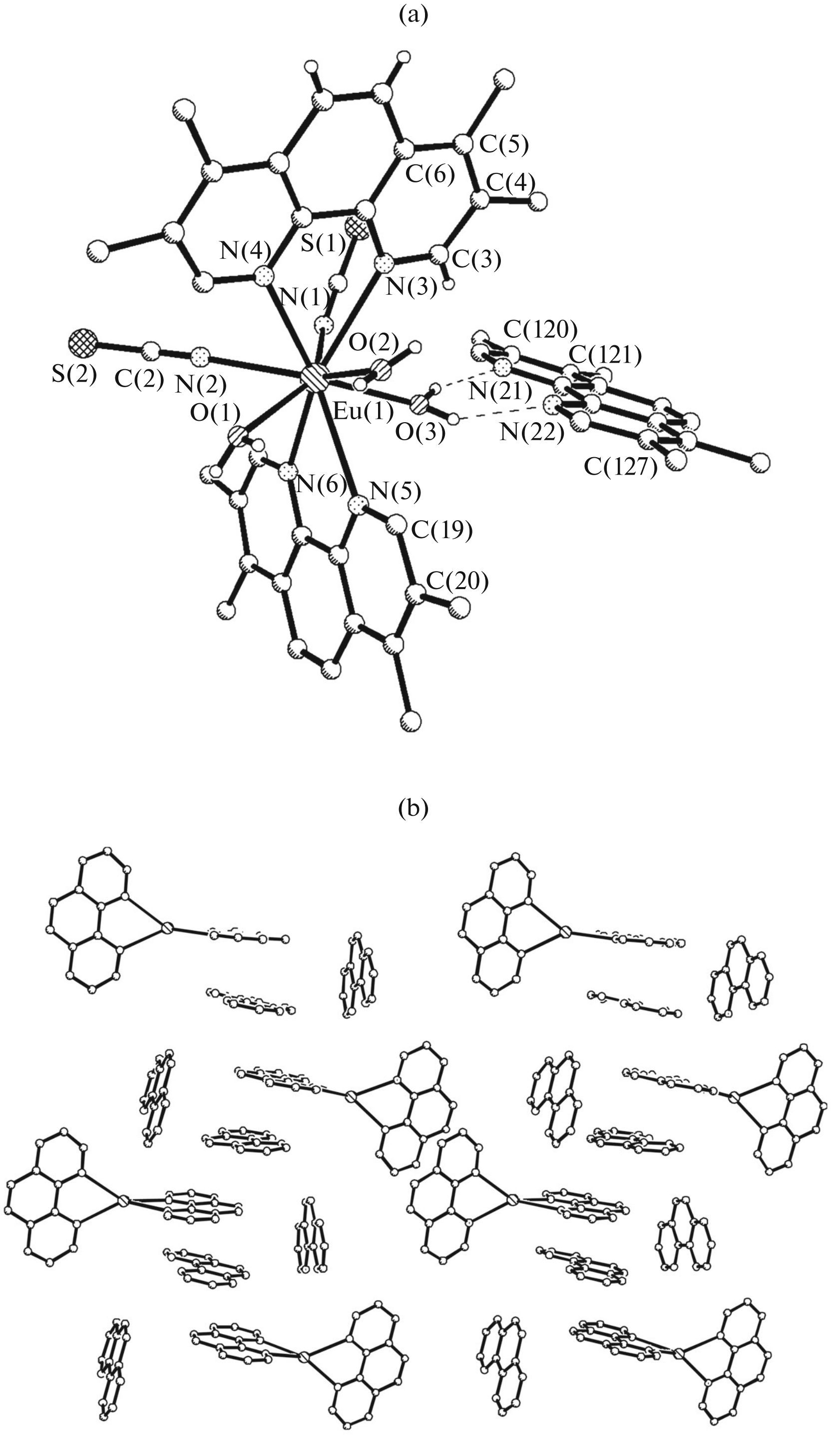

Fig. 6. (a, b) Fragments of the structure of compound **XII** (the H atoms bound to the C atoms are omitted).

the bidentate heterocyclic ligands (Bipy, Phen, and Me_4Phen) in alcohol solutions afford the molecular compounds with the coordination number 8 and coordination mode MON_7 formed by two molecules of the bidentate ligand, three NCS anions, and coordinated water molecule. The third ligand molecule is localized in the external sphere. Condensed diimines are inserted into the coordination sphere at the tempera-

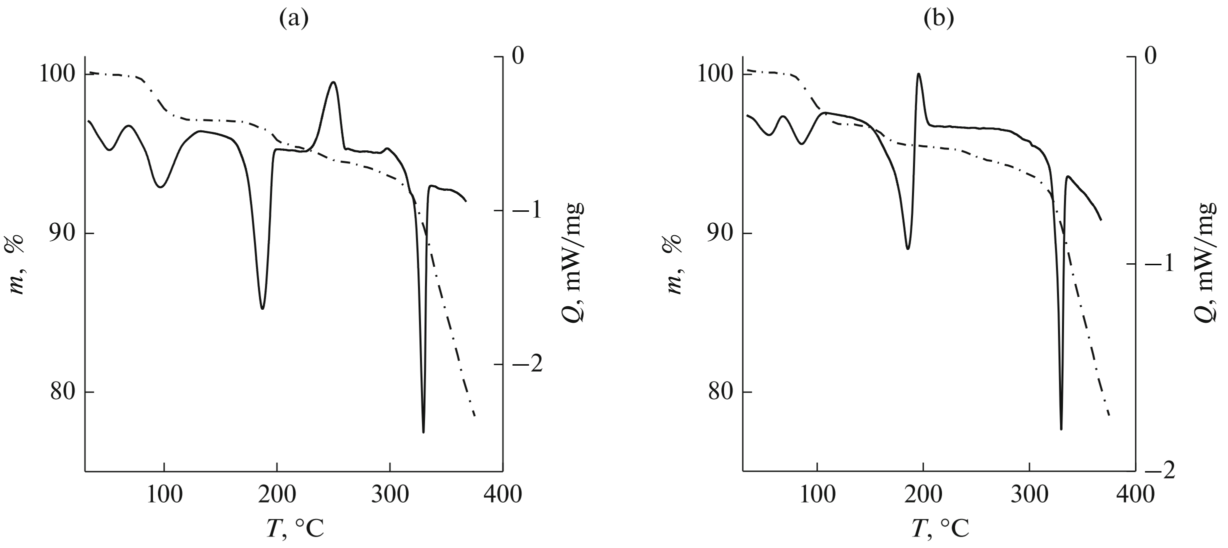

Fig. 7. (—) DSC and (— • — •) TG curves for compounds (a) **I** and (b) **II**.

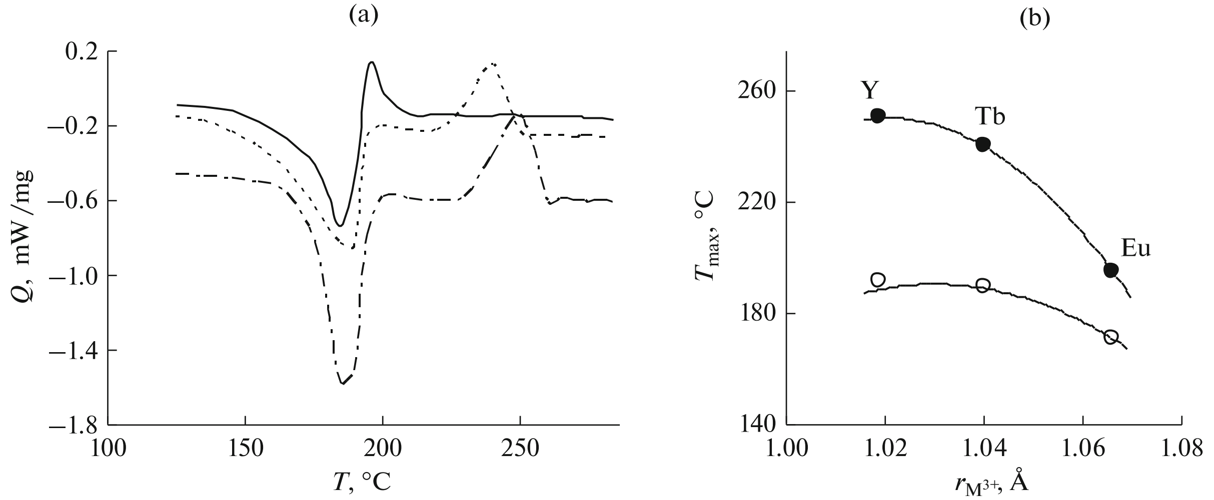

Fig. 8. (a) DSC curves in the 120–270°C range: (–) **II**, (---) **III**, and (– • – •) **I**; (b) the dependence $T_{\max}(r_{M^{3+}})$ for the compounds with (•) Me_4Phen and (o) Phen [5].

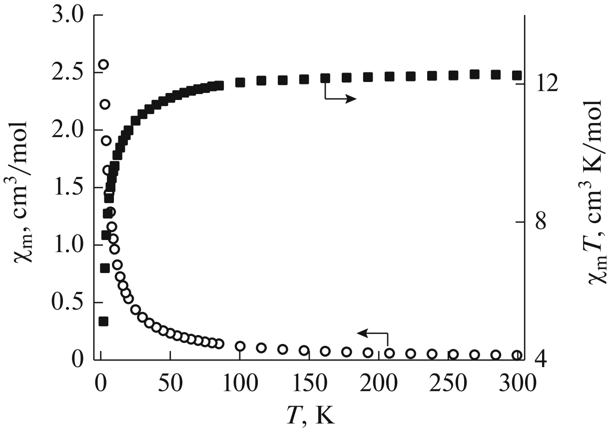

Fig. 9. Dependences χ_m and $\chi_m T$ for compound **III**.

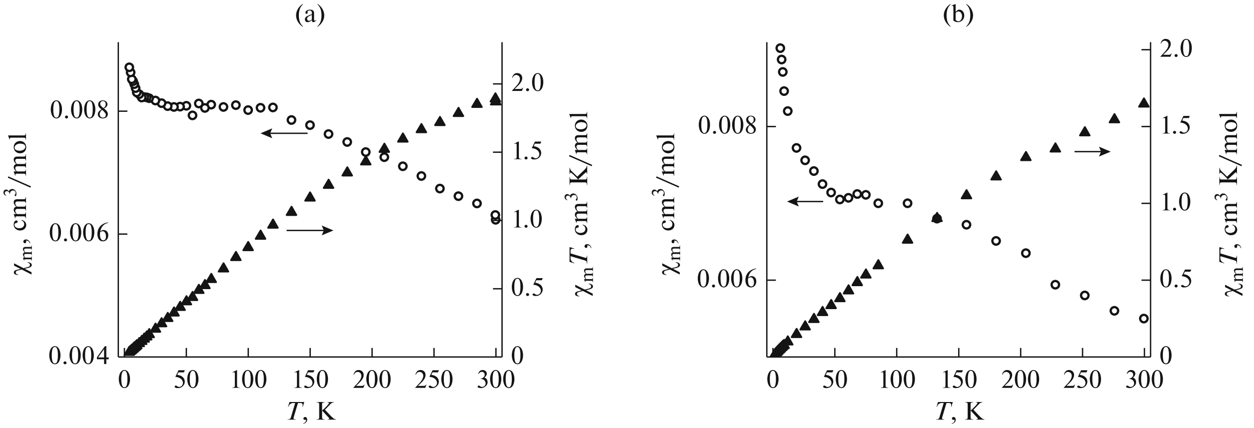

Fig. 10. Dependences $\chi_m(T)$ and $\chi_m T(T)$ for compounds (a) **II** and (b) **V**.

tures >170°C to form an intermediate with the coordination mode MN_9. The transformation temperature for the diimine coordination *exo* → *endo* is related to the ionic radius of M^{3+} and steric features of the organic ligand. The work in this area is being continued. The anionic complexes containing no solvate molecules are formed in the presence of HNCS. The impurity compounds obtained from these systems are solvated by the solvent (water, alcohols) molecules only.

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