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Yttrium Complexes with N-Donor Ligands

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Abstract—Compounds $[HBipy][Y(NCS)_4(Bipy)_2] \cdot H_2O$ (**I**), $[HPhen][Y(NCS)_4(Phen)_2]$ (**II**), and $[Y(Nic)_3(H_2O)_2]_2$ (**III**), where Bipy is 2,2'-bipyridine and Phen is 1,10-phenanthroline, are synthesized and structurally characterized by X-ray diffraction analyses (CIF files CCDC 984621, 984622, and 934971, respectively). In the anionic complexes, the coordination polyhedron of sodium is formed by eight nitrogen atoms, four of which are provided by the acido ligands and four others are given by two molecules of the N-heterocycle. In compounds **I** and **II**, the protonated and coordinated diimines together participate in stacking interactions.

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INTRODUCTION

The stable oxidation state for yttrium is Y^{3+}, and the three-charged cation forms the strongest complexes with O- and N-donor ligands or halide ions. Structural diversity of the yttrium(III) halide complexes was reviewed [1]. The coordination chemistry of yttrium with polydentate ligands has been developed intensely in the recent years. The synthesized coordination polymers are promising in the production of supramolecular devices, fluorescence sensors, or luminescence indicators frequently used in medicine and biology.

The carboxy derivatives of N-heterocyclic compounds, which are capable upon coordination of forming N,O-chelate rings with simultaneous polymerization through the COO fragments, are promising ligands for the construction of coordination polymers [2]. For example, in the coordination polymer of yttrium with chelidamic acid ($H_3L = C_7H_5NO_5$) $[YL(H_2O)_3]_n \cdot nH_2O$ [3] yttrium has a coordination number of 8, and the coordination polyhedron YNO_7 is formed by the tridentate chelating ligand L, three water molecules, and two oxygen atoms of two adjacent organic ligands. In the case of monobasic nicotinic acid (HNic is 3-pyridinecarboxylic acid), all lanthanides from La to Tm form dimers $[M(Nic)_3(H_2O)_2]_2$ [4] in which the coordination number of the cation is 8 but the coordination polyhedron is MO_8.

In this work, we studied the regularities of the reaction of HNic with yttrium thiocyanate $[Y(H_2O)_5(NCS)_3] \cdot H_2O$ in the presence of 2,2'-bipyridine (Bipy) and 1,10-phenanthroline (Phen), which made it possible to isolate and structurally characterize the anionic heteroleptic yttrium complexes, whose coordination sphere consists of eight nitrogen atoms.

EXPERIMENTAL

The following commercial reagents were used: $[Y(H_2O)_5(NCS)_3] \cdot H_2O$ (high-purity grade) [5] and HNic, Bipy, and Phen (Aldrich). All procedures were carried out in air. Elemental analyses were carried out according to 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 were recorded on a Nexus FT-IR spectrometer (Nicolet) in the range from 550 to 4000 cm^{-1} at the Center for Collective Use of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences). A Nicolet attachment (Pike technologies) was used to record attenuated total internal reflectance spectra. X-ray phase analyses were carried out on a Bruker D8 Advance diffractometer (CuK_α, Ni filter, LYNXEYE detector) at the Center for Collective Use of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences).

X-ray diffraction analysis. Experimental data for compounds **I–III** were obtained on a Bruker SMART APEX II diffractometer ($\lambda(MoK_\alpha)$) [6] (Center for Collective Use of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences), and an absorption correction was applied by the semiempirical method using the SADABS program [7]. The structures were determined by a combination of a direct method and Fourier syntheses. Hydrogen atoms were partially localized from difference Fourier syntheses and were partially calculated from geometric concepts. The refinement was performed by full-matrix anisotropic least squares taking into account hydrogen atoms. All calculations were performed using the SHELXS-97 and SHELXL-2013 programs [8].

The main structural data are presented in the table. The additional material for structures **I–III** was deposited with the Cambridge Crystallographic Data Centre (CCDC 984621, 984622, and 934971; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/DataRequest.aspx).

Synthesis of [HBipy][Y(NCS)$_4$(Bipy)$_2$] · H$_2$O (I). Weighed samples of HNic (0.356 g, 2.90 mmol) and Bipy (0.323 g, 2.07 mmol) were dissolved in water (20 mL) with slight heating, and $Y(NCS)_3 \cdot 6H_2O$ (0.385 g, 1.04 mmol) in H_2O (10 mL) was added to the solution. The obtained pink solution (pH 6) was heated at ~40°C for ~1 h during which the color became more intensive. In a week, a solid phase was formed due to isothermal evaporation, separated on a glass filter, and dried in a vacuum drying box over silica gel. The yield was 0.19 g. To obtain single crystals, the product was recrystallized from water.

For $C_{34}H_{27}N_{10}OS_4Y$ (M = 808.81)

anal. calcd., %:	C, 50.49;	H, 3.36;	N, 17.31;	S, 15.85.
Found, %:	C, 51.73;	H, 3.32;	N, 17.75;	S, 14.92.

Synthesis of [HPhen][Y(NCS)$_4$(Phen)$_2$] (II) was carried out similarly to the synthesis of compound **I** using weighed samples of HNic (0.379 g, 3.08 mmol), Phen (0.396 g, 2.00 mmol), and $Y(NCS)_3 \cdot 6H_2O$ (0.383 g, 1.03 mmol). A cream-colored solid phase was immediately isolated after yttrium hiocyanate was added, and the heterogeneous mixture was also heated at ~40°C for ~1 h. On the next day, the solid phase was separated on a glass filter and dried in a vacuum drying box over silica gel. The yield was 0.5 g. The product was recrystallized from an H_2O–EtOH (2 : 1) mixture.

For $C_{40}H_{25}N_{10}S_4Y$ (M = 862.86)

anal. calcd., %:	C, 55.67;	H, 2.92;	N, 16.23;	S, 14.86.
Found, %:	C, 56.19;	H, 3.36;	N, 17.82;	S, 16.01.

RESULTS AND DISCUSSION

Nicotinic acid is poorly soluble in water and, hence, an HNic + Bipy(Phen) solution was first prepared and then introduced into a solution of yttrium thiocyanate. The solubility of compound **I** in water is high and, therefore, the yield of compound **I** was low. The X-ray phase analysis confirmed the purity of obtained compound **I**. The yield of compound **II** was ~0.6 mmol based on yttrium, which corresponds to 60% of the amount introduced into the reaction. The analytical calculation to NCS showed that 80% of thiocyanate ions introduced into the reaction were spent to complex **II** in this case. The X-ray phase analysis confirmed the predominant presence of complex **II** in the solid phase. Filamentous crystals of HNica and cubic (plate-like) crystals of $[Y(Nic)_3(H_2O)_2]_2$ (**III**) were identified in the solid products isolated from the filtrates after compounds **I** and **II** were separated. The experimental data indicate the redistribution of yttrium in the 3HNic–2Bipy(Phen)–$Y(NCS)_3 \cdot 6H_2O$ system to form anionic forms [HBipy][Y(NCS)$_4$(Bipy)$_2$] · H$_2$O and [HPhen][Y(NCS)$_4$(Phen)$_2$], whose coordination spheres of YN_8 consist only of the N-ligands (NCS and N-heterocycles) and dimeric molecular forms with the coordination node YO_8. It should be mentioned that no formation of anionic complexes with the chloride ion and diimines was observed in $YCl_3 \cdot 6H_2O$–HNic–Bipy(Phen) solutions and we established the formation of dimers **III** only.

The consideration of the IR spectra of compounds **I** and **II** (comparison with the spectrum of the initial molecular yttrium thiocyanate) showed that the characteristic ν(CN) band of the NCS group was most informative. In the $[Y(H_2O)_5(NCS)_3] \cdot H_2O$ polyhedron, yttrium has a coordination number of 8. The N-coordinated thiocyanate is characterized by two distinct absorption lines at 2103 and 2085 cm^{-1} with an intensity ratio of ~1 : 2, which corresponds to their nonequivalent position in the structure [5]. In the spectra of compounds **I** and **II** (coordination number 8), the ν(CN) band is observed at 2050 and 2048 cm^{-1}, respectively, indicating a noticeable influence of the charge on going from $[Y(H_2O)_5(NCS)_3] \cdot H_2O$ to anionic tetrathiocyanate forms **I** and **II**.

Structure **I** is formed by complex anions [Y(NCS)$_4$(Bipy)$_2$] (Fig. 1a), cations HBipy, and crystallization water molecules. The coordination number of the yttrium atom is 8. All "active" hydrogen atoms are involved in the formation of hydrogen bonds O(N)–H···S; in addition, the *cis* conformation of HBipy results in the formation of the intramolecular hydrogen bond N–H···N. In addition to hydrogen bonds, the structural units are joined by p–π and π–π interactions. The S(4) atom participates in the p–π interaction with the HBipy protonated fragment (Fig. 1a), the distances are S(4)···C(25) 3.367(4), S(4)···N(9) 3.450(3), and S(4)···X 3.343 Å (X is the center of the C(25)–N(9) section), and the N(4)–S(4)···X angle is 135.5°. The Bipy ligands of two complexes joined by the inversion center are involved in the stacking interaction with each other (the Py planes of the rings are parallel in symmetry, and the shortest contact C(9)···C(9) is 3.514 Å). The HBipy cations joined with the complex by the N–H···S hydrogen bonds "extend" the stacking interaction to four structural units, the angle between the root-mean-square planes of the coordinated and protonated Bipy is ~9°, and the shortest contacts are C(5)···C(11) 3.418 and C(8)···C(34) 3.421 Å (Fig. 2a). Since the angle between the root-mean-square planes of HBipy and the second coordinated Bipy is ~30°, it can be asserted that no formation of infinite stacks with the stacking interaction occurs. The sulfur atoms of one of the

Selected crystallographic data and experimental conditions for compounds **I–III**

Parameter	Value		
	I	**II**	**III**
Crystal system	Triclinic	Monoclinic	Monoclinic
a, Å	9.5921(7)	12.2735(3)	9.5618(3)
b, Å	13.3012(10)	16.4337(4)	11.5893(3)
c, Å	16.1441(17)	18.8743(4)	17.8118(5)
α, deg	112.610(3)	90	90
β, deg	94.732(3)	92.9540(10)	91.3510(10)
γ, deg	107.493(2)	90	90
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
V, Å^3	1767.0(3)	3801.87(15)	1973.26(10)
Z	2	4	2
Temperature, K	183(2)	183(2)	123(2)
ρ_{calcd}, g/cm^3	1.520	1.507	1.654
μ, mm^{-1}	1.931	1.799	3.007
Crystal size, mm	0.3 × 0.18 × 0.15	0.32 × 0.25 × 0.22	0.3 × 0.25 × 0.2
$\theta_{\max}$, deg	2.28–27.53	2.07–27.91	2.76–30.11
Index range	$-12 \le h \le 12$, $-17 \le k \le 17$, $-20 \le l \le 20$	$-16 \le h \le 15$, $-21 \le k \le 21$, $-24 \le l \le 24$	$-13 \le h \le 13$, $-16 \le k \le 16$, $-25 \le l \le 25$
Collected reflections	20958	34859	26947
Independent reflections (R_{int})	8116 (0.073)	9053 (0.049)	5791 (0.0446)
Independent reflections with $I > 2\sigma(I)$	5197	6243	4407
Refined parameters	451	500	335
Goodness-of-fit	0.987	1.005	0.971
R_1, wR_2 ($I > 2\sigma(I)$)	0.0523, 0.0953	0.0383, 0.079	0.0304, 0.0718
R_1, wR_2 (all reflections)	0.1017, 0.1096	0.073, 0.089	0.0529, 0.0807
$\Delta\rho_{\max}/\Delta\rho_{\min}$, e/Å^3	0.936/–0.736	0.446/–0.355	0.459/–0.319

NCS ligands form short contacts S(1)···S(1) 3.376 Å. This value nearly coincides with a value of 3.379 Å found earlier in the structure $\{NH_4\}_2[Ga(Nta)(NCS)_2]$ [9].

Structure **II** is formed by complex cations $[Y(NCS)_4(Phen)_2]$ (Fig. 1b) and cations HPhen. The coordination number of the Y atom is 8. The mutual arrangement of two coordinated Phen ligands is that no diimine stacks directly joined by the stacking interaction can be formed in structure **II**. However, the fragments of three Phen (two coordinated cations and one protonated cation) join the complexes into chains, the angles between the Phen planes are 3° and 6°, and the shortest contacts are C(8)···C(34) 3.496, C(8)···C(35) 3.478, C(15)···C(37) 3.446, and C(25)···C(36) 3.458 Å (Fig. 2b). As in the case of structure **I**, the HBipy cations forming the stacking interaction with coordinated Phen are joined with one of the complexes by the hydrogen bond N–H···S.

Molecular complex **III** (Fig. 1c) enters into the isostructural series of lanthanides (La–Tm), and its structure is typical of binuclear lanthanide carboxylates.

In spite of the same coordination environment of yttrium in complexes **I** and **II**, the mutual arrangements of coordinated diimines are different. Two more eight-coordinate thiocyanate complexes $[M(NCS)_4(Bipy)_2]$ (M = Nb, Zr [10]) are known. These isostructural complexes have the crystallographic symmetry 222, and their structures differ substantially from those of the complexes in structures **I** and **II**. In all these compounds, the shape of the polyhedron is intermediate between a tetragonal antiprism and a trigonal dodecahedron. It is most likely that the mutual arrangement of diimines in the coordination sphere ("isomer" type) is determined by the crystal packing of the structural units.

Thus, the redistribution of the O- and N-donor ligands with the simultaneous formation of species with the uniform coordination node (either YO_8, or YN_8) was established in the studied systems. Complex **I** contains one solvate H_2O molecule, and anhydrous complex **II** is isolated from an aqueous solution in the case of Phen. The synthesis of similar compounds is of practical interest, since the N-donor ligands, NCS^- anions, and N-heterocycles increase the luminescence intensity (antenna effect) of the lanthanide complexes. The work in this direction is being continued.

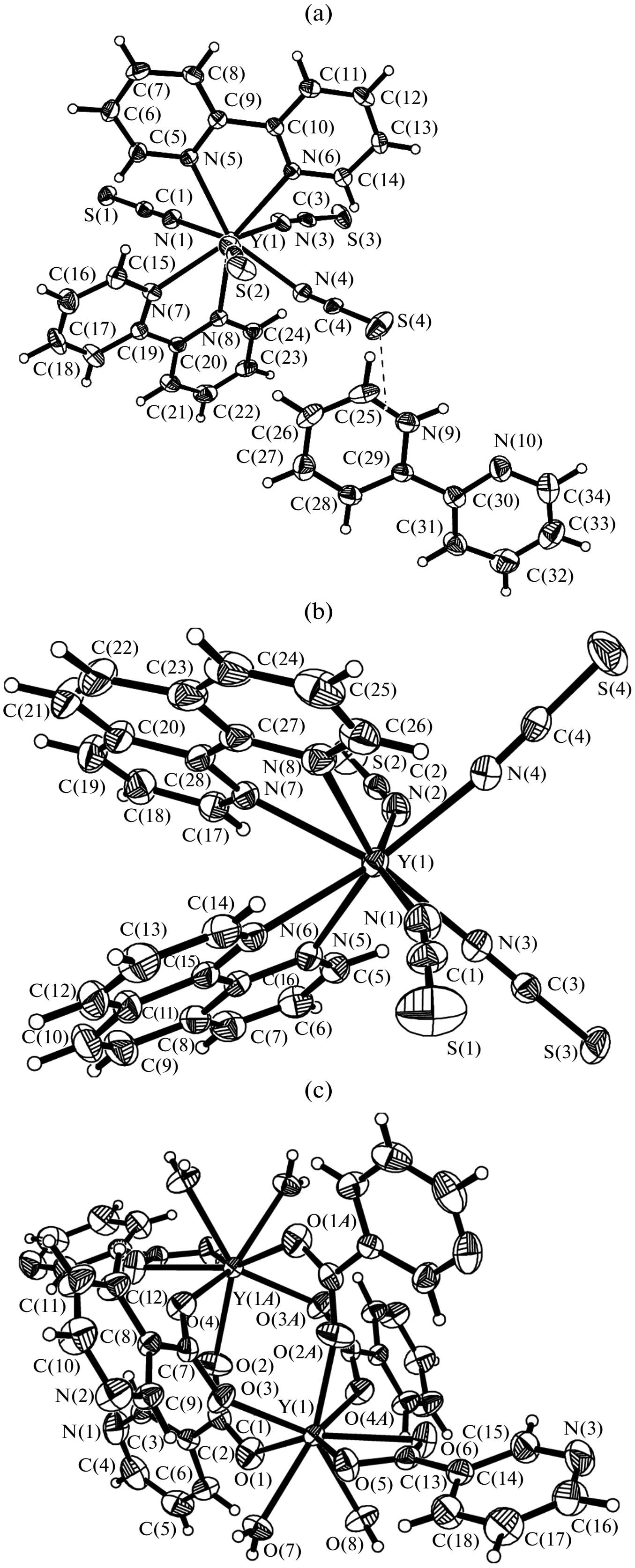

Fig. 1. Structures of complexes (a) **I**, (b) **II**, and (c) **III**.

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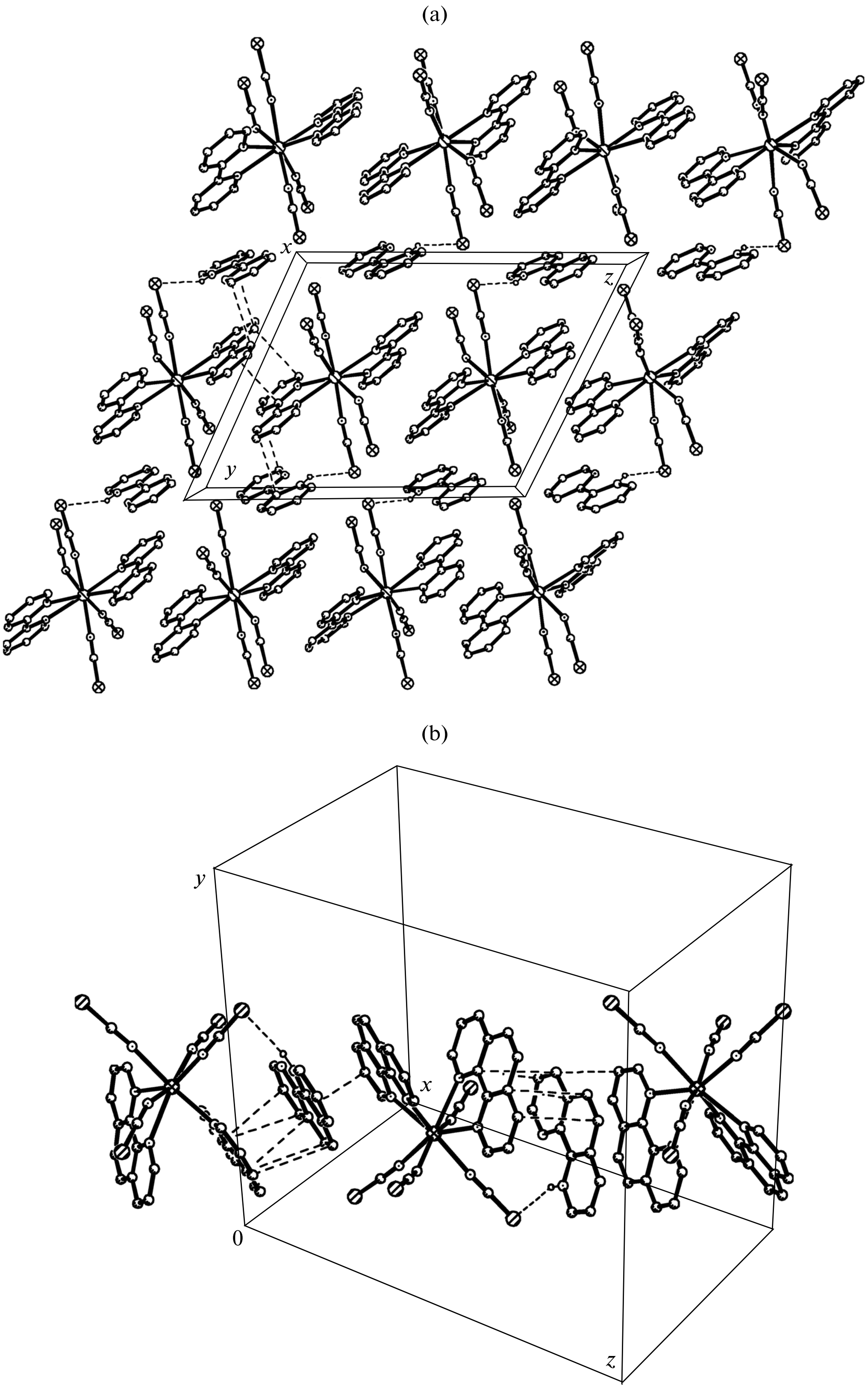

Fig. 2. Fragments of structures (a) **I** and (b) **II**.

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