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Associates of Yttrium Thiocyanate with Ditopic Phenanthroline

S. P. Petrosyants* and A. B. Ilyukhin

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
Leninskii pr. 31, Moscow, 117907 Russia
**e-mail: petros@igic.ras.ru*

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Abstract—Yttrium thiocyanate associates $[Y(H_2O)_5(NCS)_3] \cdot H_2O$ with 4,7-phenanthroline (4,7-Phen) were synthesized and structurally characterized. The monomeric yttrium complexes $[Y(H_2O)_7(NCS)](NCS)_2 \cdot 5(4,7\text{-Phen}) \cdot 5(H_2O)$, $[Y(H_2O)_5(NCS)_3] \cdot 2(4,7\text{-Phen}) \cdot 2(H_2O)$, $\{H(4,7\text{-Phen})\}_2[Y(H_2O)_7(NCS)](NCS)_4 \cdot 2(4,7\text{-Phen}) \cdot 5(H_2O)$are mainly formed in the presence of 4,7-Phen. In the associates, there are no contacts of the ditopic molecules and yttrium; the 4,7-Phen molecules are combined by stacking interactions.

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INTRODUCTION

Ditopic N-heterocycles are actively used in supramolecular chemistry for the fabrication of associates with promising functional properties. Most popular are pyrazine (Pz) and its derivatives and also diverse 4,4'-bipyridine (4,4'-Bipy) derivatives. The major array of accumulated data concerns compounds of transition elements. In recent years, the attention has switched to the design of associates with triply charged cations such as In^{3+}, Y^{3+}. For example, in the polymeric structure $[In_2Cl_6(Pz)_3]$, one Pz molecule combines *mer*-$InCl_3$ fragments into chains, while another Pz molecule links chains to form ribbons [1]. In the metal-organic layered polymer $InF_3(4,4'\text{-Bipy})$, the 4,4'-Bipy molecules are bridging [2]. However, for yttrium, in addition to the bridging coordination of 4,4'-Bipy [3], formation of the associate $[Y_2(HCa)_6(4,4'\text{-Bipy})_2(H_2O)_2] \cdot 2(4,4'\text{-Bipy})$ was established (H_2Ca is 2-hydroxycinnamic acid), one 4,4'-Bipy molecule in the associate being coordinated in the monodentate fashion and the other being a solvate molecule [4]. Unfortunately, in the case of ditopic 4,7-phenanthroline (4,7-Phen), structural data are only available for singly and doubly charged cations (CCDC, version 5.34, 2013 [5]) but in this case, too, variable bonding of 4,7-Phen can be followed, in particular, bridging and monodentate coordination and the outer-sphere association. The halide and nitrate salts of M^{2+} = Co, Cd, Zn, and Ni with 4,7-Phen form coordination polymers with the bidentate bridging position of ditopic 4,7-Phen, although analogous Cu^{2+} salts predominantly form complexes with monodentate coordination of 4,7-Phen [6].

This paper reports a study of the reaction of ditopic 4,7-Phen with yttrium aqua thiocyanate in ethanol solutions, which was used to isolate and structurally identify the outer-sphere associates of Y(III) thiocyanate complexes with ditopic N-heterocycles.

EXPERIMENTAL

The following commercial chemicals were used: $[Y(H_2O)_5(NCS)_3] \cdot H_2O$ (high-purity grade) (rare metal plant, Novosibirsk), 4,7-phenanthroline (Aldrich), EtOH, and Et_2O. An aqueous solution of HNCS was prepared by the reaction of a solution of $Ba(NCS)_2 \cdot 3H_2O$ (Vekton, reagent grade) with an equimolar amount of a H_2SO_4 solution (Fixanal).

All operations were carried out in air. Elemental analysis was done by standard procedures on an EA1108 Carlo Erba CHN-analyzer at the Center for Collective Use at the Kurnakov Institute of General and Inorganic Chemistry. The IR spectra were measured in the same Center for Collective Use on a Nexus Nicolet FT IR spectrometer in the range of 550–4000 cm^{-1}. The ATR spectra were measured using a Nicolet attachment (Pike Technologies). Powder X-ray diffraction analysis was performed on a STOE STADI P diffractometer ($CuK_{\alpha 1}$ radiation, Ge monochromator), Center for Collective Use at the Lomonosov Moscow State University.

Single crystal X-ray diffraction. Experimental data were collected on a Bruker SMART APEX II diffractometer [7] (Center for Collective Use at the Kurnakov Institute of General and Inorganic Chemistry). The absorption corrections were applied semiempirically by the SADABS program [8]. The structures were solved by combination of the direct methods and Fourier syntheses. Some hydrogen atoms were located and the other were calculated from geometric considerations. Structures **Ia**, **II–VII** were refined by the full-matrix anisotropic least-squares method with inclusion of hydrogen atoms. The crystals of **I** were of poor quality and degraded at 183 K within several hours. The structure of **I** was refined without any constraints on the geometric parameters of the molecule; therefore, despite high R_{hkl}, we have no doubts in the correctness of the proposed model. All calculations were performed using SHELXS-97 and SHELXL-97 software [9].

Selected structural data are presented in the table. Experimental data for compounds **I–VII** are deposited with the Cambridge Crystallographic Data Centre (nos. 963931–963938, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Synthesis 1: $Y(H_2O)_7(NCS)](NCS)_2 \cdot 5(4,7\text{-Phen}) \cdot 5(H_2O)$ (I). A solution of yttrium thiocyanate (0.348 g, 0.94 mmol) in 20 mL of EtOH was filtered into a solution of 4,7-Phen (0.173 g, 0.96 mmol) in 20 mL of EtOH. The bright yellow solution was concentrated at room temperature. The crystals were separated on a glass filter, washed with ether, and dried in a vacuum desiccator over silica gel. Yield 0.20 g (15% in relation to Y).

For $C_{63}H_{64}N_{13}O_{13}S_3Y$ ($M = 1380.36$)

	C	H	N	S
anal. calcd., %:	C, 54.81;	H, 4.67;	N, 13.19;	S, 6.97.
Found, %:	C, 54.14;	H, 4.51;	N, 13.25;	S, 6.49.

Synthesis 2: $[Y(H_2O)_5(NCS)_3] \cdot 2(4,7\text{-Phen}) \cdot 2(H_2O)$ (II) + $\{H(4,7\text{-Phen})\}_2[Y(H_2O)_7(NCS)](NCS)_4 \cdot 2(4,7\text{-Phen}) \cdot 5(H_2O)$ (III). A solution of yttrium thiocyanate (0.363 g, 0.98 mmol) in 20 mL of EtOH was filtered into a solution of 4,7-Phen (0.351 g, 1.95 mmol) in 20 mL of EtOH, and an aqueous solution of HNCS (2.5 mL, 1 mmol) was added. The dark pink solution was concentrated at room temperature. The crystals were separated on a glass filter, washed with ether, and dried in a vacuum desiccator over silica gel. Yield 0.34 g.

For $C_{48}H_{58}N_{13}O_{12}S_5Y$ ($M = 1258.29$)

	C	H	N	S
anal. calcd., %:	C, 45.82;	H, 4.64;	N, 14.47;	S, 12.74.
Found, %:	C, 48.12;	H, 3.76;	N, 14.33;	S, 12.45.

For $C_{27}H_{30}N_7O_7S_3Y$ ($M = 749.67$)

	C	H	N	S
anal. calcd., %:	C, 43.26;	H, 4.03;	N, 13.079;	S, 12.83.

RESULTS AND DISCUSSION

The reaction of 4,7-Phen with the molecular complex $[Y(H_2O)_5(NCS)_3] \cdot H_2O$ in ethanol solutions results in the thiocyanate ions being displaced by water molecules to give the cationic complex $[Y(H_2O)_7(NCS)]^{2+}$. The anionic ligands migrate from the coordination sphere of the molecular complex to the outer sphere of the cationic complex and, together with the nitrogen base, form associate **I**. The yield of **I** increases from 15 to 40% as the 4,7-Phen : Y ratio increases from 1 to 2. In addition to the main bulk of poor-quality crystals of **I**, the reaction products contain a well-formed impurity crystals of $[Y(H_2O)_7(NCS)](NCS)_2 \cdot 5(4,7\text{-Phen}) \cdot 6(H_2O)$ (**Ia**) with a composition differing by one water molecule. According to powder X-ray diffraction, the solid phase from synthesis 1 consists of compounds **I** (95%) and **Ia** (1–2%). As the 4,7-Phen : Y ratio was increased, a minor amount of associate based on molecular complex **II** was formed. To suppress the aquation of the molecular complex, synthesis 2 in the presence of HNCS was carried out. Indeed, according to powder X-ray diffraction data, the amount of molecular form **II** in the products of synthesis 2 increased but still it was less than half. The major product was associate **III** based on the cationic complex $[Y(H_2O)_7(NCS)]^{2+}$ with protonated and free 4,7-Phen. No associates with coordinated 4,7-Phen were detected upon these syntheses.

Examination of the IR spectra of compounds **I–III** (comparison with the spectrum of the starting molecular yttrium thiocyanate) showed that most informative is the characteristic ν(CN) band of the NCS group. In the polyhedron of $[Y(H_2O)_5(NCS)_3] \cdot H_2O$, the coordination number of yttrium is 8. The N-coordinated thiocyanate groups are responsible for two clear-cut absorption bands at 2103 and 2085 cm^{-1} with ~1 : 2 intensity ratio, which reflects their non-equivalent positions in the structure [10]. Compound **I** (the metal coordination number is 8) also accounts for two ν(CN) bands at 2066 and 2036 cm^{-1} with intensity ratio of ~2 : 1; hence, they are attributable to the presence of two outer-sphere anions and one coordinated anion in structure **I**, the frequencies being closer to the frequency for the salt KNCS (2053 cm^{-1}). The IR spectrum of the mixture **II** + **III** shows four ν(CN) bands at 2094, 2076, 2056, and 2042 cm^{-1}, which were quite consistent with the presence of molecular and cationic yttrium thiocyanate complexes and outer-sphere NCS anions.

The obtained experimental data confirm that the fused N-heterocycle induces replacement of thiocyanate ions by water molecules, the metal coordination number remaining unchanged. The introduction of the anionic ligand in the form of HNCS somewhat suppresses this process and gives associate **II** based on the molecular complex but the associate **III** based on the cationic complex is still formed predominantly.

A similar situation, i.e., the expulsion of the anionic ligand from the yttrium coordination sphere under the action of the ditopic N-heterocycle, occurs also in the reaction of $YCl_3 \cdot 6H_2O$ with 4,4'-Bipy. For example, in the hydrothermal synthesis in the pres-

Selected crystal data and X-ray experiment details for compounds **I**–**IV**

Parameter	Value							
	I	**Ia**	**II**	**III**	**IV**	**V**	**VI**	**VII**
System	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic	Tetragonal
a, Å	13.218(17)	13.3957(4)	7.4978(10)	12.8374(12)	7.8563(3)	8.034(4)	7.2575(3)	14.6626(3)
b, Å	15.46(2)	29.2140(9)	20.948(3)	13.0842(12)	12.0543(5)	9.914(5)	12.0789(5)	14.6626
c, Å	17.55(2)	17.5387(5)	11.3254(13)	20.8017(18)	13.0732(6)	14.797(5)	13.0532(6)	45.409(2)
α, deg	81.34(4)	90	90	76.026(2)	90.5440(10)	99.818(11)	68.1890(10)	90
β, deg	76.42(4)	102.8450(10)	93.010(6)	72.953(2)	103.6160(10)	98.251(15)	87.886(2)	90
γ, deg	67.45(3)	90	90	66.984(2)	91.0700(10)	92.049(13)	85.071(2)	90
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/m$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$I4_1/acd$
V, Å^3	3212(7)	6691.9(3)	1776.3(4)	3042.5(5)	1202.93(9)	1147.1(8)	1058.42(8)	9762.6(5)
Z	2	4	2	2	2	2	2	8
Temperature, K	183	296	293	296	293	296	153	153
ρ, g/cm^3	1.427	1.388	1.503	1.439	1.619	1.592	1.542	1.618
μ, mm^{-1}	1.077	1.036	1.879	1.200	3.018	3.047	3.084	2.771
Crystal size, mm	0.04 × 0.02 × 0.02	0.3 × 0.25 × 0.23	0.3 × 0.25 × 0.15	0.18 × 0.1 × 0.08	0.25 × 0.25 × 0.2	0.28 × 0.25 × 0.2	0.28 × 0.18 × 0.15	0.28 × 0.2 × 0.2
θ_{max}, deg	20	26	26	24	30.5	30	27.1	25
Range of indices	$-6 \le h \le 12$, $-9 \le k \le 14$, $-16 \le l \le 16$	$-16 \le h \le 16$, $-35 \le k \le 35$, $-21 \le l \le 21$	$-8 \le h \le 9$, $-23 \le k \le 25$, $-13 \le l \le 13$	$-14 \le h \le 14$, $-14 \le k \le 14$, $-23 \le l \le 23$	$-11 \le h \le 11$, $-16 \le k \le 17$, $-18 \le l \le 18$	$-11 \le h \le 11$, $-13 \le k \le 9$, $-15 \le l \le 20$	$-9 \le h \le 9$, $-13 \le k \le 15$, $-16 \le l \le 16$	$-17 \le h \le 17$, $-17 \le k \le 17$, $-54 \le l \le 54$
Number of collected reflections	5393	60100	10614	22316	14622	10398	9858	43658
Number of unique reflections/R_{int}	5143/0.1115	13105/0.0459	3554/0.0571	9532/0.0423	7232/0.0229	6441/0.0325	4642/0.0234	2154/0.1582
Number of reflections with $I > 2\sigma(I)$	1884	8837	2183	6825	5828	4845	4016	1000
Number of refined parameters	389	847	262	756	356	235	274	143
R_1, wR_2 ($I > 2\sigma(I)$)	0.2141, 0.4626	0.0507, 0.1309	0.0451, 0.0891	0.0576, 0.1487	0.0307, 0.0667	0.0440, 0.1232	0.0261, 0.0644	0.0306, 0.0662
R_1, wR_2 (all reflections)	0.3552, 0.4927	0.0878, 0.1479	0.1009, 0.1079	0.0875, 0.1620	0.0470, 0.0729	0.0719, 0.1488	0.0353, 0.0680	0.0969, 0.0761
GOOF	1.815	1.080	0.969	1.161	0.983	0.973	1.016	0.873
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	1.281/–1.958	0.548/–0.396	0.525/–0.391	1.013/–0.704	0.514/–0.295	0.591/–0.901	0.451/–0.447	0.396/–0.448

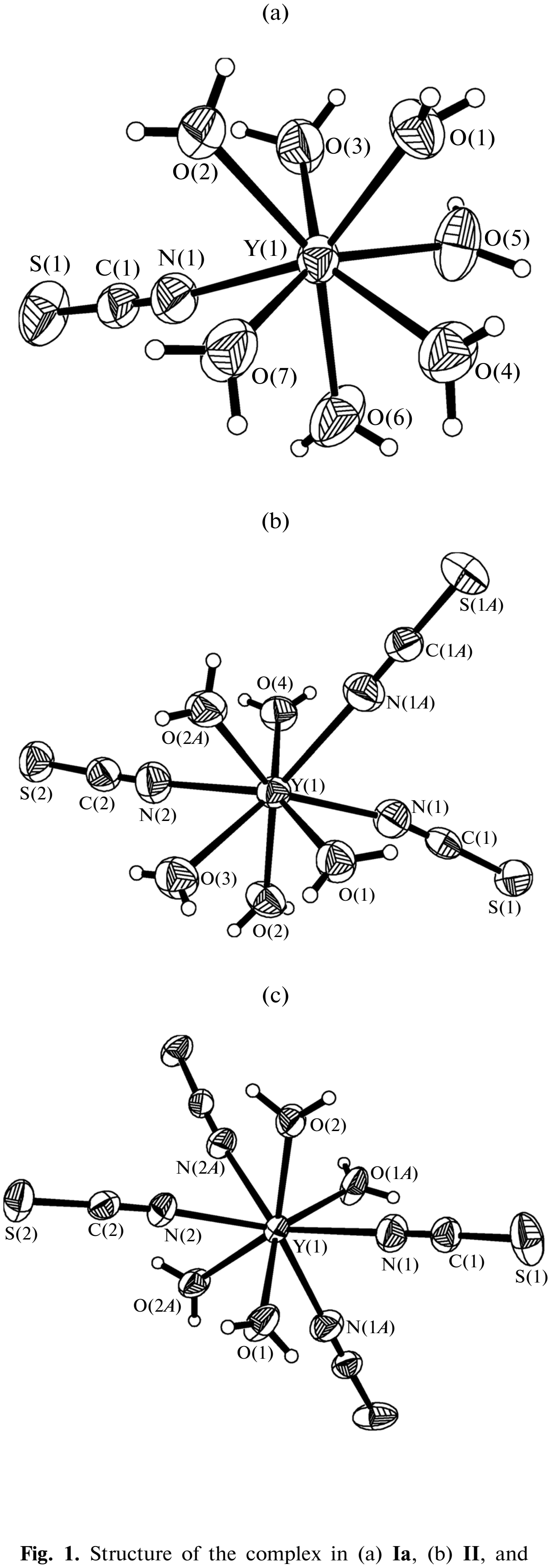

Fig. 1. Structure of the complex in (a) **Ia**, (b) **II**, and (c) **VII**.

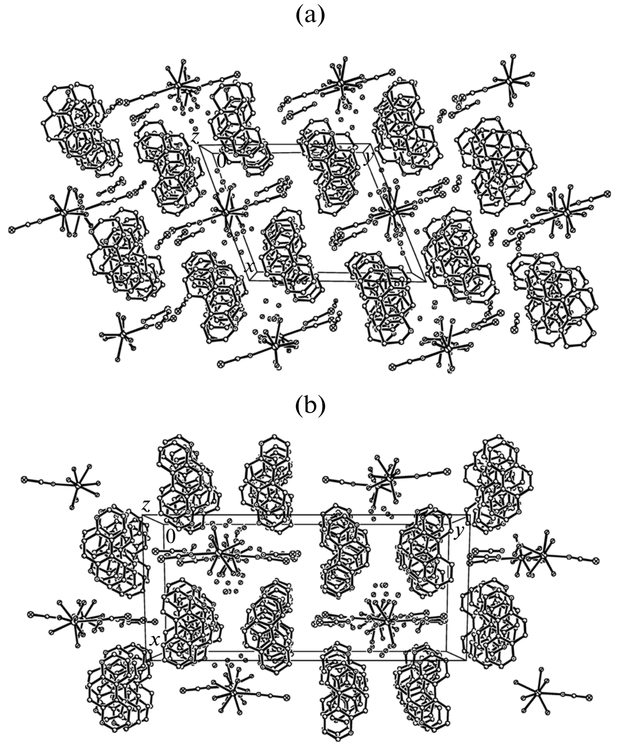

Fig. 2. Projection of structures (a) **I** and (b) **Ia** along *z* axis.

ence of HCl (170°C, 100 h), the compound $[H_2(4,4'\text{-Bipy})][Y(H_2O)_8]Cl_5 \cdot H_2O$ (**IV**) was obtained, while the solvothermal synthesis (ethanol—water, 70°C, 75 h) yielded $\{[H(4,4'\text{-Bipy})\}[Y(H_2O)_8]Cl_4 \cdot H_2O$ (**V**) . These associates were formed from the cationic aqua complex, protonated diimine, a water molecule, and chloride ions, which completely migrated to the outer sphere (no coordinated 4,4'-Bipy molecules were present).

The reaction of yttrium thiocyanate with ditopic Pz in ethanol follows a somewhat different route. For Pz : Y ≈ 3, the associate $[Y(H_2O)_5(NCS)_3] \cdot 1.5Pz \cdot H_2O$ (**VI**) based on the initial molecular yttrium complex was identified in the solid phase. By using a solution containing HNCS, the salt $\{HPz_2\}_2[Y(H_2O)_4(NCS)_4]_2 \cdot Pz$ (**VII**) was obtained. Thus, the monocyclic ditopic Pz, unlike 4,7-Phen with fused rings, does not induce aquation of the molecular yttrium complex. In the presence of Pz, the associate with the anionic yttrium complex may be formed but, as in case of 4,7-Phen, the ditopic heterocycle is not coordinated to yttrium.

Structures **I** and **Ia** are formed by the complexes $[Y(H_2O)_7(NCS)]^{2+}$ (Fig. 1a), thiocyanate ions, and 4,7-Phen and H_2O solvate molecules. The yttrium polyhedron is a square antiprism. The crystal structures of **I** and **Ia** are similar (Fig. 2a and 2b); an extended system of hydrogen bonds combines the structural units to a framework. The matrix (1 0 0/1 –2 0/0 0 –1) transforms the triclinic unit cell of **I** into the *C*-centered unit cell with the parameters

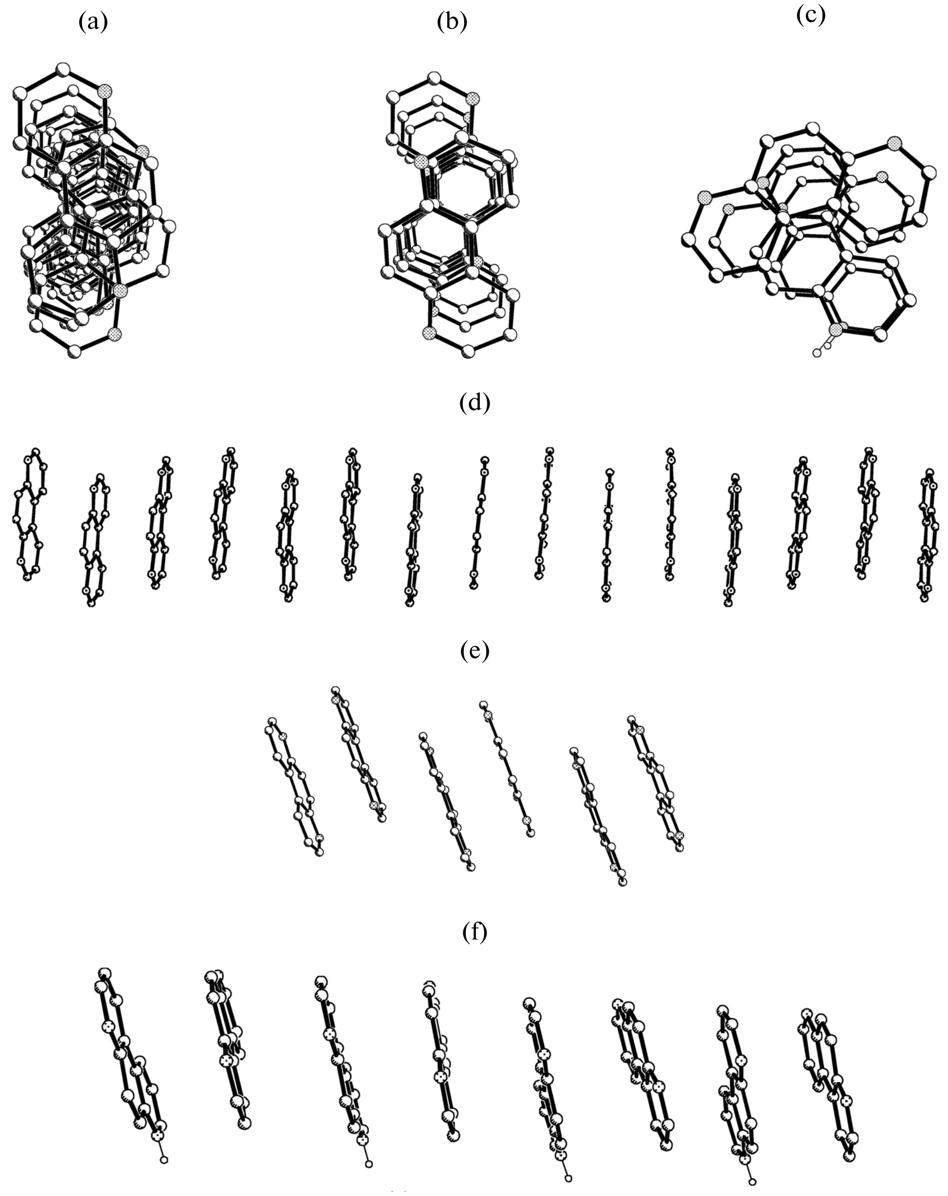

Fig. 3. Two projections of Phen stacks in structures (a, d) **Ia**, (b, e) **II**, and (c, f) **III**.

$a = 13.22$ Å, $b = 28.59$ Å, $c = 17.55$ Å; $\alpha = 86.9°$, $\beta = 103.6°$, $\gamma = 87.3°$, which do not differ much from the parameters of the monoclinic phase of **Ia** (table). The 4,7-Phen molecules form stacks (Fig. 3), one unit cell containing five crystalographically independent molecules. The distance between the neighboring 4,7-Phen molecules is ~3.5 Å (the parameter c is 17.55(2) Å and 17.5387(5) Å in **I** and **Ia**, $3.5 \times 5 = 17.5$).

The molecular complex $[Y(H_2O)_5(NCS)_3]$ (Fig. 1b) in compound **II** has crystallographic symmetry m. As in structures **I** and **Ia**, 4,7-Phen in **II** also form stacks (Figs. 3b, 3e) with a pitch of 3.4 Å.

The structure of **III** contains complexes $[Y(H_2O)_7(NCS)]^{2+}$ (in both **I** and **Ia**), monoprotonated 4,7-Phen, a thiocyanate ion, and 4,7-Phen and H_2O molecules. The protonation site of 4,7-Phen is unambiguously determined by the formation of N–H···N(NCS) hydrogen bonds (N···N 2.73 and 2.75 Å). All four crystallographically independent H_x(4,7-Phen) units are stacked; H(4,7-Phen) and 4,7-Phen alternate (Fig. 3c, 3f). The protonated ring of H(4,7-Phen) deviates from the stacks and is not involved in stacking.

In structure **IV**, the diprotonated H_2(4,4'-Bipy) cations are not involved in stacking, whereas the H(4,4'-Bipy) cations in structure **V** form stacks with non-equivalent binding of diimines. In the pair of cations related by inversion center A (Fig. 4), the shortest C···C distance is 3.41 Å; for those related by inversion center B, this distance is 3.54 Å.

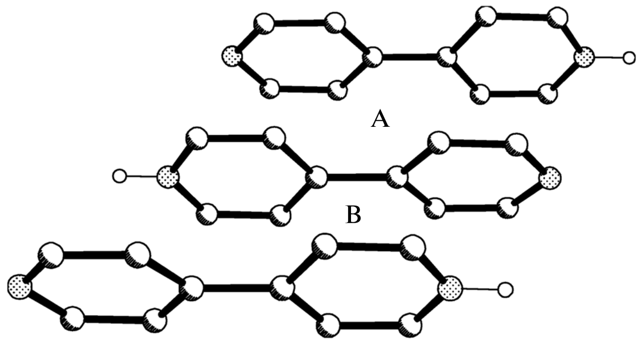

Fig. 4. Structure of the H(4,4'-Bipy) stacks in **V**.

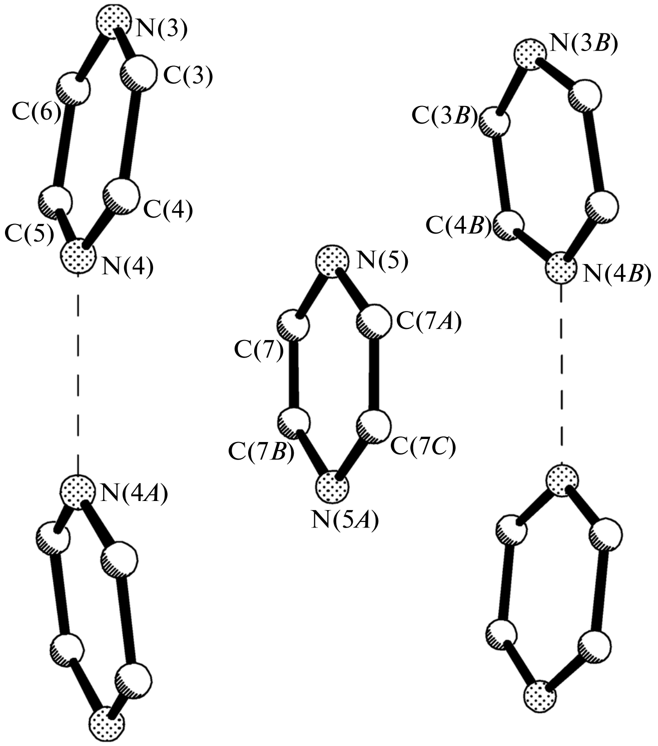

Fig. 5. Fragment of structure **VII**.

The molecular complex $[Y(H_2O)_5(NCS)_3]$ in **VI** occupies a general position; its structure is similar to that found for **II**. The shortest contact between the N and C atoms of the neighboring Pz solvate molecules in **V** is longer than 3.56 Å.

The anionic complex $[Y(H_2O)_4(NCS)_4]^-$ in structure **VII** is located on a 2 axis, the HPz cation occurs in a general position; the Pz solvate molecule has crystallographic symmetry 222. The acid hydrogen atom is disordered over two sites between the N(4) atoms related by 2 axis (Fig. 5) (N(4)···N(4*A*) 2.708 Å). The shortest non-valence contacts in the $\{HPz_2\}_2\cdot$ Pz fragment are: N(5)···N(4) 3.216, C(7)···C(4*B*) 3.406, C(7)···C(5) 3.434 Å.

Thus, associates **I–III** with cationic or molecular yttrium complexes are formed in ethanol solutions under the action of ditopic 4,7-Phen; the metal coordination number in the associates is 8. The 4,7-Phen molecules and cations in associates **I–III** form stacks with a pitch of 3.4–3.5 Å.

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