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Cobalt(II) Complexes with Pentadentate Schiff Bases 2,6-Diacetylpyridine Hydrazones: Syntheses and Structures

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Abstract—Seven new cobalt(II) complexes based on the Schiff bases, 2,6-diacetylpyridine bis(isonicotinoylhydrazone) (H_2L^1) and 2,6-diacetylpyridine bis(nicotinoylhydrazone) (H_2L^2), are synthesized and studied by X-ray diffraction analysis: $[Co(H_2L^1)(NCS)_2] \cdot 2.25H_2O$ (**I**), $[Co(H_2L^2)(NCS)_2] \cdot CH_3OH$ (**II**), $[Co(H_2L^2)(NCS)(H_2O)]NCS$ (**III**), $[Co(H_4L^1)(NCS)_2](NO_3)_2 \cdot 2H_2O$ (**IV**), $[Co(H_4L^1)(NCS)_2][Co(NCS)_4] \cdot 0.75H_2O$ (**V**), $[Co(H_4L^2)(NCS)_2][Co(NCS)_4] \cdot 1.75H_2O$ (**VI**), and $[Co(H_2L^2)(NCS)(CH_3OH)]_2[Co(NCS)_4] \cdot 2CH_3OH$ (**VII**) (CIF files CCDC 941186 (**I**), 1457906 (**Ia**), 1457905 (**II**), 941187 (**III**), 1457907 (**IV**), 1457908 (**V**), 1457909 (**VI**), and 941188 (**VII**)). The organic ligands in the complexes act as pentadentate neutral H_2L or doubly protonated $(H_4L)^{2+}$ coordinated through the same set of donor atoms N_3O_2. In all compounds **I–VII**, the coordination polyhedron of the Co^{2+} ion in a complex with the Schiff bases has a shape of a pentagonal bipyramid. The hydrazones are arranged in the equatorial plane of the bipyramid. Its axial vertices are occupied by the nitrogen atoms of the NCS^- anions in compounds **I**, **II**, and **IV–VI** and by the nitrogen atoms of NCS^- and oxygen of the water molecule in compound **III** or methanol in compound **VII**. The NO_3^- anions or $[Co(NCS)_4]^{2-}$ complex anions obtained by the reactions are involved along with the NCS^- anions in the formation of compounds **IV–VII**.

Keywords: cobalt(II) complexes, pentadentate Schiff bases with 2,6-diacetylpyridine hydrazone fragment, X-ray diffraction analysis

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INTRODUCTION

The compounds of transition metal ions with various polydentate Schiff bases as chelates are most studied in coordination chemistry [1, 2]. The Schiff bases containing hydrazone functional groups are attractive as ligands due to both diverse coordination modes to the metal and biological and pharmacological properties of their compounds [3–7]. The results of syntheses and structural studies of the 2,6-diacetylpyridine, nicotinoyl, and isonicotinoyl hydrazone compounds with the antimicrobial and genotoxic properties are described [8]. The analysis of the data in the Cambridge Crystallographic Data Centre [9] revealed that 2,6-diacetylpyridine bis(hydrazones) of benzoic acid or bis(semicarbazones) were mainly used as ligands in the transition metal compounds of this class (~70 structures). In the most cases, cobalt was used as a metal and almost all compounds were mononuclear. In all compounds, these ligands were coordinated via the pentadentate mode through the donor atoms N_3O_2, and the atoms of the anions or solvent molecules supplement the formation of coordination polyhedra of transition metals to pentagonal bipyramids [10–17]. Attempts to modify these Schiff bases by the introduction of various terminal functional groups to enhance their denticity gave polynuclear [18–20] or polymer structures [21].

The multifunctional character of 2,6-diacetylpyridine hydrazones appears as different coordination modes and a variety of the obtained molecular architectures: binuclear complexes with the double spiral structure in which the ligand is coordinated via the chelate bridging mode (3 + 2) [15, 16, 21], square mononuclear complexes [22], square pyramidal mononuclear complexes with the tridentate-coordinated ligand [15], binuclear (4 + 1) [17] and mononuclear complexes with the octahedral environment of the metal with a metal to ligand ratio of 1 : 2 and the tridentate N,N,N-coordination mode of the ligand [23], and other.

The cobalt(II) complexes in which the metal atom is seven-coordinated are interesting due to a high local anisotropy, depending mainly on the nature of the axial ligands [24]. The introduction of the terminal pyridine fragments into 2,6-diacetylpyridine hydrazones can result in the formation of structural building blocks for the development of polynuclear clusters or coordination polymers: materials with promising magnetic properties [25]. However, one can expect equilibrium shifting in the reaction of carbonyl group substitution in a solution using metals of different nature and/or acyl groups of hydrazone. These structures can be stabilized by the deprotonation of hydrazones, since the negatively charged oxygen forms a strong bond with the metal to generate enolate complexes [26].

We have previously presented the works on the syntheses and X-ray diffraction analyses of the vanadium(II), vanadium(IV), and iron(III) complexes with the condensation products of 2,6-diacetylpyridine and hydrazide of nicotinic and isonicotinic acids [27, 28]. In this work, we present the results of the syntheses and X-ray diffraction structural studies of seven new Co(II) complexes with ligands of 2,6-diacetylpyridine bis(iso- or nicotinoylhydrazones): $[Co(H_2L^1)(NCS)_2] \cdot 2.25H_2O$ (**I**), $[Co(H_2L^2)(NCS)_2] \cdot CH_3OH$ (**II**), $[Co(H_2L^2)(NCS)(H_2O)]NCS$ (**III**), $[Co(H_4L^1)(NCS)_2](NO_3)_2 \cdot 2H_2O$ (**IV**), $[Co(H_4L^1)(NCS)_2][Co(NCS)_4] \cdot 0.75H_2O$ (**V**), $[Co(H_4L^2)(NCS)_2][Co(NCS)_4] \cdot 1.75H_2O$ (**VI**), and $[Co(H_2L^2)(NCS)(CH_3OH)]_2[Co(NCS)_4] \cdot 2CH_3OH$ (**VII**), where H_2L^1 is 2,6-diacetylpyridine bis(isonicotinoylhydrazone), and H_2L^2 is 2,6-diacetylpyridine bis(nicotinoylhydrazone).

EXPERIMENTAL

All chemical substances and solvents (Aldrich) were used as received. The reactions were carried out under aerobic conditions.

Synthesis of compound I. A solution of 2,6-diacetylpyridine (0.16 g, 1 mmol) in methanol (8 mL) and a solution of isonicotinic acid hydrazide (0.28 g, 2 mmol) in methanol (15 mL) were poured to a solution of $Co(SCN)_2 \cdot 3H_2O$ (0.23 g, 1 mmol) in methanol (20 mL). The mixture was refluxed with continuous stirring for 2 h. A green precipitate began to form in the mixture after reflux for 20 min. The precipitate was filtered off, and the mother liquid was left to stay at room temperature. After 2 days, red-orange crystals formed in the solution and suitable for X-ray diffraction analysis were filtered off. The crystals were soluble in methanol, ethanol, and dimethylformamide and insoluble in ether. The yield was 21%.

For $C_{23}H_{23.5}CoN_9O_{4.25}S_2$

anal. calcd., %: C, 44.77; H, 3.84; N, 20.43; Co, 9.55.

Found, %: C, 44.69; H, 3.76; N, 20.37; Co, 9.50.

IR (ν, cm^{-1}): 3048 m, 2921 m, 2815 m, 2082 vs, 1633 s, 1541 s, 1438 m, 1413 m, 1378 m, 1297 vs, 1213 m, 1173 s, 1140 m, 1022 s, 1008 m, 846 s, 824 m, 747 s, 740 s, 680 m, 556 w, 546 w, 518 w, 476 m.

Synthesis of compound II. A solution of 2,6-diacetylpyridine (0.16 g, 1 mmol) in methanol (14 mL) and a solution of nicotinic acid hydrazide (0.28 g, 2 mmol) in methanol (30 mL) were poured to a solution of $Co(SCN)_2 \cdot 3H_2O$ (0.23 g, 1 mmol) in methanol (20 mL). The mixture was refluxed with continuous stirring for 3 h. Dark orange crystals were formed in a solution of the same color and were filtered off. Orange crystals suitable for X-ray diffraction analysis were formed in the mother liquid after 3 weeks of slow evaporation at room temperature. The crystals were filtered off. They were soluble in methanol, ethanol, and dimethylformamide and insoluble in ether. The yield was 19%.

For $C_{24}H_{23}CoN_9O_3S_2$

anal. calcd., %: C, 47.37; H, 3.81; N, 20.71; Co, 9.68.

Found, %: C, 47.01; H, 3.85; N, 20.62; Co, 9.58.

IR (ν, cm^{-1}): 3470 w, br, 3181 w, 3068 m, 2922 m, 2820 m, 2058 vs, 1632 s, 1594 m, 1526 s, 1420 m, 1378 m, 1309 vs, 1268 m, 1205 m, 1171 s, 1147 m, 1054 m, 1029 m, 995 m, 905 m, 812 s, 743 m, 731 s, 699 s, 674 m, 643 w, 536 w, 484 w, 472 w, 436 w.

Synthesis of compound III. A solution of 2,6-diacetylpyridine (0.08 g, 0.5 mmol) in methanol (7 mL) and a solution of nicotinic acid hydrazide (0.14 g, 1 mmol) in methanol (15 mL) were poured to a solution of $Co(SCN)_2 \cdot 3H_2O$ (0.12 g, 0.5 mmol) in methanol (10 mL). Water (4 mL) was added to the obtained mixture, and the resulting mixture was refluxed with continuous stirring for 3 h. A green precipitate began to form within 20–30 min in the mixture and was filtered off. The orange mother liquor was left to stay at room temperature for slow evaporation. Red-brown crystals suitable for X-ray diffraction analysis precipitated from the solution after 2 days and were filtered off. The crystals were soluble in methanol, ethanol, acetonitrile, and water and insoluble in ether. The yield was 28%.

For $C_{23}H_{21}N_9O_3S_2Co$

anal. calcd., %: C, 46.46; H, 3.56; N, 21.20; Co, 9.91.

Found, %: C, 46.32; H, 3.51; N, 21.09; Co, 9.78.

IR (ν, cm^{-1}): 3348 m, 3071 m, 2920 m, 2823 m, 2095 vs, 2072 vs, 1634 vs, 1601 s, 1589 s, 1545 s, 1508 m, 1436 m, 1419 m, 1376 m, 1306 vs, 1288 vs, 1212 m, 1175 vs, 1133 m, 1111 m, 1026 m, 1015 m, 994 w, 901 m, 810 m, 731 m, 698 vs, 589 w, 557 m, 542 m, 522 m, 461 w, 421 m.

Synthesis of compound IV. A solution of 2,6-diacetylpyridine (0.08 g, 0.5 mmol), isonicotinic acid hydrazide (0.14 g, 1 mmol), and pyrazine carboxamide (0.13 g, 1 mmol) in methanol (18 mL) was poured to a solution of $Co(SCN)_2 \cdot 3H_2O$ (0.12 g, 0.5 mmol) in methanol (18 mL). The mixture was refluxed with continuous stirring for 3 h. A green precipitate began to form in the mixture and was filtered, and the orange mother liquor was left to stay at room temperature. After several days, light orange crystals of prismatic habitus suitable for X-ray diffraction analysis precipitated from the solution and were filtered off. The crystals were soluble in methanol, ethanol, acetonitrile, and water and insoluble in ether. The yield was 17%.

For $C_{23}H_{25}N_{11}O_{10}S_2Co$

anal. calcd., %: C, 37.40; H, 3.41; N, 20.86; Co, 7.98.

Found, %: C, 37.56; H, 3.61; N, 20.70; Co, 8.15.

IR (ν, cm^{-1}): 3445 m, 3377 m, 3230 m, 3062 m, 2932 m, 2884 m, 2801 m, 2096 vs, 1673 m, 1658 m, 1638 s, 1612 s, 1550 s, 1499 m, 1439 m, 1375 vs, 1364 vs, 1339 vs, 1300 vs, 1238 m, 1199 m, 1175 s, 1142 m, 1104 m, 1077 m, 1004 m, 905 m, 829 s, 743 s, 674 m, 544 w, 516 w, 476 w, 422 w.

Synthesis of compound V. A solution of $Co(SCN)_2 \cdot 3H_2O$ (0.12 g, 0.5 mmol), 2,6-diacetylpyridine (0.08 g, 0.5 mmol), and isonicotinic acid hydrazide (0.14 g, 1.0 mmol) was refluxed with continuous stirring for 5 h. A green precipitate was filtered off, and the mother liquor was left to stay at room temperature for slow evaporation. After 7 days, dark green crystals of prismatic habitus precipitated from the solution and were filtered off. The crystals were suitable for X-ray diffraction analysis. They were soluble in methanol, ethanol, and acetonitrile and insoluble in ether. The yield was 15%.

For $C_{27}H_{22.5}N_{13}O_{2.75}S_6Co_2$

anal. calcd., %: C, 36.71; H, 2.57; N, 20.61; Co, 13.34.

Found, %: C, 36.56; H, 2.48; N, 20.53; Co, 12.96.

IR (ν, cm^{-1}): 3361 m, 3178 m, 3074 w, 2970 w, 2921 w, 2607 w, 2063 vs, 1656 m, 1625 s, 1595 m, 1513 m, 1454 m, 1435 m, 1376 m, 1303 s, 1268 m, 1210 m, 1174 s, 1139 m, 1108 m, 1074 m, 1017 m, 904 m, 875 w, 815 m, 779 w, 741 w, 719 m, 542 w, 503 w, 485 w, 466 w, 451 w.

Synthesis of compound VI was carried out in the same way as that of compound **V**, but nicotinic acid hydrazide was used instead of isonicotinic acid hydrazide. The crystals were soluble in methanol, ethanol, and acetonitrile and insoluble in ether. The yield was 17%.

For $C_{27}H_{24.5}N_{13}O_{3.75}S_6Co_2$

anal. calcd., %: C, 35.98; H, 2.74; N, 20.20; Co, 13.08.

Found, %: C, 35.44; H, 2.72; N, 19.79; Co, 12.76.

IR (ν, cm^{-1}): 3346 m, 2601 w, 2092 vs, 2068 vs, 1639 vs, 1605 m, 1588 m, 1572 w, 1466 w, 1417 m, 1374 m, 1306 vs, 1287 vs, 1024 m, 822 m, 811 m, 466 w.

Synthesis of compound VII. A solution of 2,6-diacetylpyridine (0.04 g, 0.25 mmol) in methanol (5 mL) and a solution of nicotinic acid hydrazide (0.07 g, 0.5 mmol) in methanol (15 mL) were added to a solution of $Co(SCN)_2 \cdot 3H_2O$ (0.06 g, 0.25 mmol) in methanol (5 mL). The mixture was refluxed with continuous stirring for 2 h and then slowly cooled to room temperature. After 2 days, green-blue crystals of prismatic habitus suitable for X-ray diffraction analysis precipitated from the solution and were filtered off. The crystals were soluble in methanol, ethanol, acetonitrile, and water and insoluble in ether. The yield was 52%.

For $C_{52}H_{54}N_{20}O_8S_6Co_3$

anal. calcd., %: C, 42.89; H, 3.74; N, 19.24; Co, 12.14.

Found, %: C, 42.73; H, 3.62; N, 19.11; Co, 12.01.

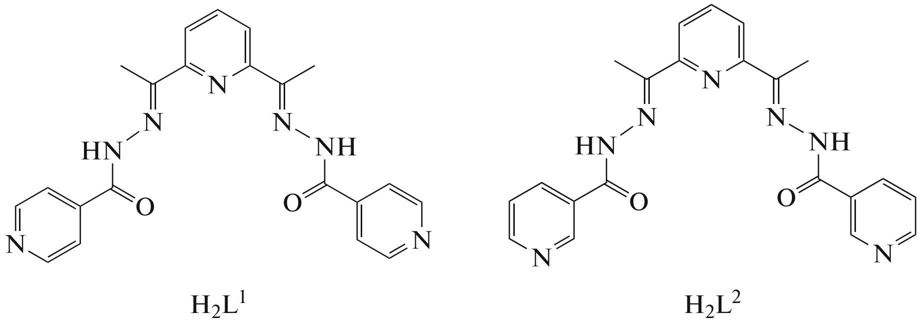
IR (ν, cm^{-1}): 3347 m, 2094 vs, 2072 vs, 1634 s, 1600 m, 1589 m, 1570 m, 1463 m, 1418 m, 1376 m, 1305 s, 1272 w, 1026 m, 820 m, 811 m, 460 w.

IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer in a range of 4000–400 cm^{-1}.

X-ray diffraction data for compounds **I–VII** were obtained on an Xcalibur E diffractometer (graphite monochromator, MoK_α radiation). The unit cell parameters were determined and experimental data were processed using the CrysAlis Oxford Diffraction Ltd. program [29]. The structures of the compounds were determined by direct methods and refined by the full-matrix least-squares method on F^2 in anisotropic approximation for non-hydrogen atoms (SHELX-97) [30]. The positions of the C and S atoms of the disordered NCS^- anion in structure **V** and the positions of some oxygen atoms of the water molecules in compounds **I** and **V–VII** with the filling coefficient of the position <1 were refined isotropically. The experiments for compound **I** were carried at both 100 K and room temperature (**Ia**). Since in compounds **V–VII** one of the coordinated NCS^- groups is disordered over two and more positions, the DFIX or SADI restraints were imposed on their geometric parameters during the structure refinement. The positions of the hydrogen atoms bound to the oxygen atoms were obtained from the difference Fourier syntheses, and the positions of all other hydrogen atoms were calculated geometrically. The experimental and refinement characteristics for structures **I–VII** are presented in Table 1. The interatomic distances and bond angles in the coordination mode are listed in Table 2. The geometric parameters of hydrogen bonds are given in Table 3. The positional and thermal parameters of the compounds were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC 941186 (**I**), 1457906 (**Ia**), 1457905 (**II**), 941187 (**III**), 1457907 (**IV**), 1457908 (**V**), 1457909 (**VI**), and 941188 (**VII**); www.ccdc.cam.ac.uk/conts/retrieving.html or deposit@ccdc.ca.ac.uk).

RESULTS AND DISCUSSION

The X-ray diffraction analyses of seven new Co(II) compounds with 2,6-diacetylpyridine bis(iso- or nicotinoyl hydrazones) **I–VII** show that the Schiff bases obtained by the condensation of 2,6-diacetylpyridine with hydrazides of isonicotinic (H_2L^1) and nicotinic (H_2L^2) acids (Scheme 1) are coordinated to the central metal atom as pentadentate neutral ligands H_2L (**I–III**, **VII**) or ligands doubly protonated at the terminal pyridine nitrogen atoms $(H_4L)^{2+}$ (**IV–VI**).



Scheme 1.

Both molecular Co(II) complexes (**I** and **II**, Figs. 1a, 1b, 2) and complexes of the ionic type were obtained as a result of using different synthesis methods. Neutral organic ligands H_2L^1 or H_2L^2 and two NCS^- anions are coordinated to the metal atom in the former complexes, whereas the latter complexes are formed by the Co^{2+} complex cations and outer-sphere inorganic or complex anions. In the complex cations of compounds **IV–VI**, two NCS^- anions along with H_2L^1 or H_2L^2 are coordinated to the metal atom. For compound **III**, these are one NCS^- anion and one water molecule. One NCS^- anion and one methanol molecule are coordinated to the metal atom in compounds **VII** and **III**. Thus, the NCS^- or NO_3^- anions compensate the positive charge of the Co^{2+} complex cation in compounds **III** and **IV**, respectively (Figs. 3a, 3b). In compounds **V–VII**, the $[Co(NCS)_4]^{2-}$ complex cation compensates the positive charge of the Co^{2+} complex cation (Figs. 4–6). In all compounds **I–VII**, the coordination polyhedron of the metal atom is a pentagonal bipyramid. The equatorial plane of the polyhedron is formed by the atoms of the pentadentate N_3O_2 ligand H_2L^1 or H_2L^2, and the nitrogen atoms of two NCS^- anions are arranged in the axial vertices in compounds **I**, **II**, and **IV–VI**. The N atom of the NCS^- anion and O atoms of the water molecule in compound **III** or methanol in compound **VII** occupy the axial vertices. The interatomic distances in the coordination mode of Co(II) in compounds **I–VII** (Table 2) lie in the following ranges: Co–N(H_2L^1 or H_2L^2, H_4L^1 or H_4L^2) 2.162(3)–2.237(2), Co–O(H_2L^1 or H_2L^2, H_4L^1 or H_4L^2) 2.176(2)–2.341(2), Co–N(NCS) 2.055(3)–2.115(3), and Co–O(H_2O or CH_3OH) 2.123(2) and 2.111(4) Å, respectively. All of them are consistent with similar distances in similar compounds [10, 11, 17, 31–34]. The coordination of these organic ligands to cobalt results in the formation of four five-membered conjugated metallocycles. The dihedral angles between the planes of the latter in compounds **I** and **III–VII** range from 0.9° to 11.1°, and those in compound **II** vary in a broader range of 6.3°–14.2°. The dihedral angles between the planes of the terminal pyridine rings (N(1), C(1)–C(5), and N(7), C(15)–C(19)) with a similar central ring (N(4), C(8)–C(12)) in compounds **I** and **III–VII** are in a range of 7.4°–24.3°, whereas those between the planes of the terminal aromatic ring lie in a range of 4.1°–27.8°, indicating an approximate planarity of the equatorial fragments of the complexes. In compound **II** these angles differ, being 17.3°, 40.2°, and 41.7°, respectively. The CNC bond angles at the nitrogen atoms of the terminal pyridine cycle in compounds **IV–VI** are somewhat larger than 120° (122.2(3)° in **IV**, 123.5(5)° and 124.3(4)° in **V**, 121.9(6)° and 121.5(8)° in **VI**), which confirms their protonation. It is known that these angles in the cationic forms of the pyridine fragments are always larger than similar angles in the neutral molecules [35]. It is also known that the CNC angle in them is sensitive to protonation [36].

Compounds **I** and **II** are formed by the molecular complexes $[Co(H_2L^1)(NCS)_2]$ and $[Co(H_2L^2)(NCS)_2]$ and crystallization molecules of water or methanol in ratios of 1 : 2.25 in compound **I** and 1 : 1 in compound **II**. The unit cell of compound **I** contains two crystallographically independent Co(II) complexes designated as **A** (in

Table 1. Crystallographic data, experimental characteristics, and refinement parameters for structures **I–VII**

Compound	**I**	**Ia**	**II**	**III**	**IV**	**V**	**VI**	**VII**
FW	617.06	608.05	608.56	594.54	738.59	883.30	901.32	1456.30
T	100	293	293	300	293	293	293	293
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$P\bar{1}$	$C2/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a, Å	25.6080(4)	25.6696(9)	8.1347(5)	14.8928(11)	12.8347(9)	9.380(5)	9.3928(7)	36.651(8)
b, Å	14.9055(3)	14.9319(5)	8.7727(4)	8.6277(7)	29.5420(12)	12.0708(14)	12.3295(4)	8.6751(8)
c, Å	20.9946(5)	21.1719(13)	18.2412(10)	20.9686(13)	10.3813(7)	16.694(9)	16.5988(9)	21.939(3)
α, deg	90	90	87.874(4)	90	90	84.07(2)	84.526(4)	90
β, deg	91.821(2)	91.686(4)	89.470(5)	102.438(7)	125.971(11)	77.28(5)	78.232(5)	105.58(2)
γ, deg	90	90	85.591(4)	90	90	87.26(2)	86.995(4)	90
V, Å^3	8009.6(3)	8111.6(6)	1296.98(12)	2631.1(3)	3185.6(3)	1833.3(15)	1872.22(19)	6719.3(19)
Z	12	12	2	4	4	2	2	4
ρ_{calcd}, g/cm^3	1.535	1.494	1.558	1.501	1.540	1.600	1.599	1.440
μ, mm^{-1}	0.849	0.836	0.869	0.855	0.740	1.296	1.273	0.983
F(000)	3810	3750	626	1220	1516	895	915	2988
Crystal sizes, mm	0.12 × 0.08 × 0.06	0.15 × 0.15 × 0.10	0.3 × 0.22 × 0.08	0.3 × 0.15 × 0.15	0.32 × 0.28 × 0.22	0.28 × 0.22 × 0.08	0.30 × 0.07 × 0.05	0.5 × 0.2 × 0.05
Range of θ, deg	2.89–26.00	2.93–25.50	3.17–26.00	3.02–26.00	2.79–25.99	2.51–25.50	2.96–25.05	2.92–26.50
Range of reflection indices	$-31 \le h \le 31$, $-18 \le k \le 18$, $-24 \le l \le 25$	$-18 \le h \le 31$, $-9 \le k \le 18$, $-25 \le l \le 25$	$-10 \le h \le 9$, $-10 \le k \le 10$, $-16 \le l \le 22$	$-18 \le h \le 18$, $-10 \le k \le 6$, $-24 \le l \le 25$	$-13 \le h \le 15$, $-3 \le k \le 36$, $-12 \le l \le 6$	$-11 \le h \le 10$, $-14 \le k \le 14$, $-20 \le l \le 20$	$-9 \le h \le 11$, $-14 \le k \le 14$, $-19 \le l \le 15$	$-34 \le h \le 46$, $-9 \le k \le 10$, $-27 \le l \le 27$
Number of measured/independent reflections	28469/7860 ($R_{int} = 0.0404$)	13185/7479 ($R_{int} = 0.0388$)	9406/5085 ($R_{int} = 0.0258$)	12738/5160 ($R_{int} = 0.0395$)	7840/3123 ($R_{int} = 0.0336$)	11797/6822 ($R_{int} = 0.0327$)	10628/6576 ($R_{int} = 0.0394$)	12644/6940 ($R_{int} = 0.0424$)
Filling, %	99.7	99.2	99.8	99.6	99.9	99.8	99.2	99.7
Number of reflections with $I > 2\sigma(I)$	6257	5188	4113	3838	2524	5038	3853	4418
Number of refined parameters	535	531	356	344	217	472	493	445
GOOF	1.020	1.012	1.009	1.007	1.004	1.007	1.006	1.004
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0465$, $wR_2 = 0.1067$	$R_1 = 0.0621$, $wR_2 = 0.1671$	$R_1 = 0.0414$, $wR_2 = 0.0942$	$R_1 = 0.0481$, $wR_2 = 0.1076$	$R_1 = 0.0465$, $wR_2 = 0.1351$	$R_1 = 0.0538$, $wR_2 = 0.1431$	$R_1 = 0.0665$, $wR_2 = 0.1495$	$R_1 = 0.0734$, $wR_2 = 0.2154$
R factor (for whole massif)	$R_1 = 0.0646$, $wR_2 = 0.1139$	$R_1 = 0.0971$, $wR_2 = 0.1859$	$R_1 = 0.0576$, $wR_2 = 0.1000$	$R_1 = 0.0719$, $wR_2 = 0.1192$	$R_1 = 0.0650$, $wR_2 = 0.1888$	$R_1 = 0.0773$, $wR_2 = 0.1600$	$R_1 = 0.1225$, $wR_2 = 0.1967$	$R_1 = 0.1144$, $wR_2 = 0.2446$
$\Delta\rho_{max}/\rho_{min}$, e Å^{-3}	0.584, –0.505	0.849, –0.534	0.473, –0.355	0.645, –0.291	0.646, –0.552	0.655, –0.541	0.618, –0.614	0.880, –0.573

Table 2. Interatomic distances and bond angles in the coordination polyhedra of structures **I–VII***

Bond	*d*, Å							
	IA	**IB**	**II**	**III**	**IV**	**V**	**VI**	**VII**
Co(1)–O(1)	2.212(2)	2.267(2)					2.226(4)	
Co(1)–O(2)	2.205(2)		2.176(2)	2.179(2)		2.234(3)	2.198(4)	2.191(3)
Co(1)–N(3)	2.218(2)	2.220(2)	2.213(2)	2.186(2)	2.217(3)	2.199(3)	2.186(5)	2.227(4)
Co(1)–N(4)	2.175(2)	2.162(3)	2.173(2)	2.181(2)	2.177(4)	2.170(4)	2.186(5)	2.190(4)
Co(1)–N(5)	2.214(2)		2.222(2)	2.237(2)		2.184(3)	2.214(5)	2.210(4)
Co(1)–N(8)	2.115(3)	2.055(3)	2.081(2)	2.075(3)	2.072(3)	2.102(4)	2.088(6)	2.064(5)
Co(1)–N(9)	2.095(3)		2.093(2)			2.079(4)	2.092(6)	
Co(1)–O(1*w*)/O(3)				2.123(2)				2.111(4)
Angle	ω, deg							
	IA	**IB**	**II**	**III**	**IV**	**V**	**VI**	**VII**
O(1)Co(1)O(2)/O(1)$^{\#1/\#2}$	78.60(7)	79.92(10)					76.9(25)	
O(1)Co(1)N(3)	70.50(8)	69.57(7)	69.17(7)	71.38(8)	70.57(9)	71.2(1)	71.1(2)	70.9(1)
O(1)Co(1)N(4)	140.55(8)	140.04(5)	139.23(7)	141.52(7)	140.64(6)	141.3(1)	141.1(2)	140.5(1)
O(1)Co(1)N(5)/N(3)$^{\#1/\#2}$	148.44(8)	149.15(8)	150.13(8)	148.29(8)	148.55(10)	148.0(1)	148.3(2)	149.0(3)
O(1)Co(1)N(8)	89.61(9)	91.31(8)	89.70(8)	91.47(10)	90.6(1)	85.9(1)	91.3(2)	88.0(2)
O(1)Co(1)N(9)/N(8)$^{\#1/\#2}$	85.03(10)	83.81(9)	82.72(8)		85.3(1)	88.7(1)	89.8(2)	
O(1)Co(1)O(1*w*)/O(3)				85.32(8)				87.8(1)
O(2)/O(1)$^{\#1/\#2}$Co(1)N(3)	149.02(8)	149.15(8)	149.23(7)	149.11(9)	148.55(10)	147.9(1)	147.9(2)	149.1(1)
O(2)/O(1)$^{\#1/\#2}$Co(1)N(4)	140.81(8)	140.04(5)	140.53(7)	140.32(8)	140.64(6)	141.5(1)	142.0(2)	141.0(2)
O(2)/O(1) $^{\#1/\#2}$Co(1)N(5)/N(3)$^{\#1/\#2}$	70.38(8)	69.57(7)	70.70(7)	70.68(8)	70.57(9)	71.0(1)	71.6(2)	70.8(1)
O(2)/O(1)$^{\#1/\#2}$Co(1)N(8)	85.97(9)	83.81(9)	89.47(8)	86.85(9)	85.3(1)	90.0(1)	88.0(2)	90.5(2)
O(2)/O(1)$^{\#1/\#2}$Co(1)N(9)/N(8)$^{\#1/\#2}$	89.03(9)	91.31(8)	86.19(9)		90.6(1)	90.5(1)	87.3(2)	
O(2)Co(1)O(1*w*)/O(3)				86.33(8)				89.0(1)
N(3)Co(1)N(4)	70.17(9)	70.59(6)	70.16(8)	70.36(8)	70.34(7)	70.5(1)	70.1(2)	69.7(2)
N(3)Co(1)N(5)/N(3)$^{\#1/\#2}$	140.59(9)	141.2(1)	139.84(8)	140.09(9)	140.7(2)	140.7(1)	140.1(2)	139.8(1)
N(3)Co(1)N(8)	91.50(10)	92.17(9)	90.13(9)	94.47(9)	88.4(1)	92.6(1)	93.9(2)	90.4(2)
N(3)Co(1)N(9)/N(8)$^{\#1/\#2}$	90.49(10)	89.95(9)	90.05(9)		93.4(1)	84.1(1)	91.3(2)	
N(3)Co(1)O(1*w*)/O(3)				90.46(8)				87.9(2)
N(4)Co(1)N(5)/N(3)$^{\#1/\#2}$	70.49(8)	70.59(6)	70.47(8)	69.73(8)	70.34(7)	70.6(1)	70.4(2)	70.2(2)
N(4)Co(1)N(8)	94.33(9)	93.18(7)	87.71(9)	95.48(10)	92.70(9)	90.8(1)	90.7(2)	94.7(2)
N(4)Co(1)N(9)/N(8) $^{\#1/\#2}$	92.36(10)	93.18(7)	100.04(9)		92.70(9)	92.4(1)	91.6(2)	
N(4)Co(1)O(1*w*)/O(3)				90.93(9)				88.4(1)
N(5)/N(3) $^{\#1/\#2}$Co(1)N(8)	93.77(9)	89.95(9)	95.91(8)	89.62(10)	93.4(1)	93.0(1)	91.5(2)	94.8(2)
N(5)/N(3) $^{\#1/\#2}$Co(1)N(9)/N(8)$^{\#1/\#2}$	88.74(10)	92.17(9)	89.22(9)		88.4(1)	92.5(1)	84.9(2)	
N(5)Co(1)O(1*w*)/O(3)				89.83(9)				89.0(2)
N(8)Co(1)N(9)/N(8)$^{\#1/\#2}$	173.30(10)	173.6(1)	171.81(9)		174.6(2)	174.3(1)	174.8(2)	
N(8)Co(1)O(1*w*)/O(3)				172.95(9)				175.8(2)
N(9)Co(1)O(1*w*)/O(3)								

* Symmetry codes:$^{\#1}$ $-x, y, -z + 1/2$ (**IB**); $^{\#2}$ $-x + 1, y, -z + 3/2$ (**IV**).

Table 3. Geometric parameters of hydrogen bonds in compounds **I–VII**

D–H···A	Distance, Å			Angle DHA, deg	Symmetry transform for A
	D–H	H···A	D···A		
			I		
N(2*A*)–H(1)···O(2*w*)	0.86	2.35	3.134(3)	151	*x* + 1/2, *y* – 1/2, *z*
N(6*A*)–H(1)···O(3*w*)	0.86	2.27	3.071(4)	155	*x*, *y* + 1, *z*
N(6*A*)–H(1)···O(3*wA*)	0.86	2.49	3.33(3)	163	*x*, *y* + 1, *z*
N(2*B*)–H(1)···O(1*w*)	0.86	2.02	2.884(3)	176	*x*, *y*, *z*
O(1*w*)–H(1)···O(2*A*)	0.85	2.27	3.095(3)	163	*x*, *y*, *z*
O(1*w*)–H(2)···N(1*B*)	0.85	2.02	2.870(3)	177	–*x* + 1/2, *y* – 1/2, –*z* + 1/2
O(2*w*)–H(1)···N(7*A*)	0.87	1.98	2.838(4)	174	*x*, *y*, *z*
O(2*w*)–H(2)···O(1*B*)	0.85	2.18	3.028(3)	174	–*x*, *y*, –*z* + 1/2
O(3*w*)–H(1)···S(1*A*)	0.90	2.53	3.425(3)	169	–*x* + 1/2, *y* – 1/2, –*z* + 1/2
O(3*w*)–H(2)···N(1*A*)	0.93	1.94	2.869(4)	173	*x*, *y*, *z*
O(3*wA*)–H(1)···N(1*A*)	0.87	2.03	2.90(3)	178	*x*, *y*, *z*
O(3*wA*)–H(2)···O(3*w*)	0.98	2.33	3.31(3)	179	–*x* + 1/2, –*y* + 1/2, –*z* + 1
O(4*w*)–H(1)···O(2*w*)	0.91	1.84	2.756(7)	180	–*x*, *y*, –*z* + 1/2
O(4*wA*)–H(2)···O(2*w*)	0.94	2.51	3.35(2)	150	*x*, *y*, *z*
			II		
O(3)–H(1)···N(7)	0.82	1.98	2.776(3)	162	*x*, *y* + 1, *z*
N(2)–H(1)···S(1)	0.86	2.68	3.459(2)	151	*x*, *y* + 1, *z*
N(6)–H(1)···O(3)	0.86	2.04	2.893(3)	175	*x* + 1, *y* – 1, *z*
			III		
N(2)–H(1)···N(9)	0.86	2.15	2.908(4)	146	*x*, –*y* + 3/2, *z* – 1/2
N(6)–H(1)···S(1)	0.86	2.76	3.583(3)	160	–*x* + 1, –*y* + 1, –*z* + 1
O(1*w*)–H(1)···S(2)	0.85	2.41	3.255(2)	174	*x*, *y*, *z*
O(1*w*)–H(2)···N(1)	0.85	1.91	2.755(3)	176	*x*, *y* – 1, *z*
			IV		
N(1)–H(1)···O(1N)	0.86	2.00	2.854(4)	171	–*x* + 1, –*y* + 1, –*z* + 1
N(2)–H(1)···O(1*w*)	0.86	2.11	2.874(5)	148	*x*, *y*, *z*
O(1*w*)–H(1)···O(4N)	0.82	2.02	2.807(5)	162	–*x*, *y*, –*z* + 1/2
O(1*w*)–H(2)···S(1)	0.91	2.65	3.390(4)	140	–*x*, *y*, –*z* + 1/2
			V		
N(1)–H(1)···S(1)	0.86	2.71	3.428(6)	142	*x*, *y* – 1, *z*
N(1)–H(1)···S(6)	0.86	2.93	3.569(6)	133	*x*, *y*, *z*
N(6)–H(1)···S(1)	0.86	2.92	3.699(4)	152	*x* + 1, *y*, *z*
N(7)–H(1)···S(3)	0.86	2.75	3.438(4)	138	–*x* + 2, –*y* + 2, –*z*
O(1*w*)–H(2)···S(2*B*)	0.78	2.28	3.03(1)	162	*x*, *y*, *z*
O(1*w*)–H(2)···S(2*A*)	0.78	2.88	3.66(1)	171	*x*, *y*, *z*
O(2*w*)–H(1)···S(2*A*)	0.85	1.83	2.62(2)	153	–*x* + 2, –*y* + 1, –*z* + 1
O(2*w*)–H(1)···S(2*C*)	0.85	1.97	2.72(2)	146	–*x* + 2, –*y* + 1, –*z* + 1
O(2*w*)–H(1)···S(2*A*)	0.85	2.11	2.94(2)	168	–*x* + 2, –*y* + 1, –*z* + 1

Table 3. (Contd.)

D–H···A	Distance, Å			Angle DHA, deg	Symmetry transform for A
	D–H	H···A	D···A		
O(2*w*)–H(1)···S(2*B*)	0.85	2.59	3.44(2)	179	–*x* + 2, –*y* + 1, –*z* + 1
VI					
N(1)–H(1)···S(4)	0.86	2.49	3.270(6)	151	*x*, *y*, *z*
N(2)–H(1)···S(1)	0.86	2.85	3.648(6)	155	*x* + 1, *y*, *z*
N(6)–H(1)···O(3*w*)	0.86	2.24	3.06(3)	159	*x* – 1, *y*, *z*
N(7)–H(1)···O(1*w*)	0.86	2.01	2.75(1)	144	*x* – 1, *y*, *z*
O(1*w*)–H(1)···O(3*w*)	0.89	2.39	3.15(3)	143	*x*, *y*, *z*
O(1*w*)–H(1)···S(2)	0.89	2.80	3.51(1)	137	*x*, *y*, *z*
O(1*w*)–H(1)···S(2*A*)	0.89	2.27	3.07(1)	150	*x*, *y*, *z*
O(1*w*)–H(1)···S(2*B*)	0.89	2.36	3.17(5)	153	*x*, *y*, *z*
O(1*w*)–H(2)···N(10)	0.79	2.56	3.34(1)	170	*x*, *y* – 1, *z*
O(2*w*)–H(1)···O(3*w*)	0.80	2.09	2.89(3)	175	*x* – 1, *y*, *z*
O(2*w*)–H(2)···S(3)	0.83	2.47	3.216(9)	150	*x*, *y* – 1, *z*
O(3*w*)–H(1)···S(2)	0.83	2.49	3.32(3)	173	*x*, *y*, *z*
O(3*w*)–H(2)···S(3)	0.79	2.74	3.52(3)	169	–*x* + 1, –*y* + 2, –*z* + 1
VII					
N(2)–H(1)···S(1)	0.86	2.80	3.634(4)	163	–*x* + 1/2, –*y* + 3/2, –*z*
N(6)–H(1)···S(3*A*)	0.84	2.80	3.588(9)	157	*x*, *y*, *z*
N(6)–H(1)···O(5)	0.84	2.08	2.92(1)	173	*x*, *y*, *z*
O(3)–H(1)···N(7)	0.87	1.93	2.758(6)	156	*x*, *y* + 1, *z*
O(4)–H(1)···O(1)	0.88	2.40	3.15(1)	144	*x*, *y*, *z*
O(4)–H(1)···O(2)	0.88	2.50	3.20(2)	137	*x*, *y*, *z*
O(4*A*)–H(1)···O(3)	0.85	2.610	3.46(2)	180	*x*, *y* – 1, *z*
O(5)–H(1)···S(3)	0.93	2.42	3.217(9)	144	*x*, *y*, *z*

the general position) and **B** (in the partial position on the 2-fold axis) (Figs. 1a, 1b), and that of compound **II** contains one crystallographically independent complex in the general position (Fig. 2). The geometric parameters of the coordination polyhedra of these three complexes (Table 2) are similar and differ only by the orientation of the NCS$^-$ anions relative to the equatorial plane CoN_3O_2. In complex **IA**, the angles between the linear anion NCS$^-$ and equatorial plane are 92.2° and 45.5°. This angle in compound **IB** is equal to 79.4°, and the angles in complex **II** are 86.3° and 46.7°.

In crystal of compound **I**, the molecules are joined into a three-dimensional framework by classical hydrogen bonds O(*w*)–H···O, O(*w*)–H···N, and O(*w*)–H···S, N–H···O(*w*) (Table 3, Fig. 7) and by weaker intermolecular hydrogen bonds of the C–H···O(*w*) type in which water molecules are involved as acceptors: C(5*A*)–H···O(2*w*) (*x* + 1/2, *y* – 1/2, *z*) (C···O 3.321, H···O 2.52 Å, angle CHO 144°), C(20*A*)–H···O(2*w*) (*x* + 1/2, *y* – 1/2, *z*) (C···O 3.275, H···O 2.33 Å, angle CHO 168°), and C(5*B*)–H···O(1*w*) (C···OS 3.112, H···O 2.35 Å, angle CHO 139°) (Fig. 3). It can be noted that in compound **I** complexes **A** and **B** are additionally bound by weak intermolecular hydrogen bonds C–H···S: C(10*A*)–H···S(2*A*) (–*x* + 1, –*y* + 2, –*z* + 1) (C···S 3.820, H···S 2.90 Å, angle CHS 174°), C(16*A*)–H···S(2*A*) (–*x* + 1/2, –*y* + 3/2, –*z* + 1) (C···S 3.674, H···S 2.88 Å, angle CHS 145°), C(11*A*)–H···S(1*B*) (*x* + 1/2, *y* + 1/2, *z*) (C···S 3.774, H···S 2.88 Å, angle CHS 161°), and C(20*B*)–H···S(2*A*) (–*x* + 1/2, –*y* + 3/2, –*z* + 1) (C···S 3.549, H···S 2.77 Å, angle CHS 139°).

The intermolecular hydrogen bonds N–H···S join complexes in crystal of compound **II** (Table 3, Fig. 8) into chains decorated by the methanol molecules due to the hydrogen bonds O–H···O. In crystal the chains are joined by the weak intermolecular hydrogen bonds C–H···O (C(16)–H···O(3) (*x* + 1, *y* – 1, *z*) (C···O

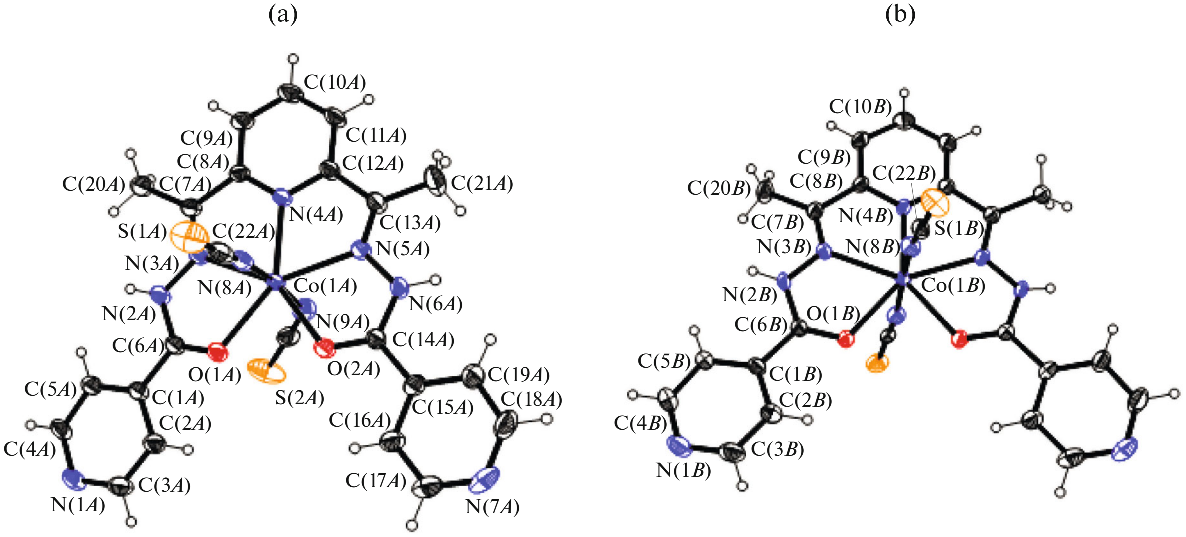


Fig. 1. Molecular structures of crystallographically independent complexes (a) **A** and (b) **B** in compound **I**.

3.142, H···O 2.40 Å, angle CHO 137°) and C(21)–H···O(3) ($x + 1, y - 1, z$) (C···O 3.340, H···O 2.39 Å, angle CHO 169°) (Fig. 4)) and C(5)–H···S(1) ($-x + 1, -y, -z + 1$) (C···S 3.816, H···S 2.92 Å, angle CHS 162°).

Compounds **III** and **IV** are of the ionic type and are formed by the complex Co(II) cations and outer-sphere anions NCS^- or NO_3^-, respectively (Figs. 3a and 3b). The mechanism of formation of the NO_3^- anions was not revealed. The independent part of the unit cell of compound **III** contains one complex cation $[Co(H_2L^2)(NCS)(H_2O)]^+$ and one anion NCS^-. The independent part of the unit cell of compound **IV** contains the $[Co(H_4L^1)(NCS)_2]^{2+}$ complex cation, two outer-sphere NO_3^- anions (on the 2-fold axis), and one water molecule. In compound **III**, compared to molecular complexes **I** and **II**, one of the coordinated NCS^- anions is substituted by the water molecule and the charges of the outer-sphere NCS^- anion are balanced, whereas the charge balance in compound **IV** is achieved by the protonation of the organic ligand. Thus, in compound **III** ligand H_2L^2 is coordinated to Co(II) as a neutral ligand, whereas in compound **IV** $(H_4L^1)^{2+}$ is coordinated as a dication. The coordination polyhedra of the metal atoms in complex cations **III** and **IV** (Fig. 3) differ only by the donor atoms in the axial vertices of the pentagonal bipyramid, and the geometric parameters are consistent with those found for compounds **I** and **II** (Table 2) and with published data [10, 11, 17, 31–34]. The NCS^- anion is oriented almost perpendicularly to the equatorial plane of the bipyramid at an angle of 86.5° in compound **III** and 84.6° in compound **IV**.

In crystal of compound **III**, the complex cations are bound into a chain by the intermolecular hydrogen bonds N(6)–H···S(1) similar to those found in compound **II** and additionally by the hydrogen bonds O(1*w*)–H···N(1) (Fig. 9a). These chains are joined into layers by the outer-sphere NCS^- anions using the intermolecular hydrogen bonds O(1*w*)–H···S(2) and N(2)–H···N(9) (Table 3). The crystal is additionally stabilized by the weak intermolecular hydrogen bonds C(9)–H···S(2) ($x, -y + 1/2, z - 1/2$) (C···S 3.811, H···S 2.90 Å, angle CHS 168°) and C(21)–H···S(1)

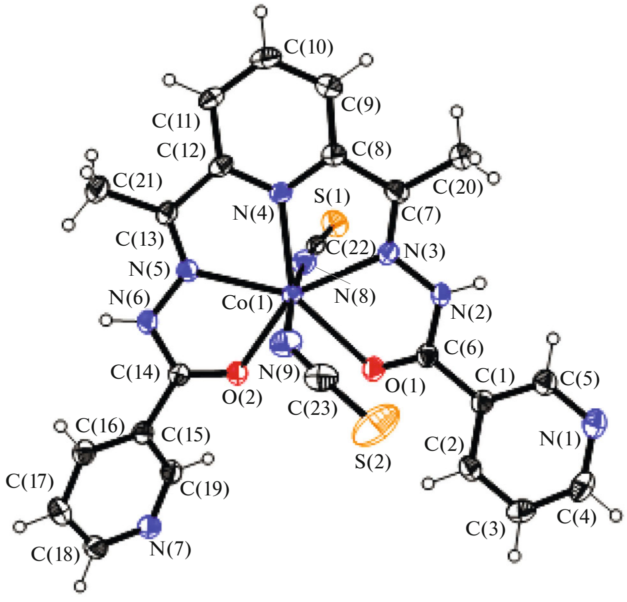


Fig. 2. Molecular structure of the complex in compound **II**.

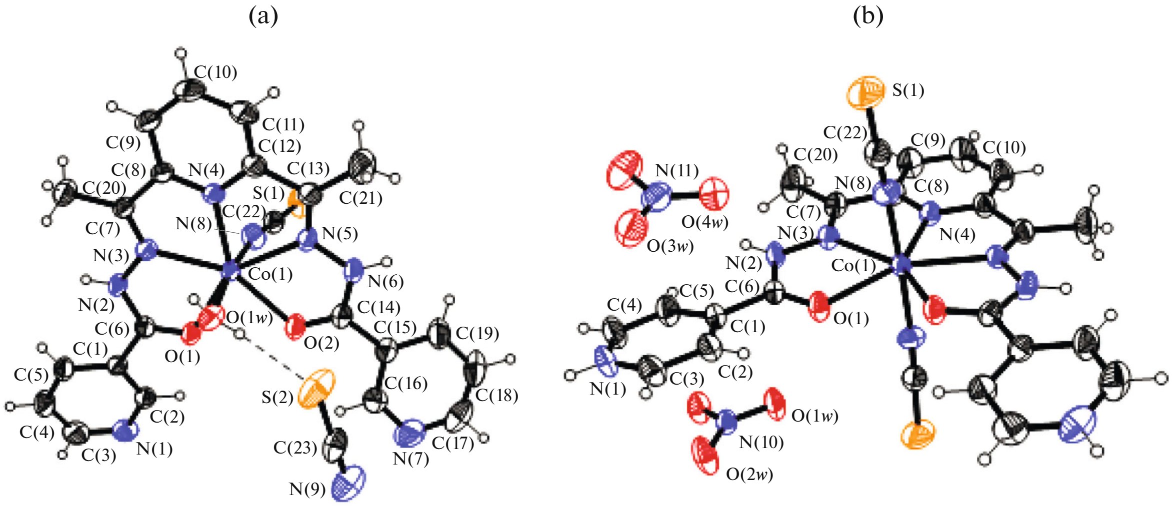


Fig. 3. Molecular structures of complexes (a) **III** and (b) **IV**.

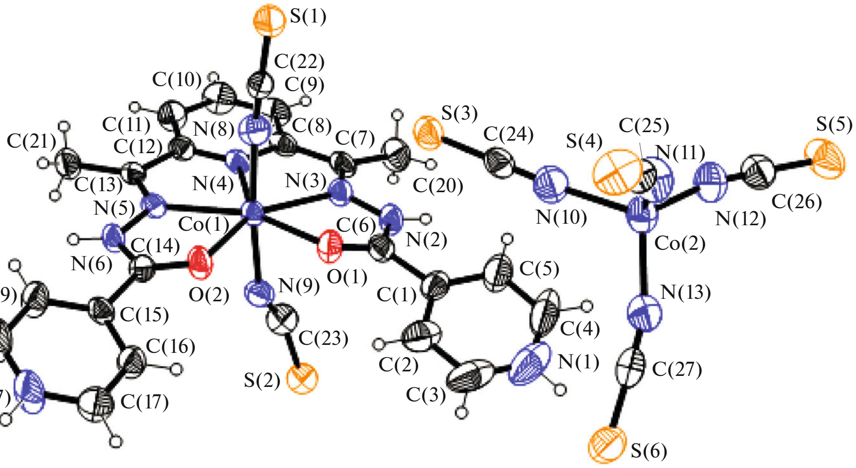


Fig. 4. Structures of the complex cation $[Co(H_4L^1)(NCS)_2]^{2+}$ and anion $[Co(NSC)_4]^{2-}$ in compound **V**.

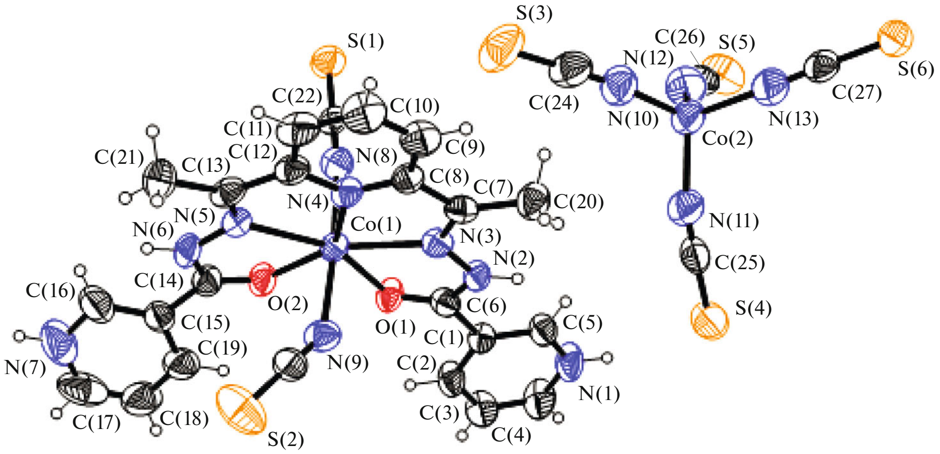


Fig. 5. Structures of the complex cation $[Co(H_4L^2)(NCS)_2]^{2+}$ and anion $[Co(NSC)_4]^{2-}$ in compound **VI**.

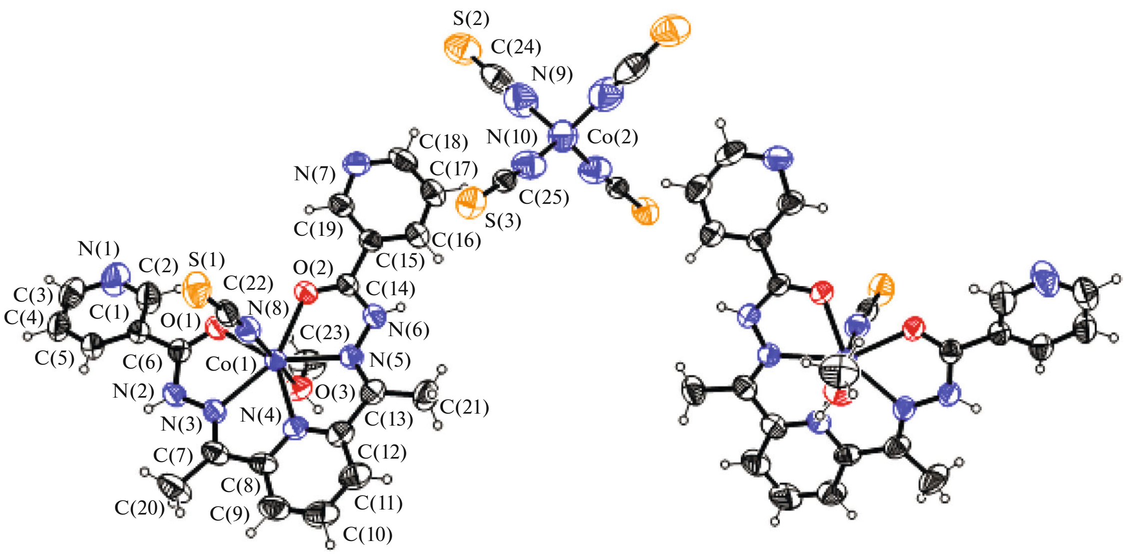


Fig. 6. Structure of the fragment $[Co(H_2L^2)(NCS)(CH_3OH)]_2[Co(NSC)_4]$ in compound **VII**.

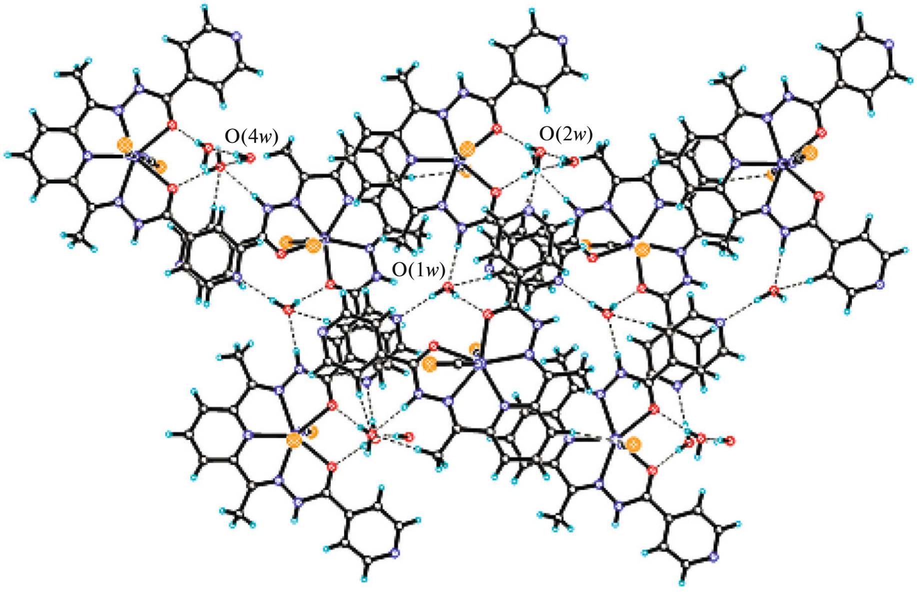


Fig. 7. Fragment of packing of the components in compound **I**.

$(-x + 1, -y + 1, -z + 1)$ (C···S 3.636, H···S 2.93 Å, angle CHS 131°).

In crystal of compound **IV**, the $[Co(H_4L^1)(NCS)_2]^{2+}$ complex cations are linked by the hydrogen bonds O(*w*)–H···S, N–H···O(*w*), and N–H···O through the water molecules and NO_3^- anion, and the second NO_3^- anion joins the hydrogen bonds O(*w*)–H···O(N) of the water molecule (Table 3, Fig. 9b). As a result, the layers are formed with the hydrophilic groups inside the layer additionally stabilized by the weak intermolecular hydrogen bonds C(4)–H···O(2N) $(-x + 1, -y + 1, -z + 1)$ (C···O 2.960, H···O 2.28 Å, angle CHO 129°), C(5)–H···O(1*w*) (C···O 3.193, H···O 2.57 Å, angle CHO 124°), and C(2)–H···O(3N) (C···O 3.286, H···O 2.38 Å, angle CHO 165°).

The independent part of the unit cells of compounds **V** and **VI** contains the complex cation $[Co(H_4L^1)(NCS)_2]^{2+}$ or $[Co(H_4L^2)(NCS)_2]^{2+}$, complex anion $[Co(NCS)_4]^{2-}$, and water molecules in a ratio of 1 : 1 : 0.75 or 1 : 1 : 1.75, respectively. The independent part of the unit cell of compound **VII** contains

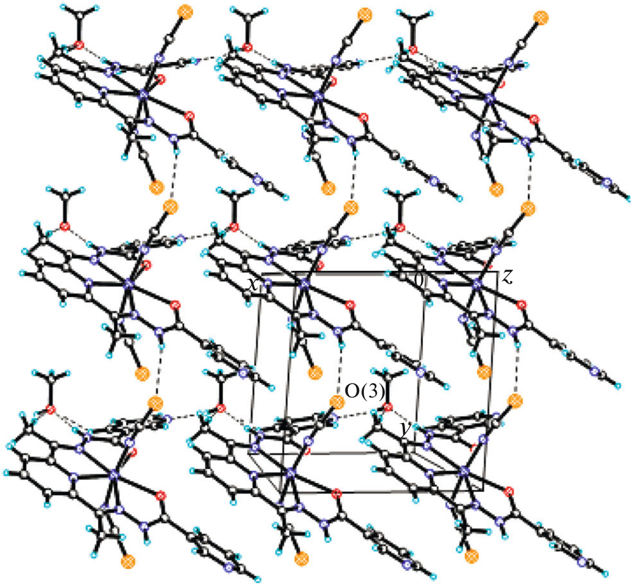


Fig. 8. Fragment of the crystal structure of compound **II**.

one complex cation $[Co(H_2L^2)(NCS)(CH_3OH)]^+$, a half of the complex anion $[Co(NCS)_4]^{2-}$ arranged on the 2-fold axis, and a methanol molecule. In complex cations of **V** and **VI**, the organic ligands, similar to those in **IV**, are protonated at the nitrogen atoms of the terminal pyridine fragments. In compounds **V** and **VI**, the NCS^- anions are coordinated to the metal in both axial positions (Figs. 10, 11). In compound **VII**, the organic ligand is neutral and the axial positions are occupied by one NCS^- anion and a methanol molecule (Fig. 12). The geometric parameters of the coordination polyhedra of the metal in the complex cations of compounds **V–VII** do not differ from those found for the previous compounds (Table 2). The angles between the linear anion NCS^- and equatorial plane are 85.3° and 56.7° (**V**), 88.3° and 53.4° (**VI**), and 88.9° (**VII**).

The complex cations in compound **V** are linked to each other by the intermolecular hydrogen bonds N–H···S into layers parallel to the (*xy*) plane. The tetrahedral complex anions $[Co(NCS)_4]^{2-}$ are arranged between the layers and are bound to the cations of the layer by the hydrogen bonds N–H···S (Table 3, Fig. 10). The structure of compound **V** is additionally stabilized by the weak intermolecular hydrogen bonds C–H···S with the sulfur atoms of the NCS^- anions as acceptors (both complex cations and anions): C(11)–H···S(2*A*) $(-x + 2, -y + 2, -z + 1)$ (C···S 3.621, H···S 2.77 Å, angle CHS 153°), C(10)–H···S(3) $(-x + 1, -y + 2, -z + 1)$ (C···S 3.758, H···S 2.88 Å, angle CHS 158°), C(17)–H···S(4) $(x + 1, y, z)$ (C···S 3.561, H···S 2.86 Å, angle CHS 133°), and C(18)–H···S(6) $(x + 1, y + 1, z)$ (C···S 3.455, H···S 2.75 Å, angle CHS 133°) (Fig. 12).

The complex cations in compound **VI** are linked with each other by the hydrogen bonds N–H···S into chains (Table 3). The latter are joined into a layer through the tetrahedral complex anions $[Co(NCS)_4]^{2-}$ and water molecules bound to the cations of the chains of the hydrogen bonds N–H···S, N–H···O(*w*), O(*w*)–H···S, and O(*w*)–H···N (Table 3, Fig. 11). The crystal structure in compound **VI** is additionally stabilized by the hydrogen bonds C–H···S: C(20)–H···S(1) $(x + 1, y, z)$ (C···S 3.643, H···S 2.85 Å, angle CHS 141°), C(20)–H···S(3) (C···S 3.508, H···S 2.75 Å, angle CHS 137°), C(3)–H···S(5) $(x, y - 1, z)$ (C···S 3.629, H···S 2.95 Å, angle CHS 131°), C(4)–H···S(6) $(-x + 2, -y + 3, -z)$ (C···S 3.611, H···S 2.86 Å, angle CHS 139°), and C(10)–H···S(6) $(-x + 1, -y + 3, -z + 1)$ (C···S 3.799, H···S 2.89 Å, angle CHS 166°) and hydrogen bonds involving acceptors of the oxygen atoms of the crystallization molecules of water: C(16)–H···O(3*w*) $(x + 1, y, z)$ (C···O 2.960, H···O 2.08 Å, angle CHO 158°) and C(21)–H···O(3*w*) $(x + 1, y, z)$ (C···O 3.400, H···O 2.46 Å, angle CHO 167°).

In compound **VII**, the complex cations $[Co(H_2L^2)(NCS)(CH_3OH)]^+$ are bound by the intermolecular hydrogen bonds N–H···S and O–H···N into ribbons joined by the complex anions $[Co(NCS)_4]^{2-}$ and solvate molecules of methanol into layers by the intermolecular hydrogen bonds N–H···O and O–H···S (Table 3, Fig. 12). In crystal the complex cations, anions, and solvate methanol molecules are additionally joined by the weak intermolecular hydrogen bonds C–H···S (C(18)–H···S(2) (C···S 3.812, H···S 2.91 Å, angle CHS 166°), C(11)–H···S(3) $(x, y + 1, z)$ (C···S 3.586, H···S 2.70 Å, angle CHS 159°), C(16)–H···O(5) (C···O 3.235, H···O 2.54 Å, angle CHO 131°), and C(21)–H···O(5) (C···O 3.080, H···O 2.28 Å, angle CHO 140°)).

In the spectra of compounds **I–VII**, it is difficult to identify the ν(NH) absorption band because of the ν(OH) bands (H_2O and CH_3OH) and a possible association of the =NH and –OH functional groups. The ν(C=O) absorption band in the spectra of the studied complexes and its shift to the long-wavelength range (1633–1635 cm^{-1}) compared to its position in the spectra of the non-coordinated ligands [21, 27] indicate both the presence of H_2L^1 and H_2L^2 in the ketone form in the complexes and the participation of the =C=O functional groups of these ligands in coordination with the metal [8, 33, 34, 37]. In the spectra of all complexes studied, the ν(C≡N) absorption bands of the NCS^- groups are very intense and appear below 2100 cm^{-1}, confirming the coordination of these ions through the nitrogen atom and/or their participation as outer-sphere ions [38] to compensate the charge of the complexing agent. The manifestation of the single intense absorption band ν(C≡N) in the spectra of compounds **I** and **II** at 2082 and 2058 cm^{-1}, respectively, indicates probably that these groups are equivalent in each complex. The presence of two very intense

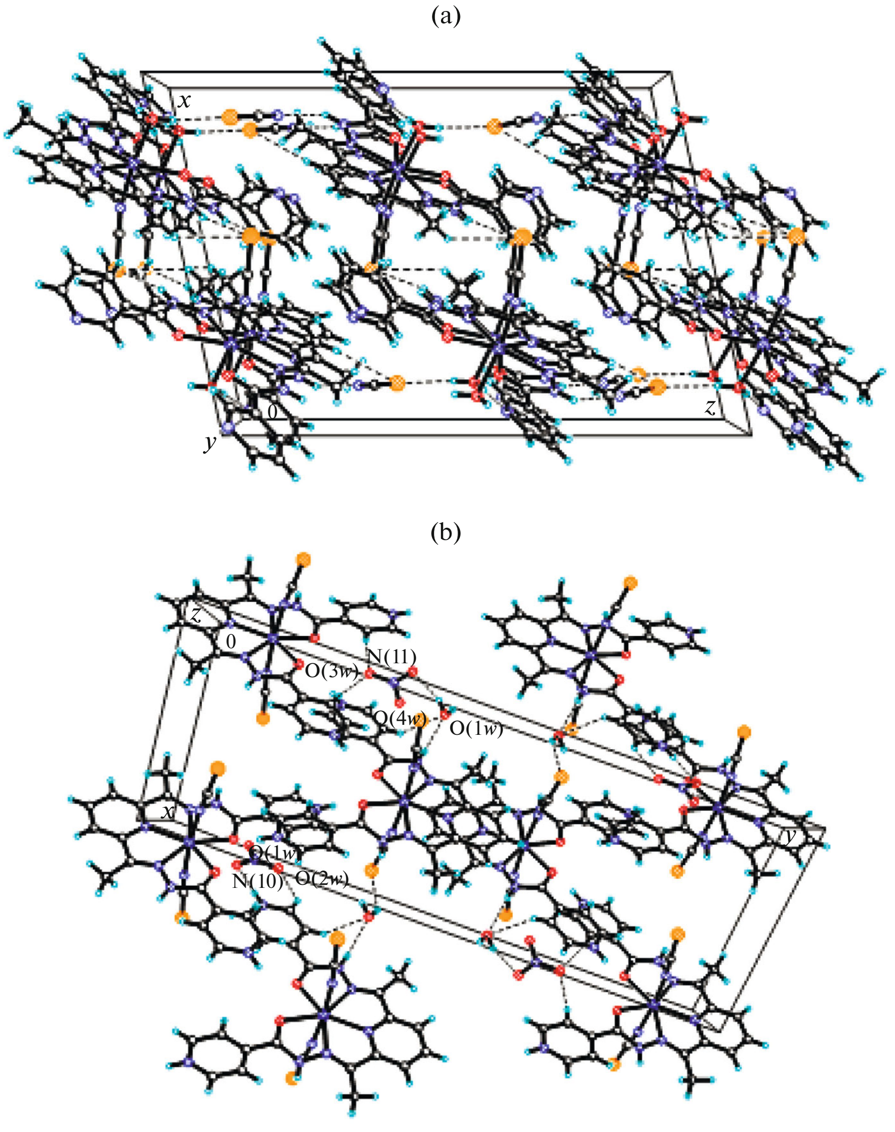


Fig. 9. Crystal structures of compounds (a) **III** and (b) **IV**.

absorption bands at 2095 and 2072 cm^{-1} in the spectrum of compound **III** can be due to different roles of the NCS$^-$ anions in the complex: coordinated and outer-sphere. The spectrum of complex **IV** contains an intense band characteristic of NCS$^-$ and two bands at 1294 cm^{-1} (very intense) and at 847 cm^{-1} (medium-intensity), which can be assigned to vibrations of the NO_3^- anions [39]. The shift of the first band to low frequencies compared to the absorbance of free NO_3^- anions is caused, probably, by the participation of these anions in the formation of hydrogen bonds with the heterocyclic nitrogen atoms of the hydrazide fragment of the ligand (this fact was confirmed by X-ray diffraction analysis). The absorbance in the form of broad bands in the spectrum of compound **IV** in a range of 2500–1800 cm^{-1} (2420, 2297, and 1877 cm^{-1}) confirms the protonation of the heterocyclic nitrogen atoms of the hydrazide fragments. The absorbance in the same range was also observed in the spectra of complexes **V** and **VI**. Two very intense absorption bands appear at 2095–2060 cm^{-1} in the spectra of complexes **V–VII** due to the presence of two types of NCS$^-$ groups: coordinated in the complex cation and in the $[Co(NCS)_4]^{2-}$ anion. The manifestation of the ν(NCS) (846–810 cm^{-1}) and δ(NCS) (476–460 cm^{-1}) absorption bands is consistent with the coordination of these anions to the metal through the nitrogen atom [38].

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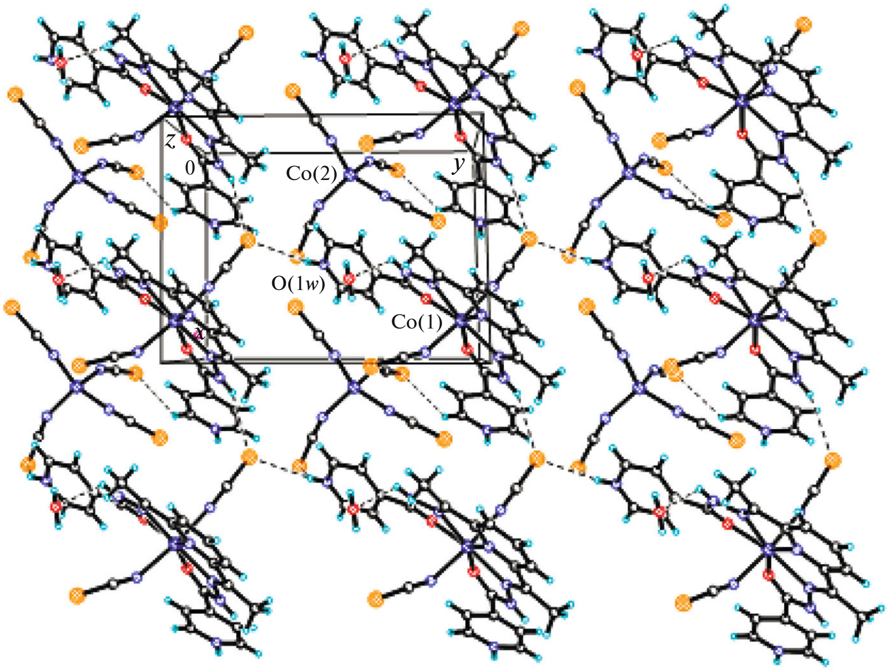

Fig. 10. Formation of the layer by the complex cations in compound **V** decorated by the complex anions.

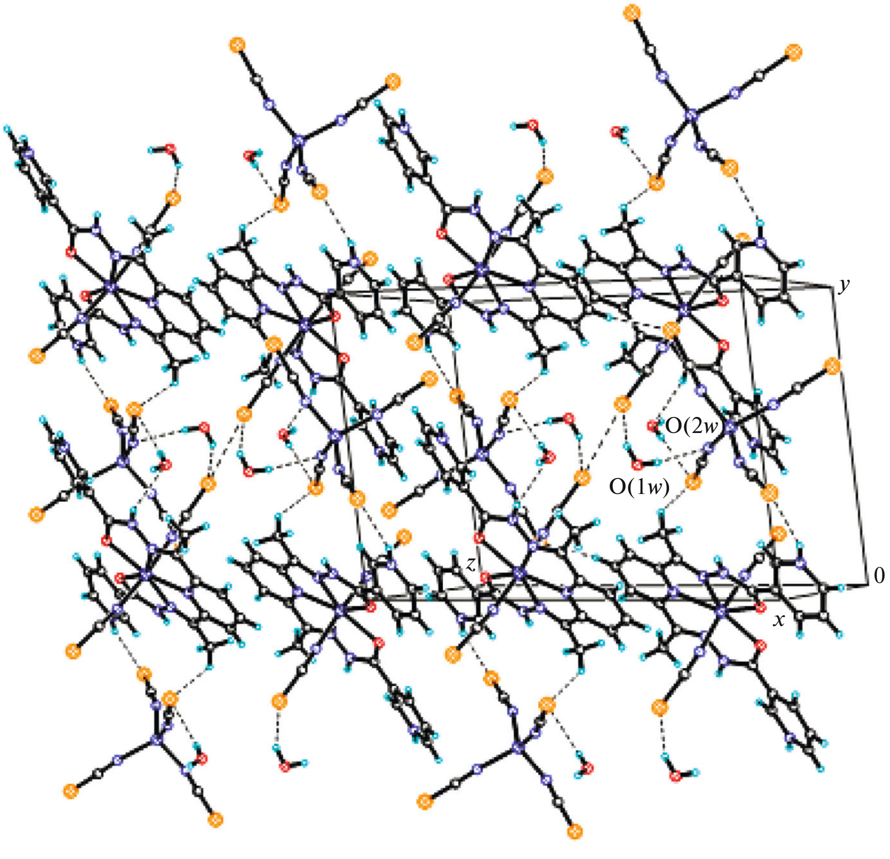

Fig. 11. Fragment of packing of the components in crystal of compound **VI**.

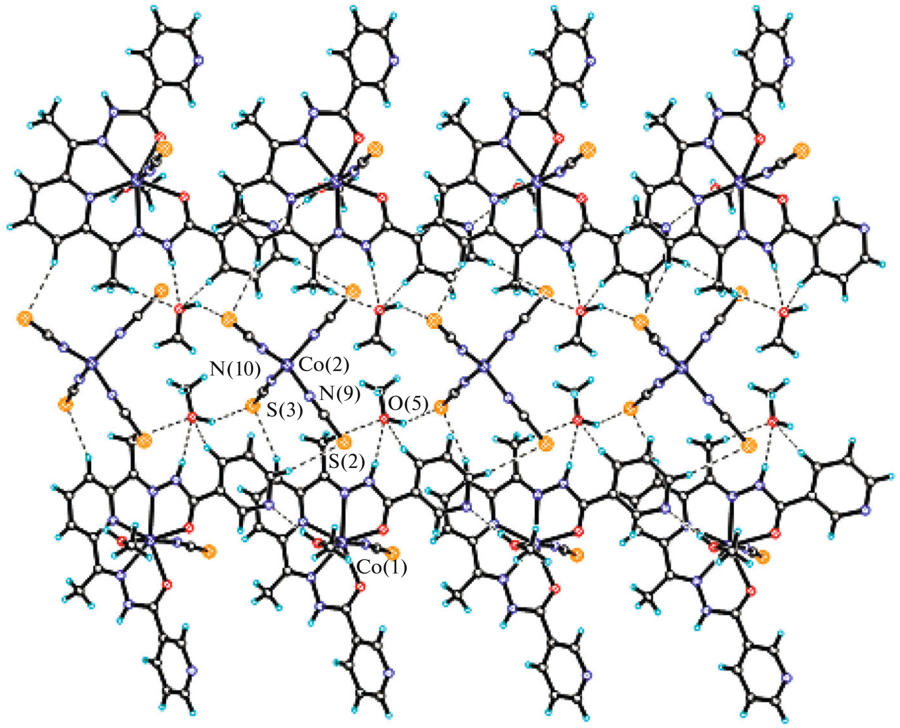

Fig. 12. Ribbons of the complex cations $[Co(H_2L^2)(NCS)CH_3OH]^+$ and anions $[Co(NCS)_4]^{2-}$ stabilized by methanol molecules in compound **VII**.

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REFERENCES

1. Davis, M.B., *Coord. Chem. Rev.*, 1997, vol. 164, p. 27.
2. Smith, D.R., *Coord. Chem. Rev.,* 1998, vol. 172, p. 457.
3. Radecka-Paryzek, W. and Gdaniec, M., *Polyhedron*, 1997, vol. 16, no. 20, p. 3681.
4. Campbell, M.J.M., *Coord. Chem. Rev.*, 1975, vol. 15, nos. 2–3, p. 279.
5. Williams, D.R., *Chem. Rev.*, 1972, vol. 72, p. 203.
6. Furst, A. and Haro, R.T., *Progr. Exp. Tumor Res.*, 1969, vol. 12, p. 102.
7. Sharma, R.P., Kothari, A.K., and Sharma, N.K., *Indian J. Derm. Vener. Lepr.*, 1995, vol. 61, p. 26.
8. Mazza, P., Orcesi, M., Pelizzi, C., et al., *J. Inorg. Biochem.*, 1992, vol. 48, p. 251.
9. Allen, F.H., *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, vol. 58, nos. 3–1, p. 380.
10. Palenik, G.J. and Wester, D.W., *Inorg. Chem.*, 1978, vol. 17, no. 4, p. 864.
11. Carcelli, M., Ianelli, S., Pelagatti, P., and Pelizzi, G., *Inorg. Chim. Acta*, 1999, vol. 292, p. 121.
12. Qin, S.-N., Chen, Z.-L., Liu, D.-Ch., et al., *Transition Met. Chem.*, 2011, vol. 36, p. 369.
13. Palenik, G.J., Wester, D.W., Rychlewska, U., and Palenik, R.C., *Inorg. Chem.*, 1976, vol. 15, no. 8, p. 1814.
14. Gudasi, K.B., Patil, S.A., Vadavi, R.S., et al., *Inorg. Chim. Acta*, 2006, vol. 359, no. 10, p. 3229.
15. Neto, B.A.D., Viana, B.F.L., Rodrigues, Th.S., et al., *Dalton Trans.*, 2013, vol. 42, p. 11497.
16. Constable, E.C., in *Comprehensive Supramolecular Chemistry*, Sauvage, J.-P., Ed., Oxford: Elsevier, 1996, vol. 9, p. 213.
17. Konar, S., Jana, A., Das, K., et al., *Polyhedron*, 2011, vol. 30, no. 17, p. 2801.
18. Mangia, A., Pelizzi, C., and Pelizzi, G., *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1974, vol. 30, p. 2146.
19. Ianelli, S., Minardi, G., Pelizzi, C., et al., *J. Chem. Soc., Dalton Trans.*, 1991, p. 2113.
20. Bonardi, A., Merlo, C., Pelizzi, C., et al., *J. Chem. Soc., Dalton Trans.*, 1991, p. 1063.
21. Naskar, S., Corbella, M., Blake, A.J., and Chattopadhyay, Sh.K., *Dalton Trans.*, 2007, vol. 11, p. 1150.
22. Plutenko, M.V., Moroz, Y.S., Sliva, T.Yu., et al., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2008, vol. 64, p. m137.
23. Bonardi, A., Ianelli, S., Pelizzi, C., et al., *Inorg. Chim. Acta*, 1995, vol. 232, nos. 1–2, p. 211.
24. Batchelor, L.J., Sangalli, M., Guillot, R.G., et al., *Inorg. Chem.*, 2011, vol. 50, p. 12045.
25. Sessoli, R., Tsai, H.L., Schake, A.R., et al., *J. Am. Chem. Soc.*, 1993, vol. 115, p. 1804.

26. Bottari, B., Maccari, R., Monforte, F., et al., *Bioorg. Med. Chem.*, 2001, vol. 9, p. 2203.
27. Bourosh, P., Bulkhak, I., Myrzak, A.I., et al., *Koord. Khim.*, 2016, vol. 42, no. 3, p. 137.
28. Bulhac, I., Deseatnic-Ciloci, A., Bourosh, P., et al., *Chem. J. Mold.*, 2016, vol. 11, no. 1, p. 39.
29. *CrysAlis RED, O. D. L. Version 1.171.34.76*, 2003.
30. Sheldrick, G., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, no. 1, p. 112.
31. Casas, J.S., Garcia-Tasende, M.S., and Sordo, J., *Coord. Chem. Rev.*, 2000, vol. 209, p. 197.
32. Deroche, A., Morgenstern-Badarau, I., Cesario, M., et al., *J. Am. Chem. Soc.*, 1996, vol. 118, p. 4567.
33. Lorenzini, C., Pelizzi, C., Pelizzi, G., and Predieri, G., *J. Chem. Soc., Dalton Trans.*, 1983, p. 2155.
34. Lorenzini, C., Pelizzi, C., Pelizzi, G., and Predieri, G., *J. Chem. Soc., Dalton Trans.*, 1983, p. 721.
35. Bis, J.A. and Zaworotko, M.J., *Cryst. Growth Des.*, 2005, vol. 5, no. 3, p. 1169.
36. Cowan, J.A., Howard, J.A.K., McIntyre, G.J., et al., *Acta Crystallogr., Sect. B: Struct. Sci.*, 2003, vol. 59, p. 794.
37. Bu, X.H., Du, M., Zhang, L., et al., *Inorg. Chim. Acta*, 2000, vol. 308, p. 143.
38. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compound*s, Wiley, 1997.
39. Nakanisi, K., *Infrared Absorption Spectroscopy*, San-Francisco: Holden Day, 1962.

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