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Coordination Polymer 4,4,10,10-Tetramethyl-1,3,7,9-Tetraazaspiro[5.5]undecane-2,8-Dione with Cobalt(II) Nitrate: Synthesis and Molecular Structure

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Abstract—The coordination polymer of cobalt(II) nitrate with bicyclic bis(urea), 4,4,10,10-tetramethyl-1,3,7,9-tetraazaspiro[5.5]undecane-2,8-dione (Sk) $\{[Co(C_{11}H_{20}N_4O_2)_2(H_2O), Co(C_{11}H_{20}N_4O_2)_2(H_2O)_2]^{4+}(NO_3^-)_4\}_n$ (**I**), is synthesized for the first time, and its atomic structure is determined (CIF file CCDC no. 925792). The crystals of compound **I** are monoclinic: space group $P2/c$, a = 26.1284(6), b = 7.1763(2), c = 17.1825(5) Å, β = 105.042(3)°, V = 3111.43(15) Å^3, ρ_{calcd} = 1.474 g/cm^3, Z = 2. The powder X-ray pattern at 293 K is refined using the Rietveld method to confirm the single-phase character of the obtained sample of powdered compound **I**: a = 26.1456(9), b = 7.1810(4), c = 17.1997(11) Å, β = 105.016(3)°, V = 3119.0(3) Å^3. The content of the major phase of compound **I** in the sample is 100 ± 1%, and impurity phases are absent. The crystal of compound **I** contains two types of chains oriented along the crystallographic direction [001] with similar structures but differed in the coordination numbers of the cobalt atoms. The Co(1) atom has a coordination number of 5 (trigonal bipyramid), and the coordination number of the Co(2) atom is 6 (octahedron). The nitrate anions are uncoordinated.

Keywords: cobalt(II), bicyclic bis(urea), tetraazaspiro[5.5]undecane, coordination polymer, structure, X-ray diffraction analysis

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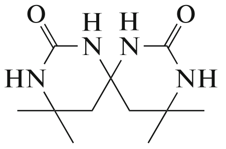
INTRODUCTION

Coordination polymers with ligands of the class of cyclic spirobis(ureas) of the undecane series are poorly studied at the moment. One of these ligands is 4,4,10,10-tetramethyl-1,3,7,9-tetraazaspiro[5.5]undecane-2,8-dione ($C_{11}H_{20}N_4O_2$, Sk).



This ligand (precursor of urea) has a series of valuable biological properties [1–5]: low toxicity (LD_{50} = 3000 mg/kg), membranotropic ability, and the ability to penetrate and accumulate in cytoplasm of mice and human leucosis cells of the lines L1210 and CEM-T4. The ligand also favors an increase in the amount of protein and a decrease in the starchiness in oats grain. The efficiency was proved for the application of some coordination compounds of Sk as stimulators of rhizogenesis in cereals [6]. The efficiency of their application as growth and development stimulators in sheep breeding was shown [7].

The following coordination polymers with Sk have previously been synthesized and described: $\{[Zn(C_{11}H_{20}N_4O_2)Cl_2]\}_n$ (CCDC 877812) [8], $\{[Cd(C_{11}H_{20}N_4O_2)(H_2O)(NO_3)_2]\}_n$ (CCDC 903387) [9], $\{[UO_2(C_{11}H_{20}N_4O_2)(NO_3)_2] \cdot 2H_2O\}_n$ (CCDC 876539) [10], $\{[Mn(C_{11}H_{20}N_4O_2)_2(H_2O)_2]^{2+}(NO_3^-)_2\}_n$ (CCDC 876570) [11], $\{[Cu(C_{11}H_{20}N_4O_2)_2(H_2O)]^{2+}(NO_3^-)_2\}_n$ (CCDC 903386) [12], and $\{[Sc_2(C_{11}H_{20}N_4O_2)_3(H_2O)_6]^{6+}(NO_3^-)_6\}_n$ (CCDC 925791) [13].

Therefore, the synthesis and study of the structures of coordination polymers of this ligand as a hard Lewis base of d metals would clarify the chemistry of its interaction with metal ions of various subgroups of the system of chemical elements.

The purpose of the present work is to synthesize the coordination polymer of cobalt(II) nitrate (hard Lewis acid) with Sk and water molecules,

$\{[Co(C_{11}H_{20}N_4O_2)_2(H_2O),\ Co(C_{11}H_{20}N_4O_2)_2(H_2O)_2]^{4+}\text{-}\left(NO_3^-\right)_4\}_n$ (**I**), and to determine its crystal structure.

EXPERIMENTAL

The following reagents were used: $Co(NO_3)_2 \cdot 6H_2O$ (reagent grade), Sk obtained according to known procedures [14, 15], and acetone (special purity grade).

Synthesis of compound I. A weighed sample of cobalt(II) nitrate hexahydrate (4.8 g, 0.0165 mol) was dissolved in acetone (20 mL), Sk (5.16 g, 0.02 mol) was added, and the mixture was magnetically stirred for 5–10 min. The obtained solution was filtered, kept for several hours for evaporation to 1/3 of the solvent, and then closed and left to stay to form crystals. The formed violet-blue crystals were filtered off, washed with acetone, and dried in air. The yield based on the ligand was ~94%. Complex **I** was stable in air.

For $C_{44}H_{86}N_{20}O_{23}Co_2$

anal. calcd., %:	C, 38.26;	H, 6.28;	N, 20.28.
Found, %:	C, 38.24;	H, 6.25;	N, 20.27.

Elemental analysis of compound **I** was carried out on an EA-3000 analyzer (EuroVector). The IR spectra of ligand Sk and synthesized complex **I** were recorded in KBr pellets on a SPECTRUM ONE FT-IR spectrophotometer (PerkinElmer) in a range of 400–4000 cm^{-1}.

X-ray diffraction analysis of compound **I** was performed on an Xcalibur 3 automated four-circle diffractometer. The structure was solved by a direct method using the SHELX-97 program package [16]. The positions of hydrogen atoms were calculated geometrically and refined by the riding model with $U_{iso} = nU_{eq}$ of the bearing atom ($n = 1.5$ for the atoms of water and methyl groups, and $n = 1.2$ for other hydrogen atoms). The structure was solved by full-matrix least squares in the anisotropic approximation for nonhydrogen atoms on F^2.

The main experimental characteristics and the unit cell parameters are presented in Table 1. Selected bond lengths and bond angles are listed in Table 2.

The X-ray diffraction results for complex **I** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC 925792; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Powder X-ray analysis for the synthesized sample of compound **I** was carried out on a Siemens D500 diffractometer (Cu radiation, graphite monochromator on the secondary beam). To confirm the purity and single-phase character of the synthesized sample, the powder X-ray pattern was refined by the Rietveld method using the single-crystal X-ray diffraction results as an initial model for the FullProf program [17]. After trituration, the sample of complex **I** was placed in a glass cell with the working volume 2 × 1 × 0.1 cm^3 for the detection of the X-ray pattern.

RESULTS AND DISCUSSION

The following characteristic bands are observed in the IR spectra of complex I and ligand Sk (ν, cm^{-1}): 3416, 3335 (HOH); 3293, 3218, 3075 (NH); 2991, 2978, 2932 (CH_3, CH_2); 1653 (C=O, amide-I); 1418, 1367 (C–N) for Sk; 3390 (HOH); 3294, 3257, 3100 (NH); 3005, 2960, 2926 (CH_3, CH_2); 1644, 1636 (C=O, amide-I); 1492, 1473, 1367 (C–N); 1385, 1046, 823 for I (δ_γ is out-of-plane bending vibration), 706 (δ_ρ is planar bending vibration) $\left(NO_3^-\right)$.

A comparison of the stretching vibrations C=O amide-I for Sk and I shows the splitting and shift to the long-wavelength range by 9 and 17 cm^{-1}, respectively, because of the nonequivalent coordination of the Sk molecules by the cobalt atoms. The shift of ν_{s+as}(NH) to the short-wavelength range from 3293, 3218, and 3075 to 3294, 3257, and 3100 cm^{-1} is also observed, which is characteristic of amino groups when the carbonyl group of the carbamide fragment is coordinated [18]. The spectrum of compound **I** exhibits absorption bands of coordinated water and a set of absorption bands of the heterocyclic rings of Sk. The free nitrate anion being a planar ion (point group D_3) has four main vibration frequencies of symmetric vibrations ν_s(NO) (1050–1060 cm^{-1}), nonsymmetric doubly degenerate stretching vibrations ν_e(NO) (1350–1400 cm^{-1}), and two frequencies of bending vibrations $\delta(NO_3)$ (810–840 and 710–730 cm^{-1}). Only three frequencies are usually active in the IR spectrum: ν_e(NO) and two $\delta(NO_3)$ [19]. Upon the coordination of the nitrate anion, its symmetry can decrease to C_s and C_{2v}. As a result, six intense lines appear in the following ranges of the IR spectrum (cm^{-1}): 970–1040 (full-symmetry vibration), 1550–1410 and 1290–1250 (stretching antisymmetric vibrations appeared as two intense lines), 830–800 (nonplanar vibration), and 780–700 and ~680 (planar bending vibration appeared as two bands) [20]. The IR spectrum of compound **I** exhibits lines at 1385, 1046, 823, and 706 cm^{-1}. This indicates that the nitrate anions are uncoordinated and arranged behind the external sphere of the polymer.

According to the X-ray diffraction data, compound **I** is coordination crystalline hydrate of the polymer. The crystal contains two types of chains in which the cobalt atoms are coordinated by the oxygen atoms of the carbonyl groups of Sk and by the water molecules (Fig. 1). The both chains are oriented along the crystallographic direction [001], and they have similar structures but differ in the coordination num-

Table 1. Main crystallographic experimental data for the structure of compound **I**

Parameter	Value
FW	1381.19
Crystal system	Monoclinic
Space group	$P2/c$
Cell parameters:	
a, Å	26.1284(6)
b, Å	7.1763(2)
c, Å	17.1825(5)
β, deg	105.042(3)
V, Å^3	3111.43(15)
Z	2
ρ_{calcd}, g/cm^3	1.474
$\mu(\text{Mo}K_\alpha)$, mm^{-1}	0.625
$F(000)$	1456
Crystal size, mm	0.07 × 0.14 × 0.27
Range of θ angles, deg	2.84–28.96
Ranges of reflection indices	$-35 \le h \le 33$, $-9 \le k \le 9$, $-23 \le l \le 20$
Number of measured reflections	27988
Number of independent reflections (R_{int})	7392 (0.0464)
Number of reflections with $I > 2\sigma(I)$	4797
Number of refined parameters	415
R factor ($I > 2\sigma(I)$)	$R_1 = 0.0477$, $wR_2 = 0.0949$
R factor over all reflections	$R_1 = 0.0907$, $wR_2 = 0.1098$
GOOF for F^2	1.022
$\Delta\rho_{\max}/\Delta\rho_{\min}$, e Å^{-3}	0.328/–0.377

Table 2. Selected bond lengths (Å) and bond angles (deg) in the structure of compound **I***

Bond	d, Å	Angle	ω, deg	Angle	ω, deg
Co(1)–O(1)	2.0918(15)	O(1)Co(1)O(1)^{i}	173.92(9)	O(4)^{vi}Co(2)O(3)	93.49(6)
Co(1)–O(2)^{ii}	1.9787(16)	O(2)^{ii}Co(1)O(1)	91.62(6)	O(4)^{v}Co(2)O(4)^{vi}	92.64(10)
Co(1)–O(5)	1.956(3)	O(2)^{iii}Co(1)O(1)	91.89(6)	O(4)^{v}Co(2)O(6*w*)	91.13(7)
Co(2)–O(3)	2.1278(15)	O(2)^{iii}Co(1)O(2)^{ii}	109.57(12)	O(4)^{v}Co(2)O(6*w*)^{iv}	175.09(7)
Co(2)–O(4)^{v}	2.0561(16)	O(5*w*)Co(1)O(1)	86.96(5)	O(4)^{vi}Co(2)O(6*w*)^{iv}	91.13(7)
Co(2)–O(6)^{iv}	2.1033(17)	O(5*w*)Co(1)O(2)^{iii}	125.22(6)	O(6*w*)Co(2)O(3)	83.22(6)
		O(3)^{iv}Co(2)O(3)	171.85(9)	O(6*w*)Co(2)O(3)^{iv}	90.77(6)
		O(4)^{v}Co(2)O(3)	92.13(6)	O(6*w*)Co(2)O(6*w*)^{iv}	85.29(10)

* Symmetry procedure: ^{i} $1 - x, +y, 1/2 - z$; ^{ii} $1 - x, -y, 1 - z$; ^{iii} $+x, -y, -1/2 + z$; ^{iv} $-x, +y, 3/2 + z$; ^{v} $-x, 1 - y, 1 - z$; ^{vi} $+x, 1 - y, 1/2 + z$.

bers of the cobalt atoms. The Co(1) atom is coordinated by four oxygen atoms O(1), O(1)^{i}, O(2)^{ii}, and O(2)^{iii} (^{i} $1 - x, y, 1/2 - z$; ^{ii} $1 - x, -y, 1 - z$; ^{iii} $x, -y, -1/2 + z$) of four Sk molecules and by the O(5*w*) atom (Fig. 2). The coordination polyhedron of Co(1) is a trigonal bipyramid in which the O(2)^{ii}, O(2)^{iii}, and O(5*w*) atoms are located in the base, whereas O(1) and O(1)^{i} are located in the axial vertices. The OCoO angles between the equatorial oxygen atoms are 125.21(6)°–109.57(12)°, and those between the axial and equatorial oxygen atoms are 86.96(5)°–91.89(6)°. The Co(2) atom is coordinated by four oxygen atoms of four Sk molecules (O(3), O(3)^{iv}, O(4)^{v}, and O(4)^{vi} ^{iv} $-x, y, 3/2 - z$; ^{v} $-x, 1 - y, 1 - z$; ^{vi} $x, 1 - y, 1/2 + z$) and two O(6*w*) and O(6*w*)^{iv} atoms of the water molecules (Fig. 3). The coordination polyhedron of the Co(2) atom is an octahedron with OCoO angles of 83.22(6)°–93.49(6)°. The nitrate anions are beyond the coordination sphere of the cobalt atoms.

Two six-membered heterocycles of the Sk ligand exist in the conformation intermediate between sofa and *twist*-boat with insignificantly twisted fragments C_{spiro}–N–C(=O)–N (torsion angles 7.3(4)°–15.6(3)°) and with the deviation of the $C(H_2)$ and $C(Me_2)$ atoms to opposite sides from the mean plane of other atoms of the cycle by 0.353(4)–0.454(5) and 0.170(5)–0.340(4) Å, respectively. In this conformation, shortened intramolecular contacts H···H 2.07–2.13 Å (a sum of the doubled van der Waals radius of hydrogen of 2.32 Å [21]) are formed between the methylene and methyl groups of different heterocycles of the chain.

Intermolecular hydrogen bonds, including those involving out-of-sphere nitrate anions, are formed in the crystal of compound **I** both inside the polymer chains and between them: N(1)–H(1)···O(7)^{vii} (^{vii} $1 - x, 1 - y, 1 - z$, H···N 2.56 Å, N–H···O 139°), N(1)–H(1)···O(8)^{vii} (H···N 2.17 Å, N–H···O 164°), N(2)–H(2)···O(2)^{iii} (H···N 2.04 Å, N–H···O 150°), N(3)–H(3)···O(1)^{ii} (H···N 2.31 Å, N–H···O 128°), N(4)–H(4)···O(9)^{vi} (H···N 2.13 Å, N–H···O 172°), O(5*w*)–H(5)···O(7)^{i} (H···O 1.83 Å, O–H···O 175°), N(5)–H(5d)···O(11)^{viii} (^{viii} $-x, y, 1/2 - z$, H···N 2.26 Å, N–H···O 166°), N(6)–H(6)···O(4)^{vi} (H···N 2.00 Å, N–H···O 157°), O(6*w*)–H(6d)···O(10)^{ix} (^{ix} $-x, 2 - y, 1 - z$, H···O 1.90 Å, O–H···O 158°), O(6*w*)–H(6e)···O(12)^{x} (^{x} $x, 2 - y, 1/2 + z$, H···O 1.94 Å, O–H···O 174°), N(7)–H(7)···O(3)^{v} (H···N 2.19 Å, N–H···O 134°), and N(8)–H(8)···O(10) (H···N 2.46 Å, N–H···O 156°). As a result, alternating layers containing the Co(1) and Co(2) atoms parallel to the [100] plane are formed in the crystal (Fig. 4).

The results of composition refinement for compound **I** using powder X-ray analysis indicate the absence of impurities. The following lattice parameters were obtained (T = 293 K): a = 26.1456(9), b = 7.1810(4), c = 17.1997(11) Å, β = 105.016(3)°, V =

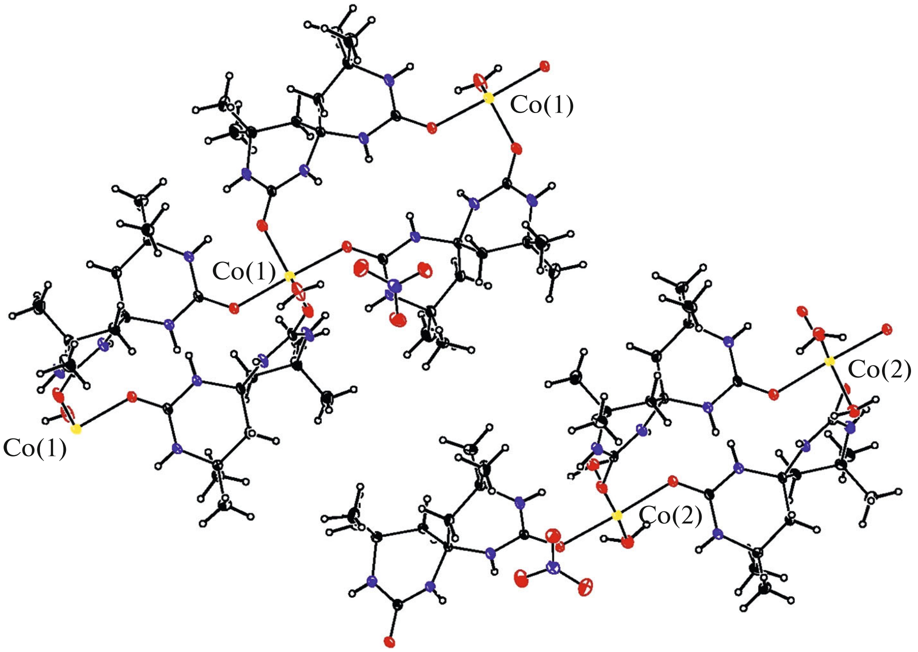


Fig. 1. Fragment of the atomic structure of compound **I**. Thermal ellipsoids of the non-hydrogen atoms are shown at the 50% probability level.

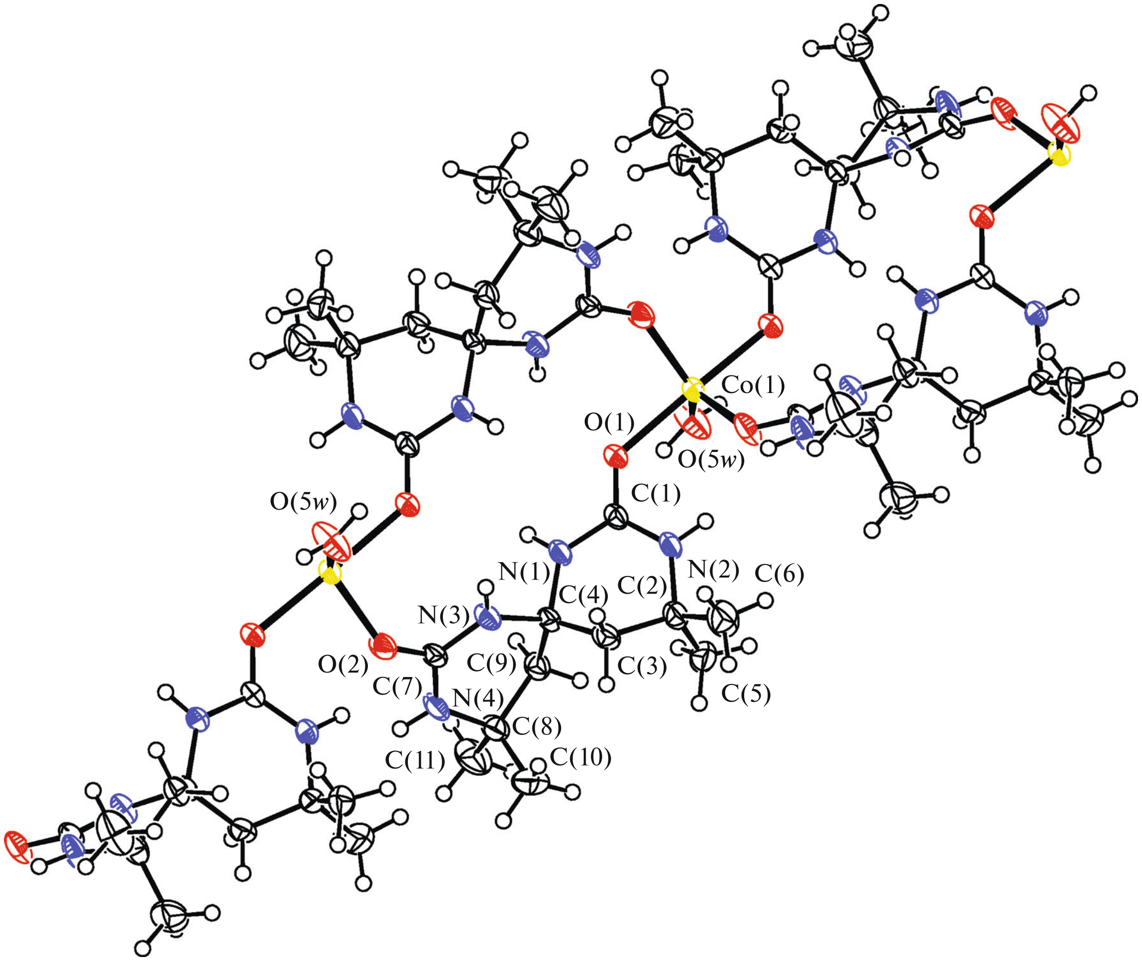


Fig. 2. Fragment of the coordination polymer in the crystal of compound **I** with the coordination number of cobalt equal to 5.

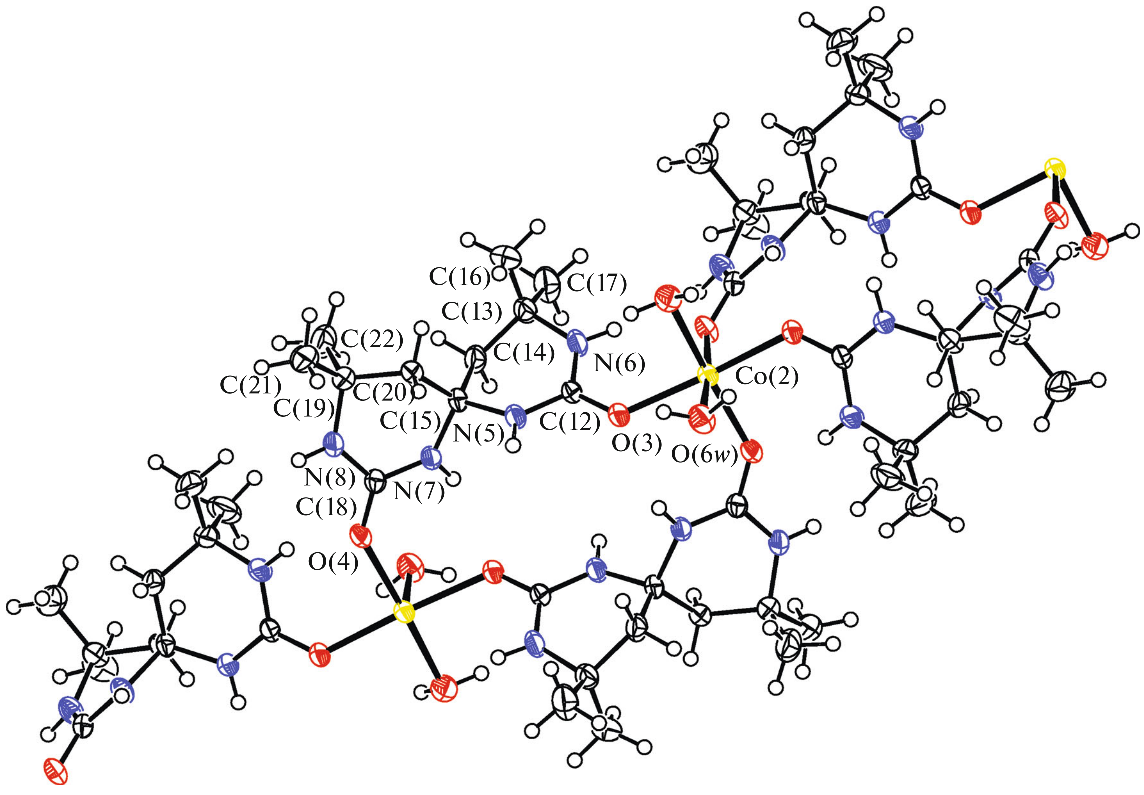


Fig. 3. Fragment of the coordination polymer in the crystal of compound **I** with the coordination number of cobalt equal to 6.

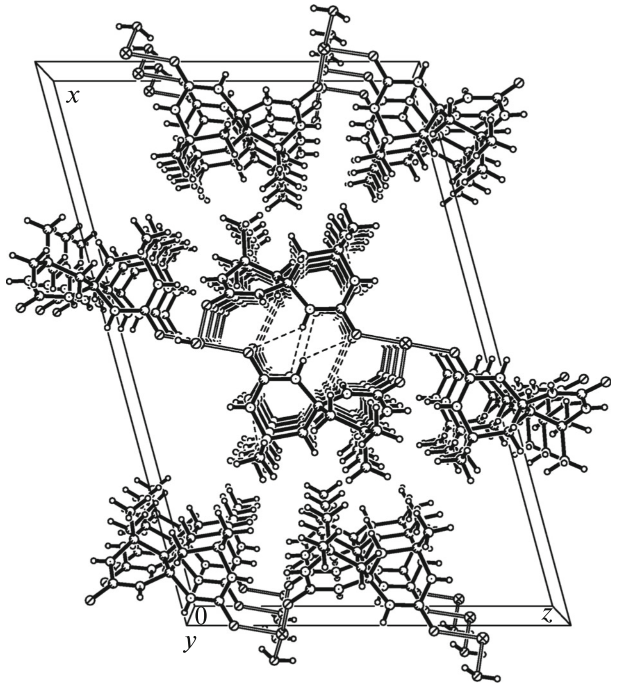


Fig. 4. Crystal packing fragment of compound **I** along the direction [001].

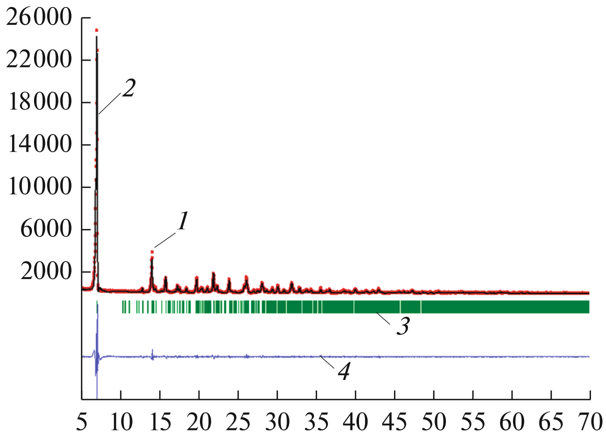


Fig. 5. Results of the refinement of the powder X-ray pattern of the sample of compound **I** using the Rietveld method: (*1*) experimental X-ray pattern, (*2*) calculated X-ray pattern, (*3*) positions of lines, and (*4*) differential curve $I_{\text{exp}}-I_{\text{calcd}}$.

3119.0(3) Å^3. The average size of crystallites in the powdered sample is 89 nm, and microstrains are nearly absent. All lines observed in the X-ray pattern correspond to the major phase, and no impurity lines are observed (Fig. 5). The content of the major phase in the sample is 100 ± 1%.

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REFERENCES

1. Mahbub, A. and Fazal Khalid, L., *Indian J. Experim. Biol.*, 1992, vol. 30, p. 1181.
2. Starikovich, L.S., Dudok, E.P., Sibirnaya, N.A., et al., *Medich. Khim.,* 2009, vol. 11, no. 1, p. 57.
3. Starikovich, L.S., Starikovich, M.A., Rechitskii, A.N., et al., *Biologichni studiï— Studia biologica*, 2009, vol. 3, no. 2, p. 93.
4. Musatov, A.G., Semyashkina, A.A., and Dashevskii, R.F., *Khranenie i Pererabotka Zerna*, 2007, no. 7, p. 38.
5. Gurevich A.S., Titov V.A., Babaeva E.V., et al., *Introduktsiya, akklimatizatsiya i kul'tivatsiya rastenii*: *Sb. nauch. tr.*, Kaliningrad: Kaliningrad Inst., 1998, p. 30.
6. Netreba E.E., *Chornomorskii Botanichnii Zh.*, 2013, vol. 9, no. 2, p. 203.
7. Kozichar, M.V., Methods for increasing the wool output of Askania fine-wool sheep, *Doctoral (Agriculture) Dissertation*, Kherson, 1998.
8. Netreba, E.E. and Fedorenko, A.M., *Uchenye Zapiski Tavricheskogo Nats. Un-ta im. V.I. Vernadskogo., Ser. Biol., Khim.*, 2012, vol. 25(64), no. 2, p. 252.
9. Netreba, E.E., *Ukr. Khim. Zh.*, 2013, vol. 79, no. 2, p. 88.
10. Netreba, E.E. and Fedorenko, A.M., *Russ. J. Coord. Chem.*, 2013, vol. 39, no. 2, p. 214.
11. Netreba, E.E. and Fedorenko, A.M.*, J. Struct. Chem.,* 2013, vol. 54, no. 2, p. 373.
12. Netreba, E.E., *J. Struct. Chem.,* 2013, vol. 54, no. 5, p. 944.
13. Netreba, E.E., *Russ. J. Inorg. Chem.*, 2014, vol. 59, no. 4, p. 315.
14. Netreba, E.E., Fedorenko, A.M., and Pavlov, A.A., *Nauch. Visnik Uzhgorod. Un-tu. Ser. Khim.*, 2011, no. 1(25), p. 107.
15. Netreba, E.E. and Papayanina, E.S., *J. Struct. Chem.*, 2014, vol. 55, no. 4, p. 722.
16. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
17. Rodriguez-Carvajal, J. and Roisnel, T., *FullProf 98 and WinPLOTR: New Windows 95/NT Applications for Diffraction,* Commission for Powder Diffraction, International Union of Crystallography, Newsletter no. 20, 1998.
18. Grigor'ev, A.I., *Vvedenie v kolebatel'nuyu spektroskopiyu neorganicheskikh soedinenii* (Introduction to Vibrational Spectroscopy of Inorganic Compounds), Leningrad: LGT*,* 1977.
19. Nakamoto, K., *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986.
20. Kharitonov, E.Yu. *Analiticheskaya khimiya. Analitika. Kn. 1.* (Analytical Chemicstry. Analytics. Book 1)*,* Leningrad: Vyssh. Shkola, 2003.
21. Zefirov, E.V. and Zorkii, O.L., *Usp. Khim.,* 1989*,* vol. 58*,* no. 5, p. 713.

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