

УДК 54–386:547.234

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SYNTHESIS AND STRUCTURE OF COORDINATION COMPOUND OF COBALT(II) 5-SULFOSALICYLATE WITH BENZOHYDRAZIDE

The new 5-sulfosalicylato cobalt coordination compound $[\text{Co}(\text{Bhz})_3]_3(\text{HSSal})_3 \cdot 7.5\text{H}_2\text{O}$ (where Bhz – benzohydrazide, HSSal^{2-} – 5-sulfosalicylate anion) has been synthesized and studied by elemental analysis, IR and diffuse reflectance spectroscopy and single-crystal X-ray diffraction.

Keywords: Benzohydrazide, 5-Sulfosalicylate, crystal structure, IR spectra

Carboxylic acid hydrazides display a wide variety of biological activities, such as antibacterial, antifungal, anthelmintic, anticonvulsant, and antitumor action [1]. Data on the structures of cobalt(II) complexes with benzohydrazide (Bhz) are relatively scarce. Previously, we synthesized some cobalt(II) benzohydrazide complexes with various anions and stated that their compositions and structures to depend on the anion of the salt taken for synthesis.

For example, for malonate, a 1:1 compound $[\text{Co}(\text{Bhz})(\text{Mal})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ is formed. Its crystals are built from $[\text{Co}(\text{Bhz})(\text{Mal})(\text{H}_2\text{O})_2]$ complex molecules and molecules of crystallization water. The Co^{2+} atom is in octahedral environment of two O atoms of the malonate ligand, N and O atoms of benzohydrazide, and two water molecules [1].

Cobalt(II) valerate and benzoate give 1:3 complexes with benzohydrazide [2], in complex of cobalt(II) phthalate this ratio is 1: 2 [3].

For maleate the composition corresponds to the formula $[\text{Co}(\text{Bhz})_3](\text{Maleate}) \cdot 4\text{H}_2\text{O}$. Its structural units are complex cations $[\text{Co}(\text{Bhz})_3]^{2+}$, maleate anions Maleate^{2-} , and crystallized water molecules [4].

Previously we have synthesized coordination compound $[\text{Co}(\text{Bhz})_3](\text{OH})\text{Cl}(\text{H}_3\text{Ssal}) \cdot \text{H}_2\text{O}$. Its structural units are $\text{Co}(\text{Bhz})_3^{2+}$ cations, OH^- and Cl^- anions, sulfosalicylic acid molecules H_3Ssal , and an H_2O molecule [5].

The aim of this work was synthesis and studying the structure of cobalt(II) 5-sulfosalicylate coordination compound with benzohydrazide.

MATERIALS AND RESEARCH METHODS

Cobalt(II) nitrate, 5-sulfosalicylic acid and benzohydrazide were of analytical grade. Carbon, hydrogen and nitrogen contents for the coordination compound were carried out on a LECO Tru Spec CHN automatic elemental analyzer. The content of cobalt was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Perkin-Elmer Optima 8000 analyser. IR spectra were recorded on a Perkin-Elmer SPECTRUM BX II FT-IR SYSTEM spectrometer at the range of $4000\text{--}400\text{ cm}^{-1}$ at room

temperature in KBr pellets. The diffuse reflection spectrum was recorded on a Lambda9 (Perkin-Elmer) spectrophotometer with MgO (100βMgO) as the standard.

Synthesis of $[\text{Co}(\text{Bhz})_3]_3(\text{HSSal})_3 \cdot 7.5\text{H}_2\text{O}$. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.91 g, 0.01 mol) was dissolved in water (5 mL), and NaOH (0.8 g, 0.02 mol) was added to the obtained solution. A formed precipitate of cobalt(II) hydroxide was filtered off, thoroughly washed with water, and transferred to a beaker with 5-sulfosalicylic acid (2.18 g, 0.01 mol). Water was added to the mixture to the complete dissolution of the cobalt(II) 5-sulfosalicylate. The solution (30 ml) of benzohydrazide (4.08 g, 0.03 mol) was added to the obtained solution, and the resulting mixture was left to stay for precipitation. The precipitate formed was filtered off, washed with water several times, and dried in a CaCl_2 desiccator to a constant weight.

After dissolving under boiling in water/ethanol/*n*-propanol (1: 1: 1) mixture, the red crystals suitable for single crystal X-ray structure determination were grown in 3 days by slow evaporation of the solvents at room temperature. Yield: 5.8 g (78%).

Anal. Calc. (%) for $\text{C}_{84}\text{H}_{84}\text{Co}_3\text{N}_{18}\text{O}_{27}\text{S}_3 \cdot 7.5\text{H}_2\text{O}$: C 46.15, H 3.85, Co 8.10, N 11.54; found (%): C46.19, H 3.70, Co 7.97, N11.39.

X-ray crystallography

Diffraction data for coordination compound were collected on a Rigaku XtaLAB AFC11 diffractometer using CuK_α radiation ($\lambda = 1.54184 \text{ \AA}$).

The collected diffraction data for $[\text{Co}(\text{Bhz})_3]_3(\text{HSSal})_3 \cdot 7.5\text{H}_2\text{O}$ (**1**) were processed with the CrysAlis PRO program [6]. The structure was solved by ShelXS and refined by the least-squares method on F^2 by ShelXL software with the following graphical user interface of OLEX² [7, 8]. Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. The hydrogen atoms were placed on geometrically calculated positions and refined as riding atoms with relative isotropic displacement parameters. Two phenyl rings of each of three crystallographically independent $[\text{Co}(\text{Bhz})_3]^{2+}$ cations are disordered over two sites with an occupancy ratio of 0.87(7): 0.13(7) (C12–C17), 0.744(15): 0.256(15) (C23–C27), 0.557(5): 0.443(5) (C42–C47), 0.612(6): 0.388(6) (C52–C57), 0.766(11): 0.251(14) (C73–C77) and 0.45(5): 0.234(11) (C83–C87), correspondingly. The crystal parameters, data collection, and refinement details are summarized in Table 1.

Table 1

Selected crystal data and structure-refinement parameters of **1**

Empirical formula	$\text{C}_{84}\text{H}_{84}\text{Co}_3\text{N}_{18}\text{O}_{27}\text{S}_3 \cdot 7.5\text{H}_2\text{O}$
Formula weight	2185.78
Temperature, K	150
Wavelength	CuK_α
Crystal system, space group	Triclinic, $P \bar{1}$
Unit cell dimensions, Å	
a , Å ; α , $^\circ$	15.91460(10); 74.5040(10)

Continuing the table 1

b , Å; β , °	17.72530(10); 73.3710(10)
c , Å; γ , °	19.17190(10); 88.0460(10)
V , Å ³	4988.41(6)
Z	2
Calculated density, g/cm ³	1.455
Absorption coeff., mm ⁻¹	5.225
F(000)	2268
Crystal size, mm	0.15 × 0.22 × 0.25
Theta range for data collection, °	3.8–68.5
Measured reflections	111977
Used in refinement	18078
Refined parameters	1487
$R[F^2 > 2\sigma(F^2)]$	0.0541
$wR(F^2)$	0.1821
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e/Å ³)	1.898, -0.306

RESULTS AND DISCUSSION

Crystal structure

Compound (**1**) crystallizes in the centrosymmetric space group $P-1$, with three Co(II) ions, nine Bhz molecules and three HSSal²⁻ anions in the asymmetric unit (Fig. 1). Benzohydrazide (Bhz) molecules are coordinated with the metal ion in a chelate mode through O and N atoms. Each metal ion is surrounded by three Bhz molecules to form [Co(Bhz)₃]²⁺ cations. Cationic [Me(Bhz)₃]²⁺ moiety was previously found in the structure of corresponding NiCl₂, Ni(NO₃)₂ and Ni(HSSal) coordination compounds with benzohydrazide [9–11]. The hydrazide group of Bhz (with the exception of N31—N32—C31—C32 part) is slightly turned relative to the bound with it phenyl ring and corresponding torsion angle N – N—C – C is in the range of 168.4 ÷ 177.3°. The significant disordering of the majority of phenyl ring in [Co(Bhz)₃]₃(HSSal)₃·7.5H₂O (**1**) most probably is caused by presence of small amount of voids (allowing the motion of the phenyl rings), which in the case of undistorted [Ni(Bhz)₃]₃(HSSal)₃·7.5H₂O·0.5(C₂H₅OH) [11] structure are filled by ethanol molecules.

The presence of the deprotonated carboxyl group of sulfosalicylate anion in **1** contributes to the inclusion in the crystal structure of a significant amount of crystallization water molecules, which are involved into the formation of hydrogen-bonded framework (Fig. 2, Table 3, Fig. 3).

Table 2

Selected bond distances (\AA) and angles ($^\circ$) in the structure 1

Bond		Angle	
Co1—N11	2.157(3)	O11—Co1—O21	92.73(9)
Co1—O11	2.071(2)	O11—Co1—O31	92.55(9)
Co1—N21	2.129(3)	O11—Co1—N21	169.14(9)
Co1—O21	2.081(2)	N21—Co1—N31	99.4(1)
Co2—N41	2.130(2)	O41—Co2—O51	89.0(1)
Co2—O41	2.067(2)	O41—Co2—O61	96.74(9)
Co2—N61	2.127(3)	O41—Co2—N61	173.45(9)
Co2—O61	2.084(2)	N41—Co2—N51	100.5(1)
Co3—N71	2.124(2)	O71—Co3—O81	90.76(8)
Co3—O71	2.093(2)	O71—Co3—O91	93.26(8)
Co3—N91	2.166(2)	O81—Co3—N91	172.42(8)
Co3—O91	2.064(2)	N81—Co3—N91	99.88(9)

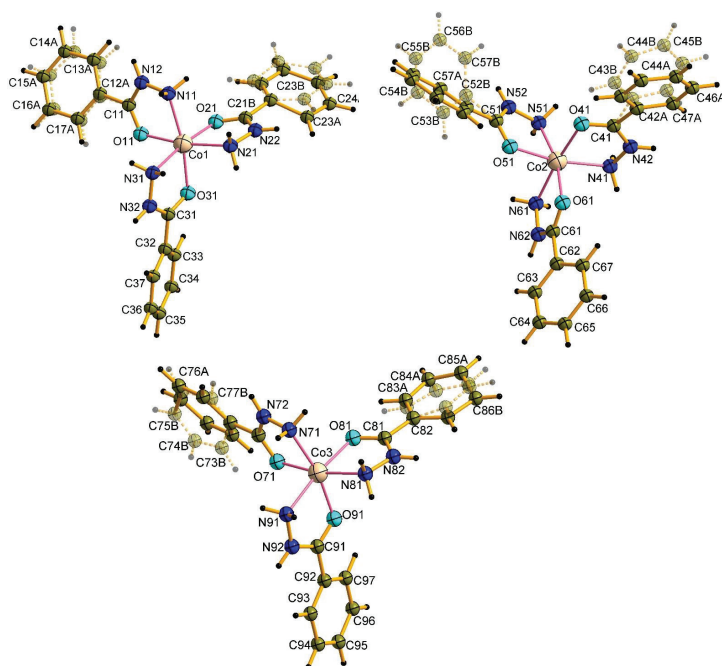
Fig. 1. Crystallographically independent $[\text{Co}(\text{Bhz})_3]^{2+}$ cations in crystal structure 1.

Table 3

Hydrogen-bond geometry (Å, °) for 1

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N11—H11A···O12 0.91		2.21	3.039 (4)	151
N11—H11B···O17 ⁱ	0.91	2.00	2.910 (3)	177
N12—H12···O5	0.88	2.07	2.941 (4)	169
N21—H21A···O14	0.91	1.87	2.755 (4)	163
N21—H21B···O22 ⁱⁱ	0.91	2.25	2.999 (3)	139
N22—H22···O3 ⁱ	0.88	2.08	2.815 (4)	140
N31—H31A···O24 ⁱⁱ	0.91	2.11	2.952 (4)	153
N31—H31B···O35 ⁱ	0.91	2.16	3.064 (4)	175
N41—H41A···O15	0.91	2.05	2.951 (3)	170
N41—H41B···O4	0.91	2.60	3.169 (4)	121
N42—H42···O3	0.88	1.96	2.803 (4)	160
N51—H51A···O34 ⁱⁱⁱ	0.91	1.96	2.816 (3)	156
N51—H51B···O32 ⁱ	0.91	1.93	2.842 (4)	175
N52—H52···O7 ⁱⁱⁱ	0.88	2.25	3.037 (4)	149
N61—H61A···O27	0.91	2.09	2.994 (3)	175
N61—H61B···S31 ⁱ	0.91	2.87	3.591 (2)	138
N61—H61B···O33 ⁱ	0.91	2.02	2.914 (3)	166
N62—H62···O6	0.88	2.04	2.816 (4)	146
N71—H71A···O23 ^{iv}	0.91	2.06	2.908 (3)	155
N71—H71B···O13 ⁱ	0.91	2.01	2.781 (3)	142
N81—H81A···O13 ⁱ	0.91	2.41	3.092 (4)	131
N81—H81A···O2	0.91	2.30	2.943 (4)	128
N81—H81B···O26 ^v	0.91	2.07	2.978 (3)	173
N82—H82···O7 ⁱ	0.88	2.04	2.891 (3)	163
N91—H91A···O23 ^{iv}	0.91	2.51	2.997 (3)	114
N91—H91A···O25 ^v	0.91	2.25	3.025 (3)	142
N91—H91B···O37 ^{vi}	0.91	2.16	3.059 (3)	169
N92—H92···O1 ^{vii}	0.88	1.99	2.823 (3)	159
O17—H17···O16	0.84	1.72	2.474 (4)	148
O27—H27···O26	0.84	1.79	2.518 (3)	144
O37—H37A···O36	0.84	1.80	2.485 (4)	138

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+1, -z$; (iii) $x, y-1, z$; (iv) $x, y, z+1$; (v) $-x+1, -y, -z+1$; (vi) $-x+1, -y+1, -z+2$; (vii) $-x+1, -y, -z+2$.

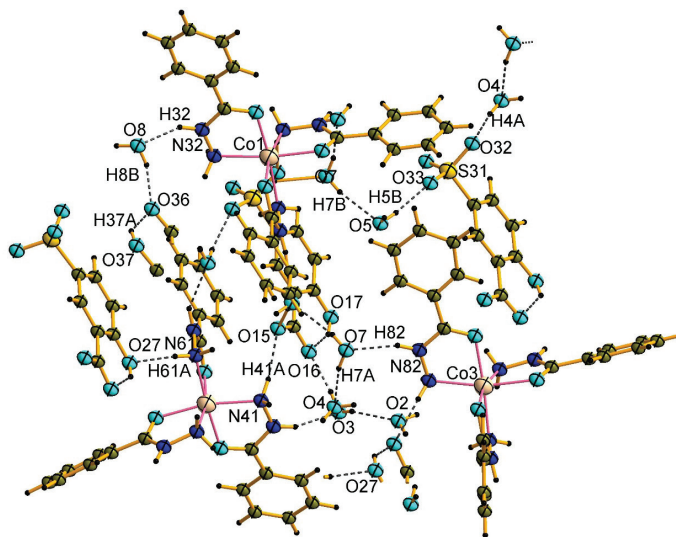


Fig. 2. H-bonded network in crystal structure 1.

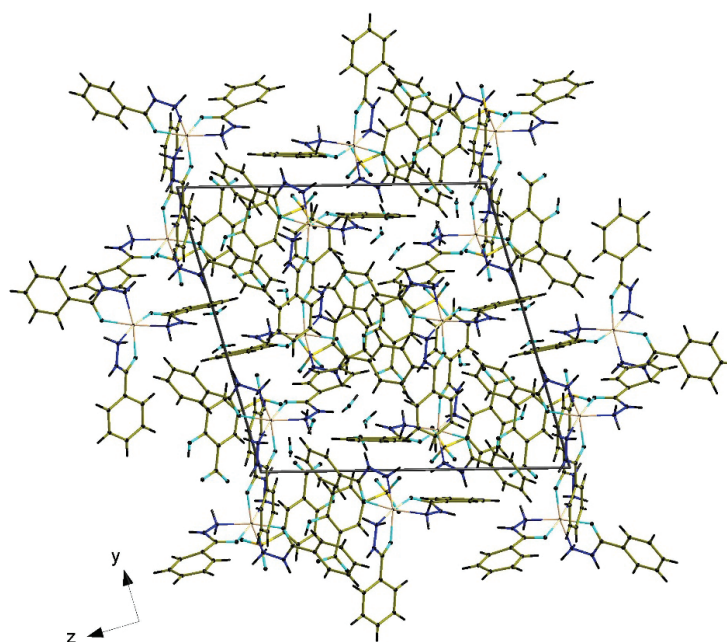


Fig. 3. A view along the *a* axis of the crystal packing of the title compound.

Analysis of the IR spectra of benzohydrazide and coordination compound (Table 4) shows that the IR spectra are in good agreement with the crystallographic data.

Table 4

Wavenumbers (frequencies, cm^{-1}) of absorption band maxima in the IR spectra of benzohydrazide and $[\text{Co}(\text{Bhz})_3]_3(\text{HSSal})_3 \cdot 7.5\text{H}_2\text{O}$

Assignment	Bzh	$[\text{Co}(\text{Bhz})_3]_3(\text{HSSal})_3 \cdot 7.5\text{H}_2\text{O}$
$\nu(\text{NH})$, $\nu(\text{NH}_2)$	3300, 3200, 3049, 3021, 2875	3333, 3256, 3066
$\nu(\text{C}=\text{O})$	1662	1636
$\delta(\text{NH}_2)$	1616	1609
$\nu_{\text{as}}(\text{COO}^-)$		1571
$\nu(\text{C}-\text{C})$		1480
$\nu_{\text{s}}(\text{COO}^-)$		1437
$\omega(\text{NH}_2)$	1350, 1299	1344, 1332
$\nu_{\text{as}}(\text{SO}_2)$		1295, 1238, 1222, 1204
$\nu(\text{CN}) + \nu(\text{N}-\text{N}) + \tau(\text{NH}_2) + \delta(\text{CCH})$	1185, 1155, 1121	1163, 1153, 1124
$\nu_{\text{s}}(\text{SO}_2)$		1078, 1031
$\nu_{\text{ring puls}} + \rho(\text{NH}_2) + \tau(\text{NH}_2)$	920, 885, 803	894, 838, 803
$\rho(\text{CCH}) + \delta(\text{CCH})$	752	785
$\nu(\text{S}-\text{O})$		671
$\delta(\text{CCN}) + \delta(\text{NCO})$	517	552
$\nu(\text{Co}-\text{N})$		440

The band appearing at 1616 cm^{-1} corresponding to the bending vibrations $\delta(\text{NH}_2)$ of benzohydrazide decreases upon complex formation to 1609 cm^{-1} . In the IR spectrum of benzohydrazide, the band with a maximum at 1662 cm^{-1} corresponds to the stretching vibrations of the $\text{C}=\text{O}$ group (amide I). This band shifts to the low frequency region by 26 cm^{-1} as compared to the frequency of uncoordinated benzohydrazide that confirms the participation of the oxygen atom in the cobalt coordination. Peak at 440 cm^{-1} in the complex spectrum was attributed to the $\text{Co}-\text{N}$ stretching vibrations.

Thus, the nature of changes of absorption bands in the IR spectra of coordination compound to bidentate chelating coordination of the benzohydrazide ligand through the oxygen and terminal nitrogen atoms with formation of five-membered chelate ring.

Comparative analysis of the positions and shapes of absorption bands of 5-sulfosalicylate anion in the IR spectrum of synthesized coordination compound shows that there is no band of the stretching vibrations of free $\text{C}=\text{O}$ group, while it shows typical carboxylate stretching bands $\nu_{\text{as}}(\text{COO}^-)$ at 1571 cm^{-1} and $\nu_{\text{s}}(\text{COO}^-)$ at 1437 cm^{-1} , therefore carboxyl group of H_3Ssal was deprotonated. In the spectrum of the complex compound the absorption bands of $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ are overlapped with the bands of stretching vibrations of the $\text{C}-\text{C}$ bonds of the aromatic rings of benzohydrazide

and anion respectively that results in an appreciable increase in their intensity. The peaks of the stretching vibrations of O-H (H_2Ssal^+) of a free carboxylic acid group are absent in complex spectrum, also indicating that both protons are deprotonated. Therefore, complex contains the $HSsal^{2-}$ anions, i.e., the SO_3H and $COOH$ groups are both deprotonated. The value of $\Delta\nu(COO^-) = \nu_{as}(COO^-) - \nu_s(COO^-)$ equal to 134 cm^{-1} indicates that the carboxylate group remains free in complexes [12]. Therefore, $HSsal^{2-}$ anions are outer sphere in cobalt complex.

The diffuse reflectance data for the complex (nm): $465 (^4T_{1g}(F) \rightarrow ^4T_{1g}(P))$, $1542 (^4T_{1g}(F) \rightarrow ^4T_{1g}(P))$ for cobalt(II) coordination compound are consistent with its octahedral structure [13].

Thus, the composition and structure of the coordination compound of cobalt(II) 5-sulfosalicylate with benzohydrazide are similar to those for the analogous nickel(II) compound [11].

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Стаття надійшла до редакції 14.03.2023

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СИНТЕЗ ТА БУДОВА КООРДИНАЦІЙНОЇ СПОЛУКИ 5-СУЛЬФОСАЛІЦИЛАТУ КОБАЛЬТУ(II) З БЕНЗГІДРАЗИДОМ

Реакцією водного розчину $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ з гідроксидом натрію добували гідроксид кобальту(II), до нього додавали 5-сульфосаліцилову кислоту. Суміш ретельно перемішували, додаючи краплинами воду до повного розчинення відповідного 5-сульфосаліцилату кобальту. До отриманого розчину додавали розчин бензогідразиду і отриману суміш залишали для осадження. Осад, що утворився, відфільтровували, кілька разів промивали водою і висушували в екзикаторі понад CaCl_2 . Після розчинення синтезованої сполуки складу $[\text{Co}(\text{Bhz})_3]_3(\text{HSSal})_3 \cdot 7.5\text{H}_2\text{O}$ при кип'ятінні в суміші вода/етанол/н-пропанол (1:1:1) червоні кристали, придатні для визначення монокристалічної рентгенівської структури, вирощували протягом 3 днів шляхом повільного випаровування розчинників при кімнатній температурі.

Сполука $[\text{Co}(\text{Bhz})_3]_3(\text{HSSal})_3 \cdot 7.5\text{H}_2\text{O}$ кристалізується в центросиметричній просторовій групі $P\bar{1}$, з трьома іонами $\text{Co}(\text{II})$, дев'ятьма молекулами Bhz і трьома аніонами HSSal^{2-} в асиметричній одиниці. Молекули бензогідразиду (Bhz) координуються з іоном металу з утворенням хелату через атоми O і N . Кожен іон металу оточений трьома молекулами Bhz , утворюючи катіони $[\text{Co}(\text{Bhz})_3]^{2+}$.

Наявність депротонованої карбоксильної групи сульфосаліцилат-аніону в $[\text{Co}(\text{Bhz})_3]_3(\text{HSSal})_3 \cdot 7.5\text{H}_2\text{O}$ сприяє включенню до кристалічної структури значної кількості молекул кристалізаційної води, які беруть участь в утворенні каркасу з водневих зв'язків.

Характер зміни смуг поглинання бензогідразиду в ІЧ-спектрах відповідає бідентатній хелатній координації бензогідразидного ліганду через кисень і термінальні атоми азоту з утворенням п'ятичленного хелатного циклу, а порівняльний аналіз положення та форми смуг поглинання 5-сульфосаліцилат-аніону показує, що обидві групи SO_3H і COOH депротоновані і аніони HSSal^{2-} є зовнішньосферними.

Дані спектру дифузного відбиття для комплексу для координаційної сполуки кобальту(II) добре погоджуються з її октаедричною структурою.

Keywords: Бензогідрозид, 5-сульфосаліцилат, кристалічна структура, ІЧ-спектри

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