

# Syntheses and Characterization of Coordination Compounds of 3d-Metal 5-Sulfosalicylates with Phenylacethydrazide: Crystal Structure of $[\text{Ni}(\text{L})_3]\text{HSSal} \cdot 3\text{H}_2\text{O}$ (L Is Phenylacethydrazide, and $\text{HSSal}^{2-}$ Is 5-Sulfosalicylic Acid Anion)

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**Abstract**—The complexes of 3d-metal 5-sulfosalicylates with phenylacethydrazide are synthesized:  $[\text{Co}(\text{L})_3]\text{HSSal} \cdot 3\text{H}_2\text{O}$  (**I**),  $[\text{Ni}(\text{L})_3]\text{HSSal} \cdot 3\text{H}_2\text{O}$  (**II**), and  $[\text{Zn}(\text{L})_3]\text{HSSal} \cdot 6\text{H}_2\text{O}$  (**III**) (L is phenylacethydrazide, and  $\text{HSSal}^{2-}$  is 5-sulfosalicylic acid anion). Compounds **I–III** are characterized by the methods of chemical analysis, IR spectroscopy, diffuse reflectance spectroscopy, luminescence, and thermogravimetry. Compound **II** is studied by X-ray diffraction analysis (CIF file CCDC no. 1819696). In the complex cation  $[\text{Ni}(\text{L})_3]^{2+}$ , the nickel atom has a face octahedral coordination mode by three O atoms and three N atoms of three bidentate chelate ligands L. The complex cations,  $\text{HSSal}^{2-}$  anions, and crystallization water molecules are joined by a branched system of hydrogen bonds. Complexes **I–III** are luminescent, and complex **III** exhibits the brightest luminescence.

**Keywords:** synthesis, IR spectroscopy, diffuse reflectance spectroscopy, luminescence, thermogravimetry, X-ray diffraction analysis, 5-sulfosalicylates of 3d metals

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## INTRODUCTION

Hydrazides of carboxylic acids can manifest various useful biological properties, in particular, bactericidal, fungicidal, antivermicular, and anticonvulsant properties. They are the starting materials for the preparation of a wide range of derivatives used as pharmaceuticals and surfactants [1]. Many metal complexes with hydrazide ligands also manifest biological activity [2]. In turn, 5-sulfosalicylic acid and its metal complexes are also biologically active: antiulcer, antimicrobial, fungicidal, and anti-inflammatory activity [3]. The compounds containing 5-sulfosalicylate anion possess luminescence properties [4–6]. It can be assumed that a combination of such potentially active fragments in one compound can be very efficient. Literature data on the complex formation of 3d metals with phenylacethydrazide (L) are lacking. We have earlier synthesized and structurally characterized the compound of nickel(II) benzoate with phenylacethydrazide:  $[\text{Ni}(\text{L})_3](\text{C}_6\text{H}_5)_2 \cdot 4\text{H}_2\text{O}$  [7]. Many structural data are available for 5-sulfosalicylates, which show that their anions in coordination com-

pounds can perform different functions. They can be mono- [6], di- [4, 5], or triply [8] deprotonated outer-sphere anions and can be coordinated via the monodentate mode through the sulfo [5, 9] and carboxy group [10] or via the bidentate mode through the carboxy group and deprotonated phenolic –OH group [11]. They can be coordinated via the bridging mode through the carboxy and sulfo groups [12] and even simultaneously through all functional groups [13]. We have earlier prepared the compound in which 5-sulfosalicylic acid is present in the undissociated form in the external sphere [14].

In this work, we describe the synthesis, structures, IR spectra, diffuse reflectance and luminescence spectra, and thermogravimetric curves of the aqua complexes of 3d-metal 5-sulfosalicylates with phenylacethydrazide:  $[\text{M}(\text{L})_3]\text{HSSal} \cdot m\text{H}_2\text{O}$  (M is cobalt(II),  $m = 3$  (**I**); M is nickel(II),  $m = 3$  (**II**); and M is zinc(II),  $m = 6$  (**III**)). The crystal and molecular structures of compound **II** (L is phenylacethydrazide, and  $\text{HSSal}^{2-}$  is 5-sulfosalicylic acid anion) were determined by X-ray diffraction analysis.

## EXPERIMENTAL

**Synthesis of complexes I–III.** 3*d*-Metal nitrate (0.01 mol) was dissolved in water (40 mL), and NaOH (0.8 g, 0.02 mol) was added to the obtained solution. A formed precipitate of 3*d*-metal hydroxide was filtered off, 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 compounds. The obtained solution was added to a solution (50 mL) of phenylacetylhydrazide (4.5 g, 0.03 mol) in methanol, and the resulting mixture was left to stay for precipitation. The precipitate formed was filtered off, washed with water, and dried in air to a constant weight. In the case of compound **II**, the crystals turned out to be suitable for X-ray diffraction analysis.

For C<sub>31</sub>H<sub>40</sub>N<sub>6</sub>O<sub>12</sub>SCo (**I**)

Anal. calcd., % C, 47.75 H, 5.13 N, 10.78 S, 4.11 Co, 7.57

Found, % C, 47.57 H, 5.47 N, 10.75 S, 4.13 Co, 7.17

For C<sub>31</sub>H<sub>40</sub>N<sub>6</sub>O<sub>12</sub>SNi (**II**)

Anal. calcd., % C, 47.75 H, 5.13 N, 10.78 S, 4.11 Ni, 7.57

Found, % C, 47.78 H, 5.41 N, 10.71 S, 4.39 Ni, 7.29

For C<sub>31</sub>H<sub>46</sub>N<sub>6</sub>O<sub>15</sub>SZn (**III**)

Anal. calcd., % C, 44.34 H, 5.48 N, 10.01 S, 3.81 Zn, 7.75

Found, % C, 44.77 H, 5.54 N, 10.43 S, 3.45 Zn, 7.37

Elemental analyses to the metal and sulfur were conducted by atomic emission spectrometry with inductively coupled plasma on a PerkinElmer Optima 8000 instrument. Analyses to carbon, hydrogen, and nitrogen were carried out on a CHN analyzer.

IR spectra were recorded on a PerkinElmer SPECTRUM BX II FT-IR SYSTEM instrument for samples as KBr pellets. Diffuse reflectance spectra were detected on a Lambda-9 spectrophotometer (Perkin-Elmer) using MgO ( $\beta_{\text{MgO}} = 100\%$ ) as a standard.

Thermogravimetric curves were measured on a Paulik–Paulik–Erdey derivatograph in air with a heating rate of 10 deg/min.

Luminescence spectra were recorded on a Fluorolog FL 3-22 spectrofluorimeter using an ozone-free xenon lamp (450 W) and an R928P photoelectric multiplier (Hamamatsu, Japan) for the UV-visible range. Excitation and luminescence spectra were corrected taking into account the radiation distribution of the xenon lamp and sensitivity of the photoelectric multiplier. The integrated intensity of luminescence ( $I_{\text{lum}}$ ) was measured from the surface area under the band contour. The luminescence quantum yield ( $\Phi$ ) of the samples was determined by the relative method using the equation

$$\Phi = \Phi_{\text{st}} \frac{(1 - R_{\text{st}}) I_x}{(1 - R_x) I_{\text{st}}},$$

where  $\Phi_{\text{st}}$  and  $\Phi$  are the quantum yields of the luminescent standard and the sample under study, respectively;  $R_{\text{st}}$  and  $R_x$  are the luminescence reflections of the standard and studied sample, respectively; and  $I_{\text{st}}$  and  $I_x$  are the integrated luminescence intensities of the standard and studied sample, respectively [15]. Sodium salicylate was used as a standard for which  $\Phi_{\text{st}} = 60\%$  in a wide range of excitation wavelengths (160–340 nm) [16]. The reflection in percentage was determined according to a described procedure [17] by scanning the luminescence monochromator in a range of 288–292 nm, whereas the excitation monochromator was fixed at  $\lambda_{\text{exc}} = 290$  nm. The reflection standard was MgO ( $R_{\text{st}} = 0.97$ ). The uncertainty of quantum efficiency determination was  $\pm 10\%$ .

**X-ray diffraction analysis of compound II.** The structure was solved by a direct method and refined by least squares in the full-matrix anisotropic approximation for all non-hydrogen atoms. The positions of hydrogen atoms in the organic ligands and in the anion were calculated geometrically and included into refinement by the riding model. Of six hydrogen atoms of three water molecules, only one atom, namely, H(7*w*), was localized and refined in the isotropic approximation. One of the phenyl groups, C(20*A*)–C(24*A*) atoms, is randomly disordered in two equally probable positions. The high *R* factor for the structure of compound **II** is determined by a poor quality of the crystal. The crystallographic data and experimental characteristics for the crystal of compound **II** are presented in Table 1. Selected bond lengths and bond angles are listed in Table 2. The geometric parameters of intra- and intermolecular bonds are given in Table 3.

The full crystallographic data for compound **II** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1819696; deposit@ccdc.cam.ac.uk or [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)).

## RESULTS AND DISCUSSION

The chemical analysis showed the ratio M : L = 1 : 3 for compounds **I–III**.

The structure of complex **II** was determined by X-ray diffraction analysis. The structural units of the crystal of compound **II** are complex cations  $[\text{Ni}(\text{L})_3]^{2+}$ , anions  $\text{HSSal}^-$ , and crystallization water molecules in a ratio of 1 : 1 : 3 (Fig. 1). The Ni atom is coordinated at the vertices of the octahedron by three oxygen atoms and three nitrogen atoms of three bidentate chelate (O,N) ligands L. When coordinating with the nickel atom, the phenylacetylhydrazide ligands (L) close three five-membered metallocycles NiNCO. The average distances are as follows: Ni–N  $2.080 \pm 0.007$  and Ni–O  $2.055 \pm 0.011$  Å. The average chelate NNiO angle is  $79.66^\circ \pm 0.57^\circ$ . The geometric parameters (Ni–N  $2.083 \pm 0.001$ , Ni–O  $2.053 \pm 0.01$  Å) and

**Table 1.** Crystallographic characteristics and experimental and structure refinement data for compound **II**\*

Parameter	Value
<i>FW</i>	773.41
Temperature, K	293(2)
Crystal system; space group	Triclinic; $P\bar{1}$
Cell parameters:	
<i>a</i> , Å	10.279(2)
<i>b</i> , Å	11.120(2)
<i>c</i> , Å	18.007(4)
$\alpha$ , deg	72.60(3)
$\beta$ , deg	78.82(3)
$\gamma$ , deg	71.91(3)
<i>V</i> , Å <sup>3</sup>	1855.4(6)
<i>Z</i> ; $\rho_{\text{calcd}}$ , g/cm <sup>3</sup>	2; 1.395
<i>F</i> (000)	804
$\mu$ , mm <sup>-1</sup>	1.857
Crystal size, mm	0.08 × 0.08 × 0.05
Diffractometer	Enraf-Nonius CAD4
Scan mode	$\omega$
Radiation; $\lambda$ , Å	CuK $\alpha$ , 1.5418
$\theta_{\text{min}}-\theta_{\text{max}}$ , deg	4.55–60.00
Range of indices	–11 ≤ <i>h</i> ≤ 11, –12 ≤ <i>k</i> ≤ 12, –20 ≤ <i>l</i> ≤ 20
Number of reflections measured/independent ( <i>R</i> <sub>int</sub> )	7435/4375 (0.020)
Number of reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	3462
Completeness for $\theta$ , %	79.2
Absorption correction	$\phi$ scan
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.8657, 0.9129
Refinement method	Full-matrix least squares for <i>F</i> <sup>2</sup>
Number of refined parameters	487
GOOF ( <i>F</i> <sup>2</sup> )	1.090
<i>R</i> <sub><i>hkl</i></sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> <sub>1</sub> = 0.085, <i>wR</i> <sub>2</sub> = 0.203
<i>R</i> <sub><i>hkl</i></sub> (for all reflections)	<i>R</i> <sub>1</sub> = 0.110, <i>wR</i> <sub>2</sub> = 0.225
Residual electron density, e/Å <sup>3</sup>	1.007, –1.395

\* Programs: APEX2, SAINT, and SADABS [18]; SIR-92 [19]; and SHELXL-2014 [20].

chelate angle NNiO ( $79.63^\circ \pm 0.47^\circ$ ) in the aforementioned compound [Ni(L)<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> · 4H<sub>2</sub>O [7] almost coincide with similar values in complex **II** with a similar composition.

Nevertheless, different geometric isomers take place in similar complex cations in the structures of compounds **I** and **IV**: *cis,trans*-meridian (*mer*) in compound **IV** and *cis,cis*-face (*fac*) with triples of N<sub>3</sub> and O<sub>3</sub> at the opposite faces of the NiN<sub>3</sub>O<sub>3</sub> octahedron in compound **II**. The structural units of the crystal of

compound **II** are joined by a branched network of hydrogen bonds O–H···O and N–H···O involving all hydrogen atoms of the NH<sub>2</sub> and NH of molecules L (as mentioned in Experimental, only one hydrogen atom of six atoms of the H<sub>2</sub>O molecules is localized): H···O 1.78–2.30, N···O 2.800–3.026, and O···O 2.475–2.804 Å and angles O(N)–H···O are 129°–180° (Table 3).

A similar stoichiometry and resembling IR spectra (Table 4) and thermogravimetric data (Table 5) assert

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

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Ni(1)–O(1)	2.048(4)	S(1)–O(5)	1.48(6)
Ni(1)–O(2)	2.066(4)	N(5)–N(6)	1.323(8)
Ni(1)–O(3)	2.051(4)	N(2)–C(1)	1.313(8)
Ni(1)–N(1)	2.085(5)	N(4)–C(2)	1.313(8)
Ni(1)–N(3)	2.083(5)	S(1)–O(4)	1.434(4)
Ni(1)–N(5)	2.073(5)	S(1)–O(5)	1.447(5)
O(1)–C(1)	1.258(7)	S(1)–O(6)	1.458(5)
O(2)–C(2)	1.234(8)	S(1)–C(25)	1.765(5)
O(3)–C(3)	1.223(8)	C(28)–O(7)	1.352(7)
N(1)–N(2)	1.415(6)	C(31)–O(8)	1.235(7)
N(3)–N(4)	1.425(7)	C(31)–O(9)	1.269(7)
S(1)–O(4)	1.434(4)		
S(1)–O(5)	1.447(5)		
Angle	$\omega$ , deg	Angle	$\omega$ , deg
O(1)Ni(1)O(2)	93.79(17)	N(6)N(5)Ni(1)	107.3(3)
O(1)Ni(1)O(3)	90.21(18)	C(1)O(1)Ni(1)	112.5(4)
O(3)Ni(1)O(2)	92.83(18)	C(2)O(2)Ni(1)	112.2(4)
O(1)Ni(1)N(1)	80.23(17)	C(3)O(3)Ni(1)	113.3(4)
O(1)Ni(1)N(3)	90.94(18)	C(1)N(2)N(1)	119.0(5)
O(1)Ni(1)N(5)	168.17(17)	C(2)N(4)N(3)	118.6(5)
O(2)Ni(1)N(1)	172.83(18)	C(3)N(6)N(5)	117.9(5)
O(2)Ni(1)N(3)	79.34(17)	N(2)C(1)C(4)	117.1(5)
O(2)Ni(1)N(5)	92.38(19)	N(4)C(2)C(11)	117.1(6)
O(3)Ni(1)N(1)	91.15(18)	N(6)C(3)C(18)	116.7(6)
O(3)Ni(1)N(3)	172.14(18)	O(1)C(1)N(2)	121.1(5)
O(3)Ni(1)N(5)	79.40(18)	O(1)C(1)C(4)	121.7(6)
N(3)Ni(1)N(1)	96.71(18)	O(2)C(2)N(4)	121.6(6)
N(5)Ni(1)N(1)	94.21(19)	O(2)C(2)C(11)	121.3(7)
N(5)Ni(1)N(3)	100.13(18)	O(3)C(3)N(6)	122.0(6)
N(2)N(1)Ni(1)	106.5(3)	O(3)C(3)C(18)	121.3(6)
N(4)N(3)Ni(1)	106.0(3)		

that the structures of the internal and external spheres for the cobalt (**I**) and zinc (**III**) complexes are the same as those for the nickel complex (**II**). The IR spectra of compounds **I–III** are presented in Table 4. The absorption bands related to vibrations of phenylacetylhydrazide were assigned taking into account published data [21–24]. A comparison of the IR spectra of free phenylacetylhydrazide and complexes **I–III** shows that the frequency of stretching vibrations of the C=O group (amide **I**) increases upon complex formation. This band usually shifts to the low-frequency range for the coordination of hydrazides through oxygen [25–31]. The unusual behavior of the band caused by the  $\nu(\text{C}=\text{O})$  vibrations is related to the fact that its frequency is decreased in the spectrum of the initial phe-

nylacetylhydrazide because of intra- and intermolecular hydrogen bonds. It has been proved as early as in 1956 that phenylacetylhydrazide both in the solid state and in concentrated chloroform solutions contains hydrogen bonds [22], and the expected frequency of the  $\nu(\text{C}=\text{O})$  band was shown to be  $\sim 1710 \text{ cm}^{-1}$ . A comparison with  $\nu(\text{C}=\text{O})$  without hydrogen bonds shows that the shift to lower frequencies is observed upon complex formation. Therefore, the frequency of the  $\nu(\text{C}=\text{O})$  band of phenylacetylhydrazide is decreased because of hydrogen bond formation more significantly than due to complex formation. For  $\omega(\text{NH}_2)$  wagging vibrations, the doublet disappears and the frequency increases compared to that of the initial phenylacetylhydrazide. The  $\nu(\text{C}-\text{C})$  bands of the aromatic ring in the IR spectra of

**Table 3.** Geometric parameters of hydrogen bonds in compound **I**\*

D—H $\cdots$ A, D $\cdots$ A	Distance, Å			Angle DHA, deg
	D $\cdots$ H	H $\cdots$ A	D $\cdots$ A	
N(1)—H(1B) $\cdots$ O(11)	0.90	2.21	3.026(7)	151
N(3)—H(3B) $\cdots$ O(6)	0.90	1.98	2.876(7)	172
N(4)—H(4C) $\cdots$ O(10)	0.86	2.00	2.829(7)	161
N(5)—H(5A) $\cdots$ O(5)	0.90	2.30	2.946(6)	129
O(7)—H(7w) $\cdots$ O(9)	0.73(5)	1.78(5)	2.475(7)	160(6)
O(11)—H(11i) $\cdots$ O(12)	0.80	1.93	2.735(7)	179
O(12)—H(12i) $\cdots$ O(6)	0.80	1.93	2.731(7)	179
N(1)—H(1A) $\cdots$ O(7) <sup>#1</sup>	0.90	2.00	2.888(6)	167
N(3)—H(3A) $\cdots$ O(8) <sup>#2</sup>	0.90	1.99	2.800(6)	171
O(10)—H(10i) $\cdots$ O(9) <sup>#2</sup>	0.80	1.90	2.702(7)	180
O(11)—H(11i) $\cdots$ O(8) <sup>#2</sup>	0.80	1.88	2.683(6)	180
N(2)—H(2A) $\cdots$ O(11) <sup>#3</sup>	0.86	1.98	2.811(6)	162
N(5)—H(5B) $\cdots$ O(4) <sup>#4</sup>	0.90	2.03	2.889(7)	160
N(6)—H(6C) $\cdots$ O(10) <sup>#5</sup>	0.86	2.14	2.966(7)	160
O(12)—H(12i) $\cdots$ O(5) <sup>#4</sup>	0.80	1.98	2.781(7)	180
O(10)—H(10i) $\cdots$ O(12) <sup>#6</sup>	0.80	2.00	2.804(7)	180
O(10) $\cdots$ N(4)			2.830(7)	
O(10) $\cdots$ O(12) <sup>#6</sup>			2.801(7)	
O(10) $\cdots$ O(9) <sup>#2</sup>			2.687(7)	
O(10) $\cdots$ N(6) <sup>#7</sup>			2.960(6)	
O(11) $\cdots$ N(1)			3.020(7)	
O(11) $\cdots$ N(2) <sup>#8</sup>			2.801(7)	
O(11) $\cdots$ O(12)			2.753(7)	
O(11) $\cdots$ O(8) <sup>#2</sup>			2.676(6)	
O(12) $\cdots$ O(6)			2.730(7)	

\* Symmetry transforms of atomic coordinates: (A) <sup>#1</sup>  $x - 1, y + 1, z$ ; <sup>#2</sup>  $x, y + 1, z$ ; <sup>#3</sup>  $-x + 1, -y + 1, -z + 1$ ; <sup>#4</sup>  $-x + 1, -y, -z + 1$ ; <sup>#5</sup>  $x - 1, y, z$ ; <sup>#6</sup>  $-x + 1, -y, -z$ ; <sup>#7</sup>  $x + 1, y, z$ ; <sup>#8</sup>  $-x, -y, -z$ .

complexes **I–III** disappear as well as the bands of symmetric vibrations  $\nu_s(\text{C–H})$  of the  $\text{CH}_2$  group. The  $\nu_{as}$  frequency of this group is split into a doublet, and the frequency of the bending  $\delta(\text{CH}_2)$  vibrations remains unchanged. The triplet at  $1130\text{--}1210\text{ cm}^{-1}$  corresponding to vibrations of various bonds involving the nitrogen atoms becomes doublet in the IR spectra of the complexes. Therefore, the character of changing the absorption bands in the IR spectra of the synthesized complexes compared to the spectrum of free phenylacetylhydrazide is caused by the participation of the oxygen and nitrogen atoms in the formation of the chelate cycle.

The absorption bands related to the vibrations of the 5-sulfosalicylate anion were assigned taking into account published data [3, 4, 32–34]. The  $\nu(\text{C=O})$  band, which appears at  $1678\text{ cm}^{-1}$  in the spectrum of

free 5-sulfosalicylic acid, disappears in the spectra of complexes **I–III**. Instead this band, the  $\nu_{as}(\text{COO}^-)$  and  $\nu_s(\text{COO}^-)$  bands appear, the difference between which (designated as  $\Delta$  in Table 4) for all the three complexes lies in a range of  $155\text{--}159\text{ cm}^{-1}$ . This corresponds to the deprotonation of the carboxy group. In the IR spectra of all complexes, the number of bands corresponding to the  $\nu(\text{SO}_2)$  vibrations decreases, which is evidently related to an increase in the symmetry of the sulfo group upon complex formation. This is consistent with the deprotonation of the  $\text{SO}_3\text{H}$  group. Thus, the absorption bands in the IR spectra of complexes **I–III** correspond to the doubly deprotonated form of the sulfur group.

The thermogravimetric curves of compounds **I–III** are almost similar: two *endo*-effects corresponding



**Table 4.** Assignment of absorption bands ( $\text{cm}^{-1}$ ) in the IR spectra of phenylacetohydrazide and its complexes with 3*d*-metal 5-sulfosalicylates

Assignment	L	H <sub>3</sub> SSal	[CoL <sub>3</sub> ]HSSal · 3H <sub>2</sub> O	[NiL <sub>3</sub> ]HSSal · 3H <sub>2</sub> O	[ZnL <sub>3</sub> ]HSSal · 6H <sub>2</sub> O
$\nu(\text{NH})$ , $\nu(\text{NH}_2)$	3294, 3200		3260 sh, 3197	3167	3260, 3199
$\nu_{as}(\text{C}-\text{H})$ ( $\text{CH}_2$ )	3030		3063, 3030	3062, 3032	3060, 3030
$\nu_s(\text{C}-\text{H})$ ( $\text{CH}_2$ )	2917				
$\nu(\text{C}=\text{O})$	1644	1678	1662	1653	1651
$\delta(\text{NH}_2)$				1614	
$\nu_{as}(\text{COO}^-)$			1598	1558	1590
$\nu(\text{C}-\text{C})_{\text{atom. ring}}$	1529				
$\delta(\text{CH}_2)$	1455		1454	1455	1455
$\nu_s(\text{COO}^-)$			1439 ( $\Delta = 159$ )	1401 ( $\Delta = 157$ )	1435 ( $\Delta = 155$ )
$\omega(\text{NH}_2)$	1352, 1265		1374	1384	1366
$\nu_{as}(\text{SO}_2)$		1234, 1203, 1165, 1134 sh	1292, 1210	1290, 1211	1291, 1210
$\nu(\text{CN}) + \nu(\text{N}-\text{N}) + \tau(\text{NH}_2) + \delta(\text{CCH})$	1205, 1156, 1137		1195, 1156	1196, 1163	1183, 1158
$\nu_s(\text{SO}_2)$		1084, 1065, 1026	1078*, 1058, 1030	1079*, 1057, 1031	1079*
$\nu_{\text{puls. ring}} + \rho(\text{NH}_2) + \tau(\text{NH}_2)$	1074, 1007		1078*, 969	1079*, 972	1079*, 1030
$\rho(\text{CCH}) + \delta(\text{CCH})$	773			759	783
$\delta(\text{CNH}) + \delta(\text{CCC})$	705, 623		695	695	700
$\nu(\text{S}-\text{O})$		663	660	652	667
$\delta(\text{CCN}) + \delta(\text{NCO})$			533	532	532

\* The vibrations of phenylacetohydrazide and 5-sulfosalicylate anion contribute to the band.

**Table 5.** Thermogravimetric data for the phenylacetylhydrazide complexes with 5-sulfosalicylates of 3d metals

Compound	Endo-effects		Exo-effects		Overall mass decrease, %
	$T, ^\circ\text{C}^*$	$\Delta m, \%$	$T, ^\circ\text{C}^*$	$\Delta m, \%$	
[CoL <sub>3</sub> ]HSSal · 3H <sub>2</sub> O	100–120 (110)	6.8	330–380 (360)	27.7	81.25
	240–330 (310)	16.1	440–600 (560)	20.4	
			900–920 (910)	4.9	
[NiL <sub>3</sub> ]HSSal · 3H <sub>2</sub> O	140–160 (150)	6.4	380–530 (500)	10.3	85.0
	260–360 (330)	44.7	530–690 (610)	22.6	
[ZnL <sub>3</sub> ]HSSal · 6H <sub>2</sub> O	90–110 (100)	2.6	250–300 (290)	23.8	91.25
	200–250 (230)	2.5	300–390 (330)	31.4	
			390–600 (500)	13.2	
			600–680 (650)	15.2	

\* The temperature of the maximum of the effect is given in parentheses.

**Table 6.** Diffuse reflectance spectral data on the nickel(II) and cobalt(II) 5-sulfosalicylate complexes with phenylacetylhydrazide

Compound	$\lambda, \text{nm}$	Assignment
[CoL <sub>3</sub> ]HSSal · 3H <sub>2</sub> O (I)	490	$^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$
	1744	$^4T_{1g}(F) \rightarrow ^4T_{2g}$
[NiL <sub>3</sub> ]HSSal · 3H <sub>2</sub> O (II)	576	$^3A_{2g} \rightarrow ^3T_{1g}(P)$
	766	$^3A_{2g} \rightarrow ^3T_{1g}$
	856	$^3A_{2g} \rightarrow ^3T_{2g}$

bution of the sulfosalicylate anion to the luminescence of the obtained compounds. The quantum yield of complex **III** measured by the relative method comparing with the luminescence standard (sodium salicylate) was 35.4%.

In complexes **II** and **I**, the radiation is considerably quenched, which is related to the energy transfer from the sulfosalicylate ion to the central metal ions. Transition metal ions with the unfilled 3d shell are characterized by a similar quenching of molecular fluorescence [36]. The efficiency of the energy transfer to the central ion-acceptor depends on the degree of overlapping of the fluorescence and absorption bands caused

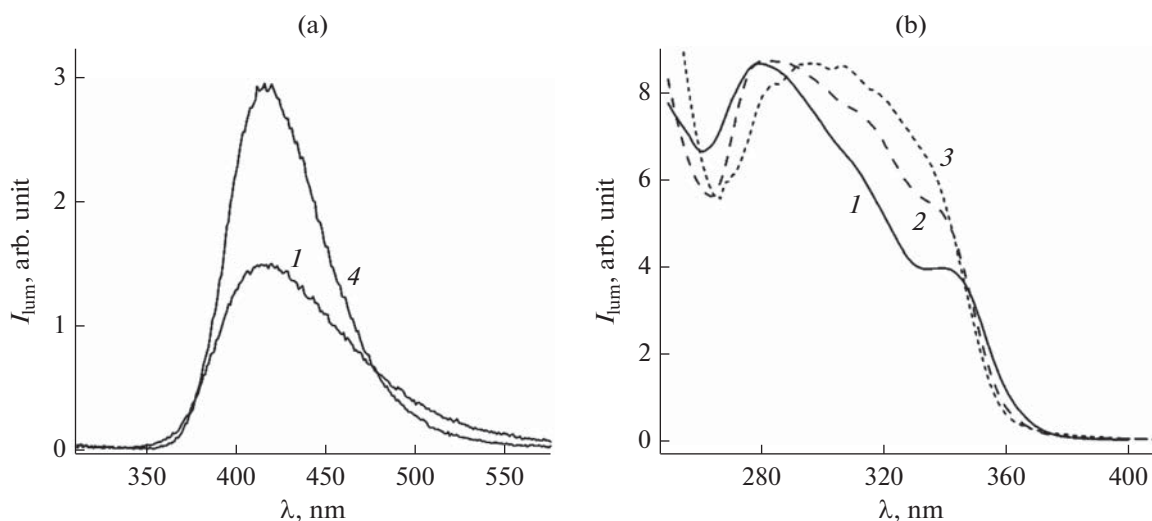
by  $d-d$  transitions. In our case, the radiation intensity for complex **II** exceeds that of compound **I** by 7.7 times. The luminescence maximum for complex **II** lies in the range of minimum absorption between the bands of the  $\pi-\pi^*$  transitions of the organic moiety and the band of the  $^3A_{2g} \rightarrow ^3T_{1g}(P)$  transition of Ni(II) with a maximum at 576 nm (Fig. 3b).

In the case of complex **I**, on the contrary, the luminescence band and  $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$  transition of Co(II) with a maximum at 490 nm are significantly overlapped (Fig. 3a). Thus, the luminescence with a quantum yield of 2.4% was detected for complex **II**,

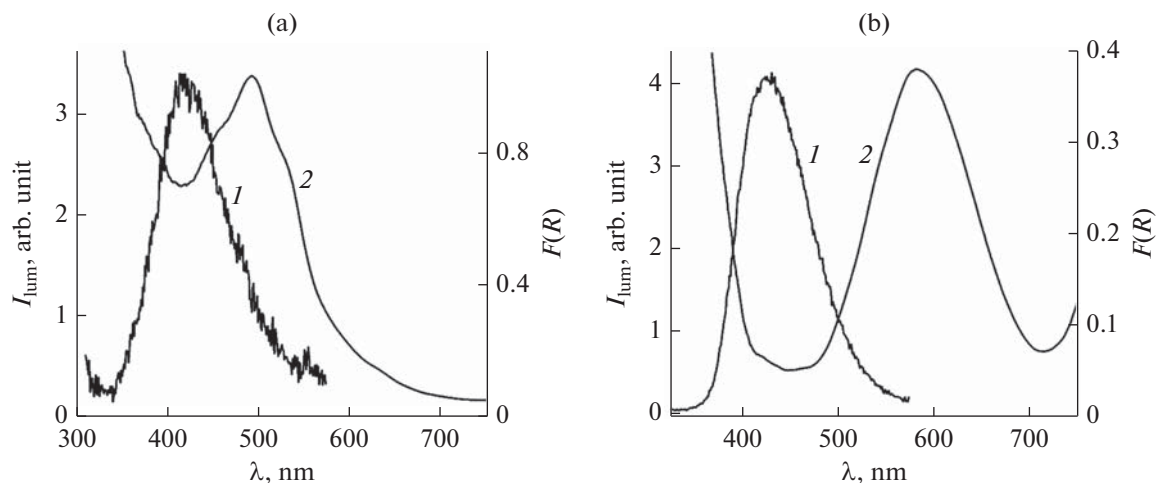
**Table 7.** Characteristics of luminescence of the phenylacetylhydrazide complexes with 3d-metal 5-sulfosalicylates

Compound	$I, \text{arb. units}$	$\lambda_{\text{lum}}, \text{nm}$	$R, \%$	$\Phi, \%$
NaSal	100.00	417	23.0	60.0
[ZnL <sub>3</sub> ]HSSal · 6H <sub>2</sub> O	69.07	416	10.3	35.6
[NiL <sub>3</sub> ]HSSal · 3H <sub>2</sub> O	4.70	425	9.9	2.4
[CoL <sub>3</sub> ]HSSal · 3H <sub>2</sub> O	0.61	416	9.8	0.3





**Fig. 2.** (a) Excitation spectra of the complexes with  $\lambda_{lum} = 420$  nm and (b) luminescence spectra with  $\lambda_{exc} = 290$  nm for (1)  $[ZnL_3]HSSal \cdot 6H_2O$ , (2)  $[NiL_3]HSSal \cdot 3H_2O$ , (3)  $[CoL_3]HSSal \cdot 3H_2O$ , and (4) sodium salicylate.



**Fig. 3.** (1) Luminescence and (2) diffuse reflectance spectra for complexes (a)  $[CoL_3]HSSal \cdot 3H_2O$  and (b)  $[NiL_3]HSSal \cdot 3H_2O$ .

whereas the value obtained for complex I (0.3%) indicates the almost complete luminescence quenching.

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