

COORDINATION
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Synthesis, IR-Spectroscopic Study and Crystal Structure of Tris(benzohydrazide)nickel(II) Dichloride Dihydrate [Ni(L)₃]Cl₂ · 2H₂O

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Abstract—Coordination compound [Ni(L)₃]Cl₂ · 2H₂O (L is benzohydrazide) has been synthesized and studied by IR spectroscopy and X-ray diffraction analysis. According to X-ray diffraction, one of the Cl[−] ions is disordered over two nonequivalent positions. The crystals are monoclinic, $a = 15.423(3)$ Å, $b = 9.697(2)$ Å, $c = 18.893(4)$ Å, $\beta = 105.99(3)^\circ$, space group $P2_1/c$, $Z = 4$. The structural units of the crystal are complex cations [Ni(L)₃]²⁺, in which ligands L are coordinated to the central atom bidentately chelating the metal atoms through the O and N atoms of the hydrazide moiety (Ni–O 2.036(4), 2.051(5), 2.047(5); Ni–N 2.095(5), 2.089(6), 2.097(6) Å). The structural units of the crystal are joined together by cation–anion electrostatic interactions and hydrogen bonds, which involve both H₂O molecules, both Cl[−] anions and the N atoms of chelate rings of the complex cation.

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Hydrazides of carboxylic acids react with transition-metal ions forming various coordination compounds. As a rule, in all these complexes irrespective of complexing metal and stoichiometry, ligands are coordinated bidentately through the oxygen atoms of the carbonyl group and the nitrogen atoms of the amino group. A number of coordination compounds of halides and sulfates of divalent 3d metals (Mn, Fe, Co, Ni, and Cu) with benzohydrazide having M : L = 1 : 3 composition were synthesized and described [1, 2]. In particular, a complex [Ni(L)₃]Cl₂ · 2H₂O (**I**) (L is benzohydrazide) was isolated for nickel(II) chloride. Based on IR spectroscopy data (using the Nujol mull technique), it was concluded that the coordination of ligand L to the metal was realized by a typical way, through the carbonyl oxygen atom and the nitrogen atom of the NH₂ group, and complex **I** had a monomeric structure. However, structural confirmation of the conclusions was lacking.

Here we describe the synthesis and the IR spectroscopy and X-ray diffraction data of crystal **I**.

EXPERIMENTAL

Synthesis. Benzohydrazide (2.04 g, 15 mmol) was dissolved in water (20 mL), and a solution of NiCl₂ · 2H₂O (1.19 g, 5 mmol) in water (20 mL) was added portionally to the obtained solution. The resulting

solution became blue. After a time, blue crystals precipitated from the solution; they were isolated, washed with a small amount of water, and dried in air to constant weight. Crystals suitable for X-ray diffraction were prepared by recrystallization from water.

IR spectra were recorded on a Frontier Perkin-Elmer FTIR spectrometer (4000–350 cm^{−1}). The samples were prepared as KBr pellets.

X-ray diffraction analysis. Structure **I** was solved by direct methods using the SHELXL-97 program [3]. Non-hydrogen atoms were refined by full-matrix least squares in the anisotropic approximation. The hydrogen atoms of ligand L were given in calculated positions and refined isotropically according to the “rider” model with the U_H parameter equal to $1.2U_j$ of basis atoms for the CH₂ groups and $1.5U_j$ for CH₃ groups.

The structural information was deposited with CCDC (no. 1030465).

The crystallographic data and details of the X-ray diffraction study of crystal **I** are listed in Table 1.

RESULTS AND DISCUSSION

Crystals **I** (Fig. 1) are built of cations [Ni(L)₃]²⁺ (L is benzohydrazide C₆H₅–C(O)–NH–NH), two anions Cl[−], one of which is disordered over two nonequivalent positions (0.53, Cl2a, 0.47, Cl2b), and

Table 1. Crystallographic parameters and refinement details for crystal **I**

Molecular formula	C ₂₁ H ₂₅ Cl ₂ N ₆ NiO ₅
FW	571.08
Color, habit	Blue prism
Size, mm	0.14 × 0.06 × 0.03
Crystal system	Monoclinic
Space group	<i>P</i> ₂ ₁ / <i>c</i>
Unit cell parameters	
<i>a</i> , Å	15.423(3)
<i>b</i> , Å	9.697(2)
<i>c</i> , Å	18.893(4)
β, deg	105.99(3)
<i>V</i> , Å ³	2716.3(9)
<i>Z</i>	4
ρ _{calc} , g/cm ³	1.396
μ, cm ⁻¹	3.196
<i>F</i> (000)	1180
Temperature, K	293(2)
Diffractometer	Enraf-Nonius Cad-4
Radiation (λ, Å)	CuK _α (1.54178)
	Graphite monochromator
θ range, deg	4.87–59.97
Reflection index ranges	–14 = <i>h</i> ≤ 9, 0 ≤ <i>k</i> ≤ 10, –18 = <i>l</i> ≤ 18
Number of reflections measured unique (<i>N</i>) with <i>I</i> > 2σ(<i>I</i>)	6326 3746 1810
Number of refined parameters	343
GOOF on <i>F</i> ²	1.135
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0647, <i>wR</i> 2 = 0.1607
<i>R</i> (on all the reflections)	<i>R</i> 1 = 0.1673, <i>wR</i> 2 = 0.2003
Δρ _{max} and Δρ _{min} , e/Å ³	3.64 and –0.12

water of crystallization molecules. Right-handed and left-handed complex cations are formed; the unit cell contains equal amounts of both complexes. The Ni atoms have an octahedral coordination formed by three O(1–3) atoms and three N(1,3,5) atoms of three bidentately chelating ligands L. Almost planar five-membered chelate rings Ni(1)N(1)N(2)C(1)O(1) (±0.01 Å), Ni(1)N(3)N(4)C(8)O(2) (±0.06 Å), and

Table 2. Bond lengths (*d*) and bond angles (ω) in the coordination polyhedron of **I**

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Ni(1)–O(1)	2.041(4)	N(1)–N(2)	1.413(7)
Ni(1)–O(2)	2.041(5)	C(1)–N(2)	1.337(8)
Ni(1)–O(3)	2.053(4)	C(8)–N(4)	1.357(8)
Ni(1)–N(1)	2.098(5)	N(3)–N(4)	1.410(8)
Ni(1)–N(3)	2.104(6)	O(3)–C(15)	1.235(8)
Ni(1)–N(5)	2.089(6)	C(15)–N(6)	1.334(9)
O(1)–C(1)	1.241(7)	N(5)–N(6)	1.418(7)
C(1)–N(2)	1.337(8)	O(2)–C(8)	1.238(8)
Angle	ω, deg	Angle	ω, deg
O(1)Ni(1)N(1)	79.7(2)	O(2)Ni(1)N(5)	173.0(2)
O(2)Ni(1)N(3)	79.7(2)	N(1)Ni(1)N(3)	97.0(2)
O(3)Ni(1)N(5)	79.3(2)	N(3)Ni(1)N(5)	96.6(2)
O(1)Ni(1)O(2)	88.4(2)	N(1)Ni(1)N(5)	95.8(2)
O(1)Ni(1)O(3)	91.1(2)	N(1)Ni(1)O(2)	90.5(2)
O(1)Ni(1)N(3)	167.7(2)	N(1)Ni(1)O(3)	169.2(2)
O(1)Ni(1)N(5)	95.6(2)	N(3)Ni(1)O(3)	93.1(2)
O(2)Ni(1)O(3)	95.0(2)		

Ni(1)N(5)N(6)C(15)O(3) (±0.03 Å) are turned in one direction and form dihedral angles with planes of their corresponding phenyl rings equal to 26°, 18°, and 6°, respectively.

The structure of the cation is similar to that found in the previously studied adduct [Co(L)₃](OH)Cl(H₃Ssal)H₂O [4], which is the inclusion compound of the molecular dimer of sulfosalicylic acid (H₃Ssal)₂ into the complex.

The bond lengths and bond angles in structure **I** are shown in Table 2.

Complex cations are located in the unit cell by layers perpendicular to the *x* axis of the crystal (Fig. 2). The interlayer space is filled with chloride ions (Cl(1), Cl(2*a*), and Cl(2*b*)) and water of crystallization molecules O(1*w*, O2*w*) linked with each other and with the cations by numerous hydrogen bonds (HB) (Table 3, Fig. 3).

Table 4 shows the assignment of absorption bands in the IR spectra of benzohydrazide L and complex **I** performed taking into account the literature data [5–7].

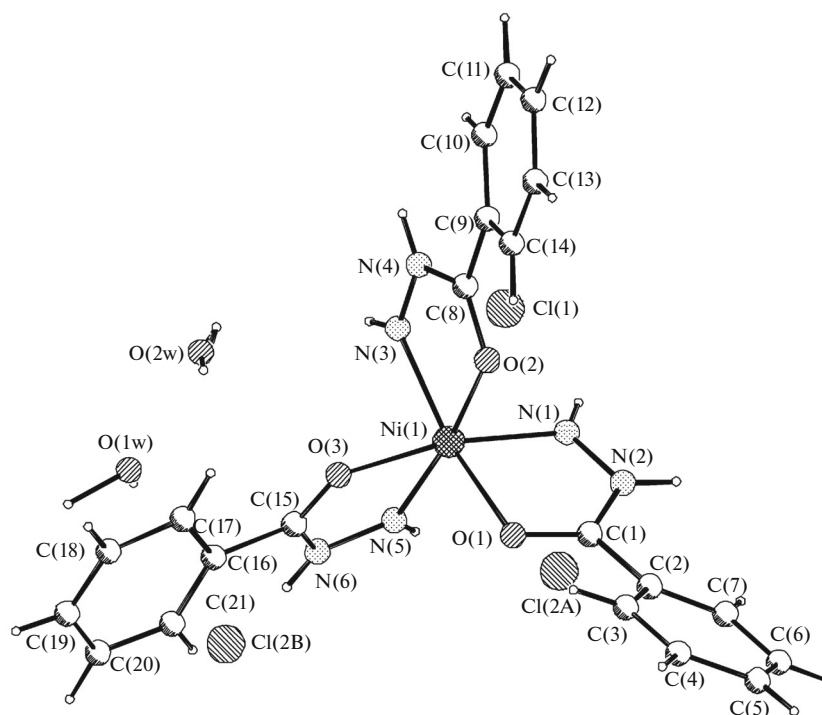


Fig. 1. Configuration of complex cation $[\text{Ni}(\text{L})_3]^{2+}$.

Table 3. Geometrical parameters of hydrogen bonds in structure I

Bond A–H...X	Length, Å*			Coordinates of the X atom
	A...X	H...X	Angle AHX, deg	
N(1)–H(1)...Cl(1)	3.343(7)	2.63	140	
N(2)–H(2)...Cl(1)	3.127(8)	2.33	154	$-x + 1, y + 1/2, -z - 1/2$
N(3)–H(3)...Cl(1)	3.242(9)			
N(4)–(H(4)...Cl(1) 1)	3.144(7)	2.36	151	$-x + 1, y + 1/2, -z - 1/2$
N(5)–H(5a)...Cl(2a)	3.269(5)	2.065	138	
N(6)–H(6b)...Cl(2b)	3.028(8)	2.58	157	
O(1w)–H1(w1)...Cl(2b)	3.165(7)	2.94	150	
O(1w)...O(2w)	2.798(6)			
O(2w)...Cl(2)	3.050(5)			$-x + 1, -y + 2, -z$

* Length N–H 0.86 Å.

Table 4. Wavenumbers (ν , cm^{-1}) of absorption band maxima in IR spectra of benzohydrazide and $[\text{Ni}(\text{L})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

Assignment	L	$[\text{Ni}(\text{L})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$
$\nu(\text{NH})$, $\nu(\text{NH}_2)$	3300, 3200, 3049, 3021, 2875	3414, 3161, 3059, 3017, 2976
$\nu(\text{C}=\text{O})$	1662	1637
$\Delta(\text{NH}_2)$	1616	1607
$\nu(\text{C}-\text{C})$ aromatic ring	1578 sh., 1567, 1488, 1447	1570, 1539, 1492, 1449
$\Omega(\text{NH}_2)$	1350, 1299	1332
$\nu(\text{CN}) + \nu(\text{N}-\text{N}) + \tau(\text{NH}_2) + \delta(\text{CCH})$	1185, 1155, 1121	1187, 1129
$\nu_{\text{br}} \text{ ring} + \rho(\text{NH}_2) + \tau(\text{NH}_2)$	1071, 920, 885, 803	1076, 1042, 1024, 1002, 929, 897, 802
$\Delta(\text{CNH}) + \delta(\text{CCC})$	685, 675, 617	689, 639, 615
$\Delta(\text{CCN}) + (\delta(\text{NCO}))$	517	543

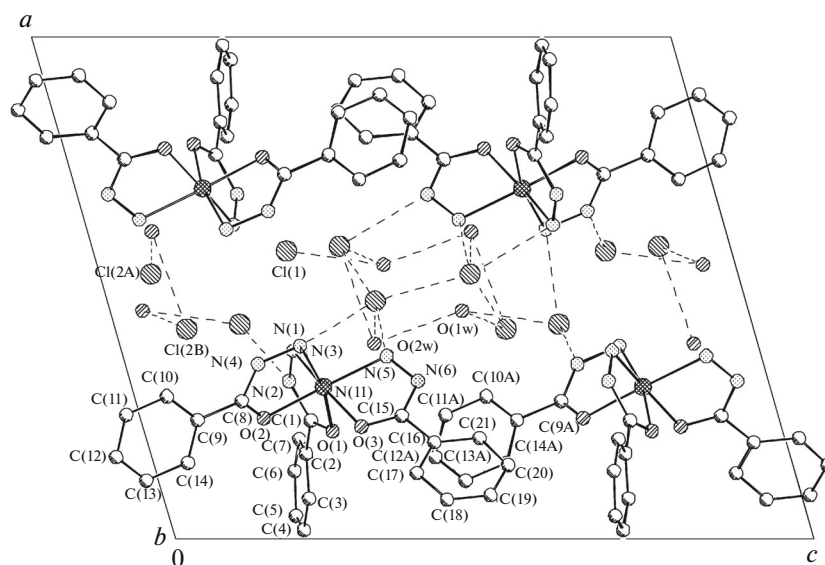


Fig. 2. Cationic layers alternating with layers, which contain the Cl^- ions and H_2O molecules.

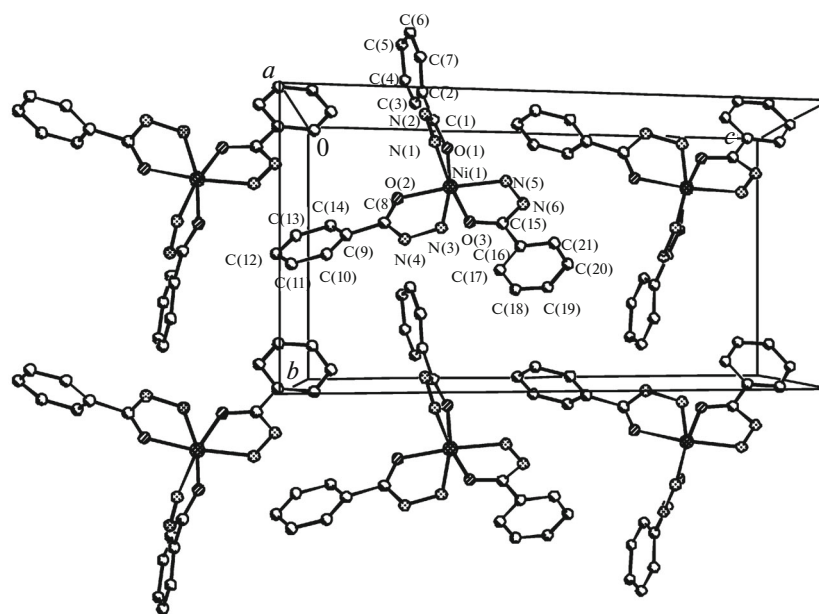


Fig. 3. The $0yz$ projection of the layer containing cations $[\text{Ni}(\text{L})_3]^{2+}$.

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). In the spectrum of complex **I**, this band shifts to the low-frequency region by 25 cm^{-1} as compared to the frequency of uncoordinated benzohydrazide, which confirms the participation of the oxygen atom in the metal coordination. The authors [1] also recorded a similar displacement by $\sim 20\text{ cm}^{-1}$ for analogous complexes. Bands of bending vibrations $\delta(\text{NH}_2)$ also decrease upon complex formation. For wagging vibrations

$\omega(\text{NH}_2)$, one band is observed in the IR spectrum of complex **I** against two absorption bands observed in the spectrum of free ligand. Bands at $\sim 1570\text{ cm}^{-1}$ correspond to the stretching vibrations of the $\text{C}-\text{C}$ bonds of the benzohydrazide aromatic ring; they slightly change upon the complexation. Thus, the nature of changes of absorption bands in the IR spectra of complex **I** corresponds to bidentately chelating coordination of benzohydrazide by the oxygen and nitrogen atoms.

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