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Mononuclear Nickel(II) and Copper(II) Coordination Compounds with Ligands Based on Acetyl(benzoyl)acetone S-Methylisothiosemicarbazones and 8-Quinolinecarboxaldehyde. Synthesis and Crystal Structure

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Abstract—Template condensation of S-methylisothiosemicarbazones of acetyl- or benzoylacetone with 8-quinolinecarboxaldehyde in the presence of nickel(II) and copper(II) ions gave four new mononuclear coordination compounds $[NiL^1]I$ (**I**), $[CuL^1I]$ (**II**), $[NiL^2]I$ (**III**), and $[CuL^2I]$ (**IV**). The chemical composition of the products was confirmed by elemental analysis, IR spectroscopy, and mass spectrometry, and the crystal structure of compounds **I** and **II** was determined by X-ray diffraction analysis (CCDC nos. 2266386, 2266387). X-ray diffraction study revealed a square planar coordination environment of the central ion of the cationic Ni(II) complex and square pyramidal geometry for the molecular Cu(II) complex.

Keywords: nickel(II), copper(II), coordination compound, S-methylisothiosemicarbazones, X-ray diffraction analysis

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INTRODUCTION

Transition metal complexes with Schiff bases with azomethine nitrogen donor atoms containing heterocyclic substituents attract considerable attention of researchers because of their unique properties and versatile applications in various fields [1].

The use of various diamine derivatives or dicarbonyl compounds in which the terminal groups are identical in functional properties as the initial blocks gives rise to various symmetrical systems. The use of hydrazine derivatives such as thio- and semicarbazides, thio- and semicarbazones, and S-alkylated thiosemicarbazones may afford asymmetric systems belonging to open-ring Schiff bases [2–11]. These compounds exhibit various biological activities, including antiviral, cytostatic, antibacterial, anticancer, and antifungal activities and catalytic activity towards a wide range of compounds [2].

It is also known that transition metal complexes based on quinoline derivatives (in particular, quinoline carboxaldehydes) exhibit bactericidal, insecticidal, fungicidal, and antitumor properties [12–15]. A combination of two active moieties, thiosemicarbazone or S-alkylisothiosemicarbazone ones, with a quinoline moiety in one molecule appears promising for the preparation of biologically active compounds. There are a number of known 3*d*-metal complexes based on semi- and thiosemicabazones of 8-quinolinecarboxaldehyde and its structurally diverse derivatives [10, 11, 16–19], including complexes able to inhibit cancer cell growth, which may allow, in the future, the use of these compounds as antitumor agents [10, 19]. Study of coordination compounds containing 8-quinolinecarboxaldehyde thiosemicarbazone [10, 16–18, 20–24] has shown that the nature of the anion and substituents in the chalcogen semicarbazide moiety of the ligand influences the composition and structure of the complexes. Thus, it is of interest to study asymmetric systems of transition metal complexes based on S-alkylisothiosemicarbazones of various β-diketones and quinolinecarboxaldehydes, which have diverse structures and useful properties.

This paper describes procedures for the synthesis and results of studies of four new asymmetric mononuclear nickel(II) and copper(II) complexes, $[NiL^1]I$ (**I**), $[CuL^1I]$ (**II**), $[NiL^2]I$ (**III**), and $[CuL^2I]$ (**IV**), with ligands obtained by the reaction of acetyl- or benzoylacetone S-methylisothiosemicarbazone hydroiodide with 8-quinolinecarboxaldehyde.

EXPERIMENTAL

Sigma Aldrich commercial chemicals (including solvents) were used as received: thiosemicarbazide (99%), methyl iodide (≥99.0% (GC)) 1,4-pentanedione (acetylacetone) (≥99%), 1-phenyl-1,3-butanedione (benzoylacetone) (99%), 8-quinolinecarboxaldehyde (≥97%), nickel(II) acetate tetrahydrate (≥98%), copper(II) acetate monohydrate (≥98%), methanol (99.8%), and triethylamine (≥99%). S-Methylthiosemicarbazide hydroiodide was prepared by a reported procedure [25], and acetyl- and benzoylacetone S-methylisothiosemicarbazone hyd-roiodides were obtained by known procedures [26, 27].

Synthesis of [NiL^1]I (I). A solution of $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.25 g, 1 mmol) in methanol (10 mL) and triethylamine (5 mL) were added to a warm (55–60°C) solution containing acetylacetone S-methylisothiosemicarbazone hydroiodide (0.32 g, 1 mmol) and 8-quinolinecarboxaldehyde (1.6 g, 1 mmol) in methanol (20 mL). The resulting brown reaction mixture was heated at reflux at 60 – 65°C for 20 min. On cooling, a dark brown crystalline solid precipitated, which was collected on a filter and washed with methanol and then with diethyl ether. The yield was ~77% (0.39 g). T_m > 360°C. pESI MS molecular ion peak: m/z = 383 $[M-I]^+$ (I, 100%).

For $C_{17}H_{17}N_4SOINi$ (M = 510.99)

Anal. calcd., %	C, 39.92	H, 3.32	N, 10.96
Found, %	C, 39.58	H, 3.30	N, 10.78

IR (ν, cm^{-1}): 3468 m, 3405 m, 3107 m, 3056 m, 3032 m, 2991 m, 2909 m, 2005 m, 1871 m, 1611 m, 1585 s, 1571 s, 1550 s, 1520 m, 1505 s, 1465 sh, 1449 s, 1423 s, 1400 w, 1376 sh, 1364 vs, 1320 m, 1314 m, 1294 m, 1270 s, 1244 m, 1223 m, 1183 s, 1146 vs, 1110 s, 1062 w, 1042 w, 1021 m, 1001 m, 979 w, 971 m, 957 w, 941 m, 923 m, 862 m, 843 s, 811 m, 793 s, 776 vs, 723 w, 703 w, 659 w, 639 w, 587 w, 549 w, 516 w, 444 vw.

Synthesis of [CuL^{1}I] (II). A solution of $Cu(CH_3COO)_2 \cdot H_2O$ (0.25 g, 1 mmol) in methanol (10 mL) and triethylamine (5 mL) were added to a warm (55–60°C) solution containing acetylacetone S-methylisothiosemicarbazone hydroiodide (0.32 g, 1 mmol) and 8-quinolinecarboxaldehyde (1.6 g, 1 mmol) in methanol (20 mL). The resulting brown reaction mixture was heated at reflux at 60–65°C for 60 min. On cooling, a dark brown solid precipitated, which was collected on a filter and washed with methanol and diethyl ether. The yield was ~67% (0.35 g). T_m = 192–194°C. pESI MS molecular ion peak: m/z = 388 $[M-I]^+$ (I, 100%).

For $C_{17}H_{17}N_4SOICu$ (M = 515.85)

Anal. calcd., %	C, 39.58	H, 3.32	N, 10.86
Found, %	C, 38.78	H, 3.27	N, 10.78

IR (ν, cm^{-1}): 3090 vw, 3063 m, 3036 m, 3000 m, 2917 m, 2841w, 2390 w, 2190 w, 1985 w, 1617 m, 1588 s, 1576 s, 1551 s, 1528 vs, 1514 sh, 1483 s, 1444 sh, 1426 s, 1370 s, 1358vs, 1320 m, 1302 s, 1272 m, 1262 s, 1241 s, 1218 m, 1205 m, 1180 w, 1157 vs, 1107 sh, 1100 s, 1094 sh, 1052 m, 1038 w, 1014 sh, 1004 s, 990 sh, 969 m, 954 w, 945 m, 923 m, 917 s, 844 sh, 836 s, 812 m, 788 s, 768 vs, 646 m, 614 m, 564 m, 540 w, 506 w, 496 m, 469 w, 431 w.

Synthesis of [NiL^2]I (III). A solution of $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.25 g, 1 mmol) in methanol (10 mL) and triethylamine (5 mL) were added to a warm (55–60°C) solution containing benzoylacetone S-methylisothiosemicarbazone hydroiodide (0.38 g, 1 mmol) and 8-quinolinecarboxaldehyde (1.6 g, 1 mmol) in methanol (20 mL). The resulting brown reaction mixture was heated at reflux at 60–65°C for 20 min. On cooling, a dark brown solid precipitated, which was collected on a filter and washed with methanol and then with diethyl ether. The yield was ~50% (0.29 g). T_m = 139–142°C. pESI MS molecular ion peak: m/z = 445 $[M-I]^+$ (I, 100%).

For $C_{22}H_{19}N_4SOINi$ (M = 573.05)

Anal. calcd., %	C, 46.11	H, 3.71	N, 10.86
Found, %	C, 45.98	H, 3.50	N, 10.79

IR (ν, cm^{-1}): 3115 w, 3087 w, 3056 w, 3028 w, 2980 w, 2923 m, 2890 w, 2873 w, 2813 w, 1672 br.w., 1624 w, 1598 m, 1585 m, 1565 m, 1521 vs, 1499 vs, 1487 vs, 1463 sh, 1453 m, 1428 s, 1399 vs, 1386 s, 1372 m, 1312 m, 1303 s, 1291 m, 1250 m, 1223 vw, 1207 w, 1185 m, 1177 m, 1167 m, 1140 m, 1112 m, 1097 m, 1089 m, 1079 m, 1049 vs, 1034 sh, 999 vw, 981 m, 970 m, 930 s, 918 m, 897 m, 876 s, 852 m, 822 s, 799 m, 776 vs, 764 vs, 720 w, 708 w, 690 vs, 677 s, 659 m, 650 m, 641 m, 630 vw, 611 m, 586 m, 559 vw, 530 m, 523 w, 507 w, 463 m, 432 m, 420 m.

Synthesis of [CuL^{2}I] (IV). A solution of $Cu(CH_3COO)_2 \cdot H_2O$ (0.25 g, 1 mmol) in methanol (10 mL) and triethylamine (5 mL) were added to a warm (55–60°C) solution containing benzoylacetone S-methylisothiosemicarbazone hydroiodide (0.38 g, 1 mmol) and 8-quinolinecarboxaldehyde (1.6 g, 1 mmol) in methanol (20 mL). The resulting brown reaction mixture was heated at reflux at 60–65°C for 60 min. On cooling, a dark brown solid precipitated, which was collected on a filter and washed with methanol and then with diethyl ether. The yield was ~50% (0.29 g). T_m = 158–160°C. pESI MS molecular ion peak: m/z = 450 $[M-I]^+$ (I, 100%).

For $C_{22}H_{19}N_4SOICu$ (M = 577.92)

Anal. calcd., %	C, 45.11	H, 3.01	N, 9.46
Found, %	C, 45.72	H, 3.31	N, 9.69

IR (ν, cm^{-1}): 3600–3200 br.w, 3055 m, 2925 m, 2587 br.w, 2315 m, 2030 br.w, 1972 br.w, 1622 s, 1586 s, 1567 s, 1534 m, 1509 s, 1482 vs, 1449 s, 1427 s, 1395 sh, 1379 vs, 1364 vs, 1334 sh, 1303 vs, 1288 sh, 1243 m, 1202 m, 1172 m, 1158 s, 1139 m, 1110 m, 1084 m, 1047 s, 1028 m, 1022 w, 985 w, 971 m, 929 m, 916 m, 896 m, 870 m, 837 m, 823 m, 799 m, 781 m, 771 s, 761 m, 716 m, 694 s, 652 m, 641 m, 581 w, 578 w, 539 w, 522 vw, 485 w, 472 w, 456 w, 424 w, 417 w.

The composition of the complexes was determined on the basis of elemental analysis, IR spectroscopy, and X-ray diffraction data; the structure of complexes was studied by mass spectrometry, IR spectroscopy, and X-ray diffraction.

IR spectra were recorded on an FT-IR Perkin-Elmer Spectrum 100 instrument in mineral oil in the 4000–400 cm^{-1} range or (ATR) in the 4000–650 cm^{-1} range.

Mass spectrometric analysis was performed on a Finningan LTQ mass spectrometer with a linear ion trap and electrospray ionization (ESI) (positive ion mode). The solutions were injected into the electrospray ion source with a syringe pump at a flow rate of 0.01 mL/min. The data were collected and processed using MassHunter Workstation Data Acquisition software for the 6200/6500 series, version B.01.03.

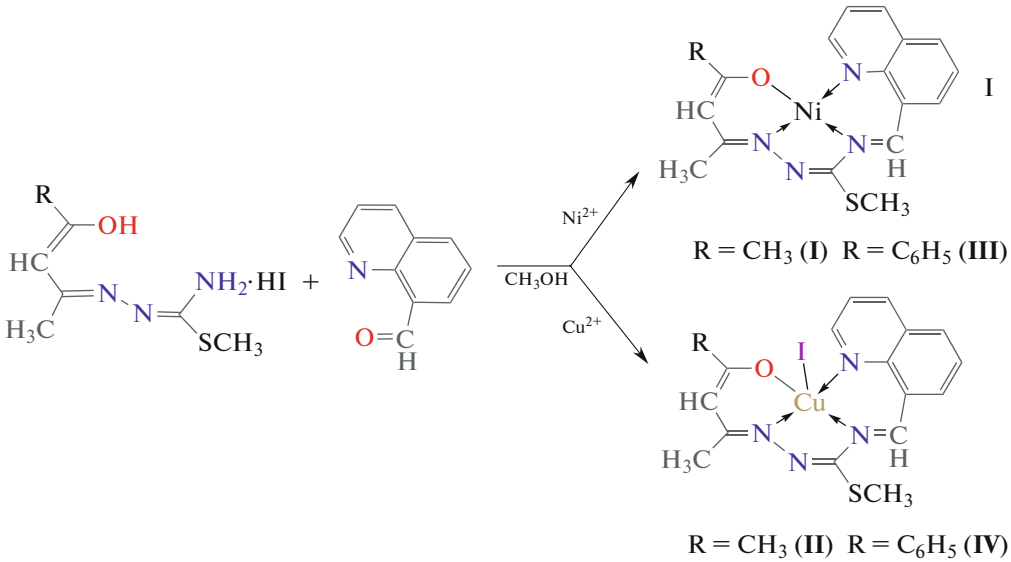
The melting points were measured on a Kofler hot stage microscope with a rheostat.

X-ray diffraction analysis of complexes **I** and **II** was carried out at room temperature on a Xcalibur E diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator, and ω-scan mode). The unit cell parameters were refined taking account of the full set of experimental data. The experimental data for **II** were integrated considering the non-merohedral twinning for the sample and refined with the contribution of 0.5639(6) and 0.4361(6) components. Although the X-ray diffraction pattern for **I** did not reveal a clear-cut twinning of the crystal, the two highest peaks in the electron density difference maps corresponded to the possible second position of the heaviest Ni and S atoms of the complex cation in 0.08 : 0.92 ratio to the major peak, while all other peaks had background values. The crystal structures were solved by the direct methods and refined by the least-squares method in the full-matrix anisotropic approximation for non-hydrogen atoms using the SHELXS-97 and SHELXL14 software [28, 29]. The hydrogen atom positions were calculated geometrically and refined isotropically in a rigid-body model. Crystallographic data and X-ray experiment details for compounds **I** and **II** are summarized in Table 1; selected interatomic distances and bond angles are listed in Table 2, and geometric parameters of hydrogen bonds are in Table 3.

The positional and thermal parameters of atoms for complexes **I** and **II** and X-ray experiment and structure refinement details are deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 2266386, 2266387) deposit@ccdc.cam.ac.uk or http://www. ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

In order to expand the range of coordination compounds based on thiosemicarbazide derivatives and 8-quinolinecarboxaldehyde, we prepared and studied four new mononuclear nickel(II) and copper(II) complexes with asymmetric tetradentate [N_3O] ligands (HL^1 and HL^2), formed upon the reaction of acetyl(benzoyl)acetone S-methylisothiosemicarbazone with 8-quinolinecarboxaldehyde, namely, $[NiL^1]I$ (**I**), $[CuL^1I]$ (**II**), $[NiL^2]I$ (**III**), and $[CuL^2I]$ (**IV**), respectively (Scheme 1). Unlike the previously studied compounds, the quinolinecarboxaldehyde moiety in **I**–**IV** is attached to the amide nitrogen atom of the isothiosemicarbazide moiety of the ligand rather than to the hydrazide atom.



Scheme 1. Synthesis of complexes **I**–**IV**.

Table 1. Crystallographic data and X-ray diffraction experiment details for the structures of **I** and **II**

Parameter	Value	
	I	**II**
Molecular formula	$C_{17}H_{17}N_4OSINi$	$C_{17}H_{17}N_4OSICu$
M	510.01	515.84
System	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a, Å	7.2706(6)	8.6354(15)
b, Å	9.970(2)	16.137(3)
c, Å	11.7873(11)	13.623(2)
α, deg	116.960(10)	90
β, deg	92.475(8)	97.928(17)
γ, deg	93.467(7)	90
V, Å^3	930.06(17)	1880.3(6)
Z	2	4
ρ(calcd.), g/cm^3	1.825	1.822
μ, mm^{-1}	2.828	2.927
F(000)	504	1012
Crystal size, mm	0.12 × 0.06 × 0.02	0.26 × 0.15 × 0.02
θ Range, deg	3.256–25.049	2.925–25.003
Ranges of reflection indices	$-8 \le h \le 8$, $-14 \le k \le 10$, $-14 \le l \le 14$	$-10 \le h \le 9$, $-19 \le k \le 19$, $-15 \le l \le 16$
Number of measured /unique reflections (R_{int})	5480/3277 (0.0737)	5899/5899 (twin)
Completeness (%)	99.7	99.9
Number of reflections with $I > 2\sigma(I)$	1382	2415
Number of refined parameters	238	230
GOOF	0.913	0.801
R factor ($I > 2\sigma(I)$)	$R_1 = 0.0773$, $wR_2 = 0.0925$	$R_1 = 0.0473$, $wR_2 = 0.0474$
R factor (for the whole array)	$R_1 = 0.1950$, $wR_2 = 0.1197$	$R_1 = 0.1345$, $wR_2 = 0.0516$
$\Delta\rho_{max}/\rho_{min}$, e Å^{-3}	0.689/–0.754	1.181/–0.756

Table 2. Selected interatomic distances and bond angles in [NiL^1]I (**I**) and [CuL^{1}I] (**II**)

Bond	d, Å		Angle	ω, deg	
	I	**II**		**I**	**II**
M(1)–N(1)	1.928(9)	2.045(6)	N(1)MN(2)	94.8(5)	92.0(3)
M(1)–N(2)	1.849(12)	1.924(6)	N(1)MN(4)	175.5(4)	164.9(2)
M(1)–N(4)	1.781(9)	1.931(6)	N(1)MO(1)	89.3(4)	93.1(3)
M(1)–O(1)	1.770(9)	1.907(5)	N(1)MI(1)		94.25(16)
M(1)–I(1)		2.906(1)	N(2)MN(4)	82.8(5)	80.7(3)
			N(2)MO(1)	174.8(4)	168.3(3)
			N(2)MI(1)		89.63(17)
			N(4)MO(1)	93.3(4)	91.9(3)
			N(4)MI(1)		98.84(17)
			O(1)MI(1)		100.52(16)

Complexes **I**–**IV** were isolated as air-stable dark brown crystals, soluble in chloroform, DMF, and DMS and insoluble in alcohols, acetone, hexane, diethyl ether, and water.

The IR spectra of the products exhibited 7 to 9 weak and medium-intensity absorption bands in the 3400–2700 cm^{-1} range; the bands can be assigned to aromatic and aliphatic (including $C-CH_3$ and $S-CH_3$) ν(C–H) modes [30]. In the case of polycyclic systems such as complexes studied here, the number of absorption bands in this region increases [30].

In the IR spectra of Ni(II) and Cu(II) complexes with L^1 (**I**, **II**) and L^2 (**III**, **IV**), the ν(C=O) absorption band shifts to lower frequency: 1550 (**I**), 1521 (**II**), 1528 (**III**), and 1482 cm^{-1} (**IV**) [31]. This pronounced shift of the carbonyl absorption bands in the spectra of complexes **I**–**IV** to lower frequencies compared to these bands for β-diketones (1720 cm^{-1} in the keto form and 1650–1600 cm^{-1} in the enol form [31]) can be attributed, along with the coordination of the carbonyl group to the metal, also to the resonance between C–O–M and C=O→M upon coordination [30].

The ν(C=C) modes of the aromatic rings occur at 1611, 1585, 1505, 1449 (**I**); 1598, 1585, 1499, 1453 (**II**); 1617, 1588, 1514, 1444 (**III**), and 1622, 1586, 1509, 1449 cm^{-1} (**IV**). The absorption bands of the methyl groups, δ_{as}/δ_s ($C-CH_3$)/δ_s ($S-CH_3$), were observed at 1465/1376/1320 (**I**), 1463/1386/1312 (**II**), 1453/1370/1320 (**III**), and 1449/1379/1334 (**IV**) cm^{-1} [30]. The $\delta_{sh}(CH)_{arom}$ modes for 1,2,3-substitution were at 1146, 1110, 1021 (**I**); 1140, 1112, 1034 (**II**); 1180, 1107 sh, 1014 (**III**); and 1139, 1110, 1028 (**IV**) cm^{-1}. The $\delta_{out\text{-}of\text{-}plane}(CH)_{arom}$ absorption bands (three adjacent unsubstituted hydrogen atoms) were located at 776 (**I**), 776 (**II**), 768 (**III**), and 761 (**IV**) cm^{-1} [32, 33]. The absorption bands for the C–S–C vibrations were observed at 657 (**I**), 659 (**II**), 646 (**III**), and 652 (**IV**) cm^{-1} [30].

The bands for the ν(M–O) + δ($C-CH_3$) modes were detected at 444 (**I**) and 432 (**III**) cm^1 (M = Ni) and at 469 (**II**) and 456 (**IV**) (M = Cu) cm^{-1} [34].

The chemical composition of complexes **I**–**IV** was established on the basis of elemental analysis data and electron impact mass spectra of chloroform–methanol solutions of samples. The spectra showed the presence of a strong $[M-I]^+$ peak (100%) at m/z = 383, 445, 388, and 450, respectively, indicating the presence of iodine in the complexes. The absence of further fragmentation of ions in the mass spectra points to the high stability of these complexes.

The structural study identified the formation of an ionic compound consisting of a mononuclear complex cation and an outer-sphere anion [NiL^1I] (**I**) and a molecular complex [CuL^1I] (**II**).

Compound **I** crystallizes in the triclinic space group $P\bar{1}$ (Table 1) and consists of the $[NiL]^+$ complex cation with a square planar geometry of the central atom and the outer-sphere iodide anion. In the cation, the monodeprotonated tetradentate open-chain ligand is coordinated to the central atom through a set of N_3O donor atoms, thus forming three coupled metallacycles, two of which are six-membered and one is five-membered (Fig. 1) The Ni–N distances are in the range of 1.781(9)–1.928(9) Å, and Ni–O distances are 1.770(9) Å (Table 2). The complex cation is additionally stabilized by weak intramolecular hydrogen bonds: C(1)–H(1)···O(1) and C(10)–H(10)···S(1) (Table 3).

In the crystal, the iodide anions are linked to the cations by intermolecular C–H···I hydrogen bonds (Fig. 2), while the complex cations dimerize via weak Ni(1)···N(2)* interactions (the interatomic distance was 3.429 Å).

Compound **II** crystallizes in the monoclinic space group $P2_1/n$ as the molecular complex [CuLI] (Fig. 3). The square-pyramidal environment of the central metal atom involves the N_3O donor atoms of the open-chain tetradentate ligand, similar to that in **I**, located in the basis plane, while the iodide anion occupies the pyramid vertex. The Cu–N distances are 1.924(6)–2.045(6); the Cu–O distance is 1.907(5), and the Cu–I distance is 2.906(1) Å. The Cu(1) atom deviates from the plane through the four donor atoms of the ligand by 0.203 Å towards the coordinated iodide anion. The Cu(II) complex, like the Ni(II) complex, is stabilized by intramolecular hydrogen bonds: C(1)–H(1)···O(1) and C(10)–H(10)···S(1) (Table 3). In the crystal, the complexes are linked to one another only by weak intermolecular C–H···I hydrogen bonds (Fig. 4).

In both complexes, the organic ligand is deprotonated at the hydroxyl group, with the oxygen atom of this group being coordinated to the metal atoms. As a result, the chemical bond lengths in the metallacycles are partially aligned due to electron delocalization among the ring atoms [35], and the charge of –1 is common to the whole ring.

Thus, mononuclear compounds with new tetradentate open-chain ligands coordinated through the set of N_3O donor atoms were prepared by template condensation of acetyl(benzoyl)acetone S-methylisothiosemicarbazone and 8-quinolinecarboxaldehyde on the Ni(II) or Cu(II) template. A distinctive feature of these ligands is attachment of the quinolinecarboxaldehyde moiety to the terminal amide nitrogen atom

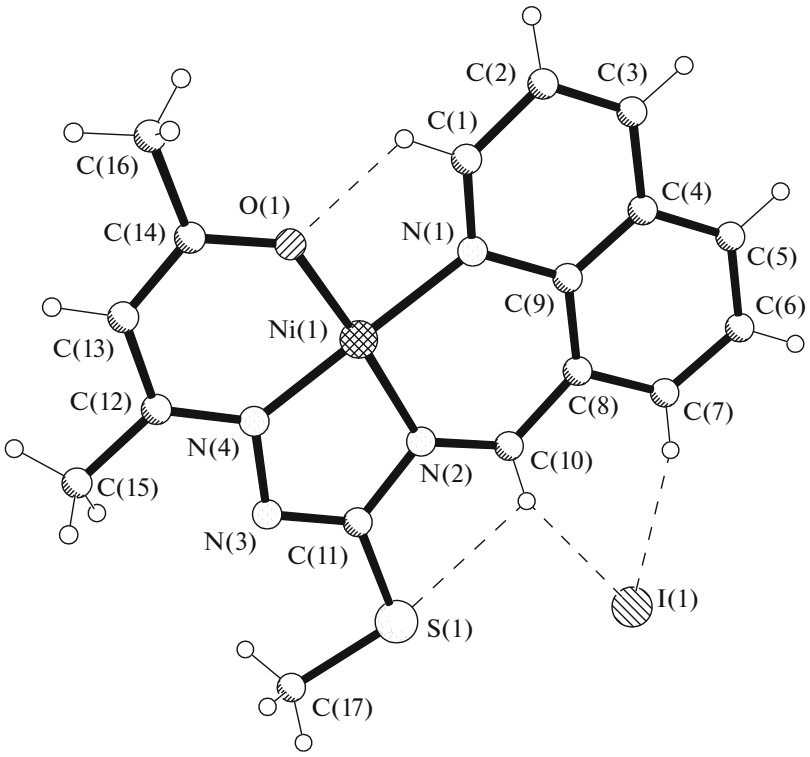


Fig. 1. Molecular structure of ionic complex **I**.

Table 3. Geometrical parameters of hydrogen bonds in compounds **I** and **II**

D–H···A contact	Distance, Å			DHA angle, deg	Coordinates of A atoms
	D–H	H···A	D···A		
			I		
C(1)–H(1)···O(1)	0.93	2.03	2.627(12)	120	x, y, z
C(2)–H(2)···I(1)	0.93	3.30	3.906(13)	125	$x, y-1, z$
C(3)–H(3)···I(1)	0.93	3.23	3.879(12)	129	$x, y-1, z$
C(7)–H(7)···I(1)	0.93	3.00	3.897(13)	162	x, y, z
C(10)–H(10)···I(1)	0.93	3.27	4.118(12)	153	x, y, z
C(10)–H(10)···S(1)	0.93	2.50	2.981(13)	112	x, y, z
C(16)–H(16C)···I(1)	0.96	3.18	4.130(10)	171	$-x+2, -y, -z+1$
			II		
C(1)–H(1)···O(1)	0.93	2.17	2.799(11)	124	x, y, z
C(10)–H(10)···S(1)	0.93	2.50	2.995(10)	113	x, y, z
C(7)–H(7)···I(1)	0.93	3.11	3.869(10)	140	$-x+3/2, y-1/2, -z+1/2$
C(17)–H(17A)···I(1)	0.96	3.22	4.057(7)	146	$-x+2, -y, -z$
C(17)–H(17B)···I(1)	0.96	3.06	4.014(7)	174	$x+1, y, z$

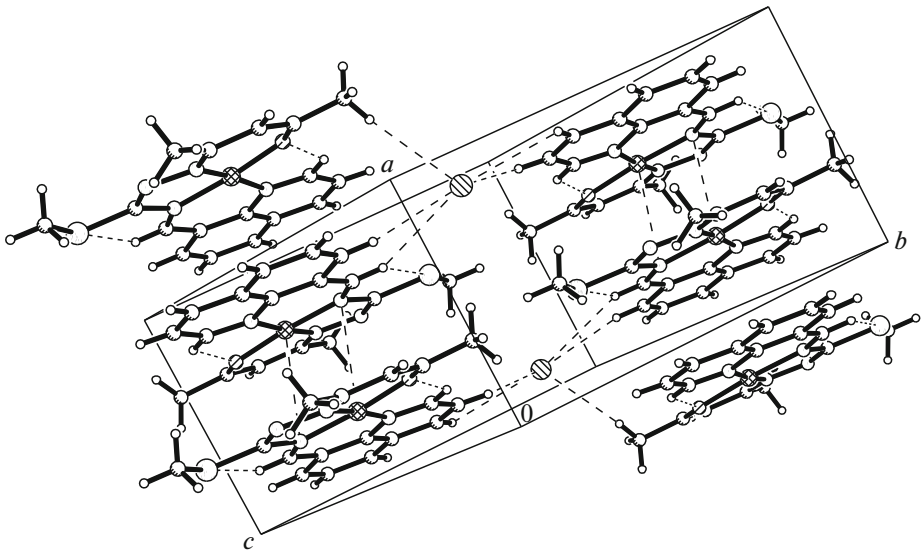


Fig. 2. Fragment of the component packing in **I**.

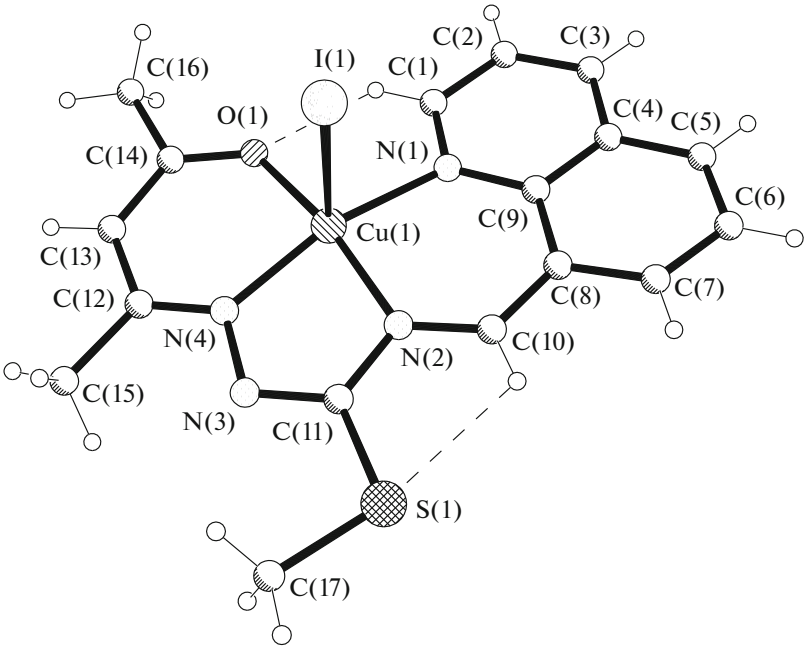


Fig. 3. Molecular structure of complex **II**.

of the isothiosemicarbazide moiety rather than to the hydrazide moiety. The Ni(II) complexes are ionic compounds with the outer-sphere iodide anion, while Cu(II) complexes are molecular compounds, with the iodide anion being coordinated to the metal atom. The proneness of these metal atoms to form characteristic coordination environments, that is, the square planar environment for Ni(II) and the square pyramidal one for Cu(II), accounts for the obtained types of structure for these complexes.

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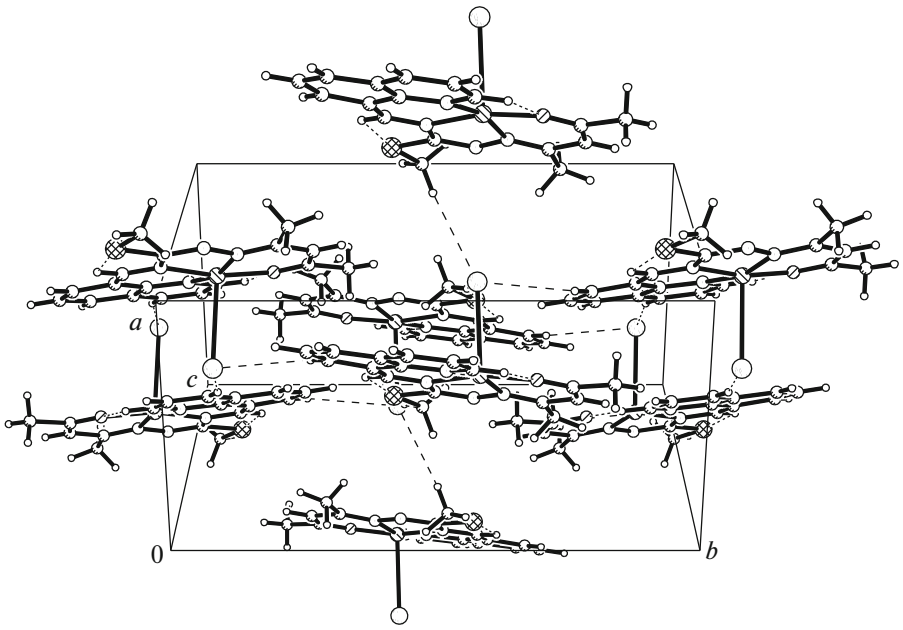

Fig. 4. Fragment of the crystal structure of **II**.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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