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# Cobalt(III) and Nickel(II) Complexes with 3-Hydroxyamino-3-Methylbutan-2-one Thiosemicarbazone: Synthesis and Structures

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**Abstract**—Condensation of 3-hydroxyamino-3-methylbutan-2-one with thiosemicarbazide afforded 3-hydroxyamino-3-methylbutan-2-one thiosemicarbazone as a new ligand ($H_2L$). Cobalt(III) and nickel(II) complexes with this ligand were obtained. The molecular formulas and structures of the thiosemicarbazone and the complexes $[Co(HL)_2]Cl \cdot 2H_2O$ (**I**) and $[Ni(H_2L)_2]Cl_2 \cdot 2.25H_2O$ (**II**) were confirmed by elemental analysis, IR spectroscopy, and X-ray diffraction (CIF files CCDC nos. 985065 ($H_2L$), 985066 (**I**), and 985067 (**II**)). The crystal structures of the ligand $H_2L$ and complexes **I** and **II** were determined. The way in which the ligand is coordinated to the metal ions, its conformational changes upon the complexation, and the packing patterns in the crystals of $H_2L$, **I**, and **II** are discussed.

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## INTRODUCTION

Transition metal complexes with chalcosemicarbazide $H_2N{-}NH{-}C(=S/Se){-}NH_2$ and its derivatives are well studied [1–4]. An analysis of the Cambridge Structural Database [5] has revealed that chalcosemicarbazones (Schiff bases) prepared by condensation of chalcosemicarbazides at the hydrazine N atom with various aldehydes and ketones can coordinate to transition metals (including Ni(II) and Co(III)) as monodentate [6, 7], bidentate [8–11], and tridentate ligands [12–17]. Dicarbonyl compounds are also known to react with chalcosemicarbazides, yielding ligands with two thio(seleno)semicarbazide fragments [18–22]. For instance, the synthesis of a Ni(II) complex with a macrocyclic ligand containing two thiosemicarbazide fragments has been reported [23]. In all these complexes, the ligands are coordinated through the chalcogen atom, most often along with the electron-donating N and O atoms of the other chelating groups. Because of this, thiosemicarbazide and its derivatives can be regarded as promising building blocks for the synthesis of novel polyfunctional organic compounds which will be used to obtain complexes with a broad spectrum of analytical and biological properties [24–26]. In complexation reactions, thiosemicarbazones show themselves as highly self-organizing species. They can vary their tautomeric form, deprotonation state, and set of electron-donating groups coordinating to the central metal atom, depending on the functional groups of a carbonyl component. This enables the synthesis of a variety of complexes differing in composition, structure, and properties.

In this study, we obtained 3-hydroxyamino-3-methylbutan-2-one thiosemicarbazone ($H_2L$) and its two complexes with Co(III) and Ni(II) and examined their structures by IR spectroscopy and X-ray diffraction.

## EXPERIMENTAL

**The ligand $H_2L$** was obtained according to a general procedure for carbazones. The synthesis involved condensation of 3-hydroxyamino-3-methylbutan-2-one with thiosemicarbazide in boiling ethanol with continuous stirring for 3 h. The product was recrystallized from ethanol. The yield of $H_2L$ was 65%, $T_m$ = 164–165°C.

IR (ν, $cm^{-1}$): 3673 w, 3415 m, 3242 s, 3196 s, 3154 s, 2971 vs, 2901 s, 1599 vs, 1506 vs, 1471 m, 1453 m, 1428 m, 1375 s, 1285 m, 1250 w, 1241 w, 1231 m, 1175 w, 1150 s, 1080 s, 1066 m, 1056 sh, 1047 sh, 1038 vs, 1021 sh, 990 w, 955 m, 938 w, 900 m, 854 s, 838 m, 748 w, 725 s, 711 sh, 696 sh.

| For $C_6H_{14}N_4OS$ | | | |
|---|---|---|---|
| anal. calcd., %: | C, 37.87; | H, 7.41; | N, 29.45. |
| Found, %: | C, 37.72; | H, 7.36; | N, 29.25. |

**Synthesis of $[Co(HL)_2]Cl \cdot 2H_2O$ (I).** A solution of $H_2L$ (0.38 g, 0.001 mol) in methanol (10 mL) was

added to a solution of $CoCl_2 \cdot 6H_2O$ (0.24 g, 0.001 mol) in water (10 mL). The reaction mixture was kept at 55–60°C for ~15 min. After a while, the resulting dark brown solution produced brown square plates soluble in water and methanol. Single crystals suitable for X-ray diffraction experiments were obtained by recrystallization from methanol. The yield of complex **I** was 0.36 g (65%).

IR (ν, $cm^{-1}$): 3416 m, 3256 s, 3160 vs, 2982 m, 2913 m, 2833 m, 1619 s, 1604 s, 1568 w, 1496 vs, 1467 s, 1442 sh, 1393 m, 1365 m, 1339 vs, 1290 m, 1201 w, 1162 s, 1124 m, 1072 m, 1046 m, 981 m, 952 m, 848 m, 784 m, 717 m, 688 w, 676 w, 655 w.

| For $C_{12}H_{30}N_8O_4S_2ClCo$ | | | | |
|---|---|---|---|---|
| anal. calcd., %: | C, 28.32; | H, 5.94; | N, 22.02; | Co, 11.58. |
| Found, %: | C, 28.20; | H,5.87; | N, 22.00; | Co, 11.78. |

**The complex $[Ni(H_2L)_2]Cl_2 \cdot 2.25H_2O$ (II)** was synthesized in a similar way from $NiCl_2 \cdot 4H_2O$. Single crystals suitable for X-ray diffraction experiments were obtained by recrystallization from methanol. The yield of complex **II** was 0.36 g (60%).

IR (ν, $cm^{-1}$): 3521 w, 3448 w, 3202 sh, 3145 vs, 3067 sh, 2979 m, 2886 m, 1627 s, 1602 m, 1552 vs, 1463 m, 1406 s, 1367 vs, 1282 s, 1237 m, 1207 m, 1156 sh, 1145 vs, 1100 m, 1083 m, 1027 m, 978 sh, 959 m, 943 w, 848 w, 823 w, 782 s, 731 m, 679 w. br.

| For $C_{12}H_{32.5}N_8O_{4.25}S_2Cl_2Ni$ | | | | |
|---|---|---|---|---|
| anal. calcd., %: | C, 26.17; | H, 5.95; | N, 20.35; | Ni, 10.66. |
| Found, %: | C, 26.12; | H, 5.98; | N, 20.22; | Ni, 10.91. |

**X-ray diffraction study.** Experimental reflection intensities were measured on Xcalibur (for $H_2L$ and **II**) and KUMA4 CCD diffractometers (for **I**) at 293 K (ω scan mode, Mo$K_\alpha$ radiation, λ = 0.71073 Å, graphite monochromator). Primary processing of the collected material for complex **I** was performed with the KUMA-Diffraction program (Wroclaw, Poland). The unit cell parameters for $H_2L$ and **II** were refined for all reflections. Selected crystallographic parameters and the data collection and refinement statistics for structures $H_2L$, **I**, and **II** are summarized in Table 1.

The crystal structures were solved by direct methods and refined by the least-squares method in the anisotropic full-matrix approximation for non-hydrogen atoms (SHELX-97) [27]. In complex **I**, the Cl atom is disordered over two positions with an occupancy factor of 0.5 (one position is in the center of symmetry). Both oxime O atoms of two coordinated monodeprotonated organic ligands $HL^-$ are disordered over two positions in a ratio of 0.5 : 0.5. Two of three water molecules are also disordered with occupancy factors of 0.5. The crystal of complex **II** is a twin crystal (BASF 0.55). The independent part of its unit cell contains four crystallographically independent complex $Ni^{2+}$ cations, eight $Cl^-$ anions, and nine water molecules (so 2.25 water molecules per Ni(II) complex); the latter occupy 13 positions. The positions of all hydrogen atoms in $H_2L$, in the crystallization water of complexes **I** and **II**, and in the functional =NH groups in complex **II** were determined in difference electron-density maps. The other H atoms were located geometrically and refined isotropically using a rigid body model. The bond lengths and bond angles in structures $H_2L$, **I**, and **II** are given in Table 2. The geometrical parameters of the hydrogen bonds are listed in Table 3. Atomic coordinates and thermal parameters for structures $H_2L$, **I**, and **II** have been deposited with the Cambridge Structural Database (nos. 985065, 985066, and 985067, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam. ac.uk).

## RESULTS AND DISCUSSION

The IR spectra of compounds containing the thiocarbonyl group is difficult to interpret because of a wide spectral range for the band of the C=S vibrations (850–1570 $cm^{-1}$), the strong effects of the atoms of adjacent chemical bonds, the possibility of thione ↔ thiol tautomerism, and other factors [28–30]. Apparently, such a wide range indicates a variety of differently interacting vibrations [31]. In the spectra of compounds in which the C=S group is bound to one or two N atoms, three bands are attributable to the vibrations of the –N–C=S fragment [28]: at 1395–1570 (–N–C=S (**I**)), 1260–1420 (–N–C=S (**II**)), and 940–1140 $cm^{-1}$ (–N–C=S (**III**)). These bands can be used for qualitative spectral analysis. In the spectrum of thiourea, similar bands appear at 1472, 1415, and 1086 $cm^{-1}$ and are considered to be contributed by the δ($NH_2$), ν(C–N), and ν(C=S) vibrations. The band at 730 $cm^{-1}$ can be assigned to the δ(NCS) vibrations [28].

The IR spectrum of the free ligand $H_2L$ shows absorption bands at 3673 (probably associated ν(OH)), 3415 and 3242 $cm^{-1}$ ($\nu_{as}(NH_2)$ and $\nu_s(NH_2)$, respectively), 3196 and 3154 (ν(NH) of secondary amine), 1599 (ν(C=N) + δ(NH)), and 1506 $cm^{-1}$ (ν(C–N)) [32]. The medium-intensity band at 1231 $cm^{-1}$ can be due to ν(C=S) [33, 34]. The bands at 1471, 1407, 1080, and 725 $cm^{-1}$ are attributable to δ(NH), ν(C–N), ν(C=S), and δ(NCS), respectively [28].

In the IR spectra of the cobalt and nickel complexes, the absorption bands $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ appear at nearly the same positions as in the spectra of the free ligand (3416 and 3256 against 3448 and 3202 $cm^{-1}$, respectively). This indicates that the

**Table 1.** Crystallographic parameters and the data collection and refinement statistics for structures $H_2L$, **I**, and **II**

| Parameter | Value | | |
|---|---|---|---|
| | $H_2L$ | **I** | **II** |
| $M$ | 190.27 | 508.94 | 550.69 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ | $C2/c$ | $Cc$ |
| Unit cell parameters: | | | |
| $a$, Å | 6.4720(5) | 31.963(6) | 16.7441(4) |
| $b$, Å | 8.6723(8) | 11.845(2) | 16.7051(3) |
| $c$, Å | 8.8594(8) | 11.531(2) | 35.4206(11) |
| α, deg | 104.174(8) | 90 | 90 |
| β, deg | 95.727(6) | 99.16(3) | 97.240(2) |
| γ, deg | 91.578(7) | 90 | 90 |
| $V$, Å$^3$ | 479.02(7) | 4310(2) | 9828.6(4) |
| $Z$ | 2 | 8 | 16 |
| $\rho_{calcd}$, g/cm$^3$ | 1.319 | 1.569 | 1.489 |
| μ, mm$^{-1}$ | 0.301 | 1.150 | 1.212 |
| $F$(000) | 204 | 2128 | 4616 |
| Crystal dimensions, mm | 0.20 × 0.20 × 0.10 | 0.30 × 0.30 × 0.10 | 0.35 × 0.25 × 0.20 |
| θ scan range, deg | 3.17–25.50 | 3.58–25.50 | 2.84–25.50 |
| Ranges of $h$, $k$, and $l$ indices | $-5 \le h \le 7$, $-10 \le k \le 10$, $-10 \le l \le 9$ | $-38 \le h \le 38$, $-10 \le k \le 14$, $-13 \le l \le 13$ | $-20 \le h \le 8$, $-18 \le k \le 20$, $-42 \le l \le 42$ |
| Number of measured/unique reflections ($R_{int}$) | 3186/1776 (0.0201) | 11116/3991 (0.0416) | 17987/11764 (0.0247) |
| Number of reflections with $I > 2\sigma(I)$ | 1444 | 3515 | 10395 |
| Number of parameters refined | 129 | 286 | 1136 |
| Completeness (θ = 25.50°), % | 99.8 | 99.6 | 99.8 |
| GOOF | 1.009 | 1.005 | 1.004 |
| $R$ factor ($I > 2\sigma(I)$) | $R_1 = 0.0488$, $wR_2 = 0.1452$ | $R_1 = 0.0671$, $wR_2 = 0.2289$ | $R_1 = 0.0502$, $wR_2 = 0.1230$ |
| $R$ factor (for all reflections) | $R_1 = 0.0607$, $wR_2 = 0.1582$ | $R_1 = 0.0755$, $wR_2 = 0.2379$ | $R_1 = 0.0583$, $wR_2 = 0.1284$ |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$, $e$ Å$^{-3}$ | 0.455, –0.438 | 0.749, –0.666 | 0.837, –0.716 |

**Table 2.** Bond lengths *d* and bond angles ω in structures $H_2L$, **I**, and **II**

| Coordination polyhedra | | | | | |
|---|---|---|---|---|---|
| Bond | *d*, Å | | | | |
| | **I** (M = Co) | **II** (M = Ni) | | | |
| | | 1 | 2 | 3 | 4 |
| M(1)–S(1*A*) | 2.220(2) | 2.396(2) | 2.423(2) | 2.408(2) | 2.399(2) |
| M(1)–N(3*A*) | 1.889(6) | 2.026(6) | 2.006(6) | 2.018(6) | 2.006(6) |
| M(1)–N(4*A*) | 1.972(7) | 2.128(7) | 2.148(7) | 2.144(6) | 2.146(6) |
| M(1)–S(1*B*) | 2.228(2) | 2.442(2) | 2.437(2) | 2.435(2) | 2.444(2) |
| M(1)–N(3*B*) | 1.895(6) | 2.016(6) | 2.031(6) | 2.014(6) | 2.017(6) |
| M(1)–N(4*B*) | 1.979(7) | 2.092(7) | 2.102(6) | 2.099(6) | 2.103(6) |
| Angle | ω, deg | | | | |
| | **I** (M = Co) | **II** (M = Ni) | | | |
| | | 1 | 2 | 3 | 4 |
| S(1*A*)M(1)N(3*A*) | 85.8(2) | 83.0(2) | 83.6(2) | 83.0(2) | 83.2(2) |
| S(1*A*)M(1)N(4*A*) | 169.3(2) | 160.5(2) | 161.2(2) | 161.3(2) | 161.7(2) |
| S(1*A*)M(1)S(1*B*) | 90.6(1) | 91.49(9) | 92.91(8) | 92.36(8) | 92.37(8) |
| S(1*A*)M(1)N(3*B*) | 95.3(2) | 103.3(2) | 103.7(2) | 103.9(2) | 102.2(2) |
| S(1*A*)M(1)N(4*B*) | 91.4(2) | 93.5(2) | 93.0(2) | 91.0(2) | 94.6(2) |
| N(3*A*)M(1)N(4*A*) | 83.5(3) | 77.6(3) | 77.6(2) | 78.3(2) | 78.6(2) |
| N(3*A*)M(1)S(1*B*) | 96.3(2) | 102.5(2) | 101.5(2) | 101.1(2) | 102.4(2) |
| N(3*A*)M(1)N(3*B*) | 177.6(3) | 172.4(3) | 171.8(3) | 172.0(2) | 173.2(2) |
| N(3*A*)M(1)N(4*B*) | 94.6(3) | 97.9(3) | 98.3(3) | 98.2(3) | 98.6(2) |
| N(4*A*)M(1)S(1*B*) | 90.6(2) | 91.2(2) | 91.0(2) | 91.2(2) | 90.7(2) |
| N(4*A*)M(1)N(3*B*) | 95.3(3) | 96.2(3) | 95.1(2) | 94.7(3) | 96.1(2) |
| N(4*A*)M(1)N(4*B*) | 89.5(3) | 90.7(3) | 89.6(2) | 91.7(2) | 89.1(3) |
| S(1*B*)M(1)N(3*B*) | 85.8(2) | 81.9(2) | 82.1(2) | 82.9(2) | 81.7(2) |
| S(1*B*)M(1)N(4*B*) | 169.1(2) | 159.4(2) | 159.9(2) | 160.7(2) | 158.6(2) |
| N(3*B*)M(1)N(4*B*) | 83.3(3) | 77.5(2) | 77.8(2) | 77.8(2) | 77.0(2) |

Free $H_2L$ molecule and the coordinated ligands $HL^-$ and $H_2L$

| Bond | *d*, Å | | | | | |
|---|---|---|---|---|---|---|
| | $H_2L$ | **I** | **II** | | | |
| | | | 1 | 2 | 3 | 4 |
| S(1*A*)–C(1*A*) | 1.685(3) | 1.728(8) | 1.703(8) | 1.673(8) | 1.696(9) | 1.696(8) |
| N(1*A*)–C(1*A*) | 1.309(4) | 1.345(10) | 1.317(10) | 1.339(10) | 1.32(1) | 1.311(10) |
| N(2*A*)–C(1*A*) | 1.356(3) | 1.277(10) | 1.35(1) | 1.33(1) | 1.354(10) | 1.350(9) |
| N(2*A*)–N(3*A*) | 1.381(3) | 1.396(9) | 1.382(9) | 1.411(9) | 1.368(9) | 1.372(8) |
| N(3*A*)–C(2*A*) | 1.271(3) | 1.304(10) | 1.296(10) | 1.259(9) | 1.288(9) | 1.304(9) |
| N(4*A*)–C(3*A*) | 1.486(3) | 1.539(10) | 1.50(1) | 1.508(10) | 1.502(10) | 1.519(10) |
| N(4*A*)–O(1*A*) | 1.444(3) | 1.42(1)/1.37(2) | 1.436(9) | 1.442(9) | 1.422(9) | 1.462(9) |
| S(1*B*)–C(1*B*) | 1.685(3) | 1.747(8) | 1.711(8) | 1.679(9) | 1.702(9) | 1.687(9) |
| N(1*B*)–C(1*B*) | 1.309(4) | 1.36(1) | 1.31(1) | 1.34(1) | 1.334(10) | 1.327(10) |
| N(2*B*)–C(1*B*) | 1.356(3) | 1.25(1) | 1.337(10) | 1.367(10) | 1.32(1) | 1.34(1) |
| N(2*B*)–N(3*B*) | 1.381(3) | 1.385(9) | 1.377(8) | 1.371(9) | 1.395(8) | 1.380(9) |
| N(3*B*)–C(2*B*) | 1.271(3) | 1.298(10) | 1.300(9) | 1.262(9) | 1.270(9) | 1.296(10) |
| N(4*B*)–C(3*B*) | 1.486(3) | 1.519(10) | 1.506(10) | 1.490(10) | 1.518(10) | 1.474(10) |
| N(4*B*)–O(1*B*) | 1.444(3) | 1.36(2)/1.40(2) | 1.423(9) | 1.443(9) | 1.445(8) | 1.427(8) |

**Table 2.** (Contd.)

| Angle | ω, deg | | | | | |
|---|---|---|---|---|---|---|
| | $H_2L$ | **I** | **II** | | | |
| | | | 1 | 2 | 3 | 4 |
| O(1*A*)N(4*A*)C(3*A*) | 109.7(2) | 114.0(8)/ 115.1(10) | 112.4(7) | 112.8(6) | 113.5(6) | 111.0(6) |
| N(1*A*)C(1*A*)N(2*A*) | 116.4(2) | 118.8(7) | 116.4(8) | 114.4(8) | 115.7(8) | 115.6(7) |
| N(1*A*)C(1*A*)S(1*A*) | 123.6(2) | 117.2(6) | 121.4(7) | 121.1(7) | 121.9(6) | 122.0(6) |
| N(2*A*)C(1*A*)S(1*A*) | 119.9(2) | 124.1(6) | 122.2(6) | 124.4(6) | 122.3(6) | 122.3(6) |
| C(1*A*)N(2*A*)N(3*A*) | 117.5(2) | 113.6(6) | 119.3(7) | 118.9(7) | 119.3(7) | 119.0(6) |
| C(2*A*)N(3*A*)N(2*A*) | 119.0(2) | 118.9(6) | 118.7(7) | 119.2(7) | 119.4(6) | 118.9(6) |
| N(3*A*)C(2*A*)C(3*A*) | 116.2(2) | 116.3(7) | 115.5(7) | 117.0(7) | 117.3(7) | 116.5(7) |
| N(3*A*)C(2*A*)C(6*A*) | 125.0(2) | 125.1(8) | 123.9(8) | 124.3(7) | 122.8(7) | 122.9(7) |
| N(4*A*)C(3*A*)C(2*A*) | 110.4(2) | 107.0(6) | 109.3(7) | 108.7(6) | 109.5(6) | 109.2(6) |
| N(4*A*)C(3*A*)C(4*A*) | 105.0(2) | 107.9(7) | 107.3(8) | 112.1(6) | 106.3(7) | 107.4(7) |
| N(4*A*)C(3*A*)C(5*A*) | 107.4(2) | 110.1(7) | 112.5(8) | 106.2(7) | 111.5(7) | 112.6(8) |
| O(1*B*)N(4*B*)C(3*B*) | | 112.6(8)/117.2(10) | 112.0(6) | 110.1(6) | 109.8(5) | 113.4(6) |
| N(1*B*)C(1*B*)N(2*B*) | | 119.7(8) | 117.4(8) | 113.9(8) | 117.4(8) | 114.9(8) |
| N(1*B*)C(1*B*)S(1*B*) | | 115.7(7) | 121.9(7) | 123.3(7) | 119.6(7) | 122.4(7) |
| N(2*B*)C(1*B*)S(1*B*) | | 124.7(6) | 120.7(6) | 122.7(6) | 123.0(6) | 122.7(6) |
| C(1*B*)N(2*B*)N(3*B*) | | 114.1(7) | 121.2(6) | 119.1(7) | 120.4(7) | 119.3(7) |
| C(2*B*)N(3*B*)N(2*B*) | | 120.3(7) | 119.4(6) | 119.3(6) | 119.3(6) | 119.7(6) |
| N(3*B*)C(2*B*)C(3*B*) | | 117.8(7) | 116.3(7) | 116.7(6) | 115.4(6) | 117.3(7) |
| N(3*B*)C(2*B*)C(6*B*) | | 125.3(8) | 123.5(7) | 123.5(7) | 125.0(7) | 122.8(7) |
| N(4*B*)C(3*B*)C(2*B*) | | 106.4(6) | 107.6(6) | 107.2(6) | 107.7(6) | 107.2(6) |
| N(4*B*)C(3*B*)C(4*B*) | | 108.3(7) | 109.6(7) | 111.3(7) | 109.8(7) | 109.0(6) |
| N(4*B*)C(3*B*)C(5*B*) | | 110.6(7) | 110.3(7) | 110.4(7) | 110.1(6) | 111.1(7) |

**Table 3.** Geometrical parameters of the intra- and intermolecular hydrogen bonds in structures $H_2L$, **I**, and **II**

| Hydrogen bond D–H···A | Distance, Å | | | Angle DHA, deg | Coordinates of the atoms A |
|---|---|---|---|---|---|
| | D–H | H···A | D···A | | |
| | | | $H_2L$ | | |
| O(1)–H(1)···N(4) | 0.82(3) | 2.06(3) | 2.835(3) | 157(3) | $-x+1, -y+1, -z$ |
| N(1)–H(2)···S(1) | 0.81(2) | 2.63(2) | 3.443(3) | 176(3) | $-x, -y, -z+1$ |
| N(2)–H(1)···O(1) | 0.81(2) | 2.44(2) | 3.224(3) | 164(2) | $-x+1, -y, -z$ |
| N(4)–H(1)···S(1) | 0.84(3) | 2.79(3) | 3.548(2) | 152(2) | $-x+1, -y, -z$ |
| | | | **I** | | |
| O(1*AA*)–H(1)···Cl(2) | 0.82 | 2.20 | 2.98(1) | 160 | $-x, y, -z+3/2$ |
| O(1*AB*)–H(1)···O(2*w*) | 0.82 | 2.15 | 2.90(3) | 152 | $x, y, z$ |
| N(1*A*)–H(1)···O(1*w*) | 0.86 | 2.32 | 3.04(1) | 143 | $x, y, z$ |
| N(1*A*)–H(2)···Cl(1) | 0.86 | 2.41 | 3.251(7) | 166 | $x, y, z$ |
| N(2*A*)–H(1)···O(1*w*) | 0.86 | 2.05 | 2.84(1) | 153 | $x, y, z$ |
| O(1*BB*)–H(1)···S(1*A*) | 0.82 | 2.74 | 2.28(1) | 124 | $x, y, z$ |
| O(1*BA*)–H(1)···N(4*A*) | 0.82 | 1.99 | 2.65(2) | 138 | $x, y, z$ |
| N(1*B*)–H(1)···O(2*w*) | 0.86 | 2.26 | 3.02(2) | 148 | $-x, -y+1, -z+1$ |
| N(1*B*)–H(1)···Cl(2) | 0.86 | 2.68 | 3.539(10) | 174 | $-x, -y+1, -z+1$ |
| N(1*B*)–H(2)···O(3*w*) | 0.86 | 2.34 | 2.98(2) | 132 | $x, y, z-1$ |
| N(1*B*)–H(2)···Cl(2) | 0.86 | 2.53 | 3.357(10) | 162 | $x, y, z-1$ |
| N(1*B*)–H(2)···O(1*AB*) | 0.86 | 2.56 | 3.28(2) | 142 | $-x, y, -z+1/2$ |
| N(2*B*)–H(1)···O(2*w*) | 0.86 | 2.10 | 2.89(2) | 152 | $x, -y+1, z-1/2$ |
| N(2*B*)–H(1)···O(3*w*) | 0.86 | 2.49 | 3.14(2) | 133 | $x, -y+1, z-1/2$ |
| O(1*w*)–H(1)···O(1*BB*) | 0.85 | 1.91 | 2.76(2) | 179 | $x, -y, z-1/2$ |
| O(1*w*)–H(1)···N(4*B*) | 0.85 | 2.61 | 3.36(1) | 149 | $x, -y, z-1/2$ |
| O(1w)–H(2)···Cl(1) | 0.85 | 2.61 | 3.36(1) | 149 | $-x+1/2, y-1/2, -z+1/2$ |
| O(2*w*)–H(1)···O(3*w*) | 0.83 | 1.93 | 2.60(3) | 137 | $x, y, z$ |
| O(2*w*)–H(2)···O(1*AB*) | 0.82 | 2.14 | 2.90(3) | 154 | $x, y, z$ |
| O(2*w*)–H(2)···N(4*A*) | 0.82 | 2.58 | 3.24(2) | 138 | $x, y, z$ |
| O(3*w*)–H(1)···O(3*w*) | 0.87 | 2.41 | 3.17(4) | 146 | $-x, y, -z+3/2$ |
| O(3*w*)–H(1)···Cl(2) | 0.87 | 2.41 | 3.28(2) | 176 | $-x, y, -z+3/2$ |
| O(3*w*)–H(2)···O(1*AB*) | 0.85 | 2.45 | 3.30(3) | 179 | $-x, y, -z+3/2$ |
| | | | **II** | | |
| O(11*A*)–H(1)···Cl(2) | 0.82 | 2.34 | 3.092(7) | 153 | $x, y-1, z$ |
| N(11*A*)–H(1)···Cl(4) | 0.86 | 2.42 | 3.210(8) | 153 | $x, y, z$ |
| N(11*A*)–H(2)···O(10*w*) | 0.86 | 2.02 | 2.82(2) | 154 | $x, y, z$ |
| N(12*A*)–H(1)···Cl(4) | 0.83(9) | 2.42(9) | 3.176(7) | 153(8) | $x, y, z$ |
| N(14*A*)–H(1)···O(5*w*) | 0.87(2) | 2.19(2) | 3.06(1) | 178(8) | $x, -y+1, z+1/2$ |
| O(11*B*)–H(1)···Cl(3) | 0.82 | 2.35 | 3.115(7) | 155 | $x, y, z$ |
| N(11*B*)–H(1)···Cl(1) | 0.86 | 2.49 | 3.285(2) | 154 | $x+1/2, y-1/2, z$ |
| N(11*B*)–H(2)···O(3*w*) | 0.86 | 2.00 | 2.83(1) | 163 | $x, y, z$ |
| N(12*B*)–H(1)···Cl(1) | 0.87(2) | 2.46(4) | 3.253(7) | 152(7) | $x+1/2, y-1/2, z$ |
| N(14*B*)–H(1)···O(11*A*) | 0.85(2) | 2.04(6) | 2.726(10) | 137(8) | $x, y, z$ |
| O(21*A*)–H(1)···Cl(7) | 0.82 | 2.33 | 3.094(7) | 155 | $x, y-1, z$ |
| N(21*A*)–H(1)···Cl(6) | 0.86 | 2.45 | 3.231(9) | 152 | $x, y, z$ |
| N(21*A*)–H(2)···O(1*w*) | 0.86 | 2.09 | 2.940(10) | 170 | $x, y, z$ |
| N(22*A*)–H(1)···Cl(6) | 0.76(9) | 2.47(9) | 3.124(7) | 145(9) | $x, y, z$ |
| N(24*A*)–H(1)···O(6*w*) | 0.88(2) | 2.16(3) | 3.03(1) | 170(8) | $x, -y, z-1/2$ |
| O(21*B*)–H(1)···Cl(5) | 0.82 | 2.55 | 3.288(9) | 150 | $x+1/2, y-1/2, z$ |
| N(21*B*)–H(1)···Cl(8) | 0.86 | 2.49 | 3.284(9) | 154 | $x, y-1, z$ |
| N(21*B*)–H(2)···O(9*w*) | 0.86 | 1.94 | 2.77(1) | 161 | $x-1/2, y-1/2, z$ |
| N(22*B*)–H(1)···Cl(8) | 0.72(9) | 2.51(9) | 3.212(7) | 164(10) | $x, y-1, z$ |

**Table 3.** (Contd.)

| Hydrogen bond D–H···A | Distance, Å | | | Angle DHA, deg | Coordinates of the atoms A |
|---|---|---|---|---|---|
| | D–H | H···A | D···A | | |
| N(24*B*)–H(1)···O(21*A*) | 0.89(2) | 1.88(2) | 2.681(10) | 148(4) | *x*, *y*, *z* |
| O(31*A*)–H(1)···Cl(8) | 0.82 | 2.36 | 3.137(7) | 158 | *x* + 1/2, *y* − 1/2, *z* |
| N(31*A*)–H(1)···Cl(5) | 0.86 | 2.40 | 3.190(8) | 153 | *x*, *y*, *z* |
| N(31*A*)–H(2)···O(7*w*) | 0.86 | 1.97 | 2.81(1) | 165 | *x* − 1/2, *y* − 1/2, *z* |
| N(32*A*)–H(1)···Cl(5) | 0.77(9) | 2.40(9) | 3.119(7) | 156(9) | *x*, *y*, *z* |
| N(34*A*)–H(1)···O(8*w*) | 0.78(2) | 2.21(3) | 3.08(1) | 173(8) | *x*, *y*, *z* |
| O(31*B*)–H(1)···Cl(6) | 0.82 | 2.69 | 3.380(7) | 142 | *x*, *y*, *z* |
| N(31*B*)–H(1)···Cl(7) | 0.86 | 2.51 | 3.300(9) | 152 | *x*, *y*, *z* |
| N(31*B*)–H(2)···O(11*w*) | 0.86 | 1.98 | 2.78(1) | 155 | *x*, *y*, *z* |
| N(31*B*)–H(2)···O(12*w*) | 0.86 | 2.13 | 2.98(2) | 169 | *x*, *y*, *z* |
| N(32*B*)–H(1)···Cl(7) | 0.83(9) | 2.42(9) | 3.237(7) | 169(8) | *x*, *y*, *z* |
| N(34*B*)–H(1)···O(31*A*) | 0.73(8) | 2.08(8) | 2.751(9) | 153(9) | *x*, *y*, *z* |
| O(41*A*)–H(1)···Cl(1) | 0.82 | 2.28 | 3.068(7) | 163 | *x*, *y*, *z* |
| N(41*A*)–H(1)···Cl(3) | 0.86 | 2.40 | 3.176(7) | 151 | *x* + 1/2, *y* + 1/2, *z* |
| N(41*A*)–H(2)···O(1*w*) | 0.86 | 2.08 | 2.92(9) | 166 | *x* + 1/2, *y* + 1/2, *z* |
| N(42*A*)–H(1)···Cl(3) | 0.85(2) | 2.31(3) | 3.126(7) | 161(8) | *x* + 1/2, *y* + 1/2, *z* |
| N(44*A*)–H(1)···O(4*w*) | 1.00(8) | 2.04(8) | 3.01(1) | 162(7) | *x*, *y*, *z* |
| O(41*B*)–H(1)···Cl(4) | 0.82 | 2.30 | 3.104(7) | 165 | *x*, *y*, *z* |
| N(41*B*)–H(1)···Cl(2) | 0.86 | 2.48 | 3.280(9) | 154 | *x*, *y*, *z* |
| N(41*B*)–H(2)···O(2*w*) | 0.86 | 1.98 | 2.82(1) | 166 | *x*, *y*, *z* |
| N(42*B*)–H(1)···Cl(2) | 0.77(10) | 2.58(10) | 3.240(7) | 145(9) | *x*, *y*, *z* |
| N(44*B*)–H(1)···O(41*A*) | 0.84(8) | 2.03(8) | 2.689(9) | 135(7) | *x*, *y*, *z* |
| O(1*w*)–H(1)···Cl(4) | 0.84 | 2.38 | 3.159(7) | 154 | *x*, *y*, *z* |
| O(1*w*)–H(2)···Cl(5) | 0.83 | 2.44 | 3.134(8) | 142 | *x*, *y*, *z* |
| O(2*w*)–H(1)···Cl(1) | 0.95 | 2.20 | 3.142(9) | 173 | *x* + 1/2, *y* + 1/2, *z* |
| O(2*w*)–H(2)···S(31*B*) | 1.05 | 2.45 | 3.505(10) | 178 | *x* + 1/2, −*y* + 3/2, *z* + 1/2 |
| O(3*w*)–H(1)···S(21*B*) | 1.05 | 2.44 | 3.491(9) | 180 | *x* + 1/2, −*y* + 1/2, *z* + 1/2 |
| O(3*w*)–H(2)···Cl(2) | 0.93 | 2.18 | 3.113(9) | 179 | *x* + 1/2, *y* − 1/2, *z* |
| O(4*w*)–H(1)···O(3*w*) | 0.85 | 2.50 | 3.356(2) | 180 | *x* − 1/2, *y* + 1/2, *z* |
| O(4*w*)–H(2)···Cl(8) | 0.96 | 2.24 | 3.205(9) | 179 | *x* + 1/2, −*y* + 3/2, *z* + 1/2 |
| O(5*w*)–H(1)···Cl(7) | 0.85 | 2.39 | 3.242(9) | 179 | *x*, *y*, *z* |
| O(5*w*)–H(2)···O(2*w*) | 0.85 | 2.49 | 3.34(2) | 179 | *x*, −*y* + 2, *z* − 1/2 |
| O(6*w*)–H(1)···Cl(2) | 0.85 | 2.37 | 3.217(8) | 179 | *x*, *y* − 1, *z* |
| O(6*w*)–H(2)···O(11*w*) | 1.07 | 2.19 | 3.21(2) | 157 | *x*, −*y* + 1, *z* + 1/2 |
| O(7*w*)–H(1)···Cl(6) | 0.98 | 2.08 | 3.053(10) | 171 | *x*, *y*, *z* |
| O(7*w*)–H(2)···S(11*A*) | 0.84 | 2.54 | 3.380(9) | 179 | *x*, *y*, *z* |
| O(8*w*)–H(1)···Cl(1) | 0.85 | 2.41 | 3.262(9) | 179 | *x*, −*y* + 1, *z* − 1/2 |
| O(8*w*)–H(2)···O(9*w*) | 0.90 | 2.34 | 3.20(2) | 159 | *x*, *y*, *z* |
| O(9*w*)–H(1)···Cl(7) | 0.85 | 2.30 | 3.142(10) | 174 | *x*, *y*, *z* |
| O(9*w*)–H(2)···S(11*B*) | 0.85 | 2.68 | 3.53(1) | 175 | *x*, −*y* + 1, *z* − 1/2 |
| O(10*w*)–H(1)···Cl(3) | 0.91 | 2.14 | 3.05(2) | 178 | *x* + 1/2, *y* + 1/2, *z* |
| O(10*w*)–H(2)···Cl(6) | 0.91 | 2.13 | 3.04(2) | 179 | *x*, *y*, *z* |
| O(11*w*)–H(1)···Cl(8) | 0.95 | 2.21 | 3.15(1) | 178 | *x*, *y*, *z* |
| O(11*w*)–H(2)···S(41*B*) | 1.01 | 2.57 | 3.57(1) | 173 | *x* − 1/2, −*y* + 3/2, *z* − 1/2 |
| O(12*w*)–H(1)···Cl(8) | 0.93 | 2.21 | 3.14(2) | 177 | *x*, *y*, *z* |
| O(12*w*)–H(2)···O(2*w*) | 0.88 | 1.92 | 2.79(2) | 177 | *x* − 1/2, −*y* + 3/2, *z* − 1/2 |
| O(13*w*)–H(1)···Cl(7) | 0.85 | 2.29 | 3.14(2) | 177 | *x*, *y*, *z* |
| O(13*w*)–H(2)···O(3*w*) | 0.85 | 1.90 | 2.75(2) | 177 | *x*, −*y* + 1, *z*–1/2 |

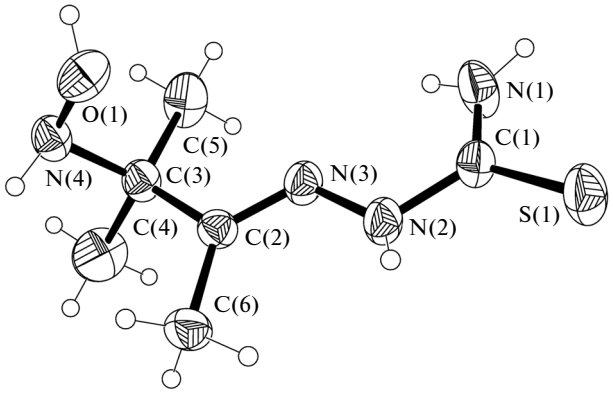


**Fig. 1.** Structure of $H_2L$ with atomic numbering.

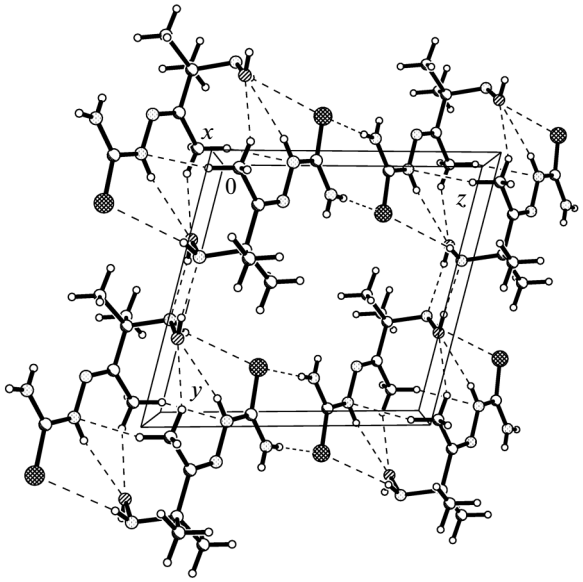


**Fig. 2.** Fragment of the layer in $H_2L$ (along the axis *x*).

$NH_2$ group of the ligand is not coordinated. Comparison of the IR spectra of $H_2L$, **I**, and **II** reveals that the intense absorption band in the spectrum of the free ligand at 3154 $cm^{-1}$ remains virtually unchanged in the spectra of the cobalt (3160 $cm^{-1}$) and nickel complexes (3145 $cm^{-1}$). Another intense band (at 3196 $cm^{-1}$) in the spectrum of the free ligand $H_2L$ is difficult to detect in the spectra of the complexes, probably, because of only one NH group involved in the coordination. Splitting of the intense band at 1599 $cm^{-1}$ in the spectrum of $H_2L$ into two bands in the spectra of the cobalt (1604 and 1619 $cm^{-1}$) and nickel complexes (1602 and 1627 $cm^{-1}$) can be due to participation of the$NH_2$ and =NH groups in hydrogen bonding. The bands at 1619 and 1627 $cm^{-1}$ should be assigned to δ(NH) (they are shifted to the higher frequencies upon hydrogen bonding [31]) and the bands at 1604 and 1602 $cm^{-1}$, to ν(C=N) [33]. The most intense absorption band in the spectrum of the free ligand (1038 $cm^{-1}$) can be due to the composite vibrations ν(–N–C=S (**II**)) [28]. It is absent from the spectra of the cobalt and nickel complexes, probably because of the sulfur atom coordinated by the metal atom. The band at 725 $cm^{-1}$ (δ(NCS)) in the spectrum of the free ligand $H_2L$ is shifted to the lower frequencies in the spectra of the cobalt and nickel complexes (717 and

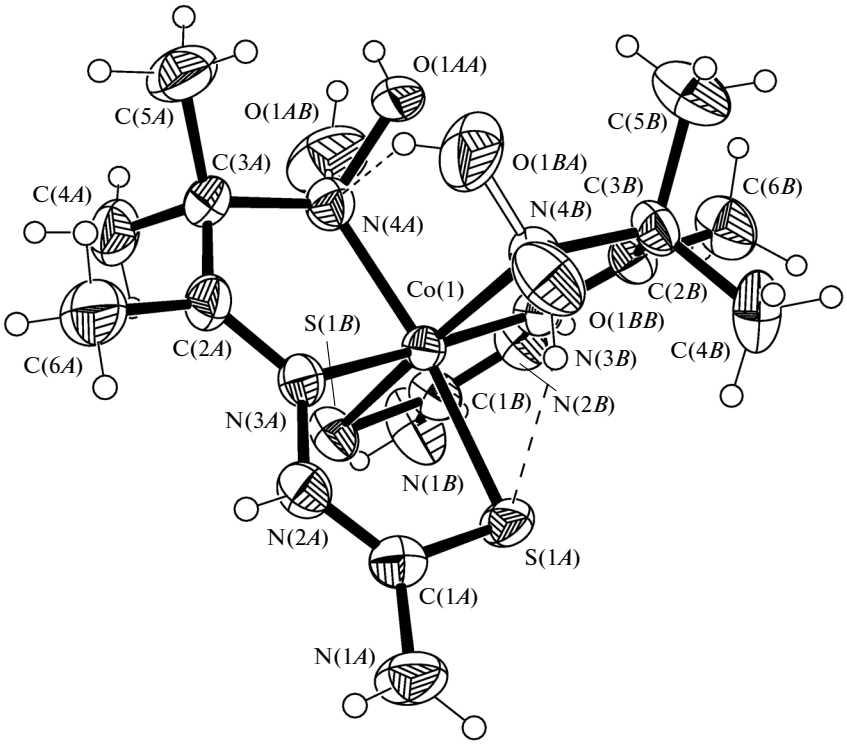


**Fig. 3.** Structure of the complex cation $[Co(HL)_2]^+$ in **I**.

731 $cm^{-1}$, respectively). This shift can also be due to the coordination of the C=S group to the metal atom.

The structure of (*E*)-2-(3-hydroxyamino-3-methylbutan-2-ylidene)hydrazinecarbothioamide ($H_2L$) is shown in Fig. 1. Its crystal is built from neutral molecules. The terminal N atoms of the thioamide group (N(1)) and the hydrazine residue (N(3)) in the thiosemicarbazide moiety are stabilized in the *trans*-configuration (*E* conformation) with respect to the N(2)–C(1) bond. The same configuration has been found in the thiosemicarbazone moieties of various derivatives [35–39]. The N(1)–C(1) and N(2)–C(1) bond lengths (1.309(4) and 1.356(3) Å, respectively) (Table 2) with the shortened terminal N(1)–C(1) bond agree with the literature data for the corresponding bonds (1.286–1.328 and 1.335–1.360 Å [35–39]) (Fig. 1). Bond length analysis for N–N, N–C, and S=C in $H_2L$ suggests their delocalization over the thiosemicarbazide moiety. The S(1)–C(1) bond length (1.685(3) Å) is also typical of the thioamide group of related molecules [35–39]. The atoms of the thiosemicarbazide moiety deviate from the plane S(1)N(1)N(2)N(3)C(1) by –0.072 to 0.081 Å; i.e., the $H_2L$ molecule is relatively planar. The deviations of the O(1) and N(4) atoms from the above plane are –2.911 and –1.992 Å, respectively.

Centrosymmetric dimers formed by both strong classic intermolecular hydrogen bonds N(4)–H···S(1) and weak intermolecular hydrogen bonds C–H···O and C–H···N are crucial for the crystal structure of the ligand (Fig. 2). In the crystal, these dimers are united into chains aligned with the axis *z* through centrosymmetric synthons $R_2^2(8)$ [40] stabilized by hydrogen bonds N(1)–H···S(1). The latter are united through centrosymmetric synthons $R_2^2(6)$ stabilized by hydrogen bonds O(1)–H···N(4).

Reactions of cobalt(II) (followed by oxidation with atmospheric oxygen) and nickel(II) salts with the thiosemicarbazone $H_2L$ gave two ionic complexes $[Co(HL)_2]Cl \cdot 2H_2O$ (**I**) and $[Ni(H_2L)_2]Cl_2 \cdot 2.25H_2O$ (**II**). The independent part of the unit cell of complex **I** contains the singly charged complex cation $[Co(HL)_2)]^+$ in the general position, the $Cl^-$ anion in the center of symmetry, and 0.5 $Cl^-$ anion in the general position (the last correlates with one water molecule of 0.5 occupancy). The independent part of the unit cell of complex **II** contains four doubly charged complex cations $[Ni(H_2L)_2]^{2+}$ and eight $Cl^-$ anions. In the complex cations of **I** and **II**, the central metal atoms show octahedral coordination (Figs. 3, 4). Their polyhedra are made up of the electron-donating NNS atoms of two tridentate ligands. The S(1) atom of the thiocarbonyl group and the N(3) atom of the

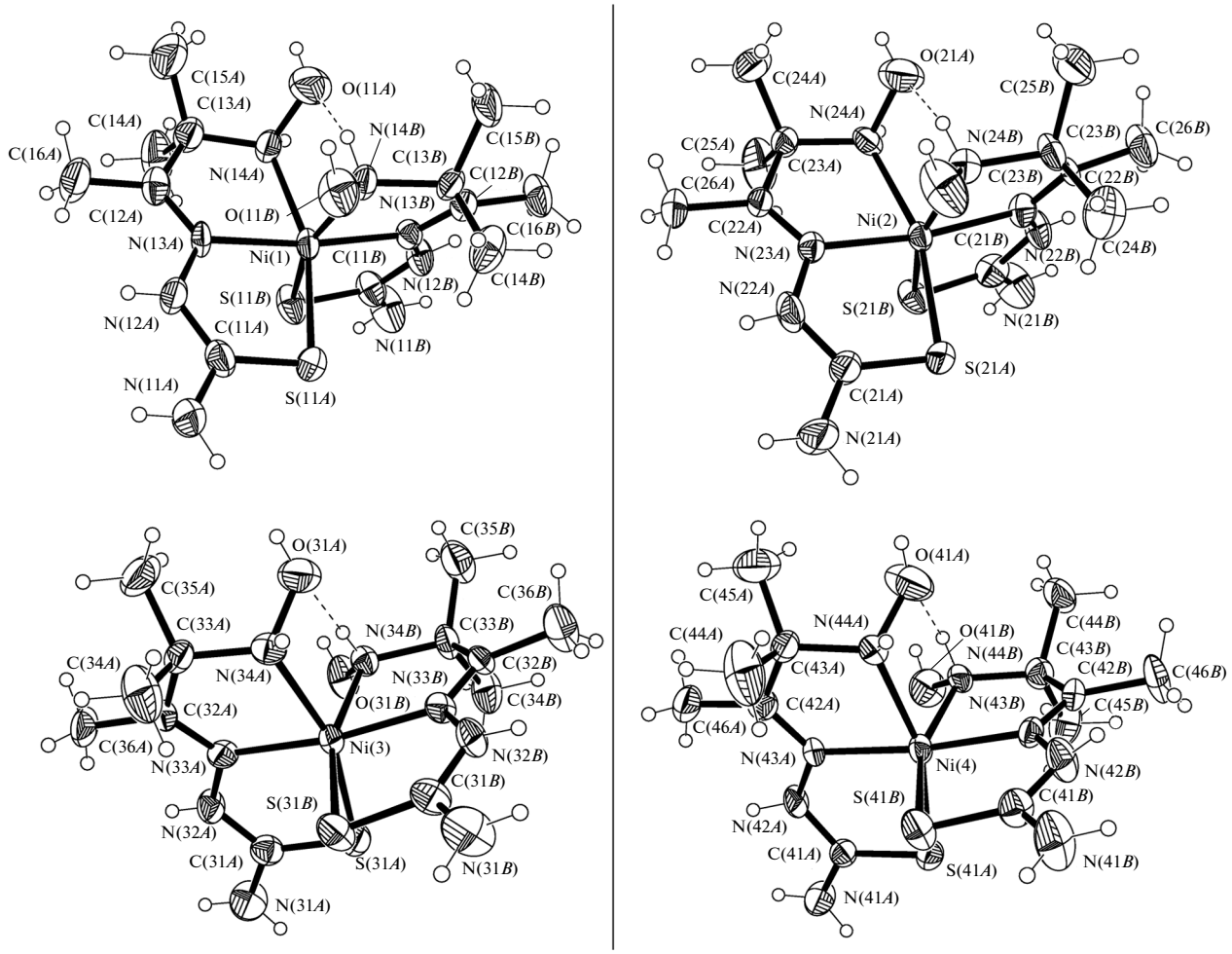


**Fig. 4.** Structure of the crystallographically independent complex cations $[Ni(H_2L)_2]^{2+}$ in **II**.

hydrazine residue in the thiosemicarbazide moieties are *trans* to each other about the N(2)–C(1) bond. In complex **II**, $H_2L$ molecules are coordinated to Ni(II) as neutral ligands, while the complex Co(III) cation in **I** contains monodeprotonated HL ligands. The M–S bond lengths agree with those found in Co(III) and Ni(II) complexes with thiosemicarbazones [12–17].

The geometry of the thiosemicarbazide moiety of $H_2L$ (Fig. 1) provides a theoretical possibility of coordination to a central transition metal ion through the terminal N(1) and N(3) atoms to form a five-membered chelate ring. However, such a coordination pattern has been reported only for a molybdenum complex with salicylaldehyde thiosemicarbazone [39]. As in most of the complexes of this class retrieved from the Cambridge Structural Database, the thiosemicarbazones in complexes **I** and **II** are coordinated to the central metal atom through the set of electron-donating atoms N(3)S(1) rather than N(1)N(3) [8–23]. For this purpose, the ligand seems to change from the *cis* (*Z*) to *trans* configuration (*E*) by rotating about the single N(2)–C(1) bond through 180°. The N(4) atom in complexes **I** and **II** can also coordinate to produce a second five-membered chelate ring. However, rotation about the single C(2)–C(3) bond is required for this coordination. Both these rotations are possible, so there are no apparent obstacles for $H_2L$ to act as a *N*,*N*,*S*-tridentate ligand. The changes in the configurations of the coordinated ligands $HL^-$ and $H_2L$ were confirmed by the torsion angles S(1)C(1)N(2)N(3), N(1)C(1)N(2)N(3), and N(3)C(2)C(3)C(4) in $H_2L$ (170.0°, –8.7°, and –111.2°), **I** (ligand A: 2.8°, –178.2°, and –12.0°; ligand B: 0°, 8.6°, and –9.9°), and **II** (complex cation 1 of ligand A: 2.5°, –177.3°, and –12.0°; complex cation 1 of ligand B: 1.6°, –176.2°, and –17.7°; complex cation 2 of ligand A: 8.7°, –172.2°, and –9.8°; complex cation 2 of ligand B: 4.5°, –177.3°, and –18.3°; complex cation 3 of ligand A: 7.5°, 171.6°, and 9.5°; complex cation 3 of ligand B: –4.0°, 176.6°, and 19.2°; complex cation 4

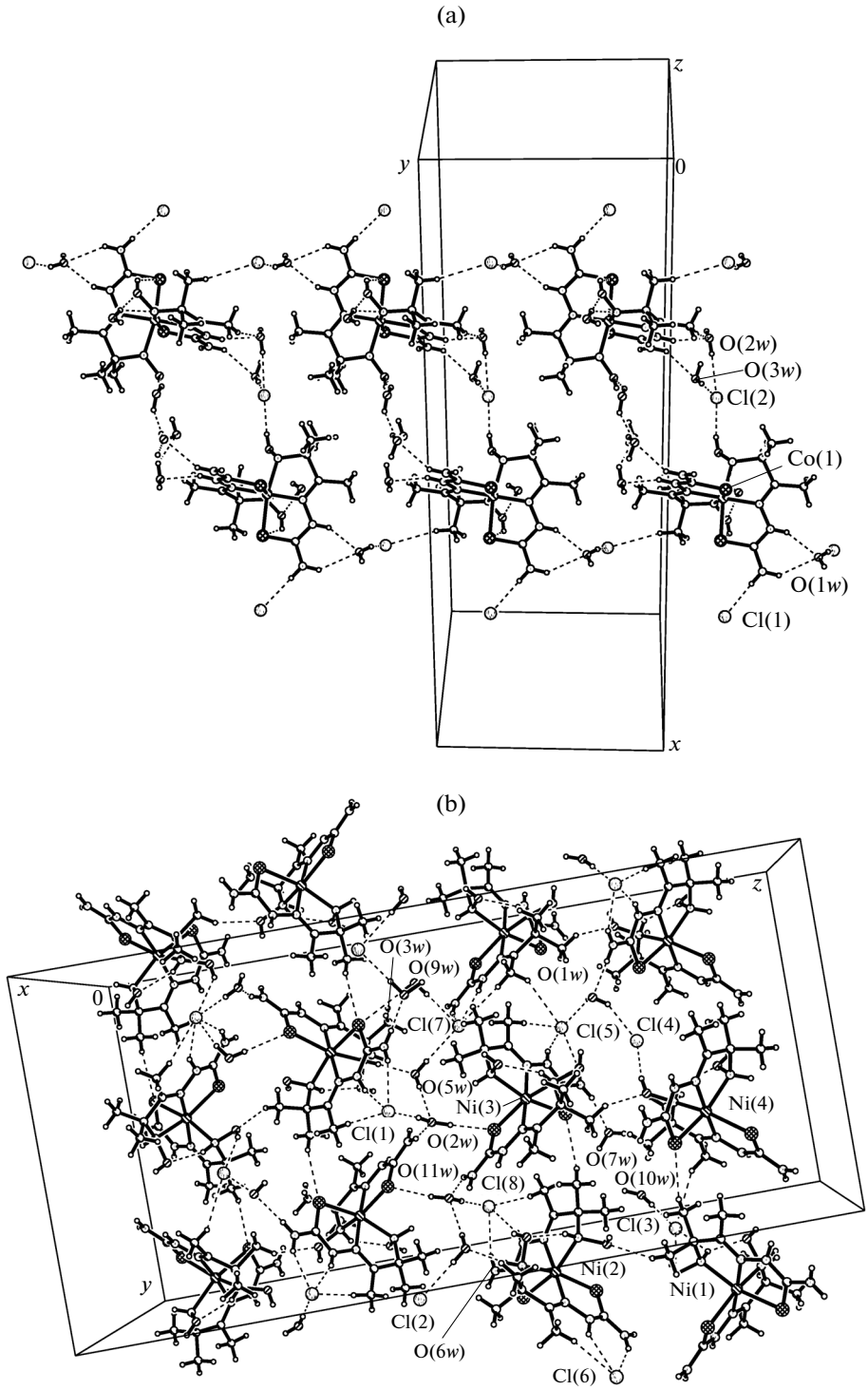


**Fig. 5.** Fragments of the crystal packing for complexes **I** (a) and **II** (b).

of ligand A: –9.7°, 173.3°, and 12.0°; complex cation 4 of ligand B: –3.0°, 176.2°, and 17.5°).

Coordination of $HL^-$ to Co(III) and that of $H_2L$ to Ni(II) produces two adjoining, nearly planar five-membered chelate rings MeSCNN and MeNCCN (Figs. 3, 4). The dihedral angles between their planes in complex **I** are 3.5° (ligand A) and 4.8° (ligand B). In complex **II**, their values are 5.3°, 4.0°, 4.2°, and 5.1° (ligand A, complex cations 1–4) and 6.2°, 4.5°, 6.4°, and 5.6° (ligand B, complex cations 1–4). Ligands A

and B in the complex cations of **I** and **II** are virtually perpendicular to each other: in structure **I**, the dihedral angle between the mean-square planes passing through the adjoining chelate rings of ligands A and B is 86.5°. In structure **II**, the corresponding angles in complex cations 1–4 are 85.0°, 93.8°, 85.1°, and 94.4°. Such a mutual arrangement of the ligands in the complex cations is stabilized by the weak intramolecular hydrogen bonds O(1*BB*)–H···S(1*A*) or O(1*BA*)–H···N(4*A*) in structure **I**. Similar bonds in **II** include N(14*B*)–H···O(11*A*), N(24*B*)–H···O(21*A*), N(34*B*)–H···O(31*A*), and N(44*B*)–H···O(41*A*) for complex cations 1–4, respectively (Table 3). The bond lengths in the coordinated organic ligands of complexes **I** and **II** differ only slightly, in agreement with the differences found in various Co(III) and Ni(II) thiosemicarbazones [7–16].

Complexes **I** and **II** form framework structures in the crystals because the complex cations $[Co(HL)_2]^+$ and $[Ni(H_2L)_2]^{2+}$ and crystallization water molecules contain many proton donors and acceptors capable of hydrogen bonding to water molecules and $Cl^-$ anions through H-bonds like N–H···O, O–H···O, N–H···Cl, and O–H···Cl (Table 3, Fig. 5). The complex cations are linked with each other mainly by the aforementioned intermolecular hydrogen bonds involving the anions and water molecules. However, structures **I** and **II** are additionally stabilized by weak intermolecular H-bonds C–H···Cl and C–H···O. In **I**, for two complex cations $[Co(HL)_2]^+$ there are one anion in the center of symmetry and another anion in the general position (the latter is disordered together with a water molecule with occupancy factors of 0.5). In addition, the complex cations in structures **I** and **II** are linked directly with each other by weak intermolecular H-bonds like C–H···S involving the methyl groups of the organic ligand as proton donors.

To sum up, we demonstrated that cobalt and nickel react with 3-hydroxyamino-3-methylbutan-2-one thiosemicarbazone (a new ligand, $H_2L$) to give 1 : 2 complexes in which the ligand can be both neutral and monodeprotonated. Conformational changes of the ligand during the complexation allow its coordination to the central metal ion through the set of electron-donating NNS atoms.

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