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**CHARACTERIZATION OF THE ADDUCTS  
OF BIS(O-ISOAMYLDITHIOCARBONATO)NICKEL(II)  
WITH HETEROCYCLIC AMINES AND X-RAY STRUCTURE OF  
BIS(O-ISOAMYLDITHIOCARBONATO)BIS(3-BROMOPYRIDINE)NICKEL(II)**

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A series of six-coordinated Ni(II) complexes, with the general formula Ni(Xan)L<sub>2</sub> (where Xan = isoamyldithiocarbonato and L = 2-bromopyridine, 3-bromopyridine, 4-acetylpyridine, 3-hydroxypyridine and 2-methoxypyridine) are synthesized and characterized by the elemental analysis and various physicochemical techniques such as magnetic susceptibility and conductivity measurements, UV-visible and infrared spectral data. Based on the electronic spectra and magnetic susceptibility measurements, an octahedral geometry is proposed for all the complexes. IR spectral data show that in all these complexes substituted pyridines coordinate to the metal ion through nitrogen atoms occupying the fifth and sixth axial positions, whereas O-alkyldithiocarbonate acts as a monoanion bidentate ligand and occupies the planar positions of octahedral structures. The structure of the adduct with 3-bromopyridine is elucidated by the single crystal X-ray diffraction method. The complex crystallizes in the triclinic space group *P*-1 with unit cell parameters  $a = 6.5855(4) \text{ \AA}$ ,  $b = 9.4984(6) \text{ \AA}$ ,  $c = 12.4518(8) \text{ \AA}$ ,  $\alpha = 87.944(5)^\circ$ ,  $\beta = 78.843(5)^\circ$ ,  $\gamma = 77.794(5)^\circ$ . The crystal structure of the molecule is stabilized by intermolecular C—H...S and C—H... $\pi$  interactions.

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**Keywords:** synthesis, dithiocarbonates, crystal structure, direct methods, interactions, octahedral.

#### INTRODUCTION

Dithiocarbonates have been known for a long time [ 1, 2 ]. Metal dithiocarbonate complexes have low solubility products and high stability constants and therefore, exhibit high efficiency for the removal of metal ions. These are extensively used as fungicides, pesticides, rubber accelerator, corrosion inhibitors, agricultural reagents and quite recently in therapy for HIV infections [ 3—5 ]. Among sulfur donating ligands, 1,1 dithiolates, which include dithiocarbamates, dithiocarbonates, and dithiocarboxylates, have invited much research attention of chemists, physicists, and biologists due to their diverse applications and interesting biological, structural, magnetic, electrochemical, and thermal properties [ 6, 7 ]. In this paper we report the synthesis and characterization of the adducts of bis(O-isoamyldithiocarbonato)nickel(II) with heterocyclic amines and the X-ray structure of bis(O-isoamyldithiocarbonato)bis(3-bromopyridine)nickel(II). The chemical structure of the title complex is shown in Fig. 1.

Fig. 1. Chemical diagram of bis(O-isoamylthiocarbonato)bis(3-bromopyridine)nickel(II)

### EXPERIMENTAL

**Synthesis.** The saturated aqueous solutions of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (2.37 g, 0.01 mol) and potassium O-isoamylthiocarbonate (4.04 g, 0.02 mol) were prepared separately and then mixed with constant stirring. Dark green precipitates formed, which were filtered immediately and dried in vacuum desiccators over anhydrous calcium chloride. The composition of the complex was established by the elemental analysis to be  $[\text{Ni}(\text{S}_2\text{COC}_5\text{H}_{11})_2]$ . The 1:2 adducts of bis(O-amylthiocarbonato)nickel(II) with substituted pyridines were prepared by stirring  $[\text{Ni}(\text{S}_2\text{COC}_5\text{H}_{11})_2]$  (1 g, 0.0026 mol) in about 70 ml of acetone for about 20 min followed by the addition of substituted pyridines [2-bromopyridine = 0.82 g, 3-bromopyridine = 0.82 g, 4-acetylpyridine = 0.62 g, 3-hydroxypyridine = 0.50 g and 2-methoxypyridine = 0.56 g (0.0052 mol)] and the mixture was again stirred for 20 min. The contents of the reaction mixture were then filtered and allowed to stand for 20–24 h, depositing shining green crystalline solids which were then washed with the solvent used in their preparation and dried over calcium chloride at room temperature.

**Materials and measurements.** Carbon, hydrogen, nitrogen and sulfur contents of the addition complexes were determined on a CHNS-932 elemental analyzer (LECO corporation, USA). Molar conductance of the adducts was determined in the millimolar solution in dimethylformamide (DMF) by a Century CC 601 digital conductivity meter. Infrared spectra of the complexes in the range  $4000\text{--}200\text{ cm}^{-1}$  were recorded using KBr pellets on a Perkin Elmer FT-IR spectrometer. The electronic spectra of the adducts were recorded in DMF on a Systronics 119 UV-Visible spectrophotometer. Magnetic moments were determined at room temperature by the VSM method (Princeton Applied Research-Model No. 155). The analytical data, molar conductance, magnetic moments, important IR bands and electronic spectral data of the isolated adducts are presented in tables.

**Data collection, structure solution and refinement.** The X-ray intensity data of a well defined crystal ( $0.30 \times 0.20 \times 0.10\text{ mm}$ ) were collected at room temperature (293K) using an X'calibur CCD area-detector diffractometer [ 8 ] with graphite monochromated  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). The cell dimensions were determined by the least-squares fit of angular settings of 4587 reflections in the  $\theta$  range from  $3.88$  to  $25.70^\circ$ . A total number of 5236 reflections were collected, out of which 2928 reflections were considered to be unique and 1798 reflections were treated as observed ( $I > 2\sigma(I)$ ). Data were corrected for Lorentz polarization and absorption factors.

The crystal structure was solved by direct methods using SHELXS97 [ 9 ] and refined by the full matrix least squares method using SHELXL97 [ 9 ] present in the WinGX program suite. All non-hydrogen atoms of the molecule were located from the *E*-map. The geometry of the molecule is determined by PLATON [ 10 ]. All the hydrogen atoms were positioned geometrically and were treated as riding on their parent C atoms, with C—H distances of  $0.93\text{--}0.97\text{ \AA}$  and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ , except for the methyl groups where  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ . The final refinement cycles yielded an *R*-factor of 0.0547 ( $wR(F^2) = 0.1486$ ) for the observed data. The residual electron density ranges from  $-0.751$  to  $0.716\text{ e/\AA}^{-3}$ . ORTEP diagram of the compound was generated using ORTEP32 [ 11 ] and packing diagram was generated using PLATON [ 10 ] software. Geometrical calculations were performed using PLATON [ 10 ] and PARST [ 12 ].

Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). CCDC-1041292 contains the supplementary crystallographic data for this paper.

### RESULTS AND DISCUSSION

The isolated adducts of bis(O-isoamylthiocarbonato)nickel(II) with substituted pyridines are microcrystalline green solids and are soluble in common organic solvents, such as acetone, chloro-

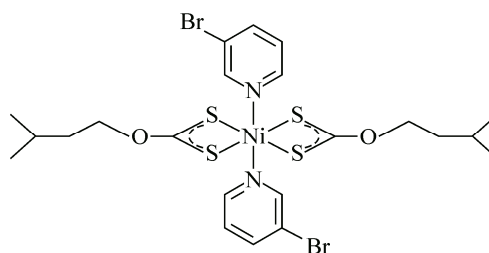


Table 1

Analytical data of the adducts of bis(*o*-isoamyldithiocarbonato)nickel(II) with substituted pyridines

S. No.	Adduct name	Mol. wt.	Yield, (%)	Colour	Found, %				Calculated, %			
					C	H	N	S	C	H	N	S
1	Bis(O-isoamyldithiocarbonato)-bis(2bromopyridine)nickel(II)	700.69	75	Blackish green	36.95	3.98	3.15	17.98	37.68	4.28	3.99	18.27
2	Bis(O-isoamyldithiocarbonato)-bis(3bromopyridine)nickel(II)	700.69	70.50	Bright green	36.85	3.75	3.3	17.90	37.68	4.28	3.99	18.27
3	Bis(O-isoamyldithiocarbonato)-bis(4acetylpyridine)nickel(II)	626.69	79	Bright green	48.90	5.17	3.98	19.97	47.04	5.45	4.77	21.81
4	Bis(O-isoamyldithiocarbonato)-bis(3hydroxypyridine)nickel(II)	574.69	75.70	Bright green	45.11	5.10	4.11	21.01	45.93	5.56	4.87	22.27
5	Bis(O-isoamyldithiocarbonato)-bis(2methoxypyridine)nickel(II)	602.69	70.70	Grassy green	47.16	5.13	4.20	20.80	47.78	5.97	4.64	21.23

Table 2

Molar conductance and magnetic data of the adducts of bis(*o*-isoamyldithiocarbonato)nickel(II) with substituted pyridines

S. No.	Molar conductance, $\text{Ohm}^{-1}\cdot\text{mol}^{-1}\cdot\text{cm}^2$	Magnetic data		S. No.	Molar conductance, $\text{Ohm}^{-1}\cdot\text{mol}^{-1}\cdot\text{cm}^2$	Magnetic data	
		$\mu_{\text{eff}}$ , B.M.	Temperature, K			$\mu_{\text{eff}}$ , B.M.	Temperature, K
1	28.67	2.99	298	4	22.58	3.15	298
2	39.76	3.20	298	5	24.37	3.19	298
3	20.38	3.17	298				

form, DMF, and dimethylsulphoxide, but insoluble in benzene, carbontetrachloride, nitrobenzene, and water. The analytical results of the adducts isolated suggest that they have the 1:2 stoichiometry and may be assigned the formula  $\text{Ni}(\text{S}_2\text{COCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3)_2\text{L}_2$  (where L = 2-bromopyridine, 3-bromopyridine, 4-acetylpyridine, 3-hydroxypyridine, and 2-methoxypyridine) (Table 1). The molar conductance measurements of the millimolar solutions of the adducts under study were carried out in DMF. The molar conductivity values are in the range of  $20.52\text{--}80.33 \text{ } \Omega^{-1}\cdot\text{mol}^{-1}\cdot\text{cm}^2$  (Table 2) suggesting that these complexes are neutral and non-ionic in character [13, 14]. The magnetic moment values of 1:2 adducts of bis(O-isoamyldithiocarbonato)nickel(II) with nitrogen donors come in the range of 3.06—3.22 BM, which is in agreement with the magnetic moment values observed for the octahedral complexes of nickel [15, 16] (Table 2). A comparison of the IR spectra of prepared adducts with those of the free ligands reveals that most bands of the free ligands are shifted from their respective positions. The C—H out-of-plane deformation bands in free substituted pyridines show red shifts while all other modes, especially the bands arising due to C—C and C—N ring stretching modes, in-plane and out-of-plane ring deformations in the free ligand show a blue shift in the adducts, indicating that substituted pyridines are coordinated to the metal ion through the nitrogen atom (Table 3). The

Table 3

Important IR bands of the adducts of bis(*o*-isoamyldithiocarbonato)nickel(II) with substituted pyridines

S. No.	Formula	$\nu_{\text{as}}(\text{C—O—C})$	$\nu_{\text{s}}(\text{C—O—C})$	$\nu(\text{C—S})$
1	$\text{Ni}(\text{S}_2\text{COC}_5\text{H}_{11})_2(\text{C}_5\text{H}_4\text{NBr})_2$	1202	1123	1033
2	$\text{Ni}(\text{S}_2\text{COC}_5\text{H}_{11})_2(\text{C}_5\text{H}_4\text{NBr})_2$	1220	1141	1031
3	$\text{Ni}(\text{S}_2\text{COC}_5\text{H}_{11})_2(\text{C}_7\text{H}_7\text{NO})_2$	1197	1136	1029
4	$\text{Ni}(\text{S}_2\text{COC}_5\text{H}_{11})_2(\text{C}_5\text{H}_5\text{NO})_2$	1210	1130	1025
5	$\text{Ni}(\text{S}_2\text{COC}_5\text{H}_{11})_2(\text{C}_6\text{H}_7\text{NO})_2$	1211	1136	1035

Table 4

Electronic spectra of the adducts of bis(*o*-isoamylthiocarbonato)nickel(II) with substituted pyridines

S. No.	$\nu_1, \text{cm}^{-1}$ ${}^3A_{2g} \rightarrow {}^3T_{2g}(\text{F})$	$\nu_2, \text{cm}^{-1}$ ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$	$\nu_3, \text{cm}^{-1}$ ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$	S. No.	$\nu_1, \text{cm}^{-1}$ ${}^3A_{2g} \rightarrow {}^3T_{2g}(\text{F})$	$\nu_2, \text{cm}^{-1}$ ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$	$\nu_3, \text{cm}^{-1}$ ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$
1	15450	21791	28180	4	15856	21122	27832
2	15468	22521	27682	5	14910	21210	27697
3	15396	21920	29470				

electronic spectra of 1:2 adducts of bis(*o*-isoamylthiocarbonato)nickel(II) have been recorded in DMF and show three bands in the range 11000–15856, 19000–22521, and 26143–27548  $\text{cm}^{-1}$ , which are assigned to:  ${}^3A_{2g} \rightarrow {}^3T_{2g}(\text{F})$  ( $\nu_1$ ),  ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$  ( $\nu_2$ ) and  ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$  ( $\nu_3$ ) transitions respectively (Table 4). These three broad bands along with shoulders show that adducts have the *trans*- octahedral geometry around the nickel (II) ion [ 17 ].

**X-ray crystallography.** The complex is centrosymmetric and comprises one  $\text{Ni}^{2+}$  cation surrounded by two chelating dithiocarbonato ligands and two monodentate pyridine ligands, having a slightly distorted octahedral  $\text{N}_2\text{S}_4$  environment. The ORTEP plot with the atomic numbering scheme of the complex is illustrated in Fig. 2. The complex crystallizes in the triclinic system, space group  $P\bar{1}$  with unit cell parameters:  $M = 701.25$ ,  $a = 6.5855(4) \text{ \AA}$ ,  $b = 9.4984(6) \text{ \AA}$ ,  $c = 12.4518(8) \text{ \AA}$ ,  $\alpha = 87.944(5)^\circ$ ,  $\beta = 78.843(5)^\circ$ ,  $\gamma = 77.794(5)^\circ$ ,  $V = 746.88(8) \text{ \AA}^3$ ,  $Z = 1$ ,  $R_1[I > 2\sigma(I)] = 0.0547$ ,  $wR_2[I > 2\sigma(I)] = 0.1486$ ,  $S$ -factor = 1.037. In the title molecular complex, the  $\text{Ni}^{2+}$  cation is located in the center of inversion.

The C—S bond lengths involving the dithiocarbonato ligands are: S1—C6 = 1.686(5)  $\text{ \AA}$  and S2—C6 = 1.674(6)  $\text{ \AA}$ . These values show a double-bond character due to delocalization over the two C—S bonds [ 18 ]. As a consequence of the carbon atom hybridization, the O1—C6 bond is shorter (1.333(6)  $\text{ \AA}$ ) than O1—C7 (1.442(7)  $\text{ \AA}$ ). The short O1—C6 bond distance is consistent with a significant contribution of the resonance form of the dithiocarbonato anion that features formal C=O and a negative charge on each of S atoms [ 19 ]. The Ni—S bond lengths involving the dithiocarbonato

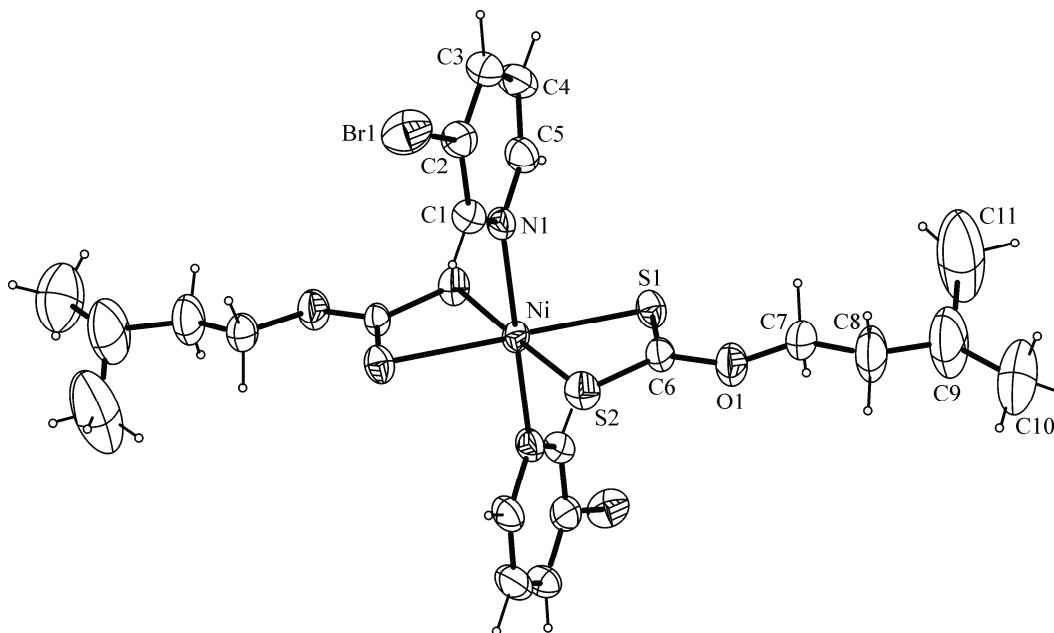


Fig. 2. ORTEP plot of the molecule with 30 % probability thermal ellipsoids.  
H atoms are shown as small spheres of arbitrary radii

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## Geometry of intra- and intermolecular hydrogen bonds

D—H...A	D—H, Å	H...A, Å	D...A, Å	$\theta(\text{DH...A})$ , deg.
C5—H5...S1 <sup>i</sup>	0.93	2.77	3.667(6)	163
C10—H10B...Cg1 <sup>ii</sup>	0.96	2.88	3.49(1)	122

Symmetry codes: <sup>i</sup>  $-x, 1-y, -z$ ; <sup>ii</sup>  $-1+x, y, 1+z$ .

Cg1 represents the center of gravity of the pyridine ring (N1/C1/C2/C3/C5/C5).

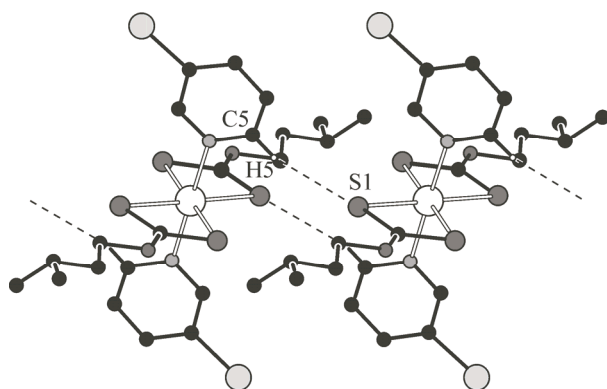


Fig. 3. Crystal structure showing intermolecular C—H...S interactions

ligands are 2.435(1) Å for Ni—S1 and 2.432(1) Å for Ni—S2, and these values of bond distances are in good agreement with those reported for other analogous Ni-dithiocarbonato complexes [20—22]. The existence of the intermolecular hydrogen bonding C5—H5...S1 (Table 5) is very important for stabilizing the molecular structure in the solid state, as shown in Fig. 3. In the crystal structure, molecules are arranged in rows along [100], forming layers parallel to (010) and (001) (Fig. 4). In addition, weak intermolecular C—H... $\pi$  interactions further stabilize and reinforce the crystal structure (Table 5). Selected bond lengths and bond angles are listed in Table 6.

## CONCLUSIONS

The adducts of Ni(isoamyldithiocarbonato)<sub>2</sub> with substituted pyridines were prepared and characterized by various physicochemical techniques such as magnetic susceptibility measurements, conductivity measurements, UV-visible and IR spectral data. Based on the electronic spectra and magnetic susceptibility measurements, the octahedral geometry has been proposed for all the complexes. IR spectral data show that in all these complexes, substituted pyridines coordinate to the metal ion through nitrogen atoms occupying the fifth and sixth axial positions, whereas O-alkyldithiocarbonate

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## Selected bond lengths (Å) and bond angles (deg.) for non-hydrogen atoms

Ni—N1	2.124(5)	O1—C7	1.442(7)	N1—Ni—N1 <sup>i</sup>	180.0(3)	N1 <sup>i</sup> —Ni—S2 <sup>i</sup>	89.5(1)
Ni—S1	2.435(1)	S1—C6	1.686(5)	N1—Ni—S2	89.5(1)	S2—Ni—S1	74.04(5)
Ni—S2	2.432(1)	S2—C6	1.674(6)	N1—Ni—S1	90.4(1)	C5—N1—Ni	121.6(4)
C6—O1	1.333(6)	Br1—C2	1.884(6)	N1 <sup>i</sup> —Ni—S2	90.5(1)	C1—N1—C5	117.4(5)
				N1—Ni—S2 <sup>i</sup>	90.5(1)	C1—N1—Ni	121.0(4)

Symmetry code(s): <sup>i</sup>  $-x+1, -y+1, -z$ .

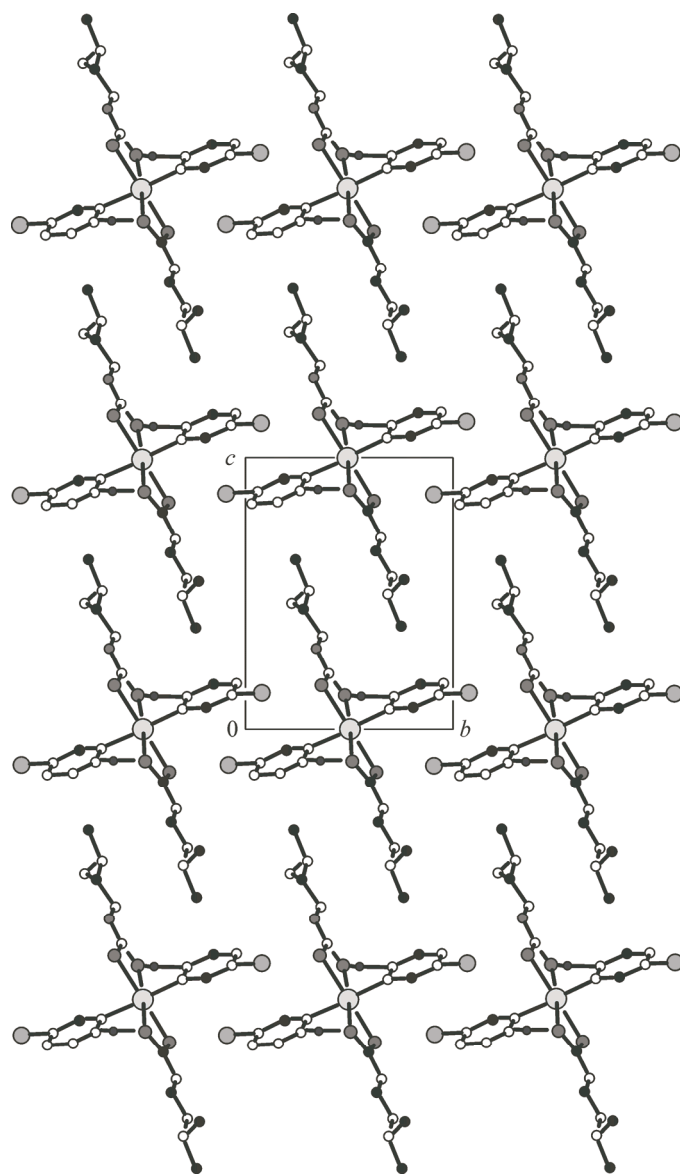


Fig. 4. Packing diagram viewed down the *a* axis

acts as a monoanion bidentate ligand and occupies the planar positions of the octahedral structures. The complex crystallizes in the triclinic space group. The coordination complex possesses the crystallographic inversion symmetry at the Ni atom. The C—S bond lengths of the thiocarboxylate group are indicative of a delocalized bond. The packing of the molecules is stabilized by intermolecular C—H...S (Fig. 4) and C—H... $\pi$  interactions. In the crystal structure, the molecules are arranged in layers parallel to (010) and (001).

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