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# Crystal structure of *trans*-diaqua-bis(methyl methylcarbamohydrazonothioato-κ$^2$*N*,*N*′) nickel(II) iodide semihydrate, $C_6H_{22}N_6O_2NiS_2I_2 \cdot 0.5H_2O$

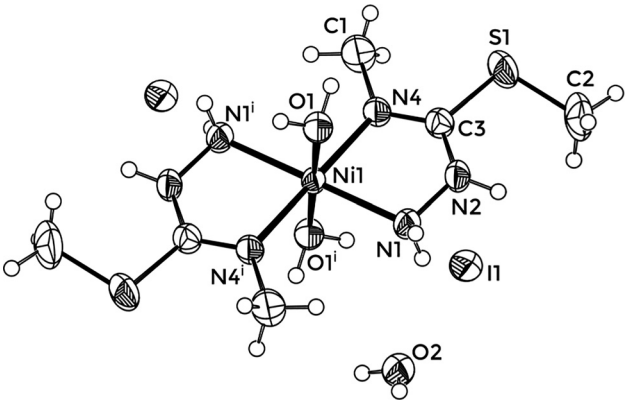


**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Purple prism |
| Size: | 0.49 × 0.18 × 0.06 mm |
| Wavelength: | Mo *Kα* radiation (0.71073 Å) |
| $\mu$: | 4.38 mm$^{-1}$ |
| Diffractometer, scan mode: | Gemini S, $\omega$ |
| $\theta_{max}$, completeness: | 29.0°, >99% |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 4196, 4196, 0.034 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 2990 |
| $N(param)_{refined}$: | 114 |
| Programs: | CrysAlis$^{PRO}$ [1], SHELX [2, 3], PLATON [4] |

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**Abstract**

$C_6H_{23}I_2N_6NiO_{2.50}S_2$, monoclinic, *C*2/*c* (no. 15), $a$ = 8.2282(4) Å, $b$ = 21.9200(7) Å, $c$ = 11.4906(4) Å, $\beta$ = 109.451(4)°, $V$ = 1954.19(14) Å$^3$, $Z$ = 4, $R_{gt}(F)$ = 0.0322, $wR_{ref}(F^2)$ = 0.1113, $T$ = 295.

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The title crystal structure is shown in the figure. Table 1 contains crystallographic data, Table 2 contains the list of the atoms including atomic coordinates and displacement parameters, and Table 3 contains selected structural parameters of title complex and closely related structures.

## Source of material

The mixture of $Ni(OAc)_2 \cdot 4H_2O$ (0.1 mmol) and $N^4$-methyl-*S*-methylisothiosemicarbazide-hydrogeniodide, L·HI, (0.2 mmol) is disolved in warm EtOH (5 mL). The solution is spontaneously evaporated to a small volume. Bluish-purple single crystals are filtered and washed with EtOH. Non-commercial ligand L·HI is obtained in the reaction of $N^4$-methyl-thiosemicarbazide and methyl-iodide in absolute ethanol during reflux for 45 min.

## Experimental details

The used crystal specimen was a non-merohedral twin. Upon determination of the twin law, simultaneous integration of reflecton intensities was performed. Deconvoluted intensity data (*SHELX* HKLF 4 format) were used for structure solution, while refinement was performed against 4152 merged reflections in *SHELX* HKLF 5 format.

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$).

| Atom | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| I1 | 0.72095(5) | 0.86708(2) | 0.46855(4) | 0.05177(17) |
| S1 | 0.2711(2) | 0.54413(7) | 0.54313(17) | 0.0626(4) |
| Ni1 | 0.250000 | 0.750000 | 0.500000 | 0.0323(2) |
| O1 | 0.5261(4) | 0.75062(17) | 0.5790(3) | 0.0423(8) |
| H1O1 | 0.578(7) | 0.7801(15) | 0.558(6) | 0.063* |
| H2O1 | 0.585(6) | 0.7216(16) | 0.561(6) | 0.063* |
| C1 | 0.2467(10) | 0.6310(3) | 0.3458(6) | 0.0684(19) |
| H1D | 0.227781 | 0.662027 | 0.283760 | 0.103* |
| H1E | 0.153729 | 0.602085 | 0.321218 | 0.103* |
| H1C | 0.353405 | 0.610437 | 0.355339 | 0.103* |
| N1 | 0.2386(5) | 0.7123(2) | 0.6647(4) | 0.0383(9) |
| H1A | 0.315(4) | 0.724(3) | 0.733(3) | 0.046* |
| H1B | 0.141(3) | 0.711(2) | 0.680(4) | 0.046* |
| C2 | 0.2285(11) | 0.5171(3) | 0.6771(8) | 0.088(2) |
| H2A | 0.123997 | 0.535209 | 0.680524 | 0.132* |
| H2B | 0.322427 | 0.528086 | 0.749695 | 0.132* |
| H2C | 0.216366 | 0.473530 | 0.672892 | 0.132* |
| N2 | 0.2738(6) | 0.6494(2) | 0.6647(4) | 0.0413(10) |
| H2 | 0.255(7) | 0.629(2) | 0.723(4) | 0.050* |
| C3 | 0.2626(6) | 0.6239(2) | 0.5540(5) | 0.0369(10) |
| N4 | 0.2544(5) | 0.65887(19) | 0.4628(4) | 0.0383(9) |
| O2[a] | 0.000000 | 0.7838(5) | 0.750000 | 0.047(2) |
| H2O2[a] | 0.046721 | 0.804361 | 0.811687 | 0.071* |

[a]Occupancy: 0.5.

Coordinates of carbon-bonded hydrogen atoms were introduced in idealized positions and refined using riding model. Their $U_{iso}$ values are approximated as $U_{iso} = kU_{eq}$ of the parent atom ($k$ = 1.2 for $sp^2$ and 1.5 for $sp^3$ hybridized atoms). Locations of hydrogen atoms bonded to heteroatoms were determined from residual electron density maps and were refined with distance restraints. Their $U_{iso}$ values are approximated as $U_{iso} = kU_{eq}$ of the parent atom ($k$ = 1.2 for nitrogen- and 1.5 for oxygen-bonded atoms). Non-coordinated water molecule was refined as a rigid group.

# Comment

## Introduction

Numerous complexes of transition metals with derivatives of *S*-alkylisothiodemicarbazide are synthesized and characterized by single crystal X-ray diffraction [5]. Besides the interesting metal-induced reactions of ligands and unusual open chain and macrocyclic structures, some of these tetra- and octadentate ligands can stabilize Cu(III), Ni(III), and Fe(IV) ions [6–10].

In Refs. [11, 12] the structure of *trans*-square-planar Ni(II) complex with *NN* bidentate *S*-methylisothiosemi-carbazide ($L^1$), i.e. $[Ni(L^1)_2]I_2$ is described. This complex is obtained in the reaction of EtOH solutions of $Ni(OAc)_2{\cdot}4H_2O$ and $L^1{\cdot}HI$ in a 1:2 M ratio. In this paper, it is shown that under the same synthetic conditions, the reaction of $Ni(OAc)_2{\cdot}4H_2O$ and L·HI results in the formation of the *trans*-octahedral complex of the formula $[NiL_2(H_2O)_2]I_2{\cdot}0.5H_2O$.

## Structural comment

The asymmetric unit of $[NiL_2(H_2O)_2]I_2{\cdot}0.5H_2O$ consists of half of the complex cation situated at a special position of site symmetry $\bar{1}$, one iodide ion, and a half water molecule with 0.5 site occupancy factor situated at two-fold rotation axis. Complex cation $[NiL_2(H_2O)_2]^{2+}$ consists of two *NN* bidentate $N^4$-methyl-*S*-methylisothiosemicarbazide ligands situated in

**Table 3:** Comparison of selected structural parameters of Ni(II) complexes with $N^4$-methyl-*S*-methylisothiosemicarbazide (L), and *S*-methyl-isothiosemicarbazide ($L^1$) ligands. Atom labels used correspond to the title complex.

| | $[NiL_2(H_2O)_2]I_2{\cdot}0.5H_2O$ | $[Ni(L^1)_2(H_2O)_2](tph){\cdot}2H_2O$ | $[Ni(L^1)_2]I_2$ | $[Ni(L^1)_2]I_2$ |
|---|---|---|---|---|
| CSD refcode | N.A. | FERLAQ | MCBNIA01 | MCBNIA |
| CCDC No. | N.A. | 262776 | 680517 | 1210100 |
| Reference | This work | [13] | [12] | [11] |
| *d*(Ni1–N1)/Å | 2.095(4) | 2.094(3) | 1.9119(16) | 1.923(10) |
| *d*(Ni1–N4)/Å | 2.046(4) | 2.027(3) | 1.8624(17) | 1.873(11) |
| *d*(Ni1–O1)/Å | 2.147(3) | 2.136(3) | – | – |
| *d*(N1–N2)/Å | 1.410(6) | 1.425(3) | 1.427(2) | 1.429(12) |
| *d*(N2–C3)/Å | 1.363(7) | 1.359(4) | 1.350(3) | 1.315(12) |
| *d*(C3–N4)/Å | 1.282(6) | 1.274(5) | 1.300(2) | 1.284(12) |
| ∠(N4–Ni1–N1)/° | 79.23(16) | 80.15(12) | 84.24(7) | 84.1(6) |
| ∠(N1–Ni1–O1)/° | 91.14(14) | 91.85(12) | – | – |
| ∠(N4–Ni1–O1)/° | 90.26(15) | 92.68(11) | – | – |

the equatorial plane, and two water molecules occupying axial positions of an octahedrally coordinated Ni(II) atom, and has an approximate 2/*m* symmetry (r.m.s.d. of atomic positions from symmetrized structure is 0.139 Å). Similar cation is observed in complex $[Ni(L^1)_2(H_2O)_2](tph)\cdot 2H_2O$, where $H_2tph$ is terephthalic acid [13]. Metal–ligand bond lengths and valence angles within the coordination polyhedron of these two structures match within ±0.02 Å, and ±1°, respectively. As expected for Ni(II) octahedral complexes, axial metal–ligand bond lengths are longer (*d*(Ni1—O1) = 2.147(3) Å) compared to equatorial (*d*(Ni1—N1) = 2.095(4) and *d*(Ni1—N4) = 2.046(4) Å).

As already mentioned, the constitution of complex cation in $[NiL_2(H_2O)_2]I_2\cdot 0.5H_2O$ is different from that found in $[Ni(L^1)_2]I_2$ [11, 12], even though syntheses were conducted under equivalent conditions. Significant differences are observed when metal–ligand bond lengths are compared to $[Ni(L^1)_2]I_2$, where nickel(II) is in a square-planar environment composed of two *S*-methylisothiosemicarbazide ligands. Namely, in $[Ni(L^1)_2]I_2$, both metal ligand bonds are shorter, and the chelate bite angle is larger. On the other hand, intraligand bond lengths of the common type in all mentioned complexes have similar values. This indicates that methylation of N4 did not significantly change the ligand structure.

A complex network of hydrogen bonds is present in the crystal structure, where all potential hydrogen bond donors are involved in bonding.

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**Conflict of interest statement:** The authors declare no conflicts of interest regarding this article.

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