# metal-organic compounds

# (5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene-$\kappa^4N^1,N^4,N^8,N^{11}$)(thiocyanato-$\kappa S$)-nickel(II) perchlorate monohydrate

## Jian-Hong Bi

Deparment of Chemistry and Chemical Engineering, Hefei Teachers College, Hefei 230061, People's Republic of China
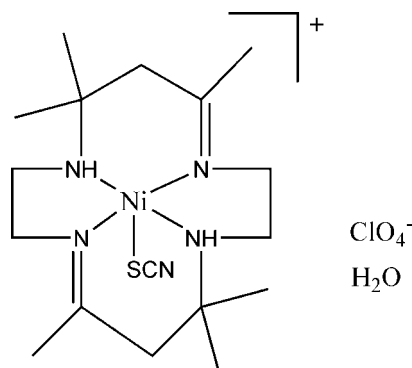
Correspondence e-mail: bi010101@126.com

In the title compound, $[Ni(SCN)(C_{16}H_{32}N_4)]ClO_4 \cdot H_2O$, the $Ni^{II}$ ion is coordinated by the four N atoms of the tetraazacyclotetradeca-4,11-diene macrocyclic ligand and by the S atom of a thiocyanate anion. The perchlorate anion is rotationally disordered around one Cl—O bond between two orientations; the occupancies refined to 0.61 (4) and 0.39 (4). Intermolecular O—H···N, N—H···O and N—H···N hydrogen bonds link two cations, two anions and two solvent water molecules into a centrosymmetric cluster. The crystal packing is further stabilized by weak intermolecular C—H···O hydrogen bonds.

## Related literature

For the crystal structures of related complexes, see: Bienko *et al.* (2007); Shen *et al.* (1999); Szalda & Fujita (1992).



## Experimental

### Crystal data

| | |
|---|---|
| $[Ni(NCS)(C_{16}H_{32}N_4)]ClO_4 \cdot H_2O$ | $\gamma = 67.3480\ (10)^\circ$ |
| $M_r = 514.71$ | $V = 1171.6\ (3)$ Å$^3$ |
| Triclinic, $P\bar{1}$ | $Z = 2$ |
| $a = 7.2678\ (11)$ Å | Mo $K\alpha$ radiation |
| $b = 8.9998\ (13)$ Å | $\mu = 1.07$ mm$^{-1}$ |
| $c = 19.513\ (2)$ Å | $T = 291$ K |
| $\alpha = 84.1430\ (10)^\circ$ | $0.49 \times 0.40 \times 0.39$ mm |
| $\beta = 87.005\ (2)^\circ$ | |

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 6103 measured reflections |
| | 4062 independent reflections |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2000) | 3247 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.623$, $T_{max} = 0.681$ | $R_{int} = 0.019$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | 299 parameters |
| $wR(F^2) = 0.109$ | H-atom parameters constrained |
| $S = 1.03$ | $\Delta\rho_{max} = 0.53$ e Å$^{-3}$ |
| 4062 reflections | $\Delta\rho_{min} = -0.90$ e Å$^{-3}$ |

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2···O2 | 0.91 | 2.28 | 3.16 (3) | 162 |
| N4—H4···N5 | 0.91 | 2.33 | 3.241 (5) | 175 |
| O5—H5F···N5 | 0.85 | 2.09 | 2.942 (6) | 178 |
| O5—H5G···N5$^i$ | 0.85 | 2.15 | 2.997 (6) | 178 |
| C3—H3A···O4$^{ii}$ | 0.97 | 2.49 | 3.450 (16) | 172 |
| C3—H3B···O2 | 0.97 | 2.48 | 3.26 (3) | 137 |
| C15—H15A···O1$^{iii}$ | 0.97 | 2.37 | 3.155 (6) | 138 |

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x+1, -y+1, -z+2$; (iii) $x-1, y+1, z$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2562).

## References

Bienko, A., Klak, J., Mrozinski, J., Boca, R., Brudgam, I. & Hartl, H. (2007). *Dalton Trans.* pp. 2681–2688.

Bruker (2000). *SADABS, SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Shen, H. Y., Liao, D. Z., Jiang, Z. H. & Yan, S. P. (1999). *Transition Met. Chem.* **24**, 581–583.

Szalda, D. J. & Fujita, E. (1992). *Acta Cryst.* C**48**, 1767–1771.

**supplementary materials**

# (5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene-$\kappa^4N^1,N^4,N^8,N^{11}$)(thiocyanato-$\kappa S$)nickel(II) perchlorate monohydrate

## J.-H. Bi

## Comment

A number of researches study azamacrocyclic systems (Bienko *et al.*, 2007; Shen *et al.*, 1999; Szalda *et al.*, 1992). Szalda reported a crystal structure of metal complex derived from tetraazacyclotetradeca-4,11-diene macrocycles (Szalda *et al.*, 1992). To investigate whether the potentially explosive perchlorate anions in this complex can be replaced by other anions to facilitate its further application, NCS$^-$ anion was used and the title complex was obtained.

The coordination geometry of Ni$^{II}$ center is shown in Fig.1. The Ni$^{II}$ center adopts a square-pyramidal coordination geometry, where four N atoms from macrocyclic ligand form an equatorial plane and one S atom from the thiocyanate anion occupies an apical position. The Ni—S bond length of 3.298 (13) Å is slightly longer than those of 3.171 (14) Å observed and discussed by Bienko *et al.* (2007).

The crystal packing is stabilized by intermolecular hydrogen bonding interactions (Table 1).

## Experimental

All solvents and chemicals were of analytical grade and were used without further purification. The mononuclear nickel(II)-diperchlorate macrocycle complex (0.538 g, 0.1 mmol), which was prepared *via* similar method as reported previously (Szalda *et al.*, 1992), was dissolved in acetonitrile (30 ml) and NH$_4$(NCS)(0.152 g, 0.2 mmol) was added. The mixture was refluxed for 2 h, and then cooled to room temperature. The green precipitate was collected, washed with a small amount of acetonitrile and dried *in vacuo*. Single crystals suitable for X-ray analysis were grown from the mother solution by slow evaporation at room temperature in air. Elemental analysis calculated for C$_{17}$H$_{34}$ClN$_5$NiO$_5$S: C 39.67, H 6.66, N 13.61%; found: C 39.71, H 6.70, N 13.57%.

## Refinement

All hydrogen atoms were geometrically positioned (C—H 0.93–0.97 Å, O–H 0.84–0.85 Å, N–H 0.91 Å) and refined as riding, with $U_{iso}$(H)=1.2–1.5 $U_{eq}$ of the parent atom. The oxygen atoms O2, O3 and O4 of the perchlorate anion were treated as disordered between two orientations with the occupancies refined to 0.61 (4) and 0.39 (4).
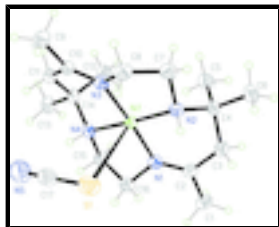
# supplementary materials

**Figures**



Fig. 1. Molecular structure of the cation of the title compound showing 30% probability displacement ellipsoids and the atomic numbering.

**(5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene- $\kappa^4 N^1, N^4, N^8, N^{11}$)(thiocyanato- κS)nickel(II) perchlorate monohydrate**

*Crystal data*

| | |
|---|---|
| $[Ni(NCS)(C_{16}H_{32}N_4)]ClO_4 \cdot H_2O$ | $Z = 2$ |
| $M_r = 514.71$ | $F_{000} = 544$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.459$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation<br>$\lambda = 0.71073$ Å |
| $a = 7.2678$ (11) Å | Cell parameters from 2923 reflections |
| $b = 8.9998$ (13) Å | $\theta = 2.5–27.7°$ |
| $c = 19.513$ (2) Å | $\mu = 1.07$ mm$^{-1}$ |
| $\alpha = 84.1430$ (10)° | $T = 291$ K |
| $\beta = 87.005$ (2)° | Block, green |
| $\gamma = 67.3480$ (10)° | $0.49 \times 0.40 \times 0.39$ mm |
| $V = 1171.6$ (3) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 4062 independent reflections |
| Radiation source: fine-focus sealed tube | 3247 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.019$ |
| $T = 291$ K | $\theta_{max} = 25.0°$ |
| φ and ω scans | $\theta_{min} = 2.1°$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2000) | $h = -8 \rightarrow 8$ |
| $T_{min} = 0.623$, $T_{max} = 0.681$ | $k = -10 \rightarrow 8$ |
| 6103 measured reflections | $l = -23 \rightarrow 16$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | H-atom parameters constrained |

$wR(F^2) = 0.109$

$w = 1/[\sigma^2(F_o{}^2) + (0.0501P)^2 + 0.9082P]$

where $P = (F_o{}^2 + 2F_c{}^2)/3$

$S = 1.03$

$(\Delta/\sigma)_{max} = 0.001$

4062 reflections

$\Delta\rho_{max} = 0.53$ e Å$^{-3}$

299 parameters

$\Delta\rho_{min} = -0.89$ e Å$^{-3}$

Primary atom site location: structure-invariant direct methods

Extinction correction: none

*Special details*

**Experimental**. The structure was solved by direct methods (Bruker, 2000) and successive difference Fourier syntheses.

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

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

|      | $x$         | $y$         | $z$          | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|------|-------------|-------------|--------------|---------------------|-----------|
| Ni1  | 0.30773 (6) | 0.73405 (4) | 0.74822 (2)  | 0.03298 (14)        |           |
| S1   | 0.77119 (17)| 0.55310 (15)| 0.69389 (7)  | 0.0742 (3)          |           |
| Cl1  | 0.83588 (13)| 0.23413 (11)| 0.87389 (5)  | 0.0488 (2)          |           |
| N1   | 0.3810 (4)  | 0.8445 (3)  | 0.81175 (14) | 0.0369 (6)          |           |
| N2   | 0.3265 (4)  | 0.5584 (3)  | 0.81554 (13) | 0.0358 (6)          |           |
| H2   | 0.4585      | 0.5040      | 0.8246       | 0.043*              |           |
| N3   | 0.2600 (4)  | 0.6153 (3)  | 0.68168 (14) | 0.0370 (6)          |           |
| N4   | 0.2731 (4)  | 0.9145 (3)  | 0.68173 (13) | 0.0358 (6)          |           |
| H4   | 0.3769      | 0.8812      | 0.6512       | 0.043*              |           |
| N5   | 0.6503 (6)  | 0.7714 (6)  | 0.5780 (2)   | 0.0895 (13)         |           |
| O1   | 1.0226 (5)  | 0.1857 (5)  | 0.8446 (3)   | 0.1262 (16)         |           |
| O2   | 0.758 (4)   | 0.401 (3)   | 0.8792 (15)  | 0.103 (6)           | 0.61 (4)  |
| O3   | 0.698 (3)   | 0.198 (3)   | 0.8398 (14)  | 0.115 (7)           | 0.61 (4)  |
| O4   | 0.889 (5)   | 0.1340 (19) | 0.9359 (6)   | 0.151 (8)           | 0.61 (4)  |
| O2'  | 0.765 (6)   | 0.150 (3)   | 0.9228 (18)  | 0.125 (11)          | 0.39 (4)  |
| O3'  | 0.724 (6)   | 0.244 (5)   | 0.8153 (16)  | 0.132 (12)          | 0.39 (4)  |
| O4'  | 0.774 (7)   | 0.381 (6)   | 0.9037 (19)  | 0.101 (10)          | 0.39 (4)  |
| O5   | 0.4522 (5)  | 0.8714 (5)  | 0.44382 (19) | 0.1003 (11)         |           |
| H5F  | 0.5099      | 0.8396      | 0.4824       | 0.120*              |           |
| H5G  | 0.4217      | 0.9727      | 0.4365       | 0.120*              |           |
| C1   | 0.4568 (6)  | 0.9196 (5)  | 0.9214 (2)   | 0.0567 (10)         |           |
| H1A  | 0.5602      | 0.9470      | 0.8977       | 0.085*              |           |
| H1B  | 0.5066      | 0.8575      | 0.9642       | 0.085*              |           |
| H1C  | 0.3455      | 1.0168      | 0.9303       | 0.085*              |           |

| | | | | |
|---|---|---|---|---|
| C2 | 0.3917 (5) | 0.8227 (4) | 0.87771 (17) | 0.0393 (7) |
| C3 | 0.3413 (5) | 0.6913 (4) | 0.91705 (18) | 0.0470 (8) |
| H3A | 0.2667 | 0.7355 | 0.9579 | 0.056* |
| H3B | 0.4658 | 0.6070 | 0.9327 | 0.056* |
| C4 | 0.2248 (5) | 0.6103 (4) | 0.88317 (17) | 0.0423 (8) |
| C5 | 0.0098 (5) | 0.7264 (5) | 0.8714 (2) | 0.0587 (10) |
| H5A | 0.0078 | 0.8222 | 0.8442 | 0.088* |
| H5B | −0.0551 | 0.7550 | 0.9150 | 0.088* |
| H5C | −0.0589 | 0.6753 | 0.8476 | 0.088* |
| C6 | 0.2333 (6) | 0.4619 (5) | 0.9316 (2) | 0.0595 (10) |
| H6A | 0.1473 | 0.4156 | 0.9148 | 0.089* |
| H6B | 0.1902 | 0.4942 | 0.9770 | 0.089* |
| H6C | 0.3676 | 0.3832 | 0.9332 | 0.089* |
| C7 | 0.2598 (6) | 0.4456 (4) | 0.78297 (19) | 0.0482 (9) |
| H7A | 0.1158 | 0.4814 | 0.7863 | 0.058* |
| H7B | 0.3180 | 0.3379 | 0.8063 | 0.058* |
| C8 | 0.3252 (6) | 0.4434 (4) | 0.70907 (19) | 0.0493 (9) |
| H8A | 0.4689 | 0.3895 | 0.7052 | 0.059* |
| H8B | 0.2635 | 0.3874 | 0.6840 | 0.059* |
| C9 | 0.2099 (7) | 0.5436 (5) | 0.5678 (2) | 0.0617 (11) |
| H9A | 0.3387 | 0.4569 | 0.5687 | 0.093* |
| H9B | 0.1862 | 0.5996 | 0.5226 | 0.093* |
| H9C | 0.1092 | 0.5004 | 0.5794 | 0.093* |
| C10 | 0.2029 (5) | 0.6592 (4) | 0.61938 (17) | 0.0404 (8) |
| C11 | 0.1245 (5) | 0.8328 (4) | 0.59141 (17) | 0.0432 (8) |
| H11A | 0.0002 | 0.8546 | 0.5685 | 0.052* |
| H11B | 0.2179 | 0.8455 | 0.5562 | 0.052* |
| C12 | 0.0857 (5) | 0.9639 (4) | 0.64053 (16) | 0.0394 (7) |
| C13 | −0.0909 (5) | 0.9766 (4) | 0.68875 (18) | 0.0466 (8) |
| H13A | −0.0751 | 0.8710 | 0.7093 | 0.070* |
| H13B | −0.2121 | 1.0222 | 0.6631 | 0.070* |
| H13C | −0.0965 | 1.0448 | 0.7242 | 0.070* |
| C14 | 0.0433 (6) | 1.1253 (4) | 0.5974 (2) | 0.0554 (10) |
| H14A | 0.0124 | 1.2101 | 0.6275 | 0.083* |
| H14B | −0.0678 | 1.1476 | 0.5680 | 0.083* |
| H14C | 0.1587 | 1.1194 | 0.5698 | 0.083* |
| C15 | 0.2952 (6) | 1.0464 (4) | 0.71649 (18) | 0.0473 (9) |
| H15A | 0.1677 | 1.1145 | 0.7353 | 0.057* |
| H15B | 0.3427 | 1.1128 | 0.6838 | 0.057* |
| C16 | 0.4423 (6) | 0.9688 (4) | 0.77314 (19) | 0.0487 (9) |
| H16A | 0.5759 | 0.9194 | 0.7542 | 0.058* |
| H16B | 0.4409 | 1.0486 | 0.8032 | 0.058* |
| C17 | 0.7045 (6) | 0.6772 (5) | 0.6252 (3) | 0.0621 (11) |

*Atomic displacement parameters ($Å^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ni1 | 0.0374 (2) | 0.0284 (2) | 0.0350 (2) | −0.01414 (17) | 0.00074 (17) | −0.00531 (16) |

| | | | | | | |
|---|---|---|---|---|---|---|
| S1 | 0.0542 (6) | 0.0768 (8) | 0.0868 (9) | −0.0221 (6) | −0.0052 (6) | 0.0040 (6) |
| Cl1 | 0.0432 (5) | 0.0483 (5) | 0.0450 (5) | −0.0061 (4) | 0.0094 (4) | −0.0117 (4) |
| N1 | 0.0370 (14) | 0.0317 (14) | 0.0435 (16) | −0.0140 (12) | 0.0022 (12) | −0.0078 (12) |
| N2 | 0.0340 (14) | 0.0309 (14) | 0.0409 (15) | −0.0111 (11) | −0.0024 (11) | −0.0012 (11) |
| N3 | 0.0396 (15) | 0.0305 (14) | 0.0428 (16) | −0.0149 (12) | 0.0008 (12) | −0.0070 (12) |
| N4 | 0.0425 (15) | 0.0315 (14) | 0.0356 (15) | −0.0164 (12) | 0.0068 (12) | −0.0078 (11) |
| N5 | 0.071 (3) | 0.098 (3) | 0.082 (3) | −0.017 (2) | 0.000 (2) | 0.007 (3) |
| O1 | 0.070 (2) | 0.144 (4) | 0.160 (4) | −0.029 (2) | 0.041 (2) | −0.062 (3) |
| O2 | 0.083 (7) | 0.074 (6) | 0.143 (16) | −0.012 (5) | −0.027 (11) | −0.026 (10) |
| O3 | 0.078 (5) | 0.119 (9) | 0.169 (19) | −0.053 (6) | −0.008 (9) | −0.040 (11) |
| O4 | 0.158 (16) | 0.151 (8) | 0.071 (5) | 0.013 (9) | −0.002 (7) | 0.027 (5) |
| O2' | 0.13 (2) | 0.110 (13) | 0.125 (17) | −0.050 (13) | 0.048 (15) | −0.002 (11) |
| O3' | 0.121 (19) | 0.15 (2) | 0.081 (13) | 0.002 (13) | −0.035 (11) | −0.040 (12) |
| O4' | 0.10 (2) | 0.10 (2) | 0.104 (17) | −0.026 (15) | 0.031 (14) | −0.071 (17) |
| O5 | 0.106 (3) | 0.114 (3) | 0.085 (3) | −0.045 (2) | −0.019 (2) | −0.004 (2) |
| C1 | 0.063 (2) | 0.063 (2) | 0.049 (2) | −0.026 (2) | −0.0088 (19) | −0.0173 (19) |
| C2 | 0.0320 (16) | 0.0397 (18) | 0.0408 (19) | −0.0060 (14) | 0.0001 (14) | −0.0115 (15) |
| C3 | 0.051 (2) | 0.052 (2) | 0.0383 (19) | −0.0191 (17) | 0.0002 (16) | −0.0057 (16) |
| C4 | 0.0389 (18) | 0.0453 (19) | 0.0405 (19) | −0.0151 (15) | 0.0031 (15) | 0.0002 (15) |
| C5 | 0.042 (2) | 0.065 (3) | 0.061 (3) | −0.0130 (18) | 0.0071 (18) | −0.003 (2) |
| C6 | 0.063 (2) | 0.065 (3) | 0.053 (2) | −0.032 (2) | 0.0009 (19) | 0.0119 (19) |
| C7 | 0.058 (2) | 0.0326 (18) | 0.058 (2) | −0.0216 (17) | −0.0078 (18) | 0.0007 (16) |
| C8 | 0.063 (2) | 0.0290 (17) | 0.058 (2) | −0.0171 (16) | −0.0087 (18) | −0.0095 (16) |
| C9 | 0.080 (3) | 0.054 (2) | 0.054 (2) | −0.024 (2) | −0.001 (2) | −0.0235 (19) |
| C10 | 0.0436 (19) | 0.0434 (19) | 0.0402 (19) | −0.0219 (16) | 0.0069 (15) | −0.0135 (15) |
| C11 | 0.0467 (19) | 0.049 (2) | 0.0362 (18) | −0.0204 (17) | 0.0019 (15) | −0.0068 (15) |
| C12 | 0.0427 (18) | 0.0382 (18) | 0.0333 (17) | −0.0118 (15) | 0.0022 (14) | −0.0020 (14) |
| C13 | 0.0398 (18) | 0.049 (2) | 0.044 (2) | −0.0088 (16) | 0.0031 (15) | −0.0065 (16) |
| C14 | 0.066 (2) | 0.044 (2) | 0.049 (2) | −0.0161 (19) | −0.0030 (19) | 0.0058 (17) |
| C15 | 0.067 (2) | 0.0337 (18) | 0.047 (2) | −0.0252 (17) | 0.0034 (17) | −0.0061 (15) |
| C16 | 0.061 (2) | 0.045 (2) | 0.053 (2) | −0.0321 (18) | 0.0022 (18) | −0.0107 (17) |
| C17 | 0.041 (2) | 0.066 (3) | 0.075 (3) | −0.015 (2) | 0.006 (2) | −0.016 (2) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Ni1—N1 | 1.880 (3) | C4—C5 | 1.522 (5) |
| Ni1—N3 | 1.888 (3) | C4—C6 | 1.538 (5) |
| Ni1—N2 | 1.916 (2) | C5—H5A | 0.9600 |
| Ni1—N4 | 1.917 (2) | C5—H5B | 0.9600 |
| Ni1—S1 | 3.2979 (13) | C5—H5C | 0.9600 |
| S1—C17 | 1.620 (5) | C6—H6A | 0.9600 |
| Cl1—O2' | 1.359 (18) | C6—H6B | 0.9600 |
| Cl1—O1 | 1.369 (4) | C6—H6C | 0.9600 |
| Cl1—O3 | 1.385 (18) | C7—C8 | 1.494 (5) |
| Cl1—O2 | 1.40 (3) | C7—H7A | 0.9700 |
| Cl1—O4' | 1.40 (4) | C7—H7B | 0.9700 |
| Cl1—O4 | 1.408 (11) | C8—H8A | 0.9700 |
| Cl1—O3' | 1.41 (3) | C8—H8B | 0.9700 |
| N1—C2 | 1.284 (4) | C9—C10 | 1.505 (5) |

| | | | |
|---|---|---|---|
| N1—C16 | 1.482 (4) | C9—H9A | 0.9600 |
| N2—C7 | 1.487 (4) | C9—H9B | 0.9600 |
| N2—C4 | 1.505 (4) | C9—H9C | 0.9600 |
| N2—H2 | 0.9100 | C10—C11 | 1.495 (5) |
| N3—C10 | 1.278 (4) | C11—C12 | 1.529 (4) |
| N3—C8 | 1.482 (4) | C11—H11A | 0.9700 |
| N4—C15 | 1.489 (4) | C11—H11B | 0.9700 |
| N4—C12 | 1.508 (4) | C12—C13 | 1.526 (4) |
| N4—H4 | 0.9100 | C12—C14 | 1.531 (4) |
| N5—C17 | 1.159 (5) | C13—H13A | 0.9600 |
| O5—H5F | 0.8500 | C13—H13B | 0.9600 |
| O5—H5G | 0.8500 | C13—H13C | 0.9600 |
| C1—C2 | 1.491 (5) | C14—H14A | 0.9600 |
| C1—H1A | 0.9600 | C14—H14B | 0.9600 |
| C1—H1B | 0.9600 | C14—H14C | 0.9600 |
| C1—H1C | 0.9600 | C15—C16 | 1.498 (5) |
| C2—C3 | 1.496 (5) | C15—H15A | 0.9700 |
| C3—C4 | 1.523 (5) | C15—H15B | 0.9700 |
| C3—H3A | 0.9700 | C16—H16A | 0.9700 |
| C3—H3B | 0.9700 | C16—H16B | 0.9700 |
| N1—Ni1—N3 | 174.53 (11) | C3—C4—C6 | 107.2 (3) |
| N1—Ni1—N2 | 92.60 (11) | C4—C5—H5A | 109.5 |
| N3—Ni1—N2 | 88.02 (11) | C4—C5—H5B | 109.5 |
| N1—Ni1—N4 | 87.93 (11) | H5A—C5—H5B | 109.5 |
| N3—Ni1—N4 | 91.75 (11) | C4—C5—H5C | 109.5 |
| N2—Ni1—N4 | 176.80 (11) | H5A—C5—H5C | 109.5 |
| N1—Ni1—S1 | 92.86 (8) | H5B—C5—H5C | 109.5 |
| N3—Ni1—S1 | 81.67 (8) | C4—C6—H6A | 109.5 |
| N2—Ni1—S1 | 92.88 (8) | C4—C6—H6B | 109.5 |
| N4—Ni1—S1 | 90.25 (8) | H6A—C6—H6B | 109.5 |
| C17—S1—Ni1 | 85.87 (14) | C4—C6—H6C | 109.5 |
| O2'—Cl1—O1 | 127.9 (17) | H6A—C6—H6C | 109.5 |
| O2'—Cl1—O3 | 75.5 (14) | H6B—C6—H6C | 109.5 |
| O1—Cl1—O3 | 115.2 (10) | N2—C7—C8 | 108.2 (3) |
| O2'—Cl1—O2 | 113.7 (19) | N2—C7—H7A | 110.0 |
| O1—Cl1—O2 | 110.6 (14) | C8—C7—H7A | 110.0 |
| O3—Cl1—O2 | 107.7 (14) | N2—C7—H7B | 110.0 |
| O2'—Cl1—O4' | 99 (2) | C8—C7—H7B | 110.0 |
| O1—Cl1—O4' | 115 (2) | H7A—C7—H7B | 108.4 |
| O3—Cl1—O4' | 119 (2) | N3—C8—C7 | 105.6 (3) |
| O2—Cl1—O4' | 21 (2) | N3—C8—H8A | 110.6 |
| O2'—Cl1—O4 | 38.1 (9) | C7—C8—H8A | 110.6 |
| O1—Cl1—O4 | 97.2 (13) | N3—C8—H8B | 110.6 |
| O3—Cl1—O4 | 109.6 (11) | C7—C8—H8B | 110.6 |
| O2—Cl1—O4 | 116.7 (11) | H8A—C8—H8B | 108.7 |
| O4'—Cl1—O4 | 96.2 (18) | C10—C9—H9A | 109.5 |
| O2'—Cl1—O3' | 103.0 (12) | C10—C9—H9B | 109.5 |
| O1—Cl1—O3' | 99.4 (17) | H9A—C9—H9B | 109.5 |
| O3—Cl1—O3' | 27.7 (17) | C10—C9—H9C | 109.5 |

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| O2—Cl1—O3' | 94.5 (16) | H9A—C9—H9C | 109.5 |
| O4'—Cl1—O3' | 113 (2) | H9B—C9—H9C | 109.5 |
| O4—Cl1—O3' | 136.4 (14) | N3—C10—C11 | 122.0 (3) |
| C2—N1—C16 | 120.5 (3) | N3—C10—C9 | 123.9 (3) |
| C2—N1—Ni1 | 130.8 (2) | C11—C10—C9 | 114.1 (3) |
| C16—N1—Ni1 | 108.6 (2) | C10—C11—C12 | 119.3 (3) |
| C7—N2—C4 | 114.5 (3) | C10—C11—H11A | 107.5 |
| C7—N2—Ni1 | 107.9 (2) | C12—C11—H11A | 107.5 |
| C4—N2—Ni1 | 114.08 (19) | C10—C11—H11B | 107.5 |
| C7—N2—H2 | 106.6 | C12—C11—H11B | 107.5 |
| C4—N2—H2 | 106.6 | H11A—C11—H11B | 107.0 |
| Ni1—N2—H2 | 106.6 | N4—C12—C13 | 109.9 (3) |
| C10—N3—C8 | 120.7 (3) | N4—C12—C11 | 106.1 (3) |
| C10—N3—Ni1 | 129.9 (2) | C13—C12—C11 | 111.4 (3) |
| C8—N3—Ni1 | 109.0 (2) | N4—C12—C14 | 111.4 (3) |
| C15—N4—C12 | 115.1 (2) | C13—C12—C14 | 109.8 (3) |
| C15—N4—Ni1 | 109.0 (2) | C11—C12—C14 | 108.3 (3) |
| C12—N4—Ni1 | 112.87 (18) | C12—C13—H13A | 109.5 |
| C15—N4—H4 | 106.4 | C12—C13—H13B | 109.5 |
| C12—N4—H4 | 106.4 | H13A—C13—H13B | 109.5 |
| Ni1—N4—H4 | 106.4 | C12—C13—H13C | 109.5 |
| H5F—O5—H5G | 108.3 | H13A—C13—H13C | 109.5 |
| C2—C1—H1A | 109.5 | H13B—C13—H13C | 109.5 |
| C2—C1—H1B | 109.5 | C12—C14—H14A | 109.5 |
| H1A—C1—H1B | 109.5 | C12—C14—H14B | 109.5 |
| C2—C1—H1C | 109.5 | H14A—C14—H14B | 109.5 |
| H1A—C1—H1C | 109.5 | C12—C14—H14C | 109.5 |
| H1B—C1—H1C | 109.5 | H14A—C14—H14C | 109.5 |
| N1—C2—C1 | 124.5 (3) | H14B—C14—H14C | 109.5 |
| N1—C2—C3 | 121.1 (3) | N4—C15—C16 | 107.5 (3) |
| C1—C2—C3 | 114.4 (3) | N4—C15—H15A | 110.2 |
| C2—C3—C4 | 120.4 (3) | C16—C15—H15A | 110.2 |
| C2—C3—H3A | 107.2 | N4—C15—H15B | 110.2 |
| C4—C3—H3A | 107.2 | C16—C15—H15B | 110.2 |
| C2—C3—H3B | 107.2 | H15A—C15—H15B | 108.5 |
| C4—C3—H3B | 107.2 | N1—C16—C15 | 106.6 (3) |
| H3A—C3—H3B | 106.9 | N1—C16—H16A | 110.4 |
| N2—C4—C5 | 110.3 (3) | C15—C16—H16A | 110.4 |
| N2—C4—C3 | 107.6 (3) | N1—C16—H16B | 110.4 |
| C5—C4—C3 | 110.8 (3) | C15—C16—H16B | 110.4 |
| N2—C4—C6 | 110.3 (3) | H16A—C16—H16B | 108.6 |
| C5—C4—C6 | 110.7 (3) | N5—C17—S1 | 176.7 (4) |
| N1—Ni1—S1—C17 | −106.07 (18) | Ni1—N1—C2—C3 | −0.1 (5) |
| N3—Ni1—S1—C17 | 73.60 (18) | N1—C2—C3—C4 | −16.4 (5) |
| N2—Ni1—S1—C17 | 161.18 (18) | C1—C2—C3—C4 | 164.7 (3) |
| N4—Ni1—S1—C17 | −18.13 (18) | C7—N2—C4—C5 | −72.0 (3) |
| N3—Ni1—N1—C2 | −110.1 (12) | Ni1—N2—C4—C5 | 53.0 (3) |
| N2—Ni1—N1—C2 | −13.6 (3) | C7—N2—C4—C3 | 167.1 (3) |
| N4—Ni1—N1—C2 | 163.2 (3) | Ni1—N2—C4—C3 | −67.9 (3) |

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|---|---|---|---|
| S1—Ni1—N1—C2 | −106.7 (3) | C7—N2—C4—C6 | 50.5 (4) |
| N3—Ni1—N1—C16 | 66.7 (12) | Ni1—N2—C4—C6 | 175.5 (2) |
| N2—Ni1—N1—C16 | 163.1 (2) | C2—C3—C4—N2 | 50.8 (4) |
| N4—Ni1—N1—C16 | −20.1 (2) | C2—C3—C4—C5 | −69.8 (4) |
| S1—Ni1—N1—C16 | 70.1 (2) | C2—C3—C4—C6 | 169.4 (3) |
| N1—Ni1—N2—C7 | 175.6 (2) | C4—N2—C7—C8 | 163.6 (3) |
| N3—Ni1—N2—C7 | −9.8 (2) | Ni1—N2—C7—C8 | 35.4 (3) |
| N4—Ni1—N2—C7 | 76 (2) | C10—N3—C8—C7 | −145.6 (3) |
| S1—Ni1—N2—C7 | −91.4 (2) | Ni1—N3—C8—C7 | 41.0 (3) |
| N1—Ni1—N2—C4 | 47.2 (2) | N2—C7—C8—N3 | −49.6 (4) |
| N3—Ni1—N2—C4 | −138.3 (2) | C8—N3—C10—C11 | 176.2 (3) |
| N4—Ni1—N2—C4 | −52 (2) | Ni1—N3—C10—C11 | −12.0 (5) |
| S1—Ni1—N2—C4 | 140.2 (2) | C8—N3—C10—C9 | −4.5 (5) |
| N1—Ni1—N3—C10 | −93.8 (12) | Ni1—N3—C10—C9 | 167.3 (3) |
| N2—Ni1—N3—C10 | 169.6 (3) | N3—C10—C11—C12 | −8.1 (5) |
| N4—Ni1—N3—C10 | −7.2 (3) | C9—C10—C11—C12 | 172.5 (3) |
| S1—Ni1—N3—C10 | −97.2 (3) | C15—N4—C12—C13 | −78.0 (3) |
| N1—Ni1—N3—C8 | 78.7 (12) | Ni1—N4—C12—C13 | 48.0 (3) |
| N2—Ni1—N3—C8 | −17.9 (2) | C15—N4—C12—C11 | 161.5 (3) |
| N4—Ni1—N3—C8 | 165.3 (2) | Ni1—N4—C12—C11 | −72.5 (3) |
| S1—Ni1—N3—C8 | 75.3 (2) | C15—N4—C12—C14 | 43.8 (4) |
| N1—Ni1—N4—C15 | −7.0 (2) | Ni1—N4—C12—C14 | 169.8 (2) |
| N3—Ni1—N4—C15 | 178.5 (2) | C10—C11—C12—N4 | 50.3 (4) |
| N2—Ni1—N4—C15 | 92.6 (19) | C10—C11—C12—C13 | −69.3 (4) |
| S1—Ni1—N4—C15 | −99.9 (2) | C10—C11—C12—C14 | 169.9 (3) |
| N1—Ni1—N4—C12 | −136.2 (2) | C12—N4—C15—C16 | 160.1 (3) |
| N3—Ni1—N4—C12 | 49.2 (2) | Ni1—N4—C15—C16 | 32.1 (3) |
| N2—Ni1—N4—C12 | −37 (2) | C2—N1—C16—C15 | −140.5 (3) |
| S1—Ni1—N4—C12 | 130.90 (19) | Ni1—N1—C16—C15 | 42.3 (3) |
| C16—N1—C2—C1 | 2.4 (5) | N4—C15—C16—N1 | −48.1 (4) |
| Ni1—N1—C2—C1 | 178.8 (2) | Ni1—S1—C17—N5 | 31 (8) |
| C16—N1—C2—C3 | −176.5 (3) | | |

*Hydrogen-bond geometry (Å, °)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N2—H2···O2 | 0.91 | 2.28 | 3.16 (3) | 162 |
| N4—H4···N5 | 0.91 | 2.33 | 3.241 (5) | 175 |
| O5—H5F···N5 | 0.85 | 2.09 | 2.942 (6) | 178 |
| O5—H5G···N5[i] | 0.85 | 2.15 | 2.997 (6) | 178 |
| C3—H3A···O4[ii] | 0.97 | 2.49 | 3.450 (16) | 172 |
| C3—H3B···O2 | 0.97 | 2.48 | 3.26 (3) | 137 |
| C15—H15A···O1[iii] | 0.97 | 2.37 | 3.155 (6) | 138 |

Symmetry codes: (i) −x+1, −y+2, −z+1; (ii) −x+1, −y+1, −z+2; (iii) x−1, y+1, z.

**Fig. 1**