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# Hydrogen-bonding and π–π stacking interactions in tris(1,10-phenanthroline-$\kappa^2N,N'$)nickel(II) bis{[1-*tert*-butylimidazole-2(3*H*)-thione-$\kappa S$]trichloridonickelate(II)} acetonitrile disolvate

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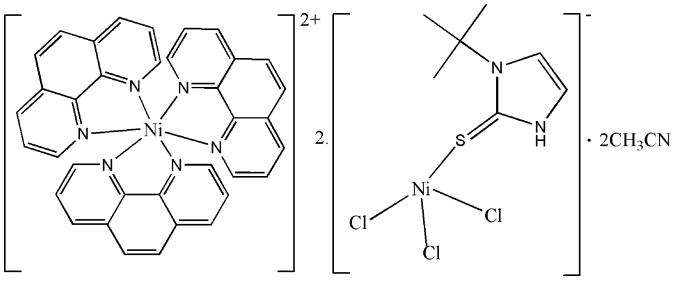
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.010 Å; disorder in main residue; $R$ factor = 0.051; $wR$ factor = 0.158; data-to-parameter ratio = 14.0.

The asymmetric unit of the title complex, $[Ni(C_{12}H_8N_2)_3][NiCl_3(C_7H_{12}N_2S)]_2\cdot 2CH_3CN$, consists of one anion, one-half of a cation and one acetonitrile molecule. The $Ni^{II}$ atom in the $[Ni(phen)_3]^{2+}$ cation (phen is 1,10-phenanthroline) lies on an inversion centre in an octahedral environment, whereas in the $[NiCl_3(tm)]^-$ anion [tm is 1-*tert*-butylimidazole-2(3*H*)-thione], the geometry is distorted tetrahedral. In the crystal structure, intermolecular C—H···Cl hydrogen bonds and π–π stacking interactions (centroid–centroid distance = 3.52 Å) lead to the formation of a three-dimensional framework. One of the methyl groups of the *tert*-butyl group of *N*-*tert*-butyl-2-thioimidazole is disordered between two equally populated positions.

## Related literature

For general background, see: Fatimi *et al.* (1994); Iradyan *et al.* (1987); Suescun *et al.* (1999); Yu *et al.* (2003); Fang & Dai (2006); Chen *et al.*, (2007); Senda *et al.* (2006). For synthesis details, see: Kister *et al.* (1979).



## Experimental

### Crystal data

$[Ni(C_{12}H_8N_2)_3][NiCl_3(C_7H_{12}N_2S)]_2\cdot 2C_2H_3N$
$M_r$ = 1324.04
Monoclinic, $C2/c$
$a$ = 22.8953 (15) Å
$b$ = 15.2934 (10) Å
$c$ = 19.9417 (19) Å
$\beta$ = 123.543 (3)°
$V$ = 5819.7 (8) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.36 mm$^{-1}$
$T$ = 298 (2) K
0.24 × 0.20 × 0.18 mm

### Data collection

Bruker Kappa APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.737, $T_{max}$ = 0.792
30921 measured reflections
5178 independent reflections
3346 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.076

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.157
$S$ = 1.07
5178 reflections
370 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.24 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.55 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N4—H4···Cl2 | 0.85 (6) | 2.37 (7) | 3.178 (6) | 160 (6) |
| C2—H2···Cl3$^{i}$ | 0.82 (7) | 2.77 (7) | 3.552 (8) | 160 (4) |
| C5—H5*C*···S1 | 0.96 | 2.75 | 3.402 (9) | 126 |
| C7—H7*A*···S1 | 0.96 | 2.68 | 3.409 (8) | 133 |
| C10—H10···Cl3$^{ii}$ | 0.93 | 2.72 | 3.557 (7) | 151 |
| C25—H25···N6$^{iii}$ | 0.93 | 2.60 | 3.502 (9) | 162 |

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2050).

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# supporting information

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# Hydrogen-bonding and $\pi$–$\pi$ stacking interactions in tris(1,10-phenanthroline-$\kappa^2N,N'$)nickel(II) bis{[1-*tert*-butylimidazole-2(3*H*)-thione-$\kappa S$]trichloridonickelate(II)} acetonitrile disolvate

**Udai P. Singh and Vaibhave Aggarwal**

## S1. Comment

2-Thioimidazole (N,*N*,*S* donors) and its alkyl derivatives have antithyroid activity and platelet inhibitory effects. (Fatimi *et al.*, 1994; Iradyan *et al.*, 1987). The literature revealed the presence of various nickel(II) complexes with phenanthroline (Suescun *et al.*, 1999; Yu *et al.* (2003); Fang & Dai, 2006; Chen *et al.*, 2007) but none with *N*-*tert*-butyl-2-thioimidazole, except the one reported recently (Senda *et al.*, 2006). The present work reports the first structure of a nickel(II) complex with *N*-*tert*-butyl-2-thioimidazole and 1,10 phenanthroline, containing a tetrahedral anion, $[Ni(tm)(Cl)_3]^-$, and an octahedral cation, $[Ni(phen)_3]^{2+}$.

The title complex (I) is centrosymmetric, ionic in nature and comprises of one complex cation $[Ni(phen)_3]^{2+}$ and two complex anions $[Ni(tm)(Cl)_3]^-$ in the unit cell (Fig. 1). The metal centre in $[Ni(phen)_3]^{2+}$ is in an octahedral environment, the equatorial plane of which is formed by four phen nitrogen atoms, and the axial positions are occupied by another two nitrogen atoms of phen, with Ni1—N bond distances in the range of 2.079 (4)–2.100 (4) Å. The dihedral angles between the meanplanes of the neighboring phen rings are 77.53°, 86.07° and 85.97°. The *cis*-angles in the octahedron deviate only slightly from 90° and the *trans* angle in the axial position is almost linear *i.e.* 170.54 (15)°. The nickel(II) atom in the $[Ni(tm)(Cl)_3]^-$ anion is coordinated by three chlorine atoms and one sulfur atom of tm in a distorted tetrahedral geometry. The Ni—Cl bond distances are in the range of 2.251 (15) to 2.275 (15) Å. In the anion the two short bond distances (Ni2—Cl3 and Ni2—Cl1 of 2.2507 (15) and 2.253 (2) Å, respectively) and two long bond distances (Ni2—S1 and Ni2—Cl2 of 2.3054 (17) and 2.2753 (16) Å, respectively) make the geometry distorted tetrahedral.

Due to the presence of several intermolecular interactions between the three chloride ions bonded to atom Ni2 and the hydrogen atoms present on the phen rings, the complex cation is linked to six complex anions (Fig. 2 and Table 1), whereas the complex anions are linked to four complex cations through C—H···Cl hydrogen bonds (Fig. 3 and Table 1). In the crystal packing of complex (I) two layers are linked by hydrogen bonds in the bc plane. The $[Ni(phen)_3]^{2+}$ cations and the $[Ni(tm)(Cl)_3]^-$ anions interact with each other via hydrogen bonds formed by the terminally coordinated chloride ions of the complex anion (Cl1, Cl2 and Cl3) and the hydrogen atoms present on the phen ligands (Fig. 4). The two complex anions also interact with one another through $\pi$–$\pi$ stacking, with a separation of ca. 3.52 Å, and intermolecular C—H···Cl and C—H···N interactions involving the hydrogen atom of the middle ring of phenanthroline and the nitrogen atom of the acetonitrile molecule present in the lattice (Table 1).

## S2. Experimental

All the reagents were of commercial grade and were used as received. N-tert-butyl-thioimidazole (tm) was synthesized by a literature method (Kister *et al.*, 1979). To a solution of $NiCl_2.6H_2O$ (1.0 mmol) in 5 ml methanol, a methanolic solution

of N-tert-butyl-2-thioimidazole (1.0 mmol) was added and the mixture stirred for 40 minutes. This mixture was then added to the solution obtained by mixing $NiCl_2.6H_2O$ (1.0 mmol) in methanol with a methanolic solution of 1,10-phenanthroline (3.0 mmol). The whole reaction mixture was stirred for a further 30 minutes. The clear solution obtained was filtered and evaporated to dryness. The solid compound obtained was dissolved in acetonitrile and green single crystals, suitable for X-ray analysis, were obtained by slow evaporation at room temperature. Yield 62%. Analysis calculated for $C_{50}H_{48}N_{10}S_2Cl_6Ni_3$: C 48.30, H 3.86, N 11.27, S 5.15%; found: C 48.24, H 3.78, N 11.21, S 5.12%. Selected IR frequencies (KBr, $\nu$, $cm^{-1}$): 725 (s), 849 (s), 1369 (w), 1575 (m), 1623 (w), 3060 (w), 3412 (s).

### S3. Refinement

One of the methyl groups of the *tert*-butyl group of N-*tert*-butyl-2-thioimidazole is disordered between two equally populated positions (C6 and C6A; H6A and H6A1; H6B and H6B1; H6C and H6C1). C-bound H atoms were placed in geometrically idealized positions, with Csp2—H = 0.93 Å and Csp3—H = 0.96 Å, and treated as riding atoms with $U_{iso}$(H) = 1.2Ueq(C). H atoms attached to the O atoms were located in a difference Fourier map and refined as riding in their as found positions, with $U_{iso}$(H) = 1.5Ueq(O).

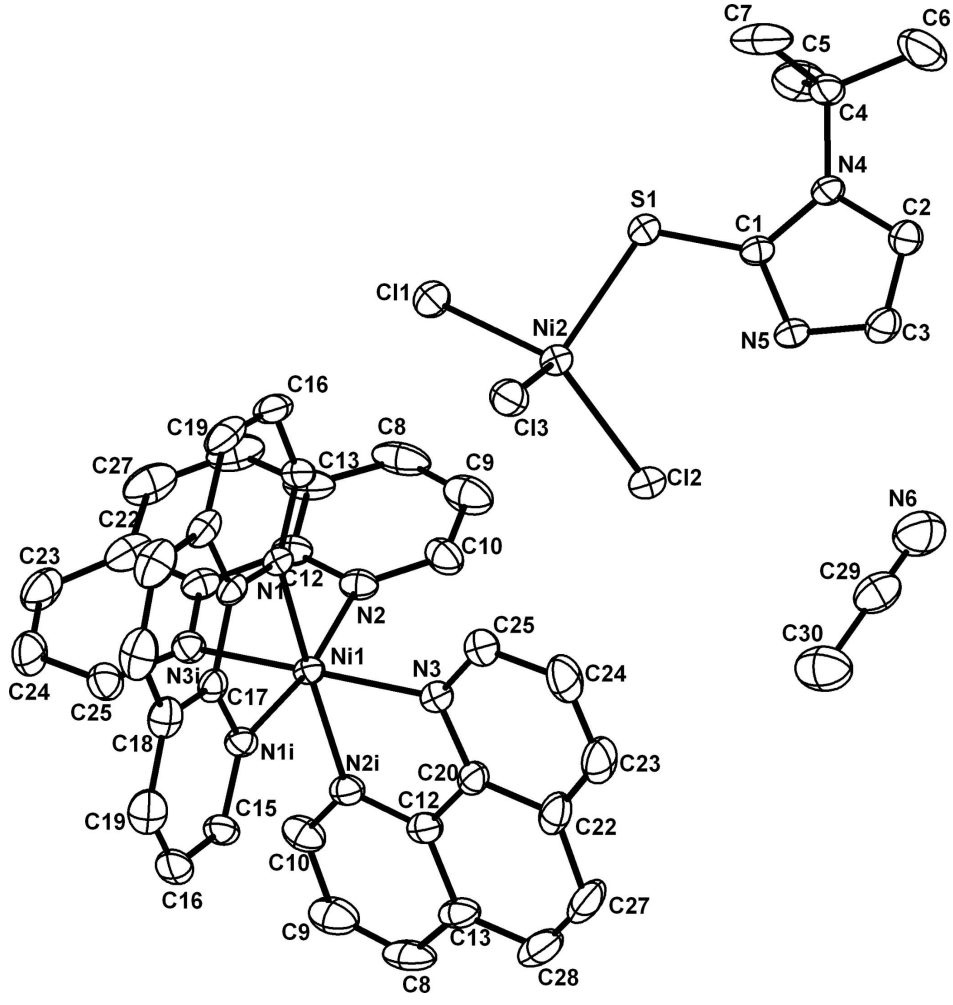


**Figure 1**

The molecular structure of the compound (I), shown with 30% probability displacement ellipsoids [H atoms have been omitted for clarity; Symmetry code: (i) -*x*, *y*, 0.5 - *z*.]

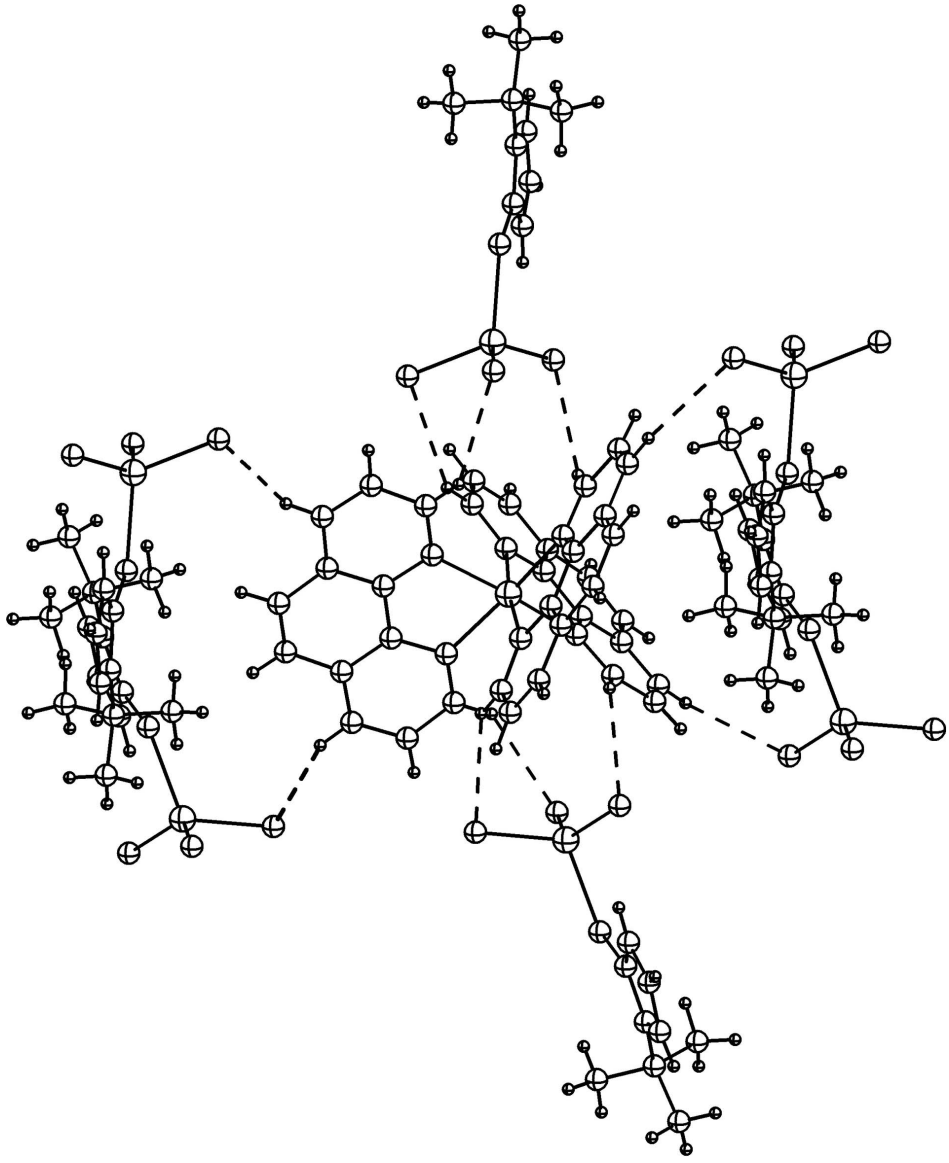

**Figure 2**

A view of the intermolecular C—H···Cl interactions involving the $[Ni(phen)_3]^+$ cation.

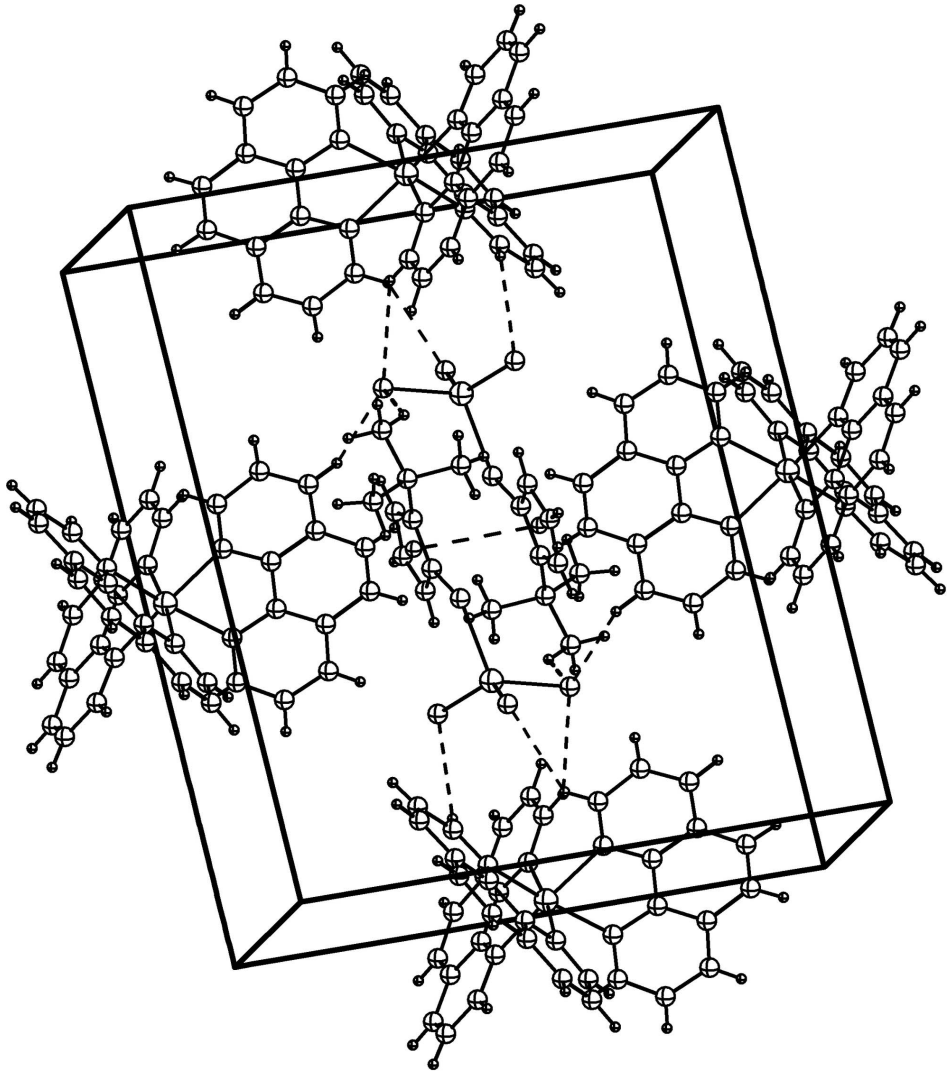

**Figure 3**

A view of the intermolecular $\pi$–$\pi$ stacking and C—H···Cl interactions involving the $[Ni(tm)(Cl)_3]^-$ anion.

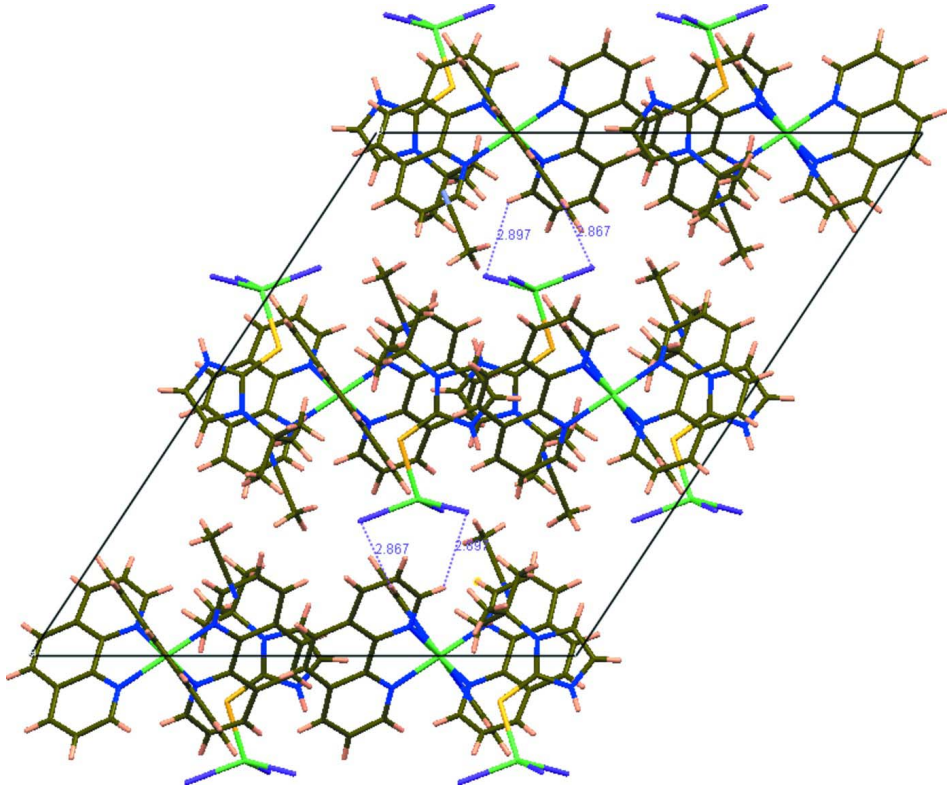


**Figure 4**

A view along the *b* axis of the crystal packing of complex (I), showing the interaction between two layers.

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*Crystal data*

$[Ni(C_{12}H_8N_2)_3][NiCl_3(C_7H_{12}N_2S)]_2\cdot 2C_2H_3N$
$M_r$ = 1324.04
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
*a* = 22.8953 (15) Å
*b* = 15.2934 (10) Å
*c* = 19.9417 (19) Å
$\beta$ = 123.543 (3)°
*V* = 5819.7 (8) Å$^3$
*Z* = 4
*F*(000) = 2720
$D_x$ = 1.511 Mg m$^{-3}$
Mo *K*$\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 5736 reflections
$\theta$ = 1.7–25.1°
$\mu$ = 1.36 mm$^{-1}$
*T* = 298 K
Block, green
0.24 × 0.20 × 0.18 mm

*Data collection*

Bruker Kappa APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.737, $T_{max}$ = 0.792
30921 measured reflections
5178 independent reflections
3346 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.076
$\theta_{max}$ = 25.1°, $\theta_{min}$ = 1.7°
*h* = −26→26
*k* = −17→17
*l* = −22→22

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.157$
$S = 1.07$
5178 reflections
370 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0987P)^2 + 2.7947P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.24$ e Å$^{-3}$
$\Delta\rho_{min} = -0.55$ e Å$^{-3}$

*Special details*

**Geometry**. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Ni1 | 0.00000 | 0.00042 (5) | 0.25000 | 0.0324 (3) | |
| N1 | 0.0571 (2) | 0.1054 (2) | 0.3259 (2) | 0.0353 (12) | |
| N2 | 0.0560 (2) | −0.0924 (2) | 0.3397 (2) | 0.0402 (12) | |
| N3 | 0.0611 (2) | −0.0069 (3) | 0.2013 (2) | 0.0394 (12) | |
| C8 | 0.1142 (3) | 0.1047 (4) | 0.3998 (3) | 0.0432 (17) | |
| C9 | 0.1465 (3) | 0.1812 (4) | 0.4422 (3) | 0.0543 (19) | |
| C10 | 0.1193 (3) | 0.2601 (4) | 0.4082 (4) | 0.060 (2) | |
| C11 | 0.0597 (3) | 0.2640 (3) | 0.3294 (3) | 0.048 (2) | |
| C12 | 0.0304 (2) | 0.1842 (3) | 0.2905 (3) | 0.0359 (17) | |
| C13 | 0.0280 (3) | 0.3432 (4) | 0.2882 (4) | 0.065 (3) | |
| C14 | 0.1128 (3) | −0.1368 (3) | 0.3578 (3) | 0.0534 (19) | |
| C15 | 0.1476 (4) | −0.1940 (4) | 0.4220 (4) | 0.069 (2) | |
| C16 | 0.1245 (4) | −0.2030 (4) | 0.4708 (4) | 0.071 (2) | |
| C17 | 0.0649 (3) | −0.1584 (3) | 0.4557 (3) | 0.0542 (19) | |
| C18 | 0.0313 (3) | −0.1036 (3) | 0.3870 (3) | 0.0424 (17) | |
| C19 | 0.1208 (3) | 0.0335 (4) | 0.2245 (3) | 0.0503 (17) | |
| C20 | 0.1528 (3) | 0.0259 (4) | 0.1814 (4) | 0.066 (3) | |
| C21 | 0.1223 (4) | −0.0231 (5) | 0.1145 (4) | 0.068 (3) | |
| C22 | 0.0604 (3) | −0.0683 (4) | 0.0887 (4) | 0.058 (2) | |
| C23 | 0.0315 (3) | −0.0582 (3) | 0.1348 (3) | 0.0410 (17) | |
| C24 | 0.0231 (4) | −0.1241 (5) | 0.0183 (4) | 0.072 (3) | |
| C25 | −0.0359 (4) | −0.1657 (4) | −0.0022 (4) | 0.071 (3) | |
| Ni2 | 0.29979 (3) | 0.96924 (4) | 0.47969 (4) | 0.0434 (2) | |
| Cl1 | 0.25801 (8) | 0.97552 (11) | 0.55872 (9) | 0.0625 (6) | |
| Cl2 | 0.27465 (7) | 0.88260 (10) | 0.37416 (8) | 0.0583 (5) | |
| Cl3 | 0.27772 (7) | 1.10207 (9) | 0.42193 (8) | 0.0528 (5) | |
| S1 | 0.41282 (7) | 0.93790 (9) | 0.58439 (8) | 0.0452 (4) | |
| N4 | 0.4404 (2) | 0.8996 (3) | 0.4710 (3) | 0.0408 (16) | |

| | | | | | |
|---|---|---|---|---|---|
| N5 | 0.5332 (2) | 0.8910 (3) | 0.5920 (2) | 0.0381 (12) | |
| C1 | 0.4636 (3) | 0.9081 (3) | 0.5493 (3) | 0.0359 (17) | |
| C2 | 0.5514 (3) | 0.8728 (4) | 0.5376 (3) | 0.0479 (19) | |
| C3 | 0.4945 (3) | 0.8778 (4) | 0.4641 (3) | 0.0481 (17) | |
| C4 | 0.5832 (3) | 0.8870 (4) | 0.6823 (3) | 0.0452 (17) | |
| C5 | 0.5869 (4) | 0.9750 (4) | 0.7181 (4) | 0.089 (3) | |
| C6 | 0.6584 (6) | 0.8705 (16) | 0.7056 (9) | 0.093 (6) | 0.75 (3) |
| C7 | 0.5581 (4) | 0.8178 (5) | 0.7141 (4) | 0.077 (3) | |
| C6A | 0.643 (2) | 0.830 (4) | 0.695 (3) | 0.093 (6) | 0.25 (3) |
| N6 | 0.3858 (4) | 0.7541 (4) | 0.3045 (4) | 0.091 (3) | |
| C26 | 0.3366 (4) | 0.7841 (4) | 0.2533 (4) | 0.066 (3) | |
| C27 | 0.2734 (4) | 0.8224 (5) | 0.1875 (5) | 0.093 (3) | |
| H8 | 0.13350 | 0.05120 | 0.42420 | 0.0520* | |
| H9 | 0.18670 | 0.17810 | 0.49400 | 0.0650* | |
| H10 | 0.14000 | 0.31130 | 0.43680 | 0.0720* | |
| H13 | 0.04640 | 0.39620 | 0.31450 | 0.0780* | |
| H14 | 0.13000 | −0.12900 | 0.32550 | 0.0640* | |
| H15 | 0.18620 | −0.22550 | 0.43130 | 0.0830* | |
| H16 | 0.14870 | −0.23950 | 0.51540 | 0.0860* | |
| H19 | 0.14210 | 0.06790 | 0.27070 | 0.0600* | |
| H20 | 0.19480 | 0.05460 | 0.19920 | 0.0790* | |
| H21 | 0.14270 | −0.02700 | 0.08520 | 0.0810* | |
| H24 | 0.04090 | −0.13130 | −0.01350 | 0.0870* | |
| H25 | −0.05840 | −0.20020 | −0.04830 | 0.0850* | |
| H2 | 0.593 (3) | 0.867 (3) | 0.555 (3) | 0.036 (14)* | |
| H3 | 0.486 (3) | 0.868 (4) | 0.409 (4) | 0.061 (16)* | |
| H5A | 0.59570 | 1.01920 | 0.69050 | 0.1340* | |
| H5B | 0.62410 | 0.97510 | 0.77410 | 0.1340* | |
| H4 | 0.397 (3) | 0.897 (3) | 0.435 (3) | 0.039 (15)* | |
| H6A | 0.67440 | 0.92000 | 0.69040 | 0.1380* | 0.75 (3) |
| H6B | 0.65930 | 0.81930 | 0.67830 | 0.1380* | 0.75 (3) |
| H6C | 0.68860 | 0.86190 | 0.76270 | 0.1380* | 0.75 (3) |
| H7A | 0.50960 | 0.82750 | 0.69350 | 0.1160* | |
| H7B | 0.58520 | 0.82040 | 0.77180 | 0.1160* | |
| H7C | 0.56360 | 0.76130 | 0.69730 | 0.1160* | |
| H5C | 0.54330 | 0.98700 | 0.71250 | 0.1340* | |
| H6A1 | 0.66990 | 0.86260 | 0.67940 | 0.1380* | 0.25 (3) |
| H6A2 | 0.62430 | 0.77870 | 0.66220 | 0.1380* | 0.25 (3) |
| H6A3 | 0.67260 | 0.81410 | 0.75030 | 0.1380* | 0.25 (3) |
| H27A | 0.24970 | 0.85310 | 0.20790 | 0.1400* | |
| H27B | 0.24340 | 0.77720 | 0.15140 | 0.1400* | |
| H27C | 0.28470 | 0.86250 | 0.15930 | 0.1400* | |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ni1 | 0.0334 (5) | 0.0360 (5) | 0.0257 (5) | 0.0000 | 0.0151 (4) | 0.0000 |
| N1 | 0.035 (2) | 0.042 (2) | 0.028 (2) | 0.0003 (18) | 0.0168 (19) | −0.0034 (18) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N2 | 0.042 (2) | 0.035 (2) | 0.034 (2) | −0.0035 (19) | 0.015 (2) | 0.0018 (17) |
| N3 | 0.039 (2) | 0.042 (2) | 0.036 (2) | −0.0011 (19) | 0.020 (2) | −0.0032 (18) |
| C8 | 0.035 (3) | 0.060 (3) | 0.030 (3) | −0.001 (2) | 0.015 (2) | −0.005 (2) |
| C9 | 0.046 (3) | 0.081 (4) | 0.034 (3) | −0.016 (3) | 0.021 (3) | −0.019 (3) |
| C10 | 0.077 (4) | 0.062 (4) | 0.055 (4) | −0.023 (3) | 0.045 (4) | −0.029 (3) |
| C11 | 0.062 (4) | 0.046 (3) | 0.051 (4) | −0.010 (3) | 0.041 (3) | −0.014 (3) |
| C12 | 0.043 (3) | 0.040 (3) | 0.035 (3) | −0.003 (2) | 0.028 (2) | −0.004 (2) |
| C13 | 0.092 (5) | 0.039 (3) | 0.087 (5) | −0.016 (3) | 0.064 (4) | −0.015 (3) |
| C14 | 0.042 (3) | 0.043 (3) | 0.057 (4) | 0.007 (3) | 0.016 (3) | −0.001 (3) |
| C15 | 0.062 (4) | 0.050 (4) | 0.063 (4) | 0.008 (3) | 0.014 (4) | 0.007 (3) |
| C16 | 0.069 (4) | 0.043 (3) | 0.046 (4) | 0.000 (3) | −0.003 (3) | 0.014 (3) |
| C17 | 0.063 (4) | 0.039 (3) | 0.034 (3) | −0.014 (3) | 0.010 (3) | 0.005 (2) |
| C18 | 0.047 (3) | 0.033 (3) | 0.035 (3) | −0.009 (2) | 0.015 (3) | −0.001 (2) |
| C19 | 0.044 (3) | 0.057 (3) | 0.051 (3) | −0.001 (3) | 0.027 (3) | −0.002 (3) |
| C20 | 0.053 (4) | 0.085 (5) | 0.078 (5) | 0.008 (3) | 0.047 (4) | 0.015 (4) |
| C21 | 0.074 (5) | 0.091 (5) | 0.064 (5) | 0.021 (4) | 0.054 (4) | 0.018 (4) |
| C22 | 0.077 (4) | 0.059 (3) | 0.051 (4) | 0.034 (3) | 0.043 (3) | 0.016 (3) |
| C23 | 0.049 (3) | 0.040 (3) | 0.034 (3) | 0.014 (2) | 0.023 (3) | 0.005 (2) |
| C24 | 0.105 (6) | 0.078 (4) | 0.051 (4) | 0.027 (4) | 0.054 (4) | 0.000 (3) |
| C25 | 0.104 (6) | 0.059 (4) | 0.041 (4) | 0.022 (4) | 0.035 (4) | −0.005 (3) |
| Ni2 | 0.0394 (4) | 0.0561 (4) | 0.0325 (4) | 0.0045 (3) | 0.0185 (3) | −0.0031 (3) |
| Cl1 | 0.0540 (9) | 0.0980 (12) | 0.0409 (8) | 0.0098 (8) | 0.0297 (7) | 0.0020 (7) |
| Cl2 | 0.0496 (8) | 0.0748 (10) | 0.0400 (8) | 0.0050 (7) | 0.0181 (7) | −0.0152 (7) |
| Cl3 | 0.0476 (8) | 0.0590 (8) | 0.0495 (9) | −0.0008 (6) | 0.0254 (7) | 0.0015 (6) |
| S1 | 0.0413 (7) | 0.0626 (8) | 0.0318 (7) | 0.0068 (6) | 0.0203 (6) | −0.0018 (6) |
| N4 | 0.042 (3) | 0.053 (3) | 0.026 (2) | 0.000 (2) | 0.018 (2) | −0.0013 (19) |
| N5 | 0.039 (2) | 0.051 (2) | 0.026 (2) | 0.0010 (19) | 0.019 (2) | 0.0021 (18) |
| C1 | 0.041 (3) | 0.040 (3) | 0.027 (3) | −0.001 (2) | 0.019 (2) | 0.002 (2) |
| C2 | 0.039 (3) | 0.067 (4) | 0.043 (3) | −0.004 (3) | 0.026 (3) | −0.003 (3) |
| C3 | 0.051 (3) | 0.061 (3) | 0.040 (3) | −0.003 (3) | 0.030 (3) | 0.000 (3) |
| C4 | 0.040 (3) | 0.065 (3) | 0.029 (3) | 0.004 (3) | 0.018 (2) | 0.006 (2) |
| C5 | 0.096 (6) | 0.076 (5) | 0.040 (4) | −0.009 (4) | 0.003 (4) | −0.008 (3) |
| C6 | 0.036 (6) | 0.183 (16) | 0.043 (6) | 0.002 (7) | 0.012 (6) | 0.004 (9) |
| C7 | 0.080 (5) | 0.091 (5) | 0.050 (4) | −0.001 (4) | 0.029 (4) | 0.023 (3) |
| C6A | 0.036 (6) | 0.183 (16) | 0.043 (6) | 0.002 (7) | 0.012 (6) | 0.004 (9) |
| N6 | 0.103 (5) | 0.105 (5) | 0.062 (4) | 0.008 (4) | 0.043 (4) | 0.005 (4) |
| C26 | 0.088 (5) | 0.066 (4) | 0.054 (4) | −0.010 (4) | 0.045 (4) | −0.002 (3) |
| C27 | 0.099 (6) | 0.080 (5) | 0.073 (5) | 0.004 (4) | 0.030 (5) | 0.006 (4) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ni1—N1 | 2.095 (3) | C21—C22 | 1.395 (12) |
| Ni1—N2 | 2.079 (3) | C22—C24 | 1.450 (10) |
| Ni1—N3 | 2.101 (5) | C22—C23 | 1.407 (10) |
| Ni1—N1$^{i}$ | 2.095 (3) | C24—C25 | 1.337 (13) |
| Ni1—N2$^{i}$ | 2.079 (3) | C8—H8 | 0.9300 |
| Ni1—N3$^{i}$ | 2.101 (5) | C9—H9 | 0.9300 |
| Ni2—Cl2 | 2.2753 (16) | C10—H10 | 0.9300 |

| | | | |
|---|---|---|---|
| Ni2—Cl3 | 2.2507 (15) | C13—H13 | 0.9300 |
| Ni2—S1 | 2.3054 (17) | C14—H14 | 0.9300 |
| Ni2—Cl1 | 2.253 (2) | C15—H15 | 0.9300 |
| S1—C1 | 1.717 (7) | C16—H16 | 0.9300 |
| N1—C8 | 1.324 (7) | C19—H19 | 0.9300 |
| N1—C12 | 1.359 (6) | C20—H20 | 0.9300 |
| N2—C18 | 1.352 (8) | C21—H21 | 0.9300 |
| N2—C14 | 1.328 (8) | C24—H24 | 0.9300 |
| N3—C23 | 1.357 (6) | C25—H25 | 0.9300 |
| N3—C19 | 1.329 (9) | C2—C3 | 1.320 (8) |
| N4—C1 | 1.349 (7) | C4—C5 | 1.504 (9) |
| N4—C3 | 1.361 (9) | C4—C6A | 1.52 (6) |
| N5—C1 | 1.354 (8) | C4—C6 | 1.536 (19) |
| N5—C2 | 1.388 (8) | C4—C7 | 1.502 (11) |
| N5—C4 | 1.510 (6) | C2—H2 | 0.82 (7) |
| N4—H4 | 0.85 (6) | C3—H3 | 1.02 (7) |
| N6—C26 | 1.118 (11) | C5—H5A | 0.9600 |
| C8—C9 | 1.393 (8) | C5—H5B | 0.9600 |
| C9—C10 | 1.355 (9) | C5—H5C | 0.9600 |
| C10—C11 | 1.402 (9) | C6—H6A | 0.9600 |
| C11—C12 | 1.402 (7) | C6—H6B | 0.9600 |
| C11—C13 | 1.418 (8) | C6—H6C | 0.9600 |
| C12—C12$^{i}$ | 1.436 (7) | C6A—H6A2 | 0.9600 |
| C13—C13$^{i}$ | 1.344 (10) | C6A—H6A3 | 0.9500 |
| C14—C15 | 1.383 (8) | C6A—H6A1 | 0.9700 |
| C15—C16 | 1.347 (13) | C7—H7B | 0.9600 |
| C16—C17 | 1.401 (12) | C7—H7C | 0.9600 |
| C17—C18 | 1.417 (7) | C7—H7A | 0.9600 |
| C17—C25$^{i}$ | 1.412 (12) | C26—C27 | 1.435 (12) |
| C18—C23$^{i}$ | 1.431 (10) | C27—H27A | 0.9600 |
| C19—C20 | 1.409 (10) | C27—H27B | 0.9600 |
| C20—C21 | 1.341 (10) | C27—H27C | 0.9600 |

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| N1—Ni1—N2 | 93.42 (13) | C8—C9—H9 | 120.00 |
| N1—Ni1—N3 | 93.77 (18) | C11—C10—H10 | 120.00 |
| N1—Ni1—N1$^{i}$ | 79.98 (13) | C9—C10—H10 | 120.00 |
| N1—Ni1—N2$^{i}$ | 170.55 (15) | C13$^{i}$—C13—H13 | 119.00 |
| N1—Ni1—N3$^{i}$ | 90.91 (18) | C11—C13—H13 | 119.00 |
| N2—Ni1—N3 | 96.30 (18) | N2—C14—H14 | 118.00 |
| N1$^{i}$—Ni1—N2 | 170.55 (15) | C15—C14—H14 | 118.00 |
| N2—Ni1—N2$^{i}$ | 93.90 (13) | C14—C15—H15 | 121.00 |
| N2—Ni1—N3$^{i}$ | 79.49 (18) | C16—C15—H15 | 121.00 |
| N1$^{i}$—Ni1—N3 | 90.91 (18) | C17—C16—H16 | 120.00 |
| N2$^{i}$—Ni1—N3 | 79.49 (18) | C15—C16—H16 | 119.00 |
| N3—Ni1—N3$^{i}$ | 173.89 (18) | N3—C19—H19 | 119.00 |
| N1$^{i}$—Ni1—N2$^{i}$ | 93.42 (13) | C20—C19—H19 | 119.00 |
| N1$^{i}$—Ni1—N3$^{i}$ | 93.77 (18) | C19—C20—H20 | 120.00 |
| N2$^{i}$—Ni1—N3$^{i}$ | 96.30 (18) | C21—C20—H20 | 120.00 |

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| Cl1—Ni2—Cl2 | 133.14 (7) | C20—C21—H21 | 120.00 |
| Cl1—Ni2—Cl3 | 104.92 (7) | C22—C21—H21 | 120.00 |
| Cl1—Ni2—S1 | 94.21 (6) | C25—C24—H24 | 119.00 |
| Cl2—Ni2—Cl3 | 100.47 (6) | C22—C24—H24 | 119.00 |
| Cl2—Ni2—S1 | 107.47 (6) | C24—C25—H25 | 119.00 |
| Cl3—Ni2—S1 | 118.25 (6) | C17$^{i}$—C25—H25 | 119.00 |
| Ni2—S1—C1 | 111.11 (19) | N4—C1—N5 | 106.5 (6) |
| Ni1—N1—C8 | 129.5 (3) | S1—C1—N5 | 128.4 (4) |
| Ni1—N1—C12 | 112.5 (3) | S1—C1—N4 | 125.1 (5) |
| C8—N1—C12 | 118.0 (4) | N5—C2—C3 | 108.5 (6) |
| C14—N2—C18 | 118.0 (4) | N4—C3—C2 | 107.3 (6) |
| Ni1—N2—C18 | 112.9 (4) | N5—C4—C6 | 110.6 (7) |
| Ni1—N2—C14 | 128.9 (4) | N5—C4—C5 | 109.7 (5) |
| Ni1—N3—C19 | 129.3 (4) | C5—C4—C6 | 104.1 (10) |
| C19—N3—C23 | 118.1 (5) | C5—C4—C7 | 111.4 (6) |
| Ni1—N3—C23 | 112.5 (4) | C5—C4—C6A | 129 (2) |
| C1—N4—C3 | 110.0 (5) | C6—C4—C7 | 112.5 (10) |
| C2—N5—C4 | 124.5 (5) | C6A—C4—C7 | 93 (2) |
| C1—N5—C2 | 107.7 (4) | N5—C4—C7 | 108.5 (5) |
| C1—N5—C4 | 127.7 (5) | N5—C4—C6A | 104.0 (19) |
| C1—N4—H4 | 121 (5) | N5—C2—H2 | 118 (4) |
| C3—N4—H4 | 128 (5) | C3—C2—H2 | 133 (4) |
| N1—C8—C9 | 122.4 (5) | N4—C3—H3 | 120 (4) |
| C8—C9—C10 | 120.1 (5) | C2—C3—H3 | 132 (4) |
| C9—C10—C11 | 119.5 (5) | C4—C5—H5A | 109.00 |
| C10—C11—C12 | 117.1 (5) | C4—C5—H5B | 110.00 |
| C12—C11—C13 | 119.2 (5) | C4—C5—H5C | 110.00 |
| C10—C11—C13 | 123.7 (5) | H5A—C5—H5B | 109.00 |
| N1—C12—C12$^{i}$ | 117.6 (4) | H5A—C5—H5C | 109.00 |
| N1—C12—C11 | 123.0 (5) | H5B—C5—H5C | 109.00 |
| C11—C12—C12$^{i}$ | 119.5 (4) | C4—C6—H6A | 110.00 |
| C11—C13—C13$^{i}$ | 121.3 (6) | C4—C6—H6B | 110.00 |
| N2—C14—C15 | 123.5 (7) | C4—C6—H6C | 109.00 |
| C14—C15—C16 | 118.6 (8) | H6A—C6—H6B | 109.00 |
| C15—C16—C17 | 121.3 (6) | H6A—C6—H6C | 109.00 |
| C16—C17—C18 | 116.1 (6) | H6B—C6—H6C | 109.00 |
| C18—C17—C25$^{i}$ | 118.7 (6) | C4—C6A—H6A2 | 110.00 |
| C16—C17—C25$^{i}$ | 125.2 (5) | C4—C6A—H6A3 | 110.00 |
| N2—C18—C23$^{i}$ | 117.6 (4) | H6A1—C6A—H6A2 | 109.00 |
| N2—C18—C17 | 122.5 (6) | H6A1—C6A—H6A3 | 109.00 |
| C17—C18—C23$^{i}$ | 119.9 (6) | H6A2—C6A—H6A3 | 110.00 |
| N3—C19—C20 | 122.1 (5) | C4—C6A—H6A1 | 109.00 |
| C19—C20—C21 | 119.5 (7) | H7B—C7—H7C | 109.00 |
| C20—C21—C22 | 120.5 (8) | C4—C7—H7A | 109.00 |
| C21—C22—C23 | 117.0 (6) | C4—C7—H7B | 109.00 |
| C21—C22—C24 | 125.7 (8) | C4—C7—H7C | 109.00 |
| C23—C22—C24 | 117.3 (7) | H7A—C7—H7B | 110.00 |
| N3—C23—C18$^{i}$ | 116.9 (6) | H7A—C7—H7C | 110.00 |

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|---|---|---|---|
| C18$^{i}$—C23—C22 | 120.3 (5) | N6—C26—C27 | 179.9 (12) |
| N3—C23—C22 | 122.8 (6) | C26—C27—H27A | 109.00 |
| C22—C24—C25 | 122.1 (8) | C26—C27—H27B | 110.00 |
| C17$^{i}$—C25—C24 | 121.6 (6) | C26—C27—H27C | 110.00 |
| N1—C8—H8 | 119.00 | H27A—C27—H27B | 109.00 |
| C9—C8—H8 | 119.00 | H27A—C27—H27C | 110.00 |
| C10—C9—H9 | 120.00 | H27B—C27—H27C | 109.00 |

| | | | |
|---|---|---|---|
| N2—Ni1—N1—C8 | 8.6 (6) | C1—N5—C2—C3 | −0.6 (7) |
| N3—Ni1—N1—C8 | −87.9 (6) | C4—N5—C2—C3 | 176.5 (5) |
| N1$^{i}$—Ni1—N1—C8 | −178.2 (6) | C2—N5—C1—N4 | 0.5 (6) |
| N3$^{i}$—Ni1—N1—C8 | 88.2 (6) | C2—N5—C4—C7 | −117.4 (7) |
| N2—Ni1—N1—C12 | −173.1 (4) | C1—N5—C4—C7 | 59.2 (8) |
| N3—Ni1—N1—C12 | 90.3 (4) | C4—N5—C1—N4 | −176.5 (5) |
| N1$^{i}$—Ni1—N1—C12 | 0.1 (4) | C2—N5—C1—S1 | −177.8 (4) |
| N3$^{i}$—Ni1—N1—C12 | −93.6 (4) | C2—N5—C4—C5 | 120.8 (7) |
| N1—Ni1—N2—C14 | −92.3 (4) | C1—N5—C4—C6 | −176.9 (11) |
| N3—Ni1—N2—C14 | 1.9 (4) | C2—N5—C4—C6 | 6.5 (12) |
| N2$^{i}$—Ni1—N2—C14 | 81.7 (4) | N1—C8—C9—C10 | 0.5 (11) |
| N3$^{i}$—Ni1—N2—C14 | 177.4 (4) | C8—C9—C10—C11 | −1.8 (11) |
| N1—Ni1—N2—C18 | 84.0 (3) | C9—C10—C11—C12 | 1.4 (11) |
| N3—Ni1—N2—C18 | 178.2 (3) | C9—C10—C11—C13 | −179.0 (7) |
| N2$^{i}$—Ni1—N2—C18 | −102.0 (3) | C12—C11—C13—C13$^{i}$ | −2.3 (11) |
| N3$^{i}$—Ni1—N2—C18 | −6.3 (3) | C10—C11—C12—N1 | 0.2 (10) |
| N1—Ni1—N3—C19 | 9.7 (5) | C13—C11—C12—C12$^{i}$ | 0.9 (10) |
| N2—Ni1—N3—C19 | −84.2 (5) | C10—C11—C12—C12$^{i}$ | −179.6 (6) |
| N1$^{i}$—Ni1—N3—C19 | 89.7 (5) | C13—C11—C12—N1 | −179.4 (6) |
| N2$^{i}$—Ni1—N3—C19 | −177.0 (5) | C10—C11—C13—C13$^{i}$ | 178.1 (8) |
| N1—Ni1—N3—C23 | −167.3 (3) | N1—C12—C12$^{i}$—C11$^{i}$ | −180.0 (6) |
| N2—Ni1—N3—C23 | 98.9 (3) | C11—C12—C12$^{i}$—N1$^{i}$ | −180.0 (6) |
| N1$^{i}$—Ni1—N3—C23 | −87.3 (3) | N1—C12—C12$^{i}$—N1$^{i}$ | 0.3 (8) |
| N2$^{i}$—Ni1—N3—C23 | 6.1 (3) | C11—C12—C12$^{i}$—C11$^{i}$ | −0.2 (9) |
| Cl3—Ni2—S1—C1 | −81.0 (2) | C11—C13—C13$^{i}$—C11$^{i}$ | 3.1 (12) |
| Cl1—Ni2—S1—C1 | 169.56 (19) | N2—C14—C15—C16 | −2.6 (9) |
| Cl2—Ni2—S1—C1 | 31.7 (2) | C14—C15—C16—C17 | 2.5 (10) |
| Ni2—S1—C1—N4 | −3.1 (5) | C15—C16—C17—C25$^{i}$ | 178.2 (6) |
| Ni2—S1—C1—N5 | 175.0 (4) | C15—C16—C17—C18 | −0.4 (9) |
| Ni1—N1—C8—C9 | 179.3 (5) | C18—C17—C25$^{i}$—C24$^{i}$ | 1.8 (9) |
| C8—N1—C12—C12$^{i}$ | 178.3 (6) | C16—C17—C25$^{i}$—C24$^{i}$ | −176.8 (7) |
| Ni1—N1—C12—C11 | −180.0 (5) | C16—C17—C18—C23$^{i}$ | 177.6 (5) |
| C12—N1—C8—C9 | 1.1 (10) | C25$^{i}$—C17—C18—N2 | 179.4 (5) |
| Ni1—N1—C12—C12$^{i}$ | −0.2 (6) | C25$^{i}$—C17—C18—C23$^{i}$ | −1.1 (8) |
| C8—N1—C12—C11 | −1.5 (9) | C16—C17—C18—N2 | −1.9 (8) |
| Ni1—N2—C18—C23$^{i}$ | 5.6 (5) | C17—C18—C23$^{i}$—C22$^{i}$ | −0.5 (8) |
| C14—N2—C18—C17 | 2.0 (7) | N2—C18—C23$^{i}$—N3$^{i}$ | −0.4 (7) |
| Ni1—N2—C18—C17 | −174.8 (4) | C17—C18—C23$^{i}$—N3$^{i}$ | −179.9 (5) |
| Ni1—N2—C14—C15 | 176.6 (4) | N2—C18—C23$^{i}$—C22$^{i}$ | 179.0 (5) |
| C14—N2—C18—C23$^{i}$ | −177.6 (4) | N3—C19—C20—C21 | 0.4 (10) |

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|---|---|---|---|
| C18—N2—C14—C15 | 0.4 (7) | C19—C20—C21—C22 | −1.8 (10) |
| Ni1—N3—C19—C20 | −175.5 (4) | C20—C21—C22—C24 | −179.1 (7) |
| C23—N3—C19—C20 | 1.3 (8) | C20—C21—C22—C23 | 1.4 (10) |
| C19—N3—C23—C22 | −1.7 (8) | C24—C22—C23—C18$^{i}$ | 1.5 (8) |
| Ni1—N3—C23—C18$^{i}$ | −5.0 (6) | C21—C22—C23—N3 | 0.4 (9) |
| C19—N3—C23—C18$^{i}$ | 177.6 (5) | C24—C22—C23—N3 | −179.2 (5) |
| Ni1—N3—C23—C22 | 175.6 (4) | C23—C22—C24—C25 | −0.9 (10) |
| C3—N4—C1—N5 | −0.3 (6) | C21—C22—C24—C25 | 179.6 (7) |
| C3—N4—C1—S1 | 178.2 (4) | C21—C22—C23—C18$^{i}$ | −179.0 (6) |
| C1—N4—C3—C2 | −0.1 (7) | C22—C24—C25—C17$^{i}$ | −0.8 (11) |
| C4—N5—C1—S1 | 5.2 (8) | N5—C2—C3—N4 | 0.5 (7) |
| C1—N5—C4—C5 | −62.7 (8) | | |

Symmetry code: (i) −*x*, *y*, −*z*+1/2.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N4—H4···Cl2 | 0.85 (6) | 2.37 (7) | 3.178 (6) | 160 (6) |
| C2—H2···Cl3$^{ii}$ | 0.82 (7) | 2.77 (7) | 3.552 (8) | 160 (4) |
| C5—H5*C*···S1 | 0.96 | 2.75 | 3.402 (9) | 126 |
| C7—H7*A*···S1 | 0.96 | 2.68 | 3.409 (8) | 133 |
| C10—H10···Cl3$^{iii}$ | 0.93 | 2.72 | 3.557 (7) | 151 |
| C25—H25···N6$^{iv}$ | 0.93 | 2.60 | 3.502 (9) | 162 |

Symmetry codes: (ii) −*x*+1, −*y*+2, −*z*+1; (iii) −*x*+1/2, −*y*+3/2, −*z*+1; (iv) *x*−1/2, −*y*+1/2, *z*−1/2.