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# Bis[1-(4-cyanobenzyl)pyrazinium] bis(1,2-dicyanoethene-1,2-dithiolato)nickelate(II)

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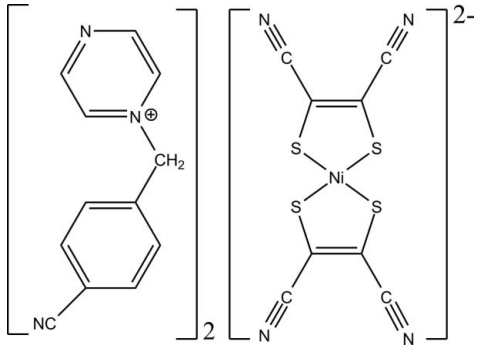
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.026; $wR$ factor = 0.074; data-to-parameter ratio = 13.4.

The asymmetric unit of the title complex, $(C_{12}H_{10}N_3)_2[Ni(C_4N_2S_2)_2]$, consists of one 1-(4-cyanobenzyl)pyrazinium cation and one half of an $[Ni(mnt)_2]^{2-}$ dianion ($mnt^{2-}$ is 1,2-dicyanoethene-1,2-dithiolate). The $Ni^{2+}$ ion is located on an inversion center and is coordinated by four S atoms from two $mnt^{2-}$ ligands, exhibiting a square-planar coordination geometry. The cation adopts a conformation where both the pyrazine ring and the benzene ring are twisted with respect to the C—C—N reference plane by 16.5 (2) and 69.8 (1)°, respectively.

## Related literature

For general background to square-planar bis-1,2-dithiolato complexes of transition metals showing potential application as magnetic or conducting materials and other properties, see: Bigoli *et al.* (2002); Duan *et al.* (2010); Pei *et al.* (2011). For the synthesis, see: Davison & Holm (1967).




## Experimental

### Crystal data

$(C_{12}H_{10}N_3)_2[Ni(C_4N_2S_2)_2]$
$M_r$ = 731.53
Monoclinic, $P2_1/n$
$a$ = 7.115 (3) Å
$b$ = 13.623 (6) Å
$c$ = 17.186 (8) Å
$\beta$ = 101.671 (5)°
$V$ = 1631.4 (13) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.89 mm$^{-1}$
$T$ = 298 K
0.30 × 0.20 × 0.15 mm

### Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{min}$ = 0.807, $T_{max}$ = 0.875
8060 measured reflections
2871 independent reflections
2586 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.020

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.074
$S$ = 1.06
2871 reflections
214 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.26 e Å$^{-3}$

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); 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); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2295).

## References

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# supporting information

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# Bis[1-(4-cyanobenzyl)pyrazinium] bis(1,2-dicyanoethene-1,2-dithiolato)nickelate(II)

**Hui Zhang, Wen-Bo Pei, Shan-Shan Yu and Xiao-Ming Ren**

## S1. Comment

Bis-1,2-dithiolene complexes of transition metals have been widely studied because of their novel properties and applications in the areas of conducting and magnetic materials, dyes, nonlinear optics, catalysis and others. These applications arise due to a combination of functional properties, specific geometries and intermolecular interactions. (Bigoli *et al.*, 2002; Duan *et al.*, 2010; Pei *et al.*, 2011). Herein we report the crystal structure of the title compound (Fig. 1).

An asymmetric unit consists of one half $[Ni(mnt)_2]^{2-}$ dianion and one 1-*N*-(4′-cyano-benzyl)-pyrazinium cation. In the $[Ni(mnt)_2]^{2-}$ moiety, the Ni atom is situated at a inversion center and is coordinated by four S atoms from two $mnt^{2-}$ ligands, forming a square-planar coordination geometry. The cation adopts a conformation where the bond lengths and bond angles were normal, and both the pyrazine ring and the phenyl ring are twisted with respect to the C8—C12—N4 reference plane with the corresponding dihedral angles of 16.5 (2)° and 69.8 (1)°.

## S2. Experimental

Disodium maleonitriledithiolate (456 mg, 2.5 mmol) and nickel chloride hexahydrate (297 mg, 1.25 mmol) were mixed under stirring in water (20 ml) and heated to boiling for about 20 min. After the red solution was filtered an aqueous solution of 1-*N*-(4′-cyano-benzyl)-pyrazinium chloride (579 mg, 2.5 mmol) was added dropwise to the filtrate. The immediately formed dark red precipitate was filtered off, washed with water and dried in vacuum (yield: 722 mg, 79%). Block shaped single crystals suitable for X-ray analysis were obtained *via* recrystallization of the corresponding complex in acetone.

## S3. Refinement

All non-hydrogen atoms were refined anisotropically, whereas the H atoms were calculated and placed to the bonded parent atoms in geometrically idealized positions (C—H = 0.93 or 0.97 Å) and refined as riding atoms, with $U_{iso}$(H) = 1.2$U_{eq}$(C).

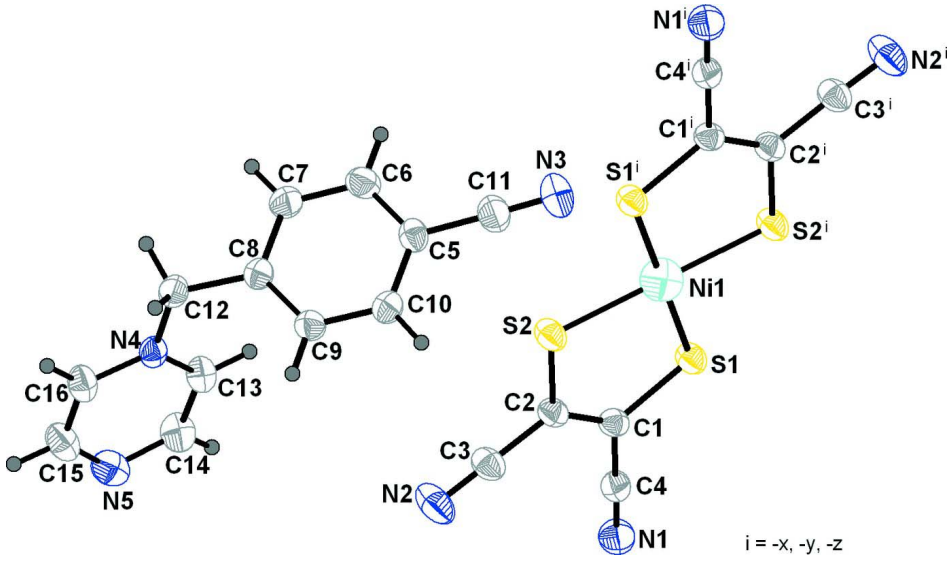


**Figure 1**

Molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level (i = -*x*, -*y*, -*z*).

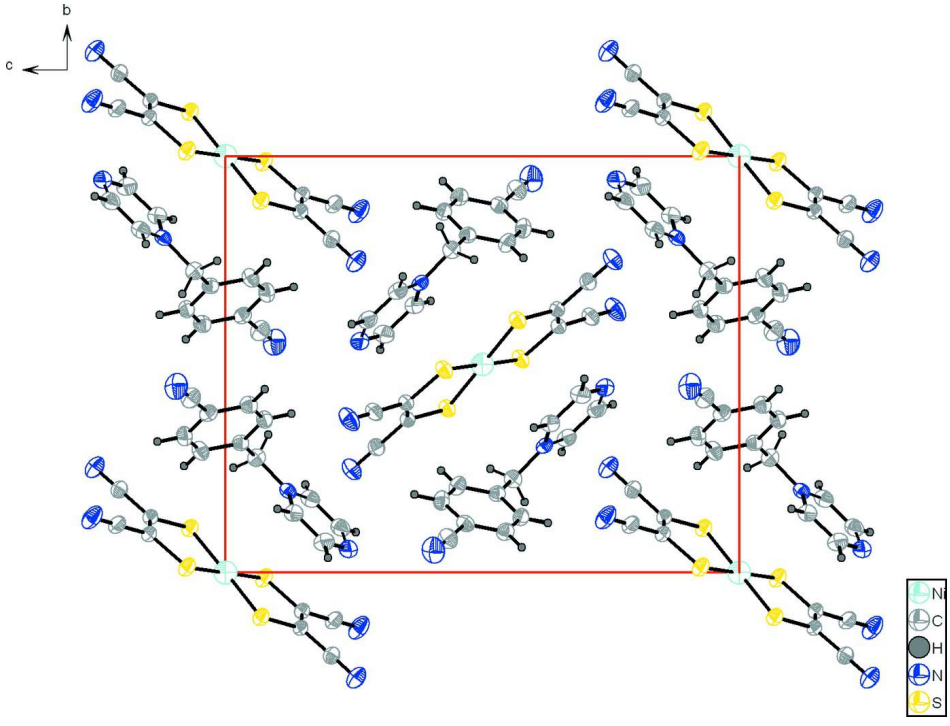


**Figure 2**

Packing diagram for (I) viewed along *a* axis.

**Bis[1-(4-cyanobenzyl)pyrazinium] bis(1,2-dicyanoethene-1,2-dithiolato)nickelate(II)**

*Crystal data*

$(C_{12}H_{10}N_3)_2[Ni(C_4N_2S_2)_2]$
$M_r$ = 731.53
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
*a* = 7.115 (3) Å
*b* = 13.623 (6) Å

$c$ = 17.186 (8) Å
$\beta$ = 101.671 (5)°
$V$ = 1631.4 (13) Å$^3$
$Z$ = 2
$F$(000) = 748
$D_x$ = 1.489 Mg m$^{-3}$
Melting point: 456 K

Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 8060 reflections
$\theta$ = 2.4–25.0°
$\mu$ = 0.89 mm$^{-1}$
$T$ = 298 K
Block, red
0.30 × 0.20 × 0.15 mm

*Data collection*

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{min}$ = 0.807, $T_{max}$ = 0.875

8060 measured reflections
2871 independent reflections
2586 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.020
$\theta_{max}$ = 25.0°, $\theta_{min}$ = 2.4°
$h$ = −8→4
$k$ = −16→15
$l$ = −20→20

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.074
$S$ = 1.06
2871 reflections
214 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.3009P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.26 e Å$^{-3}$

*Special details*

**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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Ni1 | 0.0000 | 0.0000 | 0.0000 | 0.04070 (11) |
| C1 | 0.0668 (2) | 0.13286 (12) | 0.14603 (9) | 0.0452 (4) |
| C2 | 0.2425 (2) | 0.09233 (12) | 0.14864 (10) | 0.0464 (4) |
| C3 | 0.4020 (3) | 0.11475 (13) | 0.21086 (11) | 0.0566 (4) |
| C4 | 0.0334 (2) | 0.19910 (13) | 0.20637 (10) | 0.0508 (4) |
| C5 | 0.3059 (2) | 0.61780 (13) | −0.03334 (11) | 0.0515 (4) |
| C6 | 0.4014 (3) | 0.67295 (15) | −0.08013 (11) | 0.0608 (5) |
| H6A | 0.3440 | 0.6865 | −0.1326 | 0.073* |
| C7 | 0.5826 (3) | 0.70790 (15) | −0.04870 (11) | 0.0594 (5) |
| H7A | 0.6473 | 0.7448 | −0.0805 | 0.071* |

| | | | | |
|---|---|---|---|---|
| C8 | 0.6697 (2) | 0.68900 (12) | 0.02927 (10) | 0.0473 (4) |
| C9 | 0.5730 (2) | 0.63300 (13) | 0.07578 (10) | 0.0513 (4) |
| H9A | 0.6311 | 0.6190 | 0.1281 | 0.062* |
| C10 | 0.3910 (3) | 0.59771 (13) | 0.04520 (11) | 0.0550 (4) |
| H10A | 0.3260 | 0.5608 | 0.0769 | 0.066* |
| C11 | 0.1164 (3) | 0.58128 (16) | −0.06742 (13) | 0.0670 (5) |
| C12 | 0.8708 (2) | 0.72452 (14) | 0.06029 (11) | 0.0541 (4) |
| H12A | 0.9486 | 0.6693 | 0.0833 | 0.065* |
| H12B | 0.9232 | 0.7484 | 0.0159 | 0.065* |
| C13 | 0.7384 (3) | 0.85735 (13) | 0.13272 (12) | 0.0558 (4) |
| H13A | 0.6171 | 0.8476 | 0.1014 | 0.067* |
| C14 | 0.7677 (3) | 0.92685 (15) | 0.19170 (13) | 0.0672 (5) |
| H14A | 0.6632 | 0.9643 | 0.1989 | 0.081* |
| C15 | 1.0821 (3) | 0.89226 (14) | 0.22341 (12) | 0.0658 (5) |
| H15A | 1.2038 | 0.9037 | 0.2539 | 0.079* |
| C16 | 1.0618 (3) | 0.82300 (14) | 0.16465 (11) | 0.0573 (5) |
| H16A | 1.1684 | 0.7893 | 0.1549 | 0.069* |
| N1 | 0.0083 (2) | 0.25233 (14) | 0.25432 (10) | 0.0707 (5) |
| N2 | 0.5329 (3) | 0.13221 (16) | 0.25944 (11) | 0.0842 (6) |
| N3 | −0.0327 (3) | 0.55373 (19) | −0.09570 (13) | 0.0963 (7) |
| N4 | 0.88726 (18) | 0.80422 (10) | 0.12132 (8) | 0.0455 (3) |
| N5 | 0.9357 (3) | 0.94368 (12) | 0.23882 (10) | 0.0677 (4) |
| S1 | −0.12375 (6) | 0.10653 (3) | 0.06901 (3) | 0.05089 (13) |
| S2 | 0.28315 (7) | 0.01308 (3) | 0.07488 (3) | 0.05495 (14) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ni1 | 0.04532 (18) | 0.03877 (17) | 0.03648 (17) | −0.00199 (11) | 0.00463 (12) | −0.00037 (10) |
| C1 | 0.0529 (9) | 0.0417 (8) | 0.0406 (8) | −0.0064 (7) | 0.0085 (7) | −0.0019 (7) |
| C2 | 0.0511 (9) | 0.0440 (8) | 0.0423 (8) | −0.0041 (7) | 0.0051 (7) | −0.0038 (7) |
| C3 | 0.0564 (11) | 0.0559 (10) | 0.0541 (10) | 0.0060 (8) | 0.0036 (9) | −0.0140 (8) |
| C4 | 0.0470 (9) | 0.0544 (10) | 0.0508 (9) | −0.0046 (7) | 0.0094 (8) | −0.0047 (8) |
| C5 | 0.0449 (9) | 0.0502 (9) | 0.0585 (10) | 0.0017 (7) | 0.0079 (8) | −0.0081 (8) |
| C6 | 0.0608 (11) | 0.0711 (12) | 0.0473 (10) | 0.0045 (9) | 0.0033 (8) | 0.0033 (9) |
| C7 | 0.0599 (11) | 0.0661 (11) | 0.0531 (10) | −0.0045 (9) | 0.0135 (8) | 0.0121 (9) |
| C8 | 0.0461 (9) | 0.0454 (9) | 0.0512 (9) | −0.0015 (7) | 0.0118 (7) | 0.0002 (7) |
| C9 | 0.0520 (10) | 0.0547 (10) | 0.0463 (9) | −0.0037 (8) | 0.0074 (7) | 0.0036 (7) |
| C10 | 0.0533 (10) | 0.0555 (10) | 0.0577 (10) | −0.0076 (8) | 0.0147 (8) | 0.0039 (8) |
| C11 | 0.0542 (12) | 0.0750 (13) | 0.0690 (13) | −0.0025 (10) | 0.0059 (10) | −0.0086 (10) |
| C12 | 0.0479 (9) | 0.0575 (10) | 0.0587 (10) | −0.0046 (8) | 0.0153 (8) | −0.0027 (8) |
| C13 | 0.0464 (9) | 0.0524 (10) | 0.0664 (11) | −0.0008 (8) | 0.0066 (8) | 0.0011 (8) |
| C14 | 0.0634 (12) | 0.0577 (11) | 0.0791 (14) | 0.0017 (9) | 0.0111 (10) | −0.0062 (10) |
| C15 | 0.0651 (12) | 0.0559 (11) | 0.0669 (12) | −0.0098 (9) | −0.0091 (10) | 0.0106 (9) |
| C16 | 0.0455 (9) | 0.0546 (10) | 0.0673 (11) | −0.0028 (8) | 0.0006 (8) | 0.0099 (9) |
| N1 | 0.0665 (11) | 0.0800 (12) | 0.0676 (11) | 0.0002 (9) | 0.0182 (8) | −0.0250 (9) |
| N2 | 0.0671 (11) | 0.0967 (14) | 0.0773 (12) | 0.0143 (10) | −0.0129 (10) | −0.0363 (11) |
| N3 | 0.0612 (12) | 0.1261 (19) | 0.0940 (15) | −0.0216 (12) | −0.0021 (11) | −0.0063 (14) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N4 | 0.0427 (7) | 0.0434 (7) | 0.0499 (8) | −0.0049 (6) | 0.0080 (6) | 0.0103 (6) |
| N5 | 0.0823 (12) | 0.0551 (9) | 0.0618 (10) | −0.0071 (9) | 0.0051 (9) | 0.0015 (8) |
| S1 | 0.0477 (2) | 0.0538 (3) | 0.0488 (2) | 0.00206 (18) | 0.00416 (18) | −0.00887 (18) |
| S2 | 0.0479 (3) | 0.0615 (3) | 0.0517 (3) | 0.00499 (19) | 0.0009 (2) | −0.01617 (19) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ni1—S2 | 2.1674 (9) | C8—C12 | 1.502 (2) |
| Ni1—S2$^{i}$ | 2.1674 (9) | C9—C10 | 1.382 (2) |
| Ni1—S1 | 2.1704 (7) | C9—H9A | 0.9300 |
| Ni1—S1$^{i}$ | 2.1704 (7) | C10—H10A | 0.9300 |
| C1—C2 | 1.359 (2) | C11—N3 | 1.138 (3) |
| C1—C4 | 1.430 (2) | C12—N4 | 1.498 (2) |
| C1—S1 | 1.7302 (17) | C12—H12A | 0.9700 |
| C2—C3 | 1.426 (2) | C12—H12B | 0.9700 |
| C2—S2 | 1.7334 (18) | C13—N4 | 1.330 (2) |
| C3—N2 | 1.143 (2) | C13—C14 | 1.372 (3) |
| C4—N1 | 1.139 (2) | C13—H13A | 0.9300 |
| C5—C6 | 1.376 (3) | C14—N5 | 1.322 (3) |
| C5—C10 | 1.390 (3) | C14—H14A | 0.9300 |
| C5—C11 | 1.445 (3) | C15—N5 | 1.325 (3) |
| C6—C7 | 1.378 (3) | C15—C16 | 1.368 (3) |
| C6—H6A | 0.9300 | C15—H15A | 0.9300 |
| C7—C8 | 1.382 (2) | C16—N4 | 1.337 (2) |
| C7—H7A | 0.9300 | C16—H16A | 0.9300 |
| C8—C9 | 1.384 (2) | | |

| | | | |
|---|---|---|---|
| S2—Ni1—S2$^{i}$ | 180.00 (2) | C9—C10—C5 | 119.44 (17) |
| S2—Ni1—S1 | 92.96 (3) | C9—C10—H10A | 120.3 |
| S2$^{i}$—Ni1—S1 | 87.04 (3) | C5—C10—H10A | 120.3 |
| S2—Ni1—S1$^{i}$ | 87.04 (3) | N3—C11—C5 | 178.5 (3) |
| S2$^{i}$—Ni1—S1$^{i}$ | 92.96 (3) | N4—C12—C8 | 114.59 (14) |
| S1—Ni1—S1$^{i}$ | 180.00 (2) | N4—C12—H12A | 108.6 |
| C2—C1—C4 | 121.29 (15) | C8—C12—H12A | 108.6 |
| C2—C1—S1 | 120.95 (13) | N4—C12—H12B | 108.6 |
| C4—C1—S1 | 117.76 (13) | C8—C12—H12B | 108.6 |
| C1—C2—C3 | 121.67 (15) | H12A—C12—H12B | 107.6 |
| C1—C2—S2 | 121.17 (12) | N4—C13—C14 | 118.57 (17) |
| C3—C2—S2 | 117.14 (13) | N4—C13—H13A | 120.7 |
| N2—C3—C2 | 178.3 (2) | C14—C13—H13A | 120.7 |
| N1—C4—C1 | 179.3 (2) | N5—C14—C13 | 123.76 (19) |
| C6—C5—C10 | 120.33 (16) | N5—C14—H14A | 118.1 |
| C6—C5—C11 | 118.78 (17) | C13—C14—H14A | 118.1 |
| C10—C5—C11 | 120.88 (17) | N5—C15—C16 | 122.83 (19) |
| C5—C6—C7 | 119.54 (17) | N5—C15—H15A | 118.6 |
| C5—C6—H6A | 120.2 | C16—C15—H15A | 118.6 |
| C7—C6—H6A | 120.2 | N4—C16—C15 | 119.37 (18) |
| C6—C7—C8 | 121.07 (17) | N4—C16—H16A | 120.3 |

| | | | |
|---|---|---|---|
| C6—C7—H7A | 119.5 | C15—C16—H16A | 120.3 |
| C8—C7—H7A | 119.5 | C13—N4—C16 | 119.44 (16) |
| C7—C8—C9 | 119.00 (16) | C13—N4—C12 | 123.08 (14) |
| C7—C8—C12 | 119.48 (16) | C16—N4—C12 | 117.47 (15) |
| C9—C8—C12 | 121.42 (16) | C14—N5—C15 | 115.85 (18) |
| C10—C9—C8 | 120.61 (16) | C1—S1—Ni1 | 102.41 (7) |
| C10—C9—H9A | 119.7 | C2—S2—Ni1 | 102.28 (6) |
| C8—C9—H9A | 119.7 | | |

Symmetry code: (i) $-x, -y, -z$.