

# Crystal structure of bis[1-(naphthalen-1-ylmethyl)pyridinium] bis(2,2-dicyanoethene-1,1-dithiolato- $\kappa^2S,S'$ )nickelate(II)

Miao Zhang<sup>a</sup> and Xu-Jie Xiong<sup>b\*</sup>

Received 14 July 2014

Accepted 23 July 2014

<sup>a</sup>College of Chemical Engineering, Huanggang Normal University, 438000 Huangzhou, People's Republic of China, and

<sup>b</sup>Hubei Key Laboratory for Processing and Application of Catalytic Materials, Huanggang Normal University, 438000 Huangzhou, People's Republic of China. \*Correspondence e-mail: hgxiangxj@126.com

Edited by B. Kojić-Prodić, Rudjer Boskovic Institute, Croatia

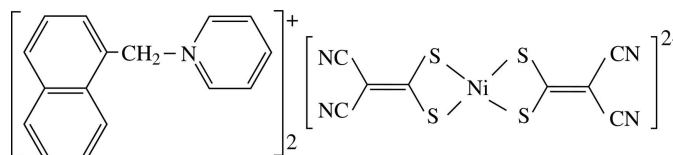
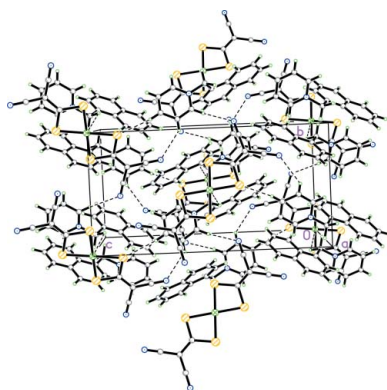
**Keywords:** bis(2,2-dicyanoethene-1,1-dithiolato)nickel(II); pyridinium; hydrogen bonding;  $\pi$ - $\pi$  interaction; crystal structure.

**Supporting information:** this article has supporting information at journals.iucr.org/e

A new ion-pair complex,  $(C_{16}H_{14}N)_2[Ni(C_4N_2S_2)_2]$  or  $(1-NaMePy)_2[Ni(imnt)_2]$ , where 1-NaMePy is 1-(4-naphthylmethylene)pyridinium and imnt is 2,2-dicyanoethene-1,1-dithiolate, was obtained by the direct reaction of  $NiCl_2$ ,  $K_2imnt$  and  $(1-NaMePy)^+Br^-$  in  $H_2O$ . The asymmetric unit contains a  $[1-NaMePy]^+$  cation and one half of an  $Ni(imnt)_2^{2-}$  anion. The  $Ni^{II}$  ion lies on an inversion centre and adopts a square-planar configuration with Ni–S bond lengths of 2.200 (1) and 2.216 (1) Å. In the  $[1-NaMePy]^+$  cation, the naphthyl ringsystem and the pyridinium ring make a dihedral angle of 90.0 (2)°. In the crystal, C–H...N and C–H...Ni hydrogen bonds, as well as  $\pi$ - $\pi$  interactions between the chelate ring and the pyridinium ring [centroid-centroid distance = 3.675 (2) Å] link the ions into a three-dimensional network.

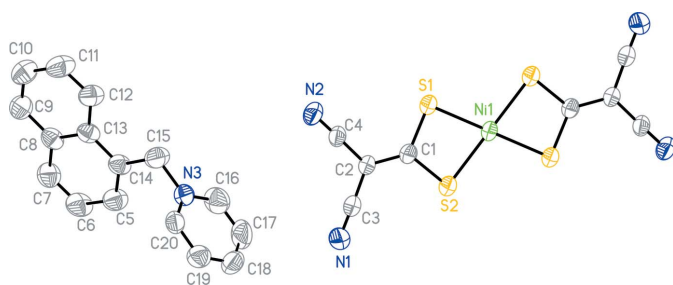
## 1. Chemical context

Transition metal complexes with dithiolate ligands such as 2,2-dicyanoethene-1,1-dithiolate (imnt) or 1,2-dicyanoethene-1,2-dithiolate (mnt) are important molecular materials with interesting electrical conductivity, superconductivity, optical and magnetic properties (Liu *et al.*, 1996; Robertson & Cronin, 2002; Ni *et al.*, 2005; Ren *et al.*, 2002; Xie *et al.*, 2002; Duan *et al.*, 2010). Recently, attempts have been made to extend the range of metal complexes containing the  $Ni(imnt)_2^{2-}$  anion, and the topology and the size of some organic cations, such as substituted benzyl pyridinium derivatives, play an important role in tuning the stacks of anions and cations of molecular materials containing the  $Ni(imnt)_2^{2-}$  anion (Liu *et al.*, 2006; Feng *et al.*, 2007). The title ion-pair complex,  $(1-NaMePy)_2[Ni(imnt)_2]$  has therefore been prepared and investigated.



## 2. Structural commentary

The asymmetric unit of the title compound consists of one  $[1-NaMePy]^+$  cation and one-half of an  $Ni(imnt)_2^{2-}$  anion located about an inversion center. The  $NiS_4$  core exhibits a square-planar configuration, with Ni–S bond lengths of 2.200 (1) and 2.216 (1) Å. The S1–Ni1–S2 bond angle within the four-membered ring (Ni1/S1/C1/S2) is 78.91 (3)°. The N1 and N2 atoms of the  $C\equiv N$  groups deviate from the Ni1/S1/C1/S2 plane by 0.078 (3) and 0.169 (3) Å, respectively. The


**Figure 1**

The molecular structure of (I), with the atom labelling and 30% probability displacement ellipsoids for non-H atoms. The other half of the anion is generated by the inversion-symmetry operation  $-x, y + \frac{1}{2}, -z + \frac{1}{2}$ .

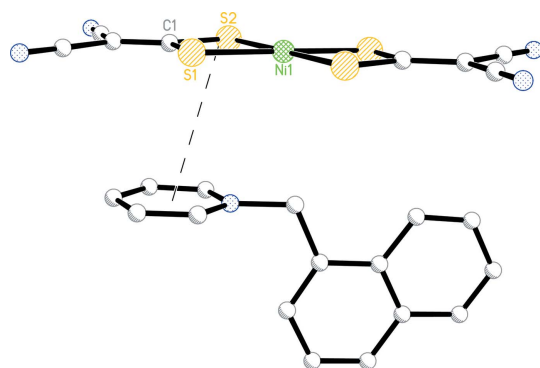
[1-NaMePy]<sup>+</sup> cation adopts a conformation in which both the naphthyl ring system and the pyridinium ring are twisted with respect to the N3/C11/C10 reference plane, making dihedral angles of 10.5 (2)° and 87.3 (3)°, respectively. The naphthyl ring system and the pyridinium ring make a dihedral angle of 90.0 (2)°.

### 3. Supramolecular features

There are three weak interactions between the Ni(imnt)<sub>2</sub><sup>2-</sup> anion and [1-NaMePy]<sup>+</sup> cation. The first is a  $\pi$ - $\pi$  contact between the chelate ring (which is defined by atoms Ni1, S1, S2, and C1) of the anion and the pyridinium ring of the cation (Fig. 2) with a distance of 3.675 (2) Å between the centroids. The second is a C—H···Ni hydrogen bond and the third is a C—H···N hydrogen bond (Table 1, Fig. 3). The combination of these weak interactions consolidates the title complex into a three-dimensional network structure (Fig. 3).

### 4. Database survey

Many ion-pair complexes containing Ni(imnt)<sub>2</sub><sup>2-</sup> anion have been reported, typical examples being [TBA]<sub>2</sub>[Ni(imnt)<sub>2</sub>] and [4NO<sub>2</sub>BzPy]<sub>2</sub>[Ni(imnt)<sub>2</sub>] [TBA is tetrabutylammonium; 4NO<sub>2</sub>BzPy is 1-(4-nitrobenzyl)pyridinium] (Liu *et al.*, 2006), [4FBzPy]<sub>2</sub>[Ni(imnt)<sub>2</sub>] [4FBzPy is 1-(4-fluorobenzyl)pyridinium] (Zhou & Ni, 2007), [Bz2NH<sub>2</sub>Py]<sub>2</sub>[Ni(imnt)<sub>2</sub>] (Bz2NH<sub>2</sub>Py is 1-benzyl-2-aminopyridinium) (Hou *et al.*, 2007),


**Figure 2**

The  $\pi$ - $\pi$  contact between the chelate ring of the anion and the pyridinium ring of the cation (shown as a dashed line).

**Table 1**

Hydrogen-bond geometry (Å, °).

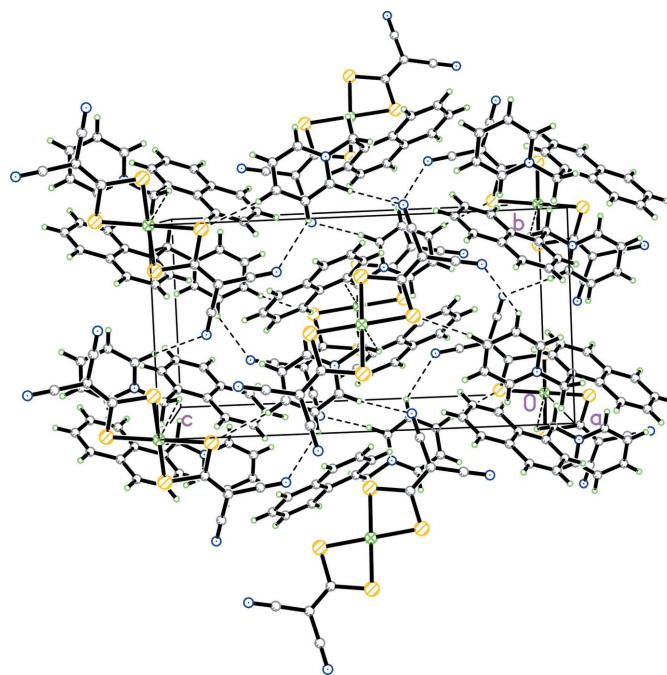
<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C19—H19···N2 <sup>i</sup>	0.93	2.60	3.265 (5)	129
C20—H20···N1 <sup>ii</sup>	0.93	2.42	3.304 (5)	160
C15—H15B···Ni1 <sup>iii</sup>	0.97	3.07	3.508 (4)	109

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

[BzDMAP]<sub>2</sub>[Ni(imnt)<sub>2</sub>] [BzDMAP is 1-benzyl-4-(dimethylamino)pyridinium] (Feng *et al.*, 2007), [2-NaMePy]<sub>2</sub>[Ni(imnt)<sub>2</sub>] and [2-NaMe-4-MePy]<sub>2</sub>[Ni(imnt)<sub>2</sub>] [2-NaMePy is 1-(2-naphthylmethyl)pyridinium; 2-NaMe-4-MePy is 1-(2-naphthylmethyl)-4-methylpyridinium] (Huang *et al.*, 2009), [Bz-4-MePy]<sub>2</sub>[Ni(imnt)<sub>2</sub>] and [Bz-4-MeQl]<sub>2</sub>[Ni(imnt)<sub>2</sub>] (Bz-4-MePy is 1-benzyl-4-methylpyridinium; Bz-4-MeQl is 1-benzyl-4-methylquinolinium) (Liu *et al.*, 2013). For a description of C—H···N and C—H···Ni hydrogen bonds, see: Huang *et al.*, (2009). For a description of  $\pi$ - $\pi$  contacts between chelate and phenyl rings, see: Molčanov *et al.* (2013).

### 5. Synthesis and crystallization

The title ion-pair complex was prepared by the direct reaction of 1:2:2 mol equiv. of NiCl<sub>2</sub>·6H<sub>2</sub>O, K<sub>2</sub>imnt and 1-(4-naphthylmethylene)pyridinium bromide in water (Huang *et al.*, 2009). The brown product obtained was purified through recrystallization from a mixed solvent of methanol and water (yield: 78%). Brown block-shaped single crystals suitable for X-ray analysis were obtained by slow evaporation of a methanol solution at room temperature after about 4 weeks.


**Figure 3**

The packing of the title compound, viewed down the *a* axis, showing the network of molecules connected by C—H···N hydrogen bonds (dashed lines).

## 6. Refinement

All H-atoms were positioned geometrically and refined using a riding model with  $d(\text{C}-\text{H}) = 0.93 \text{ \AA}$ ,  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic and  $d(\text{C}-\text{H}) = 0.97 \text{ \AA}$ ,  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for  $\text{CH}_2$  atoms. Crystal data, data collection and structure refinement details are summarized in Table 2.

## Acknowledgements

The authors thank the Doctor's Foundation of Huanggong Normal University (10CD001) and the Educational Commission of Hubei Province of China (Q20112902) for financial support.

## References

- Bruker (2000). *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Duan, H. B., Ren, X. M. & Meng, Q. J. (2010). *Coord. Chem. Rev.* **254**, 1509–1522.
- Feng, C.-W., Li, X.-R., Hou, Y. & Ni, C.-L. (2007). *Acta Cryst.* **E63**, m1762.
- Hou, Y., Huang, Q., Zuo, H. & Ni, C. (2007). *Acta Cryst.* **E63**, m2903.
- Huang, Q., Hou, Y., Zhu, H. M., Zhou, J. R., Zuo, H. R., Ni, C. L., Meng, Q. J. & Hu, X. L. (2009). *J. Coord. Chem.* **62**, 2012–2021.
- Liu, M.-G., Li, X.-Y., Lin, L.-F. & Ni, C.-L. (2006). *Acta Cryst.* **E62**, m2919–m2921.
- Liu, J. F., Liang, L. B., Dai, S. L., Huang, R. K., Guan, Q. Y., Chen, W. Q., Yang, L. M., Zhou, J. R. & Ni, C. L. (2013). *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **43**, 1492–1500.
- Liu, S. G., Liu, Y. Q., Li, Y. F. & Zhu, D. B. (1996). *Synth. Met.* **83**, 131–140.
- Molčanov, K., Jurić, M. & Kojić-Prodić, B. (2013). *Dalton Trans.* **42**, 15756–15765.
- Ni, Z. P., Ren, X. M., Ma, J., Xie, J. L., Ni, C. L., Chen, Z. D. & Meng, Q. J. (2005). *J. Am. Chem. Soc.* **127**, 14330–14338.
- Ren, X. M., Meng, Q. J., Song, Y., Lu, C. S. & Hu, C. J. (2002). *Inorg. Chem.* **41**, 5686–5692.

Table 2

Experimental details.

Crystal data	
Chemical formula	$(\text{C}_{16}\text{H}_{14}\text{N})_2[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]$
$M_r$	779.63
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	291
$a, b, c$ (Å)	11.876 (3), 9.025 (3), 17.465 (5)
$\beta$ (°)	91.808 (4)
$V$ (Å <sup>3</sup> )	1871.0 (9)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.78
Crystal size (mm)	0.36 × 0.30 × 0.21
Data collection	
Diffractometer	Bruker <i>SMART</i> CCD area detector
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2000)
$T_{\text{min}}, T_{\text{max}}$	0.762, 0.843
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	9345, 3283, 2228
$R_{\text{int}}$	0.031
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.040, 0.102, 1.04
No. of reflections	3283
No. of parameters	232
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.21, -0.15

Computer programs: *SMART* and *SAINT* (Bruker, 2000) and *SHELXTL* (Sheldrick, 2008).

- Robertson, N. & Cronin, L. (2002). *Coord. Chem. Rev.* **227**, 93–127.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Xie, J. L., Ren, X. M., Song, Y., Zhang, W. W., Liu, W. L., He, C. & Meng, Q. J. (2002). *Chem. Commun.* pp. 2346–2347.
- Zhou, A.-Q. & Ni, C.-L. (2007). *Acta Cryst.* **E63**, m3084.

## supporting information

*Acta Cryst.* (2014). E70, 115-117 [doi:10.1107/S1600536814017012]

## Crystal structure of bis[1-(naphthalen-1-ylmethyl)pyridinium] bis(2,2-dicyanoethene-1,1-dithiolato- $\kappa^2S,S'$ )nickelate(II)

Miao Zhang and Xu-Jie Xiong

### Computing details

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

### Bis[1-(naphthalen-1-ylmethyl)pyridinium] bis(2,2-dicyanoethene-1,1-dithiolato- $\kappa^2S,S'$ )nickelate(II)

#### Crystal data

(C<sub>16</sub>H<sub>14</sub>N)<sub>2</sub>[Ni(C<sub>4</sub>N<sub>2</sub>S<sub>2</sub>)<sub>2</sub>]

*M<sub>r</sub>* = 779.63

Monoclinic, *P*2<sub>1</sub>/*c*

Hall symbol: -P 2ybc

*a* = 11.876 (3) Å

*b* = 9.025 (3) Å

*c* = 17.465 (5) Å

$\beta$  = 91.808 (4)°

*V* = 1871.0 (9) Å<sup>3</sup>

*Z* = 2

*F*(000) = 804

*D<sub>x</sub>* = 1.384 Mg m<sup>-3</sup>

Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 1994 reflections

$\theta$  = 2.5–22.7°

$\mu$  = 0.78 mm<sup>-1</sup>

*T* = 291 K

Block, brown

0.36 × 0.30 × 0.21 mm

#### Data collection

Bruker SMART CCD area detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2000)

*T<sub>min</sub>* = 0.762, *T<sub>max</sub>* = 0.843

9345 measured reflections

3283 independent reflections

2228 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.031

$\theta_{\max}$  = 25.0°,  $\theta_{\min}$  = 2.3°

*h* = -13→14

*k* = -9→10

*l* = -20→20

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.040

*wR*(*F*<sup>2</sup>) = 0.102

*S* = 1.04

3283 reflections

232 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

$$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 0.1262P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$$

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.0000	0.0000	0.0000	0.06043 (19)
S1	0.03025 (7)	0.02841 (8)	0.12405 (4)	0.0697 (2)
S2	0.08762 (7)	0.21679 (9)	0.00355 (4)	0.0709 (2)
N1	0.2232 (3)	0.5408 (4)	0.11604 (17)	0.1156 (12)
N2	0.1247 (3)	0.2483 (3)	0.29836 (16)	0.0963 (9)
N3	0.2381 (2)	0.7148 (3)	0.42980 (16)	0.0805 (7)
C1	0.0909 (2)	0.1950 (3)	0.10140 (14)	0.0616 (7)
C2	0.1329 (2)	0.2957 (3)	0.15460 (14)	0.0628 (7)
C3	0.1819 (3)	0.4313 (4)	0.13254 (16)	0.0792 (9)
C4	0.1274 (3)	0.2685 (3)	0.23417 (17)	0.0704 (8)
C5	0.4644 (3)	0.7646 (4)	0.4864 (2)	0.1009 (11)
H5	0.4408	0.7981	0.4382	0.121*
C6	0.5731 (3)	0.8033 (5)	0.5164 (3)	0.1080 (13)
H6	0.6212	0.8604	0.4875	0.130*
C7	0.6062 (3)	0.7565 (4)	0.5872 (2)	0.1045 (12)
H7	0.6768	0.7843	0.6069	0.125*
C8	0.5373 (3)	0.6678 (4)	0.6314 (2)	0.0817 (9)
C9	0.5710 (3)	0.6177 (4)	0.7054 (2)	0.0983 (11)
H9	0.6410	0.6467	0.7255	0.118*
C10	0.5068 (4)	0.5308 (5)	0.7473 (3)	0.1114 (13)
H10	0.5314	0.4992	0.7956	0.134*
C11	0.4017 (4)	0.4881 (5)	0.7169 (3)	0.1169 (14)
H11	0.3563	0.4266	0.7455	0.140*
C12	0.3642 (3)	0.5342 (4)	0.6470 (2)	0.0957 (11)
H12	0.2933	0.5047	0.6286	0.115*
C13	0.4307 (3)	0.6261 (3)	0.6015 (2)	0.0769 (9)
C14	0.3947 (3)	0.6786 (4)	0.5280 (2)	0.0812 (9)
C15	0.2770 (3)	0.6348 (4)	0.4999 (2)	0.1096 (13)
H15A	0.2759	0.5292	0.4895	0.131*
H15B	0.2246	0.6539	0.5402	0.131*
C16	0.2514 (4)	0.6590 (5)	0.3620 (3)	0.1198 (14)
H16	0.2866	0.5676	0.3573	0.144*

C17	0.2150 (5)	0.7315 (7)	0.2989 (3)	0.1362 (19)
H17	0.2264	0.6917	0.2506	0.163*
C18	0.1615 (4)	0.8632 (6)	0.3060 (3)	0.1177 (15)
H18	0.1346	0.9136	0.2627	0.141*
C19	0.1477 (3)	0.9203 (4)	0.3761 (3)	0.1004 (11)
H19	0.1118	1.0109	0.3821	0.120*
C20	0.1868 (3)	0.8436 (4)	0.43750 (19)	0.0822 (9)
H20	0.1775	0.8821	0.4863	0.099*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1	0.0607 (3)	0.0696 (4)	0.0503 (3)	0.0003 (3)	-0.0087 (2)	-0.0033 (2)
S1	0.0793 (5)	0.0764 (5)	0.0527 (4)	-0.0091 (4)	-0.0100 (4)	0.0017 (4)
S2	0.0824 (5)	0.0771 (5)	0.0528 (4)	-0.0074 (4)	-0.0057 (4)	-0.0001 (4)
N1	0.173 (3)	0.094 (2)	0.080 (2)	-0.040 (2)	-0.010 (2)	0.0011 (17)
N2	0.130 (3)	0.097 (2)	0.0603 (16)	0.0021 (18)	-0.0146 (16)	-0.0046 (15)
N3	0.0765 (18)	0.083 (2)	0.0818 (19)	-0.0104 (15)	-0.0064 (15)	0.0020 (16)
C1	0.0571 (16)	0.0696 (18)	0.0577 (15)	0.0041 (14)	-0.0062 (13)	-0.0005 (14)
C2	0.0666 (18)	0.0695 (19)	0.0517 (16)	-0.0009 (15)	-0.0079 (13)	-0.0009 (14)
C3	0.100 (3)	0.081 (2)	0.0552 (18)	-0.008 (2)	-0.0128 (17)	-0.0031 (17)
C4	0.076 (2)	0.072 (2)	0.0625 (19)	0.0008 (16)	-0.0157 (15)	-0.0052 (16)
C5	0.079 (2)	0.106 (3)	0.118 (3)	-0.009 (2)	-0.004 (2)	0.026 (2)
C6	0.068 (2)	0.118 (3)	0.139 (4)	-0.026 (2)	0.012 (2)	0.022 (3)
C7	0.079 (3)	0.111 (3)	0.122 (3)	-0.014 (2)	-0.011 (2)	0.005 (3)
C8	0.065 (2)	0.071 (2)	0.109 (3)	-0.0020 (17)	0.005 (2)	-0.004 (2)
C9	0.084 (3)	0.102 (3)	0.108 (3)	0.007 (2)	-0.015 (2)	0.006 (2)
C10	0.103 (3)	0.127 (3)	0.104 (3)	0.017 (3)	-0.005 (3)	0.019 (3)
C11	0.097 (3)	0.120 (3)	0.133 (4)	0.010 (3)	0.003 (3)	0.047 (3)
C12	0.070 (2)	0.100 (3)	0.117 (3)	0.000 (2)	-0.002 (2)	0.028 (2)
C13	0.064 (2)	0.0643 (19)	0.103 (2)	0.0054 (16)	0.0043 (19)	0.0066 (18)
C14	0.063 (2)	0.077 (2)	0.103 (2)	-0.0091 (17)	-0.0005 (18)	0.0121 (19)
C15	0.086 (3)	0.119 (3)	0.122 (3)	-0.025 (2)	-0.024 (2)	0.046 (3)
C16	0.143 (4)	0.103 (3)	0.114 (3)	0.002 (3)	0.019 (3)	-0.020 (3)
C17	0.184 (5)	0.153 (5)	0.073 (3)	-0.048 (4)	0.010 (3)	-0.032 (3)
C18	0.117 (4)	0.140 (4)	0.094 (3)	-0.035 (3)	-0.030 (3)	0.034 (3)
C19	0.095 (3)	0.095 (3)	0.111 (3)	-0.003 (2)	-0.007 (2)	0.012 (3)
C20	0.088 (2)	0.086 (2)	0.072 (2)	-0.013 (2)	-0.0014 (18)	-0.0120 (19)

*Geometric parameters (Å, °)*

Ni1—S1 <sup>i</sup>	2.2000 (9)	C8—C9	1.415 (5)
Ni1—S1	2.2000 (9)	C9—C10	1.329 (5)
Ni1—S2 <sup>i</sup>	2.2160 (9)	C9—H9	0.9300
Ni1—S2	2.2160 (9)	C10—C11	1.395 (6)
S1—C1	1.718 (3)	C10—H10	0.9300
S2—C1	1.719 (3)	C11—C12	1.353 (5)
N1—C3	1.144 (4)	C11—H11	0.9300

N2—C4	1.137 (3)	C12—C13	1.409 (4)
N3—C16	1.300 (5)	C12—H12	0.9300
N3—C20	1.321 (4)	C13—C14	1.420 (4)
N3—C15	1.482 (4)	C14—C15	1.519 (4)
C1—C2	1.382 (4)	C15—H15A	0.9700
C2—C3	1.414 (4)	C15—H15B	0.9700
C2—C4	1.415 (4)	C16—C17	1.342 (6)
C5—C14	1.361 (4)	C16—H16	0.9300
C5—C6	1.421 (5)	C17—C18	1.355 (6)
C5—H5	0.9300	C17—H17	0.9300
C6—C7	1.353 (5)	C18—C19	1.344 (5)
C6—H6	0.9300	C18—H18	0.9300
C7—C8	1.395 (5)	C19—C20	1.346 (5)
C7—H7	0.9300	C19—H19	0.9300
C8—C13	1.406 (4)	C20—H20	0.9300
S1 <sup>i</sup> —Ni1—S1	180.00 (4)	C9—C10—H10	120.8
S1 <sup>i</sup> —Ni1—S2 <sup>i</sup>	78.91 (3)	C11—C10—H10	120.8
S1—Ni1—S2 <sup>i</sup>	101.09 (3)	C12—C11—C10	121.6 (4)
S1 <sup>i</sup> —Ni1—S2	101.09 (3)	C12—C11—H11	119.2
S1—Ni1—S2	78.91 (3)	C10—C11—H11	119.2
S2 <sup>i</sup> —Ni1—S2	180.00 (4)	C11—C12—C13	121.1 (4)
C1—S1—Ni1	86.09 (9)	C11—C12—H12	119.5
C1—S2—Ni1	85.56 (10)	C13—C12—H12	119.5
C16—N3—C20	120.2 (3)	C8—C13—C12	117.5 (3)
C16—N3—C15	121.3 (4)	C8—C13—C14	119.2 (3)
C20—N3—C15	118.5 (3)	C12—C13—C14	123.2 (3)
C2—C1—S1	124.5 (2)	C5—C14—C13	120.1 (3)
C2—C1—S2	126.1 (2)	C5—C14—C15	122.9 (3)
S1—C1—S2	109.42 (15)	C13—C14—C15	117.0 (3)
C1—C2—C3	121.9 (2)	N3—C15—C14	113.6 (3)
C1—C2—C4	121.3 (3)	N3—C15—H15A	108.8
C3—C2—C4	116.8 (3)	C14—C15—H15A	108.8
N1—C3—C2	178.5 (4)	N3—C15—H15B	108.8
N2—C4—C2	178.7 (4)	C14—C15—H15B	108.8
C14—C5—C6	120.3 (4)	H15A—C15—H15B	107.7
C14—C5—H5	119.9	N3—C16—C17	120.9 (4)
C6—C5—H5	119.9	N3—C16—H16	119.5
C7—C6—C5	119.6 (3)	C17—C16—H16	119.5
C7—C6—H6	120.2	C16—C17—C18	119.4 (4)
C5—C6—H6	120.2	C16—C17—H17	120.3
C6—C7—C8	121.7 (4)	C18—C17—H17	120.3
C6—C7—H7	119.1	C19—C18—C17	119.4 (4)
C8—C7—H7	119.1	C19—C18—H18	120.3
C7—C8—C13	119.0 (3)	C17—C18—H18	120.3
C7—C8—C9	122.3 (3)	C18—C19—C20	118.7 (4)
C13—C8—C9	118.6 (3)	C18—C19—H19	120.7
C10—C9—C8	122.7 (4)	C20—C19—H19	120.7

C10—C9—H9	118.6	N3—C20—C19	121.3 (3)
C8—C9—H9	118.6	N3—C20—H20	119.3
C9—C10—C11	118.4 (4)	C19—C20—H20	119.3

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

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C19—H19 $\cdots$ N2 <sup>ii</sup>	0.93	2.60	3.265 (5)	129
C20—H20 $\cdots$ N1 <sup>iii</sup>	0.93	2.42	3.304 (5)	160
C15—H15 <i>B</i> $\cdots$ Ni1 <sup>iv</sup>	0.97	3.07	3.508 (4)	109

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