

2,3-Diethylthiazolium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(III)

Etsuko Tomiyama,* Kazuaki Tomono and Kazuo Miyamura

Department of Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan
Correspondence e-mail: etomiyama@jul.rikadai.jp

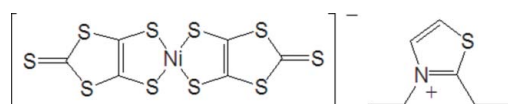
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Key indicators: single-crystal X-ray study; $T = 300$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.052; wR factor = 0.099; data-to-parameter ratio = 20.9.

In the title complex, $(\text{C}_7\text{H}_{12}\text{NS})[\text{Ni}(\text{C}_3\text{S}_5)_2]$, the dihedral angle between the thiazole ring of the cation and the plane of the anion is 8.0 (2)°. In the crystal structure, $\text{S} \cdots \text{S}$ intermolecular interactions between the anions form a distorted honeycomb structure parallel to the (002) plane, with cavities ~ 12.34 Å in diameter. The cavities are filled with cations. The cations and anions are linked *via* $\text{S} \cdots \text{S}$ [3.6657 (15) and 3.6240 (15) Å] and $\text{C}-\text{H} \cdots \text{S}$ interactions.

Related literature

For related literature, see: Abrahams *et al.* (1994); Frankenbach & Etter (1992); Gardner *et al.* (1995); Russell *et al.* (1994); Steimecke *et al.* (1979).



Experimental

Crystal data

$(\text{C}_7\text{H}_{12}\text{NS})[\text{Ni}(\text{C}_3\text{S}_5)_2]$
 $M_r = 593.61$
Monoclinic, $P2_1/c$
 $a = 8.2465$ (9) Å
 $b = 10.4325$ (12) Å
 $c = 25.382$ (3) Å
 $\beta = 93.344$ (2)°
 $V = 2179.9$ (4) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 1.95$ mm⁻¹
 $T = 300$ (1) K
 $0.29 \times 0.08 \times 0.04$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: analytical (*XPREP*; Bruker, 2000)
 $T_{\min} = 0.719$, $T_{\max} = 0.933$
13052 measured reflections
4945 independent reflections
3804 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.099$
 $S = 1.04$
4945 reflections
237 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.66$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1—S1	2.1551 (11)	Ni1—S7	2.1677 (11)
Ni1—S6	2.1613 (10)	Ni1—S2	2.1703 (10)
S1—Ni1—S6	85.02 (4)	S1—Ni1—S2	92.97 (4)
S1—Ni1—S7	177.79 (4)	S6—Ni1—S2	177.66 (4)
S6—Ni1—S7	93.13 (4)	S7—Ni1—S2	88.91 (4)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C12—H12A \cdots S6 ^{iv}	0.97	2.86	3.706 (4)	147

Symmetry code: (iv) $-x, -y + 2, -z$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997) and *KENX* (Sakai, 2002).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2476).

References

- Abrahams, B. F., Hoskins, B. F., Michail, D. M. & Robson, R. (1994). *Nature (London)*, **369**, 727–729.
Bruker (2000). *XPREP*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2001). *SAINT* (Version 6.22) and *SMART* (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEP3*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Frankenbach, G. M. & Etter, M. C. (1992). *Chem. Mater.* **4**, 272–278.
Gardner, G. B., Venkataraman, D., Moore, J. S. & Lee, S. (1995). *Nature (London)*, **374**, 792–795.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Russell, V. A., Etter, M. C. & Ward, M. D. (1994). *J. Am. Chem. Soc.* **116**, 1941–1952.
Sakai, K. (2002). *KENX*. Tokyo University of Science, Japan.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Steimecke, G., Sieler, H. J., Kirmse, R. & Hoyer, E. (1979). *Phosphorus Sulfur*, **7**, 49–55.

supplementary materials

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Comment

The control of molecular organization in the solid state is an important theme of coordination chemistry. Self-assembled metal complexes with specific network topologies attract great attention due to their potential applications as functional solid materials, as well as their fascinating framework structures, especially the 'honeycomb' structure (Gardner *et al.*, 1995). In the construction of diverse networks, there is preference for the use of directional intermolecular interactions such as hydrogen bonds (Frankenbach & Etter 1992), metal–ligand coordination bonds (Abrahams *et al.*, 1994), and donor–acceptor interactions (Russell *et al.*, 1994). This approach is based on the premise that if these interactions dominate the crystal field, then the solid-state structure should follow from the directional preferences associated with these interactions. Metal complexes with 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) ligand have drawn our attention to the role of S⋯S interaction between anions and cations, because conduction pathways between cation and anion may be constructed by S⋯S interactions. In order to explore new crystal structures of dmit complexes and to gain more insight into the structure-regulating ability of S⋯S interactions between anion and cation, the title complex salt (I) has been synthesized and analysed by X-ray crystallography.

The asymmetric unit of (I) is shown in Fig. 1. The Ni—S distances range from 2.1551 (11) to 2.1703 (10) Å, with an average of 2.163 (6) Å, and the *cis*-S—Ni—S angles range from 85.02 (4) to 93.13 (4)° (Table 1). Therefore, the NiS₄ geometry is slightly distorted square-planar. The whole [Ni(dmit)₂][−] anion is essentially planar, although the planes of the two coordinated C₃S₅^{2−} ligands make a dihedral angle of 2.83 (6)°. In the crystal structure (Fig. 2), the anions and cations are almost parallel. The dihedral angle and distance between the thiazole ring of the cation and plane of the anion are 8.0 (2)° and 3.633 Å, respectively. The C13—C12—N1—C9 [92.3 (5)°] and S11—C9—C10—C11 [−8.3 (5)°] torsion angles indicate that one of the ethyl groups is almost coplanar with the thiazolium ring and in the other group, the C(sp³)—C(sp³) bond is oriented perpendicular to the thiazolium ring. The anions are arranged in a zigzag manner along the *c* axis (Fig. 2).

In the crystal structure of (I), four S⋯S contacts shorter than 3.70 Å, the sum of van der Waals radii, are observed and are shown in Fig. 3 by dotted lines. Of the four contacts, two are between anions [S5⋯S10ⁱ and S7⋯S9ⁱⁱⁱ] and the other two are between anion and cation [S5⋯S11ⁱⁱ and S9⋯S11ⁱⁱⁱ] (see Table 1 for distances and symmetry codes); two [Ni(dmit)₂][−] anions form a quasi-dimeric structure. Inversion related anions at (*x*, *y*, *z*) and (1 − *x*, 2 − *y*, −*z*) are stacked along the *a* axis, without any significant S⋯S contacts; the shortest contact of 3.7490 (15) Å is observed between S3 and S7.

In the crystal structure, the anions form a distorted honeycomb structure parallel to the (002) plane. The cavity size is 12.34 Å in diameter as measured by the average of three Ni⋯Ni distances. The cavities are filled with cations. The cations and anions are linked through the S⋯S interactions, as mentioned above, and *via* the C12—H12A⋯S6(−*x*, 2 − *y*, −*z*) interactions [H⋯S = 2.86 Å].

The electrical conductivity of crystal measured by the two-probe alternating current method was 10^{−7} S cm^{−1} at room temperature, which is not very high among the (cation):[Ni(dmit)₂] type of 1:1 complexes.

Experimental

All starting materials were of reagent grade and used as purchased. 2,3-Diethylthiazolium bromide was synthesized as follows: Ethyl bromide (10 mmol) was mixed with 2-methylthiazole (1 mmol) and the resultant solid was filtered and washed several times by diethyl ether to give 2,3-diethylthiazolium bromide. $(\text{Bu}_4\text{N})[\text{Ni}(\text{dmit})_2]$ was synthesized according to the literature method (Steimecke *et al.*, 1979). Compound (I) was prepared by the cation-exchange method by slow interdiffusion of an acetone solution (25 ml) of $(\text{Bu}_4\text{N})[\text{Ni}(\text{dmit})_2]$ (0.05 mol) and a chloroform–methanol solution (50 ml; 4:1) of 2,3-diethylthiazolium bromide (0.10 mol) at room temperature. Black plate crystals of suitable size for X-ray diffraction and conductivity measurement were obtained.

Refinement

All H atoms were positioned geometrically and allowed to ride on their attached atoms, with C—H distances in the range 0.93–0.97 Å and $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ [or $1.5U_{\text{eq}}(\text{C})$ for methyl groups].

Figures

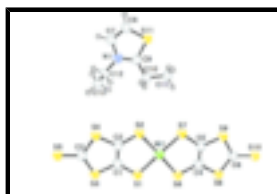


Fig. 1. An *ORTEP* (Burnett & Johnson, 1996) view of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

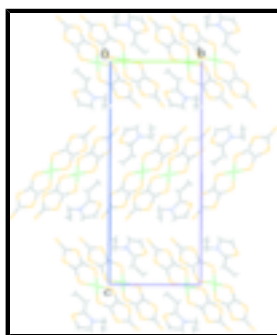


Fig. 2. The crystal packing of (I), viewed along the *a* axis.



Fig. 3. Packing of the $[\text{Ni}(\text{dmit})_2]$ anions of (I), viewed from their molecular axes. Dashed lines indicate short S...S contacts; red dashed lines are S...S contacts between anion and cation, and light blue dashed lines are S...S contacts between anions. Green lines and circles show one hexagon of the honeycomb structure.

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Crystal data

$(\text{C}_7\text{H}_{12}\text{NS})[\text{Ni}(\text{C}_3\text{S}_5)_2]$

$M_r = 593.61$

$F_{000} = 1204$

$D_x = 1.809 \text{ Mg m}^{-3}$

Monoclinic, $P2_1/c$
 Hall symbol: -P 2ybc
 $a = 8.2465$ (9) Å
 $b = 10.4325$ (12) Å
 $c = 25.382$ (3) Å
 $\beta = 93.344$ (2)°
 $V = 2179.9$ (4) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 4004 reflections
 $\theta = 2.5$ – 27.4 °
 $\mu = 1.95$ mm⁻¹
 $T = 300$ (1) K
 Plate, black
 $0.29 \times 0.08 \times 0.04$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	4945 independent reflections
Radiation source: fine-focus sealed tube	3804 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.042$
Detector resolution: 8.366 pixels mm ⁻¹	$\theta_{\text{max}} = 27.5$ °
$T = 300$ (1) K	$\theta_{\text{min}} = 2.5$ °
ω scans	$h = -10 \rightarrow 10$
Absorption correction: analytical (XPREP; Bruker, 2002)	$k = -10 \rightarrow 13$
$T_{\text{min}} = 0.719$, $T_{\text{max}} = 0.933$	$l = -30 \rightarrow 32$
13052 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.052$	H-atom parameters constrained
$wR(F^2) = 0.099$	$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
4945 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
237 parameters	$\Delta\rho_{\text{max}} = 0.66$ e Å ⁻³
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.33$ e Å ⁻³
	Extinction correction: none

Special details

Experimental. The first 50 frames were rescanned at the end of data collection to evaluate any possible decay phenomenon. Since it was judged to be negligible, no decay correction was applied to the data.

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.

Mean-plane data from final *SHELXL* refinement run:-

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Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

$$6.1704 (0.0020) x + 4.8344 (0.0022) y - 13.1376 (0.0048) z = 6.1128 (0.0016)$$

* -0.0383 (0.0007) Ni1 * -0.0106 (0.0011) S1 * -0.0476 (0.0011) S2 * 0.0304 (0.0011) S3 * -0.0189 (0.0012) S4 * 0.0678 (0.0013) S5 * -0.0729 (0.0012) S6 * -0.0221 (0.0011) S7 * -0.0154 (0.0012) S8 * 0.0405 (0.0012) S9 * 0.0746 (0.0014) S10 * 0.0095 (0.0031) C1 * -0.0134 (0.0031) C2 * 0.0276 (0.0029) C3 * -0.0376 (0.0031) C4 * -0.0171 (0.0030) C5 * 0.0434 (0.0030) C6

Rms deviation of fitted atoms = 0.0403

$$5.9897 (0.0105) x + 3.8809 (0.0123) y - 15.7207 (0.0340) z = 1.3365 (0.0105)$$

Angle to previous plane (with approximate e.s.d.) = 8.00 (0.17)

* -0.0036 (0.0025) C7 * 0.0044 (0.0023) C8 * 0.0022 (0.0020) C9 * 0.0003 (0.0022) N1 * -0.0034 (0.0018) S11

Rms deviation of fitted atoms = 0.0031

$$6.2436 (0.0026) x + 4.6387 (0.0036) y - 13.2480 (0.0082) z = 5.9160 (0.0038)$$

Angle to previous plane (with approximate e.s.d.) = 7.28 (0.18)

* 0.0074 (0.0028) C1 * 0.0043 (0.0028) C2 * -0.0037 (0.0026) C3 * -0.0031 (0.0012) S1 * 0.0054 (0.0012) S2 * -0.0068 (0.0012) S3 * -0.0147 (0.0012) S4 * 0.0112 (0.0013) S5

Rms deviation of fitted atoms = 0.0080

$$6.0849 (0.0027) x + 5.0943 (0.0037) y - 12.8985 (0.0079) z = 6.2220 (0.0020)$$

Angle to previous plane (with approximate e.s.d.) = 2.83 (0.06)

* -0.0058 (0.0028) C4 * -0.0089 (0.0028) C5 * 0.0072 (0.0028) C6 * 0.0073 (0.0012) S6 * 0.0037 (0.0012) S7 * -0.0051 (0.0012) S8 * 0.0004 (0.0012) S9 * 0.0013 (0.0014) S10

Rms deviation of fitted atoms = 0.0057

$$6.1704 (0.0020) x + 4.8344 (0.0022) y - 13.1376 (0.0048) z = 6.1128 (0.0016)$$

Angle to previous plane (with approximate e.s.d.) = 1.63 (0.05)

* -0.0383 (0.0007) Ni1 * -0.0106 (0.0011) S1 * -0.0476 (0.0011) S2 * 0.0304 (0.0011) S3 * -0.0189 (0.0012) S4 * 0.0678 (0.0013) S5 * -0.0729 (0.0012) S6 * -0.0221 (0.0011) S7 * -0.0154 (0.0012) S8 * 0.0405 (0.0012) S9 * 0.0746 (0.0014) S10 * 0.0095 (0.0031) C1 * -0.0134 (0.0031) C2 * 0.0276 (0.0029) C3 * -0.0376 (0.0031) C4 * -0.0171 (0.0030) C5 * 0.0434 (0.0030) C6

Rms deviation of fitted atoms = 0.0403

$$4.6551 (0.0255) x + 2.6266 (0.0523) y + 19.0832 (0.0922) z = 5.8094 (0.0341)$$

Angle to previous plane (with approximate e.s.d.) = 80.45 (0.22)

* 0.0000 (0.0000) C12 * 0.0000 (0.0000) C13 * 0.0000 (0.0000) N1

Rms deviation of fitted atoms = 0.0000

$$6.1704 (0.0020) x + 4.8344 (0.0022) y - 13.1376 (0.0048) z = 6.1128 (0.0016)$$

Angle to previous plane (with approximate e.s.d.) = 80.45 (0.22)

* -0.0383 (0.0007) Ni1 * 0.0095 (0.0030) C1 * -0.0134 (0.0031) C2 * 0.0276 (0.0029) C3 * -0.0376 (0.0031) C4 * -0.0171 (0.0030) C5 * 0.0434 (0.0030) C6 * -0.0106 (0.0011) S1 * -0.0476 (0.0011) S2 * 0.0304 (0.0012) S3 * -0.0189 (0.0012) S4 * 0.0678 (0.0013) S5 * -0.0729 (0.0012) S6 * -0.0221 (0.0011) S7 * -0.0154 (0.0012) S8 * 0.0405 (0.0012) S9 * 0.0746 (0.0014) S10 - 3.5538 (0.0031) N1 - 3.4707 (0.0039) C7 - 3.5866 (0.0044) C8 - 3.7369 (0.0036) C9 - 3.8162 (0.0016) S11

Rms deviation of fitted atoms = 0.0403

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3050 (4)	1.0872 (3)	0.07732 (13)	0.0325 (8)
C2	0.4172 (4)	1.0131 (3)	0.10446 (13)	0.0332 (8)
C3	0.3853 (4)	1.2187 (3)	0.16206 (13)	0.0338 (8)
C4	0.2354 (4)	0.7049 (3)	-0.09246 (13)	0.0327 (8)
C5	0.3496 (4)	0.6291 (3)	-0.06828 (13)	0.0319 (8)
C6	0.2647 (5)	0.5114 (3)	-0.15609 (13)	0.0378 (9)
C7	0.2390 (5)	0.7855 (4)	0.20018 (15)	0.0435 (10)
H7	0.2759	0.8385	0.2278	0.052*
C8	0.2956 (5)	0.6670 (4)	0.19200 (16)	0.0515 (11)
H8	0.3775	0.6280	0.2130	0.062*
C9	0.0838 (5)	0.7288 (4)	0.12669 (14)	0.0376 (9)
C10	-0.0389 (5)	0.7418 (4)	0.08211 (16)	0.0555 (12)
H10A	-0.0204	0.8220	0.0641	0.067*
H10B	-0.1458	0.7463	0.0961	0.067*
C11	-0.0377 (6)	0.6340 (5)	0.04253 (16)	0.0686 (14)
H11A	0.0641	0.6337	0.0260	0.103*
H11B	-0.1247	0.6459	0.0162	0.103*
H11C	-0.0516	0.5537	0.0602	0.103*
C12	0.0392 (5)	0.9453 (4)	0.16475 (16)	0.0515 (11)
H12A	0.0016	0.9706	0.1294	0.062*
H12B	0.1177	1.0085	0.1780	0.062*
C13	-0.1011 (6)	0.9437 (5)	0.19919 (19)	0.0725 (15)
H13A	-0.1839	0.8878	0.1842	0.109*
H13B	-0.1440	1.0289	0.2018	0.109*
H13C	-0.0657	0.9135	0.2337	0.109*
N1	0.1194 (4)	0.8188 (3)	0.16260 (12)	0.0395 (8)
Ni1	0.32928 (6)	0.85483 (4)	0.006835 (16)	0.03197 (13)
S1	0.21514 (13)	1.03771 (10)	0.01842 (4)	0.0438 (3)
S2	0.47494 (12)	0.86763 (9)	0.08067 (4)	0.0407 (2)
S3	0.25571 (12)	1.23261 (9)	0.10606 (4)	0.0405 (2)
S4	0.49365 (12)	1.07699 (10)	0.16431 (4)	0.0424 (3)
S5	0.40348 (14)	1.32933 (10)	0.20821 (4)	0.0463 (3)

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S6	0.17662 (13)	0.84662 (10)	-0.06525 (4)	0.0442 (3)
S7	0.44327 (12)	0.67219 (9)	-0.00807 (4)	0.0408 (2)
S8	0.15232 (13)	0.65050 (10)	-0.15321 (4)	0.0437 (3)
S9	0.39739 (12)	0.48947 (9)	-0.10162 (4)	0.0403 (2)
S10	0.24644 (15)	0.40762 (11)	-0.20523 (4)	0.0520 (3)
S11	0.19918 (14)	0.59741 (11)	0.13857 (4)	0.0535 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.035 (2)	0.031 (2)	0.0315 (18)	-0.0003 (16)	0.0030 (15)	-0.0022 (16)
C2	0.035 (2)	0.031 (2)	0.0331 (18)	-0.0029 (16)	0.0014 (16)	-0.0028 (15)
C3	0.036 (2)	0.032 (2)	0.0334 (18)	-0.0034 (16)	0.0042 (16)	0.0007 (16)
C4	0.037 (2)	0.032 (2)	0.0291 (18)	0.0011 (16)	0.0033 (15)	-0.0049 (15)
C5	0.034 (2)	0.029 (2)	0.0329 (18)	0.0021 (16)	0.0076 (15)	-0.0013 (15)
C6	0.043 (2)	0.037 (2)	0.0344 (19)	-0.0029 (17)	0.0071 (17)	-0.0014 (16)
C7	0.044 (2)	0.046 (3)	0.039 (2)	-0.0008 (19)	-0.0076 (18)	0.0038 (19)
C8	0.047 (3)	0.053 (3)	0.053 (2)	0.009 (2)	-0.009 (2)	0.005 (2)
C9	0.036 (2)	0.039 (2)	0.038 (2)	0.0004 (17)	0.0033 (17)	0.0067 (18)
C10	0.054 (3)	0.061 (3)	0.050 (2)	-0.004 (2)	-0.008 (2)	0.009 (2)
C11	0.064 (3)	0.090 (4)	0.051 (3)	-0.020 (3)	0.001 (2)	0.000 (3)
C12	0.058 (3)	0.038 (2)	0.058 (3)	0.011 (2)	0.001 (2)	0.009 (2)
C13	0.050 (3)	0.070 (3)	0.098 (4)	0.019 (3)	0.018 (3)	-0.004 (3)
N1	0.0415 (19)	0.0363 (19)	0.0412 (18)	0.0051 (15)	0.0081 (15)	0.0076 (15)
Ni1	0.0340 (3)	0.0310 (3)	0.0310 (2)	0.0024 (2)	0.00217 (19)	-0.0012 (2)
S1	0.0507 (6)	0.0384 (6)	0.0405 (5)	0.0122 (5)	-0.0129 (5)	-0.0072 (4)
S2	0.0422 (6)	0.0379 (6)	0.0411 (5)	0.0113 (4)	-0.0052 (4)	-0.0053 (4)
S3	0.0471 (6)	0.0326 (5)	0.0409 (5)	0.0068 (4)	-0.0058 (4)	-0.0041 (4)
S4	0.0434 (6)	0.0430 (6)	0.0395 (5)	0.0076 (5)	-0.0082 (4)	-0.0057 (4)
S5	0.0612 (7)	0.0387 (6)	0.0386 (5)	-0.0020 (5)	0.0001 (5)	-0.0068 (4)
S6	0.0548 (7)	0.0389 (6)	0.0376 (5)	0.0161 (5)	-0.0089 (5)	-0.0063 (4)
S7	0.0455 (6)	0.0402 (6)	0.0357 (5)	0.0125 (5)	-0.0052 (4)	-0.0050 (4)
S8	0.0519 (6)	0.0426 (6)	0.0355 (5)	0.0090 (5)	-0.0066 (4)	-0.0060 (4)
S9	0.0472 (6)	0.0369 (6)	0.0367 (5)	0.0092 (4)	0.0027 (4)	-0.0044 (4)
S10	0.0685 (8)	0.0462 (7)	0.0410 (6)	0.0027 (6)	0.0007 (5)	-0.0130 (5)
S11	0.0514 (7)	0.0457 (7)	0.0629 (7)	0.0097 (5)	-0.0004 (5)	-0.0047 (5)

Geometric parameters (\AA , $^\circ$)

C1—C2	1.361 (5)	C9—N1	1.329 (5)
C1—S1	1.709 (3)	C9—C10	1.480 (5)
C1—S3	1.742 (4)	C9—S11	1.686 (4)
C2—S2	1.711 (4)	C10—C11	1.509 (6)
C2—S4	1.743 (3)	C10—H10A	0.97
C3—S5	1.645 (3)	C10—H10B	0.97
C3—S4	1.727 (4)	C11—H11A	0.96
C3—S3	1.734 (4)	C11—H11B	0.96
C4—C5	1.349 (5)	C11—H11C	0.96
C4—S6	1.714 (4)	C12—N1	1.478 (5)

C4—S8	1.745 (3)	C12—C13	1.490 (5)
C5—S7	1.731 (4)	C12—H12A	0.97
C5—S9	1.742 (3)	C12—H12B	0.97
C6—S10	1.652 (4)	C13—H13A	0.96
C6—S8	1.726 (4)	C13—H13B	0.96
C6—S9	1.728 (4)	C13—H13C	0.96
C7—C8	1.342 (5)	Ni1—S1	2.1551 (11)
C7—N1	1.376 (5)	Ni1—S6	2.1613 (10)
C7—H7	0.93	Ni1—S7	2.1677 (11)
C8—S11	1.695 (4)	Ni1—S2	2.1703 (10)
C8—H8	0.93		
S5...S10 ⁱ	3.5981 (15)	S7...S9 ⁱⁱⁱ	3.4489 (13)
S5...S11 ⁱⁱ	3.6657 (15)	S9...S11 ⁱⁱⁱ	3.6240 (15)
C2—C1—S1	121.2 (3)	H11A—C11—H11B	109.5
C2—C1—S3	116.8 (3)	C10—C11—H11C	109.5
S1—C1—S3	122.0 (2)	H11A—C11—H11C	109.5
C1—C2—S2	121.3 (3)	H11B—C11—H11C	109.5
C1—C2—S4	115.1 (3)	N1—C12—C13	112.1 (3)
S2—C2—S4	123.6 (2)	N1—C12—H12A	109.2
S5—C3—S4	123.5 (2)	C13—C12—H12A	109.2
S5—C3—S3	123.5 (2)	N1—C12—H12B	109.2
S4—C3—S3	113.07 (19)	C13—C12—H12B	109.2
C5—C4—S6	121.9 (3)	H12A—C12—H12B	107.9
C5—C4—S8	116.0 (3)	C12—C13—H13A	109.5
S6—C4—S8	122.1 (2)	C12—C13—H13B	109.5
C4—C5—S7	120.9 (3)	H13A—C13—H13B	109.5
C4—C5—S9	116.2 (3)	C12—C13—H13C	109.5
S7—C5—S9	123.0 (2)	H13A—C13—H13C	109.5
S10—C6—S8	123.9 (2)	H13B—C13—H13C	109.5
S10—C6—S9	122.9 (2)	C9—N1—C7	114.7 (3)
S8—C6—S9	113.2 (2)	C9—N1—C12	125.0 (3)
C8—C7—N1	111.5 (4)	C7—N1—C12	120.2 (3)
C8—C7—H7	124.2	S1—Ni1—S6	85.02 (4)
N1—C7—H7	124.2	S1—Ni1—S7	177.79 (4)
C7—C8—S11	111.5 (3)	S6—Ni1—S7	93.13 (4)
C7—C8—H8	124.2	S1—Ni1—S2	92.97 (4)
S11—C8—H8	124.2	S6—Ni1—S2	177.66 (4)
N1—C9—C10	125.0 (3)	S7—Ni1—S2	88.91 (4)
N1—C9—S11	110.6 (3)	C1—S1—Ni1	102.48 (13)
C10—C9—S11	124.4 (3)	C2—S2—Ni1	101.99 (12)
C9—C10—C11	114.2 (4)	C3—S3—C1	97.05 (16)
C9—C10—H10A	108.7	C3—S4—C2	97.96 (17)
C11—C10—H10A	108.7	C4—S6—Ni1	102.17 (12)
C9—C10—H10B	108.7	C5—S7—Ni1	101.91 (12)
C11—C10—H10B	108.7	C6—S8—C4	97.29 (17)
H10A—C10—H10B	107.6	C6—S9—C5	97.32 (17)
C10—C11—H11A	109.5	C9—S11—C8	91.6 (2)
C10—C11—H11B	109.5		

supplementary materials

S1—C1—C2—S2	0.6 (5)	S5—C3—S3—C1	179.0 (2)
S3—C1—C2—S2	179.53 (19)	S4—C3—S3—C1	-0.9 (2)
S1—C1—C2—S4	-178.88 (19)	C2—C1—S3—C3	0.5 (3)
S3—C1—C2—S4	0.0 (4)	S1—C1—S3—C3	179.5 (2)
S6—C4—C5—S7	-0.1 (5)	S5—C3—S4—C2	-178.9 (2)
S8—C4—C5—S7	179.48 (19)	S3—C3—S4—C2	1.0 (2)
S6—C4—C5—S9	-179.16 (19)	C1—C2—S4—C3	-0.6 (3)
S8—C4—C5—S9	0.4 (4)	S2—C2—S4—C3	179.9 (2)
N1—C7—C8—S11	-0.7 (4)	C5—C4—S6—Ni1	0.9 (3)
N1—C9—C10—C11	171.1 (4)	S8—C4—S6—Ni1	-178.68 (19)
S11—C9—C10—C11	-8.3 (5)	S1—Ni1—S6—C4	177.78 (13)
C10—C9—N1—C7	-179.4 (4)	S7—Ni1—S6—C4	-1.03 (13)
S11—C9—N1—C7	0.1 (4)	C4—C5—S7—Ni1	-0.7 (3)
C10—C9—N1—C12	1.7 (6)	S9—C5—S7—Ni1	178.25 (18)
S11—C9—N1—C12	-178.7 (3)	S6—Ni1—S7—C5	0.97 (13)
C8—C7—N1—C9	0.4 (5)	S2—Ni1—S7—C5	179.83 (12)
C8—C7—N1—C12	179.3 (3)	S10—C6—S8—C4	179.5 (2)
C13—C12—N1—C9	92.3 (5)	S9—C6—S8—C4	0.5 (2)
C13—C12—N1—C7	-86.5 (5)	C5—C4—S8—C6	-0.5 (3)
C2—C1—S1—Ni1	-0.9 (3)	S6—C4—S8—C6	179.1 (2)
S3—C1—S1—Ni1	-179.79 (18)	S10—C6—S9—C5	-179.3 (2)
S6—Ni1—S1—C1	179.54 (13)	S8—C6—S9—C5	-0.3 (2)
S2—Ni1—S1—C1	0.74 (13)	C4—C5—S9—C6	-0.1 (3)
C1—C2—S2—Ni1	0.1 (3)	S7—C5—S9—C6	-179.1 (2)
S4—C2—S2—Ni1	179.52 (19)	N1—C9—S11—C8	-0.4 (3)
S1—Ni1—S2—C2	-0.50 (13)	C10—C9—S11—C8	179.1 (4)
S7—Ni1—S2—C2	178.34 (13)	C7—C8—S11—C9	0.7 (3)

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C12—H12A \cdots S6 ^{iv}	0.97	2.86	3.706 (4)	147

Symmetry codes: (iv) $-x, -y+2, -z$.

Fig. 1

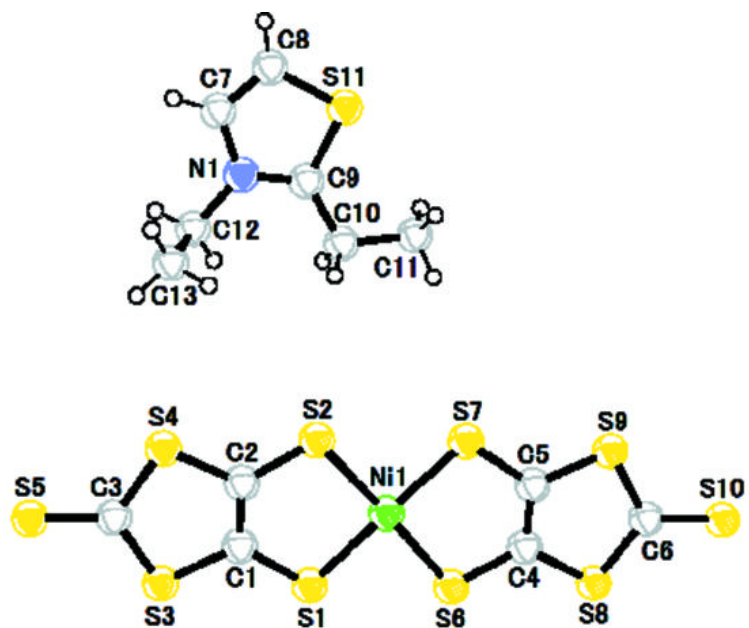


Fig. 2

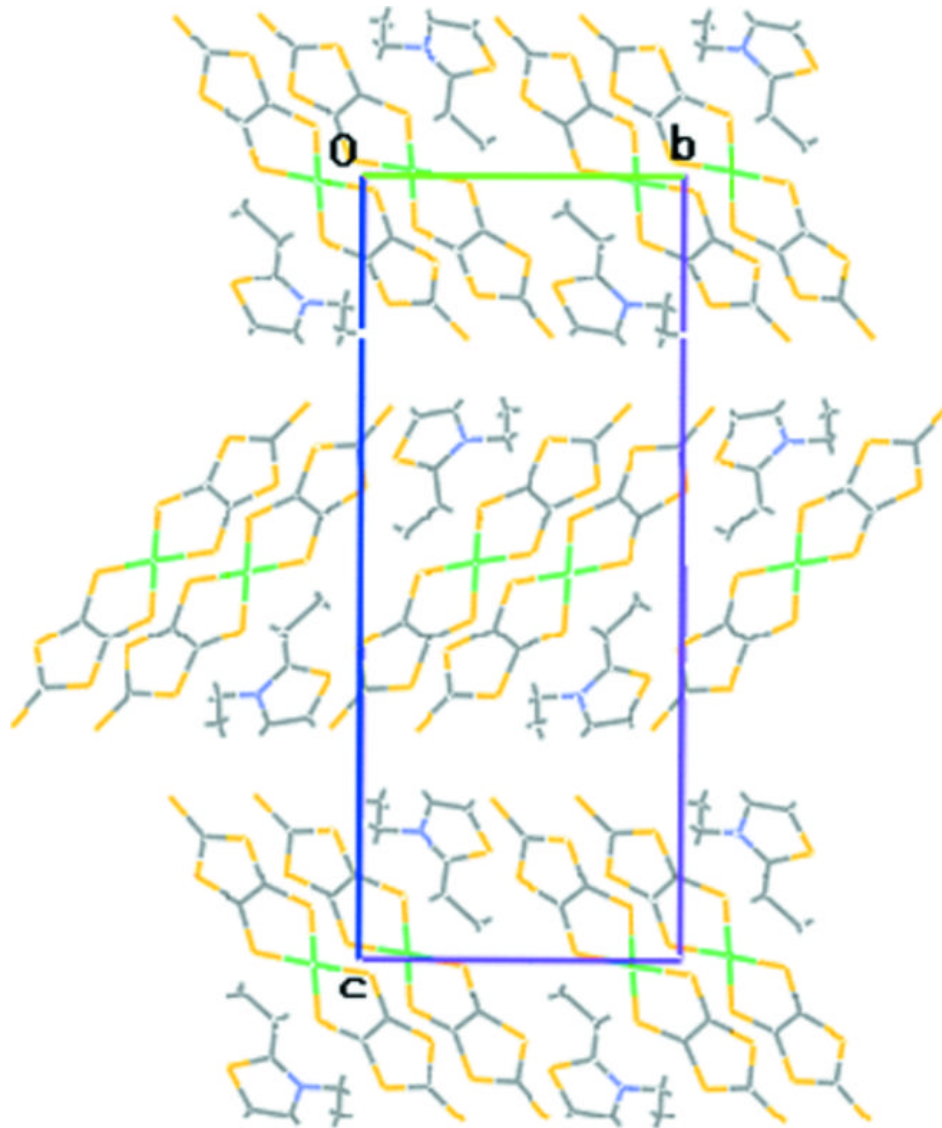


Fig. 3

