

Yi-Hang Wen<sup>a\*</sup> and  
 Qi-Wei Zhang<sup>a,b</sup>

<sup>a</sup>Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua, Zhejiang 321004, People's Republic of China, and <sup>b</sup>Department of Chemistry, Lishui University, Lishui, Zhejiang 323000, People's Republic of China

Correspondence e-mail: wyh@zjnu.cn

Key indicators

Single-crystal X-ray study  
 T = 293 K  
 Mean  $\sigma(C-C)$  = 0.005 Å  
 R factor = 0.026  
 wR factor = 0.074  
 Data-to-parameter ratio = 19.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

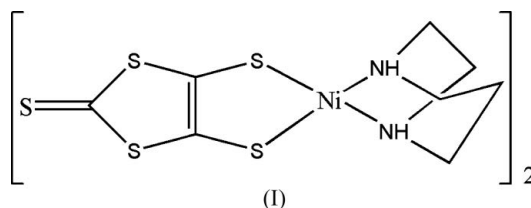
(1,4-Diazacycloheptane- $\kappa^2N,N'$ )(2-thioxo-1,3-dithiole-4,5-dithiolato- $\kappa^2S^4,S^5$ )nickel(II)

The title complex,  $[Ni(C_3S_5)(C_5H_{12}N_2)]$  or  $[Ni(dmit)(dach)]$  (dach is 1,4-diazacycloheptane and dmit is 2-thioxo-1,3-dithiole-4,5-dithiolate), crystallizes with two independent molecules per asymmetric unit. In each molecule, the central Ni<sup>II</sup> atom is coplanar with the two S atoms of one dmit ligand and two N atoms of one dach ligand. In the crystal structure, some weak S $\cdots$ S interactions and N—H $\cdots$ S and C—H $\cdots$ N hydrogen bonds are present. These interactions generate a three-dimensional framework.

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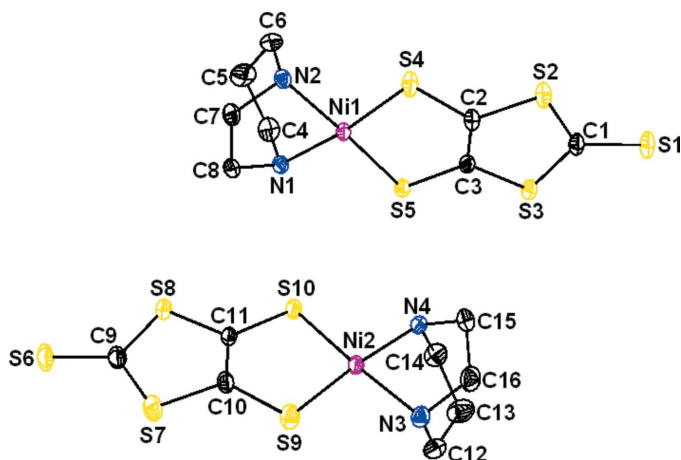
Comment

Over the past decades, transition metal complexes with bis-(dithiolate) ligands, such as dmit, have been widely studied for their semiconducting, conducting, and even superconducting properties (Akutagawa *et al.*, 2001; Aonuma *et al.*, 2001). Additionally, diazamesocyclic ligands, such as dach, occupy an important role in coordination chemistry because of their manifestation of unique conformations, exceptionally strong ligand fields and their potential for further functionalization (Mills *et al.*, 1990; Musker, 1992; Grapperhaus & Darensbourg, 1998). On combining bis(dithiolate) and diazamesocyclic ligands as a mixed-ligand system to react with transition metal salts, a series of new coordination complexes has been obtained. Here, we present the synthesis and crystal structure of the title compound,  $[Ni(dach)(dmit)]$ , (I).

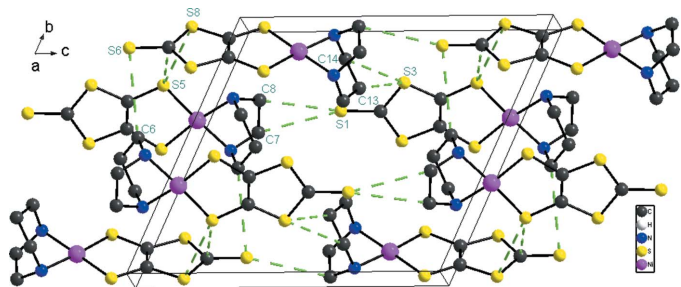


The asymmetric unit of complex (I) is illustrated in Fig. 1, and selected bond distances and angles are given in Table 1. In each molecule, the central Ni atom has a square-planar coordination environment, and is surrounded by two S atoms of one dmit ligand, with Ni—S distances 2.1505 (12)–2.1584 (10) Å, and two N atoms of a dach ligand, with Ni—N distances 1.925 (2)–1.933 (2) Å. The five S atoms of the dmit ligand are approximately coplanar; the dihedral angle of two planes defined by S4/S5/C2/C3 and S1/S2/S3/C1/C2/C3 is 5.38 (2)°. The independent molecules are linked by N—H $\cdots$ S hydrogen bonds to form a dimer (Table 2).

In the crystal structure of (I) there are some weak S $\cdots$ S interactions  $[S5\cdots S8^i = 3.5406 (14) \text{ \AA}; \text{symmetry operation: (i) } 1 - x, -y, -z]$ . Symmetry-related molecules are also connected via N—H $\cdots$ S and C—H $\cdots$ S hydrogen bonds; details are given in Table 2 and Fig. 2.



**Figure 1**  
Views of the two independent molecules of complex (I), showing the atom-labelling scheme, with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity. The two molecules are not shown in their correct relative orientation.



**Figure 2**  
A view, approximately along the *a* axis, of the crystal packing of (I). The S...S and CH...S interactions are depicted by dashed lines.

## Experimental

[Tetrabutylammonium][Ni(dmit)<sub>2</sub>] and [Ni(DACH)<sub>2</sub>](H<sub>2</sub>O)<sub>4</sub>(OAc)<sub>2</sub> were prepared according to the literature procedures (Sun *et al.*, 1996; Guo, 2002; Guo *et al.*, 2001). These two compounds (ratio 1:1) were dissolved separately in acetonitrile at room temperature and allowed to slowly diffuse in an H-shaped tube. After a few weeks, red block-shaped crystals, suitable for X-ray diffraction analysis, were obtained.

### Crystal data

[Ni(C <sub>3</sub> S <sub>5</sub> )(C <sub>5</sub> H <sub>12</sub> N <sub>2</sub> )]	<i>Z</i> = 4
<i>M<sub>r</sub></i> = 355.21	<i>D<sub>x</sub></i> = 1.791 Mg m <sup>-3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> $\alpha$ radiation
<i>a</i> = 9.3290 (19) Å	Cell parameters from 2987 reflections
<i>b</i> = 11.997 (2) Å	$\theta$ = 1.7–27.4°
<i>c</i> = 13.169 (3) Å	$\mu$ = 2.24 mm <sup>-1</sup>
$\alpha$ = 65.20 (3)°	<i>T</i> = 293 (2) K
$\beta$ = 82.81 (3)°	Block, red
$\gamma$ = 80.64 (3)°	0.30 × 0.20 × 0.20 mm
<i>V</i> = 1317.5 (6) Å <sup>3</sup>	

### Data collection

Rigaku R-AXIS RAPID diffractometer	5887 independent reflections
$\omega$ scans	4265 reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R</i> <sub>int</sub> = 0.020
<i>T</i> <sub>min</sub> = 0.590, <i>T</i> <sub>max</sub> = 0.639	$\theta$ <sub>max</sub> = 27.4°
9484 measured reflections	<i>h</i> = -12 → 12
	<i>k</i> = -15 → 15
	<i>l</i> = -17 → 16

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.027  
*wR* (*F*<sup>2</sup>) = 0.074  
*S* = 1.01  
 5887 reflections  
 301 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0378P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.52 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.43 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Ni1–N2	1.925 (2)	Ni2–N3	1.933 (2)
Ni1–N1	1.930 (2)	Ni2–N4	1.933 (2)
Ni1–S5	2.1568 (12)	Ni2–S10	2.1505 (12)
Ni1–S4	2.1584 (10)	Ni2–S9	2.1533 (9)
N2–Ni1–N1	80.11 (10)	N3–Ni2–N4	79.65 (10)
N2–Ni1–S5	171.07 (7)	N3–Ni2–S10	169.31 (8)
N1–Ni1–S5	93.09 (8)	N4–Ni2–S10	92.47 (7)
N2–Ni1–S4	92.66 (7)	N3–Ni2–S9	94.03 (8)
N1–Ni1–S4	172.73 (7)	N4–Ni2–S9	173.05 (7)
S5–Ni1–S4	94.03 (4)	S10–Ni2–S9	94.16 (4)

**Table 2**

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>
N1–H1...S10	0.88 (2)	2.87 (2)	3.527 (3)	133 (2)
N2–H2...S4 <sup>i</sup>	0.86 (2)	2.75 (2)	3.416 (3)	136 (2)
N3–H3...S1 <sup>iii</sup>	0.87 (3)	2.60 (3)	3.401 (3)	152 (2)
N4–H4...S5	0.89 (2)	2.49 (2)	3.374 (3)	173 (2)
C7–H7B...S9 <sup>iii</sup>	0.97	2.83	3.646 (3)	142
C15–H15B...S6 <sup>iv</sup>	0.97	2.87	3.771 (4)	155
C16–H16B...S6 <sup>iii</sup>	0.97	2.81	3.669 (4)	148

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

The H atoms bonded to the C atoms were positioned geometrically and refined using a riding model with C–H 0.97 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent C-atom})$ . The H atoms bonded to the N atoms were located in difference Fourier maps and refined [N–H distance = 0.857 (16)–0.894 (17) Å] with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ .

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXTL*.

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