

Wen-Jun Tong,<sup>a</sup> Ling Liu,<sup>b</sup>  
Qing-Jin Meng<sup>a</sup> and Yi-Zhi Li<sup>a\*</sup>

<sup>a</sup>Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China, and <sup>b</sup>College of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650092, People's Republic of China

Correspondence e-mail: llyjz@nju.edu.cn

#### Key indicators

Single-crystal X-ray study  
T = 293 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$   
R factor = 0.048  
wR factor = 0.079  
Data-to-parameter ratio = 16.5

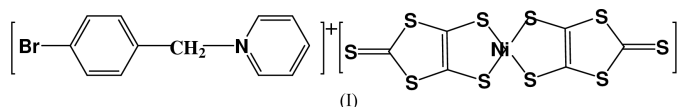
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## N-(4-Bromobenzyl)pyridinium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickel(III)

In the title compound,  $(\text{C}_{12}\text{H}_{11}\text{BrN})[\text{Ni}(\text{C}_3\text{S}_5)_2]$ , the  $\text{Ni}^{\text{III}}$  atom is coplanar with the four S atoms of two 2-thioxo-1,3-dithiole-4,5-dithiolate ligands. There are some weak  $\text{S} \cdots \text{S}$  and  $\text{Ni} \cdots \text{Ni}$  interactions between adjacent layers, resulting in a three-dimensional supramolecular network structure.

#### Comment

A great deal of work has been reported on the synthesis and characterization of different types of bis-dithiolate metal complexes. The studies on these bis-dithiolate metal compounds have been extended to other properties and uses, such as conducting Langmuir–Blodgett films, unconventional magnetic properties, and non-linear optics (NLO). Recent exploratory research on the interplay of conducting, magnetic and NLO properties in such compounds have been reported (Patrick, 1999).



In order to study the interplay of the magnetic properties, the title compound, (I), was synthesized. The crystal structure shows that the coordination around the  $\text{Ni}^{\text{III}}$  atom is approximately planar [the  $\text{Ni}-\text{S}$  bond lengths range from 2.1504 (11) to 2.1707 (12)  $\text{Å}$ ]. Two phenyl rings of different cations are parallel, while the pyridine ring is parallel to the  $\text{Ni}(\text{dmit})_2$  plane ( $\text{dmit}^{2-}$  is 2-thioxo-1,3-dithiole-4,5-dithiolate).

There are two separate components in the structure (Fig. 1); one is the  $\text{Ni}(\text{dmit})_2$  anion, the other is the substituted pyridine cations. Some non-classical hydrogen bonds ( $\text{C}-\text{H} \cdots \text{S}$ ) are found (Table 2), ranging from 3.557 (5) to 3.773 (5)  $\text{Å}$ . The anions are stacked in double layers. In these layers, there are some weak  $\text{S} \cdots \text{S}$  and  $\text{Ni} \cdots \text{Ni}$  interactions between layers and weak  $\text{S} \cdots \text{S}$  interactions between different ions in the same layer (Fig. 2). The  $\text{S} \cdots \text{S}$ ,  $\text{Ni} \cdots \text{Ni}$  and non-classical hydrogen bonds link the ions into a three-dimensional supramolecular network structure.

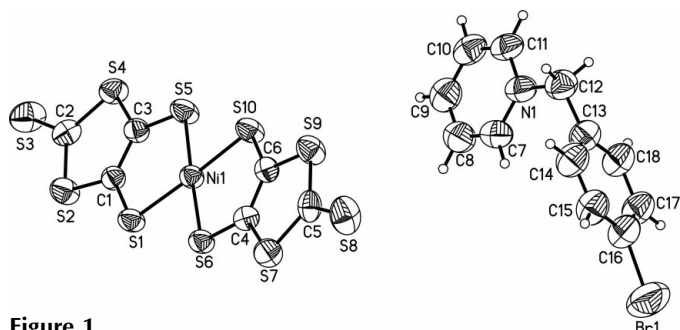
#### Experimental

A solution of NaOMe dissolved in methanol was added to a methanol solution of 4,5-bis(benzoylthio)-1,3-dithiol-2-thione, *i.e.*  $\text{dmit}(\text{COPh})_2$ . After stirring, a solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  was added. After further stirring, a solution of bromobenzylpyridine chloride was added. After further stirring, the black sediments were leached and dissolved in acetone. As the solvent slowly evaporated, well-formed crystals of (I) appeared.

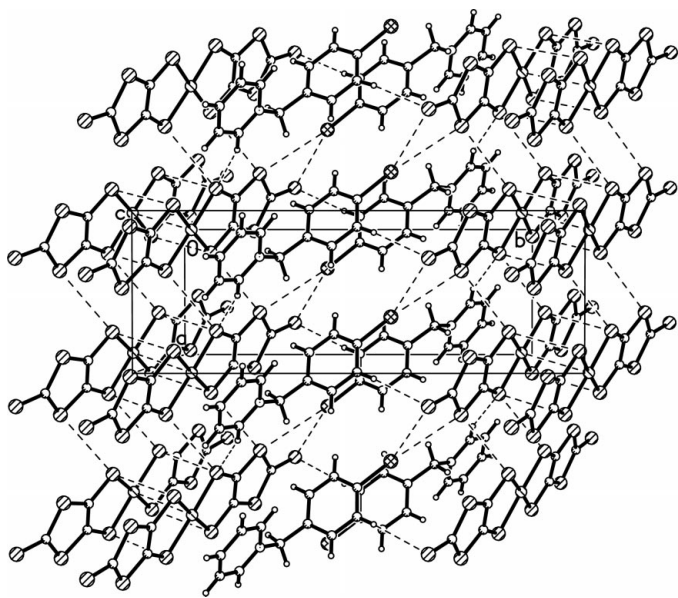
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**Figure 1**  
The molecular structure of (I), with 50% probability ellipsoids and the atom-numbering scheme.



**Figure 2**  
The packing in the crystal of (I), viewed down the *c* axis.

#### Crystal data

(C<sub>12</sub>H<sub>11</sub>BrN)[Ni(C<sub>3</sub>S<sub>5</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 700.57  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 6.275 (1) Å  
*b* = 17.438 (3) Å  
*c* = 22.839 (3) Å  
 $\beta$  = 91.87 (1)°  
*V* = 2497.8 (7) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.863 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 1002 reflections  
 $\theta$  = 2.3–17.8°  
 $\mu$  = 3.22 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Block, black  
 0.3 × 0.2 × 0.2 mm

#### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
*T<sub>min</sub>* = 0.465, *T<sub>max</sub>* = 0.523  
 12855 measured reflections

4626 independent reflections  
 2953 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.043  
 $\theta_{\text{max}}$  = 25.5°  
*h* = -7 → 7  
*k* = 0 → 21  
*l* = 0 → 27

#### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.048  
*wR*(*F*<sup>2</sup>) = 0.079  
*S* = 1.00  
 4626 reflections  
 280 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 0.113P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.45 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Ni1–S5	2.1504 (11)	S5–C3	1.690 (4)
Ni1–S6	2.1609 (11)	S6–C4	1.707 (4)
Ni1–S10	2.1664 (12)	S7–C5	1.727 (4)
Ni1–S1	2.1707 (12)	S7–C4	1.741 (4)
S1–C1	1.715 (4)	S8–C5	1.645 (4)
S2–C2	1.724 (4)	S9–C5	1.718 (4)
S2–C1	1.738 (4)	S9–C6	1.747 (4)
S3–C2	1.644 (4)	S10–C6	1.702 (4)
S4–C2	1.720 (4)	C7–N1	1.344 (5)
S4–C3	1.747 (4)	C16–Br1	1.896 (5)
S5–Ni1–S6	178.09 (5)	S5–Ni1–S1	92.93 (4)
S5–Ni1–S10	85.25 (4)	S6–Ni1–S1	88.87 (4)
S6–Ni1–S10	92.96 (4)	S10–Ni1–S1	177.60 (5)

**Table 2**

Hydrogen-bonding 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>
C8–H8...S3 <sup>i</sup>	0.93	2.70	3.557 (5)	154
C11–H11...S5 <sup>ii</sup>	0.93	2.68	3.570 (5)	161
C17–H17...S3 <sup>iii</sup>	0.93	2.85	3.773 (5)	170

Symmetry codes: (i) 1 - *x*, ½ + *y*, ½ - *z*; (ii) -*x*, 1 - *y*, 1 - *z*; (iii) 1 + *x*, 1 + *y*, 1 + *z*.

The positions of all the H atoms were fixed geometrically and constrained with a riding model.

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

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