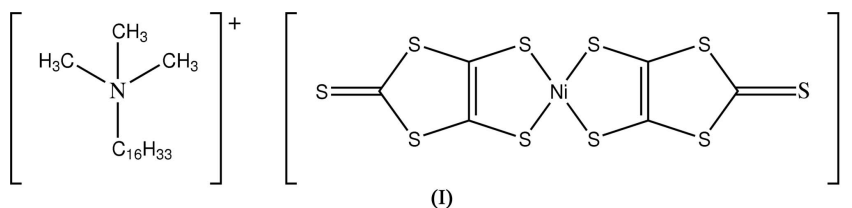


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wangyl@icm.sdu.edu.cn**Key indicators**Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.007$ Å
 R factor = 0.052
 wR factor = 0.155
Data-to-parameter ratio = 18.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**Hexadecyltrimethylammonium bis(2-thioxo-1,3-dithiole-4,5-dithiolato- κ^2S^4,S^5)nickelate(III)**

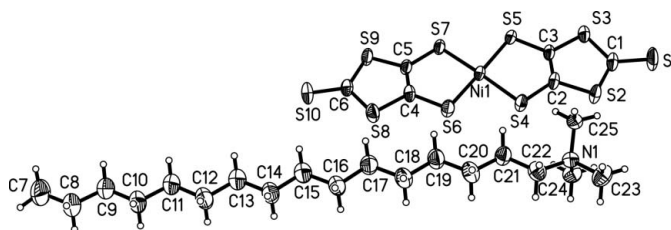
In the title complex, $(\text{C}_{19}\text{H}_{42}\text{N})[\text{Ni}(\text{C}_3\text{S}_5)_2]$, the Ni atom is coordinated by four 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) S atoms. The $[\text{Ni}(\text{dmit})_2]^-$ monoanion has a planar geometry, with the central Ni atom and the four coordinated S atoms forming an NiS_4 square plane. There are $\text{S} \cdots \text{S}$ intermolecular contacts in the crystal structure.

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Accepted 7 March 2006**Comment**

Since 1979 (Steimeck & Kirmse, 1979), metal bis(2-thioxo-1,3-dithiole-4,5-dithiolate), or bis(dmit), complexes have attracted increasing attention owing to their potential application as precursors for electrical conductors and superconductors (Cassoux, 1999; Robertson & Cronin, 2002), or as optical and photo-electrical materials (Winter *et al.*, 1992; Zuo *et al.*, 1996; Bai *et al.*, 1999; Wang *et al.*, 1999; Zhai *et al.*, 1999; Dai *et al.*, 2000; Liu *et al.*, 2002). It is well known that intermolecular interactions play an important role in the conductivities and superconductivities of $[\text{Ni}(\text{dmit})_2]^{n-}$ salts. The title salt, (I), was synthesized to study the impact of cation size on the intermolecular interactions in $[\text{Ni}(\text{dmit})_2]^-$ salts.



The molecular structure of (I) (Fig. 1 and Table 1) exhibits no distinguishing features compared to the other known structures of $[\text{Ni}(\text{dmit})_2]^-$ in terms of ligand behaviour and the coordination characteristics of the Ni ion. The $[\text{Ni}(\text{dmit})_2]^-$ anion is planar, with a maximum deviation from the least-squares plane of 0.096 (1) Å for atom S6. The NiS_4 core adopts a slightly distorted square-planar configuration.

**Figure 1**

The asymmetric unit of (I), showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size.

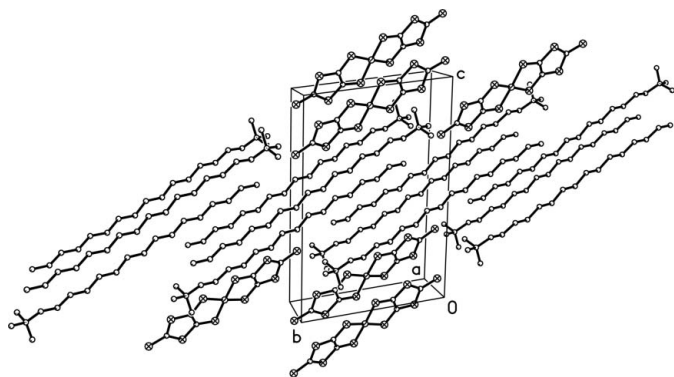


Figure 2
The packing of (I), viewed approximately along the *a* axis. H atoms have been omitted for clarity.

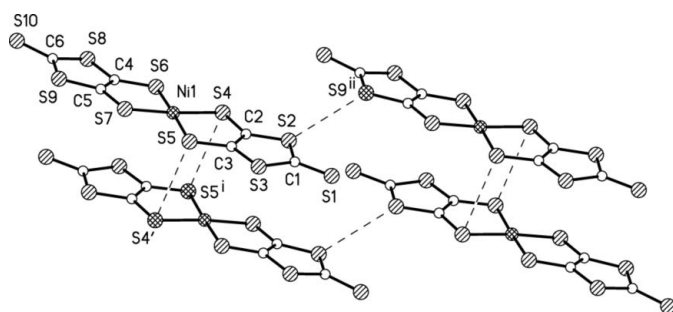


Figure 3
The packing of the $[\text{Ni}(\text{dmit})_2]^-$ anions of (I), showing the $\text{S}\cdots\text{S}$ contacts as dashed lines.

The crystal packing is shown in Fig. 2. Fig. 3 highlights the shortest $\text{S}\cdots\text{S}$ contacts which propagate the packing arrangement of the anions. By virtue of these $\text{S}\cdots\text{S}$ interactions, the $[\text{Ni}(\text{dmit})_2]^-$ anions form centrosymmetric dimers. These dimers are, in turn, linked to other dimers by translation along the *b*-axis direction, forming chains. The shortest $\text{S}\cdots\text{S}$ distance in the dimers is 3.693 (3) Å for $\text{S4}\cdots\text{S5}^i$ [symmetry code: (i) $1 - x, 1 - y, -z$] and between dimers is 3.637 (3) Å for $\text{S2}\cdots\text{S9}^{ii}$ [symmetry code: (ii) $x, 1 + y, z$]. The shortest $\text{S}\cdots\text{S}$ distance in (I) is equal to the sum of the van der Waals radii and is much larger than that in an analogue with a smaller planar cation, namely *N*-methylpyridinium (Xue *et al.*, 2003); *i.e.* a large cation appears to weaken the intermolecular interaction.

Experimental

$\text{Dmit}(\text{COPh})_2$ (0.816 g, 2 mmol) was treated with an excess of sodium methoxide (0.5 *M*) in MeOH (20 ml) under nitrogen at room temperature with stirring. To the resulting red solution, solutions of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.237 g, 1 mmol) in MeOH (20 ml) and then cetyltrimethylammonium bromide (CTAB) (0.870 g, 2.4 mmol) in MeOH (20 ml) were added. The resulting precipitate was washed with *i*-PrOH. Salt (I) was obtained by oxidizing this precipitate in acetone using I_2 according to a literature procedure (Xue *et al.*, 2003). The high optical-quality single crystals used for X-ray structure analysis were obtained by slow evaporation of an acetone solution of (I) at room temperature.

Crystal data

$(\text{C}_{19}\text{H}_{42}\text{N})[\text{Ni}(\text{C}_3\text{S}_5)_2]$
 $M_r = 735.91$
Triclinic, $P\bar{1}$
 $a = 8.051$ (5) Å
 $b = 12.240$ (5) Å
 $c = 18.316$ (5) Å
 $\alpha = 93.426$ (5)°
 $\beta = 99.218$ (5)°
 $\gamma = 100.494$ (5)°
 $V = 1744.5$ (14) Å³

$Z = 2$
 $D_x = 1.401$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 2878 reflections
 $\theta = 2.6\text{--}26.1$ °
 $\mu = 1.17$ mm⁻¹
 $T = 293$ (2) K
Plate, red
 $0.56 \times 0.27 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
 $T_{\text{min}} = 0.560$, $T_{\text{max}} = 0.892$
8662 measured reflections

6012 independent reflections
4270 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\text{max}} = 25.0$ °
 $h = -9 \rightarrow 9$
 $k = -14 \rightarrow 12$
 $l = -21 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.155$
 $S = 1.02$
6012 reflections
334 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0848P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.63$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.44$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C1—S1	1.642 (4)	C4—S8	1.746 (3)
C1—S2	1.719 (4)	C5—S7	1.709 (4)
C1—S3	1.719 (4)	C5—S9	1.726 (3)
C2—C3	1.362 (5)	C6—S10	1.645 (4)
C2—S4	1.706 (4)	C6—S8	1.708 (4)
C2—S2	1.733 (3)	C6—S9	1.726 (4)
C3—S5	1.710 (3)	Ni1—S6	2.1479 (11)
C3—S3	1.742 (3)	Ni1—S7	2.1540 (12)
C4—C5	1.347 (5)	Ni1—S5	2.1545 (11)
C4—S6	1.720 (4)	Ni1—S4	2.1592 (12)
S6—Ni1—S7	92.90 (4)	S6—Ni1—S4	87.08 (4)
S6—Ni1—S5	176.61 (5)	S7—Ni1—S4	175.07 (5)
S7—Ni1—S5	87.25 (4)	S5—Ni1—S4	93.06 (4)

All H atoms were positioned geometrically and allowed to ride on their attached atoms, with $\text{C—H} = 0.96\text{--}0.97$ Å and $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXTL* (Bruker, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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