

1-Methyl-*N*-(4-nitrobenzyl)pyridinium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)-nickelate(III)

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$

R factor = 0.056

w R factor = 0.102

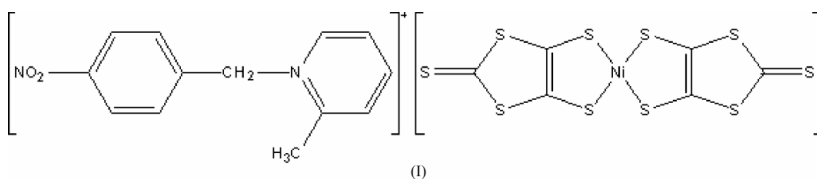
Data-to-parameter ratio = 14.3

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

The title compound, $(\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}_2)[\text{Ni}(\text{C}_3\text{S}_5)_2]$, is composed of layers of cations and anions. The Ni^{III} ion is in a planar environment, coordinated by the four S atoms of two dmit²⁻ ligands. There are some weak $\text{S}\cdots\text{S}$ and $\text{Ni}\cdots\text{S}$ interactions, and some non-classical hydrogen bonds ($\text{C}-\text{H}\cdots\text{S}$) are also observed. These interactions generate a three-dimensional framework.

Comment

A great deal of work has been reported on the synthesis and characterization of different types of bis(dithiolato)metal complexes. The studies of these bis(dithiolato)metal compounds have been extended to other properties and uses, such as conducting Langmuir–Blodgett films, unconventional magnetic properties and non-linear optics. Since the first molecular superconductor containing a transition metal complex, $(\text{TTF})[\text{M}(\text{dmit})_2]_2$ ($\text{M} = \text{Ni}$ or Pd , TTF is tetrathiafulvalene and dmit^{2-} is 2-thioxo-1,3-dithiole-4,5-dithiolate), was found by Brossard *et al.* (1986, 1989), extensive studies have been carried out on the assembled metal complexes of dmit and related compounds. The magnetic properties of substituted benzylpyridiniums have been studied in recent years, and several interesting magnetic properties, such as ferromagnetism, weak ferromagnetism, antiferromagnetism, weak antiferromagnetism and spin Peierls transitions have been found (Xie, Ren, Gao *et al.*, 2002; Xie, Ren, Song *et al.*, 2002; Ren *et al.*, 2001). In the present work, we have prepared the title salt [*N*-(4- NO_2 -benzyl)-1- CH_3 -py][$\text{Ni}(\text{dmit})_2$], (I), and determined its crystal structure.



The salt (I) has ions in a ratio of 1:1, as expected from the results of elemental analysis. The ratio of 1:1 proves that the oxidation state of nickel is +3. The coordination around the nickel ion is approximately planar (Fig. 1). The deviation of Ni1 from the Ni1/S1/S5/S6/S10 plane is 0.0089 (8) Å. The pyridine ring is approximately parallel to the $\text{Ni}(\text{dmit})_2$ plane [9.17 (17)°]. The dihedral angle between the phenyl and pyridine rings is 67.14 (13)°. There are two poles, composed of anions and cations, in the structure. Anions are grouped by weak $\text{Ni}\cdots\text{S}$ [3.694 (2) Å] and $\text{S}\cdots\text{S}$ [range 3.640 (2)–3.781 (2) Å] interactions. These groups, together with the cations, form layers through non-classical hydrogen bonds [3.489 (6) Å]. The $\text{S}\cdots\text{S}$, $\text{Ni}\cdots\text{S}$ and non-classical hydrogen

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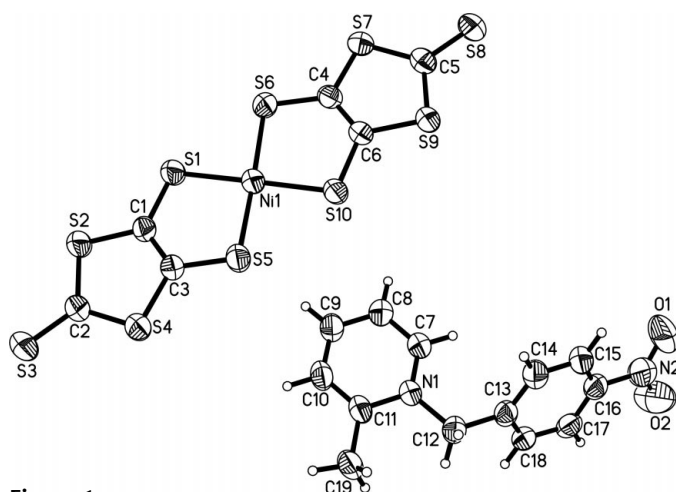


Figure 1
View of the asymmetric unit of (I), showing 50% displacement ellipsoids for non-H atoms.

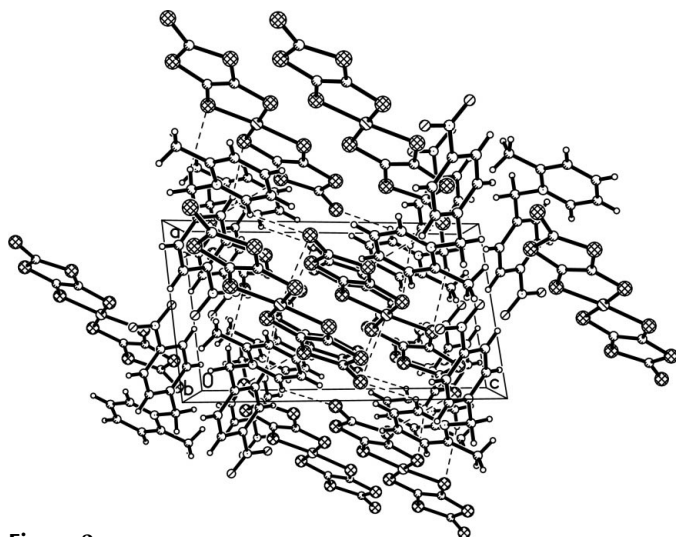


Figure 2
A view of the packing of (I), viewed along the *b* axis.

bonds link the molecules into quasi-three-dimensional layers (*viz.* the layers are finite), which stack to form the crystal structure (Fig. 2 and Fig. 3).

In another salt, [*N*-(4-Br-benzyl)-py][Ni(dmit)₂], (II), reported in our previous work (Tong *et al.*, 2002), the deviation of Ni^{III} from the Ni1/S1/S5/S6/S10 plane was 0.008 (7) Å. The pyridine ring was approximately parallel to the Ni(dmit)₂ plane [10.17 (18)°]. The dihedral angle between phenyl and pyridine rings was 81.30 (13)°. Some non-classical hydrogen bonds (C—H···S) were found [range 3.557 (5)–3.772 (5) Å]. The anions composed double-deck layers. In these layers, there were some weak Ni···Ni [3.5063 (9) Å] and S···S [3.4897 (17)–3.7625 (18) Å] interactions between layers and weak S···S [3.5840 (16)–3.7015 (15) Å] interactions between different ions in the same layer. The Ni···Ni, S···S and non-classical hydrogen bonds link the molecules into a three-dimensional framework. Thus, the coordination around the nickel is approximately planar in both salts.

Experimental

A solution of NaOMe dissolved in methanol was added to a methanol solution of 4,5-bis(benzoylthio)-1,3-dithiol-2-thione, dmit(COPH)₂. After stirring, a solution of NiCl₂·6H₂O was added. After further stirring, a solution of [*N*-(4-NO₂-benzyl)-1-CH₃-pyridine]Cl was added. The black precipitate was dissolved in acetone. As the solvent slowly evaporated, well-formed crystals of (I) appeared.

Crystal data

(C₁₃H₁₃N₂O₂)[Ni(C₃S₃)₂]
 $M_r = 680.70$
 Triclinic, $P\bar{1}$
 $a = 7.982$ (1) Å
 $b = 12.364$ (2) Å
 $c = 13.978$ (2) Å
 $\alpha = 105.43$ (1)°
 $\beta = 92.45$ (1)°
 $\gamma = 108.34$ (1)°
 $V = 1250.1$ (3) Å³

$Z = 2$
 $D_x = 1.808$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 885 reflections
 $\theta = 2.2$ – 23.4 °
 $\mu = 1.64$ mm⁻¹
 $T = 293$ (2) K
 Block, black
 0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.611$, $T_{\max} = 0.714$
 6270 measured reflections

4322 independent reflections
 2588 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$
 $\theta_{\max} = 25.0$ °
 $h = -7 \rightarrow 9$
 $k = -14 \rightarrow 14$
 $l = -12 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.102$
 $S = 1.01$
 4322 reflections
 302 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.47$ e Å⁻³
 $\Delta\rho_{\min} = -0.32$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1—S6	2.1526 (16)	C3—S5	1.709 (5)
Ni1—S5	2.1577 (16)	C3—S4	1.732 (5)
Ni1—S10	2.1599 (16)	C4—S6	1.708 (6)
Ni1—S1	2.1725 (16)	C4—S7	1.739 (5)
C1—S1	1.701 (5)	C5—S8	1.634 (6)
C1—S2	1.737 (5)	C5—S7	1.733 (6)
C2—S3	1.623 (6)	C5—S9	1.735 (5)
C2—S4	1.721 (6)	C6—S10	1.722 (5)
C2—S2	1.740 (5)	C6—S9	1.749 (5)
S6—Ni1—S5	175.72 (7)	S4—C2—S2	112.7 (3)
S6—Ni1—S10	93.35 (6)	S5—C3—S4	122.2 (3)
S5—Ni1—S10	87.64 (6)	C6—C4—S6	121.3 (4)
S6—Ni1—S1	86.27 (6)	C6—C4—S7	116.0 (4)
S5—Ni1—S1	92.95 (6)	S6—C4—S7	122.8 (3)
S10—Ni1—S1	176.97 (7)	S8—C5—S7	123.1 (3)
S1—C1—S2	123.2 (3)	S8—C5—S9	124.2 (3)
S3—C2—S4	124.5 (3)	S7—C5—S9	112.6 (3)
S3—C2—S2	122.8 (3)	S10—C6—S9	122.5 (3)

H atoms were positioned geometrically and refined with a riding model, with $U_{\text{iso}} = 1.5U_{\text{eq}}$ for methyl H atoms and $1.2U_{\text{eq}}$ for all other H atoms.

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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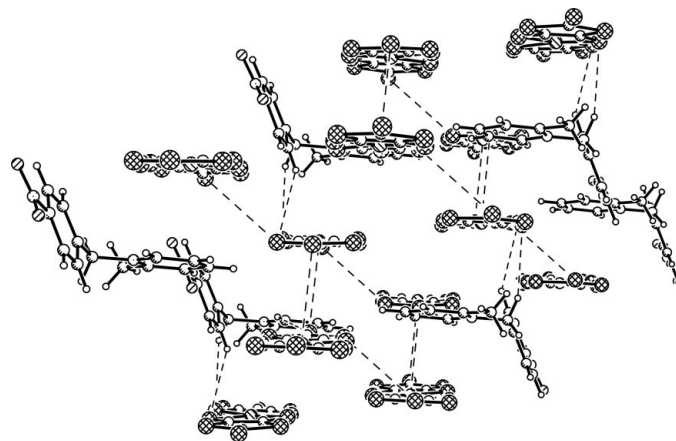


Figure 3
The packing of (I); weak interactions are indicated by dashed lines.

Xie, J.-L., Ren, X.-M., Song, Y., Zou, Y. & Meng, Q.-J. (2002). *J. Chem. Soc. Dalton Trans.* **14**, pp. 2868–2872.