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3-Methoxycarbonyl-1-methylpyridinium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(II)

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The crystal structure of the title complex, $(C_8H_{10}NO_2)[Ni(dmit)_2]$ (dmit is 4,5-dimercapto-1,3-dithiole-2-thione, $C_3H_2S_5$), is characterized by its two-dimensional S···S intermolecular interactions and can be described as an arrangement of quasi-planar $[Ni(dmit)_2]^-$ anions, separated by cation pairs. Centrosymmetric cation pairs are formed through weak C—H···O hydrogen bonds (H···O = 2.23 Å).

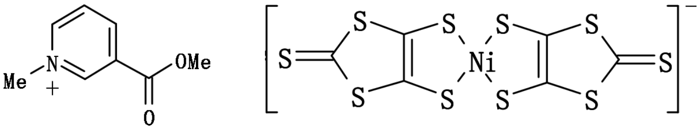
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.009 Å
R factor = 0.064
wR factor = 0.185
Data-to-parameter ratio = 19.1

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

Comment

Transition metal complexes of dmit (4,5-dimercapto-1,3-dithiole-2-thione) have received significant attention since the first open-shell molecular superconductor TTF$[Ni(dmit)_2]_2$ (TTF is tetrathiafulvalene; Bousseau *et al.*, 1986) and the first closed-shell molecular superconductor $[N(CH_3)_4][Ni(dmit)_2]_2$ (Kobayashi *et al.*, 1987) were reported. Although the closed-shell cations make no contribution to the conductivity, their sizes and shapes play a predominant role in influencing the crystal structures and consequently influencing the electronic properties. To date, most of the closed-shell cations are tetraalkylammonium; in addition, four planar aromatic cations have been reported (Miyazaki *et al.*, 1992; Veldhuizen *et al.*, 1997; Xu *et al.*, 2001), and less attention has been paid to planar cations. The synthesis of (guanidinium)$[Ni(dmit)_2]_2$ (Veldhuizen *et al.*, 1995) has aroused our interest in small planar cations, such as 3-methoxycarbonyl-1-methylpyridinium, because such cations may reduce the spacing between the conductive anions and enhance the overlap between molecular orbitals. In order to explore new dmit complexes and gain more insight into the structure–interaction of hydrogen-bond correlation (Hirose *et al.*, 2002), the title complex, (I), where a carboxyl group has been added to the pyridinium ion, has been synthesized and its structure is reported here.



(I)

The asymmetric unit of (I) contains one crystallographically independent $[Ni(dmit)_2]^-$ anion and one cation, as depicted in Fig. 1. The Ni—S distances range from 2.1571 (17) to 2.1704 (17) Å, with an average of 2.164 (9) Å, and the *cis*-S—Ni—S angles range from 85.30 (7) to 93.47 (7)°; the NiS_4 coordination thus adopts a slightly distorted square-planar configuration. Both of the coordinated $(C_3S_5)^{2-}$ anions are essentially planar, but the whole $[Ni(dmit)_2]^-$ anion is quasi-

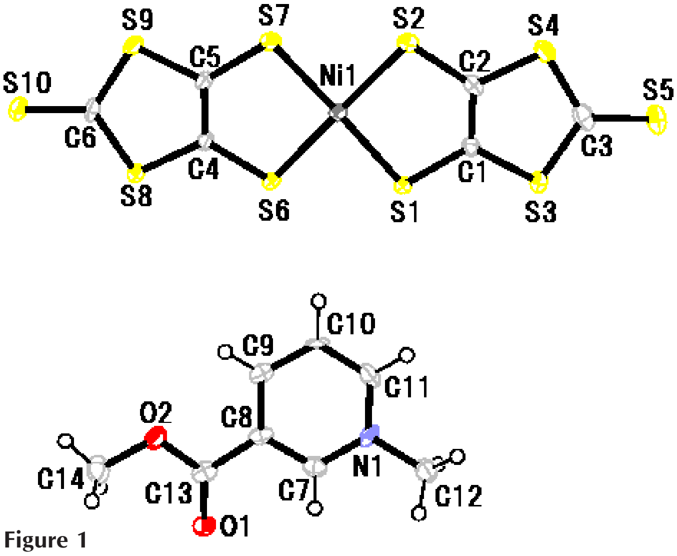


Figure 1
An *ORTEP*III view (Burnett & Johnson, 1996) of (I), showing 50% probability ellipsoids and the atom-numbering scheme.

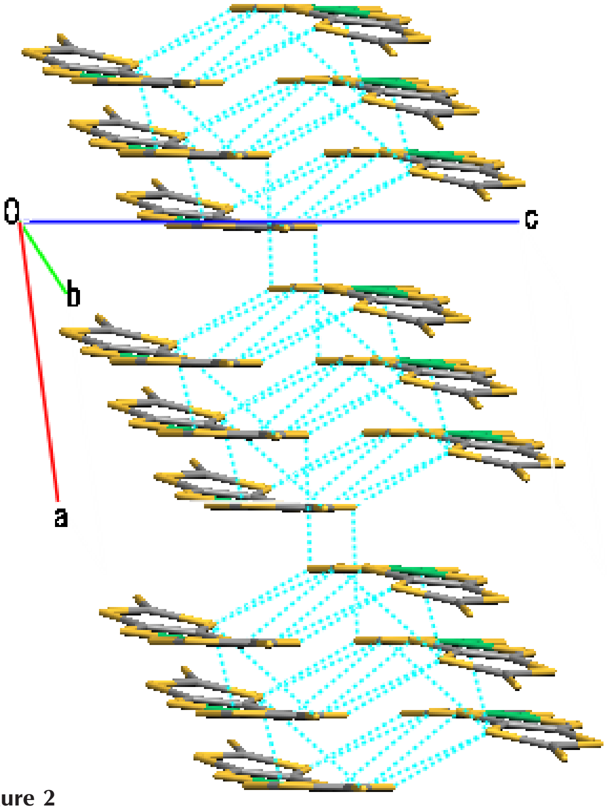


Figure 2
The packing of the $[Ni(dmit)_2]$ anions of (I) (*MERCURY*; Bruno *et al.*, 2002). Dashed lines indicate short S···S contacts.

planar, with Ni as a twist centre, as is shown by the dihedral angle of 10.3 (4)° between the planes of the two coordinated $(C_3S_5)^{2-}$ ligands.

In Fig. 2, S···S contacts shorter than 3.70 Å, the sum of van der Waals radii, are shown by dashed lines. The anions form a kind of zigzag chain *via* six intermolecular S···S interactions between neighbouring $[Ni(dmit)_2]^-$ anions (Table 1); in the crystal structure, the $[Ni(dmit)_2]^-$ anions do not form dimers. The cations form centrosymmetric pairs through weak C—H···O intermolecular hydrogen bonds; C7—H7···O1^{i}, with C···O = 3.112 (8) Å, H···O = 2.23 Å and C—H···O = 158° [symmetry code: (i) $-x$, $1 - y$, $-z$]. The aromatic rings of the cation pairs lie approximately in the *bc* plane (Fig. 3). Additionally, the structure of (I) exhibits a three-dimensional character, due to S8···S8 interactions and anion–cation Coulombic interactions. This kind of contact is not a strong interactions. In fact, the measured conductivity (by the two-probe alternating current method) of the crystal of (I) is about 1.8×10^{-8} S cm^{-1} at room temperature, which is not very high among the (cation)$[Ni(dmit)_2]$ type of 1:1 complexes.

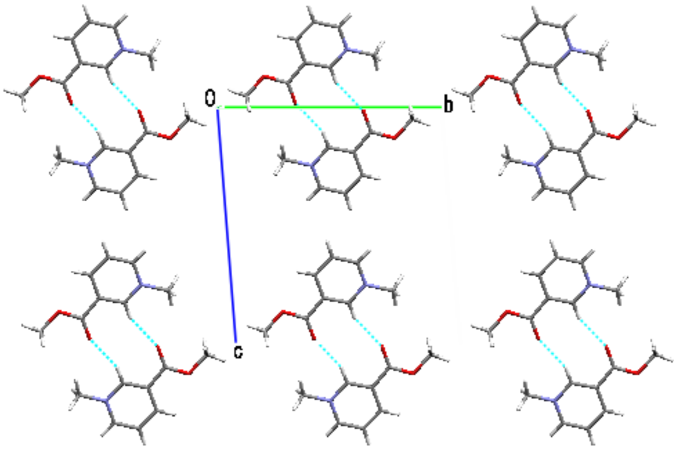


Figure 3
The packing of the cation-pair, viewed along the *a* axis (*MERCURY*; Bruno *et al.*, 2002)

Experimental

The title compound was synthesized by mixing methyl iodide (0.42 g, 3 mmol) with nicotinic acid (0.123 g, 1 mmol) in dimethylformamide (DMF, 10 ml), keeping the temperature at 357 K for several hours. The resulting solution was evaporated and washed with acetone until 3-methoxycarbonyl-1-methylpyridinium iodide precipitated. Dmit-$(COPh)_2$ (0.816 g, 2 mmol) was treated with an excess of sodium methoxide (0.5 *M*) in MeOH (20 ml) under air at room temperature with stirring. To the resulting red solution, a solution of $NiCl_2 \cdot 6H_2O$ (0.237 g, 1 mmol) in MeOH (20 ml) and 3-methoxycarbonyl-1-methylpyridinium iodide (1 mmol) in MeOH (20 ml) were added. The resulting precipitate was washed with MeOH. This precipitate was dissolved in acetone and oxidized using I_2 and NaI. Thin dark-green platelets of (I), one of which was used for the present structure determination, were obtained by slow evaporation. The compound was further purified by recrystallization from ethyl acetate in air.

Crystal data

$(C_8H_{10}NO_2)[Ni(C_3S_5)_2]$
M_r = 603.54
Triclinic, $P\bar{1}$
a = 7.2051 (19) Å
b = 12.139 (3) Å
c = 12.732 (3) Å
α = 84.319 (5)°
β = 82.170 (5)°
γ = 80.583 (5)°
V = 1085.0 (5) Å^3
Z = 2
D_x = 1.847 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2889 reflections
θ = 1.6–27.6°
μ = 1.87 mm^{-1}
T = 100 (2) K
Plate, dark green
0.19 × 0.12 × 0.02 mm

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Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: Gaussian (*XPREP* in *SAINT*; Bruker, 2001)
$T_{\min} = 0.693$, $T_{\max} = 0.967$
7209 measured reflections
4870 independent reflections
3426 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$
$\theta_{\max} = 27.6°$
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 15$
$l = -10 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.185$
$S = 1.07$
4870 reflections
255 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0961P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 1.68$ e Å^{-3}
$\Delta\rho_{\min} = -0.67$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—S6	2.1571 (17)	S9—C6	1.734 (6)
Ni1—S1	2.1610 (18)	S4—C3	1.724 (8)
Ni1—S7	2.1686 (19)	S4—C2	1.745 (6)
Ni1—S2	2.1704 (17)	S3—C1	1.739 (6)
S1—C1	1.718 (6)	S3—C3	1.743 (7)
S6—C4	1.714 (6)	S8—C6	1.719 (7)
S7—C5	1.729 (6)	S8—C4	1.745 (6)
S2—C2	1.726 (7)	S10—C6	1.649 (6)
S9—C5	1.733 (6)		
S6—Ni1—S1	85.30 (7)	S6—Ni1—S2	174.91 (7)
S6—Ni1—S7	93.31 (7)	S1—Ni1—S2	93.47 (7)
S1—Ni1—S7	177.60 (7)	S7—Ni1—S2	88.09 (7)
$\mathrm{S1\cdots S6^{i}}$	3.667 (2)	$\mathrm{S3\cdots S9^{ii}}$	3.415 (2)
$\mathrm{S3\cdots S6^{i}}$	3.600 (2)	$\mathrm{S3\cdots S10^{ii}}$	3.553 (2)
$\mathrm{S3\cdots S8^{i}}$	3.524 (2)	$\mathrm{S8\cdots S8^{iii}}$	3.614 (3)

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

All H atoms were positioned geometrically and allowed to ride on their attached atoms, with C—H distances in the range 0.93–0.96 Å and $U_{\rm iso} = 1.2U_{\rm eq}$(C) [or $1.5U_{\rm eq}$(C) for methyl groups]. In the final difference Fourier synthesis, four residual peaks in the range 0.97–1.68 e Å^{-3} were observed within 0.95 Å of the Ni atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *MERCURY* (Bruno *et al.*, (2002); software used to prepare material for publication: *SHELXL*97, *TEXSAN* (Molecular Structure Corporation, 2001), *KENX* (Sakai, 2002), *ORTEP*III and *MERCURY*.

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