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N-Ethylpyridinium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate

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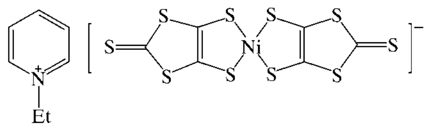
The title compound, $(C_7H_{10}N)[Ni(C_3S_5)_2]$ or (Etpy)[Ni(dmit)$_2$] (where Etpy is the *N*-ethylpyridinium cation, $C_7H_{10}N^+$, and dmit is the 2-thioxo-1,3-dithiole-4,5-dithiolate dianion, $C_3S_5^{2-}$), crystallizes in the $P\overline{1}$ space group with two molecules in the asymmetric unit. The $[Ni(dmit)_2]^-$ mono-anion has a planar D_{2h} conformation, with the central Ni atom and the four coordinated S atoms forming an NiS_4 square plane. The six-membered ring of the Etpy cation also shows good planarity, as expected. There are two main types of disorder in the two Etpy cations. Several short intermolecular interactions are present, such as S···S, Ni···S and Ni···Ni, which help to form the enhanced three-dimensional structure of the crystal.

Comment

Metal–dmit coordination anions, $[M(dmit)_2]^{x-}$ ($0 \leq x \leq 1$), as the conducting component in the $Z[M(dmit)_2]_n$ type of molecular conductors and superconductors, have attracted intense research interest over the past 20 years (Lindqvist *et al.*, 1979; Valade *et al.*, 1985; Bousseau *et al.*, 1986; Kobayashi *et al.*, 1987; Cornelissen *et al.*, 1991; Miyazaki *et al.*, 1992; Tajima *et al.*, 1993; Veldhuizen *et al.*, 1995; Fun *et al.*, 1996; Xu *et al.*, 2001). Various crystals, and consequently various conductivities, can be obtained by using different monocations in the 1:2 salts of $Z[Ni(dmit)_2]_2$, which form the most dominant group in the $Z[M(dmit)_2]_n$ family. From a synthesis point of view, conductive 1:2 $Z[Ni(dmit)_2]_2$ salts are prepared from the non-conductive precursor of 1:1 $Z[Ni(dmit)_2]$ salts. To date, most cations have been tetraalkylammonium, 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 *N*-ethylpyridinine, because such cations may reduce the spacing between the conductive anions and enhance the overlap between molecular orbitals. Thus, we synthesized the title 1:1 complex, (I), as a precursor of the 1:2 complex (Etpy)[Ni(dmit)$_2$]$_2$, which we failed to obtain, and report its structure in this paper. Surprisingly, even the 1:1 title complex shows considerable conductivity.



(I)

The unit cell of (I) contains two crystallographically independent $[Ni(dmit)_2]^-$ anions and two Etpy cations, as depicted in Figs. 1 and 2. Statistically speaking, there are no significant differences in the bond lengths and angles between the two $[Ni(dmit)_2]^-$ anions, except that the planarity of $[Ni2(dmit)_2]^-$ is more perfect than that of $[Ni1(dmit)_2]^-$. Both of the $[Ni(dmit)_2]^-$ anions have a D_{2h} symmetrical conformation and exhibit perfect planarity, with maximum deviations from the least-squares plane of 0.078 (1) Å for atom S10 in $[Ni1(dmit)_2]^-$ and 0.055 (1) Å for atom S18 in $[Ni2(dmit)_2]^-$. The NiS_4 core adopts a slightly distorted square-planar conformation. The Ni—S bond lengths range from 2.1535 (13) to 2.1751 (13) Å, with an average of 2.1612 (13) Å, and the S—Ni—S angles range from 86.65 (5) to 93.09 (5)° (Table 1). The Etpy ring is also planar, as expected. There are two types of disorder in the two Etpy cations. One type affects all four C atoms (C22, C23, C24 and C25) in one Etpy ring, with occupancies of 0.55 (2) and 0.45 (2), and the other affects atom C14 in the ethyl group of another Etpy cation, with occupancies of 0.648 (19) and 0.352 (19).

There are many S···S, Ni···S and Ni···Ni interactions between neighbouring molecules of (I) (Figs. 2 and 3). Table 2 lists all the intermolecular S···S contacts shorter than 3.60 Å (the sum of the van der Waals radii), Ni···S contacts shorter than 4.10 Å and Ni···Ni contacts shorter than 4.60 Å. The shortest intermolecular S···S contact is 3.383 (2) Å, between atoms S17 and S17^{iv} [symmetry code: (iv) $1-x, 1-y, 1-z$],

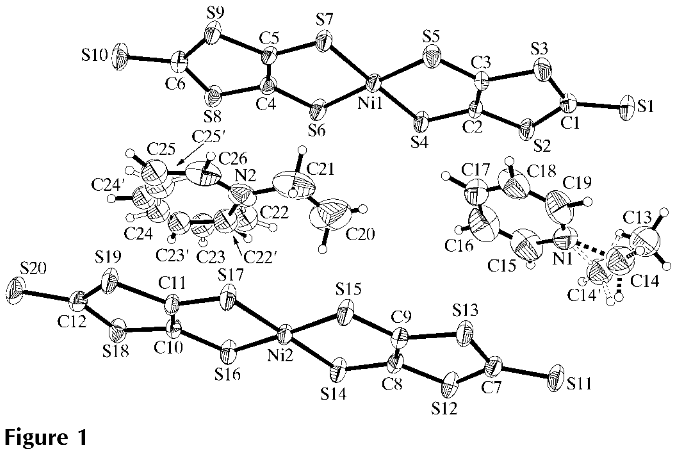


Figure 1
A view of the two independent cations and anions of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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which is shorter than the shortest value reported in the literature to date (Cornelissen *et al.*, 1991).

Referring to Figs. 2 and 3 and to Table 2, the anions of (I) form weak dimers *via* Ni···S and Ni···Ni interactions. The angle between the planes of two independent anions is 2.99 (4)°, showing the basic parallel arrangement of the two anions; the two long axes of the two planar anions are also parallel. In fact, all the planar $[Ni(dmit)_2]^-$ anions are parallel to each other. The anions form a kind of zigzag chain *via* five pairs of strong intermolecular S···S interactions between neighbouring $[Ni(dmit)_2]^-$ anions. Thus, (I) shows the typical characteristic of a one-dimensional structure required for conductivity.

Additionally, the structure of (I) exhibits a slight two- or three-dimensional character, due to Ni···Ni dimer interactions, terminal S···S interactions and anion–cation coulombic interactions. The Etpy cations are located between the anionic zigzag chains. This kind of crystal, with strong intermolecular interactions, may have a high conductivity. In fact, the measured conductivity (by the two-probe contact method) of the crystal of (I) is 5×10^{-7} S cm^{-1} at room temperature, which is quite high among the $Z[M(dmit)_2]$ type of 1:1 complexes.

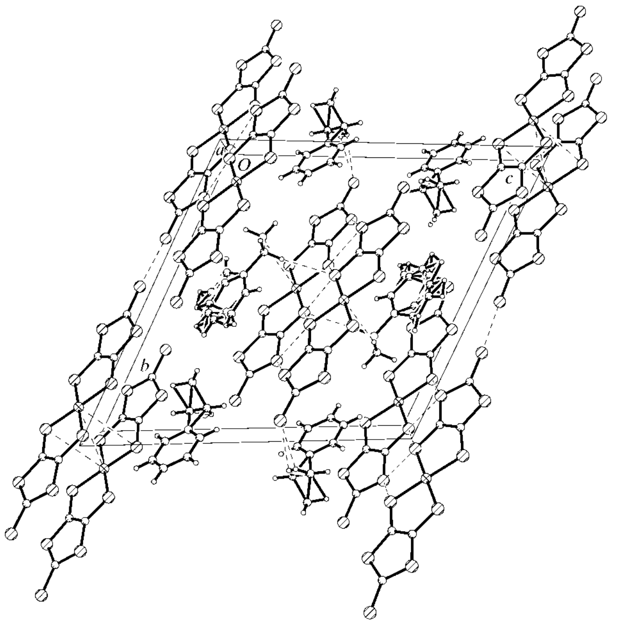

Figure 2
The crystal packing of (I), viewed along the *a* axis.

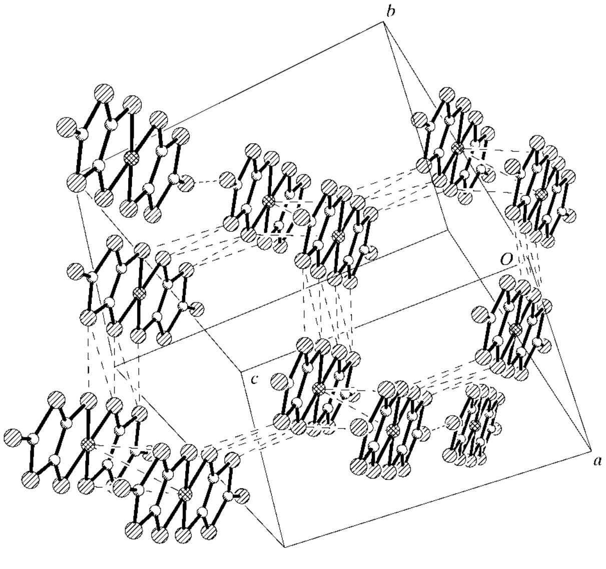

Figure 3
The packing of the $[Ni(dmit)_2]^-$ anion of (I).

Experimental

The title crystal was synthesized by WX. Ethyl iodide (15 ml) was mixed with pyridine (24 ml) and then kept at 339–341 K for several hours. The resulting solution was washed with a large excess of petroleum ether until white *N*-ethylpyridine iodide precipitated. $Dmit(COPh)_2$ (0.816 g, 2 mmol) was treated with an excess of sodium methylate (0.5*M*) in MeOH (20 ml) under nitrogen at room temperature with stirring. To the resulting red solution, solutions of $NiCl_2 \cdot 6H_2O$ (0.237 g, 1 mmol) in MeOH (20 ml) and *N*-ethylpyridine iodide (0.550 g, 2.4 mmol) in MeOH (20 ml) were added. The resulting precipitate was washed with MeOH (yield 0.555 g). This precipitate was then dissolved in acetone and oxidated using I_2/NaI. Thick black platelets of (I), one of which was used for the present structure determination, were obtained from the filtrate by slow evaporation (m.p. 470 K). The compound was further purified by recrystallization from acetone in air.

Crystal data

$(C_7H_{10}N)[Ni(C_3S_5)_2]$
$M_r = 559.61$
Triclinic, $P\bar{1}$
$a = 8.7825$ (8) Å
$b = 16.209$ (2) Å
$c = 16.7077$ (16) Å
$\alpha = 112.555$ (9)°
$\beta = 104.477$ (7)°
$\gamma = 95.876$ (10)°
$V = 2073.8$ (4) Å^3
$Z = 4$
$D_x = 1.792$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 36 reflections
$\theta = 5.3$–12.4°
$\mu = 1.94$ mm^{-1}
$T = 293$ (2) K
Prism, black
0.24 × 0.22 × 0.20 mm

Data collection

Bruker *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XSCANS*; Siemens, 1996)
$T_{min} = 0.566$, $T_{max} = 0.678$
8565 measured reflections
7056 independent reflections
4722 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 25°$
$h = -1 \rightarrow 10$
$k = -17 \rightarrow 17$
$l = -19 \rightarrow 19$
3 standard reflections every 97 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.118$
$S = 0.95$
7056 reflections
449 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 2.0853P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Extinction correction: *SHELXTL* (Bruker, 1997)
Extinction coefficient: 0.00173 (19)

Table 1
Selected geometric parameters (Å, °).

Ni1—S7	2.1540 (13)	Ni2—S17	2.1535 (13)
Ni1—S4	2.1567 (13)	Ni2—S14	2.1542 (13)
Ni1—S5	2.1612 (13)	Ni2—S16	2.1657 (13)
Ni1—S6	2.1751 (13)	Ni2—S15	2.1693 (13)
S7—Ni1—S4	179.17 (5)	S17—Ni2—S14	179.33 (6)
S7—Ni1—S5	86.65 (5)	S17—Ni2—S16	92.55 (5)
S4—Ni1—S5	92.63 (5)	S14—Ni2—S16	87.66 (5)
S7—Ni1—S6	93.09 (5)	S17—Ni2—S15	87.32 (5)
S4—Ni1—S6	87.63 (5)	S14—Ni2—S15	92.50 (5)
S5—Ni1—S6	178.32 (6)	S16—Ni2—S15	177.97 (6)

Table 2
Intermolecular S···S, Ni···S and Ni···Ni contacts (Å) shorter than the sum of the van der Waals radii.

S1···S10$^{\text{i}}$	3.520 (3)	S15···S17$^{\text{iv}}$	3.4566 (19)
S2···S4$^{\text{ii}}$	3.439 (2)	S15···S19$^{\text{iv}}$	3.450 (2)
S4···S4$^{\text{ii}}$	3.5209 (19)	S17···S17$^{\text{iv}}$	3.383 (2)
S7···S12$^{\text{iii}}$	3.5195 (19)	Ni1···S5$^{\text{v}}$	3.7586 (15)
S7···S14$^{\text{iii}}$	3.582 (2)	Ni2···S14$^{\text{vi}}$	3.6565 (15)
S9···S14$^{\text{iii}}$	3.4014 (19)	Ni1···Ni1$^{\text{v}}$	3.9778 (10)
S9···S16$^{\text{iii}}$	3.4802 (19)	Ni2···Ni2$^{\text{vi}}$	3.9768 (9)
S11···S20$^{\text{i}}$	3.467 (2)		

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

After checking their presence in the difference map, all H atoms were fixed geometrically and allowed to ride on their attached atoms, with C—H distances in the range 0.93–0.97 Å and $U_{\rm iso}$(H) values equal to $1.2U_{\rm eq}$(C).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1142). Services for accessing these data are described at the back of the journal.

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