metal-organic papers

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.008 Å
R factor = 0.040
wR factor = 0.136
Data-to-parameter ratio = 16.6

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

Benzyltrimethylammonium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(III)

The crystal structure of the title complex, $(C_{10}H_{16}N)$-$[Ni(C_3S_5)_2]$, is characterized by its three-dimensional weak $S\cdots S$ intermolecular interactions and can be described as an arrangement of quasi-planar $[Ni(dmit)_2]^-$ anions, separated by closed-shell (benzyltrimethylammonium) cations.

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$[Ni(dmit)_2]_2$ (Bousseau *et al.*, 1986) and the first closed-shell molecular superconductor $[N(CH_3)_4][Ni(dmit)_2]_2$ (Kobayashi *et al.*, 1987) were synthesized. 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. So far, most of the closed-shell cations are tetraalkyl-ammonium; in addition, four planar aromatic cations were reported (Miyazaki *et al.*, 1992; Veldhuizen *et al.*, 1997; Xu *et al.*, 2001). In order to explore new dmit complexes and gain more insight into the structure–conductivity correlations, the title complex, (I), substituting an aromatic ring for an H atom in the Me_4N^+ cation, has been synthesized and its structure reported here.

(I)
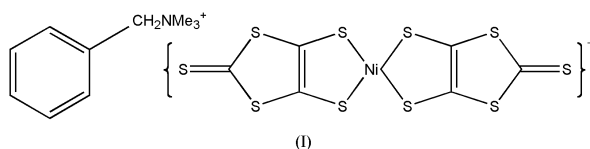
The asymmetric unit of (I) contains one crystallographically independent $[Ni(dmit)_2]^-$ anion and one cation, as depicted in Fig. 1. The Ni—S bond distances range from 2.1534 (13) to 2.1675 (14) Å, with an average of 2.1604 (13) Å, and the S—Ni—S angles range from 85.70 (5) to 93.06 (5)°; the NiS_4 coordination polyhedron 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-planar, with Ni as a twist centre, as is shown by the dihedral angle of 4.7 (3)° between the planes of the two coordinated $(C_3S_5)^{2-}$ ligands and the relatively large deviations from the least-squares plane (17 atoms) by S7 and S5, *viz*. −0.117 (1) and 0.105 (1) Å, respectively.

In Fig. 2, $S\cdots S$ contacts shorter than 3.70 Å, the sum of van der Waals radii, are shown by dashed lines and $Ni\cdots S$ contacts are shown by thin solid lines. The anions form weak face-to-face dimers, with $Ni\cdots Ni$, $Ni\cdots S6$ and $S5\cdots S8$ contacts between (shown in Table 2), and these dimers loosely stack to
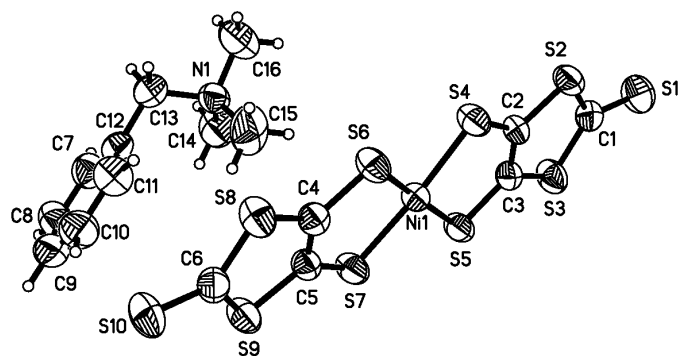
Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

form columns with lateral contacts (S2···S4). S···S contacts between terminal S atoms link neighboring columns, resulting in anion sheets parallel to the (010) plane. Along the b direction between neighboring sheets, the only short contact is S3···S9. Although the cations are located in the anionic network, three-dimensional interanionic contacts still remain. Nevertheless, this kind of three-dimensional contact is not strong. It is no surprise that the single-crystal conductivity is not very high, with a measured value of 3×10^{-7} S cm^{-1} at room temperature.

Experimental

Dmit(COPh)$_2$ (0.412 g, 1 mmol) was treated with an excess of sodium methoxide (9.0 mmol) in 20 ml MeOH under nitrogen, at room temperature with stirring. To the resulting dark-red solution, NiCl$_2$·6H$_2$O (0.118 g, 0.5 mmol) in 20 ml MeOH, and benzyltrimethylammonium bromide (0.232 g, 1 mmol) in 20 ml MeOH were added. The precipitate was washed with MeOH and dried in a vacuum desiccator. This product was recrystallized from acetone in air, to produce the title complex instead of bis(benzyltrimethylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(II), as could be deduced from its IR spectrum; 1348 [s, ν(C=C)], 1045 cm^{-1} [s, ν(C=S)].

Crystal data

(C$_{10}$H$_{16}$N)[Ni(C$_3$S$_5$)$_2$]	$D_x = 1.671$ Mg m^{-3}
$M_r = 601.66$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 38
$a = 10.3539$ (13) Å	reflections
$b = 17.0677$ (12) Å	$\theta = 5.0–12.4°$
$c = 13.5370$ (13) Å	$\mu = 1.69$ mm^{-1}
$\beta = 90.729$ (8)°	$T = 293$ (2) K
$V = 2392.0$ (4) Å^3	Plate, black
$Z = 4$	$0.34 \times 0.30 \times 0.08$ mm

Data collection

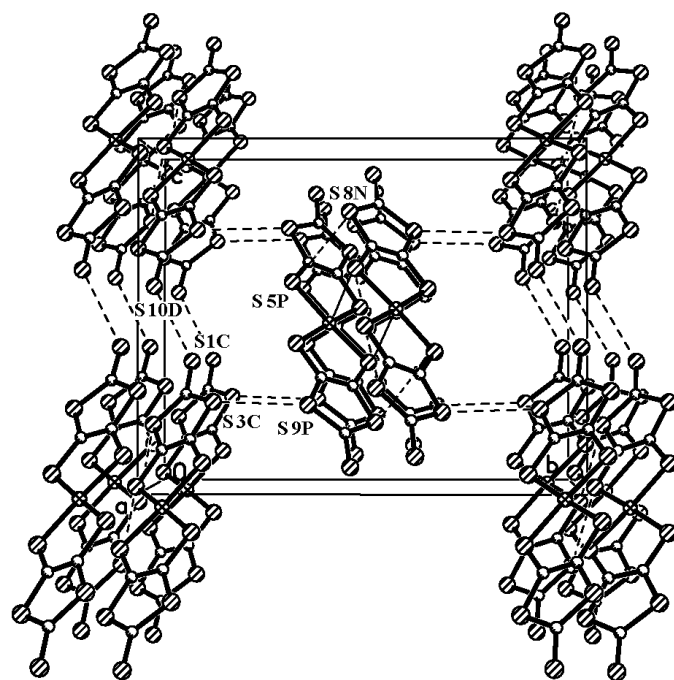|	
Bruker $P4$ diffractometer	$R_{int} = 0.030$
$\theta/2\theta$ scans	$\theta_{max} = 25.0°$
Absorption correction: ψ scan	$h = -1 \rightarrow 12$
($XSCANS$; Siemens, 1996)	$k = -1 \rightarrow 20$
$T_{min} = 0.572$, $T_{max} = 0.874$	$l = -16 \rightarrow 16$
5307 measured reflections	3 standard reflections
4204 independent reflections	every 97 reflections
2783 reflections with $I > 2\sigma(I)$	intensity decay: 2%

Figure 2
The packing of the anions, viewed along the a axis, showing weak three-dimensional intermolecular interactions. The suffix letters denote different anions.

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
$wR(F^2) = 0.136$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.80$	$(\Delta/\sigma)_{max} < 0.001$
4204 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
253 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—S4	2.1534 (13)	S5—C3	1.715 (5)
Ni1—S6	2.1564 (13)	S6—C4	1.712 (5)
Ni1—S7	2.1643 (13)	S7—C5	1.707 (4)
Ni1—S5	2.1675 (14)	S8—C6	1.736 (5)
S1—C1	1.645 (5)	S8—C4	1.736 (5)
S2—C1	1.707 (5)	S9—C6	1.728 (5)
S2—C2	1.744 (4)	S9—C5	1.747 (4)
S3—C3	1.739 (5)	S10—C6	1.633 (5)
S3—C1	1.743 (5)	C2—C3	1.356 (6)
S4—C2	1.716 (5)	C4—C5	1.364 (6)
S4—Ni1—S6	85.70 (5)	S2—C1—S3	113.1 (3)
S4—Ni1—S7	175.41 (6)	C3—C2—S4	121.8 (3)
S6—Ni1—S7	93.01 (5)	C3—C2—S2	116.1 (4)
S4—Ni1—S5	93.06 (5)	S4—C2—S2	122.1 (3)
S6—Ni1—S5	176.65 (6)	C2—C3—S5	120.8 (4)
S7—Ni1—S5	88.46 (5)	C2—C3—S3	115.7 (3)
C1—S2—C2	97.7 (2)	S5—C3—S3	123.5 (3)
C3—S3—C1	97.3 (2)	C5—C4—S6	121.2 (3)
C2—S4—Ni1	102.13 (16)	C5—C4—S8	116.4 (3)
C3—S5—Ni1	102.23 (16)	S6—C4—S8	122.4 (3)
C4—S6—Ni1	102.30 (15)	C4—C5—S7	121.1 (3)
C5—S7—Ni1	102.25 (16)	C4—C5—S9	115.0 (3)
C6—S8—C4	97.9 (2)	S7—C5—S9	123.8 (3)
C6—S9—C5	98.4 (2)	S10—C6—S9	123.4 (3)
S1—C1—S2	123.5 (3)	S10—C6—S8	124.4 (3)
S1—C1—S3	123.4 (3)	S9—C6—S8	112.2 (3)

Table 2
Intermolecular distances (Å).

S1···S10[i]	3.526 (2)	S5···S8[iv]	3.685 (2)
S2···S4[ii]	3.555 (2)	Ni1···S6[iv]	3.797 (2)
S3···S9[iii]	3.651 (2)	Ni1···Ni1[iv]	4.206 (2)

Symmetry codes: (i) $x - 1, y, 1 + z$; (ii) $-x, -y, 2 - z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $1 - x, -y, 2 - z$.

After checking their presence in a difference map, all H atoms were positioned geometrically and allowed to ride on their attached atoms, with C—H = 0.93–0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *XSCANS* (Bruker, 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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