3-Methyl-1-(1-phenylethyl)pyridinium bis(1,2-dicyanoethene-1,2-dithiolato)-nickelate(III)

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A new ion-pair complex, $(C_{14}H_{16}N)[Ni(C_4N_2S_2)_2]$ or $(PhEtPyMe)^+[Ni(mnt)_2]^-$ [$(PhEtPyMe)^+$ is 1-(1-phenylethyl)-3-methylpyridinium and mnt^{2-} is maleonitriledithiolate], crystallizing with two anions and two cations in the asymmetric unit, has been synthesized. The Ni^{III} atoms exhibit square-planar coordination geometry with four S atoms from two mnt^{2-} ligands. The cations and anions form well segregated columnar stacks along the a axis. Weak $Ni \cdots S$, $S \cdots S$ and $\pi-\pi$ interactions between anions mediate the formation of one-dimensional zigzag chains of Ni^{III} ions.

Comment

Square-planar $M(mnt)_2$ complexes are important compounds in the area of molecule-based magnetic materials (Robertson & Cronin, 2002). It has been shown that counter-cations may control the stacking pattern of the anions in these complexes and thus have a significant influence on intermolecular interactions and the resultant magnetic properties (Coomber *et al.*, 1996; Nakajima *et al.*, 2004; Uruichi *et al.*, 1998; Nishijo *et al.*, 2000). Some molecular materials with unusual magnetic properties were obtained when substituted benzylpyridinium cations were used as counterions for the $M(mnt)_2$ anion (Ni *et al.*, 2005, 2004; Xie *et al.*, 2002; Ren *et al.*, 2002). We are presently investigating the influence of substituents in the benzylpyridinium cation on the stacking pattern of $Ni(mnt)_2$ anions. Here, we report the synthesis and crystal structure of a new ion-pair complex in this series, $[PhEtPyMe]^+[Ni(mnt)_2]^-$, (I), where $(PhEtPyMe)^+$ is 1-(1-phenylethyl)-3-methyl-pyridinium and mnt^{2-} is maleonitriledithiolate.
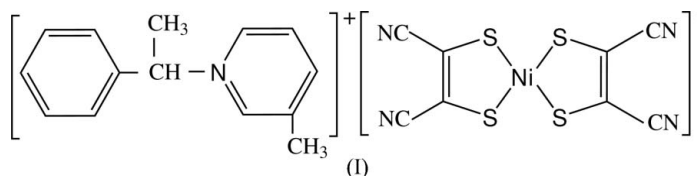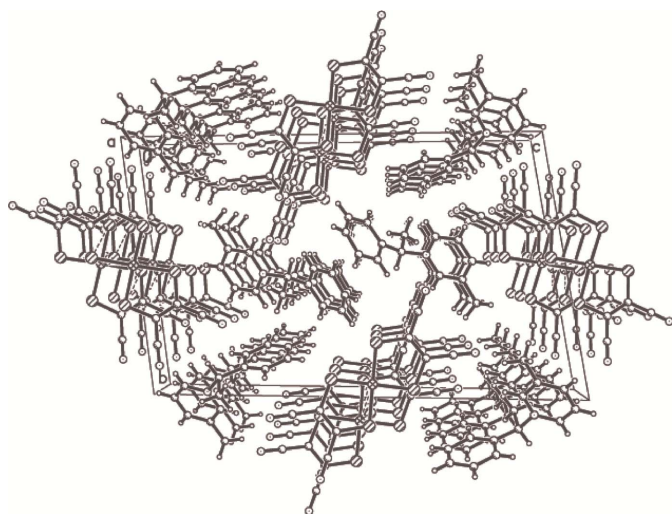

There are two symmetry-independent ion pairs in the asymmetric unit of (I) (Fig. 1). The Ni atoms of the $[Ni(mnt)_2]^-$ anions are coordinated by four S atoms and exhibit square-planar coordination geometry. The average Ni—S distances of 2.148 (2) and 2.140 (2) Å to Ni1 and Ni2, respectively, and S—Ni—S angles (Table 1) agree well with those found for other $[Ni(mnt)_2]^-$ anions (Ni *et al.*, 2005, 2004; Xie *et al.*, 2002; Ren *et al.*, 2002).

The cations adopt a conformation where the phenyl and pyridine rings are twisted relative to the reference plane defined by the atoms C23/C22/N9 or C37/C36/N10. The
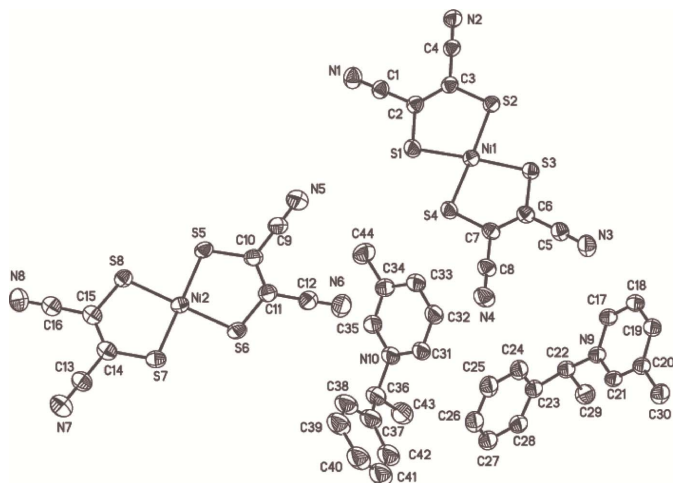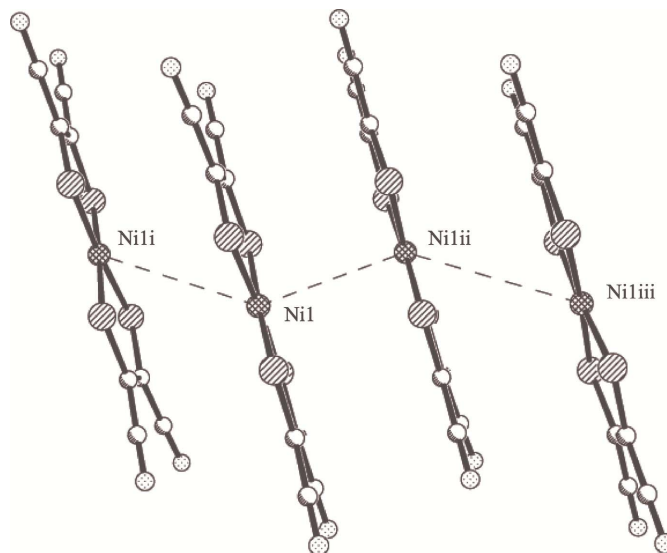
Figure 1
A view of the asymmetric unit of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

Figure 2
The crystal packing in (I).

Figure 3
A side view of one anion stack, showing the zigzag chain of Ni atoms [Symmetry codes: (i) $-x$, $1 - y$, $-z$; (ii) $1 - x$, $1 - y$, $-z$; (iii) $1 - x$, $1 - y$, $-z$.]

dihedral angles between the pyridinium and benzene rings and the corresponding reference plane are 53.5 (2) and 46.7 (2)°, respectively, for the cation containing atom N9, and 49.5 (2) and 56.4 (2)°, respectively, for the cation containing atom N10. Within the cations, the dihedral angles between the pyridine and benzene ring planes are 78.2 (2) and 82.3 (2)°, respectively.

The Ni(mnt)$_2^-$ anions and [PhEtPyMe]$^+$ cations are arranged into well segregated columnar stacks extending along the crystallographic a axis (Fig. 2). Within the stacks formed by symmetry-independent anions, there are weak Ni···S, S···S and π–π interactions. The Ni atoms are arranged into zigzag chains, with Ni···Ni distances of 3.948 (2) and 4.359 (2) Å in the anionic column containing Ni1 (Fig. 3), and of 4.032 (2) and 4.374 (2) Å in the anionic column containing Ni2. The cations form ribbons via C—H···π and π–π interactions running along the [011] direction. There are weak C—H···N interactions between the anions and cations stabilizing the crystal structure of (I).

Experimental

1-Bromoethylbenzene and 3-methylpyridine were purchased from Aldrich and used without further purification. 1-(1-Phenylethyl)-3-methylpyridinium bromide (PhEtPyMeBr) and disodium maleonitriledithiolate (Na$_2$mnt) were prepared according to published procedures (Bulgarevich *et al.*, 1994; Davison & Holm, 1967). Compound (I) was synthesized by a method analogous to that used for the preparation of [Bu$_4$N]$_2$[Ni(mnt)$_2$] (Davison & Holm, 1967). An acetone solution of I$_2$ was slowly added to an acetone solution of [PhEtPyMe]$_2$[Ni(mnt)$_2$] and the mixture was stirred for 12 h. Methanol was then added, and the mixture allowed to stand overnight; the black microcrystals that formed were filtered off, washed with methanol and dried in vacuum (yield 78%). Black block single crystals suitable for X-ray analysis were obtained by slow evaporation of an acetonitrile–propan-2-ol (1/1 v/v) solution at room temperature for about 2 weeks. Analysis, calculated for C$_{22}$H$_{16}$N$_5$NiS$_4$: C 49.18, H 3.00, N 13.03%; found: C 49.23, H 3.18, N 12.92%.

Crystal data

(C$_{14}$H$_{16}$N)[Ni(C$_4$N$_2$S$_2$)$_2$]	$V = 2413.5$ (11) Å^3
$M_r = 537.35$	$Z = 4$
Triclinic, $P\bar{1}$	$D_x = 1.479$ Mg m^{-3}
$a = 7.006$ (2) Å	Mo $K\alpha$ radiation
$b = 14.897$ (4) Å	$\mu = 1.17$ mm^{-1}
$c = 23.997$ (6) Å	$T = 293$ (2) K
$\alpha = 79.960$ (11)°	Block, black
$\beta = 81.661$ (10)°	$0.39 \times 0.31 \times 0.25$ mm
$\gamma = 80.280$ (11)°	

Data collection

Bruker SMART CCD area-detector diffractometer	11998 measured reflections
φ and ω scans	8337 independent reflections
Absorption correction: multi-scan	5250 reflections with $I > 2\sigma(I)$
(*SADABS*, Bruker, 2000)	$R_{int} = 0.036$
$T_{min} = 0.656$, $T_{max} = 0.748$	$\theta_{max} = 25.0°$

Refinement

Refinement on F^2		H-atom parameters constrained	
$R[F^2 > 2\sigma(F^2)] = 0.068$		$w = 1/[\sigma^2(F_o^2) + (0.08P)^2]$	
$wR(F^2) = 0.174$		where $P = (F_o^2 + 2F_c^2)/3$	
$S = 1.05$		$(\Delta/\sigma)_{max} = 0.008$	
8337 reflections		$\Delta\rho_{max} = 0.78$ e Å^{-3}	
581 parameters		$\Delta\rho_{min} = -0.64$ e Å^{-3}	

Table 1
Selected geometric parameters (Å, °).

Ni1—S1	2.1430 (18)	Ni2—S5	2.1367 (17)
Ni1—S4	2.1458 (16)	Ni2—S7	2.1369 (18)
Ni1—S3	2.1501 (18)	Ni2—S8	2.1400 (19)
Ni1—S2	2.1543 (16)	Ni2—S6	2.1468 (19)
S1—Ni1—S4	86.12 (6)	S5—Ni2—S7	178.32 (8)
S1—Ni1—S3	176.16 (7)	S5—Ni2—S8	87.33 (7)
S4—Ni1—S3	92.94 (6)	S7—Ni2—S8	92.33 (7)
S1—Ni1—S2	92.65 (7)	S5—Ni2—S6	92.09 (7)
S4—Ni1—S2	176.75 (7)	S7—Ni2—S6	88.22 (7)
S3—Ni1—S2	88.47 (6)	S8—Ni2—S6	178.88 (8)

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

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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