1-(2-Bromobenzyl)pyridinium bis(maleodinitriledithiolato)nickelate(III)

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In the title compound, $(C_{12}H_{11}BrN)[Ni(C_4N_2S_2)_2]$, completely segregated columnar stacks of anions and cations are observed. There are three symmetry-independent anions in the asymmetric unit (A, B and C), all of them essentially planar. Two types of anionic columns are both stacked along the b axis of the crystal; columns of the first type are made up entirely of one of the three independent anions (anion A) and have identical Ni···Ni distances of 4.1401 (10) Å, while columns of the second type are made up of alternating anions B and C and have slightly different, alternating Ni···Ni distances [4.1695 (11) and 4.0971 (11) Å]. The columns of Λ-shaped bromobenzylpyridinium cations show no π–π interactions within the stack; there are, however, short S···Br contacts between the anionic and cationic stacks.

## Comment

Several interesting physical phenomena, such as slow relaxation of magnetization and hysteresis effects not associated with three-dimensional order (Caneschi *et al.*, 2001), valence-ordering structure (Mitsumi *et al.*, 2002), spin-charge separation state (Lorenz *et al.*, 2002), and distinct magnetization plateaus (Wolf *et al.*, 2002), have been found in recent years for low-dimensional spin systems. Investigations of these phenomena have motivated corresponding theoretical research in this field (*Clay et al.*, 2003; Orignac & Citro, 2003).

(I)
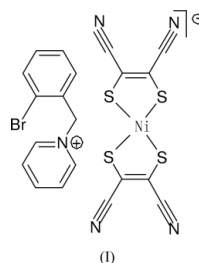
Our aim is to construct quasi-one-dimensional molecular magnetic materials involving $[M(\text{mnt})_2]^-$ anions ($M = \text{Ni}^{3+}$, Pd^{3+} or Pt^{3+}; mnt = maleodinitriledithiolate). Recently, we have developed a new class of salts, $[R\text{-BzPy}]^+[\text{Ni}(\text{mnt})_2]^-$, and found that these compounds stack into completely segregated anionic and cationic columns in the solid state. It turns out that the substituents on aromatic rings influence the stacking pattern of these salts in the solid state, thus affecting the magnetic properties of the materials (Ren *et al.*, 2002; Xie, Ren, Song, Zou & Meng, 2002; Xie, Ren, Song, Zhang *et al.*, 2002; Xie *et al.*, 2003). As part of investigating the relationships between the nature of the substituents, the stacking patterns of the compounds and their magnetic properties, we report here the crystal structure of 1-(2-bromo-
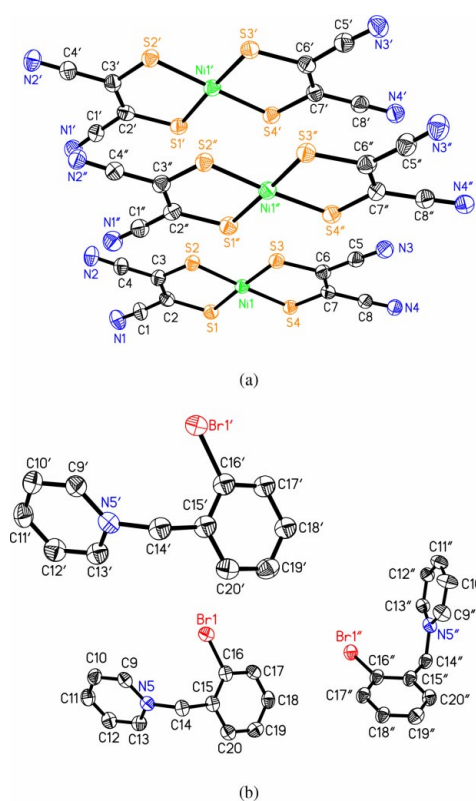
Figure 1
The anions (*a*) and cations (*b*) in the structure of (I), showing 30% probability displacement ellipsoids and the atomic labelling scheme. H atoms have been omitted.
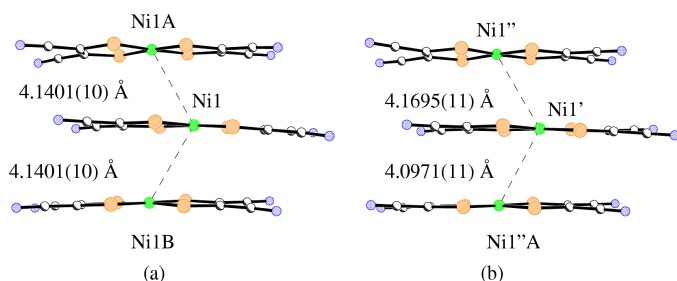
Figure 2
Two types of anionic columns: (*a*) built of anions *A* and (*b*) containing alternating anions *B* and *C*.

benzyl)pyridinium bis(1,2-dicyanoethene-1,2-dithiolato)-nickelate(III), (I), a new compound in this series.

There are three [Ni(mnt)$_2$]$^-$ anions and three 1-(2-bromo-benzyl)pyridinium cations in the asymmetric unit of (I) (Fig. 1); in the text below we refer to anions containing atoms Ni1, Ni1′, and Ni1″ as anions *A*, *B*, and *C*, respectively; similarly, cations containing atoms Br1, Br1′, and Br1″ will be referred to as cations *A*, *B*, and *C*. The Ni^{III} ions in all three independent anions exhibit square-planar coordination. The values of the Ni—S bond lengths and the S—Ni—S angles within the chelate rings in all three [Ni(mnt)$_2$]$^-$ moieties are close to each other and similar to those in previously reported related complexes (Ren *et al.*, 2001, 2002), the average values for bonds and angles being 2.1499 (14) Å and 83.83 (5)°, 2.1516 (14) Å and 83.72 (5)°, and 2.1493 (14) Å and 83.63 (5)°

for anions *A*, *B*, and *C*, respectively. The mean coordination planes of all three Ni atoms are approximately parallel, with a dihedral angle of 1.18 (3)° for the *A*/*B*, 2.58 (3)° for the *B*/*C* and 1.66 (3)° for the *A*/*C* planes.

The three symmetry-independent 1-(2-bromobenzyl)-pyridinium cations have Λ-shaped conformations with dihedral angles formed by the C14/C15/N5 plane with each of the benzene and pyridine rings being 76.6 (4) and 61.2 (3)°, 74.1 (4) and 60.2 (3)°, and 68.8 (4) and 49.0 (4)° for cations *A*, *B*, and *C* respectively.

There are two symmetry-independent anionic columns in the structure of (I), both of which are stacked along the *b* axis of the crystal (Fig. 2). Columns of the first type are built of anions, all of which are symmetry-related to anion *A*. All Ni···Ni distances between the neighbouring anions in these stacks are identical and equal to 4.1401 (10) Å. Columns of the second type are built of alternating anions *B* and *C*; therefore, there are two slightly different alternating Ni...Ni distances between the adjacent anions in these columns [4.1695 (11) and 4.0971 (11) Å].

The cationic columns show no signs of π–π stacking interactions, which is different from some of the earlier reported structures in this series (Ren *et al.*, 2002). The most significant contacts involving cations are the inter-columnar interactions between the bromine substituents of the cations and the S atoms of the anions [3.6504 (14) Å for Br1···S2^i, 3.5857 (17) Å for Br1···S4^{ii}, 3.5853 (17) Å for Br1′···S2″^{iii} and 3.7514 (14) Å for Br1″···S4″; symmetry codes: (i) *x*, *y* − 1, *z*; (ii) 1 − *x*, *y* − $\frac{1}{2}$, $\frac{3}{2}$ − *z*; (iii) 1 + *x*, *y*, *z*; see Fig. 3].

Experimental

Disodium maleodinitriledithiolate (Na$_2$mnt) was prepared following the procedure available in the literature (Davison & Holm, 1967). For the preparation of 1-(2-bromobenzyl)pyridinium bromide, mixtures of 500.2 mg (2.0 mmol) of 2-bromobenzyl bromide and 237.5 mg (3.0 mmol) of pyridine in 50 ml of acetone were refluxed for about 4 h. The product, formed as a white powder, was filtered, and washed in turn with acetone and diethyl ether, then dried *in vacuo* (yield > 85%). 237.8 mg (1.0 mmol) of NiCl$_2$·6H$_2$O, 375.1 mg (2.0 mmol) of Na$_2$mnt and 658.1 mg (2.0 mmol) of 1-(2-bromobenzyl)pyridinium bromide were directly combined in water at room temperature, the red precipitated product was filtered off, washed with water and then dissolved in about 10 ml of MeCN. 260.0 mg (1.0 mmol) of iodine was added to this solution with stirring. Three times the resulting volume of MeOH was then added and the mixture allowed to stand overnight. The resulting microcrystals were filtered off, washed with MeOH and dried *in vacuo*. Single crystals of (I) suitable for a structural study were obtained by diffusing diethyl ether into MeCN solutions of (I).

Crystal data

(C$_{12}$H$_{11}$BrN)[Ni(C$_4$N$_2$S$_2$)$_2$]	$D_x = 1.705$ Mg m^{-3}
$M_r = 588.20$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 863
$a = 31.400$ (6) Å	reflections
$b = 6.9700$ (14) Å	$\theta = 2.8$–22.3°
$c = 33.760$ (7) Å	$\mu = 2.97$ mm^{-1}
$\beta = 111.50$ (3)°	$T = 293$ (2) K
$V = 6875$ (2) Å^3	Block, brown
$Z = 12$	0.3 × 0.2 × 0.2 mm

Data collection

Bruker SMART CCD area-detector diffractometer	12054 independent reflections
φ and ω scans	7095 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.036$
($SADABS$; Bruker, 2000)	$\theta_{max} = 25.0°$
$T_{min} = 0.50$, $T_{max} = 0.55$	$h = -37 \rightarrow 34$
33754 measured reflections	$k = -8 \rightarrow 7$
	$l = -30 \rightarrow 40$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.047$	$w = 1/[\sigma^2(F_o^2) + (0.055P)^2]$
$wR(F^2) = 0.120$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
12054 reflections	$\Delta\rho_{max} = 0.55$ e Å^{-3}
838 parameters	$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—S1	2.1666 (13)	Ni1′—S3′	2.1682 (14)
Ni1—S2	2.1350 (15)	Ni1′—S4′	2.1310 (15)
Ni1—S3	2.1767 (14)	Ni1″—S1″	2.1681 (13)
Ni1—S4	2.1211 (14)	Ni1″—S2″	2.1275 (15)
Ni1′—S1′	2.1501 (13)	Ni1″—S3″	2.1450 (13)
Ni1′—S2′	2.1571 (15)	Ni1″—S4″	2.1565 (15)
S4—Ni1—S2	176.51 (5)	S4′—Ni1′—S3′	83.73 (5)
S4—Ni1—S1	94.71 (5)	S1′—Ni1′—S3′	176.57 (5)
S2—Ni1—S1	84.01 (5)	S2′—Ni1′—S3′	98.44 (5)
S4—Ni1—S3	83.63 (5)	S2″—Ni1″—S3″	93.82 (5)
S2—Ni1—S3	97.71 (5)	S2″—Ni1″—S4″	176.36 (5)
S1—Ni1—S3	177.90 (5)	S3″—Ni1″—S4″	83.64 (5)
S4′—Ni1′—S1′	94.31 (5)	S2″—Ni1″—S1″	83.61 (5)
S4′—Ni1′—S2′	176.06 (5)	S3″—Ni1″—S1″	177.05 (5)
S1′—Ni1′—S2′	83.69 (5)	S4″—Ni1″—S1″	98.98 (5)

The H atoms were placed in geometrically calculated positions (C—H = 0.93 and 0.97 Å) and included in the refinement in riding model approximation, with $U_{iso} = 1.2\ U_{eq}$ of the carrier atom.

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*.

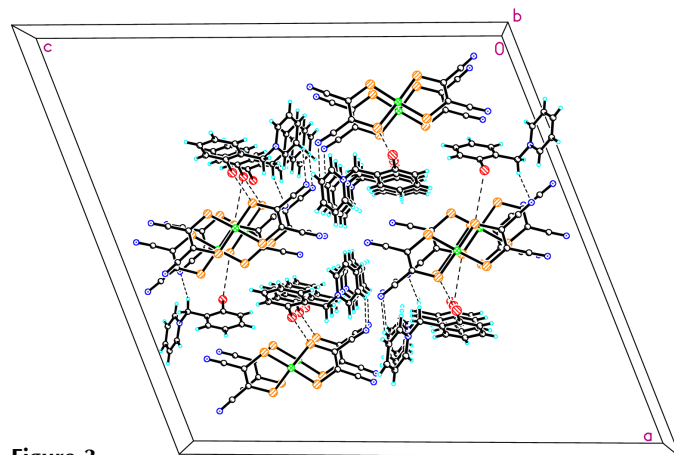**Figure 3**
Packing diagram for (I), showing the completely segregated cationic and anionic columns stacked along the *b* axis of the crystal.

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