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Bis[1-(3,5-dibromobenzyl)pyridinium] bis(1,2-dicyanoethene-1,2-dithiolato-κ^2S,S')nickelate(II)

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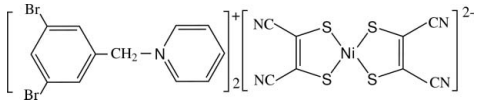
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.009 Å; R factor = 0.055; wR factor = 0.117; data-to-parameter ratio = 15.5.

In the title compound, $(C_{12}H_{10}Br_2N)_2[Ni(C_4N_2S_2)_2]$, the Ni^{II} atom of the anion lies on an inversion centre and exhibits a square-planar coordination geometry. The benzene and pyridine rings of the cation make a dihedral angle of 74.6 (3)°. The cations (*C*1 and *C*2) and anions (*A*) are arranged in a ...*C*1*C*2A*C*1*C*2A*C*1*C*2... pattern along the [$\bar{1}$10] direction and are linked by C—H···S hydrogen bonds and π–π stacking interactions involving the benzene ring [centroid–centroid separation = 3.778 (3) Å].

Related literature

For related literature, see: Liu & Ni (2006*a*,*b*); Ni *et al.* (2005); Ren *et al.* (2002); Xie *et al.* (2002).



Experimental

Crystal data

$(C_{12}H_{10}Br_2N)_2[Ni(C_4N_2S_2)_2]$
M_r = 995.13
Triclinic, $P\bar{1}$
a = 8.843 (3) Å
b = 9.415 (3) Å
c = 10.861 (4) Å
α = 77.701 (5)°
β = 78.427 (6)°
γ = 84.221 (5)°
V = 864.0 (5) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 5.46 mm^{-1}
T = 291 (2) K
0.35 × 0.30 × 0.21 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.165, T_{max} = 0.323
4584 measured reflections
3309 independent reflections
2482 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.117
S = 0.99
3309 reflections
214 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.96 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16···S1^{i}	0.93	2.75	3.591 (5)	151

Symmetry code: (i) $-x+1, -y+2, -z+1$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; 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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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2505).

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supplementary materials

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Bis[1-(3,5-dibromobenzyl)pyridinium] bis(1,2-dicyanoethene-1,2-dithiolato-κ^2S,S')nickelate(II)

Q.-B. Liao, M.-G. Liu and C.-L. Ni

Comment

Recently, some substituted benzylpyridinium cations have been introduced into the $Ni(mnt)_2$ system (mnt is maleonitriledithiolate) in order to obtain some $Ni(mnt)_2$-based molecular solids showing unusual magnetic properties (Ni *et al.*, 2005; Xie *et al.*, 2002; Ren *et al.*, 2002). We report here the crystal structure of the title compound, in which 1-(3,5-dibromobenzyl)pyridinium functions as a counterion of $Ni(mnt)_2$ anion.

As shown in Fig.1, the asymmetric unit of the title compound consists of one $C_{12}H_{10}Br_2N^+$ cation and one-half of a $[Ni(C_4N_2S_2)_2]^{2-}$ anion. The Ni^{II} ion lies on an inversion centre and exhibits a square-planar coordination geometry. The CN groups of the $[Ni(mnt)_2]^{2-}$ unit are slightly tipped out of the C1/S1/Ni1/$S2^i$/$C3^i$ plane, and the deviations from the plane are −0.116 (6) Å for N1 and 0.009 (6) Å for $N2^i$ [symmetry code: (i) $1-x, 2-y, 1-z$]. The benzene and pyridine rings of the $C_{12}H_{10}Br_2N^+$ unit form a dihedral angle of 74.6 (3)°. Atoms Br1 and Br2 deviate from the plane of the benzene ring by 0.038 (1) and 0.077 (1) Å, respectively.

Two $C_{12}H_{10}Br_2N^+$ units are linked to a $[Ni(C_4N_2S_2)_2]^{2-}$ unit through C16—H16···S1 hydrogen bonds (Table 1). The adjacent hydrogen-bonded units are cross-linked *via* weak π-π interactions between the benzene ring of the cation at (x, y, z) and ($2-x$, $1-y$, $1-z$), with a centroid-centroid separation of 3.778 (3) Å. The cations and anions involved in the above interactions are arranged alternately along the [$\bar{1}$ 1 0] direction (Fig. 2).

Experimental

The title compound was prepared by the direct reaction of $NiCl_2{\cdot}6H_2O$ (0.24 g, 1.0 mmol), disodium maleonitriledithiolate (0.37 g, 2.0 mmol) and 1-(3,5-dibromobenzyl)pyridinium bromide (0.85 g, 2.1 mmol) in water (50 ml). Red block-shaped single crystals were obtained by slow evaporation of a CH_3CN-i-PrOH (1:1) solution at room temperature over three weeks.

Refinement

All H atoms were placed in geometrically calculated positions (C—H = 0.93–0.97 Å) and treated as riding, with U_{iso} = 1.2 U_{eq}(parent atom).

Figures

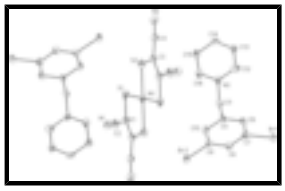

Fig. 1. The cation and anion of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted. Unlabelled atoms are related to the labelled atoms by the symmetry operation (1 − *x*, 2 − *y*, 1 − *z*).

Fig. 2. The packing of the title compound, showing a column of anions and cations.

Bis[1-(3,5-dibromobenzyl)pyridinium] bis(1,2-dicyanoethene-1,2-dithiolato-κ^2*S*,*S*')nickelate(II)

Crystal data

$(C_{12}H_{10}Br_2N)_2[Ni(C_4N_2S_2)_2]$	$Z = 1$
$M_r = 995.13$	$F_{000} = 486$
Triclinic, $P\overline{1}$	$D_x = 1.913$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 8.843$ (3) Å	Cell parameters from 904 reflections
$b = 9.415$ (3) Å	$\theta = 2.7$–27.9º
$c = 10.861$ (4) Å	$\mu = 5.46$ mm^{-1}
$\alpha = 77.701$ (5)º	$T = 291$ (2) K
$\beta = 78.427$ (6)º	Block, red
$\gamma = 84.221$ (5)º	0.35 × 0.30 × 0.21 mm
$V = 864.0$ (5) Å^3	

Data collection

Bruker SMART APEX CCD diffractometer	3309 independent reflections
Radiation source: fine-focus sealed tube	2482 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.033$
$T = 291(2)$ K	$\theta_{max} = 26.0$º
φ and ω scans	$\theta_{min} = 2.2$º
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -5 \rightarrow 10$
$T_{min} = 0.165$, $T_{max} = 0.323$	$k = -11 \rightarrow 11$
4584 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.055$	H-atom parameters constrained

$wR(F^2) = 0.117$	$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.99P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{max} = 0.001$
3309 reflections	$\Delta\rho_{max} = 0.59$ e Å^{-3}
214 parameters	$\Delta\rho_{min} = -0.96$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	1.36658 (7)	0.41523 (7)	0.40770 (6)	0.03356 (18)
Br2	0.95637 (7)	0.72824 (8)	0.73580 (6)	0.04073 (19)
C1	0.4467 (7)	0.8563 (6)	0.7832 (6)	0.0340 (13)
C2	0.3762 (8)	0.7687 (7)	0.9091 (6)	0.0384 (15)
C3	0.4290 (7)	1.0569 (7)	0.2308 (6)	0.0323 (13)
C4	0.3562 (7)	1.0604 (7)	0.1245 (6)	0.0349 (13)
C5	1.0417 (7)	0.7617 (7)	0.3449 (6)	0.0317 (13)
C6	1.1611 (7)	0.6488 (6)	0.3263 (5)	0.0298 (12)
H6	1.2019	0.6303	0.2450	0.036*
C7	1.2118 (7)	0.5708 (7)	0.4307 (6)	0.0397 (15)
C8	1.1544 (7)	0.5909 (7)	0.5510 (5)	0.0340 (13)
H8	1.1890	0.5320	0.6214	0.041*
C9	1.0407 (7)	0.7037 (7)	0.5658 (6)	0.0339 (13)
C10	0.9816 (7)	0.7898 (7)	0.4667 (6)	0.0358 (14)
H10	0.9052	0.8634	0.4797	0.043*
C11	0.9801 (7)	0.8528 (6)	0.2317 (5)	0.0330 (13)
H11A	1.0644	0.8774	0.1600	0.040*
H11B	0.9290	0.9426	0.2536	0.040*
C12	0.9136 (8)	0.6867 (7)	0.1004 (6)	0.0404 (15)
H12	1.0134	0.6912	0.0526	0.048*
C13	0.8089 (7)	0.6021 (7)	0.0802 (6)	0.0362 (14)
H13	0.8414	0.5365	0.0258	0.043*
C14	0.6588 (7)	0.6107 (6)	0.1371 (6)	0.0335 (13)
H14	0.5880	0.5571	0.1165	0.040*
C15	0.6095 (7)	0.7000 (7)	0.2271 (6)	0.0361 (14)
H15	0.5077	0.7051	0.2702	0.043*
C16	0.7215 (7)	0.7806 (6)	0.2484 (6)	0.0356 (14)
H16	0.6931	0.8472	0.3023	0.043*
N1	0.3176 (7)	0.7000 (6)	0.9957 (5)	0.0456 (14)
N2	0.2845 (6)	1.0553 (6)	0.0475 (5)	0.0373 (12)
N3	0.8642 (6)	0.7645 (6)	0.1946 (4)	0.0350 (12)
Ni1	0.5000	1.0000	0.5000	0.0337 (3)
S1	0.34573 (18)	0.87197 (16)	0.65724 (15)	0.0358 (4)
S2	0.35180 (18)	0.96071 (17)	0.37648 (15)	0.0367 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0360 (3)	0.0317 (3)	0.0297 (3)	0.0000 (2)	0.0024 (2)	−0.0077 (2)
Br2	0.0298 (3)	0.0566 (4)	0.0336 (3)	−0.0010 (3)	0.0058 (2)	−0.0158 (3)
C1	0.037 (3)	0.023 (3)	0.043 (3)	−0.008 (2)	−0.010 (3)	−0.004 (2)
C2	0.038 (3)	0.030 (3)	0.040 (3)	−0.008 (3)	0.010 (3)	−0.005 (3)
C3	0.029 (3)	0.033 (3)	0.035 (3)	−0.013 (3)	0.001 (2)	−0.010 (2)
C4	0.031 (3)	0.029 (3)	0.046 (3)	−0.007 (2)	−0.003 (3)	−0.013 (3)
C5	0.026 (3)	0.037 (3)	0.034 (3)	−0.007 (2)	0.005 (2)	−0.019 (3)
C6	0.030 (3)	0.028 (3)	0.027 (3)	−0.010 (2)	0.005 (2)	−0.001 (2)
C7	0.028 (3)	0.043 (4)	0.048 (4)	−0.011 (3)	−0.001 (3)	−0.012 (3)
C8	0.035 (3)	0.037 (3)	0.026 (3)	−0.018 (3)	0.005 (2)	0.000 (2)
C9	0.037 (3)	0.035 (3)	0.031 (3)	−0.007 (3)	−0.008 (3)	−0.006 (2)
C10	0.033 (3)	0.031 (3)	0.040 (3)	−0.001 (3)	0.001 (3)	−0.007 (3)
C11	0.036 (3)	0.028 (3)	0.029 (3)	0.002 (3)	0.000 (2)	0.000 (2)
C12	0.049 (4)	0.041 (3)	0.029 (3)	0.003 (3)	−0.018 (3)	0.006 (3)
C13	0.033 (3)	0.044 (4)	0.029 (3)	0.010 (3)	−0.012 (3)	−0.002 (3)
C14	0.034 (3)	0.024 (3)	0.047 (3)	−0.004 (2)	−0.022 (3)	−0.001 (3)
C15	0.032 (3)	0.035 (3)	0.038 (3)	−0.005 (3)	0.003 (3)	−0.006 (3)
C16	0.035 (3)	0.028 (3)	0.038 (3)	0.007 (3)	0.000 (3)	−0.002 (3)
N1	0.044 (3)	0.045 (3)	0.042 (3)	−0.026 (3)	−0.003 (3)	0.010 (3)
N2	0.036 (3)	0.039 (3)	0.031 (3)	−0.007 (2)	−0.006 (2)	0.009 (2)
N3	0.032 (3)	0.034 (3)	0.031 (3)	0.023 (2)	−0.006 (2)	0.000 (2)
Ni1	0.0298 (6)	0.0282 (5)	0.0365 (6)	0.0150 (4)	−0.0035 (4)	−0.0020 (4)
S1	0.0322 (8)	0.0298 (7)	0.0382 (8)	0.0141 (6)	−0.0039 (6)	−0.0009 (6)
S2	0.0331 (8)	0.0325 (8)	0.0396 (8)	−0.0079 (6)	0.0034 (6)	−0.0026 (6)

Geometric parameters (Å, °)

Br1—C7	1.923 (7)	C10—H10	0.93
Br2—C9	1.901 (6)	C11—N3	1.543 (9)
C1—C3^{i}	1.400 (8)	C11—H11A	0.97
C1—C2	1.490 (8)	C11—H11B	0.97
C1—S1	1.751 (7)	C12—C13	1.359 (10)
C2—N1	1.088 (8)	C12—N3	1.360 (8)
C3—C1^{i}	1.400 (8)	C12—H12	0.93
C3—C4	1.424 (9)	C13—C14	1.349 (9)
C3—S2	1.694 (6)	C13—H13	0.93
C4—N2	1.158 (8)	C14—C15	1.400 (9)
C5—C10	1.393 (8)	C14—H14	0.93
C5—C6	1.437 (8)	C15—C16	1.388 (9)
C5—C11	1.507 (9)	C15—H15	0.93
C6—C7	1.344 (9)	C16—N3	1.288 (7)
C6—H6	0.93	C16—H16	0.93
C7—C8	1.350 (9)	Ni1—S2^{i}	2.1607 (18)
C8—C9	1.399 (9)	Ni1—S2	2.1607 (18)

C8—H8	0.93	Ni1—S1^{i}	2.1795 (16)
C9—C10	1.363 (9)	Ni1—S1	2.1795 (16)
C3^{i}—C1—C2	122.6 (6)	C5—C11—H11B	110.0
C3^{i}—C1—S1	120.0 (5)	N3—C11—H11B	110.0
C2—C1—S1	116.4 (5)	H11A—C11—H11B	108.4
N1—C2—C1	174.1 (8)	C13—C12—N3	116.2 (6)
C1^{i}—C3—C4	119.8 (5)	C13—C12—H12	121.9
C1^{i}—C3—S2	120.8 (5)	N3—C12—H12	121.9
C4—C3—S2	119.1 (4)	C14—C13—C12	121.7 (6)
N2—C4—C3	172.6 (6)	C14—C13—H13	119.2
C10—C5—C6	121.1 (6)	C12—C13—H13	119.2
C10—C5—C11	118.8 (5)	C13—C14—C15	120.1 (6)
C6—C5—C11	120.1 (5)	C13—C14—H14	119.9
C7—C6—C5	117.6 (5)	C15—C14—H14	119.9
C7—C6—H6	121.2	C16—C15—C14	116.2 (6)
C5—C6—H6	121.2	C16—C15—H15	121.9
C6—C7—C8	123.6 (6)	C14—C15—H15	121.9
C6—C7—Br1	118.0 (5)	N3—C16—C15	121.0 (6)
C8—C7—Br1	118.3 (5)	N3—C16—H16	119.5
C7—C8—C9	117.5 (6)	C15—C16—H16	119.5
C7—C8—H8	121.3	C16—N3—C12	123.8 (6)
C9—C8—H8	121.3	C16—N3—C11	116.5 (5)
C10—C9—C8	123.8 (6)	C12—N3—C11	119.4 (5)
C10—C9—Br2	118.9 (5)	S2^{i}—Ni1—S2	180
C8—C9—Br2	117.3 (4)	S2^{i}—Ni1—S1^{i}	86.58 (6)
C9—C10—C5	116.4 (6)	S2—Ni1—S1^{i}	93.42 (6)
C9—C10—H10	121.8	S2^{i}—Ni1—S1	93.42 (6)
C5—C10—H10	121.8	S2—Ni1—S1	86.58 (6)
C5—C11—N3	108.5 (5)	S1^{i}—Ni1—S1	180
C5—C11—H11A	110.0	C1—S1—Ni1	101.1 (2)
N3—C11—H11A	110.0	C3—S2—Ni1	103.4 (2)

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16···S1^{i}	0.93	2.75	3.591 (5)	151

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+1.

Fig. 1

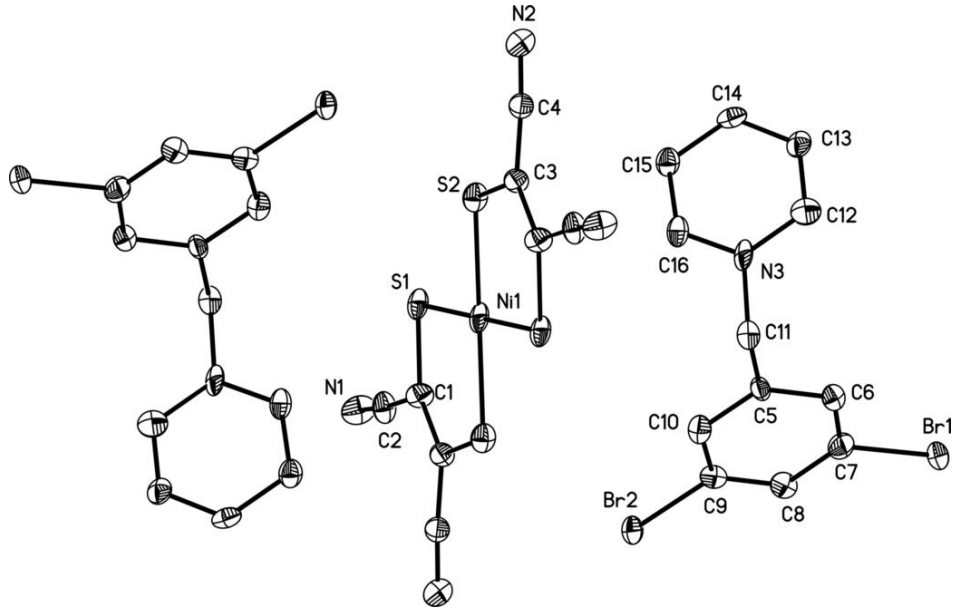
N2
C4
C14
C13
C15
C3
S2
C12
C16
N3
S1
Ni1
C11
N1
C1
C6
C10
C5
Br1
C2
C7
Br2
C9
C8

Fig. 2