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Crystal structure of bis[1-(4-bromobenzyl)pyridinium] bis(1,2-dicyanoethene-1,2-dithiolato-κ^2S,S')nickelate(II)

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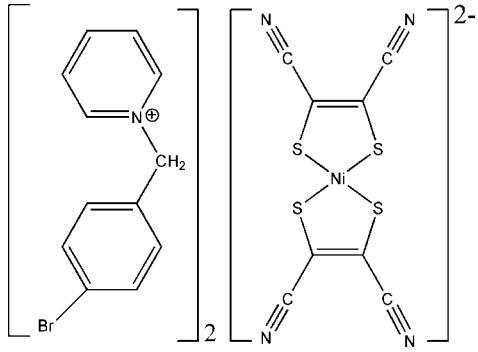
The asymmetric unit of the title salt, $(C_{12}H_{11}BrN)_2[Ni(C_4N_2S_2)_2]$, consists of one 1-(4-bromobenzyl)pyridinium cation and one half of a complex $[Ni(mnt)_2]^{2-}$ (mnt^{2-} is the maleonitriledithiolate dianion). The Ni^{2+} ion is located on an inversion centre and is coordinated by four S atoms from two mnt^{2-} ligands, exhibiting a square-planar coordination environment. In the cation, the planes of the pyridinium and benzene rings make a dihedral angle of 69.86 (19)°. The cations and anions are alternately arranged in layers parallel to (001) and are held together by non-classical C—H···N hydrogen bonds.

Keywords: crystal structure; 1-(4-bromobenzyl)pyridinium cation; maleonitriledithiolate dianion; square-planar bis-1,2-dithiolate complex; Ni^{2+} ion; hydrogen bonding.

CCDC reference: 1032163

1. Related literature

For general background to square-planar bis-1,2-dithiolate complexes of transition metals showing potential application as magnetic materials and conductors besides others, see: Duan *et al.* (2010); Pei *et al.* (2011); Ren *et al.* (2002). For the structure of a closely related compound, see: Zhang *et al.* (2011). For synthetic aspects, see: Davison & Holm (1967).



2. Experimental

2.1. Crystal data

$(C_{12}H_{11}BrN)_2[Ni(C_4N_2S_2)_2]$
M_r = 837.29
Monoclinic, $P2_1/n$
a = 9.783 (2) Å
b = 11.962 (3) Å
c = 14.858 (3) Å
β = 97.385 (7)°
V = 1724.3 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.16 mm^{-1}
T = 296 K
0.20 × 0.15 × 0.15 mm

2.2. Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.571, T_{max} = 0.649
14683 measured reflections
3040 independent reflections
2204 reflections with $I > 2\sigma(I)$
R_{int} = 0.061

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.102
S = 1.03
3040 reflections
205 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.91 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16···N2	0.93	2.49	3.384 (6)	162

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5078).

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supporting information

Acta Cryst. (2014). E**70**, m395–m396 [doi:10.1107/S1600536814024222]

Crystal structure of bis[1-(4-bromobenzyl)pyridinium] bis(1,2-dicyanoethene-1,2-dithiolato-κ^2S,S')nickelate(II)

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S1. Experimental

Disodium maleonitriledithiolate (456 mg, 2.5 mmol) and nickel chloride hexahydrate (297 mg, 1.25 mmol) were mixed under stirring in water (20 ml) and heated to boiling for about 20 min. The resuting red solution was filtered and to the filtrate was added dropwise to an aqueous solution of 1-(4′-bromobenzyl)pyridinium chloride (711.5 mg, 2.5 mmol). The dark red precipitate was filtered off, washed with water three times and dried in vacuum. The crude product was recrystallized from acetone to give red crystals (yield: 76%) with a block-like form.

S2. Refinement

The H atoms were placed on idealized positions (C—H = 0.93 Å for aromatic and 0.97 Å for methylene H atoms) and refined as riding atoms, with U_{iso}(H) = 1.2U_{eq}(C).

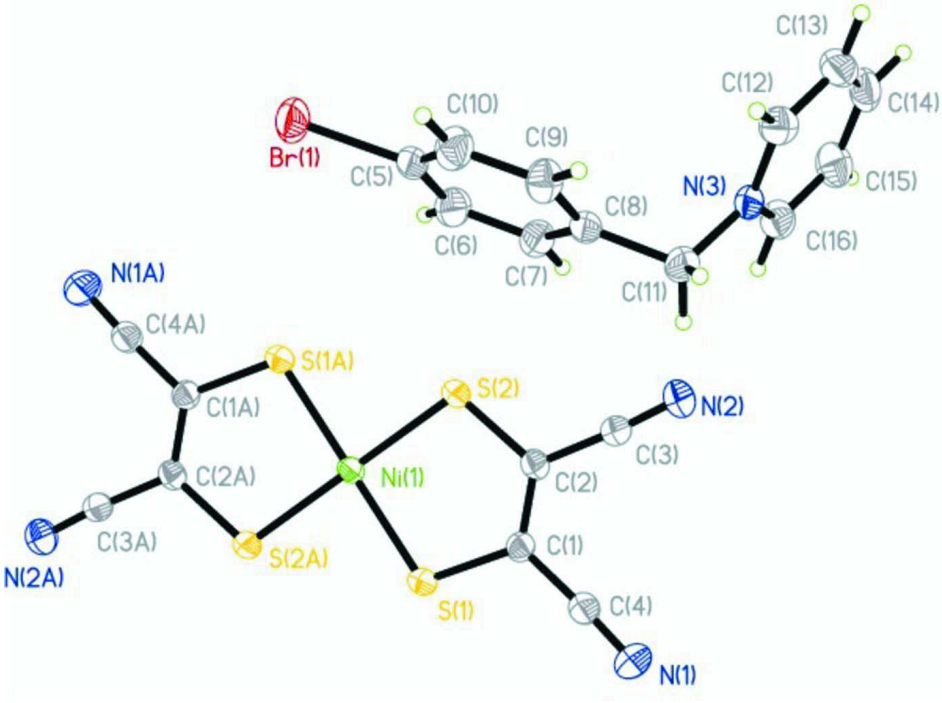

Figure 1

The molecular components of the title structure. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (A) = 1 - *x*, 1 - *y*, -*z*).]

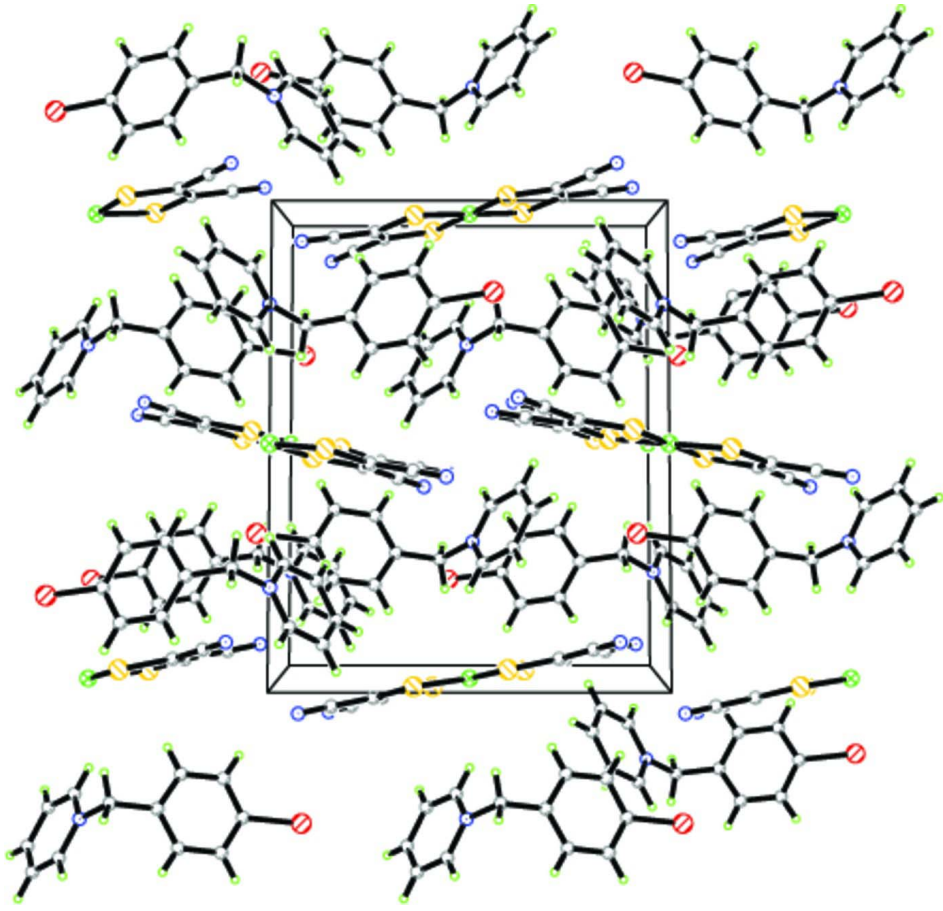

Figure 2

Packing diagram of the title structure viewed along [100]. The origin is at the upper right corner of the unit cell.

Bis[1-(4-bromobenzyl)pyridinium] bis(1,2-dicyanoethene-1,2-dithiolato-κ^2S,S')nickelate(II)

Crystal data

$(C_{12}H_{11}BrN)_2[Ni(C_4N_2S_2)_2]$
M_r = 837.29
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 9.783 (2) Å
b = 11.962 (3) Å
c = 14.858 (3) Å
β = 97.385 (7)°
V = 1724.3 (6) Å^3
Z = 2
$F(000)$ = 836
D_x = 1.613 Mg m^{-3}
Melting point: 473 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 14683 reflections
θ = 2.2–25.0°
μ = 3.16 mm^{-1}
T = 296 K
Block, red
0.20 × 0.15 × 0.15 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.571, T_{max} = 0.649
14683 measured reflections
3040 independent reflections
2204 reflections with $I > 2\sigma(I)$

R_{int} = 0.061
θ_{max} = 25.0°, θ_{min} = 2.2°
h = −11→11
k = −14→14
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.102
S = 1.03
3040 reflections
205 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 0.2393P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.91 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Ni1	0.5000	0.5000	0.0000	0.03497 (19)
Br1	−0.05497 (5)	0.44064 (4)	0.19128 (4)	0.0857 (2)
S1	0.68740 (9)	0.59888 (8)	0.02861 (6)	0.0445 (3)
S2	0.37034 (9)	0.64490 (8)	0.01000 (7)	0.0479 (3)
C3	0.4306 (4)	0.8595 (3)	0.0544 (3)	0.0472 (9)
N2	0.3771 (4)	0.9425 (3)	0.0661 (3)	0.0651 (10)
C8	0.1115 (3)	0.8032 (3)	0.2369 (3)	0.0438 (9)
C1	0.6257 (3)	0.7321 (3)	0.0478 (2)	0.0398 (8)
N3	0.0716 (3)	1.0079 (2)	0.2122 (2)	0.0426 (7)
C11	0.1688 (4)	0.9204 (3)	0.2526 (3)	0.0532 (10)
H11A	0.1894	0.9335	0.3173	0.064*
H11B	0.2544	0.9263	0.2264	0.064*
C9	0.0500 (4)	0.7490 (3)	0.3036 (3)	0.0563 (11)
H9	0.0417	0.7855	0.3579	0.068*
C5	0.0120 (4)	0.5898 (3)	0.2097 (3)	0.0537 (11)
C10	0.0009 (4)	0.6417 (4)	0.2903 (3)	0.0620 (11)
H10	−0.0392	0.6051	0.3355	0.074*
C2	0.4878 (3)	0.7516 (3)	0.0400 (2)	0.0401 (8)
C14	−0.1102 (5)	1.1646 (3)	0.1387 (3)	0.0698 (13)
H14	−0.1726	1.2181	0.1132	0.084*
C4	0.7257 (4)	0.8173 (3)	0.0722 (3)	0.0501 (9)
C15	0.0006 (5)	1.1360 (4)	0.0964 (3)	0.0710 (13)

H15	0.0142	1.1702	0.0420	0.085*
C16	0.0911 (4)	1.0574 (3)	0.1337 (3)	0.0586 (11)
H16	0.1666	1.0380	0.1049	0.070*
C12	−0.0375 (4)	1.0353 (3)	0.2544 (3)	0.0546 (10)
H12	−0.0503	0.9998	0.3084	0.066*
C6	0.0723 (4)	0.6405 (3)	0.1425 (3)	0.0622 (11)
H6	0.0794	0.6036	0.0881	0.075*
N1	0.8110 (4)	0.8818 (3)	0.0910 (3)	0.0770 (11)
C13	−0.1290 (4)	1.1141 (4)	0.2192 (3)	0.0632 (12)
H13	−0.2034	1.1335	0.2491	0.076*
C7	0.1227 (4)	0.7476 (3)	0.1569 (3)	0.0566 (11)
H7	0.1649	0.7828	0.1120	0.068*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0332 (3)	0.0344 (4)	0.0365 (4)	0.0045 (3)	0.0013 (3)	−0.0016 (3)
Br1	0.0699 (4)	0.0431 (3)	0.1335 (5)	−0.0074 (2)	−0.0270 (3)	−0.0002 (3)
S1	0.0350 (5)	0.0405 (5)	0.0563 (6)	0.0044 (4)	−0.0003 (4)	−0.0029 (5)
S2	0.0349 (5)	0.0382 (5)	0.0699 (7)	0.0047 (4)	0.0047 (5)	−0.0076 (5)
C3	0.040 (2)	0.044 (2)	0.057 (2)	−0.0019 (18)	0.0059 (18)	−0.004 (2)
N2	0.063 (2)	0.048 (2)	0.086 (3)	0.0080 (18)	0.013 (2)	−0.010 (2)
C8	0.037 (2)	0.040 (2)	0.052 (2)	0.0020 (16)	−0.0039 (17)	0.000 (2)
C1	0.041 (2)	0.038 (2)	0.039 (2)	−0.0011 (16)	0.0011 (16)	−0.0029 (16)
N3	0.0439 (18)	0.0342 (17)	0.0487 (18)	−0.0015 (14)	0.0017 (14)	−0.0087 (16)
C11	0.048 (2)	0.047 (2)	0.061 (3)	−0.0023 (18)	−0.0080 (19)	−0.002 (2)
C9	0.069 (3)	0.049 (3)	0.048 (2)	−0.002 (2)	−0.001 (2)	−0.002 (2)
C5	0.038 (2)	0.039 (2)	0.079 (3)	0.0039 (17)	−0.014 (2)	0.005 (2)
C10	0.069 (3)	0.053 (3)	0.063 (3)	−0.004 (2)	0.005 (2)	0.014 (2)
C2	0.043 (2)	0.038 (2)	0.0396 (19)	0.0048 (16)	0.0044 (15)	−0.0023 (17)
C14	0.071 (3)	0.039 (2)	0.092 (4)	0.010 (2)	−0.020 (3)	−0.003 (3)
C4	0.047 (2)	0.045 (2)	0.056 (2)	0.004 (2)	0.0011 (19)	−0.005 (2)
C15	0.086 (3)	0.053 (3)	0.075 (3)	0.009 (3)	0.010 (3)	0.013 (2)
C16	0.066 (3)	0.049 (3)	0.065 (3)	−0.003 (2)	0.025 (2)	0.005 (2)
C12	0.054 (3)	0.061 (3)	0.048 (2)	−0.003 (2)	0.005 (2)	−0.009 (2)
C6	0.063 (3)	0.055 (3)	0.069 (3)	−0.003 (2)	0.012 (2)	−0.017 (2)
N1	0.059 (2)	0.064 (3)	0.103 (3)	−0.011 (2)	−0.011 (2)	−0.016 (2)
C13	0.052 (3)	0.062 (3)	0.074 (3)	0.009 (2)	0.002 (2)	−0.020 (3)
C7	0.056 (2)	0.050 (3)	0.065 (3)	−0.005 (2)	0.016 (2)	−0.004 (2)

Geometric parameters (Å, º)

Ni1—S2^{i}	2.1642 (9)	C9—C10	1.376 (5)
Ni1—S2	2.1642 (9)	C9—H9	0.9300
Ni1—S1	2.1773 (9)	C5—C10	1.366 (6)
Ni1—S1^{i}	2.1773 (9)	C5—C6	1.366 (6)
Br1—C5	1.908 (4)	C10—H10	0.9300
S1—C1	1.740 (3)	C14—C15	1.366 (6)

S2—C2	1.737 (3)	C14—C13	1.373 (6)
C3—N2	1.146 (4)	C14—H14	0.9300
C3—C2	1.433 (5)	C4—N1	1.144 (5)
C8—C7	1.379 (5)	C15—C16	1.360 (6)
C8—C9	1.385 (5)	C15—H15	0.9300
C8—C11	1.517 (5)	C16—H16	0.9300
C1—C2	1.360 (5)	C12—C13	1.358 (6)
C1—C4	1.427 (5)	C12—H12	0.9300
N3—C16	1.343 (5)	C6—C7	1.379 (5)
N3—C12	1.346 (5)	C6—H6	0.9300
N3—C11	1.487 (4)	C13—H13	0.9300
C11—H11A	0.9700	C7—H7	0.9300
C11—H11B	0.9700		

$S2^{i}$—Ni1—S2	180.00 (5)	C6—C5—Br1	118.9 (3)
$S2^{i}$—Ni1—S1	87.84 (4)	C5—C10—C9	119.0 (4)
S2—Ni1—S1	92.16 (4)	C5—C10—H10	120.5
$S2^{i}$—Ni1—$S1^{i}$	92.16 (4)	C9—C10—H10	120.5
S2—Ni1—$S1^{i}$	87.84 (4)	C1—C2—C3	123.0 (3)
S1—Ni1—$S1^{i}$	180.0	C1—C2—S2	120.8 (3)
C1—S1—Ni1	103.21 (11)	C3—C2—S2	116.2 (3)
C2—S2—Ni1	103.42 (12)	C15—C14—C13	119.6 (4)
N2—C3—C2	175.7 (4)	C15—C14—H14	120.2
C7—C8—C9	118.7 (4)	C13—C14—H14	120.2
C7—C8—C11	120.7 (3)	N1—C4—C1	176.5 (4)
C9—C8—C11	120.6 (3)	C16—C15—C14	119.9 (4)
C2—C1—C4	122.6 (3)	C16—C15—H15	120.0
C2—C1—S1	120.3 (3)	C14—C15—H15	120.0
C4—C1—S1	117.1 (2)	N3—C16—C15	120.2 (4)
C16—N3—C12	120.4 (3)	N3—C16—H16	119.9
C16—N3—C11	120.4 (3)	C15—C16—H16	119.9
C12—N3—C11	119.2 (3)	N3—C12—C13	120.9 (4)
N3—C11—C8	112.6 (3)	N3—C12—H12	119.6
N3—C11—H11A	109.1	C13—C12—H12	119.6
C8—C11—H11A	109.1	C5—C6—C7	118.5 (4)
N3—C11—H11B	109.1	C5—C6—H6	120.7
C8—C11—H11B	109.1	C7—C6—H6	120.7
H11A—C11—H11B	107.8	C12—C13—C14	119.0 (4)
C10—C9—C8	120.7 (4)	C12—C13—H13	120.5
C10—C9—H9	119.7	C14—C13—H13	120.5
C8—C9—H9	119.7	C8—C7—C6	121.1 (4)
C10—C5—C6	122.0 (4)	C8—C7—H7	119.4
C10—C5—Br1	119.1 (3)	C6—C7—H7	119.4

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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