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

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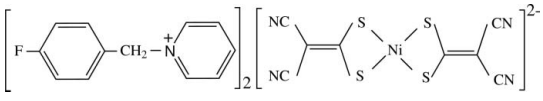
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.003 Å; R factor = 0.025; wR factor = 0.071; data-to-parameter ratio = 13.1.

A new ion-pair complex, $(C_{12}H_{11}FN)_2[Ni(C_4N_2S_2)_2]$ or $(FBzPy)_2[Ni(imnt)_2]$, where FBzPy is 1-(4-fluorobenzyl)pyridinium and imnt is 2,2-dicyanoethene-1,1-dithiolate, was obtained by the direct reaction of $NiCl_2$, K_2(imnt) and $(FBzPy)^+Br^-$ in H_2O. The asymmetric unit contains a $[FBzPy]^+$ cation and one half of the $Ni[imnt]_2^{2-}$ anion. The Ni^{II} ion lies on an inversion centre and adopts a square-planar configuration. In the $[FBzPy]^+$ cation, the benzene and pyridinium rings make a dihedral angle of 77.2 (3)°. In the crystal structure, C—H···N hydrogen bonds and π–π interactions [3.450 (3) Å] between ethenyl groups of the $Ni[imnt]_2^{2-}$ anion and the pyridinium ring of the cation generate a three-dimensional network.

Related literature

For related $Ni(imnt)_2^{2-}$ complexes, see: Liu *et al.* (1996, 2006); Feng *et al.* (2007). For related literature, see: Canadell (1999); Ni *et al.* (2007); Nishijo *et al.* (2003); Ren *et al.* (2002); Robertson & Cronin (2002); Xie *et al.* (2002).



Experimental

Crystal data

$(C_{12}H_{11}FN)_2[Ni(C_4N_2S_2)_2]$
M_r = 715.51
Triclinic, $P\overline{1}$
a = 7.085 (1) Å
b = 9.048 (1) Å
c = 13.182 (1) Å
α = 71.68 (1)°
β = 74.93 (1)°
γ = 82.11 (1)°
V = 773.19 (15) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.94 mm^{-1}
T = 291 (2) K
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.766, T_{max} = 0.836
4185 measured reflections
2695 independent reflections
2568 reflections with $I > 2\sigma(I)$
R_{int} = 0.009

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.071
S = 1.03
2695 reflections
205 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12···N1^{i}	0.93	2.59	3.471 (3)	157
C15—H15···N2^{ii}	0.93	2.60	3.337 (3)	136

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $-x+1, -y+2, -z+1$.

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: CI2509).

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supplementary materials

Acta Cryst. (2007). E**63**, m3084 [**doi:10.1107/S160053680705814X**]

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

A.-Q. Zhou and C.-L. Ni

Comment

2,2-Dicyanoethene-1,1-dithiolate (imnt) or 1,2-dicyanoethene-1,2-dithiolate (mnt) transition metal complexes have attracted cosiderable interest in molecular materials research (Liu *et al.*, 1996; Robertson & Cronin, 2002; Ni *et al.*, 2007; Ren *et al.*, 2002; Nishijo *et al.*, 2003; Xie *et al.*, 2002; Canadell, 1999). Our studies have been focused on the design, preparation, and investigation of some new salts that based on the molecular architecture of $Ni(imnt)_2^{2-}$ anions because the topology and the size of the counterions used with $Ni(imnt)_2^{2-}$ anion play an important role in tuning the stacks of anions and cations (Liu *et al.*, 1996; Liu *et al.*, 2006; Feng *et al.*, 2007).

The asymmetric unit of the title compound consists of one $[FBzPy]^+$ cation and one-half of $Ni(imnt)_2$ anion located on an inversion center; the Ni^{II} ion lies on an inversion centre. The NiS_4 core exhibits a square-planar configuration, with Ni—S distances of 2.2058 (5) and 2.2133 (5) Å. The S1—Ni1—S2 bond angle within the four-membered ring (Ni1/S1/C1/S2) is 78.80 (2)°. Atoms N1 and N2 of the –C≡N groups deviate from the Ni1/S1/C1/S2 plane by 0.607 (3) Å and 0.174 (3) Å, respectively. The $[FBzPy]^+$ cation adopts a conformation where both the benzene and pyridinium rings are twisted with respect to the N3/C11/C10 reference plane with dihedral angles of 97.7 (2)° and 95.6 (3)°, respectively. The benzene and pyridinium rings make a dihedral angle of 77.2 (3)°. The F atom deviates from the benzene plane by 0.024 (3) Å.

In the crystal structure, C—H···N type hydrogen bonds (Table 1) and π-π interactions are observed between cations and anions. The π-π interaction is observed between ethenyl groups of the $Ni(imnt)_2^{2-}$ anion and the $N3^i/C12^i—C16^i$ [symmetry code: (i) $x, -1+y, z$] ring of the cation, with the distance between atom C2 and the centroid of the ring being 3.492 (3) Å. The above interactions generate a three-dimensional network structure (Fig 2).

Experimental

The title compound was prepared by the direct reaction of $NiCl_2·6H_2O$ (0.24 g, 1 mmol), $K_2(imnt)·H_2O$ (0.48 g, 2 mmol) and $(FBzPy)^+Br^-$ (0.54 g, 2 mmol) in H_2O (50 ml). Brown crystals were obtained by slow evaporation of a CH_3CN solution at room temperature over two weeks.

Refinement

H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and refined using a riding model, with $U_{iso} = 1.2\ U_{eq}$(parent atom).

Figures

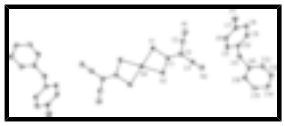

Fig. 1. The cation and anion of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. Unlabelled atoms are related to the labelled atoms by the symmetry operation (2 − *x*, −*y*, 1 − *z*).

Fig. 2. The crystal packing of the title compound, viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

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

Crystal data

$(C_{12}H_{11}FN)_2[Ni(C_4N_2S_2)_2]$	$Z = 1$
$M_r = 715.51$	$F_{000} = 366$
Triclinic, $P\overline{1}$	$D_x = 1.537$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.085$ (1) Å	Cell parameters from 3505 reflections
$b = 9.048$ (1) Å	$\theta = 2.4$–29.5º
$c = 13.182$ (1) Å	$\mu = 0.94$ mm^{-1}
$\alpha = 71.68$ (1)º	$T = 291$ (2) K
$\beta = 74.93$ (1)º	Block, brown
$\gamma = 82.11$ (1)º	0.30 × 0.25 × 0.20 mm
$V = 773.19$ (15) Å^3	

Data collection

Bruker SMART APEX CCD diffractometer	2695 independent reflections
Radiation source: fine-focus sealed tube	2568 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.009$
$T = 291(2)$ K	$\theta_{max} = 25.0$º
φ and ω scans	$\theta_{min} = 2.5$º
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -8 \rightarrow 6$
$T_{min} = 0.766$, $T_{max} = 0.836$	$k = -10 \rightarrow 10$
4185 measured reflections	$l = -15 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.025$	H-atom parameters constrained

$wR(F^2) = 0.071$	$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.1686P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
2695 reflections	$\Delta\rho_{max} = 0.19$ e Å^{-3}
205 parameters	$\Delta\rho_{min} = -0.25$ 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}
Ni1	1.0000	0.0000	0.5000	0.03971 (11)
S1	0.87140 (6)	−0.02721 (5)	0.67579 (3)	0.04361 (12)
S2	0.86668 (7)	0.23756 (5)	0.49460 (3)	0.04755 (13)
N1	0.7048 (3)	0.1351 (2)	0.91290 (14)	0.0747 (5)
N2	0.6279 (3)	0.54849 (19)	0.63808 (14)	0.0611 (4)
N3	0.33540 (19)	0.96970 (15)	0.76440 (11)	0.0391 (3)
F1	−0.34351 (17)	0.52632 (13)	0.90040 (10)	0.0665 (3)
C1	0.8128 (2)	0.17017 (19)	0.63538 (12)	0.0376 (3)
C2	0.7406 (2)	0.25975 (19)	0.70595 (13)	0.0398 (3)
C3	0.7188 (3)	0.1919 (2)	0.82093 (14)	0.0479 (4)
C4	0.6808 (2)	0.4202 (2)	0.66752 (13)	0.0440 (4)
C5	0.1503 (3)	0.64193 (18)	0.78041 (13)	0.0442 (4)
H5	0.2537	0.6311	0.7225	0.053*
C6	−0.0245 (3)	0.57681 (19)	0.79671 (14)	0.0472 (4)
H6	−0.0406	0.5234	0.7500	0.057*
C7	−0.1730 (3)	0.59274 (19)	0.88309 (14)	0.0474 (4)
C8	−0.1575 (3)	0.6725 (2)	0.95277 (14)	0.0516 (4)
H8	−0.2619	0.6824	1.0104	0.062*
C9	0.0174 (3)	0.7379 (2)	0.93532 (13)	0.0486 (4)
H9	0.0310	0.7926	0.9818	0.058*
C10	0.1731 (2)	0.72308 (17)	0.84929 (12)	0.0398 (3)
C11	0.3599 (3)	0.8020 (2)	0.82662 (15)	0.0469 (4)
H11A	0.3924	0.7936	0.8954	0.056*
H11B	0.4663	0.7510	0.7843	0.056*
C12	0.2810 (3)	1.0763 (2)	0.81891 (15)	0.0493 (4)
H12	0.2663	1.0465	0.8947	0.059*
C13	0.2468 (3)	1.2291 (2)	0.76345 (17)	0.0586 (5)
H13	0.2076	1.3029	0.8017	0.070*
C14	0.2701 (3)	1.2737 (2)	0.65203 (17)	0.0556 (5)
H14	0.2482	1.3777	0.6140	0.067*
C15	0.3260 (3)	1.1639 (2)	0.59723 (15)	0.0551 (5)
H15	0.3426	1.1920	0.5214	0.066*
C16	0.3573 (3)	1.0107 (2)	0.65574 (14)	0.0510 (4)
H16	0.3941	0.9349	0.6191	0.061*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.04242 (18)	0.04293 (18)	0.02804 (16)	0.00353 (12)	−0.00639 (12)	−0.00631 (12)
S1	0.0494 (2)	0.0426 (2)	0.0298 (2)	0.00407 (17)	−0.00642 (16)	−0.00304 (16)
S2	0.0599 (3)	0.0461 (2)	0.0271 (2)	0.00719 (19)	−0.00731 (18)	−0.00378 (17)
N1	0.1176 (16)	0.0689 (11)	0.0361 (9)	−0.0076 (11)	−0.0206 (9)	−0.0101 (8)
N2	0.0720 (11)	0.0493 (10)	0.0542 (10)	0.0051 (8)	−0.0146 (8)	−0.0078 (7)
N3	0.0380 (7)	0.0403 (7)	0.0360 (7)	0.0011 (5)	−0.0115 (5)	−0.0062 (6)
F1	0.0581 (7)	0.0592 (7)	0.0736 (8)	−0.0097 (5)	−0.0123 (5)	−0.0073 (6)
C1	0.0335 (7)	0.0442 (8)	0.0311 (8)	−0.0003 (6)	−0.0091 (6)	−0.0048 (6)
C2	0.0410 (8)	0.0451 (9)	0.0301 (8)	0.0003 (7)	−0.0100 (6)	−0.0062 (7)
C3	0.0599 (10)	0.0487 (9)	0.0353 (9)	−0.0026 (8)	−0.0115 (8)	−0.0123 (7)
C4	0.0454 (9)	0.0506 (11)	0.0350 (8)	−0.0019 (8)	−0.0084 (7)	−0.0120 (7)
C5	0.0521 (9)	0.0384 (8)	0.0366 (8)	0.0107 (7)	−0.0087 (7)	−0.0101 (7)
C6	0.0591 (10)	0.0372 (8)	0.0454 (9)	0.0052 (7)	−0.0166 (8)	−0.0119 (7)
C7	0.0506 (9)	0.0356 (8)	0.0463 (10)	0.0012 (7)	−0.0135 (8)	0.0018 (7)
C8	0.0563 (10)	0.0501 (10)	0.0354 (9)	0.0035 (8)	0.0000 (7)	−0.0058 (7)
C9	0.0647 (11)	0.0454 (9)	0.0327 (8)	0.0038 (8)	−0.0096 (7)	−0.0116 (7)
C10	0.0494 (9)	0.0317 (7)	0.0328 (8)	0.0068 (6)	−0.0136 (7)	−0.0022 (6)
C11	0.0509 (10)	0.0424 (9)	0.0454 (9)	0.0089 (7)	−0.0191 (8)	−0.0081 (7)
C12	0.0597 (11)	0.0470 (10)	0.0401 (9)	−0.0018 (8)	−0.0135 (8)	−0.0103 (8)
C13	0.0717 (13)	0.0427 (10)	0.0593 (12)	0.0000 (9)	−0.0156 (10)	−0.0129 (9)
C14	0.0527 (10)	0.0438 (10)	0.0616 (12)	−0.0072 (8)	−0.0185 (9)	0.0031 (9)
C15	0.0567 (11)	0.0613 (11)	0.0378 (9)	−0.0132 (9)	−0.0116 (8)	0.0033 (8)
C16	0.0557 (10)	0.0561 (10)	0.0381 (9)	−0.0030 (8)	−0.0068 (8)	−0.0128 (8)

Geometric parameters (Å, °)

Ni1—S1^{i}	2.2058 (5)	C6—H6	0.93
Ni1—S1	2.2058 (4)	C7—C8	1.366 (3)
Ni1—S2	2.2133 (5)	C8—C9	1.380 (3)
Ni1—S2^{i}	2.2133 (5)	C8—H8	0.93
S1—C1	1.7201 (17)	C9—C10	1.387 (2)
S2—C1	1.7163 (15)	C9—H9	0.93
N1—C3	1.142 (2)	C10—C11	1.507 (2)
N2—C4	1.145 (2)	C11—H11A	0.97
N3—C16	1.334 (2)	C11—H11B	0.97
N3—C12	1.336 (2)	C12—C13	1.368 (3)
N3—C11	1.491 (2)	C12—H12	0.93
F1—C7	1.357 (2)	C13—C14	1.366 (3)
C1—C2	1.377 (2)	C13—H13	0.93
C2—C3	1.420 (2)	C14—C15	1.364 (3)
C2—C4	1.423 (2)	C14—H14	0.93
C5—C6	1.382 (2)	C15—C16	1.378 (3)
C5—C10	1.385 (2)	C15—H15	0.93
C5—H5	0.93	C16—H16	0.93

C6—C7	1.365 (3)		
S1^{i}—Ni1—S1	180	C7—C8—H8	120.9
S1^{i}—Ni1—S2	101.201 (18)	C9—C8—H8	120.9
S1—Ni1—S2	78.799 (19)	C8—C9—C10	120.87 (16)
S1^{i}—Ni1—S2^{i}	78.799 (18)	C8—C9—H9	119.6
S1—Ni1—S2^{i}	101.201 (18)	C10—C9—H9	119.6
S2—Ni1—S2^{i}	180	C5—C10—C9	118.90 (16)
C1—S1—Ni1	85.66 (5)	C5—C10—C11	120.24 (15)
C1—S2—Ni1	85.51 (6)	C9—C10—C11	120.76 (15)
C16—N3—C12	120.66 (15)	N3—C11—C10	109.83 (13)
C16—N3—C11	119.73 (15)	N3—C11—H11A	109.7
C12—N3—C11	119.50 (14)	C10—C11—H11A	109.7
C2—C1—S2	125.81 (13)	N3—C11—H11B	109.7
C2—C1—S1	124.73 (12)	C10—C11—H11B	109.7
S2—C1—S1	109.42 (9)	H11A—C11—H11B	108.2
C1—C2—C3	120.24 (15)	N3—C12—C13	120.07 (17)
C1—C2—C4	121.83 (14)	N3—C12—H12	120.0
C3—C2—C4	117.91 (15)	C13—C12—H12	120.0
N1—C3—C2	178.5 (2)	C14—C13—C12	120.18 (19)
N2—C4—C2	178.26 (19)	C14—C13—H13	119.9
C6—C5—C10	120.72 (16)	C12—C13—H13	119.9
C6—C5—H5	119.6	C15—C14—C13	119.22 (17)
C10—C5—H5	119.6	C15—C14—H14	120.4
C7—C6—C5	118.37 (16)	C13—C14—H14	120.4
C7—C6—H6	120.8	C14—C15—C16	119.12 (17)
C5—C6—H6	120.8	C14—C15—H15	120.4
F1—C7—C6	118.43 (17)	C16—C15—H15	120.4
F1—C7—C8	118.65 (16)	N3—C16—C15	120.75 (18)
C6—C7—C8	122.93 (17)	N3—C16—H16	119.6
C7—C8—C9	118.20 (16)	C15—C16—H16	119.6

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12···N1^{ii}	0.93	2.59	3.471 (3)	157
C15—H15···N2^{iii}	0.93	2.60	3.337 (3)	136

Symmetry codes: (ii) −*x*+1, −*y*+1, −*z*+2; (iii) −*x*+1, −*y*+2, −*z*+1.

Fig. 1

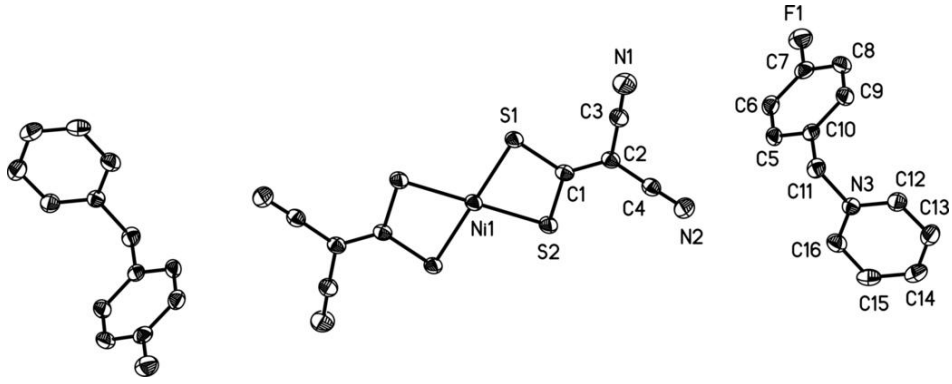
F1
C7
C8
C9
C6
C10
C5
C11
N3
C12
C13
C16
C15
C14
N1
C3
S1
C2
C1
C4
N2
Ni1
S2

Fig. 2