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Bis(2-amino-1-benzylpyridinium) bis(2,2-dicyanoethene-1,1-dithiolato-κ^2S,S')-nickelate(II)

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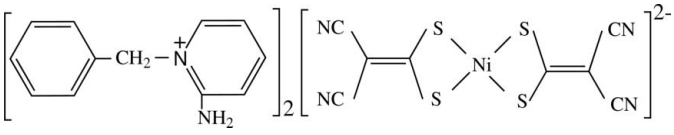
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.007 Å; R factor = 0.045; wR factor = 0.151; data-to-parameter ratio = 14.4.

A new $[Ni(imnt)_2]^{2-}$ salt ($imnt^{2-}$ is 2,2-dicyanoethene-1,1-dithiolate) with a 1-benzyl-2-aminopyridinium $[(Bz2NH_2py)^+]$ cation, $(C_{12}H_{13}N_2)_2[Ni(C_4N_2S_2)_2]$, was obtained by the direct reaction of $NiCl_2{\cdot}6H_2O$, K_2imnt and $(Bz2NH_2py)^+{\cdot}Br^-$ in water. The Ni^{II} ion lies on an inversion centre and the asymmetric unit contains a $(Bz2NH_2py)^+$ cation and one-half of the $Ni(imnt)_2^{2-}$ anion. The Ni^{II} ion adopts a square-planar coordination geometry. In the crystal structure, N—H···N and C—H···N hydrogen bonds are observed between the anions and the cations.

Related literature

For the use of $Ni(imnt)_2^{2-}$ complexes in molecular materials research, see: Liu *et al.* (1998). For related $Ni(imnt)_2^{2-}$ complexes with square-planar geometry displaying C—H···N hydrogen bonds, see: Liu *et al.* (1996, 2006); Feng *et al.* (2007).



Experimental

Crystal data

$(C_{12}H_{13}N_2)_2[Ni(C_4N_2S_2)_2]$
M_r = 709.56
Monoclinic, $C2/c$
a = 20.247 (5) Å
b = 10.764 (3) Å
c = 15.973 (4) Å
β = 105.462 (3)°
V = 3355.3 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.86 mm^{-1}
T = 291 (2) K
0.34 × 0.26 × 0.21 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.758, T_{max} = 0.840
7805 measured reflections
2951 independent reflections
1915 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.151
S = 1.05
2951 reflections
205 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4A···N2^{i}	0.86	2.25	2.986 (6)	143
C11—H11B···N2^{i}	0.97	2.58	3.490 (6)	156
C13—H13···N1^{ii}	0.93	2.51	3.329 (7)	148

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x, -y+1, -z+1$.

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: SJ2392).

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supplementary materials

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Bis(2-amino-1-benzylpyridinium) bis(2,2-dicyanoethene-1,1-dithiolato-κ^2S,S')nickelate(II)

Y. Hou, Q. Huang, H. Zuo and C. Ni

Comment

Transition metal complexes with 2,2-dicyanoethene-1,1-dithiolate have received much attention in molecular materials research (Liu *et al.*, 1998). In these complexes, the topology and the size of the counterions used with $Ni(imnt)_2^{2-}$ anions 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 structure of (I) consists of one $(Bz2NH_2py)^+$ cation and one-half of a $Ni(imnt)_2$ anion in the asymmetric unit as the Ni^{II} ion lies on an inversion centre. The $[Bz2NH_2py]^+$ cation adopts a conformation in which both the phenyl ring and pyridine ring are twisted with respect to the C10/C11/N3 plane with dihedral angles of 47.3 (2)° for the phenyl ring, 80.0 (3)° for the pyridine ring, respectively. The phenyl ring and the pyridine ring make a dihedral angle of 102.4 (3)° to one another·The N4 atom deviates from pyridine plane by 0.012 (2) Å. The NiS_4 core exhibits a square planar coordination geometry with Ni—S distances 2.2172 (12) and 2.2071 (12) Å respectively, and the S1—Ni1—S2 bond angle within the four-membered ring is 79.16 (4)°. The two N atoms of the CN groups deviate from the Ni1/S1/S2/C1 plane by −0.068 (2) Å for N1 and 0.008 (2) Å for N2.

Four different hydrogen bonds were observed in the crystal structure of (I): C4—H4A···N2, C11—H11B···N2 and C13—H13···N1 (Table 1 and Fig.2).

Experimental

The title compound was prepared by the direct reaction of $NiCl_2·6H_2O$, K_2imnt and $(Bz2NH_2py)^+Br^-$ in H_2O. Red block-like single crystals were obtained by slow evaporation of a CH_3CN solution at room temperature over about two weeks.

Refinement

H atoms bonded to the amine N atom were located in a difference map and refined with distance restraints of N—H = 0.86 (2) Å, and with U_{iso}(H) = 1.2U_{eq}(N). Other H atoms were positioned geometrically and refined using a riding model with C—H = 0.93–0.97 Å, and with U_{iso}(H) = 1.2 times U_{eq}(C).

Figures

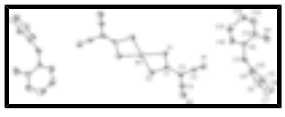

Fig. 1. The molecular structure of (I), with atom labels and 30% probability displacement ellipsoids for non-H atoms. Hydrogen atoms have been omitted and labelled atoms are related to unlabelled atoms by the symmetry operation $-x, -y, -z + 2$.

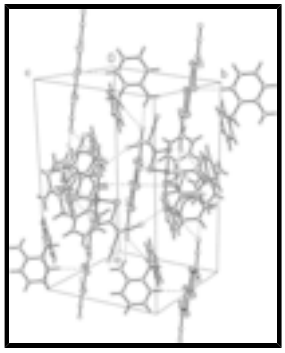

Fig. 2. The crystal packing of (I) showing the hydrogen bonds (dashed lines) between the cations and anions.

Bis(2-amino-1-benzylpyridinium) bis(2,2-dicyanoethene-1,1-dithiolato- κ^2S,S')nickelate(II)

Crystal data

$(C_{12}H_{13}N_2)_2[Ni(C_4N_2S_2)_2]$	F_{000} = 1464
M_r = 709.56	D_x = 1.405 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 3342 reflections
a = 20.247 (5) Å	θ = 2.4–27.2º
b = 10.764 (3) Å	μ = 0.86 mm^{-1}
c = 15.973 (4) Å	*T* = 291 (2) K
β = 105.462 (3)º	Block, brown
V = 3355.3 (15) Å^3	0.34 × 0.26 × 0.21 mm
Z = 4	

Data collection

Bruker SMART APEX CCD diffractometer	1915 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.034
Monochromator: graphite	θ_{max} = 25.1º
φ and ω scans	θ_{min} = 2.2º
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	*h* = −22→24
T_{min} = 0.758, T_{max} = 0.840	*k* = −12→12
7805 measured reflections	*l* = −19→19
2951 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.046	H-atom parameters constrained
$wR(F^2)$ = 0.151	$w = 1/[\sigma^2(F_o^2) + (0.086P)^2 + 1.2P]$

	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
2951 reflections	$\Delta\rho_{max} = 0.58$ e Å^{-3}
205 parameters	$\Delta\rho_{min} = -0.41$ 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	0.0000	0.0000	1.0000	0.0462 (2)
S1	0.01956 (5)	0.09604 (10)	0.88616 (6)	0.0525 (3)
S2	0.11309 (5)	0.00334 (9)	1.03689 (6)	0.0513 (3)
N1	0.1351 (2)	0.2227 (4)	0.7590 (3)	0.0906 (14)
N2	0.2833 (2)	0.0855 (4)	0.9958 (3)	0.0938 (14)
N3	0.03295 (17)	0.3881 (3)	0.42297 (19)	0.0486 (8)
N4	0.0768 (2)	0.5702 (4)	0.3819 (3)	0.0825 (12)
H4A	0.1177	0.5429	0.4039	0.099*
H4B	0.0706	0.6422	0.3578	0.099*
C1	0.10582 (19)	0.0789 (3)	0.9387 (2)	0.0467 (9)
C2	0.1580 (2)	0.1163 (4)	0.9074 (3)	0.0519 (10)
C3	0.1461 (2)	0.1762 (4)	0.8249 (3)	0.0623 (11)
C4	0.2278 (2)	0.0997 (4)	0.9569 (3)	0.0630 (12)
C5	0.1997 (2)	0.3066 (5)	0.3907 (3)	0.0756 (13)
H5	0.2252	0.3626	0.4309	0.091*
C6	0.2293 (3)	0.2487 (5)	0.3325 (4)	0.0922 (17)
H6	0.2749	0.2646	0.3346	0.111*
C7	0.1924 (3)	0.1688 (5)	0.2723 (3)	0.0878 (16)
H7	0.2124	0.1317	0.2325	0.105*
C8	0.1259 (3)	0.1428 (5)	0.2702 (3)	0.0771 (14)
H8	0.1007	0.0876	0.2292	0.092*
C9	0.0963 (2)	0.1980 (4)	0.3284 (3)	0.0623 (11)
H9	0.0512	0.1790	0.3270	0.075*
C10	0.1327 (2)	0.2820 (4)	0.3895 (2)	0.0543 (10)
C11	0.1030 (2)	0.3355 (4)	0.4583 (2)	0.0593 (11)
H11A	0.1011	0.2709	0.5000	0.071*
H11B	0.1331	0.4004	0.4889	0.071*
C12	0.0231 (2)	0.5009 (4)	0.3852 (2)	0.0547 (10)
C13	−0.0437 (3)	0.5437 (5)	0.3506 (3)	0.0735 (13)
H13	−0.0510	0.6219	0.3250	0.088*
C14	−0.0978 (3)	0.4719 (6)	0.3541 (3)	0.0826 (16)
H14	−0.1423	0.4995	0.3296	0.099*
C15	−0.0864 (3)	0.3576 (6)	0.3943 (4)	0.0835 (16)
H15	−0.1231	0.3080	0.3982	0.100*
C16	−0.0217 (3)	0.3186 (4)	0.4277 (3)	0.0712 (13)
H16	−0.0142	0.2415	0.4549	0.085*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0352 (4)	0.0506 (5)	0.0526 (4)	0.0029 (3)	0.0115 (3)	−0.0090 (3)
S1	0.0367 (5)	0.0617 (7)	0.0573 (6)	0.0055 (5)	0.0093 (4)	−0.0032 (5)
S2	0.0376 (5)	0.0602 (7)	0.0537 (6)	0.0044 (5)	0.0080 (4)	−0.0037 (5)
N1	0.073 (3)	0.104 (3)	0.103 (3)	0.020 (2)	0.038 (3)	0.037 (3)
N2	0.043 (2)	0.092 (3)	0.144 (4)	0.008 (2)	0.018 (3)	0.032 (3)
N3	0.053 (2)	0.0446 (19)	0.0499 (17)	0.0025 (15)	0.0167 (15)	0.0033 (14)
N4	0.070 (3)	0.066 (3)	0.102 (3)	−0.018 (2)	0.007 (2)	0.021 (2)
C1	0.041 (2)	0.038 (2)	0.055 (2)	0.0149 (17)	0.0029 (17)	−0.0129 (17)
C2	0.043 (2)	0.049 (2)	0.063 (2)	0.0108 (18)	0.0128 (19)	0.0061 (19)
C3	0.047 (3)	0.056 (3)	0.089 (3)	0.012 (2)	0.029 (2)	0.010 (3)
C4	0.038 (2)	0.059 (3)	0.095 (3)	0.007 (2)	0.022 (2)	0.015 (2)
C5	0.061 (3)	0.086 (4)	0.080 (3)	−0.005 (3)	0.019 (3)	−0.018 (3)
C6	0.065 (3)	0.118 (5)	0.102 (4)	0.009 (3)	0.036 (3)	−0.009 (4)
C7	0.094 (4)	0.102 (4)	0.073 (3)	0.023 (3)	0.034 (3)	−0.017 (3)
C8	0.096 (4)	0.072 (3)	0.065 (3)	−0.001 (3)	0.024 (3)	−0.011 (2)
C9	0.066 (3)	0.058 (3)	0.066 (3)	−0.001 (2)	0.022 (2)	0.003 (2)
C10	0.059 (3)	0.050 (2)	0.053 (2)	0.008 (2)	0.013 (2)	0.0070 (19)
C11	0.066 (3)	0.056 (3)	0.055 (2)	0.014 (2)	0.013 (2)	0.011 (2)
C12	0.061 (3)	0.050 (2)	0.049 (2)	−0.004 (2)	0.0066 (19)	0.002 (2)
C13	0.067 (3)	0.067 (3)	0.073 (3)	0.009 (3)	−0.005 (3)	0.002 (2)
C14	0.053 (3)	0.105 (5)	0.078 (3)	0.012 (3)	−0.002 (3)	−0.031 (3)
C15	0.061 (3)	0.099 (4)	0.100 (4)	−0.023 (3)	0.037 (3)	−0.033 (3)
C16	0.084 (4)	0.056 (3)	0.088 (3)	−0.011 (3)	0.048 (3)	−0.002 (2)

Geometric parameters (Å, °)

Ni1—S2	2.2074 (11)	C6—C7	1.356 (7)
Ni1—S2^{i}	2.2074 (11)	C6—H6	0.9300
Ni1—S1	2.2173 (11)	C7—C8	1.368 (7)
Ni1—S1^{i}	2.2173 (11)	C7—H7	0.9300
S1—C1	1.734 (4)	C8—C9	1.368 (6)
S2—C1	1.738 (4)	C8—H8	0.9300
N1—C3	1.133 (5)	C9—C10	1.389 (6)
N2—C4	1.140 (5)	C9—H9	0.9300
N3—C12	1.347 (5)	C10—C11	1.502 (6)
N3—C16	1.356 (5)	C11—H11A	0.9700
N3—C11	1.491 (5)	C11—H11B	0.9700
N4—C12	1.331 (5)	C12—C13	1.396 (6)
N4—H4A	0.8600	C13—C14	1.354 (7)
N4—H4B	0.8600	C13—H13	0.9300
C1—C2	1.345 (6)	C14—C15	1.379 (7)
C2—C3	1.428 (6)	C14—H14	0.9300
C2—C4	1.436 (5)	C15—C16	1.342 (7)
C5—C10	1.377 (6)	C15—H15	0.9300

C5—C6	1.382 (7)	C16—H16	0.9300
C5—H5	0.9300		
S2—Ni1—S2^{i}	180.000 (13)	C9—C8—C7	120.0 (5)
S2—Ni1—S1	79.16 (4)	C9—C8—H8	120.0
S2^{i}—Ni1—S1	100.84 (4)	C7—C8—H8	120.0
S2—Ni1—S1^{i}	100.84 (4)	C8—C9—C10	120.9 (4)
S2^{i}—Ni1—S1^{i}	79.16 (4)	C8—C9—H9	119.5
S1—Ni1—S1^{i}	180.0	C10—C9—H9	119.5
C1—S1—Ni1	86.03 (14)	C5—C10—C9	118.1 (4)
C1—S2—Ni1	86.24 (13)	C5—C10—C11	120.1 (4)
C12—N3—C16	119.8 (4)	C9—C10—C11	121.5 (4)
C12—N3—C11	121.6 (4)	N3—C11—C10	113.3 (3)
C16—N3—C11	118.5 (4)	N3—C11—H11A	108.9
C12—N4—H4A	120.0	C10—C11—H11A	108.9
C12—N4—H4B	120.0	N3—C11—H11B	108.9
H4A—N4—H4B	120.0	C10—C11—H11B	108.9
C2—C1—S1	125.3 (3)	H11A—C11—H11B	107.7
C2—C1—S2	126.1 (3)	N4—C12—N3	119.9 (4)
S1—C1—S2	108.6 (2)	N4—C12—C13	121.0 (4)
C1—C2—C3	121.4 (4)	N3—C12—C13	119.2 (4)
C1—C2—C4	120.9 (4)	C14—C13—C12	120.3 (5)
C3—C2—C4	117.7 (4)	C14—C13—H13	119.9
N1—C3—C2	178.4 (5)	C12—C13—H13	119.9
N2—C4—C2	179.3 (6)	C13—C14—C15	119.5 (5)
C10—C5—C6	120.4 (5)	C13—C14—H14	120.3
C10—C5—H5	119.8	C15—C14—H14	120.3
C6—C5—H5	119.8	C16—C15—C14	119.3 (5)
C7—C6—C5	120.5 (5)	C16—C15—H15	120.4
C7—C6—H6	119.8	C14—C15—H15	120.4
C5—C6—H6	119.8	C15—C16—N3	122.0 (5)
C6—C7—C8	120.0 (5)	C15—C16—H16	119.0
C6—C7—H7	120.0	N3—C16—H16	119.0
C8—C7—H7	120.0		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4A···N2^{ii}	0.86	2.25	2.986 (6)	143
C11—H11B···N2^{ii}	0.97	2.58	3.490 (6)	156
C13—H13···N1^{iii}	0.93	2.51	3.329 (7)	148

Symmetry codes: (ii) −*x*+1/2, *y*+1/2, −*z*+3/2; (iii) −*x*, −*y*+1, −*z*+1.

Fig. 1

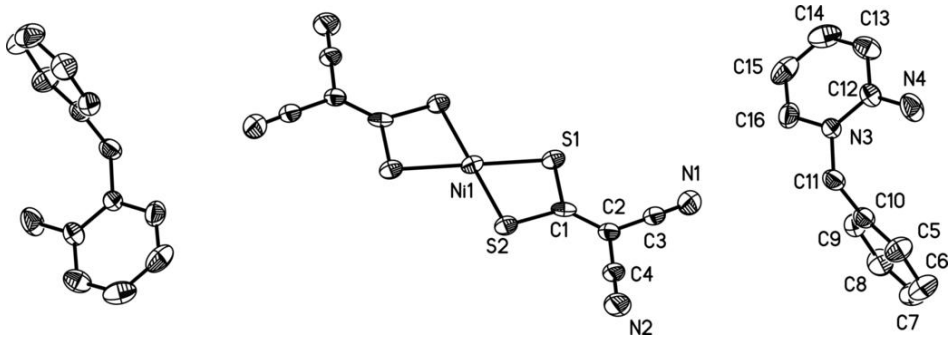
C14
C13
C15
C12
N4
C16
N3
C11
C10
C9
C5
C6
C8
C7
S1
Ni1
S2
C1
C2
C3
N1
C4
N2

Fig. 2