metal-organic compounds

Bis(piperidinium) bis(1,2-dicyanoethene-1,2-dithiolato-$\kappa^2 S,S'$)nickel(II)

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The title compound, $(C_5H_{12}N)_2[Ni(C_4N_2S_2)_2]$, is a new $[Ni(mnt)_2]^{2-}$ salt (mnt^{2-} is 1,2-dicyanoethene-1,2-dithiolate) with piperidinium $[(PIH)^+]$ cations. The Ni^{II} ion lies on an inversion centre and the asymmetric unit contains a $(PIH)^+$ cation and one half of the $[Ni(mnt)_2]^{2-}$ anion. The Ni^{II} ion exhibits a square-planar coordination geometry. In the crystal structure, weak C—H···N, C—H···S and C—H···Ni hydrogen bonds are observed between the anions and the cations.

Related literature

For background, see: Robertson & Cronin (2002). For a related $[Ni(mnt)_2]^{2-}$ complex of square-planar geometry and displaying C—H···S and C—H···Ni hydrogen bonds, see: Yang & Ni (2006). For other instances of C—H···Ni hydrogen bonds, see: Yang *et al.* (2004); Braga *et al.* (1997).
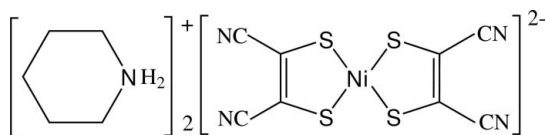
Experimental

Crystal data

$(C_5H_{12}N)_2[Ni(C_4N_2S_2)_2]$
$M_r = 511.38$
Triclinic, $P\bar{1}$
$a = 6.5959$ (9) Å
$b = 9.4351$ (13) Å
$c = 9.5669$ (13) Å

$\alpha = 91.477$ (2)°
$\beta = 100.083$ (2)°
$\gamma = 100.425$ (2)°
$V = 575.49$ (14) Å³
$Z = 1$

Mo $K\alpha$ radiation
$\mu = 1.22$ mm^{-1}
$T = 293$ (2) K
$0.41 \times 0.36 \times 0.24$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{min} = 0.622$, $T_{max} = 0.736$

3282 measured reflections
2213 independent reflections
2105 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.108$
$S = 1.07$
2213 reflections

133 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6B···N2	0.97	2.61	3.139 (4)	114
C7—H7B···N2	0.97	2.28	2.967 (4)	127
C7—H7A···S1^i	0.97	2.63	3.501 (3)	150
C7—H7B···N1^{ii}	0.97	2.29	3.124 (4)	143
C6—H6A···Ni1^i	0.97	2.82	3.420 (2)	121

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

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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2375).

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Robertson, N. & Cronin, L. (2002). *Coord. Chem. Rev.* **227**, 93–127.
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supplementary materials

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Comment

Salts containing $M(mnt)_2^{n-}$ anion have aroused great interest in recent years and the topology and the size of the counterions used with $Ni(mnt)_2^{2-}$ anions play an important role in tuning the stacks of anions and cations (Robertson & Cronin, 2002).

The structure of (I) consists of one $(PIH)^+$ cation and one-half of a $Ni(mnt)_2$ anion in the asymmetric unit as the Ni^{II} ion lies on an inversion centre. The NiS_4 core exhibits a square planar coordination geometry with Ni—S distances 2.182 (1) and 2.174 (1) Å respectively. The two N atoms of the CN groups deviate from the Ni1/S1/S2 plane by 0.392 (2) Å for N1 and 0.451 (2) Å for N2. The $(PIH)^+$ cation adopts a classical chair conformation. Five types of hydrogen bonds were observed in the crystal structure of the title complex: C6—H6B⋯N2, C7—H7B⋯N2, C7—H7A⋯S1, C7—H7B⋯N1 and C6—H6A⋯Ni1 (Table 1 and Fig. 2). C—H⋯Ni interactions are unusual but not unprecedented (Yang & Ni, 2006; Yang *et al.*, 2004; Braga *et al.*, 1997).

Experimental

The title compound was prepared by the direct reaction of $NiCl_2·6H_2O$, Na_2mnt and $(PIH)^+Cl^-$ in H_2O. Red block-like single crystals were obtained by slow evaporation of a CH_3CN solution at room temperature about two weeks.

Refinement

H atoms bonded to the piperidine N atom were located in a difference map and refined with distance restraints of N—H = 0.90 (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 = 0.97 Å, and with $U_{iso}(H) = 1.2$ times $U_{eq}(C)$.
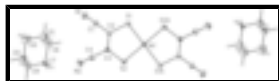
Figures

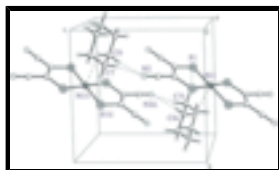Fig. 1. The molecular structure of (I), with atom labels and 30% probability displacement ellipsoids for non-H atoms.

Fig. 2. The hydrogen bonds between anions and cations.

Bis(piperidinium) bis(1,2-dicyanoethene-1,2-dithiolato-$\kappa^2 S,S'$)nickel(II)

Crystal data

$(C_5H_{12}N)_2[Ni(C_4N_2S_2)_2]$	$Z = 1$
$M_r = 511.38$	$F_{000} = 266$
Triclinic, $P\bar{1}$	$D_x = 1.476$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 6.5959$ (9) Å	Cell parameters from 2647 reflections
$b = 9.4351$ (13) Å	$\theta = 3.0–29.8º$
$c = 9.5669$ (13) Å	$\mu = 1.22$ mm^{-1}
$\alpha = 91.477$ (2)º	$T = 293$ (2) K
$\beta = 100.083$ (2)º	Block, red
$\gamma = 100.425$ (2)º	$0.41 \times 0.36 \times 0.24$ mm
$V = 575.49$ (14) Å^3	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	2213 independent reflections
Radiation source: fine-focus sealed tube	2105 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.015$
$T = 291(2)$ K	$\theta_{max} = 26.0º$
φ and ω scans	$\theta_{min} = 2.2º$
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -8 \rightarrow 7$
$T_{min} = 0.622$, $T_{max} = 0.736$	$k = -11 \rightarrow 10$
3282 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.035$	H-atom parameters constrained
$wR(F^2) = 0.108$	$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 0.3691P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
2213 reflections	$\Delta\rho_{max} = 0.63$ e Å^{-3}
133 parameters	$\Delta\rho_{min} = -0.45$ 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	0.5000	0.5000	0.0000	0.02917 (16)
S1	0.67713 (10)	0.37773 (7)	0.15080 (7)	0.03905 (19)
S2	0.24609 (10)	0.48199 (7)	0.11978 (7)	0.03761 (19)
N1	0.6624 (5)	0.2290 (3)	0.5088 (3)	0.0610 (7)
N2	0.1297 (5)	0.3650 (4)	0.4721 (3)	0.0616 (7)
N3	0.0823 (6)	−0.0310 (4)	0.7782 (5)	0.0899 (12)
H3A	0.1473	−0.0330	0.8688	0.108*
H3B	0.0572	−0.1212	0.7379	0.108*
C1	0.6037 (4)	0.2850 (3)	0.4081 (3)	0.0421 (6)
C2	0.5287 (4)	0.3541 (3)	0.2844 (3)	0.0351 (5)
C3	0.3420 (4)	0.4004 (3)	0.2707 (3)	0.0337 (5)
C4	0.2229 (4)	0.3819 (3)	0.3816 (3)	0.0406 (6)
C5	0.2229 (6)	0.0684 (4)	0.6987 (4)	0.0632 (9)
H5A	0.3568	0.0376	0.7062	0.076*
H5B	0.1593	0.0629	0.5988	0.076*
C6	0.2571 (5)	0.2211 (3)	0.7584 (3)	0.0522 (7)
H6A	0.3318	0.2282	0.8558	0.063*
H6B	0.3422	0.2840	0.7035	0.063*
C7	0.0525 (4)	0.2688 (2)	0.7541 (3)	0.0342 (5)
H7A	0.0782	0.3669	0.7951	0.041*
H7B	−0.0164	0.2688	0.6558	0.041*
C8	−0.0891 (6)	0.1742 (3)	0.8328 (4)	0.0529 (7)
H8A	−0.2225	0.2059	0.8229	0.063*
H8B	−0.0274	0.1813	0.9331	0.063*
C9	−0.1238 (6)	0.0194 (3)	0.7759 (4)	0.0585 (8)
H9A	−0.2014	0.0105	0.6791	0.070*
H9B	−0.2073	−0.0418	0.8330	0.070*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0303 (3)	0.0321 (3)	0.0261 (2)	0.00943 (17)	0.00428 (17)	0.00203 (16)
S1	0.0389 (4)	0.0475 (4)	0.0374 (4)	0.0201 (3)	0.0110 (3)	0.0122 (3)
S2	0.0332 (3)	0.0502 (4)	0.0334 (3)	0.0160 (3)	0.0073 (2)	0.0092 (3)
N1	0.0587 (16)	0.0760 (19)	0.0519 (16)	0.0217 (14)	0.0072 (13)	0.0293 (14)
N2	0.0522 (15)	0.092 (2)	0.0470 (15)	0.0183 (15)	0.0201 (13)	0.0165 (14)
N3	0.100 (3)	0.0516 (18)	0.115 (3)	0.0232 (18)	0.002 (2)	−0.0007 (18)
C1	0.0385 (14)	0.0478 (15)	0.0418 (15)	0.0110 (11)	0.0078 (11)	0.0114 (12)
C2	0.0370 (13)	0.0361 (12)	0.0326 (12)	0.0084 (10)	0.0057 (10)	0.0062 (9)
C3	0.0336 (12)	0.0365 (12)	0.0302 (12)	0.0060 (10)	0.0042 (9)	0.0032 (9)
C4	0.0367 (13)	0.0500 (15)	0.0355 (14)	0.0100 (11)	0.0055 (11)	0.0064 (11)
C5	0.059 (2)	0.0600 (19)	0.071 (2)	0.0180 (16)	0.0084 (17)	−0.0130 (16)
C6	0.0488 (17)	0.0530 (17)	0.0501 (17)	0.0038 (13)	0.0030 (13)	−0.0016 (13)
C7	0.0465 (14)	0.0247 (11)	0.0308 (12)	0.0076 (10)	0.0049 (10)	0.0020 (8)

C8	0.064 (2)	0.0479 (16)	0.0532 (17)	0.0147 (14)	0.0234 (15)	0.0085 (13)
C9	0.063 (2)	0.0414 (15)	0.068 (2)	0.0025 (14)	0.0093 (16)	0.0082 (14)

Geometric parameters (Å, °)

Ni1—S2^i	2.1739 (7)	C5—C6	1.500 (4)
Ni1—S2	2.1739 (7)	C5—H5A	0.9700
Ni1—S1^i	2.1819 (6)	C5—H5B	0.9700
Ni1—S1	2.1819 (6)	C6—C7	1.492 (4)
S1—C2	1.737 (3)	C6—H6A	0.9700
S2—C3	1.730 (3)	C6—H6B	0.9700
N1—C1	1.151 (4)	C7—C8	1.489 (4)
N2—C4	1.145 (4)	C7—H7A	0.9700
N3—C5	1.512 (5)	C7—H7B	0.9700
N3—C9	1.517 (5)	C8—C9	1.508 (4)
N3—H3A	0.9000	C8—H8A	0.9700
N3—H3B	0.9000	C8—H8B	0.9700
C1—C2	1.422 (4)	C9—H9A	0.9700
C2—C3	1.366 (4)	C9—H9B	0.9700
C3—C4	1.422 (4)		
S2^i—Ni1—S2	180.00 (4)	N3—C5—H5B	109.5
S2^i—Ni1—S1^i	92.32 (2)	H5A—C5—H5B	108.1
S2—Ni1—S1^i	87.68 (2)	C7—C6—C5	110.6 (3)
S2^i—Ni1—S1	87.68 (2)	C7—C6—H6A	109.5
S2—Ni1—S1	92.32 (2)	C5—C6—H6A	109.5
S1^i—Ni1—S1	180.00 (3)	C7—C6—H6B	109.5
C2—S1—Ni1	102.68 (9)	C5—C6—H6B	109.5
C3—S2—Ni1	102.88 (9)	H6A—C6—H6B	108.1
C5—N3—C9	110.8 (3)	C8—C7—C6	112.4 (2)
C5—N3—H3A	109.5	C8—C7—H7A	109.1
C9—N3—H3A	109.5	C6—C7—H7A	109.1
C5—N3—H3B	109.5	C8—C7—H7B	109.1
C9—N3—H3B	109.5	C6—C7—H7B	109.1
H3A—N3—H3B	108.1	H7A—C7—H7B	107.9
N1—C1—C2	179.3 (3)	C7—C8—C9	110.3 (3)
C3—C2—C1	120.4 (2)	C7—C8—H8A	109.6
C3—C2—S1	120.59 (19)	C9—C8—H8A	109.6
C1—C2—S1	119.0 (2)	C7—C8—H8B	109.6
C2—C3—C4	120.1 (2)	C9—C8—H8B	109.6
C2—C3—S2	121.05 (19)	H8A—C8—H8B	108.1
C4—C3—S2	118.9 (2)	C8—C9—N3	111.4 (3)
N2—C4—C3	178.5 (3)	C8—C9—H9A	109.3
C6—C5—N3	110.6 (3)	N3—C9—H9A	109.3
C6—C5—H5A	109.5	C8—C9—H9B	109.3
N3—C5—H5A	109.5	N3—C9—H9B	109.3
C6—C5—H5B	109.5	H9A—C9—H9B	108.0

Symmetry codes: (i) −x+1, −y+1, −z.

Hydrogen-bond geometry (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C6—H6B$\cdots$N2	0.97	2.61	3.139 (4)	114
C7—H7B$\cdots$N2	0.97	2.28	2.967 (4)	127
C7—H7A$\cdots$S1[ii]	0.97	2.63	3.501 (3)	150
C7—H7B$\cdots$N1[iii]	0.97	2.29	3.124 (4)	143
C6—H6A$\cdots$Ni1	0.97	Missing	Missing	Missing

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

Fig. 1

Fig. 2