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

Jia-Rong Zhou, Yong Hou and Chun-Lin Ni*

Department of Applied Chemistry, College of Science, South China Agricultural University, Guangzhou 510642, People's Republic of China
Correspondence e-mail: niclchem@scau.edu.cn

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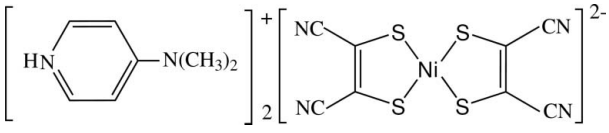
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.002 Å; R factor = 0.028; wR factor = 0.079; data-to-parameter ratio = 18.4.

The asymmetric unit of the title ion-pair complex, $(C_7H_{11}N_2)_2[Ni(C_4N_2S_2)_2]$ or $(DMAPH)_2[Ni(mnt)_2]$ [where DMAPH is 4-(dimethylamino)pyridinium and mnt is maleonitriledithiolate], consists of one cation and one half-anion, the Ni^{II} atom lying on a crystallographic centre of symmetry. The metal is coordinated by four S atoms of two mnt^{2-} ligands in a square-planar geometry. The $[Ni(mnt)_2]^{2-}$ anions (*A*) and $DMAPH^+$ cations (*C*) are stacked in an *ACCA* arrangement to form one-dimensional columns along the *a* axis, with a centroid–centroid separation between the pyridine rings of 4.032 (4) Å. The columns are linked by intermolecular N—H···N hydrogen bonds, resulting in a two-dimensional network.

Related literature

For general background, see: Robertson & Cronin (2002). For a related structure, see: (Zhou & Ren, 2006).



Experimental

Crystal data

$(C_7H_{11}N_2)_2[Ni(C_4N_2S_2)_2]$
M_r = 585.43
Monoclinic, $P2_1/c$
a = 14.1631 (12) Å
b = 6.5833 (6) Å
c = 15.0751 (13) Å
β = 114.771 (1)°
V = 1276.27 (19) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.12 mm^{-1}
T = 291 (2) K
0.46 × 0.40 × 0.15 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.628, T_{max} = 0.851
8238 measured reflections
3075 independent reflections
2744 reflections with $I > 2\sigma(I)$
R_{int} = 0.015

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.079
S = 1.08
3075 reflections
167 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···N1^{i}	0.89 (3)	2.34 (3)	3.040 (2)	135 (2)

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 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: RZ2152).

References

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supplementary materials

Acta Cryst. (2007). E**63**, m2030 [**doi:10.1107/S1600536807031157**]

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

J.-R. Zhou, Y. Hou and C.-L. Ni

Comment

The syntheses, crystal structures and properties of maleonitriledithiolate (mnt^{2-}) transition metal complexes have received much attention in many areas such as non-linear optics and magnetic and conducting materials [Robertson & Cronin, 2002]. The introduction of some organic cations was recognized to be a powerful strategy to tune the stacking pattern of the $Ni(mnt)_2$ dianion in order to obtain molecular materials with unusual magnetic properties.

The asymmetric unit of the title compound consists of one $DMAPH^+$ cation (DMAPH is 4-dimethylaminopyridinium) and one half-anion of formula $Ni(mnt)_2^{2-}$ (mnt is 1,2-dicyanoethylene-1,2-dithiolate or maleonitriledithiolate). The nickel(II) metal, which lies on a crystallographic centre of symmetry, is coordinated by four S atoms from two mnt ligands in a square planar geometry (Fig. 1). The five-membered chelating ring is essentially planar (maximum displacement 0.019 (2) Å for atom C2). The conformations of anion and cation are similar to those observed in the corresponding copper(II) complex (Zhou & Ren, 2006). The $Ni(mnt)_2$ anions (A) and $DMAPH^+$ cations (C) are stacked in a ACCA arrangement to form one-dimensional columns along the *a* axis, with a centroid···centroid separation between the pyridine rings of 4.032 (4) Å. The columns are linked by intermolecular N—H···N hydrogen bonds (Table 1) resulting in a two-dimensional network (Fig. 2).

Experimental

The title compound was prepared by the direct reaction of $NiCl_2·6H_2O$ (1 mmol, 0.24 g), Na_2mnt (2 mmol, 0.37 g) and 4-dimethylaminopyridinium chloride (2 mmol, 0.32 g) in water (60 ml). Red block-shaped single crystals were obtained by slow evaporation of a CH_3CN solution at room temperature for about two weeks.

Refinement

The pyridinium H atom was located in a difference Fourier map and refined freely. All other H atoms were placed in geometrically calculated positions with C—H = 0.93–0.96 Å, and refined using the riding atom approximation, with $U_{iso}(H)$ = 1.2 $U_{eq}(C)$ or 1.5 $U_{eq}(C)$ for the methyl groups.

Figures

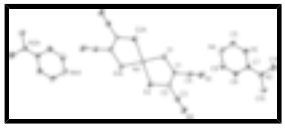

Fig. 1. The molecular structure of the title compound, with atom-labelling scheme and 30% probability displacement ellipsoids. H atoms are omitted for clarity. Atoms labelled with the suffix A are generated by the symmetry operator (−*x*, −*y*, −*z*).

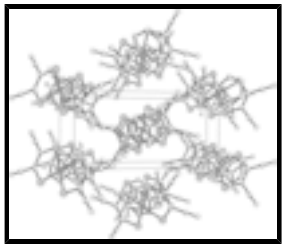

Fig. 2. A perspective view of the crystal packing of the title compound viewed along the *a* axis. H atoms are omitted for clarity.

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

Crystal data

$(C_7H_{11}N_2)_2[Ni(C_4N_2S_2)_2]$	F_{000} = 604
M_r = 585.43	D_x = 1.523 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 4341 reflections
a = 14.1631 (12) Å	θ = 2.7–29.3º
b = 6.5833 (6) Å	μ = 1.12 mm^{-1}
c = 15.0751 (13) Å	T = 291 (2) K
β = 114.7710 (10)º	Block, red
V = 1276.27 (19) Å^3	0.46 × 0.40 × 0.15 mm
Z = 2	

Data collection

Bruker SMART APEX CCD diffractometer	3075 independent reflections
Radiation source: fine-focus sealed tube	2744 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.015
T = 291(2) K	θ_{max} = 28.0º
φ and ω scans	θ_{min} = 2.7º
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	h = −10→18
T_{min} = 0.628, T_{max} = 0.851	k = −8→8
8238 measured reflections	l = −19→15

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.028	$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 0.1627P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.079	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.08	$\Delta\rho_{max}$ = 0.37 e Å^{-3}

3075 reflections	$\Delta\rho_{min} = -0.24$ e Å^{-3}
167 parameters	Extinction correction: SHELXTL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0060 (8)
Secondary atom site location: difference Fourier map	

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.0000	0.0000	0.0000	0.03144 (10)
S1	0.09496 (3)	0.27334 (6)	0.03137 (3)	0.04174 (12)
S2	0.11660 (3)	−0.16103 (6)	0.12276 (3)	0.04267 (12)
C1	0.20511 (11)	0.2056 (2)	0.13333 (11)	0.0355 (3)
C2	0.21416 (12)	0.0182 (2)	0.17392 (11)	0.0360 (3)
C3	0.30409 (13)	−0.0369 (2)	0.25921 (12)	0.0423 (4)
C4	0.28715 (12)	0.3503 (2)	0.17446 (12)	0.0418 (3)
N1	0.35347 (13)	0.4638 (2)	0.20822 (13)	0.0602 (4)
N2	0.37520 (13)	−0.0796 (3)	0.32811 (12)	0.0621 (4)
C5	0.57111 (14)	0.1127 (3)	−0.10347 (14)	0.0569 (5)
H5	0.5327	0.1986	−0.1550	0.068*
C6	0.66305 (13)	0.1782 (3)	−0.03421 (13)	0.0484 (4)
H6	0.6866	0.3081	−0.0385	0.058*
C7	0.72351 (12)	0.0507 (2)	0.04465 (11)	0.0382 (3)
C8	0.68034 (14)	−0.1433 (3)	0.04575 (14)	0.0486 (4)
H8	0.7159	−0.2338	0.0961	0.058*
C9	0.58738 (15)	−0.1975 (3)	−0.02630 (16)	0.0572 (5)
H9	0.5602	−0.3252	−0.0244	0.069*
C10	0.88001 (16)	−0.0288 (3)	0.18988 (14)	0.0552 (5)
H10A	0.8451	−0.0643	0.2302	0.083*
H10B	0.9447	0.0368	0.2290	0.083*
H10C	0.8932	−0.1495	0.1612	0.083*
C11	0.85807 (15)	0.3081 (3)	0.11201 (15)	0.0578 (5)
H11A	0.8942	0.3057	0.0705	0.087*
H11B	0.9056	0.3447	0.1771	0.087*
H11C	0.8028	0.4060	0.0876	0.087*
H4	0.472 (2)	−0.107 (4)	−0.1457 (19)	0.094 (9)*
N3	0.81502 (10)	0.1083 (2)	0.11314 (10)	0.0425 (3)
N4	0.53422 (12)	−0.0721 (3)	−0.09962 (13)	0.0596 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.02752 (15)	0.03259 (15)	0.03065 (15)	−0.00072 (9)	0.00868 (11)	0.00233 (9)
S1	0.0343 (2)	0.0353 (2)	0.0432 (2)	−0.00337 (14)	0.00413 (16)	0.00727 (15)
S2	0.0382 (2)	0.0373 (2)	0.0404 (2)	−0.00338 (15)	0.00455 (16)	0.00841 (15)
C1	0.0302 (7)	0.0374 (7)	0.0356 (7)	0.0001 (6)	0.0104 (6)	−0.0025 (6)
C2	0.0303 (7)	0.0400 (8)	0.0336 (7)	0.0018 (5)	0.0093 (6)	−0.0005 (5)

C3	0.0384 (8)	0.0399 (7)	0.0416 (9)	0.0033 (6)	0.0099 (7)	−0.0001 (6)
C4	0.0357 (8)	0.0403 (8)	0.0417 (8)	0.0008 (6)	0.0085 (6)	0.0020 (6)
N1	0.0455 (9)	0.0502 (8)	0.0626 (10)	−0.0107 (7)	0.0007 (7)	0.0012 (7)
N2	0.0491 (9)	0.0626 (10)	0.0536 (9)	0.0113 (8)	0.0008 (7)	0.0056 (8)
C5	0.0447 (9)	0.0711 (13)	0.0450 (9)	0.0119 (9)	0.0092 (8)	0.0012 (8)
C6	0.0460 (9)	0.0480 (9)	0.0476 (9)	0.0029 (7)	0.0162 (7)	0.0034 (7)
C7	0.0358 (8)	0.0428 (7)	0.0380 (8)	−0.0001 (6)	0.0174 (6)	−0.0031 (6)
C8	0.0459 (9)	0.0437 (8)	0.0549 (10)	−0.0032 (7)	0.0198 (8)	−0.0002 (7)
C9	0.0496 (10)	0.0505 (10)	0.0726 (13)	−0.0114 (8)	0.0267 (10)	−0.0149 (9)
C10	0.0484 (10)	0.0668 (12)	0.0411 (9)	0.0072 (8)	0.0095 (8)	0.0001 (8)
C11	0.0544 (11)	0.0585 (11)	0.0591 (11)	−0.0190 (9)	0.0224 (9)	−0.0131 (9)
N3	0.0368 (7)	0.0470 (7)	0.0401 (7)	−0.0027 (6)	0.0126 (5)	−0.0033 (6)
N4	0.0366 (8)	0.0743 (11)	0.0589 (10)	−0.0031 (8)	0.0113 (7)	−0.0196 (9)

Geometric parameters (Å, °)

Ni1—S2	2.1714 (4)	C7—N3	1.330 (2)
Ni1—S2^{i}	2.1714 (4)	C7—C8	1.419 (2)
Ni1—S1	2.1766 (4)	C8—C9	1.357 (3)
Ni1—S1^{i}	2.1766 (4)	C8—H8	0.9300
S1—C1	1.7278 (15)	C9—N4	1.332 (3)
S2—C2	1.7330 (15)	C9—H9	0.9300
C1—C2	1.359 (2)	C10—N3	1.452 (2)
C1—C4	1.428 (2)	C10—H10A	0.9600
C2—C3	1.426 (2)	C10—H10B	0.9600
C3—N2	1.138 (2)	C10—H10C	0.9600
C4—N1	1.140 (2)	C11—N3	1.453 (2)
C5—N4	1.335 (3)	C11—H11A	0.9600
C5—C6	1.354 (3)	C11—H11B	0.9600
C5—H5	0.9300	C11—H11C	0.9600
C6—C7	1.414 (2)	N4—H4	0.89 (3)
C6—H6	0.9300		
S2—Ni1—S2^{i}	180.00 (4)	C9—C8—C7	120.37 (17)
S2—Ni1—S1	92.200 (14)	C9—C8—H8	119.8
S2^{i}—Ni1—S1	87.800 (14)	C7—C8—H8	119.8
S2—Ni1—S1^{i}	87.800 (14)	N4—C9—C8	121.51 (18)
S2^{i}—Ni1—S1^{i}	92.200 (14)	N4—C9—H9	119.2
S1—Ni1—S1^{i}	180.00 (2)	C8—C9—H9	119.2
C1—S1—Ni1	103.03 (5)	N3—C10—H10A	109.5
C2—S2—Ni1	103.11 (5)	N3—C10—H10B	109.5
C2—C1—C4	120.26 (13)	H10A—C10—H10B	109.5
C2—C1—S1	120.95 (12)	N3—C10—H10C	109.5
C4—C1—S1	118.78 (11)	H10A—C10—H10C	109.5
C1—C2—C3	121.12 (14)	H10B—C10—H10C	109.5
C1—C2—S2	120.69 (12)	N3—C11—H11A	109.5
C3—C2—S2	118.19 (11)	N3—C11—H11B	109.5
N2—C3—C2	179.0 (2)	H11A—C11—H11B	109.5

N1—C4—C1	179.03 (19)	N3—C11—H11C	109.5
N4—C5—C6	121.62 (18)	H11A—C11—H11C	109.5
N4—C5—H5	119.2	H11B—C11—H11C	109.5
C6—C5—H5	119.2	C7—N3—C10	121.84 (15)
C5—C6—C7	120.49 (18)	C7—N3—C11	121.77 (15)
C5—C6—H6	119.8	C10—N3—C11	116.30 (15)
C7—C6—H6	119.8	C9—N4—C5	120.39 (16)
N3—C7—C6	122.23 (15)	C9—N4—H4	120.9 (18)
N3—C7—C8	122.16 (16)	C5—N4—H4	118.6 (18)
C6—C7—C8	115.61 (15)		
S2—Ni1—S1—C1	−0.14 (5)	N4—C5—C6—C7	0.4 (3)
$S2^{i}$—Ni1—S1—C1	179.86 (5)	C5—C6—C7—N3	178.82 (16)
S1—Ni1—S2—C2	0.74 (6)	C5—C6—C7—C8	−0.9 (3)
$S1^{i}$—Ni1—S2—C2	−179.26 (6)	N3—C7—C8—C9	−179.04 (17)
Ni1—S1—C1—C2	−0.76 (14)	C6—C7—C8—C9	0.7 (3)
Ni1—S1—C1—C4	179.09 (11)	C7—C8—C9—N4	0.1 (3)
C4—C1—C2—C3	1.4 (2)	C6—C7—N3—C10	−175.46 (16)
S1—C1—C2—C3	−178.76 (13)	C8—C7—N3—C10	4.3 (3)
C4—C1—C2—S2	−178.27 (12)	C6—C7—N3—C11	1.0 (2)
S1—C1—C2—S2	1.57 (19)	C8—C7—N3—C11	−179.29 (16)
Ni1—S2—C2—C1	−1.46 (14)	C8—C9—N4—C5	−0.7 (3)
Ni1—S2—C2—C3	178.86 (12)	C6—C5—N4—C9	0.4 (3)

Symmetry codes: (i) −*x*, −*y*, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···$N1^{ii}$	0.89 (3)	2.34 (3)	3.040 (2)	135 (2)

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

Fig. 1

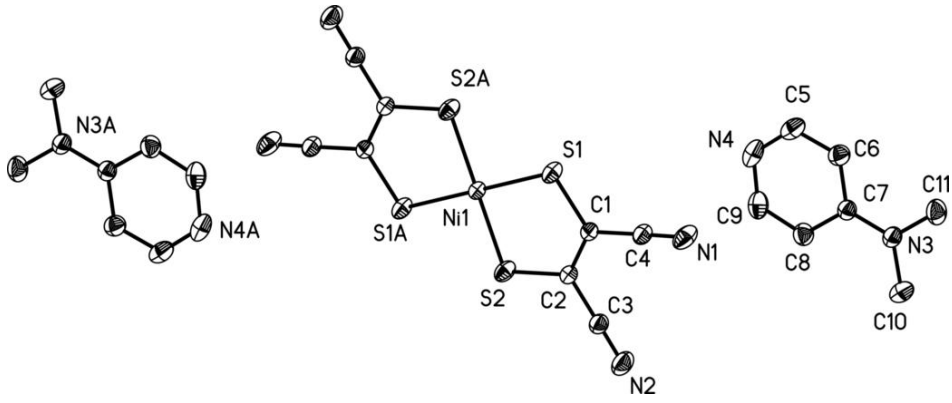
N3A
N4A
S2A
S1A
Ni1
S1
S2
C1
C2
C3
C4
N1
N2
C5
N4
C6
C7
C8
C9
C11
N3
C10

Fig. 2