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3,3'-Dimethyl-1,1'-(propane-1,3-diyl)-diimidazol-1-ium bis(1,2-dicyanoethene-1,2-dithiolato- κ^2 S,S')nickelate(II)

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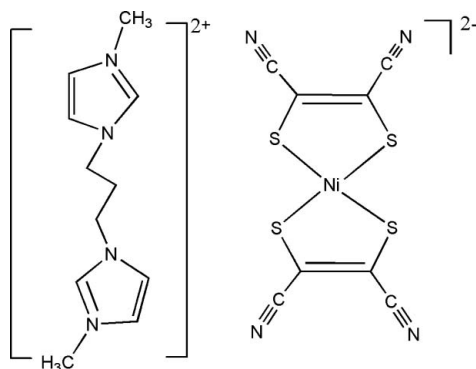
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.037; wR factor = 0.101; data-to-parameter ratio = 20.0.

In the title compound, $(\text{C}_{11}\text{H}_{18}\text{N}_4)[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]$, the asymmetric contains one half-complex, with the cation placed on a twofold axis and the anion located on an inversion center. The Ni^{II} ion in the anion is coordinated by four S atoms of two maleonitriledithiolate ligands, and exhibits the expected square-planar coordination geometry.

Related literature

For the design of functional materials, see: Robertson & Cronin (2002). For near-infrared dyes, conducting, magnetic and non-linear optical materials, see: Nishijo *et al.* (2000); Ni *et al.* (2005). For related structures, see: Ni *et al.* (2004); Ren *et al.* (2004, 2008); Duan *et al.* (2010); For the synthesis of the title compound, see: Davison & Holm (1967); Yao *et al.* (2008).



Experimental

Crystal data

$(\text{C}_{11}\text{H}_{18}\text{N}_4)[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]$
 $M_r = 545.38$
 Monoclinic, $C2/c$
 $a = 19.3683$ (15) Å
 $b = 7.3026$ (6) Å
 $c = 17.5170$ (14) Å
 $\beta = 104.167$ (1)°

$V = 2402.2$ (3) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.18$ mm⁻¹
 $T = 293$ K
 $0.4 \times 0.3 \times 0.3$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
 $T_{\text{min}} = 0.702$, $T_{\text{max}} = 0.741$
 7551 measured reflections
 2938 independent reflections
 2503 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.067$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.101$
 $S = 1.06$
 2938 reflections
 147 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.68$ e Å⁻³

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); 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: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2362).

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3,3'-Dimethyl-1,1'-(propane-1,3-diyl)diimidazol-1-ium bis(1,2-dicyanoethene-1,2-dithiolato- κ^2 S,S')nickelate(II)

Shan-Shan Yu, Hai-Bao Duan and Xiao-Ming Ren

S1. Comment

Supramolecular chemistry and molecular crystal engineering, which is the planning and utilization of crystal-oriented syntheses for the bottom-up construction of functional molecular solids from molecules and ions, are powerful tools for the assembly of designed functional materials (Robertson & Cronin, 2002). The use of bis-1,2-dithiolene complexes of transition metals as building units in the construction of such molecule based materials has received extensive attention due to their potential applications in the areas of near-infrared (near-IR) dyes, conducting, magnetic and nonlinear optical materials (Nishijo *et al.*, 2000; Ni *et al.*, 2005). Herein we report the crystal structure of the title compound (Fig. 1), which belongs to this class of materials.

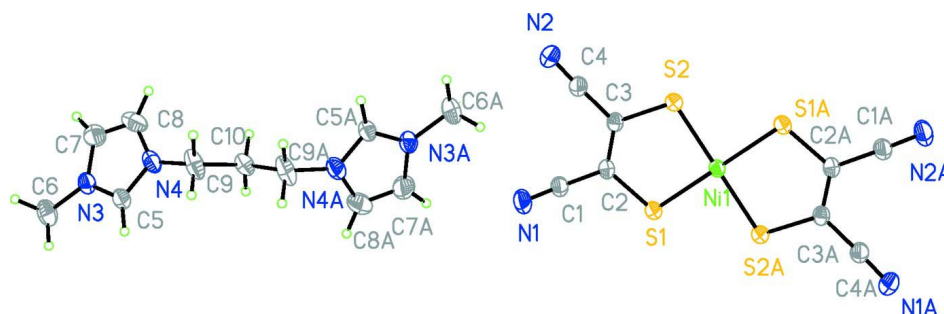
The compound crystallizes in monoclinic system, with one half of $[\text{Ni}(\text{mnt})_2]^{2-}$ dianion (*mnt* = maleonitriledithiolate) and one half of 3,3-dimethyl-1,1-(propane-1,3-diyl)diimidazol-1-ium dication in the asymmetric unit. The Ni center in the $[\text{Ni}(\text{mnt})_2]^{2-}$ anion is coordinated by four S atoms of two mnt^{2-} ligands, and exhibits the expected square-planar coordination geometry. The bond lengths and angles in the anion are in good agreement with those observed in other $[\text{Ni}(\text{mnt})_2]^{2-}$ complexes (Ni *et al.*, 2004; Ren *et al.*, 2004, 2008; Duan *et al.*, 2010).

S2. Experimental

All reagents and chemicals were purchased from commercial sources and used without further purification. The starting materials disodium maleonitriledithiolate and 1-methyl-3-(3-(1-methyl-imidazole-3-yl)propyl)-imidazolium iodide were synthesized following the literature procedures (Davison & Holm, 1967; Yao *et al.*, 2008). Disodium maleonitriledithiolate (456 mg, 2.5 mmol) and nickel chloride hexahydrate (297 mg, 1.25 mmol) were mixed under stirring in water (20 ml) at room temperature. Subsequently, a solution of 1-methyl-3-(3-(1-methyl-imidazole-3-yl)propyl)-imidazolium iodide (1.5 mmol) in methanol (10 ml) was added to the mixture, and the red precipitate that immediately formed was filtered off, and washed with methanol. The crude product was recrystallized in acetone (20 ml) to give red block crystals.

S3. Refinement

The C-bound H atoms were placed in geometrically idealized positions with C—H bond lengths fixed to 0.97 (methylene CH_2) 0.96 (methyl CH_3), and 0.93 Å (aromatic CH), and refined as riding atoms. Isotropic displacement parameters of the H atom were set at $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene and aromatic H atoms, and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

**Figure 1**

The molecular structure of the title compound, showing displacement ellipsoids at the 30% probability level.

3,3'-Dimethyl-1,1'-(propane-1,3-diyl)diimidazol-1-ium bis(1,2-dicyanoethene-1,2-dithiolato- κ^2S,S')nickelate(II)

Crystal data

(C₁₁H₁₈N₄)[Ni(C₄N₂S₂)₂]

$M_r = 545.38$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 19.3683$ (15) Å

$b = 7.3026$ (6) Å

$c = 17.5170$ (14) Å

$\beta = 104.167$ (1)°

$V = 2402.2$ (3) Å³

$Z = 4$

$F(000) = 1120.0$

$D_x = 1.508$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

$\mu = 1.18$ mm⁻¹

$T = 293$ K

Block, red

$0.4 \times 0.3 \times 0.3$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 1999)

$T_{\min} = 0.702$, $T_{\max} = 0.741$

7551 measured reflections

2938 independent reflections

2503 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.067$

$\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 2.2^\circ$

$h = -19 \rightarrow 25$

$k = -8 \rightarrow 9$

$l = -23 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.101$

$S = 1.06$

2938 reflections

147 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

$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.2056P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.31$ e Å⁻³

$\Delta\rho_{\min} = -0.68$ e Å⁻³

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ni1	0.2500	0.7500	0.0000	0.03604 (12)	
S1	0.34431 (2)	0.65936 (7)	0.08669 (3)	0.04682 (15)	

S2	0.18479 (2)	0.72779 (7)	0.08353 (3)	0.04539 (14)	
N1	0.40853 (10)	0.5664 (3)	0.29918 (11)	0.0762 (6)	
N2	0.19161 (11)	0.6190 (3)	0.28956 (11)	0.0698 (5)	
N3	0.61640 (10)	0.7743 (2)	1.00222 (10)	0.0491 (4)	
N4	0.54547 (9)	0.8708 (2)	0.89552 (10)	0.0576 (4)	
C1	0.36589 (10)	0.5949 (3)	0.24289 (11)	0.0516 (4)	
C2	0.31437 (9)	0.6359 (2)	0.17168 (10)	0.0416 (4)	
C3	0.24477 (9)	0.6629 (2)	0.17021 (10)	0.0401 (4)	
C4	0.21663 (10)	0.6392 (3)	0.23745 (11)	0.0492 (4)	
C5	0.61229 (10)	0.8655 (3)	0.93644 (11)	0.0475 (4)	
H5A	0.6506	0.9180	0.9212	0.057*	
C6	0.68163 (15)	0.7392 (3)	1.06347 (14)	0.0661 (7)	
H6A	0.7213	0.7962	1.0491	0.099*	
H6B	0.6896	0.6096	1.0689	0.099*	
H6C	0.6767	0.7889	1.1126	0.099*	
C7	0.55032 (15)	0.7161 (4)	1.00398 (16)	0.0803 (8)	
H7A	0.5380	0.6474	1.0434	0.096*	
C8	0.50654 (15)	0.7773 (5)	0.9379 (2)	0.0919 (10)	
H8A	0.4575	0.7592	0.9231	0.110*	
C9	0.52021 (13)	0.9711 (3)	0.82143 (13)	0.0750 (7)	
H9A	0.5573	1.0547	0.8150	0.090*	
H9B	0.4792	1.0439	0.8248	0.090*	
C10	0.5000	0.8508 (4)	0.7500	0.0559 (7)	
H10A	0.4602	0.7731	0.7532	0.067*	0.50
H10B	0.5398	0.7731	0.7468	0.067*	0.50

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.03490 (18)	0.03872 (19)	0.03238 (19)	-0.00051 (11)	0.00419 (13)	-0.00245 (11)
S1	0.0380 (2)	0.0625 (3)	0.0377 (2)	0.00491 (19)	0.00505 (18)	0.0005 (2)
S2	0.0379 (2)	0.0577 (3)	0.0397 (3)	0.00376 (18)	0.00789 (19)	0.00350 (19)
N1	0.0665 (12)	0.1072 (17)	0.0468 (10)	0.0188 (12)	-0.0018 (9)	0.0070 (11)
N2	0.0691 (11)	0.0954 (14)	0.0488 (10)	0.0063 (11)	0.0220 (9)	0.0090 (10)
N3	0.0537 (9)	0.0483 (9)	0.0413 (9)	-0.0086 (7)	0.0039 (7)	-0.0020 (7)
N4	0.0479 (9)	0.0663 (10)	0.0497 (9)	-0.0038 (8)	-0.0049 (7)	-0.0074 (8)
C1	0.0493 (10)	0.0627 (11)	0.0406 (9)	0.0054 (9)	0.0065 (8)	-0.0019 (9)
C2	0.0462 (9)	0.0413 (8)	0.0344 (8)	0.0003 (7)	0.0042 (7)	-0.0017 (7)
C3	0.0459 (9)	0.0382 (8)	0.0346 (8)	-0.0023 (7)	0.0069 (7)	-0.0022 (7)
C4	0.0503 (10)	0.0539 (10)	0.0423 (10)	0.0019 (8)	0.0091 (8)	0.0012 (8)
C5	0.0454 (9)	0.0498 (10)	0.0423 (10)	-0.0046 (8)	0.0012 (7)	0.0019 (8)
C6	0.0740 (15)	0.0568 (13)	0.0549 (14)	0.0002 (10)	-0.0086 (12)	0.0085 (9)
C7	0.0686 (16)	0.112 (2)	0.0614 (15)	-0.0278 (15)	0.0177 (13)	0.0053 (14)
C8	0.0446 (12)	0.140 (3)	0.087 (2)	-0.0210 (14)	0.0079 (13)	0.0053 (19)
C9	0.0783 (15)	0.0643 (13)	0.0611 (13)	0.0102 (12)	-0.0238 (12)	-0.0046 (11)
C10	0.0481 (14)	0.0592 (17)	0.0525 (16)	0.000	-0.0027 (12)	0.000

Geometric parameters (Å, °)

Ni1—S2 ⁱ	2.1603 (5)	C2—C3	1.356 (3)
Ni1—S2	2.1603 (5)	C3—C4	1.424 (3)
Ni1—S1	2.1732 (4)	C5—H5A	0.9300
Ni1—S1 ⁱ	2.1732 (4)	C6—H6A	0.9600
S1—C2	1.7334 (18)	C6—H6B	0.9600
S2—C3	1.7369 (17)	C6—H6C	0.9600
N1—C1	1.140 (2)	C7—C8	1.334 (4)
N2—C4	1.143 (3)	C7—H7A	0.9300
N3—C5	1.316 (2)	C8—H8A	0.9300
N3—C7	1.356 (3)	C9—C10	1.500 (3)
N3—C6	1.466 (3)	C9—H9A	0.9700
N4—C5	1.318 (2)	C9—H9B	0.9700
N4—C8	1.364 (4)	C10—C9 ⁱⁱ	1.500 (3)
N4—C9	1.466 (3)	C10—H10A	0.9700
C1—C2	1.426 (2)	C10—H10B	0.9700
S2 ⁱ —Ni1—S2	180.00 (3)	N3—C6—H6A	109.5
S2 ⁱ —Ni1—S1	88.018 (18)	N3—C6—H6B	109.5
S2—Ni1—S1	91.983 (18)	H6A—C6—H6B	109.5
S2 ⁱ —Ni1—S1 ⁱ	91.983 (18)	N3—C6—H6C	109.5
S2—Ni1—S1 ⁱ	88.017 (18)	H6A—C6—H6C	109.5
S1—Ni1—S1 ⁱ	180.000 (17)	H6B—C6—H6C	109.5
C2—S1—Ni1	103.27 (6)	C8—C7—N3	106.2 (2)
C3—S2—Ni1	103.64 (6)	C8—C7—H7A	126.9
C5—N3—C7	108.85 (19)	N3—C7—H7A	126.9
C5—N3—C6	125.85 (19)	C7—C8—N4	108.8 (2)
C7—N3—C6	125.3 (2)	C7—C8—H8A	125.6
C5—N4—C8	106.8 (2)	N4—C8—H8A	125.6
C5—N4—C9	124.5 (2)	N4—C9—C10	114.08 (19)
C8—N4—C9	128.5 (2)	N4—C9—H9A	108.7
N1—C1—C2	177.7 (2)	C10—C9—H9A	108.7
C3—C2—C1	121.79 (17)	N4—C9—H9B	108.7
C3—C2—S1	120.62 (13)	C10—C9—H9B	108.7
C1—C2—S1	117.55 (14)	H9A—C9—H9B	107.6
C2—C3—C4	123.12 (16)	C9—C10—C9 ⁱⁱ	108.3 (3)
C2—C3—S2	120.34 (14)	C9—C10—H10A	110.0
C4—C3—S2	116.53 (14)	C9 ⁱⁱ —C10—H10A	110.0
N2—C4—C3	177.4 (2)	C9—C10—H10B	110.0
N3—C5—N4	109.39 (19)	C9 ⁱⁱ —C10—H10B	110.0
N3—C5—H5A	125.3	H10A—C10—H10B	108.4
N4—C5—H5A	125.3		

Symmetry codes: (i) $-x+1/2, -y+3/2, -z$; (ii) $-x+1, y, -z+3/2$.