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Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$
 R factor = 0.059
 wR factor = 0.157
 Data-to-parameter ratio = 14.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

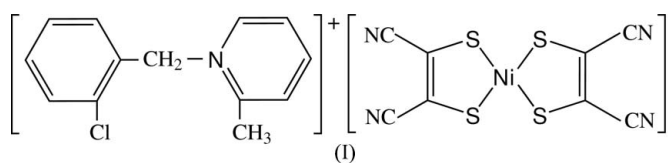
1-(2-Chlorobenzyl)-2-methylpyridinium bis(maleonitriledithiolato)nickelate(III)

The title compound is a new ionic complex, $(\text{C}_{13}\text{H}_{13}\text{ClN})\text{[Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]$ or $[\text{ClBzPyMe}][\text{Ni}(\text{mnt})_2]$ [where ClBzPyMe is 1-(2-chlorobenzyl)-2-methylpyridinium and mnt is maleonitriledithiolate]. In the anion the Ni^{III} atom is coordinated by the four S atoms of two mnt^{2-} ligands and exhibits the expected square-planar coordination geometry. In the $[\text{ClBzPyMe}]^+$ cation the benzene and pyridine rings are twisted with respect to the C/C/N plane incorporating the methylene C atom that links them. The $[\text{Ni}(\text{mnt})_2]^-$ anions and $[\text{ClBzPyMe}]^+$ cations stack into well segregated columns along the *a* axis, and the Ni^{III} ions form a one-dimensional zigzag chain through weak $\text{Ni} \cdots \text{S}$, $\text{S} \cdots \text{S}$, and π - π interactions.

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Comment

During the past few years there has been a renewed interest in maleonitriledithiolate (mnt^{2-}) transition metal complexes, which can be used as building blocks for magnetic molecular materials (Robertson & Cronin, 2002; Coomber *et al.*, 1996; Ni *et al.*, 2005). Previous studies have shown that introduction of organic cations such as benzylpyridinium derivatives as counter-cations to the $[\text{Ni}(\text{mnt})_2]^-$ anions may tune the stacking pattern of the anion and result in molecular materials with unusual magnetic properties (Xie *et al.*, 2002; Ni *et al.*, 2005; Ren *et al.*, 2002). In order to study the effects of substituted groups in the benzene and pyridine rings of a benzylpyridinium cation on the stacking pattern of $\text{Ni}(\text{mnt})_2$ complexes, we report here the synthesis and structure of the title complex $[\text{ClBzPyMe}][\text{Ni}(\text{mnt})_2]$, (I) (Fig. 1).



The cation adopts a conformation where both the benzene and pyridine rings are twisted relative to the C14/C15/N5 reference plane. The pyridine and benzene rings make dihedral angles of 79.9 (2) and 14.5 (2)°, respectively, with the C14/C15/N5 reference plane and 88.3 (2)° with each other. The Ni^{III} ion in the $[\text{Ni}(\text{mnt})_2]^-$ anion exhibits the expected square-planar coordination geometry. Bond distances and angles (Table 1) compare well with those found in other complexes containing the $[\text{Ni}(\text{mnt})_2]^-$ anion.

In the crystal structure, $[\text{Ni}(\text{mnt})_2]^-$ anions and $[\text{ClBzPyMe}]^+$ cations stack into well segregated columns along the crystallographic *a* axis (Fig. 2), and each anionic column is flanked by four cationic columns. The intracolumn $\text{Ni} \cdots \text{Ni}$ distances, alternating between 3.890 (2) and 4.327 (2) Å, are

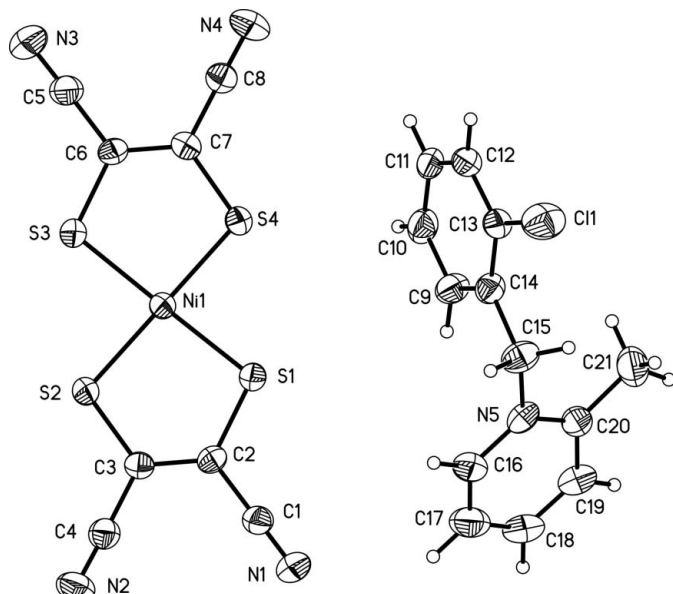


Figure 1
Structure of the title compound showing the atom-numbering scheme with 30% probability displacement ellipsoids.

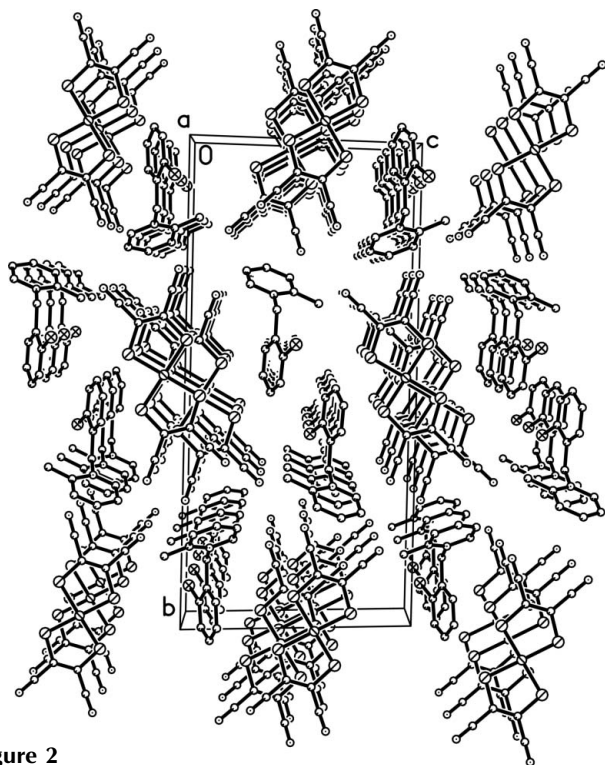


Figure 2
The crystal packing of (I). H atoms have been omitted.

significantly shorter than the intercolumn Ni...Ni distances [10.975 (2) Å]. Each Ni(mnt)₂⁻ column can therefore be considered as a one-dimensional chain by virtue of intermolecular Ni...S, S...S or π-π interactions between neighbouring anions. The anions in each individual anionic column form a zigzag alternating chain (Fig. 3) that is different from that observed in the related complex [ClBzPy][Ni(mnt)₂] (Ren *et al.*, 2002). Within a column of [ClBzPyMe]⁺ cations, there is a significant offset π-π interaction between the neighbouring

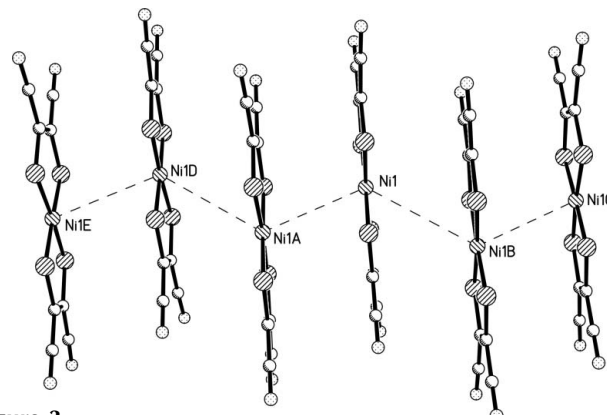


Figure 3
Side view of the anion stacking in (I) showing the alternating chain of [Ni(mnt)₂]⁻ anions; the dashed lines represent the Ni...Ni interactions at 3.890 (2) and 4.327 (2) Å.

benzene rings in adjacent cations (Fig. 4). The contact distance between C11 and the centroid of the neighbouring benzene ring is 3.725 (2) Å. These anion-anion and cation-cation contacts play an important role in stabilizing the structure.

Experimental

An acetone solution of I₂ was slowly added to an acetone solution of [ClBzPyMe]₂[Ni(mnt)₂] (Davison & Holm, 1967) and the mixture stirred for 6 h. CH₃OH was then added, and the mixture was allowed to stand overnight; black microcrystals formed and were filtered off, washed with MeOH and dried in vacuum (yield 80%). Black block-shaped crystals suitable for X-ray analysis were obtained by slow evaporation of a CH₃CN/*i*-PrOH (1:1 *v/v*) solution at room temperature for about two weeks. Analysis calculated for C₂₁H₁₃ClN₅NiS₄: C 45.22, H 2.35, N 10.05%; found: C 45.30, H 2.55, N 9.94%.

Crystal data

(C₁₃H₁₃ClN)[Ni(C₄N₂S₂)₂]
M_r = 557.76
 Monoclinic, *P*2₁/*n*
a = 6.9950 (1) Å
b = 26.658 (5) Å
c = 13.013 (3) Å
 β = 103.700 (1)°
V = 2357.5 (8) Å³
Z = 4

D_x = 1.571 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 977 reflections
 θ = 2.8–24.4°
 μ = 1.31 mm⁻¹
T = 293 (2) K
 Block, black
 0.4 × 0.25 × 0.2 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.682, *T_{max}* = 0.770
 11580 measured reflections

4141 independent reflections
 3364 reflections with *I* > 2σ(*I*)
R_{int} = 0.069
 θ_{max} = 25.0°
h = -8 → 8
k = -28 → 31
l = -14 → 15

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.059
wR(*F*²) = 0.157
S = 1.04
 4141 reflections
 290 parameters
 H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.08*P*)² + 1.2*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.50 e Å⁻³
 Δρ_{min} = -0.36 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1—S1	2.1484 (13)	N4—C8	1.129 (7)
Ni1—S2	2.1496 (14)	N5—C15	1.485 (7)
Ni1—S3	2.1416 (14)	C14—C15	1.523 (7)
Ni1—S4	2.1369 (14)	C1—C2	1.438 (7)
S1—C2	1.725 (5)	C2—C3	1.352 (7)
S2—C3	1.717 (5)	C3—C4	1.441 (7)
S3—C6	1.710 (5)	C5—C6	1.431 (7)
S4—C7	1.711 (5)	C6—C7	1.363 (7)
N1—C1	1.122 (7)	C7—C8	1.434 (7)
N2—C4	1.135 (7)	C11—C13	1.737 (6)
N3—C5	1.140 (7)		
S1—Ni1—S2	92.66 (5)	C6—S3—Ni1	103.66 (17)
S3—Ni1—S2	87.68 (5)	C7—S4—Ni1	103.94 (17)
S4—Ni1—S1	87.64 (5)	C14—C13—C11	119.3 (4)
S3—Ni1—S1	176.66 (6)	C9—C14—C15	122.3 (5)
S4—Ni1—S2	178.59 (6)	N5—C15—C14	112.4 (4)
C2—S1—Ni1	103.01 (17)	N5—C20—C21	120.4 (6)
C3—S2—Ni1	102.94 (17)		

All H atoms were placed in geometrically calculated positions (C—H = 0.93–0.97 Å) with $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{C})$ for methyl atoms or $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ otherwise.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; 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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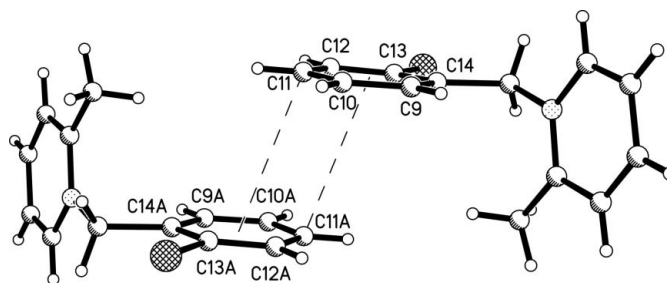


Figure 4

The offset π - π interaction between neighbouring cations. The dashed lines represent the contact distance of 3.725 (2) Å between C11 and the centroid of the neighbouring benzene ring.

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