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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 = 0.051
 wR factor = 0.131
 Data-to-parameter ratio = 14.1

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

**Bis[3-amino-1-(3-bromobenzyl)pyridinium]
 bis(maleonitriledithiolato)nickel(II)**

The title ionic complex, $(\text{C}_{12}\text{H}_{12}\text{BrN}_2)_2[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]$, crystallizes in a monoclinic unit cell, with the Ni atom on an inversion centre. All bond lengths and angles in the anions and cations are normal. The crystal structure is stabilized by intermolecular $\text{N}-\text{H}\cdots\text{S}$ and $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, and the weak $\text{C}-\text{H}\cdots\text{N}$ interactions of the anions and cations.

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Comment

In recent years, nonlinear optical (NLO) materials have attracted great interest because of their wide range of possible applications in several fields, such as laser technology, telecommunications, data storage and optical switches (Chen *et al.*, 1998; Sun *et al.*, 2001). Metal dithiolene compounds are of interest because they possess excellent photostability under laser irradiation. The ion-pair complex, $[\text{C}_6\text{H}_5\text{NR}][\text{Ni}(\text{mnt})_2]$ (*R* is *p*-nitrobenzyl and mnt is maleonitriledithiolate), is known to exhibit third-order nonlinear optical properties (Zhu *et al.*, 2000).

We report the crystal structure of the title compound, (I), another new type of ionic complex. The Ni atom lies on an inversion centre, so the asymmetric unit contains one cation and one-half anion. There are three types of weak interactions, *viz.* $\text{N}-\text{H}\cdots\text{S}$, $\text{N}-\text{H}\cdots\text{N}$ and $\text{C}-\text{H}\cdots\text{N}$ interactions (Table 2), between the anions and cations in (I) (Fig. 1). These weak interactions link the ions into two-dimensional layers, which are extended further into a three-dimensional supramolecular network structure (Fig. 2).

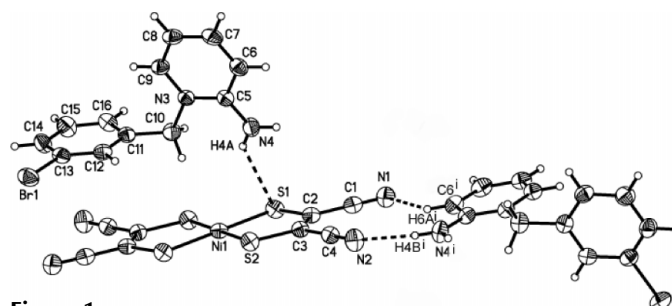
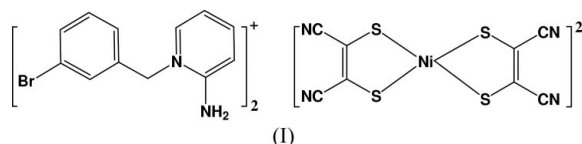


Figure 1
 A view of (I), with 30% probability displacement ellipsoids. Hydrogen bonds are indicated by dashed lines. [Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$.]

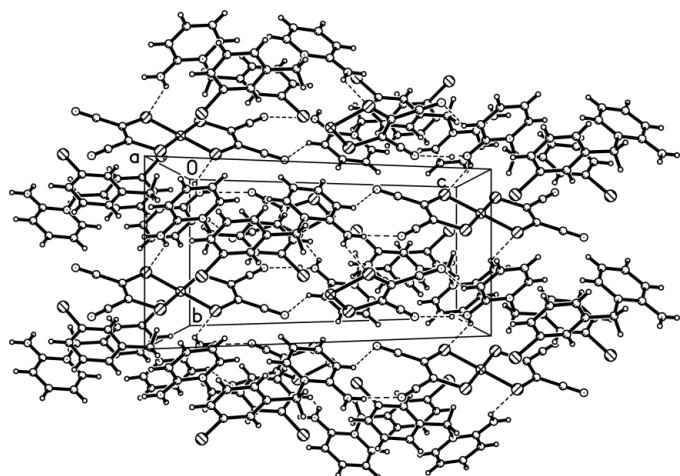


Figure 2
The crystal packing of (I). The weak intermolecular interactions are shown as dashed lines.

Experimental

3-Bromobenzyl bromide and 2-aminopyridine were purchased from Aldrich. $[N-(3\text{-Bromobenzyl})\text{-}2\text{-amino}]\text{pyridinium bromide}$ ($[\text{BrBzPyNH}_2]\text{Br}$) and disodium maleonitriledithiolate (Na_2mnt) were synthesized following published procedures (Bulgarevich *et al.*, 1994; Davison & Holm, 1967). The title complex was prepared by the direct combination of 1:2:2 molar equivalents of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2(\text{mnt})$ and $[\text{BrBzPyNH}_2]\text{Br}$ in MeOH. The red precipitate that formed was filtered off, washed with water and dried under vacuum. Single crystals suitable for X-ray analysis were obtained within two weeks from MeCN solution.

Crystal data

$(\text{C}_{12}\text{H}_{12}\text{BrN}_2)_2[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]$
 $M_r = 867.36$
 Monoclinic, $C2/c$
 $a = 27.219$ (7) Å
 $b = 8.081$ (2) Å
 $c = 20.601$ (5) Å
 $\beta = 131.01$ (1)°
 $V = 3419.5$ (15) Å³
 $Z = 4$

$D_x = 1.685$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 856 reflections
 $\theta = 2.6\text{--}23.1^\circ$
 $\mu = 3.19$ mm⁻¹
 $T = 293$ (2) K
 Block, red
 $0.3 \times 0.2 \times 0.2$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
 $T_{\min} = 0.47$, $T_{\max} = 0.53$
 16 304 measured reflections

3011 independent reflections
 2258 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.060$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -32 \rightarrow 30$
 $k = -9 \rightarrow 9$
 $l = -24 \rightarrow 22$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.131$
 $S = 0.96$
 3011 reflections
 214 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0913P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.71$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.65$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1—S2	2.1649 (11)	N4—C5	1.324 (6)
Ni1—S1	2.1662 (12)	C1—C2	1.440 (7)
S1—C2	1.735 (4)	C3—C4	1.436 (6)
S2—C3	1.727 (4)	C13—Br1	1.899 (4)
S2—Ni1—S1	92.59(5)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N4—H4A \cdots S1	0.86	2.81	3.506 (4)	140
N4—H4B \cdots N2 ⁱⁱ	0.86	2.10	2.956 (6)	175
C6—H6A \cdots N1 ⁱⁱ	0.93	2.58	3.308 (6)	136

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

All H atoms were positioned geometrically and refined as riding, with $U_{\text{iso}}(\text{H})$ set at $1.2U_{\text{eq}}$ of the parent atom. The N—H distances were set at 0.86 Å, and C—H distances were in the range 0.93–0.97 Å.

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