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Key indicators

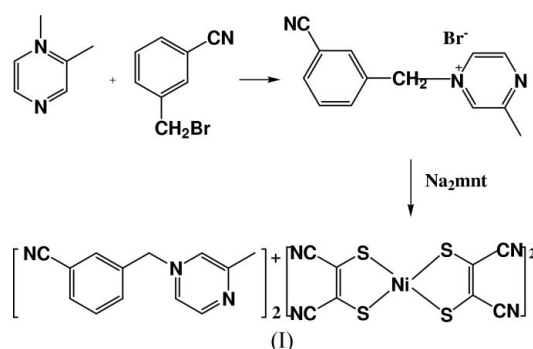
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$
 R factor = 0.055
 wR factor = 0.133
Data-to-parameter ratio = 15.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis[1-(3-cyanobenzyl)-3-methylpyrazinium]
bis(1,2-dicyanoethene-1,2-dithiolato)nickel(II)

In the title complex, $(\text{C}_{13}\text{H}_{12}\text{N}_3)_2[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2]$, the anion has slightly distorted square-planar coordination geometry, in which the Ni atom lies on an inversion center. In the crystal structure, weak $\text{C}-\text{H}\cdots\text{N}$ interactions connect anions and cations into a three-dimensional network.

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Comment

Many efforts have been focused on the study of square-planar metal-bis(dithiolene) complexes in the areas of electronic and magnetic materials, dyes, non-linear optics and catalysis (Robertson & Cronin, 2002; Cassoux *et al.*, 1991). Recently, a strategy for constructing one-dimensional molecule-based magnets based on ion-pair complexes containing $[\text{M}(\text{mnt})_2]$ ($M = \text{Ni}^{\text{II}}, \text{Ni}^{\text{III}}$; $\text{mnt}^- = \text{maleonitriledithiolate}$) and benzylpyridinium derivatives as counter-ions has been employed. They show varied magnetic exchange properties, such as ferromagnetic ordering at 2 K, a peculiar magnetic transition from ferromagnetic coupling to diamagnetism or from paramagnetic to diamagnetism and spin-Peierls-like transitions (Xie *et al.*, 2002, 2003; Ren *et al.*, 2002). They also display variable electrical properties, such as electrical conductivity, superconductivity, strong near-IR absorptions, and interesting electrical and photoelectric properties (Tajima *et al.*, 1993; Muller-Westerhoff *et al.*, 1991; Liu *et al.*, 1996). We report here the structure of the title compound, (I), in order to further understand these physical properties.



In (I), the formula unit consists of two cations and one anion. The Ni atom of the slightly distorted square-planar cation lies on an inversion center (Table 1 and Fig. 1). There are weak intermolecular interactions of the type $\text{C}-\text{H}\cdots\text{N}$ (Table 2 and Fig. 2) which connect anions and cations into a three-dimensional network.

Experimental

1-(3-Cyanobenzyl)-3-methylpyrazinium bromide ($[\text{CNBzPz}]\text{Br}$) and Na_2mnt were synthesized according to published procedures

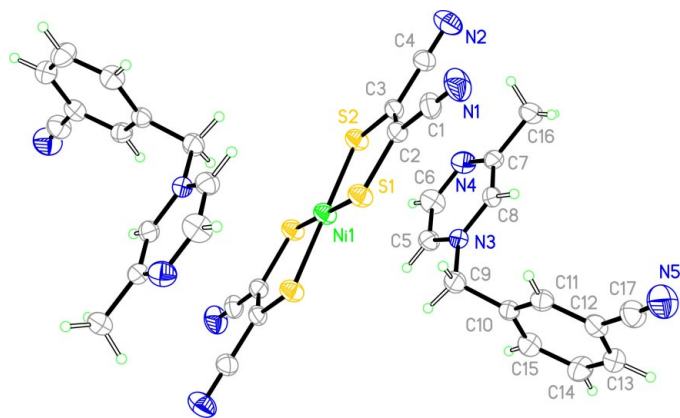


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids. The unlabeled atoms are related by the symmetry code (2 - x, 1 - y, -z).

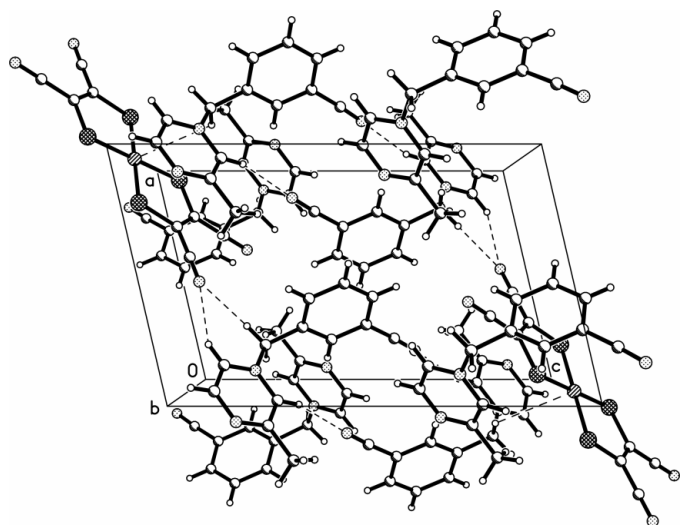


Figure 2
The crystal packing of the title compound, viewed down the *b* axis, showing C—H...N contacts as dashed lines.

(Bulgarevich *et al.*, 1994; Davison & Holm, 1967). The title compound was prepared by the direct combination of 1:2:2 molar equivalents of NiCl₂·6H₂O, Na₂mnt and [CNBzPz]Br in H₂O. A red precipitate formed, which was filtered off, washed with water and dried *in vacuo*. The resulting product was dissolved in MeCN and the solution allowed to stand for about a week, whereupon single crystals suitable for X-ray analysis were obtained.

Crystal data

(C₁₃H₁₂N₃)₂[Ni(C₄N₂S₂)₂]
M_r = 759.58
 Monoclinic, *P*2₁/*c*
a = 8.831 (2) Å
b = 14.220 (2) Å
c = 14.256 (2) Å
 β = 103.10 (1)°
V = 1743.6 (5) Å³
Z = 2

D_x = 1.447 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 951 reflections
 θ = 2.7–26.4°
 μ = 0.84 mm⁻¹
T = 293 (2) K
 Block, red
 0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 T_{\min} = 0.77, T_{\max} = 0.84
 9111 measured reflections

3401 independent reflections
 2473 reflections with $I > 2\sigma(I)$
 R_{int} = 0.019
 θ_{max} = 26.0°
 h = -10 → 10
 k = -17 → 17
 l = -10 → 17

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.055
 $wR(F^2)$ = 0.133
 S = 1.00
 3401 reflections
 224 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 1.99P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ni1—S2	2.1642 (10)	Ni1—S1	2.1735 (9)
S2—Ni1—S2 ⁱ	180	S2—Ni1—S1 ⁱ	87.91 (4)
S2—Ni1—S1	92.09 (4)	S1—Ni1—S1 ⁱ	180

Symmetry code: (i) 2 - x, 1 - y, -z.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C5—H5...N2 ⁱ	0.93	2.50	3.338 (5)	151
C8—H8...N5 ⁱⁱ	0.93	2.43	3.333 (5)	163
C9—H9B...N2 ⁱ	0.97	2.44	3.356 (5)	157

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

All H atoms were positioned geometrically and refined as riding (C—H = 0.97 Å), and given isotropic displacement parameters 1.2 (1.5 for methyl) times the U_{eq} value of the parent atom.

Data collection: SMART (Bruker, 2000); cell refinement: SMART; data reduction: SAINT (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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References

- Bruker (2000). SMART, SAINT, SHELXTL and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bulgarevich, S. B., Bren, D. V., Movshovic, D. Y., Finocchiaro, P. & Failla, S. (1994). *J. Mol. Struct.* **317**, 147–155.
 Cassoux, P., Valade, L., Kobayashi, H., Clar, R. A. & Underhill, A. E. (1991). *Coord. Chem. Rev.* **110**, 115–160.
 Davison, A. & Holm, H. R. (1967). *Inorg. Synth.* **10**, 8–26.
 Liu, S.-G., Wu, P.-J., Liu, Y.-Q. & Zhu, D.-B. (1996). *Synth. Met.* **83**, 131–140.
 Muller-Westerhoff, U. T., Vance, B. & Yoon, D. I. (1991). *Tetrahedron*, **47**, 909–932.

Ren, X.-M., Meng, Q.-J., Song, Y., Lu, C.-S. & Hu, C.-J. (2002). *Inorg. Chem.* **41**, 5686–5692.

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

Tajima, H., Inokuchi, M., Kobayashi, A., Ohta, T., Sato, R., Kobayashi, H. & Kuroda, H. (1993). *Chem. Lett.* pp. 1235–1238.

Xie, J.-L., Ren, X.-M., Gao, S., Zhang, W.-W., He, C. & Meng, Q.-J. (2002). *Chem. Commun.* pp. 2346–2347.

Xie, J.-L., Ren, X.-M., Gao, S., Zhang, W.-W., Li, Y.-Z., Lu, C.-S., Ni, C.-L., Liu, W.-L., Meng, Q.-J. & Yao, Y.-G. (2003). *Eur. J. Inorg. Chem.* pp. 2393–2396.