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#### Key indicators

Single-crystal X-ray study

$T = 294$  K

Mean  $\sigma(\text{C}-\text{C}) = 0.009$  Å

$R$  factor = 0.058

$wR$  factor = 0.159

Data-to-parameter ratio = 14.6

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

## 1-(4-Bromobenzylmethyl)pyridinium bis(benzene-1,2-dithiolato)nickelate(III)

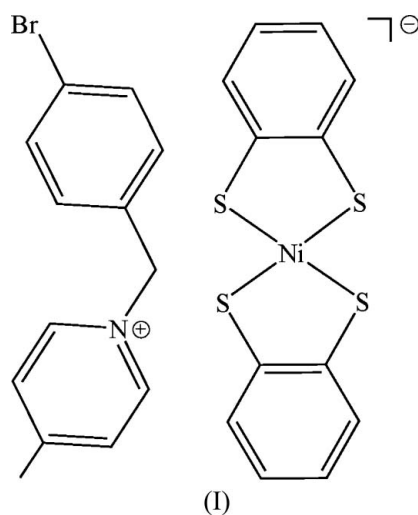
In the title compound,  $(\text{C}_{13}\text{H}_{13}\text{BrN})[\text{Ni}(\text{C}_6\text{H}_4\text{S}_2)_2]$ , the  $\text{Ni}^{\text{III}}$  atom is surrounded by four S atoms in a square-planar geometry. The asymmetric unit contains half each of two centrosymmetric anions and a single cation in a general position. The anions exhibit two packing modes, *viz.* stacked in a face-to-face fashion with an alternate arrangement of anions and cations, and stacked in a side-by-side fashion.

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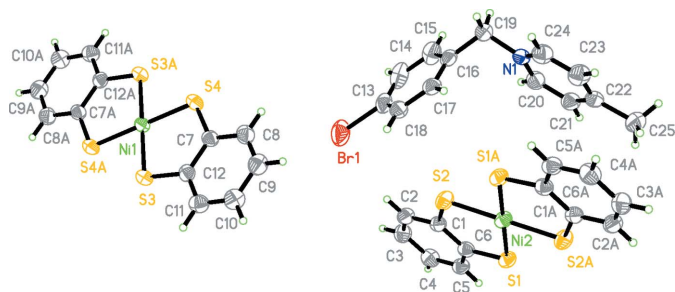
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### Comment

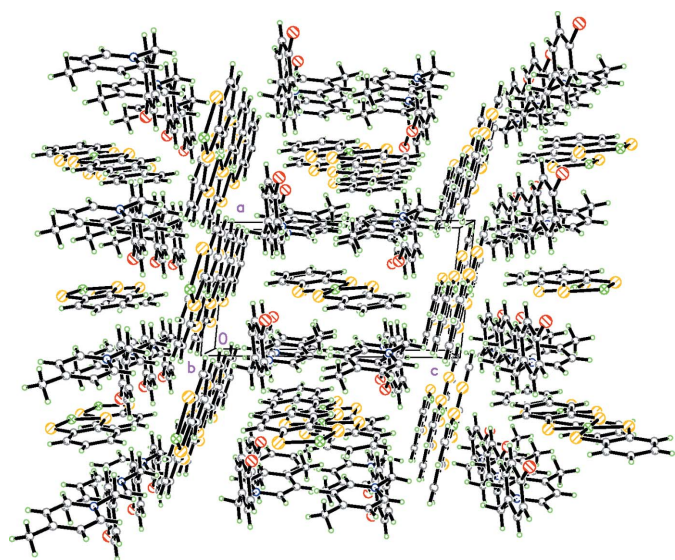
During the past two decades, an enormous amount of research has been done on the synthesis and characterization of unsaturated chalcogen ligands and/or compounds and related selenium- and oxygen-substituted analogues (Pullen & Olk, 1999), including many exciting physical phenomena such as superconductivity, field-induced spin-density waves and magnetic oscillations (Rosa *et al.*, 2004). In our previous research using benzylpyridinium derivatives ( $[\text{RBzPy}]^+$ ) as the counter-cation of  $[\text{M}(\text{mnt}^{2-})]$  (where  $M = \text{Ni}$ , Pd and Pt and  $\text{mnt}^{2-} = \text{maleodinitriledithiolate}$ ), a series of ion-pair compounds with segregated columnar stacks of cations and anions has been prepared (Ren *et al.*, 2002, 2003; Xie *et al.*, 2002). The quasi one-dimensional magnetic nature of these compounds was attributed to intermolecular  $\pi$ -orbital interactions within the anionic columns. As an extension of our work on this series of complexes, we report here the crystal structure of the title compound, (I).



The asymmetric unit of (I), contains half each of two centrosymmetric  $[\text{Ni}(\text{C}_6\text{H}_4\text{S}_2)_2]^-$  anions and one  $(\text{C}_{13}\text{H}_{13}\text{BrN})^+$  cation. In the anion, the  $\text{Ni}^{\text{III}}$  ions are surrounded by four S atoms in a square-planar geometry; the


**Figure 1**

A drawing of the title structure with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. In the Ni1 anion the suffix A corresponds to the symmetry position  $1-x, 2-y, -z$ . In the Ni2 anion the suffix A corresponds to the symmetry position  $1-x, -y, 1-z$ .


**Figure 2**

A packing diagram of (I).

Ni—S bonds and S—Ni—S angles (Table 1) are in agreement with the corresponding values in analogous complexes (Sellmann *et al.*, 1991; Xie *et al.*, 2003).

The five-membered ring A (Ni2/S1/S2/C1/C6) is not planar. Its conformation is nearly that of an envelope, with atom Ni2 at the flap position, 0.169 (3) Å from the mean plane through the other four atoms. Ring C (Ni1/S3/S4/C7/C12) is planar. The dihedral angle between the two rings of the cation is 84.60 (3)°.

In the crystal structure, the packing of the two anions is different (Fig. 2). The Ni1-containing anions stack in a side-by-side fashion, forming a one-dimensional chain along the *b* axis; the shortest distance between the adjacent Ni<sup>III</sup> ions is 7.266 (1) Å. The Ni2-containing anions stack in a face-to-face fashion with an alternating arrangement of [Ni(C<sub>6</sub>H<sub>4</sub>S<sub>2</sub>)<sub>2</sub>]<sup>−</sup> anions and [C<sub>13</sub>H<sub>13</sub>BrN]<sup>+</sup> cations such that the pyridine ring of the cation lies above the benzene ring of the anion. The shortest distance between adjacent Ni<sup>III</sup> ions is also 7.266 (1) Å. An Ni⋯Ni distance of 7.127 (1) Å is found between adjacent Ni1-containing and Ni2-containing anions.

## Experimental

Benzene-1,2-dithiol (142 mg, 1.0 mmol) was added to a solution of sodium metal (46 mg, 2.0 mmol) in absolute ethanol (25 ml), under a nitrogen atmosphere at room temperature. A solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (120 mg, 0.5 mmol) in ethanol (25 ml) was added, resulting in the mixture turning a muddy red–brown color. Following this, [BrBzPyCH<sub>3</sub>]<sup>+</sup>Br<sup>−</sup> (341 mg, 1.0 mmol) was added and the mixture allowed to stand with stirring for 1 h, and then stirred for an additional 24 h in air. The color of the mixture gradually turned green, indicating oxidation from a dianionic species to the more stable monoanionic form. The precipitate was washed with absolute ethanol and diethyl ether and then dried. The crude product was recrystallized twice from dichloromethane to give the title compound (yield 216 mg, 72%).

### Crystal data

(C<sub>13</sub>H<sub>13</sub>BrN)[Ni(C<sub>6</sub>H<sub>4</sub>S<sub>2</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 602.29  
 Triclinic, *P* $\bar{1}$   
*a* = 7.2661 (11) Å  
*b* = 12.4666 (19) Å  
*c* = 14.255 (2) Å  
 $\alpha$  = 76.446 (3)°  
 $\beta$  = 82.992 (3)°  
 $\gamma$  = 83.819 (3)°

*V* = 1241.7 (3) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.611 Mg m<sup>−3</sup>  
 Mo *K*α radiation  
 $\mu$  = 2.74 mm<sup>−1</sup>  
*T* = 294 (2) K  
 Prism, dark green  
 0.30 × 0.10 × 0.10 mm

### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
*T<sub>min</sub>* = 0.489, *T<sub>max</sub>* = 0.764

6105 measured reflections  
 4282 independent reflections  
 3257 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.034  
 $\theta_{\max}$  = 25.0°

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.058  
*wR*(*F*<sup>2</sup>) = 0.159  
*S* = 1.08  
 4282 reflections  
 293 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.6467P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 1.33 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.94 \text{ e } \text{Å}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Ni1—S3	2.1389 (14)	S2—C1	1.740 (5)
Ni1—S4	2.1460 (13)	S3—C12	1.735 (5)
Ni2—S2	2.1445 (14)	S4—C7	1.738 (6)
Ni2—S1	2.1515 (13)	C1—C6	1.390 (7)
S1—C6	1.732 (5)	C7—C12	1.397 (7)
S3—Ni1—S4	91.88 (5)	S2 <sup>ii</sup> —Ni2—S1	88.18 (5)
S3—Ni1—S4 <sup>i</sup>	88.12 (5)	C1—S2—Ni2	104.66 (18)
S2—Ni2—S1	91.82 (5)	C7—S4—Ni1	105.03 (17)

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

H atoms were positioned geometrically, with C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H atoms, respectively, and constrained to ride on their parent atoms, with *U*<sub>iso</sub>(H) = *xU*<sub>eq</sub>(C), where *x* = 1.5 for methyl H and *x* = 1.2 for all other H atoms. The highest peak is located 1.10 Å from atom Br1.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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## References

- Bruker (2000). *SADABS*, *SMART*, *SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Pullen, A. E. & Olk, R. M. (1999). *Coord. Chem. Rev.* **188**, 211–262.
- Ren, X. M., Ma, J., Lu, C. S., Yang, S. Z., Meng, Q. J. & Wu, P. H. (2003). *Dalton Trans.* pp. 1345–1351.
- Ren, X. M., Meng, Q. J., Song, Y., Lu, C. S., Hu, C. J. & Chen, X. Y. (2002). *Inorg. Chem.* **41**, 5686–5692.
- Rosa, L., Santiago, U., Cristian, V., Juan, M. C., Engenio, C., Carlos, J., Benoit, B. & Enric, C. (2004). *J. Am. Chem. Soc.* **126**, 12076–12083.
- Sellmann, D., Funfgelder, S., Knoch, F. & Moll, M. (1991). *Z. Naturforsch. Teil B*, **46**, 1601–1605.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Xie, J. L., Ren, X. M., He, C., Song, Y., Duan, C. Y., Gao, S. & Meng, Q. J. (2003). *Polyhedron*, **22**, 299–305.
- Xie, J. L., Ren, X. M., Song, Y., Zhang, W. W., Liu, W. L., He, C. & Meng, Q. J. (2002). *Chem. Commun.* pp. 2346–2347.