

Chun-Lin Ni<sup>a,b\*</sup> and  
Ming-Guo Liu<sup>a</sup><sup>a</sup>College of Chemistry and Life Science, China Three Gorges University, Hubei, Yichang 443002, People's Republic of China, and<sup>b</sup>Department of Applied Chemistry, Centre of Inorganic Functional Materials, College of Science, South China Agricultural University, Guangzhou 510642, People's Republic of China

Correspondence e-mail: niclchem@scau.edu.cn

**Bis[1-(4-bromobenzyl)-3-methylpyrazinium] bis(1,2-dicyanoethene-1,2-dithiolato- $\kappa^3S,S'$ )-nickelate(II)**

The title compound,  $(C_{12}H_{12}BrN_2)[Ni(C_4N_2S_2)_2]$ , is an ion-pair complex, isostructural with the Cl-containing analogue. The anion lies on an inversion centre and the Ni<sup>II</sup> ion is coordinated by four S atoms, giving the expected square-planar coordination geometry. The cation adopts a conformation where the benzene and pyrazine rings are twisted with respect to the plane of the central C—C—N chain which links them. C—H $\cdots$ S and  $\pi$ – $\pi$  interactions between cations and anions are observed in the crystal structure, and C—H $\cdots$  $\pi$  interactions mediate the formation of ribbons of cations.

Received 15 February 2006

Accepted 7 March 2006

**Key indicators**

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(C-C) = 0.006 \text{ \AA}$ 

R factor = 0.047

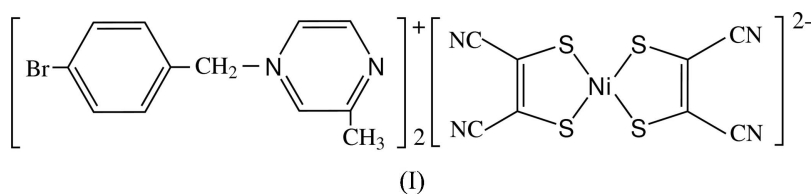
wR factor = 0.117

Data-to-parameter ratio = 14.3

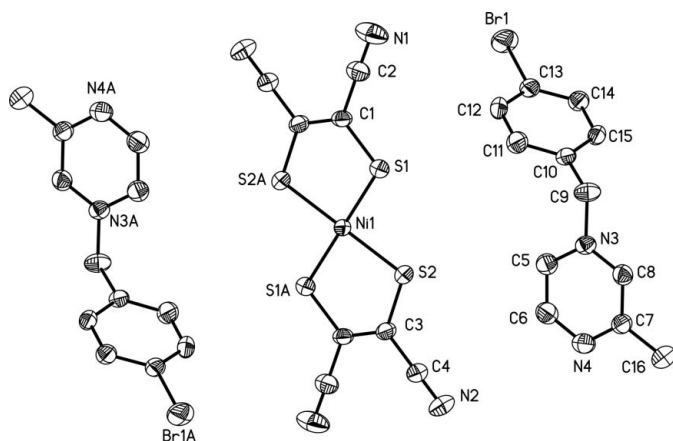
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

**Comment**

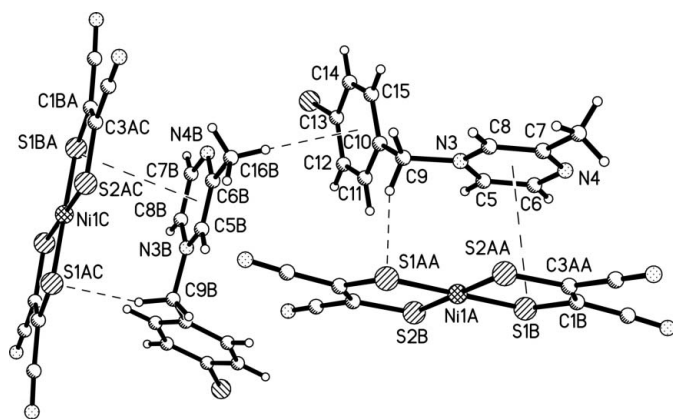
In recent years, interest has grown in the study of the introduction of the principles of supramolecular chemistry into the area of materials science, in which non-covalent interactions, such as hydrogen bonding and  $\pi$ – $\pi$  stacking interactions, have yielded new materials exhibiting novel properties (Decurtins *et al.*, 1999; Hollingsworth, 2002; Wernsdorfer *et al.*, 2002). Maleonitriedithiolate ( $mnt^{2-}$ ) transition metal complexes can be used as building blocks for magnetic molecular materials through weak  $M^{II}\cdots S$  (where  $M$  is Ni, Pd or Pt),  $S\cdots S$  or  $\pi$ – $\pi$  interactions (Pullen *et al.*, 1998; Uruichi *et al.*, 1998; Robertson & Cronin, 2002; Nishijo *et al.*, 2003; Ni *et al.*, 2004). The introduction of inorganic or organic cations as the counter-cation of  $[M(mnt)_2]^{2-}$  not only tunes the stacking pattern of the anions, but also results in molecular materials with unusual magnetic properties (Coomber *et al.*, 1996; Ren, Chen *et al.*, 2002; Ren, Meng *et al.*, 2002; Xie *et al.*, 2002; Ni *et al.*, 2005). Cation–cation or anion–cation hydrogen bonds result in the formation of two- or three-dimensional molecular magnets (Ren, Chen *et al.*, 2002; Ren, Meng *et al.*, 2002). As part of a study of the effect of substituent groups on the benzene and pyrazine rings of the benzylpyrazinium cation on the stacking pattern of  $[M(mnt)_2]^{2-}$  anions, we report here the synthesis and crystal structure of the title ion-pair complex, (I), using 1-(4-bromobenzyl)-3-methylpyrazinium (BrBzPzMe) as the cation.



Complex (I) is isostructural with  $[ClBzPzMe]_2[Ni(mnt)_2]$  (Yang *et al.*, 2004). The main structural blocks in (I) are the



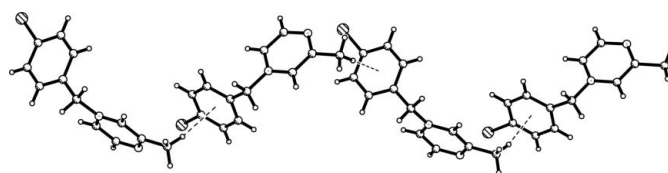
**Figure 1**  
The structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. All H atoms have been omitted for clarity. [Symmetry code: (A)  $-x, 1 - y, -z$ .]



**Figure 2**  
The anion-cation and cation-cation interactions (dashed lines) in (I). [Symmetry codes: (A)  $\frac{1}{2} - x, \frac{3}{2} + y, \frac{1}{2} - z$ ; (B)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (C)  $\frac{1}{2} + x, -y, \frac{1}{2} + z$ ; (AA)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (AC)  $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$ ; (BA)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ .]

[BrBzPzMe]<sup>+</sup> cation and the [Ni(mnt)<sub>2</sub>]<sup>2-</sup> anion, which is located on an inversion centre (Fig. 1). The [BrBzPzMe]<sup>+</sup> cation adopts a conformation where both the benzene and pyrazine rings are twisted relative to the C10/C9/N3 reference plane: the dihedral angles that the pyrazine and benzene rings make with the C10/C9/N3 plane are 38.4 (3) and 89.7 (3)°, respectively. The benzene and pyrazine rings are planar, and make a dihedral angle of 71.5 (3)°. In the [Ni(mnt)<sub>2</sub>]<sup>2-</sup> anion, the Ni<sup>II</sup> ion exhibits the expected square-planar coordination geometry. The CN groups are slightly tipped out of the coordination plane. The Ni—S bond distances are 2.1659 (10) and 2.1687 (11) Å, and the S—Ni—S bond angles within the five-membered rings are 92.64 (4)°. These values compare well with those found in the corresponding Cl complex (Yang *et al.*, 2004).

An interesting structural feature of (I) is that weak C—H...S,  $\pi$ - $\pi$  and C—H... $\pi$  intermolecular interactions are found in the crystal structure and play an important role in controlling the stacking arrangement. There are two types of weak interactions between cations and anions: C9—



**Figure 3**  
The ribbons of cations in (I) formed through C—H... $\pi$  interactions (dashed lines).

H9A...S1<sup>i</sup> [C9...S1<sup>i</sup> = 3.689 (5) Å and C9—H9A...S1<sup>i</sup> = 151°; symmetry code: (i)  $1 + x, y, z$ ] and a  $\pi$ - $\pi$  stacking interaction between the pyrazine ring and the conjugated portion of the [Ni(mnt)<sub>2</sub>]<sup>2-</sup> anion, with a distance of 3.52 (2) Å (Fig. 2). There is also a significant weak C—H... $\pi$  interaction between the methyl group C16 and the benzene ring of an adjacent cation [Fig. 2; contact distance H...centroid = 2.84 Å], so that ribbons of cations are formed (Fig. 3).

## Experimental

4-Bromobenzyl bromide and 3-methylpyrazine were purchased from Aldrich and used without further purification. 1-(4-Bromobenzyl)-3-methylpyrazinium bromide (BrBzPzMe<sup>+</sup>·Br<sup>-</sup>) was prepared by the literature method of Bulgarevich *et al.* (1994). Disodium maleonitriledithiolate, Na<sub>2</sub>mnt, was synthesized by the published procedure of Davison & Holm (1967). Compound (I) was prepared by the direct combination of 1:2:2 mole equivalents of NiCl<sub>2</sub>·6H<sub>2</sub>O, Na<sub>2</sub>mnt and BrBzPzMe<sup>+</sup>·Br<sup>-</sup> in H<sub>2</sub>O (30 ml). The resulting red precipitate was filtered off, washed with water and dried *in vacuo* (yield 88%). Single crystals of (I) suitable for X-ray analysis were grown from CH<sub>3</sub>CN by slow evaporation over a period of two weeks. Analysis, found: C 44.23, H 2.85, N, 12.78%; calculated for C<sub>32</sub>H<sub>24</sub>Br<sub>2</sub>N<sub>8</sub>NiS<sub>4</sub>: C 44.31, H 2.79, N, 12.92%. IR data (KBr,  $\nu$ , cm<sup>-1</sup>): 2215 and 2198 (C≡N), 1478 (C=C of mnt<sup>2-</sup>).

### Crystal data

(C<sub>12</sub>H<sub>12</sub>BrN<sub>2</sub>)<sub>2</sub>[Ni(C<sub>4</sub>N<sub>2</sub>S<sub>2</sub>)<sub>2</sub>]  
 $M_r$  = 867.36  
 Monoclinic,  $P2_1/n$   
 $a$  = 7.182 (2) Å  
 $b$  = 15.944 (4) Å  
 $c$  = 15.384 (4) Å  
 $\beta$  = 94.692 (10)°  
 $V$  = 1755.7 (8) Å<sup>3</sup>  
 $Z$  = 2

$D_x$  = 1.641 Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 908 reflections  
 $\theta$  = 2.9–23.6°  
 $\mu$  = 3.10 mm<sup>-1</sup>  
 $T$  = 293 (2) K  
 Block, red  
 0.25 × 0.20 × 0.15 mm

### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
 $T_{\min}$  = 0.480,  $T_{\max}$  = 0.628  
 8550 measured reflections

3085 independent reflections  
 2162 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}}$  = 0.097  
 $\theta_{\text{max}}$  = 25.0°  
 $h$  = -8 → 8  
 $k$  = -16 → 18  
 $l$  = -17 → 18

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)]$  = 0.047  
 $wR(F^2)$  = 0.117  
 $S$  = 0.92  
 3085 reflections  
 215 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0649P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}}$  = 0.032  
 $\Delta\rho_{\text{max}}$  = 0.84 e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = -0.82 e Å<sup>-3</sup>

H atoms were placed in geometrically calculated positions and refined with constrained C–H distances of 0.93, 0.96 and 0.97 Å for aromatic, methyl and methylene groups, respectively, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic and methylene})$  or  $1.5U_{\text{eq}}(\text{methyl})$ . The methyl group was allowed to refine as a rigid rotating group.

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*.

This work was funded by the President's Science Foundation of South China Agricultural University, and by China Three Gorges University.

## References

- Bruker (2000). *SMART* (Version 5.62), *SAINTE* (Version 6.02), *SHELXTL* (Version 6.10) and *SADABS* (Version 2.03). 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.
- Coomber, A. T., Beljonne, D., Friend, R. H., Brédas, J. L., Charlton, A., Robertson, N., Underbill, A. E., Kurmoo, M. & Day, P. (1996). *Nature (London)*, **380**, 144–146.
- Davison, A. & Holm, R. H. (1967). *Inorg. Synth.* **10**, 8–12.
- Decurtins, S., Pellaux, R., Antorrena, G. & Palacio, F. (1999). *Coord. Chem. Rev.* **190–192**, 841–854.
- Hollingsworth, M. D. (2002). *Science*, **295**, 2410–2413.
- Ni, C., Dang, D., Song, Y., Gao, S., Li, Y., Ni, Z., Tian, Z., Wen, L. & Meng, Q. (2004). *Chem. Phys. Lett.* **396**, 353–358.
- Ni, Z., Ren, X., Ma, J., Xie, J., Ni, C., Chen, Z. & Meng, Q. (2005). *J. Am. Chem. Soc.* **127**, 14330–14338.
- Nishijo, J., Ogura, E., Yamaura, J., Miyazaki, A., Enoki, T., Takano, T., Kuwatani, Y. & Iyoda, M. (2003). *Synth. Met.* **133–134**, 539–541.
- Pullen, A. E., Faulmann, C., Pokhodnya, K. I., Cassoux, P. & Tokumoto, M. (1998). *Inorg. Chem.* **37**, 6714–6720.
- Ren, X., Chen, Y., He, C. & Gao, S. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3915–3918.
- Ren, X., Meng, Q., Song, Y., Hu, C., Lu, C., Chen, X. & Xue, Z. (2002). *Inorg. Chem.* **41**, 5931–5933.
- Robertson, N. & Cronin, L. (2002). *Coord. Chem. Rev.* **227**, 93–127.
- Uruichi, M., Yakushi, K., Yamashita, Y. & Qin, J. (1998). *J. Mater. Chem.* **8**, 141–146.
- Wernsdorfer, W., Aliaga-Alcalde, N., Hendrickson, D. N. & Christou, G. (2002). *Nature (London)*, **416**, 406–409.
- Xie, J., Ren, X., Song, Y., Zhang, W., Liu, W., He, C. & Meng, Q. (2002). *Chem. Commun.* pp. 2346–2347.
- Yang, M., Ni, C., Zheng, Y. & Gu, W. (2004). *Acta Cryst.* **E60**, m833–m835.