

Hui Zhang,^a Xiao-Ming Ren,^{b,c,*}
 Jing-Li Xie,^d Yi-Zhi Li^d and
 Qing-Jin Meng^d

^aDepartment of Chemistry, Huangshan College, Huangshan 245021, People's Republic of China, ^bDepartment of Chemistry, Anqing Normal College, Anqing 246011, People's Republic of China, ^cMax-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, Postfach 800665, D-70569 Stuttgart, Germany, and ^dCoordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

Correspondence e-mail: x.ren@ikf.mpg.de

Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
 Disorder in solvent or counterion
 R factor = 0.044
 wR factor = 0.149
 Data-to-parameter ratio = 13.7

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

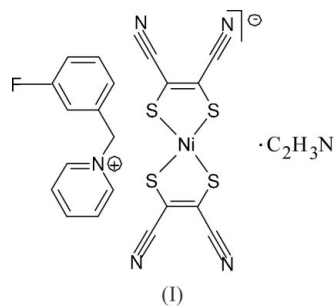
1-(3-Fluorobenzyl)pyridinium bis(maleodinitriledithiolato- $\kappa^2\text{S},\text{S}'$)nickelate(III) acetonitrile solvate

In the title compound, $(\text{C}_{12}\text{H}_{11}\text{FN})[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2] \cdot \text{C}_2\text{H}_3\text{N}$, completely segregated columnar stacks of anions and cations are observed. The anion columns have identical Ni...Ni distances of 4.2874 (9) Å. Within the cation columns, the benzene rings are parallel to each other; however the centre-to-centre distance between adjacent aromatic rings is more than 4.2 Å, and so no $\pi-\pi$ stacking interactions are found.

Comment

In recent years, many new unexpected physical phenomena have been found, especially for low-dimensional spin systems, such as slow relaxation of magnetization and hysteresis effects, which are not associated with three-dimensional order (Caneschi *et al.*, 2001), valence-ordering structure (Mitsumi *et al.*, 2002), spin-charge separation state (Lorenz *et al.*, 2002) and a distinct plateau in magnetization (Wolf *et al.*, 2002). Investigations of these phenomena motivate the corresponding theoretical research in this field (Clay *et al.*, 2003; Orignac & Citro, 2003). Our aim is to construct quasi-one-dimensional molecular magnetic materials formed by $[\text{M}(\text{mnt})_2]^-$ (M is Ni^{3+} , Pd^{3+} or Pt^{3+} ; mnt is maleodinitriledithiolate). More recently, we have developed a new class of $(R\text{-BzPy})^+[\text{Ni}(\text{mnt})_2]^-$ salt, in which $R\text{-BzPy}^+$ is the derivatives of benzylpyridinium. These compounds stack as well separated anion and cation columns in the solid state. We found that the nature of the substituents on the aromatic rings of the $R\text{-BzPy}^+$ ions affects the stacking pattern of these compounds, and further influences the magnetic properties of these compounds (Ren *et al.*, 2002; Xie, Ren, Song, Zhang *et al.*, 2002; Xie, Ren, Song, Zou & Meng, 2002; Xie *et al.*, 2003). In order to investigate the relationships between substituent effects, the stacking patterns of these compounds and the magnetic properties of the materials, we report here the crystal structure of the title compound, (I), a member of this series.

Received 24 May 2004
 Accepted 9 June 2004
 Online 19 June 2004



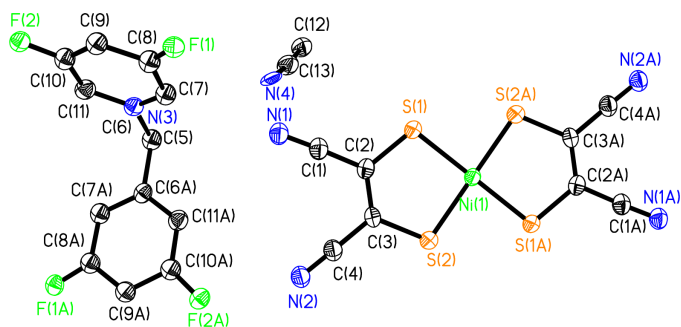


Figure 1

The structure of (I), showing 30% probability displacement ellipsoids, with the atomic numbering scheme. N(3) and C(6) are disordered on the same site; there is corresponding N/C disorder for C(6A). The single F atom is statistically distributed over the four sites shown. H atoms have been omitted.

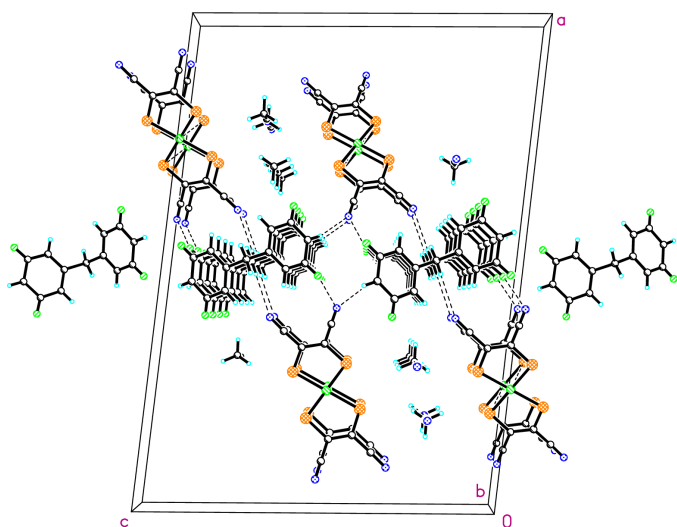


Figure 2

The completely separated stacking columns along *b* axis. Dashed lines indicate weak hydrogen-bonding interactions.

benzyl)pyridinium cation and one-half of a solvent molecule, MeCN, in the asymmetric unit. In the anion, the Ni atom lies on an inversion centre and exhibits square-planar coordination by four S atoms. The S–Ni–S bond angle for the chelate ring is 92.71 (4)°, and the two Ni–S bond lengths are very similar [2.1414 (11) and 2.1483 (10) Å]. These values are comparable to those found in other [Ni(mnt)₂][−]-based complexes (Ren *et al.*, 2001, 2002). The CN groups are nearly coplanar with the plane defined by the four S atoms, the deviations being 0.04 (5), 0.051 (5), 0.026 (5) and 0.056 (5) Å for atoms C1, C4, N1 and N2, respectively.

In the cation, which lies on a twofold rotation axis and is disordered, the dihedral angle between the aromatic ring and the C6/C5/C6A plane is 89.55 (12)°, which means that the two planes are almost perpendicular to each other.

The compound stacks in completely segregated columns of anions and cations, as illustrated by the projection along the crystallographic *b* axis shown in Fig. 2. Within the anion columns, the Ni···Ni distances between neighbouring anions are identical [4.2874 (9) Å], the plane-to-plane separation between adjacent anions is 3.541 (2) Å (Fig. 3), and the

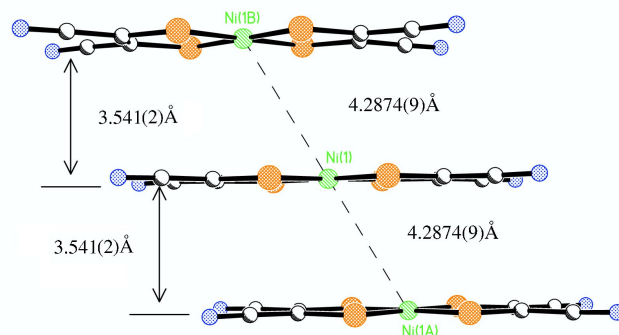


Figure 3

A uniformly spaced anion column.

shortest S···S and Ni···S contacts are 3.8362 (16) and 3.6113 (12) Å, respectively. The shortest Ni···Ni contact of between columns of [Ni(mnt)₂][−] ions is 10.613 (2) Å, which is much longer than the Ni···Ni distance between columns of [Ni(mnt)₂][−]. Within the cation columns, the benzene rings are parallel to each other; however, the centre-to-centre distance between adjacent aromatic rings is more than 4.2 Å; thus no π – π stacking interactions are found, whereas they exist in other compounds of this series (Ren *et al.*, 2002).

Experimental

Disodium maleonitriledithiolate (Na₂mnt) was prepared following the procedure described by Davison & Holm (1967). 1-(3-Fluorobenzyl)pyridinium chloride was prepared by reacting 3-fluoro-benzyl chloride with 1.5 equivalents of pyridine in refluxed acetone for about 4 h. The white microcrystalline product was filtered, and washed with acetone and diethyl ether in turn. The yield was more than 85% after drying in a vacuum. NiCl₂·6H₂O, Na₂mnt and 1-(3-fluorobenzyl)pyridinium chloride (equivalent molar ratio 1:2:2) were combined in water; the precipitated product was filtered off, washed with water and then dissolved in a little MeCN. Iodine (1 molar equivalent) was added to this solution, with stirring, at room temperature. Three times the resulting volume of MeOH was then added and the mixture was allowed to stand overnight. The resulting microcrystals were filtered off, washed with MeOH and dried in a vacuum. Single crystals of (I) suitable for structure analysis were obtained by diffusing diethyl ether into an MeCN solution of (I).

Crystal data

(C₁₂H₁₁FN)[Ni(C₄N₂S₂)₂]-C₂H₃N
M_r = 568.36
 Monoclinic, *C*2/*c*
a = 28.961 (6) Å
b = 4.2874 (9) Å
c = 20.788 (4) Å
 β = 96.53 (3)°
V = 2564.5 (9) Å³
Z = 4

D_x = 1.472 Mg m^{−3}
 Mo *K*α radiation
 Cell parameters from 454 reflections
 θ = 3.2–17.5°
 μ = 1.11 mm^{−1}
T = 293 (2) K
 Block, brown
 0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.826, *T_{max}* = 0.898
 6564 measured reflections

2512 independent reflections
 2024 reflections with *I* > 2σ(*I*)
R_{int} = 0.019
 θ_{max} = 26.0°
h = −30 → 35
k = −4 → 5
l = −25 → 25

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.149$
 $S = 1.04$
 2512 reflections
 183 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.09P)^2 + 1.99P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.78 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.57 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-----------|-------------|------------------------|-------------|
| Ni1—S1 | 2.1414 (11) | Ni1—S2 | 2.1483 (10) |
| S1—Ni1—S2 | 92.71 (4) | S1—Ni1—S2 ⁱ | 87.29 (4) |

Symmetry code: (i) $\frac{3}{2} - x, -\frac{1}{2} - y, 1 - z$.

All H atoms were placed in calculated positions ($C-H = 0.93 \text{ Å}$), with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{parent atom})$. Owing to the fact that atom C5 of the cation lies on a twofold axis, the 1-(3-fluorobenzyl)pyridinium cation is disordered. Atoms N3 and C6 occupy the same site with an occupation factor of 50% each. Moreover, the F atom is distributed over four sites, and its occupation factor on each of these sites is 25%. The disordered model was refined using the available tools in *SHELXL97*.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was funded by the National Natural Science Foundation of China (project Nos. 20171001, 29771017 and 29831010) and the Natural Science Foundation of Anhui Province of China (project No. 01012038).

References

Bruker (2000). *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Caneschi, A., Gatteschi, D., Lalioti, N., Sangregorio, C., Sessoli, R., Venturi, G., Vindigni, A., Rettori, A., Pini, M. G. & Novak, M. A. (2001). *Angew. Chem. Int. Ed.* **40**, 1760–1763.
 Clay, R. T., Campbell, D. K. & Mazumdar, S. (2003). *Synth. Met.* **135–136**, 681–682.
 Davison, A. & Holm, H. R. (1967). *Inorg. Synth.* **10**, 8–26.
 Lorenz, T., Hofmann, M., Gruninger, M., Freimuth, A., Uhrig, G. S., Dumm, M. & Dressel, M. (2002). *Nature (London)*, **418**, 614–617.
 Mitsumi, M., Kitamura, K., Morinaga, A., Ozawa, Y. & Kobayashi, M. (2002). *Angew. Chem. Int. Ed.* **41**, 2767–2771.
 Orignac, E. & Citro, R. (2003). *Eur. Phys. J. B*, **33**, 419–438.
 Ren, X. M., Li, H. F., Wu, P. H. & Meng, Q. J. (2001). *Acta Cryst.* **C57**, 1022–1024.
 Ren, X. M., Meng, Q. J., Song, Y., Lu, C. S., Hu, C. J. & Chen, X. Y. (2002). *Inorg. Chem.* **41**, 5686–5692.
 Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Wolf, B., Zherlitsyn, S., Schmidt, S. & Luthi, B. (2002). *Phys. Status Solidi A*, **189**, 389–396.
 Xie, J. L., Ren, X. M., He, C., Song, Y., Meng, Q. J., Kremer, R. K. & Yao, Y. H. (2003). *Chem. Phys. Lett.* **369**, 41–48.
 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.
 Xie, J. L., Ren, X. M., Song, Y., Zou, Y. & Meng, Q. J. (2002). *J. Chem. Soc. Dalton Trans.* pp. 2868–2872.