

# The 1:2 bis(maleonitriledithiolato)-palladium(II) complex of the *N*-(2-fluoro-4-bromobenzyl)pyridinium cation

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## Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

$R$  factor = 0.030

$wR$  factor = 0.065

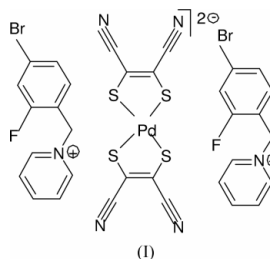
Data-to-parameter ratio = 13.6

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

In the title salt,  $(\text{C}_{12}\text{H}_{10}\text{BrFN})_2[\text{Pd}(\text{C}_4\text{N}_2\text{S}_2)_2]$  or  $[\text{N}-(2\text{-fluoro-4-bromobenzyl})\text{pyridinium}]_2[\text{Pd}(\text{mnt})_2]$ , where  $\text{mnt}^{2-}$  denotes maleonitriledithiolate, the  $\text{Pd}^{2+}$  ion is coordinated by four S atoms of two  $\text{mnt}^{2-}$  ligands in a planar geometry. The asymmetric unit is composed of one *N*-(2-fluoro-4-bromobenzyl)pyridinium cation and one-half  $[\text{Pd}(\text{mnt})_2]^{2-}$  anion. The adjacent counter-cations form dimers by  $\text{C}_{\text{py}}-\text{H}\cdots\text{F}_{\text{Ar}}$  hydrogen-bonding interactions. Anions and cations stack in alternating layers which are nearly parallel to the *bc* plane of the crystallographic unit cell.

## Comment

Recently, one-dimensional (1-D) compounds have been attracting widespread attention because of their novel physical properties, such as spin–Peierls transitions (Bray *et al.*, 1975), spin–charge separation states (Lorenz *et al.*, 2002), molecular bistabilities (Fujita & Awaga, 1999), and so on. Furthermore, more and more new quantum effects have been observed in 1-D spin systems (Caneschi *et al.*, 2001; Shiramura *et al.*, 1998).

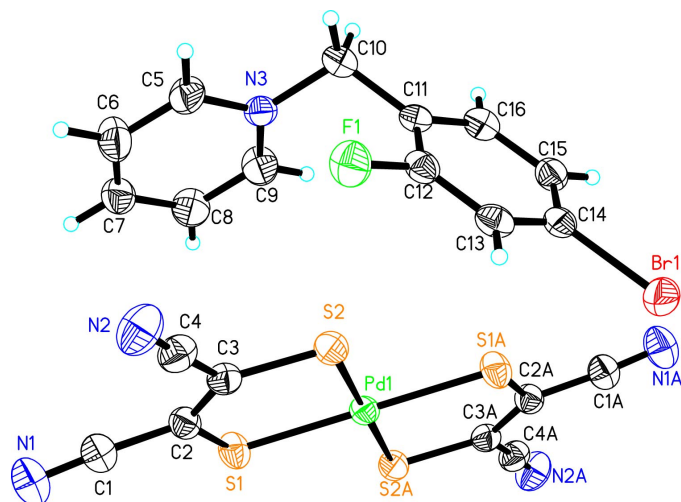


In current studies, we have developed a new class of  $[\text{R-BzPy}][\text{Ni}(\text{mnt})_2]$  salt, where  $[\text{R-BzPy}]^+$  represents a derivative of benzylpyridinium, as building blocks to construct a low-dimensional molecular solid (Ren, Meng, Song, Hu *et al.*, 2002; Ren, Meng, Song, Lu *et al.*, 2002; Xie, Ren, Song, Zhang *et al.*, 2002; Xie, Ren, Song, Zou & Meng, 2002; Xie *et al.*, 2003). We have found: (a) all  $[\text{R-BzPy}][\text{Ni}(\text{mnt})_2]$  compounds stack with well separated columns of anions and cations in the solid state, in which  $[\text{Ni}(\text{mnt})_2]^-$  anions form a spaced 1-D magnetic chain of  $s = \frac{1}{2}$  along the direction of the anion column; (b) the topology and size of the  $[\text{R-BzPy}]^+$  ion, which is related to the molecular conformation of the  $[\text{R-BzPy}]^+$  ion, can be modulated by systematic variation of the substituents in the aromatic rings, and so the stacking pattern of those complexes can be finely tuned by controlling the molecular conformation of the  $[\text{R-BzPy}]^+$  ion; (c) The magnetic coupling interactions in these systems are very sensitive to intermolecular separations. A series of complexes with almost the same stacking patterns but slightly different

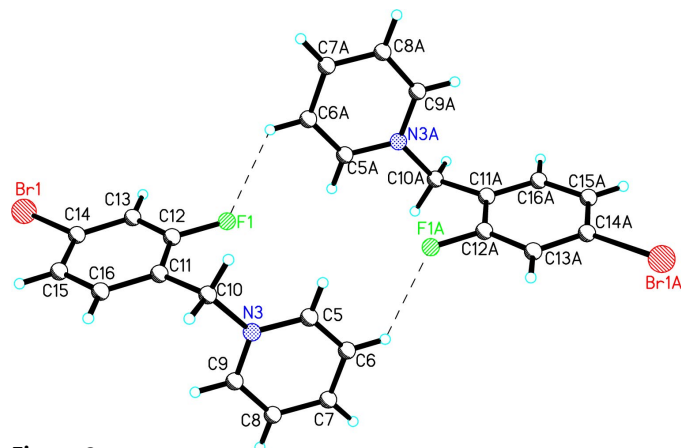
Received 19 February 2003

Accepted 5 March 2003

Online 14 March 2003



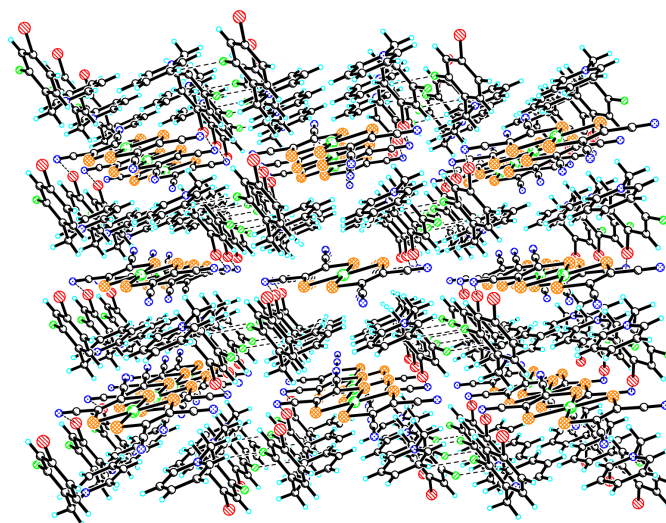
**Figure 1**  
The cation and anion of complex (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.



**Figure 2**  
The hydrogen-bonding dimer formed by adjacent cations.

intermolecular spacing has been obtained. The complexes exhibit magnetic diversity, and some reveal an unusual spin–Peierls-like phase transition. In order to further understand the relationship between magnetic properties and the stacking structures in these types of complexes, we have studied the complex  $[\text{BrFBzPy}]_2[\text{Pd}(\text{mnt})_2]$ , (I).

The asymmetric unit of (I) is composed of one *N*-(2-fluoro-4-bromobenzyl)pyridinium cation and one-half  $[\text{Pd}(\text{mnt})_2]^{2-}$  anion (Fig. 1). The  $\text{Pd}^{2+}$  ion occupies an inversion center, surrounded by four S atoms of two  $\text{mnt}^{2-}$  ligands, and exhibits a square-planar coordination geometry. The Pd–S distances are in the range 2.2872 (11)–2.2941 (10) Å, with S–Pd–S angles of between 89.56 (3) and 90.44 (3)° (Table 1). These results are in agreement with those of corresponding  $[\text{Pd}(\text{mnt})_2]^{2-}$  complexes (Bois *et al.*, 1998). The anion is almost planar, the N atoms of the CN groups being somewhat bent away from the plane, and atoms N1 and N2 deviate from the  $S_4$  plane by 0.64 (2) and 0.43 (2) Å, respectively. As for the cations, the pyridine and benzene rings twist with respect to each other, similar to the situation in an  $[\text{Ni}(\text{mnt})_2]^-$  series reported earlier by us (Ren, Meng, Song, Hu *et al.*, 2002), and



**Figure 3**  
The layered packing of alternating anions and cations.

the dihedral angles between the reference plane, N3/C10/C11, and the benzene and pyridine rings are 65.73 (16) and 59.7 (3)°, respectively. Two adjacent cations dimerize through hydrogen-bonding interactions between F1 and C6 of a neighbouring molecule (Fig. 2). The anions and cations form alternating layers, which are nearly parallel to the *bc* plane of the crystallographic unit cell (Fig. 3).

## Experimental

Disodium maleonitriledithiolate ( $\text{Na}_2\text{mnt}$ ) was prepared following the procedure of Davison & Holm (1967). *N*-(2-Fluoro-4-bromobenzyl)pyridinium chloride was prepared by reacting 2-fluoro-4-benzyl chloride with 1.5 equivalent of pyridine in refluxing acetone for 4 h. The white microcrystalline product was filtered off and washed with acetone and diethyl ether in turn; the yield is more than 86% after drying *in vacuo*. A similar method for synthesizing  $[\text{Bu}_4\text{N}]_2[\text{Pd}(\text{mnt})_2]$  (Davison & Holm, 1967) was used to prepare the title compound, (I). Well shaped, black single crystals suitable for X-ray analysis were obtained by diffusing diethyl ether into an acetonitrile solution of complex (I) for about 3 d.

### Crystal data

$(\text{C}_{12}\text{H}_{10}\text{BrFN})_2[\text{Pd}(\text{C}_4\text{N}_2\text{S}_2)_2]$   
 $M_r = 921.00$   
 Triclinic,  $P\bar{1}$   
 $a = 7.1140$  (18) Å  
 $b = 11.035$  (3) Å  
 $c = 11.851$  (3) Å  
 $\alpha = 69.564$  (4)°  
 $\beta = 89.016$  (4)°  
 $\gamma = 74.151$  (4)°  
 $V = 835.5$  (4) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.830$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 3.1$ –27.5°  
 $\mu = 3.24$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Block, black  
 0.15 × 0.10 × 0.10 mm

### Data collection

Siemens CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)  
 $T_{\text{min}} = 0.665$ ,  $T_{\text{max}} = 0.728$   
 4372 measured reflections

2907 independent reflections  
 2348 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.016$   
 $\theta_{\text{max}} = 25.0^\circ$   
 $h = -7 \rightarrow 8$   
 $k = -13 \rightarrow 13$   
 $l = -13 \rightarrow 14$

## Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.030$	$w = 1/[\sigma^2(F_o^2) + (0.025P)^2]$
$wR(F^2) = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.12$	$(\Delta/\sigma)_{\max} = 0.001$
2907 reflections	$\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
214 parameters	$\Delta\rho_{\min} = -0.47 \text{ e } \text{\AA}^{-3}$

**Table 1**Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Pd1—S1	2.2872 (11)	Pd1—S2	2.2941 (10)
S1—Pd1—S2	89.56 (3)		

**Table 2**Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C6—H6A $\cdots$ F1 <sup>1</sup>	0.93	2.40	3.079 (4)	130

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

All H atoms were placed in geometrically calculated positions (C—H = 0.93 and 0.97  $\text{\AA}$ ), with  $U_{\text{iso}} = 1.2U_{\text{eq}}$  (parent atom).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*.

This work was funded by the National Natural Science Foundation of China (project No. 20171001), the Anhui

Province Education Commission of China (project No. 2001kj162) and the Natural Science Foundation of Anhui Province of China (project No. 01012038).

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