

## 1-(4-Fluorobenzyl)pyridinium bis(maleonitriledithiolato)platinate(III)

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## Key indicators

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(\text{C}-\text{C}) = 0.023 \text{ \AA}$ 

Disorder in main residue

R factor = 0.052

wR factor = 0.135

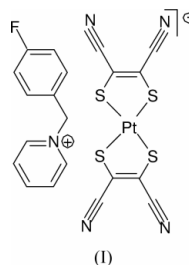
Data-to-parameter ratio = 13.7

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

In the title compound,  $(\text{C}_{12}\text{H}_{11}\text{FN})[\text{Pt}(\text{C}_4\text{N}_2\text{S}_2)_2]$ , the planar  $\text{Pt}^{\text{III}}$  complex anions stack into columns along the *b* axis, and these anionic columns are further connected by anion dimers to form a two-dimensional network in the *ab* plane. The cations stack into a two-dimensional network in the *ac* plane by weak  $\pi-\pi$  interactions. The networks of both anions and cations intercalate to give a three-dimensional solid.

## Comment

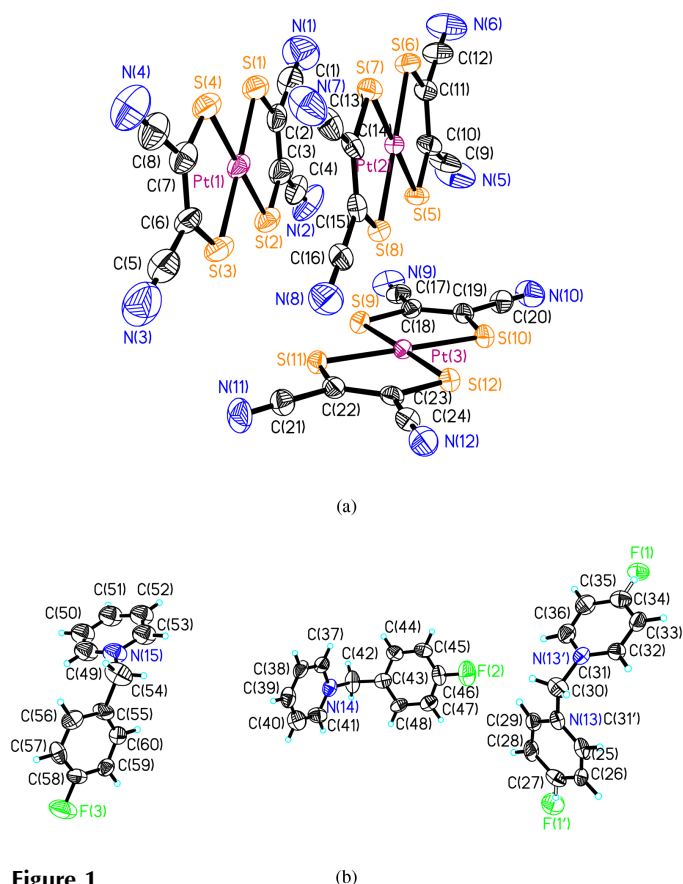
In recent years many new effects have been found for low-dimensional spin systems (Caneschi *et al.*, 2001; Wolf *et al.*, 2002; Mitsumi *et al.*, 2002; Lorenz *et al.*, 2002). Our interest is to construct quasi-one-dimensional molecule-based magnetic materials, formed by plate-like maleonitriledithiolene (mnt) anionic metal complexes  $[\text{M}(\text{mnt})_2]^-$  (*M* is  $\text{Ni}^{3+}$ ,  $\text{Pd}^{3+}$  or  $\text{Pt}^{3+}$ ). The magnetic properties of these types of low-dimensional magnetic materials are associated with columnar crystallographic packing. More recently, we have developed a new class of  $[\text{R}-\text{BzPy}]^+[\text{Ni}(\text{mnt})_2]^-$  salt, in which  $[\text{R}-\text{BzPy}]^+$  represents a derivative of benzylpyridinium, as building blocks to construct a low-dimensional molecular solid, and have found that the topology and size of the  $[\text{R}-\text{BzPy}]^+$  ion, which is related to its molecular conformation, can be modulated by systematic variation of the substituents in the aromatic rings. Therefore, the stacking pattern of these complexes can be finely tuned through controlling the molecular conformation of the  $[\text{R}-\text{BzPy}]^+$  ion. This idea motivated us to prepare a series of complexes which exhibit magnetic diversity (Ren *et al.*, 2002; Liu *et al.*, 2003; Xie, Ren, Song, Zou *et al.*, 2002; Xie, Ren, Song, Zhang *et al.*, 2002; Xie *et al.*, 2003). With the goal of extending our research and understanding the relationship between magnetic properties and stacking structures, we further pursued the study of  $[\text{RBzpy}]^+[\text{Pt}(\text{mnt})_2]^-$ , because the  $[\text{Pt}(\text{mnt})_2]^-$  anion is similar to  $[\text{Ni}(\text{mnt})_2]^-$  in both molecular structure and electronic configuration. We report here the crystal structure of the title compound, (I), which has a different packing structure from the series of  $[\text{Ni}(\text{mnt})_2]^-$ -based complexes.



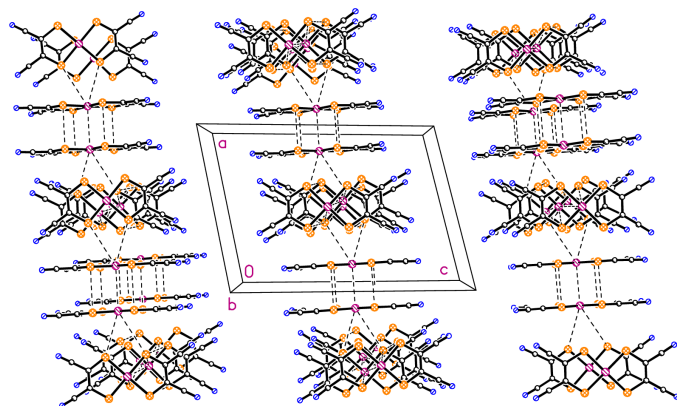
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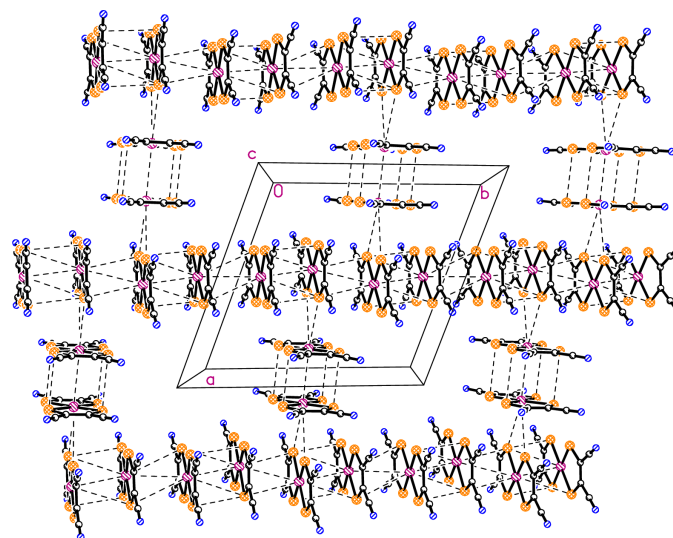


**Figure 1**  
The structure of (a) the anions and (b) the cations of complex (I), showing 30% probability displacement ellipsoids and the numbering scheme.



**Figure 2**  
The packing of anions, projected along the *b* axis.

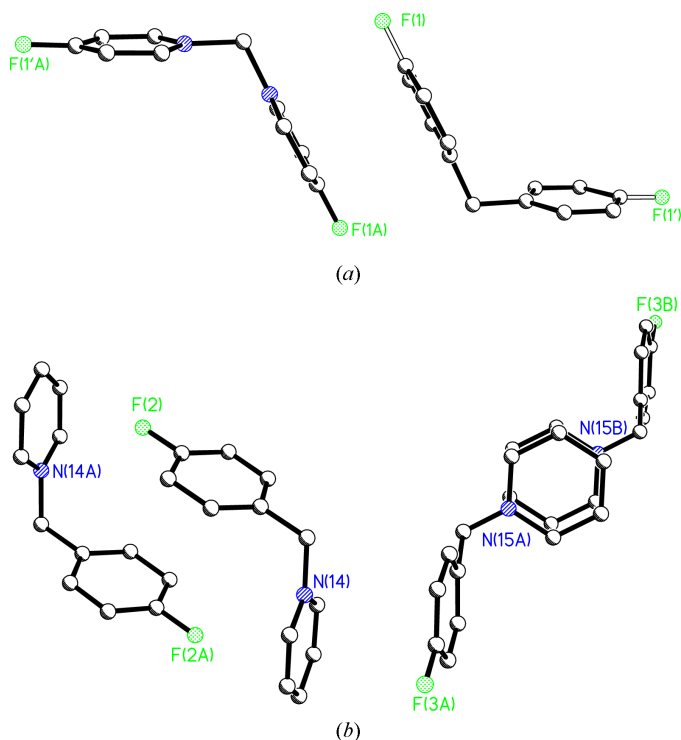
There are three anions and three cations in the asymmetric unit of (I); the Pt<sup>III</sup> ions in the three crystallographically independent [Pt(mnt)<sub>2</sub>]<sup>2-</sup> moieties are coordinated by four S atoms of two mnt<sup>2-</sup> ligands, and exhibit square-planar coordination geometry. The least-square planes of the four S atoms were calculated for each of the [Pt(mnt)<sub>2</sub>]<sup>2-</sup> moieties. The angle between the coordination planes of the Pt1 and Pt2 moieties is only 1.21 (6)°. The dihedral angle between the



**Figure 3**  
The two-dimensional anionic networks in the *ab* plane, projected along the *c* axis.

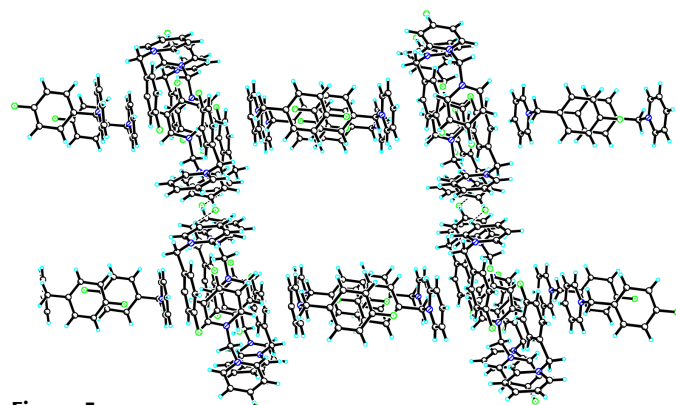
coordination planes of the Pt3 and Pt2 entries is 85.29 (6)°, so the plane including Pt3 is approximately perpendicular to the two planes including Pt1 and Pt2. The CN groups of the mnt<sup>2-</sup> ligand are out of the coordination plane in the Pt1 and Pt2 moieties, as in the series of Ni<sup>III</sup>-based complexes, the largest deviations from the coordination planes being 0.287 (15) Å for N3 and 0.160 (13) Å for N7. The average S—Pt—S chelate angle is 90.4°, and the Pt—S bond distances range from 2.250 (4) to 2.272 (3) Å; these values are in agreement with those for reported [Pt(mnt)<sub>2</sub>]<sup>2-</sup> complexes (Pullen *et al.*, 1998). One of the three independent cations, *viz.* the one involving F1, shows orientational disorder, where the positions of the pyridinium and 4-fluorophenyl moieties are interchanged. Three crystallographically independent [FBzPy]<sup>+</sup> cations have  $\Lambda$ -shaped molecular configurations; the dihedral angles between the reference plane C30/C31/N13 and the benzene and pyridine rings are 84.2 (11) and 86.4 (9)°, respectively, for the F1 cation [corresponding dihedral angles are 81.3 (11) and 76.4 (11)°, respectively, for the F2 cation and 75.2 (16) and 48.0 (11)°, respectively, for the F3 cation]. The bond lengths and angles in the cations are, generally, in close agreement with values reported for the (FBzPy)[Ni(mnt)<sub>2</sub>] complex (Xie, Ren, Song, Zhang *et al.*, 2002).

Symmetry-generated anions containing Pt1 and Pt2 stack into columns of [Pt(mnt)<sub>2</sub>]<sup>2-</sup> anions along the *b* axis; within this type of anionic column, the molecular planar separations between adjacent [Pt(mnt)<sub>2</sub>]<sup>2-</sup> anions are alternately 3.540 (2) Å between anions containing Pt1 and Pt2 and 3.634 (2) Å between anions containing Pt1 and Pt1(1 - *x*, -*y*, 1 - *z*) (Table 2). Symmetry-generated anions containing Pt3 dimerize, the separation between planes within a dimer being 3.4881 (16) Å. These dimers connect the anionic columns through S...S interactions into two-dimensional anionic networks in the *ab* plane (Figs. 2 and 3).

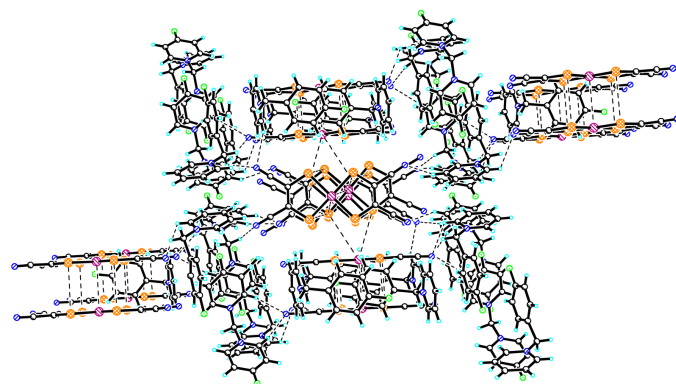
**Figure 4**

The  $\pi$ - $\pi$  interaction model between cations for (a) the F1-containing moiety (b) the F2- and F3-contained moieties. Symmetry codes are  $1 - x, 1 - y, 2 - z$  for F(1A);  $2 - x, 2 - y, 1 - z$  for F(2A);  $x, 1 + y, z$  for F(3A);  $1 - x, 1 - y, -z$  for F(3B).

There are strong  $\pi$ - $\pi$  stacking interactions between the benzene rings of cations containing F1 and F1( $1 - x, 1 - y, 2 - z$ ), which pack in a chair-like conformation with a centroid-centroid distance of 3.4591 (10) Å. There are weak  $\pi$ - $\pi$  interactions between the benzene rings of cations containing F2 and F2( $2 - x, 2 - y, 1 - z$ ), with a longer centroid-centroid distance of 4.215 (3) Å; adjacent benzene rings also stack in a chair-like conformation, but there is a shorter distance of 2.8682 (14) Å between atom F2 and the centroid of the benzene ring at ( $2 - x, 2 - y, 1 - z$ ); perhaps there is an F- $\pi$  interaction. The pyridine rings in the cations containing F3 and F3( $1 - x, -y, -z$ ) overlap in a chair-like conformation, the centroid-centroid distance being 4.203 (4) Å. The centroid-centroid distance between the benzene ring containing F3 and the neighboring pyridine ring containing N14( $x, y - 1, z - 1$ ) is 3.8694 (16) Å, the corresponding dihedral angle being 5.6 (6)° (Fig. 4). The three independence cations stack in such a way as to form a two-dimensional cationic network in the *ac* plane (Fig. 5). The anionic networks intercalate with the cationic networks to develop a three-dimensional solid (Fig. 6). Comparing these results with the series of Ni<sup>III</sup>-based complexes, it can be concluded that both the molecular conformation of benzylpyridinium derivatives and the anionic properties (for example, the radii of the M<sup>III</sup> ion, and so on) affect the stacking structure of these kinds of complexes.

**Figure 5**

The cationic networks in the *ac* plane.

**Figure 6**

Packing diagram, showing intercalating anionic and cationic networks.

## Experimental

Disodium maleonitriledithiolate (Na<sub>2</sub>mnt) was prepared following the procedure in the literature (Davison & Holm, 1967). 1-(4-Fluorobenzyl)pyridinium chloride was prepared by reacting 4-fluorobenzyl chloride with 1.5 equiv. of pyridine in refluxed acetone for 4 h; the resulting white microcrystalline product was filtered and washed with acetone and diethyl ether in turn; yield *ca* 85% after drying *in vacuo*. K<sub>2</sub>PtCl<sub>4</sub>, Na<sub>2</sub>mnt and 1-(4-fluorobenzyl)pyridinium chloride (equivalent molar ratio 1:2:2) were combined in water, and the red precipitated product was separated, washed with water and then dissolved in a little MeCN. Iodine (1.5 molar equivalent) was added to the boiling solution with stirring. Four times the resulting volume of MeOH was then added and the mixture allowed to stand overnight. The microcrystals which formed were separated, washed with MeOH and dried *in vacuo*, yield about 50%. Single crystals of (I) suitable for structure analysis were obtained by diffusing diethyl ether into an MeCN solution of (I) for a week.

### Crystal data

(C<sub>12</sub>H<sub>11</sub>FN)[Pt(C<sub>4</sub>N<sub>2</sub>S<sub>2</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 663.67  
 Triclinic, *P* $\bar{1}$   
*a* = 13.631 (3) Å  
*b* = 14.297 (4) Å  
*c* = 18.557 (5) Å  
 $\alpha$  = 99.71 (1)°  
 $\beta$  = 99.01 (1)°  
 $\gamma$  = 108.39 (1)°  
*V* = 3296.4 (15) Å<sup>3</sup>

*Z* = 6  
*D<sub>x</sub>* = 2.006 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 3.6–16.5°  
 $\mu$  = 6.79 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Block, brown  
 0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
 $T_{\min} = 0.293$ ,  $T_{\max} = 0.507$   
 16959 measured reflections

11415 independent reflections  
 7990 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.049$   
 $\theta_{\text{max}} = 25.0^\circ$   
 $h = -16 \rightarrow 16$   
 $k = -16 \rightarrow 16$   
 $l = -12 \rightarrow 22$

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.052$   
 $wR(F^2) = 0.135$   
 $S = 1.09$   
 11415 reflections  
 836 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 1.55P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 1.97 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.34 \text{ e } \text{\AA}^{-3}$

Table 1

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

Pt1—S1	2.250 (4)	Pt2—S6	2.263 (3)
Pt1—S3	2.256 (4)	Pt2—S7	2.269 (3)
Pt1—S4	2.265 (3)	Pt3—S9	2.262 (3)
Pt1—S2	2.272 (3)	Pt3—S11	2.263 (3)
Pt2—S8	2.258 (3)	Pt3—S10	2.263 (3)
Pt2—S5	2.260 (3)	Pt3—S12	2.265 (3)
S3—Pt1—S4	90.73 (13)	S8—Pt2—S7	89.97 (11)
S1—Pt1—S2	90.56 (13)	S9—Pt3—S10	90.40 (11)
S5—Pt2—S6	90.30 (11)	S11—Pt3—S12	90.33 (10)

Table 2

Contact distances ( $\text{\AA}$ ).

Pt1...Pt2	3.6423 (10)	S4...S7	3.630 (4)
Pt1...Pt1 <sup>i</sup>	3.9839 (13)	S9...S12 <sup>ii</sup>	3.471 (4)
Pt1...S7	4.045 (3)	S10...S11 <sup>ii</sup>	3.506 (4)
Pt2...S1	3.860 (3)	S9...S2	3.709 (4)
Pt3...Pt3 <sup>ii</sup>	3.4965 (11)	S9...S5	3.838 (4)
S1...S2 <sup>i</sup>	3.967 (4)	S10...S5	3.888 (4)
S3...S1 <sup>i</sup>	3.974 (4)	S11...S2	3.811 (4)
S4...S2 <sup>i</sup>	3.969 (4)	S11...S3	3.767 (4)
S2...S5	3.649 (4)	S12...S8	3.826 (4)
S3...S8	3.615 (4)		

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

All H atoms were placed in geometrically calculated positions (C—H 0.93 and 0.97  $\text{\AA}$ ) with  $U_{\text{iso}} = 1.2 U_{\text{eq}}$  (parent atom). Atoms F1 and N13 were treated as disordered, and occupancies for F1 (F1'),

C31 (N13'), and N13 (C31') were each set to 50%. The anisotropic displacement parameters of the atoms C49—C53 and N15 in one of the pyridine rings were restrained to be similar, and the geometry of another pyridine ring, C37—C41/N14, was constrained to that of a regular hexagon in order to avoid unreasonable results. The highest peak and the deepest hole of the residual density are at 0.98  $\text{\AA}$  from Pt3 and at 1.10  $\text{\AA}$  from Pt1, respectively.

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: SAINT (Siemens, 1996); 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..

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