

## 2-Methyl-1-(4-nitrobenzyl)pyridinium bis(maleonitriledithiolato)-nickelate(III)

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Received 2 January 2001

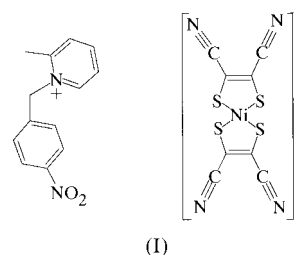
Accepted 1 June 2001

In the title complex, 2-methyl-1-(4-nitrobenzyl)pyridinium bis(1,2-dicyanoethene-1,2-dithiolato)nickelate(III), (C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>)[Ni(C<sub>4</sub>N<sub>2</sub>S<sub>2</sub>)<sub>2</sub>], the most prominent general structural feature of the complex is the completely segregated columnar stacks of anions and cations. Within the cation column, there may be stacking interactions between adjacent nitro groups and benzene rings.

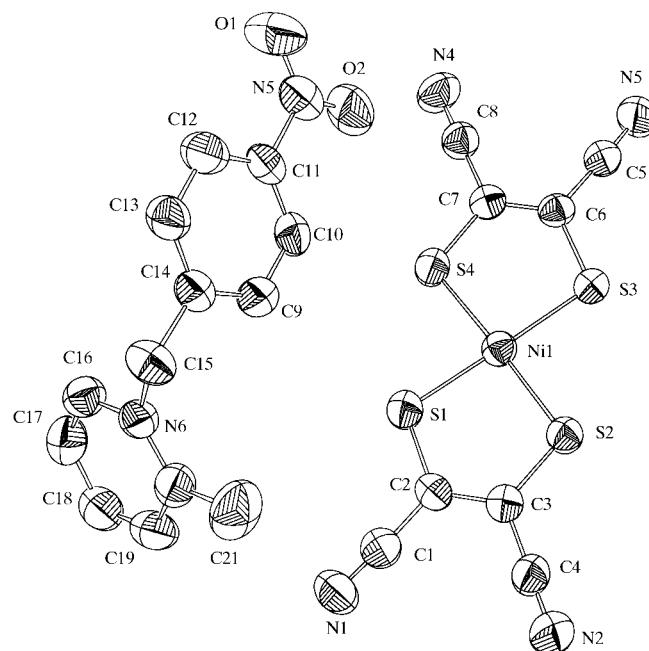
### Comment

Recently, considerable interest has been focused on low-dimensional molecular solids with novel magnetic properties, such as spin-Peierls transitions (Brown *et al.*, 1998) and room-temperature spin bistability (Fujita & Awaga, 1999). Our aim is to construct quasi-one-dimensional molecule-based magnetic materials formed by plate-like maleonitriledithiolene (mnt) anionic metal complexes [M(mnt)<sub>2</sub>]<sup>−</sup> (M is Ni<sup>III</sup>, Pd<sup>III</sup> or Pt<sup>III</sup>). These types of low-dimensional materials are associated with columnar crystallographic packing. Previous work has shown that the geometry of the counter-cations strongly influences the stacking structure of this type of material. Therefore, it is important to select particular counter-cations in order to obtain columnar crystallographic packing. The ground-state conformations of benzylpyridinium derivatives have been extensively investigated by many techniques, and results to date have indicated that the spatial orientation of the benzene and pyridine rings depends on both the electronic and steric properties of the substituents on the aryl rings (Bulgarevich *et al.*, 1994). The different conformations available to benzylpyridinium derivatives may lead to differences in the geometry of the cations sufficient to influence the stacking structures of the complexes in the solid state. As a result, the ion-pair complexes consisting of [M(mnt)<sub>2</sub>]<sup>−</sup> anions and benzylpyridinium-derived cations present a unique opportunity for the systematic investigation of the fundamental relationship between the stacking structure in the solid

and the substituents on the aryl rings. To test this idea, we prepared a series of complexes by systematically varying the substituents on the aryl rings and found that it was possible to obtain completely separated anions and cations in columnar stacking structures. We report herein the crystal structure of the title compound, (I), which has columnar packing.



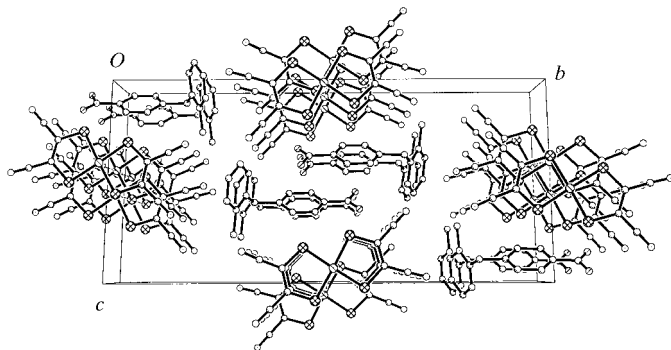
In the anion of (I), the Ni atom exhibits square-planar coordination geometry involving four S atoms, and the five-membered nickel-containing rings are slightly puckered (Fig. 1), as has been found in other [M(mnt)<sub>2</sub>]<sup>−</sup> structures (Plumlee *et al.*, 1975). The average S—Ni—S bond angle within the five-membered ring is 92.50(5)° and the average Ni—S bond distance is 2.1477(13) Å. Other chemically equivalent but crystallographically non-equivalent bond distances within the anion differ by less than three s.u.'s and compare well with those found in [Ni(mnt)<sub>2</sub>]<sup>−</sup> complexes (Brunn *et al.*, 1987). The anion is non-planar and the CN groups bend away from the plane of the four S atoms. The CN group with the largest deviation is C1≡N1 and the deviations from the plane defined by the four S atoms are 0.294(6) and 0.167(6) Å for N1 and C1, respectively. The cation adopts a conformation where the dihedral angle between the benzene ring and the C14/C15/N6 reference plane is 44.5(4)°, and the



**Figure 1**  
The molecular structure of complex (I) with the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

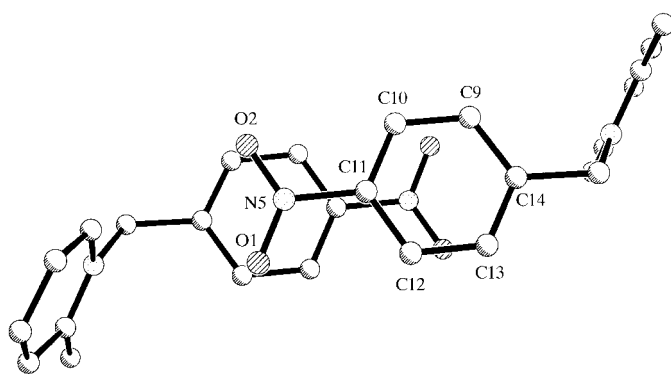
pyridine ring is twisted towards the reference plane [dihedral angle 72.3 (4)°].

The most prominent general structural features of the complex are the completely segregated stacked columns of [Ni(mnt)<sub>2</sub>]<sup>−</sup> anions and 2-methyl-1-(4-nitrobenzyl)pyridinium



**Figure 2**  
The packing diagram of (I) showing the completely separated columns of anions and cations.

cations, as revealed by the projection along the crystallographic *a* axis shown in Fig. 2. Reports of completely segregated stacked columns of [Ni(mnt)<sub>2</sub>]<sup>−</sup> anions are rare (Hobi *et al.*, 1996). The Ni···Ni distances are alternately 3.847 (1) and 4.281 (1) Å within the [Ni(mnt)<sub>2</sub>]<sup>−</sup> column. The nearest Ni···Ni contact between [Ni(mnt)<sub>2</sub>]<sup>−</sup> columns is much longer at 10.6 Å, and is longer than the Ni···Ni distance within the [Ni(mnt)<sub>2</sub>]<sup>−</sup> column. These results indicate that, compared



**Figure 3**  
A pair of cations showing the overlapping between the nitro groups and the benzene rings. H atoms have been omitted for clarity.

with intracolumnar interactions, the Ni···Ni magnetic exchange interactions between columns may be neglected. Within the 2-methyl-1-(4-nitrobenzyl)pyridinium cation column, the nitro group of one cation is stacked over the benzene ring of an adjacent cation (Fig. 3). This type of packing structure is often found in nitrobenzene derivatives (Harrowfield *et al.*, 1998). The shorter contacts between adjacent nitro groups and benzene rings are: N5···C9<sup>i</sup> 3.591 (6), N5···C10<sup>i</sup> 3.505 (6), N5···C11<sup>i</sup> 3.636 (6), O1···C9<sup>i</sup> 3.439 (6), O1···C10<sup>i</sup> 3.570 (6), O2···C12<sup>i</sup> 3.611 (6), O2···C13<sup>i</sup> 3.483 (6) and O2···C14<sup>i</sup> 3.567 (6) Å [symmetry code: (i) 2 − *x*, 1 − *y*, 1 − *z*].

## Experimental

NiCl<sub>2</sub>·6H<sub>2</sub>O, disodium maleonitriledithiolate and 2-methyl-1-(4-nitrobenzyl)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 the solution with stirring at room temperature. Three times the resulting volume of MeOH was then added and the mixture allowed to stand overnight. The microcrystals which formed were filtered off, washed with MeOH and dried *in vacuo*. Single crystals of (I) suitable for structure analysis were obtained by evaporating an MeCN-*n*-PrOH (1:1, *v/v*) solution of (I).

### Crystal data

(C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>)[Ni(C<sub>4</sub>N<sub>2</sub>S<sub>2</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 568.32  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 7.2343 (13) Å  
*b* = 26.691 (4) Å  
*c* = 12.745 (2) Å  
 $\beta$  = 104.510 (16)°  
*V* = 2382.4 (7) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.584 Mg m<sup>−3</sup>  
 Mo *K*α radiation  
 Cell parameters from 36 reflections  
 $\theta$  = 7.4–14.4°  
 $\mu$  = 1.20 mm<sup>−1</sup>  
*T* = 293 (2) K  
 Block, black  
 0.40 × 0.30 × 0.30 mm

### Data collection

Bruker *P4* diffractometer  
 2 $\theta$ / $\omega$  scans  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
*T<sub>min</sub>* = 0.646, *T<sub>max</sub>* = 0.715  
 5502 measured reflections  
 4202 independent reflections  
 2775 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.043  
 $\theta_{\max}$  = 25.0°  
*h* = −1 → 8  
*k* = −1 → 31  
*l* = −15 → 15  
 3 standard reflections  
 every 97 reflections  
 intensity decay: 6.6%

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.048  
*wR*(*F*<sup>2</sup>) = 0.124  
*S* = 1.04  
 4202 reflections  
 308 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 1.9841P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.41 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.55 \text{ e } \text{Å}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Ni1—S1	2.1407 (14)	S1—C2	1.711 (5)
Ni1—S4	2.1451 (13)	S2—C3	1.710 (5)
Ni1—S2	2.1526 (13)	S3—C6	1.725 (4)
Ni1—S3	2.1577 (13)	S4—C7	1.713 (5)
S1—Ni1—S4	85.53 (5)	N1—C1—C2	176.8 (6)
S1—Ni1—S2	92.31 (5)	N2—C4—C3	179.6 (6)
S4—Ni1—S3	92.70 (5)	N3—C5—C6	178.0 (6)
S2—Ni1—S3	89.49 (5)	N4—C8—C7	179.6 (6)

H atoms were placed in geometrically calculated positions (C—H = 0.93 Å) with *U*<sub>eq</sub>(H) = 1.2*U*<sub>eq</sub>(parent atom).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997*a*); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*b*); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by grants from the Ministry of Science and Technology of China (NKBRFSF-G9990646) and the Natural Science Foundation of China (Nos. 29771017 and 29831010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1318). Services for accessing these data are described at the back of the journal.

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