1-(2-Chlorobenzyl)pyridinium bis(maleonitriledithiolato)nickelate(III)

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In the title complex, $(C_{12}H_{11}ClN)[Ni(C_4N_2S_2)_2]$, the most prominent structural feature is the completely segregated columnar stacks of anions and cations. The neighbouring anions within the anionic column are equally spaced, with a distance of 4.0917 (8) Å between the Ni atoms. Hence, the Ni^{3+} ions form an uniformly spaced magnetic chain along the direction of the anionic stacking column.

Comment

In recent years many new effects have been found, especially for low-dimensional spin systems (Caneschi *et al.*, 2001; Wolf *et al.*, 2002; Mitsumi *et al.*, 2002; Lorenz *et al.*, 2002). Our aim is to construct quasi-one-dimensional molecule-based magnetic materials formed by plate-like maleonitriledithiolene (mnt) anionic metal complexes $[M(mnt)_2]^-$ (M is Ni^{3+}, Pd^{3+} or Pt^{3+}). The magnetic properties of these types of low-dimensional magnetic materials are associated with columnar crystallographic packing. Recently, we have developed a new class of $[R\text{-BzPy}]^+[Ni(mnt)_2]^-$ salts, using the $[Ni(mnt)_2]^-$ anion and derivatives of benzylpyridinium ($[R\text{-BzPy}]^+$) as building blocks to construct low-dimensional molecular solids. We have found that the topology and size of the $[R\text{-BzPy}]^+$ ion, which is related to its molecular conformation, can be modulated by systematic variation of the substituents on the aromatic rings. Hence, the stacking pattern of these complexes can be finely tuned through controlling the molecular conformation of the $[R\text{-BzPy}]^+$ ion. To test this idea, a series of complexes has been obtained, which exhibit magnetic diversity (Ren *et al.*, 2002; Xie, Ren, Song, Zou & Meng, 2002; Xie, Ren, Song, Zhang *et al.*, 2002; Xie, Ren, He *et al.*, 2003). In order to obtain further information concerning the nature of the effects of the substituents on the stacking pattern of these classes of ion-pair complexes, we report here the crystal structure of the title compound, (I), which has columnar packing.

(I)
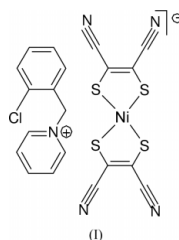
In the anion of (I), the Ni atom exhibits square-planar coordination geometry involving four S atoms. The five-membered nickel-containing rings are slightly puckered (Fig. 1), as has been found in other $[M(mnt)_2]^{n-}$ structures (Plumlee *et al.*, 1975). The average S—Ni—S bond angle
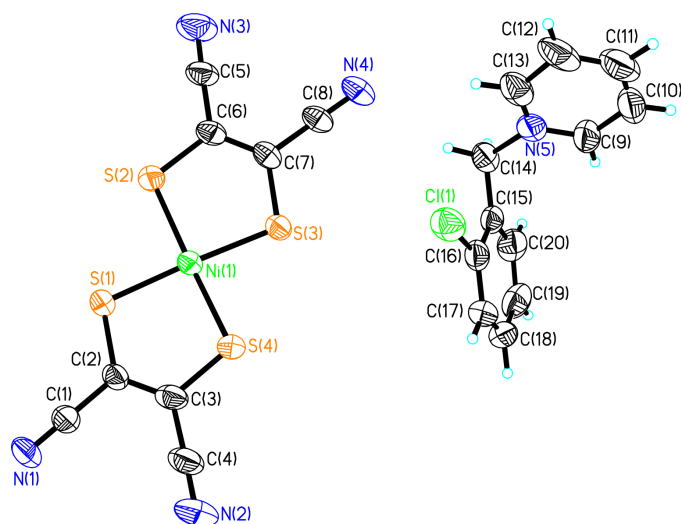
Figure 1
The structure of complex (I), showing displacement ellipsoids at the 30% probability level and the atom-numbering scheme.

Figure 2
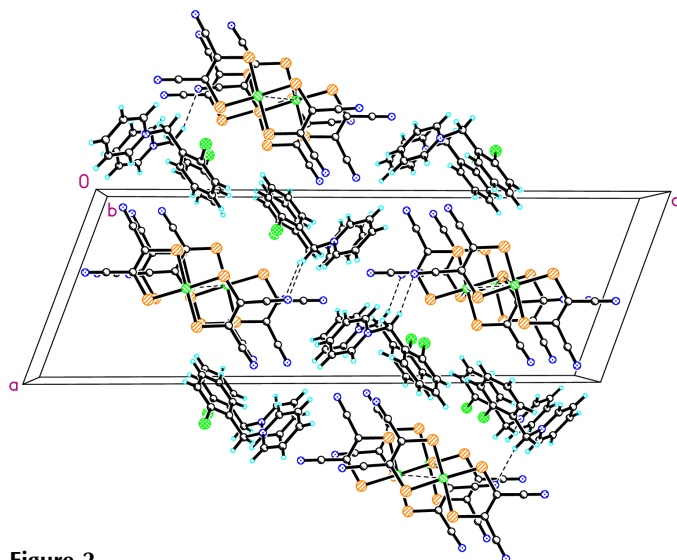Packing diagram, showing the completely separated column stacking in the **b** direction.

Figure 3
A view of the uniformly spaced anionic chain.

within the five-membered ring is 92.58 (6)° and the average Ni—S bond distance is 2.142 (2) Å. This compares well with similar bond distances and angles found in $[Ni(mnt)_2]^-$ complexes (Ren *et al.*, 2001, 2002). The anion is nearly planar; however, the CN groups bend away somewhat from the plane of the four S atoms. For example, the largest deviations from the plane defined by the four S atoms are 0.149 (6) and 0.212 (6) Å for atoms C8 and N4, respectively.

The cation adopts a Λ-shape conformation, similar to other complexes in these series. However, the dihedral angles between the aromatic rings and the reference plane deviate considerably from 90°. The pyridine ring and the C14/C15/N5 reference plane are inclined by 55.1 (4)°, and the benzene ring is twisted towards the reference plane with a dihedral angle of 75.0 (5)°. This is different from the case of 1-(4-*X*-benzyl)-pyridinium derivatives (*X* = substituent).
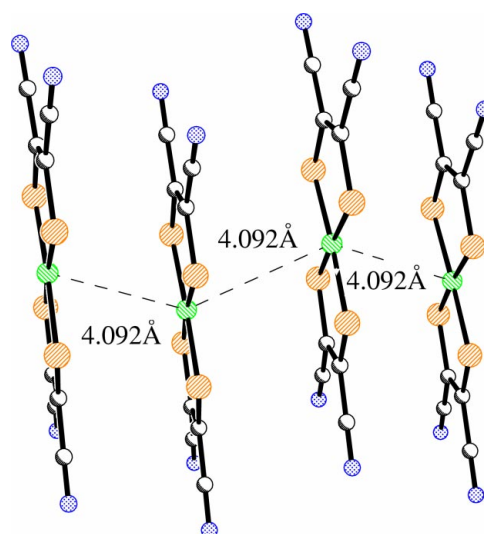
The most prominent structural features of complex (I) are the completely segregated stacking columns of the $[Ni(mnt)_2]^-$ anions and 1-(2-chlorobenzyl)pyridinium cations. This is illustrated by the projection along the crystallographic *b* axis shown in Fig. 2. Reports of completely segregated stacked columns of $[Ni(mnt)_2]^-$ anions are rare (Ren *et al.*, 2001). The Ni1···Ni1^i [symmetry code: (i) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$] distances between neighbouring anions within the $[Ni(mnt)_2]^-$ column are equal [4.0917 (8) Å]. Hence, the Ni^{3+} ions form a uniformly spaced magnetic chain along the direction of the anionic column (Fig. 3). In the magnetic chain the shortest S···S (S2···S3^i) and Ni···S (Ni1···S3^i) distances are 3.806 (2) and 3.507 (2) Å, respectively. The nearest Ni1···Ni1^{ii} [symmetry code: (ii) $-x, y - \frac{1}{2}, \frac{3}{2} - z$] contact between the $[Ni(mnt)_2]^-$ columns is 10.952 (2) Å, which is much longer than the Ni···Ni distance within the $[Ni(mnt)_2]^-$ column. These results indicate that, compared with intracolumnar interactions, the Ni···Ni magnetic exchange interactions between columns may be neglected, so this complex is an ideal magnetic chain compound. Within the column of 1-(2-chlorobenzyl)pyridinium cations, no π–π or Cl–π stacking interactions are found, which exist in 1-(4-chlorobenzyl)-pyridinium bis(maleonitriledithiolato)nickelate(III) (Ren *et al.*, 2002).

Experimental

Disodium maleonitriledithiolate (Na$_2$mnt) was prepared following a literature procedure (Davison & Holm, 1967). 1-(2-Chlorobenzyl)-pyridinium chloride was prepared by reacting 2′-chloro-benzyl-chlorine with 1.5 equivalents of pyridine in acetone and refluxing for 4 h. The product, a white microcrystalline solid, was filtered off, washed with acetone and diethyl ether in turn. The yield was more than 85% after drying *in vaccuo*. NiCl$_2$·6H$_2$O, Na$_2$mnt and 1-(2-chlorobenzyl)pyridinium chloride (equivalent molar ratio 1:2:2) were then combined in water. The resulting precipitate 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 vacuum. Crystals suitable for structure analysis were obtained by diffusing diethyl ether into a MeCN solution of (I).

Crystal data

$(C_{12}H_{11}ClN)[Ni(C_4N_2S_2)_2]$
$M_r = 543.74$
Monoclinic, $P2_1/c$
$a = 11.1294\ (14)$ Å
$b = 6.9653\ (9)$ Å
$c = 31.174\ (4)$ Å
$\beta = 110.437\ (4)°$
$V = 2264.5\ (5)$ Å^3
$Z = 4$

$D_x = 1.595$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 3.6–15.5°$
$\mu = 1.36$ mm^{-1}
$T = 293\ (2)$ K
Plate, black
$0.20 \times 0.15 \times 0.10$ mm

Data collection

Siemens CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (SHELXTL; Sheldrick, 1977b)
$T_{min} = 0.770$, $T_{max} = 0.864$
12 114 measured reflections

4443 independent reflections
2303 reflections with $I > 2\sigma(I)$
$R_{int} = 0.183$
$\theta_{max} = 26.1°$
$h = -13 \rightarrow 9$
$k = -8 \rightarrow 8$
$l = -36 \rightarrow 38$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.088$
$wR(F^2) = 0.199$
$S = 1.09$
4443 reflections
280 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.017$
$\Delta\rho_{max} = 0.72$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—S3	2.1367 (16)	Ni1—S2	2.1460 (17)
Ni1—S4	2.1356 (17)	Ni1—S1	2.1505 (16)
S3—Ni1—S4	85.58 (6)	S3—Ni1—S1	176.18 (7)
S3—Ni1—S2	92.57 (6)	S4—Ni1—S1	92.59 (7)
S4—Ni1—S2	176.87 (7)	S2—Ni1—S1	89.41 (7)

It was impossible to obtain good quality crystals. This results in a rather high R_{int} value and the fact that the crystal did not diffract significantly beyond 40° in 2θ.

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

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