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2-Amino-1-(4-chlorobenzyl)pyridinium bis(1,2-dicyanoethene-1,2-dithiolato)-nickelate(III)

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The asymmetric unit of the title compound, $(C_{12}H_{12}ClN_2)[Ni(C_4N_2S_2)_2]$, consists of one 2-amino-1-(4-chlorobenzyl)pyridinium cation and one $[Ni(mnt)_2]^-$ anion (where mnt is 1,2-dicyanoethene-1,2-dithiolate or maleonitriledithiolate). The Ni^{III} ion is coordinated by four S atoms of two mnt ligands and exhibits the expected square-planar coordination geometry. The anions and cations stack into well segregated columns along the *a* axis and the Ni^{III} atoms form a zigzag chain.

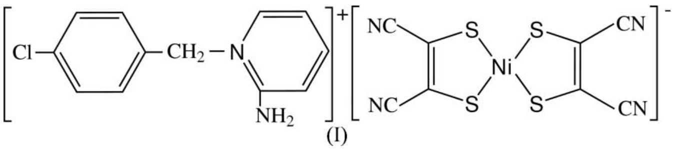
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.046
wR factor = 0.079
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.

Comment

Substituted pyridinium derivatives used as a countercation to the $[Ni(mnt)_2]^-$ anion (where mnt is 1,2-dicyanoethene-1,2-dithiolate or maleonitriledithiolate) may influence the stacking pattern of the anion and yield molecular materials with unusual magnetic properties (Robertson *et al.*, 1999; Ni *et al.*, 2004; Xie *et al.*, 2002; Ren *et al.*, 2002). Studies of anion–anion, cation–cation and anion–cation interactions play an important role in the understanding of the relationship between the physical properties and the structures of these ion-pair complexes, which is vital in the design of molecular materials. For example, the ion-pair complex containing the $[Ni(mnt)_2]^-$ anion and the 1-(4-chlorobenzyl)-4-amino-pyridinium cation exhibits an unusual magnetic transition (Ni *et al.*, 2005). We report here the synthesis and crystal structure of the title ion-pair complex, $[C_{12}H_{12}ClN_2]^+[Ni(C_4N_2S_2)_2]^-$, (I).



(I)

The asymmetric unit of (I) comprises an ion pair of $[C_{12}H_{12}ClN_2]^+$ and $[Ni(mnt)_2]^-$, as shown in Fig. 1. The Ni^{III} ion in the anion exhibits the expected square-planar coordination geometry. The phenyl and pyridine rings of the cation enclose a dihedral angle of 75.2 (2)°.

The crystal packing of the title complex is shown in Fig. 2. The $[Ni(mnt)_2]^-$ ions and $[C_{12}H_{12}ClN_2]^+$ cations stack as well segregated columns along the crystallographic *a* axis (Fig. 2). The Ni atoms of the anions form a zigzag chain (Fig. 3), with Ni$\cdots$Ni distances of 4.034 (2) and 4.247 (2) Å, which differ from the value of 3.944 Å observed in the related complex 1-(4-chlorobenzyl)-4-aminopyridinium $[Ni(mnt)_2]$ (Ni *et al.*, 2005).

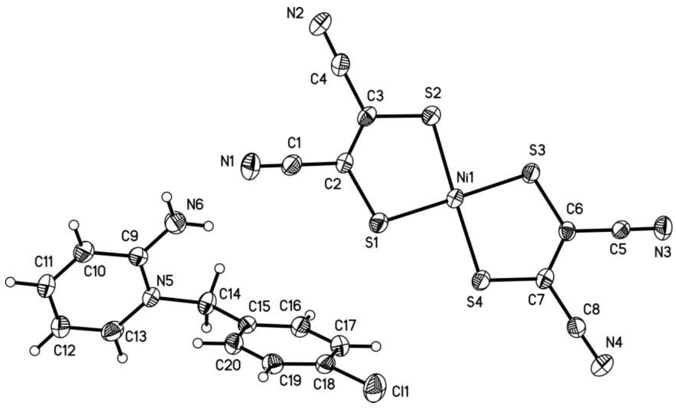


Figure 1
The structure of the title complex, showing the atom-numbering scheme, with 30% probability displacement ellipsoids.

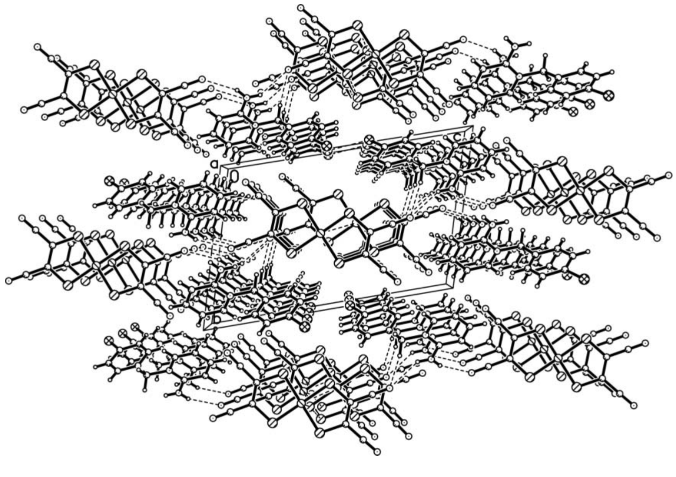


Figure 2
The crystal packing and two-dimensional network structure of (I). Dashed lines indicate the C—H···N, N—H···N and Ni···S interactions.

Experimental

The title Ni^{II} complex was prepared by the direct reaction of 1:2:2 molar equivalents of $NiCl_2·6H_2O$, Na_2mnt (Davison & Holm, 1967) and 1-(4-chlorobenzyl)-2-aminopyridinium bromide (Bulgarevich *et al.*, 1994), using a similar method for preparing $[Bu_4N]_2[Ni(mnt)_2]$. An MeCN solution (10 ml) of I_2 (0.062 mol l^{-1}) was added slowly to an acetone solution (20 ml) of $(C_{12}H_{12}ClN_2)[Ni(mnt)_2]$ (0.05 mol l^{-1}) and the mixture was stirred for 4 h. Propan-2-ol (50 ml) was then added and the mixture allowed to stand overnight. Black microcrystals were formed and these were filtered off, washed with MeOH and dried in a vacuum (yield 72%). Black block single crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of a solution in a mixture of MeCN and propan-2-ol (1:1 *v*/*v*) at room temperature for about two weeks. Analysis, calculated for $C_{20}H_{12}ClN_6NiS_4$: C 42.99, H 2.16, N 15.04%; found: C 42.87, H 2.24, N 14.93%. IR data (KBr, cm^{-1}): 3431 (NH_2), 2200 (CN), 1663, 1634, 1587, 1523 (C=C of phenyl ring and C=N of pyridine ring), 1490 (C=C of mnt^{2-}).

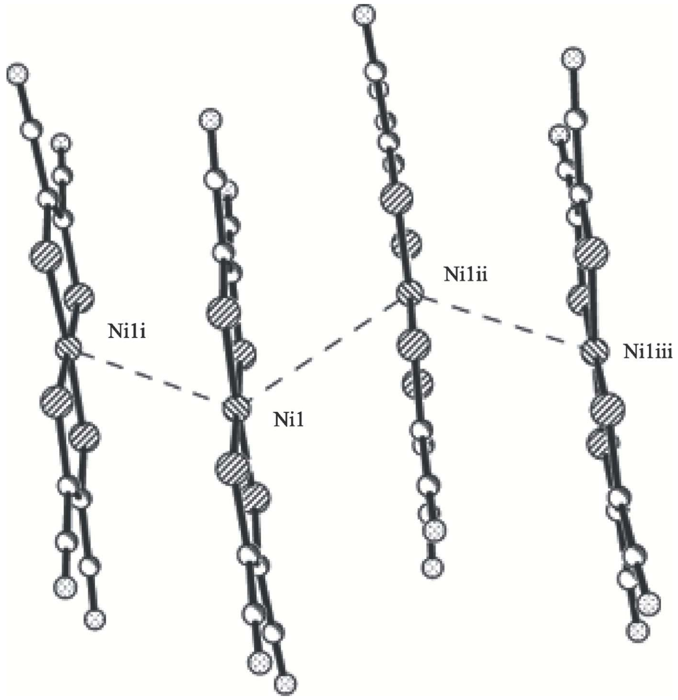


Figure 3
Side view of the anion stack of (I), showing the alternating chain of $[Ni(mnt)_2]^-$ anions. Dashed lines represent the Ni···Ni interactions at 4.034 (2) and 4.247 (2) Å.

Crystal data

$(C_{12}H_{12}ClN_2)[Ni(C_4N_2S_2)_2]$
M_r = 558.76
Triclinic, $P\bar{1}$
a = 6.891 (1) Å
b = 10.629 (2) Å
c = 16.378 (3) Å
α = 104.85 (1)°
β = 96.38 (1)°
γ = 96.66 (1)°
V = 1139.2 (3) $Å^3$
Z = 2
D_x = 1.629 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.36 mm^{-1}
T = 293 (2) K
Block, black
0.4 × 0.35 × 0.3 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.576, T_{max} = 0.657
5709 measured reflections
3944 independent reflections
2731 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 25.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.079
S = 1.06
3944 reflections
289 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.015P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.59 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.39 e $Å^{-3}$

All H atoms were placed in geometrically calculated positions, with C—H = 0.93–0.97 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

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

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