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Key indicators

Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
 R factor = 0.051
 wR factor = 0.106
Data-to-parameter ratio = 15.1

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

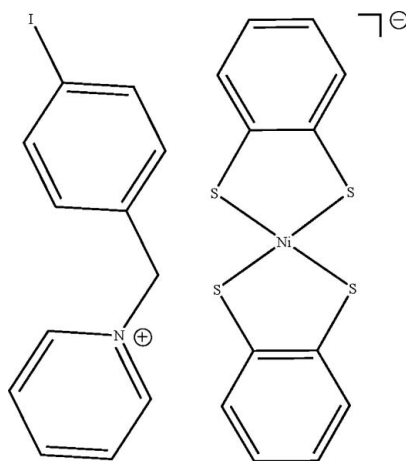
1-(4-Iodobenzyl)pyridinium bis(benzene-1,2-dithiolato)nickelate(III)

In the title compound, $(\text{C}_{12}\text{H}_{11}\text{IN})[\text{Ni}(\text{C}_6\text{H}_4\text{S}_2)_2]$, the Ni^{III} atom is surrounded by four S atoms in a square-planar geometry. The ions stack in a face-to-face fashion with an alternating arrangement of anion and cation, and a strong $\text{S} \cdots \text{I}$ interaction is observed between them.

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Comment

Recently, much attention has been focused on the coordination chemistry of unsaturated chalcogen ligands owing to their electrochemistry and photochemistry, as well as their potential applications as nonlinear optical materials (Coomber *et al.*, 1996; Akutagawa *et al.*, 2002; Xie *et al.*, 2002). In our previous research, using benzylpyridinium derivatives ($[\text{RBzPy}]^+$) as the counter-cation of $[\text{M}(\text{mnt})_2]^-$ (where $M = \text{Ni}$, Pd and Pt, and mnt_2 is maleodinitriledithiolate), a series of ion-pair compounds with segregated columnar stacks of cations and anions have been prepared (Ren *et al.*, 2002, 2003). The quasi-one-dimensional magnetic nature of these compounds was attributed to intermolecular π -orbital interactions within the anionic columns. Furthermore, for some compounds, a spin-Peierls-like transition was observed. As an extension of our work on this series of complexes, we report here the crystal structure of the title compound, (I).



(I)

In the anion of (I) (Fig. 1), the Ni atom is surrounded by four S atoms in a square-planar geometry, in which the Ni–S bonds (Table 1) are in agreement with the corresponding values in an analogous complex (Sellmann *et al.*, 1991).

The five-membered rings *A* (Ni1/S1/S2/C7/C12) and *B* (Ni1/S3/S4/C1/C6) are not planar. The conformations of rings *A* and *B* are envelopes, with atom Ni1 at the flap positions,

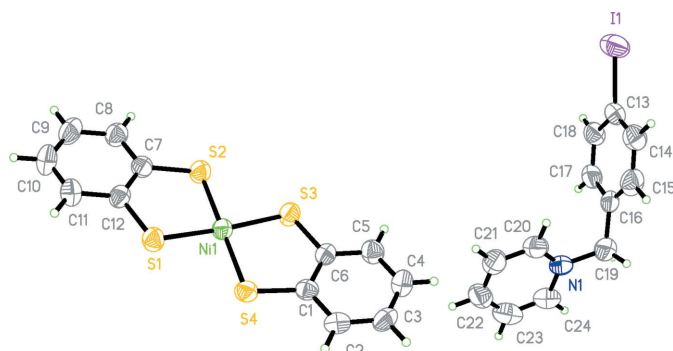


Figure 1
The asymmetric unit of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

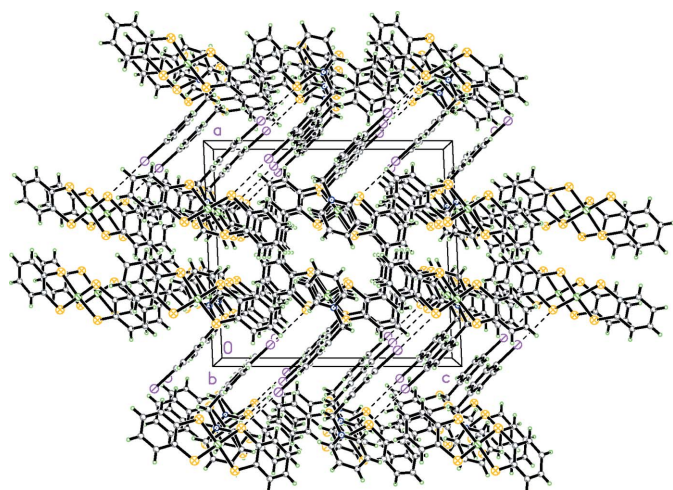


Figure 2
A packing diagram for (I). S...I interactions are shown as dashed lines.

0.072 (4) and 0.170 (3) Å from the mean planes through the other four atoms, respectively. Rings *C* (C1–C6), *D* (C7–C12), *E* (C13–C18) and *F* (N1/C20–C24) are, of course, planar, and the dihedral angles between them are *C/D* = 10.75 (4)° and *E/F* = 88.75 (3)°.

The ions stack in a face-to-face fashion with an alternating arrangement of $[\text{Ni}(\text{C}_6\text{H}_4\text{S}_2)_2]^-$ anions and $\text{C}_{12}\text{H}_{11}\text{IN}^+$ cations, such that the pyridine ring of the cation lies between the two Ni atoms of neighbouring anions, the distances between the Ni atoms and the centroid of pyridine ring are 3.995 (2) and 4.592 (3) Å. The shortest distance between adjacent Ni^{III} ions is 8.500 (1) Å. Strong S...I interactions are present, the S...I distance being 3.590 (1) Å.

Experimental

Benzene-1,2-dithiol (142 mg, 1.0 mmol) was added to a solution of sodium metal (46 mg, 2.0 mmol) in absolute ethanol (25 ml), under a nitrogen atmosphere at room temperature. A solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (120 mg, 0.5 mmol) in ethanol (25 ml) was added, resulting in the formation of a muddy red–brown colour. Following this, $[\text{IBzPy}]\text{Br}$ (375 mg, 1.0 mmol) was added and the mixture was allowed to stand with stirring for 1 h, and then stirred for an additional 24 h in air. The colour of the mixture gradually turned green, indicating oxidation from a dianionic species to the more stable monoanionic form. The

precipitate was washed with absolute ethanol and diethyl ether and then dried. The crude product was recrystallized twice from dichloromethane to give the title compound (yield 426 mg, 77%).

Crystal data

$(\text{C}_{12}\text{H}_{11}\text{IN})[\text{Ni}(\text{C}_6\text{H}_4\text{S}_2)_2]$
 $M_r = 635.25$
 Monoclinic, $P2_1/c$
 $a = 16.0187$ (18) Å
 $b = 8.5003$ (9) Å
 $c = 17.6621$ (19) Å
 $\beta = 92.408$ (2)°
 $V = 2402.8$ (5) Å³

$Z = 4$
 $D_x = 1.756$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 2.45$ mm⁻¹
 $T = 294$ (2) K
 Block, dark green
 $0.15 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\text{min}} = 0.710$, $T_{\text{max}} = 0.792$

11550 measured reflections
 4219 independent reflections
 3526 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$
 $\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.106$
 $S = 1.07$
 4219 reflections
 280 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 6.1866P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta\sigma)_{\text{max}} = 0.007$
 $\Delta\rho_{\text{max}} = 0.91$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.87$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1–S3	2.1361 (14)	Ni1–S4	2.1496 (15)
Ni1–S2	2.1441 (15)	Ni1–S1	2.1497 (14)
S3–Ni1–S2	87.45 (5)	S3–Ni1–S1	173.63 (7)
S3–Ni1–S4	91.83 (5)	S2–Ni1–S1	92.05 (6)
S2–Ni1–S4	177.34 (6)	S4–Ni1–S1	88.95 (5)

H atoms were positioned geometrically, with C–H = 0.93 and 0.97 Å for aromatic and methylene H, respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2000); software used to prepare material for publication: SHELXTL.

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References

- Akutagawa, T., Hasegawa, T., Nakamura, T. & Inabe, T. (2002). *J. Am. Chem. Soc.* **124**, 8903–8911.
 Bruker (2000). *SADABS, SMART, SAINT and SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Coomber, A. T., Beljonne, D., Friend, R. H., Brédas, J. L., Charlton, A., Robertson, N., Underbill, A. E., Kurmoo, M. & Day, P. (1996). *Nature (London)*, **380**, 144–145.
 Ren, X. M., Ma, J., Lu, C. S., Yang, S. Z., Meng, Q. J. & Wu, P. H. (2003). *Dalton Trans.* pp. 1345–1351.

Ren, X. M., Meng, Q. J., Song, Y., Lu, C. S., Hu, C. J. & Chen, X. Y. (2002). *Inorg. Chem.* **41**, 5686–5692.

Sellmann, D., Funfgelder, S., Knoch, F. & Moll, M. (1991). *Z. Naturforsch. Teil B*, **46**, 1601–1608.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Xie, J. L., Ren, X. M., Song, Y., Zhang, W. W., Liu, W. L., He, C. & Meng, Q. J. (2002). *Chem. Commun.* pp. 2346–2347.