

Decamethylferrocenium bis(2-oxo-1,3-dithiole-4,5-dithiolato- κ^2S^4, S^5)-nickelate(III) tetrahydrofuran solvate

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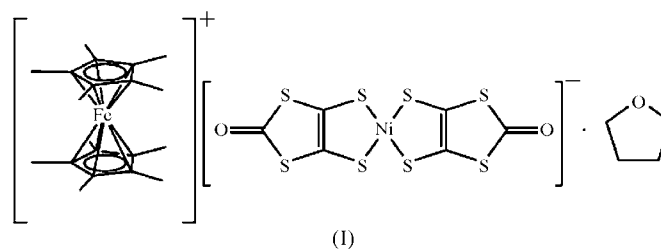
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The title compound, $[\text{Fe}(\text{C}_{10}\text{H}_{15})_2][\text{Ni}(\text{C}_3\text{OS}_4)_2] \cdot \text{C}_4\text{H}_8\text{O}$ or $[\text{Fe}(\text{Cp}^*)_2][\text{Ni}(\text{dmio})_2] \cdot \text{THF}$, where $[\text{Fe}(\text{Cp}^*)_2]^+$ is the decamethylferrocenium cation, dmio is the 2-oxo-1,3-dithiole-4,5-dithiolate dianion and THF is tetrahydrofuran, crystallizes with two independent half-anion units [one Ni atom is at the centre of symmetry ($\frac{1}{2}, \frac{1}{2}, 0$) and the other is at the centre of symmetry ($\frac{1}{2}, 0, \frac{1}{2}$)], one cation unit (located in a general position) and one THF solvent molecule in the asymmetric unit. The crystal structure consists of two-dimensional layers composed of parallel mixed chains, where pairs of cations alternate with single anions. These layers are separated by sheets of anions and THF molecules.

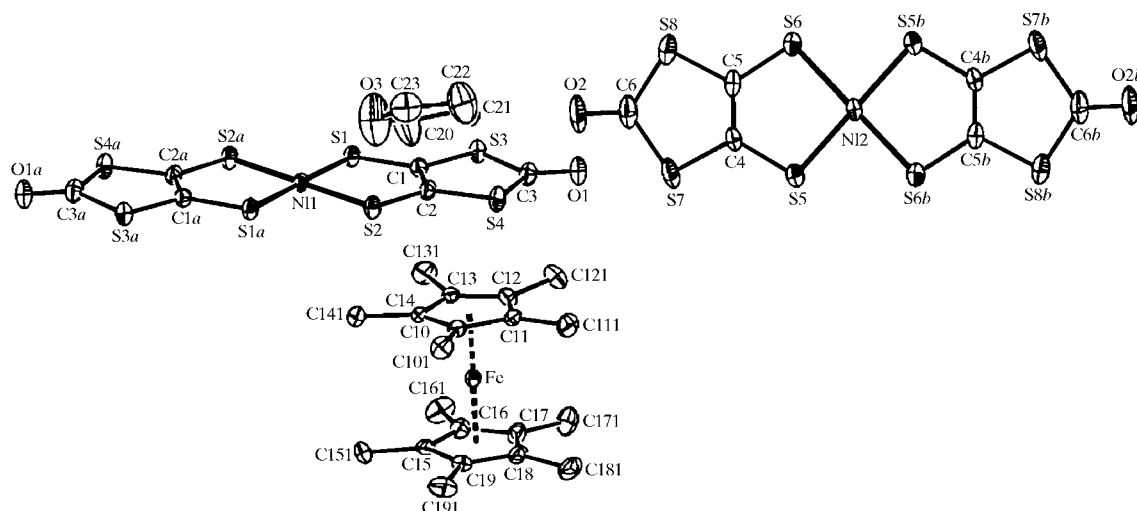
Comment

Following the report of bulk molecular magnets (Miller *et al.*, 1986; Pei *et al.*, 1986), significant research effort has been

devoted to this type of material. We have focused our attention on charge-transfer salts based on decamethylmetallocenium donors and monoanionic planar metal dithiolate acceptors, with $S = \frac{1}{2}$. These materials seem adequate to obtain new molecular magnets. The 2-oxo-1,3-dithiole-4,5-dithiolate dianion (dmio) contains several peripheral S atoms which could contribute to the existence of extended magnetic interactions, and here we report the structure of the title salt, (I).



The structure of (I) consists of $[\text{Fe}(\text{Cp}^*)_2]^+$ cations (Cp* is pentamethylcyclopentadienyl), two centrosymmetric $[\text{Ni}(\text{dmio})_2]^-$ anions and a tetrahydrofuran (THF) solvent molecule (Fig. 1). The $[\text{Fe}(\text{Cp}^*)_2]^+$ cations shows approximate C_5 local symmetry and the two Cp* rings exhibit an almost eclipsed conformation, unlike that observed in most $[\text{Fe}(\text{Cp}^*)_2]^+$ -based charge-transfer salts, which generally contain staggered conformations. The bond distances and angles in the cations and anions are in the expected ranges (Gama *et al.*, 2000). As expected, the centrosymmetric $[\text{Ni}(\text{dmio})_2]^-$ anions adopt a square-planar coordination geometry, with approximate D_{2h} local symmetry. The anions are essentially planar {the atomic deviations from the average molecular plane are less than 0.0186 Å for the $[\text{Ni}1(\text{dmio})_2]^-$ unit and less than 0.0577 Å for the $[\text{Ni}2(\text{dmio})_2]^-$ unit}. The average Ni—S distance [$\text{Ni}1\text{—S} = 2.151(2)$ Å and $\text{Ni}2\text{—S} = 2.153(2)$ Å] is in good agreement with values found in other square-planar Ni^{III} dithiolate complexes (Mahadevan *et al.*,


Figure 1

A diagram of the cation and the two independent anion units of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. H atoms have been omitted for clarity. Atoms labelled with the suffix 'a' are generated by the symmetry operation $(-x + 1, -y + 1, -z)$ and those labelled with the suffix 'b' are generated by the symmetry operation $(-x + 1, -y, -z + 1)$.

1985). The dihedral angle between the average planes of the two $[\text{Ni}(\text{dmio})_2]^-$ units is 87.79° .

The crystal structure of (I) consists of two-dimensional layers composed of parallel mixed chains, where side-by-side pairs of donors alternate with the isolated acceptor, $\cdots D^+D^+A^-D^+D^+A^- \cdots$ (Figs. 2 and 3). Within the chains, there is a net charge (+) per repeated unit ($D^+D^+A^-$), and the layers are separated by sheets of anions and THF molecules which are responsible for charge neutralization.

The supramolecular arrangement observed in (I) is similar to that reported for $[\text{Fe}(\text{Cp}^*)_2][\text{Ni}(\text{dmio})_2] \cdot \text{CH}_3\text{CN}$ (Fettouhi *et al.*, 1995). The Cp^* fragment of the cation sits above the dmio ligand of the anion. The shorter $D \cdots A$ intrachain separation ($S \cdots C$) exceeds the sum of the van der Waals radii by *ca* 4% (Bondi, 1964). The chains in the layers are quite isolated, and $S \cdots O$ short contacts (3.167 \AA) involving anions from the chains and the anionic sheets are observed (Fig. 3).

A different type of structure was observed for decamethylferrocenium charge-transfer salts based on similar

acceptors, but without solvent molecules in the crystal structure, such as $[\text{Fe}(\text{Cp}^*)_2][M(\text{dmit})_2]$, with $M = \text{Ni}$ (Broderik *et al.*, 1989) or Pt (Rabaça *et al.*, 1999), and $[\text{Fe}(\text{Cp}^*)_2][M(\text{dmio})_2]$, with $M = \text{Pd}$ or Pt (Rabaça *et al.*, 1999). For these compounds, the crystal structure consists of an arrangement of parallel stacks, where side-by-side pairs of donors alternate with face-to-face pairs of acceptors.

At high temperatures, the magnetic susceptibility of (I) follows the Curie–Weiss law, $\chi = C/(T - \theta)$, with a θ value of 10.5 K. The dominant ferromagnetic (FM) interactions can be assigned to the FM intrachain DA magnetic coupling (Rabaça *et al.*, 2003), in view of the McConnell I mechanism (McConnell, 1963), due to a spin-polarization effect in the donor, where the C atoms in the C_5 rings of the donor ligand present a negative spin density (Rabaça *et al.*, 2001).

In compound (I), the interchain contacts involving the peripheral S atoms seem to be quite weak and the anticipated increase of dimensionality in the magnetic interactions is not observed.

Experimental

Compound (I) was obtained by reaction of equimolar THF solutions of $(\text{C}_{16}\text{H}_{36}\text{N})[\text{Ni}(\text{dmio})_2]$ (Hendrickson *et al.*, 1971) and $[\text{Fe}(\text{Cp}^*)_2]\text{BF}_4$ (Muller *et al.*, 1997). The two solutions were filtered and slowly combined with constant stirring. Rapid precipitation occurred and a polycrystalline precipitate was collected *via* vacuum filtration. The precipitate was dissolved in THF. Crystals of (I) suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated THF solution.

Crystal data

$[\text{Fe}(\text{C}_{10}\text{H}_{15})_2][\text{Ni}(\text{C}_3\text{OS}_4)_2] \cdot \text{C}_4\text{H}_8\text{O}$
 $M_r = 817.70$
 Monoclinic, $P2_1/a$
 $a = 16.4733 (17) \text{ \AA}$
 $b = 11.0224 (10) \text{ \AA}$
 $c = 19.693 (2) \text{ \AA}$
 $\beta = 96.887 (9)^\circ$
 $V = 3550.0 (6) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.530 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 1.44 \text{ mm}^{-1}$
 $T = 295 (2) \text{ K}$
 Plate, dark green
 $0.50 \times 0.30 \times 0.04 \text{ mm}$

Data collection

Enraf–Nonius CAD-4
 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.613$, $T_{\max} = 0.940$
 7075 measured reflections

6873 independent reflections
 3359 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\max} = 26.0^\circ$
 5 standard reflections
 every 300 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.072$
 $wR(F^2) = 0.149$
 $S = 1.02$
 6873 reflections
 401 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0535P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.43 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$

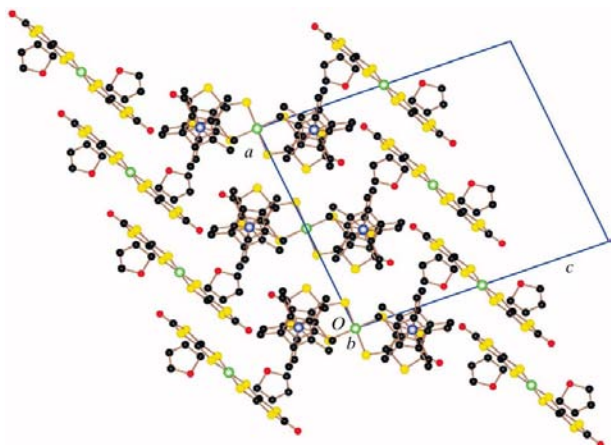


Figure 2

A packing diagram for (I), viewed along the b axis, showing a two-dimensional layer, composed of parallel mixed chains, separated by sheets of anions and tetrahydrofuran molecules.

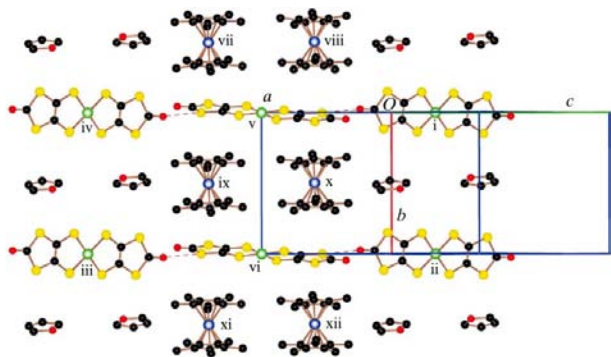


Figure 3

A packing diagram for (I), showing the details of the one-dimensional $\cdots D^+D^+A^-D^+D^+A^- \cdots$ chain and the $S \cdots O$ short contacts. [Symmetry codes: (i) x, y, z ; (ii) $x, 1 + y, z$; (iii) $1 + x, 1 + y, -1 + z$; (iv) $1 + x, y, -1 + z$; (v) $\frac{3}{2} - x, -\frac{1}{2} + y, -z$; (vi) $\frac{3}{2} - x, \frac{1}{2} + y, -z$; (vii) $\frac{3}{2} - x, -\frac{1}{2} + y, -z$; (viii) $\frac{1}{2} + x, -\frac{1}{2} - y, z$; (ix) $\frac{3}{2} - x, \frac{1}{2} + y, z$; (x) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (xi) $\frac{3}{2} - x, \frac{3}{2} + y, -z$; (xii) $\frac{1}{2} + x, \frac{3}{2} - y, z$.]

(Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SCHAKAL* (Keller, 1989) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3016). Services for accessing these data are described at the back of the journal.

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