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N-(4-Nitrobenzyl)isoquinolinium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(III)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.075
Data-to-parameter ratio = 14.1

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

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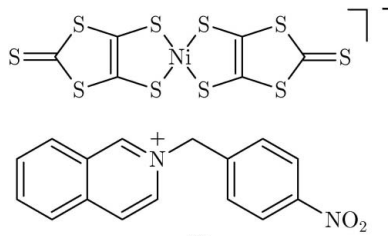
In the title compound, $(C_{16}H_{13}N_2O_2)[Ni(C_3S_5)_2]$, the Ni^{III} ion exhibits a square-planar coordination geometry with four S atoms of the two 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) ligands. Intermolecular S···S and C—H···O interactions are observed.

Comment

Extensive research has been focused on the synthesis and characterization of bis-dithiolate–metal complexes and their analogues, due to their properties and potential applications as conducting/magnetic and non-linear optical (NLO) materials (Cassoux, 1999). Amongst these, metal complexes with 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) are well known as molecular conductors.



(I)

The title compound (I) comprises $[Ni^{III}(dmit)_2]^-$ anions and *N*-(4-nitrobenzyl)isoquinolinium cations (Fig. 1), segregated into layers approximately in the (202) planes (Fig. 2). The Ni^{III} ion adopts a square-planar coordination geometry with four S atoms of the two dmit ligands, with Ni—S bond lengths ranging from 2.1466 (8) to 2.1567 (9) Å. The $[Ni^{III}(dmit)_2]^-$ anions form pairs across centres of inversion, with their least-squares planes parallel and Ni1···S5^{i} contacts of 3.795 (1) Å [symmetry code: (i) $2-x, 2-y, -z$]. Neighbouring pairs are twisted with respect to each other so that the dihedral angle between the planes of adjacent $[Ni^{III}(dmit)_2]^-$ anions is 71.2 (1)°. Intermolecular S···S interactions in this region include S2···S10^{ii} = 3.592 (1), S8···S9^{iii} = 3.389 (1) and S8···S10^{iii} = 3.560 (1) Å [symmetry codes: (ii) $\frac{1}{2}+x, 1.5-y, -\frac{1}{2}+z$; (iii) $1.5-x, -\frac{1}{2}+y, \frac{1}{2}-z$). Within the layers of $C_{16}H_{13}N_2O_2^+$ cations, the isoquinoline groups adopt offset face-to-face arrangements, and the 4-nitrobenzyl groups adopt edge-to-face arrangements (the interplanar distance of the isoquinoline rings is 3.44 Å), forming C—H···O hydrogen bonds (Table 2).

Experimental

4,5-Bis(thiobenzoyl)-1,3-dithiol-2-thione (0.812 g, 2.0 mmol) (Wang *et al.* 1998) was suspended in dry methanol (20 ml). Under nitrogen,

sodium (0.092 g, 4.0 mmol) was added at room temperature to give a bright red solution. To this solution, $NiCl_2·6H_2O$ (0.177 g, 1.0 mmol) was added. After 20 min, a solution of I_2 (0.127 g, 0.5 mmol) in methanol (10 ml) was added, followed after a further 20 min by a solution of *N*-(4-nitrobenzyl)isoquinolinium bromide (0.690 g, 2.0 mmol) in methanol (10 ml). The solution was stirred for a further 30 min and the resultant solid was collected by filtration. Evaporation of a dilute acetone solution of this powder at room temperature gave single crystals of (I) after 1–2 weeks.

Crystal data

$(C_{16}H_{13}N_2O_2)[Ni(C_3S_5)_2]$
M_r = 716.65
Monoclinic, $P2_1/n$
a = 14.746 (3) Å
b = 9.365 (2) Å
c = 19.898 (4) Å
β = 102.692 (4)°
V = 2680.6 (10) Å^3
Z = 4
D_x = 1.776 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.53 mm^{-1}
T = 293 (2) K
Block, black
0.3 × 0.2 × 0.1 mm

Data collection

Bruker SMART APEX CCD diffractometer
φ and ω scans
Absorption correction: multi-scan *SADABS* (Bruker, 2000)
T_{min} = 0.70, T_{max} = 0.85
12871 measured reflections
4702 independent reflections
3776 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 25.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.075
S = 0.98
4702 reflections
334 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.009
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—S4	2.1529 (9)	Ni1—S6	2.1466 (8)
Ni1—S5	2.1509 (9)	Ni1—S7	2.1567 (9)
S4—Ni1—S5	93.31 (3)	S5—Ni1—S6	178.66 (3)
S4—Ni1—S6	85.44 (3)	S5—Ni1—S7	87.86 (3)
S4—Ni1—S7	178.78 (3)	S6—Ni1—S7	93.40 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14···O2^{i}	0.93	2.67	3.456 (4)	143

Symmetry code: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å, U_{iso}(H) = 1.2U_{eq}(C) for aromatic H, and C—H = 0.97 Å, U_{iso}(H) = 1.2U_{eq}(C) for CH_2.

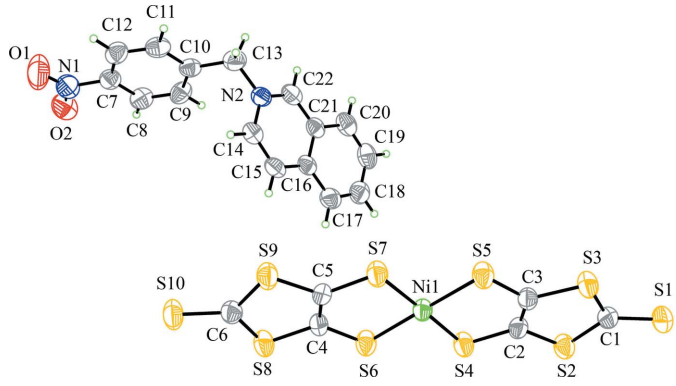


Figure 1
The cation and anion in (I), showing the atom-labelling scheme, with displacement ellipsoids drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

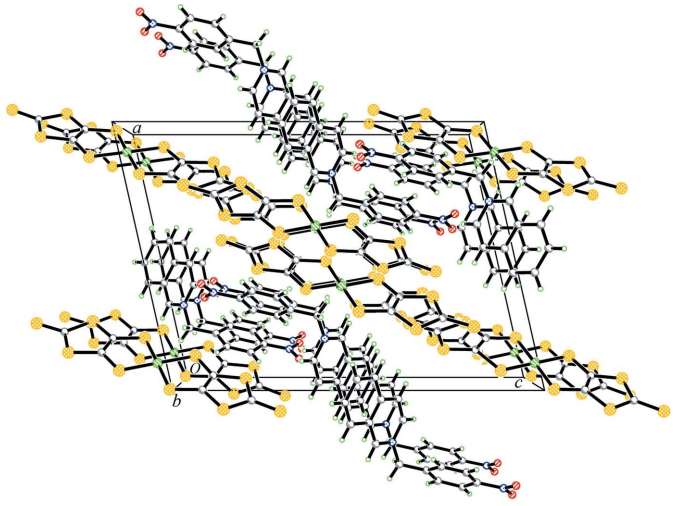


Figure 2
View of (I) along the *b* axis, showing $[Ni^{III}(dmit)_2]^-$ anions and $C_{16}H_{13}N_2O_2^+$ cations segregated into layers approximately in the (202) planes.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); 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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