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9-(2-Carboxyphenyl)-3,6-bis(diethylamino)-xanthylium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(III)

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In the title compound, $(C_{28}H_{31}N_2O_3)[Ni(C_3S_5)_2]$, the two symmetry-independent anions are located on inversion centres and adopt planar conformations with an approximate D_{2h} symmetry. The Ni atoms both show a square-planar coordination geometry. The xanthene system is planar, with the attached benzene ring twisted by 75.8 (11)° from the xanthene plane. One of the four ethyl groups of the cation is disordered. The xanthylium cation and one of the symmetry-independent 2-thioxo-1,3-dithiole-4,5-dithiolate anions are arranged into columns, with the anion sandwiched between hydrogen-bonded dimers of the cation. The second symmetry-independent anion is enclosed between these columns.

Comment

Over recent decades, transition metal bis(dithiolate) complexes have received significant attention in studies of organic conductors and superconductors (Cassoux & Valade, 1992; Kajita *et al.*, 1988; Kobayashi *et al.*, 1991, 1992; Bousseau *et al.*, 1986; Brossard *et al.*, 1988; Tajima *et al.*, 1993). Recently, we have synthesized several salts composed of $[Ni(dmit)_2]^-$, where dmit is the 2-thioxo-1,3-dithiole-4,5-dithiolate anion, and cationic dyes such as methylene blue and triphenyl-methane analogues, with the intention of using the light-absorbing nature of these dyes to modify the electronic state of the anion (Soneta & Miyamura, 2006; Soneta *et al.*, 2006). In this paper, we report the crystal structure of the title salt, $(RhB)[Ni(dmit)_2]$, (I), formed from the $[Ni(dmit)_2]^-$ anion and the highly fluorescent and photostable rhodamine dye, rhodamine B [9-(2-carboxyphenyl)-3,6-bis(diethylamino)-xanthylium, RhB].

(I)
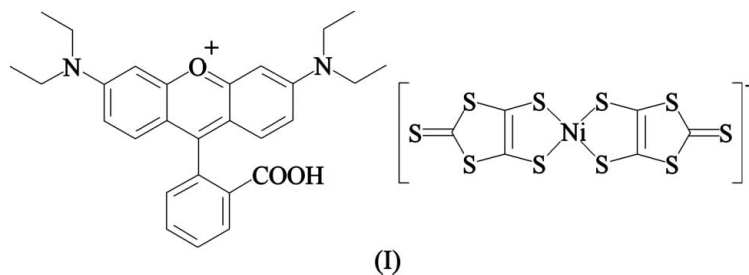
The asymmetric unit of (I) consists of two half-anions and one cation, with the anions located on inversion centres (Fig. 1). The NiS_4 core of the anions is essentially planar. The Ni—S distances in the range 2.149 (2)–2.156 (2) Å indicate that the formal charge of the Ni(dmit)$_2$ units is −1. The xanthene system is planar, with atom C9 showing the largest out-of-plane displacement of 0.058 (8) Å. The dihedral angle
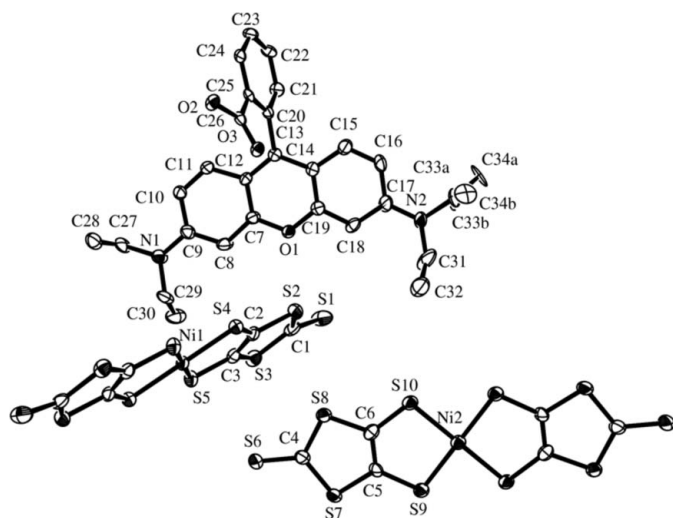
Figure 1
The structure of the components of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. Unlabelled atoms are related to labelled atoms by the symmetry code ($-x + 1$, $-y + 1$, $-z + 1$) for the anion including atom Ni1 and by the symmetry code ($-x$, $-y$, $-z$) for the anion including Ni2.
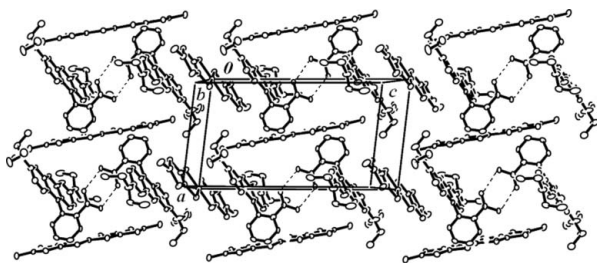

Figure 2
The crystal packing of (I). The hydrogen bonds between the carboxyl group of the RhB cations are indicated by dotted lines. H atoms have been omitted for clarity.

between the xanthene and benzene ring mean planes is 75.8 (11)°. Delocalization of the positive charge between the N atoms is evidenced by the C9—N1 and C17—N2 bonds of 1.354 (12) and 1.345 (11) Å, respectively, which show significant double-bond character.

The crystal packing of (I) is shown in Fig. 2. The arrangement of cations and anions is different from that observed in salts with 3,7-bis(diethylamino)phenothiazin-5-ium and 3,7-bis(diethylamino)phenoxazin-5-ium cations, which, like the RhB cation, possess four ethyl groups (Soneta *et al.*, 2006). There, cations and anions are arranged alternately along stacks. In (I), the xanthylium cation and one of the symmetry-independent dmit anions are arranged into columns with the anion sandwiched between hydrogen-bonded dimers of cations. The second symmetry-independent anion is enclosed between these columns. This arrangement is, in turn, similar to that observed in the salts with 3,7-bis(dipropylamino)-phenothiazin-5-ium and 3,7-bis(dibutylamino)phenothiazin-5-ium cations, *i.e.* cations with larger alkyl substituents. In these salts, the anionic complexes are pushed out of the column to occupy space separated by the elongated alkyl groups in the

intercolumn region. In the case of the title compound, the strong hydrogen bond between carboxyl groups of the RhB cations leads to a rigid RhB dimer which, together with one of the symmetry-independent anions, forms an alternating stacked column *via* electrostatic interactions.

Experimental

Crystal data

$(C_{28}H_{31}N_2O_3)[Ni(C_3S_5)_2]$	$V = 1913.5$ (13) Å^3
$M_r = 894.92$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.553$ Mg m^{-3}
$a = 10.187$ (4) Å	Mo $K\alpha$ radiation
$b = 10.752$ (4) Å	$\mu = 1.09$ mm^{-1}
$c = 18.285$ (7) Å	$T = 100$ (2) K
$\alpha = 105.729$ (7)°	Plate, black
$\beta = 96.342$ (7)°	$0.25 \times 0.24 \times 0.05$ mm
$\gamma = 91.138$ (8)°	

Data collection

Bruker SMART CCD area detector diffractometer	11478 measured reflections
φ and ω scans	8212 independent reflections
Absorption correction: analytical (*XPREP*; Bruker, 2001)	4839 reflections with $I > 2\sigma(I)$
$T_{min} = 0.772$, $T_{max} = 0.948$	$R_{int} = 0.072$
	$\theta_{max} = 28.3°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1434P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.088$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.287$	$(\Delta/\sigma)_{max} = 0.003$
$S = 1.10$	$\Delta\rho_{max} = 1.53$ e Å^{-3}
8212 reflections	$\Delta\rho_{min} = -0.74$ e Å^{-3}
479 parameters	Extinction correction: *SHELXL97* (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.0052 (14)

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2···O3^{i}	0.84	1.85	2.662 (8)	163

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

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H distances in the range 0.95–0.99 Å and an O—H distance of 0.84 Å, and with $U_{iso} = 1.2U_{eq}(C)$ or $1.5U_{eq}(C_{methyl},O)$. One of the ethyl groups is disordered over two positions (C33*A*/C34*A* and C33*B*/C34*B*). The occupancy factors of sites *A* and *B* converged at 0.48 (3) and 0.52 (3), respectively. In the final difference Fourier synthesis, the highest peak of 1.53 e Å^3 is 0.96 Å from atom Ni1.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

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SHELXTL (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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