

Bis(tetra-*n*-butylammonium) bis(2-dicyanomethylene-4,5-dimercapto-1,3-dithiole)nickel(II)

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Key indicators

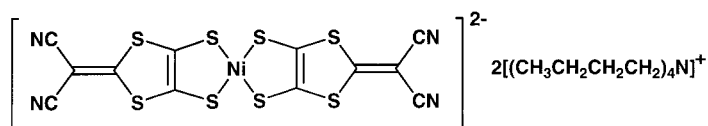
Single-crystal X-ray study
 T = 173 K
 Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$
 Disorder in solvent or counterion
 R factor = 0.093
 wR factor = 0.271
 Data-to-parameter ratio = 20.5

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

In the title complex, $(\text{C}_{16}\text{H}_{36}\text{N})_2[\text{Ni}(\text{C}_6\text{N}_2\text{S}_4)_2]$, the centrosymmetric dianion is flat. The Ni atom has square-planar coordination, with Ni—S bond lengths of 2.1836 (16) and 2.1940 (18) Å.

Comment

Recently dithiolate–metal complexes have received much attention as molecular conductors and superconductors. Several salts based on the $M(\text{dmit})_2$ system (dmit is 4,5-dimercapto-1,3-dithiole-2-thione, $M = \text{Ni}$ or Pd) have been found to become superconductors at low temperature (Brossard *et al.*, 1986; Kobayashi *et al.*, 1987; Cassoux *et al.*, 1991; Tajima *et al.*, 1993). In 2001, the first molecular metal composed of single component molecules, $[\text{Ni}(\text{tmdt})_2]$ (tmdt is trimethylenetetrafulvalenedithiolate), was discovered (Tanaka *et al.*, 2001). We have synthesized the title dithiolate–nickel complex, (I), derived from the 2-dicyanomethylene-4,5-dimercapto-1,3-dithiole ligand (Tomura & Yamashita, 1995). This ligand in the nickel complex is expected to extend the π -conjugation of the complex, resulting in decreased Coulombic repulsion. Intermolecular interactions caused by $\text{S} \cdots \text{S}$ and $\text{S} \cdots \text{N}$ heteroatom contacts may increase the dimensionality in the solid-state structure of (I) (Yamashita & Tomura, 1998). We report here the molecular and crystal structures of (I).



(I)

The dianion is located on an inversion center and is flat, with an r.m.s. deviation of 0.12 Å from the least-squares plane (Fig. 1). The central Ni atom has square-planar coordination, and the Ni1—S1 and Ni1—S2 distances and the S1—Ni1—S2 angle are 2.1940 (18), 2.1836 (16) Å and 93.29 (6)°, respectively (Table 1). These values are comparable to those in $[\text{Ni}(\text{dmit})_2]^{2-}$ complexes (Lindqvist *et al.*, 1979; Fun *et al.*, 1996).

Fig. 2 shows the packing diagram of (I), viewed along the a axis. The dianion molecules stack along the a axis, with one butyl group of the cation inserted between adjacent molecules. There are intermolecular $\text{S} \cdots \text{N}$ heteroatom contacts [3.538 (6) Å for $\text{S}4 \cdots \text{N}2^i$ and $\text{N}2 \cdots \text{S}4^i$; symmetry code: (i) $-x+1, -y+1, -z$]. The $\text{S} \cdots \text{N}$ distance is 5.6% longer than the sum of the corresponding van der Waals radii (Pauling, 1960). The two dianions associated with the $\text{S} \cdots \text{N}$ contacts are almost planar (r.m.s. deviation of fitted atoms 0.19 Å).

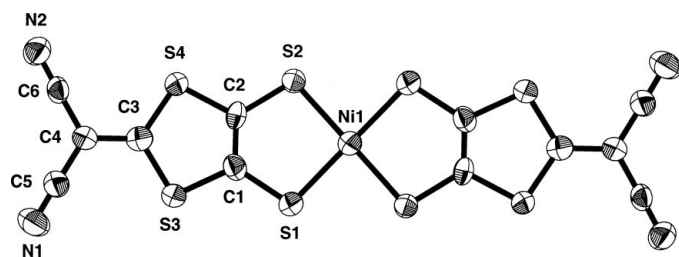


Figure 1
The molecular structure of the dianion in (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title complex was synthesized according to the literature method of Tomura & Yamashita (1995). Green–black crystals of (I) suitable for X-ray analysis were grown from an acetone solution.

Crystal data

$(C_{16}H_{36}N)_2[Ni(C_6N_2S_4)_2]$	$Z = 1$
$M_r = 1000.33$	$D_x = 1.260 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.252(4) \text{ \AA}$	Cell parameters from 4920 reflections
$b = 12.012(6) \text{ \AA}$	$\theta = 3.1\text{--}27.5^\circ$
$c = 13.867(6) \text{ \AA}$	$\mu = 0.72 \text{ mm}^{-1}$
$\alpha = 76.26(3)^\circ$	$T = 173(1) \text{ K}$
$\beta = 80.99(3)^\circ$	Plate, green–black
$\gamma = 89.69(4)^\circ$	$0.60 \times 0.20 \times 0.05 \text{ mm}$
$V = 1317.9(10) \text{ \AA}^3$	

Data collection

Rigaku/MSC Mercury CCD diffractometer	5808 independent reflections
φ and ω scans	4177 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Jacobson, 1998)	$R_{\text{int}} = 0.069$
$T_{\text{min}} = 0.672$, $T_{\text{max}} = 0.965$	$\theta_{\text{max}} = 27.5^\circ$
12833 measured reflections	$h = -10 \rightarrow 9$
	$k = -14 \rightarrow 15$
	$l = -17 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1389P)^2 + 1.6175P]$
$R[F^2 > 2\sigma(F^2)] = 0.093$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.271$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.11$	$\Delta\rho_{\text{max}} = 1.18 \text{ e \AA}^{-3}$
5808 reflections	$\Delta\rho_{\text{min}} = -0.97 \text{ e \AA}^{-3}$
283 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ni1–S1	2.1940 (18)	S4–C2	1.742 (5)
Ni1–S2	2.1836 (16)	N1–C5	1.140 (8)
S1–C1	1.732 (6)	N2–C6	1.125 (7)
S2–C2	1.735 (5)	C1–C2	1.350 (8)
S3–C3	1.720 (5)	C3–C4	1.403 (8)
S3–C1	1.735 (5)	C4–C5	1.400 (8)
S4–C3	1.701 (6)	C4–C6	1.426 (7)
S2–Ni1–S1	93.29 (6)	C1–C2–S2	122.0 (4)
C1–S1–Ni1	101.25 (19)	C1–C2–S4	116.7 (4)
C2–S2–Ni1	101.39 (18)	S4–C3–S3	115.1 (3)
C3–S3–C1	96.2 (3)	C5–C4–C6	119.4 (5)
C3–S4–C2	96.0 (3)	N1–C5–C4	179.1 (6)
C2–C1–S1	121.9 (4)	N2–C6–C4	179.0 (6)
C2–C1–S3	115.9 (4)		

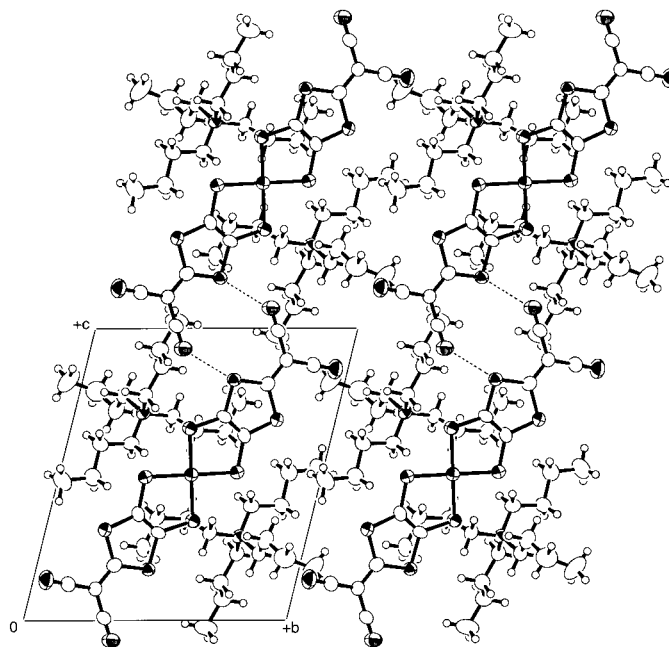


Figure 2
Packing diagram of (I), viewed along the a axis. Dotted lines show the intermolecular S...N contacts. The disordered methyl C atom with 41% occupancy has been omitted for clarity.

One terminal methyl C atom (C18) of the tetrabutylammonium cation is disordered over two sites with occupancies of 0.414 (15) and 0.586 (15). All H atoms were placed in geometrically calculated positions and refined using a riding model.

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku Corporation, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku Corporation, 2000); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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