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Tetra-*n*-butylammonium bis(2-thioxo-1,3-dithiole-4,5-dithiolato-κ^2S^4,S^5)nickelate(III)

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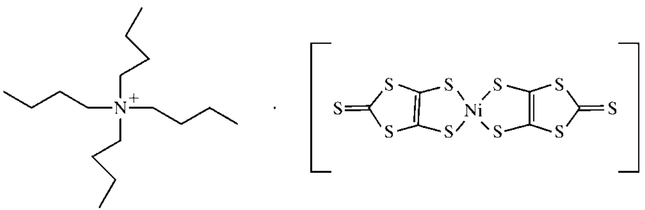
The crystal structure of the title compound, $(C_{16}H_{36}N)[Ni(C_3S_5)_2]$, is isomorphous with that of the corresponding Pt complex but different from the structures reported for compounds of the same chemical composition, and so provides a new crystalline phase of this complex. The nickel complex anion has good planarity and lies on a crystallographic inversion centre. There is disorder in the two terminal C atoms of two of the butyl chains of the tetra-*n*-butylammonium cation, the N atom of which is located on a twofold axis.

Comment

Nickel complexes of 4,5-dimercapto-1,3-dithiole-2-thione (dmit) and their π-conjugation-extended derivatives have received continued interest in the field of molecular conductors (Lei *et al.*, 1996; Narvor *et al.*, 1996; Tanaka *et al.*, 2001). Recently, the title compound, (I), was synthesized using a more direct method (see *Experimental*), instead of the common synthesis using the dibenzoyl derivative of dmit (Valade *et al.*, 1985, and references therein). It was also found that several different crystal structures of (I) have been reported (Table 2). Thus, it was postulated that compound (I) synthesized using the direct method might crystallize in a new structure, and this was the first reason for the present determination of (I). Another reason is due to the fact that the fluorescence emission spectra of (I) and the analogous bis(tetra-*n*-butylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)zincate(II) have recently been measured by us and found to be almost the same. However, it is known that the latter compound has a tetragonal coordination at the Zn centre and the former has a planar square coordination at the Ni centre, for the cases reported to date, and so the extent of delocalization of the electrons of (I) is larger than that of the Zn analogue and the compounds would be expected to have different spectra. Thus, a planar structure of the Ni–dmit complex synthesized using the current method was suspected. In order to clarify these two points, the present crystal structure determination of (I) was performed and the results are reported here.



(I)

The Ni–dmit complex anion of (I) (17 atoms) exhibits good planarity and the maximum deviation from the least-squares

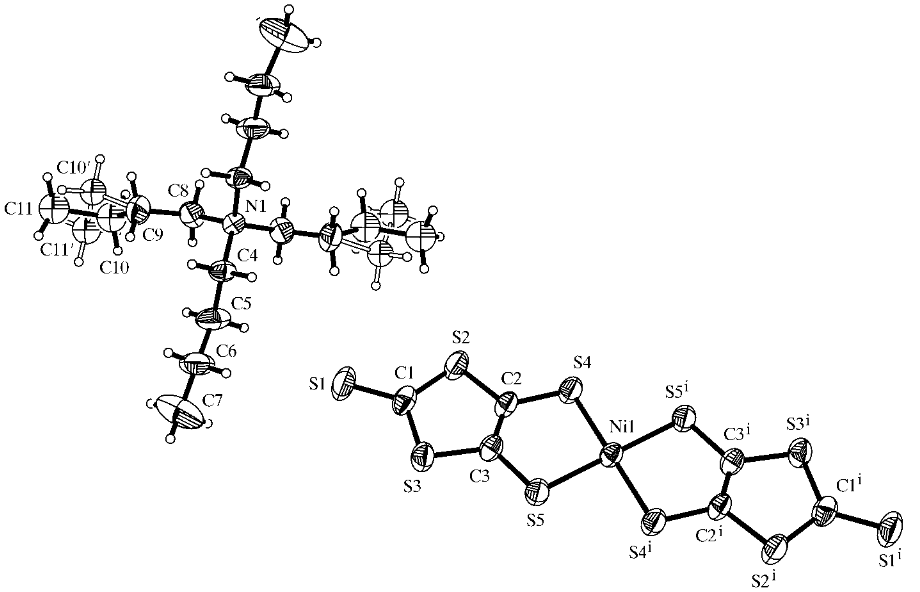


Figure 1
A view of (I) with the atomic numbering scheme; primed labels and open bonds indicate the disordered component. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x, -y, -z$.]

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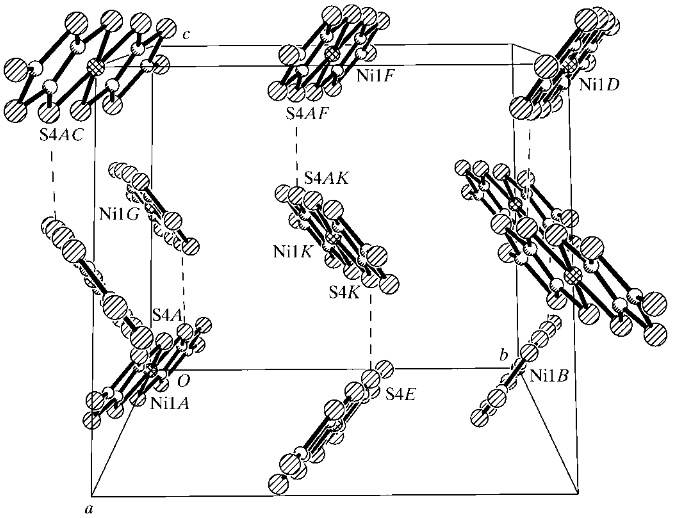

Figure 2
The packing of the nickel anion of (I).

plane is 0.043 (2) Å (for atoms S1 and S1*A*, the two terminal atoms of the anion). Thus, the close similarity of the two fluorescence emission spectra remains unexplained, assuming there are no mistakes in the spectroscopic measurements. The geometric parameters of the anion of (I) do not differ considerably from those reported (Mentzafos *et al.*, 1988; Valade *et al.*, 1985), although they agree better with the data reported by Mentzafos *et al.* (1988; Ni, $j = 2$).

The four S atoms around Ni adopt a centrosymmetric arrangement, with each pair of *trans* S atoms equivalent (Table 1). In our opinion, the four S atoms should not be regarded as equivalent, even within the range of experimental uncertainty; referring to Fig. 1 and Table 1, the Ni1—S4 and Ni1—S5 bond lengths are 2.1541 (15) and 2.1638 (15) Å, respectively, and the S4—Ni1—S5*A* and S4—Ni1—S5 bond angles are 87.37 (6) and 92.63 (6)°, respectively. A similar result was seen in the molecular structure of nickel diethyldithiocarbamate (Bonamico *et al.*, 1965). As far as the tetra-*n*-butylammonium cation is concerned (Fig. 1), two of the four butyl chains are disordered, as observed and described by Mentzafos *et al.* (1988).

The crystal packing of (I) is basically isomorphous with that of the corresponding Pt complex (Mentzafos *et al.*, 1988), but there are fairly large differences from the structures reported (Table 2) for other compounds of the same chemical composition (Mentzafos *et al.*, 1988, and references therein). Taking only the packing of the Ni complex anion into account, and referring to Fig. 2, the anions form stacks along the *c* axis. In the stack, the anions form a zigzag array and there are short S···S contacts [3.597 (2) Å for both S4···S4 and S4*A*···S4*A*] between neighbouring anions, but there are no short inter-stack S···S contacts. All of these results are in almost perfect agreement with those of the corresponding Pt complex (Mentzafos *et al.*, 1988).

Experimental

Nickel chloride hexahydrate (0.476 g, 2 mmol) was dissolved in a mixture of water, methanol and acetone (3:2:2). The resulting clear green solution was reacted with a solution of bis(tetra-*n*-butylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)zincate(II) [1.88 g, 2 mmol; prepared according to the method of Valade *et al.* (1985)] in acetone for several days, until all the solvent apart from water had evaporated completely. The resulting mixture was filtered, giving a green–black solid, and this solid was then redissolved in acetone to recrystallize. After several days, the solvent was evaporated, giving shiny stick-like green–black crystals of (I).

Crystal data

$(C_{16}H_{36}N)[Ni(C_3S_5)_2]$
$M_r = 693.91$
Monoclinic, $C2/c$
$a = 20.191$ (2) Å
$b = 13.4041$ (14) Å
$c = 12.1408$ (14) Å
$\beta = 105.554$ (8)°
$V = 3165.5$ (6) Å^3
$Z = 4$
$D_x = 1.456$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 32 reflections
$\theta = 5.1$–12.5°
$\mu = 1.29$ mm^{-1}
$T = 293$ (2) K
Prism, green–black
0.38 × 0.30 × 0.20 mm

Data collection

Bruker *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XSCANS*; Siemens, 1996)
$T_{\min} = 0.636$, $T_{\max} = 0.773$
3338 measured reflections
2791 independent reflections
1834 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 25°$
$h = -1 \rightarrow 24$
$k = -1 \rightarrow 15$
$l = -14 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.157$
$S = 1.12$
2789 reflections
155 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 7.7955P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.74$ e Å^{-3}
$\Delta\rho_{\min} = -0.53$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—S4	2.1541 (15)	S3—C1	1.732 (7)
Ni1—S5	2.1638 (15)	S3—C3	1.747 (6)
S1—C1	1.642 (6)	S4—C2	1.706 (6)
S2—C1	1.712 (7)	C2—C3	1.341 (8)
S2—C2	1.748 (5)	C3—S5	1.715 (6)
S4—Ni1—S5	92.63 (6)	S1—C1—S3	123.2 (4)
S4$^{\rm i}$—Ni1—S5	87.37 (6)	S2—C1—S3	113.3 (3)
S4—Ni1—S5$^{\rm i}$	87.37 (6)	C3—C2—S4	121.4 (4)
S4$^{\rm i}$—Ni1—S5$^{\rm i}$	92.63 (6)	C3—C2—S2	116.1 (4)
C1—S2—C2	97.5 (3)	S4—C2—S2	122.5 (4)
C1—S3—C3	97.1 (3)	C2—C3—S5	121.3 (4)
C2—S4—Ni1	102.5 (2)	C2—C3—S3	116.0 (4)
S1—C1—S2	123.5 (4)	S5—C3—S3	122.6 (4)

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

After checking their presence in the difference map, all H atoms were fixed geometrically and allowed to ride on their attached atoms, with C—H = 0.96–0.97 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Table 2
Comparison of different crystal structures with the same composition as (I).

		1†	2‡	3§	(I)
Space group		$P\overline{1}$	$P2_1/c$	$P\overline{1}$	$C2/c$
Cell parameters (Å, °)	a	12.144	14.649 (3)	11.702 (2)	20.191 (2)
	b	12.161	13.497 (3)	12.120 (2)	13.4041 (14)
	c	12.173	16.383 (4)	12.358 (2)	12.1408 (14)
	α	77.02	90	100.04 (1)	90
	β	102.95	91.14 (6)	91.93 (1)	105.554 (8)
	γ	112.88	90	105.44 (1)	90
Volume (Å^3)		1595.1	3238.6	1657.6	3165.5 (6)
Density (Mg m^{-3})		1.444	1.423	1.39	1.456
Temperature (K)		295	295	295	293 (2)
R factor (%)		0.0	5.4	3.66	5.5

† Sjolin *et al.* (1977). ‡ Lindqvist *et al.* (1982). § Mentzafos *et al.* (1988).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2001).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1555). Services for accessing these data are described at the back of the journal.

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