C(19)	0.0694 (7)	0.1228 (7)	0.5031 (5)	0.038 (4)
C(20)	−0.0242 (7)	0.2321 (7)	0.4908 (5)	0.038 (4)
C(21)	−0.2574 (9)	0.3531 (8)	0.2020 (7)	0.052 (5)
C(22)	−0.3710 (8)	0.3435 (11)	0.2443 (7)	0.067 (6)
C(23)	−0.4701 (10)	0.4270 (16)	0.2071 (11)	0.095 (9)
C(24)	−0.4553 (13)	0.5128 (12)	0.1377 (11)	0.082 (8)
C(25)	−0.3422 (17)	0.5191 (12)	0.0968 (11)	0.105 (11)
C(26)	−0.2446 (12)	0.4407 (11)	0.1300 (9)	0.079 (8)
C(27)	0.2368 (8)	−0.1524 (8)	0.1116 (6)	0.046 (4)
C(28)	0.1850 (10)	−0.2335 (9)	0.1222 (7)	0.059 (6)
C(29)	0.2304 (11)	−0.2973 (11)	0.0588 (9)	0.076 (7)
C(30)	0.3223 (11)	−0.2802 (13)	−0.0114 (9)	0.082 (8)
C(31)	0.3759 (12)	−0.2001 (13)	−0.0226 (8)	0.085 (8)
C(32)	0.3316 (10)	−0.1374 (12)	0.0414 (8)	0.075 (7)
C(33)	0.4256 (8)	−0.1942 (8)	0.4672 (6)	0.044 (4)
C(34)	0.4595 (8)	−0.3177 (9)	0.4989 (7)	0.054 (5)
C(35)	0.5581 (9)	−0.3795 (9)	0.5317 (6)	0.056 (5)
C(36)	0.6258 (9)	−0.3265 (10)	0.5343 (7)	0.065 (6)
C(37)	0.5923 (10)	−0.2044 (11)	0.5058 (8)	0.071 (7)
C(38)	0.4942 (9)	−0.1400 (9)	0.4720 (7)	0.061 (6)
C(39)	−0.0576 (8)	0.3055 (8)	0.5530 (6)	0.044 (4)
C(40)	0.0301 (11)	0.3373 (10)	0.5592 (7)	0.064 (6)
C(41)	−0.0056 (17)	0.4076 (11)	0.6181 (10)	0.089 (10)
C(42)	−0.1104 (15)	0.4368 (11)	0.6693 (9)	0.079 (8)
C(43)	−0.2003 (15)	0.4048 (11)	0.6654 (8)	0.091 (8)
C(44)	−0.1708 (9)	0.3393 (8)	0.6052 (6)	0.054 (5)

Table 2. *Selected geometric parameters* (Å, °)

Sn—Rh	2.450 (1)	Sn—Cl(1)	2.313 (3)
Sn—Cl(2)	2.318 (7)	Sn—Cl(3)	2.301 (4)
Rh—N(1)	2.028 (6)	Rh—N(2)	2.022 (9)
Rh—N(3)	2.017 (6)	Rh—N(4)	2.000 (9)
Cl(1)—Sn—Rh	116.9 (1)	Cl(2)—Sn—Rh	114.8 (1)
Cl(3)—Sn—Rh	116.0 (2)	Sn—Rh—N(1)	90.8 (2)
Sn—Rh—N(2)	91.7 (2)	Sn—Rh—N(3)	89.3 (2)
Sn—Rh—N(4)	94.4 (2)	N(1)—Rh—N(2)	90.3 (3)
N(2)—Rh—N(3)	89.9 (3)	N(3)—Rh—N(4)	89.6 (3)
N(1)—Rh—N(4)	90.2 (3)	N(1)—Rh—N(3)	179.7 (4)
N(2)—Rh—N(4)	173.8 (3)		

Structure solution and refinement: *SHELXTL-Plus* (Sheldrick, 1991).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1113). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(3-methylpyridine)bis[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato]nickel(II)

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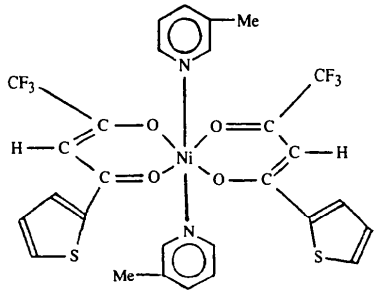
Abstract

In the title compound, $[Ni(C_8H_4F_3O_2S)_2(C_6H_7N)_2]$, the Ni atom displays distorted octahedral coordination to four coplanar O atoms from two trifluorothienylbutanedione ligands and two apical 3-methylpyridine N atoms. The two trifluorothienylbutanedione ligands, and hence the two thiophene rings, are *cis* oriented with respect to each other, whereas the 3-methylpyridine ligands are mutually *trans*. The Ni—N(1) and Ni—N(2) bond distances are 2.090 (6) and 2.104 (6) Å, respectively, and the four Ni—O distances are in the range 2.024 (5) to 2.045 (5) Å.

Comment

4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione (TTA) has been used as a lubrication additive for Cu–Cu and Cu–Fe friction couples in bearings (Kuzharov, Suchkov & Komarchuk, 1983), and its metal complex, $[Cu(TTA)_2]$, was also found to be a selective metal-transfer lubrication additive (Kuzharov, Suchkov, Kozakov & Nikol'skii, 1989). $[M(TTA)_2]$ complexes, well known

for the variety of different types of metal coordination they display, have received considerable attention. In $[Cu(TTA)_2]$ (Yu, Xu, You, Lu, Shi, Liu & Lin, 1988), $[Cu(TTA)_2(py)_2]$ (py is pyridine) (Liu, Lin, Xu, Yu & You, 1986), $[Cu(TTA)_2(bipy)]_n$ (bipy is bipyridyl) (Gou, You, Xu, Zhou, Yu, Yu & Zhu, 1991) and $[Cu(TTA)_2(C_9H_7N)_2]$ (Yu, Zhu, Xu, Gou, You, Liu & Lin, 1991), corresponding donor atoms of the TTA ligands are mutually *trans*, as are the two thiophene rings. However, the TTA ligands are *cis* in $[Cu(TTA)_2(DMSO)]$ (DMSO is dimethyl sulfoxide) (Li, You, Yao, Huang & Wang, 1987), $[Ni(TTA)_2(DMSO)]$ (Zheng, Liu, Xu, Zhou, You, Yu & Zhu, 1992), $[Cu(TTA)_2(DMF)]$ (DMF is dimethyl formamide) (Li, Xu, You, Wang & Yang, 1993) and also in the title complex, (I).



(I)

A view of the molecule is shown in Fig. 1. The Ni^{II} atom is hexacoordinated and lies in the plane formed by the four donor O atoms. Two *trans* 3-methylpyridine ligands complete the coordination. The Ni—O(*n*) (*n* = 1–4) bond distances are in the range 2.024 (5) to 2.045 (5) Å and are about 0.10 Å longer than those in $[Ni(TTA)_2(DMSO)]$ (Zheng *et al.*, 1992). The Ni—N(2) bond [2.104 (6) Å] is slightly longer than the Ni—N(1) distance [2.090 (6) Å]. The thiophene and pyridine rings are planar within experimental error. Their bond lengths and angles are unexceptional (Liu *et al.*, 1986; Zheng *et al.*, 1992). The *cis* coordination of the TTA ligands and the *trans* antiparallel arrangement of the methylpyridine ligands is probably due to spatial hindrance rather than the demands of hydrogen bonding (Liu *et al.*, 1986; Zheng *et al.*, 1992; Li *et al.*, 1993).

The bond distances and displacement parameters of the atoms of one of the thiophene rings indicate disorder involving a 180° rotation of the ring around the C(1)—C(11) bond, so that S(1) and S(1′) are composite S/C sites (see Table 1). A similar disorder was reported by Irene, Aristidis & Eugene (1987).

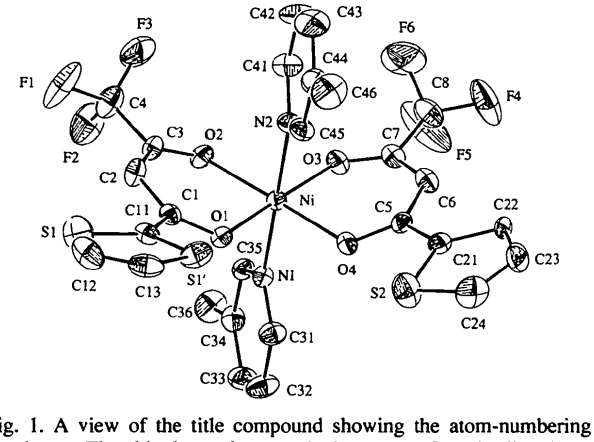


Fig. 1. A view of the title compound showing the atom-numbering scheme. The thiophene ring attached to atom C(1) is disordered so that S(1) and S(1′) are composite S/C atom sites. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

$[Ni(TTA)_2]$ was dissolved in ethanol and excess 3-methylpyridine was added until the colour of the solution changed from green to dark green. Dark-green prismatic crystals of the title complex were obtained after the solution was evaporated at room temperature for one week. Recrystallization was from ethanol.

Crystal data

$[Ni(C_8H_4F_3O_2S)_2(C_6H_7N)_2]$	Mo $K\alpha$ radiation
M_r = 687.3	λ = 0.71069 Å
Triclinic	Cell parameters from 20 reflections
$P\bar{1}$	θ = 10.33–16.01°
a = 10.320 (8) Å	μ = 0.842 mm^{-1}
b = 16.094 (7) Å	T = 296 K
c = 9.546 (4) Å	Prism
α = 105.30 (4)°	0.40 × 0.40 × 0.30 mm
β = 91.66 (5)°	Dark green
γ = 83.68 (5)°	
V = 1520 (2) $Å^3$	
Z = 2	
D_x = 1.50 Mg m^{-3}	

Data collection

Rigaku AFC-5*R* diffractometer	2653 observed reflections [$I \geq 3\sigma(I)$]
ω–2θ scans	R_{int} = 0.033
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)	θ_{max} = 25°
	$h = 0 \rightarrow 12$
	$k = -19 \rightarrow 19$
T_{min} = 0.69, T_{max} = 0.95	$l = -11 \rightarrow 11$
5685 measured reflections	3 standard reflections monitored every 250 reflections
5357 independent reflections	intensity decay: 0.2%

Refinement

Refinement on F	$w = 1/\sigma^2(F)$
R = 0.058	$(\Delta/\sigma)_{max}$ = 0.08
wR = 0.068	$\Delta\rho_{max}$ = 0.45 e $Å^{-3}$
S = 1.53	$\Delta\rho_{min}$ = −0.41 e $Å^{-3}$
2653 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
388 parameters	
H-atom parameters not refined	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Ni	0.2611 (1)	0.72674 (7)	0.4898 (1)	3.15 (4)
S(1)†	0.6884 (5)	0.8273 (3)	0.8511 (6)	7.4 (3)
S(1′)‡	0.7141 (3)	0.7629 (2)	0.5624 (4)	5.87 (2)
S(2)	0.5615 (3)	0.6119 (2)	0.1040 (3)	7.5 (2)
F(1)	0.2448 (6)	0.9627 (4)	0.9898 (8)	11.6 (4)
F(2)	0.1128 (7)	0.8715 (5)	0.9765 (7)	9.9 (4)
F(3)	0.0864 (7)	0.9555 (4)	0.8476 (8)	10.7 (4)
F(4)	−0.0656 (6)	0.7374 (6)	0.0588 (7)	11.3 (5)
F(5)	−0.1425 (7)	0.7051 (7)	0.232 (1)	14.5 (6)
F(6)	−0.0931 (8)	0.8228 (6)	0.257 (1)	14.2 (6)
O(1)	0.4426 (4)	0.7267 (3)	0.5768 (5)	3.4 (2)
O(2)	0.1851 (5)	0.8003 (3)	0.6843 (5)	3.8 (2)
O(3)	0.0856 (5)	0.7274 (3)	0.3850 (5)	4.2 (3)
O(4)	0.3488 (5)	0.6577 (3)	0.3017 (5)	3.7 (3)
N(1)	0.2302 (6)	0.6138 (4)	0.5471 (6)	3.4 (3)
N(2)	0.2888 (7)	0.8417 (4)	0.4345 (7)	3.9 (3)
C(1)	0.4768 (7)	0.7832 (5)	0.6869 (8)	3.4 (4)
C(2)	0.3885 (8)	0.8391 (6)	0.7893 (8)	4.4 (4)
C(3)	0.2564 (8)	0.8433 (5)	0.7800 (8)	3.7 (4)
C(4)	0.177 (1)	0.9093 (7)	0.899 (1)	5.9 (5)
C(5)	0.3067 (8)	0.6616 (5)	0.1775 (8)	3.7 (4)
C(6)	0.1756 (8)	0.6891 (5)	0.1468 (9)	4.3 (4)
C(7)	0.0808 (8)	0.7170 (5)	0.251 (1)	3.9 (4)
C(8)	−0.052 (1)	0.7426 (8)	0.196 (1)	6.0 (6)
C(11)	0.6176 (7)	0.7906 (5)	0.7051 (9)	3.8 (4)
C(12)	0.825 (1)	0.8228 (7)	0.792 (1)	7.0 (6)
C(13)	0.8423 (9)	0.7892 (6)	0.649 (1)	6.1 (5)
C(21)	0.4062 (8)	0.6385 (5)	0.0605 (6)	3.8 (4)
C(22)	0.3897 (7)	0.6371 (5)	−0.0918 (7)	3.2 (3)
C(23)	0.510 (1)	0.6127 (6)	−0.156 (1)	6.8 (6)
C(24)	0.612 (1)	0.5978 (7)	−0.068 (1)	6.8 (8)
C(31)	0.3165 (8)	0.5447 (6)	0.509 (1)	4.6 (4)
C(32)	0.302 (1)	0.4697 (6)	0.547 (1)	5.8 (5)
C(33)	0.195 (1)	0.4662 (6)	0.625 (1)	5.7 (5)
C(34)	0.1014 (8)	0.5369 (6)	0.6654 (9)	4.4 (4)
C(35)	0.1252 (8)	0.6100 (5)	0.6235 (8)	3.7 (4)
C(36)	−0.018 (1)	0.5382 (7)	0.752 (1)	7.1 (6)
C(41)	0.196 (1)	0.9084 (6)	0.455 (1)	5.9 (5)
C(42)	0.212 (1)	0.9822 (6)	0.414 (1)	7.6 (7)
C(43)	0.326 (1)	0.9870 (7)	0.349 (1)	7.5 (7)
C(44)	0.425 (1)	0.9209 (6)	0.327 (1)	5.4 (5)
C(45)	0.3995 (9)	0.8500 (6)	0.3735 (9)	4.4 (4)
C(46)	0.550 (1)	0.9260 (7)	0.256 (1)	8.7 (7)

† Site occupancy factor of 0.5831.
‡ Site occupancy factor of 0.7915.

Table 2. *Selected geometric parameters* (Å, °)

Ni—O(4)	2.024 (5)	N(1)—C(31)	1.32 (1)
Ni—O(1)	2.027 (5)	N(1)—C(35)	1.339 (9)
Ni—O(3)	2.044 (5)	N(2)—C(41)	1.33 (1)
Ni—O(2)	2.045 (5)	N(2)—C(45)	1.33 (1)
Ni—N(1)	2.090 (6)	C(1)—C(2)	1.42 (1)
Ni—N(2)	2.104 (6)	C(1)—C(11)	1.47 (1)
S(1)—C(12)	1.52 (1)	C(2)—C(3)	1.36 (1)
S(1)—C(11)	1.557 (9)	C(3)—C(4)	1.52 (1)
S(1′)—C(13)	1.58 (1)	C(5)—C(6)	1.42 (1)
S(1′)—C(11)	1.645 (8)	C(5)—C(21)	1.48 (1)
S(2)—C(21)	1.682 (8)	C(6)—C(7)	1.37 (1)
S(2)—C(24)	1.69 (1)	C(7)—C(8)	1.51 (1)
O(1)—C(1)	1.266 (8)	C(12)—C(13)	1.33 (1)
O(2)—C(3)	1.262 (8)	C(21)—C(22)	1.45 (1)
O(3)—C(7)	1.249 (9)	C(22)—C(23)	1.37 (1)
O(4)—C(5)	1.265 (8)	C(23)—C(24)	1.37 (1)
O(4)—Ni—O(1)	85.9 (2)	C(1)—C(11)—S(1′)	120.1 (6)
O(4)—Ni—O(3)	89.8 (2)	S(1)—C(11)—S(1′)	113.9 (5)
O(4)—Ni—O(2)	175.8 (2)	C(13)—C(12)—S(1)	117.4 (8)
O(4)—Ni—N(1)	91.7 (2)	C(12)—C(13)—S(1′)	114.3 (8)
O(4)—Ni—N(2)	89.3 (2)	C(22)—C(21)—C(5)	128.7 (7)
O(1)—Ni—O(3)	174.8 (2)	C(22)—C(21)—S(2)	113.0 (6)
O(1)—Ni—O(2)	90.4 (2)	C(5)—C(21)—S(2)	118.3 (6)
O(1)—Ni—N(1)	91.9 (2)	C(23)—C(22)—C(21)	107.2 (7)
O(1)—Ni—N(2)	88.8 (2)	C(24)—C(23)—C(22)	116.9 (8)
O(2)—Ni—O(3)	93.8 (2)	C(23)—C(24)—S(2)	111.1 (7)
O(3)—Ni—N(1)	91.2 (2)	C(41)—N(2)—Ni	122.0 (6)
O(3)—Ni—N(2)	88.2 (2)	C(45)—N(2)—Ni	121.0 (5)
O(2)—Ni—N(1)	90.3 (2)	O(1)—C(1)—C(2)	124.0 (7)
O(2)—Ni—N(2)	88.7 (2)	O(1)—C(1)—C(11)	116.6 (7)
N(1)—Ni—N(2)	178.83 (8)	C(2)—C(1)—C(11)	119.4 (7)
C(12)—S(1)—C(11)	98.5 (6)	C(3)—C(2)—C(1)	125.4 (7)
C(13)—S(1′)—C(11)	95.7 (5)	O(2)—C(3)—C(2)	129.8 (7)
C(21)—S(2)—C(24)	91.8 (5)	O(2)—C(3)—C(4)	112.4 (7)
C(1)—O(1)—Ni	124.6 (5)	C(2)—C(3)—C(4)	117.9 (8)
C(3)—O(2)—Ni	121.1 (5)	O(4)—C(5)—C(6)	124.7 (8)
C(7)—O(3)—Ni	120.5 (5)	O(4)—C(5)—C(21)	115.3 (7)
C(5)—O(4)—Ni	123.6 (5)	C(6)—C(5)—C(21)	119.9 (7)
C(31)—N(1)—C(35)	118.9 (7)	C(7)—C(6)—C(5)	123.2 (7)
C(31)—N(1)—Ni	119.7 (5)	O(3)—C(7)—C(6)	131.1 (8)
C(35)—N(1)—Ni	121.4 (5)	O(3)—C(7)—C(8)	113.7 (8)
C(41)—N(2)—C(45)	117.1 (7)	C(6)—C(7)—C(8)	115.2 (8)
C(1)—C(11)—S(1)	125.9 (7)		

The structure was solved by direct methods and difference Fourier syntheses and refined with anisotropic displacement parameters for all non-H atoms. All calculations were performed on a MicroVAX II computer with the *TEXSAN* program package (Molecular Structure Corporation, 1989).

This research was supported by a grant for a key research project from the State Science and Technology Commission of China and State Key Laboratory of Tribology of Tsinghua University.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: MU1115). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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