Intra- and intermolecular C—H···π interactions in bis[benzyl 3-(fluoren-9-ylidene)dithiocarbazato-N^3,S]-nickel(II)

S. Shanmuga Sundara Raj,[a] Hoong-Kun Fun,[a]* Ji Wu,[b] Yu-Peng Tian,[b] Fu-Xin Xie,[b] Ze-Huai Shao[b] and Sheng-Li Li[b]

[a]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]Department of Chemistry, Anhui University, Hefei, Anhui 230039, People's Republic of China
Correspondence e-mail: hkfun@usm.my

The title compound, [Ni(C₂₁H₁₅N₂S₂)₂], has a novel *cis* configuration with two fluorene moieties on the same side. The Ni atom is in a square-planar configuration. The molecular packing is stabilized by intramolecular stacking between the fluorene moieties and extensive C—H···π interactions.

Comment

Schiff base compounds having extensively conjugated π-electron systems have been reported to display second harmonic generation (Messier *et al.*, 1991; Zyss & Ledoux, 1994). It has been found (Long, 1995) that the delocalized π-conjugated electrons contribute to enhancing the non-linear optical (NLO) response through their capability for hyperpolarization. As part of our search for and study of new materials for NLO applications (Tian *et al.*, 1999), we designed and synthesized the title compound, (I), in order to explore its potential as a prospective NLO material.

(I)
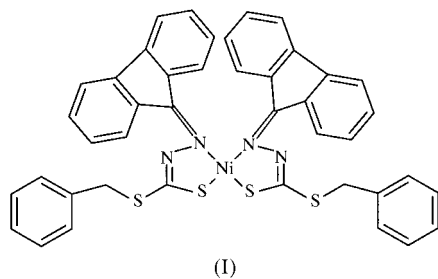
The complex molecule, which lies on a twofold axis, contains an Ni atom coordinated in a square-planar configuration with two equal Ni—S and Ni—N bonds. Most interestingly, we find that the whole molecule has a *cis* configuration. The carbazate ligand, like most dithiocarbazates (Fun *et al.*, 1996), loses a proton from the tautomeric thio

form and acts as a negatively charged bidentate ligand coordinating to nickel *via* the mercapto-S and N atoms, forming a delocalized chelate plane. However, this *cis* configuration is very rare (Liu *et al.*, 1999). The steric hindrance caused by the huge bulk of the two ligands is relieved by the stacking between the fluorene moieties of the complex molecule, which can be seen in the dihedral angle of 11.9 (1)° between the two fluorene rings. The mean distance between the centroids of the two fluorene rings is 3.345 (2) Å, which shows that there is an intramolecular interaction between the two fluorene rings. For similar reasons, one of the phenyl rings is perpendicular to both fluorene rings, with dihedral angles of 87.6 (2) and 86.4 (2)°, to avoid steric hindrance. Furthermore, the steric hindrance is further reduced by the molecules assuming a step conformation (Geremia *et al.*, 1992). The two five-membered chelate rings adopt envelope conformations and make a dihedral angle of 10.3 (1)° with one another; the mean planes are twisted through 10.7 (2)°.
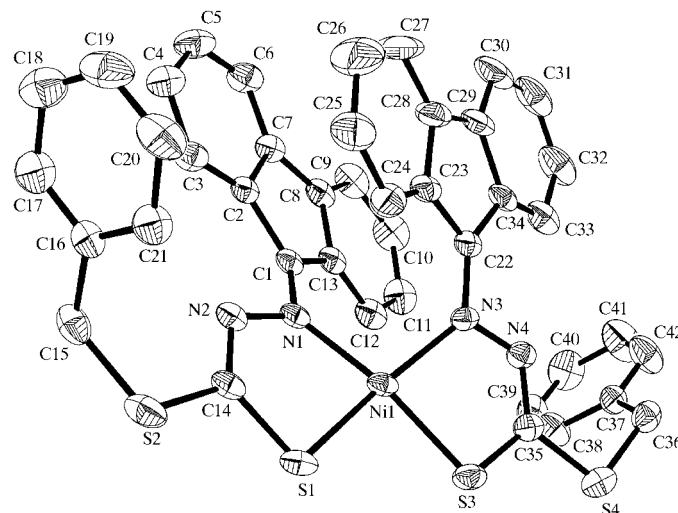

Figure 1
The structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme.

Weak intramolecular C—H···N and C—H···S interactions are responsible for the orientations of the rings. The molecules are packed as a discrete wave along the *c* axis connected by C—H···π interactions. An intramolecular C—H···π interaction between the fluorene moiety and the C16–C21 phenyl ring keeps them in an orthogonal orientation (Table 2); the dihedral angle between them is 82.5 (2)°. The other phenyl ring (C37–C42) is invloved in two C—H···π interactions.

Experimental

The title complex was prepared by mixing nickel acetate (1 mmol) and the carbazate ligand (2 mmol), prepared according to the literature method of Adel *et al.* (1991), in ethanol (30 ml) for 3 h. From the black product, single crystals were grown by slow evaporation from a dichloromethane solution of the complex containing 2-propanol.

Crystal data

$[Ni(C_{21}H_{15}N_2S_2)_2]$
$M_r = 777.65$
Monoclinic, $P2_1/n$
$a = 8.9463 (1)$ Å
$b = 21.7605 (1)$ Å
$c = 19.0038 (2)$ Å
$\beta = 100.690 (1)°$
$V = 3635.38 (6)$ Å^3
$Z = 4$

$D_x = 1.421$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7645
 reflections
$\theta = 1.44–28.37°$
$\mu = 0.801$ mm^{-1}
$T = 293 (2)$ K
Needle, black
$0.48 \times 0.14 \times 0.12$ mm

Data collection

Siemens SMART CCD area-
 detector diffractometer
ω scans
Absorption correction: empirical
 (SADABS; Sheldrick, 1996)
 $T_{min} = 0.700$, $T_{max} = 0.910$
20 413 measured reflections

6398 independent reflections
3886 reflections with $I > 2\sigma(I)$
$R_{int} = 0.088$
$\theta_{max} = 25°$
$h = -10 \rightarrow 10$
$k = -25 \rightarrow 16$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.111$
$S = 0.964$
6398 reflections
460 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0796P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.83$ e Å^{-3}
$\Delta\rho_{min} = -1.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N1	1.937 (3)	S2—C14	1.752 (4)
Ni1—N3	1.938 (4)	S2—C15	1.796 (5)
Ni1—S3	2.156 (1)	S3—C35	1.746 (5)
Ni1—S1	2.156 (1)	S4—C35	1.740 (5)
S1—C14	1.741 (5)	S4—C36	1.796 (5)
N1—Ni1—N3	100.4 (1)	S3—Ni1—S1	89.79 (5)
N1—Ni1—S3	169.4 (1)	C14—S1—Ni1	93.8 (1)
N3—Ni1—S3	85.8 (1)	C14—S2—C15	103.1 (2)
N1—Ni1—S1	85.5 (1)	C35—S3—Ni1	94.3 (2)
N3—Ni1—S1	169.4 (1)	C35—S4—C36	103.5 (2)

All H atoms were refined as riding (C—H = 0.93–0.97 Å).

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL, PARST (Nardelli, 1995) and PLATON (Spek, 1990).

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

$Cg1$, $Cg2$, $Cg3$ and $Cg4$ are the centroids of rings C16–C21, C37–C42, C8–C13 and C1/C2/C7/C8/C13, respectively.

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C3—H3A$\cdots$N2	0.93	2.43	2.947 (6)	115
C21—H21A$\cdots$S2	0.93	2.76	3.164 (5)	107
C33—H33A$\cdots$N4	0.93	2.42	2.937 (6)	115
C36—H36A$\cdots$N4	0.97	2.55	2.913 (7)	102
C38—H38A$\cdots$S4	0.93	2.73	3.153 (6)	109
C3—H3A$\cdots$Cg1	0.93	3.14	3.90	140
C15—H15B$\cdots$Cg2^i	0.97	2.96	3.80	145
C36—H36B$\cdots$Cg1^{ii}	0.97	2.90	3.63	133
C42—H42A$\cdots$Cg3^{iii}	0.93	2.97	3.89	168
C42—H42A$\cdots$Cg4^{iii}	0.93	3.28	4.11	151

Symmetry codes: (i) $\frac{3}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $x-\frac{3}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $x-1, y, z$.

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