

N1	0.5295 (2)	-0.0802 (6)	0.8572 (3)	3.07 (8)
C1	0.3407 (2)	-0.314 (1)	0.7953 (5)	4.7 (1)
C2	0.3747 (2)	-0.4671 (9)	0.8294 (5)	4.9 (1)
C3	0.4285 (2)	-0.4268 (8)	0.8624 (4)	4.1 (1)
C4	0.4474 (2)	-0.2458 (8)	0.8603 (4)	3.4 (1)
C5	0.4116 (2)	-0.0966 (9)	0.8282 (4)	3.8 (1)
C6	0.3578 (2)	-0.1342 (9)	0.7960 (5)	4.3 (1)
C7	0.5048 (2)	-0.2109 (8)	0.8932 (4)	3.6 (1)
C8	0.5846 (2)	-0.0468 (7)	0.9051 (4)	3.1 (1)
C9	0.6204 (2)	-0.1897 (9)	0.9471 (4)	4.0 (1)
C10	0.6730 (2)	-0.137 (1)	0.9882 (5)	4.9 (1)
C11	0.6881 (2)	0.046 (1)	0.9884 (5)	5.2 (2)
C12	0.6525 (2)	0.1873 (9)	0.9463 (5)	4.5 (1)
C13	0.5992 (2)	0.1423 (8)	0.9053 (4)	3.6 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Ni1—S1	2.174 (2)	C4—C5	1.403 (8)
Ni1—N1	1.915 (4)	C4—C7	1.472 (7)
S1—C13	1.755 (5)	C5—C6	1.388 (7)
C11—C1	1.734 (6)	C8—C9	1.396 (7)
N1—C7	1.281 (7)	C8—C13	1.390 (7)
N1—C8	1.440 (6)	C9—C10	1.395 (8)
C1—C2	1.401 (9)	C10—C11	1.36 (1)
C1—C6	1.347 (9)	C11—C12	1.383 (9)
C2—C3	1.390 (8)	C12—C13	1.398 (7)
C3—C4	1.374 (8)		
S1—Ni1—N1	86.1 (1)	C5—C4—C7	121.0 (5)
S1—Ni1—S1'	94.7 (2)	C4—C5—C6	119.7 (5)
N1—Ni1—N1'	97.5 (2)	C1—C6—C5	119.3 (5)
Ni1—S1—C13	94.6 (2)	N1—C7—C4	125.1 (4)
Ni1—N1—C7	127.0 (3)	N1—C8—C9	123.7 (5)
Ni1—N1—C8	113.5 (3)	N1—C8—C13	113.6 (4)
C7—N1—C8	119.3 (4)	C9—C8—C13	122.7 (4)
C11—C1—C2	117.0 (5)	C8—C9—C10	117.4 (6)
C11—C1—C6	120.0 (5)	C9—C10—C11	120.9 (6)
C2—C1—C6	123.0 (5)	C10—C11—C12	121.5 (5)
C1—C2—C3	116.9 (6)	C11—C12—C13	119.9 (6)
C2—C3—C4	121.5 (5)	S1—C13—C8	117.9 (4)
C3—C4—C5	119.5 (5)	S1—C13—C12	124.3 (4)
C3—C4—C7	119.5 (5)	C8—C13—C12	117.7 (5)
N1—Ni1—S1—C13	28.3 (2)	C7—N1—C8—C9	34.9 (7)
S1—Ni1—N1—C7	138.6 (4)	C7—N1—C8—C13	-145.6 (5)
C8—N1—C7—C4	172.4 (5)	C5—C4—C7—N1	-31.8 (8)

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

H atoms were located geometrically and then refined isotropically with fixed displacement parameters. All non-H atoms were refined anisotropically. Modified unit weights were used: if $F >$ threshold, then $w = 1.0$, if $F =$ threshold, then $w = [\text{threshold}/F]^2$, and if $F^2 <$ cutoff, $\sigma(F^2)$, then $w = 0$, where threshold = 95.15, cutoff = 2.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIMPEL* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP* (Johnson, 1965) *MolEN*. Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1204). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 1143–1145

Bis[methyl N^β -(4-methoxyphenylmethyl-ene)dithiocarbazato]nickel(II)

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Abstract

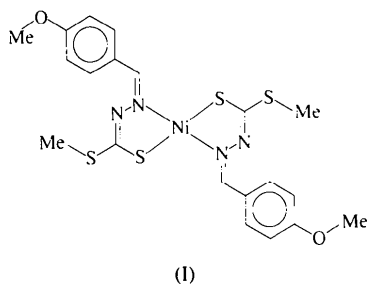
The structure of the title compound, $[\text{Ni}(\text{C}_{10}\text{H}_{11}\text{N}_2\text{OS}_2)_2]$, has been determined at 173 K. There are two independent complex molecules present in the crystal with two slightly different ligand conformations. Both independent Ni atoms lie on inversion centres.

Comment

There has been continuous interest in the chemistry of the metal complexes of Schiff bases containing N and S donor atoms because of their structural features and biological activities (Ali & Livingston, 1974; West *et al.*, 1993; Martinez & Toscano, 1995). We have reported the crystal structure of methyl N^β -(4-methoxyphenylmethyl-

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ene)dithiocarbazate (Fun *et al.*, 1996) and now describe that of its nickel(II) complex as part of our systematic studies on the chemistry of dithiocarbazates.



There are two types of complex molecules present in the crystal with different ligand conformations (*A* and *B*). Each molecule contains the same type of ligand, either *A* or *B* (see Fig. 1). The asymmetric unit consists of two halves of the two different entities.

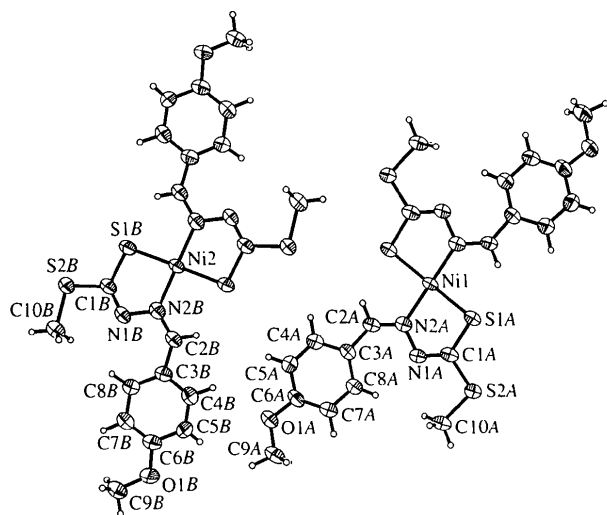


Fig. 1. A 90% displacement ellipsoid plot of the two complex molecules. The numbering scheme is given for the atoms in one asymmetric unit.

The Ni atom in each of the molecules is coordinated in a square-planar configuration with two equivalent Ni—N and Ni—S bonds. The ligand has lost a proton from its tautomeric thiol form and acts as a monoanionic bidentate ligand coordinating to nickel *via* the mercapto sulfur (S1) and β -nitrogen (N2) atoms. In the solid, the tautomeric form of the free ligand was found to be that of the thioketone, with an H atom bound to N1 and a single bond between N and C1 (Fun *et al.*, 1996). The structural differences between the free and complexed forms of the ligand are consistent with our spectroscopic observations.

Corresponding bond lengths and angles in the two complex molecules show no significant differences. However, the mean plane defined by the atoms S1, S2, C1, N1 and N2 in ligand *A* makes an angle of 7.09 (4)° with the plane of the phenyl ring, whereas in *B* the corresponding angle is 13.95 (5)° and in the uncoordinated molecule it is 5.55 (5)° (Fun *et al.*, 1996).

The complex molecules lie in the (2 $\bar{1}\bar{1}$) plane in alternate rows and form an infinite sheet. Fig. 1 shows the relative orientation of the two molecules. The intramolecular S1...H2 contacts are 2.37 (2) Å in both the complexes and the C2...S1 distances and C2—H2...S1 angles are 3.052 (2) and 3.058 (2) Å and 130 (2) and 131 (2)° for *A* and *B*, respectively; this indicates a C—H...S interaction or hydrogen bond, as was also observed in bis(methyl 3-benzylidenedithiocarbazato)-nickel(II) (Uechi & Oniki, 1982). A possible C—H...O hydrogen bond is also observed between C10A and O1B: C10A...O1Bⁱ 3.317 (3) Å, C10A—H10B...O1Bⁱ 134 (2)° [symmetry code: (i) 1 - x, 2 - y, 1 - z].

Experimental

The title complex was prepared by mixing equal volumes (20 ml) of ethanolic solutions of nickel acetate (0.5 mmol) and the ligand (1 mmol). The mixture was refluxed and stirred for 4 h. On cooling to room temperature it yielded the crystalline complex. Single crystals suitable for X-ray study were obtained by slow evaporation of a dichloromethane solution of the complex containing 2-propanol.

Crystal data

[Ni(C₁₀H₁₁N₂OS₂)₂]

M_r = 537.37

Triclinic

P $\bar{1}$

a = 8.601 (1) Å

b = 8.768 (1) Å

c = 15.008 (2) Å

α = 89.32 (1)°

β = 83.97 (1)°

γ = 81.22 (1)°

V = 1112.3 (2) Å³

Z = 2

D_x = 1.604 Mg m⁻³

Mo *K* α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 8–15°

μ = 1.274 mm⁻¹

T = 293 (2) K

Prism

0.50 × 0.34 × 0.24 mm

Black

Data collection

Siemens *P4* diffractometer

$\theta/2\theta$ scans

Absorption correction:

ψ scans (XSCANS;

Siemens, 1994)

T_{min} = 0.839, *T_{max}* =

1.000

6125 measured reflections

5099 independent reflections

4536 observed reflections

[*I* > 2 σ (*I*)]

R_{int} = 0.0173

θ_{max} = 27.5°

h = -9 → 11

k = -11 → 11

l = -19 → 19

3 standard reflections

monitored every 97

reflections

intensity decay: <3%

<i>Refinement</i>	
Refinement on F^2	$(\Delta/\sigma)_{\max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.0328$	$\Delta\rho_{\max} = 0.62 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.0942$	$\Delta\rho_{\min} = -0.67 \text{ e } \text{\AA}^{-3}$
$S = 1.063$	Extinction correction: none
5098 reflections	Atomic scattering factors
371 parameters	from <i>International Tables</i>
All H-atom parameters	for <i>Crystallography</i> (1992,
refined	Vol. C, Tables 4.2.6.8 and
$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2$	6.1.1.4)
$+ 0.1379P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

C1—N1—N2	112.52 (14)	112.16 (14)
C2—N2—N1	113.87 (14)	114.02 (14)
C2—N2—Ni	125.71 (12)	125.27 (12)
N1—N2—Ni	120.41 (11)	120.64 (11)
N1—C1—S1	124.74 (14)	124.57 (14)
N1—C1—S2	120.52 (13)	120.37 (13)
S1—C1—S2	114.74 (10)	115.06 (10)
N2—C2—C3	132.7 (2)	132.9 (2)
C4—C3—C8	117.5 (2)	117.5 (2)
C4—C3—C2	114.6 (2)	114.5 (2)
C8—C3—C2	127.9 (2)	127.9 (2)
C1—N1—N2—C2	-177.6 (2)	-169.7 (2)
N2—N1—C1—S1	-0.3 (2)	-1.9 (2)
N2—N1—C1—S2	-179.98 (12)	177.51 (12)
C10—S2—C1—N1	1.9 (2)	-1.4 (2)
C10—S2—C1—S1	-177.82 (11)	178.08 (11)
N1—N2—C2—C3	1.2 (3)	0.2 (3)
N2—C2—C3—C4	-173.8 (2)	173.9 (2)
N2—C2—C3—C8	6.7 (4)	-5.6 (4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ni1	1/2	1/2	1	0.01737 (9)
S1A	0.62483 (6)	0.68625 (6)	1.03290 (3)	0.02764 (12)
S2A	0.70250 (6)	0.94673 (6)	0.92248 (3)	0.02764 (12)
O1A	0.3417 (2)	0.6963 (2)	0.45898 (9)	0.0290 (3)
N1A	0.5527 (2)	0.7322 (2)	0.86438 (10)	0.0210 (3)
N2A	0.4895 (2)	0.5951 (2)	0.88333 (10)	0.0198 (3)
C1A	0.6165 (2)	0.7787 (2)	0.93081 (11)	0.0208 (3)
C2A	0.4292 (2)	0.5420 (2)	0.81602 (12)	0.0220 (4)
C3A	0.4167 (2)	0.5949 (2)	0.72485 (11)	0.0202 (3)
C4A	0.3274 (2)	0.5120 (2)	0.67517 (12)	0.0232 (4)
C5A	0.3045 (2)	0.5474 (2)	0.58727 (12)	0.0246 (4)
C6A	0.3715 (2)	0.6691 (2)	0.54539 (11)	0.0214 (3)
C7A	0.4611 (2)	0.7523 (2)	0.59276 (12)	0.0252 (4)
C8A	0.4833 (2)	0.7164 (2)	0.68139 (12)	0.0250 (4)
C9A	0.4133 (3)	0.8158 (3)	0.41223 (13)	0.0320 (4)
C10A	0.6657 (3)	1.0141 (3)	0.81181 (14)	0.0308 (4)
Ni2	0	0	1/2	0.01786 (9)
S1B	-0.15059 (6)	-0.12891 (6)	0.43276 (3)	0.02901 (12)
S2B	-0.22848 (6)	-0.10309 (6)	0.24716 (3)	0.02747 (12)
O1B	0.1301 (2)	0.7181 (2)	0.12956 (9)	0.0320 (3)
N1B	-0.0547 (2)	0.0795 (2)	0.31594 (10)	0.0213 (3)
N2B	0.0096 (2)	0.1227 (2)	0.39256 (10)	0.0200 (3)
C1B	-0.1318 (2)	-0.0343 (2)	0.33121 (11)	0.0208 (3)
C2B	0.0670 (2)	0.2523 (2)	0.38407 (12)	0.0231 (4)
C3B	0.0777 (2)	0.3618 (2)	0.31125 (12)	0.0220 (4)
C4B	0.1351 (3)	0.4963 (2)	0.33309 (13)	0.0318 (4)
C5B	0.1498 (3)	0.6130 (2)	0.27214 (14)	0.0346 (5)
C6B	0.1099 (2)	0.5974 (2)	0.18534 (12)	0.0239 (4)
C7B	0.0532 (2)	0.4654 (2)	0.16171 (12)	0.0248 (4)
C8B	0.0371 (2)	0.3486 (2)	0.22373 (12)	0.0246 (4)
C9B	0.0856 (3)	0.7101 (2)	0.04083 (13)	0.0305 (4)
C10B	-0.1881 (3)	0.0251 (2)	0.15629 (13)	0.0283 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

	<i>A</i>	<i>B</i>
Ni—N2	1.9351 (15)	1.9291 (15)
Ni—S1	2.1746 (5)	2.1731 (5)
S1—C1	1.728 (2)	1.731 (2)
S2—C1	1.744 (2)	1.743 (2)
S2—C10	1.800 (2)	1.796 (2)
N1—C1	1.286 (2)	1.286 (2)
N1—N2	1.407 (2)	1.406 (2)
N2—C2	1.304 (2)	1.306 (2)
C2—C3	1.449 (2)	1.451 (2)
N2—Ni—S1	86.15 (5)	85.92 (5)
C1—S1—Ni	96.16 (6)	96.10 (6)
C1—S2—C10	102.60 (9)	101.89 (9)

The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 . All H atoms were located from difference maps and refined isotropically.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC (Sheldrick, 1990). Software used to prepare material for publication: SHELXL93. Geometrical calculations: PARST (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1220). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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