Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	U_{eq}
Ni1	0	0	0	0.02512 (13)
O11	0.04507 (13)	0.0422 (2)	0.09247 (9)	0.0315 (4)
C11	0.0581 (2)	−0.0457 (3)	0.13121 (13)	0.0305 (6)
N11	0.0666 (2)	−0.0341 (2)	0.19439 (11)	0.0324 (6)
C12	0.0589 (2)	0.0859 (3)	0.22588 (15)	0.0447 (8)
C13	0.0807 (2)	−0.1424 (3)	0.2359 (2)	0.0495 (9)
O21	0.09164 (13)	0.1163 (2)	−0.04194 (9)	0.0333 (5)
C21	0.1573 (2)	0.1733 (3)	−0.01803 (13)	0.0291 (6)
N21	0.2150 (2)	0.2363 (2)	−0.05226 (11)	0.0305 (5)
C22	0.2920 (2)	0.3007 (3)	−0.0216 (2)	0.0446 (8)
C23	0.2043 (3)	0.2424 (3)	−0.12270 (14)	0.0473 (8)
O31	−0.09083 (13)	0.1420 (2)	0.00085 (9)	0.0318 (5)
C31	−0.0727 (2)	0.2471 (3)	0.02308 (14)	0.0328 (6)
N31	−0.1309 (2)	0.3389 (2)	0.02278 (13)	0.0398 (6)
C32	−0.2218 (2)	0.3243 (3)	−0.0053 (2)	0.0509 (9)
C33	−0.1067 (3)	0.4602 (3)	0.0495 (2)	0.0634 (11)
Ni2	1/2	0	1	0.03266 (15)
O41	0.41499 (14)	−0.0026 (2)	0.91995 (9)	0.0386 (5)
C41	0.3352 (2)	−0.0365 (3)	0.91658 (13)	0.0328 (7)
N41	0.2902 (2)	−0.0593 (2)	0.86211 (11)	0.0345 (6)
C42	0.3361 (3)	−0.0556 (4)	0.80101 (14)	0.0589 (10)
C43	0.1972 (2)	−0.1020 (3)	0.8593 (2)	0.0471 (8)
O51	0.60020 (13)	−0.0629 (2)	0.94236 (9)	0.0364 (5)
C51	0.5822 (2)	−0.1395 (3)	0.89842 (14)	0.0354 (7)
N51	0.6354 (2)	−0.1633 (3)	0.85043 (11)	0.0387 (6)
C52	0.7206 (2)	−0.0983 (4)	0.8447 (2)	0.0516 (9)
C53	0.6094 (3)	−0.2521 (4)	0.7998 (2)	0.0556 (10)
O61	0.53464 (14)	0.1782 (2)	0.97846 (9)	0.0383 (5)
C61	0.5549 (2)	0.2054 (3)	0.92221 (13)	0.0345 (7)
N61	0.5710 (2)	0.3183 (2)	0.90245 (11)	0.0311 (5)
C62	0.5936 (2)	0.3435 (3)	0.83554 (14)	0.0443 (8)
C63	0.5627 (2)	0.4248 (3)	0.94498 (14)	0.0399 (7)
Cl1	−0.14659 (5)	0.55618 (8)	−0.15182 (4)	0.0444 (2)
O1	−0.1503 (2)	0.5919 (4)	−0.21838 (13)	0.0922 (11)
O2	−0.2362 (2)	0.5515 (3)	−0.1297 (2)	0.0883 (10)
O3	−0.0988 (2)	0.6486 (3)	−0.1171 (2)	0.0951 (11)
O4	−0.1032 (3)	0.4405 (3)	−0.1415 (2)	0.0999 (12)
Cl2	0.35796 (6)	0.56771 (8)	0.82856 (4)	0.0503 (2)
O5	0.3970 (4)	0.5887 (4)	0.7700 (2)	0.154 (2)
O6	0.3973 (2)	0.6480 (3)	0.87646 (14)	0.0788 (9)
O7	0.3767 (2)	0.4421 (3)	0.8446 (2)	0.0872 (10)
O8	0.2650 (3)	0.5763 (5)	0.8258 (3)	0.179 (3)

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

Ni1—O31	2.037 (2)	Ni2—O41	2.040 (2)
Ni1—O11	2.051 (2)	Ni2—O61	2.040 (2)
Ni1—O21	2.063 (2)	Ni2—O51	2.055 (2)
O31—Ni1—O11'	89.05 (8)	O41''—Ni2—O61	90.67 (8)
O31—Ni1—O11	90.95 (8)	O41—Ni2—O61	89.33 (8)
O31—Ni1—O21	89.69 (8)	O41''—Ni2—O51	92.16 (8)
O31'—Ni1—O21	90.31 (8)	O41—Ni2—O51	87.84 (8)
O11'—Ni1—O21	86.45 (8)	O61—Ni2—O51	89.40 (8)
O11—Ni1—O21	93.55 (8)	O61''—Ni2—O51	90.60 (8)
C11'—O11'—Ni1—O21	−46.1 (2)	C41''—O41''—Ni2—O51	40.5 (2)
C11'—O11'—Ni1—O31	43.7 (2)	C41''—O41''—Ni2—O61	−49.0 (2)
C21—O21—Ni1—O11	9.6 (2)	C51—O51—Ni2—O41	−37.3 (2)
C21'—O21'—Ni1—O31	79.5 (2)	C51''—O51''—Ni2—O61	−53.4 (2)
C31—O31—Ni1—O11	42.9 (2)	C61—O61—Ni2—O41	−47.8 (2)
C31—O31—Ni1—O21	−50.7 (2)	C61—O61—Ni2—O51	40.1 (2)

Symmetry codes: (i) $-x, -y, -z$; (ii) $1 - x, -y, 2 - z$.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1163). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis[*N*-(4-chlorobenzylidene)-2-mercaptoanilinato]nickel(II)

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Abstract

The title structure consists of discrete [Ni($C_{13}H_9ClNS$)$_2$] molecules with each Ni atom located on a crystallographic twofold axis. The coordination around Ni is approximately square planar and *N*-(4-chlorobenzylidene)-2-mercaptoaniline acts as a monoanionic bidentate ligand [IUPAC name: 2-(4-chlorobenzylideneamino)benzenethiolato] coordinating to nickel(II) *via* the mercapto S and the imino N atoms.

Comment

Several related metal derivatives of Schiff bases have been reported (Soriano-Garcia, Toscano, Valdes-Martinez & Fernandez-G., 1985; Elerman, Fuess & Paulus, 1992). Some transition metal Schiff base complexes containing N and S donor atoms have been

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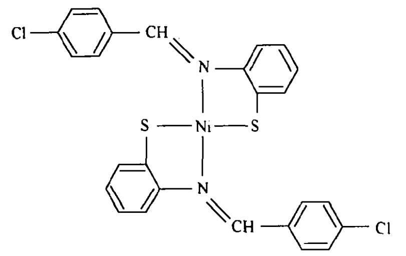
reported to possess cytotoxic activity (Das & Livingstone, 1975), and the synthesis of metal chelates of Schiff bases derived from methyl dithiocarbazate, $H_2NNHC({=}S)SCH_3$ (Das & Livingstone, 1976), or derived from 2-mercaptoaniline (Linday & Livingstone, 1967) have been reported. Here we report the structure of the title compound, (I).



(I)

The title compound exhibits approximately square-planar coordination around the Ni atom. The valence angles around Ni are between 86.1 (1) and 97.5 (2)°. N and S atoms are 0.299 (4) and 0.267 (1) Å out of the least-squares plane through atoms Ni1, N1, N1′, S1 and S1′. N1 and S1′ are located above the plane while S1 and N1′ are relatively below; Ni1 is practically in the plane with a deviation of only 0.0003 Å. Within experimental error both aromatic rings are planar. The dihedral angle between phenyl rings of the same ligand is 6.0 (9)° and that between the least-squares planes defined by N1—C8—C13—S1 and N1—Ni1—S1 is 34.4 (3)°. The bond distances and angles within the aromatic rings have usual values. The Ni—S and Ni—N distances are 2.174 (2) and 1.915 (4) Å, respectively, and appear to be in agreement with the corresponding values of 2.166 (2) and 1.921 (7) Å, respectively, observed in $[Ni(C_{14}H_{11}N_3OS)(NH)_3]$ (Soriano-Garcia, Toscano, Valdes-Martinez & Fernandez-G., 1985).

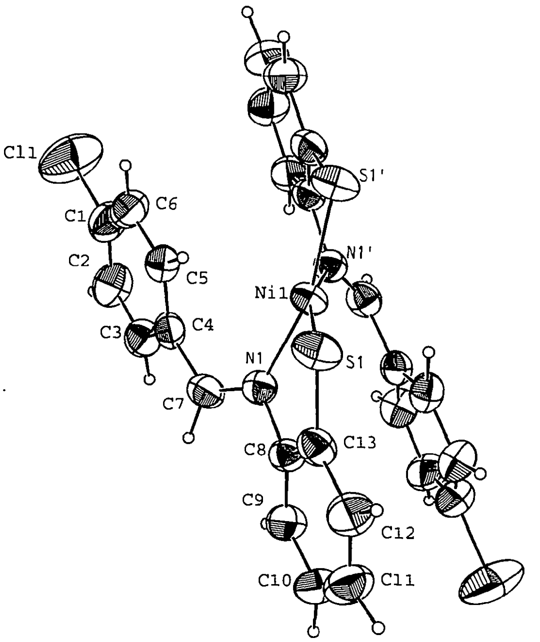


Fig. 1. *ORTEP* (Johnson, 1965) drawing displaying the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

Experimental

N-(4-Chlorobenzylidene)-2-mercaptoaniline was prepared by the condensation of 4-chlorobenzaldehyde with 2-mercaptoaniline in alcoholic solution. When the solution was treated with alkali, in the presence of nickel(II) acetate, a deeply coloured Ni^{II} complex of the Schiff base separated and was recrystallized from alcohol.

Crystal data

$[Ni(C_{13}H_9ClNS)_2]$
$M_r = 552.19$
Monoclinic
$C2/c$
$a = 25.990\,(2)$ Å
$b = 7.078\,(1)$ Å
$c = 13.203\,(1)$ Å
$\beta = 103.82\,(5)°$
$V = 2358.5\,(3)$ Å^3
$Z = 4$
$D_x = 1.555$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–18°$
$\mu = 1.24$ mm^{-1}
$T = 296$ K
Prism
0.40 × 0.15 × 0.05 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (*MolEN*; Fair, 1990)
$T_{min} = 0.877$, $T_{max} = 0.999$
2646 measured reflections
2386 independent reflections

1582 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.01$
$\theta_{max} = 26.3°$
$h = -32 \rightarrow 0$
$k = 0 \rightarrow 8$
$l = -15 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: 1.1%

Refinement

Refinement on F
$R = 0.047$
$wR = 0.050$
$S = 0.73$
1561 reflections
177 parameters
Modified unit weights (see below)

$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.98$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	B_{eq}
Ni1	1/2	0.0984 (1)	3/4	2.95 (2)
S1	0.5505 (1)	0.3066 (2)	0.8469 (1)	4.10 (3)
Cl1	0.27367 (1)	−0.3643 (4)	0.7539 (2)	9.24 (7)

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 (Å, °)*

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)
Cl1—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^{i}	94.7 (2)	C4—C5—C6	119.7 (5)
N1—Ni1—N1^{i}	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)
Cl1—C1—C2	117.0 (5)	C8—C9—C10	117.4 (6)
Cl1—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 $F^2 < \text{cutoff}.\sigma(F^2)$, 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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Bis[methyl N^β-(4-methoxyphenylmethylene)dithiocarbazato]nickel(II)

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Abstract

The structure of the title compound, $[\mathrm{Ni}(\mathrm{C_{10}H_{11}N_2OS_2})_2]$, 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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