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Crystal structure of bis[*S*-hexyl 3-(4-methylbenzylidene)dithiocarbazato-κ^2N^3,S]nickel(II)

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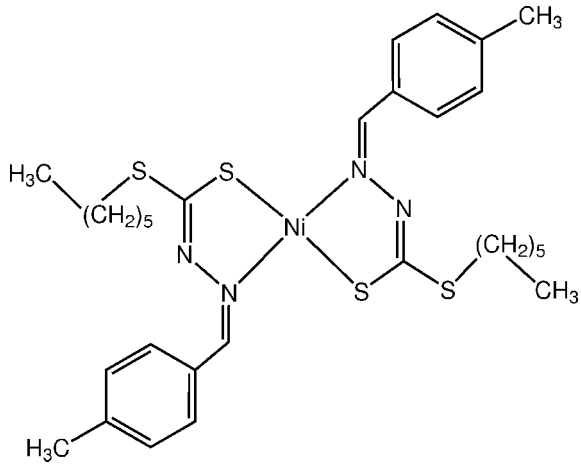
In the title complex, $[Ni(C_{15}H_{21}N_2S_2)_2]$, the Ni^{II} atom exhibits a square-planar coordination geometry and is located on an inversion centre leading to a *trans* configuration of the *N*,*S*-chelating ligands. In the crystal, the complex molecules stack at a distance of 4.6738 (3) Å along the *a* axis, which exclude any significant interactions between the aromatic rings.

Keywords: crystal structure; nickel complex; dithiocarbazate.

CCDC reference: 1035820

1. Related literature

For the structures of related complexes, see: Chan *et al.* (2008); Islam *et al.* (2011, 2014); Li *et al.* (2006); Zhang *et al.* (2004). For the structure of the ligand, see: Howlader *et al.* (2015).



2. Experimental

2.1. Crystal data

$[Ni(C_{15}H_{21}N_2S_2)_2]$
M_r = 645.62
Triclinic, $P\overline{1}$
a = 4.6738 (3) Å
b = 10.5132 (5) Å
c = 16.4789 (8) Å
α = 86.522 (3)°
β = 84.850 (3)°
γ = 79.057 (3)°
V = 791.00 (7) Å^3
Z = 1
Cu $K\alpha$ radiation
μ = 3.55 mm^{-1}
T = 173 K
0.37 × 0.08 × 0.02 mm

2.2. Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Rigaku, 1995)
T_{min} = 0.615, T_{max} = 0.932
9100 measured reflections
2834 independent reflections
2029 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.074

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.071
$wR(F^2)$ = 0.218
S = 1.09
2834 reflections
180 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.98 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ni—N1	1.933 (3)	Ni—S1	2.1775 (10)

Data collection: *RAPID-AUTO* (Rigaku, 2001); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalStructure* (Rigaku, 2010); software used to prepare material for publication: *CrystalStructure*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: DS2244).

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S1. Structural commentary

The metal is located on a crystallographic inversion centre and the two Schiff bases, in their deprotonated imino thiolate form, act as chelating ligands to the metal centre via the azomethine nitrogen N1 and thiolate sulphur S1 atoms in a trans-planar configuration as imposed by the crystal symmetry. The complex has coplanar geometry with the exception of the hexyl chains that pend hedgewise. In the complex, the Ni—S and Ni–N bond distances are of 2.1777 (11) and 1.933 (4) Å, respectively, with a S(2)—Ni—N(2) chelating angle of 86.06 (10)°. These geometrical parameters agree with those reported for similar nickel complexes either when ligands assume a *trans* (Islam, *et al.*, 2011; Islam, *et al.*, 2014; Zhang, *et al.*, 2004) or a *cis* configuration (Chan, *et al.*, 2008; Li, *et al.*, 2006). The ligand, recently reported (Howlader, *et al.*, 2015), underwent rotation about the C9—N2 by 180° in order to allow the N,S chelating behavior towards the metal. Upon coordination some salient features are observed with respect to the free ligand, and the most significant are an elongation of the C(9)—S(1) bond length (1.720 (4) Å in NiL_2 that must be compared to 1.670 (3) Å in HL, thus validating the coordination with deprotonated thiolate sulphur atom. Correspondingly the N(2)—C(9) bond length, of 1.335 (3) Å, shortens to 1.270 (6) Å in the NiL_2 complex, while the N(1)—N(2) bond length of 1.375 (3) Å in HL is slightly elongated in the complex (1.426 (5) Å, Table 1).

S2. Supramolecular features

The complexes stack at a distance of 4.6738 (3) Å (axis *a*), which exclude any significant interactions between the aromatic rings.

S3. Synthesis and crystallization

A solution of $Ni(CH_3COO)_2.4H_2O$ (0.06 g, 0.25 mmol, 8 mL methanol) was added to a solution of the ligand, S-hexyl (E)-3-(4-methylbenzylidene)dithiocarbazate, (0.15 g, 0.5 mmol, 10 mL methanol). The resulting mixture was stirred at room temperature for four hours. A dark reddish brown precipitate was formed, filtered off, washed with methanol and dried in vacuo over anhydrous $CaCl_2$. Dark reddish brown single crystals, suitable for X-ray diffraction, of the compound were obtained by slow evaporation from a mixture of chloroform and acetonitrile (1:1) after 7 days. M.P. 374 K.

S4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located geometrically and treated as riding atoms, with C—H = 0.95–0.99 Å, and with *U*iso~(H) = 1.2*U*~eq~(C) or 1.5*U*~eq~(C) for methyl H atoms.

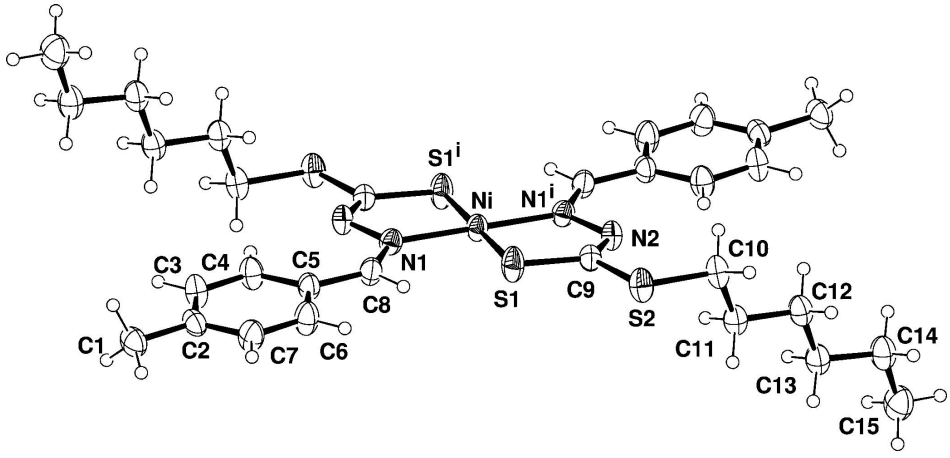

Figure 1

ORTEP drawing (ellipsoid probability at 50%) of the centrosymmetric NiL_2 complex.

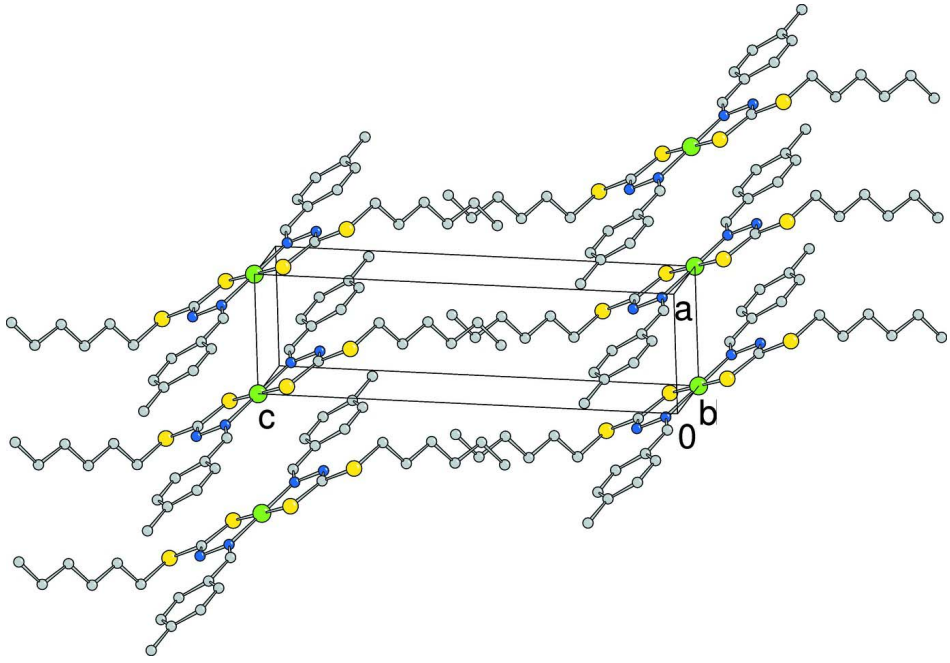

Figure 2

Crystal packing of the complex.

Bis[*S*-hexyl 3-(4-methylbenzylidene)dithiocarbazato-κ^2N^3,S]nickel(II)

Crystal data

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α = 86.522 (3)°
β = 84.850 (3)°
γ = 79.057 (3)°
V = 791.00 (7) Å^3
Z = 1
F(000) = 342.00
D_x = 1.355 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54187 Å
Cell parameters from 5923 reflections
θ = 4.3–68.2°
μ = 3.55 mm^{-1}

T = 173 K
Platelet, brown

0.37 × 0.08 × 0.02 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*ABSCOR*; Rigaku, 1995)
T_{min} = 0.615, T_{max} = 0.932
9100 measured reflections

2834 independent reflections
2029 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.074
θ_{max} = 68.2°
h = −5→5
k = −12→12
l = −19→19

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.071
$wR(F^2)$ = 0.218
S = 1.09
2834 reflections
180 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1314P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.98 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Special details

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2. R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0\ \sigma(F^2)$ is used only for calculating R-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Ni	1.0000	1.0000	1.0000	0.0372 (4)
S1	1.1112 (3)	0.83443 (10)	0.92242 (6)	0.0516 (4)
S2	1.4585 (2)	0.80909 (9)	0.76635 (6)	0.0479 (4)
N1	0.7454 (7)	0.9180 (3)	1.07644 (18)	0.0365 (8)
N2	1.3765 (7)	1.0201 (3)	0.85050 (18)	0.0405 (8)
C1	−0.0675 (10)	0.4837 (4)	1.2473 (3)	0.0514 (11)
H1A	−0.0056	0.4630	1.3025	0.077*
H1B	−0.0491	0.4035	1.2184	0.077*
H1C	−0.2717	0.5288	1.2503	0.077*
C2	0.1222 (9)	0.5695 (4)	1.2022 (2)	0.0420 (10)
C3	0.1476 (9)	0.6854 (4)	1.2321 (3)	0.0489 (11)
H3	0.0431	0.7105	1.2825	0.059*
C4	0.3184 (9)	0.7676 (4)	1.1923 (2)	0.0455 (10)
H4	0.3281	0.8471	1.2154	0.055*
C5	0.4769 (8)	0.7344 (4)	1.1181 (2)	0.0390 (9)
C6	0.4513 (10)	0.6168 (4)	1.0883 (3)	0.0522 (12)
H6	0.5555	0.5913	1.0380	0.063*
C7	0.2807 (10)	0.5349 (4)	1.1288 (2)	0.0511 (11)
H7	0.2718	0.4547	1.1063	0.061*

C8	0.6638 (9)	0.8089 (4)	1.0680 (2)	0.0418 (10)
H8	0.7429	0.7691	1.0186	0.050*
C9	1.3189 (8)	0.9071 (4)	0.8487 (2)	0.0370 (9)
C10	1.6632 (9)	0.9110 (4)	0.7013 (3)	0.0469 (11)
H10A	1.7787	0.9530	0.7355	0.056*
H10B	1.8022	0.8559	0.6632	0.056*
C11	1.4718 (9)	1.0153 (4)	0.6522 (2)	0.0463 (10)
H11A	1.3404	1.0736	0.6903	0.056*
H11B	1.3482	0.9738	0.6203	0.056*
C12	1.6461 (9)	1.0959 (4)	0.5943 (2)	0.0467 (10)
H12A	1.7684	1.1383	0.6262	0.056*
H12B	1.7784	1.0378	0.5563	0.056*
C13	1.4508 (9)	1.1991 (4)	0.5453 (2)	0.0488 (11)
H13A	1.3236	1.1563	0.5154	0.059*
H13B	1.3227	1.2580	0.5837	0.059*
C14	1.6143 (10)	1.2790 (4)	0.4849 (3)	0.0545 (12)
H14A	1.7445	1.2204	0.4468	0.065*
H14B	1.7386	1.3235	0.5147	0.065*
C15	1.4131 (11)	1.3796 (5)	0.4361 (3)	0.0670 (14)
H15A	1.3058	1.3358	0.4015	0.100*
H15B	1.5293	1.4337	0.4019	0.100*
H15C	1.2742	1.4342	0.4735	0.100*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni	0.0441 (7)	0.0337 (6)	0.0351 (5)	−0.0150 (4)	0.0033 (4)	0.0027 (4)
S1	0.0706 (9)	0.0392 (6)	0.0472 (6)	−0.0254 (6)	0.0172 (6)	−0.0036 (5)
S2	0.0571 (8)	0.0331 (6)	0.0520 (6)	−0.0121 (5)	0.0142 (5)	−0.0052 (4)
N1	0.044 (2)	0.0325 (16)	0.0337 (16)	−0.0097 (15)	0.0010 (14)	−0.0006 (13)
N2	0.045 (2)	0.0378 (18)	0.0370 (17)	−0.0105 (16)	0.0085 (15)	0.0032 (14)
C1	0.047 (3)	0.047 (2)	0.061 (3)	−0.016 (2)	−0.001 (2)	0.013 (2)
C2	0.034 (2)	0.042 (2)	0.050 (2)	−0.0104 (18)	−0.0010 (18)	0.0111 (18)
C3	0.051 (3)	0.044 (2)	0.051 (2)	−0.013 (2)	0.016 (2)	−0.0023 (19)
C4	0.053 (3)	0.034 (2)	0.049 (2)	−0.015 (2)	0.012 (2)	−0.0064 (17)
C5	0.040 (2)	0.039 (2)	0.038 (2)	−0.0142 (18)	0.0024 (18)	0.0049 (16)
C6	0.071 (3)	0.045 (2)	0.044 (2)	−0.027 (2)	0.013 (2)	−0.0083 (19)
C7	0.068 (3)	0.043 (2)	0.048 (2)	−0.027 (2)	0.004 (2)	−0.0037 (18)
C8	0.050 (3)	0.044 (2)	0.0337 (19)	−0.017 (2)	0.0048 (18)	−0.0028 (16)
C9	0.036 (2)	0.037 (2)	0.036 (2)	−0.0065 (18)	0.0024 (17)	0.0012 (16)
C10	0.049 (3)	0.039 (2)	0.050 (2)	−0.010 (2)	0.016 (2)	−0.0037 (18)
C11	0.050 (3)	0.044 (2)	0.045 (2)	−0.014 (2)	0.007 (2)	−0.0020 (18)
C12	0.048 (3)	0.043 (2)	0.049 (2)	−0.016 (2)	0.009 (2)	−0.0037 (18)
C13	0.051 (3)	0.050 (2)	0.047 (2)	−0.017 (2)	0.007 (2)	−0.0016 (19)
C14	0.061 (3)	0.047 (2)	0.056 (3)	−0.019 (2)	0.011 (2)	−0.001 (2)
C15	0.079 (4)	0.061 (3)	0.063 (3)	−0.026 (3)	0.001 (3)	0.007 (2)

Geometric parameters (Å, º)

Ni—N1	1.933 (3)	C6—C7	1.385 (5)
Ni—N1^{i}	1.933 (3)	C6—H6	0.9500
Ni—S1	2.1775 (10)	C7—H7	0.9500
Ni—S1^{i}	2.1775 (10)	C8—H8	0.9500
S1—C9	1.720 (4)	C10—C11	1.519 (5)
S2—C9	1.757 (4)	C10—H10A	0.9900
S2—C10	1.811 (4)	C10—H10B	0.9900
N1—C8	1.294 (5)	C11—C12	1.521 (5)
N1—N2^{i}	1.425 (4)	C11—H11A	0.9900
N2—C9	1.269 (5)	C11—H11B	0.9900
N2—N1^{i}	1.425 (4)	C12—C13	1.521 (6)
C1—C2	1.501 (5)	C12—H12A	0.9900
C1—H1A	0.9800	C12—H12B	0.9900
C1—H1B	0.9800	C13—C14	1.513 (5)
C1—H1C	0.9800	C13—H13A	0.9900
C2—C3	1.371 (6)	C13—H13B	0.9900
C2—C7	1.391 (6)	C14—C15	1.517 (6)
C3—C4	1.383 (5)	C14—H14A	0.9900
C3—H3	0.9500	C14—H14B	0.9900
C4—C5	1.399 (5)	C15—H15A	0.9800
C4—H4	0.9500	C15—H15B	0.9800
C5—C6	1.387 (5)	C15—H15C	0.9800
C5—C8	1.452 (5)		
N1—Ni—N1^{i}	180.00 (14)	N2—C9—S1	125.9 (3)
N1—Ni—S1	93.96 (9)	N2—C9—S2	120.3 (3)
N1^{i}—Ni—S1	86.04 (9)	S1—C9—S2	113.9 (2)
N1—Ni—S1^{i}	86.04 (9)	C11—C10—S2	113.5 (3)
N1^{i}—Ni—S1^{i}	93.96 (9)	C11—C10—H10A	108.9
S1—Ni—S1^{i}	180.0	S2—C10—H10A	108.9
C9—S1—Ni	95.86 (13)	C11—C10—H10B	108.9
C9—S2—C10	103.09 (19)	S2—C10—H10B	108.9
C8—N1—N2^{i}	113.8 (3)	H10A—C10—H10B	107.7
C8—N1—Ni	126.3 (3)	C10—C11—C12	113.2 (3)
N2^{i}—N1—Ni	119.9 (2)	C10—C11—H11A	108.9
C9—N2—N1^{i}	111.9 (3)	C12—C11—H11A	108.9
C2—C1—H1A	109.5	C10—C11—H11B	108.9
C2—C1—H1B	109.5	C12—C11—H11B	108.9
H1A—C1—H1B	109.5	H11A—C11—H11B	107.8
C2—C1—H1C	109.5	C13—C12—C11	112.4 (3)
H1A—C1—H1C	109.5	C13—C12—H12A	109.1
H1B—C1—H1C	109.5	C11—C12—H12A	109.1
C3—C2—C7	117.1 (4)	C13—C12—H12B	109.1
C3—C2—C1	121.3 (4)	C11—C12—H12B	109.1
C7—C2—C1	121.7 (4)	H12A—C12—H12B	107.9
C2—C3—C4	123.0 (4)	C14—C13—C12	114.4 (4)

C2—C3—H3	118.5	C14—C13—H13A	108.7
C4—C3—H3	118.5	C12—C13—H13A	108.7
C3—C4—C5	120.4 (4)	C14—C13—H13B	108.7
C3—C4—H4	119.8	C12—C13—H13B	108.7
C5—C4—H4	119.8	H13A—C13—H13B	107.6
C6—C5—C4	116.3 (3)	C13—C14—C15	113.0 (4)
C6—C5—C8	116.0 (3)	C13—C14—H14A	109.0
C4—C5—C8	127.8 (4)	C15—C14—H14A	109.0
C7—C6—C5	122.9 (4)	C13—C14—H14B	109.0
C7—C6—H6	118.6	C15—C14—H14B	109.0
C5—C6—H6	118.6	H14A—C14—H14B	107.8
C6—C7—C2	120.3 (4)	C14—C15—H15A	109.5
C6—C7—H7	119.9	C14—C15—H15B	109.5
C2—C7—H7	119.9	H15A—C15—H15B	109.5
N1—C8—C5	133.6 (4)	C14—C15—H15C	109.5
N1—C8—H8	113.2	H15A—C15—H15C	109.5
C5—C8—H8	113.2	H15B—C15—H15C	109.5

C7—C2—C3—C4	0.8 (6)	C4—C5—C8—N1	2.7 (8)
C1—C2—C3—C4	−179.6 (4)	$N1^{i}$—N2—C9—S1	1.8 (5)
C2—C3—C4—C5	−0.2 (7)	$N1^{i}$—N2—C9—S2	−177.5 (2)
C3—C4—C5—C6	0.0 (6)	Ni—S1—C9—N2	2.5 (4)
C3—C4—C5—C8	179.5 (4)	Ni—S1—C9—S2	−178.24 (18)
C4—C5—C6—C7	−0.2 (7)	C10—S2—C9—N2	−0.4 (4)
C8—C5—C6—C7	−179.8 (4)	C10—S2—C9—S1	−179.8 (2)
C5—C6—C7—C2	0.8 (7)	C9—S2—C10—C11	−77.3 (3)
C3—C2—C7—C6	−1.0 (6)	S2—C10—C11—C12	−176.9 (3)
C1—C2—C7—C6	179.3 (4)	C10—C11—C12—C13	179.6 (3)
$N2^{i}$—N1—C8—C5	−1.2 (7)	C11—C12—C13—C14	−178.2 (3)
Ni—N1—C8—C5	−179.8 (3)	C12—C13—C14—C15	179.1 (4)
C6—C5—C8—N1	−177.7 (4)		

Symmetry code: (i) $-x+2, -y+2, -z+2$.