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(2-{[2-(Dimethylamino)ethyl]iminomethyl}benzenethiolato-κ^3N,N',S)(4-methoxybenzenethiolato-κS)-nickel(II)

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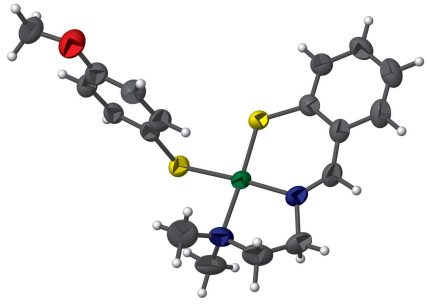
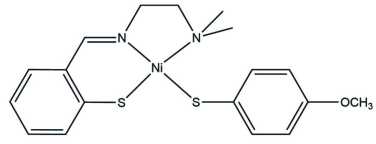
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, [Ni($C_{11}H_{15}N_2S$)(C_7H_7OS)] or [Ni($NN^{Im}S$)(4-OCH_3-PhS)] ($NN^{Im}S$ = 2-{[2-(dimethylamino)ethyl]iminomethyl}benzenethiolato), the Ni^{II} cation is coordinated by a tridentate $NN^{Im}S$ ligand and a monodentate thiolate ligand giving an N_2S_2 coordination set defining an almost square-planar environment. The Ni—N_{amine} bond in the coordination plane is approximately 0.1 Å longer than the Ni—N_{imine} bond.

3D view



Chemical scheme



Structure description

In recent years, complexes comprising an NiN_2S_2 moiety have attracted considerable interest as synthetic mimics of the NiSOD active site (Shearer & Zhao, 2006; Fiedler & Brunold, 2007; Jenkins *et al.*, 2009; Gale *et al.*, 2009, 2010; Mathruboothan *et al.*, 2010; Senaratne *et al.*, 2018). We have prepared a series of Ni^{II} complexes containing the tridentate $NN^{Im}S$ ligand ($NN^{Im}S$ = {2-{[2-(dimethylamino)ethyl]iminomethyl}benzenethiolato}) with amine, imine, and thiolate donors, and various monodentate thiolate ligands (Senaratne *et al.*, 2018). The title compound represents another in this series.

In the crystal, the molecule (Fig. 1) sits on general positions in the orthorhombic space group $Pna2_1$. The $NN^{Im}S$ ligand is essentially coplanar with the coordination sphere, with an 11.84 (17)° dihedral angle between the least-squares plane of the phenyl ring and the average plane of the N_3S donors. The thiolate substituent protrudes from the coordination plane, with an Ni—S—C angle of 109.04 (15)°. The Ni—N and Ni—S bond lengths (Table 1) are very similar to those in the previously reported members of this series. No significant intermolecular interactions are evident in the crystal structure (Fig. 2). There is a potential C—H$\cdots\pi$ interaction between the *para* C atom of the $NN^{im}S$ phenyl ring

Table 1
Selected geometric parameters (Å, °).

Ni1—S1	2.1383 (11)	Ni1—N2	1.888 (3)
Ni1—S2	2.2272 (12)	Ni1—N1	2.016 (3)
S1—Ni1—S2	85.25 (5)	N1—Ni1—S1	177.11 (12)
N2—Ni1—S1	95.97 (11)	N1—Ni1—S2	92.58 (11)
N2—Ni1—S2	173.07 (12)	C11—S1—Ni1	111.67 (14)
N2—Ni1—N1	86.41 (16)	C12—S2—Ni1	109.04 (15)

and the phenyl ring (C12–C17) of the monodentate ligand (C8···centroid 3.64 Å, C8—H8···centroid 156°).

Synthesis and crystallization

Ni(NN^{Im}S)Cl was synthesized as previously reported (Zimmerman *et al.*, 2011). Under nitrogen, NaOH (0.265 g, 7.00 mmol) was added to a solution of 4-methoxythiophenol (0.820 mL 7.00 mmol) in 10 mL methanol. After stirring for 5 min, the resulting yellow Na(4-OCH$_3$PhS) solution was added to a solution of [Ni(NN^{Im}S)Cl] (1.06 g, 3.50 mmol) in 30 ml of CH_2Cl_2. After stirring for 24 h the solution was filtered and the solvent was removed by rotary evaporation yielding 1.07 g (68.6%) of the desired title compound as a dark-brown solid. X-ray quality crystals were grown by vapor diffusion of hexanes into a CH_2Cl_2 solution.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. In the final refinement, ten reflections were omitted because they were obstructed by the beam stop.

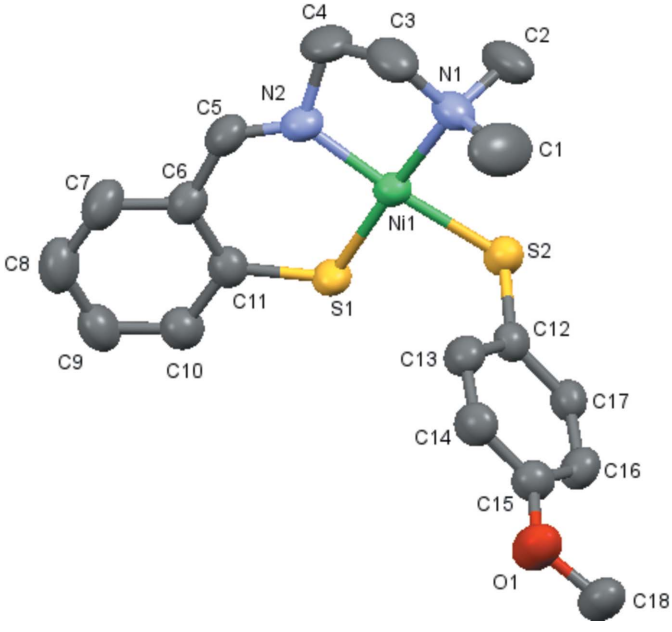


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	[Ni(C$_{11}$H$_{15}$N$_2$S)(C$_7$H$_7$OS)]
M_r	405.20
Crystal system, space group	Orthorhombic, *Pna*2$_1$
Temperature (K)	150
a, *b*, *c* (Å)	17.625 (3), 8.8348 (16), 11.677 (2)
V (Å^3)	1818.3 (6)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	1.30
Crystal size (mm)	0.63 × 0.32 × 0.19
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Numerical (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.669, 0.831
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	58307, 3969, 3439
R_{int}	0.047
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.642
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.078, 1.07
No. of reflections	3969
No. of parameters	220
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.53, −0.21
Absolute structure	Flack *x* determined using 1487 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.008 (5)

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2013* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009).

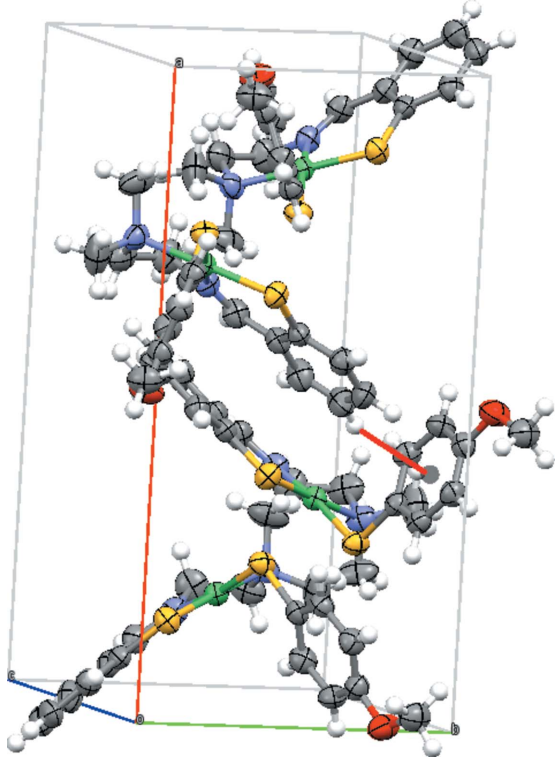


Figure 2
Packing diagram showing the C—H···π interaction as a red line.

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full crystallographic data

IUCrData (2018). **3**, x181167 [https://doi.org/10.1107/S2414314618011677]

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Crystal data

$[Ni(C_{11}H_{15}N_2S)(C_7H_7OS)]$
M_r = 405.20
Orthorhombic, $Pna2_1$
a = 17.625 (3) Å
b = 8.8348 (16) Å
c = 11.677 (2) Å
V = 1818.3 (6) Å^3
Z = 4
$F(000)$ = 848
D_x = 1.480 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9817 reflections
θ = 3.3–24.9°
μ = 1.30 mm^{-1}
T = 150 K
Block, dark brown
0.63 × 0.32 × 0.19 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed X-ray tube
Graphite monochromator
Detector resolution: 5.6 pixels mm^{-1}
φ and ω scans
Absorption correction: numerical (*SADABS*; Bruker, 2013)
T_{min} = 0.669, T_{max} = 0.831
58307 measured reflections
3969 independent reflections
3439 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 27.2°, θ_{min} = 3.7°
h = −22→22
k = −11→11
l = −14→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.078
S = 1.07
3969 reflections
220 parameters
1 restraint
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 0.4445P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Absolute structure: Flack x determined using 1487 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.008 (5)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.31015 (3)	0.79896 (5)	0.67113 (5)	0.04074 (14)
S1	0.34725 (6)	0.60772 (12)	0.57387 (8)	0.0477 (3)
S2	0.25283 (6)	0.87128 (13)	0.51019 (9)	0.0507 (3)
O1	0.47643 (19)	1.1565 (4)	0.1956 (3)	0.0694 (9)
N2	0.3471 (2)	0.7292 (4)	0.8134 (3)	0.0487 (8)
C9	0.4990 (3)	0.2846 (5)	0.6419 (4)	0.0605 (13)
H9	0.5227	0.2064	0.5991	0.073*
C15	0.4217 (3)	1.0920 (5)	0.2640 (4)	0.0516 (10)
N1	0.2763 (2)	0.9859 (4)	0.7559 (3)	0.0551 (9)
C10	0.4461 (3)	0.3780 (5)	0.5902 (4)	0.0557 (11)
H10	0.4337	0.3624	0.5119	0.067*
C16	0.3500 (3)	1.0535 (5)	0.2292 (4)	0.0529 (10)
H16	0.3342	1.0743	0.1530	0.063*
C8	0.5175 (3)	0.3052 (5)	0.7571 (5)	0.0671 (14)
H8	0.5544	0.2427	0.7927	0.080*
C11	0.4104 (2)	0.4958 (4)	0.6511 (4)	0.0452 (9)
C17	0.3007 (2)	0.9844 (5)	0.3052 (4)	0.0473 (10)
H17	0.2516	0.9566	0.2791	0.057*
C18	0.4536 (3)	1.2082 (6)	0.0876 (4)	0.0690 (14)
H18A	0.4341	1.1231	0.0426	0.104*
H18B	0.4971	1.2533	0.0480	0.104*
H18C	0.4137	1.2845	0.0967	0.104*
C14	0.4432 (3)	1.0639 (5)	0.3757 (4)	0.0542 (10)
H14	0.4925	1.0920	0.4006	0.065*
C7	0.4821 (3)	0.4157 (5)	0.8175 (4)	0.0634 (13)
H7	0.4943	0.4283	0.8962	0.076*
C5	0.3928 (3)	0.6212 (5)	0.8410 (4)	0.0529 (10)
H5	0.4046	0.6130	0.9202	0.064*
C6	0.4278 (2)	0.5124 (5)	0.7679 (4)	0.0491 (9)
C12	0.3202 (2)	0.9538 (5)	0.4186 (4)	0.0441 (9)
C4	0.3142 (3)	0.8191 (6)	0.9091 (4)	0.0694 (15)
H4A	0.3458	0.8089	0.9788	0.083*
H4B	0.2622	0.7840	0.9268	0.083*
C1	0.3012 (4)	1.1295 (6)	0.7016 (6)	0.098 (2)
H1A	0.3558	1.1248	0.6861	0.147*
H1B	0.2906	1.2143	0.7533	0.147*
H1C	0.2737	1.1442	0.6295	0.147*
C13	0.3937 (3)	0.9950 (5)	0.4524 (4)	0.0532 (11)
H13	0.4099	0.9756	0.5286	0.064*

C3	0.3131 (3)	0.9795 (7)	0.8693 (5)	0.0723 (16)
H3A	0.2847	1.0429	0.9245	0.087*
H3B	0.3656	1.0188	0.8639	0.087*
C2	0.1937 (3)	0.9892 (9)	0.7675 (5)	0.0809 (17)
H2A	0.1704	0.9943	0.6913	0.121*
H2B	0.1787	1.0783	0.8121	0.121*
H2C	0.1765	0.8973	0.8067	0.121*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0428 (3)	0.0447 (3)	0.0347 (2)	−0.00039 (19)	0.0018 (2)	−0.0028 (2)
S1	0.0554 (7)	0.0521 (6)	0.0356 (5)	0.0060 (5)	−0.0032 (4)	−0.0056 (4)
S2	0.0458 (6)	0.0612 (6)	0.0450 (5)	0.0018 (5)	−0.0011 (4)	0.0041 (5)
O1	0.0545 (19)	0.089 (2)	0.064 (2)	−0.0138 (18)	0.0003 (15)	0.0129 (18)
N2	0.057 (2)	0.054 (2)	0.0354 (17)	−0.0019 (18)	0.0011 (15)	−0.0055 (15)
C9	0.059 (3)	0.047 (2)	0.076 (4)	0.007 (2)	0.005 (2)	−0.001 (2)
C15	0.054 (3)	0.049 (2)	0.052 (2)	−0.003 (2)	0.004 (2)	0.0017 (18)
N1	0.054 (2)	0.060 (2)	0.050 (2)	0.0098 (19)	0.0007 (17)	−0.0142 (17)
C10	0.060 (3)	0.050 (2)	0.056 (3)	−0.001 (2)	0.004 (2)	0.000 (2)
C16	0.056 (3)	0.057 (3)	0.045 (2)	0.000 (2)	−0.0070 (19)	0.0035 (19)
C8	0.067 (3)	0.052 (3)	0.083 (4)	0.001 (2)	−0.016 (3)	0.010 (2)
C11	0.044 (2)	0.0406 (19)	0.051 (2)	−0.0051 (16)	−0.0015 (17)	−0.0006 (18)
C17	0.045 (2)	0.049 (2)	0.047 (2)	0.0055 (18)	−0.0063 (17)	−0.0013 (19)
C18	0.063 (3)	0.090 (4)	0.054 (3)	−0.001 (3)	0.004 (2)	0.015 (3)
C14	0.043 (2)	0.064 (3)	0.055 (2)	−0.006 (2)	−0.0051 (19)	−0.003 (2)
C7	0.079 (4)	0.054 (3)	0.058 (3)	−0.004 (2)	−0.017 (2)	0.009 (2)
C5	0.064 (3)	0.056 (3)	0.039 (2)	−0.003 (2)	−0.0086 (19)	0.0036 (18)
C6	0.054 (3)	0.046 (2)	0.048 (2)	−0.006 (2)	−0.0068 (19)	0.0034 (18)
C12	0.047 (3)	0.038 (2)	0.047 (2)	0.0042 (17)	−0.0009 (18)	−0.0012 (17)
C4	0.091 (4)	0.083 (4)	0.034 (2)	0.006 (3)	0.002 (2)	−0.013 (2)
C1	0.153 (7)	0.048 (3)	0.094 (5)	−0.004 (3)	0.023 (4)	−0.011 (3)
C13	0.055 (3)	0.063 (3)	0.042 (2)	0.003 (2)	−0.0054 (18)	−0.0016 (19)
C3	0.071 (4)	0.085 (4)	0.061 (3)	0.011 (3)	−0.003 (2)	−0.031 (3)
C2	0.056 (3)	0.121 (5)	0.065 (3)	0.021 (3)	0.003 (2)	−0.028 (3)

Geometric parameters (Å, º)

Ni1—S1	2.1383 (11)	C17—H17	0.9500
Ni1—S2	2.2272 (12)	C17—C12	1.394 (6)
Ni1—N2	1.888 (3)	C18—H18A	0.9800
Ni1—N1	2.016 (3)	C18—H18B	0.9800
S1—C11	1.740 (4)	C18—H18C	0.9800
S2—C12	1.756 (5)	C14—H14	0.9500
O1—C15	1.376 (5)	C14—C13	1.389 (6)
O1—C18	1.400 (6)	C7—H7	0.9500
N2—C5	1.289 (6)	C7—C6	1.407 (6)
N2—C4	1.488 (6)	C5—H5	0.9500

C9—H9	0.9500	C5—C6	1.427 (6)
C9—C10	1.383 (7)	C12—C13	1.403 (6)
C9—C8	1.396 (8)	C4—H4A	0.9900
C15—C16	1.370 (6)	C4—H4B	0.9900
C15—C14	1.381 (6)	C4—C3	1.492 (8)
N1—C1	1.484 (7)	C1—H1A	0.9800
N1—C3	1.475 (7)	C1—H1B	0.9800
N1—C2	1.463 (6)	C1—H1C	0.9800
C10—H10	0.9500	C13—H13	0.9500
C10—C11	1.409 (6)	C3—H3A	0.9900
C16—H16	0.9500	C3—H3B	0.9900
C16—C17	1.385 (6)	C2—H2A	0.9800
C8—H8	0.9500	C2—H2B	0.9800
C8—C7	1.357 (7)	C2—H2C	0.9800
C11—C6	1.405 (6)		

S1—Ni1—S2	85.25 (5)	H18B—C18—H18C	109.5
N2—Ni1—S1	95.97 (11)	C15—C14—H14	119.5
N2—Ni1—S2	173.07 (12)	C15—C14—C13	121.0 (4)
N2—Ni1—N1	86.41 (16)	C13—C14—H14	119.5
N1—Ni1—S1	177.11 (12)	C8—C7—H7	118.8
N1—Ni1—S2	92.58 (11)	C8—C7—C6	122.4 (5)
C11—S1—Ni1	111.67 (14)	C6—C7—H7	118.8
C12—S2—Ni1	109.04 (15)	N2—C5—H5	115.9
C15—O1—C18	117.2 (4)	N2—C5—C6	128.3 (4)
C5—N2—Ni1	132.6 (3)	C6—C5—H5	115.9
C5—N2—C4	116.8 (4)	C11—C6—C7	119.0 (4)
C4—N2—Ni1	110.6 (3)	C11—C6—C5	123.8 (4)
C10—C9—H9	120.0	C7—C6—C5	117.1 (4)
C10—C9—C8	120.0 (5)	C17—C12—S2	119.5 (3)
C8—C9—H9	120.0	C17—C12—C13	116.4 (4)
O1—C15—C14	115.5 (4)	C13—C12—S2	124.1 (3)
C16—C15—O1	125.2 (4)	N2—C4—H4A	110.5
C16—C15—C14	119.2 (4)	N2—C4—H4B	110.5
C1—N1—Ni1	113.7 (3)	N2—C4—C3	106.1 (4)
C3—N1—Ni1	106.2 (3)	H4A—C4—H4B	108.7
C3—N1—C1	106.6 (5)	C3—C4—H4A	110.5
C2—N1—Ni1	110.9 (3)	C3—C4—H4B	110.5
C2—N1—C1	108.5 (5)	N1—C1—H1A	109.5
C2—N1—C3	110.9 (4)	N1—C1—H1B	109.5
C9—C10—H10	119.3	N1—C1—H1C	109.5
C9—C10—C11	121.4 (4)	H1A—C1—H1B	109.5
C11—C10—H10	119.3	H1A—C1—H1C	109.5
C15—C16—H16	120.1	H1B—C1—H1C	109.5
C15—C16—C17	119.9 (4)	C14—C13—C12	120.8 (4)
C17—C16—H16	120.1	C14—C13—H13	119.6
C9—C8—H8	120.4	C12—C13—H13	119.6
C7—C8—C9	119.2 (5)	N1—C3—C4	108.8 (4)

C7—C8—H8	120.4	N1—C3—H3A	109.9
C10—C11—S1	116.3 (3)	N1—C3—H3B	109.9
C6—C11—S1	125.7 (3)	C4—C3—H3A	109.9
C6—C11—C10	118.0 (4)	C4—C3—H3B	109.9
C16—C17—H17	118.7	H3A—C3—H3B	108.3
C16—C17—C12	122.7 (4)	N1—C2—H2A	109.5
C12—C17—H17	118.7	N1—C2—H2B	109.5
O1—C18—H18A	109.5	N1—C2—H2C	109.5
O1—C18—H18B	109.5	H2A—C2—H2B	109.5
O1—C18—H18C	109.5	H2A—C2—H2C	109.5
H18A—C18—H18B	109.5	H2B—C2—H2C	109.5
H18A—C18—H18C	109.5		