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{3,3′-[Ethane-1,2-diylbis(methylimino)]-bis(propane-1-thiolato)}nickel(II)

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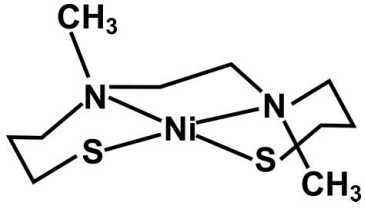
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.020; wR factor = 0.063; data-to-parameter ratio = 21.6.

The title compound, [Ni($C_{10}H_{22}N_2S_2$)], contains a square-planar Ni center coordinated by the tetradentate ligand 3,3′-[ethane-1,2-diylbis(methylimino)]dipropane-1-thiolate. Upon chelation, the N_2S_2 ligand generates one five-membered chelate ring containing the N donors and two six-membered chelate rings in chair conformations, each containing one N and one S donor. The *cis* S donors, which are not directly linked together, form an acute S—Ni—S angle of 82.965 (18)° due to ligand constraints.

Related literature

For related literature, see: Golden *et al.* (2005); Grapperhaus & Darensbourg (1998); Grapperhaus *et al.* (2004); Hatlevik *et al.* (2004); Linck *et al.* (2003); Mills *et al.* (1990); Rao *et al.* (2004); Allen (2002); Cremer & Pople (1975); Li *et al.* (2002).



Experimental

Crystal data

[Ni($C_{10}H_{22}N_2S_2$)]
M_r = 293.13
Monoclinic, $P2_1/c$
a = 8.2290 (16) Å
b = 13.304 (3) Å
c = 11.691 (2) Å
β = 92.931 (3)°
V = 1278.2 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.82 mm^{-1}
T = 100 (2) K
0.26 × 0.15 × 0.13 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.676, T_{max} = 0.779
10969 measured reflections
2986 independent reflections
2699 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.063
S = 1.02
2986 reflections
138 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2001).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2056).

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supplementary materials

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{3,3'-[Ethane-1,2-diylbis(methylimino)]bis(propane-1-thiolato)}nickel(II)

C. A. Grapperhaus, M. G. O'Toole and M. S. Mashuta

Comment

Square planar N_2S_2 nickel-thiolate complexes have been extensively studied due to their rich sulfur-based reactivity and their relevance to biological systems (Golden *et al.*, 2005; Grapperhaus & Darensbourg, 1998; Grapperhaus *et al.*, 2004; Rao *et al.*, 2004). To our knowledge the title compound represents the first structurally characterized mononuclear square planar N_2S_2 nickel thiolate complex with a three-carbon aliphatic linker between the nitrogen and sulfur donors. A diamido N_2S_2 nickel thiolate complex with a three-carbon linker has been reported as the tetraethylammonium salt (Linck *et al.*, 2003; CSD refcode IKEPIX) and its hydrate (Hatlevik *et al.*, 2004; CSD refcode WARJUV). The *x*-ray structure of a complex related to the title compound with an aliphatic two-carbon linker between the nitrogen and sulfur donors has also been reported (Grapperhaus *et al.*, 2004; CSD refcode AYIDOB).

The nickel atom of the title compound sits 0.018 (1) Å from the N_2S_2 ligand plane, which has a mean deviation of 0.047 (1) Å. Chelation of the ligand generates two nickel-containing six-membered rings and one five-membered ring. The five-membered ring containing N1 and N2 is best described as twisted, φ = 266.14 (16)° (Cremer & Pople, 1975). The six-membered rings containing N1/S1 and N2/S2 are in chair conformations with θ values of 171.52 (13) and 176.38 (12)°, respectively (Cremer & Pople 1975).

The six-membered chelate rings result in obtuse N—Ni—S bond angles. The N1—Ni—S1 and N2—Ni—S2 bond angles are 94.82 (4)° and 94.97 (4)°, respectively. In the related complex (Grapperhaus *et al.*, 2004; AYIDOB) with five-membered N—Ni—S chelates the angles are slightly accute with values of 89.87 (9)° and 88.63 (9)°. A search of the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002), yielded 27 square planar mononuclear N_2S_2Ni thiolate complexes that contain five-membered Ni—N—C—C—S chelate rings with N—Ni—S bond angles between 87.61 (7)° (Rao *et al.*, 2004; CSD refcode LAHDAA) and 91.4 (2)° (Mills *et al.*, 1990; CSD refcode VIGBES). The N1—Ni1—N2 bond angle of the title compound of 87.34 (5)° is similar to the value of 88.11 (12)° in the related complex (Grapperhaus *et al.*, 2004; AYIDOB). As a result of these bond angles and the planar nature of the donor atoms, the S1—Ni—S2 bond angle is acute with a value of 82.965 (18)°. Acute S—Ni—S bond angles, 83.40 (4)° and 84.85°, are also observed in the related structures (Linck *et al.*, 2003; IKEPIX & Hatlevik *et al.*, 2003; WARJUV) with a three-carbon linker between nitrogen and sulfur. In the related system (Grapperhaus *et al.*, 2004; AYIDOB) with all five-membered chelate rings, the corresponding S—Ni—S bond angle has a value of 95.16 (4)°.

The bond distances between the donor atoms and nickel are within expected ranges. The Ni—N bond distances of 2.0025 (13) and 2.0094 (13) Å are slightly longer than in the related system, 1.930 (3) and 1.950 (3) Å, (Grapperhaus *et al.*, 2004; AYIDOB). The Ni—S bond distances of 2.1895 (6) and 2.1842 (5) Å display the same trend as compared to AYIDOB, 2.1612 (10) and 2.1612 (10) Å (Grapperhaus *et al.*, 2004).

Experimental

The ligand, 3,3'-[ethane-1,2-diylbis(methylimino)]dipropane-1-thiol, was prepared as the HCl salt from *N*,*N*′-dimethylethylenediamine and {[(3-bromopropyl)thio]methyl}benzene by modification of analagous routes (Li *et al.*, 2002). To a degassed aqueous solution (10 ml) of NaOH (0.69 g, 17 mmol) was added the ligand·2HCl (1.3 g, 4.2 mmol) in 15 ml H_2O. To the resulting suspension was dropwise added $NiCl_2{\cdot}6H_2O$ (1.0 g, 4.2 mmol) *via* cannula. Following addition, column separation (acetonitrile/alumina) yielded the title compound (0.74 g, 60% yield). Crystals suitable for X-ray analysis were obtained upon slow diffusion of diethylether into a methanolic solution of the title compound at 275 K (2°C).

Refinement

Hydrogen atoms were placed in their geometrically generated positions and refined as a riding model. Methylene H's were included as fixed contributions with U(H) = 1.2 × U_{eq} (attached C atom) while methyl groups were allowed to ride on the attached C atom (the torsion angle which defines its orientation was allowed to refine), and these atoms were assigned U(H) = 1.5 *x* U_{eq}. The highest peak and deepest trough are located 0.74 Å from C7 and 0.84 Å from Ni1, respectively.

Figures

Fig. 1. *ORTEP-3* (Farrugia, 1997) drawing of the title compound with atom labels showing 30% probability displacement ellipsoids for non-H atoms.

{3,3'-[ethane-1,2-diylbis(methylimino)]dipropane-1-thiolato}nickel(II)

Crystal data

$[Ni(C_{10}H_{22}N_2S_2)]$	F_{000} = 624
M_r = 293.13	D_x = 1.523 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 7691 reflections
a = 8.2290 (16) Å	θ = 2.5–28.1°
b = 13.304 (3) Å	μ = 1.82 mm^{-1}
c = 11.691 (2) Å	*T* = 100 (2) K
β = 92.931 (3)°	Prism, dark purple
V = 1278.2 (4) Å^3	0.26 × 0.15 × 0.13 mm
Z = 4	

Data collection

Bruker SMART APEX CCD diffractometer	2986 independent reflections
Radiation source: fine-focus sealed tube	2699 reflections with $I > 2\sigma(I)$

Monochromator: graphite	R_{int} = 0.025
T = 100(2) K	θ_{max} = 28.1º
ω scans	θ_{min} = 2.3º
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	h = −10→10
T_{min} = 0.676, T_{max} = 0.779	k = −17→17
10969 measured reflections	l = −15→15

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.020	H-atom parameters constrained
$wR(F^2)$ = 0.063	$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 0.7704P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.02	$(\Delta/\sigma)_{max}$ = 0.001
2986 reflections	$\Delta\rho_{max}$ = 0.38 e Å^{-3}
138 parameters	$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. Data were collected with a Bruker *SMART APEX* CCD-based diffractometer using ω-scans of width 0.3° and 30 s duration at a crystal-to-detector distance of 4.908 cm. Intensity decay over the course of the data collection was evaluated by recollecting the first 50 frames of data at the end of the experiment. No significant decay was noted.

Absorption correction was based upon symmetry equivalent and repeated intensity measurements using the program *SADABS* (Sheldrick, 2001).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.77639 (2)	0.225962 (14)	0.772505 (15)	0.01001 (7)
S1	0.67345 (5)	0.37770 (3)	0.76415 (3)	0.01477 (10)
S2	0.95522 (5)	0.29130 (3)	0.66245 (3)	0.01583 (10)
N1	0.59970 (15)	0.16883 (10)	0.86457 (11)	0.0126 (3)
N2	0.88108 (15)	0.08952 (9)	0.78048 (11)	0.0120 (2)
C1	0.58399 (19)	0.40260 (12)	0.90067 (13)	0.0157 (3)
H1A	0.6724	0.4048	0.9613	0.019*
H1B	0.5325	0.4699	0.8970	0.019*
C2	0.45811 (19)	0.32662 (13)	0.93493 (14)	0.0171 (3)
H2A	0.3743	0.3194	0.8716	0.021*
H2B	0.4038	0.3521	1.0028	0.021*
C3	0.5312 (2)	0.22418 (12)	0.96266 (14)	0.0170 (3)
H3A	0.6190	0.2329	1.0230	0.020*
H3B	0.4461	0.1817	0.9951	0.020*

C4	0.6633 (2)	0.07218 (12)	0.91345 (14)	0.0186 (3)
H4A	0.5715	0.0293	0.9352	0.022*
H4B	0.7333	0.0856	0.9831	0.022*
C5	0.7599 (2)	0.01856 (12)	0.82638 (14)	0.0169 (3)
H5A	0.8168	−0.0398	0.8624	0.020*
H5B	0.6861	−0.0064	0.7631	0.020*
C6	0.93557 (19)	0.04207 (12)	0.67292 (13)	0.0144 (3)
H6A	0.8404	0.0368	0.6179	0.017*
H6B	0.9728	−0.0271	0.6911	0.017*
C7	1.07084 (19)	0.09666 (12)	0.61458 (13)	0.0153 (3)
H7A	1.1618	0.1089	0.6716	0.018*
H7B	1.1119	0.0526	0.5542	0.018*
C8	1.0188 (2)	0.19613 (12)	0.56117 (13)	0.0164 (3)
H8A	0.9275	0.1836	0.5045	0.020*
H8B	1.1105	0.2234	0.5192	0.020*
C9	0.46702 (19)	0.14717 (13)	0.77698 (15)	0.0186 (3)
H9A	0.5119	0.1118	0.7122	0.028*
H9B	0.4173	0.2104	0.7502	0.028*
H9C	0.3844	0.1050	0.8108	0.028*
C10	1.02212 (19)	0.09729 (12)	0.86542 (13)	0.0158 (3)
H10A	1.0819	0.0335	0.8681	0.024*
H10B	0.9826	0.1120	0.9413	0.024*
H10C	1.0945	0.1514	0.8427	0.024*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01079 (11)	0.00845 (11)	0.01096 (11)	0.00005 (7)	0.00226 (7)	0.00056 (7)
S1	0.0188 (2)	0.01017 (18)	0.01574 (18)	0.00216 (14)	0.00438 (15)	0.00106 (14)
S2	0.0183 (2)	0.01159 (18)	0.01839 (19)	−0.00162 (14)	0.00800 (15)	0.00055 (14)
N1	0.0120 (6)	0.0119 (6)	0.0141 (6)	0.0005 (5)	0.0016 (5)	0.0011 (5)
N2	0.0125 (6)	0.0112 (6)	0.0125 (6)	−0.0003 (5)	0.0014 (5)	0.0003 (5)
C1	0.0175 (8)	0.0137 (7)	0.0160 (7)	0.0025 (6)	0.0010 (6)	−0.0032 (6)
C2	0.0165 (8)	0.0185 (8)	0.0166 (7)	0.0038 (6)	0.0046 (6)	−0.0019 (6)
C3	0.0196 (8)	0.0178 (8)	0.0143 (7)	0.0013 (6)	0.0071 (6)	0.0017 (6)
C4	0.0195 (8)	0.0146 (8)	0.0223 (8)	0.0020 (6)	0.0080 (6)	0.0080 (6)
C5	0.0170 (8)	0.0109 (7)	0.0232 (8)	0.0004 (6)	0.0056 (6)	0.0037 (6)
C6	0.0175 (7)	0.0121 (7)	0.0136 (7)	0.0016 (6)	0.0004 (6)	−0.0030 (6)
C7	0.0162 (7)	0.0168 (8)	0.0130 (7)	0.0030 (6)	0.0030 (6)	−0.0016 (6)
C8	0.0180 (8)	0.0173 (8)	0.0142 (7)	0.0012 (6)	0.0050 (6)	0.0001 (6)
C9	0.0149 (8)	0.0169 (8)	0.0239 (8)	−0.0039 (6)	−0.0006 (6)	−0.0019 (6)
C10	0.0166 (8)	0.0182 (8)	0.0125 (7)	0.0032 (6)	−0.0015 (6)	−0.0011 (6)

Geometric parameters (Å, °)

Ni1—N1	2.0025 (13)	C4—C5	1.503 (2)
Ni1—N2	2.0094 (13)	C4—H4A	0.9900
Ni1—S2	2.1842 (5)	C4—H4B	0.9900
Ni1—S1	2.1895 (6)	C5—H5A	0.9900

S1—C1	1.8219 (16)	C5—H5B	0.9900
S2—C8	1.8281 (16)	C6—C7	1.520 (2)
N1—C9	1.486 (2)	C6—H6A	0.9900
N1—C4	1.491 (2)	C6—H6B	0.9900
N1—C3	1.497 (2)	C7—C8	1.516 (2)
N2—C10	1.4920 (19)	C7—H7A	0.9900
N2—C5	1.493 (2)	C7—H7B	0.9900
N2—C6	1.4961 (19)	C8—H8A	0.9900
C1—C2	1.516 (2)	C8—H8B	0.9900
C1—H1A	0.9900	C9—H9A	0.9800
C1—H1B	0.9900	C9—H9B	0.9800
C2—C3	1.518 (2)	C9—H9C	0.9800
C2—H2A	0.9900	C10—H10A	0.9800
C2—H2B	0.9900	C10—H10B	0.9800
C3—H3A	0.9900	C10—H10C	0.9800
C3—H3B	0.9900		
N1—Ni1—N2	87.34 (5)	C5—C4—H4A	109.7
N1—Ni1—S2	175.77 (4)	N1—C4—H4B	109.7
N2—Ni1—S2	94.97 (4)	C5—C4—H4B	109.7
N1—Ni1—S1	94.82 (4)	H4A—C4—H4B	108.2
N2—Ni1—S1	177.38 (4)	N2—C5—C4	109.24 (13)
S2—Ni1—S1	82.965 (18)	N2—C5—H5A	109.8
C1—S1—Ni1	107.53 (5)	C4—C5—H5A	109.8
C8—S2—Ni1	109.24 (6)	N2—C5—H5B	109.8
C9—N1—C4	109.14 (13)	C4—C5—H5B	109.8
C9—N1—C3	109.34 (12)	H5A—C5—H5B	108.3
C4—N1—C3	105.62 (12)	N2—C6—C7	115.69 (13)
C9—N1—Ni1	103.37 (10)	N2—C6—H6A	108.4
C4—N1—Ni1	106.44 (9)	C7—C6—H6A	108.4
C3—N1—Ni1	122.49 (10)	N2—C6—H6B	108.4
C10—N2—C5	108.41 (12)	C7—C6—H6B	108.4
C10—N2—C6	109.40 (12)	H6A—C6—H6B	107.4
C5—N2—C6	105.65 (12)	C8—C7—C6	113.83 (13)
C10—N2—Ni1	106.58 (9)	C8—C7—H7A	108.8
C5—N2—Ni1	107.17 (9)	C6—C7—H7A	108.8
C6—N2—Ni1	119.23 (9)	C8—C7—H7B	108.8
C2—C1—S1	114.99 (11)	C6—C7—H7B	108.8
C2—C1—H1A	108.5	H7A—C7—H7B	107.7
S1—C1—H1A	108.5	C7—C8—S2	114.97 (11)
C2—C1—H1B	108.5	C7—C8—H8A	108.5
S1—C1—H1B	108.5	S2—C8—H8A	108.5
H1A—C1—H1B	107.5	C7—C8—H8B	108.5
C1—C2—C3	112.73 (13)	S2—C8—H8B	108.5
C1—C2—H2A	109.0	H8A—C8—H8B	107.5
C3—C2—H2A	109.0	N1—C9—H9A	109.5
C1—C2—H2B	109.0	N1—C9—H9B	109.5
C3—C2—H2B	109.0	H9A—C9—H9B	109.5
H2A—C2—H2B	107.8	N1—C9—H9C	109.5
N1—C3—C2	116.02 (13)	H9A—C9—H9C	109.5

N1—C3—H3A	108.3	H9B—C9—H9C	109.5
C2—C3—H3A	108.3	N2—C10—H10A	109.5
N1—C3—H3B	108.3	N2—C10—H10B	109.5
C2—C3—H3B	108.3	H10A—C10—H10B	109.5
H3A—C3—H3B	107.4	N2—C10—H10C	109.5
N1—C4—C5	109.71 (13)	H10A—C10—H10C	109.5
N1—C4—H4A	109.7	H10B—C10—H10C	109.5
N1—Ni1—S1—C1	36.46 (7)	C9—N1—C3—C2	−62.81 (17)
S2—Ni1—S1—C1	−147.17 (6)	C4—N1—C3—C2	179.87 (13)
N2—Ni1—S2—C8	36.06 (7)	Ni1—N1—C3—C2	58.12 (18)
S1—Ni1—S2—C8	−145.57 (6)	C1—C2—C3—N1	−66.32 (18)
N2—Ni1—N1—C9	−99.81 (10)	C9—N1—C4—C5	72.07 (16)
S1—Ni1—N1—C9	81.68 (9)	C3—N1—C4—C5	−170.48 (13)
N2—Ni1—N1—C4	15.12 (10)	Ni1—N1—C4—C5	−38.88 (15)
S1—Ni1—N1—C4	−163.39 (9)	C10—N2—C5—C4	79.24 (15)
N2—Ni1—N1—C3	136.49 (12)	C6—N2—C5—C4	−163.58 (13)
S1—Ni1—N1—C3	−42.02 (11)	Ni1—N2—C5—C4	−35.45 (15)
N1—Ni1—N2—C10	−104.72 (10)	N1—C4—C5—N2	50.42 (17)
S2—Ni1—N2—C10	78.83 (9)	C10—N2—C6—C7	−58.73 (16)
N1—Ni1—N2—C5	11.18 (10)	C5—N2—C6—C7	−175.24 (13)
S2—Ni1—N2—C5	−165.26 (9)	Ni1—N2—C6—C7	64.21 (15)
N1—Ni1—N2—C6	130.96 (11)	N2—C6—C7—C8	−69.57 (17)
S2—Ni1—N2—C6	−45.49 (10)	C6—C7—C8—S2	63.46 (16)
Ni1—S1—C1—C2	−55.79 (12)	Ni1—S2—C8—C7	−50.50 (13)
S1—C1—C2—C3	68.03 (16)		

Fig. 1