

Bis[4-methyl-2-(4-methylphenyl-diazenyl)phenolato- κ^2 N,O]nickel(II)

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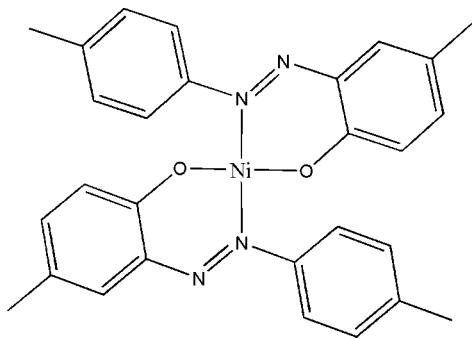
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.038; wR factor = 0.099; data-to-parameter ratio = 13.1.

In the crystal structure of the title compound, $[\text{Ni}(\text{C}_{14}\text{H}_{13}\text{N}_2\text{O})_2]$, the Ni^{II} ion is located on an inversion center and is coordinated by two 4-methyl-2-(4-methylphenyl-diazenyl)phenolate anions in a slightly distorted square-planar geometry. Within the anion, the two benzene rings are twisted from each other with a dihedral angle of $45.97(12)^\circ$. No hydrogen bonding is found in the crystal structure.

Related literature

For general background, see: Frey (2005).



Experimental

Crystal data

$[\text{Ni}(\text{C}_{14}\text{H}_{13}\text{N}_2\text{O})_2]$
 $M_r = 509.24$
 Monoclinic, $P2_1/c$
 $a = 9.5211(10)$ Å
 $b = 10.8162(11)$ Å
 $c = 12.2647(13)$ Å
 $\beta = 105.367(2)^\circ$

$V = 1217.9(2)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.83$ mm⁻¹
 $T = 293$ K
 $0.15 \times 0.15 \times 0.10$ mm

Data collection

Bruker SMART APEX
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.885$, $T_{\text{max}} = 0.920$

7063 measured reflections
 2775 independent reflections
 1890 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.099$
 $S = 1.02$
 2775 reflections

212 parameters
 All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 0.24$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³

Table 1

Selected bond lengths (Å).

Ni—O	1.8118 (16)	Ni—N1	1.8988 (18)
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Data collection: *APEX2* (Bruker, 2008); cell refinement: *S SAINT* (Bruker, 2008); data reduction: *S SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2508).

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supplementary materials

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Bis[4-methyl-2-(4-methylphenyldiazenyl)phenolato- κ^2N,O]nickel(II)

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Comment

Nickel hydride complexes are one of the most valuable catalysts and intermediates. Frey (2005) has successfully synthesized a new type of nickel hydride $\text{Ni}(\text{H})(\textit{ortho}\text{-S-C}_6\text{H}_4\text{PPh}_2)(\text{PMe}_3)_2$. In the previous work in our lab, we have reported similar reactions between nickel or cobalt hydrides and phenol derivatives. So the reaction between $\text{Ni}(\text{H})(\textit{ortho}\text{-S-C}_6\text{H}_4\text{PPh}_2)(\text{PMe}_3)_2$ and phenol derivatives was carried out to explore the acidity of the hydrogen ligand. The title compound, as an unexpected compound, was synthesized.

The molecular structure is shown in Fig. 1. The Ni^{II} ion is located in an inversion center and coordinated by two 2-(4'-methylphenylazo)-4-methylphenol anions in a square-planar geometry (Table 1). No hydrogen bonding is found in the crystal structure.

Experimental

$\text{Ni}(\text{H})(\textit{ortho}\text{-S-C}_6\text{H}_4\text{PPh}_2)(\text{PMe}_3)_2$ (1.19 g, 2.35 mmol) and 2-(4'-methylphenylazo)-4-methylphenol (0.54 g, 2.38 mmol) was mixed in $-80\text{ }^\circ\text{C}$. The mixture was stirred between $-20\text{ }^\circ\text{C}$ to $0\text{ }^\circ\text{C}$ for 18 h and a red solution was formed. Green residue was filtered off, then the solvent was removed in vacuum. The residue was extracted with pentane, and then diethyl ether. The extractions were kept in $-20\text{ }^\circ\text{C}$. The title compound was obtained from the pentane extractions as green crystals for X-ray diffraction.

Refinement

The H atoms were geometrically placed and refined isotropically.

Figures

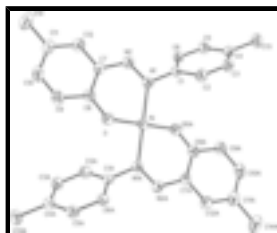


Fig. 1. View of the title compound, showing 25% displacement ellipsoids. H atoms were omitted. Symmetry code: (A) $2 - x, 2 - y, -z$.

Bis[4-methyl-2-(4-methylphenyldiazenyl)phenolato- κ^2N,O]nickel(II)

Crystal data

[Ni(C ₁₄ H ₁₃ N ₂ O) ₂]	$F_{000} = 532$
$M_r = 509.24$	$D_x = 1.389 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
Hall symbol: -P 2ybc	$\lambda = 0.71073 \text{ \AA}$
$a = 9.5211 (10) \text{ \AA}$	Cell parameters from 1666 reflections
$b = 10.8162 (11) \text{ \AA}$	$\theta = 2.6\text{--}23.4^\circ$
$c = 12.2647 (13) \text{ \AA}$	$\mu = 0.83 \text{ mm}^{-1}$
$\beta = 105.367 (2)^\circ$	$T = 293 \text{ K}$
$V = 1217.9 (2) \text{ \AA}^3$	Block, green
$Z = 2$	$0.15 \times 0.15 \times 0.10 \text{ mm}$

Data collection

Bruker SMART APEX diffractometer	2775 independent reflections
Radiation source: fine-focus sealed tube	1890 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.032$
$T = 293 \text{ K}$	$\theta_{\text{max}} = 27.6^\circ$
ω scans	$\theta_{\text{min}} = 2.2^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -12 \rightarrow 11$
$T_{\text{min}} = 0.885$, $T_{\text{max}} = 0.920$	$k = -13 \rightarrow 13$
7063 measured reflections	$l = -9 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	All H-atom parameters refined
$wR(F^2) = 0.099$	$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.1292P]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
2775 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
212 parameters	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
	Extinction correction: none

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni	1.0000	1.0000	0.0000	0.04172 (15)
N1	0.96662 (19)	0.83618 (16)	0.04286 (15)	0.0412 (4)
N2	1.02859 (19)	0.77982 (17)	0.13462 (15)	0.0448 (5)
O	1.0688 (2)	1.04670 (16)	0.14634 (14)	0.0552 (5)
C7	1.1204 (2)	0.8429 (2)	0.22272 (18)	0.0428 (5)
C1	0.8685 (2)	0.75494 (19)	-0.03615 (18)	0.0402 (5)
C6	0.9169 (3)	0.6442 (2)	-0.0673 (2)	0.0440 (5)
C4	0.6804 (3)	0.6040 (2)	-0.1919 (2)	0.0474 (6)
C5	0.8231 (3)	0.5700 (2)	-0.1455 (2)	0.0480 (6)
C2	0.7255 (3)	0.7908 (2)	-0.0813 (2)	0.0527 (6)
C12	1.1914 (3)	0.7700 (3)	0.3162 (2)	0.0524 (6)
C8	1.1345 (3)	0.9729 (2)	0.2279 (2)	0.0462 (6)
C3	0.6333 (3)	0.7146 (2)	-0.1575 (2)	0.0559 (7)
C9	1.2225 (3)	1.0238 (3)	0.3292 (2)	0.0571 (7)
C11	1.2798 (3)	0.8206 (3)	0.4119 (2)	0.0560 (7)
C10	1.2937 (3)	0.9492 (3)	0.4156 (2)	0.0595 (7)
C13	0.5765 (5)	0.5215 (4)	-0.2756 (4)	0.0741 (10)
C14	1.3546 (5)	0.7421 (5)	0.5127 (3)	0.0827 (11)
H10	1.347 (3)	0.987 (2)	0.479 (2)	0.050 (7)*
H5	0.862 (3)	0.494 (2)	-0.165 (2)	0.048 (7)*
H6	1.014 (2)	0.624 (2)	-0.0350 (18)	0.047 (6)*
H12	1.173 (3)	0.686 (2)	0.311 (2)	0.061 (8)*
H3	0.541 (3)	0.737 (2)	-0.185 (2)	0.066 (8)*
H9	1.232 (3)	1.111 (3)	0.333 (2)	0.066 (8)*
H13B	0.594 (4)	0.440 (4)	-0.253 (3)	0.127 (16)*
H13A	0.603 (5)	0.522 (4)	-0.338 (4)	0.127 (19)*
H2	0.689 (3)	0.867 (3)	-0.057 (2)	0.076 (8)*
H13C	0.491 (5)	0.541 (3)	-0.290 (3)	0.106 (15)*
H14C	1.454 (4)	0.752 (4)	0.527 (3)	0.111 (13)*
H14A	1.318 (4)	0.761 (4)	0.576 (3)	0.119 (14)*
H14B	1.341 (5)	0.663 (5)	0.504 (4)	0.16 (2)*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni	0.0496 (3)	0.0325 (2)	0.0400 (2)	-0.00195 (18)	0.00673 (18)	-0.00217 (18)
N1	0.0429 (10)	0.0346 (10)	0.0423 (10)	-0.0008 (8)	0.0046 (8)	-0.0015 (8)
N2	0.0455 (11)	0.0419 (11)	0.0439 (11)	0.0006 (8)	0.0062 (9)	0.0001 (9)
O	0.0800 (13)	0.0372 (8)	0.0422 (9)	-0.0034 (8)	0.0052 (9)	-0.0025 (8)
C7	0.0422 (12)	0.0466 (13)	0.0379 (12)	0.0001 (10)	0.0076 (10)	-0.0020 (10)
C1	0.0418 (13)	0.0339 (11)	0.0414 (12)	-0.0036 (9)	0.0047 (10)	0.0028 (9)
C6	0.0388 (13)	0.0380 (12)	0.0513 (14)	0.0008 (10)	0.0050 (10)	0.0000 (11)
C4	0.0496 (14)	0.0398 (13)	0.0466 (13)	-0.0069 (10)	0.0020 (11)	0.0021 (11)
C5	0.0507 (14)	0.0354 (13)	0.0547 (15)	0.0018 (11)	0.0085 (12)	-0.0051 (11)
C2	0.0449 (14)	0.0416 (14)	0.0648 (16)	0.0060 (11)	0.0029 (12)	-0.0021 (12)
C12	0.0568 (16)	0.0512 (16)	0.0472 (14)	0.0059 (13)	0.0103 (12)	0.0003 (12)
C8	0.0476 (14)	0.0508 (15)	0.0414 (13)	-0.0060 (10)	0.0142 (11)	-0.0070 (10)
C3	0.0388 (14)	0.0512 (15)	0.0672 (17)	0.0062 (12)	-0.0045 (12)	0.0028 (13)
C9	0.0657 (17)	0.0606 (18)	0.0435 (14)	-0.0125 (13)	0.0119 (13)	-0.0114 (12)
C11	0.0481 (14)	0.0743 (19)	0.0431 (14)	0.0056 (13)	0.0077 (11)	-0.0004 (13)
C10	0.0530 (16)	0.083 (2)	0.0392 (14)	-0.0108 (15)	0.0070 (12)	-0.0122 (14)
C13	0.067 (2)	0.061 (2)	0.075 (2)	-0.0100 (17)	-0.0148 (19)	-0.0089 (17)
C14	0.074 (3)	0.112 (4)	0.0518 (19)	0.013 (2)	-0.0005 (17)	0.013 (2)

Geometric parameters (\AA , $^\circ$)

Ni—O ⁱ	1.8118 (16)	C2—C3	1.374 (3)
Ni—O	1.8118 (16)	C2—H2	0.98 (3)
Ni—N1	1.8988 (18)	C12—C11	1.364 (3)
Ni—N1 ⁱ	1.8988 (18)	C12—H12	0.92 (2)
N1—N2	1.278 (2)	C8—C9	1.413 (3)
N1—C1	1.451 (3)	C3—H3	0.89 (2)
N2—C7	1.377 (3)	C9—C10	1.361 (4)
O—C8	1.303 (3)	C9—H9	0.95 (3)
C7—C12	1.408 (3)	C11—C10	1.397 (4)
C7—C8	1.412 (3)	C11—C14	1.513 (4)
C1—C6	1.373 (3)	C10—H10	0.91 (3)
C1—C2	1.382 (3)	C13—H13B	0.92 (4)
C6—C5	1.381 (3)	C13—H13A	0.87 (5)
C6—H6	0.93 (2)	C13—H13C	0.81 (4)
C4—C5	1.377 (3)	C14—H14C	0.92 (4)
C4—C3	1.382 (3)	C14—H14A	0.95 (4)
C4—C13	1.514 (4)	C14—H14B	0.86 (5)
C5—H5	0.95 (2)		
O ⁱ —Ni—O	180.000 (1)	C11—C12—H12	121.2 (16)
O ⁱ —Ni—N1	88.33 (8)	C7—C12—H12	116.8 (16)
O—Ni—N1	91.67 (8)	O—C8—C7	123.7 (2)
O ⁱ —Ni—N1 ⁱ	91.67 (8)	O—C8—C9	119.2 (2)

O—Ni—N1 ⁱ	88.33 (8)	C7—C8—C9	117.0 (2)
N1—Ni—N1 ⁱ	180.0	C2—C3—C4	121.8 (2)
N2—N1—C1	111.38 (17)	C2—C3—H3	119.1 (17)
N2—N1—Ni	128.07 (14)	C4—C3—H3	119.2 (17)
C1—N1—Ni	120.38 (13)	C10—C9—C8	120.7 (3)
N1—N2—C7	120.24 (19)	C10—C9—H9	122.2 (16)
C8—O—Ni	124.29 (15)	C8—C9—H9	117.0 (16)
N2—C7—C12	115.5 (2)	C12—C11—C10	117.3 (2)
N2—C7—C8	124.1 (2)	C12—C11—C14	121.8 (3)
C12—C7—C8	120.1 (2)	C10—C11—C14	120.8 (3)
C6—C1—C2	120.0 (2)	C9—C10—C11	122.8 (3)
C6—C1—N1	120.67 (19)	C9—C10—H10	117.0 (15)
C2—C1—N1	119.3 (2)	C11—C10—H10	120.2 (14)
C1—C6—C5	119.8 (2)	C4—C13—H13B	109 (2)
C1—C6—H6	117.3 (15)	C4—C13—H13A	108 (3)
C5—C6—H6	122.9 (15)	H13B—C13—H13A	101 (3)
C5—C4—C3	118.0 (2)	C4—C13—H13C	115 (3)
C5—C4—C13	121.3 (3)	H13B—C13—H13C	114 (3)
C3—C4—C13	120.8 (3)	H13A—C13—H13C	108 (4)
C4—C5—C6	121.2 (2)	C11—C14—H14C	109 (2)
C4—C5—H5	121.9 (15)	C11—C14—H14A	111 (2)
C6—C5—H5	116.9 (15)	H14C—C14—H14A	113 (3)
C3—C2—C1	119.2 (2)	C11—C14—H14B	115 (3)
C3—C2—H2	120.0 (15)	H14C—C14—H14B	104 (4)
C1—C2—H2	120.8 (15)	H14A—C14—H14B	104 (4)
C11—C12—C7	122.0 (3)		

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

Fig. 1

