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{4,4′,6,6′-Tetrabromo-2,2′-[2,2-dimethylpropane-1,3-diylbis(nitrilomethanylylidene)]diphenolato}nickel(II)

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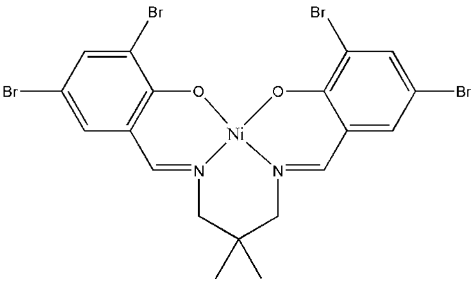
Key indicators: single-crystal X-ray study; *T* = 296 K; mean σ(C–C) = 0.005 Å; *R* factor = 0.033; *wR* factor = 0.075; data-to-parameter ratio = 16.2.

The asymmetric unit of the title compound, [Ni($C_{19}H_{16}Br_4N_2O_2$)], comprises half of a Schiff base complex. The geometry around the Ni^{II} atom, located on a twofold rotation axis, is distorted square-planar, which is supported by the N_2O_2 donor atoms of the coordinated ligand. The dihedral angle between the substituted benzene rings is 23.19 (17)°. In the crystal, a short intermolecular Br···Br [3.6475 (7) Å] interaction is present.

Related literature

For applications of Schiff bases in coordination chemistry, see: Granovski *et al.* (1993); Blower (1998). For related structures, see: Ghaemi *et al.* (2011); Kargar *et al.* (2012). For van der Waals radii, see: Bondi (1964). For standard values of bond lengths, see: Allen *et al.* (1987).



Experimental

Crystal data

[Ni($C_{19}H_{16}Br_4N_2O_2$)]
M_r = 682.69
Orthorhombic, *Pbcn*
a = 16.1125 (11) Å
b = 15.4789 (12) Å
c = 8.4734 (5) Å
V = 2113.3 (3) $Å^3$
Z = 4
Mo *Kα* radiation
μ = 8.50 mm^{-1}
T = 296 K
0.25 × 0.18 × 0.09 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.694, T_{max} = 0.871
16236 measured reflections
2086 independent reflections
1574 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.075
S = 1.05
2086 reflections
129 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.52 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.78 e $Å^{-3}$

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2421).

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supplementary materials

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{4,4′,6,6′-Tetrabromo-2,2′-[2,2-dimethylpropane-1,3-diylbis(nitrilomethanylylidene)]diphenolato}nickel(II)

Hadi Kargar, Reza Kia and Muhammad Nawaz Tahir

Comment

Schiff base complexes are one of the most important stereochemical models in transition metal coordination chemistry, with ease of preparation and structural variations (Granovski *et al.*, 1993; Blower *et al.*, (1998). In continuation of our work on the crystal structures of Schiff base metal complexes (Kargar *et al.*, 2012; Ghaemi *et al.*, 2011), we report herein on the crystal structure of the title compound.

The asymmetric unit of the title compound, Fig. 1, comprises half of a Schiff base complex. The nickel(II) atom and the central bridging C atom, C9, are located on a 2-fold rotation axis. The bond lengths (Allen *et al.*, 1987) and angles are within normal ranges and are comparable to those reported for related structures (Kargar *et al.*, 2012; Ghaemi *et al.*, 2011).

The geometry around Ni^{II} is a distorted square-planar which is supported by the N_2O_2 donor atoms of the coordinated Schiff base ligand. The dihedral angle between the substituted benzene rings is 23.19 (17)°.

In the crystal (Fig. 2), a short intermolecular $Br1\cdots Br2^{i}$ [3.6475 (7)Å; symmetry code: (i) = $-x+1/2$, $-y-1/2$, $z+1/2$] interaction is present, which is shorter than the sum of the van der Waals radius of Br atoms [3.70 Å; Bondi, 1964].

Experimental

The title compound was synthesized by adding 3,5-dibromo-salicylaldehyde-2,2-dimethyl-1, 3-propanediamine (2 mmol) to a solution of $NiCl_2$. $6H_2O$ (2.1 mmol) in ethanol (30 ml). The mixture was refluxed with stirring for half an hour. The resultant solution was filtered. Dark-green single crystals of the title compound suitable for *X*-ray structure determination were recrystallized from ethanol by slow evaporation of the solvents at room temperature over several days.

Refinement

The H-atoms were included in calculated positions and treated as riding atoms: C—H = 0.93, 0.96 and 0.97 Å for CH, CH_3 and CH_2 H-atoms, respectively, with U_{iso} (H) = k x U_{eq}(C), where k = 1.5 for CH_3 H-atoms, and = 1.2 for other H-atoms.

Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

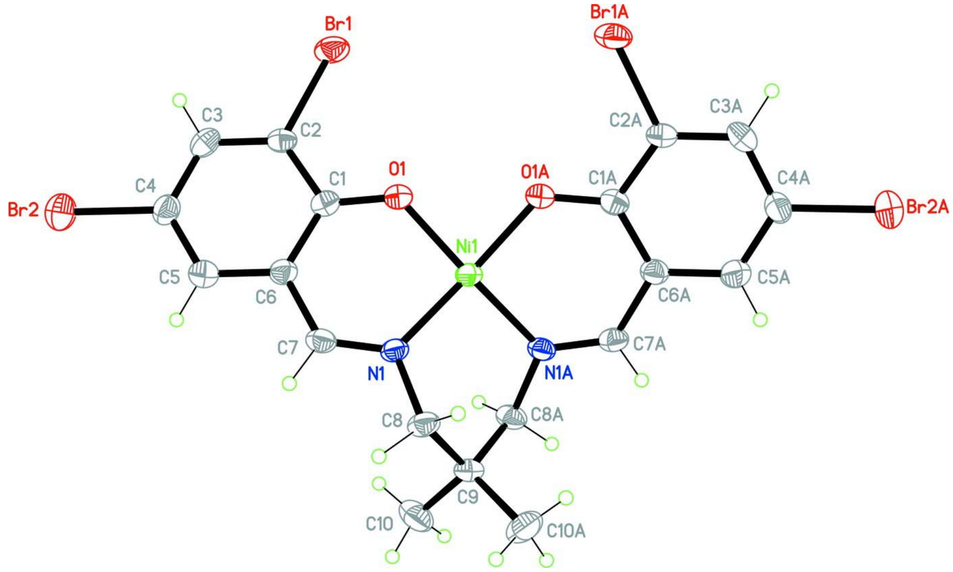

Figure 1

A view of the molecular structure of the title compound, showing 40% probability displacement ellipsoids and the atomic numbering [symmetry code: (A) = -x, y, -z+1/2].

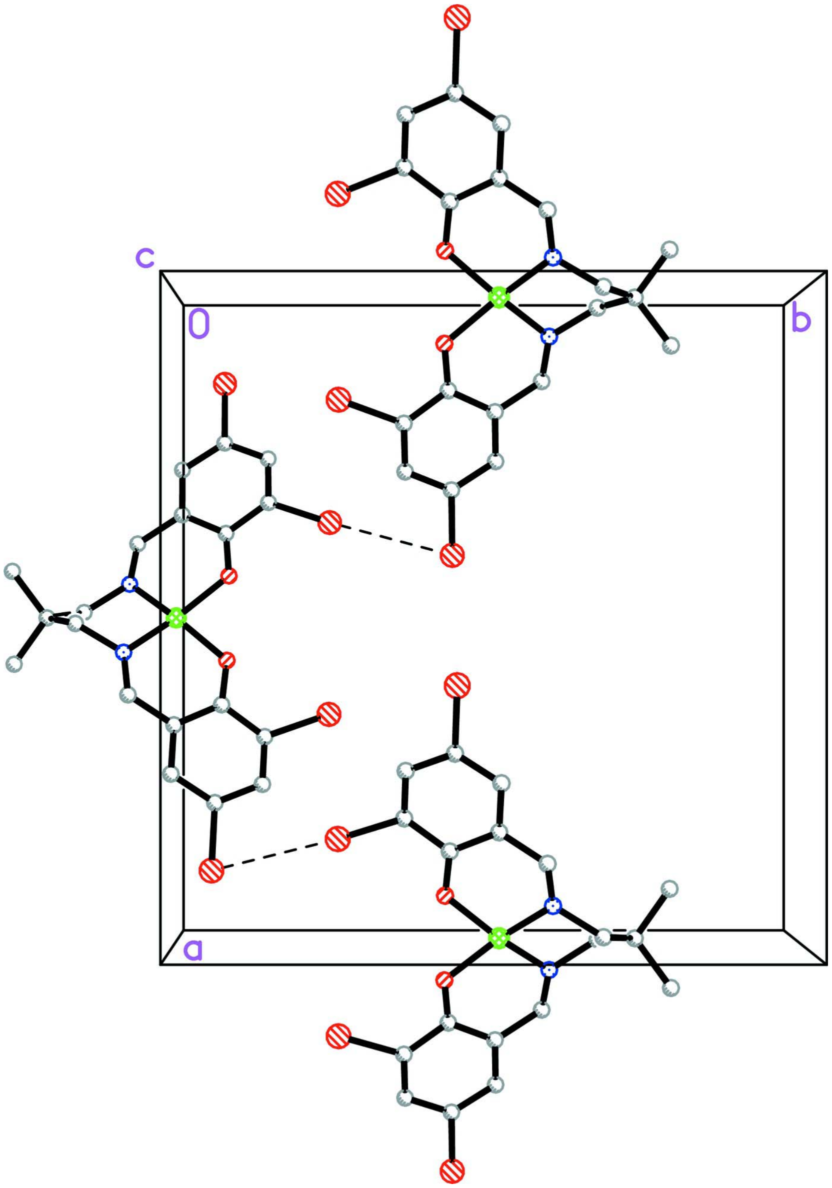

Figure 2

The crystal packing of the title compound viewed along the *c*-axis, showing how the molecules are linked via the intermolecular Br···Br interactions (dashed lines) to form chains along the *a* axis [the H atoms have been omitted for clarity].

{4,4′,6,6′-Tetrabromo-2,2′-[2,2-dimethylpropane-1,3- diylbis(nitrilomethanylylidene)]diphenolato}nickel(II)

Crystal data

[Ni($C_{19}H_{16}Br_4N_2O_2$)]	V = 2113.3 (3) Å^3
M_r = 682.69	Z = 4
Orthorhombic, *Pbcn*	F(000) = 1312
Hall symbol: -P 2n 2ab	D_x = 2.146 Mg m^{-3}
a = 16.1125 (11) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
b = 15.4789 (12) Å	Cell parameters from 2540 reflections
c = 8.4734 (5) Å	θ = 2.5–27.4°

μ = 8.50 mm^{-1}
T = 296 K

Block, dark-red
0.25 × 0.18 × 0.09 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{\min}$ = 0.694, $T_{\max}$ = 0.871

16236 measured reflections
2086 independent reflections
1574 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
$\theta_{\max}$ = 26.0°, $\theta_{\min}$ = 1.8°
$h = -19 \rightarrow 19$
$k = -14 \rightarrow 19$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.075
S = 1.05
2086 reflections
129 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
$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 0.4809P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.52 e Å^{-3}
$\Delta\rho_{\min}$ = −0.78 e Å^{-3}

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.

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 > 2sigma(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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.34274 (3)	−0.24016 (2)	0.18392 (5)	0.04218 (15)
Br2	0.10156 (3)	−0.05088 (3)	−0.14763 (7)	0.06551 (19)
Ni1	0.5000	0.02131 (4)	0.2500	0.02663 (17)
O1	0.43065 (15)	−0.06700 (15)	0.1850 (3)	0.0344 (6)
N1	0.44411 (18)	0.10588 (18)	0.1331 (3)	0.0281 (7)
C1	0.3595 (2)	−0.0600 (2)	0.1155 (4)	0.0284 (8)
C2	0.3081 (2)	−0.1331 (2)	0.0964 (4)	0.0293 (8)
C3	0.2334 (2)	−0.1309 (3)	0.0186 (4)	0.0337 (9)
H3	0.2019	−0.1809	0.0073	0.040*
C4	0.2054 (2)	−0.0533 (3)	−0.0427 (4)	0.0372 (9)
C5	0.2510 (2)	0.0203 (3)	−0.0270 (5)	0.0391 (10)
H5	0.2312	0.0721	−0.0681	0.047*
C6	0.3279 (2)	0.0180 (2)	0.0515 (4)	0.0304 (8)
C7	0.3763 (2)	0.0952 (2)	0.0563 (4)	0.0317 (8)

H7	0.3569	0.1420	−0.0017	0.038*
C8	0.4910 (2)	0.1859 (2)	0.1043 (4)	0.0334 (9)
H8A	0.4631	0.2189	0.0227	0.040*
H8B	0.5458	0.1711	0.0655	0.040*
C9	0.5000	0.2419 (3)	0.2500	0.0320 (12)
C10	0.4239 (3)	0.2995 (3)	0.2735 (5)	0.0499 (11)
H10A	0.3746	0.2647	0.2718	0.075*
H10B	0.4213	0.3415	0.1901	0.075*
H10C	0.4280	0.3286	0.3732	0.075*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0576 (3)	0.0265 (2)	0.0424 (3)	−0.00786 (19)	−0.00041 (19)	0.00544 (17)
Br2	0.0449 (3)	0.0558 (3)	0.0958 (4)	−0.0040 (2)	−0.0292 (3)	−0.0020 (3)
Ni1	0.0301 (3)	0.0205 (4)	0.0292 (3)	0.000	−0.0007 (3)	0.000
O1	0.0369 (15)	0.0238 (14)	0.0425 (14)	−0.0025 (12)	−0.0059 (12)	0.0023 (12)
N1	0.0348 (17)	0.0206 (16)	0.0290 (16)	−0.0047 (14)	−0.0020 (13)	0.0011 (13)
C1	0.033 (2)	0.027 (2)	0.0257 (18)	−0.0035 (17)	0.0038 (16)	−0.0003 (16)
C2	0.036 (2)	0.0226 (19)	0.0293 (19)	−0.0016 (16)	0.0045 (16)	0.0015 (16)
C3	0.033 (2)	0.035 (2)	0.033 (2)	−0.0105 (18)	0.0043 (16)	−0.0045 (18)
C4	0.030 (2)	0.038 (2)	0.044 (2)	−0.0040 (19)	−0.0042 (17)	−0.0042 (19)
C5	0.043 (2)	0.031 (2)	0.043 (2)	0.0032 (19)	−0.0058 (18)	−0.0022 (19)
C6	0.034 (2)	0.026 (2)	0.0315 (19)	−0.0034 (16)	−0.0011 (16)	0.0023 (16)
C7	0.040 (2)	0.023 (2)	0.0326 (19)	0.0003 (17)	0.0001 (17)	0.0042 (17)
C8	0.045 (2)	0.024 (2)	0.0313 (19)	−0.0084 (18)	−0.0001 (17)	0.0036 (16)
C9	0.038 (3)	0.020 (3)	0.038 (3)	0.000	−0.001 (2)	0.000
C10	0.057 (3)	0.040 (3)	0.053 (3)	0.019 (2)	−0.006 (2)	0.003 (2)

Geometric parameters (Å, º)

Br1—C2	1.899 (3)	C4—C5	1.362 (5)
Br2—C4	1.895 (4)	C5—C6	1.407 (5)
Ni1—O1	1.849 (2)	C5—H5	0.9300
Ni1—O1^{i}	1.849 (2)	C6—C7	1.428 (5)
Ni1—N1^{i}	1.872 (3)	C7—H7	0.9300
Ni1—N1	1.872 (3)	C8—C9	1.515 (4)
O1—C1	1.293 (4)	C8—H8A	0.9700
N1—C7	1.282 (4)	C8—H8B	0.9700
N1—C8	1.471 (4)	C9—C8^{i}	1.515 (4)
C1—C2	1.412 (5)	C9—C10^{i}	1.529 (5)
C1—C6	1.418 (5)	C9—C10	1.529 (5)
C2—C3	1.373 (5)	C10—H10A	0.9600
C3—C4	1.384 (5)	C10—H10B	0.9600
C3—H3	0.9300	C10—H10C	0.9600

O1—Ni1—O1^{i}	84.69 (15)	C5—C6—C1	121.3 (3)
O1—Ni1—N1^{i}	164.78 (11)	C5—C6—C7	118.3 (3)
O1^{i}—Ni1—N1^{i}	93.94 (11)	C1—C6—C7	120.3 (3)
O1—Ni1—N1	93.94 (11)	N1—C7—C6	126.0 (3)

O1^{i}—Ni1—N1	164.78 (11)	N1—C7—H7	117.0
N1^{i}—Ni1—N1	91.27 (17)	C6—C7—H7	117.0
C1—O1—Ni1	127.5 (2)	N1—C8—C9	113.3 (3)
C7—N1—C8	117.5 (3)	N1—C8—H8A	108.9
C7—N1—Ni1	126.0 (3)	C9—C8—H8A	108.9
C8—N1—Ni1	115.5 (2)	N1—C8—H8B	108.9
O1—C1—C2	120.4 (3)	C9—C8—H8B	108.9
O1—C1—C6	124.4 (3)	H8A—C8—H8B	107.7
C2—C1—C6	115.3 (3)	C8—C9—C8^{i}	110.2 (4)
C3—C2—C1	123.3 (3)	C8—C9—C10^{i}	107.7 (2)
C3—C2—Br1	117.8 (3)	C8^{i}—C9—C10^{i}	111.3 (2)
C1—C2—Br1	118.8 (3)	C8—C9—C10	111.3 (2)
C2—C3—C4	119.2 (3)	C8^{i}—C9—C10	107.7 (2)
C2—C3—H3	120.4	C10^{i}—C9—C10	108.7 (5)
C4—C3—H3	120.4	C9—C10—H10A	109.5
C5—C4—C3	120.9 (3)	C9—C10—H10B	109.5
C5—C4—Br2	120.4 (3)	H10A—C10—H10B	109.5
C3—C4—Br2	118.7 (3)	C9—C10—H10C	109.5
C4—C5—C6	120.0 (4)	H10A—C10—H10C	109.5
C4—C5—H5	120.0	H10B—C10—H10C	109.5
C6—C5—H5	120.0		

O1^{i}—Ni1—O1—C1	−178.8 (3)	C2—C3—C4—Br2	−179.3 (3)
N1^{i}—Ni1—O1—C1	95.7 (5)	C3—C4—C5—C6	0.5 (6)
N1—Ni1—O1—C1	−14.0 (3)	Br2—C4—C5—C6	179.8 (3)
O1—Ni1—N1—C7	6.6 (3)	C4—C5—C6—C1	−0.1 (5)
O1^{i}—Ni1—N1—C7	90.8 (5)	C4—C5—C6—C7	175.9 (3)
N1^{i}—Ni1—N1—C7	−159.1 (4)	O1—C1—C6—C5	178.0 (3)
O1—Ni1—N1—C8	−161.3 (2)	C2—C1—C6—C5	−0.9 (5)
O1^{i}—Ni1—N1—C8	−77.1 (5)	O1—C1—C6—C7	2.2 (5)
N1^{i}—Ni1—N1—C8	32.97 (18)	C2—C1—C6—C7	−176.7 (3)
Ni1—O1—C1—C2	−169.7 (2)	C8—N1—C7—C6	171.2 (3)
Ni1—O1—C1—C6	11.5 (5)	Ni1—N1—C7—C6	3.5 (5)
O1—C1—C2—C3	−177.4 (3)	C5—C6—C7—N1	174.0 (3)
C6—C1—C2—C3	1.5 (5)	C1—C6—C7—N1	−10.0 (6)
O1—C1—C2—Br1	3.1 (4)	C7—N1—C8—C9	118.4 (3)
C6—C1—C2—Br1	−177.9 (2)	Ni1—N1—C8—C9	−72.7 (3)
C1—C2—C3—C4	−1.1 (5)	N1—C8—C9—C8^{i}	35.2 (2)
Br1—C2—C3—C4	178.3 (3)	N1—C8—C9—C10^{i}	156.7 (3)
C2—C3—C4—C5	0.1 (6)	N1—C8—C9—C10	−84.3 (4)

Symmetry code: (i) $-x+1, y, -z+1/2$.