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The crystal structure of $\{N^1, N^2$ -bis[2,4-dimethyl-6-(4-(*tert*-butyl)phenyl)(phenyl)methyl]acenaphthylene-1,2-diimino- $\kappa^2 N, N'$ }-dibromido-nickel(II) – dichloromethane(1/2), $C_{64}H_{64}Br_2Cl_4N_2Ni$

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Abstract

$C_{64}H_{64}Br_2Cl_4N_2Ni$, monoclinic, $C2/c$ (no. 15), $a = 31.9723(18)$ Å, $b = 11.9826(6)$ Å, $c = 18.4722(11)$ Å, $\beta = 125.038(2)^\circ$, $V = 5794.4(6)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0536$, $wR_{ref}(F^2) = 0.1640$, $T = 273.15$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Green block
Size:	$0.05 \times 0.04 \times 0.03$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.94 mm^{-1}
Diffractometer, scan mode:	Bruker APEXII, φ and ω -scans
$\theta_{\max}$, completeness:	526.4° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	16,288, 5909, 0.023
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4631
$N(\text{param})_{\text{refined}}$:	336
Programs:	Bruker programs [1], OLEX2 [2], SHELX [3, 4]

Source of materials

The title complex was synthesized *via* the one-pot reaction of acenaphthoquinone, 2-((4-(*tert*-butyl)phenyl)(phenyl)methyl)aniline and anhydrous $NiBr_2$ with a molar ratio 1:2:1 from an acetic acid solution according to a reported method [5].

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Br1	0.54132 (2)	1.09105 (4)	0.88296 (3)	0.05779 (18)
Ni1	0.500000	0.99384 (5)	0.750000	0.03127 (18)
N1	0.45757 (10)	0.8660 (2)	0.74872 (17)	0.0282 (6)
C1	0.47673 (12)	0.7710 (3)	0.7510 (2)	0.0290 (7)
C2	0.46427 (13)	0.6540 (3)	0.7546 (2)	0.0327 (7)
C3	0.500000	0.5902 (4)	0.750000	0.0332 (10)
C4	0.500000	0.4725 (4)	0.750000	0.0396 (11)
C5	0.46259 (16)	0.4205 (3)	0.7561 (3)	0.0451 (9)
H5	0.461220	0.343056	0.756846	0.054*
C6	0.42801 (16)	0.4827 (3)	0.7608 (3)	0.0480 (9)
H6	0.403724	0.445891	0.764590	0.058*
C7	0.42818 (14)	0.6011 (3)	0.7601 (3)	0.0393 (8)
H7	0.404490	0.641610	0.763353	0.047*
C8	0.41204 (12)	0.8688 (3)	0.7483 (2)	0.0294 (7)
C9	0.41792 (13)	0.8635 (3)	0.8294 (2)	0.0329 (7)
C10	0.37360 (14)	0.8622 (3)	0.8265 (2)	0.0378 (8)
H10	0.376355	0.859389	0.879406	0.045*
C11	0.32520 (14)	0.8650 (3)	0.7474 (3)	0.0374 (8)
C12	0.32137 (13)	0.8730 (3)	0.6695 (2)	0.0338 (7)
H12	0.289157	0.876324	0.616396	0.041*
C13	0.36451 (12)	0.8763 (3)	0.6681 (2)	0.0293 (7)
C14	0.47001 (15)	0.8574 (4)	0.9156 (2)	0.0451 (9)
H14A	0.485535	0.786976	0.919692	0.068*
H14B	0.466711	0.864585	0.963884	0.068*
H14C	0.490980	0.916829	0.918209	0.068*
C15	0.27747 (16)	0.8613 (4)	0.7471 (3)	0.0540 (10)
H15A	0.247852	0.873811	0.688073	0.081*
H15B	0.279537	0.918268	0.785547	0.081*
H15C	0.274939	0.789532	0.767334	0.081*
C16	0.36089 (13)	0.8822 (3)	0.5820 (2)	0.0310 (7)
H16	0.390060	0.926721	0.594427	0.037*
C17	0.31296 (13)	0.9431 (3)	0.5094 (2)	0.0346 (7)
C18	0.30946 (16)	1.0568 (3)	0.5187 (3)	0.0489 (9)
H18	0.336088	1.093910	0.568163	0.059*
C19	0.26629 (19)	1.1156 (4)	0.4542 (3)	0.0590 (11)
H19	0.264050	1.191795	0.461106	0.071*
C20	0.22651 (16)	1.0615 (4)	0.3796 (3)	0.0573 (11)
H20	0.197711	1.100993	0.336444	0.069*
C21	0.23001 (16)	0.9512 (4)	0.3702 (3)	0.0546 (11)
H21	0.203329	0.914780	0.320323	0.066*
C22	0.27272 (15)	0.8908 (3)	0.4338 (3)	0.0449 (9)
H22	0.274466	0.814765	0.425772	0.054*
C23	0.36703 (12)	0.7663 (3)	0.5549 (2)	0.0326 (7)
C24	0.33903 (14)	0.6760 (3)	0.5507 (2)	0.0403 (8)
H24	0.316309	0.684929	0.566364	0.048*
C25	0.34420 (16)	0.5713 (3)	0.5233 (3)	0.0453 (9)
H25	0.324185	0.512216	0.519506	0.054*
C26	0.37878 (15)	0.5541 (3)	0.5015 (2)	0.0431 (9)
C27	0.40683 (16)	0.6454 (3)	0.5066 (3)	0.0465 (9)
H27	0.430344	0.636545	0.492708	0.056*
C28	0.40084 (14)	0.7503 (3)	0.5321 (2)	0.0397 (8)
H28	0.419861	0.810190	0.533739	0.048*
C29	0.38289 (17)	0.4404 (4)	0.4680 (3)	0.0525 (10)
C30	0.4377 (2)	0.4177 (5)	0.4979 (5)	0.099 (2)
H30A	0.447723	0.472759	0.472806	0.149*

Table 2: (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H30B	0.439677	0.344815	0.478382	0.149*
H30C	0.460237	0.421265	0.561215	0.149*
C31	0.3644 (3)	0.3448 (4)	0.4983 (5)	0.096 (2)
H31A	0.382381	0.347240	0.561400	0.144*
H31B	0.370820	0.274737	0.481195	0.144*
H31C	0.328418	0.352762	0.471153	0.144*
C32	0.3493 (2)	0.4431 (4)	0.3677 (3)	0.0677 (14)
H32A	0.314282	0.452744	0.347180	0.101*
H32B	0.352843	0.374261	0.345198	0.101*
H32C	0.359434	0.504119	0.347357	0.101*
Cl1	0.40937 (10)	0.8178 (2)	0.3333 (2)	0.1404 (9)
Cl2	0.29885 (8)	0.84487 (15)	0.20692 (13)	0.1120 (6)
C33	0.3463 (3)	0.8355 (6)	0.3130 (5)	0.108 (2)
H33A	0.339895	0.772661	0.338530	0.129*
H33B	0.346742	0.902481	0.342960	0.129*

The crystals of the title complex were recrystallized from the dichloromethane solution after three day. Yield 64% (based on acenaphthoquinone).

Experimental details

The structure was solved by direct methods with the SHELXS-2018 program. All H-atoms from C atoms were positioned with idealized geometry and refined isotropic ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$) using a riding model with C–H = 0.96 Å for *tert*-butyl groups, C–H = 0.93 Å for phenyl groups, C–H = 0.98 Å for C16–H16, and C–H = 0.97 Å for dichloromethane, respectively.

Comment

N,N'-bis(2,4,6-trimethylphenyl)acenaphthen-1,2-diimine and its derivatives have been synthesized as useful ligands to exploit *a*/-diimine nickel catalysts for various olefin polymerization reactions [5–16]. It is interesting that the substituent groups of these diimines affected the catalytic performance greatly. Therefore, people have a strong interest in the selection of substituent groups. Thus, we here report the single crystal structure of a new acenaphthen-1,2-diimine-based Ni(II) complex.

The title complex belongs to the acenaphthen-1,2-diimine based Ni(II) complexes. The asymmetric unit consists of one half of a ligand, one half of a Ni(II) cation, one bromide and one crystal dichloromethane molecule. The Ni(II) cation adapts an distorted tetrahedral geometry by coordinating two N atoms from the ligand and two bromido ligands. The bond lengths of Ni–N and Ni–Br are 2.037 and 2.326 Å, respectively,

which are comparable with the values of the reported results [5–17].

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