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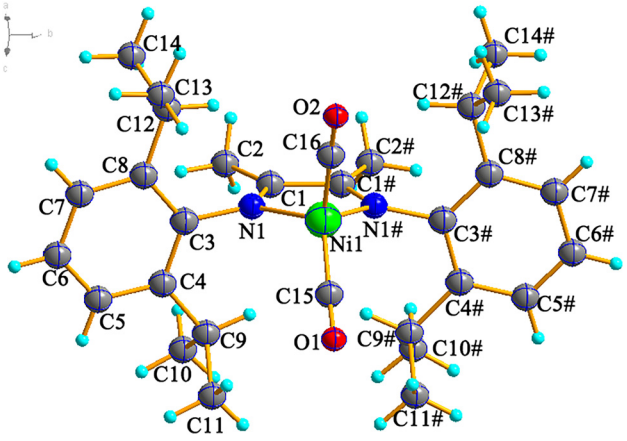
Crystal structure of dicarbonyl[*N*,*N*′-(1,2-dimethyl-1,2-ethanediylidene)bis[2,6-bis(1-methylethyl) benzenamine]-N,*N*′]nickel(0), $C_{30}H_{40}N_2NiO_2$



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Abstract

$C_{30}H_{40}N_2NiO_2$, orthorhombic, *Pnma* (no. 62), a = 12.8114(19) Å, b = 21.301(3) Å, c = 10.6536(16) Å, V = 2907.3(8) Å^3, Z = 4, $R_{gt}(F)$ = 0.0290, $wR_{ref}(F^2)$ = 0.0808, T = 273(2) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of materials

Under a nitrogen atmosphere, the grass-green Ni–Ni-bonded complex [{Ni^I(μ–L)}$_2$] (0.232 g, 0.25 mmol) (*L* = N,N^2-(1,2-dimethyl-1,2-ethanediylidene)bis[2,6-bis(1-methylethyl) benzenamine), which was synthesized from the literature [5, 6], was dissolved in 20 ml anhydrous *n*-hexane at room temperature. A CO gas stream bubbled into the solution which was stirred for 0.5 h. The color of the reaction mixture changed from grass green to purple. After then, the mixture was filtered and concentrated by vacuum to about 6 ml. The solution was stored at room temperature for about one week to afford purple crystals with yield of 82 % (0.213 g).

Table 1: Data collection and handling.

Crystal:	Purple block
Size:	0.32 × 0.25 × 0.22 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.69 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	17,151, 2634, 0.028
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2386
$N(param)_{refined}$:	172
Programs:	SHELX [1, 2], Olex2 [3], Diamond [4]

2 Experimental details

SADABS [1] was applied for absorption correction and the structure was solved and refined to convergence using the SHELXL-2014 programs [2] and OLEX2 [3]. All hydrogen atoms were positioned geometrically, with the d(C–H) = 0.97–0.99 Å, U_{iso}(H) = 1.2 times U_{eq}(C) and U_{iso}(H) = 1.5 times U_{eq}(O).

3 Comment

Many nickel complexes have been verified as good catalysts for organic chemical reactions, especially in olefin polymerization [7, 8] and alkyne cyclization [9, 10]. α-Diimine is widely used in metal coordination chemistry as a serial of nitrogen-containing bidentate ligands which can form different coordination structures with metals because of their electronic effects. Based on the above advantages and research

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.49304 (12)	0.28463 (7)	0.44437 (15)	0.0339 (4)
C2	0.58099 (16)	0.32077 (10)	0.5023 (2)	0.0639 (6)
H2A	0.5643	0.3647	0.5022	0.096*
H2B	0.6436	0.3139	0.4548	0.096*
H2C	0.5914	0.3069	0.5871	0.096*
C3	0.39049 (12)	0.37605 (7)	0.41154 (15)	0.0315 (3)
C4	0.33668 (14)	0.39501 (8)	0.51984 (16)	0.0402 (4)
C5	0.31313 (15)	0.45851 (9)	0.5324 (2)	0.0512 (5)
H5	0.2777	0.4723	0.6035	0.061*
C6	0.34122 (17)	0.50120 (9)	0.4417 (2)	0.0576 (5)
H6	0.3243	0.5434	0.4514	0.069*
C7	0.39429 (17)	0.48156 (9)	0.3368 (2)	0.0522 (5)
H7	0.4134	0.5110	0.2765	0.063*
C8	0.42029 (13)	0.41856 (8)	0.31852 (16)	0.0380 (4)
C9	0.30435 (18)	0.34916 (10)	0.62179 (19)	0.0569 (5)
H9	0.3244	0.3070	0.5941	0.068*
C10	0.3612 (3)	0.36240 (18)	0.7452 (3)	0.1153 (12)
H10A	0.4351	0.3635	0.7304	0.173*
H10B	0.3454	0.3299	0.8046	0.173*
H10C	0.3387	0.4021	0.7780	0.173*
C11	0.1866 (2)	0.34903 (15)	0.6436 (3)	0.0876 (9)
H11A	0.1652	0.3893	0.6748	0.131*
H11B	0.1691	0.3172	0.7038	0.131*
H11C	0.1514	0.3405	0.5659	0.131*
C12	0.47950 (16)	0.39838 (9)	0.20219 (16)	0.0462 (4)
H12	0.4872	0.3526	0.2056	0.055*
C13	0.5893 (2)	0.42691 (15)	0.1991 (3)	0.0824 (8)
H13A	0.5842	0.4718	0.1958	0.124*
H13B	0.6258	0.4120	0.1263	0.124*
H13C	0.6267	0.4148	0.2733	0.124*
C14	0.4192 (2)	0.41421 (14)	0.0828 (2)	0.0807 (8)
H14A	0.3502	0.3968	0.0879	0.121*
H14B	0.4548	0.3968	0.0116	0.121*
H14C	0.4146	0.4590	0.0739	0.121*
C15	0.1822 (2)	0.2500	0.3443 (3)	0.0495 (7)
C16	0.3328 (2)	0.2500	0.1435 (3)	0.0483 (6)
N1	0.41037 (10)	0.30968 (6)	0.39643 (11)	0.0283 (3)
Ni1	0.31582 (2)	0.2500	0.30825 (3)	0.03177 (13)
O1	0.09369 (17)	0.2500	0.3555 (3)	0.0926 (9)
O2	0.3380 (2)	0.2500	0.0373 (2)	0.0818 (7)

results, *α*-diimide is also favored by researchers in the synthesis of metal-organic catalysts. Here, we report a crystal structure of mononuclear nickel carbonyl complex.

In the title structure, the nickel is coordinated with four atoms those two nitrogen atoms of the ligand and two carbon atoms of CO. The title molecule is located on a mirror plane. Moreover, C1, N1, Ni1, N1#, C1# are in the same plane which is perpendicular to the plane of O1–C15–Ni1–C16–O2 (dihedral angle is 90°). In addition, as a metal catalyst, it is important to determine the oxidation state of its ligand and metal. Based on the literature [11, 12], the central core bond lengths (C1–C1# (1.475(3) Å) and C1–N1 (1.291(2)) refer to the neutral form of the ligand. Moreover, the C–O bond lengths are 1.140(3) Å and 1.133(4) Å, respectively, so the triple-bond is still retained, and therefore, the central nickel valence state has zero valence, which provides potential as a catalyst.

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