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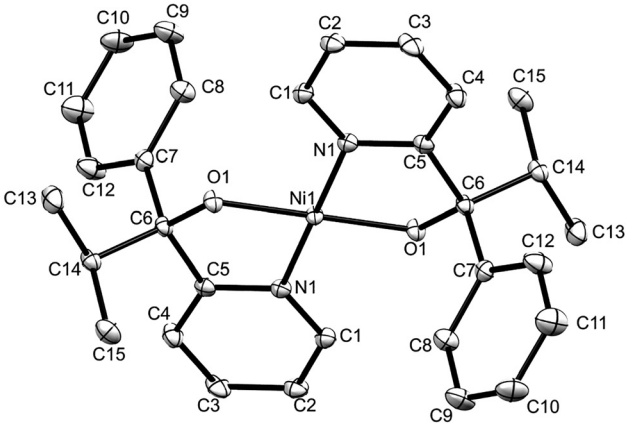
Crystal structure of bis{(2-pyridinyl)-1-phenyl-1-isopropylmethanolato-κ^2*N*,*O*}nickel, $C_{30}H_{32}N_2NiO_2$



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Abstract

$C_{30}H_{32}N_2NiO_2$, monoclinic, $P2_1/c$ (no. 14), a = 12.1250(4) Å, b = 13.6413(4) Å, c = 8.1152(3) Å, β = 108.348(2)°, V = 1274.02(7) Å^3, Z = 2, $R_{gt}(F)$ = 0.0285, $wR_{ref}(F^2)$ = 0.0711, T = 100 K.

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The molecular structure is shown in the figure (hydrogen atoms are omitted for clarity). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The synthesis was adapted from Butsch et al. [5]. A MeOH solution (5 ml) of the 2-pyridinyl-1-phenyl-1-isopropylmethanol ligand (100 mg, 0.439 mmol) was added to 6 ml of nickel chloride hexahydrate (105 mg, 0.44 mmol) in MeOH (3 ml) and acetone (3 ml). The resultant green solution was stirred overnight at room temperature. The solution was concentrated and Et_2O (20 ml) was added. The solution was cooled until a green solid formed. The solid was collected by filtration and washed with Et_2O. Single crystals were grown from slow evaporation of a mixed solvent system of MeOH and $(CH_3)_2CO$. Yield: 60%. Decomposes at >279 °C. **IR**: selected $_{max}$ (cm^{-1}): 2961, 1605, 1568, 1469, 1024, 993, 778.

Table 1: Data collection and handling.

Crystal:	Yellow shard
Size:	0.20 × 0.15 × 0.12 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.79 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13,107, 2840, 0.023
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 2470
$N(param)_{refined}$:	162
Programs:	Bruker [1], SHELX [2, 3], Mercury [4]

Experimental details

The structure was solved by direct methods using the *SHELXS* [2] program and refined. The visual crystal structure information was performed using *Mercury* [4] system software.

Comment

Pyridinyl alcoholato ligands are bidentate chelating ligands. In most cases the ligand is deprotonated when coordinated to a metal centre. The alkoxide functional group of pyridinyl alcoholato ligands allows proton-coupled electron transfer (PCET) [6, 7]. Their strong σ and π-donor properties favour the attainment of high oxidation states of coordinated transition metals. The pyridine ring

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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}
Ni1	0.500000	0.500000	0.500000	0.00988 (8)
O1	0.36466 (8)	0.43818 (7)	0.37793 (13)	0.0125 (2)
N1	0.45774 (10)	0.59457 (9)	0.32408 (15)	0.0114 (2)
C1	0.52525 (13)	0.66854 (11)	0.30139 (18)	0.0132 (3)
H1	0.602701	0.673677	0.377392	0.016*
C2	0.48517 (13)	0.73704 (12)	0.17095 (19)	0.0161 (3)
H2	0.534086	0.788576	0.156724	0.019*
C3	0.37156 (14)	0.72888 (12)	0.06090 (19)	0.0180 (3)
H3	0.341446	0.775261	−0.029423	0.022*
C4	0.30288 (13)	0.65268 (12)	0.08414 (19)	0.0165 (3)
H4	0.225161	0.646331	0.009609	0.020*
C5	0.34769 (12)	0.58551 (11)	0.21648 (18)	0.0121 (3)
C6	0.28322 (12)	0.49902 (11)	0.26290 (18)	0.0118 (3)
C7	0.19749 (13)	0.54271 (11)	0.34968 (19)	0.0132 (3)
C8	0.21814 (14)	0.52917 (12)	0.5265 (2)	0.0178 (3)
H8	0.282401	0.490625	0.591426	0.021*
C9	0.14559 (15)	0.57153 (13)	0.6093 (2)	0.0235 (4)
H9	0.160598	0.561255	0.730162	0.028*
C10	0.05241 (15)	0.62808 (13)	0.5187 (2)	0.0239 (4)
H10	0.004116	0.657792	0.576746	0.029*
C11	0.02966 (15)	0.64130 (14)	0.3417 (2)	0.0267 (4)
H11	−0.035164	0.679430	0.277403	0.032*
C12	0.10179 (14)	0.59872 (13)	0.2585 (2)	0.0220 (4)
H12	0.085489	0.607995	0.137142	0.026*
C13	0.15891 (15)	0.35066 (12)	0.1486 (2)	0.0217 (4)
H13A	0.118567	0.312781	0.044449	0.033*
H13B	0.102693	0.372933	0.204787	0.033*
H13C	0.217655	0.309320	0.229287	0.033*
C14	0.21786 (13)	0.43943 (11)	0.09763 (18)	0.0140 (3)
H14	0.156272	0.482320	0.020100	0.017*
C15	0.29924 (14)	0.40709 (12)	−0.0025 (2)	0.0195 (3)
H15A	0.362962	0.368193	0.073745	0.029*
H15B	0.331003	0.465013	−0.043003	0.029*
H15C	0.255959	0.367304	−0.102516	0.029*

provides strong binding to metal centres, which in turn increases the resistance towards degradation during catalytic runs [8]. Another advantage of these ligands is that upon coordination to a metal centre they form five-membered rings. Five-membered rings are thermodynamically stable [6]. These ligands have been coordinated to various metals and have been applied as catalysts in metathesis and oxidation reactions [6, 9–15].

The asymmetric unit consists of half a molecule of the title compound with the Ni(II) atom situated on an inversion centre. Two pyridinyl alcoholato ligands coordinate to the metal in a bidentate manner *via* the nitrogen and oxygen donor atoms. This results in a square planar geometry with bond angles around the metal centre ranging from 85.49(5)° to 180° [16]. Furthermore, the Ni–N and Ni–O bond distances are 1.872(1) and 1.834(1) Å, respectively. These bond lengths are comparable with that of a closely related 3-hydroxy-3-phenyl-(3-pyridyl-2-yl) propanenitrile derivative (Ni–N = 1.873(1) Å, Ni–O = 1.833(1) Å) [16]. Non-classical intermolecular C–H···O interactions exist between the H2 atom of the pyridinyl moiety and the O1 atom of a neighbouring molecule (C2–H2 = 0.95 Å, H2···O1 = 2.443 Å, C2···O1 = 3.385(2) Å, C2–H2···O1 = 171°, Symmetry code: 1–*x*, 1/2+*y*, 1/2–*z*.)

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