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Crystallographic report

Bis{[diacetyl-bis(2,6-isopropylphenylimine)] nickel(I)(μ-chloro)}

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The first α-diimine nickel(I) complex having a chloro bridge is reported. The centrosymmetric dinuclear structure of {[ArN═C(Me)C(Me)═NAr]NiCl}$_2$[Ar═2,6−C_6H_3(i-Pr)$_2$] features two chelating α-diimine ligands and two bridged chlorine atoms, so that a distorted tetrahedral N_2Cl_2 coordination geometry for nickel results. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; nickel; diimine; chloro bridge; monovalent

COMMENT

The centrosymmetric dinuclear structure of {ArN═C(Me)C(Me)═NAr]NiCl}$_2$ [Ar = 2, 6-C_6H_3(i-Pr)$_2$], Fig. 1, features two chelating α-diimine ligands, each of which forms approximately identical Ni–N bonds. The nickel atoms are bridged by two chlorine atoms, so that a four-coordinated N_2Cl_2 geometry results in a distorted tetrahedral geometry for each nickel atom. There is a small dihedral angle (10.40°) between the planes of N(1)–Ni(1)–N(2) and N═C–C═N. Another dihedral angle between the planes of Ni(1)–Cl(1)–Ni(1_3)–Cl(1_3) and N═C–C═N is 100.01°. To the best of our knowledge, this is the first example of a monovalent nickel complex supported by chelating α-diimine ligands and chloro bridges.[1,2]

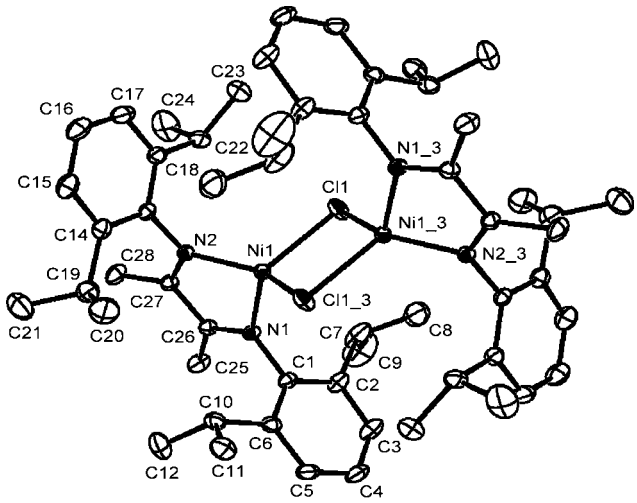

Figure 1. Molecular structure of {[ArN═C(Me)C(Me)═NAr] NiCl}$_2$[Ar = 2, 6-C_6H_3(i-Pr)$_2$]. The atoms Ni(1), Cl(1), Ni(1_3) and Cl(1_3) lie in the same plane. Key geometric parameters: Ni(1)–Cl(1) 2.2990(10), Ni(1)–N(1) 1.918(2), Ni(1)–N(2) 1.920(2), N(1)–C(1) 1.433(3), N(1)–C(26) 1.317(3), N(2)–C(13) 1.433(3), N(2)–C(27) 1.315(3) Å; Cl(1)–Ni(1)–N(1) 121.14(6), Cl(1)–Ni(1)–N(2) 117.17(5), N(1)–Ni(1)–N(2) 81.12(7), Ni(1)–N(1)–C(1) 123.2(1), Ni(1)–N(1)–C(26) 115.1(1), C(1)–N(1)–C(26) 121.8(2), Ni(1)–N(2)–C(13) 121.8(1), Ni(1)–N(2)–C(27) 115.5(1), C(13)–N(2)–C(27) 122.4(2), N(1)–C(1)–C(2) 120.8(2), N(1)–C(1)–C(6) 117.2(2), Cl(1)–Ni(1)–Cl(1_3) 91.6(7), Ni(1_3)–Cl(1)–Ni(1) 88.3(3)°.

EXPERIMENTAL

[ArN═C(Me)C(Me)═NAr]NiCl$_2$[Ar = 2,6-C_6H_3(i-Pr)$_2$] was synthesized by stirring the α-diimine[3] and (DME)NiCl$_2$[4] in toluene. 2-Ethylindene and its lithium salt were synthesized according to a literature method under argon atmosphere.[5]

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A tetrahydrofuran (THF) solution (10 ml) of 2-ethylindene lithium (0.46 g, 3.06 mmol) was added slowly into a THF suspension of [ArN=C(Me)C(Me)=NAr]$NiCl_2$[Ar = 2, 6-C_6H_3(i-Pr)$_2$] (1.63 g, 3.06 mmol) under argon atmosphere. The reaction mixture was stirred for 5 h at room temperature and filtered to give a purple solution. The solution was evaporated to dryness *in vacuo* and the residue was recrystallized from toluene at −20 °C. Purple platelet crystals suitable for X-ray structure determination were obtained in a yield of 1.90 g (65%). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.90$ [w, CH_3C=N], 1.22 [s, CH(CH_3)$_2$], 3.30 [w, CH(CH$_3$)$_2$], 6.90–7.40 [phenyl]. Intensity data were collected at 193 K on a Rigaku Mercury CCD area detector with graphite monochromated Mo Kα radiation for a purple block $0.35 \times 0.50 \times 0.12$ mm^3. $C_{56}H_{80}Cl_2N_4Ni_2$, $M = 997.58$, monoclinic, $P2_1/n$, $a = 13.737(1)$, $b = 13.9669(13)$, $c = 14.671(2)$ Å, $\beta = 103.460(4)°$, $V = 2737.5(5)$ Å^3, $Z = 2$, 6243 unique data, 4794 data with $I > 2\sigma(I)$, $R = 0.040$, $wR = 0.087$. Programs used: Crystalstructure, SHELXL-97 and ORTEP. CCDC deposition number: 227 499.

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