

[7,16-Bis(benzyloxycarbonyl)-6,18,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato- κ^4N]nickel(II)**Peter D.W. Boyd,* J.B. Challis and C.E.F. Rickard**

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Key indicatorsSingle-crystal X-ray study
 $T = 150$ K
Mean $\sigma(C-C) = 0.004$ Å
 R factor = 0.037
 wR factor = 0.104
Data-to-parameter ratio = 13.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

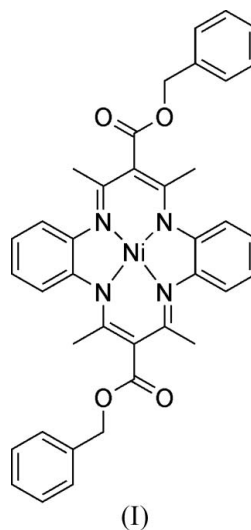
The title compound, $[Ni(C_{38}H_{34}N_4O_4)]$, is a four-coordinate nickel(II) complex of the 5,15-dihydro-7,16-bis(benzyloxycarbonyl)-6,18,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine ligand, which forms a saddle-shaped molecule with divergent concave surfaces. The molecules assemble in the crystal structure *via* C—H \cdots O interactions with the ester carbonyl O atoms and C—H $\cdots\pi$ interactions with the propanediiminate portion of the complex.

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Comment

The functionalization of dibenzotetraaza[14]annulene complexes of nickel(II) at the *meso* positions with alkoxy-carbonyl and aryloxy-carbonyl groups has recently been reported (Eilmes, Ptaszek & Zielińska, 2001). An extensive set of derivatives has been developed which are of interest as supramolecular hosts (Eilmes, Michalski & Zielińska, 2001; Eilmes *et al.*, 2002, 2003; Rodakiewicz-Nowak *et al.*, 2005). The structure of the title compound (Eilmes *et al.* 2003), (I), was determined as part of a study of dibenzotetraaza[14]annulene hosts for fullerenes. The divergent concave surfaces of tetraazaannulene complexes have been shown to interact with fullerenes in cocrystallate structures (Andrews *et al.*, 1998, 1999; Croucher *et al.*, 1999)



The molecular structure of (I) is shown in Fig. 1. The nickel tetraazaannulene complex is saddle-shaped, with two concave surfaces formed from the NiN₄ plane with either the two benzenoid rings or the two 2,4-pentanediiiminate groups. This is due to steric interactions between the methyl groups and the chelate benzene rings (C22—H22 \cdots C11 = 2.536 Å, C13—

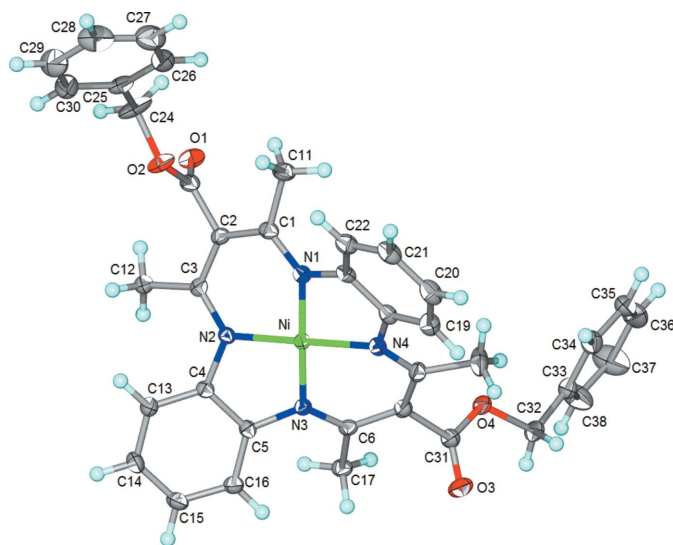


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids for non-H atoms and H atoms as arbitrary spheres (*X-SEED*; Barbour, 2001).

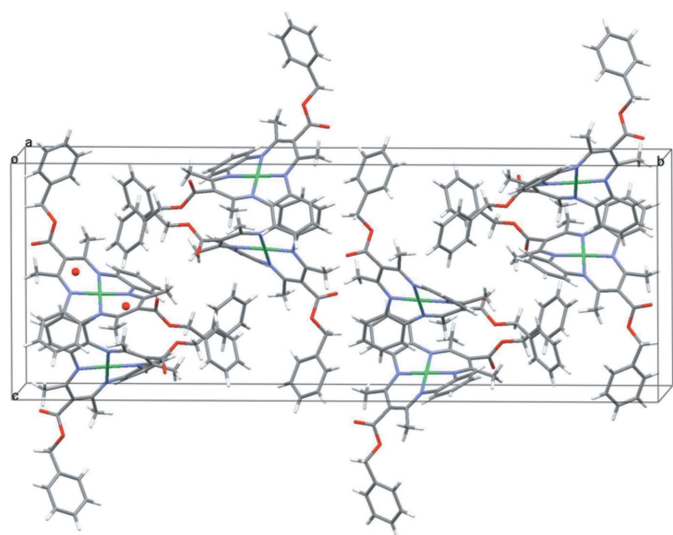


Figure 2
Packing arrangement of complex (I) in the crystal structure, showing the C–H... π interactions to the propanediiminato portion of the complex (*MERCURY*; Macrae *et al.*, 2006).

H13...C12 = 2.500 Å, C16–H16...C17 = 2.539 Å, C19–H19...C18 = 2.495 Å) (Cotton & Czuchajowska, 1990). The Ni atom, coordinated in a near-planar geometry (Table 1), lies 0.018 (1) Å out of the N₄ plane (r.m.s. deviation 0.0093 Å). The angles between the benzene ring mean planes C9/C10/C19–C22 (r.m.s. deviation 0.0135 Å) and C4/C5/C13–C16 (r.m.s. deviation 0.0147 Å) and the N₄ plane are 149.50 (9) and 151.79 (9)°, respectively, whilst in the other concave surface the angle between the pentanediiminato groups N1/N2 (r.m.s. deviation 0.0191 Å) and N3/N4 (r.m.s. deviation 0.0210 Å) and the N₄ plane are 155.67 (9) and 154.92 (11)°, respectively. The angle between the benzene planes is 121.29 (9)° and that between the pentanediiminato groups is 130.60 (9)°. These

values are comparable with those observed in the related nickel tetramethyltetraazaannulene complexes (Andrews *et al.*, 1999; Wang *et al.*, 1982). The ester groups on the methine atoms C2 and C7 are arranged *anti* with respect to the N₄ mean plane.

The molecules of (I) assemble in the crystal structure as shown in Fig. 2. A phenyl ring from the benzyl ester, C25–C30, approaches the centre of a neighbouring complex, with the H atoms on C28 and C29 centred over the N1/N2 and N3/N4 pentanediiminato groups (C28–H28...N3/N4 centroid Cg1 distance = 2.871 Å, C29–H29...N1/N2 centroid Cg2 distance = 2.880 Å). On the opposite face of the complex there are two longer C–H to centroid interactions from C14–H14 in a benzenoid ring of the complex (C14–H14...Cg1 = 2.908 Å) and a methyl group (C12–H12C...Cg2 = 3.301 Å). The two ester groups have C–H...O interactions, one, O2, with an aryl (C16–H16...O3 = 2.427 Å) and methyl (C17–H17A...O3 = 2.392 Å) H atoms, and the other, O1, with aryl (C20–H20...O1 = 2.626 Å and C21–H21...O1 = 2.539 Å) and methyl (C11–H11C...O1 = 2.587 Å) H atoms.

Experimental

Complex (I) was prepared by the method of Eilmes *et al.* (2003) and characterized by ¹H NMR and FAB mass spectrometry. Crystals were grown by layering of hexane over a CDCl₃ solution of (I).

Crystal data

[Ni(C ₃₈ H ₃₄ N ₄ O ₄)]	Z = 8
<i>M_r</i> = 669.40	<i>D_x</i> = 1.388 Mg m ⁻³
Orthorhombic, <i>Pbca</i>	Mo K α radiation
<i>a</i> = 10.6079 (2) Å	μ = 0.65 mm ⁻¹
<i>b</i> = 40.5916 (2) Å	<i>T</i> = 150 (2) K
<i>c</i> = 14.8774 (2) Å	Plate, red
<i>V</i> = 6406.08 (15) Å ³	0.36 × 0.32 × 0.16 mm

Data collection

Siemens SMART CCD area-detector diffractometer	33114 measured reflections
ω scans	5855 independent reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	4985 reflections with <i>I</i> > 2 σ (<i>I</i>)
<i>T</i> _{min} = 0.799, <i>T</i> _{max} = 0.903	<i>R</i> _{int} = 0.035
	θ _{max} = 25.4°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 14.0271P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.104$	$(\Delta/\sigma)_{\max} = 0.011$
<i>S</i> = 0.85	$\Delta\rho_{\max} = 0.27 \text{ e } \text{Å}^{-3}$
5855 reflections	$\Delta\rho_{\min} = -0.29 \text{ e } \text{Å}^{-3}$
428 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Ni–N1	1.854 (2)	Ni–N4	1.867 (2)
Ni–N3	1.856 (2)	Ni–N2	1.867 (2)
N1–Ni–N3	178.30 (9)	N1–Ni–N2	94.23 (8)
N1–Ni–N4	85.66 (9)	N3–Ni–N2	86.06 (8)
N3–Ni–N4	94.04 (9)	N4–Ni–N2	179.47 (9)

H atoms were placed in calculated positions and refined using a riding model [C–H = 0.95–0.99 Å), with $U_{\text{iso}}(\text{H})$ values of 1.2 or 1.5 times $U_{\text{eq}}(\text{C})$. Methyl groups were rotated to fit the H-atom positions to the observed electron density.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINTE* (Siemens, 1995); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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