metal-organic papers

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
H-atom completeness 91%
Disorder in solvent or counterion
R factor = 0.054
wR factor = 0.137
Data-to-parameter ratio = 12.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

A new nickel(II) complex with a [14]N4 macrocyclic ligand

The title compound, (9,20-dichloro-12,17-diphenyl-2,4,13,16-tetraazatricyclo[16.4.0.0^{6,11}]docosa-6,8,10,12,16,18,20,22-octa-ene-3,4-dionato)nickel(II) methanol hemisolvate, [Ni(C$_{30}$H$_{20}$-Cl$_2$N$_4$O$_2$)]·0.5CH$_3$OH, has a square-planar coordination geometry around the Ni^{II} ion. The two phenyl groups of the macrocyclic ligand are nearly perpendicular to the coordination plane. The solvent methanol molecule is disordered over two sites, near to a twofold axis.

Comment

The properties of macrocyclic transition metal complexes have attracted much attention (Melson, 1979; Zhang *et al.*, 2003; Wang *et al.*, 2004). As part of our ongoing investigation of macrocyclic complexes, we recently prepared the title Ni^{II} complex, (I), with a [14]N4 macrocyclic ligand and present its crystal structure here.
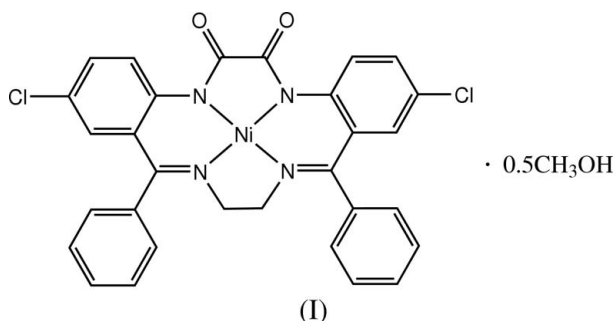
The molecular structure of (I) is shown in Fig. 1. The [14]N4 macrocyclic ligand, 2,3-dioxo-5,6:13,14-dichlorobenzo-7,12-
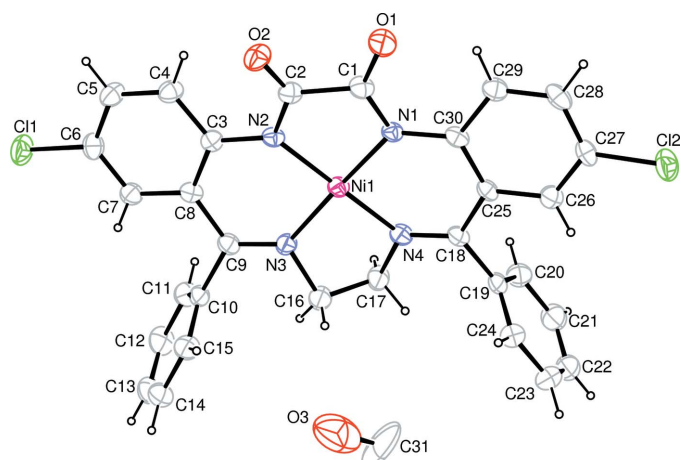

Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids (arbitrary spheres for H atoms).

diphenyl-1,4,8,11-tetraazacyclotetradeca-7,11-diene (*L*), chelates to the Ni^{II} ion *via* the deprotonated oxamide N atoms (N1 and N2) and imine N atoms (N3 and N4), to form a square-planar coordination geometry, with the maximum deviation from the mean coordination plane being 0.0668 (18) Å for atom N3. The two phenyl planes are nearly perpendicular to the coordination plane, the dihedral angles being 87.04 (14)° (the C10-ring) and 64.71 (14)° (the C19-ring). The Ni—N bonds, ranging from 1.868 (4) to 1.885 (3) Å (Table 1), are comparable with those found in related compounds (Li *et al.*, 2003).

Experimental

A methanol solution (50 ml) containing *L* (10 mmol), Ni(CH$_3$-COO)$_2$·2H$_2$O (10 mmol) and NaOH (20 mmol) was refluxed for 6 h. After cooling to room temperature, the orange precipitate which formed was separated by filtration. Single crystals of (I) were obtained by recrystallization from a methanol solution.

Crystal data

[Ni(C$_{30}$H$_{20}$Cl$_2$N$_4$O$_2$)]·0.5CH$_4$O	$D_x = 1.552$ Mg m^{-3}
$M_r = 613.63$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 833
$a = 29.869$ (9) Å	reflections
$b = 7.268$ (2) Å	$\theta = 1.5$–25.1°
$c = 26.307$ (8) Å	$\mu = 0.98$ mm^{-1}
$\beta = 113.126$ (5)°	$T = 293$ (2) K
$V = 5252$ (3) Å^3	Block, orange
$Z = 8$	$0.20 \times 0.14 \times 0.12$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	4676 independent reflections
	2876 reflections with $I > 2\sigma$
φ and ω scans	$R_{int} = 0.061$
Absorption correction: multi-scan	$\theta_{max} = 25.1°$
(*SADABS*; Sheldrick, 1996)	$h = -35 \rightarrow 33$
$T_{min} = 0.846$, $T_{max} = 0.890$	$k = -8 \rightarrow 8$
13262 measured reflections	$l = -16 \rightarrow 31$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.054$	$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2]$
$wR(F^2) = 0.137$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
4676 reflections	$\Delta\rho_{max} = 0.42$ e Å^{-3}
370 parameters	$\Delta\rho_{min} = -0.50$ e Å^{-3}

Table 1
Selected bond lengths (Å).

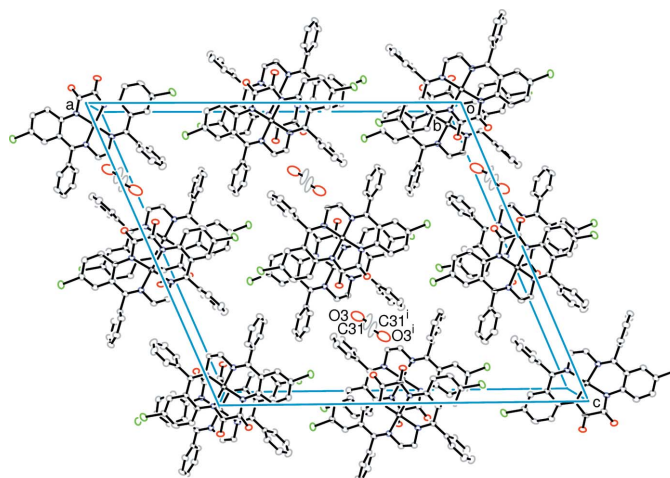|			
Ni1—N1	1.885 (3)	N2—C2	1.359 (6)
Ni1—N2	1.874 (4)	N2—C3	1.409 (5)
Ni1—N3	1.880 (4)	N3—C9	1.298 (5)
Ni1—N4	1.868 (4)	N3—C16	1.479 (6)
N1—C1	1.350 (6)	N4—C17	1.473 (6)
N1—C30	1.403 (6)	N4—C18	1.301 (6)

Figure 2
A packing diagram, showing the extensive space around the solvent methanol molecules [symmetry code: (i) $1 - x, y, 3/2 - z$].

The solvent methanol molecule, near a twofold axis, is disordered over two sites. The site occupancies were refined and converged to 0.532 (3) and 0.554 (3), and were fixed at 0.5 in the final cycles of refinement. H atoms bonded to the disordered methanol molecule were not located. Other H atoms were placed in calculated positions, with C—H = 0.93 (aromatic) or 0.97 Å (methylene) and included in the refinement in the riding-model approximation, with U_{iso}(H) = $1.2U_{eq}$(C).

Data collection: *SMART* (Bruker 1997); cell refinement: *SAINT* (Bruker 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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