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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(C-C)$ = 0.006 Å
Disorder in solvent or counterion
R factor = 0.047
wR factor = 0.159
Data-to-parameter ratio = 15.2

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

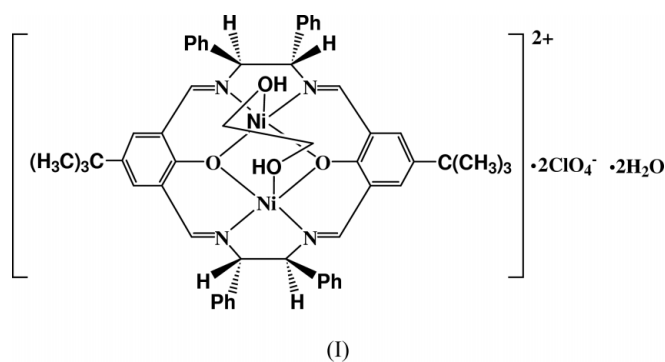
[μ -10,21-Di-*tert*-butyl-4(*S*),5(*S*),15(*S*),16(*S*)-tetraphenyl-3,6,14,17-tetraazatricyclo[17.3.1.18,12]-tetracos-1(23),2,6,8,10,12(24),13,17,19,21-decaene-23,24-diolato)(μ -ethylene glycol)-dinickel(II) diperchlorate dihydrate

Received 8 May 2003
Accepted 10 June 2003
Online 24 June 2003

In the title compound, $[Ni_2(C_{52}H_{50}N_4O_2)(C_2H_6O_2)](ClO_4)_2 \cdot 2H_2O$, the two Ni atoms are bridged by two O atoms from the Robson macrocyclic ligand, forming a parallelogram, which has a twofold axis. The macrocyclic plane is formed from an Ni_2O_2 center and four N atoms from the ligand. Above the macrocyclic plane an ethylene glycol molecule bridges the two Ni atoms, and the coordination geometry around each Ni atom is square pyramidal.

Comment

It is well known that dinuclear cores exist at the active sites of many metalloenzymes and play an essential role in biological systems (Furuta *et al.*, 1999; Arimura *et al.*, 2001). The two cavities of the Robson macrocyclic Schiff base ligand, RobsonH₂, can accommodate two metal ions, forming a planar complex [Tandon *et al.*, 1992; RobsonH₂ = 10,21-di-*tert*-butyl-4,5,15,16-tetraphenyl-3,6,14,17-tetraazatricyclo[17.3.1.18,12]-tetracos-1(23),2,6,8,10,12(24),13,17,19,21-decaene-23,24-diol]. In the present study, the chiral RobsonH₂ ligand was derived from the condensation of 2,6-diformyl-*o*-methylphenol and 1(*S*),2(*S*)-diphenyl-1,2-diaminoethane in the presence of NaOH, and the title dinuclear Ni^{II} compound, (I), was synthesized in order to investigate its biochemical effect. In this paper, the crystal structure of (I) is reported.



The two Ni atoms are bridged by O1 and O1ⁱ atoms, forming a parallelogram, which has a twofold axis (Fig. 1 and Table 1). There are also four N atoms from the ligand coordinated to the two Ni atoms in a macrocyclic plane. Above the plane, two O atoms from a glycol molecule coordinate to two Ni atoms in the axial directions. The coordination geometry around each Ni atom is square pyramidal. In the basal planes of the square pyramids, the two Ni atoms are exposed. This may be the catalytic active site of the complex. The crystal structure

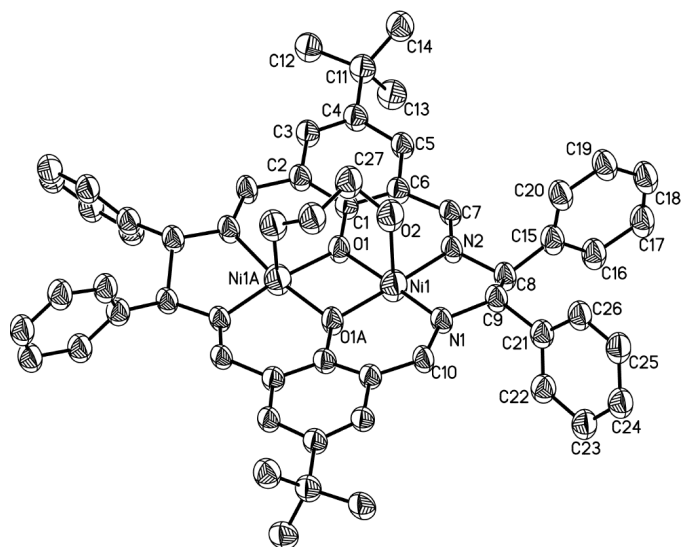


Figure 1
A view of the molecular structure of (I), showing 50% displacement ellipsoids for non-H atoms. Suffix *A* corresponds to symmetry code *i* in Table 1.

contains O—H...O intermolecular hydrogen bonds (Fig. 2 and Table 2).

Experimental

To a solution of 2,6-diformyl-4-*tert*-butylphenol (1 mmol) in 5 ml ethanol at room temperature, NaOH ethanol solution (5 ml, 0.2 *M*) was added. This mixture was stirred for 1 h and a yellow precipitate appeared. 1(*S*),2(*S*)-Diphenyl-1,2-diaminoethane (1 mmol) dissolved in ethanol was then added and the resulting mixture stirred at room temperature for 0.5 h. After that, a solution of Ni(ClO₄)₂ in ethanol (5 ml, 0.2 *M*) was added and stirring continued for another 2 h. The reaction mixture was filtered and the precipitates obtained were washed with ethanol and dried in a vacuum. Crystals of (I) were grown from an ethanol–ethylene glycol solution.

Crystal data

[Ni ₂ (C ₅₂ H ₅₀ N ₄ O ₂)(C ₂ H ₆ O ₂)]-(ClO ₄) ₂ ·2H ₂ O	Mo <i>K</i> α radiation
<i>M_r</i> = 1177.38	Cell parameters from 25 reflections
Tetragonal, <i>P</i> 4 ₂ 12	θ = 2.2–16.7°
<i>a</i> = 11.536 (3) Å	μ = 0.82 mm ⁻¹
<i>c</i> = 43.015 (3) Å	<i>T</i> = 293 (2) K
<i>V</i> = 5724 (2) Å ³	Block, orange
<i>Z</i> = 4	0.35 × 0.29 × 0.27 mm
<i>D_x</i> = 1.366 Mg m ⁻³	

Data collection

Siemens <i>P</i> 4 diffractometer	<i>R</i> _{int} = 0.011
ω scans	θ _{max} = 26.0°
Absorption correction: ψ scan (XPRED in SHELXTL; Bruker, 2000)	<i>h</i> = -9 → 13
<i>T</i> _{min} = 0.750, <i>T</i> _{max} = 0.799	<i>k</i> = -14 → 13
8048 measured reflections	<i>l</i> = -52 → 51
5296 independent reflections	3 standard reflections every 97 reflections
4763 reflections with <i>I</i> > 2σ(<i>I</i>)	intensity decay: 4.0%

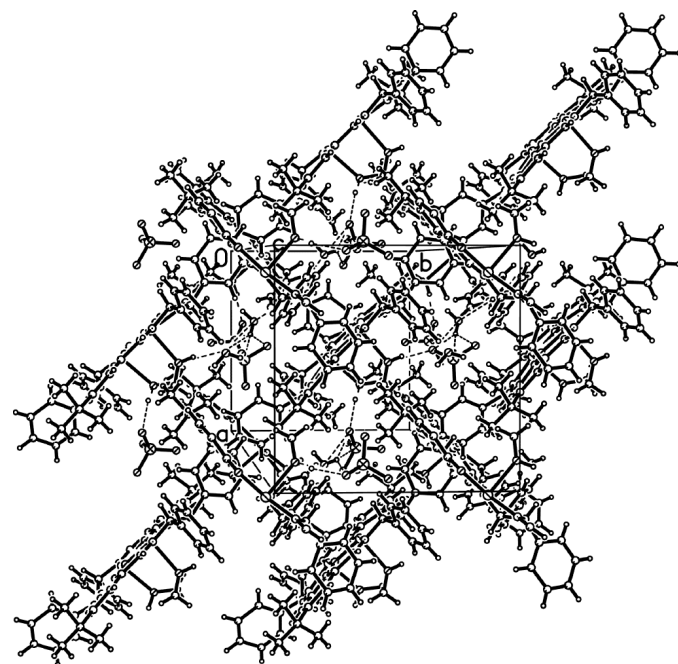


Figure 2
The crystal packing of (I), viewed approximately down the *c* axis. Dashed lines indicate the hydrogen bonds.

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.105P)^2 + 1.99P]$
$R[F^2 > 2\sigma(F^2)] = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.159$	$(\Delta/\sigma)_{\max} < 0.001$
<i>S</i> = 1.09	$\Delta\rho_{\max} = 0.49 \text{ e \AA}^{-3}$
5296 reflections	$\Delta\rho_{\min} = -0.58 \text{ e \AA}^{-3}$
348 parameters	Absolute structure: Flack (1983), 2037 Friedel pairs
H-atom parameters constrained	Flack parameter = 0.02 (2)

Table 1

Selected geometric parameters (Å, °).

Ni1—O1 ⁱ	1.837 (3)	Ni1—N1	1.901 (3)
Ni1—N2	1.874 (3)	Ni1—O2	2.347 (4)
Ni1—O1	1.899 (3)	Ni1—Ni1 ⁱ	2.8905 (12)
O1 ⁱ —Ni1—N2	172.65 (13)	O1—Ni1—O2	88.59 (12)
O1 ⁱ —Ni1—O1	78.35 (12)	N1—Ni1—O2	86.02 (14)
N2—Ni1—O1	95.77 (12)	O1 ⁱ —Ni1—Ni1 ⁱ	40.09 (8)
O1 ⁱ —Ni1—N1	96.12 (12)	N2—Ni1—Ni1 ⁱ	134.29 (10)
N2—Ni1—N1	90.18 (13)	O1—Ni1—Ni1 ⁱ	38.53 (8)
O1—Ni1—N1	171.78 (14)	N1—Ni1—Ni1 ⁱ	135.13 (10)
O1 ⁱ —Ni1—O2	96.92 (13)	O2—Ni1—Ni1 ⁱ	89.93 (8)
N2—Ni1—O2	87.26 (14)		

Symmetry code: (i) *y*, *x*, -*z*.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2A...O14	0.97	1.82	2.744 (5)	159
O3—H3B...O4	0.85	2.37	3.104 (8)	144
O4—H4C...O14 ⁱⁱ	0.85	2.17	2.898 (7)	144
O4—H4C...O12 ⁱⁱ	0.85	2.41	2.956 (8)	123

Symmetry code: (ii) 1 + *y*, *x*, -*z*.

There are two independent water molecules of crystallization. One, O3, lies on a twofold axis, while the other, O4, shows a positional disorder over two sites, each with 50% probability. The positions of all H atoms were fixed geometrically and distances to H atoms were set by the program. H atoms were fixed geometrically with distances to H atoms in the range 0.85–0.98 Å and given U_{iso} values 1.2–1.5 times the U_{eq} value of the parent atom.

Data collection: *CAD-4 SDP/VAX* (Enraf–Nonius, 1989); cell refinement: *CAD-4 SDP/VAX*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by the Science Foundation of Gansu Province of China (No. ZR001-A25-001-Z).

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