Acta Crystallographica Section E
**Structure Reports**
**Online**
ISSN 1600-5368

# [(1*RS*,7*RS*,8*RS*,14*RS*)-5,12-Dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene-$\kappa^4N^{1,4,8,11}$]nickel(II) perchlorate

**Neil F. Curtis* and David C. Weatherburn**

School of Chemical and Physical Sciences,
Victoria University of Wellington, Box 600,
Wellington, New Zealand

Correspondence e-mail: neil.curtis@vuw.ac.nz

Received 5 July 2002
Accepted 9 July 2002
Online 19 July 2002

The title compound, $[Ni(C_{24}H_{32}N_4)](ClO_4)$, has singlet ground-state nickel(II) complex cations with tetrahedrally twisted [±0.013 (4) Å] square-planar coordination by four N atoms of the 14-membered diamine–diimine tetraaza-macrocycle and perchlorate anions. A perchlorate O atom is sited near the tetragonal axis [Ni···O 2.694 (4) Å], with both N—H groups oriented towards the other side of the plane forming N—H···O hydrogen bonds to O atoms of different perchlorate ions, with no O atom near the nickel(II) tetragonal axis.

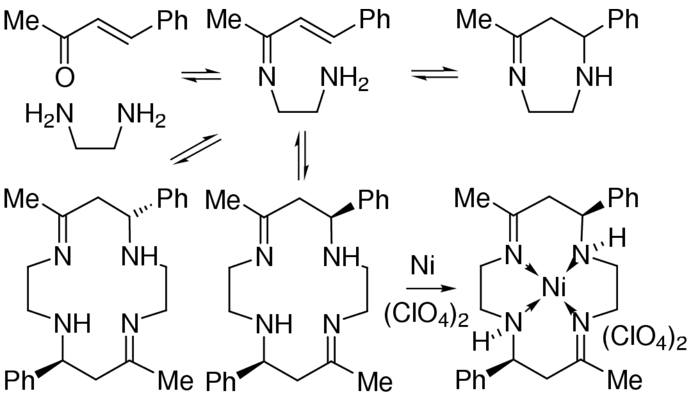
**Key indicators**

Single-crystal X-ray study
$T$ = 158 K
Mean $\sigma$(C–C) = 0.008 Å
$R$ factor = 0.041
$wR$ factor = 0.083
Data-to-parameter ratio = 13.1

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

## Comment

The *meso* macrocyclic diamine–diimine (7*RS*,14*SR*)-5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (mL) is formed by reaction of ethane-1,2-diamine with benzylidene acetone (Hideg & Lloyd, 1970; 1971; Hankovszky *et al.*, 1974). Compounds of mL with nickel(II) and copper(II) (Cook *et al.*, 1973), cobalt(III) (Curtis, 1973; Hay & Gidney, 1976) and rhodium(III) (Hay & Gidney, 1976) have been described, and the structure of *trans*-$[Cu(mL)(NO_3)_2]$ with the *trans*-C-*meso* configuration has been determined (Ferguson *et al.*, 1978).



(I)

Later work (Hankovszky *et al.*, 1979; Lloyd *et al.*, 1981) showed that solutions of 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene in polar solvents contain at least 4-methyl-6-phenyl-3-azahexa-3,5-diene-1-amine, its monocyclized derivative (the seven-membered cyclic imine 5-methyl-7-phenyl-2,3,6,7-tetrahydro-1*H*-1,4-diazapine) and the *meso* and *rac* cyclic dimers of this, mL and rL, which interconvert (see *Scheme*). The crystalline material is isomerically pure ml, but mL and rL are present in solutions in polar solvents. Reaction of ml in methanol with nickel(II) perchlo-

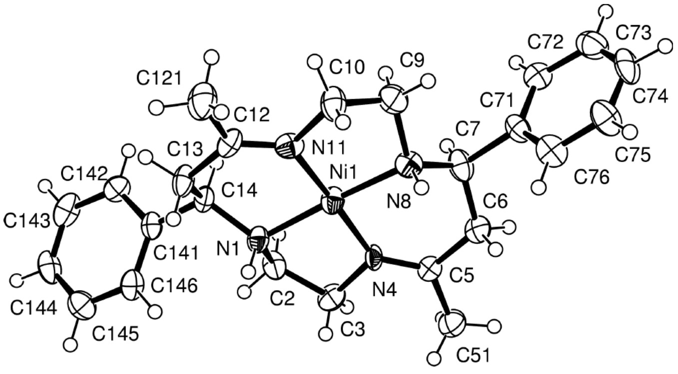


**Figure 1**
The cation of the title compound, drawn with displacement ellipsoids at the 50% probability level. H atoms are shown as circles of arbitrary radii.

rate yields a mixture of the *meso*- and *rac*-isomeric macrocycle compounds, $[Ni(mL)](ClO_4)_2$ and $[Ni(rL)](ClO_4)_2$, in proportions depending on reaction conditions (Curtis, 2001). Procedures for separating these isomeric nickel(II) compounds by crystallization of sparingly soluble bis-acetonitrile or bis-ammine adducts of $[Ni(mL)](ClO_4)_2$ have been described. The X-ray crystal structure of $[Ni(rL)](ClO_4)_2$, (I), is now reported.

The asymmetric unit of (I) contains the cation [(1*RS*,7*RS*,8*RS*,14*RS*)-5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene]nickel(II), *N*-*rac*-[Ni(rL)]$^{2+}$, shown in Fig. 1, which has approximate twofold symmetry, and two perchlorate counter-ions.

The cation has the macrocycle in square-planar coordination to singlet ground-state nickel(II), with slight [±0.013 (4) Å] tetrahedral twisting of the $N_4$ plane, with the nickel 0.077 (4) Å from this plane, displaced towards an axial perchlorate O atom (below). The bond lengths and angles about N4—C5 and N11—C12 (Table 1) confirm the presence and location of the two imine functions.

The groups N1—H1 and N8—H8 are on the same side of the molecular plane, with C7—H7 and C14—H14 on the other side, confirming the configuration 1*RS*,7*RS*,8*RS*,14*RS*, which molecular mechanics calculations indicated was least strained for this cation (Curtis, 2001).

The Ni—N distances are normal for singlet ground state nickel(II) compounds of amine–imine macrocyles, with mean values $Ni—N_{amine}$ 1.964 (6) Å and $Ni—N_{imine}$ 1.923 (6) Å, with the bond to imine N atom shorter, as is usual.

The displacement (Å, s.u. < 0.005 Å) of atoms from the $NiN_2$ chelate planes are, for the Ni1/N1/N4 plane: C2 −0.64, C3 0.01; Ni1/N8/N11 plane: C9 0.66, C10 −0.03 (both five-membered chelate rings are in asymmetric *gauche* conformations); Ni1/N4/N8 plane: C5 0.09 (C51 0.38), C6 −0.06, C7 −0.72 (C71 −0.78); Ni1/N11/N1 plane: C12 0.08 (C121 0.38), C13 −0.02, C14 −0.76 (C141 −0.93) (both six-membered chelate rings are in asymmetric twist conformations). The substituents are all equatorially oriented.

The perchlorate atom O21 is axially sited, with Ni1—O21 2.694 (4) Å, O21—Ni1—N1 93.7 (2)°, O21—Ni1—N8 90.0 (2)°, O21—Ni1—N4 98.6 (2)° and O21—Ni1—N11 86.7 (2)°. The two N—H groups are oriented towards the opposite side of the plane, hydrogen bonded to O atoms of different perchlorate ions [N8···O11$^{i}$ 2.930 (4) Å, H8···O11$^{i}$ 2.12 Å, N8—H8···O11$^{i}$ 144°; N1···O23$^{i}$ 2.856 (4) Å, H1···O23$^{i}$ 2.86 Å, Ni—H1···O23$^{i}$ 132°; symmetry code: (i) $-x+1/4$, $y+1/4$, $z+1/4$]. There is no O atom near the axial site on this side of the plane.

## Experimental

*N*-*rac*-$[Ni(rL)](ClO_4)_2$ was prepared as reported by Curtis (2001) and crystallized from an acetone/water solution.

### *Crystal data*

$[Ni(C_{24}H_{32}N_4)](ClO_4)$
$M_r = 634.13$
Orthorhombic, *Fdd*2
$a = 40.66$ (2) Å
$b = 29.40$ (1) Å
$c = 9.267$ (4) Å
$V = 11078$ (8) Å$^3$
$Z = 16$
$D_x = 1.521$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 4795 reflections
$\theta = 2.4$–23.6°
$\mu = 0.95$ mm$^{-1}$
$T = 158.2$ (2) K
Needle, orange
0.85 × 0.13 × 0.07 mm

### *Data collection*

Siemens CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: none
34536 measured reflections
4658 independent reflections
2435 reflections with $I > 2\sigma(I)$
$R_{int} = 0.106$
$\theta_{max} = 26.3°$
$h = -50 \rightarrow 50$
$k = -36 \rightarrow 36$
$l = -6 \rightarrow 11$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.083$
$S = 0.76$
4658 reflections
356 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.016$
$\Delta\rho_{max} = 0.54$ e Å$^{-3}$
$\Delta\rho_{min} = -0.36$ e Å$^{-3}$
Absolute structure: Flack (1983), 1661 Friedel pairs
Flack parameter = 0.020 (18)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ni1—N4 | 1.919 (4) | Ni1—N1 | 1.972 (4) |
| Ni1—N11 | 1.927 (4) | N4—C5 | 1.281 (6) |
| Ni1—N8 | 1.955 (4) | N11—C12 | 1.300 (6) |
| | | | |
| N4—Ni1—N11 | 174.63 (19) | N4—C5—C6 | 123.0 (5) |
| N4—Ni1—N8 | 93.64 (17) | N4—C5—C51 | 121.9 (5) |
| N11—Ni1—N8 | 86.14 (19) | C6—C5—C51 | 115.0 (4) |
| N4—Ni1—N1 | 86.12 (17) | N11—C12—C121 | 122.6 (5) |
| N11—Ni1—N1 | 93.75 (17) | N11—C12—C13 | 121.4 (5) |
| N8—Ni1—N1 | 176.3 (2) | C121—C12—C13 | 116.0 (5) |

H atoms were included in the riding-model approximation

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-32 (Johnson & Burnett, 1999); software used to prepare material for publication: *PARST* (Nardelli, 1995).

The diffraction data were collected by Professor W. T. Robinson, Chemistry Department, University of Canterbury.

We thank Dr G. J. Gainsford, Industrial Research Ltd, for assistance.

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