

[(1*RS*,4*RS*)-5,5,7,13,15,15-Hexamethyl-1,4,8,12-tetraazacyclopentadeca-7,12-diene-*N*¹,*N*⁴,*N*⁸,*N*¹²]nickel(II) diperchlorate

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Key indicators

Single-crystal X-ray study
 T = 203 K
 Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
 Disorder in solvent or counterion
 R factor = 0.042
 wR factor = 0.105
 Data-to-parameter ratio = 16.0

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

The title compound, $[\text{Ni}(\text{C}_{17}\text{H}_{34}\text{N}_4)](\text{ClO}_4)_2$, has singlet ground-state nickel(II) complex cations in tetrahedrally twisted square-planar coordination by the four N atoms of the 15-membered diamine diimine tetraazamacrocycle and disordered perchlorate anions, linked into molecular clusters by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and weak $\text{Ni}\cdots\text{O}$ interactions. The cation has approximate twofold symmetry, with bond lengths $\text{Ni}-\text{N}_{\text{amine}}$ of 1.920 (2) and 1.924 (2) \AA , and $\text{Ni}-\text{N}_{\text{imine}}$ of 1.915 (2) and 1.929 (2) \AA , and *trans*- $\text{N}-\text{Ni}-\text{N}$ angles of 165.1 (1) and 163.4 (1) $^\circ$, with the shortest $\text{Ni}\cdots\text{O}$ distance being 3.27 (3) \AA .

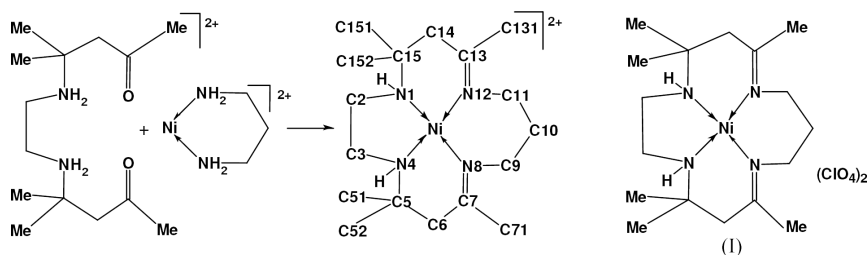
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Comment

The preparations of hexamethyl-diamine-diimine macrocycle compounds of nickel(II) and copper(II) by reactions with acetone of the metal-ion compounds of diamines with varying chain length have been described (Curtis, 1982). Reaction of equimolar amounts of tris(ethane-1,2-diamine)- and tris(propane-1,3-diamine)nickel(II) perchlorates with acetone yields $[\text{Ni}(\textit{trans}\text{-}[15]\text{diene})](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ (*trans*-[15]diene 5,7,7,13,15,14-hexamethyl-1,5,8,12-tetraazacyclopentadeca-4,12-diene) (Curtis & House, 1967; Curtis & Gainsford, 1986), while reaction of 4,4,9,9-tetramethyl-5,8-diazoniumdodecane-2,11-dione diperchlorate [formed by reaction of ethane-1,2-diammonium perchlorate with acetone (Curtis, 1982)] with (propane-1,3-diamine)nickel(II) or -copper(II) perchlorates yields 5,5,7,13,15,15-hexamethyl-1,4,8,12-tetraazacyclopentadeca-7,12-diene (*cis*-[15]diene) complex cations (Curtis & Gainsford, 1986). The structures of *N-rac*- $[\text{Cu}(\textit{cis}\text{-}[15]\text{diene})_2]\text{Cl}(\text{ClO}_4)_3$ (Gladkikh & Curtis, 1996) and *N-rac*- $[\text{Ni}(\textit{trans}\text{-}[15]\text{diene})](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ (Curtis & Gainsford, 1986) have been reported.



The title compound, 1*RS*,4*RS*- $[\text{Ni}(\textit{cis}\text{-}[15]\text{diene})](\text{ClO}_4)_2$, (I), has discrete singlet ground-state nickel(II) square-planar complex cations and perchlorate anions, linked to form molecular clusters by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonding and weak $\text{Ni}\cdots\text{O}$ interactions (Fig. 1 and Table 1). The closest $\text{Ni}\cdots\text{O}$ contact, of 3.27 (3) \AA , indicates no significant axial coordina-

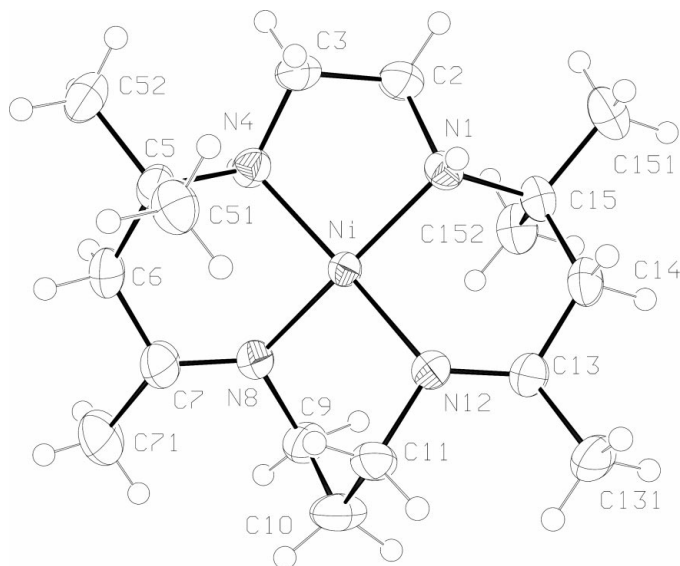


Figure 1
View of the title compound.

tion. The distances C7–N8 and N12–C13 and the angles about these atoms confirm the locations of two imine functions.

The cation shows approximate twofold symmetry through C10, Ni and the midpoint of C2–C3 (configuration *1RS,4RS*, *N-rac*). There is appreciable tetrahedral twisting of the coordination plane with displacements from the best N₄ plane of ± 0.26 Å. The chelate ring conformations and displacements of atoms from the relevant NiN₂ planes (Å, s.u. < 0.003 Å) are: N1–Ni–N4, *gauche*, C2, 0.433; C3, –0.253; N4–Ni–N8, half chair, C5, –1.99 (C51, –2.465; C52, –1.249); C6, –1.016; C7, 0.748 (C71, 0.664); N8–Ni–N12, *asym.-twist*, C9, –0.828; C10, 0.123; C11, 0.694; N12–Ni–N1, half-chair, C13, 0.618 (C131, 0.462); C14, 0.781; C15, 1.094 (C151, 1.072; C152, 2.448). The intracyclic angles at the central C atoms C5–C6–C7 and C13–C14–C15 of the trimethyl substituted chelate rings are, as usual, large (*cf.* angle C9–C10–C11).

The structure has weakly bound ‘molecules’, [Ni(*cis*-[15]diene)](ClO₄)₂, with a perchlorate ion above each face of the macrocycle, with weak Ni···O interactions, shorter for the minor oxygen sites [Ni···O12, 3.47 (1); Ni···O18, 3.27 (3), Ni···O23, 3.74 (1); Ni···O26, 3.71 (3) Å] and weak N–H···O hydrogen bonds, shorter for the major oxygen sites. These ‘molecules’ are linked by C–H···O interactions (Table 2).

The nickel(II) compound of a related 15-membered hexaaza macrocycle, which has the C⁹ and C¹¹ methylene groups of *cis*-[15]diene replaced by NH groups, has a similar structure, with the *N-rac*-configuration with approximate twofold symmetry, and with similar dimensions: Ni–N_{amine} 1.908 (4) and 1.913 (4) Å, Ni–N_{imine} 1.885 (4) and 1.902 (4) Å, and *trans*-N–Ni–N angles 167.9 (2) and 166.9 (2)° (Curtis *et al.*, 1998). The isomeric cation present for *N-rac*-[Ni(*trans*-[15]diene)](ClO₄)₂·H₂O has similar coordination geometry with Ni–N_{amine} 1.882 (4) and 1.913 (4) Å, Ni–N_{imine} 1.924 (4) and 1.896 (4) Å, and *trans*-N–Ni–N angles of 169.4 (2) and

166.1 (2)°, although this cation is saddle shaped. The general conformation and tetrahedral twisting of the NiN₄ group is also similar for *N-rac*-[Cu(*cis*-[15]diene)]₂Cl(ClO₄)₃ with *trans*-N–Cu–N angles 168.3 (3) and 158.0 (3)°.

The Ni–N distances observed for *N-rac*-[Ni(*cis*-[15]diene)](ClO₄)₂ are within the range found for singlet ground state nickel compounds of related 14-membered macrocycles for which many structures have been reported (Donnelly & Zimmer, 1999; Cambridge Structural Database, 2000), including the 14-membered homologue *N-rac*-[Ni(*cis*-[14]diene)](ClO₄)₂ [Ni–N_{amine} 1.927 (6) and Ni–N_{imine} 1.891 (6) Å] (Kilbourn *et al.*, 1969). *N-rac*-[Ni(*cis*-[15]diene)](ClO₄)₂ is unusual in that the Ni–N_{imine} distance Ni–N12 is longer than both Ni–N_{amine} distances, whereas bonds to imine nitrogen are more typically *ca* 0.03 Å shorter, as observed for *N-rac*-[Cu(*cis*-[15]diene)]₂Cl(ClO₄)₃.

The tetrahedral twisting of the N₄ plane for *N-rac*-[Ni(*cis*-[15]diene)](ClO₄)₂ is similar to that observed for other 15-membered tetraaza macrocycles coordinated to singlet ground-state nickel(II), and much greater than observed for related 14-membered macrocycle compounds, including *N-rac*-[Ni(*cis*-[14]diene)](ClO₄)₂, which has *trans*-N–Ni–N of 175.7 (3)°.

Experimental

N-rac-[Ni(*cis*-[15]diene)](ClO₄)₂ was prepared as reported by Curtis & Gainsford (1986) and crystallized from water.

Crystal data

[Ni(C₁₇H₃₄N₄)](ClO₄)₂
M_r = 552.09
Monoclinic, *P*2₁/*n*
a = 10.3529 (1) Å
b = 16.1128 (1) Å
c = 15.0400 (1) Å
 β = 107.025 (1)°
V = 2398.94 (3) Å³
Z = 4

D_x = 1.529 Mg m^{–3}
Mo *K*α radiation
Cell parameters from 8197 reflections
 θ = 1.9–27.5°
 μ = 1.08 mm^{–1}
T = 203 (2) K
Prism, orange
0.25 × 0.17 × 0.16 mm

Data collection

Siemens SMART CCD diffractometer
Area-detector ω scans
Absorption correction: multi-scan (Blessing, 1995)
*T*_{min} = 0.774, *T*_{max} = 0.879
14 323 measured reflections
5243 independent reflections

4531 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.002
 θ _{max} = 27.5°
h = –13 → 12
k = 0 → 20
l = 0 → 19
Intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.042
wR(*F*²) = 0.105
S = 1.06
5243 reflections
327 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0480P)^2 + 3.2464P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.001
 $\Delta\rho$ _{max} = 0.70 e Å^{–3}
 $\Delta\rho$ _{min} = –0.66 e Å^{–3}

Table 1

Selected geometric parameters (Å, °).

Ni—N8	1.915 (2)	Ni—N12	1.929 (2)
Ni—N4	1.920 (2)	C7—N8	1.346 (4)
Ni—N1	1.924 (2)	N12—C13	1.338 (4)
N8—Ni—N4	90.38 (10)	C7—N8—Ni	125.2 (2)
N8—Ni—N1	165.11 (11)	C9—N8—Ni	111.0 (2)
N4—Ni—N1	88.19 (9)	C11—C10—C9	112.6 (2)
N8—Ni—N12	93.73 (10)	C13—N12—C11	120.5 (2)
N4—Ni—N12	163.43 (11)	C13—N12—Ni	126.0 (2)
N1—Ni—N12	91.83 (10)	C11—N12—Ni	110.9 (2)
C7—C6—C5	120.5 (2)	N12—C13—C14	119.1 (3)
N8—C7—C6	118.3 (3)	N12—C13—C131	120.2 (3)
N8—C7—C71	120.1 (3)	C14—C13—C131	112.1 (2)
C6—C7—C71	113.1 (3)	C13—C14—C15	120.2 (2)
C7—N8—C9	120.0 (2)		

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>
N1—H1...O23	0.92	2.03	2.93 (1)	166
N1—H1...O25	0.92	2.24	3.13 (3)	163
N4—H4...O12	0.92	2.48	3.23 (1)	138
N4—H4...O14	0.92	2.17	3.06 (1)	163
N4—H4...O16	0.92	2.25	3.12 (2)	156
N4—H4...O18	0.92	2.45	3.16 (3)	134
C51—H51B...O26	0.97	2.51	2.98 (3)	110
C6—H6B...O16	0.98	2.27	3.07 (2)	137
C14—H14B...O25	0.98	2.46	3.28 (2)	140
C71—H71C...O17 ⁱ	0.97	2.48	2.96 (5)	111
C131—H13C...O15 ⁱⁱ	0.97	2.48	2.90 (5)	106

 Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, -y, -z$.

The perchlorate ions were refined as rigid groups with two sets of O-atom sites, both with large displacement parameters, O1–O4 and O5–O8 with occupancies of 0.887 and 0.123 about C11, and O21–O24 and O25–O28 with occupancies of 0.855 and 0.145 about C12, respectively.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SMART*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL93* (Sheldrick, 1993).

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