

(*C*-*rac*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane- κ^4 N)(nicotinato-*O,O'*)-nickel(II) perchlorateElena V. Basiuk,^{a*} Vladimir A. Basiuk,^b Simón Hernández-Ortega,^c Marcos Martínez-García^c and José-Manuel Saniger-Blesa^a^aCentro de Instrumentos, Universidad Nacional Autónoma de México, Circuito Exterior CU, 04510 México DF, Mexico, ^bInstituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Circuito Exterior CU, 04510 México DF, Mexico, and ^cInstituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior CU, 04510 México DF, Mexico

Correspondence e-mail: elenagd@servidor.unam.mx

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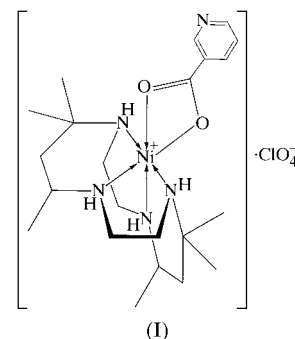
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In the title compound, $[\text{Ni}(\text{C}_6\text{H}_4\text{NO}_2)(\text{C}_{16}\text{H}_{36}\text{N}_4)]\text{ClO}_4$, the macrocyclic unit adopts a folded conformation, allowing the two carboxyl O atoms to occupy two neighbouring coordination sites and thus form an additional four-membered chelate ring. The less crowded side of the macrocycle (that with the two asymmetric C—H groups) is directed towards the nicotinate anion and the asymmetric C—CH₃ groups are directed away from it. The NH groups neighbouring the C—CH₃ groups are also directed away from the nicotinate anion, while those NH groups which are near to the geminal methyl groups are directed towards the nicotinate anion. Although the complex does not include water molecules, three types of hydrogen bond were found, involving NH groups of the macrocyclic ligand, pyridine N atoms and O atoms of the perchlorate anions.

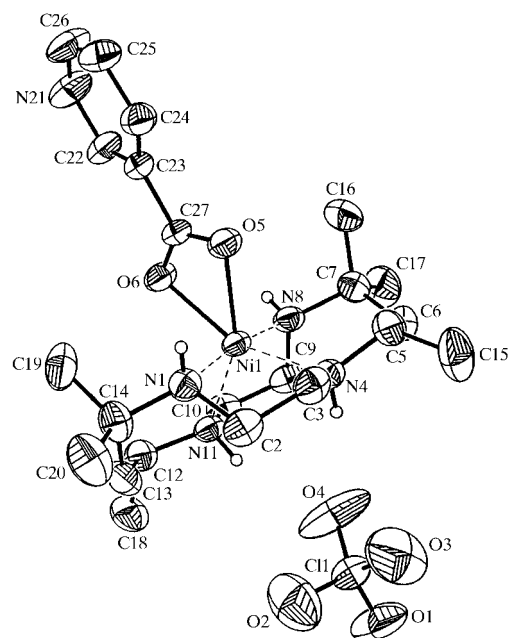
Comment

Many Ni^{II} complexes with saturated 12- to 16-membered tetraaza-macrocyclic ligands are known to exist both in a low-spin square-planar tetracoordinated form and in a high-spin octahedral hexacoordinated form (see, for example, Adam *et al.*, 1994, 1996). We are especially interested in the less studied (although known for more than three decades) 'Curtis-type' complexes with the common saturated ligand *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*rac*-Me₆[14]aneN₄) and carboxylic acids (Basiuk *et al.*, 2000; Curtis, 1964, 1968; Whimp *et al.*, 1970). In these complexes, the macrocyclic unit adopts a folded conformation, allowing the two carboxyl O atoms to occupy two neighbouring coordination sites and thus form a four-membered chelate ring. Until recently, the only known structurally characterized example of complexes of this type was $[\text{Ni}^{\text{II}}(\text{rac}\text{-Me}_6[14]\text{aneN}_4)]\text{-acetate}$

monoperchlorate (Whimp *et al.*, 1970); another example is a bridged complex, bis $[\text{Ni}^{\text{II}}(\text{rac}\text{-Me}_6[14]\text{aneN}_4)]\text{-2,5-pyridine-dicarboxylate}$ diperchlorate monohydrate, synthesized and characterized recently by us (Basiuk *et al.*, 2000). In addition, we have undertaken the preparation and X-ray analysis of the 3,5-pyridinedicarboxylic acid analogue of the latter. However, although good quality single crystals were obtained (after many unsuccessful attempts), they appeared to decay before the X-ray diffraction data collected were sufficient for structure solution.



In the present paper, we report the preparation and X-ray structure determination of another high-spin complex of the above type, namely (*C*-*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane- κ^4 N)(nicotinato-*O,O'*)nickel(II) perchlorate, (I). As in its acetate and 2,5-pyridinedicarboxylate analogues, the less crowded side of the macrocycle (that with the two asymmetric C—H groups) is directed towards the nicotinate anion and the asymmetric C—CH₃ groups are directed away from it. The NH groups of the macrocycle

**Figure 1**

The molecular structure of (I) drawn with 40% probability displacement ellipsoids. H atoms on C atoms have been omitted and H atoms on N atoms are shown as small spheres of arbitrary radii.

neighbouring the C—CH₃ groups are also directed away from the nicotinate anion, while those NH groups which are near to the geminal methyl groups are directed towards the nicotinate anion.

The macrocyclic units are folded around N1—Ni1—N8 [172.24 (13)°], with an N4—Ni1—N11 angle of 103.21 (13)°. These values are very close to the corresponding parameters for the macrocyclic unit in the bridged complex bis[Ni^{II}-(*rac*-Me₆[14]aneN₄)]-2,5-pyridinedicarboxylate diperchlorate monohydrate (*ca* 176 and 103°, respectively; Basiuk *et al.*, 2000). A dissimilarity between the two complexes occurs with the Ni—O distances, which are almost equal in the nicotinate [2.153 (3) and 2.156 (3) Å], but noticeably different in the bridged complex [2.123 (12) and 2.255 (13) Å], apparently due to a steric hindrance created by the second macrocyclic moiety. The mean Ni—N distance in (I) is 2.12 Å, which is typical for an octahedral triplet ground-state Ni^{II} atom coordinated to secondary amino groups (Whimp *et al.*, 1970).

Unlike the 2,5-pyridinedicarboxylate compound, and similar to [Ni^{II}(*rac*-Me₆[14]aneN₄)]-acetate monoperchlorate (Whimp *et al.*, 1970), complex (I) does not include water molecules. Nevertheless, there are three types of hydrogen bond involving NH groups of the macrocyclic ligand, pyridine N atoms and O atoms of the perchlorate anions (Fig. 2), namely N8—H8···N21, N4—H4···O4 and N11—H11···O4, respectively.

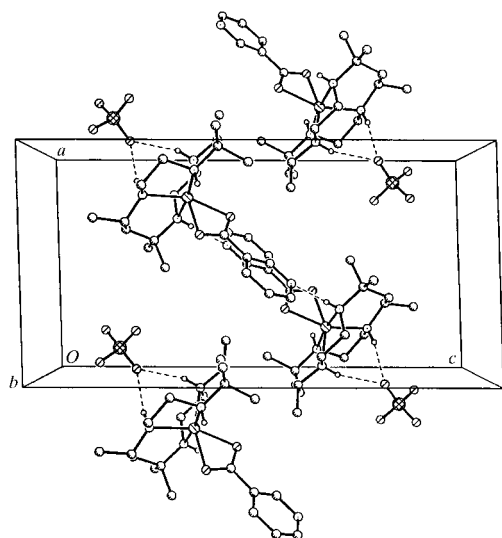


Figure 2
The packing diagram for (I).

Experimental

Caution: perchlorate salts of metal complexes are potentially explosive and should be handled with care. Nicotinic acid (Aldrich) was used without further purification. [Ni^{II}(*rac*-Me₆[14]aneN₄)](ClO₄)₂ was synthesized by complexation of the free ligand with Ni^{II} acetate in methanol, followed by the addition of perchloric acid (Curtis, 1964). The title complex was synthesized in a manner similar to that used for the 2,5-pyridinedicarboxylic acid analogue (Basiuk *et al.*, 2000), by dissolving [Ni^{II}(*rac*-Me₆[14]aneN₄)](ClO₄)₂ (0.54 g,

1 mmol) and nicotinic acid (0.25 g, 2 mmol) in water (100 ml) and adjusting the pH to *ca* 12 by adding NH₄OH. The solution was heated with stirring until half the solvent had evaporated. Violet–blue crystals of the product were filtered after standing for 2 d at room temperature. Crystals of (I) suitable for X-ray analysis were obtained by recrystallization from methanol.

Crystal data

[Ni(C₆H₄NO₂)(C₁₆H₃₆N₄)]ClO₄
M_r = 564.75
 Monoclinic, *P*2₁/*c*
a = 10.474 (2) Å
b = 13.221 (2) Å
c = 20.288 (3) Å
 β = 91.33 (1)°
V = 2808.7 (8) Å³
Z = 4

D_x = 1.336 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 50 reflections
 θ = 3.9–21.5°
 μ = 0.83 mm⁻¹
T = 293 (2) K
 Prism, violet
 0.36 × 0.24 × 0.16 mm

Data collection

Siemens *P4/PC* diffractometer
 ω scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
T_{min} = 0.755, *T_{max}* = 0.879
 5239 measured reflections
 4950 independent reflections
 2980 reflections with *I* > 2σ(*I*)

R_{int} = 0.057
 θ_{max} = 25°
h = 0 → 12
k = 0 → 15
l = -24 → 24
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.046
wR(*F*²) = 0.100
S = 0.96
 4950 reflections
 335 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.025P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.009
 $\Delta\rho_{\text{max}}$ = 0.70 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.35 e Å⁻³
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.00184 (16)

Table 1

Selected geometric parameters (Å, °).

Ni1—N4	2.097 (3)	Ni1—N1	2.141 (4)
Ni1—N11	2.101 (3)	Ni1—O6	2.153 (3)
Ni1—N8	2.127 (4)	Ni1—O5	2.156 (3)
N4—Ni1—N11	103.21 (13)	N11—Ni1—O5	157.86 (12)
N4—Ni1—N8	90.57 (14)	N8—Ni1—O5	101.28 (12)
N11—Ni1—N8	85.45 (14)	N1—Ni1—O5	85.62 (13)
N4—Ni1—N1	84.92 (14)	O6—Ni1—O5	61.43 (10)
N11—Ni1—N1	89.43 (14)	N4—Ni1—C27	128.25 (14)
N8—Ni1—N1	172.24 (13)	N11—Ni1—C27	128.51 (13)
N4—Ni1—O6	157.85 (12)	N8—Ni1—C27	94.57 (13)
N11—Ni1—O6	98.42 (12)	N1—Ni1—C27	93.17 (14)
N8—Ni1—O6	86.42 (12)	O6—Ni1—C27	30.66 (12)
N1—Ni1—O6	100.11 (12)	O5—Ni1—C27	30.78 (12)
N4—Ni1—O5	97.84 (12)		

The positional parameters of the H atoms bonded to N atoms were refined. Other H-atom positions were calculated geometrically and all H atoms were refined as riding, with *U*_{iso} = 1.2*U*_{eq} of the attached atom.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N8—H8 \cdots N21 ⁱ	0.75 (4)	2.54 (5)	3.263 (5)	161 (5)
N4—H4 \cdots O4	0.84 (4)	2.29 (5)	3.114 (6)	166 (4)
N11—H11 \cdots O4	0.86 (4)	2.26 (4)	3.064 (6)	157 (4)

Symmetry code: (i) $1 - x, -y, -z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1165). Services for accessing these data are described at the back of the journal.

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