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# (1,4,7,11,13-Pentaazacyclohexadecane-$\kappa^5N$)(perchlorato-$\kappa O$)nickel(II) Perchlorate

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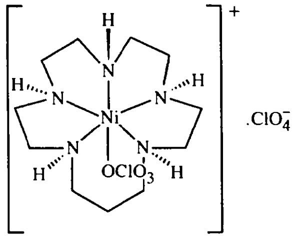
## Abstract

The crystal structure of the title compound, [$Ni(ClO_4)(C_{11}H_{27}N_5)$]$ClO_4$, shows that the $Ni^{II}$ ion is six-coordinate involving the pentadentate macrocycle and one perchlorate O atom. There are two independent molecules in the asymmeteric unit. The conformation of the ligand is in the most stable form, with the six-membered ring in a chair form and all four five-membered rings in *gauche* forms.

## Comment

Polyaza macrocyclic ligands have attracted interest from coordination chemists, but most attention has been paid to tetradentate macrocycles, less information being available for larger ring systems. The Richman & Atkins (1974) procedure allows the simple and general synthesis of larger ring systems. Reported studies have been concerned with the thermodynamics and kinetics of the metal complexes of pentaaza macrocycles in solution (Kodama & Kimura, 1978*a*,*b*; Hay, Bembi, Moodie & Norman, 1982; Hay, Bembi, McLaren & Moodie, 1984). Little work has been carried out on the crystal structures of metal complexes of pentaaza macrocycles (Bombieri *et al.*, 1982; Eigenbrot *et al.*, 1988; Tahirov *et al.*, 1993). The present paper reports the crystal structure of the title compound, [$Ni(ClO_4)(C_{11}N_5H_{27})$]$ClO_4$, (I).



(I)

The structure of (I) consists of two crystallographically independent [$Ni(ClO_4)(C_{11}N_5H_{27})$]$^+$ complex cations (denoted as molecules *A* and *B*) and two perchlorate anions. Both molecules have nearly the same conformation, and bond lengths and angles have normal values. The complex cation is six-coordinate, with five N atoms of the pentaaza macrocycle and a perchlorate O atom around the $Ni^{II}$ ion. The macrocyclic ligand is coordinated with a 5,6,5 arrangement of the chelate rings in the equational plane containing four N atoms. The N3 and N4 atoms have opposite chirality giving the *meso–syn* diasteroisomer (Bombieri *et al.*, 1982). The configurations of the four chiral amine N centers are 1*RS*, 4*RS*, 10*SR* and 13*SR*. The conformation of the ligand is the most stable form, with the six-membered ring in a chair form and all four five-membered rings in *gauche* forms. The overall geometry is similar to that of an analogous cobalt(III) complex (Bombieri *et al.*, 1982). The crystal structure is stabilized by a three-dimensional network of N—H···O hydrogen bonds, as given in Table 2. The second perchlorate anion is free in the lattice and participites in the hydrogen bonding.

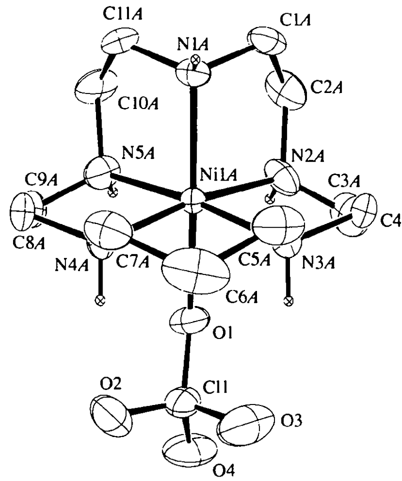


Fig. 1. The structure of molecule *A* of the title compound (molecule *B* is nearly the same as molecule *A*) showing 30% probability displacement ellipsoids. H atoms were excluded, expect for those attached to the N atoms.

## Experimental

The ligand, 1,4,7,10,13-pentaazacyclohexadecane, was prepared according to literature methods (Osvath, Curtis & Weatherburn, 1987; Richman & Atkins, 1974). Equimolar quantities of $Ni(ClO_4)_2.6H_2O$ and the ligand were mixed in methanol solution and allowed to react for 3 h in a water bath (*ca* 333 K). The resulting solution was evaporated to dryness on a rotary evaporator. Single crystals were grown by slow evaporation from a water–methanol mixture (1:1 *v*/*v*) at room temperature.

*Crystal data*

$[Ni(ClO_4)(C_{11}H_{27}N_5)]ClO_4$
$M_r = 486.99$
Monoclinic
$P2_1$
$a = 8.665\ (3)$ Å
$b = 16.681\ (2)$ Å
$c = 13.673\ (4)$ Å
$\beta = 98.49\ (3)°$
$V = 1954.7\ (9)$ Å$^3$
$Z = 4$
$D_x = 1.655$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 21 reflections
$\theta = 5.76–22.94°$
$\mu = 1.315$ mm$^{-1}$
$T = 293\ (2)$ K
Pillar
0.218 × 0.189 × 0.141 mm
Violet

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: $\psi$ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.569$, $T_{max} = 0.831$
5864 measured reflections
5864 independent reflections

2593 reflections with $I > 2\sigma(I)$
$\theta_{max} = 29.91°$
$h = -12 \rightarrow 12$
$k = -23 \rightarrow 0$
$l = 0 \rightarrow 19$
3 standard reflections every 197 reflections intensity decay: 2%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.157$
$S = 0.848$
5864 reflections
487 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.082P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.040$
$\Delta\rho_{max} = 0.606$ e Å$^{-3}$
$\Delta\rho_{min} = -0.539$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| Ni1*A*—N2*A* | 2.061 (9) | Ni1*B*—N2*B* | 2.081 (10) |
| Ni1*A*—N4*A* | 2.066 (7) | Ni1*B*—N4*B* | 2.067 (9) |
| Ni1*A*—N3*A* | 2.072 (8) | Ni1*B*—N3*B* | 2.087 (9) |
| Ni1*A*—N5*A* | 2.096 (8) | Ni1*B*—N5*B* | 2.098 (9) |
| Ni1*A*—N1*A* | 2.105 (8) | Ni1*B*—N1*B* | 2.072 (8) |
| Ni1*A*—O1 | 2.334 (7) | Ni1*B*—O5 | 2.328 (10) |
| N2*A*—Ni1*A*—N4*A* | 172.4 (4) | N2*B*—Ni1*B*—N4*B* | 170.7 (4) |
| N2*A*—Ni1*A*—N3*A* | 83.1 (4) | N2*B*—Ni1*B*—N3*B* | 84.1 (4) |
| N4*A*—Ni1*A*—N3*A* | 92.1 (3) | N4*B*—Ni1*B*—N3*B* | 91.5 (3) |
| N2*A*—Ni1*A*—N5*A* | 100.0 (4) | N2*B*—Ni1*B*—N5*B* | 101.7 (4) |
| N4*A*—Ni1*A*—N5*A* | 84.3 (4) | N4*B*—Ni1*B*—N5*B* | 82.3 (4) |
| N3*A*—Ni1*A*—N5*A* | 174.4 (3) | N3*B*—Ni1*B*—N5*B* | 173.5 (4) |
| N2*A*—Ni1*A*—N1*A* | 85.7 (3) | N2*B*—Ni1*B*—N1*B* | 84.7 (4) |
| N4*A*—Ni1*A*—N1*A* | 101.1 (3) | N4*B*—Ni1*B*—N1*B* | 104.1 (3) |
| N3*A*—Ni1*A*—N1*A* | 101.0 (3) | N3*B*—Ni1*B*—N1*B* | 99.6 (3) |
| N5*A*—Ni1*A*—N1*A* | 83.9 (3) | N5*B*—Ni1*B*—N1*B* | 84.0 (3) |
| N2*A*—Ni1*A*—O1 | 83.9 (3) | N2*B*—Ni1*B*—O5 | 80.0 (4) |
| N4*A*—Ni1*A*—O1 | 90.4 (3) | N4*B*—Ni1*B*—O5 | 92.0 (4) |
| N3*A*—Ni1*A*—O1 | 91.9 (3) | N3*B*—Ni1*B*—O5 | 91.7 (4) |
| N5*A*—Ni1*A*—O1 | 83.9 (3) | N5*B*—Ni1*B*—O5 | 86.4 (4) |
| N1*A*—Ni1*A*—O1 | 162.3 (3) | N1*B*—Ni1*B*—O5 | 159.9 (4) |

| | |
|---|---|
| Ni1*A*—N1*A*—C1*A*—C2*A* | 31.8 (11) |
| N1*A*—C1*A*—C2*A*—N2*A* | −44.8 (14) |
| Ni1*A*—N2*A*—C2*A*—C1*A* | 33.7 (12) |
| N1*A*—Ni1*A*—N2*A*—C2*A* | −12.1 (7) |
| N2*A*—Ni1*A*—N1*A*—C1*A* | −9.9 (7) |
| Ni1*A*—N2*A*—C3*A*—C4*A* | −39.0 (12) |
| N2*A*—C3*A*—C4*A*—N3*A* | 52.9 (14) |
| Ni1*A*—N3*A*—C4*A*—C3*A* | −38.1 (11) |
| N2*A*—Ni1*A*—N3*A*—C4*A* | 15.8 (7) |
| N3*A*—Ni1*A*—N2*A*—C3*A* | 12.2 (8) |
| Ni1*A*—N3*A*—C5*A*—C6*A* | 60.5 (12) |
| N3*A*—C5*A*—C6*A*—C7*A* | −70.1 (14) |
| C5*A*—C6*A*—C7*A*—N4*A* | 67.2 (14) |
| Ni1*A*—N4*A*—C7*A*—C6*A* | −54.8 (11) |
| N3*A*—Ni1*A*—N4*A*—C7*A* | 41.2 (8) |
| N4*A*—Ni1*A*—N3*A*—C5*A* | −43.1 (7) |
| Ni1*A*—N4*A*—C8*A*—C9*A* | 33.1 (12) |
| N4*A*—C8*A*—C9*A*—N5*A* | −46.6 (15) |
| Ni1*A*—N5*A*—C9*A*—C8*A* | 34.5 (13) |
| N4*A*—Ni1*A*—N5*A*—C9*A* | −11.6 (8) |
| N5*A*—Ni1*A*—N4*A*—C8*A* | −11.5 (7) |
| Ni1*A*—N5*A*—C10*A*—C11*A* | −29.4 (13) |
| N5*A*—C10*A*—C11*A*—N1*A* | 43.9 (15) |
| Ni1*A*—N1*A*—C11*A*—C10*A* | −34.2 (12) |
| N5*A*—Ni1*A*—N1*A*—C11*A* | 13.3 (8) |
| N1*A*—Ni1*A*—N5*A*—C10*A* | 8.2 (8) |
| Ni1*B*—N1*B*—C1*B*—C2*B* | 24.9 (12) |
| N1*B*—C1*B*—C2*B*—N2*B* | −43.2 (15) |
| Ni1*B*—N2*B*—C2*B*—C1*B* | 38.5 (12) |
| N1*B*—Ni1*B*—N2*B*—C2*B* | −19.6 (8) |
| N2*B*—Ni1*B*—N1*B*—C1*B* | −2.6 (8) |
| Ni1*B*—N2*B*—C3*B*—C4*B* | −26.5 (12) |
| N2*B*—C3*B*—C4*B*—N3*B* | 45.2 (14) |
| Ni1*B*—N3*B*—C4*B*—C3*B* | −39.7 (10) |
| N2*B*—Ni1*B*—N3*B*—C4*B* | 20.5 (7) |
| N3*B*—Ni1*B*—N2*B*—C3*B* | 2.9 (7) |
| Ni1*B*—N3*B*—C5*B*—C6*B* | 46.2 (13) |
| N3*B*—C5*B*—C6*B*—C7*B* | −60.4 (15) |
| C5*B*—C6*B*—C7*B*—N4*B* | 72.9 (15) |
| Ni1*B*—N4*B*—C7*B*—C6*B* | −65.7 (12) |

| | |
|---|---|
| N3*B*—Ni1*B*—N4*B*—C7*B* | 44.6 (8) |
| N4*B*—Ni1*B*—N3*B*—C5*B* | −35.1 (9) |
| Ni1*B*—N4*B*—C8*B*—C9*B* | 34.7 (11) |
| N4*B*—C8*B*—C9*B*—N5*B* | −50.7 (13) |
| Ni1*B*—N5*B*—C9*B*—C8*B* | 40.5 (12) |
| N4*B*—Ni1*B*—N5*B*—C9*B* | −17.0 (9) |
| N5*B*—Ni1*B*—N4*B*—C8*B* | −9.6 (8) |
| Ni1*B*—N5*B*—C10*B*—C11*B* | −28.3 (13) |
| N5*B*—C10*B*—C11*B*—N1*B* | 46.2 (14) |
| Ni1*B*—N1*B*—C11*B*—C10*B* | −39.6 (10) |
| N5*B*—Ni1*B*—N1*B*—C11*B* | 18.4 (7) |
| N1*B*—Ni1*B*—N5*B*—C10*B* | 5.2 (8) |

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1*A*—H1*A*···O9$^{i}$ | 0.91 | 2.29 | 3.15 (2) | 156.7 |
| N3*A*—H3*A*···O3 | 0.91 | 2.33 | 3.18 (1) | 154.5 |
| N4*A*—H4*A*···O2 | 0.91 | 2.26 | 3.11 (1) | 155.9 |
| N1*B*—H1*B*···O13 | 0.91 | 2.58 | 3.30 (2) | 136.3 |
| N1*B*—H1*B*···O14 | 0.91 | 2.35 | 3.23 (1) | 162.6 |
| N2*B*—H2*B*···O10$^{ii}$ | 0.91 | 2.32 | 3.16 (2) | 153.6 |
| N3*B*—H3*B*···O8 | 0.91 | 2.58 | 3.33 (2) | 141.2 |
| N5*B*—H5*B*···O4$^{iii}$ | 0.91 | 2.63 | 3.35 (1) | 137.0 |

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

All H-atom positions were obtained by geometrical calculation and were refined with a riding model.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1177). Services for accessing these data are described at the back of the journal.

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# Chloro(1,4,7,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴)zinc(II) Perchlorate

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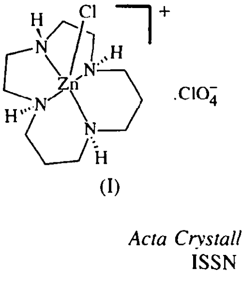
## Abstract

In the title compound, $[ZnCl(C_{10}H_{24}N_4)]ClO_4$, the coordination about the Zn$^{II}$ ion is distorted square pyramidal with the four N atoms of the macrocycle in the basal positions and the Cl ion axial. The Zn—Cl and average Zn—N bond lengths are 2.2734 (8) and 2.125 (3) Å, respectively.

## Comment

The macrocyclic ligand 1,4,7,11-tetraazacyclotetradecane (isocyclam) is an isomer of 1,4,8,11-tetraazacyclotetradecane (cyclam). The coordination behaviour of cyclam and isocyclam with transition metals has been studied extensively (Boeyens, 1983; Satake *et al.*, 1992; Tahirov *et al.*, 1993, 1995). We report here the structure of [Zn(isocyclam)Cl]ClO$_4$, (I).



(I)

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