Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis(1,4-diazacycloheptane-*N*,*N*′)nickel(II) diperchlorate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.051
wR factor = 0.141
Data-to-parameter ratio = 13.5

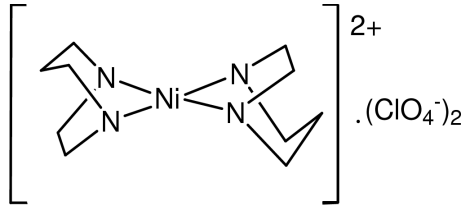
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 8 May 2001
Accepted 14 May 2001
Online 15 June 2001

The title compound, $[Ni(C_5H_{12}N_2)_2](ClO_4)_2$, consists of discrete $[Ni(C_5H_{12}N_2)_2]^{2+}$ cations and perchlorate anions. The Ni^{II} atom is at the center of symmetry and is coordinated in a square-planar manner by the nitrogen donors of a pair of mesocyclic 1,4-diazacycloheptane (DACH) ligands. Both DACH rings adopt boat conformations in the *trans* form. The perchlorate O atoms are hydrogen bonded with the nitrogen donors of the DACH rings to form a macrocycle-like system.

Comment

Mesocyclic ligands (molecules contain seven- to ten-membered rings) occupy an important place between acyclic and macrocyclic ligands. They offer several attractive features as a framework for ligand development with exceptionally strong ligand fields, unique conformational requirements and the potential for further functionalization (Musker, 1992; Grapperhaus & Darensbourg, 1998; Bu *et al.*, 2000). 1,5-Diazacyclooctane (DACO) and 1,4-diazacycloheptane (DACH) are the most typical examples of the diazamesocyclic ligands. However, by contrast with the wide investigation of DACO, structural studies on DACH are still quite rare (Musker, 1992; Allen *et al.*, 1996). As part of our effort to further develop this interesting system, we report herein the synthesis and X-ray crystal structure of a Ni^{II} complex of DACH, namely the title compound, (I).



(I)

In the complex cation, the Ni^{II} center is four-coordinated, forming an exact plane, with the Ni1 atom at the center of symmetry (Fig. 1). The Ni1—N1 and Ni1—N2 bond distances are 1.911 (4) and 1.915 (4) Å, respectively, and are nearly equivalent. The chelate N1—Ni1—N2 angle is 81.06 (17)°, and somewhat smaller than the non-chelate N1—Ni1—N2^{i} angle [symmetry code: (i) $-x, -y, -z$]. The C—C bond distances in the methylene groups of DACH are in the range 1.499 (8)–1.537 (7) Å, which are normal aliphatic C—C bonds with sp^3 hybridization. Both DACH moieties in the complex adopt the boat conformation in a *trans* form due to the centrosymmetry, which is similar to the structure of $[Ni(DACH)_2]Cl_2{\cdot}2H_2O$

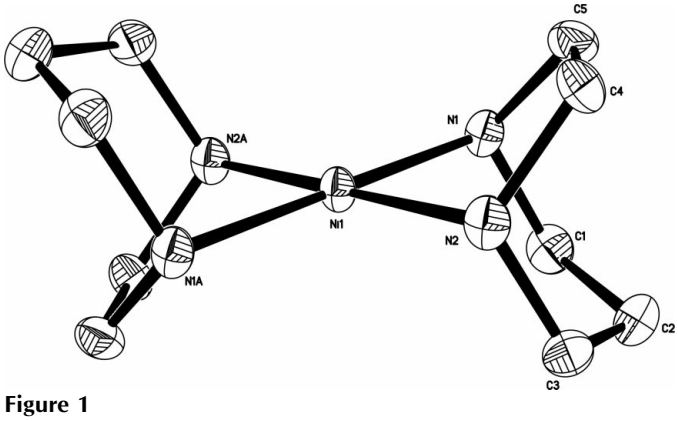


Figure 1
ORTEP view (Johnson, 1976) of the cation of the title complex with 30% probability ellipsoids.

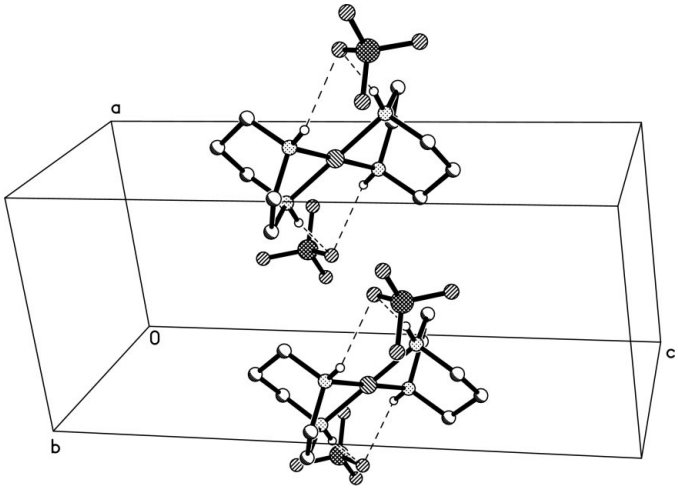


Figure 2
Molecular packing diagram in the unit cell of (I) (H atoms not mentioned in the text have been omitted for clarity).

(Hussain, 1983). The perchlorate ions have no close contacts to the Ni^{II} centers, since the shortest axial distance for Ni···O is 3.925 (3) Å.

The $[Ni(DACH)_2]^{2+}$ unit carries two perchlorate ions which are hydrogen bonded to the nitrogen donors of DACH (Fig. 2). These hydrogen bonds form a macrocycle-like ring system including a pair of N—H···O···N—H bridges, which is similar to the structure of $[Ni(DACO)_2]Br_2$ (Du *et al.*, 2000).

Experimental

A mixture of $Ni(ClO_4)_2{\cdot}6H_2O$ (220 mg, 0.6 mmol) and 1,4-diazacycloheptane (120 mg, 1.2 mmol) was dissolved in methanol (15 ml) at room temperature. A yellow powder precipitated immediately. The complex was filtered off and washed several times with anhydrous ether. Yield: 253 mg (92%). Yellow block-shaped single crystals of (I) were grown from CH_3COCH_3/CH_3OH (5:1). FT–IR data (KBr pellet, cm^{-1}): 3268 (*m*), 3123 (*m*), 3083 (*m*), 2948 (*w*), 1635 (*w*), 1473 (*m*), 1122 (*vs*), 1109 (*vs*), 988 (*m*), 636 (*s*), 626 (*s*). Analysis calculated for (I): C 26.23, H 5.28, N 12.24%; found: C 26.41, H 5.40, N 12.13%.

Crystal data

$[Ni(C_5H_{12}N_2)_2](ClO_4)_2$	$D_x = 1.724$ Mg m^{-3}
$M_r = 457.94$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3489 reflections
$a = 6.7899$ (17) Å	$\theta = 2.5$–$25.0°$
$b = 8.071$ (2) Å	$\mu = 1.45$ mm^{-1}
$c = 16.152$ (4) Å	$T = 293$ (2) K
$\beta = 94.760$ (5)°	Prism, yellow
$V = 882.0$ (4) Å^3	0.20 × 0.20 × 0.15 mm
$Z = 2$	

Data collection

Bruker SMART 1000 diffractometer	1557 independent reflections
ω scans	968 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan [*SAINT* (Bruker, 1998) and *SADABS* (Sheldrick, 1997)]	$R_{int} = 0.052$
	$\theta_{max} = 25.0°$
$T_{min} = 0.760$, $T_{max} = 0.812$	$h = -8 \rightarrow 8$
3544 measured reflections	$k = -9 \rightarrow 9$
	$l = -8 \rightarrow 19$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.051$	$w = 1/[\sigma^2(F_o^2) + (0.0750P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.141$	$(\Delta/\sigma)_{max} = 0.007$
$S = 0.98$	$\Delta\rho_{max} = 0.65$ e Å^{-3}
1557 reflections	$\Delta\rho_{min} = -0.41$ e Å^{-3}
115 parameters	

Table 1
Selected geometric parameters (Å, °).

Ni1—N1	1.911 (4)	N2—C3	1.502 (7)
Ni1—N2	1.915 (4)	C1—C2	1.519 (8)
N1—C5	1.484 (7)	C2—C3	1.499 (8)
N1—C1	1.499 (7)	C4—C5	1.537 (7)
N2—C4	1.499 (6)		
N1—Ni1—N2	81.06 (17)	C3—N2—Ni1	108.4 (3)
N1^i—Ni1—N2	98.94 (17)	N1—C1—C2	111.0 (4)
C5—N1—C1	113.3 (5)	C3—C2—C1	114.8 (5)
C5—N1—Ni1	107.2 (3)	C2—C3—N2	113.0 (4)
C1—N1—Ni1	107.7 (3)	N2—C4—C5	108.2 (4)
C4—N2—C3	112.3 (4)	N1—C5—C4	108.9 (4)
C4—N2—Ni1	106.1 (3)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*c*···O3^i	0.91	2.10	2.997 (3)	170
N2—H2*c*···O3^{ii}	0.91	2.35	3.137 (4)	144

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

The H atoms attached to C and N atoms were placed in geometrically calculated positions and included in the final refinement as riding with displacement parameters derived from the atoms to which they were bonded.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998).

We gratefully acknowledge the financial support of the National Natural Science Foundation of China (No. 29971019) and the *Trans*-Century Talents Training Program Foundation from the State Education Ministry of China.

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