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trans-Diaqua(*C-meso*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane-κ^4N)nickel(II) dichloride

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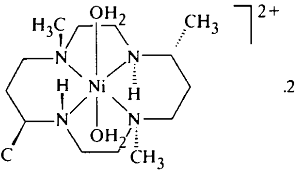
Abstract

The crystal structure of the title compound, $[Ni(C_{14}H_{32}N_4)(H_2O)_2]Cl_2$, has been determined by X-ray diffraction. The Ni^{II} ion lies on an inversion center and is six-coordinate in a distorted octahedral geometry, with the four N atoms of the macrocyclic ligand equatorial and the two water molecules axial. The tetradentate macrocyclic ligand adopts a configuration having two six-membered rings in a chair form and two five-membered rings in a *gauche* form.

Comment

The nickel(II) complex of *C-meso*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane, as with other tetraaza ligands, exists in equilibrium as a mixture of blue (paramagnetic, octahedral) and yellow (diamagnetic, square-planar) forms (Anichini *et al.*, 1977). Miyamura *et al.* (1987) reported the crystal structure of the square-planar species. In the present study, we report the isolation and X-ray structure of the *trans*-diaqua form, (I).



(I)

The title complex is octahedral around the metal center. An inversion center exists on the Ni^{II} ion. Two water molecules coordinate axially to the central Ni^{II} ion. The Ni^{II} ion and the four ligand N atoms are exactly coplanar. The ligand skeleton of the title complex takes the most stable *trans*-III conformation designated by Bosnich *et al.* (1965), with the two six-membered rings in a chair form and the two five-membered rings in a *gauche* form. The Ni1—N2 distance [2.069 (3) Å] is essentially equivalent to those found in *trans*-[Ni(1,4,8,11-tetraazacyclotetradecane)X_2] [2.067 (2) Å for X = Cl (Ito *et al.*, 1984), and 2.050 (5) and 2.060 (6) Å for X = NO_3 (Boeyens & Hancock, 1984)] and *trans*-[Ni(1,4,8,11-tetraazacyclotetradecane)(OH_2)]Cl_2 [2.072 (2) Å; Mochizuki & Kondo, 1995]. The Ni1—N1 distance of 2.113 (3) Å is considerably longer than Ni1—N2, and this value is similar to those in *cis*-(nitrato-*O*,*O*′)(*C-rac*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴)-$Ni^{II}(NO_3)$ [2.134 (2) Å; Panneerselvam *et al.*, 1999].

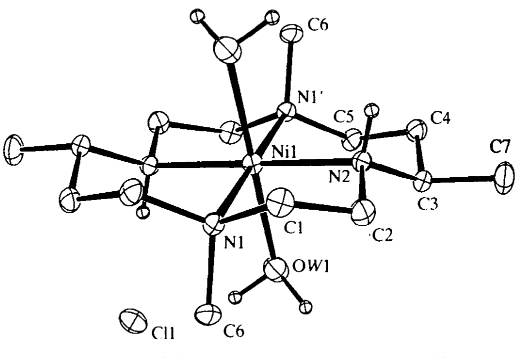


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids. H atoms are shown only on the amine N atoms and the water ligands.

This could be due to steric interaction involving the methyl group on N1 and Ni-bound water molecules. The Ni—O length is 2.216 (3) Å, which is longer than those found in *trans*-[Ni(1,4,8,11-tetraazacyclotetradecane)-$(OH_2)_2]^{2+}$ [2.176 (2) Å; Mochizuki & Kondo, 1995] and $Ni(OH_2)_6(NH_4)_2(SO_4)_2$ [2.058 (2) Å; Tahirov *et al.*, 1994]. All bond lengths and angles in the ligand moiety are normal. Hydrogen bonds (Table 2) stabilize the structure.

Experimental

C-meso-1,5,8,12-Tetramethyl-1,4,8,11-tetraazacyclotetradecane was prepared according to literature methods (Miyamura *et al.*, 1987). Nickel(II) chloride (0.42 g) and *C-meso*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane (0.45 g) were dissolved in water (100 ml) and stirred for 4 h at 333 K. The volume of the resulting solution was reduced by rotatory evaporation. Purple crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature after several days.

Crystal data

$[Ni(C_{14}H_{32}N_4)(H_2O)_2]Cl_2$
$M_r = 422.08$
Monoclinic
$P2_1/n$
$a = 8.984 (3)$ Å
$b = 11.912 (4)$ Å
$c = 9.548 (3)$ Å
$\beta = 108.34 (3)^\circ$
$V = 969.9 (6)$ Å^3
$Z = 2$
$D_x = 1.445$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.61–17.50^\circ$
$\mu = 1.289$ mm^{-1}
$T = 293 (2)$ K
Rectangular
0.48 × 0.44 × 0.36 mm
Purple

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.577$, $T_{\max} = 0.629$
1830 measured reflections
1719 independent reflections
1543 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.040$
$\theta_{\max} = 25.05^\circ$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 14$
$l = -11 \rightarrow 10$
3 standard reflections every 50 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.144$
$S = 1.132$
1719 reflections
106 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0771P)^2 + 2.0347P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.980$ e Å^{-3}
$\Delta\rho_{\min} = -0.641$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ni1—N2	2.069 (3)	N2—C2	1.481 (5)
Ni1—N1	2.113 (3)	N2—C3	1.491 (5)
Ni1—O*W*1	2.216 (3)	C1—C2	1.513 (5)
N1—C6	1.479 (5)	C3—C4	1.513 (5)
N1—C1	1.483 (5)	C3—C7	1.523 (5)
N1—C5^{i}	1.485 (5)	C4—C5	1.521 (6)
N2—Ni1—N1	86.6 (1)	C2—N2—Ni1	106.4 (2)
N2—Ni1—O*W*1	91.1 (1)	C3—N2—Ni1	117.2 (2)
N1—Ni1—O*W*1	91.7 (1)	N1—C1—C2	111.0 (3)
C6—N1—C1	108.8 (3)	N2—C2—C1	109.4 (3)
C6—N1—C5^{i}	108.1 (3)	N2—C3—C4	110.2 (3)
C1—N1—C5^{i}	109.9 (3)	N2—C3—C7	112.0 (3)
C6—N1—Ni1	116.7 (2)	C4—C3—C7	109.9 (3)
C1—N1—Ni1	101.5 (2)	C3—C4—C5	116.6 (3)
C5^{i}—N1—Ni1	111.6 (2)	N1^{i}—C5—C4	114.0 (3)
C2—N2—C3	114.0 (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*
N2—H1···Cl1^{i}	0.91	2.35	3.250 (3)	171.72
O*W*1—H1O*W*···Cl1	0.94	2.25	3.137 (3)	156.69
O*W*1—H2O*W*···Cl1^{ii}	1.00	2.26	3.236 (3)	166.69

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

All the H atoms were fixed geometrically and refined using constraint with isotropic displacement parameters ($U_{\rm iso}$ = 0.050 Å^2).

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *NRCVAX* (Gabe *et al.*, 1989). Software used to prepare material for publication: *SHELXL*97.

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trans-Diaquabis(benzoato-*O*)bis(nicotinamide-N^1)cobalt(II)

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Abstract

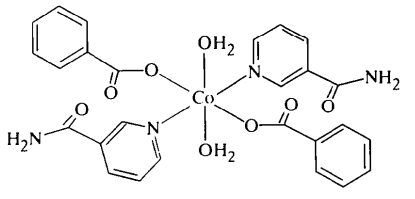
The title compound, $[Co(C_7H_5O_2)_2(C_6H_6N_2O)_2(H_2O)_2]$, is a crystallographically centrosymmetric monomeric complex in which pyridine N, and carboxylate and water O atoms form a tetragonally Jahn–Teller-distorted octahedron about the Co^{II} ion, with bond distances of 2.150 (1), 2.085 (1) and 2.141 (1) Å, respectively. There is a hydrogen bond between nicotinamide N and O atoms [N···O 2.976 (2) Å], and the non-coordinated O atom of the carboxylate group and that of nicotinamide form hydrogen bonds with water O atoms [O···O 2.580 (2) and 2.911 (1) Å, respectively].

Comment

The structures of metal complexes having different benzoic and/or nicotinic acid derivatives as ligands have been the subject of much interest in our laboratory; examples are $[Cu(C_7H_5O_3)_2(NA)_2(H_2O)_2]$ [(II); where NA is nicotinamide, $C_6H_6N_2O$; Hökelek *et al.*, 1998], $[Cu(C_7H_4NO_4)_2(DENA)_2(H_2O)_2]$ [(III); where DENA is diethylnicotinamide, $C_{10}H_{14}N_2O$; Hökelek *et al.*, 1997], $[Co(C_7H_5O_3)_2(DENA)_2(H_2O)_2]$ [(IV); Hökelek & Necefoğlu, 1997], $[M(C_7H_4NO_5)_2(H_2O)_4]$ [(V); where M = Zn^{II} and Co^{II}; Tahir *et al.*, 1997], $[Zn_2(C_7H_5O_3)_4(DENA)_2(H_2O)_2]$, [(VI); Hökelek & Necefoğlu, 1996], $[Cu(C_7H_5O_2)_2(DENA)_2]$ [(VII); Hökelek *et al.*, 1996] and $[Cu_2(C_6H_5COO)_4(DENA)_2]$ [(VIII); Hökelek *et al.*, 1995]. The structure–function–coordination relationships of the arylcarboxylate ion in Co^{II} complexes of benzoic acid derivatives change depending on the nature and position of the substituted groups in the phenyl ring, the nature of the additional ligand molecule or solvent, and the pH and temperature of synthesis (Shnulin *et al.*, 1981; Adiwidjaja *et al.*, 1978; Antsyshkina *et al.*, 1980). When pyridine and its derivatives are coordinated instead of water molecules, the structure is completely different (Catterick *et al.*, 1974).

In the $[Co(p\text{-}O_2NC_6H_4COO)_2(H_2O)_4]$ [(IX); Nadzhafov *et al.*, 1981] and $[Co(p\text{-}H_2NC_6H_4COO)_2(H_2O)_4]$ [(X); Amiraslanov *et al.*, 1979] complexes, the Co atoms are situated at centres of symmetry and are surrounded by six O atoms forming slightly distorted octahedrons. Four positions are occupied by water molecules and the other two by O atoms of the carboxyl groups of *p*-nitrobenzoato and *p*-aminobenzoato anions, respectively. In $[Co(C_7H_4NO_4)_2(NA)_2(H_2O)_2]$ [(XI); Hökelek & Necefoğlu, 1998], the Co atom is also situated at a centre of symmetry and is surrounded by four O atoms forming a slightly distorted square-planar arrangement; the pyridine N atoms of NA complete a distorted octahedral coordination.

The structure determination of the title compound, (I), was undertaken in order to determine the ligand properties of nicotinamide (NA) and benzoate ligands, and to compare the coordination geometries when the NA ligands are substituted for water in complexes (IX) and (X). The title compound is a monomeric complex with cobalt in a centre of symmetry. All ligands are monodentate and the O atoms of each water molecule and benzoate group form a slightly distorted square-planar coordination around the Co atom, which is completed to a Jahn-Teller-distorted octahedron by the pyridine N atoms of NA at distances of 2.150 (1) Å (Fig. 1). There are hydrogen bonds (Table 2) between the water O1 atom and the carboxyl O3 and nicotinamide O4 atoms, and between the nicotinamide N2 and O4 atoms. On the other hand, N2—H22 produces an H22···O3^{i} contact of 2.68 (2) Å, which is too long to be considered as a significant hydrogen bond [symmetry code: (i) $-x$, $-y$, $1-z$]. The O1···O3^{i} distance (Table 2) is shorter than the corresponding distances in complexes (XI) and (IV) [(XI): O···O 2.634 (5) Å; (IV): O···O 2.687 (5) Å].



(I)

In the carboxylate group, the C1—O2 and C1—O3 bond lengths (Table 1) are the same as in complexes (XI) and (IV) [(XI): 1.251 (2) and 1.254 (2) Å; (IV): 1.251 (6) and 1.254 (7) Å]. On the other hand, the C1—O2 bond length is shorter, while C1—O3 is the same according to the corresponding values in complexes (IX) and (X) [(IX): 1.292 (6) and 1.246 (8) Å; (X): 1.283 (4)