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Structure of (2,5,9,13,16-Pentaazaheptadecane)perchloratonickel(II) Perchlorate, $[Ni(ClO_4)(C_{12}H_{31}N_5)](ClO_4)$

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Abstract

The crystal structure of the title compound has been determined by X-ray diffraction. The coordination geometry about the Ni^{II} ion is distorted octahedral. The two five-membered chelate rings are in skew forms and the two six-membered chelate rings are in chair forms. The configuration of the four chiral N centers is (2*RS*,5*RS*,13*SR*,16*SR*). Hydrogen bonds between the amine and perchlorate groups help stabilize the crystal.

Comment

The crystal structures of transition-metal complexes of tetraamines have been studied extensively (Lu, Wu & Chung, 1986). However, the crystal structures of the complexes of pentaamines have received little attention. The ligand 2,5,9,13,16-pentaazaheptadecane can react with transition-metal ions to form very stable complexes. We report here the crystal structure of a nickel(II) complex of this ligand.

The ligand 2,5,9,13,16-pentaazaheptadecane pentahydrochloride was prepared according to the method reported by Richman & Atkins (1974). An aqueous solution of the ligand (10 g in 50 ml water) was passed through a column of Amberlite IR400 OH^- form and was added dropwise to a methanol solution (50 ml) of $Ni(ClO_4)_2.6H_2O$ (7.3 g). After evaporation of the solution, blue crystals of [Ni(2,5,9,13,16-pentaazaheptadecane)(ClO_4)](ClO_4) were formed. Blue rod-like single crystals were obtained by recrystallization in 50 vol.% methanol–water by slow evaporation.

The primary coordination sphere is a distorted octahedron comprised of five N atoms from pentaazaheptadecane and one O atom from the perchlorate ion. Ni, N(2) and N(4) are above the least-squares plane formed by N(1), N(2), N(3) and N(4), while N(1) and N(3) are below it, so that this plane undergoes a very slight tetrahedral distortion. This complex has the (2*RS*,5*RS*,13*SR*,16*SR*) configuration at the four chiral N centers. The two six-membered chelate rings exhibit chair forms and the two five-membered rings are in skew forms. The hydrogen bonds between amine groups and perchlorate groups help stabilize the crystal.

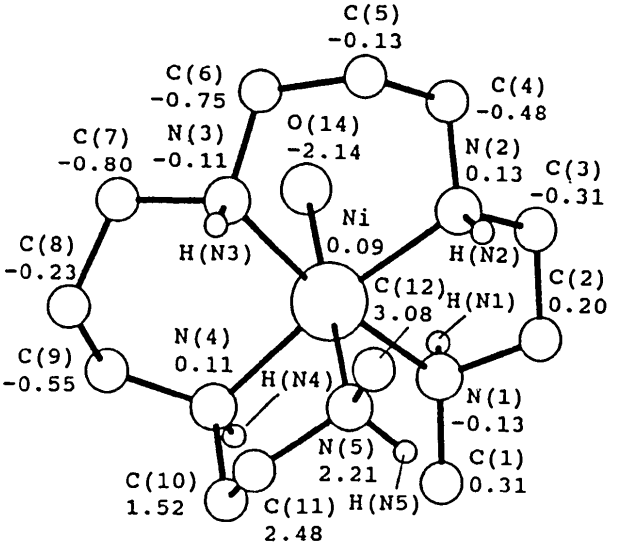

Fig. 1. A perspective view of the molecule with the atom-numbering scheme excluding the H atoms attached to the C atoms and the perchlorate ions. The displacements (Å) of the atoms from the best plane formed by the atoms N(1), N(2), N(3) and N(4) coordinated to the Ni^{II} ion are indicated.

Experimental

Crystal data

$[Ni(ClO_4)(C_{12}H_{31}N_5)](ClO_4)$
M_r = 503.023
Monoclinic
$P2_1/n$
a = 9.889 (3) Å
b = 25.239 (4) Å
c = 8.402 (2) Å
β = 92.85 (2)°
V = 2094 (1) Å^3
Z = 4
D_x = 1.595 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 8–17°
μ = 4.14 mm^{-1}
T = 298 (3) K
Rectangular pillar
0.50 × 0.43 × 0.40 mm
Blue

Data collection

AFC-5*R* diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical based on ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.715, T_{max} = 1.000
3410 measured reflections
3208 independent reflections
1457 observed reflections [$I > 2.5\sigma(I)$]
R_{int} = 0.047
θ_{max} = 30.1°
h = 0 → 11
k = 0 → 28
l = −9 → 9
3 standard reflections
frequency: 60 min
intensity variation: ±4%

Refinement

Refinement on F
$R = 0.069$
$wR = 0.080$
$S = 24.27$
1457 reflections
253 parameters
Only H-atom U's refined
Unit weights applied

$(\Delta/\sigma)_{max} = 1.554$
$\Delta\rho_{max} = 1.07$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$B_{eq} = (32\pi^2/3)\Sigma_i\Sigma_j U_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Ni	0.21065 (19)	0.11407 (8)	0.18583 (23)	3.66 (9)
Cl(1)	0.2091 (4)	0.04717 (16)	−0.1707 (4)	5.27 (17)
Cl(2)	0.1336 (4)	0.34003 (17)	1.1477 (5)	5.87 (20)
O(11)	0.1381 (20)	0.0113 (6)	−0.0929 (16)	13.7 (12)
O(12)	0.1304 (15)	0.0713 (6)	−0.2922 (14)	11.3 (9)
O(13)	0.3007 (21)	0.0216 (8)	−0.2373 (24)	18.8 (15)
O(14)	0.2493 (11)	0.0850 (4)	−0.0599 (11)	6.8 (6)
O(21)	0.0989 (15)	0.2952 (5)	1.2252 (15)	10.2 (8)
O(22)	0.1205 (15)	0.3345 (6)	0.9875 (16)	11.7 (10)
O(23)	0.2684 (16)	0.3500 (9)	1.1711 (20)	18.1 (15)
O(24)	0.068 (3)	0.3797 (6)	1.193 (3)	21.5 (19)
N(1)	0.2612 (11)	0.0328 (4)	0.2617 (13)	5.5 (6)
N(2)	0.4220 (10)	0.1225 (4)	0.2176 (11)	4.4 (5)
N(3)	0.1844 (11)	0.1878 (4)	0.0690 (12)	4.8 (5)
N(4)	0.0024 (10)	0.0963 (4)	0.1741 (13)	4.7 (5)
N(5)	0.1725 (10)	0.1420 (4)	0.4184 (11)	4.4 (5)
C(1)	0.1804 (17)	−0.0040 (6)	0.3484 (20)	7.2 (9)
C(2)	0.4039 (15)	0.0350 (6)	0.3268 (18)	6.3 (8)
C(3)	0.4826 (14)	0.0710 (7)	0.2323 (19)	6.2 (8)
C(4)	0.4940 (14)	0.1565 (7)	0.1114 (18)	6.3 (9)
C(5)	0.4336 (15)	0.2090 (7)	0.0836 (20)	6.6 (8)
C(6)	0.3031 (18)	0.2076 (6)	−0.0166 (18)	6.5 (9)
C(7)	0.0621 (17)	0.1925 (6)	−0.0456 (19)	6.6 (9)
C(8)	−0.0699 (16)	0.1768 (7)	0.0238 (18)	6.3 (8)
C(9)	−0.0871 (12)	0.1193 (7)	0.0472 (18)	6.1 (8)
C(10)	−0.0441 (13)	0.1033 (7)	0.3397 (19)	6.5 (8)
C(11)	0.0227 (13)	0.1496 (6)	0.4187 (16)	5.6 (7)
C(12)	0.2410 (14)	0.1904 (6)	0.4847 (16)	6.0 (8)

Table 2. *Geometric parameters* (Å, °)

Ni—O(14)	2.242 (9)	N(2)—C(3)	1.43 (2)
Ni—N(1)	2.20 (1)	N(2)—C(4)	1.45 (2)
Ni—N(2)	2.10 (1)	N(3)—C(6)	1.49 (2)
Ni—N(3)	2.11 (1)	N(3)—C(7)	1.51 (2)
Ni—N(4)	2.11 (1)	N(4)—C(9)	1.47 (2)
Ni—N(5)	2.13 (1)	N(4)—C(10)	1.50 (2)
N(1)—C(1)	1.44 (2)	N(5)—C(11)	1.49 (2)
N(1)—C(2)	1.49 (2)	N(5)—C(12)	1.49 (2)
O(14)—Ni—N(1)	85.1 (4)	Ni—N(1)—C(1)	128.5 (9)
O(14)—Ni—N(2)	86.3 (4)	Ni—N(1)—C(2)	105.6 (8)
O(14)—Ni—N(3)	83.3 (4)	C(1)—N(1)—C(2)	112 (1)
O(14)—Ni—N(4)	95.7 (4)	Ni—N(2)—C(3)	109.2 (8)
O(14)—Ni—N(5)	179.5 (4)	Ni—N(2)—C(4)	119.8 (8)
N(1)—Ni—N(2)	81.2 (4)	C(3)—N(2)—C(4)	112 (1)
N(1)—Ni—N(3)	167.7 (4)	Ni—N(3)—C(6)	116.0 (8)
N(1)—Ni—N(4)	91.3 (4)	Ni—N(3)—C(7)	116.1 (8)
N(1)—Ni—N(5)	95.2 (4)	C(6)—N(3)—C(7)	107 (1)
N(2)—Ni—N(3)	93.9 (4)	Ni—N(4)—C(9)	120.2 (9)
N(2)—Ni—N(4)	172.1 (4)	Ni—N(4)—C(10)	106.1 (7)
N(2)—Ni—N(5)	94.1 (4)	C(9)—N(4)—C(10)	115 (1)
N(3)—Ni—N(4)	93.9 (4)	Ni—N(5)—C(11)	105.4 (7)
N(3)—Ni—N(5)	96.4 (4)	Ni—N(5)—C(12)	121.1 (8)
N(4)—Ni—N(5)	84.0 (4)	C(11)—N(5)—C(12)	109 (1)

N(1)—H(N1)···O(11)	3.21 (2)	N(4)—H(N4)···O(11^{iii})	3.11 (2)
N(2)—H(N2)···O(22^{i})	3.12 (2)	N(5)—H(N5)···O(12^{iv})	3.06 (2)
N(3)—H(N3)···O(21^{ii})	3.15 (2)		

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

The structure was solved and refined by direct and Fourier methods with full-matrix least-squares refinement; H atoms were found by the difference Fourier method and theoretical calculation. The high value of $(\Delta/\sigma)_{max}$ results from the presence of the disordered perchlorate groups. Program used was *NRCVAX* (Gabe, Le Page, White & Lee, 1987).

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71380 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1043]

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Structure of Diiodobis(1-pyrroline)zinc(II)

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Abstract

The bis(4,5-dihydro-3*H*-pyrrole)diiodozinc(II) molecule sits on a mirror plane with the Zn atom at $y = 0.25$, one pyrroline ring lying in the plane of the mirror and the other perpendicular to it. The I atom is in a general position. Zn—I and Zn—N distances are 2.557 (1) Å, and 2.029 (7) and 2.025 (7) Å, respectively.