[N,N'-Bis(benzimidazol-2-ylethyl)-1,2-ethanediamine](nitrato-O,O')nickel(II) Nitrate†

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Abstract

The structure of the title compound, $[Ni(C_{20}H_{24}N_6)(NO_3)](NO_3)$, consists of a distorted octahedral nickel complex with the central Ni atom coordinated to two N atoms of the benzimidazole moieties, two ethylenediamine N atoms and two O atoms of one of the nitrate ions; the other nitrate ion lies in a well defined position in the lattice and plays an important role in crystal packing. The dihedral angle between the two benzimidazole rings is 85.1 (1)°. The crystal structure is stabilized by a three-dimensional network of N—H⋯O and C—H⋯O interactions, and N—H⋯O intermolecular hydrogen bonds.

Comment

Synthetic analogues of the active sites of various metalloproteins/enzymes have been used in elucidating the relationship between their structure and functions. The synthetically accessible benzimidazoles have recently become potential ligands (Thompson, Marks & Ibers, 1979) for the construction of metalloprotein/enzyme models. The nickel-tetrapyrrole-containing factor, F_{430}, is implicated in the final methane evolution step in methanogenic bacteria (Whitman & Wolfe, 1980) and has attracted considerable attention (Fassler, Pfaltz, Krautler & Eschenmoser, 1984; Hausinger, Orme-Johnson & Walsh, 1984). A mechanism has been proposed for the function of methyl coenzyme M reductase (Walsh & Orme-Johnson, 1987). The final protonation step is consistent with the hydrolysis of highly air-sensitive alkyl–Ni^I tetraaza macrocycles (Stoltzenberg & Stershic, 1987). However, other studies

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have shown that nickel(II) acetate, nickel(II) tetraethylenepentamine and nickel(II) 1,4,8,11-tetraazacyclotetradecane-5,7-dione (Fabbrizzi, Poggi & Seghi, 1985) do not convert methyl–CoM (where CoM is coenzyme M) to methane under either Ar or N_2. It is clear that the ligand activates Ni^{II} towards methyl–CoM. This ligand in F_{430} might also play an important role in activating nickel towards methyl–CoM. Here we report the crystal structure of [N,N'-bis(benzimidazol-2-ylethyl)-1,2-ethanediamine](nitrato-O,O')nickel(II) nitrate, (I), which was synthesized as part of a program of study of benzimidazole-containing ligand systems (Sivagnanam, Pandiyan & Palaniandavar, 1993), which are soft donors and will activate the Ni^{II} towards CoM.

(I)
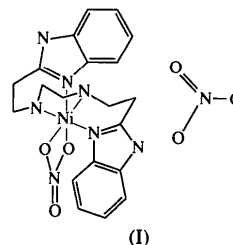
The crystal structure of the title compound consists of an octahedrally distorted metal complex cation and a nitrate anion, which are held together by a network of hydrogen bonds. The Ni atom is coordinated by one N atom of each benzimidazole moiety and the two ethylenediamine N atoms. The bidentate nitrate ion completes the coordination sphere. The metal–ligand bond lengths are not equal; the two Ni—O bonds have an average length of 2.196 (2) Å, the Ni–ligand bonds involving the amine N atoms have an average length of 2.096 (2) Å, and those involving the imine N atoms average 2.048 (2) Å. The angles N(1)—Ni—O(1), N(6)—Ni—N(3) and N(4)—Ni—O(2) all deviate somewhat from the ideal octahedral geometry value of 180° [159.98 (7), 174.33 (8) and 150.51 (7)°, respectively]. The 12 angles subtended at the metal atom by adjacent donors range from 58.59 (6) to 105.08 (8)°; the value required for a perfect octahedron is 90°. The two benzimidazole rings are planar within experimental error and make an angle of 85° with each other. The conformations adopted by the chelate rings Ni—N(6)—C(14)—C(13)—C(12)—N(4), Ni—N(4)—C(11)—C(10)—N(3) and Ni—N(3)—C(9)—C(8)—C(7)—N(1) are envelope, intermediate between envelope and half-chair, and distorted boat, respectively. Analysis of the molecular packing of the cationic and anionic units reveals the following distances: N(2)⋯O(6) 2.903 (3), N(5)⋯O(6)(1 + x, y, z) 2.817 (3), N(2)⋯O(5) 3.119 (3), N(4)⋯O(4) 3.315 (3), N(4)⋯O(5)(−x, −y, 1−z) 3.122 (3) and C(10)⋯O(5)(−x, −y, 1−z) 3.314 (3) Å, with three N—H⋯O and one C—H⋯O interaction > 3.45 Å.
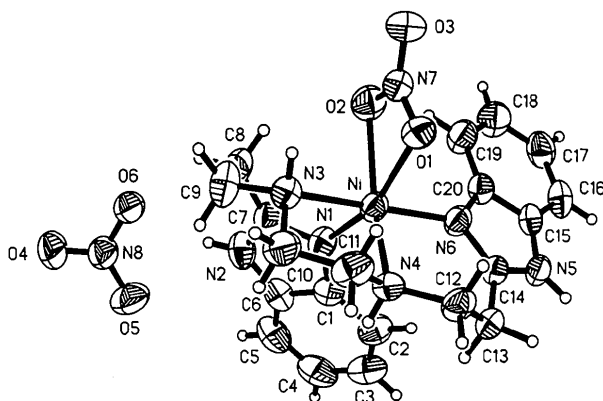
Fig. 1. The molecular structure of the title compound with the atom-labelling scheme. The displacement ellipsoids are drawn at the 50% probability level.
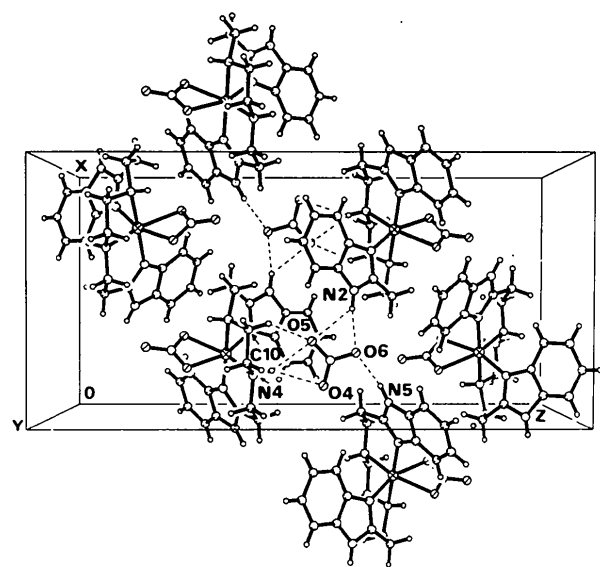

Fig. 2. A perspective drawing of the packing arrangement of the title compound. The dashed lines indicate intermolecular hydrogen bonds and hydrogen-bond interactions.

Experimental

The title compound was prepared by reaction of N,N'-bis(benzimidazol-2-ylethyl)-1,2-ethanediamine (1 mmol) dissolved in 10 ml of methanol (Sivagnanam, Pandiyan & Palaniandavar, 1993) with [Ni(NO$_3$)$_2$].6H$_2$O (1 mmol) dissolved in 5 ml of water. The blue title complex obtained was collected and dried over P$_4$O$_{10}$. 0.01 g of this nickel(II) complex was dissolved in 10 ml of methanol, which upon slow evaporation at room temperature afforded well formed crystals.

Crystal data

[Ni(C$_{20}$H$_{24}$N$_6$)(NO$_3$)](NO$_3$)
M_r = 531.18

Mo $K\alpha$ radiation
λ = 0.71073 Å

Orthorhombic
Pbca
a = 11.746 (1) Å
b = 16.535 (1) Å
c = 24.139 (1) Å
V = 4688 (1) Å^3
Z = 8
D_x = 1.505 Mg m^{-3}

Cell parameters from 25
reflections
θ = 10.0–13.7°
μ = 0.882 mm^{-1}
T = 293 K
Prismatic
0.35 × 0.26 × 0.20 mm
Light blue

Data collection

Siemens $P4$ diffractometer
$\omega/2\theta$ scans
Absorption correction:
none
4120 measured reflections
4005 independent reflections
3080 observed reflections
$[I > 2\sigma(I)]$
R_{int} = 0.030

θ_{max} = 25.0°
h = 0 → 13
k = 0 → 19
l = 0 → 28
2 standard reflections
monitored every 100
reflections
intensity decay: 2%

Refinement

Refinement on F
R = 0.034
wR = 0.065
S = 1.51
3080 reflections
341 parameters
All H-atom parameters
refined
Weighting scheme based on
measured e.s.d.'s

$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = -0.29 e Å^{-3}
Extinction correction: F_c^* =
$F_c/(1 + \chi F_c^2/\sin 2\theta)^{1/4}$
Extinction coefficient:
0.00289 (4) (isotropic)
Atomic scattering factors
from *SHELXTL-Plus*
(Sheldrick, 1990)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni	0.2502 (1)	0.0583 (1)	0.3355 (1)	0.038 (1)
O(1)	0.2999 (2)	0.1303 (1)	0.2632 (1)	0.051 (1)
O(2)	0.1799 (2)	0.0334 (1)	0.2528 (1)	0.057 (1)
O(3)	0.2204 (2)	0.1122 (2)	0.1831 (1)	0.077 (1)
O(4)	-0.3735 (2)	-0.0999 (2)	0.4760 (1)	0.083 (1)
O(5)	-0.1983 (2)	-0.1108 (2)	0.4983 (1)	0.087 (1)
O(6)	-0.2436 (2)	-0.0905 (2)	0.4136 (1)	0.075 (1)
N(1)	0.1614 (2)	-0.0213 (1)	0.3839 (1)	0.045 (1)
N(2)	0.0024 (2)	-0.0743 (1)	0.4175 (1)	0.058 (1)
N(3)	0.1128 (2)	0.1428 (1)	0.3428 (1)	0.045 (1)
N(4)	0.3297 (2)	0.1350 (1)	0.3905 (1)	0.041 (1)
N(5)	0.5584 (2)	-0.0667 (1)	0.3498 (1)	0.045 (1)
N(6)	0.3923 (2)	-0.0129 (1)	0.3275 (1)	0.042 (1)
N(7)	0.2334 (2)	0.0923 (2)	0.2314 (1)	0.051 (1)
N(8)	-0.2727 (2)	-0.1005 (2)	0.4632 (1)	0.058 (1)
C(1)	0.1893 (2)	-0.0729 (2)	0.4278 (1)	0.046 (1)
C(2)	0.2937 (3)	-0.0943 (2)	0.4506 (1)	0.054 (1)
C(3)	0.2932 (3)	-0.1476 (2)	0.4944 (1)	0.066 (1)
C(4)	0.1926 (3)	-0.1798 (2)	0.5153 (1)	0.073 (1)
C(5)	0.0896 (3)	-0.1602 (2)	0.4927 (1)	0.070 (1)
C(6)	0.0893 (2)	-0.1061 (2)	0.4490 (1)	0.053 (1)
C(7)	0.0486 (2)	-0.0243 (1)	0.3798 (1)	0.050 (1)
C(8)	-0.0201 (2)	0.0255 (2)	0.3411 (1)	0.059 (1)
C(9)	-0.0053 (2)	0.1148 (2)	0.3535 (2)	0.066 (1)
C(10)	0.1500 (2)	0.2049 (2)	0.3828 (1)	0.058 (1)
C(11)	0.2766 (2)	0.2147 (2)	0.3805 (1)	0.056 (1)
C(12)	0.4544 (2)	0.1391 (2)	0.3863 (1)	0.049 (1)
C(13)	0.5097 (2)	0.0587 (1)	0.3997 (1)	0.045 (1)
C(14)	0.4855 (2)	-0.0058 (1)	0.3583 (1)	0.040 (1)
C(15)	0.5133 (2)	-0.1174 (1)	0.3103 (1)	0.042 (1)
C(16)	0.5528 (2)	-0.1877 (2)	0.2858 (1)	0.055 (1)

C(17)	0.4845 (2)	−0.2234 (2)	0.2472 (1)	0.060 (1)
C(18)	0.3793 (3)	−0.1903 (2)	0.2331 (1)	0.064 (1)
C(19)	0.3389 (2)	−0.1210 (2)	0.2574 (1)	0.055 (1)
C(20)	0.4079 (2)	−0.0838 (1)	0.2966 (1)	0.041 (1)

Table 2. *Selected geometric parameters* (Å, °)

Ni—N(1)	2.045 (2)	Ni—N(6)	2.051 (2)
Ni—N(4)	2.060 (2)	Ni—N(3)	2.142 (2)
Ni—O(1)	2.191 (2)	Ni—O(2)	2.200 (2)
N(1)—C(7)	1.329 (3)	N(1)—C(1)	1.401 (3)
C(1)—C(2)	1.390 (4)	C(1)—C(6)	1.393 (3)
C(2)—C(3)	1.377 (4)	C(3)—C(4)	1.390 (4)
C(4)—C(5)	1.366 (4)	C(5)—C(6)	1.382 (4)
C(6)—N(2)	1.378 (3)	N(2)—C(7)	1.343 (3)
C(7)—C(8)	1.483 (4)	C(8)—C(9)	1.517 (4)
C(9)—N(3)	1.485 (3)	N(3)—C(10)	1.477 (3)
C(10)—C(11)	1.498 (4)	C(11)—N(4)	1.477 (3)
N(4)—C(12)	1.470 (3)	C(12)—C(13)	1.514 (3)
C(13)—C(14)	1.488 (3)	C(14)—N(6)	1.329 (3)
C(14)—N(5)	1.337 (3)	C(15)—N(5)	1.377 (3)
C(15)—C(16)	1.384 (3)	C(15)—C(20)	1.396 (3)
C(16)—C(17)	1.364 (4)	C(17)—C(18)	1.393 (4)
C(18)—C(19)	1.373 (4)	C(19)—C(20)	1.389 (3)
C(20)—N(6)	1.401 (3)	N(7)—O(3)	1.221 (3)
N(7)—O(1)	1.263 (3)	N(7)—O(2)	1.269 (3)
N(8)—O(4)	1.223 (3)	N(8)—O(5)	1.229 (3)
N(8)—O(6)	1.258 (3)		
N(1)—Ni—N(6)	95.71 (8)	N(3)—C(9)—C(8)	112.0 (2)
N(6)—Ni—N(4)	92.63 (8)	C(10)—N(3)—Ni	106.5 (2)
N(6)—Ni—N(3)	174.33 (8)	N(3)—C(10)—C(11)	110.2 (2)
N(1)—Ni—O(1)	159.98 (7)	N(4)—C(11)—C(10)	108.4 (2)
N(4)—Ni—O(1)	93.34 (7)	C(12)—N(4)—Ni	115.8 (2)
N(1)—Ni—O(2)	101.85 (8)	N(4)—C(12)—C(13)	111.9 (2)
N(4)—Ni—O(2)	150.51 (7)	N(6)—C(14)—N(5)	112.1 (2)
O(1)—Ni—O(2)	58.59 (6)	N(5)—C(14)—C(13)	121.3 (2)
C(7)—N(1)—Ni	119.4 (2)	N(5)—C(15)—C(20)	105.2 (2)
C(2)—C(1)—C(6)	119.9 (2)	C(14)—N(5)—C(15)	108.6 (2)
C(6)—C(1)—N(1)	108.7 (2)	C(16)—C(17)—C(18)	121.3 (3)
C(2)—C(3)—C(4)	121.8 (3)	C(18)—C(19)—C(20)	117.4 (3)
C(4)—C(5)—C(6)	117.4 (3)	C(19)—C(20)—N(6)	131.0 (2)
N(2)—C(6)—C(1)	105.7 (2)	C(14)—N(6)—C(20)	105.3 (2)
C(7)—N(2)—C(6)	108.1 (2)	C(20)—N(6)—Ni	129.6 (2)
N(1)—C(7)—C(8)	124.6 (2)	O(3)—N(7)—O(2)	122.2 (2)
C(7)—C(8)—C(9)	110.8 (2)	N(7)—O(1)—Ni	92.8 (1)
C(10)—N(3)—C(9)	112.2 (2)	O(4)—N(8)—O(5)	121.0 (3)
C(9)—N(3)—Ni	121.0 (2)	O(5)—N(8)—O(6)	118.8 (2)
N(1)—Ni—N(4)	105.08 (8)	C(12)—N(4)—C(11)	111.6 (2)
N(1)—Ni—N(3)	89.34 (8)	C(11)—N(4)—Ni	104.6 (2)
N(4)—Ni—N(3)	83.52 (8)	C(14)—C(13)—C(12)	113.9 (2)
N(6)—Ni—O(1)	91.14 (7)	N(6)—C(14)—C(13)	126.6 (2)
N(3)—Ni—O(1)	84.94 (7)	N(5)—C(15)—C(16)	132.7 (2)
N(6)—Ni—O(2)	96.45 (7)	C(16)—C(15)—C(20)	122.1 (2)
N(3)—Ni—O(2)	85.01 (7)	C(17)—C(16)—C(15)	117.2 (3)
C(7)—N(1)—C(1)	105.5 (2)	C(19)—C(18)—C(17)	122.0 (3)
C(1)—N(1)—Ni	134.8 (2)	C(19)—C(20)—C(15)	120.0 (2)
C(2)—C(1)—N(1)	131.4 (2)	C(15)—C(20)—N(6)	108.9 (2)
C(3)—C(2)—C(1)	117.6 (3)	C(14)—N(6)—Ni	124.5 (2)
C(5)—C(4)—C(3)	121.1 (3)	O(3)—N(7)—O(1)	121.6 (3)
N(2)—C(6)—C(5)	132.1 (3)	O(1)—N(7)—O(2)	116.1 (2)
C(5)—C(6)—C(1)	122.2 (3)	N(7)—O(2)—Ni	92.3 (1)
N(1)—C(7)—N(2)	112.0 (2)	O(4)—N(8)—O(6)	120.2 (2)
N(2)—C(7)—C(8)	123.3 (2)		

The H atoms of the CH and CH$_2$ groups were allowed to ride on their C atoms and were refined. The H atoms bonded to N atoms were located on a difference Fourier map at an advanced stage of anisotropic refinement and their coordinates refined.

Data collection: *SHELXTL-Plus* (Sheldrick, 1990). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Structure solution: *SHELXTL-Plus*. Structure refinement: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Preparation of material for publication: *SHELXTL-Plus* and *PARST* (Nardelli, 1983).

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(Allyl)palladium(II) Complexes with Chiral Ligands. I. (Allyl)palladium(II) Complexes with Methylenebis(oxazoline) Ligands

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Abstract

The structures of two (allyl)palladium(II) bis(oxazoline) complexes containing (*R,R*)-2,2′-(1-methylethylidene)-bis(4-benzyl-4,5-dihydrooxazole) as a chiral ligand are