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Bis[bis(benzimidazol-2-ylmethyl-*N*^{3})amine-*N*]nickel(II) Dichloride

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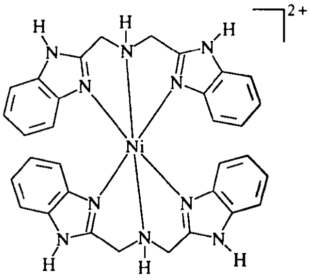
Abstract

In the title compound, $[Ni(C_{16}H_{15}N_5)_2]Cl_2$, the Ni atom has octahedral coordination, with one amine N atom and one benzimidazole N atom in axial positions and the remaining three benzimidazole and amine N atoms coordinated equatorially.

Comment

The tetrapyrrolenickel-containing factor F_{430} is implicated in the final methane evolution step of methanogenic bacteria and has attracted considerable attention (Ankel-Fuchs, Huester, Moeschel, Albracht & Thauer, 1986; Fassler, Pfaltz, Krautler & Eschenmoser, 1984; Hausinger, Orme-Johnson & Walsh, 1984). A mechanism of methane formation utilizing the nickel-containing enzyme, methyl coenzyme M reductase (methyl CoM), has been proposed (Walsh & Orme-Johnson, 1987). The final protonation step is consistent with the hydrolysis of highly air-sensitive alkylnickel(I) tetraazamacrocycles in an aqueous solution of tetraethylenepentaminenickel(II) (Stoltzenberg & Stershic, 1987). However, other studies have shown that nickel(II) acetate or (1,4,8,11-tetraazacyclotetradecane-5,7-dione)nickel(II) do not convert methyl CoM under either atmospheres of argon or H_2 (Fabbrizzi, Poggi & Seghi, 1985). It is clear that the ligand activates Ni^{II} towards methyl CoM; the ligand in F_{430} might also play an important role in activating nickel towards methyl CoM.

The synthesis of active sites of various metalloproteins/enzymes has been used to elucidate the relationship between structure and function (Thompson, Marks & Ibers, 1979; Pandiyan, Palaniandavar, Lakshminarayanan & Manohar, 1992; Pandiyan, Murali & Palaniandavar, 1995; Palaniandavar, Pandiyan, Lakshminarayanan & Manohar, 1995; Murali, Palaniandavar & Pandiyan, 1994). To overcome the difficulties of synthesizing pyrrole rings around methyl CoM, a synthetically accessible benzimidazole tridentate ligand was synthesized and complexed with a nickel(II) ion.



(I)

The recrystallization of the title complex, (I), gave air-sensitive purple crystals; a single crystal was mounted in a glass capillary tube with the mother solution. The crystal structure shows that the Ni^{II} atom is surrounded by two ligands, each acting in a tridentate manner. The N atom of the secondary amine and two N atoms of the benzimidazole groups are involved in the coordination (Fig. 1).

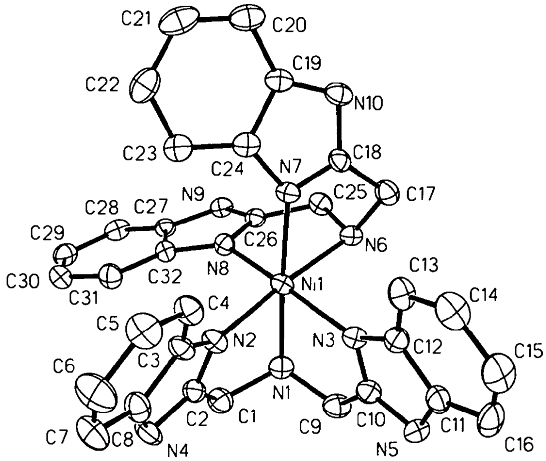


Fig. 1. The structure of the title cation, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

The geometry of (I) is *fac*-octahedral and the equatorial plane is formed by an amine and three benzimidazole N atoms. The equatorial distances between atoms N2, N6, N3 and N8, and the metal ion are 2.053 (5), 2.164 (4), 2.061 (5) and 2.057 (4) Å, respectively. The axial Ni1—N7 and Ni1—N1 distances are 2.109 (4) and 2.173 (4) Å, respectively. The benzimidazole N-atom bonds have shorter distances than those of the amine N atoms; this is due to the lone pair of electrons of the N atom being involved in resonance in the benzimidazole rings. The maximum deviations from ideal octahedral geometry are those of the angles N2—Ni1—N7, N3—Ni1—N8 and N3—Ni1—N7, with deviations of 15.2 (2), 14.8 (2) and 10.7 (2)°, respectively. The remaining 12 angles around the metal centre with adjacent donor atoms range from 79.5 (2) to 100.7 (2)° for donor atoms in *cis* positions, and from 174.3 (2) to 174.8 (2)° for donor atoms in *trans* positions.

The crystal structure is stabilized by a three-dimensional network of hydrogen bonds of the type N—H···Cl, details of which are given Table 2. The N atoms of the benzimidazole rings and amine groups are involved in hydrogen bonding. Each chloride ion is involved in three weak hydrogen bonds, with distances in the range 3.105 (6)–3.311 (5) Å. Finally, it should be mentioned that a large cavity of 149 Å^3 centred at (0,0,0.5) is observed in the lattice, without evidence for the presence of a solvent molecule in this cavity; the largest peak in the last difference Fourier map is close to Cl1.

Experimental

$NiCl_2.6H_2O$ and iminodiacetic acid were used as received from Aldrich. The ligand, bis(benzimidazol-2-ylmethyl)amine, was synthesized as reported (Nishida & Takahashi, 1988). The title compound was formed when the ligand (2.0 mmol) dissolved in methanol (10.0 ml) was added to a solution of $NiCl_2.6H_2O$ (1.0 mmol) in methanol (10.0 ml). The purple compound obtained was collected, washed with a small amount of methanol and dried over P_4O_{10}. A solution of the title complex (0.01 g) dissolved in methanol (10 ml) was allowed to evaporate. The fine purple single crystals obtained were suitable for X-ray diffraction.

Crystal data

$[Ni(C_{16}H_{15}N_5)_2]Cl_2$
$M_r = 684.27$
Triclinic
$P\bar{1}$
$a = 9.724\ (1)$ Å
$b = 11.055\ (1)$ Å
$c = 16.361\ (2)$ Å
$\alpha = 79.79\ (1)°$
$\beta = 79.19\ (1)°$
$\gamma = 73.70\ (1)°$
$V = 1643.6\ (3)$ Å^3
$Z = 2$
$D_x = 1.383$ Mg m^{-3}
$D_m = 1.391$ Mg m^{-3}
D_m measured by flotation in bromoform and benzene

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 2.53$–$10.39°$
$\mu = 0.792$ mm^{-1}
$T = 293\ (2)$ K
Irregular
0.5 × 0.3 × 0.3 mm
Purple

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: 20 ψ scans (Fait, 1991)
$T_{min} = 0.684$, $T_{max} = 0.789$
5519 measured reflections
4565 independent reflections
2944 reflections with $I > 2\sigma(I)$

$R_{int} = 0.038$
$\theta_{max} = 23°$
$h = -1 \rightarrow 10$
$k = -11 \rightarrow 12$
$l = -17 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: 6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.131$
$S = 1.072$
4559 reflections
407 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 1.0554P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.425$ e Å^{-3}
$\Delta\rho_{min} = -0.263$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0007 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ni1—N2	2.053 (5)	Ni1—N7	2.109 (4)
Ni1—N8	2.057 (4)	Ni1—N6	2.164 (4)
Ni1—N3	2.061 (5)	Ni1—N1	2.173 (4)
N8—Ni1—N3	165.2 (2)	N7—Ni1—N1	174.3 (2)
N2—Ni1—N6	174.8 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1^{i}	0.90	2.35	3.241 (5)	168
N4—H4*A*···Cl1^{ii}	0.90	2.45	3.165 (5)	137
N5—H5*A*···Cl2^{iii}	0.90	2.28	3.123 (6)	157
N6—H6···Cl1^{iv}	0.90	2.34	3.218 (5)	166
N9—H9*A*···Cl2^{v}	0.90	2.42	3.311 (5)	169
N10—H10*A*···Cl2	0.90	2.29	3.105 (6)	150

Symmetry codes: (i) $x, y, z-1$; (ii) $1-x, 1-y, 1-z$; (iii) $x, 1+y, z$; (iv) $-x, 1-y, 1-z$; (v) $-x, -y, -z$.

The crystals were unstable in the absence of the solvent. For this reason, we were unable to collect data at high diffraction angles ($\theta_{max} = 23°$).

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1270). Services for accessing these data are described at the back of the journal.

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The Secondary Explosive Tetraammine-*cis*-bis(5-nitro-2*H*-tetrazolato-N^2)cobalt(III) Perchlorate at 293 and 213 K

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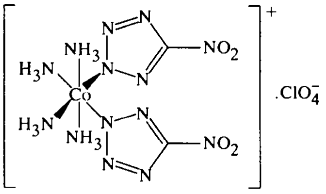
Abstract

For the title compound, $(OC\text{-}6\text{-}22)\text{-}[\mathrm{Co(CN_5O_2)_2(NH_3)_4}]\mathrm{ClO_4}$, the structure determination confirms the *cis* relationship of the two ring ligands deduced from NMR and shows that these ligands involve N-2 bonding to the Co atom. The accompanying low-temperature study suggests several O atoms of the $\mathrm{ClO_4^-}$ ion are slightly disordered rather than having large thermal displacements.

Comment

As part of an effort to elucidate fundamental properties of various substituted-tetrazolato cobalt perchlorate secondary explosives (low impact sensitivity compounds which undergo a deflagration-to-detonation transition, DDT, under the appropriate confinement) (Lieberman, 1983, 1985; Graeber & Morosin, 1983), the title compound, BNCP, proved to be a more powerful explosive and undergoes DDT more rapidly than pentaammine(5-cyanotetrazolato-N^2)cobalt(III) perchlorate, CP, used in national defense applications since 1979. More recently CP detonators have been used in oil-field completion work. The electron-withdrawing characteristics of substituents on the five-membered ligand ring alter the bonding capabilities and hence the nature of these energetic compounds (Graeber & Morosin, 1981).



BNCP

Initially the structure determined at room temperature [compound (1); coordinates deposited] yielded large anisotropic displacements for O7 and O8 of the perchlorate ion. This resulted in us performing a low temperature study which is in close agreement with that at room temperature; the corresponding displacement values were not proportionately reduced compared to those for the remainder of the structure, which is consistent with possible slight disorder, as found recently in other perchlorates (Lu, Chen & Chung, 1993; Chen, Liu, Mao, Hang & Tang, 1995).

The octahedrally coordinated Co atom consists of four Co—NH$_3$ bonds, average 1.951 (5) Å, and two

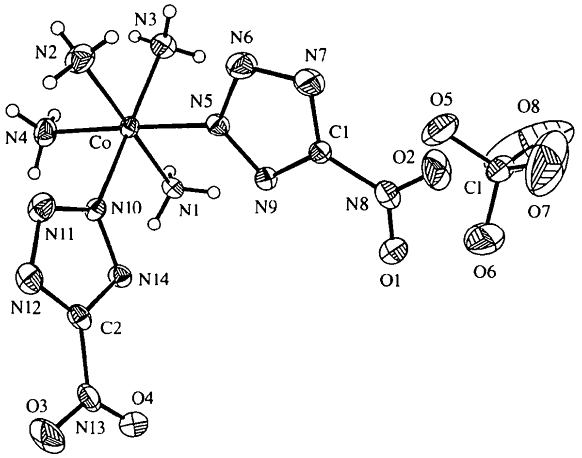


Fig. 1. The molecular structure of the BNCP cation at 213 K showing the numbering scheme and 50% probability displacement ellipsoids.

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