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Bis[bis(2-benzimidazol-2-ylethyl) sulfide]-nickel(II) Dinitrate

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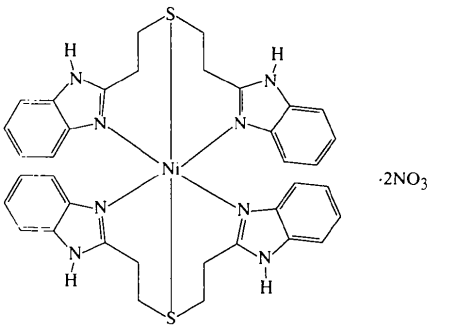
Abstract

The structure of the title compound, $[Ni(C_{18}H_{18}N_4S)_2](NO_3)_2$, consists of an octahedral nickel complex with the central Ni atom coordinated to four N atoms of the benzimidazole moieties and two S atoms. The nitrate ion lies in a well defined position in the lattice and plays an important role in the crystal packing. All four benzimidazole rings are nearly planar. The crystal structure is stabilized by a three-dimensional network of N—H···O and C—H···O hydrogen bonds.

Comment

Nickel tetrapyrrole cofactor of methanogenic bacteria, named factor F_{430} because of its absorbance maximum at 430 nm, has since been observed in all methanogens examined (Diekert, Konheiser, Piechulla & Thauer, 1981). F_{430} was shown to be the chromophore in methyl-S-CoM reductase (Ellefson, Whitman & Wolfe, 1982). F_{430} is the only known biological example of a nickel–tetrapyrrole complex (Diekert, Gilles, Jaenchen & Thauer, 1980; Pfaltz *et al.*, 1982). The structure of the methanolysis product of F_{430} has been established by Pfaltz *et al.* (1982). This enzyme catalyzes the last step in the methanogenesis, the two-electron reductive cleavage of methyl-S-CoM (methyl mercaptoethanesulfonate) to methane and HSCoM (coenzyme M, mercaptoethanesulfonate) (Ellefson & Wolfe, 1980; Nagle & Wolfe, 1983). The role of F_{430} in catalysis by the methyl S-CoM reductase has not been elucidated.

Earlier studies have shown that the ligand in F_{430} plays an important role in activating nickel towards methyl-CoM (Stoltzenberg & Stershic, 1987; Fabbrizzi, Poggi & Seghi, 1985). Here, we report the crystal structure of [bis(2-benzimidazol-2-ylethyl) sulfide]nickel(II) dinitrate, (I).



The crystal structure of the title compound consists of approximately octahedral metal complex cations and nitrate anions, which are held together by a network of hydrogen bonds. The Ni atom is coordinated by one N atom of each benzimidazole moiety and two S atoms. The average metal–ligand Ni—N and Ni—S bond lengths are 2.142 (14) and 2.554 (7) Å, respectively. The maximum angle deviations from ideal octahedral geometry are displayed by N1—Ni1—N23, N12—Ni1—N34 and S1—Ni1—S2, with values of 176.0 (1), 176.1 (1) and 174.0 (1)°, respectively. The 12 angles subtended at the metal atom by adjacent donors range from 86.8 (1) to 96.5 (1)°. The molecules consists of four nearly planar benzimidazole rings, denoted by *A*, *B*, *C* and *D*. The dihedral angles are *A*/*B* 40.5 (1), *A*/*C* 80.2 (1) and *A*/*D* 81.7 (1)°.

The crystal structure is stabilized by a three-dimensional network of hydrogen bonds of the type N—H···O and C—H···O (Desiraju, 1991), details of which are given in Table 3.

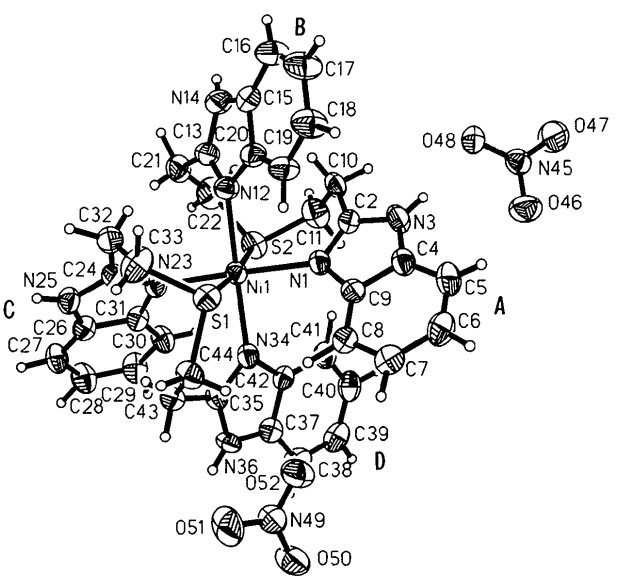


Fig. 1. The molecular structure of the title compound with the atom-labelling scheme. The displacement ellipsoids are drawn at the 50% probability level.

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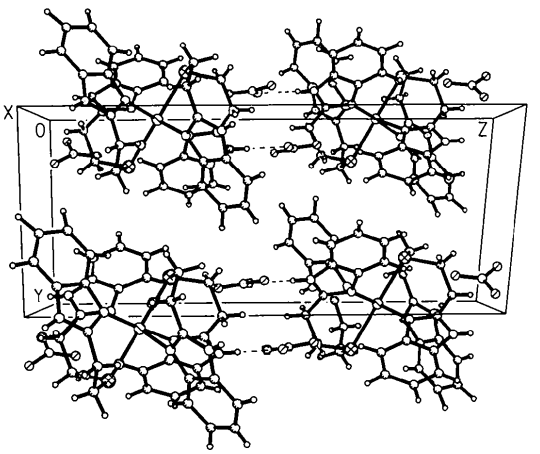

Fig. 2. A perspective drawing of the packing arrangement of the title compound. The dashed lines indicate intermolecular N—H···O hydrogen bonds.

Experimental

$Ni(NO_3)_2.6H_2O$, 3,3′-thiodipropionic acid and 1,2-diaminobenzene were used as received from Aldrich. The ligand, bis(2-benzimidazole-2-ylethyl) sulfide (bbes) was synthesized as reported by Dagdigian & Reed (1979). $Ni(bbes)_2.2NO_3$ was formed when the ligand (2.0 mmol) was dissolved in methanol (10.0 ml) and this was added with stirring to a solution of $Ni(NO_3)_2.6H_2O$ (1.0 mmol; 5.0 ml). The blue complex obtained was collected and dried over P_4H_{10}. A solution of $Ni(bbes)_2.2NO_3$ (0.01 ml) was allowed to evaporate slowly. Suitable fine blue single crystals were obtained for X-ray diffraction analysis.

Crystal data

$[Ni(C_{18}H_{18}N_4S)_2](NO_3)_2$
M_r = 827.58
Triclinic
$P\bar{1}$
a = 9.809 (4) Å
b = 10.011 (4) Å
c = 21.975 (8) Å
α = 91.77 (1)°
β = 91.62 (1)°
γ = 113.03 (2)°
V = 1983 (1) Å^3
Z = 2
D_x = 1.386 Mg m^{-3}
D_m = 1.394 Mg m^{-3}
D_m measured by flotation in bromoform and benzene

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 45 reflections
θ = 5.5–12.32°
μ = 0.652 mm^{-1}
T = 293 (2) K
Rhombohedron
0.3 × 0.2 × 0.2 mm
Blue

Data collection

Siemens $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
8301 measured reflections
6966 independent reflections
4704 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.0365
θ_{max} = 25°
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -1 \rightarrow 26$
3 standard reflections monitored every 97 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0533
$wR(F^2)$ = 0.1364
S = 1.073
6966 reflections
639 parameters
All H-atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 4.3815P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.047
$\Delta\rho_{max}$ = 0.536 e Å^{-3}
$\Delta\rho_{min}$ = −0.460 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
Ni1	0.42387 (6)	0.02663 (6)	0.25453 (3)	0.0324 (2)
S1	0.53090 (13)	0.26330 (13)	0.19816 (6)	0.0404 (3)
S2	0.34424 (15)	−0.20968 (13)	0.31014 (6)	0.0459 (3)
N1	0.3017 (4)	0.0977 (4)	0.3173 (2)	0.0354 (9)
C2	0.2999 (5)	0.0806 (5)	0.3781 (2)	0.0365 (10)
N3	0.2411 (5)	0.1664 (5)	0.4073 (2)	0.0450 (10)
C4	0.1993 (5)	0.2430 (5)	0.3637 (2)	0.0397 (11)
C5	0.1315 (6)	0.3433 (6)	0.3694 (2)	0.0518 (13)
C6	0.1009 (6)	0.3990 (6)	0.3158 (3)	0.0518 (13)
C7	0.1339 (5)	0.3546 (5)	0.2589 (2)	0.0462 (12)
C8	0.2011 (5)	0.2548 (5)	0.2535 (2)	0.0416 (11)
C9	0.2341 (5)	0.1990 (5)	0.3068 (2)	0.0353 (10)
C10	0.3451 (6)	−0.0238 (6)	0.4131 (2)	0.0451 (12)
C11	0.2790 (6)	−0.1799 (6)	0.3848 (2)	0.0540 (14)
N12	0.6090 (4)	0.1130 (4)	0.3200 (2)	0.0383 (9)
C13	0.6763 (5)	0.0318 (5)	0.3449 (2)	0.0413 (11)
N14	0.7586 (5)	0.0985 (5)	0.3961 (2)	0.0467 (10)
C15	0.7466 (5)	0.2322 (5)	0.4064 (2)	0.0409 (11)
C16	0.8068 (6)	0.3424 (6)	0.4527 (2)	0.0573 (15)
C17	0.7693 (7)	0.4613 (6)	0.4482 (3)	0.062 (2)
C18	0.6756 (6)	0.4731 (6)	0.4008 (3)	0.0560 (14)
C19	0.6161 (6)	0.3633 (5)	0.3552 (2)	0.0449 (12)
C20	0.6530 (5)	0.2414 (5)	0.3582 (2)	0.0381 (11)
C21	0.6636 (6)	−0.1152 (6)	0.3218 (2)	0.0502 (13)
C22	0.5133 (7)	−0.2378 (6)	0.3313 (3)	0.061 (2)
N23	0.5350 (4)	−0.0599 (4)	0.1911 (2)	0.0346 (9)
C24	0.6637 (5)	0.0202 (5)	0.1666 (2)	0.0347 (10)
N25	0.6899 (4)	−0.0466 (4)	0.1157 (2)	0.0405 (9)
C26	0.5710 (5)	−0.1800 (5)	0.1052 (2)	0.0377 (11)
C27	0.5407 (6)	−0.2924 (5)	0.0603 (2)	0.0464 (12)
C28	0.4095 (6)	−0.4147 (6)	0.0635 (2)	0.0532 (14)
C29	0.3120 (6)	−0.4273 (5)	0.1121 (2)	0.0502 (13)
C30	0.3416 (5)	−0.3151 (5)	0.1565 (2)	0.0452 (12)
C31	0.4729 (5)	−0.1904 (5)	0.1530 (2)	0.0359 (10)
C32	0.7714 (5)	0.1666 (5)	0.1894 (2)	0.0434 (12)
C33	0.7218 (6)	0.2904 (6)	0.1793 (3)	0.0587 (15)
N34	0.2414 (4)	−0.0439 (4)	0.1900 (2)	0.0353 (9)
C35	0.2468 (5)	−0.0279 (5)	0.1294 (2)	0.0338 (10)
N36	0.1161 (4)	−0.1129 (4)	0.0995 (2)	0.0382 (9)
C37	0.0162 (5)	−0.1873 (5)	0.1430 (2)	0.0386 (11)
C38	−0.1337 (6)	−0.2857 (5)	0.1366 (3)	0.0480 (13)
C39	−0.2032 (6)	−0.3369 (6)	0.1906 (3)	0.0527 (14)
C40	−0.1272 (6)	−0.2919 (6)	0.2481 (3)	0.0488 (13)
C41	0.0198 (5)	−0.1938 (5)	0.2540 (2)	0.0419 (11)
C42	0.0931 (5)	−0.1424 (5)	0.1996 (2)	0.0346 (10)
C43	0.3733 (6)	0.0733 (6)	0.0949 (2)	0.0405 (11)
C44	0.4366 (6)	0.2306 (5)	0.1218 (2)	0.0431 (12)
N45	0.0829 (5)	0.1543 (4)	0.5487 (2)	0.0436 (10)
O46	0.0041 (4)	0.1741 (4)	0.5062 (2)	0.0651 (11)
O47	0.0408 (5)	0.1353 (6)	0.6011 (2)	0.0822 (14)
O48	0.2077 (4)	0.1520 (4)	0.5372 (2)	0.0543 (9)
N49	0.0424 (5)	0.1760 (5)	0.0528 (2)	0.0468 (10)
O50	−0.0905 (4)	0.1051 (5)	0.0317 (2)	0.0724 (13)
O51	0.1426 (4)	0.2303 (5)	0.0173 (2)	0.0804 (14)
O52	0.0675 (4)	0.1897 (5)	0.1083 (2)	0.0652 (11)

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

Ni1—N34	2.126 (4)	Ni1—S1	2.561 (2)
Ni1—N1	2.131 (4)	S1—C33	1.846 (5)
Ni1—N23	2.153 (4)	S1—C44	1.849 (5)
Ni1—N12	2.159 (4)	S2—C11	1.836 (5)
Ni1—S2	2.547 (2)	S2—C22	1.837 (6)
N34—Ni1—N1	90.8 (1)	N1—Ni1—S1	96.5 (1)
N34—Ni1—N23	87.0 (1)	N23—Ni1—S1	86.8 (1)
N1—Ni1—N23	176.0 (1)	N12—Ni1—S1	89.1 (1)
N34—Ni1—N12	176.1 (1)	S2—Ni1—S1	174.0 (1)
N1—Ni1—N12	87.1 (1)	C33—S1—C44	101.8 (2)
N23—Ni1—N12	95.2 (1)	C33—S1—Ni1	107.2 (2)
N34—Ni1—S2	96.2 (1)	C44—S1—Ni1	107.8 (2)
N1—Ni1—S2	88.0 (1)	C11—S2—C22	102.0 (3)
N23—Ni1—S2	88.9 (1)	C11—S2—Ni1	108.3 (2)
N12—Ni1—S2	87.1 (1)	C22—S2—Ni1	107.2 (2)
N34—Ni1—S1	87.8 (1)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O48	0.85 (5)	2.04 (5)	2.883 (4)	172 (5)
N14—H14···O48^{i}	0.69 (5)	2.48 (5)	3.066 (4)	144 (5)
N25—H25···O50^{ii}	0.86 (4)	2.02 (4)	2.862 (4)	163 (4)
N36—H36···O50^{iii}	0.82 (4)	2.08 (4)	2.894 (5)	176 (4)
C8—H8···O52	1.05 (5)	2.64 (5)	3.360 (5)	126 (3)
C11—H112···O47^{iv}	1.07 (4)	2.46 (4)	3.355 (6)	141 (3)
C16—H16···O46^{ii}	0.95 (4)	2.42 (4)	3.243 (6)	147 (4)
C21—H212···O47^{i}	1.13 (5)	2.29 (5)	3.395 (5)	168 (4)
C21—H212···O48^{i}	1.13 (5)	2.60 (5)	3.399 (5)	127 (3)
C27—H27···O51^{v}	0.96 (5)	2.56 (5)	3.435 (5)	151 (4)
C32—H322···O52^{ii}	1.04 (4)	2.38 (4)	3.386 (5)	162 (4)
C44—H442···O52	0.98 (5)	2.70 (5)	3.483 (7)	138 (4)

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

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, 1991). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexakis(*N*,*N*-dimethylformamide)nickel(II) Diperchlorate

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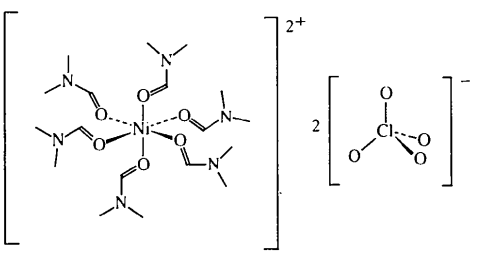
Abstract

The asymmetric unit of $[Ni(C_3H_7NO)_6](ClO_4)_2$ contains two independent ClO_4^- anions along with two independent halves of the $[Ni(dmf)_6]^{2+}$ cation, each Ni^{2+} ion being located on a centre of symmetry. The two cations differ in the orientation of the dmf ligands.

Comment

Hexakis(*N*,*N*-dimethylformamide)nickel(II) diperchlorate, $[Ni(dmf)_6](ClO_4)_2$, (I), is a potentially useful source of anhydrous Ni^{2+} for syntheses. It can be readily prepared and is surprisingly air-stable.



(I)

Fig. 1 shows the two independent $[Ni(dmf)_6]^{2+}$ cations. The cations can be distinguished by examining the conformation of the dmf ligands about the metal