metal-organic compounds

Diaquabis[N-(2-fluorobenzyl)-N-nitroso-hydroxylaminato-κ^2O,O']nickel(II)

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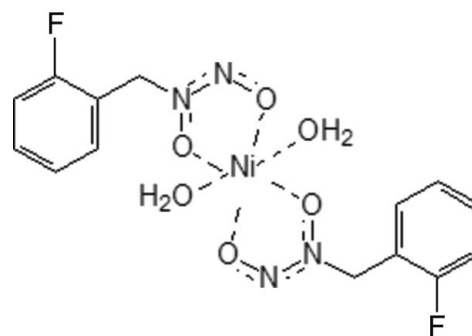Correspondence e-mail: okovalchukova@mail.ru

In the centrosymmetric title compound, $[Ni(C_7H_6FN_2O_2)_2-(H_2O)_2]$, the Ni^{II} cation is in a slightly distorted octahedral environment and is surrounded by four O atoms from the N—O groups of the organic ligands [Ni—O = 2.0179 (13) and 2.0283 (12) Å], and two water molecules [Ni—O = 2.0967 (14) Å]. The N-(2-fluorobenzyl)-N-nitrosohydroxylaminate monoanions act as bidentate chelating ligands. In the crystal, the Ni cations in the columns are shifted in such a way that the coordinated water molecules are involved in the formation of hydrogen bonds with the O atoms of the organic species of neighbouring molecules. Thus, a two-dimensional network parallel to (100) is built up by hydrogen-bonded molecules.

Related literature

For the synthesis of the potassium N-(2-fluorobenzyl)-N-nitrosohydroxylaminate salt, see: Zyuzin et al. (1997) and of the Ni complex of N-(2-fluorobenzyl)-N-nitrosohydroxylaminate, see: Kovalchukova et al. (2013). For the structures of some 3d-metal complexes with N-nitrosohydroxylamine derivatives, see: Deák et al. (1998); Okabe & Tamaki (1995); Tamaki & Okabe (1996, 1998). For the synthesis, properties and applications of other metal nitrosohydroxylaminates, see: Okabe et al. (1995); Abraham et al. (1987); Venter et al. (2009); Popov & Wendlandt (1954); Lundell & Knowles (1920); Buscarons & Canela (1974); Oztekin & Erim (2000); Yi et al. (1995); McGill et al. (2000); Shiino et al. (2001).

Experimental

Crystal data

$[Ni(C_7H_6FN_2O_2)_2(H_2O)_2]$	V = 847.5 (3) Å^3
M_r = 433.02	Z = 2
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 15.411 (3) Å	μ = 1.21 mm^{-1}
b = 7.235 (1) Å	T = 293 K
c = 7.604 (1) Å	0.75 × 0.20 × 0.05 mm
β = 91.65 (3)°	

Data collection

Enraf–Nonius CAD-4 diffractometer	1703 measured reflections
Absorption correction: part of the refinement model (ΔF) (Walker & Stuart, 1983)	1571 independent reflections
	1181 reflections with $I > 2\sigma(I)$
T_{min} = 0.427, T_{max} = 0.809	R_{int} = 0.022
	3 standard reflections every 60 min intensity decay: 0.0%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.066	
S = 1.01	$\Delta\rho_{max}$ = 0.31 e Å^{-3}
1571 reflections	$\Delta\rho_{min}$ = −0.32 e Å^{-3}
132 parameters	
2 restraints	

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H31$\cdots$O1^i	0.84 (1)	1.97 (1)	2.7987 (18)	169 (3)
O3—H32$\cdots$O2^{ii}	0.84 (1)	1.98 (1)	2.8078 (18)	170 (2)

Symmetry codes: (i) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection: CAD-4-PC (Enraf–Nonius, 1993); cell refinement: CAD-4-PC; data reduction: CAD-4-PC; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: CIFTAB97 (Sheldrick, 2008) and SHELX97.

Supporting information for this paper is available from the IUCr electronic archives (Reference: BV2230).

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supporting information

Diaquabis[*N*-(2-fluorobenzyl)-*N*-nitrosohydroxylaminato-$\kappa^2 O,O'$]nickel(II)

Olga Kovalchukova, Ali Sheikh Bostanabad, Adam Stash, Svetlana Strashnova and Igor Zyuzin

S1. Comment

N-nitrosohydroxylamine derivatives are good chelating agents which form stable complexes with a wide range of metal ions (Okabe *et al.*, 1995; Abraham *et al.*, 1987; Venter *et al.*, 2009; Popov & Wendlandt, 1954). The phenyl and naphthyl derivatives, known as cupferron and neocupferron, are reported as good analytical reagents for the determination of zirconium in its ores and metallurgical products, as well as for the separation of iron and titanium from manganese and aluminum in limestone analysis, separation and direct UV detection of lanthanides and other analyses (Lundell & Knowles, 1920; Buscarons & Canela, 1974; Oztekin & Erim, 2000). R_2N[N$_2$0$_2$] anions are smooth nonenzymatic releasers of nitric oxide in physiological media (Yi *et al.*, 1995; McGill *et al.*, 2000) and possess the property of inhibition of mushroom tyrosinase (Shiino *et al.*, 2001).

In the title compound, $C_{14}H_{16}F_2N_4NiO_6$, the Ni cation of the centrosymmetrical structure is in a slightly distorted octahedral coordination and is surrounded by four oxo O atoms of the N—O groups of the organic ligands [Ni—O = 2.0179 (13) and 2.0283 (12) Å], and two water molecules in the axial positions [Ni—O = 2.0967 (14) Å]. The described coordination type of the central atom correlates with those described previously for the dimethanolo-bis(N– nitroso-*N*-phenyl-hydroxylaminato-o,o) cobalt(II) (Deak *et al.*, 1998) and the dimethanolo-bis (*N*-nitroso-*N*-phenylhydroxy-laminato-O,O′)nickel(II) (Okabe & Tamaki, 1995). On the other hand, in the reported structure of the diaquabis[*N*-(1-naphthyl)-*N*-nitrosohydroxylaminato- O, O′] cobalt(II) (Tamaki & Okabe, 1998), the two coordinated water molecules are in the *cis* arrangement. In addition in the bis(*N*-nitroso-*N*-phenylhydroxylaminato)manganese, or manganese cupferronate (Tamaki & Okabe, 1996), the saturation of the coordination sphere of the Mn(II) cation occurs with the two O atoms of the nitroso groups of two adjacent cupferron ligands. The *N*-(2-fluorobenzyl)-*N*-nitrosohydroxylaminate monoanions act as bidentate chelating ligands. The Ni cations in the columns are shifted in such a way that the coordinated H$_2$O molecules are involved in the formation of hydrogen bonds with the O atoms of the organic species of the neighbouring molecules in the columns. Thus, the crystal lattice of the reported structure is a supramolecular architecture built up by infinite one dimensional chains of hydrogen bonded molecules.

S2. Experimental

The potassium *N*-(2-fluorobenzyl)-*N*-nitrosohydroxylaminate salt and its Ni complex was prepared (see Fig. 3) according to procedures described previously (Zyuzin *et al.*, 1997; Kovalchukova *et al.*, 2013). Single crystals of $C_{14}H_{16}F_2N_4O_6$ were grown by the slow evaporation of the ethanol solution of the diaquabis[N-(2-fluorobenzyl)-*N*-nitrosohydroxy-laminato-*O,O′*]nickel(II) powdered sample.

S3. Refinement

The structure of of $C_{14}H_{16}F_2N_4O_6$ was solved by direct method and all non-hydrogen atoms were located and refined in anisotropically. All the hydrogen atoms were located in difference electron density syntheses and included in refinement

with fixed parameters.

Figure 1

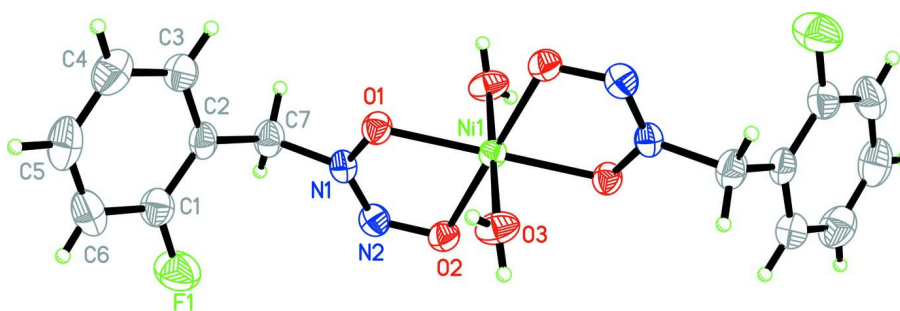*ORTEP* view of $C_{14}H_{16}F_2N_4O_6$ with atom labeling scheme (displacement ellipsoids are drawn at the 50% probability level for non-hydrogen atoms).
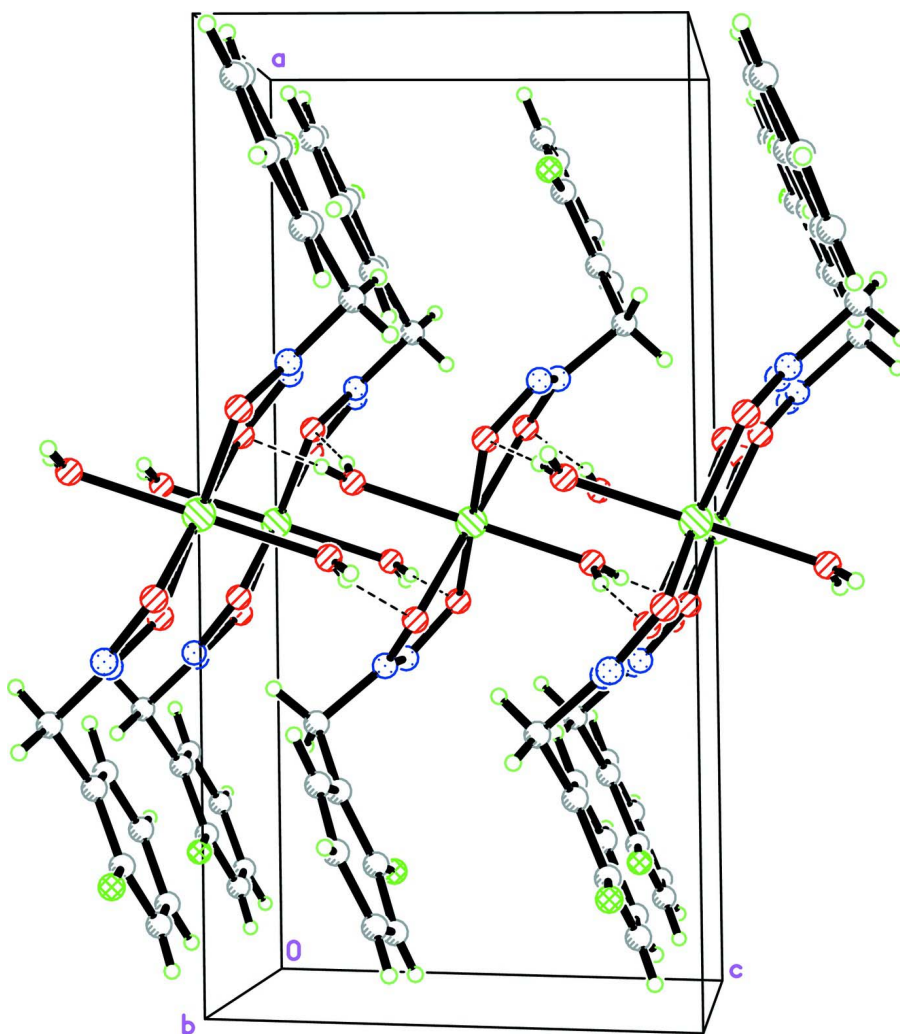

Figure 2

Molecular packing in the crystal of the complex along the crystallographic axis b.
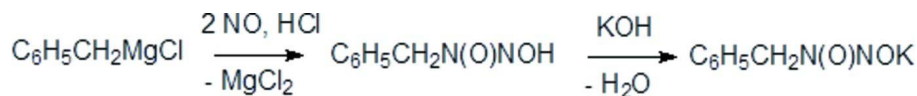
$$C_6H_5CH_2MgCl \xrightarrow[- MgCl_2]{2\ NO,\ HCl} C_6H_5CH_2N(O)NOH \xrightarrow[- H_2O]{KOH} C_6H_5CH_2N(O)NOK$$

Figure 3

The synthesis of the potassium *N*-(2-fluorobenzyl)-Nnitrosohydroxylaminate salt

Diaquabis[*N*-(2-fluorobenzyl)-*N*-nitrosohydroxylaminato-κ^2O,O']nickel(II)

Crystal data

[Ni(C$_7$H$_6$FN$_2$O$_2$)$_2$(H$_2$O)$_2$]	$F(000) = 444$
$M_r = 433.02$	$D_x = 1.697$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 15.411$ (3) Å	Cell parameters from 24 reflections
$b = 7.235$ (1) Å	$\theta = 10.9$–$12.5°$
$c = 7.604$ (1) Å	$\mu = 1.21$ mm^{-1}
$\beta = 91.65$ (3)°	$T = 293$ K
$V = 847.5$ (3) Å^3	Plate, green
$Z = 2$	$0.75 \times 0.20 \times 0.05$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	1571 independent reflections
Radiation source: fine-focus tube	1181 reflections with $I > 2\sigma(I)$
β-filter monochromator	$R_{int} = 0.022$
$\omega/2\theta$ scans	$\theta_{max} = 25.5°$, $\theta_{min} = 2.6°$
Absorption correction: part of the refinement model (ΔF)	$h = -18 \rightarrow 18$
(Walker & Stuart, 1983)	$k = 0 \rightarrow 8$
$T_{min} = 0.427$, $T_{max} = 0.809$	$l = 0 \rightarrow 9$
1703 measured reflections	3 standard reflections every 60 min
	intensity decay: 0.0%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.022$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.066$	$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2]$
$S = 1.01$	where $P = (F_o^2 + 2F_c^2)/3$
1571 reflections	$(\Delta/\sigma)_{max} < 0.001$
132 parameters	$\Delta\rho_{max} = 0.31$ e Å^{-3}
2 restraints	$\Delta\rho_{min} = -0.32$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.5000	0.5000	0.5000	0.02414 (12)
F1	0.12983 (10)	0.46369 (18)	0.3199 (2)	0.0610 (4)
O1	0.39701 (8)	0.63578 (16)	0.39297 (15)	0.0292 (3)
O2	0.41642 (8)	0.28946 (16)	0.44659 (16)	0.0312 (3)
N1	0.34766 (9)	0.51068 (19)	0.31185 (19)	0.0278 (3)
N2	0.35419 (10)	0.3370 (2)	0.3362 (2)	0.0317 (3)
C1	0.14337 (13)	0.6479 (3)	0.3049 (3)	0.0386 (4)
C2	0.22021 (12)	0.7072 (3)	0.2360 (2)	0.0329 (4)
C3	0.23158 (14)	0.8967 (3)	0.2205 (3)	0.0406 (5)
H3	0.2824	0.9423	0.1738	0.049*
C4	0.16858 (17)	1.0184 (3)	0.2733 (3)	0.0519 (6)
H4	0.1773	1.1451	0.2629	0.062*
C5	0.09283 (16)	0.9527 (3)	0.3412 (3)	0.0531 (6)
H5	0.0504	1.0354	0.3760	0.064*
C6	0.07923 (13)	0.7649 (3)	0.3581 (3)	0.0477 (5)
H6	0.0282	0.7193	0.4041	0.057*
C7	0.28684 (13)	0.5742 (3)	0.1721 (2)	0.0369 (4)
H71	0.2575	0.4679	0.1206	0.044*
H72	0.3194	0.6333	0.0805	0.044*
O3	0.45896 (10)	0.53062 (17)	0.75889 (18)	0.0371 (3)
H31	0.4344 (17)	0.628 (3)	0.790 (4)	0.075 (9)*
H32	0.4418 (15)	0.443 (2)	0.821 (3)	0.052 (7)*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.02426 (18)	0.02405 (17)	0.02409 (17)	0.00166 (12)	0.00050 (11)	0.00039 (11)
F1	0.0577 (8)	0.0447 (7)	0.0812 (10)	−0.0079 (6)	0.0135 (7)	−0.0001 (6)
O1	0.0292 (6)	0.0261 (5)	0.0321 (6)	0.0014 (5)	−0.0027 (5)	−0.0010 (5)
O2	0.0330 (7)	0.0271 (6)	0.0335 (6)	−0.0003 (5)	−0.0004 (5)	0.0022 (5)
N1	0.0243 (7)	0.0317 (7)	0.0274 (7)	0.0030 (6)	−0.0003 (6)	−0.0027 (6)
N2	0.0304 (8)	0.0317 (8)	0.0331 (7)	0.0006 (6)	0.0021 (6)	−0.0030 (6)
C1	0.0366 (11)	0.0405 (10)	0.0382 (10)	0.0008 (8)	−0.0049 (8)	−0.0023 (8)
C2	0.0286 (9)	0.0419 (10)	0.0279 (9)	0.0051 (7)	−0.0059 (7)	−0.0005 (7)
C3	0.0381 (11)	0.0441 (11)	0.0394 (10)	0.0001 (8)	−0.0046 (9)	0.0047 (8)
C4	0.0595 (14)	0.0403 (11)	0.0553 (13)	0.0083 (10)	−0.0067 (11)	0.0006 (9)
C5	0.0494 (13)	0.0590 (14)	0.0504 (13)	0.0228 (11)	−0.0050 (10)	−0.0083 (10)
C6	0.0317 (11)	0.0679 (15)	0.0434 (11)	0.0052 (10)	0.0013 (9)	−0.0062 (10)
C7	0.0351 (10)	0.0484 (10)	0.0269 (9)	0.0077 (9)	−0.0029 (8)	−0.0001 (8)
O3	0.0518 (8)	0.0300 (7)	0.0303 (6)	0.0022 (6)	0.0127 (6)	0.0008 (5)

Geometric parameters (Å, º)

Ni1—O1^i	2.0179 (13)	C2—C3	1.388 (3)
Ni1—O1	2.0179 (13)	C2—C7	1.498 (3)

Ni1—O2	2.0283 (12)	C3—C4	1.379 (3)
Ni1—O2^i	2.0283 (12)	C3—H3	0.9300
Ni1—O3	2.0967 (14)	C4—C5	1.375 (4)
Ni1—O3^i	2.0967 (14)	C4—H4	0.9300
F1—C1	1.354 (2)	C5—C6	1.381 (3)
O1—N1	1.3233 (19)	C5—H5	0.9300
O2—N2	1.302 (2)	C6—H6	0.9300
N1—N2	1.274 (2)	C7—H71	0.9700
N1—C7	1.470 (2)	C7—H72	0.9700
C1—C6	1.371 (3)	O3—H31	0.838 (10)
C1—C2	1.377 (3)	O3—H32	0.837 (10)
O1^i—Ni1—O1	180.0	C1—C2—C3	116.90 (18)
O1^i—Ni1—O2	101.70 (5)	C1—C2—C7	121.86 (17)
O1—Ni1—O2	78.30 (5)	C3—C2—C7	121.17 (18)
O1^i—Ni1—O2^i	78.30 (5)	C4—C3—C2	121.0 (2)
O1—Ni1—O2^i	101.70 (5)	C4—C3—H3	119.5
O2—Ni1—O2^i	180.0	C2—C3—H3	119.5
O1^i—Ni1—O3	85.86 (6)	C5—C4—C3	120.1 (2)
O1—Ni1—O3	94.14 (6)	C5—C4—H4	120.0
O2—Ni1—O3	93.46 (6)	C3—C4—H4	120.0
O2^i—Ni1—O3	86.54 (6)	C4—C5—C6	120.5 (2)
O1^i—Ni1—O3^i	94.14 (6)	C4—C5—H5	119.7
O1—Ni1—O3^i	85.86 (6)	C6—C5—H5	119.7
O2—Ni1—O3^i	86.54 (6)	C1—C6—C5	117.8 (2)
O2^i—Ni1—O3^i	93.46 (6)	C1—C6—H6	121.1
O3—Ni1—O3^i	180.0	C5—C6—H6	121.1
N1—O1—Ni1	106.85 (9)	N1—C7—C2	113.27 (14)
N2—O2—Ni1	112.47 (10)	N1—C7—H71	108.9
N2—N1—O1	124.40 (14)	C2—C7—H71	108.9
N2—N1—C7	117.37 (14)	N1—C7—H72	108.9
O1—N1—C7	117.96 (14)	C2—C7—H72	108.9
N1—N2—O2	114.08 (14)	H71—C7—H72	107.7
F1—C1—C6	117.94 (19)	Ni1—O3—H31	120 (2)
F1—C1—C2	118.37 (17)	Ni1—O3—H32	124.0 (18)
C6—C1—C2	123.69 (19)	H31—O3—H32	109 (3)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H31···O1^{ii}	0.84 (1)	1.97 (1)	2.7987 (18)	169 (3)
O3—H32···O2^{iii}	0.84 (1)	1.98 (1)	2.8078 (18)	170 (2)

Symmetry codes: (ii) *x*, −*y*+3/2, *z*+1/2; (iii) *x*, −*y*+1/2, *z*+1/2.