Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Hexakis(*N*,*N*-dimethylacetamide)nickel(II) bis(tetrafluoroborate) 0.17-hydrate

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Received 24 January 2006
Accepted 7 February 2006

The nickel complex of the title compound, $[Ni(C_4H_9NO)_6](BF_4)_2\cdot 0.17H_2O$, has an octahedral coordination geometry with $\overline{3}$ symmetry at the Ni ion, in which all six ligands are crystallographically equivalent. The Ni—O—C—N torsion angle [151.2 (3)°] indicates that the Ni—O bond is displaced from the direction of the lone pair of the sp^2 O atom. This is ascribed to the steric hindrance of the ligand in an octahedral environment.

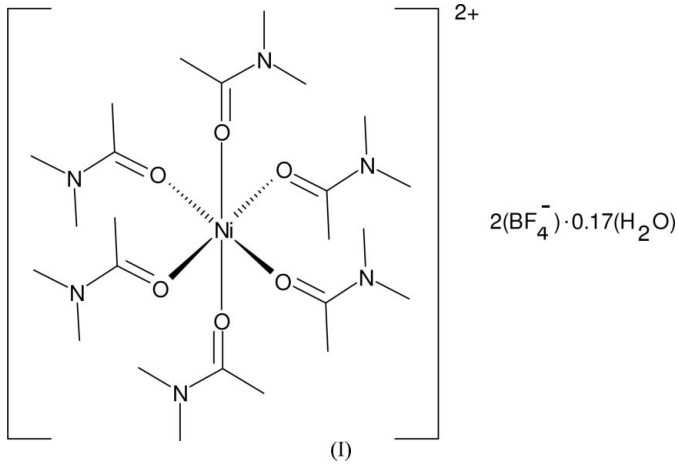
Key indicators

Single-crystal X-ray study
T = 149 K
Mean σ(C–C) = 0.006 Å
Disorder in solvent or counterion
R factor = 0.060
wR factor = 0.153
Data-to-parameter ratio = 20.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Complexation equilibria in *N*,*N*-dimethylacetamide (DMA) solution have revealed unusual coordination structures and the importance of sterically hindered solvation (Suzuki & Ishiguro, 1992). It is essential to elucidate the detailed structure of solvated cations to understand such solvent effects. Here we report the structure of the title compound, (I).



(I)

The complex cation (Fig. 1) has an octahedral structure, in which the Ni ion is located at the origin with $\overline{3}$ symmetry. Six coordinating DMA molecules are crystallographically equivalent, leading to a highly symmetrical octahedral environment. The Ni—O—C—N torsion angle [151.2 (3)°] deviates from 180°. This serves as a measure of coplanarity between the metal and the molecular plane of DMA, and indicates that Ni^{2+} is out of the DMA molecular plane. Such a deviation is absent in the analogous aluminium complex of *N*,*N*-dimethylformamide (Suzuki & Ishiguro, 1998). Therefore, it is ascribed to the steric hindrance of the acetyl methyl group of DMA in the octahedral coordination structure. In the analogous but less crowded structure of $[Ni(DMA)_4(acetonitrile)_2]^{2+}$, however, two DMA ligands are practically undis-

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torted [169.9 (2)°], whereas the other two DMA ligands show an even stronger distortion [113.4 (3)°] (Suzuki & Ishiguro, 1997).

Experimental

The title compound was prepared by dissolving nickel tetrafluoroborate hydrate (70 g) in *N*,*N*-dimethylacetamide (DMA) (100 ml) and removing the excess solvent in a rotary evaporator. Green–yellow needle-shaped crystals were precipitated from a DMA solution by the addition of diethyl ether. Single crystals were obtained by gradual cooling of the hot solution. The crystals were extremely hygroscopic; they turned into a solution within a few seconds, even in a glove box purged with argon over P_2O_5. Accordingly, a drop of the mother liquor containing the crystal was quickly transferred into a capillary tube, the liquid was then sucked out and the tube was sealed immediately. The Karl–Fischer analysis of the crystals indicated small but indefinite amounts of water, which may be from the hydrate or the solvents.

Crystal data

$[Ni(C_4H_9NO)_6](BF_4)_2\cdot 0.17H_2O$	Mo $K\alpha$ radiation
M_r = 758.13	Cell parameters from 25 reflections
Trigonal, $P\overline{3}$	θ = 13.2–14.9°
a = 12.334 (6) Å	μ = 0.61 mm^{-1}
c = 7.030 (8) Å	T = 149 (2) K
V = 926.2 (12) Å^3	Needle, yellow
Z = 1	0.40 × 0.20 × 0.20 mm
D_x = 1.359 Mg m^{-3}	

Data collection

Rigaku AFC-5 diffractometer	θ_{max} = 30.1°
ω–2θ scans	$h = 0 \rightarrow 17$
Absorption correction: none	$k = 0 \rightarrow 17$
1858 measured reflections	$l = -9 \rightarrow 9$
1588 independent reflections	3 standard reflections
1468 reflections with $I > 2\sigma(I)$	frequency: 60 min
R_{int} = 0.020	intensity decay: 5.4%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.061	$w = 1/[\sigma^2(F_o^2) + (0.105P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.153	$(\Delta/\sigma)_{max} < 0.001$
S = 1.03	$\Delta\rho_{max}$ = 0.91 e Å^{-3}
1588 reflections	$\Delta\rho_{min}$ = −0.79 e Å^{-3}
77 parameters	

Table 1
Selected geometric parameters (Å, °).

Ni—O1	2.065 (3)		
O1—Ni—O1^{i}	94.76 (11)	Ni—O1—C1	137.4 (2)
O1—Ni—O1^{ii}	85.24 (11)		
Ni—O1—C1—N1	151.2 (3)	Ni—O1—C1—C2	−29.8 (6)

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

Space group $P\overline{3}$ gave a chemically reasonable structure, in which the Ni atom was at the origin. However, two crystallographically independent DMA molecules were found, resulting in twelve-coordination instead of the expected six-coordination. Thus, the complex appeared to be two superposed octahedra, one of which could be generated from the other by a 60° rotation about the triad axis. The triad axis of a trigonal system can function as a twin axis (Buerger, 1960; Phillips, 1963; Kelly & Groves, 1970), and sixfold rotation generates a twin by pseudomerohedry (Koch, 1992). Therefore, two-component rotation twinning ($h' = -k$, $k' = h + k$, $l' = l$) was accounted for in the refinement; the twinning ratio was 0.493 (3), showing nearly perfect twinning. Methyl H atoms were positioned geometrically (C—H = 0.98 Å) and refined as riding with $U_{iso}(H) = 1.5U_{eq}(C)$, allowing for free rotation of the methyl groups. After the complex cation and the counter-anion had been located, a positive peak remained at $(0, 0, \frac{1}{2})$. Although false peaks might often appear in special positions of high symmetry, the distance of 2.993 (3) Å from this peak to the nearest atom (O1) suggested a partially occupied hydrogen-bonded water molecule. Atom O2 was treated isotropically with U_{eq} fixed at 0.03 Å^2, and its occupancy factor was optimized; atom H5 was placed at the fixed position in the direction toward O1, which represents six equivalent positions that are chemically reasonable for disordered hydrogen-bonded H atoms.

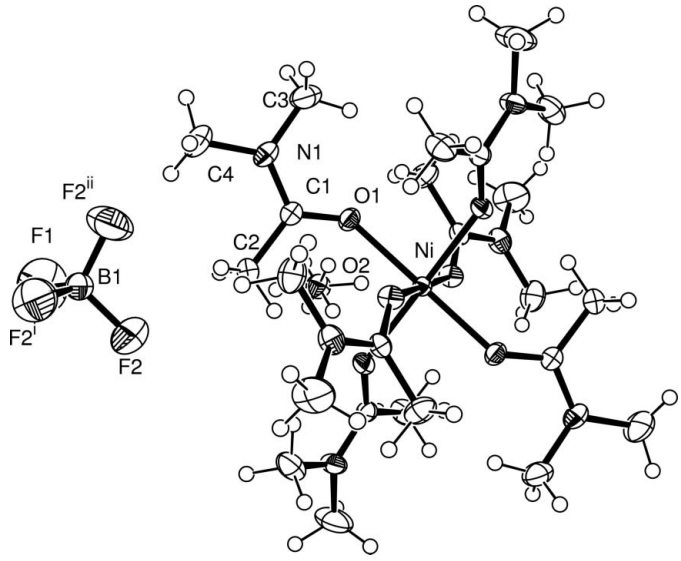

Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. The water molecule (O2) is shown with disordered H atoms. [Symmetry codes: (i) $1-x+y, -x, z$; (ii) $-y, x-y-1, z$.]

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors thank the Centre for Instrumental Analysis at the University of Toyama for their support.

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