Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

trans-Bis(acetonitrile-κN)bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-$\kappa^2 O,O'$)-nickel(II)

Heather Southerland,[a] Jeff Donovan,[a] Brendan Twamley[b] and Jamie Manson[a]*

[a]Department of Chemistry and Biochemistry, Eastern Washington University, Cheney, WA 99004-2440, USA, and [b]University Research Office, University of Idaho, Moscow, ID 83844-3010, USA
Correspondence e-mail: jmanson@ewu.edu

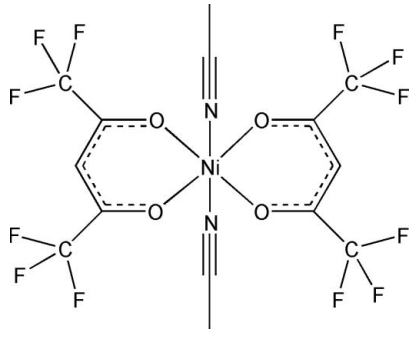
Received 27 July 2007; accepted 3 August 2007

Key indicators: single-crystal X-ray study; T = 90 K; mean σ(C–C) = 0.003 Å; R factor = 0.026; wR factor = 0.068; data-to-parameter ratio = 10.7.

The title compound, $[Ni(C_5HF_6O_2)_2(C_2H_3N)_2]$, was obtained as an unintentional by-product in the reaction of $Ni(hfac)_2$ (hfac is hexafluoroacetylacetonate) with pyrazine N,N'-dioxide in acetonitrile. The molecule is centrosymmetric and the ligands are *trans* to one another, with the Ni^{II} atom on a position with $2/m$ symmetry. The CF_3 groups are in a symmetry-imposed eclipsed conformation. The acetonitrile methyl group is involved in weak non-classical C—H···O intermolecular hydrogen bonding to the propanedionate O atoms. This forms a chain synthon parallel to the b axis. The chains are further arranged into sheets parallel to the bc plane.

Related literature

For related literature, see: Baird *et al.* (1999); Chen *et al.* (2000).



Experimental

Crystal data

$[Ni(C_5HF_6O_2)_2(C_2H_3N)_2]$
M_r = 554.93
Orthorhombic, *Cmca*
a = 20.4841 (6) Å
b = 7.1692 (2) Å
c = 13.9008 (4) Å
V = 2041.4 (1) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.08 mm^{-1}
T = 90 (2) K
0.21 × 0.20 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.805, T_{max} = 0.900
14542 measured reflections
956 independent reflections
890 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.069
S = 1.08
956 reflections
89 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5B···O1^{i}	0.93 (4)	2.56 (4)	3.381 (3)	146.5 (6)
C5—H5B···O1^{ii}	0.93 (4)	2.56 (4)	3.381 (3)	146.5 (6)

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

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2006); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *publCIF* (Westrip, 2007).

The Bruker–Siemens *SMART APEX* diffraction facility was established at the University of Idaho with the assistance of the NSF–EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA, USA.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2433).

References

Baird, I. R., Rettig, S. J., James, B. R. & Skov, K. A. (1999). *Can. J. Chem.* **77**, 1821–1833.
Bruker (2003). *SMART* (Version 5.632) and *SHELXTL* (Version 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2004). *SADABS*. Version 2004/1. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2006). *SAINT-Plus*. Version 7.23a. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, Z. N., Appelt, R. & Vahrenkamp, H. (2000). *Inorg. Chim. Acta*, **309**, 65–71.
Westrip, S. P. (2007). *publCIF*. In preparation.

 © 2007 International Union of Crystallography doi:10.1107/S1600536807038226

supplementary materials

Acta Cryst. (2007). E**63**, m2308 [**doi:10.1107/S1600536807038226**]

trans-Bis(acetonitrile-κN)bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato-$\kappa^2 O,O'$)nickel(II)

H. Southerland, J. Donovan, B. Twamley and J. Manson

Comment

The title compound, (I), is centrosymmetric with a *trans* orientation of the ligands, and is shown in Fig. 1. Although the ligand disposition around Ni1 is not perfectly perpendicular (see Table 1), the mean plane through the C and O atoms of both hexafluoroacetylacetonate (hfac) ligands and the Ni1 atom is perpendicular to the plane through the acetonitrile-Ni plane. The CF_3 groups of the hfac ligands are in a symmetry imposed eclipsed conformation.

trans-$[Cp(PPh_3)_2RuCN]_2Ni(hfac)_2$ is the only known structurally related species with a similar *trans* $Ni(hfac)_2(cyano)_2$ core (Chen *et al.*, 2000). Although the substituents on the cyano group distort the geometry, the central hfac-Ni core is also perpendicular to the N—Ni—N vector as seen in (**I**). A related ruthenium analogue, *cis*-$Ru(hfac)_2(MeCN)_2$ (Baird *et al.*, 1999) is a *cis*-isomer.

There is weak bifurcated intermolecular hydrogen bonding between the acetonitrile methyl group and the propanedionato oxygen (Fig. 2, Table 2), linking the molecules into a chain synthon parallel to the *b*-axis. The chains are further arranged into sheets parallel to the *bc* plane.

Experimental

A solution of $Ni(hfac)_2$ was added to a solution of 2 equivalents of pyrazine-dioxide in acetonitrile at room temperature. Slow evaporation of the resulting solution over five days resulted in a large crop of green parallelepiped shaped crystals (yield 73%).

Refinement

The dionato H atoms were placed in geometrically idealized positions (C—H = 0.95 Å) and constrained to ride on their parent atom, with $U_{iso}(H) = 1.2U_{eq}(C)$. Acetonitrile methyl H atoms were freely refined due to their involvement in H-bonding. The highest residual density peak and the deepest hole are located 1.00 and 0.82 Å, respectively, from atom F1.

Figures

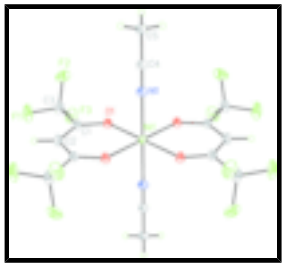


Fig. 1. The molecular structure of (I), showing 30% probability displacement ellipsoids. Only symmetry unique atoms are labelled. Hydrogen atoms are displayed as spheres of arbitrary radius.

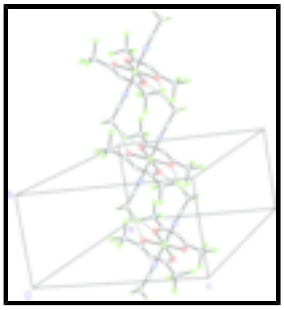


Fig. 2. Diagram showing the hydrogen-bonding pattern (dashed lines) linking the molecules into an extended chain along the b axis.

trans-Bis(acetonitrile-κ*N*)bis(1,1,1,5,5,5-hexafluoropentane-2,4-\ dionato-κ^2*O,O'*)nickel(II)

Crystal data

$[Ni(C_5HF_6O_2)_2(C_2H_3N)_2]$	F_{000} = 1096
M_r = 554.93	D_x = 1.806 Mg m^{-3}
Orthorhombic, *Cmca*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2bc 2	Cell parameters from 7181 reflections
a = 20.4841 (6) Å	θ = 2.9–30.0º
b = 7.1692 (2) Å	μ = 1.08 mm^{-1}
c = 13.9008 (4) Å	*T* = 90 (2) K
V = 2041.4 (1) Å^3	Parallelepiped, light green
Z = 4	0.21 × 0.20 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	956 independent reflections
Radiation source: normal-focus sealed tube	890 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.025
Detector resolution: 8.3 pixels mm^{-1}	θ_{max} = 25.3º
T = 90(2) K	θ_{min} = 2.0º
ω scans	*h* = −24→24
Absorption correction: multi-scan (SADABS; Bruker, 2004)	*k* = −8→8
T_{min} = 0.805, T_{max} = 0.900	*l* = −16→16
14542 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.026	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.069	$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 3.0631P]$ where $P = (F_o^2 + 2F_c^2)/3$

S = 1.08	$(\Delta/\sigma)_{max}$ = 0.001
956 reflections	$\Delta\rho_{max}$ = 0.50 e Å^{-3}
89 parameters	$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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	0.0000	0.5000	0.01765 (16)
C1	0.37064 (9)	0.1065 (2)	0.43182 (13)	0.0243 (4)
C2	0.33788 (13)	0.0000	0.5000	0.0294 (6)
H2	0.2915	0.0000	0.5000	0.035*
C3	0.33054 (10)	0.2315 (3)	0.36471 (15)	0.0344 (5)
C4	0.5000	0.3617 (4)	0.63509 (18)	0.0225 (5)
C5	0.5000	0.5185 (4)	0.7013 (2)	0.0268 (6)
H5A	0.5364 (12)	0.514 (4)	0.741 (2)	0.061 (8)*
H5B	0.5000	0.628 (6)	0.665 (3)	0.058 (12)*
F1	0.26677 (6)	0.1999 (2)	0.36833 (12)	0.0604 (5)
F2	0.33928 (7)	0.41007 (19)	0.38887 (11)	0.0531 (4)
F3	0.35020 (7)	0.2156 (2)	0.27393 (9)	0.0495 (4)
N1	0.5000	0.2359 (3)	0.58532 (15)	0.0242 (5)
O1	0.43089 (6)	0.12008 (17)	0.41713 (9)	0.0226 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0161 (3)	0.0194 (3)	0.0174 (2)	0.000	0.000	0.00028 (17)
C1	0.0214 (9)	0.0249 (9)	0.0266 (10)	0.0009 (7)	−0.0029 (7)	−0.0029 (8)
C2	0.0176 (13)	0.0353 (15)	0.0353 (15)	0.000	0.000	0.0019 (12)
C3	0.0235 (10)	0.0442 (13)	0.0354 (11)	0.0042 (9)	−0.0041 (8)	0.0075 (10)
C4	0.0246 (13)	0.0231 (13)	0.0198 (12)	0.000	0.000	0.0051 (11)
C5	0.0385 (17)	0.0209 (13)	0.0209 (14)	0.000	0.000	−0.0011 (11)
F1	0.0231 (7)	0.0842 (11)	0.0738 (10)	0.0021 (7)	−0.0135 (7)	0.0323 (9)
F2	0.0610 (9)	0.0372 (8)	0.0610 (9)	0.0183 (7)	−0.0115 (7)	0.0081 (7)
F3	0.0478 (8)	0.0700 (9)	0.0307 (7)	0.0158 (7)	−0.0109 (6)	0.0065 (6)

N1	0.0275 (12)	0.0235 (12)	0.0215 (11)	0.000	0.000	0.0008 (10)
O1	0.0204 (6)	0.0257 (7)	0.0218 (6)	0.0012 (5)	−0.0020 (5)	0.0022 (5)

Geometric parameters (Å, °)

Ni1—O1^{i}	2.0180 (12)	C2—C1^{i}	1.390 (2)
Ni1—O1	2.0180 (12)	C2—H2	0.95
Ni1—O1^{ii}	2.0180 (12)	C3—F1	1.327 (2)
Ni1—O1^{iii}	2.0180 (12)	C3—F3	1.329 (2)
Ni1—N1	2.066 (2)	C3—F2	1.335 (3)
Ni1—N1^{ii}	2.066 (2)	C4—N1	1.137 (3)
C1—O1	1.255 (2)	C4—C5	1.453 (4)
C1—C2	1.390 (2)	C5—H5A	0.93 (3)
C1—C3	1.532 (3)	C5—H5B	0.93 (4)
O1^{i}—Ni1—O1	90.90 (7)	C2—C1—C3	118.54 (18)
O1^{i}—Ni1—O1^{ii}	89.10 (7)	C1—C2—C1^{i}	122.3 (3)
O1—Ni1—O1^{ii}	180.0	C1—C2—H2	118.9
O1^{i}—Ni1—O1^{iii}	180.00 (5)	C1^{i}—C2—H2	118.9
O1—Ni1—O1^{iii}	89.10 (7)	F1—C3—F3	108.63 (18)
O1^{ii}—Ni1—O1^{iii}	90.90 (7)	F1—C3—F2	106.62 (18)
O1^{i}—Ni1—N1	91.23 (6)	F3—C3—F2	106.28 (18)
O1—Ni1—N1	88.77 (6)	F1—C3—C1	113.87 (18)
O1^{ii}—Ni1—N1	91.23 (6)	F3—C3—C1	111.43 (17)
O1^{iii}—Ni1—N1	88.77 (6)	F2—C3—C1	109.62 (17)
O1^{i}—Ni1—N1^{ii}	88.77 (6)	N1—C4—C5	178.2 (3)
O1—Ni1—N1^{ii}	91.23 (6)	C4—C5—H5A	110.5 (18)
O1^{ii}—Ni1—N1^{ii}	88.77 (6)	C4—C5—H5B	108 (2)
O1^{iii}—Ni1—N1^{ii}	91.23 (6)	H5A—C5—H5B	110 (2)
N1—Ni1—N1^{ii}	180.0	C4—N1—Ni1	177.6 (2)
O1—C1—C2	128.94 (18)	C1—O1—Ni1	124.34 (12)
O1—C1—C3	112.50 (16)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5B···O1^{iv}	0.93 (4)	2.56 (4)	3.381 (3)	146.5 (6)
C5—H5B···O1^{v}	0.93 (4)	2.56 (4)	3.381 (3)	146.5 (6)

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

Fig. 1

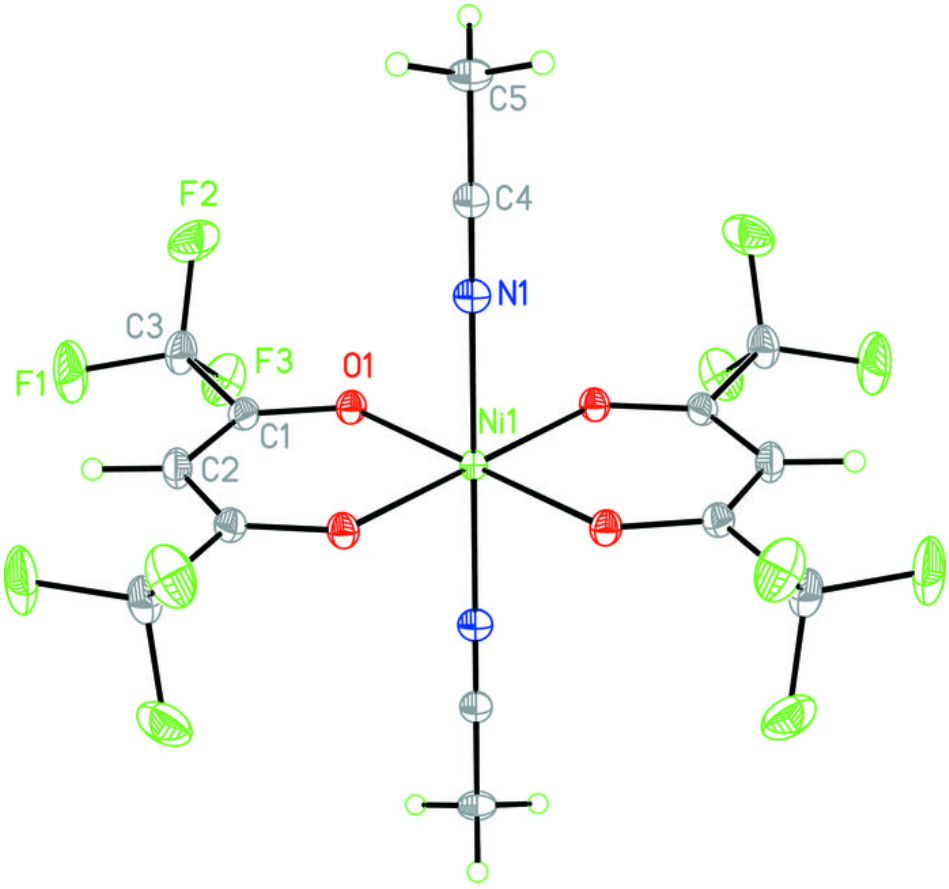
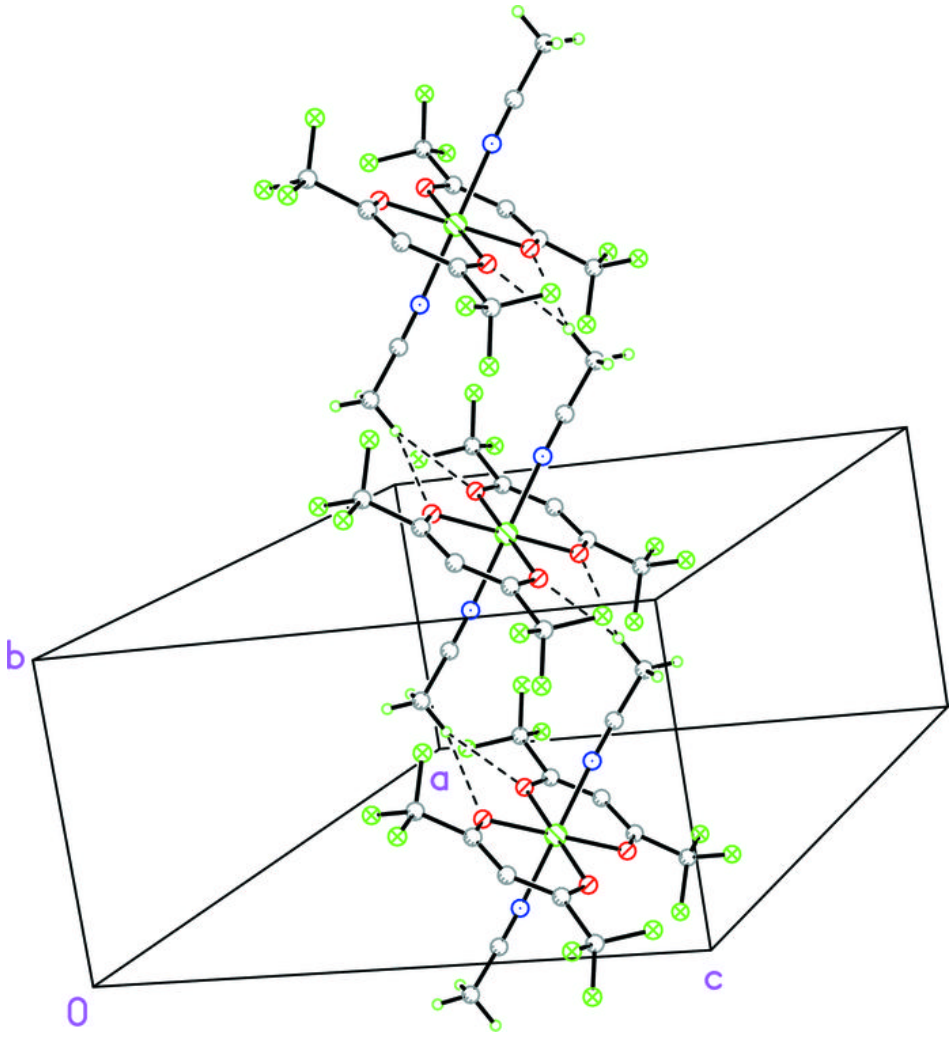



Fig. 2