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References

Breliere, C., Carre, F., Corriu, R. J. P. & Royo, G. (1988). *Organometallics*, **7**, 1006–1008.

Brutkiewicz, R. R. & Suzuki, F. (1987). *In Vivo*, **1**, 189–204.

Day, R. O., Holmes, J. M., Sau, A. C. & Holmes, R. R. (1982). *Inorg. Chem.* **21**, 281–286.

Enraf–Nonius (1979). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

Gabe, E. J. & Lee, F. L. (1981). *Acta Cryst.* A**37**, C-339.

Gurkova, S. N., Gusev, A. I., Sharapov, V. A., Alekseev, N. V., Gar, T. K. & Chromova, N. J. (1984). *J. Organomet. Chem.* **268**, 119–124.

Lazraq, Z. M., Couret, C., Declercq, J.-P., Dubourg, A., Escudie, J. & Riviere-Bandet, M. (1990). *Organometallics*, **9**, 845–848.

Lesbre, M., Mazerolles, P. & Satge, J. (1971). *The Organic Compounds of Germanium*. London: John Wiley.

Mizuta, T., Yoshida, T. & Miyoshi, K. (1989). *Inorg. Chim. Acta*, **165**, 65–71.

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Structure of *cis*-Diaquabis(hexafluoroacetylacetonato)nickel(II)

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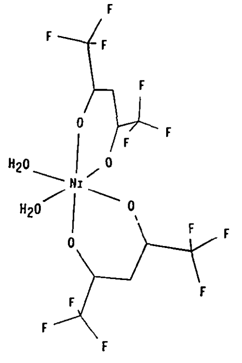
Abstract. $C_{10}H_6F_{12}NiO_6$, $M_r = 508.9$, monoclinic, $C2/c$, $a = 21.195\,(5)$, $b = 8.247\,(2)$, $c = 9.741\,(2)$ Å, $\beta = 95.91\,(2)°$, $V = 1693.6\,(7)$ Å^3, $D_x = 1.996$ Mg m^{-3}, $Z = 4$, $\mu = 1.298$ mm^{-1}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $F(000) = 1000$, $T = 298$ K, $R = 0.0369$ and $wR = 0.0645$ for 157 variable parameters ($S = 0.59$) and 1112 reflections with $F > 0\sigma(F)$. The Ni atom possesses an octahedral geometry and forms bonds to the O atoms of two chelating F_6acac ligands that occupy both axial and equatorial positions [Ni—O(1) 2.026 (3) Å; Ni—O(2) 2.027 (2) Å]. The two molecules of water are coordinated in a *cis* configuration [Ni—O(3) 2.054 (3) Å] and the structure possesses C_2 point group symmetry.

Introduction. The ability of the fluorinated derivatives of acetylacetone to form stable chelating bis adducts with many of the transition-metal elements is well established (Joshi & Pathak, 1977). In most instances stable monomeric adducts containing equatorial acac ligands are obtained. Notable exceptions include the anhydrous bis(acetylacetonato) Co^{II}, Ni^{II} and Zn^{II} complexes which possess oligomeric structures with bridging acac groups. The structures of the *trans*-diaquabis(acetylacetonato) complexes of both Co^{II} and Ni^{II} have been previously described (Bullen, 1959; Montgomery & Lingafelter, 1964) and the preparation of *trans*-$Ni(F_6acac)_2(H_2O)_2$ has been reported (Pecsok, Reynolds, Fackler, Lin & Pradilla-Sorzano, 1974). In this paper we describe the crystal structure of the previously unreported *cis*-$Ni(F_6acac)_2(H_2O)_2$ isomer.



Experimental. Crystals of the title compound were obtained in good yield following the crystallization of a product obtained by reacting one equivalent of the di(*tert*-butyl) nitroxyl free radical with one equivalent of anhydrous bis(F_6acac)Ni^{II}. Crystallization from a toluene/petroleum ether solution led to the formation of numerous well formed, multifaceted, green crystals with a trigonal prismatic habit. A regularly shaped crystal of approximate dimensions 0.30 × 0.40 × 0.60 mm was mounted on the end of a glass fiber in a random orientation. Monoclinic symmetry suggested on the basis of inter-

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axial angles and confirmed by axial rotation photographs. Intensity statistics favored a centrosymmetric cell and assignment to the space group $C2/c$ based on an examination of systematically absent reflections ($h + k = 2n + 1$; $h0l$: $l = 2n + 1$). Refined cell parameters determined from the setting angles of 20 reflections with $15 < 2\theta < 30°$. Data collection was carried out at ambient temperature using a Nicolet *R*3/*m* diffractometer utilizing the ω-scanning technique in bisecting geometry and graphite-monochromated Mo $K\alpha$ radiation. Scan rate variable, 3–20° min^{-1}; scan range, 1.5° in ω. Three standards (1$\bar{1}$0, 53$\bar{4}$, $\bar{4}\bar{4}$5) measured every 100 data showed no significant variation over the period of data collection. A total of 1147 reflections ($+h, +k, \pm l$; $h_{\max} = 22$, $k_{\max} = 8$, $l_{\max} = 10$) with $3.5 < 2\theta < 45°$ [$(\sin\theta)/\lambda_{\max} = 0.538$ Å^{-1}] were obtained and corrected for Lorentz and polarization effects. This led to 1112 unique reflections ($R_{\rm int} = 0.75\%$) that were corrected for absorption effects empirically on the basis of azimuthal scans of 8 strong reflections spanning a range of 2θ values (minimum and maximum transmission factors, 0.438 and 0.562, respectively). Structure solution carried out using the *SHELXTL PC* collection of crystallographic software (Sheldrick, 1990). Ni-atom position determined from a sharpened Patterson map; all remaining atoms located on difference Fourier maps. Ni, O, C and F atoms refined anisotropically using scattering factors, including terms for anomalous dispersion, taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Refinement based on F using weights of the form $w^{-1} = [\sigma^2(F) + 0.0116(F^2)]$. Convergence to conventional R values of $R = 0.0369$ and $wR = 0.0645$ with a goodness-of-fit of 0.59 obtained using 157 variable parameters and 1112 reflections with $F > 0\sigma(F)$. No reflections had intensities beyond the range for valid coincidence correction. For the final cycle, maximum shift/$\sigma = 0.004$ with minimum and maximum residual electron densities of -0.34 and $+0.36$ e Å^{-3}.

A view of the structure illustrating the atomic numbering scheme is presented in Fig. 1; in Fig. 2 is shown a stereoview packing diagram of the complex. Atomic positional parameters and equivalent isotropic thermal parameters for all non-hydrogen atoms are presented in Table 1.* Pertinent bond distances and angles are given in Table 2.

Discussion. The asymmetric unit consists of one half of an octahedral Ni$^{\rm II}$ complex that resides on a twofold axis of symmetry. There are no unusual intermolecular contacts and no evidence of H bonding between H_2O ligands in adjacent molecules.

The Ni atom possesses octahedral coordination geometry with a *cis* stereochemistry. In the coordination sphere of the Ni atom we find little variation in the Ni—O bond lengths which range from 2.026 (3) to 2.054 (3) Å for Ni—O(1) and Ni—O(3), respectively. Bond lengths to F$_6$acac ligands are well within the range of those observed in other octahedral bis(F$_6$acac)Ni$^{\rm II}$ complexes, despite the fact that, in the structure described here, the O atoms of these ligands occupy both axial and equatorial positions (Cervantes-Lee & Porter, 1991). This arrangement does not, however, lead to significant deviations from ideal octahedral geometry and only small variations in the interaxial angles are observed. A maximum deviation of 5.8 (1)° is found in the angle formed by bonds to the two *cis* molecules of water and this angle is acute [O(3)—Ni—O(3A) = 84.2 (1)°].

Structural features of the F$_6$acac ligands are unexceptional and will not be discussed further, except to note that alternate positions for the F atoms could be identified on difference Fourier maps. These positions were included during the completion of the structure which led to an improved model and occupancy factors that, when refined, indicated 7% static disorder.

We are not aware of the existence of any *cis*-bis(F$_6$acac) complexes of the first-row transition

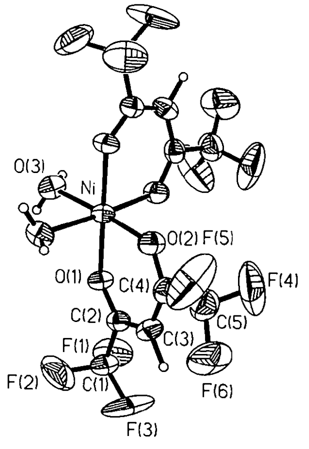

Fig. 1. A perspective view of the *cis*-Ni(F$_6$acac)$_2$(H$_2$O)$_2$ complex illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level.

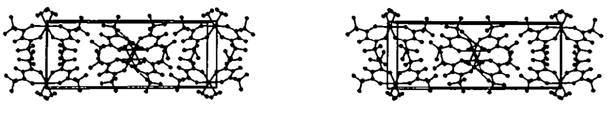

Fig. 2. A stereoview packing diagram projected down the crystallographic *c* axis.

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* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters, and CF$_3$ bond angles and distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54780 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}*
Ni	0	698 (1)	2500	32 (1)
F(1)	1756 (1)	1198 (5)	−17 (3)	84 (1)
F(2)	2045 (2)	−530 (5)	1465 (5)	112 (2)
F(3)	2406 (2)	1886 (6)	1701 (4)	118 (2)
F(4)	836 (3)	5504 (4)	4859 (5)	128 (2)
F(5)	827 (3)	3622 (6)	6315 (3)	129 (2)
F(6)	1679 (2)	4333 (5)	5544 (5)	108 (2)
†F(1A)	1805 (14)	121 (42)	448 (36)	49 (9)
†F(2A)	2271 (14)	260 (40)	2220 (31)	44 (8)
†F(3A)	2151 (21)	2296 (48)	1108 (41)	67 (11)
†F(4A)	590 (12)	4626 (36)	5672 (30)	37 (8)
†F(5A)	1404 (23)	3577 (50)	6257 (39)	71 (11)
†F(6A)	1349 (20)	5209 (47)	4842 (36)	58 (9)
O(1)	828 (1)	703 (2)	1630 (3)	38 (1)
O(2)	365 (1)	2351 (3)	3903 (2)	45 (1)
O(3)	−339 (1)	−1149 (3)	1215 (2)	46 (1)
C(1)	1901 (2)	1003 (5)	1351 (4)	51 (1)
C(2)	1326 (1)	1406 (4)	2117 (3)	37 (1)
C(3)	1408 (2)	2461 (4)	3224 (3)	45 (1)
C(4)	923 (2)	2866 (4)	4021 (3)	39 (1)
C(5)	1073 (2)	4094 (5)	5203 (5)	61 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

† Alternate positions for disordered F atoms.

metals. The intended product – a dimer containing bridging nitroxyl radicals – was not obtained, although it may have been present and subsequently cleaved by adventitious molecules of water during the process of crystallization. Evidence for dimeric transition-metal complexes containing bridging nitroxyl radicals has appeared, and further efforts are underway to establish the nature of the starting material (Caneschi, Gatteschi, Langier, Rey & Sessoli, 1988).

Table 2. *Bond lengths* (Å) *and angles* (°)

Ni—O(1)	2.026 (3)	Ni—O(2)	2.027 (2)
Ni—O(3)	2.054 (3)	O(1)—C(2)	1.254 (4)
O(2)—C(4)	1.250 (4)	C(1)—C(2)	1.530 (5)
C(2)—C(3)	1.382 (5)	C(3)—C(4)	1.391 (5)
C(4)—C(5)	1.541 (5)		

O(1)—Ni—O(2)	89.6 (1)	O(1)—Ni—O(3)	90.6 (1)
O(2)—Ni—O(3)	174.4 (1)	O(1)—Ni—O(1A)	179.8 (2)
O(2)—Ni—O(1A)	90.2 (1)	O(3)—Ni—O(1A)	89.6 (1)
O(2)—Ni—O(2A)	95.5 (1)	O(3)—Ni—O(2A)	90.2 (1)
O(3)—Ni—O(3A)	84.2 (1)	Ni—O(1)—C(2)	125.0 (2)
Ni—O(2)—C(4)	125.6 (2)	O(1)—C(2)—C(1)	113.4 (3)
O(1)—C(2)—C(3)	128.3 (3)	C(1)—C(2)—C(3)	118.4 (3)
C(2)—C(3)—C(4)	123.1 (3)	O(2)—C(4)—C(3)	127.8 (3)
O(2)—C(4)—C(5)	114.3 (3)	C(3)—C(4)—C(5)	117.9 (3)

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References

Bullen, G. J. (1959). *Acta Cryst.* **12**, 703–708.

Caneschi, A., Gatteschi, D., Langier, J., Rey, P. & Sessoli, R. (1988). *Inorg. Chem.* **27**, 1553–1557.

Cervantes-Lee, F. & Porter, L. C. (1991). *Acta Cryst.* **C47**, 1076–1077.

Joshi, K. C. & Pathak, V. N. (1977). *Coord. Chem. Rev.* **22**, 37–122.

Montgomery, H. & Lingafelter, E. C. (1964). *Acta Cryst.* **17**, 1481.

Pecsok, R. I., Reynolds, W. D., Fackler, J. P., Lin, I. & Pradilla-Sorzano, J. (1974). *Inorg. Synth.* **15**, 96–100.

Sheldrick, G. M. (1990). *SHELXTL PC. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Germany.

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Structures of Adducts formed by Indium(III) Halides and Phosphine Ligands: Tris[1,2-bis(diphenylphosphino)ethane]bis[triiodoindium(III)] and Trichlorobis(trimethylphosphine)indium(III)

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Abstract. {μ-[1,2-Bis(diphenylphosphino)ethane]-1κP:2$\kappa P'$}-bis[1,2-bis(diphenylphosphino)ethane]-1κP,2κP-bis[triiodoindium(III)], $[(InI_3)_2(C_{26}H_{24}P_2)_3]$, (1), $M_r = 2186.4$, triclinic, $P\bar{1}$, $a = 12.583$ (7), $b = 12.667$ (8), $c = 13.080$ (8) Å, $\alpha = 76.59$ (4), $\beta = 86.72$ (4), $\gamma = 79.34$ (4)°, $V = 1993$ (2) Å^3, $Z = 1$, $D_x = 1.82$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 30.3$ cm^{-1}, $F(000) = 1046$, $T = 290$ K, $R = 0.066$ for 5203 unique observed $[I/\sigma(I) \geq 2.0]$ reflections. $[InCl_3(C_3H_9P)_2]$, (2), $M_r = 373.3$, orthorhombic, $Pnma$, $a = 10.418$ (8), $b = 10.769$ (9), $c = 13.808$ (9) Å, $V = 1549$ (2) Å^3, $Z = 4$, $D_x =$

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