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Key indicators

Single-crystal X-ray study
T = 100 K
Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
R factor = 0.043
wR factor = 0.112
Data-to-parameter ratio = 11.4

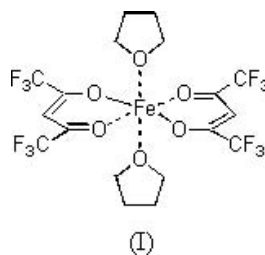
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Bis(1,1,1,5,5,5-hexafluoroacetylacetonato- $\kappa^2\text{O},\text{O}'$)-bis(tetrahydrofuran- κN)iron(II)

The title compound, $[\text{Fe}(\text{C}_5\text{HF}_6\text{O}_2)_2(\text{C}_4\text{H}_8\text{O})_2]$, crystallizes with two similar independent molecules in the asymmetric unit, in which the Fe atoms are in a slightly distorted octahedral geometry. The hexafluoroacetylacetonato (hfac) ligands are coordinated equatorially in a *trans* configuration.

Comment

Non-aqueous hexafluoroacetylacetonato(hfac)–metal complexes tend to be volatile and therefore are of general interest for applications including chemical vapour deposition of metal oxide films (Barreca *et al.*, 2000; Evans *et al.*, 2003). Tetrahydrofuran (THF) is typically chosen as a spectator ligand since it is easily incorporated by crystallization of the aqua complex from dry THF. Bis(hfac)bis(THF)metal complexes are of interest to us as precursors to water-sensitive molecular magnetic materials (Hearns *et al.*, 2004). Of the known $M(\text{hfac})_x(\text{THF})_y$ complexes, there are relatively few for which crystal structures have been obtained. These include $\text{Ni}(\text{hfac})_2(\text{THF})_2$ crystallizing in the tetragonal space group $P4_2/mnm$ (Cervantes-Lee & Porter, 1991) and $[\text{Ag}_2(\text{hfac})_2(\text{THF})]_n$ crystallizing as infinite chains in the triclinic space group $P\bar{1}$ (Evans *et al.*, 2003). $\text{Fe}(\text{hfac})_2(\text{THF})_2$, (I), reported here is a previously unknown complex and a potentially important building block for molecular magnets based on coordination complexes.



$\text{Fe}(\text{hfac})_2(\text{THF})_2$ crystallizes in the non-centrosymmetric space group, $Pna2_1$. There are two independent molecules in the asymmetric unit. A comparison of the bond lengths and angles of the two molecules shows them to be very similar but not quite identical within experimental error. The only marked differences are in the general orientations of the coordinating THF ligands and the differing rotations of the CF_3 groups about the adjoining C–C bonds (Figs. 1 and 2). Both molecules show slightly distorted octahedral coordination geometry about the Fe atom with the hfac ligands bound equatorially and the THF ligands bound axially; see Table 1 for relevant coordination bond lengths and angles.

The Fe–O bond lengths are unremarkable. The Fe–O(hfac) bond lengths are in the range 2.046 (3)–2.057 (3) Å

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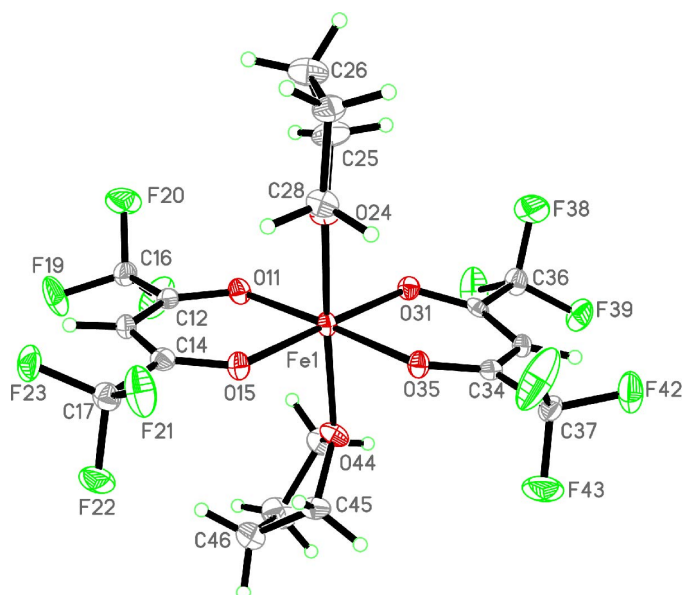


Figure 1
The structure of one of the molecules of $\text{Fe}(\text{hfac})_2(\text{THF})_2$, showing 30% probability displacement ellipsoids and the atom-labelling scheme. H atoms are represented by circles of arbitrary size.

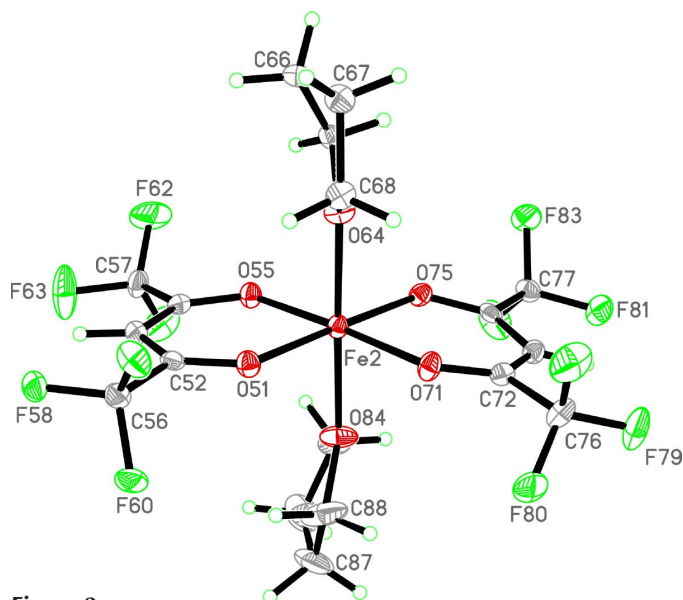


Figure 2
The structure of the second molecule of $\text{Fe}(\text{hfac})_2(\text{THF})_2$, showing 30% probability displacement ellipsoids and the atom-labelling scheme. H atoms are represented by circles of arbitrary size.

and the Fe—O(THF) bond lengths are in the range 2.114 (3)–2.167 (3) Å. These values are typical, as evidenced by examination of the Cambridge Structural Database (Version 5.25; Allen, 2002).

Experimental

The title complex was prepared by dissolving bis(hexafluoroacetylacetonato)iron(II) dihydrate in warm dry THF and precipitated upon cooling as red crystals. The precursor dihydrate complex was prepared following a general literature procedure (Izumi *et al.*, 1975). Purification of the title complex was achieved by dynamic vacuum

sublimation at 363 K and 0.01 Torr. Single crystals were grown by sublimation of the pure material under static vacuum at 383 K and 0.01 Torr for 4 d.

Crystal data

$[\text{Fe}(\text{C}_5\text{HF}_6\text{O}_2)_2(\text{C}_4\text{HF}_8\text{O})_2]$
 $M_r = 614.17$
 Orthorhombic, $Pna2_1$
 $a = 18.0117$ (5) Å
 $b = 20.2080$ (6) Å
 $c = 12.8156$ (5) Å
 $V = 4664.6$ (3) Å³
 $Z = 8$
 $D_x = 1.749$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 5860 reflections
 $\theta = 1.7$ – 27.5°
 $\mu = 0.78$ mm⁻¹
 $T = 100$ (2) K
 Plate, dark red
 $0.75 \times 0.63 \times 0.20$ mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.509$, $T_{\max} = 0.853$
 46 962 measured reflections
 7614 independent reflections

5960 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.072$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -21 \rightarrow 21$
 $k = -21 \rightarrow 24$
 $l = -13 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.113$
 $S = 1.03$
 7614 reflections
 668 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 1.4577P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.52$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.50$ e Å⁻³
 Absolute structure: Flack (1983),
 3297 Friedel pairs
 Flack parameter = 0.504 (19)

Table 1

Selected geometric parameters (Å, °).

Fe1—O35	2.046 (3)	Fe2—O75	2.047 (3)
Fe1—O31	2.046 (3)	Fe2—O71	2.048 (3)
Fe1—O11	2.051 (3)	Fe2—O55	2.048 (3)
Fe1—O15	2.053 (3)	Fe2—O51	2.057 (3)
Fe1—O24	2.134 (3)	Fe2—O64	2.114 (3)
Fe1—O44	2.167 (3)	Fe2—O84	2.139 (3)
O35—Fe1—O31	87.72 (11)	O75—Fe2—O71	87.38 (12)
O35—Fe1—O11	177.65 (14)	O75—Fe2—O55	93.64 (12)
O31—Fe1—O11	93.39 (12)	O71—Fe2—O55	177.08 (14)
O35—Fe1—O15	91.88 (12)	O75—Fe2—O51	178.62 (13)
O31—Fe1—O15	178.72 (13)	O71—Fe2—O51	92.24 (12)
O11—Fe1—O15	86.97 (12)	O55—Fe2—O51	86.68 (12)
O35—Fe1—O24	89.15 (12)	O75—Fe2—O64	91.80 (13)
O31—Fe1—O24	93.66 (12)	O71—Fe2—O64	90.46 (12)
O11—Fe1—O24	92.84 (12)	O55—Fe2—O64	92.24 (12)
O15—Fe1—O24	87.55 (12)	O51—Fe2—O64	89.52 (12)
O35—Fe1—O44	86.45 (11)	O75—Fe2—O84	87.10 (13)
O31—Fe1—O44	87.00 (12)	O71—Fe2—O84	88.74 (13)
O11—Fe1—O44	91.53 (12)	O55—Fe2—O84	88.58 (13)
O15—Fe1—O44	91.77 (12)	O51—Fe2—O84	91.57 (13)
O24—Fe1—O44	175.53 (12)	O64—Fe2—O84	178.67 (14)

H atoms were positioned geometrically and constrained as riding atoms, with $Csp^2-H = 0.95$ Å and $Csp^3-H = 0.99$ Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The Flack (1983) parameter refined to a value of 0.504 (19), indicating that the crystal was an inversion twin.

Data collection: COLLECT (Nonius, 2001); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL/PC (Sheldrick,

2001); software used to prepare material for publication: *SHELXTL/PC*.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Barreca, D., Benetollo, F., Bozza, M., Bozza, S., Carta, G., Cavinato, G., Rossetto, G. & Zanella, P. (2000). *Mater. Res. Soc. Symp. Proc.* **606**, 69–74.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Cervantes-Lee, F. & Porter, L. C. (1991). *Acta Cryst.* **C47**, 1076–1077.
- Evans, W. J., Giarikos, D. G., Josell, D. & Ziller, J. W. (2003). *Inorg. Chem.* **42**, 8255–8261.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Hearns, N. G. R., Preuss, K. E., Richardson, J. F. & Bin-Salamon, S. (2004). *J. Am. Chem. Soc.* **126**, 9942–9943.
- Izumi, F., Kurosawa, R., Kawamoto, H. & Akaiwa, H. (1975). *Bull. Chem. Soc. Jpn.* **48**, 3188–3192.
- Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.
- Sheldrick, G. M. (2001). *SHELXTL/PC*. Version 6.14 for Windows NT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.