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Dennis W. Bennett
University of Wisconsin - Milwaukee

Tasneem Siddiquee
University of Wisconsin - Milwaukee

Daniel T. Haworth
Marquette University

Sergey V. Lindeman
Marquette University, sergey.lindeman@marquette.edu

Marquette University

e-Publications@Marquette

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The crystal and molecular structure of a trifluoroacetylacetonate complex of scandium, $\text{Sc}(\text{CH}_3\text{COCHCOCF}_3)_3$

Dennis W. Bennett

Department of Chemistry, University of Wisconsin – Milwaukee, Milwaukee, WI

Tasneem A. Siddiquee

Department of Chemistry, University of Wisconsin – Milwaukee, Milwaukee, WI

Daniel T. Haworth

Department of Chemistry, Marquette University, Milwaukee, WI

Department of Chemistry, University of Wisconsin – Milwaukee, Milwaukee, WI

Sergey V. Lindeman

Department of Chemistry, Marquette University, Milwaukee, WI

The crystal and molecular structure of $\text{Sc}(\text{CH}_3\text{COCHCOCF}_3)_3$ has been determined by X-ray diffraction. The compound crystallizes as pure mer-isomer in the orthorhombic space

group *Pbca* with lattice parameters $a=15.166(8)$ Å, $b=13.560(7)$ Å, $c=19.327(10)$ Å, $\alpha=\beta=\gamma=90^\circ$, $V=3974(4)$ Å³, $Z=8$. The complex at 100 K is partially disordered in the crystal structure in an approximate 5:1 ratio with 83% fluorine population at C-11 and 17% at C-15. NMR data is compared to that previously reported.

KEY WORDS

Trifluoroacetylactonate, scandium acac, dipole moment

Introduction

We have previously reported on the syntheses and characterization of nine scandium (III) β -diketonate complexes which have a fluorosubstituent.¹ Prior to this report only three other fluorinated β -diketonates had been reported.^{2,3} The dipole moment of six of these compounds, $\text{Sc}(\text{RCOCHCOR}')_3$ increases with the fluorine content of the R' group from 4.34 to 6.18 D. A variable ¹⁹F NMR study of all compounds gave one symmetric resonance in the range of -56°C to -65°C . Since stereochemical non-rigidity has been cited as a characteristic property of six coordinate scandium complexes it was likely that these complexes were fluxional.⁴ Holm has shown that because the methyl resonance of the $\text{Sc}(\text{pmhd})_3$ ($\text{pmhd}=1\text{-phenyl-5-methylhexane-1,3-dionate}$) could not be made enantiotopic at -95°C a low rearrangement barrier was indicated; whereas, the corresponding $\text{Al}(\text{pmhd})_3$ and $\text{Ga}(\text{pmhd})_3$ complexes were non-rigid.⁴ An X-ray structural determination was undertaken of $\text{Sc}(\text{CH}_3\text{COCHCOCF}_3)_3$ to determine its conformation in the solid state and to reevaluate its ¹⁹F NMR. A comparison to the known X-ray structure of $\text{Sc}(\text{CH}_3\text{COCHCOCH}_3)_3$ will also be carried out.⁵

Table 1. Crystal Data and Structure Refinement for $\text{Sc}(\text{tfac})_3$

CCDC deposition number	298953
Empirical formula	$\text{C}_{15}\text{H}_{12}\text{F}_9\text{O}_6\text{Sc}$
Formula weight	504.21
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
Unit cell dimensions	
a (Å)	15.166 (8)
b (Å)	13.560 (7)
c (Å)	19.327 (10)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	3974(4)

Z	8
Density (calculated)	1.685 Mg/m ³
Absorption coefficient	0.483 mm ⁻¹
F(000)	2016
Crystal size	0.22×0.14×0.07 mm ³
Theta range for data collection	2.11–31.96°.
Index ranges	0 ≤ <i>h</i> ≤ 21
	0 ≤ <i>k</i> ≤ 19
	0 ≤ <i>l</i> ≤ 27
Reflections collected	64660
Independent reflections	6593 [<i>R</i> _{int} =0.0543]
Completeness to theta=31.96°	95.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9670 and 0.9012
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6593/6/329
Goodness-of-fit on <i>F</i> ²	1.020
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ =0.0562, <i>wR</i> ₂ =0.1437
<i>R</i> indices (all data)	<i>R</i> ₁ =0.0928, <i>wR</i> ₂ =0.1617
Largest diff. peak and hole	0.600 and -0.399 (eÅ ⁻³)

Experimental

The crystals of the title compound were obtained by recrystallization from ethanol-methylene chloride. A crystal (0.22×0.14×0.07 mm³) was attached to a glass fiber and mounted on a Bruker APEX Z CCD diffractometer. The data were collected at 100 K using graphite monochromatized MoK α radiation (λ =0.71073 Å) and the $\theta/2\theta$ mode in the θ range 2.11–31.96°. An absorption correction was made from semi-empirical equivalents. The structure was solved by direct methods and refined by full-matrix least squares based on *F*².⁶ A total of 64660 reflections were collected (6593 independent reflections, *R*_{int}=0.0543). The final refinement resulted in *R*=0.0562 and *wR*₂=0.1437. All hydrogen atoms were located in a series of difference Fourier syntheses and were refined isotropically, except for methyl groups, where the geometric constraints on hydrogens were put to avoid the negative effects on refinement of the corresponding fluorines. The experimental data are given in Table 1 and the structural parameters are given in Tables 2–5.

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for Sc(tfac)₃

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Sc(1)	1343(1)	7543(1)	2385(1)	27(1)

	x	y	z	U (eq)
O(1)	2057(1)	6792(1)	3138(1)	32(1)
O(2)	2386(1)	8543(1)	2471(1)	33(1)
O(3)	601(1)	8355(1)	3082(1)	34(1)
O(4)	288(1)	6562(1)	2488(1)	32(1)
O(5)	827(1)	8244(1)	1513(1)	36(1)
O(6)	1930(1)	6643(1)	1622(1)	35(1)
C(1)	3081(2)	6261(2)	3974(1)	46(1)
F(1)	3008(1)	5343(1)	3750(1)	63(1)
F(2)	3918(1)	6370(2)	4164(1)	73(1)
F(3)	2588(2)	6340(2)	4531(1)	88(1)
C(2)	2788(1)	7011(2)	3426(1)	33(1)
C(3)	3302(2)	7825(2)	3313(1)	41(1)
C(4)	3066(1)	8579(2)	2842(1)	34(1)
C(5)	3645(2)	9470(2)	2781(2)	46(1)
C(6)	-344(2)	8891(2)	3961(1)	45(1)
F(4)	-364(1)	9797(1)	3709(1)	53(1)
F(5)	-1134(2)	8725(2)	4241(1)	84(1)
F(6)	237(2)	8898(2)	4470(1)	84(1)
C(7)	-97(2)	8124(2)	3415(1)	33(1)
C(8)	-611(2)	7299(2)	3331(1)	38(1)
C(9)	-396(1)	6541(2)	2858(1)	33(1)
C(10)	-988(2)	5657(2)	2793(2)	41(1)
C(11)	428(2)	8769(2)	392(1)	48(1)
F(7)	-398(1)	8698(2)	460(2)	91(1)
F(8)	694(2)	9659(2)	496(2)	108(1)
F(9)	588(2)	8616(3)	-275(1)	104(1)
C(11)	428(2)	8769(2)	392(1)	48(1)
C(12)	919(2)	8056(2)	873(1)	39(1)
C(13)	1396(2)	7308(2)	579(2)	46(1)
C(14)	1881(2)	6626(2)	973(1)	38(1)
C(15)	2388(2)	5826(2)	602(2)	55(1)
F(7A)	2455(6)	5095(6)	1011(5)	50(2)
F(8A)	3142(6)	6230(7)	496(5)	59(3)
F(9A)	2009(7)	5657(8)	41(5)	61(3)

Note. U (eq) is defined as one third of the trace of the orthogonalized U tensor.

The ^{13}F NMR was recorded in CH_2Cl_2 , with CFCl_3 as the internal standard on a GE 300-GN instrument operating at $282(^{19}\text{F})$ MHz.

Table 3. Bond Lengths [Å] and Angles [°] for $\text{Sc}(\text{tfac})_3$

Bond lengths (Å)	
Sc(1)–O(3)	2.0720(16)
Sc(1)–O(1)	2.0804(16)
Sc(1)–O(5)	2.0879(17)
Sc(1)–O(4)	2.0893(16)
Sc(1)–O(2)	2.0911(17)
Sc(1)–O(6)	2.1120(17)
O(1)–C(2)	1.275(3)
O(2)–C(4)	1.257(3)
O(3)–C(7)	1.277(3)
O(4)–C(9)	1.260(3)
O(5)–C(12)	1.270(3)
O(6)–C(14)	1.256(3)
C(1)–F(3)	1.316(3)
C(1)–F(1)	1.323(3)
C(1)–F(2)	1.329(3)
C(1)–C(2)	1.535(3)
C(2)–C(3)	1.370(3)
C(3)–C(4)	1.414(3)
C(4)–C(5)	1.498(3)
C(6)–F(6)	1.320(3)
C(6)–F(4)	1.323(3)
C(6)–F(5)	1.332(3)
C(6)–C(7)	1.529(3)
C(7)–C(8)	1.373(3)
C(8)–C(9)	1.413(3)
C(9)–C(10)	1.503(3)
C(11)–F(7)	1.262(3)
C(11)–F(8)	1.289(3)
C(11)–F(9)	1.328(4)
C(11)–C(12)	1.534(3)
C(12)–C(13)	1.370(4)

C(13)–C(14)	1.406(4)
C(14)–C(15)	1.511(4)
Bond angles (°)	
O(3)–Sc(1)–O(1)	95.05(7)
O(3)–Sc(1)–O(5)	94.58(7)
O(1)–Sc(1)–O(5)	169.40(7)
O(3)–Sc(1)–O(4)	82.01(7)
O(1)–Sc(1)–O(4)	91.16(7)
O(5)–Sc(1)–O(4)	94.57(7)
O(3)–Sc(1)–O(2)	90.81(7)
O(1)–Sc(1)–O(2)	82.42(7)
O(5)–Sc(1)–O(2)	93.01(7)
O(4)–Sc(1)–O(2)	169.94(7)
O(3)–Sc(1)–O(6)	172.08(6)
O(1)–Sc(1)–O(6)	89.21(7)
O(5)–Sc(1)–O(6)	81.77(7)
O(4)–Sc(1)–O(6)	91.25(7)
O(2)–Sc(1)–O(6)	96.38(7)
C(2)–O(1)–Sc(1)	130.02(14)
C(4)–O(2)–Sc(1)	133.73(14)
C(7)–O(3)–Sc(1)	130.28(14)
C(9)–O(4)–Sc(1)	134.30(14)
C(12)–O(5)–Sc(1)	130.83(15)
C(14)–O(6)–Sc(1)	133.03(15)
F(3)–C(1)–F(1)	107.3(2)
F(3)–C(1)–F(2)	107.9(2)
F(1)–C(1)–F(2)	106.0(2)
F(3)–C(1)–C(2)	110.2(2)
F(1)–C(1)–C(2)	111.9(2)
F(2)–C(1)–C(2)	113.2(2)
O(1)–C(2)–C(3)	127.9(2)
O(1)–C(2)–C(1)	113.49(19)
C(3)–C(2)–C(1)	118.6(2)
C(2)–C(3)–C(4)	122.7(2)
O(2)–C(4)–C(3)	123.2(2)
O(2)–C(4)–C(5)	117.8(2)

C(3)–C(4)–C(5)	119.0(2)
F(6)–C(6)–F(4)	106.4(2)
F(6)–C(6)–F(5)	107.5(2)
F(4)–C(6)–F(5)	106.6(2)
F(6)–C(6)–C(7)	110.8(2)
F(4)–C(6)–C(7)	112.4(2)
F(5)–C(6)–C(7)	112.7(2)
O(3)–C(7)–C(8)	127.7(2)
O(3)–C(7)–C(6)	112.6(2)
C(8)–C(7)–C(6)	119.7(2)
C(7)–C(8)–C(9)	122.5(2)
O(4)–C(9)–C(8)	122.7(2)
O(4)–C(9)–C(10)	117.5(2)
C(8)–C(9)–C(10)	119.8(2)
F(7)–C(11)–F(8)	111.4(3)
F(7)–C(11)–F(9)	105.7(3)
F(8)–C(11)–F(9)	103.9(3)
F(7)–C(11)–C(12)	111.7(2)
F(8)–C(11)–C(12)	110.1(2)
F(9)–C(11)–C(12)	113.6(3)
O(5)–C(12)–C(13)	127.7(2)
O(5)–C(12)–C(11)	114.2(2)
C(13)–C(12)–C(11)	118.1(2)
C(12)–C(13)–C(14)	122.5(3)
O(6)–C(14)–C(13)	124.1(2)
O(6)–C(14)–C(15)	117.1(2)
C(13)–C(14)–C(15)	118.7(2)

Note. Symmetry transformations used to generate equivalent atoms.

Results and discussion

A drawing of the mer-molecule and its crystallographic numbering is given in Fig. 2.

The title compound gave a structure which is partially disordered in the crystal due to the mer- isomer of $\text{Sc}(\text{CH}_3\text{COCHCOCF}_3)_3$ having an approximate population of the CF_3 groups in a ratio of 5:1 with 83% population at C-11 and 17% at C-15 (Fig. 1). These are related by 180° rotation around a quasi-two-fold axis going through C(13), Sc(1) and the bisectral plane between O(1) and O(3) (Fig. 3).

Table 4. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Sc}(\text{tfac})_3$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sc(1)	23(1)	23 (1)	34(1)	2(1)	0(1)	2(1)
O(1)	32(1)	27(1)	38(1)	6(1)	-3(1)	-1(1)
O(2)	28(1)	26(1)	44(1)	3(1)	2(1)	-1(1)
O(3)	31(1)	28(1)	42(1)	-3(1)	3(1)	2(1)
O(4)	26(1)	26(1)	45(1)	-1(1)	1(1)	1(1)
O(5)	38(1)	31(1)	39(1)	5(1)	-5(1)	4(1)
O(6)	31(1)	34(1)	40(1)	-3(1)	2(1)	5(1)
C(1)	52(2)	46(1)	40(1)	3(1)	-13(1)	5(1)
F(1)	85(1)	39(1)	66(1)	11(1)	-26(1)	9(1)
F(2)	63(1)	74(1)	81(1)	14(1)	-39(1)	3(1)
F(3)	114(2)	101(2)	48(1)	26(1)	19(1)	47(1)
C(2)	34(1)	30(1)	33(1)	-2(1)	-4(1)	4(1)
C(3)	35(1)	36(1)	50(1)	-4(1)	-12(1)	-2(1)
C(4)	26(1)	27(1)	51(1)	-8(1)	7(1)	-1(1)
C(5)	32(1)	29(1)	78(2)	-7(1)	5(1)	-5(1)
C(6)	55(2)	41(1)	38(1)	-3(1)	11(1)	8(1)
F(4)	72(1)	34(1)	53(1)	-5(1)	10(1)	15(1)
F(5)	96(2)	68(1)	89(1)	-18(1)	60(1)	-3(1)
F(6)	125(2)	77(1)	51(1)	-24(1)	-31(1)	44(1)
C(7)	36(1)	29(1)	34(1)	3(1)	1(1)	10(1)
C(8)	32(1)	33(1)	48(1)	6(1)	11(1)	3(1)
C(9)	25(1)	26(1)	47(1)	7(1)	-4(1)	3(1)
C(10)	29(1)	30(1)	65(2)	6(1)	1(1)	-2(1)
C(11)	46(1)	52(2)	44(1)	14(1)	-15(1)	-12(1)
F(7)	38(1)	120(2)	116(2)	81(2)	-7(1)	2(1)
F(8)	153(3)	49(1)	122(2)	41(1)	-97(2)	-36(2)
F(9)	111(2)	159(3)	43(1)	28(2)	-14(1)	42(2)
C(11)	46(1)	52(2)	44(1)	14(1)	-15(1)	-12(1)
C(12)	36(1)	39(1)	40(1)	8(1)	-9(1)	-11(1)
C(13)	47(1)	57(2)	36(1)	-5(1)	-7(1)	-5(1)
C(14)	30(1)	41(1)	44(1)	-8(1)	2(1)	-7(1)
C(15)	45(2)	63(2)	57(2)	-23(1)	4(1)	1(1)

Note. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a'^2 U^{11} + \dots + 2hk a' b' U^{12}]$.

Our previous studies had shown that the compound has a large dipole moment (4.34 D) and only one ^{19}F NMR was observed in the range

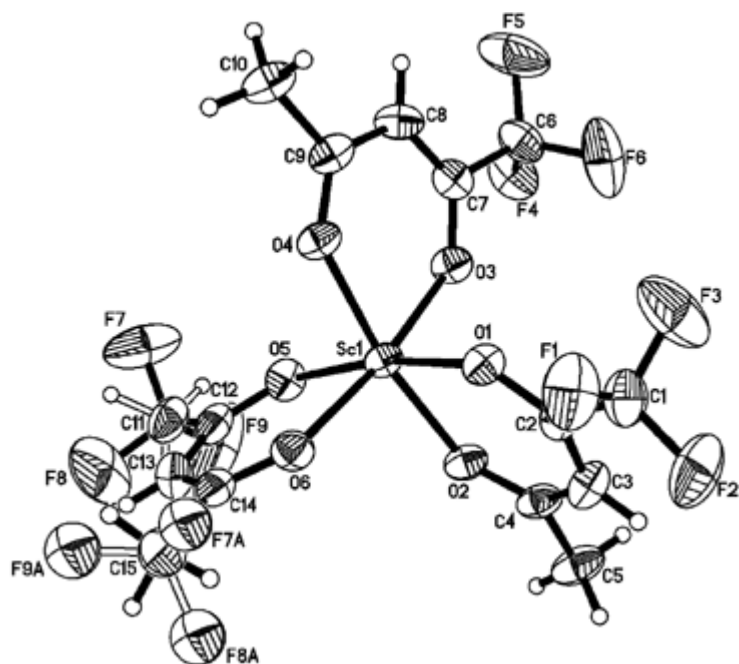


Fig. 1. ORTEP diagram showing both CF₃ contributions with C(11) having 83%.

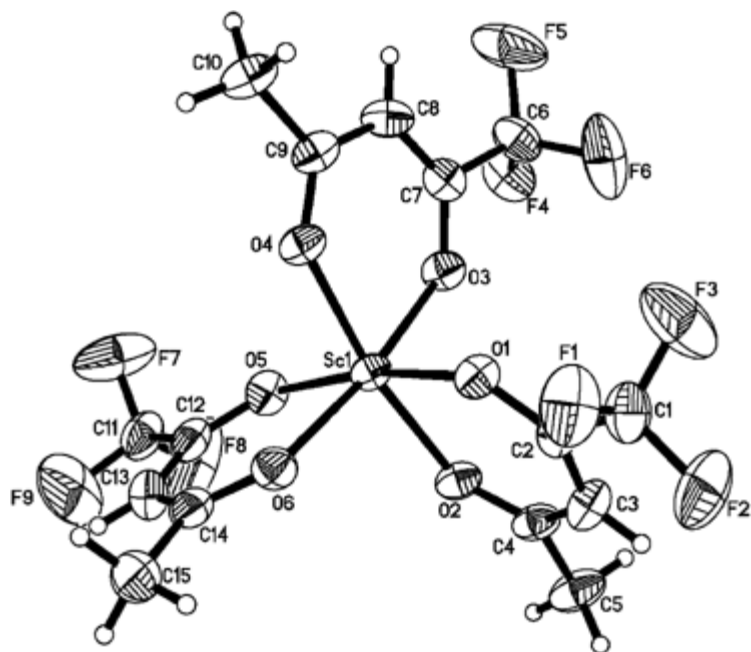


Fig. 2. The molecular structure of mer-Sc(CH₃COCHCF₃)₃. Ellipsoids are shown at the 50% probability level.

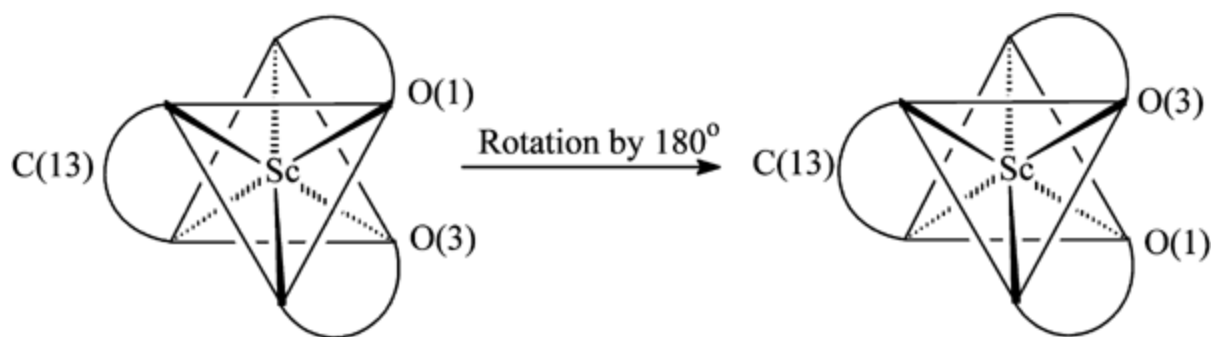


Fig. 3. Relation between the different CF₃ populations in the disordered structure.

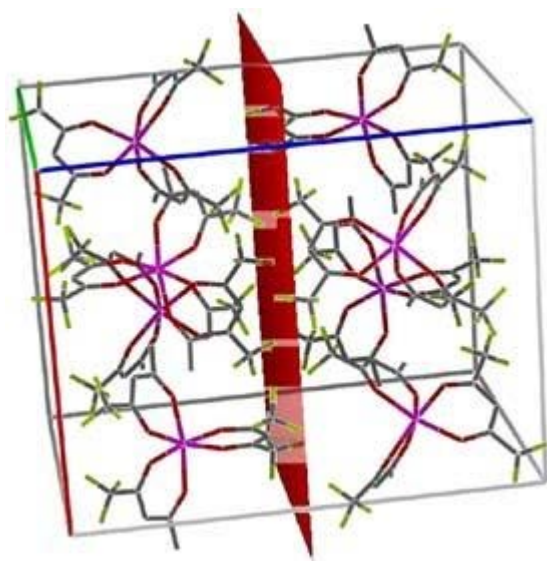


Fig. 4. Packing diagram of mer-Sc(CH₃COCHCF₃)₃ along *b*-axis.

of -56° to -65°C . While this data alone cannot be used to support stereochemical nonrigidity, a reexamination of its ^{19}F NMR shows only one CF₃ resonance at room temperature (-76.2 ppm).

Table 3 shows that the CF₃ group lengthens the C–O bond and shortens the Sc–O bond adjacent to the CF₃ group when compared to the corresponding bonds adjacent to the CH₃ groups. The acidic character of the hydrogens at C(3), C(8) and C(13) is in agreement with the shortening of the C–H bonds due to the shift of electron density toward these carbon atoms. The influence of the CF₃ group on the shorter Sc–O and larger O–C bond lengths is shown in Table 3. The Sc–O bond distances are all smaller than the 2.20 Å predicted on the basis of 0.81 Å for scandium ion using the Pauling scale. The title compound minus the

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sc(tfac)₃

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
H(15A)	129	9273	669	71
H(15B)	–9	8403	121	71
H(15C)	850	9086	79	71

	x	y	z	U (eq)
H(15D)	2868	5591	899	83
H(15E)	2635	6091	172	83
H(15F)	1991	5277	495	83
H(3)	3810(20)	7910(20)	3507(16)	55(8)
H(5A)	4220(30)	9240(30)	2783(19)	78(11)
H(5B)	3520(20)	9870(30)	3160(20)	80(11)
H(5C)	3570(20)	9860(20)	2364(17)	56(9)
H(8)	-1110(20)	7260(20)	3552(16)	51(8)
H(10A)	-1610(20)	5880(20)	2829(15)	48(8)
H(10B)	-930(20)	5300(20)	2382(16)	49(8)
H(10C)	-840(20)	5250(20)	3143(17)	57(9)
H(13)	1450(20)	7200(30)	166(19)	67(11)

CF₃ and CH₃ groups adopts a distorted octahedron (D₃) structure as indicated by the two types of O–O separation of the order of 2.742(11) and 3.046(55) Å observed in the complex. The twist angles between fac-triangle O(1)O(4)O(6) and O(2)O(3)O(5) is about 48.2° which is less than 60° required for an ideal octahedral geometry. The dihedral angles between the chelate rings are, as a result, somewhat smaller (84.7(1)°) than the ideal value, 90°. The data is similar to that reported for Sc(acac)₃.⁵ The packing diagram (Fig. 4) reveals that the CF₃ groups tend to occupy the space in a plane, on an average parallel to the *ab*-plane.

The IR spectrum shows the characteristic carbonyl stretching frequency at 1618 cm⁻¹.

X-ray diffraction powder data on mer-Sc(tfac)₃ have been reported and the indexing of the diffraction patterns were carried out using crystal data for mer-Fe(tfac)₃.^{7, 8} The data indicates that these compounds are isostructural with unit cell parameters and values in the range of data shown in Table 1.

The data taken as a whole would indicate that Sc(tfac)₃ is nonrigid in solution.

Notes

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Supplementary material

CCDC 298953 contains the supplementary crystallographic data and can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic

Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033;
email: deposit@ccdc.cam.ac.uk.

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