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Coordination Sphere Geometry of Tris(acetylacetonato)metal(III) Complexes: the Crystal and Molecular Structure of Tris(1,1,1,5,5,5-hexafluoroacetylacetonato)-iron(III)

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The molecular structure of tris(1,1,1,5,5,5-hexafluoroacetylacetonato)iron(III) has been determined by single-crystal diffractometry. The compound crystallizes in the monoclinic space group $P2_1/c$ *with cell dimensions of* $a = 9.057(4)$, $b = 13.424(5)$, $c = 21.591(16)$ Å *and* $\beta = 116.71(2)°$ ($Z = 4$, $D_m = 1.90$ g cm^{-3}, $D_x = 1.917$ g cm^{-3}). *A comparison of its coordination sphere geometry with that of tris(acetylacetonato)Fe(III) revealed no significant differences, thus strongly suggesting that the coordination sphere geometry of tris(acac)metal(III) complexes is primarily determined by the electronic configuration of the metal ion. Significant bending distortions to the chelate rings and the trifluoromethyl groups are attributed to crystal packing forces.*

Introduction

The coordination sphere geometry of tris(bidentate) chelates has been the object of investigation by a number of workers [1–3]. Sometime ago, in a comparison of the coordination octahedra of those first-row transition metal(III) tris-acetylacetonato complexes whose X-ray structures had been reported [4], we found the interesting result that the extent and type of distortion to the coordination octahedron of these complexes depended markedly on the metal^{3+} ion which was coordinated. For example, it was found that the 'bite' oxygen–oxygen atom separations were long and the other oxygen–oxygen atom separations were short for the cobalt(III) complex; whereas, the 'bite' oxygen–oxygen atom separations were short and the other oxygen–oxygen atom separations were long in the iron(III) and vanadium(III) complexes. The tris-complexes of chromium(III) and aluminum(III), on the other hand, possessed reasonably undistorted oxygen octahedra. Although Kepert [2], and recently expanded upon somewhat by Avdeef and Fackler [3], has calculated the configurations of 6-coordinate polyhedra in tris(bidentate-ligand) complexes, these including some tris(acetylacetonato)metal(III) complexes, experimentally determined X-ray diffraction values for both metal–oxygen *and* 'bite' distances were used as fixed parameters in the repulsive force calculations; thus, the more fundamental question of the origin of the forces which determine what the 'bite' distance and thus the configuration of the coordination sphere oxygen octahedron will be in a given complex remains largely unanswered. Preliminary point-charge model calculations by Prof. J. Goodisman of our department [5], in which the 'bite' distance was not a fixed parameter, indicated the possibility that all charges in the acetylacetone chelate ring must be considered. It was to determine the validity of this theory as to the source of the deviations from perfect octahedral symmetry in the coordination sphere geometry of tris(acetylacetonato)metal(III) complexes that the structure reported here was undertaken. The large inductive effect of the -CF_3 groups in tris(1,1,1,5,5,5-hexafluoroacetylacetonato)Fe(III) should give rise to a significantly different charge distribution in the chelate ring [6]; thus, the geometry of its oxygen octahedron should be significantly different from that observed for tris(acetylacetonato)Fe(III) [7], provided the chelate ring charge distribution is an important factor in determining the coordination sphere geometry.

Experimental

Tris (1,1,1,5,5,5-hexafluoroacetylacetonato) iron(III), hereafter called Fe(hfac)$_3$, was prepared by the method described by Morris *et al.* [8]. After purification of the reaction product by multiple vacuum sublimations, suitable crystals for the X-ray structure determination were grown by room-temperature vacuum sublimation. The relatively high vapor pressure of Fe(hfac)$_3$ at room temperature (23 °C) necessitated sealing all crystals used in the diffraction studies in 0.5 mm diameter Lindemann glass

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capillaries. Crystals so preserved showed no change during the X-ray data collection process. Systematic absences, observed on Weissenberg and precession photographs, were those of the centrosymmetric space group $P_{2_1/c}$ (No. 14). Unit cell dimensions were determined by carefully measuring the diffraction angle 2θ for 31 independent reflections on a GE XRD-6 Quarter-Circle diffractometer (Mo Kα, 23 °C) and by subsequently calculating a best-fit set of lattice parameters via a least-squares method. The lattice constants thus determined are: $a = 9.057$ (± 0.004) Å; $b = 13.424$ (± 0.005) Å, $c = 21.591$ (± 0.016) Å and $\beta = 116.71$ (± 0.02)°. Assuming the unit cell to contain 4 molecules of Fe(hfac)$_3$, the density was calculated to be 1.917 g/cm^3 which agrees well with the experimentally measured value of 1.90 g/cm^3 obtained by flotation in a mixture of bromoform and carbon tetrachloride.

A crystal having the approximate dimensions $0.28 \times 0.39 \times 0.52$ mm was mounted with c^* coincident with the axis of rotation ϕ. Integrated intensity data (Mo Kα) for 4122 reflections were collected out to a limit of $\sin \theta/\lambda < 0.573$ on a Canberra Industries automated GE XRD-6 diffractometer using $\theta - 2\theta$ scans of 1° per minute. Scan lengths were compensated for 2θ dependent Kα_1–α_2 spread and 30 second background counts were taken at both ends of the scan range. Two reference reflections, well separated in reciprocal space, were monitored every 40 reflections and showed no systematic changes in intensity during the data collection period. Background corrections, as well as the usual Lorentz and polarization corrections, were applied to all reflections. Because of the relatively low linear absorption coefficient of the compound for Mo Kα radiation ($\mu = 8.51$ cm^{-1}), which was also reflected in the minimal (1% or less) intensity dependence of the 006 reflection at chi = 90° to the angle phi, no absorption corrections were deemed necessary. Weights based on experimentally determined counting errors were applied. Of the 4122 measured reflections, only 1893 were considered to be observed as both high background intensities and a rapid fall-off in diffracted intensity with increasing 2θ resulted in a very large number of reflections with diffracted to background intensity ratios approaching one. The observed diffraction characteristics of this crystal are expected if one considers the low melting point of the compound (47 °C) and the relatively high vapor pressure of the solid at room temperature which is reflected in the ease with which it sublimes. The expected large thermal motion parameters for this compound were confirmed by the results of the structure refinement. The 1893 pieces of data used in the structure solution and refinement represent a data to structural parameter ratio of greater than 5 to 1 which is adequate for a well determined structure [9].

The heavy atom method was used to locate the position of the iron atom. All additional atoms were located after several subsequent Fourier maps coupled with intermediate steps of least-squares refinement of positional parameters of previously located atoms. The correctness of the structure solution was verified by an independent solution which utilized a set of direct methods programs incorporated into a crystallographic program library obtained from the National Research Council of Canada [10]. Atomic coordinate and anisotropic thermal motion parameter refinement on F's was carried out using the full-matrix least-squares program ORFLS [11] to a conventional R factor of 0.099 and a weighted R factor of 0.079. Atomic scattering factors used in the calculations were taken from the International Tables for X-Ray Crystallography, Vol. III [12]. All calculations were performed at the Syracuse University Computing Center using an IBM 360 computer. The final refined atomic coordinates are listed in Table I and the corresponding anisotropic thermal parameters are listed in Table II.

Results and Discussion

Figures 1 and 2 show the bond lengths and bond angles respectively, and also show the numbering scheme which was adopted. The fluorine atoms have been deleted from these figures for clarity. Table III gives the carbon–fluorine bond distance and angle information. An ORTEP [13] drawn stereoscopic view of the molecule is shown in Fig. 3 with envelopes of anisotropic thermal motion ellipsoids drawn at 30% probability. It can be seen from Fig. 3 and Table II that the fluorine atoms exhibit abnormally large anisotropic thermal motions. As was stated earlier, this result is not surprising considering the low melting point of the compound, the fact that it slowly sublimes even at room temperature if not suitably protected, and the observation of high background counts indicative of large amounts of thermal diffuse scattering. The anisotropic thermal motion model used in the calculation of structure factors is not an adequate one when very large anisotropic thermal motions are encountered; thus, the final agreement index R and errors in bond distances and angles, especially those involving atoms showing abnormally large thermal motions, are larger than normally expected for a structure solution with a reflection to structural parameter ratio of approximately 5 to 1. Difficulties in refining fluorine atoms because of very large anisotropic thermal motions have been observed by other workers and carbon–fluorine bond distances typically tend to show large deviations [14–17]. The presence of 18 fluorine atoms, accounting for

TABLE I. Final Atomic Coordinates (with standard deviations in parentheses).

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Fe	0.2021(2)	−0.0038(2)	0.2293(1)	C(34)	−0.0123(19)	0.0788(13)	0.3637(8)
O(11)	0.0092(11)	−0.0568(7)	0.1481(5)	C(35)	0.5714(23)	0.0957(16)	0.4240(8)
O(12)	0.1566(12)	0.1242(6)	0.1779(5)	F(11)	−0.1836(21)	−0.0982(16)	−0.0100(8)
O(21)	0.3530(12)	−0.0473(7)	0.1895(4)	F(12)	−0.3503(17)	−0.0435(10)	0.0077(7)
O(22)	0.2480(12)	−0.1359(7)	0.2795(4)	F(13)	−0.2535(14)	−0.1555(9)	0.0598(6)
O(31)	0.0640(11)	0.0346(6)	0.2764(5)	F(14)	0.0058(18)	0.3089(7)	0.1398(8)
O(32)	0.3963(10)	0.0541(7)	0.3118(5)	F(15)	0.1777(11)	0.2846(7)	0.1036(5)
C(11)	−0.0810(18)	−0.0136(16)	0.0925(8)	F(16)	−0.0640(14)	0.2763(8)	0.0392(6)
C(12)	−0.0800(22)	0.0855(14)	0.0752(8)	F(21)	0.6448(14)	−0.0466(7)	0.1770(6)
C(13)	0.0372(19)	0.1447(12)	0.1211(9)	F(22)	0.4604(12)	−0.1360(8)	0.1023(5)
C(14)	−0.2030(22)	−0.0913(15)	0.0396(7)	F(23)	0.6529(12)	−0.2030(7)	0.1856(5)
C(15)	0.0423(21)	0.2557(10)	0.1001(8)	F(24)	0.4315(15)	−0.2374(8)	0.4010(4)
C(21)	0.4489(17)	−0.1225(12)	0.2071(7)	F(25)	0.4900(10)	−0.3437(6)	0.3431(5)
C(22)	0.4652(17)	−0.1966(10)	0.2544(7)	F(26)	0.2411(11)	−0.3248(7)	0.3247(5)
C(23)	0.3613(21)	−0.1945(9)	0.2861(7)	F(31)	0.0225(12)	0.0691(12)	0.4245(5)
C(24)	0.5590(20)	−0.1264(12)	0.1695(7)	F(32)	−0.1529(11)	0.0341(8)	0.3243(6)
C(25)	0.3770(19)	−0.2804(10)	0.3401(7)	F(33)	−0.0730(14)	0.1698(9)	0.3471(6)
C(31)	0.1193(22)	0.0622(10)	0.3384(9)	F(34)	0.6628(10)	0.1481(8)	0.4020(4)
C(32)	0.2750(18)	0.0803(12)	0.3882(8)	F(35)	0.6579(11)	0.0092(9)	0.4405(5)
C(33)	0.3975(20)	0.0744(11)	0.3710(8)	F(36)	0.5860(11)	0.1293(10)	0.4812(5)

TABLE II. Anisotropic Thermal Parameters ($\times 10^4$) with Estimated Standard Deviations.
The parameters are in the form $\exp[-(h^2{}_{\beta_{11}} + k^2{}_{\beta_{22}} + l^2{}_{\beta_{33}} + 2hk_{\beta_{12}} + 2hl_{\beta_{13}} + 2kl_{\beta_{23}})]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	217(4)	69(1)	29(0)	19(2)	26(1)	3(1)	C(34)	194(34)	145(8)	61(7)	95(20)	12(13)	0(9)
O(11)	239(22)	70(7)	34(3)	8(10)	34(8)	1(4)	C(35)	362(49)	214(24)	44(7)	−2(28)	69(16)	11(10)
O(12)	248(23)	63(7)	34(3)	25(10)	25(7)	4(4)	F(11)	872(53)	545(30)	131(8)	−557(35)	273(19)	−232(14)
O(21)	276(24)	84(8)	38(4)	27(11)	58(8)	14(4)	F(12)	565(40)	194(16)	97(7)	−120(19)	−109(14)	12(8)
O(22)	229(23)	79(8)	36(3)	14(11)	30(7)	11(5)	F(13)	489(32)	206(13)	76(5)	−160(18)	59(11)	−52(7)
O(31)	220(22)	83(9)	42(4)	24(9)	47(8)	−5(4)	F(14)	936(48)	62(7)	153(8)	79(16)	275(18)	23(7)
O(32)	163(19)	98(8)	39(4)	10(10)	26(7)	1(5)	F(15)	359(26)	108(8)	105(5)	5(11)	92(10)	46(6)
C(11)	215(33)	130(19)	30(5)	−26(23)	61(11)	−13(10)	F(16)	481(34)	125(10)	105(7)	−26(14)	−57(11)	83(7)
C(12)	323(44)	72(13)	37(6)	73(20)	58(14)	16(8)	F(21)	525(31)	117(9)	129(7)	−62(13)	190(13)	−35(6)
C(13)	166(34)	85(14)	40(6)	26(18)	46(12)	3(8)	F(22)	436(28)	207(12)	56(4)	169(15)	103(9)	4(6)
C(14)	473(51)	265(24)	13(4)	−262(31)	−10(12)	2(9)	F(23)	488(28)	112(8)	90(5)	95(13)	149(10)	32(5)
C(15)	446(47)	45(11)	61(7)	57(18)	75(15)	11(7)	F(24)	733(38)	171(11)	32(3)	34(17)	78(9)	30(5)
C(21)	185(34)	88(14)	31(5)	−13(17)	36(12)	−16(7)	F(25)	348(23)	91(7)	79(4)	46(10)	82(8)	53(5)
C(22)	213(33)	63(11)	36(5)	3(15)	48(11)	13(6)	F(26)	311(22)	128(9)	85(5)	−10(11)	94(8)	36(5)
C(23)	275(40)	43(11)	25(5)	8(16)	17(12)	8(6)	F(31)	315(24)	446(23)	52(4)	154(19)	74(9)	49(8)
C(24)	333(42)	126(16)	41(6)	22(21)	51(13)	−2(8)	F(32)	336(23)	200(13)	104(6)	−19(13)	146(10)	−29(6)
C(25)	372(40)	78(11)	53(6)	90(19)	88(14)	26(7)	F(33)	509(32)	156(11)	127(7)	71(16)	196(13)	11(7)
C(31)	254(41)	55(11)	58(7)	53(18)	93(16)	21(8)	F(34)	237(20)	173(10)	56(4)	−36(11)	42(7)	−10(5)
C(32)	48(25)	130(14)	50(6)	2(16)	40(12)	6(7)	F(35)	302(23)	200(12)	74(5)	12(15)	−39(8)	43(7)
C(33)	193(37)	74(12)	27(5)	1(16)	−6(12)	−2(7)	F(36)	269(22)	356(18)	45(3)	−117(17)	55(7)	−61(7)

about 50% of the scattering power, and all of which have abnormally large thermal motions, obviously considerably affects the ability to obtain a structure solution of low uncertainty for this compound.

As the primary goal of this structure determination was its comparison with that of tris(acetylacetonato)iron(III) (Fe(acac)$_3$) in order to establish the effect, if any, of the electron withdrawing -CF$_3$ groups on the geometry of the oxygen octahedron, this aspect will be considered first. Two structures of Fe(acac)$_3$, with which a comparison may be made, have been reported; that of Iball and Morgan [7], which was obtained by a refinement of Roof's original diffraction data [18], and that of a silver

TABLE III. Carbon–Fluorine Bond Distance and Angle Information (with one estimated standard deviation in parentheses).

C(14)–F(11)	1.17(4) Å	C(11)–C(14)–F(11)	111.9(17)°
C(14)–F(12)	1.36(3)	C(11)–C(14)–F(12)	105.3(15)
C(14)–F(13)	1.15(4)	C(11)–C(14)–F(13)	119.4(17)
C(15)–F(14)	1.27(3)	C(13)–C(15)–F(14)	106.8(14)
C(15)–F(15)	1.26(3)	C(13)–C(15)–F(15)	115.6(14)
C(15)–F(16)	1.26(3)	C(13)–C(15)–F(16)	113.8(14)
C(24)–F(21)	1.29(3)	C(21)–C(24)–F(21)	113.6(14)
C(24)–F(22)	1.32(3)	C(21)–C(24)–F(22)	107.6(13)
C(24)–F(23)	1.28(3)	C(21)–C(24)–F(23)	113.1(14)
C(25)–F(24)	1.31(3)	C(23)–C(25)–F(24)	106.5(12)
C(25)–F(25)	1.31(3)	C(23)–C(25)–F(25)	108.4(12)
C(25)–F(26)	1.27(3)	C(23)–C(25)–F(26)	112.9(13)
C(34)–F(31)	1.21(3)	C(31)–C(34)–F(31)	120.3(16)
C(34)–F(32)	1.32(3)	C(31)–C(34)–F(32)	112.7(15)
C(34)–F(33)	1.32(3)	C(31)–C(34)–F(33)	109.5(15)
C(35)–F(34)	1.33(4)	C(33)–C(35)–F(34)	115.9(22)
C(35)–F(35)	1.36(3)	C(33)–C(35)–F(35)	108.8(15)
C(35)–F(36)	1.27(3)	C(33)–C(35)–F(36)	115.2(16)

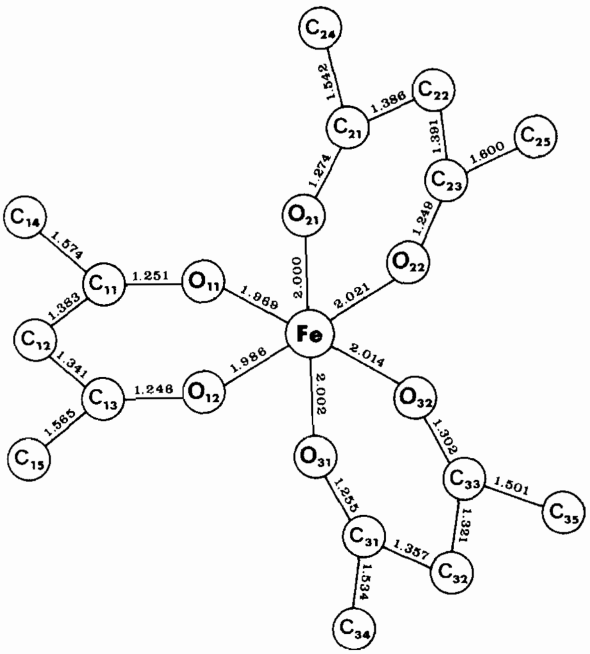

Fig. 1. Bond distances for tris(1,1,1,5,5,5-hexafluoroacetylacetonato)iron(III). The fluorine atoms have been omitted for clarity. The value of one estimated standard deviation for bond lengths involving Fe–O atoms is 0.010 Å, C–O atoms 0.020 Å, and C–C atoms approximately 0.025 Å.

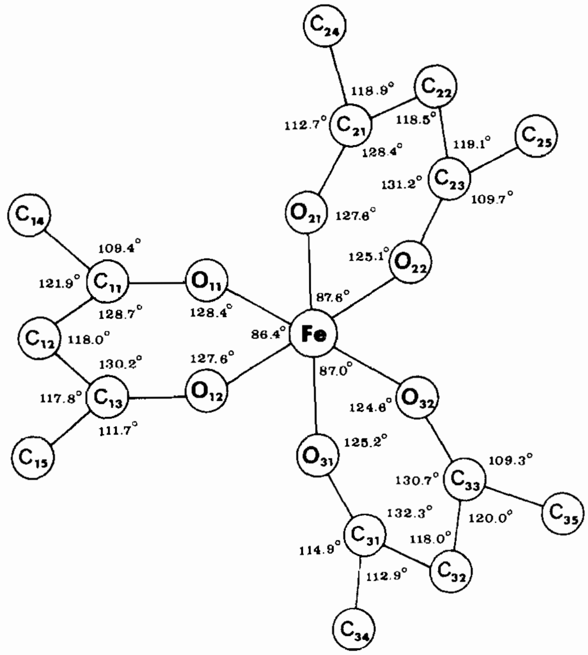

Fig. 2. Bond angles for tris(1,1,1,5,5,5-hexafluoroacetylacetonato)iron(III). The fluorine atoms have been omitted for clarity. The value of one estimated standard deviation for bond angles involving only Fe and O atoms is 0.4°, those involving Fe, O, and C atoms 1.0°, and all others approximately 1.5°.

perchlorate adduct of the monohydrate of Fe(acac)$_3$ reported by Nassimbeni and Thackeray [19]. Table IV lists the mean values of the chemically equivalent bond lengths and angles of the coordination sphere octahedra for the three structures. One notes that the agreement is very good, being well within the error limits for these structures (approx. 0.01 Å for Fe–O, 0.02 Å for O–O, and 0.5° for O–Fe–O). It is thus clear from this comparison that the

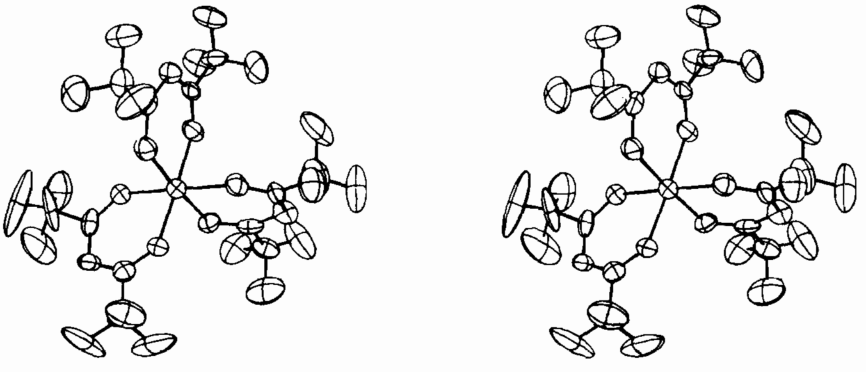

Fig. 3. A stereographic drawing of the molecule.

TABLE IV. Comparison of Chemically Equivalent Coordination Sphere Bond Lengths and Angles (average values).

Bond	$Fe(hfac)_3$[a]	$Fe(acac)_3$[b]	$Fe(acac)_3 \cdot AgClO_4 \cdot H_2O$[c]
Fe–O	1.999 Å	1.992 Å	1.998 Å
O–O (bite)	2.75 Å	2.74 Å	2.77 Å
O–O (other separations)	2.85 Å	2.84 Å	2.84 Å
O–Fe–O	87.0°	87.1°	88.0°

[a]This paper. [b]Reference 7. [c]Reference 19.

geometry of the coordination sphere octahedra of the three complexes can be considered to be essentially identical, indicating that the 'bite' oxygen–oxygen separations, the metal–oxygen bond distances, and thus the geometry of the oxygen octahedron, are determined primarily by the electronic structure of the coordinated metal ion and to a much lesser extent by the charge densities of the ligand atoms. It is very likely that small differences in the bond distances and angles do exist in the structure which are the result of the substitution of the electron withdrawing -CF_3 groups for the -CH_3 groups of the acetylacetone ligand; however, the differences are relatively small. To determine their magnitude, it would be necessary to redetermine both the $Fe(hfac)_3$ and the $Fe(acac)_3$ structures using diffraction data sets of greatly improved accuracy, which in the case of $Fe(hfac)_3$ would require data collection at a sufficiently low temperature to reduce atom thermal motions to an acceptable level.

Another aspect of the structure which is of interest is the extent of displacement of the iron atom and the carbon atoms of the trifluoromethyl groups from the plane of the acetylacetone chelate ring. The displacement of the iron atom may also be thought of as a rotation or bending of the ligand about the O–O vector of the chelate ring. Bending of the chelate ligand about the 'bite' atoms is a generally occurring feature of chelate complexes. As Prof. Lingafelter [20] has previously stated, this effect is most certainly due to steric influences; that is, packing effects in the crystal lattice. Table V presents the results of mean plane calculations for the hfac ligands in $Fe(hfac)_3$ from which it is seen that considerable bending has occurred in rings 2 and 3. The angle through which each chelate ring is bent out of the Fe–O plane about the O–O vector is 1.40°, 10.13° and 11.98° for rings 1, 2, and 3, respectively, which compares to 0.05°, 3.24° and 10.60° for $Fe(acac)_3$ [7] and 11.71°, 7.73° and 13.10° for the silver perchlorate adduct of $Fe(acac)_3$ monohydrate [19]. Although some of these bending angles are sizeable, they are not unusual for acetylacetonate complexes. A bending angle of 15.3° was observed for trans-bis(acetylacetonato)bis(4-methylpyridine)-nickel(II) [21], 19.33° for diaquabis(acetylacetonato)magnesium(II) [22], and 21.83° for diaquabis-(acetylacetonato)manganese(II) [23], all rather large angles indicating the wide range through which acetylacetone ligands may be bent while still maintaining essentially full orbital overlap as is evident from the fact that no dependence of metal–oxygen bond distances on bending angle is observed.

Results presented in Table V also show that considerable deviation of the -CF_3 groups from the planes of the acetylacetone rings is present in $Fe(hfac)_3$ and is somewhat greater than in $Fe(acac)_3$ [7]. It is very likely that this is the result of the enhanced molecular packing density of $Fe(hfac)_3$ in its crystal lattice. There is an approximate 6% decrease in free space per molecule of $Fe(hfac)_3$ in its lattice as compared to the $Fe(acac)_3$ molecule packed in its lattice. All fluorine–fluorine atom

TABLE V. Results of Mean-plane Calculations.

Plane 1		Plane 2		Plane 3	
Atom	Deviation (Å)	Atom	Deviation (Å)	Atom	Deviation (Å)
Fe	−0.035	Fe	−0.255	Fe	−0.303
*O(11)	−0.031	*O(21)	−0.015	*O(31)	−0.019
*O(12)	0.031	*O(22)	0.013	*O(32)	0.014
*C(11)	0.036	*C(21)	0.020	*C(31)	0.026
*C(12)	0.000	*C(22)	−0.005	*C(32)	−0.007
*C(13)	0.036	*C(23)	−0.013	*C(33)	−0.015
C(14)	0.212	C(24)	0.084	C(34)	0.133
C(15)	−0.018	C(25)	−0.022	C(35)	−0.023

*Atoms included in the mean-plane calculation. One estimated standard deviation is approximately 0.020 Å. Equations of the planes in an orthogonalized coordinate system are:

Plane 1: $0.8712\,X - 0.2493\,Y - 0.4229\,Z = -2.1664$
Plane 2: $-0.3735\,X - 0.5457\,Y - 0.7502\,Z = -2.8872$
Plane 3: $-0.0148\,X + 0.9647\,Y - 0.2631\,Z = -0.9043$

contacts, however, are greater than the sum of the van der Waal's radii and each fluorine atom has at least one fluorine–fluorine atom contact in the range of 2.83 to 3.22 Å with most having two contacts within this range. The -CF_3 groups are bent out of the acetylacetone ring plane in the direction which minimizes these intermolecular contacts. All fluorine–fluorine atom intermolecular contacts are approximately of the same magnitude with no consistently shorter contacts being observed for those -CF_3 groups exhibiting the greatest amount of bending.

In conclusion, the theory that the coordination sphere geometry of tris(β-diketonato)metal(III) complexes is determined by the charge density distribution in the chelate ring has been demonstrated to be incorrect. It thus seems highly probable that the electronic configuration of the metal(III) ion forming the complex is responsible for the experimentally observed coordination geometries. Structural differences, caused by the substitution of the highly electron withdrawing -CF_3 group for -CH_3, other than those features attributable to molecular packing, are seen to be smaller than the error limits of this structure determination. Crystal packing forces are seen to be able to cause sizeable bending distortions to the chelate rings and their methyl groups.

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