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Structure of Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)chromium(III) Determined by Gas-Phase Electron Diffraction

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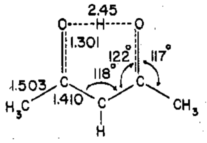
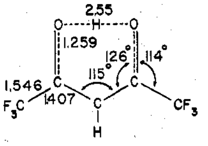
The r_g structure of tris(1,1,1,5,5,5-hexafluoroacetylacetonato)chromium(III) has been determined by gas-phase electron diffraction. The experimental data were found to be consistent with a D_3 model in which the oxygen atoms from the three ligands are arranged in a slightly distorted octahedron about the chromium atom (OCrO for the ligand = 87.0 (1.4)°). The chromium–oxygen bond length obtained (Cr–O = 1.957 (8) Å) is in close agreement with the value obtained previously by x-ray diffraction for the acetylacetonato complex of chromium [Cr–O = 1.951 (7) Å]. Structural parameters for the ligand (C–O = 1.270 (6) Å, $C–C_{ring}$ = 1.409 (14) Å, $C–CF_3$ = 1.559 (9) Å, and C–F = 1.338 (3) Å) are in excellent agreement with the values obtained in an earlier electron diffraction of the Cu(II) complex with hexafluoroacetylacetone. The experimental structure obtained was found to be inconsistent with a very successful stereochemical model for predicting the geometries of metal atom complexes involving bidentate ligands.

Introduction

Complexes involving β-ketoenolates have been reported for nearly all of the nonradioactive metals and metalloids in the periodic table.[1] The properties of these compounds have been studied by almost every known physical method. Most of this research has concentrated on the acetylacetonate (acac) complexes since they are relatively stable and easy to prepare. Fewer studies have involved the trifluoroacetylacetonate (tfa) and hexafluoroacetylacetonate (hfa) ligands, and very little is known regarding the structural consequences of fluorine atom substitution in the β-ketoenolates.

The electron diffraction structures of acetylacetone,[2,3] trifluoroacetylacetone,[3] and hexafluoroacetylacetone[4] have all been reported. Yokozeki and Bauer[5] have summarized the structural changes that result from fluorine atom substitution in these compounds. It appears that when the two methyl groups in the enol form of acetylacetone are replaced with trifluoromethyl groups, the C–O ring distance is shortened by 0.04 Å while the $C–CX_3$ bond is lengthened by about 0.04 Å. This is a rather significant inductive effect, and one might reasonably expect to see similar structural changes in the corresponding β-ketoenolate complexes with metals.





The crystal structure of $Cr(acac)_3$ was first reported by Shkol'nikova and Shugam[6] but was later revised by Morosin.[7] The structure reported by Morosin is nearly a regular octahedron about the Cr(III) atom with a Cr–O bond length of 1.951 (7) Å and an OCrO valence angle involving the two oxygens from the same ligand of 91.1°. The structural parameters for the ligand (C–O = 1.26 (2) Å, $C–C_{ring}$ = 1.39 (2) Å, and $C–CH_3$ = 1.52 (2) Å) are in fair agreement with those for acetylacetone.

One parameter of particular interest in the tris bidentate complexes is the "pitch angle" of the molecular propeller blades. The pitch angle (ϕ) may be defined as the angle of rotation of the blades (about their C_2 axes) relative to a D_{3h} (triangular prism) reference configuration. A pitch angle of 0° corresponds to a triangular prism. A regular octahedron having all 90° valence angles about the central atom would have a pitch angle of 35.26°. Typical pitch angles in acetylacetonate complexes range from 30.4° for $Sc(acac)_3$[8] to 36.7° for $Co(acac)_3$.[9] The pitch angle for $Cr(acac)_3$,[7] 35.7°, is very near the octahedral value of 35.26°; however, there is still a slight distortion from octahedral symmetry since the OCrO valence angles for the ligands in this complex are 91.1°.

A simple, yet very powerful, model for predicting the stereochemistry of tris complexes involving bidentate ligands has been proposed by Kepert.[10] In this model the ligands, which are characterized by a normalized bite, $b = O\cdots O/M–O$, are permitted to distribute themselves on the surface of a unit sphere under the influence of a repulsive pairwise interaction law. The total interaction energy is given by

$$U = \sum_{ij} a_n d_{ij}^{-n} \qquad (1)$$

where the d_{ij}'s are the distances between the ligand atoms which are bonded to the metal atom. In the case of a bidentate ligand the distance between the two atoms contributed by the ligand is fixed at the value b corresponding to the normalized bite of the ligand. For an assumed force law, the total energy is then minimized with respect to the orientation of the ligands in order to obtain optimum geometry about the metal atom.

If the bidentate ligands are all the same and symmetric, then the total energy may be written in a simpler form since all of the a_n's are equal.

$$U = a_n \sum_{ij} d_{ij}^{-n} \qquad (2)$$

Thus it is seen that the parameter a_n only serves to provide a scale factor for the total energy and that the geometry obtained by energy minimization is entirely independent of the value for this parameter. An even more remarkable observation made by Kepert is that the geometries obtained are almost totally insensitive to the choice of n (the exponent in the power law) over a wide range from $n = 1$ to $n = 12$.

For tris complexes involving symmetric bidentate ligands, application of the above model always results in a molecular geometry having D_3 symmetry. The stereochemisry of the minimum energy geometry is thus characterized by a single geometrical parameter, θ, the relative angle of twist between the upper and lower triangular faces of the polyhedron as shown in Figure 1. The twist angle, θ, and the pitch angle, ϕ, are related to each other by the equation

$$\tan \theta = \frac{b}{(4 - b^2)^{1/2}} \sin \phi \qquad (3)$$

where b is the normalized bite of the ligand. It may be seen that a regular octahedron is characterized by $\theta = 30°$ and $b = 2^{1/2}$ for which $\phi = 35.26°$.

Kepert[10] has tested this model on 82 complexes involving a variety of metal atoms and bidentate ligands and has found excellent agreement between the model and experiment. $Cr(acac)_3$ is a typical example of the agreement obtained.

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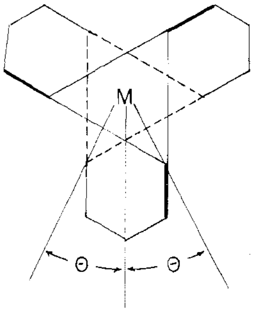

Figure 1. Definition of the stereochemical twist angle θ.

Experimentally it is found that $b = 1.43$ and $\theta = 30.8°$ for $Cr(acac)_3$, while application of the model for the case $b = 1.43$ and $n = 6$ predicts a value of $\theta = 30.5°$.

Our purpose in undertaking a structural investigation of $Cr(hfa)_3$ was threefold: (1) to obtain a precise value for the Cr–O bond length in this molecule for comparison with M–O bond lengths in other $M(hfa)_3$ complexes, (2) to compare the structure of $Cr(hfa)_3$ with that of $Cr(acac)_3$ in order to assess the effects of fluorine substitution on the molecular structure of the complex, (3) to obtain additional experimental data as a test of Kepert's model for predicting the stereochemistry of tris bidentate complexes. $Cr(hfa)_3$ is well suited for gas-phase electron diffraction investigation in spite of its large size since it possesses a high degree of symmetry and is also quite volatile.

Experimental Section

Tris(hexafluoroacetylacetonato)chromium(III) was prepared by the method of Morris and Aikens[11] and purified by recrystallization from a carbon tetrachloride solution. The electron-diffraction patterns were recorded on Kodak electron image plates using the Indiana University instrument with a 40-keV accelerating potential and camera lengths of 12 and 29 cm. The sample was introduced through a stainless steel inlet and nozzle (0.15 mm in diameter) electrically heated to 110 °C. Recorded sample pressures at this temperature ranged from 1.2×10^{-5} to 5.5×10^{-6} Torr. Exposure times for the 0.3 μA beam current employed were 5 min for both camera distances. The voltage was measured across a calibrated precision voltage divider using a digital differential voltmeter. The nozzle to plate distances were measured with a precision cathetometer. This calibration was checked against the known spectroscopic structure of CO_2 by recording CO_2 diffraction patterns under identical conditions with those used for the sample.

Two photographic plates for each camera length were selected for microphotometering on the automated Indiana University microdensitometer.[12] Corrections for saturation, sector imperfections, and plate flatness were made in the usual manner, and the levelled experimental data were interpolated at integral q $[(40/\lambda) \sin \theta/2]$ intervals for least-squares analysis.

The data were analyzed on The North Dakota State University IBM 360-50 computer using the elastic scattering factors and phase shifts of Schäfer, Yates, and Bonham[13] and the inelastic scattering factors of Tavard.[14] The details of the method of analysis have been described elsewhere.[15] Tables of experimental data and correlation and error matricies are available as supplementary material.

Data Analysis

Figure 2 illustrates the numbering scheme used in defining the structural parameters for $Cr(hfa)_3$. In order to carry out the analysis on a manageable number of geometrical parameters, the following simplifying assumptions were introduced. (1) The molecule was assumed to possess D_3 symmetry, except for the CF_3 groups. (2) The CF_3 groups were constrained to local C_3 symmetry about their respective C–C rotational axes. (3) The hfa ligands were constrained to be planar except for the two out-of-plane fluorines on each trifluoromethyl group. (4) The three hydrogen atoms, which make a negligible contribution to the overall scattering intensity, were oriented by constraining the C–H bond lengths to 1.11 Å and requiring the hydrogens to lie along the C_2 symmetry axes of the ligands.

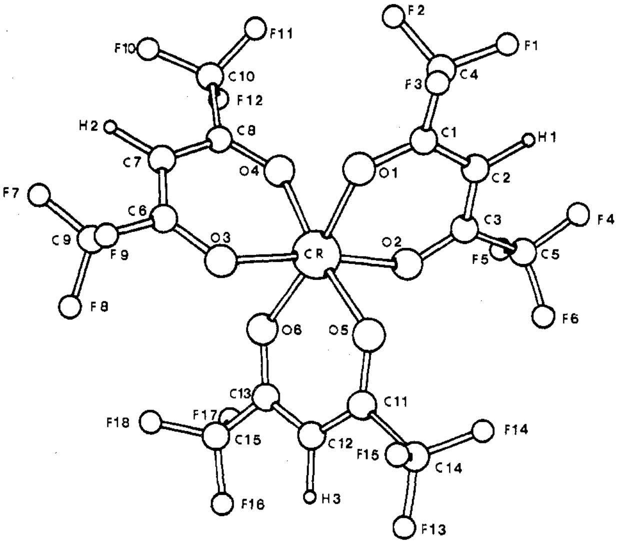

Figure 2. Numbering of the atoms in $Cr(hfa)_3$.

Table I. Structural Parameters Obtained from Least-Squares Analysis (Distances, Å; Angles, deg)

independent parameters[a]	value[b]	dependent parameters[c]	value[d]
Cr-O	1.957 ± 0.008	$O_1C_1C_2$	126.1 ± 1.4
C-O	1.270 ± 0.006	$C_4C_1C_2$	121.2 ± 1.4
C_1-C_2	1.409 ± 0.014	$C_1C_2H_1$	120.2 ± 0.8
C_1-C_4	1.559 ± 0.009	$C_1C_2C_3$	119.7 ± 1.7
C-F	1.338 ± 0.003	O_1CrO_2	87.0 ± 1.4
$O_1CrO_2/2$	43.5 ± 0.7	O_1CrO_4	86.9 ± 3.1
pitch angle	37.6 ± 2.3	O_1CrO_3	93.0 ± 1.7
CrO_1C_1	130.7 ± 1.7	O_1CrO_6	179.9 ± 2.7
$O_1C_1C_4$	112.7 ± 1.0	$O_1\cdots O_2$	2.694 ± 0.040
$C_1C_4F_1$	111.5 ± 0.4	$O_1\cdots O_4$	2.687 ± 0.080
l_{Cr-O}	0.073 ± 0.006	$O_1\cdots O_3$	2.834 ± 0.037
$l_{Cr\cdots C_4}$	0.109 ± 0.033	$O_1\cdots O_6$	3.899 ± 0.016
$l_{F_3\cdots C_1}$	0.077 ± 0.007		
$l_{F_1\cdots F_2}$	0.063 ± 0.003		
$l_{F_2\cdots O_1}$	0.102 ± 0.021		
$l_{F_2\cdots C_2}$	0.291 ± 0.117		

[a] Independent parameters varied in least-squares analysis. [b] Distances are r_g values and angles are quoted in r_α representation. Uncertainties are within the 99% confidence level. [c] Dependent parameters were derived from the r_α structure and are corrected for shrinkages. [d] The estimated standard deviations are derived by transforming the error matrix for the independent parameters.

Within the framework of the above four assumptions, it was possible to define a ten-parameter model for $Cr(hfa)_3$. The definitions of all of the parameters which were chosen as independent parameters are listed in the top half of Table I.

The above parameterization is complete except for the specification of the rotational orientation of the CF_3 groups relative to the ligand rings. The orientation of these groups forms the basis for the three models discussed in more detail below.

Vibrational amplitudes and shrinkage corrections at 383 K were calculated from the Urey–Bradley force field shown in Table II. This force field is an adaptation of the one determined by Mikami, Nakagawa, and Shimanouchi[16] for tris(acetylacetonate)iron(III) with the $-CF_3$ force constants taken from an earlier study by Shimanouchi[17] on substituted alkanes. Table II also lists a few of the l_{ij} and K_{ij} parameters calculated for the more prominent distances in the radial distribution curve (Figure 3). Only a few of the amplitude parameters for well-resolved peaks were actually varied in the

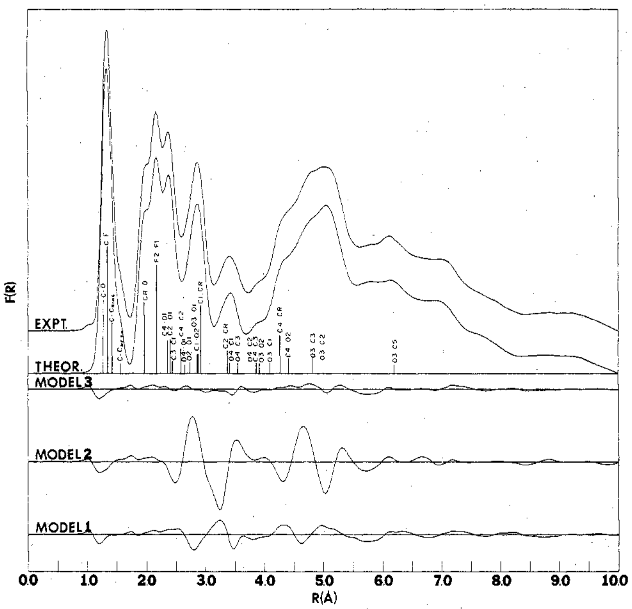

Figure 3. Levelled theoretical and experimental intensity curves for $Cr(hfa)_3$. The ordinate units are arbitrary while the abscissa is in q units ($q = (40/\lambda)\sin\theta/2$).

Table II. Force Field and Calculated Parameters for $Cr(hfa)_3$ [a]

force field parameter, mdyn Å^{-1}		force field parameter, mdyn Å	
$K(C\text{–}C_{ring})$	4.87	$H(FCF)$	0.268
$K(C\text{–}C_{meth})$	2.80	$H(CCF)$	0.310
$K(C\text{–}O)$	6.03	$H(CCC_{meth})$	0.330
$K(MO)$	1.30	$H(OCC_{meth})$	0.340
$K(C\text{–}F)$	3.75	$H(OCC_{ring})$	0.440
$K(C\text{–}H)$	4.70	$H(CCC_{ring})$	0.360
$F(F\cdots F)$	1.350	$H(CCH)$	0.190
$F(C\cdots F)$	1.30	$H(COM)$	0.030
$F(C\cdots C)$	0.40	$H(OMO_{ring})$	0.010
$F(C_{meth}\cdots O)$	0.50	$H(OMO_{ext})$	0.120
$F(C_{ring}\cdots O)$	0.60	$Y(CF3)$	0.055
$F(C_{ring}\cdots C)$	0.35	$Y(C\text{–}C_{ring})$	0.350
$F(C\cdots H)$	0.40	$Y(C\text{–}O)$	0.140
$F(C\cdots M)$	0.01	$Y(M\text{–}O)$	0.080
$F(O\cdots O_{ring})$	0.02	$E(H)$	0.157
$F(O\cdots O_{ext})$	0.02	$E(meth)$	0.400
$P(MO,MO_{ext})$	0.30	$L(OMO)$	0.130
$P(MO,MO_{ring})$	0.16		
κ	−0.073		

distance	$10^4 l_{ij}$	$10^4 K_{ij}$
Cr–O	728	129
C–O	437	136
$C\text{–}C_{ring}$	462	146
$C\text{–}C_{meth}$	494	212
C–F	470	693
$C_1\cdots Cr$	949	144
$C_2\cdots Cr$	1224	169
$C_4\cdots Cr$	940	244
$C_4\cdots C_3$	745	294
$F_2\cdots Cr$	1742	435
$F_2\cdots F_1$	607	1217
$F_1\cdots C_1$	623	590
$F_2\cdots O_1$	1628	549
$F_2\cdots C_2$	1356	547
$O_1\cdots O_2$	1475	155
$O_1\cdots O_4$	1998	146
$O_1\cdots O_6$	1092	99
$O_1\cdots O_5$	1742	129

[a] Force constants expressed in the notation of ref 16.

analysis; the remainder were constrained to their calculated values. In particular, since all of the ligand bond lengths tend to cluster under one peak of the radial distribution curve between 1.0 and 1.6 Å, the amplitude parameters for these distances were constrained to their calculated values throughout the analysis. The reader should note that the values obtained for the ligand bond lengths are therefore conditionally dependent upon the accuracy of the calculated amplitude parameters. This method of analysis, which employs both spectroscopic and diffraction data, is nevertheless a vast improvement over the alternative method of analysis which attempts to use diffraction data alone.

Three models were considered in the analysis of the experimental data. The models used are analogous to those previously employed in the study of $Cu(hfa)_2$. Various plausible orientations of the six trifluoromethyl groups were systematically explored in order to determine the preferred molecular conformation for the molecule.

It is well-known that the preferred conformation of a methyl group adjacent to a double bond (e.g., in acetone or isobutene) is the one in which one of the C—H bonds eclipses the C=C or C=O bond and that the rotational potential function is predominantly threefold. It is also well-known that a methyl group attached to an aromatic ring (e.g., in toluene) exhibits only a very small sixfold barrier to internal rotation. The situation in the case of the hfa ligand is probably somewhat intermediate between these two extremes. In this case the CF_3 group is attached to a ring which exhibits a certain degree of aromaticity; however, the strong interaction between the fluorine and oxygen atoms would probably favor a rotational potential function having both threefold and sixfold Fourier components. The relative magnitudes of these two components will determine the favored conformation or mixture of conformations observed.

The first two models tried were based on the assumption that the rotational potential function was predominantly threefold with a high barrier to internal rotation. In model 1 it was assumed that the preferred orientation of the methyl groups was the one in which one of the C–F bonds was eclipsed with the C–C partial double bond of the ligand ring. In model 2 it was assumed that one of the C–F bonds was eclipsed with the C–O partial double bond. From the difference curves shown in Figure 3, it is apparent that Model 1 is a better representation of the experimental data than model 2, although, even model 1 exhibits less than satisfactory agreement in the 3.0–6.0 Å region of the radial distribution curve.

An interesting observation may be noted regarding the difference curves shown in Figure 3 for models 1 and 2. Aside from the fact that the two error curves differ in magnitude, they are very nearly reflections of each other about the zero difference line in the 3.0–6.0 Å region of the curve. In those regions where model 1 shows negative deviations from the experimental curve, model 2 shows positive deviations and vice versa. Based upon this observation one is tempted to propose a model which is a simple mixture of these two conformations with appropriate mole fractions to be determined by least-squares analysis. Such a model is unacceptable, however, for two reasons. First, it neglects those contributions to the average structure which arise from intermediate cases in which some of the CF_3 groups are oriented in accordance with model 1 while others are oriented as in model 2. Second, it assumes that there are two separate minima in the rotational potential function separated by 60° in the torsional angle. This could only be possible if the sixfold contribution to the rotational potential function is greater in magnitude than the threefold contribution. This is not chemically reasonable, since in all molecules possessing hindered internal rotation studied to date the threefold contributions outweigh the sixfold contributions by at least 1 order of magnitude. Thus, a model involving a simple mixture of these two conformations was rejected.

On the basis of the above arguments, a third model was proposed which represents a crude approximation to a low

Table III. CR(HFA)$_3$ Conformations

conformation	G_i	E_i	weight,[a] %	F_1	F_4	F_7	F_{10}	F_{13}	F_{16}
1	1	0.0	16.55	0[b]	0	0	0	0	0
2	6	E	34.72	1[c]	0	0	0	0	0
3	3	$2E$	6.07	1	1	0	0	0	0
4	3	$2E$	6.07	0	1	1	0	0	0
5	3	$2E$	6.07	1	0	0	1	0	0
6	6	$2E$	12.14	1	0	1	0	0	0
7	6	$3E$	4.24	1	1	1	0	0	0
8	3	$3E$	2.12	1	1	0	1	0	0
9	2	$3E$	1.41	1	0	1	0	1	0
10	3	$3E$	2.12	1	1	0	0	1	0
11	6	$3E$	4.24	0	1	1	0	0	1
12	6	$4E$	1.48	1	1	0	1	0	1
13	3	$4E$	0.74	1	1	1	1	0	0
14	3	$4E$	0.74	1	1	0	1	1	0
15	3	$4E$	0.74	1	1	1	0	0	1
16	6	$5E$	0.52	1	1	1	1	1	0
17	1	$6E$	0.03	1	1	1	1	1	1

[a] The weight of each conformation was calculated by the formula weight$_i$ = $[G_i \exp(E_i/RT)]/[\Sigma_i G_i \exp(-E_i/RT)]$, where G_i is the degeneracy and E_i the energy of the conformation. R and T are the ideal gas constant and the absolute temperature, respectively. [b] 0 represents a fluorine eclipsing the partial C–C double bond. [c] 1 represents a fluorine eclipsing the partial C–O double bond.

threefold barrier to internal rotation of the CF$_3$ groups. Because of the computational complexity involved in performing a six-dimensional average over the uncorrelated hindered rotations of the six CF$_3$ groups, the assumed model was greatly simplified by including only two orientations of each CF$_3$ group. Since model 1 provided better agreement with the experimental data than model 2, it was assumed that the minimum in the threefold potential function corresponded to the orientation of the CF$_3$ group in which the C–F bond was eclipsed with the C–C ligand ring bond. Then, rather than including several orientations for each CF$_3$ group, only one additional point on the rotational potential energy function of each CF$_3$ group was included. The second orientation included was that of the transition state itself, i.e., the orientation in which the CF$_3$ group has a C–F bond eclipsing a C–O ligand ring bond as in model 2. This seems like a rather crude approximation; however, as seen below a large number of models result when one considers the six-dimensional potential energy surface and the number of thermally accessible regions of that space which are generated even by this crude approximation.

The details of the proposed model are outlined in Table III. In this model the six trifluoromethyl groups were considered to be completely independent of each other (no interaction energy between groups) and to have only two possible orientations differing in energy by a fixed quantity E. The parameter E thus crudely represents the activation energy for the threefold rotation or the barrier height per CF$_3$ group. Table III enumerates the structures, relative energies, multiplicities, and mole fractions of the various possible conformations which may be generated by considering all combinations of orientations of the six trifluoromethyl groups. The mole fractions were determined in the usual manner by taking the product of the multiplicity and Boltzmann terms and dividing by the conformational partition function. Since the energies were assumed to be additive, this model has the distinct advantage of introducing only one additional parameter, the barrier height E.

The optimum value of the parameter E was determined manually by performing several least-squares runs for fixed values of E. In each of these analyses, all of the structural parameters were permitted to vary freely. A plot of the R factor vs. the value of E in calories is shown in Figure 5. The optimum value of E, found by this technique, was 800 ± 150 cal, and as seen from the difference curves in Figure 3, this model represents a significant improvement over the two previous models. Figure 4 illustrates the final experimental and theoretical intensity curves obtained from the refinement of model 3, and the structural parameters obtained for this model are shown in Table I.

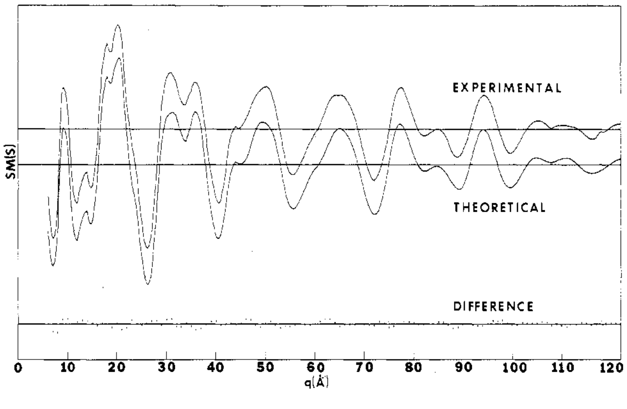

Figure 4. Theoretical and experimental radial distribution curves for Cr(hfa)$_3$. The ordinate units are arbitrary.

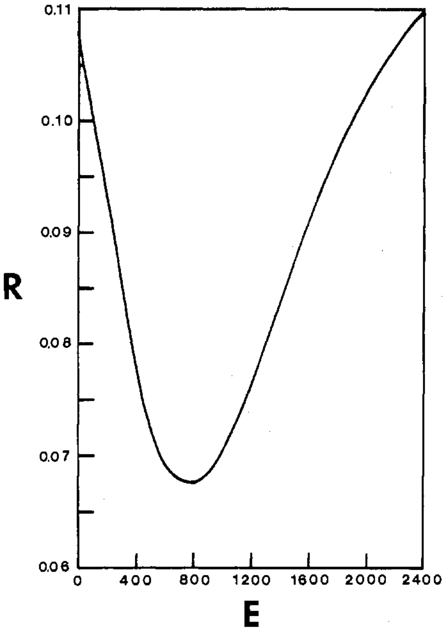

Figure 5. Conformation energy difference curve for Cr(hfa)$_3$. The abscissa is in units of calories.

Discussion

One of the principal reasons for undertaking this investigation was to obtain a precise measurement of the Cr(III)–O bond length which is to be compared with the metal–oxygen bond lengths for other hfa complexes in this series. As in the case of Cu(hfa)$_2$ studied previously,[18] the metal–oxygen bond length in Cr(hfa)$_3$ is well enough separated from the other distances in the molecule to permit a precise determination of its value. The value obtained, 1.957 (8) Å, is within the experimental uncertainty of the Cr–O bond length for Cr(acac)$_3$, 1.951 (7) Å, obtained by x-ray diffraction.

Table IV compares the ligand parameters obtained for Cr(hfa)$_3$ with those of Cu(hfa)$_2$ and other related molecules. There are no significant differences between the ligand parameters obtained for Cr(hfa)$_3$ and Cu(hfa)$_2$, and, in fact, the two parameters which are expected to be least affected by metal atom replacement, C–C$_{\text{meth}}$ and C–F, are essentially identical in the two compounds. This agreement provides an excellent cross-check on the consistency of the scale calibrations

Table IV. Comparison of Structurally Related Molecules

compound	C–O	C–C_{ring}	C–C_{meth}	C–F	OCC_{ring}	CCC_{ring}	ref	method
$Cr(hfa)_3$[a]	1.270 ± 0.006	1.409 ± 0.014	1.559 ± 0.009	1.338 ± 0.003	126.1 ± 1.4	119.7 ± 1.7	this work	E.D.[f]
$Cu(hfa)_2$[b]	1.276 ± 0.009	1.392 ± 0.015	1.558 ± 0.009	1.339 ± 0.003	127.4 ± 1.4	119.3 ± 1.8	18	E.D.
$Cr(acac)_3$[c]	1.263 ± 0.016	1.388 ± 0.021	1.517 ± 0.021		125. ± 1.0	125. ± 1.0	7	x-ray
hfa[d]	1.259 ± 0.018	1.407 ± 0.031	1.546 ± 0.008	1.337 ± 0.007	126.4 ± 1.2	115.2 ± 1.2	4	E.D.
acac[e]	1.287 ± 0.006	1.405 ± 0.005	1.510 ± 0.005		123.2 ± 1.7	118.3 ± 1.8	2	E.D.

[a] Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)chromium(III). [b] Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II). [c] Tris(2,4-pentanedionato)chromium(III). [d] 1,1,1,5,5,5-hexafluoro-2,4-pentanedione. [e] 2,4-pentanedione. [f] E.D. = electron diffraction.

for the two sets of experimental data.

Table IV also illustrates the effects of fluorine for hydrogen substitution in the metal β-ketoenolate complexes. The most pronounced effect is the lengthening of the C–C_{meth} bond length from 1.517 (21) Å in the acac complex to 1.559 (9) Å in the hfa complex. This lengthening closely parallels the lengthening of the C–C_{meth} bond which occurs in acac itself upon fluorine substitution. The decrease in the C$\overline{\cdot\cdot}$O ring distance which occurs in acac upon fluorination is not observed in the metal complex. The C$\overline{\cdot\cdot}$O bond lengths in the ligand rings of $Cr(acac)_3$ and $Cr(hfa)_3$ are the same within experimental error as are the C$\overline{\cdot\cdot}$C ring distances. In general, the agreement between the structural parameters for the hfa ligand in $Cr(hfa)_3$ and the hfa molecule itself is quite favorable.

An additional reason for studying the $Cr(hfa)_3$ molecule was to provide an additional test for the stereochemical model proposed by Kepert.[10] Using the structural parameters for $Cr(hfa)_3$ from Table I, one obtains a normalized ligand bite (O···O/M–O) for $Cr(hfa)_3$ of $b = 1.38$ (2) which is substantially smaller than the x-ray value reported for $Cr(acac)_3$, $b = 1.43$. On the basis of Kepert's model, using $b = 1.38$ and $n = 6$, one would expect a value of $\theta = 28°$ for $Cr(hfa)_3$; however, based on the observed values of the pitch angle and ligand bite for $Cr(hfa)_3$, one finds an experimental value of $\theta = 30.1°$ (1.5). This value is surprisingly close to the x-ray diffraction value obtained for $Cr(acac)_3$, $\theta = 30.8°$. It appears that for some reason $Cr(hfa)_3$ does not agree with the predictions of this otherwise rather successful stereochemical model. The only obvious structural difference between $Cr(hfa)_3$ and $Cr(acac)_3$ is the difference in the O···O nonbonded distance. In $Cr(acac)_3$, O···O = 2.79 Å, while in $Cr(hfa)_3$ this distance decreases to 2.69 Å. The Cr–O bond lengths in both compounds, however, remain the same within experimental error.

At the present time there is not sufficient data regarding structures of hfa complexes to conclude whether such anomalous behavior is characteristic of hfa complexes or is unique to the compound $Cr(hfa)_3$. Tentatively, one might speculate that the reason for this apparently anomalous behavior is that Kepert's model neglects interactions between all other atoms except those directly attached to the metal itself. It is very likely that rather strong nonbonded intractions between the fluorine atoms will have an influence on the structure. Such a conclusion will require additional experimental structural data.

The rotational models employed in the analysis of the $Cr(hfa)_3$ data are analogous to those used for $Cu(hfa)_2$, and the results obtained are very similar in nature. The barrier to internal rotation per trifluoromethyl group in $Cr(hfa)_3$, 800 ± 150 cal, is slightly (but not significantly) greater than the value obtained for $Cu(hfa)_2$, 650 ± 170 cal. As in the case of $Cu(hfa)_2$, the reader is cautioned not to attach too much chemical significance to this result since the model itself is only a first approximation to a more realistic model involving an average over a large number of points on the six-dimensional potential energy surface. These more elaborate models were not explored because of the prohibitive amount of computation time required to perform the six-dimensional average over the numerous orientations of the CF_3 groups.

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Supplementary Material Available: Experimental electron diffraction intensity data and correlation and error matrices (9 pages). Ordering information is given on any current masthead page.

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