Crystal and Molecular Structure of Chlorotris(acetylacetonato)zirconium(IV)

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Abstract: The crystal and molecular structure of chlorotris(acetylacetonato)zirconium(IV), $Zr(acac)_3Cl$, has been determined by single-crystal X-ray diffraction by analysis of 1499 independent reflections and has been refined anisotropically by least-squares methods to $R = 0.104$. Intensity data (levels $h0l$–$h10l$ and $0kl$–$3kl$) were collected with Zr-filtered Mo Kα radiation using equiinclination Weissenberg techniques. The compound crystallizes in the orthorhombic space group $Pna2_1$ with four molecules in a unit cell of dimensions $a = 15.552$ (5), $b = 8.303$ (2), and $c = 14.343$ (3) Å ($\rho_{obsd} = 1.522$ (5) g/cm^3; $\rho_{calcd} = 1.520$ g/cm^3). The molecule is monomeric with the chlorine and six acetylacetonate oxygen atoms bound to the Zr(IV) atom at the corners of a distorted pentagonal bipyramid. The chlorine atom occupies one axial position (Zr–Cl = 2.472 (6) Å), acetylacetonate ligand a spans the other axial position and one equatorial position, and acetylacetonate ligands b and c take the remaining equatorial positions. The axial Zr–O bond is ~0.06 Å shorter than the average length (2.14 Å) for the five, quite uniform, equatorial bonds. Because of extremely close O···O contacts in the equatorial plane, the pentagonal girdle of oxygen atoms is appreciably puckered. The observed distortions from ideal pentagonal-bipyramidal geometry are considered in relation to preferred eight-coordination geometries, but are attributed instead to steric effects.

Previous papers from this laboratory have described the preparation and properties of halotris(acetylacetonato) complexes of zirconium(IV) and hafnium(IV), $M(acac)_3X$ (M = Zr, X = Cl, Br, or I; M = Hf, X = Cl or Br).[2,3] Molecular weight, conductance, and infrared data indicate that these compounds are monomeric and seven-coordinate. Like most other high-coordination-number metal β-diketonates, the $M(acac)_3X$ complexes are nonrigid in solution, and attempts to obtain stereochemical information from low-temperature nmr spectra have been unsuccessful.[4,5] Consequently, a single-crystal X-ray study of a representative complex of this type, $Zr(acac)_3Cl$, was undertaken in order to confirm the seven-coordinate structure and elucidate the geometry of the coordination polyhedron.

Experimental Section

Suitable crystals of $Zr(acac)_3Cl$, prepared by the method of Pinnavaia and Fay,[2] were obtained by recrystallization from dry benzene–hexane. Under a dry nitrogen atmosphere, the moisture-sensitive crystals were mounted in 0.5-mm capillary tubes using a small amount of Apiezon N stopcock grease as an adhesive. The tubes were then sealed. Crystals mounted in this fashion displayed no visible signs of decomposition due to hydrolysis.

Preliminary examination of the crystals by precession and Weissenberg techniques established the space group to be either $Pnma$ or $Pna2_1$. The noncentrosymmetric space group[8] $Pna2_1$ was chosen on the basis of a positive text for piezoelectricity (using a Giebe-Scheibe detector designed by H. Diamant). The following lattice parameters of the orthorhombic unit cell were determined by least-squares refinement[9] of the diffraction geometry of 66 reflections measured using a Picker FACS-I four-circle diffractometer with Zr-filtered Mo Kα radiation(λ 0.71069 Å): $a = 15.552$ (5), $b = 8.303$ (2), and $c = 14.343$ (3) Å. A cell content of 4 $Zr(acac)_3Cl$ gave good agreement between the calculated density, 1.520 g/cm^3, and the experimental density, 1.522 (5) g/cm^3, determined by flotation in a carbon tetrachloride–hexane mixture.

Intensity data were collected with Zr-filtered Mo Kα radiation (Picker generator, Model 6147D, 50 kV, 22 mA) using the multiple-film, multiple-exposure equiinclination Weissenberg technique for levels $h0l$–$h10l$ and $0kl$–$3kl$; two wedge-shaped crystals having approximate dimensions 0.4 × 0.3 × 0.2 mm were employed. Relative intensities of the reflections were estimated visually by comparison with a calibration strip prepared by incremented ($I_{n+1} = 1.15I_n$) exposure of the (404) reflection. Visible reflections with an intensity less than the weakest calibration spot were assigned an intensity equal to one-half the intensity of that spot; unobserved reflections were not used.

Intralayer scaling, Lorentz–polarization corrections, and interlayer scaling were done using a least-squares technique described by Hamilton, *et al.*[10] The average scatter in the individual intensities measured for each of the 1499 unique reflections was 13.4%. No correction was made for spot contraction in upper layer Weissenberg films, and no absorption correction was applied. The linear absorption coefficient for Mo Kα radiation is 7.5 cm^{-1} for $Zr(acac)_3Cl$, which could give a maximum error from neglect of absorption corrections of <12% in any intensity or <6% in any amplitude for the crystals used. It was felt that absorption corrections would not significantly improve the reliability of the data.

The structure was determined by the heavy-atom technique using Patterson synthesis of the $|F_o|^2$ data followed by Fourier synthesis of the structure amplitudes phased by the zirconium coordinates. Initial analysis revealed atomic positions which corresponded to the approximate coordination geometry of a monocapped trigonal prism. However, subsequent refinement of this structure did not give a value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ lower than 0.27, and several interatomic distances appeared to be chemically unreasonable. Further inspection of the Fourier synthesis and least-squares re-

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(1) Procter and Gamble Fellow, 1969–1970.

(2) T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, 7, 502 (1968).

(3) R. C. Fay and T. J. Pinnavaia, *ibid.*, 7, 508 (1968).

(4) For other examples of high-coordination-number metal β-diketonates which undergo rapid stereochemical rearrangements, see (a) A. C. Adams and E. M. Larsen, *ibid.*, **5**, 228 (1966); (b) T. J. Pinnavaia and R. C. Fay, *ibid.*, **5**, 233 (1966); (c) F. A. Cotton, P. Legzdins, and S. J. Lippard, *J. Chem. Phys.*, **45**, 3461 (1966).

(5) Note, however, that π-cyclopentadienyl-containing metal β-diketonates exhibit a remarkable degree of stereochemical rigidity. Nonequivalent $-CH_3$ and $-CF_3$ environments have been observed for $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$[6] and $(\pi\text{-}C_5H_5)Zr(hfac)_3$[7] (hfac = $CF_3COCHCOCF_3^-$).

(6) T. J. Pinnavaia, J. J. Howe, and E. D. Butler, *J. Amer. Chem. Soc.*, **90**, 5288 (1968).

(7) M. Elder, J. G. Evans, and W. A. G. Graham, *ibid.*, **91**, 1245 (1969).

(8) J. A. Ibers, Ed., "International Tables for X-Ray Crystallography," Vol. I, "Symmetry Groups," The Kynoch Press, Birmingham, England, 1967, p 119.

(9) Use was made of the PICK II computer program, a revision of W. C. Hamilton's MODE I program.

(10) W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Crystallogr.*, **18**, 129 (1965). The programs for these calculations were written in this laboratory by D. M. Collins.

finement of the occupancy factor for the chlorine atom and one oxygen atom indicated that the atomic positions of these two atoms should be interchanged. Subsequent Fourier syntheses quickly revealed the rest of the structure, which displayed a geometry based on a distorted pentagonal bipyramid.

For refinement of the structure, the observed amplitudes were assigned weights according to an adaption of the Hughes weighting scheme,[11] where $w = (10/|F_o|)^2$ for $|F_o| \geq 4\,|F_{o,\min}|$ and $w = (10/4\,|F_{o,\min}|)^2$ for $|F_o| < 4\,|F_{o,\min}|$. Full-matrix least squares[12] was employed for refinement of the model having individual isotropic thermal parameters. The scattering factors used for Zr^0, Cl^0, O^0, and C^0 were those calculated by Cromer and Mann,[13] including the real part of the anomalous scattering for Zr and Cl determined by Cromer.[14,15] The value of R obtained upon convergence was 0.130. Finally, refinement of the model with fully anisotropic thermal parameters was effected by full-matrix least squares and gave an R value at convergence of 0.104. A maximum residual electron density of 2.5 electrons/Å^3 near the Zr atomic position and scattered peaks of nearly 1 electron/Å^3, indicated by a difference Fourier synthesis, precluded objective assignment of hydrogen positions.

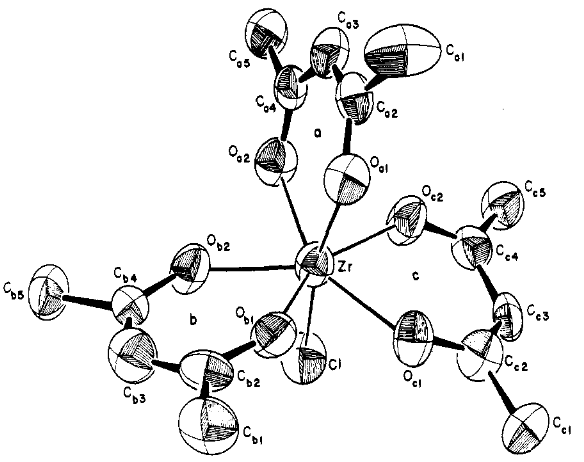

Figure 1. Model in perspective of the $Zr(acac)_3Cl$ molecule.

Results

Final atomic coordinates and thermal parameters for crystalline $Zr(acac)_3Cl$ are presented in Tables I and II, respectively.[17] The molecular geometry and the atom numbering system are shown in Figure 1. Each atom is represented by an ellipsoid consistent with the anisotropic thermal parameters in Table II and is labeled with a literal and a numerical subscript; the literal subscript identifies the particular acetylacetonate ligand (a, b, or c). The characteristic parameters of the coordination polyhedron are given in Table III, and bond lengths and angles within the acetylacetonate ligands are listed in Table IV.

Table I. Atomic Fractional Coordinates for $Zr(acac)_3Cl$[a]

Atom	10^4x	10^4y	10^4z
Zr	2202 (1)	1707 (2)	2500[b]
Cl	1246 (4)	1249 (7)	1149 (4)
O_{a1}	2788 (9)	2148 (15)	3776 (10)
O_{a2}	2472 (10)	−676 (14)	2943 (9)
O_{b1}	3002 (9)	3677 (17)	2065 (10)
O_{b2}	3132 (9)	670 (14)	1591 (11)
O_{c1}	1460 (7)	3873 (15)	2683 (10)
O_{c2}	1110 (8)	881 (16)	3285 (11)
C_{a1}	3206 (20)	2122 (28)	5386 (20)
C_{a2}	2960 (11)	1230 (26)	4498 (15)
C_{a3}	2897 (11)	−390 (25)	4523 (15)
C_{a4}	2661 (10)	−1284 (20)	3741 (13)
C_{a5}	2620 (18)	−3144 (25)	3847 (17)
C_{b1}	3897 (18)	5616 (27)	1381 (20)
C_{b2}	3570 (13)	3938 (21)	1448 (12)
C_{b3}	3943 (12)	2724 (28)	919 (15)
C_{b4}	3701 (13)	1211 (23)	1024 (13)
C_{b5}	4146 (18)	−131 (28)	406 (19)
C_{c1}	341 (17)	5863 (25)	2728 (19)
C_{c2}	666 (13)	4145 (23)	2895 (15)
C_{c3}	71 (11)	3000 (23)	3192 (12)
C_{c4}	348 (14)	1444 (23)	3421 (14)
C_{c5}	−267 (14)	217 (30)	3832 (18)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] z coordinate is arbitrary.

Discussion

Crystalline $Zr(acac)_3Cl$ contains discrete seven-coordinate molecules (Figure 1) in which the chlorine atom and the six acetylacetonate oxygen atoms are bound to the Zr(IV) atom at the corners of a distorted pentagonal bipyramid. The chlorine atom occupies one axial position, acetylacetonate ligand a spans the other axial position and one equatorial position, and acetylacetonate ligands b and c take the remaining equatorial positions. The structure is similar to those of π-cyclopentadienyltris(hexafluoroacetylacetonato)zirconium(IV), $(\pi\text{-}C_5H_5)Zr(hfac)_3$;[18] chlorotris(tropolonato)tin(IV), T_3SnCl;[19] and hydroxotris(tropolonato)tin(IV), T_3SnOH.[19] The maximum possible symmetry for this configuration is C_s-m, with the metal atom, the monodentate ligand, and bidentate ligand a lying in the mirror plane; this symmetry is closely preserved in $(\pi\text{-}C_5H_5)Zr(hfac)_3$, where the coordination polyhedron additionally approximates C_{5v} symmetry, and in the two isostructural T_3SnX complexes (X = Cl or OH). In $Zr(acac)_3Cl$, however, ligand a does not lie in a mirror plane owing to a 28°

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[11] Reference 8, Vol. II, "Mathematical Tables," 1967, p 328.

[12] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962. A revised version of the program was used in this work.

[13] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

[14] D. T. Cromer, *ibid., Sect. A*, **18**, 17 (1965).

[15] In order to identify the hkl and $\overline{hkl}$ reflections for the two crystals used and take account of the imaginary part of the anomalous dispersion for Zr^0 ($\sim$0.7), it would be necessary to carry out several refinements. Previous experience[16] indicates that the R value in this case is likely to be rather insensitive to the imaginary part of the anomalous dispersion, thus leaving ambiguity as to the sign of the reflections; even if the sign could be determined, the effect of the imaginary part on the coordinates is expected to be small. The possible minor improvement in the structure did not appear to justify the cost of additional computation.

[16] J. L. Hoard, unpublished results.

[17] A table of observed and calculated structure amplitudes from the final refinement will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

[18] M. Elder, *Inorg. Chem.*, **8**, 2103 (1969).

[19] J. J. Park, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3636 (1970).

Table II. Thermal Parameters for $\mathrm{Zr(acac)_3Cl}$[a]

Atom	Anisotropic parameters, Å² B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	Equiv isotropic B,[b] Å²
Zr	3.06 (5)	3.64 (5)	4.24 (6)	−0.15 (5)	0.36 (8)	−0.06 (8)	3.60
Cl	4.7 (2)	6.9 (3)	5.6 (2)	0.1 (2)	−0.6 (2)	−1.2 (2)	5.5
O_{a1}	3.7 (5)	4.3 (5)	5.2 (6)	−0.6 (5)	−0.5 (5)	−0.8 (5)	4.2
O_{a2}	4.5 (6)	3.4 (5)	5.6 (7)	−0.1 (5)	0.6 (6)	−0.3 (5)	4.4
O_{b1}	4.6 (7)	4.9 (6)	5.8 (7)	−0.2 (5)	0.6 (6)	1.1 (5)	5.0
O_{b2}	4.3 (6)	3.5 (5)	7.6 (8)	0.2 (5)	1.6 (6)	0.7 (5)	4.7
O_{c1}	3.6 (5)	5.1 (5)	5.9 (8)	−0.3 (4)	0.7 (5)	−1.0 (5)	4.7
O_{c2}	2.9 (6)	4.9 (7)	7.1 (9)	0.6 (5)	1.2 (6)	0.7 (6)	4.5
C_{a1}	8.9 (15)	5.3 (10)	7.4 (14)	−1.6 (10)	3.6 (12)	0.4 (10)	6.4
C_{a2}	3.1 (8)	5.5 (8)	5.1 (9)	−0.6 (6)	1.2 (7)	0.0 (8)	4.2
C_{a3}	3.4 (8)	5.6 (10)	5.6 (10)	0.6 (7)	6.5 (7)	0.2 (8)	4.7
C_{a4}	3.0 (7)	3.9 (6)	4.2 (8)	0.0 (5)	1.4 (6)	−0.1 (6)	3.5
C_{a5}	7.6 (14)	4.8 (9)	5.1 (9)	1.9 (9)	1.2 (10)	0.3 (8)	5.4
C_{b1}	7.4 (14)	5.1 (9)	7.7 (14)	−1.5 (9)	1.7 (11)	1.1 (9)	6.2
C_{b2}	4.8 (10)	4.7 (8)	3.6 (8)	−0.9 (7)	−1.0 (7)	0.4 (7)	4.2
C_{b3}	4.0 (9)	6.3 (11)	5.7 (10)	−1.0 (8)	−0.1 (8)	0.2 (9)	5.2
C_{b4}	4.2 (10)	4.7 (8)	4.5 (9)	1.0 (7)	1.3 (8)	1.4 (7)	4.2
C_{b5}	7.3 (13)	5.6 (10)	7.9 (14)	2.5 (10)	3.1 (12)	0.9 (10)	6.1
C_{c1}	7.4 (13)	4.9 (9)	8.2 (15)	2.6 (9)	0.4 (11)	0.1 (8)	6.2
C_{c2}	4.1 (8)	4.7 (9)	5.8 (10)	0.5 (7)	0.1 (7)	−0.4 (7)	4.8
C_{c3}	3.5 (7)	5.7 (9)	3.4 (7)	0.3 (7)	1.1 (6)	−0.9 (6)	3.8
C_{c4}	4.7 (9)	5.2 (10)	4.3 (8)	0.1 (8)	0.2 (7)	−0.6 (7)	4.7
C_{c5}	4.2 (9)	6.5 (11)	7.8 (14)	0.2 (8)	1.4 (10)	1.2 (10)	5.8

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. The relation between B_{ij} (Å²) and the dimensionless β_{ij} used during refinement is $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Bond Distances, Polyhedral Edge Lengths, and Bond Angles in the Coordination Group[a]

Atoms	Length, Å	Atoms	Angle, deg
Zr–Cl	2.472 (6)	Cl–Zr–O_{a1}	169.0 (4)
Zr–O_{a1}	2.076 (14)		
Zr–O_{a2}	2.120 (12)		
Zr–O_{b1}	2.148 (14)		
Zr–O_{b2}	2.129 (14)		
Zr–O_{c1}	2.152 (12)		
Zr–O_{c2}	2.150 (13)		
Cl–O_{a2}	3.579 (15)	Cl–Zr–O_{a2}	102.1 (4)
Cl–O_{b1}	3.640 (16)	Cl–Zr–O_{b1}	103.8 (4)
Cl–O_{b2}	3.039 (15)	Cl–Zr–O_{b2}	82.3 (4)
Cl–O_{c1}	3.114 (15)	Cl–Zr–O_{c1}	84.4 (4)
Cl–O_{c2}	3.086 (17)	Cl–Zr–O_{c2}	83.5 (4)
O_{a1}–O_{a2}[b]	2.677 (18)	O_{a1}–Zr–O_{a2}	79.3 (5)
O_{a1}–O_{b1}	2.782 (20)	O_{a1}–Zr–O_{b1}	82.4 (5)
O_{a1}–O_{b2}	3.406 (21)	O_{a1}–Zr–O_{b2}	108.2 (5)
O_{a1}–O_{c1}	2.962 (18)	O_{a1}–Zr–O_{c1}	88.9 (5)
O_{a1}–O_{c2}	2.900 (17)	O_{a1}–Zr–O_{c2}	86.6 (5)
O_{a2}–O_{b2}	2.461 (20)	O_{a2}–Zr–O_{b2}	70.8 (5)
O_{a2}–O_{c2}	2.530 (19)	O_{a2}–Zr–O_{c2}	72.7 (5)
O_{b1}–O_{b2}[b]	2.595 (19)	O_{b1}–Zr–O_{b2}	74.7 (5)
O_{b1}–O_{c1}	2.562 (19)	O_{b1}–Zr–O_{c1}	73.2 (5)
O_{c1}–O_{c2}[b]	2.685 (19)	O_{c1}–Zr–O_{c2}	77.2 (5)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] The "bite" of the ligand.

rotation of one of the equatorial ligands (ligand b) about its quasi-twofold axis. The direction and amount of this rotation are such as to locate the atoms Zr, Cl, $\mathrm{O_{a1}}$, and $\mathrm{O_{b2}}$ in a quasi-mirror plane (mean displacement 0.02 Å) with oxygen atoms $\mathrm{O_{b1}}$ and $\mathrm{O_{c1}}$ equivalent to $\mathrm{O_{a2}}$ and $\mathrm{O_{c2}}$, respectively.[20] Thus, the coordination polyhedron maintains approximate C_s-*m* symmetry, but this is achieved in a different manner than in the $\mathrm{T_3SnX}$ complexes. The minor departures from this symmetry that are observed seem to be due primarily to the unsymmetric arrangement of the diketonate ligands.

As already implied, the pentagonal girdle is not flat. The nature of the distortion is more clearly seen in Figure 2, which is a projection of the coordination group onto the quasi-mirror plane (Zr, Cl, $\mathrm{O_{a1}}$, $\mathrm{O_{b2}}$). The mean equatorial plane defined by the zirconium atom and the equatorial oxygen atoms (plane E in

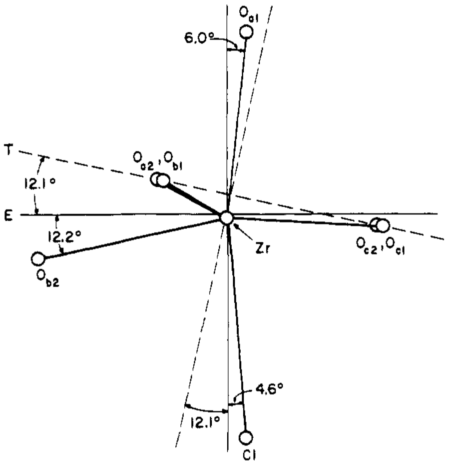

Figure 2. Projection of the coordination group of $\mathrm{Zr(acac)_3Cl}$ on the quasi-mirror plane. The equatorial plane (E) and the quasi-fivefold axis are indicated by solid lines. The trapezoidal plane (T) and its normal which passes through the zirconium atom are indicated by broken lines.

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[20] Mean planes were calculated using the method of V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, 12, 600 (1959).

Table IV. Bond Lengths (Å) and Bond Angles (Deg) in the Acetylacetonate Ligands[a]

Bond	Ligand a	Ligand b	Ligand c	Av[b]	Angle	Ligand a	Ligand b	Ligand c	Av[b]
O_1–O_2	2.677 (18)	2.595 (19)	2.685 (19)	2.65 (5)	O_1–Zr–O_2	79.3 (5)	74.7 (5)	77.2 (5)	77.1 (23)
O_1–C_2	1.31 (2)	1.27 (2)	1.29 (2)	1.29 (1)	Zr–O_1–C_2	133.0 (12)	137.4 (13)	133.4 (11)	134.3 (18)
O_2–C_4	1.29 (2)	1.28 (2)	1.29 (2)		Zr–O_2–C_4	132.7 (11)	135.6 (12)	133.6 (13)	
C_2–C_3	1.35 (3)	1.39 (3)	1.39 (3)	1.37 (3)	O_1–C_2–C_3	125.8 (19)	123.2 (18)	126.0 (17)	125.4 (13)
C_3–C_4	1.39 (3)	1.32 (3)	1.40 (3)		O_2–C_4–C_3	124.6 (16)	127.0 (18)	125.6 (18)	
C_1–C_2	1.52 (3)	1.49 (3)	1.53 (3)	1.53 (3)	O_1–O_2–C_1	115.4 (18)	116.4 (18)	116.2 (18)	115.6 (17)
C_4–C_5	1.55 (3)	1.58 (3)	1.52 (3)		O_2–C_4–C_5	117.9 (16)	114.2 (17)	113.3 (17)	
					C_2–C_3–C_4	121.9 (19)	120.6 (19)	119.8 (17)	120.8 (11)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] The number in parentheses following each averaged value is the standard deviation in a single measurement; the averaging assumes C_2 symmetry for each acetylacetonate ligand.

Figure 2) is perpendicular to the quasi-mirror plane (dihedral angle 90.0°), but the displacements of these atoms from the equatorial plane are appreciable. Displacements are −0.48 (O_{b2}), 0.39 (O_{a2}), 0.38 (O_{b1}), −0.14 (O_{c1}), −0.12 (O_{c2}), and −0.03 Å (Zr). Four of the five equatorial oxygen atoms (O_{a2}, O_{b1}, O_{c1}, O_{c2}) are coplanar (plane T in Figure 2; displacements ≤ 0.002 Å); however, the zirconium atom is displaced −0.26 Å (toward Cl) from this plane. Plane T is perpendicular to the quasi-mirror plane (dihedral angle 90.0°) and makes a dihedral angle of 12.1° with equatorial plane E.

The distortion of the pentagonal girdle is due primarily to extremely close O···O contacts in the equatorial plane. The observed contacts (Table III), which average to 2.57 Å, are 0.11–0.34 Å less than the van der Waals diameter of oxygen (2.80 Å). With the observed Zr–O bond distances (*vide infra*), a perfectly flat pentagonal girdle would require an average O···O contact of 2.52 Å. Moreover, the three inter-ring contacts would have to be less than this by an unreasonable amount since the "bite" of the acetylacetonate ligand, which defines the other two O···O contacts, generally falls in the range 2.7–2.9 Å.[21] In the observed structure the bites of ligands a and c are 2.68 Å and that of ligand b, the ligand which is twisted out of the equatorial plane, is only 2.595 (19) Å. The latter bite is ~0.07 Å shorter than any previously reported for a metal β-diketonate structure and is only ~0.04 Å longer than the hydrogen-bonded O···O contact in the enol form of hexafluoroacetylacetone.[22] This serves to emphasize the extreme crowding in the pentagonal girdle. It is also noted that the shortest inter-ring O···O contact, 2.46 Å, involves the oxygen atom, O_{b2}, which is farthest displaced from the equatorial plane.

Despite the close O...O contacts around the pentagonal girdle, the equatorial Zr–O bond distances are quite uniform and average to the surprisingly short value of 2.140 Å. This is equal to the value which would be estimated from the sum of the covalent radii for Zr(IV) in octahedral *six*-coordination[23] and is nearly 0.1 Å shorter than the average length (2.233 Å) of the equatorial Zr–O bonds in (π-C_5H_5)Zr(hfac)$_3$.[18] The axial metal–oxygen bond, Zr–O_{a1} (2.076 Å), is even shorter than the equatorial bonds (by ~0.06 Å), as is the case for (π-C_5H_5)Zr(hfac)$_3$,[18] T_3SnCl, and T_3SnOH.[19] It is a characteristic feature of pentagonal-bipyramidal geometry that there is less crowding in the region of the axial ligands, and this may be the reason, at least in part, for the shorter bond to the axial oxygen atom; the nonbonded distances between the axial and the equatorial oxygen atoms are all equal to or greater than the van der Waals contact, except that forming the bite of acetylacetonate ligand a. In view of the 2.076-Å Zr–O_{a1} bond length, it would appear that the Zr–O bond in octahedral six-coordination could be appreciably shorter than the value (2.14 Å) estimated from covalent radii. In this connection, it is relevant to observe that the Zr–F bond length in ZrF_6^{2-} (2.04 Å[24]) is 0.08 Å less than the sum of the covalent radii.[23] In addition, we note that both axial and equatorial Zr–O bond distances in Zr(acac)$_3$Cl are appreciably shorter than the average Zr–O bond length in Zr(acac)$_4$, 2.198 Å;[25] this is consistent with the lower coordination number and the higher Zr–O stretching frequencies[3] in Zr(acac)$_3$Cl.

The Zr–Cl bond length is equal to the value calculated from the covalent radii for Zr(IV) in octahedral coordination (2.47 Å[23]), and it is comparable to the Zr–Cl distances in $ZrCl_6^{2-}$ (2.44 Å[26]) and (π-C_5H_5)Zr(acac)$_2$Cl (2.50 Å[27]). Location of the chlorine atom in an axial position does not result in a reduction in the metal–chlorine bond distance as has been noted for T_3SnCl,[19] where the Sn–Cl bond is 0.11 Å shorter than the Zr–Cl bond in this structure. However, it is likely that appreciable shortening of the Zr–Cl bond is prevented by closer Cl···O contacts in Zr(acac)$_3$Cl owing to the greater distortion of the pentagonal girdle; the three significant Cl···O contacts (Table III) are ~0.1 Å shorter than those in T_3SnCl and ~0.1 Å shorter than the sum of the van der Waals radii. The longer and presumably weaker Zr–Cl bond is more reactive than the Sn–Cl bond; for example, unlike T_3SnCl,[28] Zr(acac)$_3$Cl is rapidly hydrolyzed in aqueous media.

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Bond distances and angles within the acetylacetonate ligands (Table IV) are in satisfactorily agreement with the average values compiled by Lingafelter and Braun[21] for β-diketonate structures which have been determined by three-dimensional methods. The seven atoms of each C_5O_2 acetylacetonate skeleton show only minor departures from planarity; displacements from the mean planes are ≤ 0.04 Å (average displacement 0.014 Å), except for carbon atom C_{c3} which lies 0.08 Å below (*cf.* Figure 1) the plane of ligand c. As is often found in β-diketonate structures, the chelate rings are folded along the edges (O···O) of the coordination polyhedron. Rings b and c are folded so as to bring the uncoordinated parts of the ligands closer to the chlorine atom, while ring a is folded in the direction of ring c. The dihedral angles between the ligand planes and the planes defined by the appropriate O–Zr–O group are 12.7, 6.8, and 14.5° for rings a, b, and c, respectively; the corresponding displacements of the zirconium atom from the ligand planes are 0.36, 0.19, and 0.42 Å, respectively. The folding is probably due to crystal packing. Relatively close contacts between the C_{c3}–H group and atoms O_{a1} and C_{a2} of a neighboring molecule may account for the folding of ring c as well as the displacement of carbon atom C_{c3} below the mean plane of the ligand. The bending of ring a toward ring c may result from a close intermolecular methyl–methyl contact of 3.71 Å.

Park, Collins, and Hoard[19] have pointed out that the structures of the T_3SnX complexes are closely related to the structure expected for the eight-coordinate tetrakis(tropolonato)tin(IV); the T_3SnX molecules may be described as *mmmm* dodecahedral stereoisomers[29] in which the monodentate X ligand replaces one tropolonate ligand and is located near the midpoint of an *m* edge. The resemblance to dodecahedral geometry is reinforced by the observed distortions from ideal pentagonal-bipyramidal geometry; these distortions are not expected on steric grounds, since they increase nonbonded repulsions. Park, *et al.*, have noted that neither of the other likely seven-coordination polyhedra (C_{3v} monocapped octahedron or C_{2v} monocapped trigonal prism) bears any marked geometrical resemblance to either of the preferred eight-coordination polyhedra, and this may suggest why the T_3SnX complexes prefer pentagonal-bipyramidal geometry. In view of these results, we have examined the structure of $Zr(acac)_3Cl$ in relation to eight-coordination geometries from which it might be derived. When viewed perpendicular to the mean plane of oxygen atoms O_{a1}, O_{a2}, O_{b1}, and O_{b2}, the gross appearance of the molecule is similar to $Zr(acac)_4$,[25] which exists in the solid state as the square antiprismatic *ssss* stereoisomer.[29] The ligands are attached to the "antiprism" in the same manner in $Zr(acac)_3Cl$ with the chlorine atom replacing one acetylacetonate ligand and lying near the midpoint of one of the *s* edges. Some resemblance between the observed structure and a dodecahedral configuration is also noted; this is suggested[30] by the fact that the quasi-mirror plane (Zr, Cl, O_{a1}, O_{b2}; *cf.* Figure 2) is perpendicular to the trapezoidal plane (T) defined by oxygen atoms O_{a2}, O_{b1}, O_{c1}, and O_{c2}. Neither resemblance, however, is close enough to withstand detailed geometric criteria. The average displacement of oxygen atoms O_{a1}, O_{a2}, O_{b1}, and O_{b2} from the mean plane of the "square face" of the "antiprism" is 0.20 Å,[31] and the "square" edges vary in length by ~0.3 Å. Objections to a dodecahedral description involve the location of the ligands in the quasi-mirror plane. Because the chlorine atom is located at a B site (in the notation of Hoard and Silverton[29]) and oxygen atom O_{a1} is located along an *m* edge, the observed structure does not resemble any of the six theoretically possible stereoisomers for a dodecahedral $Zr(acac)_4$ molecule. In addition, as already noted, the zirconium atom is displaced from the trapezoidal plane by 0.26 Å (*cf.* Figure 2).

Unlike the T_3SnX structures, the distortions of the $Zr(acac)_3Cl$ coordination polyhedron from ideal pentagonal-bipyramidal geometry can be understood in terms of steric effects without reference to the preferred eight-coordination geometries. Rotation of the Zr–O_{a1} and Zr–Cl bonds off the quasi-fivefold axis (*cf.* Figure 2) probably results from close contacts between O_{a1} and O_{b1}, and between Cl and O_{b2}, respectively. Distortion of the pentagonal girdle in $Zr(acac)_3Cl$ is greater than in T_3SnX because of the larger bite of the acetylacetonate ligand. Despite the considerable distortions of the pentagonal bipyramid and despite similarities between the various idealized seven-coordination polyhedra,[32] the ZrO_6Cl polyhedron in this structure bears little resemblance to the monocapped octahedron or the monocapped trigonal prism. Description in terms of the tetragonal base–trigonal base polyhedron discussed by Muetterties and Wright[32] suffers from the nonplanarity of the tetragonal base (O_{a1}, O_{a2}, O_{b1}, O_{b2}). It is not obvious why the pentagonal bipyramid is preferred in this case, but a tentative suggestion may be offered on the basis of the $M(O\frown O)_3X$ structures presently available. When X is a ligand which forms relatively strong, covalent M–X bonds (*e.g.*, X = π-C_5H_5,[18] Cl,[19] or OH[19]), the coordination group appears to prefer pentagonal-bipyramidal geometry with the X ligand in an axial position; this configuration is best suited for minimizing the M–X bond distance while maintaining relatively long X···O contacts. On the other hand, when X is a dipolar ligand which forms a relatively long M–X bond, such as H_2O in $Y(C_6H_5COCHCOCH_3)_3(H_2O)$,[33] $Yb(acac)_3(H_2O)$,[34] or $Ho(C_6H_5COCHCOC_6H_5)_3(H_2O)$,[35] the coordination group seems to prefer the monocapped octahedron or the monocapped trigonal prism.

Finally, we wish to comment on the remarkable difference in stereochemical rigidity exhibited by $Zr(acac)_3Cl$[2] and $(\pi$-$C_5H_5)Zr(hfac)_3$.[7] The cyclopentadienyl complex is considerably more rigid in solution even though its Zr–O bond distances are nearly 0.1 Å longer than those in $Zr(acac)_3Cl$.[36] Therefore, the rigidity of

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[31] This value is closer to that expected for a perfect dodecahedron than that (0.0 Å) for a perfect antiprism.[30]

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[35] A. Zalkin, D. H. Templeton, and D. G. Karraker, *ibid.*, **8**, 2680 (1969).

[36] The long Zr–O bond distances in $(\pi$-$C_5H_5)Zr(hfac)_3$ are probably due, at least in part, to tight contacts (~3.0 Å) between the equatorial oxygens and the carbon atoms of the cyclopentadienyl ring. Since

these molecules seems to be related to the steric bulk of the X ligand rather than the length (and presumably strength) of the Zr–O bonds. If the rearrangements involve Zr–O bond rupture, the maximum in the potential energy surface for (π-C_5H_5)Zr(hfac)$_3$ probably corresponds to a configuration which is reached subsequent to Zr–O bond rupture. Steric effects could also account for the greater rigidity of the cyclopentadienyl complex if the rearrangements involve a twisting mechanism.

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there are ten of these contacts, buckling of the pentagonal girdle is not feasible and approximate C_{5v} symmetry is preserved. In order to maintain reasonable ($\gtrsim$2.5 Å) O···O contacts in the flat pentagonal girdle, long Zr–O bonds are required.