those determined[5] calorimetrically which are listed in the first column.

The agreement between enthalpies from the Hammett substituent constant, E and C correlations, and ν_{OH} are excellent. For the most part those calorimetrically determined are in good agreement. The donor DMF is less well behaved and may result from problems in purification. The frequency shift for the DMF adduct is unreasonable when compared to that of DMA. As previously reported,[28] there are two donor sites in anisole, and this also could be a complicating factor in this system giving rise to a poor ν_{OH}–ΔH correlation.

The many-sided procedures for estimating ΔH on substituted phenol systems should enable one to readily estimate these enthalpies with considerable confidence. The medium effects demonstrated here must be seriously considered when pertinent to carrying out these measurements. If a measured piece of data is not consistent with the correlations presented here, the absence of medium or other complicating effects must be clearly demonstrated before one can conclude that these correlations are inapplicable. The consistency of these predictions with the Hammett substituent model should cause concern for those critics[3–5] of our correlations.

Acknowledgment. The authors acknowledge with thanks the generous support of the National Science Foundation through Grant No. 5498. T. D. E. is grateful to the Paint Research Institute for a fellowship.

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The Crystal Structure of π-Cyclopentadienylbis(acetylacetonato)chlorozirconium(IV)

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Abstract: The crystal structure of π-cyclopentadienylbis(acetylacetonato)chlorozirconium(IV), π-$C_5H_5(C_5H_7O_2)_2$-ZrCl, which crystallizes with the symmetry of the monoclinic space group $P2_1/c$, has been determined by equiinclination Weissenberg single-crystal X-ray diffraction techniques. The theoretical density (1.553 g cm^{-3}) calculated for four molecules per unit cell with the observed lattice parameters ($a = 8.42 \pm 0.01$, $b = 15.66 \pm 0.01$, $c = 15.17 \pm 0.02$ Å, $\beta = 123° 25' \pm 4'$) is in agreement with the measured value (1.556 ± 0.005 g cm^{-3}). The final discrepancy factor, $R = 0.092$, results from a full-matrix least-squares refinement of visually estimated relative intensities for 1453 reflections ($\sin \theta/\lambda \leq 0.54$ Å^{-1}, Cu Kα radiation). The observed dodecahedral stereochemical configuration of the molecule is compatible with π bonding between the cyclopentadienyl ligand and the zirconium atom and also appears to allow d_π–p_π interaction between B oxygen and the zirconium atoms. Intermolecular forces within the lattice, which exhibits distinct layers, appear to be confined to van der Waal's interactions.

The compound π-cyclopentadienylbis(acetylacetonato)chlorozirconium(IV) presents an interesting opportunity to examine the properties of three classes of ligands: a monodentate chlorine, a bidentate acetylacetonato, and a π-bonded cyclopentadienyl ligand. The preparation of the neutral complex was reported by Brainina, *et al.*,[1] who postulated an octahedral molecular configuration, with the possibility of *cis* and *trans* isomerism. The infrared absorption spectrum was cited as support for a π-bonded cyclopentadienyl ligand and was not in conflict with octahedral stereochemistry.

An analogous compound, π-$C_5H_5(C_5H_7O_2)$CrBr, has been prepared by Thomas,[2] who postulated an apparently tetrahedral molecular configuration. In both of these complexes only one stereochemical site has been attributed to the cyclopentadienyl ligand, and the acetylacetonato ligand has been depicted in the keto rather than the enol form even though the latter would allow equivalent metal–oxygen bond formation.

Considerable attention has been devoted to theoretical treatment of bonding between a central metal atom and a π-bonded cyclopentadienyl ligand. In a review of several of these calculations, Wilkinson and Cotton[3] indicate the probable formation of three bonding molecular orbitals between the metal and the ligand. This description of the π-bonding when applied to the above mixed ligand complexes might be expected to result in the stereochemistry of six- and eight-coordination for the chromium and zirconium complexes, respectively.

Several crystallographic investigations of acetylacetonato complexes have been compiled in a review by Lingafelter and Braun.[4] These authors establish the equivalence of the C–O and C–CH bond distances, an observation consistent with the enol configuration of the ligand.

A structure determination of the neutral complex, π-$C_5H_5(C_5H_7O_2)_2$ZrCl, represents an opportunity to examine the stereochemical effects of the three bonding molecular orbitals associated with the cyclopentadienyl ligand and the constraints imposed by the geometry of the acetylacetonato ligands. The four oxygen atoms from the acetylacetonato ligands and the chlorine atom

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(1) E. M. Brainina, R. Kh. Freidlina, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **138**, 1369 (1961).

(2) J. C. Thomas, *Chem. Ind.* (London), 1388 (1956).

(3) G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959).

(4) E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, **88**, 2951 (1966).

represent five unambiguous stereochemical sites for determination of the molecular geometry.

This paper reports the structural solution for π-$C_5H_5(C_5H_7O_2)_2ZrCl$ as obtained from an analysis of three-dimensional single-crystal X-ray diffraction data.

Determination of the Structure. Transparent, air-stable crystals of π-$C_5H_5(C_5H_7O_2)_2ZrCl$, which had been recrystallized in a hexagonal prismatic morphology from dry benzene, were obtained through the courtesy of Dr. T. J. Pinnavaia. Two preferred cleavage planes were observed and were later determined to be nearly parallel to the *yz* and *xz* planes.

The crystals were examined both with polarized light and by precession and equiinclination Weissenberg techniques. A unique oblique optical extinction axis and the X-ray diffraction photographs indicated the monoclinic symmetry of the unit cell. The observed extinctions, (a) $h0l$, $l = 2n + 1$ (rotation both about the *b* axis and normal to the *bc* plane) and (b) $0k0$, $k = 2n + 1$ (rotation about the normal to the *bc* plane), are in unique agreement with the requirements of space group $P2_1/c$.

The lattice parameters together with standard deviation, obtained from rotation (*b* axis) and zero-layer Weissenberg photographs exposed with Cu Kα radiation and calibrated with recrystallized NaCl ($a = 5.6387$ Å) are: $a = 8.42 \pm 0.01$, $b = 15.66 \pm 0.01$, $c = 15.17 \pm 0.02$ Å, and $\beta = 123° \, 25' \pm 4'$. The measured density of the crystal (floatation technique) is 1.556 ± 0.005 g cm^{-3}, and is in agreement with the value calculated with $z = 4$ (1.553 g cm^{-3}).

Intensity data were collected with Ni-filtered Cu radiation on a $0.12 \times 0.03 \times 0.07$ mm crystal using the multiple-film equiinclination Weissenberg technique, for levels $h0l$ through $h8l$ ($\sin \theta/\lambda \leq 0.54$ Å^{-1}). Two 12-hr exposures were made for each layer; the first employed rotation from 0 to 190° and the second from 180 to 370°. 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 (002) reflection. Reflections with an intensity less than the five-cycle calibration spot were judged too weak for comparison and were not recorded.

The structure was determined by the heavy-atom technique with application of full-matrix least-squares and Fourier programs written by A. Zalkin on either a CDC 3600 or 6600 computer. The relative intensities of the 1453 observed reflections were corrected for absorption with a program written by Coppens, *et al.*[5] The corrected intensities varied from 1.47 to 2.81 times the uncorrected values ($\mu = 74$ cm^{-1}, grid size $16 \times 6 \times 10$).

A three-dimensional Patterson map calculated with data which had been corrected for Lorentz–polarization effects revealed approximate Zr and Cl atomic positions, and a subsequent least-squares calculation on these positions produced a discrepancy index, $R = 0.308$. A Fourier series treatment of the data using the phase signs determined by the Zr and Cl atomic positions yielded approximate position parameters for the oxygen and carbon atoms of the acetylacetonato ligands and the carbon atoms of the cyclopentadienyl group. The position parameters of the hydrogen atoms were not determined.

Refinement of the Structure. Refinement of the structure was effected by application of the following parabolic weighting scheme to all recorded reflections

$$W = (A + (|F|^2 - 2B|F| + B^2)/C)^{-1}$$

where $A = 20$, $B = 10$, and $C = 30$. This equation was selected to place maximum weight on reflections having a film density compared most readily with the calibrated standard and to minimize extinction effects by placing relatively little weight on high-intensity data. No zero weighting was employed in the refinement.

A least-squares refinement of the structure computed with the weighted data and the scattering factors for C, O, Cl^- (Berghuis, *et al.*[6]), and Zr^+ (Thomas and Umeda[7]) produced a discrepancy factor, $R = 0.105$. Space group $P2_1/c$ imposes the condition $|F_{\bar{h}kl}| = |F_{hk\bar{l}}|$, and further refinement was effected by averaging the observed intensities of those reflections having the appropriate indices and then using the average intensity (1131 reflections). Subsequent least-squares refinement of the atomic positions and isotropic temperature factors produced $R = 0.092$ with changes in the parameters less than their respective standard deviations. A refinement computed with anisotropic thermal parameters yielded $R = 0.083$. As a consequence of this small change in *R* we decided to effect all subsequent calculations with the isotropic case. An additional least-squares refinement accomplished with C, O, Cl, and Zr atomic scattering factors calculated by Cromer and Waber[8] resulted in $R = 0.094$ and essentially the same parameters as those obtained previously.

Table I. Atomic Coordinates ($\times 10^4$) for π-$C_5H_5(C_5H_7O_2)_2ZrCl$

Atom	Symbol in stereographic projections	*X*	*Y*	*Z*
Zr	Z	437 (2)[a]	1657 (1)[a]	1413(1)[a]
Cl	P	3363 (7)	1006 (4)	1653 (4)
Cyclopentadienyl ligand				
C_1	C	−541 (32)	35 (16)	1192 (17)
C_2	C	−2161 (29)	532 (16)	766 (16)
C_3	C	−424 (30)	842 (17)	2539 (17)
C_4	C	665 (28)	301 (16)	2341 (16)
C_5	C	−2207 (32)	988 (17)	1529 (18)
Acetylacetonato ligands				
O_1	O	−913 (15)	1617 (10)	−244 (8)
O_2	O	−1700 (16)	2662 (9)	954 (9)
C_6	A	−2589 (26)	1920 (14)	−2078 (15)
C_7	A	−2116 (26)	2194 (15)	−989 (15)
C_8	A	−2904 (25)	2879 (14)	−851 (14)
C_9	A	−2692 (26)	3081 (15)	76 (15)
C_{10}	A	−3661 (30)	3891 (17)	172 (17)
O_3	N	1873 (16)	2237 (10)	2931 (9)
O_4	N	1676 (17)	2775 (10)	1190 (10)
C_{11}	B	2549 (31)	4253 (18)	1183 (18)
C_{12}	B	2243 (25)	3497 (16)	1687 (14)
C_{13}	B	2687 (25)	3639 (14)	2694 (15)
C_{14}	B	2499 (25)	3030 (16)	3259 (15)
C_{15}	B	3068 (25)	3170 (15)	4385 (14)

[a] The values given in parentheses are the estimated standard deviations times 10^4.

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(5) P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, **18**, 1035 (1965).

(6) J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).

(7) L H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

(8) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

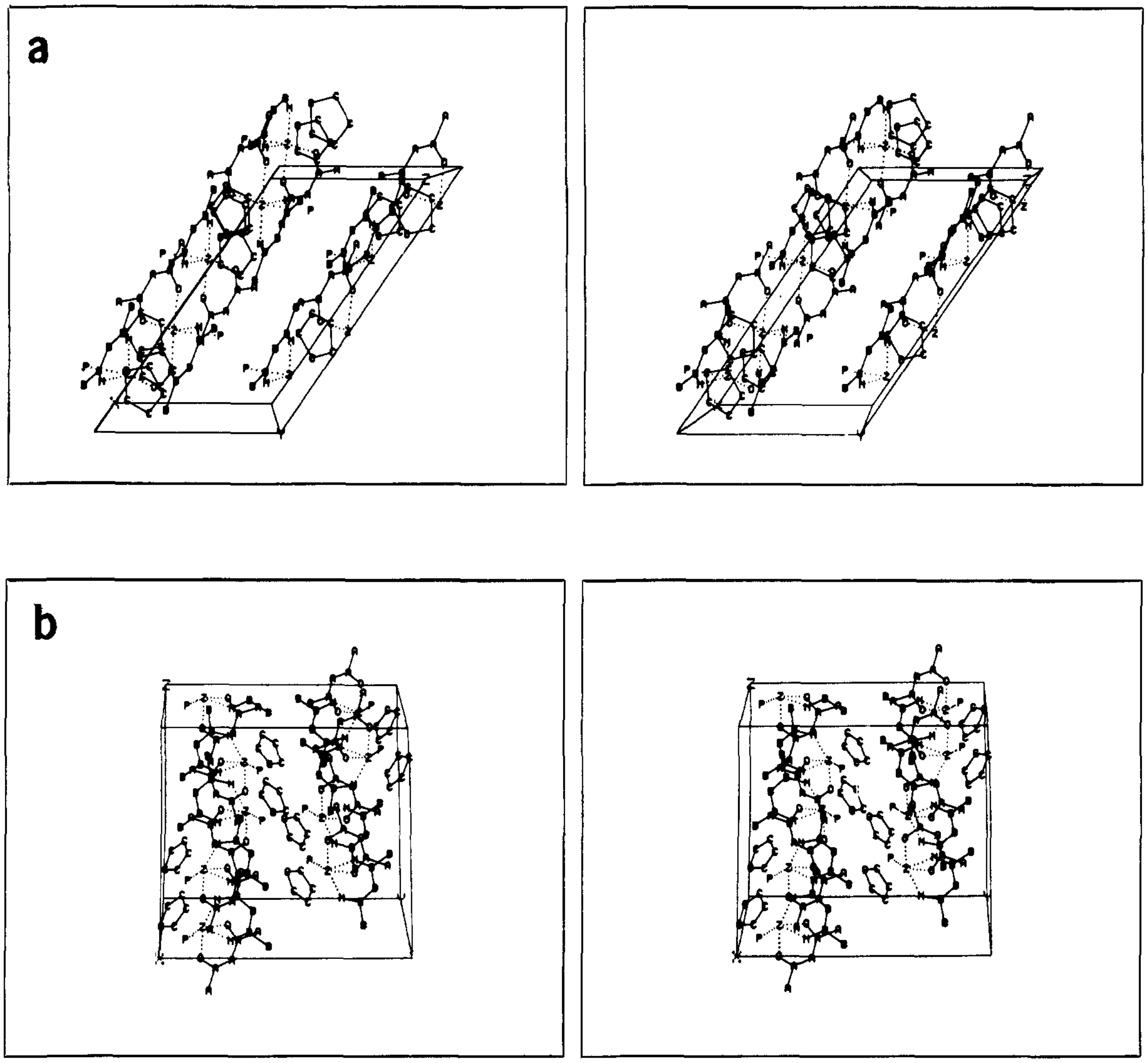

Figure 1. (a) Layer structure nearly parallel to the *yz* plane of the unit cell. (b) Less regular layer structure nearly parallel to the *xz* plane of the unit cell.

A maximum residual electron density of approximately 1.5 e Å^{-3} was indicated by comparison of a difference Fourier series with one calculated by use of F_{obsd} with F_{calcd} signs. As a consequence of this electron density which was located at the Cl and Zr atomic sites, and a large number of approximately 1 e Å^{-3} peaks, assignment of hydrogen positions seemed fortuitous and was not attempted. The position parameters for the Zr, Cl, C, and O atoms and their associated standard deviations are presented in Table I. Distances and angles were calculated from these parameters with a program, DISTAN, written by A. Zalkin; planarity was determined with a least-squares program.[9]

Description of the Structure. The arrangement of the atoms and molecules in the unit cell is displayed in Figure 1. The stereographic projections, obtained through use of a program written by A. C. Larson, may be viewed with a standard stereoscope.[10]

A layer structure, consisting of molecular units arranged nearly parallel to the *yz* plane, a cleavage plane, may be ascertained from Figure 1a. Between planes described by the O–Zr–O segment and the acetylacetonato ligand (standard deviations of ligand plane, $\sigma = \pm 0.05$ Å) is an internal fold through an angle of 15.6 ± 0.3° which draws these ligands closer together and thus favors formation of the distinct molecular layers. This flexibility of an acetylacetonato-metal bond has also been observed in tetrakis(acetylacetonato)zirconium(IV), for which Silverton and Hoard[11] report a mean fold angle of 22.6°. The cleavage plane observed to be very nearly parallel to the *xz* plane is coincident with the less regular layer arrangement which results from the staggered packing of the cyclopentadienyl groups, Figure 1b. Overlap of acetylacetonato ligands with adjacent molecules makes the presence of other cleavage planes unlikely.

The interlayer and intermolecular forces appear to be confined to van der Waal's interactions. The nearest approach between the γ-carbon atom of either acetylacetonato ligand and a chlorine atom in an adjacent layer, the most probable source of hydrogen bonding

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(9) Planarity program adapted from one described in Report No. AD 404653, Defense Documentation Center for Scientific and Technical Information, Cameron Station, Alexandria, Va., pp 21–24.

(10) Two alternative procedures are to (a) view through two low-power magnifying glasses (one for each of the images), and (b) view with a card (held perpendicular to the page) so that each eye sees only one image.

(11) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, **2**, 243 (1963).

Table II. Selected Interatomic Bond Lengths and Angles

Atom 1	Atom(s) 2	Distance, Å	Atom 1	Atom 2	Atom 3	Angle, deg
Cyclopentadienyl Ligand						
C_1	C_2	1.38 (3)[a]	C_5	C_1	C_2	104.3 (2.0)[a]
C_2	C_3	1.39 (3)	C_1	C_2	C_3	112.3 (2.0)
C_3	C_4	1.46 (3)	C_2	C_3	C_4	107.7 (2.0)
C_4	C_5	1.40 (3)	C_3	C_4	C_5	107.0 (1.9)
C_5	C_1	1.51 (3)	C_4	C_5	C_1	108.1 (1.8)
Average		1.43 (5)				107.9 (2.9)
Average Zr–C		2.55 (5)				
Zr–ligand plane		2.24 (2)				
Acetylacetonato Ligands						
Zr	O_1	2.20 (1)	O_1	Zr	O_2	80.4 (0.5)
Zr	O_2	2.11 (1)	C_4	O_1	Zr	129.9 (1.2)
O_1	O_2	2.78 (2)				
O_1	C_4	1.30 (2)	C_2	O_2	Zr	129.3 (1.2)
O_2	C_2	1.36 (2)	O_1	C_4	C_3	126.3 (2.0)
C_3	C_4	1.36 (3)	O_2	C_2	C_3	127.5 (1.7)
C_2	C_3	1.34 (3)	C_4	C_3	C_2	123.8 (1.9)
C_4	C_5	1.56 (3)	C_5	C_4	O_1	113.0 (1.7)
C_1	C_2	1.53 (3)	C_1	C_2	O_2	109.9 (1.7)
Zr	O_4O_3	2.16 (2)	O_3	Zr	O_4	77.8 (0.5)
Zr	O_3O_4	2.13 (1)	C_7	O_3	Zr	132.2 (1.1)
O_3	O_4	2.69 (2)	C_9	O_4	Zr	132.4 (1.2)
O_3	C_7	1.30 (3)	O_3	C_7	C_8	125.0 (2.0)
O_4	C_9	1.33 (3)	O_4	C_9	C_8	125.5 (1.8)
C_7	C_8	1.38 (3)	C_7	C_8	C_9	122.5 (2.1)
C_8	C_9	1.35 (3)	C_6	C_7	O_4	120.1 (1.7)
C_9	C_{10}	1.52 (3)	C_{10}	C_9	O_4	111.8 (1.8)
C_6	C_7	1.51 (3)				
Zr	Cl	2.50 (1)				

[a] The values listed in parentheses are the standard deviations of the last digit(s).

between the *yz* layers, is 3.76 ± 0.03 Å, a value equal to the sum of the van der Waal's radii for a methyl group and a chlorine atom. The molecular arrangement does not appear conducive for hydrogen-bond formation between the *xy* layers. For example, a hydrogen bond between the γ-carbon atom of the B acetylacetonato ligand and the center of the cyclopentadienyl group would require significant displacement of the hydrogen from the ligand plane. The closest approach between the interpenetrating acetylacetonato ligands (3.50 Å) is also indicative of van der Waal's molecular interactions.

Neither the orientation of the cyclopentadienyl ligand nor the intraligand oxygen atom separation appears to be seriously affected by packing considerations since space for planar expansion is apparent (Figure 1b).

Molecular Geometry. The molecular structure of π-$C_5H_5(C_5H_7O_2)_2ZrCl$ (Figure 2) exhibits only C_1 symmetry, and, as Brainina, *et al.*,[1] have indicated, may be described qualitatively as the *cis* configuration of an octahedron. A least-squares plane containing three oxygen atoms (O_1, O_2, and O_3 in Figure 2) and one chlorine atom, the possible four-coordinate plane of the octahedron, has a standard deviation of 0.06 Å. (Standard deviations of atomic positions and lattice parameters were ignored in all planarity calculations.) The two remaining octahedral sites would be occupied by the cyclopentadienyl ligand (C) and the remaining oxygen atom (O_4). The angle of intersection between the least-squares plane containing the cyclopentadienyl ligand (standard deviation 0.03 Å) and the four-coordinate plane is 3.0°. However, a significant deviation for the octahedral geometry occurs for the Zr position, which is 0.45 Å out of the four-coordinate plane.

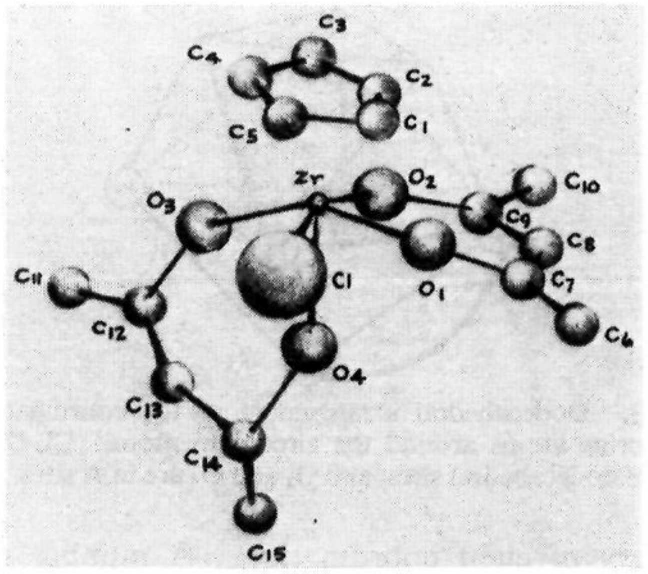

Figure 2. Molecular geometry of π-$C_5H_5(C_5H_7O_2)_2ZrCl$.

Selected interatomic bond distances and angles for the atoms contained within a single molecule are displayed in Table II. The cyclopentadienyl ligand planarity, average C–C bond length, and average bond angle are in agreement with theoretical values calculated for a ring with five equivalent bonds. The long C_1–C_5 bond distance, 1.51 Å, spans the chlorine atom site and probably results from packing effects.

A comparison between the bond lengths and angles determined for the acetylacetonato ligands in this structure and comparable parameters for octahedral transition metal complexes (Table III) is of interest. Although there is general agreement, the OMO bond angle (79.1 ± 1.3°, average deviation) for this complex differs markedly from the mean value for the octahedral complexes (93.2 ± 4.7°). The mean OZrO bond angle for this structure compares more favorably with that reported for the eight-coordinate $Zr(C_5H_7O_2)_4$ (75.0 ± 0.2°), and the Zr–O mean bond length (2.15 ± 0.04 Å) is in reasonable agreement with those reported for $Zr(C_5H_7O_2)_4$ (2.198 ± 0.009 Å) and for the $Zr(C_2O_4)_4{}^{4-}$ complex ion[12] (2.199 ± 0.009 Å). In addition, the intraligand O–C separation (2.73 ± 0.04 Å) falls midway between the mean value reported for tetrakis(acetylacetonato)zirconium(IV) (2.67 Å) and that for the octahedral complexes (2.80 Å).

Table III. Summary of Interatomic Parameters for Some Hexacoordinate Transition Metal[a] Acetylacetonato Complexes

Atom 1	Atom(s) 2	Distance, Å	Atom 1	Atom 2	Group 3	Angle, deg
O	O	2.80 (4)[b]	O	M	O	93.2 (4.7)[b]
C	O	1.27 (2)	M	O	C	125.3 (3.3)
C	CH	1.38 (2)	O	C	CH	125.6 (1.4)
C	CH_3	1.53 (3)	O	C	CH_3	124.4 (2.8)
			C	CH	C	114.0 (1.2)

[a] Metals considered are Mn, Cr, Co, and Fe; adapted from Lingafelter and Braun.[4] [b] The values contained in the parentheses are the standard deviations in the last digit(s) for the averaged values.

Zirconium compounds demonstrate a marked tendency to adopt crystalline arrangements that produce stereochemical configurations which are related to the

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(12) G. L. Glen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **2**, 251 (1963).

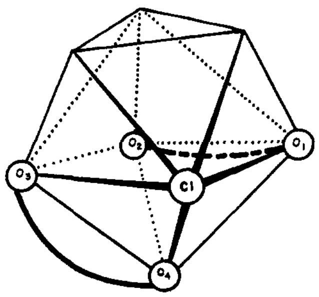

Figure 3. Dodecahedral arrangement of the coordinate oxygen and chlorine atoms around the zirconium atom. Cl, O_1, and O_3 occupy B dodecahedral sites, and O_2 and O_4 are in A sites.

geometry of eight coordination. A number of these compounds have been tabulated by Nyholm and coworkers.[13] For example, the ZrF_4 structure[14] is arranged in a square antiprismatic configuration and the ZrF_6^{2-} ion[15] has been found to crystallize as a chain-like polymer with dodecahedral links, while the $Zr(C_5H_7O_2)_4$ and $Zr(C_2O_4)_4^{4-}$ complexes are examples of discrete square antiprismatic and dodecahedral arrangements, respectively.

The π-$C_5H_5(C_5H_7O_2)_2ZrCl$ molecule may be described in terms of the stereochemistry of eight-coordination and can be shown to approximate dodecahedral geometry more closely than octahedral geometry. The dodecahedral polyhedron contains two sets of symmetry related positions which may be designated as the A and B sites in the manner of Hoard and Silverton.[16] This configuration may be constructed for the mixed ligand molecule by placing the chlorine atom and one oxygen atom from each acetylacetonato ligand in B positions and the remaining oxygen atoms in A positions (Figure 3). The observed oxygen–chlorine plane consists of an A and three B sites, and centering the zirconium atom on the S_4 axis of an ideal dodecahedron results in its displacement above this plane in the manner observed.

Dodecahedral molecular geometry is generally characterized by two sets of angles, θ_A and θ_B, and the ratio of the bond lengths. Appropriate parameters for this molecule are $\theta_A = 37.8°$ (no meaningful deviation, only one measurement), $\theta_B = 77.8 \pm 0.3°$, and Zr–O_A:Zr–O_B = 1.03 ± 0.02. Similar parameters have been calculated by Hoard and Silverton[16] for both the ideal D_{2d}-$\bar{4}2m$ ($\theta_A = 35.2°$, $\theta_B = 73.5°$, M–A:M–B = 1.03) and the hard sphere ($\theta_A = 36.9°$, $\theta_B = 69.5°$, M–A:M–B = 1.00) models. Additional characterization of a dodecahedron is obtained from a comparison of the four symmetry-related edge lengths or, more appropriately, their ratios. The values for this structure ($m/a = 1.03$, $g/a = 1.05$, and $b/a = 1.25$) may be compared with the analogous ratios for both the D_{2d}-$\bar{4}2m$ ($m/a = 1.00$, $g/a = 1.06$, and $b/a = 1.27$) and the hard sphere ($m/a = g/a = 1.00$, and $b/a = 1.25$) models. The large m/a ratio found in this work arises from the larger size of the chlorine atom which occupies one of the sites determining the only unambiguous m edge.

The possibility of d_π–p_π interaction between the oxygen atoms located at the B sites and a central metal atom has been discussed by Hoard and coworkers,[16–18] who indicate that zirconium(IV) has a favorable electronic configuration for such bonding. The mean bond ratio, Zr–O_A:Zr–O_B = 1.03, reported for the oxalato complex[16] is identical with that obtained in this solution. The contribution of the d_π–p_π interaction to the bond stability of the Zr–O_B bond is probably minor since the fold observed for the acetylacetonato-metal bond would be expected to decrease the effective overlap of these orbitals.

To check further the dodecahedral molecular configuration hypothesis, we made a series of calculations based on the θ_A and θ_B angles of the D_{2d}-$\bar{4}2m$ dodecahedron and the mean observed Zr–O bond distance (2.15 Å). The coordinates of three B and four A positions were generated by defining the z axis coincident with the S_4 axis of the dodecahedron and by assigning the first A and B sites to the xz and yz planes, respectively, and operating on them with the S_4 symmetry operations. The remaining site was determined by extending the fourth B site, generated from the above operations, to a length of 2.50 Å (the Zr–Cl bond length). Calculations based on this model produced a four-coordinate least-squares plane (one A and three B sites, $\sigma = \pm 0.04$ Å), which is comparable to the oxygen–chlorine plane of the observed molecule ($\sigma = \pm 0.06$ Å) and indicated that the origin (zirconium) was 0.64 Å from this plane. Similar calculations on three of the remaining dodecahedral sites, which may be assigned to the cyclopentadienyl ligand, established a 5.4° angle of intersection between the two planes (observed angle, 3°). The agreement between the observed structure and this model is considered reasonably good since distortion due to both repulsion and packing effects was not considered. It must be emphasized that use of the three coordination sites for the cyclopentadienyl ligand in no way implies their occupation by specific carbon atoms, but only correlates the effect of the three molecular bonding orbitals with the molecular geometry of the complex. These calculations can predict only the nearly parallel nature of the two planes; three σ bonds would require a ligand plane to metal distance of about 1.56 Å, but a distance is 2.24 Å is observed.

The molecular geometry of the complex appears to display the effect of the three bonding molecular orbitals formed between the central metal atom and the cyclopentadienyl ligand by assuming the stereochemistry of eight- rather than six-coordination. This molecular configuration presents some interesting possibilities for stereoisomerism[19] and indicates a probable octahedral configuration for the π-$C_5H_5(C_5H_7O_2)CrBr$ complex.

Acknowledgment. The assistance of K. Knox (Case-Western Reserve University) and A. Tulinsky (Michigan State University) is acknowledged. Financial assistance through a Du Pont Fellowship (J. J. S.) and from the U. S. Atomic Energy Commission (COO-716-043) is also acknowledged. Appreciation for the donation of computer programs is extended to Dr. A. Zalkin, Dr. P. Coppens, and Dr. A. C. Larson.

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