For multidentate chelates in which the complexing species makes actual use of three or more "teeth" the constraints imposed on multiple ring formation are very likely to determine the selection of the most stable stereoisomer. Certainly this appears to be the case whenever three rings branch from a single nitrogen atom, *e.g.*, the ethylenediaminetetraacetato(EDTA), nitrilotriacetato(NTA), and related complexes.[38] An uncompleted X-ray study (E. Willstadter, J. V. Silverton, and J. L. Hoard) utilizing three-dimensional data gives a qualitatively certain identification of configuration for the bisnitrilotriacetatozirconate(IV) ion in the rubidium salt. Three glycinate rings branching from a nitrogen atom at a vertex A (Fig. 1) span the edges *a*, *m*, and (one) *g* which meet at A; a twofold axis (which is also the maximum symmetry of the isolated ion) then generates the other half of the *quasi*-dodecahedral complex.

The positions of the six directly complexed atoms in the EDTA framework of the seven-coördinate[39] $[Fe(OH_2)EDTA]^-$ ion are describable in terms of Fig. 1: namely, two nitrogen atoms at adjacent vertices A, four oxygens at B. Placement of water molecules in the remaining pair of vertices A (rather than, as in the Fe(III) complex, one water molecule halfway between) would complete dodecahedral eight-coördination with retention of a twofold axis. We regard this as a highly plausible configuration for the anionic forms of discrete EDTA complexes in which the M–O bond distance is greater than about 2.15 Å. It is, indeed, the straightforward extrapolation from an octahedral sexadentate complex in which the central atom has swelled until the arms, although reaching as far as they can, leave two obvious holes to be filled by water molecules. Nearly tetrahedral bond angles are preserved at nitrogen, a condition which would appear difficult for an antiprismatic arrangement to meet. Rather more competition is to be expected from sexadentate seven-coördinate configurations, either that of $[Fe(OH_2)EDTA]^-$ or that described[40] for $[Mn(OH_2)HEDTA]^-$.

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[38] *Cf.*, J. L. Hoard, G. S. Smith, and M. Lind in "Advances in the Chemistry of Coördination Compounds," the Macmillan Co., New York, N. Y., 1961, reprints of which are available.

[39] J. L. Hoard, M. Lind, and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 2770 (1961).

[40] J. L. Hoard, B. Pedersen, S. Richards, and J. V. Silverton, *ibid.*, **83**, 3533 (1961).

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Stereochemistry of Discrete Eight-Coördination. II. The Crystal and Molecular Structure of Zirconium(IV) Acetylacetonate[1]

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Three-dimensional $\{hkl\}$ X-ray data measured for $0 < (\sin \theta)/\lambda < 0.76$ from monoclinic crystals of zirconium(IV) tetrakisacetylacetonate lead to definitive structure determination. The *quasi*-symmetry of the square antiprismatic coördination group, as also of the complete molecule, is very nearly D_2-222, the maximum for the stereoisomeric type (*ssss* in the symbolism of the preceding paper (HS)). Deviations from D_2 symmetry having probable significance are limited to the weakest links—the complexing Zr–O bonds; the dimensional integrity of the rings, extending to virtual equivalence of chemically similar bonds, is remarkably maintained in all other respects. The bond data (Table II and Fig. 2) compare favorably with a composite of the more accurate results reported by others for simpler materials. The observed lengthening, on the average, of lateral edges relative to those of square faces in the coördination group is in accord with the *a priori* analysis of HS; a significant further distortion, taken in accord with D_2, is wholly in the direction of the dodecahedral stereoisomer *mmmm* of HS.

Introduction

This paper reports a definitive structural study of zirconium(IV) tetrakisacetylacetonate, achieved through analysis of extensive three-dimensional X-ray diffraction data provided by a single crystal. We have chosen this compound for detailed study because zirconium is easily the "lightest" of the "heavy" M(IV) elements commonly forming tetrakisacetylacetonates. The pertinence to our work of the rather inconclusive structural results reported for thorium(IV) tetrakisacetylacetonate[2] and cerium(IV) tetrakisdibenzoyl methane[3] is discussed in the more general context of the first paper[4] (HS) in this series.

Experimental

The zirconium acetylacetonate used in our study was obtained through the kindness of Dr. W. C. Fernelius. As insurance against the possible need to employ the method of isomorphous

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[1] Supported in part by the U. S. Army Research Office (Durham), the National Science Foundation, and the Advanced Research Projects Agency. We thank also the Staff of the Cornell Computing Center, Mr. R. C. Lesser, Director.

[2] (a) D. Grdenić and B. Matković, *Nature*, **182**, 465 (1958); (b) *Acta Cryst.*, **12**, 817 (1959).

[3] L. Wolf and H. Bärnighausen, *ibid.*, **13**, 778 (1960).

[4] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

replacement[5] for structure determination, we prepared also the isomorphous hafnium compound. Crystals of either material, when left open to the atmosphere, decompose gradually in a process which may involve polymerization: originally clear toluene-soluble crystals become yellowish, insoluble, and amorphous. Consequently, our X-ray data were collected as speedily as possible from specimens effectively protected by thin coatings of glyptal.

Unit cell data were obtained from Weissenberg and precession photographs using CuKα radiation, and subsequently were checked on the G.E. spectrometer using MoKα radiation. The monoclinic unit cell of zirconium acetylacetonate contains four molecules and has $a = 19.86 \pm 0.02$, $b = 8.38 \pm 0.01$, $c = 14.14 \pm 0.02$ Å., $\beta = 102°50' \pm 10'$. Calculated and measured[6] densities are, respectively, 1.41 ± 0.01 and 1.415 g./cc. The space group I2/c is supported by the regular vanishings, the absence of detectable piezoelectricity, and all subsequent developments attending the successful determination of structure. Within the cited accuracy of measurement, the unit cells of the acetylacetonates of zirconium and hafnium are isodimensional.

Although a (for the most part) qualitatively correct structure for zirconium acetylacetonate was laboriously derived during 1958–1959 from photographically recorded zonal data, the structural results reported herein are based on spectrometrically measured {*hkl*} intensity data. A General Electric spectrometer assembly, including a goniostat[7] (single crystal orienter) with eucentric head, scintillation counter, and SPG-2 detector unit is utilized for counter measurement of intensities. The procedural details set forth below apply also to five other completed studies which are shortly to be reported in full.

We commonly sacrifice some part of the accuracy theoretically attainable in order that the thousands of independent reflections afforded by complex crystals of special chemical interest can be recorded at a practicable rate. Each intensity measurement employs a fixed crystal setting[7,8] in a convergent beam with take-off angle of 5–7° from the X-ray target. Filtered MoKα radiation is used along with specimens small enough to satisfy, for the given profile of the X-ray source, the requirements of the stationary crystal technique, and to keep the absolute correction for absorption along any path below 15–20%. For the coördination compounds of current interest the mean diameter of a specimen generally is 0.2–0.3 mm. Variations in the absorption correction with shape usually are ignored, even when the specimen departs significantly from the ideal spherical form. The largest diameter of our best specimen of zirconium acetylacetonate was about 70% greater than the mean diameter taken in the perpendicular plane. The linear absorption coefficient, however, is but 5.8 cm.$^{-1}$ for MoKα radiation.

We wish, on the other hand, to use a specimen large enough that all reflections of non-trivial unitary structure factor having $2\theta \gtrsim 55°$ (the MoKα equivalent of the CuKα limiting sphere) can be recorded with intensities well above background, *i.e.*, to record the basic data under conditions which permit rapid measurement with an accuracy better than 10% on the average. Achievement of this objective for specimen sizes within the range noted is more or less successful as permitted by thermal motions within the crystal. For actual specimens of comparable volume, the practicable range of intensity measurement for the salt, $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$, of the accompanying paper[9] was $2\theta < 85°$, whereas for the molecular crystal, zirconium acetylacetonate, it was barely $2\theta < 65°$. Subsequent structure analysis fully justifies the expectation that the basic CuKα sphere data are a good deal more accurate for the salt.

Following preliminary photographic study, the specimen crystal is aligned on the goniostat by procedures derived from those of Furnas.[10] A program for the Burroughs 220 computer calculates goniostat settings for all {*hkl*} within the desired range and punches them on cards, one for each {*hkl*}. The cards are ordered for convenience in the collection of data and then are printed out. The measured intensities are punched onto the original cards, which then serve as input, after sorting, for a program applying Lorentz and polarization corrections, and a scaling factor to give $|F^2|$ and $|F|$ data suitable for analysis.

We find that throughout the range $0 < 2\theta < 85°$ in which we have utilized the stationary crystal technique for intensity measurement, a computed goniostat setting based upon the weighted mean wave length of the MoKα doublet corresponds satisfactorily to the central portion of the plateau obtained on scanning. The role of spectral dispersion in modifying the intensity from a stationary crystal, and the critical dependence of the correction for this dispersion upon the effective angular breadth of the X-ray source, have been emphasized by Alexander and Smith.[11] Our experimental set-up with a crystal specimen 0.25 mm. in diameter gives so large a source breadth that the maximum correction at $2\theta = 85°$ to a measured intensity is only about 16%. Dispersion corrections to the zirconium acetylacetonate data, reaching a maximum of 5% at $2\theta = 65°$, have been disregarded.

Our procedures for estimating background corrections to the recorded intensities are illustrated for two limiting conditions of measurement: (1) thermal motions within the crystal are so large that reflections of measurable (net) intensity are confined within the CuKα (or smaller) limiting sphere, (2) thermal motions are small enough that most reflections within the CuKα sphere are well above background and many other reflections beyond the CuKα limit are definitely recordable. In the first case the background is taken as the mean of readings from opposite sides of the peak far enough away (1–2°) to ensure that the intensity has leveled off. In the second case we usually have employed a simplified and more rapid procedure for reflections having $2\theta > 20°$. During the course of rather disappointing attempts to construct balanced filters which would command confidence equally for small and large scattering angles, we noted that our specimen crystal gave a general background which did not vary appreciably with the angle ϕ,[10] was somewhat dependent upon χ[10] but was a function primarily of Bragg angle (almost completely so for $\theta < 15°$). We proceeded to map out fairly elaborate background contours and to use the resulting charts for making corrections. Central lattice rows having short spacings still need detailed attention and the whole procedure is impracticable unless the specimen is well positioned on the axis of the supporting fiber. We have extended the range of intensity measurement significantly above $2\theta = 65°$ for two crystalline materials, with benefit to the subsequent structure determinations. Our current practice, however, is to restrict intensity measurement to $2\theta < 65°$ while giving more attention to the evaluation of background corrections.

Determination and Refinement of Structure

The procedures used to determine structure for zirconium acetylacetonate were atypical in terms of our subsequent practice. The {*hkl*} intensity data became available at a time when, although lacking a basic program for three-dimensional Fourier synthesis on the newly installed Burroughs 220 computer, we did have the Eichhorn program for differential Fourier refinement[12] to use on the approximate structure derived from the earlier zonal analysis. The approximate

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[5] J. M. Robertson, "Organic Crystals and Molecules," Cornell University Press, Ithaca, N. Y., 1953.

[6] G. von Hevesy and M. Lögstrup, *Ber.*, **59B**, 1890 (1926).

[7] T. C. Furnas, Jr., and D. Harker, *Rev. Sci. Instr.*, **26**, 449 (1955).

[8] W. Cochran, *Acta Cryst.*, **3**, 268 (1950).

[9] G. L. Glen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **2**, 250 (1963).

[10] T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric X-Ray Department, Milwaukee, Wis., 1956.

[11] L. E. Alexander and G. S. Smith, *Acta Cryst.*, **15**, 983 (1962); *ibid.*, **13**, 992 (1960).

[12] *Cf.*, H. Lipson and W. Cochran, "The Determination of Crystal Structures. The Crystalline State," Vol. III, G. Bell and Sons, Ltd., London, 1953.

structure correctly placed zirconium atoms on twofold axes and all other atoms in general positions[13] of I2/c, thus classifying the four rings of a molecule into two structurally non-equivalent sets each containing a structurally equivalent pair. The originally assigned positions of several peripheral atoms were far from their true values, corresponding, indeed, to quite variable lengths for C–O and for C–C bonds within the rings. Although each ponderous cycle of differential Fourier refinement gave only a fraction of the needed movements, the trend was uniformly toward equalization of bond lengths for bonds of the same chemical type. Following sixteen cycles of refinement, of which the last two (requiring 10 hr. for a cycle) included all of the 4400 forms for $2\theta < 65°$, the structure determination had attained a nearly final state characterized as described below.

Positions of oxygen atoms and, to be sure, of zirconium had become stable, and the four structurally non-equivalent C–O bond distances showed mean deviation from the average of slightly less than 0.01 Å. Carbon positions, particularly those on the periphery of the molecule, had continued to move at ever decreasing rates toward equalization of C–C bond lengths within the ring at about 1.40 Å. and out from the ring at about 1.52 Å. The refinement process had lost nearly all impetus toward further change, presumably because the influence of the lightly scattering carbon atoms, especially the methyl carbons, was further compromised by the large thermal motions of these atoms; it is notable, however, that renewed impetus had been provided in the last two cycles by putting in the numerous, but mostly weak or unobserved, reflections from the shell, $55° < 2\theta < 65°$. ("Unobserved" reflections each were assigned an intensity count, prior to reduction to amplitudes, of half the minimum observable.) Both positional coördinates and anisotropic thermal parameters were very near their final values, but neither we nor the Computing Center felt that further 10-hr. computing cycles were in order. The value of $R = \Sigma||F_0| - |F_c||/\Sigma|F|_0$, with all 4400 observed and unobserved $\{hkl\}$ for $2\theta < 65°$ included in the calculations,[14] was 0.13.

Soon after we had made workable an efficient program for three-dimensional Fourier synthesis, an added cycle of difference synthesis[12] sufficed to demonstrate the virtual equivalence of chemically similar bonds in the ring systems. Because the earlier refinement provided a reliable phase assignment for observed amplitudes, including those of weak reflections, and rippling proved to be very small, good approximations to *quasi*-equivalence of chemically similar bonds were present also in the individual electron density functions,[15] ρ_o and ρ_c. We note further that averaged values of the bond lengths given by the last cycle of differential Fourier refinement are identical, to the appropriate number of significant figures, with those of the final structure.

TABLE I

ATOMIC COÖRDINATES IN ZIRCONIUM(IV) ACETYLACETONATE[a]

Zr in $0y^1/_4$ with $y = -0.06556$, $\sigma_y = 8 \times 10^{-5}$

Atom	10^4x	$10^4\sigma_x$	10^4y	$10^4\sigma_y$	10^4z	$10^4\sigma_z$
O_2	583	3	−2761	8	3197	5
O_3	80	3	1420	7	1580	2
O_4	1051	3	220	7	3082	4
O_5	513	3	−1550	6	1393	3
C_6	1212	5	−3161	9	3314	5
C_7	509	4	1820	9	1073	5
C_8	1743	4	−2075	14	3295	6
C_9	949	4	729	10	752	5
C_{10}	1635	3	− 435	12	3213	5
C_{11}	900	3	− 919	11	883	4
C_{12}	2254	5	699	19	3272	15
C_{13}	1290	4	−2054	12	386	5
C_{14}	1353	8	−4927	15	3507	10
C_{15}	519	6	3542	10	769	8

[a] Following submission with the manuscript for examination by referees, complete amplitude data including the (88) coefficients of the anisotropic thermal parameters have been submitted as Document No. 7391 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and by remitting $3.75 for photoprints or $2.00 for 35-mm. film in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

Table I lists the atomic coördinates together with the associated standard deviations (in fractions of the unit translations) as estimated by Cruickshank's procedure.[12] These latter, for each chemical type of atom, are highly dependent upon the markedly anisotropic Debye–Waller thermal parameters.[12] Averaged values for the thermal parameters of individual atoms range from 2.5 Å.^{2} for zirconium to about 5.0 Å.^{2} for two of the four methyl carbons. The principal axes for describing the thermal motion of zirconium lie along the required twofold axis and the two mutually orthogonal directions in the plane parallel to (001) as indicated in Fig. 1. The directions thus identified are, within the experimental accuracy, the principal axes of the molecule which approximates closely to the point group symmetry, D_2-222. The amplitude of thermal vibration for zirconium is smallest ($B = 1.26$ Å.^{2}) along the longest axis of the molecule (Fig. 1); it is much larger parallel to b (3.02 Å.^{2}) and along the third axis (3.18 Å.^{2}) of the molecule.

The complex thermal motions of the lighter atoms are not describable so concisely, although they do conform to the more obvious requirements of the molecular and packing geometry. Thus, for example, the maximum amplitude of vibration of a methyl carbon is roughly perpendicular to the mean plane of the ring to which the carbon is attached (*cf.* C_{12} in Fig. 1). The peak value of the electron density attained by either of two carbon atoms, C_{12} and C_{14}, is only about 7.0

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(13) "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham, England, 1952, Vol. I, pp. 100–101.

(14) The atomic form factors of J. Berghuis, I. M. Haanapel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, **8**, 478 (1955), were used for light atoms. The form factor used for zirconium was that of L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

(15) Positions of Fourier peaks are evaluated on the Burroughs 220 using a least-squares fitting of a gaussian to 27 points as recommended by D. P. Shoemaker, J. Donahue, V. Schomaker, and R. B. Corey, *J. Am. Chem. Soc.*, **72**, 2328 (1950).

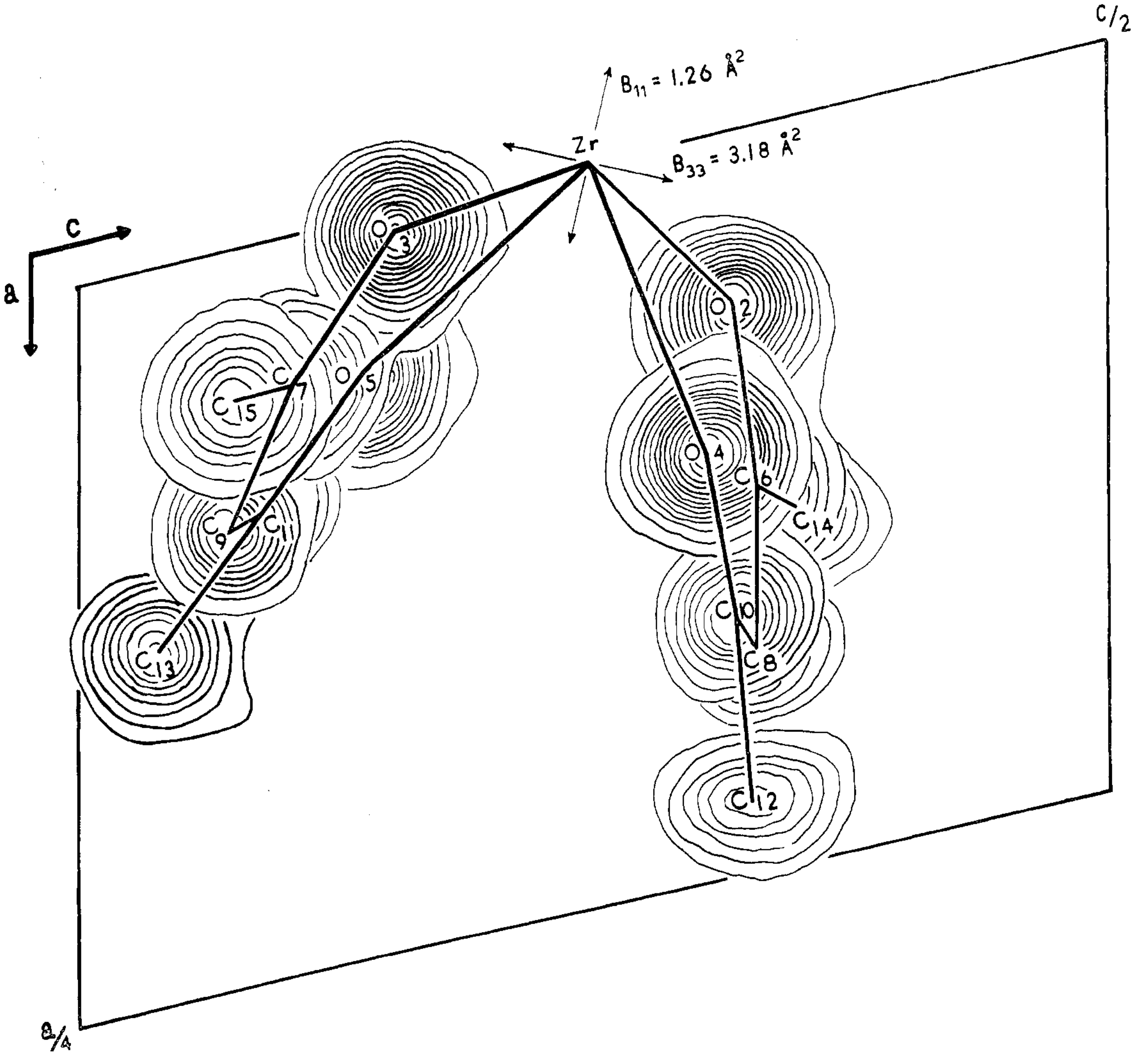

Fig. 1.—Overlay map along the *b*-axis of electron density sections through atomic centers for half a molecule centered at $0y^1/_4$.

electrons/Å.^{3}, less than half the minimum density found for carbon in $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$.[9]

When computed to include every possible reflection within the CuKα sphere, an R of 0.10 is obtained for zirconium acetylacetonate, 0.078 for $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$; the fraction of weak or unobserved reflections is much larger in the first case, the immediate consequence of much larger thermal motions. Whether the form factor used for zirconium is wholly adequate for quantitative computations is not known. Variation of absorption with specimen shape, the contributions of hydrogen to the observed amplitudes, and extinction corrections (which are significant) have been neglected in both determinations.

Discussion of Structure

Three stereoisomers, all optically active, with maximum symmetries (D_4-422, D_2-222, C_2-2) dictated by the various patterns of ring attachment, are possible for a zirconium acetylacetonate molecule having an antiprismatic inner configuration. Although a single twofold axis is all that is required of the molecule in the crystal, the pattern of ring attachment is that which permits of D_2-222 symmetry; a basis for preference of this stereoisomer is discussed in HS.[4] The approximation in the crystal to the higher symmetry is excellent, and, indeed, the approach to dimensional equality of *quasi*-chemically equivalent bond parameters for the most part is so good that we present first the idealized molecular model based upon averaged data; we then discuss individually those instances in which maximum deviations from the mean approach or exceed possible significance. Averaged values, each with the associated mean deviation, maximum deivation, and standard deviation from the mean, are listed for the distances and angles of interest in Table II.

We discuss first the ring systems for which the averaged dimensions of Table II are reproduced also in Fig. 2. Comparison of maximum with standard deviations from the means for bond lengths shows that only for the Zr–O bond is there a possibly significant deviation from the mean in the statistical sense; the individual data are considered later. The internal consistency of the O–C and C–CH bonds is particularly striking. Standard deviations for individual C–CH_3 bonds are rather variable, 0.018–0.025 Å., a reflection of differences in thermal motions for methyl carbons especially. (In Table II, $\sigma = (\Sigma\sigma_i^2/n)^{1/2}$.) Correc-

TABLE II

STEREOCHEMICAL PARAMETERS OF MOLECULE

A. Rings. Averages for Quasi-Chemically Equivalent Parameters

Bond type	Mean length, Å.	Deviations from mean, Å.		
		Av.	Max.	Std. σ
Zr–O	2.198	0.010	0.019	0.009
O–C	1.270	.006	.011	.016
C–CH	1.399	.004	.007	.018
C–CH_3	1.517	.014	.024	.022
Bond angle	**Mean value**	**Deviations from mean**		
		Av.	Max.	Std.
OZrO	74.96°	0.02°	0.02°	0.20°
COZr	133.1°	.7°	1.1°	0.78°
$(OCC)_R$	123.7°	.25°	0.6°	1.05°
$(CCC)_R$	122.5°	.3°	0.3°	1.05°
CCC_M	120.2°	.9°	1.6°	1.1°
OCC_M	116.1°	.8°	1.6°	1.0°

B. Dimensions of Antiprism. Averages for Quasi-Symmetry, D_2-222

Edge type	Mean length, Å.	Deviations from mean, Å.		
		Av.	Max.	Std.
s_r	2.674	0.009	0.009	0.013
s	2.590	.010	.010	.012
l_1	2.689	.002	.002	.017
l_2	2.812	0	0	012
l_3	2.722	.002	.002	.013

tions for libratory motion presumably would give very slightly higher bond distances corresponding to the molecule with only zero-point energy; 1.52 Å., however, is a plausible value for a C–CH_3 bond involving a trigonally hybridized carbon atom.

Deviations from the mean tend to be relatively larger for bond angles than for bond lengths. The difference (if it be taken seriously in this case) merely illustrates the principle that bond angles must yield measurably under a stress much too modest to produce perceptible changes in the associated bond lengths. Inasmuch as all of the closest contacts between molecules in the crystal are between pairs of methyl groups, some variation in bond angles involving CH_3 might be expected. The data also indicate (in a formal way) that the ring $ZrO_3C_7C_9C_{11}O_5$ is slightly more elongated than is the ring $ZrO_2C_6C_8C_{10}O_4$; deviations from the mean within each ring for the angles COZr and $(OCC)_R$ never exceed 0.45°. Detailed calculation shows that the ring skeletons, excluding zirconium, but including methyl carbons, are essentially planar: maximum deviations of atomic centers from the mean planes are 0.02 and 0.03 Å. for the respective ring types. The sum of the interior angles for the averaged ring is 711.1° (mean deviation = 0.7°), short of the 720° required for planarity. Each ring folds about a line joining the two oxygen atoms, *i.e.*, about an edge s_r of an antiprismatic square face; the mean angle of folding is 22.6 ± 0.7°.

The chemical integrity of the bond parameters for the ring systems is maintained—with one exception—to a degree of internal consistency far better than is at all probable in terms of the formally calculated standard deviations. The Zr–O bond lengths involving

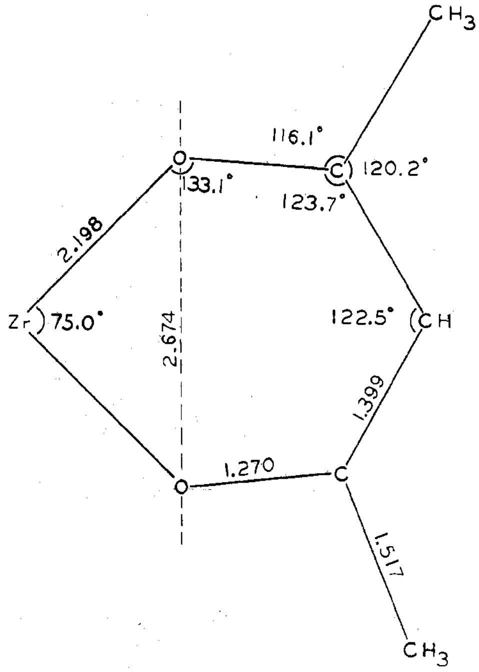

Fig. 2.—Averaged bond parameters for the acetylacetonate rings. Deviations from the average are for the most part trivial (*cf.* Table II and text). The ring is folded through 22.6° about the (dotted) line joining the oxygen atoms, *i.e.*, about a "square" edge of the antiprismatic coördination polyhedron.

O_2, O_3, O_4, and O_5 are, respectively, 2.217, 2.198, 2.194, and 2.181 Å. The maximum spread, 0.036 Å., in these values attains probable significance in the statistical sense and in the light of the remarkably consistent data otherwise characterizing the ring systems. The interpretation is straightforward: packing stresses, either in the crystal or in solution, produce strains which accumulate in the weakest links of the molecule. Inasmuch as OZrO bond angles are even more susceptible to imposed stresses (*vide infra*), the preservation of a constant OZrO bond angle within the rings is attributable mostly to the exigencies of maintaining the ring geometry, with only trivial dependence on the bond-directing capacity of the central atom.

The structure determination of vanadyl bisacetylacetonate,[16] which utilized $\{hkl\}$ data photographically recordable with CuKα radiation, affords ring bond data for comparison with ours. The shorter M–O bonds, 1.97 Å., and the larger O–M–O angle, 88°, in the vanadyl complex do not require as much folding of the ring as in zirconium acetylacetonate. Dodge, *et al.*, give 1.28 Å. for the C–O bond length, 129° and 124° for, respectively, the angles V–O–C and C–C–C in the ring, and values for the remaining ring parameters (including the methyl groups) which, to three significant figures, are identical with ours. (Dodge, *et al.*, present only averaged bond data together with the comment that "... chemically equivalent bond distances are equal to the experimental accuracy.")

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(16) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961). References to earlier, less accurate structural studies of complex acetylacetonates are given.

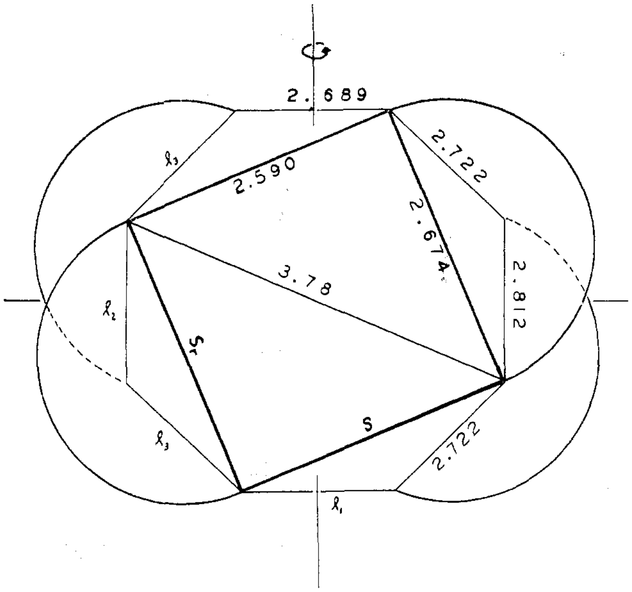

Fig. 3.—Dimensions of the antiprismatic coördination group averaged in accordance with D_2-222 (Table II). Half-circles indicate the pattern of ring attachment.

Further meaningful discussions of ring bond data in β-diketo complexes are given by Bullen,[17] Swallow and Truter,[18] and Truter,[19] who gives C–O = 1.28 Å. and C–CH = 1.40 ± 0.01 Å. as usual values for these bonds. We may expect the C–O bond length to be somewhat dependent upon the strength of the bonding interaction between oxygen and the central atom.

The antiprismatic inner configuration is described quantitatively (Table II and Fig. 3) in terms of averaged dimensions conforming to the *quasi*-symmetry of D_2-222. Maximum deviations from the mean values, never exceeding 0.010 Å., are invariably smaller than the associated standard deviations. The four edges s_r (= 2.674 Å.) are those spanned by acetylacetonate rings, *i.e.*, s_r is the intra-ring O–O separation, and the line about which the ring folding of 22.6° occurs. Two rings which emerge at opposed parallel edges of the upper rectangular face fold away from one another; the other pair of rings are similarly attached through the lower rectangular face. Because the angle between the vertical axial planes of the two pairs of ring systems is only about 45°, the molecule is of unusual, if not to say grotesque, appearance.

That the ring O–Zr–O bond angle of 74.9–75.0° is essentially the value required for an equilateral antiprism appears wholly fortuitous inasmuch as the 12 inter-ring O–Zr–O bond angles (distributed among four classes) range between 72.0 and 80.0°. Minimization of ring constraints, choice of the best packing shape, minimization of ligand repulsions within the inner coördination group—all interdependent and influenced by the angle of ring folding—appear to be the principal factors which determine the distribution in bond angles.

The shortening, on the average, of the four inter-ring "square" edges *s* (Fig. 3) relative to the lateral edges *l* is in agreement with prediction (HS).[4] The observed distribution in lateral edge lengths, in particular, the failure of two edges (2.69 Å.) spanning a twofold axis to show a significant increase over the value (2.67 Å.) for an equilateral antiprism while two edges (2.81 Å.) spanning a *quasi*-twofold axis are unexpectedly long, is not so readily understood. It is a fact, however, that the observed distortions from an antiprism, including foldings about the 3.78 Å. "diagonals" of the "rectangular" faces (the other "diagonal" length is only 3.66 Å.) are wholly in the direction to give, if carried far enough, an $Mo(CN)_8^{-4}$ type of dodecahedron. In this limit the pattern of ring attachment would be the dodecahedral *mmmm* (HS),[4] although ring folding still would limit the molecular symmetry to D_2-222 instead of the higher D_{2d}-$\bar{4}2m$. A presumably excessive increase in ring folding would be required to give the smaller ring span ($\lesssim$2.60 Å.) which, from the standpoint of ligand repulsions, would tend to stabilize the dodecahedral isomer. The observed antiprismatic stereoisomer, moreover, would be stabilized further (but in lesser degree) were a decreased ring span otherwise allowed (HS).[4]

The greater ring span (HS)[4] of the antiprismatic "pinwheel" stereoisomer *llll* (D_4-422) would minimize ring folding. This stereoisomer has superior aesthetic appeal along with a very open skeleton which might give it an unfavorably low density, both internally and for bulk packing. In the observed stereoisomer, on the other hand, the angle between the axis of the d_{z^2} orbital on zirconium and the normal to the plane of the ring skeleton (excluding Zr) is reduced by the ring folding to 20°. Although the reach is very large, interaction of d_{z^2} with the *quasi*-aromatic π-system of the ring may provide some stabilization of configuration.

The significant intermolecular distances are displayed in a diagram (Fig. 4) illustrating the packing of the molecules in crystalline zirconium acetylacetonate. The close intermolecular approaches involve pairs of methyl carbon atoms at 3.60 and 3.69 Å., respectively; other intermolecular separations range upward from 3.91 Å.

In concluding we append some remarks on accuracy having application both to the present study and to subsequent investigations in this series. We have sought to maximize resolving power and minimize rippling by extending the range of Fourier synthesis to include terms of higher frequency than has been usual. The multiplication in the number of Fourier coefficients thus included is attended by a decreasing accuracy of intensity estimation; our procedure assumes, in effect, a favorable balance from the statistics of synthesis. The excellent internal consistency of our bond parameters for the ring systems (with the completely rational exceptions noted), and the very favorable showing of these data when compared with a composite of most accurate results from other (generally simpler)

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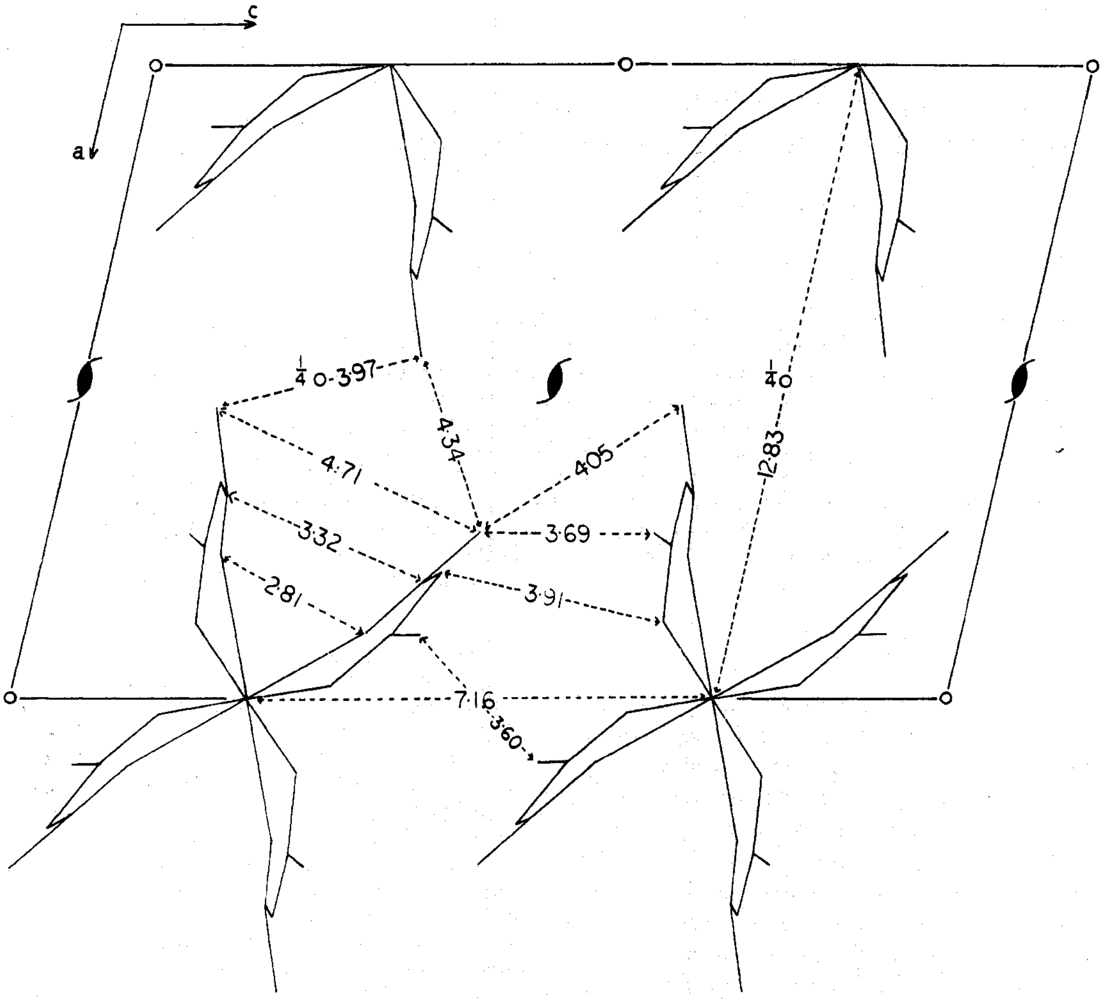

Fig. 4.—Diagram to illustrate the packing of the molecules within the crystal. General positions of I2/c are $\pm(xyz)$, $\pm(\bar{x},y,{}^1/_2 - z)$ $\pm({}^1/_2 - x, {}^1/_2 - y, {}^1/_2 - z)$, $\pm({}^1/_2 + x, {}^1/_2 - y, \bar{z})$. Molecules centered at $0y{}^1/_4$; $0\bar{y}{}^3/_4$; ${}^1/_2, {}^1/_2 - y, {}^1/_4$; ${}^1/_2, {}^1/_2 + y, {}^3/_4$, with $y = -0.0656$, are indicated.

studies, provide support for our procedure, and, at the same time, make the formally calculated standard deviations look unrealistically high. The use of $F_0 - F_c$ as a substitute[20] for the unknown error of measuring $|F_0|$, according to Cruickshank,[20] is likely to overestimate error whenever rippling corrections become trivial through the use of sufficiently extensive data. Employment of $F_0 - F_c$ as a measure of random error implies, moreover, the construction of a model based upon rather more theory and pre-existing data than are needed to determine accurately the structure of a centrosymmetric crystal. We doubt, for instance, that the form factor used for zirconium would meet the quantitative standard thus demanded, although it seems quite satisfactory for phase assignment.

We suggest that standard deviations about two-thirds as large as those tabulated (more like the presently computed probable errors) would give more rational criteria of accuracy for the present study.

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