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Stereochemistry of Eight-Coordinate Mixed-Ligand Complexes of Zirconium. II. Characterization and the Crystal and Molecular Structure of Nitratotris(acetylacetonato)zirconium(IV)[1,2]

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Abstract: The crystal and molecular structure of nitratotris(acetylacetonato)zirconium(IV), $Zr(acac)_3(NO_3)$, has been determined by single-crystal x-ray diffraction and has been refined (anisotropically for Zr, N, O, and C atoms; isotropically for H atoms) by full-matrix least-squares techniques to $R_1 = 0.030$ and $R_2 = 0.032$ using 5110 independent diffractometer-recorded reflections having $2\theta_{\mathrm{Mo}K\bar{\alpha}} < 71°$ and $I > 3\sigma(I)$. The compound crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions: $a = 9.204$ (1), $b = 15.648$ (2), $c = 13.471$ (1) Å, $\beta = 91.364$ (8)° ($\rho_{\mathrm{calcd}} = 1.543$, $\rho_{\mathrm{obsd}} = 1.538$ (5) g/cm^3). The crystal contains discrete eight-coordinate molecules in which the bidentate nitrate ligand spans an *a* edge and the three bidentate acetylacetonate ligands span *b*, *m*, and *g* edges, respectively, of a (necessarily distorted) D_{2d}-$\bar{4}2m$ dodecahedron. Distortions are in the direction of a pseudo-seven-coordinate pentagonal bipyramid. Complexing bonds to the acetylacetonate ligands are systematically shorter than those to the nitrate ligand, averaging 2.141 (1) and 2.366 (2) Å, respectively. The averaged length for all eight Zr–O bonds is 2.197 Å. Differences in the two Zr–O bond lengths within a particular chelate ring are propagated in the C–O, C–C, and N–O bonds of the ligands. The acac ligand "bite" shows significant variation with the type of polyhedral edge it spans: m (2.618 (2) Å) $< g$ (2.689 (2) Å) $< b$ (2.786 (2) Å). The ligands are planar, and the acetylacetonate methyl groups adopt a conformation in which one methyl hydrogen atom and the —CH= hydrogen atom are eclipsed. The relative merits of the observed C_1-*abmg* stereoisomer and other possible stereoisomers are discussed in terms of ligand bite, polyhedral edge lengths, and nonbonded contacts. In inert solvents, $Zr(acac)_3(NO_3)$ is a monomeric nonelectrolyte which is stereochemically nonrigid on the NMR time scale. Retention of coordination number eight in solution is suggested by the similarity of solid-state and solution-state infrared spectra.

This is the second of two papers dealing with the structure and stereochemistry of eight-coordinate mixed-ligand nitrato(acetylacetonato)zirconium complexes of the type $Zr(acac)_2(NO_3)_2$ and $Zr(acac)_3(NO_3)$. The single-crystal x-ray study reported in Part I[1] revealed that $Zr(acac)_2(NO_3)_2$ is an eight-coordinate complex in which the acetylacetonate and nitrate ligands (both bidentate) span the four *m* edges of a (necessarily distorted) D_{2d}-$\bar{4}2m$ dodecahedron (*mmmm* stereoisomer[4]). Each BAAB trapezoid of the dodecahedron[5] contains one acetylacetonate and one nitrate ligand; thus the approximate molecular point group symmetry is C_2-2. The ligand wrapping pattern observed for $Zr(acac)_2(NO_3)_2$ and the dimensions of the coordination polyhedron suggest that the relatively large bite of the acetylacetonate ligand does not permit two acac ligands to be located on the same trapezoid of a ZrO_8 dodecahedron. In support of this view, we note that $Zr(acac)_4$ adopts the alternate eight-coordination polyhedron, a D_{4d}-$\bar{8}2m$ square antiprism, with the ligands located on the *s* edges (*ssss* stereoisomer).[6]

In view of the different stereochemistries exhibited by $Zr(acac)_2(NO_3)_2$ and $Zr(acac)_4$, it was of interest to determine the structure of the intermediate mixed-ligand complex $Zr(acac)_3(NO_3)$. Neither the dodecahedral *mmmm* stereoisomer nor the antiprismatic *ssss* stereoisomer is likely for $Zr(acac)_3(NO_3)$; the former requires that two acac ligands be located on the same trapezoid, and the square antiprism is not well suited to accommodate ligands of short bite such as the nitrate ion. Possible alternative structures include (1) eight-coordinate dodecahedral stereoisomers which exhibit a ligand wrapping pattern other than *mmmm*[4] and (2) structures of reduced coordination number (CN), e.g., $Zr(acac)_3(ONO_2)$ (CN 7, nitrate monodentate) and $[Zr(acac)_3]^+[NO_3]^-$(CN 6). The results presented herein indicate that $Zr(acac)_3(NO_3)$ exists in the solid state as the previously unobserved dodecahedral *abmg* stereoisomer and is a stereochemically nonrigid monomeric nonelectrolyte in solution.

Experimental Section

Preparation and Physical Data. Nitratotris(2,4-pentanedionato)zirconium(IV), $Zr(acac)_3(NO_3)$, was prepared under a dry nitrogen atmosphere by reaction of $Zr(acac)_2(NO_3)_2$[7] with $Zr(acac)_4$[8] in anhydrous benzene. The procedure of Brainina et al.[7] was followed except that the reaction was carried out at room temperature. Recrystallization from hot benzene-hexane gave colorless prisms in 83% yield: mp 150.5–153°, lit.[7] 145–147°; mol wt 448 (cryoscopic, 0.0305 *m* nitrobenzene solution), calcd 451; molar conductance 0.43 ohm^{-1} cm^2 mol^{-1} (1.00×10^{-3} M nitrobenzene solution, 25.0°); ir (CH_2Cl_2 or benzene solution) $\nu_s(C\overset{\cdots}{-}O)$ 1570, $\nu_{as}(C\overset{\cdots}{-}O)$ 1377, ν_{as}(N-O) 1273, $\pi(NO_3^-)$ 804, $\delta(NO_3^-)$ 761, ν(Zr-O) 449, 431, and 310 cm^{-1}; ir (Nujol mull): $\nu_s(C\overset{\cdots}{-}O)$ 1569, $\nu_{as}(C\overset{\cdots}{-}O)$ obscured by Nujol absorption, ν_{as}(N–O) 1272, $\pi(NO_3^-)$ 806, $\delta(NO_3^-)$ 757, ν(Zr–O) 447, 432, and 304 cm^{-1}; NMR (CH_2Cl_2 solution, 10.0 g/100 ml, 37°) −2.00 ppm (CH_3) and −5.73 ppm (—CH═) relative to an internal reference of tetramethylsilane (1% by volume). Low temperature NMR spectra (−100 to −170°) of $CHClF_2$ solutions showed broadening of the methyl resonance; however, no structure indicative of nonequivalent methyl environments was observed.

Crystallography. The single crystals obtained from hot benzene–hexane were suitable for x-ray work when sealed under nitrogen in thin-walled glass capillaries. Weissenberg and precession photographs, used to determine the probable space group and a preliminary set of lattice constants, indicated monoclinic, 2/*m*, symmetry. The systematically absent reflections were those uniquely required by the centrosymmetric space group $P2_1/c$-C^5_{2h} (No. 14).[9] This choice was fully supported by the negative results of sensitive tests for piezoelectricity made with a Geibe–Schiebe detector and by all stages of the subsequent structure determination. Use of the accurate lattice constants given below for a unit cell containing four $Zr(acac)_3(NO_3)$ molecules gave a calculated density of 1.543 g/cm^3, in excellent agreement with the observed density of 1.538 (5) g/cm^3 measured by flotation in a hexane–carbon tetrachloride mixture.

The simple atomic arrangement in the crystal was determined by the straightforward application of the heavy-atom technique using photographically recorded and three-dimensionally correlated diffraction data whose intensities were visually estimated by comparison with a "standard" intensity strip. Nineteen interpenetrating layers of equiinclination Weissenberg and three layers of precession intensity data, 4 along *a*, 15 along *c*, and 3 along *b**, were recorded using multiple-film techniques with Zr-filtered Mo $K\bar{\alpha}$ radiation. The visually estimated intensities were reduced to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization factors. The 2135 independent data which resulted from the three-dimensional correlation of the relative $|F_o|^2$ values were used to calculate a Patterson synthesis, from which the Zr atom was located. A single difference Fourier synthesis at this point was sufficient to locate all remaining non-hydrogen atoms of the totally general-position asymmetric unit. Statistically weighted full-matrix least-squares refinement employing anisotropic thermal parameters for all non-hydrogen atoms resulted in a conventional unweighted residual, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.072 for the 1689 reflections having $\sin\theta/\lambda \leq 0.54$. Bond lengths and angles calculated from the refined structural parameters at this point indicated CN 8 for the Zr atom with the bidendate nitrate ligand spanning an *a* edge and the three bidentate acetylacetonate ligands spanning *b*, *m*, and *g* edges, respectively, of a (necessarily distorted) D_{2d} dodecahedron.[4] However, examination of the bond lengths and angles for the acetylacetonate ligand which spanned the *m* polyhedral edge revealed significant distortions from the expected geometry.[10] A difference Fourier synthesis at this point revealed no peaks with a density greater than 0.8 e/$Å^3$ and did not permit an objective assignment of hydrogen atom positions. When all attempts to improve the structural parameters of the distorted acetylacetonate ligand through additional least-squares refinement failed, it was decided to re-collect a set of diffractometer data in the hope that a more nearly complete and accurate set of diffraction data might enable us to better characterize the bonding parameters for this molecule.

A cube-shaped specimen of $Zr(acac)_3(NO_3)$ was cut from a larger single crystal, ground to a sphere 0.63 mm in diameter, and glued to the inside of a sealed glass capillary under nitrogen in a glove bag before mounting on a goniometer head. This crystal was then very carefully aligned optically on a computer-controlled four-circle Syntex $P\bar{1}$ autodiffractometer. A total of 15 high-angle ($2\theta_{MoK\bar{\alpha}} > 35°$) reflections, chosen to give a good sampling of reciprocal space and diffractometer settings, was used to align the crystal and calculate angular settings for each reflection. A least-squares refinement of the diffraction geometry for these 15 reflections, recorded at the ambient laboratory temperature of 20 ± 1° with Nb-filtered Mo $K\bar{\alpha}$ radiation (λ 0.71069 Å), gave the lattice constants: $a = 9.204 \pm 0.001$ Å, $b = 15.648 \pm 0.002$ Å, $c = 13.471 \pm 0.001$ Å, and $\beta = 91.364 \pm 0.008°$.

Intensity measurements utilized Nb-filtered Mo $K\bar{\alpha}$ radiation and the θ–2θ scanning technique with a 3° takeoff angle and a normal-focus x-ray tube. A fixed scanning rate was employed for the scan between 2θ settings 1.0° above and below the calculated Kα doublet values ($\lambda_{K\alpha_1}$ 0.70926 Å and $\lambda_{K\alpha_2}$ 0.71354 Å) of each reflection. Background counts, each lasting for half the total scan time, were taken at both ends of the scan range. A total of 8506 reflections having $2\theta_{MoK\bar{\alpha}} < 71°$ (2.0 times the number of data in the limiting Cu $K\bar{\alpha}$ sphere) was measured in concentric shells of increasing 2θ containing approximately 2100 reflections each. Scan rates of 3°/min and 2°/min were employed for those reflections having $0° < 2\theta_{MoK\bar{\alpha}} < 55°$ and $55° < 2\theta_{MoK\bar{\alpha}} < 71°$, respectively. Six standard reflections, monitored every 300 reflections, gave no indication of misalignment and/or deterioration of the crystal.

The linear absorption coefficient of the crystal[11] for Mo $K\bar{\alpha}$ radiation is 0.61 mm^{-1}, yielding a μR of 0.19 for the spherical crystal used. Since the absorption of x rays by a spherical crystal having $\mu R = 0.19$ is virtually independent of scattering angle,[12] no absorption corrections were made and the intensities were reduced to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

Of the 8506 reflections examined, 3396 were rejected as objectively unobserved by applying the rejection criterion, $I < 3.0\sigma(I)$, where $\sigma(I)$ is the standard deviation in the intensity computed from

$$\sigma^2(I) = (C_t + k^2B)$$

C_t being the total count from scanning, k the ratio of scanning time to total background time (in this case, $k = 1$), and B the total background count. The remaining 5110 observed intensities were used to locate the hydrogen atoms and refine the structure.

The structural parameters for the 26 non-hydrogen atoms were refined anisotropically to convergence using 5110 unit-weighted reflections and full-matrix least-squares techniques. A difference Fourier synthesis at this point permitted the location of all 21 hydrogen atoms in the asymmetric unit. Further cycles of unit-weighted full-matrix least-squares minimization of the function $\Sigma w(|F_o| - K|F_c|)^2$ (where K is the scale factor) which employed isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for all other atoms, led to $R_1 = 0.030$ and a conventional weighted residual, $R_2 = \{\Sigma w(|F_o| - K|F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$, of 0.030 for 5110 reflections. These and all subsequent refinement cycles employed anomalous dispersion corrections for the Zr atom[13] and a least-squares refineable extinction correction of the form $1/(1 + gI_c)^{1/2}$ (where the extinction coefficient, g, refined to a final value of 1.55×10^{-6}). Empirical weights ($w = 1/\sigma^2$) were then calculated from

$$\sigma = \sum_0^3 a_n|F_o|^n = 0.77 - (0.198 \times 10^{-1})|F_o| + (0.356 \times 10^{-3})|F_o|^2 - (0.964 \times 10^{-6})|F_o|^3$$

Table I. Atomic Fractional Coordinates in Crystalline $Zr(acac)_3(NO_3)$[a]

Atom[b]	10^4x	10^4y	10^4z
Zr	1764.5 (2)	588.4 (1)	2686.2 (1)
O_{a1}	4172 (2)	1186 (1)	2515 (1)
O_{a2}	2682 (2)	1201 (1)	1273 (1)
O_{a3}	4871 (2)	1705 (1)	1107 (2)
O_{b1}	1630 (2)	1952 (1)	2925 (1)
O_{b2}	2727 (2)	641 (1)	4124 (1)
O_{g1}	−220 (2)	862 (1)	3505 (1)
O_{g2}	155 (1)	519 (1)	1572 (1)
O_{m1}	965 (2)	−614 (1)	3239 (1)
O_{m2}	3152 (2)	−348 (1)	2070 (1)
N	3959 (2)	1376 (1)	1614 (1)
C_{b1}	1356 (4)	3305 (2)	3659 (3)
C_{b2}	1873 (2)	2396 (1)	3703 (2)
C_{b3}	2577 (3)	2097 (2)	4551 (2)
C_{b4}	2992 (2)	1261 (2)	4723 (1)
C_{b5}	3783 (5)	1034 (2)	5675 (2)
C_{g1}	−2567 (3)	1155 (2)	4063 (2)
C_{g2}	−1543 (2)	901 (1)	3262 (2)
C_{g3}	−2093 (2)	754 (2)	2299 (2)
C_{g4}	−1239 (2)	595 (1)	1499 (1)
C_{g5}	−1877 (3)	532 (2)	468 (2)
C_{m1}	500 (4)	−1991 (2)	3853 (3)
C_{m2}	1393 (3)	−1384 (1)	3264 (2)
C_{m3}	2616 (3)	−1670 (2)	2774 (2)
C_{m4}	3424 (3)	−1145 (1)	2186 (2)
C_{m5}	4685 (4)	−1481 (2)	1635 (3)

[a] Figures in parentheses are estimated standard deviations in the last significant figure. [b] Each symbol for an atom of a ligand carries a literal subscript to identify the particular polyhedral edge (*a*, *b*, *m*, or *g*) which the ligand spans and a numerical subscript to distinguish between atoms of the same element in the same ligand. Oxygen atoms of the m and g ligands which occupy idealized dodecahedral A and B sites (Figure 2) are designated by numerical subscripts of 1 and 2, respectively.

the a_n being coefficients derived from the least-squares fitting of the curve

$$||F_o| - K|F_c|| = \sum_0^3 a_n |F_o|^n$$

where the F_c values were calculated from the fully refined model using unit weighting. The final cycles of least-squares refinement utilized these weights to refine hydrogen atoms isotropically and all other atoms anisotropically together with the scale factor and extinction coefficient to give final values of 0.030 and 0.032 for R_1 and R_2, respectively, for 5110 independent reflections. During the final cycle of refinement, no parameter shifted by more than $0.27\sigma_p$, with the average shift (including shifts for hydrogen atoms) being $0.03\sigma_p$, where σ_p is the estimated standard deviation of the parameter. The final parameters from least-squares refinement cycles utilizing the empirical weights did not differ significantly from the final parameters from cycles utilizing unit weights. The atomic form factors compiled by Cromer and Mann[14] were used in all structure factor calculations.

The following programs were used on an IBM 360/65 computer for this work: MAGTAPE, SCALEUP, and SCTFT2, data reduction programs written by V. W. Day; FORDAP, Fourier and Patterson synthesis program, a modified version of A. Zalkin's original program; ORFLSE, full-matrix least-squares structure refinement program, a highly modified version of Busing, Martin, and Levy's original ORFLS; ORFFE, bond lengths and angles with standard deviations by Busing, Martin, and Levy; ORTEP2, thermal ellipsoid plotting program by C. K. Johnson; and MPLANE, least-squares mean plane calculation program from L. F. Dahl's group.

Results and Discussion

Structure in the Solid State. Final atomic coordinates and thermal parameters for crystalline $Zr(acac)_3(NO_3)$ are presented in Tables I-III.[15] A model seen in perspective of the contents of the asymmetric unit specified by the atomic coordinates of Tables I and III is illustrated in Figure 1; each non-hydrogen atom is represented by an ellipsoid having the shape, orientation, and relative size concomitant with the thermal parameters listed in Table II (hydrogen atoms are represented by small spheres not representative of their true thermal motion).

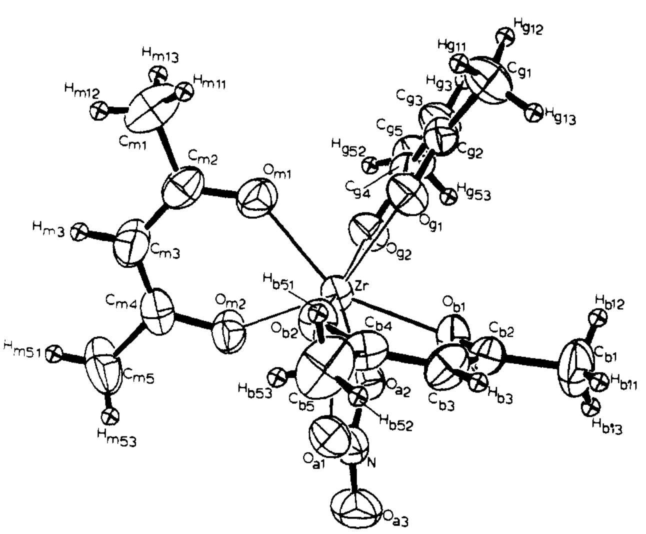

Figure 1. Perspective ORTEP drawing of the eight-coordinate $Zr(acac)_3(NO_3)$ molecule. All non-hydrogen atoms are represented by (50% probability) ellipsoids which reflect their refined anisotropic thermal parameters. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

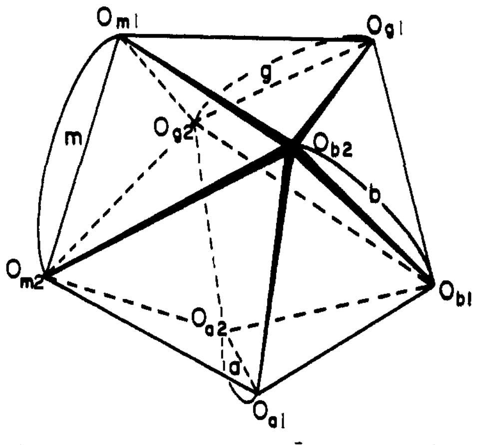

Figure 2. Conventional view of the D_{2d}-$\bar{4}2m$ dodecahedral coordination polyhedron which shows the ligand wrapping pattern observed for $Zr(acac)_3(NO_3)$. Each ligand is represented schematically by a curved line and labeled a, b, m, or g in accord with the dodecahedral edge nomenclature of Hoard and Silverton.[4] Oxygen atoms O_{a1}, O_{a2}, O_{m1}, and O_{g1} occupy dodecahedral A sites while O_{b1}, O_{b2}, O_{m2}, and O_{g2} occupy B sites of the idealized D_{2d} polyhedron. In such a polyhedron,[4] equivalent trapezoids, BAAB, lie in the mutually perpendicular mirror planes and interlock in agreement with $\bar{4}$. The ligand A sites and B sites are located, respectively, at the corners of two nonequivalent, interpenetrating D_{2d}-$\bar{4}2m$ tetrahedra, the A-site tetrahedron being elongated along the $\bar{4}$ axis and the B-site tetrahedron being compressed along the $\bar{4}$ axis. The 18 dodecahedral edges are distributed among four classes: *a* (2), *b* (4), *m* (4), and *g* (8). Each of the two mutually perpendicular twofold axes passes through the midpoints of a pair of opposite *b* edges.

The crystal contains discrete eight-coordinate molecules in which the coordinated ligand oxygen atoms are located at the vertices of a triangular dodecahedron. The coordination polyhedron and ligand wrapping pattern are shown in conventional perspective in Figure 2. In the notation of Hoard and Silverton,[4] the molecule is an *abmg* stereoisomer (point group symmetry C_1-1); the bidentate nitrate ligand spans one of the two *a* edges of the dodecahedron while each of the three acetylacetonate ligands is located along a different type of edge (*b*, *m*, or *g*).

Table II. Thermal Parameters in $Zr(acac)_3(NO_3)$[a]

Atom[b]	Anisotropic Parameters, Å²						Equiv isotropic B,[c] Å²
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	
Zr	2.65 (1)	2.74 (1)	2.46 (1)	0.29 (1)	−0.32 (1)	−0.40 (1)	2.57
O_{a1}	3.4 (1)	4.7 (1)	3.6 (1)	0.3 (1)	−0.7 (1)	0.1 (1)	3.8
O_{a2}	3.4 (1)	4.1 (1)	3.3 (1)	0.1 (1)	−0.6 (1)	0.4 (1)	3.5
O_{a3}	3.9 (1)	7.0 (1)	6.4 (1)	−0.3 (1)	0.7 (1)	2.6 (1)	5.3
O_{b1}	4.2 (1)	3.0 (1)	3.7 (1)	0.8 (1)	−0.6 (1)	−0.4 (1)	3.5
O_{b2}	3.9 (1)	3.5 (1)	2.8 (1)	0.2 (1)	−0.7 (1)	−0.1 (1)	3.3
O_{g1}	3.3 (1)	4.7 (1)	3.1 (1)	0.5 (1)	−0.1 (1)	−0.9 (1)	3.6
O_{g2}	3.0 (1)	4.5 (1)	2.9 (1)	0.2 (1)	−0.3 (1)	−0.9 (1)	3.3
O_{m1}	4.4 (1)	3.4 (1)	4.4 (1)	−0.4 (1)	0.6 (1)	−0.4 (1)	4.0
O_{m2}	4.5 (1)	3.3 (1)	4.0 (1)	0.9 (1)	0.7 (1)	−0.1 (1)	3.8
N	3.3 (1)	3.7 (1)	3.9 (1)	0.4 (1)	−0.1 (1)	0.5 (1)	3.6
C_{b1}	7.0 (2)	3.4 (1)	7.0 (2)	1.2 (1)	−0.4 (1)	−1.5 (1)	5.2
C_{b2}	3.4 (1)	3.0 (1)	4.2 (1)	−0.1 (1)	0.4 (1)	−0.7 (1)	3.5
C_{b3}	5.3 (1)	3.7 (1)	3.4 (1)	−0.7 (1)	−0.3 (1)	−1.0 (1)	3.9
C_{b4}	3.8 (1)	4.3 (1)	2.7 (1)	−0.7 (1)	−0.3 (1)	−0.3 (1)	3.5
C_{b5}	8.8 (2)	5.9 (2)	3.6 (1)	−1.0 (1)	−2.4 (1)	−0.0 (1)	5.3
C_{g1}	3.9 (1)	6.4 (1)	4.0 (1)	0.8 (1)	0.7 (1)	−0.7 (1)	4.5
C_{g2}	3.2 (1)	3.0 (1)	3.5 (1)	0.3 (1)	0.2 (1)	−0.2 (1)	3.2
C_{g3}	2.9 (1)	5.0 (1)	3.7 (1)	0.4 (1)	−0.4 (1)	−0.4 (1)	3.7
C_{g4}	3.3 (1)	2.9 (1)	3.2 (1)	0.2 (1)	−0.7 (1)	−0.2 (1)	3.1
C_{g5}	4.1 (1)	5.4 (1)	3.4 (1)	0.4 (1)	−1.2 (1)	−0.5 (1)	4.1
C_{m1}	7.7 (2)	4.8 (1)	5.5 (1)	−2.2 (1)	−0.1 (1)	0.6 (1)	5.6
C_{m2}	4.9 (1)	3.4 (1)	3.5 (1)	−0.8 (1)	−0.7 (1)	−0.1 (1)	3.8
C_{m3}	5.5 (1)	3.3 (1)	5.8 (1)	0.6 (1)	−0.1 (1)	0.4 (1)	4.6
C_{m4}	4.2 (1)	3.7 (1)	4.1 (1)	1.3 (1)	−0.5 (1)	−0.5 (1)	3.8
C_{m5}	6.5 (2)	5,6 (2)	6.9 (2)	3.0 (1)	1.3 (1)	−0.3 (1)	5.6

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; the B_{ij} in Å² are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$. [b] Atoms are labeled in agreement with Figure 1. [c] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Refined Parameters for Hydrogen Atoms in Crystalline $Zr(acac)_3(NO_3)$[a]

Atom[b]	Fractional coordinates			B,[c] Å²
	10^3x	10^3y	10^3z	
H_{b11}	155 (4)	359 (2)	419 (3)	5 (1)
H_{b12}	38 (5)	329 (3)	372 (3)	6 (1)
H_{b13}	172 (4)	361 (2)	305 (3)	5 (1)
H_{b3}	271 (3)	248 (2)	506 (2)	3 (1)
H_{b51}	309 (5)	76 (3)	608 (3)	7 (1)
H_{b52}	406 (4)	148 (3)	603 (3)	6 (1)
H_{b53}	428 (5)	63 (3)	561 (3)	6 (1)
H_{g11}	−240 (3)	83 (2)	463 (2)	3 (1)
H_{g12}	−347 (4)	111 (2)	388 (2)	4 (1)
H_{g13}	−233 (3)	175 (2)	424 (2)	4 (1)
H_{g3}	−306 (3)	79 (2)	221 (2)	2 (1)
H_{g51}	−276 (4)	52 (2)	47 (3)	6 (1)
H_{g52}	−149 (3)	8 (2)	8 (2)	4 (1)
H_{g53}	−159 (4)	107 (2)	8 (3)	6 (1)
H_{m11}	15 (4)	−168 (2)	446 (3)	6 (1)
H_{m12}	102 (5)	−246 (3)	403 (3)	8 (1)
H_{m13}	−20 (5)	−214 (3)	352 (3)	7 (1)
H_{m3}	288 (3)	−224 (2)	283 (2)	4 (1)
H_{m51}	493 (4)	−202 (2)	178 (3)	5 (1)
H_{m52}	454 (4)	−142 (3)	96 (3)	6 (1)
H_{m53}	550 (5)	−116 (3)	171 (3)	8 (1)

[a] Figures in parentheses are estimated standard deviations in the last significant figure. [b] Each symbol for a hydrogen atom carries the same (two) subscripts as the carbon atom to which it is bonded. In addition, methyl hydrogens carry a third subscript to distinguish between hydrogens on the same carbon atom. Atoms are labeled in agreement with Figure 1. [c] Isotropic thermal parameter.

Table IV. Bond Distances in the Coordination Group of $Zr(acac)_3(NO_3)$[a]

Bond[b]	Length, Å	$(Zr-O_A) - (Zr-O_B)$, Å
$Zr-O_{a1}$	2.422 (2)	
$Zr-O_{a2}$	2.309 (1)	
$Zr-O_{b1}$	2.162 (2)	
$Zr-O_{b2}$	2.112 (1)	
$Zr-O_{m1}$	2.159 (2)	0.034 (2)
$Zr-O_{m2}$	2.125 (1)	
$Zr-O_{g1}$	2.198 (1)	0.111 (1)
$Zr-O_{g2}$	2.087 (1)	
Av values:[c]		
Zr–O (acac)	2.141 (1,33,57)	
Zr–O (NO_3^-)	2.366 (2,57,57)	

[a] Figures in parentheses following individual entries are estimated standard deviations in the last significant figure. [b] Oxygen atoms carry a literal subscript to identify the particular polyhedral edge (*a*, *b*, *m*, or *g*) which the ligand spans and a numerical subscript to distinguish between atoms of the same element in the same ligand. Oxygen atoms of the m and g ligands which occupy dodecahedral A and B sites (Figure 2) are designated by numerical subscripts of 1 and 2, respectively. [c] The numbers in parentheses following each averaged value are the root mean square estimated standard deviation for an individual datum and the mean and maximum deviation from the average value.

Throughout this paper, non-hydrogen atoms are labeled with a literal and a numerical subscript; the literal subscript identifies the polyhedral edge spanned by the particular ligand (*a*, *b*, *m*, or *g*), and the numerical subscript distinguishes between atoms of the same element within that ligand. Oxygen atoms of the acetylacetonate ligands which span *m* and *g* polyhedral edges have a numerical subscript of 1 if they occupy dodecahedral A sites,[4] and 2, if they occupy B sites.[4] Each hydrogen atom is labeled with the same literal and numerical subscript as the carbon atom to which it is attached; a second numerical subscript is used to distinguish between hydrogen atoms bonded to the same carbon atom.

Bond distances, polyhedral edge lengths, and bond angles in the ZrO_8 coordination group are presented in Tables IV and V. A perspective view of the coordination polyhedron is shown in Figure 3. Description of the coordination polyhedron in terms of an idealized D_{2d}-$\bar{4}2m$ dodecahedron rather than an idealized D_{4d}-$\bar{8}2m$ square antiprism is supported by the following geometric criteria.[16] The angle be-

Table V. Polyhedral Edge Lengths and Bond Angles Subtended at the Zr(IV) Atom in the Coordination Polyhedron of $Zr(acac)_3(NO_3)$[a]

Edge type[b]	Atoms[c]	Length, Å	Atoms[c]	Angle, deg
a	O_{a1}–O_{a2}[d]	2.138 (2)	O_{a1}–Zr–O_{a2}	53.67 (5)
a	O_{m1}–O_{g1}	2.583 (2)	O_{m1}–Zr–O_{g1}	72.71 (6)
b	O_{b1}–O_{b2}[d]	2.786 (2)	O_{b1}–Zr–O_{b2}	81.33 (5)
b	O_{b2}–O_{m2}	3.203 (2)	O_{b2}–Zr–O_{m2}	98.18 (6)
b	O_{m2}–O_{g2}	3.132 (2)	O_{m2}–Zr–O_{g2}	96.07 (6)
b	O_{b1}–O_{g2}	3.175 (2)	O_{b1}–Zr–O_{g2}	96.70 (6)
m	O_{m1}–O_{m2}[d]	2.618 (2)	O_{m1}–Zr–O_{m2}	75.34 (6)
m	O_{b1}–O_{g1}	2.546 (2)	O_{b1}–Zr–O_{g1}	71.44 (6)
m	O_{a1}–O_{b2}	2.709 (2)	O_{a1}–Zr–O_{b2}	73.01 (5)
m	O_{a2}–O_{g2}	2.599 (2)	O_{a2}–Zr–O_{g2}	72.29 (5)
g	O_{g1}–O_{g2}[d]	2.689 (2)	O_{g1}–Zr–O_{g2}	77.71 (5)
g	O_{g1}–O_{b2}	2.840 (2)	O_{g1}–Zr–O_{b2}	82.38 (5)
g	O_{m1}–O_{b2}	2.795 (2)	O_{m1}–Zr–O_{b2}	81.73 (6)
g	O_{m1}–O_{g2}	2.943 (2)	O_{m1}–Zr–O_{g2}	87.76 (6)
g	O_{a1}–O_{m2}	2.641 (2)	O_{a1}–Zr–O_{m2}	70.69 (6)
g	O_{a2}–O_{m2}	2.682 (2)	O_{a2}–Zr–O_{m2}	74.28 (6)
g	O_{b1}–O_{a2}	2.716 (2)	O_{b1}–Zr–O_{a2}	74.73 (6)
g	O_{a1}–O_{b1}	2.698 (2)	O_{a1}–Zr–O_{b1}	71.85 (6)

Av Values:[e]

Edge type[b]	Atoms	Length, Å	Atoms	Angle, deg
a	O···O	2.36 (0.2,22,22)	O–Zr–O	63.2 (0.6,95,95)
b	O···O	3.07 (0.2,14,29)	O–Zr–O	93.1 (0.6,59,117)
		[3.17 (0.2,3,4)]		[97.0 (0.6,8,12)]
m	O···O	2.62 (0.2,5,9)	O–Zr–O	73.0 (0.6,12,23)
		[2.62 (0.2,6,9)]		[72,3 (0.5,5,8)]
g	O···O	2.75 (0.2,8,19)	O–Zr–O	77.6 (0.6,48,101)
		[2.76 (0.2,9,18)]		[77.6 (0.6,54,101)]

[a] Figures in parentheses following individual entries are estimated standard deviations in the last significant figure. [b] Edge nomenclature is defined in Figure 1 of ref 1. [c] Oxygen atoms carry a literal subscript to identify the particular polyhedral edge (*a*, *b*, *m*, or *g*) which the ligand spans and a numerical subscript to distinguish between atoms of the same element in the same ligand. Oxygen atoms of the m and g ligands which occupy dodedahedral A and B sites (Figure 2) are designated by numerical subscripts of 1 and 2, respectively. Atoms are labeled in agreement with Figure 1 and Tables I and II. [d] The "bite" of the ligand. [e] The numbers in parentheses following each averaged value are the root mean square estimated standard deviation for an individual datum and the mean and maximum deviation from the average value. Averaged values not enclosed in brackets include all values for the edge type; averaged values enclosed in brackets exclude edges which are also ligand bites.

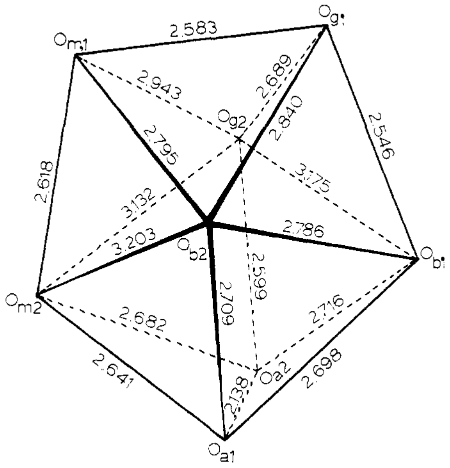

Figure 3. Perspective view (adapted from a computer-drawn diagram) of the dodecahedral coordination polyhedron as observed in the $Zr(acac)_3(NO_3)$ molecule.

Table VI. Average Polyhedron-Shape Parameters[a] for $Zr(acac)_3(NO_3)$

Parameter[b]	$Zr(acac)_3(NO_3)$[c]	MFP[d]	HSM[e]
a	1.07 (1.18)	1.17	1.20
b	1.40 (1.44)	1.49	1.50
m	1.19 (1.19)	1.17	1.20
g	1.25 (1.26)	1.24	1.20
θ_A, deg	31.6 (36.4)	35.2	36.9
θ_B, deg	75.1	73.5	69.5
Zr–O_A/Zr–O_B	1.07 (1.03)[f]	1.03	1.00

[a] See ref. 4. [b] *a*, *b*, *m*, and *g* are averaged lengths of the dodecahedral edges (Figure 2) in units of the averaged Zr–O bond distance (2.197 Å). θ_A and θ_B are the averaged angles which the Zr–O_A and Zr–O_B bonds, respectively, make with the $\bar{4}$ axis of the idealized dodecahedron. [c] Numbers not enclosed in parentheses include all polyhedral edges of a given type; numbers in parentheses do not include edges which are "bites" of ligands. [d] Most favorable coordination polyhedron, calculated (see ref 4) to minimize the closed-shell ligand repulsive energy. [e] Hard sphere model. [f] Number without parentheses represents the ratio for all eight Zr–O bonds; number in parentheses includes only the six bonds to acetylacetonate ligands.

tween the intersecting trapezoidal best planes defined by atoms Zr, O_{b1}, O_{g1}, O_{m1}, and O_{m2} and by atoms Zr, O_{a1}, O_{a2}, O_{b2}, and O_{g2} (Table X) is 88.8° vs. 90.0° for a perfect dodecahedron and 77.4° for a perfect antiprism. Values of d_T, the average displacement of coordinated ligand atoms from the trapezoidal best planes, are 0.12 and 0.06 Å, respectively (0.0 Å for a perfect dodecahedron), while the value of d_S, the mean displacement of coordinated ligand atoms from the best planes through the "antiprismatic square faces" defined by atoms O_{a1}, O_{b2}, O_{m1}, and O_{m2} and by atoms O_{a2}, O_{b1}, O_{g1}, and O_{g2}, is 0.24 Å for both faces (0.0 Å for a perfect antiprism).

Because of the chemical nonequivalence of the ligands and the unsymmetrical *abmg* ligand wrapping pattern, the ZrO_8 dodecahedron is appreciably distorted from full D_{2d}-$\bar{4}2m$ symmetry. Complexing bonds to the acetylacetonate ligands are systematically shorter (by ~0.2 Å; cf. Table IV) than those to the nitrate ligand, and two of the polyhedral edge lengths are significantly different from other edge lengths of the same type (cf. Table V) because of constraints imposed by the "bite" of the ligands. First, the *a* edge spanned by the nitrate ligand is 0.445 Å shorter than the other *a* edge. Second, the *b* edge spanned by an acetylacetonate ligand is ~0.4 Å shorter than the other three *b* edges. The acac ligand bite shows significant variation with the type of polyhedral edge it spans: *m* (2.618 (2) Å) < *g* (2.689 (2) Å) < *b* (2.786 (2) Å). The bite opens in accord with the relative lengths of the edges in the D_{2d}-$\bar{4}2m$ "most favorable" polyhedron (MFP, cf. Table VI) which minimizes closed-shell ligand repulsions;[4] however, the bite of an acac ligand (generally 2.6–2.9 Å[10]) cannot open wide enough to *properly* span a *b* edge (~3.17 Å). Apart from the *a* and *b* edges spanned by ligands, other polyhedral edges of the same type have quite similar lengths (cf. Table V). Average dodecahedral shape parameters (Table VI) are in good agreement with theoretical values given by Hoard and Silverton.[4]

As was found for $Zr(acac)_2(NO_3)_2$,[1] the Zr-O bonds directed toward the dodecahedral A sites, Zr-O_A, are significantly longer than chemically equivalent bonds directed toward the B sites, Zr-O_B. Thus the differences between Zr-O_A and Zr-O_B (Table IV) are 0.034 Å (15σ) and 0.111 Å (79σ) for the bonds to acac ligands m and g, respectively. The ratio of averaged bond distances, Zr-O_A/Zr-O_B, for bonds to the acetylacetonate ligands is 1.03, a value identical with that calculated[4] for the D_{2d}-$\bar{4}2m$ dodecahedron which minimizes closed-shell ligand repulsions (cf. Table VI).

The 0.050-Å difference between the two Zr-O bonds to acac ligand b is not so easily understood in terms of a dodecahedral model since both donor atoms, O_{b1} and O_{b2}, occupy dodecahedral B sites. However, this difference and certain other features of the geometry of the coordination polyhedron can be rationalized in terms of a distortion of the dodecahedron in the direction of a pseudo-seven-coordinate pentagonal bipyramid. It was argued in Part 1,[1] on the basis of Zr-O (acac) bond lengths, that $Zr(acac)_2(NO_3)_2$ could be regarded as a pseudo-octahedral, six-coordinate complex with each nitrate ligand being considered to occupy only one coordination site. Now the averaged Zr-O (acac) bond length in $Zr(acac)_3(NO_3)$ (2.141 Å) is intermediate between the averaged Zr-O (acac) bond lengths in $Zr(acac)_2(NO_3)_2$ (2.096 Å) and in the eight-coordinate $Zr(acac)_4$ (2.198 Å),[6] and is comparable to the averaged Zr-O (acac) bond length in the seven-coordinate, pentagonal-bipyramidal $Zr(acac)_3Cl$ (2.129 Å).[17] Moreover, the averaged $Zr-O(NO_3^-)$ bond length in $Zr(acac)_3(NO_3)$ (2.366 Å) is longer than that in $Zr(acac)_2(NO_3)_2$ (2.295 Å).[1] Consequently, it is not unreasonable to regard $Zr(acac)_3(NO_3)$ as a pseudo-seven-coordinate molecule with the bidentate nitrate ligand being considered to occupy a single coordination site. Viewed from this perspective, it is evident from Figure 3 that the coordination polyhedron is best described as a pentagonal bipyramid with atoms O_{b1}, O_{g1}, O_{m1}, O_{m2}, and the midpoint of the $O_{a1}\cdots O_{a2}$ vector in the "pentagonal" girdle and atoms O_{b2} and O_{g2} in the axial positions. The O⋯O contacts between all of the atoms in the "pentagonal" girdle are short while the Zr-O bonds to these atoms are longer than the axial bonds, $Zr-O_{b2}$ and $Zr-O_{g2}$ (cf. Table IV). Similar effects have been observed in seven-coordinate $Zr(acac)_3Cl$, SnT_3Cl,[18] and SnT_3OH[18] (T = tropolonate) where the axial metal-oxygen bonds are significantly shorter than those in the equatorial plane. Since atom O_{b2} is in an axial position while O_{b1} is in an equatorial position, the observed difference between the $Zr-O_{b1}$ and $Zr-O_{b2}$ bond lengths is rationalized. Since acac ligand g spans axial and equatorial positions on a pentagonal bipyramidal model, and A and B positions on a dodecahedral model, it could experience both effects and might be expected to exhibit the largest difference in its Zr-O bonds; the observed difference for ligand g (0.111 (1) Å, cf. Table IV) is more than twice those for ligands m and b. Also in agreement with a distortion of the dodecahedron in the direction of a pentagonal bipyramid are the values of 159.52 (7) and 140.85 (7)°, respectively, for the $O_{b2}-Zr-O_{g2}$ and $O_{m2}-Zr-O_{b1}$ angles. These angles have values of 180 and 144°, respectively, for an idealized pentagonal bipyramid, while they are equal for a D_{2d}-$\bar{4}2m$ dodecahedron (147° for MFP, 139° for HSM; cf. Table VI). Note that both polyhedra have a common mirror plane, and, with the exception of the *b* edge spanned by an acac ligand, the distortions of the dodecahedron are such as to preserve C_s-m symmetry.

Although the nitrate ligand in $Zr(acac)_3(NO_3)$ would be considered to be symmetrically bidentate according to the classification of Addison et al.,[19] the two $Zr-O(NO_3^-)$ bond lengths differ significantly (by 0.113 Å, 51σ). Neither the idealized dodecahedron nor the idealized pentagonal bipyramid requires these bonds to be inequivalent. However, the observed relative lengthening of $Zr-O_{a1}$ and shortening of $Zr-O_{a2}$ tends to equalize the lengths of the four *g* edges which connect the nitrate oxygen atoms to O_{m2} and O_{b1}.

One final observation can be made about the Zr-O bonds in the series of complexes $Zr(acac)_2(NO_3)_2$, $Zr(acac)_3(NO_3)$, and $Zr(acac)_4$. Although the Zr-O (acac) bond lengths increase in this series, the averaged lengths of all eight Zr-O bonds are essentially identical for all three complexes (2.195, 2.197, and 2.198 Å, respectively).

Table VII. Stereoisomers for a Tetrakis Chelate of the Type $M(XX)_3(YY)$[a]

Antiprismatic		Dodecahedral	
Wrapping pattern	Point group[b]	Wrapping pattern	Point group[b]
llll	C_2-2	*mmmm*	C_s-m
ssss	C_1-1	*gggg*[c]	C_1-1
llss	C_1-1	*gggg*[d]	C_1-1
ssll	C_1-1	*aabb*	C_2-2
		bbaa	C_2-2
		mmgg	C_1-1
		ggmm	C_1-1
		abmg	C_1-1
		bmga	C_1-1
		mgab	C_1-1
		gabm	C_1-1

[a] The isomers are labeled according to the nomenclature of Hoard and Silverton[4] by specifying the polyhedral edges spanned by the ligands. We distinguish between stereoisomers which have the same ligand wrapping pattern in the analogous $M(XX)_4$ complex by listing first the edge spanned by YY. Thus the *abmg* stereoisomer has YY on an *a* edge, while the *bmga* isomer has YY on a *b* edge. [b] The Schoenflies symbol is followed, after a hyphen, by the Hermann–Mauguin symbol. [c] Pseudo-S_4 wrapping pattern. [d] Pseudo-D_2 wrapping pattern.

The possible antiprismatic and dodecahedral stereoisomers for a tetrakis chelate of the type $M(XX)_4$ have been enumerated by Hoard and Silverton.[4] They pointed out that the *abmg* stereoisomer is not expected because it would require chemically equivalent XX ligands to span polyhedral edges which differ in length by fully 25%. To our knowledge, no *abmg* stereoisomer has been previously observed for any tetrakis chelate.

In the case of mixed-ligand complexes of the type $M(XX)_2(YY)_2$ and $M(XX)_3(YY)$, different bites for the XX and YY ligands may make probable ligand wrapping patterns which are not observed for the analogous $M(XX)_4$ or $M(YY)_4$ complexes. Possible stereoisomers and associated maximum point group symmetries for complexes of the type $M(XX)_3(YY)$ are listed in Table VII. The four antiprismatic stereoisomers are unlikely for $Zr(acac)_3(NO_3)$ because the square antiprism is not well-suited to accommodate ligands of short bite such as the nitrate ion. Similarly unlikely are those six dodecahedral stereoisomers in which the nitrate ligand is located on a long edge (*b* or *g*) of the dodecahedron. Of the remaining isomers (*mmmm*, *aabb*, *mmgg*, *abmg*, and *mgab*) the *mmmm* isomer may be ruled out because the bite of the acetylacetonate ligand is too large to permit two acac ligands to be located on the same trapezoid of a ZrO_8 dodecahedron; an *mmmm* structure for $Zr(acac)_3(NO_3)$ would require that nonbonded contacts along the four *g* edges which connect acac oxygen atoms decrease to an unreasonably short value of ~2.50 Å The two stereoisomers (*abmg* and *aabb*) in which the nitrate ligand is located on an *a* edge are best suited for minimizing nonbonded contacts because these isomers preserve twofold symmetry in the coordination group and the longer Zr-O bonds, $Zr-O(NO_3^-)$, are directed toward the dodecahedral A sites. The observed *abmg* stereoisomer should be preferred over the *aabb* isomer since it has only one acac ligand on a *b* edge; the acac bite is too short to *properly* span a *b* edge.

Bond lengths and angles within the acetylacetonate and nitrate ligands (Tables VIII and IX, respectively) are in excellent agreement with those found in $Zr(acac)_2(NO_3)_2$,[1] and they are in accord with the values found in other acetylacetonate[10] and nitrate[19] structures. Bond lengths in the acac ligands are illustrated in Figure 4. As was found for $Zr(acac)_2(NO_3)_2$,[1] differences between the $Zr-O_A$ and $Zr-O_B$ bond lengths (Table IV) are propagated in the C-O bond lengths of the ligands which span dodecahedral A and

Table VIII. Bond Lengths (Å) and Bond Angles (deg) in the Acetylacetonate Ligands of $Zr(acac)_3(NO_3)$[a]

Bond[b]	Ligand b	Ligand m	Ligand g	Average[c]	Angle[b]	Ligand b	Ligand m	Ligand g	Average[c]
$O_1 \cdots O_2$[d]	2.786 (2)	2.618 (2)	2.689 (2)	2.698 (2,59,88)	$Zr-O_1-C_2$	130.6 (1)	136.8 (2)	133.7 (1)	133.7 (1,21,31)
					$Zr-O_2-C_4$	132.5 (1)	137.8 (2)	137.5 (1)	135.9 (1,23,34)
O_1-C_2	1.272 (2)	1.268 (3)	1.255 (2)	1.265 (2,7,10)	$O_1-C_2-C_1$	115.8 (2)	116.3 (3)	116.5 (2)	116.0 (2,3,5)
O_2-C_4	1.282 (2)	1.280 (3)	1.290 (2)	1.284 (2,4,6)	$O_2-C_4-C_5$	116.0 (2)	115.8 (3)	115.6 (2)	
C_2-C_3	1.382 (3)	1.393 (4)	1.400 (3)	1.383 (3,9,17)	$O_1-C_2-C_3$	124.5 (2)	123.2 (2)	124.1 (2)	123.7 (2,6,8)
C_3-C_4	1.380 (3)	1.372 (4)	1.372 (3)		$O_2-C_4-C_3$	124.3 (2)	123.1 (2)	123.0 (2)	
C_1-C_2	1.501 (3)	1.496 (4)	1.503 (3)	1.498 (3,4,10)	$C_1-C_2-C_3$	119.7 (2)	120.5 (3)	119.4 (2)	120.3 (2,7,11)
C_4-C_5	1.501 (3)	1.488 (4)	1.498 (3)		$C_3-C_4-C_5$	119.7 (2)	121.0 (2)	121.4 (2)	
C_3-H_3	0.92 (3)	0.92 (3)	0.90 (3)	0.91 (3,1,1)	$C_2-C_3-C_4$	125.6 (2)	122.4 (2)	123.8 (2)	123.9 (2,11,17)
					$C_2-C_3-H_3$	117 (2)	119 (2)	117 (2)	118 (2,1,2)
					$C_4-C_3-H_3$	117 (2)	119 (2)	120 (2)	
C_1-H_{11}	0.86 (4)	1.01 (4)	0.92 (3)	0.91 (4,5,13)	$C_2-C_1-H_{11}$	114 (2)	108 (2)	111 (2)	111 (2,2,5)
C_1-H_{12}	0.90 (4)	0.91 (4)	0.86 (3)		$C_2-C_1-H_{12}$	106 (3)	111 (3)	113 (2)	
C_1-H_{13}	1.01 (4)	0.81 (4)	0.98 (3)		$C_2-C_1-H_{13}$	112 (2)	109 (3)	106 (2)	
C_5-H_{51}	0.95 (4)	0.89 (4)	0.81 (4)		$C_4-C_5-H_{51}$	106 (3)	115 (2)	112 (3)	
C_5-H_{52}	0.88 (4)	0.92 (4)	0.95 (3)		$C_4-C_5-H_{52}$	113 (3)	111 (2)	115 (2)	
C_5-H_{53}	0.78 (4)	0.91 (5)	1.02 (4)		$C_4-C_5-H_{53}$	111 (3)	114 (3)	108 (2)	
					$H_{11}-C_1-H_{12}$	98 (3)	111 (3)	109 (3)	108 (3,5,15)
					$H_{11}-C_1-H_{13}$	111 (3)	109 (4)	107 (2)	
					$H_{12}-C_1-H_{13}$	116 (3)	109 (4)	111 (3)	
					$H_{51}-C_5-H_{52}$	104 (3)	109 (3)	112 (3)	
					$H_{51}-C_5-H_{53}$	96 (4)	108 (3)	107 (3)	
					$H_{52}-C_5-H_{53}$	123 (4)	99 (3)	103 (3)	

[a] Numbers in parentheses following individual entries are the estimated standard deviations in the last significant figure. [b] Atoms numbered to agree with Figure 1 and Tables I–III. [c] The first number in parentheses following an averaged value is the root mean square estimated standard deviation for an individual datum. The second and third numbers are the mean and maximum deviation from the average value, respectively. [d] The "bite" of the ligand.

Table IX. Distances (Å) and Angles (deg) in the Nitrate Ligand of $Zr(acac)_3(NO_3)$[a]

Atoms	Distance, Å	Average[b]	Atoms	Angle, deg	Average[b]
$N-O_{a1}$	1,261 (2)	1.271 (2,10,10)	$O_{a2}-N-O_{a3}$	122.2 (2)	122.8 (2,6,6)
$N-O_{a2}$	1.281 (2)		$O_{a1}-N-O_{a3}$	123.3 (2)	
$N-O_{a3}$	1.209 (2)		$O_{a1}-N-O_{a2}$	114.5 (2)	
$O_{a1} \cdots O_{a2}$[c]	2.138 (2)				
$O_{a1} \cdots O_{a3}$	2.174 (2)	2.177 (2,3,3)	$Zr-O_{a1}-N$	93.5 (1)	95.9 (1,24,24)
$O_{a2} \cdots O_{a3}$	2.180 (2)		$Zr-O_{a2}-N$	98.3 (1)	

[a] Numbers in parentheses following individual entries are estimated standard deviations of the last significant figure. [b] The numbers in parentheses following each averaged value are the root mean square estimated standard deviation for an individual datum, the mean and maximum deviation from the average value. [c] The "bite" of the ligand.

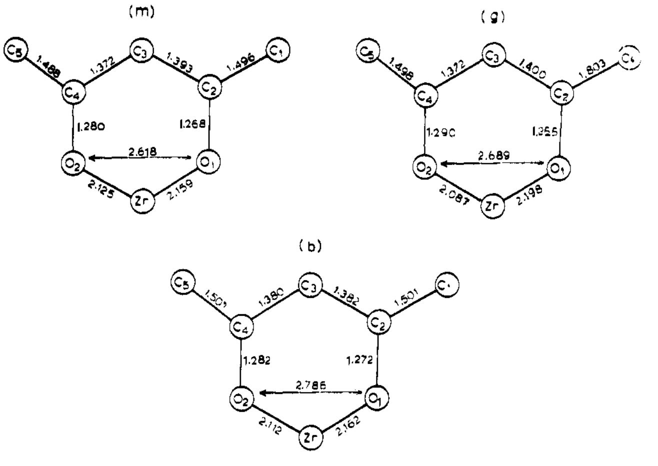

Figure 4. Bond lengths in the metal acetylacetonate groups, labeled according to the dodecahedral edge (*m*, *g*, or *b*) spanned by the ligand.

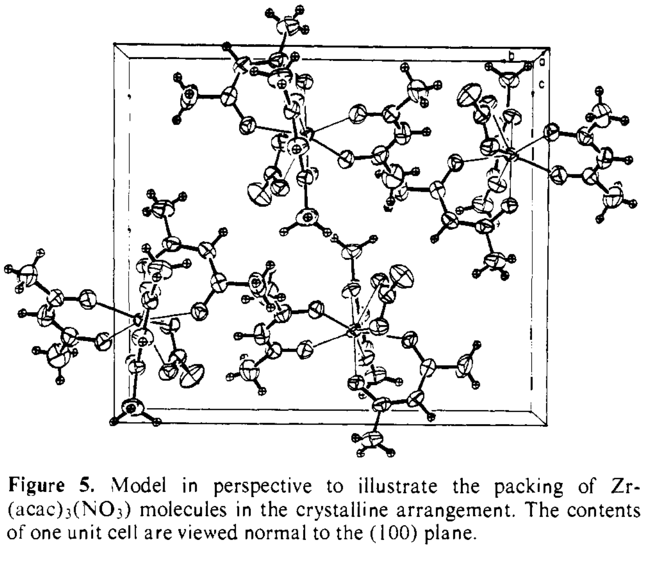

Figure 5. Model in perspective to illustrate the packing of $Zr(acac)_3(NO_3)$ molecules in the crystalline arrangement. The contents of one unit cell are viewed normal to the (100) plane.

B sites, $C-O_A$ being shorter than $C-O_B$ by 0.012 Å (3σ) and 0.035 Å (12σ) for acac ligands m and g, respectively. In each case, the shorter C–O bond is adjacent to the longer Zr–O bond, and vice versa. Even the internal C–C bonds (C_2-C_3 and C_3-C_4) of ligands m and g are inequivalent; the C–C bonds adjacent to the shorter C–O bonds are longer by 0.021 Å (4σ) and 0.028 Å (7σ) for ligands m and g, respectively. In the case of acac ligand b, which spans two dodecahedral B sites, the 0.050-Å difference in the two Zr–O bonds (Table IV) results in a small difference (0.010 Å, 3σ) in the two C–O bonds, but the internal C–C bond lengths in ligand b are essentially identical. Similar effects on the geometry of the acac ligand have been observed in tetragonally elongated γ-$Mn(acac)_3$.[20]

Table X. Least Squares Mean Planes of the Form $AX + BY + CZ = D^a$

Plane no.	Atoms	A	B	C	D
Trapezoidal Planes:					
1	Zr, O_{b_1}, O_{g_1}, O_{m_1}, O_{m_2}	−0.5380	0.0038	−0.8429	−3.9447
2	Zr, O_{a_1}, O_{a_2}, O_{b_2}, O_{g_2}	0.3491	−0.9148	−0.2030	−1.1373
Ligand Planes:					
3	N, O_{a_1}, O_{a_2}, O_{a_3}	0.3243	−0.9064	−0.2705	−1.3781
4	O_{b_1}, O_{b_2}, C_{b_1}, C_{b_2}, C_{b_3}, C_{b_4}, C_{b_5}	0.8959	0.2155	−0.3884	0.2919
5	O_{g_1}, O_{g_2}, C_{g_1}, C_{g_2}, C_{g_3}, C_{g_4}, C_{g_5}	0.1292	0.9756	−0.1776	0.4213
6	O_{m_1}, O_{m_2}, C_{m_1}, C_{m_2}, C_{m_3}, C_{m_4}, C_{m_5}	−0.5681	−0.2005	−0.7981	−3.7343
	Atoms and Their Displacements from Planes, Å				
1	Zr −0.071, O_{b_1} 0.121, O_{g_1} −0.140, O_{m_1} 0.158, O_{m_2} −0.068				
2	Zr −0.098, O_{a_1} −0.064, O_{a_2} 0.082, O_{b_2} 0.078, O_{g_2} 0.003				
3	N −0.003, O_{a_1} 0.001, O_{a_2} 0.001, O_{a_3} 0.001, Zr −0.064				
4	O_{b_1} −0.097, O_{b_2} 0.103, C_{b_1} 0.078, C_{b_2} −0.017, C_{b_3} −0.029, C_{b_4} 0.006, C_{b_5} −0.045, Zr 0.121, $H_{b_{11}}$ 0.113, $H_{b_{12}}$ 0.920, $H_{b_{13}}$ −0.663, H_{b_3} 0.016, $H_{b_{51}}$ 0.839, $H_{b_{52}}$ −0.230, $H_{b_{53}}$ −0.360				
5	O_{g_1} −0.017, O_{g_2} −0.007, C_{g_1} −0.048, C_{g_2} 0.023, C_{g_3} 0.079, C_{g_4} 0.024, C_{g_5} −0.054, Zr −0.033, $H_{g_{t1}}$ 0.560, $H_{g_{12}}$ 0.086, $H_{g_{13}}$ −0.942, H_{g_3} 0.122, $H_{g_{51}}$ 0.074, $H_{g_{52}}$ 0.494, $H_{g_{53}}$ −0.996				
6	O_{m_1} 0.001, O_{m_2} −0.008, C_{m_1} −0.027, C_{m_2} 0.008, C_{m_3} 0.041, C_{m_4} 0.006, C_{m_5} −0.021, Zr 0.211, $H_{m_{11}}$ 0.534, $H_{m_{12}}$ 0.286, $H_{m_{13}}$ −0.794, H_{m_3} 0.058, $H_{m_{51}}$ 0.085, $H_{m_{52}}$ −0.795, $H_{m_{53}}$ 0.580				

[a] *X*, *Y*, and *Z* are orthogonal coordinates measured in Å along *a*, *b*, and *c**, respectively, of the crystallographic coordinate system.

The two nitrate N-O bonds which are adjacent to the Zr-O bonds are also inequivalent; the bond adjacent to the longer Zr-O bond, N-O_{a1}, is shorter than N-O_{a2} by 0.020 Å (7σ). As expected,[19] the terminal N-O bond (1.209 Å) is the shortest of the three N-O bonds, and the O-N-O bond angle involving the coordinated oxygen atoms (114.5°) is appreciably less than 120°. The nitrate ligand is almost exactly planar (cf. Table X) while the seven atoms of each C_5O_2 acetylacetonate skelton exhibit only minor departures from planarity; displacements from the C_5O_2 mean planes are $\leq$ 0.10 Å (average displacement 0.035 Å). The Zr atom is slightly displaced from the mean plane of each ligand (cf. Table X), which implies that the chelate rings are slightly folded along the edges (O···O) of the dodecahedron. The dihedral angles between the ligand planes and the planes defined by the appropriate O-Zr-O group are 1.8, 5.8, 7.3, and 0.8° for rings a, b, m, and g, respectively.

In the case of each of the six crystallographically independent acac methyl groups, one hydrogen atom lies in (or near) the plane (Table X) of the appropriate C_5O_2 group, and this hydrogen atom is eclipsed with the hydrogen atom on the middle carbon atom (cf. Figure 1). The same conformation was found for the four methyl groups in $Zr(acac)_2(NO_3)_2$.[1]

The packing of $Zr(acac)_3(NO_3)$ molecules in the crystal is depicted in Figure 5. There are no unusually short intermolecular contacts.

Structure in Solution. $Zr(acac)_3(NO_3)$ is a monomeric nonelectrolyte in nitrobenzene, and infrared spectra of dichloromethane and benzene solutions indicate that all carbonyl groups are coordinated to the metal. The complex is probably eight-coordinate in solution, as well as in the solid state, since solid-state and solution infrared spectra are very similar. Whatever the static structure in solution, time-averaged NMR spectra[21] indicate that the molecule is stereochemically nonrigid on the NMR time scale at temperatures above −170°.

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Supplementary Material Available: observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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