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Effects of Crystal Packing on the Coordination Geometry of Eight-Coordinate Metal Chelates. Crystal and Molecular Structure of Tetrakis(1,3-diphenyl-1,3-propanedionato)zirconium(IV)

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The crystal and molecular structure of tetrakis(1,3-diphenyl-1,3-propanedionato)zirconium(IV), $Zr(bzbz)_4$, has been determined by single-crystal X-ray diffraction and has been refined anisotropically by least-squares techniques to $R_1 = 0.080$ and $R_2 = 0.072$ by using 5168 independent diffractometer-recorded reflections having $2\theta(\text{Cu K}\bar{\alpha}) \leq 110.03°$ and $|F_o| > 2\sigma(|F_o|)$. The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 25.241$ (5), $b = 10.324$ (1), and $c = 19.395$ (4) Å; $\beta = 101.72$ (1)° ($\rho_{obsd} = 1.31$, $\rho_{calcd} = 1.321$ g cm^{-3}). The crystal contains discrete eight-coordinate molecules in which the bidentate dibenzoylmethanate ligands span the *s* edges of a slightly distorted D_{4d}-$\bar{8}2m$ square antiprism to give the *ssss*-D_2 stereoisomer. Distortions are in the direction of the bicapped trigonal-prismatic $h_1h_1p_2p_2$-C_2 stereoisomer. The distortions, presumably due to the effects of crystal packing, are compared with the somewhat different distortions in the analogous $Zr(acac)_4$ complex. The Zr–O bonds in $Zr(bzbz)_4$ fall into two symmetry-inequivalent sets: Zr–O(outer) = 2.153 Å and Zr–O(inner) = 2.192 Å. The C_3O_2 portions of the chelate rings are planar, but the rings are folded (by 21.7 ± 2.2°) about the edges (O···O) of the square antiprism; all four rings are bent away from the quasi-$\bar{8}$ axis of the antiprism. The phenyl groups are twisted out of the C_3O_2 planes by angles that vary from 17.3 to 41.9°.

Introduction

Because the more common eight-coordination polyhedra are of comparable energy,[1-7] the choice of coordination polyhedron and ligand wrapping pattern in eight-coordinate tetrakis(bidentate) chelates is usually determined by secondary factors such as the matching of ligand bite with polyhedral edge lengths.[1,4] Crystal packing considerations may also influence the coordination geometry,[1] but the effects of crystal packing have not yet been well documented.

In the case of tetrakis(dithiocarbamate) complexes, the dodecahedral *mmmm*-D_{2d} stereoisomer is found in a variety of crystalline environments. Thus the $[Ta(S_2CN(CH_3)_2)_4]^+$ cation exists as the *mmmm* stereoisomer in $[Ta(S_2CN(CH_3)_2)_4]Cl\cdot CH_2Cl_2$ and $[Ta(S_2CN(CH_3)_2)_4][TaCl_6]\cdot{}^1/_2CH_2Cl_2$, and the dimensions of the dodecahedral coordination polyhedra in the two salts are closely similar.[8] The same can be said for the $[Mo(S_2CN(C_2H_5)_2)_4]^+$ cation in $[Mo(S_2CN(C_2H_5)_2)_4]Cl$ and $[Mo(S_2CN(C_2H_5)_2)_4]_2[Mo_6O_{19}]$.[9] Evidently the small normalized bite of the dithiocarbamate ligand (S···S/M–S = 1.11) favors the dodecahedral *mmmm* stereoisomer so strongly that the effects of crystal packing are unimportant.

On the other hand, crystal packing does influence coordination geometry in tetrakis(acetylacetonate) complexes, $M(acac)_4$. Two crystalline forms are known, an α form for M = Ce, Th, and U and a β form for M = Zr, Hf, Ce, Th, U, and Np.[10] The β form contains the well-established square-antiprismatic *ssss*-D_2 stereoisomer, but the α form contains the bicapped trigonal-prismatic $h_1h_1p_2p_2$-C_2 stereoisomer.[11-13] The latter isomer is related to the former by folding about the diagonal of one of the square faces of the antiprism.

The present work is prompted by an early report of still another stereoisomer in the tetrakis(β-diketonate) series. On the basis of an analysis of the badly overlapped (001) and (100) electron density projections of tetrakis(dibenzoylmethanato)cerium(IV), $Ce(bzbz)_4$, Wolf and Barnighausen[14] proposed that the isomorphous tetrakis(dibenzoylmethanates) of Ce, Th, and U have a dodecahedral *mmmm* structure. The structure of the analogous $Zr(bzbz)_4$ is unknown, but our studies of mixed-ligand complexes of the type $Zr(acac)_2(NO_3)_2$[15] and $Zr(acac)_3(NO_3)$[16] suggested that the dodecahedral *mmmm* stereoisomer is unlikely for Zr(β-diketonate)$_4$ complexes because the relatively large bite of β-diketonate ligands does not permit two such ligands to be located on the same trapezoid of a ZrO_8 dodecahedron. Brief conflicting reports that propose a square-antiprismatic structure for

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$Ce(bzbz)_4$ should also be noted.[17,18] Consequently, we have undertaken a reinvestigation of the structures of $M(bzbz)_4$ complexes in connection with our interest in the effects of crystal packing on the coordination geometry of eight-coordinate tetrakis chelates. In this paper we report that $Zr(bzbz)_4$ has an *ssss* square-antiprismatic structure that closely resembles the structure of $Zr(acac)_4$.[19]

Experimental Section

Synthesis of Tetrakis(1,3-diphenyl-1,3-propanedionato)zirconium(IV), $Zr(bzbz)_4$. Dibenzoylmethane (5.547 g, 24.7 mmol) was first converted to the sodium salt by reaction under dry nitrogen for 3 h at room temperature with sodium hydride (0.539 g, 22.5 mmol) in ~100 mL of dry diethyl ether. To the resulting thick, yellow slurry was added 1.229 g (5.27 mmol) of zirconium(IV) chloride and 2.00 mL (11.2 mmol) of 97% triethyl phosphite. The reaction mixture was allowed to reflux for 18 h. The mixture was then cooled, and the ether and triethyl phosphite were removed by vacuum distillation. The residue, after 48 h of drying in vacuo, was extracted with benzene (50 mL), and $Zr(bzbz)_4$ was precipitated as a light yellow powder by addition of hexanes (100 mL). The compound was recrystallized from a mixture of benzene and hexanes. Crystals suitable for X-ray diffraction studies were obtained by recrystallization from acetonitrile; mp 245–246 °C (lit.[20] mp 238–239 °C). Anal. Calcd for $Zr(C_{15}H_{11}O_2)_4$: C, 73.22; H, 4.51. Found: C, 73.06; H, 4.58.

Crystallography. Yellow, elongated crystals of $Zr(bzbz)_4$ were mounted in 0.3-mm diameter Lindemann glass capillaries to prevent possible decomposition.[21] Preliminary Weissenberg and precession photographs indicated the crystal system to be monoclinic. The observed systematic absences, $h0l$ for $l \neq 2n$ and $0k0$ for $k \neq 2n$, uniquely determine the space group to be $P2_1/c$-C_{2h}^5 (No. 14).[22] The following unit cell parameters were determined from the least-squares refinement of the setting angles for 12 reflections that had been automatically centered on a Picker FACS-I computer-controlled four-circle diffractometer using nickel-filtered Cu $K\bar{\alpha}$ radiation (λ = 1.5418 Å): a = 25.241 (5) Å, b = 10.324 (1) Å, c = 19.395 (4) Å, and β = 101.72 (1)°. The observed density of 1.31 g cm^{-3}, measured by flotation in hexane–carbon tetrachloride, is in good agreement with the calculated density of 1.321 g cm^{-3} for four molecules of $Zr(bzbz)_4$ (mol wt 984.22) per unit cell.

Intensity data were collected at ambient temperature on a Picker FACS-I four-circle automated diffractometer using the θ–2θ scan technique and Ni-filtered Cu $K\bar{\alpha}$ radiation. A total of 6189 independent reflections having $2\theta \leq 110.03°$ were collected. Each peak was scanned at the rate of 1°/min over a range in 2θ of 1.6° plus an allowance for the dispersion of Cu $K\alpha_1$ and Cu $K\alpha_2$ radiation; background counts of 40-s duration were taken at both ends of the scan. Reflections having counting rates greater than 10000 counts/s were automatically attenuated by inserting copper foil into the path of the diffracted beam until the intensity was reduced to less than that value. The intensities of three standard reflections were monitored periodically at intervals of 50 reflections; for each standard reflection the maximum deviation from the mean intensity was less than 5.1%.

The intensity data were corrected for background, use of attenuators, absorption, and Lorentz and polarization factors (Lp). Standard deviations were calculated from

$$\sigma^2(|F_o|) = (C + k^2B)/4|F_o|^2(Lp)^2$$

wherein C is the count of the scan, B is the total background count, and k is the ratio of the scanning time to background time. Only those reflections (5168) having $|F_o| > 2\sigma(|F_o|)$ were considered observed. The absorption correction was made by using a local variation of Alcock's program[23,24] (μ = 24.0 cm^{-1}; crystal dimensions 0.11 × 0.11 × 0.21 mm).

Structure Determination and Refinement. The structure was solved by application of Patterson and Fourier techniques and was refined by full-matrix least-squares methods using anisotropic thermal parameters for all nonhydrogen atoms. Typically, positional and anisotropic thermal parameters for approximately 14 atoms were allowed to vary in each cycle of refinement, a different set of atoms being refined in successive cycles. Hydrogen atoms were located from a difference Fourier synthesis, and their calculated coordinates (based on C atom positions) and isotropic thermal parameters (based on the thermal parameters of the adjacent C atom) were included in least-squares calculations but were not refined. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where empirical weights $w = 1/\sigma^2$. In the final cycles of refinement no parameter varied by more than 0.35 (the average was 0.05) of its estimated standard deviation, and the discrepancy indices

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$$

were 0.080 and 0.072, respectively. A final difference Fourier map showed no anomalous features; the strongest peak (0.59 e/Å^3) was near the position of the Zr atom.

Scattering factors for Zr^0, O^0, and C^0 were taken from Cromer and Mann.[25] Anomalous dispersion corrections, real and imaginary, for Zr were obtained from Cromer.[26] Calculations were performed on Prime 300 and IBM 370/168 computers using programs listed in a previous paper.[27]

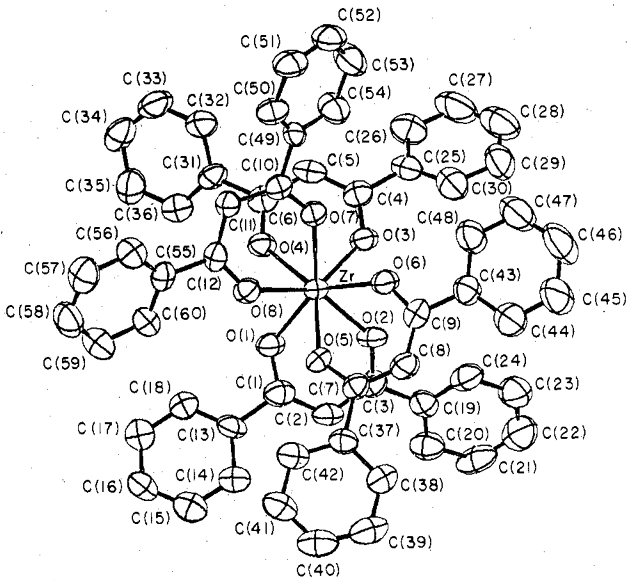

Figure 1. ORTEP drawing of the eight-coordinate $Zr(bzbz)_4$ molecule viewed along the quasi-$\bar{8}$ axis of the ZrO_8 coordination group.

Results and Discussion

Final atomic coordinates and thermal parameters for $Zr(bzbz)_4$ are presented in Tables I and II. Tables of observed and calculated structure factor amplitudes are available.[28] The molecular geometry and atom numbering scheme are illustrated in Figure 1.

The crystal contains discrete eight-coordinate molecules which occupy general positions of the space group $P2_1/c$. The coordination polyhedron is best described as a slightly distorted D_{4d}-$\bar{8}2m$ square antiprism with the bidentate dibenzoylmethanate ligands spanning the *s* edges to give the *ssss*-D_2 stereoisomer. The same isomer has been found in crystalline $Zr(acac)_4$.[19]

Bond distances, polyhedral edge lengths, and bond angles in the ZrO_8 coordination group are presented in Tables III and IV. Edge nomenclature[19] is defined in Figure 2, which compares averaged dimensions of the coordination polyhedra in $Zr(bzbz)_4$ and $Zr(acac)_4$. The Zr–O bonds in $Zr(bzbz)_4$ fall into two symmetry-inequivalent sets in accord with the idealized D_2 symmetry of the coordination group. Four of the oxygen atoms occupy "inner" sites, which lie directly above (or below) the nearest-neighbor chelate ring on the opposite square face of the antiprism (Figure 1). The other four oxygen atoms are located in "outer" sites, which are further removed from the same near-neighbor chelate ring. The Zr–O(inner) and Zr–O(outer) bond lengths are separately quite uniform (Table III), but the Zr–O(outer) bonds (average 2.153 Å) are significantly shorter than the Zr–O(inner) bonds (average 2.192 Å). It is interesting to note that the shorter bonds extend to the B sites[1] of the corresponding dodecahedral *gggg*-D_2

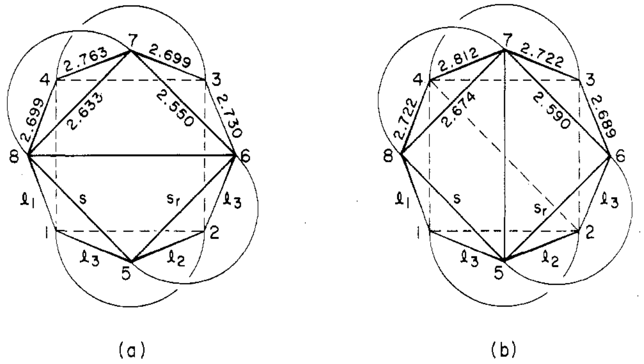

Figure 2. Dimensions of the square-antiprismatic coordination polyhedra in (a) $Zr(bzbz)_4$ and (b) $Zr(acac)_4$[19] averaged in accord with approximate D_2-222 symmetry. The vertices of both polyhedra have been numbered in agreement with the oxygen atom numbering system in Figure 1, but note that a different system is used for $Zr(acac)_4$ in ref 19. The square faces are slightly folded about the indicated diagonals.

stereoisomer (vide infra). The averaged length of all eight Zr–O bonds in $Zr(bzbz)_4$ (2.172 Å) is 0.026 Å less than the averaged Zr–O bond length in $Zr(acac)_4$ (2.198 Å[19]); this difference parallels differences in stability constants,[29] which show that dibenzoylmethanate complexes are, in general, more stable than the acetylacetonate analogues. The edges of the $Zr(bzbz)_4$ coordination polyhedron are correspondingly shorter than the edges of the $Zr(acac)_4$ polyhedron (Figure 2), except for l_1, which is 0.041 Å longer. The longer l_1 edge in $Zr(bzbz)_4$ appears to be related to a different square-face folding pattern in the two complexes (vide infra).

Polyhedron-shape parameters for $Zr(bzbz)_4$ (Table V) are in excellent agreement with values for $Zr(acac)_4$ and with theoretical values for the "most favorable polyhedron" (MFP).[1] In both complexes the ratio l/s is greater than unity, as predicted for the MFP. The polyhedral edge lengths follow the order $s < s_r < l_3 < l_2$, with $l_1 > l_3$ in $Zr(bzbz)_4$ and $l_1 < l_3$ in $Zr(acac)_4$. The normalized bite of the ligand ($s_r \simeq 1.21$) is in the range where the *ssss*-D_2 stereoisomer is expected to be one of the most stable of the possible square-antiprismatic and dodecahedral stereoisomers.[4]

The idealized square-antiprismatic coordination group is slightly distorted in both $Zr(bzbz)_4$ and $Zr(acac)_4$, but the distortions move the two complexes along reaction paths[30] in the direction of two different stereoisomers, the bicapped trigonal-prismatic $h_1h_1p_2p_2$-C_2 stereoisomer for $Zr(bzbz)_4$ and the dodecahedral *mmmm*-D_{2d} stereoisomer for $Zr(acac)_4$. In the case of $Zr(bzbz)_4$, the two square faces of the idealized antiprism are nearly parallel (dihedral angle = 0.4°), but the face defined by oxygen atoms O(5), O(6), O(7), and O(8) is slightly folded about the O(6)···O(8) diagonal (Figure 2). This diagonal (3.567 Å) is nearly 0.20 Å shorter than the O(5)···O(7) diagonal (3.762 Å). Displacements of the four oxygen atoms from the mean plane of this "square" face are ±0.029 Å (Table IX). In contrast, the other quadrilateral face bounded by O(1), O(2), O(3), and O(4) is planar to within 0.002 Å (Table IX), though the two face diagonals have slightly different lengths (O(1)···O(3) = 3.630 Å; O(2)···O(4) = 3.697 Å) owing primarily to the different lengths of the Zr–O(inner) and Zr–O(outer) bonds. The folding of one square face of the antiprism, while maintaining quasi-C_2 symmetry, is a distortion in the direction of the bicapped trigonal-prismatic $h_1h_1p_2p_2$ stereoisomer,[13] the isomer found in the α crystalline form of $Ce(acac)_4$ and $Th(acac)_4$.[11]

The geometry of the ZrO_8 coordination polyhedron may be further characterized by the δ and φ angles[13,30] (Table VI), polyhedron-shape parameters that refer to the corresponding reference dodecahedron. The reference dodecahedron has b

Table I. Final Atomic Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $Zr(bzbz)_4$[a]

atom	10^4x	10^4y	10^4z	B,[b] Å^2
Zr	2441.5 (2)	83.1 (6)	2453.0 (3)	3.04 (2)
O(1)	1722 (2)	1254 (5)	2260 (2)	3.9 (2)
O(2)	2709 (2)	2002 (4)	2209 (2)	3.7 (2)
O(3)	3066 (2)	734 (4)	3315 (2)	3.8 (2)
O(4)	2082 (2)	−47 (5)	3387 (2)	3.8 (1)
O(5)	2199 (2)	130 (5)	1295 (2)	3.8 (2)
O(6)	3167 (2)	−317 (4)	2065 (2)	3.9 (2)
O(7)	2800 (2)	−1716 (4)	2939 (2)	3.7 (1)
O(8)	1837 (2)	−1375 (4)	2148 (2)	3.6 (1)
C(1)	1574 (3)	2152 (8)	1800 (4)	4.5 (3)
C(2)	1924 (3)	3038 (7)	1595 (4)	4.5 (3)
C(3)	2484 (3)	2969 (7)	1850 (4)	4.0 (2)
C(4)	3194 (3)	465 (7)	3972 (4)	4.0 (2)
C(5)	2836 (3)	−106 (7)	4339 (3)	4.3 (2)
C(6)	2283 (3)	−270 (6)	4036 (4)	4.0 (2)
C(7)	2446 (3)	423 (6)	808 (4)	3.7 (2)
C(8)	3007 (3)	388 (7)	887 (4)	4.3 (3)
C(9)	3343 (3)	−15 (7)	1514 (4)	4.0 (2)
C(10)	2615 (3)	−2790 (7)	3090 (3)	3.4 (2)
C(11)	2076 (3)	−3178 (7)	2896 (4)	4.0 (2)
C(12)	1709 (3)	−2442 (7)	2405 (3)	3.4 (2)
C(13)	981 (3)	2178 (7)	1498 (4)	3.9 (2)
C(14)	785 (3)	2645 (9)	813 (4)	5.5 (3)
C(15)	245 (4)	2579 (10)	544 (5)	6.7 (3)
C(16)	−120 (3)	2103 (9)	916 (5)	5.8 (3)
C(17)	74 (3)	1669 (9)	1595 (5)	6.0 (3)
C(18)	614 (3)	1691 (8)	1874 (4)	4.8 (3)
C(19)	2854 (3)	4040 (8)	1727 (3)	4.0 (2)
C(20)	2664 (3)	5283 (7)	1544 (4)	5.2 (3)
C(21)	3046 (4)	6240 (7)	1485 (4)	5.2 (3)
C(22)	3587 (4)	5969 (10)	1586 (5)	6.7 (4)
C(23)	3758 (3)	4739 (9)	1766 (5)	6.2 (3)
C(24)	3396 (4)	3781 (8)	1843 (4)	4.9 (3)
C(25)	3755 (3)	843 (7)	4328 (4)	4.3 (2)
C(26)	3906 (4)	1063 (9)	5046 (4)	6.4 (3)
C(27)	4436 (4)	1419 (11)	5331 (5)	7.5 (4)
C(28)	4804 (4)	1554 (10)	4911 (6)	7.2 (4)
C(29)	4663 (3)	1374 (10)	4200 (6)	6.8 (4)
C(30)	4133 (3)	1011 (8)	3916 (5)	5.9 (3)
C(31)	1895 (3)	−705 (7)	4475 (3)	3.9 (2)
C(32)	2036 (3)	−1664 (8)	4983 (4)	5.2 (3)
C(33)	1674 (4)	−2005 (9)	5393 (4)	5.6 (3)
C(34)	1185 (4)	−1425 (9)	5320 (4)	5.1 (4)
C(35)	1041 (3)	−488 (9)	4808 (5)	5.9 (3)
C(36)	1395 (3)	−131 (8)	4379 (4)	5.3 (3)
C(37)	2097 (3)	790 (7)	117 (4)	4.0 (2)
C(38)	2296 (3)	1526 (8)	−376 (4)	5.5 (3)
C(39)	1951 (4)	1874 (9)	−1006 (4)	5.8 (4)
C(40)	1428 (4)	1453 (9)	−1146 (4)	6.1 (3)
C(41)	1228 (4)	743 (10)	−663 (5)	6.6 (4)
C(42)	1566 (3)	415 (8)	−30 (4)	5.5 (3)
C(43)	3941 (3)	−186 (8)	1584 (4)	4.5 (2)
C(44)	4223 (4)	367 (12)	1125 (5)	7.4 (4)
C(45)	4777 (4)	197 (14)	1214 (6)	8.3 (6)
C(46)	5050 (3)	−527 (14)	1753 (5)	7.9 (5)
C(47)	4772 (4)	−1094 (11)	2207 (5)	7.4 (4)
C(48)	4222 (3)	−903 (9)	2137 (4)	5.8 (3)
C(49)	3023 (3)	−3713 (7)	3494 (3)	3.4 (2)
C(50)	2964 (3)	−5038 (8)	3415 (4)	4.5 (3)
C(51)	3361 (3)	−5878 (8)	3748 (4)	5.1 (3)
C(52)	3815 (3)	−5387 (8)	4190 (4)	5.3 (3)
C(53)	3869 (3)	−4074 (9)	4292 (5)	6.2 (3)
C(54)	3479 (3)	−3234 (8)	3934 (5)	5.1 (3)
C(55)	1143 (3)	−2893 (7)	2154 (3)	3.4 (3)
C(56)	989 (3)	−4173 (8)	2142 (4)	4.7 (3)
C(57)	455 (4)	−4523 (8)	1869 (5)	5.7 (3)
C(58)	86 (3)	−3582 (10)	1611 (4)	6.0 (3)
C(59)	226 (3)	−2307 (10)	1614 (5)	6.0 (3)
C(60)	758 (3)	−1965 (8)	1880 (4)	4.7 (2)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Equivalent isotropic thermal parameters were calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$. See Table II for anisotropic thermal parameters.

Table II. Final Anisotropic Thermal Parameters for $Zr(bzbz)_4$[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zr	3.29 (3)	3.10 (3)	2.80 (2)	0.22 (3)	0.37 (2)	0.56 (3)
O(1)	4.4 (3)	4.5 (3)	3.8 (2)	1.5 (2)	1.5 (2)	1.3 (2)
O(2)	5.0 (3)	3.2 (2)	3.5 (2)	0.6 (2)	0.0 (2)	1.0 (2)
O(3)	4.6 (2)	4.0 (2)	3.1 (2)	−0.3 (2)	0.3 (2)	0.9 (2)
O(4)	4.2 (2)	4.6 (2)	2.9 (2)	0.5 (2)	0.6 (2)	0.4 (2)
O(5)	3.9 (2)	4.8 (3)	3.3 (2)	−0.5 (2)	0.9 (2)	1.0 (2)
O(6)	4.2 (2)	4.1 (3)	3.8 (2)	0.8 (2)	1.1 (2)	1.0 (2)
O(7)	3.6 (2)	3.2 (2)	4.5 (2)	0.1 (2)	0.7 (2)	0.7 (2)
O(8)	4.2 (2)	3.6 (2)	3.1 (2)	−0.6 (2)	0.4 (2)	0.0 (2)
C(1)	5.5 (4)	5.0 (4)	3.6 (4)	0.9 (4)	1.1 (3)	0.4 (3)
C(2)	5.1 (4)	4.3 (4)	4.9 (4)	0.8 (3)	0.0 (3)	1.9 (3)
C(3)	4.9 (4)	3.1 (4)	4.2 (4)	−0.3 (3)	0.9 (3)	0.0 (3)
C(4)	5.0 (4)	3.2 (4)	4.0 (4)	0.0 (3)	0.9 (3)	0.0 (3)
C(5)	5.1 (4)	4.6 (4)	3.6 (3)	0.9 (4)	−0.4 (3)	0.7 (3)
C(6)	5.6 (4)	3.0 (4)	3.9 (4)	0.2 (3)	0.9 (3)	−0.3 (3)
C(7)	4.4 (4)	3.3 (4)	3.5 (3)	−0.4 (3)	0.8 (3)	0.0 (3)
C(8)	5.0 (4)	5.4 (5)	3.2 (3)	0.1 (3)	1.4 (3)	0.5 (3)
C(9)	4.6 (3)	3.8 (4)	4.2 (3)	−0.5 (4)	1.6 (3)	−0.1 (3)
C(10)	4.1 (4)	3.3 (3)	3.1 (3)	0.2 (3)	1.0 (3)	−0.1 (3)
C(11)	3.5 (3)	4.4 (4)	4.4 (4)	0.4 (3)	1.2 (3)	0.9 (3)
C(12)	3.7 (3)	3.7 (4)	3.4 (3)	−0.9 (3)	1.0 (3)	−0.9 (3)
C(13)	3.8 (4)	4.6 (4)	3.8 (4)	1.6 (3)	0.3 (3)	0.7 (3)
C(14)	5.2 (4)	7.3 (5)	4.8 (4)	0.3 (4)	0.3 (4)	2.1 (4)
C(15)	5.7 (5)	10.0 (7)	5.5 (5)	−0.8 (5)	−0.6 (4)	1.6 (5)
C(16)	3.9 (4)	7.6 (6)	7.3 (6)	0.1 (4)	−0.8 (4)	2.2 (5)
C(17)	4.7 (4)	7.2 (6)	6.6 (5)	−0.1 (4)	1.1 (4)	1.6 (4)
C(18)	4.6 (4)	5.8 (5)	4.1 (4)	−0.1 (4)	0.9 (3)	0.8 (4)
C(19)	4.2 (4)	5.6 (5)	2.7 (3)	0.2 (3)	0.5 (3)	−0.3 (3)
C(20)	6.7 (5)	3.8 (4)	5.4 (4)	0.5 (4)	0.3 (4)	0.4 (3)
C(21)	10.6 (7)	2.8 (4)	5.1 (5)	−1.1 (4)	0.6 (5)	0.6 (3)
C(22)	8.0 (6)	6.8 (6)	6.0 (5)	−2.3 (5)	0.3 (5)	0.0 (5)
C(23)	6.3 (5)	5.8 (6)	6.6 (5)	−0.9 (4)	−0.5 (4)	0.9 (4)
C(24)	7.0 (5)	4.2 (4)	4.3 (4)	−1.0 (4)	0.4 (4)	0.8 (3)
C(25)	4.7 (4)	4.0 (4)	4.2 (4)	0.4 (3)	−0.4 (3)	0.3 (3)
C(26)	6.6 (5)	8.2 (6)	4.6 (5)	−0.3 (5)	−0.4 (4)	0.2 (4)
C(27)	7.7 (6)	10.2 (8)	6.1 (6)	0.3 (6)	−2.6 (5)	0.5 (5)
C(28)	7.1 (6)	6.6 (6)	9.1 (8)	−0.9 (5)	−3.1 (6)	0.6 (6)
C(29)	4.2 (5)	6.6 (6)	11.6 (8)	0.5 (4)	0.9 (5)	1.9 (6)
C(30)	5.2 (5)	5.7 (5)	6.8 (5)	0.2 (4)	0.4 (4)	−0.1 (4)
C(31)	5.4 (4)	4.6 (4)	2.5 (3)	−0.5 (3)	1.0 (3)	0.1 (3)
C(32)	5.4 (4)	6.7 (5)	4.1 (4)	0.4 (4)	0.8 (3)	1.1 (4)
C(33)	7.8 (6)	6.6 (5)	4.0 (4)	−1.2 (5)	0.5 (4)	1.7 (4)
C(34)	7.6 (5)	7.3 (6)	3.0 (4)	−2.6 (5)	1.5 (4)	−0.6 (4)
C(35)	5.3 (4)	7.0 (6)	6.2 (5)	−0.7 (4)	1.9 (4)	−0.2 (4)
C(36)	5.5 (4)	5.3 (5)	5.3 (4)	0.3 (4)	0.9 (3)	1.3 (4)
C(37)	4.4 (4)	4.1 (4)	3.4 (3)	0.1 (3)	0.2 (3)	0.0 (3)
C(38)	5.8 (5)	6.2 (5)	5.0 (4)	−0.5 (4)	0.9 (4)	1.4 (4)
C(39)	8.7 (6)	5.9 (5)	4.7 (4)	1.7 (5)	2.1 (4)	1.6 (4)
C(40)	8.6 (6)	6.1 (5)	4.2 (4)	0.9 (5)	−0.3 (4)	0.6 (4)
C(41)	5.9 (5)	8.8 (6)	5.9 (5)	−0.6 (5)	−1.4 (4)	1.8 (5)
C(42)	5.4 (4)	5.9 (5)	5.3 (4)	0.1 (4)	−0.1 (4)	1.5 (4)
C(43)	4.1 (3)	5.5 (4)	4.3 (4)	0.4 (3)	1.3 (3)	−0.1 (4)
C(44)	5.5 (5)	13.8 (9)	6.2 (5)	0.6 (6)	1.6 (4)	2.8 (6)
C(45)	4.6 (5)	22.0 (14)	7.8 (6)	1.9 (7)	2.5 (4)	5.4 (8)
C(46)	3.9 (4)	19.5 (13)	6.7 (6)	1.7 (6)	1.2 (4)	0.4 (7)
C(47)	5.1 (5)	10.9 (8)	7.1 (6)	1.1 (5)	−0.3 (4)	0.6 (6)
C(48)	4.4 (4)	9.1 (6)	5.0 (4)	0.2 (4)	1.2 (3)	0.0 (4)
C(49)	2.5 (3)	5.0 (4)	3.3 (3)	0.5 (3)	0.9 (3)	0.7 (3)
C(50)	5.9 (4)	3.2 (4)	5.1 (4)	0.7 (4)	1.0 (3)	0.7 (4)
C(51)	6.5 (5)	4.0 (4)	6.0 (5)	1.6 (4)	1.4 (4)	1.2 (4)
C(52)	5.8 (5)	5.4 (5)	5.7 (5)	1.9 (4)	1.0 (4)	1.8 (4)
C(53)	4.6 (4)	5.7 (5)	8.8 (6)	0.5 (4)	−0.5 (4)	0.8 (5)
C(54)	4.8 (4)	3.7 (4)	7.6 (5)	0.5 (3)	0.1 (4)	0.4 (4)
C(55)	3.9 (3)	4.4 (4)	3.0 (3)	−0.4 (3)	1.5 (3)	−0.8 (3)
C(56)	4.6 (4)	4.5 (4)	5.1 (4)	0.4 (3)	1.0 (3)	−0.6 (3)
C(57)	6.3 (5)	5.6 (5)	5.8 (5)	−1.5 (4)	1.2 (4)	−1.2 (4)
C(58)	4.5 (4)	8.9 (7)	5.4 (5)	−1.2 (4)	0.1 (4)	−0.6 (5)
C(59)	4.6 (4)	7.1 (6)	6.5 (5)	0.8 (4)	−0.2 (4)	0.4 (5)
C(60)	3.8 (4)	5.3 (4)	4.9 (4)	−0.3 (3)	0.1 (3)	0.4 (4)

[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 Å^2 are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$.

Table III. Bond Distances in the Coordination Group of $Zr(bzbz)_4$[a]

Zr–O(outer)	length, Å	Zr–O(inner)	length, Å
Zr–O(1)	2.151 (4)	Zr–O(2)	2.177 (5)
Zr–O(3)	2.161 (5)	Zr–O(4)	2.188 (4)
Zr–O(6)	2.158 (5)	Zr–O(5)	2.206 (4)
Zr–O(8)	2.140 (4)	Zr–O(7)	2.195 (4)
av[b]	2.153 (5, 7, 13)	av[b]	2.192 (4, 9, 15)

[a] Numbers in parentheses are estimated standard deviations in 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 and the mean and maximum deviation from the averaged value.

Table IV. Polyhedral Edge Lengths and Bond Angles Subtended at the Zr(IV) Atom in the Coordination Group of $Zr(bzbz)_4$[a]

edge, type[b]	atoms	length, Å	atoms	angle, deg
s_r	O(1)···O(2)[c]	2.631 (7)	O(1)–Zr–O(2)	74.9 (2)
s_r	O(3)···O(4)[c]	2.642 (6)	O(3)–Zr–O(4)	74.8 (2)
s_r	O(5)···O(6)[c]	2.636 (6)	O(5)–Zr–O(6)	74.3 (2)
s_r	O(7)···O(8)[c]	2.623 (6)	O(7)–Zr–O(8)	74.5 (2)
s	O(1)···O(4)	2.569 (6)	O(1)–Zr–O(4)	72.6 (2)
s	O(2)···O(3)	2.520 (6)	O(2)–Zr–O(3)	71.0 (2)
s	O(5)···O(8)	2.569 (6)	O(5)–Zr–O(8)	72.4 (2)
s	O(6)···O(7)	2.542 (6)	O(6)–Zr–O(7)	71.5 (2)
l_1	O(1)···O(8)	2.744 (6)	O(1)–Zr–O(8)	79.5 (2)
l_1	O(3)···O(6)	2.716 (6)	O(3)–Zr–O(6)	77.9 (2)
l_2	O(2)···O(5)	2.760 (6)	O(2)–Zr–O(5)	78.1 (2)
l_2	O(4)···O(7)	2.766 (6)	O(4)–Zr–O(7)	78.3 (2)
l_3	O(1)···O(5)	2.687 (6)	O(1)–Zr–O(5)	76.1 (2)
l_3	O(2)···O(6)	2.699 (6)	O(2)–Zr–O(6)	77.0 (2)
l_3	O(3)···O(7)	2.682 (6)	O(3)–Zr–O(7)	76.0 (2)
l_3	O(4)···O(8)	2.727 (6)	O(4)–Zr–O(8)	78.1 (2)

edge type[b]	atoms	av length,[d] Å	atoms	av angle,[d] deg
s_r	O···O	2.633 (6, 6, 10)	O–Zr–O	74.6 (2, 2, 3)
s	O···O	2.550 (6, 19, 30)	O–Zr–O	71.9 (2, 6, 9)
l_1	O···O	2.730 (6, 14, 14)	O–Zr–O	78.7 (2, 8, 8)
l_2	O···O	2.763 (6, 3, 3)	O–Zr–O	78.2 (2, 1, 1)
l_3	O···O	2.699 (6, 14, 28)	O–Zr–O	76.8 (2, 8, 13)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Edge nomenclature is defined in Figure 2. [c] The "bite" of the ligand. [d] 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.

Table V. Average Polyhedron-Shape Parameters

shape parameter[a]	$Zr(bzbz)_4$[b]	$Zr(acac)_4$[c]	MFP[d]	HSM[e]
s_r	1.212	1.217	1.190	1.215
s	1.174	1.178	1.190	1.215
l_1	1.257	1.223	1.258	1.215
l_2	1.272	1.279	1.258	1.215
l_3	1.243	1.238	1.258	1.215
l/s[f]	1.051	1.040	1.057	1.000
θ_{13}	57.4	58.9[g]	57.3	59.2
θ_{24}	57.9	56.9[g]	57.3	59.2
θ_{57}	58.7	56.9[g]	57.3	59.2
θ_{68}	56.1	58.9[g]	57.3	59.2

[a] s_r, s, l_1, l_2, and l_3 are averaged lengths of the edges of the square antiprism (see Figure 2) in units of the averaged Zr–O bond distance (2.172 Å for $Zr(bzbz)_4$ and 2.198 Å for $Zr(acac)_4$). θ_{ij} is the averaged angle (deg) which the Zr–O(*i*) and Zr–O(*j*) bonds make with the $\bar{8}$ axis of the idealized square antiprism. [b] This work. [c] Calculated from data in ref 19. [d] Most favorable coordination polyhedron calculated[1] to minimize the closed-shell repulsive energy. [e] Hard-sphere model. [f] Average value; includes all l, s, and s_r edges. [g] These angles correspond to those in column two though the atom numbering system in ref 19 is not the same as that used in this paper.

Table VI. δ and φ Parameters (deg) for $Zr(bzbz)_4$ and $Zr(acac)_4$ and Theoretical Values for Idealized Eight-Coordination Polyhedra[a]

			theoret values[d]		
$Zr(bzbz)_4$[b]	$Zr(acac)_4$[c]		D_{4d}[e]	C_{2v}[f]	D_{2d}[g]
$\delta_{13} = 0.2$	$\delta_{24} = 3.2$	δ	0.0	0.0	29.5
$\delta_{68} = 3.5$	$\delta_{57} = 3.2$	δ	0.0	21.8	29.5
$\delta_{18} = 47.3$	$\delta_{25} = 49.6$	δ	52.4	48.2	29.5
$\delta_{36} = 47.6$	$\delta_{47} = 49.6$	δ	52.4	48.2	29.5
$\varphi_{1476} = 21.2$	$\varphi_{4365} = 22.8$	φ	24.5	14.1	0.0
$\varphi_{3258} = 20.9$	$\varphi_{2187} = 22.4$	φ	24.5	14.1	0.0

[a] See text for a definition of δ_{ij} and φ_{ijkl}. [b] This work. [c] Calculated[11] from the data in ref 19. [d] References 13 and 30. [e] Square antiprism. [f] Bicapped trigonal prism. [g] Dodecahedron.

edges that are defined by the folding of the quadrilateral faces of the antiprism and/or by the shorter of the two quadrilateral face diagonals. Thus, in the case of $Zr(bzbz)_4$ (Figure 2), the reference dodecahedron has *b* edges O(1)···O(3), O(6)···O(8), O(1)···O(8), and O(3)···O(6); therefore, the two BAAB trapezoids are defined by O(1), O(4), O(7), and O(6) and by O(3), O(2), O(5), and O(8), and the reference dodecahedral stereoisomer is the *gggg*-D_2 isomer. The angle labeled δ_{ij} (Table VI) is the dihedral angle between the two triangular faces that join along the dodecahedral *b* edge O(*i*)···O(*j*); φ_{ijkl} is a measure[13,30] of the nonplanarity of the trapezoid defined by O(*i*), O(*j*), O(*k*), and O(*l*). (The dihedral angle between the mean planes of the two trapezoids in $Zr(bzbz)_4$ is 83.7°, far from the value of 90° for a perfect dodecahedron.) The δ and φ values for $Zr(bzbz)_4$ confirm that the coordination polyhedron most closely approximates a D_{4d} square antiprism. The extent of folding of one of the square faces ($\delta_{68} = 3.5°$) suggests that the observed structure lies ~15% of the way along the reaction path between the square-antiprismatic *ssss*-D_2 stereoisomer and the bicapped trigonal-prismatic $h_1h_1p_2p_2$-C_2 stereoisomer; the latter isomer is in turn the waypoint of a reaction path between the *ssss*-D_2 isomer and the dodecahedral *gggg*-D_2 isomer.[31,32]

In $Zr(acac)_4$, both square faces of the antiprism are folded by the same amount ($\delta_{24} = \delta_{57} = 3.2°$; cf. Table VI and Figure 2) since the molecule is located on a crystallographic twofold axis that lies perpendicular to the quasi-$\bar{8}$ axis of the antiprism. The observed structure is ~10% of the way along the reaction path between the antiprismatic *ssss*-D_2 stereoisomer and the dodecahedral *mmmm*-D_{2d} stereoisomer. $Zr(acac)_4$ and $Zr(bzbz)_4$ are distorted in the direction of different dodecahedral stereoisomers because of different square-face folding patterns. In $Zr(acac)_4$ the folds connect oxygen atoms in inner sites, whereas in $Zr(bzbz)_4$ the fold connects oxygen atoms in outer sites (cf. Figure 2).

Despite the differences in the distortions exhibited by $Zr(acac)_4$ and $Zr(bzbz)_4$, it is evident that crystal packing has only a relatively small effect on the geometry of the ZrO_8 coordination group. The present work does not clarify the coordination geometry of $Ce(bzbz)_4$[14,17,18] since $Ce(bzbz)_4$ and $Zr(bzbz)_4$ crystallize in different space groups. Our preliminary attempts to grow crystals of $Ce(bzbz)_4$ have been unsuccessful; only twinned crystals have been obtained.

Bond lengths and bond angles within the dibenzoylmethanate ligands of $Zr(bzbz)_4$ are presented in Table VII, and averaged values are summarized in Figure 3. For the most part, deviations from the averaged values are statistically insignificant. The averaged values are compared in Table VIII with corresponding averaged parameters for $Zr(acac)_4$[19] and other metal dibenzoylmethanates.[33-36]

The dimensions of the chelate rings in $Zr(bzbz)_4$ and $Zr(acac)_4$ are essentially identical except that $Zr(bzbz)_4$ has a shorter ligand bite (by 0.026 Å), which parallels its shorter Zr–O bond lengths. The ligand bite in $Zr(bzbz)_4$ is appre-

Table VII. Bond Lengths (Å) and Bond Angles (deg) in the Dibenzoylmethanate Ligands of $Zr(bzbz)_4$[a]

Distances

O(1)–C(1)	1.290 (8)	C(13)–C(14)	1.407 (9)	C(38)–C(39)	1.396 (10)
O(2)–C(3)	1.283 (8)	C(14)–C(15)	1.359 (10)	C(39)–C(40)	1.366 (11)
O(3)–C(4)	1.281 (8)	C(15)–C(16)	1.371 (11)	C(40)–C(41)	1.365 (12)
O(4)–C(6)	1.281 (8)	C(16)–C(17)	1.383 (11)	C(41)–C(42)	1.387 (10)
O(5)–C(7)	1.270 (7)	C(17)–C(18)	1.362 (10)	C(42)–C(37)	1.369 (10)
O(6)–C(9)	1.276 (7)	C(18)–C(13)	1.385 (10)	C(43)–C(44)	1.373 (11)
O(7)–C(10)	1.261 (7)	C(19)–C(20)	1.392 (10)	C(44)–C(45)	1.386 (12)
O(8)–C(12)	1.277 (7)	C(20)–C(21)	1.402 (11)	C(45)–C(46)	1.355 (14)
av[b]	1.277 (8, 6, 16)	C(21)–C(22)	1.368 (12)	C(46)–C(47)	1.364 (13)
C(1)–C(2)	1.385 (10)	C(22)–C(23)	1.365 (12)	C(47)–C(48)	1.383 (11)
C(2)–C(3)	1.404 (9)	C(23)–C(24)	1.377 (10)	C(48)–C(43)	1.376 (10)
C(4)–C(5)	1.389 (9)	C(24)–C(19)	1.366 (10)	C(49)–C(50)	1.382 (10)
C(5)–C(6)	1.411 (9)	C(25)–C(26)	1.386 (10)	C(50)–C(51)	1.383 (10)
C(7)–C(8)	1.395 (9)	C(26)–C(27)	1.390 (12)	C(51)–C(52)	1.382 (11)
C(8)–C(9)	1.398 (9)	C(27)–C(28)	1.360 (14)	C(52)–C(53)	1.373 (11)
C(10)–C(11)	1.396 (9)	C(28)–C(29)	1.367 (13)	C(53)–C(54)	1.389 (10)
C(11)–C(12)	1.409 (9)	C(29)–C(30)	1.392 (11)	C(54)–C(49)	1.379 (9)
av[b]	1.398 (9, 7, 13)	C(30)–C(25)	1.374 (11)	C(55)–C(56)	1.377 (10)
C(1)–C(13)	1.493 (9)	C(31)–C(32)	1.392 (10)	C(56)–C(47)	1.395 (10)
C(3)–C(19)	1.497 (10)	C(32)–C(33)	1.372 (11)	C(57)–C(58)	1.368 (11)
C(4)–C(25)	1.498 (9)	C(33)–C(34)	1.355 (11)	C(58)–C(59)	1.363 (12)
C(6)–C(31)	1.491 (9)	C(34)–C(35)	1.382 (11)	C(59)–C(60)	1.384 (10)
C(7)–C(37)	1.496 (9)	C(35)–C(36)	1.387 (10)	C(60)–C(55)	1.390 (9)
C(9)–C(43)	1.498 (9)	C(36)–C(31)	1.373 (10)	av[b]	1.378 (11, 11, 29)
C(10)–C(49)	1.503 (9)	C(37)–C(38)	1.393 (10)		
C(12)–C(55)	1.490 (8)				
av[b]	1.496 (9, 3, 7)				

Angles

Zr–O(1)–C(1)	129.9 (5)	C(1)–C(2)–C(3)	121.4 (7)	C(25)–C(26)–C(27)	119.3 (9)
Zr–O(2)–C(3)	134.8 (4)	C(4)–C(5)–C(6)	122.0 (6)	C(26)–C(27)–C(28)	120.6 (9)
Zr–O(3)–C(4)	134.4 (5)	C(7)–C(8)–C(9)	121.9 (6)	C(27)–C(28)–C(29)	121.4 (9)
Zr–O(4)–C(6)	132.7 (4)	C(10)–C(11)–C(12)	119.9 (6)	C(28)–C(29)–C(30)	117.9 (10)
Zr–O(5)–C(7)	133.3 (4)	av[b]	121.3 (6, 7, 14)	C(29)–C(30)–C(25)	122.1 (9)
Zr–O(6)–C(9)	135.2 (4)	C(1)–C(13)–C(14)	120.7 (7)	C(30)–C(25)–C(26)	118.8 (8)
Zr–O(7)–C(10)	134.8 (4)	C(3)–C(19)–C(20)	121.9 (7)	C(31)–C(32)–C(33)	119.1 (8)
Zr–O(8)–C(12)	136.2 (4)	C(4)–C(25)–C(26)	123.2 (8)	C(32)–C(33)–C(34)	121.8 (8)
av[b]	133.9 (4, 15, 40)	C(6)–C(31)–C(32)	120.9 (7)	C(33)–C(34)–C(35)	119.0 (8)
O(1)–C(1)–C(13)	114.3 (7)	C(7)–C(37)–C(38)	121.7 (7)	C(34)–C(35)–C(36)	120.7 (8)
O(2)–C(3)–C(19)	116.1 (6)	C(9)–C(43)–C(44)	122.6 (7)	C(35)–C(36)–C(31)	119.4 (8)
O(3)–C(4)–C(25)	115.2 (6)	C(10)–C(49)–C(50)	121.5 (6)	C(36)–C(31)–C(32)	120.0 (7)
O(4)–C(6)–C(31)	116.2 (6)	C(12)–C(55)–C(56)	123.6 (7)	C(37)–C(38)–C(39)	119.7 (8)
O(5)–C(7)–C(37)	116.0 (6)	av[b]	122.0 (7, 8, 16)	C(38)–C(39)–C(40)	119.9 (8)
O(6)–C(9)–C(43)	114.3 (6)	C(1)–C(13)–C(18)	120.8 (6)	C(39)–C(40)–C(41)	120.8 (8)
O(7)–C(10)–C(49)	115.5 (5)	C(3)–C(19)–C(24)	117.7 (7)	C(40)–C(41)–C(42)	119.5 (8)
O(8)–C(12)–C(55)	116.3 (6)	C(4)–C(25)–C(30)	118.0 (7)	C(41)–C(42)–C(37)	121.1 (8)
av[b]	115.5 (6, 7, 12)	C(6)–C(31)–C(36)	119.1 (7)	C(42)–C(37)–C(38)	119.0 (7)
O(1)–C(1)–C(2)	124.1 (7)	C(7)–C(37)–C(42)	119.3 (7)	C(43)–C(44)–C(45)	120.7 (9)
O(2)–C(3)–C(2)	122.3 (7)	C(9)–C(43)–C(48)	119.0 (7)	C(44)–C(45)–C(46)	120.6 (10)
O(3)–C(4)–C(5)	122.9 (7)	C(10)–C(49)–C(54)	119.6 (7)	C(45)–C(46)–C(47)	119.2 (8)
O(4)–C(6)–C(5)	123.3 (7)	C(12)–C(55)–C(60)	117.4 (7)	C(46)–C(47)–C(48)	120.8 (9)
O(5)–C(7)–C(8)	123.6 (6)	av[b]	118.9 (7, 9, 19)	C(47)–C(48)–C(43)	120.2 (8)
O(6)–C(9)–C(8)	123.3 (6)	C(13)–C(14)–C(15)	118.7 (8)	C(48)–C(43)–C(44)	118.4 (7)
O(7)–C(10)–C(11)	125.3 (6)	C(14)–C(15)–C(16)	123.0 (8)	C(49)–C(50)–C(51)	121.2 (7)
O(8)–C(12)–C(11)	123.1 (6)	C(15)–C(16)–C(17)	118.1 (8)	C(50)–C(51)–C(52)	119.5 (8)
av[b]	123.5 (7, 6, 18)	C(16)–C(17)–C(18)	120.4 (8)	C(51)–C(52)–C(53)	119.9 (7)
C(2)–C(1)–C(13)	121.5 (7)	C(17)–C(18)–C(13)	121.3 (7)	C(52)–C(53)–C(54)	120.3 (8)
C(2)–C(3)–C(19)	121.6 (6)	C(18)–C(13)–C(14)	118.5 (7)	C(53)–C(54)–C(49)	120.3 (8)
C(5)–C(4)–C(25)	121.9 (6)	C(19)–C(20)–C(21)	117.6 (8)	C(54)–C(49)–C(50)	118.8 (7)
C(5)–C(6)–C(31)	120.5 (6)	C(20)–C(21)–C(22)	121.8 (8)	C(55)–C(56)–C(57)	120.2 (7)
C(8)–C(7)–C(37)	120.4 (6)	C(21)–C(22)–C(23)	118.9 (9)	C(56)–C(57)–C(58)	119.3 (8)
C(8)–C(9)–C(43)	122.4 (6)	C(22)–C(23)–C(24)	120.9 (9)	C(57)–C(58)–C(59)	121.9 (8)
C(11)–C(10)–C(49)	119.2 (5)	C(23)–C(24)–C(19)	120.5 (8)	C(58)–C(59)–C(60)	118.6 (8)
C(11)–C(12)–C(55)	120.5 (6)	C(24)–C(19)–C(20)	120.3 (8)	C(59)–C(60)–C(55)	121.1 (8)
av[b]	121.0 (6, 9, 18)			C(60)–C(55)–C(56)	118.9 (7)
				av[b]	120.0 (8, 10, 30)

[a] Numbers in parentheses are estimated standard deviations in 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 and the mean and the maximum deviation from the average value.

ciably shorter than in the less crowded $Cu(bzbz)_2$,[33,34] Pd-$(bzbz)_2$,[35] and $Ho(bzbz)_3(H_2O)$,[36] and the chelate ring C–C–C bond angle in $Zr(bzbz)_4$ is correspondingly smaller. Apart from the M–O–C bond angles, which are a function of the M–O distance, the O–M–O bond angle, and the degree of planarity in the chelate ring, other ligand bond distances and bond angles in $Zr(bzbz)_4$ and the other metal dibenzoylmethanates are closely similar (cf. Table VIII).

The five atoms of each C_3O_2 1,3-propanedionate skeleton exhibit only minor departures from planarity; displacements

Table VIII. Comparison of Averaged Ligand Parameters for $Zr(bzbz)_4$, $Zr(acac)_4$, and Other Metal Dibenzoylmethanates

parameter	Zr-$(bzbz)_4$[a]	Zr-$(acac)_4$[b]	Cu-$(bzbz)_2$[c]	Pd-$(bzbz)_2$[d]	Ho-$(bzbz)_3$-(H_2O)[e]
A. Interatomic Distances (Å) in the Chelate Ring					
M–O	2.172	2.198	1.911	1.96	2.290
O···O	2.633	2.674	2.776	2.85	2.77
C$\overset{..}{-}$O	1.277	1.270	1.300	1.29	1.27
C$\overset{..}{-}$C	1.398	1.399	1.403	1.37	1.39
C–C_6H_5-(CH_3)	1.496	1.517	1.496	1.50	1.50
B. Bond Distances (Å) in the Phenyl Groups					
C–C	1.378[f]		1.399	1.39	1.36
C. Bond Angles (deg) in the Chelate Ring					
O–M–O	74.6	75.0	93.2	93	74.6
M–O–C	133.9	133.1	127.2	124	136
O–C–C	123.5	123.7	123.5	126	124
C–C–C	121.3	122.5	125.3	126	125
O–C–C_6H_5-(CH_3)	115.5	116.1	115.5	113	116
C–C–C_6H_5-(CH_3)	121.0	120.2	121.0	121	119
D. Fold of the Chelate Ring about O···O (deg)					
α[g]	21.7	22.6	~0	~0	~0
E. Twist of the Phenyl Groups about the C–C_6H_5 Bond (deg)					
φ[h]	26.9		7.0	7.0	15

[a] This work. [b] Reference 19. [c] Reference 33 (cf. also ref 34). [d] Reference 35. [e] Reference 36. [f] Values of 1.380[37] and 1.389 Å[38] have been reported for Hbzbz, the enol form of the ligand. [g] Dihedral angle between the C_3O_2 ligand plane and the MO_2 plane. [h] Dihedral angle between the C_3O_2 ligand plane and the C_6 phenyl planes.

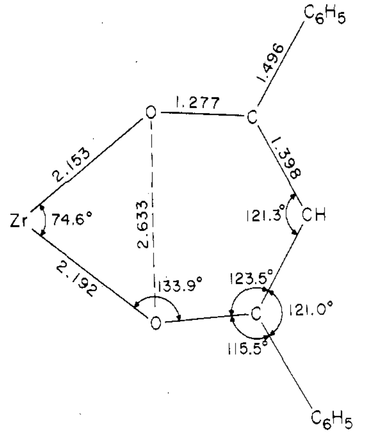

Figure 3. Averaged bond distances and angles in the dibenzoylmethanate chelate rings. Deviations from the average are given in Tables III, IV, and VII. The rings are folded through an averaged angle of 21.7° about the dashed line that joins the two oxygen atoms.

from the C_3O_2 mean planes are ≤0.07 Å (average displacement 0.027 Å; cf. Table IX). However, the Zr atom is displaced from the mean plane of each ligand by 0.5–0.7 Å, which implies that the chelate rings are appreciably folded about the s_r edges (O···O) of the square antiprism. The dihedral angles between the ligand planes and the planes defined by the appropriate O–Zr–O group are 24.3, 23.5, 21.2, and 18.0° (average 21.7 ± 2.2°); the direction of the fold in all four rings is such as to bend the rings away from the quasi-$\bar{8}$ axis of the antiprism. In $Zr(acac)_4$ the chelate rings are folded, again away from the quasi-$\bar{8}$ axis, through a remarkably similar angle (22.6 ± 0.7°).[19] On the other hand, no folding of the chelate rings is observed in $Cu(bzbz)_2$,[33] $Pd(bzbz)_2$,[35] and $Ho(bzbz)_3(H_2O)$,[36] despite the fact that the O–M–O bond angle in these complexes varies from 93.2° to 74.6°.

Table IX. Least-Squares Mean Planes of the Form $AX + BY + CZ = D$[a]

plane	atoms	A	B	C	D
1	O(1), O(2), O(3), O(4)	0.2265	−0.8025	−0.5519	−2.6241
2	O(5), O(6), O(7), O(8)	0.2320	−0.8000	−0.5533	−0.2700
3	O(1), O(2), C(1), C(2), C(3)	0.1953	−0.5859	−0.7865	−3.4065
4	O(3), O(4), C(4), C(5), C(6)	0.2853	−0.9237	−0.2557	−0.4859
5	O(5), O(6), C(7), C(8), C(9)	−0.0003	−0.9510	−0.3091	−0.8931
6	O(7), O(8), C(10), C(11), C(12)	0.4337	−0.4826	−0.7609	−0.7916

plane	displacements of atoms from planes, Å
1	O(1), 0.002; O(2), −0.002; O(3), 0.002; O(4), −0.002
2	O(5), 0.028; O(6), −0.029; O(7), 0.029; O(8), −0.028
3	O(1), 0.054; O(2), −0.061; C(1), −0.053; C(2), −0.012; C(3), 0.071; Zr, −0.707
4	O(3), −0.013; O(4), −0.007; C(4), 0.031; C(5), −0.036; C(6), 0.024; Zr, −0.699
5	O(5), −0.004; O(6), 0.010; C(7), −0.001; C(8), 0.011; C(9), −0.016; Zr, 0.630
6	O(7), 0.036; O(8), −0.018; C(10), −0.053; C(11), 0.031; C(12), 0.005; Zr, 0.540

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

Factors which can influence the folding of β-diketonate chelate rings in the square-antiprismatic *ssss* stereoisomer include (1) a tendency to reduce the M–O–C bond angle toward a value more nearly in accord with sp^2 hybridization at the oxygen atom, (2) π-bonding interactions between the empty metal d_{z^2} orbital and π-donor orbitals on the ligands,[6] and (3) crystal packing effects. The relative importance of these factors is difficult to assess, but it is clear from the stereoscopic packing diagram in Figure 4 that crystal packing is improved by folding the chelate rings away from the quasi-$\bar{8}$ axis. The molecules stack along the crystallographic b axis, with the angle between the quasi-$\bar{8}$ axis and the b axis being 36.7°. The effect of the observed ring folding is to decrease the molecular volume by flattening the molecules with respect to the quasi-$\bar{8}$ direction. There are no unusually short in-

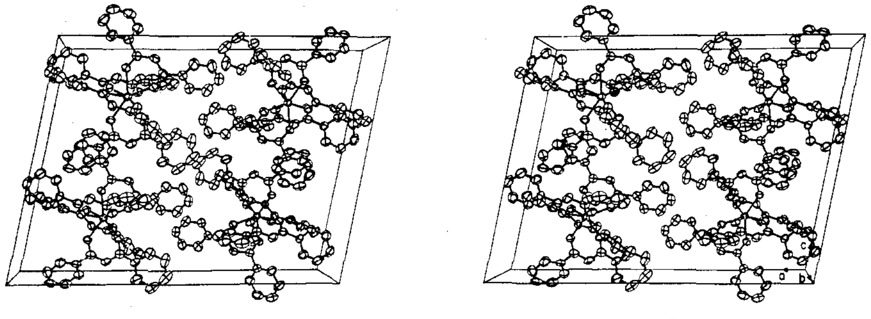

Figure 4. Stereoscopic view of the packing in crystalline $Zr(bzbz)_4$. The contents of one unit cell are viewed normal to the (010) plane.

termolecular contacts in this structure. The shortest contacts (3.36 Å) involve phenyl carbon atoms for which the sum of the van der Waals radii is 3.40 Å.[39]

As a check on the accuracy of this structure, it is gratifying to find that the averaged C–C bond length in the phenyl groups (1.378 ± 0.011 Å) is in good agreement with the values found for crystalline benzene (1.392 Å[40]) and other metal dibenzoylmethanates (cf. Table VIII). The phenyl groups are planar, with the average displacement of the 48 carbon atoms from the mean planes of the eight phenyl rings being 0.007 Å (maximum displacement 0.017 Å). However, the phenyl groups are twisted out of the plane of the C_3O_2 portion of the ligand by angles that vary from 17.3° to 41.9° (average 26.9°; cf. Table VIII).

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Registry No. $Zr(bzbz)_4$, 17455-33-3.

Supplementary Material Available: A listing of structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

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Crystal Structure of Rubidium Fluoroxysulfate. Characterization of the Fluoroxysulfate Anion[1]

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The rubidium salt of the recently identified fluoroxysulfate anion, $FOSO_3^-$, has been characterized by single-crystal X-ray diffraction. $RbFOSO_3$ crystallizes in the centrosymmetric triclinic space group, $P\bar{1}$, with unit cell constants $a = 5.503$ (2) Å, $b = 5.623$ (1) Å, $c = 7.603$ (3) Å, $\alpha = 100.64$ (2)°, $\beta = 106.72$ (2)°, $\gamma = 93.22$ (2)°, and $Z = 2$. The X-ray data refine to an $R_F = 0.067$ for 664 reflections with $F^2 > \sigma F^2$. The fluoroxysulfate anion has distorted tetrahedral coordination with each central sulfur atom bound to four oxygens. The S–O bond distances are 1.435 (8), 1.426 (8), 1.441 (7), and 1.652 (9) Å. The O–F bond distance is 1.412 (10) Å, and the S–O–F bond angle is 107.8 (6)°. Each Rb^+ cation is coordinated to nine oxygen atoms and two fluorine atoms.

Introduction

Appelman et al.[2] have recently reported the preparation of rubidium and cesium fluoroxysulfates, $Rb^+FOSO_3^-$ and $Cs^+FOSO_3^-$. Both materials were shown to be powerful oxidizing and fluorinating agents. Infrared, Raman, and NMR spectra of these salts are consistent with the formulation of the anion as a fluoroxyion or hypofluorite, $FOSO_3^-$. Although other hypofluorites are known, they are all neutral molecules that are gases at room temperature. The fluoroxysulfates are the first saltlike hypofluorites to be isolated and as such are particularly amenable to detailed structure determination by X-ray diffraction. Preliminary X-ray powder diffraction photographs of the two salts indicated them to be isomorphous. Inasmuch as the rubidium salt was more readily obtainable in the crystalline form, the structure of this material has been completely determined in the present study.

Experimental Section

Preparation of Material. Rubidium fluoroxysulfate was prepared by passing fluorine (20 mol % in N_2) through a 1.3 M solution of rubidium sulfate at 0 °C.[2] The precipitate was separated by cen-

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