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An Example of the Monocapped Octahedral Form of Heptacoordination. The Crystal and Molecular Structure of Tris(1-phenyl-1,3-butanedionato)aquoyttrium(III)[1]

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The crystal and molecular structures of tris(1-phenyl-1,3-butanedionato)aquoyttrium(III), $Y(C_6H_5COCHCOCH_3)_3 \cdot H_2O$, have been determined from 4820 independent, nonzero reflections collected with a counter diffractometer. The compound crystallizes in the triclinic space group $P\bar{1}$ with two molecules in a unit cell of dimensions: $a = 6.214 \pm 0.005$ Å, $b = 12.462 \pm 0.008$ Å, $c = 19.299 \pm 0.008$ Å, $\alpha = 95° 37' \pm 3'$, $\beta = 104° 53' \pm 3'$, and $\gamma = 96° 20' \pm 3'$ ($\rho_{obsd} = 1.36 \pm 0.02$ g cm^{-3}; $\rho_{calcd} = 1.37$ g cm^{-3}). The structure, including hydrogen atoms, was solved from Patterson and electron density maps and refined by least-squares methods to a conventional unweighted R factor of 5.9%. The molecules are monomeric with the yttrium being at the center of a distorted octahedron of chelate oxygen atoms (average $Y-O_{chelate} = 2.28$ (1) Å) capped on one face by the water molecule ($Y-O_{water} = 2.341$ (3) Å). The β-diketonate ligands wrap asymmetrically (two phenyl groups up, one down) about the coordination polyhedron and exhibit characteristic folding to aid packing. All intermolecular distances are indicative of normal nonbonded contacts except in a direction parallel to the crystallographic a axis where hydrogen bonding is indicated.

Introduction

Tris(β-diketonate) chelates of the trivalent lanthanides usually crystallize from protonic or coordinating solvents with one to three molecules of solvent.[3-8] Attempts to remove the solvent molecules generally lead to solvolysis and decomposition of the tris chelate, and it has generally been thought that at least one of the solvent molecules is coordinated to the lanthanide ion. Thus it would be considered quite likely that the monosolvate phases contain heptacoordinate metal atoms. As part of an investigation of the solid-state and solution properties of various β-diketonate complexes of yttrium(III),[9,10] we decided to test this structural possibility and thus carried out a single-crystal X-ray analysis on $Y(BZA)_3 \cdot H_2O$ where BZA is the benzoylacetonate or 1-phenyl-1,3-butanedionate ion, $C_6H_5COCHCOCH_3^-$.

Experimental Procedure

Crystalline $Y(BZA)_3 \cdot H_2O$ was prepared by allowing Na(BZA) and YCl_3 in a 3:1 ratio to react in aqueous ethanol and was purified by recrystallization from the same solvent. The compound is air sensitive, melts at 114–115°, is soluble in most nonpolar organic solvents, and appears to be monomeric in benzene as it has an osmometrically determined molecular weight of 587. *Anal.* Calcd for $YC_{30}H_{29}O_7$: C, 61.02; H, 4.92. Found: C, 61.0; H, 4.80. Analyses and molecular weight determinations were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

The predominant crystal habit is one of triclinic needles, and a parallelepiped of approximate dimensions 0.6 × 0.1 × 0.1 mm was chosen for the subsequent X-ray work and sealed in a thin-walled Lindemann glass capillary.

Preliminary Weissenberg (0*kl* and 1*kl* levels) and precession (*hk*0, *hk*1, *h*0*l*, and *h*1*l* levels) photographs indicated one of the triclinic space groups P1 or $P\bar{1}$, and afforded approximate unit cell dimensions. By use of a General Electric XRD-5 manually operated single-crystal diffractometer with Cu Kα radiation, $\lambda(K\alpha_1)$ 1.5405 Å, $\lambda(K\alpha_2)$ 1.5443 Å, the unit cell dimensions were then derived by a method described elsewhere.[11] This procedure yielded $a = 6.214 \pm 0.005$ Å, $b = 12.462 \pm 0.008$ Å, $c = 19.299 \pm 0.008$ Å, $\alpha = 95° 37' \pm 3'$, $\beta = 104° 53' \pm 3'$, and $\gamma = 96° 20' \pm 3'$. A Delaunay reduction[12] did not reveal any higher symmetry. The density was determined by flotation in aqueous calcium chloride solutions as 1.36 ± 0.02 g cm^{-3}, and this agrees well with the calculated density of 1.37 g cm^{-3} for a formula weight of 589.9, $Z = 2$, and a unit cell volume of 1423 Å^3.

Intensity data were collected on a General Electric quarter-circle automated XRD-6 diffractometer equipped with a Datex control unit, and the crystal was so aligned that its a^* axis coincided with the ϕ axis of the instrument. The distances from the crystal to the source and from the crystal to the circular screening aperture (2°) were 5.73 and 7.05 in., respectively. Cu Kα radiation, filtered by nickel foil, was used to measure 5397 independent reflections within the sphere $\theta \leq 70°$. The intensities were measured with a scintillation counter with the pulse height discriminator set to receive 95% of the Cu Kα radiation with the window centered on the Cu Kα peak. A θ–2θ scan technique was employed. Each intensity was obtained by recording the counts, P, from a 2θ scan at 4°/min from $2\theta_{calcd} - 1.33°$ to $2\theta_{calcd} + 1.33°$ and stationary background counts for 20 sec at each of the limits of the scan (B_1, B_2). Assuming that the background varies linearly (or gives an equivalent integrated total) through the scan range, the intensity is given by $I = P - (B_1 + B_2)$. Several strong reflections which exceeded the linear response range of the counter were remeasured with a lower current and were scaled to the other data by using medium intensity reflections measured with both current settings. Periodic checks of three standard reflections showed a maximum variation, having no 2θ dependence, of ±2% which was random with time. Thus there was no evidence for significant crystal decomposition.

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[1] This work was supported in part by the National Science Foundation under Grant No. 7034X.

[2] Arthur D. Little Predoctoral Fellow, 1966–1967.

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[6] R. C. Ohlmann and R. G. Charles, *J. Chem. Phys.*, **40**, 3131 (1964).

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TABLE I

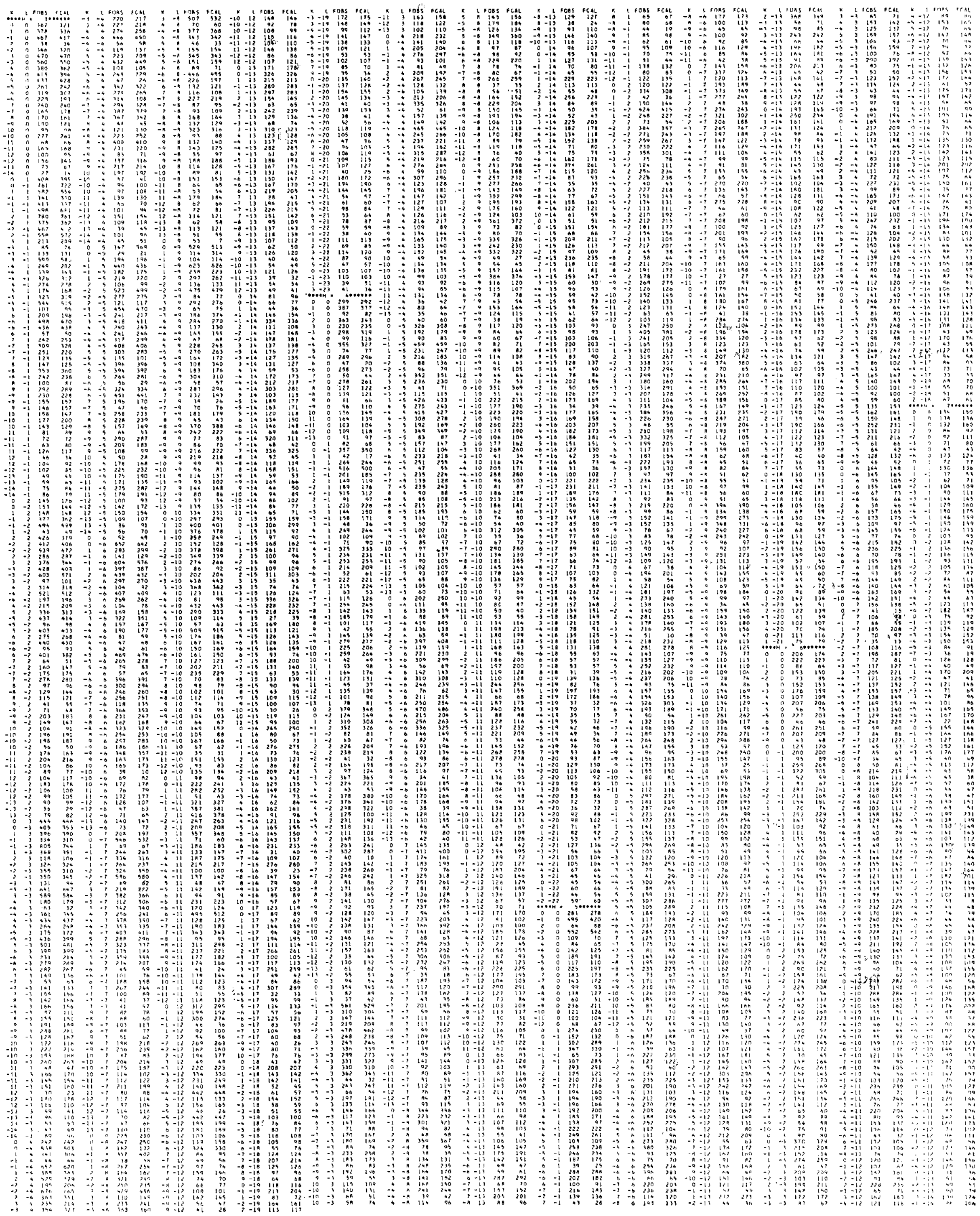
OBSERVED AND CALCULATED STRUCTURE AMPLITUDES ($\times 10$) (IN ELECTRONS) FOR $Y(BZA)_3 \cdot H_2O$

Because of the limitations of the quarter-circle instrument, only a limited amount (~700 reflections) of the Friedel-related data ($\bar{h}\bar{k}\bar{l}$) was collected; no systematic differences in intensities due to anomalous dispersion could be detected. Consequently, it was considered likely that the space group was the centrosymmetric $P\bar{1}$.

Statistically insignificant reflections (577) were rejected using the criteria: (1) $I < 0$; (2) $I \leq 3(P + B_1 + B_2)^{1/2}$. The remaining 4820 reflections were corrected for Lorentz and polarization effects and a set of $|F_o|^2$ and $|F_o|$ values (on a relative scale) was thus obtained.

Appreciable variations in the intensities of the $h00$ reflections were observed as a function of crystal orientation; ϕ scans of several of these reflections evidenced variations of 15%. Conse-

TABLE I (*Continued*)



quently, absorption corrections (μ = 34.7 cm^{-1}), based on the equations of the crystal faces, were applied to the data for the final stages of refinement.

Solution and Refinement of the Structure

A three-dimensional Patterson map readily revealed the positions of all atoms except the carbon atoms in two phenyl rings whose images overlapped. This ease of location of the light atoms as well as the subsequent successful refinement confirms the choice of space group P$\bar{1}$.

The structure was solved by conventional least-squares and Fourier calculations. For atoms other than hydrogen, the scattering factors used during this analysis were those of Cromer and Waber,[13] while the scattering factors used for hydrogen were those experimentally determined for H atoms in biphenyl by Mason and Robertson.[14] Anomalous dispersion corrections for yttrium, both real ($\Delta f'$ = $-$0.75 e$^-$) and imaginary ($\Delta f''$ = 2.20 e$^-$) parts, applied to the calculated struc-

[13] D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

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ture amplitudes[15a] were those given by Dauben and Templeton.[15b] The function minimized during the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ is the observed structure amplitude, $|F_c|$ is the calculated structure amplitude, and w is the weighting factor.

Four cycles of full-matrix least-squares refinement of the scale factor and positional and isotropic thermal parameters for all atoms, excluding hydrogens, led to a discrepancy index of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.089$. The weighted residual, $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$, using unit weights was 0.095. At this point, absorption corrections and an experimental weighting scheme similar to that of Doedens and Ibers[16] ($w = [\sigma(F)]^{-2}$) were introduced. A difference Fourier map using only the low-angle data ($(\sin \theta)/\lambda \leq 0.40$) revealed all 29 hydrogen atoms. The next cycle of refinement of all parameters for the 67 atoms showed the hydrogen atoms to be refining reasonably. The yttrium atom was next assigned an anisotropic temperature factor of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, and two final cycles of refinement of positional and thermal parameters for all atoms resulted in convergence with $R_1 = 0.059$ and $R_2 = 0.083$. An R factor test[17] validated both the anisotropic model and the model including the hydrogen atoms at the 99.5% confidence level.

During the last cycle of refinement, no positional or thermal parameter shifted more than one-fourth or one-half, respectively, of its estimated standard deviation. A final difference Fourier map computed at this point showed a peak of 0.90 e$^-$/Å^3 in the vicinity of a methyl group. All other peaks were less than 0.72 e$^-$/Å^3 and could readily be attributed to anisotropic motion of the light atoms. The error introduced into the model by our neglect of the vibration (anisotropic refinement of all atoms was beyond the capacity of the IBM 360-65 computer used) was also reflected by the final standard deviation for an observation of unit weight being 2.09, higher than the expected value of unity. Our experimental weighting scheme satisfied Cruickshank's criterion,[18] and a comparison of the observed and final calculated structure amplitudes did not suggest that a correction for extinction was necessary.

The following programs for the IBM 7094 and 360 computers were used in the structure analysis and interpretation: (1) a modified version of D. P. Shoemaker, MIT X-ray goniometer package, MIXG-2 (1962); (2) M. J. Bennett, general data reduction program, PMMO; (3) a modified version of A. Zalkin, Fourier analysis program, FORDAP; (4) W. C. Hamilton, absorption correction program, GONO9; (5) C. T. Prewitt, full-matrix crystallographic least-squares program, SFLS5 (1966); (6) J. S. Wood, molecular geometry with estimated standard deviations, MGEOM (1964); (7) D. P. Shoemaker, crystallographic bond distance, bond angle, and dihedral angle program, DISTAN (1963); (8) R. C. Elder, data presentation program, PUBTAB.

Results

Table I lists the observed structure amplitudes, $10|F_o|$, and the final calculated structure amplitudes, $10|F_c|$, each in electrons. The molecular geometry and light-atom numbering scheme are shown in Figure 1, while Figure 2 depicts a selected portion of the crystal structure projected on the ab plane. The final fractional coordinates and thermal parameters for all atoms are given in Table II with the listed standard deviations

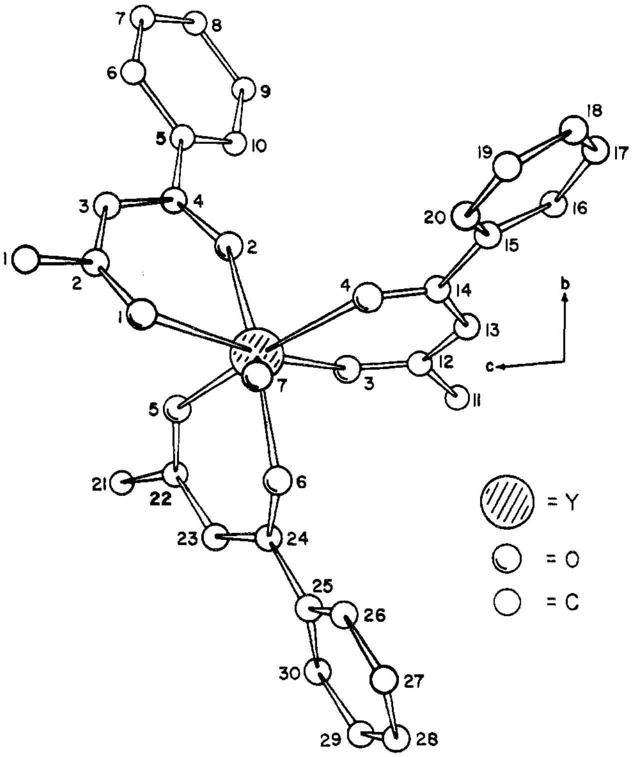

Figure 1.—The molecular structure projected on the bc plane.

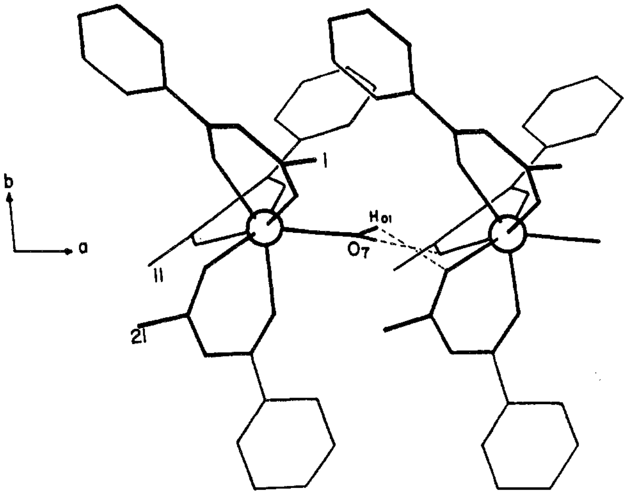

Figure 2.—(001) projection of a selected portion of the crystal structure showing hydrogen bonding parallel to the crystallographic a axis.

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[15] (a) C. T. Prewitt, Ph.D. Thesis, Massachusetts Institute of Technology, 1962, p 163; (b) C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

[16] R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967). Our weighting scheme differs only in that $p = 0.045$.

[17] W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

[18] D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press Inc., New York, N. Y., 1965, p 113.

TABLE II

FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS[a]

Atom	x	y	z	Isotropic B, Å^2	Atom	x	y	z	Isotropic B, Å^2
Y	0.22040 (5)	0.06298 (3)	0.28734 (2)	3.160[b]	C_{28}	0.1915 (12)	−0.4973 (6)	0.1573 (4)	6.96 (13)
O_1	0.4515 (6)	0.1484 (3)	0.3939 (2)	4.84 (6)	C_{29}	0.0214 (11)	−0.4971 (5)	0.1896 (4)	6.68 (13)
O_2	0.0645 (5)	0.2123 (2)	0.3129 (2)	4.39 (5)	C_{30}	−0.0057 (10)	−0.4025 (5)	0.2292 (3)	5.75 (11)
C_1	0.6417 (11)	0.2526 (5)	0.5047 (3)	6.54 (12)	O_7	0.5955 (5)	0.0545 (2)	0.2882 (2)	4.32 (5)
C_2	0.4475 (8)	0.2296 (4)	0.4380 (2)	4.38 (8)	H_3	0.299 (13)	0.356 (6)	0.468 (4)	6.3 (1.2)
C_3	0.2820 (8)	0.2972 (4)	0.4279 (2)	4.46 (8)	H_6	0.120 (8)	0.492 (3)	0.437 (2)	5.1 (7)
C_4	0.0997 (7)	0.2865 (3)	0.3658 (2)	3.66 (7)	H_7	−0.156 (10)	0.603 (5)	0.426 (3)	8.8 (1.2)
C_5	−0.0701 (7)	0.3654 (3)	0.3591 (2)	3.95 (7)	H_8	−0.548 (10)	0.554 (5)	0.336 (3)	8.4 (1.2)
C_6	−0.0276 (9)	0.4643 (4)	0.4029 (3)	5.22 (9)	H_9	−0.588 (8)	0.379 (4)	0.257 (2)	5.7 (9)
C_7	−0.1982 (10)	0.5313 (5)	0.3947 (3)	5.89 (10)	H_{10}	−0.329 (9)	0.266 (4)	0.271 (3)	7.0 (9)
C_8	−0.4009 (11)	0.5020 (5)	0.3451 (3)	6.32 (12)	H_{13}	−0.085 (12)	0.047 (6)	0.036 (4)	6.9 (1.0)
C_9	−0.4429 (11)	0.4020 (5)	0.3005 (3)	6.14 (11)	H_{16}	−0.096 (9)	0.189 (4)	−0.006 (3)	6.6 (1.0)
C_{10}	−0.2755 (9)	0.3355 (4)	0.3076 (3)	4.76 (8)	H_{17}	0.035 (11)	0.318 (5)	−0.082 (3)	8.4 (1.1)
O_3	−0.1271 (5)	0.0098 (2)	0.2034 (2)	4.21 (5)	H_{18}	0.473 (9)	0.407 (4)	−0.038 (3)	7.1 (1.0)
O_4	0.2473 (5)	0.1311 (2)	0.1848 (2)	4.28 (5)	H_{19}	0.725 (10)	0.332 (4)	0.077 (3)	7.6 (1.1)
C_{11}	−0.4230 (10)	−0.0592 (5)	0.0998 (3)	5.83 (11)	H_{20}	0.541 (10)	0.221 (4)	0.138 (3)	7.5 (1.1)
C_{12}	−0.1952 (8)	0.0059 (4)	0.1355 (2)	4.22 (7)	H_{23}	−0.109 (13)	−0.276 (6)	0.328 (4)	6.9 (1.2)
C_{13}	−0.0793 (9)	0.0598 (4)	0.0924 (3)	4.82 (9)	H_{26}	0.455 (11)	−0.239 (5)	0.213 (3)	8.8 (1.3)
C_{14}	0.1275 (7)	0.1266 (3)	0.1206 (2)	3.80 (7)	H_{27}	0.500 (9)	−0.391 (4)	0.139 (3)	6.7 (1.0)
C_{15}	0.2160 (8)	0.1996 (4)	0.0733 (2)	4.35 (8)	H_{28}	0.216 (9)	−0.580 (4)	0.128 (3)	6.6 (1.0)
C_{16}	0.0783 (11)	0.2282 (5)	0.0113 (3)	5.97 (11)	H_{29}	−0.111 (9)	−0.571 (4)	0.186 (3)	7.9 (1.0)
C_{17}	0.1648 (13)	0.3018 (6)	−0.0285 (4)	7.69 (15)	H_{30}	−0.143 (10)	−0.404 (4)	0.252 (3)	8.4 (1.1)
C_{18}	0.3860 (13)	0.3442 (6)	−0.0068 (4)	7.42 (15)	H_{1A}	0.638 (8)	0.304 (4)	0.512 (2)	7.0 (9)
C_{19}	0.5296 (11)	0.3120 (5)	0.0531 (4)	6.65 (3)	H_{1B}	0.773 (8)	0.276 (4)	0.481 (2)	7.7 (8)
C_{20}	0.4428 (9)	0.2413 (4)	0.0939 (3)	5.12 (9)	H_{1C}	0.637 (8)	0.190 (4)	0.517 (2)	6.1 (8)
O_5	0.0256 (5)	−0.0126 (3)	0.3609 (2)	4.52 (6)	H_{11A}	−0.519 (8)	−0.012 (4)	0.094 (2)	8.2 (8)
O_6	0.2307 (6)	−0.1169 (3)	0.2669 (2)	4.58 (6)	H_{11B}	−0.387 (8)	−0.114 (4)	0.113 (2)	7.5 (8)
C_{21}	−0.2128 (10)	−0.1217 (5)	0.4129 (3)	6.02 (11)	H_{11C}	−0.411 (8)	−0.076 (4)	0.059 (3)	6.5 (8)
C_{22}	−0.0613 (8)	−0.1089 (4)	0.3627 (2)	4.26 (8)	H_{21A}	−0.112 (8)	−0.101 (4)	0.447 (3)	5.8 (8)
C_{23}	−0.0274 (8)	−0.2021 (4)	0.3227 (3)	4.65 (8)	H_{21B}	−0.246 (8)	−0.195 (4)	0.410 (2)	7.7 (8)
C_{24}	0.1156 (7)	−0.2022 (3)	0.2771 (2)	3.95 (7)	H_{21C}	−0.344 (9)	−0.127 (4)	0.381 (2)	7.5 (8)
C_{25}	0.1402 (8)	−0.3059 (4)	0.2371 (2)	4.33 (8)	H_{O1}	0.726 (8)	0.074 (4)	0.333 (2)	7.1 (8)
C_{26}	0.3212 (10)	−0.3077 (4)	0.2057 (3)	5.49 (10)	H_{O2}	0.657 (8)	0.041 (4)	0.250 (2)	6.8 (8)
C_{27}	0.3447 (12)	−0.4032 (5)	0.1670 (4)	6.79 (13)					

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digit listed. [b] The value of B is the equivalent isotropic thermal parameter corresponding to the anisotropic thermal vibration tensor having the following components: β_{11}, 0.01634 (10); β_{12}, 0.00608 (3); β_{33}, 0.00252 (1); β_{12}, 0.00137 (3); β_{13}; 0.00168 (2); β_{23}, 0.00036 (1).

being derived from the inverse matrix of the final least-squares refinement cycle. The hydrogen atoms are labeled according to the light atoms to which they are bonded (*i.e.*, H_3 is bonded to C_3, H_{11A} to C_{11}, and H_{O1} to O_7). Pertinent intramolecular dimensions are listed in Tables III and IV, and Table V summarizes the characteristic parameters of the coordination polyhedron. The best weighted least-squares planes through portions of the molecule are given in Table VI.

Discussion

The racemic crystal structure of $Y(BZA)_3 \cdot H_2O$ is built up by staggered molecular chains (each chain containing only one enantiomer) running parallel to the crystallographic *a* axis. Moreover, there is distinct evidence for intermolecular hydrogen bonding in this direction as illustrated in Figure 2. The pertinent geometry involving the water of hydration (H_{O1}–O_5' = 2.23 Å, O_7–O_5' = 2.93 Å, O_7–H_{O1}–O_5' = 126°, and H_{O2}–O_3' = 1.86 Å, O_7–O_3' = 2.73 Å, O_7–H_{O2}–O_3' = 157°—where primes denote translationally related atoms) is comparable with other O–H···O configurations in hydrogen-bonded crystals.[19] Other interactions involving H_{O1} and H_{O2} can be regarded as normal van der Waals contacts. The packing of the molecules in the other lattice directions is dictated in large part by intermolecular interactions of the bulky phenyl groups, and these contacts appear to be normal.

The molecular structure, illustrated in Figure 1, shows the yttrium atom to be seven-coordinate, as expected. Since even the more symmetrical of the possible seven-coordinate geometries[20] differ but little from one another and conformational interconversions require relatively slight angular changes, the geometry observed for any actual molecule may be in large measure a reflection of constraints placed on the complex by ligand steric requirements and packing considerations. Nevertheless, in the present instance the coordination polyhedron of oxygen atoms about the central metal atom may be adequately described as a distorted monocapped octahedron (idealized C_{3v} (3m) symmetry). The oxygen atom of the water of hydration (Y–O_7 = 2.341 (3) Å) lies 1.73 Å above the center of one face of the distorted octahedron consisting of the six oxygen atoms from the β-diketonate ligands which are nearly equidistant from the yttrium atom (average Y–O_{1-6} = 2.28 (1) Å). The octahedron is

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(19) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p 259.

(20) *Cf.* E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967), for a complete discussion of these idealized geometries.

Table III

Intramolecular Distances in $Y(BZA)_3 \cdot H_2O$[a]

Ligand 1		Ligand 2		Ligand 3		Weighted Averages	
Atoms	Distance(Å)	Atoms	Distance (Å)	Atoms	Distance(Å)	Atoms[b]	Distance(Å)
$Y-O_1$	2.268(3)	$Y-O_3$	2.325(3)	$Y-O_5$	2.293(3)		
$Y-O_2$	2.260(3)	$Y-O_4$	2.265(3)	$Y-O_6$	2.248(3)		
O_1-C_2	1.264(6)	O_3-C_{12}	1.263(5)	O_5-C_{22}	1.268(5)	O-C	1.267(2)
O_2-C_4	1.266(5)	O_4-C_{14}	1.264(5)	O_6-C_{24}	1.276(5)		
C_2-C_3	1.388(7)	$C_{12}-C_{13}$	1.406(7)	$C_{22}-C_{23}$	1.396(7)	C_m-C	1.399(3)
C_3-C_4	1.405(6)	$C_{13}-C_{14}$	1.399(7)	$C_{23}-C_{24}$	1.403(7)		
C_1-C_2	1.499(8)	$C_{11}-C_{12}$	1.508(8)	$C_{21}-C_{22}$	1.521(8)	C_t-C	1.503(3)
C_4-C_5	1.510(6)	$C_{14}-C_{15}$	1.507(6)	$C_{24}-C_{25}$	1.482(6)		
C_5-C_6	1.384(7)	$C_{15}-C_{16}$	1.385(8)	$C_{25}-C_{26}$	1.409(7)	C_p-C_p	1.389(2)
C_6-C_7	1.407(8)	$C_{16}-C_{17}$	1.399(9)	$C_{26}-C_{27}$	1.384(9)		
C_7-C_8	1.359(9)	$C_{17}-C_{18}$	1.359(11)	$C_{27}-C_{28}$	1.391(10)		
C_8-C_9	1.403(9)	$C_{18}-C_{19}$	1.391(10)	$C_{28}-C_{29}$	1.358(10)		
C_9-C_{10}	1.388(8)	$C_{19}-C_{20}$	1.391(8)	$C_{29}-C_{30}$	1.391(9)		
$C_{10}-C_5$	1.388(7)	$C_{20}-C_{15}$	1.387(7)	$C_{30}-C_{25}$	1.395(7)		
C_1-H_{1A}	0.65(5)	$C_{11}-H_{11A}$	0.88(5)	$C_{21}-H_{21A}$	0.78(5)		
C_1-H_{1B}	1.06(5)	$C_{11}-H_{11B}$	0.79(5)	$C_{21}-H_{21B}$	0.90(5)		
C_1-H_{1C}	0.84(5)	$C_{11}-H_{11C}$	0.82(5)	$C_{21}-H_{21C}$	0.88(5)		
C_3-H_3	0.99(6)	$C_{13}-H_{13}$	1.08(6)	$C_{23}-H_{23}$	1.03(6)	C-H	1.09(1)
C_6-H_6	0.98(4)	$C_{16}-H_{16}$	1.09(5)	$C_{26}-H_{26}$	1.10(6)		
C_7-H_7	0.99(6)	$C_{17}-H_{17}$	1.19(7)	$C_{27}-H_{27}$	1.22(5)		
C_8-H_8	1.17(6)	$C_{18}-H_{18}$	1.20(5)	$C_{28}-H_{28}$	1.18(5)		
C_9-H_9	1.05(5)	$C_{19}-H_{19}$	1.17(6)	$C_{29}-H_{29}$	1.15(5)		
$C_{10}-H_{10}$	1.03(5)	$C_{20}-H_{20}$	0.98(6)	$C_{30}-H_{30}$	1.05(6)		

Atoms	Distance(Å)
$Y-O_7$	2.341(3)
O_7-H_{O1}	1.01(5)
O_7-H_{O2}	0.92(5)

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digits listed. [b] Carbon atom subscripts are: m, methylene; t, terminal; p, phenyl.

distorted mainly by a spreading apart of the three atoms (O_1, O_4, and O_6) defining the capped face. As a result, the yttrium atom is 0.33 Å below the best $O_1-O_5-O_3-O_4$ plane, and the angles O_1-Y-O_7, O_4-Y-O_7, and O_6-Y-O_7 increase to 70.2, 76.8, and 76.9°, respectively, from the idealized 54.7°. Moreover, the angles O_1-Y-O_4, O_1-Y-O_6, and O_4-Y-O_6 expand to 117.9, 115.0, and 106.3, while O_2-Y-O_3, O_2-Y-O_5, and O_3-Y-O_5 contract to 83.1, 83.8, and 80 8°, respectively. Doubtless, the chelating ligand requirement of an O-O distance in the range of 2.7 Å (the mean of the actual distances is 2.76 Å) also contributes to the distortion of the polyhedron whose dimensions are given more fully in Table V.

A similar type of sevenfold coordination for a lanthanide ion has recently been reported for tris(diphenylpropanedionato)aquoholmium.[21] In this structure, the water molecule (with presumed disordering of the hydrogen atoms) is located on a crystallographic threefold axis passing through the holmium atom, and the six oxygen atoms from the symmetric ligands are at the corners of an octahedron which also has undergone substantial trigonal distortion. For the $Y(BZA)_3 \cdot H_2O$ molecule as a whole, however, there is no threefold axis because one of the asymmetric β-diketonate ligands (C_{1-10}) reverses its mode of chelation as may be seen in Figure 1. This structural feature probably reflects both intra- and intermolecular packing requirements. Because of the lability of lanthanide β-diketonate systems in solution,[9] it is probable that the observed solid-state configuration of this complex is by no means the only one to be found in solutions of the compound.

Bond distances and angles within the chelate rings show excellent agreement with the average values for other β-diketonate structures which have been accurately determined by three-dimensional methods.[22,23] Each of the three ligand fragments ($C_{n1}-C_{n2}-O-C_{n3}-C_{n4}-O-C_{n5}$, where $n = 0, 1, 2$) is essentially planar but makes a dihedral angle with the plane of the O-Y-O group. This kind of folding along the O-O line is often found in these chelate rings.[24] The dihedral angles between the ligand planes and the planes defined by the appropriate O-Y-O groups are 4.4, 7.0, and 12.7°, as outlined in Table VI. To minimize further intermolecular repulsions and to aid packing, the three planar phenyl rings are not coplanar with the remainders of the chelate rings to which they belong but are instead tilted by 16.0, 21.7, and 15.6°.

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TABLE IV

BOND ANGLES IN $Y(BZA)_3 \cdot H_2O$[a]

Ligand 1		Ligand 2		Ligand 3		Weighted Averages	
Atoms	Angle(°)	Atoms	Angle(°)	Atoms	Angle(°)	Atoms[b]	Angle(°)
O_1-Y-O_2	75.0(0.1)	O_3-Y-O_4	73.7(0.1)	O_5-Y-O_6	75.3(0.1)	O-Y-O	74.7(0.1)
Y-O_1-C_2	135.4(0.3)	Y-O_3-C_{12}	133.8(0.3)	Y-O_5-C_{22}	133.3(0.3)		
Y-O_2-C_4	136.1(0.3)	Y-O_4-C_{14}	137.8(0.3)	Y-O_6-C_{24}	134.7(0.3)		
O_1-C_2-C_3	124.9(0.4)	O_3-C_{12}-C_{13}	125.2(0.4)	O_5-C_{22}-C_{23}	125.1(0.4)	O-C-C_m	124.5(0.2)
O_2-C_4-C_3	123.8(0.4)	O_4-C_{14}-C_{13}	123.8(0.4)	O_5-C_{24}-C_{23}	124.1(0.4)		
C_2-C_3-C_4	124.3(0.4)	C_{12}-C_{13}-C_{14}	123.2(0.4)	C_{22}-C_{23}-C_{24}	124.3(0.4)	C-C_m-C	123.9(0.2)
O_1-C_2-C_1	115.4(0.4)	O_3-C_{12}-C_{11}	116.1(0.4)	O_5-C_{22}-C_{21}	116.3(0.4)	O-C-C_t	115.7(0.2)
O_2-C_4-C_5	115.6(0.4)	O_4-C_{14}-C_{15}	116.7(0.6)	O_6-C_{24}-C_{25}	115.8(0.4)		
C_1-C_2-C_3	119.7(0.4)	C_{11}-C_{12}-C_{13}	118.7(0.4)	C_{21}-C_{22}-C_{23}	118.6(0.4)	C_t-C-C_m	119.6(0.2)
C_3-C_4-C_5	120.6(0.4)	C_{13}-C_{14}-C_{15}	119.5(0.4)	C_{23}-C_{24}-C_{25}	120.2(0.4)		
C_4-C_5-C_6	122.1(0.4)	C_{14}-C_{15}-C_{16}	122.4(0.4)	C_{24}-C_{25}-C_{26}	118.6(0.4)		
C_4-C_5-C_{10}	118.0(0.4)	C_{14}-C_{15}-C_{20}	118.5(0.4)	C_{24}-C_{25}-C_{30}	123.5(0.4)		
C_5-C_6-C_7	118.4(0.5)	C_{15}-C_{16}-C_{17}	120.5(0.6)	C_{25}-C_{26}-C_{27}	119.4(0.5)	C_p-C_p-C_p	119.9(0.1)
C_6-C_7-C_8	122.1(0.5)	C_{16}-C_{17}-C_{18}	119.9(0.7)	C_{26}-C_{27}-C_{28}	121.5(0.6)		
C_7-C_8-C_9	119.3(0.6)	C_{17}-C_{18}-C_{19}	120.5(0.7)	C_{27}-C_{28}-C_{29}	119.3(0.6)		
C_8-C_9-C_{10}	119.2(0.5)	C_{18}-C_{19}-C_{20}	119.6(0.6)	C_{28}-C_{29}-C_{30}	120.4(0.6)		
C_9-C_{10}-C_5	121.0(0.5)	C_{19}-C_{20}-C_{15}	120.3(0.5)	C_{29}-C_{30}-C_{25}	121.3(0.5)		
C_{10}-C_5-C_6	119.9(0.4)	C_{20}-C_{15}-C_{16}	119.1(0.5)	C_{30}-C_{25}-C_{26}	118.0(0.5)		

Atoms	Angle(°)
H_{O1}-O_7-H_{O2}	106(4)

[a] Numbers in parentheses are the estimated standard deviations occurring the last digits listed. [b] Carbon atom subscripts are: m, methylene; t, terminal, p, phenyl.

TABLE V

CHARACTERISTIC PARAMETERS OF THE COORDINATION POLYHEDRON

Atoms	Dist, Å[a]	Atoms	Angle, deg[b]
O_1–O_2	2.756 (5)	O_1–O_5–O_3	96.1
O_3–O_4	2.754 (4)	O_5–O_3–O_4	101.0
O_5–O_6	2.774 (4)	O_3–O_4–O_1	82.9
O_1–O_4	3.884 (4)	O_4–O_1–O_5	78.9
O_1–O_5	3.024 (5)	O_1–O_2–O_4	82.8
O_5–O_3	2.993 (4)	O_5–O_2–O_3	59.0
O_2–O_3	3.042 (4)	O_1–O_6–O_4	63.1
O_2–O_5	3.040 (4)	O_5–O_6–O_3	63.0
O_2–O_4	3.104 (4)		
O_6–O_1	3.808 (5)	O_1–Y–O_7	70.2
O_6–O_4	3.611 (4)	O_4–Y–O_7	76.8
O_6–O_3	2.948 (4)	O_6–Y–O_7	76.9
O_1–O_7	2.653 (4)	O_1–Y–O_4	117.9
O_4–O_7	2.861 (4)	O_1–Y–O_6	115.0
O_6–O_7	2.855 (4)	O_4–Y–O_6	106.3
		O_2–Y–O_3	83.1
		O_2–Y–O_5	83.8
		O_3–Y–O_5	80.8
		O_2–Y–O_6	155.0

[a] Numbers in parentheses are estimated standard deviations occurring in the last digits listed. [b] All angles have estimated standard deviations of 0.1°.

TABLE VI

BEST WEIGHTED LEAST-SQUARES PLANES[a] AND DIHEDRAL ANGLES

Atoms	Plane	L	M	N	D	Mean dev, Å
YO_1O_2	1	−0.6968	−0.5196	0.4945	2.6719	0.00
$O_1O_2C_{1-5}$	2	−0.6850	−0.5773	0.4444	0.2596	0.01
C_{5-10}	3	−0.5620	−0.4794	0.6740	3.8796	0.01
YO_3O_4	4	−0.4142	0.8559	0.3096	1.7777	0.00
$O_3O_4C_{11-15}$	5	−0.4947	0.8408	0.2198	1.4873	0.08
C_{15-20}	6	−0.3598	0.7469	0.5591	2.0492	0.01
YO_5O_6	7	0.6742	−0.0739	0.7349	3.8085	0.00
$O_5O_6C_{21-25}$	8	0.5839	−0.2746	0.7640	4.3530	0.02
C_{25-30}	9	0.3631	−0.4186	0.8325	5.3509	0.01
$O_1O_3O_4O_5$	10	−0.5159	0.8450	0.1410	1.2210	0.10
$O_1O_4O_6$	11	0.9803	0.1883	0.0599	−0.1409	0.00

Planes	Dihedral angle, deg	Planes	Dihedral angle, deg
1–2	4.4	2–3	16.0
4–5	7.0	5–6	21.7
7–8	12.7	8–9	15.6

[a] The equations of the planes are $LX + MY + NZ = D$ in orthogonal coordinates. The matrix to transform from triclinic to orthogonal coordinates is

$$\begin{matrix} 6.1761 & -0.6854 & 0.0 \\ 0.0 & 12.4620 & 0.0 \\ -5.1970 & -1.8889 & 18.4899 \end{matrix}$$

and $X = ax$, $Y = by$, $Z = cz$.

Finally, in comparison with other yttrium β-diketonate structures, it should be noted that the average yttrium–chelate oxygen distance in $Y(BZA)_3 \cdot H_2O$ of 2.28 (1) Å reflects, in part, the expected bond shortening due to a change in the coordination polyhedron about yttrium. For the distorted square-antiprismatic coordination observed[25] in $Y(C_5H_7O_2)_3 \cdot 3H_2O$, the corresponding distance is 2.366 Å, while for the dodecahedral eightfold coordination found[10] in $Cs[Y(CF_3COCHCOCF_3)_4]$, the mean Y–O distance is 2.323 (8) Å.

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