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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE HEPTADENTATE COORDINATION COMPLEX TRIS(DIPHENYLPROPANEDIONATO) AQUOHOLMIUM, $\text{Ho}(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)_3 \cdot \text{H}_2\text{O}$

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CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT
OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720

The Crystal and Molecular Structure of the Heptadentate Coordination Complex

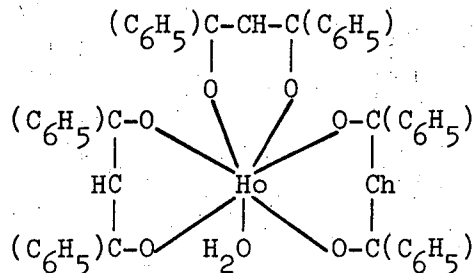
Tris(diphenylpropanedionato)aquoholmium, $\text{Ho}(\text{C}_6\text{H}_5\text{COCHCO}_6\text{H}_5)_3 \cdot \text{H}_2\text{O}^1$

BY ALLAN ZALKIN, DAVID H. TEMPLETON, AND DAVID G. KARRAKER²

$\text{Ho}(\text{C}_6\text{H}_5\text{COCHCO}_6\text{H}_5)_3 \cdot \text{H}_2\text{O}$, tris(diphenylpropanedionato)aquoholmium, crystallizes in space group R3 with one molecule per rhombohedral cell. The dimensions of the triply primitive hexagonal cell are $a = 22.713$ and $c = 6.334 \text{ \AA}$. The measured density is 1.48 g/cc; the calculated X-ray density is 1.50 g/cc. The structure was determined from measurements with Cu K α radiation of 1365 independent (in the sense of the point group) reflections, including 120 Friedel pairs. It was refined to $R = 0.031$ with anisotropic temperature factors on all but the hydrogen atoms. The holmium atom, on the three-fold axis, has a novel seven-fold coordination. The six oxygen atoms of the diphenylpropanedionato ligand are at distances 2.275 and 2.305 \AA from holmium at the corners of an octahedron which has substantial trigonal distortion. The water molecule, on the three-fold axis, is 2.39 \AA from holmium and caps the above octahedron; its hydrogen atoms are presumed to be in disordered positions. The molecule as a whole has the appearance of a three-bladed propeller, each blade of which consists of a planar six-membered ring consisting of a holmium, two oxygen, and three carbon atoms; the planes of the two phenyl groups are twisted by ten and nineteen degrees to the above plane.

Introduction

Holmium in the trivalent state, like other rare earth elements, reacts with dibenzoylmethane³ to form a complex with the structure:



The water molecule is known to be firmly bound, and Hoard⁴ in 1961 suggested this heptadentate structure for some similar complexes. The structure determination was undertaken in order to ascertain the coordination geometry about the holmium atom, and to investigate the nature of the hydration of the water molecule in this material. Recently the structure of tris(1-phenyl-1,3-butanedionato)aqueoyttrium⁵ was reported which also has this same seven-fold coordination. The results of the two determinations are in excellent agreement.

Experimental

$\text{Ho(C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5\text{)}_3 \cdot \text{H}_2\text{O}$ was prepared by adding holmium trichloride to a refluxing mixture of dibenzoylmethane, acetone, and potassium hydroxide. Yellow crystals of the compound crystallized from the filtered and cooled solution. This procedure is from preparation No. 17 as described by Melby et al.³

A crystal fragment of dimensions 0.15 × 0.15 × 0.10 mm was cleaved from a needle and glued to a pyrex fiber. A preliminary set of Weissenberg

films had shown the crystal to be rhombohedral with the fiber parallel to the hexagonal c axis. Cell dimensions were measured using a G.E. XRD-5 X-ray diffraction apparatus equipped with a quarter-circle Eulerian cradle and a molybdenum anode tube, ($\lambda_{K\alpha 1} = 0.70926 \text{ \AA}$, $\lambda_{K\alpha 2} = 0.71354 \text{ \AA}$, and $\lambda_{K\beta} = 0.632253 \text{ \AA}$). Cell dimensions were determined from a series of 2θ measurements along the hexagonal $00l$ and $h00$ directions using peaks where $K\beta$, $K\alpha 1$, and $K\alpha 2$ X-rays were resolved. All measurements were made at room temperature, i.e., $\sim 23^\circ$.

The crystal was transferred to a quarter-circle type automatic G.E. diffractometer. The intensity measurements were made using a Cu anode X-ray tube set at a take-off angle of 2° and operated at 35 kvp and 20 ma. The diffracted beam was filtered by a Ni foil just ahead of the scintillation counter. The θ - 2θ scanning technique was used; scanning began at 0.6° in 2θ ahead of the $K\alpha 1$ position and continued to 0.6° beyond the $K\alpha 2$ position at a rate of $1^\circ/\text{min}$. Backgrounds were taken at 0.4° ahead of and beyond the scan limits. The net intensity I was then calculated to be

$$I = C - (B_1 + B_2)(T_c / 2T_b) .$$

C is the total counts in the scan time T_c . B_1 and B_2 are the two stationary backgrounds which were each counted for $T_b = 10$ seconds. The data included 1366 independent reflections. Fourteen intensities were less than their estimated standard deviations, of which two were actually recorded as zero. One reflection, $(24, -12, 3)$, was deleted from the data set due to a recording error by the automatic diffractometer, i.e., a background was erroneously

recorded as zero. As the diffractometer was no longer functioning at the time of this discovery, we did not remeasure this datum. The final results are based on 1365 independent reflections. In this data set there are 120 Friedel pairs, i.e., $h,k,0$ and $h+k,\bar{h},0$ sets. The data were corrected for Lorentz and polarization effects. No correction was made for absorption. The absorption coefficient for Cu $K\alpha$ X-rays is $\mu = 44 \text{ cm}^{-1}$, and $\mu R \approx 0.3$. The error in the data is estimated to be about 20% for the extreme situation.

The standard deviations of the intensities and the structure factors were estimated as follows. The standard deviation of I is

$$\sigma(I) = [C + (\tau_c/2\tau_b)^2 (B_1 + B_2) + (qI)^2]^{1/2},$$

where q is an arbitrary fraction of the intensity which has been included to account for such non-random errors in the data as absorption, extinction, and the lack of stability of the electronic circuits of the instrument. The standard deviation of the structure factor is taken as

$$\sigma(F) = F_0 - \sqrt{(F_0^2 - s\sigma(I)/L_p)},$$

where s is the scaling factor in the equation, $F_0 = \sqrt{(sI/L_p)}$. For the reflections where $I \leq \sqrt{\sigma(I)}$, $\sigma(F) = \sqrt{(s\sigma(I)/L_p)}$. L_p is the Lorentz-polarization factor.

Our unpublished full-matrix least-squares program minimizes the function R_2 , where $R_2 = \sum_w (\Delta F)^2 / \sum_w F_0^2$; F_0 and F_c are the observed and calculated structure factors, and ΔF is the difference of their magnitudes.

The weighting factor w is $1/\sigma^2(F)$. The program accommodates both the real and imaginary parts of the dispersion correction.

Scattering factors for neutral holmium, carbon, oxygen, and hydrogen atoms were used.^{6,7} The real and imaginary dispersion corrections for holmium are -14.02 and 3.52 electrons respectively.⁸ The anisotropic temperature factor has the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. B_{ij} values in Å^2 units are reported for the thermal parameters:

$$B_{ij} = 4\beta_{ij}/a_i^* a_j^*, \text{ where } a_i^* \text{ is the } i\text{th reciprocal cell length.}$$

Results

Unit Cell and Space Group.---The space group is R3 and contains a single formula unit in the unit cell. The cell dimensions of the triply primitive hexagonal cell at 23° are: $a_h = 22.713 \pm 0.012$ and $c_h = 6.334 \pm 0.004$ Å; the errors are subjective estimates. The observed density from flotation in a mixture of ethylene dichloride and carbon tetrachloride at 25° is 1.48 g/cc, and the calculated X-ray density is 1.501 g/cc.

Determination of the Structure.---The holmium atom is in the special position (0,0,z). As the space group is polar, the origin was arbitrarily placed at the Ho atom, i.e., $z = 0.0$. A Fourier summation phased by Ho, all signs positive, was calculated, but because the holmium structure is centric this function shows two images of the structure. Some of the largest peaks were selected and their positions refined by least-squares using isotropic temperature factors. Atoms were rejected if their thermal parameters became

excessively large. This procedure resulted in a structure of eight atoms in addition to holmium which refined to $R = 0.25$, where $R = \Sigma |\Delta F| / |F_o|$. A second Fourier was calculated using structure factors phased on the above results, and the same procedure was continued. A total of fifteen atoms were deduced and the structure at this point refined to an R value of 0.14. Unfortunately the structure did not make chemical sense, and a third Fourier based on these latest results was calculated. We arrived at the final trial structure by shifting some atoms to their inverse position such that the resulting molecule made chemical sense. This final trial structure refined to an R value of 0.10.

The above calculations were performed with the 120 Friedel pairs averaged together according to the Laue symmetry. The averaging was undone, and a least squares refinement of the structure with this expanded data, but without the imaginary anomalous dispersion term included for holmium, yielded an R value of 0.099; the inclusion of this term reduced R to 0.097. Anisotropic temperature factors on holmium further reduced R to 0.065; and the application of anisotropic temperature factors to the carbon and oxygen atoms lowered R to 0.036.

A difference Fourier was calculated to search for hydrogen atoms. A peak of significant electron density, 0.16 to 0.34 electrons, was found nearby every location where a hydrogen atom was calculated to be. There were many spurious peaks in the map as well which had electron densities comparable to the hydrogen peaks. An attempt to refine the hydrogens on the carbon atoms was partially successful. Several of the temperature factors went to fairly high values, and H(6) moved to within 0.4 angstroms of C(6). We finally

decided to put each hydrogen atom in at a calculated location of 1.0 angstrom away from its associated carbon atom. Isotropic temperature factors were assigned that gave each hydrogen atom the comparable average mean-square displacement of the carbon atom it was bonded to. The hydrogen atoms associated with the water molecule are disordered according to a symmetry argument, i.e., the water oxygen atom is on a three-fold axis. The difference Fourier shows a ring of electron density that peaks at (0.01, -0.01, 0.49) with a value of 0.22 electrons. This is an appropriate location for these hydrogen atoms, but no attempt was made to refine them, as we have no convenient way of handling this type of disorder in our least-squares program.

The concluding refinements of the structure resulted in a final R factor of 0.031 using all 1365 data. The weighted R factor, R_2 , was 0.039. The standard deviation of an observation of unit weight was 1.14. The maximum shift of any parameter was less than two percent of its standard deviation after the last cycle. The list of observed and calculated structure factors are shown in Table I, the final positional parameters are shown in Table II, the anisotropic thermal parameters in Table III, and the assumed isotropic thermal parameters for hydrogen in Table IV.

A refinement of the inverse structure resulted in an increase in both R and R_2 to 0.046 and 0.062 respectively. This is confirmation that the absolute configuration of the molecule in this particular crystal is correct. We have not made a correlation of the absolute configuration with respect to morphology or any other physical property.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS IN TRIS(DIPHENYLPROPANEDIONATO)AQUOHOLMIUM

OBSERVED AND CALCULATED STRUCTURE FACTORS OF TRIS(DIPHENYLPROPANEDIONATO)AQUOHOLMIUM. FCA(10,0,1) = 3834

Table with multiple columns containing numerical data for observed and calculated structure factors. The data is organized in a grid-like format with various sub-headers and values.

TABLE II
POSITIONAL PARAMETERS^a

ATOM	X	Y	Z
HO	.0000(*0) ^b	.0000(*0) ^b	.0000(*0) ^c
H2O	.0000(*0) ^b	.0000(*0) ^b	.3771(8)
O(1)	.0670(2)	-.0170(2)	-.2373(6)
O(2)	.1090(2)	.0724(2)	.1015(6)
C(1)	.1305(2)	.0073(2)	-.2610(7)
C(2)	.1801(2)	.0583(3)	-.1378(9)
C(3)	.1681(3)	.0892(2)	.0330(8)
C(4)	.1517(2)	-.0224(2)	-.4359(8)
C(5)	.2166(4)	-.0029(7)	-.4883(22)
C(6)	.2336(4)	-.0287(7)	-.6544(24)
C(7)	.1887(4)	-.0758(4)	-.7747(15)
C(8)	.1244(4)	-.0916(5)	-.7455(17)
C(9)	.1071(3)	-.0640(4)	-.5786(14)
C(10)	.2268(3)	.1450(2)	.1486(9)
C(11)	.2183(4)	.1619(3)	.3491(10)
C(12)	.2722(5)	.2152(4)	.4598(13)
C(13)	.3360(5)	.2511(4)	.3601(17)
C(14)	.3450(4)	.2339(3)	.1718(16)
C(15)	.2918(3)	.1817(3)	.0587(12)
H(2)	.2300(*0)	.0740(*0)	-.1740(*0)
H(5)	.2520(*0)	.0310(*0)	-.3920(*0)
H(6)	.2820(*0)	-.0140(*0)	-.6870(*0)
H(7)	.2020(*0)	-.0960(*0)	-.8920(*0)
H(8)	.0900(*0)	-.1250(*0)	-.8460(*0)
H(9)	.0590(*0)	-.0770(*0)	-.5530(*0)
H(11)	.1720(*0)	.1360(*0)	.4150(*0)
H(12)	.2650(*0)	.2270(*0)	.6060(*0)
H(13)	.3750(*0)	.2890(*0)	.4340(*0)
H(14)	.3910(*0)	.2600(*0)	.1080(*0)
H(15)	.2990(*0)	.1700(*0)	-.0870(*0)

^aStandard deviations appear in parenthesis. An asterisk indicates

a parameter that has not been allowed to refine.

^bSpecial position parameters fixed by symmetry.

^cPolar space group origin fixed at $z = 0.0$ for Ho.

TABLE III
ANISOTROPIC THERMAL PARAMETERS^a

ATOM	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
HO	5.11(2)	5.11(*0) ^b	3.38(2)	2.56(*0) ^b	.00(*0) ^b	.00(*0) ^b
H ₂ O	7.15(20)	7.15(*0) ^b	2.82(21)	3.57(*0) ^b	.00(*0) ^b	.00(*0) ^b
O(1)	4.54(13)	5.58(14)	4.49(14)	2.42(11)	-.41(11)	-1.42(12)
O(2)	5.65(16)	5.74(15)	4.44(15)	2.75(13)	-.87(13)	-1.37(12)
C(1)	4.60(18)	4.57(17)	4.17(17)	2.49(15)	-.55(14)	-.61(14)
C(2)	4.49(19)	5.36(21)	5.52(24)	1.98(17)	-.52(17)	-1.35(18)
C(3)	5.41(21)	4.45(18)	4.31(17)	2.39(16)	-1.25(16)	-.80(15)
C(4)	4.31(18)	4.29(18)	5.52(22)	2.30(15)	-.39(16)	-.97(17)
C(5)	4.70(28)	16.29(86)	17.14(100)	3.33(40)	-1.32(40)	-11.96(86)
C(6)	5.12(30)	16.16(86)	17.74(107)	3.35(41)	.64(44)	-10.74(85)
C(7)	7.11(33)	7.91(36)	9.71(47)	3.93(29)	.83(32)	-3.27(35)
C(8)	7.74(38)	12.17(57)	10.47(57)	5.61(39)	-1.86(36)	-6.70(50)
C(9)	5.79(28)	10.89(47)	9.17(46)	4.48(31)	-1.33(28)	-5.32(41)
C(10)	6.24(25)	4.17(18)	5.36(22)	2.54(18)	-1.72(19)	-.83(17)
C(11)	8.04(34)	7.04(30)	5.68(27)	4.84(28)	-2.57(26)	-2.30(24)
C(12)	11.49(57)	8.67(42)	7.50(38)	7.05(46)	-4.06(41)	-4.11(35)
C(13)	8.74(45)	5.83(29)	11.20(58)	3.58(30)	-5.17(45)	-3.19(35)
C(14)	7.15(34)	5.61(27)	10.47(53)	1.75(25)	-3.69(36)	-1.35(32)
C(15)	6.55(29)	5.30(24)	7.08(33)	1.61(21)	-2.47(26)	-.59(23)

^aStandard deviations appear in parenthesis. An asterisk indicates a parameter that has been restrained.

^bThe symmetry of the special position of Ho and H₂O restrain their thermal parameters as follows: $2B_{12} = B_{22} = B_{11}$, and $B_{23} = B_{33} = 0$.

TABLE IV
ISOTROPIC THERMAL PARAMETERS^a

ATOM	B
H(2)	5.30
H(5)	13.60
H(6)	13.70
H(7)	8.20
H(8)	9.90
H(9)	8.50
H(11)	6.40
H(12)	8.30
H(13)	8.60
H(14)	8.40
H(15)	6.90

^aThese estimated values were not allowed to refine in the least squares.

Description of Structure.--The basic unit in this structure is a unimolecular species that consists of all of the atoms in the chemical formula. A projection of the molecule down the three-fold axis is shown in Fig. 1. The holmium atom, on the three-fold axis is surrounded by a distorted octahedron of six oxygen atoms from the organic ligands and a seventh oxygen from the water. The water oxygen is also on the three-fold axis and caps the expanded triangular face made up of three O(2) oxygen atoms; the O(2)-O(2) distance is 3.78 Å as opposed to an O(1)-O(1) distance of 3.03 Å in the opposing face. A list of some interatomic distances and their standard deviations is shown in Table V. The angles about holmium and water are given in Table VI.

The water molecule sits directly above the holmium atom at a distance of 2.39 Å. It has six oxygen atoms as nearest neighbors; three O(2) atoms 2.80 Å distant which are in the same coordination complex about the holmium, and three O(1) atoms at 3.00 Å distant that are in the adjacent coordination complex. With three-fold symmetry inherent in the water position, it must be concluded that the water hydrogen atoms are disordered. A study of the geometry to the adjacent 3 O(1) atoms at 3.00 Å does not suggest any orderly hydrogen bond schemes for the water, i.e., the O(1)-H₂O-O(1) angles are 61° and are much too tight to be hydrogen bond angles.

The overall complex resembles a right-handed three-bladed propeller, this being the absolute configuration of this particular crystal. The phenyl rings are twisted from the plane of the propanato portion of the complex. The phenyl group consisting of atoms C(4) through C(9) is twisted ~10° from the plane made up of atoms O(1), C(1), and C(2); the phenyl group consisting of atoms C(10) through C(15) is twisted ~19° from the plane defined by O(2), C(3), and C(2). This twisting is discernible in the stereographic picture shown in Fig. 2.

TABLE V

INTERATOMIC DISTANCES IN TRIS(DIPHENYLPROPANEDIONATO)AQUOHOLMIUM^a

Atom	Atom	Dist(Å)	Atom	Atom	Dist(Å)
Ho	- 3 O(2)	2.275(4)	O(2)	- C(1)	2.90(1)
Ho	- 3 O(1)	2.305(7)	C(1)	- C(2)	1.38(1)
Ho	- H ₂ O	2.39(2)	C(1)	- C(4)	1.50(1)
H ₂ O	- 3 O(2)	2.80(1)	C(2)	- C(3)	1.39(1)
H ₂ O	- 3 O(1)	3.00(1)	C(3)	- C(10)	1.49(1)
O(1)	- C(1)	1.27(1)	C(4)	- C(9)	1.33(1)
O(1)	- C(4)	2.35(1)	C(4)	- C(5)	1.35(1)
O(1)	- C(2)	2.35(1)	C(5)	- C(6)	1.35(1)
O(1)	- C(9)	2.76(1)	C(6)	- C(7)	1.29(2)
O(1)	- O(2)	2.77(1)	C(7)	- C(8)	1.33(1)
O(1)	- C(3)	2.91(1)	C(8)	- C(9)	1.38(1)
O(1)	- 2 O(1)	3.03(1)	C(10)	- C(11)	1.37(1)
O(1)	- O(2)	3.10(1)	C(10)	- C(15)	1.40(1)
O(2)	- C(3)	1.27(1)	C(11)	- C(12)	1.41(1)
O(2)	- C(10)	2.36(1)	C(12)	- C(13)	1.41(1)
O(2)	- C(2)	2.35(1)	C(13)	- C(14)	1.30(2)
O(2)	- C(11)	2.78(1)	C(14)	- C(15)	1.40(1)

^aStandard deviations appear in parenthesis.

TABLE VI

HOLMIUM AND WATER CENTERED ANGLES^a

H ₂ O - Ho - O(1)	130.7(2)
H ₂ O - Ho - O(2)	73.6(2)
O(1)- Ho - O(1)	82.1(3)
O(1)- Ho - O(2)	74.6(3)
O(1)- Ho - O(2)	154.7(3)
O(1)- Ho - O(2)	85.1(2)
O(2)- Ho - O(2)	112.4(2)
Ho - H ₂ O - O(1)	144.4(2)
Ho - H ₂ O - O(2)	51.4(2)
O(1)- H ₂ O - O(1)	60.5(3)
O(1)- H ₂ O - O(2)	163.3(2)
O(1)- H ₂ O - O(2)	109.9(3)
O(2)- H ₂ O - O(2)	85.1(3)
O(1)- H ₂ O - O(2)	103.1(3)

^aStandard deviations in parenthesis.

Figure 3 shows the geometry in one blade of the molecule. A least squares plane calculated through the six atoms consisting of O(1), C(1), C(2), C(3), O(2), and Ho, shows that the deviations from this plane are, in order as listed above, -0.01, 0.02, 0.0, -0.02, 0.02, and -0.01 Å respectively.

There is sizeable thermal motion in the two phenyl rings. This is apparent from the thermal parameters, and the stereographic view of the molecule in Fig. 2 gives a picture of the nature of the thermal motion. The phenyl ring consisting of atoms C(4) through C(9) appears to be oscillating in and out of its plane about an axis passing through C(4) and C(7). The other phenyl ring, C(10) through C(11), seems to be vibrating in the plane of the phenyl ring itself. It is not surprising that the bond lengths in these rings are shorter than expected. No correction has been made for this effect in the C-C bond lengths of the phenyl groups, and no effort has been expended to do this as the benzene geometry is well established and is not a significant part of this structure determination.

These results are in excellent agreement with those reported by Cotton and Legzdins⁵ for $Y(C_6H_5COCHCOCH_3) \cdot H_2O$. The chemical difference of the two materials is that one contains an Y atom for a Ho atom, and a methyl group with each phenyl group. In the yttrium compound the complex has no symmetry and all three organic ligands are independently determined. Other than the distances involving the heavy atoms, there are no significant differences in the bond distances and angles in the comparable portions of the two structures. The Ho-H₂O distance is 0.05 Å longer than the Y-H₂O distance, and the ligand Ho-O distances are both 0.02 Å longer than the comparable Y-O distances.

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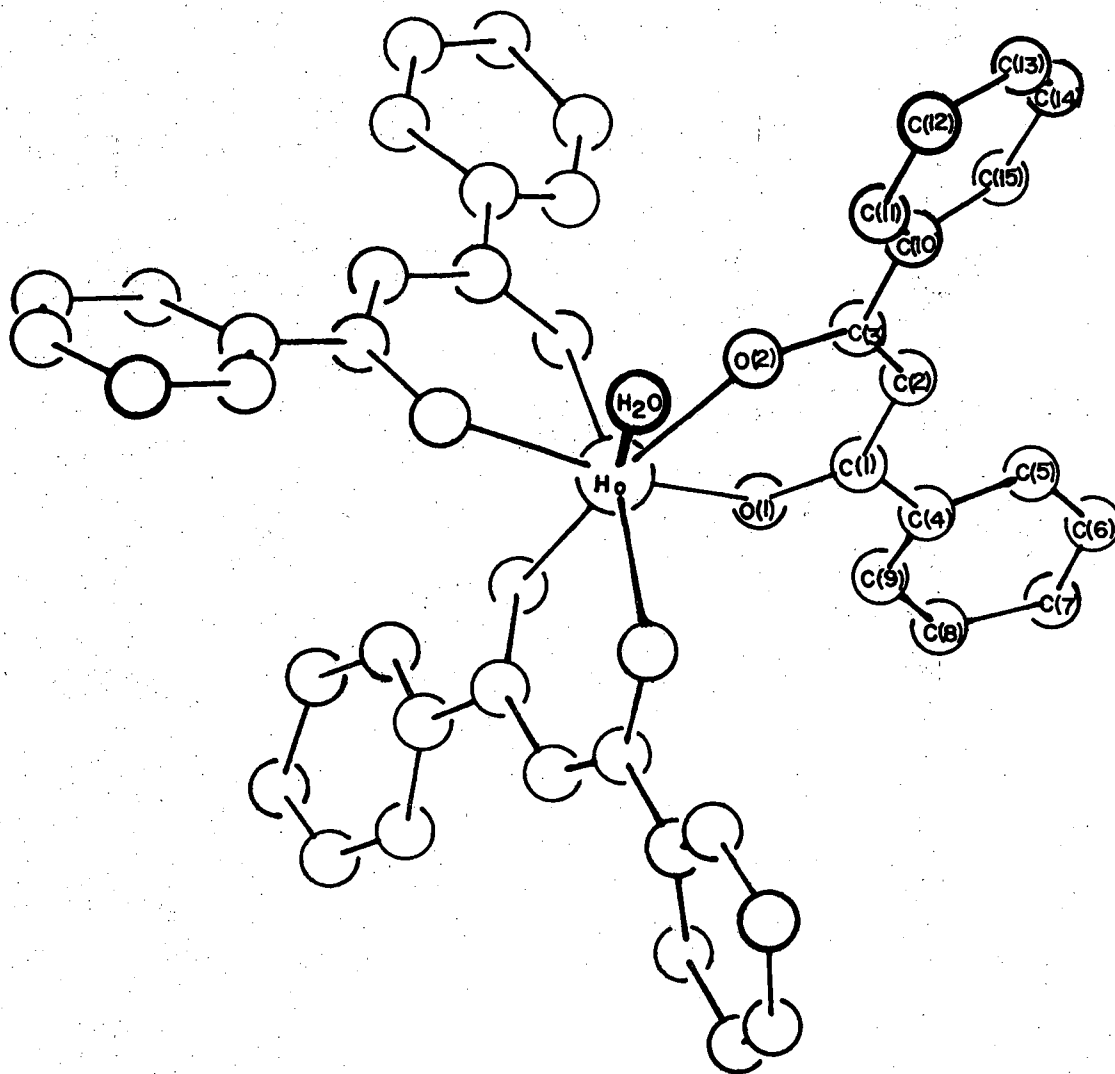
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Figure Captions

Fig. 1. The molecular unit of tris(diphenyl propanedionato)aquoholmium projected down the 3-fold axis. The water molecule is directly above Ho but has been displaced slightly in this drawing to better show the structure off.

Fig. 2. A stereographic pair drawing of the molecule of tris(diphenyl propanedionato)aquoholmium.

Fig. 3. Some distances and angles of the ligands about holmium. The estimated standard deviations of the angles is about 0.5° , and of the distances is about 0.02 A.



XBL 678-4409

Fig. 1

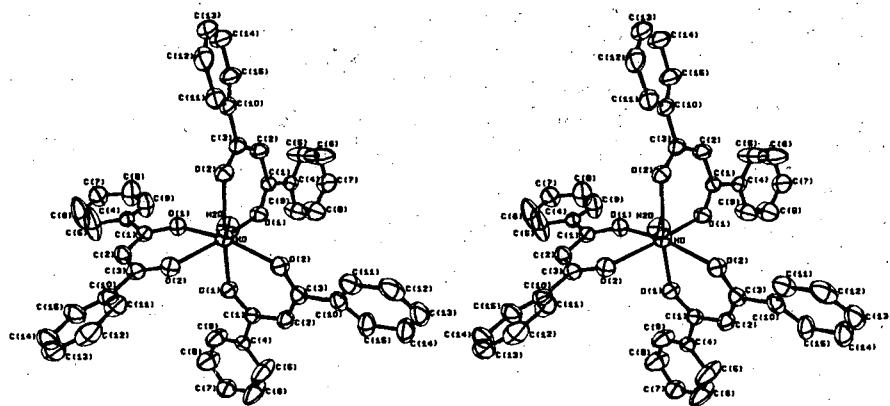
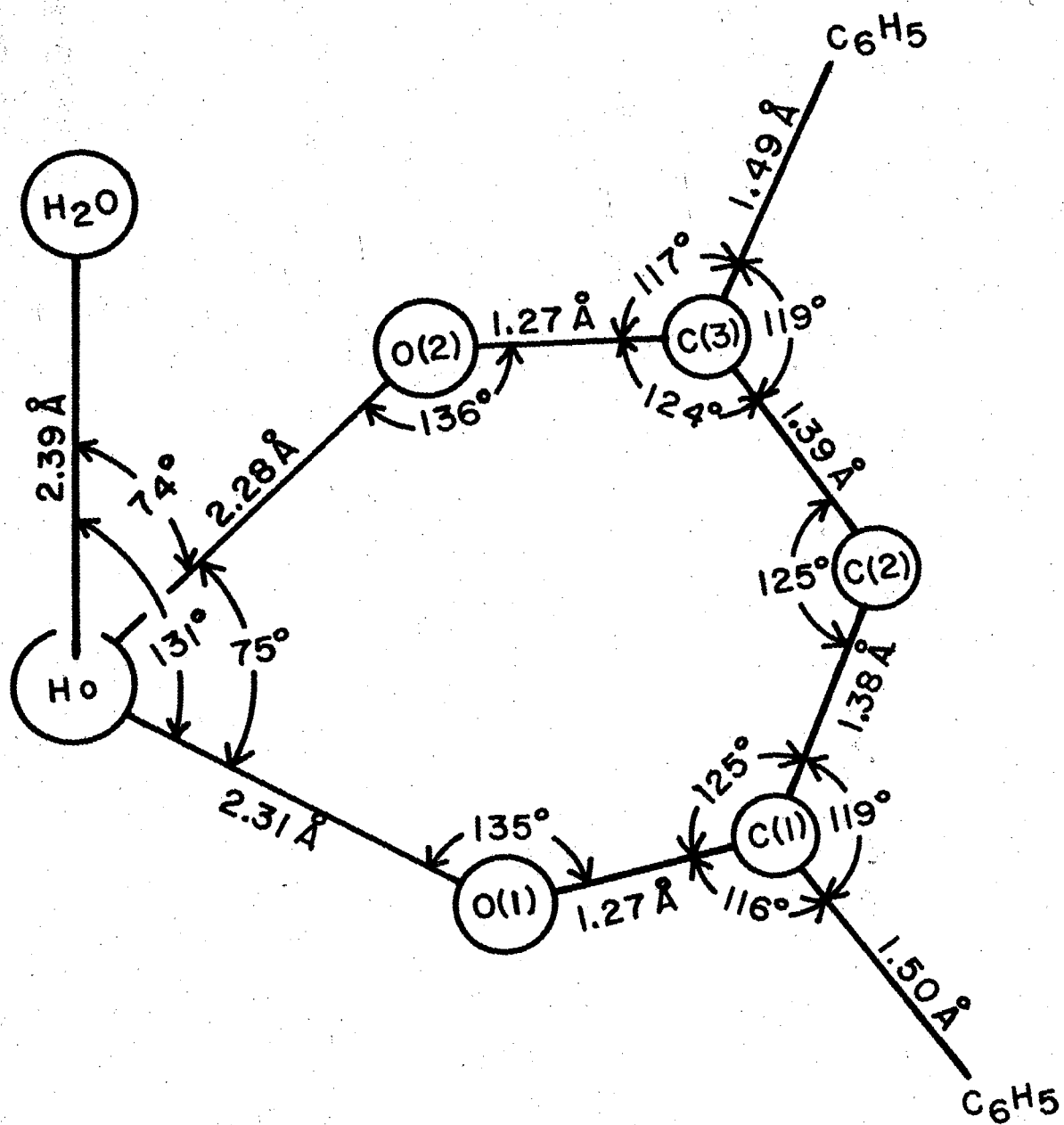


Fig. 2



XBL 6811-6173

Fig. 3

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