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Crystal and Molecular Structure of the Decacoordinate Complex Tris(bicarbonato)tetraaquoholmium(III) Dihydrate, $Ho(H_2O)_4(HCO_3)_3 \cdot 2H_2O$

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The crystal and molecular structure of tris(bicarbonato)tetraaquoholmium(III) dihydrate ($Ho(H_2O)_4(HCO_3)_3 \cdot 2H_2O$, triclinic, $P\bar{1}$, $a = 9.18$ (2) Å, $b = 11.59$ (1) Å, $c = 6.73$ (1) Å, $\alpha = 88.87$ (6)°, $\beta = 112.45$ (8)°, $\gamma = 71.54$ (6)°, $Z = 2$, Mo Kα radiation) has been determined by three-dimensional X-ray analysis. The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares analysis to a final conventional discrepancy factor ($R = [\Sigma ||F_o| - |F_c||]/\Sigma |F_o|$) of 0.039 for 1621 observed reflections ($F_o > 2\sigma_{F_o}$). The holmium moiety containing four coordinated water molecules and three bidentate bicarbonate groups is 10-coordinate and assumes a distorted s-bicapped square-antiprismatic geometry. The average Ho–(H_2O) bond length is 2.36 Å and the Ho–(bicarbonate oxygen) lengths vary from 2.442 (9) to 2.557 (9) Å with the exception of one distance (2.817 (11) Å) which appears to have been lengthened due to steric repulsion effects. Extensive intermolecular hydrogen bonding is also prevalent and has been characterized.

Introduction

Lanthanide chemistry has attracted a great deal of interest recently, due, in no small part, to the capability of the lanthanide metal ions to acquire large coordination numbers. Of considerable interest, then, are the preferred ground-state geometries of some of the higher coordination schemes. As discussed by Muetterties and Wright[1] and by Karraker,[2] there are many factors which govern the formation of high-coordination compounds. One of these is the size of the metal ion; *i.e.* the larger the metal ion, the more likely the formation of a species of high coordination number. Another important consideration is the ligand itself and the constraints it places on the system. As is readily apparent, a multidentate ligand imposes more steric requirements than does a monodentate ligand. And, finally, ligand–ligand repulsions also dictate the geometry of the system and hence the coordination number.

For 10-coordination, two idealized polyhedra consistent with an sp^3d^5f hybridization scheme are the s-bicapped dodecahedron of D_2 symmetry and the s-bicapped square antiprism of D_{4d} symmetry shown in Figure 1. The similarity of the two polyhedra is demonstrated in Figure 2, in which an s-bicapped square antiprism is distorted sufficiently to produce the s-bicapped dodecahedron. Crystallographic studies of 10-coordinate compounds previously reported in the literature were done on the complexes of the larger lanthanide and actinide metals, *e.g.*, La, Ce, and U. The geometries of such compounds approximate both the s-bicapped dodecahedron[3-5] and the s-bicapped square antiprism.[6,7]

In order to determine unequivocally the preferred ground-state geometry for 10-coordination, a compound composed of very small, identical, noninteracting, monodentate ligands surrounding the metal ion in an isolated environment would be required. In the absence of such idealized compounds, one one must examine the structures of 10-coordinate compounds involving a small metal ion bound to the same type of atoms, *e.g.*, oxygen, with the least amount of constraints imposed by the smallest number of bidentate ligands possible. Having the smallest possible number of bidentate ligands thus introduces the fewest geometrical restrictions on the system, and if the bidentate ligands are small, the ligand–ligand repulsions should be reduced. In addition, using a small lanthanide metal ion instead of one of the larger ones implies that the more stable configuration would predominate, since reducing the size of the coordination sphere increases strain on the high-coordination system due to ligand repulsions. Therefore, a sample of tris(bicarbonato)tetraaquoholmium(III) dihydrate ($Ho(H_2O)_4(HCO_3)_3 \cdot 2H_2O$) was prepared for three-dimensional X-ray analysis.

Experimental Section

Preparation. The holmium bicarbonate compound can be prepared in several ways. The two methods employed in this laboratory will be presented here. Starting with an aqueous 1 *M* $HoCl_3 \cdot 6H_2O$ solution, the holmium carbonate was produced by adding Na_2CO_3 to the solution and filtering off the carbonate precipitate. Then by acidifying the carbonate, a bicarbonate was produced and the acid–water azeotrope was boiled off. Slow evaporation of the bicarbonate solution yielded crystals of varying degrees of hydration. A greater yield of the title compound was realized from a rather novel preparation scheme. A 1 *M* $HoCl_3 \cdot 6H_2O$ solution of pH 3 was added to a saturated aqueous solution of sucrose ($C_{12}H_{22}O_{11}$). The resulting acidic solution was heated sufficiently to boil off the HCl-H_2O azeotrope (108.6°), and then additional heating was employed to eliminate the excess water. Gradual degradation of sucrose to bicarbonate in the acidic solution coupled with slow evaporation yielded soft, light orange, prismatic crystals suitable for X-ray analysis.

Crystal Data. A nearly spherical crystal of dimension 0.2 mm was mounted on the end of a glass fiber with Duco cement and was coated with a thin layer of commercial nail polish to isolate it from the atmosphere. From preliminary precession photographs, it was apparent that the compound crystallized in the triclinic crystal system. A least-squares refinement[8] of the six lattice constants based on the $\pm 2\theta$ measurements of 13 strong reflections determined by left–right, top–bottom beam splitting on a previously aligned four-circle diffractometer (Mo Kα radiation, λ 0.71069 Å), at 25°, yielded $a = 9.18 \pm 0.02$ Å, $b = 11.59 \pm 0.01$ Å, $c = 6.73 \pm 0.01$ Å, $\alpha = 88.87 \pm 0.06°$, $\beta = 112.45 \pm 0.08°$, and $\gamma = 71.54 \pm 0.06°$. A calculated density of 2.44 g/cm^3 for two molecules per unit cell is in good agreement with the observed density of 2.40 ± 0.05 g/cm^3, determined by the flotation method.

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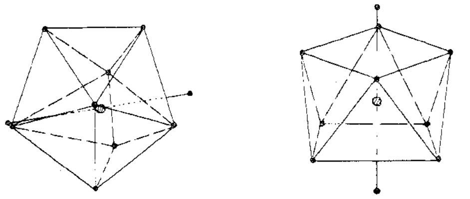
Table I. Final Atom Positional[a] and Thermal[b] Parameters

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ho	944(1)[c]	2260(0)	3961(1)	90(1)	38(1)	126(2)	-15(0)	47(1)	-8(1)
Ow1	2566(10)	1787(10)	1880(16)	138(17)	94(9)	202(31)	-29(11)	79(19)	-22(13)
Ow2	649(10)	4271(7)	2605(14)	147(14)	41(6)	270(27)	-31(8)	91(17)	-12(10)
Ow3	-1047(12)	2780(8)	337(15)	166(17)	61(8)	202(25)	-42(9)	6(17)	-7(11)
Ow4	514(11)	454(7)	2712(14)	121(15)	48(7)	234(26)	-24(8)	65(17)	-29(11)
O1	-1384(11)	2006(8)	4616(17)	164(16)	75(9)	350(33)	-37(10)	135(20)	-3(13)
O2	-1570(11)	3863(8)	4160(16)	162(16)	76(8)	411(36)	-30(9)	147(21)	-43(14)
O3	-3531(10)	3459(8)	4722(16)	110(15)	101(9)	360(34)	-15(9)	88(18)	11(14)
O4	1783(11)	3296(7)	7330(14)	182(18)	75(8)	260(28)	-40(9)	100(19)	-41(13)
O5	3592(10)	2610(9)	5988(15)	106(14)	108(10)	250(29)	-17(9)	38(17)	-37(15)
O6	4164(11)	3601(8)	8709(15)	166(16)	99(9)	251(29)	-48(10)	25(19)	-69(14)
O7	3836(12)	143(9)	6056(15)	200(18)	146(11)	202(28)	-79(12)	83(19)	-20(14)
O8	1966(10)	751(7)	7360(13)	132(15)	63(7)	212(24)	-13(9)	59(16)	8(11)
O9	4174(11)	-886(8)	8952(16)	151(16)	90(9)	301(32)	-33(10)	45(19)	23(15)
Ow5	3014(11)	4849(9)	1683(16)	122(15)	79(8)	261(32)	-31(9)	31(18)	-14(13)
Ow6	2782(11)	-1345(8)	1869(16)	137(16)	78(8)	185(26)	-30(9)	13(16)	-31(12)
C1	-2207(11)	3123(9)	4507(16)	44(16)	47(10)	103(28)	6(10)	27(17)	3(12)
C2	3220(12)	3187(9)	7391(18)	73(18)	32(8)	158(33)	13(10)	28(21)	1(14)
C3	3357(11)	-18(8)	7476(14)	66(16)	31(8)	33(24)	-4(10)	0(17)	27(12)
Hw1	206(22)	214(16)	18(34)						
H'w1	326(25)	155(21)	250(40)						
Hw2	167(22)	458(16)	250(30)						
H'w2	-24(23)	505(17)	277(29)						
Hw3	-153(24)	237(18)	-29(34)						
H'w3	-189(24)	338(19)	30(32)						
Hw4	130(23)	-30(17)	287(31)						
H'w4	-61(26)	22(18)	269(34)						
H1	-201(22)	194(16)	304(32)						
H5	384(22)	317(17)	529(33)						
H8	98(22)	33(16)	740(29)						
Hw5	373(24)	495(18)	247(35)						
H'w5	329(24)	428(18)	92(33)						
Hw6	389(24)	-176(17)	311(34)						
H'w6	280(24)	-115(18)	101(36)						

[a] The positional parameters for all non-hydrogen atoms are presented in fractional unit cell coordinates (x 10^4). Positional parameters for hydrogen atoms are (x 10^3).

[b] The β_{ij} are defined by: $T = \exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} \bullet 2kl\beta_{23})\}$. For all hydrogen atoms an isotropic thermal parameter of 4.5 was assigned.

[c] In this and succeeding tables, estimated standard deviations are given in parentheses for the least significant figures.



s-bicapped dodecahedron D_2 s-bicapped square antiprism D_{4d}

Figure 1. Idealized polyhedra for decacoordination.

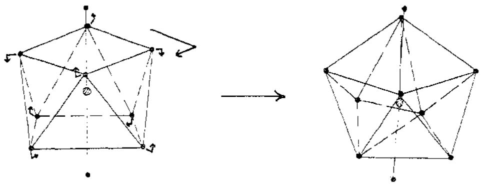


Figure 2. Formation of dodecahedral geometry *via* distortion of square antiprism.

Collection and Reduction of X-Ray Intensity Data. Data were collected at room temperature using an automated four-circle diffractometer designed and built in the Ames Laboratory. The upper full circle was purchased from STOE and is equipped with encoders (Baldwin Optical) and drive motors. The design of the base allows the encoders to be directly connected to the main θ and 2θ shafts, using solid- and hollow-shaft encoders, respectively. The diffractometer is interfaced to a PDP-15 computer in a realtime mode and is equipped with a scintillation counter. Zirconium-filtered Mo Kα radiation was used for data collection. A scan rate of 0.1 sec/step of 0.01° in θ was employed with a variable-scan range of 35 steps plus 1 step per 1° θ. Stationary-crystal, stationary-counter background counts of a quarter of the scan time were taken at the beginning and end of each scan. Before each scan a peak height measurement was made, and, in order to be scanned, the reflection had to exceed the background by more than six counts. If the reflection met this criterion, the ω setting was adjusted slightly, if necessary, to maximize the peak intensity. Within a 2θ sphere of 45° ($(\sin\theta)/\lambda = 0.538$ Å^{-1}), all data in the *hkl*, *h̄kl*, *h̄k̄l*, and *hk̄l* octants were measured in

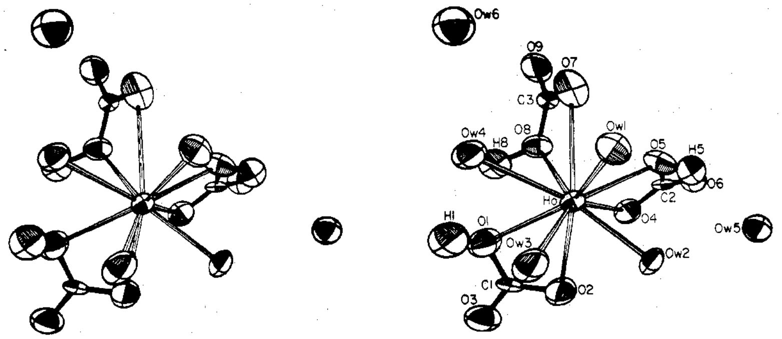


Figure 3. Stereographic view of $Ho(H_2O)_4(HCO_3)_3 \cdot 2H_2O$.

this manner, using a takeoff angle of 4.5°. Of the 1761 reflections examined, 1709 met the peak height criterion and were scanned to obtain the integrated intensities.

As a general check on electronic and crystal stability, the intensities of three standard reflections were remeasured every 25 reflections. These standard reflections were not observed to vary significantly throughout the entire period of data collection.

The intensity data were corrected for Lorentz-polarization effects, and, since the crystal was nearly spherical, the minimum and maximum transmission factors differed by ~4% for $\mu R = 1.3$, and no absorption correction was made. The estimated error in each intensity was calculated by

$$\sigma_I^2 = C_T + 2C_B + (0.03C_T)^2 + (0.03C_B)^2$$

where C_T and C_B represent the total count and background count, respectively, and the factor 0.03 represents an estimate of nonstatistical errors. The estimated deviations in the structure factors were calculated by the finite-difference method.[9] Of the 1709 independent reflections, 1621 were considered observed ($>2\sigma_{F_o}$).

Solution and Refinement of Structure

Based on examination of the Howells, Phillips, and Rogers[10] statistical test for a center of symmetry, the space group was assumed to be $P\bar{1}$. The position of the holmium atom was obtained from analysis of a three-dimensional Patterson function. The remaining atoms were found by successive structure factor [11] and electron density map calculations.[12] In addition to positional parameters for all atoms, the anisotropic thermal parameters for all nonhydrogen atoms were refined by a full-matrix least-squares procedure,[11] minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$, to a final conventional discrepancy factor of $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.039$. The largest ratio of shift of parameter to standard deviation in the final refinement cycle for nonhydrogen atoms was 0.87, and examination of observed and calculated structure factors revealed no appreciable extinction effects. The scattering factors used were those of Hanson, *et al.*,[13] modified for the real and imaginary parts of anomalous dispersion.[14]

The final positional and thermal parameters are listed in Table I. The standard deviations were calculated from the inverse matrix of the final least-squares cycle. Bond lengths and bond angles are listed in Tables II and III, respectively.[15,16]

Table II. Selected Interatomic Distances (Å) for $Ho(H_2O)_4(HCO_3)_3 \cdot 2H_2O$

Ho–Ow1	2.364 (10)	C3–O8	1.277 (12)
Ho–Ow2	2.380 (8)	C3–O9	1.215 (12)
Ho–Ow3	2.343 (10)		
Ho–Ow4	2.362 (8)	Hydrogen Bonding Distances	
Ho–O1	2.442 (9)	Hw2–Ow5	1.64 (19)
Ho–O2	2.515 (9)	H'w5–(O6)'	2.01 (21)
Ho–O4	2.557 (9)	Ow2- - -Ow5	2.735 (13)
Ho–O5	2.460 (10)	Ow5- - -(O6)'	2.824 (14)
Ho–O7	2.817 (11)	Hw4–Ow6	1.86 (20)
Ho–O8	2.518 (9)	Ow6–(Hw3)'	1.96 (20)
C1–O1	1.259 (13)	Ow4- - -Ow6	2.684 (12)
C1–O2	1.244 (13)	Ow6- - -(Ow3)'	2.735 (12)
C1–O3	1.219 (13)	O9- - -(Ow6)'	2.842 (14)
C2–O4	1.270 (13)	(H'w6)'–O9	2.27 (21)
C2–O5	1.257 (14)	Bites of Bicarbonate Groups	
C2–O6	1.209 (13)	O1- - -O2	2.111 (12)
C3–O7	1.228 (13)	O4- - -O5	2.131 (13)
		O7- - -O8	2.151 (13)

Table III. Bond Angles (deg) for $Ho(H_2O)_4(HCO_3)_3 \cdot 2H_2O$

Ow1-Ho-Ow2	79.1 (3)	O1-Ho-O4	91.5 (3)
Ow1-Ho-Ow3	75.5 (4)	O1-Ho-O5	138.7 (3)
Ow1-Ho-Ow4	78.1 (4)	O1-Ho-O7	109.0 (3)
Ow1-Ho-O1	146.2 (4)	O1-Ho-O8	68.1 (3)
Ow1-Ho-O2	142.7 (3)	O2-Ho-O4	68.3 (3)
Ow1-Ho-O4	121.8 (3)	O2-Ho-O5	112.9 (3)
Ow1-Ho-O5	72.4 (3)	O2-Ho-O7	147.7 (3)
Ow1-Ho-O7	69.1 (3)	O2-Ho-O8	101.2 (3)
Ow1-Ho-O8	116.0 (3)	O4-Ho-O5	50.2 (3)
Ow2-Ho-Ow3	72.1 (3)	O4-Ho-O7	90.6 (3)
Ow2-Ho-Ow4	140.5 (3)	O4-Ho-O8	69.7 (3)
Ow2-Ho-O1	118.1 (3)	O5-Ho-O7	63.5 (3)
Ow2-Ho-O2	68.9 (3)	O5-Ho-O8	82.3 (3)
Ow2-Ho-O4	75.0 (3)	O7-Ho-O8	47.1 (3)
Ow2-Ho-O5	71.6 (3)	O1-C1-O2	115.0 (9)
Ow2-Ho-O7	130.7 (3)	O1-C1-O3	122.8 (10)
Ow2-Ho-O8	144.4 (3)	O2-C1-O3	122.2 (9)
Ow3-Ho-Ow4	71.2 (3)	O4-C2-O5	115.0 (10)
Ow3-Ho-O1	82.5 (4)	O4-C2-O6	122.4 (11)
Ow3-Ho-O2	76.8 (4)	O5-C2-O6	122.6 (11)
Ow3-Ho-O4	138.6 (3)	O7-C3-O8	118.3 (9)
Ow3-Ho-O5	135.1 (3)	O7-C3-O9	121.2 (10)
Ow3-Ho-O7	130.1 (3)	O8-C3-O9	120.5 (10)
Ow3-Ho-O8	140.9 (3)	H1-O1-C1	97 (10)
Ow4-Ho-O1	70.7 (3)	H5-O5-C2	102 (12)
Ow4-Ho-O2	115.4 (3)	H8-O8-C3	116 (8)
Ow4-Ho-O4	144.3 (3)		
Ow4-Ho-O5	129.5 (3)	Hw4-Ow6-(Hw3)'	103 (8)
Ow4-Ho-O7	68.0 (3)	Hw2-Ow5--(O6)'	125 (6)
Ow4-Ho-O8	75.0 (3)	O9--(Ow6)'-(Hw4)'	132 (5)
O1-Ho-O2	50.4 (3)	O9--(Ow6)'-(Hw3)"	100 (6)

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(15) W. R. Busing, K. O. Martin, and H. A. Levy, "OR FFE, a Fortran Crystallographic Function and Error Program," U. S. Atomic Energy Commission Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

Description and Discussion

Tris(bicarbonato)tetraaquoholmium(III) dihydrate is 10-coordinate with the holmium atom bound to four water oxygen atoms (average distance 2.362 Å; *cf.* Table II) and six bicarbonate oxygens. Two waters of hydration are associated with each molecule and provide crystalline stability through hydrogen bonding. A stereographic view of the molecule is provided in Figure 3.[17]

The holmium-(bicarbonate oxygen) lengths vary from 2.442 (9) to 2.557 (9) Å with the exception of one long (2.817 (11) Å) distance. The latter distance appears to be dictated by the packing of that particular bicarbonate group around the holmium atom. Generally, the two oxygen atoms within a bicarbonate group which are bound to the metal are at different distances from the central ion. The bicarbonate oxygen to which the hydrogen atom is bound is found to be closer to the metal ion by an average of 0.08 Å (2.442 (9)-2.460 (10) Å, compared with 2.515 (9)-2.557 (9) Å) excluding the bicarbonate group containing the long Ho-O distance mentioned earlier.

The bidentate nature of the bicarbonate groups is evidenced by the corresponding bites (*cf.* Table II) and by the O-C-O angles. As can be seen in Table III, the metal-bound oxygen-carbon-oxygen angles are significantly smaller than the other oxygen-carbon-oxygen angles in the bicarbonate groups. The bites and angles are consistent with those reported by Shinn and Eick in a paper describing the structure of a 10-coordinate lanthanum compound containing bidentate carbonate groups.[4] It is also apparent that the carbon anisotropic thermal motion in all bicarbonate groups is predominantly out-of-plane motion (*cf.* Table I and Figure 3).

The geometry of $Ho(H_2O)_4(HCO_3)_3 \cdot 2H_2O$ approximates that of the s-bicapped square antiprism more closely than that of the s-bicapped dodecahedron (*cf.* Figures 1 and 3). Ow1, Ow4, O8, and O5 define one distorted square plane, and Ow2, Ow3, O1, and O4 define the other (see Table IV). The justification for calling the geometry distorted square antiprismatic *vs.* dodecahedral is provided in Table V, where it is seen that the angles Ow1-Ow4-O8, Ow4-O8-O5, etc. approximate 90° more closely than they do the approximate alternating 77 and 100° consistent with the s-bicapped dodecahedron. In addition, the dodecahedral model requires, based on energy considerations,[18] that $\theta_A = 32.8°$ and $\theta_B = 77.0°$, where θ_A and θ_B are the two angles by which a dodecahedron is normally described.[19] In this compound, θ_A corresponds to the Ow1-Ho-O7 type angles which average 58.9° (*cf.* Table III), and θ_B corresponds to O5-Ho-O7 type angles which average 69.2°. The average of θ_A and θ_B in this compound is approximately 64.1° which is in good agreement with the energetically favored θ angle of 64.8°[18] consistent with an s-bicapped square antiprism. Having defined the distorted square-antiprismatic planes as previously mentioned, the two capping atoms then become O7 and O2.

It is interesting to note that one of the capping atoms, O7, is the one which is involved in the longest holmium-oxygen distance. As can be seen in Table V, the capping atom-plane atom distances are similar for O7 and O2, thus indicating that if O7 were closer to the holmium atom, ligand-ligand repulsions would decrease stability. To account further for the long (2.817 (11) Å) distance between Ho and O7, a close examination of intermolecular interatomic distances is required.

Table IV. Equations of Least-Squares Planes[a] and Dihedral Angles

Plane I fitting (Ow2-Ow3-O1-O4):

$0.8099X - 0.5798Y + 0.0888Z + 2.7344 = 0$

Atom	Distance from Plane (Å)
Ow2	−0.254
Ow3	0.237
O1	−0.178
O4	0.195
Ho	1.024
O2	−1.446

Plane II defined by (Ow2-Ow3-O1):

$0.8234X - 0.4893Y + 0.2866Z + 2.2094 = 0$

Atom	Distance from Plane (Å)
O4	0.952
O2	−1.132
Ho	1.242

Plane III fitting (Ow1-Ow4-O5-O8):

$0.7907X - 0.5534Y + 0.2620Z + 0.0440 = 0$

Atom	Distance from Plane (Å)
Ow1	0.145
Ow4	−0.139
O5	−0.132
O8	0.126
Ho	−1.162
O7	1.594

Plane IV defined by (Ow1-Ow4-O8):

$0.7346X - 0.6494Y + 0.1965Z + 0.3441 = 0$

Atom	Distance from Plane (Å)
O5	−0.555
Ho	−1.289
O7	1.425

Plane V fitting (Ho-Ow1-O7-O8):

$0.3200X + 0.8036Y + 0.5019Z - 3.4543 = 0$

Atom	Distance from Plane (Å)
Ho	0.048
Ow1	−0.041
O7	0.042
O8	−0.049

Plane VI fitting (Ho-Ow3-O2-O4):

$0.3383X + 0.8727Y - 0.3520Z - 1.9254 = 0$

Atom	Distance from Plane (Å)
Ho	−0.301
Ow3	0.212
O2	−0.116
O4	0.204

Plane VII fitting (Ho-Ow4-O5-O7):

$-0.6388X - 0.1136Y + 0.7609Z - 1.5170 = 0$

Atom	Distance from Plane (Å)
Ho	0.170
Ow4	−0.131
O5	−0.130
O7	0.091

Plane VIII fitting (Ho-Ow2-O1-O2):

$0.1756X + 0.2441Y + 0.9537Z - 2.8674 = 0$

Atom	Distance from Plane (Å)
Ho	0.124
Ow2	−0.112
O1	−0.132
O2	0.120

Dihedral Angles

Plane	Plane	Angle	Plane	Plane	Angle
I	III	169.9°	V	VIII	43.0°
II	IV	168.3°	VI	VII	−54.3°
V	VI	50.7°	VI	VIII	−86.4°
V	VII	85.1°	VII	VIII	54.1°

[a] Planes are defined as $c_1X + c_2Y + c_3Z - d = 0$, where X, Y, and Z are cartesian coordinates which are related to the triclinic cell coordinates (x, y, z) by the transformations:

$$X = xa \sin\gamma + zc\,\{(\cos\beta - \cos\alpha\cos\gamma)/\sin\gamma\},$$

$$Y = xa\cos\gamma + yb + zc\cos\alpha, \quad \text{and}$$

$$Z = zc\left(\frac{\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}}{\sin\gamma}\right)$$

Table V. Selected Distances (Å) and Angles (deg) Describing Polyhedral Geometry

Distances of Interest

O7- - -Ow1	2.961 (14)	O5- - -Ow1	2.851 (14)
O7- - -Ow4	2.920 (13)	O1- - -O4	3.578 (14)
O7- - -O5	2.795 (14)	O4- - -Ow2	3.010 (13)
O2- - -Ow2	2.772 (13)	Ow2- - -Ow3	2.781 (12)
O2- - -Ow3	3.020 (14)	Ow3- - -O1	3.155 (14)
O2- - -O4	2.848 (13)	Ow1- - -O8	4.142 (14)
Ow1- - -Ow4	2.978 (14)	Ow4- - -O5	4.361 (13)
Ow4- - -O8	2.972 (13)	Ow2- - -O1	4.135 (12)
O8- - -O5	3.277 (13)	Ow3- - -O4	4.585 (14)

Selected Angles

Ow1-Ow4-O8	88.2 (3)	Ow3-O1-O4	85.5 (3)
Ow4-O8-O5	88.4 (3)	O1-O4-Ow2	77.2 (3)
O8-O5-Ow1	84.7 (4)	O4-Ow2-Ow3	104.6 (3)
O5-Ow1-O4	96.8 (4)	Ow2-Ow3-O1	88.1 (4)

Intermolecular hydrogen bonding through waters of crystallization is depicted in Figure 4, and the corresponding distances are presented in Table II. In addition, there appears to

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(16) See paragraph at end of paper regarding supplementary material.

(17) C. A. Johnson, "OR TEP-II: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," U. S. Atomic Energy Commission Report ORNL-3794 (2nd Revision with Supplemental Instructions), Oak Ridge National Laboratory, Oak Ridge, Tenn., 1970. All drawings depict 70% probability ellipsoids.

(18) A. R. Al-Karaghouli and J. S. Wood, *Inorg. Chem.*, 11, 2293 (1972).

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

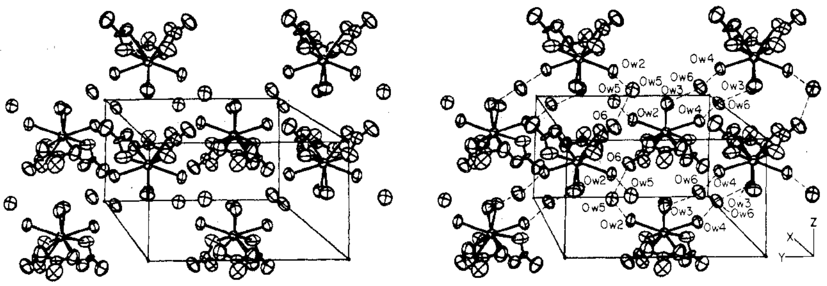

Figure 4. Stereographic drawing of the $Ho(H_2O)_4(HCO_3)_3 \cdot 2H_2O$ unit cell and adjacent moieties.

be a weak, but significant, interaction between the oxygen atom of water 6 (Ow6) of an adjacent moiety with O9 of the bicarbonate group containing O7 as shown in Figure 5. The O9- - -(Ow6)′ distance is 2.842 (14) Å and the angles O9-(Ow6)′-(Hw4)′ and O9-(Ow6)′-(Hw3)″ average 116° (*cf.* Tables II and III), thus indicating a hydrogen-bond-like interaction. The interaction of O9 with the water of crystallization also affects the spatial positions of the other oxygen atoms within the same bicarbonate group. As seen in Figure 5, the interaction of O9 and (Ow6)′ causes O7 to be moved further from the holmium atom, thus producing the long Ho-O bond (2.817 (11) Å) observed. Consequently, the coupling of the ligand-ligand repulsions and the hydrogen-bond-like interaction with O9 substantiate the fact that the Ho-O7 distance is somewhat longer than the other holmium-oxygen distances.

In conclusion, although the bonding of the bicarbonate groups and the holmium atom seems somewhat electrostatic in nature, it should be acknowledged that the molecule does approximate an idealized geometry (bicapped square antiprismatic) rather nicely. Furthermore, since this compound contains the smallest lanthanide ion of any 10-coordinate complex whose three-dimensional X-ray analysis has been reported to date, it is conceivable to conclude that the more energetically favored geometry would be more predominant in this compound than in previously reported compounds. Therefore, the structure of tris(bicarbonato)tetraaquoholmium(III) dihydrate supports the results of ligand-ligand repulsion calculations for D_{4d} *vs.* D_2 geometries,[18] which indicate that the D_{4d} (bicapped square-antiprismatic) geometry is energetically favored as the preferred ground-state geometry for decacoordination.

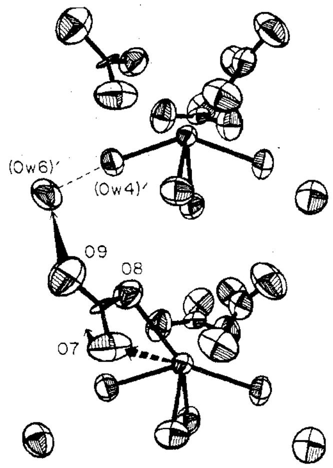

Figure 5. View depicting the O9- - -(Ow6)′ hydrogen bond and the corresponding lengthening of the Ho-O7 distance.

Registry No. $Ho(H_2O)_4(HCO_3)_3 \cdot 2H_2O$, 52239-55-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2535.