nance with the structural results on the two known examples[1,6]) was followed almost immediately by the discovery[26] of a d^8 complex with a planar $M-SO_2$ geometry and concomitant rationalization of the result in molecular orbital terms. But there is no anticipation on theoretical grounds for the η^2 mode of coordination of SO_2 to be found in the literature nor has there yet appeared an ex post facto rationalization.

It may be that as the number of structurally characterized SO_2 complexes increases, our ability to predict geometries will also improve. It clearly is an interesting question whether the η^2 mode of bonding of SO_2 will remain rare or whether the two known structures are the forerunners of a large class of compounds. The bent mode of bonding of NO to transition metals was novel in 1968[2] and is now probably as common as the linear mode.

Acknowledgment. This work was kindly supported by the National Science Foundation (Grant CHE 76-10335). We are indebted to Matthey-Bishop, Inc., for the loan of precious metal used in this study. We thank Dr. R. R. Ryan and Dr. D. C. Moody for informative preprints of their recent results.

Registry No. $RuCl(NO)(\eta^2-SO_2)(P(C_6H_5)_3)_2 \cdot CH_2Cl$, 66701-48-2.

Supplementary Material Available: Root-mean-square amplitudes of vibration (Table IV) and a listing of structure amplitudes (Table V) (38 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of the Decacoordinate Compound ((Hydroxyethyl)ethylenediaminetriacetato)diaquolanthanum(III) Trihydrate

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Received March 31, 1978

The crystal and molecular structure of the trihydrate of ((hydroxyethyl)ethylenediaminetriacetato)diaquolanthanum(III), $La[(O_2CCH_2)_2NCH_2CH_2N(CH_2CH_2OH)(CH_2CO_2)(H_2O)_2] \cdot 3H_2O$ (triclinic, $P\bar{1}$, $a = 9.476$ (2) Å, $b = 10.947$ (3) Å, $c = 9.391$ (2) Å, $\alpha = 108.18$ (2)°, $\beta = 104.66$ (3)°, $\gamma = 79.31$ (3)°, $Z = 2$, 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 a full-matrix least-squares procedure to a final conventional discrepancy factor, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, of 6.4% for 1637 observed reflections ($F_o > 2\sigma_{F_o}$). This molecule crystallizes as a dimer, utilizing the crystallographic center of symmetry. The eight coordination sites satisfied by (hydroxyethyl)ethylenediaminetriacetate include five solely from one group—including one from the oxygen of the hydroxyethyl group—two by a sharing of a carboxymethyl oxygen between the two lanthanum atoms, and one from the carboxymethyl oxygen from the ligand primarily coordinated to the other lanthanum atom. The lanthanum cations are decacoordinate, with a geometry approximating the bicapped square antiprism.

Introduction

Powell and Burkholder have demonstrated that the Gd–Eu and Eu–Sm separation factors in cation-exchange elution with ammonium ethylenediaminetetraacetate (EDTA) can be augmented by increasing the temperature from 25 to 92 °C and have shown that similar enhancements should occur in the cases of Ho–Dy and Dy–Tb pairs when (hydroxyethyl)ethylenediaminetriacetate (HEDTA) is the eluent.[1] The stabilities of the four heaviest HEDTA chelate species (Tm–Lu) are not affected by this increase in temperature, whereas the stabilities of the remaining lanthanide HEDTA species vary significantly with temperature. This difference may be explained by the assumption that the HEDTA ligand always forms pentadentate bonds to the four smaller lanthanides (Lu^{3+} through Eu^{3+}) and hexadentate bonds to those lanthanides larger than Eu^{3+} at temperatures approaching 0 °C, with the remaining coordination sites being occupied by water molecules.

There have been numerous articles recently on compounds exhibiting large coordination numbers, and considerable controversy has arisen over the preferred geometry in cases of high coordination numbers. Thus, the crystal structure determination of LaHEDTA was undertaken in order to provide further information on the coordination of the HEDTA ligand to the lighter lanthanides and the geometry of the resulting complex.

Experimental Section

Crystal Data. Well-formed white rhombohedral crystals of LaHEDTA were supplied by J. E. Powell of this laboratory and were used without further purification. A crystal of approximate dimensions 0.4 × 0.4 × 0.2 mm was mounted on a glass fiber. Preliminary precession photographs indicated that the compound crystallized in

0020-1669/78/1317-2138$01.00/0

Table I. Final Positional[a] Parameters for LaHEDTA[b,c]

atom	x	y	z
La	684 (1)	−2042 (0)	−1146 (1)
O1	1340 (9)	−3440 (7)	−3662 (10)
O2	4059 (9)	−306 (9)	−2529 (11)
O3	2149 (9)	−643 (7)	−1799 (9)
O4	2097 (8)	−5750 (8)	426 (9)
O5	1220 (8)	−4262 (7)	−811 (9)
O6	956 (8)	988 (7)	3442 (9)
O7	1186 (8)	−61 (6)	1112 (9)
Ow1	−1534 (8)	−3295 (7)	−2638 (9)
Ow2	−974 (8)	−1928 (7)	710 (8)
Ow3	−513 (10)	−3763 (8)	3613 (9)
Ow4	−2667 (10)	−1662 (8)	3714 (9)
Ow5	4083 (10)	2279 (12)	4334 (12)
N1	3681 (9)	−2870 (8)	−1074 (10)
N2	2321 (10)	−2311 (8)	1731 (10)
C1	4399 (13)	−3221 (12)	362 (13)
C2	3890 (12)	−2273 (12)	1739 (13)
C3	3742 (15)	−4056 (12)	−2404 (15)
C4	2811 (14)	−3856 (14)	−3882 (16)
C5	4434 (13)	−1855 (13)	−1186 (17)
C6	3470 (13)	−878 (11)	−1933 (13)
C7	2144 (14)	−3558 (10)	1911 (13)
C8	1820 (11)	−4600 (10)	391 (13)
C9	1865 (14)	−1232 (10)	2990 (12)
C10	1320 (11)	−21 (11)	2500 (14)
H1	551 (19)	−334 (13)	46 (14)
H2	407 (15)	−406 (16)	15 (14)
H3	397 (16)	−138 (16)	166 (15)
H4	452 (16)	−249 (13)	269 (16)
H5	474 (19)	−432 (13)	−256 (14)
H6	320 (15)	−481 (14)	−219 (14)
H7	308 (14)	−306 (15)	−411 (14)
H8	301 (15)	−464 (16)	−474 (17)
H9	68 (17)	−380 (13)	−477 (19)
H10	473 (15)	−129 (14)	−6 (17)
H11	514 (17)	−242 (14)	−191 (15)
H12	137 (17)	−355 (13)	241 (15)
H13	298 (18)	−385 (14)	258 (16)
H14	265 (17)	−115 (13)	386 (17)
H15	106 (17)	−169 (14)	319 (14)

[a] The positional parameters are presented in fractional coordinates ($\times 10^4$ for the nonhydrogen atoms, $\times 10^3$ for the hydrogen atoms). [b] The anisotropic thermal parameters for the nonhydrogen atoms are given in the supplementary material. For the hydrogen atoms the isotropic temperature factor was defined as 2.0. No water hydrogens were refined. [c] In this and succeeding tables, estimated standard deviations are given in parentheses for the least significant figures.

Table II. Selected Interatomic Distances (Å) for LaHEDTA

(a) Bonding Distances

La–N1	2.750 (8)	C1–C2	1.508 (16)
–N2	2.819 (9)	C3–C4	1.500 (19)
av	2.785 ± 0.035	C5–C6	1.501 (19)
La–O1	2.534 (8)	C7–C8	1.525 (14)
–O3	2.520 (10)	C9–C10	1.497 (17)
–O5	2.490 (8)	av	1.506 ± 0.010
–O7	2.534 (6)	O1–C4	1.430 (16)
av	2.520 ± 0.018	O2–C6	1.234 (19)
La–O7′	2.629 (6)	O4–C8	1.246 (14)
La–O6′	2.745 (8)	av	1.240 ± 0.006
La–Ow1	2.543 (7)	O3–C6	1.260 (15)
–Ow2	2.563 (9)	O5–C8	1.262 (15)
av	2.553 ± 0.010	av	1.261 ± 0.001
N1–C1	1.480 (16)	O6–C10	1.235 (12)
–C3	1.498 (14)	O7–C10	1.265 (16)
–C5	1.470 (19)		
N2–C2	1.493 (16)		
–C7	1.471 (16)		
–C9	1.476 (13)		
av	1.481 ± 0.011		

(b) Distances Describing Polyhedral Geometry

O6′–O7′	2.176 (11)	Ow2–O5	3.185 (10)
O6′–Ow1	3.027 (13)	Ow2–Ow1	2.987 (10)
O6′–O1	3.114 (10)	Ow2–O7′	3.114 (12)
O6′–O3	2.988 (10)	O5–N1	3.109 (13)
N2–N1	3.065 (14)	O5–O1	3.112 (14)
N2–O7	2.675 (11)	O5–Ow1	2.952 (10)
N2–Ow2	3.016 (11)	N1–O1	2.839 (11)
N2–O5	2.781 (10)	N1–O3	2.782 (12)
O7–O7′	2.668 (10)	Ow1–O1	3.072 (13)
O7–O3	2.945 (13)	O1–O3	3.142 (10)
O7–Ow2	3.031 (12)	O3–O7′	3.289 (12)
O7–N1	3.883 (10)	O7′–Ow1	3.548 (10)

the triclinic crystal system. Final unit cell parameters, obtained from a least-squares fit of ±2θ values for 14 independent reflections (Mo Kα radiation, λ 0.709 54 Å) at 30 °C, yielded a = 9.476 (2) Å, b = 10.947 (3) Å, c = 9.391 (2) Å, α = 108.18 (2)°, β = 104.66 (3)°, and γ = 79.31 (3)°. A calculated density of 1.90 g cm^{-3} for two molecules per unit cell is in excellent agreement with the observed density of 1.88 ± 0.02 g cm^{-3}, determined by the flotation method.

Collection and Reduction of X-ray Intensity Data. Data were collected at room temperature using a technique and apparatus described by Rohrbaugh and Jacobson.[2] Within a 2θ sphere of 40° ($(\sin\theta)/\lambda = 0.481$ Å^{-1}) all data in the hkl, $hk\bar{l}$, $h\bar{k}l$, and $h\bar{k}\bar{l}$ octants were measured. The intensity data were corrected for absorption and Lorentz–polarization effects. The minimum and maximum transmission factors were 0.38 and 0.62, respectively (μ = 25.1 cm^{-1}). The estimated error in each intensity was calculated by $\sigma_I^2 = C_T + C_B + (0.03C_T)^2 + (0.03C_B)^2 + (0.03C_N/A)^2$ where C_T, C_B, C_N, and A are the total count, background count, net count, and absorption factor, 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.[3] Of the 1815 independent reflections, 1637 were considered observed ($>2\sigma_{F_o}$).

Solution and Refinement of the Structure. The position of the lanthanum atom was obtained from the analysis of a three-dimensional Patterson function. The remaining nonhydrogen atoms were found by successive structure factor[4] and electron density map calculations.[5] The hydrogen positions in the HEDTA ligands were calculated except for those in the associated water molecules. In addition to the positional parameters, the anisotropic thermal parameters for all nonhydrogen atoms were refined by a full-matrix least-squares procedure, minimizing the function $\sum(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$, to a final conventional residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ = 6.4% and a corresponding weighted residual of 6.7%. The scattering factors for the nonhydrogen atoms were those of Hanson et al.,[6] modified for the real and imaginary parts of anomalous dispersion.[7] For hydrogen the scattering factors of Stewart et al. were used.[8]

The final positional parameters are listed in Table I; the anisotropic temperature factors and a table of structure factor amplitudes are available as supplementary material. The standard deviations were calculated from the inverse matrix of the final least-squares cycle. Bond lengths and bond angles are listed in Table IIa and Table IIIa, respectively.[9]

Description and Discussion

Original characterization of this lanthanum complex indicated an approximate formula LaHEDTA·$4.5H_2O$. However, refinement of the crystal structure showed that this compound crystallizes as a centrosymmetric dimer, with five water molecules associated with each lanthanum moiety. The lanthanum ions of ((hydroxyethyl)ethylenediaminetriacetato)diaquolanthanum(III) trihydrate are ten-coordinate, as seen in Figure 1.[10] Eight of the coordination sites are satisfied by the HEDTA ligand. Of these eight sites, five are solely from one group (N1, N2, O3, O5, and the hydroxyethyl oxygen O1), two are filled by a sharing of a carboxymethyl oxygen between the two lanthanum atoms (O6), and one is filled by a carboxymethyl oxygen from the HEDTA ligand coordinated to the other lanthanum atom (O7). The remaining two sites are filled by water molecules (Ow1 and Ow2). Three water molecules of hydration (Ow3, Ow4, and Ow5) are associated with each moiety. A unit cell diagram is shown in Figure 2.

Three of the lanthanum–oxygen (HEDTA) distances are equal (2.53 Å), cf. Table IIa, and one (La–O5) is slightly

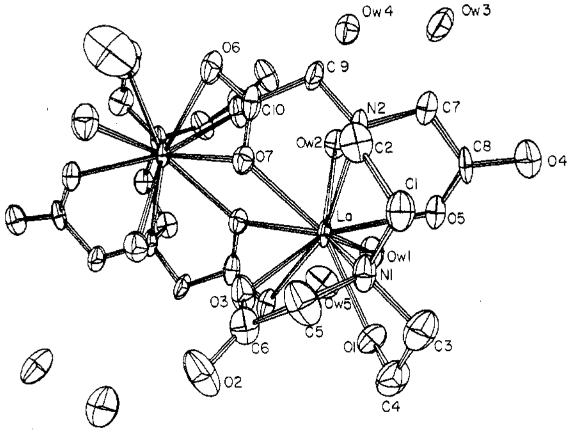

Figure 1. View of the LaHEDTA dimer. Thermal ellipsoids are drawn at the 50% probability level.

shorter (2.490 Å). The bond distances between the lanthanum atom and the bridging oxygen atoms are significantly longer, however, being 2.629 and 2.745 Å. These two long distances seem to be dictated by distortion from the ideal geometry imposed by dimerization and by the fact that bridging oxygen atoms frequently have longer associated bonds. The bond angles associated with these bridging atoms are also indicative of this distortion, particularly the angles C10–O6–La′ (91.6°) and C10–O7–La′ (96.8°), where the prime indicates the atom related by the inversion operation.

The carboxymethyl groups are planar as expected. For the nonbridging groups, the distances C–Oc average 1.261 Å, slightly longer than the C–Ou average distance of 1.240 Å (cf. Table IIa), where Oc is a coordinated oxygen atom and Ou is an uncoordinated oxygen atom. The average angles are C–C–Oc = 118.4, C–C–Ou = 118.1, and Oc–C–Ou = 123.3° (cf. Table IIIa).

There are many similarities between the structure of LaHEDTA and that of LaEDTA, reported by Lind, Lee, and Hoard,[11] as would be expected, since the HEDTA ligand differs from the EDTA ligand only in that one of the carboxymethyl groups of EDTA has been replaced by a hydroxyethyl group. One of the questions we sought to answer in this investigation was whether the hydroxyethyl group is coordinated in LaHEDTA, as is the corresponding carboxymethyl group in the EDTA complex. Moeller and Horwitz had suggested that while spectral data could not be used to determine whether this group was coordinated, dehydration studies, the generally poor coordinating ability of this group, and similarities between HEDTA and EDTA materials suggest that it is not.[12] However, our structural results show that the hydroxy oxygen (O1) is indeed coordinated, being at a distance of 2.534 Å from the lanthanum.

While the EDTA complex does not crystallize as a centrosymmetric dimer, the configuration of the ethylenediamine and glycinate rings, and thus the geometry about the lanthanum atom in the LaEDTA complex, is very similar to that in the LaHEDTA complex. As shown by Lind et al.,[10] ruffling of the five-membered rings can be viewed as a consequence of the coordination of the ligand to the lanthanum atom, and the degree of ruffling can be estimated by the sum of those interior bond angles, since this sum always decreases from the maximum value of 540° as the ring increasingly distorts from the planar configuration. Alternately, one may use the ruffling parameters ϕ_1 and ϕ_2 as defined by Lee[13] or the distances of the member atoms from the least-squares plane drawn through those member atoms. For LaHEDTA, such information is given in Table IIIc, Table IIId, and Table IV, respectively. The ring La–N1–C1–C2–N2 would be expected to be particularly distorted due to the small N1–La–N2 angle of 65.9° (65.3°) and the two approximately tetrahedral angles at C1 and C2, 112.2 and 113.2° (112.9 and 115.2°), respectively. (The values in parentheses refer to LaEDTA.) Inspection of Table IIIc and Table IV shows this to be the case. The ring La–N1–C3–C4–O1 would also be expected to be quite ruffled, for much the same reasons, and once again inspection of the table shows this to be the case. The angles N–La–Oc are also small relative to 108°, the angle expected for a regular pentagon, averaging 62.1° (60.0°). Correspondingly, the angles La–Oc–C have opened up to an average value of 125.0° (127.0°), although a similar opening has not occurred for the angles La–N–C, which average 109.4° (110.9°).

Muetterties and Wright have suggested that two geometries for decacoordination with symmetry consistent with sp^{3}d^{5}f hybridization are the bicapped square antiprism (BSAP) and the bicapped dodecahedron (BD).[14] These two geometries shown in Figure 3 are both basically constructed from squares skewed from each other by 45°, but the BD geometry differs from the BSAP one in that the two "squares" are not planar and are slightly closer together for BD geometry (see below). Al-Karaghouli and Wood have described these two geometries by θ angles,[15] but unfortunately these angles do not refer to the same thing. In the case of the BSAP geometry the θ angle is defined as in Figure 3 and should be 64.8° for the ideal figure. However, for the BD geometry, the angles θ_A, θ_B, and θ_C, defined by Al-Karaghouli and Wood, do not refer to the angles formed by the capping atom and a member of the "square", and two more angles have to be defined (see Figure 3), namely, θ_1 (60.8°) and θ_2 (74.3°), angles which average 67.5°. Al-Karaghouli and Wood note that the geometry based on the square antiprism is favored energetically.[15] The same

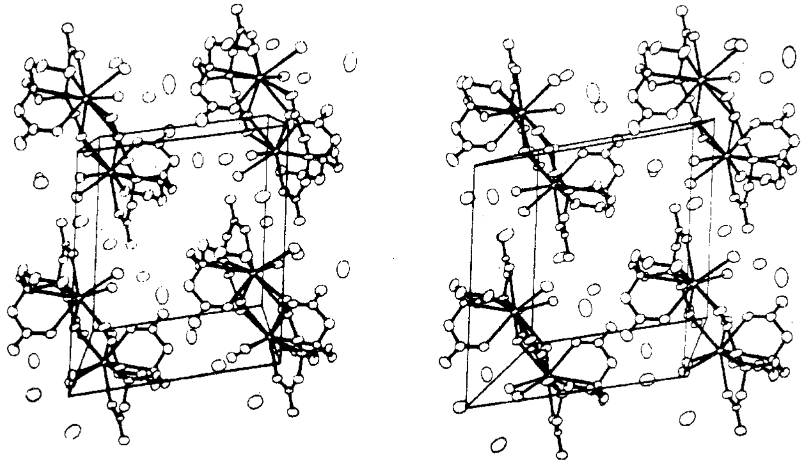

Figure 2. Unit cell drawing for LaHEDTA.

Table III. Selected Interatomic Angles (deg) for LaHEDTA

(a) Bond Angles

Bond Angles around the La^{3+} Cation			
O6′–La–O7′	47.6 (2)^a	N1–La–O7	93.1 (2)
N2–La–O7	39.5 (2)^a	O6′–La–O7	102.8 (2)
O7–La–O7′	62.2 (2)	N2–La–O3	103.2 (3)
N1–La–O3	62.4 (3)	O6′–La–Ow2	108.5 (2)
N2–La–O5	62.7 (3)^a	N2–La–O7′	116.5 (2)
N1–La–O1	63.9 (2)	N1–La–O6′	119.4 (3)
N1–La–N2	65.9 (3)^a	O1–La–O7′	119.5 (3)
N2–La–Ow2	67.5 (2)^a	O5–La–O7	121.4 (2)
O3–La–O6′	68.6 (2)^a	N2–La–Ow1	122.4 (3)
O6′–La–Ow1	69.1 (2)^a	N2–La–O1	122.6 (2)
Ow1–La–Ow2	70.6 (2)	N1–La–Ow1	128.6 (2)
O3–La–O7	70.9 (3)	N1–La–Ow2	132.0 (2)
O5–La–Ow1	71.2 (2)	O3–La–O5	133.3 (2)
N1–La–O5	71.6 (3)	O3–La–Ow1	133.8 (3)
O1–La–O6′	71.9 (2)^a	O5–La–O6′	134.5 (2)
O7–La–Ow2	72.5 (2)	O7–La–Ow1	136.8 (4)
O7′–La–Ow2	73.3 (3)	N1–La–O7′	139.8 (3)
O1–La–Ow1	73.8 (3)	O1–La–Ow2	141.1 (2)
O1–La–O3	76.4 (3)	O3–La–Ow2	141.4 (2)
O1–La–O5	76.5 (3)	O1–La–O7	146.3 (3)
O5–La–Ow2	77.7 (3)	O5–La–O7′	147.7 (6)
O3–La–O7′	79.0 (2)	N2–La–O6′	162.3 (2)
O7′–La–Ow1	85.9 (2)		
Tetrahedral Angles			
La–N1–C3	105.6 (6)	La–N1–C1	110.6 (7)
La–N2–C2	106.4 (7)	La–N2–C9	110.8 (6)
La–N2–C7	110.1 (6)	La–N1–C5	111.1 (6)
		av	109.1 ± 2.2
C1–N1–C5	108.8 (9)	C7–N2–C9	110.4 (10)
C1–N1–C3	109.0 (9)	C3–N1–C5	111.6 (11)
C2–N2–C9	109.2 (8)	av	109.8 ± 1.0
C2–N2–C7	109.8 (9)		
C10–C9–N2	111.5 (10)	C8–C7–N2	113.3 (10)
C2–C1–N1	112.2 (9)	C6–C5–N1	115.4 (10)
C4–C3–N1	113.0 (10)	av	113.1 ± 1.2
C1–C2–N2	113.2 (9)		
C3–C4–O1	107.7 (12)		
Trigonal Angles			
C5–C6–O2	117.3 (11)	C9–C10–O6	119.6 (12)
C7–C8–O4	117.3 (10)	av	118.1 ± 1.1
C5–C6–O3	117.0 (13)	C9–C10–O7	119.3 (9)
C7–C8–O5	119.0 (10)	av	118.4 ± 1.0
O6–C10–O7	121.0 (11)	O2–C6–O3	125.4 (11)
O4–C8–O5	123.5 (9)	av	123.3 ± 1.8
Other Angles			
La–O1–C4	124.1 (7)	La–O7–C10	125.0 (7)
La–O3–C6	127.7 (8)	av	126.3 ± 1.8
La–O5–C8	128.4 (6)		
La′–O7–La	117.8 (3)	La′–O6–C10	91.6 (7)
La′–O7–C10	96.8 (6)		

[a] θ angles as defined by Al-Karaghouli and Wood.[15]

(b) Angles Describing Polyhedral Geometry

O1–O6′–Ow1	60.0 (3)	Ow2–O5–N1	103.1 (3)
Ow1–O6′–O7′	84.3 (4)	O5–N1–O7	76.7 (2)
O7′–O6′–O3	77.3 (3)	N1–O7–Ow2	90.1 (2)
O3–O6′–O1	61.9 (2)	O7–Ow2–O5	89.6 (3)
Ow2–N2–O5	66.5 (3)	Ow1–O1–O3	98.5 (3)
O5–N2–N1	64.0 (3)	O1–O3–O7′	87.9 (3)
N1–N2–O7	84.8 (4)	O3–O7′–Ow1	87.0 (2)
O7–N2–Ow2	64.0 (3)	O7′–Ow1–O1	84.5 (3)
O1–N1–O3	68.0 (3)	O6′–O1–Ow1	58.6 (3)
O3–N1–O7	49.1 (2)	Ow1–O1–O5	57.0 (3)
O7–N1–N2	43.3 (2)	O5–O1–N1	62.8 (3)
N2–N1–O5	53.5 (3)	N1–O1–O3	55.2 (2)
O5–N1–O1	62.9 (3)	O3–O1–O6′	57.1 (2)
O3–O7–O7′	71.5 (3)	O6′–O3–O1	61.0 (2)
O7′–O7–Ow2	65.9 (3)	O1–O3–N1	56.9 (2)
Ow2–O7–N2	63.4 (3)	N1–O3–O7	85.3 (4)
N2–O7–N1	51.8 (3)	O7–O3–O7′	50.3 (2)
N1–O7–O3	45.6 (2)	O7′–O3–O6′	40.2 (2)
O7–Ow2–N2	52.5 (3)	O3–O7′–O7	58.1 (3)
N2–Ow2–O5	53.2 (2)	O7–O7′–Ow2	62.7 (3)
O5–Ow2–Ow1	57.0 (2)	Ow2–O7′–Ow1	52.8 (2)
Ow1–Ow2–O7′	71.1 (3)	Ow1–O7′–O6′	58.1 (3)
O7′–Ow2–O7	51.4 (2)	O6′–O7′–O3	62.4 (3)
Ow2–O5–N2	60.3 (2)	O7′–Ow1–O6′	37.6 (2)
N2–O5–N1	62.4 (3)	O6′–Ow1–O1	61.4 (3)
N1–O5–O1	54.3 (3)	O1–Ow1–O5	62.2 (3)
O1–O5–Ow1	60.8 (3)	O5–Ow1–Ow2	64.9 (2)
Ow1–O5–Ow2	58.1 (2)	Ow2–Ow1–O7′	56.1 (2)

(c) Ring Angle Sums

ring members	ring angle sum	ring members	ring angle sum
La–O3–C6–C5–N1	533.6	La–N2–C7–C8–O5	533.5
La–O1–C4–C3–N1	514.3	La–N2–C9–C10–O7	526.1
La–N1–C1–C2–N2	508.3		

(d) Ruffling Angular Parameters for LaHEDTA[13]

ring members	ϕ_1	ϕ_2	type
La–O3–C6–C5–N1	18	12	aλ
La–O1–C4–C3–N1	37	−20	eλ
La–N1–C1–C2–N2	30	38	
La–N2–C7–C8–O5	21	−4	eλ
La–N2–C9–C10–O7	23	−16	aλ

conclusion has been reached by King[16] and also by Lin and Williams for the case of "soft-sphere ligands".[17]

On the experimental side, the literature seems to be somewhat divided. Some ten-coordinate compounds whose structures have been accurately determined have been classified as BSAP,[2,15,18,19] others have been classified as BD,[20-22] and a good number either have not been specified or else closely conform to neither of the above idealized geometries.[11,23-31] In point of fact, only small distortions are required to convert from one geometry to the other. Ideally, one would prefer a ten-coordinate compound where all ligands are identical. As soon as this is not the case, the distortions introduced can make it difficult if not impossible to refer confidently to one idealized geometry or the other. A comparison of the two geometries, using for example the structures of LaEDTA, LaHEDTA, and the decacoordinate tris(bicarbonato)tetraaquoholmium(III) dihydrate, studied earlier in this laboratory[2] and hereinafter referred to as "HoBicarb", will serve to point out these similarities.

As mentioned above, the structures of LaEDTA and LaHEDTA are very similar, with the five-membered rings of these compounds forming a more relaxed environment than that formed by the four-membered rings of HoBicarb. These four-membered rings, defined by the holmium atom and the bicarbonate groups, have an average "bite" of 2.15 Å, as compared to the 2.78-Å N–O bite and 3.06-Å N–N bite of the lanthanum compounds. Thus, HoBicarb demonstrates a more distorted configuration than the lanthanum compounds.

Making the assumption of BSAP geometry, the θ angles for HoBicarb, LaEDTA, and LaHEDTA average 64.1, 64.3, and 64.1°, respectively; assuming BD geometry gives average θ_1 and θ_2 values of 58.9 and 69.2°, 62.4 and 66.2°, and 60.4 and

Table IV. Equations of Least-Squares Planes[a, b]

Atom	Dist from Plane, Å	Atom	Dist from Plane, Å
Plane I Fitting O1–O3–O7′–Ow1			
$-0.16848X + 0.48007Y - 0.86089Z = 1.00472$			
O1	0.172	Ow1	−0.152
O3	−0.160	La	−1.144
O7′	0.140	O6′	1.538
Plane II Fitting N1–O7–Ow2–O5			
$0.25170X - 0.39413Y + 0.88391Z = 1.14232$			
N1	−0.065	O5	0.080
O7	0.065	La	−1.147
Ow2	−0.080	N2	1.677
Plane III Fitting La–N1–C5–C6–O3			
$-0.02778X - 0.29529Y - 0.95500Z = 1.53327$			
La	0.030	C6	0.112
N1	0.105	O3	−0.029
C5	−0.159		
Plane IV Fitting La–N1–C3–C4–O1			
$-0.41488X - 0.89104Y + 0.18413Z = 1.24778$			
La	0.057	C4	−0.215
N1	−0.223	O1	0.036
C3	0.344		
Plane V Fitting La–N1–C1–C2–N2			
$-0.33674X - 0.92429Y - 0.17967Z = 1.79778$			
La	−0.026	C2	−0.350
N1	−0.092	N2	0.190
C1	0.278		
Plane VI Fitting La–N2–C7–C8–O5			
$0.96308X - 0.09211Y - 0.25295Z = 0.99406$			
La	−0.078	C8	0.056
N2	0.163	O5	0.054
C7	−0.195		
Plane VII Fitting La–N2–C9–C10–O7			
$0.98331X + 0.15927Y - 0.08788Z = 0.44993$			
La	−0.168	C10	−0.104
N2	0.248	O7	0.242
C9	−0.218		

[a] Planes are defined as $c_1X + c_2Y + c_3Z = d$, where X, Y, and Z are cartesian coordinates which are related to the triclinic cell coordinates (x, y, z) by the transformations $X = xa \sin\gamma + zc\cdot(\cos\beta - \cos\alpha\cos\gamma)\sin\gamma$, $Y = xa\cos\gamma + yb + zc\cos\alpha$, and $Z = zc(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}/\sin\gamma$. [b] The dihedral angle between plane I and plane II is 6.98°.

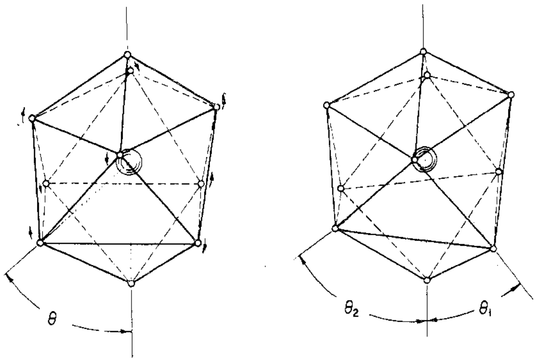

Figure 3. Idealized decacoordinate geometries: left, the bicapped square antiprism, showing the θ angle of Al-Karaghouli and Wood;[15] right, the bicapped dodecahedron, showing the θ_1 and θ_2 angles defined herein. Arrows on the left figure indicate how the BD geometry may be attained by a distortion of the BSAP geometry.

67.8°. The averaged θ angles seem to indicate the BSAP geometry is followed in all three cases, but the deviations from BD geometry are not large. However, large departures from ideality occur in all three structures. HoBicarb is the most distorted, with angles of 47.1 and 50.4°, LaEDTA is the least distorted, and LaHEDTA is intermediate, with one angle of 47.6°, the angle defined by the only four-membered ring of LaHEDTA (as discussed further, below). It thus seems to be difficult to decide on either geometry due to θ-angle arguments alone.

Table V

(a) Dihedral Angles for LaHEDTA[a]

atom 1	atom 2	dihedral angle, deg	angle type
O6′	O3	53.80[b]	A1
O6′	Ow1	58.13	A1
N2	N1	68.42	A1
N2	Ow2	55.73	A1
O6′	O7′	75.24	A2
O6′	O1	52.95	A2
N2	O7	66.73	A2
N2	O5	53.64	A2
O3	O7′	22.42	B1
Ow1	O1	46.66	B1
O7	Ow2	32.01	B1
O5	N1	40.75	B1
O7′	Ow1	18.17	B2
O1	O3	27.58	B2
N1	O7	8.91	B2
Ow2	O5	31.60	B2
O7	O7′	59.35	C1
O5	O1	36.98	C1
O3	O7	52.92	C2
O7′	Ow2	52.56	C2
Ow1	O5	53.90	C2
O1	N1	61.18	C2
Ow2	Ow1	60.15	C3
N1	O3	67.69	C3

(b) Dihedral Angles (deg) for LaHEDTA, LaEDTA, and HoBicarb, Assuming BD Geometry

angle	angle for ideal BD geometry	LaHEDTA	LaEDTA	HoBicarb
A1	67.34	59.02 ± 5.64	60.93 ± 3.90	65.98 ± 10.98
A2	50.71	62.39 ± 7.50	59.93 ± 1.48	59.79 ± 7.95
B1	40.77	35.46 ± 9.16	30.10 ± 4.81	32.69 ± 6.19
B2	11.77	21.57 ± 8.78	24.95 ± 9.57	24.49 ± 20.53
C1	72.22	48.17 ± 11.19	50.16 ± 0.58	62.69 ± 5.90
C2	61.63	55.14 ± 3.52	57.70 ± 5.29	53.08 ± 5.74
C3	46.28	63.92 ± 3.77	59.28 ± 7.19	53.66 ± 8.88

(c) Dihedral Angles (deg) for LaHEDTA, LaEDTA, and HoBicarb, Assuming BSAP Geometry

angle	angle for ideal BSAP geometry[c]	LaHEDTA	LaEDTA	HoBicarb
A	56.36	60.58 ± 7.87	60.43 ± 2.99	61.38 ± 10.63
B	30.80	28.51 ± 11.35	27.52 ± 8.00	28.59 ± 15.71
C	56.19	55.59 ± 8.50	56.21 ± 6.30	55.63 ± 7.87

[a] There are three general classes of dihedral angles for both the BSAP and BD geometries: (A) between two faces sharing an edge defined by a capping atom and an atom on the "square"; (B) between two faces sharing an edge defined by two atoms, both on the same "square"; and (C) between two faces sharing an edge defined by two atoms, which are on each of the two "squares". The nonplanarity of the "squares" of the BD geometry introduces a subclass to each of these classes. [b] The given atoms define the edge shared by the two adjacent triangular faces for which the dihedral angle is reported. [c] If the BD geometry is classed (incorrectly) as BSAP, A, B, and C angles of 59.03 ± 8.32, 26.27 ± 14.50, and 60.44 ± 9.25°, respectively, result.

Another indicator of the molecular geometry is the separation of the least-squares planes passing through the "squares" of the two configurations. If χ is defined as (average plane separation)/(average bond length), χ = 0.76 ± 0.08 for the BD geometry and 0.85 ± 0 for the BSAP geometry. For HoBicarb, χ = 0.87 ± 0.09; for LaEDTA, χ = 0.85 ± 0.10; and for LaHEDTA, χ = 0.88 ± 0.10. These values would also tend to indicate BSAP geometry.

Muetterties and Guggenberger[32] have devised a set of dihedral angles to describe various coordination geometries. At the suggestion of one of the reviewers, we extended this idea to ten-coordinate geometry. Table Va shows the dihedral angles for LaHEDTA; Table Vb shows the dihedral angles for the idealized BSAP geometry and the dihedral angles for LaHEDTA, LaEDTA, and HoBicarb, assuming BSAP geometry; Table Vc shows similar data for BD geometry. These tabulations tend to indicate BSAP geometry, once again.

Finally, for both BSAP and BD geometries, the angle formed by (capping $atom_1$)–(central atom)–(capping $atom_2$) should be 180°. In the highly distorted HoBicarb, this angle is 147.7°; in LaEDTA, it is 169.5°; and in LaHEDTA, it is 162.3°. The better value for LaEDTA as opposed to LaHEDTA can be explained by noting that for LaEDTA the capping atoms are a nitrogen and a water oxygen, whereas in LaHEDTA, the capping atoms are a nitrogen and one of the bridging carboxymethyl oxygens. Presumably the capping water oxygen in LaEDTA is better able to assume an idealized position than its counterpart in LaHEDTA, which is a member of the only four-membered ring found in that structure, a ring with a bite that is significantly less (2.18 Å) than the bites of the five-membered rings.

In summary, LaHEDTA seems to best approximate the BSAP geometry but does depart significantly from ideality. However, it does seem that the more relaxed five-membered rings of both LaEDTA and LaHEDTA allow these molecules to coordinate in a more idealized geometry than the more highly distorted HoBicarb.

Acknowledgment. This work was supported by the U.S. Department of Energy, Division of Basic Energy Sciences.

Registry No. La[HEDTA$(H_2O)_2$]·3H_2O, 66632-99-3.

Supplementary Material Available: A listing of anisotropic temperature factors and structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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