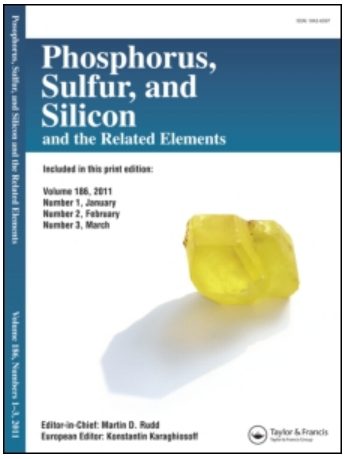

Phosphorus, Sulfur, and Silicon and the Related Elements

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Crystal Structure of the Gadolinium Trihydrogenohydroxy-1 Ethane Bis(Phosphonate)-1,1'' Trihydrate

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CRYSTAL STRUCTURE OF THE GADOLINIUM TRIHYDROGENOHYDROXY-1 ETHANE BIS(PHOSPHONATE)-1,1′ TRIHYDRATE

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(Received April 26, 2001)

The title complex salt $Gd[C(CH_3)(OH)(PO_3H)(PO_3)],3H_2O$ is obtained by progressive dissolving of gadolinium carbonate in an aqueous solution of hydroxyethylidenebisphosphonic acid (HEBP). This compound crystallizes with the orthorhombic space group Pbca *(n°61) and* a = *9.690(1) Å,* b = *9.744(2) Å,* c = *20.585(4) Å, V = 1943.7(5) Å^3, and Z = 8. The coordinence of Gadolinium is 8 and the corresponding polyhedra are associated two by two by sharing an edge to form centrosymmetric "bipolyhedra." The crystal cohesion is assumed by one interligand hydrogen bond and mainly by the hydrogen bond network given by the three water molecules. This compound, where the ligand is tri-ionized, is totally different from the other known lanthanide salts (Ln = Ho, Er, Y) where mono- and di-ionized HEBP ligands coexist with the ratio 1/1.*

Keywords: Crystal structure; gadolinium; hydroxyethylidenebisphosphonate

INTRODUCTION

The hydroxyethylidenebisphosphonic tetraacid (HEBP) $H_3C(OH)(PO_3H_2)_2$ is able to give a great variety of metallic cation complexes.[1] So, with Lanthanides it gives salts as $Ln[C(CH_3)(OH)(PO_3H)(PO_3H_2)][C(CH_3)(OH)(PO_3H)_2],5.5H_2O$, where the ligands HEBP coexist with the ionization degrees 1 and 2. The isostructural compounds (with Ln = Ho, Er, and Y) were obtained in the crystallized state and their crystal structure determined.[2–4] With Gadolinium a new crystallized salt, totally different, with the chemical formula $Gd[C(CH_3)$

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$(OH)(PO_3H)(PO_3)],3H_2O$, was obtained where only one kind of trionized HEBP ligand exists in the structure.

RESULTS AND DISCUSSION

The study complex salt was prepared by progressive addition of gadolinium carbonate in a 30% aqueous solution of boiling HEBP acid with an equimolecular proportion. After cooling and filtering of the insoluble particles, orthorhombic crystals were obtained by slow evaporation at room temperature. The experimental and refinement conditions and the final results of refinement are given in Table I. The atomic

TABLE I Experimental and Refinement Conditions

RX source	Enraf-Nonius CAD4 FR590
Monochromator	Graphite
Wavelength (Å)	0.70926
Temperature (K)	295
Formula unit	$Gd[C(CH_3)(OH)(PO_3H)(PO_3)],3H_2O$
Formula weight ($g \cdot mole^{-1}$)	414.30
Space group	*Pbca* (n°61)
Cell parameters	
a(Å)	9.690(1)
b(Å)	9.744(2)
c(Å)	20.585(4)
Volume ($Å^3$)	1943.7(5)
Z	8
d calcd. ($g \cdot cm^{-3}$)	2.831
Reciprocal space	$-14 \leq h \leq 14; 0 \leq k \leq 14; 0 \leq l \leq 30$
Scan mode	$\omega/2\theta$
Intensity reference reflections	0 0 −10; 0 −6 2; −2 0 10
Position reference reflections	−7 −5 −1; 7 1 3; 1 4 −14
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	1.22
Linear absorption coef. (cm^{-1})	68.39
F(000)	1576
Measured reflections	13,269
Unique reflections	6006
Internal R	0.0287
Reflexions used in final refinement $I_o \geq 3\sigma(I_o)$	1194
Absorption correction	Difabs[4]
coef. min.	0.709
coef. max.	1.292
average	0.963
Max. peak height in final difference map ($e.Å^{-3}$)	1.08
$R = \sum \lvert F_o - F_c \rvert^2 / \sum \lvert F_o \rvert$	0.0289
$R_w = \sum w(\lvert F_o - F_c \rvert^2 / \sum w \lvert F_o \rvert^2)^{1/2}$	0.0303
$(w = [\sigma(\lvert F_o \rvert)^2 + (k\lvert F_o \rvert)^2]^{-1})$ GFIT	1.61

scattering factors of the non-gadolinium atoms are from *SHELXS86* program.[5] Those of Gadolinium come from the *International Tables for Crystallography*[6] and are corrected for the anomalous dispersion ($f' = -0.1653$, $f'' = 3.9035$). The crystal structure was solved by the Patterson—heavy atom method using the *SHELXS86* program[5] and the figures were obtained with the *Ortep-3 for Windows* (version 1.05) program.[7] In spite of a relative precision, the hydrogen atoms were located by successive Fourier-difference synthesis followed by refinements on F^2 and using the total matrix. A last series of two refinement cycles of the atomic coordinates and of the anisotropic thermal parameters gave $R = 0.0289$, $R_w = 0.0303$, and GFIT = 1.61. The atomic coordinates and the equivalent isotropic and anisotropic thermal parameters are given in Tables II and III. Table IV gives the main interatomic distances and valence angles.

TABLE II Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Nonhydrogen Atoms; Isotropic Thermal Parameters for Hydrogen Atoms

ATOM	X	Y	Z	⟨U⟩
Gd	0.29100(3)	0.99591(4)	0.49127(2)	0.015(1)
P1	0.4929(2)	0.7195(2)	0.5474(1)	0.013(1)
P2	0.2308(2)	0.7448(2)	0.6211(1)	0.017(1)
O1	0.4961(6)	0.8747(6)	0.5294(3)	0.017(4)
O2	0.3947(7)	0.6404(6)	0.5043(3)	0.021(5)
O3	0.6372(6)	0.6634(6)	0.5521(3)	0.023(5)
O4	0.2114(6)	0.8783(6)	0.5860(3)	0.021(5)
O5	0.1615(6)	0.6225(6)	0.5911(3)	0.018(4)
O6	0.1735(8)	0.7683(8)	0.6921(4)	0.028(6)
O7	0.4346(8)	0.5698(7)	0.6525(3)	0.026(5)
E1	0.3906(7)	0.8782(7)	0.3951(3)	0.025(6)
E2	0.1985(8)	0.0953(8)	0.3821(4)	0.030(6)
E3	0.2777(13)	0.9396(9)	0.2683(4)	0.050(9)
C1	0.4159(9)	0.7085(8)	0.6292(4)	0.017(6)
C2	0.4840(13)	0.8054(12)	0.6772(5)	0.027(9)
H6	0.20(2)	0.70(2)	0.702(10)	0.22(8)
H7	0.37(2)	0.54(2)	0.646(8)	0.15(6)
H8	0.44(1)	0.78(1)	0.720(6)	0.05(3)
H9	0.409(9)	0.897(8)	0.668(4)	0.04(2)
H10	0.55(1)	0.82(1)	0.678(7)	0.06(5)
H1e1	0.457(9)	0.870(9)	0.404(4)	0.01(2)
H2e1	0.37(1)	0.897(9)	0.354(5)	0.03(2)
H1e2	0.175(9)	0.168(9)	0.389(4)	0.02(2)
H2e2	0.11(1)	0.03(1)	0.368(5)	0.06(3)
H1e3	0.29(3)	1.03(2)	0.25(1)	0.2(1)
H2e3	0.17(2)	0.91(3)	0.24(1)	0.2(1)

Estimated standard deviations in parenthesis. $\langle U \rangle = 1/3 \Sigma U_{ij} (a_j \times b_j)(a_j^* \times b_j^*)$.

TABLE III Anisotropic Thermal Parameters ($\times 10^3$) for Nonhydrogen Atoms

ATOM	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Gd	14.5(2)	15.3(2)	15.7(2)	−0.9(2)	0.3(1)	0.1(2)
P1	13.6(9)	11.0(8)	16.7(10)	−0.4(8)	0.0(8)	0.1(8)
P2	20.3(11)	14.4(9)	16.5(9)	0.3(8)	1.1(9)	−1.2(10)
O1	20(3)	17(3)	16(3)	4(2)	−4(2)	−2(2)
O2	21(3)	23(3)	21(3)	−7(2)	6(2)	−3(3)
O3	17(3)	27(3)	28(3)	−4(3)	−5(3)	9(3)
O4	19(3)	17(3)	29(3)	8(2)	2(2)	−5(3)
O5	12(3)	17(3)	27(3)	−7(2)	−4(2)	0(2)
O6	31(4)	33(4)	21(4)	0(3)	7(3)	−1(3)
O7	31(4)	23(3)	26(4)	10(3)	−6(3)	−4(3)
E1	17(3)	34(4)	25(4)	−1(3)	3(3)	−2(3)
E2	39(4)	26(3)	29(4)	4(3)	7(3)	3(4)
E3	72(8)	49(5)	30(5)	−9(3)	4(4)	−11(5)
C1	21(4)	16(4)	14(4)	−5(3)	2(3)	2(3)
C2	32(6)	35(6)	16(5)	−9(4)	−5(4)	−13(5)

Estimated standard deviations in parenthesis.

The HEBP ligand is tri-ionized by loss of two hydrogen atoms of the P1—O_3 phosphonate group and one hydrogen atom of the P2—O_3H phosphonate group. It complexes 4 Gd^{3+} with two of which by a bidentate bound (Figure 1). The oxygen atoms of the P1—O_3 group are all linked

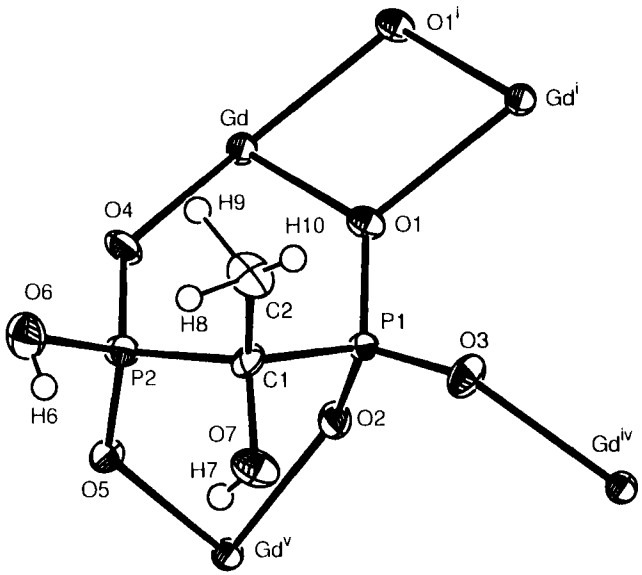

FIGURE 1 The $HEBP^{3-}$ Ligand. Symmetry code: [i]: −x, −y, −z; [iv]: 0.5 + x, 0.5 − y, −z; [v]: 0.5 − x, 0.5 + y, z.

TABLE IV Main Interatomic Distances (Å) and Main Valence Angles (°)

$HEBP^{3-}$ ligand			
C1—O7	1.445(10)	P1—O2	1.512(6)
C1—C2	1.518(11)	P1—O3	1.504(6)
C1—P1	1.845(8)	P2—O4	1.499(6)
C1—P2	1.836(8)	P2—O5	1.501(6)
P1—O1	1.558(6)	P2—O6	1.582(7)
P1—C1—P2	107.5(4)	C2—C1—O7	108.2(7)
P1—C1—C2	112.4(6)	P2—C1—C2	111.4(6)
P1—C1—O7	107.8(5)	P2—C1—O7	109.5(6)
O1—P1—O2	111.5(3)	O4—P2—O5	115.8(4)
O1—P1—O3	110.5(3)	O4—P2—O6	106.0(4)
O2—P1—O3	115.9(4)	O5—P2—O6	109.8(4)
O1—P1—C1	106.4(3)	O4—P2—C1	109.5(4)
O2—P1—C1	104.5(3)	O5—P2—C1	108.7(3)
O3—P1—C1	107.2(4)	O6—P2—C1	106.6(4)
C2—H8	1.01(13)	O6—H6	0.7(2)
C2—H9	1.17(9)	O7—H7	0.7(2)
C2—H10	0.63(13)		
C1—C2—H8	104(6)	H8—C2—H9	94(7)
C1—C2—H9	96(4)	H8—C2—H10	116(15)
C1—C2—H10	125(14)	H9—C2—H10	118(14)
P2—O6—H6	89(15)	C1—O7—H7	102(14)
Gd coordination polyhedron			
Gd—O1	2.441(5)	Gd—O4	2.390(6)
Gd—$O1^{i}$	2.455(5)	Gd—$O5^{v}$	2.441(6)
Gd—$O2^{v}$	2.299(6)	Gd—E1	2.483(6)
Gd—$O3^{iv}$	2.330(6)	Gd—E2	2.606(7)
O1—Gd—$O2^{v}$	153.6(2)	$O2^{v}$—Gd—O4	86.9(2)
O1—Gd—$O3^{iv}$	108.8(2)	$O2^{v}$—Gd—$O5^{v}$	75.0(2)
O1—Gd—O4	76.6(2)	$O2^{v}$—Gd—E1	132.8(2)
O1—Gd—$O5^{v}$	79.6(2)	$O2^{v}$—Gd—E2	66.7(2)
O1—Gd—E1	73.5(2)	$O3^{iv}$—Gd—O4	77.7(2)
O1—Gd—E2	137.4(2)	$O3^{iv}$—Gd—$O5^{v}$	141.2(3)
$O1^{i}$—Gd—$O2^{v}$	111.3(2)	$O3^{iv}$—Gd—E1	68.6(2)
$O1^{i}$—Gd—$O3^{iv}$	144.5(2)	$O3^{iv}$—Gd—E2	72.4(2)
$O1^{i}$—Gd—O4	131.2(2)	O4—Gd—$O5^{v}$	67.4(2)
$O1^{i}$—Gd—$O5^{v}$	74.2(2)	O4—Gd—E1	123.7(2)
$O1^{i}$—Gd—E1	76.9(2)	O4—Gd—E2	140.5(2)
$O1^{i}$—Gd—E2	87.1(2)	$O5^{v}$—Gd—E1	146.2(2)
$O1^{i}$—Gd—O1	67.7(2)	$O5^{v}$—Gd—E2	127.2(2)
$O2^{v}$—Gd—$O3^{iv}$	87.3(2)	E1—Gd—E2	67.5(2)

Hydrogen bonds

A H B	A—H	A—B	H—B	A—Ĥ—B
O6—H6·····$E3^{vii}$	0.7(2)	2.76(1)	2.1(2)	153(20)
O7—H7·····$O4^{v}$	0.7(2)	2.713(9)	2.2(2)	139(18)
E1—H1e1····$O5^{iv}$	0.67(9)	2.72(1)	1.99(9)	163(9)

(Continued on next page)

TABLE IV Main Interatomic Distances (Å) and Main Valence Angles (°) *(Continued)*

E1—H2e1···E3	0.89(9)	2.90(1)	2.0(1)	165(9)
E2—H1e2···E1^{v}	0.76(9)	2.90(1)	2.15(9)	173(9)
E2—H2e2···O7^{iv}	1.1(1)	3.10(1)	2.1(1)	173(9)
E3—H1e3···O6^{ii}	1.0(2)	3.28(1)	2.3(2)	173(22)
E3—H2e3···O6^{vii}	1.2(2)	2.75(1)	2.0(3)	117(17)

Estimated standard deviations in parenthesis. Symmetry code: ^{i}:−x, −y, −z; ^{ii}: 0.5 − x, −y, 0.5 + z; ^{iii}: 0.5 + x, y, 0.5 − z; ^{iv}: 0.5 + x, 0.5 − y, −z; ^{v}: 0.5 − x, 0.5 + y, z; ^{vi}: −x, 0.5 + y, 0.5 − z; ^{vii}: x, 0.5 − y, 0.5 + z.

to gadolinium cations with one of them (O2) to two Gd^{3+}. The P2-O_3H phosphonate group is only linked to two Gd^{3+} by the oxygen atoms O4 and O5 while O6 is carrier of the unique remaining hydrogen atom (H6). This dissymmetrical behaviour of the two phosphonate groups is expressed by very different pseudo-torsion angles (Table V) and an intermediate conformation between eclipsed and staggered configurations (Figure 2).

The $HEBP^{3-}$ ligands are directly linked together by only one hydrogen bond, O7-H7···O4^{v} with the shortest O···O distance (2.713(9) Å) of the any other hydrogen bonds existing in this structure (Table IV). All the other hydrogen bonds implying the $HEBP^{3-}$ ligands involve the water molecules. So, the oxygen atom O6 is acceptor of two hydrogen bonds from two E3 type water molecules and O7 is acceptor of a hydrogen bond given by E2. Lastly, the hydrogen atom H6 gives a hydrogen bond to E3 (Table IV).

TABLE V Pseudo-Torsion Angles (°) and Main Planes of Atoms (the Shifts of the Outplane Atoms given are in Å) for bisphosphonate group

O1—P1	P2—O4	17.3(3)	C2—C1	P1—O1	−50.4(6)
O2—P1	P2—O5	21.6(3)	C2—C1	P2—O4	70.4(6)
O3—P1	P2—O6	36.8(5)	O7—C1	P1—O2	72.3(5)
			O7—C1	P2—O5	−42.5(5)

2P1—C1—P2 plane: $-0.1791x \pm 0.9736y \pm 0.1417z + 9.2778 = 0$

O3	0.269(6)	O6	−0.331(8)

C2-C1-O7 plane: $0.8576x \pm 0.0658y \pm 0.5101z + 3.6055 = 0$

H7	−0.42(17)	H9	−0.58(9)
H8	−0.80(12)	H10	0.51(14)
Gd	0.226(1)		

Estimated standard deviations in parenthesis.

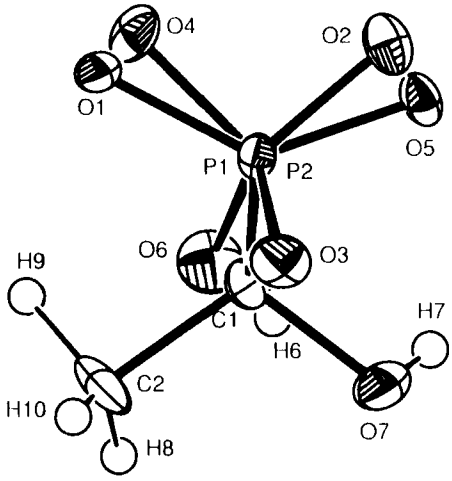

FIGURE 2 $HEBP^{3-}$ ligand projection in the plane perpendicular to the P1···P2 direction.

The P—O bond lengths depend firstly upon the fact that they carry or not a hydrogen atom but also if they are involved in the formation of hydrogen bonds or coordinated to Gd^{3+}. The shortest values concern the P—O^- and P=O indistinguishable kinds of bonds, which are about 1.50 Å while for P2—O6—H this value is 1.582 Å. It is remarkable that the P1—O1 bond (1.558(6) Å) is abnormally long in spite of there is no hydrogen atom. This is can be assigned to the coordination of O1 with two Gd^{3+}. It is also remarkable that for each phosphonate group the average of the three P—O lengths are very similar: respectively, 1.525 Å and 1.527 Å for P1—O_3 and P2—O_3. These values are completely in agreement with the average value of 1.526 Å calculated for all the known HEBP salts.[1]

The coordination of Gadolinium is 8. The coordination polyhedra are irregular square base antiprisms and are associated two by two by sharing the $O1\cdots O1^i$ edge to make individualized centrosymmetric "bipolyhedra" Gd_2O_{14} (Figure 3). Each Gd^{3+} is linked to two water molecules, E1 and E2, and to 4 $HEBP^{3-}$ ligands, 2 by monodentate bond, 2 by bidentate bond (Figure 4).

The three water molecules, named E1, E2, E3, take a prominent part in the cohesion of the crystal structure according to very different ways. E1 is coordinated to Gd^{3+} and is donnor of two hydrogen bonds: one towards O5 from the P2—O_3 group of $HEBP^{3-}$, one towards E3, and is acceptor of a hydrogen bond from E2. E2 is also coordinated to Gd^{3+},

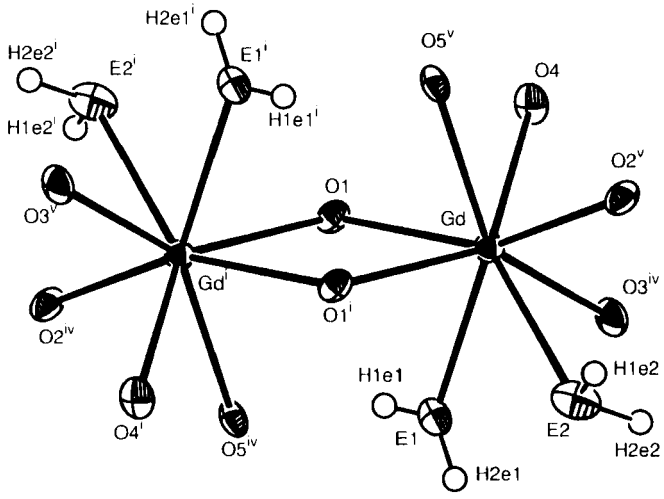

FIGURE 3 Gadolinium "Bipolyhedra." Symmetry code: ^{i}: $-x, -y, -z$; ^{iv}: $0.5+x, 0.5-y, -z$; ^{v}: $0.5-x, 0.5+y, z$.

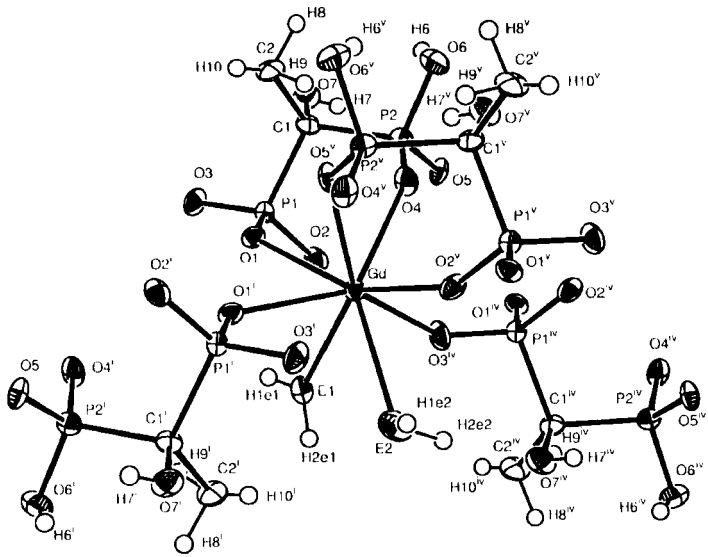

FIGURE 4 Gadolinium surrounding. Symmetry code: ^{i}: $-x, -y, -z$; ^{iv}: $0.5+x, 0.5-y, -z$; ^{v}: $0.5-x, 0.5+y, z$.

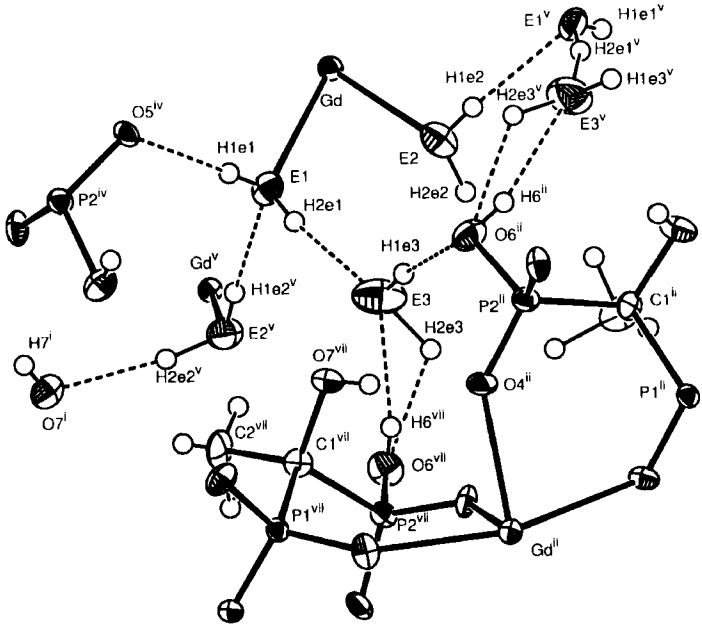

FIGURE 5 Water molecule chaining. Symmetry code: [i]: $-x, -y, -z$; [ii]: $0.5-x, -y, 0.5+z$; [iv]: $0.5+x, 0.5-y, -z$; [v]: $0.5-x, 0.5+y, z$; [vii]: $x, 0.5-y, 0.5+z$.

is donnor of two hydrogen bonds: one towards O7 of the alcohol group of the $HEBP^{3-}$ ligand, one towards E1, but is not acceptor of a hydrogen bond. E3 is not coordinated to Gd^{3+} but is donnor of two hydroegen bonds towards the oxygen atom O6 of two $HEBP^{3-}$ ligands and is acceptor of two hydrogen bonds, one given by E1, one by H6 from the P2–O_3H phosphonate group of the $HEBP^{3-}$ ligand. So, the $HEBP^{3-}$ ligands and the Gd^{3+} coordination polyhedra are linked together by exchange of hydrogen bonds involving bridges with one or two water molecules (Figure 5). Figure 6 shows a general view of the crystal structure of $Gd[C(CH_3)(OH)(PO_3H)(PO_3)],3H_2O$.

CONCLUSION

The crystal structure of $Gd[C(CH_3)(OH)(PO_3H)(PO_3)],3H_2O$ is original and very different from these of hydroxyethylidenebisphosphonate of Y, Ho, and Er, particularly about the Gd^{3+} cation. In this structure, Gd^{3+} is 8-coordinated instead of 7, the coordination polyhedra are associated two by two by sharing an edge making centrosymmetric Gd_2O_{14}

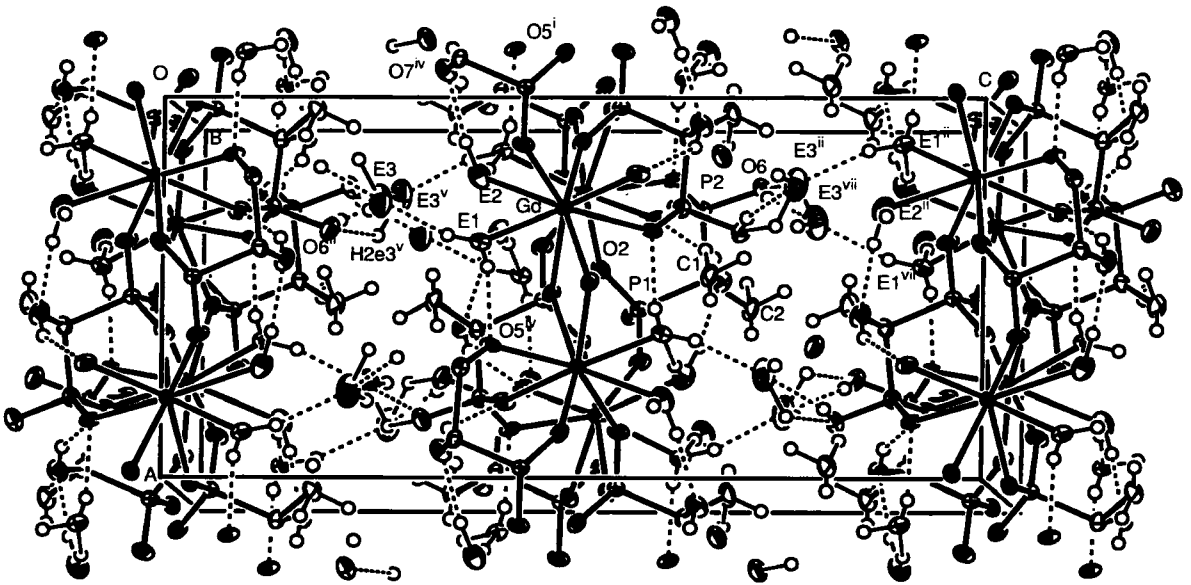

FIGURE 6 General view of the crystal structure of $Gd[C(CH_3)(OH)(PO_3H)(PO_3)],3H_2O$. Symmetry code: [i]: −x, −y, −z; [ii]: 0.5 − x, −y, 0.5 + z; [iii]: 0.5 + x, y, 0.5 − z; [iv]: 0.5 + x, 0.5 − y, −z; [v]: 0.5 − x, 0.5 + y, z; [vi]: −x, 0.5 + y, 0.5 − z; [vii]: x, 0.5 − y, 0.5 + z.

"bipolyhedra" instead of independent LnO_7 polyhedra. Lastly, the HEBP ligands are tri-ionized and are linked together with only one hydrogen bond.

DEDICATION

With great emotion, the coauthors, NQD and JPS, inscribe this article to the memory of their coworker Marie-Renée Lee, deceased accidentally in 1993.

REFERENCES

[1] J.-P. Silvestre, Nguyen Quy Dao, and Y. Leroux, *Heteroatom Chemistry*, **12,** 73 (2001), supplement to the Special Issue on the chemistry and biochemistry of bisphosphonates and aminophosphonates, **11**(7), (2000).
[2] J.-P. Silvestre, Nguyen Quy Dao, Y. Leroux, M. Wozniak, and D. Pareau, *Rapport du PIRSEM-CNRS*, **3,** 279 (1986).
[3] L. M. Shkol'nikova, A. A. Masyuk, G. V. Polanchuk, L. V. Krinitskaia, E. G. Afonin, A. L. Poznyak, and V. E. Zavodnik, *Sov. J. Coord. Chem.*, **15,** 1424 (1989).
[4] R. Rochdaoui, *Thèse de Doctorat*, Ecole Centrale Paris (1991).
[5] G. M. Sheldrick, *SHELXS86*, Program for Crystal Structure Determination, Univ. of Cambridge, England (1986).
[6] *International Tables for Crystallography*, C, 501 and 220, Edited by A. C. J. Wilson (Kluwer Academic Publishers, Dordrecht/Boston/London).
[7] L. J. Farrugia, *Ortep 3 for Windows 1.05*, <www.http://www.chem.gla.ac.uk/~louis/ortep3>.
[8] N. Walker and D. Stuart, *Acta Cryst.*, **A39,** 158 (1983).