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A Survey of the Behavior of the Hydroxybisphosphonic Function in Crystallized Acids, Metallic Salts, and Some Related Compounds

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ABSTRACT: *The flexibility and the different degrees of ionization of the hydroxybisphosphonic function provide numerous possibilities for the complexation of metallic and organic cations to molecules possessing these functions. The properties of this class of compounds are very interesting for different industrial and medical applications. They depend in a large part on the nature of the hydrocarbonated chain substituted to CH_3 in hydroxyethylidenebisphosphonic acid and of the number and the position of the bisphosphonic groups grafted on this chain.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:73–89, 2001

INTRODUCTION

The crystal structure of the hydroxyethylidenebisphosphonic acid (HEBP) monohydrate $H_3C–C(OH)(PO_3H_2)_2 \cdot H_2O$ was the first solved concerning this class of compounds [1]. This molecule is shown in Figures 1 and 2. The hydroxybisphosphonic function -$C(OH)(PO_3H_2)_2$ is a tetraacid with only one strong acidity.

Alone in an infinitely diluted medium, the HEBP

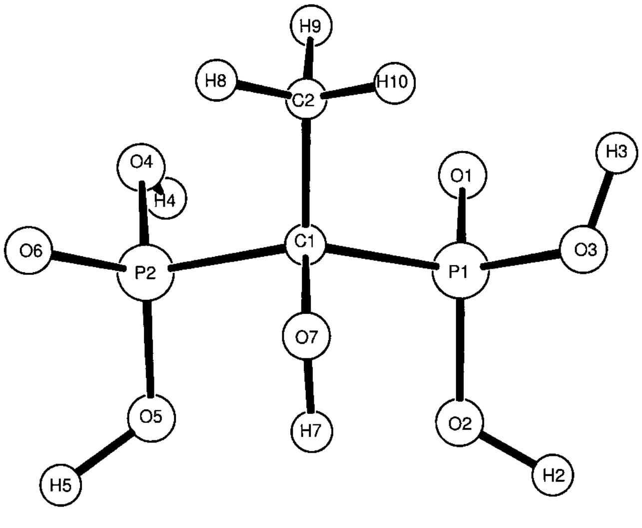

FIGURE 1 The molecule of hydroxyethylidenebisphosphonic acid with the chosen standardization for the atom names. (In the case of other compounds the hydrogen atoms eventually linked to O1 and O6 are named respectively H1 and H6).

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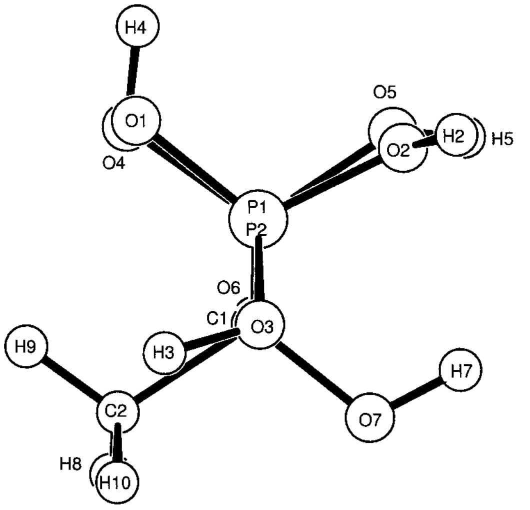

FIGURE 2 View of the molecule of hydroxyethylidenebisphosphonic acid showing the shifting between the two phosphonate groups: orthogonal projection perpendicular to the plane of the figure along the P1 (upper)–P2 (lower) axis.

molecule presents many free rotations. This is the case of each PO_3H_2 group and CH_3 and H atoms of the P–OH group. In these conditions, this molecule would show a symmetry plane defined by O7–C1–C2. In the crystallized state, all these free rotations are locked by intermolecular hydrogen bonds or involving water molecules or by the complexation of cations in salts with loss of the symmetry plane. So, because of its numerous possibilities of ionization and its flexibility of conformation, the HEBP function is able to give a great variety of complexes. We have classified these compounds in three groups: (1) the hydroxyethylidene bisphosphonic acid and its metallic salts, (2) the different bisphosphonated acids and complex salts, and (3) the tetraphosphonate salts.

This article presents the compilation of crystal structure data to show the behavior of the hydroxybisphosphonic function in the crystallized state.

For further comparison and discussion, the atoms of the hydroxybisphosphonic function were renamed for all the compounds found in the literature following the convention used in Figures 1 and 2.

CRYSTAL STRUCTURE SYMMETRY AND UNIT CELL PARAMETERS

Tables 1–3 give the space group and unit cell parameters and volume for all compounds available in the literature; among them 44 nonisostructural structures are listed. All the compounds, except **24**, **25**, and **28** (i.e., <7%) crystallize in centrosymmetric groups with generally a low symmetry group; 27.3% in triclinic $P\bar{1}$ (space group 2); 52.3% in monoclinic space group 14 ($P2_1/c$, $P2_1/n$, $P2_1/a$). Only four compounds (**2** and **15**, Table 1; **24** and **28**, Table 2) crystallize in orthorhombic space groups, respectively: *Pcab* (space group 61), *Pbca* (s.g. n°61), $Pca2_1$ (space group 29) and $Pna2_1$ (space group 33). The volume occupied by the ligand HEBP is about 200 Å^3, and after considering the volume of cations, water molecules, esterification groups, and substitution of the CH_3 group, it can be observed that the compacity is nearly the same for all the compounds.

THE P–O AND C–O BONDS

Tables 4–6 give the P–O and C–O distances for each compound with averages for each PO_3 group (columns 12 and 13), for the two PO_3 groups together (column 14), and for all the P–O and C–O bonds (column 15). For P–OH groups the P–O lengths are generally greater than 1.55 Å. It is not possible to distinguish P = O from P–O$^-$ bonds: they generally have lengths less than 1.51 Å. When the hydrogen atom is shared between two P–O or one P–O and one water molecule, the P–O length is generally about 1.52–1.53 Å. Whatever their number, the influence of hydrogen bonds received or involved cation coordinence bonds is not systematic: it is not significant from one compound to another and even also in a same compound. Thus two anomalies can be observed for the compound 21 (Table 5), which presents an inversion of the P–O bond lengths: P–O bonds carrying an H atom are shorter than P–O bonds without an H atom, and the C–OH group is ionized by loss of the hydrogen atom. On the other hand, the P–O length average in PO_3 groups is very similar for all the compounds (1.526 Å), and a compensation can be frequently observed between the two PO_3 groups and sometimes even with the C–O length of the C–OH group as it can be seen with the different calculated average values.

Then again these averages are not dependent on the ionization degree of the PO_3H_2 groups or on their esterification.

At last we can observe that they are the oxygen atoms O3 and O6 which are the most frequently carriers of an H atom, particularly in the case of the HEBP acid and its metallic salts. This is globally true whatever the ionization degree of the hydroxybisphosphonic group. So, for the 40 compounds that are not isomorphous or esterified, the 119 remaining hydrogen atoms are distributed as follows:

> 26.9% on P1–O3, 21.0% on P2–O6, 14.7% on P2–O4 and P1–O2, 12.2% on P2–O5 and 10.5% on P1–O1. This is a consequence of the volume oc-

TABLE 1 HEBP Acid and Metallic Complexes: Unit Cell Parameters

No.	*Compound*	*Space Group*	*Z*	*a(Å)*	*b(Å)*	*c(Å)*	*α(°)*	*β(°)*	*γ(°)*	*V(Å³)*	*Ref.*
1a	$(LH_4).H_2O$	$P2_1/c$	4	7.011(3)	17.613(7)	7.143(3)		108.57(7)		836.2	[1]
1b*	$(LH_4).H_2O$	$P2_1/c$	4	6.981(3)	17.55(3)	7.107(9)		108.6(1)		825.2	[2,22]
2a	$Na(LH_3).H_2O$	$Pcab$	8	18.773(3)	11.834(4)	7.500(3)				1666(2)	[3,23]
2b	$Na(LH_3).H_2O$	$Pbca$	8	7.499(3)	11.830(5)	18.779(6)				1666	[4]
3	$Na_2(LH_2).4H_2O$	$P\underline{2}_1/c$	4	10.598(4)	5.993(2)	18.262(6)		91.77(1)		1159.34	[5]
4	$K(LH_3).2H_2O$	$P\underline{I}$	2	7.499(1)	11.015(2)	6.679(3)	101.92(3)	109.92(3)	78.03(1)	501.8	[6]
5	$NH_4(LH_3).2H_2O$	$P\underline{I}$	2	7.562(1)	11.156(1)	6.668(2)	99.78(2)	109.08(2)	79.65(1)	519.2	[6]
6a	$Rb(LH_3).2H_2O$	$P\underline{I}$	2	6.627(5)	7.592(5)	11.066(3)	79.82(4)	80.69(4)	71.24(5)	516(5)	[7]
6b	$Rb(LH_3).2H_2O$	$P\underline{I}$	2	7.602(3)	11.066(3)	6.627(4)	99.29(5)	108.84(5)	79.79(5)	516.0	[8]
bc*	$Rb(LH_3).2H_2O$	$P\underline{I}$	2	6.623(7)	7.597(7)	11.053(10)	79.78(8)	80.69(8)	71.17(8)	514.7	[9]
7	$Cs(LH_3).2H_2O$	$P\underline{I}$	2	7.729(1)	11.125(2)	6.587(3)	95.89(3)	107.59(3)	81.56(1)	533.0	[8]
8	$Ca(LH_2).2H_2O$	PI	2	6.961(3)	8.085(4)	9.729(4)	106.26(7)	106.08(7)	60.33(5)	450.4	[10]
9	$Sr(LH_3)_2.4H_2O$	$C2/c$	4	18.411(9)	12.769(6)	8.323(5)		100.72(6)		1922(25)	[11,23]
10a	$Cd(LH_2).2H_2O$	$P2_1/n$	4	14.229(3)	5.613(1)	11.521(3)		93.06(1)		918.8(4)	[12]
10b	$Hg(LH_2).2H_2O$	$P2_1/n$	4	14.346(4)	5.692(2)	11.621(4)		95.17(2)		945(1)	[12]
11	$Pb(LH_2).H_2O$	$P2_1/c$	4	10.896(6)	8.297(5)	10.317(6)		109.82(6)		877(2)	[13,22]
12	$Y(LH_3)(LH_2)$ $5.5H_2O$	$P2_1/n$	4	10.451(2)	11.395(3)	17.173(3)		94.28(1)		2039.5(7)	[14,15]
13	$Ho(LH_3)(LH_2)$ $5.5H_2O$	$P2_1/n$	4	10.447(2)	11.382(2)	17.129(4)		94.32(3)		2031.1(7)	[15]
14a	$Er(LH_3)(LH_2)$ $5.5H_2O$	$P2_1/n$	4	10.432(1)	11.398(2)	17.134(2)		94.35(2)		2031.6(5)	[15]
14b	$Er(LH_3)(LH_2)$ $5.5H_2O$	$P2_1/n$	4	10.434(2)	11.407(4)	17.163(4)		94.33(2)		2036.9	[16]
15	$Gd(LH).3H_2O$	$P\underline{b}ca$	8	9.7125(5)	9.741(1)	20.53(3)				1942.5(3)	[17]
16	$Cu_3(LH)_2.6H_2O$	$P\underline{I}$	1	9.891(3)	8.784(3)	6.221(2)	103.24(2)	98.94(2)	106.26(2)	494.93	[18,24]
17	$K_3Na_2Cu(L)_2$ $12H_2O$	PI	2	11.951(3)	6.220(1)	11.789(2)	113.17(1)	108.94(2)	97.56(1)	727.4	[19]

Estimated standard deviations in parenthesis.
$L = [(H_3C)(OH)C(PO_3)_2]^{4-}$.
Compounds **1b*** and **6c***, crystal structures solved by neutron diffraction.

cupied by the hydrophobic methyl group or its substitutings.

Table 7 retails the distribution of the hydrogen atoms for each ionization degree.

CONFORMATION OF THE HYDROXYBISPHOSPHONATE FUNCTION (TABLES 8–10 AND FIGURE 2)

From one compound to an another, the P1–C1–P2 angles are similar with a 10% deviation at most. The highest and smallest values are respectively 106.3(2)° (compound **45**, Table 9) and 116.0(8)° (compound **36**, Table 9) with a general average of 111.7° (111°42′), not far from the theoretical value (109°28′) of the valence angle in sp^3 hybridization of the carbon atom.

The relative displacement between the two PO_3 groups of the hydroxybisphosphonic function (Figure 2) can be measured by the pseudo-torsion angles P1–O1/P2–O4, P1–O2/P2–O5 and P1–O3/P2–O6. Generally these three angles have the same direction of rotation, which depends only on the choice of the asymmetric unit. So, a negative sign is only given when one angle has a direction of rotation opposite to the other two or if these directions are different between two HEBP functions, which exist in the same asymmetric unit (examples: compounds **1, 12–14** [Table 8], **22** and **45**, [Table 9]). The values of these angles correspond to a not far from eclipsed conformation for a great majority of compounds. Only the compounds **24, 31, 37, 48**, and perhaps also **32** present a rather staggered configuration. So the distribution of the values of the pseudo-torsion angles is very large: from 0.1(3)° (compound **21**, Table 9) to 58.3(5)° (compound **37**, Table 9). These angles depend on the cation complexation mode and of the hydrogen bonds given or received by the oxygen atoms.

CATION COMPLEXATION MODE: TABLES 11–13

The hydroxybisphosphonate groups can complex the cations in four different ways: (1) by a monodentate bond involving an oxygen atom of one of the two PO_3

TABLE 2 Other Varied Bisphosphonated Acids and Complexes: Unit Cell Parameters

No.	*Compound*	*Space Group*	*Z*	*a(Å)*	*b(Å)*	*c(Å)*	*α(°)*	*β(°)*	*γ(°)*	*V(Å³)*	*Ref.*
18	$EDA(LH_3)$	$P\underline{2}_1/c$	4	6.867(1)	11.665(2)	10.977(2)		101.66(9)		861.2(2)	[20]
19	$2A3MP(LH_3).H_2O$	$P1$	2	8.083(2)	12.595(9)	7.174(3)	106.24(6)	92.40(4)	87.15(5)	700.1(6)	[21]
20	$(2A4MP)_2(LH_{3.5})(LH_{2.5})$ $3H_2O$	$P2_1/c$	4	7.3400(8)	21.200(5)	18.807(2)		93.96(1)		2919.6(6)	[21]
21	$(NH_4)_6Mo_6O_{17}(LH)_2.10H_2O$	$P\underline{2}_1/c$	4	8.636(2)	31.255(4)	16.619(5)		96.82(2)		4454	[25]
22	$(NH_4)_3MoO_2(LH_2)$ $(LH).6.75H_2O$	$P1$	2	9.215(1)	9.383(1)	15.470(3)	101.43(1)	97.70(1)	99.01(1)	1298(2)	[26]
23	$Na_4(NH_4)MoO_2(H)(L)_2$ $15H_2O$	$C2/c$	4	11.980(4)	13.876(3)	19.410(6)		106.03(2)		3101	[27]
24	$H(NH)(CH_3)_2(HMBP).H_2O$	$Pca2_1$	4	12.839(3)	7.290(2)	10.142(2)				949.2(6)	[28]
25	$(OH)(NH_3)(CH_2)_2(HMBP)$	$P2_1$	2	6.626(1)	9.971(1)	6.924(1)		110.56(1)		428.3(2)	[28]
26	$(NH_3)(CH_2)_3(LH_3)$	$P2_1/n$	4	10.503(3)	10.952(3)	8.028(2)		98.55(3)		913.18	[29]
27	$(NH_3)(CH_2)_5(LH_3)$	$P2_1/c$	4	6.960(2)	13.127(5)	12.056(3)		95.89(2)		1095.6(6)	[30]
28	$(NH_3)(CH_2)_5(LH_3).H_2O$	$Pna2_1$	8	12.002(9)	13.778(8)	14.131(22)				2336.8	[31]
29	$Zn[(NH_3)(CH_2)_3(LH_2)]_2.2HO$	$P2_1/c$	4	12.589(5)	13.582(4)	12.447(6)		110.0(1)		1999.9	[31] [32]
30	$Cd[(NH_3)(CH_2)_3(LH)].H_2O$	$P2_1/n$	4	12.478(5)	14.581(4)	5.765(14)		98.1(1)		1038.4	[31] [32]
31	$[(H_3C)O(H)(CH_3)]$ $[(CH_3)(CH_2)_3(LH_3)]$	$P\bar{1}$	2	11.404(3)	10.426(3)	6.199(5)	92.07(1)	95.90(1)	110.45(1)	684.89	[31]
32	$(NH_3)(CH_2)_3(LH_{3.5})_2.2H_2O$	$P2_1/n$	8	14.808(4)	10.342(3)	13.494(4)		98.95(2)		2041.4	[33] [24]
33	$(L)(CH_3)_4$	$P\bar{1}$	2	8.915(3)	8.786(3)	8.226(3)	116.02(2)	95.78(2)	87.63(2)	576.06	[34] [24]
34	$(C_6H_5)(L)(CH_3)_4$	$P2_1/n$	4	14.743(4)	8.494(2)	12.318(3)		104.35(2)		1494.4	[34] [24]
35	$(C_6H_5)(L)(CH_2C_6H_5)_4$	$P2_1/c$	4	14.427(2)	27.941(2)	8.246(2)		107.0(1)		3178.8	[35] [36]
36	$(CH_3)(L)(CH_2C_6H_5)_4$	$P2_1/c$	4	10.968(7)	8.766(3)	29.681(11)		103.1(1)		2778.9	[36]
37	$NH_3(CH_2)_5(LH_3)$	$P2_1/n$	8	10.160(4)	21.347(5)	10.700(3)		95.25(2)		2310.9	[37]
38	Betaine bis(dihydroxyphosphinoyl)-2,2 *N*(2′,3′,4′-H pyrolyl) pyrrolidin	$P2_1/n$	4	11.538(3)	11.168(5)	9.440(4)		91.59(2)		1215.9	[37]
39	$Cu[(NH_3(CH_2)_3(LH_2)_2]_2$ $2H_2O$	$P2_1/c$	4	12.622(4)	13.524(4)	12.521(3)		110.82(6)		1997.8	[37] [38]
40	$Cu_{1/2}[(NH_3(CH_2)_5(LH_2)_2]$ $2H_2O$	$P2_1/n$	4	7.396(3)	13.189(3)	13.822(3)		102.89(5)		1314.3	[37] [38]
41	$[H_2N(CH_2CH_3)_2]_2Cu(LH_2)_22H_2O$	$P2_1/c$	2	7.495(3)	11.473(4)	14.947(7)		96.81(4)		1276(2)	[39]
42	$[H_2N(CH_2CH_3)_2]_2Co(LH_2)_2$ $2H_2O$	$P2_1/c$	2	7.359(1)	11.586(2)	15.130(3)		96.18(1)		1282.5(7)	[39]
43	$[H_2N(CH_2CH_3)_2]_2Mg(LH_2)_2$ $2H_2O$	$P2_1/c$	4	7.360(1)	11.583(2)	15.135(3)		96.16(3)		1282.4(4)	[40]
44	$[H_2N(CH_2CH_3)_2]_2Zn(LH_2)_2$ $2H_2O$	$P2_1/c$	4	7.366(1)	11.577(2)	15.115(2)		96.22(2)		1281.4(3)	[40]
45	$Cu(LH_2)(bipyridil).4H_2O$	$P\bar{1}$	2	8.309(2)	10.362(2)	10.811(2)	91.53(1)	90.57(2)	93.43(1)	928.74	[16]
46	$NaCu(LH_2)Cl.3H_2O$	$P2_1/c$	4	12.219(4)	8.608(2)	12.427(3)		115.87(3)		1176(1)	[41]

Estimated standard deviations in parentheses.

EDA, ethylenediammonium, 2A3MP, 2-amino 3-methyl pyridinium, 2A4MP, 2-amino 4-methyl pyridinium, L, $[(H_3C)(OH)C(PO_3)_2]^{4-}$.

groups, never the oxygen atom of the C–OH group; (2) by a bidentate bond given by one oxygen atom from each PO_3 group, never from the same PO_3 group or from a PO_3 and C–OH group; (3) by a tridentate bond given only by one oxygen atom from each PO_3 group and from the C–OH group; and (4) by a tetradentate bond; this case is exceptional and concerns exclusively the compound **17** (Table 11) $K_4Na_2Cu[(H_3C)(OH)C(PO_3)_2]_2 \cdot 12H_2O$: for one of the potassium atoms the four bonds are given by two oxygen atoms of each PO_3 group.

For the different cations under investigation, all these possibilities can coexist, and the cation coordination can be completed or not by water molecules. The cation coordination polyhedra can be independent or linked together by sharing summits,

TABLE 3 Bis-HEBP Complexes (DHHTP and DHOTP): Unit Cell Parameters

No.	*Compound*	*Space Group*	*Z*	*a(Å)*	*b(Å)*	*c(Å)*	α(°)	β(°)	γ(°)	*V(Å³)*	*Ref.*
47	$(H_3O)_2$(DHHTP)$2H_2O$	*C*2/*c*	4	19.935(3)	9.925(2)	10.195(3)		108.51(2)		1912.8(7)	[42]
48	Na_2(DHHTP).$4H_2O$	$P2_1/a$	2	10.472(2)	10.645(4)	9.160(2)		92.12(2)		1024.9(5)	[43]
49	K_2(DHHTP).$2H_2O$	$C\underline{2}/c$	4	19.914(5)	9.813(3)	10.046(2)		107.83(2)		1872.5(7)	[42]
50	Cu(DHHTP).$10H_2O$	$P\underline{\mathrm{I}}$	1	9.820(5)	7.636(4)	9.543(2)	109.00(1)	113.09(1)	76.39(1)	617(1)	[44]
51	$[(H)O(CH_2)_2]_2$(DHOTP).$2H_2O$	$P\underline{\mathrm{I}}$	1	10.052(10)	9.336(9)	8.282(12)	98.4(1)	104.9(1)	106.6(1)	699.82	[31]
52	Ca(DHOTP).$6.8H_2O$	$P\mathrm{I}$	1	11.168(5)	11.032(6)	5.138(7)	91.9(1)	91.0(1)	91.4(1)	632.37	[31]
53	Cu_2(DHOTP).$12H_2O$	*C*2/*c*	4	31.956(2)	6.034(9)	18.510(3)		128.6(1)		2789.9	[31]

Estimated standard deviations in parentheses. DHHTP, 1,6-dihydroxyhexylidene-1,1,6,6-tetraphosphonate; DHOTP, 1,8-dihydroxyoctilidene-1,1,8,8-tetraphosphonate.

edges, faces, or alternatively summit and edge forming mono-, bi- or tridimensional chainings. The polyhedra can also be associated two by two following independent bipolyhedra (compounds **47–49**, Table 13). The possibilities are very diverse, and there is no rule involving the nature of the cation.

WATER MOLECULE

The water molecules take a prominent part in the cohesion of the crystal structures. All the compounds crystallize with water molecules, sometimes with a great number, except compounds **18, 25–27, 31, 33–38** (Table 2). Various kinds of water molecules can be distinguished and coexist in a crystal structure: (1) water molecules taking part in the cation coordination; (2) water molecules connecting the ligands following varying manners by bridges involving one or two H_2O and even three with starry arrangement (compounds **12–14**, Table 1); (3) statistical water molecules with a random distribution on different uncompletely occupied crystallographic sites; and (4) exceptionally a water molecule can play the role of a cation by ionization as H_3O^+ (compound **47**, Table 13).

All these water molecules are involved as donors of two hydrogen bonds and acceptors of zero, one or two hydrogen bonds. We can consider that the last two sorts of water molecules play the role of genuine cement between the bisphosphonated ligands.

NETWORK OF HYDROGEN BONDS

The hydrogen bonds that are given by the remaining hydrogen atoms on the phosphonate groups, the C–OH group and the water molecules give very complex and various networks. In a large part of the compounds they alone ensure the tridimensional cohesion of the structure. Unfortunately the atomic position of the hydrogen atoms are generally not well determined by X-ray diffraction, particularly when these atoms seem to be exactly shared between two oxygen atoms of PO_3 groups of two ligands related by a centre of symmetry. Only two structures were solved by neutron diffraction (compounds **1b** and **6c**) and these studies show clearly that such bonds are not symmetric and not perfectly linear with the hydrogen atom nearer one of the two involved oxygen atoms. It would be very interesting also to solve other ambiguities concerning for example the case of the hydrogen atoms of NH_2 or NH_3 groups which seem to give hydrogen bonds towards P–O groups or two H_2O groups or one P–O and one H_2O group (examples: compounds **32, 37–40**, Table 5).

CONCLUSION

The present article sums up according to the literature some characteristics of the behavior of the hydroxybisphosphonic function as can be observed in the structural studies of its salts and other related compounds. It is noteworthy that the oxidation states, the conformation possibilities, and the various networks of hydrogen bonds can greatly change depending on the substitutions, the nature of the complexing cations, and the role of the water molecules. Some of the derivated compounds with this hydroxybisphosphonic function have been therefore successfully applied in different industrial applications, and in the medical field [50–57].

TABLE 4 HEBP Acid and Metallic Complexes: P–O and C–O Bond Lengths (Å) with Indication of the Involving of O Atom in Cation Coordinence Bonds, Hydrogen Bonds, and of Hydrogen-Carrying O Atoms

Compound No.	*Cation*	*Anion*	*No. of H_2O*	*P1–O1*	*P1–O2*	*P1–O3*	*P2–O4*	*P2–O5*	*P2–O6*	*C1–O7*	*Average P1–O*	*Average P2–O*	*Average P–O*	*Average P–O + C–O*	*Ref.*
1a (RX)		0	1	1.507(3) R3R4	1.537(2) H	1.559(3) H	1.550(3) H	1.541(2) H w	1.505(2) R2R7	1.440(4) H w	1.534	1.532	1.533	1.520	[1]
1b* (N)		0	1	1.496(2) R3R4	1.534(2) H	1.554(2) H	1.546(2) H	1.534(2) H w	1.486(2) R2R7	1.426(1) H w	1.528	1.525	1.527	1.512	[2] [22]
2a	Na	LH_3^-	1	1.483(4) Cw	1.533(2) H CR5	1.553(2) H w	1.589(2) H C	1.520(2) C	1.501(3) R3R7	1.435(6) H C	1.523	1.530	1.527	1.513	[3] [23]
2b	Na	LH_3^-	1	1.488(2) Cw	1.527(4) H CR5	1.551(4) H w	1.559(4) H C	1.514(4) C	1.508(2) R3R7	1.441(3) H C	1.522	1.527	1.525	1.513	[4]
3	2Na	LH_2^{2-}	4	1.508 CR2	1.584 H C	1.499 www	1.511 Cww	1.503 C	1.576 H w	1.444 H C	1.530	1.530	1.530	1.518	[5]
4	K	LH_3^-	2	1.487(3) ww	1.527(3) h5 CCR5	1.571(3) H w	1.492(3) CR3	1.528(3) h2 C	1.565(4) H C	1.448(3) H CC	1.528	1.528	1.528	1.517	[6]
5	NH_4	LH_3^-	2	1.487(2) ww	1.530(2) h5 R5n	1.576(2) H w	1.493(2) Rn	1.520(2) h2 R	1.562(2) H n	1.441(3) H nn	1.531	1.525	1.528	1.516	[6]
6a (RX)	Rb	LH_3^-	2	1.487(3) ww	1.530(3) h5 CCR5	1.571(4) H w	1.492(3) CR3	1.528(3) h2 C	1.554(3) H C	1.458(5) H CC	1.529	1.525	1.527	1.517	[7]
6b (RX)	Rb	LH_3^-	2	1.479(6) ww	1.524(5) h5 CCR5	1.575(6) H w	1.493(6) CR3	1.529(5) h2 C	1.555(5) H C	1.441(9) H CC	1.526	1.526	1.526	1.514	[8]
6c* (N)	Rb	LH_3^-	2	1.483(3) ww	1.521(2) h5 CCR5	1.573(3) H w	1.487(3) CR3	1.527(2) h2 C	1.558(3) H C	1.431(2) H CC	1.526	1.524	1.525	1.511	[9]
7	Cs	LH_3^-	2	1.495(3) Cww	1.517(3) h5 CCR5	1.583(3) H w	1.497(3) CCR3	1.541(3) h2 CCC	1.559(3) H C	1.438(4) H CC	1.532	1.532	1.532	1.518	[8]
8	Ca	LH_2^{2-}	2	1.549(3) H R1w	1.507(3) Cw	1.530(3) H R3w	1.595(3) H w	1.496(4) C	1.505(4) CC	1.457(5) H C	1.529	1.532	1.530	1.520	[10]
9	Sr	2 LH_3^-	4	1.500(5) R3w	1.485(5) CCR4	1.548(6) H	1.556(5) H	1.494(5) CCCC	1.543(5) H w	1.440(9) H CC	1.511	1.531	1.521	1.509	[11] [23]
10	Cd (Hg)	LH_2^{2-}	2	1.510(3) Cw	1.522(3) CC	1.552(3) H	1.503(3) Cw	1.511(3) Cw	1.567(3) H w	1.453(4) H C	1.522	1.527	1.528	1.517	[12] [22]
11	Pb^{2+}	LH_2^{2-}	1	1.507(2) CR7	1.506(5) CC	1.570(5) H	1.499(5) Cw	1.513(5) CC	1.581(5) H	1.450(8) H w	1.528	1.531	1.529	1.518	[13] [22]
12	Y	LH_3^-	5.5	1.496(3) CR7^2	1.556(3) H w*	1.528(3) H	1.509(3) Cw	1.494(3) C	1.553(3) H w*w*	1.444(5) H	1.527	1.519	1.523	1.511	[14] [15]
		LH_2^{2-}		1.509(3) CR7^1	1.512(3) Cw	1.558(3) H w*	1.503(3) C	1.513(3) C	1.558(3) H	1.450(5) H	1.526	1.525	1.526	1.515	

TABLE 4 (continued) HEBP Acid and Metallic Complexes: P–O and C–O Bond Lengths (Å) with Indication of the Involving of O Atom in Cation Coordinence Bonds, Hydrogen Bonds, and of Hydrogen-Carrying O Atoms

Compound No.	Cation	Anion	No. of H_2O	*P1–O1*	*P1–O2*	*P1–O3*	*P2–O4*	*P2–O5*	*P2–O6*	*C1–O7*	*Average P1–O*	*Average P2–O*	*Average P–O*	*Average P–O + C–O*	*Ref.*
13	Ho	LH_3^-	5.5	1.500(3)	1.551(3)	1.539(3)	1.506(3)	1.485(3)	1.553(3)	1.430(5)	1.530	1.515	1.522	1.509	[15]
				CR7²	H w*	H	Cw	C	H w*w*	H					
		LH_2^{2-}		1.504(3)	1.515(3)	1.555(3)	1.500(3)	1.503(3)	1.560(3)	1.440(5)	1.525	1.521	1.523	1.511	
				CR7¹	Cw	H w*	C	C	H	H					
14a	Er	LH_3^-	5.5	1.495(3)	1.553(3)	1.540(3)	1.507(3)	1.489(3)	1.556(3)	1.429(5)	1.529	1.517	1.523	1.510	[15]
				CR7²	H w*	H	Cw	C	H w*w*	H					
		LH_2^{2-}		1.508(3)	1.507(3)	1.558(3)	1.501(3)	1.507(3)	1.559(3)	1.443(5)	1.524	1.522	1.523	1.512	
				CR7¹	Cw	H w*	C	C	H	H					
14b	Er	LH_3^-	5.5	1.502(4)	1.560(4)	1.543(4)	1.513(4)	1.495(4)	1.557(4)	1.442(6)	1.535	1.522	1.528	1.516	[16]
				CR7²	H	H	Cw	C	H	H w					
		LH_2^{2-}		1.511(4)	1.511(4)	1.561(4)	1.504(4)	1.500(4)	1.563(4)	1.445(6)	1.528	1.522	1.525	1.514	
				CR7¹	Cw	H w*	C	C	H	H w					
15	Gd	LH^{3-}	3	1.557(6)	1.516(6)	1.508(6)	1.495(6)	1.497(6)	1.581(7)	1.449(10)	1.527	1.524	1.526	1.515	[17]
				CC	C	C	CR7	Cw	H	H ww					
16	3Cu²⁺	LH^{3-}	6	1.530(8)	1.522(9)	1.494(7)	1.510(8)	1.505(9)	1.544(10)	1.471(14)	1.515	1.520	1.518	1.511	[18]
				Cw	CCww	C	CR7	CCw	H	H CCw					[24]
17		L^{4-}	12	1.509(3)	1.537(2)	1.513(3)	1.522(3)	1.547(2)	1.512(3)	1.453(5)	1.520	1.527	1.523	1.513	[19]
				ww	w	w	R7w		ww	H w					
	K1,K2			C1	C1,C1	C1	C1	C1,C1	C2						
	Na_2			C		C	C								
	Cu²⁺				CC			CC		CC					

Estimated standard deviations in parentheses.

1b* and **6c***, crystal structures solved by neutron diffraction; L = $[(H_2C)(OH)C(PO_3)_2]^4$; H, hydrogen atom totally linked to the oxygen atom of the corresponding P–O or C–O groups; h, hydrogen atom shared between the oxygen atoms of two P–O groups; R, hydrogen bond given by a POH group, and the number following R indicates the POH donor group; R7¹, hydrogen bond from the P–O7–H group of the first ligand; R7², hydrogen bond from the P–O7–H group of the second ligand; w, hydrogen bond given by a water molecule; w*, hydrogen bond given by a random water molecule or a normal water molecule but shared between two receiver P–O–H groups or shared between one P–O–H group and another water molecule; n, hydrogen given by an ammonium group; C, cation coordinence bond (C1 or C2 when a cation occupies two crystallographic sites).

TABLE 5 Other Varied Bisphosphonated Acids and Complexes: P–O and C–O Bond Lengths (Å) with Indication of the Involving of O Atom in Cation Coordinence Bonds, Hydrogen Bonds, and of Hydrogen-Carrying O Atoms

No.	*Compound*		*P1–O1*	*P1–O2*	*P1–O3*	*P2–O4*	*P2–O5*	*P2–O6*	*C1–O7*	*Aver-age P1–O*	*Aver-age P2–O*	*Aver-age P–O*	*Average P–O + C–O*	*Ref.*
18	EDA(LH$_3$)		1.538(2) H	1.547(2) H n	1.505(2) R5R7	1.509(1) R2n	1.550(2) H	1.522(1) R1n	1.448(2) H n	1.530	1.527	1.529	1.517	[20]
19	2A3MP(LH$_3$).H2O		1.494(2) R5w	1.538(2) H	1.547(2) H	1.513(2) R2n	1.563(2) H	1.491(2) n	1.452(3) H w	1.526	1.522	1.524	1.514	[21]
20	(2A4MP)$_2$(LH$_{3.5}$)(LH$_{2.5}$) 3H$_2$O	1:	1.517(2) h r2^2	1.532(2) H	1.532(2) h r6	1.565(2) H	1.497(2) R4^{2}n	1.523(2) h r3wn	1.440(3) H	1.527	1.528	1.528	1.515	[21]
		2:	1.505(2) R2^1	1.537(2) h r1^{1}n^1	1.529(2) H	1.553(2) H	1.499(2) R4^{1}n	1.517(2) R3n^1	1.439(3) H n	1.524	1.523	1.523	1.511	
21	(NH$_4$)$_6$Mo$_6$O$_{17}$(LH)$_2$ 10H$_2$O	1:	1.529(6) C	1.542(9) CC	1.518(9) H nn	1.510(8) Cw	1.550(9) CC	1.494(9) H wn	1.46(1) C	1.530	1.518	1.524	1.515	[25]
		2:	1.516(7) C	1.557(8) CC	1.509(7) H nn	1.522(7) Cw	1.548 CC	1.508 H nn	1.46(1) Cn	1.527	1.526	1.527	1.517	
22	(NH$_4$)$_3$MoO$_2$(LH$_2$)	1:	1.555(4) H	1.524(4) CR7^2	1.505(4) nnn	1.498(4) nww	1.555(4) H C	1.509(4) nw	1.442(7) H	1.528	1.521	1.524	1.513	[26]
	(LH).6.75H$_2$O	2:	1.547(5) H	1.532(4) CR7^{1}w	1.498(4) nnn	1.496(5) n	1.566(4) C	1.507(4) nww	1.453(7) H	1.526	1.523	1.524	1.514	
23	Na$_4$(NH$_4$)[MoO$_2$(H)(L)$_2$]. 15H$_2$O		1.514(7) Cw	1.541(6) CR7w	1.518(6) wn	1.497(6) Cwn	1.573(7) C	1.508(6) ww	1.46(1) H C	1.524	1.526	1.525	1.516	[27]
24	(H)(CH$_3$)$_2$N[HC(PO$_3$H$_2$)(PO$_3$H)].H$_2$O		1.491(3) nw	1.505(3) R6	1.577(3) H n	1.496(3) R3w	1.547(3) H R	1.522(3) H	—	1.524	1.522	1.523	—	[28]
25	(NH$_3$)(CH$_2$)$_2$(LH$_3$)		1.507(1) R5n	1.506(2) R6R7	1.572(1) H n	1.483(2) R3	1.550(2) H	1.555(2) H	1.441(2) H n	1.528	1.529	1.529	1.516	[28]
26	(NH$_3$)(CH$_2$)$_3$(LH$_3$)		1.481(3) R5n	1.530(3) H	1.552(3) H	1.494(3) R3R7n	1.561(3) H	1.511(3) R2n	1.438(4) H n	1.521	1.522	1.522	1.510	[29]
27	(NH$_3$)(CH$_2$)$_5$(LH$_3$)		1.500(2) R6R7	1.575(2) H n*	1.502(2) R4n*n*	1.545(3) H	1.493(2) R2n*n*	1.558(2) H	1.436(3) H n*	1.526	1.532	1.529	1.516	[30]
28	(NH$_3$)(CH$_2$)$_5$(LH$_3$).H$_2$O	1:	1.473(1) R2^{2}w*	1.544(1) H	1.551(4) H n*n*	1.487(1) R5^{2}n*	1.564(1) H	1.499(3) R3n^2	1.455(2) H	1.523	1.517	1.520	1.510	[31]
		2:	1.455(1) R2^{1}n^1*	1.559(1) H n*	1.523(2) R6n*	1.483(1) R5^{1}R7^1	1.561(2) H w*	1.565(4) H n^1*	1.406(2) H n^1*	1.512	1.540	1.526	1.509	
29	Zn[(NH$_3$)(CH$_2$)$_3$(LH$_2$)]$_2$ 2H$_2$O	1:	1.508(6) R4w	1.496(6) Cn^2*	1.565(3) H n^2*	1.558(6) H n^2*	1.508(6) CR7^{2}n	1.506(6) R3n	1.445(10) H	1.523	1.524	1.524	1.512	[31] [32]
		2:	1.506(6) Cn*	1.525(6) CR7^{1}R4	1.564(7) H n^1*	1.596(7) H n*	1.481(6) C	1.525(6) R3n*w*	1.375(11) H n^1*w	1.532	1.534	1.533	1.510	
30	Cd[(NH$_3$)(CH$_2$)$_3$(LH)].H$_2$O		1.501(9) Cn	1.544(7) CC	1.528(7) H$_x$ R6$_y$nw	1.496(6) Cw*	1.516(8) Cnw*	1.523(7) H$_y$ R3$_x$	1.443(11) H C	1.524	1.512	1.518	1.507	[31] [32]
31	[(H$_3$C)O(H)(CH$_3$)] [(CH$_3$)(CH$_2$)$_3$(LH$_3$)]		1.557(3) H	1.484(3) R7o*	1.546(3) H	1.498(3) R6o*	1.504(3) R3o*	1.573(3) H o*	1.442(4) H R1	1.529	1.525	1.527	1.515	[31]
32	(NH$_3$)(CH$_2$)$_3$(LH$_{3.5}$)$_2$ 2H$_2$O	1:	1.523(2) H R2^{2}w*	1.513(2) h R4n*	1.552(2) H n	1.548(2) H w*	1.503(2) R4^{2}n*	1.508(3) R3^2	1.438(4) H R	1.529	1.520	1.525	1.512	[33] [24]
		2:	1.510(2) R5w*	1.527(2) h R1^1	1.523(3) H	1.537(2) H w*	1.553(2) H n	1.490(3) wn	1.448(4) H n^1	1.517	1.527	1.523	1.513	

TABLE 5 (continued) Other Varied Bisphosphonated Acids and Complexes: P–O and C–O Bond Lengths (Å) with Indication of the Involving of O Atom in Cation Coordinence Bonds, Hydrogen Bonds, and of Hydrogen-Carrying O Atoms

No.	*Compound*	*P1–O1*	*P1–O2*	*P1–O3*	*P2–O4*	*P2–O5*	*P2–O6*	*C1–O7*	*Aver-age P1–O*	*Aver-age P2–O*	*Aver-age P–O*	*Average P–O + C–O*	*Ref.*
33	(L)$(CH_3)_4$	1.573(3)	1.568(3)	1.456(3)	1.556(2)	1.566(3)	1.470(3) R7	1.437(4) H	1.532	1.531	1.532	1.518	[34] [24]
34	(C_6H_5)(L)$(CH_3)_4$	1.550(3)	1.571(3)	1.460(3) R7	1.446(3)	1.566(3)	1.572(3)	1.426(4) H	1.527	1.528	1.528	1.513	[34] [24]
35	(C_6H_5)(L)$(CH_2C_6H_5)_4$	1.563(2)	1.466(2) R7	1.566(2)	1.565(2)	1.458(3)	1.568(2)	1.441(4) H	1.532	1.530	1.531	1.518	[35] [36]
36	(CH_3)(L)$(CH_2C_6H_5)_4$	1.561(12)	1.464(12) R7	1.549(14)	1.588(12)	1.432(13)	1.532(14)	1.435(21) H	1.525	1.517	1.521	1.509	[36]
37	$NH_3(CH_2)_5(LH_3)$ 1:	1.589(8) H	1.489(8) R5^{2}n^{2}*	1.511(7) R1R3^{2}	1.513(8) R7^{2}n*n^{2}*	1.560(8) H n^{2}	1.552(8) H R6^{2}	1.463(13) H n	1.530	1.542	1.536	1.525	[37]
	2:	1.466(8) R7^{1}n	1.555(8) H n^{1}*	1.578(9) H	1.478(8) R5^{1}n^{1}*	1.540(8) n^{1}*	1.569(8) H R6^{1}	1.408(13) H	1.533	1.529	1.531	1.513	
38	Betaine bis(dihydroxyphosphinoyle)-2,2N(2′,3′,4′-H pyrolyle) pyrrolidine	1.523(4) h n*	1.535(4) H	1.499(4) R6	1.516(4) h	1.508(4) R2n*	1.542(4) H	—	1.519	1.522	1.521	—	[37]
39	$Cu_2[(NH_3(CH_2)_3(LH_2)_2]_4$ $4H_2O$ 1:	1.506(6) R4r3w	1.498(6) Cn*	1.560(5) H n*	1.571(6) H n*	1.508(6) CR7^{2}n	1.502(6) r3n	1.432(9) H	1.521	1.527	1.524	1.511	[37] [38]
	2:	1.504(6) Cn*	1.502(6) CR4R7^{1}	1.537(6) H n*	1.560(6) H n*	1.503(6) C	1.503(6) R3n*ww	1.465(10) H n*	1.514	1.522	1.518	1.511	
40	$Cu_{1/2}[(NH_3(CH_2)_5(LH_2)_2]$ $2H_2O$	1.478(7) R4w	1.500(7) CC R7nw*w*	1.568(6) H n*	1.568(7) H w	1.498(7) CCw*w*	1.517(7) R3n	1.437(11) H	1.515	1.528	1.522	1.509	[37] [38]
41	$[H_2N(CH_2CH_3)_2]_2Cu(LH_2)_2$ $2H_2O$	1.500(5) R4w	1.517(5) Cn*	1.559(5) H	1.569(5) H w	1.514(5) Cn*	1.505(5) R3n	1.453(8) H	1.525	1.529	1.527	1.517	[39]
42	$[H_2N(CH_2CH_3)_2]_2Co(LH_2)_2$ $2H_2O$	1.505(2) R4w	1.510(2) Cn*	1.561(2) H	1.572(2) H w	1.510(2) Cn*	1.509(2) R3n	1.448(3) H	1.525	1.530	1.528	1.516	[39]
43	$[H_2N(CH_2CH_3)_2]_2Mg(LH_2)_2$ $2H_2O$	1.508(1) R4w	1.509(1) Cn*	1.561(2) H	1.574(1) H w	1.511(1) Cn*	1.508(1) R3n	1.456(2) H	1.526	1.531	1.529	1.518	[40]
44	$[H_2N(CH_2CH_3)_2]_2Zn(LH_2)_2$. $2H_2O$	1.505(2) R4w	1.508(2) Cn*	1.560(2) H	1.572(2) H w	1.510(2) Cn*	1.508(2) R3n	1.447(3) H	1.524	1.530	1.527	1.516	[40]
45	$Cu(LH_2)$(bipyridil).$4H_2O$	1.570(2) H	1.514(2)	1.492(2) ww	1.567(2) H	1.508(2)	1.505(2) R4w	1.447(3) H w	1.525	1.527	1.526	1.515	[16]
46	$NaCu(LH_2)Cl.3H_2O$	1.513(3) CC	1.509(3) CC	1.567(3) H	1.515(3) CC	1.518(3) CR3	1.559(3) H w	1.457(4) H	1.526	1.531	1.529	1.518	[41]

Estimated standard deviations in parentheses.

EDA, ethylenediammonium; 2A3MP, 2-amino 3-methyl pyridinium; 2A4MP, 2-amino 4-methyl pyridinium; L = $[(H_3C)(OH)C(PO_3)_2]^{4-}$; H, hydrogen atom totally linked to the oxygen atom of the corresponding P–O or C–O groups; h, hydrogen atom shared between two P–O groups; R, hydrogen bond given by a P–O–H group (*r* for a partial or shared hydrogen bond) (the following number indicates the P–O–H donor group) R^{1} and R^{2}, the exponent indicates that the hydrogen bond is given by a P–O–H group of the other HEBP ligand when the structure includes two ligands which are crystallographically independent; o*, shared hydrogen bond given by an oxonium group (compound **30**); n, hydrogen bond given by an ammonium group; n* when this bond is shared between two P–O–H groups (an exponent precises if this bond is given by the other ligand when the crystal structure includes two ligands which are crystallographically independent); w, hydrogen bond given by a water molecule; w*, hydrogen bond given by a random water molecule or shared between two P–O–H groups or between one P–O–H group and another water molecule.

TABLE 6 Bis-HEBP Complexes (DHHTP and DHOTP): P–O and C–O Bond Lengths (Å) with Indication of the Involving of O Atom in Cation Coordinence Bonds, Hydrogen Bonds, and of Hydrogen-Carrying O Atoms

N°	*Cation*	*Ionization of Each HEBP*	*No. of H2O*	*P1–O1*	*P1–O2*	*P1–O3*	*P2–O4*	*P2–O5*	*P2–O6*	*C1–O7*	*Average P1–O*	*Average P2–O*	*Average P–O*	*Average P–O + C–O*	*Ref.*
47	$H3O^+$	$2 \times 1^-$	2	1.524(2) h wr	1.545(2) H C	1.528(2) h Cw	1.505(2) R5R7	1.565(2) H C	1.523(2) CCR2	1.438(3) H CC	1.532	1.531	1.532	1.518	[42]
48	$2Na^+$	$2 \times 1^-$	4	1.517(2) R3w	1.516(2) CR4	1.543(2) H C	1.533(2) H w	1.484(2) CC	1.568(3) H	1.457(4) H Cw	1.525	1.528	1.527	1.517	[43]
49	$2K^+$	$2 \times 1^-$	2	1.519(2) h wr	1.541(2) H C	1.523(2) h Cw	1.499(2) R5R7	1.565(2) H C	1.523(2) CCR2	1.439(3) H CC	1.528	1.529	1.528	1.516	[42]
50	Cu^{2+}	$2 \times 1^-$	10	1.545(4) H	1.518(4) h CC	1.518(5) h r	1.512(5) R2	1.511(5) CCr	1.556(4) H	1.466(7) H	1.527	1.526	1.527	1.518	[44]
51	$2[HO^+(CH_3)_2]$	$2 \times 1^-$	4	1.542(9) H	1.491(8) R5o*	1.511(8) R1ww*	1.511(8) w*o*	1.534(8) H o*	1.536(7) H R7	1.414(15) H o*	1.515	1.527	1.521	1.506	[31]
52	Ca^{2+}	$2 \times 1^-$	6.8	1.530(6) H ww	1.495(5) C	1.585(6) H	1.497(6) CR7	1.506(5) Cw	1.616(5) H w	1.457(11) H w	1.537	1.540	1.538	1.527	[31]
53	$2Cu^{2+}$	2×1^2	12	1.517(6) CR7	1.560(6) H w	1.507(7) R2w	1.505(6) Cw	1.502(5) Cww	1.566(7) H	1.450(10) H w	1.528	1.524	1.526	1.515	[31]

Estimated standard deviations in parentheses.

H, hydrogen atom totally linked to the oxygen atom of the corresponding P–O or C–O groups; h, hydrogen atom shared by the oxygen atoms of two P–O groups; R, hydrogen bond (r for partial or shared hydrogen bond) from a POH group (the number following R indicates the POH donor group); w, hydrogen bond given by a water molecule; w*, hydrogen bond given by a random water molecule or a normal water molecule but shared between two receiver P–O–H groups or shared between one P–O–H group and another water molecule; o*, shared hydrogen bond given by an oxonium group; C, cation coordinence bond.

TABLE 7 Distribution of the Hydrogen Atoms (Number and Percentage) on the P–OH Groups

Ionization	*P1–O1*	*P1–O2*	*P1–O3*	*P2–O4*	*P2–O5*	*P2–O6*	*Number of H Atoms*
LH_3^-	7	12	14	4.5	10.5	15	63
	11.1%	19.0%	22.2%	7.1%	16.7%	23.8%	
LH_2^{2-}	3	2	11	8	1	6	31
	9.7%	6.5%	35.5%	25.8%	3.2%	19.4%	
LH^{3-}	1	0	2.5	0	0	4.5	8
	12.5%	0	31.3%	0	0	56.3%	
LH, $LH_{3.5}^{0.5-}$, $LH_{2.5}^{1.5-}$	1.5	3.5	4.5	5	2	0.5	17
Total	12.5	17.5	32	17.5	13.5	26	119
	10.5%	14.7%	26.9%	14.7%	11.3%	21.8%	

TABLE 8 HEBP Acid and Metallic Complexes: P–C–P Angle (°) and Pseudo-Torsion Angles (°) between PO_3 Groups

No.	*Compound*	*P1–C1–P2*	*P1–O1:P2–O4*	*P1–O2:P2–O5*	*P1–O3:P2–O6*	*Average Rotation*	*Ref.*
1a	$(LH_4)\cdot H_2O$	115.1(2)	3.2(1)	7.6(1)	−2.8(1)	2.7	[1]
1b*	$(LH_4)\cdot H_2O$	114.50(6)	3.3(1)	7.4(1)	−2.6(1)	2.7	[2,22]
2a	$Na(LH_3)\cdot H_2O$	113.3(2)	15.0(2)	10.6(2)	39.2(2)	21.6	[3,23]
2b	$Na(LH_3)\cdot H_2O$	113.7(1)	15.1(2)	10.3(2)	40.2(2)	21.9	[4]
3	$Na_2(LH_2)\cdot 4H_2O$	113.9	13.5	7.1	4.9	8.5	[5]
4	$K(LH_3)\cdot 2H_2O$	113.5(2)	13.8(1)	14.9(1)	15.7(2)	14.8	[6]
5	$NH_4(LH_3)\cdot 2H_2O$	113.3(2)	13.2(1)	12.2(1)	18.6(2)	14.7	[6]
6a	$Rb(LH_3)\cdot 2H_2O$	113.0(1)	15.3(1)	13.6(1)	19.5(1)	16.1	[7]
6b	$Rb(LH_3)\cdot 2H_2O$	113.5(3)	15.6(1)	13.9(1)	19.5(1)	16.3	[8]
6c*	$Rb(LH_3)\cdot 2H_2O$	114.1(2)	15.4(1)	13.5(1)	19.5(1)	16.1	[9]
7	$Cs(LH_3)\cdot 2H_2O$	112.9(2)	18.5(3)	21.0(3)	16.4(2)	18.6	[8]
8	$Ca(LH_2)\cdot 2H_2O$	113.7(3)	20.8(1)	23.1(1)	31.2(2)	25.0	[10]
9	$Sr(LH_3)_2\cdot 4H_2O$	113.3(3)	4.5(3)	6.4(3)	3.0(3)	4.6	[11,23]
10	$Cd(LH_2)\cdot 2H_2O$	110.5(2)	6.4(1)	9.9(1)	18.7(2)	11.7	[12,22]
11	$Pb(LH_2)\cdot H_2O$	114.2(4)	3.9(2)	3.6(3)	0.7(3)	2.7	[13,22]
12	$Y(LH_3)(LH_2)\cdot 5.5H_2O$						[15]
	LH_3^{-1}	111.3(2)	4.2(1)	1.4(1)	−3.1(1)	0.8	
	LH_2^{-2}	107.1(2)	0.6(1)	0.7(2)	−7.0(2)	1.9	
13	$Ho(LH_3)(LH_2)\cdot 5.5H_2O$						[15]
	LH_3^{-1}	111.1(2)	3.8(1)	0.8(1)	−3.3(1)	0.4	
	LH_2^{-2}	106.9(2)	0.5(1)	0.9(2)	−7.5(3)	2.0	
14a	$Er(LH_3)(LH_2)\cdot 5.5H_2O$						[15]
	LH_3^{-1}	110.4(2)	3.8(1)	1.2(1)	−3.4(1)	0.5	
	LH_2^{-2}	106.6(2)	0.8(1)	0.6(1)	−7.5(2)	2.0	
14b	$Er(LH_3)(LH_2)\cdot 5.5H_2O$						[16]
	LH_3^{-1}	110.6(3)	3.6(1)	1.0(1)	−3.0(1)	0.5	
	LH_2^{-2}	106.5(3)	0.5(1)	0.4(1)	−8.4(2)	2.5	
15	$Gd(LH)\cdot 3H_2O$	107.7(2)	17.4(3)	21.6(3)	36.8(4)	25.3	[17]
16	$Cu_3(LH)_2\cdot 6H_2O$	107.9(6)	5.3	8.0	13.5	8.9	[18,24]
17	$K_4Na_2Cu(L)_2\cdot 12H_2O$	111.4(2)	8.1(2)	8.5(1)	13.6(2)	10.1	[19]

Estimated standard deviations in parentheses.

Compounds **1b*** and **6c***, crystal structures solved by neutron diffraction; $L = [(H_3C)(OH)C(PO_3)_2]^{4-}$.

TABLE 9 Other Various Bisphosphonated Acids and Complexes: P–C–P angle (°) and Pseudo-Torsion Angles (°) between PO_3 Groups

No.	*Compound*	*P1–C1–P2*	*P1–O1, P2–O4*	*P1–O2, P2–O5*	*P1–O3, P2–O6*	*Average Rotation*	*Ref.*
18	$EDA(LH_2)$	115.8(1)	19.1	39.9	21.9	27.0	[20]
19	$2A3MP(LH_3)\cdot H_2O$	115.7(1)	6.0(1)	2.5(1)	11.9(1)	6.8	[21]
20	$(2A4MP)_2(LH_{3.5})(LH_{2.5})\cdot 3H_2O$						[21]
	$LH_{3.5}^{0.5-}$	112.8(2)	15.5	16.1	17.6	16.4	
	$LH_{2.5}^{1.5-}$	112.8(2)	14.7	15.3	16.5	15.5	
21	$(NH_4)_8Mo_6O_{17}(LH)_2\cdot 10H_2O$	111.4(6)	1.5(4)	1.9(4)	2.0(6)	1.8	[25]
		110.4(5)	1.1(3)	0.1(3)	2.7(5)	1.3	
22	$(NH_4)_3MoO_2(LH_2)(LH)\cdot 6.75H_2O$	111.7(3)	7.8(2)	−1.5(3)	−6.9	−0.2	[26]
		111.5(3)	6.9(3)	6.5(3)	−3.5(5)	3.3	
23	$Na_4(NH_4)MoO_2(H)(L)_2\cdot 15H_2O$	112.7(4)	12.5(3)	10.6(3)	15.6(4)	12.9	[27]
24	$(H)(CH_3)_2N[HC(PO_3H_2)(PO_3H)]\cdot H_2O$	113.4(8)	33.4(1)	43.9(1)	67.6(2)	48.3	[28]
25	$(NH_3)(CH_2)_2(LH_3)$	110.66(8)	25.4(1)	25.8(1)	33.1(1)	28.1	[28]
26	$(NH_3)(CH_2)_3(LH_3)$	113.5(2)	8.6(1)	0.3(1)	1.8(2)	3.6	[29]
27	$(NH_3)(CH_2)_5(LH_3)$	113.6(2)	14.0(1)	20.7(1)	47.4(2)	27.4	[30]
28	$(NH_3)(CH_2)_5(LH_3)\cdot H_2O$	112.1(1)	10.3(1)	14.6(1)	18.3(1)	14.4	[31]
		110.9(1)	24.4(1)	28.5(1)	43.3(1)	32.1	
29	$Zn[(NH_3)(CH_2)_3(LH_2)]_2\cdot 2H_2O$	110.3(4)	4.3(3)	0.8(3)	16.4(4)	7.2	[31,32]
		113.6(5)	17.7(3)	12.5(3)	42.0(4)	24.1	
30	$Cd[(NH_3)(CH_2)_3(LH)]\cdot H_2O$	108.8(6)	7.9(4)	9.3(3)	22.8(5)	13.3	[31,32]
31	$[(H_3C)O(H)(CH_3)][(CH_3)(CH_2)_3(LH_3)]$	108.4(2)	36.3(1)	39.6(1)	51.3(2)	42.4	[31]
32	$(NH_3)(CH_2)_3(LH_{3.5})_2\cdot 2H_2O$	111.0(2)	26.2(1)	27.7(1)	53.0(2)	35.6	[33,24]
		112.1(2)	23.9(1)	31.9(1)	46.4(2)	34.1	
33	$L(CH_3)_4$	119.3(2)	5.4(1)	1.5(1)	7.6(2)	4.8	[34,24]
34	$(C_6H_5)L(CH_3)_4$	111.7(2)	22.4(1)	30.0(1)	34.6(2)	29.0	[34,24]
35	$(C_6H_5)L(CH_2C_6H_5)_4$	115.8(2)	16.6(1)	15.2(1)	27.4(1)	19.7	[35,36]
36	$(CH_3)L(CH_2C_6H_5)_4$	116.0(8)	17.4(1)	18.9(1)	31.3(1)	22.5	[36]
37	$NH_3(CH_2)_6(LH_3)$	111.7(6)	41.6(3)	47.0(3)	58.3(5)	49.0	[37]
		108.6(5)	28.6(4)	36.2(4)	54.6(5)	39.9	
38	Betaine bis(dihydroxyphosphinoyle)-2,2 N(2′,3′,4′-H pyrolyle) pyrrolidine	114.6(3)	0.1	2.2	1.3	1.2	[37]
39	$Cu_2[(NH_3(CH_2)_3(LH_2)_2]_4\cdot 4H_2O$	110.0(4)	3.9	0.3	14.6	6.3	[37,38]
		113.5(4)	15.6	11.2	38.1	21.6	
40	$Cu_{1/2}[(NH_3(CH_2)_6(LH_2)_2]\cdot 2H_2O$	110.3(5)	0.2	4.8	15.0	6.7	[37,38]
41	$[H_2N(CH_2CH_3)_2]_2Cu(LH_2)_2\cdot 2H_2O$	109.7(3)	8.5(2)	14.1(2)	13.6(2)	12.1	[39]
42	$[H_2N(CH_2CH_3)_2]_2Co(LH_2)_2\cdot 2H_2O$	111.9(1)	7.5(1)	12.5(1)	9.8(1)	9.9	[39]
43	$[H_2N(CH_2CH_3)_2]_2Mg(LH_2)_2\cdot 2H_2O$	111.41(9)	7.0(1)	12.2(1)	9.8(1)	9.7	[40]
44	$[H_2N(CH_2CH_3)_2]_2Zn(LH_2)_2\cdot 2H_2O$	111.7(1)	7.4(1)	12.7(1)	9.9(1)	10.0	[40]
45	$NaCu(LH_2)Cl\cdot 3H_2O$	106.3(2)	2.1(1)	1.2(1)	−8.1(2)	−1.6	[16]
46	$(NH_3)(CH_2)_5(LH_3)\cdot H_2O$	112.1(1)	10.3(1)	14.6(1)	18.3(1)	14.4	[41]
		110.9(1)	24.4(1)	28.5(1)	43.3(1)	32.1	

Estimated standard deviations in parentheses.
EDA, ethylenediammonium; 2A3MP, 2-amino 3-methyl pyridinium; 2A4MP, 2-amino 4-methyl pyridinium; L $= [(H_3C)(OH)C(PO_3)_2]^{+}$.

TABLE 10 Bis-HEBP Complexes (DHHTP and DHOTP): P–C–P angle (°) and Pseudo-Torsion Angles (°) between PO_3 Groups

No.	*Compound*	*P1–C1–P2*	*P1–O1, P2–O4*	*P1–O2, P2–O5*	*P1–O3, P2–O6*	*Average Rotation*	*Ref.*
47	$(H_3O)_2[(H_3O_6P_2)(OH)C(CH_2)_4C(OH)(P_2O_6H_3)]\cdot 2H_2O$	111.3(1)	17.7(1)	23.7(1)	32.1(2)	24.5	[42]
48	$Na_2[(H_3O_6P_2)(OH)C(CH_2)_4C(OH)(P_2O_6H_3)]\cdot 4H_2O$	108.3(2)	35.7(1)	32.3(1)	53.6(2)	40.5	[43]
49	$K_2[(H_3O_6P_2)(OH)C(CH_2)_4C(OH)(P_2O_6H_3)]\cdot 2H_2O$	111.4(1)	19.2(1)	25.8(1)	35.7(1)	26.9	[42]
50	$Cu[(H_3O_6P_2)(OH)C(CH_2)_4C(OH)(P_2O_6H_3)]\cdot 10H_2O$	110.4(3)	9.9(2)	10.7(2)	23.4(3)	14.7	[44]
51	$[(H)O(CH_2)_2]_2[(H_3O_6P_2)(OH)C(CH_2)_6C(OH)(P_2O_6H_3)]\cdot 4H_2O$	111.2(6)	13.2(4)	14.9(4)	16.5(5)	14.9	[31]
52	$Ca[(H_3O_6P_2)(OH)C(CH_2)_6C(OH)(P_2O_6H_3)]\cdot 6.8H_2O$	111.7(4)	20.8(3)	24.5(2)	35.9(3)	27.1	[31]
53	$Cu2[(H_2O_6P_2)(OH)C(CH_2)_6C(OH)(P_2O_6H_2)]\cdot 12H_2O$	110.7(4)	7.6(3)	14.0(3)	18.7(4)	13.4	[31]

Estimated standard deviations in parentheses.

TABLE 11 HEBP Metallic Complexes: Cation Coordinence with Extreme and Average Cation-Oxygen Distances (Å)

No.	*Compound*	*Cation (M)*	*Coordinence of The Cation*	*Nature and Number of the Ligand-Cation Bonds*[a]	*Number of Coordinated H_2O*	*M–O Min.*	*M–O Max.*	*M–O average (all bonds)*	*Short Description of the Polyhedra Chaining*	*Ref.*
2a	$Na(LH_3) \cdot H_2O$	Na^+	6	B, T	1	2.300(4)	2.471(4)	2.395	Independent polyhedron	[3,23]
2b	$Na(LH_3) \cdot H_2O$	Na^+	6	B, T	1	2.294(2)	2.463(4)	2.393	Independent polyhedron	[4]
3	$Na_2(LH_2) \cdot 4H_2O$	Na^+	5	M, B	2	2.302	2.857	2.471	Monodimensional chains by alternation of shared edge and summit	[5]
		Na^+	6	B, T	1	2.303	2.453	2.348		
4	$K(LH_3) \cdot 2H_2O$	K^+	7	2M, B, T	0	2.701(3)	3.109(4)	2.879	Monodimensional chains by shared edge	[6]
6a	$Rb(LH_3) \cdot 2H_2O$	Rb^+	7	2M, B, T	0	2.887(3)	3.230(2)	3.030	Monodimensional chains by shared edge	[7]
6b	$Rb(LH_3) \cdot 2H_2O$	Rb^+	7	2M, B, T	0	2.889(6)	3.224(4)	3.028	Monodimensional chains by shared edge	[8]
6c*[b]	$Rb(LH_3) \cdot 2H_2O$	Rb^+	7	2M, B, T	0	2.888(3)	3.226(2)	3.028	Monodimensional chains by shared edge	[9]
7	$Cs(LH_3) \cdot 2H_2O$	Cs^+	11	M, 2B, 2T	0	3.070(3)	3.678(3)	3.366	Monodimensional chains by shared edge	[8]
8	$Ca(LH_2) \cdot 2H_2O$	Ca^{2+}	8	B, T	3	2.352(4)	2.608(3)	2.476	Monodimensional chains by shared edge	[10]
9	$Sr(LH_3)_2 \cdot 4H_2O$	Sr^{2+}	8	2M, 2T	0	2.554(5)	2.678(5)	2.605	Monodimensional chains by shared edge	[11,23]
10	$Cd(LH_2) \cdot 2H_2O$	Cd^{2+}	6	M, B, T	0	2.219(2)	2.508(3)	2.312	Monodimensional chains by shared edge	[12]
11	$Pb(LH_2) \cdot H_2O$	Pb^{2+}	6	4M, B	0	2.343(5)	2.910(5)	2.851	Monodimensional chains by shared edge	[13,22]
12	$Y(LH_3)(LH_2) \cdot 5.5H_2O$	Y^{3+}	7	M, 3B	0	2.225(5)	2.910(5)	2.581	Independent polyhedron	[14,15]
13	$Ho(LH_3)(LH_2) \cdot 5.5H_2O$	Ho^{3+}	7	M, 3B	0	2.235(3)	2.404(3)	2.313	Independent polyhedron	[15]
14a	$Ho(LH_3)(LH_2) \cdot 5.5H_2O$	Er^{3+}	7	M, 3B	0	2.226(3)	2.401(3)	2.306	Independent polyhedron	[15]
14b	$Er(HEBP)_2 \cdot 5.5H_2O$	Er^{3+}	7	M, 3B	0	2.221(4)	2.398(4)	2.306	Independent polyhedron	[16]
15	$Ho(LH_3)(LH_2) \cdot 5.5H_2O$	Gd^{3+}	8	2M, 2B	0	2.299(6)	2.601(6)	2.429	Polyhedra associated 2 by 2 by shared summit	[17]
16	$Cu_3(LH)_2 \cdot 6H_2O$	Cu^{2+}	5	M, B	2	1.917(9)	1.968(8)[d] 2.347(8)[c]	1.948[d] 2.028[c]	Independent polyhedron	[18,24]
		Cu^{2+}	6	2T	0	1.947(8)	1.990(8)[d] 2.45(8)[c]	1.969[d] 2.129[c]	Independent polyhedron	
17	$K_4Na_2Cu(L)_2 \cdot 12H_2O$	$K(1)^+$	8	M, B, Q	1	2.706	3.156	2.926	All the polyhedra are joined:	[19]
		$K(2)^+$	6	M	5	2.682	2.962	2.766	Na to K(1) by shared face	
		Na^+	5	M, B	2	2.290	2.418	2.346	Na to K(2) by shared edge	
		Cu^{2+}	6	2T	0	1.944(3)[d]	1.970(2)[d] 2.667(3)[c]	1.957[d] 2.194[c]	K(1) to K(1) by shared edge Cu to 4K(1) by shared edge	

Estimated standard deviation in parentheses.

[a] M, monodentate bond; B, bidentate bond; T, tridentate bond; Q, tetradentate bond, (the number of each follows the symbol).

[b] **6c***, crystal structures solved by neutron diffraction.

[c] These values correspond to the great distances: Cu–apical oxygen atoms, due to the Jahn-Teller effect, and the average value is calculated for the six bonds.

[d] These values concern the other distances: Cu–O and the corresponding average.

TABLE 12 Other Various Bisphosphonated Acids and Complexes: Cation Coordinence with Extreme and Average Cation-Oxygen Distances (Å)

No.	Compound	Cation (M)	Cation coord.	Nature and Number of the Ligand-Cation Bonds[a]	Numb. of coordinated H_2O	M–O (min)	M–O (max)	M–O average (all bonds)	Description of the Polyhedra Chaining	Ref.
21	$(NH_4)_5Mo_6O_{17}(LH)_2 \cdot 10H_2O$	$Mo(1)^{6+}$	6	T	0	1.696(9) 1.700(8)	2.346(7) 2.337(6)	1.991 1.991	Monodimensional chain: Shared face	[25]
		$Mo(2)^{6+}$	6	B	0	1.708(9) 1.699(0)	2.310(7) 2.299(6)	1.980 1.974	Shared summit	
		$Mo(3)^{6+}$	6	B	0	1.699(9) 1.708(6)	2.259(7) 2.228(6)	1.963 1.959	Shared summit between 2 Mo(3)	
		$N(1)H_4^+$	5	M, B_{Mo}	2	2.74(2)	3.07(2)	2.90	Complex chaining: Shared summits between NH_4	
		$N(2)H_4^+$	4	B, M_{Mo}	1	2.79(1)	2.98(1)	2.91	coordination polyhedra or associated	
		$N(3)H_4^+$	4	B, M_{Mo}	1	2.74(1)	2.89(1)	2.83	Mo coordination polyhedra and NH_4 coordination	
		$N(4)H_4^+$	4	M, B	1	2.83(1)	3.10(1)	2.97	polyhedra	
		$N(5)H_4^+$	5	$3M_{Mo}$	2	2.84(2)	3.02(1)	2.90	2.87	
		$N(6)H_4^+$	4	$3M_{Mo}$	1	2.82(1)	2.92(1)			
22	$(NH_4)_3MoO_2(LH_2)(LH), 6.75H_2O$	Mo6 +	6	2B	0	1.681(4)	2.253(4)	1.965	Independent polyhedron	[26]
		$N(1)H_4^+$	4	4M	0	2.825(5)	2.897(6)	2.866	Linked by shared summits	
		$N(2)H_4^+$	5	3M	2	2.82(1)	2.921(8)	2.866		
		$N(3)H_4^+$	4	3M	1	2.826(7)	3.017(7)	2.914		
23	$Na_4(NH_4)MoO_2(H)(L)_2 \cdot 15H_2O$	$Na(1)^+$	5	B	3	2.372(7)	2.502(6)	2.413	Independent polyhedron	[27]
		$Na(2)^+$	6	M	5	2.393(7)	2.49(1)	2.434	Chaining by shared edge and shared summit	
		NH_4^+	4	2B	0	2.780(7)	2.871(7)	2.826	Independent polyhedron	
		Mo^{6+}	6			1.958(5)	2.187(6)			
29	$Zn[(NH_3)(CH_2)_3(LH_2)]_2 \cdot 2H_2O$	Zn^{2+}	6	M, 2B	1	2.005(5)	2.222(6)	2.096	Independent polyhedron	[31,32]
30	$Cd[(NH_3)(CH_2)_3(LH)] \cdot H_2O$	Cd2 +	6	M, B, T	0	2.186(7)	2.485(7)	2.299	Independent bioctahedron by shared edge	[31,32]
39	$Cu_2[(NH_3(CH_2)_3(LH_2)_2]_4 \cdot 4H_2O$	Cu^{2+}	6	M, 2B	1	1.936(6)^{b} 2.295(7)^{c}	2.051(5)^{b} 2.393(7)^{c}	1.992^{b} 2.334^{c}	Independent polyhedron	[37,38]
40	$Cu_{1/2}[(NH_3(CH_2)_5(LH_2)_2] \cdot 2H_2O$	Cu^{2+}	6	2B	2	1.963(6)^{b} 2.397(7)^{c}	1.982(6)^{b} 2.397(7)^{c}	1.973^{b} 2.397^{c}	Independent octahedron	[37,38]
41	$[H_2N(CH_2CH_3)_2]_2Cu(LH_2)_2 \cdot 2H_2O$	Cu^{2+}	6	2B	2	1.960(4)^{b}	1.996(5)^{b} 2.443(6)^{c}	1.978^{b} 2.133^{c}	Independent octahedron	[39]
42	$[H_2N(CH_2CH_3)_2]_2Co(LH_2)_2 \cdot 2H_2O$	Co^{2+}	6	2B	2	2.064(4)	2.179(2)	2.108	Independent octahedron	[39]
43	$[H_2N(CH_2CH_3)_2]_2Mg(LH_2)_2 \cdot 2H_2O$	Mg^{2+}	6	2B	2	2.050(1)	2.152(1)	2.085	Independent octahedron	[40]
44	$[H_2N(CH_2CH_3)_2]_2Zn(LH_2)_2 \cdot 2H_2O$	Zn^{2+}	6	2B	2	2.056(1)	2.200(2)	2.111	Independent octahedron	[40]
45	$Cu(LH_2)(bipyridil) \cdot 4H_2O$	Cu^{2+}	5	B (2N)	1	1.936(2)^{b} 1.999(2)^{d}	1.944(2)^{b} 2.006(2)^{d} 2.258(2)^{e}	1.940^{b} 2.003^{d} 2.029^{e}	Independent tetragonal basis pyramid	[16]
46	$NaCu(LH_2)Cl \cdot 3H_2O$	Na^+	5	2B (1Cl)	0	2.348(3)	2.592(4) 2.782(2)^{f}	2.437 2.506^{f}	Chains of alternately NaO_5 and CuO_6 polyhedra linked together by shared edges	[41]
		Cu^{2+}	6	2B (2Cl)	0	1.959(3)^{b} 2.694(1)^{g}	2.006(2)^{b} 2.894(1)^{g}	1.984^{b} 2.794^{g}		

Estimated standard deviations in parentheses.

$L = [(H_3C)(OH)C(PO_3)_2]^{4-}$.

[a] M: monodentate bond; B: bidentate bond; T: tridentate bond, (the number of each follows the symbol).

[b] These values concern the other distances Cu–O and the corresponding average.

[c] These values correspond to the great distances Cu—apical oxygen atoms due to the Jahn-Teller effect and the average value is calculated for all the six coordinence bonds.

[d] These values concern the distances Cu-N and their average.

[e] These values concern the distance Cu-O(H_2) and the average calculated for all the five coordinence bonds.

[f] These values concern the distance Na-Cl and the average calculated for all the five coordinence bonds.

[g] These values concern the distances Cu-Cl and the average calculated for all the six coordinence bonds.

TABLE 13 Bis HEBP (DHHTP and DHOTP) Complexes: Cation Coordinence with Extreme and Average Cation–Oxygen Distances (Å)

No.	*Compound*[a]	*Cation (M)*	*Coordinence of the Cation*	*Nature and Number of the Ligand-Cation Bond*[b]	*Number of Coordinated H_2O*	*M–O Min*	*M–O Max*	*M–O Average*	*Description of the Polyhedra Chaining*	*Ref.*
47	$(H_3O)_2[DHHTP]\cdot 2H_2O$	H_3O^+	8	3M, 2B	1	2.909(4)	3.355(4)	3.029	Independent bipolyhedron with 4 shared oxygen atoms	[42]
48	$Na_2[DHHTP]\cdot 4H_2O$	$2Na^+$	6	2M, T	1	2.289(3)	2.884(3)	2.451	Independent bioctahedron with 2 shared oxygen atoms	[43]
49	$K_2[DHHTP]\cdot 2H_2O$	$2K^+$	8	3M, 2B	1	2.814(2)	3.202(2)	2.953	Independent bipolyhedron with 4 shared oxygen atoms	[42]
50	$Cu[DHHTP]\cdot 10H_2O$	Cu^{2+}	6	2B	2	1.943(5)	1.952(5) 2.437(6)	1.948 2.111	Independent octahedron	[44]
52	$Ca[DHOTP]\cdot 6.8H_2O$	Ca^{2+}	6	2T	0	2.270(4)	2.350(5)	2.316	Independent octahedron	[31]
53	$Cu_2[DHOTP]\cdot 12H_2O$	Cu^{2+}	5	M, B	2	1.933(5)*	1.990* 2.291	1.954* 2.021	Independent square base pyramid	[31]

Estimated standard deviations in parentheses

[a] DHHTP, 1,6-dihydroxyhexylidene-1,1,6,6-tetraphosphonate; DHOTP, 1,8-dihydroxyoctilidene-1,1,8,8-tetraphosphonate.

[b] M, monodentate bond; B, bidentate bond; T, tridentate bond. The number of each follows the symbol.

[c] These values concern the other distances Cu-O and the corresponding average.

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