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Supporting Information

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1 Interactions with one phosphate

Here we present the results of the aluminum interaction with ligands that have one phosphate group, as it was already mention in our job, mono- di- and triester phosphates were studied. Three different anions and one neutral molecule were considered: methylphosphate dianion (MeP^{2-}) , hydrogen methylphosphate anion ($HMeP^{1-}$), see figure 1(a-d), both of them were considered due to pKa values of methyl phosphate are 1.54 and 6.3,[1] dimethylphosphate anion ($dMeP^{1-}$), see figure 1(e-f), 4-hydroxy-tetrahydro-3furanyl-methylphosphate anion ($THFolMeP^{1-}$), see figure 1(g-h), and trimethylphosphate (tMeP) see figure 1(i-j). The monodentate and bidentate binding structures were considered for each complex. The term bidentate is used when two water molecules are displaced by two oxygen from the same phosphate group, while a monodentate complex is formed when just one water molecule is replaced for one oxygen from the phosphate group. All the figures referred in this supplementary material are the ones in our job.

1.1 Structures

In the cluster $[Al(H_2O)_6]^{3+}$, the distances Al-O were 1.91 Å in good agreement with the bibliography,[2] when the substitution reaction occurred those distances get distorted. We observe that the distance Al-O from the phosphate tend to shorten while the Al-O from the water in position trans with respect to the substitution tend to lengthen, a common fact in hydrolyzed cluster,[3] indeed the same case is present, with even larger distortions, when one of the water molecule gets hydrolyzed. This occurrence is known as a trans-influence[4–6] induced by σ donor ligands groups on the water molecules in trans position with respect to them. But due to the electronic structure of Al^{3+}, *s* and *p* orbital donor, we observe a cis and trans influence, which means that not only the trans-coordination gets lengthen but also the cis-coordination ligands. Because of the variety and complexity of the different structures, these effects are not always "easy to see", see Table 1.

We can see the trans-cis influence if we look close at the values displayed in Table 1, but before that, take a look again to the figure ??, we can notice that in the monodentate case, the substitution occur in O1, the trans place is the O2 and the hydrogen bond take place in the O3 in most of the cases, but in the dianion, were a hydrolysis undergoes and in the ligand with ring were another hydrogen bond undergoes in the place O4. With this information in mind now we look at Table 1 but just to the (md) labeled complexes, which are the monodentate. We can see that not only the distances from the substituted places, Al-O1, but also the ones were the water take part of the hydrogen bond, Al-O3, are shortened. The places trans and cis to those are lengthened.

If we now try to do the same with the bidentate complexes, labeled in Table 1 as (bd), we first have to take into account that in those complexes the substituted places are O1 and O2, the trans to these position are O3 and O4 while O5 and O6 are in cis position. We can see that for the dianion, we got the same trend as before, shortened for the substituted distances Al-O1 and Al-O2, lengthened for the rest of them, but this is not the case for the mono-anion. We know that the interaction metal ion-ligand is mainly electrostatic, that means that the bidentate substitution, in the case of the monoanion, is going to be weaker owing to the sharing of one negative charge from both oxygen that are taking part in the substitution. We can see this effect in the distance from Table 1, Al-O1 shrunk only 0.01$\mathring{A}$ and Al-O2 gets elongated 0.01$\mathring{A}$, the trans position do not change and the cis places get elongated till 1.95 $\mathring{A}$. For the neutral molecule, the disparity is even bigger, one of the substitution, the one with the free oxygen got shortened till 1.87 $\mathring{A}$ but the other got elongated till 2.05$\mathring{A}$, the trans places got shortened and the cis a bit elongated.

In all the monodentate complex at least one strong (short) hydrogen bond is formed – from 1.50 $\mathring{A}$ till 1.96 $\mathring{A}$–, moreover a hydrolysis takes place with the dianion ligand, where two hydrogen bonds are formed. The THFolMeP^{1-} also form two hydrogen bonds, not only in the monodentate complex, but also in the bidentate complex with the difference in the oxygen atoms involve in those hydrogen bonds. The other bidentate complex that formed a hydrogen bond is the dianion ligand.

1.2 Energies

2 Interactions with two phosphates

Here we present the models for four phosphate systems, the details were well explain in our job.

The ligands studied in the first group were dimethyl diphospate dianion (dMeDP^{2-}, fig.3(a-d)), hydrogen methyl diphosphate dianion (HMeDP^{2-}, fig.3(e-h)), methyl diphosphate tri-anion (MeDP^{3-},fig.3(i-k)) and hydroxy-methyltetrahydrofuran-diphosphate dianion (MeTHFolDP^{2-}, fig.2(l-

Table 1: One phosphate - structure.

L	Distance (Å)					
	Al-O1	Al-O2	Al-O3	Al-O4	Al-O5	Al-O6
methyl phosphate di-anion						
[Al5w-MeP]$^{1+}$(md)	1.838	1.972	1.803	2.001	1.967	1.976
[Al4w-MeP]$^{1+}$(bd)	1.857	1.872	1.935	1.929	1.993	1.964
methyl phosphate anion						
[Al5w-HMeP]$^{2+}$(md)	1.818	1.939	1.880	1.926	1.957	1.956
[Al4w-HMeP]$^{2+}$(bd)	1.896	1.920	1.910	1.914	1.954	1.953
dimethyl phosphate anion						
[Al5w-dMeP]$^{2+}$(md)	1.815	1.942	1.880	1.926	1.957	1.956
[Al4w-dMeP]$^{2+}$(bd)	1.896	1.917	1.910	1.915	1.957	1.954
4-hydroxy-tetrahydro-3-furanyl methyl phosphate anion						
[Al5w-THFolMeP]$^{2+}$(md)	1.814	1.936	1.892	1.912	1.949	1.973
[Al4w-THFolMeP]$^{2+}$(bd)	1.915	1.921	1.920	1.914	1.920	1.954
trimethyl phosphate						
[Al5w-tMeP]$^{3+}$(md)	1.826	1.922	1.910	1.910	1.938	1.939
[Al4w-tMeP]$^{3+}$(bd)	1.874	2.051	1.889	1.885	1.930	1.928

(md) monodentate complex
(bd) bidentate complex

n)).

In this second group the ligands used were 1-3-propyl-bi(methylphosphate) dianion (Propbi(MeP)$^{2-}$, fig.4(a-c)), methyltetrahydrofuran-bi(methylphosphate) dianion (MeTHFbi(MeP)$^{2-}$, fig.4(d-f)), hydroxymethyltetrahydrofuran-bi(mehtylphosphate) dianion (MeTHFolbi(MeP)$^{2-}$, fig.4(g-j)) and bi-(hydroxymethyltetrahydrofuran)-methylphosphate dianion (bi(MeTHFol)MeP^{2-} fig.4(k-l)).

The third group is represented by 1,2-Ethanediyl bisphosphate (EBP, fig.5(a-f)).

At the end these three models are going to be compared with an even simpler case; two independent phosphate diester, dMeP^{1-}, fig.5(g-h).

2.1 Structures

Within the ligands in this group the substitution mode can take place in three different ways, (1) the mono-coordinate monodentate mode (mcmd), that is when just one water molecule is replace by one oxygen from the ligand, (2) the mono-coordinate bidentante mode (mcbd), that means two water molecule are substituted with two oxygen belonging to one of the two phosphates groups, and

Table 2: One phosphate interaction, units: kcal mol^{-1}.

L	Gas phase			Aqueous phase			ΔG_{sol}
	ΔE_f	ΔH_f	ΔG_f	ΔE_f	ΔH_f	ΔG_f	
methyl phosphate di-anion							
[Al5w-MeP]$^{1+}$(md)	-622.92	-621.98	-618.78	-76.41	-76.41	-71.02	-81.95
[Al4w-MeP]$^{1+}$(bd)	-598.74	-599.55	-607.56	-58.69	-58.09	-60.81	-82.92
methyl phosphate anion							
[Al5w-HMeP]$^{2+}$(md)	-324.11	-324.92	-322.15	-39.97	-39.97	-36.00	-189.18
[Al4w-HMeP]$^{2+}$(bd)	-307.47	-309.53	-317.53	-20.63	-20.04	-23.78	-181.54
dimethyl phosphate anion							
[Al5w-dMeP]$^{2+}$(md)	-326.60	-327.13	-324.48	-40.52	-40.52	-36.22	-185.87
[Al4w-dMeP]$^{2+}$(bd)	-311.73	-313.73	-323.25	-21.40	-20.80	-25.06	-175.89
4-hydroxy-tetrahydro-3-furanyl methyl phosphate anion							
[Al5w-THFolMeP]$^{2+}$(md)	-322.71	-323.08	-319.87	-36.07	-36.06	-30.21	-178.56
[Al4w-THFolMeP]$^{2+}$(bd)	-322.06	-323.43	-329.46	-24.77	-24.17	-24.77	-163.49
trimethyl phosphate							
[Al5w-tMeP]$^{3+}$(md)	-74.14	-74.19	-73.89	-14.79	-14.79	-10.11	-355.76
[Al4w-tMeP]$^{3+}$(bd)	-30.54	-33.04	-43.46	18.98	19.54	16.17	-359.87

(md) monodentate complex
(bd) bidentate complex

(3) the di-coordinate monodentate (dcmd), which involves two oxygen atoms from two different phosphoryl groups.

In the case of the ligand dMeDP^{2-}, in the mcmd case, a hydrolysis takes place and two strong hydrogen bonds are present, the shortest of them is between the hydrogen that went to the phosphate group and the hydroxyl group left in the aluminum it has about 1.41 Å, the other is a bit longer with 1.62 Å. The mcbd complex have a strong (short) hydrogen bond about 1.38 Å, and the dcmd complex has one of about 1.69 Å. The last complex with dMeDP^{2-} ligand is a tri-coordinate complex, were it is bi-dentate with respect to one phosphate and mono-dentate with respect to the other, tcbdmd.

Again we can see the influence trans-cis in this structures. It actually can be seen clearly in the mcmd and dcmd structures, but not much in the mcbd and tcbdmd structures were there is a case of sharing charge, the same case than the anions in the previous section. Looking at the figure 3(a) we get that the distance Al-O1 and Al-O3 are the distance that should get shortened for the mcmd complex, one for the substitution, the other for the hydrolysis and indeed that is the result in Table 3, they got shrunk till 1.85 and 1.81 Å respectively. In the dcmd case, from figure 3(c) we get that Al-O1 and Al-O2 are the distances that should get shortened by the substitution, in Table 3 we see that these distances got till 1.83-1.84 $\AA$. All the other distances in this two complexes got elongated, as it is expected from the trans-cis influence.

In the NAD/ADP-like group we can directly compare the structures of the complexes: [Al4w-dMeDP]$^{1+}$(figure 3(c)), [Al4w-HMeDP]$^{1+}$ (figure 3(g)) and [Al4w-MeTHFolDP]$^{1+}$ (figure 3(l)), they not only have in common the charge but also the dcmd structure with two adjacent phosphates. All three complexes have quite similar structures, as it is showed in the upper part of Table 3. The main difference is that the complex within the ring has two hydrogen bonds more than the others even though they are longer. It is noticed that in these complexes with diphosphate ligands, the trans-cis influence is also present, getting the substituted oxygen shorter distance with aluminum and the others longer.

In the RNA/DNA-like group, different small molecules from the simplest to more complicated ligands were used. The substitution reaction occurred with two phosphates groups placed in the different extreme of the molecule, as it was mention before, the phosphates are separated by three carbon, as it is the case in those big molecules.

The three next ligands were studied in the mono-coordinate and bi-coordinate form, in addition the two asymmetrical ligands have two different mono-coordinate structure, when the substitution occur from the phosphate group on the ring (furanyl-side) it is label as "fs", on the contrary when the substitution takes place with the phosphate group on the methyl, it is label as "ms".

In Table 3 is recognized that the three mcmd complexes [Al5w-PropbiMeP] $^{1+}$, [Al5w-MeTHFbiMeP]$^{1+}_{fs}$ and [Al5w-MeTHFolbiMeP]$^{1+}_{fs}$, have similar structures, in figure 4 (a), (d) and (g) are shown two strong hydrogen bonds (1.65 – 1.96 $\AA$) and one of the water ligands undergoes hydrolysis, this one also makes an hydrogen bond (1.46 – 1.49 $\AA$), that in total make three hydrogen bonds for these complexes.

On the other side, the mcmd complexes [Al5w-MeTHFbiMeP]$^{1+}_{ms}$ and [Al5w-MeTHFolbiMeP]$^{1+}_{ms}$ have three strong hydrogen bonds but no water molecule underwent hydrolysis, see figure 4 (e) and (h). In these two complexes the distance of the hydrogen bonds are shorter, they go from 1.29 – 1.72 $\AA$. There are two feature that are different from the other mcmd complexes. First, the water ligand in place O3 did not go under hydrolysis, that makes that the distance Al-O3 do not shrink that much as it did in the other complexes, here it reach 1.87–1.88 $\AA$, while before it reached 1.81 $\AA$. Second, here the water in place O5 is part of two hydrogen bond, that makes the distance Al-O5 shrink more that it did before, it got till 1.88-1.89 $\AA$, while in the other mcmd complexes it actually elongated till 1.95–1.96$\AA$.

With the ligand Propbi(MeP)$^{2-}$ we also did the mcbd structure, see figure 4 (b). In this structure, again the sharing of one negative charge between the two oxygens that participate in the substitution, makes longer bonds distance between Al and the O from the phosphates. The water in position 5 goes under hydrolysis, the distance Al-O5 get shortened till 1.8Å, while its trans position Al-O6 get lengthened till 2.03Å.

In the last place the dcmd complexes, see figures 4(c), (f), (i), (j) and (k), show that both of the complexes with the ring-ligands [Al4w-MeTHFbiMeP]$^{1+}$, [Al4w-MeTHFolbiMeP]$^{1+}$, [Al4w-bi(MeTHFol)MeP]$^{1+}_{C5}$ and [Al4w-bi(MeTHFol)MeP]$^{1+}_{C3}$ have two strong and symmetrical hydrogen bonds, while the [Al4w-PropbiMeP]$^{1+}$ complex has two asymmetrical hydrogen bonds. These differences can be reflected in the data of Table 3 where the last compound mentioned shows a small difference from the other two in the distances Al-O5 and Al-O6.

The trans-cis influence is present in all this complexes, since the oxygen in the substitution places together with the ones in the hydroxyl group and the ones in the water that take place in the hydrogen bonds got shortened, but the others got lengthened.

For the DPG-like molecule it is possible to have di-, tri-, and tetra-anion. The complex mcmd where considered with the di- and tri-anion. Again the effect trans-cis is present in these complexes. The main difference is that the tri-anion ligand goes under hydrolysis in the water position 3, while in the di-anion there is a strong hydrogen bond in this position, the shortened in the distance Al-O3 can be appreciated in Table 3. The complex mcbd was done just for the tri-anion, (it was considered the most suitable for this complex). In Table 3 can be seen the trans-cis effect, where the position substituted for the ligand and the water that went under hydrolysis (O5) got shortened, while the others got lengthened.

The complex dcmd was considered for all of the three anions. Once again, it is possible appreciate the trans-cis effect. The di-anion ligand, [Al4w-DPE^{1+}](dcmd), is the simplest one, the position where the substitution occur, Al-O1 and Al-O2, the bond distance were reduced and all the others were elongated. In the tri-anion ligand, the water in position 5 went under hydrolysis, thus the distance Al-O5 got shortened. In the tetra-anion, not only the water in position 5 but also the one in position 6 went under hydrolysis, hence, the distance Al-O6 also got reduced.

For the last case, in oder to distinguish the influence of the anchoring in the two phosphate groups, two water molecule were substituted for two independent dMeP^{1-} molecules in trans and cis positions see figure 5(g) and (h). From Table 3 we can see that the trans-complex is the symmetric one, while the figure 5(g,h) shows that even though in both structures two hydrogen bonds are present the shortest hydrogen bonds are in the cis-complex.

From Table 3, we can see that the distances in these complexes are quite similar to the previous bi-coordinate complexes with some differences due to the different water ligands that take places in the hydrogen bonds, we can say that in the cis-complex the distances Al-O4 and Al-O5 are equivalent to the Al-O5 and Al-O6 of the previous bi-coordinate complexes respectively, while in the trans-complex those are equivalent to Al-O3 and Al-O4 respectively.

Table 3: Two phosphates - structure.

L	Distance (Å)					
	Al-O1	Al-O2	Al-O3	Al-O4	Al-O5	Al-O6
NAD-like						
[Al5w-dMeDP]$^{1+}$(mcmd)	1.847	1.979	1.808	1.982	1.957	1.970
[Al4w-dMeDP]$^{1+}$(mcbd)	1.906	1.929	1.930	1.925	1.886	1.978
[Al4w-dMeDP]$^{1+}$(dcmd)	1.833	1.842	1.967	1.962	1.959	1.961
[Al3w-dMeDP]$^{1+}$(tcbdmd)	1.951	1.964	1.862	1.928	1.915	1.950
ADP-like						
[Al5w-HMeDP]$^{1+}$(mcmd)	1.836	2.007	1.807	1.998	1.900	2.008
[Al4w-HMeDP]$^{1+}$(mcbd)	1.908	1.929	1.930	1.926	1.885	1.976
[Al4w-HMeDP]$^{1+}$(dcmd)	1.841	1.834	1.939	1.962	1.958	1.962
[Al3w-HMeDP]$^{1+}$(tcbdmd)	1.955	1.964	1.863	1.926	1.914	1.948
[Al4w-MeTHFolDP]$^{1+}$(dcmd)	1.872	1.855	1.950	1.949	1.951	1.948
[Al5w-MeDP]^{0}(mcmd)	1.836	2.007	1.807	1.998	1.900	2.008
[Al4w-MeDP]^{0}(mcbd)	1.899	1.884	1.962	1.975	1.830	2.048
[Al4w-MeDP]^{0}(dcmd)	1.857	1.859	1.995	1.996	1.823	2.014
[Al5w-MeTHFolDP]^{0} (mcmd)	1.845	1.994	1.806	1.982	1.958	2.000
[Al4w-MeTHFolDP]^{0} (dcmd)	1.873	1.897	1.983	1.995	1.816	2.007
RNA/DNA-like						
[Al5w-Propbi(MeP)]$^{1+}$(mcmd)	1.838	1.995	1.807	1.987	1.964	1.973
[Al4w-Propbi(MeP)]$^{1+}$(mcbd)	1.953	1.929	1.941	1.969	1.801	2.034
[Al4w-Propbi(MeP)]$^{1+}$(dcmd)	1.833	1.825	1.965	1.993	1.934	1.971
DNA-like						
[Al5w-MeTHFbi(MeP)]$^{1+}_{fs}$(mcmd)	1.843	1.969	1.806	2.014	1.951	1.983
[Al5w-MeTHFbi(MeP)]$^{1+}_{ms}$(mcmd)	1.840	1.978	1.869	1.998	1.885	1.962
[Al4w-MeTHFbi(MeP)]$^{1+}$(dcmd)	1.834	1.845	1.983	1.990	1.941	1.937
RNA-like						
[Al5w-MeTHFolbi(MeP)]$^{1+}_{fs}$(mcmd)	1.842	1.988	1.821	2.000	1.929	1.983
[Al5w-MeTHFolbi(MeP)]$^{1+}_{ms}$(mcmd)	1.839	1.976	1.875	1.994	1.883	1.962
[Al4w-MeTHFolbi(MeP)]$^{1+}$(dcmd)	1.835	1.845	1.985	1.988	1.941	1.939
[Al4w-MeTHFolbi(MeP)]$^{1+}_{fs}$(mcbd)	1.922	1.957	1.961	1.946	1.801	2.033
[Al4w-bi(MeTHFol)MeP]$^{1+}_{C5}$(dcmd)	1.833	1.849	1.977	1.991	1.935	1.944
[Al4w-bi(MeTHFol)MeP]$^{1+}_{C3}$(dcmd)	1.835	1.845	1.981	1.989	1.936	1.943
DPG-like						
[Al5w-EBP]$^{1+}$ (mcmd)	1.832	1.961	1.898	1.970	1.918	1.942
[Al4w-EBP]$^{1+}$ (dcmd)	1.813	1.834	1.999	1.962	1.938	1.969
[Al5w-EBP]^{0} (mcmd)	1.842	2.033	1.809	1.952	1.964	1.982
[Al4w-EBP]^{0} (mcbd)	1.886	1.891	1.974	1.974	1.831	2.054
[Al4w-EBP]^{0} (dcmd)	1.868	1.852	2.026	2.029	1.824	2.000
[Al4w-EBP]$^{1-}$ (dcmd)	1.879	1.880	2.072	2.100	1.863	1.858
two dimethyl phosphate anion						
[Al4w-2(dMeP)]$^{1+}_{trans}$(dcmd)	1.835	1.835	1.936	1.936	1.987	1.987
[Al4w-2(dMeP)]$^{1+}_{cis}$(dcmd)	1.843	1.839	2.005	1.920	1.937	1.975

(md) monodentate complex

(bd) bidentate complex

(mc) mono-coordinate complex

(dc) di-coordinate complex

(tc) tri-coordinate complex

2.2 Energies

Table 4: Two phosphates interaction, units: kcal mol^{-1}.

L	Gas phase			Aqueous phase			ΔG_{sol}
	ΔE_f	ΔH_f	ΔG_f	ΔE_f	ΔH_f	ΔG_f	
NAD-like							
[Al5w-dMeDP]$^{1+}$(mcmd)	-578.09	-579.05	-574.23	-59.24	-59.24	-52.74	-83.27
[Al4w-dMeDP]$^{1+}$(mcbd)	-549.61	-552.62	-558.52	-42.55	-41.96	-44.26	-90.46
[Al4w-dMeDP]$^{1+}$(dcmd)	-572.64	-574.40	-579.98	-55.28	-54.69	-55.01	-79.75
[Al3w-dMeDP]$^{1+}$(tcbdmd)	-553.61	-557.08	-573.34	-35.74	-34.56	-43.18	-74.52
ADP-like							
[Al5w-HMeDP]$^{1+}$(mcmd)	-578.41	-579.64	-575.01	-58.98	-58.98	-52.53	-83.67
[Al4w-HMeDP]$^{1+}$(mcbd)	-547.81	-551.26	-557.28	-41.50	-40.91	-42.73	-91.56
[Al4w-HMeDP]$^{1+}$(dcmd)	-578.39	-580.29	-585.81	-58.21	-57.61	-58.77	-79.07
[Al3w-HMeDP]$^{1+}$(tcbdmd)	-550.54	-554.52	-570.78	-34.53	-33.34	-41.64	-76.94
[Al4w-MeTHFolDP]$^{1+}$ (dcmd)	-566.33	-568.61	-573.88	-54.29	-53.70	-52.30	-78.57
[Al5w-MeDP]^{0}(mcmd)	-849.92	-851.68	-846.99	-91.65	-91.65	-86.21	-64.16
[Al4w-MeDP]^{0}(mcbd)	-838.17	-840.84	-846.49	-77.86	-77.27	-79.21	-57.63
[Al4w-MeDP]^{0}(dcmd)	-863.11	-864.66	-869.62	-92.44	-91.85	-93.00	-48.29
[Al5w-MeTHFolDP]^{0} (mcmd)	-827.23	-827.21	-821.91	-86.47	-86.47	-79.97	-56.74
[Al4w-MeTHFolDP]^{0} (dcmd)	-832.66	-833.46	-838.40	-86.33	-85.74	-86.65	-46.89
RNA/DNA-like							
[Al5w-Propbi(MeP)]$^{1+}$(mcmd)	-567.71	-567.88	-562.31	-63.40	-63.40	-55.49	-81.54
[Al4w-Propbi(MeP)]$^{1+}$(mcbd)	-553.48	-555.14	-560.86	-47.17	-46.58	-47.91	-75.36
[Al4w-Propbi(MeP)]$^{1+}$(dcmd)	-577.32	-578.43	-582.61	-63.96	-63.36	-62.36	-68.06
DNA-like							
[Al5w-MeTHFbi(MeP)]$^{1+}_{fs}$(mcmd)	-568.78	-568.92	-563.69	-61.67	-61.67	-53.55	-76.29
[Al5w-MeTHFbi(MeP)]$^{1+}_{ms}$(mcmd)	-576.20	-579.02	-572.03	-70.84	-70.84	-61.90	-76.31
[Al4w-MeTHFbi(MeP)]$^{1+}$(dcmd)	-583.77	-585.49	-589.30	-69.77	-69.18	-67.69	-64.78
RNA-like							
[Al5w-MeTHFolbi(MeP)]$^{1+}_{fs}$(mcmd)	-583.72	-584.40	-577.63	-69.29	-69.29	-59.24	-78.61
[Al5w-MeTHFolbi(MeP)]$^{1+}_{ms}$(mcmd)	-573.27	-575.96	-568.63	-69.94	-69.94	-60.31	-78.57
[Al4w-MeTHFolbi(MeP)]$^{1+}$(dcmd)	-581.15	-582.95	-586.71	-68.81	-68.21	-66.37	-66.51
[Al4w-MeTHFolbi(MeP)]$^{1+}_{fs}$(mcbd)	-546.61	-548.53	-554.41	-43.65	-43.06	-45.02	-77.46
[Al4w-bi(MeTHFol)MeP]$^{1+}_{C5}$(dcmd)	-572.94	-574.82	-578.81	-67.49	-66.90	-65.01	-74.57
[Al4w-bi(MeTHFol)MeP]$^{1+}_{C3}$(dcmd)	-577.27	-579.14	-582.72	-68.77	-68.18	-67.44	-70.75
DPG-like							
[Al5w-EBP]$^{1+}$(mcmd)	-553.31	-554.60	-549.10	-59.23	-59.23	-49.76	-88.26
[Al4w-EBP]$^{1+}$(dcmd)	-564.21	-566.18	-571.01	-59.96	-59.36	-58.50	-75.04
[Al5w-EBP]^{0}(mcmd)	-825.82	-826.21	-819.65	-93.32	-93.32	-83.48	-51.41
[Al4w-EBP]^{0}(mcbd)	-798.82	-801.59	-807.35	-73.36	-72.77	-73.74	-53.93
[Al4w-EBP]^{0}(dcmd)	-838.30	-840.26	-844.04	-95.37	-94.77	-92.65	-36.15
[Al4w-EBP]$^{1-}$(dcmd)	-1076.86	-1079.51	-1083.26	-121.11	-120.52	-119.62	-72.80
two dimethyl phosphate anion							
[Al4w-2(dMeP)]$^{1+}{}_{trans}$(dcmd)	-546.06	-546.36	-540.16	-70.83	-70.83	-60.74	-58.64
[Al4w-2(dMeP)]$^{1+}{}_{cis}$ (dcmd)	-543.06	-543.79	-537.40	-70.26	-70.26	-61.58	-62.24

(md) monodentate complex
(bd) bidentate complex
(mc) mono-coordinate complex
(dc) di-coordinate complex
(tc) tri-coordinate complex

3 Interactions with three phosphates

We employed hydrogen-methyl-triphosphate trianion $[\text{HMeTP}]^{3-}$, methyl-triphosphate $[\text{MeTP}]^{3-}$, hydrogen-methyl-hydroxy-tetrahydrofuranyl-triphosphate trianion $[\text{HMeTHFolTP}]^{3-}$ and methyl-hydroxy-tetrahydrofuranyl-triphosphate trianion $[\text{MeTHFolTP}]^{3-}$ in order to see if the ribose-like ring has any effect.

3.1 Structures

From the previous sections we can expect that the mono-coordinate complexes would be a favorable product, but less favored than the bi-coordinate or even a tri-coordinate complex. The mcmd and mcbd structures were done with the simplest ligand molecule and indeed they were the less stable products. In this section two different tri-coordinate and bi-coordinate structures were studied, the dcmd structure could be with the phosphates in α, β position or in β, γ position, the tcmd structure is when each of the three phosphates make a bond with Al while tcbdmd is when just two phosphoryl groups are involved, one of them in a bi-dentate form and the other in a mono-dentate form. The nomenclature for the phosphates is the accepted in literature, where the phosphoryl groups, starting with the group closest to the methyl (or hydroxy-tetrahydrofuranyl, THFol) are referred to as the α, β and γ phosphates.

From figure 6 (c,d,g,h,j,k,m,n) we can appreciate that in all the di-coordinate structures at least two hydrogen bonds are formed, one stronger with the terminal phosphate group that remain uncoordinated, and another a bit longer with the phosphate from the other extreme, except in the case of $[\text{Al4w-HMeTHFolTP}]_{\alpha,\beta}$ where the last hydrogen bond is replaced by two hydrogen bonds with the OH groups from the THFol. In the structure of all complexes the trans-cis influence is present. We can see this influence in the dcmd complexes in Table 5, the distance Al-O from the substitution Al-O1 and Al-O2 get shrunk, while their trans places, Al-O3 and Al-O4, get lengthened not in the same amount due to the hydrogen bonds concerned in each compound. The oxygen from a water molecule involved in a hydrogen bond tend to get shorter distance Al-O, as we can appreciate in Table 5 from the distances Al-O5, in di-coordinate complexes, where the water molecule is part of an even stronger hydrogen bond of about 1.37 – 1.41 Å, this Al-O5 distances can reach 1.89Å or even shorter in the case of hydrolysis, while a lengthened take place in its trans position in the coordination sphere of aluminum, in this cases the distance Al-O6 reached 2.03Å.

In the other side, the distances of the tri-coordinate complexes, a shortened of the three distances Al-O that take place in the substitution reaction are appreciated, Al-O1, Al-O2, Al-O3 reached 1.85–1.87 Å and at the same time, a corresponding lengthened in the rest of the distance Al-O from the water coordination 1.96–2.03Å. In this complexes there was no structural effect due to the additional ring in the ligand.

Table 5: Three phosphates - structure.

L	Distance (Å)					
	Al-O1	Al-O2	Al-O3	Al-O4	Al-O5	Al-O6
			ATP-like			
[Al5w-HMeTP]$_{\gamma}$ (mcmd)	1.815	1.976	1.871	1.972	1.898	1.978
[Al4w-HMeTP]$_{\gamma}$ (mcbd)	1.926	1.910	1.925	1.932	1.883	1.980
[Al4w-HMeTP]$_{\alpha,\beta}$ (dcmd)	1.835	1.841	1.973	1.963	1.904	1.977
[Al4w-HMeTP]$_{\beta,\gamma}$ (dcmd)	1.853	1.841	1.977	1.985	1.886	1.989
[Al3w-HMeTP](tcmd)	1.845	1.870	1.871	1.978	1.957	1.976
[Al3w-HMeTP](tcbdmd)	1.925	1.937	1.831	1.950	1.942	1.983
[Al4w-HMeTHFolTP]$_{\alpha,\beta}$ (dcmd)	1.857	1.834	1.958	2.003	1.906	1.947
[Al4w-HMeTHFolTP]$_{\beta,\gamma}$ (dcmd)	1.853	1.841	1.976	1.982	1.891	1.985
[Al3w-HMeTHFolTP](tcmd)	1.848	1.870	1.872	1.975	1.956	1.974
[Al4w-MeTP]$^{1-}_{\alpha,\beta}$ (dcmd)	1.852	1.859	2.002	1.998	1.813	2.026
[Al4w-MeTP]$^{1-}_{\beta,\gamma}$ (dcmd)	1.873	1.863	2.012	2.028	1.837	1.938
[Al3w-MeTP]$^{1-}$(tcmd)	1.865	1.874	1.848	1.941	1.979	2.005
[Al4w-MeTHFolTP]$^{1-}_{\alpha,\beta}$ (dcmd)	1.870	1.856	1.996	2.052	1.815	1.993
[Al4w-MeTHFolTP]$^{1-}_{\beta,\gamma}$ (dcmd)	1.872	1.864	2.012	2.026	1.836	1.938
[Al3w-MeTHFolTP]$^{1-}$(tcmd)	1.868	1.875	1.848	1.938	1.979	2.003

3.2 Energies

Table 6: Three phosphates interaction, units: kcal mol^{-1}.

L	Gas phase			Aqueous phase			ΔG_{sol}
	ΔE_f	ΔH_f	ΔG_f	ΔE_f	ΔH_f	ΔG_f	
				ATP-like			
[Al5w-HMeTP]$_{\gamma}$ (mcmd)	-766.90	-769.97	-764.25	-72.47	-72.48	-63.70	-92.67
[Al4w-HMeTP]$_{\gamma}$ (mcbd)	-720.87	-723.99	-731.53	-45.97	-45.38	-46.92	-108.57
[Al4w-HMeTP]$_{\alpha,\beta}$ (dcmd)	-798.21	-799.96	-805.48	-73.90	-73.31	-72.70	-60.39
[Al4w-HMeTP]$_{\beta,\gamma}$ (dcmd)	-801.36	-804.10	-809.52	-75.94	-75.35	-74.54	-58.20
[Al3w-HMeTP](tcmd)	-809.52	-812.44	-827.70	-76.97	-75.79	-82.14	-47.58
[Al3w-HMeTP](tcbdmd)	-766.03	-769.01	-785.74	-52.89	-51.71	-59.46	-66.86
[Al4w-HMeTHFolTP]$_{\alpha,\beta}$ (dcmd)	-776.13	-778.53	-780.74	-78.00	-77.41	-74.07	-79.35
[Al4w-HMeTHFolTP]$_{\beta,\gamma}$ (dcmd)	-793.87	-796.70	-800.74	-77.14	-76.55	-76.79	-62.07
[Al3w-HMeTHFolTP](tcmd)	-801.44	-804.70	-818.62	-77.73	-76.54	-83.08	-50.44
[Al4w-MeTP]$^{1-}_{\alpha,\beta}$ (dcmd)	-1040.29	-1041.26	-1045.86	-96.13	-95.54	-94.65	-105.66
[Al4w-MeTP]$^{1-}_{\beta,\gamma}$ (dcmd)	-1062.88	-1065.26	-1069.00	-108.02	-107.43	-107.40	-95.27
[Al3w-MeTP]$^{1-}$(tcmd)	-1055.25	-1059.33	-1073.26	-105.41	-104.23	-109.68	-93.25
[Al4w-MeTHFolTP]$^{1-}_{\alpha,\beta}$ (dcmd)	-987.89	-988.62	-991.38	-100.50	-99.90	-97.18	-130.02
[Al4w-MeTHFolTP]$^{1-}_{\beta,\gamma}$ (dcmd)	-1034.19	-1035.92	-1039.52	-109.29	-108.70	-109.22	-93.91
[Al3w-MeTHFolTP]$^{1-}$(tcmd)	-1024.52	-1028.13	-1041.94	-106.42	-105.24	-111.96	-94.20

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