Electronic Supplementary Material (ESI) for RSC Advances.

Aluminum interaction with 2-3-diphosphoglyceric acid. A computational study.

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Supporting Information List:

1. Methodology assessment (Table S1)
2. The studied 13 Al-(2,3-DPG) complexes (Figure S2).
3. The studied 7 Al-(2,3-DPG)(Citr) complexes (Figure S3).

1 Methodology assessment

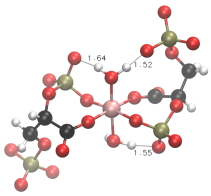
In order to assess that the methodology employed in this article was reliable, single-point calculations were carried out at the B3LYP/6-31++G(d,p) optimized structures by using three functionals (PBE0, M06-2X and BP86) and a triple-ζ basis set (6-311++G(3df,2p). The results are shown in Table S1, and compared with the original values computed at B3LYP/6-311++G(3df,2p) (Figure 1).

Table S1: Reaction energies in kcal mol^{-1} at physiological pH calculated with different DFT functionals: B3LYP, PBE0, M06-2X and BP86. The same basis set (6-311++G(3df,2p) was employed for all the calculations.

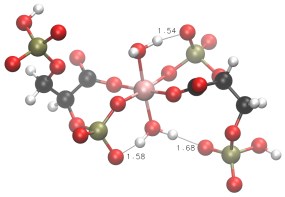
Structure	ΔG_{aq}^{Phys}(B3LYP)	ΔG_{aq}^{Phys}(PBE0)	ΔG_{aq}^{Phys}(M06-2X)	ΔG_{aq}^{Phys}(BP86)
Complexes 1:1				
$[Al(DPG)_{AC}(H_2O)_4]^{2-}$	-118.40	-122.57	-124.90	-120.01
$[Al(DPG)_{AC}(H_2O)_4]^{1-}$	-99.05	-103.85	-106.67	-102.29
$[Al(DPG)_{BC}(H_2O)_4]^{2-}$	-102.82	-106.62	-108.24	-105.26
$[Al(DPG)_{BC}(H_2O)_4]^{1-}$	-95.43	-99.04	-100.70	-97.63
$[Al(DPG)_{AB}(H_2O)_4]^{2-}$	-119.33	-123.42	-125.87	-121.13
$[Al(DPG)_{ABC}(H_2O)_3]^{2-}$	-123.54	-128.95	-132.00	-127.86
$[Al(Citr)(H_2O)_3]^{1-}$	-123.46	-127.18	-125.00	-124.97
Complexes 1:2				
$[Al(DPG)_{2,AC}(H_2O)_2]^{7-}$	-134.01	-139.71	-143.31	-136.75
$[Al(DPG)^{\dagger}_{2,AC}(H_2O)_2]^{5-}$	-127.06	-132.43	-136.01	-129.25
$[Al(DPG)^{\ddagger}_{2,AC}(H_2O)_2]^{5-}$	-118.34	-123.63	-129.72	-120.28
$[Al(DPG)^{**}_{2,AC}(H_2O)_2]^{5-}$	-116.34	-121.71	-125.64	-118.59
$[Al(DPG)^{***}_{2,AC}(H_2O)_2]^{6-}$	-133.66	-139.29	-142.98	-136.31
$[Al(DPG)^{*}_{2,AC}(H_2O)_2]^{7-}$	-130.03	-135.11	-140.40	-132.35
$[Al(DPG)_{2,AB}(H_2O)_2]^{7-}$	-136.85	-143.07	-149.13	-139.25
$[Al(DPG)^{\dagger}_{2,AB}(H_2O)_2]^{5-}$	-119.36	-125.54	-132.85	-121.61
$[Al(DPG)^{\ddagger}_{2,AB}(H_2O)_2]^{5-}$	-122.66	-129.15	-137.54	-124.25
$[Al(DPG)^{**}_{2,AB}(H_2O)_2]^{5-}$	-116.56	-122.05	-128.77	-118.06
$[Al(DPG)^{*}_{2,AB}(H_2O)_2]^{7-}$	-140.89	-147.35	-153.84	-143.24
$[Al(DPG)^{*,\ddagger}_{2,AB}(H_2O)_2]^{5-}$	-123.74	-129.80	-139.29	-124.98
$[Al(DPG)_{2,ABC}]^{7-}$	-128.43	-137.66	-144.18	-118.81
$[Al(Citr)_2]^{5-}$	-181.28	-184.37	-179.10	-181.25
Complexes 1:1:1				
$[Al(DPG)_{AC}(Citr)(H_2O)]^{6-}$	-161.39	-165.83	-166.12	-162.08
$[Al(DPG)^{***}_{AC}(Citr)(H_2O)]^{5-}$	-156.79	-148.47	-150.24	-144.46
$[Al(DPG)_{AB}(Citr)(H_2O)]^{6-}$	-156.64	-161.03	-162.34	-156.94
$[Al(DPG)^{***}_{AB}(Citr)(H_2O)]^{5-}$	-144.17	-161.01	-161.37	-157.02
$[Al(DPG)^{****}_{AB}(Citr)(H_2O)]^{5-}$	-152.52	-157.07	-158.92	-152.90
$[Al(DPG)_{ABC}(Citr)]^{6-}$	-157.82	-160.52	-160.24	-157.90
$[Al(DPG)^{***}_{ABC}(Citr)]^{5-}$	-149.90	-152.49	-151.97	-150.08

* Different ligand substitution position. † Both phosphates of group B are protonated. ‡ Both phosphates of group A are protonated. ** Different phosphate group are protonated in each ligand. *** One phosphate of group B is protonated. **** One phosphate of group A is protonated.

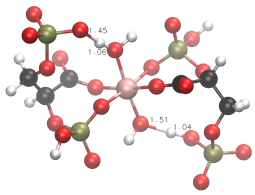
Figure S2: The 13 studied 1:2 Al-(2,3-DPG) complexes. The subscripts indicate the coordination mode of 2,3-DPG to Al(III) and the superscripts refer to the protonation states of the phosphates groups: (bb) both phosphates of group B are protonated, (aa) both phosphates of group A are protonated, (ab) different phosphate groups are protonated in each ligand, (b) one phosphate of group B is protonated, (a) one phosphate of group A is protonated, * different ligand substitution positions. The formation energies (ΔG_{aq}^{Phys}) are shown in kcal/mol.



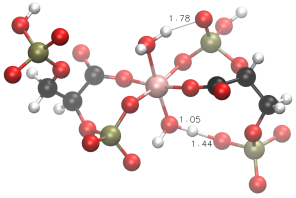
$[Al(2,3\text{-}DPG)_{2,AC}(H_2O)_2]^{7-}$
-134.01



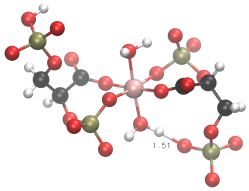
$[Al(2,3\text{-}DPG)^{bb}_{2,AC}(H_2O)_2]^{5-}$
-127.06



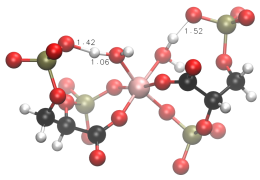
$[Al(2,3\text{-}DPG)^{aa}_{2,AC}(H_2O)_2]^{5-}$
-118.34



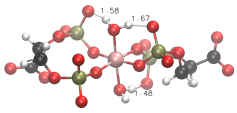
$[Al(2,3\text{-}DPG)^{ab}_{2,AC}(H_2O)_2]^{5-}$
-116.34



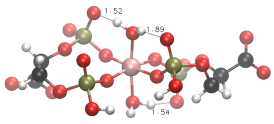
$[Al(2,3\text{-}DPG)^{b}_{2,AC}(H_2O)_2]^{6-}$
-133.66



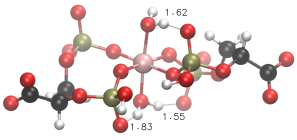
$[Al(2,3\text{-}DPG)^{*}_{2,AC}(H_2O)_2]^{7-}$
-130.03



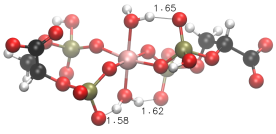
$[Al(2,3\text{-}DPG)_{2,AB}(H_2O)_2]^{7-}$
-136.85



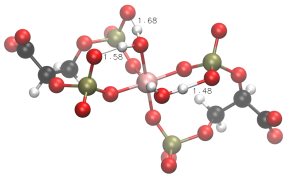
$[Al(2,3\text{-}DPG)^{bb}_{2,AB}(H_2O)_2]^{5-}$
-119.36



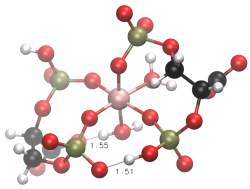
$[Al(2,3\text{-}DPG)^{aa}_{2,AB}(H_2O)_2]^{5-}$
-122.66



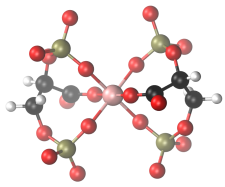
$[Al(2,3\text{-}DPG)^{ab}_{2,AB}(H_2O)_2]^{5-}$
-116.56



$[Al(2,3\text{-}DPG)^{*}_{2,AB}(H_2O)_2]^{7-}$
-140.89

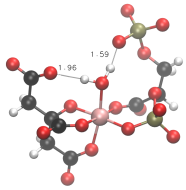


$[Al(2,3\text{-}DPG)^{*,aa}_{2,AB}(H_2O)_2]^{5-}$
-123.74

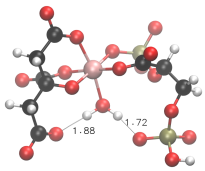


$[Al(2,3\text{-}DPG)_{2,ABC}(H_2O)_2]^{7-}$
-128.43

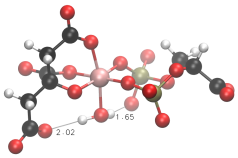
Figure S3: The 7 studied ternary structures, Al-(2,3-DPG)(Citr) complexes. The subscripts indicate the coordination mode of 2,3-DPG to Al(III) and the superscripts refer to the protonation states of the phosphates groups: (b) one phosphate of group B is protonated, (a) one phosphate of group A is protonated. The formation energies (ΔG_{aq}^{Phys}) are shown in kcal/mol.



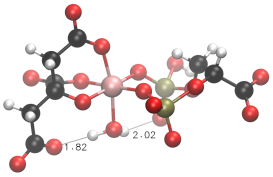
$[Al(2,3\text{-}DPG)_{AC}(Citr)]^{6-}$
-161.39



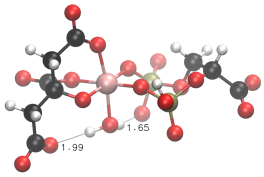
$[Al(2,3\text{-}DPG)^{b}_{AC}(Citr)]^{5-}$
-156.79



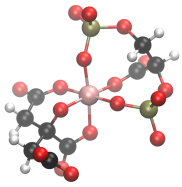
$[Al(2,3\text{-}DPG)_{AB}(Citr)]^{6-}$
-156.64



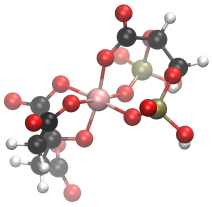
$[Al(2,3\text{-}DPG)^{b}_{AB}(Citr)]^{5-}$
-144.17



$[Al(2,3\text{-}DPG)^{a}_{AB}(Citr)]^{5-}$
-152.52



$[Al(2,3\text{-}DPG)_{ABC}(Citr)]^{6-}$
-157.82



$[Al(2,3\text{-}DPG)^{b}_{ABC}(Citr)]^{5-}$
-149.90