CHEMISTRY
A EUROPEAN JOURNAL

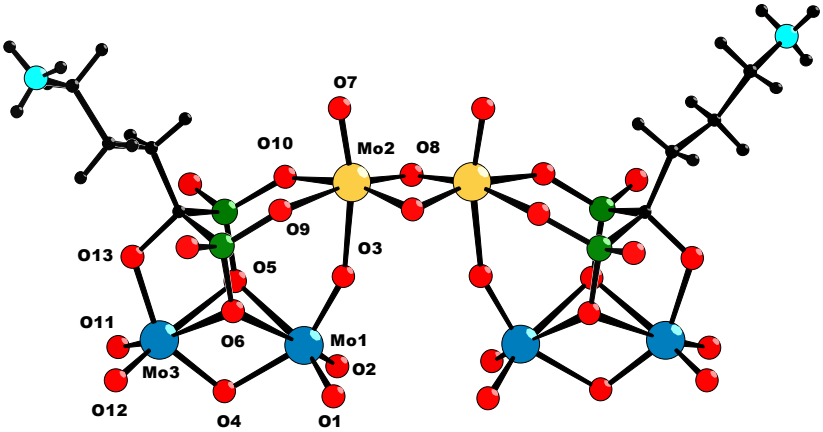
Supporting Information

Tetra- to Dodecanuclear Oxomolybdate Complexes with Functionalized Bisphosphonate Ligands: Activity in Killing Tumor Cells

Jean-Daniel Compain,[a] Pierre Mialane,[a] Jérôme Marrot,[a] Francis Sécheresse,[a] Wei Zhu,[b] Eric Oldfield,*[b, c] and Anne Dolbecq*[a]

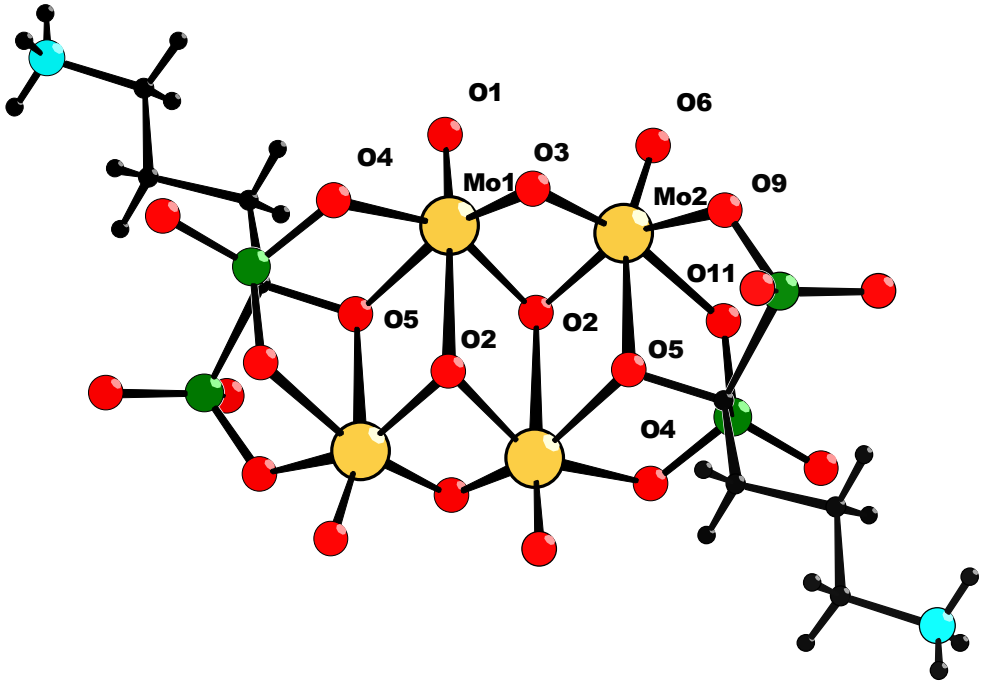
chem_201001626_sm_miscellaneous_information.pdf

Figure SI1. Ball and stick representation with partial atomic labeling scheme, selected bond distances and valence bond calculations in the anion of **1**.



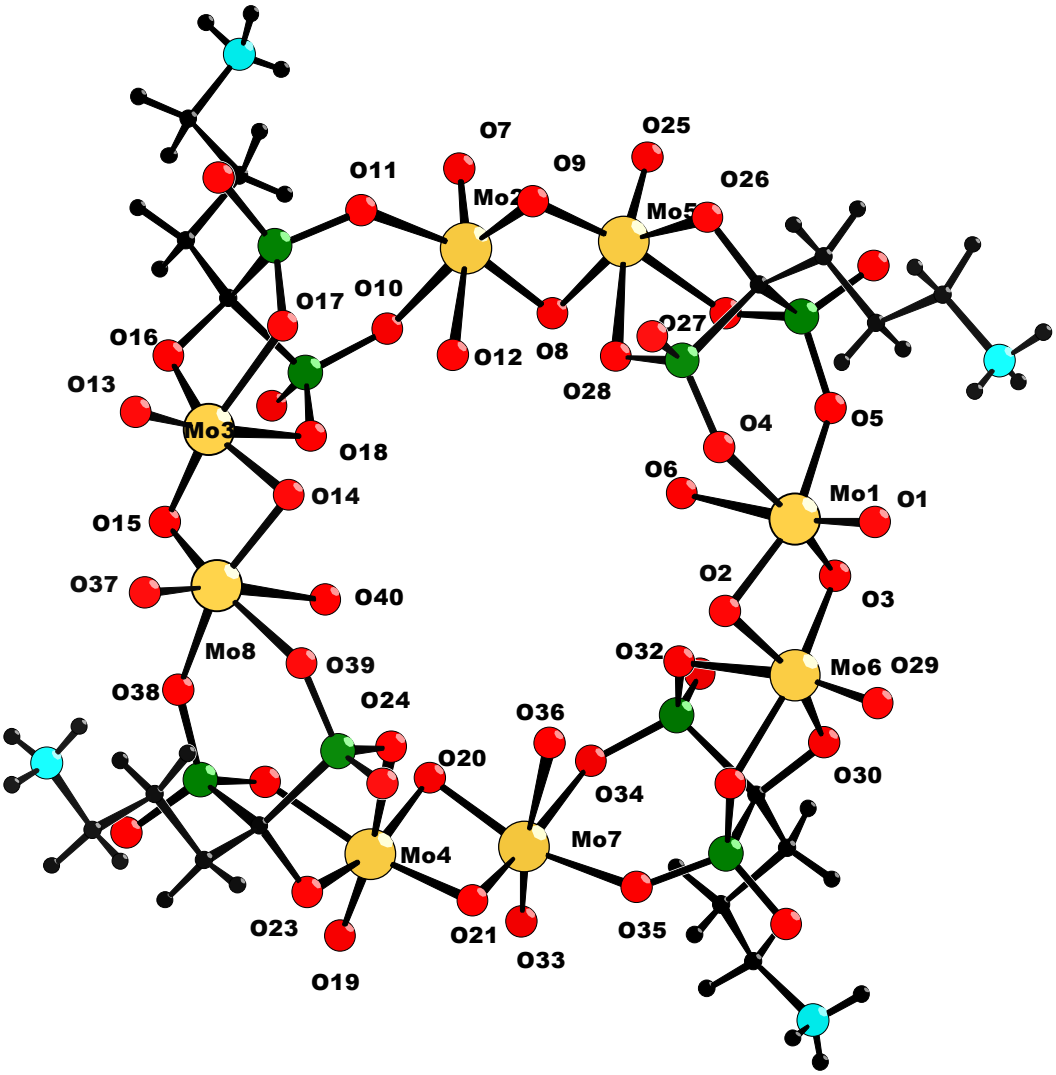
Mo(1)-O(2)	1.714(5)	S**(Mo1) = 6.2**
Mo(1)-O(1)	1.721(6)	
Mo(1)-O(3)	1.773(5)	
Mo(1)-O(4)	2.019(5)	
Mo(1)-O(5)	2.318(5)	
Mo(1)-O(6)	2.331(5)	
Mo(1)-Mo(3)	3.2078(10)	
Mo(2)-O(7)	1.709(5)	S**(Mo2) = 5.2**
Mo(2)-O(8)	1.933(5)	
Mo(2)-O(8)#1	1.951(5)	
Mo(2)-O(9)	2.110(5)	
Mo(2)-O(10)	2.129(5)	
Mo(2)-O(3)	2.139(5)	
Mo(2)-Mo(2)#1	2.5774(12)	
Mo(3)-O(11)	1.707(8)	S**(Mo3) = 5.9**
Mo(3)-O(12)	1.725(7)	
Mo(3)-O(4)	1.863(5)	
Mo(3)-O(13)	1.962(5)	S**(O13) = 1.74**
Mo(3)-O(5)	2.355(5)	
Mo(3)-O(6)	2.363(6)	

Figure SI2. Ball and stick representation with partial atomic labeling scheme, selected bond distances and valence bond calculations in the anion of **2**.



Mo(1)-O(1)	1.672(4)	**S(Mo1) = 5.2**
Mo(1)-O(2)	1.943(4)	
Mo(1)-O(3)	1.954(4)	
Mo(1)-O(4)	2.064(4)	
Mo(1)-O(5)	2.076(4)	
Mo(1)-O(2)#1	2.493(4)	
Mo(1)-Mo(2)	2.5805(6)	
Mo(2)-O(6)	1.682(4)	**S(Mo2) = 5.1**
Mo(2)-O(2)	1.936(3)	
Mo(2)-O(3)	1.961(4)	
Mo(2)-O(9)	2.071(4)	
Mo(2)-O(11)	2.119(4)	
Mo(2)-O(5)#1	2.356(4)	**S(O5) = 1.81**

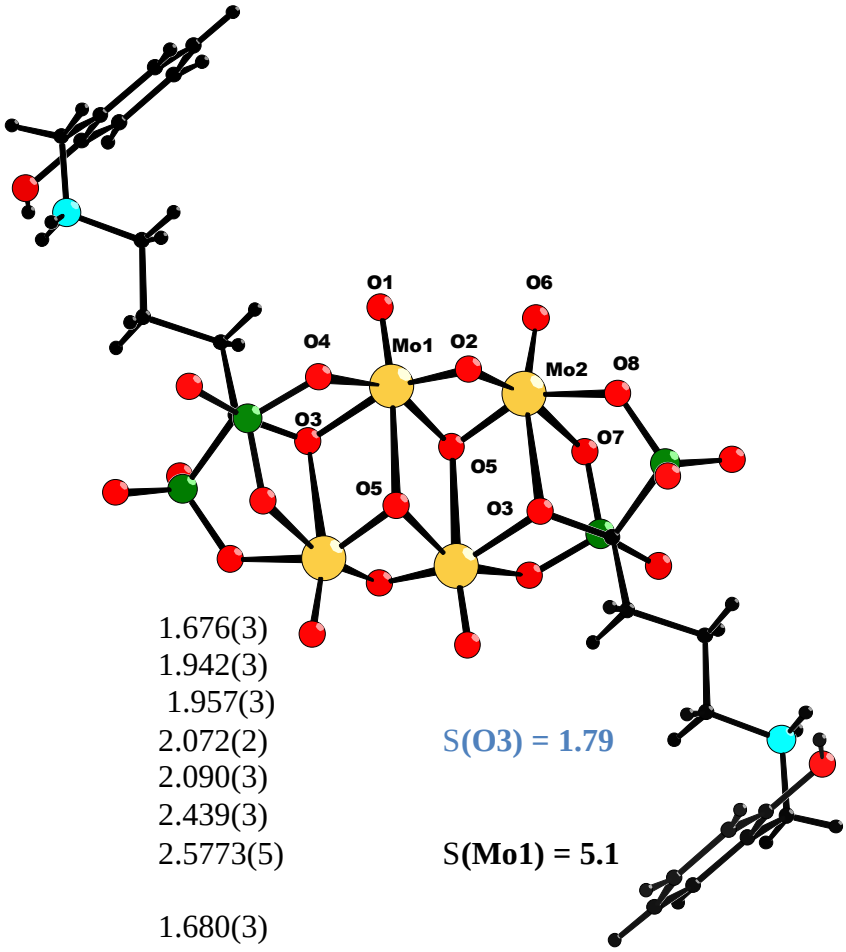
Figure SI3. Ball and stick representation with partial atomic labeling scheme, selected bond distances and valence bond calculations in the anion of **3**.



Mo(1)-O(1)	1.681(4)	S(**Mo1**) = **5.2**
Mo(1)-O(2)	1.932(4)	
Mo(1)-O(3)	1.946(4)	
Mo(1)-O(4)	2.074(4)	
Mo(1)-O(5)	2.079(4)	
Mo(1)-O(6)	2.408(4)	S(**O6**) = **0.26**
Mo(1)-Mo(6)	2.5834(7)	
Mo(2)-O(7)	1.681(4)	S(**Mo2**) = **5.2**
Mo(2)-O(8)	1.938(4)	
Mo(2)-O(9)	1.942(4)	
Mo(2)-O(10)	2.072(4)	
Mo(2)-O(11)	2.092(4)	
Mo(2)-O(12)	2.416(4)	S(**O12**) = **0.25**
Mo(2)-Mo(5)	2.5968(7)	

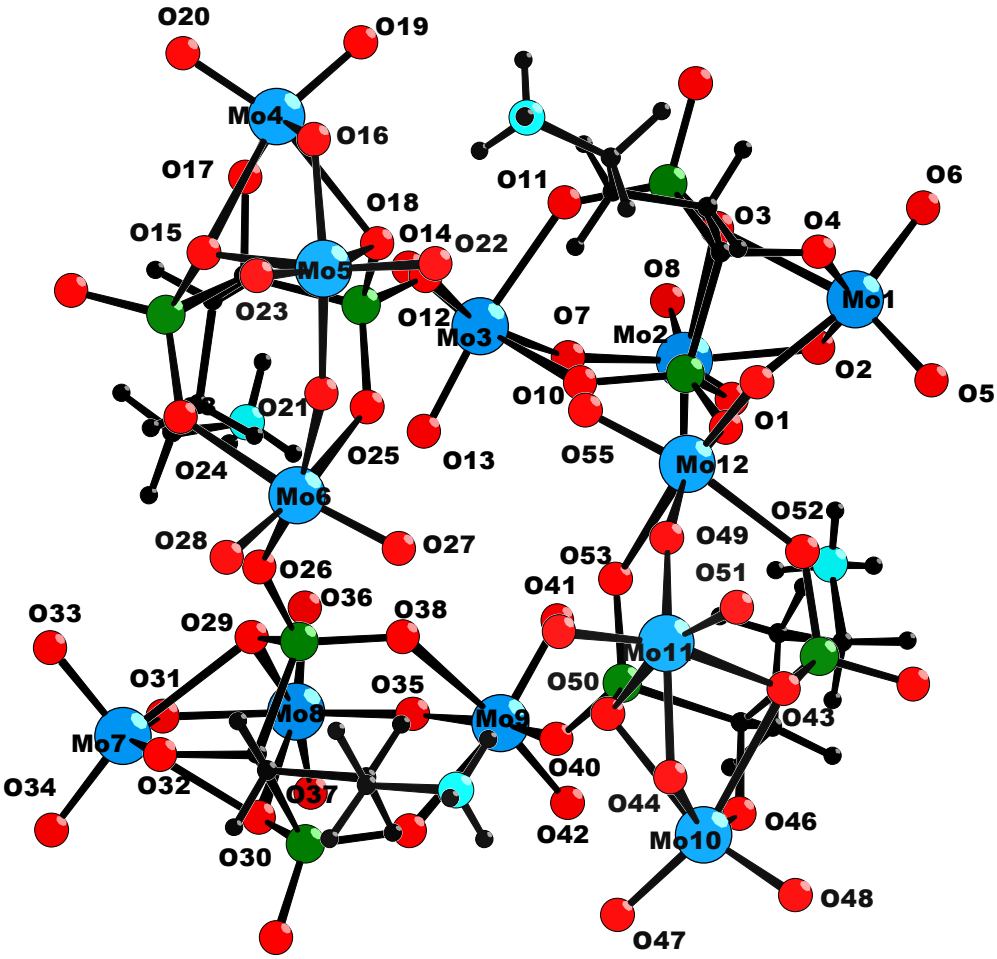
Mo(3)-O(13)	1.703(4)	S**(Mo3) = 5.1**
Mo(3)-O(15)	1.951(4)	
Mo(3)-O(14)	1.952(4)	
Mo(3)-O(16)	2.036(4)	**S(O16) = 1.76**
Mo(3)-O(17)	2.129(4)	
Mo(3)-O(18)	2.310(4)	
Mo(3)-Mo(8)	2.5921(7)	
Mo(4)-O(19)	1.702(4)	S**(Mo4) = 5.1**
Mo(4)-O(20)	1.937(4)	
Mo(4)-O(21)	1.951(4)	
Mo(4)-O(23)	2.056(4)	**S(O23) = 1.62**
Mo(4)-O(22)	2.090(4)	
Mo(4)-O(24)	2.357(4)	
Mo(4)-Mo(7)	2.5758(7)	
Mo(5)-O(25)	1.704(4)	S**(Mo5) = 5.1**
Mo(5)-O(9)	1.944(4)	
Mo(5)-O(8)	1.948(4)	
Mo(5)-O(26)	2.057(4)	**S(O26) = 1.63**
Mo(5)-O(27)	2.110(4)	
Mo(5)-O(28)	2.287(4)	
Mo(6)-O(29)	1.705(5)	S**(Mo6) = 5.2**
Mo(6)-O(2)	1.934(4)	
Mo(6)-O(3)	1.941(4)	
Mo(6)-O(30)	2.045(4)	**S(O30) = 1.54**
Mo(6)-O(31)	2.116(4)	
Mo(6)-O(32)	2.311(4)	
Mo(7)-O(33)	1.695(4)	S**(Mo7) = 5.1**
Mo(7)-O(20)	1.929(4)	
Mo(7)-O(21)	1.949(4)	
Mo(7)-O(34)	2.100(4)	
Mo(7)-O(35)	2.111(4)	
Mo(7)-O(36)	2.358(4)	**S(O36) = 0.29**
Mo(8)-O(37)	1.692(4)	S**(Mo8) = 5.1**
Mo(8)-O(14)	1.942(4)	
Mo(8)-O(15)	1.950(4)	
Mo(8)-O(38)	2.071(4)	
Mo(8)-O(39)	2.076(4)	
Mo(8)-O(40)	2.413(4)	**S(O40) = 0.25**

Figure SI4. Ball and stick representation with partial atomic labeling scheme, selected bond distances and valence bond calculations in the anion of **4**.



Mo(1)-O(1)	1.676(3)	
Mo(1)-O(5)#1	1.942(3)	
Mo(1)-O(2)	1.957(3)	
Mo(1)-O(3)	2.072(2)	**S(O3) = 1.79**
Mo(1)-O(4)	2.090(3)	
Mo(1)-O(5)	2.439(3)	
Mo(1)-Mo(2)	2.5773(5)	**S(Mo1) = 5.1**
Mo(2)-O(6)	1.680(3)	
Mo(2)-O(5)#1	1.935(2)	
Mo(2)-O(2)	1.954(3)	
Mo(2)-O(8)	2.055(3)	
Mo(2)-O(7)	2.118(3)	
Mo(2)-O(3)#1	2.336(3)	**S(Mo2) = 5.2**
Mo(4)-O(18)	1.674(2)	
Mo(4)-O(14)	1.944(3)	
Mo(4)-O(15)	1.957(2)	
Mo(4)-O(19)	2.056(3)	
Mo(4)-O(20)	2.070(3)	
Mo(4)-O(14)#2	2.490(2)	
Mo(4)-Mo(3)	2.5755(6)	**S(Mo3) = 5.2**
Mo(3)-O(13)	1.674(3)	
Mo(3)-O(15)	1.942(3)	
Mo(3)-O(14)	1.944(3)	
Mo(3)-O(17)	2.044(3)	
Mo(3)-O(16)	2.120(3)	
Mo(3)-O(19)#2	2.359(2)	**S(Mo4) = 5.2**

Figure SI5. Ball and stick representation with partial atomic labeling scheme, selected bond distances and valence bond calculations in the anion of **5**.



Mo(1)-O(6)	1.698(4)	
Mo(1)-O(5)	1.711(6)	
Mo(1)-O(2)	1.876(5)	S**(Mo1) = 6.03**
Mo(1)-O(4)	1.943(4)	S(O4) = 1.77
Mo(1)-O(3)	2.363(5)	
Mo(1)-O(1)	2.374(3)	
Mo(2)-O(8)	1.694(6)	
Mo(2)-O(9)	1.711(4)	
Mo(2)-O(7)	1.872(4)	
Mo(2)-O(2)	1.968(5)	S**(Mo2) = 6.04**
Mo(2)-O(3)	2.277(4)	
Mo(2)-O(1)	2.421(4)	
Mo(3)-O(14)	1.695(5)	
Mo(3)-O(13)	1.716(3)	
Mo(3)-O(7)	1.912(4)	
Mo(3)-O(12)	2.059(4)	S**(Mo3) = 5.99**
Mo(3)-O(11)	2.180(3)	
Mo(3)-O(10)	2.236(4)	
Mo(4)-O(20)	1.699(6)	
Mo(4)-O(19)	1.705(4)	
Mo(4)-O(16)	1.887(5)	S**(Mo4) = 6.05**
Mo(4)-O(17)	1.942(4)	S(O17) = 1.84

Mo(4)-O(15)	2.328(3)	
Mo(4)-O(18)	2.377(5)	
Mo(5)-O(23)	1.693(5)	
Mo(5)-O(22)	1.720(6)	
Mo(5)-O(21)	1.867(4)	
Mo(5)-O(16)	1.954(4)	**S(Mo5) = 6.04**
Mo(5)-O(15)	2.287(5)	
Mo(5)-O(18)	2.432(4)	
Mo(6)-O(28)	1.698(4)	
Mo(6)-O(27)	1.698(5)	
Mo(6)-O(21)	1.905(4)	
Mo(6)-O(26)	2.051(4)	**S(Mo6) = 6.09**
Mo(6)-O(24)	2.179(5)	
Mo(6)-O(25)	2.238(3)	
Mo(7)-O(34)	1.697(3)	
Mo(7)-O(33)	1.704(6)	
Mo(7)-O(31)	1.901(4)	**S(Mo7) = 6.02**
Mo(7)-O(32)	1.938(4)	**S(O32) = 1.86**
Mo(7)-O(29)	2.356(3)	
Mo(7)-O(30)	2.367(5)	
Mo(8)-O(37)	1.703(4)	
Mo(8)-O(36)	1.706(4)	
Mo(8)-O(35)	1.876(4)	
Mo(8)-O(31)	1.956(4)	**S(Mo8) = 6.00**
Mo(8)-O(30)	2.267(4)	
Mo(8)-O(29)	2.378(4)	
Mo(9)-O(42)	1.695(5)	
Mo(9)-O(41)	1.708(3)	
Mo(9)-O(35)	1.921(4)	
Mo(9)-O(40)	2.067(4)	**S(Mo9) = 6.00**
Mo(9)-O(39)	2.162(3)	
Mo(9)-O(38)	2.248(4)	
Mo(10)-O(48)	1.702(6)	
Mo(10)-O(47)	1.709(4)	
Mo(10)-O(44)	1.882(5)	**S(Mo10) = 6.01**
Mo(10)-O(46)	1.936(4)	**S(O46) = 1.88**
Mo(10)-O(45)	2.358(5)	
Mo(10)-O(43)	2.394(3)	
Mo(11)-O(51)	1.685(5)	
Mo(11)-O(50)	1.708(6)	
Mo(11)-O(49)	1.883(4)	
Mo(11)-O(44)	1.958(4)	
Mo(11)-O(43)	2.273(5)	**S(Mo11) = 6.09**
Mo(11)-O(45)	2.429(4)	
Mo(12)-O(56)	1.695(4)	
Mo(12)-O(55)	1.713(5)	
Mo(12)-O(49)	1.880(4)	
Mo(12)-O(54)	2.070(4)	**S(Mo12) = 6.08**
Mo(12)-O(52)	2.163(5)	
Mo(12)-O(53)	2.249(3)	

Figure SI6. Details of the intramolecular hydrogen bond interactions between the amino group of the **Ale** ligand and bridging and terminal oxygen atoms of the Mo framework.

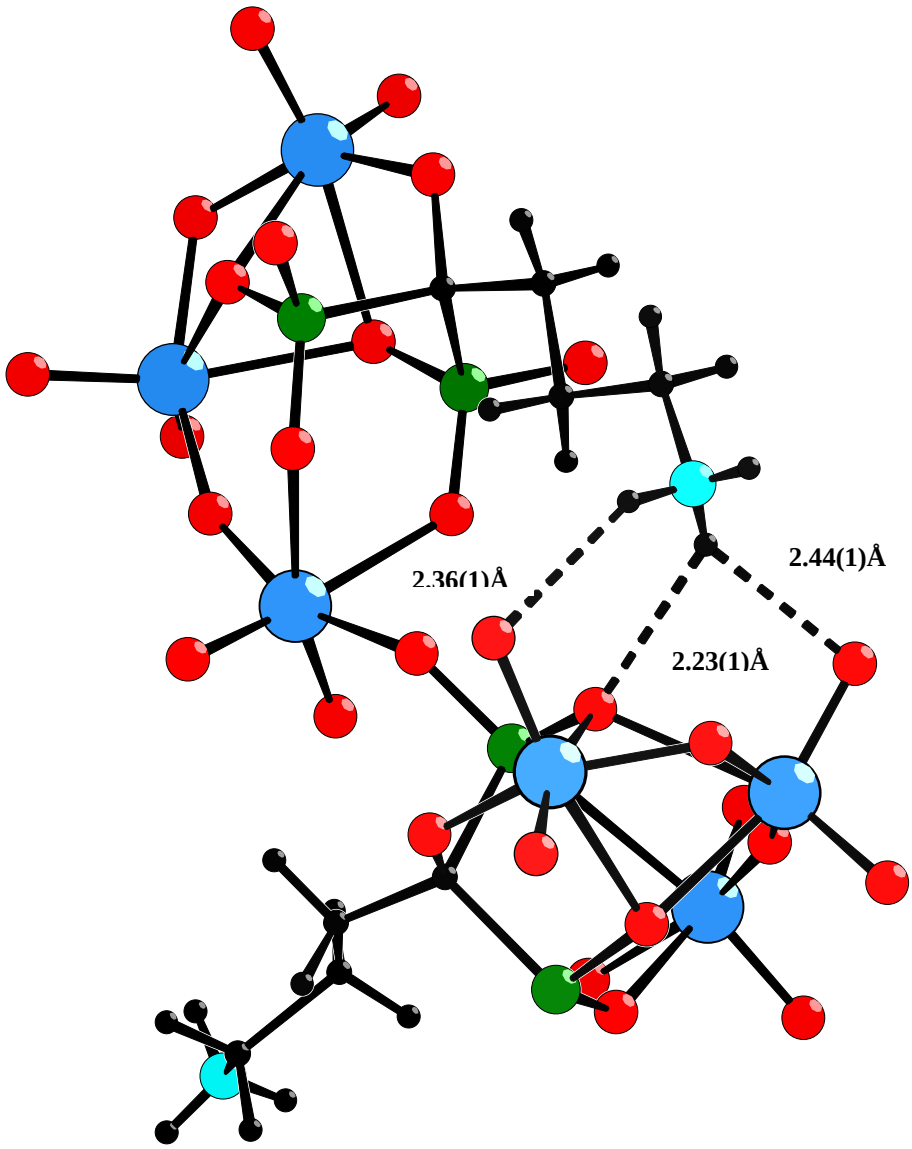


Figure SI7. ^{31}P NMR spectrum of a) a freshly prepared synthetic solution of **1** and b) a solution of **3** dissolved in water.

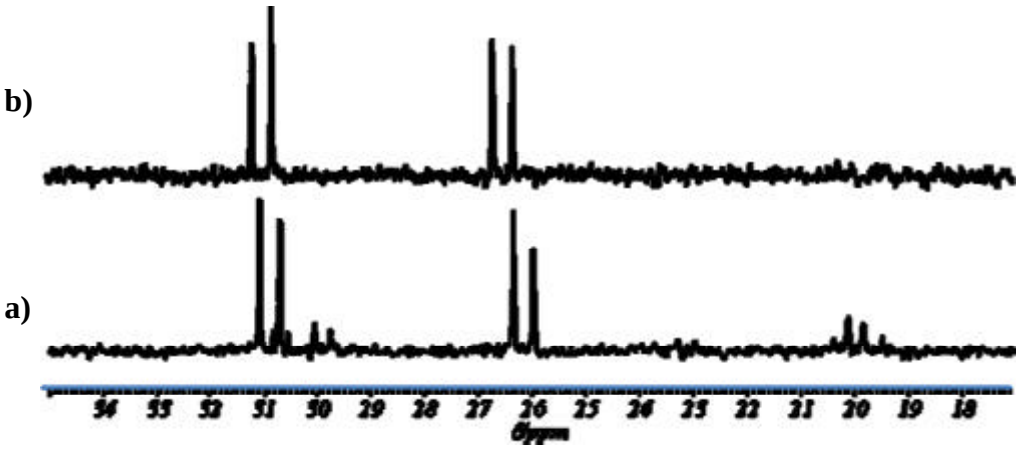


Figure SI8. ^{31}P NMR spectrum of freshly prepared synthetic solutions of a) **2** and b) **4**.

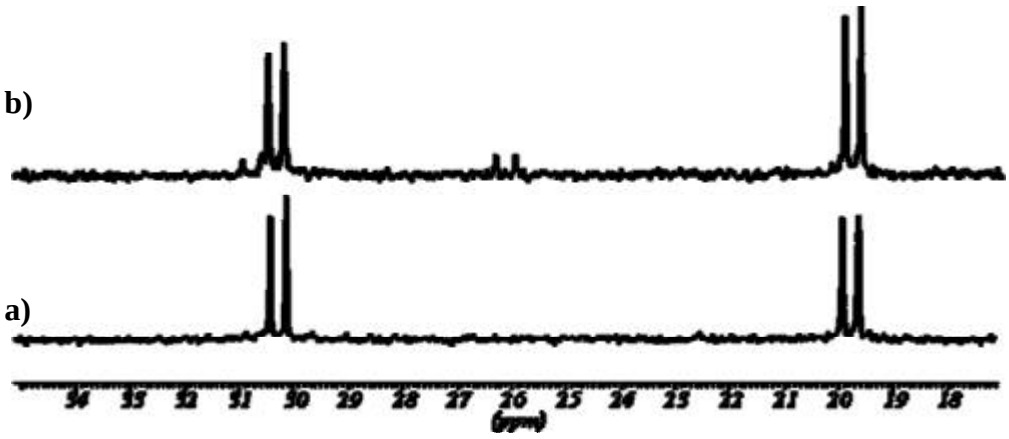


Figure SI9. Evolution with time of the relative concentration of **2** (¦), **3** (?) and of the sum of the concentrations of the unidentified X1 and X2 species (?) (see Figure 8). X1 and X2 are assumed to contain 4 phosphorus each