Unusual solidification and phosphate binding to benzimidazole cations in the presence of water

Sarah E. Clifford[a], Marcin Runowski[a], Nalini Parthasarathy[a], Céline Besnard[b], Xavier Melich[a] and Alan F.Williams*[a]

Supplementary material

Table S1 pK_a values in 1:1 water : ethanol mixtures at 22°C

	pK_{a1}	pK_{a2}	pK_{a3}
2	4.46(3)	6.20(1)	
3	4.82(2)	6.48(1)	
(1,4)-bis(*N*-methyl-benzimidazol-2-onium)butane, **6**	5.04(3)	6.48(1)	
4	4.96(4)	6.32(2)	
5	5.45(6)	6.68(4)	
N-methyl imidazolonium	6.07(1)		
H_3PO_4	3.27(16)	8.58(16)	13.53(15)
H_3AsO_4	3.59[a]	8.45[a]	13.0[a]
H_2SO_4	-3 (fixed)	3.47[a]	

[a] Values taken from Martell, A.E., Smith, R.M. NIST Critically Selected Stability Constants of Metal Complexes, Database 46, Version 6.0, NIST Standard Referenced Data, 2001.

Table S2. Stability constants β_{abc} for complexes $(PO_4)_aL_b(H)_c$ in 1:1 water : ethanol mixtures at 22°C

Cation LH_2^{2+}	β_{216}	β_{215}	β_{214}	β_{213}
2	60.40(6)	55.62(7)	49.34(5)	40.64(6)
3	61.67(3)	56.65(4)	50.25(2)	41.42(3)
4	61.01(3)	55.95(4)	49.68(3)	40.68(3)
5	61.63(5)	56.33(7)	49.57(4)	40.79(4)

Table S3. Stability constants β_{abc} for complexes $(AsO_4)_aL_b(H)_c$ in 1:1 water : ethanol mixtures at 22°C

Cation	β_{216}	β_{215}	β_{214}	β_{213}
2	β_{216} = 58.89(2)	β_{213} = 39.42(3)	β_{212} = 30.38(3)	β_{211} = 17.72(4)
3	β_{216} = 60.18(3)	β_{213} = 39.71(8)	β_{212} = 31.08(4)	β_{211} = 18.77(6)
4	β_{114} = 35.42(2)	β_{111} = 39.71(8)		
5	β_{216} = 58.89(2)	β_{213} = 39.42(3)		

Table S4 pK_a values for 1-ω-diamines in 1:1 water : methanol mixtures at 22°C and 0.5 M ionic strength.

Diamine	pKa_1	pKa_2
1,2-diaminoethane	7.46(3)	10.58(2)
1,3-diaminopropane	9.29(3)	11.16(2)
1,4-diaminobutane	10.15(5)	11.66(3)
1,5-diaminopentane	10.42(10)	11.70(8)

Table S5. Stability constants β_{abc} for complexes $(PO_4)_aL_b(H)_c$ in 1:1 water : ethanol mixtures at 22°C

L	β_{216}	β_{215}	β_{214}	β_{213}	β_{212}	β_{211}
1,2-diaminoethane			48.53(9)	40.23(4)	29.64(1)	18.73(5)
1,3-diaminopropane		59.05(3)	50.38(3)	39.3(3)	28.0(6)	16.94(17)
1,4-diaminobutane		60.81(5)	52.05(5)	41.04(8)	29.80(6)	17.0(3)
1,5-diaminopentane	70.51(1)	63.28(2)	55.45(2)	46.87(3)	35.81(5)	24.01(5)

Figure S1 Ortep drawing of [**4**]2(H_2PO_4), ellipsoids at 50%

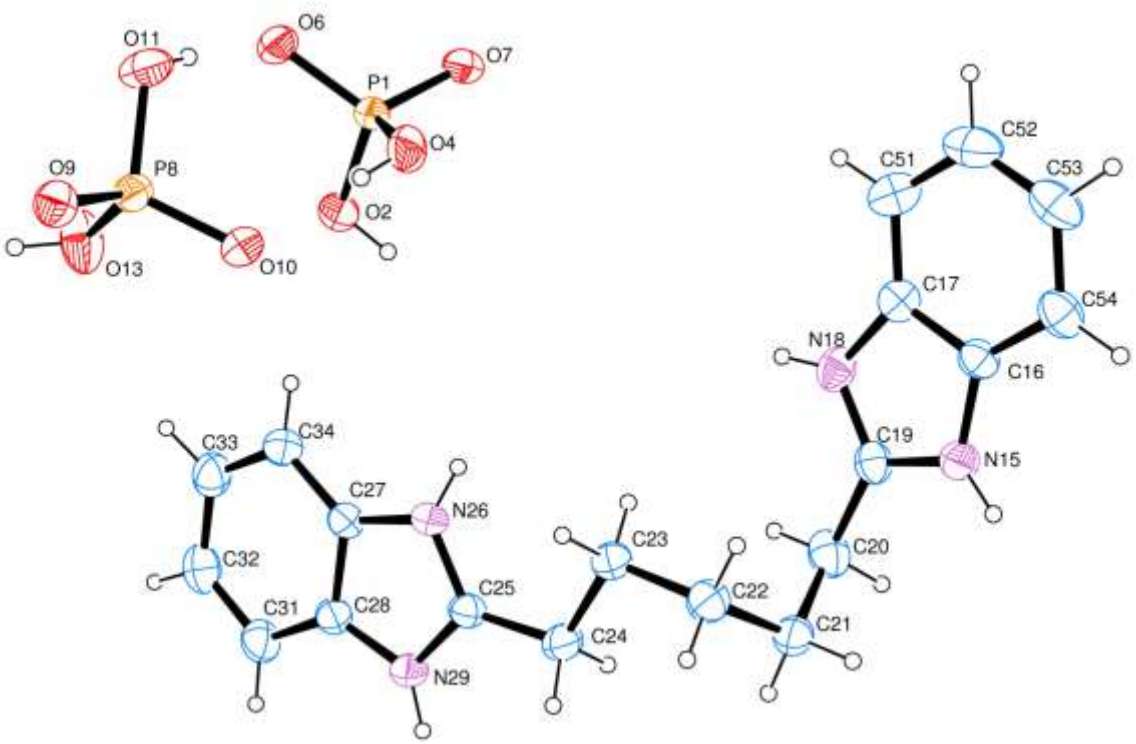

Table S6 Selected geometric parameters (Å, °) for [**4**]2(H_2PO_4)

P1—O2	1.5721	(11)	C21—C22	1.515	(2)
P1—O4	1.5715	(12)	C22—C23	1.527	(2)
P1—O6	1.5080	(10)	C23—C24	1.523	(2)
P1—O7	1.5028	(11)	C24—C25	1.486	(2)
P8—O9	1.5055	(11)	C25—N26	1.3331	(17)
P8—O10	1.5015	(10)	C25—N29	1.3380	(17)
P8—O11	1.5680	(12)	N26—C27	1.3885	(18)
P8—O13	1.5671	(12)	C27—C28	1.3910	(19)
N15—C16	1.3873	(18)	C27—C34	1.390	(2)
N15—C19	1.3312	(18)	C28—N29	1.3849	(19)
C16—C17	1.388	(2)	C28—C31	1.390	(2)
C16—C54	1.390	(2)	C31—C32	1.378	(2)
C17—N18	1.3890	(19)	C32—C33	1.397	(2)
C17—C51	1.388	(2)	C33—C34	1.378	(2)
N18—C19	1.3300	(19)	C51—C52	1.381	(3)
C19—C20	1.490	(2)	C52—C53	1.395	(3)
C20—C21	1.532	(2)	C53—C54	1.383	(2)
O2—P1—O4	107.09	(6)	C20—C21—C22	114.24	(13)
O2—P1—O6	106.65	(6)	C21—C22—C23	115.95	(13)
O4—P1—O6	109.86	(6)	C22—C23—C24	111.93	(12)
O2—P1—O7	111.04	(6)	C23—C24—C25	114.08	(12)
O4—P1—O7	106.65	(7)	C24—C25—N26	126.40	(12)
O6—P1—O7	115.30	(6)	C24—C25—N29	124.59	(12)
O9—P8—O10	114.98	(6)	N26—C25—N29	108.99	(12)
O9—P8—O11	106.27	(6)	C25—N26—C27	109.04	(11)
O10—P8—O11	110.70	(6)	N26—C27—C28	106.45	(12)
O9—P8—O13	111.18	(6)	N26—C27—C34	131.81	(13)
O10—P8—O13	106.16	(7)	C28—C27—C34	121.73	(14)
O11—P8—O13	107.37	(7)	C27—C28—N29	106.36	(12)
C16—N15—C19	108.90	(12)	C27—C28—C31	121.62	(14)

N15—C16—C17	106.52	(12)	N29—C28—C31	132.00	(14)
N15—C16—C54	131.38	(14)	C28—N29—C25	109.12	(12)
C17—C16—C54	122.10	(14)	C28—C31—C32	116.62	(15)
C16—C17—N18	106.22	(13)	C31—C32—C33	121.60	(15)
C16—C17—C51	121.63	(15)	C32—C33—C34	122.09	(15)
N18—C17—C51	132.15	(15)	C27—C34—C33	116.30	(15)
C17—N18—C19	109.04	(12)	C17—C51—C52	116.41	(16)
N15—C19—N18	109.32	(13)	C51—C52—C53	121.92	(16)
N15—C19—C20	125.33	(14)	C52—C53—C54	121.83	(16)
N18—C19—C20	125.35	(14)	C16—C54—C53	116.11	(16)
C19—C20—C21	113.28	(13)			

Table S7. Data for hydrogen bonds [**4**]2(H_2PO_4)

Donor, D	Hydrogen, H	Acceptor, A	D-H, Å	H…A, Å	D...A, Å	Angle D-H-A (°)	Equivalent position for A
O2	H21	O7	0.85(2)	1.77(2)	2.6246(16)	176(2)	1-x,-y,1-z
O4	H41	O10	0.76(2)	1.85(2)	2.6072(17)	176.8(18)	
O11	H111	O6	0.779(19)	1.837(19)	2.6125(16)	173(2)	
O13	H131	O9	0.85(3)	1.70(3)	2.5416(18)	176.3(18)	2-x,1-y,2-z
N15	H151	O9	0.879(19)	1.819(19)	2.6766(18)	165(2)	1-x,1-y,1-z
N18	H181	O6	0.85(2)	1.83(2)	2.669(2)	171.8(19)	1-x,-y,1-z
N26	H261	O7	0.84(2)	1.866(19)	2.6716(18)	160.5(19)	1-x,-y,1-z
N29	H291	O10	0.87(2)	1.88(2)	2.7152(18)	162(2)	2-x,1-y,1-z
C21	H211	O9	0.99(2)	2.58(2)	3.531(2)	161.2(15)	x,y,-1+z

Figure S2 Ortep drawing of [**2**]SO_4.3H_2O, ellipsoids at 50%

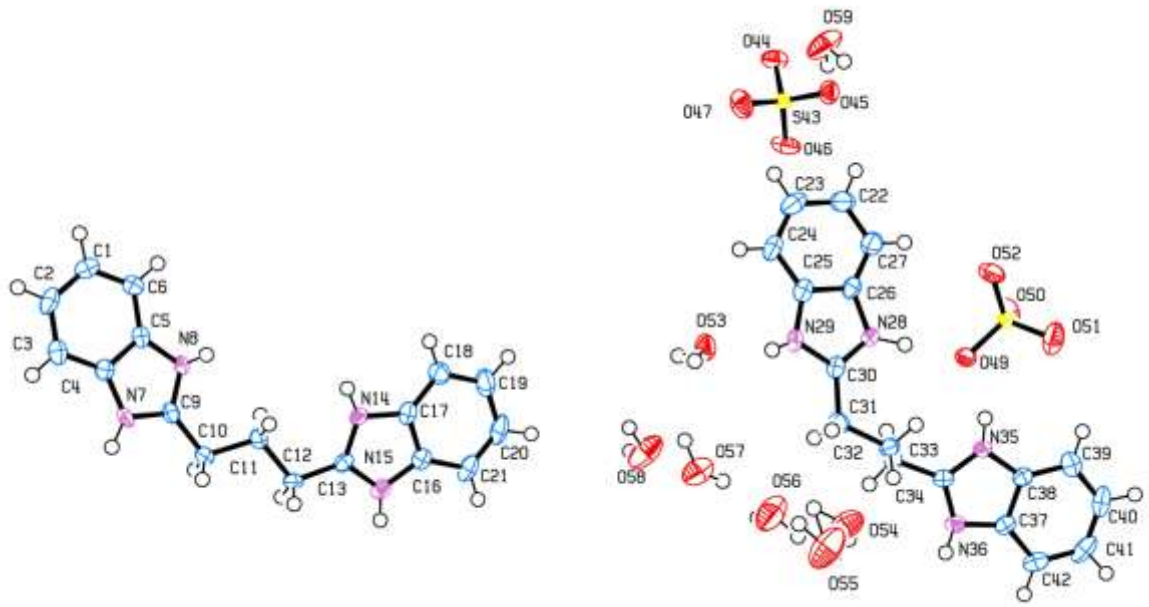

Table S8. Selected geometric parameters (Å, °) for [**2**]SO_4.3H_2O

C1—C2	1.404	(4)	C25—C26	1.394	(3)
C1—C6	1.379	(3)	C25—N29	1.380	(3)
C2—C3	1.376	(4)	C26—C27	1.375	(4)
C3—C4	1.399	(3)	C26—N28	1.407	(3)
C4—C5	1.390	(3)	N28—C30	1.318	(3)
C4—N7	1.391	(3)	N29—C30	1.340	(3)
C5—C6	1.398	(3)	C30—C31	1.497	(3)
C5—N8	1.378	(3)	C31—C32	1.531	(3)
N7—C9	1.323	(3)	C32—C33	1.531	(3)
N8—C9	1.334	(3)	C33—C34	1.494	(3)
C9—C10	1.492	(3)	C34—N35	1.328	(3)
C10—C11	1.525	(3)	C34—N36	1.325	(3)
C11—C12	1.525	(3)	N35—C38	1.380	(3)
C12—C13	1.486	(3)	N36—C37	1.394	(3)
C13—N14	1.331	(3)	C37—C38	1.400	(3)
C13—N15	1.332	(3)	C37—C42	1.389	(3)
N14—C17	1.390	(3)	C38—C39	1.385	(3)
N15—C16	1.397	(3)	C39—C40	1.377	(4)
C16—C17	1.378	(3)	C40—C41	1.394	(4)
C16—C21	1.397	(3)	C41—C42	1.385	(4)
C17—C18	1.402	(3)	S43—O44	1.4929	(17)
C18—C19	1.376	(3)	S43—O45	1.4800	(17)
C19—C20	1.409	(4)	S43—O46	1.4650	(18)
C20—C21	1.371	(4)	S43—O47	1.4661	(17)
C22—C23	1.404	(4)	S48—O49	1.4925	(16)
C22—C27	1.380	(3)	S48—O50	1.4639	(17)
C23—C24	1.375	(4)	S48—O51	1.4642	(17)
C24—C25	1.397	(3)	S48—O52	1.4655	(18)
C2—C1—C6	122.0	(2)	C25—C26—C27	121.9	(2)
C1—C2—C3	121.8	(2)	C25—C26—N28	105.4	(2)
C2—C3—C4	116.8	(2)	C27—C26—N28	132.7	(2)
C3—C4—C5	121.1	(2)	C22—C27—C26	117.0	(2)
C3—C4—N7	132.6	(2)	C26—N28—C30	109.47	(19)
C5—C4—N7	106.2	(2)	C25—N29—C30	109.3	(2)
C4—C5—C6	122.2	(2)	N29—C30—N28	109.1	(2)
C4—C5—N8	106.8	(2)	N29—C30—C31	122.7	(2)
C6—C5—N8	131.0	(2)	N28—C30—C31	128.2	(2)
C5—C6—C1	116.1	(2)	C30—C31—C32	115.93	(19)
C4—N7—C9	108.51	(18)	C31—C32—C33	112.91	(18)
C5—N8—C9	108.47	(19)	C32—C33—C34	112.11	(18)
N8—C9—N7	110.0	(2)	C33—C34—N35	122.51	(19)
N8—C9—C10	125.79	(19)	C33—C34—N36	127.1	(2)
N7—C9—C10	124.2	(2)	N35—C34—N36	110.33	(19)
C9—C10—C11	111.36	(18)	C34—N35—C38	108.90	(18)
C10—C11—C12	112.39	(18)	C34—N36—C37	108.20	(19)
C11—C12—C13	110.73	(17)	N36—C37—C38	106.36	(19)
C12—C13—N14	125.0	(2)	N36—C37—C42	132.3	(2)
C12—C13—N15	125.6	(2)	C38—C37—C42	121.3	(2)
N14—C13—N15	109.3	(2)	C37—C38—N35	106.2	(2)
C13—N14—C17	108.85	(19)	C37—C38—C39	121.8	(2)
C13—N15—C16	108.7	(2)	N35—C38—C39	132.0	(2)
N15—C16—C17	106.36	(19)	C38—C39—C40	116.7	(2)
N15—C16—C21	132.0	(2)	C39—C40—C41	121.7	(2)
C17—C16—C21	121.6	(2)	C40—C41—C42	122.0	(2)
N14—C17—C16	106.7	(2)	C37—C42—C41	116.5	(2)

N14—C17—C18	130.7	(2)	O44—S43—O45	107.80	(10)
C16—C17—C18	122.5	(2)	O44—S43—O46	108.37	(10)
C17—C18—C19	115.7	(2)	O45—S43—O46	110.01	(11)
C18—C19—C20	121.5	(2)	O44—S43—O47	109.45	(11)
C19—C20—C21	122.5	(2)	O45—S43—O47	110.25	(10)
C16—C21—C20	116.1	(2)	O46—S43—O47	110.89	(10)
C23—C22—C27	121.3	(2)	O49—S48—O50	109.18	(11)
C22—C23—C24	122.1	(2)	O49—S48—O51	108.80	(11)
C23—C24—C25	116.2	(2)	O50—S48—O51	109.29	(10)
C24—C25—C26	121.5	(2)	O49—S48—O52	107.73	(10)
C24—C25—N29	131.7	(2)	O50—S48—O52	110.67	(11)
C26—C25—N29	106.8	(2)	O51—S48—O52	111.13	(11)

Table S9. Data for hydrogen bonds for [**2**]SO_4.3H_2O

	D—H	H···*A*	*D*···*A*		*D*—H···*A*
N14—H141···O45iii	0.84	1.95	2.775	(3)	166
N15—H151···O59vi	0.91	1.85	2.686	(3)	152
N8—H81···O44iii	0.83	1.87	2.685	(3)	167
C3—H31···O46vii	0.95	2.59	3.399	(3)	143
C2—H21···O44vii	0.95	2.60	3.342	(3)	135
N7—H71···O52viii	0.89	1.79	2.676	(3)	175
N35—H351···O49	0.89	1.80	2.644	(3)	159
N36—H361···O46ii	0.91	1.91	2.676	(3)	141
N28—H281···O49	0.97	1.78	2.743	(3)	173
C27—H271···O52	0.95	2.51	3.303	(3)	141
N29—H291···O53	0.79	1.93	2.665	(3)	156
O53—H532···O51iii	0.96	1.81	2.723	(3)	159
O54—H542···O47ii	0.96	1.96	2.921	(6)	176
O54 —H551···O47ii	1.22	1.92	2.921	(6)	136
O56—H561···O47iv	0.96	2.15	2.993	(3)	147
O57—H571···O56	0.96	1.82	2.752	(3)	164
O57—H572···O51iii	0.96	1.89	2.825	(3)	164
O58—H581···O57vi	0.96	1.83	2.791	(3)	178
O58—H582···O50iii	0.96	1.84	2.796	(3)	177
O59 —H592···O45	0.96	1.84	2.790	(3)	168

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) *x*+1/2, −*y*+1, *z*−1/2; (iii) *x*−1/2, −*y*+1, *z*+1/2; (iv) *x*+1/2, −*y*+1, *z*+1/2; (v) *x*+1, *y*, *z*; (vi) *x*−1, *y*−1, *z*; (vii) *x*, *y*−1, *z*+1; (viii) *x*−1, *y*−1, *z*+1.

-1/2+x,1-y,1/2+z

Figure S3 Ortep drawing of $(\mathbf{4})_2(H_2PO_4)_2(HPO_4).4H_2O$, ellipsoids at 50%

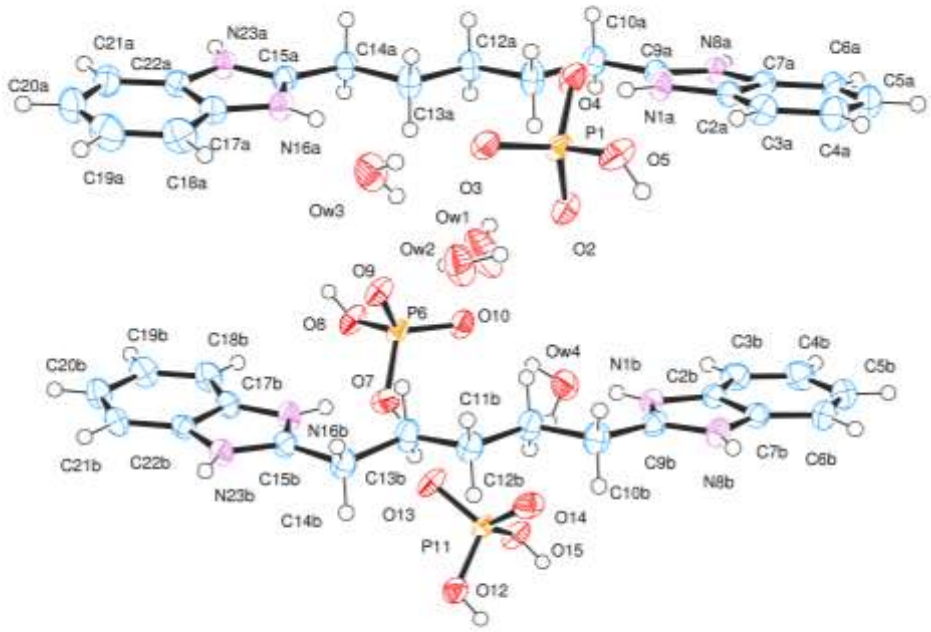

Table S10 Geometric parameters (Å, º) for $(\mathbf{4})_2(H_2PO_4)_2(HPO_4).4H_2O$

P1—O2	1.5140	(12)	N16A—C17A	1.386	(2)
P1—O3	1.5306	(11)	N16A—C15A	1.332	(2)
P1—O5	1.5776	(12)	C13A—C14A	1.517	(2)
P1—O4	1.5255	(11)	C13A—C12A	1.521	(2)
P6—O8	1.5588	(12)	N8A—C7A	1.388	(2)
P6—O10	1.4999	(12)	N8A—C9A	1.332	(2)
P6—O7	1.5775	(12)	C18B—C19B	1.378	(3)
P6—O9	1.5066	(12)	C18B—C17B	1.389	(2)
P11—O12	1.5680	(12)	C17A—C22A	1.393	(2)
P11—O14	1.5058	(12)	C17A—C18A	1.388	(2)
P11—O15	1.5562	(12)	C3B—C2B	1.385	(2)
P11—O13	1.5123	(11)	C3B—C4B	1.378	(3)
N8B—C7B	1.384	(2)	C3A—C4A	1.377	(2)
N8B—C9B	1.334	(2)	C14A—C15A	1.488	(2)
N23B—C15B	1.329	(2)	N16B—C15B	1.329	(2)
N23B—C22B	1.390	(2)	N16B—C17B	1.386	(2)
N23A—C22A	1.385	(2)	C13B—C14B	1.526	(2)
N23A—C15A	1.334	(2)	C13B—C12B	1.521	(2)
C7B—C2B	1.393	(2)	C2B—N1B	1.388	(2)
C7B—C6B	1.389	(2)	C6B—C5B	1.384	(3)
C21A—C22A	1.389	(2)	N1B—C9B	1.332	(2)

C21A—C20A	1.381	(3)	C4B—C5B	1.397	(3)
C2A—N1A	1.387	(2)	C11A—C10A	1.514	(2)
C2A—C7A	1.396	(2)	C11A—C12A	1.519	(2)
C2A—C3A	1.390	(2)	C4A—C5A	1.401	(3)
N1A—C9A	1.329	(2)	C20A—C19A	1.395	(3)
C20B—C19B	1.402	(3)	C11B—C12B	1.522	(2)
C20B—C21B	1.384	(2)	C21B—C22B	1.393	(2)
C10B—C11B	1.520	(2)	C10A—C9A	1.491	(2)
C10B—C9B	1.486	(2)	C14B—C15B	1.491	(2)
C6A—C7A	1.396	(2)	C19A—C18A	1.377	(3)
C6A—C5A	1.384	(2)	C17B—C22B	1.397	(2)
O2—P1—O3	112.35	(7)	C18B—C19B—C20B	121.63	(16)
O2—P1—O5	108.64	(6)	N23A—C22A—C21A	131.87	(16)
O2—P1—O4	111.76	(7)	N23A—C22A—C17A	106.53	(14)
O3—P1—O5	106.31	(7)	C21A—C22A—C17A	121.59	(16)
O4—P1—O3	110.32	(6)	C15A—C14A—C13A	113.70	(13)
O4—P1—O5	107.17	(8)	C15B—N16B—C17B	109.48	(13)
O8—P6—O7	106.01	(8)	C12B—C13B—C14B	114.40	(14)
O10—P6—O8	108.76	(7)	C3B—C2B—C7B	121.87	(16)
O10—P6—O7	109.59	(7)	C3B—C2B—N1B	131.59	(15)
O10—P6—O9	116.40	(8)	N1B—C2B—C7B	106.53	(14)
O9—P6—O8	110.53	(6)	C5B—C6B—C7B	116.37	(16)
O9—P6—O7	105.02	(7)	C9B—N1B—C2B	108.62	(13)
O14—P11—O12	108.63	(7)	C3B—C4B—C5B	121.77	(17)
O14—P11—O15	111.15	(8)	C10A—C11A—C12A	114.66	(14)
O14—P11—O13	114.37	(7)	C3A—C4A—C5A	121.65	(16)
O15—P11—O12	108.00	(7)	C21A—C20A—C19A	121.54	(18)
O13—P11—O12	107.94	(7)	C10B—C11B—C12B	113.19	(14)
O13—P11—O15	106.54	(6)	C20B—C21B—C22B	116.69	(15)
C9B—N8B—C7B	108.90	(13)	C9A—C10A—C11A	112.76	(13)
C15B—N23B—C22B	109.08	(13)	C15B—C14B—C13B	111.92	(13)
C15A—N23A—C22A	108.65	(13)	C18A—C19A—C20A	122.20	(18)
N8B—C7B—C2B	106.37	(14)	C6A—C5A—C4A	122.18	(16)
N8B—C7B—C6B	132.06	(15)	C13B—C12B—C11B	109.81	(14)
C6B—C7B—C2B	121.58	(16)	N8B—C9B—C10B	123.73	(14)
C20A—C21A—C22A	116.55	(17)	N1B—C9B—N8B	109.58	(14)
N1A—C2A—C7A	106.48	(13)	N1B—C9B—C10B	126.68	(14)
N1A—C2A—C3A	131.18	(14)	C11A—C12A—C13A	110.22	(13)
C3A—C2A—C7A	122.34	(14)	C6B—C5B—C4B	121.81	(17)
C9A—N1A—C2A	108.80	(13)	N1A—C9A—N8A	109.70	(14)
C21B—C20B—C19B	121.92	(16)	N1A—C9A—C10A	125.46	(14)
C9B—C10B—C11B	114.06	(14)	N8A—C9A—C10A	124.83	(14)
C5A—C6A—C7A	116.35	(15)	C19A—C18A—C17A	116.36	(18)
C15A—N16A—C17A	108.71	(13)	N23B—C15B—N16B	109.24	(14)
C14A—C13A—C12A	113.80	(14)	N23B—C15B—C14B	125.78	(14)
C9A—N8A—C7A	108.84	(13)	N16B—C15B—C14B	124.97	(14)
C19B—C18B—C17B	116.51	(15)	N23A—C15A—C14A	124.23	(14)
C6A—C7A—C2A	121.08	(15)	N16A—C15A—N23A	109.65	(14)
N8A—C7A—C2A	106.18	(13)	N16A—C15A—C14A	126.11	(14)
N8A—C7A—C6A	132.73	(15)	C18B—C17B—C22B	122.31	(15)
N16A—C17A—C22A	106.44	(14)	N16B—C17B—C18B	131.75	(15)
N16A—C17A—C18A	131.80	(16)	N16B—C17B—C22B	105.93	(14)
C18A—C17A—C22A	121.76	(16)	N23B—C22B—C21B	132.79	(14)
C4B—C3B—C2B	116.60	(16)	N23B—C22B—C17B	106.26	(13)
C4A—C3A—C2A	116.39	(15)	C21B—C22B—C17B	120.94	(15)

Table S11 Hydrogen-bond geometry (Å, º) for (**4**)$_2$(H_2PO_4)$_2$(HPO_4).4H_2O

D—H···*A*	*D*—H	H···*A*	*D*···*A*		*D*—H···*A*
O8—H8···O2i	0.84	1.67	2.4867	(16)	164
O12—H12···O3ii	0.84	1.72	2.5502	(16)	170
O15—H15···O4ii	0.84	1.67	2.5118	(16)	174
O5—H5···O9iii	0.84	1.72	2.5483	(16)	167
O7—H7···O13	0.84	1.70	2.5316	(16)	168
N8*B*—H8*B*···O13iii	0.88	1.77	2.6451	(17)	172
N23*B*—H23*B*···O3iv	0.88	1.84	2.6916	(17)	164
N23*A*—H23*A*···O14v	0.88	1.73	2.6000	(17)	169
N1*A*—H1*A*···O4	0.88	1.82	2.6587	(17)	159
N16*A*—H16*A*···O*W*3	0.88	1.86	2.7048	(18)	160
N8*A*—H8*A*···O10vi	0.88	1.80	2.6662	(17)	167
N16*B*—H16*B*···O7	0.88	1.92	2.7670	(17)	161
N1*B*—H1*B*···O*W*4	0.88	1.83	2.6641	(17)	159
O*W*4—H*W*4*A*···O14	0.87	1.86	2.7127	(19)	168
O*W*4—H*W*4*B*···O10	0.87	1.86	2.7314	(17)	178
O*W*3—H*W*3*A*···O3	0.87	2.06	2.8804	(18)	158
O*W*3—H*W*3*B*···O*W*2	0.87	1.97	2.795	(2)	159
O*W*1—H*W*1*A*···O9	0.86	1.88	2.693	(2)	157
O*W*2—H*W*2*A*···O2	0.85	1.96	2.7363	(19)	153
O*W*2—H*W*2*B*···O*W*1	0.85	2.09	2.832	(3)	145

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*+1, *y*+1, *z*; (iii) *x*−1, *y*, *z*; (iv) −*x*+1, −*y*+1, −*z*+2; (v) *x*, *y*−1, *z*; (vi) −*x*+1, −*y*+1, −*z*+1.