Anhydrates and/or hydrates in nitrate, sulphate and phosphate salts of 4-aminopyridine, (4-AP) and 3,4-diaminopyridine (3,4-DAP): the rôle of the water molecules in the hydrates.

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Electronic Supplementary Information

Table S1. Crystallographic data

	(4-APH$^+$) (NO_3^-)	**(3,4-DAPH$^+$) (NO_3^-)**	**(3,4-DAPH$_2^{2+}$) (NO_3^-)$_2$. H_2O**	**(4-APH$^+$) (HSO_4^-)**	**(4-APH$^+$)$_2$ (SO_4^{2-}). H_2O**	**(3,4-DAPH$^+$)$_2$ (SO_4^{2-}). $2H_2O$**	**(3,4-DAPH$_2^{2+}$) (SO_4^{2-}). $2H_2O$**	**(4-APH$^+$) ($H_2PO_4^-$). H_2O**	**(3,4DAPH$^+$) ($H_2PO_4^-$)**
CCDC Dep. N	959234	959237	959238	959233	959236	959239	959240	959235	959232
Formula	$C_5H_7N_3O_3$	$C_5H_8N_4O_3$	$C_5H_{11}N_5O_7$	$C_5H_7N_2O_4S$	$C_{10}H_{16}N_4O_5S$	$C_{10}H_{20}N_6O_6S$	$C_5H_{13}N_3O_6S$	$C_5H_{11}N_2O_5P$	$C_5H_{10}N_3O_4P$
M.w.	157.14	172.15	253.19	192.19	304.33	352.38	243.24	210.13	207.13
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic	tetragonal	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	Pbca	$P2_1/n$	P-1	$I4_1/a$	P-1	P-1	I2/a
a /Å	9.1718(6)	7.0735(5)	17.0057(11)	10.9507(4)	6.4515(2)	15.2902(10)	6.9429(3)	7.2785(4)	14.6204(10)
b /Å	6.9081(4)	11.0546(8)	12.7153(4)	6.4615(2)	8.4229(2)	15.2902(10)	10.2338(5)	7.9141(4)	7.6631(4)
c /Å	10.8243(7)	9.4018(6)	9.1321(3)	11.2614(3)	12.4728(8)	13.2563(7)	14.5568(8)	8.9022(6)	16.002(2)
α / º	90	90	90	90	96.429(7)	90	103.319(2)	77.651(6)	90
β / º	93.617(7)	92.308(7)	90	102.988(2)	97.523(7)	90	100.970(3)	71.756(5)	97.234(9)
γ / º	90	90	90	90	95.349(7)	90	92.592(3)	67.405(5)	90
V /Å^3	684.46(7)	734.57(9)	1974.66(16)	776.45(4)	663.70(5)	3099.2(3)	983.78(8)	447.07(4)	1778.6(3)
T / K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
Crystal shape	block	block	block	plate	needle	Lath	plate	block	plate
Colour	colourless	colourless	colourless	colourless	colourless	colourless	colourless	colourless	colourless
Z	4	4	8	4	2	8	4	2	8
All reflns	3555	7979	21219	10095	6593	15657	17819	5766	8398
Un. reflns	1542	1680	2254	1776	3023	1716	4492	2031	2030
R_{int}	0.0256	0.0442	0.0320	0.0298	0.0115	0.1342	0.0878	0.0122	0.0424
$R1_{obs}$[I>2σ(I)]	0.0518	0.0338	0.0283	0.0330	0.0326	0.0608	0.0540	0.0270	0.0332
$R1_{all\_}$	0.0579	0.0409	0.0301	0.0409	0.0375	0.1166	0.0975	0.0308	0.0405
wR2(obs)	0.1411	0.0853	0.0747	0.0944	0.0326	0.1500	0.1163	0.0726	0.0973
wR2 (all)	0.1433	0.0884	0.0757	0.1000	0.1134	0.1721	0.1362	0.0791	0.1008

Table S2. hydrogen bonds

	D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)	Symm
(4-APH$^+$)(NO$_3^-$)						
Fig1a	N(1)-H(1)···O(1)	0.88	1.90	2.776(2)	175	2-x,-1/2+y,1/2-z
Fig1a	N(1)-H(1)···O(2)	0.88	2.63	3.205(3)	124	2-x,1/2+y,1/2-z
Fig1a	N(4)-H(4A)···O(3)	0.88	2.10	2.948(3)	161	1-x,1-y,-z
Fig1a	N(4)-H(4B)···O(1)	0.88	2.10	2.930(3)	157	1-x,-1/2+y,1/2-z
Fig1a	N(4)-H(4B)···O(3)	0.88	2.53	3.280(3)	144	1-x,-1/2+y,1/2-z
Fig1a	C(2)-H(2)···O(2)	0.95	2.46	3.362(3)	159	2-x,1-y,-z
Fig1c	C(6)-H(6)···O(2)	0.95	2.47	3.342(3)	153	x,1/2-y,1/2+z
Fig1a	C(5)-H(5)···O(3)	0.95	2.62	3.362(3)	137	1-x,1/2+y,1/2-z
(3,4-DAPH$^+$)(NO$_3^-$)						
Fig 2a	N(1)-H(1)···O(5A)	0.87(2)	2.08(2)	2.942(1)	171(1)	-
Fig 2a	N(1)-H(1)···O(5B)	0.87(2)	2.56(2)	3.119(1)	123(1)	-
Fig 2a	N(3)-H(3A)···O(5B)	0.88(2)	2.10(2)	2.966(2)	168(1)	1/2-x,1/2+y,3/2-z
Fig 2a	N(3)-H(3B)···O(5A)	0.85(2)	2.18(2)	2.983(1)	157(1)	x,y,1+z
Fig 2c	N(4)-H(4A)···O(5C)	0.88(2)	2.16(2)	2.994(1)	158(1)	-x,-y,1-z
Fig 2a	N(4)-H(4B)···O(5C)	0.89(2)	2.07(2)	2.935(1)	165(1)	x,y,1+z
Fig 2a	C(2)-H(2)···O(5B)	0.95(2)	2.48(2)	3.081(2)	121(1)	-
Fig 2a	C(6)-H(6)···O(5B)		2.66(2)	3.579(2)	162.9(1)	1/2-x,-1/2+y,1/2-z
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Fig3a	N(1)-H(4)···O(2)	0.87(1)	2.00(1)	2.77(1)	147(1)	x,1+y,z
Fig3a	N(1)-H(4)···O(1)	0.87(1)	2.66(1)	3.21(1)	122(1)	-x,1-y,1-z
Fig3a	N(2)-H(5)···O(5)	0.93(1)	2.10(1)	2.91(1)	143(1)	-
Fig3b	N(2)-H(5)···O(2)	0.93(1)	2.21(1)	2.78(1)	118(1)	x,1/2-y,-1/2+z
Fig3b	N(2)-H(6)···O(3)	0.88(1)	2.19(1)	3.00(1)	152(1)	-x,1/2+y,1/2-z
Fig3b	N(2)-H(6)···O(3)	0.88(1)	2.48(1)	2.92(1)	112(1)	x,1/2-y,1/2+z
Fig3a	N(3)-H(7)···O(4)	0.84(2)	2.05(2)	2.865(1)	161(1)	-
Fig3a	N(3)-H(8)···O(6)	0.83(1)	2.13(1)	2.944(1)	168(1)	1-x,1/2+y,1/2-z
Fig3b	N(2)-H(9)···O(5)	0.87(1)	1.96(1)	2.823(1)	169(1)	x,1/2-y,1/2+z
Fig3b	N(2)-H(9)···O(6)	0.87(1)	2.49(1)	3.122(1)	129(1)	x,1/2-y,1/2+z
-	C(2)-H(1)···O(3)	0.91(1)	2.44(1)	3.049(1)	125(1)	-x,1/2+y,1/2-z
Fig3a	C(2)-H(1)···O(1)	0.91(1)	2.55(1)	3.183(1)	127(1)	-x,1-y,1-z
-	C(2)-H(1)···O(3)	0.91(1)	2.57(1)	3.128(1)	120(1)	x,1/2-y,1/2+z
Fig3a	C(3)-H(2)···O(6)	0.98(1)	2.25(1)	3.117(1)	147(1)	x,1+y,z
Fig3a	C(4)-H(3)···O(4)	0.93(1)	2.56(1)	3.427(1)	156(1)	1-x,1/2+y,1/2-z
(3,4-DAPH$_2^{2+}$)(NO$_3^-$)$_2$.H$_2$O						
Fig 5a and 6a	N(1)-H(1)···O(6)	0.88	1.90	2.775(1)	170	1+x,1/2-y,1/2+z
Fig 5a and 6a	O(1W)-H(1W)···O(2)	0.83(1)	2.50(1)	3.033(1)	123(1)	-1/2+x,1/2-y,-z
Fig 6c	O(1W)-H(1W)···O(3)	0.83(1)	1.95(1)	2.779(1)	180(2)	-1/2+x,1/2-y,-z
Fig 5a, 6a, 6b	O(1W)-H(2W)···O(4)	0.84(1)	1.89(1)	2.735(1)	178(2)	-
Fig 6b	N(3)-H(3A)···O(3)	0.91	1.88	2.781(1)	172	3/2-x,-1/2+y,z
	N(3)-H(3B)···O(2)	0.91	2.58	2.948(1)	105	-
Fig 5a and 6a	N(3)-H(3B)···O(1W)	0.91	2.09	2.971(1)	162	1/2+x,1/2-y,-z
Fig 5a and 6a	N(3)-H(3C)···O(1W)	0.91	1.90	2.786(1)	166	1/2+x,y,1/2-z

Fig 5a and 6a	N(4)-H(4A)···O(1)	0.88	2.54	3.269(1)	141	x,1/2-y,-1/2+z
Fig 5a and 6a	N(4)-H(4A)···O(2)	0.88	2.28	2.902(1)	128	x,1/2-y,-1/2+z
Fig 5a and 6a	N(4)-H(4B)···O(4)	0.88	2.54	3.327(1)	150	1+x,1/2-y,-1/2+z
Fig 5a and 6a	N(4)-H(4B)···O(6)	0.88	2.16	2.970(1)	153	1+x,1/2-y,-1/2+z
Fig 5a and 6a	C(2)-H(2)···O(1W)	0.95	2.53	3.163(1)	124	1/2+x,y,1/2-z
Fig 5a and 6a	C(2)-H(2)···O(2)	0.95	2.59	3.433(1)	148	x,1/2-y,1/2+z
Fig 5a and 6a	C(5)-H(5)···O(4)	0.95	2.40	3.261(1)	150	1+x,1/2-y,-1/2+z
-	C(6)-H(6)···O(1)	0.95	2.56	3.340(1)	140	2-x,-1/2+y,1/2-z
Fig 5a and 6a	C(6)-H(6)···O(1)	0.95	2.64	3.220(1)	120	-1+x,1/2-y,-1/2+z
(4-APH^{+}) (HSO$_4^{-}$)						
Fig 8b	N(1)-H(1)···O(1)	0.88	2.02	2.851(2)	158	2-x,1-y,1-z
Fig 8b	N(2)-H(2A)···O(1)	0.84(2)	2.06(2)	2.897(2)	175(2)	3/2-x,1/2+y,3/2-z
Fig 8b	N(2)-H(2B)···O(4)	0.88(2)	2.05(2)	2.928(2)	177(2)	1-x,1-y,1-z
Fig 8a	O(3)-H(3A)···O(2)	0.95(3)	1.62(3)	2.566(1)	175(2)	3/2-x,-1/2+y,1/2-z
(4-APH^{+})$_2$(SO$_4^{2-}$).H$_2$O						
Fig 11b	N(1')-H(1')···O(2)	0.88	2.23	2.951(4)	138	x,1+y,z
Fig 9a	N(4')-H(4'A)···O(1W)	0.88	1.97	2.810(3)	158	1-x,1-y,-z
Fig 9a	O(1W)-H(1W)···O(2)	0.84(2)	2.02(1)	2.828(2)	162(2)	x,1+y,z
Fig 9a	N(4')-H(4'B)···O(2)	0.88	1.96	2.823(3)	166	-
Fig 9a	O(1W)–H(2W)···O(4)	0.84(2)	1.97(2)	2.798(2)	170(2)	-1+x,1+y,z
Fig 9a	N(11)-H(11)···O(3)	0.88	1.89	2.712(2)	154	x,1+y,z
Fig 9a	N(14)-H(14A)···O(3)	0.88	2.00	2.875(2)	175	-
Fig 11b	N(14)-H(14B)···O(1)	0.88	1.96	2.817(2)	165	-1+x,y,z
-.	C(2')-H(2')···O(1W)	0.95	2.56	3.323(4)	137	1-x,2-y,-z
-	C(5')-H(5')···O(1)	0.95	2.53	3.357(6)	146	-
-	C(6')-H(6')···O(4)	0.95	2.41	3.228(7)	144	x,1+y,z
-	C(12)-H(12)···O(4)	0.95	2.45	3.378(2)	166	-1+x,1+y,z
-	C(16)-H(16)···O(3)	0.95	2.51	3.342(2)	146	2-x,1-y,1-z
(3,4-DAPH^{+})$_2$(SO$_4^{2-}$).2H$_2$O						
Fig 13 b	N(1)-H(1A)···O(2)	0.88	1.90	2.774(4)	172	1+x,y,z
Fig 13 b and c	N(1)-H(1A)···O(2)	0.88	2.57	3.154(4)	125	5/4-y,1/4+x,5/4-z
Fig 13 c	N(2)-H(2A)···O(10)	0.88	2.12	2.940(4)	156	1-x,1-y,1-z
Fig 13 b	N(2)-H(2B)···O(1)	0.88	2.07	2.950(4)	178	-
Fig 13 b	N(3)-H(3B)···O(1)	0.88	2.10	2.976(4)	177	-
Fig 13 c	N(3)-H(3C)···O(10)	0.88	2.32	3.149(4)	158	3/4-y,1/4+x,1/4+z
Fig 13 a	O(10)-H(10A)···O(2)	0.88(5)	2.05(5)	2.866(3)	156(5)	-
Fig 13 a	O(10)-H(10B)···O(1)	0.88(5)	1.88(5)	2.740(3)	167(5)	3/4-y,-1/4+x,3/4-z
(3,4-DAPH$_2^{2+}$) (SO$_4^{2-}$).2H$_2$O						
Fig 15b	O(1)-H(1A)···O(14)	0.83(3)	1.99(3)	2.773(3)	157(3)	-
Fig 15a and 15b	O(1)-H(1B)···O(22)	0.86(3)	1.96(3)	2.796(3)	163(3)	1-x,1-y,1-z
Fig 15b	O(2)-H(2A)···O(11)	0.85(3)	1.97(3)	2.813(3)	169(4)	-
Fig 15a	O(2)-H(2B)···O(23)	0.85(3)	1.88(3)	2.731(3)	179(4)	-
Fig 15a	O(3)-H(3A)···O(4)	0.85(3)	2.16(3)	2.975(3)	161(3)	-

Fig 15a	O(3)-H(3B)···O(1)	0.85(4)	2.07(4)	2.871(3)	155(4)	-1+x,y,z
Fig 15a	O(4)-H(4A)···O(2)	0.86(4)	1.83(3)	2.683(3)	171(4)	-
Fig 15a	O(4)-H(4B)···O(21)	0.87(5)	2.03(5)	2.850(3)	156(5)	-x,1-y,1-z
Fig 17a	N(11)-H(11)···O(23)	0.88	2.25	2.939(4)	135	-x,1-y,-z
Fig 17a	N(11)-H(11)···O(24)	0.88	2.11	2.952(4)	159	-x,1-y,-z
Fig 17a	N(12)-H(12A)···O(13)	0.85(3)	1.91(3)	2.740(4)	165(3)	-1+x,y,z
Fig 17a	N(12)-H(12C)···O(12)	0.98(4)	1.80(4)	2.758(4)	167(4)	-x,1-y,-z
Fig 17a	N(12)-H(12B)···O(11)	0.93(4)	1.83(4)	2.742(4)	167(3)	-
Fig 17a	N(13)-H(13A)···O(13)	0.88	2.06	2.907(4)	160	-x,-y,-z
Fig 17a	N(13)-H(13B)···O(3)	0.88	2.01	2.858(4)	160	-
Fig 17b	N(21)-H(21)···O(12)	0.88	1.85	2.714(3)	167	x,1+y,1+z
Fig 17b	N(21)-H(21)···O(13)	0.88	2.59	3.220(3)	129	x,1+y,1+z
Fig 17b	N(22)-H(22A)···O(22)	0.82(3)	2.05(3)	2.866(3)	175(3)	1-x,2-y,1-z
Fig 17b	N(22)-H(22A)···O(23)	0.82(3)	2.55(3)	2.995(4)	116(2)	1-x,2-y,1-z
Fig 17b	N(22)-H(22B)···O(21)	0.97(3)	2.47(3)	2.863(4)	104(2)	x,1+y,z
Fig 17b	N(22)-H(22B)···O(1)	0.97(3)	1.93(3)	2.876(4)	165(2)	1-x,2-y,1-z
Fig 17b	N(22)-H(22C)···O(21)	0.99(4)	1.76(4)	2.739(4)	170(4)	-x,2-y,1-z
Fig 17b	N(23)-H(23A)···O(4)	0.88	2.13	2.920(4)	149	x,1+y,z
Fig 17b	N(23)-H(23B)···O(24)	0.88	1.96	2.810(4)	161	-
Fig 17b	N(23)-H(23A)···O(22)	0.88	2.51	3.109(4)	126	1-x,2-y,1-z
-	C(12)-H(12)···O(14)	0.95	2.36	3.194(4)	146	-x,1-y,-z
-	C(22)-H(25)···O(2)	0.95	2.56	3.162(4)	121	-x,2-y,1-z
(4-APH$^+$) ($H_2PO_4^-$). H_2O						
Fig 18 a	N(1)-H(1)···O(1W)	0.88	1.91	2.766(2)	165	1-x,1-y,1-z
Fig 18 c	O(1W)-H(1W)···O(1)	0.81(2)	1.92(2)	2.731(2)	174(2)	1-x,1-y,2-z
Fig 18 c	O(1W)-H(2W)···O(2)	0.84(2)	1.90(2)	2.739(2)	174(2)	-
Fig 18 a	O(3)-H(3A)···O(1)	0.84	1.75	2.583(2)	170	-x,1-y,2-z
Fig 18 a	O(4)-H(4A)···O(2)	0.84	1.75	2.575(1)	166	1-x,-y,2-z
Fig 18 a	N(4)-H(4B)···O(1W)	0.88	2.12	2.976(2)	165	2-x,-y,1-z
Fig 18 a	N(4)-H(4C)···O(1)	0.88	2.07	2.944(2)	174	1-x,-y,2-z
Fig 18 a	C(2)-H(2)···O(3)	0.95	2.34	3.262(2)	163	-
(3,4DAPH$^+$) ($H_2PO_4^-$)						
Fig 19 a	N(1)-H(1)···O(2)	0.88	1.87	2.716 (2)	162	-
-	N(2)-H(2A)···O(3)	0.88	2.42	3.226(2)	152	1/2+x,1-y,z
-	N(2)-H(2B)···O(1)	0.88	2.30	3.167(2)	169	1-x,1-y,-z
Fig 19 a	O(3)-H(3)···O(2)	0.88	1.79	2.627(2)	178	1/2-x,3/2-y,1/2-z
Fig 19 c	N(3)-H(3A)···O(2)	0.88	2.10	2.907(2)	152	x,3/2-y,-1/2+z
Fig 19 a	N(3)-H(3B)···O(1)	0.88	2.01	2.882(2)	169	1-x,1-y,-z
Fig 19 a	O(4)-H(4)···O(1)	0.84	1.74	2.570(2)	172	1/2-x,1/2-y,1/2-z
-	C(2)-H(2)···O(3)	0.95	2.54	3.368(2)	146	1/2+x,1-y,z
-	C(5)-H(5)···O(4)	0.95	2.46	3.411(2)	179	x,3/2-y,-1/2+z