Electronic Supplementary Material (ESI) for CrystEngComm.

Structural variety and dehydration in 3-aminopyridine–hypodiphosphoric acid–water system

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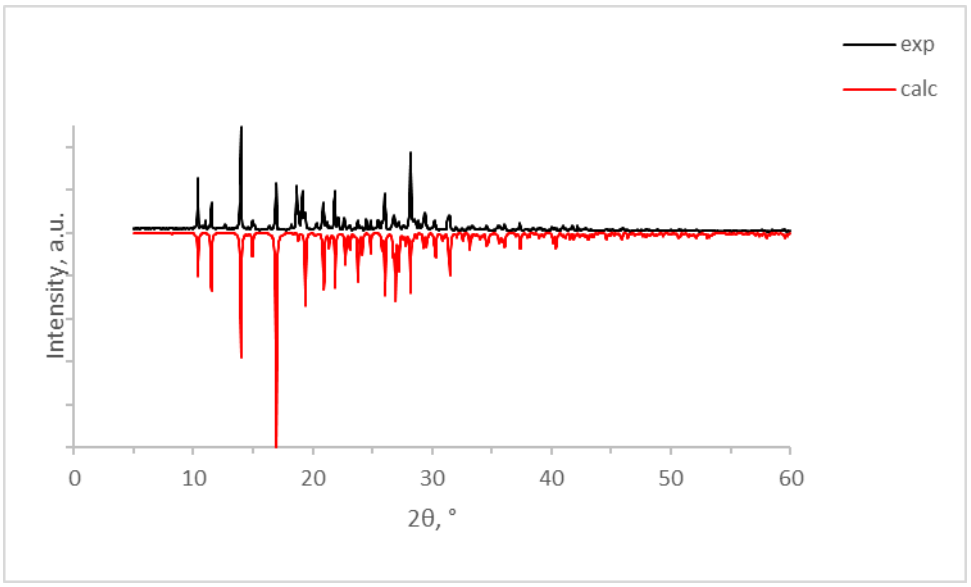
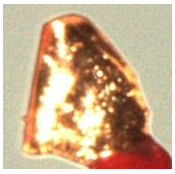
Supporting information

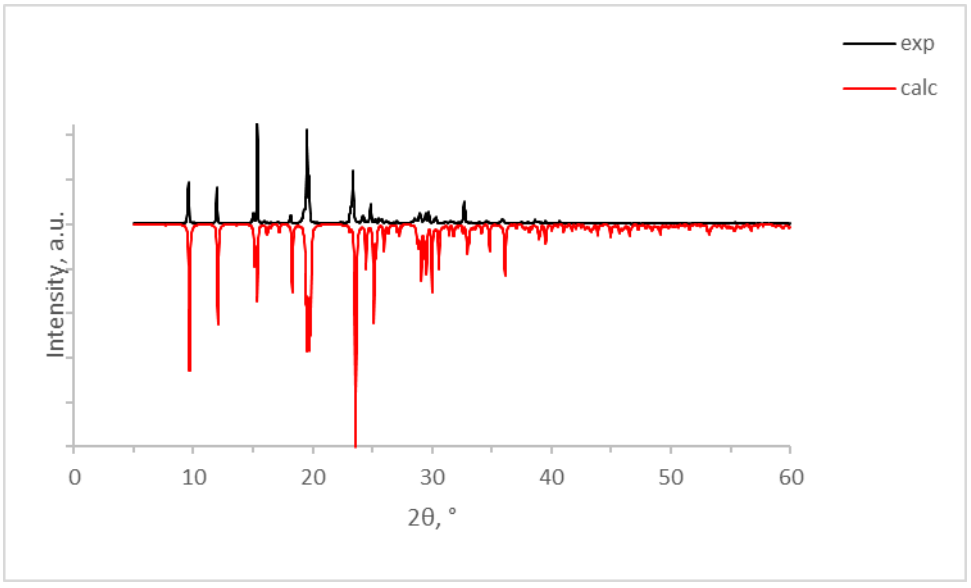


(a)



(b)

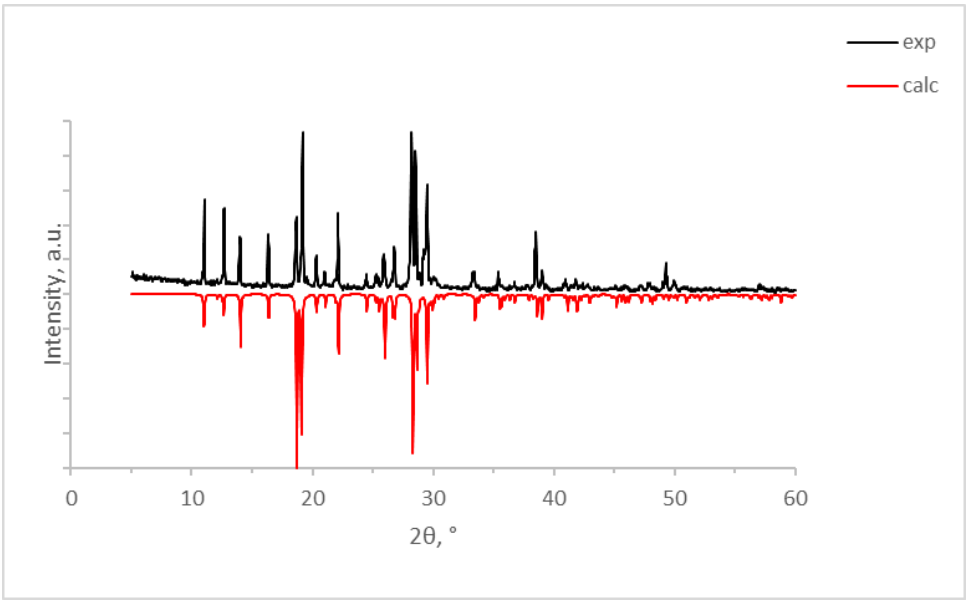
Figure S1. (a) X-ray powder diffraction pattern for (**1**) (black line) compared with the theoretical diffraction pattern of (**1**)-HTP (red line; shown upside down). **(b)** Microscopic image of (**1**) crystal.



(a)

(b)

Figure S2. (a) X-ray powder diffraction pattern for (**3**) (black line) compared with the theoretical diffraction pattern of (**3**) (red line; shown upside down). **(b)** Microscopic image of (**3**) crystal.



(a)

(b)

Figure S3. (a) X-ray powder diffraction pattern for (**5**) (black line) compared with the theoretical diffraction pattern of (**5**) (red line; shown upside down). **(b)** Microscopic image of (**5**) crystal.

FT-IR analyses of compounds were performed using nujol mulls technique with a wavelength between 4000 to 400 cm^{-1}. The recorded spectra are shown in Figures S4-S6. The absorption frequencies around 2925, 1462, 1377 cm^{-1} are derived from nujol. Absorption frequencies 3398-3311 cm^{-1} (N-H stretching), 3198-3128 cm^{-1} (C–H stretching), 2725-2669 cm^{-1} (N/O–H stretching), 1658-1612 cm^{-1} (N-H in-plane bending), 1582-1290 cm^{-1} (aromatic C=C stretching), 950-700 cm^{-1} (ring breathing), 670-620 cm^{-1} (NH_2 out-of-plane bending) and 560-552 cm^{-1} (C-N-C out-of-plane bending) confirm the 3-aminopyridinium ring in the crystals. The visible bands between 1350-1260 cm^{-1} correspond to the P-O(H) group, so it can be concluded that the hypodiphosphate anions are not completely deprotonated. In the frequency range 1154-894 cm^{-1} bands from the P-O functional group are visible, and in the range 724-449 cm^{-1} – O-P-O groups.

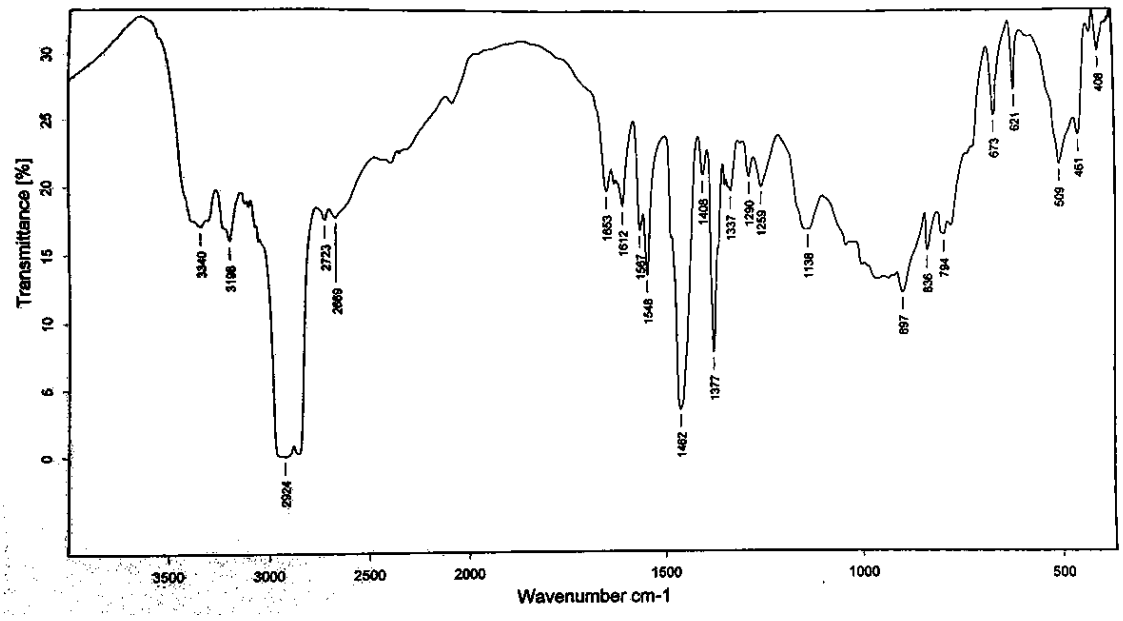


Figure S4. FT-IR spectrum of (**1**).

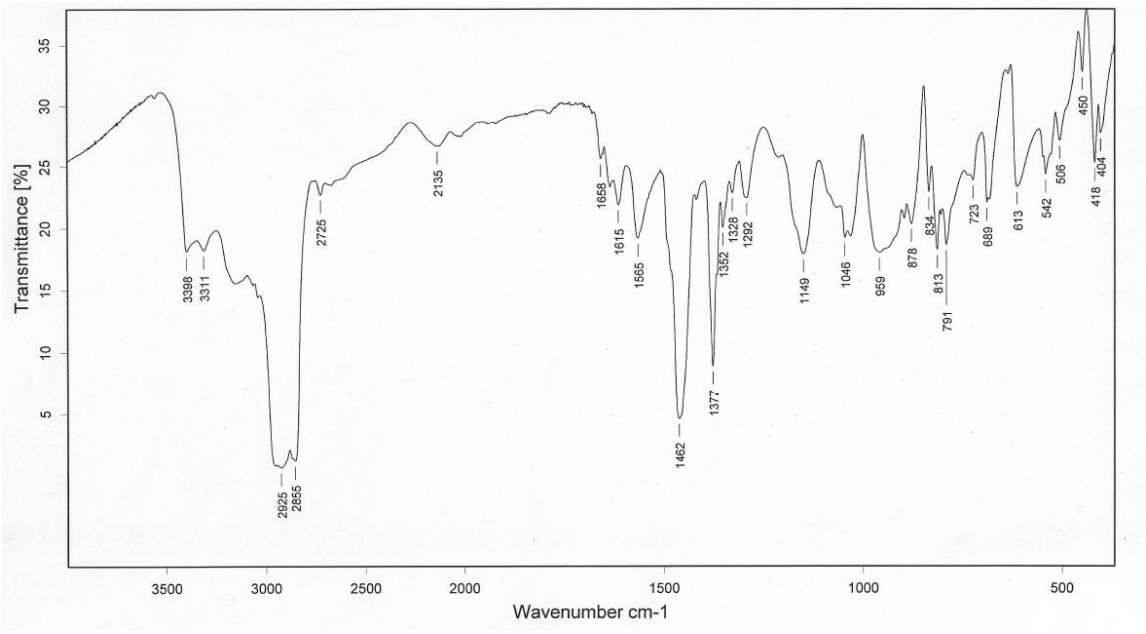


Figure S5. FT-IR spectrum of (**3**).

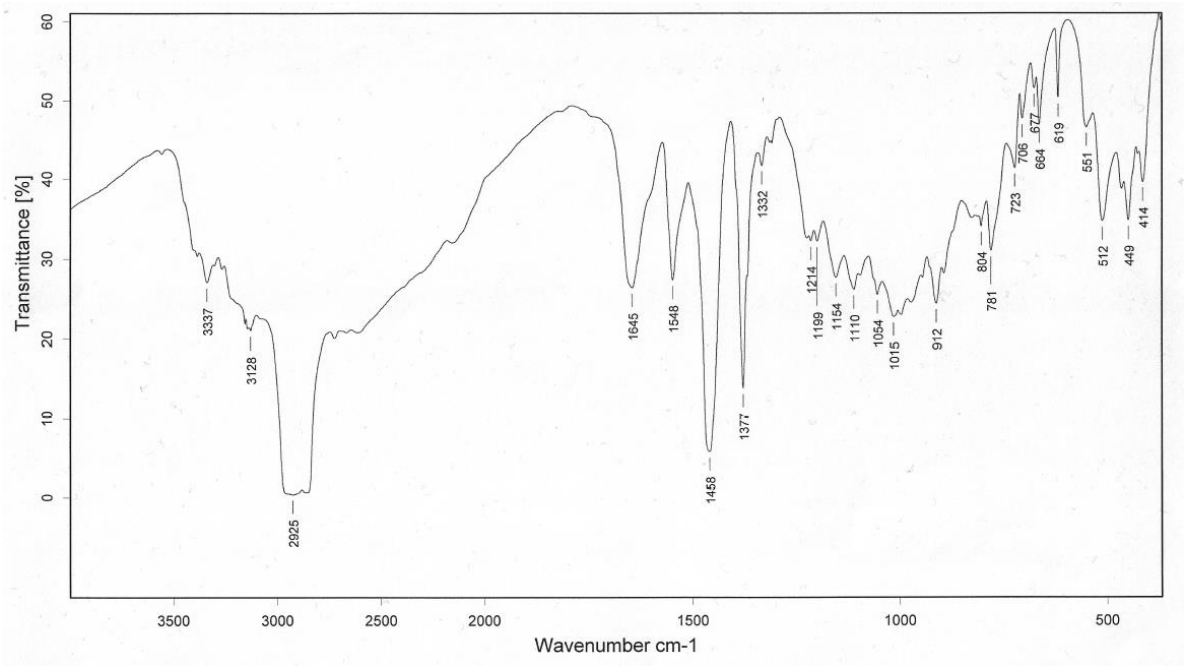
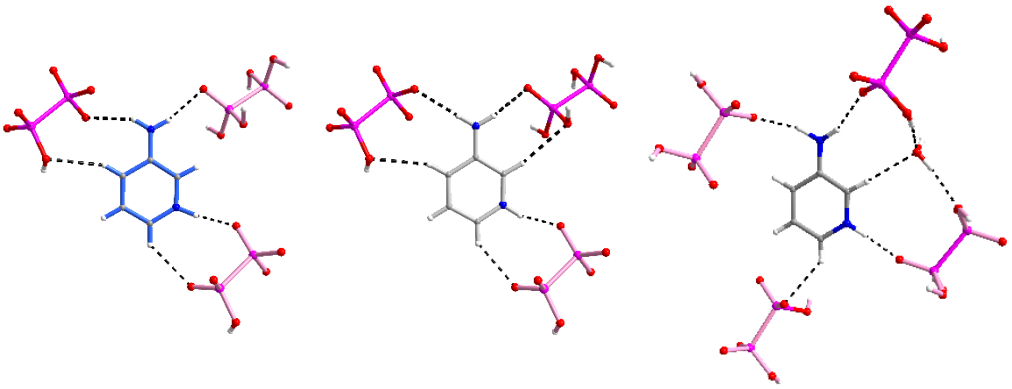


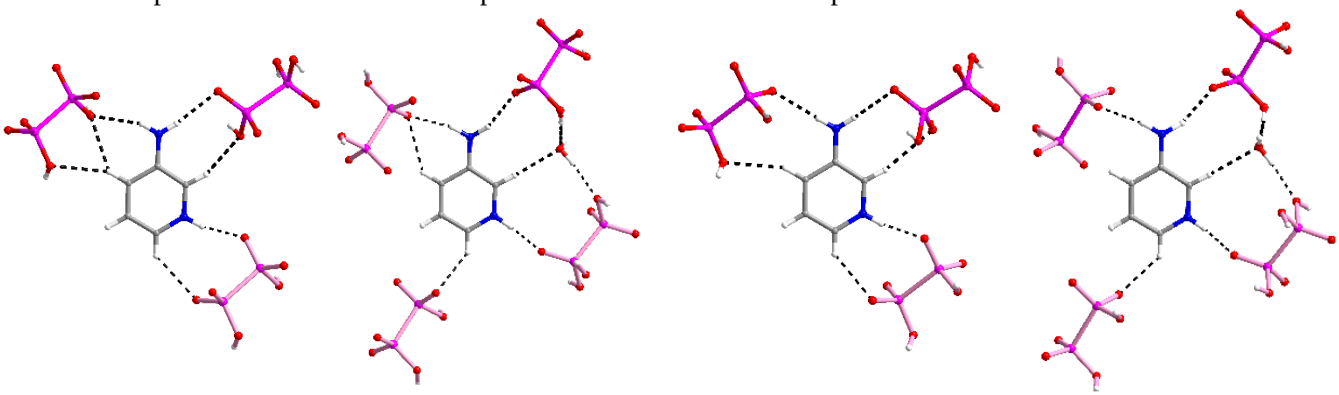
Figure S6. FT-IR spectrum of (**5**).

Almost all atoms of the cation in (**1**) are involved in 3-aminopyridinium···hypodiphosphate contacts (the exception is C5 atom). Characteristic motifs are observed – $R_2^2(10)$ and $R_2^2(9)$ – involving N3 or N1 nitrogen atom, an adjacent carbon atom and one or two oxygen atoms from hypodiphosphate anions. In the case of *C* and *D* of (**1**)-LTP cations, the NH_2 group is involved in $R_2^2(6)$ ring formation. In *B* and *C* cations, water molecules are also involved in the formation of 3ap···PP supramolecular motifs, giving rise to $R_3^3(10)$ ring.



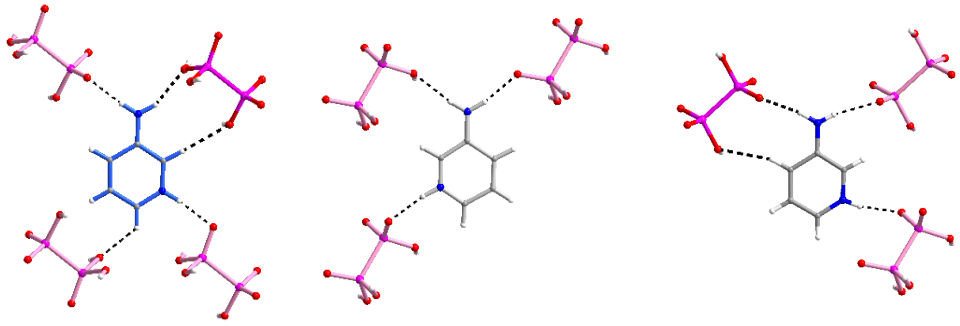
(**1**)-HTP

3ap–*A* 3ap–*X* 3ap–*B*



(**1**)-LTP

3ap–*A* 3ap–*B* 3ap–*C* 3ap–*D*



(**2**)

3ap–*A* 3ap–*X* 3ap–*B*

Figure S7. Hydrogen bond connections between the anions and the cations in the crystals of (**1**) and (**2**).

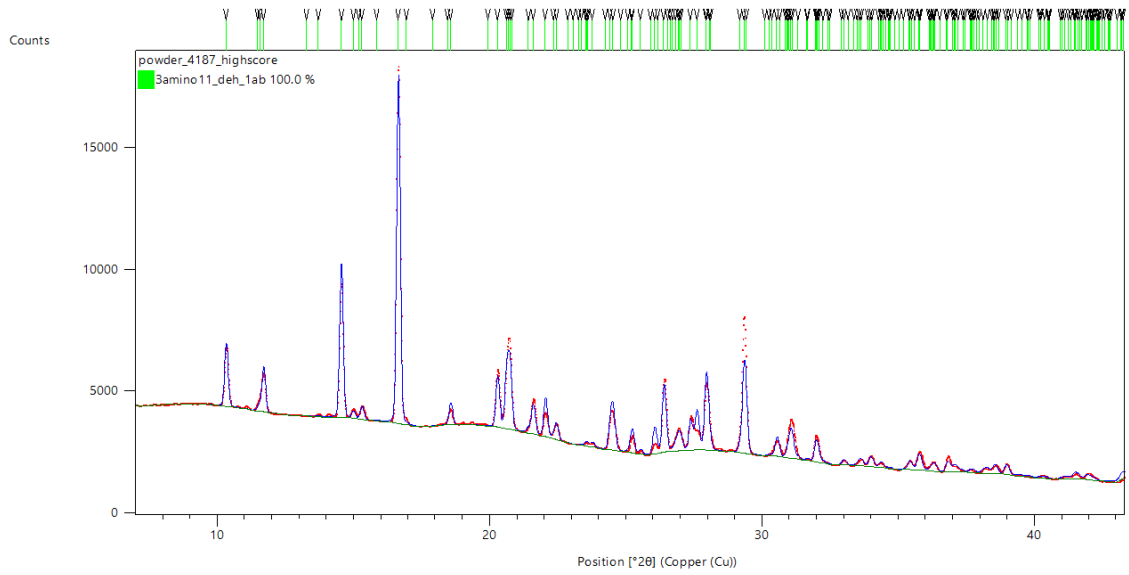


Figure S8. The powder diffraction pattern (range 2θ 7–43°) for (**2**) obtained in the dehydration process of (**1**) performed on a Boetius PHMK apparatus at 390 K.

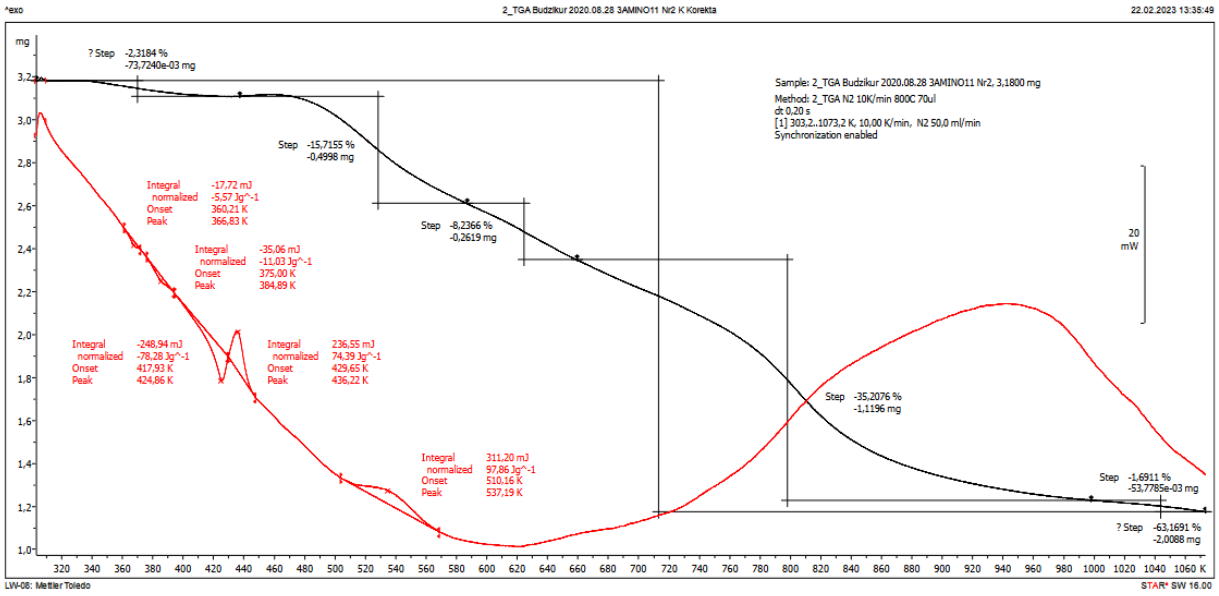


Figure S9. The TGA curve for (**1**) (m = 3.1800 mg).

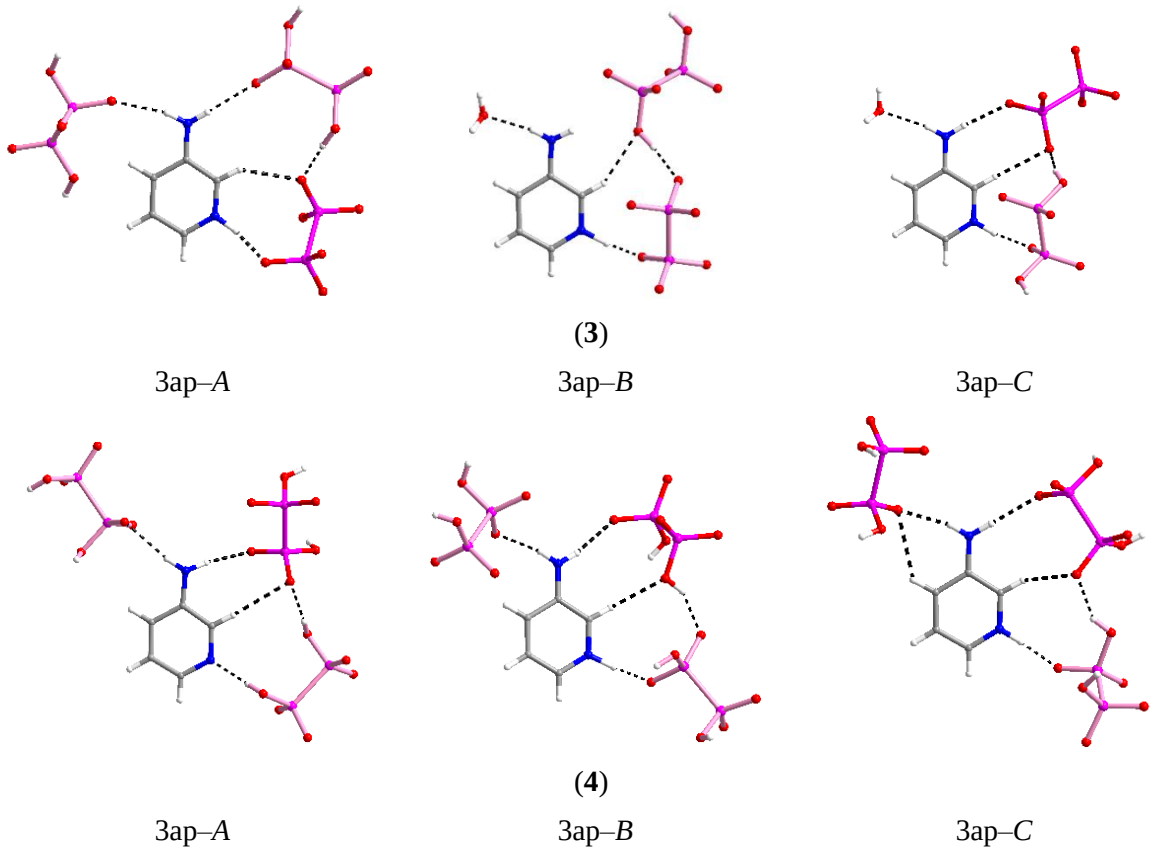


Figure S10. Hydrogen bond connections between the anions and the cations in the crystals of (**3**) and (**4**).

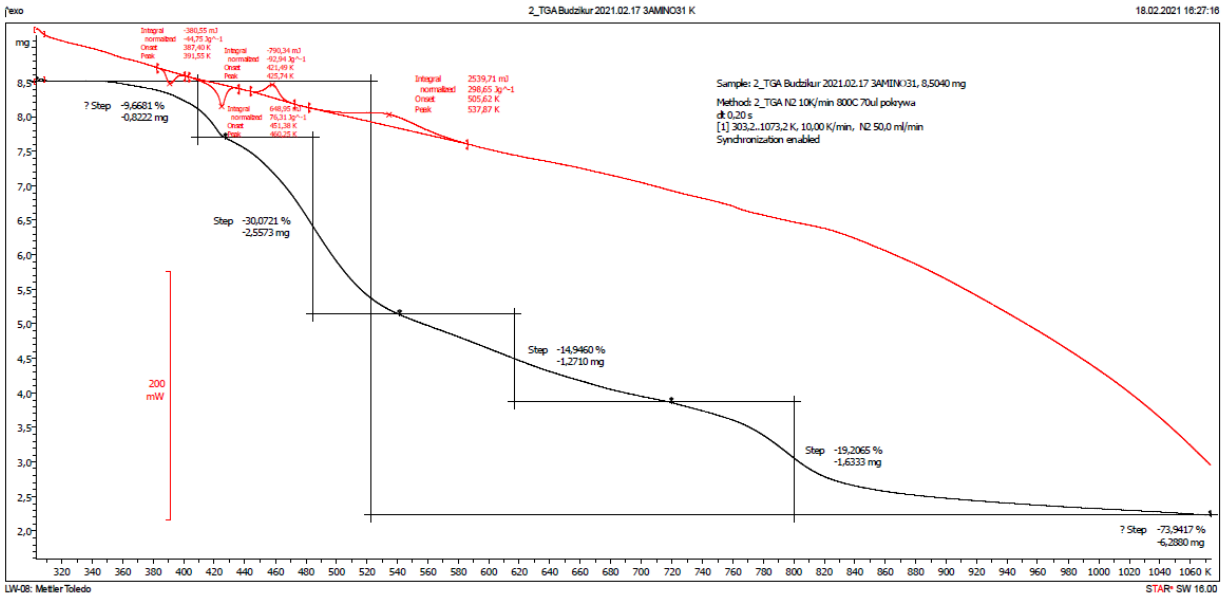
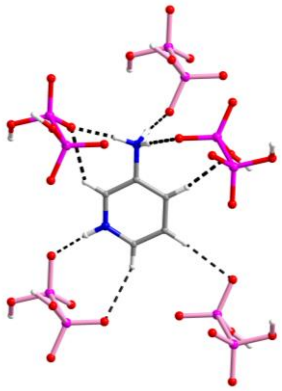


Figure S11. The TGA curve for (**3**) (m = 8.504 mg).



(**5**)

Figure S12. Hydrogen bond connections between the anions and the cation in the crystal of (**5**).

Table S1. Selected geometric parameters (Å, °) for (**1**)-HTP

P1*A*—O1*A*	1.5017(8)	P2*A*—O6*A*	1.5645(8)
P1*A*—O2*A*	1.5202(7)	P1*B*—O1*B*	1.4879(8)
P1*A*—O3*A*	1.5652(8)	P1*B*—O2*B*	1.5454(8)
P1*A*—P2*A*	2.1842(5)	P1*B*—O3*B*	1.5489(7)
P2*A*—O4*A*	1.5012(8)	P1*B*—P1*B*^{i}	2.1827(6)
P2*A*—O5*A*	1.5110(9)		
O1*A*—P1*A*—O2*A*	114.51(4)	O4*A*—P2*A*—P1*A*	107.98(4)
O1*A*—P1*A*—O3*A*	112.15(4)	O5*A*—P2*A*—P1*A*	108.03(3)
O2*A*—P1*A*—O3*A*	107.32(4)	O6*A*—P2*A*—P1*A*	104.47(3)
O1*A*—P1*A*—P2*A*	108.11(3)	O1*B*—P1*B*—O2*B*	114.43(5)
O2*A*—P1*A*—P2*A*	107.27(3)	O1*B*—P1*B*—O3*B*	113.34(5)
O3*A*—P1*A*—P2*A*	107.13(4)	O2*B*—P1*B*—O3*B*	104.78(4)
O4*A*—P2*A*—O5*A*	117.05(5)	O1*B*—P1*B*—P1*B*^{i}	110.91(4)
O4*A*—P2*A*—O6*A*	112.80(4)	O2*B*—P1*B*—P1*B*^{i}	106.89(4)
O5*A*—P2*A*—O6*A*	105.72(5)	O3*B*—P1*B*—P1*B*^{i}	105.85(3)
O1*A*—P1*A*—P2*A*—O4*A*	43.59(4)	O1*B*—P1*B*—P1*B*^{i}—O1*B*^{i}	180
O2*A*—P1*A*—P2*A*—O4*A*	−80.38(5)	O2*B*—P1*B*—P1*B*^{i}—O1*B*^{i}	54.63(5)
O3*A*—P1*A*—P2*A*—O4*A*	164.66(4)	O3*B*—P1*B*—P1*B*^{i}—O1*B*^{i}	−56.68(5)
O1*A*—P1*A*—P2*A*—O5*A*	171.07(4)	O1*B*—P1*B*—P1*B*^{i}—O2*B*^{i}	−54.63(5)
O2*A*—P1*A*—P2*A*—O5*A*	47.10(4)	O2*B*—P1*B*—P1*B*^{i}—O2*B*^{i}	180
O3*A*—P1*A*—P2*A*—O5*A*	−67.87(5)	O3*B*—P1*B*—P1*B*^{i}—O2*B*^{i}	68.69(5)
O1*A*—P1*A*—P2*A*—O6*A*	−76.71(4)	O1*B*—P1*B*—P1*B*^{i}—O3*B*^{i}	56.68(5)
O2*A*—P1*A*—P2*A*—O6*A*	159.32(4)	O2*B*—P1*B*—P1*B*^{i}—O3*B*^{i}	−68.69(5)
O3*A*—P1*A*—P2*A*—O6*A*	44.35(5)	O3*B*—P1*B*—P1*B*^{i}—O3*B*^{i}	180

Symmetry code: (i) −*x*, −*y*, −*z*+1.

Table S2. Selected geometric parameters (Å, °) for (**1**)-LTP

P1*A*—O1*A*	1.5038(7)	P2*B*—O4*B*	1.4916(7)
P1*A*—O2*A*	1.5224(7)	P2*B*—O5*B*	1.5434(7)
P1*A*—O3*A*	1.5667(7)	P2*B*—O6*B*	1.5530(7)
P1*A*—P2*A*	2.1837(5)	P1*C*—O1*C*	1.5077(7)
P2*A*—O4*A*	1.5047(7)	P1*C*—O2*C*	1.5144(7)
P2*A*—O5*A*	1.5105(7)	P1*C*—O3*C*	1.5624(8)
P2*A*—O6*A*	1.5676(8)	P1*C*—P2*C*	2.1836(5)
P1*B*—O1*B*	1.4918(7)	P2*C*—O4*C*	1.5051(7)
P1*B*—O2*B*	1.5483(7)	P2*C*—O5*C*	1.5212(7)
P1*B*—O3*B*	1.5515(7)	P2*C*—O6*C*	1.5678(7)
P1*B*—P2*B*	2.1834(5)		
O1*A*—P1*A*—O2*A*	114.37(4)	O4*B*—P2*B*—O5*B*	115.11(4)
O1*A*—P1*A*—O3*A*	112.28(4)	O4*B*—P2*B*—O6*B*	112.83(4)
O2*A*—P1*A*—O3*A*	107.59(4)	O5*B*—P2*B*—O6*B*	105.28(4)
O1*A*—P1*A*—P2*A*	108.21(3)	O4*B*—P2*B*—P1*B*	110.76(4)
O2*A*—P1*A*—P2*A*	106.70(3)	O5*B*—P2*B*—P1*B*	106.49(3)
O3*A*—P1*A*—P2*A*	107.32(3)	O6*B*—P2*B*—P1*B*	105.69(3)
O4*A*—P2*A*—O5*A*	117.06(4)	O1*C*—P1*C*—O2*C*	116.65(4)
O4*A*—P2*A*—O6*A*	112.59(4)	O1*C*—P1*C*—O3*C*	113.05(4)
O5*A*—P2*A*—O6*A*	105.99(4)	O2*C*—P1*C*—O3*C*	106.28(4)
O4*A*—P2*A*—P1*A*	107.76(3)	O1*C*—P1*C*—P2*C*	107.99(3)
O5*A*—P2*A*—P1*A*	107.82(3)	O2*C*—P1*C*—P2*C*	108.05(3)
O6*A*—P2*A*—P1*A*	104.89(4)	O3*C*—P1*C*—P2*C*	104.01(4)
O1*B*—P1*B*—O2*B*	113.86(4)	O4*C*—P2*C*—O5*C*	114.49(4)
O1*B*—P1*B*—O3*B*	113.96(4)	O4*C*—P2*C*—O6*C*	112.14(4)
O2*B*—P1*B*—O3*B*	104.49(4)	O5*C*—P2*C*—O6*C*	107.42(4)
O1*B*—P1*B*—P2*B*	110.74(4)	O4*C*—P2*C*—P1*C*	107.98(3)
O2*B*—P1*B*—P2*B*	105.96(3)	O5*C*—P2*C*—P1*C*	107.63(3)
O3*B*—P1*B*—P2*B*	107.24(3)	O6*C*—P2*C*—P1*C*	106.83(3)
O1*A*—P1*A*—P2*A*—O4*A*	43.02(4)	O3*B*—P1*B*—P2*B*—O5*B*	−179.89(3)
O2*A*—P1*A*—P2*A*—O4*A*	−80.50(4)	O1*B*—P1*B*—P2*B*—O6*B*	56.64(4)
O3*A*—P1*A*—P2*A*—O4*A*	164.40(4)	O2*B*—P1*B*—P2*B*—O6*B*	−179.43(3)
O1*A*—P1*A*—P2*A*—O5*A*	170.22(4)	O3*B*—P1*B*—P2*B*—O6*B*	−68.26(4)
O2*A*—P1*A*—P2*A*—O5*A*	46.70(4)	O1*C*—P1*C*—P2*C*—O4*C*	−43.50(4)
O3*A*—P1*A*—P2*A*—O5*A*	−68.40(4)	O2*C*—P1*C*—P2*C*—O4*C*	−170.49(4)
O1*A*—P1*A*—P2*A*—O6*A*	−77.14(4)	O3*C*—P1*C*—P2*C*—O4*C*	76.86(4)
O2*A*—P1*A*—P2*A*—O6*A*	159.33(4)	O1*C*—P1*C*—P2*C*—O5*C*	80.59(4)
O3*A*—P1*A*—P2*A*—O6*A*	44.24(4)	O2*C*—P1*C*—P2*C*—O5*C*	−46.41(4)

O1*B*—P1*B*—P2*B*—O4*B*	179.16(4)	O3*C*—P1*C*—P2*C*—O5*C*	−159.06(4)
O2*B*—P1*B*—P2*B*—O4*B*	−56.91(4)	O1*C*—P1*C*—P2*C*—O6*C*	−164.30(4)
O3*B*—P1*B*—P2*B*—O4*B*	54.26(4)	O2*C*—P1*C*—P2*C*—O6*C*	68.70(4)
O1*B*—P1*B*—P2*B*—O5*B*	−55.00(4)	O3*C*—P1*C*—P2*C*—O6*C*	−43.95(4)
O2*B*—P1*B*—P2*B*—O5*B*	68.93(4)		

Table S3. Selected geometric parameters (Å, °) for (**2**)

P1*A*—O1*A*	1.483(4)	P2*A*—O6*A*	1.563(4)
P1*A*—O2*A*	1.551(4)	P1*B*—O1*B*	1.510(3)
P1*A*—O3*A*	1.558(4)	P1*B*—O2*B*	1.511(3)
P1*A*—P2*A*	2.1837(18)	P1*B*—O3*B*	1.566(4)
P2*A*—O4*A*	1.501(4)	P1*B*—P1*B*^{i}	2.189(2)
P2*A*—O5*A*	1.504(4)		
O1*A*—P1*A*—O2*A*	115.4(2)	O4*A*—P2*A*—P1*A*	108.92(17)
O1*A*—P1*A*—O3*A*	115.4(2)	O5*A*—P2*A*—P1*A*	106.16(16)
O2*A*—P1*A*—O3*A*	101.3(2)	O6*A*—P2*A*—P1*A*	105.63(16)
O1*A*—P1*A*—P2*A*	110.69(17)	O1*B*—P1*B*—O2*B*	114.2(2)
O2*A*—P1*A*—P2*A*	106.04(16)	O1*B*—P1*B*—O3*B*	108.8(2)
O3*A*—P1*A*—P2*A*	107.17(16)	O2*B*—P1*B*—O3*B*	110.9(2)
O4*A*—P2*A*—O5*A*	117.1(2)	O1*B*—P1*B*—P1*B*^{i}	108.77(16)
O4*A*—P2*A*—O6*A*	108.4(2)	O2*B*—P1*B*—P1*B*^{i}	108.41(16)
O5*A*—P2*A*—O6*A*	110.0(2)	O3*B*—P1*B*—P1*B*^{i}	105.39(16)
O1*A*—P1*A*—P2*A*—O4*A*	77.9(3)	O1*B*—P1*B*—P1*B*^{i}—O1*B*^{i}	180
O2*A*—P1*A*—P2*A*—O4*A*	−156.2(2)	O2*B*—P1*B*—P1*B*^{i}—O1*B*^{i}	55.3(2)
O3*A*—P1*A*—P2*A*—O4*A*	−48.7(2)	O3*B*—P1*B*—P1*B*^{i}—O1*B*^{i}	−63.5(2)
O1*A*—P1*A*—P2*A*—O5*A*	−49.0(2)	O1*B*—P1*B*—P1*B*^{i}—O2*B*^{i}	−55.3(2)
O2*A*—P1*A*—P2*A*—O5*A*	76.8(2)	O2*B*—P1*B*—P1*B*^{i}—O2*B*^{i}	180
O3*A*—P1*A*—P2*A*—O5*A*	−175.6(2)	O3*B*—P1*B*—P1*B*^{i}—O2*B*^{i}	61.2(2)
O1*A*—P1*A*—P2*A*—O6*A*	−165.8(2)	O1*B*—P1*B*—P1*B*^{i}—O3*B*^{i}	63.5(2)
O2*A*—P1*A*—P2*A*—O6*A*	−39.9(2)	O2*B*—P1*B*—P1*B*^{i}—O3*B*^{i}	−61.2(2)
O3*A*—P1*A*—P2*A*—O6*A*	67.6(2)	O3*B*—P1*B*—P1*B*^{i}—O3*B*^{i}	180

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Table S4. Hydrogen-bond geometry (Å, °) for (**1**)-HTP

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
O3*A*—H3*PA*···O1*W*	0.758(15)	1.839(16)	2.5906(12)	171.3(16)
O6*A*—H6*PA*···O1*A*^{I}	0.880(14)	1.674(15)	2.5253(10)	161.9(14)
O2*B*—H2*PB*···O5*A*^{II}	1.12(3)	1.36(3)	2.4745(10)	179(2)
O3*B*—H3*PB*···O2*A*	1.03(2)	1.45(2)	2.4648(12)	167.8(19)
N1*A*—H1*N*···O4*A*	0.927(19)	1.832(18)	2.750(5)	170.3(17)
N3*A*—H3*A*1···O1*B*^{III}	0.87	2.20	3.043(4)	165
N3*A*—H3*A*2···O5*A*^{IV}	0.87	2.51	3.283(4)	148
N3*A*—H3*A*2···O6*A*^{IV}	0.87	2.38	3.142(4)	146
***C*4*A*—H4*A*···O3*A*^{IV}**	0.94	2.59	3.443(4)	151
C*6*A*—H6*A*···O1*A	0.94	2.56	3.296(5)	135
N1*X*—H1*N*···O4*A*	0.861(18)	1.832(18)	2.668(5)	163.2(18)
N3*X*—H3*X*1···O1*B*^{III}	0.87	2.35	3.132(4)	150
N3*X*—H3*X*2···O5*A*^{IV}	0.87	2.23	3.089(4)	170
***C*4*X*—H4*X*···O3*A*^{IV}**	0.94	2.56	3.445(4)	157
C*6*X*—H6*X*···O1*A	0.94	2.47	3.262(4)	142
N1*B*—H1*NB*···O1*B*	0.880(16)	1.797(16)	2.6623(13)	167.2(16)
N3*B*—H3*B*1···O1*A*^{V}	0.972(15)	2.026(16)	2.9571(14)	159.9(12)
N3*B*—H3*B*2···O2*A*^{VI}	1.033(16)	1.974(16)	2.9682(14)	160.6(13)
***C*2*B*—H2*B*···O1*W*^{V}**	0.94	2.41	3.3502(17)	177
***C*4*B*—H4*B*···O2*B*^{IV}**	0.94	2.62	3.3698(17)	137
***C*6*B*—H6*B*···O5*A*^{VII}**	0.94	2.44	3.1996(15)	138
O1*W*—H1*W*1···O3*B*^{VIII}	0.83	1.96	2.786	170
O1*W*—H1*W*2···O4*A*^{I}	0.83	1.94	2.7653(11)	172

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

Table S5. Hydrogen-bond geometry (Å, °) for (**1**)-LTP

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
O3*A*—H3*PA*···O1*W*	0.859(16)	1.725(16)	2.580	173.2(16)
O6*A*—H6*PA*···O4*C*^{I}	0.749(17)	1.795(18)	2.5199(10)	162.7(18)
O2*B*—H2*PB*···O2*A*	0.80(2)	1.67(2)	2.4485(10)	165(2)
O3*B*—H3*PB*···O2*C*	1.09(2)	1.37(2)	2.4658(10)	178(2)
O5*B*—H5*PB*···O5*A*	1.19(3)	1.26(3)	2.4551(10)	177(2)
O6*B*—H6*PB*···O5*C*	0.81(2)	1.66(2)	2.4609(10)	166(2)
O3*C*—H3*PC*···O1*A*^{II}	0.757(18)	1.788(19)	2.5217(10)	162.9(19)
O6*C*—H6*PC*···O2*W*	0.834(16)	1.740(16)	2.570	173.4(16)
N1*A*—H1*NA*···O4*A*	0.853(14)	1.857(15)	2.6964(11)	167.5(14)
N3*A*—H3*A*1···O6*A*^{III}	0.825(15)	2.312(16)	3.0766(12)	154.4(14)
N3*A*—H3*A*2···O4*B*^{IV}	0.859(15)	2.197(15)	3.0500(12)	171.8(13)
***C*4*A*—H4*A*···O6*A*^{III}**	0.95	2.60	3.3431(13)	135
C*6*A*—H6*A*···O1*A	0.95	2.52	3.2767(12)	137
N1*B*—H1*NB*···O1*B*	0.884(13)	1.774(13)	2.6551(11)	174.7(13)
N3*B*—H3*B*1···O5*C*^{III}	0.941(14)	2.050(14)	2.9689(12)	165.0(12)
N3*B*—H3*B*2···O4*C*^{V}	0.975(17)	2.039(18)	2.9723(11)	159.5(14)
***C*2*B*—H2*B*···O2*W*^{V}**	0.95	2.35	3.3016(13)	176
***C*4*B*—H4*B*···O3*B*^{III}**	0.95	2.56	3.2935(12)	135
***C*6*B*—H6*B*···O2*C*^{VI}**	0.95	2.48	3.2432(13)	137
N1*C*—H1*NC*···O1*C*	0.837(13)	1.875(13)	2.7046(11)	170.9(13)
N3*C*—H3*C*1···O2*C*^{VII}	0.837(14)	2.191(14)	3.0106(12)	166.3(14)
N3*C*—H3*C*2···O1*B*^{VIII}	0.878(13)	2.198(13)	3.0668(13)	169.8(11)
***C*2*C*—H2*C*···O3*B*^{VIII}**	0.95	2.53	3.4654(12)	167
***C*4*C*—H4*C*···O6*C*^{VII}**	0.95	2.53	3.4149(13)	155
C*6*C*—H6*C*···O4*C	0.95	2.47	3.2576(13)	140
N1*D*—H1*ND*···O4*B*	0.855(15)	1.842(15)	2.6675(11)	161.7(15)
N3*D*—H3*D*1···O2*A*^{VII}	0.946(15)	2.021(15)	2.9490(12)	166.6(13)
N3*D*—H3*D*2···O1*A*^{IX}	0.981(17)	1.969(17)	2.9131(11)	160.7(13)
***C*2*D*—H2*D*···O1*W*^{IX}**	0.95	2.40	3.3488(14)	174
***C*4*D*—H4*D*···O5*B*^{VII}**	0.95	2.60	3.3874(12)	140
***C*6*D*—H6*D*···O5*A*^{X}**	0.95	2.40	3.1206(13)	133

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

Table S6. Hydrogen-bond geometry (Å, °) for (**2**)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*A*—H2*PA*···O1*B*^{I}	0.73(7)	1.77(7)	2.501(5)	179(9)
O3*A*—H3*PA*···O4*A*^{II}	0.99(7)	1.56(7)	2.538(5)	169(6)
O6*A*—H6*PA*···O2*B*	0.73(7)	1.81(7)	2.532(5)	170(8)
O3*B*—H3*PB*···O5*A*	0.73(10)	1.90(10)	2.607(5)	162(11)
N1*A*$^{A—H1NA}$*A*···O1*A*^{III}	0.88	1.93	2.804(9)	173
N3*A*$^{A—H3A1}$*A*···O2*A*	0.88	2.05	2.883(9)	157
N3*A*$^{A—H3A2}$*A*···O4*A*^{IV}	0.88	1.93	2.808(9)	173
*C*2*A*$^{A—H2A}$*A*···O6*A*	0.95	2.45	3.398(17)	178
*C*6*A*$^{A—H6A}$*A*···O3*A*^{V}	0.95	2.47	3.093(13)	123
N1*X*$^{B—H1NX}$*B*···O4*A*^{IV}	0.88	1.91	2.779(13)	170
N3*X*$^{B—H3X1}$*B*···O6*A*	0.88	2.10	2.962(12)	167
N3*X*$^{B—H3X2}$*B*···O1*A*^{III}	0.88	1.94	2.808(13)	168
N1*B*$^{B—H1NB}$*B*···O5*A*^{VI}	0.80(7)	1.90(7)	2.683(6)	168(7)
N3*B*$^{B—H3B1}$*B*···O2*B*	0.91(7)	2.05(7)	2.928(6)	162(6)
N3*B*$^{B—H3B2}$*B*···O1*B*^{VII}	0.81(6)	2.15(6)	2.937(6)	165(6)

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

Table S7. Temperature dependence of sample composition during (**1**)→(**2**) dehydration as refined by Rietveld method (unknown decomposition product content is not taken into account).

Temperature, K	(**1**)-LTP, %	(**1**)-HTP, %	(**2**), %
110	100	0	0
295	0	98	2
300	0	95	5
305	0	91	9
310	0	86	14
315*	0	79	21
320*	0	70	30
325*	0	61	39
330*	0	50	50
330 (after 3 hours)*	0	0	100

* - unknown impurity is present in the sample

Table S8. Selected geometric parameters (Å, °) for (**3**)

P1*A*—O1*A*	1.5229(10)	P1*B*—O1*B*	1.5012(10)
P1*A*—O2*A*	1.5259(10)	P1*B*—O2*B*	1.5165(10)
P1*A*—O3*A*	1.5378(10)	P1*B*—O3*B*	1.5760(10)
P1*A*—P1*A*^{i}	2.1884(7)	P1*B*—P1*B*^{ii}	2.1922(7)
O1*A*—P1*A*—O2*A*	112.45(6)	O1*B*—P1*B*—O2*B*	116.57(6)
O1*A*—P1*A*—O3*A*	112.00(6)	O1*B*—P1*B*—O3*B*	111.40(6)
O2*A*—P1*A*—O3*A*	110.35(6)	O2*B*—P1*B*—O3*B*	106.42(6)
O1*A*—P1*A*—P1*A*^{i}	107.84(5)	O1*B*—P1*B*—P1*B*^{ii}	108.96(5)
O2*A*—P1*A*—P1*A*^{i}	106.73(4)	O2*B*—P1*B*—P1*B*^{ii}	108.00(4)
O3*A*—P1*A*—P1*A*^{i}	107.16(5)	O3*B*—P1*B*—P1*B*^{ii}	104.79(4)
O1*A*—P1*A*—P1*A*^{i}—O1*A*^{i}	180	O1*B*—P1*B*—P1*B*^{ii}—O1*B*^{ii}	180
O2*A*—P1*A*—P1*A*^{i}—O1*A*^{i}	58.96(6)	O2*B*—P1*B*—P1*B*^{ii}—O1*B*^{ii}	52.48(7)
O3*A*—P1*A*—P1*A*^{i}—O1*A*^{i}	−59.26(7)	O3*B*—P1*B*—P1*B*^{ii}—O1*B*^{ii}	−60.67(6)
O1*A*—P1*A*—P1*A*^{i}—O2*A*^{i}	−58.96(6)	O1*B*—P1*B*—P1*B*^{ii}—O2*B*^{ii}	−52.48(7)
O2*A*—P1*A*—P1*A*^{i}—O2*A*^{i}	180	O2*B*—P1*B*—P1*B*^{ii}—O2*B*^{ii}	180
O3*A*—P1*A*—P1*A*^{i}—O2*A*^{i}	61.78(6)	O3*B*—P1*B*—P1*B*^{ii}—O2*B*^{ii}	66.84(6)
O1*A*—P1*A*—P1*A*^{i}—O3*A*^{i}	59.26(7)	O1*B*—P1*B*—P1*B*^{ii}—O3*B*^{ii}	60.67(6)
O2*A*—P1*A*—P1*A*^{i}—O3*A*^{i}	−61.78(6)	O2*B*—P1*B*—P1*B*^{ii}—O3*B*^{ii}	−66.84(6)
O3*A*—P1*A*—P1*A*^{i}—O3*A*^{i}	180	O3*B*—P1*B*—P1*B*^{ii}—O3*B*^{ii}	180

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*, −*y*+1, −*z*+1.

Table S9. Selected geometric parameters (Å, °) for (**4**)

P1—O1	1.5102(19)	P2—O4	1.501 (2)
P1—O2	1.5227(19)	P2—O5	1.515(2)
P1—O3	1.5587(19)	P2—O6	1.5678(19)
P1—P2	2.1763(9)		
O1—P1—O2	115.49(11)	O4—P2—O5	114.61(11)
O1—P1—O3	108.47(10)	O4—P2—O6	109.03(11)
O2—P1—O3	111.18(11)	O5—P2—O6	111.92(11)
O1—P1—P2	110.06(8)	O4—P2—P1	107.30(8)
O2—P1—P2	104.16(8)	O5—P2—P1	110.80(8)
O3—P1—P2	107.13(8)	O6—P2—P1	102.39(9)
O1—P1—P2—O4	73.55(12)	O3—P1—P2—O5	65.49(12)
O2—P1—P2—O4	−50.83(11)	O1—P1—P2—O6	−171.74(12)
O3—P1—P2—O4	−168.71(12)	O2—P1—P2—O6	63.88(12)
O1—P1—P2—O5	−52.24(12)	O3—P1—P2—O6	−54.00(12)
O2—P1—P2—O5	−176.63(11)		

Table S10. Hydrogen-bond geometry (Å, °) for (**3**)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*B*—H3*PB*···O1*A*	0.90(2)	1.64(2)	2.5314(14)	170(2)
N1*A*—H1*NA*···O2*A*	0.95(2)	1.63(2)	2.5671(16)	169(2)
N3*A*—H3*A*1···O2*B*^{III}	0.87(2)	2.13(2)	2.9762(17)	164.3(18)
N3*A*—H3*A*2···O1*B*^{IV}	0.87(2)	2.12(2)	2.9606(17)	162.6(17)
*C*2*A*—H2*A*···O1*A*^{I}	0.95	2.41	3.1899(18)	140
*C*4*A*—H4*A*···O1*B*^{IV}	0.95	2.50	3.2769(18)	139
N1*B*—H1*NB*···O3*A*	1.08(2)	1.45(3)	2.5206(16)	174(2)
N3*B*—H3*B*1···O2*B*^{I}	0.85(2)	2.59(2)	3.3158(18)	144.2(16)
N3*B*—H3*B*1···O3*B*^{I}	0.85(2)	2.55(2)	3.3002(18)	148.7(16)
N3*B*—H3*B*2···O1*W*^{V}	0.86(2)	2.00(2)	2.8503(18)	168.0(18)
*C*2*B*—H2*B*···O3*B*^{I}	0.95	2.37	3.2427(19)	152
N1*C*—H1*NC*···O2*B*	0.95(2)	1.67(2)	2.6138(16)	171.7(19)
N3*C*—H3*C*1···O1*W*^{VI}	0.83(2)	2.05(2)	2.8646(19)	167.9(19)
N3*C*—H3*C*2···O3*A*^{II}	0.86(2)	2.07(2)	2.9063(19)	162.4(19)
*C*2*C*—H2*C*···O1*A*^{II}	0.95	2.48	3.4217(19)	174
O1*W*—H1*W*1···O1*B*	0.84	1.87	2.7058(14)	176
O1*W*—H1*W*2···O2*A*	0.84	1.88	2.7155(14)	177

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*, −*y*+1, −*z*+1; (iii) *x*+1, *y*, *z*; (iv) *x*+1, −*y*+1/2, *z*+1/2; (v) −*x*+1, *y*+1/2, −*z*+1/2; (vi) −*x*, *y*+1/2, −*z*+3/2.

Table S11. Hydrogen-bond geometry (Å, °) for (**4**)

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
O3—H3*P*···N1*A*	0.84	1.77	2.556(3)	155
O6—H6*P*···O1^{I}	0.84	1.79	2.549(3)	149
N3*A*—H3*A*1···O5^{II}	0.90(5)	2.23(4)	3.083(3)	159(4)
N3*A*—H3*A*2···O2^{I}	0.89(4)	2.08(4)	2.934(3)	161(3)
***C*4*A*—H4*A*···O3^{III}**	0.95	2.58	3.176(4)	121
***C*5*A*—H5*A*···O3^{III}**	0.95	2.59	3.178(4)	121
N1*B*—H1*NB*···O2^{I}	1.05(4)	1.54(4)	2.589(3)	175(4)
N3*B*—H3*B*1···O4^{IV}	0.87(4)	1.93(4)	2.783(3)	168(3)
N3*B*—H3*B*2···O2	0.84(4)	2.13(4)	2.945(3)	165(4)
***C*2*B*—H2*B*···O6**	0.95	2.39	3.272(3)	154
N1*C*—H1*NC*···O5^{V}	0.92(4)	1.69(4)	2.609(3)	174(4)
N3*C*—H3*C*1···O4^{VI}	0.83(4)	2.01(4)	2.812(3)	162(4)
N3*C*—H3*C*2···O5	0.95(5)	2.09(4)	3.005(3)	161(4)
***C*2*C*—H2*C*···O1**	0.95	2.31	3.154(3)	147

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

Table S12. Temperature dependence of sample composition during (**3**)→(**4**) dehydration as refined by Rietveld method (unknown decomposition product content is not taken into account).

Temperature, K	(**3**), %	(**4**), %
100	100	0
295	100	0
300	100	0
305	100	0
310	100	0
315	100	0
320	100	0
325	100	0
330	100	0
335	96	4
340	91	9
345	84	16
350	74	26
355*	57	43
360*	32	68
360 (after 30 minutes)*	19	81

* - unknown impurity is present in the sample

Table S13. Selected geometric parameters (Å, °) for (**5**)

P1—O1	1.5012(18)	P2—O4	1.5022(19)
P1—O2	1.5250(16)	P2—O5	1.5217(17)
P1—O3	1.581(2)	P2—O6	1.5811(18)
P1—P2	2.1914(11)		
O1—P1—O2	116.85(10)	O4—P2—O5	115.90(10)
O1—P1—O3	111.58(10)	O4—P2—O6	109.39(11)
O2—P1—O3	106.78(10)	O5—P2—O6	108.90(10)
O1—P1—P2	105.22(7)	O4—P2—P1	106.53(8)
O2—P1—P2	108.87(7)	O5—P2—P1	107.23(8)
O3—P1—P2	107.16(7)	O6—P2—P1	108.65(7)
O1—P1—P2—O4	46.50 (11)	O3—P1—P2—O5	40.69(11)
O2—P1—P2—O4	−79.49(11)	O1—P1—P2—O6	164.25(11)
O3—P1—P2—O4	165.37(10)	O2—P1—P2—O6	38.27(12)
O1—P1—P2—O5	−78.19(11)	O3—P1—P2—O6	−76.88(11)
O2—P1—P2—O5	155.83(11)		

Table S14. Hydrogen-bond geometry (Å, °) for (**5**)

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
O3—H3*P*···O5^{I}	0.82(4)	1.77(4)	2.582(3)	168(4)
O6—H6*P*···O2^{II}	0.92(5)	1.65(5)	2.573(3)	176(4)
N1—H1*N*···O2	0.91(4)	1.73(4)	2.630(3)	174(3)
N3—H3*N*2···O1^{III}	0.91	1.80	2.704(3)	171
N3—H3*N*1···O4^{IV}	0.91	1.80	2.699(3)	167
N3—H3*C*···O5^{V}	0.91	1.82	2.718(3)	171
C2—H2···O1^{III}	0.95	2.39	3.131(3)	134
C4—H4···O6^{IV}	0.95	2.46	3.375(3)	162
C5—H5···O5^{VI}	0.95	2.43	3.381(3)	174

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