Supporting information

Rietveld refinement was carried out using the program GSAS.[1] Peak profiles of reflections in the range 2θ = 3.03 - 42.26º were modelled with a split-type pseudo-Voigt peak profile function.[2,3] The March-Dollase function was used to correct for preferred orientation.[4] The background was modelled by a Chebyshev polynomial of the first kind with 20 parameters. The U_{iso} values of identical atom types were coupled and a small damping was applied during all refinement stages.

Apart from the hydrogens of the water molecules and the hydrogens at the exocyclic nitrogens of the melamines, nine hydrogens had to be positioned to neutralize the charge. In the crystal-structure models found with Organa, two (of the three) endocyclic nitrogens of each melamine moiety are at a hydrogen-bonding distance to NH_2 groups of neighboring melamine moieties (see Table SI 1) and hardly can accommodate extra hydrogens. The remaining endocyclic nitrogen of each of the four (independent) melamines has a short contact with an oxygen atom of an orthophosphate, suggesting a hydrogen bond and a single protonation of the melamines (see the discussion of the typical bonding characteristics in melamine phosphates below). The presence of two dihydrogenphosphates and one monohydrogenphosphate in the asymmetric part of the unit cell, as concluded from the solid-state NMR results, is also consistent with a single protonation of the melamines. The five remaining hydrogens had to be distributed over the three non-equivalent orthophosphates. During the later stages of the refinement, an analysis of the short contacts led to the identification of five potential hydrogen bridges between the orthophosphate moieties (see Table SI 1), but it was not possible to establish a more detailed bonding of these hydrogens within the bridges.

In order to avoid distortion of the model, in the refinement process all bond lengths and bond angles in the molecules were restrained using ideal values and associated s.u's.[5] As ideal restraint values for melamine bond distances and angles, averages of corresponding quantities were used, calculated from MP, MPy, MPoly and other melamine salts with a positively charged (+1) melamine moiety found in the CSD.[6] Since no assumption was made about the protonation of orthophosphates, averages of single (1.57 Å) and double (1.46 Å) bonds[7] were used as ideal

restraint values for all P-O distances. The ideal tetrahedral geometry (109.5º) was used to restrain the O-P-O bond angles. The non-hydrogen atom s.u.'s of the restraints in melamine were taken as 1% and 5% for bond distances and bond angles, respectively, and 5% for both distances and angles in orthophosphates. For hydrogen atoms at melamine and water moieties, the respective s.u.'s were taken as 0.01% and 0.05%. Hydrogens on phosphates were calculated. Planar-group restraints[5] were imposed to the melamines with s.u.'s being 0.05Å for all melamine atoms. Initially, strong restraints (with weighting factor f = 1000, defined in reference 5) were applied and reduced stepwise until finally the restraints were removed (f = 0). As the restraints became smaller, the P-O bond distances at the assumed hydrogen bridges became different, so of each particular bridge suggesting which of the oxygens was likely to accommodate the hydrogen and which rather had a double-bond character. In this way the remaining five hydrogens were positioned, resulting in the protonation scheme shown in Figure 6. After completion of the protonation scheme, the ideal restraint values for bond distances were changed in accordance with their proposed bonding to distinguish between single and double bonds[7], respectively. The corresponding s.u.'s were taken as 1%. It should be noted that refinement of other protonation schemes for these five hydrogens led to similar results (R_{wp} differ less than 0.5%) so Rietveld refinement is not decisive in this respect.

The structure model obtained after the unrestrained refinement ($R_{wp} \sim 0.076$) was not completely satisfactory because of some minor distortion of bond lengths and bond angles, especially in the melamine moieties and therefore it was decided to keep soft restraints ($f \sim 10$).[8] The R_{wp} obtained after the final refinement (0.080) was close enough to the limiting full pattern decomposition value (0.074) obtained using the structural-model-independent Le Bail profile fitting.[9] For completeness, it is noted that attempts to refine the model in space group P1 and application of more complex preferred orientation correction formulas did not lead to any significant improvement of the results.

Table SI 1 Hydrogen-bonding geometry (Å, º). Potential hydrogen bonds were calculated with PLATON[10] up to a 4 Å limit of donor-acceptor distances for the weak hydrogen bonds.[11]

Donor --- H....Acceptor	D – H	H...A	D...A	D - H...A
N(1) -- H(10) .. O(76)^{i}	0.861(4)	1.999(3)	2.839(3)	164.7(4)
N(1) -- H(11) .. O(62)^{ii}	0.859(4)	2.296(14)	3.090(13)	153.6(4)
N(2) -- H(12) .. N(33)^{i}	0.860(4)	2.059(10)	2.914(9)	172.0(4)
N(2) -- H(13) .. O(68)	0.860(2)	2.429(13)	3.062(12)	131.0(6)
N(2) -- H(13) .. O(72)^{iii}	0.860(2)	2.642(14)	3.322(14)	136.8(6)
N(6) -- H(14) .. N(34)^{iv}	0.860(4)	2.076(9)	2.931(9)	172.7(4)
N(6) -- H(14) .. N(36)^{iv}	0.860(4)	2.901(4)	3.547(3)	133.4(3)
N(6) -- H(15) .. O(65)^{v}	0.860(2)	2.416(13)	3.074(13)	133.7(6)
N(6) -- H(15) .. O(75)^{iii}	0.860(2)	2.549(9)	3.163(10)	129.1(5)
N(16) -- H(25) .. O(73)^{vi}	0.860(4)	2.342(13)	3.079(13)	144.0(4)
N(16) -- H(26) .. O(69)^{vii}	0.860(4)	2.329(5)	2.989(5)	133.7(3)
N(17) -- H(27) .. N(48)^{viii}	0.861(4)	2.084(10)	2.943(9)	175.9(4)
N(17) -- H(28) .. O(73)^{ii}	0.860(3)	2.612(13)	3.192(13)	125.8(5)
N(17) -- H(28) .. O(77)^{ix}	0.860(3)	2.755(4)	3.379(3)	130.7(4)
N(21) -- H(29) .. N(49)^{x}	0.860(4)	2.171(9)	3.020(9)	169.5(4)
N(21) -- H(30) .. O(74)^{ii}	0.860(3)	2.414(6)	3.120(4)	139.8(4)
N(21) -- H(30) .. O(78)^{i}	0.860(3)	2.351(3)	2.959(2)	128.0(4)
N(31) -- H(40) .. O(65)^{i}	0.860(4)	2.108(13)	2.923(13)	157.9(5)
N(31) -- H(41) .. O(68)^{i}	0.860(4)	2.043(13)	2.865(12)	159.6(5)
N(32) -- H(42) .. N(2)^{i}	0.860(4)	2.923(3)	3.586(2)	135.3(3)
N(32) -- H(42) .. N(3)^{i}	0.860(4)	2.019(9)	2.870(9)	169.7(4)
N(32) -- H(43) .. O(62)^{iii}	0.860(3)	2.560(14)	3.279(14)	141.8(6)
N(36) -- H(44) .. N(4)^{iv}	0.860(4)	2.021(9)	2.875(9)	171.6(4)

N(36) -- H(44) .. N(6)^{iv}	0.860(4)	2.880(3)	3.547(3)	135.8(3)
N(36) -- H(45) .. O(67)^{iii}	0.860(3)	2.861(13)	3.480(13)	130.4(5)
N(36) -- H(45) .. O(76)^{v}	0.860(3)	2.337(4)	3.014(2)	135.8(5)
N(46) -- H(55) .. O(78)^{xi}	0.860(4)	2.049(3)	2.891(3)	165.8(3)
N(46) -- H(56) .. O(77)^{xi}	0.860(4)	2.070(3)	2.869(3)	154.3(3)
N(47) -- H(57) .. N(18)^{viii}	0.859(4)	2.048(9)	2.905(9)	175.3(4)
N(47) -- H(58) .. O(70)^{ii}	0.860(3)	1.949(8)	2.802(8)	171.1(5)
N(51) -- H(59) .. N(19)^{x}	0.859(4)	2.109(9)	2.964(9)	172.8(4)
N(51) -- H(60) .. O(63)^{ii}	0.860(3)	2.724(13)	3.402(13)	136.8(5)
N(51) -- H(60) .. O(64)^{ii}	0.860(3)	2.376(12)	3.220(12)	166.7(5)
N(5) -- H(79) .. O(72)^{iii}	0.861(3)	1.973(15)	2.811(15)	164.1(7)
N(5) -- H(79) .. O(75)^{iii}	0.861(3)	2.494(9)	3.110(10)	129.1(6)
N(35) -- H(80) .. O(67)^{iii}	0.861(3)	1.842(15)	2.694(15)	170.4(7)
N(35) -- H(80) .. O(75)^{iii}	0.861(3)	2.760(9)	3.334(10)	125.5(6)
N(50) -- H(81) .. O(63)^{ii}	0.861(3)	1.926(13)	2.782(13)	172.5(7)
N(20) -- H(82) .. O(73)^{ii}	0.861(3)	2.603(13)	3.194(12)	126.8(5)
N(20) -- H(82) .. O(74)^{ii}	0.861(3)	1.837(4)	2.673(4)	163.2(6)
O(69) -- H(83) .. O(72)^{iii}	0.9002	1.6669	2.566(12)	176.76
O(69) -- H(83) .. O(76)^{xii}	0.9002	2.8612	3.304(6)	111.88
O(74) -- H(84) .. O(62)	0.9003	1.6506	2.550(13)	176.64
O(74) -- H(84) .. O(63)	0.9003	2.8416	3.394(13)	120.98
O(75) -- H(85) .. O(67)^{xiii}	0.9001	1.6534	2.549(11)	172.86
O(75) -- H(85) .. N(35)^{xiv}	0.9001	2.8216	3.334(10)	117.49
O(64) -- H(86) .. O(73)	0.9001	1.6175	2.517(12)	177.53
O(70) -- H(87) .. O(63)^{ii}	0.9001	1.6518	2.551(13)	176.34
O(70) -- H(87) .. N(47)^{xiv}	0.9001	2.9397	2.802(8)	72.40
O(76) -- H(88) .. O(69)^{xi}	0.860(4)	2.741(6)	3.304(6)	124.4(3)
O(76) -- H(88) .. O(72)	0.860(4)	2.044(12)	2.805(11)	147.1(5)
O(77) -- H(89) .. O(63)	0.860(4)	2.765(13)	3.278(12)	119.8(4)
O(77) -- H(89) .. O(65)	0.860(4)	1.751(13)	2.598(13)	168.1(6)

O(77) -- H(90) .. O(67)^{xiv}	0.860(4)	2.183(12)	2.978(12)	153.7(5)
O(77) -- H(90) .. O(69)^{xiv}	0.860(4)	2.611(6)	3.257(5)	132.8(3)
O(77) -- H(90) .. O(76)	0.860(4)	2.678(5)	2.985(3)	102.5(3)
O(76) -- H(91) .. O(77)	0.860(3)	2.713(5)	2.985(3)	100.0(3)
O(76) -- H(91) .. O(78)	0.860(3)	2.491(3)	3.269(2)	150.9(5)
O(78) -- H(92) .. O(62)^{iii}	0.860(3)	2.652(12)	3.211(12)	123.7(3)
O(78) -- H(92) .. O(64)^{iii}	0.860(3)	2.247(7)	2.950(7)	139.0(4)
O(78) -- H(92) .. O(76)	0.860(3)	2.737(3)	3.269(2)	121.4(2)
O(78) -- H(93) .. O(68)	0.860(3)	2.008(12)	2.820(12)	156.9(4)

* Symmetry codes: (i) 1-x,1-y,1-z; (ii) 2-x,1-y,1-z; (iii) -1+x,y,z; (iv) -x,1-y,-z; (v) -1+x,y,-1+z; (vi) -1+x,-1+y,z; (vii) x,-1+y,z; (viii) 2-x,-y,1-z; (ix) 2-x,1-y,2-z (x) 1-x,-y,-z; (xi) x,-1+y,-1+z; (xii) x,y,-1+z; (xiii) 1+x,y,z; (xiv) x,y,1+z; (xv) -1+x,y,1+z.

References

(1) Larson, A.C.; Von Dreele, R. B. General Structure Analysis System (GSAS). Report LAUR 86-748 Los Alamos National Laboratory, NM 87545, USA, **1994**.

(2) Van Laar, B.; Yelon, W.B. *J. Appl. Cryst.* **1984***,17*, 47.

(3) Finger, L.W.; Cox, D.E.; Jephcoat, A.P. *J. Appl. Cryst.* **1994**, *27*, 892.

(4) Dollase, W. A. *J. Appl. Cryst.* **1986**, *19*, 267.

(5) Von Dreele, R.B. *J. Appl. Cryst.* **1999**, *32*, 1084.

(6) Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31.

(7) Colvin, M. E.; Evleth, E.; Akacem, Y. *J. Am. Chem. Soc.* **1995**, *117*, 4357.

(8) Nowell, H.; Afftield, J. P.; Cole, J. C., *Acta Crys. Sect. B.* **2002**, *58*, 835.

(9) Le Bail, A.; Duray, H.; Fourquet, J.L. *Mat. Res. Bull.* **1988**, *23*, 447.

(10) Spek, A.L. PLATON. Utrecht University, The Netherlands, **2001**.

(11) Giacovazzo, G.; Monaco, H. L.; Artioli, G.; Viterbo, D.; Ferraris, G.; Gilli, G.; Zanotti, G.; Gatti, M. *Fundamentals of Crystallography 2nd ed.*; Oxford University Press: New York, 2002, p. 592.