Supplementary Information

Same but different: structural diversity of cytidine 5′-monophosphate (CMP) (an)hydrates

Oskar Kaszubowski[a]*, Katarzyna Ślepokura[a], Jakub Wojciechowski[b]

[a] University of Wrocław, Faculty of Chemistry, 14. F. Joliot-Curie, 50-383 Wrocław, Poland

[b] Rigaku Europe SE, 167 Hugenottenallee, 63263 Neu-Isenburg, Germany

* Corresponding author; email: oskar.kaszubowski@uwr.edu.pl

TABLE OF CONTENTS

Table S1. Crystal data, experimental and refinement details for triclinic crystals.

	CMP·2H$_2$O (**I**)	CMP·H$_2$O (**II**)	CMP·0.5H$_2$O (**III**)	CMP (**IV**)
Chemical formula	C$_9$H$_{14}$N$_3$O$_8$P·2H$_2$O	C$_9$H$_{14}$N$_3$O$_8$P·H$_2$O	C$_9$H$_{14}$N$_3$O$_8$P·0.5H$_2$O	C$_9$H$_{14}$N$_3$O$_8$P
M_r	359.23	341.22	332.21	323.20
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*1	*P*1	*P*1	*P*1
a, *b*, *c* (Å)	4.8019(6), 8.3731(9), 9.5127(15)	4.7963(8), 8.247(3), 9.040(3)	4.7974(8), 8.2932(10), 16.861(3)	4.7896(8), 8.1312(14), 8.4477(12)
α, β, γ (°)	76.71(2), 80.38(2), 86.60(2)	70.65(2), 86.70(3), 84.89(2)	101.48(2), 92.04(2), 95.55(2)	76.85(2), 79.75(2), 83.99(2)
V (Å^3)	366.91(9)	335.89(18)	653.29(18)	314.55(9)
Z	1	1	2	1
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
T (K)	100	100	100	100
μ (mm^{-1})	2.25	2.37	2.39	2.43
Crystal size (mm)	0.10 × 0.04 × 0.01	0.08 × 0.03 × 0.02	0.10 × 0.04 × 0.01	0.06 × 0.03 × 0.03
D_c (g·cm^{-3})	1.626	1.687	1.689	1.706
Correction for absorption effect	Multi-scan	Multi-scan	Multi-scan	Gaussian
T_{min}, T_{max}	0.948, 1.000	0.889, 1.000	0.797, 1.000	0.915, 0.996
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4863, 2088, 2060	3244, 1600, 1215	6382, 3095, 2725	3810, 1640, 1592
R_{int}	0.014	0.033	0.031	0.021
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.626	0.592	0.628	0.624
$R[F^2 > 2\sigma(F^2)]$, wR(F^2), S	0.027, 0.075, 1.06	0.098, 0.285, 1.17	0.074, 0.206, 1.06	0.049, 0.137, 1.10
No. of reflections	2088	1600	3095	1640
No. of parameters	217	203	396	194
No. of reistrants	10	12	6	3
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.39	0.98, −0.59	0.90, −0.61	0.56, −0.50
Flack Parameter	−0.01(2)	−0.18(12)	0.16(5)	0.03(4)
CCDC No.	2385027	2385028	2385029	2385030

Table S2. Crystal data, experimental and refinement details for monoclinic crystals.

	CMP (**VI**)
Chemical formula	$C_9H_{14}N_3O_8P$
M_r	323.20
Crystal system	Monoclinic
Space group	$P2_1$
a, b, c (Å)	4.843(4), 8.646(8), 15.726(2)
α, β, γ (°)	90, 93.68(1), 90
V (Å^3)	657.1(8)
Z	2
Radiation type	200 kV electron beam, λ = 0.0251 Å
T (K)	100
D_c (g·cm^{-3})	1.633
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3305, 2214, 1583
R_{int}	0.126
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.625
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.132, 0.350, 1.15
CCDC No.	2385031

Selected crystal data for CMP·H_2O (**V**) reported at CCDC (WIWZOV[1]):

	CMP·H_2O (WIWZOV) (**V**)
Chemical formula	$C_9H_{14}N_3O_8P\cdot H_2O$
M_r	341.22
Crystal system	Monoclinic
Space group	$P2_1$
a, b, c (Å)	4.8521(1), 8.2910(2), 17.0486(5)
α, β, γ (°)	90, 90.465(2), 90
V (Å^3)	685.82(3)
Z	2
T (K)	150

Table S3. Crystal data, experimental and refinement details for orthorhombic crystals.

	CMP·1.5H$_2$O (**VII_LT**)	CMP·1.5H$_2$O (**VII_HT**)	CMP·H$_2$O (**VIII**)	CMP (**IX**)
Chemical formula	C$_9$H$_{14}$N$_3$O$_8$P·1.5H$_2$O	C$_9$H$_{14}$N$_3$O$_8$P·1.5H$_2$O	C$_9$H$_{14}$N$_3$O$_8$P·H$_2$O	C$_9$H$_{14}$N$_3$O$_8$P
M_r	350.22	350.22	341.22	323.20
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12$	$P2_12_12_1$	$P2_12_12_1$
a, b, c (Å)	8.4220(14), 35.163(6), 9.693(2)	8.4629(16), 35.212(7), 4.8658(8)	8.367(2), 34.158(7), 4.8236(9)	8.338(2), 31.318(7), 4.8912(10)
α, β, γ (°)	90, 90, 90	90, 90, 90	90, 90, 90	90, 90, 90
V (Å^3)	2870.5(9)	1450.0(5)	1378.6(5)	1277.2(5)
Z	8	4	4	4
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
T (K)	100	200	100	100
μ (mm^{-1})	2.26	2.24	2.31	2.40
Crystal size (mm)	0.14 × 0.13 × 0.02	0.14 × 0.13 × 0.02	0.14 × 0.13 × 0.02	0.14 × 0.13 × 0.02
D_c (g·cm^{-3})	1.621	1.604	1.644	1.681
Correction for absorption effect	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{min}, T_{max}	0.721, 1.000	0.610, 1.000	0.691, 1.000	0.719, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19770, 5485, 4917	10362, 2812, 2712	10019, 2682, 2598	12419, 2594, 2498
R_{int}	0.025	0.026	0.033	0.043
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.628	0.626	0.628	0.628
$R[F^2 > 2\sigma(F^2)]$, wR(F^2), S	0.046, 0.146, 1.15	0.042, 0.103, 1.09	0.075, 0.211, 1.12	0.120, 0.318, 1.10
No. of reflections	5485	2812	2682	2594
No. of parameters	422	231	201	194
No. of reistrants	9	9	6	−
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.38	0.55, −0.30	0.72, −0.55	1.31, −0.73
Flack Parameter	−0.004(14)	0.008(11)	0.037(19)	0.105(16)
CCDC No.	2385032	2385033	2385034	2385035

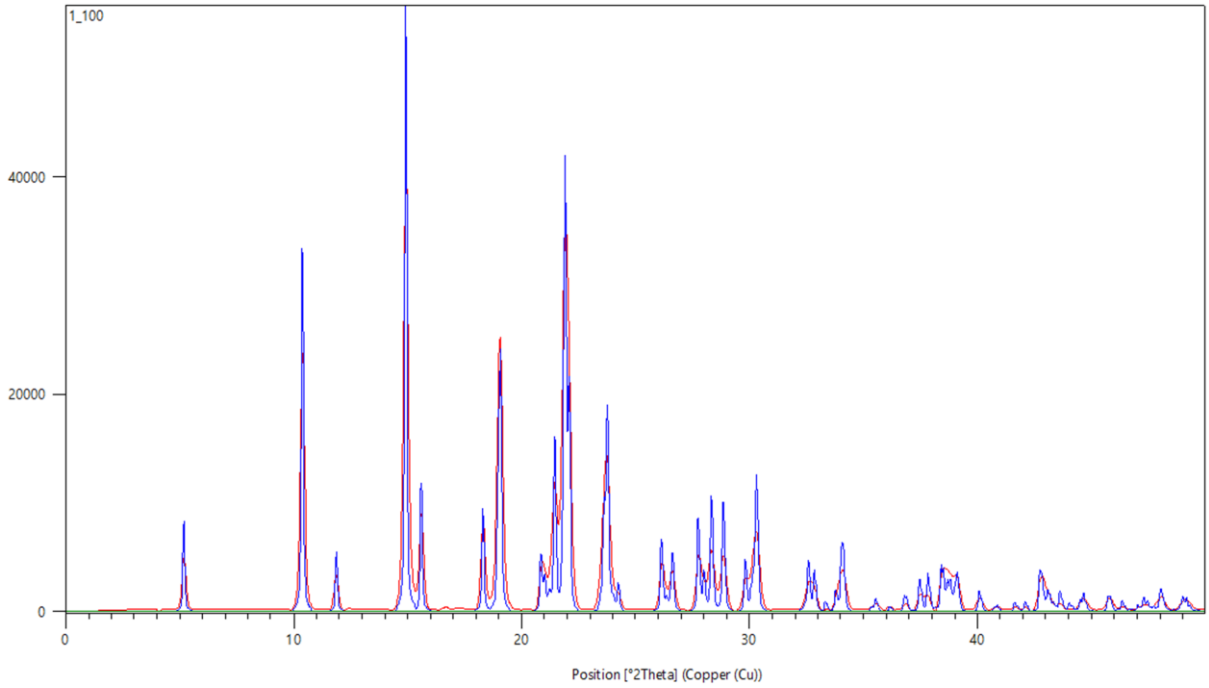

Figure S1. Comparison of experimental powder diffraction pattern of commercially available (red) and simulated powder diffraction pattern of WIWZOV (blue) monoclinic monohydrate.

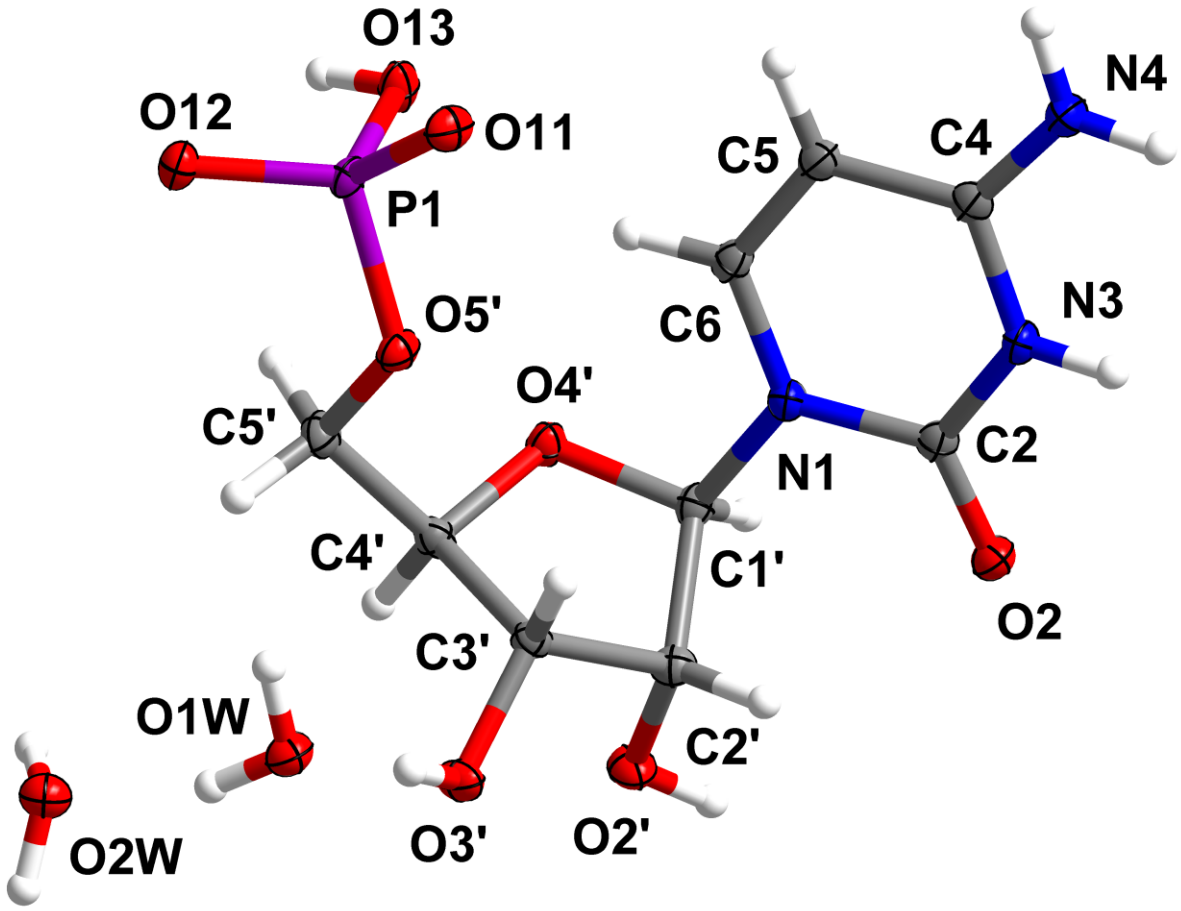

Figure S2. Asymmetric unit of triclinic crystal CMP·2H$_2$O (**I**). Displacement ellipsoids are shown at the 50% probability level.

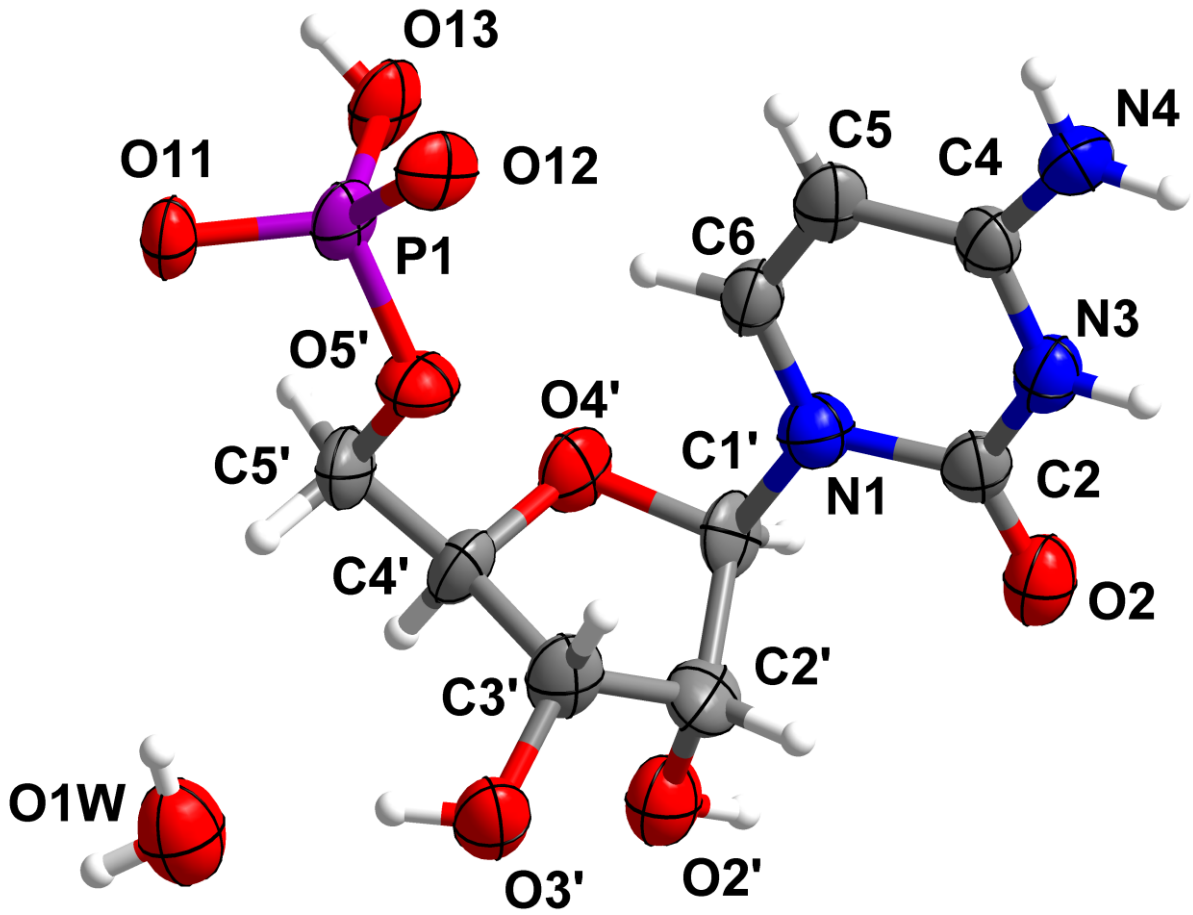

Figure S3. Asymmetric unit of triclinic crystal CMP·H_2O (**II**). Displacement ellipsoids are shown at the 50% probability level.

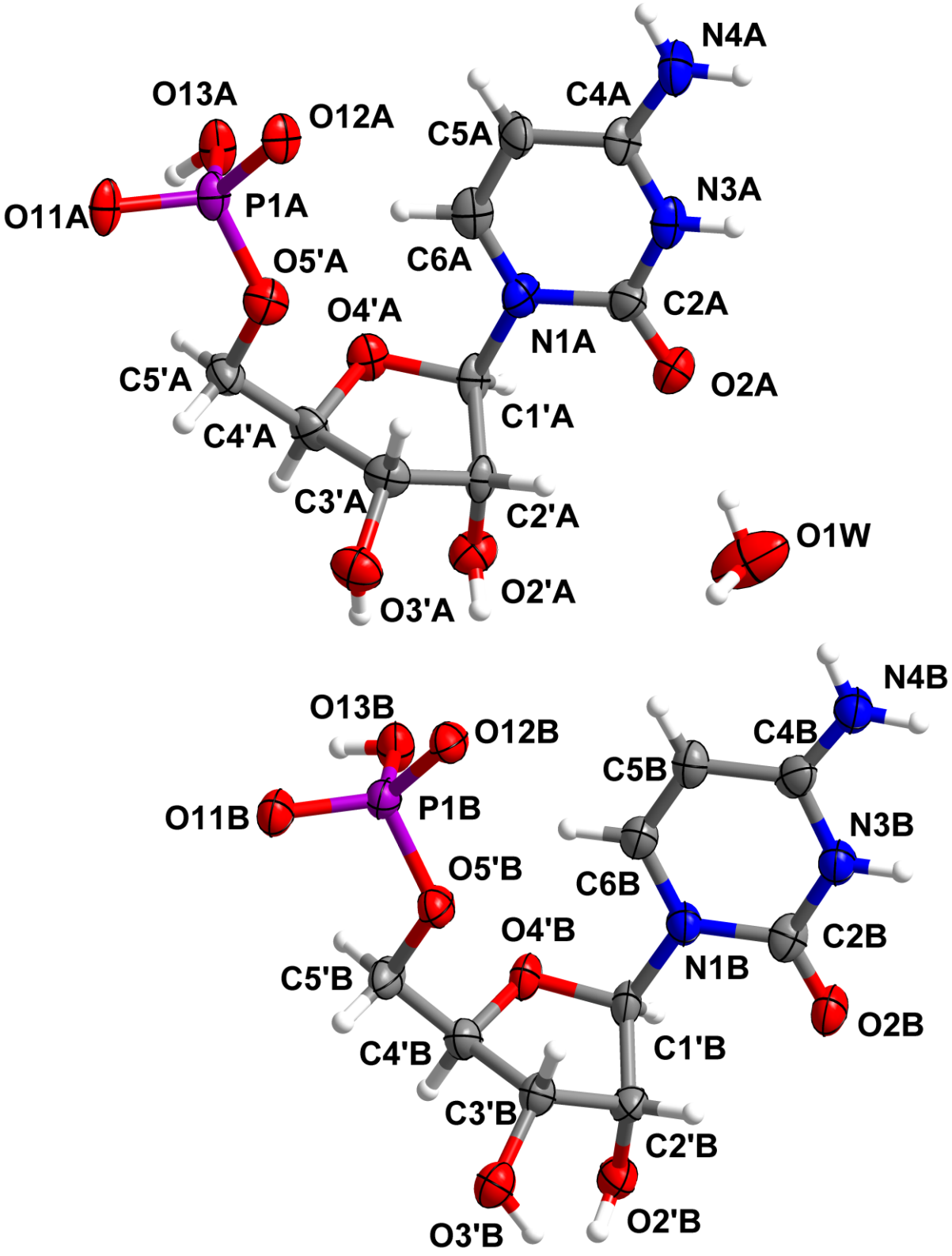

Figure S4. Asymmetric unit of triclinic crystal CMP·0.5H_2O (**III**). Displacement ellipsoids are shown at the 50% probability level.

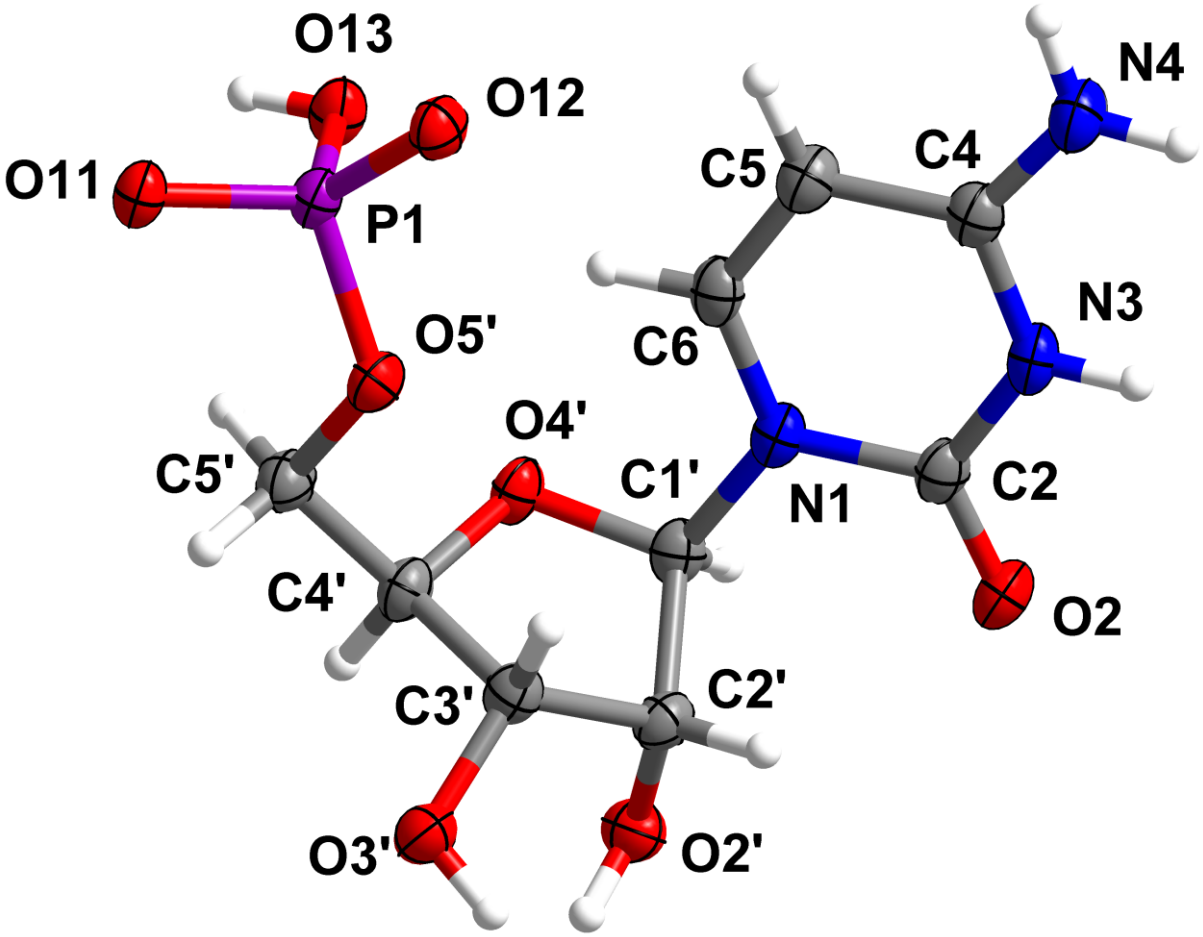

Figure S5. Asymmetric unit of triclinic crystal CMP (**IV**). Displacement ellipsoids are shown at the 50% probability level.

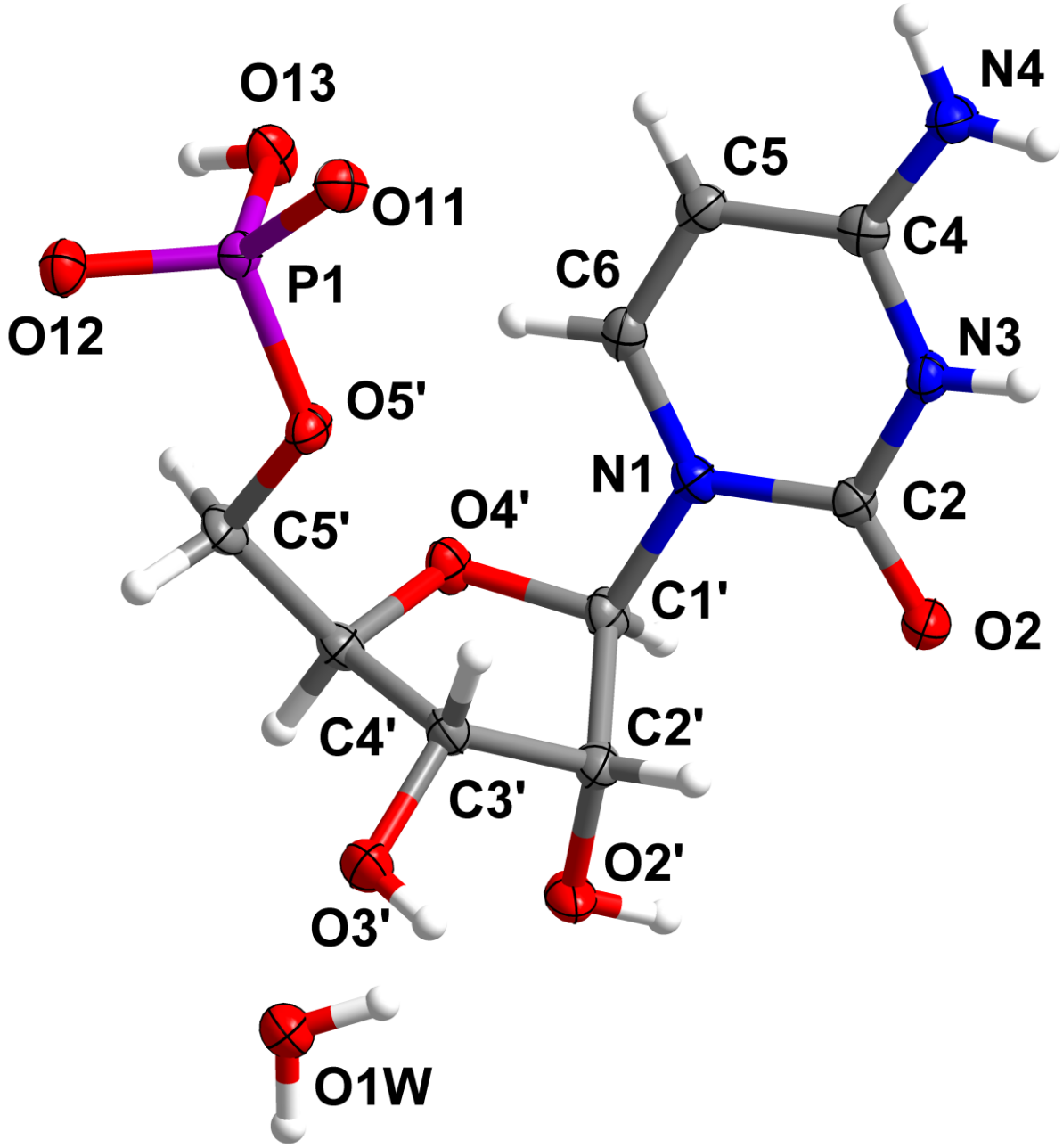

Figure S6. Asymmetric unit of monoclinic crystal CMP·H_2O (WIWZOV) (**V**). Displacement ellipsoids are shown at the 50% probability level. Atom labelling scheme has been adapted to the remaining structures.

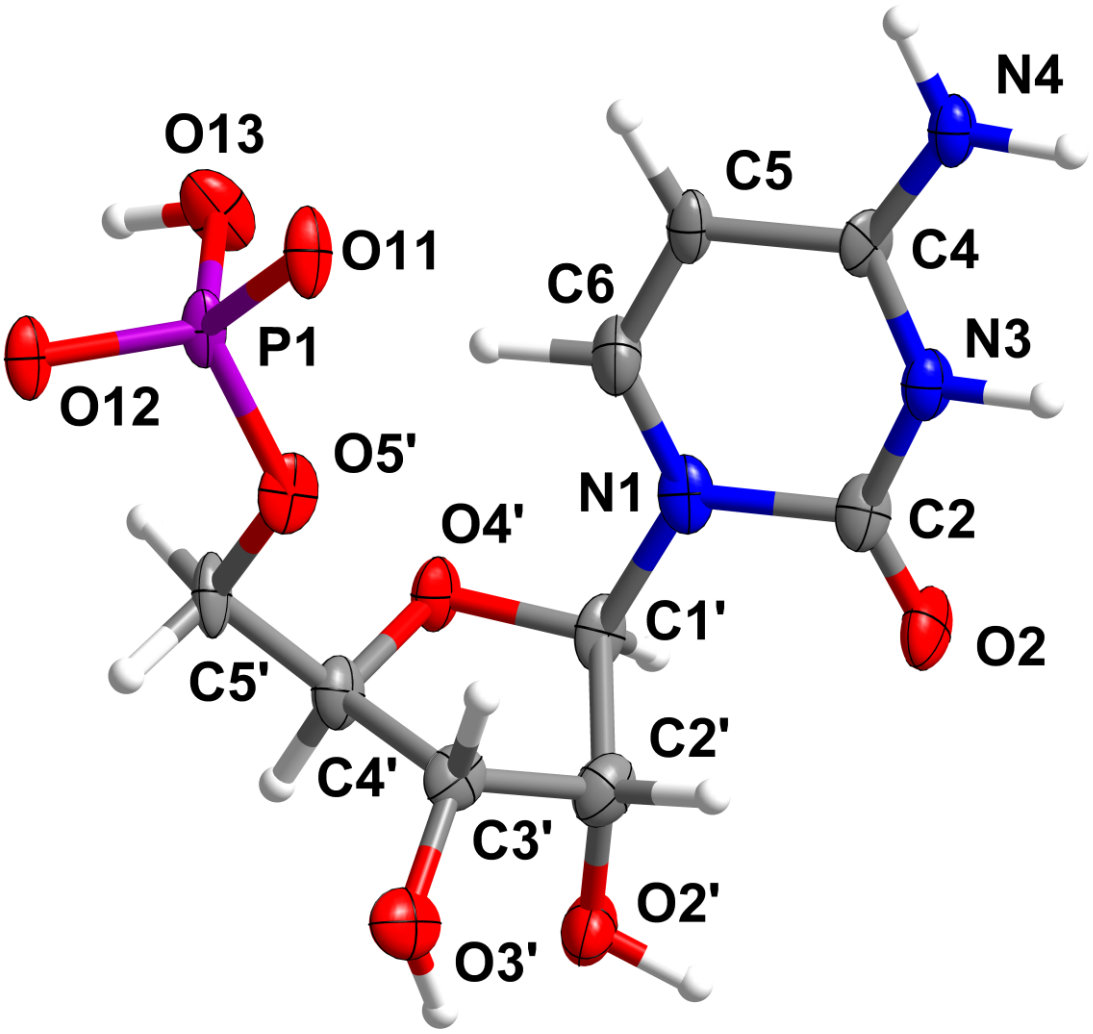

Figure S7. Asymmetric unit of monoclinic crystal CMP (**VI**). Displacement ellipsoids are shown at the 50% probability level.

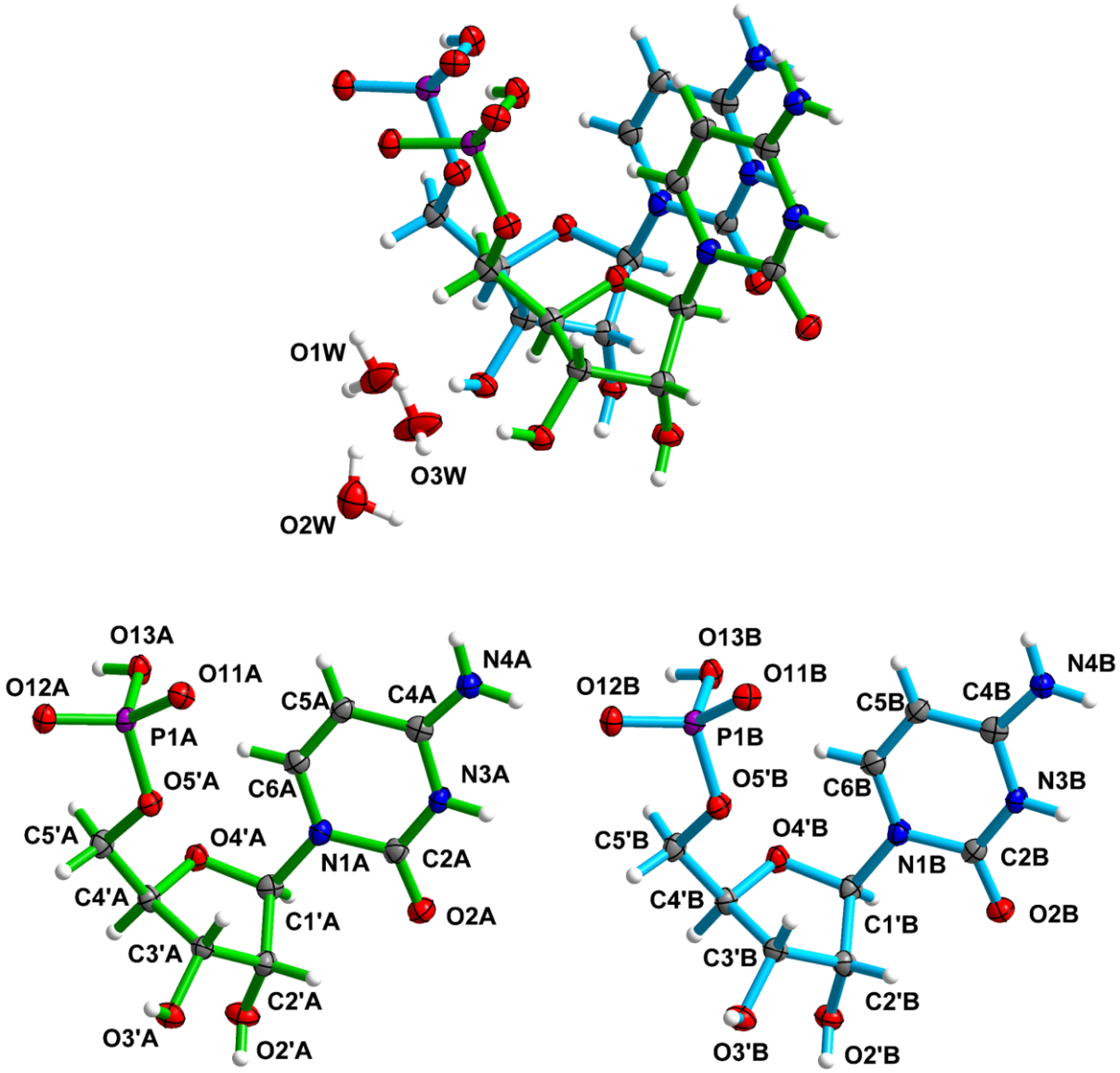

Figure S8. Asymmetric unit of low-temperature phase of orthorhombic crystal CMP·1.5H_2O (**VII_LT**) (top) and atom-numbering scheme of zwitterions A and B (bottom). Displacement ellipsoids are shown at the 50% probability level.

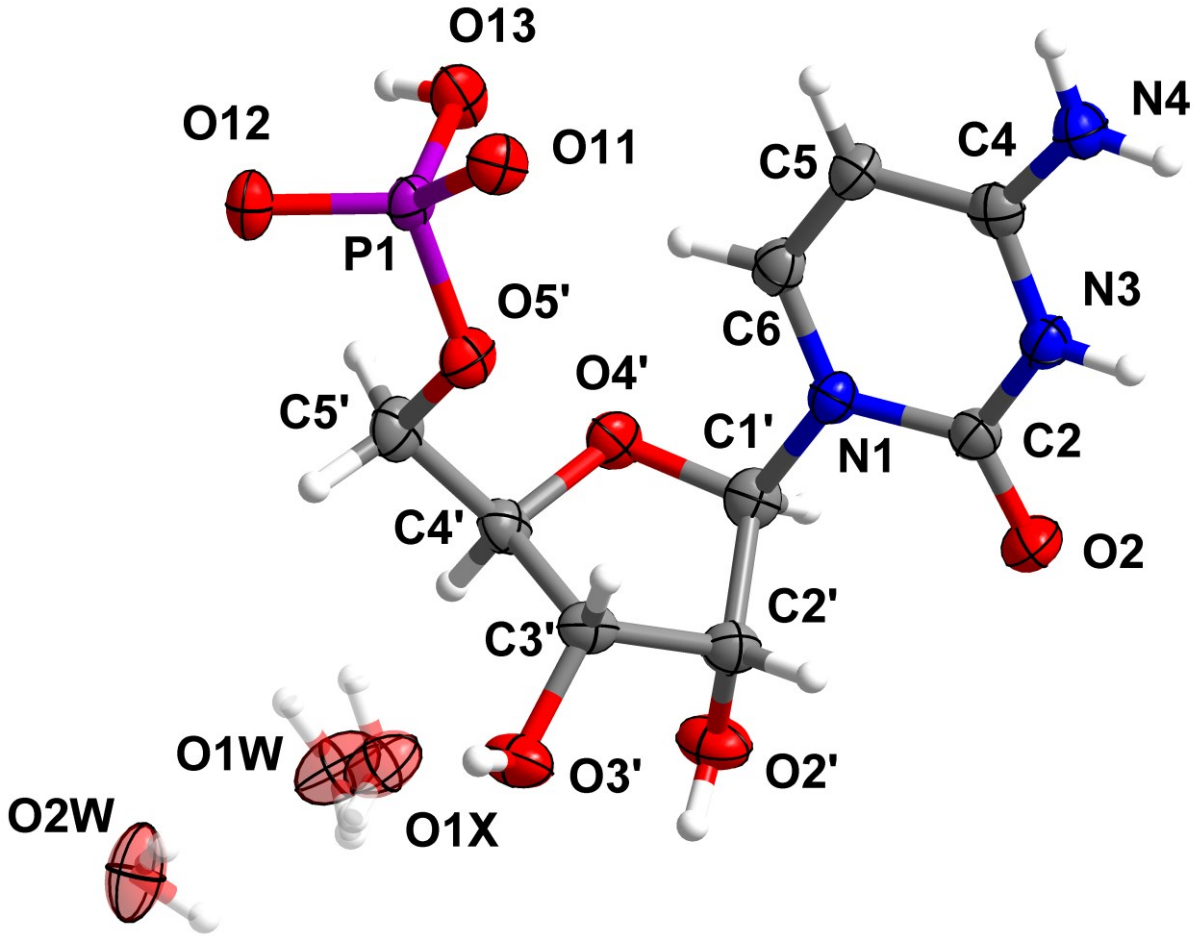

Figure S9. Asymmetric unit of high-temperature phase of orthorhombic crystal CMP·1.5H_2O (**VII_HT**). Displacement ellipsoids are shown at the 50% probability level. Transparent ellipsoids and bonds represent atoms with <1 site occupation factors values.

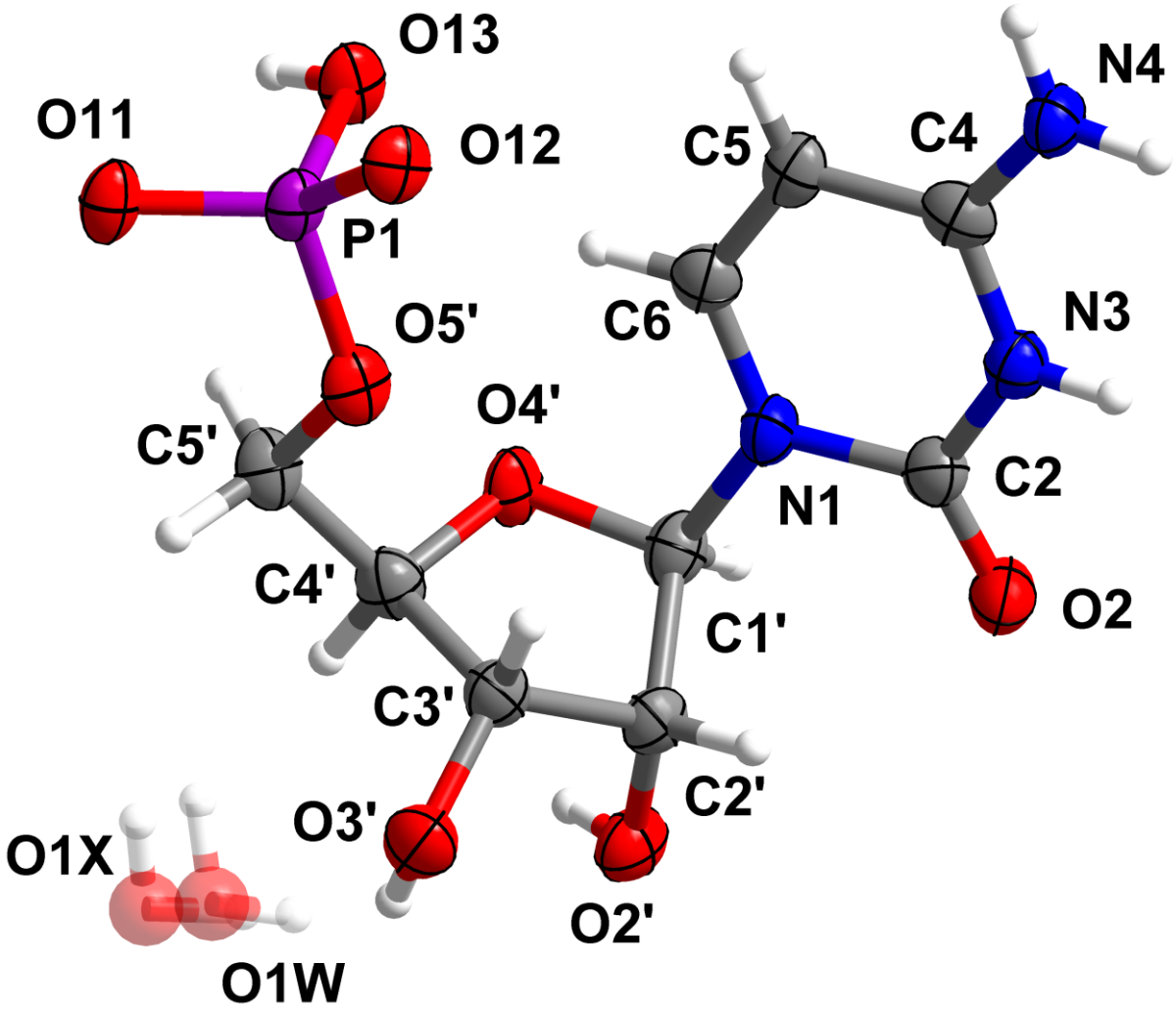

Figure S10. Asymmetric unit of orthorhombic crystal CMP·H_2O (**VIII**). Displacement ellipsoids are shown at the 50% probability level. Transparent spheres and bonds represent atoms with <1 site occupation factors values.

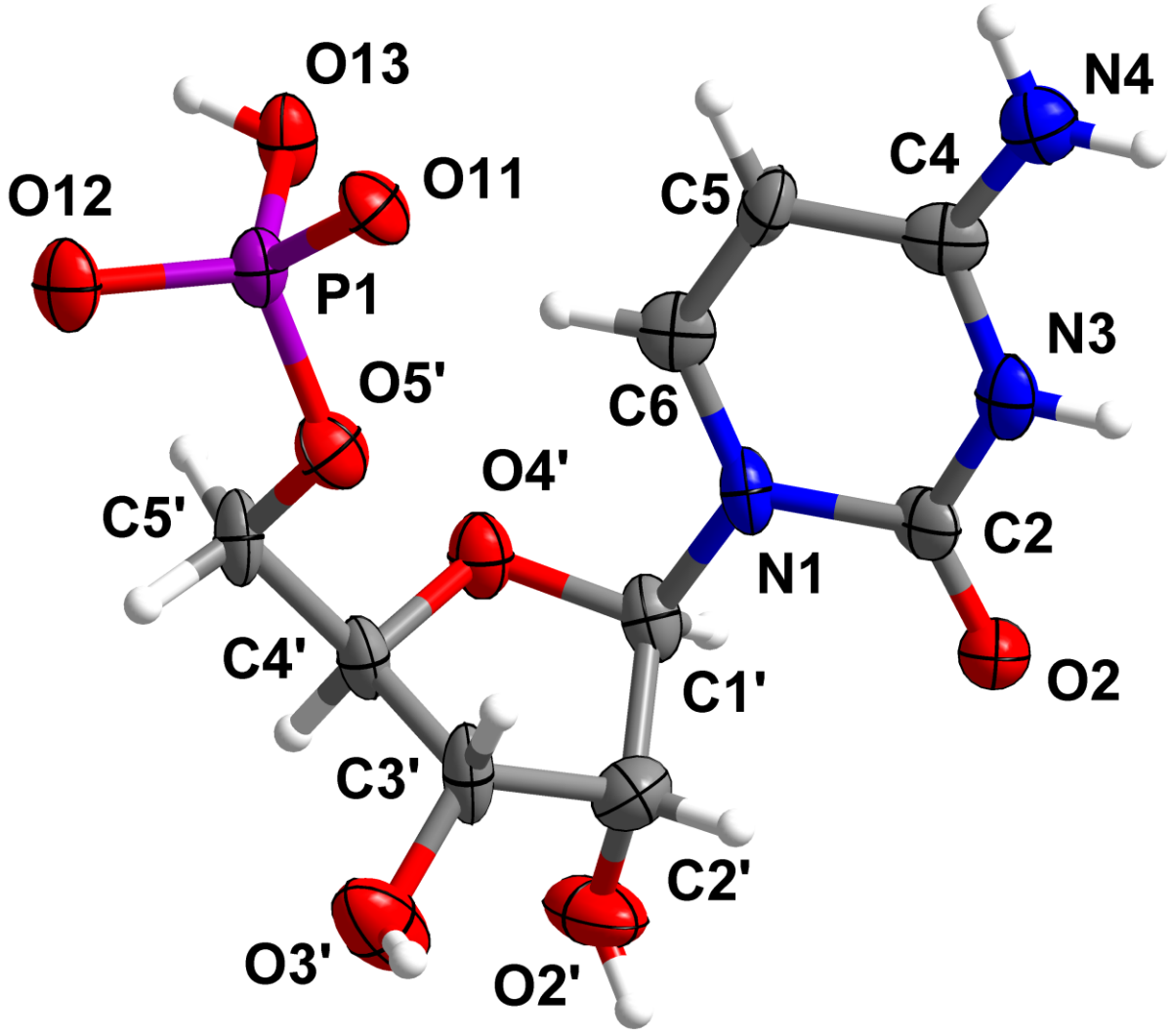

Figure S11. Asymmetric unit of orthorhombic crystal CMP (**IX**). Displacement ellipsoids are shown at the 50% probability level.

Table S4. P−O bonds lengths (Å) and selected valence angles and torsion angles values (°) for triclinic crystals CMP·2H2O (**I**), CMP·H2O (**II**), CMP·0.5H2O (**III**), CMP (**IV**), monoclinic crystals CMP·H2O (WIWZOV) (**V**), CMP (**VI**) and orthorhombic crystals CMP·1.5H2O (**VII_LT**), CMP·1.5H2O (**VII_HT**), CMP·H2O (**VIII**) and CMP (**IX**).

	P1−O5′	P1−O11	P1−O12	P1−O13	O11−P1−O5′	O12−P1−O5′	O13−P1−O5′	C2−N1−C1′−O4′	P1−O5′−C5′−C4′	O5′−C5′−C4′−O4′	O5′−C5′−C4′−C3′
I	1.6002(19)	1.4986(19)	1.4996(19)	1.5761(19)	103.99(10)	110.83(10)	104.77(10)	−177.6(2)	143.28(18)	−67.0(3)	51.1(3)
II	1.596(11)	1.499(10)	1.505(10)	1.576(12)	109.9(6)	106.6(6)	102.6(6)	−175.8(12)	151.5(12)	−66.7(19)	52(2)
III (A)	1.586(8)	1.494(7)	1.517(7)	1.564(7)	111.9(4)	104.5(4)	103.6(4)	−173.2(8)	142.4(8)	−63.6(11)	54.2(12)
III (B)	1.614(8)	1.493(8)	1.509(7)	1.562(8)	109.4(4)	105.5(4)	103.9(4)	−176.3(9)	145.2(8)	−62.8(11)	56.1(12)
IV	1.603(4)	1.502(3)	1.502(4)	1.585(4)	110.9(2)	104.9(2)	104.27(19)	−175.2(4)	143.5(3)	−63.7(5)	55.0(6)
V	1.599(2)	1.493(2)	1.494(2)	1.581(2)	106.21(12)	109.23(13)	105.08(13)	−177.4(2)	154.6(2)	−71.2(3)	47.8(4)
VI	1.584(17)	1.503(19)	1.517(15)	1.592(14)	107.6(9)	110.5(10)	106.2(9)	−174.0(12)	153.4(11)	−70.5(17)	50(2)
VII_LT (A)	1.598(3)	1.493(3)	1.495(3)	1.577(3)	105.88(15)	110.26(15)	105.00(15)	−178.7(3)	151.5(2)	−69.9(4)	49.3(4)
VII_LT (B)	1.595(3)	1.492(3)	1.498(3)	1.576(3)	106.00(15)	109.81(15)	105.11(15)	−177.2(3)	149.8(2)	−69.0(4)	50.1(4)
VII_HT	1.598(3)	1.488(3)	1.495(3)	1.575(3)	105.82(16)	109.98(17)	104.85(17)	−176.9(3)	151.6(3)	−68.8(4)	50.1(5)
VIII	1.592(6)	1.487(5)	1.492(5)	1.570(5)	110.6(3)	105.6(3)	105.0(3)	−178.5(6)	151.5(5)	−71.0(7)	46.9(8)
IX	1.605(10)	1.481(9)	1.521(10)	1.583(10)	107.1(5)	109.4(5)	104.6(5)	−174.2(10)	156.1(9)	−72.5(14)	50.8(15)

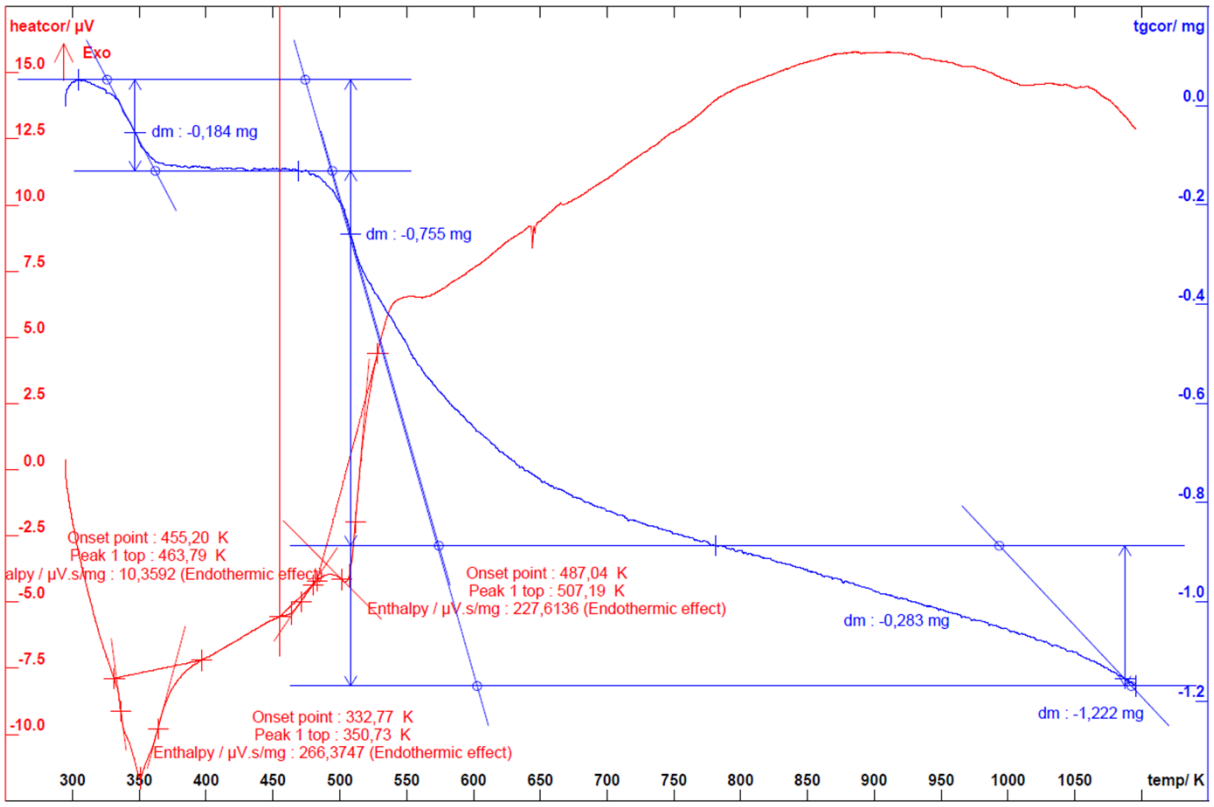

Figure S12. TGA (blue) and DTA (red) curves of triclinic crystals CMP·2H_2O (mass of sample = 1.950 mg).

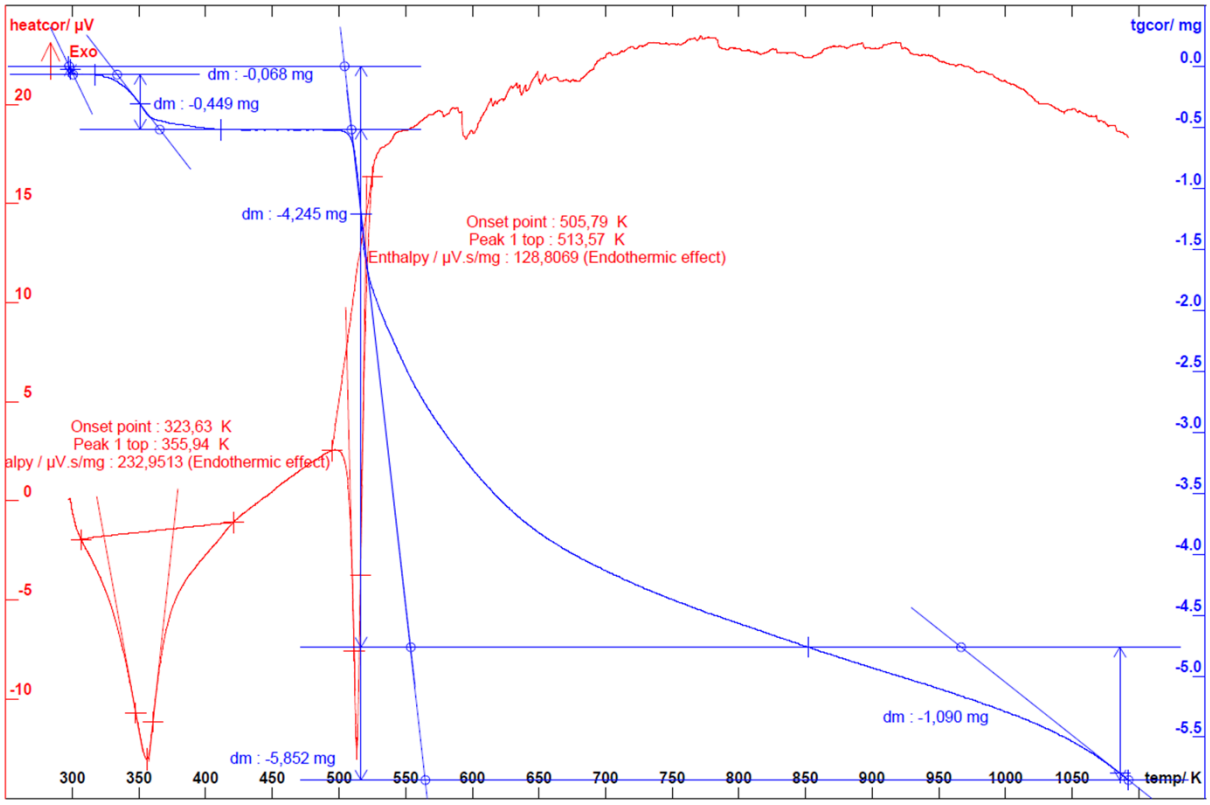

Figure S13. TGA (blue) and DTA (red) curves of monoclinic crystals CMP·H_2O (mass of sample = 9.584 mg).

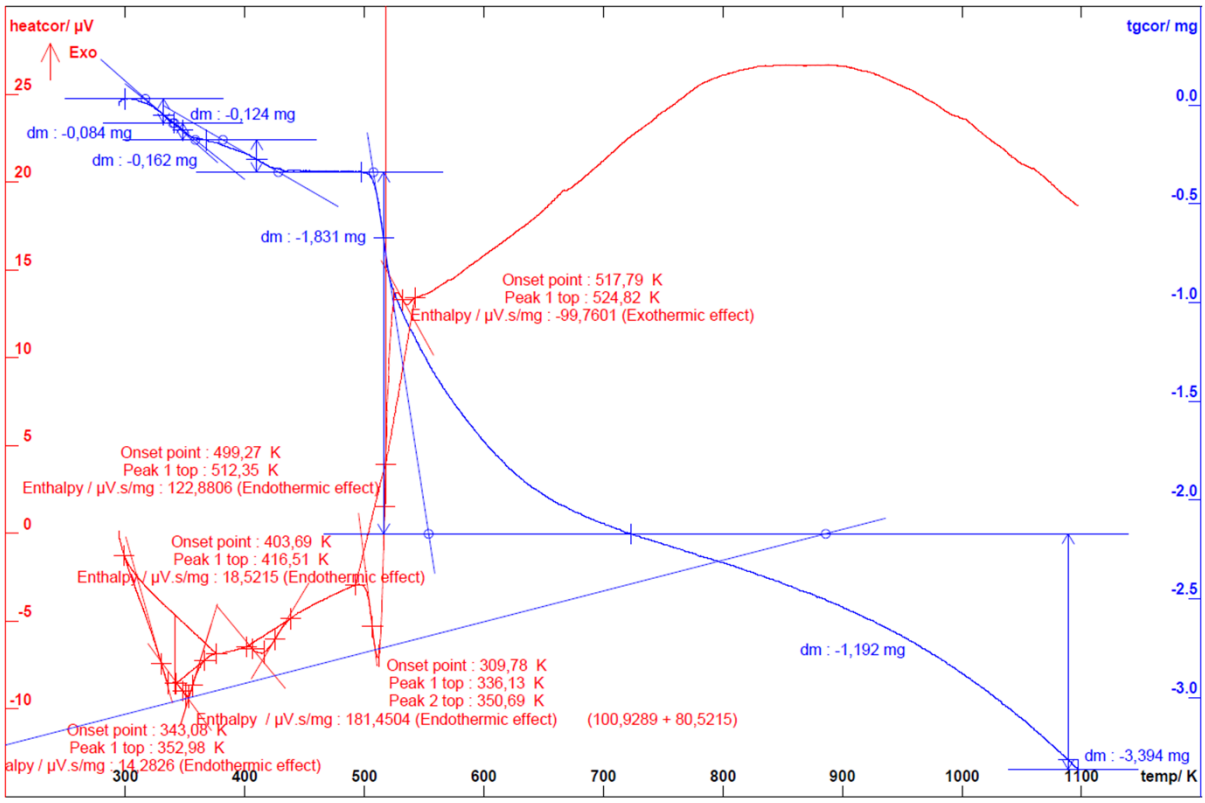

Figure S14. TGA (blue) and DTA (red) curves of orthorhombic crystals CMP·1.5H_2O (mass of sample = 4.722 mg).

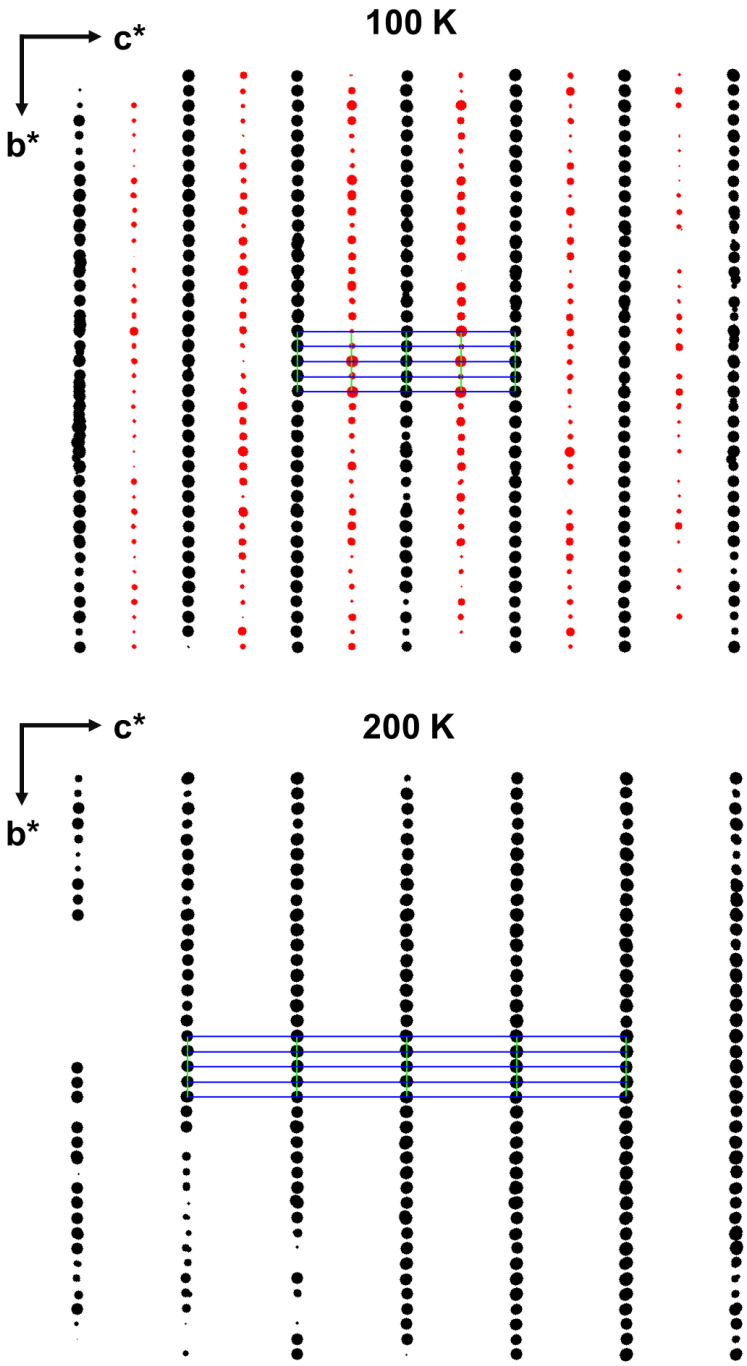

Figure S15. Diffraction pattern of low- (top) and high-temperature (bottom) phases of orthorhombic CMP·1.5H_2O crystal. Visible superstructure weak reflections (red) in the direction of the c* axis in LT phase.

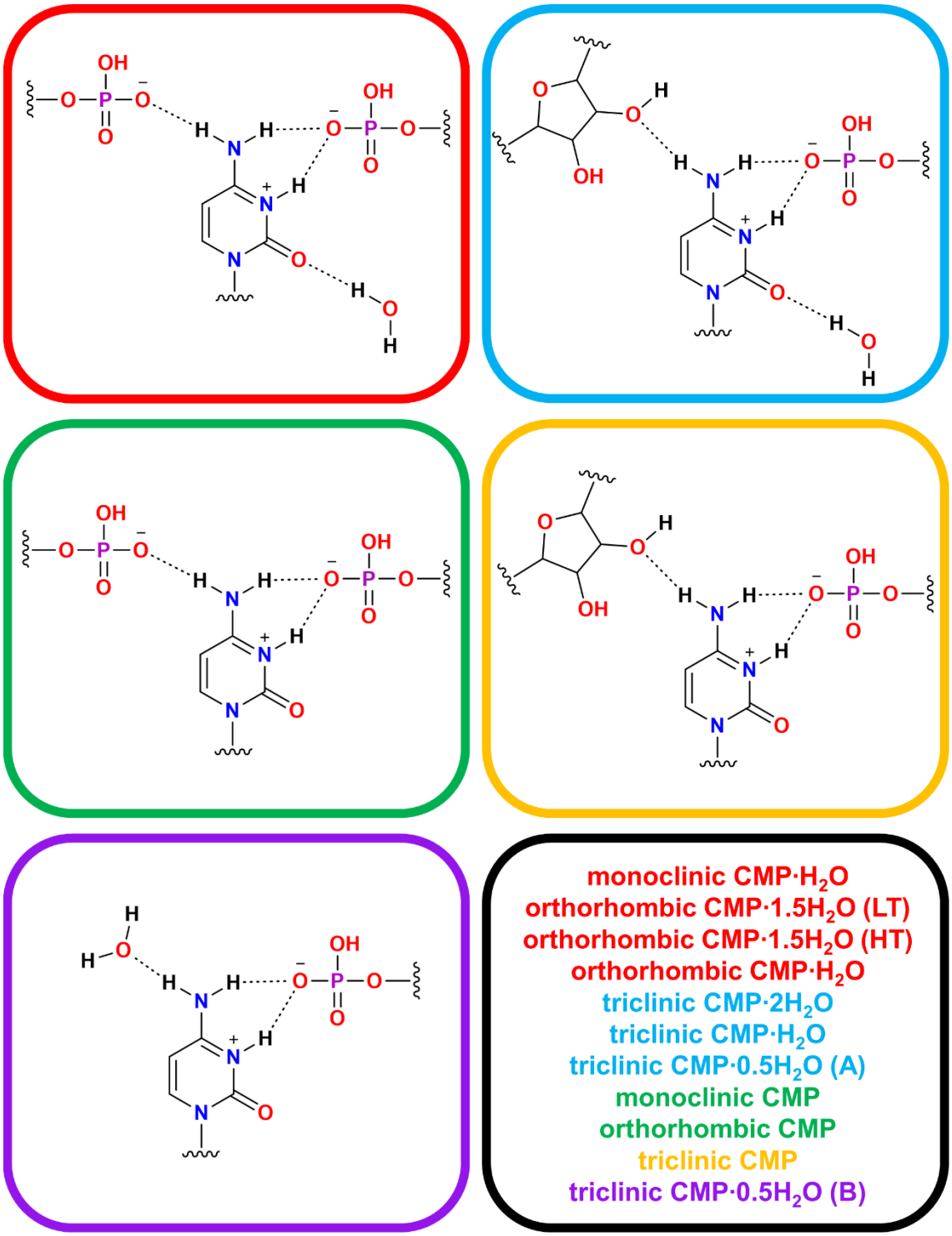

Figure S16. Supramolecular motifs formed by cytosine in individual crystals. Individual motifs and crystals in which they appear are marked with the same colour.

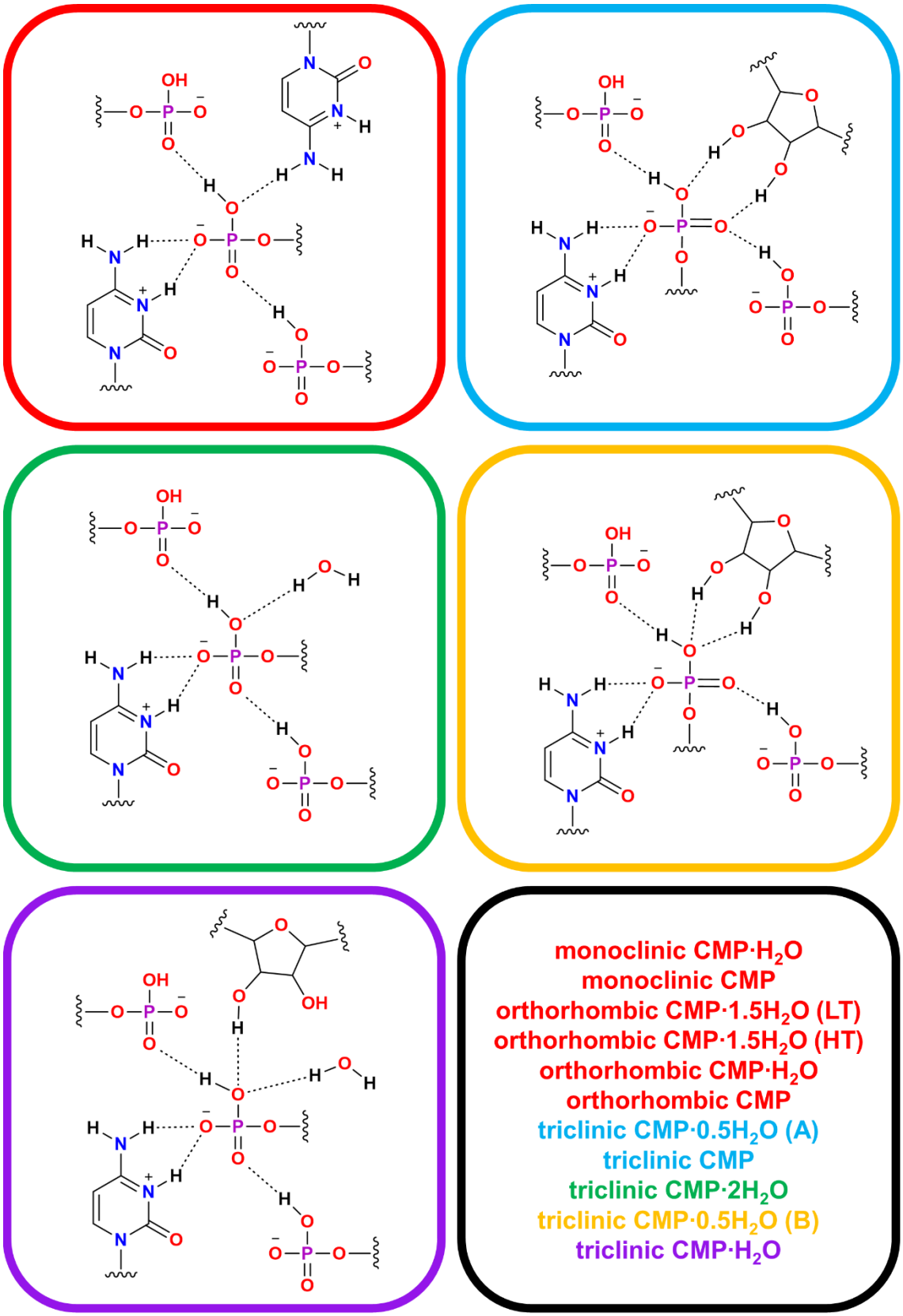

Figure S17. Supramolecular motifs formed by phosphate in individual crystals. Individual motifs and crystals in which they appear are marked with the same colour.

Table S5. Geometric parameters (Å, °) of the hydrogen bonds for triclinic crystal CMP·2H2O (**I**).

D−H···A	D−H	H···A	D···A	D−H···A
O13−H13···O11^{i}	0.84	1.78	2.601(3)	166
O2′−H2O···O2W^{ii}	0.84	1.89	2.730(3)	178
O3′−H3O···O1W	0.84	1.83	2.670(3)	176
O1W−H1W···O2^{iii}	0.84	1.94	2.719(3)	154
O1W−H2W···O2W^{iv}	0.84	2.00	2.795(3)	159
O2W−H3W···O11	0.84	1.80	2.634(3)	176
O2W−H4W···O1W^{v}	0.84	1.88	2.720(3)	173
N3−H3···O12^{vi}	0.88	1.78	2.626(3)	160
N4−H41···O12^{vi}	0.88	2.25	2.965(3)	138
N4−H42···O3′^{vii}	0.88	2.01	2.878(3)	169
C6−H6···O13	0.95	2.40	3.285(3)	154
C6−H6···O5′	0.95	2.59	3.195(3)	122

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

Table S6. Geometric parameters (Å, °) of the hydrogen bonds for triclinic crystal CMP·H2O (**II**).

D−H···A	D−H	H···A	D···A	D−H···A
O13−H13···O12^{i}	0.84	2.01	2.681(13)	136
O2′−H2O···O12^{ii}	0.84	2.30	2.914(17)	130
O3′−H3O···O1W	0.84	1.79	2.619(17)	167
O1W−H1W···O2^{iii}	0.84	2.06	2.78(2)	144
O1W−H2W···O12^{iv}	0.84	2.25	2.823(18)	126
N3−H3···O11^{v}	0.88	1.89	2.703(16)	154
N4−H41···O11^{v}	0.88	2.08	2.834(15)	143
N4−H41···O2′^{vi}	0.88	2.61	3.238(17)	129
N4−H42···O3′^{vii}	0.88	1.95	2.790(17)	158
C6−H6···O5′	0.95	2.45	3.055(16)	122
C3′−H3′···O4′^{viii}	1.00	2.62	3.289(19)	124
C4′−H4′···O3′^{i}	1.00	2.46	3.29(2)	140
C5′−H5′1···O1W	0.99	2.58	3.41(2)	141

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

Table S7. Geometric parameters (Å, °) of the hydrogen bonds for triclinic crystal CMP·0.5H$_2$O (**III**).

D−H···A	D−H	H···A	D···A	D−H···A
O13A−H13A···O12A^{i}	0.84	2.03	2.580(9)	122
O2′A−H2OA···O12B	0.84	1.92	2.724(11)	161
O3′A−H3OA···O12B	0.84	2.29	3.042(11)	149
O13B−H13B···O12B^{i}	0.84	1.86	2.668(11)	160
O2′B−H2OB···O13A^{ii}	0.84	1.95	2.749(11)	158
O3′B−H3OB···O12A^{ii}	0.84	2.01	2.761(10)	149
O3′B−H3OB···O13A^{ii}	0.84	2.54	3.209(12)	137
O1W−H1W···O2′A^{iii}	0.84	2.13	2.803(12)	137
O1W−H2W···O2A	0.84	1.93	2.751(13)	166
N3A−H3A···O11A^{iv}	0.88	1.74	2.605(10)	166
N3B−H3B···O11B^{iv}	0.88	1.88	2.681(11)	150
N4A−H41A···O11A^{iv}	0.88	2.45	3.108(12)	132
N4A−H42A···O2′B^{v}	0.88	2.42	3.049(12)	129
N4B−H41B···O11B^{iv}	0.88	1.97	2.733(12)	145
N4B−H42B···O1W	0.88	1.88	2.728(14)	162
C6A−H6A···O13A	0.95	2.59	3.506(13)	162
C6A−H6A···O5′A	0.95	2.49	3.182(12)	130
C6B−H6B···O13B	0.95	2.56	3.457(14)	158
C6B−H6B···O5′B	0.95	2.47	3.102(13)	124
Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*, *y*+1, *z*+1; (iii) *x*−1, *y*, *z*; (iv) *x*−1, *y*+1, *z*; (v) *x*−1, *y*−1, *z*−1.				

Table S8. Geometric parameters (Å, °) of the hydrogen bonds for triclinic crystal CMP (**IV**).

D−H···A	D−H	H···A	D···A	D−H···A
O13−H13···O12^{i}	0.84	1.79	2.588(5)	157
O2′−H2O···O13^{ii}	0.84	1.96	2.764(5)	159
O3′−H3O···O12^{ii}	0.84	1.96	2.763(5)	159
N3−H3···O11^{iii}	0.88	1.76	2.595(6)	158
N4−H41···O11^{iii}	0.88	2.22	2.924(6)	137
N4−H42···O2′^{iv}	0.88	2.37	3.027(6)	131
C6−H6···O13	0.95	2.54	3.435(7)	158
C6−H6···O5′	0.95	2.45	3.100(6)	126
Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*, *y*, *z*−1; (iii) *x*−1, *y*−1, *z*; (iv) *x*−1, *y*, *z*+1.				

Table S9. Geometric parameters (Å, °) of the hydrogen bonds for monoclinic crystal CMP·H_2O (WIWZOV) (**V**).

D−H···A	D−H	H···A	D···A	D−H···A
O13−H13···O11^{i}	0.84(5)	1.76(5)	2.588(3)	171(4)
O2′−H2O···O1W^{ii}	0.86(6)	1.95(6)	2.768(4)	158(4)
O3′−H3O···O1W^{iii}	0.77(5)	2.02(5)	2.780(4)	174(5)
O1W−H1W···O2^{iv}	0.90(5)	2.09(5)	2.888(3)	148(4)
O1W−H2W···O2′	0.86(5)	1.90(5)	2.743(4)	167(4)
N3−H3···O12^{v}	0.84(4)	1.84(4)	2.637(3)	158(4)
N4−H42···O11^{vi}	0.91(4)	1.89(5)	2.787(4)	169(4)
N4−H41···O12^{v}	0.82(4)	2.10(5)	2.820(4)	146(4)
C6−H6···O13	0.95	2.54	3.330(4)	140

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

Table S10. Geometric parameters (Å, °) of the hydrogen bonds for monoclinic crystal CMP (**VI**).

D−H···A	D−H	H···A	D···A	D−H···A
O13−H13···O11^{i}	0.98	1.63	2.59(2)	163
O2′−H2O···O3′^{ii}	0.98	1.74	2.67(2)	155
O3′−H3O···O2^{iii}	0.98	2.37	3.16(2)	136
N3−H3···O12^{iv}	1.03	1.73	2.69(2)	152
N4−H42···O11^{v}	1.01	1.74	2.75(2)	176
N4−H41···O12^{iv}	1.01	1.97	2.798(19)	137
C6−H6···O13	1.08	2.62	3.55(2)	144

Symmetry codes: (i) *x*φ1, *y*, *z*; (ii) φ*x*+2, *y*φ1/2, φ*z*+1; (iii) φ*x*+2, *y*+1/2, φ*z*+1; (iv) *x*+1, *y*φ1, *z*; (v) φ*x*+2, *y*φ1/2, φ*z*.

Table S11. Geometric parameters (Å, °) of the hydrogen bonds for low-temperature phase of orthorhombic crystal CMP·1.5H_2O (**VII_LT**).

D−H···A	D−H	H···A	D···A	D−H···A
O13A−H13A···O11B	0.84	1.78	2.598(4)	164
O2′A−H2OA···O3′B^{i}	0.84	1.93	2.763(4)	175
O3′A−H3OA···O3W	0.84	1.81	2.640(5)	170
O13B−H13B···O11A^{ii}	0.84	1.77	2.592(4)	167
O2′B−H2OB···O3′A^{iii}	0.84	1.87	2.699(4)	171
O3′B−H3OB···O1W	0.84	1.81	2.631(5)	164
O1W−H1W···O2B^{iv}	0.87	1.98	2.759(4)	150
O1W−H2W···O2W^{v}	0.91	2.46	3.357(6)	169
O2W−H4W···O2′B^{i}	0.84	1.93	2.770(4)	178
O2W−H3W···O1W	0.84	2.08	2.746(5)	136
O3W−H5W···O2A^{iv}	0.84	1.90	2.733(5)	170
O3W−H6W···O2W^{vi}	0.84	2.01	2.735(5)	145
N3A−H3A···O12B^{vii}	0.88	1.80	2.628(4)	155
N4A−H42A···O11A^{viii}	0.88	1.91	2.778(4)	168
N4A−H41A···O12B^{vii}	0.88	2.13	2.853(4)	140
N3B−H3B···O12A^{ix}	0.88	1.81	2.633(4)	155
N4B−H42B···O11B^{x}	0.88	1.91	2.779(4)	172
N4B−H41B···O12A^{ix}	0.88	2.14	2.864(4)	139
C6A−H6A···O13A	0.95	2.51	3.313(5)	143
C6B−H6B···O13B	0.95	2.49	3.321(5)	147

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

Table S12. Geometric parameters (Å, °) of the hydrogen bonds for high-temperature phase of orthorhombic crystal CMP·1.5H$_2$O (**VII_HT**).

D−H···A	D−H	H···A	D···A	D−H···A
O13−H13···O11^{i}	0.84	1.79	2.612(4)	166
O2′−H2O···O3′^{ii}	0.84	1.92	2.740(5)	166
O3′−H3O···O1W	0.84	1.80	2.60(2)	159
O3′−H3O···O1X	0.84	1.81	2.65(2)	177
O1−H2W···O2^{iii}	0.84	1.88	2.71(2)	166
O1X−H2X···O2^{iii}	0.84	2.00	2.79(2)	157
O2W−H3W···O2′^{ii}	0.84	1.91	2.733(9)	166
N3−H3···O12^{iv}	0.88	1.80	2.625(5)	156
N4−H42···O11^{v}	0.88	1.91	2.779(5)	171
N4−H41···O12^{iv}	0.88	2.14	2.869(5)	140
C6−H6···O13	0.95	2.53	3.364(5)	146

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

Table S13. Geometric parameters (Å, °) of the hydrogen bonds for orthorhombic crystal CMP·H$_2$O (**VIII**).

D−H···A	D−H	H···A	D···A	D−H···A
O13−H13···O12^{i}	0.84	1.79	2.593(6)	160
O2′−H2O···O2′^{ii}	0.84	2.24	2.832(5)	128
O3′−H3O···O1W^{iii}	0.84	1.78	2.531(14)	148
O3′−H3O···O1X^{iii}	0.84	1.88	2.674(15)	157
O1W−H2W···O2^{iv}	0.84	1.94	2.728(15)	157
O1W−H1W···O3′	0.84	1.99	2.757(16)	150
O1X−H2X···O2^{iv}	0.84	1.94	2.743(14)	160
O1X−H1X···O3′	0.84	1.99	2.770(14)	155
N3−H3···O11^{v}	0.88	1.78	2.615(8)	159
N4−H41···O11^{v}	0.88	2.20	2.918(8)	138
N4−H42···O12^{vi}	0.88	1.88	2.757(8)	172
C6−H6···O13	0.95	2.47	3.268(9)	141
C3′−H3′···O4′^{vii}	1.00	2.55	3.252(9)	127
C4′−H4′···O3′^{i}	1.00	2.47	3.316(10)	143

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

Table S14. Geometric parameters (Å, °) of the hydrogen bonds for orthorhombic crystal CMP (**IX**).

D−H···A	D−H	H···A	D···A	D−H···A
O13−H13···O11^{i}	0.84	1.97	2.620(13)	133
O2′−H2O···O2^{ii}	0.84	2.28	2.885(13)	130
O3′−H3O···O3′^{iii}	0.84	1.98	2.802(12)	166
N3−H3···O12^{iv}	0.88	1.85	2.657(15)	152
N4−H42···O11^{v}	0.88	1.92	2.789(15)	170
N4−H41···O12^{iv}	0.88	2.10	2.821(17)	139
C6−H6···O13	0.95	2.59	3.393(16)	142
C2′−H2′···O2′^{vi}	1.00	2.51	3.233(19)	129
C4′−H4′···O3′^{vii}	1.00	2.49	3.293(16)	137

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

Table S15. Lone pair (lp)···π distances (Å) between oxygen atoms of ribose (O4′) and phosphate (O11 or O12) and cytosine ring for triclinic crystals CMP·2H$_2$O (**I**), CMP·H$_2$O (**II**), CMP·0.5H$_2$O (**III**), CMP (**IV**), monoclinic crystals CMP·H$_2$O (WIWZOV) (**V**), CMP (**VI**) and orthorhombic crystals CMP·1.5H$_2$O (**VII_LT**), CMP·1.5H$_2$O (**VII_HT**), CMP·H$_2$O (**VIII**) and CMP (**IX**).

	lp oxygen atom	lp···centroid	lp···plane
I	O4′^{i}	3.362(2)	3.147(2)
	O12^{ii}	2.989(2)	2.879(2)
II	O4′^{i}	3.461(12)	3.112(12)
	O11^{ii}	2.945(11)	2.927(11)
III (A)	O4′A^{iii}	3.323(9)	3.078(78)
	O11A^{ii}	2.939(8)	2.788(8)
III (B)	O4′B^{iii}	3.267(8)	3.079(8)
	O11B^{ii}	2.995(8)	2.936(8)
IV	O4′^{iii}	3.302(4)	3.030(4)
	O11^{iv}	2.870(4)	2.805(4)
V	O4′^{i}	3.484(2)	3.210(2)
	O12^{iv}	2.936(2)	2.907(2)
VI	O4′^{i}	3.572(14)	3.330(14)
	O12^{iv}	3.048(13)	2.999(14)
VII_LT (A)	O4′B^{v}	3.531(3)	3.330(3)
	O12A^{iii}	3.015(3)	2.925(3)
VII_LT (B)	O4′A	3.429(3)	3.198(3)
	O12B^{iii}	3.973(3)	2.915(3)
VII_HT	O4′^{v}	3.490(3)	3.261(4)
	O12^{iii}	3.026(4)	2.960(4)
VIII	O4′^{v}	3.699(5)	3.364(5)
	O11^{iii}	2.973(5)	2.938(5)
IX	O4′^{v}	3.322(94)	3.090(91)
	O12^{iii}	2.930(94)	2.890(95)

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

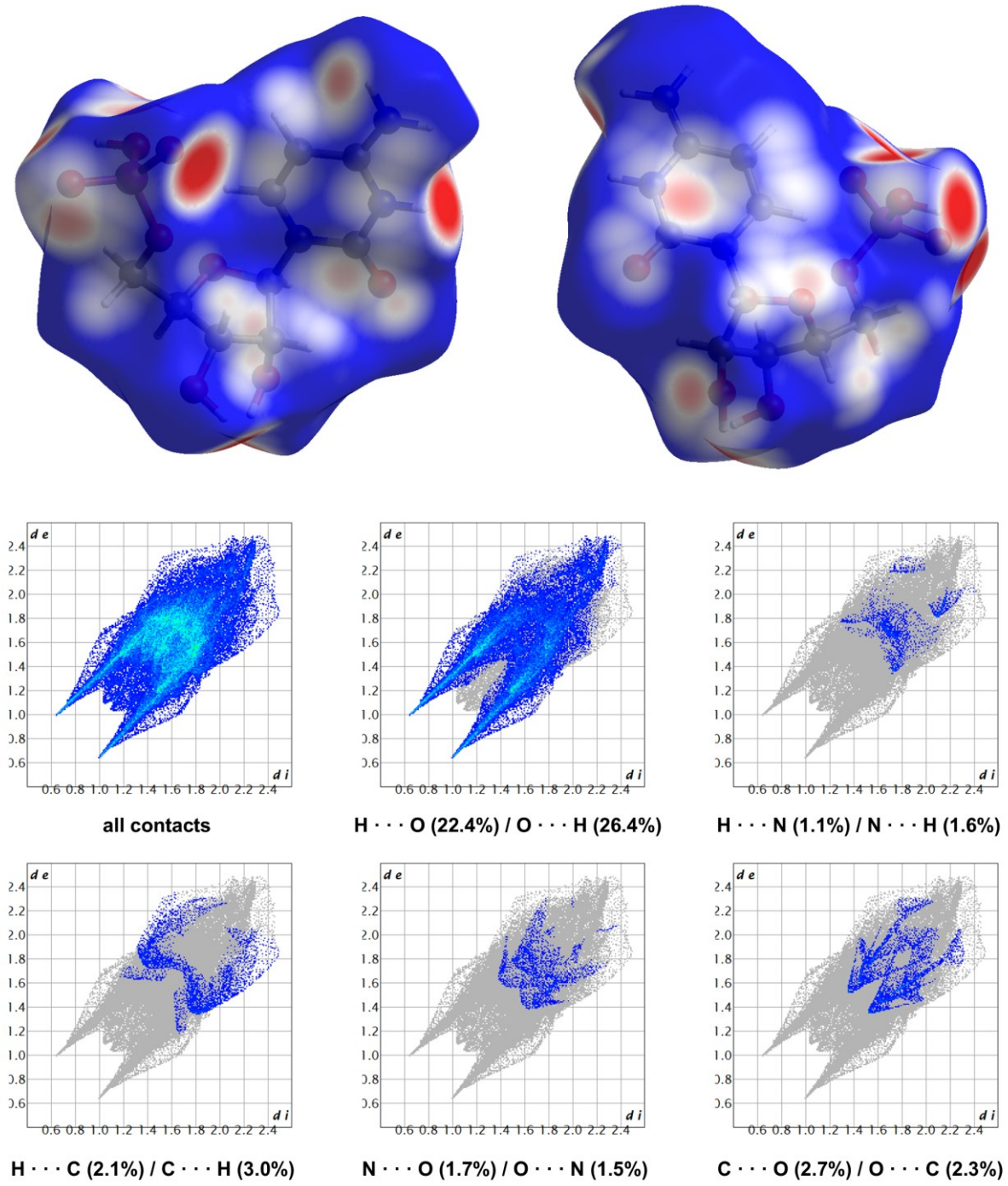

Figure S18. Front and back views of the Hirshfeld surface of the CMP zwitterion in triclinic anhydrous crystal: d_{norm} [from −0.5 (blue) to 0.5 Å (red)] mapped on the surface (top), and 2D fingerprint plots with selected types of contacts and their contribution to the surface area.

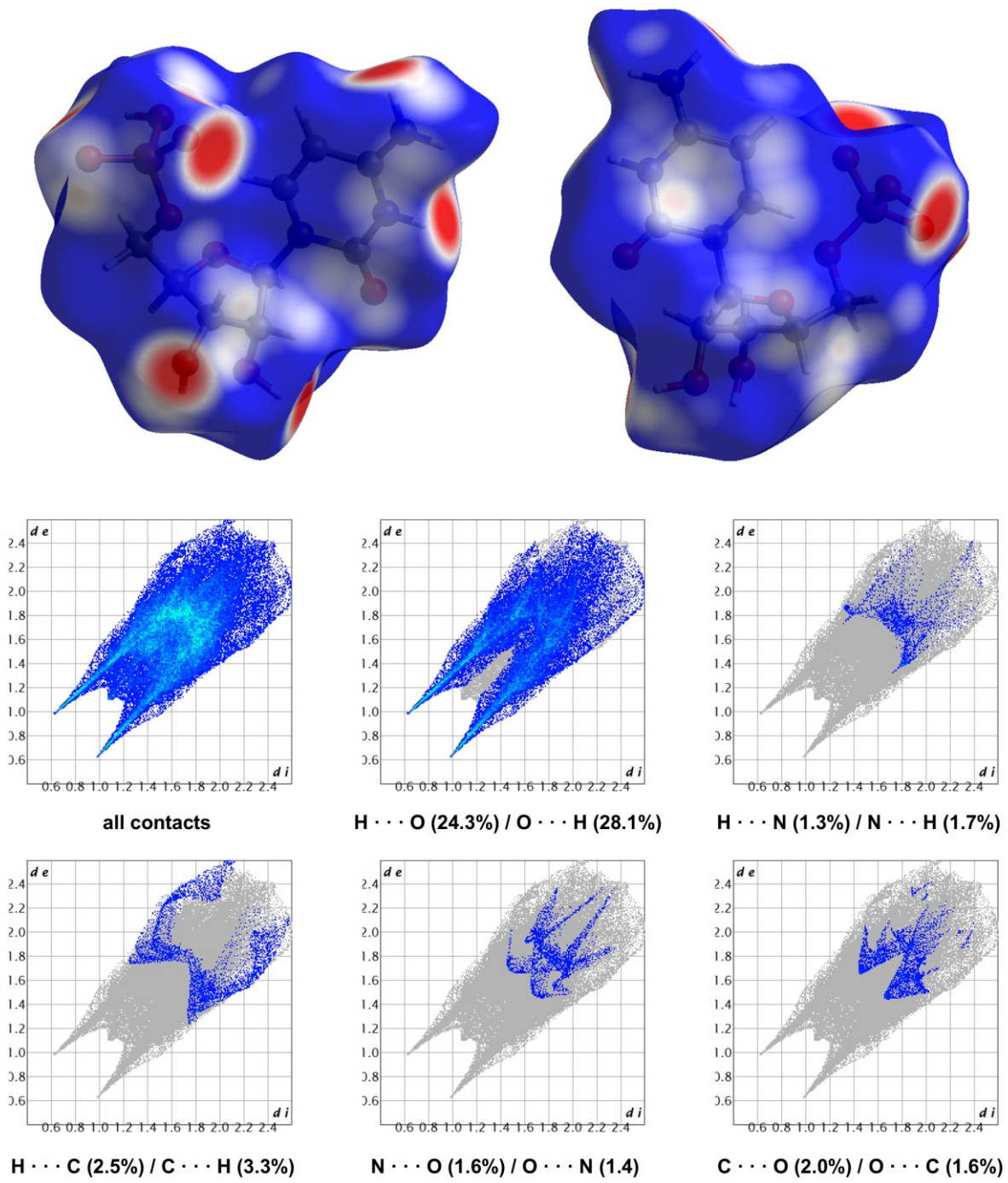

Figure S19. Front and back views of the Hirshfeld surface of the CMP zwitterion in monoclinic anhydrous crystal: d_{norm} [from −0.5 (blue) to 0.5 Å (red)] mapped on the surface (top), and 2D fingerprint plots with selected types of contacts and their contribution to the surface area.

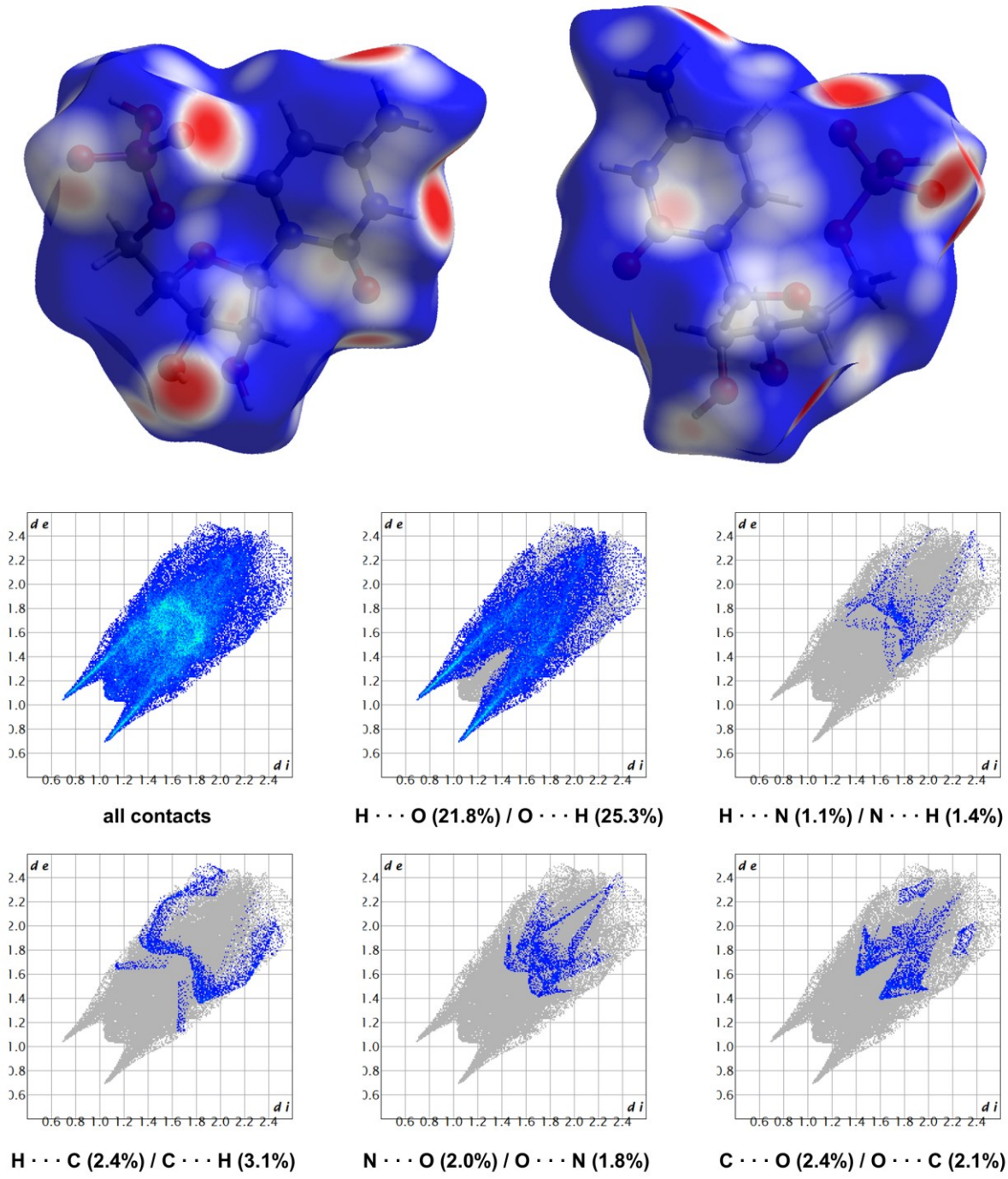

Figure S20. Front and back views of the Hirshfeld surface of the CMP zwitterion in orthorhombic anhydrous crystal: d_{norm} [from −0.5 (blue) to 0.5 Å (red)] mapped on the surface (top), and 2D fingerprint plots with selected types of contacts and their contribution to the surface area.

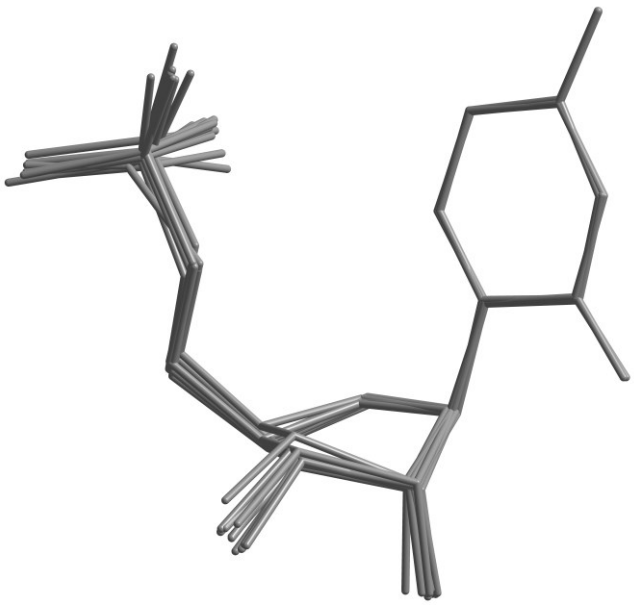

Figure S21. Comparison of the conformation of all CMP zwitterions graphically superimposed with cytosine N1, C2, N3, C4, C5 and C6 atoms. Hydrogen atoms were omitted for clarity.

REFERENCES

[1] A. Houlton, L. Mistry, P. G. Waddell, CCDC 2305187: Experimental Crystal Structure Determination, 2023.