Electronic Supplementary Material (ESI) for CrystEngComm.


# Supplementary Information

## Structural aspects of dehydration and rehydration in adenosine 5′-diphosphate (ADP)–potassium–water system

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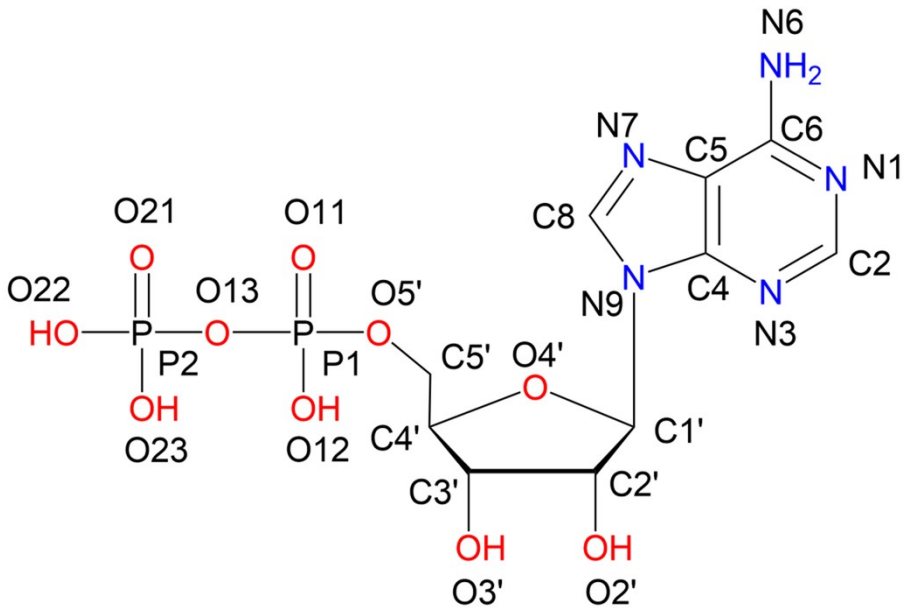



**Fig. S1** Atom numbering scheme for reported structures. ADP in neutral form is shown.

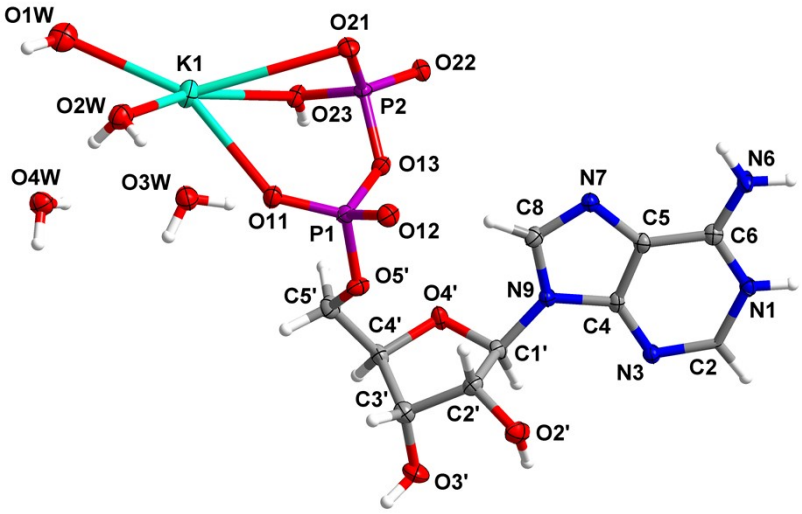



**Fig. S2** Asymmetric unit of crystal K(ADP)·4$H_2O$ (**I**). Displacement ellipsoids are shown at the 50% probability level.

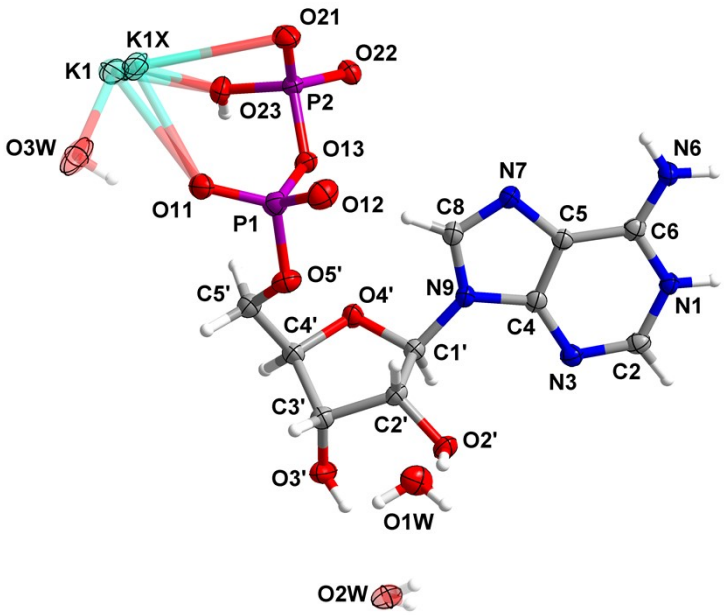



**Fig. S3** Asymmetric unit of crystal K(ADP)·2$H_2O$ (**II**). Transparent ellipsoids and bonds represent atoms with <1 site occupation factors values. Displacement ellipsoids are shown at the 50% probability level.

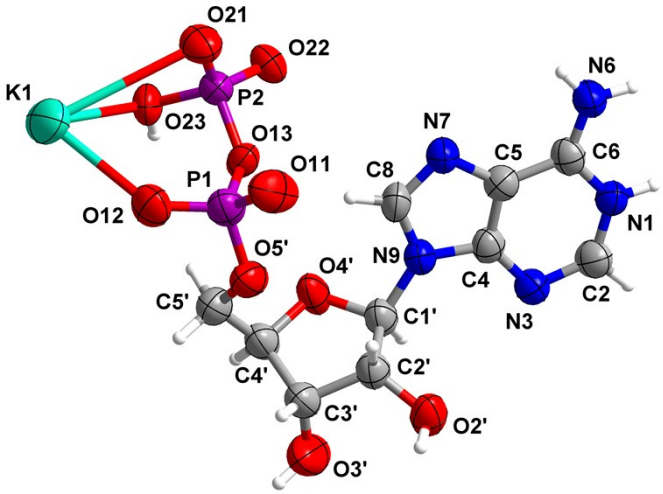



**Fig. S4** Asymmetric unit of crystal K(ADP) (**III**). Displacement ellipsoids are shown at the 50% probability level.

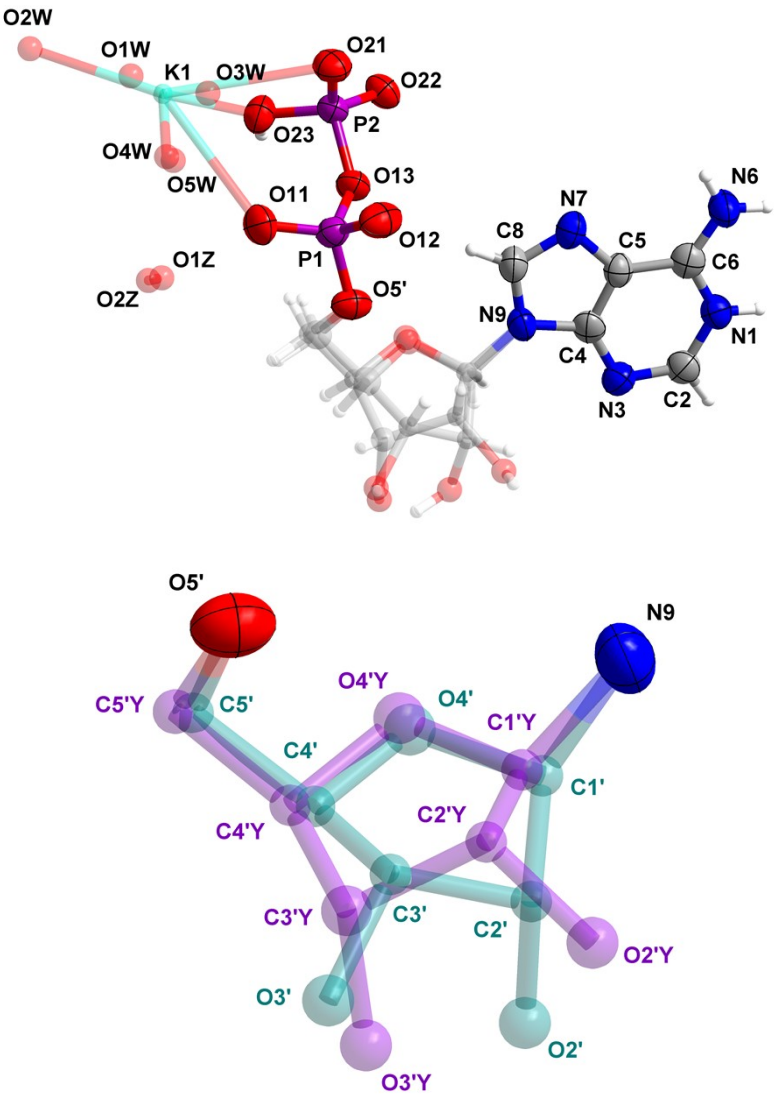



**Fig. S5** Asymmetric unit of crystal $(H_5O_2)K(ADP)_2 \cdot 4.25H_2O$ (**IVa**). Transparent spheres, ellipsoids and bonds represent atoms with <1 site occupation factors values. Displacement ellipsoids are shown at the 50% probability level. Disordered ribose fragment with atom labels is shown below.

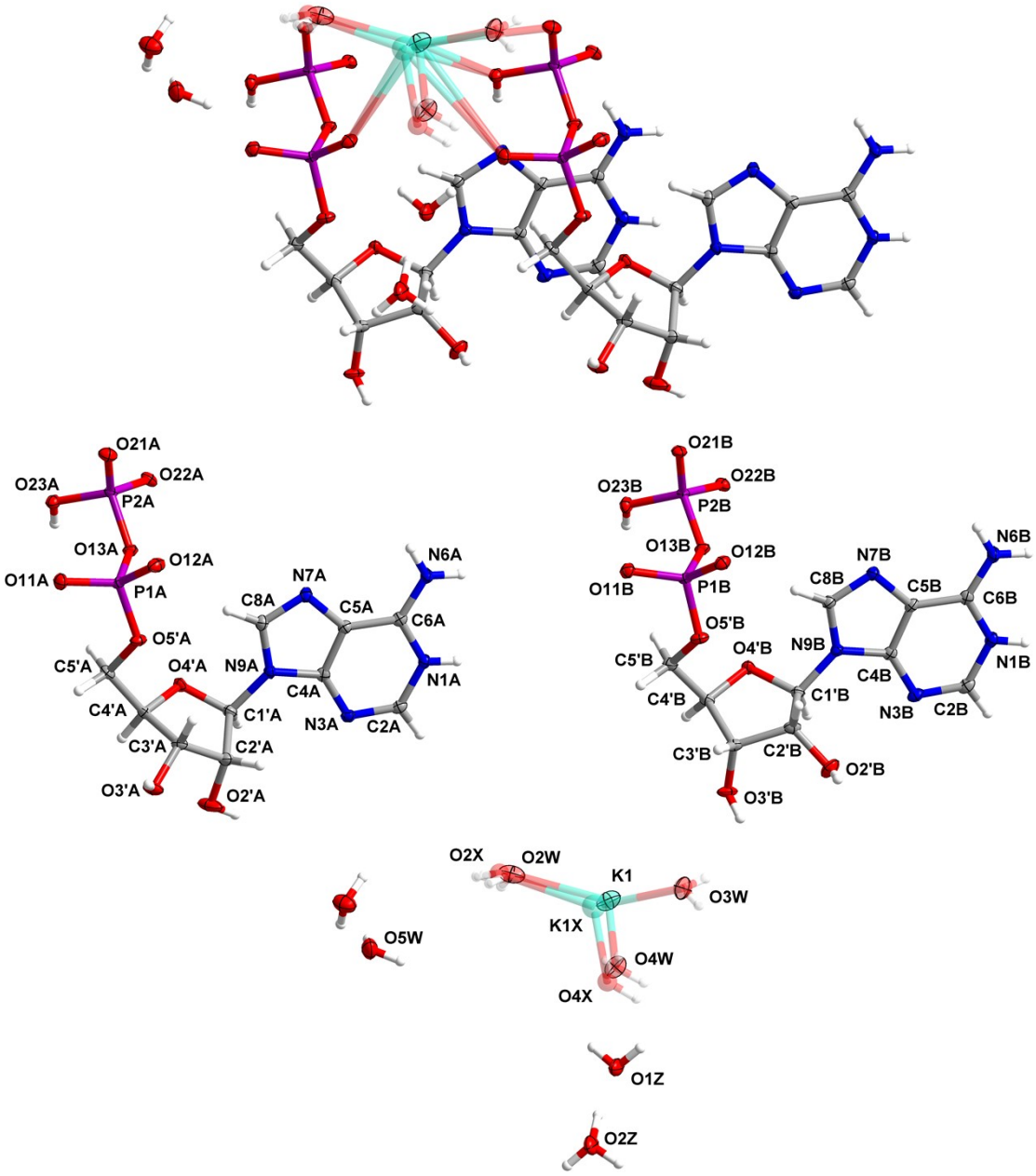



**Fig. S6** Asymmetric unit of crystal $(H_5O_2)K(ADP)_2 \cdot 4.25H_2O$ (**IVb**). Transparent spheres, ellipsoids and bonds represent atoms with <1 site occupation factors values. Displacement ellipsoids are shown at the 50% probability level. Two $ADP^-$ anions and $K^+$ cations, Zundel cation and water molecules with atom labels are shown below.

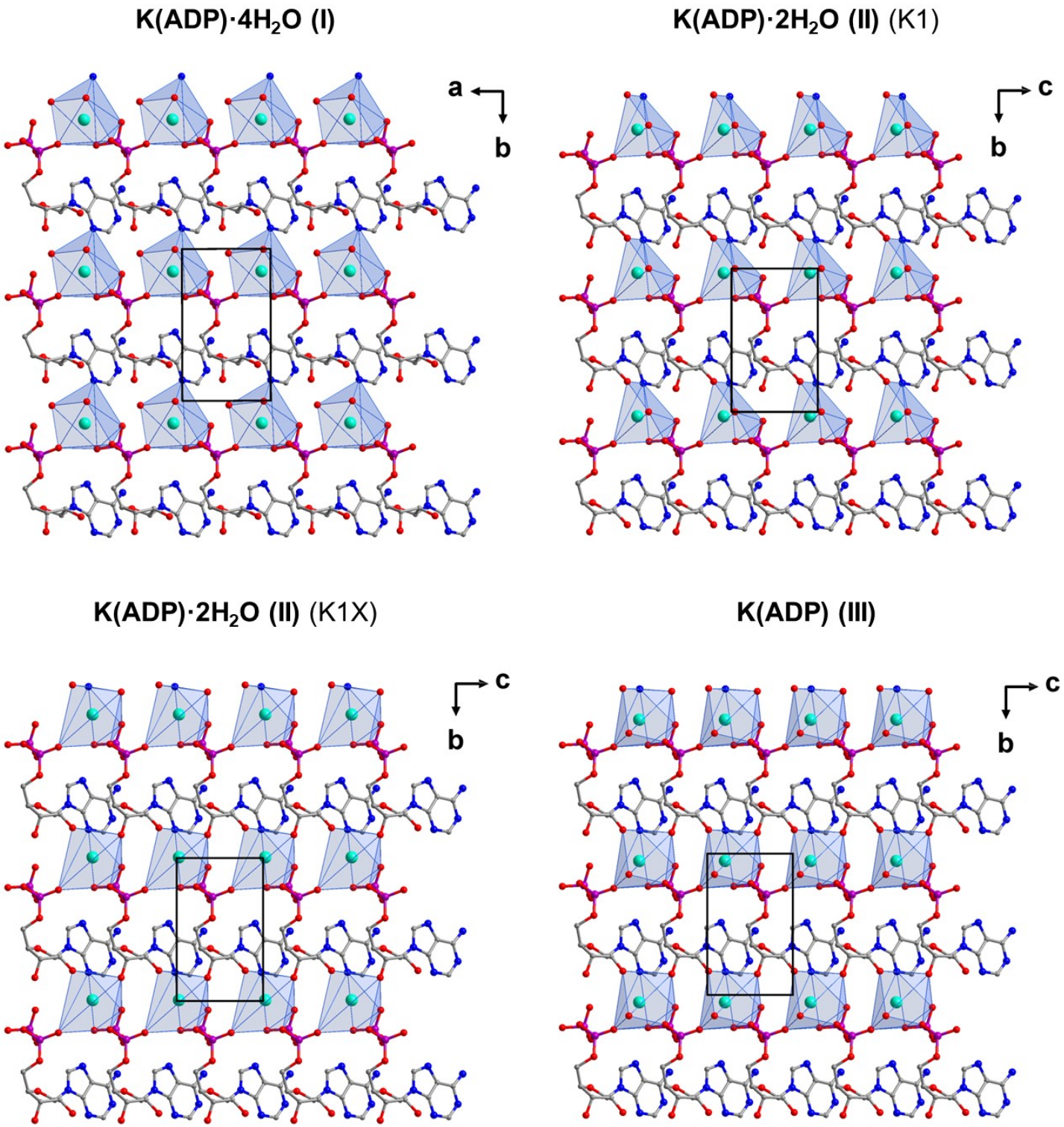



**Fig. S7** Comparison of packing diagrams of structures **I**, **II** and **III**. For **II**, two diagrams with different potassium ions are shown (K1 and K1X; SOF = 0.5). Hydrogen atoms and selected water molecules are omitted for clarity.

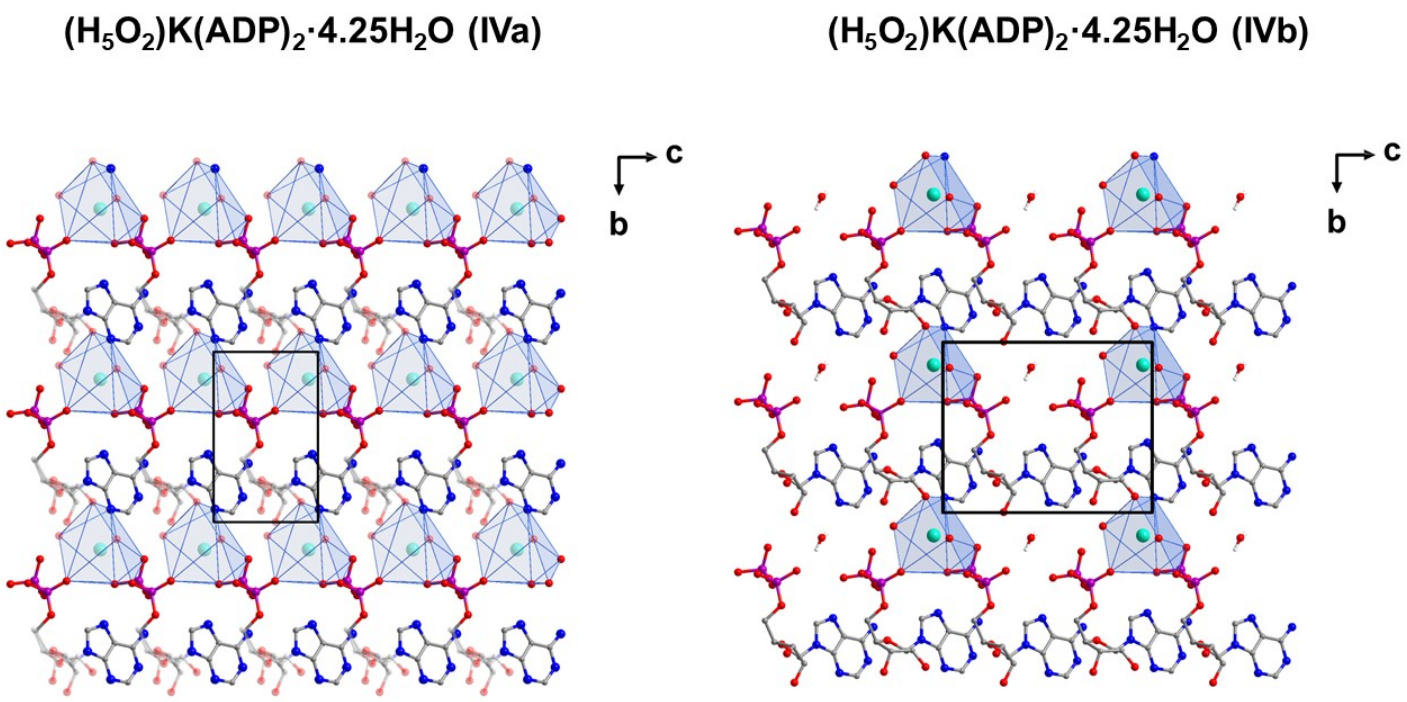



**Fig. S8** Comparison of packing diagrams of structures **IVa** and **IVb**. For **IVb**, disorder of potassium cations and water molecules is omitted and diagram for only one potassium ion is shown (K1; SOF = 0.744(7)). Disordered parts in **IVa** are presented with transparent atoms, bonds and polyhedra. Selected water molecules, oxygen atoms of Zundel cation and hydrogen atoms are omitted for clarity.

**Table S1** P–O bonds lengths [Å] and selected valence angles and torsion angles values [°] for K(ADP)·4$H_2O$ (**I**), K(ADP)·2$H_2O$ (**II**), K(ADP) (**III**) and ($H_5O_2$)K(ADP)$_2$·4.25$H_2O$ (**IVa** and **IVb**).

| | I | II | III | IVa | | IVb | |
|---|---|---|---|---|---|---|---|
| | | | | – | Y | A | B |
| P1–O5′ | 1.594(3) | 1.602(3) | 1.600(7) | 1.577(6) | | 1.588(2) | 1.585(2) |
| P1–O11 | 1.481(3) | 1.480(3) | 1.469(7) | 1.472(6) | | 1.486(2) | 1.490(2) |
| P1–O12 | 1.487(3) | 1.483(3) | 1.490(8) | 1.464(6) | | 1.493(2) | 1.493(2) |
| P1–O13 | 1.620(3) | 1.617(3) | 1.601(6) | 1.600(6) | | 1.605(2) | 1.6047(19) |
| P2–O13 | 1.609(3) | 1.604(3) | 1.589(6) | 1.611(5) | | 1.617(2) | 1.620(2) |
| P2–O21 | 1.487(3) | 1.482(3) | 1.470(7) | 1.471(6) | | 1.486(2) | 1.485(2) |
| P2–O22 | 1.497(3) | 1.499(3) | 1.499(6) | 1.511(5) | | 1.505(2) | 1.503(2) |
| P2–O23 | 1.570(3) | 1.575(3) | 1.572(6) | 1.569(5) | | 1.575(2) | 1.563(2) |
| O5′–P1–O11 | 112.81(17) | 111.99(18) | 107.0(4) | 112.9(4) | | 112.56(12) | 112.29(12) |
| O5′–P1–O12 | 103.80(16) | 106.47(19) | 111.5(4) | 105.2(3) | | 105.34(12) | 105.95(12) |
| O5′–P1–O13 | 100.27(15) | 99.26(15) | 99.0(4) | 100.5(3) | | 99.84(11) | 100.58(11) |
| O11–P1–O12 | 119.71(16) | 119.16(19) | 118.8(5) | 117.9(4) | | 118.64(13) | 117.43(12) |
| O11–P1–O13 | 109.48(15) | 108.96(16) | 109.5(4) | 109.8(3) | | 109.75(12) | 109.55(12) |
| O12–P1–O13 | 108.94(16) | 109.15(18) | 109.3(4) | 109.1(4) | | 109.00(12) | 109.68(12) |
| O13–P2–O21 | 110.36(16) | 110.11(17) | 111.0(4) | 110.5(3) | | 111.11(12) | 110.27(11) |
| O13–P2–O22 | 103.87(15) | 104.93(16) | 104.8(3) | 103.1(3) | | 102.92(11) | 103.08(11) |
| O13–P2–O23 | 105.51(16) | 104.32(16) | 104.0(4) | 105.0(3) | | 104.47(11) | 105.33(11) |
| O21–P2–O22 | 117.84(16) | 117.43(17) | 117.8(4) | 117.2(3) | | 117.55(12) | 116.58(12) |
| O21–P2–O23 | 108.00(16) | 108.71(18) | 108.5(4) | 110.2(3) | | 109.17(13) | 109.43(12) |
| O22–P2–O23 | 110.57(16) | 110.52(17) | 109.9(4) | 109.9(3) | | 110.73(12) | 111.41(12) |
| P1–O13–P2 | 130.09(17) | 131.56(18) | 133.3(4) | 131.6(4) | | 131.07(13) | 131.52(13) |
| O4′–C1′–N9–C4 | −144.4(3) | −149.6(4) | −147.8(8) | −154.5(8) | −150.6(9) | −157.8(2) | −152.7(2) |
| O5′–C5′–C4′–O4′ | −70.2(4) | −63.7(4) | −62.3(11) | −82.6(13) | −61.4(11) | −68.9(3) | −61.7(3) |
| O5′–C5′–C4′–C3′ | 48.8(4) | 57.1(5) | 57.4(11) | 43.9(14) | 65.6(12) | 49.3(3) | 60.3(3) |
| P1–O5′–C5′–C4′ | 148.2(3) | 143.7(3) | 142.3(7) | 151.3(6) | 150.4(6) | 157.68(18) | 143.62(18) |
| P2–O13–P1–O5′ | 148.6(2) | 156.6(2) | 157.3(6) | 162.2(5) | 162.2(5) | 166.06(17) | 155.39(17) |
| O13–P1– O5′–C5′ | −62.9(3) | −64.2(3) | −61.9(8) | −64.5(10) | −71.5(8) | −73.8(2) | −64.9(2) |

**Table S2** Pseudorotation parameters ($P$, $\tau_m$) and Cremer & Pople puckering parameters ($q_2$, $\phi_2$) for K(ADP)·4$H_2O$ (**I**), K(ADP)·2$H_2O$ (**II**), K(ADP) (**III**) and ($H_5O_2$)K(ADP)$_2$·4.25$H_2O$ (**IVa** and **IVb**).

| | **I** | **II** | **III** | **IVa** | | **IVb** | |
|---|---|---|---|---|---|---|---|
| | | | | **–** | **Y** | **A** | **B** |
| $P$ [°] | 158.3(4) | 165.1(4) | 165.9(11) | 1.8(11) | 159.2(12) | 18.4(3) | 147.7(3) |
| $\tau_m$ [°] | 40.9(3) | 38.0(3) | 31.9(6) | 37.4(7) | 37.9(8) | 36.0(2) | 33.2(2) |
| $q_2$ [Å] | 0.397(4) | 0.371(4) | 0.305(10) | 0.362(11) | 0.363(12) | 0.353(3) | 0.315(3) |
| $\phi_2$ [°] | 70.2(6) | 77.0(6) | 77.4(18) | 271.8(18) | 71.0(18) | 286.9(5) | 60.6(5) |

**Table S3** Geometric parameters of the hydrogen bonds for K(ADP)·4$H_2O$ (**I**).

| *D*–H···*A* | *D*–H [Å] | H···*A* [°] | *D*···*A* [Å] | *D*–H···*A* [°] |
|---|---|---|---|---|
| O23–H23···N7$^{i}$ | 0.84 | 1.85 | 2.688(4) | 175 |
| O2′–H2O···O2W$^{iv}$ | 0.84 | 1.94 | 2.730(4) | 157 |
| O3′–H3O···O2′$^{v}$ | 0.84 | 2.53 | 3.201(4) | 137 |
| O3′–H3O···O3W$^{vi}$ | 0.84 | 2.21 | 2.805(4) | 128 |
| N1–H1···O22$^{vii}$ | 0.88 | 1.80 | 2.658(4) | 165 |
| N6–H61···O21$^{vii}$ | 0.88 | 2.03 | 2.899(4) | 171 |
| N6–H62···O22$^{viii}$ | 0.88 | 2.07 | 2.832(4) | 144 |
| C1′–H1′···O1W$^{iv}$ | 1.00 | 2.21 | 3.149(5) | 156 |
| C2′–H2′···O3W$^{ix}$ | 1.00 | 2.52 | 3.285(5) | 133 |
| C3′–H3′···O2′$^{v}$ | 1.00 | 2.48 | 3.227(5) | 131 |
| C4′–H4′···O2′$^{i}$ | 1.00 | 2.46 | 3.225(5) | 133 |
| C2–H2···O21$^{iv}$ | 0.95 | 2.34 | 3.276(5) | 169 |
| C8–H8···O13 | 0.95 | 2.43 | 3.367(5) | 169 |
| O1W–H1W···O21$^{i}$ | 0.84 | 1.99 | 2.778(4) | 157 |
| O1W–H2W···O3′$^{ii}$ | 0.84 | 2.17 | 2.924(5) | 149 |
| O2W–H3W···O3W | 0.84 | 1.96 | 2.802(5) | 177 |
| O3W–H5W···O4W$^{viii}$ | 0.84 | 1.90 | 2.721(4) | 165 |
| O3W–H6W···O12$^{x}$ | 0.84 | 2.07 | 2.895(4) | 166 |
| O4W–H7W···O12$^{i}$ | 0.84 | 1.94 | 2.764(4) | 168 |
| O4W–H8W···O11$^{x}$ | 0.84 | 1.95 | 2.753(4) | 161 |

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

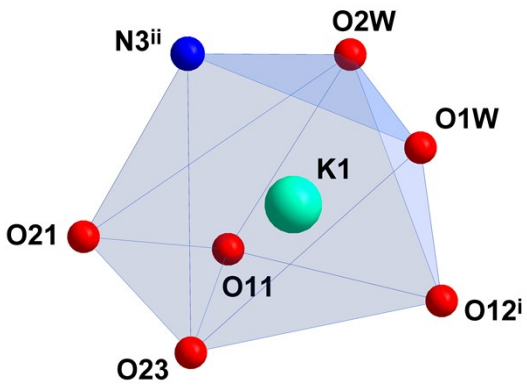



**Fig. S9** Coordination polyhedron of potassium ion in K(ADP)·4$H_2O$ (**I**). Symmetry codes are given in Table S4.

**Table S4** K−O and K−N bonds lengths [Å] in K(ADP)·4$H_2O$ (**I**).

| | |
|---|---|
| K1−O11 | 2.731(3) |
| K1−O12$^{i}$ | 2.805(3) |
| K1−O21 | 3.305(3) |
| K1−O23 | 2.816(3) |
| K1−N3$^{ii}$ | 3.593(4) |
| K1−O1W | 2.731(4) |
| K1−O2W | 2.753(3) |

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

**Table S5** Geometric parameters of the hydrogen bonds for K(ADP)·2$H_2O$ (**II**).

| *D*–H···*A* | *D*–H [Å] | H···*A* [°] | *D*···*A* [Å] | *D*–H···*A* [°] |
|---|---|---|---|---|
| O23–H23···N7$^{i}$ | 0.84 | 1.96 | 2.794(5) | 169 |
| O2′–H2O···O1W | 0.84 | 1.80 | 2.610(4) | 162 |
| O3′–H3O···O2W | 0.84 | 1.95 | 2.770(8) | 164 |
| O3′–H3O···O2W$^{iv}$ | 0.84 | 1.99 | 2.803(8) | 161 |
| N1–H1···O22$^{v}$ | 0.88 | 1.81 | 2.662(4) | 161 |
| N6–H61···O21$^{v}$ | 0.88 | 2.07 | 2.921(5) | 163 |
| N6–H62···O22$^{vi}$ | 0.88 | 2.00 | 2.758(5) | 143 |
| C4′–H4′···O2′$^{i}$ | 1.00 | 2.58 | 3.519(5) | 157 |
| C2–H2···O21$^{viii}$ | 0.95 | 2.21 | 3.063(5) | 149 |
| C8–H8···O13 | 0.95 | 2.25 | 3.186(5) | 168 |
| O1W–H1W···O11$^{ix}$ | 0.84 | 1.91 | 2.709(4) | 159 |
| O1W–H2W···O12$^{x}$ | 0.84 | 1.90 | 2.725(5) | 168 |
| O2W–H4W···O12$^{xi}$ | 0.84 | 1.98 | 2.814(7) | 176 |
| O2W–H3W···O3W$^{viii}$ | 0.84 | 2.08 | 2.845(8) | 151 |
| O2W–H3W···O3W$^{ix}$ | 0.84 | 2.08 | 2.845(8) | 151 |
| O3W–H5W···O11 | 0.84 | 2.36 | 3.082(3) | 145 |

Symmetry codes: $^{(i)}$ *x*, *y*, *z*−1; $^{(iv)}$ −*x*+1, −*y*+2, *z*; $^{(v)}$ −*x*+1/2, *y*+1/2, −*z*+2; $^{(vi)}$ *x*, *y*, *z*+1; $^{(viii)}$ *x*, *y*+1, *z*+1; $^{(ix)}$ −*x*+1, −*y*+1, *z*+1; $^{(x)}$ −*x*+1, −*y*+1, *z*; $^{(xi)}$ *x*, *y*+1, *z*.

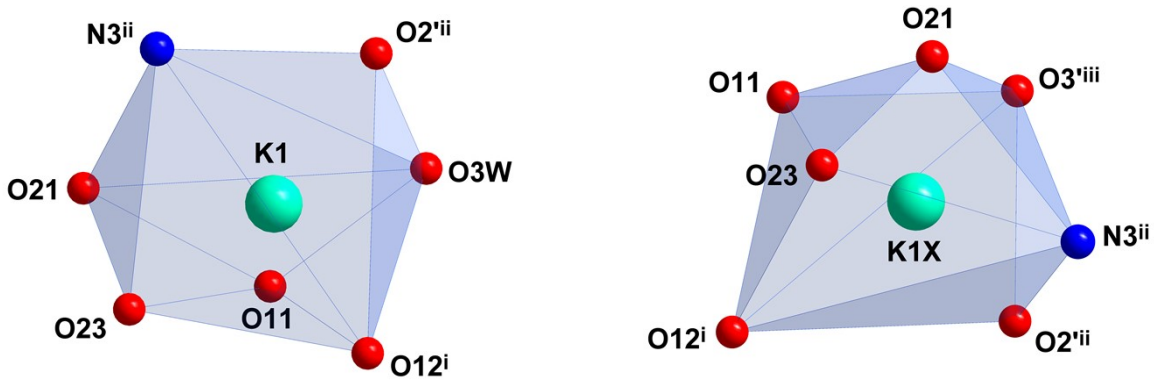



**Fig. S10** Coordination polyhedra of potassium ions in K(ADP)·2$H_2O$ (**II**). Symmetry codes are given in Table S6.

**Table S6** K–O and K–N bonds lengths [Å] in K(ADP)·2$H_2O$ (**II**).

| | | | |
|---|---|---|---|
| K1–O11 | 2.919(4) | K1X–O11 | 2.654(4) |
| K1–O12$^{i}$ | 2.821(5) | K1X–O12$^{i}$ | 3.506(5) |
| K1–O21 | 3.397(4) | K1X–O21 | 3.068(4) |
| K1–O23 | 2.789(4) | K1X–O23 | 3.122(4) |
| K1–O2′$^{ii}$ | 2.881(4) | K1X–O2′$^{ii}$ | 2.751(4) |
| K1–N3$^{ii}$ | 3.206(4) | K1X–O3′$^{iii}$ | 2.915(5) |
| K1–O3W | 3.226(4) | K1X–N3$^{ii}$ | 3.122(4) |

Symmetry codes: $^{(i)}$ *x*, *y*, *z*−1; $^{(ii)}$ *x*, *y*−1, *z*−1; $^{(iii)}$ *x*, *y*−1, *z*.

**Table S7** Geometric parameters of the hydrogen bonds for K(ADP) (**III**).

| *D*–H···*A* | *D*–H [Å] | H···*A* [°] | *D*···*A* [Å] | *D*–H···*A* [°] |
|---|---|---|---|---|
| O23–H23···N7$^{i}$ | 0.82 | 2.01 | 2.811(11) | 167 |
| O2′–H2O···O12$^{v}$ | 0.82 | 1.91 | 2.692(10) | 158 |
| O3′–H3O···O11$^{iii}$ | 0.82 | 2.21 | 2.918(13) | 145 |
| N1–H1···O22$^{vi}$ | 0.86 | 1.86 | 2.686(9) | 161 |
| N6–H61···O21$^{vi}$ | 0.86 | 2.09 | 2.912(10) | 159 |
| N6–H61···O22$^{vi}$ | 0.86 | 2.61 | 3.257(9) | 133 |
| N6–H62···O22$^{vii}$ | 0.86 | 2.00 | 2.744(10) | 144 |
| C2–H2···O21$^{viii}$ | 0.93 | 2.21 | 3.012(12) | 145 |
| C8–H8···O13 | 0.93 | 2.25 | 3.156(11) | 165 |

Symmetry codes: $^{(i)}$ *x*, *y*, *z*−1; $^{(iii)}$ −*x*+3/2, −*y*+1, *z*−1/2; $^{(v)}$ −*x*+3/2, −*y*+1, *z*+1/2; $^{(vi)}$ −*x*+1, *y*+1/2, −*z*+5/2; $^{(vii)}$ *x*, *y*, *z*+1; $^{(viii)}$ *x*, *y*+1, *z*+1.

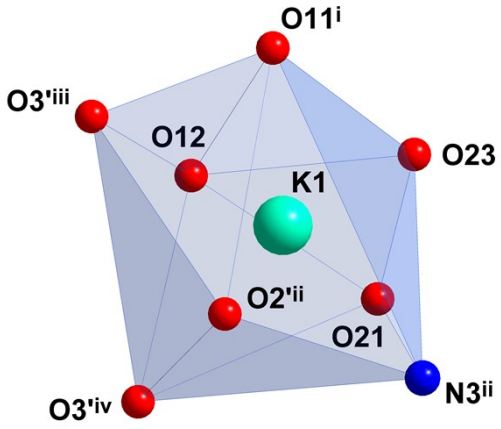



**Fig. S11** Coordination polyhedron of potassium ion in K(ADP) (**III**). Symmetry codes are given in Table S8.

**Table S8** K−O and K−N bonds lengths [Å] in K(ADP) (**III**).

| | |
|---|---|
| K1−O11$^{i}$ | 2.798(8) |
| K1−O12 | 2.694(8) |
| K1−O21 | 3.365(8) |
| K1−O23 | 2.886(7) |
| K1−O2′$^{ii}$ | 2.792(8) |
| K1−O3′$^{iii}$ | 3.413(10) |
| K1−O3′$^{iv}$ | 3.525(11) |
| K1−N3$^{ii}$ | 3.165(8) |

Symmetry codes: $^{(i)}$ *x*, *y*, *z*−1; $^{(ii)}$ *x*, *y*−1, *z*−1; $^{(iii)}$ −*x*+3/2, −*y*+1, *z*−1/2; $^{(iv)}$ *x*, *y*−1, *z*.

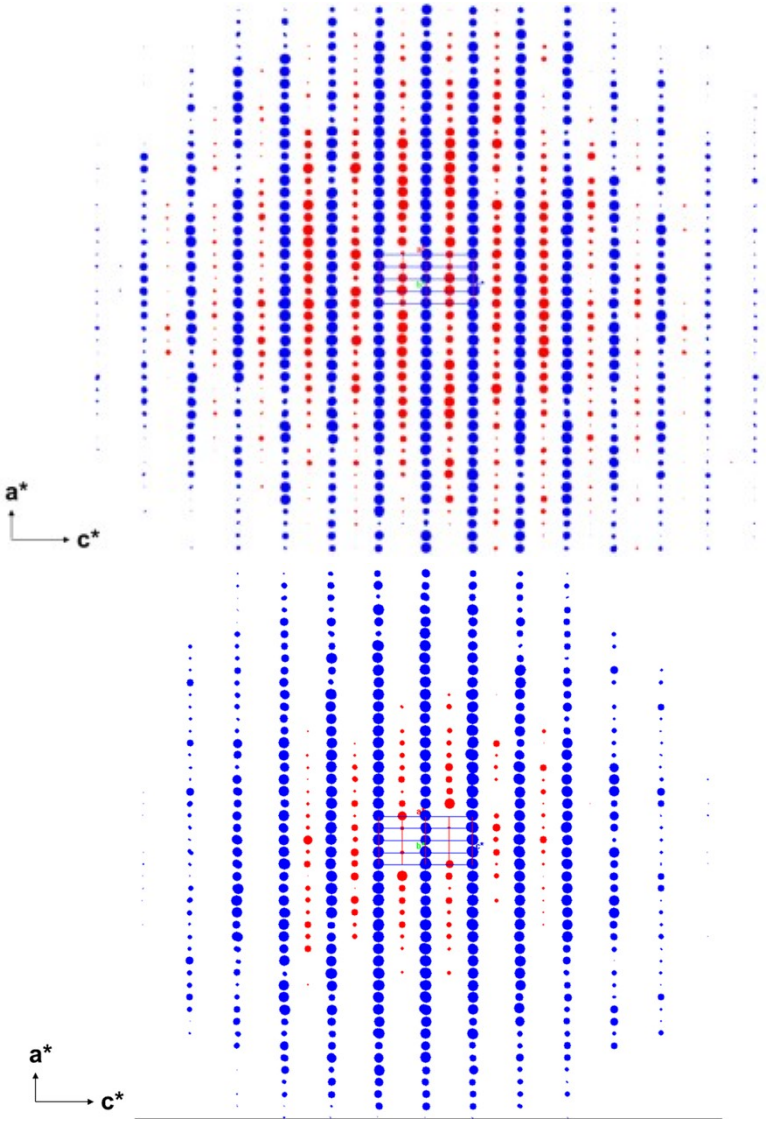



**Fig. S12** Diffraction pattern of $(H_5O_2)K(ADP)_2 \cdot 4.25H_2O$ at 100 K (top) and 280 K (bottom). Projection of the Ewald sphere along the *b** axis. Visible superstructure reflections (red) in the direction of the *c** axis. Visible reduction in the number of weak reflections with increasing temperature.

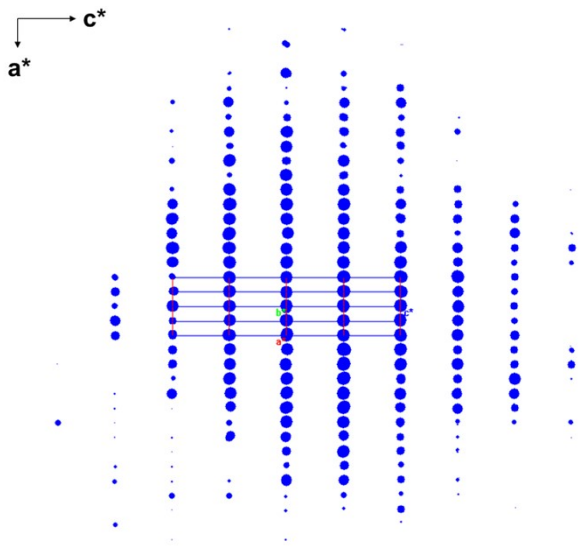



**Fig. S13** Diffraction pattern of $(H_5O_2)K(ADP)_2 \cdot 4.25H_2O$ at 300 K without superstructure reflections. Projection of the Ewald sphere along the *b** axis.

**Table S9** Geometric parameters of the hydrogen bonds for $(H_5O_2)K(ADP)_2 \cdot 4.25H_2O$ (**IVb**).

| *D*–H···*A* | *D*–H [Å] | H···*A* [°] | *D*···*A* [Å] | *D*–H···*A* [°] |
|---|---|---|---|---|
| O23A–H23A···N7B | 0.85(4) | 1.88(4) | 2.721(3) | 173(3) |
| O2′A–H2OA···O1W$^{iv}$ | 0.84 | 1.92 | 2.726(4) | 160 |
| O3′A–H3OA···O12B$^{v}$ | 0.84 | 1.87 | 2.708(3) | 176 |
| N1A–H1A···O22B$^{vii}$ | 0.81(4) | 1.86(4) | 2.675(3) | 178(3) |
| N6A–H61A···O21B$^{vii}$ | 0.88 | 1.97 | 2.848(3) | 172 |
| N6A–H62A···O22B$^{viii}$ | 0.88 | 1.95 | 2.763(3) | 152 |
| C2′A–H2′A···O4X$^{v}$ | 1.00 | 2.46 | 3.259(17) | 136 |
| C2A–H2A···O21B$^{iv}$ | 0.95 | 2.24 | 3.170(4) | 167 |
| O23B–H23B···N7A$^{iii}$ | 0.78(4) | 1.93(4) | 2.699(3) | 169(4) |
| O2′B–H2OB···O5W$^{v}$ | 0.84 | 1.85 | 2.676(3) | 169 |
| O3′B–H3OB···O2′A$^{vi}$ | 0.84 | 2.06 | 2.831(3) | 153 |
| O3′B–H3OB···O3′A$^{vi}$ | 0.84 | 2.26 | 2.784(3) | 120 |
| N1B–H1B···O22A$^{vii}$ | 0.84(4) | 1.84(4) | 2.670(3) | 172(4) |
| N6B–H61B···O21A$^{vii}$ | 0.88 | 1.99 | 2.860(3) | 171 |
| N6B–H62B···O22A | 0.88 | 2.00 | 2.816(3) | 155 |
| C1′B–H1′B···O2W$^{ix}$ | 1.00 | 2.18 | 3.082(9) | 149 |
| C1′B–H1′B···O2X$^{ix}$ | 1.00 | 2.20 | 3.04(3) | 141 |
| C2B–H2B···O21A$^{ix}$ | 0.95 | 2.36 | 3.268(4) | 160 |
| C8B–H8B···O13B | 0.95 | 2.57 | 3.486(4) | 163 |

| | | | | |
|---|---|---|---|---|
| O1W−H1W···O12A$^{iii}$ | 0.84 | 2.08 | 2.782(3) | 140 |
| O1W−H2W···N3A$^{x}$ | 0.84 | 2.37 | 3.060(3) | 140 |
| O2W−H3W···O3′B$^{i}$ | 0.84 | 2.07 | 2.867(8) | 158 |
| O2W−H4W···O21B | 0.84 | 1.91 | 2.693(8) | 154 |
| O2X−H3X···O3′B$^{i}$ | 0.84 | 1.83 | 2.64(3) | 161 |
| O2X−H4X···O21B | 0.84 | 2.03 | 2.75(3) | 143 |
| O3W−H5W···O21A | 0.84 | 1.85 | 2.618(9) | 151 |
| O3W−H6W···O2′A$^{i}$ | 0.84 | 1.83 | 2.500(10) | 136 |
| O4W−H7W···O3′B$^{v}$ | 0.84 | 2.40 | 3.051(6) | 135 |
| O4W−H7W···O5W$^{xii}$ | 0.84 | 2.41 | 3.121(6) | 143 |
| O4W−H8W···O11A | 0.84 | 2.06 | 2.814(6) | 150 |
| O4X−H7X···O5W$^{xii}$ | 0.84 | 2.42 | 3.244(18) | 166 |
| O4X−H8X···O11A | 0.84 | 2.30 | 2.868(18) | 125 |
| O5W−H9W···O1W | 0.84 | 2.00 | 2.808(4) | 162 |
| O5W−H10W···O3′A$^{xi}$ | 0.84 | 2.23 | 3.040(3) | 163 |
| O1Z−H1Z···O11A | 0.84 | 1.84 | 2.673(3) | 173 |
| O1Z−H2Z···O12B | 0.84 | 1.85 | 2.669(3) | 166 |
| O2Z−H12Z···O1Z | 1.01(6) | 1.49(6) | 2.487(4) | 168(6) |
| O2Z−H3Z···O11B$^{v}$ | 0.84 | 1.67 | 2.507(3) | 172 |
| O2Z−H4Z···O12A$^{xi}$ | 0.84 | 1.68 | 2.520(3) | 176 |

Symmetry codes: $^{(i)}$ *x*, *y*−1, *z*; $^{(iii)}$ *x*, *y*, *z*−1; $^{(iv)}$ *x*, *y*+1, *z*+1; $^{(v)}$ −*x*+3/2, −*y*+1, *z*+1/2; $^{(vi)}$ −*x*+3/2, −*y*+2, *z*−1/2; $^{(vii)}$ −*x*+1, *y*+1/2, −*z*+1/2; $^{(viii)}$ *x*, *y*, *z*+1; $^{(ix)}$ *x*, *y*+1, *z*; $^{(x)}$ *x*, *y*−1, *z*−1; $^{(xi)}$ −*x*+3/2, −*y*+1, *z*−1/2

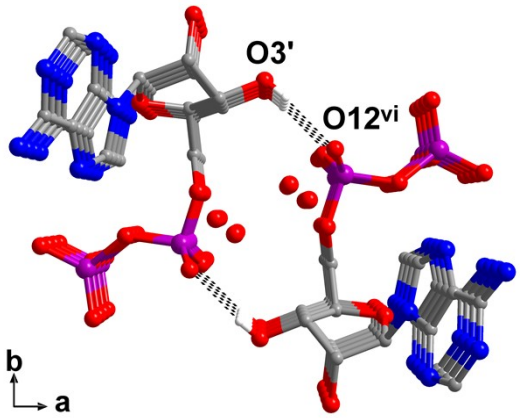



**Fig. S14** Location of the disordered Zundel cation oxygen atoms between the bilayers in crystal **IVa**. For clarity, the atoms of one of the positions of the disordered sugar ring (Y) and most of the hydrogen atoms are omitted. Selected hydrogen bonds are marked with black dotted lines. Symmetry codes are given in Table S11.

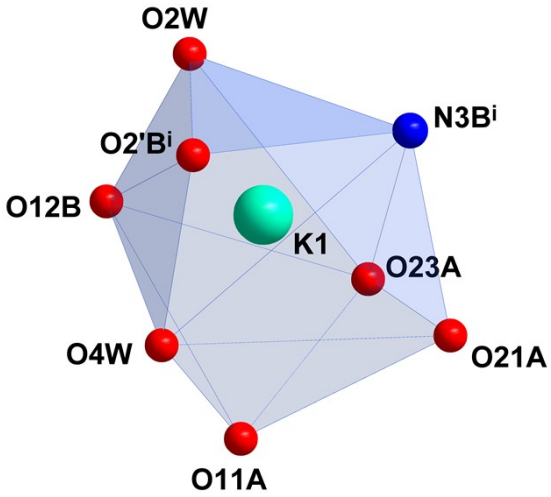



**Fig. S15** Coordination polyhedron of potassium ion in $(H_5O_2)K(ADP)_2 \cdot 4.25H_2O$ (**IVb**). Symmetry codes are given in Table S10.

**Table S10** K−O and K−N bonds lengths [Å] in $(H_5O_2)K(ADP)_2{\cdot}4.25H_2O$ (**IVb**).

| | |
|---|---|
| K1−O11A | 3.540(3) |
| K1−O21A | 3.373(4) |
| K1−O23A | 3.103(3) |
| K1−O12B | 3.308(3) |
| K1−O2′B$^{i}$ | 2.949(3) |
| K1−N3B$^{i}$ | 3.077(3) |
| K1−O2W | 2.671(9) |
| K1−O4W | 2.691(5) |

Symmetry codes: $^{(i)}$ *x*, *y*−1, *z*.

**Table S11** Geometric parameters of the hydrogen bonds for $(H_5O_2)K(ADP)_2{\cdot}4.25H_2O$ (**IVa**).

| *D*−H···*A* | *D*−H [Å] | H···*A* [°] | *D*···*A* [Å] | *D*−H···*A* [°] |
|---|---|---|---|---|
| O23−H23···N7$^{i}$ | 0.82 | 1.92 | 2.720(9) | 164 |
| O2′−H2O···O3′Y$^{iv}$ | 0.82 | 2.19 | 2.94(18) | 152 |
| O3′−H3O···O12$^{vi}$ | 0.82 | 2.04 | 2.815(13) | 159 |
| N1−H1···O22$^{viii}$ | 0.86 | 1.86 | 2.694(8) | 163 |
| N6−H61···O21$^{viii}$ | 0.86 | 2.01 | 2.868(9) | 172 |
| N6−H62···O22$^{ix}$ | 0.86 | 2.02 | 2.795(9) | 150 |
| C2−H2···O21$^{vii}$ | 0.93 | 2.36 | 3.262(10) | 164 |
| O2′Y−H2OY···O4W$^{v}$ | 0.82 | 1.72 | 2.43(4) | 144 |
| O2′Y−H2OY···O5W$^{v}$ | 0.82 | 1.91 | 2.68(4) | 158 |
| O3′Y−H3OY···O2W$^{vii}$ | 0.82 | 2.17 | 2.80(3) | 133 |
| C1′Y−H1′Y···O2W$^{vii}$ | 0.98 | 2.23 | 3.16(3) | 157 |

Symmetry codes: $^{(i)}$ *x*, *y*, *z*−1; $^{(iv)}$ −*x*+1, −*y*+2, *z*; $^{(v)}$ −*x*+1, −*y*+1, *z*+1; $^{(vi)}$ −*x*+1, −*y*+1, *z*; $^{(vii)}$ *x*, *y*+1, *z*+1; $^{(viii)}$ −*x*+1/2, *y*+1/2, −*z*+2; $^{(ix)}$ *x*, *y*, *z*+1.

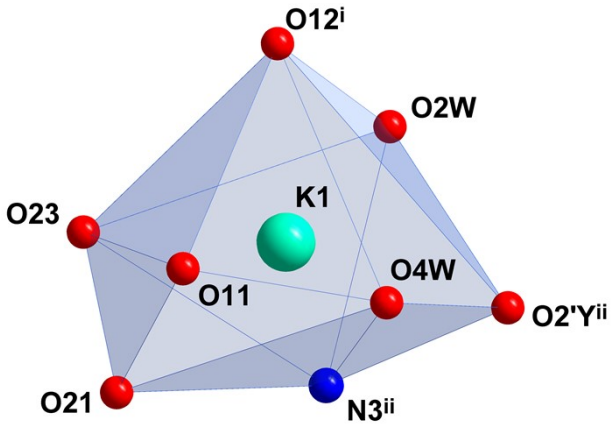



**Fig. S16** Coordination polyhedron of potassium ion in $(H_5O_2)K(ADP)_2 \cdot 4.25H_2O$ (**IVa**). Symmetry codes are given in Table S12.

**Table S12** K−O and K−N bonds lengths [Å] in $(H_5O_2)K(ADP)_2 \cdot 4.25H_2O$ (**IVa**).

| | |
|---|---|
| K1−O11 | 3.225(12) |
| K1−O12$^{i}$ | 3.111(12) |
| K1−O21 | 3.44(12) |
| K1−O23 | 3.087(11) |
| K1−O2'Y$^{ii}$ | 3.53(19) |
| K1−N3$^{ii}$ | 3.178(12) |
| K1−O2W | 2.81(2) |
| K1−O4W | 2.71(4) |

Symmetry codes: $^{(i)}$ *x*, *y*, *z*−1; $^{(ii)}$ *x*, *y*−1, *z*−1.

**Table S13** Values of deformation parameters of the analyzed coordination polyhedra from idealized shapes calculated in the *Shape* program for crystals K(ADP)·4$H_2O$ (**I**), K(ADP)·2$H_2O$ (**II**), K(ADP) (**III**) and ($H_5O_2$)K(ADP)$_2$·4.25$H_2O$ (**IVa** and **IVb**).

| Idealized shape and symmetry | HP-7[a] ($D_{7h}$) | HPY-7[b] ($C_{6v}$) | PBPY-7[c] ($D_{5h}$) | COC-7[d] ($C_{3v}$) | CTPR-7[e] ($C_{2v}$) | JPBPY-7[f] ($D_{5h}$) | JETPY-7[g] ($C_{3v}$) |
|---|---|---|---|---|---|---|---|
| K(ADP)·4$H_2O$ (**I**) | | | | | | | |
| K1 | 25.317 | 17.918 | 7.628 | 7.823 | **5.492** | 9.193 | 14.940 |
| K(ADP)·2$H_2O$ (**II**) | | | | | | | |
| K1 | 23.025 | 15.798 | 12.868 | 9.094 | **8.029** | 15.258 | 11.426 |
| K1X | 31.098 | 20.394 | 8.360 | 4.623 | **3.154** | 10.580 | 17.189 |

| Idealized shape and symmetry | JETBPY-8[h] ($D_{3h}$) | JGBF-8[i] ($D_{2d}$) | TDD-8[j] ($D_{2d}$) | SAPR-8[k] ($D_{4d}$) | CU-8[l] ($O_h$) | HBPY-8[m] ($D_{6h}$) | HPY-8[n] ($C_{7v}$) | OP-8[o] ($D_{8h}$) |
|---|---|---|---|---|---|---|---|---|
| K(ADP) (**III**) | | | | | | | | |
| K1 | 23.406 | 12.655 | **5.429** | 7.930 | 14.348 | 16.059 | 19.718 | 26.577 |
| ($H_5O_2$)K(ADP)$_2$·4.25$H_2O$ (**IVa**) | | | | | | | | |
| K1 | 19.401 | 12.832 | **9.272** | 9.578 | 16.271 | 16.753 | 16.320 | 30.287 |
| ($H_5O_2$)K(ADP)$_2$·4.25$H_2O$ (**IVb**) | | | | | | | | |
| K1 | 17.463 | 11.945 | **9.440** | 11.647 | 18.950 | 18.038 | 18.537 | 30.375 |

Idealized shapes:

[a] HP-7 – Heptagon
[b] HPY-7 – Hexagonal pyramid
[c] PBPY-7 – Pentagonal bipyramid
[d] COC-7 – Capped octahedron
[e] CTPR-7 – Capped trigonal prism
[f] JPBPY-7 – Johnson pentagonal bipyramid J13
[g] JETPY-7 – Johnson elongated triangular pyramid J7
[h] JETBPY-8 – Johnson elongated triangular bipyramid J14
[i] JGBF-8 – Johnson gyrobifastigium J26
[j] TDD-8 – Triangular dodecahedron
[k] SAPR-8 – Square antiprism
[l] CU-8 – Cube
[m] HBPY-8 – Hexagonal bipyramid
[n] HPY-8 – Heptagonal pyramid
[o] OP-8 – Octagon

**Table S14** Lengths of lp···π (lp···centroid and lp···plane) interactions of oxygen atoms and adenine six- and five-membered rings.

| | Six-membered ring | | Five-membered ring | |
|---|---|---|---|---|
| | lp···centroid [Å] | lp···plane [Å] | lp···centroid [Å] | lp···plane [Å] |
| | | K(ADP)·4$H_2O$ (**I**) | | |
| O4′$^{i}$ | 2.947(3) | 2.885(3) | – | – |
| O22$^{ii}$ | 3.473(3) | 3.117(3) | 3.511(3) | 3.118(3) |
| O23$^{ii}$ | 3.207(3) | 3.048(3) | – | – |
| | | K(ADP)·2$H_2O$ (**II**) | | |
| O4′$^{iii}$ | 2.864(3) | 2.826(3) | – | – |
| O22$^{iv}$ | 3.422(3) | 3.174(3) | 3.541(3) | 3.142(3) |
| O23$^{iv}$ | 3.378(3) | 3.133(3) | – | – |
| | | K(ADP) (**III**) | | |
| O4′$^{iii}$ | 2.950(6) | 2.896(5) | – | – |
| O22$^{v}$ | 3.499(6) | 3.310(6) | 3.718(6) | 3.299(6) |
| O23$^{v}$ | 3.475(8) | 3.188(7) | – | – |
| | | ($H_5O_2$)K(ADP)$_2$·4.25$H_2O$ (**IVa**) | | |
| O4′$^{iii}$ | 3.014(7) | 2.878(8) | – | – |
| O4′Y$^{iii}$ | 3.161(8) | 3.029(8) | – | – |
| O22$^{iv}$ | 3.612(5) | 3.115(5) | 3.553(5) | 3.092(5) |
| O23$^{iv}$ | 3.185(5) | 3.108(5) | – | – |
| | | ($H_5O_2$)K(ADP)$_2$·4.25$H_2O$ (**IVb**) (A) | | |
| O4′B$^{iii}$ | 3.151(2) | 2.904(2) | – | – |
| O22A$^{ii}$ | 3.473(2) | 2.945(2) | 3.274(2) | 2.937(2) |
| O23A$^{ii}$ | 3.193(2) | 3.098(2) | – | – |
| | | ($H_5O_2$)K(ADP)$_2$·4.25$H_2O$ (**IVb**) (B) | | |
| O4′A | 3.071(2) | 2.944(2) | – | – |
| O21B$^{vi}$ | – | – | 3.791(2) | 3.762(2) |
| O22B$^{vi}$ | 3.677(2) | 3.020(2) | 3.711(2) | 2.993(2) |
| O23B$^{vi}$ | 3.167(2) | 3.115(2) | – | – |

Symmetry codes: $^{(i)}$ *x*-1, *y*, *z*; $^{(ii)}$ -*x*+1, *y*+1/2, -*z*+1/2; $^{(iii)}$ *x*, *y*, *z*+1; $^{(iv)}$ -*x*+1/2, *y*+1/2, -*z*+1; $^{(v)}$ -*x*+1, *y*+1/2, -*z*+3/2; $^{(vi)}$ -*x*+1, *y*+1/2, -*z*-1/2

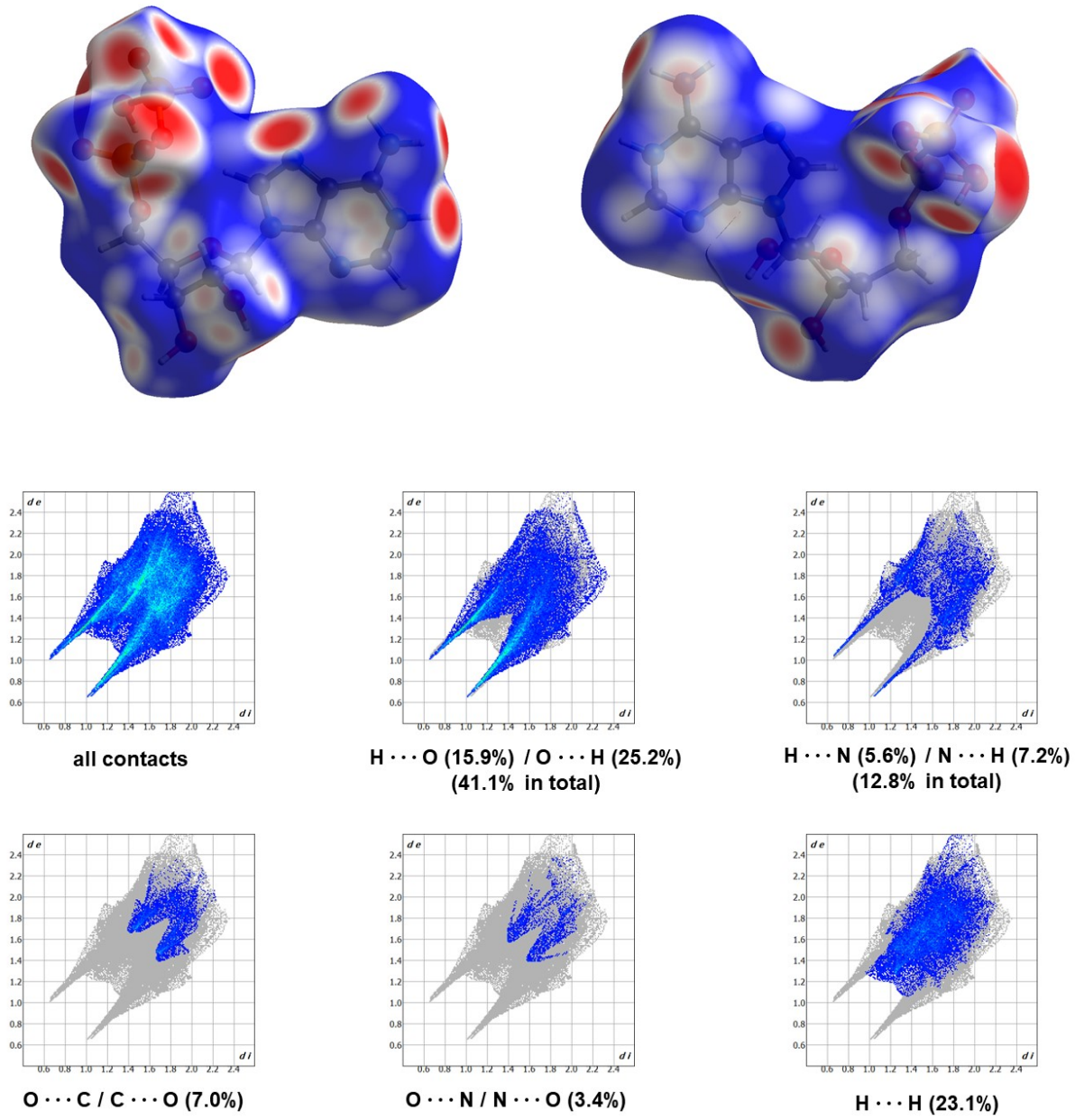
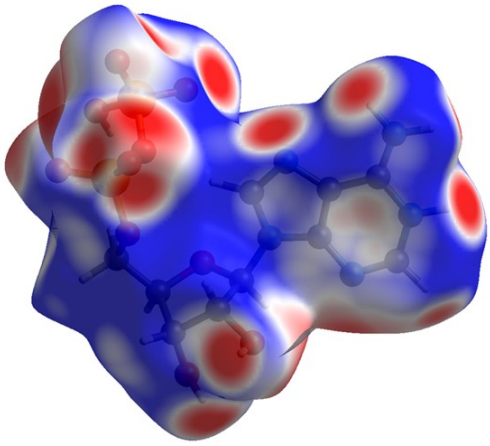
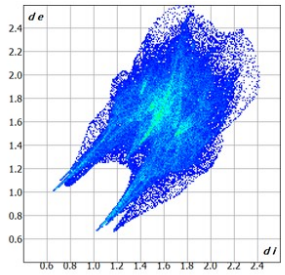
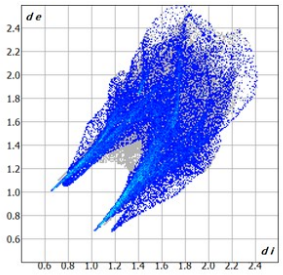



**Fig. S17** Hirshfeld surface of the $ADP^-$ anion (front and back side) in K(ADP)·4$H_2O$ (**I**): $d_{norm}$ [from −0.5 (blue) to 0.5 Å (red)] mapped on the surface (top), and 2D fingerprint plots with selected types of contacts and their contribution to the surface area (bottom).

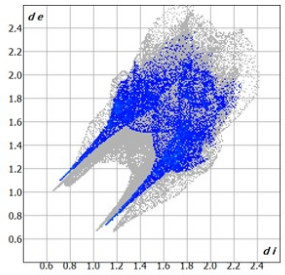




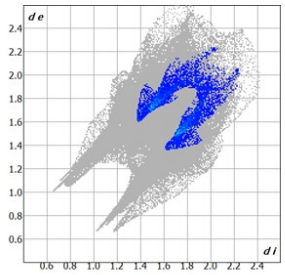

all contacts



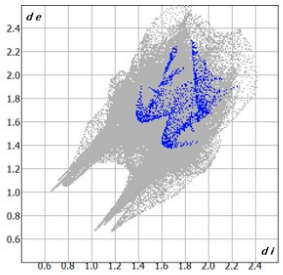

H · · · O (14.6%) / O · · · H (22.2%)
(36.7% in total)



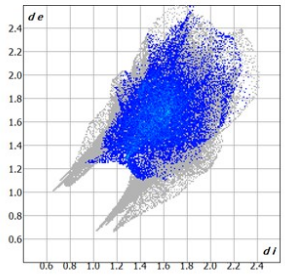

H · · · N (6.3%) / N · · · H (7.5%)
(13.8% in total)




O · · · C / C · · · O (6.5%)




O · · · N / N · · · O (2.0%)




H · · · H (23.0%)

**Fig. S18** Hirshfeld surface of the $ADP^-$ anion in K(ADP)·2$H_2O$ (**II**): $d_{norm}$ [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 (bottom).

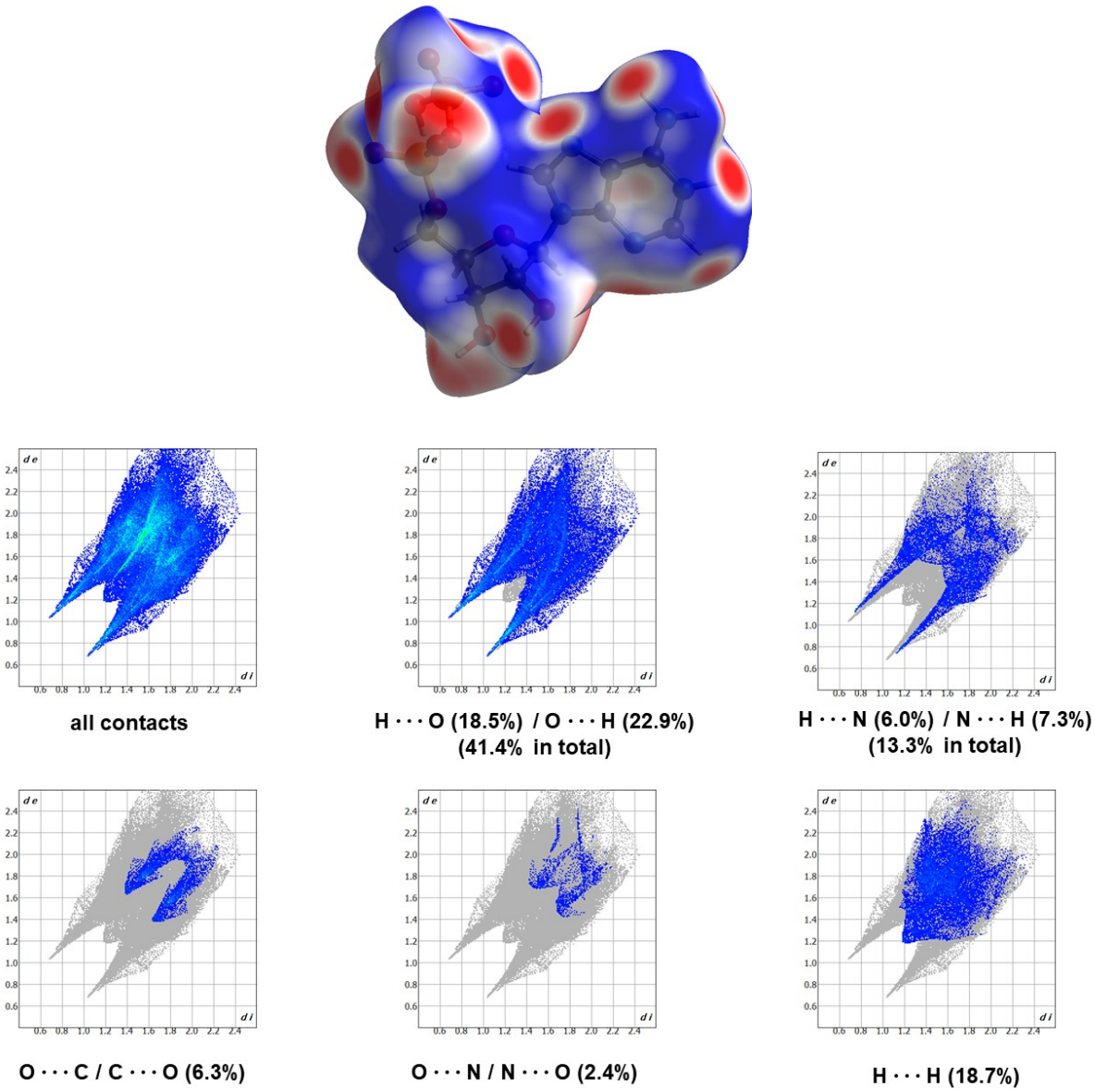



**Fig. S19** Hirshfeld surface of the $ADP^-$ anion in K(ADP) (**III**): $d_{norm}$ [from –0.5 (blue) to 0.5 Å (red)] mapped on the surface (top), and 2D fingerprint plots with selected types of contacts and their contribution to the surface area (bottom).

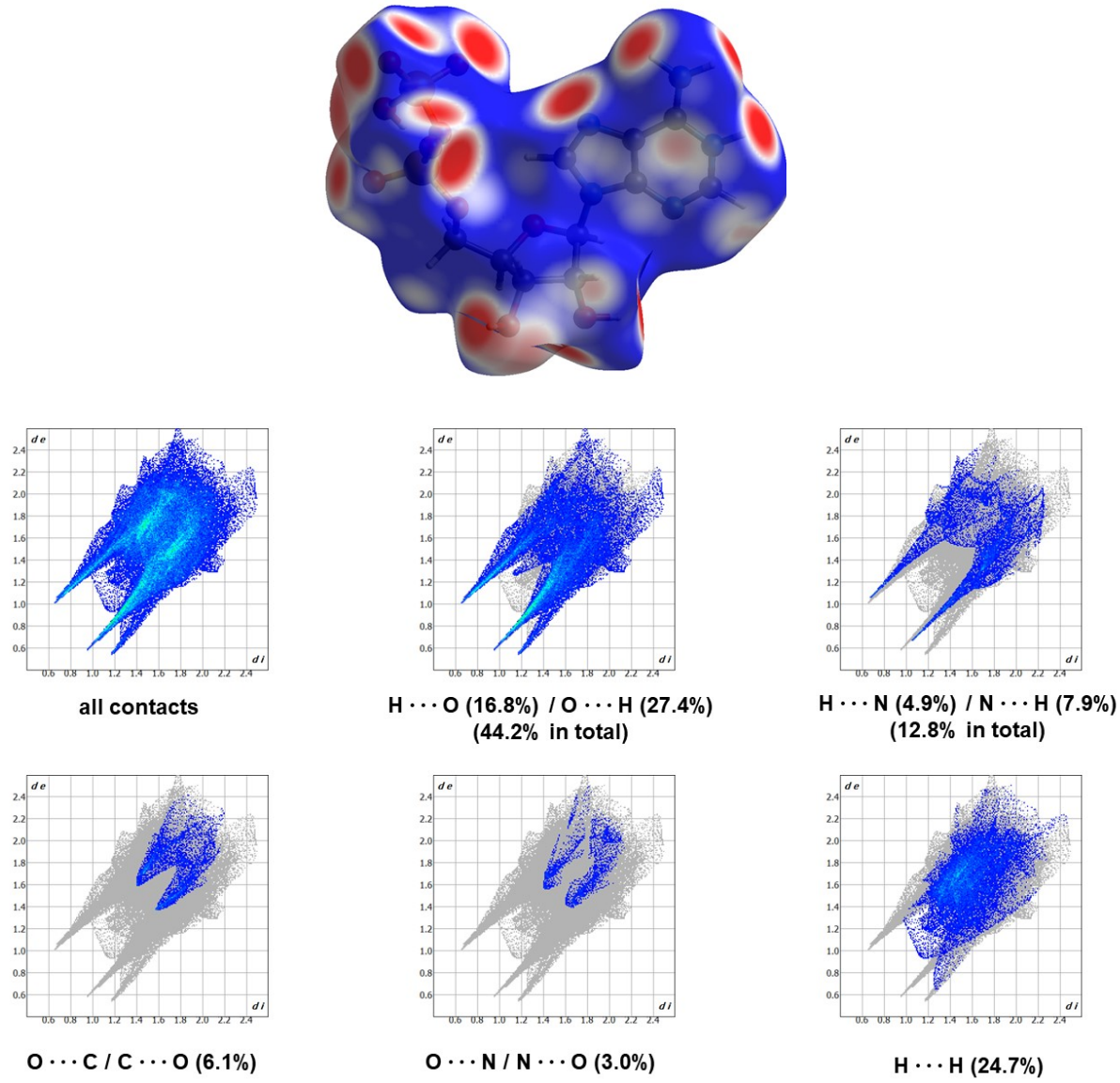
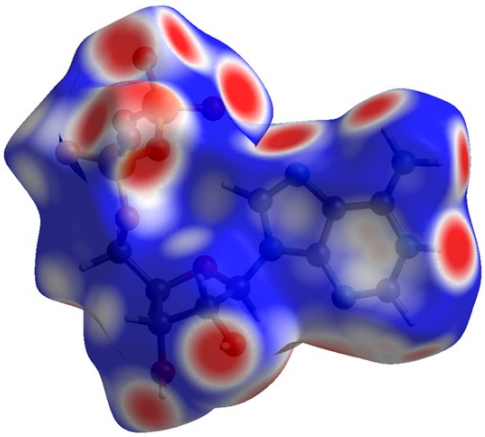
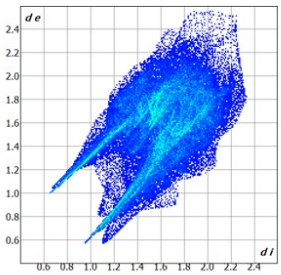
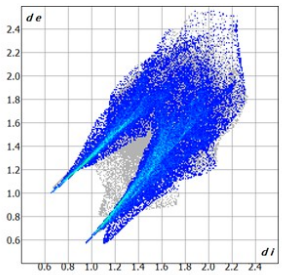



**Fig. S20** Hirshfeld surface of the $ADP^-$ anion A in low-temperature phase of $(H_5O_2)K(ADP)_2 \cdot 4.25H_2O$ (**IVb**): $d_{norm}$ [from –0.5 (blue) to 0.5 Å (red)] mapped on the surface (top), and 2D fingerprint plots with selected types of contacts and their contribution to the surface area (bottom).

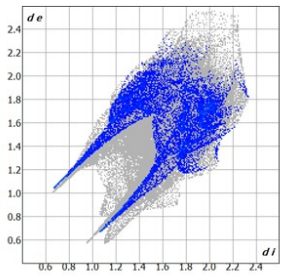




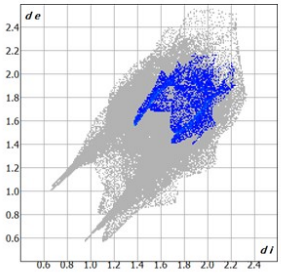

all contacts



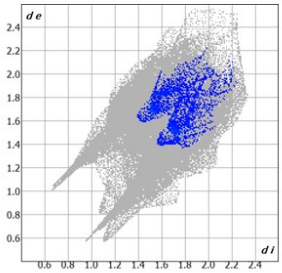

H · · · O (15.8%) / O · · · H (27.6%)
(43.4% in total)



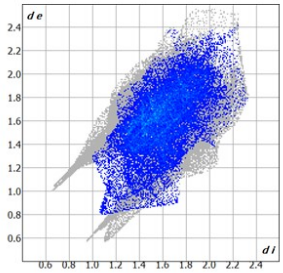

H · · · N (4.8%) / N · · · H (6.6%)
(12.8% in total)




O · · · C / C · · · O (5.5%)




O · · · N / N · · · O (4.0%)




H · · · H (25.6%)

**Fig. S21** Hirshfeld surface of the $ADP^-$ anion B in low-temperature phase of $(H_5O_2)K(ADP)_2 \cdot 4.25H_2O$ (**IVb**): $d_{norm}$ [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 (bottom).

**Table S15** Estimated percentage content of K(ADP)·2$H_2O$ and K(ADP) form in the sample during the dehydration based on series of micro-PXRD measurements.

| Temperature [K] | K(ADP)·2$H_2O$ | K(ADP) |
|---|---|---|
| 100 | 100.0 | 0.0 |
| 250 | 100.0 | 0.0 |
| 255 | 100.0 | 0.0 |
| 260 | 100.0 | 0.0 |
| 265 | 100.0 | 0.0 |
| 270 | 100.0 | 0.0 |
| 275 | 100.0 | 0.0 |
| 280 | 100.0 | 0.0 |
| 285 | 100.0 | 0.0 |
| 290 | 100.0 | 0.0 |
| 295 | 100.0 | 0.0 |
| 300 | 96.5 | 3.5 |
| 305 | 93.1 | 6.9 |
| 310 | 91.0 | 9.0 |
| 315 | 86.4 | 13.6 |
| 320 | 80.4 | 19.6 |
| 325 | 72.5 | 27.5 |
| 330 | 66.1 | 33.9 |
| 335 | 56.9 | 43.1 |
| 340 | 47.3 | 52.7 |
| 345 | 35.2 | 64.8 |
| 350 | 19.7 | 80.3 |
| 355 | 8.2 | 91.8 |
| 330 | 4.1 | 95.9 |
| 330 | 3.8 | 96.2 |
| 330 | 0.5 | 99.5 |
| 100* | 4.8 | 95.2 |

(*) Based on diffraction pattern of the sample after dehydration after two days.

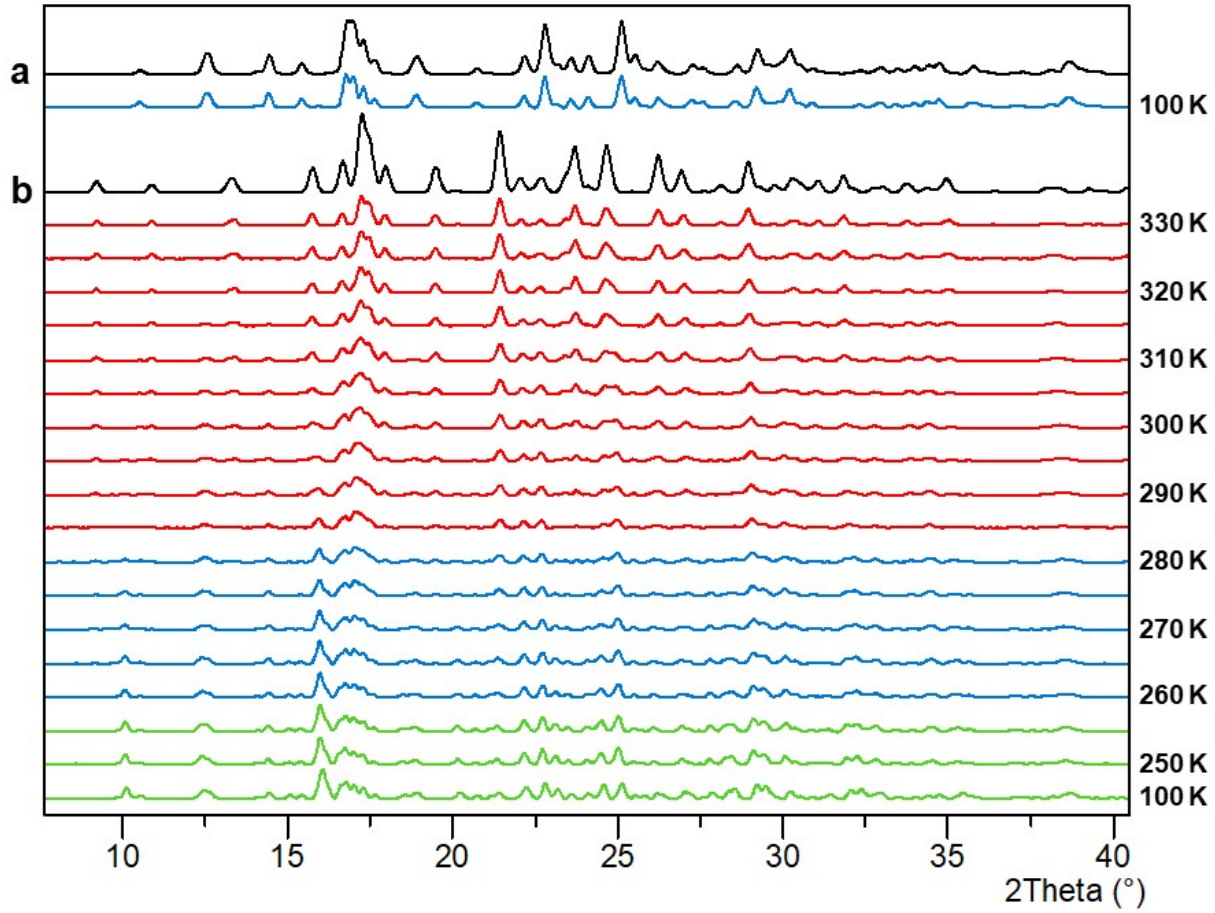



**Fig. S22** The variable temperature micro-powder X-ray diffraction patterns ($2\theta$ range 7.5–40.5°) for mixture of **I** and **II** (55:45) recorded at 100–330 K. Patterns for which the tetrahydrate phase was the dominant form are marked in green, for dihydrate dominant – in blue and anhydrous phase – in red. Theoretical (calculated) diffraction patterns for **II** (a) and **III** (b) are marked in black.

**Table S16** Estimated percentage content of K(ADP)·4$H_2O$, K(ADP)·2$H_2O$ and K(ADP) form in the sample during the dehydration based on series of micro-PXRD measurements.

| Temperature [K] | K(ADP)·4$H_2O$ | K(ADP)·2$H_2O$ | K(ADP) |
|---|---|---|---|
| 100 | 55.9 | 44.1 | 0.00 |
| 250 | 52.2 | 47.8 | 0.00 |
| 255 | 50.9 | 49.1 | 0.00 |
| 260 | 49.3 | 50.7 | 0.00 |
| 265 | 44.8 | 47.9 | 7.3 |
| 270 | 39.1 | 46.8 | 14.1 |
| 275 | 31.8 | 46.0 | 22.2 |
| 280 | 24.0 | 43.9 | 32.1 |
| 285 | 15.6 | 41.8 | 42.6 |
| 290 | 8.1 | 40.2 | 51.7 |
| 295 | 3.6 | 38.0 | 58.4 |
| 300 | 1.2 | 35.3 | 63.5 |
| 305 | 0.0 | 30.4 | 69.6 |
| 310 | 0.0 | 22.9 | 77.1 |
| 315 | 0.0 | 11.4 | 88.6 |
| 320 | 0.0 | 5.8 | 94.2 |
| 325 | 0.0 | 1.6 | 98.4 |
| 330 | 0.0 | 0.1 | 99.9 |
| 100* | 0.0 | 0.0 | 100.0 |

(*) Based on diffraction pattern of the sample after dehydration after two days.

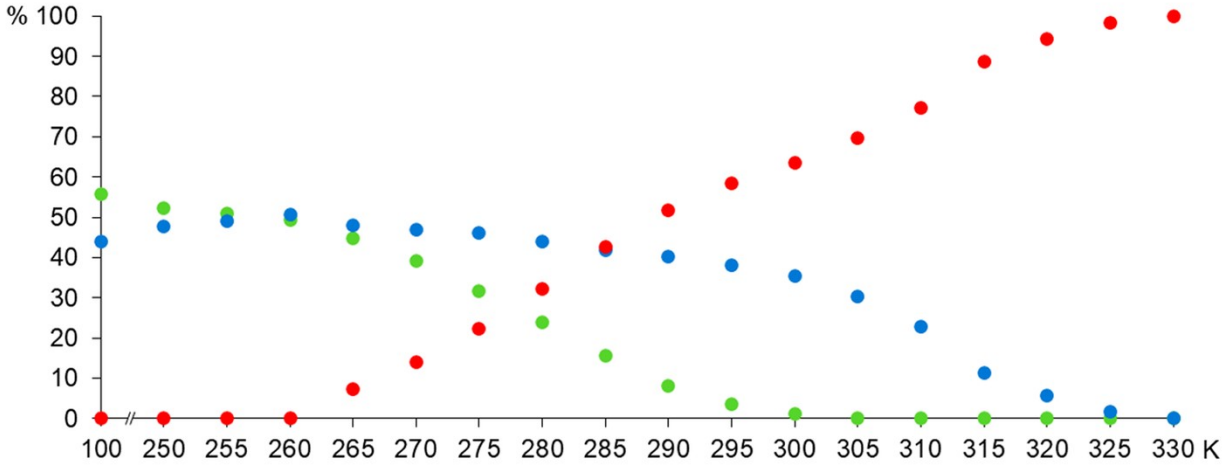



**Fig. S23** Estimated percentage content of K(ADP)·4$H_2O$ (marked in green), K(ADP)·2$H_2O$ (marked in blue) and K(ADP) form (marked in red) in the sample during the dehydration based on series of micro-PXRD measurements.

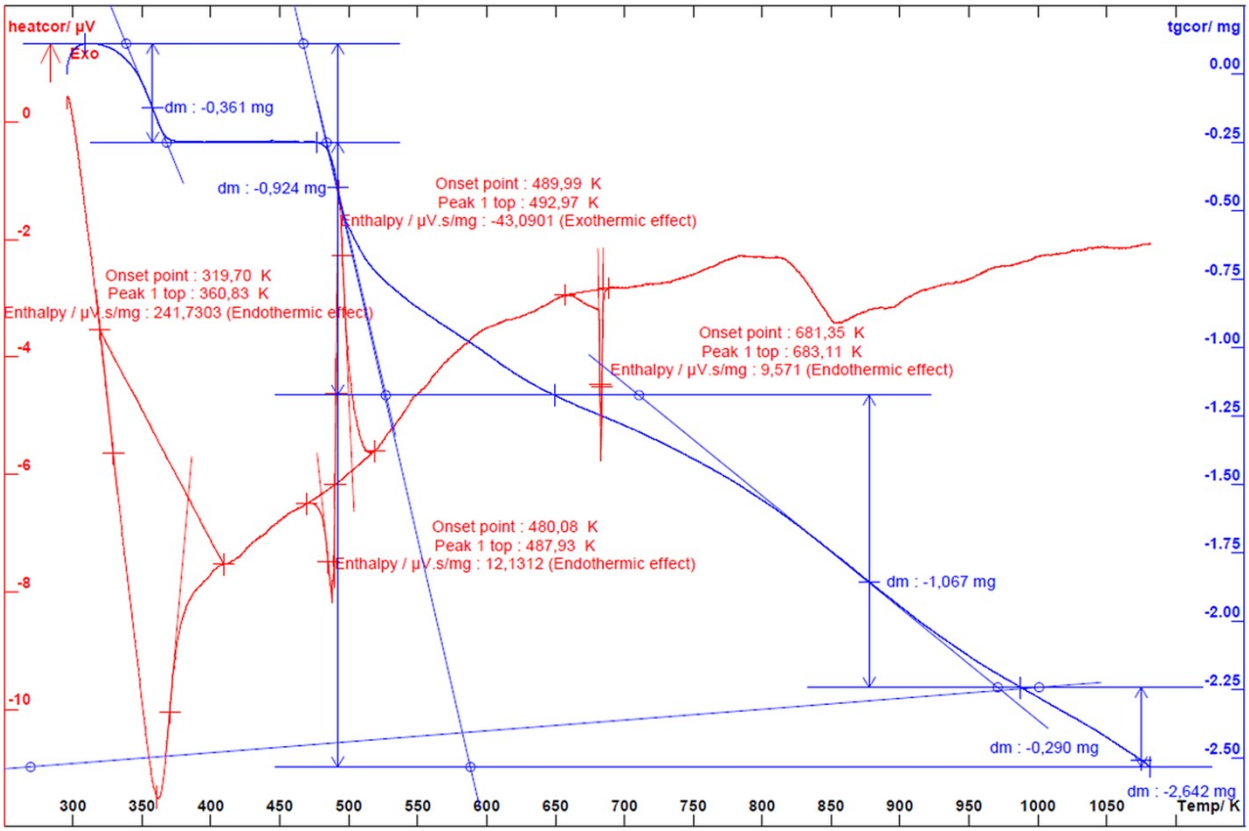



**Fig. S24** TGA/DTA curves for **II** (mass of sample = 5.192 mg).

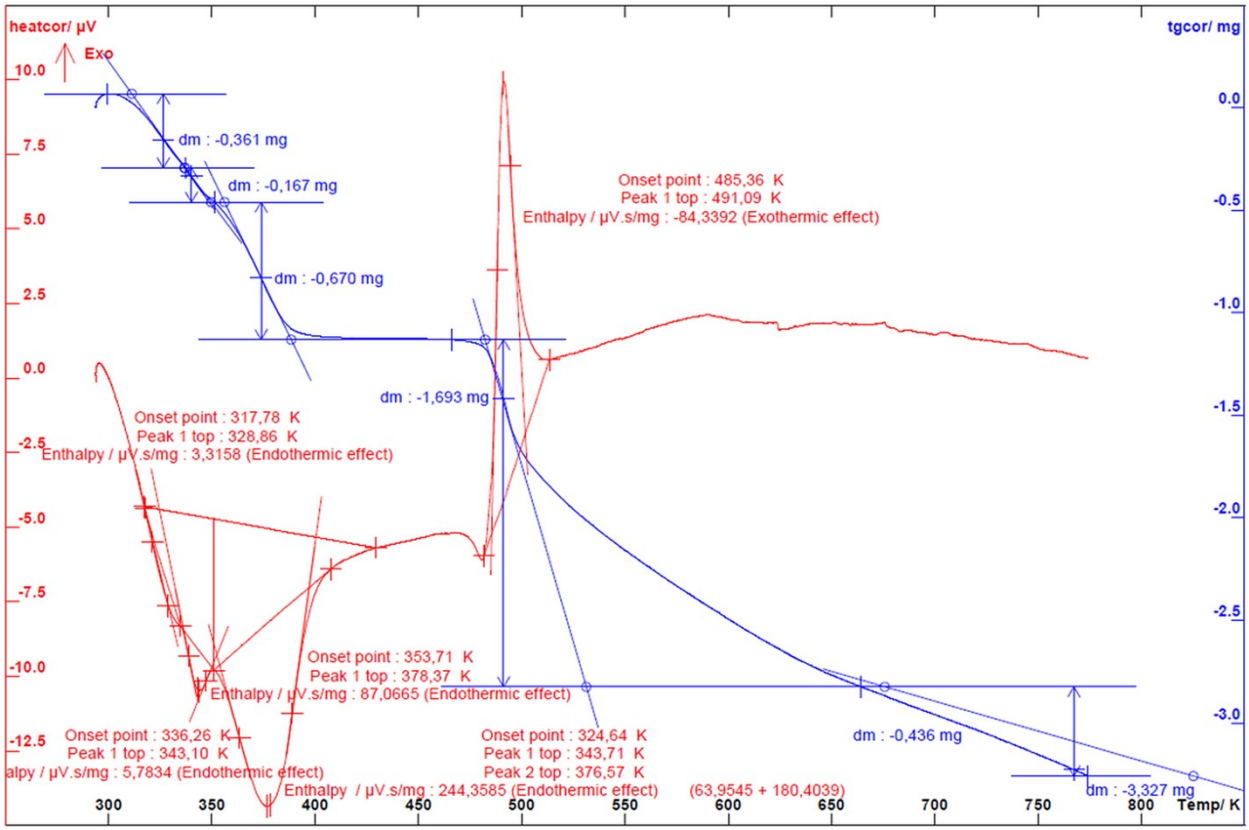



**Fig. S25** TGA/DTA curves for mixture of **I** and **II** (mass of sample = 9.712 mg).