

Short Note

Supramolecular Hydrogen-Bond *Motifs* in Chiral and Racemic Molecular Salts: A Comparison of (*S*)-2-Methyl Piperizinium Hydrogen Phosphite Monohydrate, $C_5H_{14}N_2 \cdot HPO_3 \cdot H_2O$ and (*R,S*)-2-Methyl Piperizinium Hydrogen Phosphite 2.23 Hydrate, $C_5H_{14}N_2 \cdot HPO_3 \cdot 2.23H_2O$

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Abstract: The crystal structures of $C_5H_{14}N_2 \cdot HPO_3 \cdot H_2O$ (**1**) and $C_5H_{14}N_2 \cdot HPO_3 \cdot 2.23H_2O$ (**2**) are described and compared. Compound **1** contains homochiral (*S*)-2-methyl piperizinium cations, hydrogen phosphite ions and water molecules. The components are linked by N–H···O and O–H···O hydrogen bonds into a three-dimensional network. In compound **2**, racemic (*R,S*)-2-methyl piperizinium cations combine with the same anions and water molecules to generate a far more complex, high symmetry “supramolecular” structure, which features distinctive $R^6_6(12)$ loops and helical $C(2)$ chain hydrogen-bonding *motifs* involving the water molecules. Crystal data: **1** ($C_5H_{17}N_2O_4P$), $M_r = 200.18$, orthorhombic, $P2_12_12_1$ (No. 19), $Z = 4$, $a = 8.564$ (5) Å, $b = 9.593$ (6) Å, $c = 11.607$ (6) Å, $V = 953.6$ (9) Å³, $R(F) = 0.066$, $wR(F^2) = 0.081$. **2** ($C_5H_{19.47}N_2O_{5.24}P$), $M_r = 222.49$, trigonal, $R\bar{3}$ (No. 148), $Z = 18$, $a = 31.075$ (2) Å, $c = 6.1875$ (4) Å, $V = 5174.5$ (6) Å³, $R(F) = 0.044$, $wR(F^2) = 0.107$.

Keywords: molecular salt; supramolecular network; O–H···O hydrogen bonds

1. Introduction

Supramolecular chemistry—the “chemistry of molecular assemblies and intermolecular bonds” [1] is an area of contemporary chemical research to which crystallography makes a key contribution. The

(non-covalent) intermolecular interaction *par excellence* is arguably the hydrogen bond and much work has been carried out in this area, for which a recent two-volume review edited by Mingos *et al.* [2] may serve as a starting point for further reading.

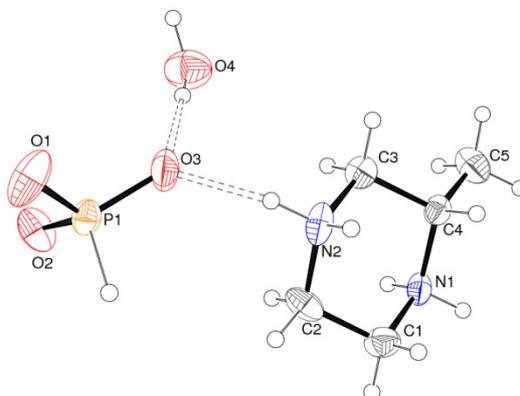
As a small contribution to this area, we now describe the syntheses and crystal structures of two related molecular salts, *viz.*, $C_5H_{14}N_2 \cdot HPO_3 \cdot H_2O$ (**1**) and $C_5H_{14}N_2 \cdot HPO_3 \cdot 2.23H_2O$ (**2**), which contain homochiral (*S*)-2-methyl piperizinium and racemic (*R,S*)-2-methyl piperizinium cations, respectively, combined with the same simple inorganic anion and water molecules of crystallization. This also follows on from our previous studies of hydrogen-bonding patterns in molecular salts containing oxo-anions, for example piperizinium hydrogen phosphite monohydrate, $C_4H_{12}N_2 \cdot HPO_3 \cdot H_2O$ [3], in which supramolecular anion–water chains occur.

2. Results and Discussion

2.1. Structure of $C_5H_{14}N_2 \cdot HPO_3 \cdot H_2O$ (**1**)

Compound **1** is a hydrated molecular salt in which double proton transfer from phosphorus acid to (*S*)-2-methyl piperizine has occurred: the asymmetric unit contains one $[C_5H_{14}N_2]^{2+}$ cation, one $[HPO_3]^{2-}$ anion and one water molecule of crystallisation (Figure 1). Its space group of $P2_12_12_1$ (see experimental section) is of course consistent with the presence of the homochiral organic molecule. The geometrical parameters for the component species in **1** are unexceptional: the cation [mean C–C = 1.515 (7) Å; mean C–N = 1.486 (7) Å] adopts a typical chair conformation with the pendant methyl group in an equatorial position, as is usually seen for this species in the solid state [4]. The N2–C3–C4–C5 and C1–N1–C4–C5 torsion angles are 175.5 (5) and 179.7 (6)°, respectively. The hydrogen phosphite dianion possesses typical geometrical parameters [mean P–O = 1.506 (4) Å; mean O–P–O = 112.0 (3)°] and the P atom is displaced from the plane of its three attached O atoms by 0.434 (3) Å. As expected [5], the P–H vertex is not involved in bonding (or hydrogen bonding) to other species.

Figure 1. The molecular structure of **1** showing 50% displacement ellipsoids. The N2–H2b···O3 and O4–H2···O3 hydrogen bonds are shown as double-dashed lines.



The packing for **1** features N–H···O and O–H···O hydrogen bonds (Table 1). All four N–H vertices of the cation make N–H···O links to different hydrogen phosphite O atoms. The bond involving H2b is

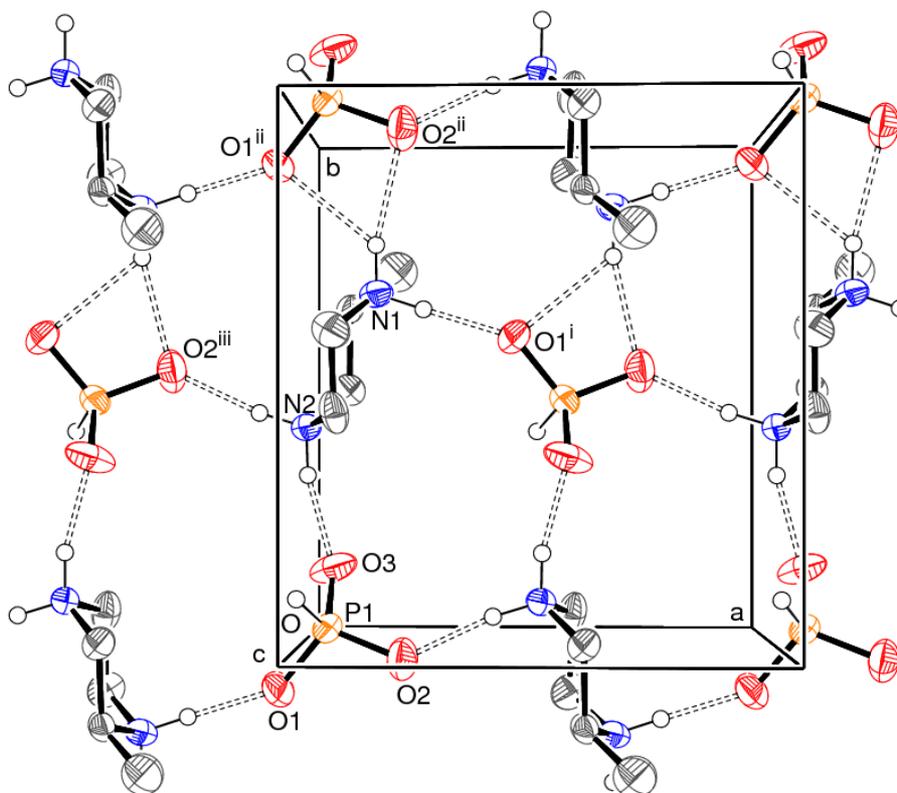
a bifurcated N–H···(O,O) link to two oxygen atoms in the same dianion (bond angle sum for H2b = 359.9°). Taken together, these bonds link the cations and anions into (001) sheets (Figure 2). Within the sheets, $R_4^2(11)$ and $R_4^3(15)$ loops, using the graph-set notation of Bernstein *et al.* [6], are apparent.

Table 1. Hydrogen-bond geometries for **1**.

Bond	D–H	H···A	D···A	D–H···A
N1–H1A···O1 ⁱ	0.90	1.72	2.617 (6)	179
N1–H1B···O2 ⁱⁱ	0.90	2.19	3.073 (6)	167
N1–H1B···O1 ⁱⁱ	0.90	2.33	2.958 (6)	127
N2–H2B···O3	0.90	1.79	2.662 (6)	164
N2–H2A···O2 ⁱⁱⁱ	0.90	1.79	2.688 (6)	172
O4–H2···O3	0.84	1.91	2.741 (7)	172
O4–H3···O2 ^{iv}	0.93	1.91	2.838 (7)	179

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (ii) $x, 1+y, z$; (iii) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (iv) $\frac{1}{2}-x, -y, -1/2+z$.

Figure 2. Partial packing diagram for **1** showing part of an (001) cation/anion sheet. Hydrogen bonds are shown as double-dashed lines. See Table 1 for symmetry codes.

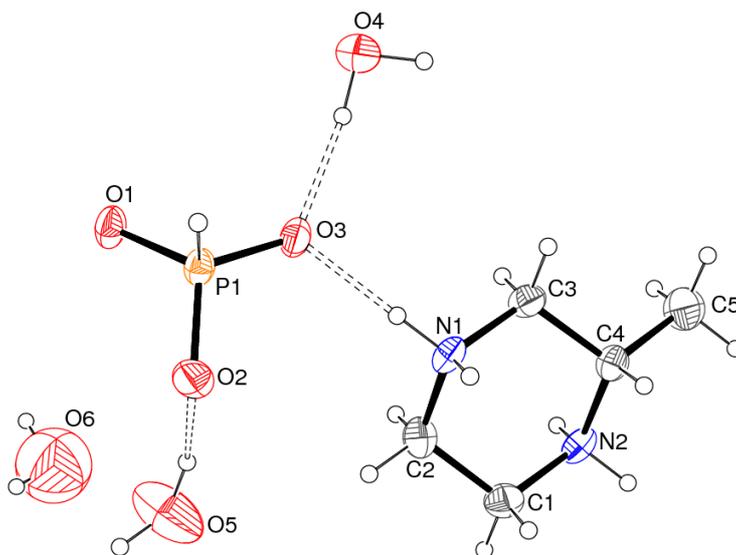


Finally, the water molecule of crystallisation in **1** makes two O–H···O hydrogen bonds to link the (001) cation/anion sheets into a three-dimensional array. Overall, the phosphite oxygen atoms O1, O2 and O3 accept two, three and two hydrogen bonds each, respectively.

2.2. Structure of $C_5H_{14}N_2 \cdot HPO_3 \cdot 2.23H_2O$ (**2**)

The asymmetric unit of compound **2** contains one cation, one anion and three water molecules of crystallisation, one of which is partially occupied (Figure 3). The pendant methyl group of the cation has an equatorial orientation and the N1–C3–C4–C5 and C1–N2–C4–C5 torsion angles are 176.6 (2) and -177.5 (2) $^\circ$, respectively. Otherwise, the key geometrical parameters in **2** barely differ from those for the equivalent species **1**: mean C–C = 1.513 (4) Å; mean C–N = 1.482 (4) Å; mean P–O = 1.512 (2) Å; mean O–P–O = 112.5 (2) $^\circ$; displacement of the P atom from its three attached O atoms = 0.4240 (13) Å. The centrosymmetric crystal symmetry (space group $R\bar{3}$) generates a statistical mixture of the two enantiomers of the organic cation, which is consistent with the racemic starting material.

Figure 3. The molecular structure of **2** showing 50% displacement ellipsoids. The N1–H1c \cdots O3, O4–H41 \cdots O3 and O5–H51 \cdots O2 hydrogen bonds are shown as double-dashed lines.

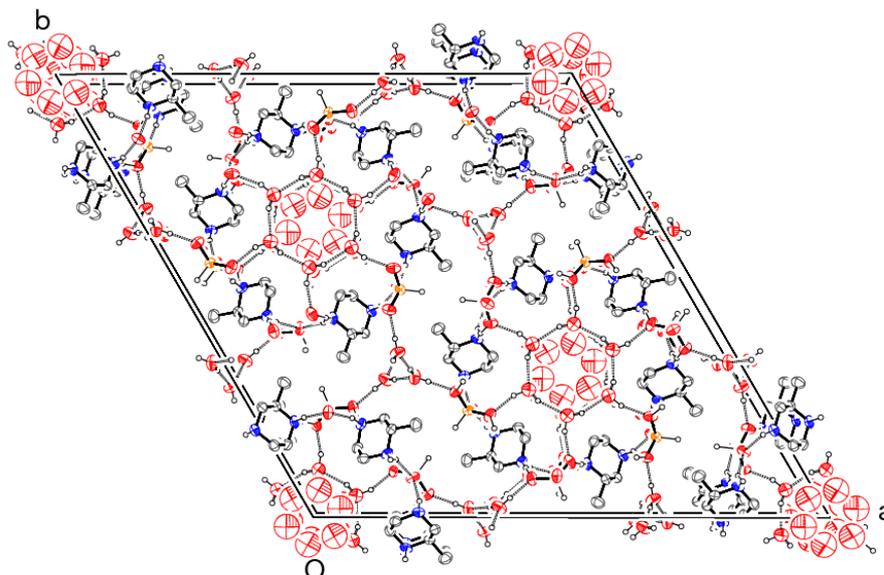


The complex unit-cell packing in **2** (Figure 4) can be broken down as follows. Alternating six-rings of the O5- and O6-water molecules stack about the $\bar{3}$ symmetry axis located at ($x = 0, y = 0$) and symmetry-equivalent positions. The O5 species are well ordered and almost in the same plane as the $\bar{3}$ -axis inversion centre at (0, 0, 1/2). They combine to form a distinctive “daisy-chain” motif of a six-ring of O5–H19 \cdots O5 hydrogen bonds, resulting in an $R_6^6(12)$ loop [6]. So far as we can ascertain from the present refinement, within any one loop, the hydrogen bonds are well ordered and all aligned in the same sense (either clockwise or anticlockwise). The O5–H18 vertex makes a hydrogen bond to an O atom of a nearby hydrogen phosphite group.

Due to two short, symmetry generated, oxygen \cdots oxygen contacts [O \cdots O = 1.610 (18) Å], the O6 water molecule must be partially occupied with a maximum site occupancy of $1/3$ [the refined site occupancy of 0.230 (11) is slightly lower than this value]. The H atoms associated with this disordered

species were geometrically placed in reasonable positions to form hydrogen bonds, and their locations should be regarded as less certain than those of the other atoms.

Figure 4. The unit-cell packing for **2** viewed approximately down the *c* axis direction. Hydrogen bonds are shown as double-dashed lines. The C-bound H atoms are omitted for clarity and all the orientations of the disordered O6 atoms are shown.



The $\bar{3}$ axis generates six hydrogen phosphite groups to encapsulate each O5 water-molecule ring and a $[\text{C}_3\text{H}_{14}\text{N}_2]^{2+}$ cation wedges between each adjacent phosphite pair and interacts with them by means of $\text{N-H}\cdots\text{O}$ bonds. These hydrogen bonds also link to further rings of anions both above and below the plane of the cations, to result in infinite [001] tubes: the cations in any six-ring circuit have alternating *R* and *S* chiralities at their C4 atoms. The cation/anion tubes (Figure 5) thus serve as “supramolecular wrappers” to encapsulate the O5/O6 water molecules, or alternately, we may envisage that the O5/O6 water molecule columns serve to “template” the ionic components of the structure.

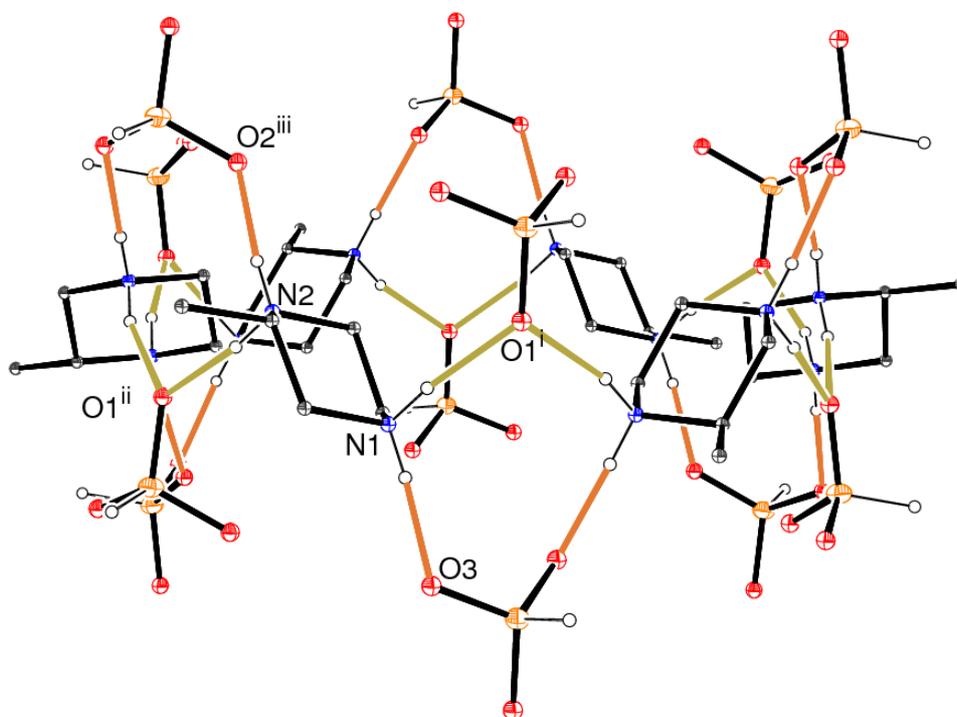
Table 2. Hydrogen-bond geometries for **2**.

Bond	<i>D</i> –H	H \cdots A	<i>D</i> \cdots A	<i>D</i> –H \cdots A
N1–H1C \cdots O3	0.90	1.75	2.648 (3)	176
N1–H1D \cdots O1 ⁱ	0.90	1.83	2.701 (3)	164
N2–H2C \cdots O1 ⁱⁱ	0.90	1.80	2.680 (3)	166
N2–H2D \cdots O2 ⁱⁱⁱ	0.90	1.77	2.665 (3)	173
O4–H41 \cdots O3	0.93	1.82	2.746 (3)	172
O4–H42 \cdots O4 ^{iv}	0.92	1.81	2.724 (2)	171
O5–H51 \cdots O2	0.98	1.89	2.830 (3)	161
O5–H52 \cdots O5 ^v	0.89	2.05	2.829 (3)	147
O6–H61 \cdots O5 ^{vi}	0.90	2.01	2.912 (7)	180
O6–H62 \cdots O6 ^{vii}	0.90	2.04	2.942 (5)	180

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

Finally, the hydrogen phosphite O3 atom accepts a hydrogen bond from the O4 water molecule, by way of an O4–H16···O3 interaction and an O4–H17···O4 (water-to-water) hydrogen bond completes the structure. These infinite [001] chains of water-molecule hydrogen bonds entwine about either a 3_1 or a 3_2 symmetry axis [at $(x = 1/3, y = 1/3)$ and symmetry-equivalent locations], hence generating $C(2)$ helices of hydrogen bonds. Around any O5-centred column, the O4–H17···O4 helices propagate in alternating clockwise and anticlockwise senses.

Figure 5. A slice of a “supramolecular wrapper” of hydrogen bonded cations and anions in **2**, viewed approximately normal to the c axis direction. Hydrogen bonds to the μ^2 -bridging O1 atom and $\mu^1 + \mu^1$ O2+O3 atoms are shown as brass and mandarin lines, respectively. The C-bound H atoms are omitted for clarity. The most direct transit about the wrapper generates an $R^6_{12}(42)$ loop [5]. See Table 2 for symmetry codes.



3. Experimental Section

Compound **1** was prepared by dissolving (*S*)-2-methyl piperazine (Aldrich, 99%, 0.10 g; 1.00 mmol) and H_3PO_3 (0.082 g; 1.00 mmol) in 2 mL distilled water at room temperature. A few tiny, colorless rods of **1** were observed after a few days as the water evaporated from a watch glass. Repeated attempts to grow larger, better quality crystals were unsuccessful and glassy/amorphous residues were usually the result.

To prepare compound **2**, (*R,S*)-2-methyl piperazine (Aldrich, 98%, 1.00 g; 10.0 mmol) and H_3PO_3 (0.82 g; 10.0 mmol) were dissolved in 10 mL distilled water at room temperature. Colorless needle-shaped crystals of **2** grew over the course of a few days as the solvent evaporated.

The single-crystal data for **1** and **2** were collected using a Bruker SMART1000 CCD diffractometer (graphite monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) at room temperature. Suitable crystals

were selected and mounted on thin glass fibers with cyanoacrylate adhesive and intensity data were collected with the aid of the SMART program. Data reduction with SAINT then proceeded in each case and the structures were solved by direct methods with SHELXS. The resulting atomic models were refined against $|F|^2$ with SHELXL [7] and the “observed data” threshold for calculating the $R(F)$ residuals was set as $I > 2\sigma(I)$.

The small crystal of **1** was a feeble scatterer, which may correlate with the high R_{Int} value. Disappointingly, refinement of the Flack absolute structure parameter [8] for **1** was inconclusive [refined value = $-0.2(3)$] and therefore the S configuration for atom C5 was assigned based on the stated absolute structure of the starting material. The C-, N- and P-bound H atoms were placed in idealised locations (C–H = 0.96–0.97 Å, N–H = 0.90 Å, P–H = 1.32 Å) and refined as riding atoms. The water H atoms were located in a difference map and refined as riding atoms in their as-found relative locations. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ was applied in all cases.

For **2**, the C-, N- and P-bound H atoms were treated in the same way as the equivalent atoms in **1**. The H atoms attached to O4 and O5 were located in a difference map and refined as riding atoms in their as-found relative locations. The H atoms attached to O6 were placed in chemically reasonable positions to achieve O–H···O hydrogen bonds and refined as riding atoms. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ was applied in all cases. Atom O6 and its attached H atoms have refined site occupancies of 0.230 (11). A PLATON [9] void-space analysis indicated a small amount of free space in the vicinity of (0, 0, 1/2), in the centre of the O5 daisy chain. An O atom placed there refined to zero site occupancy in a few cycles. Full refinement details are given in the deposited cifs.

Crystal data for **1**: colorless rod, $0.04 \times 0.01 \times 0.01$ mm, $\text{C}_5\text{H}_{17}\text{N}_2\text{O}_4\text{P}$, $M_r = 200.18$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 8.564(5)$ Å, $b = 9.593(6)$ Å, $c = 11.607(6)$ Å, $V = 953.6(9)$ Å³, $Z = 4$, $F(000) = 432$, $T = 293$ K, $\rho_{\text{calc}} = 1.394$ g cm⁻³, $\mu = 0.272$ mm⁻¹, 5970 reflections measured ($-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-8 \leq l \leq 14$; $5.50^\circ \leq 2\theta \leq 52.00^\circ$), $R_{\text{Int}} = 0.247$, 1104 merged reflections, 507 with $I > 2\sigma(I)$, 110 parameters, $R(F) = 0.066$, $wR(F^2) = 0.081$, $w = 1/[\sigma^2(F_o^2) + 0.0035P^2]$, where $P = (F_o^2 + 2F_c^2)/3$, min./max. $\Delta\rho = -0.21, +0.22$ e Å⁻³. Cambridge Database deposition number: CSD-840886.

Crystal data for **2**: colorless needle, $0.45 \times 0.04 \times 0.03$ mm, $\text{C}_5\text{H}_{19.46}\text{N}_2\text{O}_{5.23}\text{P}$, $M_r = 222.49$, trigonal, $R\bar{3}$ (No. 148), $a = 31.075(2)$ Å, $c = 6.1875(4)$ Å, $V = 5174.5(6)$ Å³, $Z = 18$, $F(000) = 2167$, $T = 296$ K, $\rho_{\text{calc}} = 1.285$ g cm⁻³, $\mu = 0.240$ mm⁻¹, 11694 reflections measured ($-37 \leq h \leq 38$, $-38 \leq k \leq 27$, $-7 \leq l \leq 7$; $4.54^\circ \leq 2\theta \leq 52.00^\circ$), $R_{\text{Int}} = 0.067$, 2270 merged reflections, 1419 with $I > 2\sigma(I)$, 120 parameters, $R(F) = 0.044$, $wR(F^2) = 0.107$, $w = 1/[\sigma^2(F_o^2) + 0.0541P^2]$, where $P = (F_o^2 + 2F_c^2)/3$, min./max. $\Delta\rho = -0.15, +0.24$ e Å⁻³. Cambridge Database deposition number: CSD-840887.

4. Conclusions

The crystal structures of the two title hydrated molecular salts have been described. Although they contain the same simple building units, differing only in the homochiral/racemic nature of the cations, their crystal structures are very different. The structure of **1** might be regarded as “typical” of a hydrated molecular salt [10,11] and similar networks of hydrogen bonds have been seen in many related structures [12,13]: it seems that the chiral nature of the cation in **1** imparts no notable properties

whatsoever to the extended structure. Indeed, the supramolecular connectivity in **1** closely resembles that in the centrosymmetric $C_4H_{12}N_2 \cdot HPO_3 \cdot H_2O$ [3].

The complex, high symmetry, centrosymmetric structure of **2** is quite different, and the differences seem to extend beyond the replacement of the chiral organic cation by its racemic congener. It is perhaps most notable that hydrogen bonding involving the water molecules in **2** appear to play such a critical role in establishing the supramolecular structure in terms of the “daisy chains” and helices described above, although we most certainly do not claim that these *motifs* are “novel” or previously unseen in other structures [14].

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