

Hydrogen bonding in 2,2',2''-(nitrilotrimethylene)-
tripyridinium hydrogenphosphate tetrakis(per-
chlorate) dihydrate and related compounds

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Key indicators

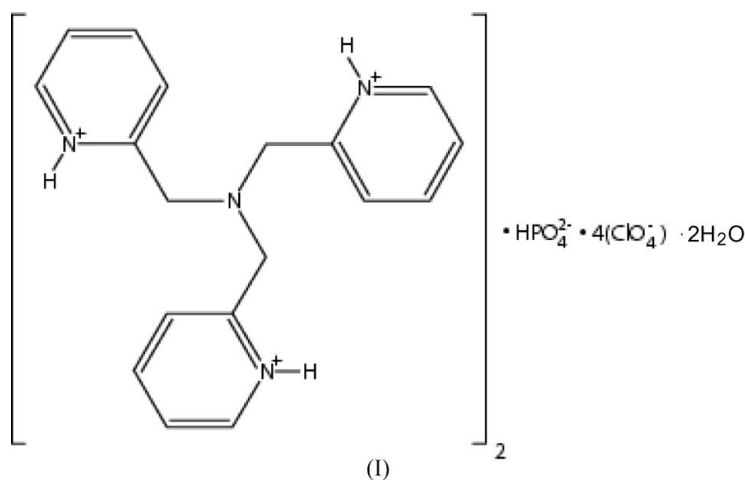
Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.053
 wR factor = 0.051
Data-to-parameter ratio = 14.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title salt, $2\text{C}_{18}\text{H}_{21}\text{N}_4^{3+} \cdot \text{HPO}_4^{2-} \cdot 4 \text{ClO}_4^- \cdot 2\text{H}_2\text{O}$, the protons of each of the pyridyl N atoms are hydrogen bonded to one HPO_4^{2-} ion. In one 2,2',2''-(nitrilotrimethylene)tripyridinium cation, all three pyridine N atoms are hydrogen bonded to the same oxygen and the ligand has approximate threefold symmetry; in the other, there are two hydrogen bonds to one O atom, and only one to the third O atom, resulting in an asymmetric ligand. The hydrogen-bonding modes observed in this and related compounds are discussed and their geometries compared.

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Comment

For tris(2-pyridylmethyl)amine (TPA) (Anderegg & Wenk, 1967), later NMR measurements (Anderegg *et al.*, 1986) showed the pyridyl N atoms to be the acidic ones. TPA is a potentially tetradentate ligand and has been used to study coordination in metal complexes; it is usually tetradentate, but can be tridentate with a pendant methyl pyridine group. $\text{H}_4\text{TPA}^{4+}$ does not seem to exist, but three structures have been determined containing the $\text{H}_3\text{TPA}^{3+}$ ion, $[\text{H}_3\text{TPA}](\text{ClO}_4)_3$, (II) (Britton *et al.*, 1991), $[\text{H}_3\text{TPA}](\text{NO}_3)(\text{SO}_4)$, (III) (Hazell *et al.*, 1999), and $[\text{H}_3\text{TPA}]\text{I}_3$, (IV) (Karmazin *et al.*, 2003). In (II), each pyridyl N atom is hydrogen bonded to a separate O atom, but in (III), (IV) and in molecule 2 (that containing N2) of the title salt, (I), all are hydrogen bonded to the same atom. In molecule 1 of (I) (that containing N1), two N atoms are hydrogen bonded to one O atom and the third to another (Fig. 1). The three modes are shown in Fig. 2.



In (II), (III) and (IV), the ammine N is on a crystallographic threefold axis, this is not the case for (I). HPO_4^{3-} has the expected geometry, *i.e.* $\text{P}-\text{OH} = 1.586$ (3) Å and $\text{P}=\text{O} =$

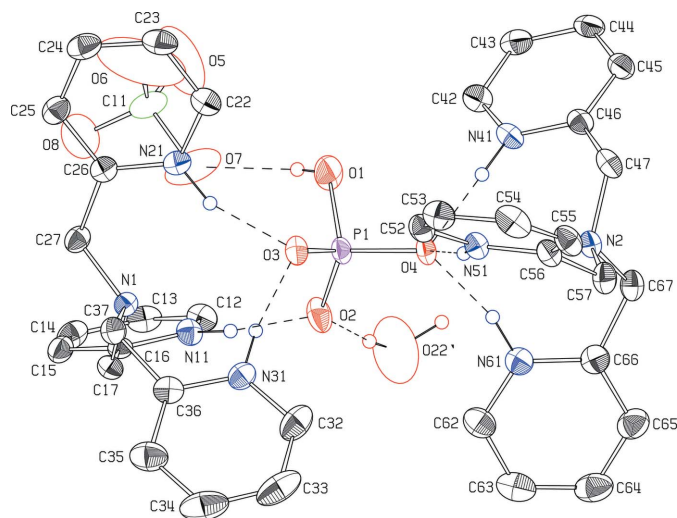


Figure 1
View of $[\text{H}_3\text{TPA}]_2(\text{HPO}_4)$ showing the labelling of the non-H atoms and hydrogen bonds (dashed lines) to HPO_4^{2-} . Displacement ellipsoids are drawn at the 50% probability level; H atoms are shown as small circles of arbitrary radius. Dashed lines indicate hydrogen bonds. Colour code: phosphorous magenta, chlorine green, oxygen red, nitrogen blue, carbon black; H atoms have the same colour as the atom to which they are bonded.

1.518 (2)–1.528 (2) Å, the long $\text{P}=\text{O}$ bond being that to O4, which is hydrogen bonded to three N atoms. The $\text{O}-\text{P}-\text{O}$ angles are in the range 103.0 (1)– 111.7 (1)°, the smaller angles involving the long $\text{P}-\text{OH}$ bond. In category (a), the pyridine rings are twisted further out of the plane through the CH_2 groups than they are in (b), resulting in shorter $\text{N}_{\text{py}}-\text{N}_{\text{py}}$ distances in (a). In (c), the $\text{N}_{\text{py}}-\text{N}_{\text{py}}$ distances for the two N atoms hydrogen bonded to the same O atom are similar to those in (a), whereas in (c) the distances to that hydrogen bonded to only one oxygen are over 0.5 Å longer. The geometry of $\text{H}_3\text{TPA}^{3+}$ is thus similar to that in the tetradentate metal complexes in four cases, whilst in the fifth it is more like the tridentate complexes with a pendant nitrogen.

Experimental

The crystals were provided by Hans Toftlund of The University of Southern Denmark

Crystal data

$2\text{C}_{18}\text{H}_{21}\text{N}_4^{3+}\cdot\text{HO}_4\text{P}^{2-}\cdot 4\text{ClO}_4^- \cdot 2\text{H}_2\text{O}$
 $M_r = 1116.64$
 Monoclinic, $P2_1/c$
 $a = 16.1366$ (7) Å
 $b = 12.8104$ (6) Å
 $c = 23.832$ (1) Å
 $\beta = 100.988$ (1)°
 $V = 4836.1$ (4) Å³

$Z = 4$
 $D_x = 1.533$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.37$ mm⁻¹
 $T = 120$ K
 Plate, colourless
 $0.44 \times 0.44 \times 0.14$ mm

Data collection

Siemens SMART CCD diffractometer
 ω rotation scans with narrow frames
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.692$, $T_{\text{max}} = 0.953$

45366 measured reflections
 13850 independent reflections
 9018 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 29.8^\circ$

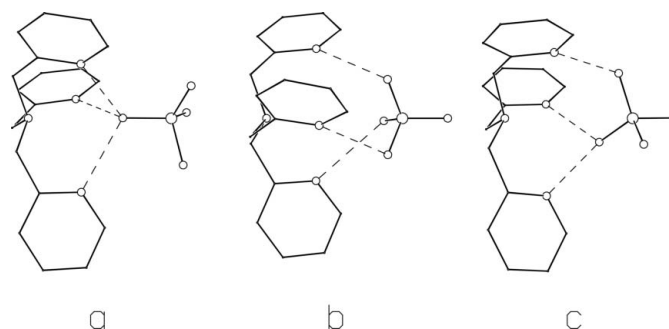


Figure 2
Modes of hydrogen bonding (dashed lines): (a) (III), (IV) and molecule 2 of (I), (b) (II) and (c) molecule 1 of (I).

Refinement

Refinement on F
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.051$
 $S = 1.04$
 9018 reflections
 644 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma_{\text{cs}}(F^2) + B + (1 + A)F^2]^{1/2}$,
 $|F|^2$, with $A = 0.03$, $B = 0.5$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.81$ (8) e Å⁻³
 $\Delta\rho_{\text{min}} = -1.12$ (8) e Å⁻³

Table 1

Selected torsion angles (°).

N1–C17–C16–N11	66.4 (3)	N2–C47–C46–N41	43.2 (4)
N1–C17–C16–C15	–116.5 (3)	N2–C47–C46–C45	–140.3 (3)
N1–C27–C26–N21	26.1 (4)	N2–C57–C56–N51	39.3 (4)
N1–C27–C26–C25	–156.5 (3)	N2–C57–C56–C55	–143.7 (3)
N1–C37–C36–N31	50.2 (3)	N2–C67–C66–N61	37.1 (4)
N1–C37–C36–C35	–132.2 (3)	N2–C67–C66–C65	–145.4 (3)

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O1–HO1 ⁱ ⋯O7	0.69 (4)	2.00 (4)	2.675 (4)	165 (5)
O21–HO21 ^a ⋯O22	0.96	1.82	2.756 (5)	163
O21–HO21 ^b ⋯O9	0.96	2.07	2.895 (5)	143
O22–HO22 ^a ⋯O2 ⁱ	0.96	1.84	2.796 (4)	174
O22–HO22 ^b ⋯O5 ⁱⁱ	0.96	1.93	2.861 (5)	163
N11–HN11⋯O2	0.95	1.68	2.578 (3)	156
N21–HN21⋯O3	0.95	1.76	2.648 (3)	155
N31–HN31⋯O3	0.95	1.72	2.658 (3)	169
N41–HN41⋯O4	0.95	1.78	2.724 (3)	172
N51–HN51⋯O4	0.95	1.78	2.719 (3)	167
N61–HN61⋯O4	0.95	1.76	2.688 (3)	166

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

H atoms for the cation were placed in calculated positions ($\text{C}-\text{H}$ and $\text{N}-\text{H} = 0.95$ Å), with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ for the atom to which they are bonded. Coordinates and an isotropic displacement parameters were refined for the H atom of HPO_4^{2-} ; those of the water molecules were kept fixed at the positions obtained from a difference map, with $U_{\text{iso}}(\text{H}) = 0.15$ Å². The maximum electron-density peak is located 0.91 Å from atom O7.

Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999) and KRYSTAL (Hazell,

1995); program(s) used to refine structure: modified *ORFLS* (Busing *et al.*, 1962) and *KRYSTAL*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *KRYSTAL*; software used to prepare material for publication: *KRYSTAL*.

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