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4-[2-(4-Pyridyl)ethyl]pyridinium nitrate trihydrate

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The title compound, $C_{12}H_{13}N_2^+\cdot NO_3^-\cdot 3H_2O$ [where $C_{12}H_{13}N_2^+$ is the monoprotonated form of 1,2-bis(4-pyridyl)ethane (BPEH$^+$)] is monoclinic, space group $P2_1/c$, and contains two empirical formulae in the asymmetric unit. The compound has cationic $[\mathrm{BPEH}]_n^{n+}$ organic layers, alternating in the **b** direction with anionic $[(NO_3)\cdot 3H_2O]_n^{n-}$ inorganic layers. Hydrogen bonds between 4-pyridyl and 4-pyridinium groups, and between nitrate ions and water molecules, give rise to chains and two-dimensional hydrogen-bonding networks, respectively.

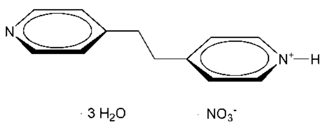
Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.003 Å
R factor = 0.076
wR factor = 0.222
Data-to-parameter ratio = 12.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

1,2-Bis(4-pyridyl)ethane (BPE) has been successfully employed in the synthesis of novel metal–organic frameworks (see, for example, Fugita *et al.*, 1994; Wang *et al.*, 1999; Bourne *et al.*, 2001). We have focused our attention on this organic ligand to obtain novel crystal structures with Cd^{2+} and Co^{2+} ions, produced under hydrothermal conditions and in the presence of carboxylic acids and triethylamine (TEA) (Almeida Paz *et al.*, 2002, 2002*a*). We have also found that, under the same experimental conditions, the absence of TEA can lead to the formation of a double-layered salt of BPE with trimesic acid residues (Almeida Paz *et al.*, 2002*b*). The title compound, (I), was obtained in the presence of Cd^{2+} ions and, to our knowledge, is the first crystal structure of a BPE salt with a typical inorganic ion (NO_3^-).



(I)

The structure determination of (I) reveals the presence of two BPE molecules in the asymmetric unit, both present in the typical *anti* conformation (Hennigar *et al.*, 1997) and with one protonated 4-pyridyl group, BPEH$^+$ (Fig. 1). Adjacent BPEH$^+$ cations are linked *via* strong $N^+—H\cdots N$ hydrogen bonds (Table 2), forming an infinite one-dimensional chain, which runs along the **a** direction (Fig. 2). These chains are close-packed in the *ab* plane, generating a positively charged $[\mathrm{BPEH}]_n^{n+}$ organic layer, which alternates with an inorganic layer composed of nitrate ions and water molecules (Figs. 3 and 4). This negatively charged inorganic layer, $[(NO_3)\cdot 3H_2O]_n^{n-}$, is formed by an extensive and strong hydrogen-bonding network (Table 2), and can be described as the alternation of two graph sets, $R_6^8(14)$ and $R_6^6(14)$ (Fig. 3). In this layer, each water O atom acts as a single acceptor (with

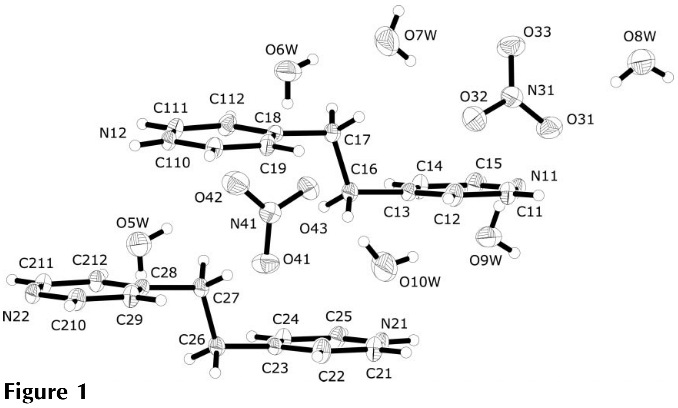


Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 30% probability level, and showing the labelling scheme for non-H atoms.

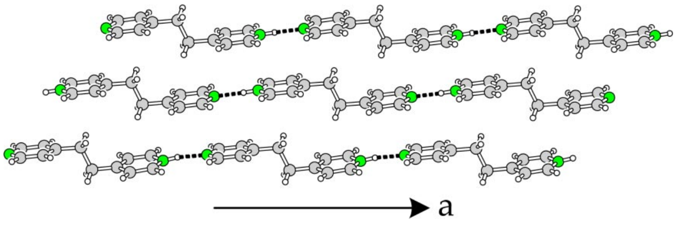


Figure 2
View, along the *b* axis, of the $[\mathrm{BPEH}]_n^{n+}$ organic cationic layer, showing the packing of the one-dimensional BPEH^+ chains.

an adjacent water molecule) and as a double donor, donating the attached H atoms to a neighbouring water molecule and a nitrate ion (Fig. 3). An interesting feature in the crystal structure arises from the bifurcated donor nature of atoms O6*W* and O9*W*, with H6*A* and H9*A*, respectively, being almost equidistant from the O atoms in the neighbouring nitrate ions (Table 2). This suggests that the hydrogen-bonding interactions are very likely to be between the water molecules and the conjugated π system in the nitrate ions (Fig. 3, top).

Experimental

All chemicals were obtained from commercial sources and were used as received. To a solution of $\mathrm{Cd(NO_3)_2{\cdot}4H_2O}$ (0.629 g, Aldrich) in distilled water (11.60 g), 1,2-bis(4-pyridyl)ethane (BPE, 0.382 g, Aldrich) was added, and the resulting mixture was stirred thoroughly for 1 h at ambient temperature. The suspension, with a $\mathrm{Cd^{2+}}$:BPE:$\mathrm{H_2O}$ molar ratio of 1.00:1.02:315, was placed in a Parr stainless steel teflon-lined reaction vessel (21 ml, 70% full). The reaction was performed under autogeneous pressure and static conditions in a preheated oven at 418 K, using a previously reported temperature profile (Almeida Paz *et al.*, 2002). The microcrystalline product was placed inside a refrigerator for 24 h, after which crystals of the title compound were separated manually.

Crystal data

$\mathrm{C_{12}H_{13}N_2^{+}{\cdot}NO_3^{-}{\cdot}3H_2O}$
$M_r = 301.30$
Monoclinic, $P2_1/c$
$a = 11.7751\ (4)$ Å
$b = 16.1980\ (7)$ Å
$c = 15.8787\ (4)$ Å
$\beta = 90.175\ (2)^\circ$
$V = 3028.58\ (18)$ Å^3
$Z = 8$
$D_x = 1.322$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15908 reflections
$\theta = 1.0$–25.0°
$\mu = 0.11$ mm^{-1}
$T = 180\ (2)$ K
Block, colourless
$0.46 \times 0.39 \times 0.12$ mm

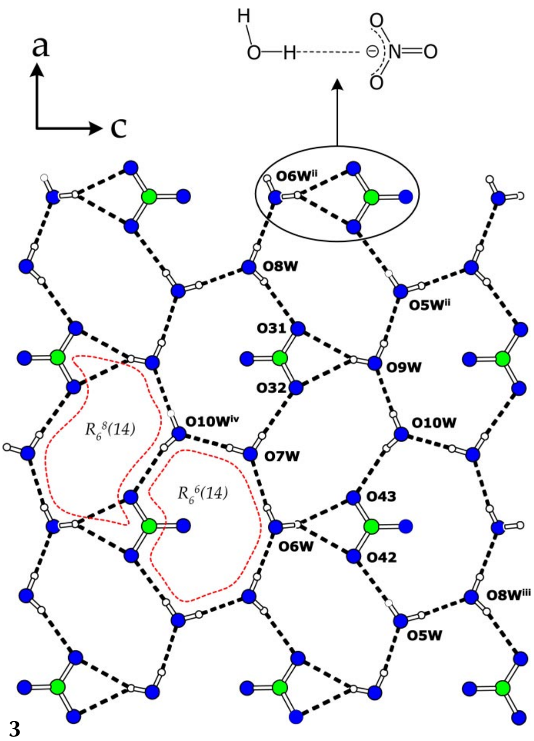


Figure 3
View, along the *b* axis, of the $[(\mathrm{NO_3}){\cdot}3\mathrm{H_2O}]_n^{n-}$ anionic inorganic layer, showing the two-dimensional hydrogen-bonding network (dashed lines) between the nitrate ions and the water molecules. For hydrogen-bonding geometry and symmetry codes, see Table 2.

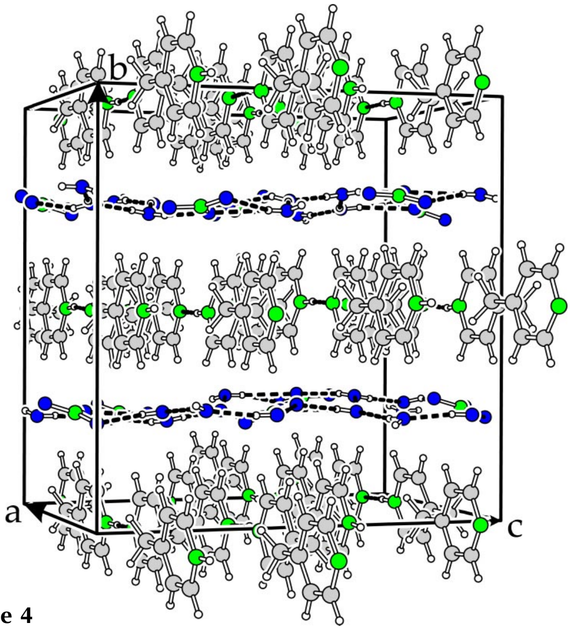


Figure 4
Perspective view of (I), showing the hydrogen-bonding network (dashed lines).

Data collection

Nonius KappaCCD diffractometer
Thin-slice ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.953$, $T_{\max} = 0.987$
21624 measured reflections
5304 independent reflections
3982 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 25.1^\circ$
$h = -14 \rightarrow 14$
$k = -18 \rightarrow 19$
$l = -18 \rightarrow 18$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.076$
$wR(F^2) = 0.222$
$S = 1.06$
5304 reflections
423 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1132P)^2 + 1.9726P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.026$
$\Delta\rho_{\max} = 0.71$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N31—O33	1.224 (3)	N41—O41	1.221 (3)
N31—O31	1.230 (3)	N41—O42	1.246 (3)
N31—O32	1.257 (3)	N41—O43	1.250 (3)
O33—N31—O31	121.9 (3)	O41—N41—O42	121.0 (2)
O33—N31—O32	120.8 (3)	O41—N41—O43	121.4 (3)
O31—N31—O32	117.3 (2)	O42—N41—O43	117.5 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12—H12N···N11$^{\rm i}$	0.88 (1)	1.77 (1)	2.650 (3)	171 (4)
N21—H21N···N22$^{\rm ii}$	0.88 (1)	1.78 (1)	2.654 (3)	171 (4)
O5*W*—H5*A*···O42	0.78 (2)	2.08 (2)	2.858 (3)	172 (4)
O5*W*—H5*B*···O8*W*$^{\rm iii}$	0.78 (2)	1.90 (2)	2.676 (4)	176 (4)
O6*W*—H6*A*···O43	0.78 (2)	2.24 (2)	2.979 (3)	158 (4)
O6*W*—H6*A*···O42	0.78 (2)	2.30 (2)	2.966 (3)	144 (3)
O6*W*—H6*B*···O7*W*	0.78 (2)	2.02 (2)	2.785 (4)	169 (4)
O7*W*—H7*A*···O32	0.78 (2)	2.11 (2)	2.900 (4)	173 (4)
O7*W*—H7*B*···O10*W*$^{\rm iv}$	0.77 (2)	1.88 (2)	2.654 (5)	174 (5)
O8*W*—H8*A*···O31	0.77 (2)	2.10 (2)	2.829 (4)	157 (4)
O8*W*—H8*B*···O6*W*$^{\rm ii}$	0.78 (2)	1.94 (2)	2.705 (4)	172 (4)
O9*W*—H9*A*···O31	0.78 (2)	2.26 (2)	3.003 (3)	160 (4)
O9*W*—H9*A*···O32	0.78 (2)	2.29 (2)	2.957 (3)	144 (3)
O9*W*—H9*B*···O5*W*$^{\rm ii}$	0.78 (2)	2.00 (2)	2.767 (3)	165 (4)
O10*W*—H10*A*···O9*W*	0.78 (2)	1.94 (2)	2.713 (4)	172 (4)
O10*W*—H10*B*···O43	0.77 (2)	2.17 (3)	2.860 (4)	150 (4)

Symmetry codes: (i) $1+x, y, z$; (ii) $x-1, y, z$; (iii) $1+x, \frac{3}{2}-y, z-\frac{1}{2}$; (iv) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

H atoms bound to C atoms were placed in calculated positions and allowed to ride during subsequent refinement, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. H atoms bonded to N and O atoms were located in difference Fourier maps and refined with a single isotropic displacement parameter common to all H atoms. N—H distances were restrained to 0.88 Å. O—H and H···H distances were also restrained, in order to ensure a reasonable geometry for the water molecules.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL* (Bruker, 2001); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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