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Hexane-1,6-diammonium dipicrate dihydrate

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Key indicators

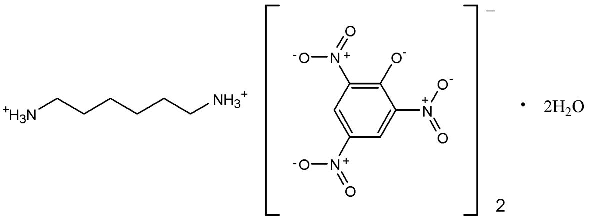
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.040
wR factor = 0.120
Data-to-parameter ratio = 11.3

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

The title salt, $C_6H_{18}N_2^{2+}\cdot 2C_6H_2N_3O_7^-\cdot 2H_2O$, consists of one hexane-1,6-diammonium cation, two picrate anions and two water molecules of crystallization. The cation lies across a centre of symmetry. The O atoms of the water molecules, and the phenolate group and nitro groups of the picrate anions act as acceptors to form N—H···O and O—H···O hydrogen bonds. In the crystal structure, this leads to the formation of a three-dimensional network.

Comment

Recently, organometallic and coordination complexes have emerged as potential building blocks for second-order nonlinear optical (NLO) materials (Long, 1995). The applications of NLO are supported by the observation that organic molecules containing π-electron systems asymmetrized by electron-donor and electron-acceptor groups are highly polarizable entities, in which problems of transparency and crystal growth may arise from their molecular crystal packing (Pecaut & Bagieu-Beucher, 1993). Picric acid acts not only as an acceptor to form various π-stacking arrangements but also as an acidic ligand to form salts through electrostatic or hydrogen-bonding interactions (In *et al.*, 1997). The structure of the title compound, (I), was analysed in order to study the packing mode of the molecules in the crystal structure and the details of the hydrogen-bonding interactions.



(I)

A view of the independent ions and water molecule of (I) with the atomic numbering scheme is shown in Fig. 1. X-ray analysis confirmed that compound (I) consists of hexane-1,6-diammonium cations and phenolate anions. The cation in (I) lies across a centre of inversion and the anion occupies a general position. The ions are connected through several kinds of hydrogen bonds (Table 1), and an H atom is transferred to form the salt.

The C—O bond length of the phenolate [1.248 (2) Å] corresponds to a partial double bond, implying that the negative charge located on the phenolate O atom is delocalized. The N—O bond distances of the nitro groups of the trinitrophenolate anion are typical of double bonds.

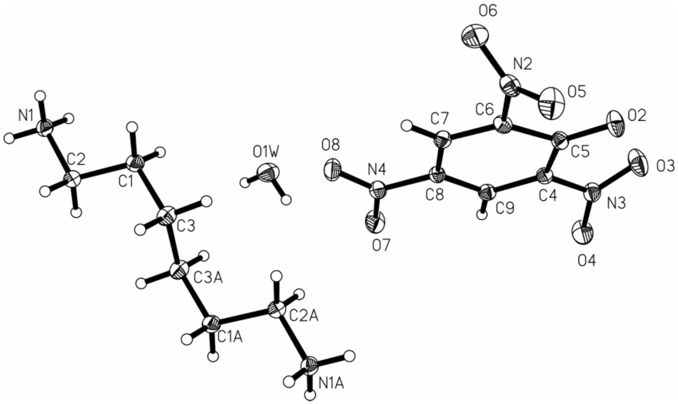


Figure 1
The components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level [symmetry code: (*A*) $-x$, $1-y$, $1-z$].

Analysis of the crystal packing of (I) shows that there exist a number of O—H···O and N—H···O hydrogen bonds, with D···A distances ranging from 2.803 (2) to 3.173 (3) Å. The hexane-1,6-diammonium cations form a one-dimensional substructure in the form of a chain extending in the *a* direction. These chains are linked by the anions and the water molecules into an overall three-dimensional structure (Fig. 2).

Experimental

All reagents and solvents were used as obtained without further purification. Picric acid (2 mmol, 458 mg) and hexane-1,6-diamine (1 mmol, 116 mg) were dissolved in 30% ammonia (10 ml). The mixture was stirred for *ca* 10 min to obtain a clear solution. On allowing the solution to stand in air overnight, with release of ammonia gas, large light-yellow crystals were formed. These were isolated, washed three times with water and dried in a vacuum desiccator using $CaCl_2$ (yield 65%). Elemental analysis found: C 35.61, H 4.53, N 18.67%. calculated for $C_{18}H_{26}N_8O_{16}$: C 35.42, H 4.29, N 18.36%.

Crystal data

$C_6H_{18}N_2^{2+}\cdot 2C_6H_2N_3O_7^{-}\cdot 2H_2O$
$M_r = 610.47$
Triclinic, $P\bar{1}$
$a = 7.165$ (1) Å
$b = 8.215$ (2) Å
$c = 11.316$ (2) Å
$\alpha = 101.36$ (3)°
$\beta = 101.31$ (3)°
$\gamma = 92.57$ (3)°
$V = 637.9$ (2) Å^3
$Z = 1$
$D_x = 1.589$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 900 reflections
$\theta = 2.3$–27.5°
$\mu = 0.14$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.48 × 0.38 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.923$, $T_{\max} = 0.956$
3381 measured reflections
2229 independent reflections
1771 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$
$\theta_{\max} = 25.0°$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 9$
$l = -13 \rightarrow 12$

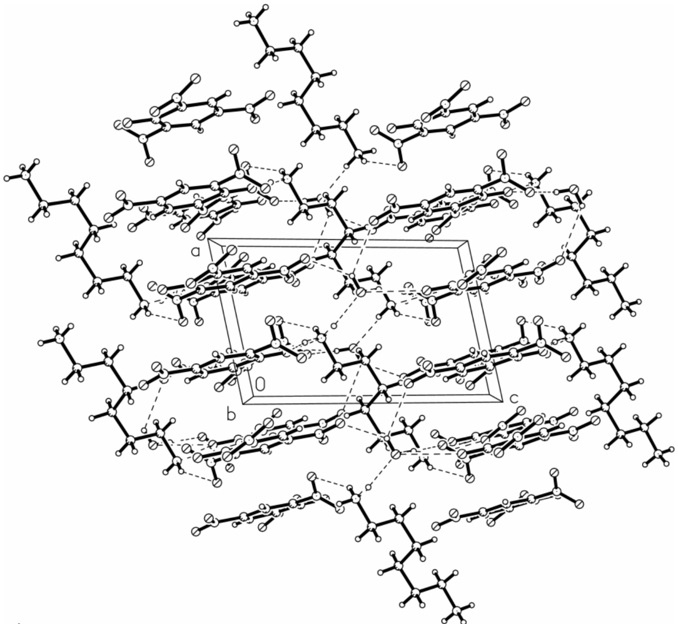


Figure 2
The crystal packing of (I), viewed along the *b* axis, showing the hydrogen bonds as dashed lines.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.120$
$S = 0.91$
2229 reflections
198 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0715P)^2 + 0.3169P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O2$^{\rm i}$	0.89	2.01	2.803 (2)	147
N1—H1*A*···O3$^{\rm i}$	0.89	2.25	2.931 (2)	133
N1—H1*B*···O6$^{\rm ii}$	0.89	2.38	3.173 (3)	149
N1—H1*E*···O1*W*$^{\rm iii}$	0.89	1.95	2.811 (3)	164
O1*W*—H1*G*···O2$^{\rm ii}$	0.79 (3)	2.18 (3)	2.892 (2)	150 (3)
O1*W*—H1*G*···O5$^{\rm ii}$	0.79 (3)	2.35 (3)	2.948 (3)	133 (3)
O1*W*—H1*H*···O7$^{\rm iv}$	0.84 (4)	2.56 (4)	3.153 (3)	129 (3)
O1*W*—H1*H*···O7	0.84 (4)	2.36 (4)	3.056 (3)	141 (3)

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

The H atoms bonded to atoms C3 and N1 were constrained to ride on the parent atom, with distances of 0.97 and 0.89 Å, respectively, and $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}$(parent C or N atom). The H atoms on the other C atoms were also constrained to ride on the parent C atom, with distances of 0.97 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(C). H atoms H1*G* and H1*H*, bonded to water O1*W*, were found in a difference electron-density map and were refined isotropically.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996) ; data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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