

Ethylenediammonium 4-nitroanthranilate dihydrate

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$

R factor = 0.045

wR factor = 0.137

Data-to-parameter ratio = 14.2

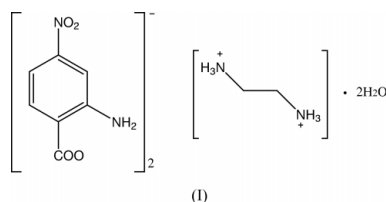
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of ethylenediammonium 4-nitroanthranilate dihydrate, $[(\text{C}_2\text{H}_{10}\text{N}_2)^{2+} \cdot 2(\text{C}_7\text{H}_5\text{N}_2\text{O}_4)^- \cdot 2(\text{H}_2\text{O})]$, shows a three-dimensional hydrogen-bonded polymer in which both of the amine groups of ethylenediamine are protonated and each gives a total of four hydrogen-bonded interactions with oxygen and amine N atoms of the anthranilate anions as well as with the water molecules. The centrosymmetrically related anthranilate species are also linked directly to the water molecules, and give a double-chain structure down the *b* axis.

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Comment

Ethylenediamine (ethane-1,2-diamine = en) reacts with acids to give stable crystalline salts, and because of the relative similarity of the dissociation constants of en ($\text{pK}_{\text{a}1} = 7.3$; $\text{pK}_{\text{a}2} = 10.1$), both amine groups are protonated, even in reactions with weak organic acids. With the enH_2^{2+} species, as is the case with protonated primary amine groups, the $-\text{NH}_3^+$ hydrogens may be involved in up to six intermolecular hydrogen-bonding interactions with suitable acceptor atoms. The resulting hydrogen-bonded polymer structures acquire considerable crystal stability together with enhanced melting points. This is seen with the en salts of the relatively strong nitro-substituted benzoic acids, e.g. 3,5-dinitrobenzoic acid (DNBA), $[(\text{enH}_2)^{2+} 2(\text{DNBA})^-]$ (Nethaji *et al.*, 1992; Lynch *et al.*, 1994), while crystallization often includes lattice water molecules, increasing the structure-making e.g. ethylenediammonium 5-nitrosalicylate hydrate, $[(\text{enH}_2)^{2+} 2(5\text{-NSA})^- \cdot \text{H}_2\text{O}]$ (Smith & Hartono, 2002). With the bifunctional 3,5-dinitrosalicylic acid (DNSA), the rare occurrence of the $(\text{DNSA})^{2-}$ species has been observed in the salt $[(\text{enH}_2)^{2+} (\text{DNSA})^{2-}]$ (Smith *et al.*, 2002). Our interest lies in the characterization of the hydrogen-bonding interactions of the nitro-substituted aromatic acids with Lewis bases. The structure of the title compound, obtained from the reaction of 4-nitroanthranilic acid (4-NAA) with en as a hydrate, described in terms of the centrosymmetric molecular unit (the unit cell contents) $[(\text{en})^{2+} 2(4\text{-NAA})^- \cdot 2(\text{H}_2\text{O})]$, (I), is reported here.



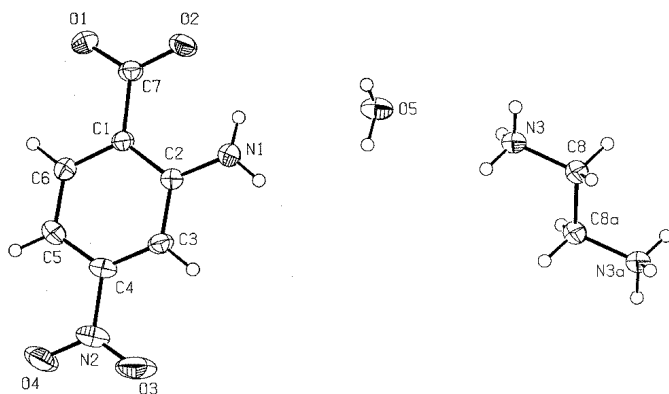


Figure 1
Molecular configuration and atom-naming scheme for the individual 4-NAA anion, the en cation and the water species in (I). Non-hydrogen atoms are shown as 40% probability ellipsoids

The structure determination of (I) shows that both the primary amine groups of ethylenediamine are protonated (Fig. 1). A hydrogen bond is found between an amine–H and an oxygen of the carboxyl group of the 4-NAA anion [N1–H1A...O2; 2.694 (2) Å]. The 4-NAA anions, one unit cell apart along the *b* axis, are linked by N1–H1B...O1(*x*, 1 + *y*, *z*) hydrogen bonds to form an infinite one-dimensional chain. The molecules in the chain are linked to those in the inversion-related chain (1 – *x*, –*y*, 1 – *z*) by the water molecules, through O–H...O hydrogen bonds, to form a double-chain structure (Fig. 2). These 4-NAA anion chains stack down the *a* axis and are linked by the (enH₂)²⁺ cations as well as the water molecules, giving a three-dimensional polymer (Fig. 3). A full hydrogen-bond listing is given in Table 1.

Experimental

The synthesis of the title compound was carried out by heating, under reflux for 10 min, 1 mmol quantities of 4-nitroanthranilic acid (2-amino-4-nitrobenzoic acid = 4-NAA) and ethylenediamine (en) in 50 ml of 80% ethanol/water. After concentration to *ca.* 30 ml, partial room temperature evaporation of the hot-filtered solution gave red crystals.

Crystal data

C ₂ H ₁₀ N ₂ ²⁺ ·2C ₇ H ₅ N ₂ O ₄ [–] ·2H ₂ O	<i>Z</i> = 1
<i>M_r</i> = 460.42	<i>D_x</i> = 1.524 Mg m ^{–3}
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 6.6473 (5) Å	Cell parameters from 2947 reflections
<i>b</i> = 7.0748 (5) Å	<i>θ</i> = 3.0–28.3°
<i>c</i> = 11.2317 (8) Å	<i>μ</i> = 0.13 mm ^{–1}
<i>α</i> = 76.686 (2)°	<i>T</i> = 293 (2) K
<i>β</i> = 77.660 (2)°	Plate, red
<i>γ</i> = 89.525 (2)°	0.40 × 0.30 × 0.20 mm
<i>V</i> = 501.67 (6) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	2052 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>φ</i> and <i>ω</i> scans	<i>R_{int}</i> = 0.046
Absorption correction: none	<i>θ_{max}</i> = 28.6°
4462 measured reflections	<i>h</i> = –8 → 8
2475 independent reflections	<i>k</i> = –9 → 9
	<i>l</i> = –15 → 14

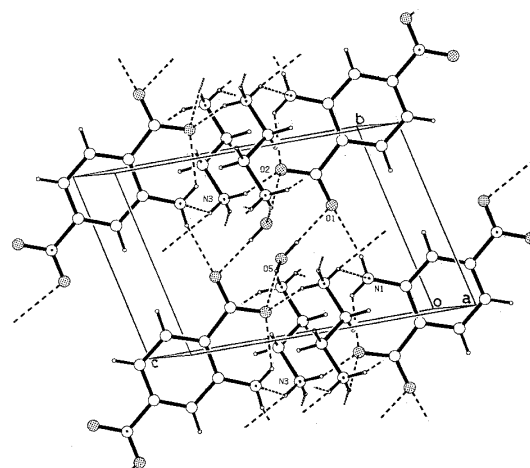


Figure 2
A view of the double-chain formation by 4-NAA and water molecules.

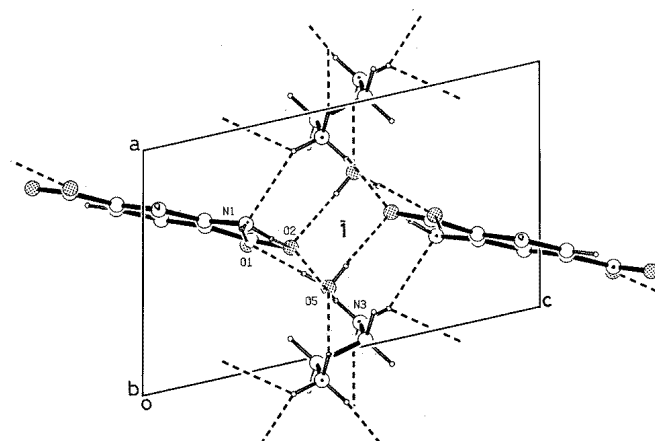


Figure 3
Packing in the unit cell, viewed down *b*, showing hydrogen-bonding associations as dashed lines.

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.045
wR(*F*²) = 0.137
S = 1.07
 2475 reflections
 174 parameters

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0745P)^2 + 0.0989P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.010$$

$$\Delta\rho_{\max} = 0.26 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{Å}^{-3}$$

Table 1

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1–H1A...O2	0.88 (2)	2.04 (2)	2.6935 (17)	130.8 (18)
N1–H1B...O1 ⁱ	0.82 (2)	2.12 (2)	2.9258 (17)	167.8 (17)
N3–H3A...O5 ⁱⁱ	0.90 (2)	1.95 (2)	2.7960 (18)	157.5 (19)
N3–H3B...O3 ⁱⁱⁱ	0.87 (2)	2.41 (2)	3.0564 (18)	130.9 (17)
N3–H3B...N1 ^{iv}	0.87 (2)	2.52 (2)	3.1847 (18)	133.8 (18)
N3–H3C...O2 ⁱ	0.917 (19)	1.937 (19)	2.8250 (17)	162.5 (14)
O5–H5A...O1 ⁱ	0.84 (2)	1.91 (2)	2.7429 (16)	179 (2)
O5–H5B...O2 ^v	0.79 (3)	2.18 (3)	2.9647 (16)	171 (3)
C6–H6...O1	0.93	2.41	2.7454 (16)	101

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

H atoms involved in hydrogen-bonding interactions (H1A, H1B, H3A, H3B, H3C, H5A, H5B) were located from a difference Fourier map and their positional and isotropic displacement parameters were refined. Others were included in the refinement at calculated positions as riding models. For refined H atoms, the N–H range is 0.87 (2)–0.92 (2) Å; the O–H (water) values are 0.79 (3) and 0.84 (2) Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXTL*.

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