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## Key indicators

Single-crystal X-ray study  
 $T = 293$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.046  
 $wR$  factor = 0.135  
Data-to-parameter ratio = 11.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

## A co-crystal of ethylenediammonium bis(3,5-dinitrobenzoate) and 3,5-dinitrobenzoic acid

The co-crystal of ethylenediammonium bis(3,5-dinitrobenzoate) and 3,5-dinitrobenzoic acid, namely ethylenediammonium–3,5-dinitrobenzoate–3,5-dinitrobenzoic acid (1/2/2),  $\text{C}_2\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{C}_7\text{H}_3\text{N}_2\text{O}_6^- \cdot 2\text{C}_7\text{H}_4\text{N}_2\text{O}_6$ , has as the asymmetric unit one 3,5-dinitrobenzoic acid molecule, one 3,5-dinitrobenzoate ion and one-half of the ethylenediammonium ion, as this cation lies on an inversion centre. Each ethylenediammonium ion is hydrogen bonded to four benzoate ions and two benzoic acid molecules.

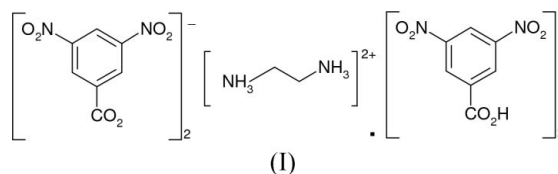
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## Comment

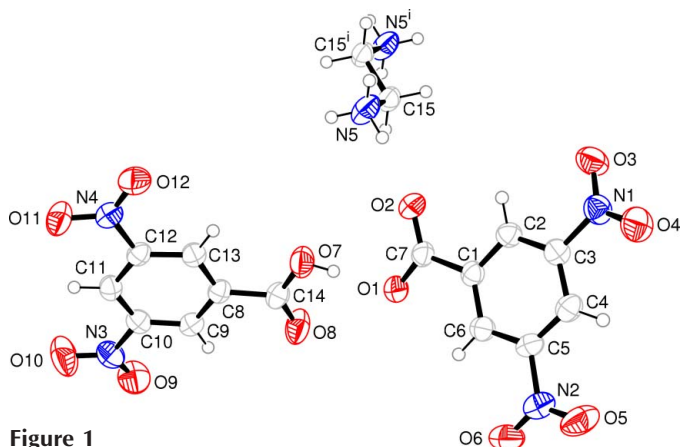
During experiments to measure the solubility of the monoclinic form of ethylenediammonium bis(3,5-dinitrobenzoate), cocrystals, (I), of this salt with 3,5-dinitrobenzoic acid were obtained.



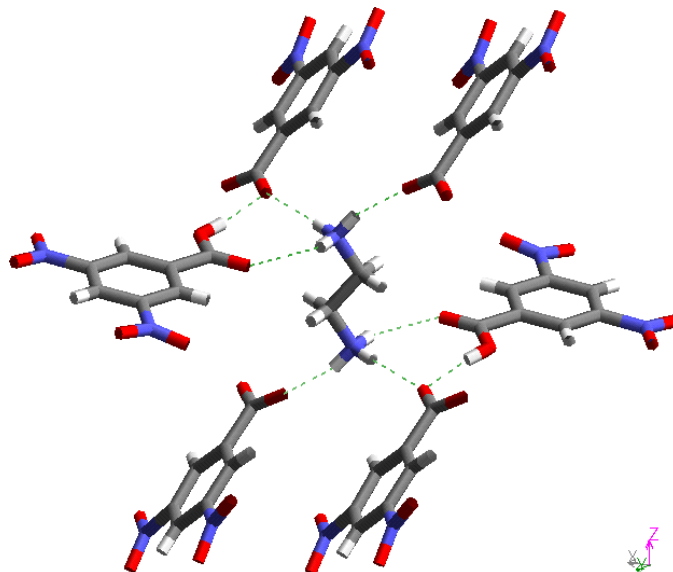
To measure the solubility of ethylenediammonium bis(3,5-dinitrobenzoate) as a function of pH at 323 K, a suspension of the salt in water was prepared and allowed to equilibrate (Jones *et al.*, 2005). In one experiment, the pH was found to be unusually low for a slurry of this salt and the experiment was stopped, but the sample continued to be held at 323 K. The cocrystals grew as pale-yellow prisms and were recovered on filtration of the slurry. Formation of these cocrystals was not observed in other solubility measurements at higher pH. Protonated 3,5-dinitrobenzoic acid is only expected to be present below pH 5 at 323 K (de Levie *et al.*, 1999).

In the crystal structure, both a protonated and a deprotonated 3,5-dinitrobenzoic acid molecule are present in the asymmetric unit. The ethylenediammonium ion lies on an inversion centre so that only one-half of the ion is in the asymmetric unit. Fig. 1 shows the structure and atom labelling.

Each ethylenediammonium ion is hydrogen bonded to four benzoate ions and two benzoic acid molecules (Fig. 2). The crystal structure contains hydrogen-bonded chains of ethylenediammonium and benzoate ions along the  $a$  axis in the motif  $C_2^2(6)$  (Fig. 3), hydrogen-bonded dimers of benzoate ions with benzoic acid molecules with an  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bond through atom H7 in the motif  $D_1^1(2)$ , and dimers of ethylenediammonium ions hydrogen bonded to the carbonyl group of a benzoic acid molecule in the motif  $D_1^1(2)$ . The benzoate ions in this structure all lie in one plane and the benzoic acid molecules all lie in another orientation.



**Figure 1**  
View of the asymmetric unit of (I), including the whole ethylenediaminium ion, which is on an inversion centre. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i)  $-x, -y, -z$ .]



**Figure 2**  
Hydrogen bonding (dashed lines) between the ethylenediaminium and 3,5-dinitrobenzoate ions and the 3,5-dinitrobenzoic acid molecules.

### Experimental

Monoclinic ethylenediaminium bis(3,5-dinitrobenzoate) was prepared by precipitation from a mixture of solutions of ethylenediamine (0.0145 mol) and 3,5-dinitrobenzoic acid (0.029 mol; supplied by Sigma–Aldrich, 99%) in ethanol (50 ml). An excess of monoclinic ethylenediammonium bis(3,5-dinitrobenzoate) (0.0145 mol) was suspended in water (40 ml) at 323 K with stirring. The solution pH was recorded as 3.79. After 20 h, stirring was stopped and the suspension was held at 323 K for 5 d. The suspension was filtered and pale-yellow prisms were observed in the powder of the monoclinic ethylenediammonium bis(3,5-dinitrobenzoate).

#### Crystal data

$C_2H_{10}N_2^{2+} \cdot 2C_7H_3N_2O_6^{-}$   
 $2C_7H_4N_2O_6$   
 $M_r = 908.6$   
 Triclinic,  $P\bar{1}$   
 $a = 7.0452$  (3) Å  
 $b = 11.2345$  (4) Å  
 $c = 11.7627$  (5) Å  
 $\alpha = 91.838$  (2)°  
 $\beta = 96.230$  (2)°  
 $\gamma = 98.710$  (1)°  
 $V = 913.72$  (6) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.651$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 5294 reflections  
 $\theta = 1.0$ – $25.0$ °  
 $\mu = 0.15$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prism, pale yellow  
 $0.3 \times 0.2 \times 0.1$  mm

#### Data collection

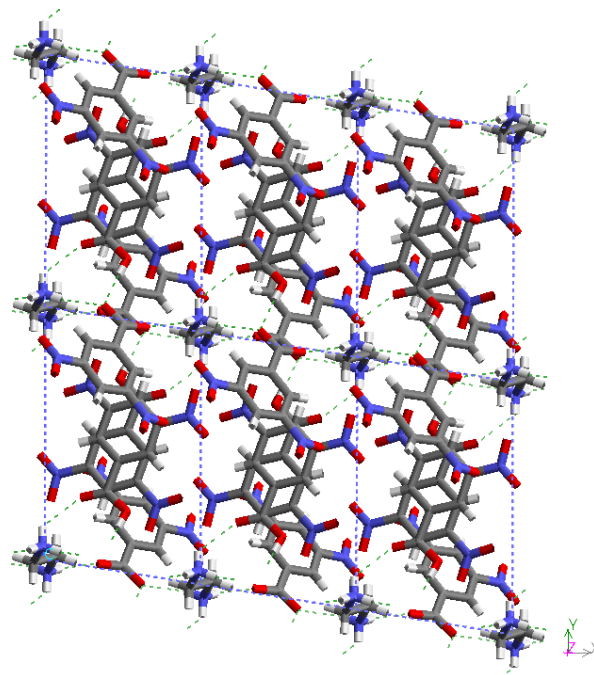
Nonius KappaCCD diffractometer  
 Thick-slice  $\phi$  and  $\omega$  scans to fill asymmetric unit  
 Absorption correction: multi-scan (Blessing, 1995)  
 $T_{\min} = 0.916$ ,  $T_{\max} = 0.986$   
 8852 measured reflections

3241 independent reflections  
 2256 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.046$   
 $\theta_{\text{max}} = 25.2$ °  
 $h = -8 \rightarrow 8$   
 $k = -13 \rightarrow 13$   
 $l = -14 \rightarrow 12$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.136$   
 $S = 1.01$   
 3241 reflections  
 294 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.20$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.21$  e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.016 (4)



**Figure 3**  
Unit cell contents, viewed along the  $c$  axis, showing hydrogen-bonded chains (dashed lines) along the  $a$  axis.

**Table 1**  
Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$            | $D-H$    | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---------------------------|----------|--------------|--------------|----------------|
| O7–H7···O1                | 0.83 (1) | 1.68 (1)     | 2.507 (2)    | 173 (4)        |
| N5–H5A···O2               | 0.89     | 1.88         | 2.732 (3)    | 161            |
| N5–H5B···O8 <sup>ii</sup> | 0.89     | 2.17         | 2.820 (3)    | 129            |
| N5–H5C···O1 <sup>ii</sup> | 0.89     | 2.02         | 2.899 (3)    | 170            |

Symmetry code: (ii)  $x + 1, y, z$ .

All H atoms attached to C and N atoms were fixed using a riding model, with C–H distances 0.93 Å ( $C_{Ar}H$ ) and 0.97 Å ( $CH_2$ ), and N–H distances 0.89 Å. The  $U_{iso}(H)$  values were set equal to  $1.2U_{eq}$  of the carrier atom for these H atoms. The hydroxy H atom was located in a Fourier difference map and the coordinates were refined with the O–H bond distance restrained to 0.82 (1) Å.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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