Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

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

Helen P. Jones, Amy L. Gillon‡ and Roger J. Davey*

Colloids, Crystals and Interfaces Group, School of Chemical Engineering and Analytical Sciences, The University of Manchester, PO Box 88, Manchester M60 1QD, England

‡ Current address: Pharmaceutical R&D, Pfizer Global R&D (IPC 435), Ramsgate Road, Sandwich, Kent CT13 9NJ, England.

Correspondence e-mail:
h.jones-2@postgrad.manchester.ac.uk

Received 6 April 2005
Accepted 13 May 2005
Online 21 May 2005

The co-crystal of ethylenediammonium bis(3,5-dinitrobenzoate) and 3,5-dinitrobenzoic acid, namely ethylenediaminium–3,5-dinitrobenzoate–3,5-dinitrobenzoic acid (1/2/2), $C_2H_{10}N_2^{2+}\cdot 2C_7H_3N_2O_6^{-}\cdot 2C_7H_4N_2O_6$, 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.

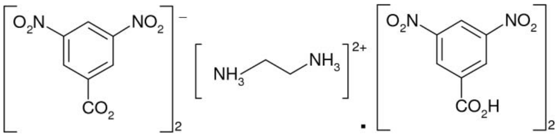
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.046
wR factor = 0.135
Data-to-parameter ratio = 11.0

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

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.



(I)

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 O—H···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.

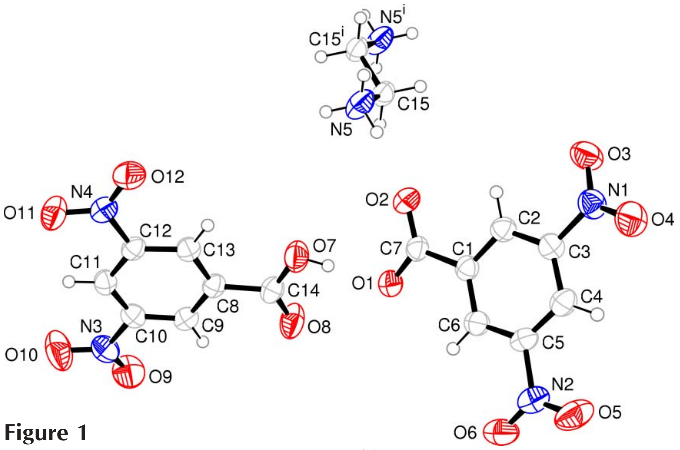


Figure 1
View of the asymmetric unit of (I), including the whole ethylenediaminium ion, which is on an inversion centre. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x, -y, -z$.]

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

$C_2H_{10}N_2^{2+}\cdot 2C_7H_3N_2O6^{-}\cdot$-
$2C_7H_4N_2O_6$
$M_r = 908.6$
Triclinic, $P\overline{1}$
$a = 7.0452$ (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^3

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

Data collection

Nonius KappaCCD diffractometer
Thick-slice φ and ω 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 $I > 2\sigma(I)$
$R_{\rm int} = 0.046$
$\theta_{\max} = 25.2°$
$h = -8 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 12$

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

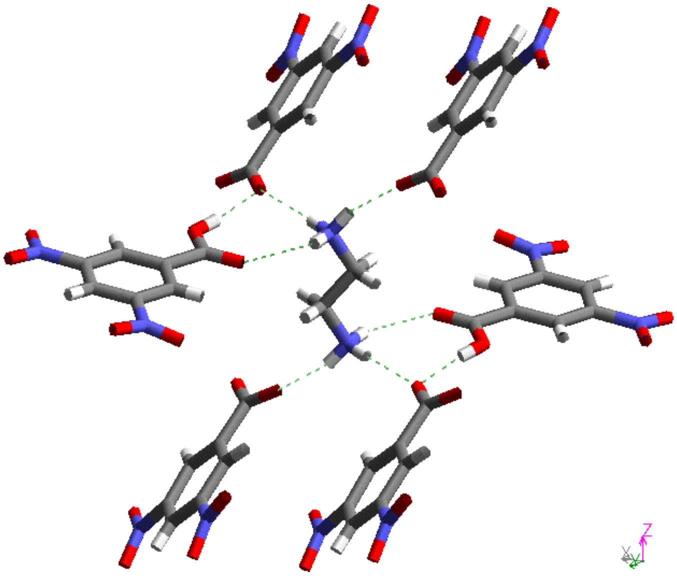


Figure 2
Hydrogen bonding (dashed lines) between the ethylenediaminium and 3,5-dinitrobenzoate ions and the 3,5-dinitrobenzoic acid molecules.

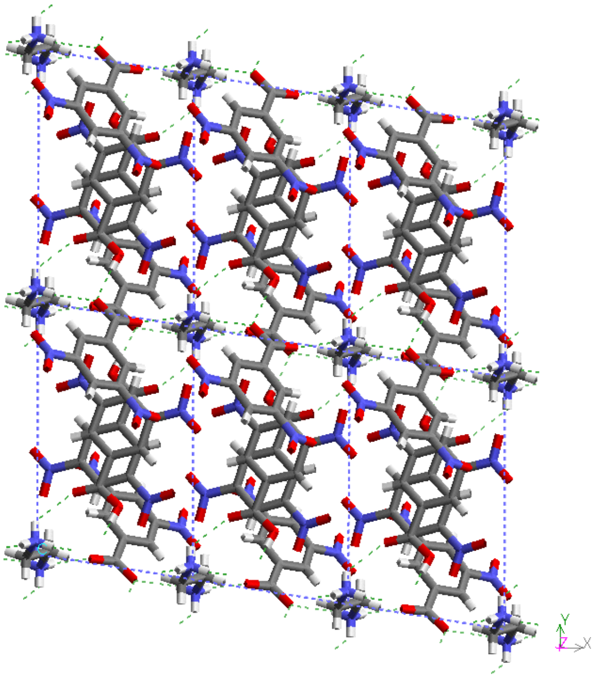


Figure 3
Unit cell contents, viewed along the *c* axis, showing hydrogen-bonded chains (dashed lines) along the *a* axis.

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

D—H···A	D—H	H···A	D···A	D—H···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^{ii}	0.89	2.17	2.820 (3)	129
N5—H5C···O1^{ii}	0.89	2.02	2.899 (3)	170

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

o1824 Jones *et al.* • $C_2H_{10}N_2^{2+}\cdot 2C_7H_3N_2O_6^{-}\cdot 2C_7H_4N_2O_6$ *Acta Cryst.* (2005). E**61**, o1823--o1825

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).

The authors thank Sanofi–Aventis Ltd for funding.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Jones, H. P., Davey, R. J. & Cox, B. G. (2005). *J. Phys. Chem. B*, **109**, 5273–5278.

Levie, R. de (1999). *Aqueous Acid–Base Equilibria and Titrations*. New York: Oxford University Press.

Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Acta Cryst. (2005). E**61**, o1823–o1825 Jones *et al.* • $C_2H_{10}N_2^{2+}\cdot 2C_7H_3N_2O_6^{-}\cdot 2C_7H_4N_2O_6$ **o1825**