Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Tris(2-ethylammonio)amine–4-nitrobenzoate–water (1/3/2)

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The asymmetric unit of the title compound, $C_6H_{21}N_4^{3+}\cdot 3C_7H_4NO_4^{-}\cdot 2H_2O$, consists of two triply protonated base molecules, six benzoate anions and four water molecules, one of which is unequally disordered across two adjacent sites in an extensive hydrogen-bonded network.

Received 3 July 2003
Accepted 14 July 2003
Online 24 July 2003

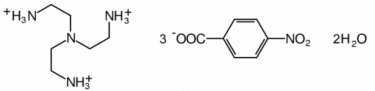
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.006 Å
H-atom completeness 98%
Disorder in solvent or counterion
R factor = 0.059
wR factor = 0.206
Data-to-parameter ratio = 12.2

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

Comment

Tris(2-aminoethyl)amine has been used extensively as a tripod ligand for the coordination of metal centres, and numerous structures exist containing coordinated tris(2-aminoethyl)-amine. However, a search of the April 2003 release of the Cambridge Structural Database (Allen, 2002) reveals that there are only ten structures where tris(2-aminoethyl)amine has been used as an organic base for which all three amine groups are protonated. None of these structures contains an organic acid. As part of a series of studies investigating the organic salt structures of multi-amine-containing aliphatic compounds with benzoic acid derivatives, we characterized the structure of the title compound, (I).



(I)

Interestingly the asymmetric unit of (I) consists of two triply protonated base molecules, six benzoate anions and four water molecules, one of which is unequally disordered across two adjacent sites (occupancies of O41*W* and O42*W* are 60 and 40%, respectively). Although the hydrogen-bonding network (Table 1) is extensive, the placement of molecules in the lattice is unexpectedly simple. The two bases, both adopting a tripod conformation and both facing in the same direction, line up along the *b* cell direction. Anions *B*, *C*, *D* and *F*, all benzoates, stack in the same orientation also along the *b* cell direction. The two remaining benzoates, anions *G* and *H*, lie perpendicular to the stacked benzoates and down the centre of the unit cell, forming what could be loosely described as a plane at $z = \frac{1}{2}$. The water molecules are then dispersed between the ions in suitable voids. Although H atoms were not located for the two components of O4*W*, the O41*W* and O42*W* atoms are 2.639 (6) and 2.810 (6) Å, respectively, from O11*H* and 3.400 (6) and 3.342 (6) Å from the back of N10*E*, suggesting their involvement in hydrogen bonds.

Experimental

1:3 Molar amounts of tris(2-aminoethyl)amine and 4-nitrobenzoic acid were refluxed in ethanol for 20 min. Total evaporation of the solvent gave yellow prisms of (I) (m.p. 457 K).

Crystal data

$C_6H_{21}N_4^{3+} \cdot 3C_7H_4NO_4^- \cdot 2H_2O$
$M_r = 683.647$
Triclinic, $P\overline{1}$
$a = 14.095\ (1)$ Å
$b = 14.697\ (1)$ Å
$c = 17.1308\ (7)$ Å
$\alpha = 103.758\ (5)^\circ$
$\beta = 99.715\ (6)^\circ$
$\gamma = 105.898\ (7)^\circ$
$V = 3209.5\ (3)$ Å^3
$Z = 4$
$D_x = 1.415$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 6$–14°
$\mu = 0.12$ mm^{-1}
$T = 298\ (2)$ K
Prism, yellow
$0.60 \times 0.50 \times 0.50$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (*Xtal*3.2; Hall *et al.*, 1992)
$T_{\min} = 0.952$, $T_{\max} = 0.977$
11 786 measured reflections
11 286 independent reflections
5646 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.011$
$\theta_{\max} = 25.0^\circ$
$h = 0 \rightarrow 16$
$k = -17 \rightarrow 16$
$l = -20 \rightarrow 20$
3 standard reflections every 200 reflections intensity decay: 15%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.206$
$S = 1.03$
11 286 reflections
922 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1205P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.63$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4A—H41A···O11$C^{\rm i}$	0.89	1.91	2.787 (4)	168
N4A—H42A···O10$B^{\rm i}$	0.89	2.30	2.938 (4)	128
N4A—H42A···O11$B^{\rm i}$	0.89	2.37	3.086 (4)	137
N4A—H42A···O10$C^{\rm ii}$	0.89	2.63	3.130 (5)	116
N4A—H43A···O11$B^{\rm ii}$	0.89	1.98	2.839 (4)	162
N7A—H71A···O11$C^{\rm i}$	0.89	1.85	2.703 (5)	161
N7A—H72A···O1$W^{\rm iii}$	0.89	1.91	2.748 (4)	156
N7A—H73A···O42W	0.89	1.68	2.495 (11)	151
N7A—H73A···O41W	0.89	2.23	3.119 (8)	173
N10A—H11A···O10$F^{\rm i}$	0.89	2.18	3.061 (4)	169
N10A—H11A···O11$F^{\rm i}$	0.89	2.27	2.902 (4)	128
N10A—H12A···O10$C^{\rm i}$	0.89	2.50	3.162 (5)	132
N10A—H12A···O11$B^{\rm ii}$	0.89	2.53	2.995 (4)	114
N10A—H13A···O11$D^{\rm ii}$	0.89	2.01	2.841 (4)	155
N4E—H41E···O2W	0.89	1.98	2.815 (5)	156
N4E—H42E···O10$D^{\rm i}$	0.89	1.98	2.849 (3)	164
N4E—H43E···O11$F^{\rm iv}$	0.89	2.30	2.968 (4)	132
N4E—H43E···O11$F^{\rm ii}$	0.89	2.48	3.017 (4)	119
N7E—H71E···O10$F^{\rm iv}$	0.89	2.03	2.873 (4)	157
N7E—H72E···O10$D^{\rm i}$	0.89	1.98	2.838 (3)	162
N7E—H73E···O11$G^{\rm i}$	0.89	1.90	2.742 (4)	158
N10E—H11E···O10$D^{\rm i}$	0.89	2.01	2.859 (4)	160
N10E—H12E···O10$B^{\rm i}$	0.89	1.88	2.734 (4)	159
N10E—H13E···O3$W^{\rm iii}$	0.89	1.86	2.733 (5)	166
O1W—H11···O10$G^{\rm v}$	0.81 (3)	1.92 (3)	2.722 (4)	171 (4)
O1W—H12···O11$G^{\rm i}$	0.81 (2)	2.02 (3)	2.805 (4)	166 (5)
O2W—H21···O10$C^{\rm ii}$	0.80 (5)	2.03 (4)	2.625 (4)	129 (4)
O2W—H22···O10$B^{\rm i}$	0.81 (3)	2.19 (2)	2.943 (5)	154 (5)
O3W—H31···O10H	0.82 (5)	2.03 (3)	2.812 (6)	177 (7)
O3W—H32···O11$H^{\rm iii}$	0.82 (5)	2.03 (5)	2.821 (6)	163 (5)

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

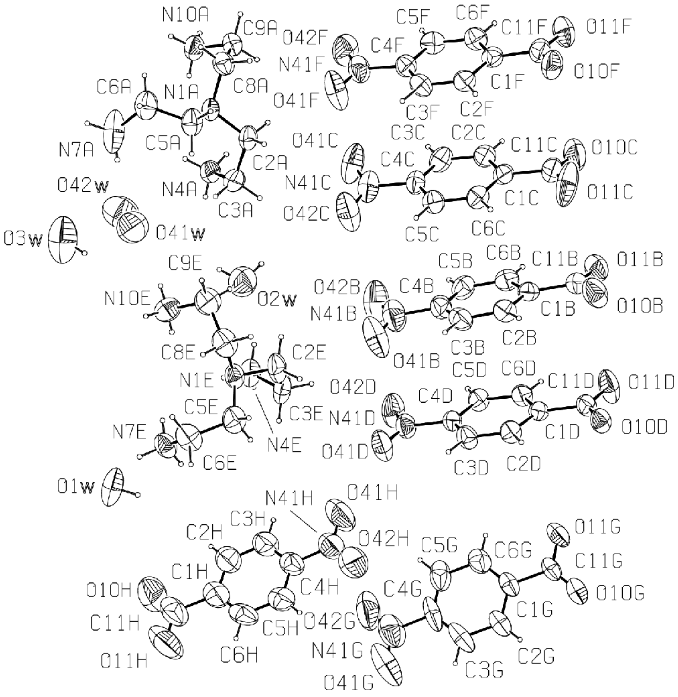


Figure 1
The asymmetric unit of the title compound (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. For clarity, anions *G* and *H* have been moved and are not in a position that can be directly compared with the positions of the other ions.

All H atoms on the N atoms were initially located in difference syntheses but were then included in the refinement (along with all non-water H atoms) at calculated positions as riding atoms, with N—H set at 0.89 Å and C—H set at 0.97 (CH_2) and 0.93 Å (Ar—H), and isotropic displacement parameters were set equal to $1.25U_{\rm eq}$ of the parent atom. All water H atoms, except those for O4*W*, were introduced at calculated positions, and their positional parameters were refined with restrained O—H distances of 0.811 Å and H···H distances of 1.3 Å, and with $U_{\rm iso} = 1.25U_{\rm eq}$(O). No H atoms were included for O4*W*. Residual electron density of 0.63 e Å^{-3} was located 1.71 Å from O4*W*. The first four unassigned peaks in the difference map are found near O2*W*–O4*W* and their respective H atoms but are too far from the O atoms to be considered as alternative H atoms.

Data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *Xtal*3.2 (Hall *et al.*, 1992); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*97 (Spek, 1997); software used to prepare material for publication: *SHELXL*97.

The author thanks the EPSRC's Chemical Database Service at Daresbury.

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