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Key indicators

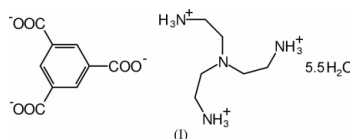
Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
H-atom completeness 98%
Disorder in solvent or counterion
 R factor = 0.063
 wR factor = 0.208
Data-to-parameter ratio = 13.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tris(2-ammonioethyl)amine benzene-
1,3,5-tricarboxylate 5.5-hydrate

The structure of the title compound, 2,2',2''-nitrilotri(ethylammonium) benzene-1,3,5-tricarboxylate 5.5-hydrate, $\text{C}_6\text{H}_{21}\text{N}_4^{3+}\cdot\text{C}_9\text{H}_3\text{O}_6^{3-}\cdot 5.5\text{H}_2\text{O}$, comprises the 1:1 organic salt of tris(2-ammonioethyl)amine and benzene-1,3,5-tricarboxylate in a complex hydrogen-bonded network which also includes four full water molecules and two with partial occupancies of 0.80 (2) and 0.70 (2).

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Comment

A search of the April 2003 release of the Cambridge Structural Database (Allen, 2002) reveals that both benzene-1,3,5-tricarboxylic acid and cyclohexane-1,3,5-tricarboxylic acid are involved in the structures of 61 salt, adduct, clathrate or hydrate complexes. Of these structures, 17 incorporate molecules that do not contain either an amine group or heterocyclic N atom, whereas the remaining structures do contain other molecules with these features. Of the latter structures, only five contain molecules with three or more N atoms, available for protonation from the acid H atoms, in the same molecule. Three of these are large selective tripod molecules (Ballester *et al.*, 1997, 2001), while the other two are derivatives of 1,4,8,11-tetraazacyclotetradecane (Burchell *et al.*, 2001) and 1,3,5-triaminocyclohexane (Menger *et al.*, 2002). Interestingly, the structures of neither tricarboxylic acid analogue with tris(2-aminoethyl)amine have been determined. Separate mixing of the two triacids with tris(2-aminoethyl)amine resulted in crystals and subsequent determination of the structure of the organic salt of only the benzene analogue with the tripod amine.



The 1:1 organic salt, (I), of benzene-1,3,5-tricarboxylate with tris(2-ammonioethyl)amine consists of both ions in a complex hydrogen-bonded network which also includes four water molecules and two partial-occupancy water molecules (Fig. 1). Two of the base ammonium groups (N4A and N7A) associate through all their H atoms to different carboxylate O atoms (except for N4A—H43A...O5W), while the third ammonium group (N10A) associates through two of its H atoms to three of the water molecules (O1W, O2W and O6W), the third H atom (H11A) associating to O52B. Of the water molecules, O1W—O4W mostly associate to carboxylate O atoms (O3W—H31 and O4W—H41 associate to O6W),

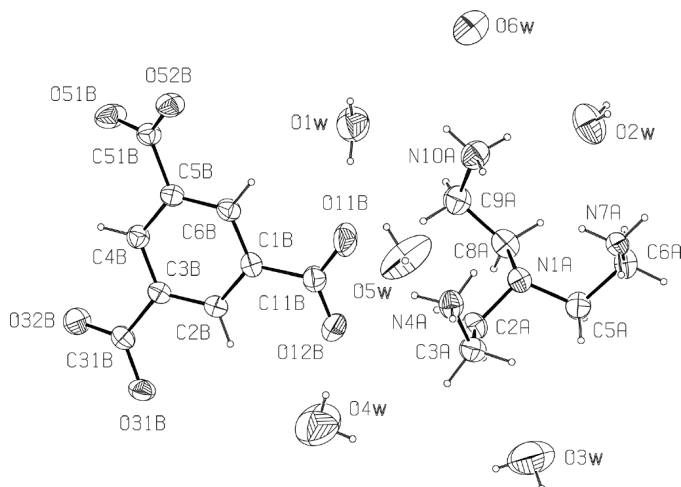


Figure 1
The molecular configuration and atom-numbering scheme for the title compound, showing 50% probability displacement parameters.

whereas O5W and O6W associate to other water molecules, although O6W is 2.916 (3) Å from N10A(1 - x, 1 - y, 1 - z). Partial occupancies for O5W [0.80 (2) occupancy] and O6W [0.70 (2) occupancy], giving a total of 5.5 water molecules in the asymmetric unit, best fits the CHN analysis of the crystals (found: C 39.3, H 7.6, N 12.4%; C₁₅H₃₅N₄O_{11.5} requires C 39.6, H 7.7, N 12.3%). Residual electron density of 0.68 e Å⁻³ was located 1.01 Å from O2W and is essentially equidistant from the two H atoms, creating H—O2W—peak angles of 46–47°. The first four unassigned peaks in the difference map closely proximate O1W—O4W and their respective H atoms but are not in suitable positions to be considered as alternative H atoms.

Experimental

Equimolar amounts of benzene-1,3,5-tricarboxylic acid and tris(2-aminoethyl)amine were refluxed in ethanol for 20 min. Total evaporation of the solvent gave colourless prisms (m.p. 453 K).

Crystal data

C₆H₂₁N₄³⁺·C₉H₃O₆³⁻·5.5H₂O
M_r = 455.47
 Triclinic, *P* $\bar{1}$
a = 9.5850 (10) Å
b = 10.7110 (10) Å
c = 12.980 (2) Å
 α = 72.790 (10)°
 β = 73.670 (10)°
 γ = 62.93 (8)°
V = 1116.5 (8) Å³

Z = 2
D_x = 1.355 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 6–14°
 μ = 0.12 mm⁻¹
T = 298 (2) K
 Prism, colourless
 0.60 × 0.50 × 0.50 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 2θ/ω scans
 Absorption correction: ψ scan (*Xtal3.2*; Hall *et al.*, 1992)
T_{min} = 0.930, *T_{max}* = 0.942
 4196 measured reflections
 3937 independent reflections
 2940 reflections with *I* > 2σ(*I*)

R_{int} = 0.027
 θ_{max} = 25.0°
h = 0 → 11
k = -11 → 12
l = -14 → 15
 3 standard reflections every 200 reflections
 intensity decay: 25%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.063
wR(*F*²) = 0.208
S = 1.17
 3937 reflections
 289 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.1270P)^2 + 0.3227P]$$

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

$$(\Delta/\sigma)_{\text{max}} < 0.001$$

$$\Delta\rho_{\text{max}} = 0.68 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.50 \text{ e } \text{Å}^{-3}$$

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>
N4A—H41A···O11B	0.89	2.11	2.944 (3)	156
N4A—H41A···O12B	0.89	2.43	3.168 (3)	141
N4A—H42A···O52B ⁱ	0.89	1.97	2.847 (3)	166
N4A—H43A···O31B ⁱⁱ	0.89	2.05	2.885 (4)	155
N4A—H43A···O5W	0.89	2.59	3.113 (3)	118
N7A—H71A···O52B ⁱ	0.89	2.06	2.921 (3)	162
N7A—H72A···O31B ⁱⁱⁱ	0.89	1.91	2.796 (3)	176
N7A—H73A···O51B ^{iv}	0.89	1.90	2.760 (4)	162
N10A—H11A···O52B ⁱ	0.89	1.89	2.771 (3)	169
N10A—H12A···O1W	0.89	2.17	2.917 (3)	141
N10A—H12A···O6W ⁱ	0.89	2.39	2.916 (3)	118
N10A—H13A···O2W	0.89	1.92	2.758 (3)	157
O1W—H11···O11B ⁱ	0.88 (3)	1.89 (3)	2.755 (3)	170 (3)
O1W—H12···O11B	0.90 (4)	2.02 (4)	2.921 (4)	173 (3)
O2W—H21···O32B ⁱⁱⁱ	0.86 (3)	1.84 (3)	2.694 (2)	171 (3)
O2W—H22···O31B ^v	0.84 (4)	2.06 (4)	2.828 (4)	153 (3)
O3W—H31···O6W ⁱⁱ	0.85 (3)	1.97 (3)	2.814 (2)	173 (3)
O3W—H32···O32B ^{iv}	0.86 (3)	1.97 (3)	2.814 (3)	170 (3)
O4W—H41···O6W ⁱⁱ	0.86 (3)	1.90 (3)	2.730 (2)	162 (3)
O4W—H42···O12B	0.89 (3)	1.85 (3)	2.730 (3)	172 (3)
O5W—H51···O3W ^{vi}	0.85 (3)	2.03 (3)	2.878 (3)	180 (3)
O5W—H52···O1W ⁱ	0.84 (3)	2.13 (3)	2.916 (2)	156 (3)
O6W—H61···O4W ^{vi}	0.85 (3)	2.11 (3)	2.955 (3)	180 (3)

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

All H atoms on the amines 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 to 0.89 Å and C—H set to 0.97 Å (CH₂) and 0.93 Å (Ar—H) and the isotropic displacement parameters were allowed to refine. All water H atoms, except H31, H41, H61 and H62, were then located in difference syntheses and positional parameters were refined, while the isotropic displacement parameters were set equal to 1.25*U*_{eq}(O). Atoms H31, H41, H61 and H62 were included at calculated positions and positional parameters refined, while the isotropic displacement parameters were set equal to 1.25*U*_{eq}(O). No suitable position for H62 could be located without causing intermolecular H62···H distances of < 2.0 Å.

Data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *Xtal3.2* (Hall *et al.*, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON97* (Spek, 1997); software used to prepare material for publication: *SHELXL97*.

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