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Crystal structure of 1,3,5,7-tetraazaadamantane-1,3-diium 2,5-dicarboxyterephthalate, $C_{16}H_{18}N_4O_8$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.15 × 0.15 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.13 mm ⁻¹
Diffractometer, scan mode:	APEX CCD, ϕ and ω scans
$2\theta_{\max}$, completeness:	28.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7546, 2068, 0.041
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1326
$N(\text{param})_{\text{refined}}$:	144
Programs:	Bruker [7], SHELX [8, 9]

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Abstract

$C_{16}H_{18}N_4O_8$, monoclinic, $C2/m$ (no. 12), $a = 14.517(4)$ Å, $b = 18.006(7)$ Å, $c = 6.916(3)$ Å, $\beta = 116.97(3)^\circ$, $V = 1611.2(11)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0497$, $wR_{\text{ref}}(F^2) = 0.1387$, $T = 296(2)$ K.

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The salt-type title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

All reagents and solvents were purchased from commercial sources and used as received. An aqueous solution (5 mL) of hexamethylenetetramine (70 mg, 0.5 mmol) and an ethanolic solution (5 mL) of 1,2,4,5-benzene tetracarboxylic acid

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
H2O ^a	0.874(3)	0.0239(9)	0.976(9)	0.10(3)*
O1A ^a	0.8488(6)	0.0628(4)	1.0003(8)	0.083(3)
O1B ^a	0.8873(6)	0.0694(3)	0.9735(9)	0.077(3)
C1	0.80234(18)	0.09111(12)	0.8080(3)	0.0412(6)
C2	0.75693(14)	0.03864(10)	0.6152(3)	0.0277(4)
C3	0.71038(14)	0.07486(10)	0.4163(3)	0.0252(4)
H1	0.7098	0.1265	0.4167	0.030*
C4	0.66478(13)	0.03908(10)	0.2172(3)	0.0238(4)
C5	0.62023(15)	0.09157(11)	0.0252(3)	0.0286(4)
C6	0.5000	0.38010(16)	0.5000	0.0365(7)
H6	0.4656	0.4122	0.3765	0.044*
C7	0.36991(16)	0.28844(13)	0.3321(3)	0.0398(5)
H7A	0.3436	0.3207	0.2061	0.048*
H7B	0.3162	0.2572	0.3561	0.048*
C8	0.47141(18)	0.28868(13)	0.7120(3)	0.0389(5)
H8A	0.5069	0.3216	0.8423	0.047*
H8B	0.4214	0.2583	0.7378	0.047*
C9	0.5000	0.19030(15)	0.5000	0.0332(7)
H9	0.4499	0.1606	0.5217	0.040*
N1	0.42276(13)	0.33437(10)	0.5225(3)	0.0357(4)
N2	0.55084(13)	0.23931(9)	0.6922(2)	0.0327(4)
H2	0.5821	0.2104	0.8100	0.039*
O2	0.77891(14)	0.15570(9)	0.7872(2)	0.0505(5)
O3	0.62778(12)	0.15884(8)	0.0596(2)	0.0398(4)
O4	0.57607(12)	0.06621(9)	−0.1684(2)	0.0440(4)
H10 ^a	0.579(3)	0.014(3)	−0.176(6)	0.053*

^aOccupancy: 0.5.

(130 mg, 0.5 mmol) were mixed, and the solution was allowed to stand at room temperature. Colorless plate crystals were obtained after three days (yield 40 mg, 20%).

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Experimental details

H atoms bound to C atoms were placed in calculated positions and refined as riding on their parent atoms, with C–H = 0.93 Å (aromatic), C–H = 0.96 Å (methylene), and with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2 U_{\text{eq}}(\text{C})$ for all other H atoms. The H atoms bound to N and O atoms were found from the Fourier difference map.

Comment

Multicarboxylates are widely used as building blocks for the construction of supramolecular structures, not only because they have versatile coordination modes to metal ions, but also because they are hydrogen bonding acceptors and donors [1–3]. Meanwhile, hexamethylenetetramine (hmt), having four N atoms, also can be involved in hydrogen bonding to generate diamond-type supramolecular networks [4, 5]. With this in mind, we have become interested in the preparation of supramolecular structures based on the multicarboxylates and hexamethylenetetramine. Herein, we report the salt-type crystal structure [6] based on 1,2,4,5-benzene tetracarboxylic acid (H₄btc) and hexamethylenetetramine, [H₂hmt][H₂btc].

The asymmetric unit of the title compound consists of one half of a [H₂hmt]²⁺ cation and one half of a [H₂btc]^{2−} anion, resulting in a 1:1 salt. In the structure, the two protons of the former 1,2,4,5-benzene tetracarboxylic acid were transferred to two N atoms of hexamethylenetetramine. Each [H₂hmt]²⁺ cation is hydrogen-bonded with two adjacent [H₂btc]^{2−} anions, and each [H₂btc]^{2−} anion is also hydrogen-bonded with two adjacent [H₂hmt]²⁺ cations to form [2 + 2] dimers through four medium strong N2–H2...O3 hydrogen bonds (N2–H2...O3 = 2.689(2) Å).

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