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Crystal structure of tetrakis(melaminium) 1,2,4,5-benzenetetracarboxylate octahydrate, $(C_3H_7N_6)_4[C_6H_2(COO)_4] \cdot 8H_2O$

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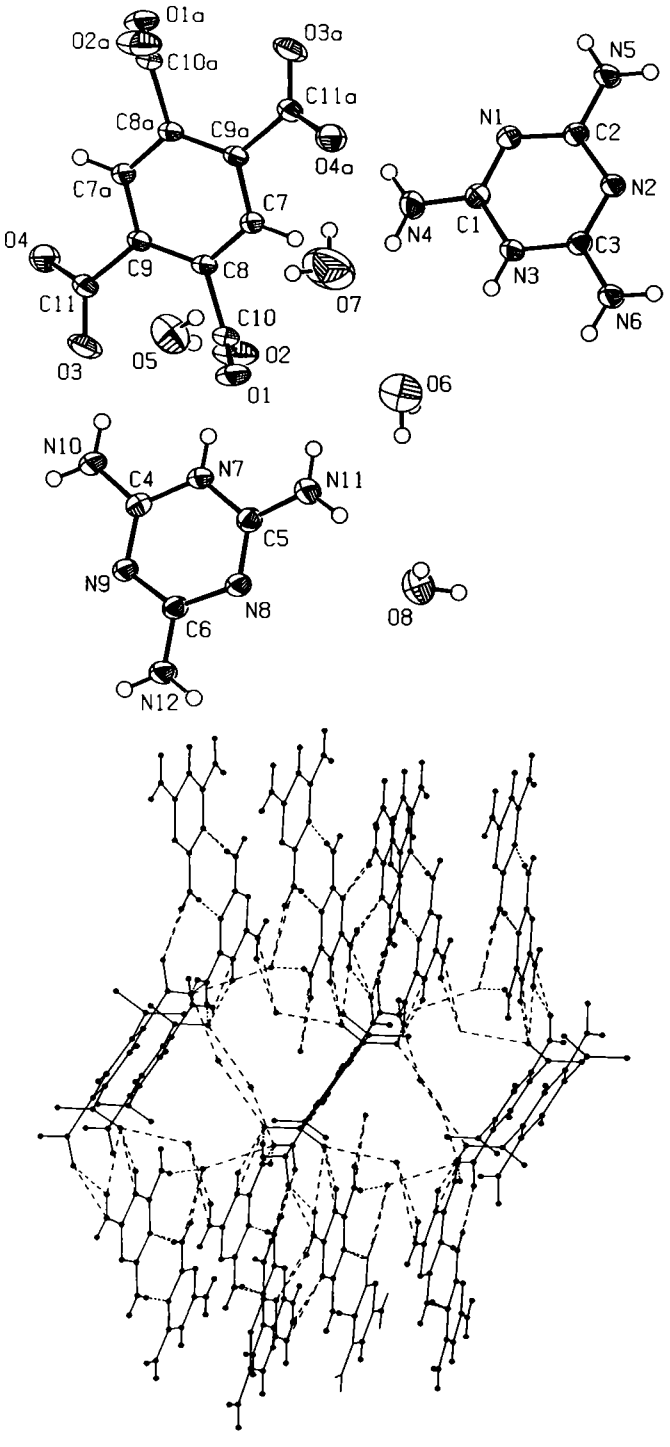

Abstract

$C_{22}H_{46}N_{24}O_{16}$, triclinic, $P\bar{1}$ (no. 2), a = 7.0706(6) Å, b = 9.7952(8) Å, c = 14.790(1) Å, α = 105.879(1)°, β = 91.608(1)°, γ = 96.254(1)°, V = 977.6 Å^3, Z = 1, $R_{gt}(F)$ = 0.049, $wR_{ref}(F^2)$ = 0.150, T = 295 K.

Source of material

Melamine (0.063 g, 0.5 mmol), 1,2,4,5-benzenetetracarboxylic acid (H_4btec; 0.12 g, 0.5 mmol), and NaOH (0.02 g, 0.5 mmol) were added to a H_2O solution (12 ml) in a Teflon-lined stainless steel reactor. The mixture was heated at 385 K for 3 days, and then slowly cooled down to room temperature. Colorless crystals of the title compound were obtained.

Discussion

The design and synthesis of supramolecular coordination polymeric networks, especially those constructed by hydrogen bonding and intermolecular weak interactions have been a field of rapid growth due to their special physical properties and potential application in functional materials. Of particular interest are compounds that are capable of forming very strong hydrogen bonds like some salts of pyromellitic acid. The 1,2,4,5-benzenetetracarboxylic acid, also known as pyromellitic acid, possesses several interesting characteristics: (a) it has four carboxyl groups which may be completely or partially deprotonated, inducing rich coordination modes and allowing interesting structures with higher dimensions; (b) it can act not only as hydrogen-bond acceptor but also as hydrogen-bond donor, depending upon the numbers of deprotonated carboxyl groups [1-8].

The structure of the title compound comprises four melamine cations, a 1,2,4,5-benzenetetracarboxylate anion and four water molecules (figure, top). Three carboxyl groups of 1,2,4,5-benzenetetracarboxylic acid are all deprotonated and a melamine-ring accepts a proton coming from a 1,2,4,5-benzenetetracarboxylic acid molecule to produce the melamine cation. It is noteworthy that hydrogen bonding and intermolecular weak interactions play an important role in the structure of the title compound, as shown in figure, bottom. There are several kinds of hydrogen bonding are present in the structure: (a) hydrogen bonding between water molecules and melamine nitrogen atoms with an N—O distances of 2.984 Å, 2.879 Å, 3.032 Å and 2.872 Å, respectively; (b) hydrogen bonding of carboxylate molecules and melamine hydrogen atoms with an N—O distance of 2.713 Å, 2.922 Å, 3.156 Å, 2.764 Å, 2.837 Å and 3.326 Å; (c) hydrogen bonding of melamine hydrogen atoms/melamine nitrogen atoms (N—N distance is 3.005 Å, 3.211 Å, 2.944 Å, 3.031 Å and 2.934 Å, respectively. An extended three-dimensional network structure with hydrogen bonds contributes to the stability of the structure.

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Table 1. Data collection and handling.

Crystal:	colorless block, size 0.25 × 0.37 × 0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.30 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	56.52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9056, 4691
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3932
$N(param)_{refined}$:	286
Programs:	SHELXS-97 [9], SHELXL-97 [10]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(7)	2*i*	0.5344	0.7588	0.4551	0.035
H(3')	2*i*	0.4017	0.2814	0.2388	0.031
H(4A)	2*i*	0.2698	0.5900	0.2274	0.044
H(4B)	2*i*	0.3223	0.5061	0.2925	0.044
H(5A)	2*i*	0.3342	0.2302	−0.1275	0.039
H(5B)	2*i*	0.2803	0.3775	−0.0923	0.039
H(6A)	2*i*	0.4949	−0.0151	0.0843	0.037
H(6B)	2*i*	0.4878	0.0570	0.1867	0.037
H(7')	2*i*	0.1036	0.7625	0.7409	0.033
H(10A)	2*i*	−0.0057	1.0296	0.9160	0.039
H(10B)	2*i*	0.0116	0.9805	0.8123	0.039
H(11A)	2*i*	0.2416	0.4456	0.7219	0.043
H(11B)	2*i*	0.1932	0.5478	0.6690	0.043
H(12A)	2*i*	0.1401	0.7272	1.0919	0.042
H(12B)	2*i*	0.2000	0.5852	1.0445	0.042
H(1W)	2*i*	0.7589	0.8761	0.6612	0.092
H(2W)	2*i*	0.9467	0.8938	0.6371	0.092
H(3W)	2*i*	0.2907	0.4574	0.4716	0.178
H(4W)	2*i*	0.1967	0.4605	0.4273	0.178
H(5W)	2*i*	0.9975	0.7404	0.5081	0.142
H(6W)	2*i*	0.8762	0.7019	0.4265	0.142
H(7W)	2*i*	0.8245	0.1436	0.7322	0.079
H(8W)	2*i*	0.9928	0.2359	0.7440	0.079

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	2*i*	0.5065(2)	0.7717(2)	0.65581(9)	0.0668(9)	0.0420(7)	0.0335(7)	0.0150(6)	0.0055(6)	0.0247(6)
O(2)	2*i*	0.2004(2)	0.7809(2)	0.6209(1)	0.0568(9)	0.077(1)	0.0426(8)	−0.0115(8)	0.0007(7)	0.0370(8)
O(3)	2*i*	0.3680(3)	1.0818(2)	0.74586(9)	0.103(1)	0.0547(9)	0.0210(6)	0.0440(9)	0.0181(7)	0.0163(6)
O(4)	2*i*	0.2371(2)	1.2294(1)	0.67959(9)	0.0627(9)	0.0384(7)	0.0329(7)	0.0264(6)	0.0171(6)	0.0131(5)
C(7)	2*i*	0.5206(3)	0.8557(2)	0.4730(1)	0.0477(9)	0.0222(7)	0.0200(7)	0.0107(6)	0.0059(6)	0.0081(5)
C(8)	2*i*	0.4375(2)	0.9138(2)	0.5570(1)	0.0393(8)	0.0256(7)	0.0178(7)	0.0074(6)	0.0041(6)	0.0102(5)
C(9)	2*i*	0.4166(2)	1.0596(2)	0.5849(1)	0.0402(8)	0.0257(7)	0.0167(6)	0.0105(6)	0.0051(6)	0.0082(5)
C(10)	2*i*	0.3757(3)	0.8152(2)	0.6162(1)	0.052(1)	0.0278(7)	0.0175(7)	0.0037(7)	0.0040(6)	0.0101(6)
C(11)	2*i*	0.3345(3)	1.1286(2)	0.6779(1)	0.049(1)	0.0285(8)	0.0196(7)	0.0126(7)	0.0095(6)	0.0078(6)
N(1)	2*i*	0.3079(2)	0.4129(1)	0.07577(9)	0.0365(7)	0.0224(6)	0.0235(6)	0.0091(5)	0.0002(5)	0.0076(5)
N(2)	2*i*	0.3973(2)	0.1744(1)	0.01954(9)	0.0327(7)	0.0238(6)	0.0214(6)	0.0100(5)	0.0021(5)	0.0080(5)
N(3)	2*i*	0.3877(2)	0.2853(1)	0.18171(9)	0.0372(7)	0.0247(6)	0.0186(6)	0.0089(5)	0.0016(5)	0.0082(5)
N(4)	2*i*	0.3052(2)	0.5131(2)	0.2362(1)	0.059(1)	0.0283(7)	0.0247(7)	0.0176(7)	0.0008(6)	0.0046(5)
N(5)	2*i*	0.3156(2)	0.3019(2)	−0.0814(1)	0.0512(9)	0.0297(7)	0.0221(6)	0.0177(6)	0.0037(6)	0.0106(5)
N(6)	2*i*	0.4737(2)	0.0580(2)	0.1289(1)	0.0453(8)	0.0279(7)	0.0229(6)	0.0150(6)	0.0022(5)	0.0098(5)
C(1)	2*i*	0.3332(2)	0.4054(2)	0.1632(1)	0.0282(7)	0.0230(7)	0.0251(7)	0.0063(5)	0.0014(6)	0.0066(6)
C(2)	2*i*	0.3415(2)	0.2960(2)	0.0061(1)	0.0265(7)	0.0239(7)	0.0238(7)	0.0062(5)	0.0013(5)	0.0083(5)
C(3)	2*i*	0.4197(2)	0.1716(2)	0.1086(1)	0.0247(7)	0.0234(7)	0.0239(7)	0.0052(5)	0.0015(5)	0.0081(5)
N(7)	2*i*	0.1134(2)	0.7451(1)	0.79465(9)	0.0392(7)	0.0255(6)	0.0222(6)	0.0083(5)	0.0035(5)	0.0110(5)
N(8)	2*i*	0.1858(2)	0.5877(1)	0.88237(9)	0.0354(7)	0.0248(6)	0.0251(7)	0.0100(5)	0.0058(5)	0.0098(5)
N(9)	2*i*	0.0886(2)	0.8195(1)	0.95865(9)	0.0344(7)	0.0240(6)	0.0243(6)	0.0092(5)	0.0061(5)	0.0103(5)
N(10)	2*i*	0.0205(2)	0.9655(2)	0.8668(1)	0.0475(8)	0.0269(7)	0.0283(7)	0.0133(6)	0.0046(6)	0.0133(5)
N(11)	2*i*	0.2054(2)	0.5264(2)	0.7213(1)	0.0540(9)	0.0294(7)	0.0250(7)	0.0137(6)	0.0065(6)	0.0070(5)
N(12)	2*i*	0.1640(2)	0.6650(2)	1.0414(1)	0.0571(9)	0.0312(7)	0.0246(7)	0.0213(7)	0.0090(6)	0.0128(5)
C(4)	2*i*	0.0741(2)	0.8443(2)	0.8751(1)	0.0253(7)	0.0236(7)	0.0271(7)	0.0040(5)	0.0021(5)	0.0105(6)
C(5)	2*i*	0.1685(2)	0.6177(2)	0.8009(1)	0.0271(7)	0.0243(7)	0.0266(7)	0.0047(6)	0.0039(6)	0.0081(6)
C(6)	2*i*	0.1458(2)	0.6919(2)	0.9592(1)	0.0285(7)	0.0247(7)	0.0260(7)	0.0080(6)	0.0052(6)	0.0104(6)
O(5)	2*i*	0.8645(3)	0.9300(2)	0.6743(1)	0.062(1)	0.068(1)	0.0475(9)	0.0049(9)	−0.0008(8)	0.0077(8)
O(6)	2*i*	0.3124(5)	0.4941(3)	0.4265(2)	0.224(4)	0.072(2)	0.063(1)	0.013(2)	0.030(2)	0.023(1)
O(7)	2*i*	0.9236(4)	0.6733(3)	0.4706(2)	0.105(2)	0.118(2)	0.060(1)	0.007(2)	−0.022(1)	0.030(1)
O(8)	2*i*	0.8790(3)	0.2267(2)	0.7605(1)	0.066(1)	0.0465(8)	0.0437(8)	0.0148(7)	0.0131(7)	0.0056(6)

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References

1. Cao, R.; Sun, D. F.; Liang, Y. C.; Hong, M. C.; Tatsumi, K.; Shi, Q.: Syntheses and Characterizations of Three-Dimensional Channel-like Polymeric Lanthanide Complexes Constructed by 1,2,4,5-Benzenetetracarboxylic Acid. Inorg. Chem. **41** (2002) 2087-2094.
2. Cao, R.; Shi, Q.; Sun; D. F.; Hong, M. C.; Bi, W. H.; Zhao, Y. J.: Syntheses and Characterizations of Copper(II) Polymeric Complexes Constructed from 1,2,4,5-Benzenetetracarboxylic Acid. Inorg. Chem. **41** (2002) 6161-6168.
3. Jiang, Y. S.; Yu, Z. T.; Liao, Z. L.; Li, G. H.; Chen, J. S.: Syntheses and photoluminescent properties of two uranyl-containing compounds with extended structures. Polyhedron **25** (2006) 1359-1366.
4. Shi, Q.; Cao, R.; Sun, D. F.; Hong, M. C.; Liang, Y. C.: Solvothermal syntheses and crystal structures of two metal coordination polymers with double-chain structures. Polyhedron **20** (2001) 3287-3293.

5. Rochon, F. D.; Massarweh, G.: Study of the aqueous reactions of metallic ions with benzenetetracarboxylate ions: Part 1. Crystal structures of compounds of the types $[M(H_2O)_6][C_6H_2(COO)_2(COOH)_2]$ (M = Mn, Co and Ni) and $Ni(H_2O)_5(C_6H_2(COO)_4)Ni(H_2O)_5 \cdot 6H_2O$. Inorg. Chim. Acta **304** (2000) 190-198.
6. Ganesan, S. V.; Natarajan, S.: Synthesis and Structures of New Pyromellitate Coordination Polymers with Piperazine as a Ligand. Inorg. Chem. **43** (2004) 198-205.
7. Ghosh, S. K.; Bharadwaj, P. K.: Puckered-Boat Conformation Hexameric Water Clusters Stabilized in a 2D Metal-Organic Framework Structure Built from Cu(II) and 1,2,4,5-Benzenetetracarboxylic Acid. Inorg. Chem. **43** (2004) 5180-5182.
8. Wang, Y. B.; Zhuang, W. J.; Jin, L. P.; Lu, S. Z.: New lanthanide coordination polymers of 1,2,4,5-benzenetetracarboxylic acid and 4,4'-bipyridine with 1D channels. J. Mol. Struct. **737** (2005) 165-172.
9. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
10. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.