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Structure of *N,N′,N″*-tris(carboxymethyl)-1,3,5-benzenetricarboxamide trihydrate

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The title compound, $C_{15}H_{15}N_3O_9 \cdot 3H_2O$, crystallizes in the centrosymmetric space group $R\bar{3}$ with a = 13.642(5), b = 13.642(5), c = 18.692(5) Å, D_{calc} = 1.440 g cm^3, and z = 6. An extensive three-dimensional hydrogen bonded network is observed. The network arises from 15 hydrogen bonds per asymmetric unit. Six identical N—H···O hydrogen bonds are formed between two triacid molecules, which results in the face-to-face dimerization of the two triacid molecules. The dimers form extended sheets through hydrogen bond interaction with water molecules. The sheets are held together by hydrogen bonds via the water molecules. The planes of the benzenoid ring are parallel to each other.

KEY WORDS: Triacid molecules; hydrogen bond interaction; water molecules.

Introduction

In our study of hydrogen bonded molecular assemblies, the title compound, (I), was synthesized. It crystallizes in the centrosymmetric space group $R\bar{3}$, a space group not very common for organic compounds. But, because of the three carboxyl groups in the title compound, the space group $R\bar{3}$ provides the best packing arrangement in the unit cell. However, the three carboxyl groups of the triacid do not form an eight-membered, dimeric hydrogen bonded cycle as in other compounds we have studied.[1]

Experimental

The triacid was synthesized by treating 1,3,5-benzenetricarbonyl trichloride with glycine methyl ester in $CHCl_3$. The triester product, upon hydrolysis with 3 equivalents of NaOH in water, gave the triacid. The title compound was crystallized from water by gas-phase neutralization[2] of a solution of the triacid in aqueous sodium hydroxide.

Data collection was carried out on an Enraf-Nonius CAD4 diffractometer. Table 1 lists the data collection and refinement details. Fractional atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2. Selected bond lengths and angles are listed in Table 3.

Results and discussion

A view of the hydrated molecule is shown in Fig. 1. The $\bar{3}$ axis passes through the center of the molecule shown in Fig. 2. As listed in Table 4, there are 15 hydrogen bonds in this structure, which fall into three identical, symmetry-related sets. Each set corresponds to the five H-bonds formed by the donors and acceptors of one of the three arms attached to the benzenoid ring. The triacid molecule has the conformation in which all three arms are pointed to one side of the plane of the benzenoid ring. Such a conformation results in a self-comple-

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Table 1. Crystal Data and Structure Refinement for $C_{15}H_{15}N_3O_9 \cdot 3H_2O$

CCDC deposit no.	CCDC-1003/5578
Color/shape	Colorless/fragment
Empirical formula	$C_{15}H_{21}N_3O_{12}$
Formula weight	435.35
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Trigonal
Space group	$R\bar{3}$ (No. 148)
Unit cell dimensions	
a = 13.642(5) Å α = 90°.	
b = 13.642(5) Å β = 90.0°.	
c = 13.692(5) Å γ = 120.0°.	
Volume	3012.6(18) Å^3
Z	6
Density (calculated)	1.440 mg/m^3
Absorption coefficient	0.126 mm^{-1}
Diffractometer/Scan	CAD4/ω-2θ scans
F(000)	1368
Crystal size	0.30 × 0.20 × 0.20 mm^3
Theta range for data collection	3.27 to 25.00°.
Index ranges	$-11 <= h <= 14$, $-16 <= k <= 8$, $-22 <= l <= 17$
Reflections collected	1943
Independent reflections	1174 [R(int) = 0.0169]
Absorption correction	Psi-scan
Max. and min. transmission	0.9974 and 0.9538
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1174/0/111
Goodness-of-fit on F^2	1.082
Final R indices [$I > 2$ sigma(I)]	$R1$ = 0.0432, $wR2$ = 0.1110
R indices (all data)	$R1$ = 0.0499, $wR2$ = 0.1174
Largest diff. peak and hole	0.283 and −0.207 e·Å^{-3}

Table 2. Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $C_{15}H_{15}N_3O_9 \cdot 3H_2O$

	x	y	z	U(eq)[a]
O(1)	3597(1)	637(1)	4545(1)	56(1)
O(2)	2585(1)	−166(1)	6139(1)	54(1)
N(3)	3105(1)	1561(1)	5706(1)	41(1)
O(4)	5416(1)	1505(1)	4821(1)	70(1)
C(5)	290(1)	−839(1)	5979(1)	34(1)
C(6)	1134(1)	294(1)	5978(1)	33(1)
C(7)	2339(1)	548(1)	5951(1)	37(1)
C(8)	4260(1)	1848(2)	5574(1)	45(1)
C(9)	4371(1)	1256(1)	4924(1)	42(1)
OW	4510(2)	−432(2)	6292(1)	97(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Lengths [Å] and Angles [°] for $C_{15}H_{15}N_3O_9 \cdot 3H_2O$[a]

O(1)−C(9)	1.199(2)
O(2)−C(7)	1.229(2)
N(3)−C(7)	1.330(2)
N(3)−C(8)	1.442(2)
O(4)−C(9)	1.303(2)
C(5)−C(6)#1	1.384(2)
C(5)−C(6)	1.391(2)
C(6)−C(5)#2	1.384(2)
C(6)−C(7)	1.502(2)
C(8)−C(9)	1.508(3)
C(7)−N(3)−C(8)	121.72(15)
C(6)#1−C(5)−C(6)	120.38(14)
C(5)#2−C(6)−C(5)	119.61(14)
C(5)#2−C(6)−C(7)	123.08(13)
C(5)−C(6)−C(7)	117.27(12)
O(2)−C(7)−N(3)	122.54(14)
O(2)−C(7)−C(6)	120.60(14)
N(3)−C(7)−C(6)	116.85(14)
N(3)−C(8)−C(9)	112.39(14)
O(1)−C(9)−O(4)	124.0(2)
O(1)−C(9)−C(8)	124.36(15)
O(4)−C(9)−C(8)	111.63(14)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + y, -x, z$ #2 $-y, x - y, z$.

mentary shape of the molecule, which facilitates dimerization.

The five bonds in each set fall into two groups: a group of two identical bonds having a N···O distance of 2.920 Å with an N−H···O angle 159°; and a group

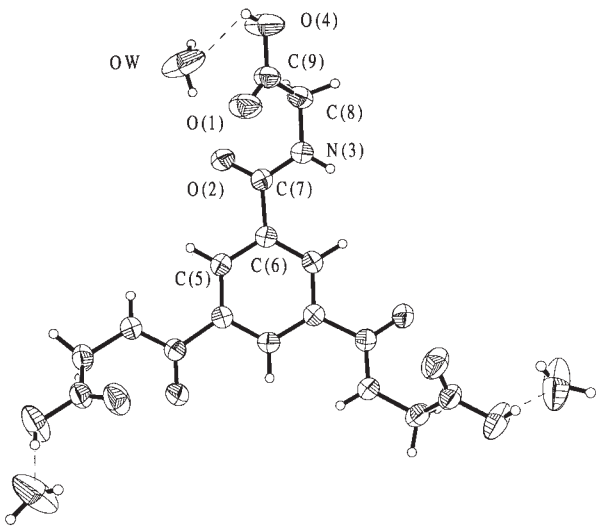

Fig. 1. Molecular structure of the title compound.

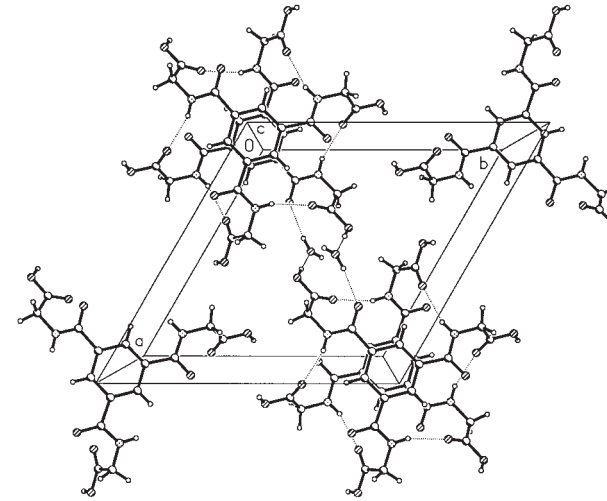

Fig. 2. Packing diagram of the title compound viewed down the *c* axis.

of three bonds having $O_d \cdots O_a$ distances ranging from 2.58 to 2.89 Å with O−H···O angles ranging from 160 to 178°. The same set of the hydrogen bonding interactions can then be characterized as follows. One arm of a triacid molecule interacts with two arms of another molecule by inserting itself into the space between the two arms of the other molecule. The amide H1 atom forms an H-bond with the carboxylic O1 acceptor on one of the two arms of the other molecule, and the carboxylic O1 acceptor forms still another, but identical H-bond with the amide H2 atom of the second arm of the other triacid molecule. Thus, two triacid molecules form six identical H-bonds between their O1 and H1 atoms, with an N···O distance of 2.920 Å and an N−H···O angle of 159°, causing a face-to-face dimerization of the two molecules. In the second group of one set, the amide O-atom acceptor, O2, forms a hydrogen bonds with the water H-atom, HW1 with an O2···OW distance of 2.839 Å and an O2···HW1−OW angle of 160°. The second H-atom, HW2,

Table 4. Hydrogen Bond Length (Å) and Angles (°) for $C_{15}H_{15}N_3O_9 \cdot 3H_2O$[a]

D−H···A	D−H	H···A	D···A	D−H···A
N3−H1···O1[i]	0.83	2.13	2.920(2)	159(2)
O4−H4···OW[ii]	0.82	1.76	2.576(2)	178.6(1)
OW−HW1···O2	0.81	2.06	2.839(3)	160(4)
OW−HW2···O2[iii]	0.87	2.03	2.895(3)	171(5)

[a] Symmetry code: (i) $x - y, x, -z$; (ii) $-x, -y, -z$; (iii) $2/3 + y, 1/3 - x + y, 1/3 - z$.

interacts with another amide O2 of an adjacent molecule, forming an H-bond with an O2···OW distance of 2.895 Å and an OW—HW2···O2 angle of 171°. The last H-bond of the second set involves the interaction between the carboxylic H-atom, H4, and OW, the water O-atom acceptor. This bond is the shortest among all 5 bonds of the same set with an O4···OW distance of 2.576 Å and an O4—H4···OW angle of 178.6°. This donor-acceptor distance is below average for organic O···O hydrogen bonds of about 2.77 Å,[3] while the distances of the other two O···O H-bonds are above average. The dihedral angle between the amide group plane and the plane of the benzenoid ring is 21.24°.

As mentioned in the abstract, crystal packing involves the formation of sheets by triacid dimers, via the hydrogen bonded network of O4—H4···OW—HW1···O2. The packing of the sheets involves the hydrogen bonded network of O2···HW1—OW—HW2···O2 that links three molecules in two different sheets.

Acknowledgments

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