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Crystal structure of guanidinium tetrapropylammonium bis(hydrogencarbonate) dihydrate, $C_{15}H_{40}N_4O_8$

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Abstract

$C_{15}H_{40}N_4O_8$, monoclinic, *Cc* (no. 9), $a = 25.986(3)$ Å, $b = 8.3450(6)$ Å, $c = 21.1358(15)$ Å, $\beta = 90.877(6)^\circ$, $V = 4582.9(6)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0357$, $wR_{ref}(F^2) = 0.0916$, $T = 296(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colorless plate
Size:	$0.38 \times 0.16 \times 0.05$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.09 mm^{-1}
Diffractometer, scan mode:	APEX2, φ and ω
θ_{max} , completeness:	23.7° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8322, 4217, 0.019
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3517
$N(\text{param})_{\text{refined}}$:	523
Programs:	SHELX [1, 2], Bruker [3]

Source of material

1,2,4,5-tetrakis(4-carboxyphenyl)benzene and tetrapropylammonium hydroxide (30% aqueous solution) were dissolved in small amount of water/ethanol (v/v, 1:2) to yield clean solution with the participation of guanidine hydrochloride (A. R.). After vigorous stirring for an hour, the solution was set aside to generate colorless plate crystals of the title compound after about 2 weeks. The aromatic acid was not present in the obtained crystalline phase. It can be concluded

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
O1	0.26820(10)	−0.0439(3)	0.09179(12)	0.0720(7)
H1	0.2891(15)	−0.095(5)	0.117(2)	0.108*
O1W	0.17440(12)	0.6009(3)	0.20479(13)	0.0707(7)
H1WA	0.1627(19)	0.612(5)	0.2425(11)	0.106*
H1WB	0.1867(18)	0.693(3)	0.195(2)	0.106*
N1	0.04595(11)	0.7994(3)	0.01959(13)	0.0502(7)
C1	−0.00372(14)	0.7119(4)	0.03113(18)	0.0567(9)
H1A	−0.0124	0.6506	−0.0065	0.068*
H1B	0.0021	0.6361	0.0653	0.068*
O2	0.19009(10)	0.0554(3)	0.09360(11)	0.0655(7)
O2W	0.13140(11)	0.6658(5)	−0.36468(18)	0.0973(10)
H2WA	0.1478(18)	0.744(4)	−0.380(3)	0.146*
H2WB	0.1520(16)	0.593(5)	−0.352(3)	0.146*
N2	−0.19118(11)	1.1797(3)	0.77811(13)	0.0471(6)
C2	−0.04944(17)	0.8138(5)	0.0475(2)	0.0770(12)
H2A	−0.0549	0.8943	0.0150	0.092*
H2B	−0.0429	0.8685	0.0874	0.092*
O3	0.21937(10)	−0.0886(3)	0.17489(12)	0.0702(7)
C3	−0.09696(17)	0.7109(7)	0.0529(2)	0.0890(14)
H3A	−0.1258	0.7770	0.0634	0.133*
H3B	−0.1036	0.6580	0.0133	0.133*
H3C	−0.0916	0.6322	0.0855	0.133*
O3W	0.37202(12)	0.1012(5)	−0.11960(14)	0.0940(10)
H3WA	0.372(2)	0.145(6)	−0.1563(14)	0.141*
H3WB	0.3970(15)	0.035(5)	−0.116(2)	0.141*
N3	0.28407(13)	0.0776(4)	−0.04013(16)	0.0777(10)
H3D	0.2833	0.0383	−0.0025	0.093*
H3E	0.3118	0.0721	−0.0616	0.093*
C4	0.06118(15)	0.8990(4)	0.07693(16)	0.0558(9)
H4A	0.0923	0.9576	0.0672	0.067*
H4B	0.0343	0.9772	0.0842	0.067*
O4W	0.06654(13)	0.6502(5)	−0.25316(18)	0.1129(12)
H4WA	0.0948(15)	0.667(7)	−0.273(3)	0.169*
H4WB	0.061(2)	0.549(3)	−0.259(3)	0.169*
N4	0.24370(13)	0.2051(4)	−0.12278(15)	0.0691(9)
H4C	0.2167	0.2488	−0.1392	0.083*
H4D	0.2715	0.1994	−0.1442	0.083*
O4	0.15079(12)	0.3434(4)	−0.17025(13)	0.0825(8)
C5	0.07044(16)	0.8069(4)	0.13744(17)	0.0639(10)
H5A	0.1001	0.7376	0.1328	0.077*
H5B	0.0408	0.7401	0.1461	0.077*
N5	0.20037(13)	0.1544(4)	−0.03166(15)	0.0693(9)
H5C	0.1731	0.1979	−0.0476	0.083*
H5D	0.2000	0.1160	0.0061	0.083*
O5	0.06988(13)	0.4249(5)	−0.16358(16)	0.1065(12)
C6	0.07965(18)	0.9213(5)	0.19207(18)	0.0758(12)
H6A	0.0855	0.8612	0.2303	0.114*
H6B	0.1093	0.9863	0.1837	0.114*
H6C	0.0501	0.9888	0.1969	0.114*
N6	0.01729(12)	0.6958(3)	−0.40152(15)	0.0626(8)
H6D	0.0455	0.6882	−0.3799	0.075*
H6E	0.0178	0.6902	−0.4421	0.075*
O6	0.10500(11)	0.2749(4)	−0.08837(13)	0.0765(8)
H6	0.0760(11)	0.291(6)	−0.071(2)	0.115*
C7	0.08630(14)	0.6728(4)	0.00641(18)	0.0552(9)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H7A	0.0873	0.5981	0.0416	0.066*
H7B	0.0757	0.6134	−0.0310	0.066*
N7	−0.06954(12)	0.7299(4)	−0.40657(17)	0.0736(9)
H7C	−0.0984	0.7448	−0.3882	0.088*
H7D	−0.0685	0.7242	−0.4472	0.088*
O7	0.01666(10)	0.3090(3)	−0.03477(12)	0.0679(7)
C8	0.13982(16)	0.7357(6)	−0.0035(2)	0.0802(12)
H8A	0.1395	0.8089	−0.0392	0.096*
H8B	0.1509	0.7951	0.0337	0.096*
N8	−0.02793(12)	0.7246(4)	−0.31044(15)	0.0693(8)
H8C	0.0001	0.7171	−0.2885	0.083*
H8D	−0.0568	0.7378	−0.2918	0.083*
O8	−0.02207(11)	0.4235(4)	−0.11735(14)	0.0883(9)
H8	0.0089(10)	0.427(7)	−0.131(3)	0.132*
C9	0.17736(18)	0.6027(6)	−0.0157(2)	0.0919(14)
H9A	0.2110	0.6470	−0.0218	0.138*
H9B	0.1783	0.5311	0.0199	0.138*
H9C	0.1668	0.5449	−0.0529	0.138*
O9	−0.06723(12)	0.3627(4)	−0.03617(14)	0.0941(10)
C10	0.04008(17)	0.9141(4)	−0.03604(17)	0.0626(10)
H10A	0.0158	0.9972	−0.0246	0.075*
H10B	0.0730	0.9655	−0.0429	0.075*
O10	−0.12304(10)	0.2705(3)	0.25737(12)	0.0686(7)
C11	0.0222(2)	0.8402(5)	−0.09755(18)	0.0844(13)
H11A	0.0478	0.7645	−0.1119	0.101*
H11B	−0.0096	0.7820	−0.0909	0.101*
O11	−0.15950(10)	0.3275(4)	0.16466(13)	0.0773(8)
C12	0.0135(3)	0.9648(6)	−0.1470(2)	0.122(2)
H12A	0.0022	0.9146	−0.1856	0.183*
H12B	−0.0122	1.0388	−0.1331	0.183*
H12C	0.0451	1.0214	−0.1541	0.183*
O12	−0.20531(9)	0.3268(3)	0.25178(11)	0.0579(6)
H12	−0.2299(12)	0.353(5)	0.2252(17)	0.087*
C13	−0.20440(14)	1.0742(4)	0.72163(15)	0.0531(8)
H13A	−0.1750	1.0065	0.7130	0.064*
H13B	−0.2327	1.0046	0.7330	0.064*
C14	−0.21912(16)	1.1622(4)	0.66153(16)	0.0618(10)
H14A	−0.2514	1.2182	0.6673	0.074*
H14B	−0.1929	1.2410	0.6519	0.074*
C15	−0.2245(2)	1.0455(5)	0.60743(19)	0.0838(12)
H15A	−0.2338	1.1024	0.5695	0.126*
H15B	−0.1924	0.9912	0.6015	0.126*
H15C	−0.2507	0.9684	0.6169	0.126*
C16	−0.23471(14)	1.2950(4)	0.79196(17)	0.0522(9)
H16A	−0.2246	1.3599	0.8281	0.063*
H16B	−0.2388	1.3665	0.7561	0.063*
C17	−0.28614(15)	1.2209(5)	0.8053(2)	0.0705(11)
H17A	−0.2832	1.1515	0.8420	0.085*
H17B	−0.2972	1.1562	0.7695	0.085*
C18	−0.32542(18)	1.3491(6)	0.8174(2)	0.0919(14)
H18A	−0.3580	1.3003	0.8259	0.138*
H18B	−0.3147	1.4121	0.8532	0.138*
H18C	−0.3286	1.4168	0.7808	0.138*
C19	−0.18125(16)	1.0690(4)	0.83360(16)	0.0586(9)
H19A	−0.2121	1.0064	0.8404	0.070*
H19B	−0.1542	0.9948	0.8222	0.070*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
C20	−0.1660(2)	1.1481(5)	0.89538(19)	0.0788(12)
H20A	−0.1348	1.2098	0.8896	0.095*
H20B	−0.1930	1.2212	0.9080	0.095*
C21	−0.1572(2)	1.0264(6)	0.9462(2)	0.1031(16)
H21A	−0.1476	1.0795	0.9849	0.155*
H21B	−0.1883	0.9664	0.9523	0.155*
H21C	−0.1302	0.9550	0.9340	0.155*
C22	−0.14388(14)	1.2812(4)	0.76450(18)	0.0553(9)
H22A	−0.1519	1.3493	0.7285	0.066*
H22B	−0.1376	1.3507	0.8006	0.066*
C23	−0.09506(16)	1.1932(6)	0.7510(3)	0.0903(14)
H23A	−0.1006	1.1208	0.7157	0.108*
H23B	−0.0850	1.1298	0.7877	0.108*
C24	−0.05293(18)	1.3086(7)	0.7357(2)	0.0986(15)
H24A	−0.0219	1.2503	0.7272	0.148*
H24B	−0.0627	1.3702	0.6991	0.148*
H24C	−0.0471	1.3791	0.7710	0.148*
C25	0.22351(14)	−0.0254(4)	0.12147(16)	0.0519(8)
C26	0.10875(18)	0.3516(5)	−0.14343(19)	0.0690(11)
C27	−0.02480(17)	0.3602(5)	−0.05995(19)	0.0620(10)
C28	−0.16055(15)	0.3076(4)	0.22337(18)	0.0542(9)
C29	0.24250(16)	0.1467(4)	−0.06488(18)	0.0574(9)
C30	−0.02670(14)	0.7160(4)	−0.37248(18)	0.0544(9)

that bicarbonate should be derived from carbon dioxide during the stirring process.

Experimental details

Hydrogen atoms bound to carbon and nitrogen atoms are introduced by a riding model. The coordinates of the hydrogen atoms at water molecules are refined freely. U_{iso} parameters are fixed for all hydrogen atoms.

Comment

A guanidinium cation is a perfect triangular potentially hydrogen-bonded motif due to its planar configuration and multiple $-NH_2$ groups. Obviously, if another hydrogen-bond acceptor can be provided to cooperate with guanidine/guanidinium, it can generate interesting hydrogen bonding schemes. The bicarbonate is clearly a good choice to interact with guanidine/guanidinium, because it can be regarded as excellent hydrogen bond donor and acceptor. In the related crystal structures involving aromatic acids and tetraalkylammonium ions [4–7], it can be found these two ions were often used to construct hydrogen-bonded

frameworks, but the title compound and its structure has not been reported before.

In the asymmetric unit of the title compound, there are four independent bicarbonate ions, four water molecules, two guanidine ions and two tetrapropylammonium cations. Observing the structure, it can be found that each two bicarbonate ions firstly connect with each other to form the dimer by the intermolecular $O-H \cdots O$ interactions, then the dimers link with two guanidine ions and four water molecules to yield the three-dimensional framework with cavities by different $O-H \cdots O$ and $N-H \cdots O$ contacts. To obtain the stable crystal structure, those cavities are filled with tetrapropylammonium cations to form the close-packed structure. Apparently, although guanidine and bicarbonate are very simple molecules, they still can construct complicated hydrogen-bonded network with the suitable conditions. Bond lengths and angles in the ions are all in the expected ranges [8].

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References

- Sheldrick, G. M.: SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
- Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112–122.
- Bruker. APEX2 and SAINT. Bruker AXS Inc., Madison, WI, USA (2007).
- Mak, T. C.; Xue, F.: Supramolecular rosette ribbon constructed from guanidinium and hydrogen carbonate ions in the crystal engineering of hydrogen-bonded networks. *J. Am. Chem. Soc.* **122** (2000) 9860–9861.
- Han, J.; Yau, C. W.; Chan, C. W.; Mak, T. C.: Anionic host layers constructed with guanidinium–hydrogen carbonate dimer 2:1 rosette-ribbons and bridging carboxylate connectors. *Cryst. Growth Des.* **12** (2012) 4457–4465.
- Han, J.; Yau, C. W.; Lam, C. K.; Mak, T. C.: Designed supramolecular assembly of hydrogen-bonded anionic rosette layers. *J. Am. Chem. Soc.* **130** (2008) 10315–10326.
- Lam, C. K.; Xue, F.; Zhang, J. P.; Chen, X. M.; Mak, T. C.: Hydrogen-bonded anionic rosette networks assembled with guanidinium and C_3 -symmetric oxoanion building blocks. *J. Am. Chem. Soc.* **127** (2005) 11536–11537.
- Li, X.; Zhu, L.: Crystal structure of guanidinium tetraethylammonium carbonate dihydrate, $C_{10}H_{30}N_4O_5$. *Z. Kristallogr. NCS* **232** (2017) 939–940.