

Hydrogen bonding in the perhydrate and hydrates of 1,4-diazabicyclo[2.2.2]octane (DABCO) †

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The crystal structures of the bis(perhydrate), the monohydrate, and the hexahydrate of 1,4-diazabicyclo[2.2.2]octane (DABCO) were determined by single-crystal X-ray diffraction to investigate the hydrogen bonding architectures. The bis(perhydrate) revealed helical chains of hydrogen peroxide molecules forming a 3-D network by interaction with the diamine. In the monohydrate, water and diamine molecules are alternately linked. In the hexahydrate, cyclic water aggregates create cavities which are occupied by DABCO molecules doubly hydrogen-bonded to the water framework of the cage.

Introduction

1,4-Diazabicyclo[2.2.2]octane (DABCO, triethylenediamine) is widely used as a catalyst¹ and complexing ligand. Numerous crystal structures of salts² and addition compounds of DABCO, such as adducts with trimethyl aluminium,³ boron trifluoride and boranes,⁴ and coordination polymers with metal ions have been published.⁵ Charge-transfer interactions of DABCO with bromine⁶ and carbon tetrabromide⁷ resulting in crystalline complexes have also been reported. The supramolecular self-assembly of zinc porphyrins was found to be induced by coordination with DABCO.⁸ Furthermore, cocrystallization phenomena of DABCO with phenols⁹ have successfully been employed for the separation of phenolic natural products by molecular recognition.¹⁰ Finally, the well-known hydrogen peroxide adduct¹¹ of DABCO is of special interest as a source of anhydrous hydrogen peroxide. Although there has been a report about its instability,¹² it is nonetheless a valuable reagent for synthetic applications. It is, of course, fascinating to compare the structure of crystalline hydrogen peroxide¹³ and, notably, hydrogen peroxide dihydrate¹⁴ with those of other perhydrates, for example, the closely related molecular complex of DABCO *N,N'*-dioxide with hydrogen peroxide and water.¹⁵ There are some other perhydrate structures known, *e.g.* with urea,¹⁶ adenine,¹⁷ triphenylphosphine oxide,¹⁸ hexamethylenetetramine *N*-oxide,¹⁹ and simple salts.^{20,21} In general, the H₂O₂ molecule adopts a skew conformation in these compounds, but a planar conformation²¹ has also been observed. Moreover, the DABCO/H₂O system has been investigated, with the phase diagram indicating the occurrence of two hydrates.²² Whereas structures

of DABCO itself have been reported,²³ to this date no crystal structures of the known monohydrate²⁴ and hexahydrate²⁵ have been published. The structures of these hydrates are of particular interest, since morphologies of water clusters²⁶ with amines are the subject of scrutiny in biology and are of fundamental importance in life sciences. A considerable number of unusual water aggregates has been documented in the literature.²⁷ DABCO is certainly a structure-directing agent,²⁸ but lattice architectures of addition compounds are not determined by only a single component. Inherently, hydrogen bonding interactions between H₂O, H₂O₂, the tertiary diamine, and among (H₂O)_n assemblies must be considered to play a significant role. The strategy behind crystal engineering involves the understanding of these interactions and then employing this knowledge for the design of new solids. Here we report the new crystal structures of and hydrogen bonding in the bis(perhydrate), the monohydrate, and the hexahydrate of DABCO in an effort to elucidate combinations of compounds which by themselves form highly interesting structures, *i.e.* DABCO, H₂O₂, and H₂O.

Experimental

DABCO bis(perhydrate) (**1**). Hydrogen peroxide (35%, 1 ml) was added dropwise to a stirred solution of DABCO (0.56 g, 5 mmol) in anhydrous THF (7.5 ml) at 5 °C. After 15 min, the precipitate was collected by centrifugation, washed with cold THF (2 × 1.5 ml) and briefly dried *in vacuo*. IR (neat): 3090, 2969, 2944, 2879, 2742, 1455, 1352, 1317, 1057, 997, 916, 833, 777 cm⁻¹. Thermomicroscopy revealed a phase transition at 70 °C and the onset of decomposition at 130 °C, differential scanning calorimetry showed an exothermic peak at 140 °C. For single crystals, a test tube was charged with hydrogen peroxide (30%, 1 ml) which was frozen in liquid nitrogen. A layer of THF (3 ml) was added and frozen. Finally, a solution of DABCO (280 mg, 2.5 mmol) in THF (2 ml) was added on top and again frozen. This concoction was allowed to thaw in the refrigerator to 5 °C, and crystals were harvested after 48 h. Compared with the single crystals, the bulk material contained considerable impurities as demonstrated by XRPD (Fig. S1).† The monohydrate is the most likely major contamination.

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† Electronic supplementary information (ESI) available: Crystallographic information files for **1–3**, X-ray powder diffraction patterns, additional views and details of the water framework of **3**. CCDC reference numbers 634612–634614. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b807303a

Table 1 Crystal data and refinement details of compounds 1–3

Compound	1	2	3
Empirical formula	C ₆ H ₁₂ N ₂ 1.7(H ₂ O) ₂ 0.3(H ₂ O)	2(C ₆ H ₁₂ N ₂) 2(H ₂ O)	C ₆ H ₁₂ N ₂ 6(H ₂ O)
Formula weight	176.20	260.38	220.27
Crystal system	Tetragonal	Monoclinic	Triclinic
Space group	I4 ₁ /a	C2/c	P-1
a/Å	12.0860(17)	21.822(4)	12.5426(10)
b/Å	12.0860(17)	6.2155(16)	12.6014(9)
c/Å	12.0361(19)	10.7703(18)	17.2689(13)
α/°			99.590(6)
β/°		100.225(13)	108.320(6)
γ/°			99.448(6)
V/Å ³	1758.1(4)	1437.6(5)	2485.6(4)
T/K	173(2)	173(2)	173(2)
Z	8	4	8
D _x /g cm ⁻³	1.33	1.20	1.18
μ/mm ⁻¹	0.11	0.08	0.10
F ₀₀₀	768	576	976
Crystal size/mm	0.31 × 0.16 × 0.16	0.24 × 0.24 × 0.20	0.24 × 0.22 × 0.14
θ range for data collection	2.38–26.95	1.90–24.75	1.28–22.75
Index ranges	−15 < h < 15, −15 < k < 15, −15 < l < 14	−25 < h < 25, −7 < k < 7, −12 < l < 12	−13 < h < 13, −13 < k < 13, −18 < l < 18
Reflections collected	6709	4063	16189
Independent reflections	948 (R _{int} = 0.042)	1209 (R _{int} = 0.042)	4779 (R _{int} = 0.052)
Reflections with I > 2σ(I)	789	936	3680
Data/restraints/parameters	948, 0, 66	1209, 0, 109	4779, 8, 591
Goodness-of-fit on F ²	1.084	1.088	1.038
Final R indices [I > 2σ(I)]	R ₁ = 0.0563, wR ₂ = 0.1378	R ₁ = 0.0599, wR ₂ = 0.1293	R ₁ = 0.0519, wR ₂ = 0.1201
R indices (all data)	R ₁ = 0.0739, wR ₂ = 0.1534	R ₁ = 0.0819, wR ₂ = 0.1380	R ₁ = 0.0718, wR ₂ = 0.1302
Δρ _{max} , Δρ _{min} /e Å ⁻³	0.20, −0.15	0.15, −0.13	0.17, −0.18

DABCO monohydrate (**2**). Deionized water (90 μl, 5 mmol) was added to a stirred solution of DABCO (0.56 g, 5 mmol) in anhydrous THF (5 ml) at room temperature. The solution was refrigerated (5 °C) for 20 h, the crystals were collected by centrifugation, washed (2 ml cold THF), and briefly dried *in vacuo*. Mp 107–108 °C. IR (neat): 3388, 3226, 2963, 2938, 2872, 1681, 1455, 1315, 1057, 992, 906, 835, 770, 749 cm⁻¹.

DABCO hexahydrate (**3**). Deionized water (540 μl, 30 mmol) was added to a stirred solution of DABCO (0.56 g, 5 mmol) in anhydrous THF (8 ml) at 28 °C. The solution was refrigerated (5 °C) for 20 h, the crystals were collected by centrifugation, washed (5 ml cold THF), and briefly dried *in vacuo*. Recrystallization of the product (230 mg) by dissolving it in THF (1.5 ml) at 30 °C and cooling to 18 °C yielded large needles. Mp 32–33 °C. IR (neat): 3230, 2963, 2938, 2872, 1679, 1455, 1315, 1057, 992, 905, 835, 771, 748, 595 cm⁻¹.

Crystal structure determination

Colorless crystals of **1**, **2**, and **3** were covered in inert oil, mounted in plastic cryoloops (Litholoops, Molecular Dimensions) and subsequently cooled in a 173 K nitrogen stream generated by a 700 Series Oxford Cryostream. X-Ray intensity data were collected on a Stoe IPDS-2 imaging plate diffractometer equipped with a graphite monochromator (Mo Kα radiation, λ = 0.71073 Å). Intensities were measured by the rotation method (90 ω-scans at a fixed φ-angle of 0°). Data reduction including intensity integration, background corrections as well as Lorentz and polarization correction was performed with the Stoe X-AREA package.²⁹ The structures were solved by direct methods using the SIR2002 program suite.³⁰ All non-hydrogen

atoms of the molecule were obtained from an *E*-map. Full-matrix least-squares refinement on *F*² was carried out using the SHELXL97³¹ software. All hydrogen atoms (except those of water molecules) were geometrically fixed and allowed to ride on the corresponding carrier atoms with C–H = 0.98–0.99 Å and *U*_{iso}(H) = 1.2 *U*_{eq}(C) of the attached C atom, and hydrogen atoms on water molecules were located in a difference Fourier map and refined isotropically subject to O–H restraints of 0.85(2) Å and additional H···H restraints of 1.35(2) Å by using the DFIX command in SHELX97. Crystallographic data and

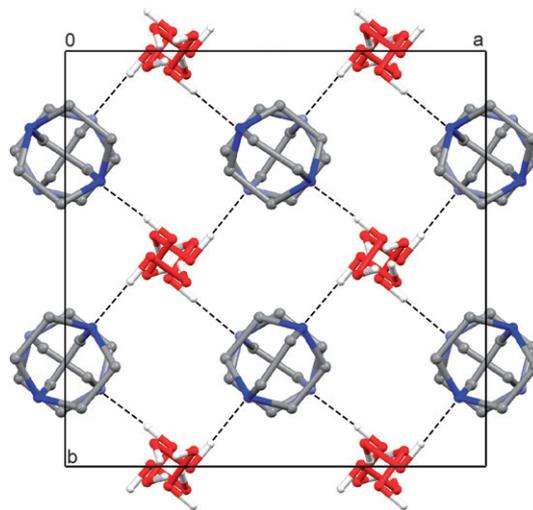


Fig. 1 Crystal packing of DABCO bis(perhydrate) **1** viewed along the *c*-axis. Hydrogens on carbon atoms omitted, and substitutional disorder not shown for clarity.

structure refinement details are given in Table 1. Some special details are worth mentioning. Although the initial model of the perhydrate **1** seemed to be a reasonable starting point, the least-squares calculations based on F^2 using anisotropic displacement parameters converged to an unconvincing unweighted R_1 index of about 0.18. Therefore, a possible twinning by merohedry was considered to explain the difficulties during the refinement. Assuming the mirror plane $m_{[1-10]}$ as the element of twinning, the TWIN3.0 software³² clearly indicated the presence of twinning by merohedry and provided an estimation of the volume fractions of the two domains (3 : 7). After the introduction of this twin model into the refinement calculations, the value of R_1 immediately dropped to 0.057. It was also found that the oxygen positions were not fully occupied. Careful refinement led to a H_2O_2 occupancy of 0.85 and a 0.15 probability of the presence of water molecules on H_2O_2 sites. Hydrogen atoms of the H_2O molecule were not located.

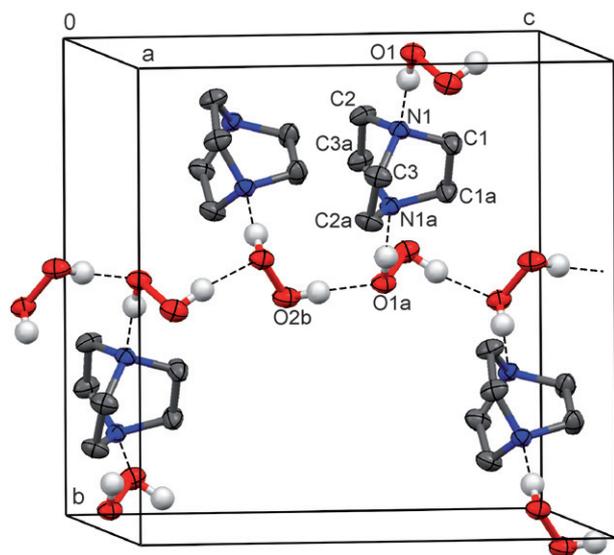


Fig. 2 Part of the crystal structure of DABCO bis(perhydrate) **1** showing one hydrogen peroxide chain formed by hydrogen bonds in the direction of the c -axis. Hydrogens on carbon atoms omitted. Symmetry code used to generate equivalent atoms: (a) $1 - x, 1/2 - y, z$; (b) $1/4 - y, -1/4 + x, -1/4 + z$.

A first indexing of the diffraction data of the hexahydrate **3** indicated an unrealistically large monoclinic C -centered unit cell of about $19\,900 \text{ \AA}^3$. However, a more detailed investigation based on precession-type reconstructions of reciprocal space clearly showed that the diffraction pattern could be interpreted as a superposition of two identical triclinic lattices in different orientations. The diffraction data of the two domains were integrated simultaneously including an overlap check (approximately 16% of the reflections were overlapping). The final choice of the one domain used for structure determination was based on the average $I/\sigma(I)$ ratio. For the refinement, only the completely non-overlapping, well resolved reflections of the larger domain have been considered. The hydrogen atoms in **3** are not well ordered due to two H_2O molecules (O10 and O18) which are each connected to symmetry-related molecules by inversion centres. This necessary disorder affects the whole hydrogen bonding network. Thus, each H_2O molecule has up to four hydrogen positions with occupancies between 0.25 and 1. Therefore, only hydrogen atoms bonding to the DABCO nitrogen atoms were refined, and the others were omitted from the model.

The crystallographic data of compounds **1–3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 634612 (**1**), 634613 (**2**), and 634614 (**3**).

Results and discussion

DABCO bis(perhydrate)

Several methods of preparation of compound **1** are known,¹¹ but single crystals for X-ray diffraction could not be obtained by literature procedures. However, a suitable crystal was grown by the diffusion method, as described in the Experimental section. A highly symmetric cell was observed containing half a DABCO molecule in the asymmetric unit, the other half was generated by a twofold axis (symmetry equivalent: $1 - x, 1/2 - y, z$). The molecules are located in rows on the $\bar{4}$ -axes of space group $I4_1/a$, *i.e.* the orientation of adjacent molecules is coupled by rotoinversions (Fig. 1). The axis of a single DABCO molecule is coincident with a line through the center of the C2–C2a–C3–C3a plane and the midpoint of the C1–C1a vector. It adopts a slightly twisted conformation (N1–C1–C1a–N1a torsion angle $6.2(4)^\circ$, N1–C2–C3a–N1a torsion angle $6.7(4)^\circ$). Thus, the symmetry of the DABCO molecules conforms to point group $2 (= C_2)$. The H_2O_2 molecule exhibits a skew geometry with a torsion angle of

Table 2 Hydrogen bonding parameters of compounds **1–3**. Distances in \AA and angles in $^\circ$

Compound	Interaction	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$	Symmetry code for A
1	O1–H \cdots N1	0.91	1.75	2.659(3)	179	
	O2–H \cdots O1	0.91	1.73	2.632(4)	171	$3/4 - y, -3/4 + x, 1/4 + z$
2	O1–H \cdots N1	0.86	2.09	2.949(6)	176	
	O1–H \cdots N2	0.86	2.11	2.973(7)	178	$1 - x, 1 - y, 1 - z$
3	O1–H \cdots N1	0.86	1.86	2.719(4)	178	
	O2–H \cdots N2	0.88	1.86	2.735(3)	176	
	O4–H \cdots N3	0.87	1.85	2.708(3)	170	
	O12–H \cdots N4	0.85	1.86	2.714(4)	176	
	O6–H \cdots N11	0.87	1.86	2.719(4)	175	$1 - x, -y, -z$
	O7–H \cdots N22	0.89	1.84	2.729(3)	180	$1 - x, 1 - y, -z$
	O17–H \cdots N33	0.87	1.86	2.723(3)	171	$1 + x, y, 1 + z$
	O16–H \cdots N44	0.87	1.85	2.710(4)	176	$1 - x, 2 - y, 1 - z$

110°. The O1–O2 bond length is 1.443(4) Å, in agreement with previously reported values.³³ The substitutional disorder of H₂O₂ and H₂O molecules is a result of the unstable nature of this compound, as also observed in ammonium oxalate perhydrate.³³ The hydrogen peroxide molecules interact with the diamine and with each other, forming a three-dimensional framework. Thus, each O1 donates one hydrogen bond to the amine nitrogen and accepts one from O2 of another H₂O₂ molecule to form a helix in the direction of the crystallographic *c*-axis (Fig. 2). The geometrical parameters of the hydrogen bonds are summarized in Table 2.

Remarkably, it was observed that the temperature during the crystallization process affected the purity of the bulk precipitate. Thus, a purer product was obtained at +5 °C than at –5 °C, as

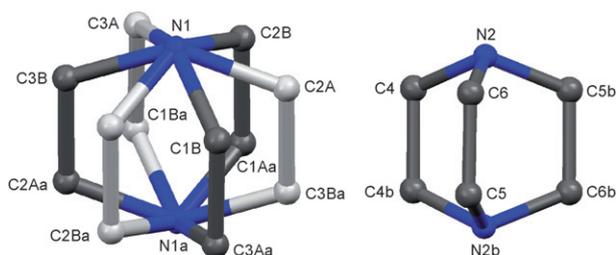


Fig. 3 Disordered and ordered DABCO molecules in the monohydrate **2**. Symmetry code: (a) $1/2 - x, 1/2 - y, 1 - z$; (b) $1 - x, y, 1/2 - z$.

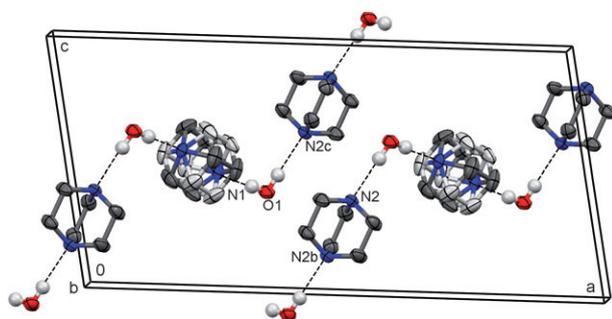


Fig. 4 Hydrogen bonding in DABCO monohydrate **2**. Hydrogens on carbon atoms are omitted. Symmetry transformations used to generate equivalent atoms: (b) $1 - x, y, 1/2 - z$; (c) $1 - x, 1 - y, 1 - z$.

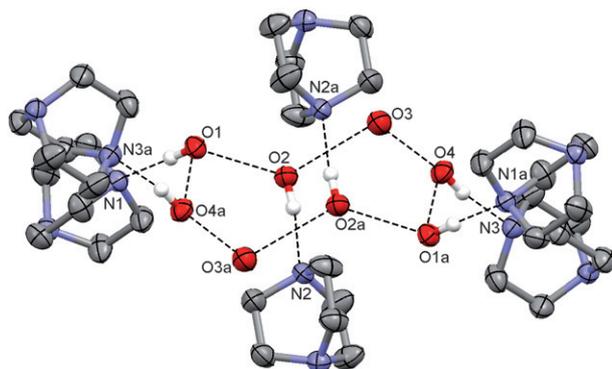


Fig. 5 View of the centrosymmetric water ring in **3** to which six DABCO molecules are coordinated. Symmetry code: (a) $1 - x, 1 - y, -z$.

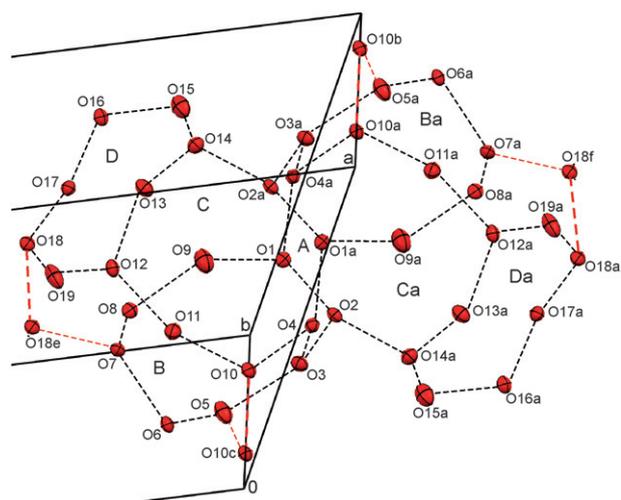


Fig. 6 Cyclic water octamer network present in the hexahydrate **3**, showing the rings B, C, D adjacent to the centrosymmetric ring A. The O10...O10' and O18...O18' linkages completing a 10-membered ring are shown in red. Symmetry code: (a) $1 - x, 1 - y, -z$; (b) $1 + x, y, z$; (c) $-x, 1 - y, -z$; (e) $1 - x, 1 - y, 1 - z$; (f) $x, y, -1 + z$.

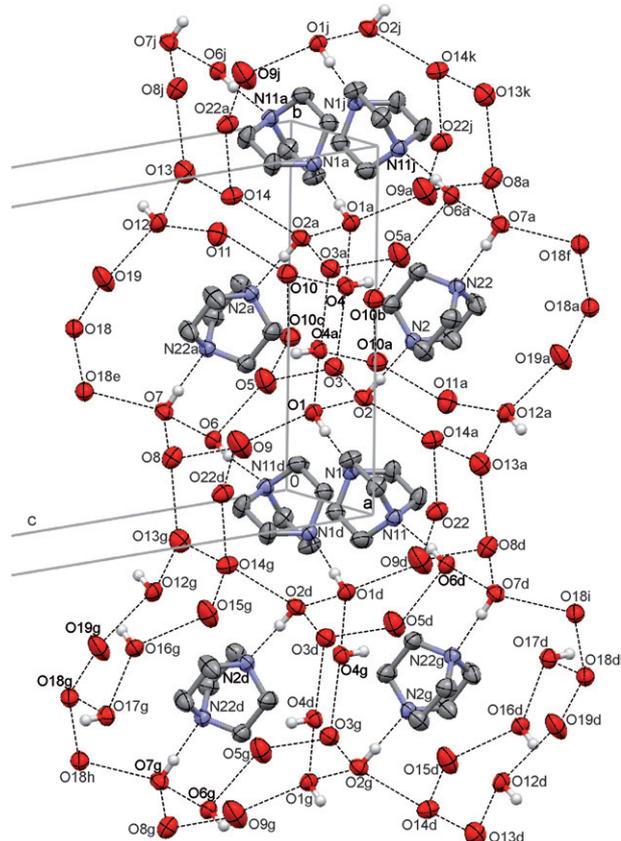


Fig. 7 Columns of DABCO units **1** and **2** in the direction of the *b*-axis surrounded by the water network in **3**. Symmetry code: (a) $1 - x, 1 - y, -z$; (b) $1 + x, y, z$; (c) $-x, 1 - y, -z$; (d) $1 - x, -y, -z$; (e) $1 - x, 1 - y, 1 - z$; (f) $x, y, -1 + z$; (g) $x, -1 + y, z$; (h) $1 - x, -y, 1 - z$; (i) $x, -1 + y, -1 + z$; (j) $x, 1 + y, z$; (k) $1 - x, 2 - y, -z$.

judged by XRPD (Fig. S1).† Impurities most likely include the monohydrate.

DABCO monohydrate

The monohydrate of DABCO is readily obtained by combining the appropriate amounts of the diamine and water in THF. The principal architecture of the structure is not unexpected. The water and diamine molecules are alternately linked by hydrogen bonds. However, every other DABCO molecule is disordered with a 1 : 1 occupancy. The symmetry of the two DABCO entities present in the unit cell is shown in Fig. 3. The ordered molecules reside on crystallographic twofold rotation axes of space group $C2/c$ running parallel to the crystallographic b -axis. Again, the axis of a single molecule is coincident with a line through the center of the C5–C5b–C6–C6b plane and the midpoint of the C4–C4b vector. The symmetry of the molecule is, therefore, C_2 . However, it deviates only slightly from the ideal D_{3h} geometry, since the respective torsion angles are only $1.2(4)$ and $0.6(4)^\circ$. The components of the disordered DABCO molecule were generated by inversion. Compared to DABCO itself, there is no close packing in the structure of the hydrate **2**. The hydrogen bonding parameters are shown in Table 2. The $N1\cdots O1\cdots N2$ angle is $102.4(5)^\circ$. The hydrogen bonding pattern is depicted in Fig. 4.

DABCO hexahydrate

The hexahydrate of DABCO is easily prepared by mixing the appropriate amounts of the components in THF, and large needles are obtained by cooling the solution.

The asymmetric unit contains four DABCO and 24 water molecules. Close inspection of the structure revealed an intricate network of H-bonded water molecules. Eight water molecules are 3-coordinate (O5, 9, 11, 13, 15, 19, 21, and 23), and eight are 4-coordinate (O3, 8, 10, 14, 18, 20, 22, and 24) bonded to other water molecules. Each of the remaining eight water molecules (O1, 2, 4, 6, 7, 12, 16, and 17) coordinates to three other water molecules and a DABCO molecule. Discrete 5-, 6-, 8- and 10-membered water rings create cavities which are occupied by DABCO molecules doubly hydrogen-bonded to the water framework of the cage, with $N\cdots O$ distances ranging from 2.71 to 2.74 Å. The hydrogen bonding parameters are shown in Table 2. Remarkably, the water molecules form a centrosymmetric cyclic $(H_2O)_8$ cluster (ring A), to which six DABCO molecules are coordinated (Fig. 5) and around which the other cyclic water assemblies (8-membered rings B, C, D, Ba, Ca, and Da) are grouped (Fig. 6). A cyclic water decamer is formed by bridging the rings B, C, and D through $O10\cdots O10'$ and $O18\cdots O18'$ linkages (Fig. 6). Although not all hydrogen atoms were located, the existence of the hydrogen-bonded water aggregates

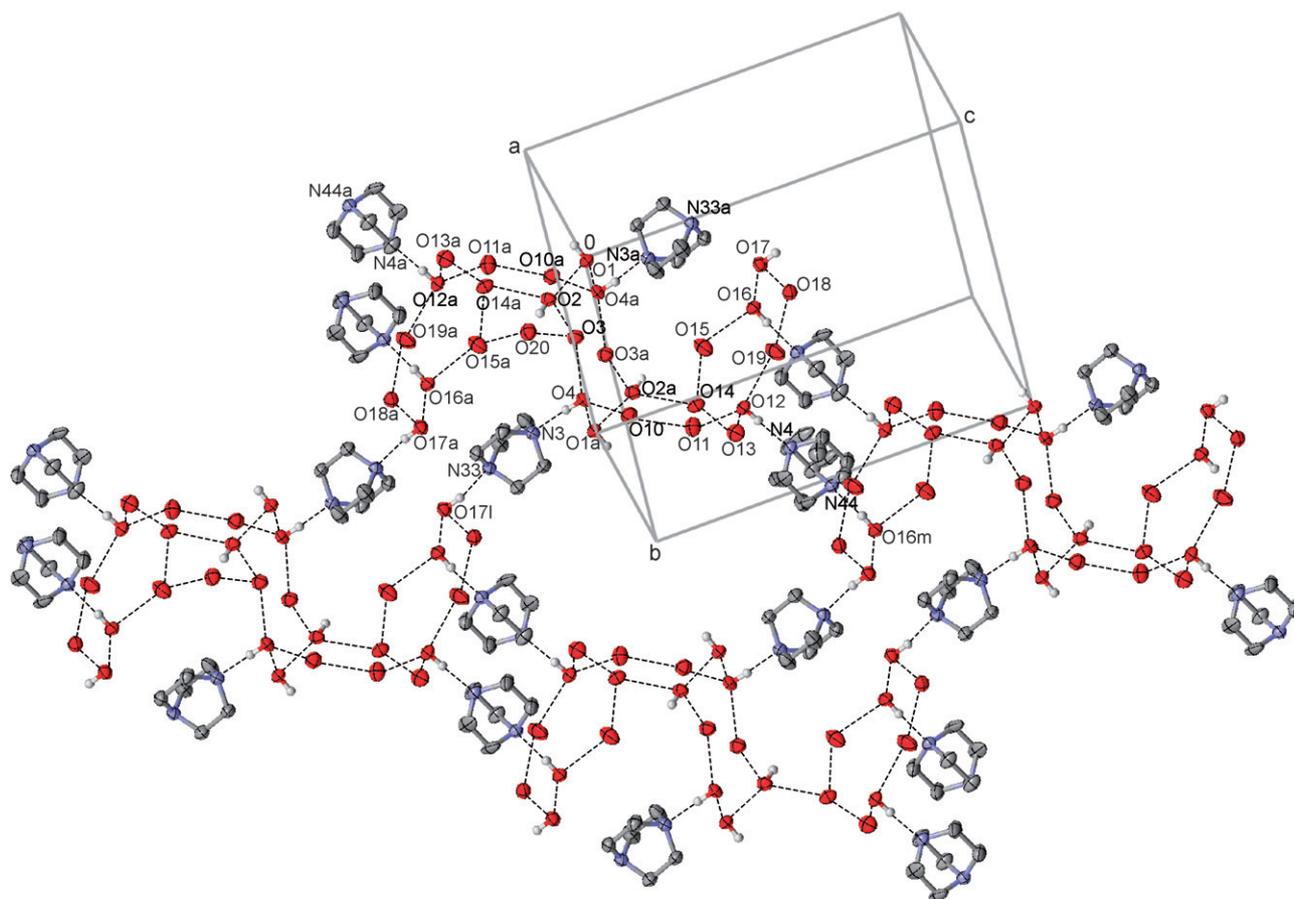


Fig. 8 Layer of DABCO units 3 and 4 connected by a water network in **3**. Disorder of DABCO unit 4 omitted for clarity. Symmetry code: (a) $1 - x, 1 - y, -z$; (l) $-1 + x, y, -1 + z$; (m) $1 - x, 2 - y, 1 - z$.

is based on the short O...O distances (shorter than the sum of van der Waals radii of 3.04 Å). The O...O distances and O...O...O angles in the water octamers are within the ranges 2.71–2.86 Å and 84–146°, respectively. The average O...O distance is 2.79 Å, and the average O...O...O angle is 114°. The clusters are linked through O10...O10' and O18...O18' inversions, whereupon the structural unit is repeated to produce the supramolecular array. Geometry details of the water aggregates are given in the ESI.† The symmetry of the DABCO molecules is almost D_{3h} . The DABCO units 1 and 2 (containing atoms N1 and N2) form columns in the direction of the *b*-axis (Fig. 7). The arrangement of the DABCO units 3 and 4 (containing atoms N3 and N4) is best rationalized as layers parallel to the (111) plane (Fig. 8). One of the DABCO molecules (N4) is orientationally disordered with occupancies of 0.50 : 0.50. The observed XRPD of the bulk material **3** was in satisfactory agreement with the pattern calculated from single crystal data (Fig. S2).†

It must be noted that polyhedral clathrate hydrates of amines, such as *tert*-butylamine,^{34,35} diethylamine,^{35,36} hexamethylenetetramine,³⁷ have been reported earlier. Other cyclic (H₂O)₈ clusters have been described recently in a copper complex³⁸ and a calixarene.³⁹ A different cyclic water decamer has been previously published.⁴⁰ Hydrogen-bonded water networks have been observed in cocrystals of DABCO with 5-nitrouracil⁴¹ and in a β-cyclodextrin inclusion complex with DABCO,⁴² but they do not contain the motifs reported here.

In summary, we have characterized the bis(perhydrate) **1** and two hydrates of the bicyclic tertiary diamine DABCO. We have found chains of hydrogen peroxide molecules in compound **1**, alternately linked water and diamine molecules in the monohydrate **2**, and an unprecedented polyhedral water cluster in the hexahydrate **3**, reminiscent of clathrate hydrate structures. Correct prediction of crystal structures is still in its infancy, as a quite interesting experiment has recently demonstrated.⁴³ As a matter of fact, the structure of the monohydrate could be reasonably predicted whereas the architecture of the hexahydrate was quite unexpected.

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Supplementary information

Hydrogen Bonding in the Perhydrate and Hydrates of 1,4-Diazabicyclo[2.2.2]octane (DABCO)

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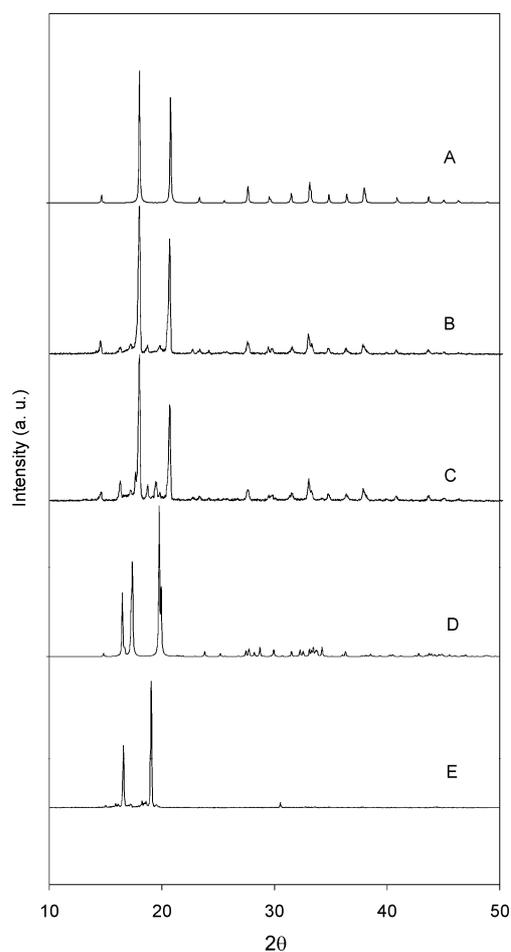


Fig. S1 The calculated XRPD pattern of DABCO bis(perhydrate) **1** (A) and observed (at 173 K) patterns of bulk **1** crystallized at +5°C (B), at -5°C (C), the monohydrate **2** (D), and sublimed DABCO (E).

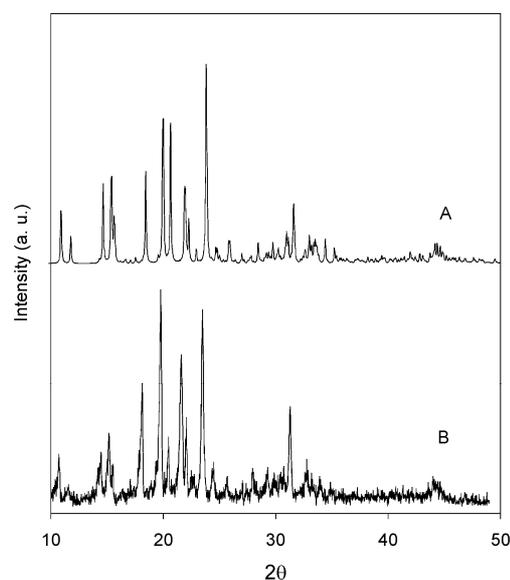


Fig. S2 The calculated (A) and observed (B) XRPD pattern of DABCO hexahydrate **3** at 173 K.

Table S1 Interatomic distances (Å) and angles (°)
 for the hexahydrate **3**

		O(14)-O(2)#1	2.788(12)
		O(14)-O(15)	2.829(10)
		O(15)-O(16)	2.713(6)
		O(15)-O(20)#1	2.822(7)
		O(16)-N(44)#8	2.710(4)
		O(16)-O(23)#9	2.783(4)
		O(16)-O(17)	2.815(3)
		O(17)-N(33)#10	2.723(3)
		O(17)-O(24)#3	2.796(6)
		O(17)-O(18)	2.804(11)
		O(18)-O(18)#5	2.77(2)
		O(18)-O(7)#5	2.779(11)
		O(18)-O(19)	2.815(10)
		O(19)-O(24)#11	2.819(6)
		O(20)-O(21)	2.774(6)
		O(20)-O(15)#1	2.822(7)
		O(20)-O(11)#2	2.824(7)
		O(21)-O(6)#4	2.780(4)
		O(21)-O(22)	2.823(12)
		O(22)-O(14)#1	2.73(2)
		O(22)-O(23)	2.751(12)
		O(22)-O(9)#3	2.788(12)
		O(23)-O(24)	2.740(6)
		O(23)-O(16)#12	2.783(4)
		O(24)-O(8)#3	2.722(12)
		O(24)-O(17)#3	2.796(6)
		O(24)-O(19)#13	2.819(6)
		N(11)-O(6)#3	2.719(4)
		N(22)-O(7)#1	2.729(3)
		N(33)-O(17)#14	2.723(3)
		N(44)-O(16)#8	2.710(4)
		N(1)-O(1)-O(9)	93.20(16)
		N(1)-O(1)-O(2)	103.48(11)
		O(9)-O(1)-O(2)	136.42(17)
		N(1)-O(1)-O(4)#1	102.31(11)
		O(9)-O(1)-O(4)#1	105.80(19)
		O(2)-O(1)-O(4)#1	109.35(11)
		N(2)-O(2)-O(1)	101.57(10)
O(1)-N(1)	2.719(4)		
O(1)-O(9)	2.724(7)		
O(1)-O(2)	2.786(3)		
O(1)-O(4)#1	2.823(3)		
O(2)-N(2)	2.735(3)		
O(2)-O(3)	2.787(6)		
O(2)-O(14)#1	2.788(12)		
O(3)-O(4)	2.784(5)		
O(3)-O(20)	2.795(13)		
O(3)-O(5)	2.821(7)		
O(4)-N(3)	2.708(3)		
O(4)-O(10)	2.813(11)		
O(4)-O(1)#1	2.823(3)		
O(5)-O(6)	2.720(7)		
O(5)-O(10)#2	2.808(11)		
O(6)-N(11)#3	2.719(4)		
O(6)-O(21)#4	2.780(4)		
O(6)-O(7)	2.809(3)		
O(7)-N(22)#1	2.729(3)		
O(7)-O(18)#5	2.779(11)		
O(7)-O(8)	2.793(6)		
O(8)-O(24)#3	2.722(12)		
O(8)-O(9)	2.789(7)		
O(8)-O(13)#6	2.865(6)		
O(9)-O(22)#3	2.788(12)		
O(10)-O(11)	2.766(12)		
O(10)-O(10)#2	2.77(2)		
O(10)-O(5)#2	2.808(11)		
O(11)-O(12)	2.805(4)		
O(11)-O(20)#2	2.824(7)		
O(12)-O(19)	2.713(7)		
O(12)-N(4)	2.714(4)		
O(12)-O(13)	2.779(4)		
O(13)-O(14)	2.754(11)		
O(13)-O(8)#7	2.865(6)		
O(14)-O(22)#1	2.73(2)		

N(2)-O(2)-O(3)	105.95(14)	O(1)-O(9)-O(8)	136.1(3)
O(1)-O(2)-O(3)	121.08(16)	O(22)#3-O(9)-O(8)	100.5(4)
N(2)-O(2)-O(14)#1	86.4(3)	O(11)-O(10)-O(10)#2	122.9(6)
O(1)-O(2)-O(14)#1	126.0(2)	O(11)-O(10)-O(5)#2	99.3(4)
O(3)-O(2)-O(14)#1	106.9(2)	O(10)#2-O(10)-O(5)#2	84.4(4)
O(4)-O(3)-O(2)	110.2(2)	O(11)-O(10)-O(4)	120.8(4)
O(4)-O(3)-O(20)	112.8(3)	O(10)#2-O(10)-O(4)	107.5(6)
O(2)-O(3)-O(20)	100.6(2)	O(5)#2-O(10)-O(4)	115.5(4)
O(4)-O(3)-O(5)	105.2(2)	O(10)-O(11)-O(12)	144.1(2)
O(2)-O(3)-O(5)	134.9(2)	O(10)-O(11)-O(20)#2	101.3(2)
O(20)-O(3)-O(5)	90.2(3)	O(12)-O(11)-O(20)#2	113.81(16)
N(3)-O(4)-O(3)	106.00(16)	O(19)-O(12)-N(4)	98.37(15)
N(3)-O(4)-O(10)	98.1(2)	O(19)-O(12)-O(13)	119.00(17)
O(3)-O(4)-O(10)	94.0(3)	N(4)-O(12)-O(13)	98.89(12)
N(3)-O(4)-O(1)#1	101.85(10)	O(19)-O(12)-O(11)	122.89(19)
O(3)-O(4)-O(1)#1	137.64(17)	N(4)-O(12)-O(11)	99.35(12)
O(10)-O(4)-O(1)#1	113.0(3)	O(13)-O(12)-O(11)	111.08(12)
O(6)-O(5)-O(10)#2	138.2(3)	O(14)-O(13)-O(12)	122.6(3)
O(6)-O(5)-O(3)	122.2(2)	O(14)-O(13)-O(8)#7	117.1(3)
O(10)#2-O(5)-O(3)	96.5(3)	O(12)-O(13)-O(8)#7	118.91(17)
N(11)#3-O(6)-O(5)	96.72(15)	O(22)#1-O(14)-O(13)	92.7(6)
N(11)#3-O(6)-O(21)#4	99.59(12)	O(22)#1-O(14)-O(2)#1	126.9(7)
O(5)-O(6)-O(21)#4	119.83(18)	O(13)-O(14)-O(2)#1	117.1(3)
N(11)#3-O(6)-O(7)	102.95(11)	O(22)#1-O(14)-O(15)	98.9(5)
O(5)-O(6)-O(7)	105.99(18)	O(13)-O(14)-O(15)	129.4(4)
O(21)#4-O(6)-O(7)	125.45(12)	O(2)#1-O(14)-O(15)	94.2(4)
N(22)#1-O(7)-O(18)#5	105.9(3)	O(16)-O(15)-O(20)#1	145.2(2)
N(22)#1-O(7)-O(8)	97.34(15)	O(16)-O(15)-O(14)	119.9(3)
O(18)#5-O(7)-O(8)	96.9(2)	O(20)#1-O(15)-O(14)	94.4(3)
N(22)#1-O(7)-O(6)	101.05(10)	N(44)#8-O(16)-O(15)	99.03(15)
O(18)#5-O(7)-O(6)	138.2(2)	N(44)#8-O(16)-O(23)#9	98.93(12)
O(8)-O(7)-O(6)	110.81(15)	O(15)-O(16)-O(23)#9	116.94(16)
O(24)#3-O(8)-O(9)	94.3(3)	N(44)#8-O(16)-O(17)	99.16(11)
O(24)#3-O(8)-O(7)	106.1(2)	O(15)-O(16)-O(17)	129.07(18)
O(9)-O(8)-O(7)	117.1(3)	O(23)#9-O(16)-O(17)	106.52(11)
O(24)#3-O(8)-O(13)#6	109.3(3)	N(33)#10-O(17)-O(24)#3	84.41(15)
O(9)-O(8)-O(13)#6	90.2(2)	N(33)#10-O(17)-O(18)	104.1(2)
O(7)-O(8)-O(13)#6	132.9(2)	O(24)#3-O(17)-O(18)	97.8(3)
O(1)-O(9)-O(22)#3	121.8(3)	N(33)#10-O(17)-O(16)	101.67(10)

O(24)#3-O(17)-O(16)	146.38(14)
O(18)-O(17)-O(16)	112.3(3)
O(18)#5-O(18)-O(7)#5	113.1(6)
O(18)#5-O(18)-O(17)	108.5(6)
O(7)#5-O(18)-O(17)	110.9(3)
O(18)#5-O(18)-O(19)	88.6(4)
O(7)#5-O(18)-O(19)	106.5(4)
O(17)-O(18)-O(19)	127.4(4)
O(12)-O(19)-O(18)	145.2(3)
O(12)-O(19)-O(24)#11	120.0(2)
O(18)-O(19)-O(24)#11	94.0(3)
O(21)-O(20)-O(3)	115.4(3)
O(21)-O(20)-O(15)#1	96.2(2)
O(3)-O(20)-O(15)#1	92.8(3)
O(21)-O(20)-O(11)#2	118.8(2)
O(3)-O(20)-O(11)#2	106.1(2)
O(15)#1-O(20)-O(11)#2	125.2(3)
O(20)-O(21)-O(6)#4	121.76(18)
O(20)-O(21)-O(22)	112.2(3)
O(6)#4-O(21)-O(22)	122.4(3)
O(14)#1-O(22)-O(23)	111.5(6)
O(14)#1-O(22)-O(9)#3	99.7(5)
O(23)-O(22)-O(9)#3	95.1(4)
O(14)#1-O(22)-O(21)	92.9(6)
O(23)-O(22)-O(21)	127.4(4)
O(9)#3-O(22)-O(21)	126.8(5)
O(24)-O(23)-O(22)	111.0(3)
O(24)-O(23)-O(16)#12	123.48(18)
O(22)-O(23)-O(16)#12	123.0(3)
O(8)#3-O(24)-O(23)	98.8(2)
O(8)#3-O(24)-O(17)#3	122.9(3)
O(23)-O(24)-O(17)#3	114.9(2)
O(8)#3-O(24)-O(19)#13	91.3(3)
O(23)-O(24)-O(19)#13	129.5(3)
O(17)#3-O(24)-O(19)#13	99.6(2)

Symmetry transformations used to generate
equivalent atoms:

#1 $-x+1,-y+1,-z$ #2 $-x,-y+1,-z$ #3 $-x+1,-y,-z$
#4 $-x,-y,-z$ #5 $-x+1,-y+1,-z+1$ #6 $x,y-1,z$
#7 $x,y+1,z$ #8 $-x+1,-y+2,-z+1$ #9 $x+1,y+1,z+1$
#10 $x+1,y,z+1$ #11 $x,y+1,z+1$ #12 $x-1,y-1,z-1$
#13 $x,y-1,z-1$ #14 $x-1,y,z-1$

The atom numbering is in accordance with
the CIF file CCDC 634614.