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A spiral-like chain from a hydrogen-bonded cyclic dichloride containing a water dimer in a quaternary diammonium dichloride trihydrate[#]

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Abstract. The reaction of benzyl chloride with tetramethylethylenediamine (tmen) results in the formation of the quaternary diammonium dichloride trihydrate (dbtmen)$Cl_2 \cdot 3H_2O$ **1** (dbtmen is N,N′-dibenzyl-N,N,N′,N′-tetramethylethylenediammonium) in good yields. **1** crystallises in the monoclinic $P2_1/c$ space group and its structure consists of N,N′-dibenzyl-N,N,N′,N′-tetramethylethylenediammonium dication, two chloride anions and three crystal water molecules all of which are located in general positions. The organic dication is H-bonded to the chloride anions and the crystal waters with the help of intra- and intermolecular C–H···Cl and C–H···O interactions, while the chloride anions are linked to the crystal waters via O–H···Cl interactions. One of the crystal waters is linked through an intermolecular O–H···O bond with another water resulting in the formation of a water dimer. The O–H···Cl and O–H···O interactions between the chloride anions and water molecules lead to the formation of a five-membered $\{O_3Cl_2\}$ cyclic dichloride containing a water dimer. The five-membered rings are linked into a chain with the aid of a O–H···Cl interaction. The organic cations are organised in zigzag fashion on either side of the chain and are further linked to the anionic water chain via weak C–H···O and C–H···Cl interactions, leading to the supramolecular organisation of the rings into a spiral-like of chain.

Keywords. N,N′-dibenzyl-N,N,N′,N′-tetramethylethylenediammonium; C–H···Cl, C–H···O, O–H···Cl and O–H···O interactions; cyclic dichloride; water dimer; spiral-like chain.

1. Introduction

Compounds containing organic cations and inorganic anions provide novel supramolecular networks with interesting structural features such as chirality in ethylenediammonium sulphate[1] or formation of a bilayer in 2-aminoanilinium perchlorate,[2] formation of sulphate anion helices in *o*-phenylenediammonium sulphate sesquihydrate[3] etc. The networks become quite interesting when the cation and anion can participate in H-bonding interactions. In crystalline hydrates, the supramolecular organisation of the cations, anions or the molecule itself, can lead to the formation of channels or cavities which can function as a host, trapping guest molecules especially water in the form of small hydrogen bonded clusters. The results of a systematic search of the Cambridge Crystallographic Database for organic crystals containing water molecules, which show the diversity of hydrogen-bonding interactions among water molecules,[4] have been recently published.[5,6] Studies on water clusters are of current research interest[7] as evidenced by the several recent theoretical[8–10] and experimental[11–27] investigations in this area. Small water clusters have been characterized spectroscopically[28–30] and clusters with $n = 2, 4, 6, 8, 10, 12, 16, 18$ and 45 have been observed crystallographically.[11–27] The simplest water cluster $(H_2O)_2$ has been crystallographically characterized in the cavity of a cryptand,[25] and also in metal–organic framework materials.[26,27] During the course of our investigations of compounds derived from organic ammonium

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[#] Dedicated to Prof. Sabyasachi Sarkar on the occasion of his 60th birthday

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cations containing inorganic anions like tetrathiomolybdate[31–33] and tetrathiotungstate[34–36] we have identified a supramolecular water dimer in the crystal structure of a quaternary diammonium dichloride trihydrate (dbtmen)$Cl_2\cdot 3H_2O$ **1** (dbtmen is N,N′-dibenzyl-N,N,N′,N′-tetramethylethylenediammonium) and these results are described in this paper.

2. Experimental

All the chemicals used in this study were of reagent grade and were used as received. Infrared spectra were recorded on a Shimadzu FT-IR spectrometer (IR Prestige-21) in the range 4000–400 cm^{-1}. The samples were prepared as KBr-diluted pellets in the solid state and the infrared signals referenced to polystyrene bands. Electronic spectra were recorded in water using matched quartz cells on a Shimadzu (UV-2450) spectrophotometer. Isothermal weight loss studies were carried out in a temperature controlled oven. TG-DTA studies were performed in Ar atmosphere in the temperature range 30° to 400°C on a Netzsch Simultaneous Thermal analyses apparatus. A heating rate of 10°C/min was chosen for the measurement.

2.1 *Preparation of (dbtmen)$Cl_2\cdot 3H_2O$* **1**

Benzyl chloride (2·5 ml) was slowly added in drops to a cooled solution of tetramethylethylenediamine (tmen) (1·5 ml) dissolved in CH_3CN (5 ml) with constant stirring. (**Caution!** Benzyl chloride is lachrymatory and hence the synthesis is to be performed in a well-ventilated fume cupboard.) The reaction is exothermic in nature and initially the reaction mixture appears turbid. When the addition of benzyl chloride was complete copious amounts of white solid separated out. The product was filtered and washed with ether and dried in air. Yield: 3·35 g (83%). Recrystallization of this product from water afforded crystalline blocks of **1** suitable for X-ray studies.

Analysis – Found (calc.) for $C_{20}H_{30}N_2Cl_2\cdot 3H_2O$, **1**: C 56·31 (56·72); H 8·31 (8·58); N 5·68 (6·61); Cl 15·91 (16·74)%.

IR data in cm^{-1}: 3429 (*s*), 3360 (*s*), 3234 (*m*), 3028 (*s*), 3011 (*s*), 2998 (*s*), 2962 (*w*), 1620 (*m*), 1477 (*s*), 1461 (*s*), 1414 (*m*), 1395 (*w*), 1216 (*m*), 1164 (*w*), 1082 (*w*), 1033 (*w*), 1002 (*m*), 975 (*m*), 927 (*m*), 885 (*s*), 781 (*s*), 725 (*s*), 705 (*s*), 628 (*s*), 538 (*m*), 499 (*w*).

2.2 *Single crystal X-ray diffractometry*

Intensity data for **1**, were collected on a Stoe Image Plate Diffraction System using graphite monochromated Mo-K_α radiation at 170 K. The intensities were corrected for Lorentz polarization effects. The structure was solved with direct methods using SHELXS-97[37] and refinement was done against F^2 using SHELXL-97.[37] All non-hydrogen atoms were refined using anisotropic displacement parameters. The C–H hydrogen atoms were positioned with idealized geometry and refined isotropically using a riding model. The positions of the O–H hydrogen atoms were located in the difference map, their bond lengths set to ideal values and were refined isotropic using a riding model with O–H = 0·86 Å. The O3 atom of one of the water molecules is disordered and was refined using a split model. The technical details of data acquisition and some selected crystal refinement results are summarized in table 1.

Table 1. Crystal data and structure refinement for N,N′-dibenzyl-N,N,N′,N′-tetramethylethylenediammonium dichloride trihydrate **1**.

Molecular formula	$C_{20}H_{36}Cl_2N_2O_3$
Formula weight	423·41
Temperature	170(2) K
Wavelength	0·71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 22·0744(15) Å b = 9·0525(7) Å c = 11·5433(7) Å β = 97·82(1)°
Volume	2285·2(3) $Å^3$
Z	4
Density (calculated)	1·231 Mg/m^3
Absorption coefficient	0·305 mm^{-1}
$F(000)$	912
Crystal size	0·5 × 0·4 × 0·4 mm^3
Theta range for data collection	2·44 to 26·92°
Index ranges	$-20 \le h \le 28$, $-11 \le k \le 11$, $-14 \le l \le 14$
Reflections collected	10799
Independent reflections	4782 [R(int) = 0·0458]
Completeness to theta = 26·92°	96·4%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4782/0/249
Goodness-of-fit on F^2	1·032
Final R indices [$I > 2\text{sigma}(I)$]	$R1$ = 0·0484, $wR2$ = 0·1388
R indices (all data)	$R1$ = 0·0620, $wR2$ = 0·1464
Largest diff. peak and hole	0·284 and –0·339 $eÅ^{-3}$

3. Results and discussion

The synthesis of the hydrated organic diammonium dichloride **1** was accomplished by reacting the organic diamine tmen with benzyl chloride in a 1 : 2 molar ratio in CH_3CN followed by recrystallization from water. This method is essentially similar to the one employed by us for the synthesis of the corresponding dibromide dihydrate.[38] It is interesting to note that, unlike the related unbenzylated dichloride $(tmenH_2)Cl_2$ ($tmenH_2$ is N,N,N′,N′-tetramethylethylenediammonium) which is anhydrous,[39] **1** crystallizes as a trihydrate. The compound analyzed satisfactorily for the proposed formula. The electronic spectrum of **1** exhibits a signal at ~263 nm which can be assigned to the charge transfer of the aromatic moiety. The proton magnetic resonance spectrum of **1** in (D_2O) exhibits four sharp singlets at δ 7·41 ppm (*s*, 10H), δ 4·49 ppm (*s*, 4H), δ 3·86 ppm (*s*, 4H), 3·02 (*s*, 12H), which can be assigned to the resonance absorptions of the aromatic, benzylic, methylene and methyl protons respectively. The observed chemical shifts are in the range observed for the corresponding dibromide dihydrate.[38] The IR spectrum of the hydrated dichloride exhibits intense signals for the O–H stretching vibrations bands at 3429, 3360 cm^{-1} and these values are about 35 cm^{-1} lower in energy as compared to the corresponding H-bonded dibromide dihydrate which absorbs at 3464 and 3394 cm^{-1}. The signal at 1616 cm^{-1} can be assigned for the O–H bending vibration in **1** and this value is very close to that (1620 cm^{-1}) observed in the dibromide. Several bands in the mid IR can be attributed to the vibrations of the organic cation.

The quaternary diammonium dichloride trihydrate **1** crystallizes monoclinic in the centrosymmetric space group $P2_1/c$ with all atoms located in general positions. The structure of **1** consists of $(dbtmen)^{2+}$ dication, two chloride anions and three crystal water molecules (figure 1). The bromide analogue of **1** namely $(dbtmen)Br_2{\cdot}2H_2O$ is a dihydrate and crystallizes in the triclinic $P\bar{1}$ space group.[38] It is interesting to note that the pair of unbenzylated dihalides of tmen viz. $(tmenH_2)X_2$ (X = Cl, Br) are anhydrous and $(tmenH_2)Cl_2$ crystallizes in the triclinic $P\bar{1}$ space group[39] while $(tmenH_2)Br_2$ crystallizes in the monoclinic $P2_1/c$ space group.[40] The observed C–C and C–N bond lengths as well as the bond angles of the organic cation in **1** (table 2) are in the normal range and are in good agreement with those observed for the corresponding dibromide dihydrate $(dbtmen)Br_2{\cdot}2H_2O$.[38] The unbenzylated $(tmenH_2)X_2$ (X = Cl, Br) compounds exhibit very strong N–H···X (X = Cl, Br) interactions between the organic cation and the anion. However, such interactions are not possible in **1** in view of the tetraalkylation of the N atoms.

An analysis of the crystal structure reveals that the organic cation, the chloride anions and the crystal waters are involved in four varieties of H-bonding interactions namely C–H···Cl, C–H···O, O–H···O and O–H···Cl (table 3). The chloride anions function as H-bond acceptors and the organic cation as H-bond donors while the crystal waters function as H-bond acceptors as well as donors. Both the Cl^- ions are H-bonded to the organic cation with the aid of several C–H···Cl interactions and to two of the crystal water molecules via O–H···Cl interactions (figure 2). The organic cation is further linked to the crystal water molecules via C–H···O bonds (figure 2). The O–H···O interaction between two of the crystal water molecules and the O–H···Cl bonds to the two chloride ions result in the formation of a five-membered cyclic dichloride $\{O_3Cl_2\}$ unit (only the O and Cl but not the H atoms are considered). The two crystal water molecules are linked to the two chloride ions via five short O–H···Cl hydrogen bonds ranging from 2·32 to 2·37 Å. These interactions can account for the observed lower energies of the O–H vibrations in the IR spectrum. The Cl···H distances are much shorter compared to 2·95 Å, the sum of their van der

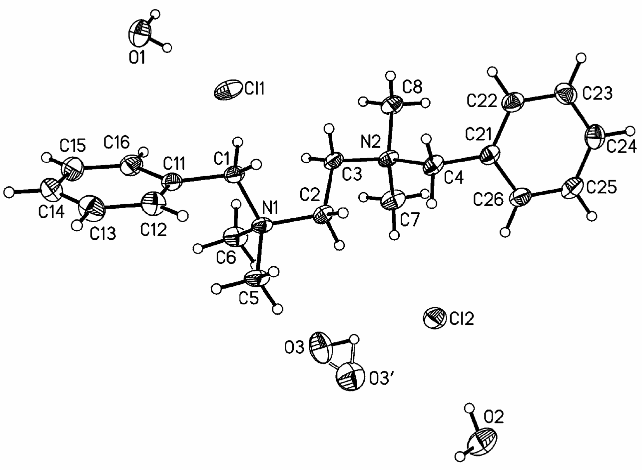

Figure 1. The asymmetric unit of $(dbtmen)Cl_2{\cdot}3H_2O$ **1** showing the atom-labelling scheme. The O3 atom is disordered. Displacement ellipsoids are drawn at the 50% probability level except for the H atoms, which are shown as spheres of arbitrary radius.

Table 2. Selected bond lengths [Å] and bond angles [°] for **1**.

Bond lengths			
N(1)–C(6)	1·503(2)	N(2)–C(3)	1·508(2)
N(1)–C(5)	1·508(2)	N(2)–C(4)	1·528(2)
N(1)–C(2)	1·509(2)	C(1)–C(11)	1·504(2)
N(1)–C(1)	1·527(2)	C(2)–C(3)	1·530(3)
N(2)–C(8)	1·505(2)	C(4)–C(21)	1·498(3)
N(2)–C(7)	1·506(2)		
Bond angles			
C(6)–N(1)–C(5)	108·31(13)	C(7)–N(2)–C(3)	111·39(14)
C(6)–N(1)–C(2)	111·29(14)	C(8)–N(2)–C(4)	110·40(14)
C(5)–N(1)–C(2)	106·45(13)	C(7)–N(2)–C(4)	111·21(14)
C(6)–N(1)–C(1)	111·16(14)	C(3)–N(2)–C(4)	108·83(13)
C(5)–N(1)–C(1)	110·33(13)	C(11)–C(1)–N(1)	115·10(14)
C(2)–N(1)–C(1)	109·18(13)	N(1)–C(2)–C(3)	112·35(14)
C(8)–N(2)–C(7)	108·55(14)	N(2)–C(3)–C(2)	113·11(14)
C(8)–N(2)–C(3)	106·37(13)	C(21)–C(4)–N(2)	115·35(14)

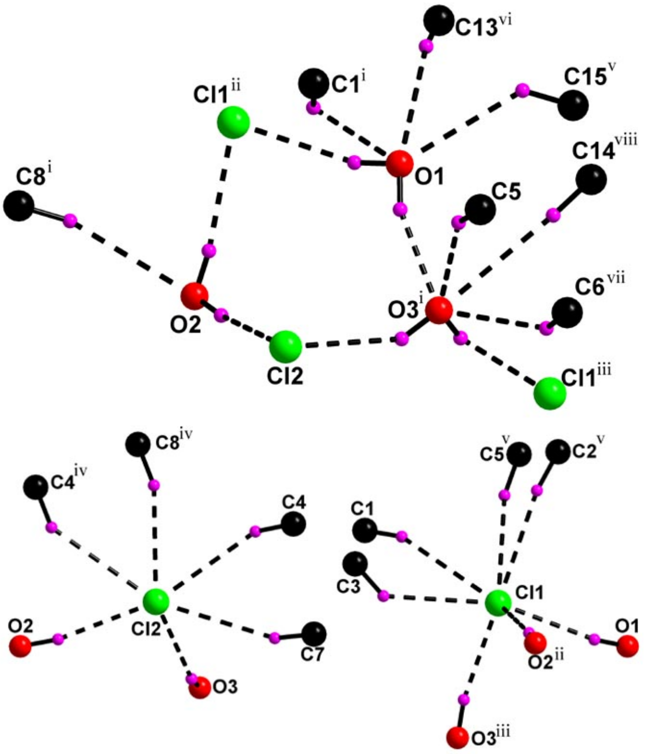

Figure 2. A view of the surroundings of the crystal water molecules showing the O–H···O, O–H···Cl and C–H···O interactions (top); The environment of the chloride anions showing the O–H···Cl and C–H···Cl interactions (bottom). Symmetry codes: (i) *x*, *y*, *z* – 1 (ii) *x*, *y*, *z* + 1 (iii) *x*, –*y* + 1/2, *z* + 1/2 (iv) *x*, –*y* + 3/2, *z* – 1/2 (v) *x*, –*y* + 3/2, *z* + 3/2 (vi) –*x* + 1, –*y* + 1, –*z* (vii) –*x* + 1, *y* + 1/2, –*z* + 1/2 (viii) –*x* + 1, –*y* + 1, –*z* + 1.

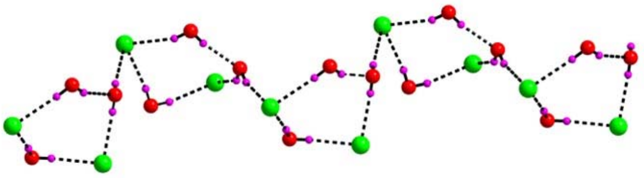

Figure 3. Formation of a chain of H-bonded five-membered rings. The rings are linked with the aid of O3-H2O3···Cl1 interaction.

Waals radii[41] and are accompanied by O–H···Cl angles ranging from 143 to 172°. Cl2 is involved in two short O–H···Cl interactions one each with O2 and O3 while Cl1 makes three short Cl···H contacts, one each with all the oxygen atoms. In the five-membered ring, Cl1 is hydrogen bonded to O1 and O2. The O3–H2O3···Cl1 interaction links one five-membered ring with the next leading to the formation of a H-bonded chain of five-membered rings (figure 3). The five-membered ring contains a supramolecular water dimer due to the linking of 01 with O3. The observed O1···O3 distance of 2·806 Å in **1** is comparable with the reported O···O distances for water dimers in other environments.[25–27] The formation of the H-bonded chain of five-membered rings can be explained by comparing the structure of **1** with that of the corresponding dibromide dihydrate (dbtmen) $Br_2 \cdot 2H_2O$. In the dibromide compound a H-bonded four membered cyclic dibromide unit $\{O_2Br_2\}$ was observed and the four-membered rings were isolated but not linked into a chain as in **1**. The four O–H···Br interactions between the bromide and the two crystal water molecules ranging from 2·472 to 2·528 Å in the dibromide compound resulted in the formation of alternating layers of (dbtmen)$^{+2}$ cation and cyclic hydrogen-bonded dibromides. This structural difference can be attributed to the different de-

Table 3. Hydrogen-bonding geometry (Å, °) for (dbtmen)$Cl_2 \cdot 3H_2O$ **1**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<DHA
O1–H1O1···O3^{i}	0·86	1·99	2·806(7)	159
O1–H2O1···Cl1	0·86	2·37	3·199(10)	163
O2–H1O2···Cl1^{ii}	0·86	2·36	3·218(6)	172
O2–H2O2···Cl2	0·86	2·34	3·185(2)	168
O3–H1O3···Cl2	0·86	2·35	3·081(7)	143
O3–H2O3···Cl1^{iii}	0·86	2·32	3·147(2)	162
C4–H4A···Cl2^{iv}	0·99	2·88	3·706(6)	146
C8–H8B···Cl2^{iv}	0·98	2·72	3·634(2)	156
C4–H4B···Cl2	0·99	2·80	3·741(5)	153
C7–H7B···Cl2	0·98	2·83	3·735(5)	154
C1–H1B···Cl1	0·99	2·84	3·766(8)	156
C3–H3A···Cl1	0·99	2·72	3·504(11)	137
C5–H5B···Cl1^{v}	0·98	2·78	3·681(3)	153
C2–H2B···Cl1^{v}	0·99	2·79	3·700(3)	154
C1–H1A···O1^{i}	0·99	2·60	3·439(2)	143
C15–H15···O1^{v}	0·95	2·64	3·348(15)	132
C13–H13···O1^{vi}	0·95	2·62	3·500(11)	155
C8–H8C···O2^{i}	0·98	2·68	3·589(6)	154
C6–H6A···O3^{vii}	0·98	2·64	3·493(10)	146
C5–H5C···O3	0·98	2·51	3·402(6)	152
C14–H14···O3^{viii}	0·95	2·70	3·635(8)	167

Symmetry codes: (i) $x, y, z - 1$ (ii) $x, y, z + 1$ (iii) $x, -y + 1/2, z + 1/2$ (iv) $x, -y + 3/2, z - 1/2$ (v) $x, -y + 3/2, z + 3/2$ (vi) $-x + 1, -y + 1, -z$ (vii) $-x + 1, y + 1/2, -z + 1/2$ (viii) $-x + 1, -y + 1, -z + 1$

grees of hydration of **1** and the dibromide. Unlike in the dibromide, the H-bonded five-membered cyclic {O_3Cl_2} units in **1** are linked into a spiral-like chain (figure 4). The seven C–H···O distances ranging from 2·51 to 2·70 Å and the eight C–H···Cl distances ranging from 2·72 to 2·88 Å indicate several weak contacts[42] between the organic cation and the anionic water chain. The supramolecular organization of the organic cations in a zigzag fashion on either side of the anionic water chain to promote weak non-bonding interactions can probably explain the spiral-like shape of the chain.

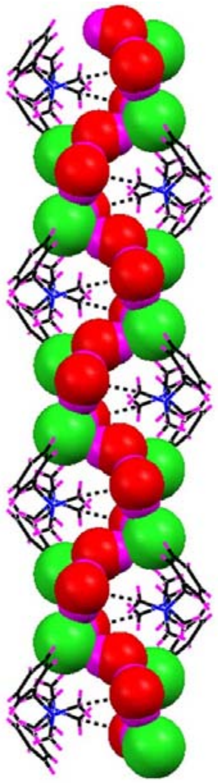

Figure 4. Supramolecular organization of the five-membered {Cl_2O_3} rings into a spiral-like chain. The organic cations are organised in zigzag fashion on either side of the chain.

The thermal stability of (dbtmen)$Cl_2 \cdot 3H_2O$ **1** was investigated by isothermal weight loss studies as well as TG-DTA measurements. A mass loss of around 11% was observed when **1** is heated at 100°C on a water bath for about 10 min. The observed mass change is slightly less than that to that expected (12·75%) for the loss of three moles of water. The observed mass loss of **1** after heating at 150°C is about 12·62% and this value is in very good agreement with that expected for the emission of three moles of water. However, the IR spectrum of the heat-treated product was very similar to that of the starting material indicating that the anhydrous sample is quite moisture-sensitive and reabsorbs water. Our several attempts to record the IR spectrum of the dehydrated sample

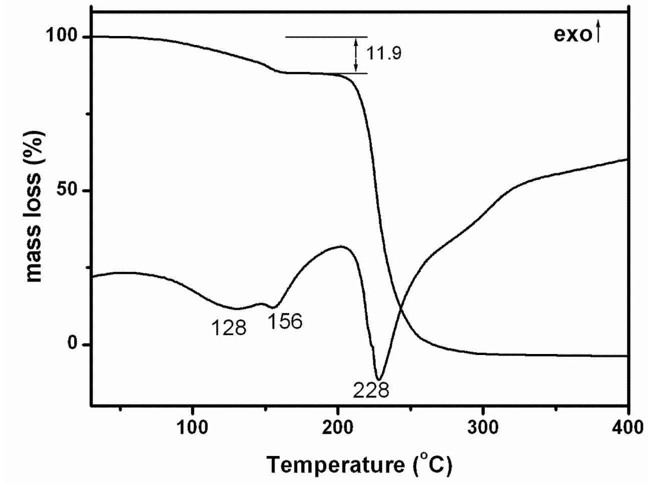

Figure 5. TG-DTA curves for (dbtmen)$Cl_2 \cdot 3H_2O$ **1** (decomposition in flowing Ar).

were not successful. The affinity of the dehydrated sample for moisture can also be evidenced by the fact that the bulk of the dehydrated sample regains its original weight by just exposure to air within 10 min. The IR spectrum of this final product is identical to that of **1**. It is to be noted that in the case of the corresponding bromide analogue the rehydration experiment was performed by equilibrating the anhydrous dibromide over water in a dessicator.[36] It is also noted that extended exposure times or equilibration over water of the anhydrous product does not result in the formation of any other product containing more than three moles of water. The TG-DTA experiment gave a very similar result and the thermogram (figure 5) exhibits endothermic events with a broad signal at around 128°C and another signal at 156°C, which can be attributed to the dehydration of **1**. On further heating, the anhydrous compound formed, undergoes endothermic decomposition at around 228°C. The compound is fully pyrolysed without leaving any residue.

4. Conclusions

In summary, we have described the synthesis, spectral, thermal and structural characterization of the organic diammonium dichloride trihydrate (dbtmen)$Cl_2 \cdot 3H_2O$ **1**, which exhibits four varieties of H-bonds. The O–H···Cl and O–H···O interactions between the chloride anions and the crystal water molecules lead to the formation of cyclic dichloride rings containing water dimers. The rings thus formed are linked into spiral-like chains with the help of O–H···Cl interactions. The organic cations are organised on either side of the anionic water chain and linked by weak C–H···O and C–H···Cl interactions. Compound **1** emits water on heating and reabsorbs water when the dehydrated sample is exposed to air or moisture. The present work constitutes an example of the identification of a water dimer in a quaternary diammonium dichloride.

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Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 614322 (1). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

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