

A novel hydrogen-bonded cyclic dibromide in an organic diammonium salt[#]

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MS received 23 September 2005; revised 2 January 2006

Abstract. The organic diammonium salt N,N'-dibenzyl-N,N,N',N'-tetramethylethylenediammonium dibromide dihydrate, (dbtmen)Br₂·2H₂O (**1**), was prepared by the reaction of N,N,N',N'-tetramethylethylenediamine (tmen) with benzyl bromide. **1** crystallizes in the triclinic space group $P\bar{1}$ with the following unit cell dimensions for C₂₀H₃₄Br₂N₂O₂ (M = 494.31): $a = 8.6672(6)$ Å, $b = 11.7046(8)$ Å, $c = 11.7731(8)$ Å, $\alpha = 76.988(8)^\circ$, $\beta = 88.978(8)^\circ$, $\gamma = 76.198(8)^\circ$, $V = 1129.26(13)$ Å³, $Z = 2$. Three components, namely the (dbtmen)²⁺ dication, two bromide anions and two crystal water molecules constitute the structural arrangement of **1**. H₂O molecules are linked to bromide anions via O–H···Br hydrogen bonding interactions resulting in the formation of a four-membered {O₂Br₂} cyclic dibromide. The {O₂Br₂} units and the dications are arranged as alternating layers extending in the crystallographic bc plane. The arrangement of anions and cations may be viewed as a typical lamellar structure. The crystal water molecules can be removed by heating **1** at 140°C and the anhydrous dibromide thus formed can be fully rehydrated as evidenced by IR spectra and X-ray powder patterns.

Keywords. N,N'-dibenzyl-N,N,N',N'-tetramethylethylenediammonium dibromide; hydrogen bonding interactions; cyclic dibromide.

1. Introduction

In recent years, organic amines have been extensively used as structure-directing agents for the construction of novel supramolecular assemblies as evidenced by the structural characterization of several new materials, which exhibit interesting molecular architectures. The important as well as often observed structural features in several of these compounds are the weak H-bonding interactions between the organic amine/ammonium cation and the crystal or coordinated water or other electronegative sites in the rest of the molecule. N–H···O or O–H···N hydrogen bonding interactions give rise to a variety of structurally diverse materials¹ that trap small clusters of water molecules in the host lattice.^{2–5} In this context, organic diamines like N,N,N',N'-tetramethylethyl-

enediamine (tmen), 1,3-propanediamine (1,3-pn), piperazine (pip) etc. have been shown to be useful structure directors for the synthesis of novel polyoxomolybdates as well as a variety of open-framework metal phosphates and metal carboxylates.^{6–10} The usefulness of the weak N–H···O bonding interactions for the formation of unusual structural architecture has been recently demonstrated in the case of a hydrated mono perchlorate salt of *o*-phenylenediamine.¹¹ In this compound the perchlorate anion, the monoprotonated *o*-phenylenediamine cation and the crystal water assemble with the aid of N–H···O as well as O–H···O hydrogen bonding interactions into a unique hydrogen-bonded network consisting of a hydrophobic double layer with a hydrophilic gallery in it.

In our research, we investigate the reactions of organic diamines with group VI oxo and thiometalates and have synthesized and structurally characterized several oxochromates,^{12–14} tetrathiomolybdates^{15–19} and tetrathiotungstates.^{20–24} These sub-

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[#]Dedicated to Prof S Chandrasekaran on the occasion of his 60th birthday

stances exhibit weak H-bonding interactions in the form of N–H...X (X = O or S) bonds between the organic cation and the oxochromate or tetrathiometalate anions. In all the tetrathiomolybdate and tetrathiotungstate compounds $[\text{MS}_4]^{2-}$ (M = Mo, W) structurally characterized by us, we have observed that one or two of the M–S bonds are elongated, which is attributed to H-bonding interactions. Our work with $[\text{WS}_4]^{2-}$ has shown that organic amines can be used as cationic handles to distort the $[\text{WS}_4]^{2-}$ tetrahedron by varying the H-bonding interactions.²⁴ In order to understand the importance of H-bonding interactions in the structural chemistry of tetrathiotungstates, we investigated the reactions of $[\text{WS}_4]^{2-}$ with organic amines which differ in terms of their steric bulk and the number of potential H donor atoms. During the course of this investigation, a fully alkylated diammonium dihalide was sought as a precursor for the synthesis of a reference $[\text{WS}_4]^{2-}$ compound that should be devoid of cation–anion interactions in the form of weak H-bonding interactions. Such a tetraalkylated salt **1** was prepared by benzylating tmen. Interestingly, a structure determination of **1** revealed the presence of a hydrogen bonded cyclic dibromide unit. Further, the title compound can be reversibly hydrated. We wish to present the results of these investigations in this paper.

2. Experimental

All the chemicals used in this study were of reagent grade and used as received. Infrared spectra were recorded on a Shimadzu FT-IR spectrometer (IRPrestige-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. X-ray powder pattern were recorded on an ITAL System (APD 2000) X-ray diffractometer using Cu–K α radiation. TG–DTA studies were performed in Ar atmosphere in the temperature range 20°C to 500°C on a Netzsch simultaneous thermal analyses apparatus. A heating rate of 4°C/min was chosen for the measurement.

2.1 Preparation of $(\text{dbtmen})\text{Br}_2 \cdot 2\text{H}_2\text{O}$ **1**

The diamine tmen (1.3 ml) was dissolved in ~10 ml of CH_3CN . This diluted amine solution was cooled and benzyl bromide (2.3 ml) was added in drops

with continuous stirring over 10–15 min. (Caution! Benzyl bromide is lachrymatory and hence the reaction has to be performed in a well-ventilated fume cupboard.) When addition is complete, copious amounts of white crystalline solid slowly separated out. The crystalline product was isolated by filtration, washed with isopropanol (20 ml), followed by ether (20 ml) and finally dried in air. Yield (4.0 g). Crystallisation of this material from water afforded X-ray quality crystals of $(\text{dbtmen})\text{Br}_2 \cdot 2\text{H}_2\text{O}$.

Analysis – found (calc) for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{Br}_2 \cdot 2\text{H}_2\text{O}$: C 48.63 (48.59), H 7.01 (6.95), N 5.68 (5.67)%.

IR data in cm^{-1} : 3464 (s), 3394 (s), 3226 (w), 3020 (s), 3007 (sh), 1616 (m), 1485 (s), 1463 (s), 1454 (s), 1396 (w), 1355 (w), 1213 (m), 1080 (w), 1033 (w), 995 (m), 964 (w), 941 (m), 921 (m), 893 (m), 864 (s), 786 (s), 744 (s), 729 (s), 713 (s), 578 (s), 513 (w), 495 (w), 462 (w).

UV–Vis data (water): 262 nm ($\epsilon = 640 \text{ l mol}^{-1} \text{ cm}^{-1}$).

¹H NMR ($\text{D}_2\text{O}-d_6$) (**d** in ppm): 7.44 (s, 10H), 4.53 (s, 4H), 3.91 (s, 4H), 3.06 (s, 12H).

2.2 Preparation of $(\text{dbtmen})\text{Br}_2$ **2**

A powdered sample of **1** (0.488 g) was heated in a temperature controlled oven at 140°C for ~20 min. This resulted in the formation of the anhydrous compound. The observed mass loss of 7.65% is in very good agreement with the expected value (7.29%) for the loss of two moles of water.

IR data in cm^{-1} : 3026 (m), 2981 (s), 2885 (w), 2804 (w), 1581 (w), 1469 (s), 1448 (s), 1398 (m), 1361 (w), 1219 (m), 1076 (w), 1003 (m), 975 (m), 927 (s), 891 (s), 867 (s), 842 (w), 821 (w), 779 (s), 721 (s), 702 (s), 619 (w), 513 (w), 486 (w), 462 (w).

2.3 Reversible hydration studies

The anhydrous compound **2** was prepared as mentioned above. A powdered sample of the water-free compound (0.451 g) was equilibrated over water in a dessicator for ~30 min. This resulted in the formation of the starting dihydrate **1** in quantitative yield. The IR spectrum of the rehydrated product is identical to that of **1**.

2.4 Single crystal X-ray diffractometry

Intensity data for **1** were collected on a Stoe Image Plate Diffraction System using graphite monochro-

mated Mo–K α radiation at 170 K. The intensities were corrected for Lorentz polarization effects. The structure was solved with direct methods using SHELXS-97²⁵ and refinement was done against F^2 using SHELXL-97.²⁶ All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and refined using the riding model with fixed isotropic displacement parameters. The technical details of data acquisition and some selected crystal refinement results are summarized in table 1. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 284867 (1). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

Table 1. Technical details of data acquisition and selected refinement results for (dbtmen)Br₂·2H₂O, **1**.

Compound	(dbtmen)Br ₂ ·2H ₂ O (1)
Formula	C ₂₀ H ₃₄ Br ₂ N ₂ N ₂ O ₂
Temperature [K]	170 (2)
Wavelength [pm]	71.073
Space group	$P\bar{1}$
<i>a</i> [Å]	8.6672 (6)
<i>b</i> [Å]	11.7046 (8)
<i>c</i> [Å]	11.7731 (8)
<i>a</i> [°]	76.988 (8)
<i>b</i> [°]	88.978 (8)
<i>g</i> [°]	76.198 (8)
Volume [Å ³]	1129.26 (13)
<i>Z</i>	2
<i>m</i> [mm ⁻¹]	3.605
<i>F</i> (000)	508
Molecular weight [g/mol]	494.31
Density (calcd.) [g cm ⁻³]	1.454
Crystal size (in mm)	0.5 × 0.2 × 0.2
<i>hkl</i> range	–11/11; –15/15; –15/15
<i>2q</i> range	4.5°–56°
Reflections collected	9858
Reflections unique	5133
Data (<i>F</i> _o > 4 <i>s</i> (<i>F</i> _o))	4162
<i>R</i> _{int}	0.0319
Min/Max transmission	0.5628/0.6349
<i>r</i> [e/Å ³]	–0.721/0.464
Parameters	236
<i>R</i> ₁ [<i>F</i> _o > 4 <i>s</i> (<i>F</i> _o)] ^a	0.0297
<i>WR</i> ₂ for all unique data	0.0760
Goodness of fit	1.007

^a*R*₁ = $\sum||F_o| - |F_c||/\sum|F_o|$

3. Results and discussion

Synthesis of the organic diammonium salt **1** was accomplished by reacting the organic diamine tmen with benzyl bromide in a 1 : 2 molar ratio in CH₃CN followed by recrystallisation from water. The compound analysed satisfactorily for the proposed formula. Reaction of **1** with (NH₄)₂[WS₄] afforded the highly insoluble complex (dbtmen)[WS₄]. The high insolubility of this compound in aqueous as well as non-aqueous solvents including DMF and DMSO precluded the preparation of a suitable crystalline material for single-crystal structure investigations. However, the presence of the organic cation as well as [WS₄]²⁻ could be inferred from IR spectra and the formulation is consistent with analytical data.

The electronic spectrum of **1** exhibits a signal at ~260 nm which can be assigned to the charge transfer of the aromatic moiety. The proton magnetic resonance spectrum of **1** exhibits four sharp singlets at *d* 7.44 (s, 10H), *d* 4.53 (s, 4H), *d* 3.91 (s, 4H), 3.06 ppm (s, 12H), which can be assigned to the resonance absorptions of the aromatic, benzylic, methylene and methyl protons respectively. The IR spectrum of the hydrated dibromide exhibits strong bands at 3464, 3394 cm⁻¹ assignable to the stretching vibration of O–H, while the O–H bending vibration was located at 1616 cm⁻¹. Several bands in the mid IR region can be attributed to the vibrations of the organic cation. **1** can be dehydrated to form the corresponding anhydrous compound by heating at ~140°C. Formation of the water-free compound **2** can be evidenced from the IR spectrum of calcined **1**, which is devoid of the O–H bands at 3464, 3394 and 1616 cm⁻¹.

The organic dibromide dihydrate **1** crystallizes in the triclinic space group $P\bar{1}$ (table 1) with all atoms located in general positions. The asymmetric unit of **1** consists of discrete N,N'-dibenzyl-N,N',N'-tetramethylethylenediammonium cations, two bromide ions and two crystal water molecules (figure 1). Selected bond lengths and bond angles are collected in table 2. The observed C–C and C–N bond lengths are in good agreement with those found in other compounds containing the tmen moiety.^{17,20,27} The crystal water molecules in **1** are hydrogen-bonded with two bromide ions forming a novel four-membered cyclic dibromide {O₂Br₂} (only the O and Br but not the H atoms are considered) (figure 2). The two bromide ions are linked to H₂O via four O–H...Br hydrogen bonds ranging from 2.472 to 2.528 Å. Br...H distances are quite short compared to 3.05 Å,

the sum of the van der Waals radii²⁸ of Br and H. The details of the H-bonding parameters are summarized in table 3. Both Br1 and Br2 are involved in two O–H...Br interactions each. The large values of the O–H...Br angles indicate that these bonds are quite strong which is further evident from the values of the Br...O distances ranging from 3.306 to 3.359 Å. As a result of these H-bonds, alternating layers of the organic cation and the cyclic hydrogen-bonded

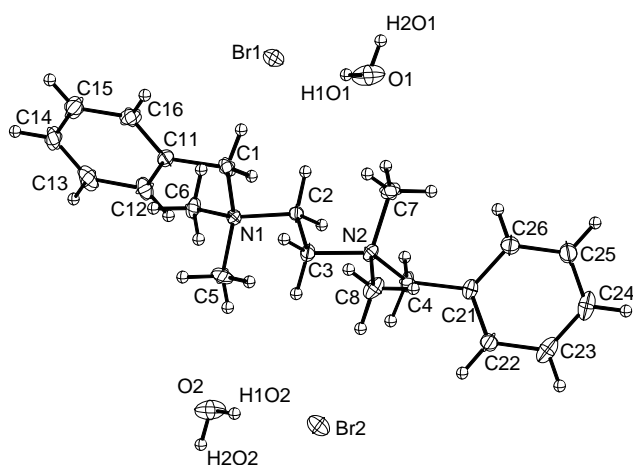


Figure 1. Crystal structure of (dbtmen)Br₂·2H₂O (**1**) with labeling and displacement ellipsoids drawn at the 50% probability level.

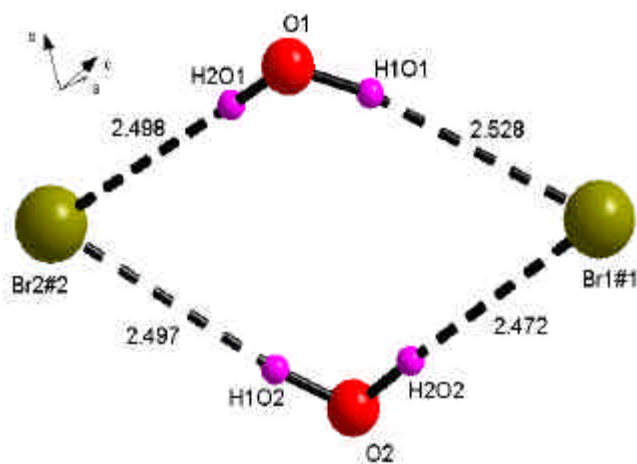


Figure 2. View of the four-membered cyclic dibromide along *a* axis showing O–H...Br interactions (given are the intermolecular O–H...Br distances in Å and dashed lines indicate hydrogen bonding). Colour codes: O red, Br green and H purple [symmetry codes: #1 = *x*, *y*, *z* + 1, #2 = *x*, *y*, *z* – 1].

dibromides are formed extending in the crystallographic *bc* plane. A search of the Cambridge structure database for organic bromides revealed that similar hydrogen-bonded bromide units have also been reported earlier in some imidazolium and pyridinium bromides.^{29–35} O...Br distances, which are of the order of 3.293 to 3.363 Å in these compounds, are comparable with the observed values for **1**. To the best of our knowledge, the present structure constitutes the first example of such a unit in a tetraalkyldiammonium dibromide. In the unbenzylated compound (tmenH₂)Br₂ it has been reported that the cation is linked to the anion via N–H...Br bonds.²⁷ Similar cation–anion interactions (N–H...S) have also been observed in (tmenH₂)[MoS₄].¹⁷ In view of the tetraalkylation of the N atom no N–H...X interactions are possible in **1**. Hence the formation of the layer structure of **1** can be attributed to the tetraalkylation of N. In **1** the interlayer interactions between the anions and cations can be of van der Waals type and/or electrostatic in nature as no interactions are observed other than the O–H...Br bonds. A view of (dbtmen)Br₂·2H₂O showing the alternating layers of cations and anions in the [010] plane is depicted in figure 3. The phenyl rings in each layer are arranged one below the other. The perpendicular distance between adjacent phenyl rings in the alternating layers is about 4.697 Å, which indicates the

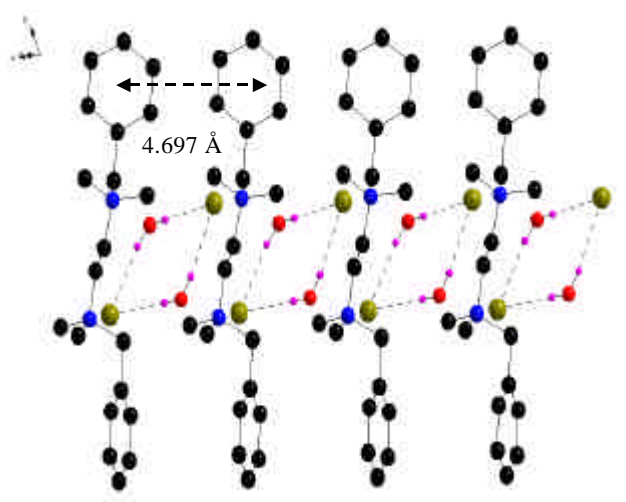


Figure 3. View of compound **1** showing alternating layers of organic (dbtmen)²⁺ cations (dashed lines indicate hydrogen bonding). The H atoms of the (dbtmen)²⁺ cation are omitted for clarity. The perpendicular distance of 4.697 Å between the rings indicates absence of stacking interactions. Colour codes: C black, N blue, O red, Br green and H purple.

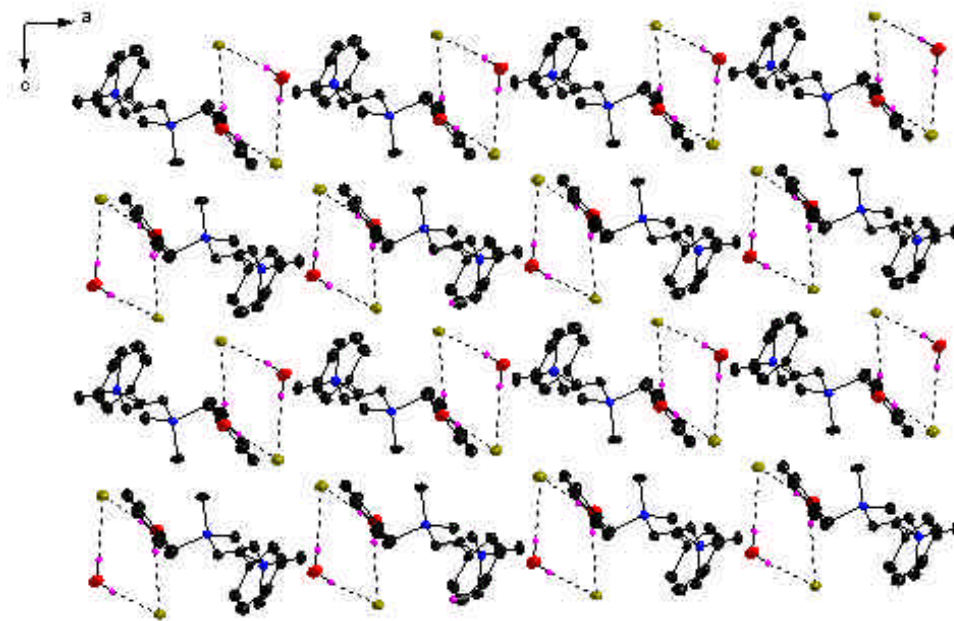


Figure 4. Hydrogen bonded cyclic dibromides occupying the pores between alternating layers of organic cations in the crystallographic *ac* plane. The H atoms of the organic cation are not shown. Colour codes: C black, N blue, O red, Br green and H purple.

Table 2. Selected geometric parameters (Å, degrees) for (dbtmen)Br₂·2H₂O, **1**.

<i>Bond lengths</i>			
C(1)–C(11)	1.513 (3)	C(11)–C(12)	1.396 (3)
C(1)–N(1)	1.540 (3)	C(12)–C(13)	1.400 (3)
N(1)–C(6)	1.500 (3)	C(13)–C(14)	1.379 (4)
N(1)–C(5)	1.502 (2)	C(14)–C(15)	1.387 (4)
N(1)–C(2)	1.517 (2)	C(15)–C(16)	1.394 (3)
C(2)–C(3)	1.530 (3)	C(21)–C(26)	1.391 (3)
C(3)–N(2)	1.517 (2)	C(21)–C(22)	1.400 (3)
N(2)–C(7)	1.506 (3)	C(22)–C(23)	1.393 (3)
N(2)–C(8)	1.506 (3)	C(23)–C(24)	1.378 (4)
N(2)–C(4)	1.528 (3)	C(26)–C(25)	1.391 (3)
C(4)–C(21)	1.511 (3)	C(24)–C(25)	1.394 (4)
C(11)–C(16)	1.392 (3)		
<i>Bond angles</i>			
C(11)–C(1)–N(1)	114.10 (17)	C(16)–C(11)–C(12)	119.51 (19)
C(6)–N(1)–C(5)	109.56 (17)	C(16)–C(11)–C(1)	119.78 (19)
C(6)–N(1)–C(2)	110.85 (15)	C(12)–C(11)–C(1)	120.6 (2)
C(5)–N(1)–C(2)	110.38 (16)	C(11)–C(12)–C(13)	119.7 (2)
C(6)–N(1)–C(1)	110.41 (16)	C(14)–C(13)–C(12)	120.1 (2)
C(5)–N(1)–C(1)	110.32 (16)	C(13)–C(14)–C(15)	120.5 (2)
C(2)–N(1)–C(1)	105.26 (15)	C(14)–C(15)–C(16)	119.7 (2)
N(1)–C(2)–C(3)	112.09 (17)	C(11)–C(16)–C(15)	120.4 (2)
N(2)–C(3)–C(2)	112.69 (17)	C(26)–C(21)–C(22)	119.06 (19)
C(7)–N(2)–C(8)	108.49 (16)	C(26)–C(21)–C(4)	120.97 (19)
C(7)–N(2)–C(3)	110.46 (15)	C(22)–C(21)–C(4)	119.9 (2)
C(8)–N(2)–C(3)	106.02 (17)	C(23)–C(22)–C(21)	120.1 (2)
C(7)–N(2)–C(4)	111.53 (17)	C(24)–C(23)–C(22)	120.4 (2)
C(8)–N(2)–C(4)	110.58 (15)	C(25)–C(26)–C(21)	120.6 (2)
C(3)–N(2)–C(4)	109.63 (15)	C(23)–C(24)–C(25)	119.9 (2)
C(21)–C(4)–N(2)	114.27 (16)	C(26)–C(25)–C(24)	119.9 (2)

absence of stacking interactions. The two phenyl rings in each cation are perpendicular to each other, which is evident from figure 4 where a view of the structure along the b axis is shown.

The thermal stability of $(\text{dbtmen})\text{Br}_2 \cdot 2\text{H}_2\text{O}$ was investigated using DTA-TG measurements. On heating, the compound starts emitting water at around 90°C , which is accompanied by a sharp endothermic event in DTA curve at 111°C (figure 5). A single mass step of 7.4% (expected mass loss is 7.3%) can be attributed to the emission of two moles of crystal

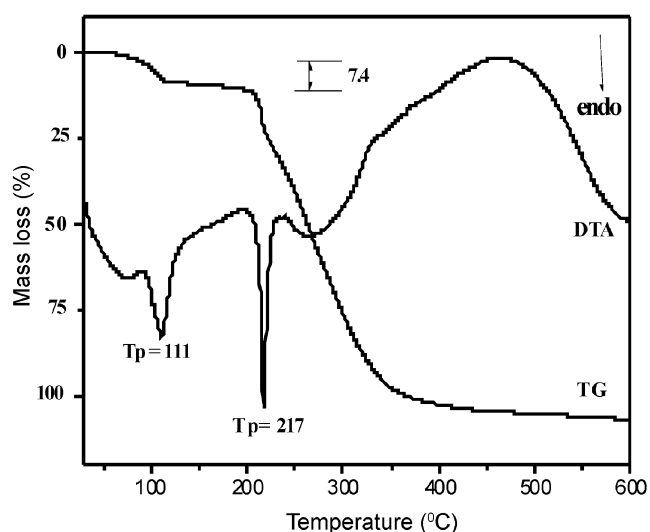


Figure 5. TG-DTA curves for $(\text{dbtmen})\text{Br}_2 \cdot 2\text{H}_2\text{O}$, **1** (decomposition in flowing Ar; T_p is peak temperature).

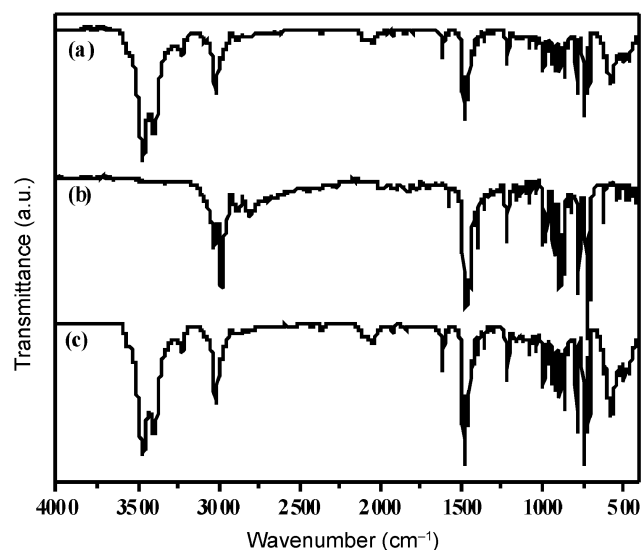


Figure 6. IR spectra of (a) pristine $(\text{dbtmen})\text{Br}_2 \cdot 2\text{H}_2\text{O}$, **1**; (b) anhydrous $(\text{dbtmen})\text{Br}_2$, **2**; (c) rehydrated $(\text{dbtmen})\text{Br}_2$.

water, which are involved in the formation of the cyclic dibromide. The loss of water is complete at about 140°C . On further heating the anhydrous compound starts decomposing endothermically ($T_p = 218^\circ\text{C}$) and pyrolysis till 600°C results in a small amount ($\sim 6\%$) of black residue of carbon indicating incomplete decomposition. **1** can be reversibly hydrated. Re-hydration behaviour of the dehydrated sample was studied using IR spectroscopy and X-ray powder diffraction. $(\text{dbtmen})\text{Br}_2 \cdot 2\text{H}_2\text{O}$ was heated to 140°C in an oven for the complete emission of crystal water and the IR spectrum of the calcined sample **2** showed the absence of the O-H bands at 3464 , 3394 cm^{-1} . In addition the bands at 941 , 744 and 578 cm^{-1} in **1** are not observed in **2**. It has been reported that the gas phase vibrational spectra of the $\text{Br}^- (\text{HBr})_n$ ($n = 1-3$) clusters exhibit signals at 888 and 976 cm^{-1} for the H-bonded $\text{Br}^- (\text{HBr})_2$ fragment.³⁶ Interestingly the missing signals in the anhydrous compound are observed when the calcined compound **2** is exposed to moisture indicating that these signals originate from the H-bonded cyclic $\{\text{O}_2\text{Br}_2\}$ unit. The remaining signals in the spectrum of **2** are observed at the same positions as for the hydrated compound. On exposure to water vapour, the calcined compound **2** is converted to the original dihydrate as evidenced by the IR spectrum of the rehydrated compound (figure 6). The X-ray powder pattern of the calcined sample is very similar to that

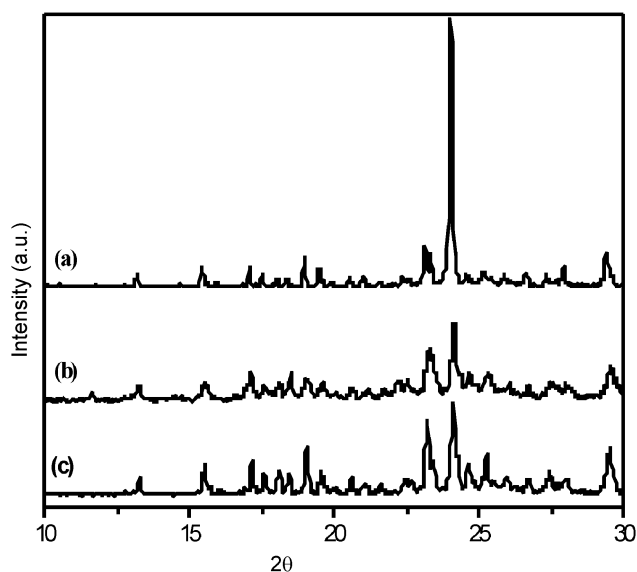


Figure 7. X-ray powder pattern of (a) pristine $(\text{dbtmen})\text{Br}_2 \cdot 2\text{H}_2\text{O}$, **1**; (b) calcined $(\text{dbtmen})\text{Br}_2 \cdot 2\text{H}_2\text{O}$, **2**, and (c) rehydrated $(\text{dbtmen})\text{Br}_2$.

Table 3. Hydrogen-bonding geometry (Å, °) for (dbtmen)Br₂·2H₂O, **1**.

D–H...A	d(D–H)	d(H...A)	d(D...A)	<DHA	Symmetry code
O1–H1O1...Br1	0.840	2.528	3.359	170.23	
O1–H2O1...Br2	0.840	2.498	3.337	176.31	<i>x, y, z – 1</i>
O2–H1O2...Br2	0.840	2.497	3.329	170.61	
O2–H2O2...Br1	0.840	2.472	3.306	171.77	<i>x, y, z + 1</i>

of the starting dihydrate (figure 7) indicating that the overall structure of **1** still remains intact after the water molecules are removed.

4. Conclusions

The organic diammonium dibromide (dbtmen)Br₂·2H₂O **1** has been synthesized by reacting tmen with benzyl bromide in CH₃CN. The hydrated dibromide has been unambiguously characterised by elemental analysis, spectroscopic techniques and X-ray crystal structure determination. Compound **1** emits water on heating and reabsorbs water when the dehydrated sample is exposed to moisture. The structure of **1** consists of the (dbtmen)²⁺ dication and a four-membered cyclic dibromide formed by O–H...Br hydrogen bonding interactions between crystal water molecules and bromide anions. The presence of the cyclic dibromide in the crystal structure of **1** as well as the tetraalkylation around N leads to a layer structure wherein the cations and anions are packed as alternating layers in the crystallographic *bc* plane. It would be of interest to verify if such a layer like arrangement is the preferred structure motif for tetraalkylated ammonium compounds with other anions like molybdates, phosphates etc. Efforts in this direction are underway in our laboratories.

Acknowledgements

BRS thanks Prof K S Rane and Dr V S Nadkarni for helpful discussions and Mr P Raghavaiah for the CCDC search. The TG-DTA carrier used in this study was procured under a Department of Science and Technology, (DST) New Delhi supported project. We are grateful to the Department of Science and Technology, Govt. of India and the University Grants Commission, New Delhi for financial support.

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