Synthesis and Structural Characterization of *N*,*N*′-Dipropyl-*N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediammonium Dichloride and Dibromide

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N,*N*′-Dipropyl-*N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediammonium dichloride (**1**) and dibromide (**2**) were prepared by the reaction of *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediamine and the corresponding 1-halopropane. The structures of the compounds were characterized by single-crystal X-ray diffraction. $\mathbf{1}\cdot 2H_2O$ crystallizes in the triclinic crystal system, space group $P1$, with $Z = 1$, and **2** in the monoclinic crystal system, space group $P2_1/c$, with $Z = 2$. The crystal structures of the salts consist of discrete dications and halide anions. The packing in $\mathbf{1}\cdot 2H_2O$ consists of layers of cations with the chloride anions and water molecules forming hydrogen-bonded chains between the cation layers. In **2**, the strongest H···Br hydrogen bonds of 2.8138(6) and 2.8187(7) Å link the cations and anions into double-stranded chains. In both salts, cations and anions are also linked together by a further weak C–H···Cl/Br hydrogen bonding network.

Key words: *N*,*N*′-Dipropyl-*N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediammonium Dichloride/Dibromide, X-Ray Crystallography

Introduction

Crystal structures of 26 *N*,*N*,*N*,*N*′,*N*′,*N*′-hexaalkyl-1,2-ethylenediammonium salts with a varying complexity of both cations and anions are currently known [1]. The anions generally show extended structures forming one-, two-, or three-dimensional networks. Some illustrative examples of such structures contain polyiodidoargentate [2 – 5], polyiodidoplumbate [6 – 9], and single-strand polytetratelluride [10] anions. The units $[SnI_3]^{3-}$ [11, 12], $[SnI_4]^{2-}$ [12], and $[TlBr_5]^{-}$ [13] appear as discrete anions in the solid state, but secondary bonding interactions link them into polynuclear networks.

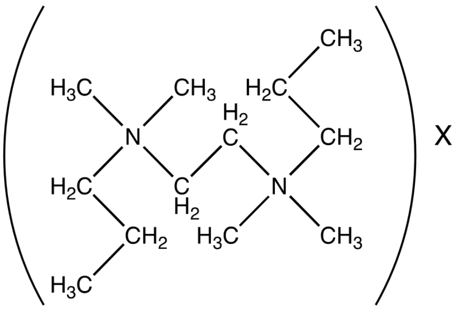

Fig 1. Molecular formula of $\{Me_2PrN(CH_2)_2NMe_2Pr\}Cl_2$ (**1**) and $\{Me_2PrN(CH_2)_2NMe_2Pr\}Br_2$ (**2**).

Structural information on hexaalkyl-1,2-ethylenediammonium salts containing simple anions such as halides or pseudohalides is rather sparse comprising $\{Me_2BuN(CH_2)_2NMe_2Bu\}Br_2\cdot 2H_2O$ [14], $\{Me_3N(CH_2)_2NMe_3\}I_2$ [15], $\{Me_2[Et(CH_2)_n]N(CH_2)_2NMe_2[(CH_2)_nEt]\}X_2$ (X = Br, $n = 10$ [16]; X = I, $n = 10, 14$ [17]), and $\{Me_3N(CH_2)_2NMe_3\}(SCN)_2$ [18]. In some of these crystals, hydrogen bonding networks lead to the formation of extended supramolecular structures.

In this Note we extend the series of simple halides and report the preparation and crystal structures of *N*,*N*′-dipropyl-*N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediammonium dichloride $\{Me_2PrN(CH_2)_2NMe_2Pr\}Cl_2\cdot 2H_2O$ ($\mathbf{1}\cdot 2H_2O$) and dibromide $\{Me_2PrN(CH_2)_2NMe_2Pr\}Br_2$ (**2**) (Fig. 1).

Experimental Section

*$\{Me_2PrN(CH_2)_2NMe_2Pr\}Cl_2$ (**1**)*

The compound was prepared by mixing 27 mL (0.180 mol) of *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediamine and 40 mL (0.454 mol) of 1-chloropropane at 60 °C. After a period of 5 d under dinitrogen, the solid product was filtered, washed with ethyl acetate and recrystallized from ethanol. Yield: 27 g (*ca.* 50 %). The product is hygroscopic, and the crystal structure determination showed that the crystals contained two water molecules per formula unit. – Anal. calcd. for $C_{12}H_{34}Cl_2N_2O_2$ (309.31): calcd. C 46.58, H 11.08, N 9.06; found C 46.77, H 11.58, N 9.19. The product could be dried at 127 °C overnight. – $C_{12}H_{30}Cl_2N_2$ (273.15): calcd. C 52.72, H 11.07, N 10.25; found C 52.70, H 11.35, N 10.40.

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Table 1. Details of the crystal structure determination of $\mathbf{1} \cdot 2H_2O$ and **2**.

	$\mathbf{1} \cdot 2H_2O$	**2**
Formula	$C_{12}H_{34}Cl_2N_2O_2$	$C_{12}H_{30}Br_2N_2$
M_r	309.31	362.20
T (K)	120	120
Crystal size, mm^3	$0.20 \times 0.20 \times 0.10$	$0.25 \times 0.25 \times 0.20$
Crystal system	triclinic	monoclinic
Space group	$P1$	$P2_1/c$
a, Å	8.0885(16)	6.5132(13)
b, Å	8.1002(16)	15.672(3)
c, Å	8.4342(17)	8.2767(17)
α, deg	64.60(3)	90
β, deg	70.08(3)	109.67(3)
γ, deg	62.97(3)	90
V, Å^3	437.3(2)	795.5(3)
Z	1	2
$F(000)$	170	372
D_{calcd}, g cm^{-3}	1.18	1.51
$\mu(MoK_\alpha)$, mm^{-1}	0.4	5.1
θ range, deg.	3.31 – 25.00	2.92 – 25.99
Refl. measd. / unique	5766 / 2668	10215 / 1550
R_{int}	0.056	0.0189
No. of parameters / restraints	183 / 7	77 / 0
x(Flack)	0.11(7)	–
R_1 $[I \geq 2\sigma(I)]$[a]	0.0524	0.0173
wR_2 (all data)[b]	0.1348	0.0398
GoF (F^2)[c]	1.069	1.067
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.34 / −0.37	0.29 / −0.28

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$ and A and B are constants adjusted by the program; [c] $\mathrm{GoF} = S = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

{$Me_2PrN(CH_2)_2NMe_2Pr$}Br_2 (2)

The compound was synthesized using the same procedure as for **1** by mixing 30 mL (0.200 mol) of *N,N,N′,N′*-tetramethyl-1,2-ethylenediamine and 40 mL (0.439 mol) 1-bromopropane. Yield: 57 g (79 %). – $C_{12}H_{30}Br_2N_2$ (362.20): calcd. C 39.77, H 8.35, N 7.74; found C 39.59, H 8.91, N 7.61.

Structure determination

Diffraction data for $\mathbf{1} \cdot 2H_2O$ and **2** were collected at 120 K on a Nonius Kappa CCD diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å). Crystal data and the details of the structure determinations are given in Table 1. Structures were solved by Direct Methods using SHELXS-97 [19] and refined using SHELXL-97 [19]. After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic displacement parameters, the hydrogen atoms bound to carbon atoms were placed in calculated positions (C–H = 0.99 and 0.98 Å in the case of methylene hydrogen atoms and methyl hydrogen atoms, respectively). In the final refinement the calculated hydrogen atoms were riding on the carbon atom they are bonded to. The isotropic displacement parameters of the hydrogen atoms were fixed at 1.2 (methylene hydrogens) or 1.5 (methyl hydrogens) times that of the corresponding carbon atom. The hydrogen atoms of the water molecules were located from the difference Fourier map, and their positions were refined isotropically with the O–H distance loosely constrained at 0.85(1) Å. Their displacement parameters were set to 1.5 U_{eq}(O). The scattering factors for the neutral atoms were those incorporated with the programs.

The intensity statistics strongly indicated that $\mathbf{1} \cdot 2H_2O$ is non-centrosymmetric in the triclinic space group $P1$. However, the initial structure determination was carried out assuming the centrosymmetric space group $P\bar{1}$. It was found that the atoms in the cation indeed showed the presence of an inversion center. The refinement in the centrosymmetric space group $P\bar{1}$ resulted, however, in disorder between the chloride anions and the water molecules that occupied the same atomic sites with the site occupation factors of *ca.* 0.5. Furthermore, the final refinement turned out to be very poor (R_1 = 0.2092, wR_2 = 0.4837). When the refinement was carried out in the non-centrosymmetric space group $P1$, fully ordered sites for both chloride ions and water molecules could be refined with reasonably good R_1 and wR_2 values (see Table 1). The atoms Cl1 and O2 occupied positions that were nominally equivalent with respect to the hypothetical inversion center. The same was true to the atom pair Cl2/O1. The cation was symmetric with respect to this nominal center of symmetry.*

CCDC 827120 and 827121 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

{$Me_2PrN(CH_2)_2NMe_2Pr$}X_2 (X = Cl, Br) are conveniently synthesized by the reaction of *N,N,N′,N′*-tetramethyl-1,2-ethylenediamine with the corresponding 1-halopropane. The crystal structures of $\mathbf{1} \cdot 2H_2O$ and **2** together with the numbering scheme are shown in Fig. 2. The asymmetric unit of $\mathbf{1} \cdot 2H_2O$ contains one cation, two independent anions and two water molecules, whereas the asymmetric unit of **2** consists of half of the cation and one anion.

In both $\mathbf{1} \cdot 2H_2O$ and **2**, the two *n*-propyl chains of the cations are in *anti* configuration with respect to the

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*The symmetry check by the program CHECKCIF [20] suggested, however, that the structure might be centrosymmetric, after all. Since the symmetry is broken only by the two atom pairs (Cl1/O2 and Cl2/O1) it is possible that, this symmetry break is not detected by CHECKCIF.

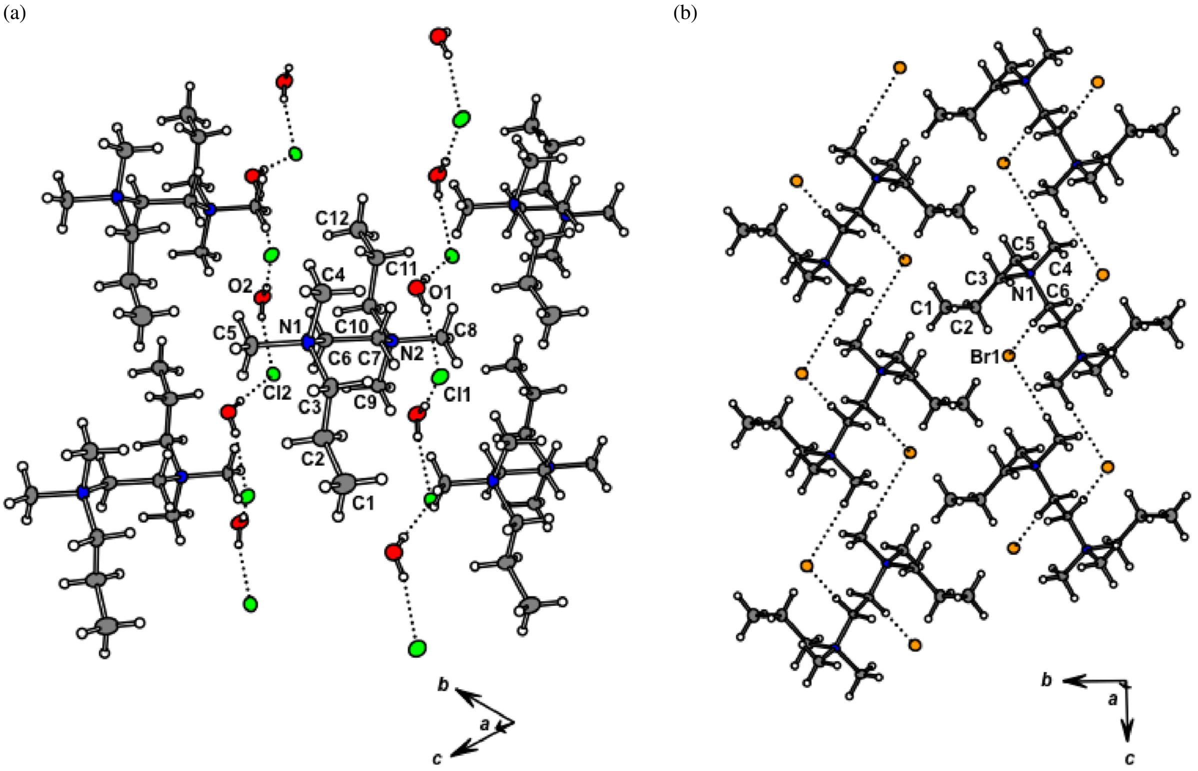

Fig. 2 (color online). The crystal structures of (a) $\{Me_2PrN(CH_2)_2NMe_2Pr\}Cl_2\cdot 2H_2O$ (**1**$\cdot 2H_2O$) and (b) $\{Me_2PrN(CH_2)_2NMe_2Pr\}Br_2$ (**2**) indicating the numbering of atoms. The displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (deg) of **1**$\cdot 2H_2O$: N1–C3 1.523(3), N1–C4 1.505(3), N1–C5 1.507(3), N1–C6 1.509(3), N2–C7 1.508(3), N2–C8 1.500(3), N2–C9 1.511(3), N2–C10 1.519(3), C1–C2 1.532(4), C2–C3 1.517(4), C6–C7 1.524(3), C10–C11 1.522(4), C11–C12 1.529(4); C3–N1–C4 108.8(2), C3–N1–C5 109.7(2), C3–N1–C6 113.3(2), C4–N1–C5 107.6(2), C4–N1–C6 110.4(2), C5–N1–C6 106.9(2), C7–N2–C8 107.6(2), C7–N2–C9 110.0(2), C7–N2–C10 112.5(2), C8–N2–C9 107.5(2), C8–N2–C10 110.6(2), C9–N2–C10 108.5(2), N1–C3–C2 115.1(2), N1–C6–C7 112.2(2), N2–C7–C6 112.7(2), N2–C10–C11 114.9(2), C1–C2–C3 108.3(3), C10–C11–C12 109.0(2). Selected bond lengths (Å) and angles (deg) of **2**: N1–C3 1.516(2), N1–C4 1.503(2), N1–C5 1.509(2), N1–C6 1.511(2), C1–C2 1.520(2), C2–C3 1.512(2), C6–C6′ 1.529(3); C3–N1–C4 109.0(1), C3–N1–C5 109.6(1), C3–N1–C6 113.0(1), C4–N1–C5 107.4(1), C4–N1–C6 110.3(1), C5–N1–C6 107.4(1), N1–C3–C2 114.8(1), N1–C6–C6′ 111.7(2), C1–C2–C3 110.1(2). Symmetry operation of primed atoms: $-x$, $-y$, $1-z$.

N-$(CH_2)_2$-N skeleton. The N–C bond lengths range from 1.500(3) to 1.523(3) Å, and the C–C distances from 1.517(4) to 1.532(4) Å in **1** and from 1.503(2) to 1.516(2) Å and from 1.512(2) Å to 1.529(3) Å in **2**. The bond lengths and angles of the cations are within their normal ranges and can be compared to the corresponding values of $\{Me_2BuN(CH_2)_2NMe_2Bu\}^{2+}$ [13] and $\{Me_2EtN(CH_2)_2NMe_2Et\}^{2+}$ [10, 12].

The packing in **1**$\cdot 2H_2O$ consists of layers of cations, as shown in Fig. 2(a). The chloride anions and water molecules form chains with hydrogen bonds of 2.29(5)–2.32(3) Å between the cation layers. Similar hydrogen bonding contacts between the halide anions and water molecules are found in $\{PhMe_2N(CH_2)_2NMe_2Ph\}Cl_2\cdot 3H_2O$ [H···Cl is 2.3148(5)–2.3648(5) Å] [21], $\{PhMe_2N(CH_2)_2NMe_2Ph\}Br_2\cdot 2H_2O$ {H···Br is 2.43(5)–2.46(5) Å [22] and 2.4722(3)–2.5275(4) Å [23]}, and $\{BuMe_2N(CH_2)_2NMe_2Bu\}Br_2\cdot 2H_2O$ [H···Br is 2.26(5) and 3.33(6) Å] [14], though the geometric arrangements vary. $\{PhMe_2N(CH_2)_2NMe_2Ph\}Cl_2\cdot 3H_2O$ shows a branched chain of alternating anions and water molecules [21], $\{PhMe_2N(CH_2)_2NMe_2Ph\}Br_2\cdot 2H_2O$ has four-membered Br···H_2O rings [22, 23], and $\{BuMe_2N(CH_2)_2NMe_2Bu\}Br_2\cdot 2H_2O$ exhibits a very asymmetric arrangement in the single-stranded chain with one very long H···Br distance [14].

There is also an extensive three-dimensional hydrogen bonding network (< 2.9 Å) between the anions and the cations in **1** $\cdot 2H_2O$. Cl1 shows four close Cl···H hydrogen bond contacts in the range 2.690(1) – 2.840(1) Å, and Cl2 five contacts of 2.612(1) – 2.876(1) Å.

In **2**, the strongest H···Br hydrogen bonds of 2.8138(6) and 2.8187(7) Å link the methyl hydrogens in one cation through the bridging bromide anion to the methylene hydrogen of the adjacent cation forming double-stranded chains, as shown in Fig. 2(b). It is interesting to note that the thiocyanate anion in $\{Me_3N(CH_2)_2NMe_3\}(SCN)_2$ behaves the same way by showing close contacts between the nitrogen atom of the thiocyanate and the methyl hydrogens on one hand, and also between the sulfur atom and methylene hydrogens on the other hand [18].

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