Random Interstitial Halide Accommodation in an α,ω-Alkylidene-diammonium Template

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

N,N,N',N'-Tetramethylethylenediammonium diiodide $[Me_2HNCH_2]_2I_2$ (**1**) as well as a set of I/Br- (**2**) and Br/Cl-mixed-halide salts (**4** and **5**) have been prepared, and their structures determined by single crystal X-ray diffraction. The results show the $[Me_2HNCH_2]_2{}^{2+}$ dication to be a highly flexible template for halide inclusion, thereby tolerating the assembly of anions of different size, with phase widths of $0 \leq x \leq 2$ for a monoclinic form with $[Me_2HNCH_2]_2I_{2-x}Br_x$ and $0 \leq x \leq 1$ for a triclinic form with $[Me_2HNCH_2]_2Br_{2-x}Cl_x$. The isotypic mixed halide compounds $[Me_2HNCH_2]_2IBr$ (**2**) and $[Me_2HNCH_2]_2BrCl$ (**4**) exhibit a statistical distribution of the anions in a structure of space group $P2_1/c$ which is also found for the pure diiodide $[Me_2HNCH_2]_2I_2$ (**1**). With an excess of chloride ($x > 1$ for $Br_{2-x}Cl_x$) this structure is converted into that of the pure dichloride, $[Me_2HNCH_2]_2Cl_2$ (**6**), with space group $P\bar{1}$. In all cases the halide anions are trapped in voids between the dications and fixed to the ammonium centers by strong N-H$\cdots$X and weak C-H$\cdots$X hydrogen bonding.

Key words: N,N,N',N'-Tetramethylethylenediammonium Dihalides, Mixed Halides, Hydrogen Bonding, Template, Anion Trapping

Introduction

Among the weakly attractive intermolecular forces, hydrogen bonding unquestionably is the most prominent chemical bonding [1]. The attractive interactions between closed-shell atoms [2] most frequently observed for nd^{10} species like the univalent cations of the coinage metals in general [3], and for gold(I) in particular (metallophilicity, aurophilicity [4]), and also for ns^2 and ns^{2}p^6 species [2,5], are of comparable energy only for the heaviest atoms where relativistic effects lead to significant contributions [6,7]. In modern molecular and crystal engineering hydrogen bonding has been employed for the construction of organic supramolecular systems in solid, liquid or gas phase because of its strength and directivity [1], more often than not following classical examples which are abundant in nature.

Aside from using their high potential as chelating or bridging ligands for main group and transition metals [8], α,ω-diaminoalkane molecules [9] and also α,ω-diammonioalkane cations [10] have been considered successfully as templates for the assembly of ionic components. The presence of N$^+$-H groups as the key functionalities for hydrogen bonding in the latter to-gether with the conformational flexibility of the hydrocarbon backbone make the α,ω-diammonioalkane cations ideal candidates for highly efficient and flexible templating agents in crystal engineering aiming at controlled anion inclusion. With the first representative featuring the shortest alkane chain in the series, the N,N,N',N'-tetramethylethylenediammonium dication $[tmedaH_2]^{2+}$, the solid state structures of the di*chloride* [11] and the di*bromide* [12] salts have recently been determined and shown to crystallize in different structures, although without major consequences for the overall structural pattern, which – regarding the cation-anion contacts – is dominated by strong hydrogen bonding. In order to study the flexibility of the N,N,N',N'-tetramethylethylenediammonium dication as a template for halide anions of different sizes, we became interested firstly in the structure of the 'missing link' in the series, the di*iodide*, and secondly in the phase widths of the corresponding *mixed halide* systems.

Results and Discussion

N,N,N',N'-Tetramethylethylenediammonium diiodide, $[tmedaH_2]I_2$, (**1**) and the two mixed salts with a

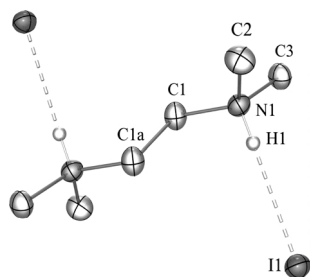Fig. 1. Molecular structure of $[Me_2HNCH_2]_2I_2$. Displacement ellipsoids are drawn at the 50% probability level, the unlabelled atoms are related to the labelled ones by a center of inversion. Selected bond lengths (Å) and angles (°): N1-C1 1.492(3), N1-C2 1.492(3), N1-C3 1.495(3), C1-C1A 1.531(4); C1-N1-C2 113.9(2), C1-N1-C3 110.3(2), C2-N1-C3 110.1(2); hydrogen bonds: N1-H1 0.82(3), H1···I1 2.589(7), N1···I1 3.400(2); N1-H1···I1 175.1(3).

I/Br and Br/Cl ratio of 1 : 1 (**2**) and (**4**) have been obtained in good yields as colorless materials by reacting tmeda with solutions of stoichiometric amounts of the corresponding hydrogen halides. All compounds were found to be readily soluble in hot methanol, and recrystallization from this solvent yielded crops of uniform, needle shaped crystals, the proposed composition of which was confirmed by microanalysis. Single crystal X-ray structure determinations revealed that compounds **1**, **2** and **4** were isotypic and furthermore isotypic to the previously characterised di*bromide* (**3**) [12], indicating statistical distribution of the mixed anions and a high tolerance of the adopted structure type regarding the size of the interstitial halides involved.

1, **2** and **4** crystallize in the monoclinic space group $P2_1/c$ with two formula units in the unit cell. The structure of the cations is determined by a center of inversion which is located in the middle of the central C-C bond, requiring an all-staggered *anti* configuration of the cations with the C-N bonds connecting to the two positively charged nitrogen atoms pointing in opposite directions. As expected, the coordination geometries around the ammonium centers are essentially tetrahedral, with an average C-N-C bond angle of 111.4°. This value as well as the C-C distances of 1.531(4) (**1**), 1.528(4) (**2**) and 1.519(5) (**4**) Å and the (average) C-N distance of 1.493 Å are in perfect agreement with those observed for the corresponding di*chloride* [111.2°; 1.526 and 1.491 Å] and di*bromide* salts [111.7°; 1.57 and 1.467 Å], respectively [11, 12].

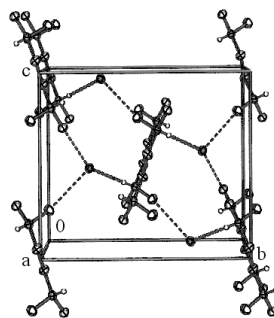The most prominent feature observed in the structures is the strong hydrogen bonding between the am-

Fig. 2. Unit cell packing diagram of **1**, showing the N-H···I and I···C_2 contacts.
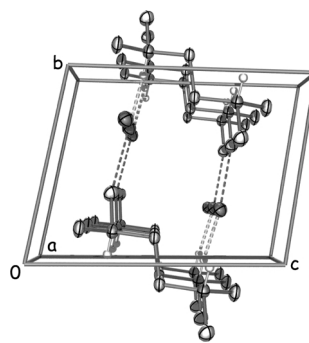

Fig. 3. Unit cell packing diagram of **6**, showing the N-H···Cl and Cl···C contacts.

monium centers and the halide counter ions, which is depicted for compound **1** in Fig. 1. The N···I distance of 3.400(2) Å shows the expected increase over the N···X separations of 3.012(3) and 3.183(3) Å of the corresponding $[tmedaH_2]^{2+}$ di*chloride* and di*bromide* salts and compares well with the N···I distance of 3.46(4) Å observed for trimethylammonium iodide [13]. The positions of the hydrogen atoms are not unambiguous, and the refined N-H distances may probably be too short owing to the inherent inadequacy of the methodology, but give a clear indication that the hydrogen atoms are more tightly bound to the nitrogen centers rather than to the halides [H···I: 2.589(7) (**1**), H···I/Br: 2.427(7) (**2**) and H···Br/Cl 2.160(6) (**4**) Å]. In all compounds the centroid of the three carbon atoms C1, C2, C3 attached to the nitrogen atom under consideration lies on the X···N vector within experimental error. Thus, the N-H···X hydrogen bonds must be approximately linear which firstly supports the geometry found experimentally [N-H···I: 175.1(3)° (**1**), N-H···I/Br: 175.7(3)° (**2**) and 175.1(3)° (**4**)], and secondly is indicative of particularly strong hydrogen bonding.

Table 1. Crystal data, data collection, and structure refinement for compounds **1 – 6**.

	[tmedaH$_2$]$^{2+}$ 2I$^-$ (**1**)	[tmedaH$_2$]$^{2+}$ I$^-$Br$^-$ (**2**)	[tmedaH$_2$]$^{2+}$ 2Br$^-$ (**3**) [12]	[tmedaH$_2$]$^{2+}$ Br$^-$Cl$^-$ (**4**)	[tmedaH$_2$]$^{2+}$ Br$_{0.4}^-$Cl$_{1.6}^-$ (**5**)	[tmedaH$_2$]$^{2+}$ 2Cl$^-$ (**6**)
Crystal data						
Formula	C$_6$H$_{18}$N$_2$I$_2$	C$_6$H$_{18}$N$_2$IBr	C$_6$H$_{18}$N$_2$Br$_2$	C$_6$H$_{18}$N$_2$BrCl	C$_6$H$_{18}$N$_2$Br$_{0.4}$Cl$_{1.6}$	C$_6$H$_{18}$N$_2$Cl$_2$
M$_r$	372.02	325.03	278.05	233.58	206.91	189.12
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	P2$_1$/c	P2$_1$/c	P2$_1$/c	P2$_1$/c	P$\bar{1}$	P$\bar{1}$
a [Å]	5.6512(1)	5.5505(2)	5.479(2)	5.3863(3)	5.7140(5)	5.7109(2)
b [Å]	11.2641(3)	11.0318(4)	10.827(5)	10.6204(6)	6.2077(5)	6.1387(3)
c [Å]	9.4189(2)	9.2468(4)	9.137(4)	8.9965(6)	7.9650(8)	7.9985(3)
α [°]	90	90	90	90	76.556(4)	76.326(4)
β [°]	94.968(1)	95.089(1)	95.5(4)	95.150(2)	79.630(4)	78.882(4)
γ [°]	90	90	90	90	72.124(6)	71.869(2)
V [Å^3]	597.31(2)	563.97(4)	539.5(5)	512.56(5)	259.71(4)	256.76(2)
ρ_{calc} [g cm^{-3}]	2.07	1.91	1.71	1.51	1.32	1.22
Z	2	2	2	2	1	1
F(000)	348	312	276	240	109	102
μ(Mo-K$_\alpha$) [cm^{-1}]	52.16	63.30	38.85	42.13	20.04	5.75
Data collection						
T [°C]	−130	−130	+25	−130	−130	−130
Measured reflections	16009	15821	1183	18459	11545	6660
Unique reflections	1165 [R$_{int}$ = 0.029]	1015 [R$_{int}$ = 0.026]	753	924 [R$_{int}$ = 0.034]	893 [R$_{int}$ = 0.031]	887 [R$_{int}$ = 0.030]
Absorption correction	DELABS [15]	DELABS [15]	–	DELABS [15]	DELABS [15]	DELABS [15]
T$_{min}$/T$_{max}$	0.589/0.876	0.742/0.928	–	0.604/0.882	0.433/0.811	0.400/0.795
Refinement						
Refined parameters	50	50	50	50	50	50
Final R values [I ≥ 2σ(I)]						
R1^a	0.0164	0.0163	0.0265	0.0246	0.0328	0.0253
wR2^b	0.0430	0.0399	0.0289	0.0556	0.0865	0.0628
ρ_{fin}(max/min) [eÅ^{-3}]	0.618/−0.396	0.365/−0.242	0.62	0.255/−0.218	0.389/−0.260	0.198/−0.158

^{a} $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; ^{b} $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0204$ (**1**), 0.0000 (**2**), 0.0000 (**4**), 0.0445 (**5**), 0.0139 (**6**); $b = 0.29$ (**1**), 0.41 (**2**), 0.52 (**4**), 0.14 (**5**), 0.10 (**6**).

The hydrogen-bonded Z-shaped 'molecular' units [tmedaH$_2$]X$_2$ are aligned in parallel strings along the *a* axis of the unit cell, with the strings slightly tilted with respect to the *ac*-plane. The hydrogen bonds are pointing upwards and downwards mainly in the direction of the *b* axis and the halide anions are trapped in voids formed between two neighboring strings tilted in opposite directions. Additionally, as depicted in Fig. 2 for compound **1**, each halide has distant contacts with two methyl groups of [tmedaH$_2$]I$_2$ units of two different strings. The shortest non-bonding distances to non-hydrogen atoms are I⋯C2 3.719(3) and I⋯C3 3.639(3) Å.

The corresponding values of the di*bromide* and the (average) values of the *mixed halides* **2** and **4** with their statistical distribution of the anions are Br⋯C2 3.587 and Br⋯C3 3.508 Å, Br/I⋯C2 3.628 and Br/I⋯C3 3.551 Å, and Br/Cl⋯C2 3.504 and Br/Cl⋯C3 3.438 Å, respectively. As a consequence of the orientation of the components and the differ-

ences in the distances, the unit cells of the isotypic compounds show their main variation in the *b* direction [*b* = 10.620(1) (Cl/Br), 10.827(5) (Br/Br), 11.032(1) (Br/I), 11.264(1) (I/I) Å]. The larger voids required for the intercalation of bigger anions are generated by the alignment of the strings at a greater distance in the *b*-direction, whereas the *a* and *c* axis are less effected by this 'cell-breathing' process (see Table 1) which allows for the high flexibility of the template (tmedaH$_2$)$^{2+}$ dication for halide inclusion.

However, a further decrease of the size of the anion is not tolerated, and the pure di*chloride* salt [tmedaH$_2$]Cl$_2$ (**6**) crystallizes in the triclinic space group P$\bar{1}$ with Z = 1 [11], although with only minor consequences for the cation/anion arrangement in their supramolecular assembly. The results of the redetermined structure of the di*chloride* also reveal a dication in an *anti*-conformation with the chloride counter ions tightly attached *via* strong hydrogen bonding [N⋯Cl 3.017(3) Å, N-H⋯Cl 176.4(3)°]. The result-

ing Z-shaped units line up into parallel strings along the *a* axis, with the central C-C bonds of the dications almost vertically oriented with respect to the *ac* plane. The main structural difference as compared to the isotypic family of **1**, **2** and **4** arises from the relative orientation of the neighboring strings, which codetermine the accommodation of the counter ions through $H_3C\cdots Cl$ contacts. In contrast to the situation described above for the monoclinic series, the strings in the triclinic series are arranged in an eclipsed way in direction of the *b* axis, thereby giving rise to voids which allow for only one such contact per chloride anion [$Cl\cdots C2$ 3.512(3) Å]. This triclinic packing obviously is less flexible with respect to the size of the intercalated anions, since it is abandoned in favour of the monoclinic packing if equal amounts of Cl^- and Br^- are provided in the synthesis. However, when an excess of HCl is supplied in the presence of only smaller amounts of HBr in the reaction with tmeda, *mixed halides* up to the composition $[Me_2HNCH_2]_2Br_{0.4}Cl_{1.6}$ (**5**) can be isolated, which turned out to be isotypic to the di*chloride*, showing that the dichloride phase on its part is capable to accommodate the larger bromide ions up to at least 20% of the halide capacity.

Conclusion

The present study has shown that N,N,N',N'-tetramethylethylenediammonium di*iodide* and di*bromide* are isotypic (monoclinic, space group $P2_1/c$) and that the cation template tolerates the accommodation of mixed Br/I stoichiometries. With increasing contents of Br^-, the unit cell shrinks mainly affecting the crystallographic *b* axis. By contrast, introduction of Cl^- into the di*bromide* salt leads to a transformation into the triclinic form (space group $P\bar{1}$) characteristic of the pure di*chloride*. The latter can accommodate only up to 20% of Br^- before the transformation occurs. Regardless of the crystal system, the structures can be described as a packing of $XHNMe_2CH_2CH_2NMe_2NHX$ 'molecules' in an *all-trans*-conformation with the halide anions fixed tightly to the ammonium centers *via* strong, linear N-$H\cdots X$ hydrogen bonds.

Experimental Section

Preparation of compounds

N,N,N',N'-*Tetramethylethylenediammonium diiodide*, *$[Me_2HNCH_2]_2I_2$* (**1**): 1.00 g (8.6 mmol) of N,N,N',N'-tetramethylethylenediamine (tmeda) was dissolved in 50 ml

of methanol, followed by the slow addition of 3.28 g of an aqueous solution of HI (67% HI, 17.2 mmol). The reaction mixture was stirred for 1 h, and the colorless precipitate was collected and recrystallized twice from boiling methanol. Yield: 91% (2.90 g, 7.80 mmol), m.p. 254 °C (dec.). – ^{1}H NMR (d^6-DMSO, room temperature) $\delta = 9.47$ (br., s, 2 H, N-*H*), 3.51 (s, 4 H, C*H$_2$*), 2.89 (s, 12 H, C*H$_3$*) ppm. – ^{13}C{^{1}H} (d^6-DMSO, room temperature) $\delta = 50.5$ (*C*H$_2$), 43.0 (*C*H$_3$) ppm. – Analysis for $C_6H_{18}I_2N_2$: calcd. C 19.37, H 4.88, I 68.22, N 7.53; found C 19.61, H 4.86, I 67.88, N 7.58.

N,N,N',N'-*Tetramethylethylenediammonium bromide iodide*, *$[Me_2HNCH_2]_2BrI$* (**2**): Following the same procedure using 1.00 g (8.6 mmol) of tmeda and a mixture of 2.11 g of a solution of HBr in acetic acid (33% HBr, 8.6 mmol) and 1.64 g of an aqueous solution of HI (67% HI, 8.6 mmol). The colorless crystalline precipitate was collected and recrystallized twice from boiling methanol. Yield: 88% (2.46 g, 7.6 mmol), m.p. 255 °C (dec.). – ^{1}H NMR (d^6-DMSO, room temperature) $\delta = 9.64$ (br., s, 2 H, N-*H*), 3.49 (s, 4 H, C*H$_2$*), 2.85 (s, 12 H, C*H$_3$*) ppm. – ^{13}C{^{1}H} (d^6-DMSO, room temperature) $\delta = 50.6$ (*C*H$_2$), 42.8 (*C*H$_3$) ppm. – Analysis for $C_6H_{18}BrIN_2$: calcd. C 22.17, H 5.58, Br 24.6, I 39.0, N 8.62; found C 22.09, H 5.65, Br 23.6, I 40.6, N 8.56.

N,N,N',N'-*Tetramethylethylenediammonium bromide chloride*, *$[Me_2HNCH_2]_2BrCl$* (**4**): Following the same procedure using 1.00 g (8.6 mmol) of tmeda and a mixture of 2.11 g of a solution of HBr in acetic acid (33% HBr, 8.6 mmol) and 0.85 g of an aqueous solution of HCl (37% HCl, 8.6 mmol). The colorless crystalline precipitate was collected and recrystallized twice from boiling methanol. Yield: 89% (1.78 g, 7.6 mmol), m.p. 274 °C (dec.). – ^{1}H NMR (d^6-DMSO, room temperature) $\delta = 10.18$ (br., s, 2 H, N-*H*), 3.50 (s, 4 H, C*H$_2$*), 2.84 (s, 12 H, C*H$_3$*) ppm. – ^{13}C{^{1}H} (d^6-DMSO, room temperature) $\delta = 50.7$ (*C*H$_2$), 42.6 (*C*H$_3$) ppm. - Analysis for $C_6H_{18}BrClN_2$: calcd. C 30.85, H 7.77, N 11.99; found C 31.01, H 7.89, N 11.78.

$[Me_2HNCH_2]_2Br_{0.4}Cl_{1.6}$ (**5**): Following the same procedure using 1.00 g (8.6 mmol, 1 eq.) of tmeda and a mixture of 1.27 g of a solution of HBr in acetic acid (33% HBr, 5.2 mmol, 0.6 eq.) and 1.19 g of an aqueous solution of HCl (37% HCl, 12.1 mmol, 1.4 eq.). The colorless crystalline precipitate was collected and recrystallized twice from boiling methanol. Yield: 79% (1.40 g, 6.8 mmol), m.p. 284 °C (dec.). – ^{1}H NMR (d^6-DMSO, room temperature) $\delta = 10.52$ (br., s, 2 H, N-*H*), 3.49 (s, 4 H, C*H$_2$*), 2.82 (s, 12 H, C*H$_3$*) ppm. – ^{13}C{^{1}H} (d^6-DMSO, room temperature) $\delta = 50.0$ (*C*H$_2$), 42.9 (*C*H$_3$) ppm. – Analysis for $C_6H_{18}Br_{0.4}Cl_{1.6}N_2$: calcd. C 34.83, H 8.77, N 13.54; found C 34.58, H 8.99, N 13.01.

N,N,N',N'-*Tetramethylethylenediammonium dichloride*, *$[Me_2HNCH_2]_2Cl_2$* (**6**): Following the same procedure using 1.00 g (8.6 mmol) of tmeda and 1.7 g of an aqueous solu-

tion of HCl (37% HCl, 17.2 mmol). The colorless crystalline precipitate was collected and recrystallized twice from boiling methanol. Yield: 85% (1.38 g, 7.3 mmol), m. p. 288 °C (dec.). – ^{1}H NMR (d^6-DMSO, room temperature) $\delta = 10.66$ (br., s, 2 H, N-H), 3.48 (s, 4 H, CH_2), 2.82 (s, 12 H, CH_3) ppm. – ^{13}C{^{1}H} (d^6-DMSO, room temperature) $\delta = 50.7$ (CH_2), 43.0 (CH_3) ppm. – Analysis for $C_6H_{18}Cl_2N_2$: calcd. C 38.11, H 9.59, Cl 37.5, N 14.81; found C 38.13, H 9.62, Cl 37.5, N 14.79.

X-ray structure determinations

Specimens of suitable quality and size were mounted at the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-K$_\alpha$ radiation. The structures of the dichloride (**6**) and the diiodide (**1**) salts were solved by a combination of direct methods (SHELXS-97) [14] and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97). Refinements of the mixed-halide crystals [Br/I, (**2**) and Cl/Br (**4**) and (**5**)] were performed by using the atomic coordinates of the diiodide (**1**) and the dichloride (**6**), respectively. The s.o.f.'s of the anion sites in the mixed halides **2**, **4**, and **5** were refined and then fixed in the final stage of the refinements. In all cases, the obtained data gave no indication for the presence of super-structures. Displacement parameters were treated anisotropically for all non-hydrogen atoms. The methyl and methylene hydrogen atoms of the dications were calculated and allowed to ride on their parent atoms with fixed isotropic contributions, whereas the ammonium hydrogen atoms were located and included into the refinements with isotropic contributions. Further information on crystal data, data collection and structure refinement are summarized in Table 1. The corresponding information on the dibromide salt **3** [12] was included for comparison. Displacement parameters and complete tables of interatomic distances and angles of compounds **1**, **2**, **4**, **5**, and **6** have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDC- 247438 – 247442.

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