Polybromides

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[C$_4$MPyr]$_2$[Br$_{20}$]: Ionic-Liquid-Based Synthesis of a Three-Dimensional Polybromide Network**

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In memory of Hans-Georg von Schnering

Ionic liquids (IL) are claimed to exhibit a range of exceptional properties. This includes a wide liquid range (−50 to +400 °C), an excellent thermal stability (up to 400 °C), a wide electrochemical window (−4 V to +4 V), and a low vapor pressure.[1] They can be composed of hundreds of different cation/anion combinations, which allows a specific fine-tuning of their solvent properties (e.g. polarity, miscibility with other solvents, solubility of starting material, magnetic/luminescent properties).[1,2] Based on their exceptional features, ionic liquids can provide opportunities for chemical synthesis that differ significantly from conventional solvents, such as liquid NH$_3$ or SO$_2$, hydrothermal and solvothermal synthesis to classical molten alkali-metal halides.[3] To date, ionic liquids have already had a considerable impact on organic synthesis,[4] synthesis of nanoparticles,[5] in catalysis,[6] or the development of inert electrolytes.[7] However, the comparatively high costs and a dramatic drop in quality when contaminated with even traces of water or impurities stemming from the synthesis or thermal decomposition of ionic liquids, on the other hand, are drawbacks.

Taking the exceptional properties of ionic liquids for granted, the question arises whether they offer any benefit to inorganic synthesis. Exploration of this area has just begun. Some first results, such as a fascinating germanium clathrate or the chemistry of weakly coordinating anions (WCAs), suggest that ionic liquids indeed may give access to unique compounds and chemical reactions as compared to conventional solvents in inorganic chemistry.[8]

As a part of our studies,[9] we have explored the stability of ionic liquids towards strongly oxidizing halogens with a view to forming halogen-rich compounds. To this context, the polyhalides represent textbook chemistry and have been of particular interest for many years.[10] To date the class of the polyhalides is dominated by the polyiodides exhibiting a generalized composition $[I_{n+m}]^{m-}$ (with $n \times I^0$ and $m \times I^-$).[11] Their structural versatility is considered to be derived from the donor–acceptor interaction between the Lewis bases I$^-$ and [I$_3$]$^-$ and the Lewis acid I$_2$. These subunits act as "building blocks" and can be combined to extended polyiodide anions, such as [I$_{26}$]$^{3-}$ or [I$_{29}$]$^{3-}$.[11b,12] Considering iodine contacts up to the sum of the doubled van der Waals radii (i.e. 420 pm), a description as infinite one-, two-, or three-dimensional networks is often viable.[13] More details regarding the huge number of different polyiodides are summarized in a Review by Svenson and Kloo.[10]

Owing to their increasing reactivity and vapor pressure, knowledge on the lighter halogens and polyhalides is much more limited. In fact, polybromides are limited to [Br$_3$]$^-$, linear [Br$_4$]$^{2-}$, Z-shaped [Br$_8$]$^{2-}$, and ring-type [Br$_{10}$]$^{2-}$.[14] Moreover, $[C_5H_6S_4Br]^+[(Br_3)^-(^1/_2\,Br_2)]$ and $[H_4Tppz^{4+}][(Br^-)_2(Br_4)^{2-}]$ (Tppz: tetra(2-pyridyl)pyrazine) are one-dimensional (1D) polybromide networks.[15] And with $[TtddBr_2]^{2+}[(Br^-)_2(Br_2)_3]$ ($[TtddBr_2]^{2+}$: 4,5,9,10-tetrathiocino-[1,2-*b*:5,6-*b*′]-1,3,6,8-tetraethyl-diimidazolyl-2,7-dibromdithionium) a two-dimensional (2D) infinite polybromide network has been reported recently.[16] Finally, [Cl$_3$]$^-$ and V-shaped [(Cl$_3$)(Cl$_2$)]$^-$ are the only known polychlorides.[17] The existence of polyfluorides in addition to [F$_3$]$^-$ is still part of a controversial discussion.[18]

By carrying out the synthesis in ionic liquids, we have now prepared [C$_4$MPyr]$_2$[Br$_{20}$] (C$_4$MPyr: *N*-Butyl-*N*-methylpyrrolidinium), the first three-dimensional (3D) polybromide network. According to an alternative description, $[C_4MPyr]_2[Br^-]_2\cdot 9(Br_2)$, the compound contains nine dibromine molecules, a remarkable amount and the highest amount of bromine ever observed—except for the element itself. The compound was obtained with a yield of about 90 % by dissolving elemental bromine in an equimolar mixture of the ionic liquids [C$_{10}$MPyr]Br (C$_{10}$MPyr: *N*-decyl-*N*-methylpyrrolidinium) and [C$_4$MPyr]OTf (OTf: triflate). The [C$_{10}$MPyr]Br serves as a "bromide donor", and [C$_4$MPyr]OTf acts as a "liquifier" to establish an eutectic mixture that is a liquid even below room temperature. This property is necessary for the growth of suitable single crystals as the resulting deep red, highly sensitive crystals melt at about +9 °C.

According to single-crystal structure analysis, [C$_4$MPyr]$_2$[Br$_{20}$] is triclinic with space group $P\bar{1}$.[19] The compound consists of a central bromide anion (Br1) that is coordinated by six dibromine molecules (Figure 1). Note that all the central bromide anions are equivalent by inversion symmetry. Four of the Br$_2$ molecules serve as direct linkers between two central bromide anions (Br1). The remaining two dibromine molecules (Br3-Br4, Br5-Br6) are also linked

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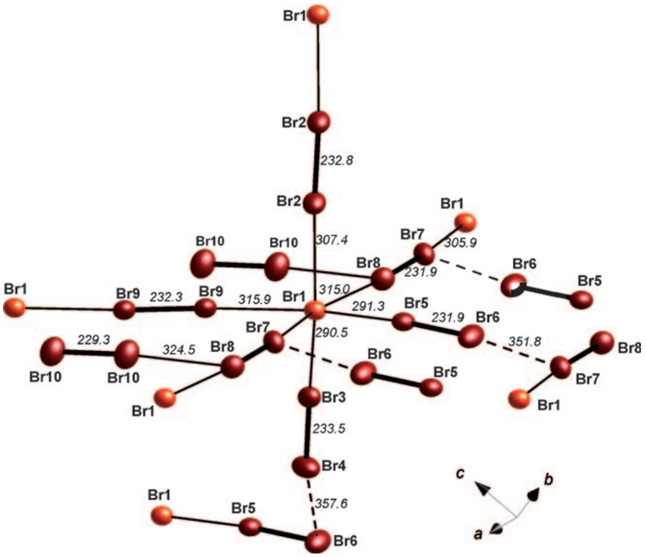

Figure 1. $[\mathrm{C_4MPyr}]_2[\mathrm{Br}_{20}]$ with the central bromide anion (Br1, light red) as the network node with coordinating dibromine molecules (Br_2, dark red) as linkers (all Br–Br distances in pm; all thermal ellipsoids set at 50% probability).

to the central bromide (Br1), and to another dibromine molecule (Br5-Br6, Br7-Br8) that is further away (352 and 358 pm) and perpendicular to the first. This arrangement results in a connectivity between Br1 atoms through three (Br1-Br5-Br6···Br7-Br1) and four (Br1-Br3-Br4···Br6-Br5-Br1) bromine atoms (Figure 1). Beside the octahedral coordination of Br_2 molecules around the central bromide, finally, an additional dibromine molecule (Br10-Br10) is attached to Br8 (Figure 1).

Three different types of Br-Br distances are observed in $[\mathrm{C_4MPyr}]_2[\mathrm{Br}_{20}]$. The shortest distances (229–234 pm) represent the dibromine molecules and are slightly elongated in comparison to the element in the solid state (227 pm).[3] Next, distances between dibromine molecules and the central bromide anion range from 291 to 316 pm. And finally even longer distances, between 325 and 358 pm, are observed between different dibromine molecules. These distances are still significantly below the doubled van der Waals radius of bromine (370 pm; Figure 1, Table 1). A classification of $[\mathrm{C_4MPyr}]_2[\mathrm{Br}_{20}]$ in view of known polyhalides is not straightforward. Since the Br^-–(Br_2) distance for two dibromine molecules is about 5% shorter (291 pm on average) than to the remaining four (311 pm on average), a polymerized V-shaped (∡:102°) $[\mathrm{Br}_5]^-$ anion might be postulated. Such a $[\mathrm{Br}_5]^-$ ion has not yet been reported. On the other hand, the Br–Br distances are much more similar to each other than the intramolecular/intermolecular distances in the polyiodides with common subunits $[\mathrm{I}_{n+m}]^{m-}$ (with $n\times\mathrm{I}^0$ and $m\times\mathrm{I}^-$).[11] As a consequence, describing $[\mathrm{C_4MPyr}]_2[\mathrm{Br}_{20}]$ as a 3D network $^3_\infty[(\mathrm{Br}^-)_2(\mathrm{Br}_2)_9]$ is much more meaningful. And this 3D network is established without involving any element other than bromine. In addition to the unique 3D network as well as the surprisingly high coordination of the central bromide by dibromine molecules, the compound contains an even higher amount of the halogen (i.e. $\mathrm{Br}^0{:}\mathrm{Br}^- = 18{:}2 = 9.00$) than the most iodine-rich polyhalide $\mathrm{Fc_3I_{29}}$ ($\mathrm{I}^0{:}\mathrm{I}^- = 26{:}3 = 8.67$, Fc: ferrocenium).[11b]

Table 1: Br–Br distances (below the doubled van der Waals radius of 370 pm) of $[\mathrm{C_4MPyr}]_2[\mathrm{Br}_{20}]$ and selected reference compounds.

Compound[a]	Br–Br [pm] (shortest distances)	Br–Br [pm] (distances < 370 pm)	Reference
$[\mathrm{C_4MPyr}]_2[\mathrm{Br}_{20}]^{2-}$	229–234	291–316 (Br^-–Br_2) 352–358 (Br_2–Br_2)	
Br_2 (solid)	227	331 within layers (399 between layers)	[3]
$[\mathrm{Q}^+][\mathrm{Br}_3]^-$	246–265	–	[14b]
$[\mathrm{Q}^+]_2[\mathrm{Br}_8]^{2-}$	235–266	317–369	
$[\mathrm{Dpfz}^+]_2[\mathrm{Br}_{10}]^{2-}$	274–294	347–350	[14c]
$[\mathrm{C_5H_6S_4Br}]^+[\{\mathrm{Br}_3\}^-(^1/_2\,\mathrm{Br}_2)]$	233–255	321–344	[15a]
$[\mathrm{H_4Tppz}^{4+}][(\mathrm{Br}^-)_2\{\mathrm{Br}_4\}^{2-}]$	242–297		[15b]
$[\mathrm{TtddBr}_2]^{2+}[(\mathrm{Br}^-)_2(\mathrm{Br}_2)_3]$	236–241	304–370	[16]

[a] Q^+: quinuclidinium; Dpfz: 1,5-Diphenylformazan.

Structurally the bromine network in $[\mathrm{C_4MPyr}]_2[\mathrm{Br}_{20}]$ can be formally rationalized based on distorted, corner-sharing $[(\mathrm{Br}^-)(\mathrm{Br}_2)_4(2\,\mathrm{Br}_2)_2]^-$ octahedra (Figure 2). The distortion originates from the different Br^-–Br_2 distances and because the interlinking of the central bromide (Br1) involves in four

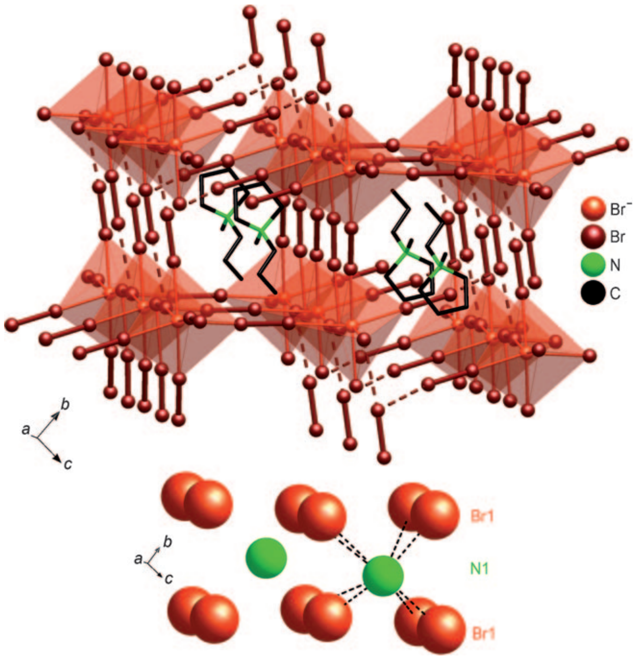

Figure 2. Top: $^3_\infty[(\mathrm{Br}^-)_2(\mathrm{Br}_2)_4(2\mathrm{Br}_2)_2(\mathrm{Br}_2)]$ network in $[\mathrm{C_4MPyr}]_2[\mathrm{Br}_{20}]$ established by distorted corner-sharing $[(\mathrm{Br}^-)(\mathrm{Br}_2)_4(2\,\mathrm{Br}_2)_2]^-$ octahedra (light red) with the central bromide anion (Br1) as the network node that is interlinked by dibromine molecules (dark red with bold line). The $[\mathrm{C_4MPyr}]^+$ ion serves as a templating agent in between the polybromide 3D networks. Bottom: The correlation with a distorted CsCl-type structure, visualized by considering only the central bromide anion and the nitrogen atom as the center of the cation.

cases a single dibromine and in two cases two dibromine molecules. Note that the ninth dibromine molecule (Br10-Br10) is not bound to Br1 (Figure 1). Thus, a $^{3}_{\infty}[(Br^-)_2(Br_2)_4(2Br_2)_2(Br_2)]$ network is obtained that includes $[C_4MPyr]^+$ ions as a kind of a template. Even the shortest C–H···Br distances (292 pm, cf. Figure S1 in the Supporting Information) are longer than what is typically discussed as bromine-hydrogen-bridge bonding (240–290 pm).[20] The long-ranging Madelung-type charge interaction between $[C_4MPyr]^+$ and the anionic network is nevertheless an important aspect with respect to the stability of the 3D polybromide. Noteworthy, the structure of $[C_4MPyr]_2[Br_{20}]$ can also be described as a distorted CsCl-type of structure (Figure 2). This becomes clear when only considering the central bromide anion (Br1) and the nitrogen atom as the center of the cation. With this interpretation, the Br^- serves as a network node that is interconnected by dibromine linkers.

Polybromides and bromine-containing compounds are very rare to date. Typically, they consist of anionic bromidometallate-like building units and complexes such as $[Cu_2Br_6]^{2-}$, $[Se_2Br_{10}]^{2-}$, $[Sb_2Br_9]^{3-}$ or $[(Me_3P)AuBr_3]$, which are most often bridged together by one or two dibromine molecules.[21] In this respect, $[(C_4H_9)_4N]^+{}_2[Pt_2Br_{10}]^{2-}(Br_2)_7$ represents the compound with the highest bromine content to date.[22] Furthermore, $[TtddBr_2]^{2+}[(Br^-)_2(Br_2)_3]$—discussed above—is the only example of an infinite polybromide 2D network without any additional element being involved.[16] Nevertheless in this compound a certain stabilization occurs through the interaction with sulfur and hydrogen atoms of the respective cations. As a result, $[C_4MPyr]_2[Br_{20}]$ is—to our knowledge—the first polybromide 3D network that is established exclusively by bromine atoms.

In view of the unique features of $[C_4MPyr]_2[Br_{20}]$ a final question remains: What is special about the ionic liquid? In this case, the stability of the eutectic mixture $[C_{10}MPyr]Br/[C_4MPyr]OTf$ towards oxidation is a clear benefit. Even more important, however, is the low vapor pressure of dibromine in this eutectic ionic liquid. Qualitatively this can be rationalized just by looking at the gas phase above molten $[C_4MPyr]_2[Br_{20}]$ crystals at room temperature (Figure 3). In contrast to the pure element, the characteristic deep brown color of dibromine in the gas phase is missing. This finding closely correlates to the frequently reported low vapor pressure/high solubility of gases (e.g. H_2, Ar, CO_2) in ionic liquids.[1,2,23] Thermogravimetry allows the thermal decomposition to be quantified in detail (Figure 3); $[C_4MPyr]_2[Br_{20}]$ decomposes with four steps: a) 60–190 °C (16.7 %), b) 190–290 °C (28.1 %), c) 290–420 °C (23.7 %), d) 420–550 °C (25.1 %). Although several reactions may certainly occur in parallel (e.g., evaporation of dibromine, radical bromination, evaporation of HBr, fragmentation of $[C_4MPyr]^+$), it is possible to rationalize the decomposition as follows: a) $-2\,Br_2$ (calcd 17.0 %), b) $-7\,HBr$ (calcd 30.0 %), c) $-2\,C_3H_6Br_2$ (calcd 21.4 %), d) $-C_6H_{10}NBr_3/C_6H_{11}NBr_2$ (calcd 31.5 %). The overall good agreement between experiment and calculation further shows the phase purity of $[C_4MPyr]_2[Br_{20}]$.

The real surprise, however, is that no loss of dibromine occurred up to a temperature as high as +60 °C. This low tendency of dibromine to evaporate can be regarded as a crucial aspect for the success of the preparation of bromine-rich compounds, such as the polybromide 3D-network $[C_4MPyr]_2[Br_{20}]$. In this respect, ionic liquids can open a doorway to novel halogen-rich compounds and an extension of the chemistry of the halogens. Moreover, ionic liquids may serve as a reservoir for bromine storage that—because of the low vapor pressure—allows a safer handling of the highly reactive halogens in laboratories.

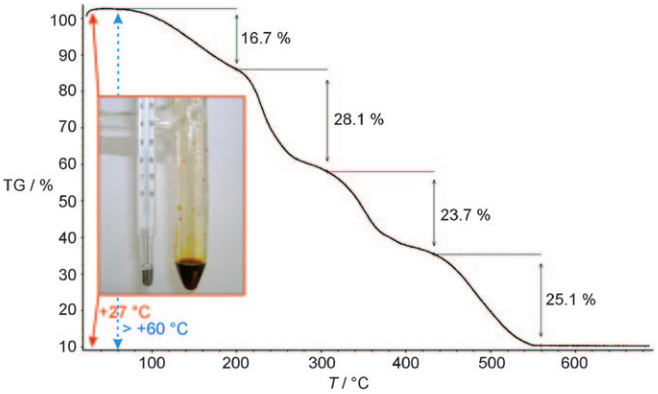

Figure 3. Photograph of liquid $[C_4MPyr]_2[Br_{20}]$ at +27 °C and thermogravimetry of the pure compound indicating a four-step weight loss between +60 °C and +560 °C.

Experimental Section

All synthetic work and sample manipulation was performed using standard Schlenk techniques or glove boxes. By adding an excess of dibromine to an eutectic, equimolar mixture of the ionic liquids $[C_{10}MPyr]Br$ and $[C_4MPyr]OTf$, a light red solution was obtained. Cooling the mixture from room temperature to −15 °C results in a precipitation of $[C_4MPyr]_2[Br_{20}]$ as well as in a partial crystallization of the ionic liquids. Deep red, highly adhesive single crystals were obtained by slowly thawing this mixture to +5 °C. At temperatures of +9 °C $[C_4MPyr]_2[Br_{20}]$ compound is completely dissolved again. A suitable single crystal of $[C_4MPyr]_2[Br_{20}]$ was selected at −20 to −15 °C under cooled nitrogen flow and mounted in perfluoropolyalkylether oil on top of a glass fiber. The red crystals of $[C_4MPyr]_2[Br_{20}]$ are extremely sensitive towards moisture and contact to air. $[C_4MPyr]_2[Br_{20}]$ can be obtained in large quantities with about 90 % yield.

Thermogravimetry (TG) and differential thermoanalysis (DTA) were performed with a STA409C device (Netzsch, Selb, Germany). The measurements were performed in dried nitrogen. The sample was selected under a flow of cool nitrogen (20 mg in corundum crucibles) and then heated from room temperature to +700 °C at a rate of 10 °C min^{-1}. Note that minor amounts of black carbon remain inside the crucible.

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[19] Data collection was performed at 200 K on an IPDS II image plate diffractometer (Stoe, Darmstadt) using graphite-monochromatized $\mathrm{Mo}_{\mathrm{K}\alpha}$ (71.073 pm) radiation and a low-temperature device. After data reduction by X-RED (Stoe, Data Reduction Program, Version 1.14, Darmstadt **1999**), space-group determination was carried out on the basis of systematic absences by XPREP (Stoe, Data Reduction Program, Version 1.14, Darmstadt **1999**). Structure solution and refinement were performed by direct methods and refined by full-matrix least-squares against F^2 with SHELXTL (Bruker, Structure Solution and Refinement Package, Version 5.1, Karlsruhe **1998**). All non-hydrogen atoms were refined with anisotropic displacement parameters. The position of the hydrogen atoms could not be fixed by Fourier refinement and was therefore modeled based on idealized C–H bonds. X-SHAPE (Stoe, Crystal Optimisation for Numerical Absorption Correction, Version 1.06, Darmstadt **1999**) was used to apply a numerical absorption correction based on crystal-shape optimization. Illustrations of the crystal structures were prepared via DIAMOND (Crystal Impact, Visuelles Informationssystem für Kristallstrukturen, Version 3.0d, Bonn **2005**). $C_{18}H_{40}N_2Br_{20}$: $M_r = 1882.6$, triclinic, $P\bar{1}$, $a = 847.5(2)$, $b = 1099.6(2)$, $c = 1313.8(3)$ pm, $\alpha = 88.77(3)$, $\beta = 80.12(3)$, $\gamma = 75.85(3)°$, $V = 1169(3) \times 10^6$ pm^3, $Z = 2$, $\rho(\text{calcd}) = 2.67$ g cm^{-3}, $\mu = 17.13$ cm^{-1}, $T = 200(1)$ K; 5839 observed reflections, of which 3627 are independent ($R_{\text{int}} = 0.049$), 185 parameters, $R1 = 0.044$ ($I > 2\sigma(I)$), $wR2 = 0.105$ (all data), GooF = 0.984. CCDC 811451 contains 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.

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