

I$_6^{2-}$ Anion Composed of Two Asymmetric Triiodide Moieties: A Competition between Halogen and Hydrogen Bond

Martin van Megen and Guido J. Reiss *

Institut für Anorganische Chemie und Strukturchemie, Lehrstuhl für Material- und Strukturforschung, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf, Germany; E-Mail: martin.megen@uni-duesseldorf.de

* Author to whom correspondence should be addressed; E-Mail: reissg@hhu.de; Tel.: +49-211-81-13164; Fax: +49-211-81-14146.

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**Abstract:** The reaction of 1,8-diaminoctane with hydroiodic acid in the presence of iodine gave a new polyiodide-containing salt: 1,8-diaminooctane bis(triiodide), (H$_3$N-(CH$_2$)$_8$-NH$_3$)[I$_3$]$_2$. The title compound has been characterized by crystallographic and spectroscopic methods. The polyiodide ion is the first example of a hydrogen bonded I$_6^{2-}$ dianion consisting of two very asymmetric triiodide components with I–I distances of 2.7739(4) and 3.1778(4) Å interacting by a weak halogen bond (I···I: 3.5017(2) Å). The structural parameters of the triiodide anions, derived from X-ray crystallographic data, are in good agreement with the Raman and Far-IR spectroscopic results.

**Keywords:** polyiodide; 1,8-diaminooctane; triiodide; crystal structure; IR and Raman spectroscopy

1. Introduction

The term “polyiodide” defines an extended part of salt structures which fulfill the general formula I$_{2n+m}$($n = 1–4$, $m =$ integer) [1–4]. They are built from I$, I_3^-$ and I$_2$ subunits and are known for their strong tendency to concatenate, forming extended motifs connected by halogen bonding [5–9]. Accurate relativistic correlated quantum chemical calculations of the halogen bond of the triiodide anion have been reported [10]. Some more complex polyiodides have been theoretically investigated in the recent years [11,12], and the general theory of halogen bonding has been improved [13–15]. There
is also a general interest in diaminiumalkane iodide/triiodide systems derived from the knowledge that the choice of the diaminium cation significantly modifies the redox potential in dye-sensitized solar cells (DSSC) [16–21]. They play an important role in other electrochemical processes, e.g., lithium iodide batteries [22,23] or hydrogen production as well [24]. It is also well known that polyiodide chains, in the solid state, conduct the electric current by a Grotthuss-like mechanism [25,26]. Therefore the structures of chain-type polyiodides can be considered as a snapshot and model systems of this phenomenon. In the recent years several groups have synthesized different compounds using stick-shaped molecules and ions. There are several interesting classes of compounds in which the rod-shaped building blocks determine the shape and pore size of the framework [27,28]. The rod-shaped building blocks can be understood as tectons used for the crystal engineering of new functional materials [29,30]. It has been shown, especially for polyiodides, that tailored materials can be constructed, and that their structures fit with the lengths and shapes of the tectons used [31–39]. This selective and robust synthetic protocol for solid polyiodides using rod-shaped tectons or templates is now generally termed \textit{dimensional caging} [31]. Salts constructed by α,ω-diaminiumalkanes represent an interesting class of organic-inorganic hybrid materials with a number of different structural arrangements including: layered materials [40]; hydrogen bonded frameworks as host systems for unusual species [41]; large-pore zeolites [42]; non-metal frameworks [43] and metal-frameworks [44,45]. We have already shown that the semi-flexible cationic α,ω-diaminiumalkanes are useful tectons for the construction of new polyiodides [46–49]. In this report we describe the structural and the spectroscopic properties of a halogen bonded $I_6^{2−}$ anion.

\section*{2. Results and Discussion}

\subsection*{2.1. Crystal Structure}

From the reaction of 1,8-diaminoctane with hydroiodic acid in the presence of a 1.5 molar excess of iodine dark-red crystals of 1,8-diaminiumoctane bis(triiodide) (\textit{18dbt}) were obtained. A higher excess of iodine gave the title compound together with elemental iodine. Experiments with a lower excess of iodine gave a hitherto not completely characterized compound with the stoichiometry 1,8-diaminiumoctane/I = 1/3.5. The asymmetric unit of \textit{18dbt} consists of one half of a 1,8-diaminiumoctane dication located around a center of inversion and one triiodide anion in the centrosymmetric space group $P\overline{1}$. The cation shows an all-trans extended conformation with bond lengths and angles in the expected ranges (Table 1). In the \textit{18dbt} the rod-shaped 1,8-diaminiumoctane dications are connected to the polyiodide substructure via medium strong hydrogen bonds. Each hydrogen atom of the aminium group donates one hydrogen bond to one neighboring iodine atom. The N···I distances of 3.592(4), 3.653(5) and 3.688(4) Å indicate that the strengths of the bonds are similar. One iodine atom (I1) of the formal triiodide anion accepts three hydrogen bonds, whereas the two other iodine atoms are not involved in any hydrogen bonding (Figure 1; Table 2). The I–I distances of 2.7739(4) and 3.1778(4) Å in the $I_3^−$ subunits are significantly more asymmetric than those in similar triiodide anions discussed so far [50,51], whereas the bond angle within these triiodide units shows typical 178°.
The asymmetry of this triatomic arrangement seems to be engendered in first instance by the electron drawing influence of the three hydrogen bonds accepted by the terminal iodine atom I1. Therefore, the structure could alternatively be understood as an inclusion compound with iodine molecules strongly coordinated to an electron-poor iodide anion. The distance between two neighboring triiodide anions in this structure is 3.5017(2) Å, which falls in the typical range of secondary I–I halogen interactions [5]. In contrast, the angle of 163° between the two units is unexpectedly acute. The arrangement found may be compared to that of two I3− ions (I–I distances within the I3− unit of 2.87 and 3.01 Å) trapped in a van der Waals hole of a hydrogen-bonded framework, which are separated by 3.63 Å [33]. Hence, the arrangement of two very asymmetric triiodide ions may be understood as the second, in this case hydrogen bonded, example of an I62− anion.
Figure 2. The staircase-shaped hydrogen bonded motif in $\text{18dbt}$. Each staircase-shaped unit (shadowed) is constructed by two cyclic elements with the graph-set descriptor $R^2_{4}(8)$. The polyiodides and the alkan-diyl units connect these hydrogen-bonded strands to a three-dimensional framework (symmetry code: $' = 2 - x, -y, 2 - z$).

The hydrogen bonds between the dications and the polyiodide anions form a three-dimensional framework. Following the typical design of $\alpha,\omega$-diaminiumalkane polyiodide salts [46–49], the rod-shaped building blocks are arranged approximately parallel to each other. Each hydrogen atom of the aminium group donates one un-bifurcated hydrogen bond to a neighboring iodine center (Figure 2). The structure shows the eight membered hydrogen-bonded ring-motif $R^2_{4}(8)$ [52] which is well known for diaminiumalkyl polyiodides [46,49]. These ring motifs form staircase-shaped one-dimensional hydrogen-bonded units along [100] (Figure 2). The polyiodides and the alkan-diyl units connect the hydrogen-bonded strands to a three-dimensional framework (Figure 3).

Figure 3. A view along [100] shows the crosslinking between the one dimensional, staircase-shaped hydrogen-bonded strands.
2.2. Spectroscopy

The Raman spectroscopic results (Supplementary Materials, Figure S3) are in good agreement with those of the X-ray crystal structure analysis. The very strong band at 165 cm\(^{-1}\) and a weak one at \(~100\) cm\(^{-1}\) are typical for extremely asymmetric triiodide anions [26,53,54]. The high/low ratio of these bands has been discussed as a quantitative measure of the triiodide anion’s asymmetry. Typical values for asymmetrical and symmetrical triiodides are \(~1.5\) and \(~1.2\), respectively [26,55]. For \(18dbt\) a ratio of 1.6 was found, which excellently reproduces the crystallographic results of a very asymmetric triiodide anion. The far-IR spectrum of \(18dbt\) (Supplementary Materials, Figure S1) has the disadvantage that most bands are broad. But the spectrum independently verifies the presence and the position of a characteristic strong band at 165 cm\(^{-1}\).

3. Experimental

**Synthesis:** All chemicals were obtained from commercial sources and used as purchased. In a typical reaction 0.25 g (1.6 mmol) of 1,8-diaminooctane (Sigma-Aldrich, 98%, Steinheim, Germany) and 0.61 g (2.4 mmol) of iodine (subl. \(\geq\)99%) were mixed, then stirred in 10 mL of aqueous hydroiodic acid (Sigma-Aldrich, \(\geq\)57%, Steinheim, Germany), and heated up to ca. 370 K yielding a dark-red solution. Upon slow cooling to room temperature, dark-red, shiny crystals were formed at the bottom of the reaction vessel within one - two days.

**General considerations:** Mid-IR spectra of a powder sample were measured at room temperature on an Excalibur FTS 3500 spectrometer (Digilab, Germany) with an apodized resolution of 2 cm\(^{-1}\) using a MIRacle ATR unit (Pike Technologies, Madison, WI, USA) in the region of 4000–530 cm\(^{-1}\). The far-IR spectra were measured on an IFS 113 V spectrometer (Bruker Optics, Leipzig, Germany) with an apodized resolution of 2 cm\(^{-1}\) in the range of 500–25 cm\(^{-1}\) using polyethylene pellets. Raman spectra of powder samples were recorded on a MultiRam spectrometer (Bruker Optics, Leipzig, Germany) with an apodized resolution of 8 cm\(^{-1}\) equipped with a Nd-YAG laser: 1064 nm and a RT-InGaAs-detector in a backscattering geometry (4000–70 cm\(^{-1}\), 128 scans, 10 mW). Elemental analyses (C, H, N) were performed with an Euro EA3000 instrument (HEKA-Tech, Wegberg, Germany). Elemental analysis of iodine: A sample of 100 mg of \(18dbt\) was dissolved in 15 mL of a water/aceton (10:1) mixture. After adding some drops of acetic acid and heating up to approximately 370 K zinc powder was added until the solution turned colorless. Filtering off the surplus of zinc yielded a clear solution which was analyzed by a classical precipitation titration (AgNO\(_3\) solution, 0.1 mol/L; potentiometric endpoint; Ag // Ag/AgCl electrodes) [56]. The melting point was determined using the Mettler-Toledo melting point system MP90 (range: 300–500 K, rate: 2 K/min).

**Analytical data:** Melting point: 446 K. Elemental analysis found: C, 10.7; H, 2.5; N, 3.4.; I, 83.3. Calc. for \(C_8H_{22}N_2I_6\): C, 10.6; H, 2.4; N, 3.1; I, 83.9%.

**Spectroscopic data:** The Far-IR, Mid-IR and Raman spectra are shown in the Supplementary Materials section.

**Crystal structure determination:** The thin platelet crystals (plate face: \{100\}) were grown from the mother liquor of \(18dbt\). Several specimens of these crystals, that seemed to be suitable for X-ray diffraction, were harvested from the bulk samples. The crystals were mounted on an Oxford Xcalibur.
four-circle diffractometer [57] equipped with an EOS detector and a CryoJet cooling device ($T = 100$ K). In all cases the investigated specimens were non-merohedrally twinned. Data collection was performed with a crystal to detector distance of 45 mm and an omega-scan width of 1°/frame collecting a complete dataset up to $2\theta = 60°$. Indexing and determination of the twin law ($-1.00, 0.00, 0.00, -0.24, 0.97, 0.07, -0.12, 0.97, -0.97$ which is approximately a $180°$ rotation about $-0.157, 0.981, 0.111$ in direct space) followed the standard routine verified by a visual inspection via a reciprocal space viewer. Absorption correction was applied using indexed faces [57]. Structure solution by Direct Methods [58] using the data of one separated component always yielded all iodine atom positions. Secondary structure solution and simultaneous successive refinement of the primary structure using the SHELX program [58] yielded an almost complete model. As the refinement had reached an advanced stage, the method of Pratt, Coyle and Ibers [59] was used to process a dataset including both twin components (final twin ratio: 0.4755(6)/0.5245(6)). The hydrogen atoms were included at the latest stages of the refinement with restrained N-H and C-H distances. For the $U_{iso}$ values of the NH$_3$ group’s hydrogen atoms one common value was refined, whereas the $U_{iso}$ values of hydrogen atoms attached to carbon atoms were calculated ($U_{iso} = 1.2U_{eq}(C)$). Selected crystallographic data are listed in Table 3.

**Table 3.** Crystallographic data for the title structure.

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C$<em>8$H$</em>{22}$I$_6$N$_2$</th>
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<tr>
<td>$b$ (Å)</td>
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<tr>
<td>$c$ (Å)</td>
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</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>76.531(2)</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>78.842(2)</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>84.574(2)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)/Z</td>
<td>523.46(2)/1</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>8.888</td>
</tr>
<tr>
<td>Absorption correction</td>
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<td>$T_{min}/T_{max}$</td>
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<tr>
<td>Reflections**/reflections ($I &gt; 2\sigma(I)$)</td>
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</tr>
<tr>
<td>$\theta$ range (°)</td>
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</tr>
<tr>
<td>$R(F)[I &gt; 2\sigma(I)]/wR(F^2)$ [all data]</td>
<td>0.0341/0.0888</td>
</tr>
<tr>
<td>Parameters / restraints / completeness</td>
<td>87/9/100%</td>
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<tr>
<td>$\Delta$ρ$<em>{max}/\Delta$ρ$</em>{min}$ (e Å$^{-3}$)</td>
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* unmerged twin refinement.

4. Conclusions

This contribution is part of the recent efforts of several groups to synthesize new polyiodide containing hybrid materials and to understand the principles of caging small polyiodide anions [31–34,36–38] and iodine molecules [60–62]. The hydrogen bonded framework of 1,8-diaminioctane bis(triiodide),
(H$_3$N-(CH$_2$)$_8$-NH$_3$)$_2$I$_3$, is constructed by one-dimensional staircase-shaped motifs which are connected with each other by polyiodide and alkan-diyl units. If we played the role of ‘devil’s advocate’ the structure could also be described as a hydrogen bonded framework of dications and iodide anions featuring oblong voids each filled with two iodine molecules. But as Lee et al. [63] have shown by an extensive database analysis, besides the stronger I$^-$I bonds typical for I$_3^-$ and I$_2$ subunits also long-range interactions are reasonable. The poliyiodide substructure may therefore be considered as a hydrogen bonded I$_6^{2-}$ anion consisting of two triiodide anions interacting by a weak halogen bond. The approximately linear triiodide subunit exhibits an extreme asymmetry. The structural properties of the poliyiodide moiety have been verified by Raman and Far-IR spectroscopy.

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Conflicts of Interest

The authors declare no conflict of interest.

References


47. Reiss, G.J. Personal communication to the Cambridge Structural Database, deposition number CCDC 786078, Cambridge, UK, 2010.


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