Crystal Engineering of a New Layered Polyiodide Using 1,9-Diammoniononane as a Flexible Template Cation

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The reaction of 1,9-diaminononane with hydroiodic acid in the presence of iodine gave a compound best described as 1,9-diammoniononane bis-triiodide iodine, \((\text{H}_3\text{N}-(\text{CH}_2)_9\text{NH}_3)\)[I\(_3\)]\(_2\)·I\(_2\). The structure is built from two crystallographically independent I\(_3^-\) anions, which are connected via secondary I···I interactions to the iodine molecules, and the 1,9-diammonioalkane cations are connected via weak hydrogen bonds to neighbouring iodine atoms. By a cooperative phenomenon, the shape and the functionality of the cation lead to a solid state structure that includes a polyiodide substructure with the formula \(2\infty [\text{I}_8]^{2-}\) or \(2\infty [\text{I}_1\cdot\text{I}_2\cdot\text{I}_3]^{2-}\). is best described as a brick-shaped layered array. Its rectangular pores fit excellently with the hydrogen bonding functionality as well as with the conformational needs of the 1,9-diammoniononane template. The Raman spectrum shows typical bands of coordinated triiodide anions and iodine molecules. The thermal analysis (DSC/TG) of the title compound indicates decomposition at temperatures above 210°C.

Key words: Structure Determination, Crystal Engineering, Polyiodide, Diammonioalkane, Hydrogen Bonding

Introduction

It is well known that rod-like \(\alpha,\omega\)-diammonioalkane cations [1] and \(\alpha,\omega\)-diaminoalkane molecules [2] are potent templates for the Crystal Engineering of layered structures, and especially for the synthesis of layered aluminium phosphates [3] and zincophosphates [4]. For their flexibility they have also been used for Crystal Engineering of hydronium cations with unusual topology, trapped in an inorganic framework [5], and as special spacers they are able to connect metal clusters [6]. Two points of a template-controlled synthesis are very important: Firstly the shape of the template in all of its stable conformers. Secondly, the chemical functionality of a potential template, e.g. the ability to form hydrogen bonds which is one of the key properties of the template. In most cases a compromise of these two and of various other factors that are less important determines the principal features of the solid-state structures.

Solid materials containing polyiodides have attracted much attention because these compounds show electrical conduction ranging from values typical for insulators to values of typical metals [7]. Magnetic materials containing polyiodide species have also been synthesized [8]. As a matter of fact iodine-rich iodides are very numerous and various iodine-iodides have been structurally characterized [9, 10]. Most iodine-iodide clusters and polymers are built up by the well known \(\text{I}_5^-\) ion and discrete \(\text{I}_2\) molecules linked together by medium strong to weak halogen-halide interactions. It is also known that the structure and stability of complex iodine-iodide anions and polymers are strongly dependent on the shape and functionality of the templating counter cations [10]. Our interest in polyiodide containing compounds is twofold: on the one hand we want to synthesize new polyiodides by a template controlled synthesis, on the other hand the metallic appearance of the resulting solids may have potential for electrically conducting compounds. For the 1,10-diammoniodecane it has already been shown that \(\alpha,\omega\)-diammonioalkane species are flexible templates able to stabilize different polymeric polyiodides [11].

Results and Discussion

The title compound can formally be described by the formula \((\text{H}_3\text{N}-(\text{CH}_2)_9\text{NH}_3)[\text{I}_3]_2\cdot\text{I}_2\). There are two crystallographically independent \(\text{I}_5^-\) anions and one
Table 1. Bond lengths (\(\text{Å}\)), angles and torsion angles (\(^{\circ}\)) for the title compound.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance ((\text{Å}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1-I2</td>
<td>3.0776(19)</td>
</tr>
<tr>
<td>I4-I5</td>
<td>2.916(17)</td>
</tr>
<tr>
<td>I7-I8</td>
<td>2.766(16)</td>
</tr>
<tr>
<td>I6-I7</td>
<td>3.4870(20)</td>
</tr>
<tr>
<td>I1-I2-I3</td>
<td>178.39(2)</td>
</tr>
<tr>
<td>I4-I5-I6</td>
<td>178.7(2)</td>
</tr>
<tr>
<td>C-C distances: 1.52(1) – 1.55(1)</td>
<td></td>
</tr>
<tr>
<td>N1-C1</td>
<td>1.512(11)</td>
</tr>
<tr>
<td>C-C distances: 1.52(1) – 1.55(1)</td>
<td></td>
</tr>
<tr>
<td>N-C-C and C-C-C angles: 111.0 – 117.0</td>
<td></td>
</tr>
</tbody>
</table>

\(^{\frac{1}{1}}\)x, \(-1+y, z\); \(^{\frac{2}{1}}\)x, y, z + 1.

Fig. 1. View along [100] on a layer of the title compound showing the excellent fit of the diammonioalkane cations (white and grey spheres) and the polyiodide anions (dark grey spheres).

iodine molecule in the asymmetric unit. All bond lengths of the I\(^{3-}\) anions and the iodine molecule are in the expected range (Table 1). Both crystallographically independent I\(^{3-}\) anions show two slightly different I-I distances. These species together with their symmetry-related ones are connected via weak to medium strong I-I interactions (Table 1) to form a polyiodide substructure best described as stacked layers parallel to the \(bc\) plane. Each layer features rectangular 18-membered, aneled rings accommodating the 1,9-diammoniononane cations. The rings are arranged like bricks in a wall (Fig. 1), and the polyiodide substructure could be expressed with the formula \(2\text{[I}_8\text{]}^{2-}\). A space filling plot impressively demonstrates that the polyiodide network fits perfectly in two dimensions with the cationic template (Fig. 1, lower part). From an analysis of the packing of the polyiodide layers it is obvious that the polyiodide layers are arranged staggered relative to the neighboring layers satisfying the needs of packing and hydrogen bonding (Fig. 2).

A detailed investigation of the hydrogen bonding network of the 1,9-diammoniononane cationic template shows that two of five relevant hydrogen bonds are found to connect an iodine atom of the same layer while three hydrogen bonds are found to connect iodine atoms of neighboring layers. As a consequence of the needs of packing and hydrogen bonding the flexible 1,9-diammoniononane cation appears in an unusual

Fig. 2. View along [100] showing the stacking of the \(2\text{[I}_8\text{]}^{2-}\) polyiodide substructure.

Fig. 3. Detailed view of the hydrogen bonding between the 1,9-diammoniononane cation and the polyiodide substructure (displacement ellipsoids are shown at the 50\% probability level, H atoms are drawn with an arbitrary radius, hydrogen bonds are only shown for the central diammonioalkane cation).
conformation with one ammonio group rotated away from the most stable all-trans conformation (N1-C1-C2-C3 65.2(11), Fig. 3). The iodine molecules (I7 and I8) of the polyiodide network are however, owing to their low basicity and as building units at the long faces of the polyiodide boxes, not involved in any hydrogen bonding (Fig. 3).

The vibrational spectroscopic investigation has shown that the characteristic bands expected for the diaminononanone as well as those characterizing the [I\textsubscript{8}]\textsuperscript{2-} entities are present. The Raman spectrum measured at room temperature shows broad bands for the polyiodide substructure in the typical range [12]. A shoulder at 217 cm\textsuperscript{-1} may result from free iodine in the gas phase due to the decomposition of the solid state compound during the measurement [13].

Conclusion

As a cooperative phenomenon, the shape and functionality of the 1,9-diammoniononanone cation lead to a solid state structure with a polyiodide substructure best described as a layered compound with 18 membered rings that are arranged like bricks in a wall. The 1,9-diammoniononanone cation acts as a flexible template for the construction of this new polyiodide salt. Characteristic bands in the Raman spectrum in the range of 100–250 cm\textsuperscript{-1} confirm the presence of coordinated triiodide anions and iodine molecules well known from numerous Raman spectroscopic investigations for I\textsubscript{3} \textsuperscript{-} and I\textsubscript{2} containing compounds [12].

Experimental Section

Synthesis

0.25 g (1.6 mmol) of 1,9-diammononanone was dissolved in 15 ml of 65\% [w/w] aqueous hydroiodic acid. Addition of 0.81 g (3.2 mmol) of iodine and heating at 100 °C yielded a black solution. Crystallization at room temperature gave within 2 weeks 1.0 g of dark, shiny crystals (53.9\% yield).

Crystallographic study

Single crystals of the title compound suitable for X-ray diffraction were selected from the bulk samples. A platelet with the dimensions 0.8 × 0.4 × 0.1 mm\textsuperscript{3}, was sealed in a thin walled glass capillary and mounted on a Stoe one circle diffractometer IPDS I (Image Plate Diffraction System) [14]. Data collection was achieved at a crystal-detector distance of 60 mm and a phi range of 0–360° for 327 exposures. Data reduction included a Lorentz and a polarisation correction as well as a numerical absorption correction using indexed faces of the crystal (T\textsubscript{min}/T\textsubscript{max}: 0.064/0.443) [15]. The unit cell constants were refined from 5000 quasi-centered reflections extracted from the data set. Structure solution by Direct Methods in the centrosymmetric space group PI and secondary structure solution by difference Fourier synthesis were successful [16]. After refinement of all non-hydrogen atoms using anisotropic displacement parameters, all H atom positions were obtained from successive difference Fourier synthesis [17]. The H atoms attached to C atoms were included using a riding model to achieve convergence in the final stages of the refinement. The atomic coordinates of the H atoms of the ammonium group were refined freely with their N-H distances restrained to plausible values. One common U\textsubscript{iso}-value has been refined for the H atoms of each CH\textsubscript{2} and NH\textsubscript{3} group.

[C\textsubscript{9}H\textsubscript{24}I\textsubscript{8}N\textsubscript{2}], M = 1175.50, triclinic, space group P\textbar, a = 8.368(3), b = 10.628(6), c = 15.163(5) Å, α = 87.40(5)°, β = 80.86(4)°, γ = 86.59(5)°, V = 1328.1(9) Å\textsuperscript{3}, T = 293 K, Z = 2, R\textsubscript{free} = 2.939 g cm\textsuperscript{-3}, μ(Mo-K\textsubscript{α}) = 93.36 cm\textsuperscript{-1}, 19175 reflections measured (R\textsubscript{max} = 0.0522), 2θmax = 52.0°, −10 ≤ h ≤ 10, −13 ≤ k ≤ 13, −18 ≤ l ≤ 18, 4853 reflections unique. 3940 reflections observed (with F\textsuperscript{2} > 2σ(F\textsuperscript{2})), full matrix least squares refinement of 180 parameters on F\textsuperscript{2}, wR2 (all data) = 0.0757(w = 1/σ\textsuperscript{2}(F\textsuperscript{2}) + (0.025P\textsuperscript{2} + 2.50P\textsuperscript{1/2}) where P = (F\textsuperscript{2} + 2F\textsuperscript{2}))/3), R1(F\textsuperscript{2} > 2σ(F\textsuperscript{2})) = 0.0320, GooF = 1.070, σ/σ\textsubscript{max} = 0.017, Δρ\textsubscript{min}/Δρ\textsubscript{max} = −0.964/0.923 eÅ\textsuperscript{-3}.

Supporting information available: Crystallographic data (excluding structure factors have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-195123. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Thermal analysis

A combined DSC and thermogravimetric measurement showed that the title compound begins to decompose rapidly at temperatures above 210 °C (Netzsch, Jupiter STA 449, range: RT to 300 °C, 5 °C/min, α-Al\textsubscript{2}O\textsubscript{3} as reference compound). A strong endothermic effect at 144 °C gives way to exothermic events that lead to a sharp maximum at 163 °C. The enthalpy of this phase transition has been determined to be 15.1 kJ mol\textsuperscript{-1} (ΔH\textsubscript{p} = 240.6 J g\textsuperscript{-1}) at a temperature of 143.0 °C (T\textsubscript{max}; 144.7 °C, T\textsubscript{onset}; 146.4 °C), not related to effects of one of the starting materials and without a loss of weight, may be related to a phase transition of the title compound at this temperature.

Vibrational spectroscopy

Infrared spectroscopy: The infrared spectra were recorded on a Bio-Rad FTS 3500 IR-spectrometer with a resolution of 2 cm\textsuperscript{-1}. A single crystal of the dimensions 0.1 × 0.2 × 1 mm\textsuperscript{3} was mounted on the liquid nitrogen cooled ZnSe plate of the ATR-accessory unit (MIRacle, PIKE Technologies, Madison), scan range 4000–650 cm\textsuperscript{-1}; ν = 3413br, 3156sh, 3043, 3012, 2980sh,
2921 vs, 2850 vs, 1863 br, 1621 w, 1563 s, 1466 vs, 1431 sh, 1386 w, 1315 w, 1271 vw, 1126 w, 966 w, 915 w, 874 w, 828 vw, 785 w, 753 vw, 736 w, 720 w cm$^{-1}$.

**Raman spectroscopy:** Single crystal sample, FT-Raman Accessory (BioRad, Krefeld, Germany) attached to IR-Spectrometer FTS 3500, 1283 mW, Y AlG laser, liquid nitrogen cooled germanium detector, resolution: 4 cm$^{-1}$, scan range: 3500 – 70 cm$^{-1}$:

$\nu = 2888$ vw, 1565 vw, 1468 vw, 1435 vw, 175 sh (I$_2$), 217 sh (I$_2$ vapor from partial decomposition [12]), 154 vs (I$_3^-$, $\nu_3$), 102 vs (I$_3^-$, $\nu_1$) cm$^{-1}$. The bands at 154 and 102 cm$^{-1}$ are broad in contrast to those of pure iodine measured as a reference material (189, 178 cm$^{-1}$). Due to the frequency of the Y AlG laser used for the Raman experiment this organic-inorganic composite material was heated rapidly. As a consequence of this heating I$_2$ vapor can also be detected as a shoulder in the Raman spectrum.


