Crystal Engineering of a New Layered Polyiodide Using 1,9-Diammonionononane 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-diammonionononane bis-triiodide iodine, $(H_3N\text{-}(CH_2)_9\text{-}NH_3)[I_3]_2 \cdot I_2$. The structure is built from two crystallographically independent I_3^- anions, which are connected *via* secondary $I^{\cdots}I$ 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 $^2_\infty[I_8]^{2-}$ or $^2_\infty[I_3 \cdot I_2 \cdot I_3]^{2-}$, 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-diammonionononane 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 α,ω-diammonioalkane cations [1] and α,ω-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 I_3^- ion and discrete 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 α,ω-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 $(H_3N\text{-}(CH_2)_9\text{-}NH_3)[I_3]_2 \cdot I_2$. There are two crystallographically independent I_3^- anions and one

Table 1. Bond lengths (Å), angles and torsion angles (°) for the title compound.

I1-I2	3.0776(19)	I2-I3	2.8506(18)
I4-I5	2.9167(17)	I5-I6	2.9902(18)
I7-I8	2.7664(16)	I3-I4	3.8369(23)
I6-I7	3.4870(20)	I1-I4[i]	4.2004(17)
I1-I8[ii]	3.3579(19)		
I1-I2-I3	178.39(2)	I4-I5-I6	177.52(2)
N1-C1	1.512(11)	N2-C9	1.516(9)
C-C distances: 1.52(1) – 1.55(1)			
N-C-C and C-C-C angles: 111.0 – 117.0			
N1-C1-C2-C3	65.2(11)	C1-C2-C3-C4	−174.9(7)
C2-C3-C4 C5	177.7(7)	C3-C4-C5-C6	−173.7(6)
C4-C5-C6-C7	177.9(6)	C5-C6-C7-C8	−175.3(6)
C6-C7-C8-C9	178.6(6)	N2-C9-C8-C7	178.7(5)

[i] $x, -1+y, z$; [ii] $x, y, z+1$.

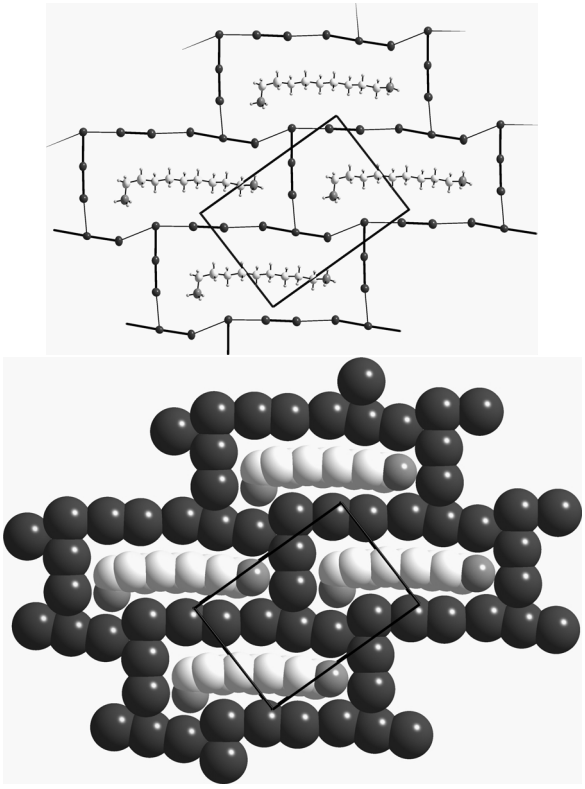

Fig. 1. View along [100] on a layer of the title compound showing the excellent fit of the diammonioalkane cations (white and grey spheres) and the polyiodide anions (dark grey spheres).

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

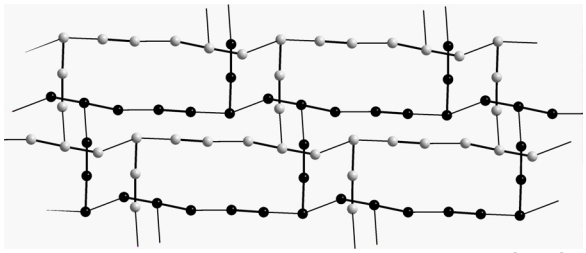

Fig. 2. View along [100] showing the stacking of the $^2_\infty[I_8]^{2-}$ polyiodide substructure.

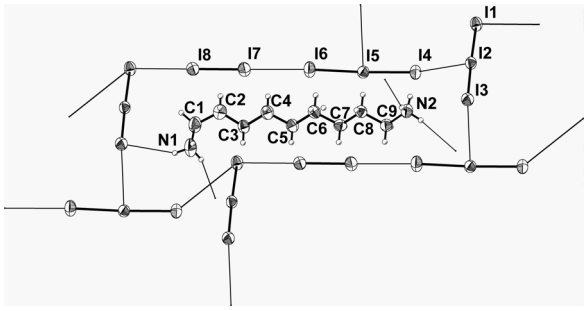

Fig. 3. Detailed view of the hydrogen bonding between the 1,9-diammoniononane cation and the polyiodide substructure (displacement ellipsoids are shown at the 50% probability level, H atoms are drawn with an arbitrary radius, hydrogen bonds are only shown for the central diammonioalkane cation).

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, annelated 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 $^2_\infty[I_8]^{2-}$. 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

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 diammoniononane as well as those characterizing the $[I_8]^{2-}$ 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^{-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-diammoniononane 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-diammoniononane 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^{-1} confirm the presence of coordinated triodide anions and iodine molecules well known from numerous Raman spectroscopic investigations for I_3^- and I_2 containing compounds [12].

Experimental Section

Synthesis

0.25 g (1.6 mmol) of 1,9-diaminononane 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 $0.8 \times 0.4 \times 0.1$ mm^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_{min}/T_{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 $P\bar{1}$ 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_{iso}-value has been refined for the H atoms of each CH_2 and NH_3 group.

$C_9H_{24}I_8N_2$, $M = 1175.50$, triclinic, space group $P\bar{1}$, $a = 8.368(3)$, $b = 10.628(6)$, $c = 15.163(5)$ Å, $\alpha = 87.40(5)°$, $\beta = 80.86(4)°$, $\gamma = 86.59(5)°$, $V = 1328.1(9)$ $Å^3$, $T = 293$ K, $Z = 2$, $\rho_{ber.} = 2.939$ g cm^{-3}, μ(Mo-K$_\alpha$) = 93.36 cm^{-1}, 19175 reflections measured ($R_{int} = 0.0522$), $2\theta_{max} = 52.0°$, $-10 \le h \le 10$, $-13 \le k \le 13$, $-18 \le l \le 18$, 4853 reflections unique, 3940 reflections observed (with $F^2 > 2\sigma(F^2)$), full matrix least squares refinement of 180 parameters on F^2, $wR2$ (all data) = $0.0757(w = 1/[\sigma^2(F_o{}^2) + (0.025P)^2 + 2.50P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3)$), $R1(F^2 > 2\sigma(F^2)) = 0.0320$, GooF = 1.070, σ/su_{max}: 0.017, $\Delta\rho_{min/max}$: −0.964/0.923 e/$Å^3$.

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_2O_3 as reference compound). A strong endothermic effect at 144 °C (T_{onset}: 143.0 °C, T_{max}: 144.7 °C, T_{offset}: 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^{-1}. A single crystal of the dimensions $0.1 \times 0.2 \times 1$ mm^3 was squeezed on to the ZnSe plate of the ATR-accessory unit (MIRacle, PIKE Technologies, Madison), scan range 4000 – 650 cm^{-1}: ν = 3413br, 3156sh, 3043, 3012, 2980sh,

2921vs, 2850vs, 1863br, 1621w, 1563s, 1466vs, 1431sh, 1386w, 1315w, 1271vw, 1126w, 966w, 915w, 874w, 828vw, 785w, 753vw, 736w, 720w cm^{-1}.

Raman spectroscopy: Single crystal sample, FT-Raman Accessory (BioRad, Krefeld, Germany) attached to IR-Spectrometer FTS 3500, 1283 mW, YAG-laser, liquid nitrogen cooled germanium detector, resolution: 4 cm^{-1}, scan range: 3500 – 70 cm^{-1}: ν = 2888vw, 1565vw, 1468vw, 1435vw, 175sh (I_2), 217sh (I_2 vapor from partial decomposition [12]), 154 vs (I_3^-, ν_3), 102 vs (I_3^-, ν_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 YAG 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.

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