

Two New Polyiodides in the 4,4'-Bipyridinium Diiodide/Iodine System

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The reaction of bipyridine with hydroiodic acid in the presence of iodine gave two new polyiodide-containing salts best described as 4,4'-bipyridinium bis(triiodide), $C_{10}H_{10}N_2[I_3]_2$, **1**, and bis(4,4'-bipyridinium) diiodide bis(triiodide) tris(diiodine) solvate dihydrate, $(C_{10}H_{10}N_2)_2I_2[I_3]_2 \cdot 3I_2 \cdot 2H_2O$, **2**. Both compounds have been structurally characterized by crystallographic and spectroscopic methods (Raman and IR). Compound **1** is composed of I_3^- anions forming one-dimensional polymers connected by interionic halogen bonds. These chains run along [101] with one crystallographically independent triiodide anion aligned and the other triiodide anion perpendicular to the chain direction. There are no classical hydrogen bonds present in **1**. The structure of **2** consists of a complex I_{14}^{4-} anion, 4,4'-bipyridinium dication and hydrogen-bonded water molecules in the ratio of 1 : 2 : 2. The I_{14}^{4-} polyiodide anion is best described as an adduct of two iodide and two triiodide anions and three diiodine molecules. Two 4,4'-bipyridinium cations and two water molecules form a cyclic dimer through N–H...O hydrogen bonds. Only weak hydrogen bonding is found between these cyclic dimers and the polyiodide anions.

Key words: Polyiodide, 4,4'-Bipyridine, Triiodide, Crystal Structure, Raman Spectroscopy

Introduction

Polyiodides are extended parts of salt structures that fulfill the general formula I_{2m+n}^{n-} ($n = 1-4$, $m = \text{integer}$) [1]. They are built by I^- , I_3^- and I_2 units and are characterized by their strong tendency to concatenate to extended motifs by halogen bonding [2]. There is also a general interest in the azaniumalkane iodide/triiodide systems as they are known to modify the redox chemistry in dye-sensitized solar cells [3]. Polyiodides also play important roles in other electrochemical processes, *e. g.* lithium iodide batteries [4]. Furthermore, polyiodide chains conduct the electric current by a Grotthuss-like mechanism [5] in the solid state. Higher polyiodides can therefore be considered as a snapshot of this phenomenon. Even though hundreds of polyiodide-containing structures have been reported, not for all the simple stoichiometries a structurally characterized example is known. The concept of *crystal engineering* gave the chase for still unknown polyiodides a significant boost [6]. In the recent past several groups have synthesized new compounds consisting of stick-shaped cationic tectons [7] and polyiodides whose structures fit with the lengths and shapes

of the templates used [8]. This selective and robust synthetic protocol for solid polyiodides is now termed *dimensional caging* [8a]. Especially the semi-flexible cationic α , ω -diazaniumalkane tectons have successfully been used for the *dimensional caging* of polyiodides ($H_3N(CH_2)_nNH_3I_2 \cdot x I_2$; $n = 3$ [9a], 6 [9b], 7 [9c], 9 [9d], 10 [9e]). For pyridinium [10], 4,4'-bipyridinium [8d, 11] and 2,2'-bipyridinium [12] cations it has already been shown that they are able to stabilize polyiodides. We now report on two novel polyiodide salts constructed by the aid of the dicationic 4,4'-bipyridinium template.

Results and Discussion

From the reaction of 4,4'-bipyridine with hydroiodic acid in the presence of iodine two crystalline phases were obtained, rod-shaped, dark-red crystals as the primary, and hexagonal, dark-red prisms as the secondary product. They were found to be 4,4'-bipyridinium bis(triiodide) ($C_{10}H_{10}N_2[I_3]_2$, **1**, and the bis(4,4'-bipyridinium) diiodide bis(triiodide) tris(diiodine) dihydrate, $(C_{10}H_{10}N_2)_2I_2[I_3]_2 \cdot 3I_2 \cdot 2H_2O$, **2**, respectively.

4,4'-Bipyridinium bis(triiodide) (**1**)

All ionic parts in the structure of 4,4'-bipyridinium bis(triiodide) (**1**) are located on special positions (with crystallographic $2/m$ symmetry). One triiodide (I1/I2) anion lies on a mirror plane, whereas the second crystallographically independent triiodide anion (I3/I4) is aligned along the two-fold axis in the monoclinic space group $C2/m$ (Fig. 1).

The shortest I...I distance between neighboring chains is 4.1026(1) Å. 4,4'-bipyridinium dications have torsional flexibility about the central C–C single bond, and planar 4,4'-bipyridinium dications as well as those with a significant torsion are well known [14]. The dication in **1** exhibits a planar geometry (Table 1). The H...I distances of the N-H and C-H groups are out of the range of classical hydrogen bonds with values above 3.1 Å [15], even though the 4,4'-bipyridinium dication is well known to form such bonds, *e.g.* in the related diiodide compound [14]. The distances between parallel polyiodide chains and neighboring layers are in the range of the van der Waals radii.

The Raman spectroscopic results are in very good agreement with those of the crystal structure analysis. For a centrosymmetric I_3^- anion with $D_{\infty h}$ symmetry one Raman active band from the centrosymmetric stretching vibration ($\nu_1 \approx 110 \text{ cm}^{-1}$) is predicted by selection rules. For related compounds it has been shown that the IR-active and Raman-forbidden anti-symmetric stretching band ($\nu_3 \approx 145 \text{ cm}^{-1}$) and the bending mode ($\nu_2 \approx 75 \text{ cm}^{-1}$) are sometimes detectable as much weaker bands [13, 16]. In the Raman

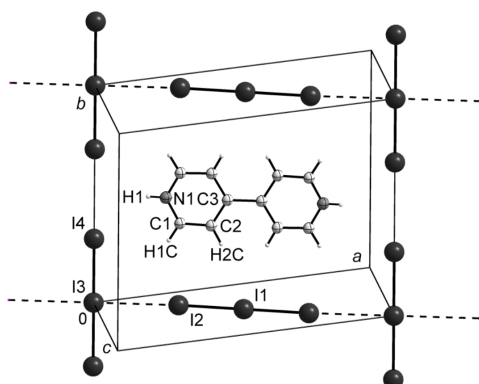


Fig. 1. A characteristic part of the structure of **1**. The triiodide chains run along [101], and a 4,4'-bipyridinium dication fills the gap between them. The almost planar dication is nearly exactly aligned (maximum deviation: 0.06 Å) along the plane defined by the two neighboring polyiodide chains shown (atoms are drawn with arbitrary radii).

Table 1. Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **1** and **2** with estimated standard deviations in parentheses.

Compound 1 ^a					
I1–I2	2.9168(2)	I2–I3	3.7468(1)		
I3–I4	2.9190(2)	N1–C1	1.322(3)		
C1–C2	1.377(3)	C2–C3	1.384(3)		
C3–C3'	1.495(6)	N1–C1–C2	120.0(2)		
C1–N1–C1''	122.2(3)	C1–C2–C3	120.2(2)		
C2–C3–C2''	117.5(3)	C2–C3–C3'	121.24(15)		
C1''–N1–C1–C2	−0.9(6)	N1–C1–C2–C3	−0.4(5)		
C1–C2–C3–C2''	1.6(5)	C1–C2–C3–C3'	−176.7(3)		
Compound 2 ^b					
I1–I2	3.4005(6)	I2–I3	3.2522(5)		
I1–I1'	2.7744(9)	I3–I4	2.7618(5)		
I4–I5	3.5649(5)	I5–I6	3.0478(5)		
I6–I7	2.8361(5)	C3–C4	1.485(7)		
N–C distances	1.328(7) – 1.337(7)	C–C _{aromat.}	1.393(8) – 1.393(8)		
I1–I2–I3	108.88(1)	I2–I3–I4	177.51(2)		
I3–I4–I5	174.91(2)	I4–I5–I6	176.19(2)		
I1'–I1–I2	174.84(2)	I5–I6–I7	175.57(2)		
C2–C3–C4–C8	27.5(8)	C9–C3–C4–C5	26.8(8)		
	D–H	H...A	D...A	Angle	
	N1–H1N...O1	0.77(6)	2.31(6)	2.880(6)	132(6)
	N2–H2N...I2	0.76(6)	2.78(6)	3.534(4)	169(6)

^a Symmetry codes: ' 1 – x, 1 – y, 1 – z; '' x, 1 – y, z.

spectrum of **1** the centrosymmetric stretching vibration is found at 113 cm^{-1} as a very strong band besides a weak band at 158 cm^{-1} for ν_3 . According to the 'rule of mutual exclusion' [17], only the bands for ν_2 and ν_3 should be visible in the far-IR spectrum, but as in the Raman spectrum, several bands are found in this region. In the mid-IR range from 900–1700 cm^{-1} the Raman spectrum shows the typical bands for the 4,4'-bipyridinium dication [18]. Although the structure motif of a one-dimensional I_3^- polymer is very common, to the best of our knowledge, a chain structure with 'crossed' triiodide anions was so far not described in the literature [1]. The 4,4'-bipyridinium dications fill the gaps between the anionic chains perfectly and hence, this suggests that the cations act as templates for the construction of this unusual connectivity in a one-dimensional triiodide polymer.

Bis(4,4'-bipyridinium) diiodide bis(triiodide) tris(diiodine) dihydrate (**2**)

The structure of **2** is built by I_{14}^{4-} polyiodide anions and cationic units that are composed of two 4,4'-bipyridinium cations and two water molecules to form a cyclic dimer. The I_{14}^{4-} polyanion is located on an

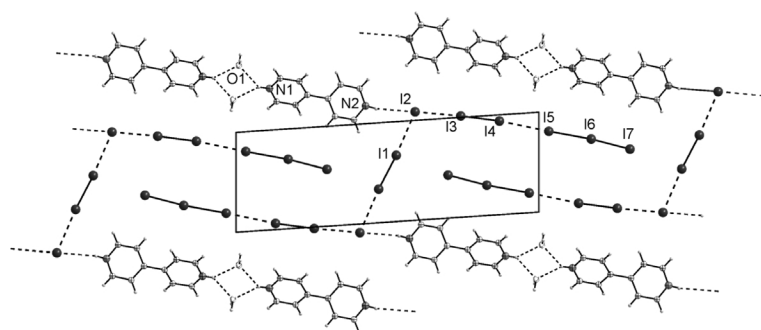


Fig. 2. View along [100] on the layered structure of **2** constructed by I_{14}^{4-} polyiodide anions and hydrogen-bonded cyclic dimers consisting of two 4,4'-bipyridinium cations and two water molecules (atoms are drawn as spheres with arbitrary radii).

inversion center in the triclinic space group $P\bar{1}$ forming a Z-shaped arrangement (Fig. 2). The I–I contacts within the I_{14}^{4-} anion vary from 2.76 to 3.56 Å and must be interpreted as bonding interactions (Table 1). Even though there is a relatively short secondary I...I distance of 3.2522(5) Å between I2 and I3, this value is clearly out of the range known for very asymmetric triiodides [19]. According to the I–I distances determined, this new anion is best described as a species that consists of two iodides, three iodine molecules and two triiodide anions. The I–I bonds in the formal iodine molecules are only slightly elongated (2.76, 2.77 Å) compared to the experimental value determined for elemental iodine (2.715 Å) [20] and similar to values reported for I_2 units in related compounds [12a, 21]. The bonding situation of atom I2 (Fig. 2) is also comparable with the polyiodide in the structure of 2,2'-bipyridine pentaiodide [12a] where one iodide anion is coordinated by three iodine molecules. In the structure of **2** the third iodine molecule is replaced by the heterocycle with its N–H⁺ group forming a weak hydrogen bond to I2. The bond lengths in the formal I_3^- anion (I5–I6–I7) are in the typical range for asymmetric triiodide anions (3.0478(5), 2.8361(5) Å) [16].

The bond lengths within the 4,4'-bipyridinium dication are as expected (Table 1). The two individually planar heteroarenes of the dication are twisted against each other by 27° about the C3–C4 bond. Two 4,4'-bipyridinium cations and two water molecules form a hydrogen bonded cyclic dimer (Fig. 3; graph set: $R_2^2(4)$ [22]). The N–H...O hydrogen bonds are in the expected range (Table 1). These long stretched tectons are connected to the I_{14}^{4-} anion only by weak N–H...I hydrogen bonds to form layers in the crystallographic *bc* plane (Fig. 2).

In the 200–50 cm^{-1} region the Raman spectrum of **2** shows the expected absorption bands. There are bands at 165 and 150 cm^{-1} which are typical for io-

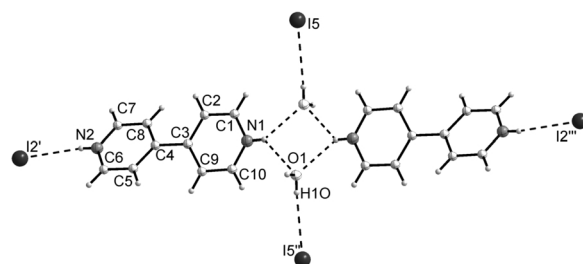


Fig. 3. The rod-shaped, hydrogen-bonded cyclic dimer consisting of two 4,4'-bipyridinium cations and two water molecules with their hydrogen-bonded neighbors present in **2** (symmetry codes: ' $1-x, 2-y, 1-z$; '' $-x, 1-y, -z$; ''' $-1+x, -1+y, -1+z$; atoms are drawn as spheres with arbitrary radii).

dine molecules attached to donors [16], and a broad, slightly split band at 110 cm^{-1} which must be attributed to stretching vibrations of the triiodide anion. The Raman spectrum shows in the region between 3000 and 600 cm^{-1} the bands which are typical for the 4,4'-bipyridinium cation (1016, 1293, 1522, 1642 cm^{-1}) [18]. There are at least two polyiodide-containing structures that have the same charge to iodine ratio (1 : 3.5) as **2** [23]. In both cases the structures are built by isolated I_8^{2-} anions and additional triiodide anions not bonded to each other. To the best of our knowledge an I_{14}^{4-} polyiodide has not previously been observed [1, 23].

Conclusion

We have shown that the 4,4'-bipyridinium cation is able to serve as a template for the synthesis of two topologically new polyiodide-containing compounds. Since aromatic azanium cations, like the 4,4'-bipyridinium cation, are poor hydrogen bond donors, non-covalent interactions between the cations and anions play a more important role than in related azanium-alkyl compounds. The flexibility of the dication by

conformational rotation about the central C–C bond is important to fit this component into the polyiodide ‘matrix’. We expect that a variation of the length of the cationic aromatic template will lead to new types of polyiodide compounds that might be able to give a deeper understanding of the I···I and I···H–C interactions in these hybrid materials.

Experimental Section

General considerations

All chemicals were obtained from commercial sources and used as purchased. In a typical reaction, 0.25 g (1.6 mmol) of 4,4'-bipyridine and 0.81 g (3.2 mmol) of iodine were stirred in 10 mL of 57 % aqueous hydroiodic acid and heated at 100 °C yielding a dark colored suspension. Upon slow cooling to r. t., dark-red, rod-shaped, shiny crystals were formed on the surface of the suspension. Additionally reddish, hexagonal platelets crystallized from the suspension after three to four days at ambient temperature at the bottom of the reaction vessel. The rod-shaped crystals are composed of 4,4'-bipyridinium cations and triiodide anions as 4,4'-bipyridinium bis(triiodide), (C₁₀H₁₀N₂)[I₃]₂, **1**, whereas the hexagonal crystals contain additional iodine and water: Bis(4,4'-bipyridinium) diiodide bis(triiodide) tris(diiodine) dihydrate, (C₁₀H₁₀N₂)₂I₂[I₃]₂ · 3I₂ · 2H₂O, **2**. Mid-IR spectra were measured at r. t. on an Excalibur FTS 3500 spectrometer (Digilab, Germany) with an apodized resolution of 2 cm⁻¹ using a MIRacle ATR unit (Attenuated Total Reflection, Pike technologies, Madison, USA) in the region of 4000–530 cm⁻¹. The far-IR spectra were measured using an IFS 113 V (Bruker Optics, Germany) with an apodized resolution of 2 cm⁻¹ in the range of 500–25 cm⁻¹ using polyethylene pellets. Raman spectra were recorded on a MultiRam spectrometer (Bruker Optics, Germany) with an apodized resolution of 8 cm⁻¹ equipped with a Nd-YAG laser: 1064 nm and a RT-InGaAs-detector (4000–70 cm⁻¹, 128 scans, 10 mW). Elemental analyses (C, H, N) were performed with a Euro EA3000 instrument (HEKA-Tech, Germany). The melting points were determined using the Mettler-Toledo melting point system MP90 (range: RT–220 °C, 2° min⁻¹). For each compound the measurements were repeated three times to verify the observations.

4,4'-Bipyridinium bis(triiodide) (**1**)

Mid-IR (single crystal, ATR): ν (cm⁻¹) = 3414(s, br), 3209(vs), 3159(vs), 3087(vs), 3064(vs), 2927(s), 2583(m, br), 2534(w), 2458(w), 1950(w), 1619(m), 1589(vs), 1469(s), 1352(w), 1288(w), 1226(m), 1193(s), 1112(w), 1133(w), 1054(w), 981(m), 880(w), 813(w), 743(s), 698(m). – Far-IR (PE pellet): ν (cm⁻¹) = 250(w), 149(s),

Table 2. Crystal structure data for **1** and **2**.

Compound	1	2
Formula	C ₁₀ H ₁₀ N ₂ I ₆	C ₁₀ H ₁₂ N ₂ I ₇ O
<i>M_r</i>	919.60	1064.52
Crystal size, mm ³	0.46×0.08×0.02	0.12×0.09×0.02
Crystal system	monoclinic	triclinic
Space group	<i>C</i> 2/ <i>m</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	13.4014(3)	7.2145(4)
<i>b</i> , Å	9.9405(2)	7.3380(4)
<i>c</i> , Å	7.43708(17)	21.5080(11)
α , deg	90	92.515(4)
β , deg	106.844(2)	93.729(4)
γ , deg	90	107.163(5)
<i>V</i> , Å ³	948.24(4)	1083.24(10)
<i>Z</i>	2	2
<i>D</i> _{calcd.} , g cm ⁻³	3.22	3.26
μ , mm ⁻¹	9.8	10.0
Absorption corr.	analytical	analytical
<i>T</i> _{min} / <i>T</i> _{max}	0.214 / 0.822	0.414 / 0.827
<i>F</i> (000), e	804	930
<i>T</i> , K	103	105
λ , Å	0.71073	0.71073
2 θ _{max} , deg	54.94	50.00
Completeness, %	99.2	99.1
Measured / indep. refl.	6064 / 1144	19496 / 3794
<i>R</i> _{int}	0.0218	0.0311
Ref. parameters / restraints	62 / 0	197 / 0
<i>R</i> [<i>F</i> ≥ 4 σ (<i>F</i>)]	0.0115	0.0216
<i>wR</i> (<i>F</i> ² , all refl.)	0.0268	0.0470
<i>S</i> (GoF)	1.06	1.22
$\Delta\rho$ _{min/max} , e Å ⁻³	−0.37 / 0.52	−0.57 / 0.84

120(vs, br), 87(s, br), 65(m). – Raman (powder sample): ν (cm⁻¹) = 3863(w), 3226(vw), 3082(vw), 1641(w), 1598(vw), 1518(w), 1282(w), 1227(w), 1015(w), 549(vw), 227(m), 158 (ν_3 (I₃⁻), m), 113 (ν_1 (I₃⁻), vs). – M. p.: 179 °C. – Elemental analysis: C₁₀H₁₀N₂I₆ (921.6): calcd. C 13.0, H 1.1, N 3.0; found C 12.6, H 1.0, N 2.6; (I₂ vapor pressure).

Bis(4,4'-bipyridinium) diiodide bis(triiodide) tris(diiodine) dihydrate (**2**)

Mid-IR (single crystal, ATR): ν (cm⁻¹) = 3375(vs, br), 3212 (vs), 3097(s, sh), 1760(w, br), 1663(m), 1626(m), 1594(m), 1520(w), 1473(w), 1445(w), 1354(w), 1192(m), 1143(m), 1017(vw), 932(vw), 898(vw), 846(w), 812(w), 885(w), 761(w), 722(w), 701(w). – Raman (powder sample): ν (cm⁻¹) = 3089(m), 2829(w), 1642(s), 1591(w), 1522(m), 1351(w), 1293(s), 1216(m), 1195(m), 1094(w), 1058(w), 1045(w), 1016(s), 973(w), 902(w), 843(w), 815(w), 764(m), 657(w), 640(w), 616(w), 549(m), 471 (m, br), 393(w), 326(m), 308(m), 267(s), 165(vs), 150(vs, sh), 110(s, br), 75(s, br). – M. p.: 176 °C. – Elemental analysis: C₂₀H₂₄N₄O₂I₁₄ (2129.1): calcd. C 11.3, H 1.1, N 2.6; found C 10.3, H 1.2, N 2.5; (I₂ vapor pressure).

Crystal structure determinations

Single crystals of both compounds suitable for X-ray diffraction were harvested from the bulk samples. For **1** a needle-shaped, dark-red, shiny crystal and for **2** an isometric, black, shiny specimen were selected. These crystals were mounted on an Oxford Xcalibur four-circle diffractometer [24] equipped with an EOS detector and a cooling device. Data collection and reduction followed the standard routine yielding a completeness of more than 99% of reflections necessary for the Laue class. Absorption correction was applied using indexed faces. Structure solution by Direct Methods [25] always yielded all iodine atom positions. Secondary structure solution and simultaneous successive refinement of the primary structure yielded an almost complete model. In the latest stages of the refinement of **1**, the positional parameters of all atoms were refined freely. For all

hydrogen atoms isotropic displacement parameters and for the non-hydrogen atoms anisotropic displacement parameters were refined. For **2** the hydrogen atoms of the CH groups were included using a riding model (AFIX 43) [25] whereas the two hydrogen atoms of the NH groups were refined freely with a common U_{iso} value. For all non-hydrogen atoms anisotropic positional coordinates and displacement parameters were refined freely. Further crystallographic details are summarized in Table 2.

CCDC 841545 and 841546 contain 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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