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Synthesis and X-ray Structure of [H_3O^+·18-crown-6][I_7^-]. A New Infinite Sawhorse Geometry for I_7^- Crystallized from a Liquid Clathrate Medium

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The synthesis and structural characterization of polyiodides has been a rich area of investigation for over 100 years.[1] Various degrees of catenation and a wide variety of geometrical arrangements have been found. These generally depend on interactions with neighboring ions as well as the size and type of associated cation. The presence of a large cation stabilizes dissociation of polyiodides into iodides and I_2, and the situation in which more than one I_2 is coordinated to I^- is limited to very large cations.[1] The I_7^- ion has been previously found in a three-dimensional array,[3] a twisted ladder arrangement,[4] and a zig/zag ladder.[5] In each of these the I_7^- is comprised of discrete units of I_2 and I_3^-. In this communication we report the synthesis of [H_3O^+·18-crown-6][I_7^-] in which the I_7^- fragment exists in a new infinite sawhorse configuration comprised of I_2 and I^- units. This is part of our on-going investigation of oxonium-based complexes[6-8] which form liquid clathrates.[9-11]

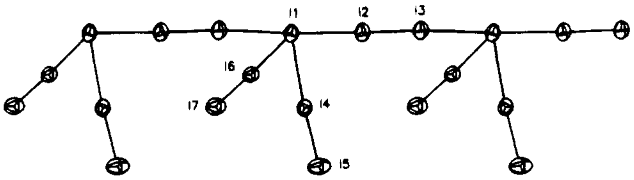

Figure 1. Structure of the I_7^- anion showing the infinite sawhorse polymeric array.

Table 1. Bond Distances (Å) and Angles (deg) for [I_7^-] in [H_3O^+·18-crown-6][I_7^-]

	Bond Distances		
I(1)−I(2)	3.426(3)	I(1)−I(3)	3.354(3)
I(1)−I(4)	3.249(3)	I(1)−I(6)	3.252(3)
I(2)−I(3)	2.764(3)	I(4)−I(5)	2.735(4)
I(6)−I(7)	2.748(4)		
	Bond Angles		
I(2)−I(1)−I(3)	177.0(1)	I(2)−I(1)−I(4)	100.93(8)
I(3)−I(1)−I(4)	81.94(8)	I(2)−I(1)−I(6)	84.76(8)
I(3)−I(1)−I(6)	94.34(8)	I(4)−I(1)−I(6)	90.91(8)
I(1)−I(2)−I(3)	178.9(1)	I(1)−I(3)−I(2)	177.0(1)
I(1)−I(4)−I(5)	174.3(1)	I(1)−I(6)−I(7)	176.8(1)

The title compound, [H_3O^+·18-crown-6][I_7^-], was synthesized by reaction of moist 18-crown-6 with HI(g) in toluene, eq 1.[12]

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(12) Experimental Data: A 1.32 g (0.005 mol) sample of 18-crown-6 was moistened with 0.09 mL (0.005 mol) of distilled water, and then approximately 30 mL of toluene was added. The solution was bubbled with HI(g), which was generated by dissolving 15.0 g of I_2 in 6.0 mL of hydroiodic acid and allowing the solution to drop onto an excess of red phosphorus. After about 10 min, a deep red colored liquid clathrate settled from the slightly orange colored upper layer. The liquid clathrate layer had the composition [H_3O^+·18-crown-6]-[I_7^-]·3.6 C_7H_8, as determined by ^1H NMR. From the liquid clathrate layer, red crystals of the title complex grew over a 6 day period. ^1H NMR (60 MHz, ppm): δ 1.79 ($-CH_3$), δ 2.91 ($-CH_2-$), δ 6.68 (aromatics), δ 9.45 (H_3O^+). Anal. Calcd: C, 12.30; H, 2.32; I, 75.82. Found: C, 12.35; H, 2.28; I, 73.88.

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A liquid clathrate of composition $[H_3O^+{\cdot}18\text{-crown-6}][I_7^-]{\cdot}3.6$

$$18\text{-crown-6} + H_2O + HI(g) \xrightarrow{\text{toluene}} [H_3O^+{\cdot}18\text{-crown-6}][I_7^-] \qquad (1)$$

C_7H_8 formed almost immediately. Other syntheses of I_7^- complexes involved the treatment of I_2 with an iodide salt in a suitable solvent.[3-5] In our case, the formation of I_2 is presumably due to the facile aerial oxidation of I^- to I_2.[13]

The X-ray crystal structure reveals that the $[I_7^-]$ anion exists as a polymeric species in which the monomer consists of a central I^- bonded to three I_2 units, establishing a sawhorse polyhalide structure (Figure 1).[14-16] Selected bond distances and angles are given in Table 1. The I—I bond lengths in the I_2 units range from 2.735(4) to 2.764(3) Å, which are approximately 0.07 Å longer than in elemental I_2.[17] The I—I distance between the central I^- and the I_2 units ranges from 3.252(3) to 3.426(3) Å. This distance compares favorably with those found in other polyiodide structures, where for example the I_3^- to I_2 distance is 3.476(2) to 3.520(1) Å in *N*-methyl-γ-picolinium heptaiodide.[4] In addition to the formation of I_7^- units, each of these has a further bond with neighboring I_7^- species through a head-to-tail interaction of the I^- of one I_7^- and an I_2 fragment on the next. This distance, 3.426(3) Å, which is similar to the distance within the I_7^- unit indicates that the polyiodide chain exists as a polymeric structure of infinite length where I_2 units link together V-shaped fragments arising in an infinite sawhorse configuration (Figure 1).

Interactions between the I_7^- chains exceed 3.81 Å, which is similar to interion distances in $[\text{theobromine}{\cdot}H^+]_4[I_{16}^{4-}]$[18] and $[\text{benzamide}]_2[HI_3]$.[19] While these interion distances are slightly shorter than the van der Waals radii, they are sufficiently weak to consider $(I_7^-)_n$ as discrete polyiodide chains. A structure related to the present case has been found in $[(C_5Me_5)_2Cr_2I_3^+]_2[I_{16}^{2-}]$, where a central I^- ion is coordinated by *four* I_2 fragments.[20]

The O(oxonium)$\cdot\cdot\cdot$O(crown) distances of the $[H_3O^+{\cdot}18\text{-crown-6}]$ cation are well within the range for hydrogen bonding (2.73(1)–2.79(1) Å).[21] The O(oxonium) resides 0.09 Å out of the plane defined by the crown ether oxygen atoms. This suggests the oxonium ion is nearly *planar*, as in a previously reported *planar* H_3O^+ ion where the oxonium ion resided 0.10 Å out of the plane of the crown.[22] *Pyramidal* geometry has also been established for the H_3O^+ ion where the oxonium ion sits 0.61 Å out of the plane of the crown oxygen atoms.[23]

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Supporting Information Available: Tables giving crystallographic data, positional and thermal parameters, and bond lengths and angles (4 pages). Ordering information is given on any current masthead page.

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(14) Crystal Data: $C_{12}H_{27}O_7I_7$, monoclinic $P2_1/n$; a = 9.540(5) Å, b = 21.983(6) Å, c = 14.170(5) Å, β = 99.62(4)°, V = 2930 Å^3, Z = 2, μ = 36.9 cm^{-1} (Mo Kα); solved by direct methods, least-squares refinement using 3005 absorption corrected, observed reflections, $F_o > 3\sigma(F_o)$, $2° < 2\theta < 45°$; R = 0.086, R_w = 0.096.

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