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})_{2}I_{2}[I_{3}]_{2}·3I_{2}·2H_{2}O, 2. Both compounds have been structurally characterized by crystallographic and spectroscopic methods (Raman and IR). Compound 1 is composed of I₃⁻ 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 I₁₄⁴⁻ anion, 4,4′-bipyridinium dications and hydrogen-bonded water molecules in the ratio of 1:2:2. The I₁₄⁴⁻ 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