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Crystallographic and Theoretical Studies on the Role of Halogen-Halide Synthons in the Structures Of (nYP)X, (nYP)₂CuX₄ and Cu(nYP)₂X₂. Firas Awwadi, Roger Willett, Kirk Peterson, Brendan Twamley, Dept. of Chemistry, Washington State Univ., Fulmer Hall, Pullman, WA 99164 USA.

Recently, halogen-halogen synthons have received much interest and debate. Halogen-halide interactions, a special case of these synthons, have not been studied in much detail. We have investigated their role in the crystal structure determinations of (nYP)X, where n = 2, 3 or 3 and nYP⁺ denotes either an n-chloro or n-bromopyridinium cation, Y = Cl or Br and X = Br, Cl or I. The data indicates that the Y...X⁻ synthon is characterized by an almost linear C-Y...X⁻ angle and Y...X⁻ distance less than the sum of the van der Waals radii - on average the distances are ca. 0.17Å (Cl-X) and 0.41Å (Br-X) shorter. This indicates, qualitatively, that the bromine-halide interaction is stronger than the chlorine-halide interaction. The charge effect on these interactions was studied using the following systems: (nBP)₂CuX₄ and Cu(nbp)₂X₂ where nbp = n-bromopyridine, nBP = n-bromopyridinium cation and X = Br⁻ or Cl⁻. The bromine-halide distances are 0.3-0.4Å and 0.0-0.2Å less than the sum of van der Waals radii of the bromine atom and the corresponding halide anion for (nBP)₂CuX₄ and Cu(nbp)₂X₂ respectively. The data indicates that the charge assisted halogen-halide interactions are stronger than unassisted ones. In these salts and complexes, the interactions all have the same directionality and therefore the same synthon; however the interactions have different strengths. Quantum mechanical calculations were performed to model and calculate their relative strength. The *ab initio* calculations showed the bromine-halide interaction strength is comparable to that of hydrogen bond and increases as the size of the halide anion decreases.