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PREPARATION AND STRUCTURES OF SOME NOVEL, SELENIUM-IODINE CATIONS

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We recently prepared quantitatively, and determined the crystal structure of $S_2I_4(AsF_6)_2$. In this salt the $S_2I_4^{2+}$ has a distorted right triangular prismatic structure, with the S - S and I - I distances indicative of bond orders 2.33 and 1.33 respectively. In fact, the S - S distance [1.83(1) Å] is the shortest observed distance in an isolated compound, and therefore the $S_2I_4^{2+}$ cation contains a much sought after 3pπ - 3pπ bond. We speculated that the geometry of $S_2I_4^{2+}$, that maximises π bonding within the cation, might be a consequence of the near equality of the ionisation potentials of S_2 [9.36(2) eV] and I_2 [9.3995(1) eV]. To explore this hypothesis, we attempted to synthesise analogous cations. In one reaction we prepared $Se_2I_4(Sb_2F_{11})_2$ [I.P. Se 8.33(3) eV] essentially quantitatively from elemental selenium and $I_2Sb_2F_{11}$. The structure of $Se_2I_4^{2+}$ can be viewed as two eclipsed SeI_2^+ units joined by a long Se - Se bond [2.841(2) Å], similar in length to the transannular bond in Se_8^{2+} [2.84(1) Å] and considerably longer than that in Se_8 [2.336(6) Å]. The geometry of $Se_2I_4^{2+}$ is similar to that of the isoelectronic $S_2O_4^{2-}$ the bonding in which has been the subject of interest and controversy for some years. In an attempt to prepare $S_7I^+MF_6^-$ [M = As, Sb], $[Se_6I^+]$-$[MF_6^-]$ were prepared containing the poly-iodo-cyclo-hexaselenium cation. The hexaselenium rings of a chair conformation are joined to two neighbouring hexaselenium rings by two weak [2.736(3) Å] exocyclic 1,4-axial selenium-iodine bonds. Another selenium-iodine cation will also be discussed.