Preparation and X-Ray Crystal Structure of Se₂I₄(Sb₂F₁₁)₂ containing the Eclipsed Diselenium Tetraiodide(2+) Cation

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$Se_2I_4(Sb_2F_{11})_2$ has been prepared and its structure determined by single crystal X-ray diffraction; the $Se_2I_4^{2+}$ cation has an eclipsed $S_2O_4^{2-}$ type structure with two SeI_2^+ units joined by a weak selenium–selenium bond [2.841(2) Å] and very weak iodine–iodine interactions [3.756(2), 3.661(2) Å].

Recently the salts S_7IMF_6 (M = As, Sb),[1] [$(S_7I)_2I$] $(SbF_6)_3\cdot2As\text{-}F_3$,[2,3] $(S_7I)_4S_4(AsF_6)_6$,[3,4] and $S_2I_4(AsF_6)_2$[5] containing novel sulphur–iodine cations have been prepared and characterised. $S_2I_4(AsF_6)_2$ contains a distorted right triangular prismatic $S_2I_4^{2+}$ cation with sulphur–sulphur and iodine–iodine bond lengths indicative of bond orders 2.33 and 1.33, respectively. The cation may be regarded as consisting of $S_2^{0.66+}$ and $2I_2^{0.66+}$ units, weakly bonded together by electrons in π^* orbitals. Thus, π bonding in each dimer unit is maximized. The bonding situation may arise from the near equality of the ionization potentials (I.P.) of S_2 [9.36(2) eV] and I_2 [9.3995(12) eV].[6] To explore this hypothesis, we attempted to synthesize analogous cations. In one reaction we prepared $Se_2I_4(Sb_2F_{11})_2$ [I.P. Se_2 8.88(3) eV][6] quantitatively according to equation (1). The structure was determined by X-ray diffraction.

$$2I_2Sb_2F_{11}(\text{ref. 7}) + 2Se \xrightarrow[\text{room temp.}]{SO_2} Se_2I_4(Sb_2F_{11})_2 \qquad (1)$$
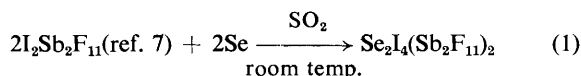
Crystal Data: $Se_2I_4(Sb_2F_{11})_2$, $M = 1570.50$, triclinic, space group $P\bar{1}$ (C_i^1), $a = 17.915(2)$, $b = 9.276(1)$, $c = 8.001(1)$ Å, $\alpha = 96.04(1)$, $\beta = 95.22(1)$, $\gamma = 91.83(1)°$, $U = 1316 \text{Å}^3$, $Z = 2$, $D_c = 3.97 \text{ Mg m}^{-3}$, $\mu(\text{Mo-}K_\alpha) = 11.62 \text{ mm}^{-1}$, $\lambda(\text{Mo-}K_\alpha) = 0.710 69$ Å. Data were collected for $5° \leqslant 2\theta \leqslant 45°$, 3438 unique reflections, 2647 observed ($I \geqslant 2\sigma$).

The data were corrected for absorption and the structure was solved by direct methods. Least-squares refinement, with anisotropic thermal parameters for all atoms, gave final residuals: $R = 0.046$ and $R_w = 0.067$.† The structure con-
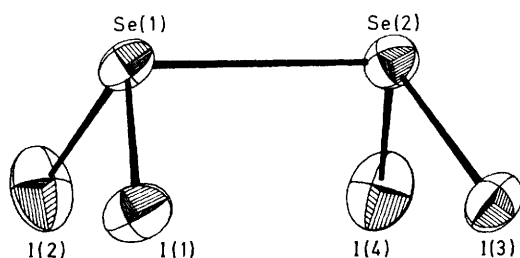

Figure 1. Structure of $Se_2I_4^{2+}$. Bond lengths and angles: Se(1)–Se(2) 2.841(2), Se(1)–I(1) 2.450(2), Se(1)–I(2) 2.436(2), Se(2)–I(3) 2.457(2), and Se(2)–I(4) 2.443(2) Å; I(1)–Se(1)–I(2) 106.95(8), I(3)–Se(2)–I(4) 105.47(8), I(1)–Se(1)–Se(2) 100.47(7), I(2)–Se(1)–Se(2) 98.07(7), I(3)–Se(2)–Se(1) 101.03(7), and I(4)–Se(2)–Se(1) 101.26(7)°. Contacts (I–I ⩽ 4.00, I–F ⩽ 3.10, and Se–F ⩽ 3.00 Å): I(1)–I(3) 3.756(2), I(2)–I(4) 3.661(2), I(1)–I(2) 3.926(2), I(3)–I(4) 3.899(2), I(1)–F(24) 2.998(12), I(2)–F(2) 3.080(11), I(3)–F(28) 2.888(11), I(4)–F(3) 2.955(11), Se(1)–F(1) 2.835(10), Se(1)–F(8) 2.915(13), Se(1)–F(23) 2.909(11), Se(2)–F(1) 2.988(12), and Se(2)–F(23) 2.922(11) Å. Torsion angles: I(1)–Se(1)–Se(2)–I(3) 1.7 and I(2)–Se(1)–Se(2)–I(4) 2.3°.

† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, West Germany. Any request should be accompanied by the full litera-ture citation for this communcation.

sists of discrete $Se_2I_4^{2+}$ and $Sb_2F_{11}^-$ ions with definite anion–cation interactions.

The eclipsed structure of the $Se_2I_4^{2+}$ cation (Figure 1) only superficially resembles that of $S_2I_4^{2+}$. It can be described as two 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][8] and the shorter selenium–selenium bond in Se_4N_4 [2.748(9) Å][9] and considerably longer than that in Se_8 (α) [2.336(6) Å].[10] This structure is similar to that of $S_2O_4^{2-}$,[11,12] the bonding in which is of considerable interest.[13,14] The S–S bond in $S_2O_4^{2-}$ [2.389,[11] 2.386(2) Å[12]] is much longer than that in S_8 [2.05 Å].[14] The arrangement of atoms about the long bond between trico-ordinate selenium atoms in Se_8^{2+} and Se_4N_4, and analogous sulphur atoms in S_8^{2+},[15] S_4N_4,[16] and $S_2O_4^{2-}$ are, like the iodine atoms in $Se_2I_4^{2+}$, in eclipsed configurations. The bonding in $Se_2I_4^{2+}$ may be described by valence bond (V.B.) structure I,
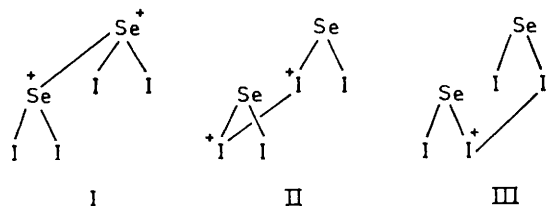
with small contributions from structures II and III. [I(1)–I(3) and I(2)–I(4) are 3.756(2) and 3.661(2) Å, respectively, significantly less than twice the sum of the van der Waals' radius of iodine of 4.00 Å[17]]. The selenium–selenium bond in $Se_2I_4^{2+}$ is longer than that in Se_8, possibly because of the presence of positive charges on adjacent selenium atoms (I), and, in addition, because the selenium–selenium bond order is less than one (as implied by V.B. structures II and III). Alternatively, the $Se_2I_4^{2+}$ cation may be regarded as two SeI_2^+ radical cations, joined, in part, by overlap of the odd electron in each of the π^* SeI_2^+ molecular orbitals (see Figure 2) resulting in some bonding between all six atoms and a formal selenium–

π, Bonding	π, Nonbonding	π^*, Antibonding
Occupancy 2e	2e	1e
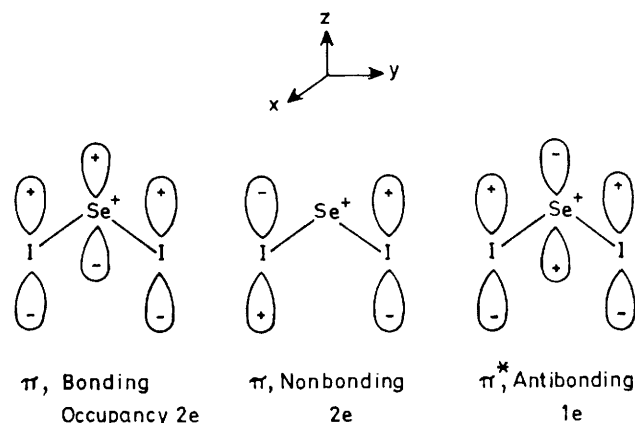
Figure 2. The SeI_2^+ radical cation's π M.O.'s derived from p_z selenium and iodine A.O.'s.

iodine bond order of 1.25 (net $0.5\,\pi$ bond per SeI_2^+ unit, see Figure 2). Interestingly, the selenium–iodine bond lengths in $Se_2I_4^{2+}$ [2.450(2), 2.436(2), 2.457(2), and 2.443(2) Å] are somewhat shorter than those in SeI_3^+ [2.511(2), 2.513(2), and 2.510(2) Å] in SeI_3SbF_6.[18] Both of these approaches account for the eclipsed geometry of the $Se_2I_4^{2+}$ cation. $Se_2I_4^{2+}$ is clearly very different from its $S_2I_4^{2+}$ analogue; although both have cluster-like characteristics, both may contain $\pi^*-\pi^*$ bonds, and both are different from the isoelectronically similar but conventional σ-bonded $trans$-P_2I_4.[19]

This is the first reported structural determination of a binary selenium–iodine species although salts of SeI_3^+[20] and SeI_6^{2-}[21] have been prepared previously. Binary neutral selenium iodides have not been isolated.[22]

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