The I_4^{2+} cation. *X*-Ray Crystal Structures of $(I_4^{2+})(AsF_6^-)_2$ and $(I_4^{2+})(Sb_3F_{14}^-)(SbF_6^-)$

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The I_4^{2+} cation has been fully characterised for the first time by the preparation of the compounds $(I_4^{2+})(AsF_6^-)_2$ and $(I_4^{2+})(Sb_3F_{14}^-)(SbF_6^-)$ and the determination of their structures by *X*-ray crystallography; the I_4^{2+} cation has a rectangular structure and may be considered to consist of two I_2^+ cations held together by two rather weak bonds.

The I_2^+, I_3^+, and I_5^+ cations have been prepared and characterised in solution in several highly acidic media such as H_2SO_4 and HSO_3F; several crystalline salts of these ions have also been isolated.[1] The structures of $I_2^+Sb_2F_{11}^-$, $I_3^+AsF_6^-$, and $I_5^+SbF_6^-$ have been determined by *X*-ray crystallography.[2–4] In one of the early studies on the cation I_2^+ it was observed that on cooling a solution of the cation in HSO_3F the colour of the solution changed from an intense blue to a deep red-brown at about −80 °C and at the same time the paramagnetism of the solution decreased considerably.[5] These results were explained by assuming that at low temperature the paramagnetic I_2^+ ion dimerizes to the diamagnetic I_4^{2+} cation. Cryoscopic and conductimetric measurements on solutions of $I_2^+SO_3F^-$ in fluorosulphuric acid were also consistent with the formation of I_4^{2+} at −78 °C.[5] However, no information on the structure of this species was obtained at that time. We now describe the isolation and structure determination of two crystalline salts of the I_4^{2+} cation.

When iodine was allowed to react with an excess of AsF_5 in solution in SO_2 at room temperature over a period of 48 h black crystals were obtained on slow removal of the solvent. These were shown by an *X*-ray crystallographic study to be the compound $I_4(AsF_6)_2$. When the same reaction was carried out in solution in SO_2ClF there was an immediate precipitation of a red amorphous powder. Crystalline $I_4(AsF_6)_2$ was obtained on crystallizing the red amorphous powder from SO_2. When SbF_5 and iodine in a 2:1 mole ratio were allowed to react in solution in SO_2 at room temperature a dark green solution was obtained. After filtration of a small amount of a white insoluble material (probably SbF_3 or an $SbF_3{\cdot}SbF_5$ compound), black crystals of $I_4Sb_4F_{20}$ were obtained by slow removal of the solvent. The main reaction can probably be represented by equation (1). The product was characterised by

$$2I_2 + 4SbF_5 \rightarrow I_4(Sb_3F_{14})(SbF_6) \qquad (1)$$

an *X*-ray crystallographic determination of its structure. When the black crystals of either compound are powdered they become bright red in colour.

Resonance Raman spectra were obtained from both solids by excitation with the 514.5 nm argon ion line. Both solids gave a single Raman line at 232 cm^{-1} together with several overtones. This frequency differs only slightly, but nevertheless significantly, from the stretching frequency of the I_2^+ ion which is observed at 238 cm^{-1} in the Raman spectrum.[6]

Crystal data: $I_4^{2+}(AsF_6^-)_2$, $M = 885.44$, monoclinic, space group $A2/m$,† $a = 5.907(2)$, $b = 9.815(5)$, $c = 12.514(6)$ Å, $\beta = 103.71(4)°$, $U = 704.9(6)$ Å^3, $Z = 2$, $D = 4.17$ g cm^{-3}. *X*-Ray data with $2\theta < 55°$ were collected with a Syntex P2$_1$ diffractometer and Mo-K_α radiation. The structure was solved by the use of the heavy-atom method and currently $R = 0.132$ and $R_W = 0.147$ based on 488 unique reflections. For $I_4^{2+}(Sb_3F_{14}^-)(SbF_6^-)$, $M = 1374.59$, monoclinic, space group $P2_1/c$, $a = 8.425(1)$, $b = 15.980(3)$, $c = 16.804(3)$ Å, $\beta = 100.53(1)°$, $U = 2225.7(7)$ Å^3, $Z = 4$, $D = 4.10$ g cm^{-3}. *X*-Ray data with $2\theta < 55°$ were collected with a Nicolet P3 diffractometer with Mo-K_α radiation. The structure was solved by the use of the heavy-atom method and currently $R = 0.092$ and $R_W = 0.093$ based on 2658 unique reflections.‡

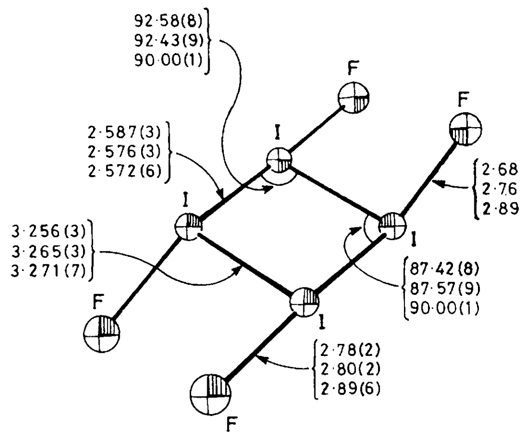

Figure 1. One of the cations from $I_4(SbF_6)(Sb_3F_{14})$. The bond lengths (Å) and angles (°) are listed in order for the cation in $I_4(AsF_6)_2$ and the two cations in $I_4(SbF_6)(Sb_3F_{14})$.

The bond lengths and angles for the cation in $I_4(AsF_6)_2$ and the two independent cations in $I_4(Sb_3F_{14})(SbF_6)$ are summarized in Figure 1. The I_4^{2+} cation is rectangular and the dimensions vary little between the three cations. It can best be described as two I_2^+ cations bonded together by two relatively weak bonds. The shorter of the two I–I distances is only slightly longer than that for I_2^+ in $I_2(Sb_2F_{11})$[2] (2.578 *vs.* 2.557 Å). The weak bonds are much shorter than the sum of the van der Waals radii (4.2 Å) and the average is comparable to the longest distances found in I_5^- (3.264 *vs.* 3.17 Å).[7] Each iodine atom forms a weak interaction with a fluorine atom of the anion. The average length of this interaction is much shorter than the iodine–fluorine van der Waals distance (2.78 *vs.* 3.46 Å). These fluorine atoms are roughly collinear with the short I–I bonds, but there is considerable flexibility since the I–I–F angles range from 132 to 175°.

Birchall and Myers[8] have shown that the Mössbauer spectra of both $I_4(AsF_6)_2$ and $I_4(Sb_3F_{14})(SbF_6)$ are consistent with the

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† This is an unconventional setting of $C2/m$. The matrix for conversion into the $C2/m$ cell is (001/0−10/100).

‡ 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, W. Germany. Any request should be accompanied by the full literature citation for this communication.

stereochemistry of the iodine found by *X*-ray crystallographic studies. They have also shown that the Mössbauer spectrum of a frozen solution of $I_2Sb_2F_{11}$ in HSO_3F is essentially identical to that of the solid crystalline compounds thus confirming the earlier suggestion that I_2^+ dimerizes to I_4^{2+} at low temperature in solution in HSO_3F.[5]

The interaction between the two I_2^+ ions may be described as a four-centre two-electron bond so that each of the long I - - - I bonds has a bond order of 0.5. The four-centre orbital can be considered to be formed from the half-filled π^* antibonding orbitals on each I_2^+. This model is consistent with the long I–I distances and the diamagnetism of the cation. Similar bonds between pairs of sulphur atoms have been found in $(S_3N_2^+)_2$ [9] and between sulphur and iodine atoms in $S_2I_4^{2+}$.[10]

It is interesting to note that both the I_4^{2+} salts crystallize at room temperature whereas in the previous studies on solutions of $I_2^+SO_3F^-$ in HSO_3F, evidence for the formation of I_4^{2+} was obtained only at low temperatures.

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