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# Preparation and characterization of $M_3X_3AsF_6$ (M=S, Se; X=Cl, Br)

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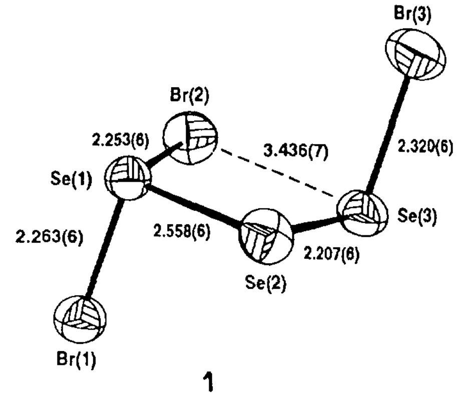
There are numerous neutral sulfur and selenium fluorides, but no stable neutral iodides. In contrast, there are several examples of sulfur and selenium iodine cations, e.g. $AsF_6^-$, $SbF_6^-$ or $Sb_2F_{11}^-$ salts of $S_2I_4^{2+}$, $S_7I^+$, $(S_7I)_2I^{3+}$, $Se_2I_4^{2+}$, $Se_6I_2^+$, $SeI_3^+$ and $(Se_6I^+)_n$, but no examples of fluoro cations with the exception of $SF_3^+$ and $SeF_3^+$. These iodine cations contain examples of stable $S_7$ and $Se_6$ rings, and stable S–I and Se–I bonds [1]. The structures have cluster-like geometries, arising from intercationic contacts. There is chalcogen–chalcogen bond alternation leading to long and short chalcogen–chalcogen distances which imply the presence of $np\pi$–$np\pi$ ($n \geqslant 3$) bonds, that we have proposed [2] arise from positive charge delocalization. This thesis is supported by the structures of $Se_3Br_3^+$ and $S_3Br_3^+$ [3], and more recently by those of $Se_3Cl_3^+$ and $S_3Cl_3^+$ ($AsF_6^-$ salts) [4]. $Se_3Br_3AsF_6$ and $S_3Br_3AsF_6$ were prepared quantitatively by the reaction of the chalcogen, bromine and $AsF_5$, e.g. as outlined in Eq. (1):

$$3S_8 + 12Br_2 + 12AsF_5 \xrightarrow{\text{liquid } SO_2} 8S_3Br_3AsF_6 + 4AsF_3 \qquad (1)$$

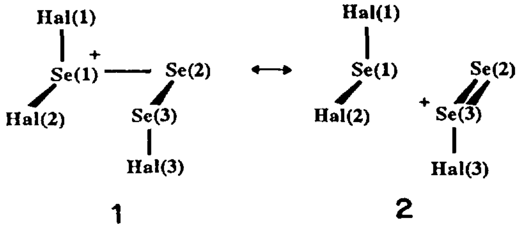
The chlorides were prepared by the reaction of $XCl_3^+$ and 2X (X=S, Se) in $SO_2$ in essentially quantitative yield.

Both $Se_3Br_3^+$ and $Se_3Cl_3^+$ adopt $Hal_2X^+XXHal$ (Hal=Br, Cl) geometries, the smallest unit in which chalcogen–chalcogen bond alternation is possible, as illustrated for $Se_3Br_3^+$ in **1**.



**1**

The structures of the $S_3Cl_3^+$ and $S_3Br_3^+$ are disordered, but are consistent with the presence of $Hal_2S^+SSHal$ cations with similar geometries to those of their selenium analogues. Their FT-Raman spectra have been obtained and peaks assigned to $AsF_6^-$, $Hal_2S^+$, S–Hal, S–S (long) and S–S (short), and by comparison with related bond distances and stretching frequencies, Hal–S and S–S bond distances were estimated. The S–S bond distances implied bond orders similar to those of the selenium analogues (ca. 0.4 and 1.6). Hence the structure of the cations can be represented, as illustrated for the selenium case, by the resonance structures **1** and **2**, with **1** being of slightly greater importance than **2**, i.e. the positive charge



**1** **2**

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delocalization leads to chalcogen–chalcogen pπ–pπ bonding.

This valence bond view of the bonding is supported by ab initio Gaussian 92 STO-3G* calculations on $S_3Cl_3^+$ which give an optimized geometry similar to that estimated from the Raman data, an energy 50 kJ $mol^{-1}$ higher for this structure with the S–S distances equal and 107 kJ $mol^{-1}$ higher for the structure with the S–Cl bond that makes intercationic contact translated by 180°, thus removing the intercationic contact. In addition, the molecular orbitals from extended Hückel calculations, using the observed geometry, show evidence for a strong σ- and a π-bond between the strongly bound sulfurs, and a weak σ-bond in the long S–S region.

## References

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