The Crystal Structure of Trifluoroselenium(IV) μ-Fluoro-bis[pentafluoroniobate(V)]

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THE adduct formed by the interaction of bromine trifluoride and antimony pentafluoride has recently been shown[1] to have a crystal structure consistent with a largely ionic formulation, BrF_2^+ SbF_6^-. There is a substantial interaction between the ions through fluorine bridging.

To investigate the SeF_3^+ ion, the existence of which has not been demonstrated in the solid state, we have studied the interaction of selenium tetrafluoride and niobium pentafluoride. The reaction has been reported[2] to yield the compound SeF_4,NbF_5, which we have found as a minor product, isostructural[3] with SeF_4,TaF_5, with a rhombohedral unit cell, $a = 8\cdot99$ Å, $\alpha = 93°$. A further minor product, which forms orthorhombic crystals, $a = 8\cdot02$, $b = 7\cdot13$, $c = 11\cdot09$ Å, has been shown by a three-dimensional crystal structure analysis[3] to be $SeOF_2,NbF_5$. The structure is very similar to that[4] of $SeOCl_2,SbCl_5$ with a bridging oxygen atom linking the selenium and niobium atoms.

The major product formed monoclinic crystals and our structure analysis has shown the compound corresponds to the formula $SeF_4,2NbF_5$. The molecular geometry of this adduct is consistent with a formulation $(SeF_3^+)(Nb_2F_{11}^-)$, with substantial interaction between the ions through fluorine bridging, as for BrF_3,SbF_5.[1]

Crystal data were determined photographically using Weissenberg and precession techniques with Cu-K_α radiation: Nb_2SeF_{14}, $M = 530\cdot8$, monoclinic, $a = 7\cdot60 \pm 0\cdot01$, $b = 17\cdot38 \pm 0\cdot02$, $c = 8\cdot80 \pm 0\cdot01$ Å, $\beta = 103\cdot4 \pm 0\cdot2°$ $U = 1113$ Å^3 Space group $P\ 2_1/c$ (C^5_{2h}, No. 14). The volume is consistent with $Z = 4$, since with 56 fluorine atoms in the unit cell, the volume per fluorine atom is 20 Å^3, the same value as in similar structures. Intensity data were determined photometrically from integrated Weissenberg films, giving 1330 independent reflections. The niobium and selenium atom positions were determined from the three-dimensional Patterson function and the fluorine atom positions from subsequent electron-density maps. Full-matrix least-squares refinement of positional and isotropic temperature parameters has led to a value of 0·09 for R.

The atomic arrangement is shown in the Figure. The two niobium atoms have an approximately octahedral co-ordination by fluorine atoms, with equal bond distances to the bridging fluorine atom between them, within experimental error. This bridge bond-length (2·05 Å) is the same as the bridge bond-length (2·06 Å) in the tetrameric unit of niobium pentafluoride[5] itself, and the $Nb_2F_{11}^-$ ion can be considered as derived from a cleavage of the tetramer. The other Nb–F distances show considerable variation but those nearest to the selenium atom are lengthened. We consider that this lengthening, and the comparatively short distances of these fluorines from selenium show a definite interaction.

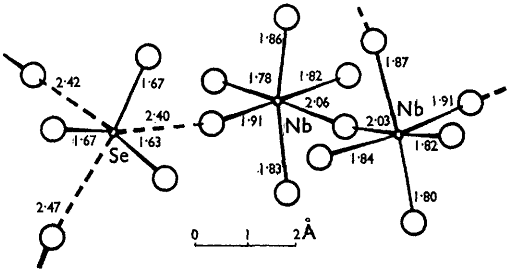

FIGURE. *Projection down* [001]. Estimated standard deviations in bond lengths are ± 0·02 Å.

The selenium atom is closely co-ordinated by three fluorine atoms at $1\cdot66 \pm 0\cdot03$ Å, and with all the F–Se–F angles equal to $94 \pm 0\cdot5°$ this SeF_3 unit has C_{3v} symmetry. However the three fluorine atoms from neighbouring $Nb_2F_{11}^-$ ions at 2·40, 2·42, and 2·47 Å complete a distorted octahedral co-ordination around the selenium atom. The distances between these atoms are very large, (3·37, 3·64, and 4·00 Å) and we suggest that this is due to the presence of the selenium non-bonding electron pair, filling a seventh co-ordination position, in the triangular octahedral face defined by these fluorine atoms. This arrangement for seven-co-ordination has been found in the Group A rare-earth sesquioxide structure.[6] Such a position for the non-bonding electron pair would also correspond to an approximately tetrahedral arrangement for the three terminal fluorine atoms and the lone-pair around the selenium atom.

The structure can be considered as derived predominantly from the ionic formulation $SeF_3^+Nb_2F_{11}^-$, with some contribution from the covalent arrangement with Nb_2F_{11} units linked through *cis*-bridging fluorine atoms to distorted octahedral SeF_6 units.

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