Fluoride Crystal Structures. Part XX.[1] Niobium Pentafluoride–Antimony Pentafluoride

By **A. J. Edwards,** Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham B15 2TT

Crystals of the title adduct are triclinic, space group $P\bar{1}$, $a = 5{\cdot}64$, $b = 9{\cdot}58$, $c = 7{\cdot}38$ Å, $\alpha = 87{\cdot}2$, $\beta = 99{\cdot}9$, $\gamma = 106{\cdot}5°$. The structure was determined from photographic data by Patterson and Fourier methods and refined by three-dimensional least-squares methods to R 0·065 for 906 reflections. The structure consists of a zigzag endless chain arrangement with alternating antimony and niobium atoms linked by *cis*-bridging fluorine atoms. Both metal atoms have a distorted octahedral co-ordination by fluorine atoms, the distortion being greater for niobium, consistent with a substantial contribution to the structure from the ionic form $[NbF_4]^+[SbF_6]^-$.

CONSIDERABLE interest has recently been shown in the interactions between pentafluorides. An n.m.r. study[2] of niobium pentafluoride dissolved in antimony pentafluoride concluded that dissolution rather than reaction occurred, although it was suggested that a fairly strong interaction was involved. More recently a detailed n.m.r. and Raman spectroscopic study[3] of complex formation between antimony pentafluoride and the pentafluorides of niobium and tantalum has been reported. The results of this work were consistent with formation in the liquid state of neutral, fluorine-bridged polymers, with mixed, *cis*-bridged transition-metal and antimony units, rather than ionic species. It was suggested that these polymers were ' fluxional ' on the n.m.r. time-scale, as were the neutral molecules MF_4,-Sb_nF_{5n-1} (M = Nb or Ta) formed in solution in sulphuryl chloride fluoride.

The crystal structure of the 1 : 1 adduct between niobium and antimony pentafluorides was briefly reported previously[4] and is now described in detail.

EXPERIMENTAL

Niobium and antimony pentafluorides were prepared by the fluorination of the metal powders at 250°. An excess of antimony pentafluoride was distilled onto niobium pentafluoride in a rigorously dried Pyrex glass apparatus. On warming to room temperature, a colourless solution was formed. On continuous pumping, colourless, thin plate crystals, m.p. *ca.* 45 °C, sublimed from the sticky solid produced. These crystals could not be freed from liquid antimony pentafluoride and an alternative preparation was attempted.

A mixture of the two pentafluorides, containing a slight excess of the niobium compound, was prepared and crystals obtained by sublimation at 40—50 °C. These needle crystals had m.p. 60 °C and were subsequently shown to be the 1 : 1 adduct. The aforementioned lower-melting plate crystals were probably the 1 : 2 adduct, $NbF_5,2SbF_5$. (Two solids with m.p.'s 40—45 and 50—56 °C were obtained from mixtures with TaF_5 and SbF_5 of 1 : 2·01 and 1 : 1·13 respectively in the n.m.r. and spectroscopic study.[3])

Single crystals of the product, which were needles elongated along the a axis, were obtained by sublimation in a temperature gradient in evacuated Pyrex capillaries as described previously.[5]

Crystal Data.—$F_{10}NbSb$, $M = 405$, Triclinic, $a = 5{\cdot}64 \pm 0{\cdot}01$, $b = 9{\cdot}58 \pm 0{\cdot}01$, $c = 7{\cdot}38 \pm 0{\cdot}01$ Å, $\alpha = 87{\cdot}2 \pm 0{\cdot}3$, $\beta = 99{\cdot}9 \pm 0{\cdot}3$, $\gamma = 106{\cdot}5 \pm 0{\cdot}3°$, $U = 377$ Å^3, $Z = 2$, $D_c = 3{\cdot}57$, $F(000) = 364$. Space group $P\bar{1}$ (C_i^1, No. 2). Cu-K_α ($\lambda = 1{\cdot}5418$ Å) and Mo-K_α ($\lambda = 0{\cdot}7107$ Å; $\mu = 56$ cm^{-1}) radiations. Single-crystal precession and Weissenberg photographs.

The density of the crystals was not measured but $Z = 2$ was assumed since the volume per fluorine atom is then

---

[1] Part XIX, A. J. Edwards, *J.C.S. Dalton*, 1972, 816.

[2] T. K. Davies and K. C. Moss, *J. Chem. Soc.* (*A*), 1970, 1054.

[3] P. A. W. Dean and R. J. Gillespie, *Canad. J. Chem.*, 1971, **49**, 1736.

[4] A. J. Edwards, *Chem. Comm.*, 1970, 820.

[5] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1970, 1891.

18·8, similar to the value of 17·6 Å^3 in niobium[6] and antimony[7] pentafluorides.

Structure Determination.—Integrated intensities were collected about the *a* axis (layers 0—5*kl*) by use of Mo-K_α radiation and a Nonius integrating camera. The relative intensities of 906 independent reflections were measured with a photometer of similar design to that described by Jeffery,[8] and were corrected for Lorentz and polarisation factors; no absorption corrections were applied for a crystal with dimensions perpendicular to the needle axis of *ca.* 0·1 mm.

A three-dimensional Patterson synthesis was calculated but considerable difficulty was experienced in its interpretation. One of the largest peaks was ultimately found to arise from a build-up of fluorine–fluorine vectors parallel to the *a* axis. An interpretation, based on the relative heights of the peaks, was eventually made in the non-centrosymmetric space group $P1$ with two antimony and two niobium atoms in general positions. This arrangement gave R 0·26 with structure factors calculated by use of scattering factors for neutral atoms from ref. 9. A three-dimensional electron density map, based on the heavy atom positions gave the positions of 20 independent fluorine atoms. Refinement of the positional and isotropic temperature factors and layer scale-factors by full-matrix least-squares methods, showed one niobium atom with a very low temperature factor and one antimony atom with a correspondingly high temperature factor. When the identities of these two atoms were interchanged, the arrangement was approximately centrosymmetric. The atoms were therefore redefined in the centrosymmetric space group $P\bar{1}$ and refinement continued. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimised, initially with unit weights, and, during the final stages, with $\sqrt{w} = |F_o|/23$ when $|F_o| \leqslant 23$ and $\sqrt{w} = 23/|F_o|$ when $|F_o| > 23$. The final parameter shifts were $< 0{\cdot}1\,\sigma$ and an analysis of the variation of $w\Delta^2$ with increasing $\sin\theta/\lambda$ and with increasing $|F_o|$ was satisfactory. The final R was 0·064. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20493 (9 pp., 1 microfiche).*

Final positional parameters and isotropic temperature factors are listed in Table 1 and interatomic distances and angles in Table 2.

TABLE 1

Final atomic positional and thermal parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U/Å^2
Sb	−0·0336(3)	0·3150(2)	0·7657(2)	1·93(4)
Nb	0·3375(3)	0·2205(2)	0·3794(2)	1·53(4)
F(1)	−0·1084(35)	0·1219(20)	0·7739(24)	4·21(34)
F(2)	0·0355(28)	0·5077(16)	0·7054(19)	2·84(26)
F(3)	0·2324(34)	0·3360(20)	0·9449(24)	3·97(33)
F(4)	−0·2578(37)	0·3256(21)	0·9163(26)	4·22(34)
F(5)	−0·3061(27)	0·2928(15)	0·5604(19)	2·59(24)
F(6)	0·1726(25)	0·3024(15)	0·5833(19)	2·59(26)
F(7)	0·3045(27)	0·0735(16)	0·5486(20)	2·92(26)
F(8)	0·4319(27)	0·4145(17)	0·3387(20)	2·80(25)
F(9)	0·5002(29)	0·1615(16)	0·2209(20)	3·00(27)
F(10)	0·0268(28)	0·1671(16)	0·2494(20)	3·04(28)

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) In the chain

Sb–F(1)	1·78(2)	Nb–F(7)	1·83(2)
Sb–F(2)	1·82(2)	Nb–F(8)	1·81(2)
Sb–F(3)	1·79(2)	Nb–F(9)	1·81(2)
Sb–F(4)	1·85(2)	Nb–F(10)	1·79(2)
Sb–F(5)	1·94(2)	Nb$^{\mathrm{I}}$–F(5)	2·16(2)
Sb–F(6)	1·95(2)	Nb–F(6)	2·18(2)
F(1) ··· F(3)	2·58(3)	F(6) ··· F(7)	2·54(2)
F(1) ··· F(4)	2·66(3)	F(6) ··· F(8)	2·53(2)
F(2) ··· F(3)	2·67(2)	F(7) ··· F(9)	2·82(2)
F(2) ··· F(4)	2·68(2)	F(8) ··· F(9)	2·76(2)
F(3) ··· F(4)	2·71(3)	F(6) ··· F(10)	2·73(2)
F(1) ··· F(5)	1·57(2)	F(7) ··· F(10)	2·75(2)
F(2) ··· F(5)	2·52(2)	F(8) ··· F(10)	2·80(2)
F(4) ··· F(5)	2·62(2)	F(9) ··· F(10)	2·73(2)
F(1) ··· F(6)	2·54(2)	F(5) ··· F(6$^{\mathrm{I}}$)	3·00(2)
F(2) ··· F(6)	2·56(2)	F(5) ··· F(7$^{\mathrm{I}}$)	2·56(2)
F(3) ··· F(6)	2·66(2)	F(5) ··· F(8$^{\mathrm{I}}$)	2·49(2)
F(5) ··· F(6)	2·65(2)	F(5) ··· F(9$^{\mathrm{I}}$)	2·76(2)
F(1)–Sb–F(3)	92·7(8)	F(7)–Nb–F(6)	78·3(6)
F(1)–Sb–F(4)	94·3(8)	F(7)–Nb–F(9)	102·0(7)
F(1)–Sb–F(5)	87·3(7)	F(7)–Nb–F(10)	98·8(7)
F(1)–Sb–F(6)	85·7(7)	F(8)–Nb–F(6)	78·0(6)
F(2)–Sb–F(3)	95·3(7)	F(8)–Nb–F(9)	99·8(7)
F(2)–Sb–F(4)	93·8(8)	F(8)–Nb–F(10)	102·1(7)
F(2)–Sb–F(5)	84·1(6)	F(9)–Nb–F(10)	98·7(6)
F(2)–Sb–F(6)	85·3(6)	F(6)–Nb–F(10)	86·1(6)
F(3)–Sb–F(6)	90·2(7)	F(5)–Nb$^{\mathrm{I}}$–F(7$^{\mathrm{I}}$)	79·5(6)
F(3)–Sb–F(4)	96·2(8)	F(5)–Nb$^{\mathrm{I}}$–F(8$^{\mathrm{I}}$)	77·0(6)
F(5)–Sb–F(4)	87·6(7)	F(5)–Nb$^{\mathrm{I}}$–F(9$^{\mathrm{I}}$)	87·8(6)
F(5)–Sb–F(6)	86·0(5)	F(5)–Nb$^{\mathrm{I}}$–F(6$^{\mathrm{I}}$)	87·4(5)
F(1)–Sb–F(2)	168·0(7)	F(7)–Nb–F(8)	147·1(6)
Sb–F(6)–Nb	162·9(8)	Sb–F(5)–Nb	164·0(8)
F(1) ··· F(7)	2·23(2)	F(1) ··· F(7$^{\mathrm{I}}$)	3·35(3)
F(4) ··· F(3$^{\mathrm{I}}$)	2·95(3)	F(10) ··· F(9$^{\mathrm{I}}$)	2·93(2)

(*b*) Contacts <3·5 Å

F(2) ··· F(8$^{\mathrm{II}}$)	2·95(2)	F(2) ··· F(9$^{\mathrm{II}}$)	3·49(2)
F(3) ··· F(8$^{\mathrm{II}}$)	3·46(3)	F(6) ··· F(8$^{\mathrm{II}}$)	2·99(2)
F(8) ··· F(8$^{\mathrm{II}}$)	2·82(3)	F(2) ··· F(2$^{\mathrm{III}}$)	2·99(3)
F(2) ··· F(5$^{\mathrm{III}}$)	2·97(2)	F(2) ··· F(6$^{\mathrm{III}}$)	3·03(2)
F(2) ··· F(8$^{\mathrm{III}}$)	2·90(2)	F(2) ··· F(10$^{\mathrm{III}}$)	3·27(2)
F(4) ··· F(8$^{\mathrm{III}}$)	3·32(3)	F(5) ··· F(2$^{\mathrm{III}}$)	2·97(2)
F(5) ··· F(8$^{\mathrm{III}}$)	3·23(2)	Nb ··· F(1$^{\mathrm{IV}}$)	3·34(2)
F(1) ··· F(7$^{\mathrm{IV}}$)	2·96(2)	F(1) ··· F(9$^{\mathrm{IV}}$)	2·98(2)
F(1) ··· F(10$^{\mathrm{IV}}$)	2·95(2)	F(7) ··· F(7$^{\mathrm{IV}}$)	3·29(3)
F(7) ··· F(10$^{\mathrm{IV}}$)	3·03(2)	F(7) ··· F(7$^{\mathrm{V}}$)	3·12(3)
F(7) ··· F(9$^{\mathrm{V}}$)	3·09(2)	Nb ··· F(3$^{\mathrm{VI}}$)	3·35(2)
F(8)z ··· F(3$^{\mathrm{IV}}$)	2·98(2)	F(9) ··· F(3$^{\mathrm{VI}}$)	3·04(2)
F(10) ··· F(1$^{\mathrm{VI}}$)	3·48(2)	F(10) ··· F(3$^{\mathrm{VI}}$)	2·91(2)
F(10) ··· F(4$^{\mathrm{VI}}$)	3·25(2)		

The Roman numerals as superscripts refer to atoms in the positions:

I	$-1 + x, y, z$	IV	$-x, -y, 1 - z$
II	$1 - x, 1 - y, 1 - z$	V	$1 - z, -y, z$
III	$-x, 1 - y, 1 - z$	VI	$x, y, -1 + z$

DISCUSSION

The structure consists of an endless zigzag chain arrangement as shown in Figures 1 and 2. Alternating niobium and antimony atoms are linked through asymmetric *cis*-fluorine bridges, and four terminal fluorine atoms complete a distorted octahedral co-ordination around each metal atom. The mean Sb–F(terminal) and Sb–F(bridge) distances are 1·81 and 1·95 Å respectively; the corresponding Nb–F distances are 1·81 and 2·17 Å. The larger difference between terminal and

---

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[6] A. J. Edwards, *J. Chem. Soc.*, 1964, 3714.

[7] A. J. Edwards and P. Taylor, *Chem. Comm.*, 1971, 1376.

[8] J. W. Jeffery, *J. Sci. Instr.*, 1963, **40**, 494.

[9] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, p. 202.

bridge bond distances for niobium is matched by a larger deviation from 90° for the angles in the octahedral co-ordination around the niobium atom (see Table 2).

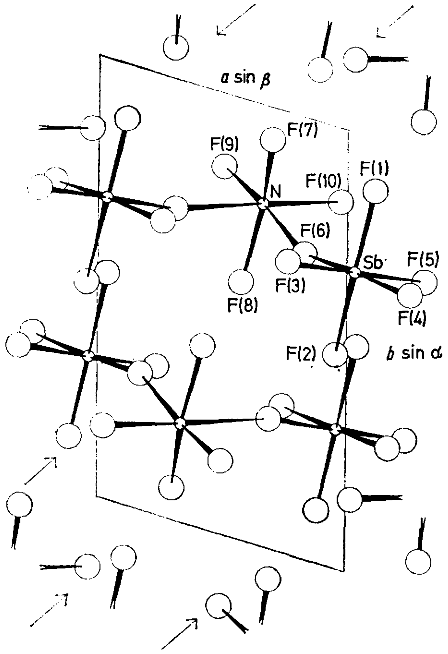

FIGURE 1 Projection of the structure down [001] showing the atom numbering and the approximate close packing. The close-packed layers are indicated by the arrows

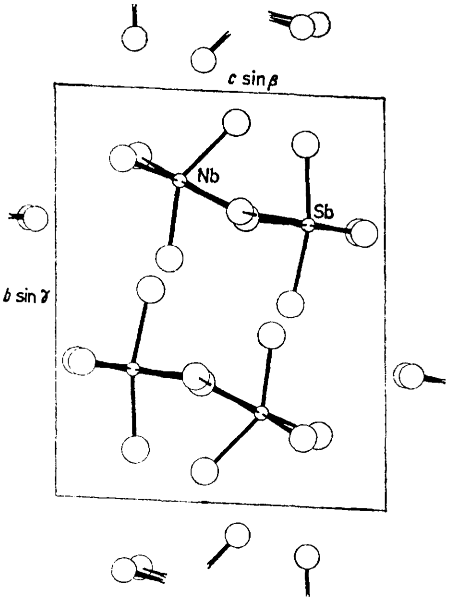

FIGURE 2 Projection of the structure down [100] showing the endless-chain arrangement and a comparison of the distortion around the niobium and antimony atoms

The zigzag endless chain arrangement is very similar to that found[10] in the structure of vanadium pentafluoride but the distortion in the present case, leading to asymmetric bridges and to a closer association of the bridging fluorine atom with the antimony atom than with the niobium atom, indicates a contribution to the structure from the ionic form [NbF$_4$]$^+$[SbF$_6$]$^-$.

Both antimony and niobium pentafluorides are good fluoride-ion acceptor molecules, as shown, for example, by the formation of adducts with bromine trifluoride[11] and selenium tetrafluoride.[5] These adducts have structures in the solid state which are best formulated in terms of ions, [BrF$_2$]$^+$[SbF$_6$]$^-$ and [SeF$_3$]$^+$[NbF$_6$]$^-$. However, these ionic formulations are insufficient to describe the structures completely, since considerable interionic interactions are involved. These interactions indicate some tendency to fluoride ion donation by the two pentafluorides, and this is supported by the tetrameric structures, with symmetric fluorine bridges, of the pentafluorides themselves.[6,7]

The unequal distortion of the fluoride co-ordination, described above, shows that antimony pentafluoride is a stronger fluoride-ion acceptor than niobium pentafluoride. If the fluoride ion were completely transferred to give the [NbF$_4$]$^+$ species, then this cation should have a regular tetrahedral configuration, with F–Nb–F angles of 109° 28′. The angles F(9)–Nb–F(10) (99°) and F(7)–Nb–F(8) (147°) can be considered to be distorted towards the tetrahedral value, from the octahedral angles of 90 and 180° respectively. In the tetrameric structure of niobium pentafluoride itself,[6] a contribution to the structure can be considered from the ionic form [NbF$_4$]$^+$F$^-$. In this [NbF$_4$] unit the F–Nb–F angles which correspond to those given for the 'cation' are 100 and 165°; the contribution from the ionic form is therefore greater in the adduct than in NbF$_5$, as would be expected if SbF$_5$ has the greater fluoride-ion acceptor strength. The Nb–F(bridge) distance in the pentafluoride is also smaller than that in the adduct by 0·11 Å.

The comparison in the case of antimony pentafluoride and the adduct shows the opposite effect, although it is less marked than for the niobium compound. Thus, in the tetrameric structure of the pentafluoride[7] the Sb–F(bridge) distance is 2·02 Å, 0·07 Å longer than the Sb–F(bridge) distance in the adduct, and the angles corresponding to the tetrahedral (SbF$_4$]$^+$ species are 162 and 102°, compared with 168 and 96° in the adduct.

The mean Nb–F–Sb angles are 163·5°, closer to the value of 180° required for occupation of adjacent octahedral holes in cubic close packing than to that of 132° for hexagonal close packing. In the structure of vanadium pentafluoride[10] the V–F–V angle is 150° and the fluorine atom arrangement is related to hexagonal close packing with considerable distortion. In the projection of the structure down [001] shown in Figure 1, the planes of atoms are indicated and the layer sequence corresponds to cubic close packing, repeating every fourth layer. The distortion of the bridge angle can be correlated with a displacement of the niobium atom from

---

[10] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), **1969**, 1651.

[11] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), **1969**, 1467.

the centre of the octahedral hole, away from the bridging fluorine atoms.

The endless-chain arrangement found for the adduct supports the suggestion of Dean and Gillespie[3] that similar chain arrangements are present in liquid mixtures of the two pentafluorides. It would appear probable that a similar zigzag chain arrangement would be formed for an adduct $[NbF_4]^+[Sb_2F_{11}]^-$ since similar chain arrangements have been shown to exist in the solid state for[12] $[SeF_3]^+[Nb_2F_{11}]^-$ and[13] $[BrF_4]^+[Sb_2F_{11}]^-$.

I thank Imperial Chemical Industries Limited (Mond Division) for the gift of a fluorine cell, and Dr. T. A. Hamor for his amended versions of the computer programmes FORDAP, ORFLS, and ORFFE. All calculations were carried out on an English Electric KDF 9 Computer, and I thank the staff at Birmingham University Computer Centre for their assistance.

[2/805 *Received*, 10*th April*, 1972]

[12] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1970, 1491.

[13] K. O. Christie, personal communication.