Preparation and Characterisation of Adducts of Bismuth Pentafluoride and Antimony Pentafluoride by Vibrational Spectroscopy, *X*-Ray Powder Diffraction, and Single-crystal *X*-Ray Crystallography [†]

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Adducts between BiF_5 and SbF_5 were prepared in liquid WF_6 at room temperature. Sublimation of the product gave various volatile crystalline products with analyses corresponding to $BiF_5(SbF_5)_3$, $BiF_5(SbF_5)_2$, $BiF_5(SbF_5)_{1\cdot5}$, and $(BiF_5)_nSbF_5$ (n = 2, 3, or 20.6). The adducts $(BiF_5)_nSbF_5$ (n = 1 or 1.5), were also prepared. The $BiF_5(SbF_5)_n$ (n = 1.5, 2, or 3) adducts were of low melting point and of higher volatility than $(BiF_5)_nSbF_5$ ($n \geqslant 1$). Single-crystal *X*-ray diffraction studies showed that $BiF_5(SbF_5)_n$ (n = 2 or 3) were isomorphous with tetrameric $(NbF_5)_4$, and an *X*-ray powder diffraction photograph of $BiF_5(SbF_5)_{1\cdot5}$ was very similar to that of $BiF_5(SbF_5)_n$ (n = 2 or 3), indicating that it was also isostructural with $(NbF_5)_4$. The $BiF_5(SbF_5)_3$ structure likely consists of disordered $BiF_5(SbF_5)_3$ tetramers, and $BiF_5(SbF_5)_2$ likely consists of a mixture of disordered $BiF_5(SbF_5)_3$ and $(BiF_5.SbF_5)_2$ tetramers in the appropriate ratios. The molecular-beam mass spectra of $SbF_5(BiF_5)_n$ (n = 2 or 3) show fragment ions attributable to BiF_5 and SbF_5 as well as various associated pentafluoride clusters, including $BiF_5(SbF_5)_3$ for the n = 3 adduct. The vibrational spectra of $BiF_5(SbF_5)_n$ (n = 1.5, 2, or 3) were similar and indicative of the presence of SbF_5 and BiF_5 units joined by *cis*-bridged fluorine atoms. $(BiF_5)_nSbF_5$ (n = 1, 1.5, 2, 3, or 20.6), were shown by *X*-ray powder diffraction photography to be isomorphous with polymeric *trans*-bridged BiF_5 and therefore to consist of disordered BiF_5 and SnF_5 units linked by *trans*-bridged fluorine atoms. The *trans*-bridged polymeric BiF_5-type structure of the adducts was further supported by their vibrational spectra. The behaviour of BiF_5-$(SbF_5)_n$ (n = 2 or 3) in WF_6 solution is discussed. An estimated phase diagram for the system BiF_5–SbF_5 was constructed.

The pentafluorides of Group 5B elements are an important and intriguing group of ' simple ' binary compounds. It is well established that phosphorus pentafluoride (m.p. −93.8 °C, b.p. 84.6 °C) [1] and arsenic pentafluoride (m.p. −79.8 °C, b.p. −53.2 °C) [1] are trigonal bipyramidal monomers in the gas phase,[2] and are likely monomeric in all states, in view of their physical properties [1] and similarity of vibrational spectra in all phases.[3,4] In contrast, antimony pentafluoride (m.p. 8.3 °C, b.p. 141 °C) [1] is a cyclic tetramer in the solid state [5] and a *cis*-bridged polymer of uncertain molecular weight in the liquid state.[1,3,6] In the gas phase, SbF_5 is associated, the degree of which has been measured as a function of temperature and pressure.[1-3] The identity of the cyclic trimer $(SbF_5)_3$ in the gas phase has been confirmed by electron diffraction.[7] Bismuth pentafluoride (m.p. 151.4 °C, b.p. 230 °C) [1] is a *trans*-bridged polymer in the solid state,[8] likely polymeric in the liquid phase,[1] and, as is the case for SbF_5, associated species have been detected by mass spectroscopy in the gas phase.[9,10] The enthalpy of polymerisation of SbF_5 has been estimated [11] as −18.5 kJ mol^{-1}. All these pentafluorides are strong Lewis acids. The relative acidities have been established from various studies [12,13] to decrease in the order $SbF_5 > AsF_5 > PF_5$. However we have shown [4] that SO_2F_2, a very weak base, forms a weak adduct, $SO_2F_2{\cdot}AsF_5$, with arsenic pentafluoride at low temperatures, but a similar adduct was not formed with SbF_5. It might be expected that BiF_5 would be a better Lewis acid than SbF_5, but several studies show that the reverse is the case.[14,15] We have shown that PF_5, itself a strong Lewis acid, acts as a base towards SbF_5, a stronger acceptor, to form the ionic salt $[PF_4]^+[Sb_3F_{16}]^-$.[16] Arsenic pentafluoride did not form an adduct under similar conditions.[16] Kolditz and Rehak [17] reported that the pentafluorides of antimony and bismuth formed an adduct of composition $BiF_5{\cdot}2SbF_5$ but no evidence for its structure was presented. In this work we sought to confirm the existence of this adduct, to determine what other adducts could be formed between BiF_5 and SbF_5, and to determine their structures. A preliminary account of this work has been reported.[18]

Experimental

Reagents and Apparatus.—Unless otherwise stated, apparatus, materials, and techniques were as previously described.[19,20] *X*-Ray powder diffraction photographs (Cu-K_α radiation λ = 1.541 Å) were obtained using a Debye–Sherrer camera of radius 114.6 mm with a Straumanis film mount. Cell dimensions were obtained according to ref. 21. Reflections with $2\theta > 90°$ were not included in the analysis because their lines were broad. BiF_5 (Ozark-Mahoning) was used directly and shown to be pure by Raman spectroscopy and *X*-ray powder photography. SbF_5 (Ozark-Mahoning) was purified by double vacuum distillation at room temperature (r.t.). WF_6 (Ozark-Mahoning) was stored over NaF prior to use. Solids were manipulated in a Vacuum Atmosphere's Dry Box equipped with a Dri-Train.

Preparation of BiF_5–SbF_5 *Adducts.*—In a typical reaction SbF_5 (1.83 g, 8.44 mmol) and WF_6 (2.50 g) were condensed onto BiF_5 (0.77 g, 2.53 mmol) in a Pyrex glass vessel attached to a Monel metal vacuum line *via* a 1KS4 stainless-steel Whitey valve and Teflon Swagelok compression fittings.

[†] *Supplementary data available* (No. SUP 56053, 14 pp.): atomic co-ordinates, thermal parameters, and structure factors for BiF_5-$(SbF_5)_3$; *X*-ray powder diffraction data for $(BiF_5)_nSbF_5$ (n = 1, 2, 3, or 20.6); Raman spectra of $BiF_5(SbF_5)_3$ (powdered, in WF_6, and liquid at 45 °C) and $(BiF_5)_nSbF_5$ (n = 2 or 3) (powdered); i.r. spectra of $BiF_5(SbF_5)_n$ (n = 1, 1.5, or 2) and $(BiF_5)_3SbF_5$. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix.

Table 1. Preparation of BiF_5–SbF_5 adducts

Preparation no.	BiF_5 : SbF_5 mole ratio	Total weight/g	WF_6/g	Crude product	Sublimation products/g 1st	2nd	3rd	4th	5th	6th	7th	Final residue [a]/g
1	1 : 3.34	2.6	2.50	Tetramer [b,c]	0.661 [d] Tetramer $BiF_5(SbF_5)_3$ (1) [f] m.p. 39 °C	0.590 [d] Tetramer	0.087 [d] Tetramer and chain (trace)	0.063 [e] Chain $(BiF_5)_2SbF_5$ (14) [f]				0.22
2	1 : 3.20	2.79	3.50	Tetramer [c]	0.374 [d] Tetramer	0.439 [d] Tetramer	0.150 [d] Tetramer					0.45
3	1 : 2.24	2.70	1.77	Tetramer and chain [g]	0.960 [d] Tetramer $BiF_5(SbF_5)_2$ (5) [d] m.p. 42 °C	0.133 [d] Tetramer	0.099 [e] Tetramer and chain (trace)					0.83
4	1 : 2.26	2.92	5.88	Tetramer and [g] chain (trace)	0.473 [d] Tetramer $BiF_5(SbF_5)_2$ (6) [f] m.p. 43 °C	0.373 [d] Tetramer	0.156 [d] Tetramer and chain (trace)					1.06
5	1 : 1.05	1.71	3.78	Tetramer and [g] chain (trace)	0.076 [d] Tetramer	0.04 [d] Tetramer	0.020 [e] Chain and tetramer (trace)	0.020 [e] Tetramer and chain (trace)	0.437 [e] Chain $(BiF_5)_3SbF$ (15) [c]			0.19
6	1.7 : 1.0	1.42	2.11	Tetramer and [g] chain (trace)	0.514 [d] Chain	0.105 [e] Chain	0.072 [e] Chain $(BiF_5)_{20.6}SbF_5$ (16) [e]	0.060 [e] Chain				0.41
7	1.0 : 3.0	3.51	2.86	Tetramer [c]	0.093 [d] Tetramer $BiF_5(SbF_5)_3$ (2,3) [f] m.p. 38—39 °C	0.189 [d] Tetramer $BiF_5(SbF_5)_3$ (4) [f]	0.121 [e] Tetramer	0.263 [e] Tetramer	0.302 [e] Tetramer $BiF_5(SbF_5)_2$ (7,8) [f] m.p. 42—43 °C	0.171 [e] Tetramer	0.157,[e] 0.53 Tetramer $BiF_5(SbF_5)_{1.5}$ (9,10) [f] m.p. 47—77 °C	0.53

[a] Vibrational spectra showed this residue contained Bi–F and Sb–F bonds but the nature of the final white residue was not further studied. The sum of all the sublimation products and final residue was not necessarily equal to the weight of total crude product because of loss of sample on each operation. [b] Structural type determined from Raman and *X*-ray powder photography. *cis*-Fluorine bridged material isomorphous with NbF_5 is designated as tetramer. Material isomorphous with BiF_5 and therefore *trans*-fluorine bridged, is designated as chain. [c] White paste. [d] Clear white crystals. [e] White cloudy crystals. [f] Number in parentheses is analysis sample number in Table 2. [g] White solid (rather than paste).

Table 2. Elemental analysis (%)[a] for BiF_5–SbF_5 adducts

Sample		Calc.			Found		
no.	Compound	Bi	Sb	F	Bi	Sb	F
1	$BiF_5(SbF_5)_3$	21.90	38.30	39.80	21.65	38.05	40.00
2					21.75	37.95	39.65
3						38.30[b]	
4					21.80	38.50	39.55
5	$BiF_5(SbF_5)_2$	28.35	33.00	38.65	28.20	33.30	38.40
6					28.05	32.70	38.45
7					28.55	32.85	38.35
8						33.15[b]	
9	$BiF_5(SbF_5)_{1.5}$	33.20	29.05	37.75	32.80	29.10	38.05
10						27.65[b]	
11	$BiF_5{\cdot}SbF_5$	40.15	23.40	36.50	40.35	23.10	36.60
12	$(BiF_5)_{1.5}SbF_5$	46.60	18.10	35.30	46.20	17.85	35.30
13						18.35[b]	
14						16.50[b]	
15	$(BiF_5)_2SbF_5$	50.70	14.75	34.55	48.05?	13.95?	37.15?
16	$(BiF_5)_3SbF_5$	55.55	10.80	33.65	55.10	10.65	34.00
17	$(BiF_5)_{20.6}SbF_5$	66.45	1.90	31.65	66.40	1.85	31.10

[a] Unless otherwise specified analyses were performed by Alfred Bernhardt, W. Germany. [b] Analyses performed in-house by means of atomic absorption of solutions in 20% HCl by volume and calibration of atomic absorption spectra against standards with appropriate quantities of NaF.

SbF_5 is soluble in WF_6, whereas BiF_5 appears not to be. A clear solution over a white solid (BiF_5) was obtained at r.t. and the mixture was stirred overnight. The volatiles (WF_6) were transferred to another vessel in a closed system, leaving a white paste-like substance of the same weight as that of the SbF_5 and BiF_5 starting materials. The paste appeared to become drier on grinding in the dry box, presumably by WF_6 and/or SbF_5 evaporation. The solid was placed in a glass vessel (*ca.* 12 cm long and 2.2 cm diameter), which was evacuated and flame sealed. It was then placed on top of an oven in a sloping position, with the bottom of the tube at 28—30 °C and the top at 22—24 °C. Clear crystals collected in the cooler part of the tube after several hours and appreciable amounts had collected after 1 or 2 d. The crystals were removed, the unsublimed residue transferred to another similar vessel, and the vessel again similarly evacuated, sealed, and heated. The process was repeated several times and the results of this and similar experiments are given in Table 1. The empirical formulae of some of the sublimation products given in Table 1 are based on chemical analyses given in Table 2. The melting points of various sublimation products are also included in Table 1.

Preparation of $(BiF_5)_nSbF_5$ *Adducts Isomorphous with* BiF_5 *with Maximum Incorporation of* SbF_5.—(1) BiF_5 (0.99 g) and SbF_5 (1.52 g) were reacted in WF_6 overnight as described above. The Raman spectrum of the solid product of average composition $BiF_5(SbF_5)_{2.15}$ showed it to contain mostly a *cis*-bridged tetramer, isomorphous with NbF_5,[22] and a small amount of material isomorphous with BiF_5 [8] (see below). The product was ground and subjected to a dynamic vacuum at r.t. for 5 h. The Raman spectrum of the residue showed it to contain a small but larger amount of the *trans*-bridged product than prior to pumping. The product was reground and the process repeated four times with pumping times of 3, 3.2, 0.4, and 0.7 h respectively, until the residue did not contain any detectable (Raman) amount of *cis*-bridged adduct. Elemental analysis of this material (Table 2, sample 11) showed that it was $BiF_5{\cdot}SbF_5$.

(2) BiF_5 (1.07 g) and SbF_5 (0.80 g) were reacted overnight in WF_6 (8.25 g) with stirring in a two-bulbed vessel incorporating a medium sintered glass frit. The mixture was filtered and the less soluble portion washed with WF_6 by condensing the latter back across the frit and refiltering. This was repeated several times and the WF_6 was then removed. The insoluble portion contained $(BiF_5)_nSbF_5$ of the *trans*-bridged type with *n* large. The soluble material (1.05 g), a mixture of *cis*- and *trans*-bridged adducts, was placed in another similar vessel and WF_6 (3.00 g) added. The solution was filtered once and

Table 3. Mass spectra (relative intensities) of $BiF_5(SbF_5)_2$ and $BiF_5(SbF_5)_3$

Ion	$BiF_5(SbF_5)_3$ T^a = 26 °C	$BiF_5(SbF_5)_2$ T^a = 17 °C
Sb	4	*b*
SbF	8	2
SbF_2	63	32
SbF_3	30	9
SbF_4	100	100
Bi	8	3
BiF	6	9
BiF_2	22	43
BiF_3	0.4	*b*
BiF_4	35	96
Sb_2F_9	19	30
$SbBiF_5$	0.3	
$SbBiF_6$	0.2	
$SbBiF_7$	1	5
$SbBiF_9$	10	25
Bi_2F_5	0.1	1
Bi_2F_7	0.1	1
Bi_2F_9	1	8
Sb_3F_{14}	0.1	1
Sb_2BiF_{12}	0.06	0.5
Sb_2BiF_{14}		1
$SbBi_2F_{11}$		*c*
$SbBi_2F_{12}$	*d*	*c*
$SbBi_2F_{14}$	0.04	
Sb_3BiF_{14}	*d*	
Sb_3BiF_{15}	*d*	
Sb_3BiF_{17}	0.04	

[a] Source temperature. [b] Not detected. [c] Detected at low intensity (<0.5) at higher temperature (*T* = 45—50 °C). [d] Detected at *T* = 60 °C, at approximately the same levels as other $SbBi_2$ and Sb_3Bi ions. Minor peaks $Sb_2F_5^+$ to $Sb_2F_8^+$ also found at low levels.

Table 4. Vibrational spectra (cm^{-1})[a] of $BiF_5(SbF_5)_3$ and SbF_5

$BiF_5(SbF_5)_3$					SbF_5		
Raman[b]		I.r.[b] Powder[d]	Raman in SbF_5 solution[c,e]	Raman[b] WF_6 solution[f]	Raman Liquid[g]	I.r. Liquid[g]	Tentative assignments
Powder	Liquid[c]						
		748 (sh)				742s	Terminal SbF_4 stretches
738vw		734 (sh)					
710m	712m (p)		714s (p)	711s (p)	716s (p)		
698w (sh)		700s				705s	
673vw (sh)	673vw (sh)	666m				669s	
668m	668m (p)		667s (p)	668 (sh) (p)	668s (p)		
649vw		648m					Terminal BiF_4 stretches
633w	632w (sh) (dp)	622s	632w (sh) (dp)	632w (dp)			
620ms	621m (p)		622m (p)	622m (p)			
604s	602s (p)	605w	603s (p)	603s (p)			
~500vvw,br		488s,br				~450w,br	Sb–F–Sb and Bi–F–Sb bridging stretches
	330w,br (p)		330w,br (p)		349vw,br (p)		
308vw	296w,br (sh) (dp)		300w (dp)		302w (dp)	~310w,br	
271m	268w (dp)		268w (dp)	268m (dp)	268w (dp)		
233m			223w,br (dp)		231w,br (dp)		
220m	192w,br (dp)		196w (dp)	200w (dp)		~200w,vbr	
186w			182w (dp)	189w (dp)	189w (dp)		
154vw	147w,br (dp)		150w,br (dp)	148w (dp)	140w,br (p)		
116vw	126w,br (dp)		132w,br (p)	126w,br (dp)			

[a] dp = Depolarised, p = polarised. [b] The actual spectrum is deposited in SUP 56053. [c] Taken at ~45 °C. [d] Powdered solid between AgCl plates. [e] $BiF_5(SbF_5)_3 \cdot SbF_5$ = 1 : 4.4 mol ratio. [f] WF_6 lines have been deleted, mol ratio $BiF_5(SbF_5)_3 : WF_6$ = 1 : 7.0. [g] The values are consistent with those quoted in refs. 6 and 32.

Table 5. Vibrational spectra (cm^{-1})[a] of $BiF_5(SbF_5)_2$ and $BiF_5(SbF_5)_{1.5}$

$BiF_5(SbF_5)_2$			$BiF_5(SbF_5)_{1.5}$			
Raman		I.r.[b] Powder[d]	Raman		I.r.[b] Powder[d]	Tentative assignments
Powder	Liquid[c]		Powder	Liquid[e]		
		748 (sh)			747 (sh)	Terminal SbF_4 stretches
738vw		734 (sh)	738vw		722s	
710m	712m (p)		708m	740m (p)		
698mw (sh)		698s	696ms		696s	
		665m				
668m	667m (p)		668m	667m (p)		
648vw		646m	649vw		659s	Terminal BiF_4 stretches
632w	632w (sh) (dp)	620s	633m	632w (dp)	617s	
620ms	621m (p)		620ms	620m (p)		
604s	602s (p)	605 (sh)	603s	600s (p)	600 (sh)	
			500vvw,br?		515m,br	Sb–F–Sb and Bi–F–Sb bridging stretches
~500vvw,br		488s,br				
			~420vvw,br?		467m,br	
	330w,br (p)			330w,br		
308vw	296w,br (sh) (dp)		308vw			
271m	268w (dp)		271m	268w (dp)		
223m			223m			
	192m,br (dp)			192w,br (dp)		
186w			186w			
155vw	149w,br (dp)		153vw	147w,br (dp)		
116vw	128w,br (p)		116w	126w,br (p)		

[a] dp = Depolarised, p = polarised. [b] The actual spectrum is included in SUP 56053. [c] Taken at ~45 °C. [d] Powdered solid between AgCl plates. [e] Taken at ~75 °C.

the WF_6 removed. The Raman spectrum and *X*-ray powder diffraction photograph of the less soluble portion showed that it did not contain any *cis*-bridged adduct. Elemental analysis (Table 2, samples 12 and 13) supports the formulation $(BiF_5)_{1.5}SbF_5$.

Preparation of Single Crystals.—(1) $BiF_5(SbF_5)_2$. Powdered $BiF_5(SbF_5)_2$ was added to carefully dried, thin-walled silica capillaries (o.d. 0.3 mm) and flame sealed under atmospheric pressure. A number of capillaries were placed in a glass tube and placed on top of an oven such that the lower part of the capillaries were at *ca*. 28—30 °C. Crystals which grew by sublimation were examined every 4 d until a suitable crystal for *X*-ray diffraction studies was found. After the *X*-ray photographic work was complete, the Raman spectrum of the single crystal was obtained and found to be identical to that

Table 6. Vibrational spectra (cm^{-1}) [a] of BiF_5 and $SbF_5(BiF_5)_n$ ($n \geqslant 1$)

BiF_5[b]		$BiF_5{\cdot}SbF_5$		$(BiF_5)_2SbF_5$	$(BiF_5)_{20.6}SbF_5$		
Raman	I.r.[b]	Raman	I.r.[b]	Raman	Raman	I.r.[b]	Tentative assignments [c]
			710s			721s	e_u SbF_4 antisymmetric stretch
				702vvw			
			686 (sh)			683s	Combination? or as above?
		667w	668 (sh)	677w	677w		a_g SbF_4 in-phase stretch
				626vw			b_g SbF_4 out-of-phase stretch
	627s	622vw	620s	617vw		623 (sh)	e_u BiF_4 antisymmetric stretch
595s [d]		598s	597 (sh)	598s	595s	598 (sh)	a_g BiF_4 in-phase stretch
570w		572w		572w	570w		b_g BiF_4 out-of-phase stretch
			500mw,br			520w,br	a_u Bi–F–Sb bridging stretch
	450m		450m,br			450w,br	a_u Bi–F–Bi bridging stretch
		304vw		304vw	304vw		b_g SbF_4 deformation
255w	220m	255w		255w	255w		b_g BiF_4 deformation
167w,br [d]		165w,br		165w,br	166w,br		e_g BiF_4 tilt

[a] The Raman spectra of polycrystalline $(BiF_5)_nSbF_5$ (n = 2 or 3) and the i.r. spectra of $(BiF_5)_nSbF_5$ (n = 1 or 3) are included in SUP 56053. [b] Reported in ref. 32. [c] The assignments have been made by assuming that the symmetry of each Bi and Sb unit is C_{4h}. Description of modes follows that given in ref. 32. The presence of peaks forbidden by the mutual exclusion rule indicates that the symmetry about the heavy atoms is less than C_{4h}. [d] The weak band at 101 cm^{-1} [$\nu_2(a_g)$] reported for BiF_5[32] was not clearly observed in our spectra.

of an analysed sample of $BiF_5(SbF_5)_2$. Peaks were absent at 1 058 cm^{-1}, the strongest peak in the Raman spectrum of WF_4O[23] which is isostructural with NbF_5, and could be formed by partial hydrolysis of WF_6.

(2) $BiF_5(SbF_5)_3$. A large crystal, obtained from the first sublimation product of preparation 2, Table 1, was identified as $BiF_5(SbF_5)_3$ from its Raman spectrum. A small crystal suitable for *X*-ray studies was then cut from the larger crystal.

Single Crystal X-*Ray Analysis*.—$BiF_5(SbF_5)_2$. Monoclinic, $a = 9.69(1)$, $b = 14.37(2)$, $c = 5.26(1)$ Å, $\beta = 95.6(3)°$, $U = 728(4)$ Å^3, $M = 737.46$, $Z = 8/3$, $D_c = 4.48$ Mg m^{-3}, $F(000) = 853.33$, $\mu(\text{Mo-}K_\alpha) = 21.1$ mm^{-1}, space group $C2/m$ (Cm or $C2$) established from precession photographs.

$BiF_5(SbF_5)_3$. Monoclinic, $a = 9.704(3)$, $b = 14.353(4)$, $c = 5.266(2)$ Å, $\beta = 95.59(3)°$, $U = 730(1)$ Å^3, $M = 954.20$, $Z = 2$, $D_c = 4.34$ Mg m^{-3}, $F(000) = 832$, $\mu(\text{Mo-}K_\alpha) = 17.7$ mm^{-1}, space group $C2/m$ (Cm or $C2$).

Cell parameters of $BiF_5(SbF_5)_3$ were determined by least-squares fit to the centred co-ordinates of 12 reflections on a Picker FACS-I diffractometer using Mo-K_α radiation, $\lambda = 0.710\,69$ Å. In both cases, various over-exposed photographs showed no evidence for the existence of a superlattice.

Mass Spectra.—Mass spectra of $BiF_5(SbF_5)_n$ (n = 2 or 3) were obtained using a molecular-beam mass spectrometer [24,25] constructed to investigate reactive fluorides by Dr. M. J. Vasile of Bell Laboratories, N.J., U.S.A. The results are given in Table 3.

Physical Properties of $BiF_5(SbF_5)_n$ *and* $(BiF_5)_nSbF_5$ *Adducts*.—Crystals of $BiF_5(SbF_5)_n$ (n = 2 or 3) are well defined, clear, and colourless. The adducts showed no signs of decomposition (Raman) on heating in a sealed tube in an oven at 100 °C for 16 h. They both have relatively sharp melting points (n = 2, 42—43 °C; n = 3, 38—39 °C); $BiF_5(SbF_5)_{1.5}$ melts over the range 47—77 °C and is partially converted to the chain adduct on heating to *ca.* 80 °C for 0.5 h.

Crystals of $(BiF_5)_nSbF_5$ ($n \geqslant 1$) are white, cloudy, and irregular in shape. They did not have sharp melting points, but gave some liquid at 106 (n = 1), 112 (n = 1.5), 122 (n = 3), and 145 °C (n = 20.6). A complete liquid phase was not obtained even at 152 °C, the melting point of BiF_5.[2] The Raman spectra of the solid after the m.p. determination showed the adducts to contain less SbF_5.

Table 7. Unit-cell parameters of $(BiF_5)_nSbF_5$ (n = 1, 2, 3, or 20.6)

Compound	a/Å	c/Å	U/Å^3	Z
$BiF_5{\cdot}SbF_5$ [a]	6.565(1)	4.165 1(7)	179.52(6)	2 [b]
$(BiF_5)_2SbF_5$	6.576(3)	4.167(2)	180.2(1)	2 [b]
$(BiF_5)_3SbF_5$	6.587(2)	4.176(1)	181.2(1)	2 [b]
$(BiF_5)_{20.6}SbF_5$	6.573(2)	4.205(4)	181.7(2)	2 [b]
BiF_5 [c]	6.569(2)	4.219(4)	182.1(1)	2 [b]

[a] Observed and calculated $1/d^2$ (Å^{-2}) values and intensities are deposited in SUP 56053. [b] Two units of MF_5 per unit cell. [c] Consistent with previous results.

Results and Discussion

Preparation of $BiF_5(SnF_5)_n$ *Adducts*.—A solution of SbF_5 in WF_6 reacts with BiF_5, which does not appear to be soluble in WF_6, to give a product of average composition $BiF_5(SbF_5)_n$ (in our experiments $3.5 > n > 1.4$). Various sublimation products were obtained from the mixtures (see Table 1 and Experimental section). These products were of two distinct types. A more volatile highly crystalline product of relatively low melting point gave *X*-ray powder diffraction photographs similar to those of Kolditz's $BiF_5(SbF_5)_2$.[17] The vibrational spectra of these adducts were very similar and highly suggestive of a *cis*-bridged polymer (Tables 4 and 5). The less volatile, less highly crystalline product did not have a sharp melting point, had characteristic vibrational spectra (Table 6), and powder photographs that were similar to BiF_5 (see Table 7). Thus, Raman spectroscopy and *X*-ray powder photography allow a ready differential of the two classes of adducts.

Of the more volatile class of adduct, three different products $BiF_5(SbF_5)_n$ (n = 3, 2, or 1.5) were identified. Their vibrational spectra (Table 4 and 5) and powder photographs were all very similar. The melting points of $BiF_5(SbF_5)_3$ (38—39 °C) and $BiF_5(SbF_5)_2$ (42—43 °C) were not very different, but eight different chemical analyses from six different samples fitted well for one or the other of these formulations (Table 2). In all cases the more volatile material analysed as $BiF_5(SbF_5)_3$ and the slightly less volatile, as $BiF_5(SbF_5)_2$; we did not obtain an analysis that gave an intermediate result. The

Table 8. Unit-cell parameters of $BiF_5(SbF_5)_3$, $BiF_5(SbF_5)_2$, and NbF_5

Compound	a/Å	b/Å	c/Å	β/°	U/Å^3	Space group
$BiF_5(SbF_5)_3$	9.704(3)	14.353(4)	5.266(2)	95.59(3)	730(1)	$C2/m$ [a]
$BiF_5(SbF_5)_2$	9.69(1)	14.37(2)	5.26(1)	95.6(3)	728(4)	$C2/m$ [b]
NbF_5 [c]	9.62(1)	14.43(2)	5.12(1)	96.1(3)	706	$C2/m$ [a]

[a] Data refined in $C2/m$. [b] Space group probably $C2/m$. [c] Ref. 22.

behaviours of $BiF_5(SbF_5)_2$ and $BiF_5(SbF_5)_3$ in WF_6 solution were also different. Thus it is reasonably certain that the two distinct adducts $BiF_5(SbF_5)_n$ (n = 2 or 3) were prepared in our experiments. Although the difference in melting points of the two adducts is small, we judge it to be real. The related pairs of adducts $NbF_5{\cdot}SbF_5$ (m.p. 60), $NbF_5(SbF_5)_2$ (45),[26] $TaF_5{\cdot}1.13SbF_5$ (50—56), and $TaF_5{\cdot}2.01SbF_5$ (40—45 °C)[27] also have rather similar melting points. $BiF_5(SbF_5)_{1.5}$ (Table 2, sample 9) did not have a sharp melting point (47—77 °C) and unlike the other two adducts gave some of the less volatile *trans*-bridged polymer on heating at 75 °C for *ca.* 0.5 h, and on resolidification. The formulation of $BiF_5(SbF_5)_2$ was given by Kolditz and Rehak[17] on the basis of bismuth and antimony analyses. The melting point was reported as 50—60 °C. It is possible that this material was a mixture of $BiF_5(SbF_5)_3$, $BiF_5(SbF_5)_2$, and $BiF_5(SbF_5)_{1.5}$, or that it was $BiF_5(SbF_5)_2$ which underwent some decomposition (hydrolysis?) prior to, or during, the melting point determination.

The composition of five of the *trans*-fluorine bridged $(BiF_5)_nSbF_5$ adducts (n = 1, 1.5, 2, 3, or 20.6) were established from chemical analyses (Table 2). The BiF_5 richer adducts (n = 2, 3, or 20.6) were prepared by sublimation (see Table 1). The $BiF_5{\cdot}SbF_5$ adduct was obtained by pumping a sample of average composition $BiF_5(SbF_5)_{2.15}$. Pumping on $BiF_5(SbF_5)_2$ gave *trans*-bridged $BiF_5{\cdot}SbF_5$, possibly by loss of the more volatile $BiF_5(SbF_5)_3$ and rearrangement of the less volatile $(BiF_5{\cdot}SbF_5)_2$ tetramers to the *trans*-bridged BiF_5 type structure. A *trans*-bridged adduct analysing as $(BiF_5)_{1.5}SbF_5$ was formed as an insoluble product from a solution of the *cis*-bridged tetramer in WF_6 solution.

X-Ray Powder Diffraction Studies and the Structures of $BiF_5(SbF_5)_n$ *(n = 1.5, 2, or 3)*.—The unit-cell dimensions and diffractometer intensity data indicate that $BiF_5(SbF_5)_3$ is isomorphous with NbF_5[22] (see Table 8) and that it is likely to have the space group $C2/m$. Of the three compounds, only the 1 : 3 adduct could have a structure in which the Sb and Bi atoms are ordered without involving a superlattice. This compound was therefore chosen for a more detailed investigation. NbF_5 essentially consists of tetramers with niobium atoms lying at the corners of a square and bridging fluorine atoms linking the metal atoms with an NbFNb angle of *ca.* 180°. In $(SbF_5)_4$,[5] on the other hand, the four antimony atoms are bridged by two fluorine atoms with a SbFSb angle of 170° and two with an FSbF angle of 141°. In the space group $C2/m$, half the metal ions occupy the 4(g) sites[28] at $\pm(0, y, 0; \tfrac{1}{2}, \tfrac{1}{2} + y, 0)$ and the rest occupy 4(i) at $\pm(x, 0, z; \tfrac{1}{2} + x, \tfrac{1}{2}, z)$, so that if this is the correct space group the metals are disordered or partially disordered with either of 4(g) or 4(i) occupied only by antimony. If the space groups $C2$ and Cm are considered either of the 4(i) of 4(g) sites can split to become two two-fold sites, thus permitting a fully ordered structure to be described. These possibilities were all explored, but no evidence of an ordered structure was found. Refinement of a disordered model using the NbF_5 structure as a starting point gave a final residual of 0.14. The fluorine positions were not well defined and a difference synthesis showed a number of peaks close to atomic positions presumably due to the inaccuracy of an averaged model. The structure of $BiF_5(SbF_5)_3$ therefore almost certainly consists of disordered $BiF_5(SbF_5)_3$ tetramers.

Unit-cell dimensions and precession photographic intensity data showed that $BiF_5(SbF_5)_2$ was also isomorphous with tetrameric NbF_5. The average stoicheiometry $BiF_5(SbF_5)_2$ may be achieved by a random disordered 1 : 1 mixture of $BiF_5(SbF_5)_3$ and $(BiF_5{\cdot}SbF_5)_2$ tetramers. The $(BiF_5{\cdot}SbF_5)_2$ tetramers themselves reasonably consist of alternating BiF_5 and SbF_5 groups. It is possible that the $(BiF_5{\cdot}SbF_5)_2$ tetramers are stabilised by the presence of $BiF_5(SbF_5)_3$ without which they rearrange. The adduct $BiF_5(SbF_5)_{1.5}$ also likely consists of an appropriate number of $BiF_5(SbF_5)_3$ and $(BiF_5{\cdot}SbF_5)_2$ tetramers as its *X*-ray powder diffraction photograph is essentially identical to those of $BiF_5(SbF_5)_n$ (n = 2[17] or 3).

Mass Spectra of $BiF_5(SbF_5)_n$ *(n = 2 or 3)*.—The mass spectrum of $BiF_5(SbF_5)_3$ (Table 3) implies that the neutral species $BiF_5{\cdot}SbF_5$, Bi_2F_{10}, Sb_2F_{10}, Sb_3F_{15}, $BiF_5{\cdot}Sb_2F_{10}$, and $BiF_5{\cdot}Sb_3F_{15}$ exist in the vapour over solid $BiF_5(SbF_5)_3$. Presumably $BiF_5(SbF_5)_3$ dissociates in the gas phase at low pressure to Sb_2F_{10}, $BiF_5{\cdot}SbF_5$, and $BiF_5{\cdot}Sb_2F_{10}$, which may themselves dissociate (*e.g.* into SbF_5 and BiF_5) or rearrange (thus accounting for Bi_2F_{10}). Trimers and dimers have been observed by mass spectroscopy in gaseous antimony and bismuth pentafluoride, as have tetramers and pentamers of antimony pentafluoride.[9,10] Not surprisingly, the mass spectrum of $BiF_5(SbF_5)_2$ is similar to that of $BiF_5(SbF_5)_3$ except that bismuth-containing ions are more abundant and ions derived from the neutral $BiF_5(SbF_5)_3$ were not detected. It is noted that the relative intensities of the various species do not necessarily reflect the abundance of associated ions. The lower molecular weight ions can be produced on electron impact of the more highly associated clusters.[10] That this was the case was shown from phase relationships using a molecular-beam mass spectrometer.[29] It was also shown[29] that none of the ionic species is polar.

Vibrational Spectra of $BiF_5(SbF_5)_n$ *(n = 3, 2, or 1.5)*.—Raman spectra of $BiF_5(SbF_5)_n$ (n = 3, 2, or 1.5) (see Tables 4 and 5) are similar except that, with increasing n, peaks in the 660—750 cm^{-1} region increase in intensity relative to the peaks in the 600—660 cm^{-1} region. However, a shoulder at *ca.* 698 cm^{-1} increases in intensity with decreasing n. Corresponding i.r. spectra are also similar, although peaks are broad and less well defined for $BiF_5(SbF_5)_{1.5}$.

The i.r. and Raman spectra in the 660—750 cm^{-1} region are similar to that of SbF_5 (liquid), it is therefore reasonable to assign peaks in this region to SbF_4 terminal units (of C_{2v} symmetry), and the polarised peaks at 712 and 668 cm^{-1} probably correspond to the symmetrical equatorial and axial stretch. Peaks in the 600—670 cm^{-1} region are probably attributable to BiF_4 terminal groups (of C_{2v} symmetry) and the polarised peaks at 620 and 602 cm^{-1} may therefore be reasonably assigned to the equatorial and axial symmetric stretches respectively. The strong broad band in the i.r. at 470—515 cm^{-1} is reasonably assigned to bridging Bi–F–Sb and/or Sb–F–Sb stretches. The vibrational spectra are therefore consistent with a *cis*-bridged structure, with BiF_4 and SbF_4 terminal units linked by bridging fluorines for all three adducts. Similar arguments have been used to support *cis*-bridged structures for $VF_5{\cdot}SbF_5$,[30] $TaF_5{\cdot}1.13SbF_5$, $NbF_5{\cdot}2.13SbF_5$,[27] NbF_5,[27] and SbF_5.[6,31]

The Raman spectra of $BiF_5(SbF_5)_n$ ($n = 3$, 2, or 1.5) are very similar in the solid and liquid states and for $n = 3$, in WF_6 solution, implying that the *cis*-bridged tetrameric structure persists both in the solution and the liquid state. However, the vibrational spectra of $BiF_5(SbF_5)_3$ are similar to those of $BiF_5(SbF_5)_2$ and $BiF_5(SbF_5)_{1.5}$, which are very likely made up of $BiF_5(SbF_5)_3$ and $(BiF_5{\cdot}SbF_5)_2$ units in appropriate ratios, thus indicating that the vibrational spectrum of $BiF_5(SbF_5)_3$ is not very different from that of $(BiF_5{\cdot}SbF_5)_2$.

The symmetric antimony–fluorine stretches in $BiF_5(SbF_5)_n$ ($n = 3$, 2, or 1.5) at 712 and 668 cm^{-1} are, on average, only very slightly lower in frequency than the corresponding stretches in liquid SbF_5, suggesting that these adducts are largely covalent with a small ionic contribution to the overall structure, *e.g.* $[BiF_4]^+[Sb_3F_{16}]^-$ in $BiF_5(SbF_5)_3$, consistent with the greater Lewis acidity of SbF_5.[14,15]

Behaviour of $BiF_5(SbF_5)_n$ *(n = 2 or 3) in* WF_6 *Solution.*— $BiF_5(SbF_5)_n$ ($n = 2$ or 3) (0.3 and 0.49 g respectively) both dissolve in WF_6 (0.66 and 1.32 g respectively) to give clear solutions. However, a precipitate quickly forms after dissolution of $BiF_5(SbF_5)_2$, whereas precipitation occurs after 20 min for $BiF_5(SbF_5)_3$. It is possible that $BiF_5(SbF_5)_2$ dissolves to give $BiF_5(SbF_5)_3$ and $(BiF_5{\cdot}SbF_5)_2$ tetramers in solution. The $(BiF_5{\cdot}SbF_5)_2$ tetramers may polymerise leading to the observed precipitate of *trans*-bridged $(BiF_5)_{1.5}SbF_5$. The enrichment of bismuth pentafluoride in the precipitate, relative to a $SbF_5{\cdot}BiF_5$ composition, may be accounted for by redistribution reactions during the polymerisation of $(BiF_5{\cdot}SbF_5)_2$ and/or by the loss of antimony pentafluoride, as $BiF_5(SbF_5)_3$, from the precipitate into solution. A separate experiment confirmed that an insoluble chain adduct, on washing with WF_6, becomes enriched with bismuth pentafluoride, at the same time giving the tetrameric adduct in solution.

$BiF_5(SbF_5)_3$ probably exists as such in WF_6 solution but undergoes a slow redistribution reaction leading to $(SbF_5)_4$ and $(SbF_5{\cdot}BiF_5)_2$. The latter may then polymerise leading to the observed precipitate.

X-Ray Powder Diffraction Studies and Structures of $(BiF_5)_nSbF_5$ *(n = 1, 2, 3 or 20.6).*—*X*-Ray powder diffraction photographs of $(BiF_5)_nSbF_5$ ($n = 1$, 2, 3, or 20.6) were all similar, both in the position and intensity distribution of the lines, to that of bismuth pentafluoride and were indexed on the basis of tetragonal unit cells of similar dimensions (Table 7). The adducts $(BiF_5)_nSbF_5$ ($n = 1.5$ or >21) also had similar powder photographs. It is therefore reasonable to conclude that they are all isomorphous and isostructural. All the adducts therefore have *trans*-bridged linear structures similar to that of bismuth pentafluoride, for which the structure had been determined from single-crystal work.[8] The structure of bismuth pentafluoride contains one asymmetric unit of BiF_5 per unit cell. The $(BiF_5)_nSbF_5$ adducts must therefore comprise disordered SbF_5 and BiF_5 units in appropriate ratios. A plot of the unit-cell volumes of BiF_5 and the various $(BiF_5)_nSnF_5$ adducts *versus* mol% SbF_5 gives a fairly good straight line.

The major changes in the cell parameters occur in the *c* axis (parallel to the chain axis), which shortens with increasing SbF_5 content. The value of *c* (Table 7) is the distance between two adjacent heavy atoms and twice the average heavy atom–bridging fluorine bond distance. The values of *c* in the *trans*-bridged $(BiF_5)_nSbF_5$, and the distance between two heavy atoms in the *cis*-bridged tetramer $(SbF_5)_3BiF_5$ [4.147(6) Å], are fitted by the equation $d_{calc.} = 0.0904x + 4.118$ for $x(BiF_5)$-$(1 - x)SbF_5$. This suggests that *cis*- and *trans*-bridging fluorine bond distances are essentially equal for a given composition. The *a* axis remains essentially constant in all the adducts (see Table 7).

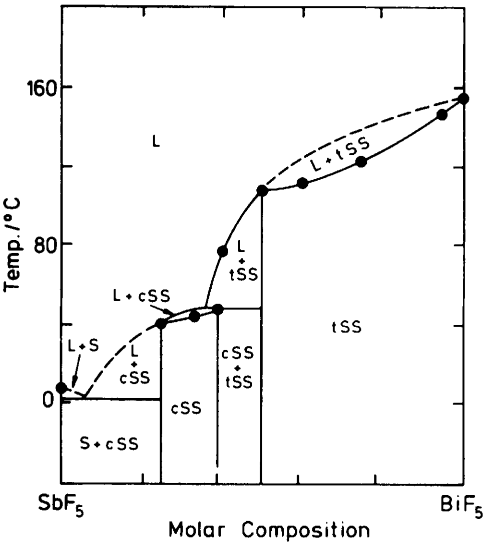

Figure. Estimated phase diagram for the system BiF_5–SbF_5. All melting-point data are included: cSS = *cis*-bridged solid solution; tSS = *trans*-bridged solid solution; L = liquid; and S = crystalline SbF_5

Vibrational Spectra of $(BiF_5)_nSbF_5$ *Adducts.*—The vibrational data for these and other related adducts are presented in Table 6, or in the preliminary communication.[18] The Raman peaks in all the adducts occur at *ca.* 677, 625, 618, 595, 570, 304, 255, and 167 cm^{-1}. The relative intensities of the set at *ca.* 595, 570, 255, and 167 cm^{-1} are approximately identical to those of $(BiF_5)_\infty$ itself;[31,32] this set is attributed to a 'BiF_6' unit consisting of a planar BiF_4 linked to neighbouring BiF_4 or SbF_4 units *via* two *trans*-bridging fluorine atoms. Consistently, the peaks increase in relative intensity as the BiF_5 content in the adduct increases. The relative intensities of a weaker set occur at *ca.* 677, 625, and 304 cm^{-1}, and are therefore attributed to 'SbF_6' units. The i.r. spectra of the $(BiF_5)_nSbF_5$ adducts are also similar, except that the peak at 720 cm^{-1} increases in intensity with increasing SbF_5 content, and that at 620 cm^{-1} increases with BiF_5 content. Therefore, by comparison with the i.r. spectrum of BiF_5, the peaks at 620 and 720 cm^{-1} are readily assigned to the e_u antisymmetric BiF_4 and SbF_4 stretching vibrations. The broad weak peak at *ca.* 450—500 cm^{-1} is assigned to Bi–F–Bi and Bi–F–Sb stretching vibrations. Thus, the vibrational spectra of these $(BiF_5)_nSbF_5$ adducts strongly support a *trans*-bridged $(BiF_5)_\infty$ structure, similar to that of BiF_5 itself.

A comparison of the stretching frequencies of the planar BiF_4 units in BiF_5 and the $(BiF_5)_nSbF_5$ adducts (Table 6) shows that they are not very different, thus suggesting the adducts have substantial covalent character. A more sensitive indication of the ionicity of the adduct could be deduced from the frequencies of the bridging Bi–F and Sb–F vibrations. Unfortunately, these vibrations appear as broad peaks and separate Bi–F and Sb–F assignments were not possible.

The BiF_5–SbF_5 *Phase Diagram.*—The principal aims of this work were to elucidate the structural and preparative chemistry of BiF_5–SbF_5 adducts. However, sufficient data were obtained on the melting behaviour of these adducts to deduce some aspects of the phase diagram, as shown in the Figure.

The melting point of BiF_5 itself,[1] and the incongruent melting points of the *trans*-bridged adducts, lie on a smooth curve whose form is typical of the solidus curve for a solid solution. The reactivity of the melts prevented determination of the corresponding liquidus curve, shown as a dashed line in the Figure. Although there thus appears to be a continuum of solid solutions between $BiF_5{\cdot}SbF_5$ and BiF_5 at the solidus line, compounds with ordered structures and definite stoicheiometries may well occur at lower temperatures.

Of the three *cis*-bridged tetrameric adducts that were isolated, $BiF_5(SbF_5)_3$ and $BiF_5(SbF_5)_2$ melted congruently, or nearly so, whereas $BiF_5(SbF_5)_{1.5}$ melted incongruently. From these observations, we deduce the presence of a peritectic point near 47 °C and 35 mol% BiF_5. Since the tetrameric adducts are isostructural, we assume that solid solutions exist between them. Our observations of only certain stoicheiometric compositions can be explained in terms of fractional sublimation. We show $BiF_5(SbF_5)_{1.5}$ as the BiF_5-rich limit of the *cis*-bridged solid solution series. However, it is possible that this compound is metastable, and that the equilibrium limit is at lower BiF_5 content.

The region of the phase diagram below 25 mol% BiF_5 could not be examined in detail because of supercooling of the SbF_5-rich liquids. However, the observation of pasty products at $SbF_5 : BiF_5$ ratios $\geqslant 3.0$ is consistent with the eutectic behaviour that we indicate for this region (Figure). Also, although SbF_5 is a *cis*-bridged tetramer in the solid state,[5] the conformation of this tetramer differs from that of the NbF_5-type structure adopted by the *cis*-bridged BiF_5–SbF_5 adducts, so solid solution formation is not anticipated to any degree between $(SbF_5)_4$ and $BiF_5(SbF_5)_3$.

Conclusions

The SbF_5-rich $BiF_5(SbF_5)_n$ (n = 1.5, 2, or 3) adducts consist of *cis*-bridged tetramers like[5] solid $(SbF_5)_4$. The BiF_5-rich $(BiF_5)_nSbF_5$ ($n \geqslant 1$) adducts adopt *trans*-bridged polymeric BiF_5 structures.[8] Presumably the energy difference between a *trans*-bridged and a *cis*-bridged arrangement is not very great, given the right environment either arrangement can be adopted. That the $BiF_5{\cdot}SbF_5$ adduct has a *trans*-bridged structure suggests that the energy difference between a bismuth *trans*- and *cis*-bridged arrangement is greater than that between an antimony *trans*- and *cis*-bridged arrangement. Why $(BiF_5)_\infty$ and $(SbF_5)_4$ have *trans*- and *cis*-fluorine bridged structures respectively remains an open question.

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