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Short Communication

Products of the incomplete fluorination of antimony metal

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Recently, Edwards and Slim [1] have reported that fluorination of antimony metal in a sloping reactor produces a high-melting material from which two different crystalline compounds may be obtained. The two materials have monoclinic and triclinic unit cells, and the triclinic compound has been characterised as $Sb_{11}F_{43}$. The unit cell contains five SbF_6^- anions and a polymeric cation $[Sb_6F_{13}]^{5+}$ in which separate SbF_2^+ and $Sb_2F_5^+$ units can be distinguished [1].

In an independent investigation, we have shown that fluorination of antimony in a flow system produces SbF_5 and a mixture of yellow and white high-melting solids. Vacuum sublimation of the mixture at -140 °C produced a white crystalline solid from which we have isolated many single crystals. X-Ray crystallographic analysis of the individual crystals has revealed data consistent with the parameters associated with SbF_3 [2] and $Sb_{11}F_{43}$ [1] only.

Chemical analysis of bulk material from several preparations indicates, in each case, overall composition close to 66% SbF_3 and 34% $Sb_{11}F_{43}$.

The main features of the Raman spectrum of $Sb_{11}F_{43}$ were obtained from successive scans of a few single crystals of the compound in an evacuated capillary (see Table 1). The bands at 654 (s), 582 (m, br) and 288 (m, br) cm^{-1} can be assigned to the ν_1, ν_2 and ν_5 modes of octahedral SbF_6^-, and that at 663 (m) cm^{-1} can probably be correlated with ν_3. The appearance of the ν_3 vibration in the Raman is an indication of a reduction of symmetry of the SbF_6^- octahedra in $Sb_{11}F_{43}$. This is consistent with the X-ray data [1] . Weak but broad bands in the 445 and 490 cm^{-1} region are probably associated with $\nu(SbF_2^+)$ and $\nu(Sb_2F_5^+)$.

Raman spectra of the bulk material (see Table 1) closely resemble that of the single crystals but more detail is apparent. Thus peaks at 279 and 290, 588 and 654, together with the shoulder at 659 cm^{-1}, can be associated with ν_5 (which is split), ν_2 and ν_1 of SbF_6^- respectively, and that at 676 cm^{-1} with ν_3. There is ambiguity about the assignment of the peak at 659 cm^{-1}

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TABLE 1

Raman		IR		Raman		
Single crystal $Sb_{11}F_{43}$	Bulk material $Sb_{11}F_{43}$	Bulk material $Sb_{11}F_{43}$	Assignment	SbF_3[3(a)]	SbF_3[3(b)]	$SbF_3 \cdot SbF_5$ (B) [7]
	60 (w)		lattice vibrations			
	91 (w)				98 (mw)	
	122 (vw)			116 (w, sh)	125 (mw)	
	148 (w)			148 (w)	153 (mw)	~139 (w, br)
	174 (w)			176 (mw)	173 (mw)	
				197 (vw)		
	220 (vw, br)			218 (w)	220 (w)	
				226 (vvw)	233 (vw)	
				247 (w)	257 (w)	
	279 (m)		$\nu_5(SbF_6^-)$	279 (mw)	284 (mw)	280 (mw)
288 (m, br)	290 (m)					295 (w, sh)
445 (vw, br)						~445 (mw, br)
	460 (m, br)		SbF_3	465 (m, br)	462 (s)	
490 (vw, br)	494 (w, sh)		?			
	498 (m)	496 (m, br)	SbF_3	499 (s, sp)	503 (vs)	
	526 (vw)		?			521 (m, br)
	533 (w)		?			
		558 (m, br)				
	567 (w, sh)		$\nu_2(SbF_6^-)$			563 (m, sh, br)
582 (m, br)	588 (ms)					578 (m, br)
	614 (w)		?			625 (w, br)
	654 (s)		$\nu_1(SbF_6^-)$			651 (s)
654 (s)	659 (w, sh)					658 (ms)
663 (w, sh)						
	678 (w, br)	670 (s)	$\nu_3(SbF_6^-)$			678 (w, br)
		676 (sh)				

vvw = very very weak, vw = very weak, w = weak, mw = medium weak, ms = medium strong, s = strong, vs = very strong, br = broad, sh = shoulder, sp = sharp.

since it might also be assigned to ν_3. The broad peaks at 460 and 498 cm^{-1} can probably be assigned to SbF_3 [3]. The broad nature of the peaks, however, suggests unresolved fine structure which may result from the presence of the SbF_2^+ and $Sb_2F_5^+$ cations in $Sb_{11}F_{43}$. The remaining peaks between 494 and 558 cm^{-1} are in a region which has been correlated with the stretching frequencies of bridging Sb·····F bonds in complexes such as $XeF_2 \cdot SbF_5$ [4, 5] and $KrF_2 \cdot SbF_5$ [6]. In this case, the bands are almost certainly associated with SbF_2^+, $Sb_2F_5^+$ and the long Sb·····F bridging bonds which unite them in the $[Sb_6F_{13}]^{5+}$ ion [1]. As in the case of the spectrum of the single crystals, the forbidden ν_3 mode appears in the Raman. The fact that ν_1, ν_2 and ν_5 are split is also indicative of a reduction in symmetry of the SbF_6^- ion and the fact that it exists in two different environments in the solid. Thus the Raman data is totally consistent with the white bulk material being a mixture of $Sb_{11}F_{43}$ and SbF_3. This is also supported by the infrared spectrum (see Table 1).

There is a close relationship between the Raman spectrum of the SbF_3/$Sb_{11}F_{43}$ mixture and that of Gillespie *et al.* on $SbF_5 \cdot SbF_3$ (B form), which is formed by reaction of antimony metal with excess of SbF_5 in liquid SO_2. It may be that $SbF_5 \cdot SbF_3$ (B) is $Sb_{11}F_{43}$ rather than $SbF_5 \cdot SbF_3$ (A) as suggested by Edwards and Slim [1], or a mixture of $Sb_{11}F_{43}$ and SbF_3.

Material sublimed from our original yellow and white solid at temperatures in excess of 240 °C had a different Raman spectrum from $Sb_{11}F_{43}$ and the bulk material (which sublimed at 140 °C). The spectrum suggests that this new material contains the $Sb_2F_{11}^-$ ion, and it seems likely that it is the monoclinic phase observed by Edwards and Slim [1].

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