

## Intercalation of Antimony Pentafluoride and Antimony Pentachloride into Graphite: Antimony-121 Mössbauer Evidence for the Oxidation States Present

By Jack G. Ballard and Thomas Birchall,\* Department of Chemistry, McMaster University, 1200 Main St. W., Hamilton, Ontario L8S 4M1

Antimony-121 Mössbauer data are reported for  $\text{SbF}_5$  and  $\text{SbCl}_5$  intercalated into graphite. The spectra show that these halides enter the graphite lattice with reduction of  $\text{Sb}^{\text{V}}$  to  $\text{Sb}^{\text{III}}$ .

LALANCETTE AND LAFONTAINE<sup>1</sup> reported that antimony pentafluoride can be intercalated into graphite to give a solid which is much easier to handle than pure  $\text{SbF}_5$ . Because of our interest in the <sup>121</sup>Sb Mössbauer spectra of antimony halides, this procedure appeared to be a convenient way of examining  $\text{SbF}_5$  and perhaps  $\text{SbCl}_5$ , both of which are highly reactive liquids. Mössbauer data for both these halides have been previously reported<sup>2,3</sup> but only at liquid-nitrogen temperatures with the resulting low percentage absorptions. It therefore seemed advisable to reinvestigate these molecules under carefully controlled conditions, and intercalation into graphite appeared to offer a convenient means for achieving this. The data reported below show that when these halides enter the graphite lattice reduction to  $\text{Sb}^{\text{III}}$  occurs in both cases.

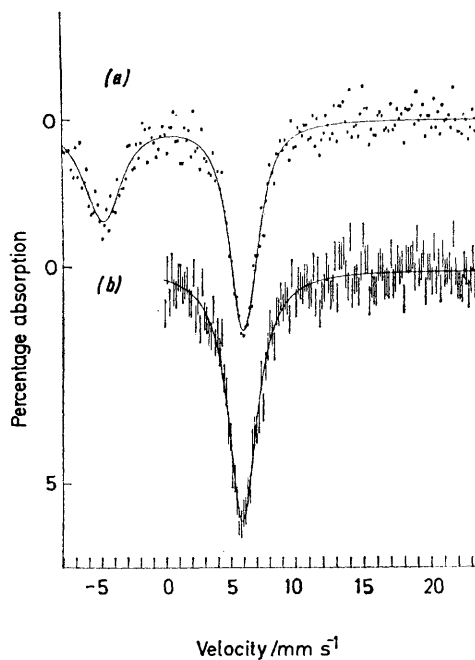
### EXPERIMENTAL

**Preparation of Samples.**—The procedure of Lalancette and Lafontaine was followed.<sup>1</sup> The parent halides were commercial samples which were first carefully purified by repeated distillation under dry nitrogen and finally *in vacuo*. All the manipulations of the purified halides were carried out in a dry box. Samples of these powders were then prepared for Mössbauer analysis by pressing the appropriate amount of compound into a sample holder cooled to 4 K, and the spectrum was recorded on equipment which has already been described.<sup>4</sup> For comparison purposes, we also recorded spectra for the halides by subliming the pure materials directly on to a thin Al window which had been cooled to 4 K. The graphite samples contained 10 mg  $\text{Sb cm}^{-2}$ . Spectra were recorded using a  $\text{BaSn}(\text{Sb})\text{O}_3$  source at room temperature and are referenced against  $\text{InSb}$  at 4 K. Data were computer fitted in each case to both a single Lorentzian lineshape and to a quadrupole-split spectrum. Velocity calibrations were made by means of a He-Ne laser interferometer system and with a standard iron foil and <sup>57</sup>Co-in-Pd source.

### RESULTS AND DISCUSSION

We find that  $\text{SbCl}_5$ , like  $\text{SbF}_5$ ,<sup>1</sup> is intercalated quite rapidly into the graphite lattice. The resulting free-flowing powders were much easier to handle than the pure liquids and Mössbauer samples were prepared much more conveniently than by the methods previously employed.<sup>3</sup> It was immediately obvious from the spectra obtained that, in addition to the expected strong absorption in the antimony(v) region of the spectrum, a

weaker absorption was also visible in the antimony(III) region (Figure). Antimony(III) absorptions were present for both  $\text{SbCl}_5$  and  $\text{SbF}_5$  intercalates, but none was detected in the spectra of the pure compounds. Clearly



Antimony-121 Mössbauer spectrum at 4 K of  $\text{SbCl}_5$  intercalated into graphite: (a) each resonance fitted to an eight-line pattern; (b) antimony(v) region only fitted to a single Lorentzian

these pentahalides do not enter the graphite lattice without some reaction occurring, contrary to what has been reported. Lalancette and Lafontaine<sup>1</sup> found that the  $\text{Sb}:\text{F}$  ratio was unchanged at 1:5, and since we have established that there is reduction of  $\text{Sb}^{\text{V}}$  to  $\text{Sb}^{\text{III}}$  it seems reasonable to suppose that carbon-halogen bond formation takes place to preserve the 1:5 stoichiometry. A similar reduction-oxidation process has also been noted for arsenic halides intercalated into graphite.<sup>5</sup>

The Mössbauer parameters obtained are similar to the previously reported values<sup>2,3</sup> (Table). Antimony pentafluoride gave a small positive quadrupole coupling, although the fitting to a single Lorentzian line was

<sup>3</sup> J. G. Stevens and L. H. Bowen, 'Mössbauer Effect Methodology,' Plenum Press, New York, 1970, vol. 5, p. 27.

<sup>4</sup> T. Birchall and A. F. Reid, *J. Solid State Chem.*, 1975, **13**, 351.

<sup>5</sup> L. Chun-Hsu, H. Selig, M. Rabinovitz, I. Agranat, and S. Sarig, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 9.

<sup>1</sup> J. M. Lalancette and J. Lafontaine, *J.C.S. Chem. Comm.*, 1973, 815.

<sup>2</sup> V. S. Shpinel, V. A. Bryukhanov, V. Kothekar, B. Z. Iofa, and S. I. Semenov, *Faraday Soc. Symposia*, 1967, **1**, 69.

equally as good. Such a splitting would be expected from a somewhat distorted octahedral arrangement about antimony. Antimony pentachloride on the other hand, whether intercalated or sublimed, consistently gave a

isomer shifts than when sublimed directly on to the Mössbauer probe. This may be an indication that these Lewis acids are involved in a significant way with the C-X halogen. The isomer shift for sublimed  $\text{SbCl}_5$

Antimony-121 Mössbauer data for antimony halides

Compound	Sample preparation	Isomer shift	Quadrupole coupling mm s <sup>-1</sup>	Line-width	$\chi^2$ (degrees of freedom)	Type of fit
$\text{SbF}_5$	Intercalated into graphite $\text{C}_{27}(\text{SbF}_5)$	10.6	4.4	2.5	201 (195)	8 lines both sites
		-6.3				
		10.6	4.5	2.5	137 (142)	8 lines $\text{Sb}^{\text{V}}$ site only
	Sublimed	10.4		2.9	139 (140)	1 line $\text{Sb}^{\text{V}}$ site only
		10.2	8.7	2.2	263 (250)	8 lines
		10.3		2.8	629 (500)	1 line
	Ref. 3	10.79				
$\text{SbF}_3$	Ref. 3	-6.04	19.6			
$\text{SbCl}_5$	Intercalated into graphite $\text{C}_{40}(\text{SbF}_5)$	5.9	-5.0	2.2	220 (195)	8 lines both sites
		5.0				
		5.9	-3.9	2.3	188 (151)	8 lines $\text{Sb}^{\text{V}}$ site only
	Sublimed	5.5		2.57	181 (150)	1 line $\text{Sb}^{\text{V}}$ site only
		5.2	-5.7	2.3	236 (250)	8 lines
		5.2		2.4	529 (500)	1 line
	Ref. 3	5.44	-4.4			
$\text{SbCl}_3$	Ref. 3	-5.24	12.2			

The spectra of the  $\text{C}_{100}(\text{SbX}_3)$  composition were the same within experimental error.

small negative  $eQV_{zz}$  value regardless of the sign of the initial estimates for the computer fitting. This negative value is certainly consistent with the trigonal-bipyramidal structure reported by Ohlberg.<sup>6</sup> However, other workers<sup>7,8</sup> have suggested that  $\text{SbCl}_5$  exists as  $[\text{SbCl}_4]$ - $[\text{SbCl}_6]$  at low temperatures, and Stevens and Bowen<sup>3</sup> have discussed the consequences of this possibility on the Mössbauer spectrum. The isomer shift of  $[\text{SbCl}_6]^-$  is 5.7 mm s<sup>-1</sup> and we have evidence that the shift of  $[\text{SbCl}_4]^+$  is 4.5 mm s<sup>-1</sup>.<sup>9</sup> The large difference in these two values mitigates against the  $\text{SbCl}_5$  resonance being a composite of  $[\text{SbCl}_4]^+$  and  $[\text{SbCl}_6]^-$  resonances, and indeed we were unable to synthesise a spectrum from these resonances which would fit the relatively narrow observed resonance.

The two halides when intercalated had slightly higher

agrees quite well with the literature value,<sup>3</sup> but there is a significant difference for  $\text{SbF}_5$ . Since the earlier workers gave no indication that the  $\text{SbF}_5$  they used had been distilled prior to sample preparation, we believe it likely that their sample contained impurities (fluoride oxides) and that our lower value of 10.22 mm s<sup>-1</sup> is the correct shift for pure  $\text{SbF}_5$ . The weak absorptions in the antimony(III) regions of the intercalated samples have isomer shifts which are close to those for  $\text{SbF}_3$  and  $\text{SbCl}_3$ . Unfortunately the poor statistics for these resonances did not allow us to abstract reliable quadrupole-coupling data which would confirm these assignments.

We thank the National Research Council of Canada for support.

[6/214 Received, 2nd February, 1976]

<sup>6</sup> S. M. Ohlberg, *J. Amer. Chem. Soc.*, 1959, **81**, 811.

<sup>7</sup> W. Bues, F. Derniray, and W. Brocker, *Spectrochim. Acta*, 1974, **A30**, 1709.

<sup>8</sup> R. F. Schneider and J. V. DiLorenzo, *J. Chem. Phys.*, 1967, **47**, 2343.

<sup>9</sup> J. G. Ballard and T. Birchall, unpublished work.