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The Synthesis and Characterization by Infrared and Raman Spectroscopy of some Ammine, Methylamine, Di- and Tri-methylamine and Aniline Complexes of Group VB (As, Sb and Bi) Trihalides

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The preparation of ammines of formula $MX_3 \cdot NH_3$ (where M = As, Sb and Bi; X = Br and I) and $SbCl_3 \cdot 2NH_3$ are described. 1:1 complexes of mono-, di, trimethylamine and aniline with some antimony and bismuth trihalides have also been isolated. Infrared and Raman spectra are reported for the compounds in the solid state and the spectra are interpreted to indicate that the complexes are mononuclear. The configuration of the monoammine and amine compounds is most probably based on a trigonal bipyramidal structure with the N donor ligand occupying an axial position and the lone pair of electrons occupying an equatorial site.

Introduction

As part of an investigation into the reactions of metal oxides with ammonium halides at elevated temperatures, we have found that in the case of the trivalent oxides of the Group VB elements (As, Sb and Bi), ammine adducts of the trihalides are formed. Ammine complexes of this type are reported in the literature as early as 1830 [1] but there appears to be considerable doubt as to their stoichiometry. No work has been published characterizing these compounds although a number of spectral and X-ray crystal structure investigations have been carried out on complexes of the Group VB trihalides with nitrogen containing donors such as butylamine [2], trimethylamine [3, 4], aniline [5], pyridine [6] and 2,2′-bipyridine [7].

We describe here the isolation and characterization of the compounds $MX_3 \cdot NH_3$ (where M = As, Sb and Bi; X = Br and I) and $SbCl_3 \cdot 2NH_3$. A preliminary report has been published [8]. Some amine complexes of methylamine, dimethylamine, trimethylamine and aniline with selected antimony and bismuth trihalides have also been prepared.

Experimental

Starting Materials

Commercially available reagents were used without further purification. Diethyl ether and benzene were dried over molecular sieves.

Synthesis

Ammine complexes

The ammine complexes (Table I) were prepared by one or more of the following methods.

(a) The metal oxide, M_2O_3, and the finely ground ammonium halide (50% excess) were intimately mixed and placed in a pyrex glass boat which was then inserted into the reaction zone of a horizontal tube furnace** (633–638 K) similar to that

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**The windings were such that a decreasing temperature gradient was maintained from the reaction zone to the exit end of the furnace. The reaction temperature was determined by Differential Thermal Analysis of the reaction mixture.

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TABLE I. Preparation, Properties and Analysis of Ammine Complexes.

Compound	Method of Preparation*	Colour	Decomp. Point (K)	Analysis/Found (Calc.)				
				M	X	N	H	NH_3
$AsBr_3 \cdot NH_3$	b	Yellow	499	22.4	72.5			5.4
				(22.6)	(72.3)			(5.1)
$AsI_3 \cdot NH_3$	a,b	Dark Red	553	15.7	80.5	2.9	0.9	
				(15.9)	(80.6)	(3.0)	(0.6)	
$SbCl_3 \cdot 2NH_3$	b	White	461	46.3	40.8			13.1
				(46.5)	(40.6)			(13.0)
$SbBr_3 \cdot NH_3$	a,b	Yellow	473†	32.3	63.2			4.4
				(32.2)	(63.3)			(4.5)
$SbI_3 \cdot NH_3$	a,b	Dark Red	487	23.1	72.9	2.8	0.7	
				(23.4)	(73.3)	(2.7)	(0.6)	
$BiBr_3 \cdot NH_3$	b	Yellow Green	479	44.5	51.3			3.5
				(44.9)	(51.5)			(3.7)
$BiI_3 \cdot NH_3$	a,c	Red	433	34.6	63.1	2.5		
				(34.5)	(62.8)	(2.3)		

*See Experimental. †Sublimation temp.

TABLE II. Analytical Data for Amine Complexes.

Compound	Colour	Analysis/Found (Calc.)				
		M	X	N	H	C
$SbCl_3 \cdot NH_2CH_3$	White	47.1	41.0	5.2	2.1	4.6
		(47.0)	(41.1)	(5.4)	(1.9)	(4.6)
$SbCl_3 \cdot NH_2C_6H_5$	White	37.9	33.1	4.4	2.2	22.4
		(37.7)	(33.2)	(4.2)	(2.6)	(21.9)
$SbBr_3 \cdot NH_2CH_3$	Yellow	31.0	61.4	3.6	1.5	3.2
		(31.0)	(61.1)	(3.6)	(1.3)	(3.1)
$SbBr_3 \cdot NH(CH_3)_2$	Pale Yellow	30.2	59.0	3.3	1.8	5.8
		(30.0)	(59.0)	(3.4)	(1.7)	(5.9)
$SbBr_3 \cdot N(CH_3)_3$	Pale Yellow	29.1	57.2	3.1	2.3	8.2
		(29.0)	(57.0)	(3.3)	(2.1)	(8.6)
$SbBr_3 \cdot NH_2C_6H_5$	Yellow	26.8	52.8	3.1	1.5	15.8
		(26.5)	(52.8)	(3.5)	(2.2)	(18.5)
$BiBr_3 \cdot NH_2CH_3$	Yellow	43.4	49.9	2.5	1.0	2.3
		(43.6)	(50.0)	(2.9)	(1.0)	(2.5)
$BiBr_3 \cdot NH(CH_3)_2$	Yellow	42.0	48.8	2.5	1.1	3.5
		(42.3)	(48.6)	(2.8)	(1.4)	(4.9)
$BiBr_3 \cdot N(CH_3)_3$	Pale Yellow	41.3	47.0	2.3	1.7	6.0
		(41.2)	(42.2)	(2.8)	(1.8)	(7.1)
$BiBr_3 \cdot NH_2C_6H_5$	Yellow	38.6	44.3	2.6	1.3	13.3
		(37.8)	(43.7)	(3.2)	(1.5)	(12.3)

described by Berg and Hartlage [9]. Dry nitrogen was passed over the reaction mixture and under the influences of the temperature gradient and the carrier gas the solid reaction product, MX_3 and NH_4X were deposited in fairly well-resolved bands along the glass liner tube. After cooling, the liner tube was removed from the furnace and the portion containing the ammine complex cut out. The product was scraped out, washed free from MX_3 with benzene and dried *in vacuo*.

(b) Dry NH_3 was bubbled through molten MX_3 or, in the case of $SbCl_3 \cdot 2NH_3$, through a solution of $SbCl_3$ in ether. A precipitate was formed immediately on entry of NH_3*. The solid product was washed free

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*If the ammonia is passed for a prolonged period, NH_4X is observed in the solid product indicating ammonolysis.

from unreacted MX_3 or $SbCl_3$ with either benzene or ether and dried *in vacuo.*

(c) Dry NH_3 was passed over heated BiI_3 (373 K) until a red product formed. The product was ground to a fine powder which was then heated and subjected to further reaction with NH_3. The processes were repeated until all the BiI_3 had reacted (as indicated by X-ray powder diffractometry).

Amine complexes

The general procedure adopted for the preparation of methylamine, dimethylamine and trimethylamine complexes was to add a benzene solution of the appropriate amine to a benzene or ether solution of the trihalide which was in slight excess. The precipitate was washed with benzene and dried *in vacuo.* Wade and Willey [10] have reported the preparation of trimethylamine complexes of some Group VB trihalides.

The aniline complexes were prepared by the method of Hulme and Scruton [11]. A warm solution of aniline in benzene was added to a stirred solution of MX_3 in warm benzene ($MX_3:NH_2C_6H_5 = 1:1.5$). The solid product was washed with benzene and dried *in vacuo.* In the case of $BiBr_3 \cdot NH_2C_6H_5$, ether was used as solvent and the reactants were mixed in a 1:1 mol ratio. The preparation of aniline complexes of SbX_3 (X = Cl, Br) has been described by Sumarokova and Kuidina [12] and Bowen *et al.* [13] using stoichiometric proportions of the reagents.

To the authors' knowledge the isolation of $SbBr_3 \cdot NH_2CH_3$, $SbBr_3 \cdot NH(CH_3)_2$, $SbCl_3 \cdot NH_2CH_3$, $BiBr_3 \cdot NH_2CH_3$, $BiBr_3 \cdot NH(CH_3)_2$, $BiBr_3 \cdot N(CH_3)_3$ and $BiBr_3 \cdot NH_2C_6H_5$ has not been reported.

The isolated compounds and their analytical data are listed in Table II.

Deuterated Ammine Complexes

ND_4Br and ND_4I were prepared by repeated dissolution of the ammonium halide in D_2O and evaporation of the solution to dryness *in vacuo.* About 80% conversion was obtained. Only those compounds requiring solid ND_4X for their preparation (method (a)) were produced.

Analytical Procedures

Carbon, hydrogen and nitrogen were estimated by microanalysis carried out by Mr J. Kent and Mr P. Nobbs, Department of Chemistry, University of Queensland. In some cases total NH_3 was determined by heating the sample with a solution of sodium hydroxide and absorbing the evolved ammonia in excess standard hydrochloric acid. Standard methods of analysis were used to determine other elements.

Physical Measurements

Room temperature infrared spectra (4000–400 cm^{-1}) were recorded on a Perkin-Elmer 225 spectrophotometer from samples pressed into KBr discs or as Nujol and hexachlorobutadiene mulls supported between potassium bromide plates. There was no evidence for bromide exchange in the preparation of KBr discs. Low temperature (~100 K) spectra of Nujol mulls and KBr discs were recorded using an evacuable glass cryostat fitted with KBr windows.

Far-infrared spectra (400–50 cm^{-1}) of samples as Nujol mulls between high density polythene plates were obtained at room temperature using a Beckman-RIIC IR-720 Fourier spectrophotometer. Low temperature spectra of Nujol mulls were also recorded using the Beckman-RIIC variable temperature unit.

A Cary model 82 laser spectrometer was used to record the Raman spectra of compounds. The solid samples were sealed in 1 mm diameter glass capillary tubes and low temperature spectra (~100 K) were obtained using an Oxford Instruments CF100 continuous flow cryostat cooled with liquid nitrogen. Either 515 nm (Ar^+) or 647 nm (Kr^+) were used as excitation wavelengths with a power of 50–100 mW at the sample.

Wavenumber values are considered accurate to ±5 cm^{-1} due to the generally broad nature of the bands in the spectra.

Results and Discussion

$AsCl_3$ and $BiCl_3$ appear to be particularly susceptible to ammonolysis ($MCl_3 + 6NH_3 \rightleftarrows M(NH_2)_3 + 3NH_4Cl$) and although other workers [1, 14, 15] have described the preparation of ammine adducts of As and Bi, we were unable to isolate compounds of this type.

The ammine complexes are, in general, stable in air, practically insoluble in common solvents but hydrolysed by water. Only solid state spectra could be measured and no molecular weights could be determined. Mass spectra did not yield a parent molecular ion but rather the fragmentation pattern for MX_3. All compounds decomposed without melting except for $SbBr_3 \cdot NH_3$ which sublimed unchanged at atmospheric pressure and *in vacuo.*

Infrared and Raman spectra were recorded at room temperature and at ~100 K. In general, bands were sharper in the low temperature spectra and consequently more features appeared. Only the low temperature spectra are listed in Table III. Wavenumber values at room temperature are not significantly different. Proposed assignments are indicated. In Table IV, selected frequencies for the solid state spectra of the amine complexes at room temperature are listed for comparison purposes.

TABLE III. Vibrational Spectra (cm^{-1}) and Assignments for $MX_3 \cdot nNH_3$.[a]

$AsBr_3 \cdot NH_3$		$AsI_3 \cdot NH_3$		$SbCl_3 \cdot 2NH_3$		$SbBr_3 \cdot NH_3$		$SbI_3 \cdot NH_3$		$BiBr_3 \cdot NH_3$		$BiI_3 \cdot NH_3$		Approx. Assign.
R	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	IR	
18w		15m				12w		11w						Lattice Modes δXMN and ρMX_3
26m		20sh				20w		18m						
31s		22m				29w		24w						
34s		25sh				35m		29s				27m		
54sh		31s				47sh		40m				38w		
58sh		37sh		38s		51sh		46s						
64m		46m				57s		49s						
67m		52m		53m		60sh		51s		51w				
73m		58m				66m		53m		61sh		53s		
82mw		60sh				74m		57m		65m		65m		
		69m		67m		89w		70w				80w		
		78w		77w		95w								
107w	110sh			96w	104w	105w				104w				
128w					122m									
144w					157w									
161w	157sbr	96m	91m	178w	178s		120m	86m	92m	115w	113s	90s		δMX_3
		110w	109w					124sh	124sh			102m	102vw	
		133w										115m		
		149vw				141w	155m							
		162vw		245w	227m						148m			
217s	205sh	179vs	164s	267w	274s	182s	187s	149s	151s	165m	170s	127m	128w	$\nu(M-X)$
		186sh												
246s		195s		287ms	293sh	216s	204sh	169sh	175sh	192s	192sh	139s	142w	$\nu(M-X)$
			216sh	308sh								154m		
			244vw					216vw					181vw	
	323m		322m		343sh		318w		278w		295s		265s	$\tau(NH_3)$
				433m	426s									$\delta(NSbN)$
	595s		573s		548m		520m		529m		502m		475m	$\nu(M-N)$
682vw					666s		630w		623m					ρNH_3
			820w				745w		747w					ρNH_3
1406vw	1397s	1396vw	1380s	1405vw	1400s	1402vw	1395s	1396vw	1391s	1400vw	1396s	1389w	1390s	δNH_3
3020vw	3022sh		3040m		3000sh				3000w				3000w	$\nu(N-H)$
	3102s				3140m		3110m		3107m		3084m		3110m	$\nu(N-H)$

[a] s = strong; m = medium; w = weak; br = broad; sh = shoulder; v = very.

TABLE IV. Selected Frequencies (cm^{-1}) for Amine Complexes (ambient temp.).

Complex	$\nu(M-X)$		$\delta(MX_3)$		$\nu(M-N)$ Infrared
	Raman	Infrared	Raman	Infrared	
$SbCl_3 \cdot NH_2CH_3$	274mbr	275mbr		158sbr	542wbr
		309sh			
	322s				
$SbCl_3 \cdot NH_2C_6H_5$		269s		138sh	388m
		291s		156sbr	
		320s			
$SbBr_3 \cdot NH_2CH_3$	189s	187sbr	113vw	112sbr	543mbr
			162m	147w	
$SbBr_3 \cdot NH(CH_3)_2$		183sbr	110vw	113mbr	542wbr
	196m				
	217m	230m			
$SbBr_3 \cdot N(CH_3)_3$	173sh	173sh	112wbr	113w	534mwbr
	181m	188m		127w	
	209m	200s			
$SbBr_3 \cdot NH_2C_6H_5$		190vw		96m	374m
		205m		120s	
				143m	
$BiBr_3 \cdot NH_2CH_3$	189m	170s		116sbr	508m
	214m				
$BiBr_3 \cdot NH(CH_3)_2$	164w	170s	111w		505w
	179sh			128m	
	187m	188s	136w		
	199s	198sh			
$BiBr_3 \cdot N(CH_3)_3$		146w	112m	108m	507w
	161m	152w		119sh	
	184s	172s			
$BiBr_3 \cdot NH_2C_6H_5$		141brsh		113s	372m
		177s			

Because the aniline complexes were easily decomposed by laser radiation, even in an unfocussed beam of low intensity, only infrared spectra were measured.

Vibrations Associated with the NH_3 Moiety

N–H stretching bands

A broad band, or bands, mainly appearing in the infrared spectra about 3100–3000 cm^{-1} may be attributed to N–H stretching. Hydrogen bonding may contribute to the broadening and together with coordination, to the shift to lower frequencies compared with NH_3 [16]. On deuteration, the band shifted to ~2300 cm^{-1} ($\nu_{N-H}/\nu_{N-D} = 1.35$).

NH_3 deformation and rocking bands

A study of the spectra of known ammine complexes [16] shows that degenerate bending and symmetric bending modes occur approximately in the 1650–1550 and 1400–1100 cm^{-1} ranges respectively, and that NH_3 rocking modes occur in the range 950–600 cm^{-1}. In the spectra of all of the ammines, bands were observed at about 1400 cm^{-1} which are attributed to the symmetric NH_3 deformations. These bands are shifted on deuteration and several bands corresponding to deformations of NH_2D, NHD_2 and ND_3 species were observed in the region 1400–1000 cm^{-1}. No bands were observed in any of the spectra in the 1600 cm^{-1} region and it can only be assumed that the asymmetric deformation vibrations give rise to extremely weak signals.

With the exception of $BiI_3 \cdot NH_3$ and $BiBr_3 \cdot NH_3$, the compounds displayed broad, weak bands in the range 820–620 cm^{-1} which are assigned to NH_3 rocking.

NH_3 torsional bands

Infrared spectra of the ammine complexes of $AsBr_3$, AsI_3, $BiBr_3$ and BiI_3, exhibited strong to medium bands in the range 325–265 cm^{-1}. In the infrared spectra of $SbBr_3 \cdot NH_3$ and $SbI_3 \cdot NH_3$ weak, broad bands occurred at 318 and 278 cm^{-1} respectively. These bands have been assigned to the NH_3 torsional mode (*cf.*, CH_3 torsions in organic compounds have been assigned to bands in the range 280–222 cm^{-1} [17]). On deuteration, the bands at 278 cm^{-1} ($SbI_3 \cdot NH_3$), 295 cm^{-1} ($BiBr_3 \cdot NH_3$) and 265 cm^{-1} ($BiI_3 \cdot NH_3$) move to 230, 225 and 222 cm^{-1} respectively (τ_{NH_3}/τ_{ND_3} = 1.20, 1.30 and 1.20 respectively). In $SbCl_3 \cdot 2NH_3$, the NH_3 torsional modes occur close to the region of the intense Sb–Cl stretching modes. The infrared band at 343 cm^{-1} is tentatively assigned to a torsional mode.

Vibrations Associated with the MX_3 Moiety

M–X stretching bands

Using the vibrational frequencies for the simple metal halides [18] as a guide it is possible to tentatively assign bands in the 300–120 cm^{-1} region to M–X stretching vibrations. Although the stretching frequencies assigned are lower than those known for the simple halides, they are in general agreement with M–X stretching frequencies proposed for other complexes of the Group VB trihalides [19–21]. Further justification for these assignments comes from the obvious halogen dependency and metal dependency of the band positions. That is, for given M, ν(M–X) decreases as the mass of X increases (Cl to Br to I) and for given X, ν(M–X) decreases as the mass of M increases. For halides of similar structure the expected frequency ratios ν(M–Cl):ν(M–Br):ν(M–I) are 1:0.70–0.75:0.55–0.60 [20]. Corresponding ratios were calculated from the frequencies assigned to ν(M–X) in Table III and the values 1:0.68–0.75:0.55–0.60 indicate that these *ammine complexes are structurally similar.*

The bands assigned to M–X stretching modes in the amine complexes are listed in Table IV. Frequencies assigned to Sb–Cl stretching modes in $SbCl_3 \cdot NH_2CH_3$ and $SbCl_3 \cdot NH_2C_6H_5$ agree well with those assigned to the ammine complex $SbCl_3 \cdot 2NH_3$. $SbCl_3 \cdot NH_2C_6H_5$ is known to be a mononuclear species [11] and the good agreement for the ν(Sb–Cl) modes indicates the absence of bridging in $SbCl_3 \cdot 2NH_3$ and $SbCl_3 \cdot NH_2CH_3$. Comparison of Tables III and IV shows that the bands assigned to ν(Sb–Br) in the ammine complex correspond, in frequency and intensity, to bands in the spectra of the amine complexes of antimony. It is therefore probable that the methylamine and ammine complexes are also mononuclear. A similar conclusion may be drawn for the Bi complexes.

MX_3 deformation bands

Assignment of frequencies to MX_3 deformation modes is complicated by possible overlap with lattice modes which are likely to occur below 100 cm^{-1}. The assigned frequencies are in general agreement with frequencies proposed in other Group VB complexes [20] and, as with the M–X stretching frequencies, they exhibit halogen and metal dependency. Frequencies assigned to these modes in the amine complexes in Table IV compare well with those assigned to the ammines.

M–N Stretching Vibrations

In many ammine complexes of transition metals the M–N stretching bands have been assigned to the 500 cm^{-1} frequency region [16]. Schumann and Roth [22] in their studies on the reaction of phenylazide with triphenylstannyl-diphenylarsine and bis-(triphenylstannyl)-phenylarsine assigned the As–N stretching frequencies in resulting compounds to 502 and 504 cm^{-1} respectively. Meinema and Noltes [23] have assigned Sb–N stretching frequencies in some mono- and bisdiethylaminostibines to the region 565–455 cm^{-1}. More recently Ando *et al.* [24] reported Bi–N stretches in $Bi(NEt_2)_3$ and $Bi(NPr_2)_3$ (where Et = ethyl and Pr = n-propyl) at 550, 270 cm^{-1} and 408, 322 cm^{-1} respectively. In the present work the ammine (and the mono, di and trimethylamine) complexes exhibit bands in the range 595–475 cm^{-1} which may be assigned to the M–N stretching mode. The frequencies for the ammines exhibit the expected metal dependency. On deuteration a shift to lower frequencies of ~35 cm^{-1} would be expected but no detectable shift was observed. This is probably due to the general broadness of the band and the possible contributions from incompletely deuterated species, NH_2D and NHD_2.

In the aniline complexes, bands occurring at 388 ($SbCl_3 \cdot NH_2C_6H_5$), 374 ($SbBr_3 \cdot NH_2C_6H_5$) and 372 ($BiBr_3 \cdot NH_2C_6H_5$) cm^{-1} have been assigned to the M–N stretching modes respectively. Ahuja *et al.* [25] and Jungbauer and Curran [26] measured the far-infrared spectra of aniline complexes of a number of transition and non transition metal halides and have assigned bands in the range 450–350 cm^{-1} to M–N modes. The shift of the Sb–N and Bi–N stretches to lower frequencies in complexes employing ligands such as aniline compared with ammonia and the methylamines, is probably due to the heavier mass of these ligands together with the electron withdrawing effect of the benzene ring which tends to decrease the strength of the M–N bond.

NMN Deformation Vibrations

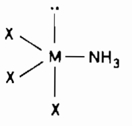
According to Nakamoto [16], NMN deformation frequencies are likely to occur in the range 550–300 cm^{-1}. The band at ~430 cm^{-1} observed in the spectra of $SbCl_3 \cdot 2NH_3$ has been assigned to this deformation mode.

XMN Deformation Modes

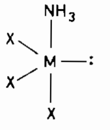
XMN deformation and MX_3 rocking modes probably occur with low wavenumber values in the lattice region.

Proposed Molecular Configurations for Ammine Complexes

Based on trigonal bipyramidal stereochemistry for M (10 electron valence shell) the following models may be considered for



(a)



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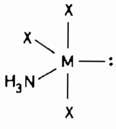

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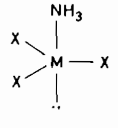
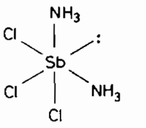


(d)

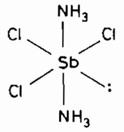
$MX_3 \cdot NH_3$. The highest possible symmetry for configurations (a), (b), (c) and (d) is C_s, C_s, C_s and C_{3v} respectively.

The appearance of more than two features in the M–X stretching region in the combined infrared and Raman spectra for the ammines would preclude the C_{3v} configuration (A_1 + E) and indicate that the molecules possess one of the configurations exhibiting C_s symmetry ($2A' + A''$). With several exceptions, amine and aniline complexes also exhibit more than two bands. The M–X stretching frequencies observed are comparable to those obtained by Ahlijah and Goldstein [19] for tetra-alkylammonium salts of mixed tetrahalogeno-complexes of the type $[R_4N][MX_3Y]$. It is reasonable to assume that these complexes exhibit a trigonal bipyramidal configuration with C_s symmetry. Information whether (a), (b) or (c) is the correct model cannot be obtained solely from the measured infrared and Raman spectra of the solids. However, since X-ray studies on $SbCl_3 \cdot NH_2C_6H_5$ [11] and X-ray and spectral studies on $AsCl_3 \cdot NMe_3$ [3, 4] showed the molecules to have a configuration corresponding to (b), it is probable that the configuration of the monoammine, amine and aniline complexes corresponds also to (b). The possibility that the isolated molecule may have C_{3v} symmetry (d) but undergoes symmetry lowering due to site symmetry effects cannot be discounted.

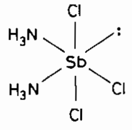
For the complex $SbCl_3 \cdot 2NH_3$ there are two donor N atoms and VSEPR theory predicts the metal atom to be surrounded by six electron pairs based on an octahedral configuration. Possible configurations are (e), (f) and (g) with C_s, C_{2v} and C_s symmetry respectively.



(e)



(f)



(g)

Three infrared and Raman active (coincident) Sb–Cl stretching modes are predicted for all configurations, and at least three bands are observed in the Sb–Cl stretching region. It is not possible to obtain information on the symmetry of the molecule from vibrational data alone. Hulme *et al.* [5] and Cameron and Killean [6] have shown by single crystal X-ray studies that $SbCl_3 \cdot 2NH_2C_6H_5$ and $AsCl_3 \cdot 2NC_5H_5$ have molecular configurations corresponding to (e). On the other hand Lipka and Wunderlich [7] report a distorted octahedral stereochemistry for Sb in $SbCl_3 \cdot 2,2'$-bipyridine which contains a T-shaped $SbCl_3$ moiety (corresponding to (g)).

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