Table V. Raman Frequencies of Molten $AlCl_3$-$TeCl_4$ Mixtures (cm^{-1})[a]

$AlCl_3$: $TeCl_4$ = 0:1 250°, A	$AlCl_3$: $TeCl_4$ = 1:1 200°, B	$AlCl_3$: $TeCl_4$ = 2:1 150°, C	Assignment
	392 vs, p	395 vs, p	ν_1 (A_1) $TeCl_3^+$
381 vs, p			(A_1) $TeCl_4$
	371 m, dp	378 m, dp	ν_3 (E) $TeCl_3^+$
351 m, dp			(E) $TeCl_4$
	344 m, p	345 m, p	ν_1 (A_1) $AlCl_4^-$
		311 m, p	(A_1) $Al_2Cl_7^-$
281 vw, dp?			(B_1) $TeCl_5^-$
	169 m, p?	169 m, p?	ν_2 (A_1) $TeCl_3^+$
151 m, dp			(E) $TeCl_4$
	147 m, dp	147 m, dp	ν_4 (E) $TeCl_3^+$

[a] Key: m, medium; s, strong; v, very; w, weak; dp, depolarized; p, polarized.

amount of $AlCl_4^-$ present, the mass balance demands that the rest of Al(III) is present as Al_2Cl_6. A calculation similar to that used by Oye, *et al.*,[18] of the mole fraction equilibrium constant $K = x_{Al_2Cl_6}x_{AlCl_4}{}^{-2}/x_{Al_2Cl_7}{}^{-2}$ was performed. It was assumed that the Raman intensity is proportional to the concentration. The intensities of the strongest bands for $AlCl_4^-$ and $TeCl_3^+$ used were obtained from the mean of three spectra of 1:1 composition and the 2:1 composition of $AlCl_3$-$TeCl_4$. A value for K of about 2×10^{-2} was obtained. This value fits reasonably well with the values from the MCl-$AlCl_3$ systems, where K can be calculated to be 0.8×10^{-2}, 2.6×10^{-2}, and 4.96×10^{-2} for KCl,[18] NaCl,[29] and NaCl[30] at 170-240, 190, and 175°, respectively. It is here worthwhile mentioning that in contrast to the MCl-$AlCl_3$ systems no miscibility gap is found in the $TeCl_4$-$AlCl_3$ system. An explanation for this is probably that the M^+ ions (M = Li, Na, K, Cs) are not able to form uncharged species with the anions of the melt to the same degree as the polar $TeCl_3^+$ and that the uncharged species are completely miscible with Al_2Cl_6. That there is strong interaction between the ions in the system can be seen from the frequency change of the symmetrical stretching vibration of the $TeCl_3^+$ complex. As the anions become less and less able to polarize (*i.e.*, as one goes from Cl^- to $AlCl_4^-$ to $Al_2Cl_7^-$ and $AlCl_4^-$), the frequencies 381, 392, and 395 cm^{-1}, respectively, are obtained for the position of the band due to the symmetrical stretching vibration.

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Registry No. $KAlCl_4$, 13821-13-1; $TeCl_4$, 10026-07-0; $AlCl_3$, 7446-70-0; $TeCl_3^+$, 43644-19-5; $TeCl_5^-$, 44246-02-8; $TeCl_6^{2-}$, 20057-66-3; KCl, 7447-40-7.

(29) H. A. Oye and D. M. Gruen, *Inorg. Chem.*, 3, 836 (1964).
(30) L. G. Boxall, H. L. Jones, and R. A. Osteryoung, *J. Electrochem. Soc.*, 120, 223 (1973).

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Vibrational Spectra and Bonding in Acetonitrile Complexes of Group Va Pentahalides

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Complete solid-state Raman and infrared spectra have been obtained for the acetonitrile adducts of arsenic pentafluoride and antimony pentachloride. In addition, Raman depolarization data are presented for the acetonitrile and SO_2 solutions of these systems. The results are in accord with the X-ray structure of $SbCl_5 \cdot NCCH_3$ which is a molecular solid with octahedral coordination (~C_{4v} symmetry) about the central metal atom. In general, the metal-halogen vibrations correlate well in relative frequency and intensity with those of similar complexes having approximately C_{4v} symmetry. The measured Raman shifts for the MN stretch (including the revised assignment of the previously reported data for the SbF_5 complex) are ~277 cm^{-1} for $SbF_5 \cdot NCCH_3$, 270 cm^{-1} for $AsF_5 \cdot NCCH_3$, and 222 cm^{-1} for $SbCl_5 \cdot NCCH_3$. The respective force constants for each of these complexes are 1.9, 1.9, and 1.1 mdyn/Å. The relationship between the constants of the fluoride and the chloride complexes for antimony (*i.e.*, $SbF_5 \cdot NCCH_3 > SbCl_5 \cdot NCCH_3$) is just opposite to that calculated for the acetonitrile complexes of the boron halides. An attempt to stabilize the "nonexistent" molecule $AsCl_5$ as the acetonitrile complex proved unsuccessful.

Introduction

Strong Lewis acids, particularly the binary metal halides, and their adducts find use in a host of well-known reactions. For example, they have long served as catalysts[2] and intermediates[3] in Friedel-Crafts and related reactions. In the past, reports involving the use of group IIIa halides dominated the literature; since the earyl 1960's, however, interest in the pentahalides of the group Va elements has increased. One major instance is the use of antimony pentafluoride in the formation and stabilization of simple carbonium ions.[4]

A variety of simple molecular and ionic $MX_5 \cdot L$ complexes (~C_{4v} symmetry) exist, including such species as $AsF_5 \cdot NCCH_3$,[5] $AsF_5 \cdot N(CH_3)_3$,[5] $AsF_5 \cdot SO_2$,[5] $AsF_5 \cdot PF_3$,[6] AsF_5Cl^-,[7] AsF_5Br^-,[7] AsF_5OH^-,[5] $SbF_5 \cdot NCCH_3$,[5] $SbF_5 \cdot$dioxane,[5] $SbF_5 \cdot$py,[5] $SbF_5 \cdot SO_2$,[5] $SbF_5 \cdot PF_3$,[6] $SbF_5 \cdot P(C_6H_5)_3$,[6] $SbF_5 \cdot As(C_6H_5)_3$,[6] SbF_5OH^-,[5,8] $SbCl_5 \cdot OP(CH_3)_3$,[9] $SbCl_5 \cdot OPCl_3$,[9] $SbCl_5 \cdot CH_3NO_2$,[10] $SbCl_5 \cdot$DMF,[11] $SbCl_5 \cdot$DMSO,[9,11] and $SbCl_5 \cdot$

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[1] To whom correspondence should be addressed.
[2] G. A. Olah in "Friedel-Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Interscience, New York, N. Y., 1963, Chapter IV.
[3] G. A. Olah and M. W. Meyer, ref 2, Chapter VIII.
[4] For example: G. A. Olah and G. Liany, *J. Amer. Chem. Soc.*, 95, 3792 (1973), and preceding papers in this series.
(5) The following review of the halides of arsenic and antimony discusses some of the specific compounds listed in the text as well as many others: L. Kolditz, *Halogen Chem.*, 2, 115 (1967), and references therein.
(6) R. D. W. Kemmitt, V. M. McRae, R. D. Peacock, and I. L. Wilson, *J. Inorg. Nucl. Chem.*, 31, 3674 (1966).
(7) L. Kolditz and H. -P. Krause, *Z. Chem.*, 7, 157 (1967).
(8) W. A. Mazeika and H. M. Neumann, *Inorg. Chem.*, 5, 309 (1966).
(9) I. Lindqvist, "Inorganic Adduct Molecules of Oxo-Compounds," Academic Press, New York, N. Y., 1963, and references therein.
(10) L. Riesel and H. -A. Lehman, *Z. Chem.*, 7, 316 (1967).

$NCCH_3$.[12,13] Most of the recent reports do contain vibrational spectra, but these are limited to narrow energy ranges and a single isotopic species. Indeed, except for the previous paper in this series,[14] no comprehensive spectroscopic assignments for the MX_5 moiety of any group Va pentahalide complex are available.

The data presented here on $AsF_5 \cdot NCCH_3$ and $SbCl_5 \cdot NCCH_3$ in conjunction with those already reported for $SbF_5 \cdot NCCH_3$[14] are employed to explore the influence of the central atom and attached halogens on the donor-acceptor bond. The consequence of changing halogens is not at all obvious. For example, among the boron halides, simplistic electronegativity arguments to the contrary, the relative order of acidity determined from heats of fromation is $BBr_3 \geqslant BCl_3 > BF_3$,[15] which is in the same sequence as the relative donor-acceptor bond strengths given by the force constants.[16] Qualitative chemical evidence seems to indicate just the opposite influence of halogen on the acidity of group Va pentahalides.

Experimental Section

Except where noted below all procedures were similar to those reported in the previous paper.[14]

Infrared Spectra. Far-infrared spectra (450-60 cm^{-1}) were collected on a Perkin-Elmer 180 with the factory-installed far-infrared option. For the mid-infrared region (4000-400 cm^{-1}), this same instrument was employed for $AsF_5 \cdot NCCH_3$ samples, whereas a Beckman IR-9 was used for $SbCl_5 \cdot NCCH_3$ samples. Each of these instruments was occasionally checked with atmospheric water and CO_2 bands or with liquid indene and peak positions were corrected to within $\pm 2.0\ cm^{-1}$.

As with $SbF_5 \cdot NCCH_3$,[14] samples of the adducts were prepared for infrared spectroscopy by layering the reactants on an AgCl sample plate at $-196°$. However, owing to its high volatility, AsF_5 was deposited in more and thinner layers with acetonitrile and annealing was performed at a lower temperature than before, $-60°$. There was no indication of uncomplexed Lewis acid or base in any of the spectra.

Raman Spectra. All Raman data for the adducts were gathered on a Spex 1401 0.85-m double monochromator and sampling optics of our own design. Extensively modified Spex photon counting equipment was used in conjunction with an RCA C31034 photomultiplier. The green 514.5-nm or blue 488.0-nm line of an argon ion laser or the red 647.1-nm line of a krypton ion laser (both light-feedback stabilized Spectra Physics 164 Models) was used to illuminate the sample. For $SbCl_5 \cdot NCCH_3$, using the 647.1-nm exciting line, laser power at the sample typically ranged from 100 to 300 mW and the spectral resolution was 0.5-2.5 cm^{-1}. In the case of the $AsF_5 \cdot NCCH_3$ systems, using 514.5- or 488.0-nm radiation, laser power at the sample was 300-400 mW and the band pass was 0.8-1.5 cm^{-1}. The observed wave number shifts should be good to about $\pm 1.0\ cm^{-1}$.

Data for each sample were collected on a strip chart recorder, as well as digitally on magnetic tape (typically at 0.83-cm^{-1} intervals). Digital data were processed on a CDC 6400 computer by program RAMAN.[17] In every case, the conventional 90° viewing geometry was employed, with the incident beam taken to be the z axis, the collection optics then being along the x axis.

In addition to the usual room-temperature spectra, studies of the $SbCl_5 \cdot NCCH_3$ and $AsF_5 \cdot NCCH_3$ compounds at lower temperatures (down to about $-110°$) were obtained in a Miller-Harney type cell.[18]

Reagents. $SbCl_5$ (Baker and Adamson reagent grade, Specialty Chemicals Division, Allied Chemical Corp.) was repeatedly distilled at room temperature under high vacuum until the Raman spectra showed no trace of free Cl_2. AsF_5 (Pflautz and Baum) was purified by fractional distillation under high vacuum. Details of the purification of CH_3CN, CD_3CN, and $CH_3C^{15}N$ are given in the previous paper.[14]

Attempted Preparation of $AsCl_5$. About 1 ml (~2 g) of $AsCl_3$ was distilled into a 0.25-in. o.d. Pyrex tube at $-196°$, followed by an excess of chlorine. After sealing off under vacuum, the mixture was warmed to room temperature. A Raman spectrum of the bright yellow liquid showed only bands assignable to the two parent molecules.

Attempted Preparation of $AsCl_5 \cdot NCCH_3$. Approximately equimolar quantities (<10 mmol, estimated from the volume of the liquids) were distilled into a 0.25-in. Pyrex tube containing an excess of acetonitrile. The tube was sealed under vacuum (with the reactants cooled to $-196°$); then the mixture was allowed to warm slowly to room temperature. The initial mixture was a yellow, free-flowing liquid. After several days the color began to fade and the solution became more viscous. A few days later some light-colored crystals appeared. Although a reaction had occurred, the Raman spectrum gave no indication of features which might be attributed to an $AsCl_5 \cdot L$ species or to complexed acetonitrile.

Results

Selection Rules. As expected, the spectra fully confirmed the assumption that $AsF_5 \cdot NCCH_3$ is structurally similar to $SbCl_5 \cdot NCCH_3$, which has approximately C_{4v} symmetry (octahedral coordination) about the antimony atom.[12] Considered as a rigid structure, the highest symmetry possible for the isolated $MX_5 \cdot NCCH_3$ [M = As, Sb; X = F, Cl] molecule is C_s, for which the selection rules predict 30 fundamentals. More reasonable, particularly for solutions of the complexes, is a nonrigid structure in which the methyl group rotates freely with respect to the four equatorial halogen atoms. As shown in the previous paper,[14,19,20] selection rules derived from the corresponding permutation group yield 21 fundamentals: 8 A_1, 1 A_2, 2 B_1, 1 B_2, and 9 E.[21] Of these, the A_1 and E modes are both Raman and infrared active, the B_1 and B_2 species are Raman active, and the A_2 mode is silent.

Even if the molecule were strictly rigid on the infrared time scale, a local symmetry approximation to the selection rules would be physically reasonable. This is true because of the rather wide separation of the frequencies attributed to the MX_5- and -$NCCH_3$ moieties and the spatial remoteness of the MX_5- portion from the -$NCCH_3$ part of the complex. This local symmetry model results in the same overall symmetry designations and activities as those outlined for the nonrigid model. In particular, the acetonitrile portion (~C_{3v}) should exhibit 4 A_1 and 4 E fundamentals, while 4 A_1, 2 B_1, 1 B_2, and 4 E modes[21] are expected for the MX_5N- portion (~C_{4v}). In addition, there is an MNC deformation belonging to the species E and an A_2 torsional mode. The designation and approximate description of these 21 fundamentals are given in Table I.

Assignments. Tables II and III give the assignments for the infrared and Raman bands of solid $AsF_5 \cdot {}^{14}NCCH_3$ and $SbCl_5 \cdot {}^{14}NCCH_3$. The complete set of spectroscopic data for the solid D- and ^{15}N- substituted species and Raman data for the sulfur dioxide solutions of the normal isotopic molecules, as well as the assignments for the analogous isotopic variants of $SbF_5 \cdot NCCH_3$, may be found in Tables II-VII of ref 20.

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(11) M. Burgard, G. Kaufman, and R. Rohmer, *C. R. Acad. Sci., Ser. C*, **267**, 689 (1968).

(12) H. Binas, *Z. Anorg. Allg. Chem.*, **352**, 271 (1967).

(13) M. Burgard and I. MacCordick, *Inorg. Nucl. Chem. Lett.*, **6**, 599 (1970).

(14) D. M. Byler and D. F. Shriver, *Inorg. Chem.*, **12**, 1412 (1973).

(15) H. C. Brown and R. R. Holmes, *J. Amer. Chem. Soc.*, **78**, 2173 (1956).

(16) D. F. Shriver and B. Swanson, *Inorg. Chem.*, **10**, 1354 (1971).

(17) D. F. Shriver, R. Lloyd, and W. Davis, XXI Mid-America Symposium on Spectroscopy, Final Program, Chicago, Ill., 1970, p 46.

(18) F. A. Miller and B. M. Harney, *Appl. Spectrosc.*, **24**, 291 (1970).

(19) See also Appendix I of ref 20.

(20) D. M. Byler, Ph.D. Dissertation, Northwestern University, 1974.

(21) For the sake of consistency with the crystal structure of $SbCl_5 \cdot NCCH_3$, the xz and yz mirror planes were chosen to be the dihedral planes (σ_d) bisecting the two vertical planes (σ_v) containing the equatorial halogens. Note that α_{xy} now transforms as B_1 while $\alpha_{x^2-y^2}$ transforms as B_2.

Table I. Numbering and Approximate Description of the Fundamental Vibrations of $MX_5 \cdot NCCH_3$ (M = As or Sb; X = F or Cl)[a]

A_1 class	
ν_1	CH_3 str
ν_2	CN str
ν_3	CH_3 def
ν_4	CC str
ν_5	MX′ axial str
ν_6	MX_4 equatorial str
ν_7	MX_4 out-of-plane def
ν_8	MN str
A_2 class	
ν_9	torsion
B_1 class	
ν_{10}	MX_4 equatorial str
ν_{11}	MX_4 out-of-plane def
B_2 class	
ν_{12}	MX_4 in-plane def
E class	
ν_{13}	CH_3 str
ν_{14}	CH_3 def
ν_{15}	CH_3 rock
ν_{16}	MX_4 equatorial str
ν_{17}	CCN def
ν_{18}	X′-MX_4 wag
ν_{19}	N-MX_4 wag
ν_{20}	MX_4 in-plane def
ν_{21}	MNC def

[a] This numbering scheme differs slightly from that originally employed in ref 14.

Table II. Observed Infrared and Raman Frequencies (cm^{-1}) for Solid $AsF_5 \cdot {}^{14}NCCH_3$

Infrared (196°)	Raman (~22°)	Assignment
	~105 (~25)[a]	ν_{21}
	239 (10)	ν_{19}
281 w	270 (6)	ν_8
324 w	325 (17)	ν_{20}
362 s	365 (6)	ν_7
377 s	384 (12)	ν_{18}
~390 sh, w		(?)
435 m	436 (13)	ν_{17}
	603 (10)	ν_{10}
671 ms	673 (100)	ν_6
718 vs	715 (46)	ν_5
734 vs	~740 (2)	ν_{16}
962 mw	959 (~2)	ν_4
1030 mw	1030 (~2)	ν_{15}
1364 mw	1364 (33)	ν_3
1410 mw, br	1414 (~3)	ν_{14}
2315[b] ms	2311[b] (14)	$\nu_3 + \nu_4$
2350[b] s	2342[b] (33)	ν_2
2950 mw	2948 (41)	ν_1
3023 mw	3021 (3)	ν_{13}

[a] Relative Raman intensities (0–100) are given in parentheses.
[b] The values given for $\nu_3 + \nu_4$ and ν_2 are uncorrected for Fermi resonance coupling; the corrected values are 2325, 2340 cm^{-1} for the infrared spectrum and 2320, 2332 cm^{-1} for the Raman data, respectively.

Table III. Observed Infrared and Raman Frequencies (cm^{-1}) for Solid $SbCl_5 \cdot {}^{14}NCCH_3$

Infrared (196°)	Raman (~22°)	Assignment
	13 (<1)[a]	Lattice vibrations
	19 (2)	
	23 (8)	
	32 (10)	
	35 (~6)	
	39 (~9)	
	46 (11)	
	94 (4)	ν_{21}
	135 (33)	ν_{20}
166 m	169 (11)	ν_{18}
~175 sh	~174 sh[b] (~1)	ν_7
	187 (23)	ν_{12}
219 m	211 (1)	ν_{19}
232 w	222 (1)	ν_8
	295[c] (16)	ν_{10}
	301[c] (9)	$\nu_{18} + \nu_{20}$
~341 m	344 (100)	ν_6
~352 s	348 (<30)	ν_5
	352 sh[b] (<10)	$\nu_{12} + \nu_{18}$; $2\nu_7$
	367 (~1)	ν_{16}
370 vs		
	371 (3)	
	377 (<1)	$2\nu_{12}$ (?)
	~381 (<1)	$\nu_{10} + \nu_{21}$ (?)
~386 sh (?)		?
396 w	396 (2)	ν_{17}
402 mw	402 (0)	
	477 (0)	(?)
	675 (0)	(?)
~789 w		$2\nu_{17}$
	792 (0)	
~802 vw		
948 vs	945 (1)	ν_4
1022 m	1022 (0)	ν_{15}
1353 vs	1353 (8)	ν_3
1356 m		
1398 w	1405 (0)	ν_{14}
~1415 w		$\nu_{15} + \nu_{17}$
	2252 (0)	(?)
	2267 (0)	(?)
2289[d] s	2286[d] (6)	$\nu_3 + \nu_4$
2323[d] vs	2316.5[d] (9)	ν_2
	2693 (0)	$2\nu_3$
2934 ms	2930 (18)	ν_1
~3004 w	3000 br (0)	ν_{13}

[a] Relative Raman intensities (0–100) are given in parentheses.
[b] These bands are resolved as distinguishable features only at temperatures below −10°. [c] The values given for ν_{10} and $\nu_{18} + \nu_{20}$ are uncorrected for Fermi resonance coupling; the corrected values are 297 and 299 cm^{-1}, respectively. [d] The values given for $\nu_3 + \nu_4$ and ν_2 are uncorrected for Fermi resonance coupling; the corrected values are 2303, 2309 cm^{-1} for the infrared spectrum and 2299, 2305 cm^{-1} for the Raman spectrum, respectively.

In no case do any of the fundamental frequencies show a marked temperature dependence. Therefore, the quoted infrared frequencies obtained at *ca.* −196° can be compared directly with the Raman shifts for runs at ambient temperature. In the following discussion, data for the normal isotopic molecules are given without comment or by listing the Lewis acid, while those for the isotopically substituted species are designated by listing the Lewis acid and the enriched element, *e.g.*, AsF_5-${}^{15}N$ = $AsF_5 \cdot {}^{15}NCCH_3$. Unless stated otherwise, the frequencies cited in the text are an average of the infrared and Raman data. Assignments for the eight acetonitrile fundamentals are not discussed as they follow those given previously for $SbF_5 \cdot NCCH_3$.[14]

$AsF_5 \cdot NCCH_3$: 750-500 cm^{-1}. Excluding the A_2 torsion, only five stretches and seven deformations involve the central metal atom. Displacements along the metal-halogen bonds heavily contribute to four of the stretching vibrations—the unique MX′ axial stretch [$\nu_5(A_1)$] and the three MX_4 equatorial stretches [$\nu_6(A_1)$, $\nu_{10}(B_1)$, and $\nu_{16}(E)$].

Assignments for the AsF stretching region of the arsenic pentafluoride adduct closely parallel those previously reported for $SbF_5 \cdot NCCH_3$.[14] As often observed for molecules with lighter central atoms, the four bands come at higher frequencies for the arsenic complexes than for those of antimony. For the former the A_1 vibrations are at ~716 and ~672 cm^{-1}, while for the latter they are found at ~666 and ~642 cm^{-1}. The B_1 stretch is seen only in the Raman spectra at ~604 and 598 cm^{-1}, while the E fundamental appears strongly in the infrared spectra ~733 and ~685 cm^{-1}, respectively. The corresponding Raman band appears as an extremely weak feature in the spectra of the arsenic compounds and not at all in those of the SbF_5 complexes. None of these vibrations exhibit a significant frequency shift upon acetonitrile isotopic substitution, phase change (solid to solution), or temperature.

We prefer to assign the higher frequency A_1 vibration as the axial stretch because of its greater intensity in the infrared spectra relative to that of the other A_1 mode.

$AsF_5 \cdot NCCH_3$: 400-50 cm^{-1}. The remaining eight bands associated with the central metal atom lie in this portion of the spectrum: five MX deformations (1 A_1, 1 B_1, 1 B_2, and 2 E), the N-MX_4 wag (E), and the MNC deformation (E). In addition, the inactive torsional mode A_2 probably occurs here. These assignments were by far the most difficult, even with the help of data from related $MF_5 \cdot L$ systems.[22-26] As the data for the AsF_5 complex allow a clearer understanding of this region than was possible when the spectra of $SbF_5 \cdot NCCH_3$ were initially analyzed,[14] we present some revised assignments for the latter adduct.

For the arsenic complexes, six bands (two of which are polarized) are seen in the Raman spectra, with four corresponding bands observed in the infrared spectra. The two very weak, polarized features appear at 365 and 270 cm^{-1} in the Raman solution spectra for the normal isotopic molecules (Figure 1). The band at higher frequency is assigned to the totally symmetric AsF_4 out-of-plane deformation ν_7 and is also seen as a medium strong infrared peak. The other fundamental, which probably corresponds to a weak infrared band at 281 cm^{-1}, must then be ν_8 (AsN stretch, A_1). With isotopic substitution ν_7 does not change appreciably in frequency; in contrast, ν_8 decreases to 260 cm^{-1} (AsF_5-D) and 267 cm^{-1} (AsF_5-^{15}N) in the Raman spectra with similar shifts found also in the infrared spectra.

Teller-Redlich product rule[27] calculations corroborate the assignments for the eight A_1 block frequencies. The observed ratio

$$\prod_{n=1}^{8} \left[\frac{\nu_n(AsF_5\text{-D})}{\nu_n(AsF_5\text{-H})}\right]$$

differs by less that 1% from the predicted value (0.507 *vs.* 0.504). With ^{15}N substitution the discrepancy is somewhat larger (~4%), the respective values for the observed and the theoretical ratios being 0.975 and 0.936.

The intense band at ~384 cm^{-1} in the infrared spectra, with a weak, depolarized Raman counterpart, must be of E symmetry. Because it is unaffected by isotopic substitution (Figure 1), it is unlikely to be linked to symmetry coordinates involving the metal-nitrogen bond. By elimination, this narrows the choice to either the F′-AsF_4 wag (E) or the AsF_4 deformation (E).[28-33]

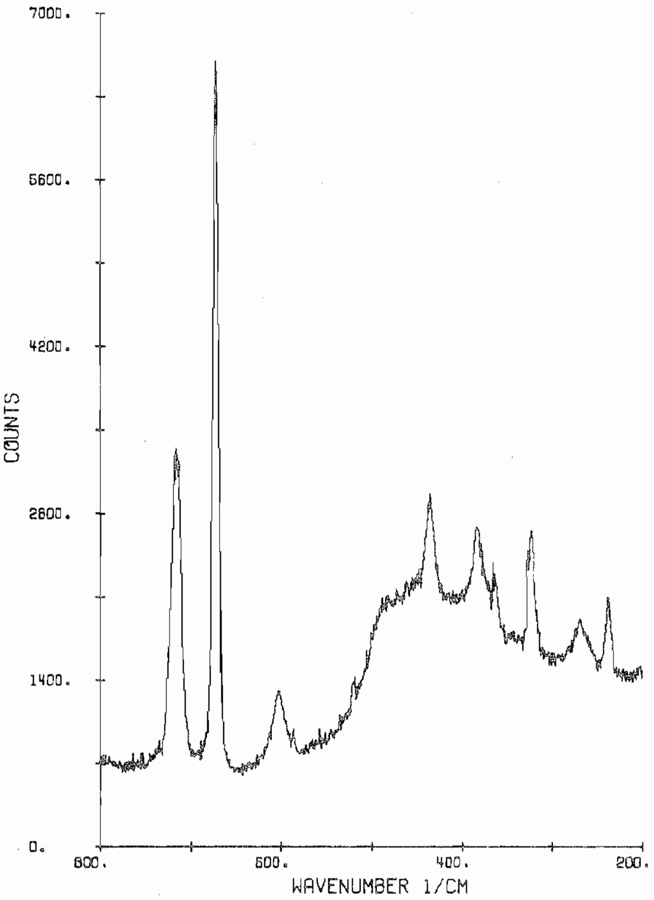

Figure 1. Raman spectrum of polycrystalline $AsF_5 \cdot {}^{14}NCCH_3$ (200–800 cm^{-1}). The broad, asymmetric band underlying the $AsF_5 \cdot N$-deformations is due to Raman scattering from the Pyrex sample tube.

The remaining weak infrared band at 324 cm^{-1} corresponds to a weak, depolarized feature in the Raman spectra. This, too, must belong to the E symmetry class. Isotopic substitution at the nitrogen produces little change in its frequency; deuteration, on the other hand, causes a decrease of 11 cm^{-1} in the Raman spectra and ~18 cm^{-1} in the infrared spectra and a corresponding increase in intensity. Since ν_8 (AsN stretch, A_1) is some 55 cm^{-1} lower in frequency, it seems implausible to assign the 324-cm^{-1} peak as ν_{19} (N-AsF_4 wag, E), and it is much too high in energy to be the AsNC deformation. The only possibility that survives is ν_{20} (AsF_4 in-plane deformation, E).

A weak, depolarized band in the Raman spectra at 240 (AsF_5-H), 232 (AsF_5-D), and 237 cm^{-1} (AsF_5-^{15}N) must be ν_{19} (N-AsF_5 wag, E), even though its infrared counterpart is not observed. It cannot be ν_{12} (AsF_4 in-plane deformation, B_2) because ν_{12} is the lone coordinate of the B_2 class and the Teller-Redlich product rule ratio for this symmetry block equals 1.000.[34] Therefore, the position of this vibration must remain constant during isotopic substitution. Likewise, it cannot be ν_{11} (AsF_4 out-of-plane deformation, B_1). The B_1 class product rule ratio is again 1.000,[34] and therefore the fact that the other member of this class, ν_{10} (~604 cm^{-1}),

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(22) SeF_5Cl: K. O. Christe, C. J. Schack, and E. C. Curtis, *Inorg. Chem.*, 11, 583 (1972).

(23) TeF_5OH: H. J. Burger, *Z. Anorg. Allg. Chem.*, 360, 97 (1968).

(24) SeF_5^-, TeF_5^-: K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, 11, 1679 (1972).

(25) IF_5O: D. F. Smith and G. M. Begun, *J. Chem. Phys.*, 45, 2001 (1965).

(26) BrF_5, IF_5: (a) G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, 42, 2236 (1963); (b) H. Selig and H. Holzman, *Isr. J. Chem.*, 7, 417 (1969).

(27) W. J. Jones in "Infra-Red Spectroscopy and Molecular Structure," M. Davies, Ed., Elsevier, Amsterdam, 1963, Chapter IV, pp 134–137.

(28) It is unclear whether δ(X′-MX_4 wag) or δ(MX_4 deformation) should be of higher energy. Christe and his coworkers assigned the former as being at higher frequency than the latter in SeF_5Cl,[22] SF_5O^-,[29] SF_5^-,[24] SeF_5^-,[24] and TeF_5^-,[24] on the basis of previous assignments for the SF_5Cl molecules by Griffiths[30] and by Woodward, *et al.*[31] Neither of these last two reports, however, give any reason for the stated preference. Adams, on the other hand, prefers the alternative assignment for $InCl_5^-$ [32] and $InCl_5(H_2O)^-$ [33] [*i.e.*, $\delta(MX_4) > \delta(X'\text{-}MX_4)$]. The choice shown in Table I is given simply as a matter of convenience.

(29) K. O. Christe, C. J. Schack, D. Pilipovich, E. C. Curtis, and W. Sawodny, *Inorg. Chem.*, 12, 620 (1973).

(30) J. E. Griffiths, *Spectrochim. Acta, Part A*, 23, 2145 (1967).

(31) L. H. Cross, H. L. Roberts, P. Goggin, and L. A. Woodward, *Trans. Faraday Soc.*, 56, 945 (1960).

(32) D. M. Adams and R. R. Smardzewski, *J. Chem. Soc. A*, 714 (1971).

(33) D. M. Adams and D. C. Newton, *J. Chem. Soc., Dalton Trans.*, 681 (1972).

(34) No translations or rotations, or vibrations involving an isotopically substituted atom, belong to either of the B symmetry classes; therefore, all of the exponents in the product rule equation[27] are zero and the product ratio becomes identically equal to 1.000.

remains constant during isotopic substitution requires ν_{11} to stay fixed also.

The only other observed band yet unassigned is a broad, medium-intensity, Raman band at ~104 cm^{-1}. Again there is no corresponding infrared peak, but isotopic frequency changes (to ~95 [AsF_5-D] and ~102 cm^{-1} [AsF_5-^{15}N]) rule out its assignment to either of the B mode deformations.[34] The alternative is ν_{21} (AsNC deformation, E), which would be expected to be of very low energy.

That ν_{11} (AsF_4 out-of-plane deformation, B_1) is not seen is understandable; this fundamental is either very weak or not observed for other $MF_5 \cdot L$ type complexes.[22-26] The absence of the B_2 deformation ν_{12} is more troubling. It is quite possible, however, that this band is accidentally degenerate with one of the other observed deformations.

The deformation region for the antimony pentafluoride adducts begins some 100 cm^{-1} lower (~290 cm^{-1})[14] than that for the arsenic systems. This time only five bands are found in the Raman spectra (two of which are polarized), while there is one, very broad, ill-defined band in the far-infrared spectra. The weak, polarized Raman band at ~290 cm^{-1} is probably ν_7 (SbF_4 out-of-plane deformation, A_1) while the very weak, polarized feature at ~277 cm^{-1} (SbF_5-H) and at ~274 cm^{-1} (SbF_5-D) may be assigned to the SbN stretch, ν_8 (A_1). A very weak, depolarized peak about 261 cm^{-1} is likely to be ν_{19}, the N-SbF_4 wag (E), since it too moves to smaller wave number values upon deuteration. A strong, broad infrared band is centered at ~267 cm^{-1} but is too poorly resolved even at −196° to aid in the assignments.

The remaining two observed Raman bands are at 183 and ~96 cm^{-1} for the normal isotopic complex. The former has a deuterium isotope shift of about −3 cm^{-1} while the latter decreases *ca.* 10 cm^{-1}. Neither of these is found in the infrared spectra; nevertheless, comparison of relative peak positions and intensities with those measured for the arsenic spectra leads to their probable assignment as ν_{20} (SbF_4 in-plane deformation, E) and ν_{21} (SbNC deformation, E).

One E mode is yet unobserved: the F′-SbF_4 wag (ν_{18}). Its absence may best be explained by assuming it to be accidentally degenerate with ν_7 (~290 cm^{-1}) and to contribute to the relative peak height of this latter band. Again the two deformations belonging to the B symmetry classes are missing from the observed spectrum. The arguments presented above for the arsenic complexes apply here with equal validity.

$SbCl_5 \cdot NCCH_3$: 425–275 cm^{-1}. The four metal-chlorine stretches (2 A_1, 1 B_1, and 1 E), as well as the CCN deformation (ν_{17}, E), belong in this portion of the spectrum of $SbCl_5 \cdot NCCH_3$. Although the molecular symmetry about the antimony approaches C_{4v}, the site group for the crystalline solid is only C_s.[12] Indeed, there is some evidence for site group splitting on the E modes; overall, however, the assignments bear out a C_{4v} local symmetry approximation rather well.

Spectral data for a number of antimony pentachloride complexes exist in the literature including $SbCl_5 \cdot CH_3NO_2$,[10] $SbCl_5 \cdot$DMF,[11] $SbCl_5 \cdot$DMSO,[11] $SbCl_5 \cdot H_2O$,[11] and $SbCl_5 \cdot NCCl$,[13] as well as $SbCl_5 \cdot NCCH_3$.[13] None of these gives a complete spectrum and of the few assignments attempted, several appear to be in error.

More helpful, particularly for the deformation region to be discussed shortly, are very detailed vibrational studies for $InCl_5^-$,[32,35] $TlCl_5^-$,[36,37] $M(NO)Cl_5^-$,[38] and $M(CO)Cl_5^-$ [39] [where M = Os, Ru, Ir, or Rh]. Reports concerning $InCl_5(H_2O)^-$,[33] $NbCl_5 \cdot NCCH_3$,[40] $NbCl_5Br^-$,[41] and $TaCl_5Br^-$ [41] were also consulted.

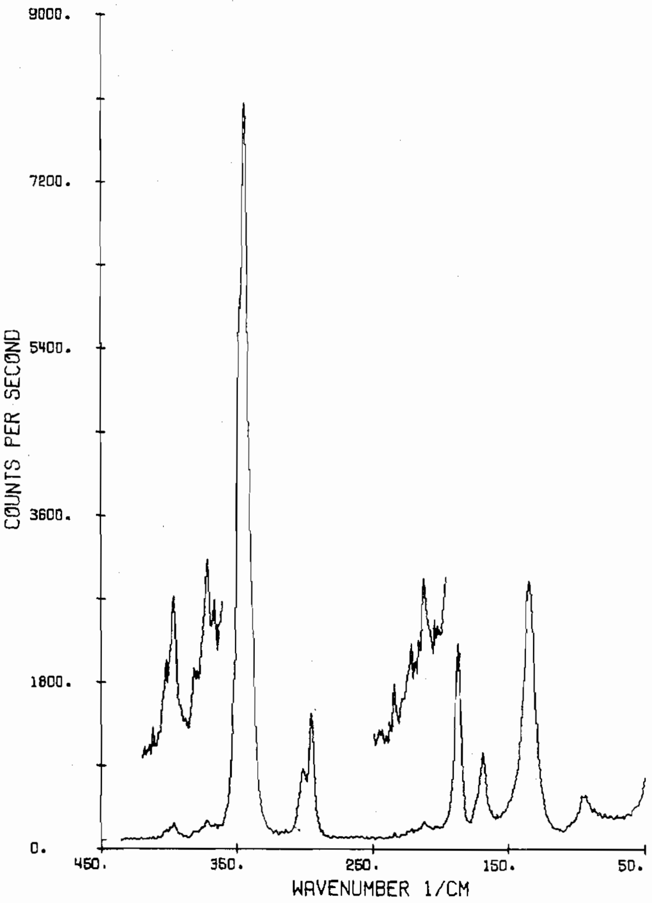

Figure 2. Raman spectrum of polycrystalline $SbCl_5 \cdot {}^{14}NCCH_3$ (50–450 cm^{-1}). Several very weak features are shown at 10 times the normal ordinate expansion.

As with the fluoride complexes, there are two very strong Raman bands, which in this instance are at 344 and 348 cm^{-1} (Figure 2) and logically belong to ν_5 (SbCl′ axial stretch, A_1) and ν_6 ($SbCl_4$ equatorial stretch, A_1). The corresponding infrared bands for the solid are slightly displaced to 340 and 350 cm^{-1}. Solution data reveal two polarized bands: one at 340 cm^{-1} is very strong; the other is medium weak and broad and is centered at 361 cm^{-1}.

The very strong infrared fundamental at 370 cm^{-1} has a weak Raman analog about 371 cm^{-1} and must be of E symmetry. Deuteration results in small (~2 cm^{-1}) positive frequency shifts. Clearly, then, it is not the CCN deformation but must be ν_{16} ($SbCl_4$ equatorial stretch, E). Site group splitting may be responsible for a somewhat weaker Raman feature about 367 cm^{-1}. The CCN deformation, ν_{17} (E), appears at 399 cm^{-1} for the normal molecule and shifts to 368 cm^{-1} upon deuteration. Again there is evidence of site group splitting in the solid-phase spectra of the normal isotopic molecule: two bands are seen in both the Raman and the infrared spectra at ~395 and 401.5 cm^{-1}.

(35) S. R. Leone, B. Swanson, and D. F. Shriver, *Inorg. Chem.*, 9, 2189 (1970).

(36) D. F. Shriver and I. Wharf, *Inorg. Chem.*, 8, 2167 (1969).

(37) G. Joy, A. Gaughan, I. Wharf, D. F. Shriver, and J. P. Dougherty, submitted for publication.

(38) M. J. Cleare, H. P. Fritz, and W. P. Griffith, *Spectrochim. Acta, Part A*, 28, 2013 (1972).

(39) M. J. Cleare, H. P. Fritz, and W. P. Griffith, *Spectrochim. Acta, Part A*, 28, 2019 (1972).

(40) G. A. Ozin and R. A. Walton, *J. Chem. Soc. A*, 2236 (1970).

(41) G. A. Ozin, G. W. A. Fowles, D. J. Tidmarsh, and R. A. Walton, *J. Chem. Soc. A*, 642 (1969).

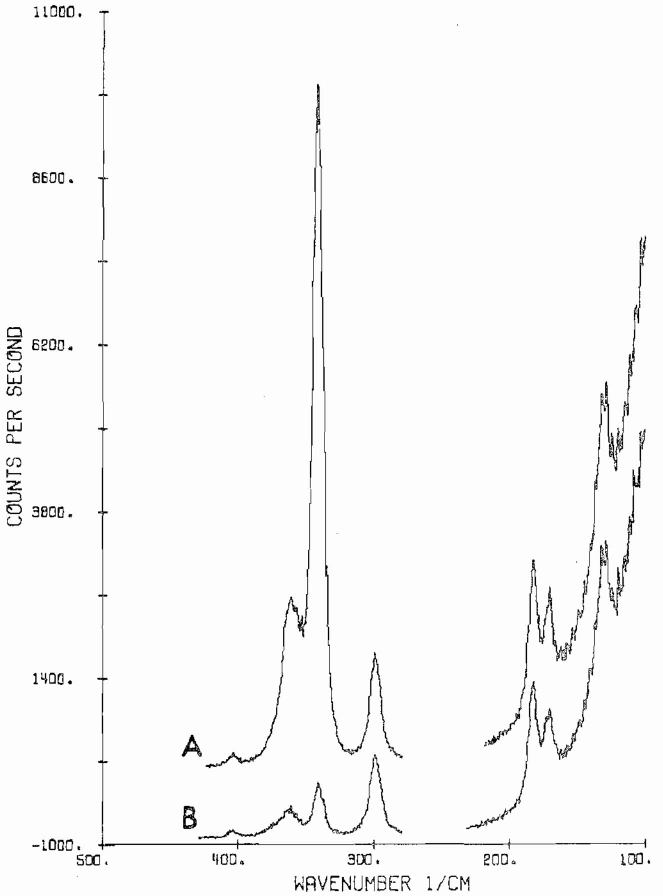

Figure 3. Raman spectra of a solution of $SbCl_5 \cdot {}^{14}NCCH_3$ in liquid SO_2 (100–500 cm^{-1}). For A, the electric vector of the incident beam was perpendicular to the direction in which the scattered light was observed; for B, the electric vector of the incident beam was parallel to the direction in which the scattered light was observed.

Two moderately weak features at 295 and 300 cm^{-1} in the Raman spectrum of the solid (Figure 2) remain to be discussed. Solution spectra (Figure 3) reveal only a single, depolarized band of comparable intensity at 299 cm^{-1}. Because of the absence of any infrared bands between 330 and 240 cm^{-1}, these must belong to one of the B classes. In particular, one must be the B_1 $SbCl_4$ equatorial stretch (ν_{10}). The origin of the weaker vibration in the solid phase at 301 cm^{-1} may perhaps be traced to the $\nu_{18} + \nu_{20}$ combination[42] (the Cl'-$SbCl_4$ wag and the $SbCl_4$ in-plane deformation, both class E). Its unusual intensity is the result of Fermi resonance coupling with ν_{10}. After the usual corrections,[43] the values for the fundamental and the combination band are 297 and 299 cm^{-1}, respectively. Why the second band is missing from the solution spectra remains uncertain. Perhaps it lies close enough to ν_{10} so as not to be resolved as a separate peak. That ν_{20} decreases about 4 cm^{-1} in frequency upon dissolution lends credence to such an assumption.

$SbCl_5 \cdot NCCH_3$: 275–200 cm^{-1}. Two very weak peaks appear in the Raman spectra of the solid at 211 and 222 cm^{-1} ($SbCl_5$-H). Deuteration causes a drop to lower wave number (205 and 215 cm^{-1}, respectively). The matching room-temperature infrared vibrations manifest themselves at somewhat higher frequency (~215 and ~223 cm^{-1}), the former being moderately intense while the latter is weaker and less well resolved. Although no depolarization ratios are available (these bands being too weak to be seen in solution spectra), on the basis of the isotopic shifts, it is reasonable to attribute them respectively to ν_{19} (N-$SbCl_4$ wag, E) and ν_8 (SbN stretch, A_1). This choice gives an A_1 block Teller-Redlich product rule ratio of 0.509, compared to a theoretical value of 0.503, for an error of just over 1%. Also, as expected for smaller, less polarizable elements such as nitrogen, the relative Raman intensities for these two bands are of the same order of magnitude as those of the acetonitrile modes and are very much weaker than most of the antimony-chlorine vibrations.

One striking feature of these two fundamentals is the conspicuous temperature dependence. The E mode drops about 3 cm^{-1} per 100°K dip in temperature, and the symmetric stretch decreases almost 5 cm^{-1} in the same interval.

$SbCl_5 \cdot NCCH_3$: 200–10 cm^{-1}. The five SbCl deformations (1 A_1, 1 B_1, 1 B_2, and 2 E) and the SbNC deformation (E) should all be found below 200 cm^{-1}. Of the three bands actually observed in this region of the solution spectra none were polarized (Figure 3). Two other vibrations were seen only for the solid. The weak, depolarized Raman band at 170 cm^{-1} is paired with a medium-strong infrared fundamental at 166 cm^{-1} and must be one of the two E type SbCl deformations (ν_{18} or ν_{20}). A nearby shoulder (~175 cm^{-1}) in both techniques is of either E or A_1 symmetry. (The Raman feature was resolved only at temperatures below −10° in the spectrum of the solid.) Because of its relative intensity and its proximity to the previously assigned E mode, we felt it likely to be ν_7 ($SbCl_4$ out-of-plane deformation, A_1).

Of the three remaining bands, only the one at ~94 cm^{-1} in the solid-phase Raman (Figure 2) could be given a reasonably sure assignment. Its disposition as the SbNC deformation (ν_{21}, E) agrees quite well with previous assignments for the equivalent coordinates in $AsF_5 \cdot NCCH_3$ and $SbF_5 \cdot NCCH_3$. That a decrease of ~8 cm^{-1} was observed for the deuterated analog lends further support to this interpretation.

Three coordinates are left for which to account, but only two bands have not yet been assigned. These two features at 187 and 135 cm^{-1} are found only in the Raman spectra and are depolarized. Since the two B class deformations are assigned to higher frequencies than the A_1 or E modes for the thoroughly studied $InCl_5^{\,-}$ [32,35] ion (C_{4v}), one can reasonably hypothesize that the 187-cm^{-1} band is ν_{12} ($SbCl_4$ in-plane deformation, B_2) while the 135-cm^{-1} vibration is the remaining E mode (ν_{20}). This latter choice is in accord with the earlier assumption that the Raman shift at 300 cm^{-1} is a combination band of the fundamentals at 170 and 135 cm^{-1} in Fermi resonance with ν_{10} (B_1) at 295 cm^{-1}. As argued previously, ν_{11} ($SbCl_4$ out-of-plane deformation, B_1) is probably too weak to be discerned.

Seven other features, all of which shift with temperature, appear in the solid-phase Raman spectra between 10 and 50 cm^{-1}. They are assigned as lattice vibrations.

Discussion

The results of this vibrational spectroscopic investigation of the acetonitrile adducts of arsenic pentafluoride and antimony pentachloride, together with those of the previously reported antimony pentafluoride complex,[14] provide the most comprehensive set of data and assignments now available for any $MX_5 \cdot L$ type complex of a group Va metal pentahalide. As expected, the data are in accord with simple molecular complexes having approximately C_{4v} symmetry at the central metal atom. All eight predicted A_1 class fundamentals were located as polarized bands in the Raman solution spectra of

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(42) For C_{4v} symmetry, the combination of these two modes results in $A_1 + A_2 + B_1 + B_2$.

(43) J. Overend, ref 27, Chapter X, pp 350–353.

the fluoride systems. Although the ν_7 and ν_8 (A_1) bands were imperceptible in the solution spectra of $SbCl_5 \cdot NCCH_3$, they were successfully assigned to weak features in the solid-phase spectra. Based on these data, a vibrational analysis yielded the A_1 block symmetry force constants for each of these systems of complexes (Table VII and Appendix).

The most significant changes in the acetonitrile portion of these molecules after complex formation are associated with ν_2 (CN stretch, A_1), ν_4 (CC stretch, A_1), and ν_{17} (CCN deformation, E). All of these move to higher frequencies, their values generally following the trend $\nu(AsF_5 \cdot L) > \nu(SbF_5 \cdot L) > \nu(SbCl_5 \cdot L) > \nu(L)$ where L = acetonitrile. The k_{CN} ($=F_{22}$) force constants conform to the same pattern (Table VII), free acetonitrile trailing the others with a value of 17.4 ± 0.8 mdyn/Å.[44] Because results on the acetonitrile portion are ancillary to the central theme of this project, readers desiring further discussion of these matters should refer to Swanson and Shriver's comments on the $BX_3 \cdot NCCH_3$ molecules [X = F, Cl, or Br].[16,45]

Of particular importance are the observed trends in the frequencies and force constants of the metal-nitrogen stretch. The general order for both is $SbF_5 \cdot L \sim AsF_5 \cdot L > SbCl_5 \cdot L$ (L = acetonitrile). The calculated force constants for the fluoride species are equal (~1.9 mdyn/Å) within statistical error, even though the antimony adduct exhibits a slightly higher frequency. By contrast, the value for the antimony pentachloride complex is significantly smaller ($k_{SbN} = 1.1$ mdyn/Å). The trend toward a higher N–Sb force constant for SbF_5 than for $SbCl_5$ adducts is exactly opposite that of the acetonitrile boron trihalides where k_{B-N} is greater for the BCl_3 than the BF_3 adduct.[16]

Upon adduct formation, BF_3 is distorted from a planar to a pyramidal geometry, and as this distortion is increased, MO calculations show that the acceptor orbital of BF_3 decreases smoothly in energy.[16] This energy decrease, which corresponds to greater acceptor strength, occurs from increased s character in the vacant orbital and from decreased π-antibonding character as the B–F π bonding is reduced by the angular distortion.[46] Even with tetrahedral bond angles around boron, the π donation from F to B may interfere with σ donation from the lone pair of an added Lewis base.[47] The pπ–pπ boron-halogen interaction is stronger for the two second-period elements boron and fluorine than for boron and chlorine. Therefore, resistance to distortion and competing π bonding will be greater for BF_3 than BCl_3, making BF_3 the poorer electron acceptor.

In contrast with boron acceptors, pπ–pπ bonding to the halide should be much less important with fourth- and fifth-period acceptors such as As and Sb. Also, involvement of d orbitals in the bonds of these heavy elements will tend to reduce the influence of halogen-metal π bonding even further, because pπ–dπ bonds, which involve the d_{xz}, d_{yz}, and d_{xy} orbitals, are orthogonal to the remaining d orbitals, which are involved in σ bonding. It is therefore reasonable that the strengths of donor-acceptor bonds formed by SbX_5 will be dominated by the electronegativity of the halides and not by the effects of π bonding which appear to determine relative acceptor strengths of the boron halides.

Interestingly, the SbN and AsN stretching force constants are equal within experimental error for the pentafluoride-acetonitrile adducts, indicating that the donor-acceptor bond energy is nearly the same for both. Even on the basis of reported chemical properties, no distinct difference between the relative strengths of the two Lewis acids may be discerned.

The other key aspect of this study of these group Va acetonitrile adducts lay in the detection of recognizable, systematic patterns characteristic of such $MX_5 \cdot L$ complexes. As with other such species of C_{4v} symmetry[10,11,13,22-26,29-33,35-41] the metal-halogen stretch region appears to be the most symptomatic. In general, one finds two strong, polarized Raman bands as well as a weak, depolarized peak some 40-65 cm^{-1} lower in frequency. The infrared spectra in the same region have three medium to very strong bands. In the infrared spectra the highest frequency feature is very strong and is found 15-25 cm^{-1} above its nearest neighbors. (Upon occasion a weak Raman feature is observed at this same frequency.) The two lower energy infrared bands are usually of strong to medium intensity and closely correspond to the polarized Raman vibrations.

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Appendix. Calculation of the A_1 Block Force Constants for $AsF_5 \cdot NCCH_3$, $SbF_5 \cdot NCCH_3$, and $SbCl_5 \cdot NCCH_3$

The A_1 block symmetry force constants for the acetoni-

Table IV. Molecular Parameters and Internal Coordinates for $MX_5 \cdot NCCH_3$ (M = As or Sb; X = F or Cl)

Bond Lengths, Å

r	C–H	1.102[a]	R	M–X	1.64 (MX = AsF)[d]
d	C–C	1.46[b]			1.85 (MX = SbF)[e]
D	C≡N	1.18[b]	l	M–X′	2.36 (MX = SbCl)[b]
L	M–N	2.02 (M = As)[c]			
		2.23 (M = Sb)[b]			

Bond Angles,[f] deg

α	HCH	109.47	γ	NMX	90.0
β	CCH	109.47	δ	XMX	90.0
ϵ	CCN	180.0	ζ	XMX′	90.0
ρ	MNC	180.0			

A_1 Block Symmetry Coordinates

$$S_1 = (1/\sqrt{3})(\Delta r_1 + \Delta r_2 + \Delta r_3)$$
$$S_2 = \Delta D$$
$$S_3 = (1/\sqrt{n})[m(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) - (\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)]^g$$
$$S_4 = \Delta d$$
$$S_5 = \Delta l$$
$$S_6 = (1/2)(\Delta R_1 + \Delta R_2 + \Delta R_3 + \Delta R_4)$$
$$S_7 = (1/2\sqrt{2})[(\Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3 + \Delta\gamma_4) - (\Delta\zeta_1 + \Delta\zeta_2 + \Delta\zeta_3 + \Delta\zeta_4)]$$
$$S_8 = \Delta L$$
$$S_R = (1/\sqrt{n})[m(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) + (\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)]^g$$
$$S_{R'} = (1/2\sqrt{2})[(\Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3 + \Delta\gamma_4) + (\Delta\zeta_1 + \Delta\zeta_2 + \Delta\zeta_3 + \Delta\zeta_4)]$$
$$S_{R''} = (1/2)(\Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3 + \Delta\delta_4)$$

[a] Average values from $NCCH_3$: C. C. Costain, *J. Chem. Phys.*, 29, 864 (1958). [b] Average values from $SbCl_5 \cdot NCCH_3$.[12] [c] The observed difference between r(Sb–F) and r(As–F) is 0.21 Å and is in close agreement with Pauling's estimates: L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 224. [d] Average values from $ClF_3 \cdot AsF_5$: H. Lynton and J. Passmore, *Can. J. Chem.*, 49, 2539 (1971). [e] Average values from $SbF_5 \cdot SO_2$[49] and $[XeF_3^+][Sb_2F_{11}^-]$ for terminal r(Sb–F): D. E. McKee, A. Zalkin, and N. Bartlett, *Inorg. Chem.*, 12, 1713 (1973). [f] Idealized to highest possible symmetry. [g] $m = -\sqrt{3} \cdot \cos\beta/\cos(\alpha/2)$; $n = 3(m^2 + 1)$. When $\alpha = \beta = 109.47°$ (*i.e.*, the tetrahedral angle), $m = 1$ and $n = 6$.

(44) B. I. Swanson, Ph.D. Dissertation, Northwestern University, 1970, Appendix A.

(45) B. Swanson and D. F. Shriver, *Inorg. Chem.*, 9, 1406 (1970).

(46) The F–B–F angle in a complex is not necessarily 109° because the degree of BF_3 distortion is expected to vary from one donor to the next, with strong donors leading to F–B–F nearer the tetrahedral value.

(47) D. G. Brown, R. S. Drago, and T. F. Bolles, *J. Amer. Chem. Soc.*, 90, 5706 (1968).

Table V. Observed and Calculated A_1 Block Frequencies for Three Isotopic Varieties of $AsF_5 \cdot NCCH_3$ (cm^{-1})

	$AsF_5 \cdot {}^{14}NCCH_3$			$AsF_5 \cdot {}^{14}NCCD_3$			$AsF_5 \cdot {}^{15}NCCH_3$		
Assignment	Obsd	Calcd	Δ[a]	Obsd	Calcd	Δ	Obsd	Calcd	Δ
ν_1 (CH_3 str)	2947.8	2946.2	1.6	2114.9	2118.9	−4.0	2947.5	2946.2	1.3
ν_2 (CN str)	2332.3[b]	2335.7	−3.4	2338.6	2338.7	−0.1	2308.0[b]	2304.3	3.7
ν_3 (CH_3 def)	1363.8	1364.9	−1.1	1097.0	1094.2	2.8	1363.9	1364.9	−1.0
ν_4 (CC str)	962.1	964.2	−2.1	878.5	875.0	3.5	952.6	953.6	−1.0
ν_5 (AsF′ str)	715.0	715.5	−0.5	715.0	714.7	0.3	715.8	715.5	0.3
ν_6 (AsF_4 str)	673.3	673.3	−0.0	673.0	673.3	−0.3	673.7	673.3	0.4
ν_7 (AsF_4 def)	364.6	364.8	−0.2	363.1	362.0	1.1	363.5	364.4	−0.9
ν_8 (AsN str)	270.3	269.0	1.3	259.7	261.1	−1.4	267.2	267.3	−0.1

[a] The average deviation is 1.4 cm^{-1} for the three molecules [$\Delta = \nu(\text{obsd}) - \nu(\text{calcd})$]. [b] The values given for ν_2 of $AsF_5 \cdot {}^{14}NCCH_3$ and $AsF_5 \cdot {}^{15}NCCH_3$ have been corrected for Fermi resonance with $\nu_3 + \nu_4$.

Table VI. Observed and Calculated A_1 Block Frequencies for Two Isotopic Varieties of $SbF_5 \cdot NCCH_3$ and $SbCl_5 \cdot NCCH_3$ (cm^{-1})

	$SbF_5 \cdot {}^{14}NCCH_3$			$SbF_5 \cdot {}^{14}NCCD_3$			$SbCl_5 \cdot {}^{14}NCCH_3$			$SbCl_5 \cdot {}^{14}NCCD_3$		
	Obsd	Calcd	Δ[a]	Obsd	Calcd	Δ	Obsd	Calcd	Δ[c]	Obsd	Calcd	Δ
ν_1 (CH_3 str)	2948.0	2944.7	3.3	2113.0	2117.7	−4.7	2930.1	2929.2	0.9	2104.7	2106.3	−1.6
ν_2 (CN str)	2329.0[b]	2330.2	−1.2	2335.0	2333.6	1.4	2304.5[b]	2307.1	−2.6	2312.9	2311.0	1.9
ν_3 (CH_3 def)	1364.0	1365.3	−1.3	1099.0	1097.6	1.4	1353.3	1355.6	−2.3	1093.6	1093.5	0.1
ν_4 (CC str)	965.0	966.8	−1.8	877.0	874.1	2.9	944.5	947.4	−2.9	856.3	850.2	6.1
ν_5 (SbX′ str)	663.0	664.1	−1.1	665.0	664.0	1.0	348.5	348.4	0.1	347.9	348.0	−0.1
ν_6 (SbX_4 str)	641.0	641.0	0.0	641.0	641.0	0.0	344.0	344.3	−0.3	344.7	344.3	0.4
ν_7 (SbX_4 def)	290.0	292.6	−2.6	289.0	288.1	0.9	173.5	173.8	−0.3	173.0	172.6	0.4
ν_8 (SbN str)	277.0	278.3	−1.3	274.0	271.8	2.2	221.6	222.1	−0.5	215.7	215.9	−0.2

[a] The average deviation is 1.7 cm^{-1} for $SbF_5 \cdot {}^{14}NCCH_3$ and $SbF_5 \cdot {}^{14}NCCD_3$ [$\Delta = \nu(\text{obsd}) - \nu(\text{calcd})$]. [b] The values given for ν_2 of $SbF_5 \cdot {}^{14}NCCH_3$ and $SbCl_5 \cdot {}^{14}NCCH_3$ have been corrected for Fermi resonance with $\nu_3 + \nu_4$. [c] The average deviation is 1.3 cm^{-1} for $SbCl_5 \cdot {}^{14}NCCH_3$ and $SbCl_5 \cdot {}^{14}NCCD_3$.

trile complexes of AsF_5, SbF_5, and $SbCl_5$ were calculated using the iterative least-squares program FPERT and the associated program GMAT (both locally modified).[48] The individual eigenvalues were weighted as $w_i = 1/\lambda_i$.

Molecular parameters used to calculate the G matrix are summarized in Table IV and were estimated from several sources. Since the angles ClSbCl = 89°, ClSbCl′ = 95°, and NSbCl = 85° for $SbCl_5 \cdot NCCH_3$[12] and FSbF = 87.5°, FSbF′ = 94.4°, and NSbF = 85.6° for $SbF_5 \cdot SO_2$[49] are all within 5° of being perpendicular, the 12 angles about the metal were taken to be 90° for all three adduct systems. In addition, the MNC and CCN angles were set equal to 180° while all the CCH and HCH angles were idealized as being tetrahedral.

Tables V and VI summarize the observed frequencies which were used for these force constant calculations. Raman data for the solids were the choice throughout except in the four instances. Infrared values were used for ν_4 for the AsF_5 species and for ν_1, ν_2, and ν_4 for the SbF_5 adducts.

As with most large molecules, insufficient data preclude an unconstrained general valence force field (GVFF) analysis. Therefore, for the first approximation just two interaction constants (F_{28} and F_{34}) and the eight primary constants were given nonzero values, and only the four primary constants involving the MX_5-N- vibrations were refined. The initial values for the acetonitrile constants, including F_{28} and F_{34}, were transferred from those for $BF_3 \cdot NCCH_3$;[45] those for AsF_5-N- were estimated from SeF_5Cl,[11] and those for SbF_5-N- were scaled from the previous values for the AsF_5-N- constants by assuming that $k(TeF_5^-)/k(SeF_5^-)$ is proportional to $k(SbF_5 \cdot NCCH_3)/k(AsF_5 \cdot NCCH_3)$.[24] Estimated constants for $SbCl_5$-N- were obtained from $SbCl_6^-$ [50] using a transference scheme analogous to that proposed by Ozin for relating $k(NbCl_5Br^-)$ to $k(NbCl_6^-)$.[41]

In the final refinement, both F_{78} and F_{34} were allowed to refine simultaneously with all eight primary constants to achieve the values summarized in Table VII. An attempt also to include F_{28} in the refinement of the $AsF_5 \cdot NCCH_3$ data failed. Earlier calculations in which F_{78} was the only unconstrained interaction constant gave a reasonable fit for the observed and calculated frequency parameters but resulted in an unacceptable potential energy distribution (PED) for ν_7 and ν_8 of the $AsF_5 \cdot NCCH_3$ complexes. The predominant contributor in these cases for these frequencies was S_8 and S_7, respectively. The addition of F_{34} brought an immediate change; the PED's now showed the predominant contributor in each case (except for the deuterated molecule, $SbF_5 \cdot NCCH_3$) to be the symmetry coordinate previously assigned to that frequency.

Large uncertainties in the exact frequency value for ν_8 of $SbF_5 \cdot NCCH_3$, which appears in the Raman spectrum as an unresolved shoulder, may help account for the discrepancy in the PED for ν_7 and ν_8 in this particular case.[51] Another contributing factor may be that ν_7 and ν_8 lie very close in energy to one another and are heavily mixed.

A variety of numerical experiments were performed to test the significance of the similar force constants for k_{AsN} and k_{SbN}. For both molecules it was found that a small deterioration in overall fit and in the fitted isotopic shifts was obtained by fixing F_{88} at a variety of values above and below 1.88 mdyn/Å. Therefore, within the calculated statistical uncertainty of *ca.* ±0.2 mdyn/Å, the As-N and Sb-N force constants are indistinguishable. The final fit between the observed and calculated frequency parameters is pre-

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(48) (a) R. G. Snyder and J. H. Schactschneider, *Spectrochim. Acta*, 19, 85 (1963). (b) Programs GMAT and FPERT are described more fully by J. H. Schactschneider, "Vibrational Analyses of Polyatomic Molecules," Parts V and VI, Technical Reports 231-64 and 57-65, Shell Development Co., Emeryville, Calif., 1964 and 1965.

(49) (a) J. W. Moore, H. W. Baird, and H. B. Miller, *J. Amer. Chem. Soc.*, 90, 1358 (1968); (b) J. W. Moore, H. W. Baird, and H. B. Miller, unpublished X-ray data.

(50) P. Labonville, J. R. Ferraro, M. C. Wall, S. M. C., and L. G. Basile, *Coord. Chem. Rev.*, 7, 257 (1972).

(51) This same kind of phenomenon was observed for the analogous symmetry coordinates (the BN stretch and the BF_3 deformation) for $BF_3 \cdot NCCH_3$.[16]

Table VII. A_1 Block Symmetry Force Constants

	$AsF_5 \cdot NCCH_3$	$SbF_5 \cdot NCCH_3$	$SbCl_5 \cdot NCCH_3$
F_{11}[a]	4.994 (5)[b]	4.99 (1)	4.936 (8)
F_{22}	18.38 (3)	18.26 (6)	18.00 (4)
F_{33}	0.584 (3)	0.583 (6)	0.570 (2)
F_{44}	5.27 (8)	5.32 (5)	5.30 (3)
F_{55}	4.34 (2)	4.20 (4)	1.78 (2)
F_{66}	5.07 (2)	4.60 (4)	2.48 (3)
F_{77}	1.00 (12)	1.08 (4)	1.08 (3)
F_{88}	1.87 (25)	1.88 (8)	1.09 (2)
F_{28}	−0.25[c]	−0.25[c]	−0.25[c]
F_{34}	−0.41 (2)	−0.41 (1)	−0.38[c]
F_{78}	0.10 (6)	0.34 (2)	0.17 (22)

[a] The subscripts identify F_{kl} with the corresponding symmetry coordinates k and l defined in Table IV. Force constants F_{33} and F_{77} are in units of mdyn Å/radian^2 while F_{34} and F_{78} are in units of mdyn/radian. All other force constants are in units of mdyn/Å.
[b] Least-squares standard deviations, given in parentheses, represent the deviation in the last decimal place(s) of a given force constant.
[c] These force constants were constrained during refinement. The other 25 unlisted force constants were constrained to zero.

Table VIII. Potential Energy Distribution[a]

	$AsF_5 \cdot NCCH_3$	$SbCl_5 \cdot NCCH_3$
ν_1	100% V_{11}	99% V_{11}
ν_2	87% V_{22} + 10% V_{44}	87% V_{22} + 11% V_{44}
ν_3	105% V_{33} + 8% V_{44} − 13% V_{34}	104% V_{33} + 8% V_{44} − 13% V_{34}
ν_4	7% V_{22} + 82% V_{44} + 9% V_{88}	8% V_{22} + 83% V_{44}
ν_5	93% V_{55}	85% V_{55} + 9% V_{77} + 8% V_{88}
ν_6	100% V_{66}	100% V_{66}
ν_7	7% V_{55} + 64% V_{77} + 32% V_{88} − 7% V_{78}	11% V_{55} + 7% V_{77} + 85% V_{88} − 8% V_{78}
ν_8	32% V_{77} + 56% V_{88} + 6% V_{78}	86% V_{77} + 6% V_{78}

[a] Contributions less than 6% have been omitted.

sented in Tables V and VI. The PED's presented in Table VIII for $AsF_5 \cdot NCCH_3$ hold approximately for $SbF_5 \cdot NCCH_3$, while those for $SbCl_5 \cdot NCCH_3$ are significantly different.

Registry No. $AsF_5 \cdot NCCH_3$, 17632-27-8; $SbF_5 \cdot NCCH_3$, 19106-78-6; $SbCl_5 \cdot NCCH_3$, 19106-78-6.

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Amide and Fluoroxy Derivatives of *N*-Perfluoroacylhexafluoroisopropylidenimines

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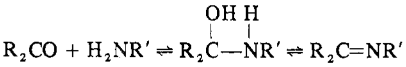
$LiN{=}C(CF_3)_2$ readily undergoes metathetical reactions with perfluoroacyl halides to give perfluoroacylimines. The new acylimines, $R_fC(O)N{=}C(CF_3)_2$ ($R_f = CF_3, C_2F_5$), are susceptible to polar addition of XY (XY = HF, HCl, ClF) across the C=N bond to yield the corresponding secondary and tertiary amides, $R_fC(O)NXCY(CF_3)_2$. Direct fluorination of $CF_3C(O)N{=}C(CF_3)_2$ under catalytic conditions produces a fluoroamide, $CF_3C(O)NFCF(CF_3)_2$, from saturation of the C=N function and a fluoroxy compound $CF_3CF(OF)NFCF(CF_3)_2$ from further addition across the C=O bond.

The acid-catalyzed reaction of aldehydes or ketones with amines has been the most commonly used preparation as a direct one-step route to imines.



$$R_2CO + H_2NR' \rightleftharpoons R_2\overset{OH}{\overset{|}{C}}-\overset{H}{\overset{|}{N}}R' \rightleftharpoons R_2C{=}NR'$$

Middleton and Krespan[1] employed this facile one-step procedure in the synthesis of hexafluoroisopropylidenimine, $(CF_3)_2C{=}NH$,[2] and the electrophilic nature of the C=N[1-11] link has been thoroughly elucidated. The electron-withdrawing substituents (CF_3) on the imine carbon enhance the electrophilicity of the C=N bond making it very susceptible to nucleophilic attack. Reactive carbon–nitrogen multiple bonds, however, are not limited to imines as is demonstrated by nucleophilic additions to polar isocyanates ($R{-}N{=}C{=}O \leftrightarrow R{-}N^{\delta-}{-}C^{\delta+}{=}O$)[12,13] and nitriles ($R{-}C{\equiv}N \leftrightarrow R{-}C^{\delta+}{=}N^{\delta-}$).[14,15] Though other polar carbon–nitrogen multiple bonds are electrophilic also, the imine usually is much more susceptible to addition. Generalized addition to carbon–nitrogen multiple-bond linkages has been illustrated by the reaction of chlorine monofluoride when it reacted as a chlorofluorinating agent.[11,14,16,17] Although studies involving nucleophilic or polar addition have been prevalent in recent years, it is noteworthy that a number of papers have appeared dealing with the direct fluorination of carbon–nitrogen multiple bonds.[5,18-20]

(1) W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).
(2) Y. V. Zeifman, N. P. Gambaryan, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, 153, 1334 (1963).
(3) Y. V. Zeifman, N. P. Gambaryan, and I. L. Knunyants, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1431 (1965).
(4) C. G. Krespan and W. J. Middleton, *Fluorine Chem. Rev.*, 1, 145 (1967).
(5) J. K. Ruff, *J. Org. Chem.*, 32, 1675 (1967).
(6) D. M. Gale and C. G. Krespan, *J. Org. Chem.*, 33, 1002 (1968).
(7) O. Glemser and S. P. von Halasz, *Chem. Ber.*, 102, 3333 (1969).
(8) K. Niedenzu, K. R. Blick, and C. D. Miller, *Inorg. Chem.*, 9, 975 (1970).
(9) K. Niedenzu, C. D. Miller, and F. C. Nahm, *Tetrahedron Lett.*, 28, 2441 (1970).
(10) S. P. von Halasz and O. Glemser, *Chem. Ber.*, 103, 553 (1970).
(11) R. F. Swindell, L. M. Zaborowski, and J. M. Shreeve, *Inorg. Chem.*, 10, 1635 (1971).
(12) S. Ozaki, *Chem. Rev.*, 72, 457 (1972).
(13) G. H. Sprenger, K. J. Wright, and J. M. Shreeve, *Inorg. Chem.*, 12, 2890 (1973).
(14) J. B. Hynes and T. E. Austin, *Inorg. Chem.*, 5, 488 (1966).
(15) P. H. Ogden, *J. Org. Chem.*, 33, 2518 (1968).
(16) D. D. Moldavskii and V. G. Temchenko, *J. Gen. Chem. USSR*, 39, 1362 (1969).
(17) D. E. Young, L. R. Anderson, and W. B. Fox, *Chem. Commun.*, 7, 395 (1970).
(18) B. C. Bishop, J. B. Hynes, and L. A. Bigelow, *J. Amer. Chem. Soc.*, 85, 1606 (1963).
(19) B. C. Bishop, J. B. Hynes, and L. A. Bigelow, *J. Amer. Chem. Soc.*, 86, 1827 (1964).
(20) J. B. Hynes, B. C. Bishop, P. Bandyopadhyay, and L. A. Bigelow, *J. Amer. Chem. Soc.*, 85, 83 (1963).