Considering only the cations to form hydrated species, the competitive equilibria may be written

$$Cd^{2+} + nH_2O \rightleftarrows Cd(H_2O)_n^{2+} \quad K_H$$

$$Cd^{2+} + Br^- \rightleftarrows CdBr^+ \quad K_{10}$$

The latter equilibrium constant is derived from the association of the solutes in the anhydrous molten salt solvent. The measured equilibrium constant in the hydrous melt may thus be written

$$\frac{1}{K_1} = \frac{([Cd^{2+}] + [Cd(H_2O)_n^{2+}])[Br^-]}{[CdBr^+]}$$

$$= \frac{1}{K_{10}} + \frac{K_H}{K_{10}} a_{H_2O}{}^n$$

The analogy between this equation and that of the quasilattice model is apparent and not surprising, since the latter also corresponds to the mass action principle, applied to bonds on the quasilattice. The left-hand curve in Figure 2 shows a plot of the reciprocal equilibrium constants *vs.* the square of the activity of water. The water activities were obtained from our previously reported isopiestic measurements[4,11] and from earlier measurements by Ewing.[31] The slope of this plot gives the ratio of the equilibrium constants for hydration and association, leading to the value for the hydration equilibrium constant, $K_H = 2 \times 10^3$.

One possible interpretation of this calculation, although there are insufficient data as yet to be conclusive, is that hydration of cadmium may proceed *via* addition of two water molecules, *i.e.*, that water-water interactions in the coordination spheres of the ions may play a significant role in the buildup of the hydration shells as water is added to an anhydrous molten salt. It would imply also strong entropy effects since the bulk of the water is associated with the calcium nitrate solvent, although the cadmium-water interaction is stronger than the calcium water interaction on the basis, *e.g.*, of the water activities.[11] Cooperative addition of two water molecules may not be unreasonable, although additional data are needed to test the possibility. Formation of water dimers in organic solvents has been reported on the basis of both thermodynamic and nmr results.[32]

The tacit assumption of only cation hydration needs to be reexamined for hydrous melts. As water is added to a molten salt, water dipoles probably orient themselves between a cation and an anion, the negative end adjacent to a cation and the positive end adjacent to an anion. With filled hydration shells, the structure may be determined largely by the orientation of water dipoles toward the cations, but even with appreciable differences between cation-water and anion-water interactions, entropic effects must produce significant contributions from anion-water interactions. Additional measurements at higher and lower water contents are in progress to test this interpretation of the competitive association and hydration equilibria.

Registry No. $CdBr^+$, 15691-37-9; $CdBr_2$, 7789-42-6; cadmium, 7440-43-9.

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[31] W. W. Ewing and W. R. Guyer, *J. Amer. Chem. Soc.*, **60**, 2707 (1938).

[32] D. R. Cogley, M. Falk, J. N. Butler, and E. Grunwald, *J. Phys. Chem.*, **76**, 855 (1972); W. L. Masterton and M. C. Gendrano, *ibid.*, **70**, 2895 (1968).

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Infrared and Raman Spectra of Acetonitrile-Antimony Pentafluoride

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Infrared and Raman spectral data are reported for three isotopic variants of solid $SbF_5 \cdot NCCH_3$, and Raman polarization data are presented for acetonitrile and SO_2 solutions. The data are in full accord with a molecular adduct of local C_{4v} symmetry for the SbF_5N moiety. Furthermore, selection rules for the local symmetry approximation are identical with those based on the permutation group, E_{24}, which represents the situation of free methyl group rotation. Bands characteristic of coordinated SbF_5 are discussed.

Introduction

Although a variety of different complexes having the general formula $SbF_5 \cdot L$ ($\sim C_{4v}$) exist,[1] there are no detailed assignments available for the SbF_5 moiety in such species. Vibrational data on SbF_5 complexes are of general interest because of the extensive use of antimony pentafluoride as a strong Lewis acid[2] and is of specific interest to us in our vibrational study of the unusual sulfur dioxide adduct $SbF_5 \cdot SO_2$.[3]

The adduct with acetonitrile was chosen for several reasons. First, this complex is easily prepared[1c] and is quite stable (in the absence of moisture) at room temperature. Second, the vibrational spectra of acetonitrile[4] and also of its 1:1 adducts with the boron trihalides[5] are well known, there being available in the literature complete vibrational analyses. Finally, and most important, acetonitrile has only one fundamental

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[1] For example: (a) SbF_5OH^-: J. E. Griffiths and G. E. Walrafen, *Inorg. Chem.*, **11**, 427 (1972); W. A. Mazeika and H. M. Neumann, *ibid.*, **5**, 309 (1966); (b) $SbF_5 \cdot PF_3$: R. D. W. Kemmitt, V. M. McRae, R. D. Peacock, and I. L. Wilson, *J. Inorg. Nucl. Chem.*, **31**, 3674 (1969); (c) $SbF_5 \cdot NCCH_3$, $SbF_5 \cdot py$, $SbF_5 \cdot$dioxane: L. Kolditz and W. Rehak, *Z. Anorg. Allg. Chem.*, **342**, 32 (1966).

[2] For example: (a) J. Bacon and R. J. Gillespie, *J. Amer. Chem. Soc.*, **93**, 6914 (1971); (b) G. A. Olah, J. R. DeMember, R. H. Schlosberg, and Y. Halpern, *ibid.*, **94**, 156 (1972).

[3] D. M. Byler and D. F. Shriver, unpublished data.

[4] (a) Gas phase: F. W. Parker, A. H. Nielson, and W. H. Fletcher, *J. Mol. Spectrosc.*, **1**, 107 (1957); W. H. Fletcher and C. S. Shoup, *ibid.*, **10**, 300 (1963); (b) liquid phase: B. Swanson and D. F. Shriver, unpublished infrared spectra; D. M. Byler and D. F. Shriver, unpublished Raman spectra.

[5] (a) B. Swanson and D. F. Shriver, *Inorg. Chem.*, **9**, 1406 (1970); (b) D. F. Shriver and B. Swanson, *ibid.*, **10**, 1354 (1971).

below 800 cm^{-1}, and that falls in a region in which no bands attributable to SbF_5 are present. Because the donor-acceptor SbN bond is of particular interest, but is difficult to assign, the isotopically substituted species $^{14}NCCD_3$ and $^{15}NCCH_3$ were also employed, in addition to normal $^{14}NCCH_3$.

Experimental Section

Infrared Spectra. The far-infrared spectra (450-70 cm^{-1}) were recorded on a Beckman IR-11, and those from 400 to 4000 cm^{-1} were obtained on a Beckman IR-9. Both instruments were occasionally checked with atmospheric water and CO_2 bands to ensure that they are calibrated to within ±1.0 cm^{-1}. Spectra were taken using a Wagner-Hornig type low-temperature infrared cell[6] fitted with KBr end windows and an AgCl sample plate for the 400-4000 cm^{-1} region and with polyethylene plates for the far-infrared region.

Owing to the hygroscopic nature of the adducts, all sample preparations were performed on a vacuum line. A small amount (~0.3 mmol) of CH_3CN was first frozen onto the sample plate at −196°, followed by a similar quantity of SbF_5 and a final layer of CH_3CN (~1 mmol). The sample plate was allowed to warm to about −30° at which point the two compounds reacted. Finally, excess acetonitrile was distilled out at −30° leaving the 1:1 adduct. Spectra were recorded at *ca.* −196, −78, and 0°. There was no indication of uncomplexed SbF_5 or CH_3CN in any of the spectra.

Because SbF_5 appears to react at room temperature with KBr, polyethylene, and perhaps even AgCl, care was taken to avoid reaction temperatures above about −15° and to use clean windows and sample plates for each run.

Raman Spectra. The Raman data was collected using a Spex 1400-II double monochromator with photon-counting detection.[7] The green 514.5-nm line of an argon ion laser (Spectra Physics 164 or Coherent Radiation Model 52G) was employed as the exciting line. The observed Raman shifts are estimated to be accurate to at least ±4 cm^{-1}. Laser power at the sample of ~400 mW and a spectral band pass of 1.5-2.0 cm^{-1} were employed for the solid polycrystalline samples. For solutions, power at the sample ranged from 100 to 300 mW and the monochromator band pass was *ca.* 1 cm^{-1}. Ninety degree scattering geometry was employed in all runs.

In order to optimize the signal-to-noise ratio in the measurement of depolarization ratios, the electric vector of the laser beam was rotated through 90° on successive scans (Spectra Physics Model 310-21 polarization rotator) and scattered light was passed through a quartz wedge scrambler.[8] Depolarization ratios were estimated from peak heights.

Reagents. SbF_5 (Peninsular Chemical Research) was twice distilled at room temperature under high vacuum. Infrared and Raman spectra for the resulting viscous liquid agreed with literature reports.[9] CH_3CN (reagent grade, Matheson Coleman and Bell) was refluxed over P_2O_5, distilled, and then stored over dry Linde 5A molecular sieves. CD_3CN (estimated >95% D from spectra of liquid[4b]) and $CH_3C^{15}N$ (>95% ^{15}N; Isomet, Inc., Palisades Park, N. J.) also were distilled and stored over molecular sieves.

Results

Assignments. The initial assumption, which the spectra subsequently confirmed, was that $SbF_5 \cdot NCCH_3$ is structurally similar to $SbCl_5 \cdot NCCH_3$, which has approximately C_{4v} symmetry (octahedral coordination) about the Sb atom.[10] Considered as a rigid structure, the highest symmetry possible for the $SbF_5 \cdot NCCH_3$ molecule is C_s, for which the selection rules predict 30 fundamentals. More reasonable is a nonrigid structure in which the methyl group rotates freely with respect to the four equatorial fluorines. As shown in the Appendix, the 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.[11] 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 rigid on the infrared time scale,

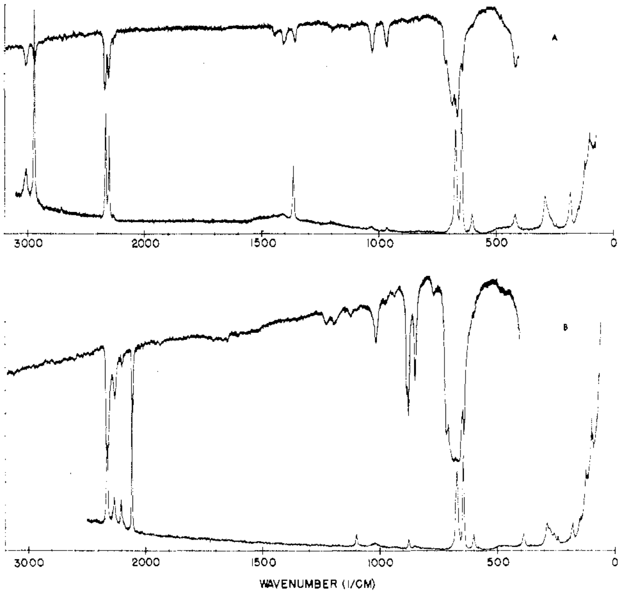

Figure 1. Infrared and Raman spectra of polycrystalline $SbF_5 \cdot NCCH_3$ (spectra A) and $SbF_5 \cdot NCCD_3$ (spectra B). In each case the upper curves are the infrared spectra (*ca.* −196°); the lower ones are the Raman spectra (~25°). [The intensity of several low-frequency features in the Raman spectra (*viz.*, ~243 cm^{-1} and those below ~150 cm^{-1}) changed upon readjustment of the sample in the laser beam and therefore appear to be spurious.]

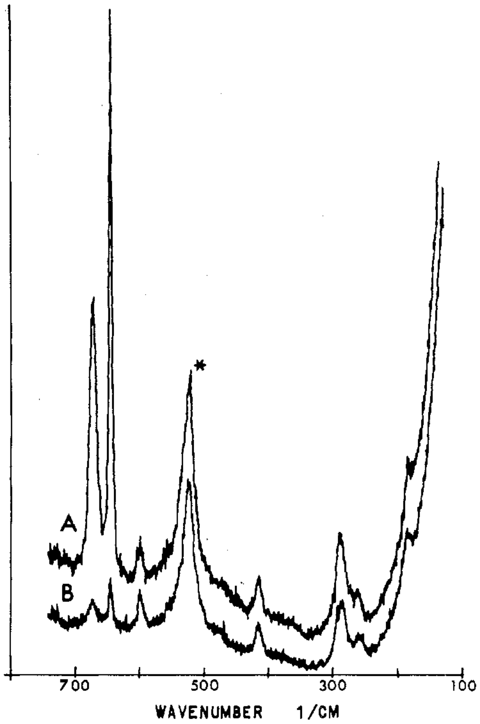

Figure 2. Raman spectra of a solution of $SbF_5 \cdot NCCH_3$ in liquid SO_2 (~25°): A, electric vector of the incident beam perpendicular to the direction in which the scattered light was observed; B, electric vector of the incident beam parallel to the direction in which the scattered light was observed. [The peak marked by the asterisk is due to the solvent.]

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(6) (a) E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 296 (1950); (b) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, p 95.

(7) I. Wharf and D. F. Shriver, *Inorg. Chem.*, **8**, 914 (1969).

(8) Method 5 of C. D. Allemand, *Appl. Spectrosc.*, **24**, 348 (1970). For this geometry the theoretical maximum value of ρ is $^6/_7$ (0.857).

(9) A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2929 (1969); I. R. Beattie, K. M. S. Livingston, G. A. Ozin, and D. J. Reynolds, *J. Chem. Soc. A*, 958 (1969).

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

(11) The vertical planes $\sigma_v(xz)$ and $\sigma_v(yz)$ were chosen to contain the equatorial fluorines.

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 SbF_5 and $NCCH_3$ moieties and the spatial remoteness of the SbF_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 ($\sim C_{3v}$) should exhibit 4 A_1 and 4 E fundamentals, while 4 A_1, 2 B_1, 1 B_2, and 4 E modes[11] are expected for the SbF_5N portion ($\sim C_{4v}$). In addition, there is an SbNC deformation belonging to the species E and an A_2 torsional mode.

The designation and approximate description of these 21 fundamentals is given in Table I. In the following discussion, data for the normal isotopic molecule are given without comment, while those for isotopic species are designated by listing the enriched element, *e.g.*, $^{15}N = SbF_5 \cdot {}^{15}NCCH_3$.

Assignments for the observed infrared and Raman bands are given in Table II. In no case do any of the fundamental frequencies show a marked temperature dependence. Therefore, infrared frequencies are usually quoted for spectra obtained at *ca.* −196°, while Raman shifts are for runs at ambient temperature. Assignments for the acetonitrile portion of the molecule are aided by data on the boron trihalide adducts,[5] while those for the SbF_5N portion were aided by data for $SbF_5 \cdot SO_2$,[3] SeF_5Cl,[12] and TeF_5OH.[13]

4000–2000 cm^{-1}. This region contains three fundamentals, ν_1 (CH_3 stretch, A_1), ν_2 (CN stretch, A_1) and ν_{13} (CH_3 stretch, E), which are easily assigned.[5] As observed for other acetonitrile adducts, a strong band due to the $\nu_3 + \nu_4$ combination (CH_3 deformation and CC stretch, respectively) borrows intensity from ν_2.[5] Correcting the infrared data for Fermi resonance, we find a value of *ca.* 2329 cm^{-1} for ν_2 of the normal isotopic molecule and *ca.* 2304 cm^{-1} for the ^{15}N species. For the D adduct, in which ν_2 is unaffected by Fermi resonance, ν_2 occurs at 2335 cm^{-1}.

2000–750 cm^{-1}. Except for ν_{17} (CCN deformation), the remaining acetonitrile fundamentals fall within this part of the spectra. For the H isotopic molecules these four bands [ν_3 (CH_3 deformation, A_1), ν_4 (CC stretch, A_1), ν_{14} (CH_3 deformation, E) and ν_{15} (CH_3 rock, E)] occur between 950 and 1425 cm^{-1}; in the case of the deuterated complex they are observed between 825 and 1100 cm^{-1}. Of these modes, ν_3 and ν_{15} occur essentially unchanged from the parent;[4b] ν_4 shows an increase of *ca.* 44 cm^{-1} to 965 cm^{-1} (H), 877 cm^{-1} (D), and 956 cm^{-1} (^{15}N); and ν_{14} exhibits a decrease compared with the parent of *ca.* 43 cm^{-1} to *ca.* 1404 cm^{-1} (H, ^{15}N) and of *ca.* 20 cm^{-1} to 1017 cm^{-1} (D). The shift in ν_4 is probably due to mixing of this fundamental with the SbN symmetric stretch mode, in a manner similar to that observed for the boron trihalide–acetonitrile systems.[5]

Several weak features in the infrared spectra, particularly those at 1127 and 1198 cm^{-1}, exhibit a marked increase in intensity with increasing temperature. Similar bands in the deuterated species seem not to be affected by temperature changes.

Table I. Numbering and Approximate Description of the Fundamental Vibrations of $SbF_5 \cdot NCCH_3$

A_1 Class	
ν_1	CH_3 str
ν_2	CN str
ν_3	CH_3 def
ν_4	CC str
ν_5	SbN str
ν_6	SbF′ axial str
ν_7	SbF_4 equatorial str
ν_8	SbF_4 out-of-plane def
A_2 Class	
ν_9	torsion
B_1 Class	
ν_{10}	SbF_4 equatorial str
ν_{11}	SbF_4 out-of-plane def
B_2 Class	
ν_{12}	SbF_4 in-plane def
E Class	
ν_{13}	CH_3 str
ν_{14}	CH_3 def
ν_{15}	CH_3 rock
ν_{16}	SbF_4 equatorial str
ν_{17}	CCN def
ν_{18}, ν_{19}	F′–SbF_4 def SbF_4 in-plane def
ν_{20}	N–SbF_4 def
ν_{21}	SbNC def

Table II.[a] Observed Infrared and Raman Frequencies (cm^{-1}) for Solid $SbF_5 \cdot {}^{14}NCCH_3$

Infrared (−196°)	Raman (~25°)	Assignment
	~45	?
	~65	?
	~95	?
113 mw(?)		?
	183 (1)[b]	ν_{12}
267 vs, br	~261 sh	ν_{19}
	~277 sh	ν_{18}
	290 (1)	ν_8
412.5 mw	417 (1)	ν_{17}
	~500 (0) vbr	?
	602 (1)	ν_{10}
641 m	646 (6)	ν_7
663 vs	673 (4)	ν_6
671 w		ν_5
714 m		$2\nu_{12} + \nu_{19}; \nu_3 - \nu_7; \nu_{14} - \nu_{16}$
~826 vw		$2\nu_{17}$
~874 vw		$\nu_{10} + \nu_{18}$
~901 vw[c]		?
~930 vw[c]		$\nu_6 + \nu_{19}; \nu_7 + \nu_8; \nu_6 + \nu_{18}; \nu_{16} + \nu_{19}$
965 mw	966 (0)	ν_4
974 sh		$\nu_8 + \nu_{16}$
1027 mw[c]	1031 (0)	ν_{15}
1127 w[c]		$\nu_{14} - \nu_{18}$ (?)
~1153 vw		$\nu_{14} - \nu_{19}$ (?)
~1198 w[c]	~1198 (0)	$2\nu_{10}$
1358 mw	1364 (2)	ν_3
1404 mw	1407 (0)	ν_{14}
1443 w		$\nu_{15} + \nu_{19}$
2276 w		$\nu_1 - \nu_{16}; \nu_1 - \nu_6$
2312 m [2325][d]	2308 (3)	$\nu_3 + \nu_4$
2342 ms [2329][d]	2339 (4)	ν_2
	2711 (0)	$2\nu_3$
2948 mw	2948 (10)	ν_1
3021 mw	3019 (1)	ν_{13}

[a] A supplementary table containing infrared and Raman data for the solid D- and ^{15}N- substituted species as well as Raman data for acetonitrile and sulfur dioxide solutions of the normal isotopic molecule will appear following these pages in the microfilm edition of this volume of this journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1412. [b] Relative intensities (0–10) are given in parentheses for the Raman data. [c] These bands grow in intensity as temperature increases. [d] Values corrected for Fermi resonance are given in brackets for infrared data.

750–550 cm^{-1}. Both SbF and SbN stretching frequencies are expected in this region but the spectra are dominated by the former. The SbF_5 stretching modes of A_1 and E symmetry are expected to be active in infrared and Raman spectra. However the E-type SbF_4 stretch, ν_{16}, is not observed in the Raman spectrum. (With other $MX_5 \cdot L$ complexes this Raman band is either weak or unobserved.[12,13]) The two A_1 modes are observed by both techniques and are polarized in Raman solution spectra. The stronger infrared band at ~665 cm^{-1} is provisionally assigned as ν_6 (the axial

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

(13) H. J. Burger, *Z. Anorg. Allg. Chem.*, 360, 97 (1968).

Table III. Character Table for the Permutation Symmetry Group E_{24}

E_{24}	E	(123)(4567) (132)(4765)	(123)(46)(57) (132)(46)(57)	(4567) (4765)	(123) (132)	(123)(4765) (132)(4567)	(46)(57)	(23)(46)* (12)(46)* (31)(46)* (23)(57)* (12)(57)* (31)(57)*	(23)(47)(56)* (12)(47)(56)* (31)(47)(56)* (23)(45)(67)* (12)(45)(67)* (31)(45)(67)*		
A_1	1	1	1	1	1	1	1	1	1	z	$z^2, x^2 + y^2$
A_2	1	1	1	1	1	1	1	−1	−1	R_z	
B_1	1	−1	1	−1	1	−1	1	1	−1		$x^2 - y^2$
B_2	1	−1	1	−1	1	−1	1	−1	1		xy
E_1	2	$\sqrt{3}$	1	0	−1	$-\sqrt{3}$	−2	0	0		
E_2	2	1	−1	−2	−1	1	2	0	0		
E_3	2	0	−2	0	2	0	−2	0	0	$(x, y)(R_x, R_y)$	xz, yz
E_4	2	−1	−1	2	−1	−1	2	0	0		
E_5	2	$-\sqrt{3}$	1	0	−1	$\sqrt{3}$	−2	0	0		
Γ_{tot}	36	8	−8	8	36	8	−8	8	6		

SbF stretch), while the weaker feature at 641 cm^{-1} is assigned as ν_7 (the equatorial SbF_4 stretch). The remaining SbF stretch, ν_{10} (B_1 symmetry), is Raman active only and is assigned to a weak band at 600 cm^{-1} in the Raman spectrum which has no infrared counterpart.[14]

The assignment of the SbN stretching frequency, ν_5, proved to be quite difficult. Initially a feature at 715 cm^{-1} which appears on the side of the strong 685-cm^{-1} infrared band was assigned as ν_5. However, the expected Raman counterpart is not observed and this choice leads to an error of *ca.* 4% in the Teller-Redlich product rule calculation for the 8 A_1 frequencies. If on the other hand, ν_5 is assigned to an infrared band at 671 cm^{-1} for the normal isotopic compound, 648 cm^{-1} for the ^{15}N compound, and *ca.* 641 cm^{-1} for the D adduct (*i.e.*, obscured by ν_7 = 641 cm^{-1}), then the product rule ratios differ by less than 1% from those predicted theoretically: observed for D and ^{15}N respectively, 0.499 and 0.931; calculated, 0.503 and 0.939. The absence of these features in the Raman spectra is probably due to the very high intensity of ν_6 and ν_7 in this region. Nevertheless, this assignment is tentative.

550-300 cm^{-1}. The only observed fundamental is ν_{17} (CCN deformation, E) at 413 (H), 386 (D), and 409 cm^{-1} (^{15}N). These constitute shifts of *ca.* +35 cm^{-1} from the corresponding parent isotopic species.[4b]

300-25 cm^{-1}. A series of deformation modes falls in this region: 5 SbF deformations (1 A_1, 1 B_1, 1 B_2, and 2 E), 1 N-SbF_4 deformation (E), and the SbNC deformation (E). In addition the inactive torsional mode A_2 probably occurs here. Because many of the bands are weak and several appear as shoulders, it was difficult to obtain accurate depolarization ratios from the Raman solution spectra. Therefore assignments in this region are necessarily more tentative than those given above.

In the infrared region only one strong, very broad band is observed *ca.* 267 cm^{-1}. This approximately corresponds to two barely discernible shoulders in the Raman spectrum of the normal isotopic molecule at *ca.* 260 and *ca.* 275 cm^{-1}. The former is definitely depolarized in acetonitrile solution spectra. These features are quite distinct in spectra of the deuterated complex and are assigned as ν_{18} and ν_{19}, the two SbF_4 degenerate, asymmetric deformations of E symmetry. A stronger, polarized band at 290 cm^{-1} in the Raman is assigned as ν_8, the symmetric SbF_4 deformation (A_1). The only other band that was definitely observed is a weak, depolarized Raman peak at *ca.* 182 cm^{-1}. Since a corresponding infrared band is not observed, this feature is presumed to belong to one of the B modes; ν_{12} (SbF_4 in-plane deformation, B_2) was selected because the other B deformation mode (ν_{11}, B_1) is expected to be weaker and has not been observed for similar C_{4v} species.[12] The two remaining E modes apparently occur below 150 cm^{-1} but no bands were observed which could be definitely assigned to them.

Discussion

The present work provides the most complete spectroscopic data and assignments yet available for an antimony pentafluoride adduct $SbF_5 \cdot L$. The results are in accord with a simple molecular complex of C_{4v} local symmetry and not with ionic structures such as $[SbF_4L_2]^+[SbF_6]^-$.[1c] The SbF stretching region of $SbF_5 \cdot NCCH_3$ is particularly characteristic. In Raman spectra, two very strong polarized bands are observed around 673 and 646 cm^{-1}, and a weak depolarized SbF stretch is observed at 600 cm^{-1}. The infrared spectrum shows two very strong features at 685 and 665 cm^{-1} as well as a medium-intensity band at 641 cm^{-1}. In analogous adducts, frequencies of these Raman and infrared features may be expected to vary somewhat depending upon the nature of L; however, the general frequency range and pattern should prove to be useful in the identification of other antimony pentafluoride adducts.

The foregoing observations for $SbF_5 \cdot NCCH_3$ are to be contrasted with the two strong and polarized bands at 720 and 672 cm^{-1} for the Raman spectrum of liquid SbF_5 and the presence of at least three very strong infrared bands in the 760-500-cm^{-1} range.[9,15] Spectra of the acetonitrile adduct also are easily distinguished from those of SbF_6^-, which has bands in the Raman spectrum about 665 cm^{-1} (vs, polarized) and 575 cm^{-1} (w, depolarized) and in the infrared spectrum *ca.* 665 cm^{-1} (vs).[1a]

Of interest in the spectra of the acetonitrile portion of $SbF_5 \cdot NCCH_3$ is the magnitude of the increase in ν_{CN}, 61 cm^{-1}, which is significantly less than that observed for the acetonitrile-boron trihalides, where shifts on the order of 100 cm^{-1} are observed.[5] If, as has been proposed, the increase in ν_{CN} is related to the acidity of the attached Lewis acid, we would conclude that SbF_5 is weaker than BF_3. However this order of acidity appears unlikely from qualitative observations on these two acids. For example, $HSbF_6$ appears to exist in liquid HF[16] while HBF_4 does not.[17]

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(14) Because of the difficulty in obtaining polarization data on this weak feature rather large standard deviations result: $\rho = 0.73 \pm 0.15$ for SO_2 solution and 0.75 ± 0.15 for acetonitrile solution.

(15) (a) L. E. Alexander and I. R. Beattie, *J. Chem. Phys.*, **56**, 5829 (1972); (b) D. M. Byler, unpublished spectra.

(16) H. H. Hyman, L. A. Quarterman, M. Kilpatrick, and J. J. Katz, *J. Phys. Chem.*, **65**, 123 (1961).

Similarly, although a weak $BF_3 \cdot SO_2$ complex reportedly exists below *ca.* −96°,[18] the 1:1 $SbF_5 \cdot SO_2$ adduct is stable above room temperature under a moderate partial pressure of SO_2 and SbF_5.[19] While fragmentary, the evidence suggests that the shift in ν_{CN} is not directly related to acid strength.

Normal-coordinate analysis of $SbF_5 \cdot NCCH_3$ is being deferred until the completion of spectroscopic work on related group V acetonitrile adducts.

Registry No. $SbF_5 \cdot NCCH_3$, 19106-78-6; $SbF_5 \cdot NCCD_3$, 38894-62-1; $SbF_5 \cdot {}^{15}NCCH_3$, 38894-63-2.

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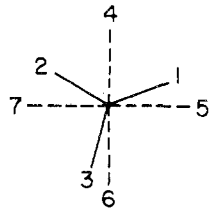
Appendix

Classification of the normal modes of vibration for a nonrigid molecule requires the use of a permutation symmetry group.[20] In the case of $SbF_5 \cdot NCCH_3$ as a nonrigid species in which the methyl group is free to rotate about the *z* axis (containing the FSbNCC backbone), the appropriate permutation symmetry group, which we call E_{24}, is isomorphous with D_{6h}. It has 8 symmetry classes and is of order 24, as shown in Table III. Using the numbering given in Scheme I, the 24 symmetry operations are denoted by standard permutation notation.[20] Table III also gives the reducible representation[21] for the 36 degrees of freedom for the $SbF_5 \cdot NCCH_3$ molecule, as well as the species which contain the translations, rotations, and polizability tensor elements. The reducible representation for the fundamental molecular vibrations consists of $8\ A_1 + 1\ A_2 + 2\ B_1 + 1\ B_2 + 9\ E_3$. The A_1 and E_3 species are Raman and infrared active, while the B_1 and B_2 vibrations are Raman active only. The A_2 mode is inactive.

Scheme I. Viewing down the *z* Axis with the Methyl Group toward the Observer



A direct correlation of E_{24} with C_{3v} and C_{4v} is not possible since the latter are not subgroups of the permutation group. Nevertheless, the similarity between the vibrational representations of the rigid and nonrigid models is immediately apparent.[22]

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(21) As with Turrell's molecule,[20b] for each permutation on the "heavy" skeletal atoms two at a time [*e.g.*, the operation (46)(57)], each unpermuted atom contributes −1 to the character of that operation. On the other hand, permutations on all four equatorial fluorines in a cyclic fashion [*e.g.*, the operation (4567)] requires that each unpermuted atom contributes +1.

(22) Since all of the degenerate vibrations predicted by the nonrigid model belong to one species, E_3, the subscript 3 has no importance for the purpose of comparing the results of the two models. Hence, for simplicity, throughout the body of the paper we refer to this species as E.

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Reaction between Ethylenediaminetetraacetic Acid and Carboxylatopentaaquochromium(III) Complexes

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The kinetics of the reaction between EDTA and three carboxylatopentaaquochromium(III) complexes were studied in the pH range 3.0–3.5. The acetato, formato, and trifluoroacetato complexes all react to form the Cr(III)-EDTA complex substantially faster than does hexaaquochromium(III). Under comparable conditions the acetato complex reacts faster than hexaaquochromium(III) by a factor of 10^3. Simple first-order kinetics were not observed for the carboxylato complexes even under conditions of constant EDTA concentration and pH. The absorbance–time profiles could be analyzed assuming irreversible formation and decay of an intermediate species. Although the intermediate's identity was not established, the reactivity order of the carboxylato complexes (acetato > formato > trifluoroacetato) is the same for both its formation and disappearance. A mechanism is proposed in which the carboxylate's unbound oxygen provides nucleophilic assistance for the replacement of a cis water molecule. The likelihood that this mechanism is responsible for several other cases of unexpected lability in chromium(III)-substitution reactions is discussed.

Introduction

The ligand substitution reactions of acidopentaaquochromium(III) complexes have been the subject of several recent articles.[1-8] They include reports that coordinated iodide[4] as well as O-bonded sulfite[6] and nitrite[7,8] can increase the lability of chromium(III). We have studied another example of labilization by a coordinated ligand: the rate enhancement of EDTA complex formation by a

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