Notes

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Vibrational Spectroscopic Study of Some Oxo Adducts of Antimony Pentachloride

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Received August 6, 1974 AIC405424

A large number of addition complexes of antimony pentachloride are known[1] and the crystal structures have been established for some of them.[2–6] Byler and Shriver[7] have recently studied in detail the vibrational spectra of the complex $SbCl_5{\cdot}NCCH_3$, which can be considered as a model for $SbCl_5{\cdot}L$ complexes of C_{4v} symmetry. It seemed of interest to study some complexes of antimony pentachloride with oxygen donor ligands in order to compare the spectra of the two moieties $NSbCl_5$ and $OSbCl_5$. Moreover, various differences would be expected since the system $Sb{\leftarrow}N{\equiv}C$ is linear whereas the system $Sb{\leftarrow}O{-}X$ (X = Se, P, C, ...) is always bent in an oxygen donor complex. In the present work, the influence of the donor strength of the ligands is also studied and the vibrational spectra of adducts with strong donors (DMF, $(CH_3)_3PO$) are compared with those formed with weak donors ($OPCl_3$, $OSeCl_2$, $OSCl_2$). Since normal modes of the organic part of the complexes appear in the range 50–500 cm^{-1} characteristic of the "Cl_5SbO" modes, deuteration ($SbCl_5{\cdot}DMF$-h_7, $SbCl_5{\cdot}DMF$-d_7) as well as isotypic molecules ($SbCl_5{\cdot}OPCl_3$, $SbCl_5{\cdot}OP(CH_3)_3$) have been used for proposing an assignment.

Experimental Section

Spectra. Infrared spectra were recorded on a Beckman IR-12 instrument between 400 and 4000 cm^{-1}, using the KBr pellet technique. Far-infrared spectra were obtained with a Fourier interferometer Polytec FIR 30.

The Raman spectra of samples sealed in Pyrex tubes were recorded with a Coderg PHO spectrophotometer. The green 514.5-nm line of an argon ion laser (Spectra Physics 164) and the red 632.8-nm line of a He–Ne laser (OIP 181 E) served as exciting lines. The samples were contained in a chamber filled with a heat-transfer gas.

Preparation of the Complexes. Two standard procedures were used. $SbCl_5{\cdot}DMF$-h_7, $SbCl_5{\cdot}OP(CH_3)_3$, $SbCl_5{\cdot}OPCl_3$, and $SbCl_5{\cdot}OSeCl_2$ were obtained by mixing a solution of the ligand in dichloromethane (carbon tetrachloride for $SbCl_5{\cdot}DMF$-d_7) with a solution of antimony pentachloride in the same solvent in stoichiometric proportions. Crystals were formed by cooling the resulting solution near 0 °C and recrystallization was carried out in the same solvent. Crystalline $SbCl_5{\cdot}OSCl_2$ was obtained by direct addition of the antimony pentachloride to the liquid ligand followed by cooling.

Reagents. $SbCl_5$ (Merck for chromatography), DMF-d_7 (Merck), DMF-h_7, $OPCl_3$, and $OSCl_2$ (Fluka puriss), and $OSeCl_2$ (Alfa Inorganics) were used without further purification. $OP(CH_3)_3$ was obtained by the procedure described in ref 8 and checked for purity by its ir and Raman spectra and by analysis of C, H, and P.

Results and Discussion

Although the whole range (33–4000 cm^{-1}) of the spectra was studied, only the results relative to the $OSbCl_5$ moiety are discussed. The assignments are based on C_{4v} symmetry.

$\nu(a_1)$(Sb–O). In the case of $SbCl_5{\cdot}DMSO$,[9] this vibrational mode is observed in the 450–500 cm^{-1} region and by deuteration of the ligand it is decreased by about 20 cm^{-1}. Very similar behavior is observed for the $SbCl_5{\cdot}DMF$ complex for which the ν(Sb–O) vibration appears at 430 cm^{-1} in the DMF-h_7 adduct and at 405 cm^{-1} in the DMF-d_7 adduct. For the other complexes, this vibration could easily be assigned at 390, 395, and 463 cm^{-1} in the Raman spectra of $SbCl_5{\cdot}OSCl_2$, $SbCl_5{\cdot}OPCl_3$, and $SbCl_5{\cdot}OSeCl_2$ complexes, respectively, and it was found to be sensitive to temperature changes in all complexes studied; generally, an increase of about 10 cm^{-1} is observed when the temperature is lowered from 293 to 77 K (Tables I and II). Moreover, the Raman band corresponding to this vibration is polarized (Figure 1), which confirms the proposed assignment.

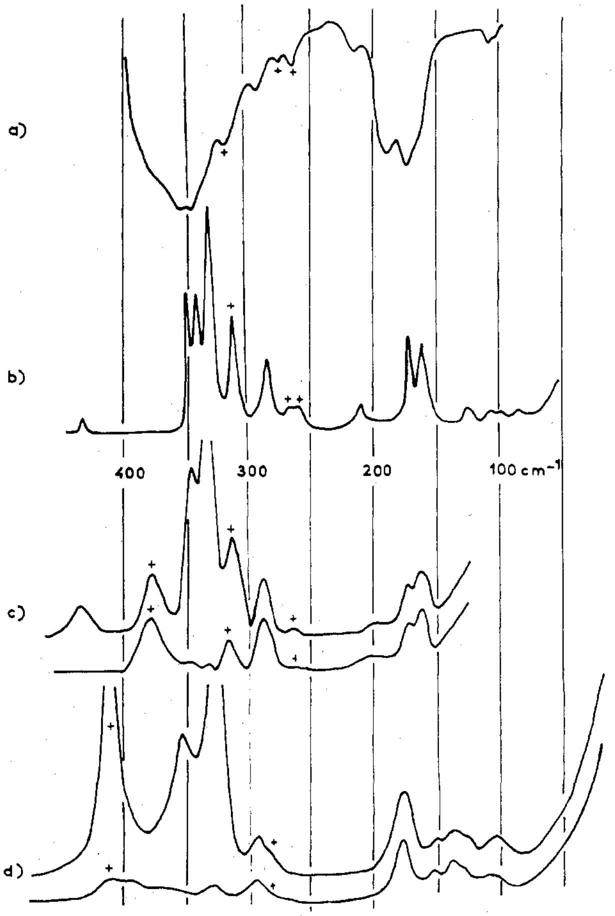

Figure 1. Raman and ir spectra of $SbCl_5{\cdot}L$ in the range 50–450 cm^{-1}: (a) ir spectrum of $SbCl_5{\cdot}OP(CH_3)_3$ in the solid state (ordinary temperature); (b) Raman spectrum of $SbCl_5{\cdot}OP(CH_3)$ in the solid state (ordinary temperature); (c) Raman spectrum of $SbCl_5{\cdot}OP(CH_3)_3$ in CH_3CN solution; (d) Raman spectrum of melted $SbCl_5{\cdot}OSeCl_2$. A cross (+) signifies a line which does not belong to the $OSbCl_5$ moiety.

ν(Sb–Cl). The normal modes corresponding to the Sb–Cl bonds appear in the 280–380-cm^{-1} region. The Raman spectra of the complexes, in solution or in the fused state, are very similar and regulary show (Figure 1) (a) a depolarized band of medium intensity between 280 and 300 cm^{-1}, (b) a very strong polarized band between 325 and 350 cm^{-1}, (c) a strong polarized band between 345 and 365 cm^{-1}, and (d) a weak band or a shoulder on the strong band near 360 cm^{-1}. In the

Table I. Raman and Ir Spectra in the Range 30–450 cm^{-1} for $SbCl_5 \cdot OSCl_2$, $SbCl_5 \cdot OSeCl_2$, $SbCl_5 \cdot DMSO$, and $SbCl_5 \cdot DMF$[a]

$SbCl_5 \cdot OSCl_2$	$SbCl_5' \cdot OSeCl_2$			$SbCl_5' \cdot DMSO$	$SbCl_5 \cdot DMF$-h_7		$SbCl_5 \cdot DMF$-d_7		
Ra(LT)	Ra(LT)	Ra(90 °C)	Ir(OT)	Ra(OT)	Ra(OT)	Ir(OT)	Ra(OT)	Ir(OT)	Assignments
				42 vw	36 vw		36 vw		Lattice and bending vibrations
				56 vw	47 m		46 m		
89 w	90 vw		87 m	85 vw	66 vw		65 vw		
				100 vw	76 w		71 w		
	111 m	108 dp		115 vw	101 sh		90 sh		
	124 w		120 sh	127 w	125 w	125 vw	125 w		
	138.5 vw	132 dp	133 sh		138 w	135 sh	133 w	138 sh	
143 m	146.5 m	142 dp	145 sh	143 m					
153 m	158.5 m	156 dp	157 s						
169 w	171.5 w	172 dp	170 s	164 s	171 sh	170 vs	171 sh, m	173 vs	
176 vw									
187.5 s	184.5 s	181 dp	180 sh	177 vs	177 s		176 s		$\delta(b_2)(ClSbCl)$
216 w	199 m		195 sh	202 w	198 vw	193 sh	188 vw	187 sh	$\delta(e)(OSbCl)$
219 w				206 w	211 vw	212 m	204 vw	207 m	
				248 vw		240 vw		261 w	Ligand vibrations
	288 w	285 w	283 m			263 vw		269 w	
299 s	297.5 m	293.5 dp		286 w	290 s	292 w	290 s	291 w	$\nu(b_1)(SbCl_4)$
	306.5 m		305 sh, vw	296 m					
326 w									Ligand vibration
343.5 s	329.5 s	327 p	327 sh	327 vs	325 vs	324 w	322 vs	324 w	$\nu(a_1)(SbCl_4)$
345.5 s									
357.5 m	345.5 s			346 s	345 s		344 s	347 sh	$\nu(a_1)(SbCl_{\mathbf{ax}})$
364 s	351 s	353 p	345 sh	350 s	351 s	353 s	351 vs	352 s	
	367 vw	368 dp	360 vs	366 w		363 s		362 s	$\nu(e)(SbCl_4)$
390 m	463 m	440 dp		500 m	422 vw	422 m			
		450 dp			432 vw		405 w	405 s	$\nu(a_1)(SbO)$
					440 vw	438 m			

[a] Key: w, weak; m, medium; s, strong; v, very; sh, shoulder; p, polarized; dp, depolarized; Ra, Raman; LT, 77 K; OT, ordinary temperature.

Table II. Raman and Ir Spectra in the Range 30–450 cm^{-1} for $SbCl_5 \cdot OP(CH_3)_3$ and $SbCl_5 \cdot OPCl_3$[a]

$SbCl_5 \cdot OP(CH_3)_3$			$SbCl_5 \cdot OPCl_3$		
Ir(OT)	Ra(OT)	Ra (CH_3-CN soln)	Ir(OT)	Ra(LT)	Assignments
	60 vw				Lattice and bending vibrations
	90 w				
105 vw	104 vw				
	114 w		120 m		
	131 w			132 w	
			149 sh	145.5 m	
165 sh	165 m	165 m	166 s	154 m	
172 s				169 vw	
				176 vw	
	176 m	175 dp		182 m	$\delta(b_2)(ClSbCl)$
187 s	186 vw			213 w	$\delta(e)(OSbCl)$
210 w	215 w	215 dp	213 w	217.5 w	
240 vw					
261 vw	266 vw	267 dp	265 sh		Ligand vibrations
271 vw	271 vw				
290 vw	288 m	289 dp	298 dp	300.5 m	$\nu(b_1)(SbCl_4)$
				303.5 sh	
317 vw	317 m	314 p			Ligand vibrations
	334 vs	336 p	330 sh	340 vs	$\nu(a_1)(SbCl_4)$
				341.5 vs	
345 sh	344 s		345 sh, s	360 m	$\nu(a_1)(SbCl_{\mathbf{ax}})$
351 vs	352 s	350 p	365 sh, s	367.5 m	
372 sh			375 vs	373.5 vw	$\nu(e)(SbCl_4)$
448 m	445 s	438 p	395 sh	395 m	$\nu(a_1)(SbO)$

[a] Key: w, weak; m, medium; s, strong; v, very; sh, shoulder; p, polarized; dp, depolarized; Ra, Raman; LT, 77 K; OT, ordinary temperature.

case of molten $SbCl_5 \cdot OSeCl_2$, a weak, depolarized band is observed at 368 cm^{-1}. It is interesting to compare this spectroscopic behavior to that of analogous complexes in which C_{4v} symmetry around the antimony atom is more effective, i.e., $SbX_5 \cdot NCCH_3$ (X = Cl, F).[7,10] In solution, the spectra of antimony pentachloride–oxygen donor complexes are almost identical with those of $SbX_5 \cdot NCCH_3$. Using this model and assuming C_{4v} symmetry around the Sb atom, the observed bands can be assigned as follows: $\nu(b_1)(SbCl_4)$, 280–310 cm^{-1}; $\nu(a_1)(SbCl_4)$, 325–350 cm^{-1}; $\nu(a_1)(SbCl_{ax})$, 345–365 cm^{-1}; $\nu(e)(SbCl_4)$, 368 cm^{-1} for $SbCl_5 \cdot OSeCl_2$.

Generally, the spectra of the solids (Tables I and II) are more complex and the analogy between the various compounds is not good as that found for solutions. The strong band close to 350–365 cm^{-1} in the spectra of solutions corresponds to two bands separated by 4–8 cm^{-1}. This feature is also observed with complexes of $SbCl_5$ with nitriles other than CH_3CN.[11] Three possibilities can be invoked to explain such a fact: an isotopic shift due to ^{35}Cl and ^{37}Cl, the presence of a harmonic or combination mode enhanced by a Fermi resonance, and finally a factor group splitting. In this last hypothesis, in the factor group analysis of $SbCl_5 \cdot DMF$, $SbCl_5 \cdot OPCl_3$, and $SbCl_3 \cdot OP(CH_3)_3$, one expects two Raman-active modes for each nondegenerate internal mode.

The mode assigned to $\nu(e)(SbCl_4)$ always corresponds to a strong absorption band in the ir spectra whereas the Raman spectra exhibit a very weak corresponding band or none at all. This is frequently observed with molecules of C_{4v} symmetry.[7,10,12]

The $\nu(b_1)(SbCl_5)$ vibration, which is not observed in the ir spectra of $SbCl_5 \cdot NCCH_3$, is ir and Raman active for the oxygen donor complexes studied and this shows clearly the influence of the site group (C_1 or C_s) in these complexes. In the Raman spectra of the solids, the band corresponding to the $\nu(b_1)(SbCl_5)$ vibration is sometimes split, and as in the case of $SbCl_5 \cdot NCCH_3$,[7] this splitting can be explained by a Fermi resonance with the combination of two bending modes (127 + 164 = 291 cm^{-1} in $SbCl_5 \cdot DMSO$ and 138.5 + 158.5 = 297 cm^{-1} in $SbCl_5 \cdot OSeCl_2$).

Bending Vibrations. Six bending modes due to the $OSbCl_5$ moiety ($A_1 + B_1 + B_2 + 3\,E$) and one due to $\delta(SbOX)$ (X = C, S, P, Se) are expected in the low region. As observed for $SbCl_5 \cdot NCCH_3$,[7] the Raman spectra of the complexes in solution or in the melt show only depolarized bands which must be assigned to non totally symmetric vibrations. For $SbCl_5 \cdot DMF$ and $SbCl_5 \cdot DMSO$, the two weak bands near 200 cm^{-1} which are depolarized and sensitive to the deuteration

Table III. Raman Stretching Frequencies for $OPCl_3$, $OSeCl_2$, and $OSCl_2$ Coordinated to $SbCl_5$ at 77 K and Frequency Shifts ($\Delta\nu$) Due to the Coordination (cm^{-1})[a]

$SbCl_5 \cdot OPCl_3$		$SbCl_5 \cdot OSeCl_2$		$SbCl_5 \cdot OSCl_2$		Assignments
ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	(M = P, Se, S)
629 vw	+40	405.5 sh, m	+55	490.5–495 w	+50	$\nu(MCl)_{asym}$
632						
529 w	+40	412.5 vs	+25	515–520 w	+25	$\nu(MCl)_{sym}$
1161 sh	−140	757	−195	1160–1164.5	−165	$\nu(MO)$
		765 w		1075.5 w		

[a] Key: w, weak; m, medium; sh, shoulder; v, very.

are assigned to bending modes (OSbCl) of e symmetry.

The bending vibration $\delta(b_2)$(ClSbCl) can be easily assigned since it is expected to appear near 170 cm^{-1} when allowance is made for correlation between this mode and its corresponding mode $\delta(f_{2g})$(ClSbCl) appearing at 170 cm^{-1} in the Raman spectrum of the $SbCl_6^-$ anion.[13] The Raman spectra of all of the complexes studied present a strong depolarized band at 180 ± 10 cm^{-1} which has been assigned to the b_2 mode.

Ligand Vibration Shifts. $POCl_3$ and $SeOCl_2$ give molecular complexes with $SbCl_5$ and are coordinated through the oxygen atom.[5,6] In the Raman spectra of these adducts, the coordination is shown by the shifts of the symmetric and asymmetric normal modes ν(PCl), ν(SeCl), ν(PO), and ν(SeO) with respect to the spectra of the free oxychlorides[14,15] (Table III). As expected, the ν(PCl) and ν(SeCl) frequencies are increased whereas ν(PO) and ν(SeO) are strongly lowered. As shown by normal-coordinate analysis carried out on some adducts of Lewis acids,[9,16] these latter shifts arise simultaneously from the weakening of the force constants K(M–O) (M = Se, P) and the mechanical coupling generally observed between the M–O and Sb–O oscillators. Comparison between the spectra of free $OSCl_2$[17] and the $SbCl_5 \cdot OSCl_2$ adduct shows the same trend and is in agreement with the expected molecular structure of the complex.

Influence of the Donor Strength of the Ligands. Antimony pentachloride has been used by Gutmann[18] to define the donor strength of various Lewis bases from thermodynamic measurements. From x-ray crystallographic data, Lindqvist[3] and Weiss and Chevrier[2] have shown the relation between the donor strength and the Sb–O bond length in some oxygen donor complexes. From vibrational spectra, it is possible to correlate the position of the ν(SbO) vibration with the donor strength of the ligand; a definite decrease of the corresponding frequency is observed when the donor strength decreases. However, this mode has been shown to be strongly coupled with modes of the ligand by using deuteration (DMSO and DMF) and by carrying out a normal-coordinate analysis in the case of $SbCl_5 \cdot$DMSO.[9] Consequently, there is no simple correlation between the ν(SbO) frequency and the donor strength.

The Sb–Cl modes appear to be more directly related to the donor strength of the ligands. Their frequencies are decreased when the strength of the donors is increased. This trend appears clearly in the case of DMSO and $OSCl_2$ complexes, in which a difference of 10–15 cm^{-1} is observed for the ν(SbCl) stretching modes. The three oxychlorides can by classified in a similar manner. Using the position of the strongest Raman band, the order is as follows: $OSCl_2$ (344 cm^{-1}) < $OPCl_3$ (341 cm^{-1}) < $OSeCl_2$ (329.5 cm^{-1}). Further, it has been possible using these results to propose a molecular structure for $SbCl_5 \cdot OVCl_3$, $OVCl_3$ being a weak donor with a $\nu(a_1)(SbCl_4)$ frequency at 350 cm^{-1}.[19]

Registry No. $SbCl_5 \cdot OSCl_2$, 58298-20-7; $SbCl_5 \cdot OSeCl_2$, 58298-21-8; $SbCl_5 \cdot$DMSO, 23058-09-5; $SbCl_5 \cdot$DMF-h_7, 12075-62-6; $SbCl_5 \cdot$DMF-d_7, 58298-22-9; $SbCl_5 \cdot OP(CH_3)_3$, 37979-80-9; $SbCl_5 \cdot OPCl_3$, 18116-31-9.

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Fluorosulfates of the Lanthanide Elements

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Received April 10, 1975 AIC50261B

Fluorosulfates of scandium, yttrium, and most of the lanthanide elements in oxidation state III have been prepared by the action of peroxydisulfuryl difluoride upon anhydrous carbonates of the metals. When oxides of Nd, Sm, and Eu were used in place of carbonates, only part of the solid reacted.

Experimental Section

Synthesis. Peroxydisulfuryl difluoride, $S_2O_6F_2$, was prepared by allowing sulfur trioxide to react with fluorine.[1] Carbonates of the metals were produced by dissolving the appropriate oxide in dilute nitric acid and adding sodium bicarbonate to give a precipitate. The solid was washed with water followed by methanol. It was powdered in a mortar and dried for several hours at 110 °C. Oxides of metals used in these preparations were of a quality in which at least 99.9% of the rare earth element was the one desired.

In a typical preparation, about 1 mmol of a freshly prepared carbonate was placed in a Pyrex glass bulb which could be attached to a vacuum line by a ground joint and later closed by a Fischer and Porter Lab Crest valve having a Teflon stem. The vessel was held at about 70 °C and evacuated until it reached constant weight. It was then cooled to −183 °C, and peroxydisulfuryl difluoride, $S_2O_6F_2$, was added in sufficient amount to be present in excess for the reaction. When the vessel stood at room temperature or somewhat higher for about 15 h the following reaction occurred

$$M_2(CO_3)_3 + 3S_2O_6F_2 \rightarrow 2M(SO_3F)_3 + 3CO_2 + 1.5O_2$$