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Vibrational Spectra of the Molecular Adducts of $SbCl_3$ with Some Amides

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The molecular adducts formed between $SbCl_3$ and some aliphatic or aromatic amides are studied by infrared and Raman spectroscopy. The stability constants relative to the formation of adducts of 1:1 (K_1) and 1:2 (K_2) stoichiometry are calculated in C_6H_6 and in $CHCl_3$; in these solvents, $K_1 > K_2$.

The enthalpies of complex formation are weak (9.5 to 13.5 kJ mol^{-1}). The frequency shifts of the $\nu_{C=O}$ and the ν_{Sb-Cl} vibrations are discussed in function of electronic charge transfer effects.

The results suggest that the structure of the adducts may be different in the liquid and in the solid state.

Introduction

Some molecular adducts of $SbCl_3$ with carbonyl donors have been studied by infrared or Raman spectroscopy and it has been concluded that coordination occurs through the oxygen of the carbonyl group [1–5].

Although the stability constants of acetophenone [6–7], benzophenone [8–9] and γ-butyrolactam [4] with $SbCl_3$ have been determined in organic solvents, very few thermodynamic parameters have been reported for these addition compounds. In this work, we have determined the formation constant and the enthalpy of complex formation of this Lewis acid with the following amides: N,N-dimethylacetamide (DMA), dimethylformamide (DMF), N,N-dimethylbenzamide (DMBA), N-methylacetamide (NMA), benzamide (BA). The perturbations of the vibrational spectrum of $SbCl_3$ in solution and in the solid state are also discussed.

Experimental

The infrared spectra were recorded on Perkin-Elmer 325 and 180 spectrophotometers using cells with NaCl, Kbr, CsI and polyethylene windows. The temperature of the liquids was measured with a thermistance immersed in the cell. Raman spectroscopic measurements were carried out on a Coderg T800 spectrophotometer equipped with a 164 Ar^+ Laser (514.5 and 488 nm).

The solvents (*pur.* for spectroscopy) and the amides were distilled and dried on molecular sieves 4 Å.

$SbCl_3$ was utilized without further purification and kept under vacuum. The complexes in the solid state were prepared from equimolar mixtures of both components, recrystallized in diethylether and further handled in a dry nitrogen atmosphere.

Results and Discussion

Thermodynamic Parameters

The stability constants K_1 and K_2 are defined by the expressions

$$K_1 = \frac{[AD]}{[A]\,[D]} \text{ and } K_2 = \frac{[AD_2]}{[AD]\,[D]}$$

where [A] and [D] represent the equilibrium concentrations of $SbCl_3$ and amide, and [AD] and $[AD_2]$ the equilibrium concentrations of complexes of 1:1 and 1:2 stoichiometry. The K_1 and K_2 values are calculated by a method described in a previous publication [5] and the concentration of free donor is evaluated from the absorbance of the $\nu_{C=O}$ stretching band. The analytical concentration of $SbCl_3$ varies between 0.01 and 0.06 *M*. To avoid the auto-association of the primary and secondary amides, the analytical concentrations are maintained between 0.005 and 0.06 *M*; for higher concentrations, a second band appears at the low frequency side of the ν_{NH} or $\nu_{C=O}$ band, indicating dimerization of the amide molecule.

The formation enthalpy (ΔH_1^0) of the complexes of 1:1 stoichiometry is calculated from the K_1 values at two different temperatures.

The K_1 and K_2 values, listed in Table I, result from about fifteen experimental determinations.

These results show that in solution, the principal complex species is AD and that there is also a small amount of AD_2 species. The predominance of adducts of 1:1 stoichiometry is confirmed by the appearance of an isosbestic point in the $\nu_{C=O}$ region (Figure 1). Similar results were also obtained for the adducts of $SbCl_3$ with acetophenone [6–7] and 3-MeO benzamide [4].

TABLE I. Stability Constants K_1 and K_2 for the Adducts of $SbCl_3$ with Some Amides, T° = 298 °K.

Amide	Solvent	$K_1(dm^3 mol^{-1})$	$K_2(dm^3 mol^{-1})$
DMF	$CHCl_3 (\epsilon = 4.80)$	40.5 ± 1.9[a]	0.5 ± 1.5[a]
NMA	$CHCl_3$	46.2 ± 3.1[a,b]	2.4 ± 0.6[a,b]
DMA	$CHCl_3$	28.9 ± 0.3[a,b]	0.6 ± 0.5[a,b]
BA	$CHCl_3$	37.8 ± 1.8	5.3 ± 0.8
DMBA	$CHCl_3$	44.8 ± 2.5	3.8 ± 0.2
DMA	$C_2H_4Cl_2 (\epsilon = 10.23)$	338 ± 29	9.8 ± 0.3
DMF	$C_6H_6 (\epsilon = 2.28)$	229 ± 15	1 ± 0.6
NMA	C_6H_6	118 ± 11[b]	19.4 ± 2.3[b]
DMA	C_6H_6	274 ± 6[b]	3.3 ± 0.2[b]

[a] T° = 303 °K. [b] Values taken from reference 5.

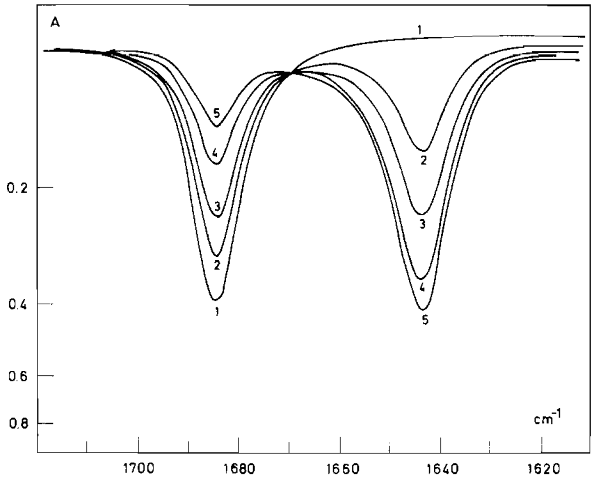

Figure 1. Infrared spectrum (1700–1600 cm^{-1}) of mixtures of $SbCl_3$ and DMF in benzene. Concentration of DMF = 0.026 *M*. Concentration of $SbCl_3$: (1) = 0; (2) = 0.007 *M*; (3) = 0.014 *M*; (4) = 0.026 *M*; (5) = 0.039 *M*.

There is no clear relation between the K values and the basic strength of the amide or the dielectric constant of the medium. As pointed out by Duyckaerts [7], the specific interactions between the solvent and the donor or acceptor molecules influence the stability of these complexes. The K_1 values are lower in $CHCl_3$ than in C_6H_6 and this fact can be explained by the formation of $C{=}O...HCCl_3$ hydrogen bonds which counter the further addition of the $SbCl_3$ molecule.

The relative donor ability of the amides toward $SbCl_3$ is found to be:

in C_6H_6: DMA > DMF > NMA
in $CHCl_3$: NMA > DMF > DMA

showing that only in C_6H_6, which does not specifically interact with the amides, the basic strength of the electron donors is preserved (pK_a of DMA = −0.19 and pK_a of NMA = −0.49).

The formation of an adduct of a Lewis acid with a carbonyl donor brings about a frequency lowering of the $\nu_{C=O}$ vibrations. The observed shifts are reported in Table II.

The lowering of the $\nu_{C=O}$ stretching vibration can be related to the weight of the dative structure, $b^2 + abS$ defined by the theory of Mulliken [12]. In this expression, a and b are the coefficients of the wave function in the no-bond and dative state and S is the overlap integral. It can be shown that

$$\frac{k^0 - k^c}{k^c - k^1} \simeq \frac{b^2 + abS}{1 - (b^2 + abS)}$$

TABLE II. Wavenumber of the $\nu_{C=O}$ Vibration in the Free and Complexed Amides Molecules, and Weight of the Dative Structure $b^2 + abS$.

Amide	Solvent	$\nu_{C=O}$ free (cm^{-1})	$\nu_{C=O}$ compl (cm^{-1})	$\Delta\nu_{C=O}$ (cm^{-1})	$b^2 + abS$
DMF	$CHCl_3$	1672	1643	29	0.07
NMA	$CHCl_3$	1670	1630	40	0.10
DMA	$CHCl_3$	1635	1597	38	0.10
BA	$CHCl_3$	1677	1645	32	0.08
DMBA	$CHCl_3$	1623	1590	33	0.09
DMA	$C_2H_4Cl_2$	1645	1593	52	0.14
DMF	C_6H_6	1685	1644	41	0.10
NMA	C_6H_6	1685	1628	57	0.15
DMA	C_6H_6	1659	1599	60	0.16

TABLE III. K_1 Values at 323 °K, Enthalpy and Entropy of Complex Formation for Some of the Adducts of SbCl$_3$ with Amides.

Amide	Solvent	$K_1^{323\,°K}$ (dm^3 mol^{-1})	$-\Delta H_1^\circ$ (kJ mol^{-1})	$-\Delta S_1^\circ$ (J mol^{-1} K^{-1})
DMF	CHCl$_3$	32 ± 0.9	9.6	1
NMA	CHCl$_3$	33.7 ± 1.5	12.6	9.6
DMA	CHCl$_3$	22.4 ± 0.6	10.5	6.7
BA	CHCl$_3$	27.8 ± 0.8	10	3.3
DMBA	CHCl$_3$	34.2 ± 2.9	10.9	12.6
DMA	C$_2$H$_4$Cl$_2$	224 ± 12	13.4	3.3

TABLE IV. Wavenumber of the $\nu_{s\,Sb-Cl}$ and $\nu_{as\,Sb-Cl}$ Vibrations in the Free and Complexed SbCl$_3$ Molecule[a].

Amide	Solvent	ν_s free (cm^{-1})	ν_s compl (cm^{-1})	$\Delta\nu_s$ (cm^{-1})	ν_{as} free (cm^{-1})	ν_{as} compl (cm^{-1})	$\Delta\nu_s$ (cm^{-1})
DMF	CH$_2$Cl$_2$	369	358	11	344	337	7
NMA	CH$_2$Cl$_2$	369	356	13	344	334	10
DMA	CH$_2$Cl$_2$	369	354	15	344	334	10
DMA	C$_6$H$_6$	366	339	27	339	304	35
BA	CH$_2$Cl$_2$	369	357	12	344	335	9
DMBA	CH$_2$Cl$_2$	369	356	13	344	335	10

[a] Infrared results; the ν_{Sb-Cl} Raman bands are 1 cm^{-1} lower.

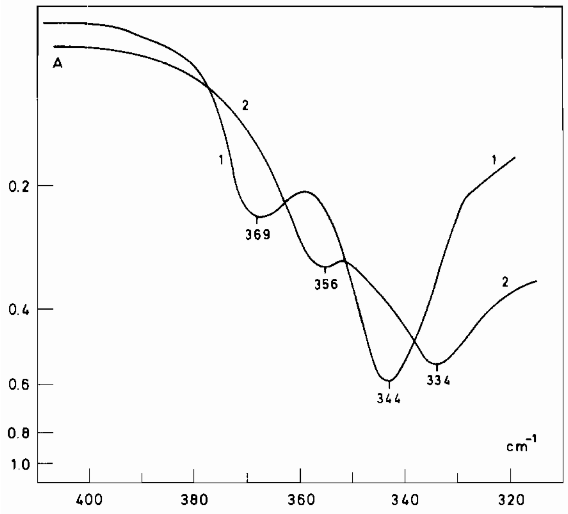

Figure 2. Infrared spectrum in the ν_{Sb-Cl} region of mixtures of SbCl$_3$ and NMA in CH$_2$Cl$_2$. Concentration of SbCl$_3$ = 0.057 *M*. Concentration of DMF: (1) = 0; (2) = 0.13 *M*.

where k^0 and k^c are the force constants of the free and complexed carbonyl bond; k^1, the force constant of the same bond in the dative state was found to be approximately equal to 600 Nm^{-1} [13]. The calculated values of $b^2 + abS$ are also listed in Table II. These values – like the K_1 values – are weaker in CHCl$_3$ than in C$_6$H$_6$ and this can be explained by the concurrent charge transfer in the C=O...H–C hydrogen bond. In the three mentioned solvents, the charge transfer remains moderate, suggesting that the complexes between the amides and SbCl$_3$ in solvents of low dielectric constants are essentially non-ionic in nature. The low molar conductivity of Sb(III) halide–tetramethyldithiooxamide complexes also suggests a non electrolytic behaviour for these adducts [14].

The formation enthalpies and entropies for the 1:1 complex are listed in Table III. These results show that the $-\Delta H_1^\circ$ and $-\Delta S_1^\circ$ values are weak for all the studied complexes. Low $-\Delta H_1^\circ$ and $-\Delta S_1^\circ$ were also obtained for the adducts of ZnCl$_2$ and SnCl$_4$ with benzamide derivatives [4]. Gutman and Czuba [2] however reported a higher value for the DMA·SbCl$_3$ complex (36 kJ mol^{-1}) in 1,2-dichloroethane as solvent. Further the $-\Delta H_1^\circ$ values obtained in CHCl$_3$, do not reflect the intrinsic basicity of the amides. In 1,2-dichloroethane, where the charge transfer is more pronounced, the enthalpy of complex formation is somewhat higher.

ν_{Sb-Cl} Vibrations in Solution

Complex formation with a donor brings about a lowering of the ν_{as} and ν_s Sb–Cl bands [15–17]. The wavenumbers of these two vibrations are indicated in Table IV and the infrared spectrum in the ν_{Sb-Cl} range is reported in Figure 2 for the NMA adduct.

No splitting of the ν_{Sb-Cl} vibrations has been observed in solution and this fact suggests that the C_{3v} structure of the SbCl$_3$ molecule is not substantially deformed by complex formation with an amide.

For the adduct of the same Lewis acid with tributylphosphate, Roland *et al.* [16], however, reported three ν_{Sb-Cl} bands in the Raman spectrum, suggesting a C_{2v} or C_s structure.

In C_6H_6, the ν_{Sb-Cl} band is observed at 3–5 cm^{-1} lower than in CH_2Cl_2; this fact can be explained by a weak specific interaction between this solvent and $SbCl_3$ [18–20]; as suggested many years ago by Daash [21], a great separation of charge does not occur in this complex and this is confirmed by the small differences observed in C_6H_6 and CH_2Cl_2. The frequency shifts listed in Table IV are related to the charge transfer taking place from the oxygen of the carbonyl group to the d vacant orbital of the Sb atom. Figure 3 shows that the $\Delta\nu_{Sb-Cl}$ values are related to b^2 + abS (these two parameters are compared in $CHCl_3$ and in CH_2Cl_2 which do not strongly differ). Moreover, it appears from this figure that the extrapolated curves go not far from the origin and this fact suggests that the b^2 + abS values, computed from a vibrational mode of the donor molecule, are approximately correct.

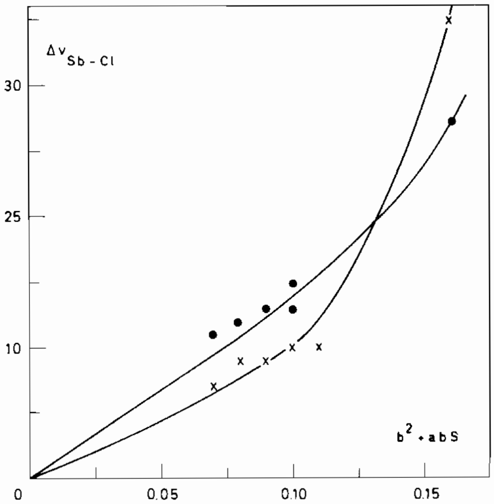

Figure 3. $\Delta\nu_{Sb-Cl}$ as a function of b^2 + abS. ● $\Delta\nu_s$; × $\Delta\nu_{as}$.

The bending vibrations lying between 160 and 120 cm^{-1} did not show any appreciable change on complex formation, either in the infrared or in the Raman spectrum.

DMA·$SbCl_3$ Adduct in the Solid State

The elemental analysis of the DMA·$SbCl_3$ adduct has been performed in the Laboratory of Dr. Malissa [22]. The analytical data are reported in Table V and show that in the solid state the molecular adduct is also characterized by a 1:1 stoichiometry.

In the ν_{Sb-Cl} region, the Raman spectrum of the DMA·$SbCl_3$ adduct is characterized by the presence of *three* diffusion bands at 335, 324 and 305 cm^{-1} (Figure 4), suggesting that the three Sb–Cl bonds are no more equivalent in the solid DMA·$SbCl_3$ adduct. In the free $SbCl_3$ crystal, Tramer [23] reported bands at 343, 320 and 315 cm^{-1} and showed that the degenerate frequency is split in the crystal state; this effect should be ascribable to the non equivalence of the three Sb–Cl bonds whose lengths are equal to 2.35 and 2.37 Å respectively [24]. In the solid DMA·$SbCl_3$ adduct, the splitting of the degenerate frequencies is a little more pronounced than in the free molecule, suggesting that one of the Sb–Cl bonds is more stretched than the two others. This shows that the most probable structure is similar to that of the Aniline–$SbCl_3$ adduct, where the configuration about the antimony is that of a distorted trigonal bipyramid [25]; in this complex, a chlorine and a nitrogen atom occupy the axial position and the Sb–Cl distance (2.51 Å) is markedly longer than the two Sb–Cl bonds in the equatorial position (2.33 Å).

TABLE V. Analytical Data for the DMA·$SbCl_3$ Adduct.

Calculated (%)				Found (%)			
Sb	38.62	O	5.07	Sb	38.90	O	5.27
Cl	33.74	C	15.24	Cl	33.51	C	15.07
N	4.44	H	2.88	N	4.33	H	2.81

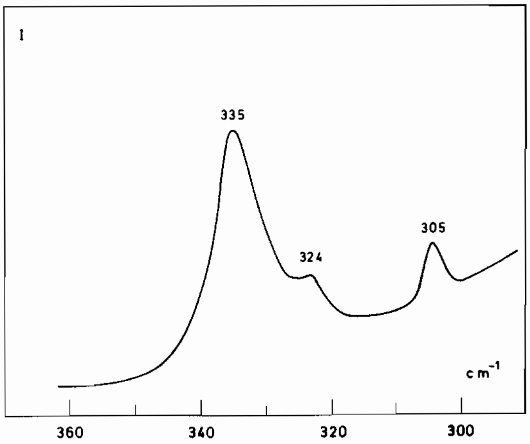

Figure 4. Raman spectrum of the solid DMA·$SbCl_3$ adduct (Ar^+ Laser with a power of 150 mW. Slit = 200 μ).

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