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Vibrational spectroscopic study of some benzonitrile complexes of antimony pentachloride

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Abstract—Complexes of antimony pentachloride were prepared with benzonitrile, 2,3- and 4-methylbenzonitriles, and 2,3-; 2,4-; 2,5- and 3,4-dimethylbenzonitriles of the type $SbCl_5 \cdot L$. All the isolated solids were non-electrolytes in nitromethane. The i.r. and Raman spectral data of the complexes are in good agreement with local C_{4v} symmetry for the $SbCl_5N$ moiety. A classification of the donor strength of benzonitriles is proposed.

INTRODUCTION

Numerous studies have been made in the last few years on addition complexes of antimony pentachloride with different bases [1]. Of particular interest are those studies on the vibrational spectra of $SbCl_5 \cdot L$ complexes, with C_{4v} symmetry, where L is a nitrogen donor such as: NCBr and NCCl [2], $NCCH_3$ [3, 4] and NCR [R = CCl_3, CH_2Cl, CH_2CH, $(CH_3)_3C$, (C_6H_5), $NC(CH_2)_nCN$] (n = 1, 2, 3, 4) [5] or an oxygen donor such as DMSO [6, 7], DMF [6, 8], $OSeCl_2$, $OSCl_2$ [8], $OP(CH_3)_3$ [8, 9] and $OPCl_3$ [9].

The present paper describes the studies made on the addition compounds of antimony pentachloride and benzonitrile (BN), 2-methylbenzonitrile (2-MBN), 3-methylbenzonitrile (3-MBN), 4-methylbenzonitrile (4-MBN), 2,3-dimethylbenzonitrile (2,3-DMBN), 2,4-dimethylbenzonitrile (2,4-DMBN), 2,5-dimethylbenzonitrile (2,5-DMBN) and 3,4-dimethylbenzonitrile (3,4-DMBN) to compare the variation in some of the physical properties of the complexes with the parameters of the ligand substituents.

EXPERIMENTAL

Materials

Antimony pentachloride (Carlo Erba) was vacuum distilled. Solid nitriles (Merck or Fluka) were recrystallized from benzene or benzene–petroleum ether. Liquid nitriles (Merck or Fluka) were dried and distilled through a vigreux column under reduced pressure, the middle fractions being collected. Benzene (Merck) for spectrophotometry was used without further purification. The other solvents, cyclohexane, 1,2-dichloroethane and nitromethane (Carlo Erba or Merck) were dried and purified by standard methods.

Preparation of complexes

All preparations and sampling were made in a dry-box, which was continuously flushed with dry nitrogen.

The complexes were prepared by dropwise addition at room temperature of a solution of the nitrile (24.9 mmol) in dry cyclohexane (25 cm^3) to a solution of the antimony pentachloride (3.2 cm^3 approx. 24.9 mmol) in the same solvent (50 cm^3) under continuous stirring. The mixture was stirred for about 2–3 h. The precipitate was filtered off, washed several times with cyclohexane, recrystallized from hot 1,2-dichloroethane and dried *in vacuo* at room temperature.

Analytical procedure

C, N and H were analysed with a Perkin–Elmer 240 apparatus in the Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Zaragoza, Spain. Chloride was determined as AgCl and Sb was determined volumetrically [10]. The analytical results, together with some physical properties, are given in Table 1.

Physical measurements

Infrared spectra were recorded as Nujol or Hexachlorobutadiene mulls between CsI plates (4000–250 cm^{-1}) and polyethylene windows (500–180 cm^{-1}) on a Perkin–Elmer I.R.-180 spectrophotometer. The Raman spectra, of samples sealed in Pyrex tubes, were recorded with a Jarrell-Ash spectrophotometer model 25–300. The red

Table 1. Analytical data, found % (calcd. %) and molar conductivity Ω_M (ohm^{-1} mol^{-1} cm^2) in 10^{-3} M. Nitromethane solution at 20°C for benzonitrile derivative complexes

	Sb	Cl	C	N	H	Colour	M.p.ºC	Λ_M
$SbCl_5 \cdot$BN	30.00(30.27)	43.83(44.08)	20.88(20.90)	3.21(3.48)	1.32(1.25)	White	130	25.9
$SbCl_5 \cdot$2-MBN	28.77(29.25)	42.20(42.60)	22.84(23.09)	3.11(3.36)	1.81(1.69)	White	90	22.7
$SbCl_5 \cdot$3-MBN	29.10(29.25)	42.01(42.60)	22.56(23.09)	3.17(3.36)	1.85(1.69)	Pale yellow	87 dec.	21.2
$SbCl_5 \cdot$4-MBN	28.92(29.25)	42.05(42.60)	22.70(23.09)	2.94(3.36)	1.77(1.69)	Yellow	90 dec.	19.8
$SbCl_5 \cdot$2,3-DMBN	27.91(28.30)	40.81(41.20)	24.46(25.13)	3.21(3.25)	2.13(2.11)	Pale yellow	85	16.3
$SbCl_5 \cdot$2,4-DMBN	28.10(28.30)	40.92(41.20)	25.00(25.13)	3.12(3.25)	2.33(2.11)	Pale yellow	100	17.5
$SbCl_5 \cdot$2,5-DMBN	28.06(28.30)	40.99(41.20)	25.02(25.13)	3.14(3.25)	2.25(2.11)	Yellow	90	19.9
$SbCl_5 \cdot$3,4-DMBN	28.03(28.30)	40.87(41.20)	24.98(25.13)	3.20(3.25)	2.17(2.11)	Light beige	80	21.1

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632.8 nm line of a He–Ne laser (Spectra Physics 125) and the green 514.5 nm line of an Ar^+ (Coherent Radiation Model 52) served as exciting lines. The Raman spectra were recorded at room temperature in benzene (400–200 cm^{-1}) and 1,2-dichloroethane (250–80 cm^{-1}) solutions.

The conductivity measurements were carried out employing a Metrohm Herisau, model E-518, at 20°C for 10^{-3} M solutions in nitromethane.

RESULTS AND DISCUSSION

The analytical data (Table 1) suggest that the general formula for these complexes is $SbCl_5{\cdot}L$. For a stoichiometry of this type there are two possible structures: a molecular one and an ionic one $[SbCl_6]^-$ $[SbCl_4L_2]^+$ [11]. Conductivity measurements of the compounds in nitromethane (Table 1) display a non-electrolyte behaviour in this solvent [12]. These data and the results of i.r. and Raman spectroscopy (*vide infra*) are in agreement with the molecular structure of the complexes.

If we consider the ligand to be a point mass, the molecule $SbCl_5{\cdot}L$ would have approximately a C_{4v} symmetry, for which 15 normal vibrations are expected: $4A_1 + 2B_1 + B_2 + 4E$. Of these, the A_1 and E modes are both Raman and i.r. active and the B_1 and B_2 species are Raman active. Moreover, by group theory five stretching modes can be expected for this symmetry: three A_1 modes which represent the SbN, $SbCl_{ax.}$ and $SbCl_4$ stretches, and the B_1 and E modes, which are $SbCl_4$ stretching vibrations.

Table 2 gives the bands observed in the 80–400 cm^{-1} region for i.r. and Raman spectra. A typical spectrum is shown in Fig. 1.

The intense to very intense band, observed in i.r. in the 350–370 cm^{-1} range, is attributed to the A_1 symmetry $\nu(SbCl_{ax.})$ mode. This same band is generally observed in Raman spectra as a polarized band of medium to very high intensity. The occasional observed splitting of this band in the Raman spectrum could be considered to be due to the isotopic effect of the ^{35}Cl and ^{37}Cl, to a combination band at around 185 cm^{-1} and 165 cm^{-1} in Fermi resonance with the $A_1\nu(SbCl_{ax.})$ or to an harmonic of the band at *ca* 175 cm^{-1}.

On the other hand, the band which is observed in the i.r. spectrum as a shoulder in the 330–340 cm^{-1} region generally appears in the Raman spectrum as the most intense band and, as it is polarized, it is assigned to the $A_1\nu(SbCl_4)$ mode.

The medium intensity and depolarized band observed in the 290–310 cm^{-1} region of the Raman spectrum does not appear in the i.r. spectrum and can be assigned to the $B_1\nu(SbCl_4)$. At times this band is observed to be split, which can be interpreted as due to a combination of the fundamental bands at *ca* 165 and 135 cm^{-1}, in Fermi resonance with the $B_1\nu(SbCl_4)$ mode.

In certain cases, a band appears in the i.r. spectrum in the 365–375 cm^{-1} region. This band is not observed in the Raman spectrum of the solution but it appears as a band of very low intensity in the Raman spectrum of the solid state. This is likewise often observed for the E mode in molecules with C_{4v} symmetry [4, 13], and it was therefore assigned to the E mode $\nu(SbCl_4)$.

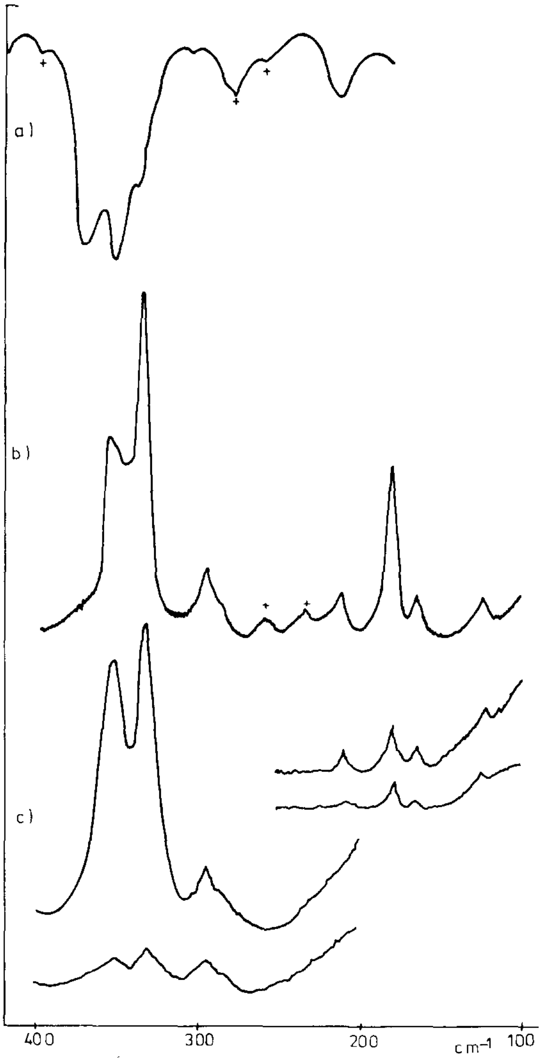

Fig. 1. Infrared and Raman spectra of $SbCl_5{\cdot}$3,4-DMBN: (a) i.r. spectrum of the adduct in the solid state; (b) Raman spectrum in the solid state; (c) Raman spectrum in the range 200–400 cm^{-1} in benzene and of 80–250 cm^{-1} in 1,2-dichloroethane solutions, the upper and lower curves denote two directions of polarization (perpendicular and parallel respectively). A cross (+) signifies a line which does not belong to the $NSbCl_5$ moiety.

With regard to the $A_1\nu(SbN)$ vibration, bibliographic data are frequently contradictory. KAWAI and KANESAKA [2], however, assign to this mode to the vibration at 209 and 213 cm^{-1} in $Cl_5Sb{\cdot}NCCCl$ and $Cl_5Sb{\cdot}NCBr$ respectively. BYLER and SHRIVER [4] assign this same vibration at 220 cm^{-1} in $Cl_5SbNCCH_3$. MASSON *et al.* [5] have later made the assignment in the 200–240 cm^{-1} region for $SbCl_5$ adducts with different nitriles.

All compounds obtained in the present study display in the i.r. a band of medium to weak intensity, and of

Table 2. Infrared and Raman frequencies (cm^{-1}) for the $SbCl_5N$ moiety in the complexes

BN			2-MBN			3-MBN			
i.r.	Raman Solid	Raman Soln.	i.r.	Raman Solid	Raman Soln.	i.r.	Raman Solid	Raman Soln.	Assignments
	83 m			98 m	102 m,dp		95 m	93 w,dp	lattice vibrations
	112 m	110 w,dp		123 w	127 w,dp		102 m	100 w,dp	
							125 w		
	131 m	131 m,dp		142 m			140 m	138 m,dp	$E\ \delta(SbCl_4)$
	167 m	162 w,dp		168 w	170 w,dp		170 m	174 m,dp	$E\ \delta(Cl_{ax.}SbCl_{eq.})$
	184 m	183 w,dp		183 m	183 w,dp		183 m	189 m,dp	$B_2\ \delta(SbCl_4)$
228 m	235 w	232 w, p	223 w	220 vw	225 w, p	214 m	220 w	220 w, p	$A_1\ \nu(SbN)$
263 s			262 w	257 vw		265 sh			ligand vibrations
276 s			276 vw			280 m			
	296 m	297 w,dp		290 m	295 w,dp		295 m	294 w,dp	$B_1\ \nu(SbCl_4)$
	300 m	300 w,dp							
325 sh			322 sh			324 sh			ligand vibration
340 sh	338 vs	333 vs,p	345 sh	340 vs	336 m,p	343 sh	342 vs	340 vs,p	$A_1\ \nu(SbCl_4)$
350 s,br	350 s	352 sh,p	366 vs	370 m	354 m,p	357 vs	350 sh	354 vs,p	$A_1\ \nu(SbCl_{ax.})$
	355 s	354 vs,p			365 m,p		360 m		
370 sh	367 vw					372 sh			$E\ \nu(SbCl_4)$
	374 vw								

4-MBN			2,3-DMBN			2,4-DMBN			
i.r.	Raman Solid	Raman Soln.	i.r.	Raman Solid	Raman Soln.	i.r.	Raman Solid	Raman Soln.	Assignments
	105 w			94 w	92 vw		95 w	92 vw	lattice vibration
	130 m	131 m,dp		140 m,b	136 m,dp		130 m	136 m,dp	$E\ \delta(SbCl_4)$
	169 w	166 vw		165 vw	162 vw		164 vw		$E\ \delta(Cl_{ax.}SbCl_{eq.})$
				174 w	172 w,dp		175 w	176 m,dp	$A_1\ \delta(SbCl_4)$
	195 m	190 m,dp		184 m	180 m,dp		189 w	187 vw	$B_2\ \delta(SbCl_4)$
224 w	230 vw		230 w	232 w	233 w,p		217 m	219 m,p	$A_1\ \nu(SbN)$
260 w			265 w			262 w			ligand vibrations
276 vw	272 vw		275 sh			278 w			
	295 m	294 m,dp		295 m	300 m,dp		295 m	295 m,dp	$B_1\ \nu(SbCl_4)$
	305 w								
325 sh			322 sh						ligand vibration
343 sh	340 vs	342 vs,p	348 sh	342 vs	344 s,p	335 sh	328 s	327 vs,p	$A_1\ \nu(SbCl_4)$
358 vs	364 m	366 vs,p	358 vs	362 m	359 vs,p	350 vs	352 sh	350 s,p	$A_1\ \nu(SbCl_{ax.})$
							356 s	354 sh,p	
						370 sh			$E\ \nu(SbCl_4)$

2,5-DMBN			3,4-DMBN			
i.r.	Raman Solid	Raman Soln.	i.r.	Raman Solid	Raman Soln.	Assignments
	95 w	97 w,dp		108 w	108 w,dp	lattice vibrations
	105 vw					
	117 w	112 vw,dp				
	134 m	132 m,dp		126 w	126 w,dp	$E\ \delta(SbCl_4)$
	168 w	169 w,dp		165 w	168 w,dp	$E\ \delta(Cl_{ax.}SbCl_{eq})$
	190 m	183 w,dp		185 s	185 m,dp	$B_2\ \delta(SbCl_4)$
230 m	230 vw	237 vw	210 w	211 w	214 w,p	$A_1\ \nu(SbN)$
				225 vw		ligand vibration
257 m			255 sh	253 vw		
278 vw			278 w			
	295 m	294 m,dp		288 sh	293 m,dp	$B_1\ \nu(SbCl_4)$
	310 w			296 m		
325 sh			320 sh			ligand vibration
340 sh	340 vs	341 vs,p	336 sh	334 vs	332 vs,p	$A_1\ \nu(SbCl_4)$
				349 sh		$A_1\ \nu(SbCl_{ax.})$
366 vs	370 m	363 vs,p	350 vs	354 s	355 s,p	
			369 vs			$E\ \nu(SbCl_4)$

weak to very weak intensity in Raman. This band is polarized in the 210–230 cm^{-1} region and we attribute it to the ν(SbN) mode with A_1 symmetry.

The assignment of deformation vibrations, to be found below 210 cm^{-1}, cannot be made without ambiguity due to the fact that the bands observed below this frequency in the Raman spectrum for 1,2-dichloroethane solution were not polarized, and also due to the fact that it was impossible to make an i.r. spectrum in this region because of instrumental limitations. In spite of this, a tentative assignment has been made (Table 2) of some of the bands, by comparing them with those of the study on the $SbCl_5$ adduct with acetonitrile [4]. Hence, the low intensity band at around $165 cm^{-1}$ could be one of the *E* types of in-plane deformation $\delta(SbCl_4)$ or a wag $\delta(Cl_{ax.}SbCl_{eq.})$.

As type *B* deformations are assigned to higher frequencies than those of A_1 or *E* modes, the band at around $185 cm^{-1}$ can reasonably be assigned to the in-plane bending $\delta(SbCl_4)$ with B_2 symmetry. The band at around $135 cm^{-1}$ was assigned to the in-plane bending $\delta(SbCl_4)$ with *E* symmetry. The latter assignment is in agreement with the idea that the band at around $300 cm^{-1}$, in the Raman spectrum, is a combination of the fundamental bands, at 165 and $135 cm^{-1}$, in Fermi resonance with the stretching $\nu(SbCl_4)$ with B_1 symmetry.

Nevertheless in all cases it was observed that the i.r. and Raman spectra of the organic part of the complex, with respect to that of the free ligand, underwent certain variations [14], such as shifts in frequency and changes in intensity of certain bands. The largest shift observed is in the $\nu(CN)$ vibration (Table 3) and the fact that this shift takes place at higher frequencies could indicate that coordination is brought about through the nitrogen to the antimony.

Finally, antimony pentachloride has been used by various authors to define the donor strength of various Lewis bases, using thermodynamic [15], crystallographic [9, 16] and vibrational [5, 8] data. The shift in the valency vibration $\nu(CN)$ of the complexes enabled us to establish the following order of donor strength of the different benzonitriles:

BN < 3-MBN < 2,5-DMBN $\simeq$ 2-MBN < 2,3-DMBN < 4-MBN $\simeq$ 3,4-DMBN < 2,4-DMBN.

This sequence is practically the same as that followed by the electronic constants of the substituents. A clearer example is given in Fig. 2 where $\Delta\nu(CN)$ is plotted vs σ. The fact that in this plot there is an almost linear correlation suggests that, in these cases, the donor strength depends on the electronic effects of the substituents and that the steric effects are either null or very small.

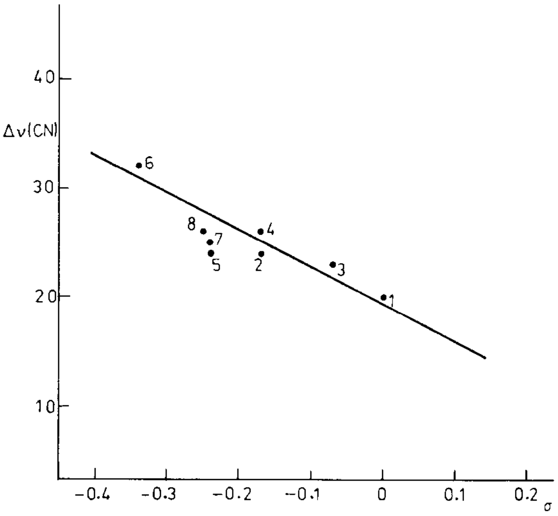

Fig. 2. Plot of $\Delta\nu(CN)$ against Hammett or Taft parameters (σ): (1) BN; (2) 2-MBN; (3) 3-MBN; (4) 4-MBN; (5) 2,3-DMBN; (6) 2,4-DMBN; (7) 2,5-DMBN and (8) 3,4-DMBN.

Table 3. Infrared spectra results in the $\nu(CN)$ region (cm^{-1})

Base	Base	Adduct	Δ ν (CN)
BN	2230 s	2250 s	20
2-MBN	2226 vs	2250 vs	24
3-MBN	2229 vs	2252 vs	23
4-MBN	2229 s	2255 m	26
2,3-DMBN	2224 vs	2248 vs	24
2,4-DMBN	2221 vs	2253 s	32
2,5-DMBN	2225 vs	2250 s	25
3,4-DMBN	2225 s	2251 s	26

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