Complexes of Antimony Pentachloride with Some 4-Substituted Pyridine N-Oxides

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The complexes $SbCl_5 \cdot L$ (where L = 4-methoxy-pyridine N-oxide, 4-chloropyridine N-oxide, 4-cyano-pyridine N-oxide, 4-nitropyridine N-oxide and 3-ethyl carboxilatepyridine N-oxide) have been isolated and investigated by conductivity, UV and IR spectral measurements. The IR spectra in the range 600–250 cm^{-1} are consistent with a C_{4v} symmetry. The N–O stretching vibration was insensitive to the substituent variations in the complexes with 4-Z-pyO ligands (where Z = CH_3O, CH_3, H, Cl, CN, NO_2). There is no linear correlation between the Sb–O stretching modes and the σ_{pyo} parameters. A better correlation of the latter with the π–π^* ligand band position was found.

Introduction

The interaction of antimony(III) and (V) chlorides with pyridine N-oxide and some pyridine N-oxide derivatives was investigated in a preceding work [1]. Furthermore we considered interesting to extend the number of systems studied, including other 4-substituted ligands, in order to discuss the variation of some physical properties of the complexes with substituent parameters of the ligands [2]. Therefore, the interaction between antimony pentachloride and 4-methoxypyridine N-oxide (4-CH_3O-PyO), 4-chloropyridine N-oxide (4-Cl-PyO), 4-cyanopyridine N-oxide (4-CN-PyO), 4-nitropyridine N-oxide (4-NO_2-PyO) was investigated and the results are now described. This paper also includes the preparation and properties of the adduct $SbCl_5 \cdot EtNNO$ (where EtNNO is 3-Ethylcarboxylatepyridine N-oxide).

Experimental

Materials

Antimony pentachloride (Carlo Erba) was vacuum distilled. The aromatic amine oxides (Fluka or Aldrich) were recrystallized from 1,2-dichloroethane. Solvents were purified by the usual methods.

Preparation of Complexes

$SbCl_5 \cdot 4$-Cl-PyO. The aromatic amine oxide (0.7526 g, 0.0058 mol) was dissolved in 40 ml of dry 1,2-dichloroethane and the solution was added dropwise to a magnetically stirred antimony pentachloride solution (0.5 ml, approx. 0.004 mol) in 25 ml of the same solvent. The white solid formed was isolated by filtration, recrystallized from hot 1,2-dichloroethane and vacuum dried.

A similar preparation was carried out with the other complexes. $SbCl_5 \cdot EtNNO$ was recrystallized from dichloromethane. $SbCl_5 \cdot 4$-NO_2-PyO and $SbCl_5 \cdot 4$-CN-PyO were not recrystallized because of their scarce solubility in organic solvents of low dielectric constant. They were washed with 1,2-dichloroethane and vacuum dried.

Although all the complexes were quite stable to hydrolysis (the 4-CH_3O-PyO adduct was apparently unchanged by air moisture) they were handled, as far as possible, in a dry box.

Analytical Procedure

C, N and H were analyzed with a Perkin–Elmer 240 apparatus in the Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Zaragoza (Spain). The analytical results, together with some physical properties, are given in Table I.

Physical Measurements

These were carried out employing the apparatus which has been described previously [1]. Dielectrometric titrations were not performed due to the low solubility of the complexes in nonpolar solvents. The π–π^* ligand band position in the $SbCl_5 \cdot 4$-NO_2-PyO adduct was not localized with acceptable precision, because the spectrum shows time variation, indicating a possible decomposition of the compound with UV radiation. The molar conductivities have been measured in acetonitrile.

Results and Discussion

The conductometric titrations in 1,2-dichloroethane are shown in Fig. 1. The specific conductivity of the solutions (χ) decreases until a donor/acceptor

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TABLE I. Analytical and Physical Data of Complexes.

Compound	% C	% N	% H	Colour	M.P. (°C)[b]	Λ[c]
SbCl$_5$·4-Cl-PyO	13.97 (14.01)[a]	3.06 (3.27)	0.86 (0.94)	White	255	3
SbCl$_5$·4-NO$_2$PyO	13.61 (13.68)	5.78 (6.38)	0.75 (0.92)	Pale Yellow	255–260	5
SbCl$_5$·4-CH$_3$O-PyO	16.89 (16.99)	3.04 (3.30)	1.38 (1.66)	Yellow	220	2
SbCl$_5$·4-CN-PyO	18.50 (17.19)	6.76 (6.68)	0.93 (0.96)	White	250	12
SbCl$_5$·EtNNO	20.89 (20.61)	2.82 (3.01)	1.76 (1.95)	White	137–140	9

[a]Theoretical percentage in brackets. [b]Some complexes undergo colour change before melting. Above the m.p. liquids are yellow or red. [c]Concentration in acetonitrile ~$10^{-3}M$ (ohm^{-1} cm^2 mol^{-1}). Under similar conditions, 1:1 electrolytes normally exhibit Λ = 120–160 ohm^{-1} cm^2 mol^{-1} [5].
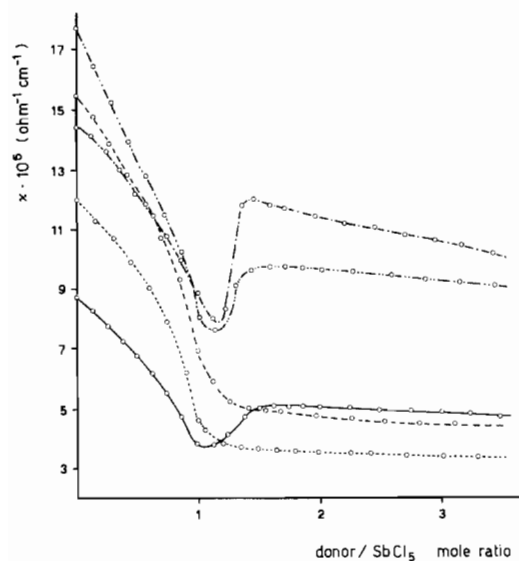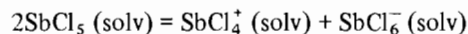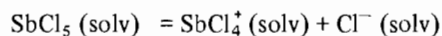

Figure 1. Conductometric titrations in 1,2-dichloroethane of SbCl$_5$ with ····· 4-CH$_3$O-PyO, ········ EtNNO, —— 4-Cl-PyO, ----- 4-CN-PyO, ····· 4-NO$_2$-PyO.

Figure 2. Correlations of σ_{PyO} with the π–π^* band position in the free ligands (O) and complexes (Δ).

molar ratio (MR) of approx. 1 is reached. Beyond this point, the χ values are nearly constant. This behavior is consistent with a weak ionization of the initial halide solutions. Although the acetonitrile ionization–dissociation mechanism of SbCl$_5$ has been studied in detail [3, 4], the proposed equilibria:

$$SbCl_5 \text{ (solv)} = SbCl_4^+ \text{ (solv)} + Cl^- \text{ (solv)}$$

$$2SbCl_5 \text{ (solv)} = SbCl_4^+ \text{ (solv)} + SbCl_6^- \text{ (solv)}$$

cannot be extrapolated to 1,2-dichloroethane, due to the different properties of this solvent. Nevertheless, any ionic equilibria existing in the initial acceptor solutions will be retrograded by the transformation of the halide molecular form in the non-electrolyte (see Table I and Ref. 5) SbCl$_5$·L adduct. This would give a decrease of the specific conductivity until the MR 1 is reached, in agreement with the experimental data.

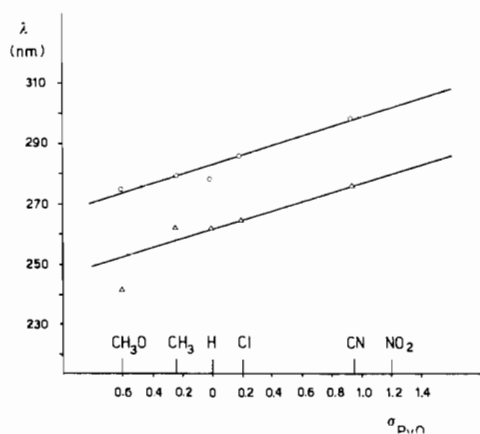The π–π^* ligand band position corresponding to the UV spectra of the complexes and the free ligands

is plotted *versus* σ_{PyO} in Fig. 2 (the values of PyO and 4-PicO [1] are included). The λ_{max} in the non-coordinated bases apparently shows a linear correlation with the sigma parameters (except for 4-NO$_2$-PyO), following a sequence according to the modification of the π^* orbital energy with the ring substituents [6]. Theoretical studies [7] associate this band with a charge transfer from the oxygen atom of the N–O group to the ring. For this reason, the band position will be affected by the donor–acceptor process. In fact, the adduct spectra showed a blue shift (Fig. 2) in agreement with the preceding literature work [1, 8, 9].

This blue shift can be justified by a drain of electron density from the oxygen to the metal. This drain raises the oxygen electronegativity, decreasing its contribution to the π system of the ligand and increasing the π^* orbital energy. Nevertheless, the linearity of λ_{max} *versus* σ_{PyO}, apparently decreases with electron-releasing substituents on the ring (really, there is too few data for concluding a diminishing linearity in these adducts or a different sequence of λ_{max} *versus* σ_{PyO} as compared with the systems with electron-withdrawing substituents). This discontinuity can be an evidence of a different mechanism in the metal–oxygen bond (sigma–pi or

TABLE II. More Relevant IR Data (cm⁻¹) of Ligands and Complexes.

Compound	ν_{N-O}	ν_{Sb-Cl}			ν_{Sb-O}
4-CH₃O-PyO	1205 vs	−			−
SbCl₅·4-CH₃O-PyO	1190 vs	355 s,	335 s,	320 m	450s
4-PicOª	1249 vs	−			−
SbCl₅·4-PicOª	1200 vs	360 s,	345 vs,	330 m	440 s
PyO	1250 vs	−			−
SbCl₅·PyOª	1192 vs	350 vs,	315 m		400 s
4-Cl-PyO	1245 vs	−			−
SbCl₅·4-Cl-PyO	1190 vs	360 s,	345 vs,	320 sh	405 w
4-CN-PyO	1275 vs	−			−
SbCl₅·4-CN-PyO	1195 vs	365 m,	340 vs,	320 sh	435 m
4-NO₂-PyO	1270 vs	−			−
SbCl₅·4-NO₂-PyO	1190 vs	350 sh,	340 vs		420 m
EtNNO	1270 vs	−			−
SbCl₅·EtNNO	1190 vs	350 vs,	315 sh		425 m

ªRef. 1.

sigma only) in the bases with positive or negative σ_{PyO} (*vide infra*).

The more relevant IR frequencies are given in Table II. The metal–halogen stretching modes have been assigned as in [1]. Their numbers are consistent with a C_{4v} symmetry in the adducts. Although in some complexes the three bands necessary for symmetry requirements are not present, we feel that the missing ones are obscured by the strong broad bands in Table II.

The bands around 850 cm⁻¹ in the complexes (assigned to δ_{N-O}) undergo a small position modification with respect to the free ligands and they are not included in Table II. This behavior is shown by complexes of FeCl₃ [10] and Cd(SCN)₂ [11] with aromatic amine oxides and these results could be interpreted in terms of two effects [11]: a) coordination of the N–O group which would raise the frequencies and b) decrease of double bond character which would yield the opposite effect.

The N–O stretching mode shows a shift towards lower wavenumbers. This is in agreement with the bond through the oxygen atom. This mode is practically insensitive to the effects of the substituents on the ring, as occurs in preceding works [10, 11, 12, 15].

In the assignment of ν_{Sb-O} we have considered the studies with the same ligands [10, 12] and their position in GaCl₃ complexes [13]. The assignment of this stretching mode is more tentative than the others, due to the complicated spectra of the ligands in this zone and to the possibility of its modification [14].

The plot of ν_{Sb-O} versus σ_{PyO} is V-shaped. This trend was interpreted [10, 14] in terms of combination of two effects. In the complexes with electron-releasing substituents, the antimony–oxygen bond is dominated by the sigma donation of the bases. In the bond of the adducts with electron-withdrawing substituents, the antimony–oxygen back π-bonding effect predominates. The same explanation is proposed by Michelson *et al.* [12] to justify the insensitivity of ν_{N-O}.

Acknowledgment

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