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Donor–Acceptor Compounds. IX*. Pyridine, 2-, 3- and 4-Methylpyridine N-oxides Complexes with $SbCl_3$ and $SbCl_5$.

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The interaction of $SbCl_3$ and $SbCl_5$ with pyridine, 2-, 3- and 4-picoline N-oxides by spectrophotometric, dielectrometric and conductometric titrations has been investigated. The formation of complexes in 1:1 and 1:2 molar ratio for $SbCl_3$ and adducts 1:1, when the acceptor was $SbCl_5$, is confirmed. The dipole moments of the formed complexes have been calculated. The following adducts: $SbCl_3 \cdot PyO$, $SbCl_3 \cdot (4\text{-}PicO)_2$, $SbCl_5 \cdot PyO$, $SbCl_5 \cdot 2\text{-}PicO$, $SbCl_5 \cdot 3\text{-}PicO$, and $SbCl_5 \cdot 4\text{-}PicO$ have been isolated and their most significatives IR frequencies are reported and assigned. Those located within 600–250 cm^{-1} range are consistent with a C_{4v} symmetry for $SbCl_5$ complexes. All the isolated solids are non-electrolytes in acetonitrile.

Introduction

The coordination chemistry of the pyridine N-oxide and its derivatives has been the subject of recent revisions[1,2]. As far as the behaviour of these bases with acceptors which contain non-transitional elements is concerned, the interaction with halides and haloderivatives of Te, P, Si, Ge, Sn, Pb, B[2], Al[3] and In[4] has been studied. The preparation of the adduct $SbCl_5 \cdot PyO$ has been also described[5]. On the other hand, there has recently been reported the isolation and properties of the adducts formed by the bases previously mentioned and $Sb(OR)Cl_4$[6].

The results obtained from the study of complex formation between $SbCl_3$ or $SbCl_5$ and pyridine N-oxide (PyO, C_5H_5NO) and picoline N-oxides (2-PicO, 3-PicO, 4-PicO; C_6H_7NO) are now reported.

Experimental

Materials

Acetonitrile, 1,2-dichloroethane and dichloromethane were purified by usual methods. Benzene Carlo Erba for Spectrophotometry was dried over Molecular Sieves 4 A. Antimony pentachloride Carlo Erba was vacuum distilled. Antimony trichloride Merck was purified by sublimation under vacuum. Pyridine N-oxides Fluka were recrystallized from acetone and benzene.

Preparation of Complexes

The adducts $SbCl_3 \cdot L_n$ (n = 1 or 2) were prepared in benzene or in 1,2-dichloroethane by mixing solutions which contained the acceptor and the donor in a proportion slightly higher than the 1:2 acceptor/donor molar ratio (MR). When L = PyO, the compound was isolated in benzene, washed with acetone and then vacuum dried. When L = 2-PicO and 3-PicO, using 1,2-dichloroethane, solids which contained a mixture of the adducts 1:1 and 1:2 were obtained. For L = 4-PicO the complex was prepared in 1,2-dichloroethane, washed with the same solvent and vacuum dried.

The adducts $SbCl_5 \cdot L$ were isolated in 1,2-dichloroethane, except $SbCl_5 \cdot 3\text{-}PicO$ which was prepared in a mixture of the above mentioned solvent and ciclohexane. The donor and the acceptor were then mixed in an approximately 1:1 molar ratio. When L = PyO or 4-PicO, the reaction proved to be strongly exothermic and produced the immediate formation of a precipitate which was washed several times with hot 1,2-dichloroethane. When L = 2-PicO and 3-PicO, it was necessary to eliminate most of the solvent and to cool the solution to induce the precipitation.

Analytical Procedure

Sb(III) was determined volumetrically[7]. 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 the colour and the melting points of the adducts are given in Table I.

Physical Measurements

Conductometric and spectrophotometric studies were carried out employing the apparatus described in a

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TABLE I. Analytical and Some Physical Data of Antimony(III) and (V) Chlorides–Pyridine and Picoline N-Oxides Complexes

Compound	Colour	M.P. (° C)	%M	%C	%N	%H
$SbCl_3 \cdot PyO$	White	105–110	36.94(37.67)[a]	19.85(18.60)	4.80(4.30)	1.71(1.50)
$SbCl_3 \cdot (4\text{-PicO})_2$	Pale Yellow	135	27.55(27.28)	32.19(32.20)	6.31(6.20)	3.21(3.10)
$SbCl_5 \cdot PyO$	White	190	---------	15.26(15.20)	3.56(3.50)	1.35(1.20)
$SbCl_5 \cdot 2\text{-PicO}$	Yellow	110–120	---------	19.00(17.60)	3.70(3.40)	2.01(1.70)
$SbCl_5 \cdot 3\text{-PicO}$	Yellow	155–160	---------	18.30(17.60)	3.50(3.40)	1.88(1.70)
$SbCl_5 \cdot 4\text{-PicO}$	White	235	---------	17.45(17.60)	3.36(3.40)	1.78(1.70)

[a] The theoretical percentage is given in brackets.

previous paper[8]. The dipole moments were determined in benzene, at 25° C, on the basis of the method described by Guggenheim[9], using dielectrometric titrations and refraction index measurements[10, 11]. The IR spectra were recorded in potassium bromide pellets or Nujol mulls in polyethylene windows using a Beckman IR-20A spectrophotometer. As far as possible, a dry box was used for manipulations.

Results and Discussion

$SbCl_3$

The progress of the reaction between pyridine N-oxide and antimony(III) chloride in 1,2-dichloroethane was studied titrimetrically by spectrophotometry and conductometry.

The conductometric curves (Fig. 1) show increases of specific conductivity until it reaches a maximum for the MR 1:2, where it begins to decrease. Until it reaches MR 1:1 curve variation is practically linear. Similar behaviour was observed when confronting $SbCl_3$ with DMSO, TBP, and HMPA[12]. As suggested in these cases, this conductivity increase could be due to slight ionization processes of the type:

$$\text{Sb–Cl} + \text{L} \rightleftarrows (\text{Sb–L})^+ + \text{Cl}^-$$

superimposed on the formation equilibrium of the adducts,

$$SbCl_3 + nL \rightleftarrows SbCl_3 \cdot L_n \ (n = 1 \text{or } 2)$$

The spectrophotometric measurements were centred in the bands of the ligands. According to theoretic studies[13], the associated transition with the bands imply a charge transfer from the N–O oxygen to the ring. This phenomenon should be affected when the oxygen atom involves part of its free electron pairs in a donor–acceptor process.

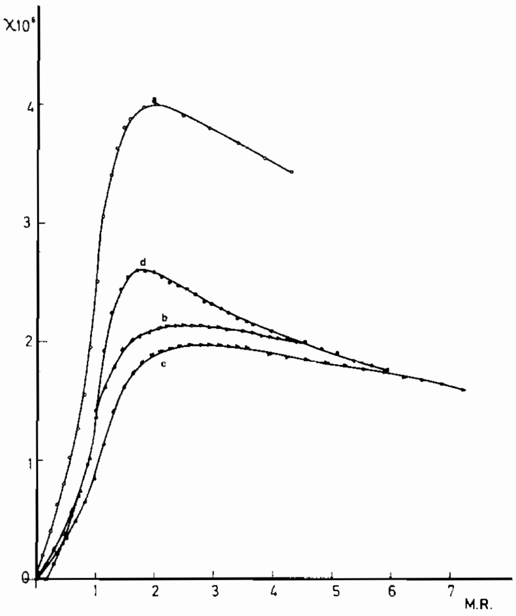

Figure 1. Conductometric titrations in 1,2-dichloroethane of $SbCl_3$ with: (a) PyO, (b) 2-PicO, (c) 3-PicO, (d) 4-PicO.

In the spectrophotometric titrations, a blue shift of the π–π^* band was observed when the MR was 1:1 or 1:2. In the first case, the displacements occurred between 3 and 6.5 nm, being greater when L = 4-PicO and lesser when L = 2-PicO. The hypsochromic shift was less significant for the MR 1:2. Similar behaviour was observed in complexes of titanyl, zirconyl and uranyl perchlorates with pyridine N-oxides[14, 15].

The dielectrometric titrations together with refractometric data allowed the calculations of Guggenheim parameters α and ν, and the dipole moments of the adducts 1:1 and 1:2 (Table II). The results are compatible with bipyramidal–trigonal structures for the $SbCl_3 \cdot L$ complexes, with a lone pair of the central atom in a coordination position, a situation similar to the one found for the $SbCl_3 \cdot C_6H_5NH_2$ adduct in solid state[16]. The values of the moments of the $SbCl_3 \cdot L_2$ compounds proved too low for an octahedral structure with an active pair and the donor molecules in *cis* position – a coordination found by Hulme *et al.*[17] in solid phase for the complex $SbCl_3 \cdot (C_6H_5NH_2)_2$. This discrepancy is justifiable if an equilibrium between *cis* and *trans* forms exists in solution.

Only two of the adducts isolated have shown a defined composition (Table I). The adduct $SbCl_3 \cdot$

TABLE II. Dipole Moments of Complexes in Benzene at 25° C.

Complex	a	ν	μ(D)	μ_{L-A} (D)
$SbCl_3 \cdot PyO$	39.6053	2.7255	10.5[a]	--------
$SbCl_3 \cdot (PyO)_2$	35.8803	2.2206	11.4[a]	--------
$SbCl_3 \cdot$ 2-PicO	28.4559	0.3743	9.3	--------
$SbCl_3 \cdot$ (2-PicO)$_2$	23.2537	0.3599	9.7	--------
$SbCl_3 \cdot$ 3-PicO	22.1540	0.3990	8.2	--------
$SbCl_3 \cdot$ (3-PicO)$_2$	18.1886	0.5574	8.5	--------
$SbCl_3 \cdot$ 4-PicO	31.1642	0.2032	9.8	--------
$SbCl_3 \cdot$ (4-PicO)$_2$	26.3477	0.4205	10.3	--------
$SbCl_5 \cdot PyO$	36.3453	0.7944	11.4[a]	5.8
$SbCl_5 \cdot$ 2-PicO	31.3913	0.3366	10.8	5.2
$SbCl_5 \cdot$ 3-PicO	33.7786	0.4329	11.2	5.4
$SbCl_5 \cdot$ 4-PicO	45.4977	0.0294	13.1	7.1

[a] The error of this values is greater than the others because they have been calculated from very diluted solutions.

TABLE III. More Relevant IR Frequencies (cm^{-1}) of Compounds.

Compound	ν_{N-O}	ν_{Sb-Cl}	ν_{Sb-O}
PyO	1250 vs	--------	--------
2-PicO	1250 vs	--------	--------
3-PicO	1278 vs	--------	--------
4-PicO	1249 vs	--------	--------
$SbCl_3 \cdot PyO$	1200 vs	320 s, 300 s	360 m
$SbCl_3 \cdot$ (4-PicO)$_2$	1200 vs, 1192 vs	320 w, 290 m	375 m
$SbCl_5 \cdot PyO$	1192 vs	350 vs, 315 m	400 s
$SbCl_5 \cdot$ 2-PicO	1195 vs	360 vs, 345 vs, 320 m	410 s
$SbCl_5 \cdot$ 3-PicO	1242 m	360 vs, 345 vs, 320 m	405 s
$SbCl_5 \cdot$ 4-PicO	1200 vs	360 s, 345 vs, 330 m	440 s

(4-PicO)$_2$ exhibited in acetonitrile a molar conductivity (for a solution $10^{-3}M$) of 2.5 ohm^{-1} cm^2 mol^{-1} showing a non-electrolytic nature[18]. The compound $SbCl_3 \cdot PyO$ was practically insoluble in this solvent.

Because of complex formation the IR spectra presented (Table III) a shift towards lower frequencies for the ν_{N-O} band exhibited by the free ligands. This is indicative of coordination through the N–O oxygen. In the complex $SbCl_3 \cdot (4\text{-PicO})_2$, a splitting of this band was observed, which could be caused by the coupling of the vibrations of both molecules of ligand in the solid. The δ_{N-O} and γ_{C-H} ligand modes undergo modifications of little significance. In Table III, ν_{Sb-O} and ν_{Sb-Cl} modes are assigned in a very tentative form. The uncertainty comes from the facility with which bands can be mistaken in the complexes of $SbCl_3$ and $AsCl_3$[19]. The antimony–oxygen bands appear in these systems at lower frequencies than in the corresponding adducts of $SbCl_5$ (*vide infra*) in agreement with the acid forces of the two antimony halides[19].

$SbCl_5$

The conductometric titrations in 1,2-dichloroethane showed inflexions around the MR 1 : 1 and conductivity variations with time in the proximities of this point, suggesting the presence of various superimposed equilibria of mutual influence.

The UV spectra of acceptor–donor mixture in MR 1 : 1 show blue shifts of π–π^* bands of the ligands between 9 and 17 nm and also increases in the extinction coefficients. Again the lesser shift corresponds to 2-PicO and the greater to 4-PicO.

The dielectrometric titrations (Fig. 2) together with refractometric data allow the calculation of the dipole moments of the adducts 1 : 1 (Table II) which do not disagree with those given in the literature[20–24]. These values can be related with the moments of the donor–acceptor bonds in making certain structural considerations. On the basis of a C_{4v} configuration for the adducts in solution (structure confirmed in solid state by the IR spectra, *vide infra*) and supposing an angle Sb–O–N = 120° (very frequent value in the complexes of pyridine N-oxides of diverse geometry[25]), the components of the total dipolar moment could be expressed as:

$$\begin{aligned} \mu_x &= \mu_L \cos 30 \\ \mu_y &= 0 \\ \mu_z &= \mu_{Sb-Cl} + \mu_{L-A} + \mu_L \cos 60 \end{aligned} \qquad (1)$$

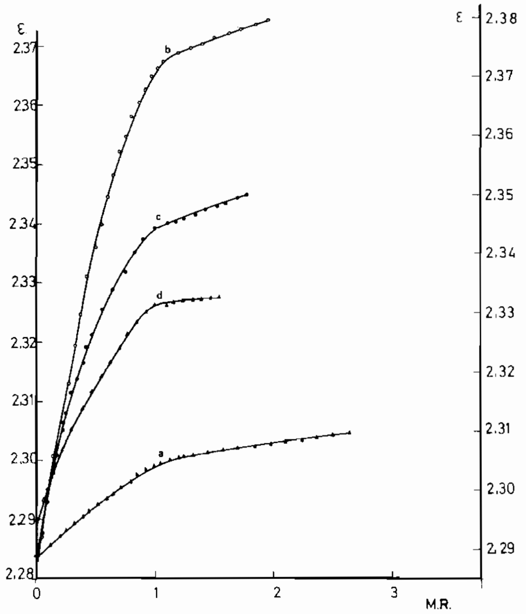

Figure 2. Dielectrometric titrations in benzene of $SbCl_5$ with: (a) PyO, (b) 2-PicO, (c) 3-PicO, (d) 4-PicO. The right ordinate axis is for curve b. The concentration of initial acceptor solutions is between 2–8 × $10^{-3}M$.

where xy is the plane containing the four equatorial chlorines, μ_L the dipole moment of the pyridine N-oxides, and μ_{Sb-Cl} and μ_{L-A} the moments of Sb–Cl and donor–acceptor bonds, respectively. Smyth[26] proposes a value of 2.6 D for μ_{Sb-Cl}. Supposing that the partial cession of the base pair increases the bond polarity, a value of 3 D could be considered acceptable for this moment. The values taken for μ_L were μ_{PyO} = 4.2 D[27], $\mu_{2\text{-PicO}}$ = 3.9 D[25]*, $\mu_{3\text{-PicO}}$ = 4.3 D[27] and $\mu_{4\text{-PicO}}$ = 4.5 D[27]. Substituting these values in (1), the moments of donor–acceptor bonds of Table II are obtained. Although the quantitative aspect of these values could be affected by the assumptions made above, since the error would probably affect all the complexes in the same way, the qualitative sequence of μ_{L-A} should prove to be fundamentally correct. On the other hand these values proved to agree with those stated in the literature for the strong acceptors and donors[23], but higher than those found when $SbCl_5$ interacts with weaker donors[24]. This indicates an important charge transfer from the donor to the acceptor and a greater basicity for 4-PicO as was expected according to the values of σ_{PyNO}[1,28] for the different oxides.

The isolated complexes have the general stoichiometry $SbCl_5 \cdot L$ (Table I). The adducts of 2-PicO and 3-PicO retain an excess of ligand, mainly the first one. Because of the crystallization difficulty shown by these complexes, such excess could not be eliminated. Adducts are non-conducting in acetonitrile[18], with values of molar conductivity (for solutions $10^{-3}M$) between 1–2 ohm^{-1} cm^2 mol^{-1}.

The IR spectra show shifts of the ν_{N-O} frequency towards lower wavenumbers (Table III). The δ_{N-O} bands is displaced in the same way. The ν_{Sb-Cl} was assigned taking into account the position of this band in $SbCl_5$[29] and the fact that an increase of coordination in the Sb(V) environment should lower the frequency of vibration of these bonds[30]. The bands found are in agreement with C_{4v} structures for the complexes, so that such a situation could imply the existence of three ν_{Sb-Cl} and one ν_{Sb-O} IR active bands situated in the analyzed zone[31]. Furthermore, the values of Table III match qualitatively with the position of the bands shown by $SbCl_5Br^-$ ion[31].

The assignment of the band ν_{Sb-O} in $SbCl_5 \cdot PyO$ implied choosing between two absorptions recorded at 400 and 440 cm^{-1}, the latter being next to the frequencies ν_{Sb-O} reported in literature[6,32]. Nevertheless, this band also appears in $SbCl_3 \cdot PyO$, so that it is probably originated from the ligand. This was considered by Brown *et al.*[3] and Kawasaki *et al.*[33] in the complexes they prepared with pyridine N-oxide. Therefore it appears more suitable to consider the band situated at 400 cm^{-1} as ν_{Sb-O}.

For the rest of $SbCl_5$ complexes, ν_{Sb-O} has been assigned taking the adduct of PyO as reference. The sequence obtained agrees qualitatively with that expected from the different pyridine and picoline N-oxide basicities. Nevertheless the plot of ν_{Sb-O} *versus* σ_{PyNO} shows a poor linear relation between both quantities, possibly due to the bands ν_{Sb-O} not being 'pure' because they contain a mixture of ligand bands[34].

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References

1 R.G. Garvey, J.H. Nelson and R.O. Ragsdale, *Coord. Chem. Rev., 3,* 375 (1968).
2 N.M. Karayannis, L.L. Pytlewski and C.M. Mikulski, *Coord. Chem. Rev., 11,* 93 (1973).
3 D.H. Brown, D.T. Stewart and D.E.H. Jones, *Spectrochim. Acta, 29 A,* 213 (1973).
4 D.H. Brown and D.T. Stewart, *J. Inorg. Nucl. Chem., 32,* 3751 (1970).
5 G. Hilgetag and H. Teichman, *Chem. Ber., 96,* 1446 (1963).

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* Estimated.

6 R.C. Paul, H. Madan and L. Chadha, *J. Inorg. Nucl. Chem., 36,* 737 (1974).

7 F. Bermejo, "Tratado de Química Analítica Cuantitativa", 1ª Ed, Imprenta del Seminario Conciliar, Santiago de Compostela, 1958.

8 J.R. Masaguer and J.S. Casas, *Anal. Real Soc. Esp. Fis. y Quim., 69,* 997 (1973).

9 E.A. Guggenheim, *Trans. Faraday Soc., 45,* 714 (1949); *47,* 573 (1951).

10 E.N. Gur'yanova, *Russ. Chem. Rev., 37,* 836 (1968).

11 J.R. Masaguer, M.R. Bermejo, J.S. Casas, A. Castiñeiras and J. Sordo, *Anal. Real Soc. Esp. Fis. y Quim., 69,* 1093 (1973).

12 V. Gutman and H. Czuba, *Mh. Chem., 100,* 708 (1969).

13 K. Seibold, G. Wagnière and H. Labhart, *Helv. Chim. Acta, 52,* 789 (1969).

14 P. Rama Murthy and C.C. Patel, *Can. J. Chem., 42,* 856 (1964).

15 V. Krishnan and C.C. Patel, *Can. J. Chem., 43,* 2685 (1965).

16 R. Hulme and J.C. Scruton, *J. Chem. Soc. A,* 2448 (1968).

17 R. Hulme, D. Mullen and J.C. Scruton, *Acta Cryst., A 25,* S171, (1969).

18 J.R. Masaguer, J. Romero and A. Sousa, *Acta Científica Comp., 8,* 1 (1971).

19 J.D. Smith, "Arsenic, Antimony and Bismuth"; "Comprehensive Inorganic Chemistry", J.C. Bailar, H.J. Eméleus, R. Nyholm and A.F. Trotman-Dickenson Eds., Pergamon Press, Oxford (1973).

20 R.C. Paul and S.L. Chadha, *J. Inorg. Nucl. Chem., 31,* 1679 (1969).

21 R.C. Paul, H.R. Singal and S.L. Chadha, *J. Chem. Soc. A,* 1849 (1969).

22 R.C. Paul, B.R. Sreenathan and S.L. Chadha, *J. Inorg. Nucl. Chem. 28,* 1225 (1966).

23 J.R. Masaguer and J. Sordo, *Anal. Real Soc. Esp. Fis. Quim., 69,* 1255 (1973).

24 S.R. Jain and S. Soundarajan, *Z. anorg. allg. Chem., 337,* 214 (1965).

25 A. Sánchez, *Tesis Doctoral,* Facultad de Ciencias, Universidad de Santiago de Compostela, 1975.

26 C.P. Smyth, *J. Phys. Chem., 41,* 209 (1937).

27 A.L. McClellan, "Tables of Experimental Dipole Moments", Vol. 1, Freeman, 1963.

28 C. Klofutar, S. Paljk and Barlic, *Spectrochim. Acta, 29 A,* 1069 (1973).

29 G.L. Carlson, *Spectrochim. Acta, 19,* 1291 (1973).

30 R.J.H. Clark, *Spectrochim. Acta, 19,* 1291 (1963).

31 C.J. Adams and A.J. Downs, *J. Inorg. Nucl. Chem., 34,* 1829 (1972).

32 A. Schmidt, *Z. anorg. allg. Chem., 362,* 129 (1968).

33 Y. Kawasaki, M. Hori and K. Uenaka, *Bull. Chem. Soc. Japan, 40,* 2463 (1967).

34 D.M. Adams, "Metal–Ligand and Related Vibrations", pag. 246, Arnold, London, 1967.