KURZE MITTEILUNGEN

Bis am 20. des Monats bei der Redaktion eingehende Kurze Mitteilungen werden in der Regel am 15. des folgenden Monats veröffentlicht
Es werden auch Manuskripte aus dem Ausland angenommen

Infrared Spectra of 2-Amino Pyridine and its Addition Compounds with Certain Inorganic Halides

Addition compounds of 2-amino-pyridine with certain inorganic halides like $SbCl_3$, $SbCl_5$, $BiCl_3$, $TiCl_4$, $SnCl_4$ and $SnBr_4$ have been prepared. The stoichiometric composition of the various adducts has been established. Infrared spectra of all the adducts have been recorded in the medium infrared region (4000–650 Cm^{-1}). The assignments for the bands are given.

Introduction

No literature seems to be available on the addition compounds of 2-aminopyridine, although it is expected to possess electron donating properties. The present work was undertaken with a view to find out the possibility of complex formation between 2-aminopyridine and some inorganic halides like $SbCl_3$, $SbCl_5$, $BiCl_3$, $TiCl_4$, $SnCl_4$ and $SnBr_4$. Infrared spectra of the adducts in the medium infrared spectral region (4000 – 650 Cm^{-1}) are also reported and the various bands are discussed to understand the changes in vibrational spectrum which the 2-aminopyridine molecule undergoes on complex formation.

Experimental

Preparation: Dry, distilled benzene was used as solvent in the preparation of all the complexes except for bismuth trichloride which was found soluble only in methyl acetate. E. Merck's GR Grade methyl acetate was dried, distilled and used as solvent for the preparation of the $BiCl_3$ adduct. 2-Aminopyridine was a Reagent Grade May and Baker product and was used without further purification. $SnCl_4$ and $SbCl_5$ were Riedel products, whereas $TiCl_4$ and $SnBr_4$ were BDH products. These were used without further purification. All the complexes were prepared by mixing, in desired proportions, the accurately weighed amounts of 2-aminopyridine and inorganic halide dissolved in the appropriate solvent. All the operations were carried out under anhydrous conditions. Adducts were dried *in vacuo* under anhydrous conditions. All the adducts were hygroscopic, well defined solid products.

Analytical: All the adducts were analyzed for their N, halogen and metal contents to establish the stoichiometric composition. Nitrogen was determined by the Kjeldahl method. Halogen was determined volumetrically by Volhard's method.[2] Antimony was determined volumetrically[3] by the potassium bromate method. Bismuth was estimated gravimetrically[4] by precipitating BiOI with potassium iodide. Tin[5] and titanium[6] were also determined by precipitation with cupferon. Analytical data and stoichiometric compositions are listed in Table 1.

Infrared Spectra: A Perkin-Elmer model 221 double beam infrared spectrophotometer equipped with sodium chloride optics was used to record the spectra in the sepctral region 4000 – 650 cm^{-1}. All the spectra were recorded in KBr disc. The bands observed in the spectrum of 2-aminopyridine and its adducts are listed in Table 2.

Discussion

To our knowledge no data on infrared spectra of 2-aminopyridine seem available in the literature. However, the infrared and Raman spectroscopic behaviour of pyridine[7–12] has been studied thoroughly. We find that most of the pyridine bands appear in the infrared spec-

Table 1. Analytical Data of Various 2-Aminopyridine Adducts (Calculated Data in Parenthesis)

S. No.	Acceptor	% N	% Halogen	% Metal	Stoichiometry Acceptor : Donor	Colour
1.	$SbCl_3$	8.62 (8.69)	32.75 (33.06)	37.42 (37.76)	1 : 1	golden
2.	$SbCl_5$	7.09 (7.12)	44.98 (45.14)	29.98 (30.94)	1 : 1	dark yellow
3.	$BiCl_3$	6.81 (6.84)	25.59 (26.03)	72.68 (73.10)	1 : 1	colourless
4.	$TiCl_4$	14.28 (14.82)	37.12 (37.58)	12.20 (12.44)	1 : 2	dark yellow
5.	$SnCl_4$	12.20 (12.48)	30.85 (31.65)	26.50 (26.44)	1 : 2	colourless
6.	$SnBr_4$	7.99 (8.94)	50.32 (51.02)	18.80 (18.94)	1 : 2	yellow

Table 2. Vibrational Frequencies of 2-Aminopyridine and its Adducts with Inorganic Halides

Assignment	Frequencies in Cm^{-1} 2-aminopyridine	Adducts with: $SbCl_3$	$SbCl_5$	$BiCl_3$	$TiCl_4$	$SnCl_4$	$SnBr_4$
	3333_{vs}	3333_{vs}	3448_s	3448_s	3448_s	3448_s	3448_{vs}
	3175_{vs}	3175_{vs}	3279_s	3279_s	3279_s	3333_s	3279_{vs}
	1626_{s*}	–	–	–	–	–	–
$\nu 8a$	1600_s	1667_{m+}	1681_{vs+}	1681_{vs+}	1681_{vs+}	1667_{s+}	1667_{vs+}
$\nu 8b$	1562_s	1619_s	1639_{vs}	1639_{vs}	1639_{vs}	1639_{vs}	1639_{vs}
$\nu 19a$	1481_w	1538_w	1562_w	1562_w	1562_w	1538_w	1562_w
$\nu 19b$	1439_{vs}	1471_w	1481_w	1481_w	1481_w	1481_m	1492_m
		1408_s	1418_{vw}	1418_{vw}	1418_{vw}	–	1429_{vw}
$\nu 14$	1324_{vs}	1379_s	1389_m	1389_m	1389_m	1389_m	1389_m
	1274_{vs}	1324_s	1333_s	1333_m	1333_m	1333_m	1333_s
$\nu 15$	1156_{vs}	1235_{vs}	1242_w	1242_w	1242_w	1250_w	1250_m
$\nu 18a$	1136_{vs}	1162_s	1176_m	1163_w	1170_w	1170_m	1174_m
$\nu 12$	1060_w	1117_w	1124_w	1124_{vvw}	1124_{vvw}	–	1124_{vvw}
	1036_w	1044_w	–	–	–	–	1053_{vw} 1031_w
$\nu 1$	985_m	990_w	1000_w	1000_w	1000_w	1000_w	1000_m
$\nu 17a$	955_w	958_{vw}	–	–	–	957_w	–
$\nu 10b$	855_w	857_w	862_w	862_w	$893_{w\ broad}$	865_{vw}	862_m
$\nu 11$	766_s	761_s	763_{s+} 748_s	754_s	763_s	769_{m+} 746	766_{vs+} 748_{vs}
$\nu 4$	735_s 688_m	714_s 661_m	704_s –	709_m –	709_w –	704_s 671_{vw}	704_s –

* = triplet, + = doublet, w = weak, vw = very weak, vvw = very very weak, s = strong, vs = very strong, m = medium

trum of 2-aminopyridine without any major change and are easily recognizable. Furthermore, the infrared spectrum of γ-picoline has been discussed by Cook[13] in greater detail. It seems possible to identify most of the 2-aminopyridine bands with those of the pyridine and the γ-picoline molecule from the knowledge of the substitution pattern of the NH_2 group in 2-position in the pyridine ring. In the following part of the discussion, we have attempted to correlate the 2-aminopyridine vibrations with those of pyridine and γ-picoline for which complete and unambiguous assignments are available. This has greatly helped in following the bands in the adducts. Assignments for pyridine vibrations follow those of Wilmshurst and Bernstein[9].

Ring Vibrations: Similar to pyridine there are four characteristically strong bands in the spectrum of 2-aminopyridine with maxima at 1600, 1562, 1481 and 1439 cm^{-1}. In the case of pyridine, they have been attributed to C—C and C—N vibrations, which give rise to two symmetric and two antisymmetric in plane ring deformation frequencies. The band at 1626 cm^{-1} which appears as a shoulder, has been attributed to an overtone. Individual bands are discussed below.

$\nu 19b$: The strong 2-aminopyridine band at 1439 cm^{-1} which can be assigned to this in plane antisymmetric ring deformation, on co-ordination moves to higher frequencies showing an increase of the order of 32–53 cm^{-1} and is diminished in intensity.

$\nu 1$: A band of medium intensity appearing in the 2-aminopyridine spectrum at 985 cm^{-1} is also attributable to this totally symmetric mode of ring breathing. On co-ordination the band moves to higher frequencies by 5–15 cm^{-1}.

$\nu 4$: This out of plane vibration mode of ring deformation appearing at 735 cm^{-1} in the 2-aminopyridine spectrum, on co-ordination decreases in frequency by 16–26 cm^{-1}.

C—H Vibrations: ν 15 (in plane, antisymmetric hydrogen bending) and $\nu 18a$ (in plane totally symmetric hydrogen bending), appear in the 2-aminopyridine spectrum as strong bands at 1156 and 1136 cm^{-1}, respectively. On co-ordination they show a general increase in frequency.

$\nu 17a$ (out of plane C—H deformation) and $\nu 10b$ (out of plane antisymmetric, C—H deformation) appear in 2-aminopyridine as weak bands at 955 cm^{-1} and 855 cm^{-1}, and are not much affected by co-ordination. $\nu 11$ (out of plane C—H deformation) observed as a strong band at 766 cm^{-1} shows an irregular behaviour as it decreases in frequency in some adducts while it increases in others.

A medium intensity band observed in 2-aminopyridine at 668 cm^{-1}, which does not appear in most of the adducts can be assigned to a combination mode ($\nu 18a - \nu 18b$).

No assignment is available for a strong 2-aminopyridine band at 1274 cm^{-1}, which on co-ordination appears at 1324 cm^{-1} in the $SbCl_3$ adduct and at 1333 cm^{-1} in other adducts.

ν19a: The strong band at 1481 cm^{-1} in the 2-aminopyridine spectrum corresponds to this in plane, totally symmetric ring stretching mode. On co-ordination, the band shows a general increase in frequency by 57–81 cm^{-1} and is diminished in intensity.

ν8b: A strong band at 1562 cm^{-1} in the 2-aminopyridine spectrum can be unmistakenly assigned to the in plane antisymmetric ring vibration. The band moves to higher frequencies in all the adducts showing an increase of the order of 57–77 cm^{-1} without any noticeable change in intensity.

ν8a: Another strong 2-aminopyridine band at 1600 cm^{-1} seems to arise also from the in plane, totally symmetric ring stretching mode. The band moves to higher frequencies by 67 to 81 cm^{-2} in various adducts, without any apparent change in intensity. – The origin of weak bands in the region 1408 – 1429 cm^{-1}, observed in various adducts, is not clear.

ν14: The strong 2-aminopyridine band at 1324 cm^{-1} can be assigned to the in plane antisymmetric ring deformation mode of vibration. On co-ordination the band moves to higher frequencies by 55–65 cm^{-1} in the adducts.

ν12: A weak band at 1060 cm^{-1} seems to arise from this symmetric in plane ring breating mode. The band shows an increase in frequency of the order of 57–64 cm^{-1} in various adducts.

Some generalizations follow from the above discussion. It appears that on co-ordination out of plane vibrations decrease in frequency, whereas in plane vibrations actually show an increase. Systematic and large variations are found only in bands involving C—C and C—N vibrations. This could be expected since the complex formation involves the nitrogen lone pair electrons. In the complex these electrons form co-ordinate bonds which are expected to have an influence on the other ring bonds.

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