232. *Complexes of Boron Trichloride with Pyridine and Piperidine.*

By N. N. GREENWOOD and K. WADE.

The properties of fused boron trichloride–pyridine, m. p. 115° and boron trichloride–piperidine, m. p. 184°, are reported and interpreted in terms of ionic equilibria of the type $2BCl_3,C_5H_xN \rightleftharpoons [(C_5H_xN)_2BCl_2]^+[BCl_4]^-$ where $x = 5$ or 11; the degree of ionic dissociation is about 1%. There is also some evidence for a compound $BCl_3,2C_5H_5N$ melting incongruently at 56°. Except for the higher m. p., volatility and heat of formation the 1 : 1 piperidine complex is remarkably similar to its pyridine analogue. At their respective m. p.s the densities of BCl_3,C_5H_5N and $BCl_3,C_5H_{10}NH$ are 1·3511 and 1·2059 g. ml.$^{-1}$; the dynamic viscosities are 3·186 and 2·539 cp.; and the specific conductivities are $1·696 \times 10^{-3}$ and $1·644 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$. The infrared spectra of the complexes and of pyridinium chloride and tetrachloroborate are also discussed and new assignments suggested for some of the bands in the pyridine derivatives.

SINCE it was first reported [1] the 1 : 1 addition compound boron trichloride–pyridine has been used in preparative chemistry [2] and several of its physical properties have been determined. Thermochemical studies in nitrobenzene solutions [3] and dipole-moment

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[1] Gerrard and Lappert, *J.*, 1951, 1020.

[2] *Idem, Chem. and Ind.*, 1952, **71**, 53.

[3] Brown and Holmes, *J. Amer. Chem. Soc.*, 1956, **78**, 2173.

measurements in benzene solutions [4] have established that the electron-acceptor strength of boron trichloride towards pyridine is greater than that of boron trifluoride and less than that of boron tribromide. In these solutions the complex can be formulated as a simple addition compound $C_5H_5N{\rightarrow}BCl_3$ and the complex is monomeric and non-conducting in benzene.[4] A similar structure was found by *X*-ray crystallography for solid boron trifluoride–pyridine.[5] However, in the molten state some ionic dissociation occurs,[6] and this paper reports a study of the fused compound. There appears to be no published information on the related complex boron trichloride–piperidine which was first prepared during this work.[6] It was studied to investigate the effect of removing the aromatic character of the ligand on the properties of the complex. Experimental techniques have been described previously.[7]

RESULTS

Pyridine, m. p. −41°, was purified by fractionation and then freed from last traces of moisture by treatment, first, with finely ground sodium hydride and then by distillation from a small amount of boron trichloride, m. p. −107°. Addition of pyridine to boron trichloride in a vessel fitted with a spring-loaded tap gave a eutectic at −108° (8 moles % of pyridine) and a sharp maximum at the 1 : 1 ratio, corresponding to the compound BCl_3,py, m. p. 115°. Further addition of pyridine (Fig. 1) decreases the m. p.; there is some indication of an incongruently melting compound BCl_3,2py at 56° and the eutectic occurs at −45° (87 moles % of pyridine). The m. p. diagram of the system boron trichloride–piperidine could not be obtained in the same way because of the high vapour pressure of the components over the reaction mixture at temperatures required to melt the complex. Thus the m. p. of the complex (184°) is 80° above the b. p. of piperidine and 5° above the critical temperature [8] of boron trichloride. Nevertheless it was established that addition of either component to the 1 : 1 mixture lowered its m. p., thereby indicating that this composition represents the stoicheiometry of a true compound.

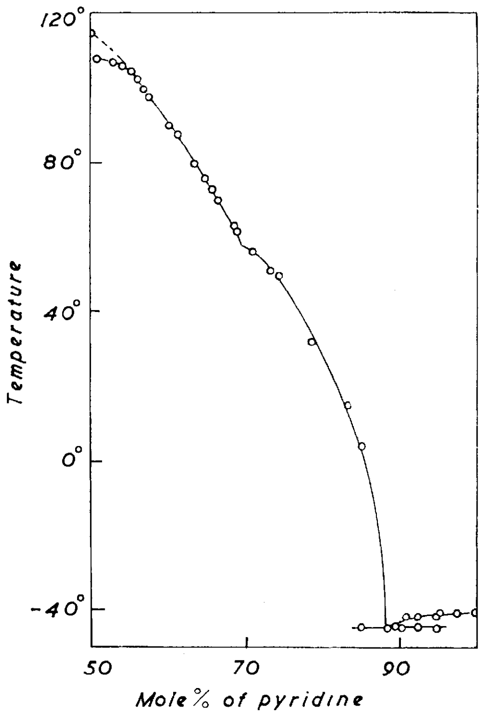

FIG. 1. *System boron trichloride–pyridine.*

Boron Trichloride–Pyridine.—The complex was prepared (*a*) by direct reaction of appropriate weights of ligand and acceptor in a vacuum system, or (*b*) by addition of boron trichloride to an excess of pyridine followed by removal of the excess of pyridine in a vacuum. The compound crystallized as large, transparent, colourless, hexagonal plates from benzene (Found: C, 30·9; H, 2·7; N, 6·9; Cl, 54·3. Calc. for $C_5H_5NBCl_3$: C, 30·6; H, 2·6; N, 7·1; Cl, 54·2%). However, the preferred method of purification before the determination of physical properties was by repeated, slow recrystallization from the melt under a vacuum in a vessel sealed directly to the measuring apparatus.

The density of fused boron trichloride–pyridine was measured at approximately 3° intervals in the range 109—143° by means of an all-glass, double-capillary pyknometer, and interpolated

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[4] Bax, Katritzky, and Sutton, *J.*, 1958, 1254, 1258.

[5] Zvonkova, *Kristallografiya*, 1956, **1**, 73.

[6] Greenwood, Wade, and Perkins, Proc. I.U.P.A.C. Congress (Inorganic Chemistry Section), Paris, 1957, p. 491, Butterworths Scient. Publ., 1958.

[7] Greenwood and Wade, *J.*, 1958, 1663.

[8] Parker and Robinson, *J.*, 1927, 2977.

values at 5° intervals are in Table 1. The experimental values can be represented to 1 in the last decimal place by the equation:

$$d_4^t = 1{\cdot}3511 - 8{\cdot}932 \times 10^{-4}(t - 115)$$

The molar volume, V_M, is 145·29 ml. at 115°. The surface tension was determined simultaneously from the difference in height of the liquid in the two capillaries and the experimental values (± 1 dyne cm.$^{-1}$) lead to the relation

$$\gamma = 41{\cdot}2 - 0{\cdot}105(t - 115) \text{ dyne cm.}^{-1}.$$

The molar surface free energy, $\gamma V_M^{2/3}$, is 1130 dyne ml.$^{2/3}$ mole$^{-2/3}$ at 115° and the Eötvös constant k is 2·38. The parachor is constant in the range studied and has the value $[P] = 368$,

FIG. 2. *Conductivity* (○) *and viscosity* (●) *of boron trichloride–pyridine.*

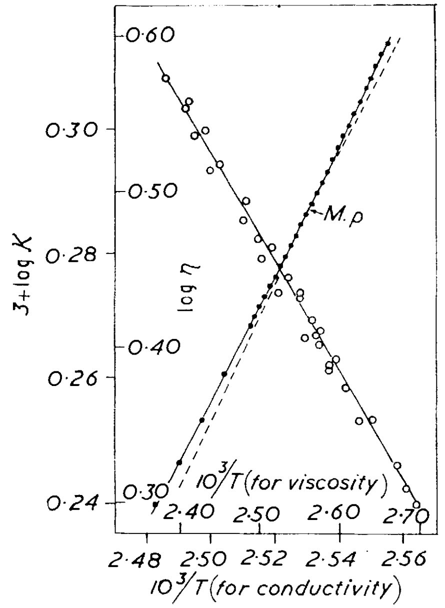
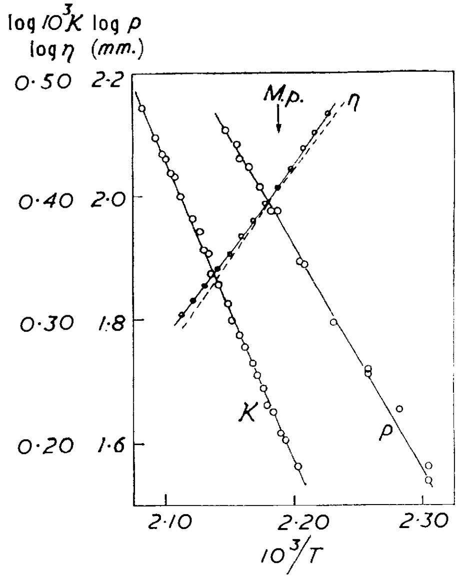


FIG. 3. *Conductivity, viscosity, and vapour pressure of boron trichloride–piperidine.*



compared with a value of 347 calculated on the basis of a covalent addition compound by McGowan's method.[9]

The viscosity was measured at 1° intervals in the range 102—138° and then less frequently up to 149° by means of a sealed glass viscometer which employed the weir principle to maintain a constant mean head of liquid at the various temperatures. The dynamic viscosity, η, is plotted logarithmically in Fig. 2 which indicates a certain deviation from linearity, especially in the region of the m. p. Above this temperature the activation energy of viscous flow, E_η, is 4·76 kcal. mole^{-1} but at lower temperatures it increases to 5·02 kcal. mole^{-1}. Values of the viscosity at 5° intervals are listed in Table 1.

The electrical conductivity of three samples of purified boron trichloride–pyridine was determined; in each case the resistance of the cell increased before attaining a reproducible, equilibrium value after about 12 hr. For example, at 118°, an initial conductivity of $2{\cdot}525 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$, obtained directly after fusion, decreased by 30% to an equilibrium value of $1{\cdot}762 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$. It was then possible to determine the variation of conductivity with temperature in the range 115—130° at half-degree intervals, interpolated values at 5° intervals being summarized in Table 1. The experimental values are plotted logarithmically in Fig. 2 to illustrate the scatter of points, which is rather larger than usual for

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[9] McGowan, *Rec. Trav. chim.*, 1956, **75**, 193.

measurements on complexes of this type. For this reason, the values in Table 1 are given only to three significant figures. The activation energy for conduction, E_κ, is 3·94 kcal. mole^{-1}. The molar conductivity ($\mu = \kappa V_M$) is also listed in Table 1; E_μ is 4·32 kcal. mole^{-1} which approaches the value for the activation energy of viscous flow. Because of this, the product of molar conductivity and dynamic viscosity, $\mu\eta$, varies little with temperature, as illustrated in the last column of Table 1. These values indicate [10] about 1% of ionic dissociation in the melt.

TABLE 1. *Properties of fused boron trichloride complexes.*

Temp.	d_4^t	γ (dyne cm.$^{-1}$)	η (cp.)	$10^3\kappa$ (ohm^{-1} cm.$^{-1}$)	μ (ohm^{-1} cm.^{2} mole^{-1})	$\mu\eta$
Pyridine						
110°	1·3556	42·5	3·460	(1·54)	(0·230)	(0·796)
115	1·3511	41·0	3·170	1·67	0·248	0·784
120	1·3467	40·6	2·944	1·80	0·263	0·774
125	1·3422	40·1	2·733	1·94	0·284	0·776
130	1·3378	38·5	2·539	2·06	0·301	0·766
135	1·3333	39·7	2·367	—	—	—
140	1·3288	38·3	2·215	—	—	—
145	1·3243	37·8	2·082	—	—	—
		p(mm.)				
Piperidine						
175	1·2137	63	2·966	(1·270)	(0·215)	(0·638)
180	1·2090	78	2·727	1·478	0·248	0·675
185	1·2050	95	2·501	1·687	0·283	0·708
190	1·2013	115	2·318	1·929	0·325	0·753
195	1·1968	136	2·156	2·190	0·370	0·795
200	1·1916	—	2·006	2·512	0·426	0·855
205	1·1877	—	(1·87)	2·834	0·483	0·904

A d.c. experiment at 122° gave a decomposition potential of about 1 ± 0·1 v. The value was not reproducible because electrolysis resulted in charring and carbonation at the anode; this deposit increased the resistance of the cell continuously and irreversibly. No gas was evolved at either electrode.

Boron Trichloride–Piperidine.—The compound was purified by fractional crystallization or vacuum-sublimation. Considerable difficulty was experienced in loading the dilatometer for density and surface-tension measurements because of the formation of bubbles in the capillaries as a result of the high vapour pressure of the complex at its m. p. Experimental values of the density were reproduced with a mean deviation of 4 in the last decimal place by the equation:

$$d_4^t = 1{\cdot}2050 - 8{\cdot}65 \times 10^{-4}(t - 185)$$

A satisfactory run of surface tension measurements was not achieved but an approximate value of $\gamma = 34$ dyne cm.$^{-1}$ was obtained at the m. p. As the molar volume is 167·80 at the m. p. this corresponds to a parachor of 405 (calc. 375).

The vapour pressure of boron trichloride–piperidine was measured directly in an evacuated, totally immersed U-tube manometer carrying a side-arm for the complex. The mercury was degassed at high temperature before each experiment and the observed differences in height were corrected for the variation in density of mercury with temperature. Interpolated values are given in Table 1. When $\log p$ is plotted against $1/T°$, as in Fig. 3, the slope decreases slightly above the m. p. and corresponds to a heat of vaporization of the liquid of 17·7 kcal. mole^{-1}. Likewise the heat of sublimation of the solid is 18·2 kcal. mole^{-1} but this difference is probably not far outside experimental error and should not be taken to imply a heat of fusion of 0·5 kcal. mole^{-1}. Extrapolation of the vapour-pressure data to 760 mm. gives b. p. 239°.

The viscosity of boron trichloride–piperidine was measured at 2° intervals between 175° and 200° and values are incorporated in Table 1. The activation energy of viscous flow varied from 6·72 at lower temperatures to 6·31 kcal. mole^{-1} at higher temperatures. The ratio $E_\eta : \Delta H_{\text{vap}}$ is therefore about 1 : 2·7.

The specific conductivity showed no variation with time at the m. p. At 195° it increased by less than 0·1% in 2 hr. and at 207° the increase was still only 2·5% in 10 hr. Measurements were made at 1° intervals and interpolated results are shown in Table 1; they lead to an activation energy for conduction of 11·3 kcal. mole^{-1}, which is about twice the value observed for

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[10] Greenwood and Martin, *J.*, 1953, 1427.

other addition compounds of the Group III trihalides. Table 1 indicates that, at their respective m. p.s, the two complexes have very similar specific, molar, and reduced conductivities. This leads to the unexpected conclusion that saturation of the aromatic ring, in particular presence of the NH group, has little influence on the degree of ionic dissociation of the complexes with boron trichloride and gallium trichloride.[11]

The decomposition potential of boron trichloride–piperidine is 0·25 v at 187°. No gas was evolved at either electrode but there was considerable charring round the anode when the current was raised above 1 ma.

Infrared Spectra.—These were recorded on a Unicam S.P. 100 spectrometer and typical spectra are shown in Figs. 4 and 5. Pyridine and piperidine were examined as liquid films. The complexes were studied as potassium bromide discs. In each case the apparent ε values were calculated from the peak heights of the absorption maxima. Spectra for benzene solutions gave essentially the same results. Benzene is not an ideal solvent for spectroscopic work, especially for pyridine compounds, but it was chosen so that the work would be comparable with the study of dipole moments which had been carried out in this solution.[4] The spectra of pyridinium chloride and pyridinium tetrachloroborate were also observed for comparison.

DISCUSSION

The trichlorides of Group III show an interesting variation in the stoicheiometry of their complexes with pyridine. Boron trichloride forms a 1 : 1 complex and there is possibly also a tendency to form an incongruently melting 1 : 2 compound BCl_3,2py. A compound $(BCl_3)_2$,py was not reported at the time that $(BF_3)_2$,py and $(BBr_3)_2$,py were obtained at low temperatures, though all three trihalides form 2 : 1 complexes with triethylamine.[12] Aluminium trichloride forms both 1 : 1 and 1 : 2 complexes with pyridine [13,14] and also, apparently, a 1 : 3 complex.[13] Gallium trichloride forms 1 : 1 and 1 : 2 complexes but no 1 : 3 complex.[7,11] In each case the 1 : 1 complex is the more stable. By contrast, indium trichloride forms no 1 : 1 or 1 : 2 complexes with pyridine, the stable adduct being $InCl_3$,3py.[15] Indium tri-iodide–pyridine has, however, been reported.[16] Thallium trichloride forms 1 : 2 and 1 : 3 complexes.[17] There is thus a trend to greater co-ordination of pyridine with increasing atomic number of the Group III acceptor atom. The same trend is also shown with other ligands.

No complexes of piperidine with the Group III trihalides have previously been reported except for those with gallium trichloride and tribromide.[7,11,18] Such complexes are undoubtedly stable and their absence from the literature merely reflects the comparatively scanty attention paid to this ligand. A compound boron trichloride–dimethylamine, m. p. 127—137°, has been established.[19] This is analogous to boron trichloride–piperidine, the difference between the two compounds being that the two methyl groups in dimethylamine are substituted by a bridging trimethylene group in piperidine.

A detailed interpretation of the physical properties of boron trichloride–pyridine and –piperidine would follow closely the methods outlined in recent papers on gallium trichloride–pyridine [7] and –piperidine [11] and need not be repeated here. All four compounds are remarkably similar. It has been suggested [6] that the complexes have structures of the type $[py_2BCl_2]^+[BCl_4]^-$. A detailed examination of the infrared spectra of the solids does not decide unambiguously in favour of this and is probably more consistent with the formula $py\rightarrow BCl_3$ at least for the solid state and in benzene solution. The

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[11] Greenwood and Wade, *J.*, 1958, 1671.

[12] Brown, Stehle, and Tierney, *J. Amer. Chem. Soc.*, 1957, **79**, 2020.

[13] Van Dyke and Crawford, *J. Amer. Chem. Soc.*, 1951, **73**, 2022.

[14] Eley and Watts, *J.*, 1952, 1914.

[15] Renz, *Z. anorg. Chem.*, 1903, **36**, 101; Dennis and Geer, *J. Amer. Chem. Soc.*, 1904, **26**, 437; Peraldo-Bicelli, *Ann. Chim.* (*Italy*), 1958, **48**, 749.

[16] Schumb and Crane, *J. Amer. Chem. Soc.*, 1938, **60**, 306.

[17] Meyer, *Z. anorg. Chem.*, 1900, **24**, 347; Renz, *Ber.*, 1902, **35**, 1111; Berry, Lowry, and Goldstein, *J.*, 1928, 1752; Abbott, *Iowa State Coll. J. Sci.*, 1943, **18**, 3.

[18] Greenwood, *J. Inorg. Nuclear Chem.*, 1958, **8**, 234.

[19] Brown, *J. Amer. Chem. Soc.*, 1952, **74**, 1219.

question of the structure of the ions formed in the molten state is therefore unanswered and no advance can be made on our previous inferences,[7] though it seems clear that the fused compounds are ionically dissociated to the extent of about 1%. The infrared spectra of pyridine and piperidine are very markedly altered during complex formation and several regions merit further discussion.

B–N *Stretching Frequency.*—Fig. 4 indicates that the strong band at 1113 cm.$^{-1}$ (ε 55) occurs only in the spectrum of boron trichloride–pyridine; it appears to be associated with the formation of the co-ordinate B–N bond. In benzene solution the band lies at 1100 cm.$^{-1}$ (ε 390). These values compare with 1112 cm.$^{-1}$ for solid boron trifluoride–pyridine,[20] 1105 cm.$^{-1}$ for trimethylboron–ammonia,[21] and 1090—1102 cm.$^{-1}$ (ε 155—340) for a series of complexes BX_3,py in chloroform solution (X = H, F, Cl, Br).[22] The B–N frequency would be expected to lie at higher wave numbers for alkylamine–boron complexes because of their greater electron-donor properties. Consistently with this the band appears at 1245 cm.$^{-1}$ (ε 41) in boron trichloride–piperidine (see Fig. 5). The band is a well-resolved doublet in benzene solution, the maxima lying at 1220 cm.$^{-1}$ (ε 85) and 1236 (ε 83). The bands which occur in chloroform solutions of BH_3,NMe_3 at 1250 cm.$^{-1}$ (ε 30) and BF_3,NMe_3 at 1249 (ε 160) have likewise been assigned to the B–N stretching frequency,[22] and values of 1255 and 1248 cm.$^{-1}$ have been recorded for this vibration in the Raman and infrared spectra of BH_3,NMe_3 and BD_3,NMe_3.[23] Where partial double-bonding can occur between boron and nitrogen as a result of back-donation from the non-bonding electrons on nitrogen [*e.g.*, in covalent compounds such as $Me_2B{\cdot}NHPh$ and $(R_2N)_3B$] the B–N frequency apparently shifts to wave numbers as high as 1350 cm.$^{-1}$.[24] Very recently,[25] the assignment of bands in the 1100—1250 cm.$^{-1}$ region to the B–N stretching mode has been disputed and

FIG. 4. *Infrared spectra of pyridine* (*A*) *and complexes. B = pyridinium chloride; C = pyridinium tetrachloroborate; D = boron trichloride–pyridine.*

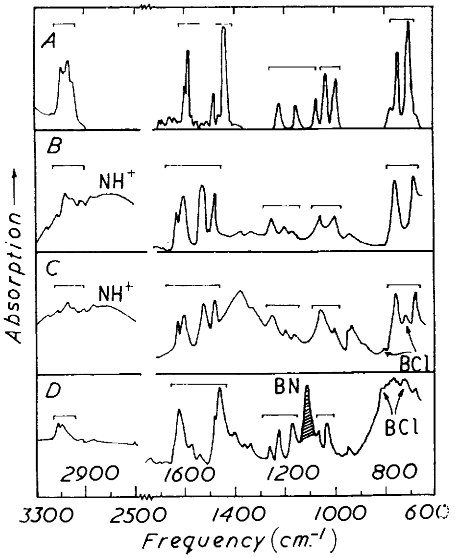
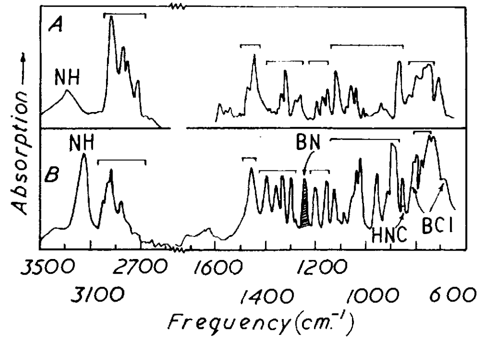


FIG. 5. *Infrared spectra of piperidine* (*A*) *and boron trichloride–piperidine* (*B*).



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[20] Luther, Mootz, and Radwitz, *J. prakt. Chem.*, 1957, **5**, 242.

[21] Goubeau and Becker, *Z. anorg. Chem.*, 1952, **268**, 1, 113.

[22] Katritzky, *J.*, 1959, 2049.

[23] Rice, Caliano, and Lehmann, *J. Phys. Chem.*, 1957, **61**, 1222.

[24] Becher, *Z. anorg. Chem.*, 1957, **289**, 262; Bellamy, Gerrard, Lappert, and Williams, *J.*, 1958, 2412.

[25] Taylor and Cluff, *Nature*, 1958, **182**, 390.

cogent evidence has been adduced in favour of assigning this mode to frequencies in the region 650—750 cm.$^{-1}$. Unequivocal evidence on this was not obtained in the present work because of complications due to the occurrence of B–Cl vibrations in the same region, but further work is being undertaken to clarify this point. It remains true, however, that the formation of a dative B–N bond is accompanied by the appearance of a strong band near 1100—1250 cm.$^{-1}$ the exact position of which can be correlated with the relative donor strength of the ligand, but which does not show the isotope doublet structure expected for a vibration involving the motion of the boron atom.

B–Cl *Frequencies*.—Comparison of the spectra of pyridinium chloride and pyridinium tetrachloroborate shown in Fig. 4 reveals two new bands in the latter compound at 717 (ε 130) and 799 cm.$^{-1}$ (ε 10) which, by comparison with the spectrum of carbon tetrachloride,[6] can be assigned to the ν_3 and $(\nu_2 + \nu_3)$ modes of the tetrahedral BCl_4^- ion. Similar bands recur in the spectrum of solid boron trichloride–pyridine at 723 (ε 150) and 799, 813 cm.$^{-1}$ (ε 45), and in solid boron trichloride–piperidine at 690 (ε 38) and 798 cm.$^{-1}$ (ε 70). However, the same assignment does not necessarily follow since the frequency of the asymmetrical B–Cl vibration of the $L \rightarrow BCl_3$ grouping is likely to fall in the same region. For example, the benzene solution of boron trichloride–pyridine, which is known [4] to contain predominantly the undissociated species $C_5H_5N \rightarrow BCl_3$, has bands at 729 ($\varepsilon$ 550) and 816 cm.$^{-1}$ (ε 120). The asymmetrical B–Cl frequency in a chloroform solution of the pyridine adduct was observed at 818 cm.$^{-1}$ (ε 55).[22] A further argument against assigning these bands to the BCl_4^- ion in these complexes is that this implies the presence of cationic species $L_2BCl_2^+$ to restore the correct 1 : 1 stoicheiometry; the B–Cl frequencies in such cations will differ from those in the tetrachloroborate anion but no other new frequencies are observed in this region which can be assigned in this way. Moreover, it has recently been shown [26] that the infrared spectra of alkylammonium tetrachloroborates invariably have a very strong and well-defined doublet at about 660, 700 cm.$^{-1}$ and three bands of medium intensity at 1265, 1382, and 1449 cm.$^{-1}$. A corresponding series of bands does not appear for the pyridine or the piperidine complex of boron trichloride and we believe that, in the solid state and in solution, the complexes are best represented as the simple adducts $L \rightarrow BCl_3$.

N–H$^+$ *and* N–H *Stretching Frequencies*.—The region 1600—2800 cm.$^{-1}$ is almost free from absorption by pyridine and boron trichloride–pyridine but the two pyridinium complexes (Fig. 4) show a fairly strong and very broad absorption band between 2600 and 2800 cm.$^{-1}$. This is the N–H$^+$ stretching frequency [27] and has maxima at 2840 (ε 61) and 2740 cm.$^{-1}$ (broad, ε 65) for the chloride, and at 2830 (ε 170) and 2760 cm.$^{-1}$ (broad, ε 170) for the tetrachloroborate. Of more interest is the variation in the N–H stretching frequency of piperidine which occurs on complex-formation. Fig. 5 shows that the broad, medium-intensity band at 3291 cm.$^{-1}$ (ε 33, $\Delta\nu_{\frac{1}{2}}{}^{a}$ 132 cm.$^{-1}$) in liquid piperidine becomes narrower and more intense in the complex, the band occurring at 3157 cm.$^{-1}$ (ε 75, $\Delta\nu_{\frac{1}{2}}{}^{a}$ 32 cm.$^{-1}$) in the solid and at 3169 cm.$^{-1}$ (ε 85, $\Delta\nu_{\frac{1}{2}}{}^{a}$ 40 cm.$^{-1}$) in benzene solution. The piperidine N–H stretching frequency is known to occur at 3347—3350 cm.$^{-1}$ in chloroform [28] or carbon tetrachloride solution.[29,30] When the spectrum of the pure compound itself is obtained as a liquid film, however, the increased extent of intermolecular hydrogen-bonding reduces the force constant of the N–H bond and so lowers the frequency to 3291 cm.$^{-1}$ (Fig. 5) (cf. 3280 cm.$^{-1}$ for the liquid [28]). When the non-bonding pair of electrons on the nitrogen is involved in donor–acceptor interaction, the N–H bond is weakened even further and the frequency drops to 3157 cm.$^{-1}$ (Fig. 5). The shift is thus greater that that observed when piperidine co-ordinates to Pt(II),[30,31] Pd(II),[31]

[26] Kynaston and Turner, *Proc. Chem. Soc.*, 1958, 304.

[27] Chenon and Sandorfy, *Canad. J. Chem.*, 1958, **36**, 1181.

[28] Marion, Ramsay, and Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 305.

[29] Russell and Thompson, *J.*, 1955, 483; *Proc. Roy. Soc.*, 1956, *A*, **234**, 318.

[30] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.

[31] *Idem*, *J.*, 1956, 2712; *J.*, 1958, 3203.

or Rh(I),[32] where the lowest N–H stretching frequency observed was 3211 cm.$^{-1}$ for *trans*-[PPr$^n_3$,pip,PtI$_2$]. In this group of three transition metals the extent of the shift can be correlated with the relative electron-acceptor strength of the metal, as, in a series of secondary amines, the intensity of the band can be correlated with the acidity of the amine.[29] These observations are now extended to the much more powerful electron-acceptor, boron trichloride, and it is clear that increasing the electron drift from the nitrogen atom increases the intensity and decreases the frequency of the N–H stretching vibration.

Changes in the Spectrum of Pyridine on Co-ordination.—The infrared spectrum of the pyridine molecule is considerably modified when the non-bonding pair of electrons on the nitrogen atom is donated into the vacant orbital of an electron-acceptor. The effects on frequency and intensity might be expected to depend both on the symmetry of the vibration and on the chemical nature of the bond involved. The detailed assignment of frequencies in the spectrum of pyridine has been the subject of some controversy but most of the points at issue have now been resolved and the following discussion is based on the assignments given by Wilmshurst and Bernstein [33] using the nomenclature of Kline and Turkevitch.[34] The pyridine molecule contains eleven atoms and thus has 27 (*i.e.*, $3n - 6$) fundamental modes of vibration. The molecule is planar, with a twofold axis of symmetry (C_{2v}) through the nitrogen atom and the γ-carbon atom. The 27 modes are therefore divided into four classes: ten modes are in the plane of the ring and are symmetrical with respect to the C_{2v}-axis (class A_1); nine are in the plane of the ring but antisymmetrical with respect to the C_{2v}-axis (class B_1); five modes involve out-of-plane vibrations which are antisymmetric to the two-fold axis (class B_2); and the remaining three modes, which are forbidden in the infrared region, are out-of-plane, symmetrical vibrations (class A_2). The 27 modes are numbered 1—20 with suffixes *a*, *b* where necessary to distinguish degenerate vibrations.[34]

The first strong band at the low-frequency end of the spectrum of pyridine shown in Fig. 4 occurs at 705 cm.$^{-1}$ (ε 150), [B_2, 11 (out-of-plane C–H deformation)]. The maximum is shifted about 25 cm.$^{-1}$ to shorter frequencies in the complexes and has comparable, but generally weaker, intensity; it occurs at 684 cm.$^{-1}$ (ε 103) in pyridinium chloride, at 677 cm.$^{-1}$ (ε 220) in pyridinium tetrachloroborate, and at 681 cm.$^{-1}$ (ε 45) in boron trichloride–pyridine. (In the following paragraphs the data for the three complexes will be given in the above order without naming the compounds each time.) The shoulder at 675 cm.$^{-1}$ is probably a combination band (18*a*–16*b*) (calculated frequency, 667 cm.$^{-1}$).

The pyridine band at 748 cm.$^{-1}$ (ε 74) [B_2, 4 (out-of-plane ring deformation)] is moved to slightly higher frequencies and enhanced in intensity: 759 cm.$^{-1}$ (ε 91), 753 cm.$^{-1}$ (ε 220), 751 and 769 cm.$^{-1}$ (ε 55 and 70). Results [20] on the pyridine complexes of boron trifluoride and aluminium trichloride are consistent with this, the maxima occurring at 777 and 760 cm.$^{-1}$, but the effect is apparently absent when iodine is the electron-acceptor.[35] The weak absorption at 773 cm.$^{-1}$ is possibly a combination band (16*a* + 16*b*) (calculated frequency 779 cm.$^{-1}$). This appears in the boron trichloride complex at 785 cm.$^{-1}$ but not in the pyridinium complexes.

The region between 800 and 980 cm.$^{-1}$ contains only very weak pyridine bands [36,37] which were not observed with the film thickness recorded in Fig. 4. The complexes, however, show enhanced absorption in this region, the principal maximum occurring at 940 (ε 20), 934 (ε 100), and 943 cm.$^{-1}$ (ε 11). This is close to the weak pyridine fundamental at 942 cm.$^{-1}$ [B_2, 5 (out-of-plane C–H deformation)].

Pyridine has a characteristic group of five sharp bands in the region 990—1230 cm.$^{-1}$.

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[32] Chatt, Duncanson, Shaw, and Venanzi, *Discuss. Faraday Soc.*, 1958, **26**, 131.
[33] Wilmshurst and Bernstein, *Canad. J. Chem.*, 1957, **35**, 1183.
[34] Kline and Turkevitch, *J. Chem. Phys.*, 1944, **12**, 300.
[35] Ham, Rees, and Walsh, *Nature*, 1952, **169**, 110.
[36] Corrsin, Fax, and Lord, *J. Chem. Phys.*, 1953, **21**, 1170.
[37] Long, Marfin, Hales, and Kynaston, *Trans. Faraday Soc.*, 1957, **53**, 1171.

The two stronger bands are ring breathing frequencies and the other three are in-plane C–H deformations. All five can be recognised in the complexes, though sometimes with considerably altered frequencies and intensities. The band at 995 cm.$^{-1}$ (ε 38) [A_1, 1 (totally symmetric, in-plane, breathing frequency)] moves to 1003 (ε 35) and 1005 cm.$^{-1}$ (ε 94) in the pyridinium complexes but is shifted by 40 cm.$^{-1}$ and diminished in intensity in the boron trichloride adduct to 1034 cm.$^{-1}$ (ε 20). The same band has been listed [22] for chloroform solutions of the pyridine adducts of borine (1020 cm.$^{-1}$, ε 10), boron trichloride (1024 cm.$^{-1}$, ε 15), and boron tribromide (1025 cm.$^{-1}$, ε 32) but was assigned to a C–H in-plane deformation.* Typical of other values for the frequency of this vibration in pyridine derivatives are 1025 cm.$^{-1}$ for solid boron trifluoride–pyridine,[20] 1025 cm.$^{-1}$ for aluminium trichloride–pyridine,[20] 1017 cm.$^{-1}$ for pyridine *N*-oxide,[38] 1001—1004 cm.$^{-1}$ for salts of the cation $C_5H_5NI^+$,[39] and 1005 cm.$^{-1}$ for pyridine–iodine.[35,40] There appears to be a rough correlation between the strength of the donor–acceptor bond and the extent to which the symmetrical breathing frequency of the ring is increased.

The second breathing frequency [A_1, 12] occurs at 1034 cm.$^{-1}$ (ε 40) in pyridine and is apparently shifted by about 25 cm.$^{-1}$ in the complexes: 1059 (ε 35), 1056 (ε 150), 1063 cm.$^{-1}$ (ε 16). The band occurs in the crystalline adducts of pyridine with boron trifluoride and aluminium trichloride [20] at 1070 and 1055 cm.$^{-1}$ and in chloroform solutions of pyridine adducts with borine and boron trifluoride [22] at 1060 (ε 10) and 1067 cm.$^{-1}$ (ε 105, shoulder) though these last two lines were assigned to C–H in-plane deformations (class B_1). It is surprising that no corresponding line was found in our benzene solution of boron trichloride–pyridine, or in a chloroform solution of this compound.[22] A new line, absent from the solid complexes, does appear at 1138 cm.$^{-1}$ (ε 13) in the benzene solution but its origin is not clear. In contrast with the behaviour of the 1034 cm.$^{-1}$ pyridine band in the six complexes just mentioned, the band remains almost unaltered in position in pyridine oxide,[38] pyridine–iodine,[39] and pyridine–I$^+$ salts,[39] though it is considerably diminished in intensity.

The three C–H in-plane deformations which occur in the region 1070—1220 cm.$^{-1}$ in pyridine itself are shifted to considerably higher frequencies in the complexes and become more bunched together. The detailed changes are listed in Table 2 in which band 1 is 18*a* (class A_1), band 2 is 15 (class B_1), and band 3 comprises two modes which differ only in the motion of the γ-C–H bond with respect to the nitrogen atom, *viz.*, 3(B_1) and 9(A_1).

TABLE 2. C–H *in-plane deformation frequencies and intensities.*

	Band 1			Band 2			Band 3			
Compound	ν (cm.$^{-1}$)	ε	δ (cm.$^{-1}$)	ν (cm.$^{-1}$)	ε	δ (cm.$^{-1}$)	ν (cm.$^{-1}$)	ε	δ (cm.$^{-1}$)	Δ(3 − 1) (cm.$^{-1}$)
py	1072	21	—	1152	16	—	1220	17	—	148
py,HCl	1168	20	96	1198	26	46	1252	33	32	84
py,$HBCl_4$	1166	80	94	1200	94	48	1250	140	30	84
py,BCl_3	1169	20	97	1225	17	73	1262	11	42	93
py,BCl_3 (soln.)	1164	20	92	1220	90	68	1260	13	40	96
py,BF_3 (ref. 20)	1162	m	90	1227	m	75	1268	w	48	106
py,$AlCl_3$ (ref. 20)	1164	st	92	1224	m	72	1250	w	30	86

The last column of Table 2 shows that the frequency difference, Δ, between the first and the third band, decreases from 148 in pyridine to about 90 cm.$^{-1}$ in the complexes, owing to the fact that band 1 shifts some 95 cm.$^{-1}$ whereas band 3 moves only about 35 cm.$^{-1}$ (see columns headed δ in Table 2). It may be significant that band 1 is the only mode in this region which involves a C–H stretching vibration (on the γ-carbon atom) in addition to the C–H bending motions on the other four carbon atoms.

* Further information is required before one can decide definitely between these two assignments.

[38] Costa and Blasina, *Z. phys. Chem.* (*Frankfurt*), 1955, **4**, 24.

[39] Zinbaro and Tolberg, *J. Amer. Chem. Soc.*, 1959, **81**, 1353.

[40] Glusker and Thompson, *J.*, 1955, 471.

It is hard to compare Table 2 with Katritzky's data [22] because of differing assignments and the possibility of band overlapping. The band which occurs [22] at 1158 (ε 15) and 1160 cm.$^{-1}$ (ε 20) in chloroform solutions of boron trichloride- and boron tribromide-pyridine has been assigned to class B_1 though it is very similar to band 1 (class A_1) which occurs near 1165 cm.$^{-1}$ (ε 20) in our complexes. The band at 1165 cm.$^{-1}$ (ε 170) in borine-pyridine was assigned to the BH_3 bending mode; [22] this would clearly swamp any contribution from the in-plane C–H deformation 18*a*. The band occurs at 1165 cm.$^{-1}$ (ε 310) in boron trifluoride–pyridine and was assigned to the asymmetric $^{10}BF_3$ vibration.[22] However, the ^{11}B-component at 1125 cm.$^{-1}$ (ε 280) has lower intensity despite the fact that ^{11}B is four times as abundant as ^{10}B, and some other contribution to the total intensity of the 1165 cm.$^{-1}$ band in this compound is indicated. (The same difficulty arises with the assignment of the corresponding band in boron trifluoride–trimethylamine, where the peak assigned to $^{11}BF_3$ occurs only as a shoulder on the $^{10}BF_3$ band and has only half its intensity.) Bands corresponding to bands 2 and 3 in Table 2 were not recorded for the chloroform solutions of the complexes,[22] presumably because of interference by the solvent band in this region.

The spectrum of pyridine is clear between 1230 and 1430 cm.$^{-1}$ except for a very weak band at 1375 cm.$^{-1}$ (ε 3) [B_1, 14 (in-plane antisymmetric ring deformation involving C–C and C–N stretching modes)]. Absorption in this region is considerably enhanced in the complexes and gives rise to two (or three) maxima at about 1335, 1375 cm.$^{-1}$ (and 1404 cm.$^{-1}$). These are not fully accounted for but it is clear that the band at 1375 cm.$^{-1}$ cannot be assigned to the tetrachloroborate combination band at 1382 cm.$^{-1}$ [26] since it occurs in pyridinium chloride as well as the tetrachloroborates. The same statement applies to band 3 in Table 2, which cannot be assigned to the tetrachloroborate combination band at 1265 cm.$^{-1}$.

The four principal bands between 1430 and 1600 cm.$^{-1}$ are due to C–C, C–N stretching vibrations, two of which give rise to symmetric and two to antisymmetric in-plane ring deformations. The band at 1583 cm.$^{-1}$ (ε 76) carries a satellite at 1597 cm.$^{-1}$ (ε 31) due to Fermi resonance of 8*a* with (1 + 6*a*). This satellite disappears, as expected, in the spectra of the complexes because the frequency-shifts in the fundamentals move the frequency of the combination band away from the resonance condition. With this modification, the four bands are recognisable in the complexes, though they are slightly more spread and occur at higher frequencies (see Table 3). Between bands 19*b* and 19*a* in pyridine there is a weak band at 1458 cm.$^{-1}$ (ε 8) which is just discernible in the three complexes in the same position relative to the two main peaks but at 1501, 1501, and 1481 cm.$^{-1}$. It appears to be a combination band but it is not possible to decide between three alternatives, all of which are within 10 cm.$^{-1}$ of the observed band: (18*a* + 16*b*), (16*a* + 18*b*), (11 + 4). The band has previously been assigned to a class A_1 fundamental (presumably 19*a*) involving an in-plane ring deformation.[22]

TABLE 3. *In-plane ring deformation frequencies and intensities.*

	(1). 19*b*(B_1)			(2). 19*a*(A_1)			(3). 8*b*(B_1)			(4). 8*a*(A_1)			Δ(4 − 1)
Compound	ν	ϵ	δ	ν	ϵ	δ	ν	ϵ	δ	ν	ϵ	δ	(cm.$^{-1}$)
py	1439	130	—	1483	26	—	1572	8	—	1583	76	—	144
py,HCl	1481	65	42	1530	82	47	1603	63	31	1631	40	48	150
py,$HBCl_4$	1480	190	41	1526	180	43	1599	140	27	1629	120	46	149
py,BCl_3	1462	49	23	1540	9	57	1576	12	4	1624	28	41	162
py,BCl_3 (soln.) ...	1462	180	23	1541	7	58	1576	13	4	1622	60	39	160
										1634	65	51	172

Little systematic change can be detected in the intensity of the four bands listed in Table 3; the two central bands (19*a*, 8*b*) are considerably enhanced in the pyridinium compounds and become comparable with the outer pair (19*b*, 8*a*). This is less pronounced for the boron trichloride complex. Similar features can be noted in the spectra of other pyridine adducts,[20,22] including the curious splitting of the 8*a*-band in benzene and chloroform solutions of boron trichloride–pyridine though the band is a singlet in the solid state; the corresponding band for chloroform solutions of pyridine complexes with borine, boron trifluoride, and tribromide is also a singlet.[22]

The effects of complex formation on the C–H stretching modes near 3000—3100 cm.$^{-1}$ are obvious form Fig. 4. Detailed discussion is not profitable because of poor resolution and the overlapping of the broad N–H$^+$ absorption in the pyridinium complexes. In summary, co-ordination decreases the frequency of C–H out-of-plane deformations but increases the frequencies of all other modes; the increase is greatest for C–H in-plane deformations but is also considerable for in-plane ring deformations; the increase is less for ring breathing modes and least for out-of-plane ring deformations.

Changes in the Spectrum of Piperidine on Co-ordination.—The infrared absorption spectrum of piperidine is much more complicated than that of pyridine and complete assignment of the 46 fundamentals has not been carried through. However, comparison of the Raman [41] and infrared spectra,[42] together with the known frequency ranges of typical vibrations in organic compounds, enables most of the bands to be assigned to chemically identifiable groups of atoms. Fig. 5 shows that co-ordination of boron trichloride to piperidine alters both the frequency and the intensity of these bands considerably and tends to enhance the weaker bands to strengths comparable with those of the stronger bands, especially in the region 900—1400 cm.$^{-1}$. The effect on the N–H stretching frequency at 3291 cm.$^{-1}$ has already been mentioned (p. 1136).

There are four clearly defined C–H stretching frequencies (cm.$^{-1}$) at 2722 (ε 43), 2797 (ε 70), 2841 (ε 93), and 2923 (ε 230); these shift to slightly higher frequencies in the complex but are considerably diminished in intensity: 2750 (ε 7), 2803 (ε 12), 2857 (ε 24), and 2933 (ε 49). The main band in the complex also carries two satellites on the high-frequency side.

The two H–C–H bending modes occur at 1443 (ε 42) and 1468 (ε 18) and are replaced by a single band at 1456 (ε 50).

Four of the H–C–C wagging vibrations are shifted about 20 cm.$^{-1}$ to higher frequencies; the fifth remains almost unchanged. Intensities in the complex become more nearly equal to that of the most intense wagging mode except for the lowest-frequency member which remains weak:

Piperidine: 1260 (ε 14), 1279 (ε 11), 1319 (ε 30), 1332 (ε 14), 1388 (ε 7).

BCl_3,pip: 1280 (ε 13), 1299 (ε 43), 1332 (ε 45), 1354 (ε 35), 1391 (ε 43).

Three H–C–C twisting modes in piperidine occur at 1151 (ε 17), 1170 (ε 14), and 1194 (ε 11). The first and third of these are shifted slightly but considerably enhanced in the complex: 1156 (ε 39) and 1200 (ε 35). The central peak was not observed in the crystalline complex but appeared as a very weak band at 1179 cm.$^{-1}$ in benzene solution. A fourth twisting mode at 1010 cm.$^{-1}$ also disappears in the complex.

There are five ring vibrations in piperidine. These retain the same general appearance in boron trichloride–piperidine and intensities are again about trebled, except for the highest-frequency component which remains almost unaltered. The two bands of lowest frequency shift to higher frequencies, and the next two bands shift a similar amount to lower frequencies. The precise data are:

Piperidine: 862 (ε 36), 941 (ε 10), 1038 (ε 18), 1055 (ε 19), 1119 (ε 29).

BCl_3,pip: 892 (ε 100), 956 (ε 45), 1021 (ε 65), 1036 (ε 46), 1126 (ε 33).

The H–N–C deformation apparently moves from 822 (ε 14) to 855 (ε 41); this is the largest frequency shift of any of the piperidine modes on complexing except for that of the N–H stretching vibration itself.

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[41] Kohlrausch and Stockmann, *Z. phys. Chem.*, 1936, *B*, **31**, 382.

[42] Voetter and Tschamler, *Monatsh.*, 1953, **84**, 134.

The three H–C–C rocking modes are scarcely altered in position but are more intense and better resolved in the complex. The presence of B–Cl vibrations in this region makes specific assignments less definite, but it seems likely that the three piperidine bands at 749 (ε 34), 770 (shoulder), and 800 cm.$^{-1}$ (ε 24) correlate with the adduct's bands at 745 (ε 125), 772 (ε 60), and 798 cm.$^{-1}$ (ε 70). The band at 705 (ε 25) shifts to 725 cm.$^{-1}$ (ε 125).

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