467. *The Infrared Spectra of Some New Compounds of Boron Trifluoride, Boron Trichloride, and Sulphur Trioxide.*

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In some work on the properties of liquid hydrogen chloride as an ionizing solvent, a number of new compounds, containing the groups PH_4^+, PCl_4^+, SO_3Cl^-, BCl_4^-, and BF_3Cl^-, have been prepared, together with some others, such as $POCl_3,BCl_3$ and $POCl_3,BF_3$. In this paper their infrared spectra together with the infrared spectra of some similar compounds are reported and discussed. It is concluded that $POCl_3,BCl_3$ and $POCl_3,BF_3$ have the $Cl_3PO\rightarrow BCl_3$ and $Cl_3PO\rightarrow BF_3$ structures.

IN previous papers [1,2] the authors reported the preparation of the following compounds: $Me_4N^+BCl_4^-$, $Et_4N^+BCl_4^-$, $PCl_4^+BCl_4^-$, $PH_4^+BCl_4^-$, $Me_4N^+BF_3Cl^-$, $Et_4N^+BF_3Cl^-$, $NOBF_3Cl$, $PH_4^+BF_3Cl^-$, $PCl_4^+BF_3Cl^-$, $Me_4N^+SO_3Cl^-$, and $PCl_4^+SO_3Cl^-$. The infrared spectra of these compounds are now recorded together with those of $POCl_3,BCl_3$, $POCl_3,BF_3$, Et_2O,BF_3, C_5H_5N,BF_3, and C_5H_5N,BCl_3, in the range 4000—400 cm.$^{-1}$. The spectra have been analysed, and the characteristic frequencies of the BCl_4^-, BF_3Cl^-, SO_3Cl^-, PCl_4^+, and PH_4^+ ions determined, and as far as possible a vibrational assignment has been made. From the infrared spectra of $POCl_3,BCl_3$ and $POCl_3,BF_3$ it is concluded that in these compounds co-ordination to the boron takes place through the oxygen and a B–O stretching frequency has been assigned. In $POCl_3,BF_3$ the absence of a B–Cl stretching frequency rules out the possibility of a $POCl_2^+BF_3Cl^-$ structure.

EXPERIMENTAL

Materials.—The preparations and analyses of the compounds have been given in previous papers,[1,2] except for those compounds described below. The diethyl ether–boron trifluoride complex was made as described in *Inorg. Synth.*, 1957, vol. V. The pyridine–boron trifluoride complex was made by adding dry pyridine to the boron trifluoride–ether complex and distilling off excess of the ether complex with the displaced ether. The pyridine–boron trichloride complex was made by distilling excess of boron trichloride on to frozen pyridine in a vacuum-line, allowing the mixture to warm gradually, and distilling off the excess of boron trichloride.

Apparatus and Method.—The infrared spectra of the compounds were taken with a Perkin–Elmer 21, double-beam, continuously recording spectrophotometer. A rock-salt prism was used in the range 4000—650 cm.$^{-1}$, and a potassium bromide prism in the range 800—400 cm.$^{-1}$. Solids were finely powdered in an agate mortar and made into a mull, either with Nujol or with hexachlorobutadiene. The mull was then smeared between rock-salt or potassium bromide plates. Liquids were similarly smeared as thin films.

RESULTS AND DISCUSSION

(*A*) *Infrared Spectrum of the* BCl_4^- *Ion.*—The infrared spectra of Me_4N^+, Et_4N^+, $C_5H_5NH^+$, PH_4^+, and PCl_4^+ tetrachloroborates were taken, and the contribution of the BCl_4^- ion was identified by comparison with the infrared spectra of other salts of the same cations. The spectra contained two strong bands at about 692 and 664 cm.$^{-1}$, and three weak bands at about 1275, 1380, and 1460 cm.$^{-1}$, all attributable to the BCl_4^- ions. Kynaston and Turner [3] have reported on the infrared spectra of tetramethylammonium and potassium tetrachloroborate. Our results for the above salts are in good agreement with theirs.

The BCl_4^- ion, like the isoelectronic carbon tetrachloride molecule, should be tetrahedral and have only two fundamental vibration frequencies active in the infrared, ν_3

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[1] Waddington and Klanberg, *Naturwiss.*, 1959, **46**, 578.

[2] Waddington and Klanberg, preceding papers.

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

and ν_4. By comparison with the infrared spectrum[4] of carbon tetrachloride ($\nu_4 = 305$ cm.$^{-1}$), only one of these, ν_3, will be expected to be active above 400 cm.$^{-1}$. In fact, two peaks are active in the infrared, split by almost exactly the same amount in all cases. There are two possible explanations of this splitting. It may be due to the two isotopic species $^{10}BCl_4^-$ and $^{11}BCl_4^-$, or it may be due to the interaction by Fermi resonance of the combination $\nu_1 + \nu_4$, which has the same symmetry as ν_3, with ν_3, as a result of which it is shifted and gains in intensity. Two reasons suggest that the latter explanation is correct: first, the splitting is larger than one would expect for the two isotopic species and, secondly, a similar splitting is observed in carbon tetrachloride (ν_3, $\nu_1 + \nu_4$; 797, 768 cm.$^{-1}$). It is noteworthy that the splitting in carbon tetrachloride, 29 cm.$^{-1}$, is almost exactly the same as that in BCl_4^-, 28—30 cm.$^{-1}$. We therefore conclude that the strong peaks at 692 and 664 cm.$^{-1}$ in the BCl_4^- spectrum are ν_3 and $\nu_1 + \nu_4$. The fact that the strongest combination bands in the infrared spectrum of carbon tetrachloride are $2\nu_1 + 2\nu_4$, $\nu_1 + \nu_4 + \nu_3$, and $2\nu_3$ (1529, 1546, 1575 cm.$^{-1}$) suggests fairly strongly that the three bands in the infrared spectrum of BCl_4^-, 1275, 1380, 1460 cm.$^{-1}$, may be given the same assignment.

(*B*) *Infrared Spectrum of the* PCl_4^+ *Ion.*—The infrared spectra of the PCl_6^-, BCl_4^-, BF_3Cl^-, and SO_3Cl^- salts of PCl_4^+ were taken, and the contribution of the PCl_4^+ ion was identified by comparison with the infrared spectra of other salts of the same anions. The spectra contained two strong bands at about 584 and 650 cm.$^{-1}$ and three weak bands at about 1160, 1215, and 1309 cm.$^{-1}$, all attributable to the PCl_4^+ ion.

The PCl_4^+ ion, like the isoelectronic silicon tetrachloride molecule, should be tetrahedral and have only two fundamental frequencies active in the infrared, ν_3 and ν_4. By comparison with the infrared spectrum[5] of silicon tetrachloride ($\nu_4 = 221$ cm.$^{-1}$) only one of these, ν_3, will be expected to be active above 400 cm.$^{-1}$. In fact, two strong peaks are active in the infrared region. One of these must be ν_3, and the other is probably $\nu_1 + \nu_4$, since this is observed close to ν_3 in the infrared spectrum of silicon tetrachloride ($\nu_3 = 621$ cm.$^{-1}$; $\nu_1 + \nu_4 = 647$ cm.$^{-1}$). Of the three weak bands at 1160, 1215, and 1309 cm.$^{-1}$ in the spectrum of PCl_4^+, the one at 1309 cm.$^{-1}$ is by far the strongest and the others are very weak. They are probably the three combination bands $2\nu_1 + 2\nu_4$, $\nu_1 + \nu_4 + \nu_3$, and $2\nu_3$.

(*C*) *Infrared Spectrum of the* PH_4^+ *Ion.*—The infrared spectra of phosphonium iodide, tetrachloroborate, and trichlorofluoroborate were taken, and the contribution of the PH_4^+ ion was identified by comparison with the infrared spectra of other salts of the same anions and by comparison with the infrared spectrum of phosphine. This last step was necessary because of the high dissociation pressure of the compounds, phosphine being one of the dissociation products. The infrared spectrum of phosphonium iodide has previously been studied[6] in detail at —190°. Only two fundamental frequencies of the PH_4^+ ion, ν_3 and ν_4, are active in the infrared region and both these are found in all three compounds. They are observed at the following frequencies (in cm.$^{-1}$): PH_4I, ν_3 2345, ν_4 945; PH_4BCl_4, ν_3 2445, ν_4 982; PH_4BF_3Cl, ν_3 2380, ν_4 980. It should be noted that quite large shifts have taken place in ν_3 in going from phosphonium iodide to the tetrachloroborate, comparable to the size of shifts encountered in ammonium salts and quite unlike the constancy in value of ν_3 found in PCl_4^+. However, the combination and overtone bands $2\nu_4$ and $\nu_2 + \nu_4$ which occur in many ammonium salts are not found, and the intensities of ν_3 and ν_4 are much lower than in the ammonium ion, probably because of the much lower polarity of the P–H than of the N–H bond.

(*D*) *Infrared Spectrum of the* SO_3Cl^- *Group.*—The SO_3Cl^- group has the C_{3v} symmetry and should have six fundamental vibration frequencies, all infrared active. The spectrum of the group is very similar to that of the SO_3F^- group, whose infrared spectrum has been examined and assigned by Sharp[7] and whose Raman spectrum has been studied by

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[4] Herzberg, " Infrared and Raman Spectra," van Nostrand, New York, 1945.
[5] Smith, *J. Chem. Phys.*, 1953, **21**, 1997.
[6] Martinez and Wagner, *J. Chem. Physics*, 1957, **27**, 1110.
[7] Sharp, *J.*, 1957, 3761.

Siebert.[8] The infrared spectra of $PCl_4^+SO_3Cl^-$ and $Me_4N^+SO_3Cl^-$ were taken, and the contribution of the SO_3Cl^- ion was identified by comparison with the infrared spectra of other salts of the same cations. The results are given in Table 1, with Sharp's results for SO_3F^- for comparison.

It will be seen that the present assignment of frequencies is slightly different from that of Sharp, who, on the evidence of SO_3F^- alone, assigned the peak at 1277 cm.$^{-1}$ to $\nu_2(A_1) + \nu_5(E)$ and that at 1299 to $\nu_4(E)$. The evidence from the infrared spectrum of SO_3Cl^- seems to indicate a reversal of this assignment.

(*E*) *Infrared Spectrum of the* BF_3Cl^- *Group.*—Like the SO_3Cl^- group, this group has the C_{3v} symmetry, with 6 fundamental vibration frequencies, all active in the infrared region. It is isoelectronic with chlorotrifluoromethane, whose infrared spectrum has been examined by Thompson and Temple.[9] The infrared spectra of tetramethylammonium, tetrachlorophosphonium, phosphonium, and nitrosyl chlorotrifluoroborates were recorded, and the contribution of the BF_3Cl^- group was identified by comparison with the infrared spectra of other salts of the same cations. The frequencies and assignments are given in Table 2, together with the corresponding assignments in chlorotrifluoromethane for comparison.

(*F*) *Infrared Spectra of* $POCl_3,BF_3$ *and* $POCl_3,BCl_3$.–There are two possible structures for these compounds: they can either be $POCl_2^+BF_3Cl^-$ and $POCl_2^+BCl_4^-$ or $Cl_3PO\rightarrow BF_3$ and $Cl_3PO\rightarrow BCl_3$. The infrared spectra of both these compounds have been recorded and compared with these of $(C_2H_5)_2O\rightarrow BF_3$, BF_3Cl^-, C_5H_5N,BF_3,[10] C_5H_5N,BCl_3, and BCl_4^-. The assignment of frequencies in $POCl_3,BF_3$ is unequivocally in favour of the $Cl_3PO\rightarrow BF_3$.

TABLE 1. *The infrared spectrum of the* SO_3Cl^- *group* (*cm.*$^{-1}$).

Me_4NSO_3Cl	PCl_4SO_3Cl	KSO_3F	Assignment
535	540		S–Cl stretch ν_2 (A_1)
565	562	565	sym. SO_3 deform. ν_3 (A_1)
585	580	583	asym. SO_3 deform. ν_5 (E)
		732	S–F stretch ν_2 (A_1)
		970	
1044	1044	1073	sym. S–O stretch ν_1 (A_1)
1150	1160		ν_2 (A_1) + ν_5 (E)
1275	1250	1277	asym. S–O stretch ν_4 (E)
		1299	ν_2 (A_1) + ν_5 (E)

TABLE 2. *The infrared spectra of the* BF_3Cl^- *group* (*cm.*$^{-1}$).

PCl_4BF_3Cl	PH_4BF_3Cl	$NOBF_3Cl$	Me_4NBF_3Cl	CF_3Cl	Assignment
466			456	478	sym. X–F def. ν_3 (A_1)
556		522 533	520 544	561	asym. X–F def. ν_5 (E)
650		645	645	783	X–Cl stretch ν_2 (A_1)
		765	767		ν_6 (E) + ν_3 (A_1)
844 880			854 887	1092 1102 1112	sym. X–F stretch ν_1 (A_1)
	1028 1063	1040 1077	1037 1071	1210 1265	asym. X–F stretch ν_4 (E)
1200	1195	1194	1198		ν_2 (A_1) + ν_5 (E)

No peak which can be reasonably assigned to a B–Cl stretching mode can be found in the infrared spectrum of the compound, so no BF_3Cl^- cation can be present. Furthermore, a peak, assigned to the B–O stretching mode, is found close to that in the diethyl ether–boron trifluoride complex. The absorption bands found in the infrared spectrum of phosphorus oxychloride–boron trifluoride, their assignments, and the relevant parts of the infrared spectra of some other compounds are given in Table 3.

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[8] Siebert, *Z. anorg. Chem.*, 1957, **289**, 15.

[9] Thompson and Temple, *J.*, 1948, 1442.

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

The interpretation of the infrared spectrum of phosphorus oxychloride–boron trichloride is less unequivocal. It is not possible on the B–Cl stretching frequencies alone to decide between the two possible structures. However, the presence of the additional frequency at 1190 cm.$^{-1}$, which we assign to B–O stretching, by comparison with phosphorus oxychloride–boron trifluoride and diethyl ether–boron trifluoride, and which could not occur in the $Cl_2PO^+BCl_4^-$ structure, is strong evidence in favour of the Cl_3PO,BCl_3 structure. The spectra of these compounds are given in Table 4.

One of the most interesting features of the infrared spectra of the boron trifluoride and trichloride complexes with phosphorus oxychloride is that the P–O stretching frequencies are hardly shifted at all from that of the unco-ordinated phosphorus oxychloride: $POCl_3$, 1290—1300 cm.$^{-1}$; $POCl_3,BF_3$, 1298 cm.$^{-1}$; $POCl_3,BCl_3$, 1293 cm.$^{-1}$. This is in marked contrast to the behaviour of the phosphorus oxychloride adducts with stannic chloride and titanium tetrachloride prepared by Sheldon and Tyrer,[11] who found the frequency lowered by as much as 75 cm.$^{-1}$. Of course, it is just possible that the assignments of the P–O and B–O frequencies could be reversed in these two compounds, but this seems improbable, particularly as the frequencies at 1290 in $POCl_3,BCl_3$ and $POCl_3,BF_3$ seem to have much the same shape and intensity as that in phosphorus oxychloride itself. An explanation of the difference in these results and those of Sheldon and Tyrer may be that since neither boron trifluoride nor boron trichloride has any available *d*-orbitals on the central atom in the P–O–B bond there can be no *pπ–dπ* bond between the oxygen and the boron and hence no delocalization of the π-electrons in the P=O bond. However, in stannic chloride and titanium tetrachloride vacant *d*-orbitals are readily available on the central metal atom and hence the π-electrons of the P=O bond can readily co-ordinate into the *d*-shell of the metal producing a *pπ–dπ* bond between the oxygen and the tin or titanium with

TABLE 3. *The vibration spectra of some* BF_3 *adducts* (*cm.*$^{-1}$).*

$POCl_3,BF_3$		$(C_2H_5)_2O,BF_3$		C_5H_5N,BF_3		BF_3Cl^-		BF_4^-	
ν	Assmt.	ν	Assmt.	ν	Assmt.	ν	Assmt.	ν	Assmt.
486						456	Sym. B–F deform.		
532	BF_3, asym. deform.	520 530	$-B^{10}F_3$, $-B^{11}F_3$ asym. deform.	517 525	$-B^{10}F_3$, $-B^{11}F_3$ asym. deform.	521 532	$-B^{10}F_3$, $-B^{11}F_3$ asym. deform.	522 535	$B^{10}F_4^-$, $B^{11}F_4^-$ ν_4
579									
						645	B–Cl stretch		
755	$\nu_6 + \nu_3$; combin. band	759	Combination band	744	Combination band	766	$\nu_6 + \nu_3$	770	Weak ν_1 (forbidden)
936 945 955	sym. BF_3 stretch	876 900	sym. BF_3 stretch	893 912	sym. BF_3 stretch	854 887	sym. BF_3 stretch		
1030 1062	asym. BF_3	1025 1065	asym. BF_3	1125 1165	asym. BF_3 stretch	1040 1077	asym. BF_3 stretch	1033 1058	ν_3
1150	B–O stretch	1166	B–O stretch	1249	B–N stretch				
1298									

* $POCl_3$ has frequencies 484, 588, and 1290 cm.$^{-1}$.

TABLE 4. *The vibration spectra of some* BCl_3 *adducts.*

$POCl_3$	$POCl_3,BCl_3$		C_5H_5N,BCl_3		BCl_4^-	*W*
ν	ν	Assmt.	ν	Assmt.	ν	Assmt.
484	482					
588	585					
	667 700	B–Cl stretch	715 757	B–Cl stretch	663 690	$\nu_1 + \nu_4$ ν_3
	1190	B–O stretch	1103	B–N stretch		
1290	1293				1275	$2\nu_1 + 2\nu_4$
					1380	$\nu_1 + \nu_4 + \nu_3$
					1460	$2\nu_3$

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[11] Sheldon and Tyrer, *J. Amer. Chem. Soc.*, 1958, **80**, 4775; 1959, **81**, 2290.

subsequent delocalization of the π-electrons across the P–O–Sn bonds, increasing the Sn–O bond strength but weakening the P=O bond. This weakening is then reflected in the infrared spectra.

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