

351. Preparation and Infrared Spectra of Some Tetrachloroborates.

By W. KYNASTON, B. E. LARCOMBE, and H. S. TURNER.

Some alkali-metal and ammonium tetrachloroborates have been prepared by cold milling at atmospheric pressure. The infrared absorption spectra are recorded and briefly discussed.

MANY salts of tetrafluoroboric acid are known. The existence of tetrachloroborates has only recently been established, though it had been suggested previously that the anion is present in certain adducts of boron trichloride with halogen compounds.¹ More concrete evidence has been the preparation by a high-temperature reaction of potassium, rubidium, and caesium tetrachloroborates,² and by the preparation and examination of the infrared absorption spectra of quaternary and other ammonium tetrachloroborates;³ and, on the basis of isotope studies,⁴ the halogen exchange between boron trichloride and quaternary ammonium chlorides has been explained as involving a tetrachloroborate ion as intermediate. Tetrachloroborates have also been obtained by disproportionation following the reaction of certain primary and secondary amines with boron trichloride.⁵ Compounds containing mixed complex ions $[RBX_{3-n}Y_n]^-$ (where R is alkyl or vinyl and X and Y are fluorine, chlorine, or bromine) have been prepared recently.⁶

Earlier we obtained substituted ammonium tetrachloroborates by reaction of boron trichloride with finely divided ammonium chlorides in boiling chloroform; the reaction is sometimes complicated by elimination of hydrogen chloride, with formation of borazane adducts $RR'R''NBCl_3$, the borazenes $RR'N:BCl_2$, and the borazoles $(RN:BCl)_3$, and the degree of reaction depends on the state of division of the chloride. A much more satisfactory and widely applicable method is to mill the chloride at room temperature with glass beads in chloroform containing an excess of boron trichloride, the reactive surface of insoluble chlorides being continually re-exposed and much purer tetrachloroborates obtained: earlier failures, e.g., by Greenwood and Wade,¹ almost certainly arose through too small a surface for reaction. Besides the substituted ammonium tetrachloroborates which may also be prepared in boiling chloroform, ammonium tetrachloroborate itself and the higher alkali-metal tetrachloroborates have been made. Lithium and sodium chlorides did not give the tetrachloroborates, as was also found by Muetterties² in his high-temperature studies, but potassium and caesium chlorides (rubidium was not tried) react smoothly. The potassium and caesium salts contained 87% and 88% respectively of the tetrachloroborates and with the thermodynamically favourable conditions of a cold reaction practically complete conversion would be expected with longer or more efficient milling. The only other metal chloride investigated, barium chloride, did not react. Ammonium tetrabromoborate was also prepared in this way.

The tetrahalogenoborates examined were white solids which reacted instantly and vigorously with water to give boric acid, hydrogen halide, and the parent base. All were stable in dry air at room temperature. Lappert^{1b} observed that while pyridinium tetrachloro- and tetrabromo-borate lost hydrogen halide when heated, giving the pyridine-boron trihalide adducts, the reverse reaction did not take place. We have observed the same behaviour with trimethylamine-boron trichloride, but it is known⁶ that the reaction

¹ (a) Geuther, *J. prakt. Chem.*, 1874, **8**, 354; Meerwein and Maier-Hüser, *ibid.*, 1932, **134**, 51; Greenwood and Wade, *J.*, 1956, 1527; Wiberg and Heubaum, *Z. anorg. Chem.*, 1935, **222**, 98; Martin, *J. Phys. Chem.*, 1947, **51**, 1400; Groeneveld, *Rec. Trav. chim.*, 1952, **71**, 1152; Lappert, *J.*, 1953, 2784; Hewitt and Holiday, *J.*, 1953, 530; (b) Lappert, *Proc. Chem. Soc.*, 1957, 121.

² Muetterties, *J. Amer. Chem. Soc.*, 1957, **79**, 6563.

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

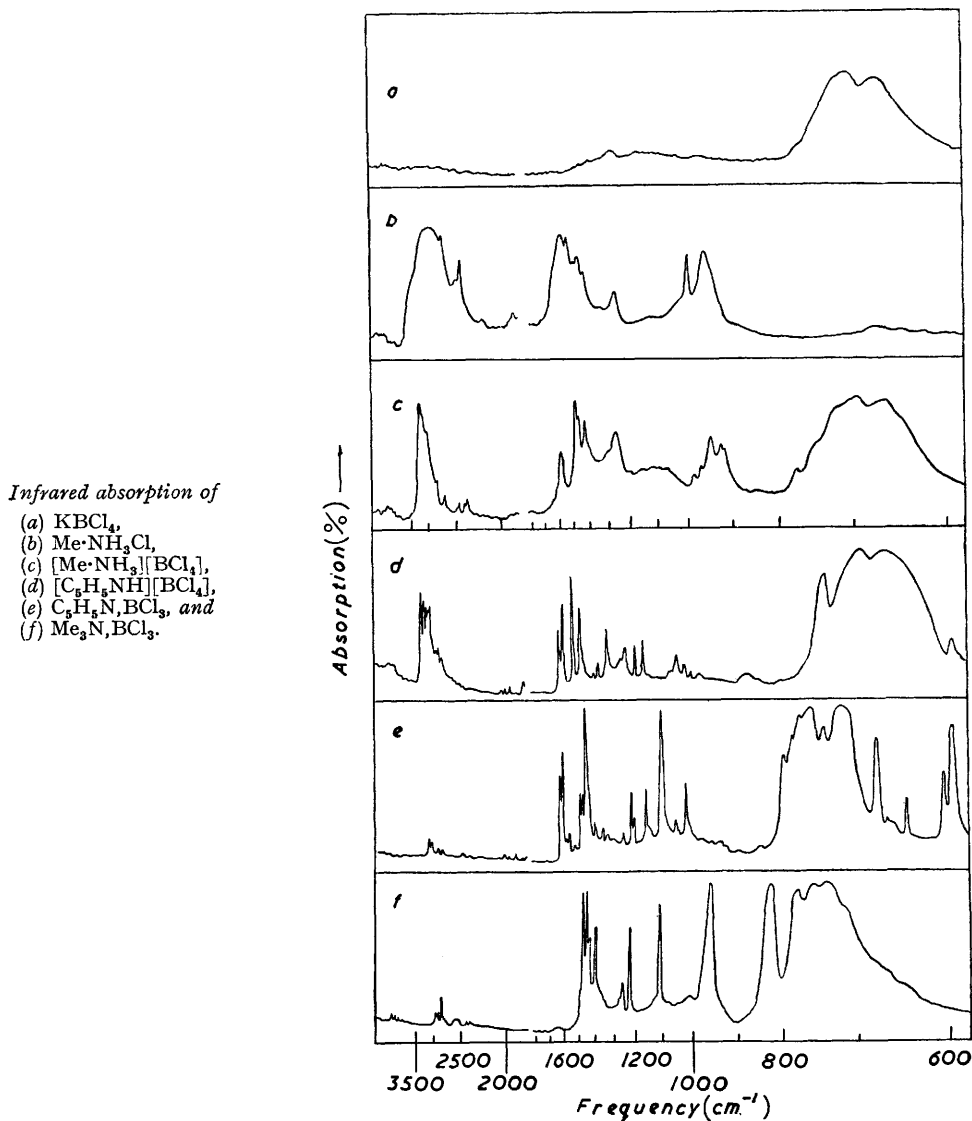
⁴ Herber, *J. Amer. Chem. Soc.*, 1958, **80**, 5080.

⁵ Gerrard and Mooney, *Chem. and Ind.*, 1958, 1259; Gerrard, Hudson, and Mooney, *ibid.*, 1959, 432.

⁶ Brinckman and Stone, *Chem. and Ind.*, 1959, 254.

$\text{Me}_3\text{N}\cdot\text{BEtF}_2(\text{s}) + \text{HCl}(\text{g}) \longrightarrow [\text{Me}_3\text{NH}][\text{BEtF}_2\text{Cl}](\text{s})$ does take place. Presumably in this case the B-N bond is weakened by the positive inductive effect of the ethyl group, and the nitrogen atom is sufficiently negative to take up a proton.

That the compounds we have obtained are tetrachloroborates is confirmed by their characteristic infrared absorption: for the alkali-metal and tetra-alkylammonium compounds there is no other reasonable structure; the same absorption is present in the



product from the highly hindered ethyldi-isopropylamine,⁷ and ammonium or substituted ammonium ions are demonstrable in the ammonium tetrachloroborates. The typical absorption spectra of solid tetrachloroborates (Fig. 1a, c, d) show a very broad strong band in the 630—750 cm^{-1} region. The potassium salt shows also weak bands at 1449, 1382, and 1265 cm^{-1} , but these are obscured for the ammonium salts by CH deformation and CH_3 and NH_3 rocking vibrations. With ammonium tetrabromoborate there is a strong broad band

⁷ Hunig and Kiessel, *Chem. Ber.*, 1958, **91**, 380.

with maxima at 607 and 586 cm^{-1} attributable to the tetrabromoborate ion. Bands measured are given in Table 1, where the tetrahalogenoborate maxima are enclosed in square brackets.

For the quaternary ammonium salts the main absorption band differs little from that in the alkali-metal salts, but in other ammonium salts the band is broader and subsidiary maxima, not always fully resolved, appear in the 700—750 cm^{-1} region. This suggests that there is a small interaction of the tetrachloroborate ion with the ammonium ion and examination of the 3 μ region suggests slight hydrogen-bonding of the ammonium ions.

Waddington⁸ measured the infrared frequencies of the ammonium ion in a number of monobasic salts. The effect of hydrogen-bonding would be to lengthen the N-H bond and consequently to shift the N-H stretching band ν_3 to a lower frequency; frequencies observed lie between 3100 cm^{-1} for ammonium fluoride and 3332 cm^{-1} for the tetrafluoroborate. The frequency of the other infrared-active fundamental of the ammonium ion ν_4 , which is at about 1400 cm^{-1} and would be expected to be increased by hydrogen-bonding, shows no clear movement. In ammonium tetrachloroborate, ν_3 has the high value 3249 cm^{-1} (ν_4 1407 cm^{-1}), but the presence of the weak band at 1756 cm^{-1} (presumably the combination frequency $\nu_4 + \nu_6$) suggests that there is enough residual hydrogen-bonding to prevent free rotation. Although our sample of ammonium tetrachloroborate contained about 9% of ammonium chloride comparison of the spectrum with other materials of lower tetrachloroborate content suggests that the band was not merely due to the ammonium chloride present.

In the spectra of the aliphatic substituted ammonium chlorides and of pyridinium chloride, the following assignments accord with those of previous workers: ^{9,10} NH_3^+ , 3100—2900s, 2800—2400m; NH_2^+ , 3000—2700s, 2450m; NH^+ , 2700—2400s cm^{-1} . With the corresponding tetrachloroborates (Table 1) these bands are absent or very weak, and instead other stronger and sharper bands occur between 3300 and 3100 cm^{-1} ; this is where, it has been calculated,¹⁰ the N-H stretching frequencies of free unbonded substituted ammonium ions would be found, and this is borne out for those salts in which hydrogen bonding is inherently unlikely. Thus in methylammonium tetrafluoroborate these bands are found at 3282 and 3223 cm^{-1} ; in the corresponding tetrachloroborate the values are 3214 and 3158 cm^{-1} , and from this comparison and because the tetrachloroborate band is more complex than for the alkali-metal salts it seems likely that there is some small residual hydrogen-bonding or a perturbation of the free N-H vibrations by crystal forces.¹¹ The same is probably true to varying extents of the other substituted ammonium tetrachloroborates.

The effect of the anion on the cation is particularly marked with the pyridinium salts. Solid pyridinium chloride shows weak bands at 3206 and 3134 cm^{-1} as well as the broad, strong band near 2490 cm^{-1} and two bands of medium intensity at 2108 and 1990 cm^{-1} . It has been suggested¹¹ that the two weak bands around 3200 cm^{-1} are attributable to a proportion of unbonded NH^+ groups perturbed only by crystal forces. In pyridinium perchlorate, in which much less hydrogen-bonding might be expected, the broad band is still present, but at 2740 cm^{-1} . For pyridinium tetrachloroborate (Fig. 1d) and the mercurichloride ¹² $[\text{C}_5\text{H}_5\text{NH}]^+[\text{HgCl}_3]^-$ there is no absorption between 2800 and 2200 cm^{-1} , and instead there are very strong sharp bands at 3256 and 3239 cm^{-1} , and at 3225 and 3164 cm^{-1} , respectively. In these salts hydrogen-bonding may well be completely absent.

We have been unable to undertake an infrared examination of all the compounds^{1a} regarded as tetrachloroborates, but we examined the pyridine-boron trichloride adduct

⁸ Waddington, *J.*, 1958, 4340.

⁹ Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen and Co. Ltd., London, p. 259; Witkop, *Experientia*, 1954, 10, 420; Heacock and Marion, *Canad. J. Chem.*, 1956, 34, 1782; Stone, Craig, and Thompson, *J.*, 1958, 52.

¹⁰ Chenon and Sandorfy, *Canad. J. Chem.*, 1958, 36, 1181.

¹¹ Dodd and Stephenson, "Hydrogen Bonding," Pergamon Press, London, 1959, p. 177.

¹² Evans and Kynaston, unpublished work.

formulated¹³ as $[(C_5H_5N)_2BCl_2]^+[BCl_4]^-$. The conductivity of the molten compound provides evidence of dissociation into ions, and two infrared bands not present in the components might, on comparison with the bands of the isoelectronic molecule carbon tetrachloride, reasonably be ascribed to the tetrachloroborate ion.¹³ Bax, Katritzky, and Sutton¹⁴ have, however, shown by molecular-weight and conductivity determinations that the adduct is monomeric and negligibly dissociated into ions in benzene solution. A comparison of the infrared absorption spectrum of the solid compound with that of pyridinium tetrachloroborate proves the absence of the tetrachloroborate ion. A comparison of trimethylamine-boron trichloride and trimethylammonium tetrachloroborate leads to a similar conclusion. The absorption spectra of pyridine- and trimethylamine-boron trichloride in chloroform solution have previously been recorded, with tentative partial assignment of the bands by Katritzky,¹⁵ in good agreement with our own results apart from small solvent effects.

EXPERIMENTAL

Potassium and caesium chlorides were commercial products. The substituted ammonium halides were either commercial products or were prepared from the free amines, and were dried at $\sim 100^\circ/0.1$ mm. Boron trichloride was purchased in cylinders from British Drug Houses Ltd. and used without further purification. Boron tribromide, supplied by Borax Consolidated Ltd., was distilled before use. Chloroform, a laboratory grade, was dried over calcium chloride and kept over phosphoric anhydride.

Analyses were normally carried out by standard microanalytical methods. Boron was determined by a combustion procedure.¹⁶ Some of the ammonium tetrahalogenoborates were hydrolysed and the solutions titrated for halide and boric acid; the amine present was estimated by distillation and titration.

M. p.s were determined in sealed hard-glass tubes. The result commonly depended on the rate of heating: the tube was therefore first immersed in a bath about 10° below the m. p. and then heated rapidly.

Preparation of Tetrachloroborates.—(a) *By cold milling.* The halide (0.050 g.-mol.) and glass beads (40–80 g.) were placed in a heavy-walled cylindrical round-bottomed bottle bearing a B19 socket. This vessel was attached to a vacuum-manifold and heated at $100^\circ/0.005$ mm. for 15 min. to remove any remaining traces of water. While the bottle was chilled to -80° boron trichloride (6.44–8.78 g., 0.055–0.075 mole; 10–50% excess) was distilled in, followed by chloroform (30–60 ml.). (When boron tribromide was used it was added from a pipette under nitrogen.) The apparatus was then filled with dry nitrogen at atmospheric pressure and the bottle was detached and closed by an adaptor with a tap through which the bottle was roughly evacuated (to ~ 10 cm.). The bottle was allowed to warm to room temperature and shaken. The tap and the B19 joint were both lubricated with a heavy Fluorolube grease (supplied by Imperial Chemical Industries Limited, General Chemicals Division) which had a satisfactory resistance to chloroform and boron halides. In most cases the product of the reaction was a suspension of a solid and this was filtered under dry nitrogen (it was convenient to exclude the beads by using a coarse sieve), washed with chloroform and light petroleum (b. p. 40 – 60°), and dried in a current of nitrogen. In a few cases the product was a two-phase liquid system, which was evaporated to dryness *in vacuo*. The results of a number of preparations are summarised in Table 2. The degree of conversion of the halide into the halogenoborate depended on a number of factors, including the efficiency of milling and the solubility of the halide in the solvent used. In the preparations described no attempt was made to find a minimum reaction time. Chloroform was the most satisfactory solvent since many ammonium halides are appreciably soluble in it, but other solvents such as toluene or light petroleum have also been used.

(b) *In refluxing chloroform.* The halide (0.150 mole) in chloroform (200 ml.) was milled

¹³ Greenwood, Wade, and Perkins, XVIth Internat. Congress Pure Appl. Chem., Paris, 1957.

¹⁴ Bax, Katritzky, and Sutton, *J.*, 1958, 1258.

¹⁵ Katritzky, *J.*, 1959, 2049.

¹⁶ Corner, *Analyst*, 1959, **84**, 41.

with glass beads in a glass-topped preserving jar on a roller mill at room temperature for 24–48 hr. The suspension was transferred through a coarse sieve to a 1-l. 3-necked flask fitted with a double-surface condenser surmounted by a solid carbon dioxide-cooled cold-finger condenser, a Vibromixer agitator impeller, and an inlet, *via* a small cold-finger condenser attached to the third neck, for boron trichloride and nitrogen. A flexible seal between the impeller and the flask was made by a polyvinyl chloride Pyrotenax single-way sleeve H.V. 2311 (made by Hellermann Ltd., Crawley) which had a satisfactory resistance to the vapour above the reaction mixture. The suspension was stirred under nitrogen while refluxing gently and boron trichloride was admitted at the rate of ~1 drop of liquid every 2 seconds until an excess was present, as indicated by an increase in the amount condensing on the exit cold-finger. Refluxing was continued for about an hour after which the cold-finger condenser was warmed

TABLE I.

CsBCl ₄	1450w, 1376w, 1261w, [752sh, 692s, 661s]
NH ₄ Cl*	3134s, 3043s, 2805m, 2010w, 1756m, 1443sh, 1402s
NH ₄ BCl ₄ *	3249s, 3147sh, 3053s, 2821m, 1756m, 1407s, 1260sh, 1112w, [756sh, 722s, 694s, 665s, 649s]
[Bu ^t NH ₃]Cl	3223w, 3119m, 2957s, 2890s, 2805s, 2709s, 2597s, 2503s, 2407w, 2298w, 2208w, 2074s, 1967w, 1773w, 1612m, 1578w, 1511s, 1474m, 1465w, 1397s, 1371s, 1365s, 1298s, 1216s, 1156w, 1139w, 1022w, 994w, 935w, 885w, 733w, 667w
[Bu ^t NH ₃][BCl ₄]	3223s, 3174s, 3135m, 3089m, 2992s, 2923s, 2876s, 2787w, 2691w, 2572w, 2464w, 2083w, 2017w, 1586s, 1490s, 1483s, 1407s, 1401s, 1382s, 1372s, 1291s, 1215sh, 1200m, 1076w, 954w, 936w, 868w, [748sh, 709s, 675s, 650s]
[Me ₂ NH ₂]Cl*	3198w, 2985s, 2937s, 2850s, 2781s, 2513w, 2464w, 2144w, 1904w, 1583s, 1481s, 1438w, 1417w, 1255m, 1232m, 1082m, 1040w, 1020s, 883s, 865s
[Me ₂ NH ₂][BCl ₄]*	3201s, 3163s, 3130s, 3041m, 3011m, 2974m, 2934sh, 2906sh, 2821w, 2781m, 2737w, 2712w, 2437w, 2420w, 2372w, 1579s, 1465s, 1455s, 1434m, 1411m, 1393s, 1356m, 1270m, 1230w, 1074w, 1018m, 1005s, 873m, 800s, [748s, 714sh, 691s, 658s]
[Me ₃ NH]Cl*	3111w, 3007m, 2957s, 2916sh, 2863w, 2685s, 2623s, 2524s, 2474s, 2417sh, 2144w, 1483s, 1445m, 1415m, 1401w, 1384w, 1259s, 1242w, 1164w, 1069w, 987s, 820w
[Me ₃ NH][BCl ₄]*	3185s, 3022w, 2968m, 2920m, 2850w, 2670m, 2520m, 2470m, 2422sh, 1479s, 1470s, 1449m, 1411m, 1378m, 1275m, 1043w, 985m, 975s, 811w, [753m, 705s, 689s, 661s]
[Et ₃ NH]Cl	2980m, 2946m, 2886w, 2812w, 2774w, 2744w, 2623s, 2607s, 2575sh, 2537m, 2503s, 2362w, 1483s, 1478s, 1440m, 1395s, 1380m, 1363w, 1330w, 1186m, 1172m, 1076sh, 1071m, 1035s, 851m, 810m
[Et ₃ NH][BCl ₄]	3142s, 3002m, 2988m, 2950m, 2890w, 2805w, 2750w, 2709w, 2677w, 2467w, 1476s, 1470s, 1459s, 1444s, 1420m, 1408m, 1387s, 1358m, 1311w, 1288m, 1266w, 1172m, 1153m, 1088w, 1063m, 1053m, 1039m, 1010m, 892m, 837m, 806m, 779w, [733sh, 697s, 659s]
[EtPr ⁱ ₂ NH]Cl	3142w, 2985s, 2937s, 2781m, 2640s, 2602s, 2570s, 2524s, 2494s, 2422m, 1488m, 1477m, 1470m, 1438s, 1403s, 1392s, 1378m, 1365m, 1334w, 1320m, 1295w, 1260w, 1185s, 1160m, 1137s, 1120w, 1100m, 1067s, 1023s, 951w, 938sh, 933w, 921w, 879w, 848w, 786w, 780m
[EtPr ⁱ ₂ NH][BCl ₄]	3163s, 2990m, 2947m, 2880w, 2694w, 1490m, 1484sh, 1464m, 1410sh, 1402s, 1386s, 1382sh, 1365w, 1305m, 1180m, 1155m, 1130m, 1110m, 1082m, 1059m, 1015m, 947w, 938w, 924m, 915sh, 778m, 768m, [728s, 699s, 667s, 650sh]
[Me ₄ N]Cl*	3100w, 3021m, 2950w, 2923m, 2850w, 2787w, 2744w, 2570w, 2474w, 2371w, 1490s, 1405m, 1358w, 1299w, 1135w, 1118w, 1082w, 1020w, 959s, 949s, 917w
[Me ₄ N][BCl ₄]*	3033m, 2961m, 2753w, 2583w, 2481w, 2355w, 1482s, 1414m, 1288w, 948s, [723s, 695s, 665s]
[Et ₄ N]Cl	2984s, 2942s, 2888sh, 2290w, 1483s, 1461s, 1409s, 1376m, 1320m, 1184s, 1083m, 1030m, 1008m, 958w, 803s, 795sh
[Et ₄ N][BCl ₄]	2982s, 2940m, 2880w, 1475sh, 1463s, 1401s, 1308s, 1271m, 1184s, 1124w, 1076m, 1032s, 1021sh, 1003s, 971w, 948w, 890w, 798s, 789s, 761w, [718s, 693s, 667s]
NH ₄ Br	3135s, 3032s, 2802m, 1708w, ~1430sh, 1398s
[NH ₄][BBr ₄]	3146s, 3032s, 2801m, 1714w, 1428sh, 1398s, 1271m, 1106w, [607s, 586s]
K[BF ₄]	1303w, [1119sh, 1054s, 1032s], 772w
[MeNH ₃]F	3134—2445s, 2272s, 2040w, 1957m, 1795w, 1773w, 1669m, 1573m, 1474m, 1445m, 1309m, 1228w, 1164w, 1124w, 1011s, 929w, 890w, 722w
[MeNH ₃][BF ₄]	3282s, 3223s, 3111m, 3059m, 2992m, 2869w, 2768w, 2544w, 2430w, 1618s, 1520s, 1468m, 1432m, 1382w, 1296s, 1261m, 1164sh, [1063sh, 1025s], 985s, 921s, 769w, 723w

TABLE 1. (Continued.)

Curve		
a	K[BCl ₄]*	1447vw, 1382vw, 1261vw, [703s, 668s]
b	[MeNH ₂]Cl*	3081s, 2980s, 2870s, 2781m, 2484w, 1910w, 1578s, 1535s, 1465w, 1424w, 1261w, 1001s, 958s
c	[MeNH ₂][BCl ₄]*	3220s, 3155sh, 3022s, 2834m, 2741m, 2510w, 2437w, 2404w, 1582s, 1490s, 1481s, 1459s, 1426m, 1259s, 1102w, 972w, 956w, 923m, 912m, 780m, [750sh, 722sh, 696s, 668s, 647sh]
d	[C ₅ H ₅ ·NH][BCl ₄]*	3256s, 3239s, 3190s, 3138s, 3107s, 3096s, 3081s, 3021w, 2985w, 2964w, 2930w, 2923w, 2902w, 2869w, 2805w, 2050w, 2017w, 1980w, 1860w, 1638m, 1606s, 1540s, 1486s, 1409w, 1386m, 1370w, 1335s, 1262m, 1246sh, 1241m, 1200s, 1168s, 1076w, 1050m, 1028w, 1008w, 988w, 876w, 743s, [694s, 666s]
e	C ₅ H ₅ N·BCl ₃ *	3143w, 3134m, 3093m, 3071w, 3048w, 2927w, 2528w, 2040w, 2008w, 1842w, 1639m, 1624s, 1573w, 1495m, 1482m, 1462s, 1404w, 1358w, 1334w, 1257w, 1219m, 1211w, 1158m, 1101s, 1055w, 1024m, 805s, 789sh, 779s, 762s, 743s, 720s, 677s, 645m, 612m, 605s
f	Me ₃ N·BCl ₃ *	3043w, 3021w, 2957m, 2923w, 2889w, 2843w, 2685w, 2524w, 2474w, 2236w, 1481s, 1463s, 1449m, 1409m, 1405m, 1265w, 1230m, 1113s, 1019w, 963s, 833s, 786s, 755s, 743s, 722sh

s = strong; m = medium; w = weak; sh = shoulder.

* These spectra will appear in the DMS Index (Butterworths) on spectral cards numbered 6000 onwards.

TABLE 2. Preparation of tetrahalogenoborates, M[BXY₃], from MX and BY₃ by milling.

MX	BY ₃	BY ₃ (excess) %	Time (hr.)	Con- version (%)	Found (upper)/calc. (lower) (%)					M. p.
					C	H	N	Cl	B	
Me ₄ NCl	BCl ₃	10	66	87	24.2	6.2	6.6	58.4	5.0	264 ^o ^a
					21.2	5.3	6.2	62.5	4.8	
Me ₃ NHCl	... BCl ₃	13	112	91.5	18.0	5.2	6.8	64.2	4.75	160—163
					16.9	4.7	6.6	66.7	5.1	
Me ₂ NH ₂ Cl	... BCl ₃	54	140	98	13.1	5.2	6.9	70.8	5.7	110—112
					12.1	4.0	7.05	71.4	5.4	
MeNH ₂ Cl	BCl ₃	48	112	90	7.1	3.6	8.3	74.5	5.8	150—152
					6.5	3.1	7.6	76.9	5.9	
Et ₄ NCl*	BCl ₃	67	120	95	33.8	7.6	5.75	48.8	4.0	222—224
					33.9	7.2	5.0	50.2	3.8	
Et ₃ NHCl*	BCl ₃	39	112	98	29.3	6.5	5.9	55.1	4.2	71—75
					28.2	6.3	5.5	55.7	4.3	
Pr ₂ EtNHCl ^a	BCl ₃	25	19	97	33.2	6.85	4.85	49.3	4.2	109—110
					33.9	7.2	5.0	50.2	3.8	
C ₅ H ₅ NHCl	BCl ₃	18	88	~100	25.8	2.5	5.8	60.9	4.85	119—121
					25.8	2.6	6.0	61.0	4.65	
NH ₄ Cl	... BCl ₃	50	160	91	—	3.0	8.75	81.7	6.3	166—170
					—	2.35	8.2	83.2	6.35	
NH ₄ Br	BBr ₃	21	64	60	—	—	5.2	—	2.8 ^e	^a
					—	1.15	4.0	—	3.1	
NH ₄ Br	BCl ₃	22	40	94	—	2.9	8.5	64.1 ^e	4.3	^a
					—	1.86	6.5	65.9 ^e	5.0	
CsCl	BCl ₃	13	112	87	—	—	—	46.1	3.45	
					—	—	—	49.8	3.80	
KCl	BCl ₃	66	116	88.5	—	—	—	71.0	5.55 ^f	
					—	—	—	74.1	5.65	
Bu ^t NHCl ^b	BCl ₃	—	—	97	21.5	4.7	7.7	61.5	5.5	162—167 ^a
					21.1	5.3	6.2	62.5	4.8	

^a The product was a two-phase liquid system. ^b Prepn. in boiling chloroform. ^c Total halogen, as Cl. ^d Decomp. ^e Found: Br, 87.7. Calc.: Br, 91.8%. ^f Found: K, 20.5. Calc.: K, 20.4%.

to room temperature and excess of boron trichloride was swept out in a current of nitrogen. Finally the product was cooled and filtered off. This method proved to be less convenient than cold milling and gave inferior results. Ammonium tetrachloroborate could not be made in this way.

Most of the tetrahalogenoborates were insoluble in those solvents (*e.g.*, carbon tetrachloride, chloroform, light petroleum, benzene, diethyl ether) with which they did not react, but tetraethylammonium, triethylammonium, and ethyldi-isopropylammonium tetrachloroborate

formed two-phase liquid systems with chloroform at or slightly above room temperature. The smaller, upper, less dense phase in each case contained the bulk of the tetrachloroborate, with a very dilute solution below.

Infrared Spectra.—The tetrahalogenoborates are too reactive to allow their absorption spectra to be measured satisfactorily in potassium chloride discs, but mulls in liquid paraffin and hexachlorobutadiene were satisfactory if prepared in a dry box.

The spectra were measured on a double-beam recording grating spectrometer designed and constructed in this laboratory.¹⁷ Several spectra of tetrachloroborates, together with the corresponding chlorides, are reproduced in the Figure. The absorption bands of other tetrahalogenoborates are listed in Table 1. The spectra of the pyridine-boron trichloride and trimethylamine-boron trichloride adducts are reproduced for comparison with pyridinium tetrachloroborate.

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NATIONAL CHEMICAL LABORATORY, D.S.I.R.,
TEDDINGTON, MIDDLESEX.

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¹⁷ Hales, *J. Sci. Instr.*, 1959, **36**, 264.
