

Spectroscopic studies of Lewis acid-base complexes—I

Vibrational spectra and assignments for trimethylamine complexes of boron halides*

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Abstract—Infrared and Raman spectra of 1:1 complexes of trimethylamine with boron trifluoride, boron trichloride and boron tribromide have been obtained in the solid state. Samples studied included those isotopically enriched in B^{10} as well as those containing the natural isotopic ratio of B^{11} to B^{10} . On the basis of isotopic shifts and trends of frequencies within the series, vibrational assignments of the observed frequencies are proposed.

INTRODUCTION

LEWIS acid-base complexes have been of considerable chemical interest for many years. Not only do they provide examples in which chemical reaction and bond formation may occur without the usual complications of an initial bond rupture, but also they frequently play an important role in the reactions of the very interesting compounds of the third group elements. Spectroscopic studies, which can be expected to contribute greatly to the specific information about these compounds as well as to their broader aspects, have not been extensive. The continuing interest and importance of these compounds to inorganic chemistry and to catalytic processes warrant a greater degree of spectroscopic study than has yet appeared.

Trimethylamine (TMA) is well known as one of the stronger Lewis bases while the boron halides are recognized as typical Lewis acids. The well characterized 1:1 solid molecular complexes which are formed when trimethylamine reacts with BF_3 [1–3], BCl_3 [4–6] or BBr_3 [7] provide an excellent series of compounds for investigation. The BI_3 complex apparently has not been reported. X-ray diffraction work on the boron trifluoride complex [8] has shown that this molecule possesses C_{3v} symmetry with a dative bond between the boron and nitrogen atoms. The BF_3 group, which is planar in the free state, is distorted into a pyramid in the complex with smaller

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changes occurring in the amine half of the molecule. The structures of the TMA complexes with the other two boron halides are presumed to be similar to that of the fluoride although no data are available.

Infrared frequencies of the boron trifluoride complex as a solid and in solution have been reported in two papers [9, 10] and in an unpublished report [11]. Vibrational assignments based on these data have been proposed but points of disagreement exist. No Raman results have been located for this compound and the infrared data are restricted to the rock salt region.

Both Raman and infrared studies have been published for trimethylamine-boron trichloride [9-12]. Katritzky, and Peterson and Bauer discussed assignments in some detail and the latter workers carried out force constant calculations based on their assignments. The only Raman work is that by GOUBEAU and co-workers [12] who reported frequencies only. Their results disagree with the infrared data.

Infrared studies of the trimethylamine-boron tribromide complex [7, 10] are quite incomplete and limited to the rock salt region. Only a few assignments have been suggested and Raman work does not appear to have been done. No spectral results for any of the complexes in which the boron was isotopically enriched in B^{10} have been found.

The incompleteness of the experimental data and the fragmentary and conflicting vibrational assignments for these molecules make a thorough spectroscopic study of the series desirable.

EXPERIMENTAL

Reagents

Boron trichloride and boron tribromide containing the natural 4:1 isotopic abundance of B^{11} to B^{10} were obtained from commercial sources and used without other purification than a preliminary trap to trap distillation. A commercial sample of the diethyl etherate of boron trifluoride was vacuum distilled to give a clear liquid and was not purified further.

Isotopically enriched boron containing 92 per cent B^{10} was obtained from the Atomic Energy Commission in the form of KBF_4 . This was decomposed under vacuum at $750^\circ C$ to give boron trifluoride. Boron-10 enriched BCl_3 and BBr_3 were prepared from BF_3 by the halogen exchange method described by GAMBLE [13]. A small amount of KBF_4 containing 99 per cent boron-11 was obtained from the Oak Ridge National Laboratory and was used in the preparation of one sample of the BF_3 complex. Anhydrous trimethylamine was purified by allowing it to stand over P_2O_5 at $-78^\circ C$ to remove traces of water and of mono- and dimethylamines.

Preparation of complexes

The trimethylamine-boron trifluoride complexes were prepared by bubbling trimethylamine vapor through an ice-cold solution of diethyl ether-boron trifluoride

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[11] C. C. PETERSON and S. H. BAUER, *The Infrared Spectra of Lewis Salts*, N.R.L. Report, Department of Chemistry, Cornell University (1955).

[12] J. GOUBEAU, M. RAHTZ and H. J. BECHER, *Z. anorg. allgem. Chem.* **275**, 11 (1954).

[13] E. O. GAMBLE, *Inorganic Syntheses*, III, p. 27. McGraw-Hill, New York (1950).

complex in excess diethyl ether. The solid complex which precipitated was separated from excess solvent, dissolved in cold absolute methanol, and passed through a short column of activated charcoal. Sufficient methanol was then pumped from the filtrate to cause partial precipitation of solid which was separated from the mother liquor and dried in vacuum to remove traces of solvent. Recrystallization from hot alcohol was tried but spectroscopic examination showed decomposition had occurred to give tetrafluoroborate ion as one of the products. The same or a similar decomposition was found to occur very slowly when the complex was allowed to stand and consequently spectra were obtained from freshly purified material.

Adducts of TMA with the normal and enriched boron trichloride and tribromide were prepared by direct combination of the reactants in benzene [6, 7]. The products were recrystallized from absolute ethanol in a manner similar to that for the BF_3 complex and excess solvent was removed in vacuum. The following melting points were observed: TMA: BF_3 , 144–146°C, lit. [2, 3], 138–147°C; TMA: BCl_3 , 241–243°C, lit. [6], 242–243°C; TMA: BBr_3 , 234–236°C, lit. [7], 238–240°C. Powder X-ray diffraction data of the boron trifluoride complex agreed with values calculated from the single crystal data [8].

Spectroscopic techniques

Infrared spectra were recorded using a Perkin-Elmer Model 21 spectrophotometer equipped with CaF_2 , NaCl and KBr prisms over the range between 400 and 3500 cm^{-1} . Calibration of each spectrum was made with an indene-camphor-cyclohexanone standard [14]. The low frequency region was also examined using a Beckman IR-4 equipped with a CsBr prism through the courtesy of American Cyanamid Company. All samples were prepared in KBr discs using precautions to eliminate traces of water. Several concentrations were employed for each compound to provide the best rendition of both high and low intensity bands.

Raman spectra of the solid complexes were obtained by pressing the pure crystalline powders into discs 1–3 mm thick using the same die as for the KBr pellets. These semi-translucent discs were illuminated on one side by spectrally pure Hg 4358 radiation and the light from the opposite side was collected and passed into the spectrograph. The light source consisted of an AH-4 mercury arc lamp which provided a fairly small arc of high intrinsic intensity but without such an extremely high continuous background that it could not be removed by filtering. Both absorption and interference type filters were used for the latter purpose and the spectral purity of the exciting light was judged as good or better than that customarily employed for the Raman effect of liquids using a Toronto arc and standard filters. The excess exciting light accompanying the Raman frequencies was reduced significantly before entering the spectrograph by multiple reflections from interference filters [15, 16]. The thickness of the sample which, in this method, determines the intensity of the Raman scattering [17] was adjusted to an optimum value by trial and

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[17] M. C. TOBIN, *J. Opt. Soc. Am.* **49**, 850 (1959).

error. Spectra were recorded photographically using Eastman IIa-O spectrographic plates whose sensitivity had been increased by preheating at 60°C for 12–24 hr under anhydrous conditions. Wavelength measurements of the Raman lines were made both on plates and microphotometer tracings. The tabulated data represent mean values obtained from several spectra. In the case of BCl_3 and BBr_3 complexes, spectra of the loose crystals also were obtained using the instrument at the American Cyanamid Company [17]. These results were particularly valuable in the low frequency region below about 400 cm^{-1} .

EXPERIMENTAL RESULTS

The experimental frequencies and assignments for the trimethylamine complexes of normal and isotopic varieties of boron trifluoride, boron trichloride and boron tribromide are listed respectively in Tables 1, 2 and 3. Infrared spectra of the compounds are reproduced in Figs. 1 and 2 in which the spectra chosen for presentation were selected to show the principal features most clearly. Many more frequencies were observed for all compounds than have previously been reported. The agreement between the infrared and Raman results in the present study is quite satisfactory, the small differences found being no more than might be expected from experimental error.

The infrared spectra of the BF_3 and BCl_3 complexes (Fig. 1) show good qualitative agreement with the tracings of PETERSON and BAUER [11], with due allowance for the difference in resolution. However, marked disagreement was found with the Raman data reported by GOUBEAU [12] for the BCl_3 complex. In particular, the four strongest bands observed in the present investigation at 383, 535, 826 and 967 cm^{-1} are all missing in his list of frequencies and it is possible that the substance he examined may not have been sufficiently well characterized. Literature results for the BBr_3 complex are rather limited but agreement was noted for the few values available.

DISCUSSION OF ASSIGNMENTS

Complexes of the formula $(\text{CH}_3)_3\text{NBX}_3$ possess 45 fundamental vibrations which, on the basis of C_{3v} symmetry, comprise $10A_1'$, $5A_2$ and $15E$ modes. The A_1 and E frequencies are allowed in both the Raman and infrared, while the A_2 fundamentals are inactive in both. The classification, numbering and a simplified description of the various fundamentals are given in Table 4.

From a spectroscopic point of view, the study of Lewis complexes has an advantage in that the formation of the dative bond perturbs but does not radically change the nature of the interacting species. Since the structural study of the BF_3 complex [8] has shown that the configuration of the amine half of the compound does not differ markedly from that of the free base, a similarity in the frequencies of the free and combined amine is to be expected. On the other hand, the distortion of the planar structure of the free boron halides plus changes in their force constants caused by rehybridization may be expected to alter the vibrational frequencies of the BX_3 group significantly. In both cases, the magnitude of the frequency shifts can serve as a qualitative indication of the extent of perturbation of the two groups resulting from the formation of the dative bond.

Table 1. Infrared and Raman frequencies observed for various isotopic varieties of $(\text{CH}_3)_3\text{NBF}_3$ (in cm^{-1})

Natural (81% B^{11}) Boron			92% B^{10} Enriched	
Infrared (KBr pellet)	Raman (crystal)	Assignment	Infrared (KBr pellet)	Raman (crystal)
3033 w	3030 s	ν_{16}	3035 w	3035 s
3013 m		ν_{17}	3016	
2971 sh		$\nu_{19} + \nu_{20}$	2976 vw	
2954 s	2967 s	ν_1	2956 s	2967 s
2924 vw			2925 vw	
2890 w	2889 m	ν_{18}	2890 w	2885 m
2868 vw			2868 vw	
2845 vw			2845 vw	
2807 vw	2802 sh	ν_2	2807 vw	2806 sh
99% B^{11} enriched			92% B^{10} enriched	
1487 m		ν_{19}	1487 m	
1480 w		ν_{20}	1480 w	
1469 w	1473 vs	ν_3	1470 w	1473 vs
1454 w			1457 w	
1412 vw	1413 vw	ν_4		1420 vw
1271 vw		$\nu_6 + \nu_{26}$	1270 sh	
1255 w	1253 w	ν_{22}	1255 w	1255 w
1208 w			1211 w	
1175 sh	1178 vvw	$\nu_6 + \nu_{27}$	1180 sh	1178 vvw
1142 s, br		ν_{25}	1165 s, br	1165 vvw
			1136 vvw	
			1122 vw	
1104 m	1105 w	ν_{23}	1109 w	1114 w
1017 vw		$\nu_7 + \nu_9$	1014 vw	
991 w	988 s	ν_{24}	987 w	991 s
932 s	935 w, sh	ν_8	952 s	
841 s	842 s	ν_6	838 m	847 s
692 m	694 s	ν_7	696 m	700 s
640 vw		$2\nu_9$	643 vvw	640 w
547 w	545 vw	ν_{10}	550 w	545 vw
			536 vw	
519 vw, sh	513 vw	$2\nu_{30}?$	525 w	518 vw
464 vvw?			465 vvw?	
430 w	428 vvw	ν_{26}	431 w	429 vw
	372 vw	?		
340 w		ν_{27}	340 w	
320 w		ν_9	323 vw	

Methyl group frequencies

The bands associated with the stretching and deformation motions of the methyl groups in the complexes are well isolated from the rest of the frequencies and a detailed discussion of their assignments does not appear necessary. As commonly happens, the overtones of the methyl deformation frequencies resonate with the C—H stretching fundamentals to complicate the pattern of bands in the 2900 cm^{-1} region. Complexing might be expected to have relatively little effect on these frequencies but it is interesting to note that the formation of the dative bond apparently changes the degree of coupling between the methyl deformation modes so that the accidental degeneracy present in the free amine is reduced in the complex. This effect is most pronounced in the BCl_3 case. The methyl group rocking modes are relatively well isolated between 1100 and 1270 cm^{-1} except in the BF_3 complex whose spectrum in this region contains a B—F stretching mode plus overtones. The B—F fundamental is identifiable by its intensity, sensitivity to isotopic substitution

Table 2. Infrared and Raman frequencies observed for normal and B¹⁰ enriched varieties of (CH₃)₃NBCl₃ (in cm⁻¹)

Natural boron		Assignment	92 % B ¹⁰ enriched	
Infrared (KBr pellet)	Raman (crystal)		Infrared (KBr pellet)	Raman (crystal)
3479 vvw		$\nu_{16} + \nu_{26}$	3470 vvw	
3417 vvw		$\nu_8 + \nu_{18}$	3425 vvw	
3360 vvw		$\nu_9 + \nu_{17}$		
3305 vvw		$\nu_1 + \nu_9$	3305 vvw	
3233 vvw		$\nu_1 + \nu_{27}$	3233 vvw	
3075 vw		$\nu_{18} + \nu_{29}, \nu_2 + \nu_{27}$	3072 vw	
3044 w	3035 s	ν_{16}	3043 w	3035 s
3026 w	3020 sh	ν_{17}	3025 w	3023 sh
2972 sh		$2\nu_{19}$		
2964 m	2966 s	ν_1	2962 m	2965 s
2922 w	2922 vw	$\nu_3 + \nu_{20}$	2922 w	2922 vw
2889 w	2887 w	ν_{18}	2889 w	2888 w
2843 w		$2\nu_4^*$	2842 w	
2804 vw	2802 w	ν_2	2804 vw	2806 w
2748 vw		$\nu_{19} + \nu_{22}$	2745 vw	2740 vw
2713 vvw		$\nu_3 + \nu_{22}, \nu_5 + \nu_{19}$	2715 vvw	
2694 vvw		$\nu_5 + \nu_{20}$	2694 vvw	
2677 vw		$\nu_{21} + \nu_{22}$	2677 vw	
2555 vw		$\nu_3 + \nu_{23}$	2557 vw	
2521 vw		$2\nu_{22}, \nu_4 + \nu_{23}$	2521 w	
2461 vw		$2\nu_5$	2461 vw	
2426 vvw		$\nu_1 - \nu_8$	2427 vvw	
2367 w		$\nu_4 + \nu_{24}$	2371 w	
2235 w		$\nu_4 + \nu_6$	2238 w	
2231 sh		$2\nu_{23}$	2229 sh	
2196 vvw		$\nu_5 + \nu_{24}$	2193 vvw	
2155 vvw		$\nu_4 + \nu_7$	2181 vvw	
2055 vvw		$\nu_5 + \nu_6$		
		$\nu_7(\text{B}^{10}) + \nu_{22}$	2028 vvw	
2002 vvw		$\nu_8 + \nu_{20}$	2000 vvw	
1980 vvw		$\nu_3 + \nu_8$		
1942 vvw		$\nu_6 + \nu_{23}$	1945 vvw	
1923 vw		$2\nu_{24}, \nu_{19} + \nu_{26}$	1926 vw	
1890 vvw		$\nu_3 + \nu_{26}$	1892 vvw	
1792 vw		$\nu_6 + \nu_{24}$	1795 vw	
1734 vw		$\nu_{20} + \nu_{28}$	1734 vw	
1710 vw		$\nu_{20} + \nu_{29}$	1712 vw	
1680 vvw		$\nu_5 + \nu_{26}$	1680 vvw	
1650 vvw		$\nu_8 + \nu_{23}$	1625 vvw	
1571 vw		$\nu_6 + \nu_7$	1598 vw	
1553 vvw		$\nu_{23} + \nu_{26}$	1553 vvw	
1506 sh		$\nu_8 + \nu_{24}$	1506 sh	
1485 s	1481 sh?	ν_{19}	1486 s	1481 sh?
1465 s	1459 sh?	ν_{20}	1463 s	
1451 m	1447 s	ν_3	1451 m	1449 s
1412 m		ν_{21}	1412 m	
1408 m	1409 vw	ν_4	1408 m	1410 vw
1344 vw		$\nu_{10} + \nu_{24}$	1344 vw	

Table 2 (contd.)

Natural boron		Assignment	92 % B ¹⁰ enriched		
Infrared (KBr pellet)	Raman (crystal)		Infrared (KBr pellet)	Raman (crystal)	
1263 m	1263 vw	ν_{22}	1264 m		
1232 s	1231 w	ν_5	1232 s	1232 w	
1116 s	1115 w	ν_{23}	1116 s	1116 w	
976 sh		$\nu_8 + \nu_{26}$	976 sh		
965 vs	967 s	ν_{24}	965 vs	968 s	
837 sh?			840 sh?		
833 vs	826 s	ν_6	835 vs	828 s	
786 m		$\left\{ \begin{array}{l} \nu_{25}(\text{B}^{10}) \\ \nu_7(\text{B}^{10}) \\ 2\nu_{10} \end{array} \right.$	783 vs		
	750-790		$\nu_{25}(\text{B}^{11})$	770 m	773 m
			$\nu_7(\text{B}^{11})$	761 w	
765 sh?		$\nu_{26} + \nu_{27}, \nu_9 \div \nu_{10}$	757 vw?		
755 vs		$\nu_{10} + \nu_{27}$	748 w		
746 m	744 ms		721 w		
721 w			648 vw		
650 vw		ν_8	540 vw	536 s	
538 vw	535 s	ν_{26}	443 m	445 w	
443 m	445 w	ν_{10}	381 w	383 s	
381 w	383 s	ν_9	337 m	333 sh	
337 m	332 w	ν_{27}		269 w	
	271 w	ν_{28} or ν_{29}		256 w	
	255 w	ν_{29} or ν_{30}		183 w	
	183 w				

s = strong, m = medium, w = weak, sh = shoulder, etc.; * perturbed by Fermi resonance

and by comparison with the spectra of the other complexes. Assignments of the methyl rocking modes to some extent are arbitrary but have been made on the basis of the assignments for the free amine. Overlapping occurs in the case of the BF₃ complex, and the B¹⁰ and B¹¹ spectra of this compound show characteristic differences in the 1100 cm⁻¹ region.

Amine frequencies

Vibrational frequencies and assignments for free trimethyl amine are available in the literature [18, 19] and appear reasonably well established. As expected, the corresponding frequencies of the complexes were easy to identify since they were not markedly shifted in position. The symmetric C—N stretching mode at 826 cm⁻¹ in the free amine shifts to 842 cm⁻¹ in the BF₃ complex, but is observed at about 830 cm⁻¹, essentially unaffected, in the other two compounds. KATRITSKY [10] assigned this band to the asymmetric B—Cl stretch in the chloride complex but, in view of the evidence from the other two complexes plus the lack of a significant isotope effect, this does not appear to be correct. The asymmetric C—N stretching fundamental, ν_{24} , is more sensitive to the attaching group, the band at 1043 cm⁻¹ in the

[18] J. R. BARCELO and J. BELLANATO, *Spectrochim. Acta* **8**, 27 (1956).

[19] E. J. ROSENBAUM, D. J. RUBIN and C. R. SANDBERG, *J. Chem. Phys.* **8**, 366 (1940).

Table 3. Infrared and Raman frequencies observed for normal and B¹⁰ enriched varieties of (CH₃)₃NBBr₃ (in cm⁻¹)

Natural boron		Assignment	92 % B ¹⁰ enriched	
Infrared (KBr pellet)	Raman (crystal)		Infrared (KBr pellet)	Raman (crystal)
3061 vvw		$\nu_{18} + \nu_{29}$	3063 vvw	
3036 w	3030 m	ν_{16}	3036 w	3025 m
3021 vw		ν_{17}	3023 vw	
			3014 vw	
2956 s	2960 s	ν_1	2954 m	2957 s
2948 vw		$\nu_{19} + \nu_{20}$		
2919 vvw	2912 vw	$2\nu_{20}$	2917 vw	2915 vvw
2882 w	2883 w	ν_{18}	2882 w	2880 w
2851 vw		$\nu_3 + \nu_4$		
2798 vw	2797?	ν_2	2797 vw	
2729 vvw		$\nu_{20} + \nu_{22}$	2731 vvw	
2698 w		$\nu_3 + \nu_{22}$		
2664 vw		$\nu_4 + \nu_{22}$	2664 vw	
2549 vw		$\nu_3 + \nu_{23}$	2550 vw	
2512 vw		$2\nu_{22}$	2512 vw	
			2496 vvw	
2465 vvw			2465 vvw	
2445 vvw		$\nu_{19} + \nu_{24}$	2445 vvw	
2413 vvw		$\nu_{20} + \nu_{24}$	2413 vvw	
2397 vvw		$\nu_3 + \nu_{24}$	2397 vvw	
2347 vw			2351 vw	
		$\nu_4 + \nu_6$	2234 sh	
2223 vw		$2\nu_{23}$	2223 vw	
2130 vvw		$\nu_3 + \nu_{25}$	2154 vvw	
		$\nu_5 + \nu_{19}$	2005 vvw	
1982 vvw		$\nu_8 + \nu_{20}$		
1953 vvw		$\nu_7 + \nu_{22}$	1972 vvw	
1908 vvw		$2\nu_{24}$	1909 vvw	
		$\nu_3 + \nu_{26}$	1879 vvw	
1762 vvw		$\nu_3 + \nu_9$	1770 vvw	
		$\nu_5 + \nu_8$	1745 vvw	
		$\nu_3 + \nu_{10}?$	1706 vw	
1588 vvw		$\nu_9 + \nu_{22}$	1574 vw	
			1559 vvw	
1546 vw		$\nu_{23} + \nu_{26}$		
1540 sh		$\nu_5 + \nu_9$	1539 vvw	
1522 vvw		$\nu_{10} + \nu_{22}$	1520 vvw	
1484 s	1484 vw, sh	ν_{19}	1483 s	1480 vw, sh
			1476 sh	
1461 s	1460 sh	ν_{20}	1461 s	
1448 m	1448 s	ν_3	1448 m	1448 s
1410 s	1408 vvw	ν_4, ν_{21}	1409 s	1408 vvw
1345 vw	1345 vvw	$\nu_6 + \nu_8$	1346 vw	
1260 w		ν_{22}	1259 w	
1226 s	1227 m	ν_5	1225 s	1227 m
1165 vw		$\nu_7 + \nu_{26}$		

Table 3 (contd.)

Natural Boron		Assignment	92 % B ¹⁰ enriched	
Infrared (KBr pellet)	Raman (crystal)		Infrared (KBr pellet)	Raman (crystal)
		$\nu_{25} + \nu_{26}$	1131 vw	1140 vw
1113 s	1115 w	ν_{23}	1113 s	1115 w
1021 vw		$\nu_6 + \nu_{27}$	1020 vw	
957 vs	959 s	ν_{24}	955 vs	960 s
827 vs	826 s	ν_6	830 vs	826 s
			772 w	
752 m		$\nu_9 + \nu_{26}$	751 m	
732 s		$\nu_8 + \nu_{27}$		
707 s		$\nu_{25}(\text{B}^{10})$	706 vs	700 m
	689 m	ν_7		720 m
		$\nu_{25}(\text{B}^{11}), \nu_8 + \nu_{29}$	678	
677 vs	673 m	$\nu_{25}(\text{B}^{11})$		
518 w	516 m	ν_8	520 w	518 m
434 m	434 m	ν_{26}	434 m	435 m
316 m	318 w	ν_9	316 m	318 w
	275 s	ν_{10}		275 s
	194 w	ν_{27}		195 w
	184 m	ν_{29}		182 m

free base shifting successively to 989, 965 and 958 cm^{-1} in the fluoride, chloride and bromide.

The asymmetric NC_3 deformation mode shifts slightly to higher frequencies from 425 cm^{-1} in the free base to 430, 443 and 434 cm^{-1} in the respective complexes, while the symmetric mode decreases in magnitude from 365 cm^{-1} to 320, 337 and 316 cm^{-1} . The isotopic sensitivity of all of these bands was small. It is of interest to note that the symmetric NH_3 deformation mode in the spectra of NH_3 complexes is significantly higher in frequency than it is in free NH_3 [20, 21]. This is contrary to the relative positions assigned here for the symmetric NC_3 deformation but attempts at assigning a frequency to the NC_3 mode higher than that observed in the free base clearly led to less satisfactory results.

BF_3 group frequencies

Assignment of frequencies primarily involving the complexed BF_3 group can be made by reference to the spectra of free BF_3 and of the BF_4^- ion. The latter represents the limiting case in which full conversion of the boron to an sp^3 hybridization and a tetrahedral structure has been achieved. Frequency data for all the boron halides have been summarized by WENTINK and TIENSUU [22] while the spectra of the BF_4^- ion have been discussed by GOUBEAU and BUES [23], and by

[20] S. I. MIZUSHIMA and I. NAKAGAWA, *J. Chem. Phys.* **23**, 1367 (1955).

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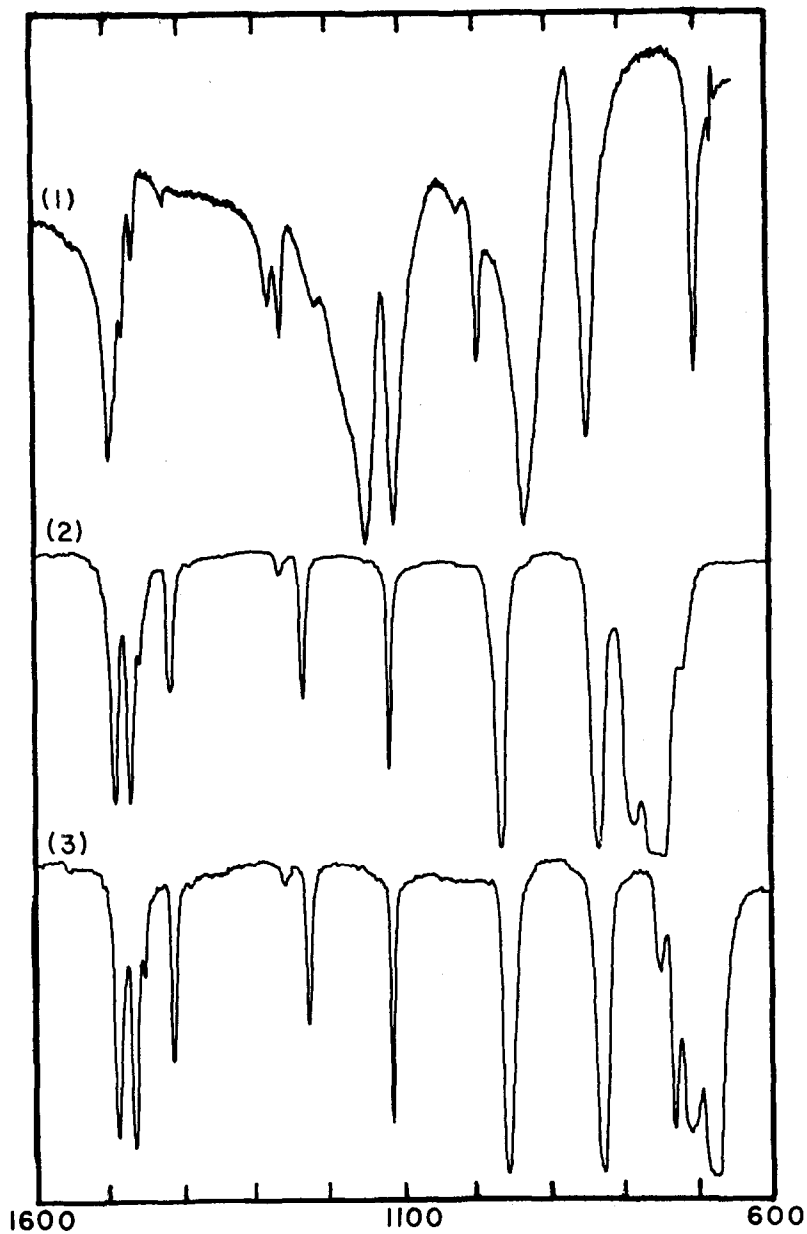


Fig. 1. Infrared spectra of trimethylamine complexes of boron halides in the NaCl region. (1) BF_3 (99% B^{11}), (2) BCl_3 (81% B^{11}), (3) BBr_3 (81% B^{11}).

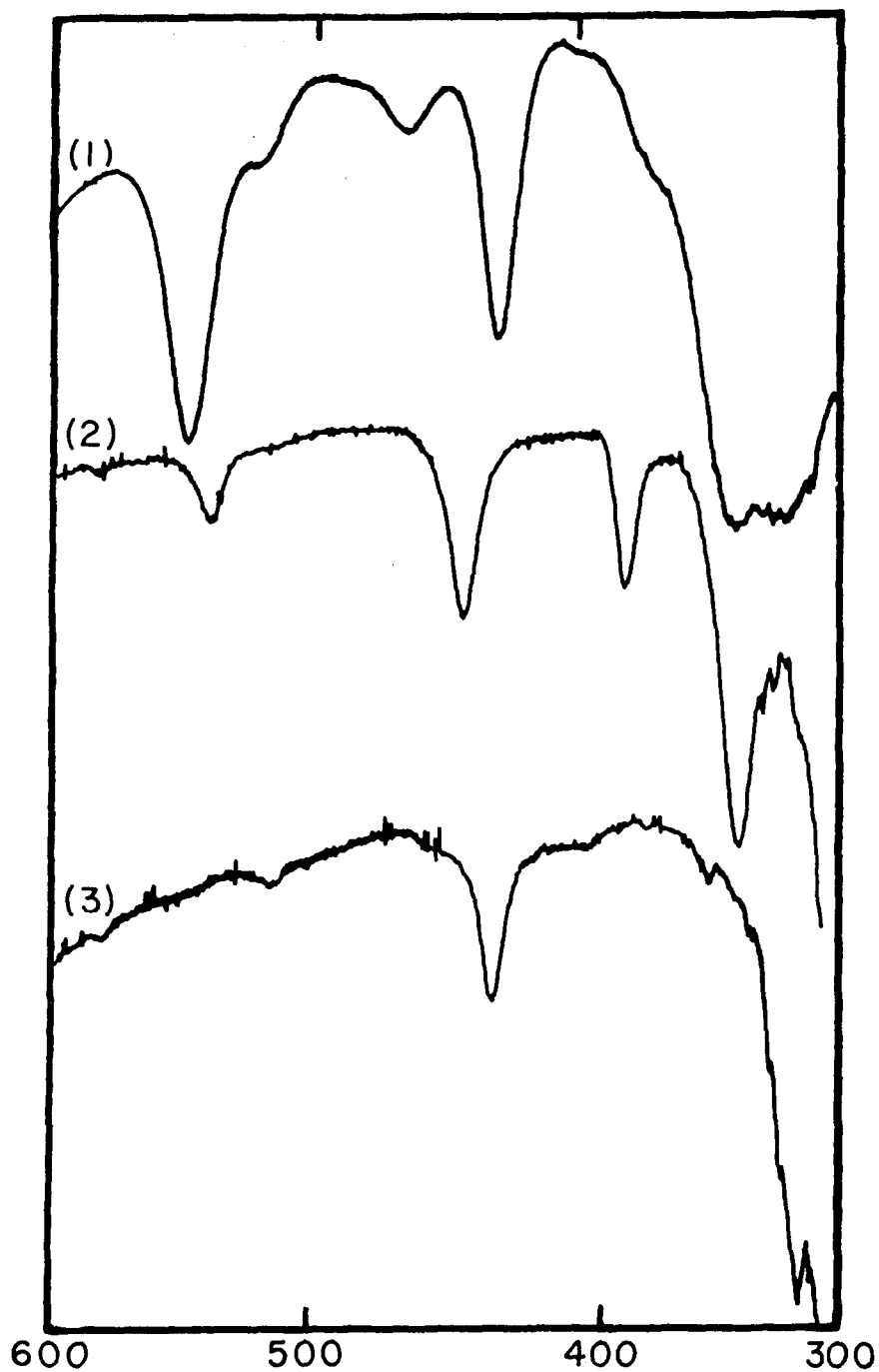


Fig. 2. Infrared spectra of trimethylamine complexes of boron halides in the KBr region. (1) BF_3 (99% B^{11}), (2) BCl_3 (81% B^{11}), (3) BBr_3 (81% B^{11}).

Table 4. A description of vibrational modes for $(\text{CH}_3)_3\text{N}:\text{BX}_3$

Number	Symmetry	Description
1	a_1	$\nu^s\text{CH}$ —out-of-phase C—H stretch
2	a_1	$\nu^s\text{CH}$ —in-phase C—H stretch
3	a_1	$\delta^s\text{CH}_3$ —out-of-phase CH_3 deformation
4	a_1	$\delta^s\text{CH}_3$ —in-phase CH_3 deformation
5	a_1	$\rho^s\text{CH}_3$ — CH_3 rock
6	a_1	$\nu^s\text{CN}$ —C—N stretch
7	a_1	$\nu^s\text{BN}$ —B—N stretch
8	a_1	$\nu^s\text{BX}$ —B—X stretch
9	a_1	$\delta^s\text{C}_3\text{N}$ — C_3N deformation
10	a_1	$\delta^s\text{BX}_3$ — BX_3 deformation
11	a_2	$\nu^a\text{CH}$ —out-of-phase C—H stretch
12	a_2	$\delta^a\text{CH}_3$ —out-of-phase CH_3 deformation
13	a_2	ρCH_3 — CH_3 rock
14	a_2	τCH_3 — CH_3 torsion
15	a_2	τBN —torsion about molecular axis
16	e	$\nu^a\text{CH}$ —out-of-phase C—H stretch
17	e	$\nu^a\text{CH}$ —out-of-phase C—H stretch
18	e	$\nu^a\text{CH}$ —in-phase C—H stretch
19	e	$\delta^a\text{CH}_3$ —out-of-phase CH_3 deformation
20	e	$\delta^a\text{CH}_3$ —out-of-phase CH_3 deformation
21	e	$\delta^a\text{CH}_3$ —in-phase CH_3 deformation
22	e	ρCH_3 — CH_3 rock
23	e	ωCH_3 — CH_3 wag
24	e	$\nu^a\text{CN}$ —C—N stretch
25	e	$\nu^a\text{BX}$ — $\nu^a\text{BX}$ stretch
26	e	$\delta^a\text{C}_3\text{N}$ — C_3N deformation
27	e	$\delta^a\text{BX}_3$ — BX_3 deformation
28	e	τCH_3 — CH_3 torsional motion
29	e	ρTMA —TMA rock
30	e	ρBX_3 — BX_3 rock

Table 5. Assignments of the skeletal fundamental frequencies of trimethylamine-boron halide complexes (in cm^{-1})

Fundamental	Boron trifluoride		Boron trichloride		Boron tribromide		Approximate description
	B^{11}	B^{10}	B^{11}	B^{10}	B^{11}	B^{10}	
A_1 Class							
ν_6	842	847	833	835	827	830	C—N stretch
ν_7	692	696	746	770	689	720	B—N stretch
ν_8	932	952	538	540	518	520	B—X stretch
ν_9	320	323	337	337	316	316	NC_3 deformation
ν_{10}	547	550	381	381	275	275	BX_3 deformation
E Class							
ν_{24}	989	989	965	965	958	958	C—N stretch
ν_{25}	1142	1165	755	783	677	706	B—X stretch
ν_{26}	430	431	443	443	434	434	NC_3 deformation
ν_{27}	340	340	270	270	194	195	BX_3 deformation
ν_{29}	—	—	183	183	183	183	NC_3 rock
ν_{30}	—	—	—	—	—	—	BX_3 rock

GREENWOOD [24]. In addition, frequencies and assignments for the complex, H_3NBF_3 , are available [21, 25] and a spectroscopic study has been reported for the pyridine: BF_3 complex [26].

Modes involving motions of fluorine atoms commonly show unusually intense infrared absorptions and correspondingly weak Raman intensities. Accordingly, the asymmetric B—F stretching fundamental is assigned to the broad, intense infrared band at 1142 cm^{-1} which exhibits a significant B^{10} isotope shift. This frequency was too weak to be observed in the Raman spectrum of the normal species although a very weak line was observed in the spectrum of the isotopic species. Its isotope sensitivity and its absence in the spectra of the other complexes confirm its identity.

The situation with respect to the symmetric B—F stretching mode is somewhat more complicated. Normal coordinate calculations on H_3NBF_3 [27] have shown that the B—F and B—N stretching motions are strongly mixed to give two modes better described as out-of-phase and inphase symmetric NBF_3 stretchings. A similar situation undoubtedly exists in the TMA complex. Since the out-of-phase motion should have an appreciable dipole moment change and involve a significant motion of the boron atom, this fundamental is assigned to the strong infrared band at 932 cm^{-1} which shifts to 952 cm^{-1} on isotopic substitution. Its Raman intensity is low as might be expected. The corresponding in-phase or breathing mode, ν_7 , is assigned to the strong Raman band at 694 cm^{-1} which shows a negligible isotope effect.

In the B—F deformation region, a pair of weak lines having the typical appearance of a Fermi doublet is observed in the Raman spectrum of both isotopic species. The higher of the two at about 545 cm^{-1} is assigned as the symmetric BF_3 deformation on the basis of its greater infrared intensity while the lower at about 512 cm^{-1} , is probably the overtone of the unobserved BF_3 rocking mode. The asymmetric-deformation, ν_{27} , is assigned to a band at 340 cm^{-1} in good agreement with a corresponding fundamental of the BF_4^- ion.

BCl_3 group frequencies

Although the spectrum of free BCl_3 is well known [20], that of the BCl_4^- ion is incomplete [28, 29]. The missing frequencies can be estimated from those of the isoelectronic CCl_4 molecule, however, and in addition, numerous data are available for molecules containing the CCl_3 group [30]. As in the fluoride molecule, the asymmetric chlorine stretch, ν_{25} , should be strong in the infrared and exhibit a significant isotope shift. The logical choice is the intense band at 755 cm^{-1} which shifts to 783 cm^{-1} in the B^{10} compound. The appearance of the spectrum in this region is somewhat confused by overlapping with ν_7 and the presence of an overtone. However,

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[26] H. LUTHER, D. MOOTZ and F. RADWITZ, *J. Prakt. Chem.* **277**, 242 (1958).

[27] R. C. TAYLOR, *Boron-Nitrogen Chemistry*, Ch. 6, Advances in Chemistry Series No. 42, The American Chemical Society (1964).

[28] N. N. GREENWOOD and K. WADE, *J. Chem. Soc.* 1130 (1960).

[29] T. C. WADDINGTON and F. KLANBERG, *J. Chem. Soc.* 2339 (1960).

[30] LANDOLT-BORNSTEIN, **6**, Auflage, I. Band, *Atom- und Molekular Physik*, 2. Teil, Molekeln I.

the intensities are altered in the Raman effect and ν_7 can be distinguished more clearly.

Two strong Raman bands at 535 and 383 cm^{-1} were observed which, on the basis of their intensity, appear to be the symmetric BCl_3 stretching and deformation modes. Their positions agree well with assignments in molecules containing the CCl_3 group; for example, in 1,1,1-trichloroethane the corresponding frequencies fall at 525 and 343 cm^{-1} . The remaining bands in the low frequency region can be assigned less reliably and the evidence is not sufficient to allow an unequivocal decision among all possible choices. The assignment of the asymmetric BCl_3 deformation to the Raman band at 271 cm^{-1} is made on the basis of its somewhat greater intensity and sharpness than the band at 256 cm^{-1} .

BBr₃ group frequencies

No reference data other than the assignments of the free acid were found for the BBr_3 group although frequencies for a few organic compounds containing the CBr_3 group are available. However, most assignments could be made in a fairly straightforward manner except for the bands observed in the region between 650 and 750 cm^{-1} . The infrared spectrum of the natural compound showed an intense band at 677 cm^{-1} with progressively weaker bands occurring at 707, 732 and 752 cm^{-1} (Fig. 1); the B^{10} enriched compound showed a very strong band at 706 cm^{-1} with a much weaker band at 751 cm^{-1} . The Raman effect, however, exhibited only two moderately intense bands at 673 and 689 cm^{-1} and at 700 and 720 cm^{-1} in the spectra of both the natural and enriched complexes respectively. The high infrared intensity and significant isotope shift suggest that the infrared bands at 677 and 706 cm^{-1} arise from the asymmetric B—Br stretching motion, ν_{25} , in the two isotopic species. The latter frequency also appears in the spectrum of the natural compound because of the appreciable amount of B^{10} present. The Raman bands at 673 and 700 cm^{-1} of the respective species are assigned to the same fundamental, the small difference from the infrared values probably arising from the difference in state. The other fundamental expected in this region and likely to have appreciable intensity in the Raman effect is ν_7 , a breathing type of motion involving the B—N bond. This mode is assigned to the remaining two Raman frequencies at 689 and 720 cm^{-1} in the two isotopic compounds. Failure to observe ν_7 in the infrared spectrum is not unexpected in view of the nature of the vibration. The infrared band at 752 cm^{-1} can easily be disposed of as a combination but the remaining moderately intense band at 732 cm^{-1} in the spectrum of the natural compound remains somewhat of a puzzle. The closest combination to this band is $\nu_8 + \nu_{27} = 713 \text{ cm}^{-1}$ which is appreciably different and lower in frequency. It is possible that the 732 cm^{-1} band is an overtone or combination involving an inactive frequency, perhaps enhanced by resonance, but if this is so, it is odd that it is completely absent from the spectrum of the B^{10} species.

The symmetric B—Br stretch, ν_8 , is assigned to the band at 516 cm^{-1} which, at first sight, might seem much too high when compared to the symmetric stretch in free BBr_3 at 280 cm^{-1} . However, this is not a valid comparison since the boron atom does not move in the symmetric vibration of the planar free halide whereas its amplitude undoubtedly is appreciable in the symmetric vibration of the pyramidal

halogen structure in the complex. In fact, the rather small difference in ν_8 between the chloride and bromide complexes indicates that the principal contribution to the reduced mass in the two cases comes from the boron atom.

Complex frequencies

The formation of the dative bond converts six external degrees of freedom into vibrational modes which can be described qualitatively as a B—N stretch, degenerate $(\text{CH}_3)_3\text{N}$ and BX_3 rocking modes and the torsion of the two ends around the molecular axis. Of these, the torsion is inactive and the rocking modes are likely to be so low in frequency that their observation or positive identification will be difficult. In the case of the B—N stretch, a study of several isotopic varieties of H_3NBH_3 [31] has located the uncoupled dative bond frequency at about 750 cm^{-1} . However coupling effects with other skeletal frequencies undoubtedly will be present in most molecules containing terminal atoms heavier than hydrogen and it is questionable whether the dative bond can be said to have a characteristic bond frequency in such cases [27]. The fundamental, ν_7 , which nominally would be the dative bond stretch, probably is better described as a breathing type of motion of the NBX_3 skeleton as mentioned earlier. It is assigned at nearly the same frequency, 692 and 689 cm^{-1} , in the fluoride and bromide, respectively, but is significantly higher and at approximately the position of the uncoupled B—N frequency in the chloride. No conclusions regarding the dative bond itself appear justified in the absence of a normal coordinate analysis.

CONCLUSIONS

Although there are minor details in each of the spectra for which explanations are unsatisfactory or lacking, by and large the picture presented for the principal features of the spectra of the three complexes appears consistent and logical. Since some final assignments were arrived at only by considering trends in the series, the advantage of having data from several closely related molecules can scarcely be overemphasized. Identification of the rocking modes associated with the two halves of the complexes and the one active torsional mode could not be made and must await more satisfactory data for the low frequency region.

Those fundamentals primarily associated with the acid portion of the complex in general were observed to fall intermediate between the corresponding frequencies of the free acid and the observed or extrapolated frequencies of the BX_4^- ion. Because of the marked change in the geometry of the acid accompanying complex formation together with the extensive coupling among the low frequency modes, it is difficult to draw conclusions from the frequencies themselves regarding changes in bonding in the acid half of the complex.

In the case of fundamentals associated with the amine half, frequency shifts are more significant since structural changes are less severe than in the case of the acid. Two important factors have been recognized [32] as effecting the strength of amine N—C or N—H bonds when complexes are formed. The first is an increase in the

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[32] V. N. FILIMONOV and D. S. BYSTROV, *Optics and Spectroscopy*, **12**, 31 (1962).

amount of *s* character in the sigma bonds resulting from changes in hybridization concomitant with the formation of the dative bond. This has the effect of increasing the bond strength. The second is the polarizing effect of the acid group which tends to bind the electrons in the bonding orbitals more tightly around the nitrogen and reduce the electron density in the valence bonds. The latter appears to predominate in the present case, since both C—N frequencies in the complexes are lower than in the free amine. Data in the literature for other complexes show similar effects [32].

Factors influencing the forces involved in angle deformations are more numerous and less well understood than those for bond stretching and the interpretation of frequency changes is correspondingly more difficult. Reference has already been made to the fact that the symmetric NC_3 deformation has been assigned to a lower frequency than in the free amine, a direction contrary to that found in ammonia complexes. Structural data for the $\text{TMA}:\text{BF}_3$ complex [8] indicate a rather large increase in the CNC angle from 108° to 114° upon complexation, a change which also suggests that the restoring forces in the CNC deformation have increased. Corresponding structural data for $\text{NH}_3:\text{BF}_3$ are not available but confirmation of the present NC_3 deformation assignment by data from the deuterated amine appears desirable before any discussion is attempted.

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