Inorganica Chimica Acta, 10 (1974) 191–195

Infrared Spectra of the Trimethylamine Adducts of mono- and di-Haloboranes

P. J. BRATT, K. R. SEDDON* and I. A. STEER
Donnan Laboratories, The University, Liverpool, U.K.
Received January 31, 1974

The infrared spectra (4000–200 cm^{-1}) of the adducts $Me_3N \cdot BH_2X$ and $Me_3N \cdot BHX_2$ (where X = Cl,Br, or I) are reported. Vibrational assignments are proposed, using the group vibration approximation.

Introduction

Although the adducts $Me_3N \cdot BX_3$ (X = F, Cl, Br)[1] and $Me_3N \cdot BH_3$[2,3] have been the subject of rigorous vibrational analysis, the spectra of the adducts $Me_3N \cdot BH_2X$ and $Me_3N \cdot BHX_2$ have not been interpreted. Partial assignments for the more complex spectra of $Et_3N \cdot BH_2X$ (X = H, Cl, Br, I or Ph)[4] have been made, and the infrared spectra of $Me_3N \cdot BH_2Cl$ and $Me_3N \cdot BHCl_2$ have been reported in part[5], but no assignments made. In view of the increased interest in these adducts,[6,7] and the dearth of detailed spectroscopic assignments for compounds of the general type $LBXH_2$ and LBX_2H, the present work was undertaken.

Experimental

The complexes $Me_3N \cdot BH_2X$ and $Me_3N \cdot BHX_2$ (X = Cl, Br, I) were prepared and purified as described elsewhere.[6] The infrared spectra were recorded on a Perkin–Elmer 225 spectrophotometer, the samples being mulled with nujol and hexachlorobutadiene and placed between CsI plates.

Results and Discussion

The infrared spectra of the complexes $Me_3N \cdot BXY_2$ (if X = H, Y = Cl, Br or I: if Y = H, X = Cl, Br or I) have been analysed using the group vibration approximation, the vibrations arising from the amine group being considered separately from those arising from the borane group. This approach is well justified, since the configuration of Me_3N in $Me_3N \cdot BF_3$ has been shown to differ very little from that of the free base,[8] and the group vibrations of Me_3N were only slightly modified in the spectra of the complexes $Me_3N \cdot BX_3$.[1] The Me_3N group has C_{3v} symmetry, giving vibrational modes according to ($7a_1 + 4a_2 + 11e$). There are thus 18 infrared active bands, eleven of which are doubly degenerate. The $NBXY_2$ group has C_s symmetry, giving vibrational modes according to ($6a' + 3a''$): 9 infrared active bands. A list of the infrared allowed bands, together with their descriptions and frequency number, are given in Table I. The treatment ignores the three low-frequency rocking modes which do not arise within the approximation.

Monohalogenated Trimethylamine–Boranes

The infrared spectra of the compounds, $Me_3N \cdot BH_2X$, together with their assignments are listed in Table II. The vibrations arising from the trimethylamine group will be considered first. The bands due to the methyl stretching modes (ν_1, ν_2, ν_8, ν_9, ν_{10}) and methyl deformation modes (ν_3, ν_4, ν_{11}, ν_{12}, ν_{13}) are in discrete portions of the spectra (3100–2800 and 1500–1350 cm^{-1} respectively), and have been well characterised for other compounds elsewhere.[1,9,10] There are numerous overtones and combination bands in the region, but no attempt has been made to assign these, since the symmetry of the molecule permits all possible combinations, and multiple indistinguishable assignments are possible. The assignment of the CH_3 rocking and wagging modes (ν_5, ν_{14}, ν_{15}) is complicated, however, by the occurrence of the BH_2 deformation modes (ν_{22}, ν_{26}) in the same spectral region (1300–1000 cm^{-1}). Assignment was accomplished by comparing the spectra of the complexes with those of $Me_3N \cdot BHX_2$ and $Me_3N \cdot BX_3$,[1] thus identifying the $\delta(BH_2)$ modes; the CH_3 modes then being assigned by analogy with the literature. Some of the bending and wagging modes are split into doublets, owing to the symmetry of the complex actually being lower than C_{3v} (*i.e.* a breakdown of the group vibration approximation). The C–N stretching frequencies (ν_6, ν_{16}) and the C_3N deformation modes (ν_7, ν_{17}) were also assigned by comparison with the spectra of $Me_3N \cdot BHX_2$ and $Me_3N \cdot BX_3$.

The position of the B–H stretching frequencies (ν_{21}, ν_{25}) was in the expected region (2600–2200 cm^{-1}). All the asymmetric bands showed the anticipated splitting due to the boron-isotope effect. The symmetric

---

* To whom correspondence should be addressed at St. Catherine's College, Oxford OX_1 $_3$UJ, U.K.

TABLE I. Description of Vibrational Modes for $(CH_3)_3N \cdot BXY_2$.

No.	Symmetry	Description	
Me_3N			
ν_1	a_1	$\nu(CH)_{sym}$	out-of-phase C–H stretch
ν_2	a_1	$\nu(CH)_{sym}$	in-phase C–H stretch
ν_3	a_1	$\delta(CH_3)_{sym}$	out-of-phase CH_3 deformation
ν_4	a_1	$\delta(CH_3)_{sym}$	in-phase CH_3 deformation
ν_5	a_1	$\varrho(CH_3)_{sym}$	CH_3 rock
ν_6	a_1	$\nu(C\text{–}N)_{sym}$	C–N stretch
ν_7	a_1	$\delta(C_3N)_{sym}$	C_3N deformation
ν_8	e	$\nu(CH)_{as}$	out-of-phase C–H stretch
ν_9	e	$\nu(CH)_{as}$	out-of-phase C–H stretch
ν_{10}	e	$\nu(CH)_{as}$	in-phase C–H stretch
ν_{11}	e	$\delta(CH_3)_{as}$	out-of-phase CH_3 deformation
ν_{12}	e	$\delta(CH_3)_{as}$	out-of-phase CH_3 deformation
ν_{13}	e	$\delta(CH_3)_{as}$	in-phase CH_3 deformation
ν_{14}	e	$\varrho(CH_3)$	CH_3 rock
ν_{15}	e	$\omega(CH_3)$	CH_3 wag
ν_{16}	e	$\nu(CN)_{as}$	C–N stretch
ν_{17}	e	$\delta(C_3N)_{as}$	C_3N deformation
ν_{18}	e	$\tau(CH_3)$	CH_3 torsional motion
$NBXY_2$			
ν_{19}	a′	$\nu(BN)$	B–N stretch
ν_{20}	a′	$\nu(BX)$	B–X stretch
ν_{21}	a′	$\nu(BY)_{sym}$	symmetrical B–Y stretch
ν_{22}	a′	$\delta(BY_2)_{sym}$	symmetrical BY_2 deformation
ν_{23}	a′	$\delta(NBX)$	NBX deformation
ν_{24}	a′	$\varrho(BXY_2)$	BXY_2 rock
ν_{25}	a″	$\nu(BY)_{as}$	asymmetrical B–Y stretch
ν_{26}	a″	$\delta(BY_2)_{as}$	asymmetrical BY_2 deformation
ν_{27}	a″	$\tau(BXY_2)$	BXY_2 torsional motion

TABLE II. Infrared Spectra of $Me_3N \cdot BH_2X$ (units of cm^{-1}).

X = Cl	X = Br	X = I	Assignments	
3022 w	3021 w	3020 w	ν_8	
		3015 vw	[a]	
3008 w	3005 m	3001 m	ν_9	
	2975 vw, sh	2964 vw	[a]	
2951 m	2951 m	2945 m	ν_1	
2927 w	2925 w	2914 w	ν_{10}	
2895 w	2895 w	2881 w	ν_2	
2870 vw	2867 vvw	2857 w	[a]	
2834 w	2833 w	2827 w	[a]	
2800 w	2797 w	2794 w	[a]	
2732 w	2719 w	2735 w	[a]	
	2689 w	2556 w	[a]	
2443 sh	2475 s, sh	2480 m	ν_{25}	$\nu(B^{10}H)_{as}$
2414 s	2425 s	2437 s		$\nu(B^{11}H)_{as}$
–	–	2355 w	ν_{21}	$\nu(B^{10}H)_{sym}$
2346 m	2337 m	2328 m		$\nu(B^{11}H)_{sym}$
2258 w	2245 w	2245 w	[a]	
2218 w	2195 w	2165 w	[a]	
2188 vw	2153 w	2097 w	[a]	
	2012 vw		[a]	
1482 s	1482 s	1480 s	ν_{11}	
1468 s	1470 s	1455 s	ν_{12}	

Table II. (Cont.).

X = Cl	X = Br	X = I	Assignments
1447 m	1446 m	1442 m	ν_3
1436 vw	–	1430 vw	ν_{13}
1404 m	1403 s	1406 s	ν_4
		1395 sh	[a]
–	–	–	ν_{14}
1248 m	1253 m	1248 m	ν_5
	1245 m	1241 m	
1186 s	1175 s	1171 s	ν_{26} $\delta(BH_2)_{as}$
1132 vs	1127 sh	1121 sh	ν_{15}
	1117 s	1108 s	
1094 s	1080 s	1057 s, br	ν_{22} $\delta(B^{10}H_2)_{sym}$
1083 s, sh	1067 s, sh	1040 s, br	$\delta(B^{11}H_2)_{sym}$
1006 m	1004 m	1000 m	ν_{16}
984 m	977 w	974 m	
948 w	937 w	932 w	
	924 vw	920 vw	
893 w, sh	878 w, sh	871 w, sh	
845 s	844 s	846 s	ν_6
705 m	710 m	717 m	ν_{19} $\nu(B^{10}N)$
693 s	698 s	703 s	$\nu(B^{11}N)$
666 m	592 m	549 m	ν_{20} $\nu(B^{10}X)$
645 s	572 s	533 s	$\nu(B^{11}X)$
471 w	464 m	460 m	
426 vw	418 w	412 w	ν_{17}
338 w	338 w	339 w	ν_7
	304 vw		
315 m	265 m	244 w	

[a] Combination or overtone bands; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

$\nu(B^{10}H)$ bands in $Me_3N\cdot BH_2Cl$ and $Me_3N\cdot BH_2Br$ are probably masked by the broad asymmetric $\nu(B^{11}H)$ bands. The position of the asymmetric $\delta(BH_2)$ mode (ν_{26}) is close to that assigned in the spectra of $py\cdot BH_2Ph$[11] and $Me_3N\cdot BH_3$,[3] but at higher energy than that assigned to $Et_3N\cdot BH_2X$ complexes.[4] The symmetric mode (ν_{22}), which is split due to the B^{10}, B^{11} isotope effect, is also at a higher energy than those assigned to $Et_3N\cdot BH_2X$ complexes.[4] The bands due to the boron–nitrogen and boron–halogen stretching frequencies were also readily identifiable due to the isotopic splitting pattern. The positions of these bands agree well with the literature values for similar complexes, although there is little data available for complexes containing B–Br and B–I bonds.

Dihalogenated Trimethylamine–Boranes

The infrared spectra of the compounds $Me_3N\cdot BHX_2$, together with their assignments, are listed in Table III. The assignment of the bands due to the trimethylamine was straightforward, the procedure being identical to that adopted for the mono-halogenated derivatives. However, the reason for the changing position of the asymmetric C–N stretching frequency (ν_{16}) with change of halogen is not obvious, and was not found to the same extent in the series $Me_3N\cdot BX_3$[1] or $Me_3N\cdot BH_2X$. However, it was reported that the asymmetric C–N stretching frequency was sensitive to the nature of the attached groups, whereas the symmetrical frequency (ν_6) was not.[1]

None of the bands assigned to $\nu(BH)$ showed the expected boron isotope effect, although they were asymmetric upon the high frequency side ($\nu(BH)$ is not split in the spectrum of $BHCl_2$[12] or $BHBr_2$[13] either). Moreover, only $Me_3N\cdot BH_2Cl$ showed an isotope effect upon the NBH deformation mode (ν_{23}). However, the B–N and B–X stretching modes do show the expected splittings. ν(B–N) was in the same region as in the $Me_3N\cdot BH_2X$ series, but the assignment of ν(B–X) was complicated by overlap between the ν(B–N) and ν(B–Cl) bands (for $Me_3N\cdot BHCl_2$) and overlap between $\nu(B^{11}I)_{as}$ and $\nu(B^{10}I)_{sym}$ (for $Me_3N\cdot BHI_2$). However, the position of ν(B–X) compares well with the assignment for the monohalogenated derivatives. Although the assignments of the BX_2 deformation modes must be tentative, they all show the correct isotope splitting, and also obey the empirical rule that $2\delta(AB) \leqq \nu(AB)$.

TABLE III. Infrared Spectra of $Me_3N \cdot BHX_2$ (units of cm^{-1}).

X = Cl	X = Br	X = I	Assignments
3032 w	3031 w	3019 w	ν_8
3014 m	3011 m	3006 m	ν_9
2958 m	2954 m	2945 m	ν_1
2928 w	2921 w	2916 w	ν_{10}
2891 w	2884 w	2875 w	ν_2
2840 vw	2846 vw	2855 vw	[a]
	2808 vw	2830 vw	[a]
	2723 vw	2737 vw	[a]
	2688 vw		[a]
2471 s	2500 s	2514 s	ν_{20} $\nu(BH)$
		2456 vw, sh	[a]
2371 vw	2367 vw	2355 vw	[a]
2343 vw	2338 vw	2335 vw	[a]
2247 vw	2255 vw	2235 vw	[a]
2193 vw	2178 vw	2160 vw	[a]
2127 vw			[a]
2068 vw	2097 vw		[a]
1483 s	1485 s	1478 s	ν_{11}
1464 s	1460 s	1457 s	ν_{12}
1447 m	1450 s	1445 s	ν_3
1432 vvw	1432 vw	1430 vw	ν_{13}
1406 m	1409 s	1400 s	ν_4
1257 sh	1260 w	1254 w	ν_{14}
1246 m	1243 s	1240 m	ν_5
1241 m	1240 sh	1226 m	
1127 s	1128 s	1122 s	ν_{15}
1113 m	1114 m	1108 m	
1094 vw			
1063 s	1050 s	1047 s	ν_{23} $\delta(NBH)$
1039 s			
972 s	996 s	958 s	ν_{16}
	964 s	935 s	
860 sh	860 sh	844 sh	
836 s	834 s	833 s	ν_6
762 vw			
732 w, sh	729 m, sh	731 m	ν_{19} $\nu(B^{10}N)$
712 s	714 s	716 s	$\nu(B^{11}N)$
	690 w, sh		
–	680 m, sh	600 s	ν_{25} $\nu(B^{10}X)_{as}$
697 s	651 s	576 vs	$\nu(B^{11}X)_{as}$
–	625 s	–	ν_{21} $\nu(B^{10}X)_{sym}$
668 m	609 s	552 s	$\nu(B^{11}X)_{sym}$
499 w	489 m	483 w	
442 vw	427 w	416 vw	ν_{17}
384 w	418 vw		
	320 vw		
355 sh	307 w, sh	301 sh	ν_{26} $\delta(B^{10}X_2)_{as}$
346 m	297 m	293 m	$\delta(B^{11}X_2)_{as}$
322 br	265 sh	259 sh	ν_{22} $\delta(B^{10}X_2)_{sym}$
	258 m	247 m	$\delta(B^{11}X_2)_{sym}$
244 sh	226 w, sh	(<200)	
226 m	216 m		

[a] Overtone or combination bands.

General Discussion

Study of the two series, $Me_3N \cdot BH_2X$ and $Me_3N \cdot BHX_2$, has produced assignments for most of the important fundamental infrared active modes of these species. Since many of the assignments were arrived at by comparison of trends in the spectra of these compounds, the importance of the analyses of these two parallel series cannot be overstated. Good correlation with the assignments for the complexes $Me_3N \cdot BX_3$[1] was obtained, and the effect of the lower symmetry of the mono- and di-halogenated species was observed.

Acknowledgements

We would like to thank Dr. M. P. Brown for useful discussions and Dr I. J. Worrall for the use of the facilities at the University of Lancaster. We would also like to thank the S.R.C. for a maintenance grant (to P.J.B.) and I.C.I. for the award of a fellowship (to K.R.S.).

References

1 R.L. Amster and R.C. Taylor, *Spectrochim. Acta, 20,* 1487 (1964).
2 B. Rice, R.J. Galiano and W.J. Lehmann, *J. Phys. Chem., 61,* 1222 (1957).
3 R.C. Taylor, *Advances in Chemistry Series,* No. 42, p. 59 (1964).
4 J.N.G. Faulks, N.N. Greenwood and J.H. Morris, *J. Inorg. Nuclear Chem., 29,* 329 (1967).
5 J.W. Wiggins and G.E. Ryschkewitsch, *Inorg. Chim. Acta, 4,* 33 (1970).
6 M.P. Brown, R.W. Heseltine, P.A. Smith and P.J. Walker, *J. Chem. Soc. (A),* 410 (1970).
7 P.J. Bratt and M.P. Brown, to be published.
8 S. Geller and J.L. Hoard, *Acta Cryst., 4,* 399 (1951).
9 J.R. Barceló and J. Bellonato, *Spectrochim. Acta, 8,* 27 (1956).
10 J.N. Gayles, *Spectrochim. Acta, 23A,* 1521 (1967).
11 J.F. Douglass, *J. Am. Chem. Soc., 84,* 121 (1962).
12 C.D. Bass, L. Lynds, T. Wolfram and R.E. De Wames, *Inorg. Chem., 3,* 1063 (1964).
13 S.K. Wason and R.F. Porter, *J. Phys. Chem., 69,* 2461 (1965).