The Chlorotrimethylammonium and Bromotrimethylammonium Cations

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Three methods are described for the preparation of the chloro- and bromo-trimethylammonium cations as a series of salts including the perchlorates and fluorosulphates. The vibrational and n.q.r. spectra are reported and discussed in relation to the bonding in the ions. Halogen and interhalogen adducts of trimethylamine have also been studied, and it is concluded that halogenotrimethylammonium cations are not present in these species.

In the study of the addition compounds of chlorine, bromine, and iodine with simple aliphatic tertiary amines, such as trimethylamine, the existence of discrete halogenotrialkylammonium cations has been suggested, but they have never been isolated.

Hantzch and Graf[1] studied the reaction between aqueous trimethylamine and hypochlorite, and, finding that the products included chlorodimethylamine and methanol, suggested the formation of the chlorotrimethylammonium ion as an intermediate, accounting for these products by the reactions (1) and (2). Ellis and Soper[2] also studied this reaction and from kinetic and spectroscopic evidence reached the same conclusion as the previous workers, suggesting that the initial fast reaction was formation of the chloronium cation followed by attack of this on trimethylamine, which, after hydrolysis of the intermediate species, formed methanol, and the dimethyl- and trimethyl-ammonium cations.

$$N(CH_3)_3 + HOCl + H^+ \longrightarrow N(CH_3)_3Cl^+ + H_2O \quad (1)$$

$$N(CH_3)_3Cl^+ + H_2O \longrightarrow N(CH_3)_2Cl + CH_3OH + H^+ \quad (2)$$

Böhme and Krause[3] considered that the best representation of addition compounds such as $N(CH_3)_3Br_2$ was $N(CH_3)_3Br^+Br^-$ and that this ionisation was responsible for the 16-fold increase in conductivity of a solution of trimethylamine and bromine in a mixture of sulphur dioxide and tetrachloromethane at −20 °C, over the conductivity of the individual reactants. In this mixture sulphur dioxide could act as a Lewis acid to cause ionisation [equation (3)].

$$N(CH_3)_3Br_2 + SO_2 \longrightarrow N(CH_3)_3Br^+ + SBrO_2^- \quad (3)$$

On dissolving $N(CH_3)_3Cl_2$ in 0.01 mol dm^{-3} H_2SO_4 Ellis and Soper[2] found that the absorption spectrum did not correspond to $N(CH_3)_2Cl$, Cl_2, or OCl^- formation, although the oxidising power was still maintained. The freezing point of such a solution was also consistent with ionisation to the chlorotrimethylammonium cation. This type of solution has been used in the work reported in this paper, to precipitate solid species containing the chlorotrimethylammonium cation.

Böhme and Boll[4] obtained a solid product which they suggested contained the chlorotrimethylammonium cation when equimolar mixtures of trimethylamine, antimony pentachloride, and chlorine were mixed in tetrachloromethane. The solid product gave an oxidising reaction towards iodide ion, but the amount of iodine liberated was much less than expected for a pure compound.

In this work cations of the form NR_3Cl^+ and NR_3Br^+ are prepared and their vibrational spectra studied. In the case of the chloro-compounds the ^{35}Cl n.q.r. spectra were also recorded.

The cations were prepared by three methods. The simplest method is to treat the corresponding *N*-halogenoamine with a strong alkylating agent. Methyl fluorosulphate, dimethyl sulphate, and methyl perchlorate were found to react in this way, whereas iodomethane reacted to form species containing anions of the type $NR_2(ICl)_2^-$ and $NR_2(IBr)_2^-$,[5] and in the presence of weaker alkylating agents such as methyl nitrate and methyl trifluoroacetate only decomposition products of the chloroamines were observed. The second method used was the reaction of the known chlorine adduct of the trialkylamine with a strong Lewis acid such as boron trichloride. This corresponds to the type of reaction used by Böhme and Boll,[4] except that they mixed all three components together simultaneously. This is likely to generate the trimethylamine–Lewis acid adduct as well as the required product. The third method was the dissolution of the chlorine adduct of the trialkylamine in water, a solution which is reported to contain the required types of cations,[2] and the precipitation of a salt of the cation by adding a soluble salt of a large, singly charged anion, such as perchlorate or tetrafluoroborate.

In all these cases isolable crystalline solids were obtained which decomposed only slowly at room temperature. The bromine-containing species were less stable than the chloro-compounds and proved more difficult to analyse.

EXPERIMENTAL

N-Chlorodimethylamine was prepared from dimethylamine and *N*-chlorosuccinimide by the method of Ruschig *et al.*[6] *N*-Bromodimethylamine was prepared in a similar manner using *N*-bromosuccinimide; however, the product was extracted into tetrachloromethane and used in this solvent because of the instability of the pure compound. The observed i.r. and u.v. absorption spectra corresponded to those reported by Heasley *et al.*[7] Methyl perchlorate was prepared in solution in tetrachloromethane from iodomethane and silver perchlorate by the method of Hammond.[8] Methyl fluorosulphate was prepared by the exchange reaction between dimethyl sulphate and fluorosulphuric acid as described by Alder.[9] Other reagents were obtained commercially and purified, where necessary, by standard techniques.

Carbon, hydrogen, and nitrogen microanalyses were obtained by combustion using a Perkin-Elmer 240 elemental analyser. Where necessary the compounds were destroyed by oxygen-flask combustion before analysis for the other elements. Chlorine and bromine were analysed by potentiometric titration against silver nitrate in an aqueous acetone mixture. Boron was determined by atomic absorption spectrophotometry. Sulphur was analysed as sulphate by titration with barium perchlorate solution.[10] Fluorine was analysed as fluoride ion by ion exchange to form aqueous hydrogen fluoride, and the acid determined by titration with base.[11] The mass of the compounds corresponding to a one-electron oxidising agent (the equivalent mass) was determined by addition of a large excess of aqueous iodide and titration of the liberated iodine with sodium thiosulphate solution.[12]

Infrared spectra were run in the range 250—4 000 cm^{-1} using a Perkin-Elmer model 457 spectrophotometer, and in the 40—400 cm^{-1} using a Beckman-RIIC RS720 interferometric spectrometer. Ultraviolet and visible spectra were recorded on a Unicam SP 800 spectrometer. Nuclear quadrupole resonance spectra were obtained at 77 K on a mid-range Decca spectrometer (5—60 MHz), using Zeeman modulation. Resonance frequencies were determined within an accuracy of ±10 kHz by interpolation between frequency markers, calibrated by means of an Advance Instruments T.C. 16 frequency counter.[13]

Preparations.—Trimethylamine–chlorine adduct, $N(CH_3)_3Cl_2$. Trimethylamine (1 cm^3, 0.013 mol) was transferred under vacuum into a small flask, and onto this was condensed trichlorofluoromethane (Freon 11) (7 cm^3) and the mixture warmed to −23 °C at which temperature the system was a single liquid phase. The solution was then frozen to 77 K and chlorine (0.5 cm^3, measured at 190 K; 0.012 mol) condensed in, followed by more Freon 11 (5 cm^3). Formation of the adduct as a white precipitate occurred smoothly on warming the mixture to 190 K. After allowing 15 min for completion of the reaction, the remaining trimethylamine and solvent was distilled from the flask leaving a fine, pale yellow powder. The product was very light and easily sucked into the vacuum line. This was prevented by introducing a porosity 3 sinter between the flask and the vacuum line. The yield of 1.58 g corresponded to quantitative conversion based on the chlorine used (Found: C, 28.25; H, 6.35; Cl, 54.95; N, 10.85. Calc. for $C_3H_9ClN_2$: C, 27.7; H, 7.00; Cl, 54.55; N, 10.77%). The i.r. spectrum, the important bands of which are listed in Table 2, showed no evidence for $N(CH_3)_3H^+$ or C–Cl bands. The u.v. absorption spectrum in 0.01 mol dm^{-3} sulphuric acid agreed with that found by Ellis and Soper.[2]

Chlorotrimethylammonium methyl sulphate, $[N(CH_3)_3Cl][SO_3(OCH_3)]$. Dimethyl sulphate (1 cm^3, 0.01 mol) was dissolved in dry diethyl ether (10 cm^3), and the solution degassed on the vacuum line. Chlorodimethylamine (0.7 g, 0.008 8 mol) was condensed onto the frozen solution and the mixture warmed to −5 °C and held at this temperature for 2 h. The fine white solid precipitate was filtered in a nitrogen-filled dry-box to yield 1.32 g of the salt. This represents a 73% conversion of the chloramine (Found: C, 23.45; H, 5.95; Cl, 17.9; N, 7.00; S, 15.95; relative equivalent mass as oxidising agent, 104.1. $C_4H_{12}ClNO_4S$ requires C, 23.35; H, 5.85; Cl, 17.25; N, 6.80; S, 15.55%; relative equivalent mass as an oxidising agent, 102.8).

Chlorotrimethylammonium fluorosulphate, $[N(CH_3)_3Cl][SFO_3]$. Methyl fluorosulphate (1 cm^3, 0.012 5 mol) was condensed into a flask containing degassed tetrachloromethane (5 cm^3). Chlorodimethylamine (0.1 g, 0.001 3 mol) was condensed onto this mixture which was then warmed to −5 °C for 10 min. All the volatile material was then pumped away leaving 0.2 g of a fine white powder. This represents an 83% conversion based on the chloroamine used (Found: C, 18.25; H, 4.60; Cl, 18.5; F, 10.0; N, 7.10; S, 16.6. $C_3H_9ClFNO_3S$ requires C, 18.6; H, 4.65; Cl, 18.35; F, 9.80; N, 7.25; S, 16.55%).

Chlorotrimethylammonium perchlorate, $[N(CH_3)_3Cl][ClO_4]$. *Method* (*a*). A solution of methyl perchlorate (0.46 g, 0.004 mol) in tetrachloromethane (5 cm^3) was degassed on the vacuum line and chlorodimethylamine (0.351 g, 0.004 4 mol) condensed into it at 77 K. After *ca.* 5 min at room temperature a white solid began to form, and after 10 min the mixture was filtered through a sinter in a nitrogen-filled dry-box and the solid washed with a small quantity of dry tetrachloromethane (Found: C, 18.7; H, 4.75; Cl, 36.7; N, 7.35. $C_3H_9Cl_2NO_4$ requires C, 18.55; H, 4.65; Cl, 36.6; N, 7.20%).

Method (*b*). Freshly prepared $N(CH_3)_3Cl_2$ (1 g, 0.007 7 mol) was dissolved in cold distilled water (5 cm^3). To this was added an equal volume of a saturated solution of sodium perchlorate in water, and the fine white microcrystalline product precipitated after a few seconds. The solid was filtered by suction on a sinter, washed with a little ice-cold water, and dried under vacuum to a free-flowing white powder (yield 0.3 g, 20%) (Found: C, 18.4; H, 4.45; Cl, 36.2; N, 7.95; relative equivalent mass as an oxidising agent, 99.7. $C_3H_9Cl_2NO_4$ requires C, 18.55; H, 4.65; Cl, 36.6; N, 7.20%; relative equivalent mass as an oxidising agent, 97.0). The i.r. spectrum of the salt, the main features of which are listed in Table 2, agreed well with that of the sample prepared by alkylation. The u.v. absorption spectrum of the salt dissolved in 0.01 mol dm^{-3} H_2SO_4 showed the peak corresponding to $N(CH_3)_3Cl_2$ dissolved in the same solvent.

Chlorotrimethylammonium tetrafluoroborate, $[N(CH_3)_3Cl][BF_4]$. This was prepared in exactly the same manner as the corresponding perchlorate above, except that a saturated solution of sodium tetrafluoroborate was used as the precipitant. Again the product formed quickly as a fine white crystalline solid (yield 0.4 g, 29%) (Found: C, 19.45; H, 5.10; B, 5.85; Cl, 19.4; F, 41.5; N, 7.60. $C_3H_9BClF_4N$ requires C, 19.85; H, 4.95; B, 5.95; Cl, 19.6; F, 41.9; N, 7.70%). The n.q.r. spectrum is listed in Table 1 and the main features of the i.r. spectrum in Table 2.

Lithium hexafluorophosphate, sodium azide, and thiocyanate did not give precipitates when used in place of the sodium perchlorate.

Chlorotrimethylammonium tetrachloroborate, $[N(CH_3)_3Cl][BCl_4]$. Freshly prepared trimethylamine–chlorine adduct (0.532 g, 0.004 1 mol) was added to an ampoule capped by a greaseless tap (Rotaflo TF6/24). An excess (7.92 g, 0.067 6 mol) of boron trichloride was then condensed into the tube, and the mixture agitated for 39 h at room temperature. The volatiles were then distilled from the mixture and the tube reweighed. From the mass of solid remaining, 90.4% conversion into the tetrachloroborate had occurred. The i.r. spectrum showed bands due to the tetrachloroborate anion and peaks due to the cation (Table 2).

Bromotrimethylammonium fluorosulphate, $[N(CH_3)_3Br][SFO_3]$. In a nitrogen-filled dry-box methyl fluorosulphate (0.4 cm^3) was added to a 0.8 mol dm^{-3} solution (5 cm^3) of *N*-bromodimethylamine in tetrachloromethane. After a few seconds a white precipitate formed. This was filtered from the solvent by suction and washed with dry solvent (Found: C, 15.9; H, 4.80; Br, 31.45; F, 8.30; N, 5.60; S, 12.2. $C_3H_9BrFNO_3S$ requires C, 15.15; H, 3.80; Br, 33.6; F, 8.00; N, 5.90; S, 13.45%). The peaks in the i.r. spectrum attributable to the skeletal modes of the cation are listed in Table 2.

Bromotrimethylammonium perchlorate, $[N(CH_3)_3Br][ClO_4]$. Bromotrimethylammonium fluorosulphate (0.5 g) prepared as above was dissolved in the least quantity of ice-cold water. To this was added a saturated solution of sodium perchlorate, precipitating the white solid product which was filtered onto a sinter, washed with ice-cold water, and dried under vacuum. The peaks in the i.r. spectrum attributable to the skeletal modes of the cation are listed in Table 2.

RESULTS AND DISCUSSION

From the above methods of preparation, and the fact that weighings and analyses could be performed satisfactorily at room temperature, it is clear that the chloro- and bromo-cations studied are quite stable in the solid phase in the presence of a large stable anion such as tetrafluoroborate or fluorosulphate. These materials were found to be stable indefinitely in sealed containers at −25 °C. At room temperature no significant decomposition occurred during 30 min, but a chlorine-like smell was noticeable above the solid after a few hours.

Nuclear Quadrupole Resonance Spectra.—All the compounds that were prepared by the direct alkylation method did not give n.q.r. signals, even when care was taken to crystallise the salts very slowly. The two ^{35}Cl n.q.r. spectra that were obtained were those of the perchlorate and tetrafluoroborate salts precipitated from aqueous solution. The i.r. spectra did not show any significant difference between the samples prepared by these two methods, and, as the signal-to-noise ratio observed (2 : 1) was quite small, it is likely that the n.q.r. signal was observed from the samples crystallised from water because these samples were composed of more perfect crystals. The frequencies observed are listed in Table 1 together with those of some related compounds, as are the coupling constants assuming an asymmetry parameter of zero. The values from this work have previously been reported by Lynch and Waddington [14] in a more general discussion of the n.q.r. spectra of chlorine bonded to Group 5 elements. The average frequency observed for the ^{35}Cl resonance in the $N(CH_3)_3Cl^+$ cation (56.0 MHz) is slightly higher than that observed in molecular chlorine (54.78 MHz),[15] indicating that the electron-withdrawing power of the $N(CH_3)_3{}^+$ group is stronger than that of a chlorine atom. An estimate of the electronegativity of the $N(CH_3)_3{}^+$ group, using the method of Chandra and Chandra [16] based on Gordy's definition of electronegativity from nuclear screening considerations,[17,18] gave a value of 3. This is approximately equal to the value for chlorine, implying the absence of ionic character in the bond. Assuming this, the Townes and Daily method [19] indicated that the *s*-orbital character of the chlorine bonding orbital in the cation was negligible. The ^{35}Cl quadrupole coupling constant of $N(CH_3)_3Cl^+$ is almost twice that of the isostructural $P(CH_3)_3Cl^+$ ion (assuming $\eta = 0$); this may be due to two effects, the greater electronegativity of nitrogen and possible phosphorus *d*-orbital participation in partial P–Cl π-bond formation. Similar effects operate in the isostructural species $C(CH_3)_3Cl$ and $Si(CH_3)_3Cl$. The ^{35}Cl n.q.r. ratios are very similar: $\nu_Q[N(CH_3)_3Cl^+]/\nu_Q[P(CH_3)_3Cl^+] = 1.924$; $\nu_Q[C(CH_3)_3Cl]/\nu_Q[Si(CH_3)_3Cl] = 1.887$. The increase in ^{35}Cl frequency from $N(CH_3)_2Cl$ to $N(CH_3)_3Cl^+$ is to be expected because of the positive polarity enchancement of the nitrogen by the methylation.

TABLE 1

Chlorine-35 n.q.r. frequencies for the chlorotrimethylammonium cation and analogous species, at 77 K

Compound or ion	$\nu(^{35}Cl)$/MHz	$\dfrac{e^2Qq/h(^{35}Cl)}{MHz}$	Ref.
$N(CH_3)_3Cl^+$ ClO_4^-	56.09		*a*
$N(CH_3)_3Cl^+$ BF_4^-	55.89		*a*
$N(CH_3)_3Cl^+$ (average)	55.99	112	*a*
$P(CH_3)_3Cl^+$	29.09	58.2	*b*
$C(CH_3)_3Cl$	31.065	62.1	*c*
$Si(CH_3)_3Cl$	16.46	32.9	*d*
$N(CH_3)_2Cl$	43.67		*a*
$CH(CH_3)_2Cl$	31.94		*e*

[a] This work. [b] K. B. Dillon, R. J. Lynch, R. N. Reeve, and T. C. Waddington, *J.C.S. Dalton*, 1976, 1243. [c] R. Livingston, *J. Chem. Phys.*, 1952, **20**, 1170. [d] H. O. Hooper and B. J. Bray, *J. Chem. Phys.*, 1960, **33**, 334. [e] B. P. Dailey, *J. Chem. Phys.*, 1960, **33**, 1641.

Infrared Spectra.—The observed i.r. spectra for the cations as various salts together with their assignments are given in Table 2. The vibrational assignments were made by considering the species $N(CH_3)_3X^+$ as a five-atom structure with C_{3v} symmetry and all methyl groups equivalent. This method has been used successfully in considering complexes of the type $N(CH_3)_3XY$ [20,21] and in $C(CH_3)_3Cl$,[22] which is isoelectronic with the chlorine-containing cation. This assumes that all absorption frequencies observed above 1 000 cm^{-1} are predominantly

TABLE 2

Frequencies and assignments for the i.r. spectra of halogenotrimethylammonium cations

	$N(CH_3)_3Cl^+$					$N(CH_3)_3Br^+$	
Assignment	ClO_4^-	BF_4^-	$SO_3(OCH_3)^-$	SFO_3^-	BCl_4^-	ClO_4^-	SFO_3^-
ν(N–X) A_1	403	403	400	400	400	325	325
ν(C–N) A_1	815	815	810	820	815	805	805
ν(C–N) E	935	935	940	940	940	945	945
$\delta(NC_3)$ A_1	336	335	335	335	330	295	295

CH modes. For the C_{3v} skeleton of these ions there should be three non-degenerate (A_1) and three doubly degenerate (E) vibrational modes, all of which will be i.r. active.

From Table 2 the absorptions at 815 and 935 cm^{-1} are assigned to the A_1 and E carbon–nitrogen stretching modes, in accordance with the corresponding modes in a variety of trimethylamine–acceptor complexes as well as trimethylamine itself. Previous assignments[21] for $N(CH_3)_3ICl$ are listed in Table 3 to show this correspondence.

TABLE 3

Frequencies and assignments for the i.r. spectra of trimethylamine–halogen and –interhalogen adducts

	Trimethylamine complex					
Assignment	Cl_2	Br_2	I_2	ICl	IBr	BrCl
ν(N–X)	336	166	148	196	172	302
ν(C–N)	800	800	801	809	807	800
ν(C–N)	962	989	999	993	996	985
$\delta(NC_3)$	324	320	365	434	434	435
$\delta(NC_3)$	544	494	468	471, 490	482	500
$\rho(NC_3)$		267			269	
ν(X–Y)	348	224	188	249	206	278
δ(NXY)	88	70	50	147	90	
Ref.	This work	20	20	21	21	This work

The nitrogen–chlorine stretching vibration (A_1) was assigned to the band at 403 cm^{-1}. This was confirmed by a shoulder at 398 cm^{-1} of about a third the intensity of the main peak. This is assigned to the (N–^{37}Cl) vibration. If the trimethylamino-group is treated as a point of relative atomic mass 59, the force constant assumed to be constant with changing isotope mass, and the simple harmonic approximation used, then the splitting between the peaks should be 7 cm^{-1}. The observed splitting (5 cm^{-1}), together with the fact that the observed relative intensities of the peaks correspond to the expected 3 : 1 due to the chlorine isotope abundance, confirm the assignment of this band.

The vibration observed at 335 cm^{-1} is either an NC_3 deformation or NC_3 rocking mode. It seems likely that, in view of the low intensity of the NC_3 rocking modes observed in the trimethylamine–halogen addition compounds,[20,21] the rather weak absorption at 335 cm^{-1} is derived from either of the NC_3 deformation modes, and most probably the symmetric mode since this appears the stronger in the spectrum of $C(CH_3)_3Cl$. The missing NC_3 deformation and rocking modes were not detectable even using very strong mulls in the far-i.r. region (40—350 cm^{-1}).

Similar assignments are made for the bromo-cation (Table 2), when the two higher-frequency absorptions at 805 and 945 cm^{-1} are assigned to the A_1 and E carbon–nitrogen stretching frequencies. There is a 60 cm^{-1} reduction in value for the carbon-halogen stretching frequency on going from $C(CH_3)_3Cl$ to $C(CH_3)_3Br$. The same reduction is also observed in the nitrogen–halogen stretching frequencies of the *N*-halogenodimethylamines. Of the two frequencies observed for the bromo-cation (325 and 295 cm^{-1}) it seems likely that the higher corresponds to the nitrogen–bromine stretching frequency as this would correspond to a 78 cm^{-1} reduction in frequency from the chlorine-containing ion. The absorption at 295 cm^{-1} is then assigned to the $A_1(NC_3)$ deformation mode. As in the case of the chloro-cation, no absorptions were found which could be attributed to the two low-frequency E modes.

The i.r. spectrum of $N(CH_3)_3Cl_2$ is reported in Table 3 and for this species the bands have shifted significantly from the positions in the simple chloro-cation and the NC_3 skeletal modes have a much closer parallel with those of the bromine adduct, the assignments for which (Table 3) are those of Gayles.[20] The N–Cl stretching frequency is significantly lower than that found in $N(CH_3)_3Cl^+$. This fact, and the observation of a Cl–Cl stretching frequency at 348 cm^{-1}, indicates considerable Cl–Cl bonding.

Conclusion.—This work demonstrates that the halogenotrimethylammonium cations are stable species in the solid phase when paired with stable and moderately large counter anions, but that the halogen and interhalogen adducts of trimethylamine are best described by covalent forms.

The authors thank R. J. Lynch for help in running the n.q.r. spectra and R. Coult for performing the halogen and boron analyses. One of us (N. D. C.) thanks the S.R.C. for a research studentship.

[9/1287 *Received*, 13*th August*, 1979]

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