Preparation and Structures of Halidelon Complexes of Carbon Tetrahalides and Tetrahalogenoethylenes

By **J. A. Creighton** * and **K. M. Thomas**, Chemical Laboratory, University of Kent, Canterbury

The preparation is reported of 33 crystalline compounds of tetra-alkylammonium halides with carbon tetrahalides and with tetrabromo- and tetraiodo-ethylene. The Raman and i.r. spectra are discussed, in conjunction with X-ray data, in terms of the site symmetries of the halogenocarbon molecules in these molecular complexes, and lattice force constants and vibrational amplitudes are calculated. The halide ion–carbon tetrahalide distances are considerably less than the sum of the ionic and van der Waals' radii by an amount which increases in the same order, $Cl^- < Br^- < I^-$, as the halide ion–CBr_4 lattice force constant. This together with Raman intensities of the lattice vibrations strongly indicates that the compounds should be regarded as donor–acceptor complexes.

TETRABUTYLAMMONIUM CHLORIDE and bromide are remarkably soluble in carbon tetrachloride and a brief report that tetrabutylammonium chloride forms solid complexes with CCl_4 has been published,[1] but no data on the structures of these complexes were given. There is also evidence, from the u.v. spectra of dilute solutions of tetrabutylammonium bromide and iodide in carbon tetrachloride, in support of the formation of complexes of the solute ion-pairs with molecules of the solvent,[2,3] and from the decrease in the stability constant of the complex on passing from iodide to bromide solutions it was concluded that the halide ion is bound to CCl_4 by donor–acceptor interaction rather than by electrostatic forces.[3] Several other complexes of carbon tetrahalides or tetrahalogenoethylenes with potential donors, such as ammonia, triethylamine, triphenylphosphine, hexamethylenetetramine, pyridine, piperidine, triethylenediamine, pyrazine, benzene, *p*-xylene, mesitylene, and hexamethylbenzene have been reported,[4] and these have generally been regarded as charge-transfer compounds, although for the benzene complexes evidence has been presented that the interaction is not of the donor–acceptor type.[5]

This paper reports the formation of a considerable number of crystalline adducts of carbon tetrahalides or tetrahalogenoethylenes with tetra-alkylammonium halides. The preparation and vibrational spectra of 33 of these compounds is given together with some X-ray powder data, and their structures and bonding are discussed. A preliminary report of this work has already been published.[6] An analogous series of compounds of tetra-alkylphosphonium halides with carbon tetrahalides has also been prepared.[7] The vibrational spectra, structures, and equilibrium data on the 1 : 1 complexes of halide ions with CCl_4 and CBr_4 which exist in solution in aprotic solvents will be the subject of a later publication.

EXPERIMENTAL

Tetramethyl-, tetraethyl-, and tetrapropyl-ammonium halides were dried by heating *in vacuo*. Aqueous solutions of tetrabutylammonium halides, prepared from the hydroxide, were evaporated *in vacuo*; the solute was taken up in dichloromethane and dried (CaH_2), filtered and evaporated. The resulting anhydrous tetrabutylammonium halide was dissolved in carbon tetrachloride and stored over calcium hydride.

The crystalline adducts, for which analytical data are given in Table 1, were precipitated by mixing roughly stoicheiometric amounts of solutions of the anhydrous tetra-alkylammonium halide and the tetrahalogenomethane. The tetramethylammonium compounds were prepared in methanol solution or, in the case of the CI_4 adduct, in a mixture of methanol and dichloromethane, while the tetraethylammonium and tetrapropylammonium compounds were prepared from solutions in dichloromethane or acetonitrile. The tetramethylammonium halide–CBr_4 adducts could also be precipitated from solutions in methanol. The stoicheiometry of the products was established by varying the proportions of reactants. The carbon tetrachloride complexes dissociate slowly both in air and *in*

---

[1] D. H. McDaniel and R. M. Dieters, *J. Amer. Chem. Soc.*, 1966, **88**, 2607.

[2] M. J. Blandamer, T. E. Gough, and M. C. R. Symons, *Trans. Faraday Soc.*, 1966, **62**, 301.

[3] P. C. Dwivedi and C. N. R. Rao, *Spectrochim. Acta*, 1970, **26A**, 1535.

[4] P. Datta and G. M. Barrow, *J. Amer. Chem. Soc.*, 1965, **87**, 3053; W. C. Dehn and A. H. Dewey, *ibid.*, 1911, **33**, 1588; D. P. Stevenson and G. M. Coppinger, *ibid.*, 1962, **84**, 149; G. Heublein, *Z. Chem.*, 1965, **5**, 305; A. N. Sharpe and S. Walker, *J. Chem. Soc.*, 1964, 2340; T. Dahl and O. Hassel, *Acta Chem. Scand.*, 1966, **20**, 2009; 1968, **22**, 372; J. P. Lorand, *Tetrahedron Letters*, 1971, 2511; G. W. Chantry, H. A. Gebbie, and H. N. Mirza, *Spectrochim. Acta*, 1967, **23A**, 2749; R. F. Weimer and J. M. Prausnitz, *J. Chem. Phys.*, 1965, **42**, 3643; F. J. Strieter and D. H. Templeton, *ibid.*, 1962, **37**, 161; F. Doerr and G. Buttgereit, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 861.

[5] D. A. Bahnick, W. E. Bennet, and W. B. Person, *J. Phys. Chem.*, 1969, **73**, 2309.

[6] J. A. Creighton and K. M. Thomas, *J. Mol. Structure*, 1971, **7**, 173.

[7] J. A. Creighton and T. J. Sinclair, unpublished work.

vacuo or when washed with light petroleum; under these conditions the CBr_4 compounds with smaller cations are quite stable. The adducts of CI_4 are yellow in contrast to CI_4 which is red, but they darken slowly on standing in air.

Attempts to prepare crystalline adducts of C_2Cl_4, C_2Cl_6, and C_6Cl_6 by their addition to concentrated solutions of Et_4NCl in dichloromethane or of Bu_4NCl in carbon tetrachloride were unsuccessful. Similar attempts to prepare solid complexes of Et_4NCl, Et_4NBr, Et_4NI, and Bu_4NCl with CH_2Cl_2, $SiCl_4$, or $SiBr_4$, or of P_4 with Et_4NBr were also unsuccessful, and there was no Raman evidence for compounds of Et_4NCl with CH_2Cl_2, $SiCl_4$ (see, however, ref. 8) or $SiBr_4$ in CH_2Cl_2 solution. With CH_2Br_2 and CH_2I_2, Et_4NCl and Et_4NBr gave solid compounds which the Raman spectra showed to be complexes of these molecules but no reproducible analyses could be obtained. Similar variable results were obtained with complexes of CBr_4 with tetrabutylammonium chloride or bromide prepared from solutions in CCl_4, due presumably to the ready loss of CBr_4 from these complexes with large cations.

TABLE 1

Analytical data

	Found (%)				Required (%)			
	C	H	N	X	C	H	N	X
$Me_4NCl,2CBr_4$	9·35	1·55	1·75		9·3	1·55	1·8	
* $Me_4NBr,2CBr_4$	9·0	1·75	1·75		8·8	1·45	1·7	
$Me_4NI,2CBr_4$	8·85	1·7	1·65		8·35	1·4	1·6	
* $Me_4NCl,2CI_4$	6·1	0·85	1·4		6·25	1·05	1·2	
* $Me_4NBr,2CI_4$	6·2	1·1	1·3		6·05	1·0	1·15	
* $Me_4NI,2CI_4$	5·95	0·8	1·25	92·04	5·8	0·9	1·1	92·15
$Me_4NBr,2C_2I_4$	8·05	1·3	1·3		7·9	1·0	1·15	
† Et_4NCl,CCl_4				11·2				11·1
† Et_4NBr,CCl_4				22·2				22·0
Et_4NCl,CBr_4	22·15	4·65	2·9		21·7	4·05	2·8	
Et_4NBr,CBr_4	20·3	3·9	2·55		19·95	3·7	2·6	
Et_4NI,CBr_4	18·7	3·4	2·3		18·35	3·4	2·4	
* Et_4NCl,CI_4	15·85	3·1	1·85		15·8	2·9	2·05	
* Et_4NBr,CI_4	14·9	2·85	1·9		14·8	2·75	1·9	
* Et_4NI,CI_4	14·1	2·7	1·85	81·75	13·9	2·6	1·8	81·9
Et_4NCl,C_2I_4	17·35	3·25	1·95		17·20	2·85	2·0	
Et_4NBr,C_2I_4	16·5	3·2	1·8		16·2	2·7	1·9	
Et_4NI,C_2I_4	15·45	2·6	1·65		15·2	2·55	1·8	
Et_4NBr,CHI_3	18·3	3·85	2·25		17·9	3·5	2·3	
Et_4NI,CHI_3	17·1	3·45	2·05		16·6	3·25	2·15	
$Et_4NBr,CHBr_3$	23·8	4·95	3·1		23·35	4·95	3·0	
$Et_4NI,CHBr_3$	21·5	4·3	2·7		21·2	4·1	2·75	
Et_4NCl,C_2Br_4	23·2	4·0	2·9		23·55	3·9	2·75	
Et_4NBr,C_2Br_4	21·8	4·15	2·6		21·65	3·6	2·55	
Et_4NI,C_2Br_4	19·05	3·1	2·25		19·95	3·35	2·35	
Pr_4NCl,CBr_4	31·6	5·75	3·05		28·2	5·05	2·53	
* Pr_4NBr,CBr_4	26·25	4·75	2·45	66·85	26·05	4·7	2·35	66·9
Pr_4NI,CBr_4	24·3	4·05	2·05		24·5	4·35	2·15	
* Pr_4NCl,CI_4	20·85	3·6	2·0		21·0	3·8	1·9	
* Pr_4NBr,CI_4	19·75	3·4	1·6		19·85	3·55	1·8	
* Pr_4NI,CI_4	18·55	3·25	1·85	76·35	18·7	3·35	1·7	76·25
Pr_4NCl,C_2I_4	21·75	3·7	1·8		22·3	3·7	1·85	
Pr_4NBr,C_2I_4	21·25	3·3	1·8		21·0	3·5	1·75	
* Pr_4NI,C_2I_4	20·05	3·5	1·6	75·15	20·1	3·35	1·7	74·85
Pr_4NBr,C_2Br_4	27·25	4·7	2·4		27·75	4·6	2·3	
Et_3NHCl,CBr_4	18·0	3·55	2·85		17·9	3·4	3·0	
Et_3NHBr,CBr_4	16·2	2·6	2·55		16·3	3·1	2·7	

X = Br, I.

* See text. † X = Ionizable halogen.

Raman spectra were recorded with a Coderg PH1 spectrometer with O.I.P. 150 mW helium–neon laser, and the frequencies are accurate to ± 2 cm^{-1}. I.r. spectra in the range 80—360 cm^{-1} were measured with a R.I.I.C. FS 720 interferometer and FTC 100 wave analyser with a resolution of 4 cm^{-1}, and above 200 cm^{-1} with a Perkin-Elmer 225 spectrophotometer. Analytical data in Table 1 were obtained with a Hewlett Packard 185 CHN analyser except for those marked with an asterisk which are due to A. Bernhardt Mikroanalytisches Laboratorium. *X*-Ray powder photographs were recorded with a Guinier camera with Cu-K_α (1·55418 Å) and the intensities were estimated by eye.

Structures and Vibrational Assignments.—The Raman and i.r. spectra of all the compounds showed the following features: (i) bands due to the tetra-alkylammonium cations, which have been omitted from the data shown in Tables 2—6; (ii) bands whose frequencies closely resemble those of the parent halogenoalkane, for which vibrational data are also in Tables 2—6 for comparison; (iii) bands below 110 cm^{-1} which are attributed to lattice vibrations. These observations indicate that the compounds are molecular complexes in which the halogenoalkane molecules are loosely bound in the lattice. This

---

[8] I. R. Beattie and K. M. Livingston, *J. Chem. Soc.* (*A*), 1969, 857.

TABLE 2

Raman spectra of crystalline carbon tetrahalide complexes (700—40 cm^{-1})

	ν_3	ν_1	ν_4	ν_2	Other bands
CCl$_4$ (liquid)	790, 762m	459vs	314s	218s	
CBr$_4$ (solution)	670m	269vs	183ms	127m	
CI$_4$ (solid)	555m	178vs	123ms	90m	
Me$_4$NCl,2CBr$_4$	668m	263vs	187s	146w	49·5vs
Me$_4$NBr,2CBr$_4$	663s	262vs	186s	151vw	47·5vs
Me$_4$NI,2CBr$_4$	659m	258vs	182s		45vs
Me$_4$NCl,2Cl$_4$	571m	186vs	127m		45s
Me$_4$NBr,2CI$_4$	571m	187vs	127m		
Me$_4$NI,2CI$_4$	571m	186vs	127m		45s
Et$_4$NCl,CCl$_4$	780s, 747w	436vs	316s	236w	86vs
Et$_4$NBr,CCl$_4$	780s, 747w	435vs	317m	232w	74vs
Et$_4$NI,CCl$_4$	776s, 743w	433vs	316vs	228w	67vs
Et$_4$NCl,CBr$_4$	670s, 673sh	252vs	186s, 184s	145w	114m, 99vs, 78w, 70w, 58sh, 53w
Et$_4$NBr,CBr$_4$	669s	250vs	184s	142w	83m, 75s, 50w
Et$_4$NI,CBr$_4$	663s	248vs	185s	136w	67vs
Et$_4$NCl,CI$_4$	581w	177vs	129m		105s
Et$_4$NBr,CI$_4$	579w	176vs	128m		78s
Et$_4$NI,CI$_4$	574w	176vs	127m	112w	69s
Pr$_4$NCl,CBr$_4$	667m, 645w	251vs	184sh, 177mw	134w	99sh, 77m
Pr$_4$NBr,CBr$_4$	664m, 647w	250vs	187sh, 183mw, 176mw	133w	64m
Pr$_4$NI,CBr$_4$	660m, 650w	249vs	186sh, 181w, 175mw	133w	111vw, 55m
Et$_3$NHCl,CBr$_4$	672m, 663m, 658sh	257vs	185m, 180m, 160w	130w	162w, 118vw, 108vw, 74w
Et$_3$NHBr,CBr$_4$	668m, 660m	255vs	184ms, 181m	134w, 119w	68w, 56w

TABLE 3

Infrared spectra of crystalline carbon tetrahalide complexes (700—60 cm^{-1})

	ν_3	ν_1	ν_4	ν_2	Other bands
Me$_4$NCl,2CBr$_4$	669vs		187s		96vs,br 78sh (102vs, 84s) *
Me$_4$NBr,2CBr$_4$	667vs		187s		102sh, 80m, 68vs (81s, 72vs) *
Me$_4$NI,2CBr$_4$	662vs		184s		73sh, 64vs, (75s, 68vs) *
Me$_4$NCl,2CI$_4$	574vs		127s		97w, 63vs
Me$_4$NBr,2CI$_4$	574vs		126s		96w, 64vs
Me$_4$NI,2CI$_4$	572vs		126s		62vs
Et$_4$NBr,CCl$_4$					(80vs, 73vs, 60w, 53m) *
Et$_4$NCl,CBr$_4$	668vs		187s	146 *	110vs, 98sh, 78s, 56sh, (113vs, 82m, 71m, 55m) *
Et$_4$NBr,CBr$_4$	667vs		185vs	145w	110w, 75vs, 66vs, 52sh (86vs, 72m, 65m, 53m)*
Et$_4$NI,CBr$_4$	662vs	247w	182vs	137w	97w, 74s, 63vs (78vs, 62m, 54m, 48m) *
Et$_4$NCl,CI$_4$	580s		128vs		113vs,br, 64m (119vs, 104sh, 75m, 66m, 48m) *
Et$_4$NBr,CI$_4$	577s		128s		78vs (88vs, 76sh, 65m, 59m, 44m) *
Et$_4$NI,CI$_4$	573s		127vs	112w	96w, 67vs
Pr$_4$NCl,CBr$_4$	666vs, 641vs	252m	188m, 178m		104vs,br, 85vs,br
Pr$_4$NBr,CBr$_4$	662vs, 641vs, 666sh	251m	187sh, 183m, 176m		69vs
Pr$_4$NI,CBr$_4$	662vs, 645vs, 665sh	249w	185sh, 183m, 176m	150sh, 140s	113sh, 81w, 64vs
Pr$_4$NCl,CI$_4$	560sh, 553vs	170w	142s, 123s	100w	66m, 60vs
Pr$_4$NBr,CI$_4$	565sh, 557vs	169w	142vs, 124sh	98w	62m
Pr$_4$NI,CI$_4$	559s, 552vs	169w	143m, 122s, 118sh	95m	65m, 49vs
Et$_3$NHCl,CBr$_4$	670vs, 659vs, 650sh	257w	186w, 168vs	128w	100s
Et$_3$NHBr,CBr$_4$	668s, 660vs	256w	186s	120vs, 130s	105s, 95s

* Observed at −196 °C.

conclusion is in agreement with X-ray structural data on some of the compounds in terms of which a detailed discussion of the vibrational spectra may be made.

TABLE 4

Assignments of lattice bands of Et_4N^+ compounds

		Translational modes	Librational modes
Et_4NCl,CBr_4	Raman	114m, 99vs; 78w 70w	58sh, 53w
	I.r.	113vs; 82m, 71m	55m
Et_4NBr,CBr_4	Raman	83m, 75s	50w
	I.r.	86vs; 72m, 65m	53m
Et_4NI,CBr_4	Raman	67vs	
	I.r.	78vs; 62m, 54m	48m
Et_4NCl,CI_4	Raman	105s	
	I.r.	119vs, 104sh; 75m, 66m	48m
Et_4NBr,CI_4	Raman	78s	
	I.r.	88vs, 76sh; 65m, 59m	44m
Et_4NBr,CCl_4	Raman	74vs	
	I.r.	80vs; 73vs, 60m	53m

$Me_4NX,2CBr_4$ *Compounds*.—The frequencies of CBr_4 in Table 2 are for solutions in carbon tetrachloride and differ slightly from data published previously.

Preliminary analysis of X-ray data from single crystals of $Me_4NBr,2CBr_4$ shows that the space-group is $F\bar{4}3m(T_d^2)$ with four molecules per unit cell and a cubic cell constant of 12·253 ± 0·008 Å.[9] The lattice is a NaCl-like arrangement of Me_4N^+ and halide ions with one CBr_4 molecule at the site of T_d symmetry at the centre of each primitive cube and with the C–Br bonds directed towards the halide ions. X-Ray powder photographs of $Me_4NCl,2CBr_4$ and $Me_4NI,2CBr_4$ (indexed in ref. 10) show that these compounds are isomorphous with $Me_4NCl,2CBr_4$, with cubic cell constants of 12·137 ± 0·008 Å and 12·517 ± 0·008 Å respectively. There is, therefore, no reduction in the symmetry of CBr_4 by the crystal field in any of these compounds, and consistent with this, no splitting of bands or change in Raman or i.r. activity of the internal vibrations of complexed CBr_4 is observed, as shown in Tables 2 and 3. The frequencies and intensities of these internal vibrations are also similar to those of free CBr_4. The largest change is in ν_2 which is *ca.* 20 cm^{-1} higher in frequency and very weak in the Raman spectrum, while ν_1 and ν_3 show shifts of *ca.* 5 cm^{-1} to lower frequencies. It is evident from these small shifts that the internal forces in the CBr_4 molecules are not greatly affected by the external forces which hold the molecules at the lattice sites, in agreement with the X-ray measurement on $Me_4NBr,2CBr_4$ which shows normal C–Br bond lengths.[9]

TABLE 5

Raman spectra (cm^{-1}) of solid C_2X_4 complexes

	ν_1	ν_5	ν_2	ν_6	ν_3	Other bands
C_2I_4	1466w	775w	184vs	149m	110m	
$Me_4NBr,2C_2I_4$	1462w	769m, 755sh	183vs	147s, 135m	112w	98w
Et_4NCl,C_2I_4	1459w	764m, 752sh	177vs	147s, 137sh	112w	
Et_4NBr,C_2I_4	1457w	763m, 754sh	175vs	144sh, 137s	110w	34w
Et_4NI,C_2I_4	1451w	752m, 744sh	172vs, 169sh	133vs	109w	41w
Pr_4NCl,C_2I_4	1456w	760m, 749sh	177vs	142sh, 136s	111w	92w
Pr_4NBr,C_2I_4	1455w	763m, 755m, 746sh	176vs	142m, 135s	111w	58m
Pr_4NI,C_2I_4	1447w	749m, 733sh	171vs	135vs	112w	54m
C_2Br_4	1547m	880w	265vs	208m	144m	
Et_4NCl,C_2Br_4	1529w	872sh, 867m	254vs	206m	154w	
Et_4NBr,C_2Br_4	1527w	868sh, 864m	253vs, 232m	204s, 196sh	151w	739w, 722w, 177w
Et_4NI,C_2Br_4	1532w	862m	253vs, 234w	198vs, 189m	149w	739w, 139vw, 111w
Pr_4NBr,C_2Br_4	1535w	871m, 862m	256vs, 238w	207s, 202s, 194sh	150w	745w

TABLE 6

Infrared spectra (cm^{-1}) of C_2I_4 complexes

	$\nu_6 + \nu_{11}$	ν_9	ν_{11}	ν_7	ν_{12}	ν_{10}	Other bands
C_2I_4	676	639	525	226	131	95	
Me_4NBr,C_2I_4	664w	618w	516w	231sh, 238sh	141sh, 134m	97	111sh, 177m, 83vs
Et_4NCl,C_2I_4	683w	616w	520w	247m	142m		128vs, 97s, 71m
Et_4NBr,C_2I_4	659w	609w	516w	242, 238m	136s	101vs	90vs, 78sh
Et_4NI,C_2I_4	659w	609w	514w	231m	132m	98m	65m, 51m
Pr_4NCl,C_2I_4	656w	607w	512w	240m	137s		124vs, 100vs, 85vs
Pr_4NBr,C_2I_4	657w	609w	511w	237m	133s	100s	85vs, 68s
Pr_4NI,C_2I_4		595w	509w	245m	133s	94s	60vs

The translational lattice vibrations in these compounds, whose frequencies give a measure of these external forces, are of species $3f_2$ of the factor-group T_d. These vibrations are more usefully classified however as $f_{2g} + 2f_{1u}$ of the factor-group of the space-group $Fm3m(O_h^5)$ which results from regarding Me_4N^+ as a point mass. It then follows that one of the vibrations, which involves contrary translation of the two CBr_4 molecules in the primitive cell, is Raman-active only, while the other two translatory vibrations are i.r.-active only. These predictions are in complete accord with the spectra summarized in Tables 2 and 3; the Raman spectra of all the compounds show a single intense lattice band, while the i.r. spectra all show one broad band at room temperature, which at −190° is re-

---

[9] P. T. Clarke, personal communication.

[10] K. M. Thomas, Ph.D. Thesis, University of Kent, 1971.

solved into two overlapping bands. The frequencies of these bands, and of the lattice vibrations of the compounds Et_4NX,CBr_4, are discussed in a later section.

Et_4NX,CBr_4 *Compounds.*—*X*-Ray data on single crystals of Et_4NCl,CBr_4 show that the space-group is $\bar{I}_4$ (S_4^2) with two molecules per unit cell, $a = b = 8{\cdot}06 \pm 0{\cdot}03$ Å, $c = 12{\cdot}31 \pm 0{\cdot}04$ Å.[9] The structure is similar to that of $Me_4NBr,2CBr_4$ but with only half of the tetrahedral sites occupied by CBr_4 molecules and with a small tetragonal distortion of the lattice. The effect of the tetragonal distortion is to reduce the symmetry of the sites occupied by the CBr_4 molecules to D_{2d}, and the conformation adopted by the Et_4N^+ ions further reduces this to S_4. This reduced site symmetry splits the degenerate vibrations of CBr_4 into doublets $[e(T_d) \longrightarrow a + b\ (S_4);\ f_2(T_d) \longrightarrow b + e\ (S_4)]$ of which the *b* and *e* components are i.r.-active and all components are Raman-active. The splittings of ν_3 and ν_4 are observed in the Raman spectrum (Table 2) but are too small to be seen in the i.r. with the available instrumental resolution. The splitting of ν_2 is evidently too small to be seen in either spectra but the i.r.-activity conferred on the *b* component of ν_2 is observed.

Systematic absences in the *X*-ray powder photographs (indexed in ref. 10) of the other two compounds Et_4NBr,CBr_4 and Et_4NI,CBr_4 are consistent with face-centred cubic lattices. The cubic cell constants are $11{\cdot}91 \pm 0{\cdot}02$ Å and $12{\cdot}11 \pm 0{\cdot}02$ Å respectively. The lattices are probably similar to that of Et_4NCl,CBr_4 but with no tetragonal distortion; the space-group remains $\bar{I}_4$ (S_4^2) (though now pseudo-cubic) due to the probable S_4 symmetry of the Et_4N^+ ions, and the site symmetry of the CBr_4 molecules is again S_4. In agreement with this the spectra show the predicted i.r.-activity of ν_2 (*b* component in S_4 symmetry), but presumably due to the absence of the tetragonal distortion the splittings of the degenerate vibrations of CBr_4 are too small to be observed in either the i.r. or Raman spectra.

The assignment of the lattice vibrations of the Et_4N^+ compounds is less straightforward than for the Me_4N^+ compounds. The two triply degenerate translational modes which result if the Et_4N^+ ions are regarded as point masses, are each split into doublets of species $b + e$ in the lower factor-group symmetry S_4 which results when the effect of the S_4 point symmetry of the Et_4N^+ ions is included. For Et_4NCl,CBr_4 one of these pairs of vibrations may reasonably be assigned to the most intense lattice bands (99vs, 114m, sh) in the Raman spectrum, coinciding with the broad i.r. band at 113 cm^{-1}. Lattice force-constant calculations indicate that the other doublet must be near 70 cm^{-1} for the lattice force constants to be comparable to those in $Me_4NCl,2CBr_4$ (see below), and is most probably 71,82 cm^{-1} in the i.r. spectrum, corresponding to a weak doublet in the Raman spectrum. The assignment for Et_4NBr,CBr_4 and Et_4NI,CBr_4 is exactly analogous as shown in Table 4, and is supported by the observation that all four translational frequencies show a smooth decrease from chloride to iodide. The remaining lowest observed band which shows a much smaller shift with change of anion is then a librational mode, most probably of Et_4N^+ since the i.r. and Raman bands due to libration of CBr_4 molecules are expected to be very weak. There are two librational modes (a_1, *e*, point symmetry S_4) of Et_4N^+, both of which are Raman-active while only the *e* mode is i.r.-active, but only in Et_4NCl,CBr_4 have both modes been detected.

Other CBr_4 *Compounds.*—The splitting of degenerate bands and the appearance of ν_1 with medium intensity in the i.r. spectra indicate low crystal symmetries in the triethylammonium and tetrapropylammonium compounds. The frequencies and intensities of the bands, notably of ν_2, approach those of free CBr_4 as the size of the cation increases, and the strong Raman lattice bands, assigned to translation of halide ions against CBr_4, decrease in frequency until presumably below the lower limit of observation of 40 cm^{-1}. These results indicate that for larger cations the CBr_4 molecules are less tightly bound in the lattice, in agreement with the observed decrease in stability of these compounds with increase of cation size.

CI_4 *Compounds.*—The spectra of the tetramethylammonium and tetraethylammonium compounds of CI_4 follow the pattern of the CBr_4 compounds. Thus only fairly small shifts are observed in the fundamentals ν_1, ν_3, and ν_4 of CI_4, and ν_2 was too weak to observe in the Raman spectra, except in Et_4NI,CI_4 where it is 22 cm^{-1} higher than in free CI_4. There seems little doubt therefore that the CI_4 compounds are all pseudo-cubic with structures similar to the corresponding CBr_4 complexes, and this is confirmed by the *X*-ray patterns for Et_4NCl,CI_4 and Et_4NBr,CI_4, which show[10] these compounds to be isomorphous with Et_4NBr,CBr_4, with cubic cell constants of $12{\cdot}292 \pm 0{\cdot}2$ Å and $12{\cdot}481 \pm 0{\cdot}02$ Å respectively.

CCl_4 *Compounds.*—Previous vapour pressure studies[1] on solutions of tetrabutylammonium chloride in carbon tetrachloride have shown the occurrence of the compounds $Bu_4NCl,\frac{1}{2}CCl_4$, Bu_4NCl,CCl_4, and $Bu_4NCl,5CCl_4$. The compounds were suggested to be salts of the CCl_5^- ion, and tetraethylammonium chloride was reported to have no interaction with CCl_4.

We have now prepared the compounds Et_4NCl,CCl_4 and Et_4NBr,CCl_4 by the addition of carbon tetrachloride to solutions of the tetraethylammonium halides in dichloromethane or acetonitrile. The compounds readily lose CCl_4 and the results of microanalyses were variable, but Volhard determinations of ionizable halogen in larger samples showed them to be 1 : 1 complexes as indicated in Table 1. The Raman spectra in Table 2 also show that they are molecular complexes of CCl_4 with structures probably similar to the CBr_4 adducts, and this is confirmed by the *X*-ray powder pattern of Et_4NBr,CCl_4 which may be indexed to a cubic lattice with a cell constant of $11{\cdot}58 \pm 0{\cdot}02$ Å.[10] As in the CBr_4 complexes, ν_2 is weaker and displaced to higher frequency than in free CCl_4, while ν_1 is displaced to lower frequency, and in consequence the Fermi resonance of $\nu_1 + \nu_4$ with ν_3 is affected, the higher component, which is then evidently mainly ν_3, becoming much the stronger. The most intense Raman lattice bands are lower in frequency than in the corresponding CBr_4 compounds despite the smaller mass of CCl_4, and this reflects the lower stability of the CCl_4 adducts.

C_2X_4 *Complexes.*—The Raman and i.r. spectra of these compounds are given in Tables 5 and 6 along with the spectra of the parent halogenoalkanes.[11,12] Bands due to ν_8 (b_{2g}) which are weak in the parent halogenoalkanes, were not observed from any of the complexes and this vibration is therefore omitted from Table 5. The ν_5

---

[11] E. J. Fleurie and W. D. Jones, *Spectrochim. Acta*, 1969, **25A**, 653.

[12] D. E. Mann, J. H. Meal, and E. K. Plyler, *J. Chem. Phys.*, 1956, **24**, 1018.

band of C_2I_4, reported as the strongest band in the Raman spectrum of this substance,[11] was found here to be weak relative to ν_2, as is reported for C_2Br_4,[12] and its qualitative intensity given previously [11] is thus probably in error.

All the spectra of the C_2X_4 complexes show marked changes in intensities from those of the parent halogenocarbons, but as for the CX_4 adducts changes in the frequencies and splitting of bands are fairly small, consistent with their formulation as molecular halogenocarbon complexes. The greatest intensity change in the Raman spectra is in ν_6 which is intensified relative to the strongest band ν_2, but ν_5 is also strengthened and ν_3 weakened in all the compounds. In contrast all bands in the carbon–iodine stretching region of the i.r. spectra are weak. All the frequencies are lower than in the parent halogenocarbon except for ν_3 and ν_{10} which are scarcely affected, and ν_7 and ν_{12} which are slightly increased in frequency.

The frequencies ν_2, ν_5, and ν_6 are split in most of the compounds, ν_2 by *ca.* 20 cm^{-1} in some of the complexes of C_2Br_4, and since all these vibrations are non-degenerate in the free molecule, the splitting must arise from correlation-field splitting, rather than from low C_2X_4 site symmetries. Indeed the absence of i.r.-active vibrations of the free molecule in the Raman spectra suggests that the sites occupied by C_2X_4 molecules are probably centrosymmetric. The observation of correlation-field splitting indicates that the primitive cells contain more than one C_2X_4 molecule, and the structure of these complexes, containing planar C_2X_4 molecules, are thus probably less simple than those of the complexes of tetrahedral CX_4 molecules.

The intense translational lattice bands associated with relative motion of C_2X_4 molecules and halide ions were not found in the Raman spectra above the lower limit of observation of 40 cm^{-1}. Weak bands at 739 cm^{-1} in Et_4NBr,C_1Br_4 and Et_4NI,C_2Br_4 and at 745 cm^{-1} in Pr_4NBr,C_2Br_4 are possibly $\nu_{10} + \nu_{11}$ (b_{1g}) = 754 cm^{-1}.[12]

DISCUSSION

Of particular interest in these compounds is the nature of the interaction between the halide ions and perhalogenoalkane molecules. The strongly basic properties of halide ions in aprotic conditions is well known, and several reports have been given of complexes of perhalogenoalkanes with neutral donor molecules such as nitrogen bases or aromatic hydrocarbons,[4] in at least some of which compounds it is probable that the bonding interaction is due to charge transfer. However the halogenomethane molecules are highly polarizable, and the alternative possibility arises in the compounds described here that the interaction is predominantly an electrostatic ion–induced dipole effect. A distinction between these two possibilities may be made by a study of the effect of change of halide ion on the interatomic distances and lattice vibrational properties, and the following discussion relates mainly to the data for the CBr_4 complexes. From the general similarity between the CBr_4 and the other halogenomethane complexes, it is most probable, however, that the conclusions are applicable also to these other complexes.

Interatomic Distances.—The CBr_4 bond lengths in $Me_4NBr,2CBr_4$ and Et_4NCl,CBr_4 have been shown [9] to be unchanged within experimental error from that in free CBr_4. Assuming this to be true also of the halogenomethane bond lengths in the other complexes for which powder *X*-ray data were recorded, the halogen–halide ion distance may be calculated from the cubic cell constant. These distances are given in Table 7, accompanied, in parentheses, by the amount by which these distances are less than the sum of the respective van der Waals' and Pauling ionic radii. For each compound this distance is significantly short and increases in the order $Cl^- < Br^- < I^-$. This is the expected order for charge-transfer interaction, being the order of decreasing halide-ion ionization potential, but is the inverse of that expected for electrostatic interactions from size considerations. The shortening of the halide ion–halogenomethane distance along the series of halogenomethanes, which increases in the order $CCl_4 < CBr_4 < CI_4$, parallels both the order of increasing polarizability and decreasing energy of the lowest acceptor orbitals,[13] and is thus consistent with either type of interaction.

TABLE 7

Halogen–halide ion distances and force constants in carbon tetrahalide complexes

	$X^- \cdots Y$ (Å)	*K* (mdyn $Å^{-1}$)
$Me_4NCl,2CBr_4$	3·305(0·45)	0·13
$Me_4NBr,2CBr_4$	3·357(0·54)	0·15
$Me_4NI,2CBr_4$	3·472(0·64)	0·16
Et_4NCl,CBr_4	3·190(0·57)	0·10—0·14
Et_4NBr,CBr_4	3·207(0·69)	0·13—0·15
Et_4NI,CBr_4	3·294(0·82)	0·17—0·19
Et_4NBr,CCl_4	3·250(0·50)	
Et_4NCl,CI_4	3·223(0·74)	
Et_4NBr,CI_4	3·305(0·79)	

The $Br \cdots I^-$ distance is greater in $Me_4NI,2CBr_4$ than in Et_4NI,CBr_4, and this is attributed to the greater number of CBr_4 acceptor molecules around each I^- ion in the Me_4N^+ compound (eight as against four in Et_4NI,CBr_4). In $Me_4NCl,2CBr_4$ and $Me_4NBr,2CBr_4$ this effect is augmented by a $Br \cdots Br$ contact between adjacent CBr_4 molecules which occurs if the $Br \cdots X^-$ distance is less than 3·38 Å; in the Et_4NX,CBr_4 compounds this type of contact does not occur since only every other tetrahedral site between Et_4N^+ and X^- ions is occupied by CBr_4.

Lattice Vibrations.—In order to interpret the frequencies and Raman intensities of the lattice vibrations, approximate force constants and lattice vibrational amplitudes of the Me_4N^+ and Et_4N^+ compounds with CBr_4 were calculated from the translational frequencies (room temperature values) by the method of Shimanouchi.[14] Point masses were assumed for R_4N^+ and CBr_4, and the small tetragonal distortion in Et_4NCl,CBr_4 was neglected. To this approximation the crystals are all cubic and the secular equations for the

---

[13] T. Yonezawa, H. Kato, H. Saito, and K. Fukui, *Bull. Chem. Soc. Japan*, 1962, **35**, 1814.

[14] T. Shimanouchi, M. Tsuboi, and T. Miyazawa, *J. Chem. Phys.*, 1961, **35**, 1597.

triply degenerate lattice vibrations may be derived by a one dimensional calculation. This treatment ignores interactions between the lattice modes and the internal vibrations of R_4N^+ and CBr_4, but since the lowest f_2 internal vibration, ν_4 of CBr_4, is 80 cm^{-1} higher than the highest lattice frequency the inaccuracies arising from this are likely to be small compared to those due to approximations in the force field. For the Et_4N^+ compounds it was consequently necessary also to ignore the splitting of the translational modes into *b* and *e* components, and the mean of the frequencies as given in Table 9 were used in the calculations.

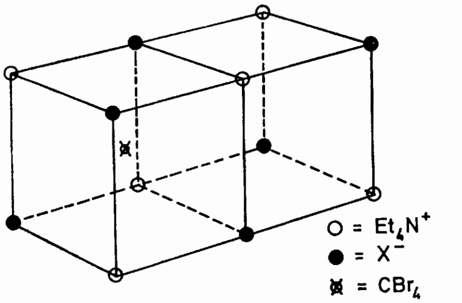

FIGURE 1 The primitive cell of Et_4NX,CBr_4

The primitive cell of the tetraethylammonium compounds is shown in Figure 1; that for the tetramethylammonium compounds is similar but with a CBr_4 molecule at the centre of both unit cubes. Following Shimanouchi [14] the most important crystal forces were assumed to arise from the nearest neighbour interactions $R_4N^+ \cdots X^-$, $R_4N^+ \cdots CBr_4$ and $X^- \cdots CBr_4$ associated with diagonal force constants, H, J, and K. Also in the Me_4N^+ compounds an interaction constant k between $X^- \cdots CBr_4$ displacements involving a common X^- ion was included, this being considered chemically a more realistic way of taking into account the effect of a near-contact between the two CBr_4 molecules in a primitive cell than a diagonal force constant for $CBr_4 \cdots CBr_4$ stretching. All other force constants were neglected. The $\boldsymbol{G}$ and $\boldsymbol{F}$ matrix elements and the symmetry co-ordinates, including those S_a of the acoustic modes which must be included in the amplitude calculations, are given in Table 8.

For both the Me_4N^+ and Et_4N^+ compounds there is one more force constant than frequency, and the whole range of real solutions for which the interionic force constant H is positive was therefore investigated. For each value of H there were two solutions corresponding to the two possible assignments of the i.r.-active translational modes, but one of these was easily rejected by inspection. The resulting range of values of the force constants is shown in Figure 2. For the Me_4N^+ compounds, although three of the four force constants could be varied over a fairly wide range, the X^-–CBr_4 stretching force constant K varied by less than 7% throughout the whole range of real solutions, and the mean values given in Table 7 are thus well determined (subject to the approximations in the force field) by the observed frequencies. For the Et_4N^+ compounds a larger range of real solutions resulted in wider limits on the possible values of K. However it is reasonable to assume that the interionic force constant H is not significantly different from its values in the Me_4N^+ compounds, and probably lies in the range 0·01—0·04 mdyn Å^{-1}. Somewhat tighter limits may thus be placed on K than is indicated in Figure 2, and these limits are given in Table 7. It may be seen from Figure 2 that over the whole range of solutions for the Me_4N^+ and Et_4N^+ compounds, the values of K are in the expected order for donor–acceptor complexes, $Cl^- < Br^- < I^-$; $CCl_4 < CBr_4 < CI_4$, in agreement with the conclusions reached above from interatomic distances and contrary to the order of strengths expected for predominantly electrostatic forces.

TABLE 8

Symmetry co-ordinates and $\boldsymbol{G}$ and $\boldsymbol{F}$ matrix elements for the translational lattice vibrations of $Me_4NX,2CBr_4$ and Et_4NX,CBr_4. (n, x, c, and μ_n, μ_x, μ_c denote respectively one dimensional displacement co-ordinates and inverse masses of R_4N^+, X^-, and CBr_4; S_a is for the acoustic mode)

Symmetry co-ordinates, $Me_4NX,2CBr_4$: $S_1(f_{2g}) = (c_1 - c_2)/\sqrt{2}$, $S_2(f_{1u}) = (n - x)/\sqrt{2}$, $S_3(f_{1u}) = (n + x - c_1 - c_2)/2$, $S_a(f_{1u}) = (n + x + c_1 + c_2)/2$. Et_4NX,CBr_4: $S_1(f_{1u}) = (x - n)/\sqrt{2}$, $S_2(f_{1u}) = (2c - n - x)/\sqrt{6}$, $S_a(f_{1u}) = (n + x + c)/\sqrt{3}$

$\boldsymbol{G}$ *matrix*, $Me_4NX,2CBr_4$: $g_{11} = \mu_c$, $g_{22} = (\mu_n + \mu_x)/2$, $g_{23} = g_{2a} = (\mu_n - \mu_x)/\sqrt{8}$, $g_{33} = g_{aa} = (\mu_n + \mu_x + 2\mu_c)/4$, $g_{3a} = (\mu_n + \mu_x - 2\mu_c)/4$. Et_4NX,CBr_4: $g_{11} = (\mu_n + \mu_x)/2$, $g_{1a} = -\sqrt{2}g_{12} = (\mu_x - \mu_n)/\sqrt{6}$, $g_{22} = (\mu_n + \mu_x + 4\mu_c)/6$, $g_{2a} = (2\mu_c - \mu_n - \mu_x)/\sqrt{18}$, $g_{aa} = (\mu_n + \mu_x + \mu_c)/3$

$\boldsymbol{F}$ *matrix*, $Me_4NX,2CBr_4$: $f_{11} = 4(J + K + k)/3$, $f_{22} = 4H + 4(J + K - k)/3$, $f_{23} = 8(J - K + k)/3\sqrt{2}$, $f_{33} = 8(J + K - k)/3$, $f_{12} = f_{13} = f_{aa} = f_{1a} = f_{2a} = f_{3a} = 0$. Et_4NX,CBr_4: $f_{11} = 4H + 2(J + K)/3$, $f_{12} = 2(J - K)/\sqrt{3}$, $f_{22} = 2(J + K)$, $f_{aa} = f_{1u} = f_{2a} = 0$

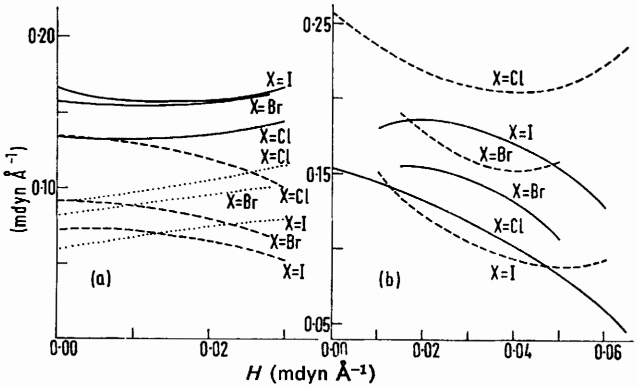

FIGURE 2 The range of the lattice vibrational force constants J (– – – –), K (——) and k (· · · ·) for $Me_4NX,2CBr_4$ and Et_4NX,CBr_4; (a) = $Me_4NX,2CBr_4$ and (b) = Et_4NX,CBr_4

The Cartesian vibrational amplitudes for unit displacement in the normal co-ordinates are given by $\tilde{\boldsymbol{U}}\boldsymbol{L}$, where $\boldsymbol{L}$ is the normalized eigenvector matrix of $\boldsymbol{GF}$ expressed in Cartesian symmetry co-ordinates and the acoustic symmetry co-ordinate is included so that the amplitudes are in relation to a fixed centre of gravity. Amplitudes were calculated corresponding to $H = 0{\cdot}015$ mdyn Å^{-1}, which is near the centre of the range of solutions of ***GF*** for the Me_4N^+ compounds. The results given in Table 9 show that the higher and lower frequency f_{1u} vibrations of the Me_4N^+ compounds may be loosely described, respectively, as vibrations of Me_4N^+ and X^- against the rest of the lattice, while in the Et_4N^+ compounds the higher frequency involves mainly X^-–CBr_4 stretching, with the lower predominantly motion of Et_4N^+ against the rest of the lattice. As previously discussed, the lowest frequency translational mode (f_{2g}) of the Me_4N^+ compounds involves only contrary motion of the two CBr_4 molecules in the primitive cell.

TABLE 9

Relative lattice vibrational amplitudes for $H = 0{\cdot}015$ mdyn Å^{-1}

	ν/cm^{-1}	CBr_4	X^-	Me_4N^+
$Me_4NCl,2CBr_4$	102	0·0108	0·0279	−0·1099
	84	−0·0099	0·1617	0·0109
	49·5	±0·0388	0·0000	0·0000
$Me_4NBr,2CBr_4$	84	0·0111	0·0109	−0·1108
	72	−0·0127	0·1057	−0·0002
	48	±0·0388	0·0000	0·0000
$Me_4NI,2CBr_4$	78	−0·0134	0·0063	0·1087
	65	−0·0131	0·0818	−0·0226
	45	±0·0388	0·0000	0·0000
Et_4NCl,CBr_4	106	0·0171	−0·1596	0·0001
	76·5	−0·0267	−0·0267	0·0754
Et_4NBr,CBr_4	80	0·0303	−0·0887	−0·0227
	68·5	−0·0158	−0·0529	−0·0730
Et_4NI,CBr_4	72·5	0·0334	−0·0679	−0·0189
	58	−0·0142	−0·0397	0·0751

The highest frequency translational vibration of the Et_4N^+ compounds and the lowest of the Me_4N^+ compounds are notable for their high Raman intensity, and Table 9 shows that these are the only Raman-active modes in which there is a large amplitude of X^-–CBr_4 stretching. The high Raman intensity of these modes, which is a characteristic of vibrations involving covalent bonds, is thus further evidence for donor–acceptor interaction between the halide ions and CBr_4. In contrast, for an electrostatic-bonding model the Raman intensity would be expected to be low,[15] and certainly very much smaller than that, for example, of the internal CBr_4 vibrations.

It is thus concluded that all the complexes described here are of the donor–acceptor type and that in the CX_4 complexes there is presumably donation of charge from the halide ions into the vacant low-lying a_1^* and f_2^* orbitals, which are of suitable symmetry to accept charge from tetrahedrally distributed halide ions. In common with other donor–acceptor complexes, these compounds show bands in the near u.v. in diffuse reflectance. Unfortunately the bands were very broad and only in the CBr_4 complexes, where several band components were discernable, was there a definite shift with change of anion. In view of the poor quality of the spectra no detailed analysis was attempted.

We thank the S.R.C. for a research studentship (K. M. T.).

[1/1546 *Received, August 25th,* 1971]

---

[15] J. H. R. George, J. A. Rolfe, and L. A. Woodward, *Trans. Faraday Soc.*, 1953, **49**, 375; T. V. Long and R. A. Plane, *J. Chem. Phys.*, 1965, **43**, 457.