Pentachloro- and Pentabromo-titanate(IV) ions

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The reactions between titanium(IV) chloride and tetra-alkylammonium chlorides and between titanium(IV) bromide and tetra-alkylammonium bromides, in solution in dichloromethane, have been studied by Raman and i.r. spectroscopy. The five-co-ordinate ions $[TiCl_5]^-$ and $[TiBr_5]^-$ have been clearly identified for the first time. These ions and the other singly charged species $[Ti_2Cl_9]^-$ and $[Ti_2Br_9]^-$ are the only anions detected by Raman spectroscopy in the dichloromethane solutions. The preparations of the tetrabutylammonium salts $[Bu_4N][TiCl_5]$ and $[Bu_4N][TiBr_5]$ and of tetraphenylarsonium pentachlorotitanate are described, but the corresponding salts of the smaller tetraethyl- and tetrapropyl-ammonium cations are shown to be $[Et_4N]_2[Ti_2Cl_{10}]$, $[Et_4N]_2[Ti_2Br_{10}]$, and $[Pr_4N]_2[Ti_2Cl_{10}]$ with binuclear halogen-bridged anions.

ALTHOUGH several pentachloro-anionic species have now been well established, including the ions $[InCl_5]^{2-}$, $[TlCl_5]^{2-}$, $[GeCl_5]^-$, $[SnCl_5]^-$, $[CuCl_5]^{3-}$, and $[CdCl_5]^{3-}$,[1-5] there have been no reports of the existence of the corresponding chlorine-bridged dimeric species $[M_2Cl_{10}]^{n-}$. (A statement [6] that earlier workers [7] had identified the complex $[Cl_4P]_2[Sn_2Cl_{10}]$ appears to be the result of a mistranslation.) This is in contrast to the situation with the uncharged molecular species where, with the probable exception of phosphorus pentachloride,[8] all the known pentachlorides have been shown to exist both as MCl_5 molecules and as chlorine-bridged dimers, in several cases with both forms existing even in the solid or liquid states.[9-11]

This paper reports the identification of the trigonal-bipyramidal ions $[TiCl_5]^-$ and $[TiBr_5]^-$, both in solution and as their tetrabutylammonium salts. Since the $[Ti_2Cl_{10}]^{2-}$ ion has already been established in the salt $[Cl_4P]_2[Ti_2Cl_{10}]$ by *X*-ray studies,[6] this work provides the first example where both the $[MCl_5]^-$ and $[M_2Cl_{10}]^{2-}$ ions are known. The tetraethylammonium salt, however, which was earlier suggested [3] to contain $[TiCl_5]^-$ ions, is shown to be $[Et_4N]_2[Ti_2Cl_{10}]$, and the analogous bromo-complex is also reported. It is thus clear that the anion structure adopted in these halogenotitanates is dependent on the size of the cation, as the following series of tetraethylammonium, tetrapropylammonium, tetrabutylammonium, and tetraphenylarsonium salts established in this study shows: $[Et_4N]_2[Ti_2Cl_{10}]$, $[Pr_4N]_2[Ti_2Cl_{10}]$, $[Bu_4N][TiCl_5]$, $[Ph_4As][TiCl_5]$; and $[Et_4N]_2[Ti_2Br_{10}]$ and $[Bu_4N][TiBr_5]$.

RESULTS AND DISCUSSION

Salts of the $[Ti_2Cl_{10}]^{2-}$ *and* $[Ti_2Br_{10}]^{2-}$ *Ions.*—The Raman spectrum of $[Cl_4P]_2[Ti_2Cl_{10}]$ has already been published [12] and this has been confirmed in the present study. When allowance is made for the bands due to the cations, the Raman spectra of the $[PCl_4]^+$ salt and of the corresponding tetraethyl- and tetrapropyl-ammonium salts are closely similar, notably in the presence of the two strong bands at 305—310 and 380—385 cm^{-1} (Table 1). It is thus clear beyond doubt that both these quaternary ammonium salts are salts of the $[Ti_2Cl_{10}]^{2-}$ ion, which has already been established as the anion in the $[PCl_4]^+$ salt.[6]

TABLE 1

Vibrational spectra (cm^{-1}) of the $[Ti_2Cl_{10}]^{2-}$ and $[Ti_2Br_{10}]^{2-}$ ions

$[Et_4N]_2[Ti_2Cl_{10}]$		$[Pr_4N]_2[Ti_2Cl_{10}]$	$[Cl_4P]_2[Ti_2Cl_{10}]$		$[Et_4N]_2[Ti_2Br_{10}]$	
I.r. [a]	Raman	Raman	I.r.	Raman [b]	I.r.	Raman
427m						
385vs	389vs	381vs	377vs	382vs	308s	300s
346vs	355m	351m	350vs	361m	276vs, br	
				342m		
317s	308s	309s	315s	309s	190s	192vs
			278m			
212m	233w	244w	223m, br	243		
182w	187 [c]	190 [c]	196w	187s	131mw	
170m			172m		112mw	
154w			153w	136m	100w	
				132m		
				128 (sh)		
			114w	117s	76mw	
83m			92w	64s	54w	

sh = Shoulder and br = broad.

[a] Ref. 3. [b] Ref. 12. [c] Medium-intensity shoulder on an emission line of the laser.

There is also a close similarity between the i.r. spectra of $[Cl_4P]_2[Ti_2Cl_{10}]$ and of the corresponding $[Et_4N]^+$ salt, although this is not immediately clear from the published data.[3,12] This is because of the listing of a number of bands of the $[PCl_4]^+$ salt as shoulders without an estimate of their relative intensities. We, therefore, remeasured the i.r. spectra of both these salts. Several

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[1] D. F. Shriver and I. Wharf, *Inorg. Chem.*, 1969, **8**, 2167; D. S. Brown, F. W. B. Einstein, and D. G. Tuck, *ibid.*, p. 14.

[2] I. R. Beattie, T. Gilson, K. Livingston, V. Fawcett, and G. A. Ozin, *J. Chem. Soc.* (*A*), 1967, 712.

[3] J. A. Creighton and J. H. S. Green, *J. Chem. Soc.* (*A*), 1968, 808.

[4] M. Matsui, S. Koda, S. Ooi, H. Kuroya, and I. Bernal, *Chem. Letters*, 1972, 51; I. Bernal, N. Elliott, and R. Lalancette, *Chem. Comm.*, 1971, 803.

[5] K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1111; T. V. Long, A. W. Herlinger, E. P. Epstein, and I. Bernal, *ibid.*, 1970, **9**, 459.

[6] T. J. Kistenmacher and G. D. Stucky, *Inorg. Chem.*, 1971, **10**, 122.

[7] P. Reich and W. Wieker, *Z. Naturforsch.*, 1968, **B23**, 739.

[8] R. W. Suter, H. C. Knachel, U. P. Petro, J. H. Howatson, and S. G. Shore, *J Amer. Chem. Soc.*, 1973, **95**, 1474; T. Kennedy, D. S. Payne, R. I. Reed, and W. Snedden, *Proc. Chem. Soc.*, 1959, 133.

[9] W. Bues, F. Demiray, and H. A. Øye, *Z. phys. Chem.* (*Frankfurt*), 1973, **84**, 18.

[10] W. Bues, F. Demiray, and W. Brockner, *Spectrochim. Acta*, 1974, **A30**, 1709; K. Olie, C. C. Smitskamp, and H. Gerding, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 129.

[11] R. F. W. Bader and A. D. Westland, *Canad. J. Chem.*, 1961, **39**, 2306; R. A. Walton and B. J. Brisdon, *Spectrochim. Acta*, 1967, **A23**, 2489.

[12] D. Nicholls and K. R. Seddon, *Spectrochim. Acta*, 1972, **A23**, 2399.

of the weak bands and shoulders in the spectrum of the $[PCl_4]^+$ salt reported previously[12] were not confirmed, and the remaining bands were all sufficiently well resolved for an estimate of their relative intensities to be made. The published spectrum of the $[Et_4N]^+$ salt[3] was confirmed below 340 cm^{-1} with the addition of a weak band at 154 cm^{-1}. These new measurements, showing the close similarity between the i.r. spectra of the two salts, are listed in Table 1.

In the earlier report of the i.r. spectrum of the $[Et_4N]^+$ salt[3] it was suggested that this salt contained $[TiCl_5]^-$ rather than $[Ti_2Cl_{10}]^{2-}$ ions, because of the absence of prominent bands in the region 250—300 cm^{-1} expected for chlorine-bridge stretching. With much stronger evidence supporting the formulation of this salt as $[Et_4N]_2[Ti_2Cl_{10}]$, it now seems likely by analogy with published assignments for Nb_2Cl_{10}, Ta_2Cl_{10}, and Re_2Cl_{10}[13] that these bridge-stretching modes of the $[Ti_2Cl_{10}]^{2-}$ ion (b_{2u} and b_{3u}; point group D_{2h}) are at 317s and 212m cm^{-1} in the i.r. spectrum, with Raman counterparts (a_g and b_{1g}) at 308s and 233w cm^{-1}. This is similar to the assignment already suggested for these modes in the $[PCl_4]^+$ salt.[12] The possibility that the 317 cm^{-1} i.r. band, assigned above to bridge stretching, is due instead to ν_3 of $[TiCl_6]^{2-}$ ions present as an impurity is ruled out by our observation that ν_1 of $[TiCl_6]^{2-}$ (320 cm^{-1} in $[Et_4N][TiCl_6]$)[14] is absent from the Raman spectrum of the same sample.

TABLE 2

Vibrational spectra (cm^{-1}) of the $[TiCl_5]^-$ and $[TiBr_5]^-$ ions

$[Bu_4N][TiCl_5]$		$[Bu_4N][TiBr_5]$		$SbCl_5$ (l)[a]		Assignment
Raman	I.r.	Raman	I.r.	Raman	I.r.	
408w	411m		341s 310 (sh)	397 (2)	395vs	ν_5, e'
	355s		293vs, br		371vs	ν_3, a_2''
348vs[b]		209		357 (10)		ν_1, a_1'
302vw				307 (4)	306w	ν_2, a_1'
193m	190m			177 (4)	172s	ν_6, e'
	178m				154m	ν_4, a_2''
166m				165 (2)		ν_8, e''
	66m		57mw	72		ν_7, e' or lattice

[a] Ref. 3, Raman relative intensities are given in parentheses. [b] For $[Ph_4As][TiCl_5]$, ν_1 was observed at 249vs cm^{-1}.

TABLE 3

Comparison of the most intense Raman bands (cm^{-1}) of species $[MX_4]^{n-}$, $[MX_5]^{(n+1)-}$, and $[MX_6]^{(n+2)-}$ (X = Cl or Br)

A		B		$\frac{1}{2}$(A + B) = C	D		D − C
$[InCl_4]^-$	321[a]	$[InCl_6]^{3-}$	277[b]	299	$[InCl_5]^{2-}$	294[a]	−5
$[TlCl_4]^-$	312[a]	$[TlCl_6]^{3-}$	264[b]	288	$[TlCl_5]^{2-}$	279[a]	−9
$GeCl_4$	397	$[GeCl_6]^{2-}$	309[a]	353	$[GeCl_5]^-$	348[a]	−5
$SnCl_4$	367[a]	$[SnCl_6]^{2-}$	309[a]	338	$[SnCl_5]^-$	338[a]	0
$SnBr_4$	220[a]	$[SnBr_6]^{2-}$	182[a]	201	$[SnBr_5]^-$	202[a]	+1
$[PCl_4]^+$	451[a]	$[PCl_6]^-$	355[a]	403	PCl_5	393[a]	−10
$[SbCl_4]^-$	342[c]	$[SbCl_6]^{3-}$	267[b]	305	$[SbCl_5]^{2-}$	348[d]	+43[d]
$[SbCl_4]^+$	353[a]	$[SbCl_6]^-$	333[a]	343	$SbCl_5$	353[e]	+10
$TiCl_4$	388[a]	$[TiCl_6]^{2-}$	320[f]	354	$[TiCl_5]^-$	349	−5
$TiBr_4$	230[a]	$[TiBr_6]^{2-}$	190[f]	210	$[TiBr_5]^-$	208	−2

[a] S. D. Ross, 'Inorganic Infrared and Raman Spectra,' McGraw-Hill, London, 1972. [b] T. Barrowcliffe, I. R. Beattie, P. Day, and K. Livingston, *J. Chem. Soc.* (*A*), 1967, 1810. [c] G. Y. Ahlijah and M. Goldstein, *J. Chem. Soc.* (*A*), 1970, 326. [d] Ref. 15. [e] Ref. 2. [f] Ref. 14.

Also reported in this paper is the salt $[Et_4N]_2[Ti_2Br_{10}]$. This formulation as a salt of a binuclear anion is less certain than for $[Et_4N]_2[Ti_2Cl_{10}]$. The complex is very dark in colour and only its strongest Raman bands could be recorded (Table 1), and furthermore the i.r. spectrum was poorly defined with a broad absorption throughout the Ti–Br stretching region due to partly overlapping bands. However, these data are sufficient to show that this complex is not a salt of $[TiBr_5]^-$, whose frequencies are reported in Table 2. It is, therefore, concluded that it is the salt $[Et_4N]_2[Ti_2Br_{10}]$, analogous to the chloro-complex, and the data in Table 4 lend some support to this conclusion.

The $[TiCl_5]^-$ *and* $[TiBr_5]^-$ *Ions.*—Evidence for the $[TiCl_5]^-$ ion was first obtained when attempting to study the $[Ti_2Cl_{10}]^{2-}$ ion in solution for Raman polarization measurements. The Raman spectrum of a solution of equimolar amounts of tetrabutylammonium chloride and $TiCl_4$ in dichloromethane showed no evidence of the characteristic 385 cm^{-1} band of the $[Ti_2Cl_{10}]^{2-}$ ion, but instead gave rise to a strong, highly polarized, band at 348 cm^{-1} ($\rho < 0.1$). Addition of several volumes of light petroleum to this solution precipitated a complex which also showed this strong Raman band (Table 2), and whose analysis was consistent with the composition $[Bu_4N][TiCl_5]$. A similar procedure using tetrabutylammonium bromide and $TiBr_4$ gave solutions showing a strongly polarized band at 209 cm^{-1}, and on precipitation of the solute a complex of composition $[Bu_4N][TiBr_5]$ was obtained which also showed this band.

In order to establish the assignment of these bands to the five-co-ordinate $[TiCl_5]^-$ and $[TiBr_5]^-$ ions, Table 3 shows a correlation of the strongest Raman bands (the symmetric breathing frequencies ν_1) of the series $[MX_4]^{n-}$, $[MX_5]^{(n+1)-}$, and $[MX_6]^{(n+2)-}$ (X = Cl or Br) for which there are well established data. Where small differences exist in the frequencies reported for different salts, Table 3 lists those relating to the salt with the largest cation or to solution measurements.

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[13] (*a*) I. R. Beattie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc.* (*A*), 1968, 2765; (*b*) D. A. Edwards and R. T. Ward, *ibid.*, 1970, 1617.

[14] W. van Bromswyk, R. J. H. Clark, and L. Maresca, *Inorg. Chem.*, 1969, **8**, 1395.

In each case the strongest Raman band of the $[MX_5]^{(n+1)-}$ species lies within ± 10 cm^{-1} of the mean of the ν_1 frequencies of $[MX_4]^{n-}$ and $[MX_6]^{(n+2)-}$, with the exception of the lone-pair ion $[SbCl_5]^{2-}$ where the strongest Raman band is unexpectedly high in frequency and has been discussed in this respect by Beattie *et al.*[15] In contrast the strongest Raman bands of the dimeric M_2X_{10} species are normally at higher frequencies, especially the bands of molecules or ions with low mass ratios $m_M : m_X$, as shown in Table 4. These correlations thus provide a clear spectroscopic differentiation (for $m_M : m_X \lesssim 2.5 : 1$) of five-co-ordinate MX_5 species from their bridged dimers, using only the frequencies of the strongest Raman bands and without analysis of the details of the spectra. For $[TiCl_5]^-$ and $[TiBr_5]^-$ the strongest Raman bands are within only 5 cm^{-1} of the mean of the TiX_4 and $[TiX_6]^{2-}$ frequencies, and their identification as five-co-ordinate species thus seems beyond doubt.

TABLE 4

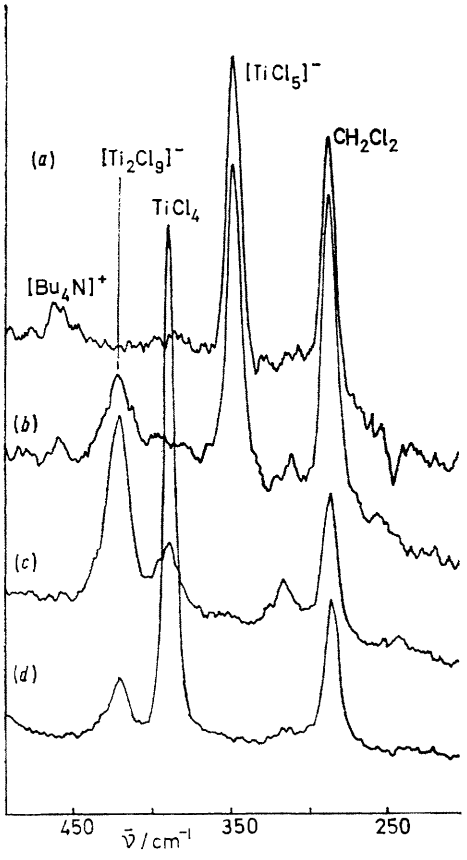
Most intense Raman bands (cm^{-1}) of MX_5 and M_2X_{10} species, and their mass ratios $m_M : m_X$

	A		B	B − A	$m_M : m_X$
$[TiBr_5]^-$	209	$[Ti_2Br_{10}]^{2-}$	300	91	0.60
$NbBr_5$	234 [a]	Nb_2Br_{10} [b]	291	57	1.16
$[TiCl_5]^-$	348	$[Ti_2Cl_{10}]^{2-}$	389	41	1.35
$TaBr_5$	240 [a]	Ta_2Br_{10} [b]	266	26	2.26
$NbCl_5$	394 [a]	Nb_2Cl_{10} [b]	416	22	2.62
$TaCl_5$	406 [a]	Ta_2Cl_{10} [b]	418	12	5.10

[a] I. R. Beattie and G. A. Ozin, *J. Chem. Soc.* (*A*), 1969, 1691.
[b] Ref. 13*a*.

The frequencies and intensities for the $[TiCl_5]^-$ ion closely resemble the pattern of bands shown by other trigonal-bipyramidal pentachloro-species, and their assignment in Table 2 on the basis of D_{3h} symmetry is thus straightforward by analogy with that for $SbCl_5$.[3] For $[TiBr_5]^-$, only the strongest Raman band could be recorded because of the dark red colour of this ion. Only a partial assignment could therefore be made for $[TiBr_5]^-$. This assignment is also given in Table 2, and is notable in showing the order $\nu_3 \gg \nu_1$ also observed for PCl_5 [2] but not for other MCl_5 species and which is consistent with the high mass ratios $m_{Br} : m_{Ti}$ and $m_{Cl} : m_P$.

The observation that $[Bu_4N][TiCl_5]$ and $[Bu_4N][TiBr_5]$ are soluble in dichloromethane with no significant change in their Raman spectra is itself further evidence that these are salts of the singly charged $[TiX_5]^-$ ions, since salts of doubly charged ions are usually either insoluble in this low dielectric-constant solvent or dissolve with dissociation of the doubly charged ion. An interesting illustration of this insolubility of multiply charged ions in dichloromethane was seen when a solution of $TiCl_4$ was titrated with tetrapropylammonium chloride in this solvent. The only salts which precipitated during the titration were $[Et_4N]_2[Ti_2Cl_{10}]$ and $[Et_4N]_2[TiCl_6]$, which were formed as the ratio $TiCl_4 : Cl^-$ approached 1 : 1 and 1 : 2 respectively ($[Pr_4N][Ti_2Cl_9]$ also precipitates in the early stages of the titration if concentrated solutions are used). The $[Ti_2Cl_{10}]^{2-}$ and $[TiCl_6]^{2-}$ ions were not detected in the solutions by Raman spectroscopy, however, the only chloro-species observed being $TiCl_4$ and the singly charged $[Ti_2Cl_9]^-$ and $[TiCl_5]^-$ ions. Spectra showing the variations in the intensities of the Raman bands of these solution species as $TiCl_4$ was titrated with tetrabutylammonium chloride in dichloromethane solution are reproduced in the Figure. These were obtained by placing the reaction vessel directly in the Raman spectrometer and are therefore not of high quality, but they are reproduced to show how effectively this titration may be followed by Raman spectroscopy. The Figure also shows a weak band at 318 cm^{-1} which reached a maximum intensity at $TiCl_4 : Cl^- = 3 : 1$ and which may be due to a further solute species $[Ti_3Cl_{13}]^-$.



Raman spectra of solutions prepared by titrating tetrabutylammonium chloride with $TiCl_4$ in dichloromethane. Mol ratios $[Bu_4N]Cl : TiCl_4$ are (*a*) 1.0, (*b*) 0.8, (*c*) 0.5, and (*d*) 0.1 : 1

The $[Ti_2Cl_9]^-$ *and* $[Ti_2Br_9]^-$ *Ions.*—Raman spectra of the salts $[Et_4N][Ti_2Cl_9]$ and $[Et_4N][Ti_2Br_9]$ were also recorded in the course of this study (Table 5). I.r. spectra of both these salts have been reported previously,[3,16] but the published measurements on the bromo-complex were only above 200 cm^{-1} and these have therefore now been extended to lower frequencies. Raman spectra of solutions of $[Bu_4N][Ti_2Cl_9]$ and $[Bu_4N][Ti_2Br_9]$ in dichloromethane were also recorded,

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[15] I. R. Beattie, F. C. Stokes, and L. E. Alexander, *J.C.S. Dalton*, 1973, 465.

[16] R. J. H. Clark and M. A. Coles, *J.C.S. Dalton*, 1972, 2454.

and these showed bands at 420 (polarized) and at 317 (vs, polarized) and 192m cm^{-1} respectively.

TABLE 5

Vibration bands (cm^{-1}) of the $[Ti_2Cl_9]^-$ and $[Ti_2Br_9]^-$ ions

$[Et_4N][Ti_2Cl_9]$		$[Et_4N][Ti_2Br_9]$			
Raman	I.r.*	Raman	I.r.	Assignment	
420vs		317vs		a_1'	ν_t
	416vs		324vs	a_2''	
396m		292m		e''	
384m	379vs	281 (sh)	276vs	e'	
	268m		182m	a_2''	ν_b
233	230w	192m	192w (sh)	e'	
	188w		143w		
	171w	92m	91w		
	74w		70mw		
	57w		57w		

* Ref. 3.

The $[Ti_2Cl_9]^-$ ion has been shown by *X*-ray studies to have the expected D_{3h} symmetry with three bridging chlorine atoms,[6] and the vibrational spectra in Table 5 qualitatively resemble the spectra of the $[Tl_2Cl_9]^{3-}$ ion [13a] which also has this structure. A vibrational assignment has been proposed for $Cs_3[Tl_2Cl_9]$ based on single-crystal Raman studies,[13a] and the partial assignments given in Table 5 are made by analogy with this. All four terminal stretching modes of both $[Ti_2Cl_9]^-$ and $[Ti_2Br_9]^-$ were observed, of which three are Raman active (a_1', e', and e'') and two i.r. active (a_2'' and e'), and the assignment follows straightforwardly from a comparison of the Raman and i.r. spectra. Of the four bridge-stretching modes (a_1', a_2'', e', and e''), however, only two were observed for each salt and the assignment of these is thus less certain. The possibility that the Raman band of $[Ti_2Br_9]^-$ at 192 cm^{-1}, which is one of the frequencies assigned to bridge stretching, is ν_1 of $[TiBr_6]^{2-}$ ions present as an impurity is ruled out by the absence of ν_3 of $[TiBr_6]^{2-}$ (243 cm^{-1}) [14] from the i.r. spectrum of the same sample.

The highest frequencies of both $[Ti_2Br_9]^-$ (320—280 cm^{-1}) and of $[Ti_2Br_{10}]^{2-}$ (310—270 cm^{-1}) at first seem very high for terminal metal–bromine stretching modes, which normally lie in the range 180—240 cm^{-1} for octahedrally co-ordinated metal atoms. This, however, presumably reflects the fact that all the terminal modes of $[Ti_2Br_9]^-$ and $[Ti_2Br_{10}]^{2-}$ involve considerable motion of the relatively light titanium atoms. Thus similar high frequencies are observed for the asymmetric stretching modes ν_5 of $[TiBr_5]^-$ (341 cm^{-1}) and ν_3 of $[TiBr_6]^{2-}$ (243 cm^{-1}) [14] which also involve motions of the titanium atoms, whereas the symmetric stretching frequencies ν_1 of these ions are much lower (209 and 190 cm^{-1}, respectively). For the corresponding chloro-species the masses of the titanium and chlorine atoms are more closely similar and the symmetric and asymmetric stretching frequencies are thus closer together: $[Ti_2Cl_9]^-$ (420—380); $[Ti_2Cl_{10}]^{2-}$ (390—340); $[TiCl_5]^-$ [348 (ν_1) and 411 (ν_5)]; and $[TiCl_6]^{2-}$ [320 (ν_1) and 316 (ν_3) cm^{-1}].[14]

EXPERIMENTAL

Tetraethylammonium and tetraphenylarsonium chloride were dehydrated by treating with thionyl chloride and removing volatiles *in vacuo*. Tetrapropyl- and tetrabutylammonium halides and $[Et_4N]Br$ were rendered anhydrous by standing their solutions in dichloromethane over calcium hydride. Dichloromethane was purified by treating with titanium(IV) chloride, fractionally distilling under dry nitrogen, and standing over calcium hydride.

All preparations and manipulations of halogenotitanate salts were carried out in a dry-bag flushed with dry nitrogen. Exposure to moist air or use of unpurified dichloromethane solvent resulted in products showing spurious spectral bands. The complexes $[Cl_4P]_2[Ti_2Cl_{10}]$, $[Et_4N]_2[Ti_2Cl_{10}]$, and $[Et_4N][Ti_2Cl_9]$ were prepared as described previously.[3,12] Contamination of $[Et_4N]_2[Ti_2Cl_{10}]$ with $[Et_4N][Ti_2Cl_9]$ or $[Et_4N]_2[TiCl_6]$ was avoided by using a slight excess of $TiCl_4$ in the preparation; $[Et_4N][Ti_2Cl_9]$ which was then present in the product was removed from the less soluble $[Et_4N]_2[Ti_2Cl_{10}]$ by washing with 5% nitromethane in dichloromethane. Analogous procedures using anhydrous tetrapropylammonium chloride in dichloromethane solution yielded precipitates of $[Pr_4N][Ti_2Cl_9]$ and $[Pr_4N]_2[Ti_2Cl_{10}]$. Similarly, slow addition of a dry solution of $[Et_4N]Br$ to 2 mol equiv. of $TiBr_4$ in dichloromethane yielded dark red $[Et_4N][Ti_2Br_9]$; [16] using equimolar amounts, a black precipitate of *tetraethylammonium μ-dibromo-octabromodititanate* was obtained (Found: Br, 68.95. $C_{16}H_{40}Br_{10}NTi_2$ requires Br, 69.15%).

Tetrabutylammonium pentachlorotitanate was prepared by mixing equimolar amounts of $[Bu_4N]Cl$ and $TiCl_4$ in dichloromethane solution and precipitating the product by addition of several volumes of sodium-dried light petroleum. In order to ensure equimolar amounts before precipitation it was found convenient to monitor the Raman spectrum of the dichloromethane solution and to add reagents until only solute bands due to $[TiCl_5]^-$ were observed (Found: Cl, 37.9. $C_{16}H_{36}Cl_5NTi$ requires Cl, 37.75%). *Tetraphenylarsonium pentachlorotitanate* was similarly prepared from $[Ph_4As]Cl$ and $TiCl_4$ in dichloromethane solutions. Using $[Bu_4N]Br$ and $TiBr_4$ a similar procedure yielded dark red *tetrabutylammonium pentabromotitanate* (Found: Br, 57.95. $C_{16}H_{36}Br_5NTi$ requires Br, 57.9%).

Spectral Measurements.—Raman spectra were recorded with a Coderg PH1 spectrometer with a 150 mW He–Ne laser. I.r. spectra above 200 cm^{-1} were measured with a Perkin-Elmer 225 spectrophotometer and from 400 to 40 cm^{-1} with a Beckman-R.I.I.C. FS720 interferometric spectrometer. The solid samples were examined as petroleum-jelly mulls prepared in a nitrogen-flushed dry-bag, and the caesium iodide plates used to support the mulls for measurements above 200 cm^{-1} were protected from contact with the mulls by thin films of Polythene.

We thank the S.R.C. for the award of a research studentship (to C. S. C.).

[4/2725 *Received*, 30*th December*, 1974]