Mono- and Bi-nuclear Anionic Derivatives of Methyltitanium Trichloride and Methyltitanium Tribromide and Related Complexes

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Treatment of methyltitanium trichloride or methyltitanium tribromide with tetra-alkylammonium halides in dichloromethane at 0 °C yields three different series of complex salts depending on the mole ratios of the reactants. They are: type A, $R[Me_2Ti_2X_7]$ or $R[Me_2Ti_2X_6Y]$; type B, $[R]_2[Me_2Ti_2X_8]$ or $[R]_2[Me_2Ti_2X_6Y_2]$; type C, $[R]_2[MeTiX_5]$ or $[R]_2[MeTiX_3Y_2]$, where X, Y = Cl or Br. The complexes are deeply coloured solids, very sensitive to air and moisture; although they are much more stable thermally than methyltitanium trichloride or methyltitanium tribromide themselves, they are nevertheless only stable for short periods at room temperature. On the basis of i.r. spectral studies and other considerations, the type A complexes are believed to contain, in the solid state, anions of the $Ti_2Cl_9^-$ type (*i.e.* two octahedra with a shared face), the type B complexes anions of the $Ti_2Cl_{10}^{2-}$ type (*i.e.* two octahedra with a shared edge), and the type C complexes mononuclear octahedral anions. The structures of the complexes in solution are discussed with reference to temperature-range n.m.r. studies. The TiC stretching frequencies in the complex anions occur in the range 461—504 cm^{-1}, and the titanium–methyl group n.m.r. resonances in the range τ 7·28—7·60 (dichloromethane solutions). This resonance occurs at τ 7·09 for methyltitanium trichloride and τ 7·45 for methyltitanium tribromide (dichloromethane solutions). The new complex $Et_4N[Ti_2Br_9]$ is reported. Brief reports of both oxygen and sulphur dioxide insertions into titanium–carbon bonds are included. The structure of methyltitanium trichloride in the solid state is discussed.

IT is generally found that complexes of the early transition metals which involve the metal–carbon σ-bond are rather labile and this fact is considered to be closely associated with the ability of alkyltitanium compounds to act as Ziegler–Natta catalysts for the polymerisation of α-olefins.[1-5] Although there is a very large literature relating to such catalyst mixtures (often titanium halides with aluminium alkyls), it is only recently that attention has been directed to the isolation and characterisation of definite complexes incorporating the titanium–carbon σ-bond. Key studies by Thiele and co-workers have shown that both methyltitanium tri-

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[1] P. Cossee, *Rec. Trav. chim.*, 1966, **85**, 1151.

[2] W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533.

[3] P. S. Braterman and R. J. Cross, *J.C.S. Dalton*, 1972, 657.

[4] M. R. Collier, M. F. Lappert, and M. M. Truelock, *J. Organometallic Chem.*, 1970, **25**, C36.

[5] C. Beerman and H. Bestian, *Angew. Chem.*, 1959, **71**, 618.

chloride [6] and tetramethyltitanium [7,8] act as Lewis acids, even if somewhat less effectively than titanium tetrachloride. The thermal stabilities of the five-co-ordinate 1 : 1 complexes of tetramethyltitanium with monodentate ligands are lower than those of the six-co-ordinate 1 : 2 complexes, which in turn are lower than those of six-co-ordinate 1 : 1 complexes with bidentate ligands; for each type of complex, the thermal stability depends on the nature (presumably the electronegativity) of the donor atom(s) of the ligand(s) in the manner $O <$ N (aliphatic) $<$ P (aliphatic) $<$ N (aromatic). Clark and McAlees have characterised a series of complexes of methyltitanium trichloride with both symmetrical [9] and unsymmetrical [10] bidentate ligands with the conclusions that the complexes (a) are six-co-ordinate monomers, (b) have a thermal stability order (in respect of the donor atoms of the ligands) of $O < N < S < P \sim As$, (c) all possess the meridional configuration at low temperatures, and (d) have stereochemistries such that the more electronegative donor atom of an unsymmetrical bidentate ligand preferentially co-ordinates *trans* to the methyl group. Amplification of this work is expected to lead to a more detailed understanding of the mechanism of the Ziegler–Natta polymerisation process, in particular in respect of the optimum nature and disposition of the ligands attached to the Me–Ti moiety.

Other studies involving the titanium(IV)–carbon σ-bond have led to the characterisation of complexes of methyltitanium trichloride with monodentate ligands,[11,12] of tris(dialkylamino)titanium alkyls,[13,14] of titanium complexes of the type $(\pi\text{-}C_5H_5)_2Ti(R)Cl$,[15] of dimethyltitanium 2-methyl-2,4-pentanediolate $(CH_3)_2Ti(C_6H_{12}O_2)$,[16] of dibenzyltitanium diethoxide and its derivatives,[17] dimethyldiphenyltitanium, methyltribenzyltitanium and its 2,2′-bipyridyl derivative,[18] tetrabenzyltitanium,[18-22] and of alkoxymethyltitanium halides.[23] These compounds are invariably more stable thermally than tetramethyltitanium or methyltitanium halides, and it is generally believed [2] that the main reason for this is that the additional ligands block the co-ordination sites necessary for the decomposition reactions to take place. Recently, a series of kinetically stable complexes of the early transition metals with the trimethylsilylmethyl group have been prepared [2] in which the common method for the destruction of metal–carbon bonds, that of alkene elimination, is not possible.

In the present work, methyltitanium trichloride and methyltitanium tribromide have been treated with tetraethylammonium halides (and in one case with tetraphenylarsonium chloride) in order to gain further information about the titanium–carbon σ-bond and to assess the influence of ionic lattice stabilisation thereon. The system proved to be more complicated than expected, and three different series of anions were isolated from the reaction mixtures. Two of these proved to be binuclear anions, based on the faced-shared $Ti_2Cl_9^-$ ion and on the edge-shared $Ti_2Cl_{10}^{2-}$ ion, and the third series was based on the more obvious mononuclear dinegative ion of the $TiCl_6^{2-}$ type. A brief report of the properties of the chloro-anions has appeared.[24] Studies of both oxygen and sulphur dioxide insertion into the titanium–methyl bond are also reported.

EXPERIMENTAL

Starting Materials.—Hexane and dichloromethane were dried by their being refluxed over lithium aluminium hydride under nitrogen and degassed by alternate freezing and melting *in vacuo.* Hexane was distilled from a potassium mirror and dichloromethane distilled from lithium aluminium hydride under nitrogen prior to use. The methyltitanium trihalides were prepared according to the methods of de Vries [25] and Thiele [26] in the manner described previously,[9] and stored as concentrated hydrocarbon solutions (in *ca.* 6 mmol quantities) in sealed vacuum ampoules at −78° in the absence of light.

Tetraethylammonium halides (B.D.H. Ltd.) were dried by being heated (at *ca.* 100°) *in vacuo* for 3 h. The solids were dissolved in dichloromethane (*ca.* 1 mol l^{-1} of solvent) and the resultant solutions refluxed with freshly powdered calcium hydride and degassed. The supernatant solution above the calcium hydride was removed for use by syringe. Similar procedures were used for tetraphenylarsonium chloride and tetrabutylammonium chloride.

Preparation of the Complexes.—The apparatus used is shown in Figure 1. A rubber tubing connection to a combined vacuum/nitrogen line was used to maintain a positive pressure of purified nitrogen in the apparatus during the addition of the reagents by syringe, and during the subsequent reactions. Filtration of the products was facilitated by tilting the apparatus and applying a slight vacuum *via* taps 2 or 3 as appropriate.

The ampoule containing the methyltitanium trihalide and occluded hydrocarbon solvent was attached to the apparatus by a rubber tubing connection as shown. The

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[7] K.-H. Thiele and J. Müller, *Z. anorg. Chem.*, 1968, **362**, 113.

[8] J. Müller and K.-H. Thiele, *Z. anorg. Chem.*, 1968, **362**, 120.

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[14] H. Bürger and H.-J. Neese, *J. Organometallic Chem.*, 1970, **21**, 381.

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[16] H. Sugahara and Y. Shuto, *J. Organometallic Chem.*, 1970, **24**, 709.

[17] K.-H. Thiele and W. Schäfer, *Z. anorg. Chem.*, 1970, **379**, 63.

[18] P. Zdunneck and K.-H. Thiele, *J. Organometallic Chem.*, 1970, **22**, 659.

[19] K. S. Boustany, K. Bernauer, and A. Jacot-Guillarmond, *Helv. Chim. Acta*, 1967, **50**, 1305.

[20] U. Giannini and U. Zucchini, *Chem. Comm.*, 1968, **16**, 940; U. Zucchini, E. Abizatti, and U. Giannini, *J. Organometallic Chem.*, 1971, **26**, 357.

[21] G. R. Davies, J. A. J. Jarvis, and B. T. Kilbourn, *Chem. Comm.*, 1971, 1511.

[22] D. G. H. Ballard and P. W. van Lienden, *Makromol. Chem.*, 1972, **154**, 177.

[23] K. Clauss, *Ann. Chem.*, 1968, **711**, 19.

[24] R. J. H. Clark and M. Coles, *Chem. Comm.*, 1971, 1587.

[25] H. de Vries, *Rec. Trav. chim.*, 1961, **80**, 866.

[26] K.-H. Thiele, P. Zdunneck, and D. Boumgant, *Z. anorg. Chem.*, 1970, **378**, 62.

scored ampoule was broken open inside the tubing connection and the concentrated methyltitanium trihalide solution (*ca.* 6 mmol), produced on warming the ampoule to *ca.* −20°, was filtered under slight vacuum into the cooled flask A. Traces of insoluble decomposition products were removed at the frit. Dichloromethane (20 ml) was syringed into flask A *via* the serum cap and tap 1 and the resultant solution was then filtered into the cooled flask B. The tetraethylammonium halide solution (2·5 mmol for the type A complexes, 6 mmol for the type B complexes, and 12 mmol for the type C complexes) was then syringed into flask A in the manner described above. The apparatus was tilted and the tetraethylammonium halide solution was allowed to filter slowly under gravity (taps 2 and 3 connected to nitrogen) into the cooled (*ca.* −10°), magnetically stirred, methyltitanium trihalide solution. Any suspended calcium hydride transferred with the tetraethylammonium halide solution was removed at the frit. The reaction was instantaneous, a dark violet suspension and solution (2 : 1, type A complex) was produced initially, changing to a dark red solution and a red or brown precipitate as the 1 : 1 mole ratio of reactants was approached (type B complex). Addition of further tetraethylammonium halide solution beyond the 1 : 1 mole ratio resulted in the precipitation of the blue or black 1 : 2, type C complexes from the dark red solution. The yields of products were maximised by cooling to −78° (2 : 1 and 1 : 1 complexes); the suspensions were back-filtered at the frit and the solids collected thereon. The complexes were washed with hexane (20 ml) which had been syringed into flask B *via* the serum cap and tap 4; the hexane was removed at the frit by filtration. The complexes were dried by evacuation *via* tap 3 for 2 h, the filtrate in flask A being frozen by immersion in a liquid-nitrogen bath. By admitting a fast flow of nitrogen to the evacuated apparatus *via* tap 2 the solid product was transferred from the frit to flask B. This flask was then disconnected from the apparatus under a fast flow of nitrogen and quickly attached to a product manifold. Flask B was then immediately evacuated *via* tap 4, the serum cap having been replaced by a connection to the vacuum line. The product was dried *in vacuo* for a further hour before being sealed in the manifold.

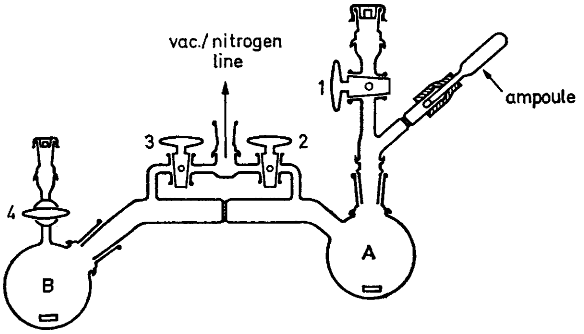

FIGURE 1 Apparatus used for the preparation of the complexes

The addition of dichloromethane solutions of tetraphenylarsonium chloride (2 mmol) and tetrabutylammonium chloride (2 mmol) to methyltitanium trichloride (5 mmol) in dichloromethane at −20° produced dark violet solutions. The complex $[Ph_4As][Me_2Ti_2Cl_7]$ was precipitated from the solution after addition of hexane, cooling and partial vacuum evaporation of solvent. Similar procedures failed to produce any solid material from the tetrabutylammonium chloride experiment and the invariably produced dark violet gum was not characterised.

The new enneabromide, $Et_4N[Ti_2Br_9]$, was prepared by similar methods, care being taken to ensure that the ratio tetraethylammonium : titanium did not exceed 1 : 4. Thus tetraethylammonium bromide in dichloromethane was added slowly to a well stirred solution of titanium tetrabromide in dichloromethane. The dark red-brown complex, which is slightly redder than the complex $[Et_4N]_2[TiBr_6]$, precipitated after a few seconds.

Insertion Reactions.—The complex $[Et_4N][Me_2Ti_2Cl_7]$ was found to insert oxygen into the titanium–carbon bonds to form the corresponding methoxo-derivative, $[Et_4N][(MeO)_2Ti_2Cl_7]$. The insertion reaction was carried out in dichloromethane solution in the manner described previously.[9,27] It is believed that the other complexes behave similarly, but the matter was not investigated quantitatively.

Sulphur dioxide was also found to insert into titanium–carbon bonds. This reaction was first investigated with the parent methyltitanium trihalides as follows. Dry hexane (20 ml) was added to methyltitanium trichloride (*ca.* 4 mmol) with stirring and cooling to −78°. Dry sulphur dioxide was then condensed into this solution for 90 min with the result that a brown solid precipitated. The latter turned yellow on being allowed to warm to room temperature. It was then filtered off, washed with hexane and dried *in vacuo* for *ca.* 2 h. The solid is insoluble in liquid sulphur dioxide, hexane, dichloromethane, benzene, and tetrachloroethylene, and is instantly hydrolysed by water to give a white precipitate. The analytical figures for this compound were a little variable, and suggested the formation of a mixture of the compounds $(MeSO_2)TiCl_3$ and $(MeSO_2)_2TiCl_2$, m.p. 107—109° (Found: C, 8·2; H, 2·0; Cl, 38·1; Ti, 19·4. $CH_3Cl_3O_2STi$ requires C, 5·1; H, 1·3; Cl, 45·6; Ti, 20·5. $C_2H_6Cl_2O_4S_2Ti$ requires C, 8·7; H, 2·2; Cl, 25·6; Ti, 17·3%).

On carrying out the same process with methyltitanium tribromide (*ca.* 4 mmol) a brown precipitate was formed initially, which, on being allowed to warm to room temperature, changed to an orange-red powder. This compound was dried as described above, and had closely similar properties to the above chloro-compound. The analytical figures on the compound were consistent with the formulation $(MeSO_2)_2TiBr_2$, m.p. 70—71° (Found: C, 6·3; H, 1·5; Br, 42·7; Ti, 13·6. $C_2H_6Br_2O_4S_2Ti$ requires C, 6·6; H, 1·6; Br, 43·6; Ti, 13·1%).

Sulphur dioxide was also found to insert into the titanium–carbon bond of other methyltitanium compounds, *e.g.* $MeTiCl_3(MeOCH_2\cdot)_2$ and $MeTiCl_3(MeSCH_2\cdot)_2$, but in no case could the products be characterised. This type of reaction was therefore not pursued further.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed in this Department. Titanium was analysed gravimetrically as titanium dioxide. Weighed samples of the complexes were hydrolysed with aqueous acetone, dried at 70° and finally ignited at 850°. Halogens were estimated potentiometrically with silver nitrate solution. Samples of the complexes were hydrolysed with aqueous acetone *in vacuo* and warmed with potassium hydroxide before acidification and titration. The analytical data on the complexes are included in Table 1. The compounds proved to be very difficult to analyse on account of their thermal instability.

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[27] R. J. H. Clark and A. J. McAlees, *J.C.S. Dalton*, 1972, 640.

Spectra.—The i.r. spectra of the complexes were recorded on a Perkin-Elmer 225 spectrometer, the samples being prepared in a nitrogen-filled dry box and placed between caesium iodide plates.

Attempts were made to record the Raman spectrum of methyltitanium trichloride using a Spex 1401 spectrometer equipped with Ar^+ and Kr^+ laser sources. However, the compound proved to be insufficiently stable to any laser line even at −196° for the satisfactory recording of its Raman spectrum.

N.m.r. spectra of the complexes were recorded on dichloromethane solutions in sealed tubes using a Varian associates HA100 instrument. The samples (*ca.* 20 g l^{-1}) were made up in an apparatus and by a procedure described previously (Figure 4 of ref. 9). The τ values are given with reference to that of the solvent, dichloromethane (τ 4·67).

TABLE 1

Analytical data and other properties of the anionic derivatives of methyltitanium trichloride and methyltitanium tribromide

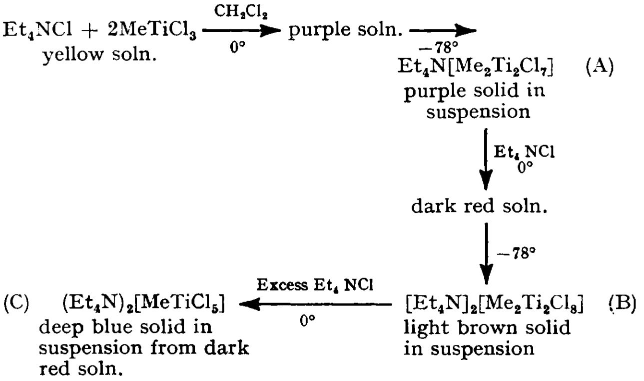
<table>
<tr><th rowspan="2">Formua</th><th rowspan="2">Colour</th><th rowspan="2">Chemical [a] shift τ 27°</th><th colspan="6">Found (%)</th><th colspan="6">Calculated for (%)</th></tr>
<tr><th>C</th><th>H</th><th>N</th><th>Ti</th><th>Cl</th><th>Br</th><th>C</th><th>H</th><th>N</th><th>Ti</th><th>Cl</th><th>Br</th></tr>
<tr><td>$Et_4N[Me_2Ti_2Cl_7]$</td><td>Dark violet</td><td>7·31</td><td>23·0</td><td>5·1</td><td>2·3</td><td>18·9</td><td>48·1</td><td></td><td>23·8</td><td>5·2</td><td>2·8</td><td>19·0</td><td>49·2</td><td></td></tr>
<tr><td>$Ph_4As[Me_2Ti_2Cl_7]$</td><td>Dark violet</td><td>7·34</td><td></td><td></td><td></td><td></td><td>32·4</td><td></td><td></td><td></td><td></td><td></td><td>32·8</td><td></td></tr>
<tr><td>$Et_4N[Me_2Ti_2Cl_6Br]$</td><td>Dark violet</td><td>7·28</td><td>21·8</td><td>4·9</td><td>2·3</td><td>18·4</td><td colspan="2">55·6</td><td>21·9</td><td>4·8</td><td>2·6</td><td>17·5</td><td colspan="2">53·3</td></tr>
<tr><td>$Et_4N[Me_2Ti_2ClBr_6]$</td><td>Dark violet-brown</td><td>7·51</td><td>14·9</td><td>3·3</td><td>1·7</td><td>11·9</td><td colspan="2">62·2</td><td>15·6</td><td>3·4</td><td>1·8</td><td>12·4</td><td colspan="2">66·8</td></tr>
<tr><td>$Et_4N[Me_2Ti_2Br_7]$</td><td>Dark violet-brown</td><td>7·52</td><td>14·1</td><td>3·1</td><td>1·4</td><td>11·5</td><td></td><td>67·0</td><td>14·7</td><td>3·2</td><td>1·7</td><td>11·7</td><td></td><td>68·6</td></tr>
<tr><td>$Et_4N[Ti_2Br_9]$</td><td>Red-brown</td><td></td><td>10·2</td><td>2·2</td><td>1·4</td><td>10·3</td><td></td><td>75·9</td><td>10·2</td><td>2·1</td><td>1·5</td><td>10·1</td><td></td><td>76·1</td></tr>
<tr><td>$[Et_4N]_2[Me_2Ti_2Cl_8]$</td><td>Light brown</td><td>7·56</td><td>30·6</td><td>7·3</td><td>3·9</td><td>13·2</td><td>41·4</td><td></td><td>32·2</td><td>6·9</td><td>4·2</td><td>14·3</td><td>42·3</td><td></td></tr>
<tr><td>$[Et_4N]_2[Me_2Ti_2Cl_6Br_2]$</td><td>Orange-brown</td><td>7·57</td><td>28·6</td><td>6·0</td><td>3·6</td><td>13·1</td><td colspan="2">50·0</td><td>28·5</td><td>6·1</td><td>3·7</td><td>12·6</td><td colspan="2">49·1</td></tr>
<tr><td>$[Et_4N]_2[Me_2Ti_2Cl_2Br_6]$</td><td>Yellow-brown</td><td>7·59</td><td>22·4</td><td>4·7</td><td>2·8</td><td>10·1</td><td colspan="2">61·5</td><td>23·1</td><td>4·9</td><td>3·0</td><td>10·2</td><td colspan="2"></td></tr>
<tr><td>$[Et_4N]_2[Me_2Ti_2Br_8]$</td><td>Dark red</td><td>7·60</td><td>21·2</td><td>4·5</td><td>3·4</td><td>9·2</td><td></td><td>61·6</td><td>21·1</td><td>4·5</td><td>2·7</td><td>9·3</td><td></td><td>62·3</td></tr>
<tr><td>$[Et_4N]_2[MeTiCl_5]$</td><td>Dark blue</td><td>Insol.</td><td>39·6</td><td>8·3</td><td>5·3</td><td>9·5</td><td>35·4</td><td></td><td>40·8</td><td>8·7</td><td>5·6</td><td>9·6</td><td>35·4</td><td></td></tr>
<tr><td>$[Et_4N]_2[MeTiCl_3Br_2]$</td><td>Black</td><td>Insol.</td><td>35·3</td><td>7·5</td><td>4·8</td><td>8·0</td><td>18·6</td><td>27·7</td><td>34·6</td><td>7·5</td><td>4·7</td><td>8·1</td><td>18·0</td><td>27·1</td></tr>
<tr><td>$[Et_4N]_2[MeTiCl_2Br_3]$</td><td>Black</td><td>Insol.</td><td>29·7</td><td>6·2</td><td>4·0</td><td>7·3</td><td colspan="2">44·5</td><td>32·2</td><td>6·8</td><td>4·4</td><td>7·6</td><td colspan="2">49·0</td></tr>
<tr><td>$[Et_4N]_2[MeTiBr_5]$</td><td>Black</td><td>Insol.</td><td>28·0</td><td>5·8</td><td>3·8</td><td>6·2</td><td></td><td>55·1</td><td>28·2</td><td>6·0</td><td>3·9</td><td>6·6</td><td></td><td>55·3</td></tr>
</table>

[a] Chemical shifts (CH_3–Ti) are calculated assuming the dichloromethane solvent resonates at τ 4·67. The τ-values of methyltitanium trichloride and methyltitanium tribromide in dichloromethane are 7·09 and 7·45 respectively. The τ-value of methyltitanium trichloride in C_2Cl_4 and in benzene solutions has recently been reported to be 7·22 and 7·80 respectively. J. F. Hanlan and J. D. McCowan, *Canad. J. Chem.*, 1972, **50**, 747.

Diffuse reflectance spectra in the visible and u.v. were recorded on a Cary 14 spectrometer. The samples, diluted with magnesium oxide, were enclosed in a silica faced airtight holder.

RESULTS AND DISCUSSION

The anionic derivatives of methyltitanium trichloride have been prepared according to the following typical reaction scheme:



Three types of anionic derivative can be formed:

Type (A) $[R][Me_2Ti_2X_7]$ and $[R][Me_2Ti_2X_6Y]$;
Type (B) $[R]_2[Me_2Ti_2X_8]$ and $[R]_2[Me_2Ti_2X_6Y_2]$;
Type (C) $[R]_2[MeTiX_5]$ and $[R]_2[MeTiX_3Y_2]$,

where X,Y = Cl or Br and R is usually Et_4N.

Some properties of the complexes are summarised in Tables 1 and 2. Type A complexes are dark violet, have proton chemical shifts of τ 7·30 ± 0·02 (X = Cl, Y = Br) and τ 7·51 ± 0·01 (X = Br, Y = Cl) and titanium–carbon stretching frequencies, ν(TiC), of 487 ± 1 cm^{-1} (X = Cl, Y = Br) and 473 ± 1 cm^{-1} (X = Br, Y = Cl). Type B complexes are brown or red, have a chemical shift of τ 7·58 ± 0·02, and ν(TiC) of 500 ± 4 cm^{-1}, while type C complexes are dark blue-black, are insoluble in dichloromethane, and have ν(TiC) of 465 ± 4 cm^{-1}. The complexes, although thermally more stable than the parent methyltitanium trihalides, are only stable for short periods at room temperature and are rapidly decomposed on exposure to the atmosphere. The complexes can be stored at −30° in the absence of light but decomposition, as evidenced by the presence of titanium(III), is detectable after *ca.* 1 month. A notable exception is the dark blue type C complex $[Et_4N]_2[MeTiCl_5]$, which, although it is extremely moisture-sensitive, is indefinitely stable *in vacuo* at room temperature and is unaffected by dry oxygen. It is perhaps significant that this salt would have higher lattice energy than any other type A, B, or C salt. The complexes derived from methyltitanium tribromide are more sensitive than those from methyltitanium trichloride to both temperature and the atmosphere.

The type A and type B complexes appear to have similar solubilities in dichloromethane and the course of the reactions to form types A, B, and C complexes, on the addition of a tetraethylammonium halide solution to a methyltitanium trihalide solution, is detectable visually. The insoluble type C complexes were precipitated from the dark red solution of the type B complex as soon as the 1 : 1 mole ratio of reactants was exceeded.

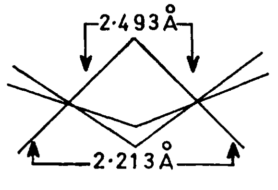
TABLE 2

Infrared spectra of the complexes (510—220 cm^{-1}) and the band assignments

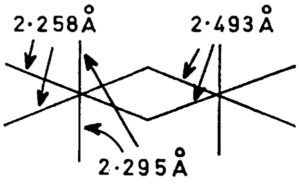
Complex	ν(TiC)	$\nu(\mathrm{TiCl})_{\mathrm{ter}}$	$\nu(\mathrm{TiCl})_{\mathrm{br}}$	$\nu(\mathrm{Ti\,Br})_{\mathrm{r}}$
Type A complexes, $Ti_2Cl_9^-$ ion type				
$[PCl_4][Ti_2Cl_9]$ [a]		412vs,br 379s	279m 230m	
$[Et_4N][Ti_2Cl_9]$ [b]		419vs,br 378s	267m 229w	
$[Et_4N][Me_2Ti_2Cl_7]$	487ms	406s 379vs	260s	
$[Et_4N][Me_2Ti_2Cl_6Br]$	486ms	408s 378vs	261m	320wm
$[Et_4N][Me_2Ti_2ClBr_6]$	472ms	384m		318vs 291vs 280vs
$[Et_4N][Me_2Ti_2Br_7]$	474ms			319vs 296vs 281vs
$[Et_4N][Ti_2Br_9]$				325vs 278vs
$[Et_4N][(MeO)_2Ti_2Cl_7]$ [c]		402vs,br 368vs,br	284s 269m	
Type B complexes, $Ti_2Cl_{10}^{2-}$ ion type				
$[PCl_4]_2[Ti_2Cl_{10}]$ [d]		373vs, 354s 315wm		
$[Et_4N]_2[Me_2Ti_2Cl_8]$	504s	363vs,br 328vs,br		
$[Et_4N]_2[Me_2Ti_2Cl_6Br_2]$	501s	364vs,br 336s,sh		298ms 255w
$[Et_4N]_2[Me_2Ti_2Cl_2Br_6]$	497s	351vs		291vs,br 240w
$[Et_4N]_2[Me_2Ti_2Br_8]$ [e]	499s			293vs,br 265m,sh
Type C complexes, TiX_6^{2-} ion type				
$[Et_4N]_2[TiCl_6]$ [f]		316vs,br		
$[Et_4N]_2[MeTiCl_5]$ [g]	469m	308vs,br		
$[Et_4N]_2[MeTiCl_3Br_2]$	463m	320vs,br		245wm
$[Et_4N]_2[MeTiCl_2Br_3]$	461m	310vs,br		245vs,br
$[Et_4N]_2[MeTiBr_5]$ [h]	462m			250vs
$[Et_4N]_2[TiBr_6]$ [f]				243vs

[a] The PCl_4^+ cation gives rise to absorption bands at *ca.* 650vs and 248m cm^{-1} which are attributed to the $\nu_3(t_2)$ and $\nu_4(t_2)$ fundamentals respectively. The tetraethylammonium cation, however, gives rise only to very weak bands in this region. [b] This salt was first characterised by J. A. Creighton and J. H. S. Green, *J. Chem. Soc.* (*A*), 1968, 808. [c] The MeOTi groups give rise to the following characteristic absorption bands: ν(CO), 1092vs,br; ν(TiO), 624vs and 612vs cm^{-1}. [d] See footnote *a*; the ν_3 and ν_4 fundamentals of the cation occur at *ca.* 645vs and 247wm cm^{-1} respectively. [e] Weak unassigned bands occur at 350 and 212 cm^{-1}. [f] Refs. 34 and 35. [g] A weak band at 230 cm^{-1} was not assigned. [h] A weak-medium band occurs in the i.r. spectrum of this compound at 315 cm^{-1}. While this observation would naturally suggest the presence of chloride impurity in the salt, careful analyses indicated the complete absence of chloride. The band possibly arises from the methyl group rocking mode, but this could not be proven.

Structures and Infrared Spectra of the Complexes.— The structures of the anions in the complexes of types A and B are considered to be basically the same as those of the anions $Ti_2Cl_9^-$ and $Ti_2Cl_{10}^{2-}$, as recently determined[28] for the salts $[PCl_4][Ti_2Cl_9]$ and $[PCl_4]_2[Ti_2Cl_{10}]$, *viz.*,



A



B

The average titanium–chlorine (bridging) bond length in the $Ti_2Cl_9^-$ ion is identical with that in the $Ti_2Cl_{10}^{2-}$ ion, and closely similar to that in other titanium(IV) complexes involving chlorine bridges[29] *e.g.* $[TiCl_4,POCl_3]_2$ and $[TiCl_4,MeCOOEt]_2$. The terminal TiCl bond lengths are 0·28 Å shorter for A and 0·20 Å shorter for B than the bridging ones, which is also typical for bridged octahedral complexes of titanium(IV).

The basis for the assignment of structure of the $[Me_2Ti_2Cl_7]^-$ and $[Me_2Ti_2Cl_6Br]^-$ ions is the close similarity between the terminal titanium–chlorine stretching frequencies, $\nu(\mathrm{TiCl})_{\mathrm{ter}}$, for these ions (407 ± 1 and 378 ± 1 cm^{-1}) and those for two salts of the $Ti_2Cl_9^-$ ion (415 ± 4 and 378 ± 1 cm^{-1}) *cf.* Table 2. The titanium–chlorine bridge stretching frequencies of the $[Me_2Ti_2Cl_7]^-$ and $[Me_2Ti_2Cl_6Br]^-$ ions are also closely similar to those

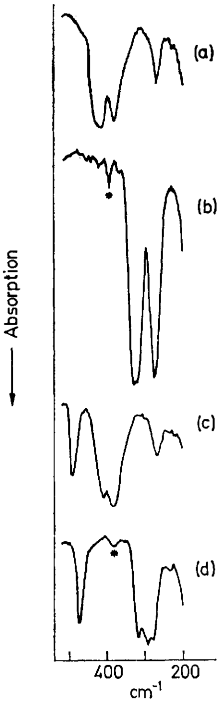


FIGURE 2 Infrared spectrum (500—220 cm^{-1}) of the tetraethylammonium salts of (a), $Ti_2Cl_9^-$; (b), $Ti_2Br_9^-$; (c), $[Me_2Ti_2Cl_7]^-$; and (d), $[Me_2Ti_2Br_7]^-$ ions (the asterisk indicates cation absorption)

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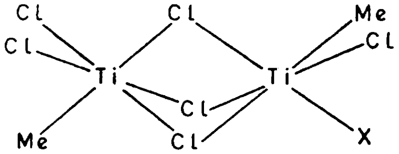
[28] T. J. Kistenmacher and G. J. Stucky, *Inorg. Chem.*, 1971, **10**, 122.

[29] R. J. H. Clark, 'The Chemistry of Titanium and Vanadium, Elsevier, Amsterdam, 1968.

of the $Ti_2Cl_9^-$ ion, occurring in the range 228—279 cm^{-1}. Similar assignments have been made previously[30] for the structurally similar $Tl_2Cl_9^{3-}$ ion, for which $\nu(TlCl)_{ter}$ occur at 279—265 cm^{-1} and $\nu(TlCl)_{br}$ occur at 222—180 cm^{-1}. The terminal and bridging TlCl stretching frequencies of the $Tl_2Cl_9^{3-}$ ion are nearer one another than is the case for the corresponding TiCl stretching frequencies of the $Ti_2Cl_9^-$ ion, and presumably this is associated with the fact that the terminal and bridging TlCl bond lengths of the $Tl_2Cl_9^{3-}$ ion differ[31] by only 0·12 Å, whereas the terminal and bridging TiCl bond lengths of the $Ti_2Cl_9^-$ ion differ[28] by 0·28 Å. The i.r. spectra of this and related ions are given in Figure 2.

The TiBr stretching frequency of the $[Me_2Ti_2Cl_6Br]^-$ ion occurs at the relatively high value of 320 cm^{-1} which is consistent only with the bromine atom occupying a terminal position; accordingly the chlorine atoms must be in bridging positions.

The appearance of only a single i.r.-active band in the Ti–C stretching region of the spectra of the $[Me_2Ti_2Cl_7]^-$ and $[Me_2Ti_2Cl_6Br]^-$ ions suggests that the two methyl groups in each case are not strongly coupled and hence that they are associated with different titanium atoms (as indeed would be expected on the basis of the methods of preparation of the anions). The structures of the anions are thus considered to be:



(X = Cl or Br)

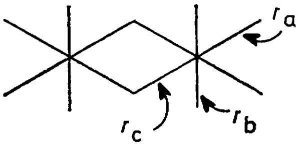
The existence of the stereochemical isomers possible for each of the above ions could not be detected in the solid state, although an exchange between isomers in solution is indicated by the n.m.r. data.

Similar arguments are applicable to the $[Me_2Ti_2Br_7]^-$ and $[Me_2Ti_2ClBr_6]^-$ ions. From the high value found for the TiCl stretching frequency of the latter ion (384 cm^{-1}) it is inferred that the chlorine atom occupies a terminal position. The reference compound, $Et_4N[Ti_2Br_9]$, which has apparently not previously been reported, has terminal TiBr stretching frequencies of 325 and 278 cm^{-1} (a_2'' and e'') and, consistent with this, the TiBr stretching frequencies of the other bromine-containing ions also occur in this region (318 ± 1, 293 ± 3 and 280 ± 1 cm^{-1}). The ratio $\nu(TiBr):\nu(TiCl)$ for corresponding vibrations of the $Ti_2X_9^-$ ions is *ca.* 0·75, similar to that found for many other systems.[32]

The key type B ion, the $Ti_2Cl_{10}^{2-}$ ion, is very similar structurally to the neutral halide Nb_2Cl_{10}. A comparison of pertinent structural and vibrational data on these two species is drawn in Table 3. For both species, $r_a < r_b \ll r_c$, and the associated MCl stretching frequencies are similar, but lower for the titanium(IV) species than for the niobium(V) species on account of the oxidation state change.[32]

TABLE 3

Comparison of *X*-ray data (Å) and i.r. data (cm^{-1}) on M_2Cl_{10} species



	r_a	r_b	r_c
$Ti_2Cl_{10}^{2-}$ [a]	2·258	2·295	2·493
Nb_2Cl_{10} [b]	2·250	2·302	2·555
	$\nu(MCl)_{ter}$	$\nu(MCl)_{ter}$	$\nu(MCl)_{br}$
$Ti_2Cl_{10}^{2-}$ [c]	373vs 354s	315m	<220
Nb_2Cl_{10} [d]	412sh 400s	359s	254m,br 226m

[a] T. J. Kistenmacher and G. J. Stucky, *Inorg. Chem.*, 1971, **10**, 122. [b] A. Zalkin and D. E. Sands, *Acta Cryst.*, 1958, **11**, 615. [c] This work. [d] I. R. Beattie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc.* (*A*), 1968, 2765.

The basis for the structural assignment for the $[Me_2Ti_2Cl_8]^{2-}$ and $[Me_2Ti_2Cl_6Br_2]^{2-}$ ions is the similarity between the terminal TiCl stretching frequencies of these ions (328—363 cm^{-1}) and the corresponding ones for the $Ti_2Cl_{10}^{2-}$ ion (354—373 cm^{-1}); the methyltitanium species have slightly lower frequencies because replacement of chlorine by a (less electronegative) methyl group results in a lowering of the effective positive charge on the titanium atom, *cf.* similar results for methyltin compounds.[33] The loss of the 315 cm^{-1} band of the $Ti_2Cl_{10}^{2-}$ ion (attributed in Table 3 to a terminal TiCl stretching frequency of the 'vertical' TiCl bonds, *i.e.* those associated with the bond length r_b) from the spectra of the methyltitanium anions, suggests that it is in the r_b positions that the two methyl groups become attached. The TiCl bridge stretching frequencies for these ions lie below 220 cm^{-1}. The highest terminal TiBr stretching frequencies occur at *ca.* 290 cm^{-1}, and a weaker one occurs at *ca.* 250 cm^{-1}.

The appearance of only a single band in the i.r. spectra of type B compounds attributable to a TiC stretching frequency is taken to imply, in agreement with the conclusion above, that the methyl groups are attached to different titanium atoms and probably *anti* to one another. The *ca.* 15 cm^{-1} upward shift in the TiC stretching frequency of these ions from its value in the type A ions (a shift in the reverse direction from that found for the terminal TiCl stretching frequencies) suggests that in type B anions, the methyl group is *trans* to a terminal chlorine atom (whereas it *must* be

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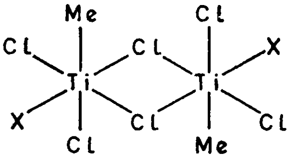
[30] I. R. Beattie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc.* (*A*), 1968, 2765.

[31] J. L. Hoard and L. Goldstein, *J. Chem. Phys.*, 1935, **3**, 199.

[32] R. J. H. Clark, *Spectrochim. Acta*, 1965, **21**, 955.

[33] R. J. H. Clark, A. G. Davies, and R. J. Puddephatt, *J. Chem. Soc.* (*A*), 1968, 1828.

trans to a bridging one in type A anions). Thus the structures proposed for these ions are:



(X = Cl or Br)

The type B complexes derived from methyltitanium tribromide have similar structures. From the high value (351 cm^{-1}) for the TiCl stretching frequency of the $[Me_2Ti_2Cl_2Br_6]^{2-}$ ion it is concluded that the chlorine atoms are terminal. The mixed halogeno-anions are not mixtures of the parent $[Me_2Ti_2X_8]^{2-}$ ions as evidenced by their i.r. spectra, and by the fact that they may be recrystallised unchanged from dichloromethane.

The type C anions are considered to be mononuclear on the basis that the TiCl and TiBr stretching frequencies of these anions are nearly identical with those of the mononuclear TiX_6^{2-} and $TiX_4Y_2^{2-}$ (X, Y = Cl or Br) anions [34,35] (Table 2). The broadness of the peaks in the TiCl and TiBr stretching frequency regions of the mixed halogeno-anions does not permit precise stereochemical conclusions to be drawn relating to the relative co-ordination positions of the chlorine and bromine atoms.

It is worth noting the empirical relationship (Figure 3) between the highest i.r.-active TiCl stretching frequency and the shortest TiCl bond length within a titanium(IV) compound. This smooth relationship lends credence to the procedure adopted herein of inferring the structure of the complex anions from their highest i.r.-active TiCl or TiBr stretching frequency. The large downward shift of this frequency in the order type A > type B > type C is clearly to be related to the stepwise increase in formal negative change carried by each titanium atom *viz.*, 1/2, 1 and 2 respectively.

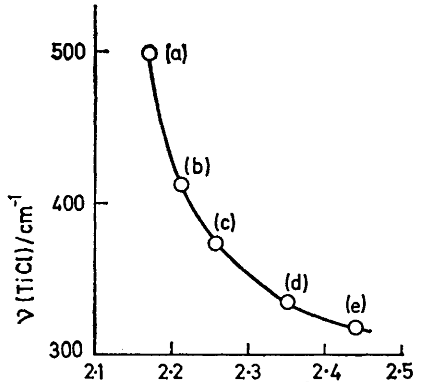


FIGURE 3 Relationship between the shortest TiCl bond length in a titanium(IV) compound and the highest i.r.-active TiCl stretching frequency. Data taken from refs. 28 and 29; (a), $TiCl_4$; (b), $[PCl_4][Ti_2Cl_9]$; (c), $[PCl_4]_2[Ti_2Cl_{10}]$; (d), Cs_2TiCl_6; (e) $TiCl_4,2(C_{10}H_{16}As_2)$

Diffuse Reflectance Spectra.—The diffuse reflectance spectra of the binuclear anions all display medium absorption at *ca.* 18,000 cm^{-1} (Figure 4) which may be assigned (by analogy with the similar assignment made for the 25,000 cm^{-1} band of methyltitanium trichloride) [36] to an $n \longrightarrow \sigma^*$ transition *i.e.* to a transition from the highest non-bonding chlorine π-molecular orbital to the σ* orbital antibonding between the carbon and the titanium atom. Consistent with this, the corresponding $Ti_2Cl_9^-$ and $Ti_2Cl_{10}^{2-}$ ions do not show these low frequency electronic transitions. In the blue, both types of ion display strong absorption which shifts to the red as bromine replaces chlorine in the ion. Such bands are attributable to the invariably very halogen-sensitive $n \longrightarrow \pi^*$ transitions such as have been reported, for example, for certain salts of the TiX_6^{2-} ions.[37,38]

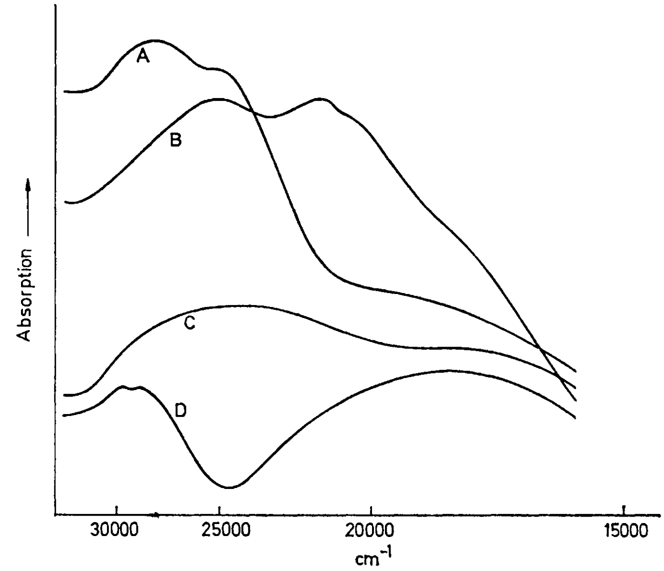


FIGURE 4 Diffuse reflectance spectra of the tetraethylammonium salts of (a), $[Me_2Ti_2Cl_8]^{2-}$; (b), $[Me_2Ti_2Br_8]^{2-}$; (c), $[Me_2Ti_2Br_7]^-$; (d), $[Me_2Ti_2Cl_7]^-$ ions

The diffuse reflectance spectra of the complexes $[Et_4N]_2[MeTiX_5]$, X = Cl or Br, likewise contain a medium band at *ca.* 17,000 cm^{-1} which is assigned to the $n \longrightarrow \sigma^*$ transition (Table 4). This band is most clearly seen in the spectrum of the $[MeTiCl_5]^{2-}$ ion, and it has no counterpart in the spectrum of the $TiCl_6^{2-}$ ion (Figure 5). The $n \longrightarrow \pi^*$ transitions, which occur in virtually the same positions in the $[MeTiX_5]^{2-}$ and the TiX_6^{2-} ions, move *ca.* 7300 cm^{-1} on changing from X = Cl to X = Br.

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

[35] R. J. H. Clark, L. Maresca, and R. J. Puddephatt, *Inorg. Chem.*, 1968, **7**, 1603.

[36] C. Dijkgraaf and J. P. G. Rousseau, *Spectrochim. Acta*, 1969, **25A**, 1455.

[37] B. J. Brisdon, T. E. Lester, and R. A. Walton, *Spectrochim. Acta*, 1967, **23A**, 1969.

[38] J. L. Ryan, *Inorg. Chem.*, 1969, **8**, 2058.

Other Physical Measurements.—Although the complexes gave the appearance of being crystalline, very few lines were found in their powder photographs. Accordingly we were unable to establish whether the complexes within each group were isomorphous.

The extremely low thermal stability of the complexes in suitable solvents precluded any conductance measurements.

N.m.r. Studies.—The chemical shifts (τ) of the methyl protons (Me–Ti) of the types A and B complexes, together with those of the parent methyltitanium trihalides, are given in Table 1. The tetraethylammonium cation resonated at *ca.* τ 6·8 and *ca.* τ 8·6, well removed from the region associated with the Me–Ti resonance.

TABLE 4

Lowest frequency charge transfer bands of relevant mononuclear species (cm^{-1}) (DR = diffuse reflectance measurement)

Compound	Solvent	$n \longrightarrow \sigma^*$	$n \longrightarrow \pi^*$		
$MeTiCl_3$ [a]	n-hexane	25,000w,sh	43,000vs		
$TiCl_4$ [b]	C_6H_{12}		34,840s		*ca.* 42,500s
$TiBr_4$ [b]	C_6H_{12}		27,100s,sh	28,700s	34,900vs
$[Et_4N]_2[MeTiCl_5]$ [c]	DR	17,000m	25,000sh	28,800s	
$[Et_4N]_2[TiCl_6]$ [c]	DR		25,000sh	28,550vs	33,100vs
$[Et_4N]_2[MeTiBr_5]$ [c]	DR	17,750m		21,550vs	25,150vs
$[Et_4N]_2[TiBr_6]$ [c]	DR		17,750sh	21,400vs	25,700vs

[a] Ref. 36. R. J. H. Clark and C. J. Willis, *Inorg. Chem.*, 1971, **10**, 1118. [c] This work.

The proposed stoicheiometry was supported by signal integration.

The chemical shift of the Me–Ti protons provides an indication of the relative electron density at the titanium centre. Thus the chemical shift of the methyl protons in methyltitanium tribromide (τ 7·45) is greater than that in methyltitanium trichloride (τ 7·09) as a consequence of the lower electronegativity of bromine than of chlorine. A similar correlation between methyl proton chemical shifts and halogen electronegativities has been observed for the π-cyclopentadienyl (cp) compounds $cp_2Ti(Me)X$, X = Cl, Br, or I.[39] The cyclopentadienyl protons, on the other hand, are successively deshielded in the order Cl < Br < I and this is postulated as being due to the overriding effect on the ring protons of $p\pi$–$d\pi$ back-bonding from the halogen to the titanium atom.

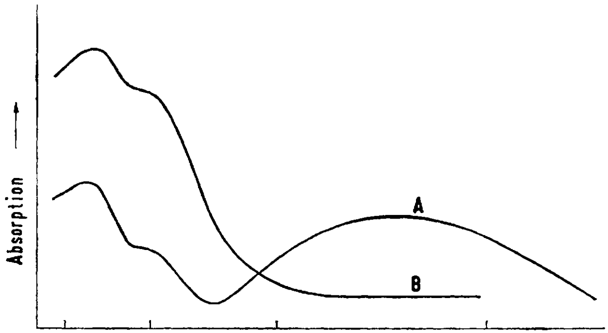

FIGURE 5 Diffuse reflectance spectra of the tetraethylammonium salts of (a), $[MeTiCl_5]^{2-}$; and (b), $TiCl_6^{2-}$ ions

The types A and B anions have higher chemical shifts than the parent methyltitanium trihalides partly owing to the increase from four to six in the co-ordination number of the metal atom. A similar effect has been noted for the six-co-ordinate neutral complexes of methyltitanium trichloride.[9,10] An increase in chemical shift is to be expected and is found on increasing the anionic change from that in the type A complexes to that in the type B complexes. The type C complexes could not be investigated owing to their insolubility in appropriate solvents. Bromine-containing species have, as expected on electronegativity grounds (*vide supra*), higher chemical shifts than analogous chlorine-containing species. However, the similar chemical shifts of the $[Me_2Ti_2Cl_8]^{2-}$ and $[Me_2Ti_2Br_8]^{2-}$ ions (difference 0·04 τ) contrasts with the large difference (0·36 τ) between the chemical shifts of the parent methyltitanium trihalides. This situation is brought about by the negative charge carried by the type B anions, which results (possibly owing to the more effective $p_\pi \longrightarrow d_\pi$ back-bonding in the charged anions, which will be greater from chlorine than from bromine) in a similar charge density at the titanium atom in both the $[Me_2Ti_2Cl_8]^{2-}$ and the $[Me_2Ti_2Br_8]^{2-}$ions. The behaviour of the type A ions, $[Me_2Ti_2Cl_7]^-$ and $[Me_2Ti_2Br_7]^-$ is intermediate in all respects.

To investigate the possibility that the observed n.m.r. signals, as a result of intermolecular exchange, were an average of those of dissociated species produced on solution of the complexes, an equimolar solution of the ions $[Me_2Ti_2Cl_6Br]^-$ and $[Me_2Ti_2Cl_6Br_2]^{2-}$ was studied. The solution exhibited the signals due to the individual ions only at −90°. At 27°, only one sharp signal was observed, the chemical shift of which was equal to the average of the chemical shifts of the constituent ions. The coalescence temperature was −82°. These results indicate that an intermolecular exchange process was taking place which was fast on the n.m.r. time scale at room temperature. Variable temperature n.m.r. studies provided no evidence of similar intermolecular exchange in solutions of solely the type B anions. The low temperature spectra of these complexes were remarkable only for the maintenance of the extremely sharp Me–Ti signal which showed little variation in chemical shift (0·05 p.p.m.) with temperature even to −100°. The spectrum of a dilute solution of the $[Me_2Ti_2Br_8]^{2-}$ ion

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[39] H. C. Beachell and S. A. Butter, *Inorg. Chem.*, 1965, **4**, 1133.

exhibited a weak signal at τ 7·37, which is attributable to a decomposition product. Identical weak signals were observed in some samples of the $[Me_2Ti_2Cl_2Br_6]^{2-}$, $[Me_2Ti_2Br_7]^-$, and $[Me_2Ti_2ClBr_6]^-$ ions, the intensities and chemical shifts of which were independent of temperature. The lack of evidence for exchange between species produced in solutions of the type B ions suggests that the possible dissociation

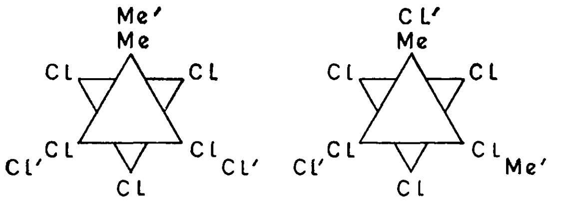
$$[Me_2Ti_2Cl_8]^{2-} \rightleftharpoons 2[MeTiCl_4]^-$$

is not taking place to any significant extent, and thus that the ions retain their binuclear structure in solution.

It is noteworthy that for both the chloride and the bromide complexes the average of the chemical shifts of the type B anion and of the parent methyltitanium trihalide corresponds to that of the appropriate type A anion. One possible explanation of this observation is that type A anions dissociate as follows in solution,

$$2[Me_2Ti_2X_7]^- \rightleftharpoons [Me_2Ti_2X_8]^{2-} + 2MeTiX_3$$

and that exchange between the species produced is fast on the n.m.r. time scale. To investigate this possibility, we studied the temperature range n.m.r. spectra of the type A anions. In each case, a broadening of the methyl group proton signal was observed at *ca.* −70°, which in the $[Me_2Ti_2Cl_7]^-$ and $[Me_2Ti_2Cl_6Br]^-$ ions was resolved at lower temperatures into two signals. These resolved signals were separated, however, by only 0·05 p.p.m. at −100° as against the 0·36 p.p.m. separation expected if the species $[Me_2Ti_2Cl_8]^{2-}$ and $MeTiCl_3$ had been produced. Thus we do not consider that such an equilibrium is set up in solution. It seems more likely that the exchange process which is being frozen out in the case of type A ions is an intramolecular one, which involves exchange between different stereochemical isomers. There are two of these for the $[Me_2Ti_2Cl_7]^-$ ion, one in which the two methyl groups are *cis* (*i.e. trans* to the same bridging chlorine atom) and the other in which they are *gauche* (*i.e. trans* to different bridging chlorine atoms):



The broadening of the signals of the type A anions at low temperature therefore probably represents the slowing of an intramolecular exchange between the *cis* and *gauche* isomers.* A further pair of isomers is possible for the mixed type A anions, $[Me_2Ti_2X_6Y]^-$. If the halide Y occupies a terminal site of the binuclear anion, as was indicated by the solid state i.r. spectra, the methyl groups bound to each titanium atom will be non-equivalent. However, the difference between the chemical shifts of such methyl groups would be small and unlikely to result in a detectable splitting of an averaged signal on slowing the exchange by lowering the temperature.

On the basis of the n.m.r. studies it is considered that types A and B anions maintain their binuclear structures in dichloromethane solution, and this conclusion is supported by the observation that the tetraethylammonium salts of the $[Me_2Ti_2Cl_7]^-$, $[Me_2Ti_2Br_7]^-$, $[Me_2Ti_2Cl_8]^{2-}$, and $[Me_2Ti_2Br_8]^{2-}$ ions may be recrystallised unchanged from this solvent (i.r. evidence).

Insertion Reactions.—The complex $[Et_4N][Me_2Ti_2Cl_7]$ in dichloromethane solution is found to react rapidly with molecular oxygen with the result that an oxygen atom is inserted into each titanium–carbon bond. The resulting yellow methoxo-compound, $(Et_4N)[(MeO)_2Ti_2Cl_7]$ has an i.r. spectrum which is closely similar to that of the starting material although with the loss of the band attributable to ν(TiC) and the gain of peaks at 1092 and *ca.* 620 cm^{-1} attributable to ν(CO) and ν(TiO) respectively *cf.* Table 2. This appears to be a general reaction of methyltitanium compounds.[9,10,27] but the corresponding reactions of the other complexes reported herein were not investigated in detail.

A similar investigation of sulphur dioxide insertion reactions was made in the first instance on methyltitanium trichloride and methyltitanium tribromide. In the case of the trichloride the final yellow product appeared to be a mixture of $(MeSO_2)TiCl_3$ and $(MeSO_2)_2TiCl_2$, a product which is apparently analogous to the reported product of its reaction with molecular oxygen,[5] *viz.* $(MeO)TiCl_3{\cdot}(MeO)_2TiCl_2$. However, sulphur dioxide reacts with methyltitanium tribromide to form the single product, the orange-red solid $(MeSO_2)_2TiBr_2$. The titanium–halogen stretching frequencies in these metal sulphinates, ν(TiCl) 390 cm^{-1}, ν(TiBr) 320 cm^{-1}, indicate that the metal atom is six-co-ordinate. The SO stretching frequencies give rise to strong, broad bands at 875 and 945 cm^{-1} (chloride), and at 870 and 955 cm^{-1} (bromide).

The insertion of sulphur dioxide into titanium–methyl bonds has recently been reported elsewhere [40] in the case of the π-cyclopentadienyl compound $(\pi\text{-}C_5H_5)_2TiMe_2$, which yields on this treatment the sulphinate $(\pi\text{-}C_5H_5)_2Ti(O_2SMe)_2$. Unfortunately the insolubility of the present compounds precluded molecular weight and n.m.r. studies, and thus monomeric as well as oxygen-bridged polymeric structures are possible.

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* It is possible that the intermolecular exchange processes envisaged above may proceed at a rate faster than that observed to occur between the six-co-ordinate anions $[Me_2Ti_2Cl_6Br]^-$ and $[Me_2Ti_2Cl_6Br_2]^{2-}$. The view that exchange processes are much faster in four-co-ordinate than six-co-ordinate compounds is supported by the observation that mixtures of methyltitanium trichloride and methyltitanium tribromide display only a single methyl group proton signal at a τ-value which is the (mole-fraction) weighted average of the τ-values of the parent compounds. This is true down to −100°, so that even at this low temperature, methyl group exchange is fast on the n.m.r. time scale. The argument for assigning the splitting of signals due to the type A complexes at low temperature to an intramolecular exchange process remains valid unless it is proposed that an intermolecular exchange process between species could proceed at a rate faster than an intramolecular exchange process in the individual species.

[40] P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometallic Chem.*, 1971, **33**, 181.

Comments on the Structure of Methyltitanium Trichloride and Methyltitanium Tribromide.—It is a matter of some interest that methyltitanium trichloride and methyltitanium tribromide change colour from nearly black in the solid state to yellow in non-polar solvents. It is not known whether the colour change is associated with a structural change in the molecule. In this connection it is worth noting that the m.p.s of the methyltitanium halides (in so far as they are known) are closely similar to those of the methyltin halides (Figure 6). In the series $Me_{4-n}SnI_n$, the m.p. increases uniformly with increase in n in a behaviour typical of molecular solids as their polarisabilities increase. On the other hand, the m.p.s of the corresponding chlorides, $Me_{4-n}SnCl_n$, go through a maximum as n changes from zero to four. This behaviour of the m.p.s is associated with a change from molecular solids ($n = 0$ or 4) to a chlorine-bridged polymer ($n = 2$),[41] and this structural change undoubtedly takes place on account of the much bigger dipole moment of the methyltin chlorides than the methyltin iodides. Unfortunately, the structure of methyltin trichloride has not yet been elucidated, but from its m.p. it would appear to be weakly associated. The very close similarity between the m.p.s of the corresponding tin and titanium compounds suggests that methyltitanium trichloride may be found to be isostructural with methyltin trichloride.

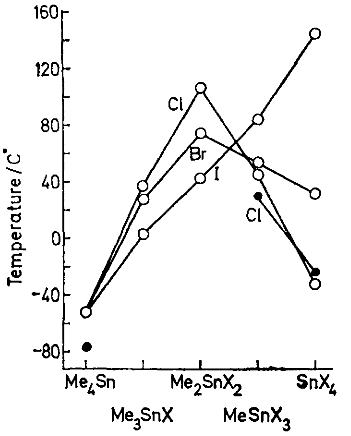

FIGURE 6 Melting points of the methyltin and methyltitanium halides; ○, tin compounds; ● titanium compounds

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[41] A. G. Davies, H. J. Milledge, D. C. Puxley, and P. J. Smith, *J. Chem. Soc.* (*A*), 1970, 2862.