Binuclear Anionic Derivatives of Methyltitanium Trichloride

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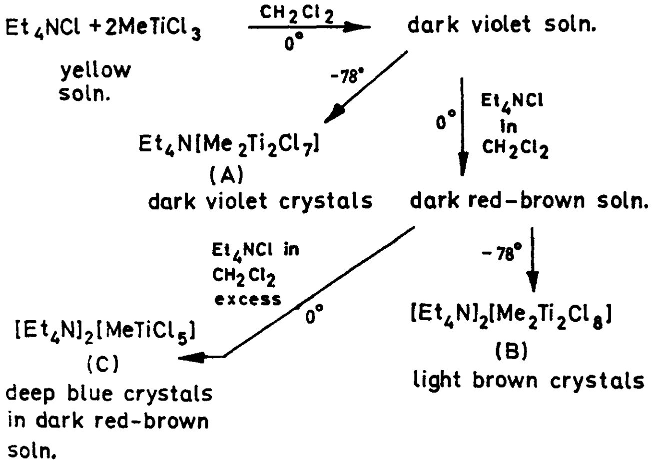
Summary Treatment of methyltitanium trichloride with tetraethylammonium chloride or tetraethylammonium bromide yields three series of anions (depending on the mole ratios used), two of which are binuclear.

METHYLTITANIUM TRICHLORIDE is known to form adducts with both monodentate[1] and bidentate ligands[2,3] in which the titanium atom has a co-ordination number of six. In view of the role of alkyltitanium compounds in the Ziegler–Natta polymerisation of olefins, the mechanism for which may involve ionic species,[4] it seemed important to attempt to isolate and study specific alkyltitanium compounds in which the alkyltitanium moiety is part of an ionic lattice. To this end we have treated methyltitanium trichloride with tetraethylammonium chloride and with tetraethylammonium bromide in dichloromethane at 0° and, depending on the mole ratios of the reactants, isolated three different types of complex salt. The reaction Scheme is given below for the case of tetraethylammonium chloride as precipitant.

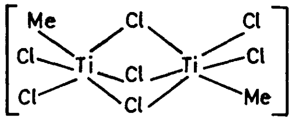


SCHEME

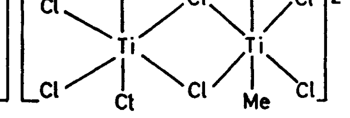
Tetraethylammonium bromide reacts similarly with methyltitanium trichloride to give the salts $Et_4N[Me_2Ti_2Cl_6Br]$, $(Et_4N)_2[Me_2Ti_2Cl_6Br_2]$, and $(Et_4N)_2[MeTiCl_3Br_2]$. Despite the thermal, hydrolytic, and oxidative instability of these compounds, they have all been isolated and characterised satisfactorily by carbon, hydrogen, nitrogen, halogen, and titanium analyses.

Type A complexes are dark violet, have a chemical shift of τ 7·31 $\pm$ 0·03 in dichloromethane and a TiC stretching frequency of 487 $\pm$ 3 cm^{-1}, type B complexes are brown, have a chemical shift of τ 7·57 and a TiC stretching frequency of 502 $\pm$ 2 cm^{-1} while type C complexes are dark blue-black, are insoluble in dichloromethane and have aTiC stretching frequency of 466 $\pm$ 1 cm^{-1}. All the compounds are more stable thermally than methyltitanium trichloride itself.

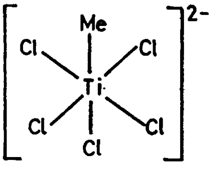
Detailed i.r. and other studies of these complexes lead to the conclusions that type A complexes contain anions of the $[Ti_2Cl_9]^-$ type (*i.e.* two octahedra with a shared face), type B complexes contain anions of the $[Ti_2Cl_{10}]^{2-}$ type (*i.e.* two octahedra with a shared edge), and type C complexes contain the mononuclear octahedral anions.



(A)



(B)



(C)

The main basis for the structural assignment for the type A complexes lies in the very close similarity between the terminal TiCl stretching frequencies of these complexes and those of the complex $[PCl_4][Ti_2Cl_9]$, which is known from *X*-ray diffraction work[5] to contain a binuclear anion of type A. Similarly, the terminal TiCl stretching frequencies of type B complexes are similar to those of the complex $[PCl_4]_2[Ti_2Cl_{10}]$, which is known to contain a binuclear edged-shared anion,[5] while the titanium–halogen stretching frequencies of the type C complexes closely resemble those

TABLE

I.r. spectra of the anions in the metal–halogen stretching frequency region

Type A Complexes

Assignment	$Et_4N[Me_2Ti_2Cl_7]$	$Et_4N[Me_2Ti_2Cl_6Br]$	$PCl_4[Ti_2Cl_9]$	$Et_4N[Ti_2Cl_9]$[a]
$\nu(TiCl)_{ter}$	407 s 376 vs	408 s 378 vs	412 vs, br 379 s	419 vs, br 378 s
$\nu(TiBr)_{ter}$	260 s	320 wm	279 m	267 m
$\nu(TiCl)_{br}$	228 m	261 m	230 m	229 w?

Type B Complexes

Assignment	$[Et_4N]_2[Me_2Ti_2Cl_8]$	$[Et_4N]_2[Me_2Ti_2Cl_6Br_2]$	$[PCl_4]_2[Ti_2Cl_{10}]$
$\nu(TiCl)_{ter}$	363 vs, br 328 vs, br	364 vs, br 336 s, sh	373 vs 354 s, 315 m
$\nu(TiBr)_{ter}$	*ca.* 240 w, br	298 ms	
$\nu(TiCl)_{br}$		255 w	

Type C Complexes

Assignment	$[Et_4N]_2[MeTiCl_5]$	$[Et_4N]_2[MeTiCl_3Br_2]$	$[Et_4N]_2[TiCl_6]$[b]	$[Et_4N]_2[TiBr_6]$[b]
$\nu(TiCl)_{ter}$	308 vs, br	320 vs, br	316 vs, br	
$\nu(TiBr)_{ter}$		245 wm		243 s

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

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

of the $[Et_4N]_2[TiCl_6]$ and $[Et_4N]_2[TiBr_6]$ ions, which are known to contain mononuclear anions. For complexes of types A and B, apart from the probability that the methyl groups are attached to different titanium atoms, the relative positions of these groups have not been established for certain.

The role of the solvent (ϵ 9·08) in permitting the isolation of these three series of anions is under further investigation. The salts themselves represent the first characterised ionic derivatives of an alkyltitanium species.

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[1] G. A. Razuvaev and L. M. Bobinova, *Doklady Akad. Nauk S.S.S.R.*, 1963, **152**, 1363.
[2] K.-H. Thiele and K. Jacob, *Z. anorg. Chem.*, 1968, **356**, 195.
[3] R. J. H. Clark and A. J. McAlees, *J. Chem. Soc. (A)*, 1970, 2026; *Inorg. Chem.*, 1971, **10**, in the press.
[4] C. E. H. Bawn and A. Ledwith, *Quart. Rev.*, 1962, **16**, 361.
[5] T. J. Kistenmacher and G. J. Stucky, *Inorg. Chem.*, 1971, **10**, 122.