

Hexahalogenotitanates(III)

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ALTHOUGH the $[\text{TiCl}_6]^{3-}$ anion is believed to be formed by tervalent titanium in fused chloride melts, its simple salts have not been isolated. We have prepared the pyridinium salt as an orange solid by two routes:—(1) The direct reaction of titanium(III) chloride with an excess of anhydrous pyridinium chloride, followed by removal of the excess with chloroform at room temperature, and (2) The reaction of pyridinium chloride with tris-(acetonitrile)trichlorotitanium(III) in chloroform-acetonitrile. The use of tetraethylammonium

chloride and bromide in the second method, gave not the expected hexahalogeno-salts but $(\text{Et}_4\text{N})\text{[TiCl}_4(\text{MeCN})_2]$ and $(\text{Et}_4\text{N})\text{[TiCl}_3\text{Br}(\text{MeCN})_2]$ respectively, and under the same conditions tris-(acetonitrile)tribromotitanium(III) and tetraethyl ammonium bromide gave $(\text{Et}_4\text{N})\text{[TiBr}_4(\text{MeCN})_2]$. $(\text{C}_5\text{H}_5\text{N})_3\text{[TiCl}_4\text{Br}_2]$ was prepared by the reaction of tripyridinotribromotitanium(III) with liquid anhydrous hydrogen chloride.

In the case of $(\text{C}_5\text{H}_5\text{N})_3\text{[TiCl}_6]$, X-ray powder photography showed the absence of pyridinium

chloride and indicated an orthorhombic unit cell of dimensions: $a = 16.0$, $b = 16.8$, $c = 20.8$ Å. The compound had the expected infrared spectrum (650—3500 cm^{-1}) for a pyridinium cation,² and a magnetic moment at room temperature of 1.66 B.M.

The diffuse reflectance spectra (*cf.* table) in every case showed a single peak with a distinct shoulder, corresponding to the ${}^2T_{2g} \rightarrow {}^2E_g$ transition. These peaks fit into the previously reported³ ligand-field order, since replacement of chloride by bromide and acetonitrile gave respectively red and blue shifts.

TABLE
Diffuse reflectance spectra

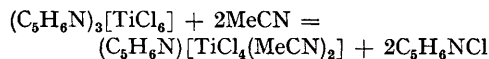
Compound	Peaks (cm^{-1})	
$(\text{C}_5\text{H}_6\text{N})_3[\text{TiCl}_6]$	10,990 sh	12,740
$(\text{C}_5\text{H}_6\text{N})_3[\text{TiCl}_4\text{Br}_2]$	10,260 sh	12,350
$(\text{Et}_4\text{N})[\text{TiCl}_4(\text{MeCN})_2]$	14,290 sh	15,040
$(\text{Et}_4\text{N})[\text{TiBr}_4(\text{MeCN})_2]$	12,740	14,810 sh.

¹ D. M. Gruen and R. L. McBeth, "VIIth International Conference on Co-ordination Chemistry," Stockholm, 1962 Butterworths, p. 27.

² P. H. C. Mitchell, *J. Inorg. Nuclear Chem.*, 1961, **21**, 392.

³ G. W. A. Fowles, R. A. Hoodless, and R. A. Walton, *J. Chem. Soc.*, 1963, 5873.

Conductivity studies could not be made to confirm the proposed number of ions since the compounds were oxidised by such solvents as nitrobenzene. In acetonitrile, pyridinium hexachlorotitanate(III) dissolved to give a green solution with a spectrum almost identical with the diffuse reflectance spectrum of $(\text{Et}_4\text{N})[\text{TiCl}_4(\text{MeCN})_2]$, although the original salt was recovered unchanged on evaporation of the solvent. It is therefore considered that in such a solution there is a reversible dissociation:—



Salts of the analogous vanadium(III) and chromium(III) anions $[\text{MCl}_6]_3^-$ have also been prepared.

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