

Complexes of Bivalent Titanium

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THE only complex compound of titanium(II) previously reported appears to be $\text{TiCl}_2 \cdot 2\text{C}_3\text{H}_7\text{NO}$.¹ We have now found that the methyl cyanide adducts of titanium(II) chloride and bromide ($\text{TiX}_2 \cdot 2\text{CH}_3\text{CN}$) can be prepared quite readily by direct reaction of the halides with excess of methyl cyanide. Furthermore, the methyl cyanide may be readily replaced by a number of other ligands, and in this way the following compounds have been prepared: $\text{TiCl}_2 \cdot 2\text{L}$ ($\text{L} = \text{C}_4\text{H}_8\text{O}$, $\text{C}_5\text{H}_{10}\text{O}$, py, $\frac{1}{2}$ bipyr, and $\frac{1}{2}$ phen), and $\text{TiBr}_2 \cdot \text{bipyr}$. The compounds are very dark brown in colour, apart from the bipyridyl and phenanthroline complexes

which are dark blue. They are readily oxidised by air, and with water liberate hydrogen with the formation of pale yellow solutions.

The stoichiometry of the complexes has been established firmly by elemental analyses, but information on their molecular complexity is hindered by their lack of solubility in solvents with which they do not react. The methyl cyanide and pyridine complexes are sufficiently soluble in the anhydrous parent ligands to give solutions that are virtually non-conducting at approximately 10^{-3}M strength ($\Lambda_{\text{M}} < 10 \text{ ohm}^{-1}\text{cm}^2$ in all cases). The magnetic moments of all the compounds at room

temperature fall in the range 0.99—1.21 B.M., and thus agree with the value of 1.17 B.M. previously reported for $\text{TiCl}_2 \cdot 2\text{C}_3\text{H}_7\text{NO}$. These values are well below the spin-only value, and in accord with polymeric structures (probably six-co-ordinate and related to those of the dihalides themselves).

As the compounds are easily oxidised, spectra measurements, especially of far infrared, are very difficult. Each of the chloride complexes showed a band between 300 and 320 cm^{-1} that may be attributed to a Ti-Cl stretching mode, since titanium(II) chloride itself shows a weak band around 290 cm^{-1} . The spectra of the bromide complexes are less reliable but show broad bands around 280 cm^{-1} .

Visible spectra have been measured on the solids and on solutions in the parent ligands and while these spectra are generally disappointing because of rising absorptions above 10,000 cm^{-1} , weak shoulders are observed. With $\text{TiCl}_2 \cdot 2\text{CH}_3\text{CN}$ in CH_3CN solution, for instance, the spectrum shows

shoulders at $\sim 9,700 \text{ cm}^{-1}$ and 14,000 cm^{-1} . These peaks may be compared to the values 7,600 cm^{-1} and 14,500 cm^{-1} reported by Oye and Gruen² for a solution containing bivalent titanium in a fused chloride melt. The considerable shift of the lower energy peak is to be expected since methyl cyanide produces a larger ligand field than chloride ion. The origin of the strong broad absorption at higher energy is unclear, but a similar effect was observed in the diffuse reflectance spectrum of TiCl_2 .³ This absorption appears to be ligand independent and presumably arises from the polymeric titanium(II) halide structures. The low energy is clearly inconsistent with the $X(\pi) \rightarrow \text{Ti}(d)$ transitions found in titanium(III) and titanium(IV) compounds.

We hope to synthesise less polymeric titanium(II) complexes and will shortly be making temperature-dependent magnetic susceptibility measurements on those complexes we have already prepared.

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¹ P. Ehrlich and W. Siebert, *Z. anorg. Chem.*, 1960, **303**, 96.

² H. A. Oye and D. Gruen, *Inorg. Chem.*, 1964, **3**, 836.

³ R. J. H. Clark, *J. Chem. Soc.*, 1964, 417.