

952. Complexes of Tervalent Titanium.

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Reaction of tribromobis(trimethylamino)titanium(III) with 1,4-dioxan, 1,4-thioxan, *N*-methylmorpholine, and methylcyanide gave compounds of the types $\text{TiBr}_3, 3\text{L}$ or $\text{TiBr}_4, 2\text{L}$, depending upon the ligand used. Reaction of the analogous chloride compound, $\text{TiCl}_3, 2\text{NMe}_3$, with 1,4-thioxan and *N*-methylmorpholine gave compounds $\text{TiCl}_3, 2\text{L}$. The spectroscopic and magnetic properties of these complexes have been investigated at room temperature and the *Dq* values for the ligands reported.

ALTHOUGH several complexes of titanium(III) chloride have been prepared and characterised recently,¹⁻³ very few complexes of titanium(III) bromide are known. Fowles and co-workers^{1,4} have prepared the adducts $\text{TiBr}_3, 3\text{L}$ for $\text{L} = \text{pyridine}$ and methyl cyanide, and the trimethylamine adduct $\text{TiBr}_3, 2\text{NMe}_3$, which can be readily prepared by the reaction of excess of the amine with titanium(IV) bromide.¹

Titanium(III) bromide is not a very convenient starting material for the preparation of bromo complexes of trivalent titanium since, although it can be prepared⁵ by reduction of titanium(IV) bromide with hydrogen, the yield is low and the product is often impure. We have accordingly investigated further the reduction of titanium(IV) bromide by trimethylamine, and found that the trivalent complex $\text{TiBr}_3, 2\text{NMe}_3$ can be obtained pure and in high yield. This compound dissolves readily in a variety of co-ordinating solvents (L) with the displacement of co-ordinated trimethylamine, and the formation of new compounds $\text{TiBr}_3, n\text{L}$. All the isolated complexes were soluble in excess of the ligand, and the spectra of these solutions have been examined.

The visible spectra of titanium(III) compounds usually show a single broad asymmetric peak, the asymmetry sometimes producing a shoulder on the main ligand-field peak. This doublet appears because titanium is not in a perfectly octahedral field; even when the ion

¹ Fowles and Hoodless, *J.*, 1963, 33.

² Clark, Lewis, Machin, and Nyholm, *J.*, 1963, 379.

³ Fowles, Hoodless, and Walton, *J.*, 1963, 5873.

⁴ Duckworth, Fowles, and Hoodless, *J.*, 1963, 5665.

⁵ Sherfey, *Inorg. Syntheses*, 1960, 6, 57.

is surrounded by six equivalent ligands there is believed to be a tetragonal distortion;⁶ in complexes such as $\text{TiBr}_3 \cdot 3\text{L}$, the departure from octahedral symmetry may be even greater. These distortions result in a splitting of the 2E_g and ${}^2T_{2g}$ terms. The two peaks are accordingly assigned to the transitions ${}^2A_{1g} \leftarrow {}^2B_{2g}$ and ${}^2B_{1g} \leftarrow {}^2B_{2g}$, so that the separation of these peaks gives a measure of the splitting of the upper 2E_g term. The distortion in the ground state (${}^2T_{2g}$) can be estimated from measurements of the magnetic susceptibility over a temperature range.²

At room temperature, the magnetic moments of our trivalent titanium complexes should be close to 1.73 B.M., since the asymmetric ligand field may result in the quenching of any orbital angular momentum.⁷ Titanium(III) chloride is antiferromagnetic,⁸ but Klemm and Krose⁹ report that there is no evidence for this type of behaviour with titanium(III) bromide. The observed magnetic moments of most complexes of titanium(III) chloride occur in the range 1.60—1.73 B.M.,¹⁻⁴ but the bromide complexes are generally found to have moments somewhat below 1.60 B.M. If the bromo complexes and their chloro analogues have the same basic symmetry (*e.g.*, C_{2v}), then the lower magnetic moments observed for the bromo compounds are unexpected, since the axial asymmetry should be greater for the bromo complexes (the ligand-field strength being $\text{L} > \text{Cl} > \text{Br}$ for the compounds examined), and low symmetry tends to produce spin-only values.¹⁰ One possible explanation for the low moments is that they are caused by a trace of titanium(IV) impurity, since the bromide complexes are oxidised far more readily than the chloride analogues. Considerable care was taken to prevent such oxidation, however, and other explanations must also be considered. It may be that, in the solid state, different distortions arise in the two series of compounds, because of different crystal packing. Alternatively, the chloro and bromo complexes may differ in their symmetries. Thus C_{3v} is just as likely as C_{2v} for any particular compound, and the low moments for the bromo complexes could be explained on the assumption that they tend more towards the C_{3v} symmetry. The spectra of the complexes show that none of the compounds have a purely C_{3v} symmetry, because the visible peak is very unsymmetrical, and with $\text{TiCl}_3 \cdot 3\text{MeCN}$ shows a distinct shoulder.

The reaction of $\text{TiBr}_3 \cdot 2\text{NMe}_3$ with excess of dioxan gave the product $\text{TiBr}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$; the analogous chloro compound was also obtained by this procedure, although the direct reaction of TiCl_3 with dioxan yields the 1 : 2 or 1 : 1 adducts, depending upon the reaction period.³ The infrared spectra of dioxan complexes may be used to determine whether one or both of the oxygen atoms are co-ordinated to the metal, since upon co-ordination the peaks at 1125 and 883 cm^{-1} (associated with the C—O—C system) disappear, and new peaks appear at lower wavenumbers.³ With the chloride complexes it was found³ that, whereas both co-ordinated and unco-ordinated oxygen atoms were present in roughly equal amounts for the 1 : 3 and 1 : 2 adducts, with the 1 : 1 compound nearly all the oxygen atoms were co-ordinated. The bromide complex $\text{TiBr}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$ has an infrared spectrum that is virtually identical with that of the chloro analogue, and it would seem that only one of the two oxygen atoms in the dioxan molecule is co-ordinated with titanium.

The diffuse reflectance spectrum of $\text{TiBr}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$ shows a peak at 14,100 cm^{-1} with a shoulder at 12,500 cm^{-1} [cf. Fig. 1(a)], but a single peak at 13,600 is observed for a solution of the complex in dioxan. These spectra are similar to those found for $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$, apart from a small shift to lower wavenumbers; this shift agrees with the view that $\text{Cl} > \text{Br}$ in ligand field strength. The chloride complex also showed a peak at $\sim 20,000 \text{ cm}^{-1}$; Clark *et al.*² have observed a peak in this region in similar systems and have tentatively assigned this to a charge-transfer transition. We believe, however, that this absorption

⁶ Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 73.

⁷ Figgis and Lewis, "Modern Co-ordination Chemistry," Interscience Publishers, 1960, p. 430.

⁸ Lewis, Machin, Newnham, and Nyholm, *J.*, 1962, 2036.

⁹ Klemm and Krose, *Z. anorg. Chem.*, 1947, **253**, 209.

¹⁰ Figgis, *Trans. Faraday Soc.*, 1961, **57**, 198.

may arise through an interaction transition $[\text{Ti(III)} \rightarrow \text{Ti(IV)}]$,⁶ as a result of a trace of Ti(IV) impurity.

Reaction of $\text{TiX}_3 \cdot 2\text{NMe}_3$ with 1,4-thioxan gave the compounds $\text{TiX}_3 \cdot 2\text{C}_4\text{H}_8\text{OS}$; the spectra of these compounds in thioxan solution (cf. Fig. 2) showed peaks at 15,000 and 14,200 cm^{-1} for the chloride and bromide, respectively, and once again the slight difference can be explained by the ligand field order $\text{Cl} > \text{Br}$. These spectra differ from the diffuse reflectance spectrum of the 1 : 1 adduct $\text{TiCl}_3 \cdot \text{C}_4\text{H}_8\text{OS}$,³ which showed a single peak at 13,500 cm^{-1} . The 1500 cm^{-1} shift observed on passing from the 1 : 1 to the 1 : 2 adduct arises because thioxan produces a stronger ligand field than the chloride ion. When the 1 : 1 adduct was prepared by refluxing titanium(III) chloride with thioxan, a soluble portion was obtained, and the spectrum of this showed a shoulder at 15,000 cm^{-1} , which suggests that some of the soluble 1 : 2 adduct was formed in the reaction.

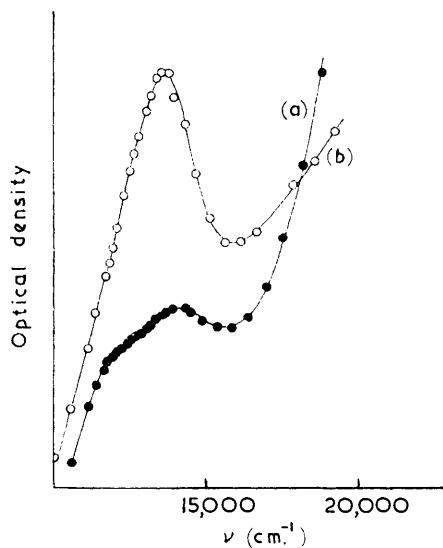


FIG. 1. (a) Reflectance spectrum of $\text{TiBr}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$; (b) Spectrum of $\text{TiBr}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$ in dioxan solution.

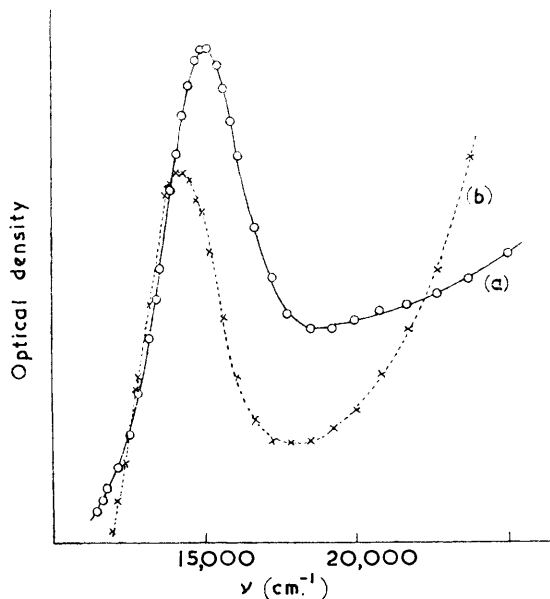


FIG. 2. (a) Spectrum of $\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{OS}$ in thioxan; (b) Spectrum of $\text{TiBr}_3 \cdot 2\text{C}_4\text{H}_8\text{OS}$ in thioxan.

The infrared spectra of the 1 : 2 thioxan adducts do not enable us to decide unambiguously whether bonding occurs through the sulphur or oxygen atoms of thioxan. A strong band was observed at 1103 cm^{-1} (asymmetric C-O-C stretch) which is the same as that found for the free ligand, and an additional strong absorption was found at 960 cm^{-1} . The presence of the former band suggests that the oxygen atom is not co-ordinated, but it is not possible to obtain positive evidence for co-ordination through sulphur, since the C-S-C stretching frequencies are very weak; we were unable to detect any differences between the spectra of the complex and that of the ligand in the appropriate region (600–700 cm^{-1}), however. In the complexes of quadrivalent titanium, $\text{TiX}_4 \cdot 2\text{C}_4\text{H}_8\text{OS}$,¹¹ the sulphur atom is believed to be co-ordinated to titanium.

The reaction of *N*-methylmorpholine with $\text{TiBr}_3 \cdot 2\text{NMe}_3$ gave the 1 : 3 adduct, whereas the 1 : 2 adduct was formed in the analogous chloride reaction; there seems to be no obvious explanation for this difference. The spectra of these complexes in solution in methylmorpholine (cf. Fig. 3) show peaks at 15,000 and 14,250 cm^{-1} for the chloride and

¹¹ Fowles and Walton, *J.*, in the press.

bromide complexes, respectively. The infrared spectra of the adducts show that bonding is through the oxygen rather than through the sterically hindered nitrogen atom, since the symmetric C-O-C stretching frequency (found at 870 cm^{-1} in the free ligand) is split and shifted to lower wavenumbers in the complexes. This is in marked contrast to the morpholine complex, $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_9\text{ON}$, where bonding is through the nitrogen atom.³

Methyl cyanide reacted with $\text{TiBr}_3 \cdot 2\text{NMe}_3$ to form the adduct $\text{TiBr}_3 \cdot 3\text{MeCN}$, which was prepared previously by the direct reaction of methyl cyanide with the tribromide.⁴ The spectrum of the complex, both as a solid and in methyl cyanide solution, showed one broad asymmetric peak at $15,500\text{ cm}^{-1}$. The distortion in the excited state (δ'), which is the energy difference between the ${}^2A_{1g} \leftarrow {}^2B_{2g}$ and ${}^2B_{1g} \leftarrow {}^2B_{2g}$ transitions, amounts to 2400 cm^{-1} for the chloride complex, but an accurate value cannot be assigned to the corresponding bromide complex, because the asymmetric peak does not yield a separate

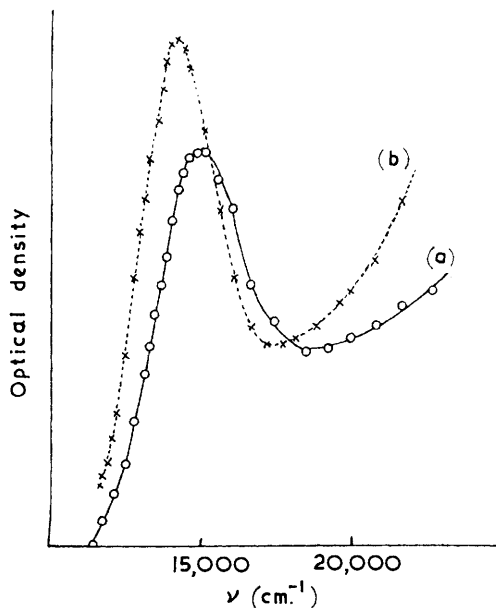


FIG. 3. (a) Spectrum of $\text{TiCl}_3 \cdot 2\text{C}_5\text{H}_{11}\text{NO}$ in *N*-methylmorpholine; (b) Spectrum of $\text{TiBr}_3 \cdot 3\text{C}_5\text{H}_{11}\text{NO}$ in *N*-methylmorpholine.

shoulder. It is clear, however, that the separation of the components of the 2E_g term is less for the bromide complex than for its chloride analogue. This agrees with our suggestion that the symmetry of the bromo complex tends towards C_{3v} .

Whereas the spectra of solutions and the diffuse reflectance spectra are virtually the same for the methyl cyanide complexes, this is not true for all complexes. Thus, with the dioxan complexes, $\text{TiX}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$, the spectra of solutions show a single peak, but a distinct shoulder is found in the diffuse reflectance spectra. A possible explanation is that while the distortion for the species in solution is not sufficiently great for the appearance of a second peak or shoulder (the ligand field for $\text{C}_4\text{H}_8\text{O}_2$ is much less than that of MeCN), further distortions may arise in the solid state through interaction between neighbouring molecules; this interaction may occur between the unco-ordinated oxygen atoms of one or more dioxan ligands and nearby titanium atoms. Support for this hypothesis is provided by the observation that a doublet diffuse reflectance spectrum is also found for the morpholine complex $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_4\text{NO}$, but not for complexes formed with monofunctional ligands such as tetrahydrofuran.

If a Dq value of 1370 cm^{-1} is used for titanium(III) octahedrally co-ordinated with chloride ions,² and values of 1510 and 1360 cm^{-1} are taken for the respective complexes $\text{TiCl}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$ and $\text{TiBr}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$, then a Dq value of 1080 cm^{-1} is obtained for titanium(III)

octahedrally co-ordinated with bromide ions (assuming Jørgensen's rule of average environment¹² is valid). A value of 1030 cm^{-1} is obtained if calculations are based on the values 1720 and 1550 cm^{-1} for the complexes $\text{TiCl}_3 \cdot 3\text{MeCN}$ ^{2,4} and $\text{TiBr}_3 \cdot 3\text{MeCN}$.

EXPERIMENTAL

Reactions were carried out by standard vacuum line procedures, great care being taken to exclude traces of moisture.

Materials.—Titanium(III) chloride, which was supplied by Union Carbide, was used without further purification. Reaction of this with trimethylamine in a double ampoule gave good yields of the soluble adduct, $\text{TiCl}_3 \cdot 2\text{NMe}_3$, which was obtained as blue crystals.¹ The double ampoule consisted of two jointed ampoules separated by a sintered disc and a constriction, the whole system being sealed under vacuum.

Reaction of titanium(IV) bromide with trimethylamine in a double ampoule gave a dark red solid. After a few hours a green solution was obtained, which, on filtration and removal of excess of trimethylamine, left the green crystalline adduct $\text{TiBr}_3 \cdot 2\text{NMe}_3$. The process of filtration and distillation was repeated at intervals, over a period of three weeks, to give a good yield of the adduct (Found: Br, 59.1; Ti, 11.7. $\text{TiBr}_3 \cdot 2\text{NMe}_3$ requires: Br, 59.1; Ti, 11.8%).

Reaction of $\text{TiBr}_3 \cdot 2\text{NMe}_3$ with 1,4-Dioxan.—A dark green solution resulted which, on removal of excess of dioxan, left a green solid (Found: Br, 44.4; Ti, 9.3. $\mu = 1.45$ B.M. $\text{TiBr}_3 \cdot 3\text{C}_4\text{H}_8\text{O}_2$ requires: Br, 43.4; Ti, 8.7%).

Reaction of $\text{TiBr}_3 \cdot 2\text{NMe}_3$ with 1,4-Thioxan.—A green-brown solution was formed at room temperature, which left a yellow-brown solid on removal of excess of thioxan (Found: C, 20.2; H, 4.6; Br, 47.6; Ti, 9.5; $\mu = 1.60$ B.M. $\text{TiBr}_3 \cdot 2\text{C}_4\text{H}_8\text{OS}$ requires: C, 19.4; H, 3.3; Br, 48.35; Ti, 9.7%).

Reaction of $\text{TiBr}_3 \cdot 2\text{NMe}_3$ with N-Methylmorpholine.—A dark yellow-green solution resulted from which a yellow-brown solid was obtained (Found: Br, 40.9; N, 6.9; Ti, 8.8; $\mu = 1.49$ B.M. $\text{TiBr}_3 \cdot 3\text{C}_5\text{H}_{11}\text{NO}$ requires: Br, 40.6; N, 7.1; Ti, 8.1%).

Reaction of $\text{TiBr}_3 \cdot 2\text{NMe}_3$ with Methyl Cyanide.—The resulting dark green solution left a yellow-green solid on removal of excess of methyl cyanide (Found: Ti, 11.9; Br, 56.7; N, 10.0; $\mu = 1.50$ B.M. $\text{TiBr}_3 \cdot 3\text{MeCN}$ requires: Br, 58.35; N, 10.2; Ti, 11.7%).

Reaction of $\text{TiCl}_3 \cdot 2\text{NMe}_3$ with 1,4-Thioxan.—A dark green solution yielding a green solid (Found: Ti, 14.0; Cl, 29.7; C, 27.5; H, 5.0; $\mu = 1.58$ B.M. $\text{TiCl}_3 \cdot 2\text{C}_4\text{H}_8\text{OS}$ requires: Ti, 13.2; Cl, 29.4; C, 26.5; H, 4.5%).

Reaction of $\text{TiCl}_3 \cdot 2\text{NMe}_3$ with N-Methylmorpholine.—A blue-green solution resulted, from which a green solid was isolated (Found: C, 32.0; H, 6.6; Cl, 29.3; N, 7.8; Ti, 12.7; $\mu = 1.62$ B.M. $\text{TiCl}_3 \cdot 2\text{C}_5\text{H}_{11}\text{NO}$ requires: C, 33.7; H, 6.2; Cl, 29.85; N, 7.9; Ti, 13.4%).

Analysis.—Titanium, halogen, and nitrogen were determined as previously described.¹³ Carbon and hydrogen were determined by a professional analyst.

Spectra.—Infrared spectra were measured for Nujol mulls, by using Unicam S.P. 200 and Infracord (KBr) spectrophotometers. Visible spectra were measured on a Unicam S.P. 500 instrument fitted with a reflectance attachment.

Magnetic Susceptibilities.—A Gouy type of balance was used, and measurements were made at room temperatures only.

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¹² Jørgensen, 10^e Conseil de l'Institut International de Chimie Solvay, 1956, p. 355.

¹³ Fowles and Nicholls, *J.*, 1959, 990.