

5. The Reaction of Titanium Halides with Tertiary Amines.

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Titanium(IV) chloride and bromide reacted with trimethylamine to give simple adducts $\text{TiX}_4\cdot\text{NMe}_3$, that were monomeric in benzene solution. An excess of the amine reduced titanium to the trivalent state and gave the compounds $\text{TiX}_3\cdot 2\text{NMe}_3$; these were also prepared by direct reaction of trimethylamine with the appropriate trihalide. Pyridine also reduced titanium(IV) halides. Titanium(III) chloride with pyridine or γ -picoline gave 1 : 3 adducts, and with α -picoline a 1 : 2 adduct. The spectra of these compounds have been measured and interpreted.

ANTLER and LAUBENGAYER¹ found that titanium(IV) chloride with trimethylamine in the gas phase gave a mixture which could be partly separated by sublimation. They obtained some evidence for the formation of a simple adduct $\text{TiCl}_4\cdot\text{NMe}_3$, and characterised a trivalent titanium complex $\text{TiCl}_3\cdot 2\text{NMe}_3$; the latter was also synthesised directly from titanium(III) chloride. Beattie and Leigh² have also commented on the formation of

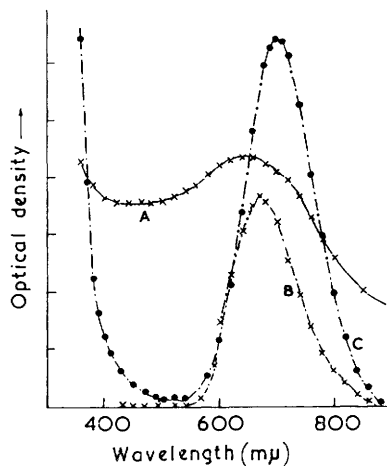


FIG. 1. Spectra of $\text{TiCl}_3\cdot 2\text{NMe}_3$ (A) solid and (B) in NMe_3 , and of $\text{TiBr}_3\cdot 2\text{NMe}_3$ (C) in NMe_3 .

titanium(III) in the reaction of titanium(IV) chloride with trimethylamine. We have now isolated the simple 1 : 1 adducts of trimethylamine with titanium(IV) chloride and bromide. Molecular-weight measurements show that these adducts are monomeric in benzene solution, so that the titanium atoms have the unusual co-ordination number of five. With titanium(IV) chloride there is also some evidence for the subsequent formation of a 1 : 2 adduct before reduction.

The bromide reduction product, $\text{TiBr}_3\cdot 2\text{NMe}_3$, has been isolated and characterised as a complex of trivalent titanium; it has also been prepared by the direct reaction of titanium(III) bromide with trimethylamine. Both $\text{TiX}_3\cdot 2\text{NMe}_3$ complexes are formally five co-ordinate. Trimethylamine is the only organic solvent in which the complexes dissolve without reaction, and the solutions show (cf. Fig. 1) fairly broad absorption bands centred at $14,900$ and $14,280\text{ cm}^{-1}$ for the chloride and bromide, respectively. The diffuse reflectance spectrum of the chloride complex shows a similar band at $15,380\text{ cm}^{-1}$. The analogous vanadium(III) compounds, $\text{VX}_3\cdot 2\text{NMe}_3$, are soluble and monomeric in benzene, and dipole-moment measurements indicate that they have *trans*-trigonal-bipyramidal configurations.³ Since the titanium compounds are less volatile and less soluble, they are

¹ Antler and Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 5250.

² Beattie and Leigh, *J. Inorg. Nuclear Chem.*, 1961, **23**, 55.

³ Duckworth, Fowles, and Williams, *Chem. and Ind.*, 1962, 1285.

likely to be polymerised in the solid, probably through chlorine-chlorine bridging. This bridging can be broken by electron-donor solvents and therefore the compounds dissolve in trimethylamine (other solvents such as methyl cyanide displace the co-ordinated amine). The presence of a single absorption peak suggests that the titanium atoms have an octahedral configuration both in the solid and in solution; this peak is then attributed to the $T_{2g} \rightarrow E_g$ transition. The asymmetrical nature of the ligand field results in a modest splitting of E_g level and a broadening of the band. The position of the peak differs in the two compounds by about 600 cm^{-1} , the chloride complex having the band with the higher wavenumber, as might be expected; this band shifts by a further 500 cm^{-1} in the solid, presumably because the titanium atom now has four chlorine and two trimethylamine ligands, compared with three chlorine and three trimethylamine ligands in solution.

The complexes have magnetic susceptibilities close to the spin-only value, as would be expected for octahedral complexes with a fairly unsymmetrical field.⁴ The chloride complex obeys the Curie-Weiss law over a temperature range $90\text{--}291^\circ\text{K}$, with $\theta = 32^\circ$.

Attempts to make analogous triethylamine complexes were unsuccessful, reaction being incomplete. However, titanium(IV) chloride and bromide gave the 1:1 adduct, together with some tervalent titanium complex. The 1:1 adduct $\text{TiCl}_4 \cdot \text{N}(\text{Et})_3$ was prepared by mixing solutions of the reactants in light petroleum. When the solvent was moist, the product was a white precipitate consisting of hydrated titanium(IV) oxide to which triethylamine was strongly attached. The white products previously considered^{5,6} as "tetra-aminates" may also be hydrolysed.

Titanium(IV) chloride forms a 1:2 adduct with pyridine,⁷ but with an excess of pyridine the titanium is reduced to the tervalent state. The oxidation products of pyridine have not been identified. No chloropyridines were produced, however, and the chlorine atom "lost" by titanium(IV) chloride appeared quantitatively as pyridinium hydrochloride. The complex $\text{TiCl}_3 \cdot 3\text{py}$, which is the probable product, has been prepared by direct reaction of titanium(III) chloride with pyridine. It gives a non-conducting solution in pyridine, but behaves as a typical 1:1 electrolyte in methyl cyanide (cf. Table 1). The compound

TABLE 1.
Molar conductivities (in $\text{ohm}^{-1} \text{ cm}^2$).

	$\text{TiCl}_3 \cdot 3\text{py}$	$\text{TiCl}_3 \cdot 3\gamma\text{-Picoline}$	Et_4NBr
In MeCN	149	131	159
In $\text{C}_2\text{H}_5\text{N}$	8	—	134

TABLE 2.
Absorption spectra.

Compound	State	Absorption peaks (cm^{-1}) (ϵ in parentheses)			
$\text{TiCl}_3 \cdot 2\text{NMe}_3$	Solid	15,380			
	NMe_3 soln.	14,900			
$\text{TiBr}_3 \cdot 2\text{NMe}_3$	NMe_3 soln.	14,280			
$\text{TiCl}_3 \cdot 3\text{py}$	Solid	24,690	16,670		
	py soln.	24,100	24,100	16,530	
	MeCN soln.	42,550 (1400)	35,710 (2600)	25,640 (495)	16,670 (23)
$\text{TiCl}_3 \cdot 3\gamma\text{-pic}$	Solid	24,390	16,810		
	$\gamma\text{-pic}$ soln.	25,000	16,670		
	MeCN soln.	42,550 (1700)	35,710 (460)	32,260 (350)	25,970 (960) 16,530 (45)
$\text{TiCl}_3 \cdot 2\alpha\text{-pic}$	Solid		16,950		
	$\alpha\text{-pic}$ soln.	25,640	16,000		

is evidently a simple adduct which ionises in methyl cyanide solution to give $[\text{TiCl}_2\text{py}_3(\text{MeCN})]\text{Cl}$; the ionisation must be reversible since the original compound can

⁴ Figgis and Lewis, "Modern Co-ordination Chemistry," Interscience Publ., Inc., New York, 1960, p. 430.

⁵ Trost, *Canad. J. Chem.*, 1952, **30**, 835.

⁶ Prasad and Tripathi, *J. Indian Chem. Soc.*, 1957, **34**, 749.

⁷ Emeléus and Rao, *J.*, 1958, 4245.

be recovered unchanged from solution. We believe that the octahedral environment of titanium is retained by co-ordination of a molecule of methyl cyanide.

The spectrum of the compound (cf. Table 1 and Figs. 2 and 3), both in the solid and in solution, shows two peaks in the visible region. Since the titanium atom has an unsymmetrical ligand field surrounding it, the two peaks might be considered to arise through splitting of the E_g level, but this is unlikely⁸ since the splitting amounts to some 8000 cm^{-1} . Further, the two peaks have quite different intensities. The first peak has an extinction coefficient of 23, which is typical for a $d-d$ transition, whereas the second peak has a much higher value (500) and is more likely to be a charge-transfer band of relatively low intensity. Barnum⁹ has recently examined the spectra of the acetylacetonate complex of trivalent titanium and obtained two very similar peaks; that with the higher extinction coefficient was

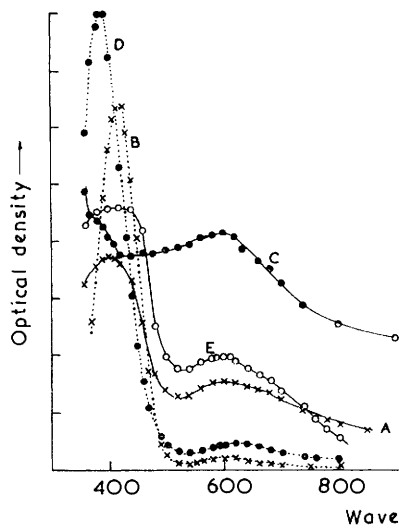


FIG. 2.

FIG. 2. Spectra of $\text{TiCl}_3 \cdot 3\text{py}$ (A) solid and (B) in pyridine, of $\text{TiCl}_3 \cdot 2\alpha\text{-pic}$ (C) solid and (D) in $\alpha\text{-picoline}$, and of $\text{TiCl}_3 \cdot 3\gamma\text{-pic}$ (E) solid.

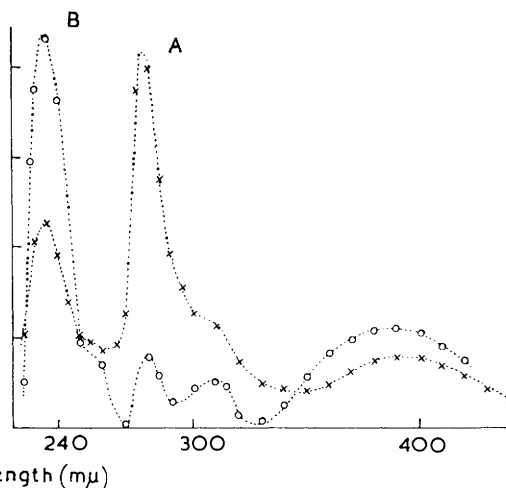


FIG. 3.

FIG. 3. Spectra of (A) $\text{TiCl}_3 \cdot 3\text{py}$ and (B) $\text{TiCl}_3 \cdot 3\gamma\text{-pic}$.

assigned to a transition from the titanium d_ϵ level to an antibonding π -orbital (π_4) of the acetylacetonate groups. Jørgensen¹⁰ has studied a number of pyridine complexes of trivalent rhodium and iridium and concluded that there is always a band in the 30,000—35,000 cm^{-1} region that can be attributed to the transition of a d -electron from the metal atom to an antibonding π -orbital of the pyridine ligand. Titanium(III) is more easily oxidised, so the analogous electron-transfer band in titanium(III)-pyridine complexes should occur at lower wavenumbers; the band around 25,000 cm^{-1} is assigned to this transition.

The bipyridyl complex of overall composition $\text{TiCl}_3 \cdot 1.5\text{bipy}$, also shows two peaks,^{11,12} but in this case the peaks have similar extinction coefficients and both appear to be $d-d$ transitions. The compound is ionic, and it is considered¹² that two different titanium species are present, one cationic and the other anionic, so that each species,

⁸ Liehr and Ballhausen, *Ann. Phys.*, 1958, **3**, 304.

⁹ Barnum, *J. Inorg. Nuclear Chem.*, 1961, **21**, 221; **22**, 183.

¹⁰ Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 151; "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, p. 191.

¹¹ Fowles and Hoodless, unpublished observations.

¹² Lewis and Nyholm, personal communication.

gives rise to a separate band. Analogous formulations for the pyridine complex, e.g., $[\text{Ti py}_4\text{Cl}_2][\text{Ti py}_2\text{Cl}_4]$, are excluded since the compound is non-conducting in pyridine.

The spectrum of the compound in methyl cyanide solution (cf. Fig. 3) shows two further peaks in the ultraviolet region, at 35,720 and 42,600 cm^{-1} , respectively. One of these is clearly the $\pi \rightarrow \pi^*$ transition associated with the pyridine ligands, and by analogy with Jørgensen's findings¹⁰ for the iridium complexes we suggest that this transition has the higher wavenumber. The other peak may be due to an electron transfer involving the co-ordinated molecule of methyl cyanide, since a peak is found in an almost identical position for the $\text{TiCl}_3 \cdot 3\text{MeCN}$ complex.¹¹

The infrared spectrum of the complex closely resembles that of pyridine and confirms the presence of co-ordinated pyridine and the absence of pyridinium ions.¹³ In the potassium bromide region, however, the complex shows additional peaks at 635 and 438 cm^{-1} . These may be associated with titanium-chlorine stretching modes, since the spectrum of titanium(IV) chloride shows strong bands in the 500–600 cm^{-1} region.¹⁴ Titanium-nitrogen stretching frequencies are unlikely to be found in this region, since although cobalt-nitrogen frequencies [in cobalt(III) ammines] have now been assigned¹⁵ to 400–500 cm^{-1} , the heavier pyridine ligands should lower the frequency considerably.

γ -Picoline with titanium(III) chloride gives an analogous 1:3 adduct, but only two molecules of α -picoline are taken up; it seems likely that the α -methyl group tends to restrict attachment of the third α -picoline ligand. The visible spectrum of the γ -picoline adduct (cf. Fig. 2) is very similar to that of the pyridine adduct both in the solid and in solution, and the two bands may be assigned to a $d-d$ and an electron-transfer transition to the ligand, respectively, as before. There is, however, an additional peak of modest intensity in the near-ultraviolet region which may be the $n \rightarrow \pi^*$ transition of the ligand, present only as a shoulder in the pyridine complex but now more apparent because it is sufficiently modified (through co-ordination of the ligand) to be no longer obscured by the methyl cyanide-titanium electron-transfer band. In α -picoline solution the α -picoline adduct shows the usual two visible peaks, but in the solid state the band at higher wavenumbers is much less clearly defined. It is possible that the adduct is dimeric in the solid state, through chlorine-chlorine bridging, but takes up an additional molecule of α -picoline when dissolved in the ligand. The spectrum in solution should then resemble the spectra of the pyridine and the γ -picoline adducts, but in the solid state the smaller number of α -picoline groups would lead to a modification of the charge-transfer bands.

The infrared spectra of both the γ - and the α -picoline adducts resemble those of the appropriate ligands fairly closely (all bands within 20 cm^{-1}) except in the potassium bromide region. The adducts show additional strong peaks at 543, 498, and 490 cm^{-1} , and at 647 and 432 cm^{-1} , for the γ - and α -picoline compounds, respectively. Some of these will be associated with titanium-chlorine stretching modes.

Titanium(III) chloride also reacts with 2,6-lutidine under reflux, but only one molecule of the ligand appears to be taken up, presumably because of the steric requirements of the two methyl groups.

EXPERIMENTAL

Because of the extreme ease with which the products were hydrolysed, all experiments were carried out in closed vacuum-systems.

Reaction of Titanium(IV) Chloride with Trimethylamine.—Mixing benzene solutions of the reactants at room temperature, followed by isolation, within 10 min., gave the yellow 1:1 adduct [Found: Ti, 19.0; Cl, 55.9; N, 5.8%; *M*, 259 (0.9% solution in benzene). $\text{TiCl}_4 \cdot \text{NMe}_3$

¹³ Mitchell, *J. Inorg. Nuclear Chem.*, 1961, **21**, 382.

¹⁴ Dove, Creighton, and Woodward, *Spectrochim. Acta*, 1962, **18**, 267; Rao, *Z. anorg. Chem.*, 1960, **304**, 176.

¹⁵ Nakamoto, Morimoto, and Fujita, Proc. 7th Internat. Conference on Coordination Chemistry, p. 1A7.

TABLE 3.
 TiX₄-NMe₃ reaction products

Run	Reaction time	Insoluble product				Soluble product			
		Ti (%)	X (%)	N (%)	Ti : X : N	Ti (%)	X (%)	N (%)	Ti : X : N
TiCl ₄									
1	10 mins.	20.1	57.0	5.3	1.00 : 3.83 : 0.91 *	18.1	48.8	6.9	1.00 : 3.64 : 1.30 *
2	2 years	12.4	48.9	7.3	1.00 : 5.34 : 2.03 †	18.8	33.4	10.8	1.00 : 2.40 : 1.96 §
TiBr ₄									
1	1 day	8.6	67.2	3.0	1.00 : 4.66 : 1.19 †	—	—	—	1.00 : 2.51 : 1.91 ¶
2	3 months	6.5	65.2	4.7	1.00 : 6.03 : 2.47 ‡	12.4	57.0	7.2	1.00 : 2.76 : 1.99 ¶

* Yellow product. † Yellow-green product. ‡ Red product. § Blue-green product. ¶ Green product.

requires Ti, 19.2; Cl, 57.0; N, 5.6%; *M*, 249]. The product was diamagnetic ($\chi_M - 66 \times 10^{-6}$ c.g.s.).

Reaction with an excess of liquid amine at room temperature in an ampoule also gave a yellow solid, but the amine solution gradually assumed a green colour. Amine-soluble and -insoluble products were isolated by filtration (cf. Table 3). The soluble product gave a mauve solution in sulphuric acid.

Reaction of Titanium(III) Chloride with Trimethylamine.—The chloride slowly reacted with, and partly dissolved in, trimethylamine to give a blue solution. A sealed system, consisting of two ampoules separated by a sinter-disc, was used to prepare good yields of the soluble *adduct*, which was obtained as blue crystals (Found: Ti, 18.0; Cl, 39.6; N, 9.7. TiCl₃, 2NMe₃ requires Ti, 17.6; Cl, 39.1; N, 10.3%). The compound was insoluble in benzene, chlorobenzene, carbon tetrachloride, and "iso-octane," and dissolved with reaction in methyl cyanide, nitrobenzene, and dioxan. The magnetic susceptibility μ was 1.73, 1.66, and 1.58 B.M. at 291°, 197°, and 90°K, respectively.

Reaction of Titanium(IV) Bromide with Trimethylamine.—The reaction of "iso-octane" solutions at -78° gave a red *product* [Found: Ti, 11.2; Br, 74.8; N, 3.2%; *M*, 423 (1.9% solution in benzene). TiBr₄, NMe₃ requires Ti, 11.2; Br, 74.9; N, 3.3%; *M*, 427]. The product was diamagnetic ($\chi_M = -103 \times 10^{-6}$ c.g.s.). A dark red solid and solution were formed at first in reactions in ampoules, but the solutions became green fairly rapidly. The mixtures were separated as before, and the products analysed (cf. Table 3). The soluble green product of run 2 had a magnetic susceptibility corresponding to $\mu = 1.51$ B.M., and gave a mauve solution in sulphuric acid.

The reaction of trimethylamine with titanium(III) bromide gave a green crystalline *product* (Found: Ti, 12.4; Br, 57.2; N, 7.3. TiBr₃, 2NMe₃ requires Ti, 11.8; Br, 59.1; N, 6.9%), μ 1.67 B.M.

Reaction of Titanium Halides with Triethylamine.—When solutions of titanium(IV) chloride and triethylamine in light petroleum were mixed, a black diamagnetic *compound* was formed; this was insoluble in the usual organic solvents (Found: Ti, 16.5; Cl, 48.1; N, 4.95. TiCl₄, NEt₃ requires Ti, 16.5; Cl, 48.8; N, 4.8%). Neither the tetrachloride nor the tetrabromide reacted completely with triethylamine in ampoules, but the products contained trivalent titanium. Typical analytical figures for the products formed after reaction for several weeks gave Ti : Cl : N = 1.00 : 3.96 : 0.72 and Ti : Br : N = 1.00 : 3.95 : 0.33.

Titanium(III) chloride did not react with triethylamine under reflux.

Reaction of Titanium(IV) Chloride and Titanium(III) Chloride with Pyridine.—A yellow solid and a green solution were formed after titanium(IV) chloride and pyridine had reacted for several weeks. Filtration gave the yellow solid (Found: Ti, 13.6; Cl, 40.5; N, 8.1. TiCl₄, 2C₅H₅N requires Ti, 13.8; Cl, 40.8; N, 8.05%). The *product* was diamagnetic ($\chi_M = -90 \times 10^{-6}$ c.g.s.). The soluble product appeared to be a mixture of a trivalent titanium complex, together with pyridinium hydrochloride (Found: Ti, 11.3; Cl, 33.0; N, 9.9%; Ti : Cl : N = 1.00 : 3.94 : 2.99); it had μ , 1.42 B.M. and gave a mauve solution in sulphuric acid.

The reaction of titanium(III) chloride with pyridine gave a green solution and a green solid *adduct* (Found: Ti, 12.6; Cl, 26.9; N, 10.6. TiCl₃, 3C₅H₅N requires Ti, 12.2; Cl, 27.2; N, 10.7%), μ 1.63 B.M.

Reaction of Titanium(III) Chloride with γ -Picoline, α -Picoline, and 2,6-Lutidine.—Reaction with the two picolines was carried out in ampoules; the excess of picoline was distilled off and the product washed with benzene. γ -Picoline gave a green solid *adduct* (Found: Ti, 11.2; Cl, 24.3; N, 9.8. $\text{TiCl}_3 \cdot 3\text{C}_6\text{H}_7\text{N}$ requires Ti, 11.1; Cl, 24.6; N, 9.7%) that dissolved in, and slowly reacted with, nitromethane. α -Picoline gave a green-blue *adduct* (Found: Ti, 14.7; Cl, 31.2; N, 8.4. $\text{TiCl}_3 \cdot 2\text{C}_6\text{H}_7\text{N}$ requires Ti, 14.1; Cl, 31.2; N, 8.2%), μ 1.62 B.M. Lutidine did not react with titanium(III) chloride except under reflux; a brown solid *product* was then formed (Found: Ti, 19.7; Cl, 42.2. $\text{TiCl}_3 \cdot \text{C}_7\text{H}_9\text{N}$ requires Ti, 18.3; Cl, 40.7%).

Reaction of Titanium(III) Bromide with Pyridine.—A green solid *adduct* was formed (Found: Ti, 9.38; Br, 43.5. $\text{TiBr}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$ requires Ti, 9.13; Br, 45.7%), μ 1.56 B.M.

Analytical Procedures.—Titanium, chlorine, and bromine were determined in the usual way.¹⁶ Nitrogen was estimated by the full Kjeldahl procedure.

Spectra.—Infrared spectra were measured for Nujol mulls, by using Unicam S.P. 100 and Infracord (KBr) spectrophotometers. Visible and ultraviolet spectra were measured on a Unicam S.P. 500 instrument equipped with a reflectance attachment.

Molecular Weights.—These were measured cyroscopically for benzene solutions. The apparatus was especially designed so as to be used in conjunction with the preparative vacuum-line. The temperature change was measured by means of a thermistor.

Magnetic Susceptibilities.—These constants were measured on a Gouy-type balance, normally at room temperature only.

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¹⁶ Fowles and Nicholls, *J.*, 1959, 990.
