

833. Reaction of Titanium(IV) and Zirconium(IV) Chlorides and Bromides with Several Ligands of Groups V and VI.

By G. W. A. FOWLES and R. A. WALTON.

The reactions of titanium(IV) chloride and bromide with triphenylphosphine, triphenylarsine, pyrazine, 2,6-dimethylpyrazine, thioxan, *N*-methylmorpholine, and phthalonitrile have been studied. Some of the analogous reactions of the zirconium(IV) halides have also been examined. Isolated titanium complexes had overall compositions corresponding to either TiX_4L or $TiX_4,2L$, but only $ZrX_4,2L$ compounds were obtained. The possible configurations of these compounds are discussed with the aid of infrared spectral data. Triphenylphosphine, *N*-methylmorpholine, and phthalonitrile brought about some reduction of titanium to the trivalent state.

In this Paper we report extensions to earlier work¹ on the complexes of quadrivalent titanium and zirconium. The reactions that have been studied are those of titanium(IV) chloride and bromide with the unidentate ligands triphenylphosphine and triphenylarsine, and those of the same halides and their zirconium analogues with several potentially bidentate ligands. Table I lists the products obtained.

TABLE I.

Products of MX_4 reactions (M = Ti and Zr; X = Cl and Br).

Halide	Ligand	Product
$TiCl_4$	PPh_3	$TiCl_4,2PPh_3$
$TiBr_4$	PPh_3	Reduction to Ti(III)
TiX_4	$AsPh_3$	$TiX_4,AsPh_3$
MX_4	Pyrazine (pyz)	$MX_4,2pyz$
TiX_4	2,6-Dimethylpyrazine (dmp)	$TiX_4,2dmp$
TiX_4	Thioxan	$TiX_4,2Thioxan$
TiX_4	<i>N</i> -Methylmorpholine	Reduction to Ti(III)
ZrX_4	<i>N</i> -Methylmorpholine	$ZrX_4,2C_8H_{11}NO$
$TiCl_4$	Phthalonitrile	$TiCl_4,C_8H_4N_2$
$TiBr_4$	Phthalonitrile	Reduction to Ti(III)
$ZrCl_4$	Phthalonitrile	$ZrCl_4,2C_8H_4N_2$

Chatt and Hayter² reported the preparation of several complexes of titanium(IV) chloride with tertiary and ditertiary phosphines, but were unable to measure any physical properties because of the extreme sensitivity of the complexes to moisture. We have overcome these handling problems and measured the infrared spectra of all the complexes prepared, including $TiCl_4,2PPh_3$. Above 400 cm^{-1} the spectrum of this compound shows

¹ Fowles and Walton, *J. Less-Common Metals*, 1963, 5, 510.

² Chatt and Hayter, *J.*, 1963, 1343.

very little change from that of the unco-ordinated ligand, although the out-of-plane hydrogen deformation vibrations are split. Below 400 cm^{-1} (cf. Table 2), which is the region for titanium-chlorine stretching frequencies,³ the complex shows two strong peaks at 380 and 325 cm^{-1} ; on the assumption that the complex contains six-co-ordinate titanium (it is too insoluble in suitable solvents for molecular weight determinations), the infrared spectrum suggests a *cis*-configuration.^{4,5}

Prolonged reaction between titanium(IV) chloride and triphenylphosphine resulted in some reduction of titanium to the trivalent state; in the analogous reaction of titanium(IV) bromide this reduction was much quicker and a complex of the quadrivalent element could not be isolated.

Reduction did not take place when triphenylarsine was used as a ligand, however, but 1 : 1 adducts ($\text{TiX}_4\cdot\text{AsPh}_3$) were isolated. These compounds were very soluble in benzene, and the bromide was monomeric.

Although relatively few examples of five-co-ordinate titanium are known, the analogous trimethylamine adducts ($\text{TiX}_4\cdot\text{NMe}_3$) have been shown to be monomeric.⁶

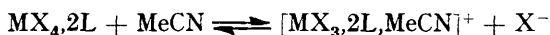
The tetrachlorides and bromides of titanium and zirconium reacted with pyrazine to give compounds $\text{MX}_4\cdot 2\text{pyz}$, and the analogous 2,6-dimethylpyrazine compounds were also prepared quite readily from the titanium halides. These compounds dissolved to a limited extent in methyl cyanide ($\sim 10^{-3}\text{M}$), and molar conductivities of 7.1 and 15.8 $\text{ohm}^{-1}\text{cm}^2$ were obtained, respectively, for solutions of $\text{TiBr}_4\cdot 2(2,6\text{-dmp})$ and $\text{ZrCl}_4\cdot 2\text{pyz}$ at 25°; a typical 1 : 1 electrolyte such as Et_4NBr has a molar conductivity of 159 $\text{ohm}^{-1}\text{cm}^2$ in methyl cyanide. The low values obtained suggest that the pyrazine and dimethyl-

TABLE 2.

Infrared spectra in the 500—250 cm^{-1} region (in Nujol mulls).

Compounds	Frequencies (cm^{-1})
Thioxan	388m, br, 340w
$\text{TiCl}_4\cdot 2\text{C}_4\text{H}_8\text{OS}$	386s, 363sh, 311w
$\text{TiBr}_4\cdot 2\text{C}_4\text{H}_8\text{OS}$	392w, 367w, 357w, 299vs, br
$\text{TiCl}_4\cdot 2\text{PPh}_3$	494m, 485sh, 442w, 432w, 380s, 325m, br
AsPh_3	469s, 311s
$\text{TiCl}_4\cdot \text{AsPh}_3$	464s, 450sh, 383s, 323m
$\text{TiBr}_4\cdot \text{AsPh}_3$	471w, 463m, 361s, 356s, 320w, 287s
$\text{Ph}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PPh}_2$	472m, 439m, 396w, 336w
$\text{TiCl}_4\cdot \text{Ph}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PPh}_2$	490w, 413w, 389m, 375m, 360s
Pyrazine (pyz)	413m
$\text{TiCl}_4\cdot 2\text{pyz}$	456m, 394s, 344w, 315w
$\text{TiBr}_4\cdot 2\text{pyz}$	452m, 406w, br, 315s, br, 299sh
2,6-Dimethylpyrazine (2,6-dmp)	440s, 282w
$\text{TiCl}_4\cdot 2(2,6\text{-dmp})$	481m, 385s, 310w
$\text{TiBr}_4\cdot 2(2,6\text{-dmp})$	483m, 385w, 303vs, br
$\text{TiCl}_4\cdot 2\text{C}_8\text{H}_4\text{N}_2$	394s, 327w

pyrazine complexes are essentially non-ionic, although it is possible that the conductivity may arise through a slight dissociation in solution:



Analogous equilibria^{1,7} have been postulated to account for the similar conductivity values obtained for methyl cyanide solutions of the bipyridyl complexes of zirconium and niobium.

Unfortunately, the complexes were not sufficiently soluble in solvents such as benzene for molecular weight measurements to be made, so that the co-ordination number of 6 for the metals cannot be proven. Since the ligands are capable of co-ordinating to the metal through either or both of the nitrogen atoms,⁸ there is the possibility of the metal's acquiring

³ Clark, *J.*, 1963, 1377.

⁴ Beattie, McQuillan, Rule, and Webster, *J.*, 1963, 1514.

⁵ Beattie, Webster, and Chantry, *J. Mol. Spectroscopy*, in the press.

⁶ Fowles and Hoodless, *J.*, 1963, 33.

⁷ Allbutt, Feenan, and Fowles, *J. Less-Common Metals*, 1964, **6**, 299.

⁸ Lever, Lewis, and Nyholm, *Nature*, 1961, **189**, 58.

TABLE 3.

Principal infrared absorption bands of pyrazine derivatives, from 1400 to 400 cm^{-1} .*All pyrazine complexes MX₄·2L:*

1350 w—m; 1305 \pm 5 vw; 1265 \pm 2 vw—w; 1230 \pm 2w—m; 1170 m; 1150 \pm 2 vs; 1126 \pm 1 m—s; 1110w; 1085 \pm 2 w—m; 1065 \pm 2 w—m; 1048 \pm 3 s—vs; 1020 \pm 3 sh; 905 \pm 5 vw—w; 805 \pm 3 vs; 700 vw; 680 vw; 600 \pm 2 w; 455 \pm 4 m—s.

In addition:

TiCl ₄ ·2pyz	983vw	975vw	748w	—	633w	—
TiBr ₄ ·2pyz	983vw	975vw	748w	—	~620w,br	—
ZrCl ₄ ·2pyz	—	—	—	~760s,br	~630,w,br	446w
ZrBr ₄ ·2pyz	—	—	—	~740s,br	—	445w

All 2,6-dimethylpyrazine complexes:

1415 \pm 1 m—s; 1285 \pm 5 m; 1258 m—s; 1193 w; 1158 \pm 2 vs; 983 \pm 2 vw—w; 952 \pm 3 w—m; 702 \pm 3 w; 560 \pm 4 m; 555 \pm 2 w; 487 \pm 2 m—s.

In addition:

TiCl ₄ ·2(2,6-dmp)	1402vw	1308vw	1033vs	883m	878s	744s	737s	—	678w	443w
TiBr ₄ ·2(2,6-dmp)	—	—	1018s	—	873w	755m	738w	728w	678w	443w

a co-ordination number higher than 6, at least in the solids. Recently, infrared spectral data have been used to determine whether the ligands act through one or both nitrogen atoms in complexes of other transition elements.^{9,10} Medium to strong bands at 960 and 1160 cm^{-1} for pyrazine and 2,6-dimethylpyrazine complexes, respectively, have been considered to show that only one nitrogen atom is co-ordinated. When both nitrogen atoms are co-ordinated, these bands are not present, presumably because the higher symmetry of the ligands gives simpler spectra. Table 3 lists the principle bands in the 1400—400 cm^{-1} region.

With the ZrX₄·2pyz complexes there is no peak at 980 cm^{-1} , and only very weak absorptions (at 975 and 983 cm^{-1}) are found for the analogous titanium compounds. The implication is that, at least in the solid state, the zirconium complexes contain eight-coordinate zirconium, the ligands bridging two metal atoms. With the titanium complexes the weakness of the observed bands suggests that some of the ligands bond through both nitrogen atoms.

2,6-Dimethylpyrazine is less likely to co-ordinate through both nitrogen atoms owing to the steric requirements of the methyl groups, and we should expect a peak at 1160 cm^{-1} ; this is present for the titanium complexes.

N-Methylmorpholine reduced both of the titanium halides to the trivalent state, but the zirconium halides gave 1:2 adducts, ZrX₄·2C₅H₁₁NO. Titanium(IV) bromide was also reduced by phthalonitrile, but the chloride yielded a 1:1 adduct, TiCl₄·C₈H₄N₂. The infrared spectra of this compound shows two titanium—chlorine stretching frequencies at 394 and 327 cm^{-1} , consistent with a *cis*-arrangement for an octahedral titanium compound TiCl₄·2L. Furthermore, the CN stretching vibration found at 2235 cm^{-1} in phthalonitrile itself, shows up as a single peak in the complex, shifted characteristically to 2285 cm^{-1} . ZrCl₄·2C₈H₄N₂, which was formed from the analogous reaction of zirconium(IV) chloride, dissolves in methyl cyanide to give a solution that is almost non-conducting. The CN stretching frequency is split into a doublet, which may indicate that only one CN group is co-ordinated to zirconium.

Titanium(IV) chloride and bromide react with thioxan to give products of overall composition TiX₄·2C₄H₈OS, the bromide complex giving an almost non-conducting solution in nitromethane. Thioxan is potentially a bidentate ligand and it is of interest to see whether both oxygen and sulphur co-ordinate to give eight-coordinate titanium, or whether only one atom co-ordinates (and if so, which). Unfortunately, molecular weight

⁹ Lever, Lewis, and Nyholm, *J.*, 1962, 1235.

¹⁰ Lever, Lewis, and Nyholm, *J.*, 1963, 3156, 5042.

measurements cannot be made because of limited solubilities, but infrared and n.m.r. measurements show fairly conclusively that co-ordination is through sulphur only. Thus, the free ligand shows strong C—O—C stretching modes at 1105 and 836 cm^{-1} , and these bands are unaltered in the titanium complexes; in contrast, the analogous bands for dioxan shift considerably when the ligand co-ordinates to the titanium halides.^{11,12} Since bonding is not apparently through oxygen it must be through sulphur, although positive infrared evidence is rather slight, because C—S—C stretching vibrations only give bands of weak intensity in the 600—700 cm^{-1} region.¹³ Thioxan itself shows three bands in this region (612vw, 662m, and 690w), and only the latter two appear in the spectra of the complexes. The metal—halogen stretching vibrations (cf. Table 2) suggest a *cis*-configuration. The n.m.r. data again favour co-ordination through sulphur. Dioxan and dithian show single peaks at 3.70 and 2.90 δ , respectively, and thioxan shows two triplets with centres at 3.85 and 2.55 δ . The same two triplets are observed for the complexes formed by the titanium(IV) halides ($\text{TiCl}_4 \cdot 2\text{C}_4\text{H}_8\text{OS}$, 4.02 and 2.95; $\text{TiBr}_4 \cdot 2\text{C}_4\text{H}_8\text{OS}$, 4.02 and 3.03 δ). The triplet associated with protons adjacent to the sulphur atom shifts about three times as much as that arising from the protons next to oxygen when thioxan co-ordinates to the titanium(IV) halides. This evidence strongly favours bonding through sulphur.

EXPERIMENTAL

The complexes were prepared in sealed ampoules either by mixing benzene solutions of the reactants or by shaking a suspension of the halide with a benzene solution of the ligand; because of the extreme ease with which the products were hydrolysed, all subsequent handling was carried out in closed vacuum systems. Analyses, and various physical measurements (*i.e.*, spectra, magnetic susceptibility, molecular weight, and conductivity) were made in the previously described manner.^{11,14} N.m.r. measurements were made on chloroform solutions using a Varian A60 instrument at room temperature with tetramethylsilane as internal reference.

Reactions of 1,4-Thioxan with TiCl_4 and TiBr_4 .—These yielded yellow and orange products, respectively (Found: C, 24.0; H, 4.2; Cl, 35.9; S, 15.6; Ti, 11.7. $\text{TiCl}_4 \cdot 2\text{C}_4\text{H}_8\text{OS}$ requires C, 24.1; H, 4.05; Cl, 35.6; S, 16.1; Ti, 12.0%. Found: C, 15.7; H, 3.2; Br, 56.2; S, 10.0; Ti, 8.4. $\text{TiBr}_4 \cdot 2\text{C}_4\text{H}_8\text{OS}$ requires C, 16.7; H, 2.8; Br, 55.5; S, 11.1; Ti, 8.3%). Both compounds were soluble in acetonitrile and nitromethane, but almost insoluble in benzene and cyclohexane. In nitromethane, the bromo-complex ($\sim 10^{-3}\text{M}$) had a conductivity (Λ_m) of 6.05 $\text{ohm}^{-1} \text{cm}^2$ at 25°.

Reaction of Triphenylphosphine with TiCl_4 .—This gave a dark red-purple diamagnetic solid (Found: C, 59.5; H, 4.7; Cl, 19.7; Ti, 6.6. $\text{TiCl}_4 \cdot 2\text{C}_{18}\text{H}_{15}\text{P}$ requires C, 60.6; H, 4.2; Cl, 19.9; Ti, 6.7%). Reaction during 4 days gave a product of similar appearance which was somewhat paramagnetic (Found: Cl, 28.2; Ti, 9.2%), μ 0.51 B.M. In the analogous reaction with TiBr_4 , the 1 : 2 adduct could not be isolated; the product, which was always paramagnetic, varied in colour from orange to dark brown depending upon the reaction time.

Reactions of Triphenylarsine with TiCl_4 and TiBr_4 .—These gave purple products with the correct analysis for $\text{TiX}_4 \cdot \text{AsPh}_4$ [Found: C, 43.2; H, 3.4; Cl, 27.4; Ti, 9.2. $\text{TiCl}_4 \cdot \text{C}_{18}\text{H}_{15}\text{As}$ requires C, 43.6; H, 3.05; Cl, 28.6; Ti, 9.7%. Found: C, 31.8; H, 2.7; Br, 47.0; Ti, 7.3%; M, 591 (1% soln. in benzene). $\text{TiBr}_4 \cdot \text{C}_{18}\text{H}_{15}\text{As}$ requires C, 32.1; H, 2.2; Br, 47.4; Ti, 7.1%; M, 674].

Reactions of Pyrazine with TiCl_4 , TiBr_4 , ZrCl_4 , and ZrBr_4 .— TiCl_4 and TiBr_4 gave 1 : 2 adducts, which were yellow and orange, respectively (Found: C, 26.3; H, 2.8; Cl, 40.1; N, 15.5; Ti, 13.1. $\text{TiCl}_4 \cdot 2\text{C}_4\text{H}_4\text{N}_2$ requires C, 27.5; H, 2.3; Cl, 40.5; N, 16.0; Ti, 13.7%. Found: C, 19.6; H, 2.6; Br, 59.3; N, 10.8; Ti, 8.9. $\text{TiBr}_4 \cdot 2\text{C}_4\text{H}_4\text{N}_2$ requires C, 18.2; H, 1.5; Br, 60.6; N, 10.6; Ti, 9.1%). The analogous 1 : 2 adducts formed by ZrCl_4 and ZrBr_4 were white and pink, respectively (Found: C, 23.1; H, 2.8; Cl, 34.7; N, 13.7; Zr, 23.2. $\text{ZrCl}_4 \cdot 2\text{C}_4\text{H}_4\text{N}_2$ requires C, 24.4; H, 2.05; Cl, 36.1; N, 14.25; Zr, 23.2%. Found: C, 16.5; H, 2.1; Br, 55.0; N, 9.5; Zr, 15.5. $\text{ZrBr}_4 \cdot 2\text{C}_4\text{H}_4\text{N}_2$ requires C, 16.8; H, 1.4; Br, 56.0; N, 9.8; Zr, 16.0%).

¹¹ Fowles, Hoodless, and Walton, *J.*, 1963, 5873.

¹² Clark, Lewis, Machin, and Nyholm, *J.*, 1963, 379.

¹³ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 353.

¹⁴ Drake and Fowles, *J.*, 1960, 1498.

Reactions of 2,6-Dimethylpyrazine with TiCl_4 and TiBr_4 .—These yielded 1:2 adducts that were yellow and deep brown, respectively (Found: C, 35.6; H, 4.1; Cl, 34.6; N, 13.6; Ti, 11.6. $\text{TiCl}_4 \cdot 2\text{C}_6\text{H}_8\text{N}_2$ requires C, 35.5; H, 4.0; Cl, 34.9; N, 13.8; Ti, 11.8%. Found: C, 24.5; H, 3.2; Br, 54.3; N, 9.6; Ti, 7.8. $\text{TiBr}_4 \cdot 2\text{C}_6\text{H}_8\text{N}_2$ requires C, 24.7; H, 2.8; Br, 54.8; N, 9.6; Ti, 8.2%).

Reactions of N-Methylmorpholine with TiCl_4 , TiBr_4 , ZrCl_4 , and ZrBr_4 .—The titanium(IV) halides reacted to give yellow-orange paramagnetic solids of variable composition, and pure compounds could not be isolated. With the zirconium(IV) halides, a slow reaction occurred (without reduction), giving compounds whose analysis approximated to $\text{ZrX}_4 \cdot 2\text{C}_5\text{H}_{11}\text{NO}$ (Found: C, 29.0; H, 6.6; Cl, 30.2; N, 5.8; Zr, 20.2. $\text{ZrCl}_4 \cdot 2\text{C}_5\text{H}_{11}\text{NO}$ requires C, 27.6; H, 5.1; Cl, 32.6; N, 6.4; Zr, 21.0%. Found: Br, 48.0; N, 4.6; Zr, 14.5. $\text{ZrBr}_4 \cdot 2\text{C}_5\text{H}_{11}\text{NO}$ requires Br, 52.1; N, 4.6; Zr, 14.9%).

Reactions of Phthalonitrile with TiCl_4 , TiBr_4 , and ZrCl_4 .— TiCl_4 gave a diamagnetic yellow solid (Found: C, 30.3; H, 1.6; Cl, 44.2; N, 8.9; Ti, 14.7. $\text{TiCl}_4 \cdot \text{C}_8\text{H}_4\text{N}_2$ requires C, 30.2; H, 1.3; Cl, 44.6; N, 8.8; Ti, 15.1%). The complex was almost insoluble in benzene but dissolved in methyl cyanide ($\Lambda_m = 2.7 \text{ ohm}^{-1} \text{ cm}^2$ at 25° for $8.6 \times 10^{-3}\text{M}$ solution). TiBr_4 was reduced by the ligand, and complexes of Ti(IV) could not be isolated. A typical experiment gave $\mu = 0.5$ B.M. after a reaction period of 1 day. ZrCl_4 reacted very slowly, to give a very pale yellow solid (Found: Cl, 29.2; Zr, 19.1. $\text{ZrCl}_4 \cdot 2\text{C}_8\text{H}_4\text{N}_2$ requires Cl, 28.9; Zr, 18.6%). A solution ($2.5 \times 10^{-3}\text{M}$) in methyl cyanide gave $\Lambda_m = 10 \text{ ohm}^{-1} \text{ cm}^2$ at 25° .

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THE UNIVERSITY, SOUTHAMPTON.

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