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2. TITANIUM

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CONTENTS

INTRODUCTION

The chemistry of titanium continues to be a vigorous and diverse area of research activity. This review attempts comprehensive coverage of the coordination chemistry of titanium; organometallic and solid-state aspects of titanium chemistry are treated selectively and, usually, in connection with some other theme. The important subject of photocatalytic reactions on TiO_2 and $SrTiO_3$ powders and semiconductor electrodes has been judged to be beyond the scope of this review and has been omitted.

During the past year, several reviews of various aspects of the organometallic chemistry of titanium have been published. These include Labinger's annual review of the literature for 1979 [1] and Thewalt's comprehensive volume in the Gmelin Handbuch on organotitanium compounds with two pentahapto ligands [2]. In addition, the special issue, Volume 200, of the Journal of Organometallic Chemistry contains a number of interesting articles that touch on organotitanium chemistry. Noteworthy are papers on metal atom synthesis of zerovalent arene compounds [3], dinitrogen fixation by transition metal compounds [4], and

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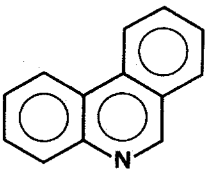
organometallic catalysts for the oligomerisation of alkenes [5]. Nugent and Haymore have reviewed the chemistry of organoimido (NR) compounds of titanium [6]. On the solid state side, two brief reviews of the intercalation chemistry of TiS_2 have appeared [7,8].

The present review covers the major journals for the 1980 calendar year and the lesser known and/or foreign journals for the period covered by Chemical Abstracts, Volume 91, Number 21 through Volume 93, Number 18.

2.1 TITANIUM(IV) COMPOUNDS

2.1.1 Halide and pseudohalide complexes

Titanium(IV) fluoride adducts of the type TiF_4L_2 (L = 3,4-benzoquinoline (phenanthridine) **(1)** or 5,6-benzoquinoline **(2)**) have been prepared by reaction of equimolar amounts of TiF_4 and the *N*-donor ligands in thf at reflux. The presence of a single ν(Ti-F) band in the IR spectra of these complexes (near 570 cm^{-1}) points to a *trans*-octahedral geometry [9].



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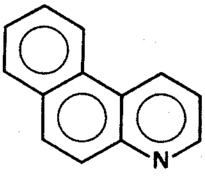

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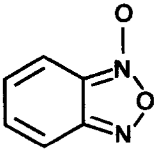
Guinier X-ray powder data indicate that the new metal fluorides Rb_3TiF_7 and Cs_3TiF_7 have the tetragonal K_3SiF_7 structure, space group *P4/mbm*. The Ti^{4+} ion is octahedrally coordinated by F^- ions $\{\bar{r}(Ti-F) = 1.91$ Å (in the Rb^+ salt) or 1.92 Å (in the Cs^+ salt)$\}$. The presence of octahedral $\{TiF_6\}$ groups in these compounds has been confirmed by Raman spectroscopy [10]. The structure of $[N_2H_6]_2F_2[TiF_6]$ consists of hydrazinium(2+) cations, fluoride anions, and discrete, nearly regular, octahedral $[TiF_6]^{2-}$ anions $\{\bar{r}(Ti-F) = 1.862$ Å$\}$; these units are connected by N-H•••F hydrogen bonds [11].

Complex fluoroanions of the type $[TiF_4X_2]^{2-}$ (X = CF_3COO, SCN or N_3) have been characterised in solution by ^{19}F NMR spectroscopy; both *cis* and *trans* isomers were observed [12].

A variety of Lewis bases react with $TiCl_4$ to give solid adducts having stoicheiometry $TiCl_4.2L$, $TiCl_4.L$, or $2TiCl_4.L$. Phenanthridine **(1)**, benzofuroxane **(3)**, and hexamethylphosphoramide (hmpa) yield $[TiCl_4L_2]$ complexes that have been



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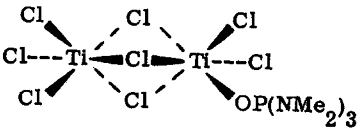
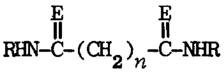
assigned a *trans*-octahedral structure on the basis of a single ν(Ti–Cl) or a single ν(Ti–L) band in their IR spectra [13-15]. The benzofuroxane ligand (3) is attached to titanium through the acyclic oxygen atom [14]. Reaction of $TiCl_4$ with hmpa (2:1 mol ratio) in nitromethane affords the dark red complex $2TiCl_4$.hmpa, which is a nonelectrolyte in dichloromethane. A confacial bioctahedral structure (4) featuring chlorine bridging and terminal attachment



(4)

of an *O*-bonded hmpa ligand has been proposed on the basis of IR and NMR evidence [15]. This structure is analogous to that of the isoelectronic $[Ti_2Cl_9]^-$ ion in $[PCl_4][Ti_2Cl_9]$ [16]. Triphenylphosphine sulphide reacts with $TiCl_4$ in benzene at reflux to give a 1:1 adduct that has been assigned a dimeric μ_2-Cl-bridged structure, $[LCl_3TiCl_2TiCl_3L]$, on the basis of molecular weight, conductance, and IR data; the IR spectra suggest that the Ph_3PS ligands are attached to titanium *via* the S atom [17]. $TiCl_4$ reacts with the bidentate amide ligands *N*,*N*'-dimethyloxamide (5), *N*,*N*'-diethyloxamide (6), *N*,*N*'-dimethyldithiooxamide (7), *N*,*N*'-diethyldithiooxamide (8), or *N*,*N*'-diethylmalonamide (9) to give solid,



$$RHN{-}\overset{\displaystyle E}{\overset{\|}{C}}{-}(CH_2)_n{-}\overset{\displaystyle E}{\overset{\|}{C}}{-}NHR$$

(5; n = 0, R = Me, E = O)
(6; n = 0, R = Et, E = O)
(7; n = 0, R = Me, E = S)
(8; n = 0, R = Et, E = S)
(9; n = 1, R = Et, E = O)

yellow or orange $TiCl_4L$ complexes, which are nonelectrolytes in nitromethane solution. Shifts in the frequencies of the ν(C–N) and ν(C–E) IR bands upon complex formation indicate a bidentate *O*,*O*- or *S*,*S*-attachment of the amide ligands, and suggest that the *S*-donor ligands are more strongly bound to titanium than the corresponding *O*-donors [18].

The enthalpies of several Lewis acid-base interactions involving $TiCl_4$ have been measured calorimetrically. The enthalpies of complex formation in benzene solution at 25 °C for $[TiCl_4\{(C_5H_{11}S)_2\}]$ (-2.9 kJ mol^{-1}) and $[TiCl_4\{(C_4H_9)_2S\}]$ (-48.1 kJ mol^{-1}) are consistent with the notion that disulphides are considerably weaker Lewis bases than monosulphides [19]. The enthalpies of formation of chlorotriphenylmethane complexes with $TiCl_4$ (-39.3 kJ mol^{-1}) and related Lewis acids indicate that Lewis acid strength toward Ph_3CCl decreases in the order [20]:

$$SbCl_5 > AlBr_3 > GaCl_3 > BCl_3 > SnCl_4 > TiCl_4 > VCl_4 > VOCl_3$$

Intercalation of graphite by $TiCl_4$ has been observed in the presence of free chlorine, but the most highly intercalated products have a Ti:C ratio of only 1:32 and $TiCl_4$ is rapidly lost upon exposure to the atmosphere [21].

Electrochemical and Raman spectroscopic studies have shown that $TiCl_4$ is present in $BaCl_2$-KCl-LiCl eutectic as the $[TiCl_6]^{2-}$ anion [22,23]. Salts of the type $[RPCl_3][Ti_2Cl_9]$ and $[RPhPCl_2][Ti_2Cl_9]$ (R = CMe_3, $CEtMe_2$, C_6H_{11}, or CPh_3) have been prepared by reaction of $TiCl_4$, PCl_3 (or $PhPCl_2$), and RCl in dichloromethane solution. These compounds behave as 1:1 electrolytes in nitromethane, and IR spectra exhibit the terminal and bridging ν(Ti-Cl) bands expected for the $[Ti_2Cl_9]^-$ anion [24]. The changes which occur upon heating $[PCl_4][Ti_2Cl_9]$ and $[PCl_4]_2[Ti_2Cl_{10}]$ have been investigated by studying their Raman spectra as a function of temperature. $[PCl_4][Ti_2Cl_9]$ melts at *ca.* 210 °C, and molten $[PCl_4][Ti_2Cl_9]$ decomposes to yield solid $[PCl_4][TiCl_5]$ and gaseous $TiCl_4$ (eqn. (1)). In $[PCl_4]_2[Ti_2Cl_{10}]$, dissociation of the dinuclear anion to give $[TiCl_5]^-$ occurs in the solid state at *ca.* 185 °C; the solid melts at *ca.* 320 °C, and $[PCl_4]^+$ and $[TiCl_5]^-$ ions are present in the melt (eqn. (2)). All of the changes in eqns. (1) and (2) are reversible [25].

$$[PCl_4][Ti_2Cl_9](s) \overset{\sim 210\ ^\circ C}{\rightleftharpoons} [PCl_4][Ti_2Cl_9](\ell) \rightleftharpoons [PCl_4][TiCl_5](s) + TiCl_4(g) \quad (1)$$

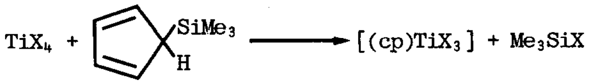
$$[PCl_4]_2[Ti_2Cl_{10}](s) \overset{\sim 185\ ^\circ C}{\rightleftharpoons} 2[PCl_4][TiCl_5](s) \overset{\sim 320\ ^\circ C}{\rightleftharpoons} 2[PCl_4][TiCl_5](\ell) \quad (2)$$

Several papers have appeared that describe the preparation and properties of organotitanium halides and pseudohalides. Two improved synthetic routes to $[(cp)TiCl_3]$ and related substituted cyclopentadienyltitanium trihalides have been reported. One involves reaction of bis(cyclopentadienyl)titanium dichlorides with SO_2Cl_2 in $SOCl_2$ at reflux (eqn. (3)) [26]. The other utilises the reagent

$$[R_2TiCl_2] + SO_2Cl_2 \longrightarrow [RTiCl_3] + SO_2 + RCl \qquad (3)$$

(R = cp or Mecp)

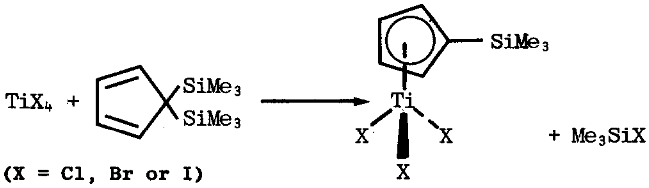
trimethylsilylcyclopentadiene (eqn. (4)). Analogous trimethylsilylcyclopentadienyl



(4)

(X = Cl, Br or I)

complexes, $[(Me_3Sicp)TiX_3]$, have been obtained by reaction of titanium(IV) halides with bis(trimethylsilyl)cyclopentadiene (eqn. (5)). Attempts to prepare adducts



(5)

(X = Cl, Br or I)

of $[(cp)TiCl_3]$, $[(cp)TiBr_3]$ and $[(Me_3Sicp)TiCl_3]$ with a variety of bidentate ligands indicate that the Lewis acidity of these complexes is much reduced from that of the parent tetrahalides; only two adducts, $[(cp)TiCl_3(phen)]$ and $[(Me_3Sicp)TiCl_3(diars)]$, could be positively identified [27]. Far IR and Raman spectra of solid and gaseous $[(cp)TiCl_3]$ and $[(cp)_2TiCl_2]$ have been reported; ring and skeletal vibrations have been assigned, and barriers to restricted rotation about the Ti-cp bonds have been calculated [28,29]. ^1H and ^{13}C chemical shifts have been reported for a series of bis(alkyl-substituted cyclopentadienyl)titanium dichlorides, $[(\eta\text{-}RC_5H_4)_2TiCl_2]$ and $[(\eta\text{-}RR'C_5H_3)_2TiCl_2]$; their ^{13}C chemical shifts can be predicted on the basis of additive contributions from the alkyl groups [30].

Stepwise electrochemical reduction of $[(cp)_2TiX_2]$ (X = Cl or Br) in thf gives $[(cp)_2TiX_2]^-$, $[(cp)_2TiX_2]^{2-}$, and $[(cp)_2TiX_2]^{3-}$. $[(cp)_2TiX_2]^-$ is stable in solution and reacts with $PPhMe_2$ to give a 1:1 adduct (EPR evidence). $[(cp)_2TiX_2]^{2-}$ dissociates into X^- and $[(cp)_2TiX]^-$, which also forms a 1:1 adduct with $PPhMe_2$ [31]. Organotitanium halides can be prepared by electrochemical oxidation of titanium metal in a cell containing an organic halide RX (R = alkyl or aryl; X = Cl, Br or I). The products are conveniently isolated as MeCN or 2,2'-bipyridine adducts, and the most commonly isolated products are $R_2TiX_2L_2$

(L = MeCN or ½bipy) [32].

Pseudohalide complexes of the type [(cp)(Mecp)TiX$_2$] (X = N$_3$, NCO, NCS or NCSe) have been synthesised, in aqueous solution at pH 2 or in thf at reflux, by reaction of [(cp)(Mecp)TiCl$_2$] with Na[N$_3$], K[OCN], K[SCN], or Na[SeCN] [33]. The corresponding [(Mecp)$_2$TiX$_2$] complexes have been prepared by similar procedures [34]. IR spectra show that the NCO, NCS and NCSe ligands in these complexes are bonded to titanium through the nitrogen atom [33,34]. Mixed isocyanate-aryloxide complexes of the type [(cp)$_2$Ti(NCO)(OAr)] have been prepared from [(cp)$_2$Ti(NCO)$_2$] and have been converted to [(cp)$_2$Ti(NCO)Br] by reaction with HBr; [(cp)$_2$Ti(NCO)Br] is relatively inert to disproportionation [35]. Related complexes of the type [(cp)(cp')TiXY] {cp' = η-C$_5$H$_3$(1-Me)(2-CHMe$_2$) or η-C$_5$H$_3$(1-Me)(3-CHMe$_2$); XY = (OAr)(Cl), (OAr)(NCS), or (Br)(NCS)} are chiral and exist as two pairs of diastereoisomers. A study of the products of substitution reactions (6) and (7) indicates that reaction (6) is stereoselective and reaction (7) is stereospecific [36].

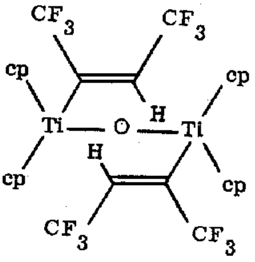
$$[(\mathrm{cp})(\mathrm{cp'})\mathrm{Ti(OAr)Cl}] \xrightarrow{\mathrm{K[NCS]}} [(\mathrm{cp})(\mathrm{cp'})\mathrm{Ti(OAr)(NCS)}] \qquad (6)$$

$$[(\mathrm{cp})(\mathrm{cp'})\mathrm{Ti(OAr)(NCS)}] \xrightarrow{\mathrm{HBr}} [(\mathrm{cp})(\mathrm{cp'})\mathrm{Ti(Br)(NCS)}] \qquad (7)$$

2.1.2 Complexes with O-donor ligands

In this section, compounds are discussed in order of increasing complexity of the *O*-donor ligand. Oxo and peroxo complexes are considered first, complexes with monodentate ligands next, and complexes with bidentate ligands last. Discussion of complexes with bidentate and polydentate ligands that contain other donor atoms in addition to oxygen is deferred to later sections dealing with the other element.

The syntheses and structures of several oxo-bridged polynuclear titanium(IV) complexes have been reported [37–40]; averaged Ti–O bond distances and Ti–$\hat{\mathrm{O}}$–Ti bond angles are summarised in Table 1. [{(cp)$_2$TiCl}$_2$O] and [{(cp)$_2$Ti(CF$_3$C=C(H)CF$_3$)}$_2$O] (**10**) are dinuclear complexes that have nearly linear



(**10**)

TABLE 1

Averaged Ti–O bond distances and Ti–O–Ti bond angles in some oxo-bridged polynuclear titanium(IV) complexes

Compound	$\bar{r}$(Ti–O)/Å	Ti–$\hat{\mathrm{O}}$–Ti	Ref.
$[\{(cp)_2TiCl\}_2O]$	1.837	173.8°	37
$[\{(cp)_2Ti(CF_3C{=}C(H)CF_3)\}_2O]$	1.856	170.0°	38
$[\{(Mecp)TiCl(\mu\text{-}O)\}_4]$	1.798	163.4°	39
$Cs_4[\{TiO(nta)\}_4].6H_2O$	1.75, 1.90	162.2°	40

Ti–O–Ti linkages and Ti–O bond lengths that indicate an appreciable amount of π-bonding involving filled p_π orbitals on oxygen and a vacant d_π orbital on titanium. In (10), all of the titanium-ligand bonds are somewhat longer than normal $\{\bar{r}(\mathrm{Ti{-}O}) = 1.856$ Å; $\bar{r}(\mathrm{Ti{-}C}_{sp^2}) = 2.239$ Å; $\bar{r}(\mathrm{Ti{-}C}_{sp}) = 2.421$ Å$\}$; this is attributed to steric effects. (10) was prepared by reaction of $[(cp)_2Ti(CO)_2]$ with hexafluorobut-2-yne in benzene solution [38]. Crystals of $[\{(cp)_2TiCl\}_2O]$ were obtained by reaction of $[(cp)_2TiCl(CH_3)]$ with traces of water in benzene solution [37]; this compound has also been prepared by oxidation of $[\{(cp)_2TiCl\}_2]$ with N_2O (eqn. (8)) [41].

$$[\{(cp)_2TiCl\}_2] + N_2O \longrightarrow [\{(cp)_2TiCl\}_2O] + N_2 \qquad (8)$$

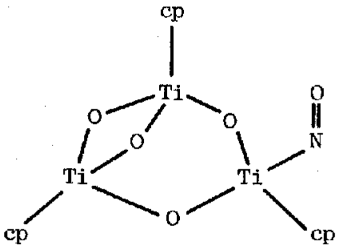
Hydrolysis of $[(Mecp)TiCl_3]$ in heptane affords the tetranuclear complex $[\{(Mecp)TiCl(\mu\text{-}O)\}_4]$ in which four $\{(Mecp)TiCl\}$ moieties are linked together by four symmetrical oxo bridges to give an eight-membered ring of alternating Ti and O atoms that has approximate D_{2d} symmetry. Once again, the Ti–O bond lengths (see Table 1) indicate an appreciable amount of Ti–O π-bonding [39]. The corresponding cyclopentadienyl derivative $[\{(cp)TiCl(\mu\text{-}O)\}_4]$ reacts with $[(cp)TiCl_3]$ to produce $[\{(cp)TiCl_2\}_2O]$ (eqn. (9)). The driving force for this

$$[\{(cp)TiCl(\mu\text{-}O)\}_4] + 4[(cp)TiCl_3] \longrightarrow 4[\{(cp)TiCl_2\}_2O] \qquad (9)$$

and related redistribution reactions has been attributed to the fact that the strong π-donor oxygen atoms prefer to be distributed over the maximum number of metal centres. This has the effect of minimising the competition among π-donors for the acceptor orbitals available on each metal centre, as well as minimising steric repulsion [42].

The $[\{TiO(nta)\}_4]^{4-}$ anion in $Cs_4[\{TiO(nta)\}_4].6H_2O$ (nta = nitrilotriethanoate) also has a tetranuclear oxo-bridged structure. Each titanium atom is six-coordinated by the tetradentate nta ligand and by two *cis* μ-oxo groups. The titanium and oxygen atoms form a centrosymmetric, puckered, eight-membered ring. However, in contrast to $[\{(Mecp)TiCl(\mu\text{-}O)\}_4]$, the oxo bridges in $[\{TiO(nta)\}_4]^{4-}$ are not symmetrical; a short Ti–O bond (1.75 Å) and a longer bond (1.90 Å) alternate [40]. It is worthy of note that the Ti–O–Ti bridges in both tetranuclear complexes exhibit appreciable deviations from linearity (*cf*. Table 1). Closely related to $Cs_4[\{TiO(nta)\}_4].6H_2O$ are the dipicolinate and iminodiethanoate complexes, $[TiO(dipic)(OH_2)].3H_2O$ and $[TiO(imda)(OH_2)].2H_2O$. These complexes may also have oxo-bridged polynuclear structures since they lack ν(Ti=O) bands in the 900–1050 cm^{-1} region of their IR spectra [40].

$[(cp)_2TiCl_2]$ reacts with $[Ti(chelate)_2(OCHMe_2)_2]$ (chelate = acac, benzac, dbzm, methyl salicylate, or the anion of salicylaldehyde) in toluene at reflux to give Me_2CHCl (1 mol) and insoluble yellow solids which have been formulated, on the basis of elemental analysis and IR spectra, as oxo-bridged complexes of the type $[(cp)_2ClTiOTi(chelate)_2(OCHMe_2)]$. A strong IR band in the region 790–820 cm has been assigned to ν(Ti–O–Ti) [43]. $[(cp)_2TiR]$ (R = Ph or Bz) reacts with NO to give a complex of stoicheiometry $Ti_3(cp)_3O_4(NO)$. This compound has been assigned an oxo-bridged structure (11) on the basis of two



(11)

^1H NMR signals for the cp ligands (relative intensities 2:1) and an IR band at 1550 cm^{-1} that can be assigned to a bent TiNO group [44].

Photolysis of benzene solutions of the peroxo(porphyrinato)titanium(IV) complexes $[Ti(O_2)(TPP)]$ and $[Ti(O_2)(TmTP)]$ ($[TPP]^{2-}$ = tetraphenylporphyrin dianion; $[TmTP]^{2-}$ = tetra-3-tolylporphyrin dianion) leads to evolution of O_2 and formation, in essentially quantitative yields, of the corresponding oxo(porphyrinato)titanium(IV) complexes. ^{18}O-labelling experiments indicate that the oxo ligand is derived exclusively from the starting peroxo complex and also that the O–O bond of the starting peroxo complex remains intact in the evolved O_2. This suggests photoinduced reductive elimination of O_2 and formation of a formal Ti(II) intermediate (eqn. (10)), followed by oxygen atom transfer from another peroxo complex (eqn. (11)). Loss of some of the O_2 as

$$[Ti^{IV}(O_2)(Por)] \xrightarrow{h\nu} [Ti^{II}(Por)] + O_2 \qquad (10)$$

$$[Ti^{II}(Por)] + [Ti^{IV}(O_2)(Por)] \longrightarrow 2[Ti^{IV}O(Por)] \qquad (11)$$

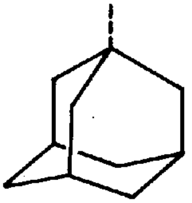
solvent oxidation products suggests that the O_2 is formed in a singlet state [45].

The peroxo- and oxotitanium(IV) complexes, $[Ti(O_2)(edta)]^{2-}$ and $[TiO(edta)]^{2-}$, have been obtained in an approximately 50:50 mixture in the first addition of O_2 to a classical titanium(III) complex, $[Ti(OH_2)(edta)]^-$. The reaction is believed to proceed *via* formation of an intermediate superoxo species (eqns. (12) and (13) [46].

$$[Ti(OH_2)(edta)]^- + O_2 \longrightarrow [Ti(O_2)(edta)]^- + H_2O \qquad (12)$$

$$[Ti(O_2)(edta)]^- + [Ti(OH_2)(edta)]^- + 2H_2O \longrightarrow [Ti(O_2)(edta)]^{2-} + [TiO(edta)]^{2-} + 2H_3O^+ \qquad (13)$$

Several new titanium(IV) alkoxides have been prepared by alcohol exchange reactions between $Ti(OCHMe_2)_4$ and the appropriate alcohol in benzene at reflux. Complexes of the type $[Ti(OR)_4]$ (R = 1-adamantyl (**12**), 2-adamantyl (**13**), or



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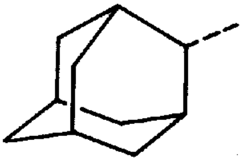


(13)

1-adamantylmethyl) were obtained as high melting, thermally stable white solids [47]. $[Ti\{OCH(CH_3)CH{=}CHCH_3\}_4]$ was isolated as a light yellow liquid (b.p. 116 °C/0.5 Torr) [48]. All of these compounds are monomeric in benzene solution.

$TiCl_3(OCH_2CH_2Cl)$ and $TiCl_2(OCH_2CH_2Cl)_2$ behave as Lewis acids toward a variety of nitrogen bases, giving insoluble solid compounds, $TiCl_3(OCH_2CH_2Cl).nL$ and $TiCl_2(OCH_2CH_2Cl)_2.nL$ (n = 1 or 2) that have been characterised by elemental analyses and IR spectra. Piperidine, morpholine, 2-, 3-, and 4-methylpyridine, and 1,2-diaminoethane afford 2:1 adducts, while

N,N,N',N'-tetramethyl-1,2-diaminoethane and *N,N*-dimethylhydrazine yield 1:1 adducts. IR bands in the region 340-410 cm^{-1}, assignable to ν(Ti-Cl), are consistent with the presence of six-coordinate titanium in these complexes [49].

The X-ray structures of $[(cp)_2Ti(OEt)Cl]$ and $[\{(cp)Cl_2Ti\}OCMe_2CMe_2O\{TiCl_2(cp)\}]$ **(14)** provide evidence for π-donation by both chloride and alkoxide ligands to

$$[(cp)Cl\overline{TiOCMe_2CMe_2O}] + [(cp)TiCl_3] \xrightarrow{C_6H_6} \underset{\textbf{(14)}}{[\{(cp)Cl_2Ti\}OCMe_2CMe_2O\{TiCl_2(cp)\}]} \qquad (14)$$

the formally coordinatively unsaturated titanium centres. Thus, the Ti-Cl distance in $[(cp)_2Ti(OEt)Cl]$ (2.405 Å) is 0.041 Å longer than the Ti-Cl distance in $[(cp)_2TiCl_2]$. This suggests that chloride and ethoxide are competitive π-donors toward titanium, and that ethoxide is the more effective π-donor. Indeed, one can consider $[(cp)_2Ti(OEt)Cl]$ to be an 18-electron complex in which the OEt ligand (considered formally as a neutral radical) behaves as a three-electron donor. In the pinacolate complex **(14)**, the high degree of coordinative unsaturation of the $\{(cp)Ti\}^{3+}$ fragment results in extensive Ti-OR and Ti-Cl π-bonding, evidenced by the shortest Ti-OR distance (1.750 Å) yet observed, the most obtuse Ti-$\hat{O}$-R angle (166.2°) yet observed, and a very short Ti-Cl distance (2.271 Å) [50]. The redistribution reaction of $[(cp)Cl\overline{TiOCMe_2CMe_2O}]$ with $[(cp)TiCl_3]$ to give compound **(14)** (eqn. (14)) provides additional evidence for Ti-OR π-bonding. This reaction goes essentially to completion, despite its unfavourable entropy change; the driving force appears to be the tendency of the π-donor oxygen atoms to be distributed over the maximum number of unsaturated metal centres [42].

$[(cp)_2Ti(CF_3SO_3)_2]$ has been prepared by reaction of $[(cp)_2TiCl_2]$ with $Ag[CF_3SO_3]$ in thf and has been found to have a covalent structure despite the low basicity of the trifluoromethanesulphonate anion. The geometry about the titanium atom is approximately tetrahedral with $\bar{r}$(Ti-O) = 2.00 Å; $\bar{r}$\{Ti-(centroid cp)\} = 2.04 Å; O-$\hat{Ti}$-O = 91.2°; and (centroid cp)-$\hat{Ti}$-(centroid cp) = 131.0° [51]. The $[(cp)_2Ti(OH_2)_2]^{2+}$ cation in $[(cp)_2Ti(OH_2)_2][ClO_4]_2.3thf$ has a closely similar structure with values of the above parameters being 2.01 Å, 2.03 Å, 90.4°, and 133.3°, respectively. $[(cp)_2Ti(OH_2)_2][ClO_4]_2.3thf$ was obtained by controlled hydrolysis of $(cp)_2Ti(ClO_4)_2$ in thf solution [52].

$TiCl_4$ reacts with $HOTeF_5$ to give $TiCl_3(OTeF_5)$, which disproportionates *via* $TiCl_2(OTeF_5)_2$ and $TiCl(OTeF_5)_3$ to give $Ti(OTeF_5)_4$, a colourless crystalline solid. The compounds $TiCl_{4-n}(OTeF_5)_n$ (n = 1-4) have been characterised in solution by ^{19}F NMR spectroscopy. $Ti(OTeF_5)_4$ behaves as a strong Lewis acid, forming a $Ti(OTeF_5)_4.2POCl_3$ adduct and reacting with $CsOTeF_5$ to give $Cs_2[Ti(OTeF_5)_6]$ [53].

Dihalophosphates and dimethylphosphinates of the type $TiCl_2(PO_2X_2)_2$ (X = F, Cl, or Me) have been synthesised by reaction of $TiCl_4$ with the appropriate trimethylsilyl ester (eqn. (15)), and also by the alternative routes indicated

$$\mathrm{TiCl_4 + 2Me_3SiOP(O)X_2 \longrightarrow TiCl_2(PO_2X_2)_2 + 2Me_3SiCl} \qquad (15)$$

(X = F, Cl or Me)

in eqns. (16) and (17). The high melting point, low solubility, and $\nu(\mathrm{PO_2})$ IR

$$\mathrm{TiCl_4 + 2X_2(O)POP(O)X_2 \longrightarrow TiCl_2(PO_2X_2)_2 + 2POX_2Cl} \qquad (16)$$

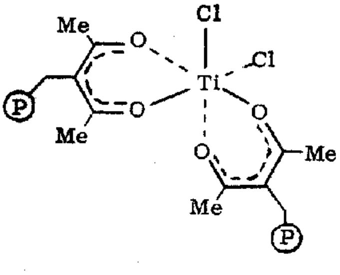
(X = F or Cl)

$$\mathrm{TiCl_4 + 2HOP(O)Me_2 \longrightarrow TiCl_2(PO_2Me_2)_2 + 2HCl} \qquad (17)$$

frequencies (ν_{as} = 1160 $\mathrm{cm^{-1}}$; ν_s = 1033 $\mathrm{cm^{-1}}$) of $\mathrm{TiCl_2(PO_2Me_2)_2}$ suggest that this compound has a polymeric structure in which the titanium atom is six-coordinate and both oxygen atoms of the $\mathrm{PO_2Me_2}$ group are attached to the metal [54,55].

Quite a number of oximate complexes of the type $\mathrm{Ti(OR)_{4-\mathit{n}}(ON{=}CR'R'')_{\mathit{n}}}$ (n = 1-4) have been prepared by reaction of $\mathrm{Ti(OR)_4}$ with an oxime in benzene solution. These complexes are monomeric in boiling benzene, except when R = Et and n = 1 or 2, in which case the degree of association is 1.2-1.7. Phenyl isocyanate inserts into the Ti-O bonds of $\mathrm{Ti\{ON{=}C(Me)C_6H_4F\}_4}$ to give $\mathrm{Ti\{ON{=}C(Me)C_6H_4F\}_{4-\mathit{n}}\{N(Ph)C(O)ON{=}C(Me)C_6H_4F\}_{\mathit{n}}}$ (n = 1-4), where the value of n depends on the stoicheiometry of the reaction mixture [56].

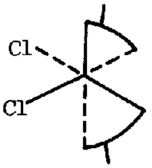
Turning to chelate complexes of titanium(IV) with *O*-donor ligands, we note first a number of synthetic and stereochemical studies of β-diketonate complexes. $\mathrm{TiCl_4}$ reacts with 4-fluoro-, 4-chloro-, or 4-bromobenzoylacetones (4-XbenzacH) or with 2-thenoyltrifluoroacetone (thtfacH) to give new complexes of the type $\mathrm{Ti(dik)Cl_3}$ or $\mathrm{Ti(dik)_2Cl_2}$, depending on the stoicheiometry of the reaction mixture. The reaction of $\mathrm{[(cp)_2TiCl_2]}$ with 4-XbenzacH (X = Cl or Br) affords complexes of the type $\mathrm{[(cp)Ti(dik)_2Cl]}$. All of these compounds are bright red solids, monomeric in boiling benzene, and nonelectrolytes in nitrobenzene [57]. The extraction of titanium(IV) from concentrated hydrochloric acid into chloroform with benzacH, thtfacH, tributylphosphate, or with mixtures of these reagents has been studied by Komatsu [58]. Cross-linked polystyrene functionalised with pentane-2,4-dionato groups reacts with $\mathrm{TiCl_4}$ in dry dichloromethane at 25 °C to give, as deep orange-red beads, the polymer bound analogue of $\mathrm{[Ti(acac)_2Cl_2]}$; the resin acts as a tetradentate ligand **(15)** towards each metal centre [59]. A series of complexes of the type $\mathrm{[(Mecp)_2Ti(acac)][Y]}$ (Y = $\mathrm{[ClO_4]}$, $\mathrm{[BF_4]}$, $\mathrm{[FeCl_4]}$, $\mathrm{[ZnCl_3(H_2O)]}$, $\mathrm{[SnCl_3]}$, $\tfrac{1}{2}\mathrm{[CdCl_4]}$, $\mathrm{[HgCl_3]}$, Br or I) has been prepared by adding a source of $\mathrm{Y^-}$ to a concentrated aqueous solution of $\mathrm{[(Mecp)_2TiCl_2]}$ that contains an excess of pentane-2,4-dione. These compounds are 1:1 electrolytes in nitrobenzene, except for $\mathrm{[(Mecp)_2Ti(acac)]_2[CdCl_4]}$, which is a 2:1 electrolyte. They



(15; Ⓟ denotes polymer backbone)

exhibit substantial downfield shifts for the ^1H NMR resonances of the acac ligand, as expected for cationic complexes [60]. A series of related cyclopentadienyl complexes, $[(cp)_2Ti(acac)][MX_4]$ (M = Ga, In, or Tl; X = Cl, Br, or I), has also been reported [61].

NMR line-broadening studies of several $[Ti(dik)_2Cl_2]$ and $[Ti(dik)_2Cl(OR)]$ complexes that contain diastereotopic isopropyl methyl groups have been carried out in an attempt to elucidate the stereochemistry and the kinetics of configurational rearrangements of these complexes. It has been found that: (i) $[Ti(acac)_2Cl(OCHMe_2)]$, $[Ti(acac)_2Br(OCHMe_2)]$, $[Ti(acac)_2Cl\{2,6\text{-}(CHMe_2)_2C_6H_3O\}]$, and $[Ti(CHMe_2COCHCOCHMe_2)_2Cl(OMe)]$ exist exclusively in CH_2Cl_2 solution as the *cis* geometrical isomer; (ii) $[Ti(CF_3COCHCOCHMe_2)_2Cl_2]$ and $[Ti(CF_3COCHCOCMe_3)_2Cl_2]$ exist in CH_2Cl_2 as an equilibrium mixture of the three geometrical isomers that have chlorine atoms in the *cis* positions, **(16)**-**(18)**; and (iii) exchange of



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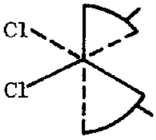

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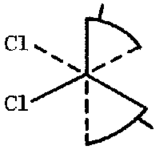


(18)

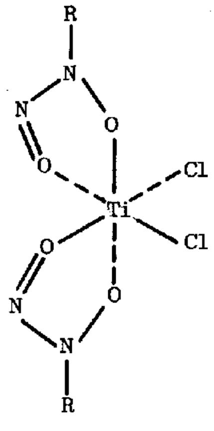
β-diketonate ring substituents in these complexes is accompanied by inversion of configuration ($\Delta \rightleftharpoons \Lambda$) at the metal centre. The authors prefer a mechanism that involves twisting about two of the four C_3 axes of the octahedral framework [62-64].

Titanium(IV) trichloroethanoate, $Ti(CCl_3CO_2)_4$, has been prepared by reaction of $TiCl_4$ with an excess of hot trichloroethanoic acid. With py, pyNO, or Ph_3PO, $Ti(CCl_3CO_2)_4$ behaves as a Lewis acid, forming $Ti(CCl_3CO_2)_4L_2$ adducts. The IR spectra and the low solubility of $Ti(CCl_3CO_2)_4$ and its adducts suggest that these complexes may be polymeric [65]. Bis(carboxylato) complexes of the type

$[(\mathrm{Mecp})_2\mathrm{Ti}(\mathrm{RCO_2})_2]$ (R = Me, Et, Pr, Ph, CH_2Cl, or $CHCl_2$) have been synthesised, in aqueous solution and in thf, by reaction of $[(\mathrm{Mecp})_2\mathrm{TiCl_2}]$ with $[\mathrm{RCO_2}]\mathrm{Na}$. An approximately 300 cm^{-1} splitting between the $\nu_{as}(CO_2)$ and $\nu_{s}(CO_2)$ IR bands in the chloroethanoate derivatives indicates that the $[CH_2ClCO_2]^-$ and $[CHCl_2CO_2]^-$ groups behave as monodentate ligands. However, a corresponding splitting of only ~100 cm^{-1} for the other carboxylate derivatives points to a bidentate attachment of the $[RCO_2]^-$ groups when R = Me, Et, Pr, or Ph. $[(\mathrm{Mecp})_2\mathrm{Ti}(\mathrm{RCO_2})_2]$ complexes with bidentate carboxylato and η^5-Mecp ligands would be 20-electron complexes; the authors propose instead that these compounds are 16-electron complexes in which one of the Mecp rings behaves as an η^1-ligand [66]. The structures of these complexes should be investigated.

A full paper has appeared reporting the He-I and He-II photoelectron spectrum of gaseous $[Ti(NO_3)_4]$. Peaks not present in the spectrum of $K[NO_3]$ are taken as evidence for strong titanium-ligand bonding involving the 4e'' (oxygen $2p_\sigma$) MO's of the nitrate ion [67].

Titanium alkyls of the type TiR_2Cl_2, TiR_3Cl, and TiR_4 (R = CH_2CMe_3 or CH_2SiMe_3) react with nitric oxide to give *N*-alkyl-*N*-nitrosohydroxylaminato complexes, $[\mathrm{Ti}\{\mathrm{ON(R)NO}\}_n\mathrm{Cl}_{4-n}]$ (n = 2, 3 or 4), which have been formulated, on the basis of IR and NMR spectroscopic evidence, as the six-coordinate complexes **(19)**-**(21)**, containing bidentate and monodentate ON(R)NO groups [44].



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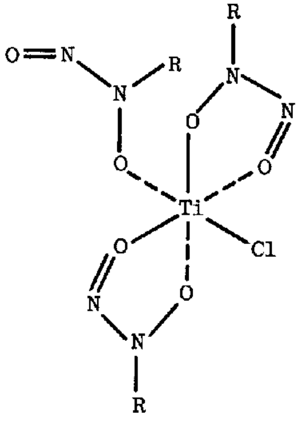

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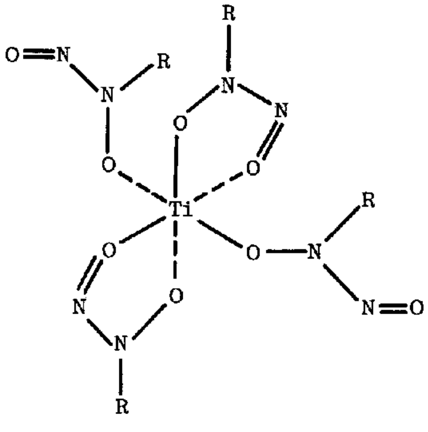

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Maluka and Tur'yan have determined stability constants for formation of oxalato and hydrogen oxalato complexes with titanium(IV) and titanium(III) in acidic aqueous solution [68]. A TGA, DTGA, and DTA study of the thermal decomposition of $TiO(C_2O_4).3.5H_2O$ indicates stepwise decomposition to TiO_2 *via*

$TiO(C_2O_4).2H_2O$ and the basic carbonate $TiO(CO_3).2TiO_2$ [69].

^{183}W NMR chemical shifts have been reported for the α-$[(cp)Ti(PW_{11}O_{39})]^{4-}$ anion; these have been interpreted in terms of a *trans* bond alternation mechanism for the delocalisation of charge [70].

2.1.3 Titanates(IV) and mixed-metal oxides

The synthesis and structure of metal titanates continues to be of interest because of the refractory and ferroelectric properties of these materials. This section discusses alkali, alkaline earth, transition metal, and lanthanide titanates, and also mixed-metal oxides such as titanoniobates and titanotantalates.

New sodium titanium dioxide bronzes $Na_xTi_4O_8$ have been synthesised by hydrothermal reactions between titanium dioxide gel and 5 *M* NaOH. The products obtained in reactions carried out at 250-300 °C have a disordered arrangement of Na^+ ions, while the products synthesised at 350-530 °C display a superlattice that results from an ordered arrangement of Na^+ ions [71]. Several new alkali metal titanoniobates and titanotantalates have been prepared by heating mixtures of TiO_2, M_2O_5 (M = Nb or Ta), and a suitable alkali metal compound, *e.g.* A_2CO_3. These mixed-metal oxides have layer or tunnel structures in which units of two or three edge-shared octahedra ($\{TiO_6\}$ or $\{MO_6\}$) are stacked together by corner sharing. In $CsTi_2NbO_7$ [72], $ATiTaO_5$ (A = K or Rb) [73], and $A_{1-x}Ti_{1-x}Nb_{1+x}O_5$ (A = K, Rb, Tl or Cs; $0 < x \leq 0.15$) [73], the octahedra stack so as to give layer structures in which puckered layer titanoniobate or titanotantalate anions are held together by the A^+ cations. In ATi_3MO_9 and $ATi_3MO_9.(A_2Ti_6O_{13})_n$ (M = Nb or Ta; n = 1, 2 or 3) [74], the A^+ cations occupy tunnels in a three-dimensional framework built up from the edge- and corner-shared octahedra.

Hydrothermal synthesis of $BaTiO_3$ affords a highly dispersed, high purity product that has a perovskite structure, although the crystal system and unit cell parameters vary with the synthesis temperature [75]. The X-ray crystal structure of $Ba_6Ti_2Nb_8O_{30}$ is similar to that of $K_6W_{10}O_{30}$, with a statistical distribution of Ti and Nb in the W sites. However, unlike $K_6W_{10}O_{30}$, which has been reported to be tetragonal (space group *P4/mbm*), $Ba_6Ti_2Nb_8O_{30}$ is orthorhombic (space group *Pbam*), despite the equality of the a and b lattice parameters; this result suggests that the structure of $K_6W_{10}O_{30}$ should be reinvestigated [76]. The phases which exist in the TiO_2-Ta_2O_5 system have been investigated in the temperature range 20-1400 °C and the composition range, Ti/(Ti + Ta), of 0-6.7 atom % [77]. The use of KF + CdF_2 (or CdO) + B_2O_3 melts as solvents for the synthesis of $CdGaTiTaO_7$ single crystals reduces the synthesis temperature by 300-400 °C relative to the 1200 °C temperature needed for solid phase synthesis; optimum compositions of the melts are reported [78]. Synthetic ilmenite, $FeTiO_4$, has been prepared by fusion of a stoicheiometric mixture of Fe_2O_3 and TiO_2

powders (eqn. (18)) [79].

$$Fe_2O_3 + 2TiO_2 \longrightarrow 2FeTiO_3 + \tfrac{1}{2}O_2 \qquad (18)$$

Shock-wave synthesis of the lanthanide titanates, Ln_2TiO_5 (Ln = Sm-Lu or Y), from a 1:1 mixture of Ln_2O_3 and TiO_2 at 1500-2000 °C and 1.0-1.5 mbar pressure affords the hexagonal modification of Ln_2TiO_5 [80]. IR and Raman spectra (1000-30 cm^{-1}) have been reported for Ln_2TiO_5 (Ln = La, Nd-Dy or Y), and the bands have been assigned on the basis of a theoretical calculation for Nd_2TiO_5 [81]. Lattice parameters, densities, and melting points have been determined for several new ferroelectric compounds that possess a layer perovskite-like structure; the following compounds were studied: $Pr_2Ti_2O_7$, $CaLaTiNbO_7$, $SrLnTiNbO_7$ (Ln = La or Pr), and $SrLnTiTaO_7$ (Ln = La, Pr or Nd) [82]. New barium lanthanum titanates, $BaLa_2Ti_nO_{2n+4}$ (n = 2, 3 or 4), have been prepared by heating stoicheiometric mixtures of $BaCO_3$, La_2O_3 and TiO_2 in air at 1250 °C, and also by heating stoicheiometric mixtures of the simple titanates (eqns. (19)-(21)).

$$BaTiO_3 + La_2TiO_5 \longrightarrow BaLa_2Ti_2O_8 \qquad (19)$$

$$BaTiO_3 + La_2Ti_2O_7 \longrightarrow BaLa_2Ti_3O_{10} \qquad (20)$$

$$BaTiO_3 + La_2Ti_2O_7 + TiO_2 \longrightarrow BaLa_2Ti_4O_{12} \qquad (21)$$

The latter approach gives the individual $BaLa_2Ti_nO_{2n+4}$ phases, while use of the oxides as starting materials yields complex multiphase mixtures [83]. Analogous isostructural series of barium lanthanide titanates, $BaLn_2Ti_3O_{10}$ (Ln = Pr-Eu) and $BaLn_2Ti_4O_{12}$ (Ln = Pr-Gd), have been synthesised at 1250 °C by reactions analogous to eqns. (20) and (21). However, phases with a stoicheiometry $BaLn_2TiO_8$ were not observed (except for Ln = La) [84].

Lanthanide titanoantimonates $LnTiSbO_6$ (Ln = La-Lu) have been prepared by heating stoicheiometric mixtures of the coprecipitated hydroxides. Two polymorphic forms of each $LnTiSbO_6$ exist in the temperature range 800-1250 °C, a low temperature metastable cubic form and a stable high-temperature modification. The high-temperature modification depends on the ionic radius of Ln^{3+}; it is hexagonal for La-Pr, orthorhombic for Nd-Gd, and monoclinic for Tb-Lu [85].

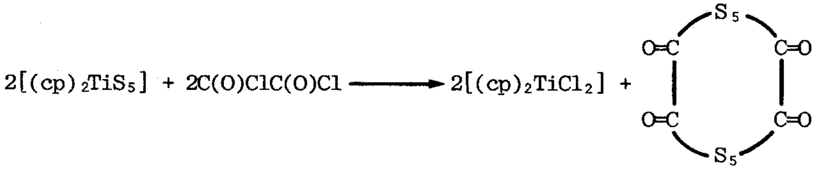
2.1.4 Complexes with S-donor ligands

TiX_4 (X = F or Cl) reacts with the sodium salt of piperazine 1,4-di(carbodithioate) to give complexes of the type $[X_2Ti\{S_2CN(CH_2CH_2)_2NC(S)SH\}_2]$. On the basis of IR spectroscopic evidence, these compounds have been assigned a.

trans-octahedral structure in which one CS_2^- group of each piperazine 1,4-di(carbodithioate) acts as a bidentate ligand while the other CS_2^- group is attached to a proton [9,86]. $[(Mecp)Ti(S_2CNMe_2)_3]$ has been prepared in aqueous and in non-aqueous media by the reaction of $[(Mecp)_2TiCl_2]$ with $Na[S_2CNMe_2]$. This compound has been assigned a seven-coordinate structure on the basis of molecular weight, conductance, and IR data; the IR spectrum shows the presence of bidentate dithiocarbamato ligands and an η^5-Mecp group [87]. A pentagonal bipyramidal geometry with the Mecp group in an axial position is likely, as has been established by X-ray diffraction for the analogous $[(cp)Ti(S_2CNMe_2)_3]$ complex [88]. The presence of more than one dithiocarbamate methyl resonance in the ^1H NMR spectrum of $[(Mecp)Ti(S_2CNMe_2)_3]$ at 30 °C indicates that stereochemical rearrangement of this compound is still slow on the NMR time scale at that temperature [87].

Chlorotris(dithioethanoato)titanium(IV), $[Ti(S_2CMe)_3Cl]$, has a seven-coordinate pentagonal bipyramidal structure in which the Cl atom occupies an axial position $\{r(Ti{-}Cl) = 2.248(2)\ \text{Å};\ r(TiS_{ax}) = 2.480(2)\ \text{Å};\ \bar{r}(Ti{-}S_{eq}) = 2.536\ \text{Å}\}$ [89]. The structure is very similar to that of $[Ti(S_2CNMe_2)_3Cl]$ [90].

An interesting reaction of $[(cp)_2TiS_5]$ has been reported by Roesky *et al.* [91]. The S_5 group of $[(cp)_2TiS_5]$ condenses with oxalyl chloride in carbon disulphide to give the 14-membered heterocyclic tetraone **(22)** (eqn. (22)).



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(22)

Solid titanium(IV) hexathiohypodiphosphate TiP_2S_6 has an extended three-dimensional structure in which each Ti^{4+} ion is attached to three bidentate chelating $[S_3PPS_3]^{4-}$ ions and each $[S_3PPS_3]^{4-}$ ion bridges between three Ti^{4+} ions. The coordination geometry of the titanium is distorted octahedral, with $r(Ti{-}S)$ ranging from 2.433 to 2.454 Å. Each titanium is a member of two four-membered $\{TiS_2P\}$ chelate rings and one five-membered $\{TiS_2P_2\}$ chelate ring [92].

2.1.5 Sulphides

Alkali intercalation compounds of layered transition metal dichalcogenides such as TiS_2 continue to be subjects of intense study because of the applicability of these materials as cathodes in the construction of high energy density batteries. The intercalation of lithium into TiS_2 is continuous over the entire composition range Li_xTiS_2 ($0 \le x \le 1$). The crystalline structure of TiS_2 is maintained upon intercalation, with only a 10% lattice expansion perpendicular to the sulphide sheets for $x = 1$. Consequently the intercalation reaction is rapid and highly reversible [93]; the mechanism of this reaction has been investigated by optical and X-ray techniques [94]. A neutron diffraction study of Li_xTiS_2 for $x = 0.12, 0.33, 0.67$ or 1.0 has shown that the lithium atoms preferentially occupy the octahedral sites in the van der Waals gap of the host TiS_2 structure. There is no evidence for three-dimensional ordering of lithium [95].

In contrast to Li_xTiS_2, Na_xTiS_2 exhibits several phases in the composition range $0 \le x \le 1$; an X-ray study indicates that these phases have different three-dimensionally ordered arrangements of sodium [96]. The presence of more than one phase in the Na-TiS_2 system is also revealed by plateaux in a plot of the voltage of the Na_xTiS_2 electrode versus the compositional parameter x [97].

A single crystal X-ray study has shown that $BaTiS_3$ is isostructural with $BaNiO_3$, $BaVS_3$, and $BaTaS_3$ (space group $P6_3/mmc$). The titanium atoms in $BaTiS_3$ are octahedrally coordinated by S atoms $\{r(\text{Ti-S}) = 2.419(5)\ \text{Å}\}$ [98].

2.1.6 *Complexes with N-donor ligands*

Mono- and bis-azido-complexes of Ti(IV) have been prepared by reaction of trimethylsilyl azide with $[TiCl(OCHMe_2)_3]$ (eqns. (23) and (24)). The

$$[TiCl(OCHMe_2)_3] + Me_3Si(N_3) \longrightarrow [TiCl(OCHMe_2)_2(N_3)] + Me_3SiOCHMe_2 \qquad (23)$$

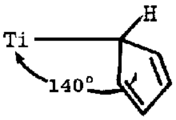
$$[TiCl(OCHMe_2)_3] + 2Me_3Si(N_3) \longrightarrow [Ti(OCHMe_2)_2(N_3)_2] + Me_3SiOCHMe_2 + Me_3SiCl \qquad (24)$$

bis-azido-complex $[Ti(OCHMe_2)_2(N_3)_2]$ is also obtained from the reaction of $Me_3Si(N_3)$ with $Ti(OCHMe_2)_4$. The reactions of the azido group in $[(cp)TiCl_2(N_3)]$ with alcohols, secondary amines or phosphines have been investigated. Trifluoroethanol displaces the $[N_3]^-$ ligand to give HN_3 and $[(cp)TiCl_2(OCH_2CF_3)]$. Displacement of $[N_3]^-$ with *cis*-butene-1,4-diol yields the mononuclear complex $[(cp)TiCl_2(OCH_2CH{=}CHCH_2OH)]$ or the dinuclear diolato-bridged complex $[Cl_2(cp)Ti(OCH_2CH{=}CHCH_2O)Ti(cp)Cl_2]$, depending on the temperature. Pyrocatechol displaces $[N_3]^-$ and one Cl^- to give $[(cp)TiCl(O_2C_6H_4)]$. The secondary amine $NHEt_2$ cleaves the Ti-Cl bond instead of the Ti-N_3 bond, yielding HCl and $[(cp)TiCl(NEt_2)(N_3)]$. Phosphines ($PR_3 = PMe_3$ or PMe_2Ph) react with $[(cp)TiCl_2(N_3)]$ to give N_2 and the phosphiniminato-complexes $[(cp)TiCl_2(N{=}PR_3)]$ [99].

$[AsPh_4]_2[TiCl_4(N_3)_2]$ has been prepared in dichloromethane from a stoicheiometric mixture of $TiCl_4$ and $[AsPh_4][N_3]$. An X-ray study reveals that the azide groups in $[TiCl_4(N_3)_2]^{2-}$ occupy *trans* positions, and their conformation gives the ion C_2 symeetry $\{r(Ti-N_1) = 2.006$ Å; $r(N_1-N_2) = 1.166$ Å; $r(N_2-N_3) = 1.169$ Å; $Ti-\hat{N}_1-N_2 = 128.1^\circ$; $N_1-\hat{N}_2-N_3 = 174.8^\circ\}$ [100].

The reaction of $TiCl_4$ with an excess of $Li[N(SiMe_3)_2]$ yields the chlorotris{bis(trimethylsilyl)amido} complex $[TiCl\{N(SiMe_3)_2\}_3]$. The resistance of this compound to complete substitution of chloride suggests the presence of considerable steric crowding due to the bulky $[N(SiMe_3)_2]^-$ ligands. This has been confirmed by X-ray crystallographic and NMR spectroscopic studies. In the solid state, $[TiCl\{N(SiMe_3)_2\}_3]$ has crystallographically imposed C_3 symmetry and a distorted tetrahedral geometry $\{r(Ti-Cl) = 2.259$ Å; $r(Ti-N) = 1.940$ Å$\}$. Crowding is evidenced by $Cl-\hat{T}i-N$ (104.1°) being less than $N-\hat{T}i-N$ (114.3°) and by $Ti-\hat{N}-Si$ proximal to Cl (116.0°) being less than $Ti-\hat{N}-Si$ distal to Cl (127.2°). Its ^1H NMR spectrum, which exhibits two equally intense resonances below the coalescence temperature of 34 °C, was interpreted in terms of restricted rotation about the Ti-N bonds. At low temperatures, the three silylamide ligands remain equivalent, but the $SiMe_3$ groups proximal and distal to chlorine are nonequivalent [101].

The di(pyrrolyl) complex $[(cp)_2Ti(\eta^1-NC_4H_4)_2]$ has been synthesised by reaction of $[(cp)_2TiCl_2]$ with (pyrrolyl)sodium in thf. This compound is formally isoelectronic with $[(\eta^5-cp)_2Ti(\eta^1-cp)_2]$, and it is structurally similar to $[(\eta^5-cp)_2Ti(\eta^1-cp)_2]$ in that both compounds contain two η^5- and two η^1-ligands. However, $[(\eta^5-cp)_2Ti(\eta^1-cp)_2]$ and $[(\eta^5-cp)_2Ti(\eta^1-NC_4H_4)_2]$ differ in that the former exhibits a $Ti-\hat{C}$-(centroid η^1-cp) angle **(23)** of 140°, consistent with sp^3 hybridisation at the carbon atom, while the latter displays a $Ti-\hat{N}$-(centroid $\eta^1-NC_4H_4$) angle **(24)** of 166°, indicative of sp^2 hybridisation at the nitrogen atom. The 166° bond angle and a short Ti-N bond length ($\bar{r} = 2.085$ Å) point to considerable $d_\pi-p_\pi$ character in the Ti-N bond [102].



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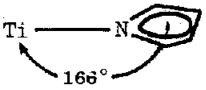
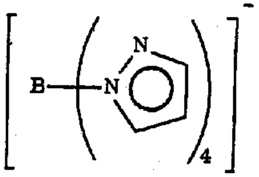


(24)

An X-ray study of $[Ti\{(NCMe_3)_2SiMe_2\}_2]$ has established a spirocyclic structure of approximate D_{2d} symmetry with planar $\{TiN_2Si\}$ rings $\{\bar{r}(Ti-N) = 1.890$ Å; $N-\hat{T}i-N = 83.4^\circ\}$ [103].

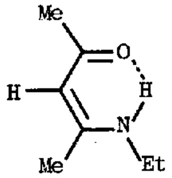
The known titanium(III) complexes $[(cp)_2TiL]^+$ (L = bipy or phen) have been oxidised with $[NO][PF_6]$ in MeCN to give the corresponding titanium(IV) dications, which have been isolated as green $[(cp)_2TiL][PF_6]_2$ salts. These compounds are the first $(cp)_2Ti(IV)$ derivatives with netural bidentate ligands to have been isolated [104].

$[Ti(BPz_4)_4]$ has been prepared by reaction of stoicheiometric amounts of $TiBr_4$ and $K[BPz_4]$ ($[BPz_4]^-$ = tetrakis(pyrazol-1-yl)borate anion **(25)**). The ^1H NMR spectrum of $[Ti(BPz_4)_4]$ indicates that only three of the four pyrazolyl groups are equivalent. This observation has been interpreted in terms of a stereochemically nonrigid eight-coordinate structure with bidentate $[BPz_4]^-$ ligands that are involved in some type of a rearrangement process [105].

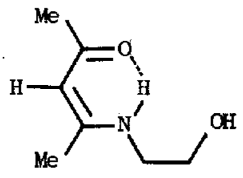


(25; $[BPz_4]^-$)

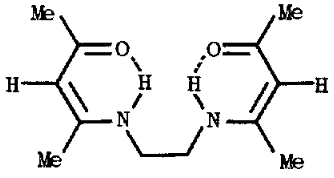
Schiff base complexes of the type $[(cp)_2TiCl(L)]$, $[(cp)_2Ti(L)_2]$, $[(cp)_2Ti(L')]$, and $[(cp)_2Ti(L'')]$ have been synthesised in refluxing thf by reaction of stoicheiometric amounts of $[(cp)_2TiCl_2]$, triethylamine, and any one of a large number of bidentate (HL), tridentate (H_2L'), and tetradentate (H_2L'') Schiff bases; one example of each type of Schiff base is shown in **(26)**-**(28)**. These compounds are monomeric nonelectrolytes in solution. On the basis of their IR and ^1H NMR spectra, they have been assigned five- and six-coordinate structures **(29)**-**(31)** in which all of the oxygen and nitrogen atoms are coordinated to the



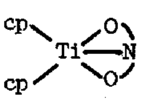
(26; HL)



(27; H_2L')



(28; H_2L'')



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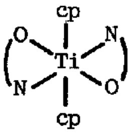

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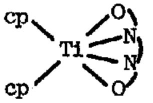
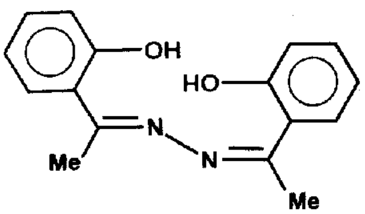


(31)

metal [106,107]. For both steric and electronic reasons, six-coordinate $(cp)_2Ti(IV)$ derivatives are unlikely; the crystal structures of these compounds should be investigated.

$Ti(OCHMe_2)_4$ reacts in benzene at reflux with a variety of dibasic tridentate Schiff bases, H_2L, in 1:1 and 1:2 mole ratios to give complexes of the type $[Ti(OCHMe_2)_2(L)]_2$ and $[Ti(L)_2]$, respectively. The Schiff bases that undergo these reactions include azines **(32)** [108], semicarbazones **(33)** [109], thiosemicarbazones **(34)** [110], and other *S*-containing tridentate Schiff bases **(35)** [111];



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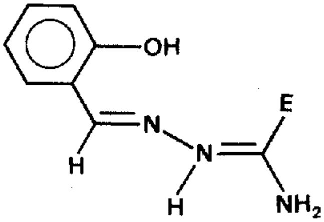
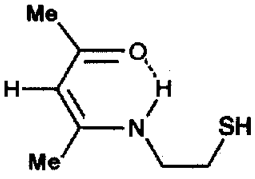


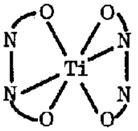
(33; E = O)

(34; E = S)



(35)

one example of each type of ligand is shown in **(32)**-**(35)**. Molecular weight measurements indicate that the $[Ti(L)_2]$ complexes are monomeric in solution, while the $[\{Ti(OCHMe_2)_2(L)\}_2]$ analogues are dimeric. Six-coordinate structures have been proposed in which $[L]^{2-}$ behaves as an *ONO* or *ONS* tridentate ligand, for example **(36)** and **(37)** for the azine complexes. Alkoxide exchange reactions



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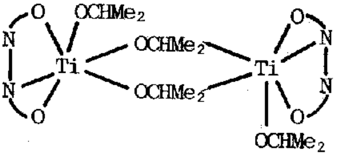
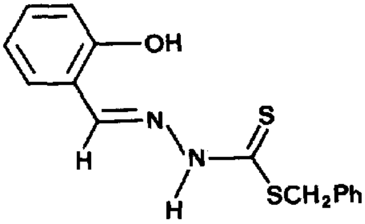


(37)

of the $[\{Ti(OCHMe_2)_2(L)\}_2]$ complexes with alcohols such as Me_3COH, 2-methylpentane-2,4-diol ($C_6H_{14}O_2$) or benzene-1,2-diol ($C_6H_6O_2$) afford the $Ti(OCMe_3)_2L$, $Ti(C_6H_{12}O_2)(L)$ or $Ti(C_6H_4O_2)(L)$ derivatives respectively [108-111].

The dithiocarbazate Schiff base H_2L **(38)** reacts with $TiCl_4$, $Ti(OCHMe_2)_4$ or $Ti(OCHMe_2)_2(L')_2$ (L' = anion of salicylaldehyde, benzoylacetone, or benzoylphenylhydroxylamine) to give $TiCl_2(L).HCl$, $[Ti(L)_2]$ or $[Ti(L)(L')_2]$, respectively. IR spectra suggest tridentate (*ONS*) attachment of $[L]^{2-}$ in $[Ti(L)_2]$, but the mode of attachment of $[L]^{2-}$ in the $[Ti(L)(L')_2]$ complexes is not yet clear [112].

Mixed-ligand complexes $[Ti(L)(L')]$ that contain the dinegative anions of two different *ONO* tridentate Schiff bases have been prepared in benzene at reflux by



(38; H_2L)

reaction of a 1:1:1 mole ratio of $Ti(OCHMe_2)_4$, H_2L and H_2L' [113,114]. *ONNO* tetradentate Schiff bases H_2L {related to (28)} react with $Ti(OCHMe_2)_4$ in benzene at reflux to give six-coordinate complexes of the type $[Ti(OCHMe_2)_2(L)]$ [115].

2.1.7 *Complexes with P-donor ligands*

$TiCl_4$ reacts with $P(NCO)_3$ or $P(CN)_3$ in benzene solution to give $TiCl_3P(NCO)_2$ or $TiCl_3P(CN)_2$, respectively (eqn. (25)). These compounds have been obtained

$$TiCl_4 + PX_3 \longrightarrow TiCl_3(PX_2) + ClX \qquad (25)$$
$$(X = NCO \text{ or } CN)$$

as somewhat impure, very hygroscopic solids. On the basis of IR spectroscopic evidence, the $P(NCO)_2$ and $P(CN)_2$ ligands are believed to be coordinated through the phosphorus atom [116].

2.1.8 *Complexes with Si-donor ligands*

$[(cp)_2Ti(SiMe_3)Cl]$ has been synthesised by reaction of $[(cp)_2TiCl_2]$ with $Al(SiMe_3)_3.Et_2O$ or $Li[Al(SiMe_3)_4].3Et_2O$. An analogous reaction with $Al(GeMe_3)_3.Et_2O$ affords the germanium analogue $[(cp)_2Ti(GeMe_3)Cl]$. The trimethylsilyl complex has a distorted tetrahedral structure with $r(Ti\text{-}Si) = 2.67$ Å; $r(Ti\text{-}Cl) = 2.31$ Å, $Cl\text{-}\hat{T}i\text{-}Si = 87^\circ$ and $cp\text{-}\hat{T}i\text{-}cp = 132^\circ$ [117]. The reaction of $[(cp)_2Ti(CO)_2]$ with $HSiCl_3$ yields a poorly characterised, extremely air-sensitive, brown solid that appears, on the basis of analytical data, to be a mixture of $(cp)_2Ti(H)(SiCl_3)$ and $(cp)_2Ti(H)(CO)(SiCl_3)$ [118].

Titanium has been incorporated into a catenated silicon ring by reaction of $[(cp)_2TiCl_2]$ with 1,4-dilithiooctaphenyltetrasilane, $Li_2Si_4Ph_8$, to yield $[(cp)_2\overline{TiSiPh_2(SiPh_2)_2Si}Ph_2]$. This compound has been characterised as a cyclometallopolysilane by means of elemental analysis, molecular weight determination, base catalysed hydrolysis, and IR, ^1H NMR, and ^{13}C NMR spectroscopy [119,120].

2.2 TITANIUM(III) COMPOUNDS

2.2.1 Halide and pseudohalide complexes

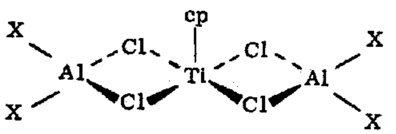
X-ray structural data have been reported for complex fluorides of the types $CsM^{II}Ti^{III}F_6$ (M^{II} = Mg, V, Mn, Fe, Co, Ni or Zn) and $CsM^{I}_{0.5}Ti^{III}_{1.5}F_6$ (M^{I} = Li, Na, K, Rb or $[NH_4]$). The former compounds are cubic with a modified pyrochlore structure of the $RbNiCrF_6$ type; the latter are cubic when M^{I} = K or Rb, monoclinic when M^{I} = Li or Na, and orthorhombic when M^{I} = $[NH_4]$ [121].

The hexamethylphosphoramide adduct $[TiCl_3(hmpa)_3]$ has been obtained as a pale blue, air-sensitive solid by reaction of $TiCl_3$ with hmpa in dry thf. Conductance measurements and IR spectra suggest that this complex has a *facial* (C_{3v}) octahedral structure in which the hmpa ligands are attached to titanium through the oxygen atom [15].

Reaction of equimolar amounts of $TiCl_4$ and the cyclic amides Me_3SiNR (R = $(CH_2)_4$ or $(CH_2)_5$) in hydrogen-containing solvents (such as benzene, toluene or dichloromethane) results in reduction to titanium(III) with formation of air-sensitive solids of composition $Ti_3Cl_9.2RNH$. This reaction is thought to involve formation of RN• free readicals and H-atom abstraction from the solvent since no reduction occurs when the reaction is performed in CCl_4; in the latter solvent, the products are the titanium(IV) adduct $3TiCl_4.2Me_3SiNR$ and the substitution derivative $TiCl_3(NR)$. Reaction of 2:1 molar mixtures of $TiCl_4$ and Me_3SiNR in benzene at reflux results in reduction and partial substitution, yielding compounds of composition $Ti_3Cl_8(NR).2RNH$. All of the titanium(III) complexes are quite insoluble in organic solvents; they are probably polymeric [122].

Reduction of $[(cp)_2TiCl_2]$ and $[Ti(acac)_2Cl_2]$ with $[Ni(cod)_2]$ does not lead to reductive coupling with formation of metal-metal bonds. Instead, only partial reduction occurs. Reduction of $[(cp)_2TiCl_2]$ in pyridine gives $[(cp)_2Ti(py)Cl]$; reduction of $[Ti(acac)_2Cl_2]$ yields $[\{Ti(acac)_2Cl\}_2]$ [123].

Ethyl-substituted trinuclear complexes $[(cp)TiAl_2Cl_{8-x}Et_x]$ (**39**; x = 1,2,3 or 4)



(39; X = Cl or Et)

have been prepared by reaction of $[(cp)TiCl_3]$ with two equivalents of ethylaluminium compounds. These complexes have been characterised by electronic and EPR spectroscopy, and their spectra have been used to study the composition of complexes formed in mixtures of $[(cp)TiAl_2Cl_8]$ and $Et_{3-x}AlCl_x$ (x = 0, 1 or 2). The stability of the $[(cp)TiAl_2Cl_{8-x}Et_x]$ complexes decreases with increasing values of x [124].

Raman spectroscopic studies have shown that titanium(III) exists in a $BaCl_2$-KCl-LiCl eutectic at 450 °C as $[TiCl_6]^{3-}$. However, in CsCl-LiCl at 450 °C, a different complex is formed, perhaps $[Ti_2Cl_9]^{3-}$ [23].

The intercalation compound $TiOCl.0.16[(cp)_2Co]$ has been prepared by heating TiOCl with a toluene solution of $[(cp)_2Co]$. X-ray powder diffraction data are consistent with a structural model in which $[(cp)_2Co]$ occupies the van der Waals gaps in the layered structure of TiOCl with the cyclopentadienyl rings perpendicular to the layers [125].

Grey-green complex cyanides of titanium(III), $K_5Ti(CN)_8$, $Rb_5Ti(CN)_8$, and $Cs_4Ti(CN)_7$, have been synthesised by reaction of $TiBr_3$ with alkali cyanides in liquid ammonia; the rubidium and caesium compounds are new. All three compounds have very similar IR and electronic spectra, which exhibit five or six ν(CN) bands and three $d \leftrightarrow d$ transitions, respectively. On this basis, all three compounds are believed to contain the seven-coordinate $[Ti(CN)_7]^{4-}$ ion. In view of the number of ν(CN) and $d \leftrightarrow d$ bands, a C_{2v} monocapped trigonal prismatic structure is most likely. Thermal decomposition of $K_5Ti(CN)_8$ *in vacuo* at 280 °C, followed by extraction of KCN with liquid ammonia, affords an almost black residue of $K_3Ti(CN)_6$. This compound exhibits only one ν(CN) IR band and displays an electronic spectrum characteristic of octahedrally coordinated titanium(III) ($10Dq$ = 22100 cm^{-1}) [126].

2.2.2 Complexes with O-donor ligands

The reactions of N_2O with $[(cp)_2Ti]$ or $[(cp)_2Ti(CO)_2]$ have been studied by Bottomley *et al.* [41]. When $[(cp)_2Ti]$ or $[(cp)_2Ti(CO)_2]$ are in excess, the products are the titanium(III) complexes $[\{(cp)_2Ti\}_2O]$ or $[\{(cp)_2Ti\}_4(CO_3)_2]$, respectively (eqns. (26) and (27)). $[\{(cp)_2Ti\}_4(CO_3)_2]$ is also obtained from the reaction of O_2 with an excess of $[(cp)_2Ti(CO)_2]$ (eqn. (28)). Both $[\{(cp)_2Ti\}_2O]$ and $[\{(cp)_2Ti\}_4(CO_3)_2]$ undergo further oxidation to the titanium(IV) polymer "$(cp)_2TiO$" in the presence of excess N_2O (eqns. (29) and (30)).

$$2[(cp)_2Ti] + N_2O \longrightarrow [\{(cp)_2Ti\}_2O] + N_2 \qquad (26)$$

$$4[(cp)_2Ti(CO)_2] + 4N_2O \longrightarrow [\{(cp)_2Ti\}_4(CO_3)_2] + 4N_2 + 6CO \qquad (27)$$

$$4[(cp)_2Ti(CO)_2] + 2O_2 \longrightarrow [\{(cp)_2Ti\}_4(CO_3)_2] + 6CO \qquad (28)$$

$$[\{(\mathrm{cp})_2\mathrm{Ti}\}_2\mathrm{O}] + \mathrm{N_2O} \longrightarrow 2\text{"}(\mathrm{cp})_2\mathrm{TiO}\text{"} + \mathrm{N_2} \qquad (29)$$

$$[\{(\mathrm{cp})_2\mathrm{Ti}\}_4(\mathrm{CO_3})_2] + 2\mathrm{N_2O} \longrightarrow 4\text{"}(\mathrm{cp})_2\mathrm{TiO}\text{"} + 2\mathrm{CO_2} + 2\mathrm{N_2} \qquad (30)$$

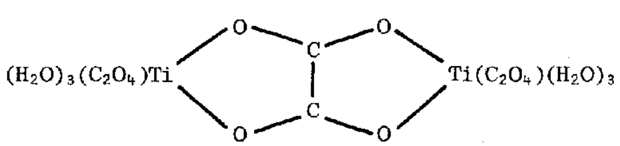
$[\{(cp)_2Ti\}_2O]$ is very reactive: it reacts with CO_2 at 20 °C in toluene to give $[\{(cp)_2Ti\}_4(CO_3)_2]$ within minutes, and it reacts with CO to yield a mixture of $[(cp)_2Ti(CO)_2]$, "$(cp)_2TiO$", and a CO_2 complex, believed to be $[\{(cp)_2Ti\}_2(CO_2)]$.

A paramagnetic intermediate has been detected in the reaction of an aqueous titanium(III) tartrate complex with oxygenated water. At pH 7-9 a singlet EPR signal (g = 2.0134) appears within 20-50 ms after mixing the solutions, which was assigned to a titanium superoxide complex [127].

Electrochemical or chemical reduction of the titanium(IV) complexes $[(cp)_2TiX_2]$ (X = OAr, $OSiR_3$, Me or Bz) or $[(cp)TiX_3]$ (X = OAr or $OSiR_3$) gives the corresponding titanium(III) radical anions $[(cp)_2TiX_2]^{\bullet-}$ or $[(cp)TiX_3]^{\bullet-}$, which rapidly rearrange, with loss of $[cp]^-$ or X^-, respectively, to yield the neutral titanium(III) derivatives $(cp)TiX_2$ [128].

The crystal and molecular structure of the 15-electron d^1 complex $[(cp)_2Ti(OAr)]$ (where OAr is the 2,6-di-tert-butyl-4-methylphenoxide ligand) has been reported {r(Ti-O) = 1.892 Å; $\bar{r}$(Ti-C) = 2.362 Å; (centroid cp)-$\hat{\mathrm{Ti}}$-(centroid cp) = 135.5°; Ti-$\hat{\mathrm{O}}$-C(Ar) = 142.3°}. It is interesting to note that this OAr ligand is ambidentate, behaving as a 6-electron-η^5-C-centred cyclohexadienonyl ligand in the 18-electron d^8 complex $[Rh(\eta^5\text{-}ArO)(PPh_3)_2]$ [129].

The powder magnetic susceptibility and crystal magnetic anisotropy of $[Ti(urea)_6][ClO_4]_3$ and $[Ti(urea)_6]I_3$ have been measured from 300 to 4.2 K [130]. Magnetic susceptibility data (300-15 K) have also been reported for the oxalate complexes $Ti_2(C_2O_4)_3(H_2O)_6.4H_2O$ and $Ti_2(C_2O_4)_3(H_2O)_5$. The former complex has a dimeric structure **(40)**, in which two seven-coordinate pentagonal-bipyramidal



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titanium(III) ions are bridged by an oxalate dianion. The bridging oxalate provides an effective path for antiferromagnetic exchange between the two titanium(III) ions, as evidenced by a rather large exchange parameter (J = $-60\ cm^{-1}$). In contrast, the partially dehydrated $Ti_2(C_2O_4)_3(H_2O)_5$ complex, of unknown structure, exhibits weak magnetic exchange interactions, and its susceptibility can be fitted to a distorted octahedral, single-ion model [131].

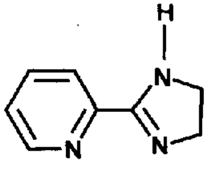
The thermal decomposition of titanium(III) oxalates has been studied by TGA, DTA and IR spectroscopy. $Ti_2(C_2O_4)_3.10H_2O$ and the hydrazine containing compound $Ti_2(C_2O_4)_3.N_2H_4.H_2C_2O_4.8.5H_2O$ both decompose to oxides *via* the carbonate $Ti_2(CO_3)_3$ [132].

Complex formation in the Ti(III)-lactic acid and Ti(III)-mandelic acid systems has been studied as a function of pH by NMR spectroscopy [133].

2.2.3 Complexes with N-donor ligands

Resonance Raman spectra of the dinitrogen-bridged complexes $[\{(cp)_2TiR\}_2(N_2)]$ (R = Ph or Bz) have been studied in the region of the intense 600 nm $^1A_g \rightarrow {}^1B_u$ electronic transition. Resonance amplification of cp, Ti-cp and Ti-N vibrational bands indicates that the 600 nm electronic transition involves significant charge transfer from the titanium atoms to the cp rings and the coordinated N_2 [134].

Complexes of the type $[(cp)_2Ti(HL)]^+$ (HL = 2-(2'-pyridyl)imidazoline **(41)**, 2-(2'-pyridyl)imidazole **(42)**, 2-(2'-pyridyl)benzimidazole **(43)** or 8-aminoquinoline **(44)**) have been prepared by reaction of HL with $[\{(cp)_2TiCl\}_2]$ in dry thf. The cations were isolated from aqueous solutions as oxygen-sensitive hexafluorophosphate salts, $[(cp)_2Ti(HL)][PF_6]$. Attempts to oxidise these titanium(III) complexes and attempts to deprotonate the coordinated ligands led to decomposition [104].



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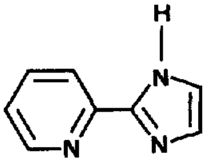

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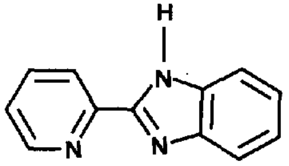

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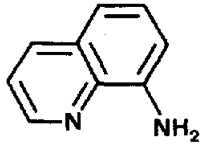
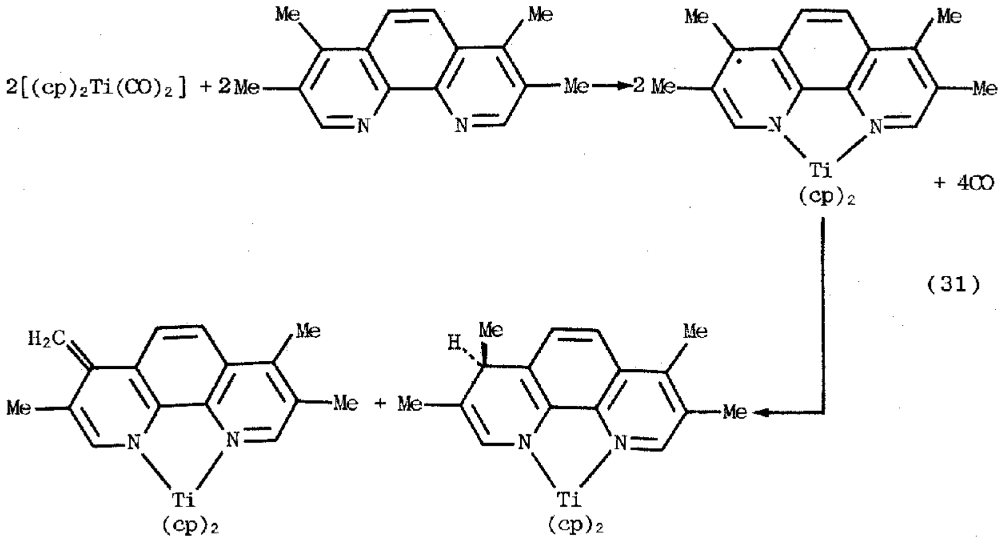


(44)

The reaction of $[(cp)_2Ti(CO)_2]$ with 3,4,7,8-tetramethyl-1,10-phenanthroline, 3,4,7,8-Me_4phen, in thf results in electron transfer upon complex formation, with subsequent dissociation of a C-H bond in a methyl group to give the 4-methylene-3,7,8-trimethyl-1,10-phenanthroline complex **(45)** and hydrogenation of the coordinated 3,4,7,8-Me_4phen radical anion to give **(46)** (eqn. (31)). Compounds **(45)** and **(46)** have been isolated as crystalline solids. In their mass spectra, they exhibit parent molecular ions that have mass one unit less (compound **(45)**) and one unit greater (compound **(46)**) than expected for $[(cp)_2Ti(3,4,7,8\text{-}Me_4phen)]$. Both compounds exhibit doublet state EPR spectra at -196 °C. The structure of **(45)** has been established by X-ray crystallography, which clearly shows the presence of the methylene group and the quinoid character of the



(31)

(45)

(46)

methylene-substituted ring [135].

Aryltitanium(III) tetraphenylporphyrin complexes [Ti(Ar)(TPP)] (Ar = Ph, 2-MeC_6H_4, or Bz) have been isolated as violet oxygen-sensitive crystals following anaerobic treatment of [TiF(TPP)] with the appropriate aryl Grignard reagents (eqn.(32)). Toluene solutions of the [Ti(Ar)(TPP)] complexes exhibit nine-line

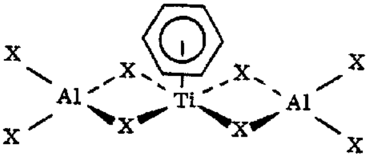
$$[\mathrm{TiF(TPP)}] + \mathrm{ArMgBr} \xrightarrow[\mathrm{thf}]{\mathrm{PhMe}} [\mathrm{Ti(Ar)(TPP)}] + \mathrm{MgBrF} \qquad (32)$$

EPR spectra, reflecting interaction of the unpaired electron with the four equivalent nitrogen nuclei of the porphyrin. The EPR and UV-VIS spectra of [Ti(Ph)(TPP)] are unaffected by the presence of pyridine, *N*-methylimidazole or thf ligands, indicating the preference of titanium(III) in this complex for five-coordination. The [Ti(Ar)(TPP)] complexes react with O_2 to give the oxotitanium(IV) complex and the corresponding biaryl (eqn. (33)) [136].

$$2[\mathrm{Ti(Ar)(TPP)}] + O_2 \longrightarrow 2[\mathrm{TiO(TPP)}] + \mathrm{Ar}_2 \qquad (33)$$

2.3 TITANIUM(II) COMPOUNDS

The distribution of halogen atoms between bridge and terminal positions in complexes of the type $[(C_6H_6)TiAl_2Cl_xBr_{8-x}]$ (x = 1-8) **(47)** has been studied in benzene solution by following the dependence on x of both the electronic spectra



(47; X = Cl or Br)

of compounds (47), and also the *g*-values in the EPR spectra of the corresponding titanium(III) complexes, $[(cp)TiAl_2Cl_xBr_{8-x}]$, obtained by reaction of compounds (47) with cyclopentadiene. Both approaches indicate preferred occupation of bridge positions by Cl atoms [137]. In the $[(C_6H_6)TiAl_2Et_xCl_{8-x}]$ and $[(C_6H_6)TiAl_2Et_xBr_{8-x}]$ systems, only the first two members, x = 1 or 2, could be observed; the (benzene)titanium(II) complexes containing more than two ethyl groups are not stable in benzene solution at room temperature. The ethyl groups occupy terminal positions [124].

The red-brown, very air-sensitive complex $[(cp)_2Ti\{P(OMe)_3\}_2]$ has been prepared by condensing sodium atoms at -100 °C into thf solutions containing $[(cp)_2TiCl_2]$ and excess trimethyl phosphite. $[(cp)_2Ti\{P(OMe)_3\}_2]$ has been characterised by elemental analysis, NMR and mass spectroscopy. It reacts cleanly with CO in pentane solution at 25 °C and 1 atm to give $[(cp)_2Ti(CO)_2]$ [138].

$K_2Ti(CN)_4$ has been synthesised by reduction of $K_3Ti(CN)_6$ with one equivalent of potassium in liquid ammonia. The electronic spectrum of $K_2Ti(CN)_4$ exhibits the three $d \leftrightarrow d$ transitions expected for octahedrally coordinated titanium(III) ($10Dq$ = 16200 cm^{-1}) [126].

A theoretical calculation of the electronic structure of TiH_2 favours a linear ($D_{\infty h}$) geometry. However, bending requires only an extremely small amount of energy [139].

2.4 TITANIUM(0) COMPOUNDS

Reduction of $[TiCl_4(dmpe)]$ with sodium amalgam in thf in the presence of butadiene affords the deep blue titanium(0) complex $[Ti(\eta\text{-}C_4H_6)_2(dmpe)]$. Unlike the analogous zirconium(0) complex, the titanium compound does not form seven-coordinate adducts with excess dmpe, PMe_3 or CO. The decreased Lewis acidity of the titanium complex in comparison with its zirconium analogue is, presumably, a steric consequence of the smaller size of the titanium atom; both complexes catalyse the dimerisation of alkenes [140].

$K_4Ti(CN)_4$ has been obtained as an extremely reactive black solid by reduction of $TiBr_3$ with potassium in liquid ammonia in the presence of excess KCN. This compound is pyrophoric, even in traces of air, and it is a powerful reducing agent, reducing 2,2'-bipyridine in liquid ammonia to $[bipy]^-$ [126].

2.5 MIXED-VALENCE COMPOUNDS

This section includes compounds in which titanium is present in more than one oxidation state, and also compounds which are not easily classified in terms of the oxidation state formalism.

The new mixed-valence titanates $Sr_2Ti_6O_{13}$ and $BaTi_8O_{16}$ have been prepared by heating mixtures of the appropriate oxides in a vacuum furnace at 1800 and 1400 °C, respectively. X-ray structural determinations show that $Sr_2Ti_6O_{13}$ is isostructural with $Ba_2Ti_6O_{13}$ and $BaTi_8O_{16}$ is isostructural with α-MnO_2. Both structures are built up from distorted $\{TiO_6\}$ octahedral units [141,142].

Reduction of TiS_2 with potassium metal at 1300 K in a KCl melt affords gray crystals of $K_{0.3}Ti_3S_4$, which has a structure of a type not previously described for alkali metal titanium sulphides. In this structure, distorted $\{TiS_6\}$ octahedra share faces and edges so as to form a three-dimensional framework that has wide channels parallel to the *c* axis of the hexagonal crystal. The channels are partially occupied by K^+ ions. Because the K^+ ions are highly mobile, this compound is of potential interest as an electrode material in battery applications [143].

An X-ray study has revealed that α-Ti_5P_3 is isostructural with β-Yb_5Sb_3. The structure contains two kinds of phosphorus atoms, surrounded by eight or seven close-neighbour titanium atoms; Ti-P distances range from 2.391 to 2.675 Å [144].

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