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2. TITANIUM

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CONTENTS

INTRODUCTION

Titanium exhibits three relatively common oxidation states and forms, in addition, a number of mixed-valence compounds. The 1979 literature on titanium is both extensive and diverse, ranging from organometallic chemistry through classical coordination chemistry to solid-state chemistry. This review presents comprehensive coverage of the coordination chemistry; organometallic and solid-state aspects of the chemistry of titanium are treated selectively and, usually, in connection with some other theme. For a comprehensive treatment of the organometallic chemistry of titanium, the reader is referred to the annual reviews by Labinger in the Journal of Organometallic Chemistry; reviews of the literature for 1977 [1] and 1978 [2] have appeared during the past year and a review of the 1979 literature is forthcoming. On the solid-state side, there exists an extensive literature on the crystal chemistry of metal titanates and the photoelectrochemical and photocatalytic properties of n-type semiconducting TiO_2. These topics are discussed briefly but are not treated comprehensively. Several review articles have been published during the past year that deal with various aspects of the solid-state chemistry of titanium. Shcherbakova et al. [3] have described the synthesis, phase equilibria, crystal chemistry, properties and uses of lanthanide titanates. Whittingham [4] has reviewed the chemistry of intercalation compounds of transition metal chalcogenides, with special emphasis on TiS_2. Wrighton [5] has summarized work on the photoelectrolysis of water using semiconducting TiO_2 and $SrTiO_3$ electrodes.

Among the more interesting developments during the past year are: the synthesis of η-cyclopentadienyltitanium derivatives of polyoxoanions; NMR studies of the kinetics of metal-centered rearrangement in octahedral Ti(IV) β-diketonates; synthesis and structural characterization of seven-coordinate monothiocarbamate complexes $[Ti(SOCNR_2)_3Cl]$ that are stereochemically rigid on the NMR time scale; studies of the reactions of $[(\eta\text{-}C_5H_5)_2Ti(CO)_2]$ with unsaturated molecules such as CO_2, PhNCO, diethyl ketomalonate, and *N,N'*-di-4-tolylcarbodiimide; studies of the reactions of titanium porphyrins; and synthetic, structural, and magnetic studies of dinuclear Ti(III) complexes in which the two titanium atoms are bridged by the dianion of a disubstituted pyrimidine. An important area that is mentioned only briefly in this review is the kinetics of electron transfer reactions in which Ti(III) serves as the reductant.

This review covers the major journals for the 1979 calendar year and the lesser known and/or foreign journals for the period covered by Chemical Abstracts, Volume 90, Number 1 to Volume 91, Number 20.

2.1 TITANIUM(IV) COMPOUNDS

2.1.1 Halide and pseudohalide complexes

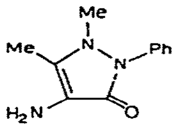
The complex fluoride $[Et_4N]_2[TiF_6] \cdot H_2O$ has been prepared by direct electrochemical oxidation of a titanium anode in PhCN or MeCN/PhCN solutions that contain $[Et_4N]F \cdot 3\ HF$ [6]. The crystal structure of $SrTiF_6 \cdot 2\ H_2O$ [7] is based on almost regular TiF_6 octahedra $\{\bar{r}(\text{Ti—F}) = 1.86\ \text{Å}\}$ and eight-coordinate SrF_5O_3 polyhedra that are linked together by bridging fluorine atoms. Five of the six fluorine atoms of each TiF_6 octahedron are corner-shared with five different SrF_5O_3 polyhedra; the sixth fluorine atom is involved in two hydrogen bonds with oxygen atoms of the two water molecules.

Several types of oxofluorotitanates(IV) have been prepared by addition of aqueous ethanoic acid solutions of appropriate cations to solutions of hydrous TiO_2 in 40% HF (Ti : F ratio = 1 : 4). Among the compounds isolated are: (a) oxotrifluorotitanates, $MTiOF_3 \cdot n\ H_2O$ (M = $[NH_4]$, Na, K, or Tl) and $[Co(NH_3)_6][TiOF_3]_3 \cdot H_2O$; (b) oxotetrafluorotitanates, $[Co(NH_3)_6]_2[TiOF_4]_3$ and $BaTiOF_4 \cdot 0.5\ H_2O$; and (c) fluorotitanates that have an oxygen : titanium ratio of 3 : 4, $K_6Ti_4O_3F_{16}$ and $Rb_5HTi_4O_3F_{16}$. Broad bands in the 700—900 cm^{-1} region of IR spectra suggest that these compounds contain —Ti—O—Ti—O— chains [8].

An ^{19}F NMR study of TiF_4 complexes with the phosphoryl ligands L (where L = tributylphosphine oxide, triphenylphosphine oxide, tributylphosphate, or hexamethylphosphoramide) in dichloromethane solution has shown that octahedral *cis*-$[TiF_4L_2]$ complexes are formed. The ^{19}F chemical shifts have been related to the donor strength of the phosphoryl ligand and have been interpreted in terms of fluorine—titanium $p\pi \rightarrow d\pi$ bonding [9].

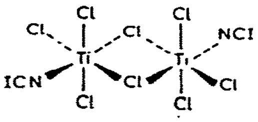
Several papers have appeared which deal with various physical properties of $TiCl_4$. A pulsed neutron diffraction study of liquid $TiCl_4$ has afforded a Ti—Cl bond length of 2.169(4) Å [10], in very good agreement with previous electron diffraction (2.169(2) Å, [11]) and reactor neutron diffraction (2.159(1) Å, [12]) values. Collisional ionization experiments [13] have yielded a value of 2.88 ± 0.15 eV for the electron affinity of $TiCl_4$; the corresponding value for $TiCl_3$ is 0.61 ± 0.17 eV. SCF-Xα molecular orbital calculations have been carried out for $TiCl_4$ [14] and the results used to interpret the UV absorption and UV photoemission spectra.

A variety of Lewis bases react with $TiCl_4$ to give solid adducts of the type $TiCl_4L$ and $TiCl_4L_2$. 4-Aminoantipyrene (1) yields a $[TiCl_4L_2]$ complex that



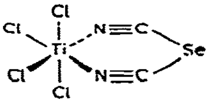
(1)

has been assigned an octahedral *trans* structure on the basis of its IR spectrum; the 4-aminoantipyrene ligands are coordinated through the carbonyl oxygen atom [15]. Diphenylsulphine gives a 1 : 1 complex $TiCl_4 \cdot Ph_2CSO$, in which the ν(CSO) vibrational frequencies are only slightly perturbed from their values in the free ligand; complex formation is attributed to a weak electrostatic interaction rather than covalent bonding. Photolysis of $TiCl_4 \cdot Ph_2CSO$ in dichloromethane solution gives the known ketone complex $TiCl_4 \cdot Ph_2CO$ plus sulphur; the mechanism appears to involve photolytic fragmentation of the sulphine complex followed by photolytic conversion of Ph_2CSO to Ph_2CO and subsequent combination of Ph_2CO and $TiCl_4$ [16]. The pseudohalogen ICN adds to $TiCl_4$ to give 1 : 1 and 1 : 2 adducts in which ICN is attached to titanium through the nitrogen atom. On the basis of the number of $\nu(C{\equiv}N)$, ν(C—I), ν(Ti—N) and ν(Ti—Cl) bands observed in IR and Raman spectra, an octahedral *trans* configuration has been assigned to $[TiCl_4(NCI)_2]$, and a dimeric C_{2h} structure (2) has been proposed for $TiCl_4(NCI)$ [17].



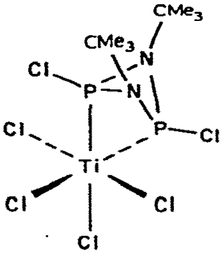
(2)

Vibrational spectra indicate that $TiCl_4$ adducts with $S(CN)_2$ and $Se(CN)_2$ adopt rather different structures [18]. $[TiCl_4\{S(CN)_2\}_2]$ has an octahedral *trans* structure in which the $S(CN)_2$ ligands are *S*-bonded to Ti. In contrast, in $TiCl_4 \cdot Se(CN)_2$, a 1 : 1 adduct, the $Se(CN)_2$ ligand appears to be *N*-bonded. A chelate structure (3) has been suggested [18], but oligomeric structures in



(3)

which $Se(CN)_2$ acts as an *N*-bonded bridging ligand may be more likely in view of the geometry of $Se(CN)_2$ [19]. $TiCl_4$ reacts with the cyclophosphazane $(Me_3CNPCl)_2$ to give a 1 : 1 adduct that has been assigned, on the basis of IR and ^{31}P NMR evidence, an octahedral *cis* structure (4) in which $(Me_3CNPCl)_2$ acts as a *P*-bonded bidentate ligand [20].



(4)

t-Butylisonitrile inserts into a Ti—Cl bond of $TiCl_4$ yielding the dimeric complex $[TiCl_3\{C(Cl)NCMe_3\}(CNCMe_3)]_2$, which contains both terminal ($\nu(C{\equiv}N) = 2200\ cm^{-1}$) and inserted ($\nu(C{\equiv}N) = 1650$—$1600\ cm^{-1}$) isonitrile ligands. The inserted isonitrile probably bridges to the second Ti atom through the imino-nitrogen atom. Attempts to induce further isonitrile insertion, by reaction of $[TiCl_3\{C(Cl)NCMe_3\}(CNCMe_3)]_2$ with chelating ligands such as 8-quinolinolate (8-HO-quin = 8-hydroxyquinoline), *N,N*-diethyldithiocarbamate (Et_2NCS_2), or bis(diphenylphosphino)ethane (dppe) led to displacement of isonitrile ligands; reaction products were $[TiCl_2\{C(Cl)NCMe_3\}(8\text{-}O\text{-quin})]$, $[TiCl_2(Et_2NCS_2)_2]$, or $[TiCl_4(dppe)]$, respectively. Displacement of inserted as well as terminal isonitrile ligands suggests that the insertion reaction is reversible [21].

Ligand exchange reactions between $TiCl_4$ and $[(\eta\text{-}C_5H_5)_2Pb]$ give $[(\eta\text{-}C_5H_5)TiCl_3]$, $[(\eta\text{-}C_5H_5)_2TiCl_2]$, and $[(\eta\text{-}C_5H_5)PbCl]$ [22]. A 1 : 1 mixture of $TiCl_4$ and IOCN in dichloromethane affords $TiCl_3NCO$ as a yellow solid; IR and Raman spectra indicate that the cyanate group is attached to Ti through the N atom [23].

Normal coordinate analyses of the chlorotitanate ions $[Ti_2Cl_{10}]^{2-}$, $[Ti_2Cl_9]^-$, and $[TiCl_5]^-$ have been carried out, and observed vibrational frequencies have been assigned [24]. The resonance Raman spectrum of $TiBr_4$ has been obtained using UV (363.8 nm) excitation. It is characterized by an intense overtone progression in the totally symmetric fundamental ν_1 and subsidiary progressions in $\nu_1 + \nu_3$, $\nu_1 + \nu_2$, and $\nu_1 + \nu_4$ [25]. The electronic absorption spectrum of TiI_4 has been reported in the region 200—600 nm [26]. In the solid state, TiI_4 exists in two crystalline forms; the solubilities and the conditions for appearance of the two forms have been studied [26].

Several papers have appeared that describe the preparation and properties of organotitanium halides and pseudohalides. Improved methods have been reported for synthesis of $[(\eta\text{-}CH_3C_5H_4)_2TiX_2]$ (X = F or Cl), and two high-yield halide-exchange routes have been described for conversion of these compounds to the bromide and iodide analogues: (a) reaction of $[(\eta\text{-}CH_3C_5H_4)_2TiCl_2]$ with BBr_3 or BI_3 in dichloromethane; and (b) reaction of $[(\eta\text{-}CH_3C_5H_4)_2TiF_2]$ with concentrated HBr or HI [27]. An EPR study of the photochemistry of $[(\eta\text{-}C_5H_5)_2TiCl_2]$ indicates that the primary photolysis process in homolytic cleavage of the Ti—C_5H_5 bond gives an $(\eta\text{-}C_5H_5)TiCl_2$ fragment and a $\dot{C}_5H_5$ radical [28]. $[(\eta\text{-}C_5H_5)_2TiCl_2]$ has been identified as the first titanium complex and the first metallocene derivative that exhibits antitumour activity [29]. The possibility of antitumour activity was suggested by the presence of a *cis*-dichlorometal moiety in a neutral complex, as in the well-known antitumour agent *cis*-$[Pt(NH_3)_2Cl_2]$. The X-ray structure of $[(\eta\text{-}C_5H_5)_2Ti(NCO)_2]$ shows that the cyanate ligands are *N*-bonded, with the Ti—N—C—O moieties being approximately linear. The expected distorted tetrahedral geometry at the Ti atom is characterized by N—Ti—N and (centroid C_5H_5)—Ti—(centroid C_5H_5) angles of 94.7 and 132.8°, respectively, and by average Ti—N and Ti—(centroid C_5H_5) distances of 2.012 and 2.055 Å, respectively [30]. Several classes of organotitanium isothiocyanate complexes have been prepared by metathesis reactions. Compounds of the type $[(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_3RR')Ti(NCS)_2]$ and $[(\eta\text{-}C_5H_3RR')_2Ti(NCS)_2]$ were obtained by reaction of KSCN with the corresponding organotitanium dichlorides; IR spectra suggest that the thiocyanate ligands are *N*-bonded [31]. Mixed thiocyanate—aryloxide complexes of the type $[(\eta\text{-}C_5H_5)_2Ti(NCS)(OAr)]$ have been prepared from $[(\eta\text{-}C_5H_5)_2Ti(NCS)_2]$ and have been converted to $[(\eta\text{-}C_5H_5)_2TiCl(NCS)]$ by reaction with HCl. The latter reactions are complicated by disproportionation of $[(\eta\text{-}C_5H_5)_2TiCl(NCS)]$ to $[(\eta\text{-}C_5H_5)_2TiCl_2]$ and $[(\eta\text{-}C_5H_5)_2Ti(NCS)_2]$ [32]. $[(\eta\text{-}C_5H_5)_2Ti(NCSe)_2]$ has been prepared by reaction of $[(\eta\text{-}C_5H_5)_2Ti(CO)_2]$ with $(SeCN)_2$; analogous reactions with $X(CN)_2$ (X = S or Se) give the new, mixed-ligand complexes $[(\eta\text{-}C_5H_5)_2Ti(CN)(NCX)]$ [33].

2.1.2 Complexes with O-donor ligands

Most of the papers published in this area report studies of alkoxy compounds and complexes with bidentate chelating ligands. This section includes complexes with bidentate ligands in which both donor atoms are oxygen. Complexes with bidentate and polydentate ligands that contain other donor atoms (e.g. S or N) in addition to oxygen are discussed later in sections dealing with the other element.

Titanium alkoxides derived from unsaturated alcohols, $Ti(OR)_4$ ($R = CH_2—CH=CH—CH_3$ [34] or $C(CH_3)_2CH=CH_2$ [35]), have been prepared by alkoxide interchange reactions between the unsaturated alcohol and titanium(IV) isopropoxide. Molecular weight measurements in boiling benzene indicate that $Ti(OC(CH_3)_2CH=CH_2)_4$ is a monomer, but $Ti(OCH_2—CH=CH—CH_3)_4$ is a dimer. A variety of 2,2,2-trifluoroethoxy derivatives of titanium have been described by Basso-Bert and Gervais [36,37]. The mixed-ligand complexes $TiCl_2(OR_f)_2$, $TiCl(OR_f)_3$, and $Ti(OCHMe_2)_2(OR_f)_2$ ($OR_f = OCH_2CF_3$) were prepared by reaction of R_fOH with $TiCl_4$ or $Ti(OCHMe_2)_4$ (eqn. (1)). How-

$$TiX_4 + n\ R_fOH \rightarrow TiX_{4-n}(OR_f)_n + n\ HX \qquad (1)$$

$$(X = Cl \text{ or } OCHMe_2)$$

ever, this approach did not afford $Ti(OR_f)_4$, even when a large excess of R_fOH was used. $Ti(OCHMe_2)_3(OR_f)$ was synthesized in highest yields by reaction of R_fOH with the corresponding methyl or diethylamide derivatives (eqns. (2) and (3)). The coordinatively unsaturated character of these

$$MeTi(OCHMe_2)_3 + R_fOH \rightarrow Ti(OCHMe_2)_3(OR_f) + CH_4 \qquad (2)$$

$$Ti(NEt_2)(OCHMe_2)_3 + R_fOH \rightarrow Ti(OCHMe_2)_3(OR_f) + Et_2NH \qquad (3)$$

fluoroalkoxy complexes is indicated by the formation of 1 : 1 adducts with R_fOH, MeCN, and EtCN, and by association in solution. Cryoscopic molecular weight measurements in benzene suggest that $TiCl_2(OR_f)_2$ and $Ti(OCHMe_2)_2(OR_f)_2$ are dimers while $TiCl(OR_f)_3$ is a trimer. Association probably occurs via bridging fluoroalkoxy groups. The fluoroalkoxy compounds undergo substitution reactions with ethanoyl chloride and pentane-2,4-dione (eqns. (4) and (5)) and insertion reactions with phenylisocyanate (eqn. (6)). The alkyltitanium

$$TiCl(OR_f)_3 + MeCOCl \rightarrow TiCl_2(OR_f)_2 + MeCOOR_f \qquad (4)$$

$$TiCl_2(OR_f)_2 + 2\ Hacac \rightarrow Ti(acac)_2Cl_2 + 2\ R_fOH \qquad (5)$$

$$TiCl(OR_f)_3 + PhNCO \rightarrow TiCl(OR_f)_2[N(Ph)COOR_f] \qquad (6)$$

derivatives $RTi(OR_f)_3$ ($R = Me$ or $PhCH_2$) have been prepared by reaction of $TiCl(OR_f)_3$ with MeLi or $PhCH_2MgCl$, respectively [36].

Closely related to $TiCl(OR_f)_3$, $TiCl_2(OR_f)_2$, and $MeTi(OR_f)_3$ are the cyclopentadienyl derivatives $[(\eta\text{-}C_5H_5)Ti(OR_f)_3]$, $[(\eta\text{-}C_5H_5)TiCl(OR_f)_2]$, and $[(\eta\text{-}C_5H_5)Ti(Me)(OR_f)_2]$. These latter compounds were prepared starting from $[(\eta\text{-}C_5H_5)TiCl_3]$ (eqns. (7)—(9)). The $Ti—OR_f$ bond of $[(\eta\text{-}C_5H_5)Ti(OR_f)_3]$

$$[(\eta\text{-}C_5H_5)TiCl_3] + 3\ LiOR_f \rightarrow [(\eta\text{-}C_5H_5)Ti(OR_f)_3] + 3\ LiCl \qquad (7)$$

$$[(\eta\text{-}C_5H_5)TiCl_3] + 2\ LiOR_f \rightarrow [(\eta\text{-}C_5H_5)TiCl(OR_f)_2] + 2\ LiCl \qquad (8)$$

$$[(\eta\text{-}C_5H_5)TiCl(OR_f)_2] + MeLi \rightarrow [(\eta\text{-}C_5H_5)Ti(Me)(OR_f)_2] + LiCl \qquad (9)$$

undergoes the expected reactions when this compound is treated with ethanoyl chloride or phenylisocyanate (eqns. (10) and (11)). The Ti—Me

$$[(\eta\text{-}C_5H_5)Ti(OR_f)_3] + MeCOCl \rightarrow [(\eta\text{-}C_5H_5)TiCl(OR_f)_2] + MeCOOR_f \qquad (10)$$

$$[(\eta\text{-}C_5H_5)Ti(OR_f)_3] + PhNCO \rightarrow [(\eta\text{-}C_5H_5)Ti(OR_f)_2(N(Ph)COOR_f)] \qquad (11)$$

bond in $[(\eta\text{-}C_5H_5)Ti(Me)(OR_f)_2]$ is cleaved by I_2, HCl and R_fOH (eqns. (12)–(14)). $[(\eta\text{-}C_5H_5)Ti(Me)(OR_f)_2]$ is an efficient catalyst for polymerisation of methyl methacrylate [37].

$$[(\eta\text{-}C_5H_5)Ti(Me)(OR_f)_2] + I_2 \rightarrow [(\eta\text{-}C_5H_5)TiI(OR_f)_2] + MeI \qquad (12)$$

$$[(\eta\text{-}C_5H_5)Ti(Me)(OR_f)_2] + 3\ HCl \rightarrow [(\eta\text{-}C_5H_5)TiCl_3] + CH_4 + 2\ R_fOH \qquad (13)$$

$$[(\eta\text{-}C_5H_5)Ti(Me)(OR_f)_2] + R_fOH \rightarrow [(\eta\text{-}C_5H_5)Ti(OR_f)_3] + CH_4 \qquad (14)$$

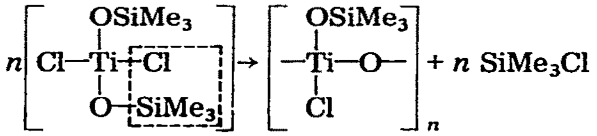
In a related study of $[(\eta\text{-}C_5H_5)Ti(OR)_3]$ (R = Et, $CHMe_2$, or CMe_3) complexes, it was found that phenylisocyanate rapidly inserts into the Ti—O bonds to give $[(\eta\text{-}C_5H_5)Ti(OR)_{3-n}(N(Ph)COOR)_n]$, where $n = 1$, 2 or 3, depending on the stoicheiometry of the reaction mixture. The insertion products exhibit a characteristic IR band at $\sim 1710\ cm^{-1}$ due to carbonyl stretching [38].

Two crystalline bimetallic alkoxides, $BaTi(OEt)_6$ and $Ba[Ti_2(OEt)_9]_2$, have been isolated upon rapid mixing of ethanol solutions of $Ti(OEt)_4$ and $Ba(OEt)_2$. These compounds have been characterized by analysis, mass spectra, IR spectra, X-ray powder patterns, and solubility measurements [39].

The formation of mono- and di-siloxy derivatives of $TiCl_4$ upon reaction of $TiCl_4$ with hexamethyldisiloxane (eqns. (15) and (16)) has been monitored by NMR spectroscopy. After 10 days, a 1 : 2 mixture of $TiCl_4$ and $O(SiMe_3)_2$ deposits an insoluble white solid which analyses for $TiOCl(OSiMe_3)$. Evidently this compound forms when $SiMe_3Cl$ is eliminated from $TiCl_2(OSiMe_3)_2$ (eqn. (17)); the IR spectrum of $TiOCl(OSiMe_3)$ is consistent with a polymeric structure that contains tetrahedral Ti(IV), terminal Ti—Cl bonds, and Ti—O—Ti bridges [40].

$$TiCl_4 + O(SiMe_3)_2 \rightarrow TiCl_3(OSiMe_3) + SiMe_3Cl \qquad (15)$$

$$TiCl_3(OSiMe_3) + O(SiMe_3)_2 \rightarrow TiCl_2(OSiMe_3)_2 + SiMe_3Cl \qquad (16)$$



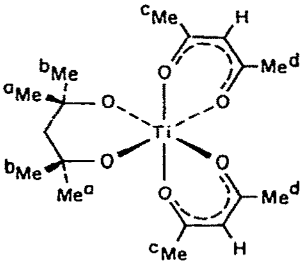
$$n\left[Cl{-}\underset{\underset{O-SiMe_3}{|}}{\overset{\overset{OSiMe_3}{|}}{Ti}}{-}Cl\right] \rightarrow \left[{-}\underset{\underset{Cl}{|}}{\overset{\overset{OSiMe_3}{|}}{Ti}}{-}O{-}\right]_n + n\ SiMe_3Cl \qquad (17)$$

Phenylmercury titanoxanes of the type $Ti(chelate)_2(OHgPh)_2$, where chelate denotes a bidentate ligand such as the anion of salicylaldehyde, 8-hydroxyquinoline or a β-diketone, have been prepared by condensation of $[Ti(chelate)_2(OCHMe_2)_2]$ with PhHgOH; two moles of isopropanol are eliminated. Condensation of $Ti(OCHMe_2)_4$ with PhHgOH gives $Ti(OHgPh)_4$ [41].

A potentiometric study of the hydrolysis of titanium(IV) in 2 M aqueous (Na, H)Cl solutions at 25°C has revealed that the Ti(IV), which is present under these conditions as TiO^{2+}, is partially hydrolyzed to form a polynuclear complex, $[(TiO)_8(OH)_{12}]^{4+}$. The value of log(K) for the hydrolysis reaction (eqn. (18)) is −1.68 ± 0.10 [42].

$$8\ TiO^{2+} + 12\ H_2O \rightleftharpoons [(TiO)_8(OH)_{12}]^{4+} + 12\ H^+ \qquad (18)$$

Turning to chelate complexes of titanium(IV) with *O*-donor ligands, we note first a number of studies of β-diketonate complexes. Procedures for synthesis of dihalobis(pentane-2,4-dionato)titanium(IV) complexes, $[Ti(acac)_2X_2]$ (X = F, Cl or Br) [43], have appeared [44]. The chelate rings of $[Ti(acac)_2Cl_2]$ have been halogenated with *N*-chlorosuccinimide, *N*-bromosuccinimide, and ICl to give the 3-halopentane-2,4-dionato analogues, $[Ti(acac\text{-}X)_2Cl_2]$ (X = Cl, Br or I, respectively) [45]. Oxobis(3-mesitylpentane-2,4-dionato)titanium(IV) has been prepared and its ^1H NMR spectrum reported in connection with a study of the magnetic anisotropy in metal β-diketonate chelate rings [46]. The kinetics and mechanism of metal-centered rearrangement in the octahedral diolatobis(pentane-2,4-dionato)titanium(IV) complexes (5) and (6) have been studied by dynamic ^1H NMR spectroscopy. Rate constants for inversion of configuration (k_{inv}) have been determined from the coalescence of the resonances of the diastereotopic diolate geminal methyl groups a and b, and values of k_{inv} have been compared with rate constants for exchange (k_{ex}) of pentane-2,4-dionate methyl groups c and d. A similar study has been carried out for *cis*-$[Ti(acac)_2(OCHMe_2)_2]$. Values of the rate constant ratio k_{inv}/k_{ex} are relatively independent of solvent, but vary between 1.0 and 2.0 depending on the nature of the diolate ligand. These results have been interpreted in terms of a twisting mechanism, with the ratio k_{inv}/k_{ex} depending on the C_3 axis (or combination of C_3 axes) about which the twist occurs [47,48]. Similar conclusions were reached earlier in a study of *cis*-dialkoxybis(β-diketonato)titanium(IV) complexes [49].



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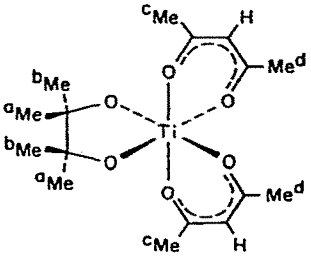
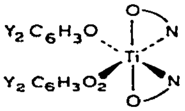


(6)

NMR line-shape studies of the closely related phenoxy complexes, *cis*-$[Ti(acac)_2(OC_6H_4X)_2]$ and *cis*-$[Ti(acac)_2(OC_6H_3Y_2)_2]$ (X = 2-Cl, 2-I, 4-Cl, 2-$CHMe_2$, 4-$CHMe_2$ or 2-Ph; Y_2 = 2,6-Cl_2 or 2,6-$(CHMe_2)_2$) have also been reported [50,51]. Rates of acac methyl group exchange are slower in the complexes that contain the more basic phenoxide ligands, which argues against a bond-rupture mechanism and favours a twist mechanism. Electronic effects appear to be more important than steric effects in determining the rates of acac methyl group exchange. Rates of inversion of the isopropyl-substituted complexes $[Ti(acac)_2(OC_6H_4X)_2]$ (X = 2-$CHMe_2$) and $[Ti(acac)_2(OC_6H_3Y_2)_2]$ (Y_2 = 2,6-$(CHMe_2)_2$) have been determined from the coalescence of the resonances of the diastereotopic isopropyl methyl groups. Inversion and acac methyl group exchange in the isopropyl-substituted complexes occur at comparable rates; however, reported values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the two processes are surprisingly different [50]. The analogous 8-hydroxyquinolinolate (8-O-quin) and 2-methyl-8-hydroxyquinolinolate (2-Me-8-O-quin) complexes, $[Ti(8\text{-}O\text{-}quin)_2(OC_6H_3Y_2)_2]$ and $[Ti(2\text{-}Me\text{-}8\text{-}O\text{-}quin)_2(OC_6H_3Y_2)_2]$ undergo inversion more slowly and may rearrange by a different mechanism [51]. These complexes have a *cis*(phenoxy), *cis*(N), *trans*(O) arrangement of donor atoms in the solid state (7) [52], and ^1H NMR spectra [51] are consistent with the same structure in solution. No other stereoisomers were detected. $\Delta \rightleftharpoons \Lambda$ inversion of the *cis*(phenoxy), *cis*(N), *trans*(O) isomer can occur in one step via a trigonal-bipyramidal axial intermediate (8). Evidence for Ti—N bond rupture is a correlation between inversion rates and Ti—N bond distances; the 2-Me-8-O-quin complex rearranges ~10^2 times faster than the 8-O-quin complex, in accord with the longer (by 0.13 Å) Ti—N bond in the 2-Me-8-O-quin complex.



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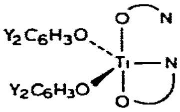
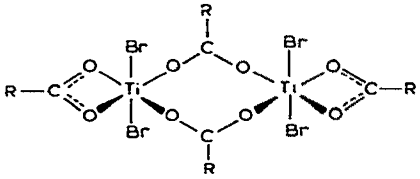


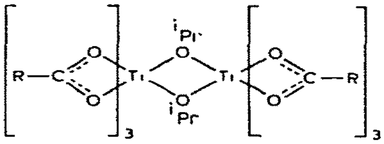
(8)

Titanium dicarboxylate dibromides $Ti(O_2CR)_2Br_2$ (R = Me, Et, $CHMe_2$, CH_2Cl, CH_2F or $CHCl_2$) have been prepared by reaction of $TiBr_4$ with the appropriate carboxylic acid. On the basis of molecular weight measurements and vibrational spectra, these compounds have been formulated as six-coordinate dimers (9) that contain bidentate and bridging carboxylate ligands [53]. Heterocyclic carboxylates of the type $Ti(O_2CR)_n(OCHMe_2)_{4-n}$, (where n = 1, 2 or 3 and RCO_2^- is the anion of furan 2-carboxylic acid, indole 3-ethanoic acid, or indole 3-butanoic acid) have been prepared in quantitative yields by reaction of $Ti(OCHMe_2)_4$ with the carboxylic acids in refluxing benzene; the value of n depends on the stoicheiometry of the reaction mixture.



(9)

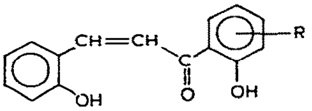
The fourth isopropoxide group could not be replaced, even on prolonged heating under reflux with an excess of carboxylic acid. $Ti(O_2CR)_3(OCHMe_2)$ (RCO_2^- = furan 2-carboxylate anion) is dimeric in refluxing benzene, and IR spectra suggest that the $Ti(O_2CR)_3(OCHMe_2)$ complexes contain bridging isopropoxide groups; an eight-coordinate structure (**10**) has been proposed



(10)

[54]. Sengupta and Dasgupta gave described a series of oxalatotitanates of the type $(BH)_2TiO(C_2O_4)_2 \cdot x\ H_2O$ and $(B'H_2)TiO(C_2O_4)_2 \cdot x\ H_2O$ (where B = pyridine, quinoline or guanidine, and B′ = 1,2-diaminoethane or 1,2-diaminopropane) [55].

Oxotitanium(IV) complexes with the mononegative anion of 2,2′-dihydroxychalcones (**11**; R = H, 3′-Me, 4′-Me, 5′-Me, or 5′-Cl) have been prepared by



(11)

reaction of the chalcones (H_2L) with $TiO(ClO_4)_2$ in ethanol; the complexes have stoicheiometry $TiO(HL)_2$. They are monomeric nonelectrolytes in nitrobenzene and exhibit a $\nu(Ti{=}O)$ IR band in the region 990—1085 cm^{-1}. Other aspects of the IR spectra suggest that the chalcones are acting as bidentate ligands, bonding to titanium through the carbonyl group and the *ortho*-hydroxyl oxygen atom; a square-pyramidal structure has been proposed [56]. Related complexes, $TiLCl_2$, that contain dinegative anions of 2,2′-dihydroxychalcones, have also been reported [57].

8-Hydroxyquinolinolate *N*-oxide complexes of the type $[Ti(C_9H_6NO_2)_2X_2]$ (X = Cl or OEt) have been synthesized by reaction of the ligand with TiX_4 in benzene; IR spectra indicate that the 8-hydroxyquinolinolate *N*-oxide anion coordinates through both oxygen atoms [58]. Reaction of $TiCl_4$ with NaO_2SeR (R = Me or Ph) in ethanenitrile affords the tetrakis(bidentate) chelates $[Ti(O_2SeR)_4]$; these compounds probably have a D_{2d}-dodecahedral structure [59]. The He-II photoelectron spectrum of the dodecahedral complex $[Ti(NO_3)_4]$ has been reported; metal—ligand bonding involves those orbitals which correlate with the $4e'$ (oxygen $2p\sigma$) m.o.'s of the nitrate ion [60]. A ^1H and ^{13}C NMR study of complex formation between Ti(IV) and malic acid ($HOOC\text{-}CHOH\text{-}CH_2\text{-}COOH$) indicates that at pH 4.0 the malate ligand complexes through the hydroxyl oxygen and the adjacent carboxylate group to give five-membered chelate rings [61].

2.1.3 Titanates and oxyanion salts

Quite a number of papers have appeared that describe the preparation, properties, and structure of alkali, alkaline earth, transition metal, and rare earth titanates. Metal titanates are of importance as ceramics, high-temperature refractory materials, and ferroelectric substances [3]. In addition, alkali metal titanates are of interest as solid-state ionic conductors.

The crystal structure of the Li^+ ion conductor $Li_2Ti_3O_7$ has been determined by X-ray diffraction. The structure consists of $Ti_{0.86}Li_{0.14}O_6$ octahedra which are joined together so as to create open channels along the orthorhombic *c* direction. These channels contain four kinds of tetrahedral sites, two of which are partially but equally occupied by the remaining Li^+ ions, and two of which are vacant. Thus, the "structural" formula can be written as $(Li_{1.72}\square_{2.28})_{0.5}(Li_{1.72}\square_{2.28})_{0.5}(Ti_{3.43}Li_{0.57})O_8$, where $\square$ represents a Li^+ ion vacancy in the partially occupied tetrahedral sites. A lack of strong anisotropy in the DC conductivity indicates Li^+ ion diffusion perpendicular to, as well as along, the channel directions. The observed structure is nicely consistent with conductivity perpendicular to the channel directions, since it allows for Li^+ ion hopping from the octahedral site through a shared face to a vacant tetrahedral site and then on to a partially occupied tetrahedral site [62].

A new member of the sodium titanate series, $Na_2Ti_9O_{19}$, has been synthesised [63] and its structure determined by high-resolution electron microscopy [64]. The non-stoicheiometric compound, $Na_{0.56}Fe_{0.28}Ti_{1.72}O_4$, has a structure in which the Na^+ ions occupy channels within a three-dimensional framework of edge- and corner-shared $(Ti, Fe)O_6$ octahedra. Because the Na^+ ion sites are only approximately half occupied, this compound should show ionic conduction along the channel directions [65]. Synthesis of the K^+ ion conductors, $K_2MTi_7O_{16}$ ($M^{2+} = Mg^{2+}$, Ni^{2+}, Zn^{2+}, or Cu^{2+}) and $K_2M_2Ti_6O_{16}$ ($M^{3+} = Al^{3+}$ or Fe^{3+}), is accelerated by the presence of KCl, which evidently forms a melt that partially dissolves the reagents and intermediate products [66].

The method commonly employed for synthesis of alkaline earth titanates by solid-phase reaction of TiO_2 and alkaline earth carbonates requires prolonged heating at high temperatures. Syntheses of $MTiO_3$ (M = Ca, Sr or Ba) can be effected more rapidly and at lower temperatures if the reactions are carried out in the presence of $Na_2[CO_3]/K_2[CO_3]$ or NaCl/KCl melts [67,68]. $BaTiO_3$ can also be prepared at quite low temperatures (600—700°C) by thermal decomposition of $BaTi(C_6H_6O_7)_3 \cdot 6\ H_2O$ ($[C_6H_6O_7]^{2-}$ = citrate) [69]. Titanium(IV) hydroxide strongly absorbs alkaline earth metal hydroxides from their aqueous solutions to give amorphous mixed metal hydroxides [70,71]. Ageing suspensions of the Sr and Ba compounds affords the hydrated titanates, $SrTiO_3 \cdot 0.9\text{—}1.0\ H_2O$ and $BaTiO_3 \cdot 1.2\text{—}1.5\ H_2O$ [70]. Thermal decomposition of the Ca compound gives a new calcium titanate, $Ca_2Ti_5O_{12}$, which has a cubic structure and is stable in the temperature range 700—1000°C [71]. The structure of $Ba_2Ti_{5.5}O_{13}$ features distorted octahedral coordination of Ti $\{\bar{r}(\text{Ti—O}) = 2.00$ Å$\}$ and 11-coordination of Ba; this compound is isostructural with $M_2Ti_6O_{13}$ (M = Na, K, or Rb) with one of three different Ti sites being only partially occupied [72].

Cr_2TiO_5 has been synthesized as a stoicheiometric single phase above 1660°C in air, and its structure has been shown to be of the V_3O_5 type [73]. A new lanthanum titanate $La_4Ti_3O_{12}$ has been prepared from the oxides at 1200—1400°C; it has a perovskite-like layer structure of hexagonal symmetry in which the Ti^{4+} ions occupy three-quarters of the perovskite type-B positions [74]. X-ray, IR, and Raman studies of $Ln_2Ti_2O_7$ (Ln = La, Pr or Nd) and the high-pressure phase of $Sm_2Ti_2O_7$ indicate that these compounds have a non-centrosymmetric monoclinic structure in which Ti exhibits tetrahedral coordination [75].

Other solid-state oxygen-containing compounds of titanium that have attracted interest during the past year are the phosphates and silicates. Titanium phosphates are of interest as inorganic ion exchangers [76—79], and because of their stability and the low cost of raw materials, they appear to be promising materials for industrial use [76]. The ion exchange properties of $Ti(HPO_4)_2$ [77], $Ti(HPO_4)_2 \cdot 0.5\ H_2O$ [76], and $Ti(HPO_4)_2 \cdot H_2O$ [77] have been investigated, and the thermal behaviour [78] and structure [79] of $Ti(HPO_4)_2 \cdot 2\ H_2O$ have been studied. The detailed structure of the dihydrate is not known, but X-ray powder patterns, density measurements, and the formation of intercalation compounds with organic molecules suggest a layer structure [79]. The complex titanium silicates, $Pb_2CoTiSi_2O_9$ and $Pb_2NiTiSi_2O_9$, have been prepared by solid-state reactions at 775—800°C. These compounds are orthorhombic and isostructural with kentrolite $Pb_2Mn_2Si_2O_9$; IR spectra indicate the presence of pyrosilicate (Si_2O_7) groups [80]. An IR and Raman study of $Ba_2TiSi_2O_8$, a pyrosilicate that contains square pyramidal TiO_5 groups, has uncovered a high-frequency Ti—O stretching mode (860 cm^{-1}) [81]. This indicates a short Ti—O distance and suggests that the X-ray structure [82] should be refined. Another interesting property of $Ba_2TiSi_2O_8$ is its luminescence, which shows an unusually long decay time (3.5 ms) [81].

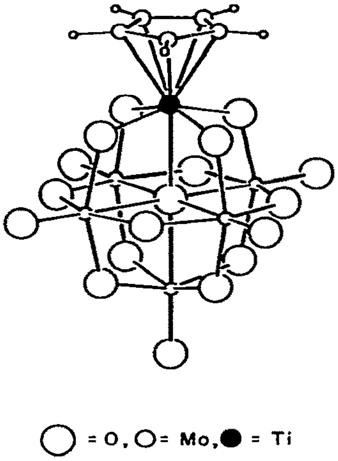
2.1.4 *η-Cyclopentadienyltitanium polyox anions*

Organometallic derivatives of polyoxoanions have attracted considerable attention because they may provide insights into the factors responsible for the reactivity of heterogeneous catalysts that have organometallic compounds supported on a metal oxide surface. The first polyoxoanion-supported organometallic complex, $[(\eta\text{-}C_5H_5)Ti(W_{11}PO_{39})]^{4-}$ was reported in 1978 by Ho and Klemperer [83]. This complex has been prepared independently by Knoth [84], who has also reported $[(\eta\text{-}C_5H_5)Ti(W_{11}SiO_{39})]^{5-}$ and $[(\eta\text{-}C_5H_5)Ti(Mo_{11}SiO_{39})]^{5-}$. Knoth has prepared these organometallic derivatives in aqueous solution at pH 5 or pH 7 by reaction of $[(\eta\text{-}C_5H_5)TiCl_3]$ with an appropriate heteropolyanion. The complexes are related to the Keggin-type anions $[W_{12}PO_{40}]^{3-}$, $[W_{12}SiO_{40}]^{4-}$, and $[Mo_{12}SiO_{40}]^{4-}$ by substitution of a

$[WO]^{4+}$ or $[MoO]^{4+}$ moiety with $[Ti(\eta\text{-}C_5H_5)]^{3+}$. ^1H and ^{31}P NMR spectra indicate that these $(\eta\text{-}C_5H_5)Ti$ derivatives may exist as two isomers, but the nature of the isomerism is not yet understood.

Klemperer and Shum [85] have synthesized the $[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$ anion by reaction of $[(\eta\text{-}C_5H_5)_2TiCl_2]$ with $[Bu_4N]_2[Mo_2O_7]$ and water in CH_2Cl_2 (eqn. (19)); the complex was isolated as a crystalline tetrabutylammonium salt. A pseudo-C_{4v} structure (12) has been assigned on the basis of

$$2(\eta\text{-}C_5H_5)_2TiCl_2 + 5[Mo_2O_7]^{2-} + H_2O$$
$$\rightarrow 2[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-} + 4\ Cl^- + 2\ C_5H_6 \qquad (19)$$



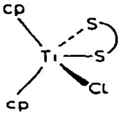
(12)

the completely resolved ^{17}O NMR spectrum, which exhibits the expected six resonance lines.

2.1.5 Complexes with S-donor ligands

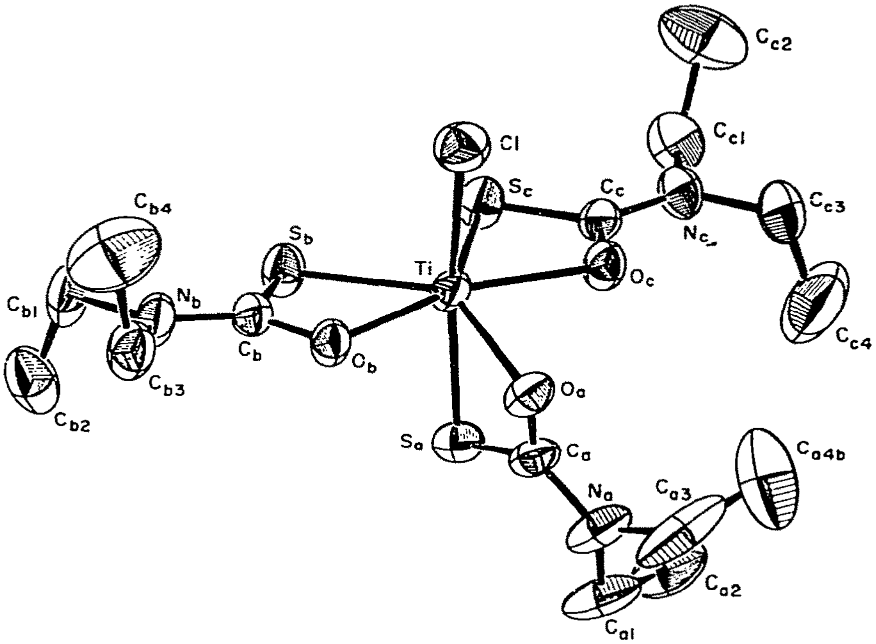
Hexamethyldisilathiane, $S(SiMe_3)_2$, reacts with $TiCl_4$ extremely rapidly to give polymeric $(Cl_2TiS)_n$ which can be converted to soluble monomeric adducts $TiCl_2S \cdot 3\ L$ (L = ethanenitrile, pyridine or tetrahydrofuran) upon treatment with strong donor solvents [40]. The first dithioacid derivatives of Ti(IV), $[Ti(dtb)_nCl_{4-n}]$ (dtb = dithiobenzoate; $n = 2$, 3 or 4), have been prepared by reaction of $TiCl_4$ with dtbH or Na[dtb]. With Na[dtb], one obtains $[Ti(dtb)_2Cl_2]$ or $[Ti(dtb)_4]$, depending on the stoicheiometry of the reaction mixture; with dtbH, the only product that could be isolated, irrespective of the ligand-to-metal ratio, is $[Ti(dtb)_3Cl]$. The $[Ti(dtb)_nCl_{4-n}]$ complexes are monomeric nonelectrolytes in solution, and the $\nu(C\overset{\dots}{-}S)$ region of IR spectra indicates bidentate attachment of the dtb ligands. Consequently, Ti is assigned coordination numbers of 6, 7 or 8 for $n = 1$, 2 or 3, respectively [86], as in the dithiocarbamate analogues, $[Ti(dtc)_nCl_{4-n}]$ [87]. The electronic spectra of [Ti(dtb)$_n$Cl$_{4-n}$] have been recorded, and interpreted in terms of metal—ligand π bonding [86]. [Ti(dtb)$_3$Cl] and the corresponding 4-methoxydithiobenzoate, [Ti(mdtb)$_3$Cl], have also been prepared by reaction of the dithioacids with $TiCl_4 \cdot 2$ EtCN. Hydrolysis of the chloro-complexes gives [{Ti(dtb)$_3$}$_2$O] and [{Ti(mdtb)$_3$}$_2$O], which have been assigned seven-coordinate oxo-bridged structures on the basis of IR spectra (ν(Ti—O—Ti) = 750 cm^{-1}) [88].

Three series of cyclopentadienyl *N*-aryl-substituted dithiocarbamato-complexes have been reported [89—91]. Six-coordinate complexes of the type [(η-C$_5$H$_5$)$_2$Ti(S$_2$CNHAr)$_2$] were synthesized by reaction of [(η-C$_5$H$_5$)$_2$TiCl$_2$] with excess [NH$_4$][S$_2$CNHAr] in aqueous solution [89], while five-coordinate complexes of the types [(η-C$_5$H$_5$)$_2$Ti(S$_2$CNHAr)Cl] [90] and [(η-CH$_3$C$_5$H$_4$)$_2$-Ti(S$_2$CNHAr)Cl] [91] were obtained by reaction of equimolar amounts of [(η-C$_5$H$_5$)$_2$TiCl$_2$] or [(η-CH$_3$C$_5$H$_4$)$_2$TiCl$_2$] and [NH$_4$][S$_2$CNHAr] in refluxing dichloromethane. All of these compounds are monomeric nonelectrolytes in solution, and IR spectra indicate bidentate attachment of the dithiocarbamate ligands. A trigonal bipyramidal structure with the two cyclopentadienyl ligands in *trans* positions has been proposed for the five-coordinate compounds [90], but NMR spectra are equally consistent with an edge-capped tetrahedral structure of C_s symmetry (13) or with a fluxional structure of lower symmetry.



(13)

Seven-coordinate *N,N*-dialkylmonothiocarbamate complexes of the type [Ti(SOCNR$_2$)$_3$Cl] (R = Me, Et, CHMe$_2$ or CH$_2$CHMe$_2$) have been prepared by reaction of TiCl$_4$ with stoicheiometric amounts of Na[SOCNR$_2$] in dichloromethane or benzene. The *N,N*-diethyl derivative has a pentagonal bipyramidal structure (14) in which the chlorine atom occupies an axial position {r(Ti—Cl) = 2.330 Å} and the monothiocarbamate ligands are oriented so as to cluster the three sulphur atoms in all-*cis* positions on one triangular face of the pentagonal bipyramid {r(Ti—S) = 2.477—2.489 Å; r(Ti—O) = 2.076—2.089 Å}. Low-temperature ^{1}H NMR spectra of [Ti(SOCNMe$_2$)$_3$Cl], viz. four methyl resonances of relative intensity 1 : 2 : 2 : 1, favour the same structure in solution. At higher temperatures, NMR line-shape changes indicate the existence of two distinct kinetic processes: (a) a low-temperature intramolecular metal-centered rearrangement process that exchanges the equatorial SOCNMe$_2$ ligands with the ligand that spans axial and equatorial sites ($\Delta G^{\ddagger}(-58.2°C) = 45.2 \pm 0.4$ kJ mol^{-1}, $\Delta H^{\ddagger} = 46.9 \pm 1.2$ kJ mol^{-1}, $\Delta S^{\ddagger} = 8.4 \pm 6.7$ J mol^{-1} K^{-1}) and (b) a high-temperature process that involves rotation about the C$\overset{\dots}{=}$N bond in the SOCNMe$_2$ ligands ($\Delta G^{\ddagger}$ (110°C) = 83.7 kJ mol^{-1}). A polytopal rearrangement mechanism involving a monocapped octahedral transition state



(14)

that maintains the all-*cis* arrangement of sulphur atoms has been suggested for the mechanism of metal-centered rearrangement. These complexes are of special interest because they are rare examples of seven-coordinate halotris(chelate) complexes that become rigid on the NMR time scale at readily accessible temperatures [92].

Alkyl thioglycolate complexes of the type $Ti(OCHMe_2)_2G$ and TiG_2 ($G = [SCH{=}C(OR)O]^{2-}$; R = Me or Et) have been synthesized by reaction of $Ti(OCHMe_2)_4$ with stoicheiometric amounts of the alkyl thioglycolate, H_2G. The isopropoxy groups of $Ti(OCHMe_2)_2G$ are replaced by *t*-butoxy groups when the isopropoxy complex is refluxed with an excess of *t*-butanol in benzene. IR spectra and molecular weight measurements indicate that the $Ti(OR)_2G$ complexes have alkoxy-bridged dimeric structures. In both the $Ti(OR)_2G$ and the TiG_2 complexes, the alkyl thioglycolates act as dinegative, bidentate ligands [93].

2.1.6 Complexes with N-donor ligands

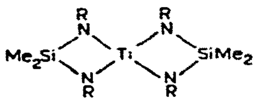
The azido-complexes $[(\eta\text{-}C_5H_5)TiCl_2(N_3)]$, $[(\eta\text{-}C_5H_5)_2TiCl(N_3)]$, $[Ti(N_3)(S_2CNEt_2)_3]$, and $[TiCl(N_3)(S_2CNEt_2)_2]$ have been synthesized by reaction of trimethylsilylazide with the appropriate metal chloride according to the general preparative route represented by eqn. (20). The phosphineiminato-

$$L_xTiCl_n + Me_3SiN_3 \rightarrow L_xTiCl_{n-1}(N_3) + Me_3SiCl \qquad (20)$$

complex $[TiCl(NPPh_3)(S_2CNEt_2)_2]$ was prepared similarly by reaction of

$Me_3SiNPPh_3$ with $[TiCl_2(S_2CNEt_2)_2]$. Reaction of $Me_3SiNPPh_3$ with $TiCl_4$ gave $[TiCl_2(NPPh_3)_2]$, even when four equivalents of $Me_3SiNPPh_3$ were used. Because of its low solubility, $[TiCl_2(NPPh_3)_2]$ may be polymeric, and high values of $\nu(P{=}N)$ (1090 and 1110 cm^{-1}) suggest chloride rather than $NPPh_3$ bridges. $[Ti(N_3)(S_2CNEt_2)_3]$ is expected to be pentagonal bipyramidal but is non-rigid on the NMR time-scale down to −60°C. $[(\eta\text{-}C_5H_5)TiCl_2(N_3)]$ reacts with PPh_3 to give a complex with a strong IR band at 1120 cm^{-1} characteristi of $[(\eta\text{-}C_5H_5)TiCl_2(NPPh_3)]$; HCl and MeCOCl cleave the Ti—N bond of $[(\eta\text{-}C_5H_5)TiCl_2(N_3)]$ yielding $[(\eta\text{-}C_5H_5)TiCl_3]$ [94].

Imido-complexes of the type $Ti(OCHMe_2)_{4-n}(NHCOR)_n$ (n = 1, 2, 3 or 4; R = Me, Ph or C_5H_4N) have been prepared in quantitative yield by reaction of $Ti(OCHMe_2)_4$ with stoicheiometric amounts of acetamide, benzamide and nicotinamide. These compounds are insoluble in common organic solvents, generally high melting, and probably polymeric. IR spectra show an unperturbed $\nu(C{=}O)$ vibration, indicating that the NHCOR ligand coordinates through the N atom [95]. *N,N′*-Dilithiated diaminosilanes, $Me_2Si(N(R)Li)_2$ (R = $CHMe_2$, Me_3C or Me_3Si) react with $TiCl_4$ in a 2 : 1 mole ratio to give spirocyclic titanium amides (15). Titanacyclobutanes (16) are obtained upon reaction of $Me_2Si(N(R)Li)_2$ with TiX_4 (X = F, Cl or Br) (1 : 1 mole ratio) or $(R_2'N)_2TiBr_2$ (R′ = Me or Et) [96].



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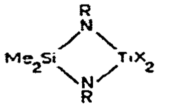
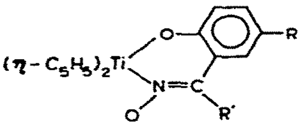


(16)

(X = F, Cl, Br, NMe_2, NEt_2)

$[(\eta\text{-}C_5H_5)_2TiCl_2]$ reacts with *o*-hydroxy oximes and with glyoximes in the presence of triethylamine to give complexes of the types (17) (R = R′ = H; R = Me and R′ = H, Me, Et or Pr); (18) (R = H or Ph), and (19). All of these oximes except dimethylglyoxime behave as dibasic ligands [97].



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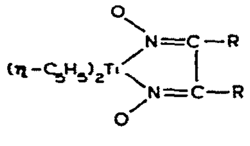

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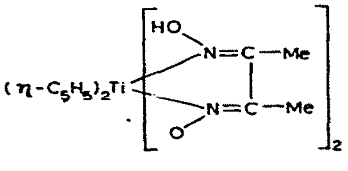
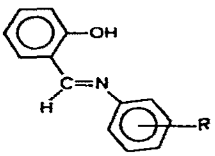


(19)

Reactions of $Ti(OCHMe_2)_4$ with the bidentate Schiff bases (20) and (21) (R = 2-Me or 4-Me) in 1 : 1, 1 : 2 or 1 : 3 mole ratios in refluxing benzene



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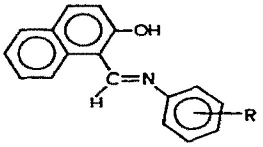
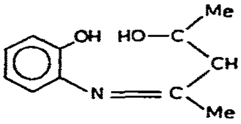


(21)

afford the complexes $[Ti(OCHMe_2)_{4-n}(SB)_n]$, where $n = 1$, 2 or 3, respectively, and SB^- is the anion of the Schiff base. The fourth $OCHMe_2$ group could not be replaced, even when reactions were carried out with an excess of Schiff base. Monomeric molecular weights in boiling benzene indicate that the Ti atom has coordination numbers 5, 6 or 7, respectively, when $n = 1$, 2 or 3 [98]. Two papers have appeared that describe Ti(IV) complexes with terdentate Schiff bases [99,100]. The complexes are of the types $Ti(SB)_2$ and $Ti(OR)_2(SB)$, where R = Me, Et or $CHMe_2$, and SB^{2-} is the dinegative anion of any one of a large number of Schiff bases; an example is pentane-2,4-dione-2-hydroxyanil (H_2AAP) (22). IR and NMR spectral evidence indi-



(22)

cates that the Schiff base ligands behave as dibasic terdentate *ONO*-donors. Titanium achieves coordination number 6 in both $Ti(SB)_2$ and $Ti(OR)_2SB$, in the latter compounds, by formation of alkoxy-bridged dimers. These dimers are in equilibrium with the monomer and with disproportionation products according to eqn. (21), but only in the case of $Ti(OCHMe_2)_2(AAP)$ is this

$$2[Ti(OR)_2(SB)] \rightleftharpoons [Ti(OR)_2(SB)]_2 \rightleftharpoons Ti(OR)_4 + Ti(SB)_2 \qquad (21)$$

equilibrium shifted significantly toward the monomeric species [99].

The mechanism of oxo—peroxo ligand substitution in Ti(IV) porphyrins (eqn. (22)) has been investigated by NMR and isotopic labelling experiments.

$$Ti(O)P + H_2O_2 \rightarrow Ti(O_2)P + H_2O \qquad (22)$$

Substitution occurs with retention of configuration and with the O—O bond of H_2O_2 remaining intact in the peroxo-complex. An associative mechanism in which the intermediate has entering and leaving ligands adjacent to each other on a single face of the porphyrin has been suggested [101].

2.2 TITANIUM(III) COMPOUNDS

2.2.1 Halide and pseudohalide complexes

Quantum mechanical calculations of the ab initio restricted-Hartree—Fock type indicate that the equilibrium geometry of TiF_3 should be trigonal planar

(D_{3h} symmetry) with a Ti—F distance of 1.83 Å [102]. The electronic ground state, $^2A_1'$, is calculated to lie 2260 cm^{-1} below the first excited state, $^2E''$, in good agreement with an EPR value of 2000 cm^{-1} [103]. The EPR spectrum of TiF_3 indicates that the molecule has a threefold axis but does not establish whether TiF_3 is planar or pyramidal. The IR spectrum of TiF_3 has been interpreted in terms of a pyramidal structure [104].

$KTiF_4$ has a crystal structure in which TiF_6 octahedra share four corners to form $(TiF_4)_n$ layers perpendicular to the orthorhombic c axis. The Ti—F distances range from 1.884 to 2.065 Å ($\bar{r}$ = 1.968 Å). The K^+ ions lie between the $(TiF_4)_n$ layers and have seven nearest-neighbour F^- ions [105].

The magnetic properties of $[TiCl_3(thf)_3]$ (thf = tetrahydrofuran) and its thermal decomposition products $[TiCl_3(thf)_2]$ and $TiCl_3 \cdot thf$ have been studied at 77—300K. The magnetic data are consistent with monomeric structures for $[TiCl_3(thf)_3]$ (confirmed by a crystal structure determination) and $[TiCl_3(thf)_2]$, and they point to a polymeric species for $TiCl_3 \cdot thf$ [106]. A related study (77—300K) of $TiCl_3 \cdot 4\ ROH$ (R = Me, Et or $CHMe_2$) and $TiCl_3 \cdot 3\ ROH$ (R = Pr, Bu or CH_2CHMe_2) shows that the Ti(III) ions are magnetically dilute in these complexes; effective magnetic moments at room temperature are 1.79—1.86 μ_B [107]. The thermal decomposition of nitrile adducts of $TiCl_3$, $TiCl_3 \cdot 3\ RCN$ (R = Me, $CH_2{=}CH$, Ph or CH_2Ph) and $TiCl_3 \cdot 4\ MeCN$, has been investigated by thermogravimetric analysis [108].

Addition of $TiCl_3$ to KCl—LiCl or CsCl—LiCl eutectics leads to formation of compounds such as $M_3[TiCl_6]$, $M_3[Ti_2Cl_9]$ or $TiCl_3 \cdot nMCl$, where M = K or Cs and n is unknown. The nature of the Ti(III) complexes present in solutions of $TiCl_3$ in alkali chloride eutectics depends on the alkali cation. Raman spectroscopy shows the presence of $[TiCl_6]^{3-}$ anions when the melt contains K^+, but a different anion, perhaps $[Ti_2Cl_9]^{3-}$, is present when the melt contains Cs^+ [109].

Interesting solids of composition $[NH_4]_3TiX_3(CN)_3$ (X = Cl or Br) have been obtained from solutions of TiX_3 and $[NH_4]CN$ in liquid ammonia. X-ray powder patterns of these solids show only lines due to $[NH_4]X$. The electronic spectrum of "$[NH_4]_3TiCl_3(CN)_3$" exhibits a d—d transition at 22 000 cm^{-1} with a shoulder at 18 500 cm^{-1}. This spectrum is very similar to that of $K_3[Ti(CN)_6]$, suggesting that the Ti(III) in "$[NH_4]_3TiCl_3(CN)_3$" is octahedrally coordinated with $[CN]^-$ ions. Consequently, these solids are formulated as mixtures of $Ti(CN)_3$ and $3[NH_4]X$. No simple cyanide of Ti(III) has been reported previously. A polymeric structure for the $Ti(CN)_3$ is suggested by a low magnetic moment (μ_{eff} = 1.31 μ_B at 20°C) and by ν(CN) IR bands characteristic of bridging and terminal cyanide ligands. Attempts to separate $Ti(CN)_3$ from the ammonium halide have thus far proved unsuccessful [110].

The new Ti(III) cyanide complex $[TiCl_2(CN)(MeCN)_2]_2$ has been synthesized by refluxing a mixture of KCN and $TiCl_4$ in ethanenitrile. A chlorine-bridged dimeric structure that contains octahedrally coordinated Ti(III) has been assigned on the basis of a cryoscopic molecular weight determination in $POCl_3$ and IR spectra (ν(Ti—Cl bridging) = 340 cm^{-1}; ν(Ti—Cl terminal) =

460 cm^{-1}; ν(C≡N, terminal cyanide) = 2150 and 2090 cm^{-1}); the complex has a room-temperature magnetic moment of 0.6 μ_B [111].

2.2.2 Compounds with O-donor ligands

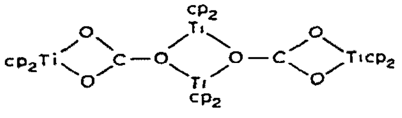
Unit cell parameters have been reported for the isomorphous series of compounds $MH(SO_4)_2 \cdot 4\,H_2O$ (M = Ti, V, Fe, Al, Ga, In or Tl) [112]. A new family of phosphates of the type $Na_3M_2(PO_4)_3$ (M = Ti, V, Cr or Fe) has been obtained by high-temperature synthesis. These compounds have structures of the $NaZr_2(PO_4)_3$ type, and therefore they may be interesting ionic conductors [113].

The spectral and magnetic properties of polymeric diisopropyl phosphate (dipp) and di-*n*-propyl phosphate (dnpp) complexes of the type $M(dipp)_3$ and $M(dnpp)_3$ (M = Ti, V, Cr, Fe, Al or Dy) have been compared as part of an effort to assess steric and inductive effects of alkyl substituents on the strength of the metal—oxygen bond in metal complexes with organophosphorus ligands. In comparison with the dnpp complexes, the dipp complexes exhibit lower values of ν(M—O), lower values of the ligand field parameter *Dq*, and higher values of the magnetic moment. These data point to a weaker M—O bond in the dipp complexes, which is attributed to a steric effect of the $CHMe_2$ substituents since inductive effects of $CHMe_2$ and Pr groups are about the same. Of the possible polymeric structures for these compounds, the authors prefer a linear, chain-like, triply-bridged structure of the type $\{M(O\text{-}P(R)_2\text{-}O)_3\}_n$ [114].

Russian workers have measured formation constants for complexes of Ti(III) with dihydrogen citrate (H_2cit^-) and oxalate. The complexes formed in aqueous solution at pH 1.0 are $[Ti(H_2cit)_2]^+$ [115] and $[Ti(C_2O_4)_n]^{+3-2n}$ (n = 1, 2 or 3) [116].

The reactions of carbon dioxide with $[(\eta\text{-}C_5H_5)_2TiCl]_2$ and $[(\eta\text{-}C_5H_5)_2Ti(CO)_2]$ have been studied by Fachinetti et al. CO_2 is deoxygenated to CO by $[(\eta\text{-}C_5H_5)_2TiCl]_2$ (eqn. (23)), while $[(\eta\text{-}C_5H_5)_2Ti(CO)_2]$ promotes the disproportionation of CO_2, yielding CO and the tetranuclear carbonato-bridged Ti(III) complex $[\{(\eta\text{-}C_5H_5)_2Ti\}_2(CO_3)]_2$ (23) (eqn. (24)).

$$CO_2 + [(\eta\text{-}C_5H_5)_2TiCl]_2 \rightarrow [\{(\eta\text{-}C_5H_5)_2TiCl\}_2O] + CO \qquad (23)$$



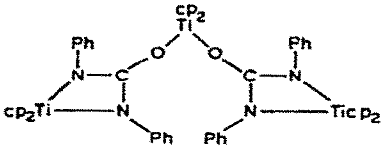
(23)

Compound (23) has

$$4[(\eta\text{-}C_5H_5)_2Ti(CO)_2] + 4\,CO_2 \rightarrow [\{(\eta\text{-}C_5H_5)_2Ti\}_2(CO_3)]_2 + 10\,CO \qquad (24)$$

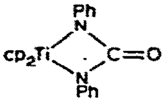
a magnetic moment of 1.70 μ_B per Ti atom at 293K, and its structure has been established by X-ray diffraction. Reactions (23) and (24) can be understood in terms of the free radical-like nature of $[(\eta\text{-}C_5H_5)_2TiCl]$ and the carbenoidlike nature of the d^2 complex $[(\eta\text{-}C_5H_5)_2Ti(CO)_2]$ [117].

Closely related to the carbonato-bridged tetranuclear complex (23) is the trinuclear diphenylureylene-bridged complex (24) obtained by the $[(\eta\text{-}C_5H_5)_2\text{-}Ti(CO)_2]$-promoted disproportionation of phenyl isocyanate (eqn. (25)). X-ray diffraction and magnetic data indicate that (24) contains a central Ti(IV) atom and two equivalent Ti(III) atoms. Complex (24) is converted in hot toluene solution to the diamagnetic mononuclear Ti(IV) complex (25) and the dinuclear Ti(III) complex (26).

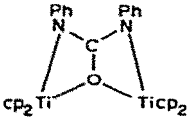


(24)

$$3[(\eta\text{-}C_5H_5)_2Ti(CO)_2] + 4\ PhNCO \rightarrow [\{(\eta\text{-}C_5H_5)_2Ti\}_3\{OC(NPh)_2\}_2] + 8\ CO \tag{25}$$



(25)

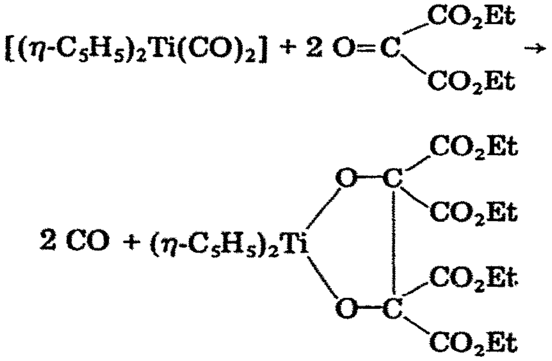


(26)

Complex (26) can be synthesized directly by reaction (26); its structure has been established by X-ray diffraction [118].

$$2[(\eta\text{-}C_5H_5)_2Ti(CO)_2] + 2\ PhNCO \rightarrow CO + [\{(\eta\text{-}C_5H_5)_2Ti\}_2\{OC(NPh)_2\}] \tag{26}$$

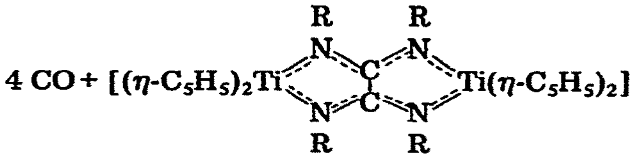
While $[(\eta\text{-}C_5H_5)_2Ti(CO)_2]$ promotes the disproportionation of CO_2 and PhNCO, it induces the reductive coupling of CO_2-like molecules such as diethyl ketomalonate (eqn. (27)) and *N,N'*-di-4-tolylcarbodiimide (eqn. (28)).



$$[(\eta\text{-}C_5H_5)_2Ti(CO)_2] + 2\ O{=}C(CO_2Et)_2 \rightarrow 2\ CO + (\eta\text{-}C_5H_5)_2Ti[OC(CO_2Et)_2]_2 \tag{27}$$

(27)

$2[(\eta\text{-}C_5H_5)_2Ti(CO)_2] + 2\ RN{=}C{=}NR \rightarrow$



(28)

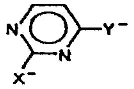
(R = 4-$CH_3C_6H_4$)

(28)

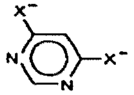
Reductive coupling of the carbonyl and imino functional groups is accompanied by oxidative addition to the $(\eta\text{-}C_5H_5)_2Ti(II)$ moiety, affording the diamagnetic Ti(IV) complex (27) and the paramagnetic Ti(III) complex (28) ($\mu_{eff} = 1.74\ \mu_B$ per Ti at 293K). The structures shown in eqns. (27) and (28) have been confirmed by a preliminary X-ray study of (27) and a completed X-ray study of (28). The bridging ligand in (28) has bond distances indicative of a C—C single bond (1.504(6) Å) and C⩦N partial double bonds (1.328(2) and 1.333(3) Å) [119].

2.2.3 Compounds with S-donor ligands

A series of dinuclear bis-bidentate bridged Ti(III) complexes of the type $[\{(\eta\text{-}CH_3C_5H_4)_2Ti\}_2B]$, where the bridging ligand B is the dianion of 2,4-dithiopyrimidine (29), 2,4-diselenopyrimidine (30), 2-thiouracil (31), 4-thiouracil (32), 4,6-dihydroxypyrimidine (33) or 4,6-dithiopyrimidine (34),

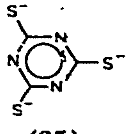


(29) X = Y = S
(30) X = Y = Se
(31) X = S, Y = O
(32) X = O, Y = S



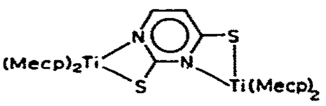
(33) X = O
(34) X = S

has been prepared by reaction in thf of $[(\eta\text{-}CH_3C_5H_4)_2TiCl]_2$ with the dianion of the substituted pyrimidine. A trinuclear derivative $[\{(\eta\text{-}CH_3C_5H_4)_2Ti\}_3B]$, where B is the trianion of trithiocyanuric acid (35), was synthesized by a



(35)

similar procedure. The structure of the 2,4-dithiopyrimidinato-complex (36)



(36)

has been established by X-ray diffraction; the Ti(III) atoms lie within 0.11 Å of the plane of the bridging ligand and are separated from each other by 6.075(2) Å. Magnetic susceptibility measurements (4.2—244K) show that some of these complexes exhibit weak ferromagnetic exchange interactions ($J = +2$ to $+3$ cm^{-1}) while others display weak antiferromagnetic interactions ($J = -1.4$ to -1.9 cm^{-1}). EPR spectra show well-resolved zero-field splittings [120—122].

$TiCl_3 \cdot 3$ thf reacts with hexamethyldisilathiane, $S(SiMe_3)_2$, in thf to give the insoluble (polymeric) grey solid $TiCl(S) \cdot 1.5$ thf and $SiMe_3Cl$. IR bands due to ν(Ti—Cl) modes are characteristic of octahedral Ti(III) [40].

The superstructures of the non-stoicheiometric titanium sulphides $TiS_{1.45}$ and $TiS_{1.51}$ have been investigated by X-ray diffraction [123] and high-resolution electron microscopy [124,125].

2.2.4 Compounds with N- and P-donor ligands

The IR spectrum of gaseous TiN has been observed, affording values for the ground state vibrational frequency ($\nu_0 = 969.6(20)$ cm^{-1}) and the rotational constants ($B_e = 0.623(6)$ cm^{-1}, $\alpha_e = 4.08(4) \times 10^{-3}$ cm^{-1}, $r_e = 1.58(1)$ Å). TiN has a $^2\Sigma$ ground state [126].

An X-ray diffraction study has shown that the dinuclear complex $[\{(\eta\text{-}C_5H_5)_2Ti(4\text{-}CH_3C_6H_4)\}_2N_2]$ has a centrosymmetric structure in which the two Ti atoms are linked in an essentially linear fashion by a dinitrogen bridge $\{r(Ti—N) = 1.962(6)$ Å, $r(N—N) = 1.162(12)$ Å$\}$. The 4-tolyl groups are σ-bonded to Ti$\{r(Ti—C) = 2.216(7)$ Å$\}$, and the two phenyl rings and the atoms of the TiN≡NTi unit are coplanar to within 0.12 Å. This latter feature enables both Ti atoms to engage in $d\pi—p\pi$ back bonding with the same π^* orbital of the N_2 ligand, thus accounting for the diamagnetism of the complex. It also makes possible delocalization of π electrons from the N_2 ligand via the Ti atoms to the phenyl groups [127].

The five-coordinate *meso*-tetraphenylporphyrinato-complex [TiF(TPP)] has been synthesized by reduction of $[TiF_2(TPP)]$ with zinc amalgam. Electrochemical reduction of $[TiF_2(TPP)]$ or chemical reduction with sodium anthracenide gives $[TiF_2(TPP)]^-$. Consistent with its coordinative unsaturation, [TiF(TPP)] adds ligands L (L = thf, PBu_3, pyridine, *N*-methylimidazole, or *N*-methylpyrrolidone) yielding [TiF(L)(TPP)], and adds F^- affording $[TiF_2(TPP)]^-$. All of these Ti(III) complexes have been characterized in solution by EPR spectroscopy; the unpaired electron is believed to reside in the $3d_{xy}$ orbital. Oxidation of [TiF(TPP)] yields a mixture of $[TiF_2(TPP)]$ and the peroxo-complex$[Ti(O_2)(TPP)]$. EPR evidence suggests that this reaction proceeds via the dioxygen adduct $[TiF(O_2)(TPP)]$ (eqns. (29) and (30)), a

$$[TiF(TPP)] + O_2 \rightleftharpoons [TiF(O_2)(TPP)] \qquad (29)$$

$$[TiF(TPP)] + [TiF(O_2)(TPP)] \rightarrow [TiF_2(TPP)] + [Ti(O_2)(TPP)] \qquad (30)$$

species which could be formulated as a superoxo-titanium(IV) complex but which appears to have a significant amount of peroxo-porphyrin cation radical-titanium(IV) character [128].

Muchnik et al. have reported an improved method for synthesis of the titanium phosphides TiP and TiP_2. Titanium and phosphorus are heated together in the presence of iodine, which evidently leads to initial formation and then decomposition of TiI_4. The titanium metal produced by this decomposition reacts smoothly with phosphorus to form TiP or TiP_2 depending on the stoicheiometry of the reaction mixture. Synthesis by this method occurs more rapidly and at lower temperatures than in the absence of iodine [129].

2.2.5 Electron transfer reactions

Titanium(III) is a common reductant in kinetic studies of electron transfer reactions. Space does not permit detailed discussion of work in this area, but several of the more important papers will be mentioned in passing. Kinetic data have been reported for oxidation of Ti(III) in acidic aqueous media by the following oxidants: $[Co(NH_3)_5(OOCCX_3)]^{2+}$ (X = H, F or Cl) [130]; $[Ru(NH_3)_5X]^{2+}$ (X = Br or I) [131]; $[Ru(NH_3)_5(OOCCH_3)]^{2+}$, $[Ru(NH_3)_5(C_2O_4)]^{+}$ and *cis*-$[Ru(NH_3)_4(C_2O_4)]^{+}$ [132]; tris-bipyridine or -phenanthroline derivatives of Os(III) [133]; I_2 and I_3^- [134]. Rate laws for these reactions exhibit a dependence on $[H^+]^{-1}$, indicating that the primary reacting Ti(III) species is $Ti(OH)^{2+}$ rather than Ti^{3+}. Reactions with the oxidants that contain ethanoate and oxalate ligands are believed to occur by an inner-sphere mechanism [130,132]; all of the other reactions appear to take place by an outer-sphere mechanism [130,131,133,134].

Reduction of $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_3)_5(H_2O)]^{3+}$ with the Ti(III)-edta (edta = ethylenediaminetetracetate) complex has been studied at pH $\leqslant$ 2 where the complex is believed to have the structure $[Ti(edtaH)(H_2O)]$. The reductions of $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5Cl]^{2+}$ follow an acid-independent path and appear to occur by an outer-sphere mechanism. However, reduction of $[Co(NH_3)_5(H_2O)]^{3+}$ exhibits an $[H^+]^{-1}$ dependence, which is attributed to reaction of the hydrolysis product $[Co(NH_3)_5(OH)]^{2+}$. The latter complex is $\sim 10^6$ times more reactive than $[Co(NH_3)_5(H_2O)]^{3+}$, suggesting that $[Co(NH_3)_5(OH)]^{2+}$ reacts by an inner-sphere mechanism that involves formation of the intermediate hydroxo-bridged complex $[(edtaH)Ti(OH)Co(NH_3)_5]^{2+}$ [135]. Electron transfer from Ti(III) to Co(III) through a pyridine-2,4,6-tricarboxylate bridge has been interpreted in terms of a two-step mechanism in which the bridging ligand is first reduced in the rate-determining step [136].

2.3 TITANIUM(II) COMPOUNDS

An X-ray study of $[\{\eta\text{-}(CH_3)_6C_6\}Ti(Cl_2AlCl_2)_2] \cdot C_6H_6$ shows that the Ti atom has square-pyramidal coordination with four Cl atoms at the base of the pyramid and the centroid of the η-hexamethylbenzene ligand at the apex. The

$\bar{r}$(Ti—C) = 2.50 Å and $\bar{r}$(Ti—Cl) = 2.615 Å distances are rather long compared with Ti—C and Ti—Cl distances in related Ti(III) and Ti(IV) complexes [137]. Magnetic susceptibility and EPR studies show that $[(\eta\text{-}C_5H_5)_2Ti(bipy)]$ has a triplet excited state that lies ~600—750 cm^{-1} above the singlet ground state. Fenske-Hall MO calculations suggest that the triplet should be described as a state in which one unpaired electron occupies an MO which is localized on the $(\eta\text{-}C_5H_5)_2Ti$ moiety while the second unpaired electron resides in the lowest energy π^* orbital of the bipyridine ligand [138]. He(I)- and He(II)-excited photoelectron spectra have been reported for $[(\eta\text{-}C_5H_5)_2Ti(CO)_2]$. The first band (6.35 eV) is assigned to ionization of a Ti 3*d* electron; a vibrational progression associated with this band (interval 2300 ± 150 cm^{-1}) is cited as evidence for significant metal—ligand back bonding involving the occupied Ti 3*d* orbital and the vacant carbonyl π^* orbitals [139].

Titanium polonide has been synthesized from the elements at 540—570°C. It has a hexagonal structure of the NiAs type [140].

2.4 MIXED-VALENCE COMPOUNDS

This section includes compounds in which titanium is present in more than one oxidation state and compounds which are not easily classified in terms of formal oxidation states. New, crystalline titanium halides having composition Ti_7Cl_{16} and Ti_7Br_{16} have been synthesized at elevated temperatures in the presence of Al_2Cl_6 and Al_2Br_6, respectively, which serve as gaseous transport agents. These compounds contain two kinds of Ti atoms, tentatively considered to be Ti(II) and Ti(IV). The structure of Ti_7Cl_{16} contains trigonal Ti_3Cl_{13} units consisting of three $Ti^{II}Cl_6$ octahedra that are joined together by edge-sharing and additionally by Ti—Ti bonds (2.954(2) Å). The three dimensional structure is built up by joining, via sharing of octahedral edges without Ti—Ti bonds, the Ti_3Cl_{13} units with one another and with $Ti^{IV}Cl_6$ octahedra. The resulting structural formula $Ti^{IV}Cl_{6/3}[Ti_3^{II}Cl_{12/3}Cl_{6/2}]_2$ is consistent with the stoicheiometry $TiCl_4 \cdot 6\ TiCl_2$ [141]. The chemical reactions of the compound $[(Ph_3P)_3PtCl]^+[Ti_3Cl_{11}]^-$ are consistent with the presence in the anion of two equivalents of Ti(III) and one equivalent of Ti(IV) [142].

Neodymium titanium bronzes of composition $Nd_{2/3+x}TiO_{3\pm y}$ $(0 \leqslant x \leqslant \frac{1}{3})$ having the perovskite structure have been synthesized from Nd_2O_3, Ti_2O_3 and TiO_2, and have been characterized by X-ray diffraction. These phases may be regarded as members of a series of solid solutions of $Nd_{2/3}TiO_3$ and $NdTiO_3$, in which the oxidation state of Ti changes from +4 to +3 [143]. Optimal conditions for synthesis of TiS_3 have been reported [144]. Several new phases have been detected in the Ti—P and Ti—Cu—P systems [145]. The diatomic molecule PtTi has been observed in a mass spectrometric study of the vapour above a high-temperature mixture of Pt and Ti. The measured dissociation energy of PtTi, $D^\circ_0 = 394 \pm 11$ kJ mol^{-1}, is indicative of multiple bonding [146].

2.5 PHOTOELECTROCHEMICAL AND PHOTOCATALYTIC PROPERTIES OF TiO_2

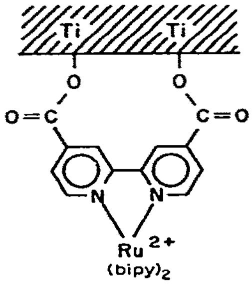
It is well known that *n*-type semiconducting TiO_2 can be employed as a photoanode in a cell for the photoelectrolysis of H_2O to H_2 and O_2 [5]. When a TiO_2 electrode is illuminated with light having an energy greater than the bandgap of 3.0 eV, electrons are excited into the conduction band, leaving positively charged holes (h^+) in the valence band. The holes migrate to the electrode surface and are able to oxidize H_2O to O_2 according to eqn. (31). H^+ ions are reduced to H_2 at a platinum counterelectrode (eqn. (32)), although this process requires a driving force of ~0.2 V in the external circuit because the conduction band of TiO_2 lies ~0.2 V below the potential for H_2 evolution. The overall cell reaction (eqn. (33)) represents a means for converting optical energy to chemical energy. The electrolysis of water can be effected with light as the only input energy source by employing a $SrTiO_3$ photoanode; in the case of $SrTiO_3$, the energies of the valence and conduction bands straddle the potentials for evolution of H_2 and O_2. Unfortunately, the band gap of $SrTiO_3$ is too large for this material to be useful in solar energy applications.

$$\text{TiO}_2\text{ anode:}\quad H_2O + 2\,h^+ \rightarrow \tfrac{1}{2}O_2 + 2\,H^+ \qquad (31)$$

$$\text{Pt cathode:}\quad 2\,H^+ + 2\,e^- \rightarrow H_2 \qquad (32)$$

$$\text{cell reaction:}\quad H_2O \xrightarrow{2h\nu} H_2 + \tfrac{1}{2}O_2 \qquad (33)$$

Several recent reports have been concerned with modification of the TiO_2 photoanode so as to increase its sensitivity to solar radiation and increase its long-term stability. Anderson et al. [147] have attached to a single-crystal *n*-type TiO_2 electrode a monolayer of a derivative of $[Ru(bipy)_3]^{2+}$; the bipyridine complex is attached via ester linkages as shown in (37). The modified electrode generates significant anodic photocurrents when irradiated with visible light ($\lambda > 450$ nm) in the absence of a supersensitizer. The light absorbed by the $[Ru(bipy)_3]^{2+}$ derivative is believed to excite an electron into the conduction band of TiO_2 with the Ru(III) complex left on the surface being subsequently reduced back to a Ru(II) complex by capture of an electron from the solution. Rauh et al. [148] have attempted to increase the sensitivity of TiO_2 and alkaline earth titanate electrodes to visible light by sub-



(37)

stituting d^n transition metal ions for Ti^{4+} to give compounds such as $Ti_{1-x}Cr_xO_{2-(x/2)}$. The idea is to introduce a valence band of non-bonding d-electron parentage between the usual valence and conduction bands characteristic of the unsubstituted materials. Several of the substituted materials were sensitized to the visible portion of the spectrum, although the photocurrent quantum yields were decreased by substitution. Subbarao et al. [149] have investigated the electrical and optical properties of fluorinated TiO_2 anodes, $TiO_{2-x}F_x$ ($x \leqslant 0.002$). The fluorinated anodes are more sensitive to long-wavelength radiation than optimally reduced TiO_{2-x} anodes, presumably because of the filling of oxygen vacancies. In addition, the $TiO_{2-x}F_x$ anodes exhibit a long-term stability that is at least as good as that of TiO_{2-x}.

When irradiated with UV light, n-type TiO_2 powders are effective photocatalysts for a number of important reactions. Reiche and Bard [150] have reported the photosynthesis of amino acids from H_2O, CH_4 and NH_3 or $[NH_4]Cl$ in the presence of aqueous suspensions of platinized TiO_2. This worl suggests that, during the initial stages of chemical evolution, synthesis of organic compounds could have occurred under the influence of solar radiation on the surface of semiconducting oxides. Reiche et al. [151] have described the photosynthetic reduction of Cu^{2+} on TiO_2 powder according to eqn. (34),

$$Cu^{2+} + H_2O \xrightarrow{2h\nu} Cu + \tfrac{1}{2}O_2 + 2\,H^+ \tag{34}$$

a reaction that has considerable potential in the removal or recovery of copper, even from dilute solutions. In a study of potential relevance to the gasification of coal, Kawai and Sakata [152] have found that irradiation of an aqueous suspension of TiO_2, RuO_2 and activated carbon produces H_2 and CO (eqn. (35)). Other reactions that are photocatalyzed by TiO_2 powders include

$$H_2O + C \xrightarrow[TiO_2\text{-}RuO_2]{2h\nu} H_2 + CO \tag{35}$$

the oxidation of N_2 to NO [153], NH_3 to N_2 and N_2O [154], and isobutane to propanone and CO_2 [155], and the reduction of CO_2 to HCOOH, HCHO, CH_3OH and CH_4 [156]. The first step in all of these reactions is presumed to be light-absorption by TiO_2, which generates electrons in the conduction band and positive holes in the valence band; the electrons subsequently serve as reducing agents, and the holes as oxidizing agents.

An earlier report of the photocatalytic decomposition of chemisorbed H_2O at the solid—gas interface of TiO_2/argon [157] has been questioned by Van Damme and Hall [158]. These workers suggest that the observed evolution of small amounts of H_2 and O_2 arises, not from a photocatalytic process, but from the photoassisted decomposition of the hydroxylated surface layer of TiO_2. This brief survey of reactions that are photocatalyzed by TiO_2 is concluded with mention of an interesting study of the photocatalytic oxidation of hydroquinone in which TiO_2 powder has been sensitized to visible light by coating the powder with phthalocyanines (MgPc or metal-free H_2Pc) [159].

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