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COORDINATION CHEMISTRY REVIEWS

1. Titanium 1993

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CONTENTS

INTRODUCTION

This review illustrates the advances in titanium chemistry as reported in the literature for 1993. The emphasis is mainly on coordination compounds with some references to organometallic compounds which may be pertinent. It is based on a search of volumes 118, 119 and 120 of *Chemical Abstracts*. In addition, major inorganic chemistry journals have been searched separately for the calendar year 1993. A review of complexes of sterically hindered thiolate ligands including those of titanium has appeared [1].

1.1 TITANIUM(IV)

1.1.1 Complexes with halide ligands

Studies on the electronic structure of MCl_4 (M = Ti, Zr and Hf) molecules by the multiple-scattering Xα (MS-Xα) method have been conducted in order to obtain energies for charge-transfer energy gaps [2]. The results are consonant with those observed experimentally.

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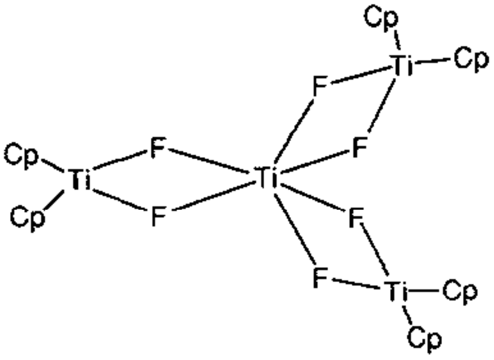
Interesting examples of the symbiosis of classical Werner coordination and organometallic chemistry have been synthesised [3]. The reaction of $[Cp_2Ti(CO)_2]$ with $[Cp_2TiF_2]$ led to the formation of the complexes (**1**) and (**2**). An X-ray structure for the former revealed the salient feature to be a distorted octahedral TiF_6 moiety. When the central Ti atom was replaced by aluminium the resulting compound was isostructural with (**1**). The Ti_2F_2 and $AlTiF_2$ rings are unsymmetrical while the central Ti and Al atoms are surrounded by the four-membered rings in a propeller-like manner. A metal-metal bonded interaction is not indicated: Ti-Ti = 3.2577(10) and Al-Ti = 3.1132(2) Å. These complexes have been studied by EPR spectroscopy.



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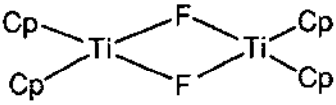

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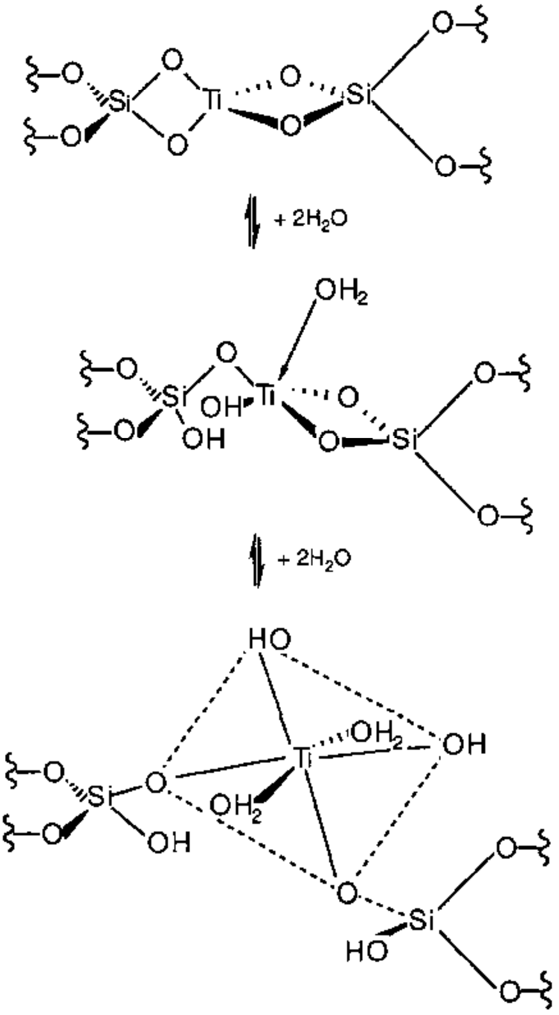
1.1.2 Complexes with oxygen donor ligands

The coupled substitution of Nb(IV) and Si(IV) for Ti(IV) and P(V)/As(V) in $KTiOPO_4$ (KTP) and $KTiOAsO_4$ (KTA) has given rise to a new series of non-linear optical materials, $KTi_{1-x}Nb_xOX_{1-x}Si_xO_4$ (X = P, As, x = 0 - 0.4) [4]. The niobium substitution in KTP and KTA did not destroy the second harmonic generation (SHG) response indicating the importance of the d^0 electronic configuration of the transition metal ion in determining the non-linear optical property of KTP and related materials.

An EXAFS multishell analysis of a titanium silicate shows that double Si-O-Ti bridges formed between $[TiO_x]$ and the $[SiO_4]$ framework tetrahedra are partially hydrolysed in the presence of water [5]. As a result, a switch from edge-sharing to corner-sharing bonding between the two units occurs as shown in (3).

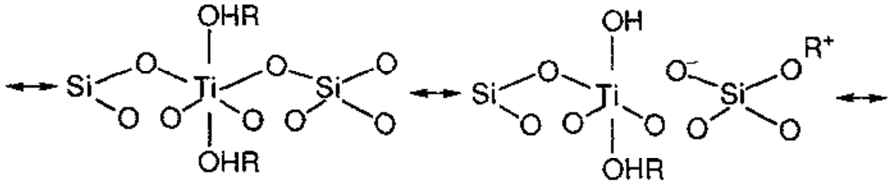
Interest in the use of heterodimetallic alkoxides as potential precursors for dimetallic oxides has led to a study on the nature of intermediates in the hydrolysis of mixed-metal alkoxides [6]. In particular, partial hydrolysis of $[LiTi(O^iPr)_5]_2$ yielded $[LiTi(O^iPr)_3]_4$ which has been characterised by ^1H and ^{13}C NMR spectroscopy and solid-state X-ray crystallography. Titanium and oxygen atoms are located in a middle layer with Li atoms in the layers above and below, supported by alkoxide bridges.



(3)

Heterodimetallic Pt-Ti complexes which may have chemotherapeutic potential in cancer treatment have been synthesised recently [7]. These complexes contain a classical platinum coordination compound linked to an organometallic titanium group *via* a bridging hydroxypyridine ligand. It is thought that with properly designed hydrolysis properties, complexes of this type may cross the cell wall intact and function as DNA chelators with titanium binding to an external phosphate and platinum binding to internal nitrogen donors. The crystal structure of *trans*-[$PtCl_2(DMSO)(NC_5H_4\text{-}2\text{-}OTi(C_5H_5)_2Cl)$] has been obtained and reveals platinum in a square planar environment with the chloride ions retaining their *trans*-orientation while the titanium centre has a distorted tetrahedral coordination.

An IR spectroscopic investigation on a large-pore β-Ti zeolite has been conducted and a new assignment for the characteristic 960 cm^{-1} IR band (Si-$O^{\delta-}$-$Ti^{\delta+}$stretching vibration) has been proposed [8]. The structural model features a changeable titanium coordination environment dependent on the presence of guest molecules. In essence, titanium coordinates to four framework oxygen atoms but also may interact with one or two more ligands (H_2O or OH^-) due to its large covalent radius thereby increasing its coordination five- or six-fold. Negative charges may be delocalised by resonance with the formation of Si-OR groups (R = Et_4N^+ or H^+) (**4**).



(**4**)

The synthesis, structure and alcoholysis of η^5-1,3-bis(trimethylsilyl)-cyclopentadienyltitanium *cis*-1,3,5-cyclohexanetrialkoxide have been described [9]. An X-ray structure indicates that the cyclopentadienyltitanium unit is bound via titanium to the trialkoxide and the average Ti-O bond distance is 1.830(2)Å. When this complex was reacted with 3 molar equivalents of methanol or ethanol in benzene, no exchange was seen after 3 hours at room temperature. When 3 molar equivalents of phenol were used, exchange occurred immediately with the precipitation of *cis*-1,3,5-cyclohexanetriol whereas when the complex was dissolved in ethanol complete exchange occurred in 15 minutes.

Interest in studying the interaction between Ziegler-Natta catalysts and esters has led to the preparation and characterization of several new Ti/Mg complexes containing carboxylate and phenoxy groups [10]. The reaction of [$TiMgCl_6 \cdot 4EtOAc$] with a variety of acids RCO_2H (R = C_6H_5, C_6H_5CHCH, p-$(CH_3)_3CC_6H_4$, and $(CH_3)_2CCH$ gave the heterodimetallic carboxylates [$TiMgCl_4(RCO_2)_2 \cdot 2EtOAc$] whereas with pivalic acid, [$TiMgCl_4\{(CH_3)_3CCO_2\}_2 \cdot 1.25EtOAc$] was obtained. In the corresponding reactions with phenol, [$TiMgCl_5(OC_6H_5) \cdot 1.25EtOAc$] and [$TiMg_2Cl_6(OC_6H_5) \cdot 2EtOAc$] were isolated.

An intercalation compound of $H_2Ti_4O_9$ with $TMpyPH_2$ has been prepared by a guest-exchange method using the $NPrH_3^+$- $H_xTi_4O_9$ intercalation compound as an intermediate [11]. The porphyrin was found to be intercalated with an inclined arrangement in the interlayer of $H_2Ti_4O_9$. Spectroscopic evidence indicates that it is present as the monomeric free-base ion. Fluorescence studies show the porphyrin is present as a monomer without stacked aggregation; the fluorescence decays rapidly indicative of interactions between porphyrin molecules in the interlayer space.

Cyclic complexes have been obtained from the reaction of Cp_2TiCl_2 with a series of substituted and unsubstituted dibasic phenols, bisphenols and binaphthols in a 1:1 molar ratio in the presence of sodium amide. The compounds were characterised on the basis of elemental analysis and IR and ^1H NMR spectroscopies [12].

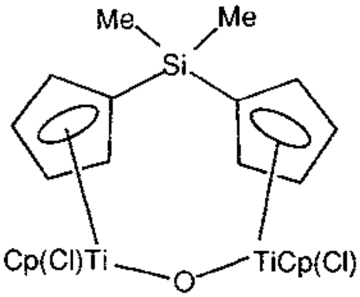
The crystal structure of [$TiCl_4(hmpa)_2$] (where hmpa is hexamethylphosphoric triamide) has been obtained [13]. The Ti atom is in an octahedral environment with the hmpa ligands bonding to the Ti atom via their O atoms and in a *trans*-orientation with respect to each other. The Ti-O bond length is 1.945(3) Å and the average Ti-Cl bond length is 2.328Å.

The reaction of $TiCl_4$ with allyl acetate ($CH_3CO_2CH_2CH=CH_2$) was studied in order to identify the preference of the coordination centre for the carbonyl oxygen or the C=C bond [14]. The resulting crystalline adduct comprises a centrosymmetric dimer in which each titanium atom is surrounded by three terminal Cl atoms, two bridging Cl atoms and one carbonyl O atom of the allyl acetate molecule forming an edge-sharing dioctahedron. The Ti....Ti distance is 3.851(4) Å and Ti-O bond length is 2.022(2) Å.

A new structural family of remarkably stable polyoxotitanate derivatives that display unusual regioselective alkoxide exchange with alcohols has recently been synthesised [15]. The alkoxides α_1 and α_2-[$Ti_{12}O_{16}$](O^iPr)$_{16}$ display very low moisture sensitivity in alcohol solution, while the alkoxide [$Ti_{11}O_{13}$](O^iPr)$_{18}$ has been identified as the sole (>95%) reaction product of $Ti(O^iPr)_4$ by approximately a half equivalent. of water in isopropanol solution.

The preparation of phosphanyl spacer-substituted metal alkoxides $(RO)_3E\text{-}X\text{-}PPh_2$ (E = Ti, Zr; X = spacer) has been documented [16]. In particular, the reaction of $HPPh_2$ with $(PrO_3)E(O_2CCH=CH_2)$ gave $(PrO_3)E(O_2CCH_2CH_2PPh_2)$ whereas $(PrO_3)Zr(O_2CCH_2PPh_2)$ was obtained by treatment of $(PrO_3)Zr(O_2CCH_2Cl)$ with $LiPPh_2$. These alkoxides were characterised by IR and ^1H and ^{31}P NMR spectroscopies.

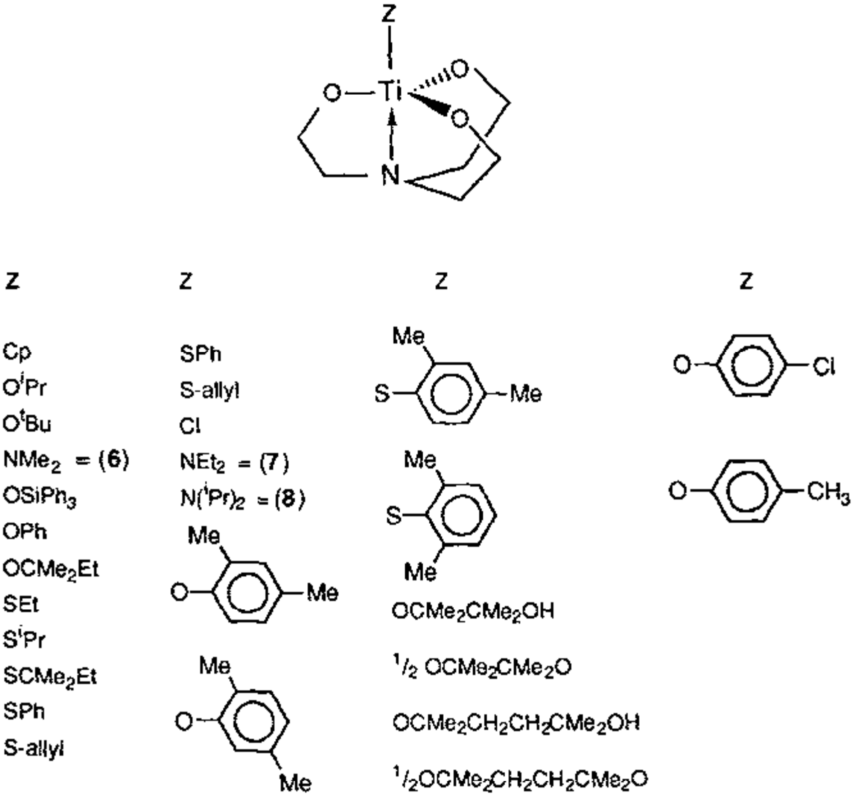
The first examples of dinuclear metallocene type complexes of titanium with the bridging ligand (dimethylsilylidene)bis(cyclopentadienyl) [$Me_2Si(\eta^5\text{-}C_5H_4)_2$]$^{2-}$ have been prepared and crystal structures of two representative complexes have been obtained [17]. In particular, the complexes [$TiCl_2Cp^*{}_2$[$\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2$] and [$TiCl_2Cp_2$[$\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2$] were obtained. When the latter was hydrolysed the μ-oxo derivative [$TiClCp]_2(\mu\text{-}O)\{\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2$] (5) resulted. These compounds were characterised by elemental analysis, IR, ^1H, ^{13}C, and ^{31}P NMR spectroscopies.



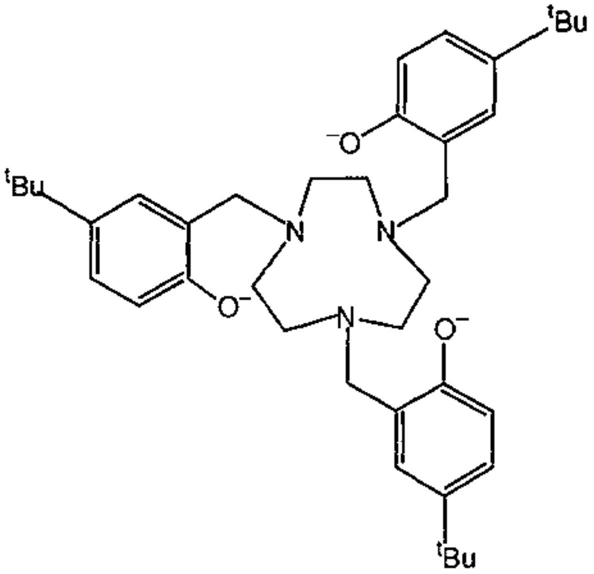
(5)

1.1.3 Complexes with oxygen and nitrogen donor ligands

The preparation of several new titanatranes has been reported [18]. In addition, the relative rates of displacement of NMe_2, NEt_2, and $N(^iPr)_2$ from (6), (7), and (8) respectively, by OH⁻ and -SH compounds has been found to be in the general order 7 >> 6 > 8. This order has been rationalised based on the relative basicities and steric properties of the NR_2 substituents.



The synthesis and coordination chemistry of 1,4,7-tris(5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane, L, (9) has been reported [19]. The reaction of trivalent first-row transition metals with the trianion afforded monomeric pseudo-octahedral complexes. The crystal structure of $[LTi^{IV}]PF_6$ has been determined, the average Ti-OAr distance was found to be 1.828Å while the Ti-N bonds vary from 2.221(9) to 2.244(8)Å. Additionally, electronic spectral data, magnetic properties and the electrochemistry for the new complexes have been reported. A study of the degree of $d_\pi - p_\pi$ bonding in the $M–O_{phenolate}$ bonds as a function of the d^n electronic configuration of the central metal ion has been carried out. It was found that the fewer the electrons in the t_{2g} valence subshell of the respective metal ion the stronger the resulting $M\text{-}O_{phenolate}$ bonds.

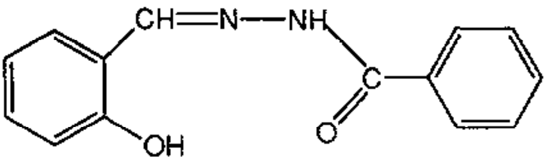


(9)

The utility of porphyrin ligands in intermetal oxygen, sulfur and selenium atom transfer involving titanium porphyrin complexes has been discussed [20].

Titanium complexes with ligands derived from 4-aminoantipyrine have been synthesised and characterised by IR and NMR spectroscopy and conductance measurements.[21].

Complexes of titanium and vanadium with the tridentate diacidic ligands salicylaldehyde benzoylhydrazone (**10**) and 2-(2'-hydroxyphenyl)-8-quinolinol (**11**) have been synthesised and characterised [22]. Mass spectrometry for the titanium compounds indicates a bis-ligand conformation.



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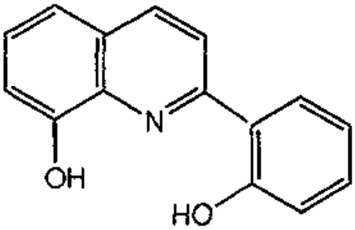

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1.1.4 Complexes with sulfur donor ligands

The high-yield synthesis (up to 85%) of $CpTi(S_2CCH_3)_3$ from (η^7-C_7H_7)TiCp and dithioacetic acid CH_3CS_2H has been described [23]. It is the first example of a group IV organometallic complex possessing dithioacetate ligands. Its X-ray structure shows it to be comprised of discrete seven coordinate molecules in which the Ti(IV) atom is at the centre of a slightly distorted pentagonal bipyramid. A Cp group occupies one axial site while two didentate dithioacetate ligands occupy four of the five equatorial sites and the remaining axial and equatorial sites are spanned by a third didentate dithioacetate ligand. The axial Ti-S distance is 2.545Å while the average equatorial Ti-S distance is 2.615Å. This compound has been fully characterised by elemental analysis, ^1H and ^{13}C NMR spectroscopy, IR, MS and X-ray crystallography.

Interest in the utility of early transition metal thiolate derivatives to serve as metalloligands and hence as synthons for heterodimetallic complexes has led to the development of synthetic routes to cyclopentadienyltitanium dithiolate derivatives. The Lewis acidity has been examined via structural, spectroscopic and theoretical studies [24]. In a related paper [25], macrocyclic titanocenedithiolate complexes were synthesised by the reaction of Cp_2TiCl_2 with extended dithiols in the presence of base. In particular, $Cp_2Ti(SCH_2CH_2)_2S$, $[Cp_2Ti(SCH_2CH_2)_2S]_2$, $[Cp_2TiCl]_2(SCH_2CH_2)_2S$, $Cp_2Ti((SCH_2CH_2CH_2)_2S)$, $[Cp_2Ti(SCH_2CH_2CH_2)_2S]_2$, $Cp_2Ti((SCH_2CH_2SCH_2)_2CH_2)$, $[Cp_2Ti((SCH_2CH_2SCH_2)_2CH_2)]_2$, and $Cp_2Ti(SCH_2CH_2SCH_2R)_2$, R = CH_3, Ph were purified and characterised. Their ability to act as metalloligands was demonstrated by the interaction of these macrocycles with Cu(I). In some instances, ring size and Lewis acidity of the metal caused a destabilisation of the Ti-S bonds giving rise to thiolate transfer reactions. A further interesting feature, the mechanism of formation of these macrocycles was also studied [26]. Electrochemical, structural and spectroscopic data suggest that a radical mechanism involving Ti(III) in the formation of Ti-S occurs. A weakening of the Ti-Cl bond upon coordination of the donor ligands is suggested by the data and evidence of the formation and subsequent reaction of Ti(III) species is presented.

1.1.5 Complexes with tellurium donor ligands

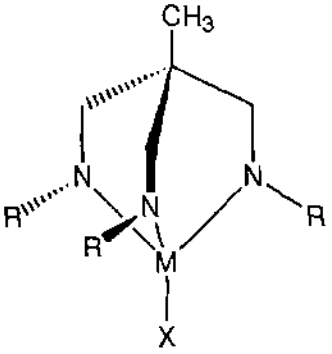
Stable bis-silyltellurolate derivatives of early transition-metal metallocenes have been prepared by both metathetical and tellurolysis routes [27]. The bis-tellurolates $Cp_2M[TeSi(SiMe_3)_3]_2$, M = Ti, Zr, and Hf were obtained in high yields. reaction with strong unhindered Lewis bases generated isolable Ti(III) species $Cp_2Ti[TeSi(SiMe_3)_3L$, L = PMe_3, PEt_3, PMe_2Ph and 2,6-$Me_2C_6H_3NC$ which could be trapped in near-quantitative yields.

1.1.6 Complexes with nitrogen donor ligands

Mono-η-cyclopentadienyl-benzamidinato compounds of titanium, zirconium and hafnium have been prepared and their ability to act as co-catalysts towards alkene polymerisation has been investigated [28]. The compound $\{Ti(\eta\text{-}C_5Me_5)[Me_3SiNC(p\text{-}C_6H_4OMe)NSiMe_3]F_2\}$ was prepared and found to be highly sensitive to oxygen and water. Its crystal structure has been determined and a preliminary study of its catalytic properties in the polymerisation of ethene and propene has been reported.

A new class of five coordinate titanium complexes containing a polyfunctional amido ligand has been synthesised [29]. Trimethylsilylation of the ligand $CH(2\text{-}C_5H_4N)(CH_2NH_2)_2$ gave the corresponding $CH(2\text{-}C_5H_4N)(CH_2NHSiMe_3)_2$ which after dilithiation and reaction with $[TiX_4(thf)_2]$ (X = Cl or Br) gave the complexes $[TiX_2\{CH(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2\}]$ as air- and moisture-sensitive orange microcrystalline solids. A single crystal X-ray analysis for the bromide derivative shows the molecule possesses C_s symmetry with the titanium atom being at the centre of a slightly distorted trigonal bipyramid with Ti-N(amido) distances being 1.842(9)Å and a Ti-N(pyridyl) distance of 2.262(12)Å. The use of the complexes as potential building blocks in the synthesis of oligonuclear complexes is being explored.

The synthesis, structures and studies of dynamic properties in solution of titanium amides of the general type (**12**) has been described [30].



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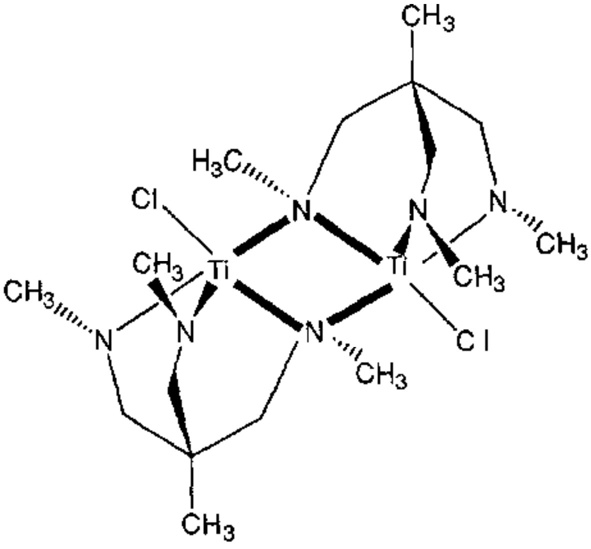


(**1 3**)

The compound $[H_3CC(CH_2NMe)_3TiCl]_2$ (**13**) was synthesised. Its X-ray crystal structure shows it to be a dimer with an idealised C_2 symmetry in which bridging amido functions bridge two halves of the molecule. The titanium interatomic distance of 3.142(3)Å rules out any direct interaction between the two metal centres. The Ti-N distances for the non-bridging amido functions lies in the range 1.839(9) - 1.879(9) Å. This dimeric structure was found to be retained in solution as shown by ^1H- and ^{13}C-NMR spectroscopy. A high degree of ligand dynamics was found and this was investigated by variable temperature NMR spectroscopic studies and phase sensitive ^1H-NOESY/EXSY spectra. A byproduct of the synthesis $[H_3CC(CH_2NSiMe_3)_2(H)CH_2NTiX]_2$ was isolated and its crystal structure obtained.

When $TiCl_4$ and $N(SiMe_3)_3$ were reacted in a sealed glass tube the titanium imide chloride $[Ti(NSiMe_3)Cl_2]_8$ was obtained [31]. Its crystal structure shows it comprises six titanium atoms linked together by chloro and trimethylsilylimido bridges in a ring structure. Additionally, two $TiCl_2$ groups are bound to the ring by two imido bridges.

An *ab initio* quantum chemical study of the elimination of small molecules HX from group 4 (M = Ti, Zr, Hf) amido complexes $L_nM(NH_2)(X)$ (X = H, CH_3, Cl, NH_2 and SiH_3 has been described [32]. This study is pertinent to the rational design of precursors for materials to be synthesised by CVD. Results indicate that the leaving group X plays a crucial role in tuning the bonding and energetics of the transition state and thus the rate of elimination of HX. The conclusion is that precursors whose design enhances the metal transannular hydrogen interaction lead to lower activation barriers for HX elimination resulting in lower processing temperatures or higher rates for a given temperature.

Several complexes of titanium with silylated aminophosphorane and sulfodiimide ligands have been obtained recently [33]. The reaction of $TiCl_4$ with $S(NSiMe_3)_2$ and $Me_2S(NSiMe_3)_2$ gave 1:1 adducts. Reaction of $TiCl_4$with $(Me_3Si)_2NPPh_2NPPh_2NSiMe_3$ gave rise to an exchange of one silyl group with a $TiCl_3$ moiety, the resulting molecule possesses a titanium atom which is four-coordinate. Reaction of $CpTiCl_3$, Cp^*TiCl_3, and Cp^*TiF_3 with $Ph_2P(NSiMe_3)_2H$ did not result in any chelate complexes.

The oxidation of bis(phthalocyaninato)titanium(IV) Pc_2Ti and bis(pthalocyaninato)tin(IV), Pc_2Sn with I_2 and HNO_3 generated the species $[Pc_2M](I_3)_{0.66}$ and $[PcM]NO_3$ respectively (M = Ti(IV), Sn(IV) [34]. Exchange of the NO_3^- group with PF_6^- has resulted in new products. The structure of $[Pc_2Ti](I_3)_{0.66}$ has been obtained from a low-temperature (–160°C) single-crystal X-ray study. Notably, two interligand C-C σ bonds observed in Pc_2Ti are no longer present, two Pc groups are staggered at an angle of 41.1° and the titanium atom is surrounded by eight inner nitrogen atoms in the form of a square antiprism with Ti-N bond distances of 2.246(7)Å. Structural and electronic features of these oxidised species were studied in order to gain a better understanding of their improved electrical conductivity properties with respect to their precursors Pc_2Ti and Pc_2Sn.

The structure of an allotropic form of [bis(trimethylsilyl)amido]dichloro(η^5-cyclopentadienyl)titanium which is used as a precursor for CVD of thin films of ceramic TiN has been obtained [35]. It is not significantly different from the previously reported monoclinic form. Titanium is in a tetrahedral environment with a noticeably short Ti-N bond length of 1.881(6) Å.

1.2 TITANIUM(III)

1.2.1 Complexes with halide ligands

The dimetallic complexes [$M_2(\mu\text{-}Cl)_2Cl_4(thf)_4$] where M = Ti or V have been prepared by recrystallisation of [$MCl_3(thf)_3$] from dichloromethane [36]. Their crystal structures have been obtained, and both dimers comprise slightly distorted edge-sharing octahedra with a Ti·····Ti separation of 3.711(3)Å and a V·····V separation of 3.619(1)Å. The metal atoms are surrounded by two terminal chlorine atoms, two bridging chlorine atoms and two oxygen atoms of the thf molecules. High catalytic activity for ethene polymerization was demonstrated for the Ti dimer.

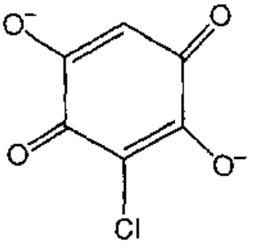
1.2.2 Complexes with hydride donor ligands

The trinuclear hydride complex [$\{(C_5Me_5)_2Ti(\mu\text{-}H)_2\}Mg$] has been synthesised and its X-ray crystal structure determined [37]. This was prepared by suspending [$(C_5Me_5)_2TiCl_2$] in dry, degassed Et_2O to which ^iPrMgCl in Et_2O was added. The complex consists of two mutually perpendicular $(C_5Me_5)_2Ti(\mu\text{-}H)_2$ fragments attached to a central pseudo-tetrahedrally Mg atom by means of four Ti-H-Mg bridges. The Ti-H distances range from 1.66 to 1.79Å while the Ti·····Ti distance is 5.7Å.

Ab initio unrestricted Hartree-Fock (UHF) calculations have been carried out for the previously characterised d^1-$Ti(BH_4)_3$ complex using both limited and extended basis sets [38]. Twenty different structures exhibiting different BH_4^- coordination modes were studied and results from these calculations are consistent with those from an electron diffraction study with a C_{3h} (η^3, η^3, η^3) structure being the lowest energy one and optimised bond lengths and angles are close to experimental values. A mechanism for exchange between bridging and non-bridging hydrogen atoms has been proposed.

1.2.3 Complexes with oxygen donor ligands

Slow intramolecular electron transfer in a Ru(III)-Ti(III) redox intermediate having a dianion derived from a dihydroxyquinone as a bridging ligand has been observed [39]. A kinetic study of Ti(III) reduction of $Ru(trien)CQ^+$ where CQ^- is the dianion of chloranilic acid, $C_6Cl_2O_4^{2-}$ (**14**) has been carried out. Reductions by Ti(III) of $Co(trien)Q^+$ and $Co(en)_2SQ^+$ where Q^{2-} and SQ^{2-} are the dianions of 2,5-dihydroxy-1,4-benzoquinone (**15**) and squaric acid (**16**) were also studied.



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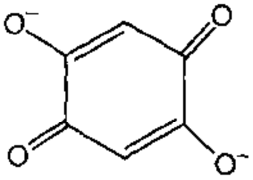

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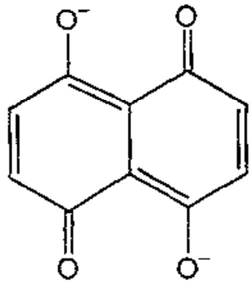

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1.2.4 Complexes with oxygen and nitrogen donor ligands

The molecular structure of $Na[Ti(H_2O)(edta)]\cdot 2H_2O$ has been determined by X-ray analysis recently [40]. The complex anion has a seven-coordinate and approximately pentagonal bipyramidal structure in which $edta^{4-}$ is a hexadentate ligand and a water molecule occupies one of the five basal sites.

The crystal and molecular structures of three Ti^{III}-edta complex salts have been obtained [41]. The complexes violet $Ba[Ti(edta)(H_2O)]\cdot 6H_2O$, reddish-violet $Na_2[Ti(edta)(H_2O)]_2\cdot NaCl\cdot 7H_2O$, and purple $K[Ti(edta)(H_2O)]\cdot 2.5H_2O$ were found to possess seven-coordinate and distorted mono-capped trigonal prismatic structures.

1.2.5 Complexes with oxygen and phosphorus donor ligands

Using crystalline $[Li(\mu\text{-}OC^tBu_2CH_2PMe_2)_2]_2$, a number of pentane-soluble derivatives including the first monomeric Ti^{III} monomeric alkoxide have been obtained [42]. In particular, the X-ray crystal structure of $[TiCl(OC^tBu_2CH_2PMe_2)_2]$ shows that there is a distorted trigonal bipyramidal geometry about the Ti atom with Ti-O bond lengths 1.841(3) and 1.843(3)Å and Ti-P bond lengths of 2.600(2) and 2.591(2)Å.

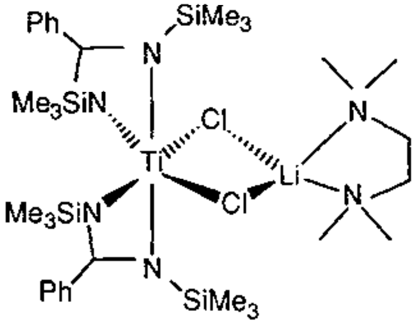
1.2.6 Complexes with sulfur donor ligands

A novel mixed-valence, quasi-two-dimensional bismuth calcium titanium(III/IV) sulfide $Bi_{6-x}Ca_xTi_5S_{16}$ ($x = 3.08$) has been synthesised and reported as a commensurate structure for the first time in the class of misfit-layer compounds [43].

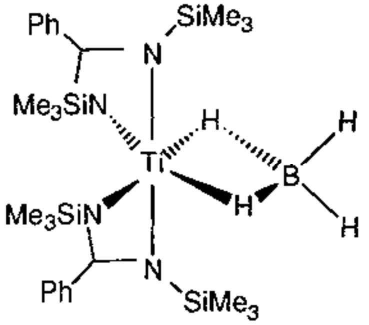
1.2.7 Complexes with nitrogen donor ligands

The preparation and structural characterization of the first bis(benzamidinato)titanium(III) chloride and its transformation into the corresponding borohydride and allyl derivatives has been reported [44]. The reaction of $TiCl_2(tmen)_2$ and $TiCl_3(thf)_3$ with 2 equivalents of

$PhC[(Me_3Si)N]_2Li(tmen)$ in thf gave rise to forest-green crystals of $\{PhC[(Me_3Si)N]_2\}_2Ti(\mu\text{-}Cl)_2Li(tmen)$, **(17)** in good yield. When the latter was reacted with $Li[BH_4]$, light brown crystals of $\{PhC[(Me_3Si)N]_2\}_2Ti(BH_4)$, **(18)** were obtained. A thermally stable Ti(III)-allyl derivative $\{PhC[(Me_3Si)N]_2\}_2Ti(\eta^3\text{-allyl})$ was obtained from the reaction of **(17)** with (allyl)MgBr in thf.



(17)



(18)

Rare examples of solid-liquid heterogeneous metathesis reactions have recently been demonstrated [45]. Thermal or frictional initiation of mixtures of $MCl_4(l)$ (M = Ti, V) and Li_3N or Li_2O gave rise to MN, Ti_xV_yN, $x = y = 0.5$, or MO_2 in 2-3 seconds via an exothermic solid-liquid metathesis reaction. In related papers [46] and [47], the generation of crystalline transition metal nitrides of various compositions M_xN_y via an exothermic solid-state metathesis reaction and MN respectively has been reported. The metal nitrides were purified by thf trituration and characterised by X-ray powder diffraction, scanning electron microscopy, energy dispersive analysis with X-rays, magnetic moment measurements, FTIR spectroscopy and microanalysis.

Studies demonstrating that when a suitable choice of ligand was employed edge-sharing dioctahedral titanium compounds possessing a Ti-Ti single bond were obtained have been reported [48]. The dinuclear compounds $Ti_2Cl_2[RNC(H)NR]_2(\mu\text{-}Cl)_2$, (R = phenyl or biphenyl) whose crystal structures have been obtained show the coordination sphere of the titanium atoms to be composed of two bridging and two chelating formamidinate ligands and two bridging chlorine atoms. The Ti-Ti distances, 2.8990(8)Å for the phenyl case, and 2.916(3)Å for the biphenyl derivative are indicative of a single bond and magnetic susceptibility studies have shown the biphenyl derivative to be diamagnetic. In addition, stoichiometric analogues $M_2Cl_6(PMe_3)_4$ where M = Ti and Zr have been prepared and characterised. X-ray crystallography and magnetic measurements indicate no appreciable Ti·····Ti interaction whereas a Zr-Zr bond exists.

1.3 TITANIUM(II)

The preparation and characterization of novel (η^2- acetylene) and bis(amine)titanium(II) porphyrin complexes has been achieved [49]. The preparation of $(TPPH_2)Ti(\eta^2\text{-}RCCR')$, ($R = R' = CH_3, CH_2CH_3, C_6H_5$; $R = CH_3$, $R' = CH_2CH_3$) has been described. These π-complexes were found to undergo simple substitution reactions with py and 4-picoline yielding the bis(ligand) complexes *trans*-$(TPPH_2)Ti(py)_2$ and *trans*-$(TPPH_2)Ti(4\text{-picoline})_2$. The structure of the latter complex was determined by single crystal X-ray diffraction. The two picoline ligands were found to be coplanar and $Ti\text{-}N_{pic}$ distance is 2.223(3)Å while the average $Ti\text{-}N_{pyrrole}$ distance is 2.047(8)Å. The strong reducing potential of Ti(II) is evident from its reactions with diazo reagents and phosphine chalcogenides.

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