Titanium is the first member of the d-block transition elements. It belongs to the group IV (sub group A) of the periodic classification. Some common properties of titanium are given in Table 1.1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>22</td>
</tr>
<tr>
<td>Atomic weight (^{12}\text{C}=12)</td>
<td>47.90</td>
</tr>
<tr>
<td>Electronic configuration</td>
<td>(\text{[Ar]}^3\text{d}^2\text{s}^2)</td>
</tr>
<tr>
<td>Melting point</td>
<td>1677°C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>3277°C</td>
</tr>
</tbody>
</table>

The most stable, the most common and extensively studied oxidation state of +4 involves the loss of \(3\text{d}^2\text{s}^2\) valence electrons. However, the element also exists in lower oxidation states, e.g., 3, 2, 1, 0, -1, and -2. Out of these, next to tetravalent state, the chemistry of tervalent titanium is studied in great detail. The valency states, 0, -1 and -2 exist in the compounds, \(\text{Li}\left(\text{Ti(bipy)}\right)_3\), \(\text{Li}_2\left(\text{Ti(bipy)}\right)_3\) 3.7THF and \(\text{Li}_2\left(\text{Ti(bipy)}\right)_3\) 5.7THF (1-3), where bipy = \(\alpha-\alpha'\) bipyridyl and THF = tetrahydrofuran. The genuineness of these oxidation states (0, -1 and -2) is not beyond doubt.
The most common coordination number of titanium is six although the compounds with coordination number 4, 5, 7 and 8 are known. The stereochemistry of titanium in the valency states 2, 0, -1 and -2 has not yet been well established.

I. FLUORO COMPOUNDS OF TITANIUM

Titanium forms TiF₄, TiO(OH)F, TiOF₂ and several types of oxofluorotitanates and peroxofluorotitanates (Table 1.2) which are described below in succession.

Table 1.2

a) Hexafluorotitanates (1-13)

\[
\text{M}_2\text{TiF}_6; \quad \text{where M}^1 = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Tl}^+, \text{NH}_4^+ \text{ and Ag}^+. \\
\text{M}_2\text{II}_{\text{TiF}_6.6\text{H}_2\text{O}; \quad \text{where M}^\text{II} = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Pb}^{2+}, \\
\text{Cd}^{2+}, \text{Zn}^{2+} \text{ and Mg}^{2+}. \\
\text{Li}_2\text{TiF}_6.2\text{H}_2\text{O, AgTiF}_6, \text{BaTiF}_6, \text{BaTiF}_6.0.5\text{H}_2\text{O, CuTiF}_6.4\text{H}_2\text{O,} \\
2\text{Co(NH}_3)_6.7\text{F}_3.3\text{TiF}_4.2\text{HF, (N}_2\text{H}_5)_2\text{TiF}_6.2\text{H}_2\text{O, (N}_2\text{H}_6)\text{TiF}_6, \\
\text{(NH}_3)_2\text{TiF}_6, \text{(NO)}_2\text{TiF}_6, \text{TiO(TiF}_6) \text{ and (AmH)}_2\text{TiF}_6 \text{ (where Am represents secondary amine).} \\
b) Heptafluorotitanates (4, 14, 15)

\text{K}_3\text{TiF}_7, (\text{NH}_4)_3\text{TiF}_7, \text{KCuTiF}_7.4\text{H}_2\text{O} \text{ and NH}_4\text{CuTiF}_7.4\text{H}_2\text{O.} \\
c) Octafluorotitanates (4, 9)
Table 1.2 (Contd.)

\[ \text{La}_{3} \text{HTiF}_{8}, \text{Cs}_{4} \text{TiF}_{8} \text{ and } (\text{N}_{2}\text{H}_{6})_{2}\text{TiF}_{8} \]

d) \( \left(\text{C}_{2}\text{H}_{5}\right)_{4}\text{N} \rightleftharpoons \text{TiF}_{5}(\text{H}_{2}\text{O}) \rightleftharpoons \text{H}_{2}^{+} \text{Ti}^{3+} \text{F}_{4} \] and \( \left(\text{C}_{2}\text{H}_{5}\right)_{4}\text{N} \rightleftharpoons \text{TiF}_{5} \rightleftharpoons \text{K}^{+} \text{Ti}^{3+} \text{F}_{4} \].

e) Peroxofluorotitanates (4, 6)

\[ \text{M}_{3}^{1-} (\text{O}_{2}) \text{TiF}_{5} \] where \( \text{M}^{1} = \text{Li}^{+}, \text{Na}^{+}, \text{K}^{+} \text{ or } \text{NH}_{4}^{+} \)

\[ \text{H}_{2} \text{Ti}(\text{O}_{2})\text{F}_{4} \text{ or, } \text{TiO}_{2}\text{F}_{2}, \text{2HF} ; \ (\text{NH}_{4})_{2}\text{Ti}(\text{O}_{2})\text{F}_{4} \text{ or, } \text{TiO}_{2}\text{F}_{2}, \text{2NH}_{4}\text{F} ; \]

\[ \text{K}_{2} \text{Ti}(\text{O}_{2})\text{F}_{4} \text{ or, } \text{BaTi}(\text{O}_{2})\text{F}_{4} \text{ or, } \text{TiO}_{2}\text{F}_{2}, \text{BaF}_{2}. \]

A. Titanium Tetrafluoride and Fluorotitanates

Titanium tetrafluoride may be prepared by direct fluorination of titanium sponge at 200° in a flow system (18,19). It can also be prepared by the following methods: (a) by direct fluorination of TiO\(_2\) at above 350°C (18), (b) by the reaction (20) of chlorine trifluoride on titanium metal in a flow system at 350°C and (c) by the thermal decomposition (21) of ammonium hexafluorotitanate at 150°C.

Titanium tetrafluoride is extremely hygroscopic. It can be readily purified by vacuum sublimation. It is soluble in aqueous HF to form hexafluorotitanate (IV) ion. Titanium tetrafluoride acts as a fluorinating agent with the
carbontetrachlorides to form fluorohydrogenomethanes (22). It forms addition compounds with nitriles, amines, arsenic ligands etc. Typical addition compounds of titanium tetrafluoride are given in the Table 1.3 below.

Table 1.3 (6)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Donor atom</th>
<th>Formula</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylamine</td>
<td>N</td>
<td>TiF₄·CH₃NH₂</td>
<td>22</td>
</tr>
<tr>
<td>Pyridine</td>
<td>N</td>
<td>TiF₄·C₅H₅N</td>
<td>22</td>
</tr>
<tr>
<td>Pyridine</td>
<td>N</td>
<td>TiF₄·C₅H₅N</td>
<td>23,24</td>
</tr>
<tr>
<td>Trimethylamine</td>
<td>N</td>
<td>TiF₄·(CH₃)₃N</td>
<td>24</td>
</tr>
<tr>
<td>Ammonia</td>
<td>N</td>
<td>TiF₄·2NH₃</td>
<td>23</td>
</tr>
<tr>
<td>α-α′-bipyridyl</td>
<td>N</td>
<td>TiF₄·C₁₀H₈N₂</td>
<td>25</td>
</tr>
<tr>
<td>O-phenylene bis-(dimethyl arsine)</td>
<td>As</td>
<td>(TiF₄)₂·C₁₀H₁₆As₂</td>
<td>26</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>O</td>
<td>TiF₄·C₆H₅CHO</td>
<td>22</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>O</td>
<td>TiF₄·2(CH₂CH₂)₂O</td>
<td>24</td>
</tr>
<tr>
<td>Ethanol</td>
<td>O</td>
<td>TiF₄·2C₂H₅OH</td>
<td>24</td>
</tr>
<tr>
<td>8-quinolinol(oxH)</td>
<td>N</td>
<td>TiF₄·oxH</td>
<td>27</td>
</tr>
<tr>
<td>8-quinolinol(oxH)</td>
<td>N</td>
<td>TiF₄·2oxH</td>
<td>27</td>
</tr>
</tbody>
</table>
From the study of the titanium tetrafluoride adducts by $^{19}$F NMR spectroscopy Dyer and Ragsdale (28) showed that bonding occur between the fluorine atoms and the titanium atom in the nitrogen base adducts. However, di-n-propylamine reacts with a chloroform solution of the tetrafluoride to produce a mixture of $\left[(C_3H_7)_2NH\right]_2TiF_6$ and the derivative, $TiCl_3N(C_3H_7)_2$ (7). Infrared studies on these and related complexes have established that Ti-F stretching frequencies occur in the 550-682 cm$^{-1}$ region (26, 29).

Buslaev et al. (30, 31) studied the hydrolysis of TiF$_4$ by $^{19}$F NMR and found the presence of TiF$_5^-$, TiF$_6^{2-}$ ions and $\left[Ti_2F_6\cdot Ti(OH)_2\right]^4_-$ in the aqueous solution. In a 40% TiF$_4$ aqueous solution they found the presence of the polynuclear species $\left[TiF_4\cdot Ti(OH)_4(H_2O)_2\right]^-$. A $^{19}$F study of the supernatant liquid from the hydrolysis of the TiF$_4$·$\text{ZNC(0)NMe}_2$ also showed the presence of TiF$_5^-$·$\text{HC(O)NMMe}_2$, TiF$_5H_2O^-$ and TiF$_6^{2-}$ ions. A new type of anion TiF$_5ROH^-$, where $R$ represents the alkyl group, was reported by Ragsdale and Stewart (31a). Recently, from the $^{19}$F NMR study of the system TiF$_4^-$·$\left(\text{Pr}_2-\text{NH}_2\right)_2TiF_6$, Dean (32) reported the formation of the species, Ti$_2F_{11}^-$, (TiF$_5$)$_n^-$, Ti$_2F_{10}^{2-}$ and Ti$_2F_9^-$. The existence of TiF$_8$ was reported (33) from the polarographic study of Ti(IV) in fluoride medium along with other ions.

Titanium tetrafluoride combines with the ionic fluorides
to give the respective hexafluorotitanates (Table 1.2). They are usually prepared by the addition of alkali and alkali metal fluorides in the correct proportions to a solution of the titanium dioxide in HF. Hexafluorotitanates of alkali metals may be prepared by many methods and some of the principal routes are summarized below (5).

<table>
<thead>
<tr>
<th>Method</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ in aqueous HF</td>
<td>MF or MHF₂ was added</td>
</tr>
<tr>
<td>TiO₂ in aqueous HF</td>
<td>Li₂CO₃ was added</td>
</tr>
<tr>
<td>TiO₂, NaF and SF₄</td>
<td>Bomb, 350°C</td>
</tr>
<tr>
<td>TiO₂, KF and KBF₄</td>
<td>Fused at 900-995°C in Argon</td>
</tr>
<tr>
<td>TiO₂ and Na₂SiF₆</td>
<td>Fused at 600°C</td>
</tr>
<tr>
<td>TiF₄ and MF</td>
<td>Flow system, 350-450°C</td>
</tr>
<tr>
<td>TiF₄, MF and BrF₃</td>
<td>Refluxed</td>
</tr>
<tr>
<td>TiBr₄ and NH₄F</td>
<td>Methanol solution</td>
</tr>
</tbody>
</table>

The hexafluorotitanates of Co²⁺, Pb²⁺, Cd²⁺, Ca²⁺ etc. are prepared by adding respective metal carbonates to a solution of TiO₂ in HF followed by the evaporation of the mixture. Miolati and Rossi (4) prepared 2Co(NH₃)₆F₃·3TiF₄·2HF by adding a solution Leutocobaltic carbonate or fluoride to HF solution of titanic acid.

Ammonium heptafluorotitanate was obtained (4) on crystallisation of a mixture of an acidic or ammoniacal solution
of \((\text{NH}_4)_2\text{TiF}_6\) and excess of \(\text{NH}_4\text{F}\). \((\text{NH}_4)_3\text{TiF}_7\) may also be prepared (14) by the reaction of \(\text{TiO}_2\) (anatase) and \(\text{TiOF}_2\) with \(\text{NH}_4\text{HF}_2\). From the phase equilibria study of the system KF-K_2TiF_6, Antipin et al. (15) reported the existence of K_3TiF_7. The compounds \(\text{NH}_4\text{CuTiF}_7\cdot4\text{H}_2\text{O}\) and \(\text{KCuTiF}_7\cdot4\text{H}_2\text{O}\) are prepared by evaporating a mixture of an aqueous solution of \(\text{CuTiF}_6\cdot4\text{H}_2\text{O}\) and \(\text{NH}_4\text{F}\) or KF.

The compound \((\text{NH}_2\text{H}_6)\text{TiF}_6\) was isolated (9) from a neutral solution obtained by the neutralization of \(\text{H}_2\text{TiF}_6\) solution with hydrazine monohydrate. \((\text{NH}_2\text{H}_6)\text{TiF}_8\) was crystallized from the above mixture but containing an excess of HF. The composition also depends on the ratio of \(\text{NH}_2\text{F}_2\) and \(\text{TiF}_4\). Marignac (4) prepared the compound \(\text{Na}_2\text{TiF}_6\cdot\text{NaHF}_2\) from the mother liquor of the preparation of sodium hexafluorotitanate which was prepared by evaporating the solution obtained by adding NaOH to a solution of the tetrafluoride until a permanent precipitate begins to form. When CsF was added to a concentrated solution of \(\text{TiF}_4\), small lustrous crystals of Cesium octafluorotitanate, Cs_4TiF_8 were produced (4).

Tetraethyl aquopentafluorotitanate was prepared by Salapala and Guerchais (16) from \(\text{Et}_4\text{NF}\) and \(\text{TiF}_4\). Kolditz and Malzahn (17) prepared the compound, \(\text{Et}_4\text{N}^+\text{TiF}_5\) from the reaction of \(\text{Et}_4\text{N}^+\text{TiCl}_5\text{CH}_3\text{CN}\) with HF.

From x-ray diffraction technique it was indicated that
the simple hexafluorotitanates exhibit polymorphism and the modification mainly depend on the method of preparation. It was also reported by Cipriani (34) from single crystal study of Na₂TiF₆ that a titanium-fluorine distance is 2.0 Å. Ibers and Holm (35) from ¹⁹F NMR study of K₂TiF₆, reported the titanium-fluorine distance 1.92 Å. Weiss et al (36, 37) studied the structure of Na₃HTiF₆ and concluded that it had orthorhombic lattice and there are four molecular units in the cell. The structure consists of very slightly distorted TiF₆⁻ octahedra, sodium ions and bifluoride ions, whereas the compound, NH₄CuTiF₇·4H₂O has a tetragonal lattice with two molecular units in the cell. X-ray work (38) has shown that the complex, NH₄CuTiF₇·4H₂O consists of infinite .......... TiF₆⁻ ..... Cu(H₂O)₄ ⁷⁺ chains connected by hydrogen bonds and does not contain any discrete TiF₇⁻ ions.

B. Titanium oxide fluorides and oxyfluorotitanates

Titanium oxide difluoride may be prepared by hydrolysis of the titanium tetrafluoride or the chlorotrifluoride. It may also be obtained by the action of aqueous or anhydrous HF on titanium dioxide. X-ray powder diffraction data (39) show that the structure consists of titanium atoms octahedrally coordinated to randomly distributed oxygen and fluorine atoms. A detailed study of the properties of the compound made by the above methods
reveal that the compound is in fact TiO(OH)F (40).

Dehnike (40) prepared the compound, titanium oxidedifluoride authentically as a yellow solid by the interaction of titanium difluoride dichloride and chlorinemonoxide in a polar solvent at 4°C.

Till now no chemical properties of titanium oxidedifluoride is known.

Quite a large number of papers have been published on oxofluorotitanates(IV). Out of these, most of the papers dealt mainly with the synthesis of alkali metal salts of oxotetrafluorotitanate(IV) from the pyrolysis and phase study of the different systems.

Bamburov et al. (41) from the study of the system KF - TiF₄ - H₂O reported the formation of K₂TiF₆·H₂O, K₂TiF₆·2H₂O and K₂TiF₆·3H₂O. At 420°C, K₂TiF₆ hydrolyses to K₂TiOF₄ and HF. The formation of K₂TiOF₄ was also supported by x-ray analysis. The thermal analysis (42) of the compound, K₂TiF₆ showed a series of endothermic effect in the temperature range 300-1000°C. The first endotherm was observed at 371°C corresponding to the polymorphic transformation of α-K₂TiF₆ to β - K₂TiF₆. The loss in weight in between 500-700°C is in agreement with the formation of K₂TiOF₄ according to the reaction, K₂TiF₆ H₂O → K₂TiOF₄. The thermal analysis of K₂TiOF₄ showed
a number of endotherms but the endotherm at 698° might be due to the formation of K₂TiO₂F₂. The results were supported by chemical and x-ray analysis. Bamburov and his coworkers (43, 44) studied the possible reactions occurring in the systems, K₂SiF₆ - TiO₂ and Na₂SiF₆ - TiO₂. According to them the following reaction takes place along with other reactions:

\[ 2M₂SiF₆ + 2TiO₂ \rightarrow 2M₂TiOF₄ + SiO₂ + SiF₄ \] (where M = Na or K)

The reaction with Na₂SiF₆ predominates above 600°C. But from the investigation of Na₂TiF₆ - SiO₂ system Chernov et al. (45), suggested the formation of Na₂TiOF₄ and Na₆Ti₃O₄F₁₀. Antipin and coworkers (46) studied the stability of potassium fluorotitanate at high temperature and suggested that the conversion occurring during the heating of K₂TiF₆ can provisionally be represented by the following scheme:

\[ \alpha \rightarrow K₂TiF₆ \rightarrow \beta \rightarrow K₂TiF₆ (300-700°) \rightarrow K₂TiOF₄ (550-700°) \]

K₂TiO₂F₂ (570-620°) \rightarrow K₂Ti₄O₉ (at 1000°). Dmitrovskii et al. (47) also from the thermal decomposition of lithium sodium, rubidium and cesium hexafluorotitanates in the absence of a protective atmosphere above 1000°C concluded that the thermal decomposition is the same as that of potassium hexafluorotitanate and the compounds of the type M₂TiOF₄ (where M = Li⁺, Na⁺, Rb⁺ and Cs⁺) are formed as intermediate. The scheme of decomposition
was supported by T.G., x-ray and chemical analysis. But, according to Esteal and Udy (48) the product of thermal decomposition of K$_2$TiF$_6$$\cdot$H$_2$O was oxpfluorotitanate of probable stoichiometry K$_2$Ti$_4$O$_8$F$_2$, which was characterised by its powder diffraction pattern.

Bamburov and Demenev (49) reported the formation of K$_2$TiOF$_4$ alongwith K$_2$TiF$_6$ from the reaction of TiO$_2$ with KF at 400°-700°. From the study of the conditions of the formation and kinetics, Fotiev and Sheinkmann (50) found that K$_2$TiOF$_4$ was formed with appreciable yield from the mixture of KF and TiO$_2$. It was also seen by them that the formation of K$_2$TiOF$_4$ was favoured by the presence of excess of KF in the mixture.

Lastochkina, Shaka and Malinko (51) from the study of the system, M$^I$M$^{IV}$F$_6$$\cdot$NH$_4$OH (KOH, NaOH) - H$_2$O where M$^I$ = Li, K, Cs and Rb, and M$^{IV}$ = Ti, Zr and Hf reported the formation of basic salts of various compositions. Thus, TiOF$_2$ - nH$_2$O and M$^I$M$^{IV}$OF$_3$ (M$^I$ = K, Rb, Cs ; M$^{IV}$ = Zr and Hf) were formed for the molar ratio $\frac{\[OH\]}{\[M^{IV}F_6\]}$ of 0.5 - 2.0. Hexafluorotitanates gave TiO(OH)F$n$H$_2$O, K$_{1.5}$TiO$_{0.75}$F$_4$$\cdot$H$_2$O and KTiO$_{1.5}$F$_2$$\cdot$0.75H$_2$O.

Burmistrova and Reznichenko (52) studied the phase composition of the components of the system, sodium chloride - sodiumfluorotitanate during the electrolysis and hydrometallurgical treatment. In the products of hydrolysis they found the presence
of Na₂TiOF₄ along with other compounds. High temperature hydrolysis reaction (53) between steam and chloride fluorotitanate and chloride fluorozirconate melts infer the formation of the compounds of the type M₂M' TiOF₄ (where M = K, Na and M' = Ti and Zr).

The reaction of K₂TiF₆ with BaCl₂ in aqueous medium at different pH was studied by Golub et al. (64). At pH = 2.36 and the ratio 1:1 the formation of BaTiOF₄.0.5H₂O was reported. They also reported (55) the same compound from the study of the systems, K₂TiF₆ - BaCl₂ - K₂CO₃ - H₂O and K₂TiF₆ - BaCl₂ - (NH₄)₂CO₃.H₂O at the ratio K₂TiF₆ : BaCl₂ = 1:1 and pH = 2.7 - 4.0.

From the study of the system, BaF₂ - TiOF₂, Ravez (56) reported the formation of Ba₃(TiOF₅)₂ and Ba₃Ti₃C₃F₁₆. Again, study of the system, PbF₂ - TiOF₂ (57) indicated the formation of Pb₃(TiOF₅)₂. The study of the system MF₂ - TiOF₂ (M = Ca and Sr) by Ravez and Hagenmuller indicated the formation of CaTiOF₄ and α-SrTiOF₄. Pausewang and Reudorft (58) prepared a series of compounds of the general formula A₂A'TiOF₅ where A and A' are the alakalimetals but the size of A > A'. The compounds were prepared by the reaction of the type,

K₂TiF₆ + TiO₂ + 2KF + 2NaF = 2K₂NaTiOF₅.
The compounds reported are; \( K_2NaTiOF_5 \), \( Rb_2NaTiOF_5 \), \( Rb_KTiOF_5 \), \( Cs_2KTiOF_5 \), \( Cs_2RbTiOF_5 \) and \( K_3TiOF_5 \).

Though a number of oxotetrafluorotitanates and oxopentafluorotitanates are known but till now no trifluorotitanate is described. However, the presence of \( TiOF_3^- \) ion in solution was reported by a number of workers (59-62).

From the potentiometric measurements, the presence of the ion \( TiOF_3^- \) along with other ions, \( TiOF_4^{2-} \) and \( TiOF^+ \) were reported (59). Polarographic analysis (60) of titanium complexes at varying \( F^- \) and \( H^+ \) concentrations showed the presence of \( \left[ Ti(OH)F_4^- \right]^- \) and \( TiF_3^- \) in solution, while those taking part in electrode reactions were \( \left[ Ti(OH)F_3^- \right]^- \) and \( \left[ Ti(OH)F_3^- \right]^- \). The cryometric determination (61) of the system \( TiO_2 + K_2TiF_6 + 4KF \) dissolved in KBr indicated the formation of \( \left[ TiOF_3^- \right]^- \) arising from the reaction \( TiO_2 + K_2TiF_6 \rightarrow 2\left[ TiOF_3^- \right]^- + 2K^+ \). The formation of \( TiOF_3^- \) ion as an activated intermediate was reported also by Reznichenko (62) from the reaction of potassium hexafluorotitanate with metallic titanium in aqueous medium. One of the ultimate products of the above reaction is \( K_2TiOF_4 \).

C. Peroxofluorotitanates

The formation of an intense yellow-orange colour by the addition of hydrogen peroxide to an acid solution of titanium(IV)
is known since 1870. This is the most sensitive reaction for the detection of titanium. It is also seen that the colour of an aqueous solution of titanium(IV) ion/H$_2$O$_2$ depends on pH, e.g., it is orange in acid solutions, yellow in the solutions of pH~8 and colourless in strongly alkaline media. Quite a number of peroxofluorotitanates are known. Amongst these ammonium salt is very stable and is soluble in water without any decomposition.

Piccini prepared hydroxyfluoropertitanic acid H$_2$Ti(O$_2$)F$_4$ or TiO$_2$F$_2$HF, in solution by adding barium oxyfluoropertitanate, in slight excess, to well-cooled dil. H$_2$SO$_4$(4-5%) contained in pt-dish.

The peroxofluorotitanates are obtained by oxidising a concentrated solution of (NH$_4$)$_2$TiF$_6$ with H$_2$O$_2$ at 20°C followed by the addition of ammonia with cooling (63). K$_2$TiO$_2$F$_4$ is reported to be formed by addition of KCl at 20°C to an aqueous solution of (NH$_4$)$_2$Ti(O$_2$)F$_5$.

Guerchais (64) reported the existence of the ions $\text{Ti}_2\text{F}_8(\text{C}_2\text{O}_4)_2$ and $\text{TiF}_4(\text{C}_2\text{O}_4)_2$ in solution from the $^{19}$F NMR study. But the details about these two ions have not been reported by the author.

Guerchais (65) also reported the formation of the compounds of the type $\text{Et}_4\text{N}_2\text{TiF}_4$ (HL = $\beta$-diketone). These were prepared by allowing the $\beta$-diketones to react with $\text{Et}_4\text{N}_2\text{TiF}_5(\text{H}_2\text{O})_2$ in acetonitrile.
II. OXALATO COMPOUNDS OF TITANATES

Ligand characterisation of oxalates: oxalate is a fascinating ligand exhibiting both bidentate and monodentate characteristics in the compound formation. The oxalate may act both as chelating ligand about a metal ion or as a bridge between two metal ions as shown below:

Titanium forms titanyloxalate, TiO(C2O4)(66), but the oxalate of the type, Ti(C2O4)2 is unknown. A number of oxalato complexes of titanium are known (67-74) which can be classified into following groups:
(i) Titanyl oxalates, e.g., $\text{M}^+\text{TiO(C}_2\text{O}_4\text{)}_2\cdot n\text{H}_2\text{O}$, where $\text{M}^+ = \text{Na}^+ ; \text{K}^+ \text{ etc.}; \text{M}^{\text{II}}\text{TiO(C}_2\text{O}_4\text{)}_2\cdot n\text{H}_2\text{O}$, where $\text{M}^{\text{II}} = \text{Co}^{2+}$, $\text{Ca}^{2+}$, $\text{Sr}^{2+}$, $\text{Ba}^{2+}$, $\text{Pb}^{2+}$ etc., and $\text{Zn}^{2+}\text{Co(NH}_3\text{)}_6\cdot \text{Ti}_3\text{O}_2\text{Cl}_2\text{(C}_2\text{O}_4\text{)}_6\cdot 5\text{H}_2\text{O}$.

(ii) Tris-oxalato complex, e.g., $\text{C}_2\text{H}_5_4\text{N}_2\text{Ti(C}_2\text{O}_4\text{)}_3\cdot 7\text{H}_2\text{O}$.

A double oxalate of iron(II) and titanium(IV) is also reported (75) which is formulated as, $\text{FeC}_2\text{O}_4\cdot 3\text{TiO}_2\text{C}_2\text{O}_4\cdot n\text{H}_2\text{O}$. In these compounds oxalate ion is acting as a bidentate group.

$\text{TiO(C}_2\text{O}_4\text{)}$ is prepared (66) by evaporating a solution of freshly precipitated hydrated titanium oxide in oxalic acid.

Potassium titanyl oxalate is prepared (67) by evaporating a mixture of hydrated titanium oxide dissolved in oxalic acid and requisite amount of $\text{K}_2\text{C}_2\text{O}_4\cdot \text{H}_2\text{O}$.

Tetraethylammonium tris-oxalatotitanate may be prepared (72) by shaking a mixture of $\text{TiCl}_4$ (1 mole) and tetraethylammonium bromide (2 moles) in dry acetone with an excess of silver oxalate for about one hour. The silver salts were centrifuged off and anhydrous ether was added to precipitate the product.

Kharkar and Patel (76) studied the system, hydrated titanium oxide-oxalic acid conductometrically and suggested the formation of four types of oxalates having molar ratios of acid to $\text{TiO}_2$ of 0.5, 1.0, 1.5 and 2.0. Babko and Dubovenko (77)
studied the system containing TiO^{++} and C_{2}O_{4}^{2-} ions by measuring the optical density of the solution in the u.v. region of the spectrum. They concluded from the study that the simplest complex TiO{C_{2}O_{4}} was formed at pH < 1 and when the pH was increased, complex anion of the type \(^{-}TiO(C_{2}O_{4})_{2}^{2-}\) were formed. Sarjuprasad and Tripathi (78) studied the oxalato complexes of Ti(IV) potentiometrically and reported the formation of four compounds, viz., TiCl_{2} = C_{2}O_{4}, Ti(C_{2}O_{4})_{2}, Ti(C_{2}O_{4})_{2}\cdot M_{2}(C_{2}O_{4}) or, M_{2}^{-} Ti(C_{2}O_{4})_{3}^{-} and Ti(C_{2}O_{4})_{2}\cdot 2M_{2}(C_{2}O_{4}) or, M_{4}^{-} Ti(C_{2}O_{4})_{4}^{-}; where M = H^{+}, Na^{+}, K^{+} or NH_{4}^{+}.

Extensive studies have been made on the thermal decomposition of oxalatotitanates on account of their scientific interest and industrial value. For example, the thermal decomposition of barium titanyl oxalate have been studied by thermogravimetry and differential thermal analysis, since barium titanate shows remarkable ferro-electric behaviour and is utilised in the ceramic industry. A number of papers have been published (79-83) regarding the mode of thermal decomposition of barium titanyl oxalate. Most recently Gopalakrishnamurthy et al. (83) studied the decomposition of barium titanyl oxalate in detail and they have suggested the following decomposition reactions:
The thermogravimetry and differential thermal analysis studies of potassium titanyl oxalate, $K_2TiO(C_2O_4)_2\cdot2H_2O$ indicate 5 plateaus corresponding to the possible products (84), $K_2TiO(C_2O_4)_2$, $K_2CO_3\cdotTiO_2$, $K_2O_2\cdotTiO_2$, $K_2CO_2\cdotTiO_2$ and $K_2OTiO$. Dollimore again reported (85) that the dehydration of potassium titanyl oxalate started at 70°C and decomposed in two stages. The final residue at 1000°C contained $K_2CO_3$ and $K_2TiO_5$. Thermal decomposition of oxalates of potassium and ammonium studied by Papazian and coworkers (86) indicated that potassium titanoyl oxalate is less stable than potassium oxalate, again ammonium titanoyl oxalate is more stable than ammonium oxalate. The thermal decomposition study (70) of cobalt titanoyl oxalate, $Co_2TiO(C_2O_4)_2\cdot7H_2O$ shows that the compound lose water molecule at 90 - 170°C and further decomposition of the compound occur at 218 - 443°C according to the reaction, $CoTiO(C_2O_4)_2\rightarrow CoTiO_3 + 2CO_2 + CO_2$.  

$BaTiO(C_2O_4)_2\cdot(4 + x)H_2O \xrightarrow{100°C} BaTiO(C_2O_4)_2\cdot4H_2O + xH_2O$

$BaTiO(C_2O_4)_2\cdot4H_2O \xrightarrow{120 - 180°C} BaTiO(C_2O_4)_2 + 4H_2O$

$2BaTiO(C_2O_4)_2 \xrightarrow{180 - 250°C} Ba_2Ti_2O_2(C_2O_4)_3\cdotCO_3 + CO$

$Ba_2Ti_2O_2(C_2O_4)_3\cdot3CO_3 \xrightarrow{250 - 450°C} Ba_2Ti_2O_2CO_3(CO_2) + 2CO_2 + 3CO$

$Ba_2Ti_2O_5CO_3(CO_2) \xrightarrow{450 - 600°C} Ba_2Ti_2O_5CO_3 + CO_2$

$Ba_2Ti_2O_5CO_3 \xrightarrow{600 - 750°C} 2BaTiO_3 + CO_2$
TG and DT analyses (87) of the compound, $\text{Co(NH}_3\text{)}_6\text{Ti}_3\text{O}_2\text{Cl}_2\text{(C}_2\text{O}_4\text{)}_6\cdot 7\cdot 6\text{H}_2\text{O}$ indicate a stable intermediate, $\text{Co(NH}_3\text{)}_6\text{Ti}_2\text{(C}_2\text{O}_4\text{)}_2\cdot 7\text{ at } 70 - 170^\circ\text{C losing both Cl and H}_2\text{O. On heating at higher temperature decomposition takes place giving rise to several products. Most recently, the thermal behaviour of PbTiO(C}_2\text{O}_4\text{)}_2\cdot 4\text{H}_2\text{O have been studied (88), using thermogravimetry, DTA, i.r. spectroscopy and x-ray. The decomposition involves 4 main steps corresponding to the dehydration of the tetrahydrate followed by the formation of a stable oxide carbonate PbTiO}_2.5\text{(CO}_3\text{)}_0.5$. 

Infra-red spectra of oxalatotitanates:

According to Fujita et al. (89) the spectra of all the oxalato complexes are essentially similar regardless of the kind of the metal and combining ratio of the metal to ligand.

The structure of the free oxalate ion is well established. It is planar with $D_{2h}$ symmetry. The i.r. spectra show bands as tabulated (90) below:

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When oxalate ion is coordinated, all of the fundamentals are more or less altered in form and frequency. As metal-oxygen bonds become stronger the effective symmetry of the ligand changes from $D_{2h}$ to $C_{2v}$. In the case of the chelate oxalate complexes the C-O bonds interacting with metal ion become longer, the other two shorter. The asymmetric (O-C-O) stretching bands shift to higher frequencies and the symmetric (O-C-O) stretching bands shift to lower frequencies and all the i.r. inactive Raman spectrum bands become i.r. active. Krishnamurthy and Harris (92) also concluded from the spectra of various

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1664*/1640</td>
<td>O-C-O assymmetric stretching ($\nu_{as}$)</td>
</tr>
<tr>
<td>1485, 1450</td>
<td>O-C-O symmetric stretching ($\nu_s$)</td>
</tr>
<tr>
<td>1335S</td>
<td>O-C-O out of plane bending (\delta)</td>
</tr>
<tr>
<td>780sh</td>
<td>O-C-O out of plane bending (\delta)</td>
</tr>
<tr>
<td>774S</td>
<td>O-C-O out of plane bending (\delta)</td>
</tr>
<tr>
<td>512</td>
<td>O-C-O out of plane bending (\delta)</td>
</tr>
<tr>
<td>298*</td>
<td>C-C stretching (\sigma)</td>
</tr>
<tr>
<td>545*</td>
<td>M-O stretching (\sigma)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} = infra red spectrum of Na$_2$C$_2$O$_4$. * Raman spectrum of K$_2$C$_2$O$_4$.H$_2$O (i.r. inactive). VS. = very sharp. S = sharp. sh = shoulder. M = metal.
oxalato complexes that the strong absorption band in the neighbourhood of 1700 cm\(^{-1}\) indicate a certain degree of covalent character of the bound oxalate in the complex.

According to Curtis (90, 91) chelate oxalato complexes can be characterised by the occurrence of a strong band in the region, 1380 - 1430 cm\(^{-1}\). The corresponding symmetric band for ionic oxalate is i.r. inactive but Raman spectrum active at 1485 cm\(^{-1}\). He also observed a strong band at 774 cm\(^{-1}\) of oxalate ion for \((O-C-O)\) deformation which is being shifted to the region 785 - 825 cm\(^{-1}\) for the chelate oxalate complexes. Again, C-C stretching vibration which is i.r. inactive (Raman band, 898) for the ionic oxalates, but found infra-red active for the chelate complexes. Same is the case with the band in the region 520-570 cm\(^{-1}\) which is absent for the ionic oxalates. It may be recalled that the oxalate not only can form chelate compounds but it can also act as a bridge between two metal ions. The oxalates may act as either "bridging bidentate" or "bridging unidentate" ligand. Curtis commented in his papers that the bridging bichelate oxalate compounds closely resemble the spectra of the ionic oxalate, however, the compounds with bi-unidentate oxalates differ from the others as there is a shift of single \(\gamma\)as \((O-C-O)\) and \(\delta\) \((O-C-O)\) bands to lower frequencies. The characteristic bands of different types of oxalato compounds are represented below (Table 1.4).
Table (91) 1.4

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Ionica(^a)</th>
<th>Bridging(^b) bidentate</th>
<th>Chelate(^c)</th>
<th>Bridging bi-unidentate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma_{as}(0-C-0))</td>
<td>1640(VS)</td>
<td>1640(VS)</td>
<td>1720(sh)</td>
<td>1567(VS)(^d) 1562(VS)(^e)</td>
</tr>
<tr>
<td>(\gamma_{s}(0-C-0))</td>
<td>1335(S)</td>
<td>1355(w)</td>
<td>1433(S)</td>
<td>1351(m) 1365(m)</td>
</tr>
<tr>
<td>(\delta(0-C-0))</td>
<td>744(S)</td>
<td>795(m)</td>
<td>775(S)</td>
<td>740(S) 760(S)</td>
</tr>
</tbody>
</table>

VS = very sharp, S = sharp, m = medium, w = weak and sh = shoulder.

\(a = \text{Na}_2\text{C}_2\text{O}_4\), \(b = \text{Nickel amine oxalate}\). \(c = \text{K}_2\text{Ni(C}_2\text{O}_4)_2\cdot6\text{H}_2\text{O}\)
\(d = \text{Ni(tet a) C}_2\text{O}_4\). \(e = \text{Ni(tet a) C}_2\text{O}_4\cdot3\text{H}_2\text{O}\).

tet a = tetramine C - racemic 5, 7, 7, 12, 14, 14 - hexamethyl-1, 4, 8, 11 tetra-azocycloptetradecane (C - meso isomer).
REFERENCES


