RESEARCH ARTICLE

CHARACTERISATION OF METAL COMPLEXES OF SUBSTITUTED FERROCENE

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ARTICLE INFO	ABSTRACT
	The multi nuclear complexes involving Si(IV), Sn(IV), Ti(IV), Zr(IV) and Hf(IV) chlorides with ferrocene derivative has not been reported nor any effort has been made to synthesize such complexes. The complexes presented in this chapter are novel in the sense that they contain four metal ions and one of them is either Si(IV), Sn(IV), Ti(IV), Zr(IV) or Hf(IV) involving ferrocene. The multinuclear complexes have been synthesized by following strict dry conditions using dry box flushed with nitrogen. In the process of synthesis of the complexes, the ferrocene derivatives, which was used as ligand.

INTRODUCTION

Describe the multinuclear complexes involving silicon (IV), tin(IV), titanium(IV), zirconium(IV), Co(II), Ni(II), Cu(II), Mn(II), Fe(III) or hafnium with ferrocene derivatives. These complexes are novel in the sense that they have three to four different metal ions in their composition. A survey of the literature shows that complexes of silicon (IV), tin (IV), titanium(IV), zirconium(IV) and hafnium(IV) with ferrocene have not been synthesized nor efforts have been made to synthesize complexes of the type that have been presented.
The present state of knowledge of ferrocene complexes and the complexes formed by silicon (IV), tin(IV), titanium(IV), zirconium(IV) and hafnium(IV) halides and pseudohalides is as follows:

Tetravalent Halides Complexes of Tin and Silicon:
Tetrahedral geometry dominantes the structural chemistry of the halides of silicon and all the tetrahalides MX_4 hydride halides $MH_n X_{4-n}$ (n= 1−3) and organometallic halides, $MR_n X_{4-n}$ (n−1−3; R = alkyl, alkenyl aryl), exhibit this stereochemistry in all phases [1].

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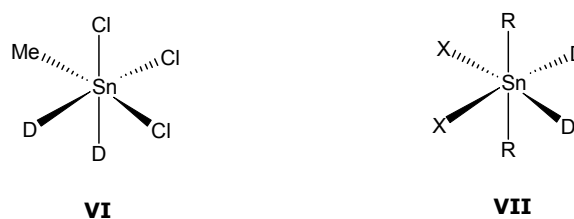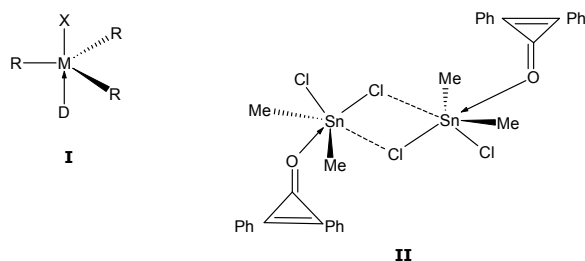[2]Chemistry department of S.S.M.V. (P.G.) College Shikarpur, Buland shahr, India.

In contrast, although the analogous tin derivatives are also tetrahedral in the vapour and liquid phases [2] the solid tin halides show a preponderance for the formation of halogen−bridged lattices. The tetrahedral compounds warrant little comment, although it is notable that the metal−halogen distance increases whilst the metal−carbon distance decreases in the series $Me_n MX_{4-n}$ as the halogen content of the molecule increases, which is consistent with a redistribution of p character in the bonds to the more electronegative ligands.

The silicon (IV), germanium (IV) and tin (IV) halides MX_4 and organometallic halides $R_{4-n} SnX_n$ are good Lewis acids and acceptros of halide and neutral donor molecules. Lewis acidity in these halides increases in the order   Si < Ge < Sn < Pb, I < Br < Cl < F and n = 1< 2 < 3 < 4, and is reflected in the stiochiometry and stability of the resulting complexes. Thus, whereas trimethylchlorosilane shows no tendency for complex formation with pyridine[3] the corresponding tin adduct, Me_3 SnCl. C_5H_5N, was the first authenticated five coordinated tin complex [4]. Coordination saturation appears to be reached in the original bipyramidal arrangement (I) with a planar (Me_3M) moiety for the monohalides, but the dihalides, trihalides and tetrahalides can form 1:2 adducts with an octahedral geometry as well as 1:1 adducts with trigonal bipyramidal geometry. In the latter, the organic groups always occupy equatorial sites.(II)

I

II

The 1:1 adduct of dimethyl tin dichloride and diphenylcyclopropene is unusual, and comprises a chlorine−bridged dimer with distorted octahedral geometry for tin[2,5] other than the usual trigonal bipyramidal geometry found in most rather 1:1 complexes such as $Ph_2 SnCl_2$ benzothiazole[6]. Two types of behaviour are observed with terdentate ligands. In some isolated cases, seven coordinated adducts with a distorted pentagonal bipyramidal geometry (III) are found[7,8] but 2,2′, 2″−terpyridine promotes displacement of halogen from tin and the formation of ionic complexes such as $[Me_2Sn (terpy)Cl^+]$ $[Me_2 SnCl_3^-]$ containing six coordinate cations and five coordinate anions[9]. Ionization of halide takes place more readily with bromine and iodine which are more weakly bonded to the Group IV elements. Thus, whereas hexamethylphosphoric triamide forms a neutral, trigonal bipyrmaidal adduct with trimethyltin chloride, the ionic complex $[Me_3Sn(hmpt)_2]^+$ $[Me_3 Sn Br_2]^-$ is formed with trimethyltin bromide. Similarly, stable ionic 1:1 adducts of the type $[Me_3 Si.D]^+ X^-$(X=Cl, Br; D = pyridine, hmpt) have been isolated from the interaction of trimethylbromo and trimethyliodo−silanes with the donor[10] whilst all four Si−T bonds are cleaved on dissolution of silicon (IV) iodide in the same solvent, from which the complex $(Sn(hmpt)_6]^{4+}$ 4I containing octahedrally coordinated silicon was isolated[11].
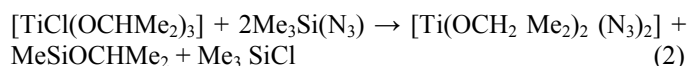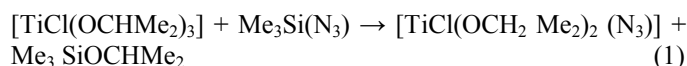

III

IV

V
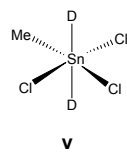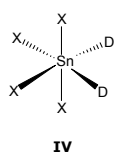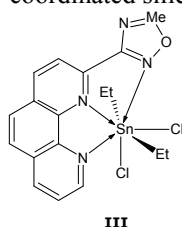
Various stereochemical permutations are observed for octahedral tin complexes. Adducts of tin (IV) chloride generally exhibit the cis geometry (IV)[12] although some examples of the trans geometry are known[13]. Reasons for the preference for the cis geometry are not obvious, but the complexes with the trans structure are those with rather bulky donor molecules. Similarly confusing are the structures adopted by the complexes of organotin trihalides and diorganotin dihalides. The two donors are trans in the 2:1 pyridine and hmpt complexes of methyltin trichloride as in (V) but the analogous DMF complex adopts the cis structure (VI)[14–15]. The two organic groups in $R_2 SnX_2$. 2L complexes are always invariably mutually trans, but again the two halide and the two donor molecules can adopt either configuration, (VII) or (VIII), depending upon the nature of the substituents[16].

VI

VII

VIII
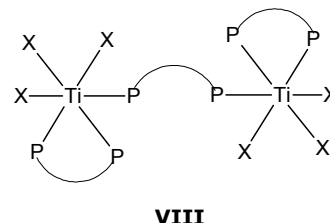
Titanium (IV) Complexes: There are a large number of complexes TiX_4 with monodentate nitrogen ligands. For TiF_4 both 1:2 and 1:1 complexes are known, the former being pseudooctahedral and the latter, because of the high Ti–F bond strength, are fluoro−bridge polymers,[17] with $TiCl_4$ and $TiBr_4$ six−coordinate monomers are the commonest adducts, viz. TiX_4L_2. The area has been well reviewed[17]. However, reactions between $TiCl_4$ and amines can, unlike reaction with oxygen donor ligands, give rise to $TiCl_4$ derivatives[17]. More work will be described here, adducts of $TiOCl_2$ with MeCN and NMe_3, for example, form $TiOCl_2L_2$, but with py the adduct $TiOCl_2 Py_{2.5}$ form. Only in the case of $TiOCl_2(−pic)_2$ and $TiOCl_2 (NMe_3)_2$, IR spectra indicate the presence of a terminal Ti=O moiety (978 cm^{-1}), the other complexes presumably having a Ti–O–Ti bridge (ca. 890 cm^{-1}). The potentially bidentate o−allylaniline complexes only via the nitrogen in TiX_4L (X = Cl, Br) to form pentacoordinate monomers; the hexacoordinate $TiBr_4L_2$ is also known.[18]

Titanium(IV) chloride and bromide form TiX_4 $(Me_2 C=N−N=CMe_2)_2$ in the presence of excess of acetone azine, but when the halides are in excess the products formed are $(TiCl_4)_4$ (ligand)$_3$ and $TiBr_4$ (ligand)$_2$ (18). Stable azides $[Ti(OPr)_2(N_3)_2]$ and $[TiCl(OPr)_2(N_3)]$ complexes are known; the azido group can be displaced by reaction with protic reagents and HN_3 is eliminated. The complexes also react with phosphines to form phosphiniminato complexes with N_2 elimination. Mono− and bis−azido complexes have been prepared as shown in equations (1) and (2).

$$[TiCl(OCHMe_2)_3] + Me_3Si(N_3) \rightarrow [TiCl(OCH_2 Me_2)_2 (N_3)] + Me_3 SiOCHMe_2 \qquad (1)$$

$$[TiCl(OCHMe_2)_3] + 2Me_3Si(N_3) \rightarrow [Ti(OCH_2 Me_2)_2 (N_3)_2] + MeSiOCHMe_2 + Me_3 SiCl \qquad (2)$$

An X−ray study of $[TiCl_4[N_3)_2]^{-2}$ reveals that the azide groups occupy trans positions. Electrolytic reduction of $TiCl_4$ in the presence of N_2 in DMSO produces a 1:1$TiCl_3$: N_2 complex. Two previously reported products from $[ReCl(N_2)(PPhMe_2)_6]_2$ and $TiCl_3$ have been shown to be derived from $TiCl_4[ReCl(N_2)(PPhMe_2)_4TiCl_4]$ and $[ReCl(N_2) (PPhMe_2)_4 TiCl_4(THF)]$ can be obtained from $TiCl_4$, the former being the first fully characterized example of a trinuclear complex containing two bridging dinitrogen ligands. Titanium tetrachloride in excess reacts with $[ReCl(N_2) (PPhMe_2)_4]$ in Et_2O to yield $[ReCl (N_2) (PPhMe_2)_4 (Ti_2Cl_6O) (Et_2O)]$, which

exhibits a very low (N_2) at 1622 cm^{-1}. The x–ray crystal structure of the product[19] of the reaction of $TiCl_4$ with $N(SiMe_3)_3$ shows to contain planar four–membered $(Ti-N)_2$ rings with planar geometry at N apparently with considerable bonding in the rings. These are linked by chlorine bridges to give five–coordinate Ti atoms in approximately trigonal bipyramidal geometry. The reaction of $TiCl_4$ with an excess of $Li[N(SiMe_3)_2]$ yields $[TiCl (N (SiMe_{32})_3]$. The resistance to complete chlorine substitution suggests considerable steric crowding due to the bulky $[N(SiMe_3)_2]^-$ ligands. Both X–ray crystallography and ^1H NMR spectrum, which exhibits two equally intense resonances below the coalescenece temperature of 34°C, has been interpreted in terms of restricted rotation about the Ti–N bonds. At low temperature the three silylamide ligands remain equivalent, but the $SiMe_3$ groups proximal and distal to chlorine are non–equivalent.

The TiF_4 and Pr_2 NH, py or NMe_3 systems have been shown to be quite complex by Drago and coworkers[20] for example, in TiF_4 rich solutions in acetone, high conductance has been explained by equation (3).

$$3TiF_4 + R_2NH \rightarrow TiF_3 (R_2NH)^+ + Ti_2 (3F^-)_3 \qquad (3)$$
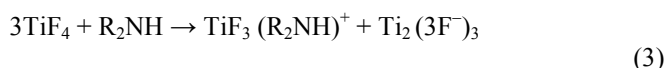
A number of dinitrile ligands (succinonitrile, glutaronitrile, adiponitrile) form $TiCl_4$ (ligand) complexes in which the nitriles bridge two titanium atoms. Reactions of $CH_2(NMe_2)_2$ or $SiMe_2 (NMe_2)_2$ with $TiCl_4$ give both chelated $TiCl_4$ (ligand) complexes and $TiCl_3 (NMe_2)$ species.[21] The five–coordinate meso–tetraphenylorphyrinate 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 anthrecenide, gives $[TiF_2(TPP)_2]^-$ consistent with its coordinate unsaturation, $[TiF (TPP)]$ adds ligands L (L=THF, PBu, pyridine, N–methylimidazole, or N–methylpyrrolidine) yielding $[TiF(L)(TPP)]$, and adds F^- affording $[TiF_2 (TPP)]^-$. All these Ti 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 $[TiF(O_2)(TPP)]$, as shown in equations (4) and (5), a species which could be formulated as a superoxotitanium (IV) complex but which appears to have a significant amount of peroxo porphyrin cation radical titanium(IV) character.[22]

$$[TiF (TPP)] O_2 \rightarrow [TiF (O_2) (TPP)-] \qquad (4)$$

$$[TiF(TPP)] + [TiF(O_2)(TPP) \rightarrow [TiF_2(TPP)+ [Ti(O_2)(TPP)]- \qquad (5)$$
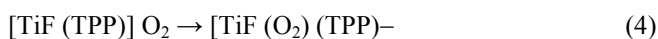
The isolation of $TiCl_3(PH_3)$ was first reported in 1832[23] $TiCl(PH_3)_2$ has also been prepared. A large number of $TiCl_4(PR_3)_2$ complexes are now known,[24] but only have $TiBr_4(PPh_3)$ and $TiBr_4(PPh_3)_2$ been prepared, the former having C_{3v} symmetry and the later a cis octahedral structure. There is some evidence for the probable existence of binuclear species of the type $Ti_2Cl_8 (PR_3)$. Titanium tetrachloride reacts with $Pt(PPh_3)_n$ (n=3,4) to yield emerald green $(TiCl_4)_2$ $Pt(TiCl_4.PPh_3)_3$, which, on heating in vacuo or treatment with more PPh_3, produces $Pt(TiCl_4.PPh_3)_3$. It is thought[25] that the former species is pentacoordinate with two axial $TiCl_4$ and

three equatorial $TiCl_4.PPh_3$ moeities bonded to platinum via the titanium atoms. Although $TiCl_4$ and $AsPh_3$ were known to complex as early as 1924, the adduct $TiCl_2 (AsPh_3)$ has only been investigated relatively recently. The reports of a bis adduct $TiCl_4 (AsPh_3)_2$ must be viewed with some suspicion. The reaction between $SbPh_3$ and $TiCl_4$ in dry benzene initially gives a deep violet solution and ultimately a gummy black solid. It is likely that reduction of $TiCl_4$ has occurred. With 1,2–bis (diphenylarsino) ethane (dpse), $TiCl_4$ forms only a 2:3 complex $[(TiCl_4)_2(dpae)_3]$ although diphos forms 1:1 and 3:2 adducts. Tetramethyldiphosphine and $TiCl_4$ react to form a deep red paramagnetic product of unknown composition, the paramagnetism suggesting that partial reduction of titanium(III) had occurred. With $TiCl_3(THF)_3$ an insoluble, moisture– and air–sensitive complex $(TiCl_3)_2 (Me_2PPMe_2)_3$ is produced, for which structure (VIII) has been proposed. Tetraethyldiphosphine does not yield any isolate complex with $TiCl_3(THF_3)^{(24)}$.
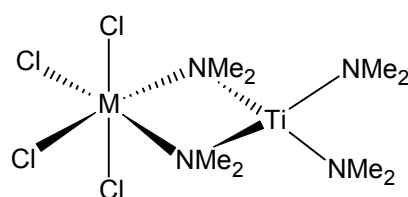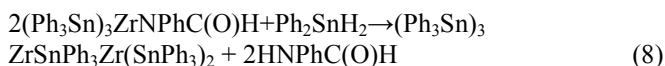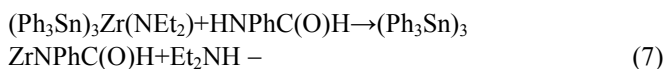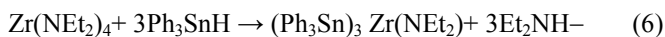
IX

Investigation of the diars complexes of the titanium(IV) halides resulted in the first example of eight–coordination in the first transition series. In $[TiCl_4(diars)_2]$ the dodecahedron contains two diars forming an elongated tetrahedron and four chlorine atoms in a flattened tetrahedron with respect to the fourfold inversion axis[25]. Although numerous attempts have been made to prepare similar complexes with a range of bidentate ligands, only those with the o–phenylene or similar backbone have proved successful. Thus 1,2–bis (dimethylarsino)–3–fluoro–or 4–fluoro–benzene form only the hexacoordinate $TiCl_4$ (ligand) complexes; presuable for fluorine–substituted ligands are poorer σ–donors. Eight–coordination is also not achieved with 1,2–bis (dimethylarsino) –3,3,4,4–tetrafluorocyclobutene (f_4 fars) or 1,2–bis (dimethylarsino) –3,3,4,4,5,5– hexafluorocyclopentene (f_6 fars), probably due to the larger As–As 'bite' of the ligands, nor with rac–o–phenylene bis (phenylmethylarsine), due to steric hindrance. However, 1,8–bis (dimethylarsino) naphthalene, which has a short As–As separation, readily forms brown $TiCl_4$ (ligand)$_2$. These results reinforced earlier conclusions about the importance of steric factors in promoting eight–coordination, but also suggest that the electronic properties of the ligands are not negligible.[26]

Zirconium (IV) and Hafnium(IV): Very little is known about cyanide complexes of zirconium(IV) or hafnium(IV). Just one compound has been reported. $[Hf(CN) N(SiMe_3)_2]_3$ with Me_3SiCN in toluene at reflux. $Zr(SnPh_3)_4$ has been obtained as a yellow solid (m.p. 70–73°C); sintering at 65°C) by reaction of $Zr(NEt_2)_4$ $ZrSnPh$ $Zr_3(SnPh_3)_3$, was prepared via the sequence of reactions in equations(6–8). The transamination with N–phenylformamide (equation 6) is necessary in order to prevent diethylaminecatalyzed

decomposition of Ph_2SnH_2 in the next reaction step. After purification by chromatography, the product was obtained in 22% yield as a yellow solid which melted at 100°C (sintering at 85°C).[27]

$$Zr(NEt_2)_4 + 3Ph_3SnH \rightarrow (Ph_3Sn)_3 Zr(NEt_2) + 3Et_2NH- \qquad (6)$$

$$(Ph_3Sn)_3Zr(NEt_2) + HNPhC(O)H \rightarrow (Ph_3Sn)_3$$
$$ZrNPhC(O)H + Et_2NH - \qquad (7)$$

$$2(Ph_3Sn)_3ZrNPhC(O)H + Ph_2SnH_2 \rightarrow (Ph_3Sn)_3$$
$$ZrSnPh_3Zr(SnPh_3)_2 + 2HNPhC(O)H \qquad (8)$$

The reactions of ammonia and aliphatic amines with zirconium(IV) chloride and hexachlorozirconate (IV) salts have been reviewed by Fowles[28]. Early work on ammonia adducts of zirconium tetrahalides is summarized in the monograph by Blumenthal. Compounds of the type $ZrCl_4.nNH$ (n=8,4 or 2)[29] and $ZrBr_4.4NH_3$[30] were prepared by reaction of the tetrahalides with gaseous ammonia. Thermal decomposition of $ZrCl_4.8NH_3$ in argon gives stepwise formation of $ZrCl_3.6NH_3$, $ZrCl.4NH_3$ and finally $ZrCl_4$[31]. Tensimetric studies indicate that the $ZrCl_4.8NH_3$ obtained upon reaction of $ZrCl_3$ $(NH_2).6NH_3$ and NH_2Cl[32]. The ammonolysis product can be freed of NH_4Cl by washing with liquid ammonia, and the resulting $ZrCl_3$ $(NH_2).nNH_3$ is converted to $ZrCl_3(NH_2).NH_3$ by heating in vacuo at 100°C[33]. The same ammonolysis products are obtained upon reaction of liquid ammonia with $M_2Zr.Cl_6$ (M = NH_4, Rb or Cs)[34]. The reaction of gaseous $ZrCl_4$ with ammonia at 300°C yields $ZrCl_4.2NH_3$, which has cubic unit cell with a=10.13A[35].

Zirconium(IV) and hafnium(IV) halides form adducts with a variety of monodentate and polydentate amines. In general, these compounds are air–and moisture–sensitive white solids (yellow when the halide is iodide), thermally stable and insoluble in most organic solvents. While zirconium(IV) chloride forms simple adducts with tertiary and secondary amines, aminolysis takes place with primary amines yielding aminobasic chlorides such as $ZrCl_2$ $(NHMe)_2.NH_2Me$ and $ZrCl_3$ $(NHR).NH_2R$ (R=Et, Pr or Bu)[36]. The reactions of amines (A=Me_3N, Et_3 N, Me_2 NH, Et_2 NH or $EtNH_2$) with the corresponding alkylammonium hexachlorozirconates $[AH]_2[ZrCl_6]$ have also been studied[37]. No reaction was observed with the tertiary amines; very slow aminolysis occurred with the secondary amines; and relatively rapid aminolysis of one Zr–Cl bond took place with ethylamine (equation 9).

$$[EtNH_3]_2[ZrCl_6] + 2EtNH_2 \rightarrow [EtNH_3]_2$$
$$[ZrCl_5(NHEt)] + [EtNH_3]Cl \qquad (9)$$
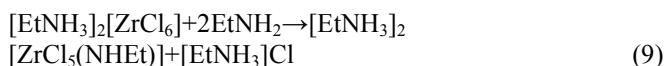
Diamines such as ethylene diamine, tetramethylethylene diamine and $SiMe_2(NMe_2)_2$ give 1:1 adducts with zirconium(IV) and hafnium(IV) halides. The (M–X) region of IR spectra of $[MX_4 (TMEDA)]$ (X = Cl or Br) and $[MCl_4 (NMe_2)_2SiMe_2]$ complexes is consistent with an octahedral cis (C_{3v}) structure. The presence of two N–methyl resonances in ^1H NMR spectra of $[ZrCl_4 (NMe_3) (SiMe_2)]$ suggests the presence of a non–planar ZrN_2Si chelate ring; the two resonances coalesce to a broad singlet at 100°C owing to a rapid ring–inversion process. Pale yellow solid adducts,

$[MCl_4Ti(NMe_2)_4]$ (M = Zr or Hf), have been prepared by displacement of trimethylamine from n–pentane suspension of $[MCl_4(NMe_3)_2]$. IR spectra of the $[MCl_4 Ti(NMe_2)_4]$ complexes suggest an octahedral cis structure about zirconium or hafnium in which Ti $(NMe_2)_4$ behaves as a bidentate chelating ligand (IX). Monodentate N–heterocyclic amines such as pyridine, substituted pyridines, benzoquinolines, imidazoles and indazoles, and bidentate amines such as 2,2'– bipyridyl and 1,10–phenanthroline react with zirconium(IV) and hafnium(IV) halides to give moisture–sensitive, diamagnetic adducts that are generally insoluble in most organic solvents. They may be prepared by prolonged stirring of a solution of the ligand and a suspension of the metal halide in an inert solvent such as benzene or dichloromethane. Alternatively, the adducts may be precipitated by mixing solutions of the ligand and metal halide in a donor solvent such as acetonitrile, ether or ethyl acetate.

Octahedral 1:2 adducts $[MX_4L_2]$ are the usual products of the reaction of zirconium (IV) or hafnium(IV) halides with monodentate N–heterocyclic amines. However, there are exceptions. Both 1:2 and 1:3 adducts have been reported for X=Cl and L=pyridine; the MCl_4 $(py)_3$ (M=Zr or Hf) complexes are converted to $[MCl_4 (py)_2]$ upon heating in vacuo for seven hours at 65–75°C. While 3,5–lutidine and 2,4–lutidine react with ZrX_4 (X=Cl, Br or I) to give the expected 1:2 adducts, the more sterically hindered 2,6–lutidine yields 1:1 adducts. IR and ^1H–NMR spectra of $ZrCl_4$ (2,6–lutidine) suggest that this complex may have a symmetrical, chlorine–bridged dimeric structure. 5,6–Benzoquinoline also gives a 1:1 adduct with zirconium(IV) chloride, whereas 3,4–benzoquinoline yields the expected 1:2 complex.

X–Ray structures of these complexes are not yet available. However, the $[MX_4L_2]$ adducts have been assigned octahedral cis or trans structures on the basis of the number of metal–halogen stretching bands in IR spectra. Cis–$[MCl_4L_2]$ complexes exhibit two or more (M–Cl) bands in the region 275–360 cm^{-1}[38], while trans–$[MCl_4 L_2]$ compounds show a single (M–Cl) band at about 335–350cm^{-1}. Both cis and trans isomers are observed and the preferred configuration is not easily rationalized in terms of the structure of the ligand. IR spectra are also useful in identifying the ligand donor atom in the case of complexes that contain ambidentate or potentially bidentate ligands. Thus, 3–cynopyridine, 2–acetylpyridine and nicotinamide behave as monodentate ligands in $[MCl_4 L_2]$ complexes, coordinating to the metal only through the pyridine nitrogen atom. Imidazoles bind to metal tetrachlorides at the unsaturated nitrogen atoms, while indazoles are attached at the pyrrole nitrogen atom. The absence of a band at 960 cm^{-1} in the IR spectra of ZrX_4 (pyrazine)$_2$ (X=Cl or Br) complexes indicates that, at least in the solid state, both pyrazine nitrogen atom are coordinated. Evidently pyrazine bridges between two metal atoms. The molar conductance of a–10^{-3} M acetonitrile solution of $ZrCl_4$(pyrazine)$_2$ is close to that expected for a nonelectrolyte; the small conductance observed may be due to slight dissociation. Unfortunately, the low solubility of the ZrX_4(pyrazine)$_2$ complexes precluded molecular weight measurements.[40] An ionic structure, $[MCl_2$ (bipy)$_3]$ $[MCl_6]$, has been suggested for the isomorphous MCl_4 (bipy)$_5$ (M = Zr or Hf) complexes, but attempts to isolate the eight–coordinate cation by preparation of the perchlorate or tetrafluoroborate salts were unsuccessful. The v(M–X) region of IR spectra of

the [MX$_4$ (bipy)] (M = Zr or Hf, X=Cl; M=Zr, X=Br) complexes is consistent with an octahedral cis (C$_{3v}$) structure. The structure of the [MX$_4$ (phen)] analogues may be more complex since IR spectra of the [MCl$_4$ (phen)$_2$] complexes exhibit five (M–Cl) bands. Molar conductances of the [ZrX$_4$L] (L=bipy or phen) complexes in acetonitrile are much less than expected for a 1:1 electrolyte, but slight dissociation in this solvent (equation 10) in indicated.

$$[ZrX_4L] + MeCN \rightarrow [ZrX_3L(MeCN)^+ + X^- \qquad (10)$$

Oxozirconium(IV) complexes of the type ZrOX$_2$L$_n$ (L=pyridine, ∝–picoline, 2–aminopyridine, 2,4–lutidine, 2,6–lutidine or quinoline; n=4 when X=Cl, Br, I or ClO; n=2 when X=NO or NCS) have been reported[41]. The corresponding 2,2$^|$– bipyridyl and 1,10–phenanthroline complexes have stoichiometries ZrO (ClO$_4$)$_2$L$_3$, ZrOX$_2$L$_2$(X=Cl, Br or I) and ZrOX$_2$L (X=NO or NCS). All of these compounds are monomeric nonelectrolytes in nitrobenzene except the perchlorate derivatives, which behave as 1:2 electrolytes. The structures of these complexes are unknown. However, several conclusions have been drawn on the basis of IR studies: (i) the nitrate ligands are bidentate; (ii) the NCS ligands bond to zirconium through the nitrogen atom; and (iii) the perchlorate compounds contain uncoordinated ClO$_4^-$ ions. A weak IR band in the 900–980 cm^{-1} region has been assigned to ν(Zr=O),[42] but the presence of the zirconyl group needs to be confirmed by X–ray diffraction since this species rarely occurs.[43]

Ferrocene derivatives as ligands

It has been established by the Pauson that Cyclo pentadienyl magnesium bromide is acted on by ferrous chloride then a very interesting aromatic system is formed iron cyclo pentadienyl or ferrocene which has been shown by x–ray analysis to have a sandwich structure.
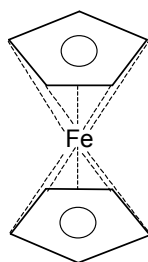
Sandwich Structure of Ferrocene

In ferrocene the cyclopentadienyl rings are much less susceptible to nucleophilic attack than the cyclopentadienyl amine and are incapable of adding electrophilic reagents. This is because the cyclopentadienyl ring of ferrocene contains the partial negative charge and not the full charge.[44–49] According to quantum mechanical calculations by mean of molecular orbital methods, it is −0.35 of electronic charge on each of the rings (+0.7 on iron). The first electrophilic substitution reaction of ferrocene was the Friedel Crafts acylation discovered by Woodward and Rosenbleum, which lead to formation of mono and di substitutes[50]. Nesmeyanov[51] and his coworkers carried out following set of reactions on ferrocene (1) Mercuration (2) Alkylation (3) Sulphonation (4) Arylation (5) Metallation and (6) Mannich condensation. Ferrocene reacts with mercuric acetate and potassium chloride

resulting in mono and bis mercurated ferrocene. This mercurated ferrocene is used in the synthesis of various substituted ferrocene[52]. Kochesh Kov firstly prepared amino ferrocene using it, which is a stronger base than the amine and incapable of undergoing diazotization.

The ambidentate nature of (–NCX) group (X = S$^-$ or Se$^-$) is well known. Introduction of this NCX in place of chlorine in the ferrocenyl bis [Mercury cury(II) chloride] opens the route for the synthesis of various adducts. The so formed ferrocenyl bis mercury (II) thio/selenocyanate, shows the behaviour of bidentate ligand[53]. 1,1$^|$–Bis (thiocyanato mercurio) ferrocene was reacted with MCl$_4$ [M=Si(IV), Sn(IV), Ti(IV), Zr(IV) and Hf(IV)] and the resulting adducts were studied by various physico–chemical analysis and are presented in chapter–II. These, adducts having three different metals in which one is either silicon, tin, titanium, zirconium or hafnium tetravalent state will be a new addition to the wealth of existing organometallic compounds. The selenocyante derivatives of the mercurated ferrocene have also been repared and in order to compare the behaivours of thiocyanate series of complexes with selenocyanate series of complexes, adducts of selenium derivative of mercurated ferrocene has been prepared and included in chapter–III. Mohugh and Smith[54] claimed to have prepared Cp$_2$ TiS$_5$ type complexes but could not offer the characterization. Ralea[55] and Coworkers prepared (Cp$_2$TiSX)$_n$ (where n=3 or 4) from Cp$_2$TiCl$_2$ and various chloro sulphides and sodium sulphides. However for the first time Kopf and Block[56] established that in all cases only Cp$_2$TiS$_5$ could be isolated. Epstein et.al[57,58] on the basis of X–ray diffraction studies have assigned a chair configuration to TiS$_5$ ring fragment of (C$_5$H$_5$)$_2$ TiS$_5$ complex.

Pentasulphide and pentaselenide complexes of bis (methyl cyclo pentadienyl) titanium(IV) and [(cyclopentadienyl) (methyl cyclo pentadienyl) titanium(IV)] have been prepared.[59,60] These complexes have been characterized by elemental analysis, IR and ^{1}H–NMR spectroscopy. Molecular weight determination and conductivity measurement, indicated these complexes to be monomeric and non electrolytic in nature. On the basis of ^{1}H NMR a chair configuration is assigned to TiS$_5$ or TiSe$_5$ ring in these complexes. Six coordinate complexes of type ML$_2$X$_2$ (where L=β–diketone and X=δ– bonded carbanions which were synthesized[61–64] include (L= acetyl acetonate), M=Sn and X=Me or ph as well as M=Pb, X=Me or Ph. Complexes having trans configuration are thermodynamically favoured[65] where as complexes with cis configuration are energetically more favourable with X ligands other than carbanions as for example in Sn(acac)$_2$Cl$_2$. Complexes of the type (A$_2$ML)$^+$X$^-$ where L − is the conjugate base of acetyl acetone, dibenzoyl methane; benzoyl acetone and trobolone, X$^-$ is BF$_4^-$, ClO$_4^-$, PF$_6^-$, ASF$_6^-$, Fe$_3$CSO$_3^-$, Cl$_2$CSO$_3^-$; Ph$_4$B$^-$, I, NCS−, NCSe−, FeCl$_4^-$, CoCl$_4^{2-}$, ZnCl$_2$(H$_2$O), SnCl$_2^-$, CdCl$_4^{2-}$ and SnCl$_6^{2-}$ and M is Ti(IV) V(IV) have been reported[66–69]. π–bonded cyclopentadienyl and methyl cyclopentadienvyl rings are identified in the IR. Spectra of these complexes by the appearance of IR–active bands which are in accordance with the assignment made by Fritz[70]. In addition to the bands complex chloro anions also appear at ~(240–390) cm^{-1}. The reaction between dichlorobis (Cyclo–pentadienyl) titanium(IV) and monohydroxy coumarins such as 7–hydroxy coumarin 4–methyl–7– coumarin, 4–methyl–7–Hydroxy coumarin,

4–phenyl–7–hydroxy coumarin, 4–methyl–6–nitro–7–hydroxy coumarin and 4–methyl–7–hydroxy coumarin and 4–methyl–8– nitro–7–hydroxy coumarin has been carried out 1:1 and 1:2 molar ratios in tetrahydrofuran in the presence of triethyl amine. Products of the type $Cp_2Ti(OCM)Cl$ and $Cp_2Ti(OCM)_2$ respectively where $[OCM]^{-1}$ is the anion of the corresponding hydroxy coumarin CMOH are obtained with dihydroxy coumarins, 6,7–dihydroxy coumarin and 4–phenyl 6,7– dihydroxy coumarin derivatives of the type $Cp_2Ti(O_2CM)$ are obtained where $[O_2CM]^{2-}$ represents the anion of the corresponding dihydroxy coumarin, CMO_2H_2. The new hydroxy coumarin derivatives have been characterized on the basis of their elemental analysis conductance electronic and IR–spectral data[71]. The hydroxy group in the 7–position is very reactive due to the electromeric effect[72]. When a nucleophilic group R– is present in the 4–position the dissociation of the hydroxy group in the 7–position decreases and the ligand becomes less acidic. But the presence of an electron withdrawing group like NO_2 in position –6 or –8 leads to the enhancement of the acidity of these coumarins. The degree of acidic character of the ligand is revealed by the amount of time taken to complete the reaction. π–cyclopentadienyl groups exhibit four strong bands at ~3100, ~1435, 12020 cm^{-1} (δCH in plane) and 820 cm^{-1} (δ C–H our of plane). An additional band also occur around 1120 cm^{-1} due to ring breathing mode. The intensity of this band varies considerably[73–75]. The electronic spectra recorded in chloroform and acetone show a single band in the region 24528–24380 cm^{-1}. Absence of d–d transitions rules out the presence of any unpaired electron in the titanium ion.

A number of dicarboxylato chelates of bis(cyclopentadienyl)–titanium(IV) and bis(indenyl) titanium(IV) have been prepared. These complexes have been characterized on the basis of molecular weight, IR spectra and analytical data. The nature of the carboxylato group linkage is also discussed[76]. In covalently bonded carboxylates, there is an increase in the asymmetric and decrease in (O–C–O) symmetric stretching[77–78]. Hence a comparison of the two frequencies with those of ionic salts on one band and covalent esters on the other, could give an idea of the metal to carboxylate group linkage. From the observations it is concluded that the linkages in the complexes have covalent character and the increasing order of degree of covalency may be expressed as: oxalate < malonate < succinate. There is an increase in the ionic character of linkage in the case of tartarate complexes probably due to the intramolecular hydrogen bonding. The appearance of medium intensity band around 1650 cm^{-1} and a broad medium band around 2650 cm^{-1} indicates that the second carbonyl is involved in hydrogen bonding[77]. The lowering of O–H frequency (3340 cm^{-1}) also supports this[78].

The increase in both the O–C–O stretching frequencies in the case of phthalate complexes may be due to the presence of aryl conjugation[79–81]. The coordination numbers 8,7,6 and 5 are exhibited by the dithiocarbamate derivatives of titanium(IV) and zirconium(IV)[82–87] (chloro) (N,N–alkylcyclohexyl–dithiocarbamato) bis(η^5–cyclopentadienyl) titanium (IV)/zirconium(IV) complexes of the type η^5–Cp$_2$M(S$_2$CNRR)Cl [where M = Ti(IV), Zr(IV), R=Me, Et and i–Pr and R^1=cyclohexyl group) have been prepared by the

reaction of stoichiometric amounts of dicyclopentadienyl titanium(IV)/Zirconium(IV) dichloride with sodium salts of dithiocarbamic acids in refluxing dichloromethane; molecular weight, conductance and IR–studies show these complexes to be monomeric non electrolytes in which the dithiocarbamate ligands are bidentate. Therefore pentacoordination has been assigned to titanium(IV)/zirconium(IV) atom in all the six complexes. The complexes have been characterized on the basis of elemental analysis, conductance infrared, PMR, electronic spectra, magnetic susceptibility and molecular weight data[80]. Sodium dithiocarbamates (NaS$_2$CNRR^1) prepared by the method described by Klopping and Kerk[89] were dried in vacuo over P_4O_{10}. Bis(η^5–cyclopentadienyl) titanium(IV)/Zirconium(IV) dichlorides were prepared by standard methods.[90] Analytical data reveal that dicyclopentadienyl– titanium(IV)/zirconium(IV) dichloride reacts with sodium dithiocarbamates in 1:1 molar proportion according to the following general equation.

$(C_5H_5)_2MCl_2$ + Na(S$_2$CNRR^1) → (C$_5$H$_5$)$_2$M(S$_2$CNRR^1)Cl + NaCl
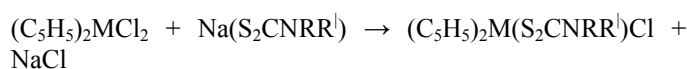
(where M=titanium/zirconium R=methyl ethyl and isopropyl groups and R^1= cyclohexyl). All the compounds are soluble in common organic solvents and are non electrolytes in nitrobenzene (ΔM=0.50 ohm^{-1} cm^2 mol^{-1}). The compounds are diamagnetic. Molecular weight measurements show them to be monomeric. One may assign a coordination number of 5 to titanium/zirconium atom in all these complexes if each cyclo pentadienyl group occupies one coordination site and the dithiocarbamate ligand is bidentate. However a coordination number of 4–would result if the dithiocarbamate ligand behaves as monodentate. R–spectra of all the complexes show one medium intensity band at ~1000 cm^{-1} which is due to two equivalent C   S stretching frequencies. This supports the bidentate character of dithiocarbamate ligands. In case the dithiocarbamate group behaves as s–bonded monodentate ligand as in Ru(NO) (S$_2$CNR$_2$)$_3$[91,92] a doublet would appear in the region 1000 ± 50 cm^{-1} due to two unequivalent C   S vibrational modes. All the prepared complexes show characteristic absorption due to C   N stretching frequency at ~1500 cm^{-1} suggesting that this bond possesses some double bond character. The bands occurring consistently at ~3110 cm^{-1} (C–H) stretching band), ~1435 cm^{-1} (asymmetric ring breathing), 1025 cm^{-1} (C–H deformation of C_5H_5 ring) and 815 cm^{-1} (C–H bending out of plane deformation) in all the compounds suggest the presence of π–bonded cyclopentadienyl groups[93]. Electronic spectra of all the complexes in chloroform and nujol mull exhibit a single band in the region 24730–24600 cm^{-1} for titanium complexes. This band may be assigned to the charge transfer bands[94,95] which is in accord with the electronic configuration (n–1)d°, nS° of titanium/zirconium in all these complexes.

Bis(carboxylato)–bis(p–biphenyl)tin(IV)complexes of the type (p–C$_6$H$_5$–C$_6$H$_4$)$_2$Sn (O$_2$CR)$_2$ (where R = –CH$_3$, –C$_2$H$_5$; n–C$_3$H$_7$ n–C$_4$H$_9$, n–C$_5$H$_{11}$; –C$_6$H$_5$; –CH$_2$Cl, –CHCl$_2$ or –CCl$_2$) have been prepared and characterized by elemental analysis molecular weight determinations conductivity measurements, IR and PMR–spectroscopy.[96] Carboxylato ligand can bind to the metal atom either as monodentate, bidentate or in ionic form as suggested by Nakamoto[97]. The separation value between ν$_2$(ν$_{as}$ OCO) and ν$_1$(OCO) was suggested <200 cm^{-1}

for bidentate and > 200 cm^{-1} for monodentate carboxylato ligand[98–101]. IR spectra of complexes obtained presently indicate that for the complexes, the separation between ν_2(1550–10 cm^{-1}) and ν_1 (1405 ± 5 cm^{-1}) is 140, 150, 150, 145, 130 and 140 cm^{-1} respectively characterizing the bidentate mode of bonding for carboxylato ligand and giving thereby a coordination number of six to tin in these complexes. Complexes of bis(cyclopentadienyl) titanium(IV) and zirconium(IV) dichloride with 4−amino−5−mercapto−3−trifluoromethyl 1,2,4−triazole, 4−benzylideneamine−5−mercapto−3−trifluoromethyl, 1,2,4−triazole; 4−furyli− deneneimine−5−mercapto 3−trifluoromethyl 1,2,4−triazole; 4−furylideneimine−5− mercapto−3−trifluoromethyl−1,2,4−triazole have been prepared and characterized on the basis of elemental analysis electrical conductance, magnetic susceptibility and spectral (electronic and infrared) data. Some phenyldithiocarbazato[102] (chloro) transition metal complexes of the type η^5−R$_2$M(S$_2$CNHNHC$_6$H$_5$)Cl (where R=cyclopentadienyl methyl cyclopentadienyl[102–104], indenyl, pyrrolyl and M=Ti(IV), Zr(IV), Oxomolybdenum(VI) have been prepared by the reaction of stoichiometric, quantities of the transition metal derivatives of the type η^5−R$_2$MCl$_2$ and phenyl hydrazinium phenyl dithiocarbazate. These complexes have been characterized on the basis of various physico−chemical studies. The complexes are monomeric non−electrolytes. Infrared spectral data show that the dithiocarbazate group behaves as a S−S bonding bidentate ligand.

Substitution on cyclopentadienyl[105–108] ring affects the stability of titanium cyclopentadienyl bond i.e. in case of (η^5−C$_5$H$_5$)TiCl$_3$, cyclopentadienyl ring is lost by alkaline hydrolysis, whereas [η^5−CH$_3$)$_5$C$_5$]TiCl$_3$ is converted only to [{η^5−(CH$_3$)$_5$C$_5$][Ti(OH)]$_n$. In the other case unlike (η^5−Cp)$_2$Ti(CH$_3$)$_2$, the yellow pentane solutions of [(η^5−(CH$_3$)$_5$C$_5$]$_2$Ti(CH$_3$)$_2$ were found to show no reactivity towards H$_2$ even at 100 atm. Pressure. It has been established that in the reaction of (η^5−C$_5$H$_5$)$_2$MCl$_2$ or (η^5−CH$_3$C$_5$H$_4$)$_2$MCl$_2$ (M =Ti, Zr or Hf) with sodium dithiocarbamates in the ratio of 1:3 one cyclopentadienyl or methyl cyclopentadienyl ring is knocked[109–116] off resulting in the formation of (η^5−C$_5$H$_5$) M(DTC)$_2$ or (η^5−CH$_3$C$_5$H$_4$) M(DTC). The present investigation was undertaken to study the interaction of (i) 1,1$^|$− Bis (Thio)/(Cyanato)/Selenato) mercurio ferrocene complexes with Silicon(IV), Tin(IV), Titanium(IV), Zirconium(IV) and Hafnium(IV) chlorides. (ii) Transition and Non−Transition metal complexes with 1−Formyl Ferrocene−3−Amino−2− Acetyl Benzofuran; (iii) Formyl Ferrocenyl orthoamino benzoyl hydrazone complexes of Aluminium(III) and Titanium(IV). (iv) Phenyl Tin cleavage by some ferrocenyl Hydrazones. (v) Metal complexes of N−Acetyl−N−Aroyl ferrocenyl Hydrazides. (vi) Lanthanide complexes of ferrocene keto acid & 2−quinolinoyl and 8−quinolinoyl hydrazines. (vii) kinetics of acid catalysed hydrolysis of N−formyl−N−aroyl ferrocenyl hydrazide. (viii) Characterization of copper(II), Nickel(II), Cobalt(II), Zinc(II), Tin(IV) and Cadmium(II) complexes with ferrocenyl− phenyl−N−Thiosemicarbazones and copper(II), cobalt(II & III), nickel(II) complexes with ferrocenyl Schiff bases. The above complexes and compounds structure was established on the basis of modern technique such as magnetic moment, PMR, NMR and spectroscopic (UV, Vis, IR) methods besides conventional molar conductance and chemical analysis, molecular weight etc.

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