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3. ZIRCONIUM AND HAFNIUM

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INTRODUCTION

Following previous practice in this series, this review attempts comprehensive treatment of the coordination chemistry of zirconium and hafnium; organometallic and solid-state aspects of the chemistry of these elements are treated selectively. Comprehensive, annual reviews of the organometallic chemistry of zirconium and hafnium may be found in the *Journal of Organometallic Chemistry*; a review of the literature for 1980 appeared during the past year [1]. A review of the chemistry of zirconocene has also been published recently [2]. On the solid state side, Alberti and Costantino have reviewed the structure and intercalation properties of layered zirconium phosphates [3]. Also published during the past year is Volume 2 of *Inorganic Reaction Chemistry* [4], which includes a summary of the reactions of aqueous Zr(IV) and Hf(IV) with a variety of analytical reagents.

The present review covers the major journals for the 1982 calendar year and the lesser known and/or foreign journals for the period covered by *Chemical Abstracts*, Volume 95, Number 19 through Volume 97, Number 20.

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3.1 ZIRCONIUM(IV) AND HAFNIUM(IV) COMPOUNDS

3.1.1 Halide complexes

Electron diffraction data for the ZrF_4 and HfF_4 molecules have been reinterpreted, yielding the equilibrium internuclear distances r_e(Zr-F) = 1.886(4) and r_e(Hf-F) = 1.893(5) Å. Force constants and the missing vibrational frequencies (cm^{-1}) ν_1 = 633(20) and ν_2 = 185(6) for ZrF_4 and ν_1 = 659(20), ν_2 = 187(6), and ν_4 = 179(6) for HfF_4 have also been determined [5]. α-ZrF_4, the high temperature polymorph of zirconium(IV) fluoride, has a tetragonal structure in which $\{ZrF_8\}$ triangular dodecahedra are linked together by sharing corners along the *a* and *b* directions, and edges and corners alternately along the *c* direction. The Zr-F bond lengths vary from 2.031(2) to 2.190(2) Å $\{r$(Zr-F) = 2.108 Å$\}$ [6].

A high-temperature mass spectrometric study has shown that the complex molecules $AZrF_5$ and AZr_2F_9 (A = K or Cs) are present in the saturated vapour of the AF-ZrF_4 systems [7]. Ethanoic acid is a convenient medium for synthesis of anhydrous potassium fluorohafnates. K_2HfF_6 and $KHfF_5 \cdot MeCOOH$ have been isolated from the KF-HfF_4-MeCOOH system, and have been characterised by chemical analysis and X-ray diffraction patterns. At 108 °C, $KHfF_5 \cdot MeCOOH$ loses ethanoic acid yielding anhydrous $KHfF_5$ [8]. The ammonium fluorometallates $[NH_4]_2[MF_6]$ (M = Zr or Hf) react with XeF_2 at 150 °C yielding $[NH_4]MF_5$, HF, dinitrogen, and xenon {equation (1)} [9]. A variety of potassium fluorosulphatozirconates have been obtained from the ZrO_2-SO_3-KF-H_2O system [10].

$$[NH_4]_2[MF_6] + nXeF_2 \longrightarrow [NH_4]MF_5 + 0.5N_2 + 4HF + 1.5Xe + (n-1.5)XeF_2 \qquad (1)$$

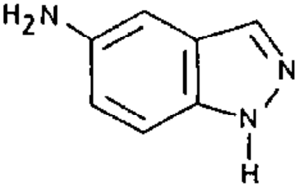
$$(n \geqslant 6; \quad M = Zr \text{ or } Hf)$$

Crystals of the ethylenediammonium salt $[H_3NC_2H_4NH_3]_3[ZrF_7]_2 \cdot 2H_2O$ contain two crystallographically independent monocapped trigonal prismatic $[ZrF_7]^{3-}$ ions $\{r$(Zr-F) = 2.059 Å$\}$ [11]. The structure of $Mn_2ZrF_8 \cdot 6H_2O$ is built up from layers of pentagonal bipyramidal $\{Mn(OH_2)_3F_4\}$ and square antiprismatic $\{ZrF_8\}$ polyhedra $\{r$(Zr-F) = 2.11 Å$\}$. The polyhedra are linked together by a sharing of F atoms and by a system of hydrogen bonds [12]. The structure of primitive-cubic $YbZrF_7$, prepared by rapid quenching from 1000 °C, has been determined by X-ray and neutron diffraction. This material is a disordered fluorine-excess ReO_3-type phase in which the coordination number of the metal is increased from six to seven. No ordering effects are observed on heating to near 200 °C, but near 400 °C there is a slow transformation to the monoclinic $YbZrF_7$ structure [13].

The following guanidinium and aminoguanidinium fluorozirconates have been isolated from aqueous media and have been characterised by chemical analysis, X-ray diffraction, IR spectroscopy, and TGA: $[CN_3H_6]_2ZrF_6$, $[CN_3H_6]_3ZrF_7$, $[CN_4H_7]_2ZrF_6$, $[CN_4H_8]ZrF_6\cdot0.5H_2O$, and $[CN_4H_8]ZrF_6\cdot H_2O$. IR spectra of these compounds and related compounds of known structure indicate that $[CN_3H_6]_3[ZrF_7]$ and $[CN_4H_7]_2[ZrF_6]$ contain mononuclear $[ZrF_7]^{3-}$ and $[ZrF_6]^{2-}$ ions, respectively, while the other compounds contain polynuclear anions having Zr-F-Zr bridges. The IR spectra suggest the presence of $[Zr_2F_{12}]^{4-}$ ions in $[CN_3H_6]ZrF_6$ and polymeric chain anions in $[CN_4H_8]ZrF_6\cdot H_2O$. The crystal structure of $[CN_4H_8]ZrF_6\cdot0.5H_2O$ contains tetranuclear $[Zr_4F_{24}]^{8-}$ units. Thermal decomposition of the $[CN_4H_8]ZrF_6\cdot nH_2O$ compounds involves loss of water at 100–120 °C and elimination of HF at 130–190 °C; the latter process yields the pentafluorozirconate $[CN_4H_7]ZrF_5$ [14].

An electron diffraction study of the $HfCl_4$ molecule at 470±15 K has established the following values of the internuclear distances and mean vibrational amplitudes: $r(\text{Hf-Cl}) = 2.316(5)$, $l(\text{Hf-Cl}) = 0.058(5)$, $r(\text{Cl}\cdots\text{Cl}) = 3.759(13)$, and $l(\text{Cl}\cdots\text{Cl}) = 0.164(11)$ Å. A combined analysis of the electron diffraction and spectral data in the harmonic approximation has been used to determine the equilibrium internuclear distance $r_e(\text{Hf-Cl}) = 2.305$ Å and the complete force field [15].

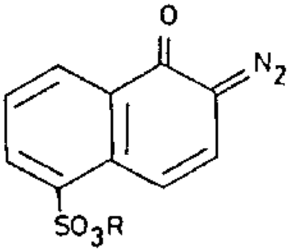
Several studies of metal tetrachloride adducts with Lewis bases have been reported. Procedures for preparation of the tetrahydrofuran adducts, $[MCl_4(OC_4H_8)_2]$ (M = Zr or Hf), in 90% yield have appeared in *Inorganic Syntheses* [16]. The moisture sensitive phosphoryl isothiocyanate adducts, $MCl_4\cdot2OP(NCS)_3$ (M = Zr or Hf), have been synthesised and have been characterised by chemical analysis, IR spectra, and X-ray diffraction [17]. Zirconium(IV) chloride reacts with 5-aminoindazole (*1*) to give the 1:2 adduct $[ZrCl_4(C_7H_7N_3)_2]$; the IR spectrum of this compound suggests that 5-aminoindazole coordinates to zirconium through the pyrrole nitrogen atom [18].



(1)

IR (4000-180 cm^{-1}) and Raman (4000-10 or 4000-50 cm^{-1}) spectra of $[MCl_4(NCMe)_2]$, $[MCl_4(NCCD_3)_2]$, and $[MCl_4(OPCl_3)_2]$ (M = Zr or Hf) have been reported, and normal coordinate calculations have been performed using a modified Urey-Bradley force field. For each compound, four ν(M-Cl) frequencies are observed in the region 375-305 cm^{-1}, consistent with an octahedral *cis* structure. The values of the M-N and M-O stretching force constants indicate that M-N bonding in the ethanenitrile adducts is stronger than M-O bonding in the $POCl_3$ adducts [19,20].

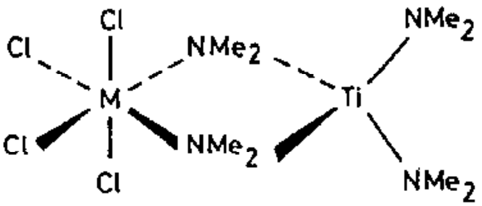
Reaction of $ZrCl_4$ or $HfCl_4$ with semicarbazide in ether affords moisture sensitive 1:1 adducts $[MCl_4(H_2N\text{-}NH\text{-}CO\text{-}NH_2)]$ (M = Zr or Hf). IR spectra suggest that the semicarbazide acts as a bidentate ligand, coordinating through the oxygen atom and a nitrogen atom of the hydrazine residue. Thermochemical measurements indicate that the hafnium complex is more stable than the zirconium analogue [21]. A ^1H NMR study has established that $ZrCl_4$ and $HfCl_4$ form 1:1 complexes [MCl_4(nqd)] with tri-*tert*-butylphenyl-1,2-naphthoquinonediazide-(2)-5-sulphonate (*2*; nqd). Equilibrium constants and thermodynamic parameters



(2 ; $R = C_6H_2(CMe_3)_3$)

for complex formation indicate that the stability of [MCl_4(nqd)] complexes increases as the metal tetrachloride varies in the order $TiCl_4$ < $ZrCl_4$ < $HfCl_4$. Rapid exchange of nqd ligands occurs by an associative mechanism; rate constants and activation parameters for the exchange process have been measured [22].

Air and moisture sensitive solid adducts, $MCl_4 \cdot Ti(NMe_2)_4$ (M = Zr or Hf) and $ZrCl_4 \cdot Ti(OPh)_4$, have been prepared by displacement of NMe_3 from pentane suspensions of $MCl_4 \cdot 2NMe_3$. IR spectra of the $MCl_4 \cdot Ti(NMe_2)_4$ complexes suggest an octahedral *cis* structure about zirconium or hafnium in which $Ti(NMe_2)_4$ behaves as a bidentate chelating ligand (*3*). In contrast, the reactions of $MCl_4 \cdot 2NMe_3$ (M = Zr or Hf) with $[(cp)_2Ti(OPh)_2]$ or $[(cp)TiCl(OPh)_2]$ in hexane or pentane result in phenoxide-chloride ligand exchange {equations (2) and (3)} [23].



(3)

$$[(cp)_2Ti(OPh)_2] + MCl_4 \longrightarrow [(cp)_2TiCl_2] + [MCl_2(OPh)_2] \qquad (2)$$

$$[(cp)TiCl(OPh)_2] + MCl_4 \longrightarrow [(cp)TiCl_3] + [MCl_2(OPh)_2] \qquad (3)$$

The formation of gas-phase complexes $ZrAlCl_7$ and $ZrAl_2Cl_{10}$ has been studied by mass spectrometry. Thermodynamic quantities for reaction (4) are

$$ZrCl_4(s) + 0.5Al_2Cl_6(g) \longrightarrow ZrAlCl_7(g) \qquad (4)$$

ΔH^{O}_{298} = 74 kJ and ΔS^{O}_{298} = 111 J K^{-1} [24]. The electrochemical behaviour of $HfCl_4$ in $AlCl_3$-NaCl melts has been investigated and an electrochemical method for efficient separation of zirconium from hafnium has been devised. Controlled-potential electrolysis of an approximately equimolar mixture of $ZrCl_4$ and $HfCl_4$ in a slightly acidic $AlCl_3$-NaCl melt (50.5 mol% $AlCl_3$) at 0.09 V *vs.* an Al(III)/Al reference electrode in a melt of the same composition results in reduction of the zirconium(IV) to solid $ZrCl_3$ with relatively little reduction of hafnium(IV). The atomic ratio Hf/Zr in the product is $\leqslant$ 0.005 [25].

Equilibrium constants for the stepwise solvolysis of $ZrCl_4$ in propan-1-ol and butan-1-ol have been determined by conductivity measurements [26].

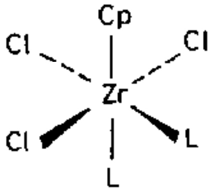
α-ZrI_4 has an orthorhombic structure, space group $Pca2_1$, in which $\{ZrI_6\}$ octahedra are linked by sharing edges [27]. Evidently, this is a different modification of ZrI_4 than the monoclinic phase, space group $P2/c$, studied earlier by Krebs *et al.* [28].

$Cs_2[ZrI_6]$ and $Cs_2[HfI_6]$ have been prepared by reaction of stoicheiometric amounts of CsI and the appropriate metal tetraiodide in an evacuated silica ampoule at 600 °C. These compounds crystallise in the $K_2[PtCl_6]$ structure; the lattice parameter of the cubic unit cell is 11.613(3) Å for $Cs_2[ZrI_6]$ and 11.609(3) Å for $Cs_2[HfI_6]$. A single-crystal X-ray study of the hafnium compound has established a Hf-I bond length of 2.829(2) Å [29]. Phase diagrams have been determined for the RbI-ZrI_4 and CsI-ZrI_4 systems. The only congruently melting compounds formed in these systems are $Rb_2[ZrI_6]$ (mp 737 °C) and $Cs_2[ZrI_6]$ (mp 788 °C). These compounds have been characterised by chemical analysis and X-ray powder patterns [30]. Far IR spectra of $A_2[ZrI_6]$ and $A_2[HfI_6]$ (A = Li, Na, K, Rb, or Cs) have been reported in the region 450-35 cm^{-1}. The zirconium compounds display a strong band in the region 195-175 cm^{-1}; the hafnium analogues exhibit a similar band at 165-145 cm^{-1} [31].

Several studies of organozirconium and organohafnium halides have been reported. $[(cp)ZrCl_3]$ has been prepared in almost quantitative yield by photoinduced chlorination of $[(cp)_2ZrCl_2]$ {equation (5)}. The product is

$$[(cp)_2ZrCl_2] + 3Cl_2 \xrightarrow[CCl_4]{h\nu} [(cp)ZrCl_3] + 1,2,3,4,5\text{-}C_5H_5Cl_5 \qquad (5)$$

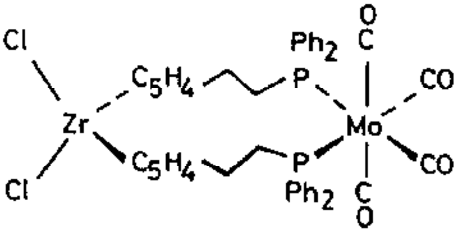
insoluble in non-coordinating solvents, but it dissolves in benzene or chloroform upon addition of two equivalents of Lewis bases (L) such as NEt_3, pyridine, ether, or thf. ^1H NMR studies of the $[(cp)ZrCl_3L_2]$ adducts indicate that stereoisomer (*4*) is the preferred product. An ether suspension of $[(cp)ZrCl_3]$ rapidly reacts with aryllithium reagents yielding $[(cp)ZrR_3]$ (R = Ph, 3-C_6H_4Me, or 4-C_6H_4Me), which also form soluble adducts with Lewis bases [32]. $Li(C_5Me_5)$ reacts with $ZrCl_4$ in toluene to give $[(\eta^5\text{-}C_5Me_5)ZrCl_3]_x$. The trialkyls $[(\eta^5\text{-}C_5Me_5)ZrR_3]$ (R = Me, CH_2Ph, or Ph), the dialkyl $[(\eta^5\text{-}C_5Me_5)ZrCl(Me)_2]$, and the alkyls $[(\eta^5\text{-}C_5Me_5)ZrCl_2R]_x$ (R = Me or CH_2Ph) have been prepared by reaction of $[(\eta^5\text{-}C_5Me_5)ZrCl_3]_x$ with a stoicheiometric amount of RMgX (X = Cl or Br) [33].



(4)

The 1,1'-ring-substituted metallocene dichlorides $[(\eta^5\text{-}C_5H_4EMe_3)_2MCl_2]$ (M = Zr or Hf; E = Si or Ge) have been synthesised by reaction of $Li(C_5H_4EMe_3)$ with the appropriate metal tetrachloride in pentane-thf [34]. The $[(\eta^5\text{-}C_5H_4SiMe_3)_2MCl_2]$ complexes have been reported previously [35]. The reaction of $Li(C_5H_4CH_2CH_2PPh_2)$ with $ZrCl_4$ yields $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2]$.

This compounds reacts with [Mo(CO)$_4$(C$_8$H$_{12}$)] and [{Rh(μ-Cl)(CO)(C$_2$H$_4$)}$_2$], respectively, to give the new heterobimetallic complexes [Cl$_2$Zr(η^5-C$_5$H$_4$CH$_2$CH$_2$PPh$_2$)$_2$Mo(CO)$_4$] (*5*) and [Cl$_2$Zr(η^5-C$_5$H$_4$CH$_2$CH$_2$PPh$_2$)$_2$Rh(CO)Cl}$_x$. The latter compound is probably a dimer (*6*) in which the zirconium complex acts as a bridging diphosphine ligand [36]. The heterobimetallic complex *trans*-[{(cp)$_2$ZrCl(CH$_2$PPh$_2$)}$_2$Rh(CO)Cl] has also been prepared and has been found to react with CO to give unexpectedly the zirconium(IV) carbonyl complex [{(cp)$_2$Zr(CO)Cl(CH$_2$PPh$_2$)}$_2$Rh(CO)Cl]; reaction of the uncomplexed [(cp)$_2$ZrCl(CH$_2$PPh$_2$)] with CO yields the expected acyl derivative [(cp)$_2$ZrCl(COCH$_2$PPh$_2$)] [37].



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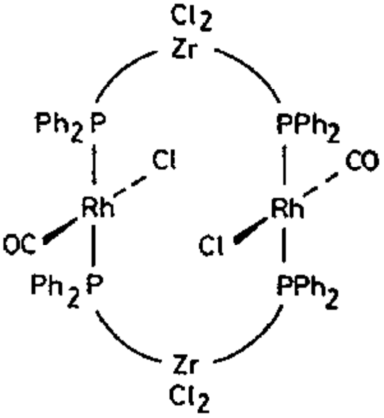


(6)

3.1.2 Complexes with oxygen-donor ligands

Infrared and Raman spectra of ZrOCl$_2\cdot$8H$_2$O in the solid state and in aqueous solution are consistent with the presence of the hydroxo-bridged tetrameric cation [Zr$_4$(OH)$_8$(OH$_2$)$_{16}$]$^{8+}$. A ν(Zr–O) band has been observed at 550 cm^{-1} in the IR spectrum, and ν(Zr–O) Raman lines have been identified at 580 cm^{-1} (polarised, ν(Zr–OH) bridging), 450 cm^{-1} (depolarised, ν(Zr–OH) bridging), and 420 cm^{-1} {ν(Zr–OH$_2$)}. No bands attributable to the Zr=O group have been observed. Upon addition of alkali to aqueous solutions of ZrOCl$_2\cdot$8H$_2$O, an additional ν(Zr–O) Raman line is observed at $\sim$530 cm^{-1}; this frequency has been assigned to stretching of the non-bridging Zr–OH bonds of the hydrolysis product [Zr$_4$(OH)$_8$(OH)$_4$(OH$_2$)$_{12}$]$^{4+}$ [38].

Oxozirconium(IV) hexamethylphosphoramide complexes of the type [ZrOX$_2$(hmpa)$_2$] (X = Cl, Br, NCS, NO$_3$, or BPh$_4$), [ZrO(hmpa)$_4$]I$_2$, and

$[ZrO(hmpa)_6][ClO_4]_2$ have been prepared by reaction of hmpa with a methanol or propanone solution of the appropriate zirconyl salt. Molecular weight and conductance measurements in nitrobenzene and dmso indicate that the $[ZrO(hmpa)_4]I_2$ and $[ZrO(hmpa)_5][ClO_4]_2$ complexes are 1:2 electrolytes, while the $[ZrOX_2(hmpa)_2]$ complexes are monomeric non-electrolytes. This result is puzzling for $ZrO(BPh_4)_2(hmpa)_2$. IR spectra of these compounds indicate that (i) hmpa is attached to zirconium *via* the oxygen atom, (ii) perchlorate is ionic, (iii) thiocyanate coordinates to zirconium through the nitrogen atom, and (iv) nitrate behaves as a bidentate ligand. A weak IR band at 900-980 cm^{-1} has been attributed to ν(Zr=O), but the existence of the Zr=O group in these compounds needs to be confirmed by X-ray diffraction [39]. Solvent extraction of $ZrCl_4$ and $HfCl_4$ from hydrochloric acid solutions by dipentyl sulphoxide, dioctyl sulphoxide, and diphenyl sulphoxide has been studied, and optimum conditions for separation of zirconium(IV) and hafnium(IV) have been reported [40].

$ZrCl_4$ and $HfCl_4$ react with LiOAr (OAr = 2,6-di-*tert*-butylphenoxide) in benzene or diethyl ether to give the aryloxide complexes $[MCl(OAr)_3]$ (M = Zr or Hf). Attempts to prepare the corresponding $MCl_2(OAr)_2$ compounds were unsuccessful. $[HfCl(OAr)_3]$ has a sterically congested, tetrahedral structure (Figure 1) with bond distances r(Hf-Cl) = 2.365(1) and r(Hf-O) = 1.938(3), 1.925(2), and 1.917(3) Å. The Hf-O-C bond angles are opened to 152-159°, which helps to relieve steric strain. Low-temperature ^{1}H NMR spectra exhibit

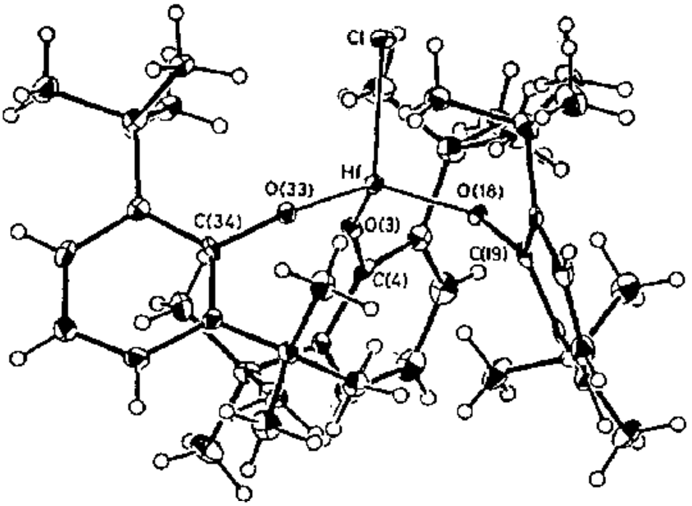
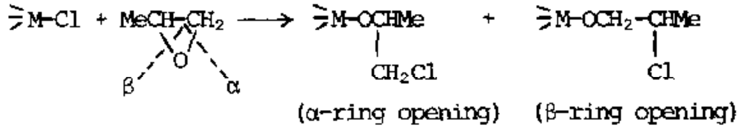


Fig. 1: A view of the $[HfCl\{OC_6H_3(CMe_3)_2\text{-}2,6\}_3]$ molecule, reproduced by permission from L. Chamberlain, J.C. Huffman, J. Keddington, and I.P. Rothwell, *J. Chem. Soc., Chem. Commun.*, (1982) 805 [41].

inequivalent *tert*-butyl groups proximal and distal to the Cl atom owing to a slowing at ∿ −60 °C of rotation about the Hf–O–Ar bonds. At −90 °C, restricted rotation of one of the *tert*-butyl groups is observed. Because the sterically bulky *tert*-butyl groups tend to protect the metal atom from nucleophilic attack, the $[MCl(OAr)_3]$ complexes are not easily alkylated though $[HfCl(OAr)_3]$ does react with LiMe to give $[Hf(Me)(OAr)_3]$ [41].

The X-ray crystal structure of (η^8-cyclooctatetraenyl)(η^3-allyl)-*tert*-butoxyzirconium has been determined. Strong Zr–O bonding involving $O(p_\pi) \rightarrow Zr(d_\pi)$ interaction is indicated by a short Zr–O bond length (1.921(2) and 1.900(2) Å in the two crystallographically independent molecules per asymmetric unit) and a large Zr–O–C bond angle (166.6(3) and 172.9(2)°) [42].

Propylene oxide inserts into the Zr–Cl bonds of $ZrCl_4$ and $[(cp)_2ZrCl_2]$ to give 2-chloro-*iso*-propoxy and 2-chloro-*n*-propoxy compounds {equation (6)} in



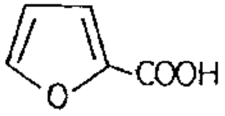
$$\geqslant M{-}Cl + MeCH{-}CH_2\,(O) \longrightarrow \geqslant M{-}OCHMe(CH_2Cl) + \geqslant M{-}OCH_2{-}CHMe(Cl) \qquad (6)$$

(α-ring opening) (β-ring opening)

relative amounts that depend on the substituents on the Zr atom. 30% α- and 70% β-ring opening is observed for $ZrCl_4$, while 90% α- and 10% β-ring opening is obtained for $[(cp)_2ZrCl_2]$ [43]. $[(cp)_2ZrCl_2]$ reacts with α-naphthol or β-naphthol in benzene solution at reflux in the presence of triethylamine to give $[(cp)_2Zr(\alpha,\beta\text{-}OC_{10}H_7)Cl]$ or $[(cp)_2Zr(\alpha,\beta\text{-}OC_{10}H_7)_2]$, depending on the stoicheiometry of the reaction mixture. The $[(cp)_2Zr(\alpha,\beta\text{-}OC_{10}H_7)_2]$ complexes have also been synthesised in aqueous solution by reaction of $[(cp)_2ZrCl_2]$ with the sodium salt of α- or β-naphthol. These complexes have been characterised by chemical analysis, IR and ^1H NMR spectroscopy. They are monomeric in boiling benzene and non-electrolytes in nitrobenzene [44].

The vapour pressure of anhydrous, crystalline hafnium(IV) perchlorate has been measured in the temperature range 30-61 °C: $\log p$ (mm Hg) = $14.407 - 4272/T$. Thermodynamic quantities for sublimation are $\Delta H° = 82 \pm 4$ kJ mol^{-1}, $\Delta S° = 220 \pm 10$ J mol^{-1}K^{-1}, and $\Delta G°_{298} = 16 \pm 5$ kJ mol^{-1}. The IR spectrum of gaseous $[Hf(ClO_4)_4]$ is not significantly different from that of crystalline $[Hf(ClO_4)_4]$ indicating no significant change in molecular structure upon vapourisation [45]. The (perchlorato)hafnates $Rb_n[Hf(ClO_4)_{4+n}]$ (n = 1 or 2) and $Cs_n[Hf(ClO_4)_{4+n}]$ (n = 1, 2 or 3) have been prepared by reaction of $[Hf(ClO_4)_4]$ with $MClO_4$ (M = Rb or Cs) in $HClO_4$ containing 20-30% free Cl_2O_7 (perchloric oleum). The same compounds can be synthesised in $HClO_4$–Cl_2O_7 by using $HfCl_4$ and MCl as starting materials. IR spectra suggest that, as n increases, the number of bidentate perchlorate ligands decreases and the number of monodentate perchlorate groups increases, thus maintaining a coordination number of eight for the hafnium atom [46].

The heterocyclic carboxylato-complexes Zr$(O_2CR)_n(OCHMe_2)_{4-n}$ (R = C_4H_3O, C_9H_8N or $C_{11}H_{12}N$; n = 1, 2 or 3) have been prepared by reaction in benzene at reflux of stoicheiometric amounts of $Zr(OCHMe_2)_4 \cdot CHMe_2OH$ and furan-2-carboxylic acid (*7*), indole-3-acetic acid (*8*), or indole-3-butyric acid (*9*). Only three of the four isopropoxide groups could be substituted, even when an excess of the carboxylic acid was used. IR spectra of the $Zr(O_2CR)_n(OCHMe_2)_{4-n}$ complexes exhibit an 80-120 cm^{-1} separation between the $\nu_s(CO_2)$ and $\nu_{as}(CO_2)$ stretching modes, suggesting a symmetrical bidentate attachment of the carboxylate ligands [47].



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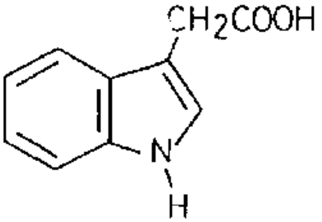

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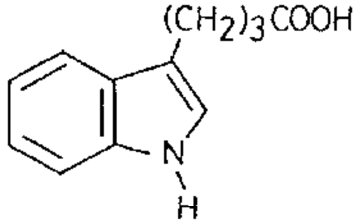
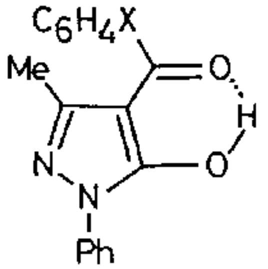


(9)

New tetrakis(β-diketonato)zirconium(IV) complexes of the type [Zr(RCOCHCOR')$_4$] (R = aryl or 2-thienyl; R' = CHF_2, CF_3, C_2F_5 or C_3F_7) have been prepared by reaction of stoicheiometric amounts of $Zr(NO_3)_4 \cdot 5H_2O$ and the appropriate β-diketone in hot ethanol-toluene. In benzene solution, these complexes are monomeric, and large dipole moments (5-7 D) point to highly polar structures. Low-temperature ^{19}F NMR spectra indicate fluxional behaviour down to -100 °C [48]. [M(RCOCHCOR)$_4$] (M = Zr or Hf; R = CMe_3) complexes have been synthesised by reaction of dipivaloylmethane with the metal tetrachlorides in absolute methanol. The stability, melting points, volatility, and X-ray diffraction patterns of these compounds have been studied [49,50].

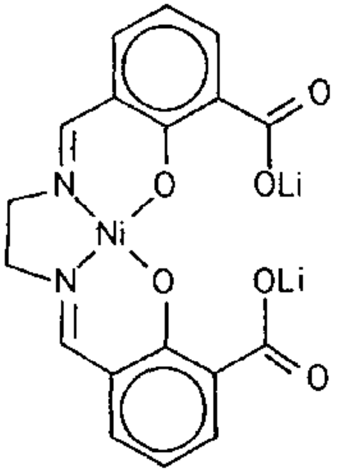
The He-II excited photoelectron spectrum of [Zr(acac)$_4$] has been reported [51]. Comparison of the band intensities with those in the He-I spectrum [52] indicates some mixing of the zirconium 4d_{xz} and 4d_{yz} orbitals with the out-of-phase combination of the oxygen lone pairs located in the plane of the ligand [51]. [Zr(acac)$_4$] reacts with polystyrene resin functionalised with 2,4-pentanedionate groups to give a polymer-bound zirconium complex [53].

Solvent extraction of hafnium(IV) with various benzoyl-substituted 1-phenyl-3-methyl-4-benzoylpyrazol-5-ones (*10*) has been studied by Navratil and Smola [54]. The lithium salt of the nickel(II) complex with the Schiff base derived from 3-formylsalicylic acid and ethylenediamine (*11*) reacts with



(10; X = 2-Cl, 4-MeO, 3-NO_2, 4-NO_2)

[$(cp)_2ZrCl_2$] in refluxing methanol or ethanol yielding the heterobimetallic complex (*12*) [55].



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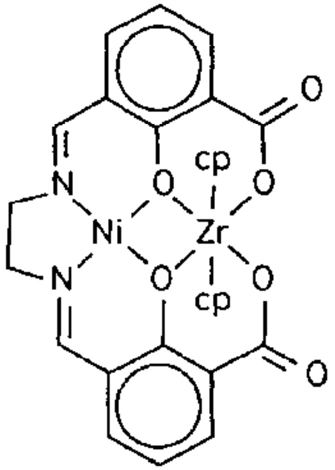


(12)

TGA, DTGA, and DTA studies of the thermal decomposition of the divalent metal zirconyl oxalates, $MZrO(C_2O_4)_2 \cdot 4H_2O$ (M = Be or Cd) and $ZnZrO(C_2O_4)_2 \cdot 6H_2O$, have been reported. These compounds decompose *via* three major steps: (i) dehydration; (ii) decomposition of the oxalates to carbonates; (iii) conversion of the carbonates to metal zirconates $MZrO_3$ [56,57].

This review does not include the chemistry of layered zirconium phosphates and the related zirconium alkylphosphonates. However, several leading references to 1982 papers on these interesting materials are noted [58-65].

3.1.3 Complexes with sulphur-donor ligands

$[(cp)_2Zr(SPh)(Me)]$ has been prepared in 60% yield by reaction for one week in the dark at room temperature of equimolar amounts of $[(cp)_2ZrMe_2]$ and PhSSPh {equation (7)} [66]. Tetramethylthiuram disulphide complexes $ZrOX_2L_2$ (X = Cl, Br, I, NCS or NO_3; L = $Me_2NC(S)S{-}SC(S)NMe_2$) have been synthesised and

$$[(cp)_2ZrMe_2] + PhSSPh \xrightarrow{\text{heptane}} [(cp)_2Zr(SPh)(Me)] + PhSMe \qquad (7)$$

have been characterised by IR spectra and thermal decomposition studies [67].

Five-, six-, seven- and eight-coordinate dithiocarbamato-complexes of the type $[M(S_2CNRR')_nCl_{4-n}]$ (n = 1, 2, 3 or 4; M = Zr or Hf; R = Et, R' = $3{-}C_6H_4Me$; R = H, R' = cyclopentyl or cycloheptyl) have been prepared by reaction of stoicheiometric amounts of MCl_4 and anhydrous $Na[S_2CNRR']$ in dichloromethane at reflux. These complexes are monomeric non-electrolytes in solution, and IR spectra indicate a bidentate attachment of the dithiocarbamate ligands. The ν(M-S) frequency decreases as n increases, consistent with an increase in the coordination number of the metal from five to eight. The frequency of the band assigned to ν(M-Cl) also decreases with increasing value of n, but the variation in ν(M-Cl) is surprisingly small (3-8 cm^{-1}) and the values of ν(M-Cl) are surprisingly high (380-400 cm^{-1}) [68,69]. Related complexes, $[(cp)_2Zr(S_2CNRR')Cl]$ and $[(cp)Zr(S_2CNRR')_3]$ (R = Et, R' = $3{-}C_6H_4Me$; R = H, R' = cyclopentyl or cycloheptyl), have been synthesised by reaction of 1:1 and 1:3 molar ratios, respectively, of $[(cp)_2ZrCl_2]$ and $Na[S_2CNRR']$. When a 1:2 molar ratio of reactants was used, only $[(cp)_2Zr(S_2CNRR')Cl]$ could be isolated. Molecular weight, conductance, and IR studies indicate that the $[(cp)_2Zr(S_2CNRR')Cl]$ and $[(cp)Zr(S_2CNRR')_3]$ complexes are five- and seven-coordinate compounds, respectively, that contain bidentate dithiocarbamate ligands [70]. Analogous $[(cp)_2Zr(S_2CNRR')Cl]$ (R = Me, Et or $CHMe_2$; R' = cyclohexyl) complexes have also been reported [71].

Phenylhydrazinium phenyldithiocarbazate, $[PhNHNH_3][S_2CNHNHPh]$, reacts with equimolar amounts of $[R_2ZrCl_2]$ {R = cp, $\eta^5{-}C_5H_4Me$, $\eta^5{-}C_9H_7$ (indenyl), or $\eta^5{-}C_4H_4N$ (pyrrolyl)} in dichloromethane at reflux yielding the phenyldithiocarbazato-complexes, $[R_2Zr(S_2CNHNHPh)Cl]$. These compounds are monomeric non-electrolytes in solution, and a single $\nu(C{=}S)$ IR band at ∿1000 cm^{-1} suggests a bidentate *S*,*S*-attachment of the dithiocarbazate ligand [72].

Tetrakis(thioacetylacetonato)zirconium(IV), $[Zr(Sacac)_4]$, has been prepared by reaction of stoicheiometric amounts of $ZrCl_4$ and Na[Sacac] in dichloromethane. $[Zr(Sacac)_4]$ has an eight-coordinate structure (Figure 2) in which the bidentate thioacetylacetonate ligands span the *s* edges of a

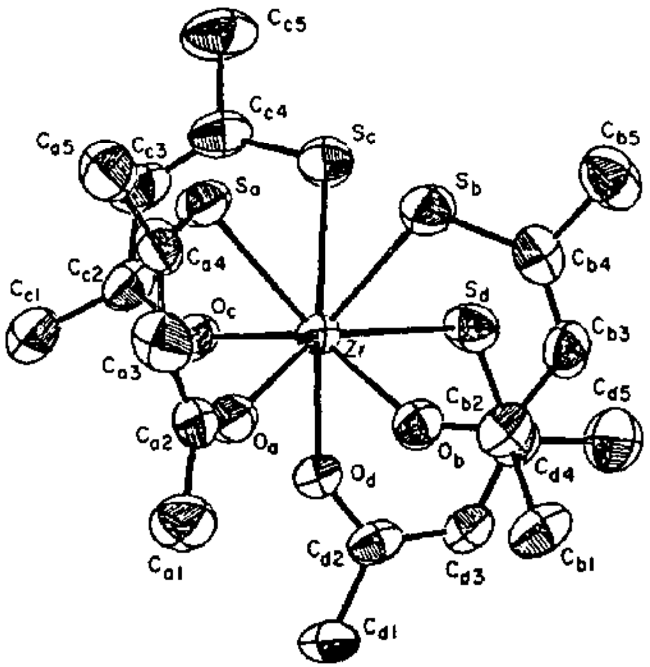


Fig. 2: The $[Zr(Sacac)_4]$ molecule viewed along the *quasi*-$\bar{8}$ of the ZrS_4O_4 coordination group [73].

(necessarily distorted) D_{4d}-$\bar{8}2m$ square antiprism. The unsymmetrical ligands are arranged so as to cluster the sulphur atoms in all *cis* positions. The observed square-antiprismatic *ssss*-C_2 stereoisomer is distorted in the direction of the dodecahedral *mmgg*-C_1 and bicapped-trigonal-prismatic $t_1t_1p_2p_2$-C_1 stereoisomers. Consistent with the former distortion, the averaged Zr-O and Zr-S bond lengths fall into two classes: $r(Zr\text{-}O_A) = 2.185$ Å; $r(Zr\text{-}O_B) = 2.132$ Å; $r(Zr\text{-}S_A) = 2.724$ Å; $r(Zr\text{-}S_B) = 2.665$ Å. $[Zr(Sacac)_4]$ is a highly fluxional molecule; ^1H NMR spectra of $[Zr(Sacac)_4]$ in $CHClF_2$ solution exhibit just two methyl resonances down to -163 °C [73].

The sulphur atoms are also clustered in all *cis* positions in the structure of tetrakis(*N*-methyl-4-thiotolylhydroxamato)hafnium(IV), $[Hf\{MeC_6H_4C(S)N(O)Me\}_4]$ (Figure 3). An analysis of polyhedral shape parameters for this molecule indicates that the coordination group most closely approximates a C_{2v}-bicapped trigonal prism. The observed stereoisomer has the $t_1t_1p_2p_2$ ligand wrapping pattern. Averaged metal-ligand bond distances are $r(Hf\text{-}O) = 2.150$ Å and $r(Hf\text{-}S) = 2.678$ Å [74].

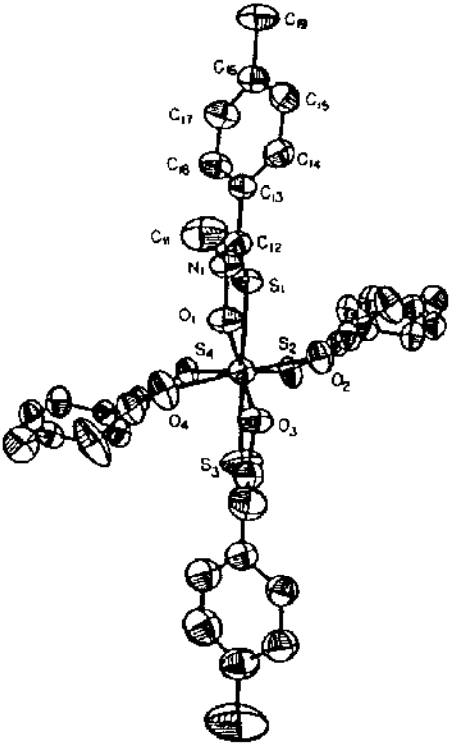


Fig. 3: Perspective view of the $[Hf\{MeC_6H_4C(S)N(O)Me\}_4]$ molecule, reproduced by permission from K. Abu-Dari and K.N. Raymond, *Inorg. Chem.*, 21 (1982) 1676 [74].

ZrP_2S_6, synthesised from the elements at 750-800 °C, has a tetragonal structure, space group $P4_2/m$, in which Zr^{4+} cations are attached to four bidentate thiohypodiphosphate $[P_2S_6]^{4-}$ anions. The $[P_2S_6]^{4-}$ anions in turn bridge between four Zr^{4+} cations to give an extended three-dimensional structure. The $\{ZrS_8\}$ coordination polyhedron is a slightly distorted D_{2d}-$\bar{4}2m$ dodecahedron $\{r(Zr{-}S_A) = 2.875(2)$ Å; $r(Zr{-}S_B) = 2.599(2)$ Å$\}$ [75].

HfOS has been synthesised as yellow, translucent, octahedral crystals about 1 mm in size by heating stoicheiometric amounts of HfO_2 and HfS_2 in the presence of small amounts of $[NH_4]Cl$ in a sealed tube at 900 °C. The same approach works for preparation of ZrOS and for the solid solutions $Zr_{1-x}Hf_xOS$ (x = 0.25 or 0.75) [76].

3.1.4 Complexes with selenium-donor ligands

The new phenylseleno-complexes $[(\eta^5\text{-}C_5H_4R)_2Zr(SePh)(Me)]$ (R = H or CMe_3) have been prepared in quantitative yield by reaction in the dark at room temperature of equimolar amounts of $[(\eta^5\text{-}C_5H_4R)ZrMe_2]$ and PhSeSePh {equation (8)}. The products of reaction (8) do not react further in the dark,

$$[(\eta^5\text{-}C_5H_4R)_2ZrMe_2] + PhSeSePh \xrightarrow{\text{heptane}} [(\eta^5\text{-}C_5H_4R)_2Zr(SePh)(Me)] + PhSeMe \quad (8)$$

but in the presence of UV light, further reaction gives the known compounds $[(\eta^5\text{-}C_5H_4R)_2Zr(SePh)_2]$ (R = H or CMe_3). The $[(\eta^5\text{-}C_5H_4R)_2Zr(SePh)_2]$ complexes can also be prepared by irradiating a mixture of $[(\eta^5\text{-}C_5H_4R)_2ZrPh_2]$ and PhSeSePh {equation (9)} [66].

$$[(\eta^5\text{-}C_5H_4R)_2ZrPh_2] + PhSeSePh \xrightarrow{\text{UV}} [(\eta^5\text{-}C_5H_4R)_2Zr(SePh)_2] + PhPh \quad (9)$$

3.1.5 Complexes with nitrogen-donor ligands

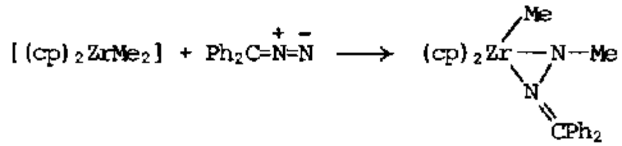
Hydrazine and substituted hydrazines react with $ZrOX_2$ in ethanol to give complexes of the type $ZrOL_4X_2$ (X = Cl, Br, I, NCS or NO_3; L = N_2H_4, $PhNHNH_2$ or Me_2NNH_2). The insolubility and thermal stability of these complexes and the presence of a ν(N-N) IR band at 960-1000 cm^{-1} suggest that these compounds have polymeric structures containing bridging hydrazine ligands. A substantial variation in the ν(M-N) frequencies indicates that the M-N bond strength decreases as L varies in the order $Me_2NNH_2 > N_2H_4 > PhNHNH_2$. The thermal stability of the $ZrOL_4X_2$ complexes decreases as X varies in the order Cl > Br > NCS > I [77].

Reaction of tetrabenzylzirconium with an excess of imidazole in thf at 50 °C yields $Zr(C_3N_2H_3)_4$ as a yellow crystalline solid {equation (10)} [78].

$$Zr(CH_2Ph)_4 + 4C_3N_2H_4 \longrightarrow Zr(C_3N_2H_3)_4 + 4MePh \quad (10)$$

Tris(pyrazol-1-yl)borato-complexes of the type $[(RBPz_3)ZrCl_3]$ (R = $CHMe_2$ or Bu) and $[\{HB(3,5\text{-}Me_2Pz)_3\}ZrCl_3]$ have been prepared by reaction of sodium salts of the tris(pyrazol-1-yl)borates with two equivalents of $ZrCl_4$. Treatment of $[\{HB(3,5\text{-}Me_2Pz)_3\}ZrCl_3]$ with one equivalent of NaOMe in toluene affords the methoxo-complex $[\{HB(3,5\text{-}Me_2Pz)_3\}Zr(OMe)Cl_2]$. ^1H and ^{13}C NMR spectra indicate that the latter compound is stereochemically rigid at 35 °C [79].

Diphenyldiazomethane reacts with $[(cp)_2ZrMe_2]$ and $[(cp)_2Zr(H)(Cl)]$ inserting into the Zr-C and Zr-H bonds, respectively {equations (11) and (12)}.



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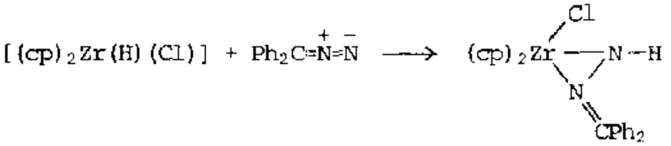

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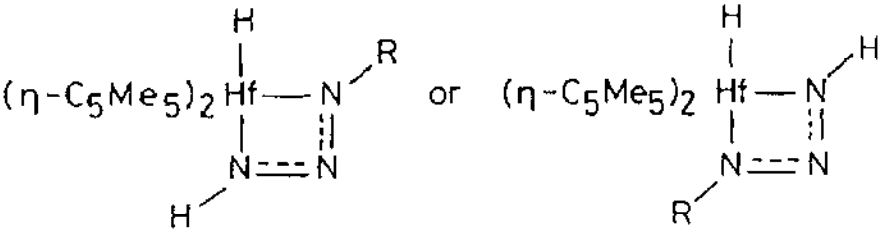
X-ray studies have shown that the resulting complexes contain η^2-*N*,*N'*-bonded hydrazonido(1-)-ligands [80]. Moderately stable triazenido-complexes of hafnium, $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{HfH(NHNNR)}]$ (R = Ph or 4-$\text{C}_6\text{H}_4\text{Me}$) (*13*) have been prepared



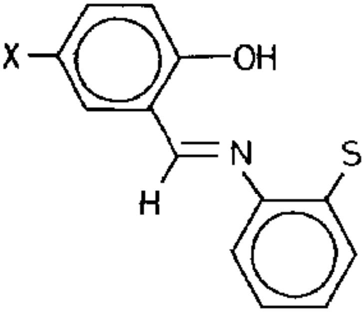
(13)

by reaction of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{HfH}_2]$ with aryl azides RN_3. Upon heating at 80 °C, complexes (*13*) lose dinitrogen yielding the arylamido-complexes $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{HfH(NHR)}]$, which can also be obtained by reaction of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{HfH}_2]$ and RNH_2. Interestingly, the ^{1}H NMR spectrum of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{HfH(NHC}_6\text{H}_4\text{Me-4)}]$ exhibits a single resonance for all thirty C_5Me_5 protons, even at -65 °C at 500 MHz. The NHR ligand should lie in a plane perpendicular to the plane bisecting the $(\eta^5\text{-C}_5\text{Me}_5)\text{-Hf-}(\eta^5\text{-C}_5\text{Me}_5)$ angle if $\text{N}(\text{p}_\pi)\rightarrow\text{Hf}(\text{d}_\pi)$ bonding is important. Evidently, the barrier to rotation about the Hf-N bond is very small. Treatment of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{HfH}_2]$, $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{HfH(NHNNR)}]$ or $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{HfH(NHR)}]$ with excess RN_3 results in rapid formation of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Hf(NHR)}_2]$ [81].

Reaction of $\text{Zr(OCHMe}_2)_4$ with *N*,*N*-diethylhydroxylamine affords the colourless, crystalline tetrakis(hydroxylaminato)-complex $[\text{Zr(ONEt}_2)_4]$. An X-ray study of the analogous titanium(IV) complex has established an eight-coordinate dodecahedral structure in which the η^2-*N*,*O*-bonded hydroxylaminate ligands span the *m* polyhedral edges. The nitrogen atoms occupy the dodecahedral A sites, and the oxyten atoms take the B sites. The ^{1}H NMR resonances of the diastereotopic methylene protons of $[\text{Zr(ONEt}_2)_4]$ coalesce at 42 °C owing to a rapid rate process ($\Delta G^\ddagger$ = 69±6 kJ mol^{-1}) that involves cleavage of the Zr-N bonds [82].

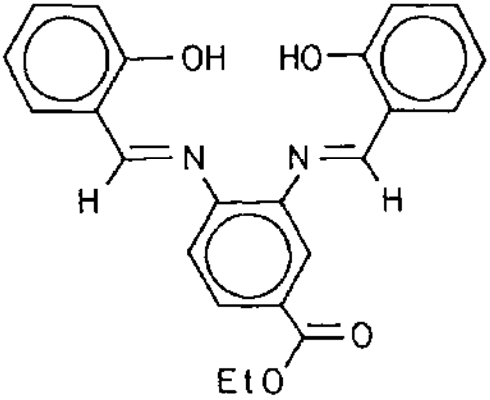
$\text{Zr(OCHMe}_2)_4\cdot\text{CHMe}_2\text{OH}$ reacts in benzene at reflux with a variety of dibasic tridentate Schiff bases H_2L in 1:1 and 1:2 mole ratios to give complexes of the type $[\{Zr(OCHMe_2)_2(L)\}_2]$ and $[Zr(L)_2]$, respectively. The Schiff bases are condensation products of pentane-2,4-dione, 2-hydroxyacetophenone, salicylaldehyde or 2-hydroxy-1-naphthaldehyde with 3-hydroxy-1-propylamine or 1-hydroxy-2-butylamine. Molecular weight measurements indicate that the $[Zr(L)_2]$ complexes are monomeric in solution, while the $[\{Zr(OCHMe_2)_2(L)\}_2]$ analogues are dimeric. Six-coordinate structures have been proposed in which $[L]^{2-}$ behaves as an *ONO*-tridentate ligand. Alkoxide exchange reactions of the $[\{Zr(OCHMe_2)_2(L)\}_2]$ complexes with 2-methyl-2,4-pentanediol afford the monomeric $[Zr(C_6H_{12}O_2)(L)]$ derivatives [83].

The reaction of hot aqueous solutions of zirconium nitrate with ethanol solutions of salicylidene 2-aminobenzothiols (*14*; H_2L) yields Schiff base complexes of the type $[Zr(OH)_2(OH_2)(L)]$. These compounds are monomeric non-electrolytes in solution, and IR spectra indicate that the $[L]^{2-}$ anions behave as *ONS*-tridentate ligands [84].



(14; H_2L; X = H, Cl, Br)

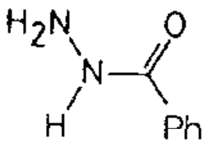
The new Schiff base *N*,*N*'-disalicylidene-3,4-phenylendiamine-1-ethylbenzoate (*15*; H_2dspeb) reacts with $Zr(OBu)_4\cdot BuOH$ in absolute ethanol at reflux to give



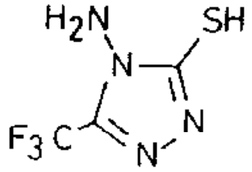
(15; H_2dspeb)

the eight-coordinate complex [Zr(dspeb)$_2$]. The presence in this compound of two uncoordinated ester groups may facilitate the synthesis of coordination polymers. However, preliminary attempts to polymerise [Zr(dspeb)$_2$] with aromatic amines have been unsuccessful owing to decomposition of [Zr(dspeb)$_2$] at the high temperatures required [85].

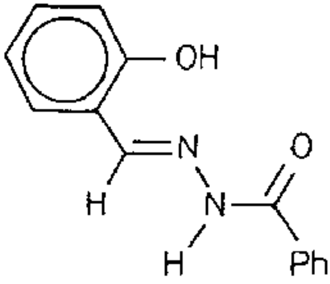
Substituted hydrazines and mercaptotriazoles such as (*16*; HL) and (*17*; HL) react with [(cp)$_2$ZrCl$_2$] to give complexes of the type [(cp)$_2$ZrCl(L)] and [(cp)$_2$Zr(L)$_2$], which are believed to contain *N*,*O*- and *N*,*S*-bonded bidentate L$^-$ ligands [86,87]. Hydrazones such as (*18*; H$_2$L') give related [(cp)$_2$Zr(L')] complexes [86].



(16 ; HL)



(17 ; HL)

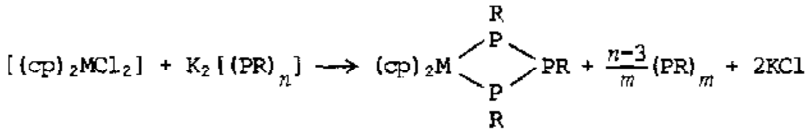


(18 ; H$_2$L')

Thermodynamic parameters for the formation of [M{N(CH$_2$COO)$_3$}]$^+$ (M = Zr or Hf) from M^{4+} and nitrilotriacetate ions have been determined from calorimetric measurements [88]. Potentiometric measurements give pK = 25.65±0.01 for [Zr(edta)] at ionic strength 0.4 in 0.2 *M* perchlorate solution [89].

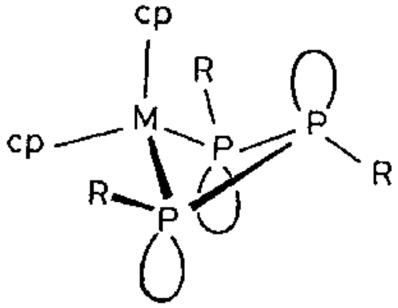
3.1.6 Complexes with phosphorus-donor ligands

[(cp)$_2$MCl$_2$] (M = Zr or Hf) complexes react in dioxane/toluene or thf with dipotassium poly(organophosphanes) K$_2$[(PR)$_n$] (R = Me, Et, CMe$_3$ or Ph; n = 3-5) to give, independent of the value of n, air-sensitive triphosphonato-chelates [(cp)$_2$M{(PR)$_3$}] {equation (13)}. A C$_s$ structure (*19*) with a folded chelate



(13)

ring and equatorial R groups has been proposed on the basis of ^{31}P and ^{1}H NMR spectra [90].



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3.1.7 *Hydride and borohydride complexes*

$[(cp)_3HfX]$ (X = H or D) complexes have been prepared by reaction of $[(cp)_4Hf]$ with $LiAlH_4$ or $LiAlD_4$ in thf [91,92], and IR and Raman spectra of solid $[(cp)_3MX]$ (M = Zr or Hf; X = H or D) have been studied. The spectra are consistent with a C_{3v} structure containing three equivalent η^5-cyclopentadienyl ligands. The frequencies of the M-X $\{\nu(Zr-H)$ 1603 cm^{-1}; $\nu(Hf-H)$ 1669 $cm^{-1}\}$ and M-cp modes indicate that the strength of the metal-ligand bonds increases on going from $[(cp)_3ZrX]$ to $[(cp)_3HfX]$ [92].

The dimeric mixed-ring hydride $[\{(\eta^5-C_5Me_5)(cp)ZrH_2\}_2]$ $\{\nu(Zr-H) = 1540$ and $1270\ cm^{-1}\}$ has been prepared by reaction of $[(\eta^5-C_5Me_5)(cp)ZrCl_2]$ with LiBu in toluene under 1 atm of H_2. Reaction of $[(\eta^5-C_5Me_5)(\eta-1,2,4-C_5H_2Me_3)ZrMe_2]$ with H_2 (80 atm) affords $[(\eta^5-C_5Me_5)(\eta^5-1,2,4-C_5H_2Me_3)ZrH_2]$ $\{\nu(Zr-H = 1585\ cm^{-1}\}$. $[(\eta^5-C_5Me_5)ZrCl_3]_x$ reacts with excess $LiBH_4$ in toluene to give $[(\eta^5-C_5Me_5)Zr(BH_4)_3]$, which is converted to $[\{(\eta^5-C_5Me_5)Zr(H)(BH_4)(\mu-H)\}_2]$ upon treatment with 8-10 equivalents of NMe_3. The IR spectrum of $[(\eta^5-C_5Me_5)Zr(BH_4)_3]$ indicates that all of the borohydride ligands are tridentate, while the spectrum of $[\{(\eta^5-C_5Me_5)Zr(H)(BH_4)(\mu-H)\}_2]$ shows the presence of bidentate borohydride, one terminal hydride $\{\nu(Zr-H) = 1628\ cm^{-1}\}$, and one bridging hydride $\{\nu(Zr-H-Zr) \approx 1450\ cm^{-1}\}$. The latter dimer fails to reduce carbon monoxide [33].

$BH_3\cdot$thf reacts with $[(cp)_2ZrMe_2]$ to give $[(cp)_2Zr(BH_4)(Me)]$ and, ultimately, $[(cp)_2Zr(BH_4)_2]$. An ^{11}B NMR study has shown that these reactions proceed *via* intermediates containing coordinated $[BH_3Me]^-$ and $[BH_2Me_2]^-$. Thus, the initial stage of the reaction involves formal insertion of BH_3 into a Zr–Me bond [93].

The He-I photoelectron spectra of $Zr(BH_4)_4$ and $Hf(BH_4)_4$ are essentially identical, in agreement with an earlier report by Downs *et al.* [94]. However, the earlier assignments have been modified with the aid of an LCAO-HFS(Xα) calculation on $Zr(BH_4)_4$. The factors that determine the relative stabilities of mono-, bi-, and tridentate attachment of borohydride ligands have been discussed in terms of a qualitative molecular orbital picture [95].

3.2 ZIRCONIUM(III) COMPOUNDS

Single crystal X-ray studies of ZrX_3 (X = Cl, Br or I) and $ZrI_{3.40}$ have confirmed that all four structures consist of chains of face-shared $\{ZrX_6\}$ octahedra with equally spaced metal atoms (Figure 4). The space group is *P*6_3*/mcm*. Bond lengths are *r*(Zr–Zr) = 3.0695(8) and *r*(Zr–Cl) = 2.5382(6) Å in $ZrCl_3$, *r*(Zr–Zr) = 3.152(1) and *r*(Zr–Br) = 2.676(3) Å in $ZrBr_3$, *r*(Zr–Zr) = 3.334(2) and *r*(Zr–I) = 2.900(2) Å in ZrI_3, and *r*(Zr–Zr) = 3.3365(6) and *r*(Zr–I) = 2.8820(9) Å in $ZrI_{3.40}$. The formula of the partially oxidised $ZrI_{3.40}$ may be written as $Zr_{0.882}I_3$ since 11.8% of the octahedral metal atom sites along the

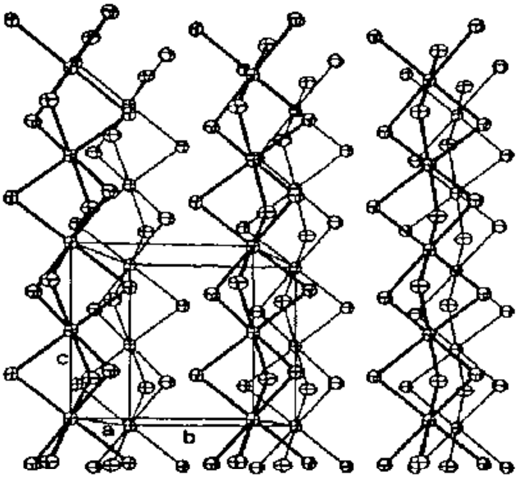
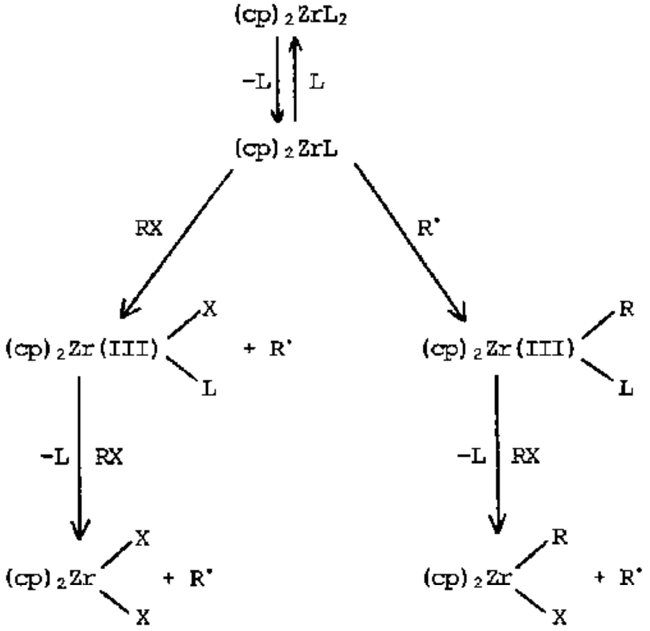


Fig. 4: The chain structure of ZrX_3 (X = Cl, Br or I) and $ZrI_{3.40}$, reproduced with permission from E.M. Larsen, J.S. Wrazel and L.G. Hoard, *Inorg. Chem.*, 21 (1982) 2619 [96].

chain are vacant. It is interesting to note that, despite the likelihood of metal-metal bonding in these d^1 compounds, the $\{ZrX_6\}$ octahedra are elongated along the chain axis. This effect, which is greatest for $ZrCl_3$, less for ZBr_3, and negligible for ZrI_3 and $ZrI_{3.40}$, has been attributed to the need to reduce repulsive electrostatic interactions between nearest-neighbour metal ions [96].

Zirconium(III) species have been observed by EPR spectroscopy in the course of oxidative-addition reactions between alkyl halides and $[(cp)_2ZrL_2]$ (L = PPh_2Me). These reactions produce $[(cp)_2ZrRX]$ and $[(cp)_2ZrX_2]$ by a proposed mechanism outlined in the scheme below. The reaction is initiated by



halogen atom abstraction producing $[(cp)_2Zr^{III}XL]$ and R˙. $[(cp)_2Zr^{III}XL]$ leads to $[(cp)_2ZrX_2]$, while capture of R˙ by $[(cp)_2ZrL]$ gives $[(cp)_2Zr^{III}RL]$ and eventually the oxidative-addition product $[(cp)_2ZrRX]$. Primary alkyl halides strongly favour formation of $[(cp)_2ZrRX]$; tertiary halides give $[(cp)_2ZrX_2]$; and secondary halides yield a mixture of the two products. This mechanism is supported by observation of an EPR signal attributed to $[(cp)_2ZrCl(PPh_2Me)]$ $\{g = 1.998;\ a\langle{}^{31}P\rangle = 21\ G;\ a\langle{}^{91}Zr\rangle = 17\ G\}$ and a second signal assigned to $[(cp)_2ZrBu(PPh_2Me)]$ $\{g = 1.983;\ a\langle{}^{31}P\rangle = 28\ G\}$. The larger ^{31}P hyperfine coupling constant for the latter compound is consistent with an increase in spin density on the phosphorus atom upon replacing the electron-withdrawing chlorine atom with an electron-releasing butyl group [97].

3.3 ZIRCONIUM(II) COMPOUNDS

Zr_6Cl_{15} crystallises in the Ta_6Cl_{15} structure, space group $Ia3d$, and is best formulated as $Zr_6Cl_{12}Cl_{6/2}$. The formal oxidation state of zirconium in this compound is +2.5. The crystal contains [Zr_6} octahedra {r(Zr–Zr) = 3.199(3) and 3.215(4) Å} edge-bridged by chlorine atoms (Figure 5). The resulting Zr_6Cl_{12} units are linked to adjacent clusters by six additional chlorine atoms that occupy exo-positions [98].

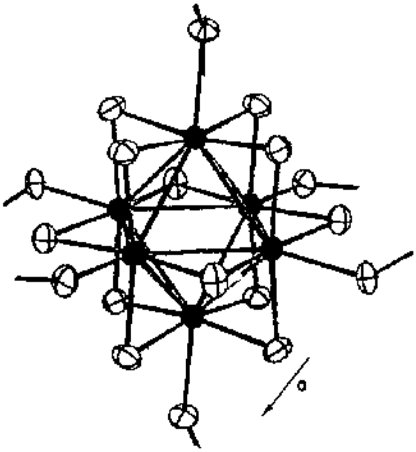


Fig. 5: A perspective view of the $Zr_6Cl_{12}Cl_6/_2$ cluster, reproduced by permission from J.D. Corbett, K.R. Poeppelmeier and R.L. Daake, *Z. Anorg. Allg. Chem.*, 491 (1982) 51 [98].

Syntheses of monoclinic ZrI_2, α-ZrI_2 [99], produce a second, orthorhombic phase, β-ZrI_2, that is isostructural with WTe_2, space group $Pmn2_1$. β-ZrI_2 contains sheets in which infinite zigzag chains of zirconium atoms {r(Zr–Zr) = 3.185(3) Å} lie between puckered hexagonal close-packed layers of iodine atoms {r(Zr–I) = 2.894–3.103 Å}. The structures of α- and β-ZrI_2 are very similar, and evidently the two phases always intergrow with one another in various proportions [100].

Crystals of Zr_6I_{12} (γ-ZrI_2) and $CsZr_6I_{14}$ have been prepared by reaction of ZrI_4, excess Zr strips, and for $CsZr_6I_{14}$, CsI at 850–925 °C for 15–40 days in tantalum containers. Zr_6I_{12}, space group $R\bar{3}$, contains a slightly trigonally compressed {Zr_6} octahedron {r(Zr–Zr) = 3.204(2) and 3.194(1) Å} edge-bridged by twelve iodine atoms. The six iodine atoms that bridge the waist edges of the octahedron also occupy exo-positions in six adjacent {Zr_6} clusters. Thus, the formula of this compound may be represented as $Zr_6I_6I_{6/2}I_{6/2}$. $CsZr_6I_{14}$, space group *Cmca*, has a related cluster structure in which unsymmetric iodine bridging produces a tetragonally distorted $\{Zr_6\}$ octahedron $\{r(Zr-Zr) = 3.29$ Å (8x) and 3.35 Å (4x)$\}$. The structure is derived from that known for Nb_6Cl_{14} and Ta_6I_{14} by addition of caesium to a large interstice [101].

Although organometallic chemistry is largely excluded from this review, we wish to note that 1982 has been a particularly active year for study of the synthesis, structure, fluxionality and reactivity of zirconium(II) and hafnium(II) diene complexes, $[(cp)_2M(diene)]$ (M = Zr or Hf) [102-108].

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