ZIRCONIUM AND HAFNIUM CHEMISTRY

E. M. Larsen

Department of Chemistry, University of Wisconsin,
Madison, Wisconsin

I. Introduction

There are several complete compilations of the literature concerning zirconium and hafnium that take the reader up to about 1960 (*62*, *344*, *420*, *558*). Since then several reviews of more limited scope have been published, one on the structural aspects of zirconium chemistry (*116*), and others on the separation of zirconium and hafnium (*578*), aqueous chemistry (*234*, *533*), and ion-exchange properties of zirconium compounds (*29*). In general, the data in the present review are drawn from publications since 1960, although references to earlier work are included where necessary to complete the picture.

The discovery that the thermal-neutron cross-section capture of zirconium containing the natural 2% hafnium content was largely due to the very high thermal-neutron cross section of the hafnium stimulated the present interest in the chemical and physical properties of these elements. The use of hafnium-free zirconium alloys for cladding nuclear fuels and the use of hafnium for control rods in nuclear reactors account for the fact that much of the recent literature deals with the reduction, purity, working properties, and alloy formation of these elements. It is interesting that another large segment of the literature deals with separation procedures, in spite of the fact that a large-scale production process for the production of reactor-grade zirconium does exist. This is accounted for by the fact that the existing solvent extraction method does not allow the direct recovery of the metal tetrachlorides from the system, but rather requires the recovery of the metal as the hydroxide and reconversion to the tetrachloride prior to metal reduction. Thus, some of the separation procedures have been directed at bypassing the aqueous phase. On the other hand, much of the research has been directed toward studies of chelating agents in the hope of finding one that shows a high discrimination factor between zirconium and hafnium.

The subject matter of this review has been limited to keep the chapter to a reasonable size. Thus, in spite of the large volume of data reported on the metal, its alloys, and many refractory compounds, none of this will be included here. In addition, no attempt is made to discuss all the published separation procedures, although a few that seem of particular interest are mentioned in the appropriate sections.

The subject matter has been organized on the basis of the metal–nonmetal bond, rather than the more conventional organization of compound type. It is immediately evident that compounds containing metal–oxygen bonds predominate, followed by compounds with metal–halogen bonds. It is hoped that this organization will bring some new insights into the chemistry of these elements.

II. Compounds Containing Metal–Hydrogen Bonds

Other than the binary hydrides (*207*), which will not be covered in this review, only a few metal–hydrogen-bonded compounds of zirconium and hafnium are presently known, the first being the borohydride $M(BH_4)_4$. Although its preparation goes back to the work of Hoekstra and Katz (*246*), it is only recently that structural studies have revealed that metal–hydrogen–boron bridges are involved in the structure. The proton NMR spectrum (*263*, *582*) of a benzene solution shows a quartet with 1 : 1 : 1 : 1 intensities, and the B^{11} NMR spectrum, also of a benzene solution, shows a quintet of 1 : 4 : 6 : 4 : 1 intensities. These spectra are consistent only with a system in which the protons are undergoing rapid exchange. The gas-phase infrared spectrum (*263*, *581*, *582*) has been interpreted as evidence for a structure with D_{4d} or D_{4h} symmetry involving hydrogen-bonded BH_4 groups,

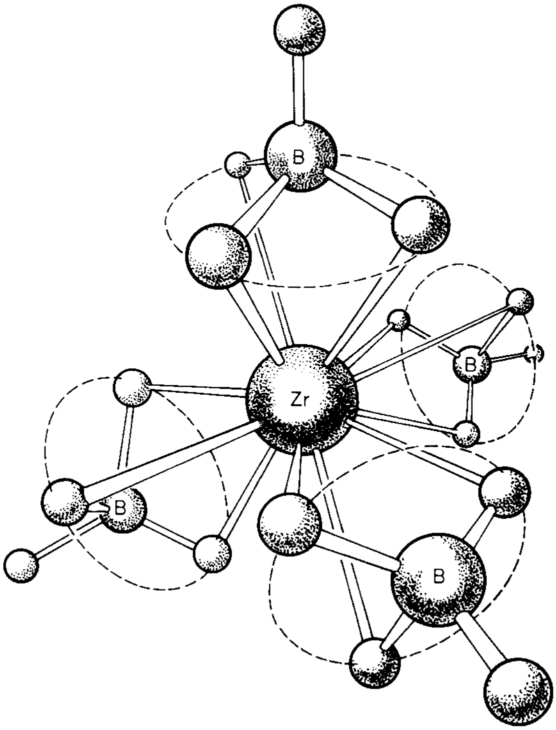
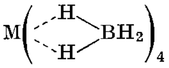


FIG. 1. One possible arrangement of borohydride groups about the zirconium atom. Reproduced by permission, from P. Bird and M. R. Churchill, *Chem. Commun.* p. 403 (1967).



$$M\left(\begin{matrix}\cdot H \\ \cdot H\end{matrix}BH_2\right)_4$$

The X-ray crystal structure (Fig. 1), on the other hand, shows that the molecule possesses full T_d symmetry of the space group $(\bar{4}3m)$. The zirconium atom is tetrahedrally surrounded by four crystallographically equivalent boron atoms (Zr–B = 2.34 ± 0.03 Å), with the symmetry of the space group requiring that each Zr–B vector is coincident with a C_3 axis. A single terminal H atom is located on this threefold axis, the B–H distance being 1.2 ± 0.4 Å. There are thus three B–H bridges per boron atom, and the zirconium is surrounded by a total of twelve bridging hydrogen atoms. The nature of the bonding in this structure has not been described, although multicentered bonds must be involved. The interpretation of the gas-phase infrared spectrum should be reconsidered on the basis of these data.

Reid *et al.* (*454*) reinvestigated the synthesis of the zirconium and hafnium borohydrides. The reaction of diborane with zirconium tetrachloride dissolved in tetrahydrofuran (THF) does not give a boron-containing product, whereas the reaction of diborane with an ether solution of zirconium tetraethoxide gives the desired metal borohydride although it is difficult to separate from the borate ester coproduct. The reaction of Katz (*246*) was run with potassium fluorozirconate in preference to the sodium salt because the potassium salt reacted more readily,

$$KHfF_5 + 2\ Al(BH_4)_3 \rightarrow Hf(BH_4)_4 + 2\ AlF_2BH_4 + KF \qquad (1)$$

but the most suitable reaction found for this synthesis is described by the equation

$$ZrCl_4 + 4\ LiBH_4 \rightarrow Zr(BH_4)_4 + 4\ LiCl \qquad (2)$$

Sodium or potassium borohydride was not successful in this synthesis. Zirconium borohydride in ether reacts with an ether solution of lithium aluminum hydride to give a white precipitate of $Zr(AlH_4)_4$ that decomposes at room temperature to give a black pyrophoric solid of unknown composition.

A hydrogen–metal bond is present in compounds formed by the action of trimethylamine on $(\pi\text{-}C_5H_5)_2Zr(BH_4)_2$ (*264*, *265*). Either white, diamagnetic $(\pi\text{-Cp})_2Zr(H)(BH_4)$[1] or white, insoluble, nonvolatile $[(\pi\text{-Cp})_2ZrH_2]_n$ is obtained depending on whether one or two moles of amine are used per mole of borohydride. The proton of the metal–hydrogen bond could not be detected by NMR, but its presence was established by the sharp IR absorption at 1945 cm^{-1}. The dihydride is postulated to have a polymeric bridging hydride structure on the basis of an absorption at 1540 cm^{-1} which is assigned to a metal–hydrogen bridging vibration. The corresponding hafnium species are said to have been prepared.

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[1] Cp, cyclopentadienyl.

III. Compounds Containing Metal–Carbon Bonds

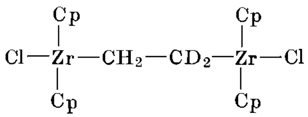
The first organometallic compound of zirconium reported was bis(π-cyclopentadienyl)zirconium dibromide (*592*). Since the initial report many new organozirconium compounds have been prepared, most of which contain at least one cyclopentadienyl ring. Only a few compounds of hafnium have been prepared, presumably because everyone assumes that hafnium behaves in a fashion identical to zirconium, a proposition which should be examined more closely.

A. ALKYL DERIVATIVES

The reaction of diazopentane with zirconium hydride at –40°C is reported (*583*) to yield dipentylzirconium, $(C_5H_{11})_2Zr$, while the reaction of ethylmagnesium chloride, ethylsodium, or ethyllithium with zirconium tetrachloride (*134*) presumably results in the production of diethylzirconium dichloride. These products have not been completely characterized.

Tetramethylzirconium was prepared (*59*) by the reaction of stoichiometric amounts of methyllithium and zirconium tetrachloride in an ether–toluene solvent mixture at –45°C. Methylation is accompanied by the appearance of a yellow color and precipitation of lithium chloride. The red liquid was recovered in poor yield by vacuum distillation at –30°C. The product decomposes at –15°C with the evolution of methane and the formation of a black color. When a mole ratio of $ZrCl_4 \cdot LiCH_3$ (1 : 6) is used, the addition of hexane to the ether/toluene solution results in a chloride-free precipitate whose elementary analysis corresponds to the composition $Li_2[Zr(CH_3)_6]$. This product decomposes at 0°C.

There is evidence for a species in which a $-CH_2-CH_2-$ group acts as a bridge between two $Cl(Cp)_2Zr$ moieties. The reaction of triethyl aluminum with $(\pi\text{-}Cp)_2ZrCl_2$ proceeds with the evolution of ethane, and the formation of an adduct containing one mole of aluminum for every mole of zirconium. The aluminum moiety can be substantially removed by treatment with THF. When tris(1,2-deuteroethyl)aluminum was used as the reagent, one mole of 1,2-deuteroethane was evolved per two moles of $(\pi\text{-}Cp)_2ZrCl_2$ used in the reaction. When the product (I), which is formulated as



$$Cl-\overset{Cp}{\underset{Cp}{Zr}}-CH_2-CD_2-\overset{Cp}{\underset{Cp}{Zr}}-Cl$$

(I)

is treated with hydrogen chloride, a second mole of deuteroethane is obtained, and (π-Cp)$_2$ZrCl$_2$ recovered from the reaction system (*517*).

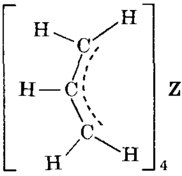
The reaction of ethylmagnesium chloride and (π-Cp)$_2$ZrCl$_2$ at 0°C in methylene chloride results in a yellow crystalline product which presumably is $C_2H_5Cp_2ZrCl$. It is a diamagnetic solid which is decomposed by light, air, or water, but is stable at 0°C under nitrogen (*518*).

B. ARYL DERIVATIVES

Attempts to prepare (σ-C$_6$H$_5$)$_2$Zr(π-C$_5$H$_5$)$_2$ have so far failed, although the corresponding titanium compound is known. The pentafluorophenyl derivative, however, has been prepared. It was first reported by Tamborski and co-workers (*552*) as the product of the reaction of pentafluorophenyllithium and (π-Cp)$_2$ZrCl$_2$ in diethyl ether. However, the reported melting point, 257°C (decomposition, dec.) does not agree with the 219°C (dec.) obtained by Chaudhari and Stone (*103*) for the product obtained from the same reaction system, and also characterized as (σ-C$_6$F$_5$)$_2$Zr(π-C$_5$H$_5$)$_2$. The extreme reactivity of this product with moisture to form (σ-C$_6$F$_5$)Zr(π-C$_5$H$_5$)$_2$OH and ultimately (π-C$_5$H$_5$)-Zr(OH)$_2$ (dec. 250°C) makes it likely that the initially reported material was hydroxylated. These compounds tend to decompose explosively near or above their melting points.

C. ALLYL DERIVATIVES

Tetraallylzirconium $(C_3H_5)_4Zr$ was prepared by the reaction of allylmagnesium chloride and zirconium tetrachloride in diethyl ether under nitrogen at −80° to −20°C (*590*). It reacts with anhydrous hydrogen chloride in ether to form red-brown $(C_3H_5)_3ZrCl$. The compound $Cp_2Zr(C_3H_5)_2$ has also been reported (*141*). The proton magnetic resonance spectrum (*53*, *54*) of a $CFCl_3$ solution of $(C_3H_5)_4Zr$ is temperature dependent with the two doublets of the AM_2X_2 spectrum broadening and moving together, coalescing at −40°C, and finally sharpening at higher temperatures to the single CH_2 doublet of the AX_4 spectrum. Simultaneously the resonance of the single proton, nine lines at −74°C,



(II)

changes to a quintet at –20°C. It is concluded that a symmetrically bonded allylic ligand as in (II) gives rise to both AM_2X_2 and the AX_4-type spectra, depending on whether the rate of internal rotation of the CH_2 groups about the bonds linking them to the central metal atom is slow (AM_2X_2) or fast (AX_4). The spectrum of the corresponding hafnium compound shows no temperature dependence, indicating that the rate of rotation is still several hundred hertz (cycles per second) even at –72°C.

D. CYCLOPENTADIENE DERIVATIVES

1. *Monocyclopentadienylmetal Trihalides*

Monocyclopentadienylzirconium trichloride has been prepared from zirconium tetrachloride by reaction with cyclopentadienylmagnesium chloride in toluene/diethyl ether solution (*240*, *241*). Both the chloride and bromide have been prepared from the corresponding tetrahalides and magnesium cyclopentadienide in xylene at 100°–110°C (*451*), or by continuous recirculation of cyclopentadiene vapor upward through a bed of zirconium trihalide (250°–300°C) resting on a glass sinter. The products were purified by sublimation. Yields were only about 15% compared to the 60–70% obtained from syntheses carried out in solution. The melting points and colors for the monocyclopentadienyl metal trihalides and for other cyclopentadienyl metal halide compounds are tabulated in Table I.

2. *Bis(π-cyclopentadienyl)metal Dihalides*

The bis(π-cyclopentadienyl)zirconium dichloride has been synthesized by a variety of routes and a variety of authors. It can be recovered from reaction systems of zirconium tetrachloride and sodium cyclopentadienide in tetrahydrofuran or ethyleneglycol dimethyl ether (*89*, *194*, *343*, *471*) or with lithium cyclopentadienide (*472*) in place of the sodium compound. The hafnium compound was prepared in a similar manner (*343*, *471*). In general, the residue obtained upon evaporation of the solvent is extracted with chloroform and the product from the extraction is recrystallized from benzene. The dichloride was also prepared (*451*) by the continuous recirculation of cyclopentadiene vapor through a bed of $ZrCl_2$ at 270°–350°C. Another route to the chloride is the reaction of zirconium tetrachloride with cyclopentadienylmagnesium chloride (*559*) in benzene; yet another involves the reaction of zirconium tetrachloride and cyclopentadiene in ethylamine as the solvent at room temperature (*367*).

Bis(π-cyclopentadienyl)zirconium dibromide was recovered from the reaction of zirconium tetrachloride with cyclopentadienylmagnesium bromide followed by treatment with anhydrous hydrogen bromide (*592*). Higher yields are obtained by the reaction of cyclopentadienylsodium (*591*) with zirconium tetrabromide in either tetrahydrofuran or 1,2-dimethoxyethane. It may also be prepared by the direct action of cyclopentadienyl vapor on zirconium dibromide, but the yields are low (*451*). Halogen exchange is also a possible route to the bromide (*473*). Bis(π-cyclopentadienyl)zirconium dichloride in benzene when treated with anhydrous hydrogen bromide yields Cp_2ZrBr_2. The iodide Cp_2ZrI_2 has also been prepared by halogen exchange (*451*, *471*). Sodium iodide in dry acetone, added to a solution of Cp_2ZrCl_2 in the same solvent, yields an immediate precipitate of sodium chloride and a green solution from which the crude diiodide is obtained by evaporation. The product is purified by sublimation. Still another route to Cp_2ZrI_2 is the reaction of zirconium tetraiodide with fused magnesium cyclopentadienide in a sealed tube at 230°C. Similar reactions with zirconium tetrachloride, tetrabromide, and tetrafluoride, and potassium hexafluorozirconate were unsuccessful (*453*).

Several groups have recorded the infrared spectra of these cyclopentadienylmetal compounds (*451*, *449*, *471*, *521*). The four strongest bands in the fundamental spectra are at 820, 1010, 1430, and 3100 cm^{-1}. These have been assigned to the CH out-of-plane bending, CH in-plane-bending, CC-stretching, and CH-stretching frequencies, respectively, and are observed in all the compounds. The ring-metal frequencies occur below 800 cm^{-1} and therefore the fundamental spectra differ in this region depending on the metal present. A combination of fundamental frequencies results in absorption above 3800 cm^{-1} which is similar for all the compounds and characteristic of a cyclopentadienyl ring bonded with fivefold symmetry to a metal atom. A single sharp CH-stretching frequency occurs at 6100–6200 cm^{-1}. Other binary combination bands containing the frequencies mentioned above are found at 3930, 4100, and 4450 cm^{-1}. The combination spectrum resulting from the vibrational modes of the cyclopentadienyl ring is insensitive to other groups attached to the metal or the overall symmetry of the molecule. The single-ring titanium and zirconium trihalides differ from the bis(π-cyclopentadienyl)metal dihalide complexes by the resolution of the band at 4030–4040 cm^{-1}.

The proton NMR spectra of these compounds consist of a single sharp line found between 6.63 to 6.78 ppm (*521*), which indicates that the five ring protons are equivalent. In addition, the dipole moments of Cp_2TiCl_2 (6.3 D) and Cp_2ZrCl_2 (5.9 D) in benzene are consistent with a structure in which there are four approximately tetrahedral bond angles (*208*).

3. *Tris(π-methylcyclopentadienyl)metal Chloride*

$(CH_3C_5H_4)_3ZrCl$ is the only representative of this class reported to date (*87*). It was prepared by the (3 hours) reaction at room temperature of sodium methylcyclopentadienide and zirconium tetrachloride in toluene. It is a yellow product with a melting point of 168°–170°C.

4. *Dicyclopentadienylzirconium and Tetracyclopentadienylzirconium*

Dicyclopentadienylzirconium was first reported by Watt (*587*) and co-workers. In a typical experiment, Cp_2ZrCl_2, naphthalene, metallic sodium, and tetrahydrofuran were stirred for 24 hours, the solvent removed, and the residue extracted with benzene. After evaporation of the benzene, the excess naphthalene was sublimed at 100°C and 10^{-2} mm leaving a purple-black chlorine-free residue of Cp_2Zr.

Tetracyclopentadienylzirconium and tetracyclopentadienylhafnium were listed (*195*) with compounds said to contain σ-bonded cyclopentadienyl groups, but no reference was cited for their preparation. Since this initial disclosure, the synthesis via the reaction of sodium cyclopentadienide and zirconium tetrachloride (*452*, *361*) has appeared in the literature, as well as the synthesis from the reaction of sodium cyclopentadienide in toluene with Cp_2ZrCl_2 (69% yield) (*76*, *85*). Tetracyclopentadienylzirconium is stable in air up to 75°C and in an inert atmosphere up to about 400°C. It hydrolyzes to zirconium oxide in water and gives $Zr(OEt)_4$ with ethanol. Its IR spectrum shows the absence of ligands of the diene type. All protons are equivalent by NMR. Tetracyclopentadienyl hafnium was prepared (*366*) by the reaction of sodium cyclopentadienide suspended in toluene and hafnium tetrachloride in benzene. The heterogeneous reaction system produced $Hf(Cp)_4$ during the course of 4 hours at 40°C. Like the zirconium homolog, the NMR spectra in chloroform consists of a singlet with a chemical shift of 5.92 relative to tetramethylsilane (TMS) and the infrared spectrum shows frequencies of π-bonded cyclopentadienyl rings. The original report of σ-bonded cyclopentadienyl rings appears to be incorrect.

5. *Metal Halide Derivatives of Substituted Cyclopentadienes*

Bis(π-methylcyclopentadienyl)zirconium dichloride (m.p. 180°–181°C) is obtained in a 38% yield (*455*, *471*) from the reaction mixture of zirconium tetrachloride and sodium methylcyclopentadienide in tetrahydrofuran. The bis(π-indenyl)zirconium dichloride and bis(π-fluorenyl)zirconium dichloride have been prepared in a similar fashion (*471*, *474*).

Whereas sodium indenide was formed in tetrahydrofuran, the metallation of fluorene was best carried out with sodium or potassium in dimethoxyethane or with potassium in diethyl ether. In either case the sodium indenide or sodium fluorenide was added to a suspension of zirconium tetrachloride in the respective solvents, whereupon a yellow or orange crystalline product was formed. The product could not be extracted with an organic solvent owing to the rapidity with which it decomposed in solution. The product could be recovered, however, by precipitation with a large excess of ether. The indenyl product $(C_9H_7)_2ZrCl_2$ melts at 264°C, but the fluorenyl product $(C_{13}H_9)ZrCl_2$ decomposes with melting.

TABLE I

ORGANOMETALLIC COMPOUNDS OF ZIRCONIUM AND HAFNIUM

Compound	Melting point (°C)	Color	Ref.
$Zr(Cp)Cl_3$	237 (dec.)	Cream	(*45*)
$Zr(Cp)Br_3$	274	Yellow	(*45*)
$Zr(Cp)I_3$	133	Red	(*45*)
$Zr(Cp)_2Cl_2$	248	Colorless	(*343*)
$Zr(Cp)_2Br_2$	260 (dec.)	Buff	(*45*)
$Zr(Cp)_2I_2$	299	Bright yellow	(*451*)
$Hf(Cp)_2Cl_2$	236	—	(*366, 451*)
$Zr(Cp)_2$	>300 (dec.)	Purple-black	(*87*)
$Zr(Cp)_3Cl$	168–170	Yellow	(*559*)
$Zr(Cp)_4$	—	—	(*85, 452*)
$Hf(Cp)_4$	207–208	—	(*366*)

Bis(π-ethylcyclopentadienyl)hafnium difluoride has been synthesized by the reaction of hafnium tetrafluoride and ethylcyclopentadiene in the presence of an organic base (*221*).

6. *Chemical Properties*

a. Exchange with Organic Acid Anions. Bis(π-cyclopentadienyl)zirconium dichloride reacts with some carboxylic acids (*79*) to give products of the general composition $CpZr(O_2CR)_3$. Thus, distillation *in vacuo* (105°C over 9 hours) of an anhydrous acetic acid solution of Cp_2ZrCl_2 gives a 66% yield of $CpZr(O_2CCH_3)_3$ [m.p. 170°C (dec.)]. The triacetato compound, in turn, reacts with benzoic acid in toluene at 100°–105°C (12 hours) to give a 56% yield of $CpZr(O_2CC_6H_5)_3 \cdot \frac{1}{2}C_6H_5CH_3$

(m.p. 209°–210°C) (*87*). From valeric acid an 87% yield of $CpZr(O_2CC_4H_9)_3$ is obtained and from heptanoic acid an 85% yield of $CpZr(O_2CC_6H_{13})_3$. The trivalerato and triheptanato(π-cyclopentadienyl) complexes have also been obtained by ligand exchange between $CpZr(acac)_2Cl$ and the respective acids at 100°C (*79*). On the other hand (*87*), the reaction of $(\pi\text{-}Cp)_2ZrCl_2$ with trifluoroacetic acid (m.p. 70°C for 1.5 hours) gave a 50% yield of the disubstituted product $Cp_2Zr(O_2CCF_3)_2$ (m.p. 116°–117.5°C).

b. Exchange with β-Diketone Anions. Bis(π-cyclopentadienyl)zirconium dichloride heated with acetylacetone to 70°–80°C for 2 hours yields (*343*) $CpZr(acac)_2Cl$ (m.p. 188°–190°C). The same product can be obtained from the reaction of $Zr(acac)_2Cl_2$ and CpNa in tetrahydrofuran for 2 hours (*343*). Benzoylacetone in benzene at 95°–100°C for 15 hours gave, in an analogous manner, $CpZr(bzac)_2Cl$ (m.p. 184°–185.5°C) in 69% yield (*343*). Bis(π-cyclopentadienyl)triacetatozirconium with acetylacetone (*79*) at 60°–65°C for 6.5 hours gave a 70% yield of $CpZr(acac)_2(O_2CCH_3)$ (m.p. 128.5°–131°C), while at 85°C ligand substitution was complete and tetrakis(acetyacetonato)zirconium(IV) was obtained.

Starting with $ZrCp_4$, three of the four cyclopentadienyl groups may be substituted by chelating ligands. In this manner π-cyclopentadienyltris(benzoylmethanato)zirconium (m.p. 186°–187°C) in 63% yield, π-cyclopentadienyltris(benzoylacetonato)zirconium (m.p. 141°–142°C) in 52% yield, and π-cyclopentadienyltris(acetylacetonato)zirconium (m.p. 163°–165.5°C) were prepared.

The complex $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ is sufficiently stereochemically rigid at room temperature to observe nonequivalent environments for methyl and the γ protons on the chelate rings (*433*). In nitrobenzene solution the compound is monomeric and a very weak electrolyte. There is no spectral evidence for uncoordinate carbonyl groups, so it is concluded that the chlorine atom and all four carbonyl groups are coordinated to the zirconium. There is only one resonance for the protons on the cyclopentadienyl ring which is taken as evidence for rapid rotation of the ring about the metal-ring axis. No stereoisomerism could be detected even on heating in benzene at 80°C for 24 hours. X-ray single-crystal data show that the geometry approximates a dodecahedron.

Graham *et al.* (*161*) have prepared and characterized $(\pi\text{-}C_5H_5)Zr(hfac)_3$. An X-ray single crystal study revealed a monoclinic cell with $a = 13.42 \pm 0.02$ Å, $b = 22.94 \pm 0.02$ Å, $c = 8.90 \pm 0.02$ Å, $\beta = 95.0 \pm 0.2°$ with space group $P2_1/n$ and four molecules in the unit cell. The molecule can be described as having a pentagonal–bipyramidal geometry in which the cyclopentadienyl ring is regarded as occupying a single axial coordination position. Two of the bidentate ligands lie in the equatorial plane, while the third ligand occupies one of the axial positions and the remaining equatorial one. The five equatorial Zr–O bonds are tilted away from the plane of the ring by 10°. Fluorine-19 NMR at –30°C shows four bands of intensity ratio 2 : 2 : 1 : 1 consistent with the X-ray structure. Upon raising the temperature the resonances due to the fluorine on the equatorial ligand coalesce near 50°C, while the fluorines on the remaining ligand require a higher temperature before exchange is observed.

Proton and ^{19}F NMR spectra of the unsymmetrical chelate π-$C_5H_5Zr(tfac)_3$ can be similarly interpreted. In addition, the spectra show the presence of two isomers in a molar ratio of 3:2. The isomers differ in the orientation of the mixed axial–equatorial ligand.

c. *Exchange with 8-Hydroxyquinoline Anion.* The compound (π-cyclopentadienyl)tris(8-quinolinolato)zirconium has been prepared by a variety of routes (*87*). Ligand exchange of the chloro groups by the anion of 8-hydroxyquinoline is easily accomplished by direct reaction of Cp_2ZrCl_2 and 8-hydroxyquinoline in benzene at 80°C during the course of 20 minutes. The hydrogen chloride produced in the reaction is eliminated as the hydrochloride of 8-hydroxyquinoline, and the product is recovered from the filtrate. The same product is obtained from the reaction of 8-hydroxyquinoline with $(Cp_2Zr(acac)_2)_2O$ in benzene at 95°–100°C for 1 hour. Here the chelate group breaks the Zr–O–Zr bond and replaces the acetylacetone groups. A third route to the synthesis of $CpZr(ONC_9H_6)_3$ is the reaction of tetrakiscyclopentadienylzirconium with 8-hydroxyquinoline in benzene at 70°–80°C for 15 minutes. A yield of 89.7% was obtained by this method. The product melts with gradual preliminary decomposition at 357°–360°C, and is readily soluble in chloroform, tetrahydrofuran, difficultly soluble in benzene, and insoluble in hexane and ethyl ether. Similarly, ligand exchange of chlorotris(π-methylcyclopentadienyl)zirconium with 8-hydroxyquinoline in benzene for 2 hours led to the production of (π-methylcyclopentadienyl)tris(8-quinolinato)zirconium (m.p. 252°–260°C) in 60% yield. All these compounds are monomers, and are stable to oxygen. The infrared spectra show absorption bands characteristic of π-bonded cyclopentadienyl rings. (π-Cyclopentadienyl)tris(8-hydroxyquinolate)hafnium was prepared by either the reaction of $(\pi\text{-}Cp)_4Hf$ or $(\pi\text{-}Cp)_2HfCl_2$ with 8-hydroxyquinoline at 80°C. The recrystallized product decomposed at 250°C.

d. *Exchange with Alkoxy Groups.* Bis(π-cyclopentadienyl)zirconiumdichloride in benzene reacts (60°C for 3 hours) with ethanol and isopropanol in the presence of triethylamine to give triethylamine hydrochloride as a precipitate, and a solution from which may be recovered $Cp_2Zr(OC_2H_5)Cl$ (m.p. 70°C, 43% yield) or $Cp_2Zr(iso\text{-}OC_3H_7)Cl$ (23% yield) (*84*). The ethoxy derivative reacts with acetylacetone at 50°C to give a 52% yield of $Cp_2Zr(acac)_2$.

Mono(π-cyclopentadienyl)zirconium trihalide reacts with an alcohol or phenol in the prescribed solvent at reflux temperatures to replace one halogen atom (*219*). Thus the tribromide and hexadecyl alcohol in diethyleneglycol dimethyl ether yields $CpZr(OC_{16}H_{33})Br_2$; indenylhafnium trifluoride and phenol in normal hexane gives $C_9H_7Hf(OC_6H_5)F_2$; from fluorenylzirconium trichloride and ethylene glycol, $[CH_2OZr(C_{13}H_9)Cl_2]_2$ is obtained, and with (phenylcyclopentadienyl)zirconium trichloride and picric acid in toluene, $(C_6H_5C_5H_4)(O_2NC_6H_4O)ZrCl_2$ results.

e. Exchange with Inorganic Anions. Bis(π-cyclopentadienyl)zirconium dichloride and lithium borohydride in diethyl ether react in 8 hours to give insoluble lithium chloride, and a solution, from which $Cp_2Zr(BH_4)_2$ may be recovered. The product when purified by sublimation *in vacuo* at 110°C yields a pale yellow solid (m.p. 155°C dec.) (*387*). If only a twofold molar excess of lithium borohydride is used, then $Cp_2ZrCl(BH_4)$ is obtained. The infrared spectrum shows strong similarities to the spectra of other cyclopentadienyl derivatives of transitional metals and typical covalent borohydrides. Some asymmetry in the cyclopentadienyl rings is implied from the splitting of the C–H-stretching frequencies.

Bis(π-cyclopentadienyl)zirconium dichloride treated with sulfuric acid in acetic anhydride gave a product in which the chlorides were replaced with HSO_4 groups and one cyclopentadienyl ring was sulfonated. The compound $Cp(C_5H_5SO_3H)Zr(OSO_3H)_2 \cdot Ac_2O$ does not melt. When treated with acetylacetone a product of composition $[(acac)_2(C_5H_4SO_3H)Zr(SO_4H)] \cdot C_5H_8O_2$ results (*83*).

Mono-π-cyclopentadienyltriacetatozirconium, $\pi\text{-}CpZr(OOCCH_3)_3$, reacts with sulfuric acid and acetic anhydride in dry dichloromethane by replacement of the acetate groups by OSO_3H groups to yield $\pi\text{-}CpZr(OSO_3H)_3 \cdot (CH_3CO)_2O$. This product with SO_3 in 1,1-dichloroethane at room temperature undergoes ring sulfonation to produce $(\pi\text{-}C_5H_4SO_3H)Zr(OSO_3H)_3$ (*193*).

A monocyclopentadienyl mixed dichlorobromo species has been reported by Gorsich (*221*), who identified $CpZrBrCl_2$ in the reaction mixture resulting from the reaction of Cp_2ZrCl_2 with bromine in trichlorobenzene as the solvent. Gorsich also prepared $(C_2H_5C_5H_4)HfF_3$ by reaction of elemental fluorine and bis(π-ethylcyclopentadienyl)hafnium difluoride in chlorinated biphenyl at 210°C.

Tetracyclopentadienylzirconium in dichloromethane reacts with nitric acid at room temperature over 2 hours to give a 67% yield of $Cp_2Zr(NO_3)_2$. This product explodes at about 185°C (*85*). Tetracyclopentadienylhafnium reacts with acids and bases in the same manner as the zirconium compound. Nitric acid and hydrogen chloride result in exchange of two of the cyclopentadienyl groups to yield Cp_2HfCl_2 (m.p. 236°C) and $Cp_2Hf(NO_3)_2$ (*366*).

f. Hydrolysis Reactions. Cyclopentadienylzirconium compounds containing Zr–O–Zr bonds have been prepared by a variety of routes. Simple hydrolysis of Cp_2ZrCl_2 in benzene in the presence of aqueous triethylamine at moderate temperatures (40°C) yields a precipitate of triethylamine hydrochloride and a solution from which a compound of composition $(Cp_2ZrCl)_2O$ is obtained (*84*, *450*). This compound is colorless, diamagnetic, and nonconducting in chloroform solution. The same product is obtained by hydrolysis of $Cp_2Zr(OC_2H_5)Cl$ in ethanol (*84*). The corresponding bromo compound has also been prepared (*474*). The reaction with amines was originally thought to yield a compound of composition $C_{10}H_9ZrCl$ (*473*), but Brainia and co-workers (*84*), Reid (*450*), and Samuel (*471*) have concluded that the products originally reported (*473*) contain Zr–O–Zr bonds. The oxygenated species show a strong complex absorption at 750–775 cm^{-1} which is assigned to the Zr–O-stretching frequency. The NMR spectrum has one sharp singlet at δ 6.34 ppm (*450*) indicating that all the protons are equivalent. The bridged structure was confirmed by mass spectral data (*450*) which show that many of the ions produced contain the Zr–O–Zr unit. Preliminary single-crystal X-ray data of $(Cp_2ZrCl)_2O$ show that the unit cell is monoclinic with $a = 13.75$ Å, $b = 7.80$ Å, $c = 18.73$ Å, and $\beta = 94°50'$. There are four molecules in the unit cell. The hafnium compound (m.p. 265°–269°C) has also been prepared (*366*).

The reaction of $(Cp_2ZrCl)_2O$ with $(CH_3)_3Al$ in benzene at 65°–70°C for 3.5 hours breaks the Zr–O bond (*546*) to give an alkyl product $(Cp)_2ZrCH_3Cl$ (m.p. 191°–193°C) in a 53% yield. The molecular weight is consistent with the formula, and the NMR shows two sharp peaks, δ 0.42 ppm $[Zr(CH_3)]$ and δ 5.78 ppm (π-Cp). The compound hydrolyzes in water to give methane in quantitative yields. There is also reference (*297*) to unpublished work on the preparation of another alkylated compound $Cp_2Zr(CH_3)I$.

A compound containing Zr–O–Zr bonds but no halogens can be obtained by hydrolysis of the product resulting from the reaction of Cp_2ZrCl_2 and phenyllithium (*77*). The compound $[(C_6H_5)_2Cp_4Zr_2O]OH_2$ (m.p. 250°–260°C) was obtained in 52% yield. The anhydrous product can be obtained by the reaction of $(Cp_4Zr_2Cl_2)O$ with phenyllithium at room temperature. When tolyllithium is used, the product $(CH_3C_6H_5)_2Cp_4Zr_2O$ (m.p. 210°–224°C) is obtained in a 44% yield. Acetylacetone replaces the two phenyl groups and two of the cyclopentadienyl groups of $[(C_6H_5)_2Cp_4Zr_2O]OH_2$ in 1 hour at 30°–35°C to yield $Cp_2(acac)_4Zr_2O$ (m.p. 164.5°–165.5°C). In contrast, acetylacetone with $Cp_4Zr_2Cl_2O$ at 40°C gives almost quantitative conversion (97%) to $Cp(acac)_2ZrCl$.

By adding water to a refluxing solution of $n\text{-}C_8H_{17}C_5H_4ZrF_3$ in acetone, a crystalline deposit of $[n\text{-}C_8H_{17}C_5H_4Zr(O)F]_4$ is obtained. Similarly, treatment of $(CH_2{=}CHC_5H_4)HfI_3$ with water (1:1) in $C_6H_3Cl_3$ at 0°C yields a compound $[CH_2{=}CHC_5H_4\ HfI_2]_2O$ (*220*).

E. Cyclopentadienylene Derivatives

The oxidation of $C_5H_5(C_5H_5Cl_2)ZrX_2$ with peroxide containing ether or oxygen in a diethyl ether solution yielded the yellow compounds $C_5H_4ZrCl_2$, $C_5H_4ZrBr_2$, and $C_5H_4ZrF_2$. The compounds are resistant to air oxidation and inert in water (*287*).

F. Arene Derivatives

Bisbenzenezirconium is assumed to have been formed in solution upon heating a mixture of zirconium tetrachloride, aluminum, and aluminum chloride in benzene. A wine-red solution was obtained, but no products were isolated (*178*, *232*).

The reaction of zirconium tetrachloride and hexamethylbenzene in the presence of aluminum and aluminum trichloride at 120°C produces a melt, which upon hydrolysis with water in the presence of methylene chloride, yields an organic-soluble species of composition $[Zr_3(C_6(CH_3)_6Cl_6]Cl$. The brown product has a magnetic moment at 303°K of 2.04 B.M. Conductivity measurements have been interpreted in terms of the trinuclear cluster cation. It decomposes in nitrogen at 20°–30°C and is rapidly oxidized by oxygen (*179*).

G. Miscellaneous Ligands

Bis(π-cyclopentadienyl)zirconium dichloride reacts with 1,4-dilithiotetraphenylbutadiene in diethyl ether under reflux conditions to give insoluble lithium chloride and methylenechloride-soluble, orange bis(π-cyclopentadienyl)-2,3,4,5-tetraphenylzirconacyclopentadiene (m.p. 140°–170°C, dec.), $(C_5H_5)_2\underline{Zr{-}CPh{=}CPhCPh{=}CPh}$, in 53% yield. The compound is decomposed in alcohols and is slowly hydrolyzed by moisture (*88*).

Bis(π-cyclopentadienyl)zirconium dichloride treated with chlorine in carbon tetrachloride yields $Cp_2(C_5H_5Cl_2)ZrCl_2$ and $Cp(C_5H_5Cl_4)ZrCl_2$, while bis(π-cyclopentadienyl)zirconium difluoride and bromine also in carbon tetrachloride yield $Cp(C_5H_5Br_4)ZrF_2$ (*288*).

Electrochemical reduction of (π-$Cp)_2ZrCl_2$ in dimethoxyethane suggests reduction first to a chloro-bridged dimer and then to a polymer (*147*).

Formation of the first heterozirconium–metal-bonded compound was reported by Lappert *et al.* (*97*), who recovered (π-$Cp)_2ClZr$–$Si(C_6H_5)_3$ as orange, sublimable crystals (~175°C) from the reaction of (π-$Cp)_2ZrCl_2$ and $(C_6H_5)_3SiLi$ in tetrahydrofuran at –50°C. The product is cleaved by gaseous HCl to give (π-$Cp)_2ZrCl_2$ and $(C_6H_5)_3SiH$. A similar reaction has been run by Coutts and Wailes (*130*) using $NaSn(C_6H_5)_3$ and $LiGe(C_6H_5)_3$. The yellow products have properties consistent with compositions for Cp_2ClZr–$Sn(C_6H_5)_3$ and Cp_2ClZr–$Ge(C_6H_5)_3$. Kingston and Lappert (*299*) have also prepared the Hf–Si, Hf–Ge, and Hf–Sn bound species.

Creemers (*132*) has reported that the reaction of triphenyltin hydride with tetrakis(diethylamino)zirconium in a mole ratio of 4:1 at 60°C under reduced pressure gave volatile diethylamine and a brown residue of crude tetrakis(triphenylstannyl)zirconium. This residue, dissolved in benzene, when purified by column chromatography, yielded a yellow eluate from which a yellow solid (m.p. 70°–73°C) was obtained. When a mole ratio of triphenyltin hydride tetrakis(amine)zirconium of 3:1 was used and the resulting product subjected to transamination with *N*-phenylformamide to prevent diethylamino-catalyzed decomposition of diphenyltin hydride which is the next reactant, a yellow product corresponding to bis[tris(triphenylstannyl)zirconyl]diphenyltin, $[(Ph_3Sn)_3ZrSnPh_2Zr(SnPh_3)_3]$, (100°C, dec.) was obtained. With the same reaction sequence but with a triphenyltin hydride and tetrakis(amino)zirconium mole ratio of 2:1, an orange-yellow polymeric compound was obtained which is thought to have alternating zirconium and tin atoms in a chain with an overall composition of $[(Ph_3Sn)_2Zr$–$SnPh_2]_n$ (160°C, dec.).

IV. Compounds with Metal–Nitrogen, Metal–Phosphorus, or Metal–Arsenic Bonds

A. METAL–NITROGEN BONDS

1. *Amine and Nitrile Adducts*

The Lewis acid properties of zirconium and hafnium tetrahalides have been studied with nitrogen bases as well as oxygen bases, although very

TABLE II

NITROGEN BASE ADDUCTS OF ZIRCONIUM (HAFNIUM) TETRAHALIDES[a]

Compound	Ref.	Compound	Ref.
$ZrF_4 \cdot 2(4\text{-}CH_3C_6H_4N)$	(*376*)	$ZrCl_4 \cdot NC(CH_2)_4CN$	(*261*)
$ZrF_4 \cdot 2\text{bipy}$	(*173*)	$ZrCl_4 \cdot NC(CH_2)_8CN$	(*261*)
$(Hf, Zr)(Cl, Br)_4 \cdot 2\text{py}$	(*52, 189, 447*)	$ZrCl_4 \cdot (C_2H_5)_2NCH_2CN$	(*262*)
$(Hf, Zr)Cl_4 \cdot 3\text{py}$	(*411, 447*)	$ZrCl_4 \cdot$phthalonitrile	(*191*)
$Zr(Cl, Br)_4 \cdot 2MeCN$	(*52, 189, 190, 411*)	$ZrCl_4 \cdot xPhNH_2$	(*411*)
$Zr(Cl, Br)_4 \cdot 2EtCN$	(*190*)	$Zr(Cl, Br)_4 \cdot N$-methylmorpholine	(*191*)
$Zr(Cl, Br)_4 \cdot 2$pyrazine	(*191*)	$(Hf, Zr)(Cl, Br)_4 \cdot$bipy	(*52, 446, 447*)
$ZrCl_4 \cdot 2NR_2H$	(*150*)	$(Hf, Zr)Cl_4 \cdot 1.5$bipy	(*109*)
$ZrCl_4 \cdot 2NR_3$	(*150*)	$(Hf, Zr)(Cl, Br)_4 \cdot$phen	(*446, 447*)
$ZrCl_4 \cdot 2(NCCH_2CN)$	(*261*)	$(Hf, Zr)(Cl, Br)_4 \cdot$temen	(*447*)

[a] temen, tetramethylethylenediamine; py, pyridine; bipy, bipyridyl; phen, *o*-phenanthroline.

little has been done with other donor atoms. Most of the work has been done with the tetrachloride, some with the bromide, and nothing or very little with the fluoride and iodide. A tabulation of the addition compounds containing metal–nitrogen bonds appears in Table II. A general review of the reactions of metal halides with ammonia and aliphatic amines has been published by Fowles (*187*).

The sparingly soluble methyl cyanide adduct acts as a nonelectrolyte in that solvent. The spectra of the zirconium tetrachloride–methyl cyanide and zirconium tetrachloride–ethyl cyanide adducts show strong absorptions at 45,660, 34,480, 27,780, and 44,250, 33,670, and 27,400 cm^{-1} (*190*) which are attributed to charge-transfer transitions. The corresponding bromides show similar transitions at a much lower frequency, 37,740, 25,510, 21,410, and 38,460, 25,380 and 20,620 cm^{-1}, respectively. The $ZrBr_4 \cdot 2MeCN$ product shows an additional peak of very high extinction coefficient at 47,390 cm^{-1} which is not found with other complexes. The rise in frequency of the C≡N mode in the ultraviolet spectra has been described as arising from a coupling of the M–N- and C≡N-stretching vibrations. The spectra of the 1:2 adducts cannot be unambiguously interpreted in terms of the stereochemistry of the molecules (*52*).

The pyrazine derivatives also show only low conductivities in acetonitrile leading to the conclusion that they are molecular in solution. The solubility is so low, however, that molecular weight determinations cannot be made (*191*). The absence of bands in the infrared spectrum of the pyrazine derivative at 960 and 1160 cm^{-1} indicates that both nitrogen atoms are coordinated in a bridge to two metal atoms. The morpholine and phthalonitrile adducts have analyses which only approximately approach the 1:2 composition (*191*).

The dinitrile adducts were obtained as powders from the reaction of excess nitrile with a suspension of zirconium tetrachloride in methylene chloride. It is interesting to note that as the methylene chain length increases, the ligand becomes bidentate to the same metal (*261*). In the dinitrile complexes, as in the methyl cyanide complexes, an increase in the C≡N-stretching frequency is observed, confirming the fact that coordination takes place through the nitrogen and not through the triple bond. With the ligand, diethylaminoacetonitrile, (*262*) it was impossible to prepare chelates in which normal coordination of the two nitrogen atoms was present because of the linearity of the CH_2–C≡N part of the molecule. The infrared spectrum of the zirconium tetrachloride adduct shows a decrease rather than the typical increase in the C≡N-stretching frequency, possibly indicating that here the triple bond is involved in chelate formation.

The report (*447*) of the formation of a 1:3 metal tetrahalide:pyridine adduct from the reaction of zirconium tetrachloride in neat pyridine is in contrast to the formation of the 1:2 adduct in the presence of a solvent. Heating the 1:3 complex under vacuum at 65°–75°C for 7 hours results in the removal of one pyridine molecule. The bromide, however, only formed the 1:2 adduct.

TABLE III

INFRARED ABSORPTION FREQUENCIES FOR TERTIARY AMINE COMPLEXES OF $ZrCl_4$, $ZrBr_4$, AND $HfCl_4$ IN THE REGION 450–245 cm^{-1}

Complex	Frequencies^a					
$ZrCl_4 \cdot 3py$		343s	330.5s	303vs		
$ZrCl_4 \cdot 2py$		339vs	332vs	300vs		
$ZrBr_4 \cdot 2py$					246vs	
$HfCl_4 \cdot 3py$				305vs	277vs	
$HfCl_4 \cdot 2py$		335m, b		303vs	283s	
$ZrCl_4 \cdot bipy$		340vs	334vs	304m	288w	
$ZrBr_4 \cdot bipy$					271vs	258vs
$HfCl_4 \cdot bipy$		341s	314vs	305vs	279m	
$ZrCl_4 \cdot phen$	361s	348.5vs	343vs	303vs	282s	
$ZrBr_4 \cdot phen$					268s	259s
$HfCl_4 \cdot phen$	347s	342.5s	331s	310vs	278.5m	
$ZrCl_4 \cdot temen$		343vs	334vs	298m	276w	
$ZrBr_4 \cdot temen$					268vs	
$HfCl_4 \cdot temen$		340s	319s	307vs	279s	

^{a} vs, very strong; s, strong; m, medium; w, weak; and b, broad.

The tertiary amines, trimethylamine and triethylamine, and the secondary amines, dimethyl, diethyl, and dipropyl, react with zirconium tetrachloride to form 1:2 addition compounds, whereas primary amines undergo ammonolysis reactions (*151*).

Metal–halogen frequencies for a number of complexes of C_{2v} symmetry are shown in Table III. There is little frequency displacement when changing the basicity of amine ligand. The additional band observed for the *o*-phenanthroline compound is indicative of some less symmetrical structural feature of this complex compared to the others.

2. *Amides, Imides, and Dialkylamino Compounds*

Zirconium tetrachloride in liquid ammonia at −35°C yields a precipitate, which after being washed with liquid ammonia has the composition Zr:Cl:N (1.00:2.90:6.04), indicating that only one chloride has been lost in an ammonolysis reaction. About 7% of the zirconium originally present remained soluble in the ammonia solution. This increased to 33% when the insoluble product was heated *in vacuo* to 100°C between washings. The insoluble material then had the composition Zr:Cl:N (1.00:2.54:5.08). The freshly formed suspensions of ammonolysis products were titrated with sodium or potassium in liquid ammonia using a conductiometric technique to follow the reaction. No definable products were obtained, although the data are interpreted in terms of imide formation, followed by metal attack of the acid imide protons (*25*).

Zirconium tribromide also reacted in liquid ammonia to give a dark brown precipitate and a similar colored solution (*25*). Addition of potassium amide resulted in the formation of additional precipitate and blue solution. The precipitate as finally recovered from the solution was black, and had the composition Zr:N:K (1.00:3.25:1.69). The presence of the blue color was taken to indicate the reduction of potassium ion to the metal and oxidation of the zirconium to the four state with the formation of ammonolyzed products.

The compound $Zr(NH_2)_2$ is said to be the product of a reaction in which $K_2Zr(SCN)_6$ in liquid ammonia is treated with potassium amide. It is an insoluble, yellow, amorphous solid (*482*).

The reactions of the hexachlorozirconate anion as the ammonium, rubidium, and cesium salts, with anhydrous liquid ammonia at –35°C, results in a soluble portion containing up to 90% of the zirconium and an insoluble portion which appears to be identical with the product obtained from the reaction of ammonia and zirconium tetrachloride, namely, $ZrCl_3(NH_2)\cdot xNH_3$ (*153*). It is probable that the hexachlorozirconate first dissolves in ammonia and then undergoes solvolysis similar to that found for reactions with aliphatic amines (*152*). The reactions which occur may be expressed in the following equations.

$$(NH_4)_2ZrCl_6 + NH_3 \rightarrow (NH_4)_2[ZrCl_5(NH_2)] + NH_4Cl \qquad (3)$$

$$(NH_4)_2[ZrCl_5(NH_2)] \rightarrow ZrCl_3NH_2 + 2\ NH_4Cl \qquad (4)$$

The rubidium and cesium salts appear to be ammonolyzed to the same extent.

The reaction of the hexachlorozirconate anion as an alkylammonium salt $(RH)_2ZrCl_6$, where $R = C_2H_5NH_2$, $(CH_3)_2NH$, $(C_2H_5)_2NH$, $(CH_3)_3N$, and $(C_2H_5)_3N$, with excess of amine (*152*), results in no product with tertiary amines, and very slow solvolysis with secondary amines. A product with a Zr:N ratio of 1:2.49 with diethylamine was obtained after 8 weeks, and a product with a Zr:N ratio of 1:2.86 with dimethyl-amine after 6 weeks. The ethylamine salt reacted rapidly with excess ethylamine to give a product corresponding to the composition $(C_2H_5NH_3)_2[ZrCl_5(NHC_2H_5)]$.

The compounds of general composition $M(NR_2)_4$, where M is zirconium and R is methyl, ethyl, *n*-propyl, or *i*-butyl were prepared either by treating the metal tetrachloride with the appropriate lithium dialkylamide or by ammonolysis of a tetrakisdialkylaminometal compound with another dialkylamine (*75*). The latter method may give dialkylamino derivatives of the type $M(NR_2)_x(NR')_{4-x}$, where R′ is ethyl, *n*-propyl, *i*-propyl, and *i*-butyl. The reaction may be expressed by the following equations.

TABLE IV

DIALKYLAMINO DERIVATIVES OF ZIRCONIUM

Compound	Boiling point (°C)/mm	Color
$Zr(NMe_2)_4$	80/0.05 (m.p. 70°C)	White
$Zr(NEt_2)_4$	120/0.1	Green
$Zr(NPr^n_2)_4$	165/0.1	Green
$Zr(NMe_2)_2(NPr^i_2)_2$	100/0.05 (subl.)	Green
$Zr(NC_6H_{12})_4$	190/0.1	Blue
$Zr(NC_7H_{14})_4$	200/0.05	Red
$Zr(NEt_2)_3(NPr^i_2)$	112/0.05	Green
$Zr(NBu^i_2)_4$	180/0.1 (subl.)	Green
$Zr(NC_5H_{10})_4$	190/0.2 (m.p. 80°C)	Brown

$$MCl_4 + 4\ LiNR_2 \rightarrow M(NR_2)_4 + 4\ LiCl$$

$$M(NR_2)_4 + xR'_2NH \rightarrow M(NR'_2)_x(NR_2)_{4-x} + xR_2NH$$

These compounds (Table IV) can be distilled or sublimed *in vacuo* and are soluble in common organic solvents, readily hydrolyzed, and converted by alcoholysis into metal alkoxides. Molecular weight determinations in boiling benzene show that the dimethylamino derivatives are significantly polymerized, whereas the diethylamino derivatives are monomeric.

The addition of tetrakis(dimethylamino)zirconium to an excess of metal carbonyl in the absence of light at room temperature caused an exothermic reaction but no evolution of carbon monoxide. The following compounds are reported: $Zr(NMe_2)_4 \cdot 2Ni(CO)_4$, $Zr(NMe_2)_4 \cdot 2Fe(CO)_4$,

TABLE V

AMINE DERIVATIVES OF ZIRCONIUM AND HAFNIUM

Composition	Color	Form	Boiling point (°C)/mm	Preparation[a]
$(\pi\text{-Cp})Zr(NMe_2)_3$	Yellow	Slightly vicous liquid	94–96/0.05	2
$(\pi\text{-Cp})_2Zr(NMe_2)_2$	Yellow	Crystals	110–120/0.05	1, 3
$(\pi\text{-Cp})_2Hf(NMe_2)_2$	Yellow	Solid	120–125/0.02	1
$(\pi\text{-Cp})_2Zr(NEt_2)_2$	Orange-yellow	Solid	120–130/0.03	1
$(\pi\text{-Cp})_2Hf(NEt_2)_2$	Yellow	Crystals	120–130/0.03	1
$[Me(\pi\text{-}C_5H_4Me)]_2Zr(NMe_2)_2$	Red-brown	Waxy solid	125–135/0.11	1
$IndZr(NMe_2)_3$	Orange	Viscous liquid	144/0.15	1
$(Me_2N)_2Zr[N(SiMe_3)_2]_2$	White	Crystals	120–140/0.04	1

[a] See text.

$Zr(NMe_2)_4 \cdot 2Mo(CO)_6$, and the corresponding hafnium compounds. The structural features of these products are unknown (*70*).

The reaction of $Zr(N(CH_3)_2)_4$ with $CH_3O_2CC{\equiv}CCO_2CH_3$ at reflux temperatures in diethyl ether or light petroleum results in –C–C– insertion into the Zr–N bond to yield $(CH_3O)_2Zr[C(CO \cdot N(CH_3)_2){:}C(CO_2CH_3) \cdot N(CH_3)_2]_2$ in 23% yield. The product melts above 240°C with decomposition (*99, 100*).

It was found (*45*) that an excess of aniline added to tetrakis(diethylamino)zirconium in the absence of a solvent, results in a distillate of diethylamine and a solid product approximating $Zr(NHPh)_4$. Aniline is lost on standing to give $Zr(NPh)(NHPh)_2$. In hydrocarbon solvents at 0°–5°C, products of composition $Zr(NR)(NHR)_2$ (where $R = Ph$, Bu, Pr, or Et) are slowly formed. When methylamine or ammonia is added to tetrakis(diethylamino)zirconium in light petroleum ether at –80°C, a precipitate is formed with a zirconium content intermediate between $Zr(NHR)_4$ and $Zr(NR)(NHR)_2$ (where $R = Me$ or H). Attempts to obtain $Zr(NH)_2$ by heating the product of the reaction between ammonia and tetrakis(diethylamine)zirconium, also gave a product with a composition between that of $Zr(NH)_2$ and $Zr(NH)(NH_2)_2$.

The chemistry of zirconium and hafnium amides has been investigated further (*101*) using the general reactions of (1) metal amide with excess protic compound, (2) metal amide with a stoichiometric amount of protic compound, and (3) the reaction of a metal chloride with lithium dimethyl amide. The compounds prepared are listed in Table V. They are all monomeric. Hafnium amides have not been described before, although there is a reference by Bradley (*70*) to the reaction of hafnium amide with carbon disulfide and metal carbonyls.

3. *Halonitrides*

Zirconium tetrahalides form addition compounds with gaseous ammonia, which when heated at an elevated temperature yield products of general composition ZrNX (*272* to *276*). The original products usually have a composition such as $Zr_{1.2}N_{1.2}I$, which when heated with ZrX_4 at 900°C for additional time, yield products which more closely conform to the composition ZrNX. The zirconium halide nitride can also be prepared from the reaction of the zirconium nitride with the corresponding halide. The chloride and bromide may be obtained in two different crystallographic forms. The low-temperature α form obtained at about 400°C is very much less stable to hydrolysis and chemical attack than the high-temperature β form. When heated (750°C for the iodide and somewhat higher temperatures for the chloride and bromide) a dark blue zirconium nitride of composition Zr_xN (where $0.940 > x > 0.812$) is obtained. At slightly lower temperatures, brown Zr_3N_4 is obtained; either product yields yellow ZrN at 1000°C. The low-temperature α forms of the chloride and bromide were always contaminated with other ammonolysis products. Purer products and better crystals can be obtained by heating in an atmosphere of ZrX_4 at 900°–1000°C, although if the heating period is too long the β forms are obtained. Heating ZrF_4 in ammonia leads to $ZrN_{0.91}F_{1.27}$ (*277*).

TABLE VI

CRYSTALLOGRAPHIC PARAMETERS OF ZrNX COMPOUNDS

	Parameter		
Compound	*a*	*b*	*c*
α-ZrNCl	4.08	3.52	8.57
α-ZrNBr	4.11_6	3.58_1	8.70_1
α-ZrNI	4.11_4	3.72_4	9.43
β-ZrNCl	2.08_1	—	9.23_4
β-ZrNBr	2.10	—	9.75

Compound	N^{3-}–N^{3-}	N^{3-}–Zr^{4+}	Zr^{4+}–X	X–X
α-ZrNBr	2.79	2.12	2.85	3.77
ZrNI	2.81	2.16	2.95	4.17
β-ZrNCl	2.80	2.12	2.68	3.74
βZrNBr	2.80	2.12	2.82	3.91

The α forms and ZrNI are orthorhombic with a FeOCl-type layer lattice (D_{2h}^{13}). Zirconium ions are tetrahedrally bonded to two nitride and two iodide ions. In the direction of the *b* axis there are I–Zr zigzag chains which are joined by Zr–N chains in the direction of the *a* axis. The β forms are hexagonal with a random sequence of XZrNNZrX layers. The $Zr_2N_2^{2+}$ unit occupies a site equivalent to Cd^{2+} in the $CdBr_2$ structure. The crystallographic coordination number of each of the ions is six. The Zr^{4+} ions sit in distorted octahedral holes formed by three nitrogens and three halogens. The halogens have three halogens from the next layers and three zirconium ions as nearest neighbors, and the nitride ions have three other nitride ions and three zirconium ions as nearest neighbors. The crystallographic parameters of these compounds are tabulated in Table VI.

4. *Dipyridyl Complexes*

The zerovalent diamagnetic complex Zr(2,2′-dipyridyl)$_3$ was prepared by treating zirconium tetrachloride in THF with three moles of dipyridyl and then with dilithium dipyridyl. Copper-colored, air-sensitive crystals were obtained from the green solution. They were soluble in dioxane, THF, pyridine, and benzene, but insoluble in water and alcohol, and only slightly soluble in ether (*242*). Elemental iodine oxidized the zirconium(0) to zirconium(IV). Addition of an excess of Li_2dipy resulted in a change of color of the THF solution from the green of the tris compound to a blue-violet color with simultaneous precipitation of black-violet shiny metallic needles. Analysis of the crystals gave the composition $Li[Zr(dipy)_3]\cdot 4THF$. The effective magnetic moment is 1.70 B.M. at room temperature. The THF could be removed by heating to 80°–200°C *in vacuo*. If elemental lithium is used as the reducing agent, black crystals are obtained from an olive-green solution that have the composition $Li_2[Zr(dipy)_3]\cdot 8THF$. In high vacuum 7.71 moles of THF can be removed. The product is pyrophoric and the solutions are easily oxidized to zirconium(IV). The effective magnetic moment is 1.10 B.M. at room temperature (*243*).

5. *Thiocyanates*

The separation of zirconium and hafnium by liquid–liquid partition of their thiocyanates, a process first reported by Fischer in 1947, is in 1969 still the most important process for the commercial production of hafnium-free zirconium (*184*, *185*, *514*). The detailed equilibrium study of the process is difficult because of the complexity of the systems and high concentrations of the electrolytes used, the ease of oxidation of thiocyanic acid, and the hydrolysis of the zirconium and hafnium ions. Although Fischer originally used ether as the solvent, presently a hexanone is used. The extractable species appears to be the neutral tetrathiocyanato species, with hafnium being preferentially extracted into the organic phase. The extraction coefficients pass through a maximum as the thiocyanate concentration increases, falling off at higher concentrations owing to the formation of nonextractable anionic species. The partition coefficients decrease with increasing HSCN concentration in the organic phase as the concentration of free solvent goes down. The addition of ammonium sulfate to the aqueous phase leads to a decrease in partition coefficients, but the decrease is greater for zirconium than for hafnium, thus improving the separation factor.

Attempts to prepare normal zirconium tetrathiocyanate by evaporating the solution resulting from mixing equivalent quantities of zirconium sulfate and barium thiocyanate yielded, after removal of the precipitated barium sulfate, only decomposition products of thiocyanic acid. If excess thiocyanic acid present is extracted with diethyl ether, only solid glass-like residues are obtained upon evaporation of the extracted solution. Attempts to salt out the product with ethanol, acetone, or dioxane give a product of composition $ZrO(NCS)_2 \cdot 2H_2O \cdot 1.5C_4H_8O_2$ (*556*). Solutions of zirconium thiocyanate, when mixed in a 1 : 3 mole ratio with a solution of an alkali metal thiocyanate, give, upon partial evaporation, large crystals of composition $M[ZrO(OH_2)(NCS)_3]H_2O$. These compounds lose one mole of water at 110°C, and a second at 160°C with decomposition. The infrared spectra (*291*) show an absorption in the 480–500 cm^{-1} range which is attributed to nitrogen-bonded thiocyanates. There is also an absorption in the 910–920 cm^{-1} region which the authors attribute to the presence of $Zr{=}O$ and which has been confirmed by Selbin (*486*). Similar compounds have been prepared with hafnium (*557*), for which the infrared spectra are very similar (*292*) with the ν HfO found in the 930–940 cm^{-1} region and the NCS deformation at 480–513 cm^{-1}.

The reaction of zirconium and hafnium with thiocyanate ion was studied spectrophotometrically (*214*) at thiocyanate concentrations over the range 0.002 to 0.18 *M*, free perchloric acid concentrations of 0.1 to 0.8 *M*, and at high metal ion concentrations. Experiments were interpreted to show that a series of complexes from $MNCS^{3+}$ to $M(NCS)_4^{8-}$ were formed. At high thiocyanic acid concentrations, the zirconium is converted to an anionic species much more readily than the hafnium.

The extraction of zirconium and hafnium thiocyanate species from aqueous solution has been studied using other solvents, among them, isobutyl ketone (*514*), diisoamylmethyl phosphate (DIAMP) (*513*), and acetophenone (*405a*). Extractions made with diisoamylmethyl phosphate from solutions containing zirconium and hafnium sulfate (10–20 gm/liter), sulfuric acid (0.1–0.5 *N*), and varying amounts of ammonium thiocyanate indicate that the species extracted has the composition $M(OH)_2(NCS)_2 \cdot 2DIAMP$.

6. *Ferrocyanides*

When a solution of zirconium oxychloride reacts with $M_4[Fe(CN)_6]$, the composition of the product depends on the initial ratio of reactants and the hydrogen ion concentration (*259*, *531*). When $Fe(CN)_6^{4-}:Zr(IV)$ is 0.25, the precipitate has the composition $[ZrO(OH)]_4[Fe(CN)_6] \cdot nH_2O$; when the ratio is 0.33, the product has the composition $[Zr_3O_3(OH)_2][Fe(CN)_6] \cdot 11H_2O$. The normal ferrocyanide is obtained at acid concentrations greater than 1 *M*. The ferrocyanide acts as an ion exchanger with properties similar to those of the phosphate. The alkali metals are absorbed and may be eluted with ammonium ions, with lithium coming off first and cesium last (*322*).

7. *Miscellaneous Ligands*

a. Schiff Bases. Zirconium oxychloride dissolved in methanol, when added to an aldehyde solution in diethyl ether, followed immediately by addition of a diethyl ether solution of benzidine ($H_2NC_6H_5C_6H_5NH_2$), results in a Schiff base condensation accompanied by precipitation of a product containing the base, zirconium, hydroxide, and chloride. In a few instances the hydroxide appeared to be absent. The insolubility in organic solvents and rather low thermal stability (dec. <100°C) suggest a polymeric structure for these products (*346*).

Bis(acetylacetonethylenediimine), (H_2L), in methanol reacted with zirconium oxychloride in the same solvent to produce ($ZrCl_2L$), which was precipitated from solution upon addition of ether. A dark resinous product of composition ZrL_2 was obtained when a mixture of solid H_2L and zirconium oxychloride was heated *in vacuo* at 250°C for 5–6 hours (*347*).

Salicyldioxime reacts with acid solutions of zirconium(IV) and hafnium(IV) to form colorless 1:1 complexes. When the pH is raised to 6.0, the product precipitates as a gelatinous mass. Chelation is assumed to be through the oxime oxygen and adjacent hydroxyl group with the loss of two protons (*350*).

b. Cupferron. N-Phenyl-*N*-nitrosohydroxylamine anion has long been used as an analytical reagent for zirconium(IV). It has been previously noted (*283*, *285*) that the composition of the cupferronates is variable and depends on time, acidity, and method of preparation. A precipitate of composition $Zr[C_6H_5N(NO)O]_4$ can be obtained from solutions of zirconium(IV) in hydrofluoric acid, concentrated nitric acid, or sulfuric acid of not less than 2 *N* (*283*).

c. 1,3-Diphenyltriazenide. Zirconium tetrachloride in dry diethyl ether or hydrocarbon, when shaken with a slight excess of the 1,3-diphenyltriazenidosilver(I) under nitrogen, gave a precipitate of silver chloride and a solution of $Zr(dpt)_4$. The product can be recovered from the solvent as a dark red crystalline compound which melts at 230°C. It is a monomer in diethyl ether (*90*).

d. 8-Hydroxyquinoline. Although 8-hydroxyquinoline has been used as a precipitant for zirconium and hafnium, its use as an analytical reagent has been negated by the difficulty of obtaining a product of known composition. It has been reported (*460*, *580*) that if 8-hydroxyquinoline is added to acid solutions of zirconium(IV) salts containing an excess of oxalic acid, followed by the addition of ammonia while the solution is heated to 80°–90°C, the precipitate formed, after washing and drying at 130°–140°C, is the stoichiometric 1:4 complex $Zr(C_9H_6ON)_4$.

e. Diantipyrinylmethane and Pyramidone. Zirconium (2×10^{-5} *M*) in HCl ranging from 0.1 to 1 *M* forms 1:2 and 1:3 complexes with diantipyrinylmethane (*37–39*). The equilibrium constant for the dissociation of this complex is 3.1×10^{-12}.

Pyramidone (pyr) forms a complex of composition $Zr(OH)_3{}^+$pyr whose instability constant is $(2.6 \pm 0.5) \times 10^{-7}$ (*505*).

Many other organic ligands have been studied for use as analytical reagents for zirconium and hafnium, but will not be treated here. This subject is adequately reviewed in the monograph by Elinson and Petrov (*162*).

B. PHOSPHORUS AND ARSENIC ATOMS AS LIGANDS

Compounds of zirconium and hafnium metal tetrahalides with the bidentate ligands $(\phi)_4As_2C_2H_4$ and $(\phi)_4P_2C_2H_4$ were prepared (*447*) by the reaction of the tetrahalide and the ligand in a suspension in benzene. These are presumably species with a coordination number of eight. The infrared absorption frequencies in the 460–250 cm^{-1} region are tabulated in Table VII.

The first diarsine complex with a known coordination number of eight was prepared from *o*-phenylenedimethyldiarsine (*110–114*) and titanium tetrachloride in THF. Similarly prepared $(Zr,Hf)Cl_4 \cdot 2$(diarsine) compounds are white, insoluble products. They do not melt but rather decompose (290° and 284°C for zirconium and hafnium, respectively).

TABLE VII

INFRARED ABSORPTION FREQUENCIES OF DITERTIARY PHOSPHINE AND DITERTIARY ARSINE COMPLEXES

Complex	Frequencies[a]					
$ZrCl_4(diph)_2$	447.5w	414w	353s	345vs	301b	
$ZrBr_4(diph)_2$						257vs
$HfCl_4(diph)_2$		415w	343s	324vs	303w	278s
$ZrCl_4(diar)_2$	457m		335vs	316vs, b		
$ZrBr_4(diar)_2$			322w		301m	281m, b
$HfCl_4(diar)_2$			340s, b		293vs, b	

[a] See Table III for abbreviations.

The strong infrared bands for the methyl rocking mode at 884 and 846 cm^{-1} and for the C–H deformation at 741 cm^{-1} of the free ligand appear 20 cm^{-1} higher in the complexes, which is consistent with bidentate chelation. The zirconium and hafnium bis(diarsine) complexes are isomorphous with the $TiX_4 \cdot 2$diarsine complex for which the crystal structure is known (Fig. 2). In this structure the point symmetry is

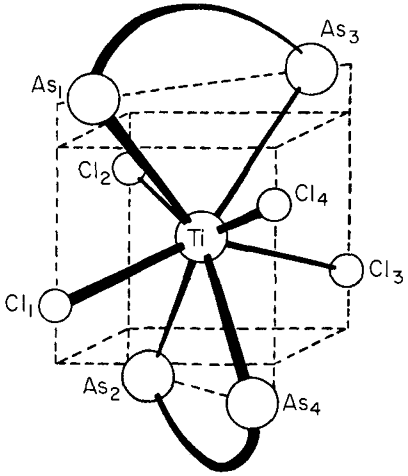


FIG. 2. Structure of $TiCl_4 \cdot 2$ diarsine. Reproduced by permission, from R. J. H. Clark, J. Lewis and R. S. Nyholm, *J. Chem. Soc.* p. 2463 (1962).

$\bar{4}2m$ with all the atoms in the molecule except the methyl groups lying on mirror planes. The eight donor atoms sit at the vertices of two interpenetrating tetrahedra, one flattened and one elongated along the fourfold axis. The chloride atoms are in positions which are potentially double-bonding by π-electron donation to the empty *d* orbitals on the metal.

It has been observed that *(110)* zirconium tetrachloride reacts immediately with diarsine in THF, whereas the reaction with hafnium tetrachloride is much slower. A similar observation was made with the bromide. This is the basis for a separation process for zirconium and hafnium. Equimolar proportions of the tetrachlorides were dissolved in THF and enough diarsine was added to precipitate 86% of the zirconium. The white precipitate which was filtered after 10 minutes was found to contain 35% of the zirconium originally present. The cost of the ligand hardly makes this a practical method of separation, but the idea of a process based on differences in rates of reaction is an important idea to pursue in other systems.

The compounds $C[CH_2PMC_6H_5]_4$ (where M = Na or K) act as quadridentate reagents, and may be used in the production of covalent spiroheterocyclic products containing zirconium. The potassium compound, with Cp_2ZrCl_2 in tetrahydrofuran, results in the precipitation of potassium cyclopentadienide and a solution from which may be recovered the product $Cl_2Zr[C(CH_2PC_6H_5)_4]ZrCl_2$, 3,3,9,9-tetrachloro-2,4,8,10-tetraphenyl-2,4,8,10-tetraphospha-3,9-dizirconaspiro[5.5]undecane, in 10% yield. The sodium compound, on the other hand, results in the precipitation of sodium chloride and a solution from which may be recovered the product in which cyclopentadienyl rings are retained in place of the chloro groups (*163*). This product is recovered almost quantitatively. It melts with decomposition at 270°C. Both products are very sensitive to air and moisture. They are soluble in tetrahydrofuran and ethyl alcohol, slightly soluble in benzene, and insoluble in hydrocarbons. They are nonelectrolytes in tetrahydrofuran.

Bis(π-cyclopentadienyl)zirconium moieties are presumed to be bridged by dialkyl-substituted phosphines in the products $[Cp_2MPR_2]_2$, obtained by the reaction of $(\pi\text{-Cp})_2ZrX_2$ with $LiPR_2$ (R = ethyl or butyl) in THF. The ethyl compound was obtained in a 71% yield of red-brown crystals which melt at 280°–282°C (dec.), and the butyl compound was obtained in a 59% yield of red-brown crystals which melt at 238°–240°C (dec.). Both compounds are sensitive to air and moisture.

V. Compounds with Metal–Oxygen or Metal–Sulfur Bonds

A. OXYGEN LIGANDS—ORGANIC MULTIDENTATE GROUPS

1. *Diketone Derivatives*

a. Tetrakis Species. Comparison of the X-ray data for tetrakis(2,4-pentanedionato)zirconium(IV) and the corresponding thorium compound of known antiprismatic structure led Grdenic and Matkovic (*222*) to assign the same structure to the zirconium compound. The definitive crystal structure was done by Silverton and Hoard (*512*) who found that the zirconium chelate does indeed have a symmetry approximating D_2-222. Of the three possible arrangements for four symmetrical bidentate ligands, the one predicted by Hoard (*244*) as the most favorable is the one found in the crystal (Fig. 3). Actually the edges of the parallel faces spanned by the ligands are somewhat shorter than the other two edges, giving rectangular rather than square faces. The two ligand rings which emerge at opposed edges of the rectangular face fold away from one another at an angle of 22.6° from the plane bearing the oxygen atoms. The mean Zr–O and C–O bond distances are 2.198 and 1.270 Å, respectively, while the mean value of the O–Zr–O bond angle is 74.96°.

A glance at the structure of tetrakis(2,4-pentanedionato)zirconium(IV) shows that one methyl group of an acetylacetone ligand on the upper face, and a second methyl group of a ligand on the lower face are aligned such that there is some interference between them. The other methyl group on each ring is free from this nonbonding interaction. If this structure is maintained in solution, and if the species is inert, then two different methyl proton resonances should be seen in the NMR spectrum of this compound. In fact (*4*), only a single methyl proton resonance at 1.83 ppm (relative to TMS) is observed in benzene at 33°C. Similarly, the chelation of four unsymmetrical bidentate ligands, as in tetrakis(1,1,1-trifluoro-2,4-pentanedionato)zirconium(IV), should yield geometrical isomers, which in solution, should show different F^{19} resonances if the species were kinetically inert. In fact (*431*), only a single fluorine-19 resonance has been observed for this compound even down to –105°C. These data suggest that the ligands are in rapid equilibrium with one another and that the existence of discreet isomers is not likely. This hypothesis was verified by both the methyl proton and fluorine resonance

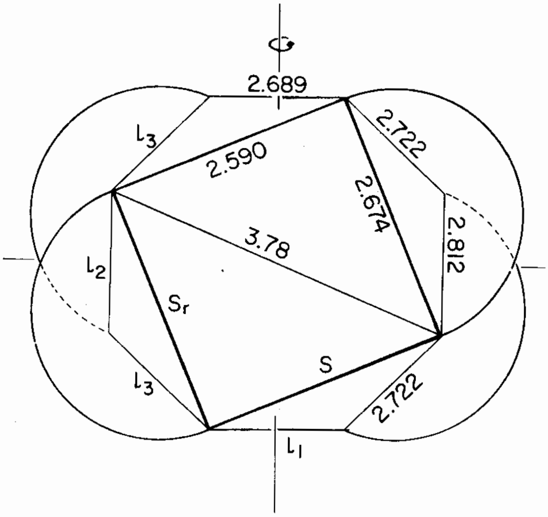


FIG. 3. Structure of tetrakis(2,4-pentanedionato)zirconium(IV). Dimensions of the antiprismatic coordination group averaged in accordance with D_2-222. Reproduced by permission, from J. V. Silverton and J. L. Hoard, *Inorg. Chem.* **2**, 246 (1963).

spectra (*4, 5, 431*) of a mixture of tetrakis(1,1,1-trifluoro-2,4-pentanedionato)zirconium(hafnium)(IV) and tetrakis(2,4-pentanedionato)-zirconium(hafnium)(IV) in benzene and other solvents. In benzene particularly, resonances for the methyl protons in species of all combinations of the two ligands, $Zr(Hf)(acac)_{4-x}(tfac)_x$, are observed. A comparison of the calculated mole fraction of each of the species based on random distribution of the ligand and the actual composition of the solutions as determined from the NMR spectra, shows that the mixed complexes are favored over $M(tfac)_4$ and $M(acac)_4$. The enthalpy changes for the exchange reactions were found to be essentially zero, while the entropy changes were 1–3 e.u. in excess of the entropy changes expected for the random scrambling of the ligands (*431*).

The kinetics of the ligand exchange between zirconium and hafnium chelates and the free β-diketone were studied by NMR techniques (*6*). The exchange of metal acetylacetonates with free ligand in chlorobenzene and the exchange of the metal trifluoroacetylacetonates with free ligand in benzene and chlorobenzene were first-order in both metal complex and free ligand. A possible mechanism for the exchange path includes: (1) the rapid breaking and reforming of one of the metal–oxygen bonds to yield a 7-coordinate species, (2) the addition of a ligand molecule to regain 8-coordination, (3) the exchange of the proton from the entering to the leaving group, (4) the rupture of the metal–oxygen bond to return a ligand molecule to solution, and (5) a metal–oxygen bond formation to return to a species in which all the ligands are bidentate. The rate of acetylacetone exchange is faster in the zirconium compounds than in the hafnium compounds, and probably means that a metal–oxygen bond breaking is involved in the rate-determining step. There is no detectable difference in the rate of exchange for trifluoroacetylacetone ligands with zirconium or hafnium complexes. It is likely that for this ligand the rate-determining step is either step (2) or step (3). The acetylacetone exchange in benzene has a different rate law. Whereas the order with respect to the metal complex is one, the order with respect to the free ligand increases as the acetylacetone ligand concentration increases. No mechanism has been presented to explain this.

The proton NMR spectra of the tetrakistropolonates of zirconium and hafnium in dimethyl sulfoxide has also been examined. The spectra are consistent with a complex in which all four ligands are equivalent, but there is no evidence for rapid exchange between the chelates and free ligands (*379*). Similarity in chemical shifts for the tropolone and chelate resonances, however, makes a definitive statement difficult. Attempts to form a 10-coordinate species with tropolone were unsuccessful (*377*).

A variety of other tetrakis, monosubstituted tris, and disubstituted bis chelates have been prepared using the following methods.

1. Metal tetrahalide and diketone

$$\mathrm{MX_4} + n\mathrm{HAA} \xrightarrow[\text{organic solvent}]{\text{reflux}} \mathrm{M(AA)}_n\mathrm{X}_{4-n} + n\mathrm{HX}$$

2. Metal chelate and diketone

$$\mathrm{M(acac)_4} + n\mathrm{HAA} \xrightarrow[\text{vacuo}]{\text{heat in}} \mathrm{M(AA)}_n\mathrm{(acac)}_{4-n} + n\mathrm{Hacac}$$

3. Metal alkoxide and diketone

$$\mathrm{M(OEt)}_{4-x}\mathrm{Cl}_x + n\mathrm{HAA} \xrightarrow{\text{benzene}} \mathrm{M(AA)}_n\mathrm{X}_{4-n} + (4-x)\mathrm{EtOH} + (x+n-4)\mathrm{HX}$$

4. Hydrated salt and diketone

$$\begin{array}{rcl} \mathrm{MOX_2\cdot 8H_2O} & & \mathrm{M(AA)}_n\mathrm{X}_{4-n} + (n-2)\,\mathrm{HX} + 9\,\mathrm{H_2O} \\ \mathrm{M(SO_4)_2\cdot 4H_2O} + n\mathrm{HAA} & \xrightarrow[\text{chloroform}]{\text{ethanol or}} & \mathrm{M(AA)}_n\mathrm{(SO_4)}_{4-n/2} + n/2\,\mathrm{H_2SO_4} + 4\,\mathrm{H_2O} \\ \mathrm{M(NO_3)_4\cdot 5H_2O} & & \mathrm{M(AA)}_n\mathrm{(NO_3)}_{4-n} + n\mathrm{HNO_3} + 5\,\mathrm{H_2O} \end{array}$$

5. Metal tetrahalide and chelate

$$\text{a.}\quad \mathrm{MX_4} + a\mathrm{M(AA)_4} \xrightarrow[\text{reflux}]{\text{THF}} (a+1)\mathrm{M(AA)}_n\mathrm{X}_{4-n}$$

$$\text{b.}\quad a\mathrm{MX_4} + b\mathrm{Fe(acac)_3} \longrightarrow a\mathrm{M(acac)}_n\mathrm{X}_{4-n} + b\mathrm{FeX_3}$$

The specific diketones and method of preparation used for the chelates are given in Table VIII. In general, the tetrakis species are white to pale yellow in color, whereas the halosubstituted species are yellow and yield yellow solutions. In many instances there are discrepancies in the melting points reported by different authors. Although the possibility of different crystalline forms cannot be dismissed, the presence of hydrolytic impurities is the most likely explanation. The data given by Fay are considered the most reliable.

b. *Substituted Bis and Tris Chelates*, $M(AA)_2X_2$ and $M(AA)_3X$. The substituted bis and tris chelates which have been prepared are presented in Table IX. Fay and Pinnavaia (*174*, *432*) have observed that the solvent is important in determining whether the product of the reaction of zirconium tetrachloride and diketone is the tris or bis product. In diethyl ether the bis product is obtained and in benzene or carbon tetrachloride at higher temperature, the tris product. Carbon tetrachloride is preferred

TABLE VIII

TETRAKIS(DIONATO)METALLATES [M(AA)$_4$]

Metal	Diketone anion	Melting point (°C)	Method of preparation[a]	Ref.
Zr	1,1,1-Trifluoro-2,4-pentanedionato	130–131	1 (CCl_4)	*(375)*
	1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato	39–42	1 (CCl_4)	*(102)*
		152–154	1 (CCl_4)	*(374)*
	2,2,6,6-Tetramethyl-3,5-heptanedionato	—	—	*(160a, 511)*
	1,3-Diphenyl-1,3-propanedionato	238–239	2, 3	*(80, 594)*
	1-*p*-Biphenylyl-1,3-butanedionato	275–277	2	*(594)*
	1,3-Bis(*p*-biphenylyl)-1,3-propanedionato	302–303	1	*(594)*
	1-Phenyl-3-*p*-biphenyl-1,3-propanedionato	254–255	3	*(594)*
	1,3-Bis(1-naphthyl)-1,3-propanedionato	276–277	3, 4	*(594)*
	1,3-Bis(2-naphthyl)-1,3-propanedionato	278–279	3	*(594)*
	1,2,3-Triphenyl-1,3-propanedionato	210–220	1	*(594)*
	3-Butyl-2,4-pentanedionato	131.5–133 (dec.)	2	*(80)*
	Tropolone	300 (subl.)	1	*(379)*
Hf	Tropolone	300 (subl.)	1	*(379)*
	1,3-Diphenyl-1,3-propanedionato	238–239	2	*(594)*
	1,1,1-Trifluoro-2,4-pentanedionato	130–131	1 (CCl_4)	*(375)*
	1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato	47.5–49.5	1 (CCl_4)	*(102)*
	1-Phenyl-1,3-butanedionato	205.5–207.5	2	*(86)*

[a] See text.

for the preparation of the bromide, since in diethyl ether only an oil is obtained. It is important in the syntheses of the monohalo species to use sufficient solvent so that the disubstituted products remain in solution and react further to give the tris-substituted product. The iodide does not yield the disubstituted product in diethyl ether, only an impure $Zr(acac)_3I \cdot Et_2O$. In isopropyl ether and in the absence of a solvent, solvent-free monoiodide can be obtained. Tetrahydrofuran seems to be the best solvent for this reaction. No route was found by which pure fluoro-substituted species could be obtained. The tetrakis(2,4-pentanedionato) species is only slowly obtained by the reaction of the tetrachloride with the diketone, because the substitution of the last chloride is very slow unless water is present. In contrast to acetylacetone, certain aryl- and trifluoro-substituted diketones do give tetrakis products readily.

Pinnavaia and Fay (*432*) have found that the zirconium and hafnium species containing the same halogen are isomorphous, but the chloro species are not isomorphous with the bromo species. The monohalogen substitution products $M(acac)_3X$, except for the iodide show no significant dissociation as observed by molecular weight and conductivity experiments. In the case of the iodide in tetrahydrofuran, the ionic species is assumed to be $Zr(acac)_3^+$. In the chloro and bromo compounds it appears that the species in solution is the 7-coordinate molecule. The infrared spectra show that all the carboxyl groups are coordinated. The dihalo species in solution are assumed to be 6-coordinate since conductance data in nitrobenzene indicate only 2–5% dissociation.

The proton NMR spectra of the mono and dihalo complexes in dichloroethane, chloroform, and benzene consist of a single methyl proton resonance. This evidence for rapid configurational rearrangement seems to exclude the existence of isomers. Even at −130°C only one methyl proton resonance is observed. The rate constant for exchange of nonequivalent hydrogens at −130°C is estimated to be about 10 sec^{-1}. The cis configuration for the dihalo species is suggested by the pronounced downfield shifts of the methyl proton resonances as the halogen content of the solvent increases. It is assumed that these shifts reflect the dipolar character of the cis dihalo molecules (*432*).

The infrared spectra (*174*) show no absorptions above 1600 cm^{-1}, except for the C–H-stretching frequencies, thus supporting the conclusion that the products are free of hydrolytic impurities. The infrared spectra of $M(acac)_2X_2$, $M(acac)_3X$, and $M(acac)_4$ are generally similar to the spectra of other metal acetylacetonates in the chelating carbonyl stretching region. The observed carbonyl frequency shifts are in accord with the expectation that a coordination number increase results in a

TABLE IX

SUBSTITUTED BIS AND TRIS CHELATES [$M(AA)_2X_2$, $M(AA)_3X$]

Metal	Diketone anion	X	Melting point (°C)	Method of preparation[a]	Ref.
$M(AA)_2X_2$					
Zr	2,4-Pentanedionato	Cl	180.5–182	1(Et_2O)	*(174)*
		Cl	236	1(Et_2O)	*(131)*
		Cl	68–78	5a	*(194)*
		Br	185–186.5	1(Et_2O)	*(174)*
Hf	2,4-Pentanedionato	Cl	186–188	1(Et_2O)	*(174)*
		Br	190–192	1(Et_2O)	*(174)*
		NO_3	148–148.5	4	*(86)*
Zr	1,3-Diphenyl-1,3-propanedionato	Cl	271–273	5a	*(80)*
		Cl	231–234	5a	*(194)*
		NO_3	254–256	4	*(594)*
		$Zr(SO_4)_3$	>350	4	*(594)*
Hf	1,3-Diphenyl-1,3-propanedionato	NO_3	237–238	4	*(86)*
Zr	3-Butyl-2,4-pentanedionato	Cl	132.5–134 (dec.)	5a	*(80)*
Hf	1-Methyl-3-phenyl-1,3-propanedionato	NO_3	189.5–190	4	*(86)*

$M(AA)_3X$				
Zr 2,4-Pentanedionato	Cl	134	1(benzene)	(*131*, *443*)
	Cl	134–136	5b	(*131*)
	Cl	159.5–161	1(benzene)	(*174*)
	Cl	156–158	1(THF)	(*80*)
	Cl	143–148	1($CHCl_3$)	(*148*)
	Br	162.5–164	1(CCl_4)	(*174*)
	I	178–183 (dec.)	5(THF)	(*174*)
	I	171–172	1(isopropylether)	(*174*)
Hf 2,4-Pentanedionato	Cl	154–156	1(benzene)5a, 5b	(*131*)
	Cl	159.5–161	1(benzene)	(*174*)
	Br	161.5–163.5	1(benzene)	(*174*)
	NO_3	157–157.5	1(benzene)	(*86*)
Zr 1-Phenyl-1,3-butanedionato	Cl	122–124	1(benzene)	(*131*)
Hf 1-Phenyl-1,3-butanedionato	Cl	125–128	1(benzene)	(*174*)
Zr 1,3-Diphenyl-1,3-propanedionato	Cl	262	3, 4	(*594*)
	Cl	256–258	1(benzene)	(*131*)
	Br	280	1(benzene)	(*594*)
	I	233	1(EtOH or $CHCl_3$)	(*594*)
	NO_3	237	1(benzene or EtOH)	(*594*)
	$FeCl_4$	170	($CHCl_3$)	(*131*)
	$AuCl_4$	—	($CHCl_3$)	(*131*)
Hf 1,3-Diphenyl-1,3-propanedionato	Cl	258–268	1(benzene)	(*131*)
	Cl	259	4	(*594*)
	Cl	261–262	5a	(*86*)
Zr 1-*p*-Biphenylyl-1,3-butanedionato	Cl	255 (dec.)	1,3(benzene)	(*594*)

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[a] See text.

M–O bond distance increase, thus decreasing the M–O bond strength and increasing the C–O bond strength. The M–O frequencies were independent of the halogen present. The assignments of M–O modes are given in Table X.

A diketone without an enolizable γ hydrogen, 3,3′-dimethylacetylacetone, reacts with zirconium tetrachloride at 0°C in methylene chloride to give upon addition of hexane, a precipitate of the adduct $ZrCl_4 \cdot CH_3COC(CH_3)_2COCH_3$ (*26*). The gray-white product is reported to have a melting point of 163°–166°C. No reaction was observed with zirconium tetrafluoride under the same conditions. Substitution of acetylacetone for the 3,3′-derivative in the reaction system yielded only $Zr(acac)_2Cl_2$.

TABLE X

INFRARED AND RAMAN ASSIGNMENTS OF THE ACETYLACETONATES AND SUBSTITUTION PRODUCTS

	ν_s M–O		ν_{as} M–O		ν M–O
Compound	IR	Raman	IR	Raman	IR range
$Zr(acac)_2X_2$	460	459	450	~450	248–304
$Zr(acac)_3X$	450	449	435	~433	260–314
$Zr(acac)_4$	—	441	421	416	251–301
$Hf(acac)_2X_2$	463	461	447	~445	250–268
$Hf(acac)_3X$	454	452	433	432	243–262
$Hf(acac)_4$	—	446	422	417	233–267

c. *Aqueous Solution Equilibria.* Although many β-diketones have been studied for use in two phase separation processes for zirconium and hafnium (*578*), relatively few quantitative determinations of formation constants have been reported.

Peshkova *et al.* (*362, 363, 424–426, 428, 429*) have calculated formation constants for the equilibria described by the general equation

$$ZrK_n^{4-n} + K^- \rightleftarrows ZrK_{n+1}^{3-n} \qquad (5)$$

for the β-diketones, benzoylacetone (Bzac), acetylacetone (Acac), thenoyltrifluoroacetone (Tta), selenoyltrifluoroacetone (Sta), selenoylacetone (Sa), and dibenzoylmethane (Dbzm) at 25°C ± 0.1°, $\mu = 1.0$, metal ion concentrations ranging from 10^{-6}–10^{-7} mole/liter and pH value of 0 to 2. At these metal and hydrogen ion concentrations, the metal ion is assumed to be monomeric. Corrections for hydrolysis of the metal ion were made on only one set of data (*507*), the assumption apparently being that such a correction was not significant. The data of Freiser on acetylacetone (*328*) are included in Table XI for comparison even though the solution concentration (2.7×10^{-5} *M* Zr) and ionic environment differ from the conditions of Peshkova.

TABLE XI

SUCCESSIVE FORMATION CONSTANTS OF β-DIKETONE CHELATES

	Ligand	$\log k_1$	$\log k_2$	$\log k_3$	$\log k_4$	Ref.
Zr	Bzac	12.71	11.86	11.34	11.08	(*429*)
	Acac	8.38	7.58	7.26	6.86	(*328*)
	Sta	11.35	10.17	10.05	9.25	(*362*)
	Sa	12.11	11.82	11.09	10.37	(*428*)
	Tta	10.93	10.81	10.38	10.30	(*363*)
Hf	Bzac	11.68	11.29	10.28	10.78	(*424*)
	Acac	7.40	7.28	6.74	6.68	(*425*)
	Sta	10.46	10.28	9.48	9.48	(*426*)
	Sa	11.61	11.07	10.96	10.57	(*428*)
	Tta	10.80	10.64	10.06	10.02	(*426*)
	Dbzm	12.42	11.63	11.37	10.97	(*424*)

2. *Carboxylic and Hydroxycarboxylic Acids*

a. Carboxylic Acids. i. Oxalic acid. The zirconium(IV) oxalate ion system is the most thoroughly studied of the group. Much of the early work centered on the difficulty of obtaining a nonhydrolyzed oxalato species. Ion exchange studies (*34*, *165*, *166*, *300*) and conductiometric and potentiometric titrations (*545*) have been used extensively to study this system, with evidence having been obtained for $Zr(C_2O_4)^{2+}$, $Zr(C_2O_4)_2$, $Zr(C_2O_4)_3^{2-}$, $Zr(C_2O_4)_4^{4-}$, and even $Zf(Hf)(C_2O_4)_5^{6-}$ at pH 5.8–6.2.

The equilibrium constants for the formation of the species described in the equation

$$M^{4+} + nH_2C_2O_4 \rightleftarrows M(C_2O_4)_n^{4-2n} + 2nH^+ \qquad (6)$$

were obtained at 2 and 4 *M* hydrogen ion and metal ion concentrations of 5×10^{-6} *M* or less (*353*). At an ionic strength of 2.0, the equilibrium constants were, for zirconium $K_1 = 2.96 \pm 0.3 \times 10^5$ and $K_2 = 4.8 \pm 1.6 \times 10^9$, and for hafnium $K_1 = 1.36 \times 10^5$ and $K_2 = 5.3 \pm 0.8 \times 10^9$. Successive equilibrium constants, defined by the net equation,

$$M(C_2O_4)_n^{4-2n} + xC_2O_4^{2-} \rightleftarrows M(C_2O_4)_{(n+x)}^{4-2(n+x)} \qquad (7)$$

at pH 1.82, metal ion concentration of $4.8 \times 10^{-5}\,M$, and an ionic strength of 0.04 (20°C) were determined to be $K_1 = 1.35 \times 10^{11}$, $K_2 = 1.5 \times 10^{9}$, $K_3 = 4.53 \times 10^{6}$, and $K_4 = 1.07 \times 10^{6}$. The maximum number of oxalates bound to the zirconium was only four. These values were obtained from data on the mobility of zirconium ions in perchloric acid and sodium perchlorate solutions as a function of the oxalate : zirconium ratio (*506*).

The normal neutral oxalate $Zr(C_2O_4)_2$ has been prepared (*228*) by adding stoichiometric quantities of oxalic acid to a solution of zirconium tetrachloride in absolute methanol. Only oxy species were obtained from aqueous solution.

Salts of the trioxalatozirconate dianion have been reported (*65*) as being prepared by the addition of alcoholic solutions of the oxychloride, oxalic acid, and ammonium nitrate in the order presented and in the mole ratio 1 : 11 : 5. The potassium salt was prepared by addition of an aqueous solution of zirconium oxychloride to an aqueous solution of potassium hydrogen oxalate followed by precipitation with an alcohol–ether mixture. These authors also claim the production of $(NH_4)_3H_3[Zr(C_2O_4)_5]\cdot 1\text{–}1.5H_2O$ using the stoichiometric quantities of reagents in alcohol solution. The normal salt was obtained by passing gaseous ammonia over the acid salt.

The spectra of the trioxalatozirconates are characterized by the appearance of a doublet at about 800 cm^{-1} which is thought to be due to δ (O=C–O) + ν (Zr–O). Also present are absorptions characteristic of bidentate oxalate groups at 1650–1730 cm^{-1} (ν C=O), 1260–1240 cm^{-1} (ν C=O), and 900 cm^{-1} [ν C–O + ν Zr–O + δ (O=C–O)] (*289*). The spectra of the pentaoxalatozirconates show two groups of bands typical of bidentate oxalate groups and in addition the intense band at about 1660 cm^{-1} attributed to the antisymmetric stretch of the "uncoordinated" COO^- group. Thus the presence of five oxalato groups does not necessarily mean that the coordination number of eight has been exceeded in this compound (*289*).

A variety of methods (*65, 228, 434*) have been used to prepare soluble tetraoxalato salts. A suitable synthesis for potassium tetraxoalatozirconate(hafnate) (*267*) free of hydroxy species is one in which a zirconium(hafnium) oxychloride solution is added to a buffered solution containing a stoichiometric amount of potassium oxalate and half the amount of oxalic acid. The potassium tetraoxalatometallate pentahydrate is then precipitated upon slow addition of ethanol.

Insoluble compounds of composition $M_2[Zr(C_2O_4)_4]\cdot nH_2O$, where $M = Ca^{2+}$, Ba^{2+}, Cd^{2+}, and Pb^{2+}, have been prepared by the addition of a soluble metal salt, usually the nitrate, to a solution of potassium tetraoxalatozirconate (*228*). The insoluble alkali metal salts also have been prepared by the addition of 0.1 *M* M^{2+} nitrate solutions to a solution of 0.1 *M* Zr(IV) in 0.2 *M* nitric acid containing excess oxalic acid. Solubility measurements of these compounds led to the following solubility products for $M_2[Zr(C_2O_4)_4]$ at 25° ± 0.5°C: $K_{sp}(\mathrm{Ca}) = 1 \times 10^{-6}$; $K_{sp}(\mathrm{Sr}) = 2 \times 10^{-7}$; $K_{sp}(\mathrm{Ba}) = 5 \times 10^{-8}$ (*507*).

The structure of the tetraoxalatozirconate(hafnate) anion in the salt $Na_4M(C_2O_4)_4 \cdot 3H_2O$ was determined by Hoard and co-workers (*212*). Figure 4 shows the idealized dodecahedral, D_{2d}-$\bar{4}2m$, structure of this anion. The oxalate ions span edges of mutually interpenetrating trapezoids, whose planes intersect in the vertical $\bar{4}$ symmetry axis. The oxalate ions are flat within experimental error, although there is a slight twist of the rings at the zirconium atom. The O–Zr–O angle within each ring is 71.3°, the Zr–O_1, Zr–O_4 distance is 2.230 ± 0.014 Å, and the Zr–O_2, Zr–O_3 distance, 2.168 ± 0.024 Å. This structure had been predicted as the most likely structure of all the arrangements possible for this highly negatively charged anion (*244*).

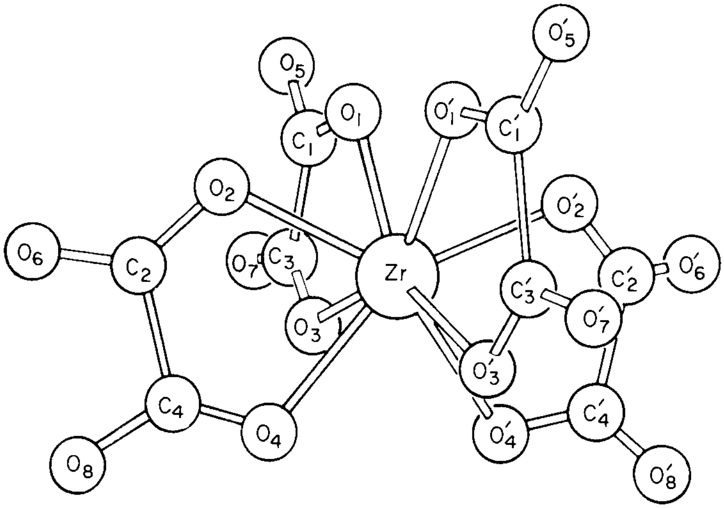


FIG. 4. Structure of the tetraoxalatozirconate anion in the salt $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$. Reproduced by permission, from G. L. Glen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.* **2**, 253 (1963).

The tetraoxalato species of zirconium and hafnium when dissolved in water produce an instantaneous increase in the hydrogen ion concentration and a corresponding quantity of a hydroxylated metallate species. In addition to hydrolysis, an aquation reaction is also likely.

A tentative value for the equilibrium constant for the reaction

$$\mathrm{Zr(C_2O_4)_4^{4-} + 2\,H_2O \rightleftarrows Zr(C_2O_4)_3(OH_2)_2^{2-} + C_2O_4^{2-}} \tag{8}$$

was found to be about 10^{-4} (*228*). This apparent lability of the oxalate ligand was confirmed in experiments using ^{13}C-labeled oxalate. Within the minimum 2 minutes required to complete the experiment, complete exchange of oxalate occurred even at 3°C, thus establishing the fact that the oxalate ligands are in rapid equilibrium with their environment (*266*).

The spectra of the tetraoxalates produced from aqueous solution is characterized by absorption bands typical of bidentate oxalate groups (*226*). Preparations from alcoholic solution, in addition, show a band of moderate intensity with a maximum at 1597 cm^{-1} which is assigned to the antisymmetric stretching frequency of the "uncoordinated" COO$^-$ group (*289*).

ii. Hydrolyzed oxalate species. We have seen that unless the oxalate and hydrogen ion concentrations are carefully controlled, hydroxy or oxo-oxolato species are obtained. The reaction of zirconium oxychloride and oxalic acid in the ratio of 2:1 in water yields upon addition of methanol and diethyl ether a precipitate of composition $\mathrm{[(ZrO)_2(C_2O_4)(H_2O)_6]Cl_2}$ (*606*). Similarly, 0.1 *M* methanol solutions of oxalic acid and zirconium oxychloride, when mixed, yield $\mathrm{ZrO(C_2O_4)\cdot 4H_2O}$.

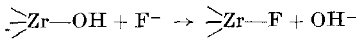
Saksin (*467*) established the presence of three zirconium complexes in solution, namely, $\mathrm{[ZrOC_2O_4(H_2O)]}$, $\mathrm{[ZrO(C_2O_4)_2^{2-}]}$, and $\mathrm{[(ZrO)_2(C_2O_4)]^{2+}}$, for which instability constants of 3.46×10^{-6}, 2.12×10^{-8}, and 3.27×10^{-9}, respectively, were calculated. Saksin also isolated a solid product of composition $\mathrm{Zr(C_2O_4)_2\cdot 2Zr(OH)_4}$. The monooxolato species has also been formulated as the hydroxo rather than oxo species. At hydrogen ion concentrations over the range 0.084–0.416 *M*, equilibrium oxalate ion concentrations of $(0.06 \text{ to } 0.153) \times 10^{-4}$ *M*, and zirconium(IV) concentrations of $(1 \text{ to } 1.8) \times 10^{-5}$ *M*, the major species in solution is said to be $\mathrm{[Zr(OH)(C_2O_4)]^+}$. For the equation

$$\mathrm{Zr(OH)_3^+ + H_2C_2O_4 \rightleftarrows [Zr(OH)(C_2O_4)]^+ + 2\,H_2O} \tag{9}$$

a relative constant of $1.3 \pm 0.2 \times 10^6$ was obtained (*598*). Potentiometric, turbidometric, and electrometric titrations (*12*) provide support for the presence of the same three species as reported by Saksin (*467*). It has been suggested that these hydroxy salts are really hydrated zirconium hydroxide sols on which the carboxylic acid is absorbed (*544*). Although this might be the case under certain circumstances, the syntheses referred to here seem to be well verified and reproducible.

Zaitsev (*606*) has prepared some of these complexes as follows. A fivefold excess of oxalic acid in alcohol added to zirconium nitrate or sulfate also in alcohol, gives after gentle heating and prolonged stirring, $H_2[ZrO(C_2O_4)_2]\cdot 3H_2O$. This compound may also be obtained from aqueous solution by dissolving a zirconium salt or the hydroxide in concentrated aqueous oxalic acid, followed by successive additions of methanol and diethyl ether to precipitate a mixture of $H_2[ZrO(C_2O_4)_2]$ and oxalic acid. The oxalic acid is washed out by alcohol. The hafnium complex was prepared in an analogous fashion. The ammonium salt is prepared by reaction of the acid with gaseous ammonia, whereas the barium salt is obtained by a double decomposition reaction. Ammonium and potassium acid salts were also prepared, although the reaction of sodium hydroxide with the acid in an alcoholic–etheral system gave only $Na(ZrO)(OH)(C_2O_4)(OH_2)$.

Zaitsev (*604*, *608*, *610*) has proposed structures for these species based on his view of the structural features thought to exist in the α, β, and γ forms of zirconium hydroxide, namely: a tetrameric square-planar array of zirconium atoms, bridged in the freshly precipitated α form, by pairs of hydroxyls, $[Zr_4(OH)_8(OH)_8]$; in the β form, prepared by precipitation from methanol, bridged alternately by oxygen atoms and pairs of hydroxyl groups, $[Zr_4O_2(OH)_4(OH)_8]$; and the γ form, obtained by aging, bridged by all oxygen atoms, $[Zr_4O_4(OH)_8]$. When reacted with oxalic acid in the mole ratio range of 0.6–0.8, pairs of terminal hydroxyl groups are replaced by oxalates to yield a product of composition $[Zr_4O_2(OH)_4(OH)_4(C_2O_4)_2]\cdot 8H_2O$. At higher oxalate:zirconium ratios of 1.1–1.5, with ammonium oxalate, the β form yields the same product, whereas the α and γ forms give $[(Zr_4O_4)(OH)_4(C_2O_4)_2]\cdot 5H_2O$. In alcoholic medium α, β, and γ retained their respective tetrameric arrangements, but substitute two pairs of the terminal hydroxyl groups for two oxalato groups. In some instances all the terminal hydroxyl groups have been replaced. Gaseous hydrogen chloride reacts with the β and γ hydroxyoxalates to give products of composition $[Zr_4(OH)_8Cl_4(C_2O_4)_2]\cdot 9H_2O$. The hydroxyl and oxo groups bonded to zirconium are determined by displacement with fluoride ion, followed by acid titration of the freed hydroxyl ions (*439*, *553*, *602*).



$$>Zr-OH + F^- \rightarrow\ >Zr-F + OH^-$$

Solubility products for the three forms at 25° ± 0.2°C at an ionic strength of 1 are estimated to be $K_{sp}\alpha = 5.0 \pm 1 \times 10^{-10}$, $K_{sp}\beta = 9.0 \pm 1 \times 10^{-12}$, and $K_{sp}\gamma = 4.9 \pm 1 \times 10^{-11}$. At pH 0.7 α is converted to β, but on lowering the pH to about 0.35, β is almost completely converted to α in

25 hours; γ also goes to α under these conditions. The analogous hafnium compounds have also been observed.

Zirconium oxalate of composition $ZrO(OH)(C_2O_4H)$ was found to have ion exchange properties (*360*), although the selectivity for the alkali metals was not favorable compared to the phosphate. The oxalate is also chemically unstable in strong base and acid solutions.

iii. Other dicarboxylic acids. Aqueous solutions of malonate $CH_2(COO^-)_2$, adipate $(CH_2CH_2COO^-)_2$, succinate $(CH_2COO^-)_2$ (*12, 573, 598*), and mercaptosuccinate (*516*) with aqueous zirconium(IV) solutions leads to the precipitation of solids with composition $[ZrO(CH_2)_n(COO^-)_2]$. The 1:1 adipate and succinate species do not dissolve in excess carboxylic acid solution indicating that the dianionic species are not formed. At metal ion concentrations of (1 to 2) × 10^{-5} M and hydrogen ion concentrations between 0.087–0.350 M, malonic and succinic acids establish the equilibrium defined by the equation

$$Zr(OH)_3^+ + H_2A \rightleftarrows Zr(OH)_3A^- + 2\ H^+$$

for which the equilibrium constants of $K_m = 28.9 \pm 3.9$ and $K_s = 28.5 \pm 4.5$ were determined.

iv. Esters of dicarboxylic acids. Coordination complexes between diesters of α,ω-dicarboxylic acids and zirconium tetrachloride have been prepared (*457*). Two types of products are obtained, a 1:1 complex in which chelate rings from five to nine atoms are formed by the ROCO groups being bidentate to the same metal and 2:1 MX_4 diester complexes in which the ROCO groups are each bidentate to a MX_4. Thus the molecule is expected to be linear with two terminal four-membered rings per ester molecule. Cryoscopic data in benzene showed that significant dimerization of the 1:1 species was occurring (*406*). Any proposed structure for the dimer would have to take in account dipole moments of 7.52, 9.21, and 8.65 D for $ZrCl_4(CO_2Et)_2$, $ZrCl_4CH_2(CO_2Et)_2$, and $ZrCl_4(CH_2CO_2Et)_2$, respectively.

b. Hydroxycarboxylic Acids. Experiments show that dicarboxylic acids without hydroxy groups, except for oxalic acid, are weaker complexing agents for zirconium and hafnium than are the α-hydroxycarboxylic acids. Ion exchange experiments were used to obtain (*463, 465*) the equilibrium constants for the formation of the 1:1 complexes of lactic acid, $CH_3CHOHCOOH$; malic acid, $CHOHCH_2(COOH)_2$; tartaric acid, $(CHOHCOOH)_2$; citric acid, $[HOOCCH_2COH(COOH)\text{-}CH_2(COOH)]$, and trihydroxyglutaric acid, $[CHOH(CHOHCOOH)_2]$, at metal ion concentrations of 1 × 10^{-5} M and a hydrogen ion concentration of 2 M (Table XII). No solid products were isolated. Trihydroxyglutaric acid and lactic acid form 1:2 complexes at these high acidities, while tartaric acid forms a 1:2 complex only at pH values greater than 5 (*416*).

TABLE XII

EQUILIBRIUM CONSTANTS FOR THE FORMATION OF COMPLEXES WITH α-HYDROXYCARBOXYLIC ACIDS

	Zr		Hf	
Acid	K_1	K_2	K_1	K_2
Lactic	190 ± 10	350 ± 150	108 ± 8	108 ± 60
Malic	172 ± 17.2	—	67 ± 5.0	—
Tartaric	310 ± 24	—	97.2 ± 2.4	—
Trihydroxy-glutaric	2580 ± 100	$(25 \pm 4.6) \times 10^4$	530 ± 40	$(16 \pm 4.0) \times 10^4$
Citric	2600 ± 432	—	348 ± 43	—

A hydroxytartrate species (*457*) forms at metal ion concentrations of $(1 \text{ to } 2) \times 10^{-5}$ *M* and hydrogen ion concentrations of 0.18 *M*. At tartaric acid concentrations of $(0.256 \text{ to } 0.770) \times 10^{-6}$ *M* the equilibrium may be described by the equation

$$Zr(OH)_3^+ + H_2C_4H_4O_6 \rightleftarrows Zr(OH)(C_4H_4O_6)^+ + 2\,H_2O \qquad (10)$$

for which the equilibrium constant is 3.21×10^5. At higher tartaric acid concentrations, $(2 \text{ to } 24) \times 10^{-3}$ *M*, the 1:2 zirconium:ligand complex is formed,

$$Zr(OH)(C_4H_4O_6)^+ + H_2C_4H_4O_6 \rightleftarrows Zr(C_4H_4O_6)_2 + H^+ + H_2O \qquad (11)$$

An equilibrium constant of 8.8 ± 1.1 was obtained at 0.88–0.264 *M* H^+. Oxy species of malic acid, $ZrO(CH_2CHOH(COO)_2)$ and $K_2ZrO(CH_2CHOH(COO)_2)_2$ (*406*), and citric acid also are reported (*300*). Polymeric lactate complexes have been reported by workers at Takeda Industries (*551*). Although a complete analysis was not given, the isolation of a polymer formulated as $M_4[Zr(OCHRCO_2)_n]$, where M is sodium or potassium and R is methyl or another alkyl, was reported. Blumenthal (*63*) has questioned whether the normal lactate will ever be formed.

The infrared spectrum of the tartaric acid complex shows (*173*) no stretch due to COOH groups, but does show the intense bands at 1600 and 1380 cm^{-1} which are assignable to the asymmetric and symmetric vibrations of the COO^- group. This indicates that all the carboxyl groups take part in complex formation. The lack of absorptions normally assigned to bending vibrations of the hydroxyl group indicate that both the OH groups of tartaric acid take part in complex formation with the removal of the protons. A similar conclusion is reached for the citric acid complex, all three carboxyl groups and the hydroxy group being bonded to the metal ion with removal of the protons. The infrared spectrum of the zirconium complex of trihydroxyglutaric acid does show an intense band at 1715 cm^{-1} indicative of the C=O stretch in nonbonded carboxyl groups. Since the spectrum also shows the absorptions at 1650 and 1370 cm^{-1} characteristic of the asymmetric and symmetric vibrations of the COO^-, the assumption is made that part of the carboxyl group is bound to the metal. It is also concluded that the zirconium forms bonds with at least two of the hydroxyl groups from which the protons are removed.

Mandelic acid has been studied extensively as an analytical reagent for zirconium (*162*) with conflicting results (*9*, *445*), the difficulty being that an excess of precipitant is difficult to remove without producing some hydroxylated species in the product. Precipitation from homogeneous solution by (*459*) hydrolysis of the ester, hydroxypropyl mandelate, was a successful route for the production of a normal mandelate which could be weighed directly after drying. Complexes of composition 1 : 4 have also been prepared with the *p*-chloro-, *p*-bromo-, and *m*-nitromandelates (*27*, *125*). Klingenberg and Theis (*304*) studied another closely related ligand, an ether, methoxyphenylacetic acid, and its *p*-chloro and *p*-bromo derivatives, but obtained no precipitate with an acidified zirconium oxychloride solution. This is in direct contrast to Liang and Wang (*338*) who report that zirconium was precipitated quantititively as a 1 : 1 complex with the same reagent from zirconium oxychloride solutions at a pH of less than 1.4.

Some physical properties and structural features of the normal tetramandelate have been reported. The solubility of the 1 : 4 mandelato complex in 2 *M* perchloric acid was determined to be 7.8×10^{-4} mole/liter (*444*), and was found to fall slowly with increasing pH to a minimum of 4×10^{-5} at pH 3.1, after which it then rose. The change in solubility was accompanied by a change in composition which involved the formation of metal oxo species. In 1958, R. W. Stromatt (*540*) concluded on the basis of infrared spectroscopy, that the tetramandelates exist as discrete 8-coordinate molecular species. This would seem to be supported by the fact (*24*) that an organic-soluble species can be extracted from aqueous solutions containing (1.0 to 8) $\times 10^{-6}$ mole/liter zirconium(IV) in 1 *M* perchloric acid with an isopentyl alcohol solution of *p*-bromomandelic acid. The normal tetramandelate precipitated from aqueous solution at the usual concentration conditions, however, is very insoluble in organic solvents and nonsublimable as well, properties not usually associated with molecular species. Considering the concentrations used in the extraction studies and the reported solubility of the tetramandelate in aqueous solutions, one cannot say that the observations are inconsistent with one another. Infrared spectral studies on the tetramandelate by Homeier (*248*) show that the product is not monomolecular in the solid state, but rather polymeric, with double minimum hydrogen bonds between the protons and oxygens of two ligand moieties acting as bridges between zirconium(IV) ions (*248*). The same product is slowly obtained by the reaction of zirconium tetrachloride and mandelic acid in anhydrous acetonitrile.

3. *Aminopolycarboxylic Acids*

a. Ethylenediaminetetraacetate. Potentiometric titration of a 1:1 mixture of zirconium(IV) (2.5×10^{-3} mole/liter) and ethylenediaminetetraacetic acid (EDTA) with base confirms the presence of a 1:1 complex in solution. The authors (*256*) propose an 8-coordinate model in which the six donor atoms of the ligand and two water molecules occupy the vertices of a square antiprism. At pH 6 an additional mole of base is taken up accompanied by formation of a polynuclear species. Beyond this region irreversible precipitation of the hydrous oxide occurs. The same authors (*258*) have determined the formation constant for the equilibrium

$$M^{4+} + 4\,L^- \rightleftarrows ML_4 \qquad (12)$$

to be $\log k = 29.0 \pm 0.05$ ($\mu = 0.01$). The data were suitably corrected for hydroxo and chloro complexing as well as metal ion polymer formation. A similar value of $\log k = 28.95$ was obtained at 20°C in 1.2 *M* HCl using an ion exchange technique to study the equilibrium (*563*). An apparent equilibrium constant was also obtained for the hafnium system (*256*). Ermakov and co-workers (*169, 170*) studied the EDTA equilibrium by ion exchange and radiotracers at low metal ion concentrations (2×10^{-6}). The EDTA concentrations ranged from $(1 \text{ to } 10) \times 10^{-6}$ *M* and the acidity from 1–2 *M* $HClO_4$. With suitable corrections for metal ion hydrolysis they report formation constants of $\log K_{Zr} = 29.0$ and $\log K_{Hf} = 29.5$.

Martel and Intorre (*258*) have also studied the hydrolysis and polymerization of the EDTA complex at metal ion concentrations of $(5 \text{ to } 40) \times 10^{-4}$ *M*. They arrived at the following equilibrium constants:

$$Zr(EDTA) + H_2O \rightleftarrows Zr(OH)(EDTA)^- + H^+ \qquad pK = 6.2 \qquad (13)$$

$$2\,Zr(EDTA) + 2H_2O \rightleftarrows Zr_2(OH)_2(EDTA)_2^{2-} + 2\,H^+ \qquad pK = 8.72 \qquad (14)$$

$$2\,Zr(OH)(EDTA)^- \rightleftarrows Zr_2(OH)_2(EDTA)_2^{2-} \qquad \log K = 3.5 \qquad (15)$$

These values are to be considered tentative since there is some drift in the values with concentration, and it is likely that the above equilibria do not completely define the system. Self-diffusion coefficients of the zirconium–EDTA complex in slightly acidic solution also indicate a considerable degree of polymerization (*417*) as do the hydrogen ion dependence data of Ermakov (*172*). In the direct analytical titration of zirconium with EDTA, polymeric species must be depolymerized. This may be accomplished by boiling the solution with 5 *N* sulfuric acid (*430*).

Proton nuclear magnetic resonance studies (*1*) of aqueous solutions of zirconium(IV) (0.3 *M*) and hafnium(IV) (0.5 *M*) in the presence of ethylenediaminetetraacetate ion also confirm the existence of the 1:1 complex in solution at pH 3.5. The system has a simple AB quartet centered at 2.61 ppm with a single ethylenic resonance upfield at 1.99 ppm.[2] The quartet is thought to arise from spin-spin interaction of the two nonequivalent methylenic protons of each acetate group. The nonequivalence arises upon bonding of the oxygen atoms and nitrogen atom of the ligand with the metal. The bonding must be reasonably nonlabile as rapid exchange would destroy the nonequivalence of the methylenic protons. An 8-coordinate model involving the six ligand donor atoms of the ligand and two water molecules in a dodecahedral symmetry is consistent with these data. As the pH is increased the NMR pattern changes to a broad central peak at 2.55 ppm (pH 5) and a single ethylenic resonance upfield, indicating that hydroxyl groups are preferentially displacing the donor atoms of the ligand, thus removing the nonequivalence of the methylenic protons. At still higher pH values the EDTA complex appears to be completely destroyed. These observations are consistent with those of earlier investigations. Hafnium solutions behave in a similar fashion, although an excess of EDTA was required to obtain solutions which remained clear over the pH range studied.

b. Nitriloacetate. Studies with the nitriloacetate anion (*258*) led to the conclusion that the bis(nitrilacetato)zirconate complex anion exists in aqueous solution as a multidentate 8-coordinate species. There are several possible stereoisomers with this quadridentate group, although there are certain geometrical and energy restraints imposed by the branching ring structure and multiple ring formation. The single-crystal X-ray studies (*245*) show that the structure of the anion in the salt $4K_2Zr[N(CH_2COO)_3]_2 \cdot H_2O$ is dodecahedral (D_{2d}) with two nitrogen atoms and two oxygen atoms at *A* vertices (Fig. 5) and four oxygen atoms

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[2] *t*-Butyl alcohol, which was used as an internal standard for chemical shift measurements, has a resonance at 1.2333 ppm downfield from the sodium salt of 3-(trimethylsilyl)-1-propane sulfonic acid.

at the B vertices. The complexing bond lengths are Zr–O^a, 2.25 Å; Zr–O^b, 2.13 Å; and Zr–N, 2.44 Å each with an estimated standard deviation of less than 0.01. The M–A/M–B ratio of 2.251/2.130 = 1.057 is significantly larger than the 1.03 found in the tetraoxalatozirconate. This probably reflects the difference in magnitude and distribution of the negative charge. The nonequivalence of the A and B sites may be explained on the basis that the d_{xy} orbital, which has its lobes passing through the midpoints of the four b edges (Fig. 6), is available for π bonding, primarily with the O^B ligands. The large Zr–N and Zr–O bond lengths require nonplanar glycine rings. The three CNC angles between the rings (110.6°–110.9°), however, are only slightly larger than the ideal tetrahedral angle. This is evidence that the ring strains are equally distributed among the rings. The crystal itself as an orthorhombic unit cell with $a = 14.84$ Å, $b = 14.83$ Å, and $c = 8.67$ Å and space group Ccc–C_{2v}.

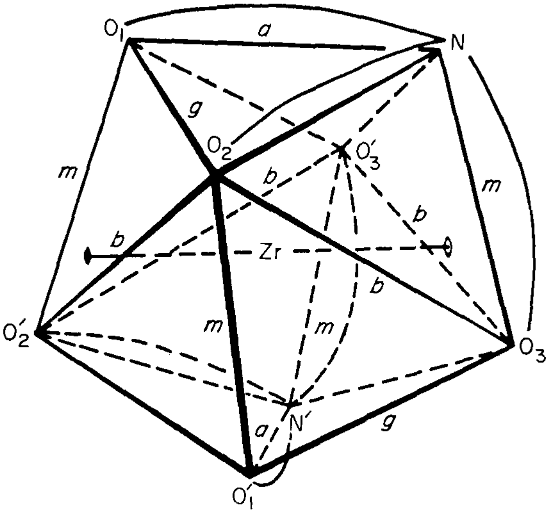

FIG. 5. Structure of the $Zr[N(CH_2COO)_3]_2^{2-} \cdot H_2O$ anion. Reproduced by permission, J. L. Hoard, E. W. Silverton, and J. V. Silverton, from *J. Am. Chem. Soc.* **90**, 2302 (1968).

The methylenic protons of the bis(nitrilacetato)zirconate anion should be distinguishable by NMR techniques, since the edges spanned by the chelate rings are different. Additionally, it presumably would show nonequivalence similar to that in the EDTA case if the bonding was nonlabile. Experimentally (*3*), only a single resonance at +0.75 ppm relative to water is observed. It may be that the chemical shifts for these protons are actually smaller than the resolution of the instrument or that fast chemical exchange is occurring.

Formation constants for the 1 : 1 complex of zirconium(IV) and nitriloacetate ion (25°C, $\mu = 0.01$) have been determined by Martell (*258*) at metal ion concentrations of $(1.7 \text{ to } 5.2) \times 10^{-3}$ *M* in chloride solution. A corrected formation constant of $\log K_{\mathrm{Zr}} = 20.8 \pm 0.1$ was calculated.

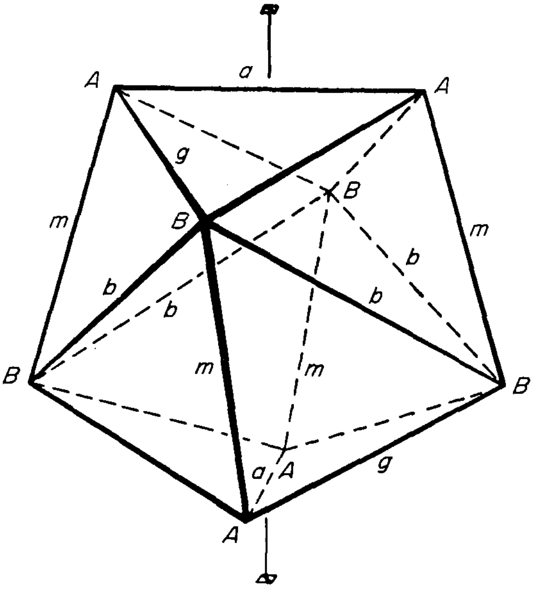

FIG. 6. The D_{2d}-$\bar{4}2m$ dodecahedron. Reproduced by permission, from J. L. Hoard, E. W. Silverton, and J. V. Silverton, *J. Am. Chem. Soc.* **90,** 2302 (1968).

A comparable constant for hafnium was not calculated owing to a lack of data for hydroxo and chloro complexing. A similar value has been obtained for the same constant by Ermako *et al.* (*169, 170*) by ion exchange techniques under vastly different conditions, namely, metal ion concentrations of 2×10^{-6} mole/liter and 0.23 *M* perchloric acid. Equilibrium constant values of $\log K_{\mathrm{Zr}} = 20.8$ and $\log K_{\mathrm{Hf}} = 20.3$ were obtained. At high metal ion concentrations (0.01–0.1 *M*) there is evidence for formation of a 2Zr:NTA complex in which hydrolyzed zirconium atoms are bridged by the nitriloacetate ion (*172*).

The anhydrous potassium bis(nitriloacetato)zirconate may be prepared by the dehydration *in vacuo* over calcium sulfate at room temperature of the hydrate which is obtained by the addition of a solution containing nitriloacetic acid (0.04 *M*) and potassium carbonate

(0.06 *M*) to a solution of zirconium oxychloride (0.02 *M*), followed by evaporation until crystal formation is observed (*331*).

c. Other Ligands. Intorre and Martell (*256*) studied the coordinating tendency of other multidentate ligands to zirconium by potentiometric titration. *N*-Hydroxyethylenediaminetriacetate (6-coordinate) forms a stable 1:1 complex in which the alcoholic hydroxyl is involved in the bonding to the metal ion. Ultracentrifugation experiments (*230*) are consistent with polymerization to a dimer over the metal ion concentration (1.6 to 9.2) × 10^{-2} *M*. The equilibrium constant for dimerization is $\log K = 2.14 \pm 0.8$ (25°C, 1.2 *M* NaCl). In this system precipitation occurred above pH 9.5.

Other multidentate species, trimethylenediaminetetraacetate, [oxybis(ethylenenitrilo)]tetraacetate, and ethylenebis[(oxyethylenenitrilo)]-tetraacetate gave unknown precipitates over most of the pH range, although ligand may have been incorporated in the product in some cases. *trans*-Cyclohexanediaminetetraacetate (DCTA) apparently formed a 1:1 complex at low pH values, but beyond pH 4 a precipitate appeared. A diethylenetriaminepentaacetate–zirconium (DTPA) 1:1 mixture, gave a precipitate at a metal ion concentration of 0.018 *M* over the whole pH range; but at 0.2 *M* metal ion, a titration curve was obtained which suggested the formation of a completely coordinated chelate in which all eight coordination sites of the metal were filled by the eight donor ligands. In very dilute solutions [2×10^{-6} mole/liter zirconium(IV)], Ermakov and co-workers (*169*, 170) determined the equilibrium constant for the formation of the 1:1 species in 0.23 *M* $HClO_4$ to be $\log K_{Zr} = 35.8$ and $\log K_{Hf} = 35.4$, and Tikhonova (*563*) at pH 0.5 and 20°C determined $\log K_{Zr}$ to be 33.96. The formation of the 1:1 complexes of zirconium(IV) and DCTA and DTPA was also studied by Pankratova (*418*).

The quadridentate ligands *N,N*-dihydroxyethylglycine and *N*-hydroxyethyliminodiacetate(HIMDA) form 2:1 chelate:zirconium complexes which are stable with respect to hydroxide precipitation even up to pH 10. These quadridentate ligands involve the bonding of the alkoxide groups at the higher pH values .The formation constant for the 1:1 HIMDA–hafnium complex in 0.123 *M* $HClO_4$ is $\log K = 14.6$ (*170*, 305).

Triethylenetetraaminehexaacetic acid forms $(MH_2L)^{\circ}$, and tetraethylenepentaminepentaacetic acid forms (MH_4L^+), in 0.5–2 *M* $HClO_4$. These complexes are about as stable as the nitriloacetic acid complex (*171*). The stability constant for the 1:1 complex with 2-hydroxytrimethylene-1,3-bis(iminodiacetic) acid is $\log K = 23.58$; with (2,2′-diaminodiethyl ether)-*N,N,N′,N′*-tetraacetic acid [2,2′-oxybis(ethyliminodiacetic acid)], it is $\log K = 24.72$; and with (2,2′-diaminodiethylsulfide-*N*,*N*,*N*′,*N*′-tetraacetic acid [2,2′-thiobis(ethyliminodiacetic acid)], it is $\log K = 23.17$ (*563*).

It is generally concluded that the order of tendency to bond to zirconium increases $R_3N < ROR < RCOO^- < RO^- < HO^- < O^{-2}$. The 5-member ring systems are more stable than the 6-membered ring systems, and a decrease in stability is observed with a decrease in the number of 5-membered rings.

Intorre and Martell (*257*) have also studied the formation of mixed chelate species in which the zirconium 1:1 complex with the hexadentate chelating ligands, ethylenediaminetetraacetic acid, *N*-hydroxyethylethylenediaminetriacetic acid, and *trans*-cyclohexanediaminetetraacetic acid, are shown to take up one mole of the bidentate ligands, 1,2-dihydroxybenzene-3,5-disulfonate; 1,8-dihydroxynaphthalene-3,6-disulfonate; 8-hydroxyquinoline-5-sulfonate, and acetylacetone (except ZrHEDTA), to form 8-coordinate 1:1:1 species. At least for the zirconium–EDTA–1,2-dihydroxybenzene-3,5-disulfonate species, there is evidence for dimerization (*230*). Additionally, the Zr:EDTA complex reacts with one mole of the bidentate ligands, 5-sulfosalicyclic acid, alizarin sulfonate, citric acid, and lactic acid to form 1:1:1 complexes; tartaric acid and pyrophosphate ions form complexes which could not be identified. The zirconium–nitriloacetic acid complex in the presence of two moles of oxalic acid or 1,2-dihydroxybenzene-3,5-sulfonate also forms 1:1:1 complexes in solution.

4. *Aromatic Polyalcohols, Carboxylic Acids, and Their Derivatives*

a. Benzoic Acid and Derivatives. In a nonaqueous solvent such as benzene, salicyclic acid reacts with the monosolvate of zirconium tetrapropoxide to yield a tris(salicylato)monoisopropoxidezirconium, which when heated reacts with loss of isopropyl alcohol and the formation of bis(salicylato)[salicylato(2^-)] zirconium. The same product is obtained when starting with zirconium tetrachloride rather than the isopropoxide. When the mole ratio of ligand to zirconium is greater than three, the product is bis[salicylato(2^-)]zirconium. Zirconium tetraisopropoxide with phenol, benzoic acid, or methylsalicylate, in benzene gives, respectively, the tetraphenoxyzirconium, tetrabenzonatozirconium, and tetrakis(methylsalicylato)zirconium (*282*).

The reaction of zirconium(IV) with 5-sulfosalicylic acid has been studied by Babko (*37*) and Deich (*142*), with the latter concluding that only a highly dissociated species exists in solution. In contrast to these observations Sheka (*284*) reports that in a zirconium (hafnium) solution of 0.02 *M* metal ion and 0.1 *M* hydrochloric acid, a 1:1 complex is formed as an insoluble precipitate with the release of one proton to the solution. Infrared data indicate that the carboxyl proton has been lost, and that no metal–oxygen double bonds are present. Analytical data indicate that there are two hydroxyls bound to the metal atom per formula unit. Complexes of *N*,*N*-bis(carboxymethyl)anthranic acid have also been studied (*149*).

b. Aromatic Polyols and Their Derivatives. Pyrocatechol(1,2-dihydroxybenzene) forms 1:1 complexes with zirconium and hafnium. Cation exchange studies at metal ion concentrations of 1×10^{-5} *M* in perchloric acid gave stability constants of $\log K_{\mathrm{Zr}} = 22.37$ and $\log K_{\mathrm{Hf}} = 22.4$. The hafnium species $\mathrm{Hf(pyg)_2^{2-}}$ was present even in 1 *M* $\mathrm{H^+}$, whereas the comparable zirconium species was not (*167*).

Increasing the number of ligand hydroxyl groups to three does not improve the chelating properties. Thus, pyrogallol (1,2,3-trihydroxybenzene) in 1 *M* HCl at metal ion concentrations of 2.5×10^{-4} *M* forms 1:1 complexes (*414*). The equilibrium data, suitably corrected for the hydrolysis of the metal ions, gave stability constants for the formation of $[\mathrm{M(OH)_2}$ pyrogallol$]$ of $\log K_{\mathrm{Zr}} = 4.06$ and $\log K_{\mathrm{Hf}} = 4.33$.

Potentiometric titrations of solutions containing 1,2-dihydroxybenzene 3,5-disulfonate (Tiron) and zirconium(IV) (0.2–0.02 *M*) with base, yields evidence (*417*) for the formation of complexes with ligand: metal ratios of 1, 2, and 3; there is no evidence for complexes of higher ratio. The ligand bonding is considered to be through the phenolic oxygens and not the oxygens of the sulfonic acid groups. All the complexes are soluble up to pH 10. At these high metal ion concentrations, more than two moles of base per mole of ligand are used indicating that zirconium atoms were picking up hydroxide, probably in the formation of polymeric species bridged by hydroxy groups.

The equation

$$\mathrm{Zr(IV)} + \mathrm{H_2A^{2-}} \rightleftarrows \mathrm{ZrA^0} + 2\,\mathrm{H^+} \qquad (16)$$

expresses the net reaction for the formation of the 1:1 complex. Intorre and Martell (*256*) studied this equilibrium at a metal ion concentration of about 10^{-3} *M* in 1.2 *M* HCl at 24.7°C, and calculated a formation constant for the 1:1 zirconium complex of $\log K_{\mathrm{Zr}} = 25.4 \pm 0.3$. Cation exchange was used to study the same equilibrium, but at vastly lower metal ion concentrations (1×10^{-5} to 1×10^{-6} *M*) and at hydrogen ion concentrations of 0.5 (*278*) and (1 to 2) *M* (*167*). The stability constant for the 1:1 hafnium complex has been reported to be $\log K_{\mathrm{Hf}} = 24.67$ (*278*) and 23.0 (*167*), while that for zirconium is $\log K_{\mathrm{Zr}} = 24.15$ (*190*). Although lower than that obtained by Martell, the data are in good agreement considering the difference in ionic environment of the two studies.

When 1,2-dihydroxy-3,5-disulfonate is added to a solution of a 1:1 Zr:EDTA complex at metal ion concentrations of (1.7 to 5.2) × 10^{-3} M, potentiometric titrations of the resulting solutions are consistent with the reactions

$$\mathrm{ZrEDTA} + \mathrm{H_2A^{-2}} \rightleftarrows \mathrm{Zr(EDTA)HA^{3-}} + \mathrm{H^+} \qquad (17)$$

$$2\ \mathrm{Zr(EDTA)HA^{3-}} \rightleftarrows [\mathrm{Zr(EDTA)A}]_2^{8-} + 2\ \mathrm{H^+} \qquad (18)$$

Equilibrium constants (*171*) for these two equilibria were calculated to be $K_1 = 0.12 \pm 0.2$ and $K_2 = (32 \pm 0.6) \times 10^{-4}$. A dimer model is proposed with two moles of chelating agent acting as bridges between two 1:1 zirconium(IV):EDTA chelate units. The ultracentrifugation experiments (*230*) are consistent with these data.

Chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonate) reacts with zirconium(IV) to form a 1:1 complex. The apparent equilibrium constant for this system at pH 2.0 and at a metal ion concentration of 5×10^{-4} M in 0.1 M KCl, was calculated to be $\log K'_{\mathrm{Zr}} = 3.63$ (*466*). The initial report (*98*) of little or no reaction appears to be incorrect. A nitroso derivative of this ligand reacts with zirconium(IV) to give a red-violet precipitate in weak acid solution (*535*).

5. *Anthraquinone and Its Derivatives*

Although alizarin-S (1,2-dihydroxyanthraquinone-3-sulfonate) has been used (*162*) for many years for the detection and estimation of zirconium and hafnium, the composition of the product formed in this system is still uncertain. Recent studies on hafnium (*43*) and zirconium (*317, 419*) complex formation by spectrophotometric methods led to the conclusion that the zirconium 1:1 complex exists in the pH range 1.0–1.8 at a metal concentration of 1×10^{-4} M. Below that pH no complex could be observed and above that pH only suspensions were obtained. Hafnium, on the other hand, is said to form the 1:2 ligand complex at metal ion concentrations of (2 to 4) × 10^{-4} mole/liter over the pH range 1.0 to 4.0. A stability constant of 10.3 ± 0.3 was reported for this species. The 1:1 complex of zirconium is extractable with *n*-butanol (*149a*).

Hoshino (*251*) has reported that the complex formed with quercetin sulfonate (a sulfonate of 3,5,7,3′,4′-pentahydroxyflavone) is a 1:1 species, whereas that formed with morin (3,5,7,2′,4′-pentahydroxyflavone) is the 1:2 species. Complex formation most likely occurs through chelation with the quinoid oxygen and the adjacent hydroxyl group (*260*).

6. *Miscellaneous Ligands*

The compound disodium-2-(3-methyl-5-oxo-1-phenyl-2-pyrazolin-4ylazo)-6,8-naphthalene disulfonate reacts with zirconium(IV) at a pH of 1.5–2 to yield a precipitate containing two moles of zirconium per mole of ligand. Trihydroxyzirconium ions are thought to be bound at the sulfonic acid sites (*436*, *437*).

The compound 3,4-dihydroxyazobenzene-2′-carboxylic acid (H_3R) forms a bright red $Zr:2H_3R$ complex in 1 *M* HCl (*318*). Coordination is presumably through the dihydroxy groups, as it is also presumed to be in the Zr:2L complexes with 3,4-dihydroxyazobenzene and 3,4-dihydroxyazobenzene-4′-sulfonate (*388*) and in the arsenazo 1:1 complex (*351*). There is no evidence for participation of the azo group in the bonding of these species.

B. OXYGEN LIGANDS—ORGANIC MONODENTATE GROUPS

1. *Acids*

When zirconium (hafnium) oxychloride is added to a boiling solution of 85% formic acid, a vigorous liberation of hydrogen chloride occurs and a microcrystalline crust forms as the solution is evaporated. The product has the composition $M_2O(OH)(HCOO)_5 \cdot 2H_2O$. The zirconium and hafnium compounds were isomorphous by X-ray powder patterns, insoluble in ether, sparingly soluble in ethanol, benzene, and chloroform and very soluble in water. The compounds lose 0.5 mole of water in the range 70°–110°C, lose a mole of formic acid between 110°–220°C to give $M_2O_2(HCOO)_4 \cdot 1.5H_2O$, and lose additional formic acid and water between 220°–350°C to yield $M_2O_3(HCOO)_2$. The hafnium compound undergoes these chemical changes at a temperature slightly lower than the zirconium compound.

The infrared spectra of the hydroxyformates (*536*) suggest the presence of hydrogen bonds by the broad absorption in the 3150–3450 cm^{-1} region. Bidentate or bridging COO^- groups are also present. The COO^- vibration observed at 1373 cm^{-1} for the zirconium species and 1382 cm^{-1} for the hafnium, is higher than that of the corresponding free ion. The asymmetric COO^- at 1553 cm^{-1} for the zirconium and 1563 cm^{-1} for the hafnium compound is below that observed for the free formate. The narrow intense bands characteristic of the M=O group are absent as are the broad bands usually associated with the formation of long M–O–M–O chains. By the process of elimination it was concluded that these oxyformates contain M–O–M or $M_2(OH)_3^{5+}$ groups or both. Titration of the hydroxyl ion released upon treatment of a sample of the oxyformate with fluoride ion suggests the presence of $\geq\mathrm{M{-}O{-}M}\leq\mathrm{OH}$ groups, and molecular weight data in cresol suggest the presence of tetrameric ions.

An acetate of similar composition, $M_2O(OH)(OAc)_5 \cdot 2H_2O$, has been prepared (*314*, *315*). Decomposition of the zirconium oxyacetate begins at 50°C with the loss of one mole of acetic acid to form crystalline $Zr_2O_2(CH_3COO)_4 \cdot 2H_2O$. At 200°C, one mole of water and one-half mole of $(CH_3CO)_2O$ per mole of zirconium are lost, leaving a product of composition $Zr_4O_5(CH_3COO)_6 \cdot 2H_2O$. The loss of another mole of $(CH_3CO)_2O$ above 275°C leads to $Zr_2O_3(CH_3COO)_2 \cdot H_2O$. The oxide is the final product. The decomposition of the hafnium salt goes slower and is completed at a higher temperature. The solubility of the hafnium compound in glacial acetic acid was considerably greater than that of the zirconium compound. As in the case of the formates, the infrared spectra lack evidence for the presence of M=O groups, and long M–O–M–O chains, but in this case the molecular weight data are consistent with a dimeric species.

The oxypropionates of zirconium and hafnium, $MO(C_2H_5COO)_2 \cdot H_2O$, are prepared (*441*) by the reaction of the oxychlorides with a twentyfold excess of concentrated propionic acid. Hydrogen chloride is evolved and upon cooling the product separates as a fine crystalline crust. The infrared spectra show a wide and fairly strong absorption over the range 3030–3400 cm^{-1} attributed to hydroxyl stretching vibrations of water molecules which are strongly hydrogen bonded to the carboxyl group. The intense narrow absorption at 800–1000 cm^{-1} associated with the presence of M=O groups is absent, but the broad band found over the range 840–970 cm^{-1} suggests the presence of O–M–O–M–O-type chains. Bands at 470 and 565 cm^{-1} in the zirconium compound and 470 and 587 cm^{-1} in the hafnium compound are apparently due to the vibrations of the M–O–M single bond. Isopiestic molecular weight determinations with cresol as the solvent gave 1200 for the zirconium compound and 1610 for the hafnium compound, suggesting that the metal species are present as tetramers.

There have been many previous studies on zirconium compounds of the so-called "fatty acids," which upon analysis are usually found to be oxy species. For example, the reaction of excess steric or palmitic acids with the isopropyl alcohol solvate of tetraisopropoxide zirconium (*280*, *281*) in benzene at reflux temperatures gives final products which are consistent with the composition $[(RCOO)_3Zr]_2O$. Actually this reaction can be carried out so as to isolate the mono- and disubstituted alkoxides, $Zr(RCOO)(OPr^i)_3$ and $Zr(RCOO)_2(OPr^i)_2$. Treatment of the disubstituted product with additional fatty acid in benzene gives products for which there is some evidence of decomposition, although one additional isopropoxide group can be replaced. Tetrasubstituted products were obtained when a suspension of zirconium tetrachloride in benzene was reacted with fatty acids at reflux temperatures. A slow evolution of hydrogen chloride was observed over a period of 14 hours, followed by the deposition of colorless crystals of the tetrasubstituted product.

A more desirable synthesis (*82,442*) for the acyloxyzirconium derivatives involves ligand exchange of the coordinated acetylacetonate ligand for the fatty acid anion, according to the equation,

$$(C_5H_7O_2)_4Zr + RCOOH \rightleftarrows (RCOO)_4Zr + 4\ C_5H_8O_2 \qquad (19)$$

With butyric, valeric, capronic, and oenanthic acids, excess acid was used. In the case of stearic, palmitic, lauric, and ω-chloroundecanoic acids, a 4:1 ratio of the reactants in benzene was used. The reaction time varied from 3 to 8 hours after which the excess acid or benzene was removed and the product was recrystallized with, in some cases, slight decomposition. The ω-chloroundecanoate, valerate, and capronate were rather viscous liquids; the oenanthate is described as a mobile liquid, while the others are light powders. If the coordination number eight of the acetylacetonate were preserved, then the COO^- group would have to function as a bidentate group to the same metal, a more reasonable alternative being that the carboxyl group bridges two metals. There are no molecular weight data available, nor other structural information so the exact nature of the products is unknown.

2. Esters

The zirconium tetrahalides react with esters to form $ZrX_4 \cdot 2$ ester adducts (*302, 303, 330, 407–410, 412*) in which, coordination number six is attained. On the basis of dipole moments (Table XIII), it is concluded that the adducts have the cis structure. This has been supported, at least in the case of $ZrCl_4 \cdot 2CH_3COOC_2H_5$, by the infrared spectrum (*330*). Cryoscopic studies in benzene solution of the 2:1 adducts of zirconium tetrachloride and ethyl formate, ethyl acetate, and ethyl butryrate show that these complexes tend to decompose to the 1:1 species, the extent of dissociation increasing with the number of carbon atoms in the acid radical. The estimated dissociation constant is about 5×10^{-4}, whereas for the ethyl acetate adduct of zirconium tetrabromide it is only 2×10^{-2}. The approximate dissociation constant of the complex zirconium tetraiodide:2 ethyl acetate is 3.5×10^{-1}. The 1:1 species were synthesized by direct reaction in benzene with strictly stoichiometric ratios of the reactants. Cryoscopic determination of molecular weights of the 1:1 complexes indicate that these complexes generally exist as dimers which show some degree of dissociation at very low concentrations in benzene. The heats of formation (*410*) in kilocalories per mole for ethyl formate, ethyl acetate, and ethyl butyrate in 1:1 complexes with zirconium tetrachloride were 20.6 for all three esters, and 24.0, 23.9, and 23.6 in the case of the 1:2 complexes. When zirconium tetrachloride in ethyl acetate is refluxed for 24 hours, there is obtained upon removal of excess ethyl acetate, a yellow crystalline compound of composition $ZrCl_2(OC_2H_5)_2 \cdot 2CH_3COOC_2H_5$ (m.p. 78°C) (*421*).

TABLE XIII

DIPOLE MOMENTS AND MELTING POINTS OF ESTER ADDUCTS

	Dipole moments and melting points[a]					
	$ZrCl_4$		$ZrBr_4$		ZrI_4	
Ester	1:1	2:1	1:1	2:1	1:1	2:1
$HCOOC_2H_5$	4.15	7.63	4.50	7.85	—	4.24
	(94°C)	—	(108°C)	—	—	—
$HCOOC_3H_7$	4.18	7.76	—	—	—	—
	—	—	—	—	—	—
$CH_3COOC_3H_5$	3.89	6.75	3.15	3.40	3.17	3.49
	(170°C)	—	(164°C)	—	—	—
$CH_3COOC_3H_7$	3.85	6.73	—	3.97	—	3.93
	(129°C)	—	—	—	—	—
$CH_3COOC_4H_9$	—	6.74	—	4.21	—	4.23
	—	—	—	—	—	—
$CH_3COOCH_2C_6H_5$	—	6.54	—	—	—	—
	—	—	—	—	—	—
$C_3H_7COOC_2H_5$	3.53	5.23	3.57	3.80	—	3.07
	(163°C)	—	(157°C)	—	—	—

[a] Numbers in parentheses are melting points.

3. *Alkoxides*

a. Preparations. Work on the alkoxides up to 1960 has been neatly summarized by Bradley (*67*). It is well known that alkoxy exchange may be used as a preparative method for new alkoxides. For instance, tetraisobutoxide zirconium was prepared (*68*) by reacting tetraisopropoxide with isobutanol and fractionally distilling the liberated isopropanol. The solvate $Zr(OBu^i)_4 \cdot BuOH$ was deposited upon concentration and cooling of the solution. At 100°C and 0.1 mm Hg the crystals softened and lost isobutanol. The tetraisobutoxyzirconium could be distilled at

213°C at 0.3 mm. Tetralkoxyzirconium compounds and trialkoxyzirconium species have been prepared also by double decomposition of tetrakisacetylacetonatozirconium and trisacetylacetonatozirconium with alcohols (*81*). The tetraalkoxy compounds of hexyl, heptyl, octyl, and nonyl alcohols were prepared in this manner with the reaction being complete in 2 to 3 hours.

$$\mathrm{Zr(acac)_4 + 4\,ROH \rightarrow (RO)_4Zr + 4\,C_5H_8O_2} \qquad (20)$$

With isopropyl and *n*-propyl alcohols the products were $(C_5H_7O_2)_3(Pr^iO)Zr$ and $(C_5H_7O_2)(Pr^nO)_3Zr$, respectively.

b. Structure. It is well established that zirconium alkoxides are polymeric compounds involving M–O coordinate bonds, and that they may be hydrolyzed under controlled conditions to form isolable intermediate oxide alkoxides $ZrO_x(OR)_{4-2x}$ which involve both condensation polymerization (Zr–O–Zr) and coordination polymerization. By an ebulliometric technique, Bradley has studied the degree of polymerization as a function of hydrolysis (*68*, *69*). An explanation of the course of the hydrolysis, which, in general, may be described by the equation

$$[\mathrm{ZrO}_{x_1}(\mathrm{OR})_{4-2x_1}]_n + (n_2x_2 - n_1x_1)\mathrm{H_2O} \rightarrow n_1/n_2[\mathrm{ZrO}_{x_2}(\mathrm{OR})_{4-2x_2}]n_2 + 2(n_2x_2 - n_1x_1)\mathrm{ROH}$$

is based on the assumption that coordination number six is preserved for zirconium throughout. In the following, n is the number average degree of polymerization and h is the degree of hydrolysis, namely, the ratio of moles of water added per mole of zirconium. Three models are considered: (1) The unsolvated trimeric alkoxide $Zr_3(OR)_{12}$ which upon hydrolysis yields a series of coordination condensation polymers of the general formula $Zr_{3(x+1)}O_{4x}(OR)_{4(x+3)}$, for which the general relationship, $n = 12/(4\text{-}3h)$ holds. (2) A solvated dimer $Zr_2(OR)_8 \cdot 2ROH$, which upon hydrolysis yields a series of linear polymers for which $n = 6/(3\text{-}2h)$. (3) A solvated monomer $Zr(OR)_4 \cdot 2ROH$, which upon hydrolysis yields products for which $n = 3/(3\text{-}h)$.

Tetraethoxyzirconium(IV) yields species upon hydrolysis which belong to both models (1) and (2). At an alkoxide concentration of 0.186 mole/1000 gm of ethanol, precipitation of insoluble polymeric material occurred at $h = 1.87$ for which $n = 10.9$. The tetrapropoxide system, on the other hand, conforms to polymers of models (1) and (2) in the early stages, but for $h = 1.0$, solvation becomes increasingly important and hence polymers based on models (2) and (3) more accurately describe the system. The absence of a precipitate is consistent with the presence of polymers based on model (3). The hydrolysis of the *n*-butyl and isobutyl alkoxides conform to model (3), although in the early stages of hydrolysis of the *n*-butyl alkoxide, model (2) polymers seem to exist. No precipitation occurs.

Hydrolysis studies of secondary and tertiary alkoxides (*69*) indicate that the degree of polymerization of secondary alkoxides in benzene is lower than for the normal alkoxides, whereas the teritary alkoxides are monomeric. Thus the hydrolysis data on tetraisopropoxide zirconium and tetra-*sec*-butoxide zirconium are consistent with the model (2) hypothesis, while the hydrolysis data of tetra-*tert*-amyloxide fit the model (3) hypothesis. Additionally, crystal structure data on tetraisopropoxide zirconium (hafnium) containing one mole of isopropanol of addition, are consistent with a dimeric structure in which each metal atom is surrounded octahedrally by oxygen atoms, two of which form a common edge between octahedra (*255*). On the other hand, recent (*72*) cryoscopic molecular weight data for zirconium (hafnium) tetraisopropoxide in very dry benzene are consistent with the presence of trimers and tetramers. The NMR spectra of freshly distilled zirconium and hafnium tetraisopropoxide in cyclohexane gave one doublet with a chemical shift corresponding to the weighted mean value of the terminal and bridging isopropoxides of a trimeric species. Upon aging three new minor doublets appeared, which at higher temperatures coalesced with the main doublet. These are believed to be due to the growth of a tetrameric species.

TABLE XIV

ORGANOSILYLOXYZIRCONIUM DERIVATIVES

Compound	Melting point (°C)	Boiling point (°C)/mm	n^a
$(Me_3SiO)_4Zr$	152	135/0.1	2.05
$(Me_2EtSiO)_4Zr$	105	105/0.1	1.20
$(MeEt_2SiO)_4Zr$	30	120/0.1	1.05
$(Et_3SiO)_4Zr$	—	147/0.1	0.98
$(Pr^nMe_2SiO)_4Zr$	60	103/0.05	1.11
$(Pr^iMe_2SiO)_4Zr$	—	110/0.1	1.01

[a] *n*, degree of polymerization.

c. Chemical Properties. Zirconium tetraisopropoxide reacts with silanols in boiling benzene or silyl acetates in boiling cyclohexane to yield organosilyloxyzirconium derivatives and the volatile alcohols. In this manner the products tabulated in Table XIV were prepared.

Tetrakistrimethylsiloxyzirconium in dioxane undergoes room temperature hydrolysis to form zirconium oxide trimethylsilyloxides according to the equation

$$n\mathrm{Zr(OSiMe_3)_4} + 2nx\mathrm{HOH} \rightarrow \mathrm{Zr}_n\mathrm{O}_{nx}\mathrm{(OSiMe_3)}_{4n-2nx} + 2nx\mathrm{HOSiMe_3} \qquad (21)$$

A number average degree of polymerization, *n*, as high as 8.4 has been obtained. Heating the initial polymers at 150°C/0.1 mm causes disproportionation to the volatile tetrakis compound and a nonvolatile more highly condensed polymer (*73*, *74*).

The hydrolysis of tertiary butoxide zirconium (0.5 mole water/mole of alkoxide) at 60°C and finally at 110°C gave a product (*78*) of composition $\mathrm{(BuO)_6Zr_2O}$ as a semisolid crystalline mass. An increased proportion of water gave solids of composition $\mathrm{(BuO)_8Zr_3O_2}$, $\mathrm{(BuO)_{10}Zr_4O_3}$, and $\mathrm{(BuO)_{32}Zr_{10}O_9}$.

The reaction of *n*-propanol, *n*-butanol, *n*-hexanol, *n*-heptanol, *n*-octanol, and *n*-nonanol with chlorotrisacetylacetonatozirconium gave monochloroalkoxides

$$\mathrm{Zr(acac)_3Cl} + 3\ \mathrm{ROH} \rightarrow \mathrm{(RO)_3ZrCl} + 3\ \mathrm{C_5H_8O_2} \qquad (22)$$

All these products were distillable at 10^{-5} mm. Long heating at elevated temperatures led to some decomposition. The compounds are viscous liquids readily soluble in cold alcohol, benzene, petroleum ether, chloroform, and diethyl ether. They are sensitive to atmospheric moisture.

The disubstituted nitrate $\mathrm{Zr(acac)_2(NO_3)_2}$ also reacts with alcohols, such as isopropyl and *n*-butyl, to give $\mathrm{(C_5H_7O_2)(C_3H_7O)Zr(NO_3)_2}$, m.p. 149°–150°C and $\mathrm{(C_5H_7O_2)}(n\text{-}\mathrm{C_4H_9O})\mathrm{Zr(NO_3)_2}$, m.p. 144°–146°C. The ethoxy derivative, m.p. 148°–152°C, may be prepared by ligand exchange of the isopropoxy derivative with ethanol.

Alcoholic solutions of the alkoxides react with alkali metal alkoxides according to the equation

$$\mathrm{MOR} + 2\ \mathrm{Zr(OR)_4} \rightarrow \mathrm{MZr_2(OR)_9} \qquad (23)$$

where $M = $ Li, Na, K, Tl, Ca, and $\mathrm{Et_4N}$ and R = ethyl, *n*-propyl, isopropyl, *n*-butyl, and *sec*-butyl (*46*). The ennea *n*-butoxides of lithium, sodium, and potassium sublime without change in composition. In benzene, the ennea ethoxide of lithium is a dimer, although the corresponding sodium compound is only slightly associated. The lithium *n*-propoxy and *n*-butoxy derivatives and the tetraethylammonium-isopropoxy derivatives are also associated in benzene. All the other products are monomeric in benzene. These ennea alkoxides hydrolyze, with the extent of hydrolysis increasing in the order MeO > EtO > Pr^iO.

4. *Ethers, Ketones, Organic Oxides, and Amides*

The ethers in general are poor bases for the metal tetrahalides. The $ZrCl_4 \cdot 2Et_2O$ addition compound decomposes at 95°C (*411*). In benzene it has a dipole moment of 4.87 D and is presumably in the cis arrangement.

The adduct with acetone is reported to be $ZrCl_4 \cdot 2(CH_3)_2O$ (*411*), although at -5°C in carbon tetrachloride, Joseph and Blumenthal (*271*) report that the product obtained is the 1:1 adduct and that the room temperature reaction yields hydrogen chloride and benzene-insoluble trichloroisopropeneoxyzirconium ($Cl_3ZrCH_2COCH_3$). The infrared spectrum of this compound shows the presence of a terminal double bond and the absence of the carbonyl stretching frequency. When methylisopropyl ketone was used in place of acetone, an analogous product was obtained, $Cl_3Zr(CH_2COC_3H_7)$.

The cyclic diether, dioxane, forms a 1:1 adduct with zirconium tetrachloride (*27*), which is similar, by X-ray powder pattern, to the titanium(IV) chloride compound. A polymeric species, in which the chair form of dioxane is coordinated to metal atoms through each oxygen, is proposed as the infrared spectrum shows no band which can be assigned to uncoordinated C–O–C stretch. A similar 1:1 complex with monothioxan is reported in which coordination must be through both the oxygen and sulfur atoms. The Zr–Cl-stretching frequency is lowered from 390 to 330–345 cm^{-1} upon complex formation.

Certain cyclic ketones dissolved in acetyl chloride when added to zirconium tetrachloride dissolved in the same solvent gave a precipitate of composition 2:1 ketone:$ZrCl_4$. The following properties were recorded for the adducts: anthrone, green, m.p. >325°C; 10-nitroanthrone, green, m.p. 251°C; 10-benzalanthrone, violet-red, m.p. 266°C; benzanthrone, red, m.p. >300°C. Zirconium tetrabromide reacted only with benzanthrone to give a red product with a melting point greater than 325°C. The tetraiodide did not react. Thermal gravimetric analysis showed an inflection at composition 1:1, but it was not possible to isolate a pure product of this composition. A decrease in the infrared carbonyl stretching frequency in the adduct compared to the pure ketone is evidence for bonding through the ketonic oxygen (*422*).

Muetterties (*376*) reports that ethers and sulfones do not react with zirconium tetrafluoride at 50°–160°C, whereas 2:1 adducts of dimethyl sulfoxide, *N*,*N′*-tetramethylurea, and dimethylformamide were formed upon refluxing a slurry of the tetrafluoride in excess base. The soluble complexes were recovered as precipitates upon addition of the solution to a mixture of toluene and ether. Clearfield reported a melting point of 206°–208°C for the dimethylformamide complex (*118*). Dimethyl acetamide also resulted in a 2 : 1 compound, although the acetamide and formamide products contained a minimum of four moles of amide per mole of tetrahalide. In the case of formamide at least, there is evidence that not all the amides are bound to the metal. The infrared spectra show that bonding is through the amide oxygen.

The reaction of zirconyl perchlorate with pyridine *N*-oxide in ethanol (*382*) gave a product of composition $ZrO(pyO)_6(ClO_4)_2$. The infrared spectrum shows that bonding is through the oxygen. A similar product was obtained with quinoline *N*-oxide (*327*). Zirconium is assumed to have a coordination number of seven in these species. The nature of the zirconium–oxygen moiety is not known.

C. OXYGEN LIGANDS—INORGANIC GROUPS

1. *Oxy-hydroxy*

The polymeric nature of the aqueous zirconium species at metal ion concentrations greater than 10^{-3} *M* and hydrogen ion concentrations of less than 1 *M* was established by the equilibrium studies of Connick *et al.* (*126–128*, *611*) and the ultracentrifugation experiments of Kraus *et al.* (*268*, *269*, *324*). The data were consistent with the existence of tetramers, $Zr_4(OH)_8^{8+}$, or trimers, $Zr_3(OH)_4^{8+}$, in solution. Low-angle X-ray studies on 2 molal zirconyl(hafnyl) oxychloride (bromide) carried out by Muha and Vaughn (*380*), show major peaks in the radial distribution functions which are reasonably consistent with a $[Hf_4(OH)_8(H_2O)_{16}]X_2$ species, although the data for zirconium solutions suggest that a more highly polymerized species might be present. Light scattering studies of zirconyl chloride in 2.80 *M* hydrochloric acid (*30*) and metal ion concentrations of 0.02–0.10 *M* lead to the conclusion that the predominant species in solution is a trimer with a total charge of three. At lower acid concentrations, such as 0.75 *M* H^+, the polymer appears to be a metal hexamer with a charge of less than 1. Approximate molecular weights for zirconium and hafnium polymers for solutions of 0.08–0.16 *M* zirconium (0.25 *M* hafnium) as determined by the method of free diffusion show the contribution of low molecular weight components is very small compared to the main polymeric form at these relatively high metal ion concentrations (*310*, *311*). Metal polymer formation is also consistent with the β-diketone extraction data of Peshkova (*427*, *429*), the metal ion dependence of electromigration (*383*), rate of dialysis (*35*), development of color with xylenol orange (*36*), diffusion coefficients (*593*), and nonmobility of zirconium hydrolysis products on chromatographic paper (*104*).

It appears likely then that the metal ion $Zr_4(OH)_8(H_2O)_{16}^{8+}$, which is present in the solid structure of $ZrOCl_2 \cdot 8H_2O$ (*576*) is also the basis for the structure of the aqueous polymer. In this ion the four zirconium atoms are at the corners of a square plane each being joined by a double hydroxy bridge. These four oxygen atoms and four more from water molecules are situated about the zirconium at the vertices of an Archimedian antiprism.

At low metal ion concentrations (10^{-6} mole/liter) and high hydrogen ion concentrations (pH, ~1.00), the ionic equilibria involving hydroxylation of the M^{4+} ion have been studied by β-diketone extraction techniques (*427*, *429*) at 25°C and ionic strength of 1. The values of β_n based on concentrations are tabulated in Table XV. From these data the hafnium(IV) species appears to be slightly less susceptible to hydrolysis compared to the zirconium(IV) species. True equilibrium constants have been determined by Solovkin and co-workers (*532*, *534*) for the hydrolysis of the Zr^{4+} ion in perchloric acid at ionic strength 1 and 25°C, by following the distribution of tracer ^{95}Zr between a perchlorate aqueous phase and a solution of thenoyltrifluoroacetone in benzene. The β_n values obtained were $\beta_1 = (3.8 \pm 0.4) \times 10^{14}$; $\beta_2 = (23.9 \pm 2.3) \times 10^{28}$; $\beta_3 = (52.0 \pm 8.5) \times 10^{42}$; $\beta_4 = .70 \times 10^{56}$. These constants are calculated for the equation:

TABLE XV

FORMATION CONSTANTS FOR HYDROXYLATION OF M^{4+} ION

Zr	Constant	Hf	Constant
β_1	$(2.10 \pm 0.2) \times 10^{14}$	β_1	1.3×10^{14}
β_2	$(1.83 \pm 0.02) \times 10^{28}$	β_2	0.77×10^{23}
β_3	$(0.83 \pm 0.01) \times 10^{42}$	β_3	0.30×10^{42}
β_4	$(0.195 \pm 0.005) \times 10^{56}$	β_4	0.10×10^{56}

$$M^{4+} + nH_2O \rightleftarrows (MOH)_n^{4-n} + nH^+ \tag{24}$$

The hydrolyzed species in equilibrium with solid zirconium hydroxide were studied by measuring the change in solubility of the hydroxide as a function of pH in dilute solution at 20° and 40°C, and in molar perchlorate solution at 20°C using a Tyndallometric method (*60*) (Table XVI). The data indicated that complexes of charges 0, +1, and +4 predominate

TABLE XVI

LOG APPARENT EQUILIBRIUM CONSTANTS FOR THE SOLUBILITY OF $Zr(OH)_4$

Equations	Equilibrium constants at:		
	20°C (*M* $NaClO_4$)	20°C	40°C
$Zr(OH)_4(s) + 4\ H^+ \rightleftarrows Zr^{4+} + 4\ H_2O$	~3.8(<4.3)	4.6(<5.0)	5.05 ± 0.18
$Zr(OH)_4(s) + 2\ H^+ \rightleftarrows Zr(OH)_2^{2+} + 2\ H_2O$	—	1.83 ± 0.13	2.01 ± 0.02
$Zr(OH)_4(s) + H^+ \rightleftarrows Zr(OH)_3^{1+} + H_2O$	0.2 ± 0.04	0.27 ± 0.03	0.06 ± 0.05
$Zr(OH)_4(s) \rightleftarrows Zr(OH)_4$	−4.36 ± 0.05	−3.90 ± 0.07	−3.91 ± 0.07
$Zr(OH)_4(s) \rightleftarrows Zr^{4+} + 4\ OH^-$	−52.0(< −51.5)	−52(< −51.6)	149.1 ± 0.2

in the molar perchlorate solutions. Apparent equilibrium constants were calculated for the tabulated equations assuming that monomolecular species were present (*60*).

The metal-bound hydroxyl groups, as before, were determined by displacement with fluoride and titration with standard acid (*605*). This method has also been adapted for distinguishing between terminal hydroxyl groups, bridging hydroxyl groups, bridging oxo groups, chain oxo groups, and Zr=O groups. A 0.1 gm sample is placed in 15 ml of water, a few drops of phenolphthalein and 15 ml of 2 *M* potassium fluoride are then added, after which the pH is adjusted to 8.0–8.2 with 0.1 *M* hydrochloric acid. The hydroxyl groups displaced are then titrated with 0.1 *M* hydrochloric acid. Freshly precipitated zirconium hydroxide, carefully washed free of ammonia gives 4 gm-equiv. of OH^- per mole of zirconium after 5–7 minutes. Hydroxide aged for 2–3 days or boiled gives only 2 gm-equiv./mole of zirconium after 5 minutes and 2 more after 10 hours. Zirconium hydroxide dried at room temperature barely reacted at all, whereas ignited zirconium oxide did not react. This technique was further refined by measuring the rate of titration of hydroxyl groups (*603*). The rate is said to be highest for nonbridging OH^- or bridging OH^-, lower for compounds containing chains of Zr–O–Zr–O–Zr and even lower for oxo bridges, Zr–O–Zr. The deoxolation of a Zr–O–Zr bridge is favored in acid solution (*602*), being rapid in 2 *N* acid (*439*), although it is sometimes necessary to heat the reaction system before adding the potassium fluoride solution.

The preparation of polynuclear products with Zr–O–Zr bonds is favored by the presence in the reaction mixture of a dehydrating agent, alcohol, or acetone. Using this principle numerous compounds have been reported (*609*). For instance, the addition of diethyl ether to a solution of zirconium oxychloride in methanol yielded a white, finely divided, crystalline precipitate with composition $Zr:Cl:OH:H_2O = 1:1.06:2.73:2.5$. The infrared spectrum indicates the absence of Zr=O groups (*290*). The data are consistent with a cation composed of two hydroxy-bridged tetrameric rings bridged by an oxygen atom. Single terminal hydroxy groups are pictured as being bound to the six similar zirconium atoms, and these appear to be replaceable by other anions, for example, oxalate. A whole series of compounds has been prepared on this basis.

It has been previously shown that freshly precipitated zirconium hydroxide washed thoroughly with water contains four hydroxy groups for every zirconium atom (*605*). This is the product designated by Zaitsev (*604*) as α-$[Zr(OH)_4]_4$. As previously mentioned there appears to be two other forms of zirconium hydroxide based on a cyclic tetramer, the β form in which the zirconium atoms are considered to be bonded alternately by two OH and two O groups, and the γ form in which all the bridging atoms are oxygen atoms. The reactivity toward acids declines from the α to γ forms. The α form is soluble in 50% potassium carbonate at 60°–80°C, whereas the β and γ forms are insoluble even on boiling. All forms take up 0.2–0.3 mole of carbonate per mole of zirconium; and with aqueous hydrogen chloride in methanol, one hydroxy group is exchanged for one chloride. The aging of these forms by boiling at 100°C or below, results in the elimination of some hydroxyl groups. The overall composition of hydroxides aged above 100°C suggests the existence of a new phase, δ $ZrO_{1.5}(OH)$, which is stable to about 400°C. This is not quite consistent with the observation that zirconium hydroxide dried at 60°C is $Zr(OH)_4$ (*56*).

It is clear that experimental data on the structure of hydrolyzed zirconium(IV) species in aqueous solution and in the solid lead to the conclusion that the zirconyl moiety Zr=O is not present (*294*, *295*), but rather an oxy- or hydroxy-bridged polymeric species. Attempts to dehydrate $ZrOCl_2 \cdot 8H_2O$ (*218*, *313*) or $ZrO(ClO_4)_2 \cdot 8H_2O$ (*55*) to obtain $ZrOX_2$ yield hydrogen chloride as one of the products before dehydration is complete. Dehnicke (*139*, *140*), however, has synthesized $ZrOCl_2$ by the reaction

$$ZrCl_4 + Cl_2O \rightarrow ZrOCl_2 + 2\,Cl_2 \qquad (25)$$

in carbon tetrachloride as the solvent. The oxychloride forms a 2:1 addition compound with $POCl_3$ and a 1:1 addition compound with pyridine. The infrared spectrum of $ZrOCl_2$ has a band at 877 cm^{-1} which is assigned to the Zr=O-stretching frequency which is not present in the spectrum of $ZrOCl_2 \cdot 8H_2O$. To account for the total absorption spectrum, however, it is necessary to postulate a model based on $(ZrO^{2+})(ZrOCl_4^{2-})$ ions, with the anion containing square-planar chlorides perpendicular to a Zr–O–Zr–O chain. Anhydrous $MOCl_2$ has also been prepared (*369*) by heating $Zr(Hf)Cl_4$ with Sb_2O_3 at 180°–320°C for 8–14 hours in a stream of gaseous chlorine. Additionally, there are reports of zirconyl (hafnyl) compounds, such as $ZrOF_2$, $KZrOF_3$, $Zr_4F_{10}O_3$, $ZrF_4 \cdot H_2O$, $Hf_4F_{12}O_2$, $HfF_4 \cdot H_2O$, and $HfOF_2$ (*290*), the isothiocyanates $M[ZrO(NCS)_3(H_2O)] \cdot H_2O$, where M = ammonium, potassium, rubidium, cesium, and pyridinium (*291*), and the corresponding hafnium compounds (*292*, *340*) with cesium and pyridinium cations, as well as $(PyH)_3[(HfO)_2(NCS)_7(H_2O)] \cdot H_2O$. The infrared spectra for all these compounds have been interpreted as showing evidence for the presence of the "M=O" moiety. Selbin (*486* has repeated much of this work and has been successful in duplicating the thiocyanate, but not the fluoride, data.

Hydrous zirconia has been shown to have cationic and anionic exchange capacities in alkaline and acid media, respectively. The early progress in this area has been adequately reviewed by Amphlett (*29*). The capacities are strongly hydrogen ion-dependent, with cation and anion capacities being equal at about pH 7. The most probable mechanism for exchange appears to be a highly specific but reversible adsorption of hydrogen ions or hydroxyl ions. The thermodynamics of anion exchange has been studied by Nancollas (*385*). Hydrous oxide used for exchange studies was prepared by the addition of aqueous ammonia to a solution of 0.2 *M* zirconyl chloride at 70°C. The resulting gelatinous precipitate was washed and air-dried at 50°C. The glassy solid was sieved and washed in a column until free of chloride. The exchange of chloride, nitrate, and thiocyanate was then studied by equilibrating 0.5 gm of exchanger at 25°C with solutions of mixed anions at a total ionic strength of 0.1 and an acid concentration of 0.01 *M*. Anion capacities previously determined were in weight of ZrO_2/meq of anion, $Cl^- = 0.517$, $NO_3^- = 0.545$, and $NCS^- = 0.542$. Thermodynamic equilibrium constants for anion equilibria were $K^{Cl}_{NO_3} = 1.04 \pm 0.1$; $K^{NCS}_{Cl} = 1.54 \pm 0.1$; and $K^{NCS}_{NO_3} = 1.94 \pm 0.2$.

Crystalline hydrous zirconia has been prepared (*115*) by refluxing slurries of hydrous zirconia or zirconium oxychloride solutions adjusted to pH values between 1 and 2.5 by addition of ammonia. Final products have an X-ray diffraction pattern characteristic of monoclinic zirconia. Cubic zirconia free of monoclinic zirconia was prepared by heating amorphous hydrous zirconia in the presence of aqueous sodium or potassium hydroxide. Cubic hydrous zirconia was stable to 650°C whereupon it reverted to the monoclinic form.

The crystal structure of monoclinic ZrO_2 has been corrected (*2*, *356*, *528*). The zirconium has sevenfold coordination with four formula units in the unit cell. Four oxygen atoms are at the base of a cube with one at one of the upper corners and the remaining two at the midpoints of the cube edge connecting the unoccupied corners. Thus there are oxygen atoms in approximately tetrahedral symmetry with Zr–O distances ranging from 2.151 to 2.285 Å, and three oxygen atoms in approximately triangular symmetry with Zr–O distances of 2.057, 2.163, and 2.051 Å. The triangular array appears to be planar with pairs of triangles sharing Zr–Zr edges and the corners of the zirconium polyhedron being shared by three such polyhedra. The remaining four corners are shared by four polyhedra. HfO_2 was found to be isomorphous (*2*). The monoclinic-tetragonal (*48*, *202*) and tetragonal-cubic conversions (*124*, *527*) have also been studied.

2. *Peroxy*

Quantitative studies made on the three component system $Zr(OH)_4$, H_2O_2, and H_2O at 0°C and −20°C (*348*) established the concentration limits for the existence of the solid phases shown in Table XVII. Attempts to wash the products free of mother liquor resulted in decomposition. The hydrates were formulated as hydroperoxides by the authors.

TABLE XVII

HYDROGEN PEROXIDE CONCENTRATION (%) LIMITS FOR EXISTENCE OF SOLID PHASES IN THE SYSTEM $Zr(OH)_4$–H_2O_2–H_2O

Temperature	Compound	Limit Lower	Limit Upper
0°C	$Zr(OH)_4$	4.23	19.05
	$ZrO_3 \cdot 2H_2O$	19.05	71.92
	$ZrO_3 \cdot H_2O$	71.92	83.13
−20°C	$Zr(OH)_4$	27.64	34.02
	$ZrO_3 \cdot 2H_2O$	34.02	70.94
	$ZrO_3 \cdot H_2O$	70.94	92.93
	ZrO_3	92.93	96.45

In acid solution, zirconium(IV) (*597*) and hafnium(IV) (*599*) have been shown to catalyze hydrogen peroxide decomposition. The intermediate metal–peroxide species formed appears to be a 1:1 complex at pH 1–2 and very low metal ion concentrations (10^{-5} *M*). In strongly acid solutions (1–2 *M* HCl), two zirconium–peroxide compounds are observed containing one and two moles of peroxide per mole of zirconium. Babko and Ul'ko (*40*) considered these compounds to be products of Zr^{4+} and ZrO^{2+} with H_2O_2. Cheng (*105*) observed that at hydrogen ion concentrations of 0.5–1.0 *M* and metal ion concentrations of 10^{-5} *M*, the complex formed with hydrogen peroxide and zirconium is so stable that the zirconium–xylenol orange complex cannot form. This is not the case with the hafnium–hydrogen peroxide complex. This differentiation was not shown when zirconium–hafnium mixtures were used. The 1:1 complex was also observed in solutions of low pH (0.7–1.75) and high metal ion concentrations (0.2 *M*) to which hydrogen peroxide is added (*286*).

A complex $(NH_4)[Zr(O_2)F_5]\cdot H_2O$ was crystallized from a solution made by dissolving freshly prepared hydrated zirconium hydroxide in cold (−5°C) 40% hydrofluoric acid, then adding excess 30% hydrogen peroxide, and finally aqueous ammonia until pH 7 is reached. The infrared spectrum showed ν_{O-O} at 839w, $\nu^{s}_{MO_2}$ at 555w, and $\nu^{as}_{MO_2}$ at 480s, br (*226*).

From sulfate solutions, the precipitate obtained upon standing at room temperature for 24 hours after the addition of 30% hydrogen peroxide to a zirconium sulfate solution containing 100 gm/liter at pH 0.1 to 0.7, corresponds to the composition $Zr_2(OO)_3(SO_4)\cdot nH_2O$, where $n = 8$ to 10 (*562*). From boiling sulfate solutions at pH values between 0.8 and 2.7 and a $Zr:SO_4$ ratio of 1:5, products are obtained which usually correspond to mixtures of the limiting compositions $(ZrO)_2OO(SO_4)\cdot nH_2O$ and $(ZrO)_3(OO)_2(SO_4)\cdot nH_2O$.

Peroxide complexes from basic solutions have also been studied (*40*), the anion $ZrO(O_2)_2^{2-}$ being reported in the pH region of 12–13. Griffith (*225*) reported that the absorption spectra of $K_4Zr(O_2)_4$ and $K_4Hf(O_2)_4$ have strong bands at 854 and 828 cm^{-1}, respectively, which likely arise from the O–O stretching or O–M–O deformation. No data are given on the source or the purity of the compounds. It has been observed that products obtained from alkaline solution contain carbonate unless precautions are taken to exclude the atmosphere from the reaction system (*332*). Thus, from solutions of composition hydrogen peroxide: sodium hydroxide:zirconium (hafnium) oxychloride (5:10:1), in which the final minimum hydroxide concentration is 0.5 *M* and the metal ion concentration ranges from 0.08 to 0.3 *M*, there is precipitated from a homogeneous solution a product of composition $Na_4[Zr_5(H_2O)_5O_6(O_2)_6]$. The water molecules are probably present as hydroxyl groups as the infrared spectrum shows strong absorption at 3350 cm^{-1}. The dry product on standing in the atmosphere takes up two moles of carbon dioxide and loses two moles of peroxide. The sodium ions are exchangeable, being replaced by potassium, magnesium, calcium, and barium. A review of the peroxide compounds of the transition metals which includes the early work on zirconium and hafnium has been written by Connor (*128*).

3. *Nitrate*

The general area of anhydrous metal nitrates has been surveyed by Addison (*10*). The anhydrous tetranitrate has been prepared (*176*) by the reaction of dinitrogen pentoxide on zirconium tetrachloride at 30°C. Nitryl chloride is evolved and an initial product of composition $Zr(NO_3)_4\cdot 0.4N_2O_5\cdot 0.6N_2O_4$ is obtained. The nitrogen oxides can be removed by heating at 100°C in 4 hours at 0.01 mm. On continued heating, the tetranitrate slowly sublimes and may be condensed in the form of colorless crystals. The compound has a high solubility in polar solvents, but reacts with compounds such as toluene to produce nitro products. The infrared spectrum of the solid includes bands in the ranges 1224–1384 (ν_1), 1575–1631 (ν_4), 983–1015 (ν_2), and 764–792 cm^{-1} (ν_3 and ν_6). The appearance of ν_4 and ν_1 requires that the metal–nitrate bonds are strongly covalent and that the nitrate groups are bidentate or bridging. The corresponding hafnium compound has also been prepared by the reaction of N_2O_5 on hydrated hafnium nitrate (*176*). The product usually was the $Hf(NO_3)_4 \cdot N_2O_5$ derivative rather than the stoichiometric nitrate (*177*). The hydrated tetranitrates, $M(NO_3)_4 \cdot 4H_2O$, also show a splitting of the ν_3 mode to ν_4 (1520–1590 cm^{-1}) and ν_1 (1290–1430 cm^{-1}), thus indicating covalently bonded nitrate groups. The zirconium and hafnium nitrates show a high degree of splitting compared to the other nitrates (*175*).

The infrared spectrum of compounds having the gross composition $Zr(NO_3)_4(H_2O)_4$ and $Zr(OH)(NO_3)_3(H_2O)_3$ were studied (*236*). The compounds were partially deuterated by exposing them to D_2O vapor in a vacuum desiccator followed by vacuum evaporation at 0° to 30°C. The strong bands centered on 1567, 1275, 1010, 796, 774, and 765 cm^{-1} are similar to those found in the anhydrous compound, and can be assigned to the fundamental vibrations of the coordinated bridging or bidentate nitrato groups. Bands characteristic of hydroxyl and water were also present. Frequencies at 443–419 and 303 cm^{-1} did not shift upon deuteration and are assigned to Zr–O bonds in which the oxygen is bonded to nitrogen and hydrogen. No bands were assigned to the nitrate ion or to the Zr=O group.

The infrared spectra of (*293*) the zirconium and hafnium nitrates having the general composition $MO(NO_3)_3 \cdot 2H_2O$, $MO(NO_3)_2 \cdot 6H_2O$, and $M_2O_3(NO_3)_2 \cdot 5H_2O$ show no evidence for MOMO chains. It is impossible to say whether the dihydrate and hexahydrate contain MO or $M(OH)_2$ groups. The hexahydrate spectrum contains bands typical of coordinated nitrato groups and uncoordinated nitrate ions as well. The intense absorption of the nitrate ion at about 1390 cm^{-1} is absent in the dihydrate and the conclusion is that water molecules displace nitrate groups from the first coordination sphere in the hexahydrate. It should be recalled that Hardy *et al.* (*236*) saw no evidence for uncoordinated nitrate ions in their compounds. The product of composition $Zr_2O_3(NO_3)_2 \cdot 5H_2O$ has been prepared (*435*) by the addition of a tenfold volume of alcohol to a 3 *M* solution of zirconium (hafnium) oxynitrate at 40°–50°C. Upon the addition of ether, precipitation of the product occurs. The infrared spectrum indicates the presence of hydroxyl groups, so the compound is better formulated as $ZrO(OH)(NO_3) \cdot 2H_2O$. The hafnium compound has also been prepared.

The crystal structure of $Zr(OH)_2(NO_3)_2(H_2O)_4$ has been determined (*358*). Chemically the structure may be considered as consisting of chains of $[Zr(OH)_2(NO_3)(OH_2)_2{}^+]_n$, which are joined by nitrate groups through hydrogen bonds. The zirconium atoms are joined by double bridges of hydroxide ions. The coordination number of the zirconium is 8 and the coordination polyhedron is a dodecahedron with triangular faces. There are two formula units per unit cell in the triclinic structure which has $a = 7.408$ Å, $b = 11.227$ Å, $c = 6.741$ Å, with $\alpha = 60.91°$, $\beta = 99.78°$, and $\gamma = 99.78°$.

TABLE XVIII

EQUILIBRIUM CONSTANTS FOR THE COMPLEXING OF M^{4+} WITH NITRATE

	Constants		
Equation	Zr	Hf	μ
$M^{4+} + NO_3^- \rightleftarrows MNO_3^{3+}$	0.92 ± 0.07	0.90 ± 0.07	$\mu = 2.0$
	0.88 ± 0.1	0.60 ± 0.05	$\mu = 4.0$
$M^{4+} + 2\,NO_3^- \rightleftarrows M(NO_3)_2^{2+}$	0.46 ± 0.1	0.55 ± 0.08	$\mu = 2.0$
	0.14 ± 0.08	0.12 ± 0.04	$\mu = 4.0$

Compounds of composition $(NMe_4)_2Zr(Hf)(NO_3)_6$ result from the reaction of liquid N_2O_4 in acetonitrile or liquid N_2O_5 on the corresponding hexachloro complexes (*41*). The hexanitrato complexes are soluble in anhydrous acetonitrile or nitromethane, but immediately decompose in water. The complexes are thermally unstable, evolving oxides of nitrogen at 130°C (Zr) or 230°C (Hf). The infrared spectrum can be assigned to covalently bonded nitrate groups. The separation of the ν_1 and ν_4 frequencies (250–320 cm^{-1}) of the hexanitratozirconate(IV), which contains unidentate nitrate groups, is markedly less than the separation observed in this region (292–407 cm^{-1}), for the tetranitrate which contains bidentate nitrate groups.

Zirconium solutions (0.324 *M*), which are 0.65–8 *M* in nitrate, absorb in the 250–260 mμ range with an intensity which is proportional to the nitrate concentration. Additional evidence for zirconium–nitrate complex formation comes from two phase distribution studies in which the distribution coefficient is found to be a function of both of the nitrate concentration and the hydrogen ion concentration. These data were interpreted to mean that the extracted compound in the aqueous phase had the composition $(ZrO)_n(NO_3)_{2n}$ (*310*).

Equilibrium constants for the formation of nitrate complexes at hydrogen ion concentrations of 2 and 4 *M* and metal ion concentrations of 5×10^{-6} *M* or less, were determined using ion exchange techniques (*353*, *465*) (Table XVIII). Activity coefficient data for aqueous zirconium and hafnium species are scarce, although there is one report (*319*) of activity coefficients for metal nitrate solutions as determined by the isopiestic method.

4. *Carbonate*

Studies of the $ZrOCl_2$–Na_2CO_3–H_2O system and the equivalent potassium carbonate (*356*) and ammonium carbonate (*339*) systems have led the authors to conclude that the solid phase contains a mixture of basic zirconium carbonates and hydroxocarbonates of composition $M[Zr(OH)_3CO_3]$ and $ZrOCO_3 \cdot nH_2O$ and that the solution phase contains anions of compositions $[ZrO(CO_3)_2]^{2-}$ and $[Zr(OH)_4(CO_3)_2]^{4-}$. The $[ZrO(CO_3)_2^{2-}]$ anion has also been obtained in a barium salt (*31*).

A more extensive set of carbonato species has been characterized by Pospelova and Zaitsev (*438*). Compounds with Zr:CO_3 ratios ranging from 1:1 to 1:4 in increments of 0.5 mole of carbonate have been prepared. The first four members of the series are looked upon as being derived from the oxo- and hydroxo-bridged tetrameric species, in which carbonate groups first replace the terminal hydroxide groups, and finally two of the bridging oxo positions. The 1:3 and 1:3.5 species are viewed as being derived from a linear dimer containing an oxo bridge and a carbonato bridge, respectively. The sodium, potassium, and guanidinium salts of the anions $[ZrOZr(OH)_4(CO_3)_2]^{2-}$, $[ZrOZr(OH)_3(CO_3)_3]^{3-}$, $[ZrOZr(OH)_2(CO_3)_4]^{4-}$, $[ZrOZr(CO_3)_5]^{4-}$, $[ZrOZr(CO_3)_6]^{6-}$, $[ZrCO_3Zr(CO_3)_6]^{6-}$, and $[Zr(CO_3)_4]^{4-}$ were prepared. For some of these species, the alkali metal cations were exchanged for the complex cations $Co(NH_3)_6^{3+}$ and $Cr(CO(NH_2)_2)_6^{3+}$. X-ray diffraction patterns were extremely complex (*215*) with no isostructural species noted.

5. *Sulfates*

The tetrahydrate of the normal sulfate $Zr(SO_4)_2 \cdot 4H_2O$ is obtained as a precipitate upon addition of sulfuric acid to an aqueous solution of zirconium(IV). Its structure consists of sheets of coordination number eight antiprisms in which zirconium is bonded by the oxygen atoms of the four water molecules and the oxygen atoms of four sulfate groups. The sulfate groups are bidentate to two metal ions and hold the layer together. The average Zr–O distance is 2.180 Å. The sheets are perpendicular to the *a* axis of the orthorhombic unit cell, and are held together by hydrogen bonds (*515*). The infrared absorption spectra of zirconium (hafnium) sulfate tetrahydrate over the range 2–15 μ have been recorded (*11*). The anhydrous normal sulfate α-$Zr(SO_4)_2$ is prepared by fuming the tetrahydrate with sulfuric acid and then heating at 350°–450°C. A vapor pressure study of the α-$Zr(SO_4)_2 \cdot H_2O$ system showed no evidence for a monohydrate, although a pentahydrate was recovered from the clear syrupy liquid resulting from the dissolution of one mole of anhydrous sulfate in eleven moles of water (*49*). Upon heating the tetrahydrate at 300°–400°C for 1 hour, β- and γ-$Zr(SO_4)_2$ are obtained. These species show a slight deficiency in sulfate compared to the α product, and have different X-ray powder patterns. Vapor phase hydration of the β product yields β-$Zr(SO_4)_2 \cdot 5H_2O$ which has an equilibrium water vapor pressure of 15.2 ± 0.1 mm at 25°C compared to 16.7 ± 0.1 mm for the α-pentahydrate (*50*). A heptahydrate has been prepared by crystallization at 0°C from saturated solutions of the anhydrous or pentahydrate phases or supersaturated tetrahydrate solution. It is stable at 0°C in contact with its saturated solution, although at room temperature it is converted directly to the tetrahydrate. If dried over P_2O_5 it decomposes to α-$Zr(SO_4)_2 \cdot 5H_2O$. X-ray data reveal the hepta- and pentahydrates to be monoclinic with unit cell parameters for heptahydrate: $a = 12.04$, $b = 6.36$, $c = 8.28$ Å, $\alpha = 93.0$, $\beta = 92.4$, $\gamma = 95.9$, $Z = 2$; for pentahydrate: $a = 11.89$, $b = 6.17$, $c = 7.56$ Å, $\alpha = 106.5$, $\beta = 95.7$, $\gamma = 104.6$, $Z = 2$. Both are built up from similar dimeric groups and can be best represented by the formulas $[Zr_2(SO_4)_4(OH_2)_8] \cdot 6H_2O$ and $[Zr_2(SO_4)_4(OH_2)_8] \cdot 2H_2O$. The coordination of the zirconium atom in each case is 8 in dodecahedral geometry. Two dodecahedra and four tetrahedral sulfates make up the common structural unit. These units are joined together through bonded and nonbonded water molecules. In the heptahydrate, four water molecules are coordinated to each zirconium with the remaining six being nonbonded and lying in sheets along the 001 plane. In the pentahydrate there are only two nonbonded water molecules. The stability of the dimeric structure depends on the hydrogen bridging between the nonbonded water molecules and adjacent layers of $Zr_2(SO_4)_4(OH_2)_8$ groups (*51*). Lower hydrates with 1.5 and 0.5 moles of water are found by Rogachev (*458*).

In contrast to the equilibrium vapor pressure measurements on the tetrahydrate, thermal decomposition studies show the stepwise loss of water, the first three moles being lost at 155°–180°C and the fourth at 290°–315°C. It has been suggested that (*32*) the two-step dehydration is associated with a structural rearrangement to give a species of composition $H_2[ZrO(SO_4)_2]$, which may contain the tetrameric $(Zr\text{–}O)_4^{8+}$ ring. A similar observation has been made on the corresponding hafnium tetrahydrate sulfate (*579*), although in this case three moles of water are lost up to temperatures of about 215°C, while the fourth is not lost until 490°C. The recovery of sodium and potassium salts from aqueous solutions of the sulfate, with the composition $M_2[ZrO(SO_4)_2]\cdot 3H_2O$ is consistent with this idea.

Many other oxygenated and hydroxylated species have been formulated (*64*), but structural data are available for only a few of them (*359*). The compounds $Zr_2(OH)_2(SO_4)_3(H_2O)_4$, $Zr(OH)_2SO_4$ [(I) and (II)] were prepared by evaporating to dryness a solution of zirconium oxychloride in dilute sulfuric acid, followed by heating the residues to temperatures of 100°–150°C, 175°–225°C, and 250°–300°C, respectively. The $Zr:SO_4$ 1:1 compounds have almost the same lattice parameters, although (II) has a slight distortion to monoclinic symmetry; the space group being $P\,2_1/n$ rather than *Pnma*. The symmetry about the zirconium is antiprismatic with the oxygen atoms of four hydroxyl groups and four sulfate groups at the vertices. The zirconium atoms and hydroxyl groups form zigzag chains with the composition $[Zr(OH)_2]_n^{2n+}$. The chains are held together by sulfate groups with each sulfate group connecting three chains. A hydrate of composition $Zr(OH)_2(SO_4)\cdot 2H_2O$ is precipitated (*64*) upon adding a 0.25 mole excess of sulfuric acid to a solution of zirconium oxychloride in methanol. This compound when treated with gaseous HCl yielded $Zr(OH)_2Cl(HSO_4)\cdot H_2O$, which was taken as evidence that some of the hydroxyl groups were terminal rather than bridging. The infrared spectra showed no evidence for the $Zr{=}O$ groups (*295*, *359*). Although the structure was formulated as a tetramer with hydroxy bridges and monodentate hydrogen sulfate groups, this seems questionable in light of the previously cited X-ray structure of the anhydrous species. A monohydrate of the same composition was precipitated by alcohol (*64*) from a solution formed from freshly precipitated $Zr(OH)_4$ and sulfuric acid in the ratio of 1 : 1.25. This compound, when treated with gaseous HCl, was recovered unchanged. This was taken to mean that the compound did not contain free hydroxyl groups, but only bridging groups. Zaitsev (*64*) reports that the composition of the product depends on the form of the hydroxide used.

Anionic species which contain zirconium and sulfate in a 1:1 ratio have also been reported (*64*). The addition of M'_2SO_4 aqueous solutions to an aqueous solution of $Zr(SO_4)_2\cdot 4H_2O$ followed by the addition of alcohol gives a fine white precipitate of composition $M'_2[Zr_4(OH)_8(SO_4)_6]\cdot 11H_2O$. The ammonium, sodium, and potassium salts have been prepared. These are looked upon as being tetrameric with oxy as well as hydroxy bridges.

The compound $Zr_2(OH)_2(SO_4)_3(H_2O)_4$ (*359*) is composed of sheets of zirconium atoms, each being connected by four sulfate groups to adjacent zirconium atoms, with eight of the sulfate groups bonded to three zirconium atoms and four sulfates bonded to two zirconium atoms. The sheets are connected by double hydroxy bridges between metal atoms. Therefore, each zirconium has eightfold coordination with the oxygen atoms of two hydroxyl groups, four sulfate groups, and two water molecules at the vertices of a dodecahedron. The metal–metal distance in the dimer is 3.545 Å. The O–O distance in the OH bridge is very short, being only 2.34 ± 0.06 Å. The crystal is monoclinic with $a = 13.056 \pm 0.002$, $b = 6.5075 \pm 0.0006$, $c = 15.092$ Å, and $\beta = 96.21 \pm 0.01$. There are four formula units per unit cell. It is interesting to note that in the compounds for which the structures have been determined, there have always been four sulfates per zirconium regardless of the stoichiometry of the compound.

TABLE XIX

EQUILIBRIUM CONSTANTS FOR THE COMPLEXING OF M^{4+} WITH SULFATE

Equation	Constant Zr	 Hf
$M^{4+} + HSO_4^- \rightleftarrows M(SO_4)^{2+} + H^+$	$K_1 = 361 \pm 12$	130 ± 6
$M^{4+} + 2HSO_4^- \rightleftarrows M(SO_4)_2 + 2H^+$	$K_2 = (2.17 \pm 0.15) \times 10^3$	$(2.09 \pm 0.01) \times 10^3$
$M^{4+} + 3HSO_4^- \rightleftarrows M(SO_4)_3^{2-} + 3H^+$	$K_3 = (4.06 \pm 1.2) \times 10^5$	—

An anionic species containing zirconium and sulfate in the ratio 1:1.5 of composition $M'_4[Zr_4(SO_4)_6(OH)_8]\cdot 6H_2O$ is obtained upon adding alcohol to a mixture of M'_2SO_4 and $Zr(SO_4)_2$ in the mole ratio 1:(1.0–2.0). No chloride exchange occurs upon exposure to gaseous hydrogen chloride leading to the conclusion that all the hydroxyl groups are bridging groups.

Anionic sulfato complexes with $Zr:SO_4$ ratios greater than 2 have also been reported (*33*). In general these are prepared by evaporating a solution of M_2SO_4, H_2SO_4, and $Zr(SO_4)_2\cdot 4H_2O$ in appropriate mole ratios until a crystalline product appears. In this way, compositions corresponding to $M_{1.5}[ZrO_{0.25}(SO_4)_{2.5}]H_2O$, $M_2[Zr(SO_4)_3]\cdot nH_2O$, $M_3[Zr(SO_4)_{3.5}]$, $M_4[Zr(SO_4)_4]\cdot 3H_2O$, $K_{4.5}H_{0.5}[Zr(SO_4)_{4.5}]\cdot 3H_2O$,

$K_6Zr(SO_4)_5 \cdot 3H_2O$, $K_{6.5}H_{1.5}[Zr(SO_4)_6] \cdot H_2O$, $K_{7.8}H_{2.2}[Zr(SO_4)_7] \cdot H_2O$, and $K_9H_3[Zr(SO_4)_8] \cdot H_2O$, where M is generally NH_4^+, Na^+, or K^+, have been prepared. X-ray diffraction patterns of each product are unique.

Qualitative observations on the nature of the soluble aqueous species present in sulfate solutions indicate that sulfate complexes are much more stable than perchlorate, chloride or nitrate complexes (*383*). Electromigration studies at SO_4:Zr ratios greater than 1:1 show that anionic sulfate complexes are formed (*384*). In spite of complexing by sulfate, hydrolysis does occur (*154*) and metal polymeric hydroxy species are formed (*595*) in 0.006 *M* zirconium solutions.

Quantitative studies (*464*, *465*) by ion exchange techniques on the complexing of the M^{4+} metal ions with sulfate ions, show that hafnium is less strongly complexed than zirconium (Table XIX). At lower hydrogen ion concentrations, the hydrogen ion dependence of the complexing is consistent with the reaction

$$H_2O + Zr^{4+} + HSO_4^- \rightleftharpoons ZrOSO_4 + 3\,H^+ \tag{26}$$

for which the equilibrium constant of 58 ± 5 was calculated (*600*). Another cationic oxygenated species $[(ZrO)_2SO_4]^{2+}$ was reported by Saksin (*468*) to have an instability constant of 1.88×10^{-9}. Whether or not this species contains a ZrO group probably should be reexamined in the light of recent evidence.

6. *Phosphate and Arsenate*

a. Amorphous Zirconium Phosphate. Zirconium phosphate of composition $PO_4/Zr = 2$ is obtained as a gelatinous amorphous precipitate when excess phosphoric acid is added to a soluble zirconium salt (*14*, *22*, *36*, *123*, *589*). Precipitates of different PO_4/Zr ratios may be obtained by altering the initial concentrations and washing procedures. Insoluble amorphous precipitates obtained upon addition of an $Na_5P_3O_{10} \cdot 6H_2O$ solution to solutions of zirconyl or hafnyl oxychloride gave M^{4+}/P_3O_{10} ratios of 5/2, 2/1, or 5/4 depending on the initial concentrations of reactants (*209*).

Amorphous products of composition $ZrO_2:P_2O_5:2H_2O$, when heated at 110°C, lose one mole of water. A second mole is lost in the range 180°–350°C (*22*, *123*) and is accompanied by the formation of P–O–P bonds, although complete conversion to ZrP_2O_7 is not achieved until temperatures of about 800°C are reached. The weight loss is compatible with an initial composition of $Zr(HPO_4)_2 \cdot nH_2O$.

A product for ion exchange use has been prepared in granular form by freezing (*487*) purified, freshly precipitated gels at a cooling rate of 5–10 cal/ml/hour. Upon unfreezing a granulated product with physical properties more desirable than the plain air-dried gel is obtained.

Early work on the exchange properties of amorphous zirconium phosphate has been summarized by Amphlett (*29*). In addition, Ahrland *et al.* (*13*, *15*) have studied the exchange behavior of representative fission product ions, for which they found an affinity order of UO_2^{2+}, Ce^{3+}, Y^{3+}, Sr^{2+}, Cs^+, Rb^+, Na^+, when amorphous gels of high PO_4/Zr ratios were used. The separation of certain transplutonium ions (*250*) on amorphous zirconium phosphate of composition $PO_4/Zr(1.34)$ having a capacity of 0.60 meq/gm at pH 2 and 75°C yielded separation factors shown in Table XX. Equilibrium was not attained rapidly at any hydrogen ion concentration, although reverse desorption attained equilibrium within 1 hour. The affinity sequence of Cf > Eu > Cm > Am > Ce is the exact reverse of that found for Dowex 50.

TABLE XX

SEPARATION FACTORS FOR TRANSPLUTONIUM ION EXCHANGE ON AMORPHOUS ZIRCONIUM PHOSPHATE[a]

Compound	Cm^{3+}/Am^{3+}	Cf^{3+}/Cm^{3+}	Eu^{3+}/Am^{3+}	Am^{3+}/Ce^{3+}
HNO_3	1.20	2.45	1.46	1.86
H_2SO_4	1.15	2.10	1.36	—

Compound	Ce^{4+}/Cm^{3+}	Ce^{4+}/Cf^{3+}	Ce^{4+}/Cm^{3+}
HNO_3	175	71.4	59.4

[a] At 75°C.

Although the effect of heat treatment of the phosphate is a decrease in ion exchange capacity (*14*, *22*, *123*, *560*), the hydrogen form of the exchanger was successfully regenerated from the ammonium form by thermal decomposition of the ammonium ion in a nitrogen atmosphere (*19*). With a flow rate of 12 liters/hour it was possible to achieve a 90% decomposition in 10 hours at 260°C with only 6% pyrophosphate condensation.

It was recognized that the hydrolytic stability of amorphous zirconium phosphate left something to be desired (*14*, *36*, *123*), although certain ratios seem to be more stable than others in water at 25°C. The hydrolytic stability of amorphous phosphate preparations of varying PO_4/Zr ratios in nitric acid solution at 75°C has been studied by Horwitz (*250*). There was no composition within the range studied which was completely stable to hydrolysis, although samples with mole ratios of PO_4/Zr, 1.34 to 1.13, showed a substantial reduction in the degree of hydrolysis. The extent of hydrolysis was at a minimum in the range of 10^{-2} *M* HNO_3 and decreased slightly with decreasing temperature.

b. Crystalline Zirconium Phosphate. Clearfield (*117*, *123*) has prepared three forms of crystalline $Zr(HPO_4)_2 \cdot nH_2O$. The monohydrate, called the α form, is the most stable. It is prepared by refluxing an amorphous preparation in phosphoric acid. In 8–12 *M* acid only 1 hour of reflux is necessary for the conversion. Another route to the preparation of crystalline zirconium phosphate involves the precipitation in the presence of a small amount of fluoride. A product of composition $PO_4/Zr = 2.0$ is obtained with a particle size of $\geqslant 20$ mesh (*20*).

Anhydrous zirconium phosphate ($PO_4/Zr = 2$) and the dihydrate are prepared by adding 100 ml of 1 *M* zirconium oxychloride$\cdot 8H_2O$ dropwise to constantly stirred, refluxing phosphoric acid solution prepared by dissolving two moles of sodium dihydrogenphosphate$\cdot H_2O$ in 200 ml of 3 *M* HCl. The zirconium phosphate gel is refluxed in its mother liquor for 25 hours and then washed until free of chloride. When air-dried, the dihydrate or γ phase was obtained; when vacuum-dried over calcium sulfate, the anhydrous α phase was obtained (*117*).

X-ray powder diagrams of crystalline $Zr(HPO_4)_2 \cdot H_2O$ (*23*, *485*) were indexed on the basis of hexagonal symmetry. Clearfield (*120*, *121*), however, has found from single-crystal studies that untwinned crystals are best described as monoclinic with $a = 9.076 \pm 0.003$ Å, $b = 5.298 \pm 0.006$ Å, $c = 16.22 \pm 0.02$ Å, and $\beta = 111.5 \pm 0.01°$. The space group is $P2_1/c$. There are four formula units per unit cell. The monohydrate has a layered structure. Each layer consists of sheets of zirconium atoms held together by phosphate bridges. The phosphate groups are situated above and below the sheets of metal atoms. Each zirconium is coordinated by six oxygen atoms arranged octahedrally about the zirconium atom. Each of these six oxygen atoms belongs to one of six different monohydrogen phosphate groups, three of which lie above the mean plane of the zirconium atoms and three of which lie below it. Each monophosphate acts as a three-way bridging ligand, coordinating three different zirconium atoms through three of its oxygen atoms. The fourth noncoordinating oxygen atom points toward an adjacent layer in the structure and presumably bears the hydrogen atom. The layers are ordered in a way such that the monohydrogen phosphate groups from adjacent layers do not lie directly opposite one another. This packing creates zeolytic cavities in which the water molecules reside. Hydrogen bonds involving the water molecules and HPO_4 groups hold the layers together. The interlayer separation in the α-zirconium phosphate structure is 7.6 Å. The distance between the mean plane of the zirconium atoms and the mean plane of the phosphorus atoms is 1.64 Å.

The β and γ structures probably contain the same two-dimensional layer structure, except that the packing is such that the HPO_4 groups in each layer are opposed to one another. An interlayer separation of 9.28 Å is predicted for the anhydrous β product. It is thought that the dihydrate is derived from the anhydrous structure by simple insertion of water molecules between the layers, giving an interlayer distance greater than 9.28 Å.

$KZr_2(PO_4)_3$ has a hexagonal structure with $a = 8.71$ Å, $c = 23.90$ Å, and space group $R\bar{3}C$ (*354*).

The ion exchange capacity of crystalline zirconium phosphate monohydrate by titration, shows the presence of two different hydrogen ion exchange sites (*123*, *237*). In the ion exchange process the cations initially displace hydrogen from the PO–H groups which are hydrogen bonded to water molecules, with the cations occupying the positions vacated by the water molecules. Crystalline zirconium phosphate exchanges hydrogen for Na^+, K^+, and Rb^+ (at high pH), but generally excludes Cs^+ (*14*, *23*, *123*, *237*), whereas Cs^+ is exchanged by the amorphous form (*23*, *589*). Multivalent ions are absorbed more strongly than univalent ions, with $Sr^{2+} \geqslant UO_2^{2+} \geqslant Ce^{3+} > Na^+$ (*23*, *386*). Clearfield (*119*) has prepared a crystalline phosphate with a capacity of 6.64 meq/gm. The second proton is exchanged only at higher pH with an accompanying elongation of the *c* axis. Strontium ion appears to occupy interlayer sites, whereas barium ion is presumably too large and is not sorbed in acid solution (*440*).

In general, the crystalline form does not hydrolyze to the extent that the amorphous form does (*19*, *123*, *237*), although ion exchange which is accompanied by an increase in distance between the layers makes the crystalline form more susceptible to hydrolysis (*23*). Since the β and γ forms of zirconium phosphate are more open, exchange of cations such as Cs^+ and Ba^{2+}, which are excluded in the α form, can occur in these forms. Since one hydrogen is opposed to the other, the theoretical capacity of 7.06 meq/gm is not achieved.

The absorption of UO_2^{2+} on phosphates of varying crystallinity was examined by Vesely *et al.* (*577*). Samples were equilibrated in an autoclave for 5–6 hours with 1.25×10^{-2} M $UO_2(NO_3)_2$ in 0.01 M HNO_3. The UO_2^{2+} up take increased from 0.01 meq/gm at 25°C to 1.88 meq/gm at 269°C. At elevated temperature the capacity of the crystalline product was greater than that of the semicrystalline product.

The ion exchange behavior of various substituted ammonium ions on crystalline zirconium phosphate has also been investigated (*448*). A nearly complete separation of various substituted ammonium ions was achieved. As measured in units of meq/ml of bed, the breakthrough capacities were: octylammonium, 0.10; ethylammonium, 0.16; methylammonium, 0.30; and ethylenediammonium 0.37. The separation of triethanolammonium, 0.18; ethanolammonium, 0.20; and ammonium ions was only partially successful. Decreasing temperature increased the breakthrough capacities.

X-ray investigations (*364*) showed that during substituted ammonium ion takeup, the two perpendicular lattice dimensions remained practically unchanged, whereas the third dimension (inner layer distance) changed with the length of the alkyl chain, the mean increase being 2.0–2.2 Å per carbon atom of the alkyl chain. An ion like the trimethylcetylammonium forms only an unimolecular layer between the anionic zirconium phosphate layers rather than a close-packed double layer of cations.

Kinetic studies on amorphous zirconium phosphate indicate that the rate-determining step is the diffusion of the ions through the exchanger with a diffusion coefficient intermediate between that of a strong sulfonic acid and the weak acid carboxylic resins (*404*). The rate-determining step in crystalline zirconium phosphate exchange also is the diffusion of ions within the exchange particles (*237*). Exchange takes place by an initial fast step followed by a slow step, both being independent of the concentration of the entering ion. This observation is consistent with the structure in which two different hydrogen ion exchange sites are present.

c. *Ion Exchange in Fused Salts.* The ion exchange properties of zirconium phosphate in fused salt eutectics has also been examined (*18*, *355*, *561*). Alkali nitrate eutectics were used at temperatures as low as 160°C (*17*, *18*) and as high as 370°–400°C (*561*). After 70 hours at 160°C in fused $LiNO_3$–KNO_3 eutectic, formation of P–O–P groups was found to be negligible. It was difficult to get unambiguous data on exchange of the alkali metal with the sodium form of zirconium phosphate because of contamination by the ions of the melt, but the order of the selectivity coefficients gave an affinity order of $Li > Na \gg K$ which is opposite that found for the same ions with zirconium phosphate in aqueous solution. Alberti *et al.* also used zirconium phosphate in the form of strips of purified glass fiber paper which were impregnated with the exchanger

(*18*). In alkali metal nitrate eutectics, absorption of the alkali metal ions, Tl^+ and Pb^{2+} was low, Ni^{2+}, Co^{2+}, UO_2^{2+}, and Eu^{3+} were exchanged to a moderate extent, and Fe^{3+} and Th(IV) were extensively exchanged.

d. Miscellaneous Properties of Zirconium Phosphate. Zirconium phosphate also has been used for membrane electrodes (*21, 355*), although their use does not seem to have been developed. Zirconium phosphate deposited on chromatographic paper has been studied as an exchanger (*336*), and zirconium phosphate has been used as a carrier for oxidizing and reducing agents (*477*).

The catalytic properties of metal–zirconium phosphate solid has also been investigated (*21, 349*). The catalysts were prepared by the ion exchange of zirconium phosphate with copper, nickel, and chromium ions. Catalytic dehydration of 2-propanol was studied at 160°–350°C, with zirconium phosphate itself giving the highest activity, yielding 97% propylene at 230°–240°C. Introduction of Cu^{2+}, Ni^{2+}, and Cr^{3+} decreased the dehydrating properties, and also decreased the catalytic isomerizing properties when tested with the cyclohexane–methylcyclopentane isomerization. The introduction of copper and nickel improved the dehydration properties of zirconium phosphate when tested on ethylbenzene.

e. Mixed Metal Phosphates. The addition of a nitric acid (5 *N*) solution of zirconium nitrate (0.37 *M*) to a solution containing 0.15 *M* phosphate and 1.8 *M* molybdate as the sodium salts, results in a solution, which when treated with nitric acid and a small amount of pyridine, gives a precipitate of pyridiniummolybdenozirconium phosphate. This product is soluble in oxygen-containing solvents such as *n*-butanol (*500, 501*). The composition is Mo : Zr : P = 12 : 1 : 1. The equilibrium constant for the formation of the zirconium complex from the aqueous molybdophosphate complex was determined to be 5.2×10^5 (*502*). A similar hafnium molybdophosphate complex has been prepared (*503*).

Zirconium and niobium phosphates may be coprecipitated to give a product which has ion exchange properties (*233*).

f. Zirconium Arsenate. Like zirconium phosphate, zirconium arsenate of varying compositions can be prepared depending on the initial mole ratios and washing conditions. The addition of excess arsenic acid to a solution of zirconium nitrate yields a precipitate, which when refluxed in concentrated nitric acid, gives a crystalline product of As/Zr = 2.0. The product loses one mole of zeolitic (*122*) water at 110°C and a second mole splits out at 450°C by condensation of arsenate groups. Crystalline products behaved similarly to the corresponding phosphate products, although at a pH of 11 almost 30% of the arsenate was solubilized. Sodium and lithium ion titration curves exhibit two end points corresponding to the replacement of two hydrogen atoms from the arsenate group. The Cs ion was not appreciably exchanged in acid solution.

The arsenate is isomorphous with the phosphate. Although high-quality single crystals were not available, the interlayer distance was determined to be 7.7 Å, compared to 7.6 Å in the phosphate. Like the phosphate, the arrangement of zicronium atoms and monohydrogenarsenates is such to produce zeolite cavities. There is one mole of cavities per formula weight.

7. *Silicate, Iodate, Chromate, Molybdate, and Tungstate*

Stoichiometric amounts of sodium iodate and zirconium sulfate dissolved in water form a white precipitate immediately. The air-dried product is amorphous, but upon exposing the precipitate to refluxing nitric acid in a Soxhlet extractor, small well-formed crystals of $Zr(IO_3)_4$ appear in the bottom of the flask. The iodate ion is bidentate (*334*) along the l edge of a nearly perfect antiprism. The average Zr–O distance is 2.206 Å. There are two formula units in the unit cell and the space group is $P4/n$. Iodates precipitated from solutions of Cl:Zr ratios <2 gave products of variable composition (*530*).

In zircon (*329*), a rather distorted antiprism is found with four Zr–O distances of 2.15 Å and four of 2.29 Å. There are four molecules in the unit cell with a space group of $I4_1/amd$.

In the compound $Zr_4(OH)_6(CrO_4)_5(OH_2)_5$, infinite chains of zirconium atoms are bonded by hydroxyl ions and chromate ions in a ratio of 3:1 so that there is a double oxygen bridge between every pair of zirconium atoms yielding $[Zr_4(OH)_6(CrO_4)_n]^{8n+}$ ions. The zirconium atoms are coordinated to seven oxygen atoms in a pentagonal pyramid configuration (*345*).

The equilibrium constants for the reaction of zirconium(IV) ion with molybdate and tungstate

$$Zr^{4+} + H_2MO_4 \rightleftarrows ZrMO_4^{2+} + 2H^+ \qquad (27)$$

were determined to be $(1.5 \pm 0.3) \times 10^4$ and about 10^4, respectively (*501*)

8. *Lewis Acid–Base Adducts*

Dimethyl sulfoxide adducts of zirconium perchlorate were prepared (*326*) by dissolving the metal perchlorate hydrate in dimethyl sulfoxide at 20°C. The addition of a large excess of benzene resulted in the precipitation of white, crystalline, $ZrO(ClO_4)_2 \cdot 8DMSO$. The infrared spectrum shows an adsorption at 1024 cm^{-1} due to the presence of unbound S=O, and another absorption at 938 cm^{-1} attributed to the S–O-stretching frequency of oxygen-bound DMSO. Upon heating this product at 185°C, two moles of DMSO are lost resulting in the 6-solvate product. The two very strong bands at 1148 and 1125 cm^{-1} are attributed to S-bonded DMSO.

Direct reaction of zirconium and hafnium tetrahalides and bromides with excess DMSO under strictly anhydrous conditions yielded products of composition $Zr(Hf)Cl_4 \cdot 9DMSO$ and $Zr(Hf)Br_4 \cdot 10DMSO$ (*482*). Attempts to recover the tetrahalides by heating only resulted in the production of tarry residues. The S–O-stretching frequency in these compounds was found to be 950 cm^{-1} for the nine-solvate and 920 cm^{-1} for the 10-solvate, which indicates that the DMSO molecules are oxygen bound.

Zirconium tetrachloride dissolved in warm dioxane, slowly added to a solution of diphenylselenoxide also in dioxane, results in the precipitation of a colorless powder of composition $2(C_6H_5)_2SeO \cdot ZrCl_4$. The infrared spectrum showed a Se–O-stretching frequency at 770 cm^{-1} (*413*).

The hafnium species extracted from a fluoride-containing aqueous phase by tri-*n*-octylphosphine oxide (TOPO) in cyclohexane were shown to be $Hf(ClO_4)_4 \cdot 1.5TOPO$ and $HfF_2(ClO_4)_2 \cdot 1.5TOPO$ (*575*). Monoisoamylmethylphosphonate (HMAMP) reacts with a zirconium nitrate solution to give white crystalline $ZrO(MAMP)_2$ (*572*).

D. SULFUR LIGANDS

Very few sulfur-bonded zirconium or hafnium compounds have been reported. Bradley (*71*) in attempting to dissolve dialkylamine compounds, $M(NR_2)_x$, where M = Zr or Hf, and R = methyl, ethyl, or *n*-propyl, in carbon disulfide, found that a vigorous reaction occurred with formation of *N*,*N'*-dialkylthiocarbamates, $M(S_2CNR_2)_4$. The dimethyl derivatives are very insoluble and nonvolatile, suggesting that they might be polymeric, but the higher alkyl derivatives are soluble and monomeric. The ligand appears to be bidentate.

A red-brown amorphous complex $ZrCl_4 \cdot 2C_4H_4S$ was isolated from the reaction of the tetrahalide in excess thiophene. The compound does not dissolve in benzene, carbon tetrachloride, or hexane (*411*). A dimethylsulfide adduct, $(CH_3)_2S \cdot ZrCl_4$ has been examined by infrared spectroscopy, but no details of the preparation have been given (*152*). In a Nujol mull it shows two bands, one weak one at 372, and a second broad band at 299 cm^{-1}.

The mixed alkoxide and thiosalicylate of zirconium was prepared by treating benzene solutions of the corresponding alkoxides with the stoichiometric quantity of thiosalicyclic acid. The isopropyl alcohol produced was fractionated out azeotropically with benzene. In this way $Zr(OPr^i)_2(C_7H_4O_2S)$, a pale yellow, benzene-soluble solid, and $Zr(C_7H_4O_2S)_2$, a light yellow, benzene-soluble solid, were prepared (*238*).

π-Cyclopentadienylzirconium dichloride reacts with *cis*-1,2-ethylene dithiolene in an acetone–methanol solvent to give orange sublimable crystals of $(Cp)_2ZrS_2C_2H_2$ (*298*).

VI. Compounds with Metal–Halogen Bonds

A. SPECIES IN AQUEOUS SOLUTIONS

The complexing of zirconium and hafnium ions by fluoride ions is quite extensive compared to chloro complexing, while complex ion formation with bromide and iodide ions is negligible. Formation constants for fluoride complexing with zirconium(IV) and hafnium(IV) calculated from the data of Connick (*126*), Buslaev (*94*), and Hume (*574*), have been summarized graphically by Goldstein (*213*). Slightly different values have been published by Bukhsh (*92*). Noren (*15a*, *401–403*) has redetermined the equilibrium constants for the reaction,

$$M^{4+} + nHF \rightleftarrows MF_n^{+4-n} + F^- \qquad (28)$$

at 20°C and in 4 *M* $HClO_4$ by extraction, emf, and cation exchange techniques. The best values obtained are tabulated in Table XXI.

TABLE XXI

EQUILIBRIUM CONSTANTS FOR FLUORIDE COMPLEXING OF ZIRCONIUM AND HAFNIUM

Atom	$K_1 \times 10^{-5}$	$K_2 \times 10^{-4}$	$K_3 \times 10^{-3}$	$K_4 \times 10^{-2}$	$K_5 \times 10^{-1}$	K_6
Zr	9 ± 1	2.6 ± 0.5	1.0 ± 0.1	1.9 ± 0.3	3.4 ± 0.6	2 ± 1
Hf	3.3 ± 0.2	1.1 ± 0.2	1.1 ± 0.2	1.6 ± 0.3	5 ± 1	3 ± 2

In agreement with other workers, the constants for the first two species are larger for zirconium than for hafnium. Noren's data yields values for K_3–K_6 which are smaller than the values reported by earlier workers, and which are essentially the same for both zirconium and hafnium. The heptafluoro ion is known to be unstable with respect to dissociation in aqueous solution (*307*).

Equilibrium data for the formation of the chloro complexes MCl^3 MCl_2^{2+}, MCl_3^{1+}, and MCl_4 have been determined using ion exchange tec niques at hydrogen ion concentrations of 2 and 4 *M* and at metal i concentrations of 5×10^{-6} or less (*353*, *465*). The values for the cumul tive formation constants are given in Table XXII. The strong absorpti

TABLE XXII

FORMATION CONSTANTS OF CHLORO COMPLEXES WITH ZIRCONIUM AND HAFNIUM

Atom	Formation constant, n				μ
	1	2	3	4	
Zr(Hf)	0.95 ± 0.05	0.12 ± 0.05	0.07 ± 0.01	0.08 ± 0.005	$\mu =$
Zr	1.1 ± 0.1	0.21 ± 0.05	0.05 ± 0.01	—	$\mu =$
Hf	0.94 ± 0.06	0.18 ± 0.05	0.08 ± 0.02	—	$\mu =$

of these elements by anion exchangers from hydrochloric acid solutions greater than 8 *M* leads to the conclusion that MCl_5^- and MCl_6^{2-} speci are formed at the higher chloride concentrations. A review of t complexing properties of zirconium and hafnium has been compiled Ermakov *et al.* (*168*).

Additional properties of chloride solutions have been studied, namel the characteristics of constant boiling hydrochloric acid solutions zirconyl chloride (*206*) and activity coefficients of zirconium oxychlori solutions (*319*). The ultraviolet spectra of hydrochloric acid solutions zirconium and hafnium have been recorded by a variety of investigato but no assignments of the spectra have been made to specific species solution (*312*, *353*, *465*, *537*).

B. BINARY COMPOUNDS

1. *Tetrahalides*

a. Fluoride. Zirconium and hafnium tetrafluorides have be reported to exist in three crystalline and one amorphous modificatio (*203*, *204*). Amorphous zirconium tetrafluoride is prepared by the reacti of fluorine gas diluted by nitrogen on zirconium tetrachloride. Condens tion of the tetrafluoride gas on a cool surface results in the formation the α form followed by the growth of crystals of the β form. This seems occur more rapidly with hafnium than zirconium. The metastable α form may also be obtained by thermal decomposition of α-$MF_4 \cdot NH_4F$, and it may be stabilized by the addition of trivalent ions such as Fe^{3+} or Ga^{3+}. The presence of 8% Fe_2O_3 in the HfO_2, or 3% Fe_2O_3 in the ZrO_2 used in the preparation of the starting $NH_4F \cdot MF$, is sufficient to stabilize the α form. On the other hand, thermal decomposition of the γ-$MF_4 \cdot NH_4F$ gives γ-MF_4 up to temperatures of 450°C for hafnium and 400°C for zirconium. The α, γ, and amorphous forms transform irreversibly to the β form at 400° to 450°C. The β form is the only one of the three which has been characterized by single-crystal X-ray diffraction (*93*). It has a monoclinic space group $I2/a$ with $a = 9.57$ Å, $b = 9.93$ Å, $c = 7.73$ Å, $\beta = 99.47°$, and $Z = 12$. The structure has been confirmed by other investigators (*28*, *91*). It consists of a three-dimensional array of distorted square antiprismatic polyhedra which are joined by sharing corners through fluorine bridges; thus the zirconium has coordination number 8 and the fluorine a coordination number of 2. The Zr–F bond distances vary from 2.03 to 2.18 Å, with the average being 2.10 Å. The solid state NMR has also been investigated (*198*).

The vapor pressures above solid α- (*201*) and β-zirconium tetrafluoride (*16*) are described by the equations in Table XXIII over the temperature ranges specified. The calculated heat of sublimation for the tetrafluoride of zirconium is some 20 kcal/mole greater than the heats of sublimation of the other tetrahalides of zirconium (Table XXIII), which is consistent with the greater complexity of the fluoride solid state compared to the probable structures of the other halides in the solid state. Zirconium tetrafluoride in the gaseous state is known to be monomeric by mass spectroscopy (*96*). Fluorine bomb calorimetry (*223*, *224*) has been used to determine the standard heats of formation of the tetrafluorides ZrF_4, -456.80 ± 0.25 kcal and HfF_4, -461.40 ± 0.85 kcal.

b. Chloride. The gas phase structure of zirconium tetrachloride is known to be tetrahedral (*296*) with the Zr–Cl distance equal to 2.32 ± 0.01 Å. The conclusion that the structure is tetrahedral in the solid state (*235*) has been questioned (*116*) because its heat of sublimation is 15 kcal/mole higher than values for compounds of known tetrahedral structure in the solid state, and, in addition, the vibration spectrum (*588a*) seems to exclude a molecular structure. A single-crystal X-ray (*325a*) analysis has revealed that zirconium tetrachloride crystallizes in the monoclinic space group $P2/C - C_{2h}^4$ with $a = 6.361 \pm 0.004$ Å, $b = 7.407 \pm 0.004$ Å, $c = 6.256 \pm 0.004$ Å, $\beta = 109.30 \pm 0°$, and $Z = 2$. The zirconium atoms sit in one-quarter of the octahedral holes of a slightly distorted cubic close-packed structure of chlorine atoms. The distorted $ZrCl_6$ octahedra share two edges to form a zigzag chain, although the common edges do not lie trans to one another. The two Zr–Cl bridge bonds have lengths of 2.498 and 2.655 Å (both ±0.003 Å) compared to the terminal bond length of 2.307 Å. Note that the terminal bond lengths are comparable to those of the tetrahedral molecule in the gas phase. The shortest zirconium–zirconium distance is 3.962 Å.

TABLE XXIII

VAPOR PRESSURE RELATIONSHIPS FOR ZIRCONIUM AND HAFNIUM TETRAHALIDES

Compound	$\log p = A - B/T$		Temperature (°K)	ΔH_s (kcal/mole)	Ref.
	A	B			
β-ZrF_4	13.5571	12430	681–913	56.9 ± 0.2	(*16*)
α-ZrF_4	12.150	10722	713–813	49.05	(*201*)
$ZrCl_{4(s)}$	11.766	5400	480–689	24.7 ± 0.3[a]	(*415*)
$ZrCl_{4(s)}$	11.83	5430	508–608	—	(*196*)
$ZrCl_{4(s)}$	11.4632	5191	<699	23.7 ± 1.0	(*145*)
$ZrCl_{4(l)}$	9.088	3427	710–741	—	(*415*)
$ZrCl_{4(l)}$	9.0421	3406	—	—	(*66*)
$ZrCl_{4(l)}$	9.4714	3750	711–773	—	(*399*)
$HfCl_{4(s)}$	11.712	5197	476–681	23.8 ± 0.3	(*415*)
$HfCl_{4(s)}$	11.64	5200	508–608	—	(*196*)
$HfCl_{4(s)}$	11.6726	5143	<685	23.5 ± 1	(*145*)
$ZrBr_{4(s)}$	12.402	5941	494–620	27.1 ± 2.2	(*479*)
$HfI_{4(s)}$	12.235	6214	536–674	28.37 ± 0.04	(*538*)
α-$HfI_{4(s)}$	19.46	10640	575–597	48.9 ± 1.3	(*538*)
β-$HfI_{4(s)}$	13.99	7370	598–645	33.7 ± 0.6	(*538*)
γ-$HfI_{4(s)}$	12.05	6125	646–678	28.2 ± 0.5	(*538*)
$HfI_{4(s)}$	9.0511	4261	548–605	26.9	(*566*)
$HfI_{4(s)}$	11.619	5814	605–668	—	(*566*)

[a] $\Delta H^0 = 27.67 \pm$ kcal/mole as reported in JANAF Thermochemical Tables (Dow Chemical Company, Midland, Michigan) based on the data of Palko (*415*).

Equilibrium properties of zirconium and hafnium tetrahalides are reported in Tables XXIII and XXIV. The vapor pressures calculated for temperatures at the triple point and above generally do not agree with the experimentally determined vapor pressure above liquid metal tetrachlorides. Densova and co-workers (*145*) note that previous investigators have neglected the curvature in the $1/T$ vs. $\log p$ plots in the region of the triple point, which probably accounts for the lack of agreement observed. They also report that the sublimation energies show minima

TABLE XXIV

PHYSICAL PROPERTIES OF ZIRCONIUM AND HAFNIUM TETRAHALIDES

Property	Ref.	$ZrCl_4$	$HfCl_4$	$ZrBr_4$	$HfBr_4$	ZrI_4	HfI_4
Melting point (°C)	*(398)*	435.5	433.2	450	424.5	500	449
	(415)	437	434	—	—	—	—
Critical temperature (°C)	*(145)*	503.5	452.5	532	473	686	643
	(394)	499	445	—	—	—	—
Triple point (°C)	*(144)*	437.3	432	—	—	—	—
	(399)	438.0	—	—	—	—	—
Critical density (gm/cm^3)	*(398)*	0.76	1.06	0.97	1.20	1.13	1.30
Vapor density (gm/cm^3)	*(394, 567)*	0.143	0.45	—	—	—	—
Liquid density (m.p.) (gm/cm^3)	*(398, 145)*	1.65	18.6	24.0	2.42	2.94	3.07
Critical pressure (atm)	*(398)*	57.4	54.0	42.9	40.5	40.7	39.0
ΔH_f° (kcal/mole)	*(229)*	−234.7	−236.7	—	—	—	—
	(199, 200)	−234.17 ± 0.28	−236.66 ± 0.29	—	—	—	—
ΔH_{vap} (kcal/mole)	*(399)*	17.1	—	—	—	—	—
	(415)	15.7 ± 0.9	—	—	—	—	—
ΔH_{fusion} (kcal/mole)	*(415)*	9.0 ± 0.9	—	—	—	—	—
	(145)	14 ± 3	18 ± 3	—	—	—	—

at 420°C for zirconium tetrachloride and at 410°C for hafnium tetrachloride, and suggest that these irregularities might be due to the presence of ionic species in the system as the melting point is approached. Species such as this have been suggested by Blumenthal (*62*), although the idea has been discounted after the diamagnetism of zirconium tetrachloride was found to be independent of temperature (*143*).

Nisel'son (*394*, *395*) has concluded that any separation process based on differences in volatility should be carried out within the temperature range 440°–475°C. Vapor pressure measurements at the triple point only lead to a separation coefficient of 1.7 (*415*). On the other hand, small quantities of zirconium-free hafnium have been prepared by gas chromatographic techniques on a synthetic, highly purified graphite column at 295°C (*543*).

The molar volumes and liquid–gas phase compositions for the $ZrCl_4$–$HfCl_4$ systems have also been studied (*144*). Nisel'son (*396*) found that the binary systems of zirconium–hafnium chlorides, and bromides and iodides as well, have unlimited solubility in the liquid and solid states. The systems $ZrCl_4$–$ZrBr_4$ and $ZrCl_4$–ZrI_4 form a continuous series of solid solutions which contains a minimum. No mention is made of the possibility of mixed halide species.

The mixed halide $ZrCl_2F_2$ has been prepared, however, not by direct reaction, but rather by the action of a stoichiometric amount of AsF_3 on $ZrCl_4 \cdot 2PCl_5$ dissolved in $AsCl_3$. The white, finely divided crystalline product precipitates from solution. It is practically insoluble in ether, benzene, petroleum ether, and carbon tetrachloride, and slightly soluble in acetonitrile (*306*).

A separation of zirconium and hafnium based on difference in rates of reaction of the tetrachlorides with molecular oxygen has been devised. The activation energies for the reaction

$$MCl_4(g) + O_2(g) \rightarrow ZrO_2 + 2\ Cl_2(g) \tag{29}$$

are 24.2 ± 2 and 18.7 ± 2 kcal/mole for zirconium and hafnium tetrachlorides, respectively. The reaction was found to be second-order (*197*), with a temperature dependence which fits the equations

$$\log k_{ZrCl_4}(\text{mm}^{-1}\text{hour}^{-1}) = 4.25 - 5.3 \times 10^3/T$$

$$\log k_{HfCl_4}(\text{mm}^{-1}\text{hour}^{-1}) = 2.9 - 4.1 \times 10^3/T$$

c. Bromide and Iodide. Now that the metals are readily available, the tetrabromide and iodide are normally prepared by direct reaction of the metals with the appropriate halogen. The tetrachloride is the normal commercial source, however, and may be used as starting material for the production of the tetrabromide and iodide by halogen exchange. Nisel'son (*400*) heated zirconium tetrachloride with sodium iodide, silicon tetraiodide, aluminum bromide and iodide, and hydrogen iodide. Best results were obtained with the aluminum halides, with amost 100% exchange occurring with the iodide in 40 minutes at a maximum of 360°C. Experiments on the thermal stability of the tetrahalides on hot surfaces confirm the fact that the iodides are the least stable, with the bromides next, and the chlorides the most stable (*568*), with hafnium halides being more stable than the corresponding zirconium compounds.

Some uncertainty remains in the exact structure of the solid state bromides and iodides. Klemn and co-workers (*301*) reported that zirconium tetraiodide possesses cubic closest packing of the iodides, with the metal atoms sitting in octahedral rather than tetrahedral holes. The actual ordering of the metal atoms was not determined. Krause and co-workers (*325*) also report that hafnium tetraiodide consists of cubic close-packed iodides with $a_0 = 11.77$ Å. Because of similar intensity and line sequence it was assumed that hafnium tetraiodide had the tin(IV) iodide structure and consequently space group T_h^6 was assigned. No mention of allotropic forms was made by Krause. Phase transformations and vapor pressure data for hafnium tetraiodide (Table XXIII) have been studied by Stevenson and Wicks (*538*) and Tsirel'niko and Ioffe (*566*). Wicks reports transition temperatures at 329° ± 3°C for an α to β transition, and 375° ± 2°C for the β to γ transition, whereas Ioffe only noted a break in the $1/T$ vs. $\log p$ plot at 332°C, which presumably is the same as that Wicks observed at 329°C. Wicks estimates the enthalpies of transition as 14.4 ± 1.1 kcal/mole for the $\alpha \rightarrow \beta$, and 5.4 ± 0.6 kcal/mole for the $\beta \rightarrow \gamma$. Ioffe reported 7.4 kcal/mole for the transition at 332°C. The structural changes accompanying these phase changes are unknown.

Klemn also reported that zirconium tetrabromide possessed a structure similar to the iodide but with tetragonal distortion. Berdonosov and co-workers (*58*), apparently unaware of Klemn's report, write that zirconium tetrabromide has a primitive cubic lattice with $a = 10.95 \pm 0.01$ Å, and assigned the space group T_h^6 by analogy with zirconium tetrachloride. Zirconium and hafnium tetrabromides seem to be structurally different than titanium tetrabromide. It is observed that titanium tetrabromide is soluble to the extent of 40% in chloroform and 30% in ethylene dichloride and carbon tetrachloride, whereas zirconium and hafnium tetrabromides are soluble to the extent of only 4% in chloroform and 0% in carbon tetrachloride (*57*).

2. *Tri- and Dihalides*

a. Preparation. i. Chemical reduction. Early work on the reduction of zirconium tetrachloride with aluminum metal in liquid aluminum chloride (*461*) yielded a zirconium trichloride which was contaminated with the oxides of zirconium and aluminum, and the aluminum metal as well. Young (*601*) was able to produce about 1 gm of pure tribromide, by carrying zirconium tetrabromide in hydrogen gas over aluminum wire at 450°C in an apparatus called a "hot-cold" tube. Schumb and Morehouse (*483*) used the same technique to prepare a "hafnium tribromide," which actually had a Br/Hf ratio of 3.2:1. There was some tendency to form the dibromide, although this was reoxidized to the tribromide upon sublimation (290°C) of the excess tetrabromide codeposited with the product. Watt and Baker (*586*) reported the preparation of zirconium triiodide by aluminum reduction when a high ZrI_4/Al ratio (5.5/1), low temperature (300°C), and long reaction time (10 weeks) were used. Attempts to produce the hafnium triiodide by aluminum reduction of the tetraiodide with aluminum metal at 350°–385°C for 2 to 14 days, followed by sublimation of the volatile halides, gave a product still contaminated with aluminum (*42*). Other metals have been used as reducing agents, but suffer from the fact that the product is difficult to separate from the resulting halide of the reducing metal.

The trichlorides, bromides, and iodides of both zirconium and hafnium were reported by Larsen and Leddy (*333*), who used finely divided zirconium or hafnium metals as the reducing agent and gaseous tetrahalides at elevated temperature (700°C), pressures (18 atm) and reaction times of 36–72 hours. The metal trihalides were deposited on the surface of the metal particles and resulted in products with initial purities ranging from 85–95%. Improved products were obtained upon grinding the samples with additional tetrahalide and reprocessing. A modification of this technique by Schläfer (*478*, *480*, *481*), who used still higher pressures (40 atm for the bromide, 60 atm for the chloride), but lower reaction temperatures (485°C for the bromide and 500°C for the chloride), with reaction times of 45 hours for the bromide and 100 hours for the chloride, resulted in the production of a tribromide which was free of metal, and a chloride of 99.6% purity. Swaroop and Flengas (*547*) eliminated the necessity of a high-pressure system by using a double-bulbed quartz reaction vessel, the tetrachloride compartment of which was held at 330°C, while the bulb holding the metal was at 700°–750°C. Under these conditions the pressure of the tetrachloride was only about 1 atm. Platinum or zirconium foil was used to line the high-temperature bulb. After 72 hours the reaction system was cooled so as to separate all the excess tetrahalide from the product. Any metal remaining in the reaction product was removed by screening. The best purity obtained was 99.2%.

Sale and Shelton (*469*) avoided the problem of metal contamination (*565*) by using a sheet of zirconium metal in place of finely divided metal, and a temperature of 510°C (for 24 hours), under which conditions the zirconium tetraiodide was liquid. The pressure within the sealed tube was only about 6.5 atm. After sublimation of the unreacted tetraiodide at 300°C, the product was recovered in the form of needlelike crystals and separated from the unreacted zirconium metal sheet. Similarly Struss and Corbett (*129*, *541*, *542*) used the same technique for the preparation of hafnium triiodide, although the composition of the phase obtained by the reaction of liquid HfI_4 (20 atm) with hafnium metal foil in a sealed tantalum container at 500°–550°C was $HfI_{3.2-3.3}$. A tantalum container was used to avoid contamination by the glass tube. Equilibration of this product with hafnium powder at 425° to 575°C gave $HfI_{3.0}$ as the lower limit of composition; the phase in equilibrium with $HfI_4(l)$ varied from $HfI_{3.46}$ at 475°C to $HfI_{3.20}$ at 550°C. There was no evidence for a lower halide even up to 1000°C.

The liquid aluminum halides have been used as solvent systems for the production of the zirconium trihalides (*211*). Tetrahalide–aluminum halide melts containing about 85 mole% Al_2X_6 react with zirconium (or aluminum) metal to give an unknown soluble blue species which is probably trivalent zirconium, from which crystals of ZrX_3 grow up from the meniscus along the side walls of the ampule. The trichloride and bromide appear to be unstable in the presence of the aluminum halide and usually yield brown products of composition $ZrCl_{2.78}$ and $ZrBr_{2.9}$. The stoichiometric iodide is always obtained. The reaction temperatures range from 250°C for the chloride to 300°C for the iodide. The insoluble trihalides are separated from excess reactants by sublimation of the excess volatile reactants and solvent.

Newnham and Watts (*391*) were successful in producing high-purity zirconium trichloride, tribromide, and triiodide from the corresponding tetrahalides by atomic hydrogen reduction in a glow discharge tube. A yield of about 0.5 gm/hour was obtained. The product was separated from unreacted tetrahalide by sublimation at 200°C for the chloride and bromide, and 260°C for the iodide under reduced pressure. Careful control of flow rates, temperature, and electrode design are required for the successful operation of this process.

Larsen and Leddy (*333*) tried the reduction of zirconium tetrafluoride with zirconium metal, but were unsuccessful. Ehrlich (*160*) substantiated this observation, but was able to obtain the trifluoride by reacting zirconium hydride with a gaseous mixture of hydrogen fluoride and hydrogen at 750°C over a period of 6 hours. The conversion was quantitative. On the other hand, the reaction of anhydrous hydrogen fluoride with zirconium metal (24 hours) gives the tetrafluoride (*378*) rather than the trifluoride, although the fluoride content of the product was low for tetrafluoride, and the X-ray powder pattern indicated the presence of some unidentified species. Murad and Hildenbrand (*381*) made a mass spectrometric study of the thermodynamic properties of Zr–F species from which he calculated standard heats of formation to be $ZrF_3(g) = -262 \pm 5$ kcal/mole, $ZrF_2(g) = -141 \pm 5$ kcal/mole and $ZrF_4(g) = -400.2 \pm 0.5$ kcal/mole.

It has been noted (*333*) that the tetraiodides are most easily reduced, followed by the bromides, and then the chlorides. In each case, the hafnium yields were slightly lower than the zirconium yields under the same experimental conditions. Newnham (*389*) noted that zirconium metal preferentially reduced zirconium in a mixture of gaseous zirconium and hafnium tetrachlorides (1.5% hafnium), thus enriching the vapor phase in hafnium, and producing a residue of zirconium trichloride with a reduced hafnium content, usually less than 0.05%. The reaction was carried out as a batch operation at 400°–450°C in vacuum and at $Zr/ZrCl_4$ mole ratios which ranged from 1 to 5. Similar observations have been reported (*164*, *323*) with aluminum as the reducing agent at 330°C and with zirconium as reducing agent at 400°C. This selective reduction of zirconium is the basis of an industrial process (*390*), although apparently it has not been developed to the point where it is competitive with the liquid–liquid extraction process.

Dihalides of uncertain purity are prepared by the disproportionation of the trihalides. Alternate routes have also been reported. Swaroop and Flengas (*549*) prepared $ZrCl_2$ of 95–99% purity by heating the trichloride and metallic zirconium at 675°C for 30–35 hours in an evacuated quartz tube lined with platinum foil. There is also a reference to the production of liquid dihalides by the reaction of the gaseous tetrahalides with loosely packed zirconium at 700°C for the chloride and 400°C for the bromide and iodide (*270*). The difluoride has been prepared (*357*) by the reaction of atomic hydrogen on thin layers of zirconium tetrafluoride at 350°C. New data on hafnium are lacking, although Corbett (*542*) has concluded that hafnium diiodide does not exist.

ii. Electrolytic reduction. Electrolytic reduction of zirconium(IV) and hafnium(IV) has been studied in a variety of solvents. Olver and Ross (*405*) studied the polarographic behavior of zirconium and hafnium tetrachlorides in acetonitrile with tetraethylammonium perchlorate as the supporting electrolyte. Three plateaus were observed which were thought to be related to reduction to the III, II, and metallic states.

The second, the III–II reduction, was well developed for zirconium only. The current on the plateaus on each of the waves was dependent on the diffusion of electroactive species to the electrode. The polarograms did not vary with time. All the waves were irreversible. Over the concentration range 0.3 to $6mM$, the half-wave potentials of the first two zirconium waves were constant within the limit of the reference stability, at −0.53 and −1.33 volts, respectively, and the first hafnium wave was also constant at −0.60 volts. For both metals, the half-wave potential of the first wave was strongly shifted to more negative potentials (−1.59 to −1.77 for zirconium and −1.63 to −1.80 for hafnium) as the concentration increased, which is not normally the behavior of irreversibly reduced species. The effect of added halide on the polarographic behavior was also examined. Solutions of iodide and M(IV) quickly turned yellow, an observation which was associated with the production of elemental iodine. It was assumed that the metal species were, in turn, reduced to the three state. In excess bromide, one irreversible wave representing a four-electron reduction was obtained and the potential was strongly affected. The hafnium system, in fact, became more negative than the supporting electrolyte. The effect of chloride was even more pronounced with 0.01 M chloride changing the millimolar zirconium potential to −1.9 volts in a single wave, whereas the same concentration of hafnium gave no reduction before the decomposition of the electrolyte.

In aqueous alcohol (5, 25, 50, and 75% by volume) and with lithium chloride as the supporting electrolyte (0.1, 0.5, and 1 M), Sancho *et al.* (*475*) observed a reversible one-electron reduction for zirconium and

TABLE XXV

APPARENT STANDARD ELECTRODE POTENTIALS WITH RESPECT TO THE CHLORINE ELECTRODE IN 1:1 MOLE KCl:NaCl[a]

Cell reaction	$-E^0$ (app.) at:		
	670°C	700°C	740°C
$Zr(s) + Cl_2(g) = (ZrCl_2)$	2.225 ± 0.006	2.200 ± 0.008	2.166 ± 0.006
$(ZrCl_2) + \frac{1}{2}Cl_2(g) = (ZrCl_3)$	1.837 ± 0.015	1.813 ± 0.020	1.784 ± 0.018
$(ZrCl_3) + \frac{1}{2}Cl_2(g) = (ZrCl_4)$	1.226 ± 0.005	1.240 ± 0.010	1.205 ± 0.015
$Zr(s) + \frac{3}{2}Cl_2(g) = (ZrCl_3)$	2.096 ± 0.009	2.071 ± 0.012	2.039 ± 0.010
$Zr(s) + 2Cl_2(g) = (ZrCl_4)$	1.888 ± 0.008	1.863 ± 0.012	1.830 ± 0.011
$Ag(s) + \frac{1}{2}Cl_2(g, 1\ atm) = (AgCl)$	0.852 ± 0.001	0.845 ± 0.001	0.835 ± 0.001
Cl^-/Cl^0	0	0	0

[a] From Ref. (*550*).

hafnium. Reduction has also been observed in dimethylsulfoxide solutions of MCl_4 (*231*).

The electroreduction of zirconium halides in alkali halide melts has led to the measurement of reversible potentials (Table XXV) in the temperature range 670°–750°C (*550*). Phase rule studies of the mixed systems preceded the cell studies and revealed that the phase diagrams of the KCl–$ZrCl_2$ and $NaCl$–$ZrCl_2$ systems were of the simple eutectic type. The liquidus curves of these binary systems were established by freezing point measurements. The melting point of pure zirconium dichloride was found to be $722° \pm 1°C$. In the potassium chloride–zirconium dichloride system, the eutectic is found at $698° \pm 1°C$ at 53.5 mole% zirconium dichloride. In the sodium chloride system the eutectic lies at $695° \pm 10°C$ at 69 mole% zirconium dichloride. No evidence was found for solid solutions in the sodium chloride system, although slight solubility was found in the potassium chloride system The solutions are thermally stable.

The melting point of pure zirconium trichloride could not be obtained because of disproportionation. Attempts to determine the phase diagram for the sodium chloride system failed because of excessive disproportionation. In the potassium chloride–zirconium trichloride system the eutectic temperature was $581° \pm 2°C$. A mixed system was used, however, since it was found that the stability of the trichloride was satisfactory in a 50:50 sodium chloride : potassium chloride melt. Powder patterns of the frozen melt at 15 mole% zirconium trichloride which had been at 750°C for 24 hours showed no evidence of the dichloride and tetrachloride. There was evidence for slight solubility of the trichloride in the solid at this composition. The reaction of zirconium metal with the trichloride in the equimolar sodium–potassium chloride melt revealed that even after the trichloride had been reduced to the dichloride, zirconium metal dissolved to the extent of 5×10^{-5} or 10^{-4} mole fraction of excess metal in the solution. Zirconium metal did not, however, appear to dissolve in the melt in the absence of zirconium dichloride.

The reversible potentials for the cell

$$\mathrm{Zr}\left|\begin{matrix}\mathrm{ZrCl_2} & (X_2) \\ \mathrm{KCl:NaCl} & (1:1)\end{matrix}\right\|\left.\begin{matrix}\mathrm{AgCl} & (X_1) \\ \mathrm{KCl:NaCl} & (1:1)\end{matrix}\right|\mathrm{Ag}$$

were measured in the $ZrCl_2$ mole fraction range 10^{-3}–10^{-4} and in the temperature range 670°–750°C (*550*). Potential measurements in the $Zr:Zr^{4+}$ system have been reported also by Yang *et al.* (*596*) in a KCl–LiCl system with a chlorine electrode. The data indicate, however, that the system was reacting during the measurements and it is doubtful that potentials can be calculated from these results. In addition, the potentials of the Zr:Zr^{4+} system have also been measured by Smirnov *et al.* (*523*) in potassium–sodium chloride melts and in magnesium–strontium chloride melts (*526*). The dependence of the potential on the radii of the dissolving salt cations (*525*) over the temperature range 650°–950°C was determined. The data of Smirnov *et al.* are in disagreement with the data of Swaroop (*550*) (Table XXV) with the Zr:Zr^{2+} and Zr:Zr^{4+} given as −1.927 and −2.000 volts, respectively. It appears that the method used to calculate the potentials is open to question. In a later publication Smirnov and co-workers (*522*) report potential vs. current data obtained at 700°C in potassium–sodium chloride melts with molybdenum electrodes. Although three distinct steps at −1.1, −1.7, and −2.1 volts were observed, the −1.1 value was attributed to reduction of oxidized molybdenum species, although in fact it probably should be assigned to the IV–III reduction.

TABLE XXVI

EQUILIBRIUM PARTIAL PRESSURES FOR THE DISPROPORTIONATION OF MX_3

	$\log_{10} P_{mm} = A - B/T$					
MX_3	A	B	Temperature (°K)	ΔH (kcal/mole)	ΔS (e.u.)	Ref.
$ZrCl_3$	11.632	6246	588–698	30.1^a	39.1 ± 1.7	(*569*)
$ZrBr_3$	8.36	4671	593–773	21.2 ± 1.7^c	25.1 ± 2.6	(*479*)
$ZrI_3{}^b$	12.47	8700	548–598	39.9 ± 2^c	—	(*470*)
	37.70	26367	623–673	120 ± 5^c	—	(*470*)

[a] $T = 298.1$°C.

[b] For Eqs. (30) and (31) as described in the text.

[c] Mean heat of disproportionation for the temperature range specified.

b. Properties—Chemical. i. Stability to oxidation–reduction. The disproportionation of the trihalides has been studied using a modification of the dew-point method to obtain the tetrachloride pressures (*569*) and direct pressure measurements (*479*) (Table XXVI). The chloride data are consistent with standard enthalpies and entropies of formation for $ZrCl_3$ of −186 kcal/mole and 36.4 e.u. and for $ZrCl_2$, −136 kcal/mole and 28.3 e.u. Data from Uchimura (*571*) lead to different values for the standard enthalpies and entropies, namely, −172 kcal/mole and 48 e.u. for $ZrCl_3$ and −118 kcal/mole and 34 e.u. for $ZrCl_2$. The standard enthalpies of formation for the hafnium chlorides are reported as -195 ± 8 kcal/mole for $HfCl_3$ and -131 ± 8 kcal/mole for $HfCl_2$(*462*).

From the study of cell potentials, the equilibrium constants for various reductions in the equimolar sodium–potassium chloride melt were calculated (*550*) (Table XXVII). The high values of the equilibrium constants indicate that zirconium metal should reduce any tetravalent or trivalent zirconium present to the divalent species. The reduction in both cases should be quantitative. It can also be predicted that zirconium trichloride in solution does not disproportionate to any significant extent, and that the reaction between zirconium dichloride and tetrachloride to produce zirconium trichloride proceeds almost to completion.

TABLE XXVII

EQUILIBRIUM CONSTANTS FOR ZIRCONIUM OXIDATION–REDUCTION REACTIONS IN 1:1 MOLE KCl:NaCl

Equation	Constants at:		
	670°C	700°C	740°C
$Zr(s) + (ZrCl_4) = 2(ZrCl_2)$	1.75×10^{7}	8.77×10^{6}	5.14×10^{6}
$Zr(s) + 3(ZrCl_4) = 4(ZrCl_3)$	2.56×10^{13}	8.90×10^{12}	3.3×10^{12}
$Zr(s) + 2(ZrCl_3) = 3(ZrCl_2)$	1.45×10^{4}	9.42×10^{3}	6.4×10^{3}
$2(ZrCl_3) = (ZrCl_2) + (ZrCl_4)$	8.22×10^{-4}	1.10×10^{-3}	1.24×10^{-3}

The disproportionation of zirconium triiodide is considered to proceed via an intermediate phase (*470*). The rates of zirconium tetraiodide effusion were measured in an effusion cell at 275°–325°C to the point where there was no further loss in weight. The temperature was raised to 350°–400°C whereupon further effusion of the tetraiodide was followed to constant weight. The heat of disproportionation for the overall process is about 40 kcal/mole. These data and the analyses of the residues are consistent with the reactions

$$8\ ZrI_3(s) \rightarrow 6\ ZrI_3 \cdot ZrI_2(s) + ZrI_4(g) \qquad (30)$$

$$6\ ZrI_3 \cdot ZrI_2(s) \rightarrow 4\ ZrI_2(s) + 3\ ZrI_4(g) \qquad (31)$$

Corbett (*542*) reports that hafnium triiodide in water, at least in part, undergoes disproportionation to the metal and the oxidation state (IV).

Ehrlich (*160*) reports that zirconium trifluoride is stable in air to 300°C, and stable to disproportionation at 850°C. In addition, it is reported as being difficulty soluble in hot water, and soluble in warm mineral acids without evolution of hydrogen. This is inconsistent with the conclusion of Straumanis (*539*) that zirconium trifluoride is an intermediate in the reaction of zirconium nitride with anhydrous hydrofluoric acid, but since it is unstable with respect to oxidation by protons the tetrafluoride and hydrogen are the final products.

The dihalides, like the trihalides, undergo disporportionation, in this case yielding the metal and the tetrahalide. There seems to be some uncertainty in the temperature at which this reaction becomes significant. For instance, the dichloride of zirconium is reported to be unstable in alkali and alkali metal melts at 400°C, on the one hand (*490*) and stable in a 50:50 sodium chloride–potassium chloride eutectic at 750°C, on the other (*550*). The stability does seem to be somewhat dependent on the cation size (*491*, *524*). There seems to be no question that the zirconium dihalides are more stable than the trihalides and their hafnium homologs. Swaroop (*549*) reports that zirconium dichloride is a black powder which is more stable in air than the trichloride and that it does not dissolve readily in water nor rapidly reduce water.

TABLE XXVIII

REACTION PRODUCTS OF ZrX_3 WITH NITROGEN LIGANDS

Compound	Color	μ_{eff}	IR Frequencies				
$ZrCl_3 \cdot 2py$	Chocolate	1.29		418s		293br	270sh
$ZrBr_3 \cdot 2py$	Red-brown	1.24		417s	382w		220br
$ZrI_3 \cdot 2py$	Yellow	1.16	472br	417s	320s		
$2ZrCl_3 \cdot 5CH_3CN$	Red-brown	0.46	440br			294s	
$2ZrBr_3 \cdot 5CH_3CN$	Brown	0.29	461br		395s	296w	223br
$2ZrI_3 \cdot 5CH_3CN$	Yellow-brown	1.10	459br		395m		
$2ZrCl_3 \cdot 3bipy$	Chocolate	1.35	434sh	416s	347sh	292s	
				403sh	315sh		278sh
$ZrBr_3 \cdot 2bipy$	Dark-brown	1.20			—		
$2ZrI_3 \cdot 3bipy$	Yellow-green	0.96			—		
$2ZrCl_3 \cdot 3phen$	Purple-brown	1.27	410s	360w	302s	265m 252sh	

ii. Coordination compounds. Fowles and co-workers (*188*, *192*) have prepared coordination compounds of zirconium trihalides and the nitrogen-containing ligands, acetonitrile, pyridine (py), bipyridyl (bipy), and phenanthroline (phen) (Table XXVIII). These compounds are insoluble in nonpolar solvents, but slightly soluble in acetonitrile. The pyridine complexes are very sensitive to moist air. In acetonitrile they are essentially nonelectrolytes, although in the case of the iodide, the behavior is that of a 1:1 electrolyte. The infrared spectrum of

$ZrCl_3py_2$ shows a Zr–Cl stretch in the same region as the binary chloride, suggesting that the same type of Zr–Cl bonding occurs in both cases. The most probable structures are halogen-bridged dimers, with the iodide dissociating in solution. The infrared spectrum of $2ZrX_3 \cdot 5CH_3CN$ does not show the cyanide stretching frequency of the free ligand. Combined with the fact that no methyl cyanide can be driven off even *in vacuo* at 100°C, one must conclude that all the methyl cyanides are chemically bound. Conductance measurements show low values for the chloride and bromide, but a higher value for the iodide complex. This suggests a situation similar to that in the pyridine complexes. With the exception of $2ZrCl_3 \cdot 3$bipy, the bipyridyl and *o*-phenanthroline complexes have conductances in methyl cyanide close to that expected for 1 : 1 electrolytes. Structures such as $[ZrX_2L_2^+][ZrX_4L^-]$ and $[ZrBr_2(\text{bipy})_2]^+$-$Br^-$ are suggested for these compositions. Conductances in solution are very low, however, and the ion pairing must be extensive.

c. Properties—Physical. i. Structures. The trihalides have been described as being bluish-gray (fluoride), black, blue-black or brown-black (chloride and bromide), and black, brown-black, or olive green (iodide). It has been commonly assumed that the brown forms are partially hydrolyzed products, although there seems to be no quantitative data to support this contention. The different colors could be related to a polymorphism similar to that found in the titanium halide systems; yet again experimental data are lacking which show this relationship. Baker and Janus (*42*) report that the black and the green forms of the iodides have the same powder patterns, and Corbett (*542*) confirms this for hafnium triiodide. Sale and Shelton (*470*) report that the brown-black form and blue-black material obtained by exposing zirconium metal to zirconium tetraiodide vapor were identical in all respects. Sale and Shelton also note that when the brown-black material is exposed to a small partial pressure of water vapor, followed by heating to about 300°C, the brown-black product is converted to a yellow-green colored compound.

Preliminary X-ray powder diffraction studies on zirconium and hafnium trihalides were carried out first by Leddy (*335*) and then more thoroughly by Holze (*247*). Holze concluded that the zirconium trihalides were isostructural with TiI_3 and the β forms of $TiBr_3$ and $TiCl_3$, on the basis of indexed powder lines obtained from samples containing a large fraction of metal. Holze assigned the space group D_{3h}^3–$P\bar{6}2m$ and carried out a limited structural analysis which indicated that these solid zirconium trihalides consisted of linear chains of Zr_2X_6 units in a close-packed lattice of halogen atoms. This assignment and the subsequently formulated structure with the zirconium atoms drawn together in pairs along the *c* axis were based on the presence of an 001 indexed line in the powder pattern. This 001 line is the only observed reflection which does not fit the systematic absences of *l* odd for all data required by the $P6_3mcm$ (D_{6h}^3) space group. This line does not appear in any of the powder patterns of Chiang (*107*), Watts (*588*), Baker (*42*, *586*), Sale (*469*), or Corbett (*542*), although it has been reported by Schläfer (*480*). An analysis of the powder data of Chiang (*135*) leads to the conclusion that in the absence of the 001 reflection, the metal atoms are regularly spaced along the *c* direction midway between the halogens at a distance corresponding to one-half of the "*c*" cell constant. This structure (β) is consistent with the space group requirements of D_{6h}^3 and is supported by the intensity data.

TABLE XXIX

X-RAY DATA FOR MX_3

Compound	Space group	a(Å)	c(Å)	c/a	$D_{\text{calcd.}}$	$D_{\text{exptl.}}$	Ref.
β-$ZrCl_3$	D_{6h}^3-$P6_3mcm$	6.36	6.14	0.965	3.05	2.95	(*135*)
β-$ZrBr_3$		6.75	6.315	0.936	4.42	4.52	(*135*)
β-ZrI_3		7.25	6.64	0.916	5.20	5.13	(*135*)
β-HfI_3		7.225	6.59	0.912	6.25	6.17	(*135*)
α-$ZrCl_3$	$P\bar{3}m1$	5.961	9.669	1.622	2.205	2.281	(*548*)

The crystal structure of a zirconium(III) chloride prepared by Swaroop and Flengas (*548*) differs greatly from the previous data. The data correspond to a structure exhibiting layer disorder. It is a BiI_3 layer structure based on a subcell with a space group $P\bar{3}m1$. The main difference between the β structure and this one is due to the positions of the metal atoms. Here the zirconium atoms are in layers *A*, *B*, and *C* normal to the *c* direction and are built up in orders such as *ABAB*, *BCBC*, or *CACA* at random. This may be equivalent to the α form of $TiCl_3$. Another set of data by Schläfer and Wille (*480*) do not correspond to any of those previously reported, and may represent an alternate method of octahedral occupancy or anion packing. A summary of the X-ray data for the α-ZrX_3 and β-ZrX_3 are given in Table XXIX.

In the β-$ZrCl_3$ there is a slight distortion of octahedra along the *c* axis. Thus, in the shared faces the Cl–Cl distance is 3.53 ± 0.01 Å, and in the remaining faces it is 3.68 ± 0.01 Å. The average Zr–Cl distance is 2.55 ± 0.01 Å and the Zr–Zr distance is 3.07 ± 0.01 Å compared to the Zr–Zr distance in the metal of 3.19 Å. Powder data by Corbett (*542*) on

HfI_3 indicates that the *a* and *c* dimensions of the hexagonal unit cell should probably be doubled and quadrupled, respectively. Single-crystal studies of Gil-Arnao (*210*), however, on $ZrBr_3$ confirm the structure previously reported (*135*).

Ehrlich (*160*) reports that the X-ray powder data for ZrF_3 are similar to TaF_3 which is known to have a rhenium trioxide-type structure.

ii. Magnetic properties. The room temperature magnetic moments of zirconium trichloride, tribromide, and triiodide, prepared by the Newnham technique, have been reported to be (*337*) only 0.4 B.M. The reduction in the magnetic moment due to spin-orbit coupling by Kotani's theory (spin-orbit coupling constant of 500), predicts that the magnetic moment should be 1.2 B.M. at room temperature. Thus, spin-orbit coupling alone does not explain the low moment, and the presence of very strong antiferromagnetic interaction including direct metal–metal bonds has been invoked to explain the data (*337*). The magnetic moment of a product formed by the dilution of zirconium trichloride in fused tetraphenylarsonium chloride (in a 1/3 mole ratio) showed a rise to 0.9 B.M., thus lending support to the existence of antiferromagnetic interactions in the pure trihalide. In contrast to these data are those of Baker and Janus (*42*) for the black and green forms of zirconium and hafnium triiodides. The susceptibilities were field-dependent, only slightly temperature-dependent, essentially the same for both forms, and considerably higher than reported by Nyholm. The purity of the products is open to question. The conflict between these two sets of data can only be resolved by further experimental work on unambiguous samples. Corbett (*542*) reports the $HfI_{3.0}$ only shows weak temperature-independent paramagnetism corresponding to μ_{eff} of 0.6 at 300°K.

Ehrlich and co-workers (*160*) measured the magnetic susceptibility of zirconium(III) trifluoride over the temperature range −183° to 20°C. They also observed a field dependence, but assumed that it was due to ferromagnetic impurities. After removing the field dependence by extrapolating to H_∞, a value of X_m of 1040 to 1260×10^{-6} c.g.s. units/mole was obtained which was only slightly temperature dependent.

The only magnetic data for the oxidation state II are those reported by Nyholm (*337*) on an unanalyzed sample. The susceptibility was low, only 150×10^{-6} c.g.s. units/mole, equivalent to 0.6 B.M., compared to the spin-only value of 2.88. Since Kotani's theory predicts only a reduction of 2.6 B.M. owing to spin-orbit coupling, antiferromagnetic interaction via direct metal–metal bonds is assumed to be operative here also.

iii. Absorption spectra. The diffuse reflection spectrum of zirconium trichloride reported by Clark (*108*) shows an intense band at 17,300 cm^{-1} with a shoulder at 21,000 cm^{-1} which is interpreted as a ligand-field band $^2E_g \rightarrow {}^2T_{2g}$ transition for zirconium(III) octahedrally coordinated to chloride ions. The bromide absorption maximum was at 16,200 cm^{-1}.

The aqueous solution spectrum of Zr(III) has also been reported. Even though the metal trihalides reduce water to give hydrogen, the rate is slow enough so that an absorption spectrum of the resulting brown solution can be obtained (*42*, *335*). A typical absorption spectrum shows a peak at 24,400 cm^{-1} and a shoulder at 22,000 cm^{-1}, which decay slowly with time. There is some question whether a disproportionation reaction occurs upon solution of the trihalide in water with the production of brown colloidal metal which contributes to the absorption spectrum (*542*).

C. TERNARY COMPOUNDS

1. *Hydrates and Hydrolysis Products*

a. Fluoro Species. Zirconium tetrafluoride dissolved in water at 100°C gives upon evaporation the 3-hydrate, $ZrF_4 \cdot 3H_2O$ (*584*). It is also obtained as the initial solid phase when it is recrystallized from aqueous hydrofluoric acid at concentrations up to 29.3% (*392*). The infrared spectrum (*309*) and NMR spectrum (*352*) indicate a normal hydrate structure rather than a zirconyl structure. Waters (*585*) has done a two-dimensional crystal structure which confirms this conclusion. The crystals are triclinic with $a = 5.94$ Å, $b = 6.96$ Å, $c = 7.55$ Å, $\alpha = 90.2°$, $\beta = 105.0°$, and $\gamma = 118.9°$. There are two molecules in the unit cell and the space group is P_1. The molecule is dimeric with each half bridged by two fluorine atoms. The other three fluorine atoms are at the vertices of a tetrahedron. The three oxygen atoms of the water molecules complete a 8-coordinate polyhedron around each metal atom. Thermodynamic properties of zirconium fluoride hydrates as determined by Hull (*252*) are given in Table XXX.

Attempts to prepare a crystalline monohydrate usually lead to products for which $n > 1$ in the composition $ZrF_4 \cdot nH_2O$. Heating the 3-hydrate in air at 80°C to constant weight gave a product with $n = 1.14$,

TABLE XXX

THERMODYNAMIC PROPERTIES OF ZIRCONIUM FLUORIDE HYDRATES

Compound	$\Delta H_{f, 298°}$	$C^0_{p, 298°}$	$S^0_{298°}$	$\Delta G^0_{f, 298°}$
$ZrF_4 \cdot H_2O$	−532.3 ± 0.6	(34.3)[a]	(35.7)	−494.7 ± 1
$ZrF_4 \cdot 3H_2O$	−674.6 ± 0.6	(53.3)	(52.5)	−603.7 ± 1

[a] Parentheses indicate best estimates.

and in vacuum at 80°C for 3 hours, $ZrF_{3.99}\cdot 0.59H_2O$ was obtained. Heating the 1.14 hydrate in vacuum caused no weight loss until 200°C where hydrogen fluoride and water were then lost simultaneously (*252*). Maricic and co-workers (*352*), however, claim that the stoichiometric monohydrate can be prepared by dehydration of the 3-hydrate at 100°C, although products for which $n > 1$ were obtained by dissolution of zirconium metal in a 1 : 1 mixture of nitric and 48% hydrofluoric acid and by the addition of hydrofluoric acid to zirconium oxychloride. Dehydration of the monohydrate in an atmosphere of HF at 400°C will yield the β-ZrF_4 (*203*). The infrared (*309*) and NMR (*352*) spectra again show that the monohydrate is not some sort of oxygenated species. There is a definite change in the crystal structure when the trihydrate is transformed into the monohydrate, but there is no drastic change in the fluorine resonance spectrum.

The hafnium tri- and monohydrates are prepared in a fashion similar to the zirconium compounds (*204*, *456*), although the stoichiometric monohydrate may be obtained directly by dehydration of the trihydrate at 80°C in nitrogen. There is a question whether the zirconium and hafnium hydrates are isostructural (*204*) or not (*456*). Whereas the thermal decomposition of $ZrF_4\cdot H_2O$ in a normal atmosphere is said to yield $ZrOF_2$ (*584*, *456*) at 300°C, the hafnium monohydrate is said to yield Hf_2OF_6 at 200°C and $Hf_3O_2F_8$ at 350°C, although Gaudreau found the intermediates $Zr(OH)_{0.15}F_{3.85}\cdot 0.8H_2O$ (at 150°–170°C) and $Zr_3(OH)_2F_{10}$.

In the three-component system HF, ZrO_2, and H_2O, Buslaev and co-workers (*95*, *392*) established that at 25°C the phase $Zr_4(OH)_6F_{10}\cdot 3H_2O$ was stable up to 7.26 wt.% HF and 10.09 wt.% ZrO_2, after which $ZrF_4\cdot 3H_2O$ separated. The trihydrate crystallizes out up to 29.28 wt.% HF with a solubility which corresponds to 35.03% ZrO_2. Additional hydrofluoric acid results in the appearance of the $HZrF_5\cdot 4H_2O$ phase which exists over the range of 29.83 to 34.53 wt.% HF. Waters (*584*) has reported that this composition exists within a range of hydrates, 1.5–6 H_2O. At still higher hydrofluoric acid concentrations, $H_2ZrF_6\cdot 2H_2O$ crystallizes out. Several other hydrates have been prepared under different conditions (*584*). Attempts to isolate them from the mother liquor failed because of HF and H_2O loss. In the corresponding hafnium system (*95*) the solid phase up to 8.83 wt.% HF is $Hf(OH)F_3\cdot 0.75H_2O$ with a solubility of 24.32 wt.% HfO_2. $HfF_4\cdot 3H_2O$ is the equilibrium solid phase over the HF concentration range 9.97–23.27 wt.% with a solubility of 44.30 wt.% HfO_2 at the highest fluoride concentration. There is a short fluoride concentration range over which both the trihydrate and the next phase, $HHfF_5\cdot 2H_2O$ coexist, but over the HF concentration range 25.36% to 27.76 wt.% only $HHfF_5\cdot 2H_2O$ is present.

The maximum solubility decreases from 44.0 to 42.90 wt.% over this fluoride concentration range. Beyond this, $H_2HfF_6 \cdot 2H_2O$ is the stable phase. Several other compositions have been isolated as hydrolysis products of $MF_4 \cdot H_2O$ (*309*). The compositions $ZrF_3OH \cdot H_2O$ and $ZrF_2(OH)_2 \cdot H_2O$ were unstable thermally to give

$$ZrF_3OH \cdot H_2O \rightarrow Zr_2F_6O \rightarrow Zr_3F_8O_2 \tag{32}$$

and

$$ZrF_2(OH)_2 \cdot H_2O \rightarrow ZrF_2(OH)_2 \rightarrow ZrF_2O \tag{33}$$

Gaudreau (*204*) has classified the zirconium oxygen fluorine compounds into four phases, three of which are nonstoichiometric, ZrO_xF_{4-2x} with $x = 0.67$, $1.30 \geqslant x \geqslant 1$, $0.67 > x > 0.44$, $0.44 \geqslant x \geqslant 0.25$. In these systems fluorine can replace oxygen in all proportions. Gaudreau (*204*) considers the HF, HfO_2, H_2O system in terms of two nonstoichiometric phases $HfF_4 \cdot xHF \cdot (3-x)H_2O$, where phase I corresponds to $1 \geqslant x \geqslant 0.8$ and phase II, $0.5 \geqslant x \geqslant 0$. For $0.8 > x > 0.5$, both phases coexist.

b. Chloro Species. Chloride solutions of zirconium and hafnium normally yield the crystalline compounds of simple empirical formula $MOCl_2 \cdot nH_2O$. The nature of the 8-hydrate has been previously discussed (*576*). The zirconium 8-hydrate is stable in the water vapor range 9.75–13.23 mm Hg at 20°C. Over concentrated sulfuric acid (40–98%), the octahydrate is dehydrated stepwise to reveal hydrates with 7.0, 6.5, 6.0, 5.5, 4.5, and 4.0 moles of water per mole of zirconium. Hafnium compounds of similar water content are also obtained. The 3-hydrate seems to be the lower limit, but cannot be obtained by dehydration. It is, however, the equilibrium solid phase for zirconium in concentrated hydrochloric acid below 45°C and for hafnium at hydrochloric acid concentrations greater than 30% and at temperatures below 60°C. The molar solubilities of the zirconium and hafnium chloro species are very similar, although at hydrogen chloride concentrations greater than 33 wt.% the hafnium species is the more soluble. At elevated temperature the system is complicated by the loss of hydrogen chloride with the production of hydrolyzed species corresponding to the composition $MO(OH)Cl \cdot nH_2O$ (*216–218, 607*).

In the presence of calcium chloride, solid phases $ZrOCl_2 \cdot 8H_2O$, $ZrOCl_2 \cdot 6H_2O$, $(ZrOCl_2)_2 \cdot CaCl_2 \cdot HCl \cdot 12H_2O$, and $ZrOCl_2 \cdot CaCl_2 \cdot 0.5HCl \cdot 10H_2O$ were found to exist (*279*).

2. *Salts of Halometallates from Aqueous Solution*

a. Fluoro Species. The anionic zirconium and hafnium fluoro species are well documented, but a substantial amount of work continues to be done with these systems. The ternary phase diagrams for the systems

ZrF_4–Na(K,Rb,Cs)F–H_2O and HfF_4–K(Rb,Cs)F–H_2O were worked out in detail (*554, 555*). In the sodium–zirconium fluoride system there are four solid phases in equilibrium with the solution. With 0.21% sodium fluoride in solution, $NaZrF_5 \cdot H_2O$ converts to Na_2ZrF_6. This exists as a solid phase up to 0.4% sodium fluoride. At concentrations between 0.465 and 1.18%, a new solid phase separates, namely, Na_5ZrF_{13}. With a further increase in sodium fluoride concentration Na_3ZrF_7 is deposited. Solubilities in gm/100 gm H_2O at 25°C are: $NaZrF_5 \cdot H_2O$, 0.37 and Na_2ZrF_6, 0.58. In the potassium and rubidium systems, $MZrF_5 \cdot H_2O$ extends up to 0.7% KF, 3% RbF, and 3.8% CsF, whereas M_2ZrF_6 exists within the MF ranges 0.76–2.63% KF, 3.54–12.65% RbF, and 5% CsF. Raising the KF and RbF concentration to 3 and 19%, respectively, leads to the separation of K_3ZrF_7 and Rb_3ZrF_7. The cesium heptafluoride does not form. In the hafnium systems the pentafluorohafnates exist as solid phases in a rather narrow interval of alkali metal fluoride concentrations. $KHfF_5 \cdot H_2O$ exists as a solid phase in KF solutions of less than 0.6%. At KF concentrations 0.7–2.23%, K_2HfF_6 crystallizes (0.98% HfF_4) and at 2.46% KF, K_3HfF_7 (1.18% HfF_4). The rubidium and cesium pentafluorohafnates exist as solid phases at RbF concentrations up to 2.5% and CsF concentrations to 4%. Rb_2HfF_6 is observed as the stable solid phase at RbF concentrations from 2.74–15.2%, while Cs_2HfF_6 is formed at CsF concentrations of 0.6%. At 17.3% RbF separation of Rb_3HfF_7 occurs. Like the zirconium system, there is no stable cesium heptafluoride of hafnium.

A detailed and precise study of the solubility of the hexafluoropotassium salts of zirconium and hafnium (*157–159*) showed that the solubility (*158*) of the zirconium salt increased with temperature from 3.304×10^{-3} to 127.819×10^{-3} gm-mole/100 gm H_2O over the temperature range 0°–100°C, while the hafnium solubility ranged from 6.079×10^{-3} to 199.950×10^{-3} gm-mole/100 gm H_2O over the same temperature

TABLE XXXI

THERMODYNAMIC PROPERTIES OF THE AMMONIUM HEPTA-, HEXA-, AND PENTAFLUOROZIRCONATES

Compound	ΔH^0	S^0	ΔG^0
$ZrF_4 \cdot 3NH_4F$ (c)[a]	-809.2 ± 0.7	(80.5)	−703.6
$ZrF_4 \cdot 2NH_4F$ (α)	-697.5 ± 0.7	(62)	−619.0
$ZrF_4 \cdot NH_4F$ (c)	-581.2 ± 0.7	(43.5)	−529.9

[a] (c) stands for crystalline.

range. An equilibrium separation coefficient of 0.434 at 20°C was reported by Egerav (*158*), whereas Nikolaev (*393*) reported 0.65 at the same temperature. The separation factor is observed to decrease as the F/M ratio increases $5 > 6 > 7$, and increases slightly as the temperature increases.

The hydrazinium fluorozirconates (hafnates) have also been prepared (*519*, *520*). A saturated solution of $N_2H_4 \cdot 2HF$ was mixed with an equivalent amount of a 20% solution of zirconium tetrafluoride. Upon evaporation 2-mm long, colorless crystals of $N_2H_6ZrF_8$ were formed. If the solutions were mixed in the mole ratio of 4.5:2, colorless crystals of trihydrazinium bis(heptafluorozirconate) were formed on evaporation. The corresponding hafnium salts were also prepared.

The hydrazinium salt decomposition started at 110°C and proceeded stepwise until it was finished at 380°C (*519*). Similarly the ammonium heptafluorozirconate (hafnate) (*204*) in flowing nitrogen or argon at 120°C decomposed to the hexafluorozirconate, which in turn decomposed to NH_4ZrF_5 which was stable to 200°C. The pentafluoride could be converted to the tetrafluoride in 1 hour at 330°C. α- and γ-NH_4ZrF_5 forms are observed as well as nonstoichiometric phases containing 1.4 and 1.7 moles of NH_4F.

The thermodynamic properties of the compounds $ZrF_4 \cdot (NH_4F)_n$ were calculated from measurements of the heats of solution of the respective compounds (Table XXXI) (*253*). The α-hexafluoro species is unstable with respect to the β form above 138°C. The anhydrous pentfluorospecies is the equilibrium phase above 4.2% Hf at 20°C, while the monohydrate is the equilibrium phase below this concentration. The standard heat of formation of the pentafluorohydrate is -651.95 ± 0.6 kcal/mole with the standard free energy of formation being -586.6 ± 1.0 kcal/mole (*254*).

The alkaline hydrolysis of ammonium and potassium hexafluorozirconates (*308*) yields $(M)ZrF_3(OH)_2 \cdot H_2O$ which are easily dehydrated. Thermal decomposition yields $(NH_4)_2Zr_4F_{12}O_3$ and at higher temperatures (240°C) $Zr_4F_{10}O_3$. The potassium salt $KZrF_3(OH)_2$ decomposes to give $KZrF_3O$. Acid hydrolysis of $MZrF_6 \cdot H_2O$ yields $K_{1.5}H_{0.5}Zr_2F_8O$ and $(NH_4)_{1.3}H_{0.7}Zr_2F_8O$.

The lithium (*249*) and copper(II) (*138*, *180*) hexafluorozirconates have been shown to contain the 6-coordinate ZrF_6^{2-}, in contrast to the ZrF_8^{4-} found in potassium salt. The compound Li_4ZrF_8 has been obtained from aqueous solutions of LiF and ZrF_4 (*316*). It has been reported to be tetragonal, with four molecules in the unit cell which has dimensions $a = 9.633 \pm 0.003$ Å and $c = 5.672 \pm 0.001$ Å. Whether this compound contains the ZrF_8^{4-} ion or not is not known, but the compound, Li_6BeF_4-ZrF_8, which is obtained from a fused system does (*484*). The crystal is also tetragonal with $a = 6.57 \pm 0.02$ Å, $c = 18.62 \pm 0.06$ Å, and with space group $D_{4h}^{19} - I_4/amd$. Around the zirconium atoms there are four equivalent F atoms at 2.05 ± 0.01 Å and four more at 2.16 ± 0.01 Å arranged as two interpenetrating tetrahedra with a common center, thus giving an irregular dodecahedron. In $Cu_2ZrF_8 \cdot 12H_2O$, the zirconium atoms are 8-coordinate, and no fluorines are shared. The crystal is monoclinic with $a = 15.895 \pm 0.013$ Å, $b = 9.652 \pm 0.01$ Å, and $c = 11.921 \pm 0.012$ Å with $\beta = 121° 47'$. The space group is $C2/c$ and there are four molecules in the unit cell. The mean Zr–F distance is 2.08 Å (*181*).

The crystal structure of $Cu_3Zr_2F_{14} \cdot 16H_2O$ was reported by Fischer (*182*). The Zr_2F_{14} species is monoclinic with two moles per unit cell, space group $P2_1/c$ and dimensions $a = 10.395$ Å, $b = 10.135$ Å, $c = 10.998$ Å, each ± 0.01 Å, and $\beta = 91° 47'$. The species $Zr_2F_{14}^{6-}$ results from the association of two square antiprisms with a common edge, thus leaving both zirconium atoms with coordination number eight. The zirconium–zirconium distance is 3.65 Å, and the mean Zr–F distance is 2.10 Å.

The compound $Na_5Zr_2F_{13}$ is crystallized from a solution containing equimolar quantities of NaHF and $ZrF_4 \cdot 3H_2O$ (*239*). The crystals are monoclinic with space group $C2m$ and $a = 11.62 \pm 0.02$ Å, $b = 5.49 \pm 0.01$ Å, $c = 8.44 \pm 0.01$ Å, and $\beta = 97.7 \pm 0.20°$. There are two formula units per unit cell. The fluorine atoms are placed at the corners of a coordination polyhedron composed of a trigonal prism and a tetragonal pyramid. Two such polyhedra joined together through the common apex of the pyramids form the complex ion $Zr_2F_{13}^{5-}$. Each zirconium thus has a coordination number of 7. The Zr–F interatomic distances range from 2.00 to 2.10 Å.

The structure of $K_2Cu(ZrF_6)_2 \cdot 6H_2O$ (*183*) is built up of $[Zr_2F_{12}^{4-}]$ anions which result from the association by a common edge, of two distorted pentagonal-bipyramidal ZrF_7 groups. The crystal is monoclinic with $a = 6.631$ Å, $b = 9.981$ Å, $c = 12.921$ Å, $\beta = 114° 12'$, $Z = 2$, and the space group is $P2_1/c$.

b. Chloro Species. Salts of composition M_2ZrCl_6, where $M = Cs^+$, Rb^+, and NH_4^+, have been prepared from aqueous solutions saturated with hydrogen chloride (*44*, *151*, *564*). The alkali metal–chloro complexes crystallize from aqueous solutions in a narrow hydrogen chloride concentration range. The minimal hydrogen chloride concentration at which the equilibrium hexachloro solid phases exist are: Cs_2ZrCl_6, 25%; Rb_2ZrCl_6, 30%; $(NH_4)_2ZrCl_6$, 35%; and K_2ZrCl_6, 38%. The cesium and rubidium salts melt congruently at 765° and 768°C, whereas the ammonium salt decomposes at 450°C (*564*). The corresponding hafnium compounds are more soluble than the zirconium compounds with the largest difference shown in the cesium and rubidium compounds. The hafnium, cesium, and rubidium compounds melt at 780° and 795°C, respectively (*44*).

3. *Salts of Halometallates from Nonaqueous Solutions*

a. Fluoro Species. Crocket and Haendler (*133*) have prepared M_2ZrF_6 species, where M = K, Rb, or Cs, by the addition of a methanol solution of zirconium tetrabromide to a concentrated solution of alkali fluoride also in methanol.

b. Chloro Species. Zirconium tetrachloride dissolves in $SOCl_2$ to the extent of 1–2% to form a solution which is more conducting than the pure solvent. This may be explained by the reaction

$$ZrCl_4 + 2\ SOCl_2 \rightleftarrows 2\ SOCl^+ + ZrCl_6^{2-} \tag{34}$$

The addition of a solution of a quaternary ammonium chloride in $SOCl_2$ to the zirconium tetrachloride solution yields a precipitate of the hexachloro complex, as expressed by the equation

$$2\ RCl + 2\ SOCl^+ + ZrCl_6^{2-} \rightarrow R_2ZrCl_6 + 2\ SOCl_2 \tag{35}$$

The compounds prepared were $[(CH_3)_4N]_2ZrCl_6$, m.p. 322°C (dec.); $[(CH_3)_3NC_6H_5]_2ZrCl_6$, m.p. 285°C (dec.); $[(CH_3)_3NC_7H_7]_2ZrCl_6$, m.p. 225°C (dec.); $[(CH_3)_2NC_6H_5 \cdot C_7H_7]_2ZrCl_6$, m.p. 217°C (dec.); and $[(C_2H_5)_3NC_7H_7]_2ZrCl_6$, m.p. 175°C (dec.). In the latter case no precipitate was obtained except upon addition of dry ethyl acetate (*476*).

The corresponding ethylammonium, dimethylammonium, diethylammonium, trimethylammonium and triethylammonium salts were prepared in ethanol (*151*) solution in which both the tetrachloride and amine were dissolved. Upon saturating the solution with hydrogen chloride, white crystalline products usually precipitated, although it was sometimes necessary to cool to 0°C. The products are all stable below 260°C, although they all darken between 260°–300°C. The recorded melting points are $[(C_2H_5)NH_3]_2ZrCl_6$, 260°C; $[(CH_3)_2NH_2]_2ZrCl_6$, 233°C; $[(C_2H_5)_2NH_2]_2ZrCl_6$, 274°C; $[(CH_3)_3NH]_2ZrCl_6$, 210°C; and $[(C_2H_5)_3NH]_2ZrCl_6$, 215°C. The dimethyl- and diethylammonium salts react slowly to give products with high Zr:N mole ratios, presumably owing to the formation of anionic species of the type $ZrCl_5(NR_2)^{2-}$.

4. *Salts of Halometallates from Fused Systems*

a. Fluoro Species. In the binary system NaF–ZrF_4 a whole series of stable phases have been shown to exist (*47*), namely, $3NaF \cdot 4ZrF_4$, $7NaF \cdot 6ZrF_4$, $3NaF \cdot 2ZrF_4$, $2NaF \cdot ZrF_4$, $5NaF \cdot 2ZrF_4$, and $3NaF \cdot ZrF_4$.

The equilibrium tetrafluoride partial pressure and free energy of formation of these phases have been determined by mass spectrometric means (*508–510*). The complex molecule $NaZrF_5$ was also shown to exist in the gas phase at 877°C.

In the binary system $NaF–HfF_4$ over the temperature range 400°–1000°C, two congruently melting compounds, Na_3HfF_7 (m.p. 860°C) and $NaHfF_5$ (m.p. 540°C), and one incongruently melting Na_2HfF_6 (m.p. 582°C) were established on crystallization from the liquids at $\leqslant 60\%$ HfF_4. One compound, Na_4HfF_8, formed at 750°C in the solid phase. There are four nonvariant points—three eutectics at 21% HfF_4, (m.p. 762°C) 42% HfF_4 (m.p. 500°C), and 52% HfF_4, (m.p. 538°C), and one peritectic, 35% HfF_4 (*496*).

In the binary system $KF–HfF_4$ (*492*) over the temperature range 400°–1000°C, four compounds were present, two of which melt congruently, K_3HfF_7 and $KHfF_5$ (m.p. 923° and 433°C, respectively), K_2HfF_6, which melts incongruently at 608°C, and K_4HfF_8, which exists in the solid phase at 730°C. The system has four eutectics: 13% HfF_4 (m.p. 766°C); 40% HfF_4 (m.p. 408°C); 57% HfF_4 (m.p. 420°C); and a peritectic at 35% HfF_4. In the ternary system $NaF–KF–HfF_4$ (*493*), the compounds M_3HfF_7, M_2HfF_6, and $MHfF_5$, form as a continuous series of solid solutions. The system has only one ternary eutectic at 27% NaF, 65% KF, and 8% HfF_4 with a melting point of 680°C.

Many other molten salt systems have been studied, some of which are $K_2ZrF_6–KCl$, $K_2ZrF_6–NaCl$, $K_2ZrF_6–KCl–NaCl$, $ZrCl_4–KF–KCl$ (*489*); $NaCl–NaF–Na_2ZrF_6$ (*488, 495, 499*); $NaCl–KCl–K_2ZrF_6–Na_2ZrF_6$ (*498*); $KF–KCl–K_2ZrF_6$ (*494*); $KBr–K_2ZrF_6$ and $KI–K_2ZrF_6$ (*106*); and $NaCl–KCl–Na_3ZrF_7–K_3ZrF_7$ (*497*).

b. Chloro Species. The binary system $MCl_4–Al_2Cl_6$ has been studied in several different laboratories with inconsistent results, which may be due to the tendency of aluminum chloride to supercool. Shor *et al.* (*504*) report that zirconium tetrachloride and aluminum chloride form a simple eutectic system without solid intermediary compounds, but possibly some limited solid solution, The composition of the eutectic at 165°C is approximately 75 mole% Al_2Cl_6, Nisel'son *et al.* (*205*) report that the eutectic temperature for both zirconium and hafnium tetrachlorides is 189°C at 71 and 81 mole% Al_2Cl_6, respectively. Denisova *et al.* (*146*), on the other hand, report a zirconium tetrachloride–aluminum chloride eutectic at 176°C and 86 mole% Al_2Cl_6, while Morozov (*373*) reports a eutectic at 71 mole% Al_2Cl_6 and 116°C, and a liquid miscibility gap from 23% $ZrCl_4$ to an unknown upper limit. None of the other authors with the exception of Korshunov (*321*) report the separation into two phases. The data of Shor's suggest that the two molecular chlorides interact in the liquid to form mixtures of essentially un-ionized complex molecules of $ZrCl_4(AlCl_3)_n$, where $n = 1, 2, 3, 4$, or higher. Shor also points out that the hafnium tetrachloride–aluminum chloride diagram of Morozov (*373*) must be wrong because the melting point depression of Al_2Cl_6 shown is 70 times larger than is compatible with the known heat of fusion for Al_2Cl_6. Nisel'son (*205*) also reports the ternary $ZrCl_4$, $HfCl_4$, Al_2Cl_6 diagram.

The compounds $M_2Zr(Hf)Cl_6$ have been synthesized by fusing calculated quantities of the simple salts in sealed quartz tubes (*371*), or by reacting gaseous zirconium tetrachloride at one atmosphere with Na(K)Cl in a double-bulbed evacuated tube in which the tetrachloride is heated to 330°C and the alkali metal chlorides are heated to 475° ± 50°C (*341*). The reaction time minimum is 24 hours under these conditions. The kinetics of this reaction (*156*) show that the reaction is diffusion controlled with the rate constant equal to $3.58 \exp(-12{,}300/RT)$ in units of $(\text{gmNa}_2\text{ZrCl}_6)^2\ \text{cm}^{-4}\ \text{hr}^{-1}$. The apparent activation energy is 12.3 kcal/mole (*156*). The potassium salt is known to be cubic (*341*), with $a_0 = 10.0818 \pm 0.003$ Å and space group *Fm*3*m*. In general the hafnium salts melt at a higher temperature than the corresponding zirconium compounds.

TABLE XXXII

VAPOR PRESSURE DATA FOR THE REACTION, $M_2M'Cl_{6(s)} \rightleftarrows M'Cl_{4(g)} + 2\ MCl_{(s)}$

Compound	$\log P(\text{mm}) = -a/t + b$		ΔH (kcal/mole)	Temperature (°C)
	a	b		
Na_2ZrCl_6	5640	8.54	25.8	432–630
K_2ZrCl_6	11300	13.40	52.0	650–790
Cs_2ZrCl_6	11360	11.80	52.0	700–800
Na_2HfCl_6	5690	8.47	26.0	450–650
K_2HfCl_6	11830	13.33	54.0	700–790
Cs_2HfCl_6	11930	10.24	54.5	740–820

The activities of Li_2ZrCl_6, Na_2ZrCl_6, and K_2ZrCl_6 in the systems $MCl–M_2ZrCl_6$ were recalculated from available vapor pressure data (*186*). Previously reported calculations (*342*) for the sodium and potassium chloride systems are now known to be in error. The calculations indicate positive deviations from ideality that decrease with increasing size of the alkali metal cation. Equilibrium constants for the dissociation of the sodium and potassium hexachlorozirconates at 535°C have average values of 87.0 ± 7.0 (Na_2ZrCl_6) and 76.0 ± 6 (K_2ZrCl_6), where the zirconium tetrachloride pressure is given in torrs. These data are consistent with the observation of Morozov (*371*) that the thermal stability of the ternary hexachlorometallates is a function of the cation size, the stability increasing with increasing size of the cation. Vapor pressure data for the dissociation are given in Table XXXII.

The phase diagrams for the binary systems MCl–Zr(Hf)Cl_4 have been studied in some detail. Lithium chloride (*155*) shows only the formation of Li_2ZrCl_6 (m.p. 535°C, $\Delta H_{\text{fusion}} = 9.30 \pm 0.8$ kcal/mole) and Li_2HfCl_6 (m.p. 557°C, $\Delta H_{\text{fusion}} = 8.80 \pm 0.65$ kcal/mole). The sodium chloride binary system is more complex. The hexachloro species Na_2ZrCl_6 (m.p. 646° ± 1°C, $\Delta H_{\text{fusion}} = 4.0 \pm 0.65$ kcal/mole) (*155*, *341*, *342*) and Na_2HfCl_6 (m.p. 600°C) (*155*) are identified. Three polymeric transitions (*370*) are claimed for the hafnium species at 384°, 440°, and 484°C, but the number of such transitions for the zirconium compound is uncertain, although discontinuities in equilibrium vapor pressures have been observed in the temperature range 350°–390°C (*155*, *320*). In addition, a Na_2ZrCl_6–NaCl (*342*) eutectic (m.p. 548°C) is found at 61.5 mole% Na_2ZrCl_6, and a Na_2HfCl_6–NaCl eutectic (m.p. 540°C) at 53.2 mole% $HfCl_4$, as well as a Na_2HfCl_6–$HfCl_4$ eutectic (m.p. 330°C) at 59.4 mole% $HfCl_4$. With potassium as the cation, K_2ZrCl_6 (m.p. 799° ± 2°C) (*341*, 342, 370) and K_2HfCl_6 (m.p. 802°C) (*370*) are identified. Two solid phase transitions are reported for the zirconium product (*155*), one in the range 614°–631°C and the other at 800°C. Two eutectics are also reported in these systems, K_2ZrCl_6–KCl (24.2 mole% $ZrCl_4$, m.p. 594°C) and K_2ZrCl_6–$ZrCl_4$ (57.8 mole% $ZrCl_4$, m.p. 220°C); K_2HfCl_6–KCl (22.4 mole% $HfCl_4$, m.p. 604°C) and K_2HfCl_6–$HfCl_4$ (62 mole% $HfCl_4$, m.p. 242°C) (*370*). No rubidium chloride system has been reported, although the reader will recall that the rubidium as well as the cesium hexachlorometallates have been prepared in aqueous solutions. In the cesium chloride-fused system (*370*), Cs_2ZrCl_6 (m.p. 805°C) and Cs_2HfCl_6 (m.p. 820°C) are reported. These melting points are considerably higher than those reported for the hexachlorometallates recovered from the aqueous solution. In addition, eutectics are reported at 15.2 mole% $ZrCl_4$, Cs_2ZrCl_6–CsCl (m.p. 572°C); at 67.2 mole% $ZrCl_4$, Cs_2ZrCl_6–$ZrCl_4$ (m.p. 286°C); at 18.4 mole% $HfCl_4$, Cs_2HfCl_6–CsCl (m.p. 590°C); and at 65.1 mole% $HfCl_4$, Cs_2HfCl_6–$HfCl_4$ (m.p. 302°C).

The binary systems of $ZrCl_4$ ($HfCl_4$) with $SnCl_4$, $ZnCl_2$, and $BiCl_3$ have also been investigated (*397*). The tetrachlorides with zinc chloride form simple eutectics at 10 wt.% $ZrCl_4$ and 14 wt.% $HfCl_4$, which melt at 308.5° and 305°C, respectively. Similarly, eutectics are formed with bismuth trichloride at 12 wt.% $ZrCl_4$ and 19wt.% $HfCl_4$ which melt at 212° and 206°C, respectively. Tin(II) chloride, on the other hand, appears to form compounds of composition $SnCl_2 \cdot 2MCl_4$ which melt incongruently at 315°C for the zirconium and at 342°C for the hafnium compound. Eutectics are formed with these compounds and $SnCl_2$ at 16 wt.% $ZrCl_4$ (m.p. 210°C) and 28.5 wt.% $HfCl_4$ (m.p. 217°C).

The ternary system NaCl, KCl, $ZrCl_4$ (*342*) shows a ternary eutectic at 36 mole% NaCl, 20 mole% $ZrCl_4$ and 44 mole% KCl with a melting point of 513° ± 3°C. In the ternary systems (*372*, *373*), Na(K)Cl–$Hf(Zr)Cl_4$–$AlCl_3$ there are five fields of primary crystallization corresponding to the separation of Na(K)Cl, $Hf(Zr)Cl_4$, $AlCl_3$, $Na_2(K_2)Hf(Zr)Cl_6$, and $NaAlCl_4$. Vapor pressure measurements show that $Zr(Hf)Cl_4$ can be freed from the main mass of $AlCl_3$ by the addition of Na(K)Cl to form nonvolatile $Na(K)AlCl_4$ (*373*).

Magnesium chloride and zirconium tetrachloride form a simple eutectic at 3.45 mole% $MgCl_2$ which has a melting point of 426°C. In the ternary system KCl–$MgCl_2$–$ZrCl_4$ there are five primary crystallization fields corresponding to the separation from the melt of $MgCl_2$, KCl, $ZrCl_4$, K_2ZrCl_6, and $KCl \cdot MgCl_2$. The interaction of K_2ZrCl_6 with $MgCl_2$ in the melt leads to the irreversible displacement of the reaction toward the side of the formation of $ZrCl_4$ and $KCl \cdot MgCl_2$, which permits the complete evaporation of volatile zirconium and hafnium chlorides from the melt (*570*). Similarly, iron(III) chloride and zirconium tetrachloride form a eutectic at 14.82 mole% zirconium tetrachloride which melts at 300°C (*368*). In the ternary system $FeCl_3$, $ZrCl_4$, NaCl, again five primary crystallization fields are present corresponding to the separation of NaCl, K_2ZrCl_6, $NaFeCl_4$, $ZrCl_4$, and $FeCl_3$. The equilibrium reaction

$$K_2ZrCl_6 + 2\ FeCl_3 = 2\ KFeCl_4 + ZrCl_4 \tag{36}$$

resulted in a small but finite vapor pressure of $FeCl_3$ at elevated temperatures (*368*, *372*).

5. *Infrared Spectra of Hexahalometallates*

a. Fluoro Species. An isolated MX_6^{2-} (O_h point group) should have six fundamental vibrational frequencies: three Raman-active ν_1, a_{1g} (polarized); ν_2, e_g (polarized) and ν_5, f_{2g}; two infrared-active ν_3, f_{1u}; ν_4, f_{1u}; and ν_6, f_{2u} which would be both infrared- and Raman-inactive. Although the stoichiometry may be MX_6, the site symmetry may be lower than O_h and, indeed, the coordination number of the metal in the solid state, particularly, may be higher than six. Peacock (*423*) studied the trends in the frequency assigned to ν_3 as a function of valency and position of the element in the periodic table. The decrease in frequency of ν_3 in TiF_6^{2-} from 560 cm^{-1} to values less than 400 cm^{-1} for ZrF_6^{2-} and HfF_6^{2-} was attributed to an increase in coordination number from 6 to 8.

Dean and Evans (*137*) recorded the Raman-active modes, ν_1 and ν_5 for the ammonium salts of the hexa- and heptafluorozirconates, and Griffith (*227*), did the same for solutions of the dioxides in 5 *M* HF. The values obtained were: ZrF_6^{2-}, 581 (ν_1), 228 (ν_5); HfF_6^{2-}, 589 (ν_1), 230 (ν_5); HfF_7^{3-}, 589 (ν_1), 230 (ν_5) (*423*), and 588 (ν_1) for zirconium dioxide in 5 *M* HF; and 593 (ν_1), 234 (ν_5) for hafnium dioxide in 5 *M* HF (*227*). These data indicate that MF_6^{2-} is an important species in all of these solutions. Dean (*137*) also looked at the ^{19}F NMR spectra of 1 *M* solutions of $(NH_4)_2ZrF_6$ and $(NH_4)_2HfF_6$. Broad peaks were observed at –73.9 ppm ZrF_6^{2-}, –33.0 ppm HfF_6^{2-}, and –152.2 ppm TiF_6^{2-}, compared to +49.8 for SiF_6^{2-}. The average lifetime of a fluorine nucleus in the two sites ZrF_6^{2-}, F^- is about 1.4×10^{-5} second compared to values $>10^{-2}$–10^{-3} second for SiF_6^{2-}, GeF_6^{2-}, SnF_6^{2-}, and TiF_6^{2-}.

TABLE XXXIII

INFRARED AND RAMAN SPECTRA OF MX_6^{n-} SPECIES

Solid state	Raman ν_1	Raman ν_2	Raman ν_5	Infrared ν_3	Infrared ν_4	Inactive ν_6
$(Et_4N)_2ZrCl_6$	327	237vw	153	290	150	90
$(Et_4N)_2HfCl_6$	333	237vw	157	288	145	80
Solutions						
$ZrCl_4$ in conc. HCl	326	225	150			
	329	237				
$HfCl_4$ in conc. HCl	331	204	152			

Smith *et al.* (*529*) have made an extensive investigation of the infrared spectra of $(NH_4)_3ZrF_7$, $(NH_4)_2ZrF_6$, NH_4ZrF_5, $NH_4ZrF_5 \cdot OH_2$, K_2ZrF_6, K_2HfF_6, Cs_2ZrF_6, and ZrF_4. The extremely broad bands in the range 380–550 cm^{-1} are assigned to M–F-stretching frequencies and those in the 350–200 cm^{-1} range to bending vibrations of the metal–fluorine complexes. Broad bands assigned as Zr–F-stretching frequencies have previously been observed by Clark (*109*) *et al.* and Muetterties (*376*) in the range 453–570 cm^{-1} for $ZrF_4 \cdot 2bipy$, $ZrF_4 \cdot 2Me_2SO$, and $ZrF_4(Me_2N)_2CO$. For Cs_2ZrF_6, the band at 500 cm^{-1} was assigned to the ν_3 mode of octahedral ZrF_6^{2-}, while the bands at 230 and 220 cm^{-1} were assigned to the ν_4 mode split into two components. Except for the cesium salt, the broadness and similarity of all the other spectra including that of ZrF_4, suggest that the anion site symmetry is low and that a coordination number greater than 6 is probable.

b. Chloro Species. In $pyH^+[MCl_6^-]$ (*109*), ν_3(M–Cl) frequencies occur at 297(Zr) and 273(Hf) cm^{-1}, which are in reasonably good agreement with the values reported by Adams (*7*, *8*) and Davis (*136*) in Et_4NMCl_6. The compounds $MCl_4 \cdot 1.5$bipy also show strong absorptions in this region at 299 and 314 cm^{-1} for the zirconium compound and 273 cm^{-1} for the hafnium compound, which is consistent with the idea that these complexes contain MCl_6^{2-} ions (*103*).

The solid state Raman and infrared spectra of Adams (*8*) and the Raman solution spectra of Davies (*136*) and Griffith (*227*) are recorded in Table XXXIII.

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