$$[\mathrm{Cu}]_\mathrm{T} = [\mathrm{Cu}]\{1 + \beta_{100}[\mathrm{A}] + \beta_{200}[\mathrm{A}]^2 + \beta_{101}[\mathrm{A}]a_\mathrm{H} + \beta_{201}[\mathrm{A}]^2a_\mathrm{H} + \beta_{202}[\mathrm{A}]^2a_\mathrm{H}^2 + \beta_{010}[\mathrm{G}] + \beta_{020}[\mathrm{G}]^2 + \beta_{030}[\mathrm{G}]^3 + \beta_{110}[\mathrm{A}][\mathrm{G}] + \beta_{111}[\mathrm{A}][\mathrm{G}]a_\mathrm{H}\}$$

$$[\mathrm{A}]_\mathrm{T} = [\mathrm{A}]\{1 + a_\mathrm{H}/K_{\mathrm{aA}3} + a_\mathrm{H}^2/K_{\mathrm{aA}2}K_{\mathrm{aA}3} + [\mathrm{Cu}](\beta_{100} + 2\beta_{200}[\mathrm{A}] + \beta_{101}a_\mathrm{H} + 2\beta_{201}[\mathrm{A}]a_\mathrm{H} + 2\beta_{202}[\mathrm{A}]a_\mathrm{H}^2 + \beta_{110}[\mathrm{G}] + \beta_{111}[\mathrm{G}]a_\mathrm{H})\}$$

$$[\mathrm{G}]_\mathrm{T} = [\mathrm{G}]\{1 + a_\mathrm{H}/K_{\mathrm{aG}2} + a_\mathrm{H}^2/K_{\mathrm{aG}1}K_{\mathrm{aG}2} + [\mathrm{Cu}](\beta_{010} + 2\beta_{020}[\mathrm{G}] + 3\beta_{030}[\mathrm{G}]^2 + \beta_{110}[\mathrm{A}] + \beta_{111}[\mathrm{A}]a_\mathrm{H})\}$$

These equations were solved for [Cu], [A], and [G] by using the Newton-Raphson method.[31] An independent check on the procedure was made by calculating the analytical concentration of titratable protons, $[\mathrm{H}]_\mathrm{T}$, from the following mass balance equation and comparing it with the known value.

$$[\mathrm{H}]_\mathrm{T} = [\mathrm{H}^+] - [\mathrm{OH}^-] + [\mathrm{HA}] + 2[\mathrm{H_2A}] + [\mathrm{HG}] + 2[\mathrm{H_2G}] + [\mathrm{CuAH}] + [\mathrm{CuA_2H}] + 2[\mathrm{CuA_2H_2}] + [\mathrm{CuAGH}] = [\mathrm{H}^+] - [\mathrm{OH}^-] + a_\mathrm{H}\{1/K_{\mathrm{aA}3} + 2a_\mathrm{H}/K_{\mathrm{aA}2}K_{\mathrm{aA}3} + 1/K_{\mathrm{aG}2} + 2a_\mathrm{H}/K_{\mathrm{aG}1}K_{\mathrm{aG}2} + [\mathrm{Cu}](\beta_{101}[\mathrm{A}] + \beta_{201}[\mathrm{A}]^2 + 2\beta_{202}[\mathrm{A}]^2a_\mathrm{H} + \beta_{111}[\mathrm{A}][\mathrm{G}])\}$$

Thus the concentration of any of the known species in solution can be calculated from its equilibrium constant and the values of [Cu], [A], and [G].

Appendix II. Solution of Differential Rate Laws Using the Runge-Kutta Method

Suppose we wish to solve the rate law

$$\mathrm{d}[\mathrm{CO_2}]/\mathrm{d}t = k_2[\mathrm{H_2A}] + k_{\mathrm{M}1}[\mathrm{Cu}][\mathrm{A}]$$

for the unknown rate constant $k_{\mathrm{M}1}$. The rate law is reduced to a form containing only [Cu], [A], and [G] as unknown concentrations

$$\mathrm{d}[\mathrm{CO_2}]/\mathrm{d}t = [\mathrm{A}](k_2a_\mathrm{H}^2/K_{\mathrm{aA}2}K_{\mathrm{aA}3} + k_{\mathrm{M}1}[\mathrm{Cu}])$$

The derivative $\mathrm{d}[\mathrm{CO_2}]/\mathrm{d}t$ is directly related to the derivative $-\mathrm{d}[\mathrm{A}]_\mathrm{T}/\mathrm{d}t$ which is equal to $\mathrm{d}[\mathrm{G}]_\mathrm{T}/\mathrm{d}t$. In fact between pH 3.5 and 4.5, $\mathrm{d}[\mathrm{CO_2}]/\mathrm{d}t = -\mathrm{d}[\mathrm{A}]_\mathrm{T}/\mathrm{d}t = \mathrm{d}[\mathrm{G}]_\mathrm{T}/\mathrm{d}t$. Thus the amount of glycine formed with respect to time is calculated in a stepwise fashion from $t = 0$ to $t = 95\%$ reaction by using an estimated value for $k_{\mathrm{M}1}$ in the rate law. A three-term Runge-Kutta equation was used to calculate the glycine concentration at each step.[32] The values of [Cu], [A], and [G] used in the rate law were calculated at each step by using the Newton-Raphson method described in Appendix I. The theoretical value of HCl added at any time is then calculated from the calculated glycine concentration. The theoretical volume-time curve is then compared with the observed volume-time curve as described in the Results and Discussion and the least-squares value of $k_{\mathrm{M}1}$ is obtained by iteration with the PITMAP method.[9]

Registry No. $\mathrm{Cu^{2+}}$, 15158-11-9; $\mathrm{H_2A}$, 1068-84-4; HG, 56-40-6; $\mathrm{CuA_2{}^{2-}}$, 49634-21-1; $\mathrm{CuA_2H_2}$, 49634-22-2.

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Synthesis of Crystalline Zirconium Trihalides by Reduction of Tetrahalides in Molten Aluminum Halides. The Nonreduction of Hafnium

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Zirconium(III) chloride, bromide, and iodide, free of the zirconium (or aluminum) reducing agent, are crystallized from zirconium(III)-containing aluminum trihalide solutions prepared by the low-temperature (230–310°) reduction of corresponding zirconium(IV) halide–aluminum trihalide solutions. Under the same experimental conditions, the rate of hafnium(IV) reduction is slow, thus allowing a separation of the two elements in naturally occurring mixtures. The separation factors are about 10, 5, and 2 for the chloride, bromide, and iodide systems, respectively. The crystal growth, which occurs at the edge of the melt, is limited (first batch yields: 5% bromide, 20% chloride, 30% iodide) by the ability to transport the soluble zirconium(III) species to the growth site and by a competing disproportionation reaction which yields, for the chloride and bromide systems only, an insoluble brown product, $(\mathrm{ZrX_2})_2\cdot\mathrm{AlX_3}$.

Introduction

Syntheses[2-12] for zirconium trichloride, tribromide, and triiodide generally have involved the reaction of gas phase zirconium tetrachloride with a solid reducing agent, usually zirconium or aluminum, under a variety of temperatures, temperature gradients, pressures, times, reaction vessel conformations, and physical forms of the reducing agents. In these procedures, the trihalide is produced on the surface of the metallic reducing agent and encapsulation of the metal by the product is a problem, although essentially eliminated with the use of foil.[11,12] Alternate syntheses reported in-

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clude atomic hydrogen reduction[13,14] of the tetrahalide in a glow discharge tube with the unreacted tetrahalide separated from the product by sublimation, electrolytic reduction of zirconium tetrahalides in alkali halide melts,[15-17] and active metal reduction in tetrachloroaluminate melts.[18] In the latter cases, separation of the product from nonvolatile melts would not be clean cut.

Ruff[2] and Newnham[6] observed that reduction of zirconium tetrachloride seemed to be facilitated by the aluminum trichloride produced when aluminum was used as the reducing agent. Corbett[12,19] similarly observed that the reduction of hafnium(IV) was improved by the presence of a limited amount of aluminum trihalide. No attempt had been made to study aluminum trihalides as solvent systems for these reductions. Here we report the low-temperature reduction of zirconium tetrahalides by zirconium or aluminum metal in aluminum trihalide solutions, a procedure for the separation of zirconium from its naturally occurring hafnium impurity, and evidence for a new ternary chloride of zirconium(II) and aluminum(III). Preliminary data[20] on the separation were reported earlier.

Results and Discussion

Although a variety of purification methods and syntheses of the zirconium and aluminum halides have been described, much of the equipment is either too unsophisticated to yield high quality products or contains joints which require a lubricant. All our procedures for the preparation of halides involve, after filling and evacuation, only sealed ampules of a variety of designs.

The reaction system consists of a solid reducing agent, either aluminum or zirconium, and an aluminum trihalide-zirconium tetrahalide mixture near the eutectic composition. The chloride system has an eutectic at 76 mol % Al_2Cl_6[21] (165°), and although no phase data are available, our observations lead to the conclusion that eutectics exist at a somewhat higher mole per cent of Al_2X_6 for the bromide and iodide systems. Extensive experiments defined the optimum conditions to be 76 to 85 mol % Al_2X_6, a ZrX_4-M mol ratio of 4-5 to 1, and reaction temperatures of 230-270° for the chloride, 270-290° for the bromide, and 310° for the iodide. The reaction times were erratic but the maximum crystal growth was usually obtained in five days; longer times were not advantageous.

The exact nature of the dissolved zirconium species in the fused chloride system is not known, and although no compound formation has been observed,[21] the zirconium tetrachloride is most certainly solvated. A model for the melt is necessary to rationalize the chemistry of this system. An important factor in any model is that at 76 mol % Al_2X_6, only three dimers or six monomers of aluminum trihalide are present for each zirconium(IV); the extent of solvation is thus limited. Solvation of the type $ZrCl_4 \cdot nAlCl_3$, where n = 1, 2, 3, and 4, has been suggested,[21] in which zirconium is coordinated to four $AlCl_4$ tetrahedra with the Zr-Cl bonds directed to the corners of a tetrahedron. However, the proclivity of Al_2X_6 to go to AlX_4^- in the presence of a halide donor,[22-25] and the general tendency of zirconium to achieve coordination number (CN) 6 or higher in condensed phases, as shown in the solid state structure of zirconium tetrachloride,[26] suggests that the tetrahedral model should be modified to a CN 6 coordination species such as $Zr(Cl_2AlCl_2)_2(Cl\text{-}AlCl_3)_2$, which contains the structural features common to zirconium tetrachloride,[26] $Co(AlCl_4)_2$[27] and $Ni(AlCl_4)_2$.[28] Although no data are available for the bromide and iodide systems, a similar model is assumed to hold.

As the liquid eutectic is raised to the reaction temperature, a soluble blue species is seen streaming off the surface of the metal reducing agent in the chloride and bromide systems, and although visually obscured in the iodide case by an intense red-orange charge transfer absorption, an analogous species, as shown by absorption spectroscopy, is present there also. The formation of this soluble species is independent of whether zirconium or aluminum is used as the reducing agent and therefore is assumed to involve a reduced zirconium species. Although the colored species has not been isolated, the observations which follow suggest that its formation may be represented by the equations

$$Zr + 3[Zr(X_2AlX_2)_2(XAlX_3)_2] \rightarrow 4Zr(X_2AlX_2)_3 \qquad (1)$$

$$Al + 3[Zr(X_2AlX_2)_2(XAlX_3)_2] \rightarrow 3Zr(X_2AlX_2)_3 + 2Al_2X_6 \qquad (2)$$

The nature of the blue species has been partially characterized by the absorption spectra (Figure 1) of the melts. Note the intense absorption in the ultraviolet which shifts to longer wavelength as the anion is changed from chloride to bromide to iodide. This absorption is also present in the spectra of all the aluminum trihalide-zirconium tetrahalide melts and is attributed to a ligand to metal charge transfer transition of the solvated zirconium tetrahalide. The feature of interest is the single broad absorption in the visible and near infrared regions of each spectrum. The coincidence of this single absorption with the most intense absorption in the diffuse reflectance spectrum (Table I) of the corresponding binary trihalides supports the conclusion that the soluble blue species contains zirconium(III) in an octahedral site, since in the solid state structure of the zirconium(III) binary halides, zirconium(III) ions are known[29] to occupy octahedral (actually D_{3d}) sites of a close-packed anion lattice. This absorption can be ascribed to a $^2T_{2g} \rightarrow {}^2E_g$ transition[30] of a d^1 ion. The absorption band is broad but this can be attributed to the increased metal-ligand vibrations at the relatively high temperature of the reaction system, the splitting of degenerate orbitals by Jahn-Teller, and spin-orbit coupling effects. Although each of the latter would be expected to cause a degree of asymmetry in the observed absorption peak, the simultaneous operation of the effects probably results in averaging and thus a broadening of the absorption

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Table I. Reflectance Spectra of Solid ZrX_3, $(ZrX_2)_2 \cdot AlX_3$, and Absorption Spectra of Zirconium(III) in Aluminum Trihalide-Zirconium Tetrahalide Melts

System	Absorption maxima, kK				Ref
Cl melt		17.4 plus intense charge transfer band beginning *ca.* 22.7			This work
Br melt		16.0 plus intense charge transfer band beginning *ca.* 20.8			This work
I melt		14.0 plus intense charge transfer band beginning in near ir			This work
$ZrCl_3$(s)	9.0	17.4		27.8	This work
		17.3	21.0 sh		30
		16.7		26.3	36
		15.6		25.8	37
$ZrBr_3$(s)		14.5		26.3	This work
		14.0		25.0	37
		16.2			30
ZrI_3(s)		13.5		26.5	This work
$(ZrCl_2)_2 \cdot AlCl_3$		16.1	20.7	27.8	This work
$(ZrBr_2)_2 \cdot AlBr_3$		13.4	20.8	27.2	This work

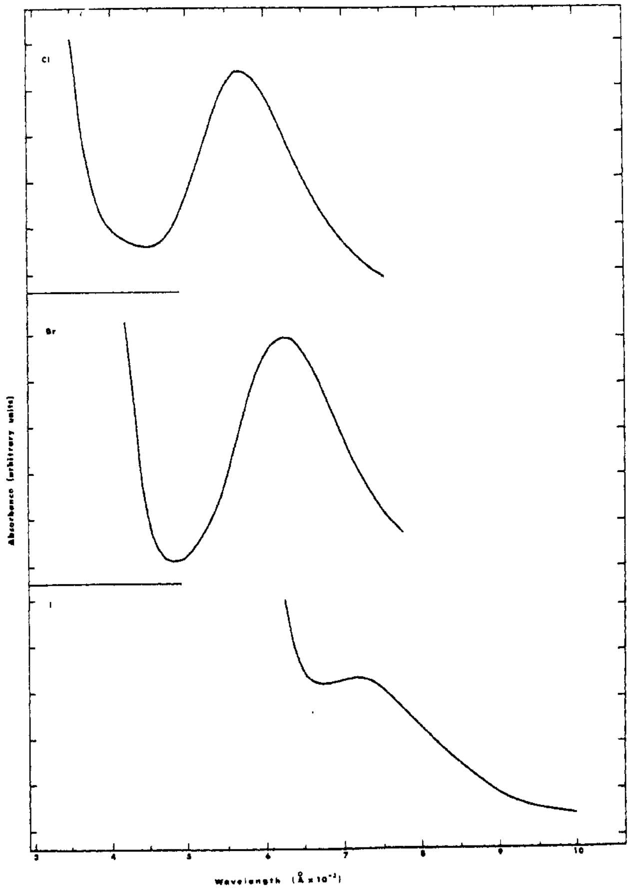

Figure 1. Absorption spectra of solvated zirconium(III) halides in liquid aluminum(III) halides.

envelope without a large degree of asymmetry.[31]

The magnitudes of the 10*Dq* values are also consistent with zirconium(III) in an octahedral field of halide ions. For the chloride system a comparison of the experimental 10*Dq* value with a calculated 10*Dq* value can be made using the data for titanium dichloride in aluminum trichloride[23] and the relationships of Jorgensen.[32] To correct for the change from a 2+ ion to a 3+ ion, the 10*Dq* value for titanium(II), 7.0 kK, is multiplied by 1.6 and to correct for the change from a 3d to a 4d species the product is multiplied by 1.45. The resulting value, 16.2, is in reasonably good agreement compared to the experimental value of 17.4. In addition, the direction and magnitude of change in 10*Dq* values with change in ligand is that expected for a CN 6 environment; $10Dq_{Cl}/10Dq_{Br}$ being 1.09 compared to 1.05 using the spectrochemical ligand parameters given by Jorgensen[32] for octahedral coordination and a constant metal oxidation state.

A magnitude for the molar absorbancy of the blue species would be helpful in confirming the octahedral environment of zirconium(III). Unfortunately, since the blue species was not isolable, only an order of magnitude value could be obtained. An absolute minimum value of 200 was established, which is consistent with a d-d transition for a second row element where a combination of spin-orbit coupling and intensity stealing from charge transfer bands can account for high absorptivities. However, if the absorbancy is as high as 1000, an alternate explanation of the spectra is required.

Additional information on the nature of the blue species comes from the observation that zirconium trihalide crystals are essentially insoluble in pure aluminum trihalide, except that a very low intensity rose color has been observed near the surface of trichloride crystals when the system is scrutinized very carefully. We have not identified the source of this color. However, the crystals are soluble in a zirconium tetrahalide containing solution of aluminum trihalide forming a soluble blue solution identical with that formed in the reduction reaction. Thus, the molecular aluminum halide dimer is incapable of attacking the chloro bridges of the zirconium trihalide solid state structure, but the solvated zirconium tetrahalide does successfully attack the solid zirconium trihalide structure. This can be rationalized if the solvated species previously proposed undergoes an electron exchange reaction in a manner similar to that occurring in the solution of anhydrous chromium(III) chloride in the presence of aqueous chromium(II) ion. An equation consistent with this idea may be written as

$$2Zr(X_2AlX_2)_2(XAlX_3)_2(soln) + 2Zr^*X_3(s) \rightarrow 2Zr(X_2AlX_2)_3(soln) + 2Zr^*(X_2AlX_2)_2(XAlX_3)_2(soln) \quad (3)$$

Owing to the similarity in spectral properties of the blue solution and the solid state binary halides, we must conclude that no direct zirconium(III)-zirconium(IV) species is formed.

Crystals of olive green trichloride, dark brown bromide, and blue-black triiodide were deposited from their respective melts. All these crystals possess a metallic sheen. The de-

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position of zirconium(III) halide crystals occurs on the glass side walls within the area wet by a thin film of melt and not generally in the bulk of the melt. Contamination of the reduced state product by the metallic reducing agent is thus eliminated. Improved crystal growth is obtained by tilting the tube furnace 20° to the horizontal to reduce the surface area wet by a liquid film of melt. This results in a desirable crystal growth of needle-like crystals at a point a centimeter or so from the lip of the meniscus. The best crystal growth is obtained in the chloride system where needles up to a centimeter in length have been obtained. The crystal growth is limited by the ability to transport the soluble zirconium species to the growth site and by a competing disproportionation reaction which results in the deposition of a brown aluminum-containing zirconium(II) compound in the melt. It appears that the crystal growth results from the decomposition of the blue species *via* the decomposition of the solvated zirconium(III) halide rather than *via* the gas phase

$$2Zr(X_2AlX_2)_3 \rightarrow 2ZrX_3(s) + 3Al_2X_6 \qquad (4)$$

although we do not have data at the present time on the composition of the vapor phase. It seems reasonable to assume that a complex gas phase species of zirconium tetrachloride does exist similar to $Nd(AlCl_4)_3$,[33] $UCl_5 \cdot AlCl_3$,[34] and $UCl_2(AlCl_4)_2$ but that the gas phase species of zirconium(III) chloride is less likely at these temperatures.

The quality of the crystals is such that they may be used for a single crystal X-ray diffraction study.[35] The single crystal data showed hexagonal Laue point symmetry D_{6h} $6/m2/m2/m$, with systematic absences indicating $P6_3/mcm$ ($D_{6h}{}^3$), $P6_3m$ ($C_{6v}{}^3$), or $P\bar{6}c2$ ($D_{3h}{}^2$) as probable space groups. The hexagonal lattice parameters of $a = 6.724 \pm 0.002$ Å and $c = 6.291 \pm 0.002$ Å, the unit cell volume of 246.35 Å^3, and calculated density of 4.46 g cm^{-3} for $Z = 2$ correspond favorably with those previously deduced from the powder data[29,36] but are of higher precision. Although the data treatment, detailed in the Experimental Section, leaves unanswered questions, the results are consistent with the structure based[29] on the centrosymmetric space group symmetry, $P6_3/mcm$, in which infinite chains of $ZrBr_6$ octahedra, joined at opposite faces, extend along the c axis. The more precise data give the distance between the metal atom and its six surrounding bromine atoms as 2.667 ± 0.001 Å, while the equally spaced zirconium atoms are 3.145 Å apart (corresponding to one-half of the c lattice parameter). It should be emphasized that in actuality the zirconium atoms may not be equally spaced in a given chain on a microscopic basis but that a crystal order-disordered structure containing regularly spaced atoms with the above distances is produced for the (X-ray) determined "average" unit cell. No evidence for a supercell was seen from the X-ray data for this crystal of $ZrBr_3$ as has been suggested for HfI_3.[19]

The crystalline products obtained *via* this low-temperature reduction route have powder patterns identical with those synthesized[29] under higher temperatures and pressure. This suggests that these parameters alone are not the only ones which account for the presumed polymorphism[36-38] of the zirconium trihalides. Not only have different powder patterns been reported,[36] but also different colors for the same compound have been observed. In some instances, the color differences may be due to particle size, for the higher energy absorption observed in the reflectance spectra (Table I) decreases markedly in intensity upon grinding and dilution, and simultaneously the intense absorption in the visible, which is essentially absent in the reflectance spectrum of macrocrystals, grows in intensity. Thus, the green macroscopic crystals yield a blue microcrystalline powder.

The competing reaction to crystal growth, which occurs in the chloride and bromide systems but not in the iodide, is observed as the formation of an insoluble, nonvolatile brown microcrystalline powder in the liquid melt. The same brown products may be obtained by digesting the binary trichloride or tribromide in the corresponding pure aluminum trihalide at relatively low temperatures (250°). The X-ray powder diffraction patterns (Table IV) show no evidence of any lines corresponding to the aluminum halides, zirconium or aluminum metal, or zirconium(III) or zirconium(IV) binary halides. The similarity in the patterns suggests that the chloride and bromide products are isostructural.

The brown solids are not soluble without undergoing a reaction so the only spectral data available are from the solid state. The reflectance spectra are not particularly revealing except for the fact that they are more complex than the corresponding spectra of the binary compounds. The infrared spectrum of the brown chloride shows three strong absorptions at 300, 440, and 555 cm^{-1} compared to the single strong absorption at 338 cm^{-1} for zirconium(III) chloride. None of the absorptions correspond to the spectrum of pure aluminum trichloride, which shows a strong absorption at 320 cm^{-1}, a weaker one at 475 and a shoulder at 500 cm^{-1}, nor to the single strong absorption at 485 cm^{-1} in pure $KAlCl_4$. The brown bromide has a similar spectrum with strong absorptions at 360, 445, and 515 cm^{-1}. There are also about a half-dozen weaker absorptions or shoulders in the spectra of the brown microcrystalline powder. These products were originally thought to be binary nonstoichiometric compounds, but spectrographic analyses indicated the presence of aluminum, and quantitative analyses by atomic absorption revealed the presence of 1 mol of aluminum to 2 of zirconium. The oxidation state of two for zirconium is compatible with the analytical data and the solution behavior of these compounds. Both dissolve in water with the vigorous evolution of hydrogen and the formation of a transitory green solution which changes to the familiar red-orange of zirconium(III) in aqueous solution. On the basis of this observation, we conclude that the oxidation state of zirconium is two. The magnetic moments at room temperature are above 2.5, but this in itself is not particularly meaningful since these compounds exhibit a field dependence which makes the magnitude of μ_B difficult to interpret. However, the magnetic properties do show differences from the zirconium(III) compounds, which lead us to conclude that the oxidation state is other than three. Inasmuch as these zirconium(II) products are obtained in the presence of aluminum trihalides, it would appear that the oxidation state (III) compound undergoes disproportionation favored by the incorporation of aluminum(III) in the structure. The chloride product corresponds closely to $(ZrCl_2)_2 \cdot AlCl_3$ and may be conceived to be formed by the reactions

$$8ZrCl_3(s) + 9Al_2Cl_6 \rightarrow 2(ZrCl_2)_2 \cdot AlCl_3 + 4Zr(Cl_2AlCl_2)_2(ClAlCl_3)_2 \qquad (5)$$

$$8Zr(Cl_2AlCl_2)_3 \rightarrow 4Zr(Cl_2AlCl_2)_2(ClAlCl_3)_2 + 3Al_2Cl_6 + 2(ZrCl_2)_2 \cdot AlCl_3 \qquad (6)$$

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Table II. Data for Some Differential Reduction Experiments

	ZrX_4		Al_2X_6		Metal				
	g	mmol	g	mmol	g	mmol	Temp, deg	Days	Sepn factor[c]
Cl^-	4.02	17.3	14.95	56.04	0.3186[a]	3.49	260	8	10.9
							300	1	
	4.08	17.5	14.99	56.22	0.0933[b]	3.46	260	8	9.6
							290	4	
Br^-	4.65	11.3	19.78	37.08	0.207[a]	2.27	270	33	5.3
	3.59	8.74	25.94	48.63	0.158[a]	1.74	270	33	6.0
I^-	3.99	6.66	17.97	22.03	0.123[a]	1.35	310	19	2.9
							360	13	
	4.01	6.70	17.68	21.69	0.366[b]	1.36	310	19	2.3
							330	13	

[a] Zirconium sponge. [b] Aluminum chips. [c] Separation factor is defined as initial Hf–Zr mole ratio divided by the final Hf–Zr mole ratio.

It seems very likely that the brown trichloride reported by Ruff[2] is in fact the same as our $(ZrCl_2)_2 \cdot AlCl_3$, as his analytical data correspond more closely to the composition of the brown powder than the trichloride.

Although the exact nature of the structural features will have to await more precise characterization, it is interesting to note that certain similar titanium compounds are known. A compound reported as $Ti(AlCl_4)_2$ (blue) which decomposes in the presence of excess aluminum chloride to give an insoluble brown powder of composition $TiAlCl_5$ has been reported by Smith, *et al.,*[39] and although the X-ray powder data for these compound are clearly different than the powder data of $(ZrX_2)_2 \cdot AlX_3$, both may belong to a structure in which M(II) and M(III) cations sit in appropriate tetrahedral and octahedral holes of a close-packed halide ion lattice.

The low temperature of reduction and the formation of nonvolatile zirconium(III) halide crystals on the container sidewalls away from the bulk of the melt suggested that this chemical system might afford a particularly good method of separating zirconium from naturally occurring hafnium in view of the known[5,6,14,18] slight difference in the ease of reduction of these two elements. Additionally, the fact that the aluminum trihalides and unreduced metal tetrahalides were volatile and thus easily transported provided a convenient separation procedure of the nonvolatile product from the volatile solvent and unreduced reactants. Experiments with hafnium tetrachloride under the same conditions used successfully in the preparation of zirconium trichloride yielded no obvious reduction products. To further test this hypothesis an equimolar $ZrCl_4$-$HfCl_4$ mixture was prepared for reduction. The trihalide crystals recovered contained only 5.5 mol % hafnium for a separation factor of 17. A few of the additional experiments using zirconium tetrahalide containing a naturally occurring amount of hafnium are tabulated in Table II. The fact that the hafnium content of the zirconium(III) halide is different for each halide is indicative that some reduction of hafnium to a lower oxidation state does occur. A differential reaction rate is also probably important in the favorable separation observed. A continuous feed and crystal harvest procedure undoubtedly would bring improvements in yield as well as in the effectiveness of separation.

The separation factors are somewhat erratic owing to the fact that upon opening the reaction ampules, which are under reduced pressure, some scattering of the contents of the ampule occurs upon pressure equilization. Additionally, the separation of the volatile and nonvolatile components may not be entirely reproducible with the existing technique.

Table III. Distribution of Hafnium in a Chloride Reduction Melt

	Wt, g	Equiv oxide wt, g	g Hf/g oxide × 10^3	g Hf × 10^3
Reactants				
$ZrCl_4$	2.34	1.24	14	17.3
Zr	0.27	0.364	0.12	0.04
				17.3
Products				
$ZrCl_3$	0.31	0.194	0.74	0.14
Ternary chloride	1.18	0.700	1.6	1.12
Reclaimed $ZrCl_4$	1.04	0.55	28.8	15.8
				17.0

It is known that the crystalline product may be contaminated with up to 1% aluminum as the chloride, a substantial portion (70%) of which may be removed by simply washing with benzene.

A hafnium balance was made on a chloride melt with the results shown in Table III. This reaction system was held at 252° for a period of 10 days. The data show that in fact the brown powder was the major product. Shorter reaction periods will reduce the total quantity of ternary compound produced and more effective sublimation procedures will reduce the hafnium content of the ternary chloride.

Experimental Section

Equipment and Technique. All the starting materials and products were sensitive to oxygen and water, therefore all procedures were carried out in dry nitrogen or *in vacuo* ($\leqslant 1\ \mu$). Solids were routinely manipulated in a stainless steel inert atmosphere box continuously swept with high purity nitrogen (min. purity 99.9975, dew point −65°). Internal water content, monitored by a Shaw portable hygrometer, was maintained at 15–30 ppm by open dishes of phosphorus pentoxide. Oxygen levels, 0–50 ppm, measured by a Westinghouse oxygen gauge, Model 203, were controlled by a heated copper-supported scavenger (BASF catalyst R3-11).

All syntheses and purifications were carried out in Pyrex ampules, the main sections of which were 30-min o.d. standard wall tubing. Multisection ampules were connected with sections of $^3/_8$-in. o.d. heavy wall tubing. All tubes were terminated with a 14/35 male joint by which they were attached to the vacuum line *via* a stopcock adapter.

X-Ray Patterns. A 114.6-mm Debye–Scherrer camera mounted on a Norelco X-ray generating unit operating at a tube voltage of 35 kV and a filament current of 18 mA was used to obtain powder patterns with nickel-filtered copper radiation. All samples were loaded into 0.3-mm Lindemann glass capillaries which were plugged with vacuum grease and then flame sealed outside of the inert atmosphere box. Typical exposure times were 12–24 hr. All patterns were recorded on Kodak NS-392T film, using a Straumanis mounting. The 2θ spacings were determined using a Norelco film illuminator and measuring device and were converted into *d* spacings using published tables. Intensities were estimated visually.

The single crystal data were obtained on a suitable zirconium tribromide needle of average diameter 0.10 mm and length 0.85 mm which was cemented to the wall of a thin-walled glass capillary with epoxy glue, evacuated, and then filled with nitrogen before sealing.

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(39) J. Byrnestad, S. von Winbush, H. L. Yakel, and G. P. Smith, *Inorg. Nucl. Chem. Lett.,* **6,** 889 (1970).

Table IV. X-Ray Powder Patterns of the Ternary Halides

Chloride			Bromide		
I	2*θ*	*d*, Å	*I*	2*θ*	*d*, Å
W	8.25	10.71			
M	9.90	8.93	MW	9.45	9.36
S	10.76	8.22	M	10.25	8.63
S	14.57	6.08	M	13.83	6.40
			VVW	15.25	5.81
			VVW	16.22	5.46
VW	18.85	4.71	VW	18.90	4.70
VW	19.82	4.48	M	20.10	4.42
M(b)	21.25	4.18	W	21.55	4.12
W	22.56	3.94	VW	22.58	3.94
W	23.63	3.77	VW	25.95	3.43
W	27.30	3.27	W	27.12	3.29
			W	28.18	3.17
M	28.50	3.13	S	28.75	3.11
W	29.36	3.04			
M	30.26	2.95	W	30.20	2.96
M	31.79	2.81	W	32.30	2.77
M	33.97	2.64	S	33.25	2.69
VS	34.97	2.57	W	36.42	2.47
M	38.24	2.35	W	37.22	2.42
M	39.05	2.31	VVW	38.48	2.34
W	40.42	2.23	W	39.75	2.27
			VW	40.78	2.21
M	41.71	2.17	VW	42.12	2.15
W	42.83	2.11	W	42.52	2.13
M	44.30	2.04	W	43.75	2.07
W	45.75	1.98	M	47.64	1.91
VW	48.83	1.87	VVW	48.92	1.862
	50.00	1.820	VVW	49.62	1.837
S(b)[a]	50.45	1.809	VVW	50.85	1.796
	50.80	1.797	VVW	51.88	1.762
VW	51.52	1.774	VVW	53.30	1.719
VW	52.52	1.742	VVW	54.52	1.683
VW	53.71	1.707	M	56.65	1.625
VW	57.45	1.604	VW	58.88	1.568
W(b)	59.27	1.559	MW	59.55	1.552
M	62.87	1.478	VVW	60.82	1.523
VW	64.08	1.453	VVW	62.70	1.482
M	66.16	1.412	VVW	63.90	1.457
W	67.47	1.388	VVW	66.85	1.399
M	73.79	1.284	VVW	67.85	1.381
W	76.92	1.239	VVW	68.75	1.365
			MW	69.70	1.349
			VVW	70.58	1.334
			VVW	72.58	1.303
			W	76.55	1.245
			W	77.30	1.234
			MW	79.00	1.212
			MW	79.62	1.204

[a] These lines appear as one intense band on film but were resolved on the powder diffractometer.

Preliminary oscillation and Weissenberg photographs confirmed[29] the hexagonal Laue point symmetry D_{6h}, $6/m2/m2/m$. The hexagonal lattice parameters were measured with Mo Kα radiation from the careful crystal alignment of 22 reflections on a full-circle, Datex-automated General Electric diffractometer. Both *hkl* and $\bar{h}kl$ intensity data, collected with Mo Kα radiation up to a 2*θ* value of 60° (beyond which there were only a few reflections above background) yielded 493 "observed" diffraction maxima with $I \geqslant 2\sigma(I)$ and 258 "unobserved" reflections with $I < 2\sigma(I)$. The "observed" data were merged by least squares to give 190 independent data. Details of the data collection reduction (including the calculation of esd's for the intensities) and merging method are given elsewhere.[40] A least-squares refinement (based on the centrosymmetric space group symmetry $P6_3/mcm$[41] which requires that the zirconium and bromine layers of atoms be equally spaced along the *c* lattice direction[42]) of the variable *x* coordinate for the bromine atom and two isotropic temperature factors (*i.e.*, one for the independent Zr and for the independent Br) converged at an unweighted R_1 of 8.3% and a weighted R_2[43] of 9.7%. Two cycles of anisotropic thermal refinement did not influence these results. The somewhat high *R* values are presumed to be mainly a consequence of the attempted absorption correction not being sufficiently precise. The final value of the fractional *x* coordinate for the crystallographically independent Br atom was found to be 0.3205 ± 0.0004, while the final isotropic thermal parameters were 2.59 ± 0.09 Å^2 for Zr and 1.96 ± 0.06 Å^2 for the Br atom.

Spectra. Infrared spectra were recorded as mulls in a Beckman I.R. 10 or Perkin-Elmer 457 spectrophotometer. Fluorolube mulls between sodium chloride plates were used for the region 4000–1300 cm^{-1} and Nujol mulls between cesium iodide plates were used for the region 1300–250 cm^{-1}. All spectra were calibrated using polystyrene film.

Diffuse reflectance spectra were obtained with a Cary Model 14 spectrophotometer equipped with a Model 1411 reflectance attachment. Magnesium carbonate was used as the reference sample and anhydrous magnesium sulfate as the diluent. The samples were loaded into paddle shaped ampules with a parallel wall separation of several millimeters.

Electronic spectra in the ultraviolet, visible, and near infrared were also recorded on a Cary Model 14 spectrophotometer in fused silica cells constructed from precision bore square tubing with a wall separation of 1 cm. The cell was connected *via* a graded seal to a spherical Pyrex reservoir (*ca.* 25 ml volume) which in turn was connected to a length of tubing which terminated in a standard 14/35 joint. The cell was loaded with a reaction mixture in the inert atmosphere box, evacuated, and sealed. To obtain a spectrum, the cell was allowed to reach thermal equilibrium and the furnace was then transferred to the Cary sample compartment. The furnace used was a modification of those used with the Beckman Model DU spectrophotometers.[44,45] After scanning was completed, the cell was removed and the melt poured into the spherical reservoir to minimize the formation of solid in the rectangular cell. The Cary was operated in normal modes with no special optical arrangement since all spectra were run at or below 320° and black-body effects are not considered significant below 500°.[44,46,47]

Reagents. Metals. Zirconium sponge obtained from the National Lead Co. had a hafnium content of 2.3% and (in ppm) Al 173, C 82, Cl 750, Cr 80, Cu 20, Fe 830, Mg 466, Mn 25, N 38, Pb 5, Si 70, Ti 20, O 785. Boron, cobalt, molybdenum, nickel, and vanadium were below the limits of detection. Zirconium powder (−325 mesh) obtained from Wah Chang, Albany, Oreg., had a hafnium content of only 0.018% and (in ppm) Al 25, C 80, Cr 100, Cu 25, Fe 570, Mg <10, Mn <10, N 412, Pb <5, Si 56, Ti <20, O 2100, Ta <200, Nb 500, B <0.2, Cd <0.3, Co <5, Mo <10, Ni 370, Sn <10, V <5, W <25, Zn <50, and H 105. Zirconium sponge used in the preparation of the tetrahalides had a hafnium content of 0.014%.

Aluminum metal (purified grade) as 8–20 mesh shot was obtained from J. T. Baker Chemical Co. High purity aluminum metal (99.999%) in lump form obtained from Research Organic/Inorganic Chemical Co. was used in certain syntheses. The aluminum powder was routinely washed with water, methanol, benzene, and sometimes trichloroethylene and thoroughly dried before use to remove possible contamination by organic species.

Metal Halides. Aluminum trichloride and zirconium tetrachloride were purified by sublimation of the commercial products.

Forty grams of aluminum trichloride was loaded with 1–3 g of aluminum metal in a 7 in. sublimation tube. After extensive degassing the tube was sealed and suspended vertically in a tube furnace and the temperature slowly raised to 230–250°. This temperature was held until the color associated with reducible impurities disappeared and no further accumulation of tarry carbonaceous products was observed. The furnace was then opened to allow solidification of the contents, after which the furnace was closed and the tube raised to allow sublimation. It was found that this procedure was far superior to distilling from the liquid melt. The process was re-

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(40) V. A. Uchtman and L. F. Dahl, *J. Amer. Chem. Soc.*, 91, 3756 (1969).

(41) For this space group the two Zr atoms are fixed in the special set 2b (0,0,0; 0,0,$^1/_2$), while the six halogen atoms were set to occupy the special set 6g (x,0,$^1/_4$; 0,x,$^1/_4$; $\bar{x}$,$\bar{x}$,$^1/_2$; $\bar{x}$,0,$^3/_4$; 0,$\bar{x}$,$^3/_4$; x,x,$^3/_4$).

(42) It is noteworthy that all three possible listed space groups demand that the metal and halogen layers of atoms be regularly spaced along the *c* lattice direction.[29]

(43) $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$ and $R_2 = [\Sigma w_i||F_o| - |F_c||^2/w_i|F_o|^2]^{1/2} \times 100$.

(44) B. R. Sundheim and J. Greenberg, *Rev. Sci. Instrum.*, 27, 703 (1956).

(45) D. M. Gruen and R. L. McBeth, *J. Inorg. Nucl. Chem.*, 9, 290 (1959).

(46) J. R. Morrey and E. E. Voiland, *Spectrochim. Acta*, 18, 1175 (1962).

(47) D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, 66, 57 (1962).

peated (*danger*, high internal pressures were often present during the first sublimation) until a colorless product and residue-free sublimate was obtained (three to six sublimations). Yields were typically 50–70%.

Forty grams of zirconium tetrachloride was loaded into an ampule, about 10 in. in length, which was thoroughly degassed and sealed. The tube was placed in a preheated tube furnace with the tetrachloride-containing end near the center of the furnace and the sealed-off end extending outside of the furnace. A temperature above 350 and below 400° was used because of the large difference in the vapor pressures of zirconium tetrachloride and iron(III) chloride in this range. The first sublimation usually yielded a considerable amount of nonsublimable residue and a sublimate which showed a concentrated yellow ring in the fore part of the sublimate. Extreme caution should be used in opening the tube owing to the possible presence of an internal pressure. The whitest fraction was removed and loaded into a second sublimation tube. The new tube was again extensively degassed before sealing. The whole tube was placed in the furnace at 400° for 24–48 hr, after which the tube was partly removed from the furnace and the product sublimed. Sublimations were continued until the product was pure white and residue-free sublimate was obtained. Yields were 40–60%.

Aluminum tribromide was prepared by direct reaction of the elements in a two-compartment tube equipped with a liquid bromine reservoir. The aluminum was loaded into the apparatus and displaced to the center of the longest ampule. Bromine, previously dried, was then thoroughly degassed and vacuum distilled into the reservoir. Typical amounts were 9.0 g of aluminum and 16 ml of bromine. The bromine was again degassed and the tube sealed off *in vacuo* with the bromine frozen. The bromine was kept frozen while the tube was placed in a furnace in a manner such that the metal was in the center of the furnace and the round end of the second collection ampule was exposed 2–3 in. beyond the furnace. After the metal reached 300°, the bromine was gradually warmed up to room temperature. The vapor pressure of the bromine was sufficient to maintain an adequate reaction rate. After the initial reaction, the product was sublimed back over the aluminum metal to ensure complete reaction. One further digestion of the product with high-purity aluminum at 260–280° followed by sublimation from a vertical position gave a residue-free sublimate. The rate of sublimation was slower than that for the chloride. The yield was 80–90%.

Zirconium tetrabromide was prepared in a manner analogous to the preparation of aluminum tribromide except that a temperature of 300–380° was used. Occasionally the bromine was condensed, product zirconium tetrabromide sublimed to the end of the tube, and the bromine brought back to room temperature. This process was repeated until the bromine was entirely consumed. Differential sublimation was continued until a residue-free colorless sublimate was obtained. The yield was about 90%.

Aluminum triiodide was prepared by the reaction of the elements with a procedure similar to that of Jolly[48] and Watt and Hall,[49] except that a sealed glass apparatus consisting of an iodine reservoir and three joined ampules was used so that the reaction and initial purification could be carried out in the same apparatus. To initiate the reaction, a small amount of iodine was flamed with a hand torch onto the metal and this area flamed until evidence for reaction was seen. It is imperative that *extreme caution* be taken to ensure that only a small amount of iodine be used to initiate the reaction. After initiation of the reaction all the iodine was sublimed into the section of the apparatus containing the remaining iodine and the reaction vessel placed in a tube furnace preheated to 350–420°, such that all of the section containing the metal and one-half of the third and empty section were in the heated zone. The rate of reaction was controlled by gradually increasing the temperature of a furnace around the iodine reservoir. After the iodine had been sublimed and reacted, the aluminum triiodide was transported to the largest end section which was then sealed. The entire tube was then suspended vertically in a 350–380° furnace and heated until the initial yellow color of the melt, due to traces of unreacted iodine, vanished. After completion of the reaction, the tube was raised in the furnace and the sublimation process carried out with the help of a cooling air stream. The digestion was repeated with a small amount of aluminum metal (0.3–0.5 g) until the melt was colorless and a colorless residue-free sublimate was obtained. Final yields were usually 90–95%.

Zirconium Tetraiodide. This compound was prepared by direct reaction of the elements[50] using a reaction tube with a separate iodine reservoir. This allowed better reaction rate control especially when large batches were prepared. The initial reaction product was resublimed over metal to ensure complete reaction of iodine and then sublimed into new tubes until a residue-free material was obtained. Yields averaged 90–95%.

Trihalides. Zirconium tetrahalide, aluminum trihalide, and 325 mesh zirconium or chips of high purity aluminum were loaded into a reaction ampule which was degassed and sealed. The ampule was placed in a tube furnace, brought up to temperature, and tilted 20° to the horizontal after the liquid phase had formed. After several hours incipient crystal growth is observed on the glass surface in the vicinity of the liquid meniscus; slow crystal growth is observed over the following several days. The furnace should be opened only infrequently, since upon cooling, the condensed vapor phase washes over the crystals resulting in some solution as observed by formation of the soluble blue species. When the crystals themselves show any evidence of decomposition to the brown powder, the reaction is terminated. To do this the angle of tilt is increased a few degrees to further separate the crystals and melt taking care not to jar the crystals into the melt. The end of the tube containing the melt is moved out of the furnace so that all condensables solidify leaving the crystals isolated. After recovering the crystals, the solids are ground up, placed in a new ampule, and the process repeated until no further growth is observed. First crop yields are low for the bromide, about 5%, but about 20% for the chloride and 30% for the iodide. The yields can be enhanced considerably by recycling.

Anal. Calcd for $ZrCl_3$: Zr, 46.17; Cl, 53.83. Found: Zr, 46.13; Cl, 53.78. Calcd for $ZrBr_3$: Zr, 27.57; Br, 72.43. Found: Zr, 27.48; Br, 72.49. Calcd for ZrI_3: Zr, 19.33; I, 80.67. Found: Zr, 19.20; I, 80.80.

Ternary Halides. The pure microcrystalline chloride compound can best be synthesized by decomposing zirconium trichloride in aluminum trichloride. To do this, an ampule containing a sintered glass frit is used. The zirconium(III) chloride is loaded into one side and the aluminum trichloride into the other. After evacuating and sealing, the aluminum trichloride is sublimed through the frit into the zirconium(III) chloride-containing side. The tube is placed horizontally in a tube furnace at 250° whereupon the disproportionation is initiated and completed during the course of several days. To recover the brown product the tube is partially removed from the furnace and the volatiles sublimed back through the frit leaving pure brown powder in the warmer zone of the reaction tube.

Alternatively, the brown powder produced in a normal reaction tube can be processed by sublimation to remove additional quantities of volatile aluminum trichloride and zirconium tetrachloride and finally sieved to remove any unreacted macro metal particles.

A final purification to remove the last traces of any aluminum trihalide not chemically bound is accomplished by placing a sample of the ternary halide in the arm of an inverted V tube containing a frit in one arm. After evacuation, purified dry benzene is transferred onto the sample by vacuum distillation. After freezing and degassing, the apparatus is sealed off. The sample may then be washed with benzene as often as seems desirable by decanting the liquid phase through the filter and then condensing it back on the sample *via* vapor phase transport. Analysis of a sample so washed gave the following. *Anal.* Calcd for Zr_2AlCl_7: Zr, 39.87, Al, 5.90, Cl, 54.23. Found: Zr, 40.7, Al, 5.75, Cl, 52.35.

Analytical Procedures. A sample of the reduced state compound (0.3 to 0.5 g) is loaded into a small push cap polyethylene vial in the inert atmosphere box. The vial is then tared, opened, and dropped immediately into a small beaker. Enough water is added to rinse the vial and dissolve the sample. In the case of the brown powder a very vigorous evolution of hydrogen gas occurs so losses *via* escape of mist must be avoided. Oxidation of the zirconium(III) samples is slower and it is advantageous to dissolve the sample in 1:1 nitric acid. After the solution has cleared, it is filtered through a tared sintered glass crucible, rinsed, and the vial and crucible dried and weighed. In the absence of aluminum, the solution is then made basic (pH 8) with ammonium hydroxide to precipitate the hydrous zirconium oxide; the precipitate is collected on filter paper, placed in a constant weight platinum crucible, dried at 110°, and ashed in a muffle furnace at 550°.

Zirconium and aluminum in the presence of each other were determined by atomic absorption, the details of which will be reported elsewhere. To the solution is added 7.0 g of anhydrous boric acid,[51] 7.5 ml of 40% aqueous hydrofluoric acid, and an amount

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(48) W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice Hall, Englewood Cliffs, N. J., 1960, pp 157-158.

(49) G. W. Watt and J. L. Hall, *Inorg. Syn.*, 4, 117 (1953).

(50) K. C. Eberly, *Inorg. Syn.*, 7, 52 (1963).

(51) B. Bernas, *Anal. Chem.*, 40, 1682 (1968).

of hydrochloric acid such that a total chloride concentration of 4% is achieved upon diluting to 250 ml. Both zirconium and aluminum are determined from this stock solution by comparing peak intensities with standard solutions which bracket the estimated unknown concentrations.

Halide concentrations were determined on the filtrates of the hydroxide precipitates by standard procedures.

The hafnium concentration in zirconium samples was determined by arc spectrographic analysis on oxide samples submitted to the National Spectrographic Laboratories, Cleveland, Ohio.

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Registry No. $\mathrm{ZrCl_3}$, 10241-03-9; $\mathrm{ZrBr_3}$, 24621-18-9; $\mathrm{ZrI_3}$, 13779-87-8; $\mathrm{(ZrCl_2)_2 \cdot AlCl_3}$, 39472-11-2; $\mathrm{Zr(Cl_2AlCl_2)_2(ClAlCl_3)_2}$, 43211-71-8; $\mathrm{Zr(Br_2AlBr_2)_2(BrAlBr_3)_2}$, 43211-72-9; $\mathrm{Zr(I_2AlI_2)_2(IAlI_3)_2}$, 43211-73-0; $\mathrm{(ZrBr_2)_2 \cdot AlBr_3}$, 39472-10-1; $\mathrm{ZrCl_4}$, 10026-11-6; $\mathrm{ZrBr_4}$, 13777-25-8; $\mathrm{ZrI_4}$, 13986-26-0; $\mathrm{AlCl_3}$, 7446-70-0; $\mathrm{AlBr_3}$, 7727-15-3; $\mathrm{AlI_3}$, 7784-23-8.

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2,4-, 2,6-, and 3,5-Lutidine Adducts of Zirconium(III) Chloride and Zirconium(IV) Chloride, Bromide, and Iodide

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Solid zirconium(III) chloride reacts with a benzene solution of lutidine (L) to form solid $\mathrm{ZrCl_3(3,5\text{-}L)_2}$ and $\mathrm{ZrCl_3(2,4\text{-}L)_{1.2-1.3}}$. It does not react with 2,6-lutidine. The small fraction of zirconium(III) in solution appears to undergo an oxidation-reduction reaction in the presence of excess lutidine. Zirconium(IV) chloride, bromide, and iodide react to form $\mathrm{ZrX_4(3,5\text{-}L)_2}$, $\mathrm{ZrX_4(2,4\text{-}L)_2}$, and $\mathrm{ZrX_4(2,6\text{-}L)}$. The product compositions of both the zirconium(III) and zirconium(IV) products are controlled by the steric effects of the methyl groups. A field dependent paramagnetism was observed for the zirconium(III) chloride adducts similar to that observed for the binary chloride itself.

Introduction

The chemistry of trivalent zirconium is relatively unexplored. Fowles and Wiley[2,3] have reported the preparation of $\mathrm{ZrX_3 \cdot 2py}$, $\mathrm{2ZrX_3 \cdot 5MeCN}$, $\mathrm{2ZrCl_3 \cdot 3L}$ (L = 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bipy)), $\mathrm{ZrBr_3 \cdot 2bipy}$, and $\mathrm{2ZrI_3 \cdot 3bipy}$ by direct reaction of zirconium(III) compounds with the ligand. Wasmund[4] reduced zirconium tetrachloride with sodium in pyridine to prepare the zirconium(III) pyridine adduct. By either route, the products possess unusual stoichiometries[2,3] or rather unsatisfactory[4] analyses suggesting that further work is necessary in the reduced state chemistry of zirconium.

Although a large variety of organic molecules possessing oxygen ligand atoms are known to form adducts with zirconium(IV) halides, oxygen-containing species did not seem to be the most suitable to study in view of the reducing properties of zirconium(III) and the strength of the zirconium(IV)-oxygen bond. Organic molecules containing nitrogen ligands appeared to be more desirable, especially those with reducing properties. As with the zirconium(III), there have been relatively few adducts prepared with zirconium(IV) halides and compounds with a nitrogen ligand atom. Diadducts, $\mathrm{ZrX_4L_2}$, are known for X = Cl and Br with the unidentate ligands MeCN and EtCN,[5-8] pyridine,[5,6,9] and pyrazine[10] and monoadducts, $\mathrm{ZrX_4L}$, with the bidentate ligands, 2,2'-bipyridyl and 1,10-phenanthroline.[5,9] A triadduct, $\mathrm{ZrCl_4(py)_3}$,[9] has also been reported. In this work the 2,4-, 2,6-, and 3,5- isomers of lutidine were used.

Discussion

The Tetrahalide Systems. With the exception of the 2,6-lutidine-zirconium tetrachloride and tetrabromide systems, the syntheses involve the reaction of solid zirconium tetrahalide suspended in benzene with a stoichiometric amount of dissolved ligand. In such a heterogeneous reaction system the reaction rates are slow and the incorporation of unreacted tetrahalide in the product is possible. However, the use of solvents in which the zirconium tetrahalides are soluble, such as acetonitrile and tetrahydrofuran, yields adducts, which, although isolable, are of erratic composition and colored. Some colored organic by-product is obtained even in the benzene systems if excess ligand is present. The amount of such by-product is small since the products obtained are identical, except for color, with those obtained using the stoichiometric amount of ligand, as shown by elemental analysis, X-ray diffraction patterns, and infrared spectra. Zirconium(IV) halides give 1:2 adducts with 2,4- and 3,5-lutidines but only the 1:1 adduct with 2,6-lutidine (Table I).

Except for the two cases cited, the lutidine adducts were recovered as the insoluble component of the reaction system. The insolubility of the products in benzene accounts for the high yields obtained. All the iodides evidenced some slight solubility as seen by the colored supernatant liquor; however,

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