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Hexafluoroacetylacetonates of Zirconium and Hafnium¹

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Zirconium tetrakis(hexafluoroacetylacetonate) and hafnium tetrakis(hexafluoroacetylacetonate) have been synthesized for possible use as precursor materials in the preparation of refractory oxides. A reasonably complete characterization of these two compounds has been obtained based on chemical analysis, differential thermal analysis, thermogravimetric analysis, infrared spectra, mass spectrometric analysis, proton and fluorine nuclear magnetic resonance, and gas chromatography. Results of the thermal decomposition of these two compounds to prepare refractory oxides are also reported.

Introduction

Metal β -diketonates are promising precursor materials for obtaining high-purity, fine-particle metal oxides with potential high-temperature applications for some of these oxides.² Recently several metal acetylacetonates have been thermally decomposed to yield metal oxides.³⁻⁷ This study was undertaken to determine the thermal decomposition characteristics of zirconium and hafnium hexafluoroacetylacetonates. The former has been reported in a note,⁸ however, neither the details of the method of preparation nor the results of chemical analysis were given, and the data⁸ reported could not be reproduced with the pure compound prepared in this investigation. In this paper the results of synthesis, characterization, and thermal decomposition of zirconium tetrakis(hexafluoroacetylacetonate), $Zr(hfa)_4$, and hafnium tetrakis(hexafluoroacetylacetonate), $Hf(hfa)_4$, are reported.

Experimental Section

Chemicals and General Experimental Conditions.—Spectrograde zirconium tetrachloride and hafnium tetrachloride used in the preparation of the corresponding complexes were obtained from Wah Chang Corp., Albany, Ore. Hexafluoroacetylacetonate [1,1,1,5,5,5-hexafluoro-2,4-pentanedione, abbreviated hereafter as Hhfa] from Peninsular ChemResearch, Gainesville, Fla., was used as received.

All operations involved in synthesis, purification, and subsequent handling of these complexes were carried out in an inert atmosphere and under anhydrous conditions. Where exposure to air was unavoidable, the time of exposure was no more than a few seconds. Reagent grade carbon tetrachloride dried over Linde Molecular Sieve 3A was used. Temperatures mentioned are all uncorrected. Immediately after purification of the compounds by vacuum sublimation melting points and infrared spectra were taken.

Zirconium Tetrakis(hexafluoroacetylacetonate), $Zr(hfa)_4$.—The zirconium compound was prepared by the reaction of zirconium tetrachloride [53 ppm of Hf; total impurity <630 ppm] and Hhfa in carbon tetrachloride. The reactants zirconium tetrachloride and Hhfa were mixed in the mole ratio of 1:4. After the hydrogen chloride evolution subsided, the mixture was refluxed for 0.5 hr and filtered. A white crystalline product (yield over 94%) was obtained from the filtrate by removing the solvent by vacuum distillation and simultaneous cooling. The crystalline product was purified by vacuum sublimation at room temperature and at a pressure of 0.03–0.02 mm. The final purified product, a colorless crystalline solid, when heated in a closed capillary tube containing nitrogen, melted completely at 39–42°, lit. mp⁸ 152–154°, to a clear colorless liquid. The melt on cooling to room temperature solidified immediately.

Hafnium Tetrakis(hexafluoroacetylacetonate), $Hf(hfa)_4$.—The hafnium compound was prepared in an identical manner in high yield using hafnium tetrachloride [165 ppm of Zr; total impurity <758 ppm]. The sublimed product, also a colorless crystalline solid, when heated in a closed capillary tube containing nitrogen started to change its appearance somewhat at 40°. This was followed by softening and finally complete melting at 47.5–49.5° to a clear, colorless liquid. The melt on cooling to room temperature solidified immediately.

Chemical Analyses and Molecular Weight.—Chemical analyses (and determination of molecular weight of the sublimed Zr compound by vapor pressure osmometry) were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Chlorine analysis for the Zr compound was done by the Ethyl Corp., Detroit, Michigan.

Infrared Spectra.—Spectra were taken with a Perkin-Elmer 521 grating infrared spectrophotometer in Nujol and in Fluorolube oil LG 160 (Fisher Scientific Co.) mulls between sodium chloride and potassium iodide (or cesium iodide) plates. Mulls were prepared and transferred to the plates in a drybox. The instrument was purged with dry helium before and during the time the spectra were recorded.

Differential Thermal Analysis and Thermogravimetric Analysis.—Dta and tga curves for the compounds were obtained from Monsanto Research Corp., Dayton, Ohio.

Mass Spectrometric Analysis.—Mass spectrometric analyses were performed by Mellon Institute, Pittsburgh, Pa. Spectra were taken on an Associated Electrical Industries MS-9 double-focusing high-resolution mass spectrometer using ionizing voltages of 10 (or 12) and 70 eV at temperatures of 130–170°. Perfluorokerosene and perfluorotributylamine were used as references. Samples were loaded directly on to the probe and immediately inserted into the source vacuum lock. For the Hf compound, the peaks from m/e 801 down were measured against the m/e 614 peak of perfluorotributylamine. All other measurements were made against the m/e 801 peak itself assuming that it was the $(C_8HF_8O_2)_3Hf^+$ peak with the calculated m/e of 800.9112. This double-measurement technique can result in double errors, such errors lying in the range of ± 20 ppm.

Nuclear Magnetic Resonance Spectra.—Proton nmr spectra

(1) Presented in part at the International Symposium on Decomposition of Organometallic Compounds to Refractory Ceramics, Metals and Metal Alloys, Nov. 28, 1967, Dayton, Ohio.

(2) K. S. Mazdiyasn, C. T. Lynch, and J. S. Smith, II, *J. Am. Ceram. Soc.*, **50**, 532 (1967).

(3) C. F. Powell, "Vapor Deposition," C. F. Powell, J. H. Oxley, and J. M. Blocher, Jr., Ed., John Wiley & Sons, Inc., New York, N. Y., 1966, pp 389–390.

(4) J. M. Mochel, U. S. Patent 3,202,054 (Aug 24, 1965).

(5) L. A. Ryabova, E. A. Gerasimova, and Ya. S. Savitskaya, *Zh. Prikl. Khim.*, **38**, 1862 (1965); *J. Appl. Chem. USSR*, **38**, 1815 (1965).

(6) L. A. Ryabova, Ya. S. Savitskaya, and R. N. Sheftal, *Zh. Prikl. Khim.*, **38**, 1863 (1965); *J. Appl. Chem. USSR*, **38**, 1817 (1965).

(7) J. A. Papke, *et al.*, Report ML-TDR-64-206, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433, Feb 1967, part III, p 30.

(8) M. L. Morris, R. W. Moshier, and R. E. Sievers, *Inorg. Chem.*, **2**, 411 (1963).

were measured in concentrated solution in carbon tetrachloride at 60 Mc at the ambient probe temperature of 37° on a Varian Associates Model A-60 spectrometer using tetramethylsilane as the internal standard. The foregoing solutions were also used for the fluorine nmr spectra. Fluorine-19 spectra were obtained from Monsanto Research Corp., Dayton, Ohio. Spectra were recorded at 25° on a Varian Associates Model V-4300-2 dual-purpose spectrometer operating at a frequency of 40.0 Mc and field strength of approximately 9986 G. Trifluoroacetic acid was used as an external reference. After the fluorine spectra were taken, proton nmr measurements were repeated 1 week after initial proton nmr on these solutions. No change in position and intensity of the proton peaks was observed.

Gas Chromatography.—A Hewlett-Packard (F & M) Model 5754 gas chromatograph (with dual column, dual thermal conductivity detector) was used. Experimental conditions were: 1 ft × 0.25 in. (o.d.) Teflon tubing containing 5% Apiezon L on Gas-Pack F (60–80 mesh); temperatures for injection port, column, and T.C. detector, 110, 70, and 108°, respectively; He flow, 60 ml/min; solvent, carbon tetrachloride; sample size, 5 μl; a millivolt recorder with attenuation, ×1; chart speed, 0.5 in./min. For identification, the eluates under the peaks corresponding to the sublimed compounds were separately trapped in capillary tubes. The white crystalline eluates could not be completely melted at the melting temperatures of the original sublimed compounds. Such behavior may be due to slight hydrolysis of the eluates during brief exposure to air before the capillary tubes were sealed and/or partial thermal decomposition during sealing. Retention times of the chelates were fairly reproducible, but some variation, particularly with change of sample size, was observed. The glass insert in the injection port was examined after the completion of the experiments; trace amounts of white residue were found. The residue could result from a nonvolatile impurity.

Thermal Decomposition.—The apparatus was a modified Sargent Micro Combustion Apparatus into which a Vycor brand glass tube 91 cm long (9-mm i.d.) was inserted. Through the glass tube dry, prepurified nitrogen was passed at a rate of 13 ml/min. A porcelain boat containing 50–70 mg of the sublimed chelate was then introduced. The chelate was volatilized on heating to about 100° by means of a heating tape wrapped around the glass tube. The chelate vapor passed through an intermediate hot zone at 178° and then into the decomposition zone where temperatures of 600° for the Zr compound and 500° for the Hf compound were maintained. With each sample, the experiment was allowed to run continuously for a period of 18 hr. The apparatus was allowed to cool to room temperature. Both the Zr chelate and the Hf chelate gave black, gray, and white deposits in that order, extending over a length of about 4 cm, the black deposits appearing at the start of the decomposition zone.

Results and Discussion

Trends in Melting Points of β-Diketonates.—In Table I melting points of a number of anhydrous metal β-diketonates are listed. It is readily apparent that the melting points observed in this investigation for the sublimed zirconium and hafnium chelates are in the expected range and are consistent with the trend that the hfa chelate of a particular metal has the lowest melting point in the chelate series: acac, tfa, hfa.

The freshly sublimed products of zirconium and hafnium chelates were colorless and somewhat transparent. On standing, both of the compounds slowly and partly turned (Hf compound more slowly) to white, opaque, and more finely divided crystals; the change was more rapid and readily apparent on their being exposed to air. With air exposure the range of melting became wider and higher for both compounds, and the melts solidi-

TABLE I
MELTING POINTS (°C) OF SOME
METAL β-DIKETONATES^a

Metal ion	acac ^b	tfa ^c	hfa
Al(III)	198	117 121–122 (<i>trans</i>)	73–74
Cr(III)	214 216	112–114 (<i>cis</i>) 154.5–155.0 (<i>trans</i>)	84–85
Fe(III)	181.3	114 (<i>trans</i>)	49
Rh(III)	260	148.5–149.0 (<i>cis</i>) 189.5–190 (<i>trans</i>)	114–115
U(IV)	176–177 dec	142–144	90
Zr(IV)	194–195	128–130	152–154 ^d 39–42 ^e
Hf(IV)	193–195 dec	125–128	47.5–49.5 ^e

^a R. W. Moshier and R. E. Sievers, "Gas Chromatography of Metal Chelates," Pergamon Press Inc., Long Island City, N. Y., 1965, pp 138–153, and references cited therein. ^b Anion of 2,4-pentanedione. ^c Anion of 1,1,1-trifluoro-2,4-pentanedione. ^d Reference 8. ^e This work.

fied very slowly on cooling to room temperature [unlike sublimed compounds]. For the Zr compound with a series of samples of increasing air exposure, complete or partial melting was observed at temperatures in the ranges 39–45, 70–85, and 142–160° (lit.⁸ mp 152–154°). Both of the sublimed compounds were found to lose weight when exposed to air and each had an odor resembling that of the free ligand, Hhfa. The air-exposed materials on vacuum sublimation at room temperature left residues much less volatile. The Zr chelate, after exposure to air several times for brief periods and after being allowed to stand in a stoppered vial for 6 months, could not be sublimed under vacuum (0.03–0.02 mm) at room temperature even in 24 hr.

Analytical results of the sublimed compounds and the corresponding materials after air exposure for several days have been obtained. The data on air-exposed materials are included to demonstrate that they are significantly different from those of the pure sublimed compounds.

Chemical Analysis.—The results of chemical analysis are shown in Table II. Chlorine was not found in the zirconium and hafnium chelates. With the exception of the fluorine analysis, the results for the sublimed compounds are close to the values calculated for the tetrakis chelates. Accuracy of fluorine analyses for compounds containing more than 40% fluorine is generally poor.⁹ The experimental data (particularly on metal analysis) for the air-exposed compounds are significantly different from those of the sublimed compounds; they are in reasonable agreement with the decrease of carbon and fluorine and increase of hydrogen and metal content expected for the monohydroxy complexes. The data for metal analysis are surprisingly close to those calculated for the monohydroxy complexes. No attempt was made in this study, however, to isolate the monohydroxy complexes. The values calculated for the zirconyl complex, one of the possible products of hydrolysis of the tetrakis chelate of zir-

(9) P. M. Maslona and P. M. Visotsky, Report AFML-TR-65-389, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433, Jan 1966.

TABLE II
ELEMENTAL ANALYSES OF HEXAFLUOROACETYLACETONATES
OF ZIRCONIUM AND HAFNIUM

	% car- bon	% hydro- gen	% fluo- rine	% metal
Calcd for $Zr(C_6HF_7O_2)_4$	26.13	0.44	49.59	9.92
Found for Zr compd sublimed ^a	25.61	0.39	46.65	10.19
	25.31	0.35	46.50	10.24
Found for Zr compd air exposed	25.09	0.67	44.23	12.75
	24.90	0.61	43.97	12.51
Calcd for $Zr(C_6HF_7O_2)_3(OH)$	24.70	0.55	46.89	12.51
Calcd for $ZrO(C_6HF_7O_2)_2$	23.04	0.39	43.73	17.50
Calcd for $Hf(C_6HF_7O_2)_4$	23.86	0.40	45.29	17.73
Found for Hf compd sublimed ^b	23.41	0.78	44.72	18.47
	23.47	0.63	44.68	18.29
Found for Hf compd air exposed	23.42	0.67	42.98	21.49
	23.18	0.71	42.90	21.59
Calcd for $Hf(C_6HF_7O_2)_3(OH)$	22.06	0.49	41.88	21.86

^a Analysis for chlorine showed none present in the compound before sublimation. ^b Analysis for chlorine showed none present.

conium, are included for comparison; they indicate very little agreement with experimental data.

Infrared Spectra.—The spectrum of sublimed $Zr(hfa)_4$ is shown in Figure 1. The positions of absorption peaks for this compound, the sublimed Hf chelate, and the corresponding air-exposed compounds are listed in Table III. Except where noted, the band

limed chelates. These peaks and their assignments are only discussed here; assignments of other bands can be made by following published work.^{8,10-12} Bands in the region $3676-3636\text{ cm}^{-1}$ are assigned to OH stretch. The peaks at 3637 (s) and 3647 (m) cm^{-1} are very sharp; the position and sharpness of these peaks may indicate the presence of one or more free hydroxyl¹³ groups. Slight hydrolysis of the sublimed Zr chelate is indicated by the presence of the extremely weak band at 3636 cm^{-1} . In the spectrum of the air-exposed Hf chelate the medium-intensity peaks at 3676 cm^{-1} , which is a little broader than the one at 3647 cm^{-1} , may be due to hydration. The peaks at 833 (sp) and 862 cm^{-1} (broader than the 833-cm^{-1} peak) may be tentatively assigned to metal-O-H bending.¹³ For the air-exposed Zr compound the peak at 833 cm^{-1} and another at $3637-3636\text{ cm}^{-1}$ were found to increase in intensity with increasing air exposure. Ir absorption bands in the region $1650-659\text{ cm}^{-1}$ have been reported⁸ for $Zr(hfa)_4$. All of those bands⁸ including one at 832 cm^{-1} are in good agreement with those in the spectrum obtained here for air-exposed and impure $Zr(hfa)_4$.

Differential Thermal Analysis.—The dta curves are shown in Figure 2. In the curve for the sublimed

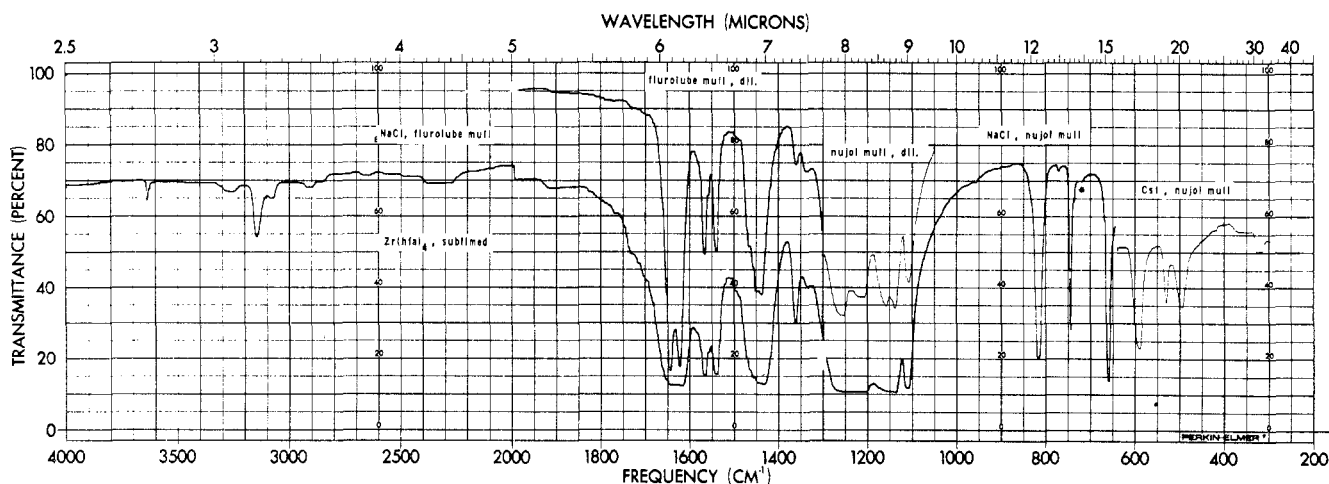


Figure 1.—Infrared spectrum of $Zr(hfa)_4$ sublimed.

TABLE III

INFRARED ABSORPTION^a OF HEXAFLUOROACETYLACETONATES OF ZIRCONIUM AND HAFNIUM IN THE REGION $4000-400\text{ cm}^{-1}$

$Zr(hfa)_4$ sublimed	(3636)		3262	3146	3078	1644	1623	1567	1541	1439	1362			
$Zr(hfa)_4$ air exposed	3637		3284	3144	3080	1653	1624	1565	1540	1475	1358			
$Hf(hfa)_4$ sublimed			3270	3150	3085	1646	1623	1569	1542	1444	1363			
$Hf(hfa)_4$ air exposed	3676	3647	(3430)	(3290)	3148	(3080)	1654	1623	1565	1540	1487	1361		
$Zr(hfa)_4$ sublimed	1257	1214	1157	1138	1108		817	745	660	592	531	495		
$Zr(hfa)_4$ air exposed	1255	1214	1156	1142	1112		833	814	744	658	600	534	498	475 sh
$Hf(hfa)_4$ sublimed	1261	1211	1158	1138	1110		814	742	656	593	530	495		
$Hf(hfa)_4$ air exposed	1256	1220	1155	1142	1112		862	810	743	657	597	532	484	456 sh

^a Extremely weak and questionable bands are enclosed in parentheses; sh, shoulder.

shapes and intensities in all four spectra are similar. In particular the spectra of the two sublimed chelates are very similar and so are those of the two air-exposed compounds. The important distinguishing feature is the presence of peaks in the regions $3676-3636$ and $862-833\text{ cm}^{-1}$ in the spectra of air-exposed compounds and the absence of these bands in the spectra of pure sub-

Zr compound there is an endothermic peak and a shoulder at 39 and 42.5° , respectively. The sublimed Hf compound gives two separate endothermic peaks at

(10) S. C. Chatteraj and R. E. Sievers, *Inorg. Chem.*, **6**, 408 (1967).

(11) H. Ogoshi and K. Nakamoto, *J. Chem. Phys.*, **45**, 3113 (1966).

(12) K. Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963.

(13) Reference 12, pp 73-76.

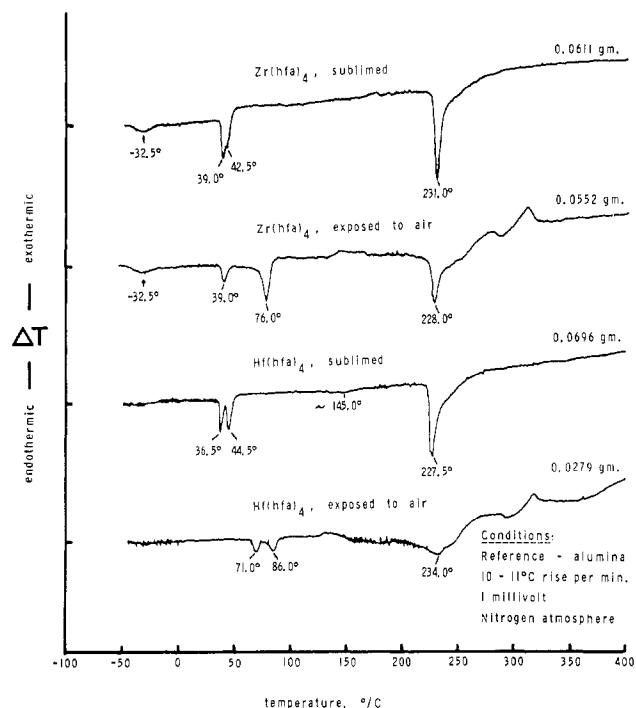


Figure 2.—Differential thermal analysis.

36.5 and 44.5°. The shoulder and the peaks, all observed in the range of melting, suggest that these compounds are dimorphic. Although only one¹⁴ crystalline modification of zirconium tetrakis(acetylacetonate) has been observed, tetrakis(acetylacetonates) of cerium, thorium, and uranium are reported to be dimorphic.¹⁴ The peaks at 231.0 and 227.5° in the curves for the sublimed Zr and Hf chelates, respectively, indicate the probable respective boiling points of these compounds. In the curves for the air-exposed compounds the peaks at 76.0, 71, and 86.0° are consistent with the wider and higher range of melting previously observed with these compounds.

Thermogravimetric Analysis.—The results of thermogravimetric analysis are shown in Figure 3. The sublimed zirconium and hafnium compounds gave almost identical curves (only one complete curve for the Zr compound is shown) through the sharp break at about 146–147° indicating that the two sublimed compounds have the same volatility. This break (weight loss of 97–98% for the sublimed compounds) gives an indication of partial decomposition at very low temperatures. This might be expected since several of the metal acetylacetonates are known to decompose¹⁵ partially within the temperature range of 150–400°. The first portions of the curves for the air-exposed materials show decreased volatility as expected; the first inflection appears in these curves at about the same temperature region as before but corresponding to a much lower weight loss.

Molecular Weights.—Determination of molecular weight in air by vapor pressure osmometry proved to be unsuitable for these moisture-sensitive compounds.

(14) D. Grdenić and B. Matković, *Acta Cryst.*, **12**, 817 (1959).

(15) J. V. Hoene, R. G. Charles, and W. M. Hickam, *J. Phys. Chem.*, **62** 1098 (1958).

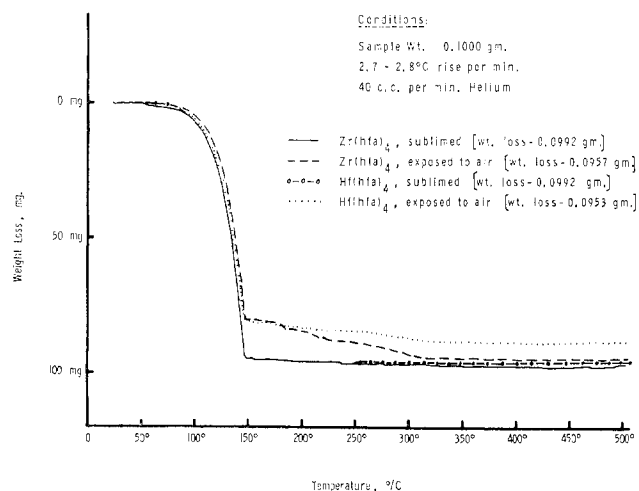


Figure 3.—Thermogravimetric analysis.

Experiments conducted in air with the sublimed Zr compound in carbon tetrachloride yielded abnormally low values (282, 292; calcd for the monomer, 919.5) because of hydrolysis.

Mass Spectrometric Analysis.—A list of the significant peaks observed in the mass spectra (70 eV) along with their assignments is given in Table IV. Weak

TABLE IV
MASS SPECTROMETRIC ANALYSIS OF
HEXAFLUOROACETYLACETONATES OF ZIRCONIUM AND HAFNIUM

Measd m/e^a	Identity	Calcd m/e
917.8527 w	Zr ⁹⁰ C ₂₀ H ₄ F ₂₄ O ₈	917.8570 ^b
898.8554 m	Zr ⁹⁰ C ₂₀ H ₄ F ₂₃ O ₈	898.8586
729.8678 w	Zr ⁹⁰ C ₁₅ H ₃ F ₁₉ O ₆	729.8674
710.8711 vs	Zr ⁹⁰ C ₁₅ H ₃ F ₁₈ O ₆	710.8689
1007.8803 w	Hf ¹⁸⁰ C ₂₀ H ₄ F ₂₄ O ₈	1007.8993 ^b
1006.8871	Hf ¹⁷⁹ C ₂₀ H ₄ F ₂₄ O ₈	1006.8986 ^b
1005.8780	Hf ¹⁷⁸ C ₂₀ H ₄ F ₂₄ O ₈	1005.8965 ^b
988.8843 m	Hf ¹⁸⁰ C ₂₀ H ₄ F ₂₃ O ₈	988.9009
818.9093 w	Hf ¹⁷⁹ C ₁₅ H ₃ F ₁₉ O ₆	818.9089
817.9049	Hf ¹⁷⁸ C ₁₅ H ₃ F ₁₉ O ₆	817.9068
800.9072 vs	Hf ¹⁸⁰ C ₁₅ H ₃ F ₁₈ O ₆	800.9112
799.9058	Hf ¹⁷⁹ C ₁₅ H ₃ F ₁₈ O ₆	799.9105
798.9026	Hf ¹⁷⁸ C ₁₅ H ₃ F ₁₈ O ₆	798.9084
797.9043	Hf ¹⁷⁷ C ₁₅ H ₃ F ₁₈ O ₆	797.9079
797.9017	Hf ¹⁷⁶ C ₁₅ H ₃ F ₁₈ O ₆	796.9060

^a Approximate intensities of peaks are indicated by the symbols: w, weak; m, medium; s, strong; v, very. ^b Parent peak.

parent peaks observed in the spectra establish that in the vapor phase these compounds are, indeed, the monomeric tetrakis chelates. Compared to the background, no significant increase in intensity of the peaks at m/e 17 and 18 corresponding to OH and H₂O, respectively, was observed in the spectra. This observation lends further support to the conclusion from infrared data that the sublimed compounds are anhydrous. Peaks at m/e 710.87 for the zirconium compound and at m/e 800.91 for the hafnium compound are very strong; they correspond to the loss of one hexafluoroacetylacetonate ligand radical from the parent compounds. Similar loss of β -diketonate ligand radi-

cals has been reported previously.¹⁶ Two interesting new types of species have been observed in this study. The first one (m/e 898.86 for the Zr compound and m/e 988.88 for the Hf compound) corresponds to loss of one fluorine from the parent tetrakis-chelated species. The second [m/e 729.87 for the Zr compound and m/e 819.91 (not shown in Table III), 818.91, and 817.91 for the Hf compound] corresponds to the addition of one fluorine to the tris-chelated species.

Nuclear Magnetic Resonance Spectra.—Proton and fluorine nmr peaks of the sublimed compounds are listed in Table V. The proton peaks are sharp and

TABLE V
PROTON AND FLUORINE MAGNETIC
RESONANCE CHEMICAL SHIFTS

Compd	CH proton chem shift, δ , ppm	Fluorine chem shift, δ , ppm	Rel fluorine peak area
Zr(hfa) ₄	-6.56	-1.96 -1.56	25 1
Hf(hfa) ₄	-6.54	-1.83 -1.41	40 1
Hhfa	-6.43 ^a -6.36 ^b	-1.87 ^c	

^a Reference 17 (10% by weight in CCl₄). Reference 18 (pure liquid). ^b Reference 19 (0.3 M in CCl₄). ^c Reference 19 (0.35 M in CCl₄).

appear in the neighborhood of CH proton peaks observed for the free ligand Hhfa¹⁷⁻¹⁹ and some of its metal chelates.^{10,20,21} It is of interest to note that fluorine peaks for Hhfa and these Zr and Hf chelates are considerably moved upfield from the peaks (-5.46, -5.42, -5.27 ppm) observed for rhodium-hfa chelates.¹⁰ Because of their very high relative peak area, the single sharp major fluorine peaks are certainly due to the tetrakis chelates. The very small minor single fluorine peaks probably originate from unidentified impurities, possibly hydrolysis products. Thus, a single proton peak and a single fluorine peak observed for each of these compounds are explained on the basis of rapid environmental averaging, a process found to occur

(16) S. J. Lippard, *J. Am. Chem. Soc.*, **88**, 4300 (1966), and references cited therein.

(17) R. L. Lintvedt and H. F. Holtzclaw, *ibid.*, **88**, 2713 (1966).

(18) J. L. Burdett and M. T. Rogers, *ibid.*, **86**, 2105 (1964).

(19) G. Fukanic, N. C. Li, W. S. Brey, and G. B. Savitsky, *J. Phys. Chem.*, **70**, 2899 (1966).

(20) S. C. Chatteraj, A. G. Cupka, Jr., and R. E. Sievers, *J. Inorg. Nucl. Chem.*, **28**, 1937 (1966).

(21) F. A. Cotton, P. Legzdins, and S. J. Lippard, *J. Chem. Phys.*, **45**, 3461 (1966).

with other eight-coordinate β -diketonate complexes.²¹⁻²³ It should be mentioned that the existence of geometrical isomers cannot be ruled out on the basis of the nmr data.

Gas Chromatography.—Under the experimental conditions the sublimed Zr and Hf compounds, in a duplicate run, gave single moderately sharp peaks with average retention times of 2 min 7 sec and 3 min 4 sec, respectively. A mixture of these two compounds, however, gave only a single peak with an average retention time of 2 min 20 sec, indicating that the Zr and Hf chelates cannot be separated under these conditions.

Thermal Decomposition.—The black and white deposits resulting from the decomposition of the Zr and Hf chelates were identified to be monoclinic ZrO₂ and HfO₂, respectively, by examination of the X-ray diffraction patterns of the powdered deposits. The black color may be caused by small amounts of amorphous carbon or oxygen deficiency²⁴ in these dioxides. The white deposit from the Zr chelate also contained a few colorless transparent thin flakes of a material. These flakes on examination by electron diffraction were identified to be also monoclinic ZrO₂. Further investigations regarding the nature, purity, and optimum conditions for the formations of these black, white, and transparent dioxide deposits are in progress.

Conclusions

Zr(hfa)₄ and Hf(hfa)₄ are volatile, moisture-sensitive compounds with mp 39-42 and 47.5-49.5° and bp 231 and 227.5°, respectively. Chemical, infrared, and mass spectrometric analyses show that the pure compounds are anhydrous. Mass spectra also show that they are monomeric. The limited nmr data are consistent with rapid environmental averaging in solution. Dta suggests they are dimorphic. Tga data show that they have the same volatility. Each compound gives a single peak when injected separately in a gas chromatograph. The compounds undergo partial decomposition at 146-147° as tga data indicate. At 500-600° they both decompose to form monoclinic dioxides.

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(22) A. C. Adams and E. M. Larsen, *Inorg. Chem.*, **5**, 228 (1966).

(23) T. J. Pinnavaia and R. C. Fay, *ibid.*, **5**, 233 (1966).

(24) R. Ruh, *J. Am. Ceram. Soc.*, **46**, 301 (1963).