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Preparation and Properties of Some Six- and Seven-Coordinate Halo(acetylacetonato) Complexes of Zirconium(IV) and Hafnium(IV)[1]

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Reported herein is the preparation and characterization of dihalobis(acetylacetonato) and halotris(acetylacetonato) complexes of zirconium(IV) and hafnium(IV), $M(acac)_2X_2$ (X = Cl or Br) and $M(acac)_3X$ (X = Cl, Br, or, when M = Zr, I). The zirconium and hafnium compounds containing the same halogen are isomorphous. The dihalides are monomeric weak electrolytes in solution; nmr chemical shifts suggest that these complexes exist as *cis* geometrical isomers. The monohalides are monomeric seven-coordinate complexes which are only very slightly dissociated in ionizing solvents when X = Cl or Br, but which are appreciably dissociated when X = I. The dissociated species of the monoiodide are markedly stabilized by tetrahydrofuran. Nmr spectra indicate that chelate rings in the halo and dihalo complexes undergo rapid configurational rearrangements; time-averaged spectra were observed even at temperatures as low as −130°. Proton chemical shifts are reported and discussed in terms of the intramolecular electric field of the complexes and dipole–induced dipole interactions between the complexes and the solvent.

Introduction

Although β-diketonate (dik) complexes are known for every nonradioactive element possessing metallic character,[2] zirconium is unique in that it is the only element which has been reported to form β-diketonates in which the metal may exhibit coordination numbers of six, seven, and eight. The known zirconium compounds are of the types $Zr(dik)_2Cl_2$,[3-6] $Zr(dik)_3Cl$,[7,8] and $Zr(dik)_4$.[6,8-10] The only zirconium diketonates reported containing halogen atoms other than chlorine are the dibenzoylmethanates $Zr(bzbz)_3Br$ and $Zr(bzbz)_3I$.[8] Hafnium is expected to form an analogous series of compounds, and indeed $Hf(dik)_3Cl$[8,11] and $Hf(dik)_4$[8,12,13] have been reported; however, a pure dihalobis(β-diketonato)hafnium compound has not yet been isolated.[11]

With the exception of the tetrakisacetylacetonates,[14] little is known concerning the constitution and stereochemistry of zirconium and hafnium diketonates. The dichlorides, $Zr(dik)_2Cl_2$, have generally been assumed to contain six-coordinated zirconium atoms;[10] however, the situation for the monohalides is considerably more confused. In the earlier literature[4,7,10] the monochlorides were formulated, on the basis of chemical properties, as ionic salts, $[Zr(dik)_3]^+Cl^-$, containing six-coordinated zirconium. More recently, Wolf and Tröltzsch have stated that infrared spectra of $Zr(bzbz)_3X$ (X = Cl, Br, or I) point to six-coordinated zirconium; however, conductivity data for the chloride and bromide suggest coordination number seven.[8] During the present investigation, two additional papers have appeared. Cox, Lewis, and Nyholm[11] have reported molecular weight data (in nitrobenzene) and conductance data (in nitromethane) for several monochlorides of zirconium and hafnium, including the acetylacetonates, $M(acac)_3Cl$; their data indicate seven-coordination. On the other hand, Doron, Belitz, and Kirschner[15] have cited molecular weight and conductance results for $Zr(acac)_3Cl$ (in benzene and butanone), which support the six-coordinated $[Zr(acac)_3]Cl$ structure.

In this paper we describe the preparation and detailed characterization of dihalobis(acetylacetonato) and halotris(acetylacetonato) complexes of zirconium and hafnium, where the halogen is chlorine, bromine, and, in one case, iodine. The bromo and iodo compounds have not been reported previously. Our results indicate seven-coordination for the monohalides and are consistent with a *cis*-octahedral configuration for the dihalides.

Experimental Section

Reagents and General Techniques.—Anhydrous zirconium(IV) chloride (99.8+%, Chemicals Procurement Laboratories, Inc.), zirconium metal powder (Alfa Inorganics, Inc.), and anhydrous hafnium(IV) chloride and −60 mesh hafnium metal powder (spectroscopic grade, <200 ppm zirconium, Wah Chang Corp.) were used as purchased without further purification. Zirconium(IV) bromide and hafnium(IV) bromide were synthesized from the elements using apparatus described by Young and Fletcher.[16] Zirconium(IV) iodide was prepared from the elements by the method of Lowry and Fay.[17] Acetylacetone (Matheson Coleman and Bell) was freshly distilled before use; the proton nmr spectrum was checked to ensure absence of impurities.

All solvents were reagent grade. Benzene, hexane, carbon

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tetrachloride, dichloromethane, 1,1,2-trichloroethene, and 3-chloropropene were dried by distillation from calcium hydride. Ethyl ether, isopropyl ether, and tetrahydrofuran were freshly distilled under dry nitrogen from lithium aluminum hydride and subsequently handled under dry nitrogen in a glove bag. Chloroform was freed of ethanol by treatment with activated alumina. 1,2-Dichloroethane was washed with a saturated solution of sodium carbonate, dried over molecular sieves, and distilled from P_4O_{10}. Nitrobenzene was purified as previously described.[18]

Since the halo and dihalo complexes are readily hydrolyzed, all operations involved in syntheses, purification, and subsequent handling of these compounds were conducted under anhydrous conditions. During preparations, a stream of dry nitrogen was passed through the reaction mixture. Filtrations were carried out using a specially designed glass-frit Büchner funnel similar to that described by Holah.[19] Recrystallizations were performed in a glass-stoppered erlenmeyer flask fitted with a side arm and stopcock. During crystallizations, solutions were kept out of contact with moist air, while being heated, by passing dry nitrogen into the side arm and over the surface of the solution. All glassware was dried at 180° and was cooled, whenever possible, in a calcium sulfate desiccator.

Dichlorobis(2,4-pentanedionato)zirconium(IV).—Acetylacetone (23.3 ml, 227 mmol) was added dropwise to a slurry of anhydrous zirconium(IV) chloride (9.35 g, 40.1 mmol) in 400 ml of refluxing ether. After allowing the reaction mixture to reflux for 12 hr, the white precipitate which had formed was filtered, washed with two 50-ml portions of ether, and then with two 50-ml portions of hexane. The yield of crude product after drying *in vacuo* at 80° for 3 hr was 8.70 g (60%). The product was recrystallized twice from benzene–hexane and obtained as colorless, prismatic crystals. The crystals were dried *in vacuo* at 80° for 0.5 hr; mp 180.5–182°, lit.[11] 233–235°. *Anal.* Calcd for $Zr(C_5H_7O_2)_2Cl_2$: C, 33.33; H, 3.92; Cl, 19.68; Zr, 25.11. Found: C, 33.12; H, 3.88; Cl, 19.64; Zr, 25.54.

Dichlorobis(2,4-pentanedionato)hafnium(IV).—This compound was prepared and purified by the same method as that used for the zirconium analog except that a 24-hr reaction time was required to ensure complete reaction, mp 186–188°. *Anal.* Calcd for $Hf(C_5H_7O_2)_2Cl_2$: C, 26.83; H, 3.15; Cl, 15.84; Hf, 39.88. Found: C, 26.74; H, 3.07; Cl, 15.89; Hf, 40.12.

Dibromobis(2,4-pentanedionato)zirconium(IV).—Acetylacetone (16.2 ml, 158 mmol) in 160 ml of ether was added dropwise to a slurry of zirconium(IV) bromide (21.6 g, 52.6 mmol) in 500 ml of ether at room temperature. After a 24-hr reaction time, the precipitate was filtered, washed with two 100-ml portions of hexane, and dried *in vacuo* at room temperature; yield, 17.7 g (75%). The crude product was recrystallized twice from benzene–hexane and obtained as bone white, prismatic crystals which were dried at 80° for 0.5 hr. Very pale yellow crystals were obtained if prolonged heating during the recrystallizations was not avoided or if the crystals were not removed from the mother liquor soon after crystallization; mp 185–186.5°. *Anal.* Calcd for $Zr(C_5H_7O_2)_2Br_2$: C, 26.74; H, 3.14; Br, 35.57; Zr, 20.30. Found: C, 26.91; H, 2.96; Br, 35.46; Zr, 20.54.

Dibromobis(2,4-pentanedionato)hafnium(IV).—This compound was prepared and purified by the same procedure as that described for the corresponding zirconium complex except that the reaction time was 32 hr; mp 190–192°. *Anal.* Calcd for $Hf(C_5H_7O_2)_2Br_2$: C, 22.39; H, 2.63; Br, 29.79; Hf, 33.27. Found: C, 22.24; H, 2.87; Br, 29.66; Hf, 33.29.

Chlorotris(2,4-pentanedionato)zirconium(IV).—Acetylacetone (13.0 ml, 127 mmol) was slowly added to a slurry of anhydrous zirconium(IV) chloride (9.00 g, 38.6 mmol) in 100 ml of refluxing benzene. After a 4-hr reaction time the product was recovered from the clear, pale yellow solution by boiling off some benzene, adding hot hexane until turbidity appeared, and cooling. The yield of crude product after drying *in vacuo* at room temperature was 15.6 g (95%). After two recrystallizations from benzene–hexane the compound was obtained as colorless, prismatic crystals which were dried *in vacuo* at 80° for 0.5 hr; mp 159.5–161°, lit. 101–102°,[7] 132–134°,[11] 143–148°,[15] 156–158°.[6,10] *Anal.* Calcd for $Zr(C_5H_7O_2)_3Cl$: C, 42.49; H, 4.99; Cl, 8.36; Zr, 21.51. Found: C, 42.26; H, 5.00; Cl, 8.36; Zr, 21.82.

This compound was also obtained unexpectedly in 26% yield upon reaction of acetylacetone and anhydrous zirconium(IV) iodide (1:3 mole ratio) in refluxing carbon tetrachloride; mp 156–158°. The product gave a positive qualitative test for chloride and a negative test for iodide. *Anal.* Calcd for $Zr(C_5H_7O_2)_3Cl$: C, 42.49; H, 4.99; Zr, 21.51. Found: C, 41.96; H, 4.88; Zr, 21.92. After two recrystallizations from benzene–hexane the melting point was 159.5–161°.

Chlorotris(2,4-pentanedionato)hafnium(IV).—The same procedure was employed as for the zirconium analog except that the reaction time was 10 hr; mp 161.5–162.5°, lit.[11] 154–156°. *Anal.* Calcd for $Hf(C_5H_7O_2)_3Cl$: C, 35.24; H, 4.14; Cl, 6.93; Hf, 34.91. Found: C, 35.46; H, 4.28; Cl, 7.03; Hf, 34.97.

Bromotris(2,4-pentanedionato)zirconium(IV).—Acetylacetone (11.9 ml, 116 mmol) was slowly added to a slurry of anhydrous zirconium(IV) bromide (9.60 g, 23.4 mmol) in 300 ml of refluxing carbon tetrachloride. After a 6.5-hr reaction time the clear yellow solution was cooled to room temperature and then decolorized by treatment with *ca.* 40 g of Norit A activated carbon which had been previously dried for 1 hr at 450° under a stream of dry nitrogen. The product was recovered by boiling off some carbon tetrachloride, adding hot hexane until appearance of turbidity, and cooling. The yield, after drying *in vacuo* at room temperature, was 6.84 g (62%). The product was recrystallized from carbon tetrachloride–hexane, and the resulting white crystals were dried *in vacuo* at 80° for 0.5 hr; mp 162.5–164°. The same melting point was obtained upon recrystallization from benzene–hexane. *Anal.* Calcd for $Zr(C_5H_7O_2)_3Br$: C, 38.46; H, 4.52; Br, 17.06; Zr, 19.47. Found: C, 38.13; H, 4.21; Br, 17.23; Zr, 19.62.

Bromotris(2,4-pentanedionato)hafnium(IV).—The same method of synthesis and purification was used as employed for the analogous zirconium compound except that the reaction time was 15 hr; mp 161.5–163.5°. *Anal.* Calcd for $Hf(C_5H_7O_2)_3Br$: C, 32.42; H, 3.81; Br, 14.38; Hf, 32.12. Found: C, 32.64; H, 3.82; Br, 14.20; Hf, 32.39.

Iodotris(2,4-pentanedionato)zirconium(IV).—Zirconium(IV) acetylacetonate[20] (9.311 g, 19.09 mmol) was added to a solution of zirconium(IV) iodide (3.812 g, 6.366 mmol) in 250 ml of tetrahydrofuran (THF). The yellow solution was stirred under argon for 1 hr at room temperature, and then the volume was reduced to *ca.* 80 ml by vacuum distillation at room temperature. The resulting white crystals were washed with four 20-ml portions of THF and were dried *in vacuo* for 16 hr at room temperature. Proton nmr spectra in dichloromethane solution indicated the presence of 1 mol of THF/mol of compound. Heating for 5 hr at 80° *in vacuo* was required to remove all of the THF. The yield was 10.75 g (82%). Because of extreme sensitivity to moisture, the product was stored *in vacuo*. The compound gradually decomposed on heating but melted rather sharply to a yellow-orange liquid in the range 178–183°, depending on the heating rate. *Anal.* Calcd for $Zr(C_5H_7O_2)_3I$: C, 34.95; H, 4.12; I, 24.62; Zr, 17.70. Found: C, 33.65, 33.80; H, 4.09, 4.25; I, 24.66; Zr, 17.66.

Reaction of zirconium(IV) iodide and acetylacetone (1:2 molar ratio) in isopropyl ether at room temperature also yielded this compound. However the product showed a distinct, but weak, hydroxyl stretching band in the infrared spectrum; mp 171–172°. *Anal.* Calcd for $Zr(C_5H_7O_2)_3I$: C, 34.95; H, 4.12; I, 24.62; Zr, 17.70. Found: C, 34.11; H, 4.43; I, 24.50; Zr, 17.71.

Tetrakis(2,4-pentanedionato)hafnium(IV) was prepared by a procedure analogous to that described for the corresponding zirconium compound.[20] Tris(2,4-pentanedionato)silicon(IV) chloride was obtained by heating tris(2,4-pentanedionato)silicon-

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Table I

X-Ray Powder Diffraction Data

$M(acac)_2Cl_2$		$M(acac)_2Br_2$		$M(acac)_3Cl$		$M(acac)_3Br$			$Zr(acac)_3I \cdot$ THF
M = Zr	M = Hf	M = Zr	M = Hf	M = Zr	M = Hf	M = Zr	M = Hf	$Zr(acac)_3I$	
7.76[a] (3)[b]	7.73 (1)	9.66 (1)	...	...	...	...	...	10.9 (1)	10.98 (2)
7.05 (7)	7.00 (7)	8.55 (2)	...	...	...	8.47 (1)	8.65 (1)	8.55 (10)	8.47 (10)
6.66 (7)	6.63 (7)	7.80 (1)	7.92 (1)	7.84 (7)	7.79 (7)	7.76 (8)	7.77 (8)	7.76 (5)	7.76 (5)
...	...	7.03 (8)	7.13 (10)	7.17 (10)	7.14 (10)	7.00 (5)	6.99 (4)	7.20 (5)	7.22 (5)
6.37 (10)	6.35 (10)	...	...	6.50 (6)	6.51 (7)	6.37 (10)	6.38 (10)	6.71 (5)	6.71 (3)
5.89 (8)	5.93 (7)	6.46 (10)	6.52 (8)	...	...	...	...	5.87 (1)	5.90 (1)
5.73 (2)	5.72 (2)	...	...	5.69 (2)	5.67 (3)	5.50 (6)	5.49 (5)	5.61 (5)	5.61 (5)
...	...	5.87 (8)	5.82 (8)	5.28 (6)	5.27 (5)	5.19 (2)	5.18 (1)	5.37 (5)	5.36 (5)
5.17 (2)	5.16 (2)	...	5.62 (1)	...	...	...	...	5.07 (1)	5.10 (3)
4.91 (2)	4.90 (2)	5.42 (1)	5.43 (1)	4.45 (3)	4.41 (1)	4.50 (2)	4.49 (1)	[c]	4.80 (1)
...	4.52 (2)	5.11 (1)	5.12 (1)	...	...	4.32 (1)	4.31 (1)	[c]	4.60 (1)
4.36 (2)	4.36 (2)	...	4.84 (1)	4.19 (4)	4.21 (5)	4.15 (4)	4.16 (5)	...	...
4.24 (1)	4.22 (1)	4.48 (1)	4.48 (3)	4.04 (4)	4.07 (5)	...	...	...	...
4.05 (6)	4.04 (5)	...	...	...	...	3.93 (4)	3.93 (5)	3.92 (5)	3.90 (5)
...	...	...	4.23 (3)	3.87 (1)	...	...	...	...	...
3.93 (1)	3.91 (1)	...	...	3.77 (1)	3.75 (1)	3.77 (6)	3.77 (5)	3.74 (3)	3.74 (3)
3.77 (7)	3.77 (5)	3.96 (2)	3.96 (1)	3.66 (4)	3.64 (1)	3.66 (1)	3.67 (1)	3.61 (10)	3.60 (10)
...	...	...	...	3.42 (4)	3.42 (5)	3.48 (6)	3.47 (5)	...	3.45 (1)
3.51 (6)	3.51 (5)	...	3.73 (5)	3.24 (4)	3.24 (5)	3.31 (5)	3.31 (5)	...	3.30 (1)
3.40 (6)	3.39 (5)	3.62 (7)	3.59 (5)	3.14 (1)	...	3.17 (2)	3.18 (3)		
3.25 (5)	3.24 (2)	...	...	3.04 (1)	3.01 (1)	3.06 (4)	3.06 (4)		
3.19 (1)	3.17 (1)	3.42 (4)	3.40 (5)	2.94 (1)	2.95 (1)	2.88 (1)	...		
3.10 (1)	3.09 (1)	...	...	2.84 (2)	2.84 (1)	2.82 (1)	2.83 (3)		
...	...	3.18 (4)	3.19 (5)	...	2.77 (1)	2.73 (4)	2.74 (3)		
2.99 (1)	2.97 (3)	...	...	2.68 (2)	2.66 (3)	2.69 (1)	...		
2.82 (1)	2.81 (3)	3.04 (4)	3.03 (2)	2.64 (1)	...	...	...		
2.69 (2)	2.67 (3)	...	...	2.56 (2)	2.55 (1)	2.59 (1)	2.59 (1)		
2.61 (2)	2.59 (3)	2.82 (4)	2.81 (2)	2.51 (1)	...	2.52 (5)	2.51 (4)		
2.54 (1)	...	...	...	...	2.44 (1)	2.43 (1)	2.42 (3)		
2.51 (1)	2.51 (3)	2.61 (2)	2.61 (2)	2.40 (2)	2.39 (1)	...	...		
2.46 (4)	2.45 (3)	...	2.55 (2)	2.35 (1)	2.35 (1)	...	...		
...	...	...	...	2.28 (2)	2.28 (3)	2.32 (5)	2.32 (4)		
2.34 (6)	2.33 (5)	2.47 (2)	2.47 (3)	2.22 (1)	...	2.25 (2)	2.24 (3)		
2.28 (2)	2.27 (2)	2.39 (4)	2.39 (2)	2.17 (1)	2.17 (2)	2.16 (2)	2.16 (4)		
2.21 (2)	2.21 (3)	2.31 (2)	2.31 (2)	...	...	2.12 (2)	2.10 (4)		
2.15 (2)	2.14 (3)	...	...	2.05 (3)	2.05 (3)	2.08 (2)	...		
		...	2.21 (2)						
		...	...						

[a] d_{hkl}, Å. [b] Visually estimated relative intensities. [c] Lines in this region were weak and diffuse.

(IV) hydrogen dichloride[21] for 5 hr at 80° *in vacuo;* loss of hydrogen chloride was verified by the nmr spectrum. Tris(2,4-pentanedionato)titanium(IV) hexachloroantimonate was prepared as described by Cox, *et al.*[11]

Physical Measurements. Melting Points.—Melting points were measured in sealed capillaries using a calibrated thermometer. Severe decomposition upon melting was noted for $Zr(acac)_3I$; all other compounds melted with only slight decomposition.

Molecular Weight and Conductance Measurements.—The techniques and equipment employed for these measurements have been previously described.[18,22]

Nuclear Magnetic Resonance Spectra.—Proton chemical shifts were obtained with a Varian A-60 spectrometer at 60.000 Mc. The magnetic field sweep was checked against the chemical shift of a 2 vol % solution of benzene in carbon tetrachloride.[23] Low-temperature spectra were recorded with a Varian HR-60 spectrometer at 60.000 Mc using the audiofrequency side-band technique for calibration of the magnetic field. Techniques for obtaining low-temperature spectra have been described in a previous paper.[24]

X-Ray Powder Patterns.—X-Ray powder patterns were obtained with nickel-filtered Cu Kα radiation using 0.5-mm glass capillaries and a Debye–Scherrer camera of 360.0-mm circumference. The diffraction patterns of at least two different capillary preparations of each compound were compared to ensure reproducibility. In addition, since the compounds are easily hydrolyzed, each compound was exposed to moist air, and diffraction patterns of anhydrous samples were checked against patterns of exposed samples in order to ensure the absence of spurious lines due to hydrolysis. With the exception of $Zr(acac)_3I$ and $Zr(acac)_3I \cdot THF$, samples had been recrystallized from benzene–hexane. The THF solvate was used as obtained from THF; $Zr(acac)_3I$ was recrystallized by slow evaporation of a dichloromethane solution under vacuum after THF had been removed at 80° *in vacuo.* Interplanar spacings and visually estimated relative intensities are listed in Table I.

Results and Discussion

Preparative Chemistry.—Zirconium(IV) and hafnium(IV) chlorides and bromides react with acetylacetone under anhydrous conditions to give substitution products plus hydrogen halide. In diethyl ether, the disubstitution products $M(acac)_2X_2$ are obtained. At higher temperatures, in refluxing benzene or carbon tetrachloride, the reaction yields higher substitution products, $M(acac)_3X$.

In syntheses of the dihalides we were careful to employ a limited amount of solvent so that the product precipitates from solution as it is formed. This minimizes the danger of converting $M(acac)_2X_2$ to $M(acac)_3X$ by homogeneous reaction with excess acetylacetone. The dichloride of zirconium has been prepared by Jantsch[4] in diethyl ether which apparently was in sufficient excess to keep the product in solution for the duration of the reaction. Using the method of Jantsch, however, Cox, Lewis, and Nyholm[11] were unable to prepare the corresponding hafnium compound, $Hf(acac)_2Cl_2$, but obtained, instead, $Hf(acac)_3Cl$. Hence, the desirability of using a limited amount of solvent is to be emphasized.

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[24] T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, **5**, 233 (1966).

In syntheses of the monohalides, $Zr(acac)_3X$ (X = Cl, Br, or I), painful experience has shown that the choice of solvent is most important. Although benzene is suitable for preparation of the chloride, this solvent yielded an intractable red oil when used in attempts to prepare the bromide. The bromide, however, is readily prepared in carbon tetrachloride. Interestingly, in our attempts to prepare the iodide in carbon tetrachloride, we found that this solvent reacted with zirconium(IV) iodide and acetylacetone to give $Zr(acac)_3Cl$. It is important, in syntheses of the monochloride and monobromide, to use sufficient solvent so that the disubstituted products remain in solution and react further to give the monohalides.

Unlike zirconium(IV) chloride and bromide, zirconium(IV) iodide does not yield the disubstitution product upon reaction with acetylacetone in diethyl ether. Instead, an impure $Zr(acac)_3I-(C_2H_5)_2O$ solvate was obtained. The ether could be removed by heating *in vacuo* for several hours at 80–100°, but simultaneous decomposition of the complex occurred. In isopropyl ether and in the absence of solvent, the solvent-free monoiodide was obtained; however, a hydroxyl stretching vibration in infrared spectra of the products indicates some hydrolysis. The pure monoiodide is best prepared by a ligand-exchange reaction between zirconium(IV) acetylacetonate and zirconium(IV) iodide (3:1 molar ratio) in dry tetrahydrofuran (THF). The compound is first obtained as a 1:1 solvate, but the THF can be removed at 80° *in vacuo* without decomposition of the complex. Although Freidlina, *et al.*,[5] have prepared the dichloride, $Zr(acac)_2Cl_2$, by ligand exchange in THF using a 1:1 molar ratio of $Zr(acac)_4$ and zirconium(IV) chloride, the analogous approach is unsuccessful for preparation of the diiodide. From the reaction of $Zr(acac)_4$ and zirconium(IV) iodide (1:1 molar ratio) in THF, we obtained instead $Zr(acac)_3I$ in 49% yield.

Our attempts to prepare a fluoro complex of zirconium were unsuccessful. No reaction was observed between zirconium(IV) fluoride and neat acetylacetone after 24 hr at 80°. The inert nature of zirconium(IV) fluoride may be attributed to its extended three-dimensional structure[25] which renders the compound highly insoluble in organic solvents. Attempted metathesis of $Zr(acac)_3Cl$ and silver(I) fluoride in acetonitrile (in absence of light) resulted in partial substitution of both chloride and acetylacetonate ligands and gave complex, unidentified products. Extensive substitution of acac ligands also occurred upon reaction of $Zr(acac)_3Cl$ with excess anhydrous hydrogen fluoride in diethyl ether.

It has been remarked that $Zr(acac)_4$ cannot be prepared by reaction of zirconium(IV) chloride with excess acetylacetone under anhydrous conditions; even after prolonged heating, the highest substitution product obtained was $Zr(acac)_3Cl$.[7] We find, by nmr spectroscopy, that heating $Zr(acac)_3Cl$ with neat acetylacetone (1:40 molar ratio) for 24 hr at 80° yields a product which is *ca.* 20% $Zr(acac)_4$. Thus, the fourth chlorine atom can be replaced by acetylacetone under anhydrous conditions, but the rate of substitution is slow. This behavior suggests a seven-coordinate structure for $Zr(acac)_3Cl$ since $Zr(acac)_3^+$ would be expected to react rapidly with acetylacetone. The ready conversion of $Zr(acac)_3Cl$ to $Zr(acac)_4$ in the presence of water[7,26] can be understood in terms of preliminary hydrolysis at the Zr–Cl bond. In anhydrous media the ease of complete substitution is apparently strongly dependent on the nature of the diketone, since certain aryl-[8] and trifluoromethyl-substituted[27] diketones readily afford the tetrakisdiketonates.

Attention is directed to serious discrepancies in melting points reported in this work and in the earlier literature for $Zr(acac)_2Cl_2$ and $Zr(acac)_3Cl$. (See Experimental Section.) Four groups of workers have prepared $Zr(acac)_3Cl$ by reaction of acetylacetone with zirconium(IV) chloride, and each group has reported a different melting point.[7,10,11,15] Our results are in best agreement with those of Freidlina, *et al.*[10] Although the possibility of several different crystalline modifications cannot be excluded, it is more likely that melting point discrepancies in previous studies of $Zr(acac)_3Cl$ are due to partial hydrolysis during synthesis or purification of the compound.

Characterization of Compounds.—X-Ray powder diffraction data presented in Table I indicate that (1) the zirconium and hafnium compounds containing the same halogen are isomorphous, (2) the chlorides and bromides are probably not isomorphous, and (3) $Zr(acac)_3I$ is definitely not isomorphous with either $Zr(acac)_3Cl$ or $Zr(acac)_3Br$. The lack of isomorphism between the monochlorides and monobromides is supported by microscopic observations which show that crystals of $Zr(acac)_3Cl$ are orthorhombic whereas $Zr(acac)_3Br$ is monoclinic. Powder patterns of $Zr(acac)_3I$ and $Zr(acac)_3I \cdot THF$ are nearly identical. Although there is evidence for some formation of $[Zr(acac)_3(THF)]^+$ in solutions of $Zr(acac)_3I$ containing THF (see below), the structure of the solid is not appreciably modified by the presence of THF. Apparently, the THF occupies holes in the lattice.

Molecular weight and conductance data are presented in Tables II and III. All of the halo complexes are monomeric in solution, although molecular weights for $Zr(acac)_3I$, which decrease somewhat with decreasing concentration, suggest some dissociation upon dilution in the case of the monoiodide. Except for the monoiodide, molar conductances (Λ) in ionizing solvents are small compared with conductances for analogous 1:1 electrolytes, $[Si(acac)_3]Cl$ and $[Ti(acac)_3][SbCl_6]$, at the same concentrations.[28] Com-

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[25] R. D. Burbank and F. N. Bensey, Jr., U. S. Atomic Energy Commission Report K-1280, 1956; *Nucl. Sci. Abstr.*, **11**, 412 (1957).

[26] E. M. Brainina and R. Kh. Freidlina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1489 (1961).

[27] M. L. Morris, R. W. Moshier, and R. E. Sievers, *Inorg. Syn.*, **9**, 50 (1967).

[28] Molar conductances for the halo zirconium and hafnium compounds exhibited some time dependence due to a bit of hydrolysis. The time dependence suggests that Λ values for these complexes may be in error by *ca.* ±25%; this uncertainty in no way affects our conclusions concerning the constitution of these compounds in solution.

TABLE II

MOLECULAR WEIGHT AND CONDUCTANCE DATA

Compound	Concn $\times 10^2$	Mol wt		Conductance	
		Found[a]	Calcd	Molarity $\times 10^3$	Λ^d
Zr(acac)$_2$Cl$_2$	2.18 *m*	353	360	10.4	0.68
Hf(acac)$_2$Cl$_2$	2.19 *m*	456	448	10.3	0.53
Zr(acac)$_2$Br$_2$	1.76 *m*	462	449	9.6	1.5
Hf(acac)$_2$Br$_2$	1.75 *m*	531	537	9.8	0.74
Zr(acac)$_3$Cl	Inf. dil	441[b]	424	10.2	0.22
Hf(acac)$_3$Cl	2.04 *m*	528	511	9.6	0.07
Zr(acac)$_3$Br	Inf. dil.	472[b]	468	9.9	0.24
Hf(acac)$_3$Br	2.02 *m*	547	556	10.1	0.38
Zr(acac)$_3$I	8.34 *M*	519[c]	515	28.6	7.0
	6.13 *M*	499[c]			
	3.71 *M*	475[c]			
[Si(acac)$_3$]Cl	. . .	. . .	. . .	10.9	25.3
[Ti(acac)$_3$][SbCl$_6$]	. . .	. . .	. . .	10.0	19.5
Zr(acac)$_4$	. . .	. . .	. . .	1.0	<0.04
Hf(acac)$_4$	. . .	. . .	. . .	1.0	<0.04

[a] Determined cryoscopically in nitrobenzene unless indicated otherwise. [b] Determined by vapor pressure osmometry in benzene at 37°; data were extrapolated to infinite dilution. [c] Determined by vapor pressure osmometry at 37° in 1,2-dichloroethane; calibration plots in this solvent were sufficiently nonlinear to make extrapolation of data to infinite dilution impractical. [d] Molar conductance, ohm^{-1} cm^2 mole^{-1}, in nitrobenzene at 25.00 ± 0.05°.

TABLE III

CONDUCTANCE DATA FOR Zr(acac)$_3$X COMPLEXES IN 1,2-DICHLOROETHANE AT 25°

Compound	Molarity $\times 10^3$	Λ, ohm^{-1} cm^2 mole^{-1}	
		In pure solvent	In pure solvent + 0.05 *M* THF
Zr(acac)$_3$Cl	1.36	0.36	0.40
Zr(acac)$_3$Br	1.27	0.36	0.71
Zr(acac)$_3$I	1.17	5	20
[Si(acac)$_3$]Cl	1.02	38.3	. . .
[Ti(acac)$_3$][SbCl$_6$]	1.06	35.5	35.4

parison of the Λ values for the M(acac)$_2$X$_2$ and M(acac)$_3$X complexes with Λ *vs.* (molarity)$^{1/2}$ plots for [Si(acac)$_3$]Cl allows the per cent dissociation to be estimated. The dihalides are *ca.* 2–5% dissociated in nitrobenzene; for the monohalides (X = Cl and Br) the per cent dissociation is *ca.* 1% or less in nitrobenzene and in 1,2-dichloroethane. Since infrared spectra indicate that all acetylacetonate carbonyl groups are coordinated,[29] the M(acac)$_2$X$_2$ and M(acac)$_3$X complexes (X = Cl and Br) may be formulated in solution as monomeric, weak electrolytes in which the metal atom exhibits, respectively, coordination numbers six and seven. Eight-coordinate structures for the monohalides, such as M(acac)$_3$(H$_2$O)X, may be eliminated on the basis of elemental analyses and infrared spectra, which confirm the absence of water.[29]

In contrast to the monochlorides and monobromides, Zr(acac)$_3$I is appreciably dissociated in solution. The molar conductance of a 0.0286 *M* solution in nitrobenzene corresponds to a degree of dissociation of *ca.* 26%; Λ of a 10^{-3} *M* solution in 1,2-dichloroethane indicates *ca.* 10% dissociation. In view of the very low conductances for the eight-coordinate M(acac)$_4$ compounds (Table II), it is apparent that observed conductances for the halo complexes result primarily from dissociation of halide rather than acetylacetonate ions. Therefore, the predominant dissociated species for Zr(acac)$_3$I are most probably Zr(acac)$_3^+$ and I$^-$. Increased dissociation for the monoiodide might be expected since the Zr–X bond should be weakest when X is iodine. Metal–halogen bond energies are not available for the Zr(acac)$_3$X complexes; however, there is a steady decrease in mean thermochemical bond energies (kcal/mole) for the zirconium tetrahalides: 117.0 (Zr–Cl), 101.5 (Zr–Br), and 82.9 (Zr–I).[30] Furthermore, the Zr–X bond should be weakened by steric factors to a greater extent in Zr(acac)$_3$I than in Zr(acac)$_3$Cl or Zr(acac)$_3$Br.

It is interesting to note (Table III) that the dissociated species of Zr(acac)$_3$I in 1,2-dichloroethane are markedly stabilized by THF. In the presence of 0.05 *M* THF, Λ of a 10^{-3} *M* solution of Zr(acac)$_3$I increased from 5 to 20 ohm^{-1} cm^2 mole^{-1}, while Λ for Zr(acac)$_3$Cl and Zr(acac)$_3$Br increased only slightly. Most likely, in the case of the iodide, THF coordinates to zirconium to give solvated cations: $\mathrm{Zr(acac)_3I + THF \rightleftarrows [Zr(acac)_3(THF)]^+ + I^-}$.

Enhanced dissociation resulting from THF coordination is supported by proton nmr spectra. On adding THF to a solution of Zr(acac)$_3$I, one might expect to observe new resonance lines downfield from the resonances of Zr(acac)$_3$I due to the appearance of the positively charged species, [Zr(acac)$_3$(THF)]$^+$. In the presence of rapid ligand exchange, which would average the acac environments in Zr(acac)$_3$I and [Zr(acac)$_3$(THF)]$^+$, one should simply observe a downfield shift in the position of the Zr(acac)$_3$I resonance lines owing to the increasing concentration of [Zr(acac)$_3$(THF)]$^+$ as THF is added to the solution. This latter phenomemon was, in fact, observed. Figure 1 shows the observed downfield shifts of the acetylacetonate ring proton (—CH═) and methyl proton resonances for Zr(acac)$_3$I. In contrast, the resonances of Zr(acac)$_3$Cl are essentially unaffected by the addition of THF. Downfield shifts of 7 cps (—CH═) and 2.5 cps (—CH$_3$) for solutions of solid Zr(acac)$_3$I·THF in dichloromethane (Table IV) are comparable to the downfield shifts for 1:1 mixtures of Zr(acac)$_3$I and THF in 1,2-dichloroethane (Figure 1). Coordination of THF in the case of the monoiodide is also indicated by downfield shifts of the THF proton resonances in the presence of Zr(acac)$_3$I. Upon addition of Zr(acac)$_3$I (0.10 *M*) to a 0.02 *M* solution of THF in 1,2-dichloroethane, a downfield shift of *ca.* 9 cps was observed for the multiplet due to THF protons in the 3,4 positions.

Proton nmr spectra of the M(acac)$_2$X$_2$ and M(acac)$_3$X complexes in dichloromethane, chloroform, and benzene consist of a single methyl and a single ring proton resonance. Chemical shifts are presented in Table IV; data for acetylacetone and the tetrakisacetylacetonates are included for comparison. The concentration dependence of the chemical shifts was checked

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(29) R. C. Fay and T. J. Pinnavaia, *Inorg. Chem.*, **7**, 508 (1968).

(30) Computed from enthalpy data in "JANAF Thermochemical Tables," compiled by the Dow Chemical Co., Midland, Mich., 1960.

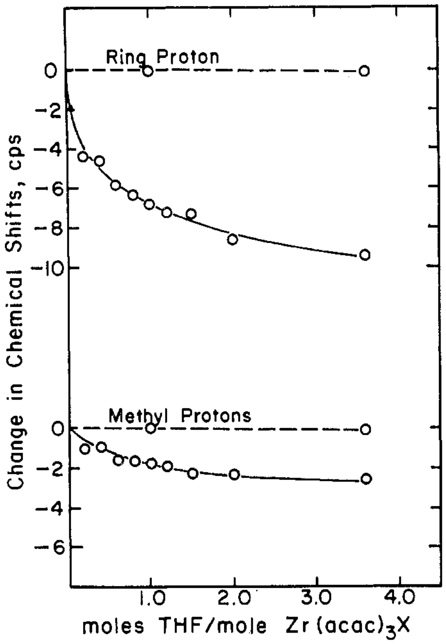

Figure 1.—The effect of THF on the chemical shifts of Zr(acac)$_3$I (solid line) and Zr(acac)$_3$Cl (broken line) in 1,2-dichloroethane at 38.5°. Concentration of Zr(acac)$_3$X is 0.10 *M*.

TABLE IV

PROTON CHEMICAL SHIFT DATA[a]

Compound	Dichloromethane		Chloroform		Benzene	
	—CH=	—CH$_3$	—CH=	—CH$_3$	—CH=	—CH$_3$
H(acac) (enol form)	−5.51	−2.01	−5.51	−2.04	−5.03	−1.65
Zr(acac)$_2$Cl$_2$	−5.99	−2.13	−5.96	−2.14	−5.18	−1.49
Hf(acac)$_2$Cl$_2$	−5.94	−2.13	−5.92	−2.14	−5.15	−1.48
Zr(acac)$_2$Br$_2$	−6.01	−2.13	−5.99	−2.15	−5.20	−1.48
Hf(acac)$_2$Br$_2$	−5.98	−2.13	−5.94	−2.14	−5.13	−1.44
Zr(acac)$_3$Cl	−5.78	−2.04	−5.77	−2.06	−5.41	−1.78
Hf(acac)$_3$Cl	−5.73	−2.03	−5.73	−2.08	−5.36	−1.77
Zr(acac)$_3$Br	−5.80	−2.04	−5.80	−2.08	−5.43	−1.77
Hf(acac)$_3$Br	−5.76	−2.04	−5.76	−2.07	−5.36	−1.76
Zr(acac)$_3$I	−5.89[b]	−2.06[b]	−5.86	−2.09	−5.42	−1.76
Zr(acac)$_4$	−5.51	−1.90	−5.48	−1.92	−5.36	−1.82
Hf(acac)$_4$	−5.48	−1.89	−5.46	−1.92	−5.33	−1.82

[a] Ppm (±0.01) relative to an internal reference of tetramethylsilane (1% by volume). Temperature is 37 ± 2°. Concentration is 10.0 g/100 ml of solvent except for the dihalides in benzene where concentration is 1.3 g/100 ml of solvent. [b] Shifts for Zr(acac)$_3$I·THF are −6.02 (—CH=) and −2.10 (—CH$_3$).

for Zr(acac)$_2$Cl$_2$ and Zr(acac)$_3$Cl in dichloromethane and benzene solutions in the concentration range 1.3–10.0 g/100 ml of solvent. Except for Zr(acac)$_2$Cl$_2$ in benzene, the concentration dependence was less than 0.03 ppm. The resonances of Zr(acac)$_2$Cl$_2$ in benzene at a concentration of 10.0 g/100 ml of solvent were shifted downfield by 0.13 (—CH=) and 0.06 ppm (CH$_3$) relative to the resonances at 1.3 g/100 ml of solvent. Since shifts at the latter concentration were within 0.02 ppm of the extrapolated, infinite dilution values, data reported in Table IV for the dihalides in benzene were obtained at this concentration.

The chemical shifts are very similar for the zirconium and hafnium compounds, although the —CH= resonances appear slightly farther downfield in the case of the zirconium complexes. The shifts show little or no dependence on the halogen, except for the —CH= resonance of Zr(acac)$_3$I in dichloromethane and chloroform, which is found *ca.* 0.1 ppm downfield relative to the signals of Zr(acac)$_3$Cl and Zr(acac)$_3$Br. The most significant trend in the data of Table IV is the pronounced downfield shift (in dichloromethane and chloroform) with increasing number of halogen atoms; the resonances appear at progressively lower field in the order M(acac)$_4$ > M(acac)$_3$X > M(acac)$_2$X$_2$. These downfield shifts are probably due to an electric field effect arising from the molecular dipole moment,[31] and the shifts suggest that the dipole moment increases in the order M(acac)$_4$ < M(acac)$_3$X < M(acac)$_2$X$_2$. Therefore, it is most likely that the dihalides exist in solution as the *cis* geometrical isomer; chemical shifts for the *trans* isomer should be similar to those for the nonpolar M(acac)$_4$ complexes.[31] Observed shifts for the dihalides are close to those found for the analogous Ti(acac)$_2$X$_2$ compounds which have been shown unequivocally to have the *cis* configuration.[18] The *cis* structure for the zirconium and hafnium compounds is also supported by infrared and Raman spectra.[29]

Another notable feature of the chemical shift data is the marked upfield shift of the resonance lines in benzene solution relative to their positions in dichloromethane and chloroform. The average upfield shifts for the —CH= and methyl resonances, respectively, are 0.14 and 0.09 ppm for M(acac)$_4$, 0.37 and 0.29 ppm for M(acac)$_3$X, and 0.80 and 0.67 ppm for M(acac)$_2$X$_2$. The solvent effect is so prominent for the dihalides that the resonances for these compounds in benzene appear at highest field rather than at lowest field as found in dichloromethane and chloroform. The upfield shifts indicate that the magnetically anisotropic, solvating benzene molecules prefer orientations which produce diamagnetic shielding at the —CH= and methyl protons. Schneider[32] has proposed a dipole–induced dipole mechanism to account for diamagnetic shielding of polar solutes in aromatic solvents. Applying Schneider's ideas, we would expect the acac end of the dipolar M(acac)$_3$X and M(acac)$_2$X$_2$ molecules (positive end of the solute dipole) to lie near the π electrons of the benzene ring. The upfield shifts should increase in the order M(acac)$_4$ < M(acac)$_3$X < M(acac)$_2$X$_2$ as the solute dipole moment increases. Although experimental dipole moments are not yet available, observed shifts are in accord with the expected trend. Similar upfield shifts in aromatic solvents have been observed previously for other dipolar metal diketonate complexes.[24,33,34]

Finally, we comment on the simplicity of nmr spectra of the halo complexes. All reasonable seven-coordinate M(acac)$_3$X structures have two or more nonequivalent methyl groups. Likewise, the M(acac)$_2$X$_2$ *cis* isomer contains two sets of methyl protons. Observation of a single methyl resonance indicates that the chelate rings undergo rapid configurational rearrangements which exchange methyl groups be-

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(31) J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc., Sect. A*, 1749 (1966).
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(33) A. C. Adams and E. M. Larsen, *Inorg. Chem.*, **5**, 228 (1966)
(34) R. G. Linck and R. E. Sievers, *ibid.*, **5**, 806 (1966).

tween the various nonequivalent environments. Similar exchange for related eight-coordinate tetrakis diketonates has been reported previously.[24,33] In the case of *cis*-Ti(acac)$_2$X$_2$ complexes, this exchange is sufficiently slow so that separate resonance lines have been observed for nonequivalent methyl groups below -26 to $-63°$.[18] The zirconium and hafnium compounds, however, are considerably more labile. Spectra of Zr(acac)$_2$X$_2$ and Zr(acac)$_3$X (X = Cl and Br) at $-108°$ in a mixture of dichloromethane and 1,1,2-trichloroethene (6:4 by volume) showed a single methyl resonance (line width, 1.4–1.8 cps). Spectra of Zr(acac)$_2$Cl$_2$, Zr(acac)$_3$Cl, and Zr(acac)$_4$ were also obtained at *ca.* $-130°$ in dichloromethane–3-chloropropene (1:1 by volume); even at this low temperature only one rather sharp methyl resonance was observed (line width *ca.* 2–3 cps). Assuming that chemical shifts between nonequivalent protons are similar to that for Ti(acac)$_2$Cl$_2$,[18] rate constants for exchange of methyl groups can be estimated to be >10 sec^{-1} at $-130.°$

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Infrared and Raman Spectra of Some Six-, Seven-, and Eight-Coordinate Acetylacetonato Complexes of Zirconium(IV) and Hafnium(IV)[1]

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Infrared (4000–70 cm^{-1}) and Raman spectra are reported for six-coordinate dihalobis(acetylacetonato) and seven-coordinate halotris(acetylacetonato) complexes of zirconium(IV) and hafnium(IV), M(acac)$_2$X$_2$ (X = Cl or Br) and M(acac)$_3$X (X = Cl, Br, or, when M = Zr, I). Spectra are also reported for the eight-coordinate acetylacetonato complexes, M(acac)$_4$ (M = Zr, Hf, Ce, or Th). Vibrational frequencies assigned to carbonyl stretching, metal–halogen stretching, and certain of the metal–oxygen stretching modes are sensitive to coordination number. The spectra indicate the *cis* configuration for the M(acac)$_2$X$_2$ complexes, and they afford confirmatory evidence for the seven-coordinate nature of the M(acac)$_3$X complexes.

Introduction

As a continuation of our study of the interesting six- and seven-coordinate halo(acetylacetonato) complexes of zirconium(IV) and hafnium(IV), M(acac)$_2$X$_2$ and M(acac)$_3$X,[3] we have obtained infrared and Raman spectra of these compounds and the related eight-coordinate complexes, M(acac)$_4$ (M = Zr, Hf, Ce, or Th). The aim of this study was twofold. First, we hoped to identify the metal–oxygen and metal–halogen stretching vibrations. The M–O and M–X stretching region should afford additional evidence for the seven-coordinate nature of the monohalides and should provide a basis for distinguishing between the possible *cis* and *trans* structures for the dihalides. Second, these series of compounds offer an excellent opportunity to investigate the way in which the vibrational frequencies depend on coordination number.

Experimental Section

Preparation and characterization of the M(acac)$_2$X$_2$ and M(acac)$_3$X complexes has been described in the preceding paper.[3] The tetrakisacetylacetonates were prepared by standard methods,[4-6] and the purity of these compounds was checked by their melting points.[4,7,8] Cerium(IV) acetylacetonate, which does not have a reproducible melting point, was satisfactorily analyzed.[9]

The starting materials used for preparation of all hafnium compounds were spectroscopic grade, <200 ppm zirconium; consequently, spectra of the hafnium compounds should be free of bands due to the zirconium analogs.

Infrared spectra in the 4000–250-cm^{-1} region were recorded using a Perkin-Elmer 521 grating spectrophotometer. The instrument was calibrated with reagent grade indene, freshly distilled from calcium hydride, and was swept with dry air while recording spectra. Solutions were contained in 0.1-mm cesium bromide cells; Nujol mulls were supported between cesium iodide plates. A fivefold frequency scale expansion was employed in the 600–250-cm^{-1} region. The maximum uncertainty in the reported frequencies is estimated to be less than 4 cm^{-1} and less than 2 cm^{-1} in the 1600–600- and 600–250-cm^{-1} regions, respectively.

Infrared spectra in the 322–70-cm^{-1} region were obtained with a Perkin-Elmer Model 301 grating spectrophotometer. This instrument was calibrated using the pure rotational bands of water vapor. Solution spectra were obtained in 0.1-mm polyethylene molded cells, and Nujol mulls were supported between polyethylene plates. The vapor of boiling nitrogen, after being warmed to room temperature, was used to purge the instrument while recording spectra. The estimated accuracy of reported frequencies in this region is ± 2 cm^{-1}.

Raman spectra were obtained in nearly saturated benzene solutions using a Cary Model 81 Raman spectrophotometer. The spectra were excited with the 4358-Å mercury line; the 4047-Å line was removed with a Kodak Wratten 2A filter.

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