rate than the acetylacetone ligands, but this has already been shown to be incorrect.

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Nuclear Magnetic Resonance Studies of Ligand Exchange for Some Group IVb β-Diketonates[1]

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The rapid ligand exchange of β-diketonate ligands which occurs upon mixing solutions of eight-coordinated group IVb meta acetylacetonates, M(acac)$_4$, and metal trifluoroacetylacetonates, M(tfac)$_4$ (M = Zr, Hf, Ce, Th), has been studied by fluorine n.m.r. spectroscopy. The ligand-exchange equilibria may be described in terms of three independent equilibrium quotients. For the zirconium system, which has been studied in most detail, the equilibrium quotients in benzene and carbon tetrachloride solutions deviate by a factor of 2–3 from the values expected for a random statistical distribution of ligands. The mixed complexes Zr(tfac)$_3$(acac), Zr(tfac)$_2$(acac)$_2$, and Zr(tfac)(acac)$_3$ are favored at the expense of Zr(tfac)$_4$ and Zr(acac)$_4$. Deviations from a statistical distribution of ligands are due to entropy changes; enthalpy changes for the ligand exchange reactions are nearly zero. The n.m.r. spectra also indicate that the group IVb β-diketonates undergo very rapid isomerization. Attempts to detect geometrical isomers at temperatures as low as −105° have been unsuccessful. Coalescence of n.m.r. lines due to ligand exchange has been observed for mixtures of Th(acac)$_4$ and Th(tfac)$_4$. Proton and fluorine chemical shifts are reported for M(acac)$_4$ and M(tfac)$_4$ in carbon tetrachloride, chloroform, and benzene solutions.

Introduction

The coordination geometries of eight-coordinate zirconium(IV), cerium(IV), and thorium(IV) acetylacetonates have been shown by X-ray diffraction to be based on a square antiprism.[2-4] Whether or not this geometry persists in solution is not known. In attempts to investigate the stereochemistry of zirconium, hafnium, cerium, and thorium β-diketonates in solution by fluorine magnetic resonance spectroscopy, we have found that these complexes undergo remarkably rapid intramolecular rearrangement. The lability of these compounds is further indicated by rapid intermolecular ligand exchange which occurs upon mixing solutions of metal acetylacetonate, M(acac)$_4$, and metal trifluoroacetylacetonate, M(tfac)$_4$. A 1:1 mixture of Zr(acac)$_4$ and Zr(tfac)$_4$, for example, exhibits four fluorine resonance lines which are assigned to Zr(tfac)$_4$ and the three mixed complexes, Zr(tfac)$_3$(acac), Zr(tfac)$_2$(acac)$_2$, and Zr(tfac)(acac)$_3$. Evidence for ligand exchange in the zirconium and hafnium systems has also been reported by Adams and Larsen using proton n.m.r. techniques.[5] The main purpose of the present paper is to describe the fluorine resonance spectra of mixtures of M(acac)$_4$ and M(tfac)$_4$ (M = Zr, Hf, Ce, Th) and to quantitatively characterize the ligand-exchange equilibria for the Zr(acac)$_4$–Zr(tfac)$_4$ system.

Experimental Section

Syntheses.—Metal acetylacetonates and trifluoroacetylacetonates used in this work were synthesized using well-known methods[6-9] with the exception of Zr(tfac)$_4$ and Hf(tfac)$_4$, which were prepared by refluxing the anhydrous metal chlorides with 10% excess trifluoroacetylacetone in benzene solution as suggested by Morris, Moshier, and Sievers.[10] The purity of the known compounds was checked by their melting points.[6,8,11] Cerium(IV) acetylacetonate was found to exhibit a melting point which varied with heating time due to decomposition. Rather sharp melting points were observed in the range 140–165°. Therefore, this compound was analyzed.

Anal. Calcd. for Ce(C$_5$H$_7$O$_2$)$_4$: C, 44.61; H, 5.36; Ce, 26.04. Found: C, 44.77; H, 5.26; Ce, 26.09.

Fluorine n.m.r. spectra of the hafnium compounds indicated that the hafnium contained *ca.* 10% zirconium.

Cerium and thorium trifluoroacetylacetonates have not been previously reported but are readily prepared using methods described for the corresponding acetylacetonates.[8,9]

Tetrakis(1,1,1-trifluoro-2,4-pentanediono)cerium(IV).—This compound was obtained as dark red, needle-shaped crystals when recrystallized from 25% benzene–75% hexane; m.p. 132–132.5°.

Anal. Calcd. for Ce(C$_5$H$_4$F$_3$O$_2$)$_4$: C, 31.92; H, 2.14; F, 30.30; Ce, 18.62. Found: C, 32.06; H, 2.33; F, 30.11; Ce, 18.82.

Tetrakis(1,1,1-trifluoro-2,4-pentanediono)thorium(IV).—Upon sublimation *in vacuo* at 100° this compound was obtained as white, anhydrous crystals. It is hygroscopic and must be handled in a dry atmosphere; m.p. 132.5–134° (sealed capillary).

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[1] Presented before the Division of Inorganic Chemistry, 150th National Meeting, American Chemical Society, Atlantic City, N. J., Sept. 1965.

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Anal. Calcd. for Th($C_5H_4F_3O_2$)$_4$: C, 28.46; H, 1.91; Th, 27.48. Found: C, 28.49; H, 1.99; Th, 27.45.

Preparation of Solutions.—All solvents were reagent grade. Benzene was dried over sodium wire before use. Chloroform was freed of ethanol by treatment with activated alumina. Carbon tetrachloride and acetone were used without further purification. In general, unless noted otherwise, the rate of solution of the diketone complexes was hastened by gentle warming.

Nuclear Magnetic Resonance Spectra.—Fluorine magnetic resonance spectra were obtained with a Varian HR-60 high-resolution spectrometer at 56.444 Mc. The spectrometer was equipped with a Varian variable temperature n.m.r. probe accessory, Model V-4340, and a dewar probe insert, Model V-4331 THR. In the temperature range 31 to $-105°$ the probe was cooled with the vapor of boiling liquid nitrogen. The boiling rate was held constant by supplying a constant current to a 250-ohm resistor immersed in the liquid. In the range 31–170°, constant temperature was maintained with preheated nitrogen gas; the flow rate was kept constant with a flow meter. Using these techniques, temperature could be maintained constant to $\pm 0.5°$. Sample temperature was measured with a calibrated copper–constantan thermocouple which was immersed in a sample tube containing chloroform or acetone (low-temperature spectra) or mineral oil (high-temperature spectra). The magnetic field sweep was calibrated using the side-band technique; fluorine chemical shifts are believed accurate to ± 0.01 p.p.m.

Proton chemical shifts were obtained with a Varian A-60 high-resolution spectrometer at 60.000 Mc. The magnetic field sweep of this instrument was periodically checked against the chemical shift of a 2% (by volume) solution of benzene in carbon tetrachloride.[12] This method of calibration was in agreement with the side-band technique. The estimated accuracy of proton chemical shifts is ± 0.01 p.p.m.

Measurement of Signal Intensities.—It is known that relative areas under absorption signals are proportional to relative concentrations of magnetic nuclei only if the product of relaxation times T_1T_2 is the same for all signals or if the radiofrequency field H_1 is small enough so that differences in T_1T_2 can be neglected.[13] Therefore, areas were studied as a function of H_1 in order to determine the maximum value of radiofrequency field below which signal areas are proportional to H_1 and independent of T_1T_2. All quantitative data were recorded below this value of the radiofrequency field. It was found that unreliable equilibrium quotients were obtained at high radiofrequency fields, where signal areas do depend on T_1T_2.

The absorption signals were recorded on a Varian Model G14 graphic recorder and integrated with a compensating polar planimeter. Signal areas used in the calculation of equilibrium quotients were integrated to within $\pm 2\%$ accuracy. In general, at least five copies of each spectrum were integrated and the results averaged in order to reduce the error caused by variations in magnetic field sweep.

Results and Discussion

Fluorine Resonance Spectra.—Figure 1 shows typical fluorine resonance spectra for equilibrium mixtures of Zr(tfac)$_4$ and Zr(acac)$_4$ in benzene solution at 31°. The ligand composition of the solutions is characterized by the quantity f_{tfac} which is defined as the molar fraction of total ligand present as tfac. The solutions may contain compounds with the five molecular formulas, Zr(tfac)$_n$(acac)$_{4-n}$ (n = 0–4). Compounds with n = 1, 2, 3, or 4 will give rise to fluorine resonance lines. In view of previous studies of the Al(tfac)$_3$–Al(acac)$_3$ system,[14] compounds with n = 1, 2, 3, or 4 should be present as geometrical isomers, and these isomers, in the absence of rapid isomerization, should be detectable by fluorine n.m.r. spectroscopy. Assuming the square antiprismatic arrangement of ligands found in the crystal for Zr(acac)$_4$,[2] as many as 54 resonance lines can arise from the 27 possible Zr(tfac)$_n$(acac)$_{4-n}$ isomers. Other reasonable geometries also predict complex fluorine n.m.r. spectra. A maximum of four lines in the observed spectra (Figure 1) indicates that rapid intramolecular rearrangement (isomerization) is occurring which averages the environments of the various nonequivalent CF_3 groups in each Zr(tfac)$_n$(acac)$_{4-n}$ molecule. Therefore, each resonance line is assigned to all CF_3 groups in the collection of isomers with the same molecular formula. The lowest field line in Figure 1 is assigned to Zr(tfac)(acac)$_3$. The next three lines, in order of increasing field, are assigned to Zr(tfac)$_2$(acac)$_2$, Zr(tfac)$_3$(acac), and Zr(tfac)$_4$. These assignments are consistent with our quantitative studies of ligand-exchange equilibria.

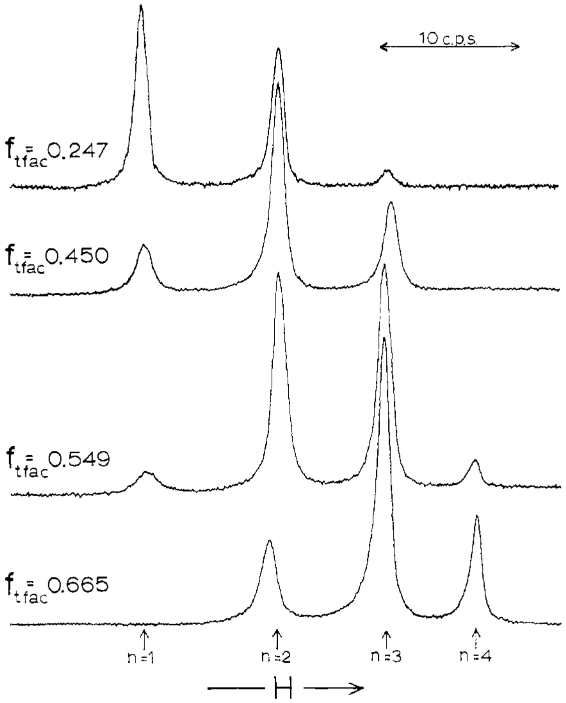

Figure 1.—Fluorine n.m.r. spectra for equilibrium mixtures of Zr(tfac)$_4$ and Zr(acac)$_4$ in benzene solution at 31°; total solute molarity is 0.25 *M*.

We have attempted to observe the geometrical isomers at low temperatures, but without success. Fluorine resonance spectra of Zr(tfac)$_4$ and Ce(tfac)$_4$ in chloroform solution at $-68°$ exhibited only one resonance line. Acetone solutions of Zr(tfac)$_4$, Hf(tfac)$_4$, Ce(tfac)$_4$, and Th(tfac)$_4$ at $-105°$ also showed a single line. Line widths at $-105°$ were *ca.* 3 c.p.s.; at room temperature, *ca.* 1.3 c.p.s.

Fluorine spectra for mixtures of M(tfac)$_4$ and M(acac)$_4$ (M = Hf, Ce, Th) in benzene solution at room temperature are presented in Figure 2. These spectra,

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[12] G. V. D. Tiers, "NMR Summary," Minnesota Mining and Manufacturing Company, St. Paul, Minn., Jan. 15, 1962.

[13] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 458.

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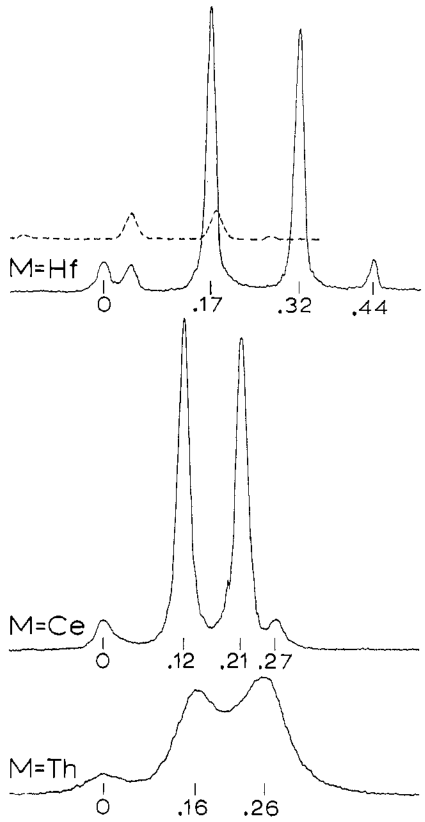

Figure 2.—Fluorine n.m.r. spectra for equilibrium mixtures of $M(tfac)_4$ and $M(acac)_4$ (M = Hf, Ce, Th) in benzene solution at 31°; $f_{tfac} = 0.550$; total solute molarity is 0.25 *M*. Dotted spectrum is spectrum of the mixture of $Zr(tfac)_n(acac)_{4-n}$ which is present as impurities when M = Hf. Spectrum for the cerium system was obtained within 6 min. after dissolution at room temperature. Chemical shifts are reported in p.p.m. relative to $M(tfac)(acac)_3$.

obtained using solutions with a ligand composition $f_{tfac} = 0.550$, exhibit qualitative similarities to the spectrum obtained for the zirconium system at the same composition (Figure 1). The spectrum for the hafnium system, after subtraction of impurity peaks due to zirconium compounds, is essentially identical with the spectrum for the zirconium system. For the cerium system, the differences in the chemical shifts are smaller, and the resonance lines are correspondingly less well resolved. Again, however, four lines are observed with approximately the same relative intensities. For the thorium system, the $Th(tfac)_4$ line is obscured due to extensive line broadening, but the other three lines show relative intensities characteristic of the zirconium system. Therefore, it may be concluded that for mixtures of $M(tfac)_4$ and $M(acac)_4$ in benzene solution, the equilibrium concentrations of $M(tfac)_n(acac)_{4-n}$ complexes are rather similar for M = Zr, Hf, Ce, and Th.

The fluorine spectrum of a mixture of $Th(tfac)_4$ and $Th(acac)_4$ in benzene ($f_{tfac} = 0.550$; total solute molarity = 0.25 *M*) was found to be strongly temperature dependent. Spectra at several selected temperatures are presented in Figure 3. At 6° the spectrum is considerably sharper than at room temperature, and the $Th(tfac)_4$ line appears as a shoulder on the high-field side of the $Th(tfac)_3(acac)$ resonance. As the temperature is increased, the four resonance lines merge into a single broad line; the broad line then sharpens above the coalescence temperature of 43°. The coalescence behavior is attributed to intermolecular ligand exchange which exchanges ligands between molecules with different molecular formulas rapidly enough to average the environments of all CF_3 groups in the entire system.

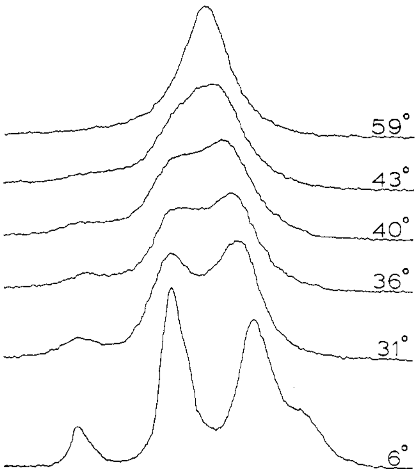

Figure 3.—Fluorine n.m.r. spectra for an equilibrium mixture of $Th(tfac)_4$ and $Th(acac)_4$ in benzene solution at several temperatures near the coalescence region; $f_{tfac} = 0.550$; total solute molarity is 0.25 *M*.

Ligand exchange in benzene solution for the zirconium, hafnium, and cerium systems occurs more slowly than for the thorium system. Spectra of previously unheated solutions[15a] of $Zr(tfac)_4$–$Zr(acac)_4$ and $Hf(tfac)_4$–$Hf(acac)_4$ ($f_{tfac} = 0.550$; total solute molarity = 0.25 *M*) are somewhat broadened but not yet coalesced to a single line at 168°. The coalescence temperature for solutions containing $Ce(tfac)_4$ and $Ce(acac)_4$ ($f_{tfac} = 0.550$; total solute molarity = 0.25 *M*) is greater than 60°.[15b]

Ligand-Exchange Equilibria for the $Zr(tfac)_4$–$Zr(acac)_4$ System.—Ligand-exchange equilibria for the $Zr(tfac)_4$–$Zr(acac)_4$ system were characterized quantitatively in benzene and carbon tetrachloride solutions. These equilibria are established rapidly at room temperature; less than 30 sec. is required for benzene solutions.

The equilibrium molar fractions of total solute as $Zr(tfac)_n(acac)_{4-n}$, $f_{Zr(tfac)_n(acac)_{4-n}} = [Zr(tfac)_n(acac)_{4-n}]/\sum_{n=0}^{4}[Zr(tfac)_n(acac)_{4-n}]$, in benzene solution at 31° are presented in Figure 4 as a function of f_{tfac}, the molar fraction of total ligand as tfac. Theoretical curves which give calculated values of $f_{Zr(tfac)_n(acac)_{4-n}}$ assuming a random statistical distribution of ligands are also included. For a random distribution of ligands, $f_{Zr(tfac)_n(acac)_{4-n}}$ may be calculated

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(15) (a) Heating mixtures of $Zr(tfac)_4$–$Zr(acac)_4$ and $Hf(tfac)_4$–$Hf(acac)_4$ at 155–170° for 50 min. gave decomposition products which lowered the coalescence temperatures. The decomposition products apparently catalyze ligand exchange. (b) Owing to more serious decomposition, the spectrum of $Ce(tfac)_4$–$Ce(acac)_4$ mixtures at 60° is coalesced to a single line after heating for 7 min. at this temperature. At 31° appreciable line broadening can be noted *ca.* 20 min. after preparing solutions.

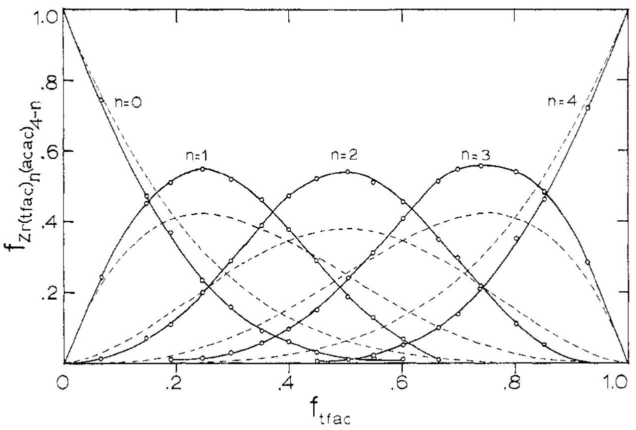

Figure 4.—Ligand-exchange equilibria for the $Zr(tfac)_4$–$Zr(acac)_4$ system in benzene solution at 31°. The molar fraction of total solute as $Zr(tfac)_n(acac)_{4-n}$ at equilibrium, $f_{Zr(tfac)_n(acac)_{4-n}}$, is plotted *vs.* the molar fraction of total ligand as tfac. Total molarity of solute is 0.25 *M*. Solid lines, experimental curves; broken lines, calculated curves assuming a random statistical distribution of ligands.

by application of elementary probability considerations. Following the approach of Calingaert and Beatty,[16] we obtain

$$f_{Zr(tfac)_n(acac)_{4-n}} = (f_{tfac})^n (f_{acac})^{4-n} \frac{4!}{n!(4-n)!}$$

where $f_{acac} = 1 - f_{tfac}$ is the molar fraction of total ligand as acac. This result does not depend on the number of geometrical isomers which may be spanned by the various molecular formulas. It is apparent, upon comparison of the experimental and calculated curves, that the mixed complexes are favored at the expense of $Zr(tfac)_4$ and $Zr(acac)_4$.

The ligand-exchange equilibria may be described by specifying three independent equilibrium quotients. We have chosen the quotients defined by the reactions

$$Zr(acac)_4 + Zr(tfac)_2(acac)_2 \xrightleftharpoons{K_1} 2Zr(tfac)(acac)_3 \quad (1)$$

$$Zr(tfac)(acac)_3 + Zr(tfac)_3(acac) \xrightleftharpoons{K_2} 2Zr(tfac)_2(acac)_2 \quad (2)$$

$$Zr(tfac)_2(acac)_2 + Zr(tfac)_4 \xrightleftharpoons{K_3} 2Zr(tfac)_3(acac) \quad (3)$$

The values of K_2 and K_3 were calculated directly from the relative intensities of observed resonance lines. Since K_1 involves the concentration of $Zr(acac)_4$, which has no fluorine resonance line, its concentration had to be calculated by difference.

TABLE I

DEPENDENCE OF EQUILIBRIUM QUOTIENTS FOR THE $Zr(tfac)_4$–$Zr(acac)_4$ SYSTEM ON SOLUTE COMPOSITION[a]

	Average values of equilibrium quotients[b]		
f_{tfac}	K_1	K_2	K_3
0.149	6.1 ± 0.3[c]	...	...
0.191	6.3 ± 0.5	...	...
0.247	6.3 ± 0.5	...	...
0.297	5.9 ± 0.3	5.5 ± 0.4	...
0.353	5.9 ± 1.0	5.9 ± 0.5	...
0.399	...	6.0 ± 0.3	...
0.450	...	6.1 ± 0.2	...
0.506	...	6.5 ± 0.8	...
0.549	...	6.5 ± 0.8	7.9 ± 0.5
0.603	...	...	7.0 ± 0.3
0.665	...	...	7.5 ± 0.2
0.699	...	...	7.2 ± 0.4
0.741	...	...	6.7 ± 0.2
0.803	...	...	7.6 ± 0.4
Mean of all spectral measurements	6.09 ± 0.21	6.08 ± 0.20	7.23 ± 0.17
Statistical equilibrium quotients	2.67	2.25	2.67

[a] Benzene solution, 31°; total molarity of solute is 0.25 *M*. [b] Average of at least five spectral measurements. [c] All errors are estimated at the 95% confidence level.

TABLE II

DEPENDENCE OF EQUILIBRIUM QUOTIENTS FOR THE $Zr(tfac)_4$–$Zr(acac)_4$ SYSTEM ON TOTAL SOLUTE CONCENTRATION[a]

	Average values of equilibrium quotients[b]		
Total molarity	K_1[c]	K_2[d]	K_3[e]
0.420	6.4 ± 1.0[f]	6.1 ± 0.3	6.9 ± 0.7
0.336	6.3 ± 0.8	5.6 ± 0.4	6.9 ± 0.3
0.252	6.1 ± 0.9	5.9 ± 0.5	7.5 ± 0.2
0.210	6.1 ± 0.6	5.9 ± 0.4	6.5 ± 0.2
0.168	6.7 ± 0.4	5.7 ± 0.4	6.2 ± 0.9
0.126	6.1 ± 0.6	5.7 ± 0.2	6.7 ± 0.3
0.105	6.3 ± 0.5	5.7 ± 0.4	7.3 ± 0.5
0.084	...	5.7 ± 0.4	7.4 ± 0.3
0.063	...	6.6 ± 1.3	7.5 ± 0.5
0.053	...	5.8 ± 0.8	7.6 ± 0.6
0.042	...	...	7.5 ± 0.8
0.032	...	...	7.3 ± 0.6
0.026	...	...	7.0 ± 0.4
0.021	...	...	7.6 ± 0.4
Mean of all spectral measurements	6.27 ± 0.20	5.86 ± 0.13	7.13 ± 0.14
Statistical equilibrium quotients	2.67	2.25	2.67

[a] Benzene solution, 31°. [b] Average of at least five spectral measurements. [c] f_{tfac} = 0.263. [d] f_{tfac} = 0.410. [e] f_{tfac} = 0.665. [f] All errors are estimated at the 95% confidence level.

Within experimental error, the equilibrium quotients in benzene at 31° were independent of both ligand composition and total solute concentration. The results, summarized in Tables I and II, indicate that activity coefficient quotients are constant for the range of compositions and concentrations studied. All three equilibrium quotients are *ca.* 2.5 times larger than expected on the basis of a random statistical distribution of ligands. Assuming that the entropy changes for the reactions are those expected for a statistical ligand distribution, the somewhat high equilibrium quotients could be accounted for if the reactions are exothermic to the extent of 0.5–0.6 kcal./mole.

In order to explore this possibility, the temperature dependence of the equilibrium quotients was studied. The results[17] are presented in Table III. Enthalpies were obtained from log *K vs.* 1/*T* plots. The data were treated by least-squares analysis including five data points at each temperature. From the least squares straight lines, free energies and entropies at

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(16) G. Calingaert and H. A. Beatty, *J. Am. Chem. Soc.*, **61**, 2748 (1939).

(17) As the temperature of the solutions increased, the spectral signal-to-noise ratio decreased; in addition, resonance lines began to overlap due to decreasing chemical shifts. These two factors determined the maximum temperature at which equilibrium data could be extracted from the spectra.

TABLE III

TEMPERATURE DEPENDENCE OF EQUILIBRIUM QUOTIENTS FOR THE $Zr(tfac)_4$–$Zr(acac)_4$ SYSTEM IN BENZENE[a]

Temp., °C.	Average values of equilibrium quotients[b]		
	K_1[c]	K_2[d]	K_3[e]
7.5	6.4 ± 0.8[f]	6.7 ± 0.4	7.0 ± 0.4
18.5	6.1 ± 0.8	6.4 ± 0.5	6.9 ± 0.8
31.2	6.7 ± 0.7	6.5 ± 0.5	7.1 ± 0.7
41.0	7.1 ± 0.9	6.2 ± 0.2	6.8 ± 0.2
53.1	5.9 ± 0.6	6.1 ± 0.9	6.9 ± 0.9
63.9	...	6.4 ± 0.4	6.8 ± 0.4
77.8	...	6.7 ± 0.3	...

[a] Total molarity of solute is 0.25 *M*. [b] Average of five spectral measurements. [c] $f_{\text{tfac}} = 0.262$. [d] $f_{\text{tfac}} = 0.411$. [e] $f_{\text{tfac}} = 0.665$. [f] All errors are estimated at the 95% confidence level.

TABLE IV

THERMODYNAMIC DATA FOR THE $Zr(tfac)_4$–$Zr(acac)_4$ SYSTEM IN BENZENE SOLUTION AT 25°

Reaction	ΔH, kcal./mole	ΔF, kcal./mole	ΔS, e.u.	Statistical ΔS, e.u.
1	0.05 ± 0.54[a]	−1.10 ± 0.14	3.4 ± 1.8	1.95
2	−0.05 ± 0.18	−1.10 ± 0.08	3.5 ± 0.7	1.61
3	0.02 ± 0.26	−1.15 ± 0.09	3.9 ± 0.9	1.95

[a] All errors are estimated at the 95% confidence level.

TABLE V

TEMPERATURE DEPENDENCE OF EQUILIBRIUM QUOTIENTS FOR THE $Zr(tfac)_4$–$Zr(acac)_4$ SYSTEM IN CARBON TETRACHLORIDE

Temp., °C.	Average values of equilibrium quotients[a]		
	K_1[b]	K_2[c]	K_3[d]
−18.5	5.9 ± 0.5[e]	5.4 ± 0.3	8.8 ± 0.7
−7.8	5.7 ± 1.2	6.4 ± 0.4	8.1 ± 1.3
7.2	6.0 ± 0.7	7.0 ± 0.4	7.7 ± 0.9
20.7	...	6.3 ± 0.4	7.4 ± 1.0
31.7	5.9 ± 0.6	6.0 ± 0.8	8.0 ± 1.1
41.0	5.8 ± 0.9	6.1 ± 0.5	7.6 ± 1.1
51.6	5.6 ± 0.1	6.9 ± 0.9	8.1 ± 0.8
63.4	5.5 ± 0.5	6.5 ± 0.5	...
79.8	5.6 ± 1.1	...	...

[a] Average of five spectral measurements. [b] $f_{\text{tfac}} = 0.260$; total molarity of solute is 0.251 *M*. [c] $f_{\text{tfac}} = 0.410$; total molarity of solute is 0.200 *M*. [d] $f_{\text{tfac}} = 0.670$; total molarity of solute is 0.100 *M*. [e] All errors are estimated at the 95% confidence level.

25° were calculated. The experimental values are collected in Table IV along with values of ΔS calculated for a random statistical distribution of ligands. Within experimental error, the enthalpy changes for all three reactions are zero. Moreover, with the possible exception of reaction 1, the values of the confidence level estimates of error indicate that deviations of the observed equilibrium quotients from statistical values cannot be accounted for by enthalpy changes. The driving force for reactions 2 and 3 involves an entropy change which, even at the lower 95% confidence limit, is more than 1 e.u. in excess of that expected for a random scrambling of ligands.

TABLE VI

THERMODYNAMIC DATA FOR THE $Zr(tfac)_4$–$Zr(acac)_4$ SYSTEM IN CARBON TETRACHLORIDE SOLUTION AT 25°

Reaction	ΔH, kcal./mole	ΔF, kcal./mole	ΔS, e.u.	Statistical ΔS, e.u.
1	−0.10 ± 0.19[a]	−1.03 ± 0.13	3.1 ± 0.8	1.95
2	0.25 ± 0.18	−1.09 ± 0.11	4.5 ± 0.7	1.61
3	−0.20 ± 0.25	−1.22 ± 0.13	3.4 ± 0.9	1.95

[a] All errors are estimated at the 95% confidence level.

Equilibrium quotients and thermodynamic data for the $Zr(tfac)_4$–$Zr(acac)_4$ system in carbon tetrachloride solution are presented in Tables V and VI. As was found for benzene solutions, the equilibrium quotients are two to three times larger than the random statistical values. Deviations from the statistical values cannot be accounted for in terms of the enthalpy changes, which are zero or nearly zero. The observed entropy changes are 1–3 e.u. in excess of the entropy changes expected for random scrambling of ligands.

In recent studies of monodentate ligand-exchange reactions on a variety of central atoms, Van Wazer and co-workers[18] have assumed that entropy changes can be attributed to randomization of ligands and that deviations of observed equilibrium quotients from statistical values are due to enthalpy changes. Although enthalpy terms probably make the major contribution to nonrandom behavior in cases where deviations from randomness are very large (*cf.* calorimetric data in ref. 18a and 18d), the present study indicates that entropy terms cannot be neglected in cases where deviations from random scrambling are less pronounced. The desirability of experimentally measuring enthalpy and entropy contributions in studies of ligand-exchange equilibria is to be emphasized.

It is suggested that the nonrandom entropy changes observed in the present work may arise from a difference in the solvation entropies of reactants and products. Solvation entropies for metal diketone complexes are not available, but the entropy of solution data reported by Jones and co-workers[19] suggest that it is not unreasonable to attribute entropy changes of 1–3 e.u. to solvation effects in benzene and carbon tetrachloride solutions. For benzene solutions, nonrandom solvation is indicated by proton chemical shift data.

N.m.r. Chemical Shifts.—Proton and fluorine chemical shift data for the trifluoroacetylacetonates and acetylacetonates of zirconium, hafnium, cerium, and thorium in carbon tetrachloride, chloroform, and benzene solutions are presented in Table VII. Data for the enol form of the β-diketones are included for comparison. The proton shifts for $Zr(tfac)_4$ and $Ce(tfac)_4$ in chloroform and benzene were investigated as a function of solute concentration in the range 1.3 to 10.0 g./100 ml. The concentration dependence was less than 0.02 p.p.m.

The proton shifts for the trifluoroacetylacetonates are about the same in carbon tetrachloride and chloroform. In benzene, however, the methyl resonances are shifted upfield by *ca.* 0.59 p.p.m.; the —CH= protons are

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(18) (a) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 139 (1964); (b) K. Moedritzer and J. R. Van Wazer, *ibid.*, **3**, 268 (1964); (c) M. D. Rausch and J. R. Van Wazer, *ibid.*, **3**, 761 (1964); (d) J. R. Van Wazer and L. Maier, *J. Am. Chem. Soc.*, **86**, 811 (1964); (e) K. Moedritzer and J. R. Van Wazer, *ibid.*, **87**, 2360 (1965).

(19) M. M. Jones, J. L. Wood, and W. R. May, *J. Inorg. Nucl. Chem.*, **23**, 305 (1961); M. M. Jones, A. T. Davila, J. E. Hix, Jr., and R. V. Dilts, *ibid.*, **25**, 369 (1963).

TABLE VII

CHEMICAL SHIFTS FOR THE TRIFLUOROACETYLACETONATES AND ACETYLACETONATES OF SOME GROUP IVb METALS[a]

	Carbon tetrachloride			Chloroform			Benzene		
	—CH=	—CH_3	—CF_3	—CH=	—CH_3	—CF_3	—CH=	—CH_3	—CF_3
H(tfac) (enol form)	−5.88	−2.21	3.89	−5.92	−2.22	3.93	−5.32	−1.38	3.84
Zr(tfac)$_4$	−5.97	−2.19	2.85	−5.99	−2.15	2.91	−5.76	−1.61	2.68
Hf(tfac)$_4$	−5.95	−2.18	3.01	−5.97	−2.15	3.05	−5.74	−1.61	2.82
Ce(tfac)$_4$	−5.80	−2.20	2.37	−5.81	−2.16	2.43	−5.56	−1.56	2.23
Th(tfac)$_4$[b]	−5.93	−2.20	2.96	−5.93	−2.15	3.02	−5.71	−1.55	2.81
H(acac) (enol form)	−5.39	−1.99	...	−5.51	−2.04	...	−5.03	−1.65	...
Zr(acac)$_4$	−5.37	−1.90	...	−5.48	−1.92	...	−5.36	−1.82	...
Hf(acac)$_4$	−5.34	−1.89	...	−5.46	−1.92	...	−5.34	−1.83	...
Ce(acac)$_4$	−5.21	−1.89	...	−5.31	−1.91	...	−5.15	−1.76	...
Th(acac)$_4$	−5.34	−1.91	...	−5.44	−1.93	...	−5.29	−1.77	...

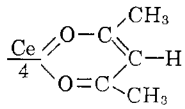
[a] Proton shifts are in p.p.m. relative to an internal reference of TMS (1% by volume). Fluorine shifts are in p.p.m. relative to an external reference of *cis*-Rh(tfac)$_3$ in the same solvent. Concentration of the *cis*-Rh(tfac)$_3$ reference in CCl_4, $CHCl_3$, and C_6H_6 is 3.0, 11.4, and 11.4 g./100 ml. of solvent, respectively. Concentration of compounds in CCl_4, $CHCl_3$, and C_6H_6 is 3.0, 10.0, and 10.0 g./100 ml. of solvent, respectively, unless noted otherwise. Temperature 35° (H^1), 31° (F^{19}). [b] Shifts measured using saturated solutions in CCl_4 (*ca.* 0.5 g./100 ml. of solvent) and $CHCl_3$ (*ca.* 8.5 g./100 ml. of solvent).

shifted in the same direction by *ca.* 0.23 p.p.m. For trifluoroacetylacetone, the corresponding upfield shifts of *ca.* 0.84 and 0.58 p.p.m. are even larger. Although there are large upfield shifts for acetylacetone in benzene, the analogous shifts for the metal acetylacetonates are much less pronounced.

These data indicate that the protons of metal diketonates experience the diamagnetic anisotropy of the benzene rings to a greater extent than does the TMS reference. Apparently the solvating benzene molecules prefer orientations which lead to diamagnetic shielding at the methyl and —CH= protons; this effect is enhanced by the presence of trifluoromethyl groups, probably due to a dipole–induced dipole mechanism as suggested by Schneider for interaction of certain polar solutes with aromatic solvents.[20] The especially large upfield shifts for the free diketones probably result from a sandwiching of the planar enol molecules between the benzene molecules. The chemical shift data support the notion that the ΔS values for the ligand-exchange reactions may involve significant contributions from entropies of solvation.

Another interesting feature of the chemical shift data concerns the proton shifts for the cerium compounds. For spectra obtained in the same solvent, the position of the methyl resonance is nearly independent of the nature of the metal ion. The same is true for the —CH= resonance with the exception of the cerium complexes. For both Ce(tfac)$_4$ and Ce(acac)$_4$ in carbon tetrachloride, chloroform, and benzene, the —CH= resonance is shifted upfield by *ca.* 0.16 p.p.m. relative to the corresponding zirconium, hafnium, and thorium compounds. We have demonstrated that the shifts are not due to small amounts of paramagnetic cerium(III) diketone complexes which might be present as low-concentration impurities. Upon addition of appreciable amounts of the cerium(III) complexes to freshly-prepared solutions of Ce(tfac)$_4$ and Ce(acac)$_4$, the —CH= chemical shifts are changed by no more than 0.02 p.p.m. In view of the fact that zirconium, cerium, and thorium acetylacetonates have the same molecular geometry in the solid state, although not the same packing arrangements,[2-4] it is rather unlikely that the differences in chemical shifts result from different molecular geometries in solution.

In contrast to zirconium, hafnium, and thorium, cerium(IV) is easily reduced to the +3 oxidation state. Therefore, the metal–diketonate bonds are expected to be more covalent in the case of the cerium complexes. Increased covalency can result from partial transfer of σ electrons and/or π electrons from the diketonate anion to cerium(IV). Ligand→metal π bonding increases the contribution of the benzenoid resonance structure



which may or may not give rise to appreciable benzenoid interatomic ring currents. It is not yet clear how large a ring current one should expect for a heterocyclic system containing atoms of such widely different electronegativities; however, the ring current is almost certain to be less than in benzene. We find no evidence for an enhancement of interatomic ring currents in the cerium complexes since the observed shifts for the —CH= proton of the cerium compounds are upfield; interatomic ring currents predict a downfield shift.

Enhancement of the two types of metal–ligand covalency (σ and π) produce opposite effects on the chemical shift of the —CH= ring proton. Ligand→cerium σ bonding should shift the —CH= resonance downfield. Partial transfer of π electrons from the diketonate anion to cerium should decrease the magnetic anisotropy of the diketonate anion, thus decreasing the local field at the —CH= proton and shifting the resonance upfield. Apparently the latter π effect is the more important.

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Proton Magnetic Resonance Study of β-Diketones and Its Application to Thermodynamic Formation Constants of Various β-Diketone Metal Chelats.

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The proton magnetic resonance spectra of sixteen β-diketones were determined. The position and character of the chemical shift for the enolic hydrogen is dependent upon the nature of the substituent group at the 1 or 3 position. There is a correlation between the dissociation constant, K_d, of the β-diketone and the position of its enolic hydrogen magnetic resonance absorption peak. A correlation also exists between the position of this peak and the thermodynamic formation constants of the β-diketone metal chelates. The character of this peak is discussed in terms of the effects which substituents might have on the intramolecular hydrogen bond. There is strong evidence that in phenyl-substituted β-diketones the phenyl group is acting as an electron-supplying group.

Inasmuch as the basicities of the β-diketones are important in determining the stabilities of their chelates, it is of interest to determine whether a useful relationship exists between basicities and spectral data. In this paper the chemical shift of the β-diketone enolic hydrogen is compared with the pK_d of the β-diketone. The values of pK_d have been determined potentiometrically by Van Uitert.[1,2] The β-diketone enolic hydrogen chemical shift is also compared with the thermodynamic formation constants of numerous β-diketone chelates. The latter relationship is believed to be the first direct correlation between proton magnetic resonance data and chelate stability to appear in the literature.

The enolic form of a β-diketone contains a strong intramolecular hydrogen bond. Infrared spectra have been used to estimate the length of this bond.[3,4] Proton magnetic resonance should also be well suited for the study of the hydrogen bond. It was observed that the width of the magnetic resonance peak for the enolic proton varied greatly depending upon the groups substituted at the 1, 2, or 3 position. This peak width was used to draw conclusions about the placement of the enolic hydrogen between the two oxygens.

Recently, Burdett and Rogers[5] have stated that in phenyl-substituted β-diketones the phenyl ring is at no time coplanar with the enolic ring. Hence, they state that the only effect of the phenyl group is electron withdrawal by induction. The data given in the present article, however, seem to support the conclusion that the phenyl group is electron-supplying through resonance.

Experimental Section

All proton magnetic resonance spectra were obtained in 2.0 *M* solutions using reagent grade carbon tetrachloride as solvent.[6] A Varian A60 nuclear magnetic resonance spectrophotometer was employed. All resonance peaks are referred to tetramethylsilane (TMS) as an internal reference with $\delta = 0$ p.p.m.

The following β-diketones were obtained from commercial sources: 1,3-diphenyl-1,3-propanedione, 1-phenyl-1,3-butanedione, 2,4-pentanedione, 1,1,1-trifluoro-3-(2-thienyl)-2,4-butanedione, 1,1,1-trifluoro-2,4-pentanedione, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 2-furoylperfluorobutyrylmethane, 2-thenoylperfluorobutyrylmethane, and 6-methyl-2,4-heptanedione.

The β-diketones listed in Table I were synthesized by condensing the appropriate ethyl ester and methyl ketone using sodium amide as the basic condensing agent. The method of preparation is described by Levine, *et al.*[7]

All the β-diketones were sufficiently pure so that no extraneous, unidentifiable peaks occurred in the proton magnetic resonance spectra.

The 3-phenyl-2,4-pentanedione was prepared by other workers[8] in this laboratory by the method[9] described below. The

$$C_6H_5CH_2COCH_3 + (CH_3CO)_2O \xrightarrow{BF_3} CH_3CO\underset{\underset{C_6H_5}{|}}{C}HCOCH_3 + CH_3COOH$$

procedure is similar to the one submitted by Denoon[9] with a modified purification method. Phenyl acetone (134 g., 1.0 mole) and acetic anhydride (55 g., 2.5 moles) are placed in a three-necked flask. The mixture is cooled in an ice bath. An inlet tube which goes below the surface of the mixture is attached to one neck of the flask through which the boron trifluoride will

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