the pseudo-tetrahedral complexes have bands at 8700–10,000 and 12,800–13,800 cm^{-1}, which they assigned on the basis of their frequencies and relatively low intensities to crystal-field transitions of the copper(II) ion in a pseudo-tetrahedral environment. The spectra of the above biquinolyl complexes are similar to those of these known pseudo-tetrahedral complexes.

Magnetism.—The magnetic data for the copper(II) 2,2′-biquinolyl complexes are presented in Table I. The measurements were performed over a temperature range of ~80–400°K and the compounds obey the Curie–Weiss law with small values of θ in the range 0 to $-8°$. The moments of the compounds lie in the range 1.9–2.0 BM and are comparable with those reported for other pseudo-tetrahedral copper(II) compounds.[15-19] Although a room-temperature moment of ~2.2 BM has been predicted for copper(II) in a tetrahedral environment,[20] distortions can appreciably lower it if the low-symmetry ligand fields produced are large compared to spin–orbit coupling. In related complexes there is some evidence for a correlation between the magnitude of the moment and distortions from planar toward tetrahedral symmetry. For example, the $CuCl_4^{2-}$ ion is planar in the compound $[Pt(NH_3)_4][CuCl_4]$ and $\mu = 1.77$ BM compared with the value of 2.0 BM in Cs_2CuCl_4, where the ion is present in the form of a flattened tetrahedron.[21] Similarly, Sacconi, Ciampolini, and Campigli[14] have commented on the fact that the magnetic moments (1.90–1.92 BM) of the distorted tetrahedral N-*sec*-alkylsalicylaldiminocopper(II) complexes are slightly higher than those (1.85–1.86 BM) of the N-*n*-alkyl-substituted planar compounds. The moments in the biquinolyl series $Cu(biq)X_2$ ($X = NO_3$, Cl, Br) steadily increase from 1.93 to 2.02 BM and the highest moment is associated with the dibromo complex, which is expected to show the greatest deviation from a planar arrangement of the two nitrogen and two halogen atoms.

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Rare Earth Chelates of 1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-4,6-octanedione[1,2]

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Received January 15, 1967

Fifteen chelates of the ligand 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, H(fod), with trivalent rare earth metal ions have been synthesized and investigated. The tris chelates are more volatile than any other known lanthanide compounds. The complexes have been characterized by their elemental analyses, infrared and nuclear magnetic resonance spectra, melting points, molecular weights, and Karl Fischer titrations. All of the complexes [except that of Sc(III), which is anhydrous] are isolated as monohydrates which can be easily dehydrated *in vacuo* over P_4O_{10}. The complexes have been studied by gas chromatography and thermogravimetric analysis. The results indicate an increase in volatility with a decrease in the radius of the central metal ion.

Introduction

Of the many rare earth chelates of β-diketones that have been described[4-7] the tris complexes generally have the most promising properties necessary for gas chromatographic elution, *i.e.*, thermal and solvolytic stability and volatility. However, the prevalence of hydration in compounds of this type seems to produce undesirable effects on the thermal stability in many cases[8-10] and attempts to elute neodymium(III) trifluoroacetylacetonate dihydrate, $Nd(tfa)_3 \cdot 2H_2O$, were unsuccessful.[11] Recently, however, Eisentraut and Sievers have used a sterically crowded ligand to preclude the formation of hydrated complexes,[12] a possibility that was suggested by Brown, Steinbach, and Wagner.[13]

It has been well demonstrated that the incorporation of fluorocarbon moieties in the ligand enhances the

(1) Abstracted in part from a thesis submitted by C. S. Springer, Jr., to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

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volatility of the resulting complex.[14,15] In order to combine the advantages gained by the substitution of fluorine and sterically crowded groups, 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, H(fod), was synthesized. The results of the investigation of 15 complexes of trivalent rare earth metal ions with this bulky fluorinated ligand are reported herein.

Experimental Section

Synthesis of 1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-4,6-octanedione, H(fod).—The β-diketonic ligand H(fod) was synthesized by a Claisen condensation[16] of ethyl heptafluorobutyrate with pinacolone.

A 2000-ml three-necked round-bottomed flask was flushed with nitrogen and fitted with a drying tube filled with Drierite. Sodium methoxide (0.2 mole, 10.87 g) (Matheson Coleman and Bell) was suspended in 150 ml of absolute diethyl ether (Mallinckrodt). Ethyl heptafluorobutyrate (0.2 mole, 48.42 g) (Peninsular ChemResearch, Inc.) was added dropwise to the stirred mixture over a period of 1 hr from a stoppered pressure-equalizing addition funnel, whereupon a cream-colored slurry resulted. A solution of pinacolone (0.2 mole, 20.04 g) (Matheson Coleman and Bell) in 50 ml of absolute diethyl ether was added from the funnel over a period of 0.5 hr. When the addition was half complete, a clear yellow solution was present in the flask. This solution was basic (pH paper) after complete addition of pinacolone. It was stirred for 2 hr and then allowed to stand overnight. Sulfuric acid (100 ml, 2 *M*) was slowly added with stirring to the ether solution. The aqueous phase generated was basic (pH paper) until all of the acid was added. The aqueous layer was separated and washed with fresh diethyl ether. The washings were combined with the original yellow organic layer; and, after partial evaporation under a stream of air, the solution was vacuum distilled in a 12-in. Vigreux column. The nmr spectrum of a middle fraction collected at 28° (1.7 mm) showed that the H(fod) was contaminated with pinacolone. The amount of H(fod) was estimated to be 32 g (55% of theoretical). The fraction collected was colorless but soon turned orange. A second distillation yielded a colorless fraction, with a pungent odor, boiling at 33° (2.7 mm), which was pure H(fod). *Anal.* Calcd for H(fod), $C_{10}H_{11}F_7O_2$: C, 40.55; H, 3.75; F, 44.90. Found: C, 40.51; H, 3.59; F, 45.02.

The ^{1}H nuclear magnetic resonance spectrum of the neat liquid showed no detectable amount of pinacolone and revealed that the pure compound is completely enolized [singlet peaks at 1.23 ($C(CH_3)_3$, relative area 9.00), 6.09 (CH, relative area 0.96), and 14.76 ppm (OH, relative area 0.93) downfield from the internal standard tetramethylsilane]. The ^{19}F nuclear magnetic resonance spectrum of the neat liquid confirmed the straight-chain structure of the perfluoropropyl group [a triplet at 3.6 ($\mathit{CF_3}CF_2$, relative area 3, coupling constant 8.5 cps), a quartet at 44.5 ($CF_2\mathit{CF_2}CO$, relative area 2, coupling constant 8.5 cps), and a singlet at 50.0 ppm ($CF_3\mathit{CF_2}CF_2$, relative area 2) upfield from the external standard trifluoroacetic acid]. The lack of observable spin–spin coupling between vicinal atoms is not uncommon for ^{19}F nuclei.[17] The colorless product darkens upon standing for several days (even when stored in a dark bottle) but no decomposition products can be detected in the proton nmr spectrum.

Syntheses of the Monoaquo Tris fod Complexes of the Lanthanide(III) and Y(III) Ions.—The hydrated rare earth(III) nitrate was prepared as described before[12] with the modification that, after dissolution of the metal oxide in concentrated HNO_3, the solvent (and HNO_3) was removed with a rotary evaporator. This provides a rapid means of obtaining the crystalline nitrates for the metals Tb through Lu and Y. For the metals La through Gd, a glassy form of the nitrate, which can be crushed with a spatula and collected, is obtained. The hydrated rare earth(III) nitrate (0.011 mole) was dissolved in the minimum amount of absolute methanol (Matheson Coleman and Bell), and the pH of the resulting solution was adjusted (between 4 and 6 as indicated by pH paper) by adding the required amount of a solution of 4.12 *M* aqueous NaOH. A solution of H(fod) (0.033 mole) in approximately 20 ml of absolute methanol was neutralized with 8.01 ml of 4.12 *M* sodium hydroxide solution. Addition of an excess of sodium hydroxide or the use of a more concentrated basic solution was avoided in order to preclude hydrolysis of the ligand. Upon addition of the first portion of the aqueous NaOH solution, the formerly homogeneous solution separated into two phases, because the unneutralized H(fod) is insoluble in the resulting solvent mixture. When an equivalent amount of base had been added, the solution became homogeneous. The two solutions were then mixed with a magnetic stirrer, and a small amount of white $NaNO_3$ precipitated immediately. The resulting mixture was added dropwise over a period of approximately 2 hr to *ca.* 400 ml of distilled water which was stirred vigorously. The solid complex precipitated, and the mixture was stirred until the precipitate was in the form of fine granules. A stirring rod was used during the precipitation to crush the granules and prevent coagulation into a tar. The final methanol concentration was kept very low to minimize the possibility of oiling. The suspended precipitate was isolated by suction filtration and air dried for approximately 1 hr.

The yields of the crude products ranged from *ca.* 74% to essentially quantitative and averaged *ca.* 87%.

The crude products were recrystallized twice by dissolving them in the minimum amount of methylene chloride (Baker Analyzed or MCB Spectroquality) at room temperature and cooling the solutions to <0°. The compounds were dried *in vacuo* (at room temperature) for *ca.* 12 hr between recrystallizations. The analytical data for the monoaquo complexes so obtained are given in Table I.

Synthesis of the Anhydrous Tris fod Complex of Sc(III).—The Sc(III) complex is obtained as a light yellow oil from the above procedure. *Anal.* Calcd for $Sc(fod)_3$, $ScC_{30}H_{30}F_{21}O_6$: C, 38.72; H, 3.25; F, 42.88; Sc, 4.83. Found: C, 38.89; H, 3.10; F, 42.82; Sc, 5.67.

Syntheses of the Anhydrous Tris fod Complexes of the Lanthanide(III) and Y(III) Ions.—All of the monohydrated complexes were dehydrated by storing in a vacuum desiccator at less than 1 mm over P_4O_{10} at room temperature for a few days. The anhydrous complexes were characterized by Karl Fischer titrations. They contained less than the minimum measurable amount of water, which averaged 0.3% for the sample sizes used. The elemental microanalyses of the anhydrous dysprosium complex are given. *Anal.* Calcd for $Dy(fod)_3$, $DyC_{30}H_{30}F_{21}O_6$: C, 34.38; H, 2.89; F, 38.07; Dy, 15.50; mol wt, 1048. Found: C, 34.40; H, 2.94; F, 37.94; Dy, 15.43; mol wt, 1030 (in $CHCl_3$).

All elemental analyses and molecular weight determinations were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The Karl Fischer titrations were carried out with a Beckman Model KF-2 Aquameter using anhydrous methanol (Matheson Coleman and Bell) as the solvent. Commercial premixed Karl Fischer reagent (Harleco) was used as the titrant, sodium tartrate dihydrate (Fisher Certified) as the primary standard, and commercial Karl Fischer Water Standard (Harleco) as the secondary standard.

Infrared and Nuclear Magnetic Resonance Spectra.—The infrared spectra were obtained with a Perkin-Elmer Infracord. Powdered samples of the hydrated chelates were suspended in a KBr matrix. Proton nmr spectra were obtained on a Varian Model A-60 spectrometer. Samples of the anhydrous diamagnetic fod chelates were dissolved in Silanar-C ($CDCl_3$ with internal TMS) (Merck) which had been dried over Linde molecu-

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TABLE I

ANALYTICAL DATA FOR $Ln(fod)_3 \cdot H_2O$ COMPLEXES[a]

		% C		% H		% F		% Ln		% H_2O		Mol wt	
Ln(III)	Color	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found[b]	Calcd	Found[c]
Lu	White	33.41	33.40	2.99	2.97	36.99	36.86	16.22	16.34	1.67	1.4 ± 0.4	1079	1070
Yb	White	33.47	33.53	3.00	3.06	37.06	37.28	16.07	16.25			1077	1065
Tm	White	33.60	33.31	3.01	2.94	37.20	37.04	15.75	15.68			1072	1060
Er	Pink	33.65	33.83	3.01	3.13	37.26	37.38	15.62	15.73			1071	1059
Y	White	36.30	36.16	3.25	3.21	40.20	40.05	8.96	8.92			992	990
Ho	Beige	33.72	33.56	3.02	3.10	37.34	37.36	15.44	15.30	1.69	2.0 ± 0.3	1068	1060
Dy	White	33.80	33.53	3.02	3.09	37.43	37.64	15.24	15.44	1.69	2.0 ± 0.3	1066	1054
Tb	White[d]	33.91	34.17	3.04	3.16	37.55	37.37	14.96	15.15			1062	1058
Gd	White	33.97	33.73	3.04	3.09	37.61	37.70	14.82	14.92			1061	1060
Eu	White[e]	34.13	33.92	3.06	3.06	37.80	37.63	14.40	14.49			1056	1050
Sm	White	34.19	34.36	3.06	3.11	37.86	37.61	14.26	14.43			1054	1049
Nd	Blue	34.39	34.42	3.07	3.18	38.08	38.21	13.77	13.83			1048	1042
Pr	Green	34.49	34.64	3.08	3.19	38.20	38.08	13.49	13.31			1044	1050
La	White	34.56	34.36	3.09	3.03	38.27	38.11	13.32	13.46	1.73	1.8 ± 0.7	1042	1020

[a] All samples, except the lanthanum complex, were vacuum pumped over silica gel for 4 hr immediately before analysis. [b] Percentage of water was determined by Karl Fischer titration. [c] Molecular weights were determined in chloroform. [d] The Tb complex fluoresces with a green color upon irradiation with ultraviolet light at 3660 A. [e] The Eu complex fluoresces with an intense red color upon irradiation with ultraviolet light at 3660 A.

lar sieves No. 13X [concentration, ~30% (w/v)]. The ^{19}F spectrum of H(fod) was obtained on a Varian Model V-4300-2 high-resolution spectrometer at 40 Mc by Messrs. J. E. Strobel and J. V. Pustinger of the Monsanto Research Corp. (Dayton Laboratory).

Gas Chromatography.—The gas chromatographic data were obtained on an F & M Model 810 research chromatograph. The column was constructed of Teflon (Du Pont) tubing of 4.5-mm i.d. The column packing was 14 cm long and consisted of 10% (w/w) SE-30 (a poly(dimethylsiloxane) supplied by General Electric) on Chromosorb W (Applied Science). The carrier gas was helium which had been passed through molecular sieves at a flow rate of 100 ml/min. The temperatures employed were: column, 171°; thermal conductivity detector, 227°; injection port, 230°. Saturated solutions of the anhydrous fod chelates in benzene (which had been dried over No. 13X molecular sieves) were injected with a microsyringe. Sample sizes ranged from 0.1 to 2 μl. The injection port was lined with a glass insert in order to reduce contact of the sample with the hot metal walls. The eluted substances were trapped at the exit port and shown to be identical with the original samples by infrared and melting point studies.

Thermogravimetric Analyses.—A Du Pont Model 950 thermogravimetric analyzer was used to obtain all thermogravimetric data. The atmosphere over the sample was helium gas (purified by passing through molecular sieves), and the flow rate was held constant throughout all experiments at 60 ml/min. The sample heating rate was 10°/min, and efforts were made to keep the sample masses used as nearly the same as possible to maximize comparability.

Results

Chelates of the trivalent rare earth ions with 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, H(fod), were isolated as the monohydrated species from the procedure outlined above. Karl Fischer titrations have been used to measure the amount of water associated with the complexes. This technique was applied to β-diketonate complexes of rare earth ions by Wagner[18] and is particularly effective for studying complexes of this type. Most of the other possible analytical methods are relatively insensitive to the amount of water present. Consequently, many of the assignments of the extent of hydration in the older literature must be considered questionable. The elemental analyses of the compounds reported in this paper fully support the Karl Fischer data. The presence of water is also confirmed by the infrared spectra, which are almost identical for all of the monohydrated complexes. The peak positions and band intensities for $Lu(fod)_3 \cdot H_2O$ are given in Table II. The broad peak at 3400 cm^{-1} undoubtedly arises from an OH stretch due to the water present.

TABLE II

INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTRA FOR $Ln(fod)_3$ COMPLEXES[a]

Infrared spectrum of $Ln(fod)_3 \cdot H_2O$.[b] cm^{-1}

3400	m, b	1380	m, sh	1070	m
2950	m	1350	s	1030	w
1620	s	1290	m	970	m
1600	s, sh	1230	s, b	940	w
1530	m, sh	1190	s, sh	910	m
1500	s	1160	s, sh	835	m
1480	s	1120	s	800	m
1390	m	1110	m, sh	750	m

Nmr spectra of $Ln(fod)_3$ complexes[c]

Ln(III)	For *t*-butyl, ppm	Rel area	For CH, ppm	Rel area
Sc	1.18	9.0	6.26	0.95
Lu	1.11	9.0	6.14	0.99
Y[d]	1.07	9.0	6.04	0.99
La	1.12	9.0	6.02	0.93

[a] Spectral notations: s, strong intensity; m, medium intensity; w, weak intensity; b, broad; sh, shoulder. [b] Obtained in a KBr matrix. [c] Obtained in deuterated chloroform at 40°, concentration ~30% w/v. Peak positions are given downfield from TMS. [d] The peaks obtained for $Y(fod)_3$ are *ca.* 13 cps broad at half peak height.

The anhydrous tris chelates, $Ln(fod)_3$, can be produced by dehydration of the monoaquo complexes in two ways. Vacuum pumping of the monohydrates over P_4O_{10} for several days will yield the anhydrous tris chelates (Experimental Section). Likewise, heating the aquated species above 100° in a flowing anhydrous at-

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mosphere causes loss of water. Mass spectroscopic results[19] for the hydrated fod chelate of lutetium show a large peak (*m/e* 18) due to water and a parent ion mass peak (*m/e* 1057, the theoretical mass of Lu(fod)$_3$ is 1061). No peak corresponding to the parent ion of the monoaquo species (*m/e* 1079) was observed in regions of higher mass to charge ratio, indicating that it either does not exist in the gas phase or is unstable. A solution of Y(fod)$_3$ in dried benzene gave the same chromatographic retention time for the complex as a solution of the monoaquo compound, implying that the compound is dehydrated in the gas phase at the temperature (170°) of the elution. Finally, thermograms obtained for hydrated fod samples revealed a 1–2% weight loss at temperatures in the vicinity of 100°, suggesting the volatilization of the mole of water present. Figure 1 shows the tga curves for Dy(fod)$_3$ and Dy(fod)$_3$·H$_2$O with the instrument weight suppression controls set for the observation of only the first 5% of weight loss. The complete loss of the water of hydration at 100° is clearly evident. The anhydrous dysprosium complex was characterized by Karl Fischer titrations and elemental analyses (see Experimental Section). Triplicate Karl Fischer titrations of the monohydrate revealed the presence of 2.0 ± 0.3% H$_2$O (see Table I). The agreement between the Karl Fischer and the thermogravimetric methods is excellent. The weight loss corresponding to 0.4% for the anhydrous compound is attributed to water picked up during transfer from the desiccator to the tga apparatus.

The anhydrous complexes are hygroscopic, those of heavier metals picking up water instantaneously upon exposure to the atmosphere, while the lighter compounds hydrate more slowly. The rapidity of hydration is illustrated by an infrared study in which Er(fod)$_3$, collected directly from the chromatographic eluate and in contact with the air only a few seconds, showed the presence of water.

The anhydrous europium complex is bright yellow, in contrast with the white monoaquo complex, but the latter emits a more intensely red fluorescence upon irradiation with ultraviolet light at 3660 A. Likewise, the green fluorescence of the terbium complex is visibly enhanced by the presence of water.

All of the anhydrous and monoaquo complexes are highly soluble in many organic solvents and insoluble in water.

Hydration of the anhydrous complexes lowers the melting point in most cases, in some rather markedly, a phenomenon which has been noted for other rare earth β-diketonate complexes by previous investigators.[8,20] The melting points of both the anhydrous and monohydrated complexes are shown in Table III. The association of 1 mole of water with the anhydrous fod complexes is evidently a totally reversible process. By drying a sample or exposing it to the atmosphere, the melting point changes in the appropriate direction.

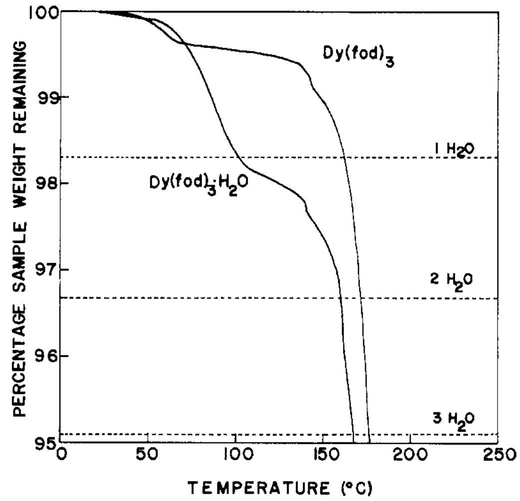

Figure 1.—Thermogravimetric curves of Dy(fod)$_3$ and Dy(fod)$_3$·H$_2$O. Conditions: carrier gas, He; flow rate, 60 ml/min; heating rate, 10°/min; sample sizes, approximately 20 mg.

Table III

The Melting Points of Rare Earth fod Complexes

	Mp,[a] °C	
Ln(III)	Anhydrous[b]	Monohydrate[c]
Lu	118–125	111–115
Yb	125–132	112–115
Tm	140–146	110–115
Er	158–164	104–112
Y	162–167	108–112
Ho	172–178	103–111
Dy	180–188	103–107
Tb	190–196	92–97
Gd	203–213[d]	60–65
Eu	205–212[d]	59–67
Sm	208–218[d]	63–67
Nd	210–215[d]	210–215[d]
Pr	218–225[d]	218–225[d]
La	215–230[d]	215–230[d]

[a] Obtained on a Thomas–Hoover capillary apparatus. [b] Stored *in vacuo* over P$_4$O$_{10}$ for at least 1 week. [c] Anhydrous samples were exposed to the atmosphere for at least 1 day to form the monohydrate. [d] Sample melted with decomposition.

The rather wide melting range exhibited by any particular fod sample in either state is indicative of the sensitivity of this property to moisture. When the white monoaquo europium complex melts, at *ca.* 60°, a colorless liquid is obtained; however, at *ca.* 100° water is given off in the form of steam bubbles producing a yellow liquid.

The nmr spectra for the anhydrous diamagnetic complexes in CDCl$_3$ at 40° are all very similar. The peak positions and relative areas are given in Table II.

The anhydrous fod compounds have been chromatographed in the vapor phase; a typical chromatogram [that of Er(fod)$_3$] is shown in Figure 2. The logarithms of the retention times and the retention volumes, relative to the hydrocarbon eicosane (n-C$_{20}$H$_{42}$), of most of the anhydrous fod chelates are plotted against the ionic radii[21] of the six-coordinate, tripositive metal ions in Figure 3. The trend of lower

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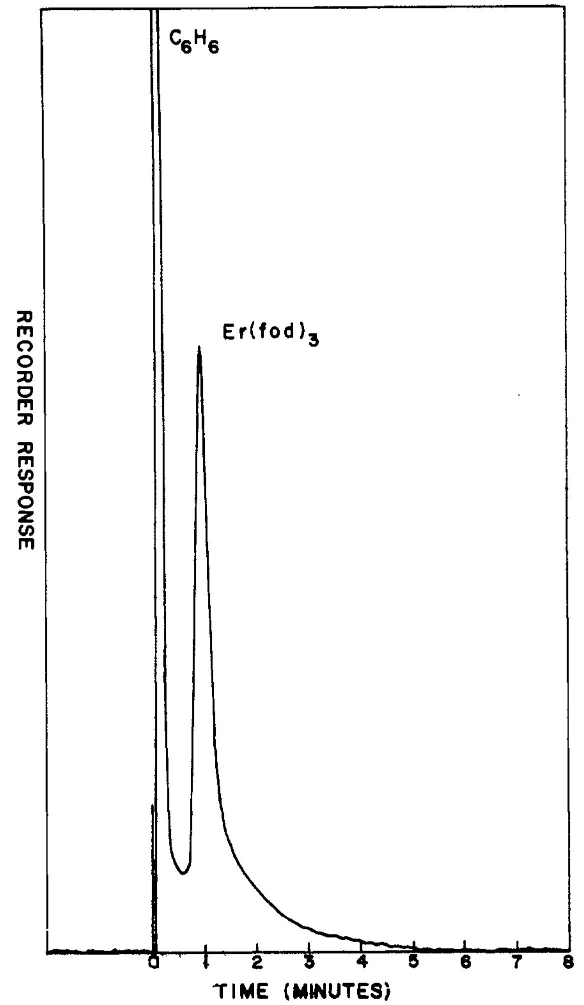

Figure 2.—Chromatogram of Er(fod)$_3$. Conditions: carrier gas, He; flow rate, 100 ml/min; column, 4.5 mm (i.d.) × 140 mm (length), 10% (w/w) SE-30 on Chromosorb W; temperature, 171°; injection port temperature, 230°; thermal conductivity detector temperature, 227°; sample injected was 0.3 µl of a saturated solution of the anhydrous complex in benzene.

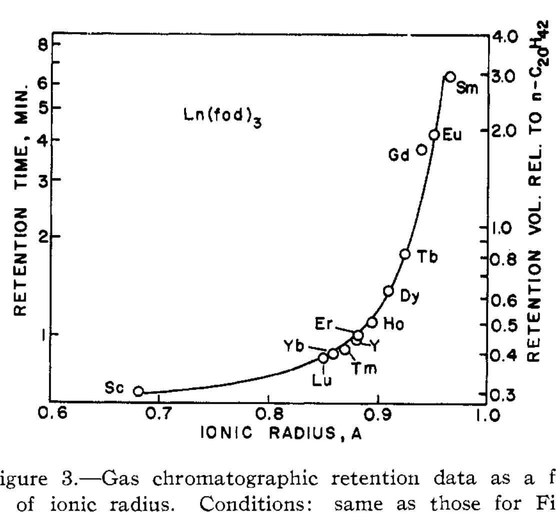

Figure 3.—Gas chromatographic retention data as a function of ionic radius. Conditions: same as those for Figure 2.

retention time with decreasing ionic radius first reported by Eisentraut and Sievers[12] is reaffirmed with the fod complexes. The retention data cannot be correlated with the mass of the complex. The significance of the ionic radius is illustrated particularly well by the yttrium value which fits smoothly on the ionic radius curve but is anomalous in either an analogous atomic number or mass curve.

The thermogravimetric curves obtained for the anhydrous fod compounds are reproduced in Figure 4. The chelates of the smaller metal ions are volatilized at lower temperatures than their larger analogs. The only exception to this trend is the thermogram of Sc(fod)$_3$ which is almost coincidental with the curve for Tm(fod)$_3$. However, the chromatographic retention time of Sc(fod)$_3$ occupies the predicted position in the radius plot (Figure 3). The tga curves represent a combined sublimation–vaporization process since each curve passes the melting temperature of the anhydrous compound (excepting Sc(fod)$_3$, a liquid at room temperature) before 100% weight loss is recorded.

Discussion

The thermal instability of hydrated tris(β-diketonate) rare earth(III) complexes has been attributed to hydrolysis, presumably giving the hydroxobis(diketonate) complex and neutral ligand, at elevated temperatures.[8–10] There are also indications that certain compounds undergo hydrolysis *in vacuo* even at room temperature.[10] There have been few reasonably well-characterized examples of dehydration without accompanying decomposition.[6,8,20]

The monohydrated fod chelates are easily transformed to the anhydrous tris complexes without hydrolysis. Since these compounds contain three bulky fluorinated ligands, the water molecule may be hydrogen bonded to an electronegative site on the ligand shell rather than coordinated to the metal ion.[22–24] Davis and Fackler have reported infrared evidence suggesting such interactions.[25] Also Cunningham, *et al.*, have shown by X-ray crystallography that one of the water molecules in $[Y(acac)_3(H_2O)_2]\cdot H_2O$ is not coordinated to the metal ion but is instead hydrogen bonded between two adjacent eight-coordinate complex molecules.[26]

The fod rare earth complexes are the most volatile lanthanide compounds known. The fluorocarbon substituent in the ligand shell markedly increases the volatilities of the complexes over those of compounds containing a similar nonfluorinated ligand. With Cr(III)[15,27] and with Al(III),[27] the tris fod complexes have been shown to have volatilities greater than those of the analogous tris acac and tris thd (2,2,6,6-tetra-

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(22) Some evidence for this possibility is found in the visible absorption spectra of the erbium fod complexes.[23] Neither the energy nor the extinction coefficient of the low-energy hypersensitive transition is appreciably affected by the addition of the water molecule. This is in contrast to the case recently reported by Taketatsu and Banks,[24] presumably involving the coordination of a seventh donor atom. The change in color of the europium complex upon hydration in carbon tetrachloride solution has been shown to be due to a shift of a ligand peak out of the visible region and not to a change in the 4f hypersensitive transition.[23]

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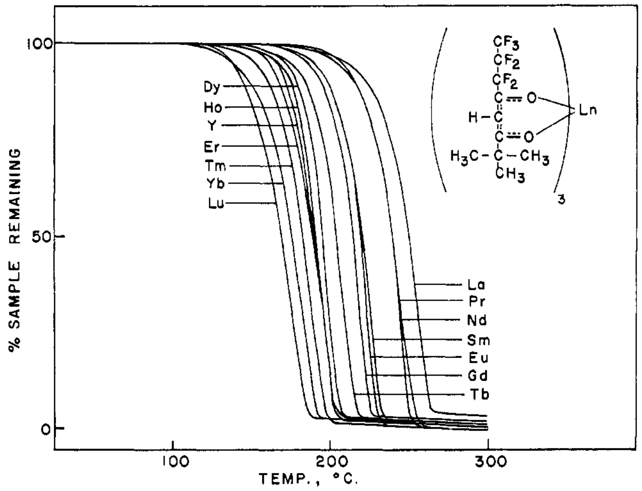

Figure 4.—Thermogravimetric curves of the rare earth fod complexes. Conditions: same as those for Figure 1 except that sample sizes were approximately 10 mg.

methyl-3,5-heptanedionate) compounds and only slightly less than those of the analogous tris tfa compounds.[27] The increased volatility of compounds containing the highly electronegative fluorocarbon ligands implies that these groups produce a more repulsive shell around the complex molecule than that in the similar hydrocarbon chelates.

Another interesting effect is demonstrated by the correlation between the lanthanide contraction and the volatilities of the tris fod chelates as evidenced by the retention data (Figure 3). The qualitative thermogravimetric data (Figure 4) prove that the chromatographic trend truly reflects the volatilities of the compounds and is not a manifestation of specific solvation effects. A similar trend in volatility has been confirmed for the rare earth thd compounds by thermogravimetric analysis.[15,27] Several possible explanations can be advanced to account for the correlation.

One might assume that the position of possible monomer–polymer equilibria would vary with ionic radius and cause the observed trend in volatility. The acetylacetonate chelates of the lanthanides tend to polymerize in solution.[28,29] Other examples of possible monomer–dimer equilibria have recently been reported.[30] One can imagine that monomer $\rightleftharpoons$ polymer transformations could take place in the condensed phase (solid, liquid, or solution as in the chromatographic experiments) in equilibrium with the monomeric gaseous species. If the larger complexes were to polymerize more extensively than the more compact members, they would be expected to exhibit a lower apparent vapor pressure. However, the molecular weight data, which are in excellent agreement with that required for monomeric species in solution (Table I), render this hypothesis improbable.

More tenable explanations concern themselves with the ways in which a change in ionic radius can affect the van der Waals forces of attraction. For tris complexes containing unsymmetrical ligands, as is the case with fod, the molecules have permanent molecular dipoles. If it is assumed that the size of the molecule decreases with the radius of the central metal ion, then it is likely that the size of the molecular dipole also decreases. In addition, all tris(β-diketonate) chelates have smaller permanent local dipoles, irrespective of the symmetry of the ligand. These could be expected either to decrease in magnitude or to become more effectively shielded as the size of the central metal ion is decreased. Finally, as the size of these pseudo-spherical molecules decreases, one would expect the polarizability to be reduced. All of these factors would be expected to decrease the dipole–dipole (molecular or local) interactions, the dipole (molecular or local)–induced dipole interactions, and the induced dipole–induced dipole interactions and consequently to increase the volatility as the ionic radius becomes smaller.

Acknowledgments.—This research was supported in part by the ARL In-House Independent Laboratory Research Funds, Office of Aerospace Research, U. S. Air Force. The authors thank the American Chemical Society for permission to publish the original experimental data here and to summarize this data in a review which is being simultaneously published in the Advances in Chemistry Series. Our thanks also go to Dr. K. J. Eisentraut for many stimulating discussions.

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