

CONTRIBUTION FROM THE AEROSPACE RESEARCH LABORATORIES, ARC,
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433**Volatile Rare Earth Chelates of 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione and 1,1,1,2,2,3,3,7,7,7-Decafluoro-4,6-heptanedione**

BY MARY FRANCES RICHARDSON* AND ROBERT E. SIEVERS

Received July 15, 1970

Rare earth tris and tetrakis chelates of 1,1,1,2,2,3,3,7,7,7-decafluoro-4,6-heptanedione (Hdfhd) have been synthesized. The hydrated tris chelates, $\text{Ln}(\text{dfhd})_3 \cdot 2\text{H}_2\text{O}$, show only slight decomposition upon volatilization. The tetrakis chelates, $\text{NH}_4\text{Ln}(\text{dfhd})_4$, are completely volatile without decomposition, as are the dimethylformamide adducts, $\text{Ln}(\text{dfhd})_3 \cdot 2\text{DMF}$. Infrared and nuclear magnetic resonance spectra and chemical analysis data suggest that the rare earths are eight-coordinate in these compounds. The effects of adduct formation and tetrakis salt formation on volatility and thermal stability were studied for the rare earth 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa) chelates. The hydrated tris-hfa chelates are thermally unstable and sublime only with considerable decomposition, whereas the compounds $\text{Ln}(\text{hfa})_3 \cdot \text{DMF}$, $\text{Ln}(\text{hfa})_3 \cdot 2\text{DMF}$, $\text{Ln}(\text{hfa})_3 \cdot \text{DMF} \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{Ln}(\text{hfa})_4$, and $\text{C}_5\text{H}_5\text{NHLn}(\text{hfa})_4$ sublime quantitatively without decomposition. 2,2-Dimethoxypropane (dmp) adducts with the formula $\text{Ln}(\text{hfa})_3 \cdot \text{dmp}$ and $\text{Ln}(\text{dfhd})_3 \cdot \text{dmp}$ are highly volatile but show slight decomposition upon volatilization. Infrared and nuclear magnetic resonance evidence suggests that the dmp is chelated to give a four-membered ring and an eight-coordinate rare earth. The volatilities of the tris and tetrakis chelates studied increase as the ionic radius of the rare earth decreases, with yttrium occupying a place near Er (whose size it resembles). It is concluded from the present data and other literature data that volatile, thermally stable rare earth chelates result when bulky, fluorine-substituted ligands are used. These ligands prevent the strong bonding of water or cause its exclusion from the coordination sphere altogether, thus minimizing or eliminating hydrolysis reactions which are a major cause of thermal instability. Prevention of hydrolysis is also accomplished by adduct formation or tetrakis salt formation.

Previous work on rare earth β -diketone chelates¹ has shown that the most volatile and thermally stable compounds are those in which the metal atom is well shielded by the ligands, thus minimizing solvation effects and interactions between the molecules. It is also known that volatility usually increases with increasing extent of fluorination of the ligand.^{1,2} The mutual effects of ligand size and degree of fluorination were examined for various rare earth β -diketone chelates in the present study. It was of interest to examine the rare earth chelates of Hdfhd;³ the high fluorination should give great volatility, while the relatively small substituents (in comparison to Hthd and Hfod) might lead to hydration and thus to hydrolytic instability at the temperatures required for sublimation.

The postulate that hydration adversely affects thermal stability and volatility⁴ has been tested in the present work. For tris chelates whose hydrates are known to be thermally unstable (*i.e.*, the hfa and dfhd chelates), two types of compounds were synthesized: adducts with the formula $\text{LnL}_3 \cdot n\text{D}$ and tetrakis chelates with the formula MLnL_4 , where Ln is a lanthanide, M is a univalent cation, L is hfa or dfhd, and D is an organic donor molecule.

Experimental Section

Analyses for C, H, N, and F and molecular weight deter-

(1) R. E. Sievers, K. J. Eisentraut, C. S. Springer, Jr., and D. W. Meek, *Advan. Chem. Ser.*, **No. 71**, 141-154 (1967).

(2) R. W. Moshier and R. E. Sievers, "Gas Chromatography of Metal Chelates," Pergamon Press, Oxford, 1965, pp 19-20, and references therein.

(3) Ligand abbreviations used in the present work are as follows: Hhfa, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; Hdfhd, 1,1,1,2,2,3,3,7,7,7-decafluoro-4,6-heptanedione; Hfod, 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione; Hthd, 2,2,6,6-tetramethyl-3,5-heptanedione; Hpta, 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione; Hacac, 2,4-pentanedione; Htfa, 1,1,1-trifluoro-4,4-pentanedione; DMF, *N,N*-dimethylformamide; dmp, 2,2-dimethoxypropane; py, pyridine.

(4) R. E. Sievers, K. J. Eisentraut, C. S. Springer, Jr., and D. W. Meek, *Advan. Chem. Ser.*, **No. 71**, 142 (1967), and references cited therein.

minations were made by Galbraith Laboratories, Knoxville, Tenn. Metal analyses were carried out either at Galbraith or by ignition of the oxalate to the oxide.⁵ Karl Fischer titrations were performed as described previously.⁶ Infrared spectra were recorded on Perkin-Elmer Infracord and Model 521 spectrophotometers in Nujol-Fluorube mulls between NaCl or KBr plates. Nmr spectra were taken on the Varian A-60 spectrometer with tetramethylsilane as an internal standard.

Thermogravimetric curves were recorded with a Du Pont Model 950 thermogravimetric analyzer under the same conditions as described by Eisentraut and Sievers.⁷

$\text{Ln}(\text{hfa})_3 \cdot (2-3)\text{H}_2\text{O}$, $\text{NH}_4\text{Ln}(\text{hfa})_4 \cdot (0-1)\text{H}_2\text{O}$, and $\text{pyHLn}(\text{hfa})_4 \cdot (0-1)\text{H}_2\text{O}$.—These compounds were synthesized according to the procedures described previously.⁸ They were characterized by their infrared spectra and by metal analyses. Anhydrous tetrakis compounds of La, Pr, and Nd were obtained by drying over $\text{Mg}(\text{ClO}_4)_2$ at atmospheric pressure.⁸

$\text{Ln}(\text{dfhd})_3 \cdot 2\text{H}_2\text{O}$.—The tris-dfhd chelates were synthesized by the ether extraction method used for tris-hfa chelates.⁸ The rare earth chlorides were used in 10-50% excess in order to prevent formation of the tetrakis salts.⁹ The ether extracts were dried over CaSO_4 and evaporated. Oils were usually obtained, which subsequently crystallized when allowed to stand in air. The compounds oiled out of every solvent from which recrystallization was attempted (benzene, hexane, methylcyclohexane, heptane, etc.; they are too soluble in oxygen-donor solvents to be recrystallized from them): Sublimation was also unsuccessful, as the compounds distill and do not crystallize on the cold finger (distillation is a poor purification method since there is partial decomposition of the complexes and the decomposition products also distil). However, analytical data are quite satisfactory for the compounds which crystallized after evaporation of the ether extracts (Table I). Nitrogen analyses were occa-

(5) M. F. Richardson, D. E. Sands, and W. F. Wagner, *Chemist-Analyst*, **56**, 65 (1967).

(6) C. S. Springer, Jr., D. W. Meek, and R. E. Sievers, *Inorg. Chem.*, **6**, 1105 (1967).

(7) K. J. Eisentraut and R. E. Sievers, *J. Inorg. Nucl. Chem.*, **29**, 1931 (1967).

(8) M. F. Richardson, W. F. Wagner, and D. E. Sands, *ibid.*, **30**, 1275 (1968).

(9) Since mixtures of the tris and tetrakis compounds cannot be separated by crystallization (they oil out together; the oily tris chelate is a good "solvent" for the tetrakis chelate), it is most important to avoid conditions under which a mixture of tris and tetrakis compounds can be formed.

TABLE I
 ANALYTICAL DATA FOR RARE EARTH-HEXAFLUOROACETYLACETONE AND -DECAFLUOROHEPTANEDIONE CHELATES

| Ln | % Ln | | % H ₂ O | | % C | | % H | | % N | | % F | | Mol wt ^a | |
|--|--------------------|--------------------|--------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|---------------------|------------------|
| | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found |
| Ln(dfhd) ₃ ·2H ₂ O | | | | | | | | | | | | | | |
| La | 12.67 | 12.49 | 3.28 | 3.53 | 23.00 | 23.16 | 0.64 | 0.81 | | | 52.00 | 52.16 | | |
| Pr | 12.83 | 12.64 | 3.28 | 3.65 | 22.97 | 23.03 | 0.64 | 0.80 | | | 51.90 | 51.61 | | |
| Nd | 13.09 | 12.90 | 3.27 | 3.38 | 22.89 | 22.96 | 0.64 | 0.74 | | | 51.75 | 51.46 | 1101 | 1140 |
| Sm | 13.57 | 13.70 | 3.25 | 3.47 | 22.77 | 22.54 | 0.64 | 0.84 | | | 51.46 | 51.44 | 1107 | 1150 |
| Eu | 13.70 | 13.91 | 3.25 | 3.56 | 22.75 | 22.54 | 0.64 | 0.69 | | | 51.39 | 51.22 | | |
| Gd | 14.10 | 14.17 | 3.23 | 2.94 | 22.63 | 22.50 | 0.63 | 0.64 | | | 51.14 | 50.98 | 1114 | 1095 |
| Tb | 14.24 | 14.39 | 3.23 | 3.36 | 22.60 | 22.36 | 0.63 | 0.68 | | | 51.07 | 51.19 | | |
| Dy | 14.51 | 14.32 | 3.22 | 3.49 | 22.52 | 22.70 | 0.63 | 0.75 | | | 50.90 | 50.97 | 1120 | 1150 |
| Ho | 14.69 | 14.51 | 3.21 | 3.20 | 22.47 | 22.63 | 0.63 | 0.72 | | | 50.79 | 50.65 | | |
| Er | 14.87 | 14.62 | 3.20 | 3.16 | 22.43 | 22.52 | 0.63 | 0.77 | | | 50.69 | 50.37 | 1124 | 1080 |
| Tm | 15.00 | 14.80 | 3.20 | 3.09 | 22.39 | 22.28 | 0.63 | 0.67 | | | 50.61 | 50.47 | 1126 | 1080 |
| Yb | 15.30 | 15.21 | 3.18 | 3.27 | 22.31 | 22.18 | 0.62 | 0.55 | | | 50.43 | 50.31 | | |
| Lu | 15.46 | 15.49 | 3.18 | 3.43 | 22.27 | 22.56 | 0.62 | 0.56 | | | 50.34 | 50.60 | | |
| Y | 8.50 | 8.32 | 3.44 | 3.21 | 24.11 | 24.01 | 0.68 | 0.64 | | | 54.48 | 54.57 | | |
| NH ₄ Ln(dfhd) ₄ | | | | | | | | | | | | | | |
| Nd | 10.51 | 10.53 | 0.0 | 0.74 | 24.50 | 23.34 | 0.59 | 0.63 | 1.02 | 1.10 | 55.39 | 53.62 | 1372 | 1137 |
| Sm | 10.90 | 10.72 | | | 24.39 | 24.15 | 0.58 | 0.72 | 1.02 | 1.07 | 55.12 | 54.25 | | |
| Eu | 11.01 | 10.92 | | | 24.36 | 23.56 | 0.58 | 0.46 | 1.01 | 0.98 | 55.06 | 53.02 | 1380 | 1445 |
| Gd | 11.34 | 11.46 | 0.0 | 0.46 | 24.27 | 23.96 | 0.58 | 0.54 | 1.01 | 1.06 | 54.85 | 54.04 | 1386 | 1386 |
| Tb | 11.45 | 11.33 | | | 24.24 | 23.42 | 0.58 | 0.43 | 1.01 | 0.95 | 54.78 | 53.67 | 1387 | 1417 |
| Dy | 11.68 | 11.34 | 0.0 | 0.52 | 24.18 | 24.10 | 0.58 | 0.70 | 1.01 | 1.23 | 54.64 | 54.86 | 1391 | 1426 |
| Ho | 11.84 | 11.77 | 0.0 | 0.49 | 24.14 | 23.85 | 0.58 | 0.43 | 1.01 | 1.02 | 54.54 | 54.75 | 1393 | 1410 |
| Er | 11.98 | 11.94 | | | 24.10 | 23.89 | 0.58 | 0.58 | 1.00 | 0.99 | 54.45 | 54.18 | | |
| Tm | 12.09 | 12.31 | | | 24.07 | 23.96 | 0.58 | 0.54 | 1.00 | 1.08 | 54.39 | 54.26 | | |
| Yb | 12.34 | 12.46 | 0.0 | 0.52 | 24.00 | 23.58 | 0.58 | 0.65 | 1.00 | 1.08 | 54.23 | 54.98 | 1401 | 1370 |
| Lu | 12.47 | 12.38 | | | 23.96 | 23.76 | 0.57 | 0.40 | 1.00 | 0.97 | 54.15 | 53.96 | | |
| Y | 6.75 | 6.95 | 0.0 | 0.51 | 25.53 | 25.41 | 0.61 | 0.52 | 1.06 | 1.10 | 57.69 | 57.88 | | |
| Y ^b | 6.75 | 6.74 | 0.0 | 0.0 | 25.53 | 25.57 | 0.61 | 0.66 | 1.06 | 1.09 | 57.69 | 57.36 | 1317 | 1290 |
| Ln(dfhd) ₃ ·2DMF | | | | | | | | | | | | | | |
| Pr | 13.98 ^c | 14.15 ^c | | | 26.88 | 27.08 | 1.42 | 1.40 | 2.32 | 2.61 | 47.17 | 41.44 | 1208 | 1670 |
| Yb | 15.89 ^d | 16.11 ^d | | | 26.14 | 26.21 | 1.38 | 1.41 | 2.26 | 2.36 | 45.95 | 45.81 | 1240 | 1280 |
| Ln(hfa) ₃ ·DMF | | | | | | | | | | | | | | |
| Pr | 16.87 | 17.05 | 0.0 | 0.38 | 25.89 | 25.84 | 1.20 | 1.28 | 1.68 | 1.80 | 40.95 | 40.86 | 835 | 832 ^e |
| Sm | 17.80 | 18.08 | | | 25.60 | 25.34 | 1.19 | 1.30 | 1.66 | 1.66 | 40.49 | 40.39 | 844 | 1010 |
| Gd | 18.47 | 18.22 | | | 25.39 | 25.44 | 1.18 | 1.37 | 1.64 | 1.77 | 40.08 | 39.96 | 851 | 966 |
| Dy | 18.47 | 19.09 | | | 25.23 | 25.19 | 1.18 | 1.22 | 1.63 | 1.71 | 39.92 | 39.91 | 857 | 946 |
| Er | 19.41 | 19.28 | 0.0 | 0.21 | 25.09 | 24.93 | 1.17 | 1.06 | 1.62 | 1.85 | 39.62 | 39.41 | 862 | 1013 |
| Lu | 20.13 | 20.28 | | | 24.87 | 24.93 | 1.16 | 1.16 | 1.61 | 1.70 | 39.34 | 39.54 | 869 | 924 |
| Y | 11.35 | 11.19 | | | 27.60 | 27.62 | 1.29 | 1.31 | 1.79 | 1.68 | 43.67 | 43.59 | 783 | 572 ^e |
| Ln(hfa) ₃ ·DMF·H ₂ O | | | | | | | | | | | | | | |
| Pr | 16.51 | 16.43 | 2.11 | 2.31 | 25.34 | 25.22 | 1.42 | 1.32 | 1.64 | 1.72 | 40.09 | 39.93 | 853 | 843 ^e |
| Sm | 17.43 | 17.22 | 2.09 | 1.42 | 25.06 | 24.84 | 1.40 | 1.26 | 1.62 | 1.69 | 39.65 | 39.47 | 863 | 865 ^e |
| Dy | 18.58 | 18.39 | 2.06 | 1.66 | 24.72 | 24.87 | 1.38 | 1.33 | 1.60 | 1.73 | 39.10 | 38.91 | 875 | 1013 |
| Er | 19.02 | 19.21 | 2.05 | 2.15 | 24.58 | 24.46 | 1.38 | 1.44 | 1.59 | 1.61 | 38.88 | 38.74 | 880 | 602 ^e |
| Y | 11.10 | 11.14 | 2.25 | 2.39 | 26.99 | 26.95 | 1.51 | 1.47 | 1.75 | 1.70 | 42.69 | 42.53 | 801 | 578 ^e |
| Ln(hfa) ₃ ·DMF | | | | | | | | | | | | | | |
| La | 15.33 | 15.21 | | | 27.83 | 28.65 | 1.89 | 2.11 | 3.09 | 3.78 | 37.74 | 34.78 | 906 | 1049 |
| Pr | 15.51 | 15.67 | | | 27.77 | 27.59 | 1.89 | 1.94 | 3.08 | 3.36 | 37.65 | 34.33 | 908 | 935 |
| Nd | 15.82 | 15.71 | | | 27.67 | 27.55 | 1.88 | 2.04 | 3.07 | 3.17 | 37.51 | 34.95 | 911 | 992 |
| Sm | 16.38 | 16.56 | | | 27.48 | 27.55 | 1.87 | 1.82 | 3.05 | 3.32 | 37.27 | 37.08 | 918 | 921 |
| Eu | 16.53 | 16.58 | | | 27.44 | 27.55 | 1.86 | 1.85 | 3.05 | 3.09 | 37.20 | 36.98 | 919 | 929 |
| Gd | 17.01 | 17.09 | | | 27.28 | 27.01 | 1.85 | 1.67 | 3.03 | 3.01 | 36.99 | 36.59 | 925 | 940 |
| Tb | 17.17 | 17.04 | | | 27.23 | 27.02 | 1.85 | 1.90 | 3.02 | 3.07 | 36.92 | 36.90 | 926 | 938 |
| Er | 17.90 | 17.78 | | | 26.98 | 26.92 | 1.83 | 1.87 | 3.00 | 2.91 | 36.59 | 36.50 | 935 | 1022 |
| Yb | 18.40 | 18.54 | | | 26.82 | 26.75 | 1.82 | 1.58 | 2.98 | 2.93 | 36.37 | 36.27 | 940 | 938 |
| Lu | 18.57 | 18.66 | | | 26.77 | 26.79 | 1.82 | 1.70 | 2.97 | 2.96 | 36.29 | 36.15 | 942 | 958 |
| Y | 10.38 | 10.15 | | | 29.46 | 29.46 | 2.00 | 2.01 | 3.27 | 3.21 | 39.94 | 39.71 | 856 | 926 |
| Ln(hfa) ₃ ·dmp | | | | | | | | | | | | | | |
| Dy | 21.01 ^d | 20.99 ^d | | | 27.05 | 27.30 | 1.70 | 1.89 | | | 38.52 | 38.34 | 888 | 937 |
| Er | 21.43 ^d | 21.34 ^d | | | 26.91 | 26.60 | 1.69 | 1.74 | | | 38.31 | 38.05 | 893 | 927 |

^a Molecular weights of Ln(dfhd)₃·2H₂O and NH₄Ln(dfhd)₄ in CHCl₃; molecular weights of the remaining compounds in benzene unless otherwise noted. ^b After sublimation. ^c As Pr₄O₇. ^d As Ln₂O₃. ^e Molecular weight in DMF. / Molecular weight in CHCl₃.

sionally performed in order to make sure that $\text{NH}_4\text{Ln}(\text{dfhd})_4$ was absent.

$\text{Ln}(\text{dfhd})_3 \cdot x\text{H}_2\text{O}$ ($x < 2$).—The hydrated dfhd chelates become oils when dried over $\text{Mg}(\text{ClO}_4)_2$ (1 day under vacuum; several weeks at atmospheric pressure). These oils pick up water from the air to form the dihydrated chelates again. However, the analytical data are not as good as desired for the anhydrous chelate. As an example, $\text{Er}(\text{dfhd})_3 \cdot 2\text{H}_2\text{O}$ yields an orange oil when stored over $\text{Mg}(\text{ClO}_4)_2$. *Anal.* Calcd for $\text{Er}(\text{dfhd})_3$, $\text{ErC}_{21}\text{H}_3\text{O}_6\text{F}_{30}$: Er, 15.37; C, 23.17; H, 0.28; F, 52.37; H_2O , 0.0. Found: Er, 15.82; C, 24.22; H, 1.07; F, 50.85; H_2O , 0.61.

Thermogravimetric data (Figure 2, curve 2) showed that the "anhydrous" compound is not significantly different in its volatility characteristics from the hydrated dfhd chelates, and further work on the "anhydrous" chelates was not carried out.

$\text{NH}_4\text{Ln}(\text{dfhd})_4$.— $\text{NH}_4\text{Er}(\text{dfhd})_4$ was obtained in the following way. A solution of NH_4dfhd (0.41 ml of concentrated NH_4OH , 4 ml of H_2O , and 2.1 g of Hdfhd) was added slowly, with stirring, to 4 ml of 0.45 *M* aqueous ErCl_3 . The precipitate was filtered, washed several times with water, and recrystallized twice from benzene. The yield of $\text{NH}_4\text{Er}(\text{dfhd})_4$ was 70%. The other rare earth tetrakis salts were prepared analogously. Analytical data are given in Table I. The tetrakis compounds tend to oil out of benzene, but crystallization occurs readily if the solutions are not too concentrated.

The tetrakis chelates obtained by recrystallization contain about 0.5% water which corresponds to $\sim 1/3$ mol of water/mol of chelate. Sublimation yields completely anhydrous chelates.

The tetrakis La and Pr salts are not obtained by the aqueous method, and the Nd compound is difficult to prepare in a high state of purity. Other methods⁸ for preparing the tetrakis La and Pr compounds also met with failure.

$\text{Ln}(\text{hfa})_3 \cdot \text{dmp}$ and $\text{Ln}(\text{dfhd})_3 \cdot \text{dmp}$.—2,2-Dimethoxypropane (dmp) was initially chosen as a dehydrating agent¹⁰ in hopes of obtaining anhydrous, unsolvated tris-hfa and -dfhd chelates. However, dimethoxypropane adducts were obtained instead. One gram of the hydrated chelate, $\text{Ln}(\text{hfa})_3 \cdot 2\text{H}_2\text{O}$ or $\text{Ln}(\text{dfhd})_3 \cdot 2\text{H}_2\text{O}$, was dissolved in ~ 5 ml of dimethoxypropane. The solution was boiled for a few seconds and then placed in a vacuum desiccator, and the excess solvent was pumped off. Crystals were sometimes obtained, but most frequently the product was an oil. Complete analytical data are given in Table I for the Dy- and Er-hfa compounds. Several other dimethoxypropane adducts (those of the hfa chelates of Pr, Sm, Gd, Ho, Yb, Lu, and Y and of Pr- and Er-dfhd chelates) were characterized only by their ir spectra and by metal analyses, which were in good agreement ($\pm 0.3\%$) with the theoretical metal contents.

Insufficient boiling of the dimethoxypropane solutions yields acetone-methanol solvates, instead of dimethoxypropane adducts (acetone and methanol are the products of the reaction of dimethoxypropane with water). Analytical data for the yttrium compound are consistent with the formulation $\text{Y}(\text{hfa})_3 \cdot \text{CH}_3\text{COCH}_3 \cdot \text{CH}_3\text{OH}$. *Anal.* Calcd for $\text{YC}_{13}\text{H}_{13}\text{O}_8\text{F}_{18}$: Y, 11.12; C, 28.50; H, 1.62; F, 42.75; mol wt 800. Found: Y, 11.05; C, 28.71; H, 1.83; F, 42.52; mol wt 805 (in CHCl_3).

$\text{Ln}(\text{hfa})_3 \cdot \text{DMF}$, $\text{Ln}(\text{hfa})_3 \cdot \text{DMF} \cdot \text{H}_2\text{O}$, $\text{Ln}(\text{hda})_3 \cdot 2\text{DMF}$, and $\text{Ln}(\text{dfhd})_3 \cdot 2\text{DMF}$.—Dimethylformamide (DMF) adducts were prepared in two ways. The first method involves adding the stoichiometric amount (1:1 or 2:1) of DMF to the solid chelate and heating gently. Droplets of water appear in the resulting oil. Vacuum drying at $\sim 60^\circ$ yields the anhydrous 2:1 and 1:1 adducts. The hydrated 1:1 adducts were obtained by air exposure of the anhydrous compounds or simply by allowing the initial preparation to cool and dry in air. The second method is essentially similar to the first, the only difference being that benzene was used as the solvent; evaporation of the benzene yielded the adducts. Analytical data are given in Table I.

Results and Discussion

Infrared and Nuclear Magnetic Resonance Spectra.

(10) K. Starke, *J. Inorg. Nucl. Chem.*, **11**, 77 (1959).

TABLE II

INFRARED SPECTRA OF $\text{Sm}(\text{dfhd})_3 \cdot 2\text{H}_2\text{O}$ AND $\text{NH}_4\text{Sm}(\text{dfhd})_4^a$

| $\text{Sm}(\text{dfhd})_3 \cdot 2\text{H}_2\text{O}$ | | $\text{NH}_4\text{Sm}(\text{dfhd})_4$ | |
|--|-----------|---------------------------------------|---------|
| 3615 m, sp | 970 m | 3650 vw | 1140 sh |
| 3510 m, br | 962 m | 3560 vw | 1119 vs |
| 3260 sh | 930 m | 3360 sh | 1094 s |
| 3145 w | 898 m | 3235 w | 1060 w |
| 1655 sh | 811 m | 3145 w | 965 sh |
| 1642 vs | 802 s | 1652 s | 960 m |
| 1624 s | 783 m | 1645 vs | 929 w |
| 1558 sh | 768 vw | 1608 m | 900 m |
| 1535 s | 747 s | 1559 sh | 800 m |
| 1475 vs | 731 w | 1540 s | 781 w |
| 1438 sh | 724 w | 1526 s | 765 vw |
| 1353 s | 677 w | 1495 s | 746 m |
| 1315 vs | 665 m | 1470 m | 724 w |
| 1270 s | 648 w | 1420 sh | 678 vw |
| 1220 vs | 628 m | 1410 m | 664 m |
| 1170 vs | 577 m | 1352 m | 648 w |
| 1155 vs | 550 m, br | 1310 vs | 620 w |
| 1145 vs | 538 m | 1272 m | 588 sh |
| 1120 vs | 528 m | 1225 vs | 576 m |
| 1096 s | 469 w | 1200 sh | 541 w |
| 1068 m | 390 w | 1178 vs | 530 w |
| 1060 m | | 1164 vs | 466 w |
| | | 1149 vs | 370 vw |

^a Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; sp, sharp; br, broad.

TABLE III
NMR SPECTRA OF SOME RARE EARTH CHELATES

| Compound | Solvent | δ^a | Rel intens | Assignment |
|--|-----------------|------------|------------|----------------------------|
| $\text{Lu}(\text{hfa})_3 \cdot 2\text{H}_2\text{O}$ | CDCl_3 | 3.28 | b | H_2O |
| | | 6.29 | b | $=\text{CH}(\text{hfa})$ |
| $\text{Lu}(\text{hfa})_3 \cdot \text{dmp}^c$ | CHCl_3 | 1.41 | 2.0 | $\text{CH}_3(\text{dmp})$ |
| | | 3.43 | 2.0 | $\text{OCH}_3(\text{dmp})$ |
| | | 6.19 | 1.0 | $=\text{CH}(\text{hfa})$ |
| dmp | CHCl_3 | 1.31 | 1.0 | CH_3 |
| | | 3.19 | 1.0 | OCH_3 |
| $\text{Y}(\text{hfa})_3 \cdot \text{CH}_3\text{COCH}_3 \cdot \text{CH}_3\text{OH}$ | CHCl_3 | 2.26 | 8 | CH_3 (acetone) |
| | | 3.58 | 3 | CH_3 (methanol) |
| | | 3.95 | 1 | OH (methanol) |
| | | 6.20 | 3 | $=\text{CH}(\text{hfa})$ |
| Acetone | CHCl_3 | 2.17 | | CH_3 |
| | | 3.47 | 3 | CH_3 |
| CH_3OH | CHCl_3 | 2.16 | 1 | OH |
| | | 2.90 | 6 | $\text{CH}_3(\text{DMF})$ |
| $\text{Lu}(\text{hfa})_3 \cdot 2\text{DMF}$ | CCl_4 | 3.03 | 6 | $\text{CH}_3(\text{DMF})$ |
| | | 6.08 | 3 | $=\text{CH}(\text{hfa})$ |
| | | 7.95 | 2 | $\text{CH}(\text{DMF})$ |
| | | 2.84 | 3 | CH_3 |
| DMF | CCl_4 | 2.97 | 3 | CH_3 |
| | | 7.93 | 1 | CH |
| | | 1.97 | 2 | $\text{CH}_3(\text{DMF})$ |
| $\text{Lu}(\text{hfa})_3 \cdot 2\text{DMF}$ | Benzene | 2.29 | 2 | $\text{CH}_3(\text{DMF})$ |
| | | 6.32 | 1 | $=\text{CH}(\text{hfa})$ |
| | | 2.02 | 1 | CH_3 |
| | | 2.43 | 1 | CH_3 |
| DMF | Benzene | 1.87 | 3.0 | $\text{CH}_3(\text{DMF})$ |
| | | 2.23 | 3.2 | $\text{CH}_3(\text{DMF})$ |
| | | 3.03 | 2.7 | H_2O |
| | | 6.32 | 3.0 | $=\text{CH}(\text{hfa})$ |
| $\text{Lu}(\text{dfhd})_3 \cdot 2\text{H}_2\text{O}$ | CDCl_3 | 3.58 | b | H_2O |
| | | 6.47 | b | $=\text{CH}(\text{dfhd})$ |
| | | 5.26 | b | NH_4 |
| $\text{NH}_4\text{Y}(\text{dfhd})_4$ | CHCl_3 | 6.58 | b | $=\text{CH}(\text{dfhd})$ |

^a In ppm downfield from an internal reference of tetramethylsilane. ^b Not determined. ^c Small peaks at 2.18 and 3.56 ppm due to methanol and acetone impurities.

—Ir and nmr spectra of the hydrated rare earth-tris-dfhd complexes show peaks due to water. The ir spectra (Table II) of the tris chelates have a broad peak at $\sim 3510 \text{ cm}^{-1}$ (OH stretching), while the nmr spectrum of $\text{Lu}(\text{dfhd})_3 \cdot 2\text{H}_2\text{O}$ has a peak at δ 3.58 ppm similar to the peak at 3.28 ppm in $\text{Lu}(\text{hfa})_3 \cdot 2\text{H}_2\text{O}$ (Table

III). The ir spectra of the ammonium tetrakis chelates are quite similar to those of the hydrated tris chelates (*cf.* the spectra of $\text{NH}_4\text{Sm}(\text{dfhd})_4$ and $\text{Sm}(\text{dfhd})_3 \cdot 2\text{H}_2\text{O}$ in Table II). The nmr spectrum of $\text{NH}_4\text{Y}(\text{dfhd})_4$ has a broad peak at δ 5.26 ppm due to NH_4^+ . The $=\text{CH}-$ resonance in the dfhd chelates appears at 6.47 ppm for $\text{Lu}(\text{dfhd})_3 \cdot 2\text{H}_2\text{O}$ and 6.57 ppm for $\text{NH}_4\text{Y}(\text{dfhd})_4$. These peaks appear at somewhat lower field than the corresponding peak in $\text{Lu}(\text{hfa})_3 \cdot 2\text{H}_2\text{O}$ (6.29 ppm). The single $=\text{CH}-$ resonance is undoubtedly due to rapid ligand exchange and/or intramolecular rearrangement of the ligands, which would average the nonequivalent protons.

The ir spectra of the DMF adducts (Table IV) shed

TABLE IV

SELECTED ABSORPTION BANDS IN THE INFRARED SPECTRA OF SOME RARE EARTH hfa AND dfhd CHELATE ADDUCTS^{a,b}

| La(hfa) ₃ ·DMF ^c | Sm(hfa) ₃ ·DMF·H ₂ O | Dy(hfa) ₃ ·DMF·H ₂ O | Nd(hfa) ₃ ·2DMF ^c |
|---|--|--|---|
| 1383 m | 1370 m | 1375 m | 1370 m |
| 1374 m | 1060 w | 1060 w | 1364 m |
| 1364 m | | 680 m | 1060 w |
| 1055 w | | | 660 w |
| 660 m | | | |
| Sm(hfa) ₃ ·2DMF ^c | Er(dfhd) ₃ ·2DMF ^c | Lu(hfa) ₃ ·dmp ^c | Er(hfa) ₃ ·CH ₃ COCH ₃ ·CH ₃ OH |
| 1370 m | 1380 m | 1390 m | 3610 w |
| 1060 w | 680 m | 1008 s | 3350 w |
| 680 m | | 965 m | 1695 s |
| | | | 1000 m |

^a Only bands which do not appear in the spectra of the corresponding hydrated tris chelates are listed. ^b Abbreviations: s, strong; m, medium; w, weak. ^c No O-H stretching frequencies observed.

some light on the coordination numbers of the rare earths in the compounds prepared. In none of the DMF adducts of the hfa and dfhd chelates is there a peak in the region 1650–1730 cm^{-1} , which is where uncoordinated carbonyl absorptions are found (the carbonyl absorption of neat DMF occurs at 1685 cm^{-1}). The carbonyl frequencies of $\text{Ln}(\text{dfhd})_3 \cdot 2\text{H}_2\text{O}$ and $\text{Ln}(\text{hfa})_3 \cdot n\text{H}_2\text{O}$ ⁸ are found at 1640–1650 cm^{-1} , and apparently the carbonyl absorption of DMF in the adducts is hidden by these strong peaks. Thus, the shift of the carbonyl stretching frequency of DMF from 1685 to \leq 1650 cm^{-1} is an indication of DMF coordination through the carbonyl group,^{11,12} giving at least seven- and eight-coordinate rare earths in the mono and bis adducts. Eight-coordination in the bis adducts and seven-coordination in the mono adducts are supported by molecular weight measurements in benzene (Table I) which show that neither dissociation of the adduct nor association to form oligomers occurs to any significant extent. We note, however, that molecular weight measurements are merely suggestive, as the structures in solution and in the solid state might be quite different.

The N—C=O bending frequency, observed at 657

cm^{-1} in pure DMF, seems to be a sensitive function of the crystal and/or molecular structure of the adducts. In the two series of compounds $\text{Ln}(\text{hfa})_3 \cdot 2\text{DMF}$ and $\text{Ln}(\text{hfa})_3 \cdot \text{DMF} \cdot \text{H}_2\text{O}$ there is an abrupt change in the position of this band as the rare earth series is traversed. For $\text{Ln}(\text{hfa})_3 \cdot 2\text{DMF}$, there is an absorption at 660 cm^{-1} and not at 680 cm^{-1} for Nd and lighter rare earths (Table IV), while Sm and heavier rare earth derivatives have a peak at 680 cm^{-1} and not at 660 cm^{-1} . In the series $\text{Ln}(\text{hfa})_3 \cdot \text{DMF} \cdot \text{H}_2\text{O}$, the change in the N—C=O bending frequency from 660 to 680 cm^{-1} occurs between Sm and Dy. The anhydrous 1:1 adducts $\text{Ln}(\text{hfa})_3 \cdot \text{DMF}$ were not studied completely across the rare earth series, but those examined had no absorption at 680 cm^{-1} . The spectra of two dfhd chelates studied, $\text{Pr}(\text{dfhd})_3 \cdot 2\text{DMF}$ and $\text{Er}(\text{dfhd})_3 \cdot 2\text{DMF}$, both exhibited a peak at 680 cm^{-1} . A shift of the N—C=O bending absorption to higher frequencies is usually taken as an indication of coordination,^{11,12} but it is apparent that coordination does not necessarily result in the shifting of this band. Single-crystal structure determinations will obviously be necessary to elucidate the factors (coordination, molecular packing, possible hydrogen bonding) which affect the position of this band.

The nmr spectra of the DMF adducts in CCl_4 indicate that the DMF is coordinated¹² as the DMF frequencies are shifted slightly downfield relative to those of uncomplexed DMF in CCl_4 (Table III). In benzene, the DMF peaks in the adducts are shifted upfield with respect to DMF in benzene. Nevertheless, molecular weights (Table I) show that the DMF molecules are coordinated in benzene.¹³ Caution should thus be exercised in interpreting the direction of shift as due to coordination or lack of coordination in various adducts, especially when benzene is the solvent (owing to diamagnetic anisotropism).

Analytical data alone are insufficient to distinguish between the compositions $\text{Ln}(\text{hfa})_3 \cdot \text{CH}_3\text{COCH}_3 \cdot \text{CH}_3\text{OH}$ and $\text{Ln}(\text{hfa})_3 \cdot \text{dmp}$. However, the nmr spectra provide conclusive proof that both types of compounds are formed (compare the spectra of $\text{Y}(\text{hfa})_3 \cdot \text{CH}_3\text{COCH}_3 \cdot \text{CH}_3\text{OH}$ and $\text{Lu}(\text{hfa})_3 \cdot \text{dmp}$ in Table III). Ir spectra support the nmr evidence, as the acetone-methanol adducts have large OH (\sim 3300 cm^{-1}) and C=O (1690 cm^{-1}) peaks which are absent in the spectra of the dmp adducts (Table IV).

The peaks in the ir spectrum of $\text{Lu}(\text{hfa})_3 \cdot \text{dmp}$ at 1390, 1008, and 965 cm^{-1} bear no clear relationship to the spectrum of dimethoxypropane, which has strong peaks at 1080, 1055, and 825 cm^{-1} which might be expected to appear in the spectra of the adducts. The lack of peak correspondence might be expected if the dimethoxypropane were chelated, as many of the frequencies would be considerably changed due to the con-

(11) E. W. Randall, C. M. S. Yoder, and J. J. Zuckerman, *Inorg. Chem.*, **5**, 2240 (1966), and references cited therein.

(12) J. E. Schwarberg, D. R. Gere, R. E. Sievers, and K. J. Eisentraut, *ibid.*, **6**, 1933 (1967).

(13) Actually, the molecular weights show that $\text{Ln}(\text{hfa})_3 \cdot 2\text{DMF}$ remains undissociated—they do not indicate how the DMF is bonded. Coordination of the DMF through oxygen is by far the most likely mode of bonding, however, since the ir spectra indicate coordination in the solid state and also because in the rare earth series coordination numbers higher than 6 are preferred.

TABLE V
 HALF-TEMPERATURES (°C) FOR THE VOLATILIZATION OF SOME RARE EARTH CHELATES^a

| Ln | Ln(dfhd) ₃ ·2H ₂ O ^b | NH ₄ Ln-(dfhd) ₄ | Ln(dfhd) ₃ ·2DMF | Ln(dfhd) ₃ ·dmp ^b | Ln(hfa) ₃ ·dmp ^b | pyHLn-(hfa) ₄ ^b | NH ₄ Ln-(hfa) ₄ | Ln(hfa) ₃ ·2DMF | Ln(hfa) ₃ ·DMF | Ln(hfa) ₃ ·DMF·H ₂ O |
|----|---|--|-----------------------------|---|--|---------------------------------------|---------------------------------------|----------------------------|---------------------------|--|
| La | | | | 205 | | 210 | | 214 | | |
| Pr | 200 | | 204 | 190 | 184 | 205 | | 205 | 199 | 198 |
| Nd | 200 | 191 | | | | 204 | | 204 | | |
| Sm | 192 | 187 | | | | 201 | 199 | 202 | 188 | 189 |
| Eu | 196 | 186 | | | | 197 | | 198 | | |
| Gd | 191 | 184 | | | | 199 | 195 | 197 | 183 | |
| Tb | 185 | 179 | | | | 194 | | 194 | | |
| Dy | 184 | 178 | | | 154 | 195 | | | 175 | 175 |
| Ho | 180 | 175 | | | | | | | | |
| Y | 177 | 178 | | | 145 | 197 | 194 | 184 | 173 | 172 |
| Er | 174 | 175 | | 158 | 145 | 189 | 197 | 185 | 169 | 169 |
| Tm | 172 | 167 | | | | | | | | |
| Yb | 165 | 168 | 179 | | | 186 | | 181 | | |
| Lu | 165 | 167 | | | 132 | 184 | 185 | 175 | 164 | |

^a The half-temperature is defined as the temperature of 50% weight loss on the tga curve for the arbitrarily chosen but fixed operating conditions described in the Experimental Section. ^b The half-temperatures of these compounds are not strictly a measure of volatility since there is some decomposition during volatilization.

straints imposed by chelation (a four-membered ring would be formed). Chelation or at least coordination is supported by the nmr spectrum of Lu(hfa)₃·dmp (Table III). The peaks at 1.31 and 3.19 ppm in dmp are shifted to lower field, to 1.41 and 3.43 ppm, in Lu(hfa)₃·dmp.

Thermogravimetric Analyses.—Some representative tga curves are shown in Figures 1 and 2. Space limita-

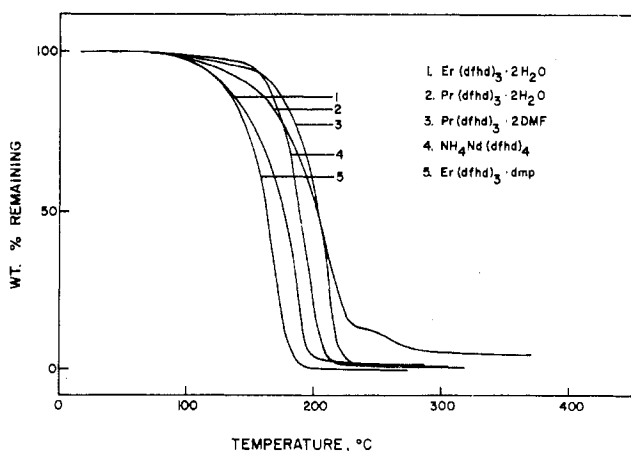


Figure 1.—Tga curves for some 1,1,1,2,2,3,3,7,7,7-decafluoro-4,6-heptanedione chelates.

tions prohibit showing all tga curves, but the half-temperatures (the temperature of 50% weight loss under the arbitrary but fixed operating conditions described in the Experimental Section) derived from the tga curves are given in Table V. The half-temperature will be used as a measure of relative volatility, as there is a good correlation between the half-temperature and the absolute vapor pressure of a compound.¹⁴ It should be emphasized, however, that the half-temperature becomes progressively less meaningful (insofar as it is a measure of relative volatility) as the extent of decomposition increases. Those cases in which partial decomposition takes place are noted in Table V.

The tga data show that the rare earth-tris-dfhd che-

(14) W. R. Wolf, Doctoral Dissertation, Kent State University, 1969.

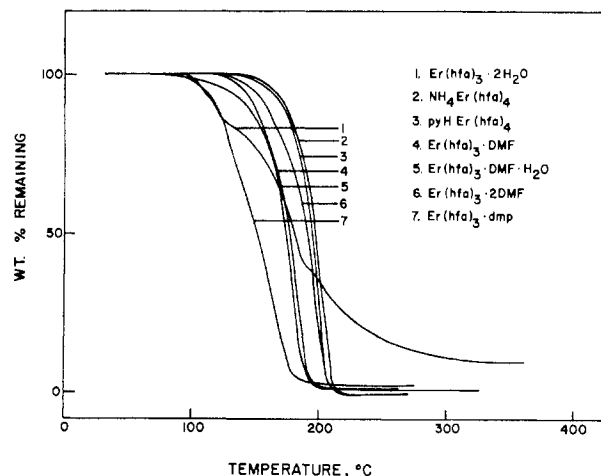


Figure 2.—Tga curves for some 1,1,1,5,5,5-hexafluoro-2,4-pentanedione chelates.

lates are quite volatile. Only the lighter rare earth chelates (La, Pr, Nd) decompose to any considerable extent, although there is slight decomposition for the heavier rare earths (*cf.* curves 1 and 2 in Figure 1). The small degree of decomposition for the dfhd chelates contrasts greatly with that for the hfa chelates Ln(hfa)₃·2H₂O, where decomposition is extensive even at the heavy end of the series (curve 1, Figure 2). The greater thermal stability of the dfhd chelates may be related to the fact that the dfhd chelates are fairly easily dehydrated at room temperature over a desiccant whereas the hfa chelates slowly decompose to nonstoichiometric products.¹⁵ Empirically this indicates that reactions of the type¹⁶ LnL₃(OH₂) → LnL₂OH + HL or those leading to further decomposition occur more readily in the hfa chelates than in the dfhd chelates. The greater bulk of the dfhd ligands should result in some steric crowding of the water molecules and thus in greater relative stability of Ln(dfhd)₃.

A quite remarkable phenomenon observed by many

(15) M. F. Richardson, Dissertation, University of Kentucky, Lexington, Ky., 1967.

(16) G. W. Pope, J. R. Steinbach, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **20**, 304 (1961).

workers^{1,2,17-19} is the generally high volatility and thermal stability of rare earth tetrakis chelates. The hfa and dfhd chelates are no exception. Particularly dramatic is the complete lack of decomposition of $\text{NH}_4\text{-Ln}(\text{hfa})_4$ ($\text{Ln} = \text{Sm-Lu}$) and $\text{pyHLn}(\text{hfa})_4$ ($\text{Ln} = \text{Pr-Lu}$) (Figure 2, curves 2, 3) as compared to the high thermal instability of $\text{Ln}(\text{hfa})_3 \cdot 2\text{H}_2\text{O}$ (e.g., Figure 2, curve 1). None of the tetrakis-dfhd chelates showed decomposition, although $\text{NH}_4\text{La}(\text{dfhd})_4$ and $\text{NH}_4\text{Pr}(\text{dfhd})_4$ could not be examined because of synthesis problems. The tetrakis chelates are quite volatile, with half-temperatures of 184–210° for the hfa chelates and 167–191° for the dfhd chelates (Table V).

Fairly extensive decomposition is observed for some of the lighter rare earth tetrakis compounds, namely, $\text{NH}_4\text{La}(\text{hfa})_4$, $\text{NH}_4\text{Pr}(\text{hfa})_4$, $\text{NH}_4\text{Nd}(\text{hfa})_4$, and $\text{pyHLA}(\text{hfa})_4$. All of these chelates form monohydrates readily,⁸ but that water is not the problem is evidenced by the fact that $\text{pyHPr}(\text{hfa})_4$ and $\text{pyHNd}(\text{hfa})_4$, which also form monohydrates, sublime without decomposition. However, decomposition apparently occurs more rapidly when the complexes are molten: $\text{NH}_4\text{La}(\text{hfa})_4$, $\text{NH}_4\text{Pr}(\text{hfa})_4$, and $\text{NH}_4\text{Nd}(\text{hfa})_4$ all melt at 195–200°, i.e., before sublimation is complete. The melts turn brown at ca. 205°, indicating that decomposition is occurring. On the other hand, $\text{NH}_4\text{Sm}(\text{hfa})_4$ melts at 212° (and the heavier rare earth chelates have even higher melting points), after sublimation in the tga apparatus is complete. The melts of $\text{NH}_4\text{Sm}(\text{hfa})_4$ and the heavier rare earth analogs also turn brown in the melting point capillaries, and were these chelates less volatile (so that they melted before sublimation was complete), they would probably exhibit the same type of decomposition observed for La–Nd.

Adduct formation, insofar as the water is displaced from the coordination sphere or is less strongly bound than in the tris-chelate hydrates, can remarkably increase the thermal stability. This strongly infers that self-hydrolysis is the dominant contributing factor to thermal instability. The 1:1 and 2:1 DMF adducts illustrate this point, as the chelates $\text{Ln}(\text{hfa})_3 \cdot \text{DMF}$, $\text{Ln}(\text{hfa})_3 \cdot 2\text{DMF}$, and $\text{Ln}(\text{dfhd})_3 \cdot 2\text{DMF}$ volatilize completely, without decomposition, for all of the rare earths (see curve 3 in Figure 1; curves 4 and 6 in Figure 2). Even the La chelates sublime without decomposition, and it will be recalled that complexes of La and some of the other light rare earths often present thermal stability problems not encountered with the more volatile heavier rare earth complexes.

The dimethoxypropane adducts resulted from an attempt to synthesize anhydrous, unsolvated $\text{Ln}(\text{hfa})_3$ and $\text{Ln}(\text{dfhd})_3$. It is unfortunate that the dmp adducts show some slight decomposition upon heating, as they have the lowest half-temperature and presumably the greatest volatility of any rare earth chelates yet known: cf. half-temperatures of 145° for $\text{Er}(\text{hfa})_3 \cdot \text{dmp}$, 158° for $\text{Er}(\text{dfhd})_3 \cdot \text{dmp}$, 160° for $\text{Er}(\text{hfa})_3 \cdot \text{DMF}$,

175° for $\text{NH}_4\text{Er}(\text{dfhd})_4$, 185° for $\text{Er}(\text{hfa})_3 \cdot 2\text{DMF}$, 188° for $\text{Er}(\text{fod})_3$,⁶ and 212° for $\text{Er}(\text{thd})_3$.⁶

General Relationships in the Volatility and Thermal Stability of Rare Earth β -Diketones

The relative effects of fluorination and ligand size on the stability and volatility of various rare earth chelates may be seen in Table VI. Thus, the chelates of

TABLE VI
COMPARATIVE EFFECTS OF LIGAND SIZE AND DEGREE OF FLUORINATION IN RARE EARTH CHELATES OF THE TYPE $\text{Ln}(\text{RCOCHCOR}')_3 \cdot n\text{H}_2\text{O}$

| Ligand | R | R' | n | Volatility characteristics |
|--------|---------------------------|---------------------------|-------------------------|---|
| Hacac | CH_3 | CH_3 | 0, 1, 2, 3 ^a | Negligibly volatile ^{a,b} |
| Htfa | CH_3 | CF_3 | 2 ^b | Slightly volatile ^b |
| Hhfa | CF_3 | CF_3 | 2, 3 ^c | Subl with considerable dec ^{b,c} |
| Hpta | $\text{C}(\text{CH}_3)_2$ | CF_3 | ? | Subl without dec (rare earths Sm-Lu) ^d |
| Hfod | $\text{C}(\text{CH}_3)_2$ | $n\text{-C}_2\text{F}_7$ | 0, 1 ^e | Subl completely without dec ^e |
| Hthd | $\text{C}(\text{CH}_3)_2$ | $\text{C}(\text{CH}_3)_2$ | 0 ^f | Subl completely without dec ^f |
| Hdfhd | CF_3 | $n\text{-C}_2\text{F}_7$ | 2 ^g | Subl with only slight dec ^g |

^a M. F. Richardson, D. E. Sands, and W. F. Wagner, *Inorg. Chem.*, **7**, 2495 (1968). ^b E. W. Berg and J. J. C. Acosta, *Anal. Chim. Acta*, **40**, 101 (1968). ^c Reference 8. ^d T. Shigematsu, M. Matsui, and K. Utsunomiya, *Bull. Chem. Soc. Jap.*, **41**, 763 (1968); M. Tanaka, T. Shono, and K. Shinra, *Anal. Chim. Acta*, **43**, 157 (1968). ^e Reference 6. ^f Reference 7. ^g This work.

Hacac are thermally unstable and not volatile, while those of Hhfa (the fluorinated analog of Hacac) do sublime, albeit with considerable decomposition. When larger ligands or ligands containing fluorine (Hpta, Hfod, Hthd, and Hdfhd) are used, the thermal stability becomes great enough to permit the volatilization, without decomposition, of the chelates. The key to preparing volatile, thermally stable rare earth chelates is thus to use bulky, fluorine-containing ligands.

One striking feature presents itself in examining the present work and other data^{1,6,7,18,20-23} related to the volatility of rare earth chelates: the volatility (as evidenced by tga half-temperatures, gas chromatographic retention times, and vapor pressure measurements) increases as the ionic radius of the rare earth decreases. This phenomenon has been observed to a greater or lesser extent in all series of volatile rare earth chelates yet known. The molecular weight is of little significance in determining the volatility within a given series of chelates. Thus, the heaviest rare earth chelates are the most volatile. On the other hand, the correlation between volatility and ionic radius of the metal is quite good.^{1,20} The position of yttrium is also explained by this correlation; its volatility is similar to that of the Er chelate, and its ionic radius (0.88 Å) is close to that of Er (0.881 Å). The great dependence of volatility on ionic radius of the rare earth implies that dipole forces are important in determining relative volatility.^{6,20} These forces should become smaller as

(20) J. E. Sicre, J. T. Dubois, K. J. Eisentraut, and R. E. Sievers, *J. Amer. Chem. Soc.*, **91**, 3476 (1969).

(21) T. Shigematsu, M. Matsui, and K. Utsunomiya, *Bull. Chem. Soc. Jap.*, **41**, 763 (1968).

(22) W. C. Butts and C. V. Banks, *Anal. Chem.*, **42**, 133 (1970).

(23) M. Tanaka, T. Shono, and K. Shinra, *Anal. Chim. Acta*, **43**, 157 (1968).

(17) S. J. Lippard, *J. Amer. Chem. Soc.*, **88**, 4300 (1966).

(18) R. Belcher, J. Majer, R. Perry, and W. I. Stephen, *J. Inorg. Nucl. Chem.*, **31**, 471 (1969).

(19) M. Ismail, S. J. Lyle, and J. E. Newberry, *ibid.*, **31**, 1715 (1969).

the radius of the metal ion decreases. Also the polar groups in the interior of the molecule should become better shielded as the molecule becomes more compact.

The difference between the half-temperatures ($T_{1/2}$) of the lighter and heavier members of a series of rare earth chelates is usually smaller for the tetrakis salts and solvated tris chelates than for anhydrous, unsolvated tris chelates. For example, $\Delta T_{1/2}$ is $\sim 60^\circ$ for $\text{Sm}(\text{pta})_3\text{-Lu}(\text{pta})_3$,²¹ $\sim 35^\circ$ for $\text{Pr}(\text{thd})_3\text{-Lu}(\text{thd})_3$,¹ and $\sim 70^\circ$ for $\text{Pr}(\text{fod})_3\text{-Lu}(\text{fod})_3$,⁶ but for the solvated and tetrakis chelates listed in Table VI, $\Delta T_{1/2}$ for the Pr (or Nd or Sm) and Lu (or Yb) members of each series ranges from a maximum of $\sim 40^\circ$ to a minimum of $\sim 10^\circ$, *i.e.*, to very little change in half-temperature as a function of ionic radius. One possible explanation of this behavior is that the adducts and tetrakis chelates are not as volatile as the unsolvated tris chelates and that dissociation must take place before vaporization occurs. However, the adducts and tetrakis chelates should become progressively more stable as the ionic radius decreases, due to a more favorable charge:radius ratio. There would thus be two opposing trends:

the increasing volatility of LnL_3 with decreasing ionic radius would be countered by increasing stability of the less volatile salts and adducts. We emphasize that more experimental evidence is needed to confirm this explanation (gas-phase molecular weights would be particularly valuable). Mass spectra have shown that MLnL_4 (M is an alkali metal) chelates can sublime as ion pairs,^{17,18} but to our knowledge little work has been done on the mechanism of volatilization of ammonium tetrakis chelates and solvated tris chelates.

Finally, it should be pointed out that water of hydration does not of necessity have a deleterious effect on the thermal stability of chelates. When the water is not coordinated to the metal or is coordinated but the metal-water bond is much more easily broken than the metal-diketonate bonds (*e.g.*, $\text{Ln}(\text{dfhd})_3 \cdot 2\text{H}_2\text{O}$ and $\text{Ln}(\text{fod})_3 \cdot \text{H}_2\text{O}$), the decomposition due to hydrolysis will be negligible.^{23a}

(23a) NOTE ADDED IN PROOF.—Because these and other related compounds are highly soluble and are better Lewis acids (due to the electron-withdrawing fluorines) than any of the other nmr paramagnetic shift reagents yet reported, we have been examining them for use in nmr spectra clarification.

CONTRIBUTION NO. 1714 FROM THE CENTRAL RESEARCH DEPARTMENT,
EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE 19898

Anomalous Reactions of Sterically Hindered Molybdenum Carbonyl Anions

By S. TROFIMENKO*

Received July 6, 1970

The sterically hindered carbonyl anion $\text{HB}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3\text{Mo}(\text{CO})_3^-$ reacts with either ArSO_2Cl or ArSCl to yield the stable, monomeric red derivatives $\text{HB}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3\text{Mo}(\text{CO})_2\text{SAr}$. A tungsten analog was prepared similarly as was the selenium analog $\text{HB}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3\text{Mo}(\text{CO})_2\text{SeAr}$. The reaction of $\text{HB}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3\text{Mo}(\text{CO})_3^-$ with aryldiazonium salts leads to blue products assigned the structure $\text{HB}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3\text{Mo}(\text{CO})_3\text{Ar}$. Thionyl chloride reacts with $(\text{C}_2\text{H}_5)_4\text{NHB}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3\text{Mo}(\text{CO})_3$ yielding a red precursor which, on contact with alumina, is converted to the green $\text{HB}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3\text{MoCl}_2\text{O}$. Nitrosation of $\text{HB}(3,5\text{-}(\text{C}_2\text{H}_5)_2\text{pz})_3\text{Mo}(\text{CO})_3^-$ gave $\text{HB}(3,5\text{-}(\text{C}_2\text{H}_5)_2\text{pz})_3\text{Mo}(\text{CO})_2\text{NO}$.

One of the several advantages of the tris(1-pyrazolyl)borate ion, $\text{HB}(\text{pz})_3^-$, over the cyclopentadienide ion as a ligand is that by appropriate substitution on the pyrazole rings one can alter the steric and/or electronic environment of the metal ion without destruction of the original symmetry of the parent ligand. It had been found before that presence of alkyl substituents in the 3 positions as in $\text{HB}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3\text{Mo}(\text{CO})_3^-$ increases the electron density on Mo, at the same time restricting the access to the metal by prospective reactants. The result is increased stability of derivatives, coupled with greater difficulty in effecting reactions that proceed through a sterically hindered transition state. For example, while nitrosation proceeds equally

well¹ for the parent $\text{HB}(\text{pz})_3\text{Mo}(\text{CO})_3^-$, for the methylated system $\text{HB}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3\text{Mo}(\text{CO})_3^-$, and even for the still more hindered $\text{HB}(3,5\text{-}(\text{C}_2\text{H}_5)_2\text{pz})_3\text{Mo}(\text{CO})_3^-$, in the reaction with allyl bromide the 3,5-methylated species is inert under conditions² where the parent reacts rapidly. On the other hand, $\text{HB}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3\text{Mo}(\text{CO})_2\text{-}\pi\text{-C}_3\text{H}_5$ has been prepared indirectly³ and is quite stable. The present paper examines some other reactions of the $\text{HB}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3\text{Mo}(\text{CO})_3^-$ species, where unusual results were obtained.

$\text{HB}(3,5\text{-}(\text{CH}_3)_2\text{pz})_3\text{Mo}(\text{CO})_3^-$ reacted readily with *p*-toluenesulfonyl chloride at room temperature yielding as the main product an air-stable red solid which was assigned structure II (Ar = *p*-tolyl) on

* Address correspondence to the Plastics Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Del. 19898.

(1) S. Trofimenko, *Inorg. Chem.*, **8**, 2675 (1969).

(2) S. Trofimenko, *J. Amer. Chem. Soc.*, **91**, 588 (1969).

(3) S. Trofimenko, *ibid.*, **91**, 3183 (1969).