Inorganica Chimica Acta, *122* (1986) L13

Synthesis of THF Adducts of Lanthanide Trihexafluoroacetylacetonate

KEMIN YAO* and GREGORY R. CHOPPIN

Department of Chemistry, Florida State University, Tallahassee, Fla. 32306-3006, U.S.A.

(Received September 3, 1986)

Interest in lanthanide β-diketonates has grown steadily over the last two decades. The stability of these compounds to heat, oxidation and hydrolysis and their solubility in organic solvents has led to their use in gas chromatography, NMR shift reagent studies and laser systems. The tris complexes have been found to be the most useful for these purposes. The fluorine substituted β-diketones are strong Lewis bases and provide increased thermal stability by minimizing hydrolysis. The addition of adduct molecules to the lanthanide tris-β-diketonates also serves to eliminate hydrate water and prevent hydrolysis. The hydrated tris hexafluoroacetylacetonatis-[$Ln(HFA)_3 \cdot mH_2O$] sublime with considerable decomposition whereas the adduct compounds $Ln(HFA)_3 \cdot DMF$, $Ln(HFA)_3 \cdot 2DMF$ (DMF = dimethylformamide) sublime quantitatively with no decomposition.

The $Ln(HFA)_3 \cdot nDMF$ (n = 1,2) compounds have been synthesized by a two step method in which the solid tris compound is prepared first [1] followed by conversion to the adduct compounds [2]. We report a method in which the adduct compounds can be prepared directly, using solvent extraction. In this work, the $Ln(HFA) \cdot (THF)$ (THF = tetrahydrofuran) compounds of Nd, Sm and Eu were synthesized and analyzed. This method is based on the solubility of the hydrates of the tris-β-diketonates in organic solvents and their strong tendency in such solvents to replace the hydrate waters by less polar adducts [3, 4].

The two procedures used are as follows.

A. Benzene Extraction

Ten mmol of the lanthanide nitrate was dissolved in 100 ml of dilute HCl solution (pH 4–6) and the pH adjusted to *ca.* 5. A benzene solution (100 ml) containing 300 mmol of the ammonium salt of hexafluoroacetylacetone (Farchan Lab., Inc.) was prepared by using stoichiometric amounts of HFA and concentrated ammonium hydroxide. Five ml of THF (Aldrich Chem. Co.) was added to the benzene solution which was shaken with the $Ln(NO_3)_3$ aqueous phase in a sepatory funnel. The benzene phase was removed, washed with small amounts of water and dried over Na_2SO_4. Evaporation of the benzene yielded the solid $Ln(HFA)_3 \cdot THF$ which was stored in a desiccator over Na_2SO_4.

TABLE I. Analysis of $Ln(HFA)_3$ THF

Compound	Ln (%)	
	Found	Calculated
$Nd[(CF_3CO)_2CH]_3 \cdot THF$	17.17 ± 0.13	17.23
$Sm[(CF_3CO)_2CH]_3 \cdot THF$	17.27 ± 0.08	17.83
$Eu[(CF_3CO)_2CH]_3 \cdot THF$	17.72 ± 0.19	17.98

B. Ether Extraction

The same procedure was followed using diethylether as the organic solvent. Evaporation of the ether yielded a viscous oil from which the $Ln(HFA)_3 \cdot THF$ compound crystallized. This compound was purified by recrystallization from 9:1 $H_2O:CH_3OH$ solvent.

The Nd and Sm compounds were prepared by *A* while the Eu compound was prepared by *B*. For analysis, the solids were dissolved in a mixture of HNO_3 and $HClO_4$ (3:1) by heating. After evaporation of the excess acid, the residue was dissolved in water, the pH adjusted with hexamethylenetetramine and the lanthanide content determined by titration with EDTA solution using xylenol orange as indicator. Table I shows the results of triplicate analyses.

The ^1H spectra of neat THF and of $Nd(HFA)_3$ THF in $CDCl_3$ were measured on the 270 MHz (Bruker) spectrometer of the FSU NMR laboratory at ambient temperature with TMS internal standard. The peaks at 3.7456 ppm and 1.8521 ppm of the α-CH_2 and β-CH_2 groups of pure THF in $CDCl_3$ were shifted to −0.7116 ppm and −2.8368 ppm, respectively, in the $Nd(HFA)_3$ THF solution. Absence of water resonance line in the spectra confirmed the anhydrous nature of the compound.

Acknowledgements

This research was supported by a contract from the USDOE-BES Division of Chemical Science.

References

1 M. F. Richardson, W. F. Wagner and D. E. Sands, *J. Inorg. Nucl. Chem.*, *30*, 1275 (1968).
2 M. F. Richardson and R. E. Sievers, *Inorg. Chem.*, *10*, 498 (1971).
3 G. M. Kramer, M. B. Dines, R. B. Hall, A. Kaldor, A. J. Jacobson and J. C. Scanlon, *Inorg. Chem.*, *19*, 1340 (1980).
4 F. Halverson, J. S. Brinen and J. R. Leto, *J. Chem. Phys.*, *40*, 2790 (1964).

---

*On leave from Department of Chemistry, Zhejiang University, Hangzhou, China.

0020-1693/86/$3.50