Lanthanide Complexes with 1,5-Diphenyl-1,3,5-pentanetrione.
An example of Anhydrous Lanthanide Complexes

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Introduction

Considerable interest has recently been focused on the coordination properties of 1,3,5-triketones. The ligands form binuclear complexes with metal (II) [1] or (III) [2] ions. However very few examples have been reported with other metal ions [3–5] and only uranyl complexes have been reported with actinide ions [4, 5]. To our knowledge, nothing is known about the lanthanide ions's behavior toward the triketones. In the present letter we report the synthesis of four lanthanide complexes with the triketone 1,5-diphenyl-1,3,5-pentanetrione (H_2DBA) in order to know if the lanthanide ions form mono or binuclear complexes with tris triketone ligand and if such compounds are anhydrous or hydrated.

Experimental

Physical Measurements

Carbon and hydrogen analyses were performed by MicAnal Laboratories, Tucson, Arizona. Lanthanide analyses were carried out by complexometric titrations with EDTA using Eriochrome Black T as the indicator [6].

Infrared spectra were recorded on a Perkin-Elmer 283 B spectrophotometer.; thermogravimetric analyses on a Perkin-Elmer TGS 2 thermobalance.

Synthesis of the Complexes

The ligand 1,5-diphenyl-1,3,5-pentanetrione (H_2-DBA) was purchased from Eastman Organic Chemical Co. and used without further purification. The lanthanum, praseodymium, neodymium and ytterbium nitrates were prepared from the respective oxides (Alfa).

The four compounds were prepared according to the general pattern reported here.

1,5-Diphenyl-1,3,5-pentanetrione (0.0175 mol) was dissolved in 30 ml 95% ethanol and 17.5 ml 1 *M* ethanolic NaOH added. To the resulting solution the appropriate lanthanide nitrate at pH = 5 (0.005 mol in 10 ml water) was added. The solid chelate precipitated and was filtered off, washed with ethanol–water and air-dried at room temperature. The yield was almost quantitative for compounds $Ln(HDBA)_3$.

The reaction between lanthanide nitrate and ligand in a 1:1 relation or with the ligand in excess gives the same compounds, $Ln(HDBA)_3$.

Results and Discussion

The ligand H_2DBA gives yellow complexes with lanthanide nitrates, soluble in common organic solvents. The analytical data suggest (Table I) anhydrous mononuclear compounds.

As was the case with Pd(II) and uranyl chelates [3, 5] with triketone ligands, we could not obtain 2:2 chelates, and the obtained compounds were always 1:3 lanthanide(III) chelates.

The infrared absorption spectra of the four compounds are very similar. The complexes show strong absorption bands in the region 1600–1500 cm^{-1}

TABLE I. Analyses of Complexes.

Compound	Found			Calculated		
	C (%)	H (%)	Metal (%)	C (%)	H (%)	Metal (%)
$La(HDBA)_3$	65.26	4.37	14.32	65.53	4.20	14.86
$Pr(HDBA)_3$	65.12	4.31	14.86	65.39	4.19	15.04
$Nd(HDBA)_3$	65.21	4.20	15.04	65.16	4.18	15.34
$Yb(HDBA)_3$	63.05	4.17	17.20	63.22	4.06	17.86

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arising from C=C and C=O vibrations and a band at 1670 cm^{-1} due to uncoordinated carbonyl groups. The region 4000–3100 cm^{-1} is very similar with those of anhydrous triketonate complexes $Cu_2(daa)_2$, $Pd(daa)_2$ [3–7] (daa = diacetylacetone), as there are no characteristic absorptions of coordinated water.

The thermogravimetric analyses show no detectable weight loss in the region between 90 and 160 °C, indicative of the absence of water in the complexes.

It is known that the lanthanide diketonates obtained from aqueous solutions are almost invariably hydrated [8, 9]. However, the lanthanide complexes reported here are anhydrous and this behavior is a surprising example of the steric requirements of the terminal groups that prevent the coordination of water molecules [10]. Unfortunately we could not obtain a single crystal for X-Ray diffraction.

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