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# Anhydrous and Hydrated Lanthanide(III) β,δ-Triketonates

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## Abstract

Complexes of the β,δ-triketones benzoylacetone and diacetylacetone with lanthanide(III) ions are reported. The compounds with the first ligand (formulated $Ln(Hbaa)_3$) are anhydrous while those with the last one (formulated $Ln(Hdaa)_3 \cdot H_2O$) are hydrated. IR and TGA analyses were carried out to confirm the anhydrous or hydrated character of the complexes. The anhydrous character of the lanthanide complexes with benzoylacetone is discussed in terms of the larger steric requirements in the terminal groups of the ligand with respect to those in the compounds with diacetylacetone.

## Introduction

In a previous letter [1] we reported the complexing behavior of dibenzoylacetone ($H_2dba$) toward the lanthanide(III) ions. The complexes among these species are mononuclear, trischelate and anhydrous with the general formula $Ln(Hdba)_3$. The anhydrous character of these complexes could be a consequence of the steric requirements of the terminal groups in the ligand, in the same way as happens for analogous systems [2, 3]. In order to know the influence of the steric hindrance of the β,δ-triketone's terminal groups on the anhydrous character of their complexes with lanthanide(III) ions, we have synthesized the complexes with the La(III), Pr(III), Nd(III) and Yb(III) ions, and the ligands benzoylacetylacetone ($H_2baa$) and diacetylacetone ($H_2daa$).

## Results

### *Complexes with Benzoylacetylacetone: $Ln(Hbaa)_3$*

These four complexes are yellow powders soluble in polar and non-polar organic solvents (but nof in hexane) and insoluble in water. They melt with decomposition at 92–95 °C. The elemental analyses suggest a 1:3 metal:ligand ratio for all these complexes.

The thermogravimetric analyses for all the complexes show decomposition patterns and no evidence for the presence of coordinated water. Infrared spectra of the four compounds are qualitatively identical. The region of 4000 to 3100 $cm^{-1}$ is nearly flat; this points out the absence of the stretching modes of water and consequently the anhydrous character of the complexes. An absorption due to the uncoordinated keto group is present at 1700 $cm^{-1}$, which is known to appear in mononuclear β,δ-triketonates [4, 5]. Between 1600 and 1500 $cm^{-1}$ there are 3 bands (the maxima of the spectra) that are typical of the C=C and C=O vibrations of this kind of chelates [5, 6, 7].

### *Complexes with Diacetylacetone: $Ln(Hdaa)_3 \cdot H_2O$*

These complexes were obtained as brilliant powders with a characteristic nuance of yellow for every metal, *viz.* lanthanum: soft yellow, praseodymium: yellowish green, neodymium: pinkish yellow, and ytterbium: deep yellow. As in the case of the benzoylacetylacetone complexes, these ones melt with decomposition at 89–91 °C and are dissolved by common organic solvents, but hydrolized by water. The elemental analyses also suggest a 1:3 ratio (metal to ligand). For the four complexes, the thermogravimetric analyses show the presence of 1 mol of water per mol of the complex; the water is eliminated at 130–140 °C. The infrared spectra of the four compounds are almost identical. There is a very wide band centered at 3380 $cm^{-1}$ due to the stretching modes of water; as in the case of the $Ln(Hbaa)_3$ complexes, the band at 1700 $cm^{-1}$ of the uncoordinated carbonyl is also present as well as the maxima of the spectra in the regions due to the C=C and C=O vibrations of the chelate ring.

## Discussion

For the lanthanide(III) β-diketonates, analogous to the present complexes, it has been proved that the presence of the terminal bulky groups in the ligand

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allows the obtainment of anhydrous complexes [8, 9]; however, it has also been shown that terminal phenyl groups in β-diketonates are not bulky enough to avoid the hydrated character of the lanthanide(III) complexes [10, 11]. This evidence points out that in the case of the lanthanide(III) β,δ-triketonates, the anhydrous character of the complexes might be a consequence of some other factors not present in the analogous β-diketonates. One of these additional factors could be the free carbonyl present. In this way, the anhydrous character of dibenzoylacetone [1] and benzoylacetylacetone complexes might be a consequence of a combination of steric shieldings by bulky phenyl groups and uncoordinated keto groups. In the diacetylacetone complexes, this combination is deficient and the Ln(III) complexes are hydrated.

## Experimental

### *Physical Determinations*

Metal content was determined by EDTA titration with xylenol orange as indicator [12]. C, H elemental analyses were performed in commercial laboratories. IR spectra were obtained on a Perkin-Elmer 283-B, and TG analyses on a Perkin-Elmer TGS 2 thermobalance.

### *Synthesis of the Complexes*

Benzoylacetylacetone was prepared by the method of Harris *et al.* [13], and diacetylacetone by the method of Collie and Reilly [14]. Nitrates of the lanthanides prepared from their respective oxides (Alfa) were used. The complexes were obtained as follows·

#### $Ln(Hbaa)_3$

0.0049 mol of $H_2$baa are dissolved in 35 ml of 0.14 M NaOH solution in ethanol–water (1:1). While the solution is stirred, 0.00163 mol of the lanthanide nitrate at pH 5.5 in 30 ml of water are added. Five minutes later, 150 ml of distilled water are added slowly with stirring, to precipitate the complex as a yellow solid. It is separated by vacuum filtration, washed with 5% ethanol solution in water, and then with distilled water. The solid is air dried.

#### $Ln(Hdaa)_3 \cdot H_2O$

0.007 mol of diacetylacetone are dissolved in 5 ml of 1.4 M NaOH solution in water, then 0.0045 mol of the lanthanide nitrate at pH 5.5 in 10 ml of water are added drop by drop with stirring. After 2 min, the resulting solution is extracted with three 15 ml dichloromethane portions. The organic phase is filtered and the solvent is eliminated under reduced pressure. The dry solid residue is redissolved in dry dichloromethane, filtered, and again the solvent is eliminated under reduced pressure. The dry residue is scraped from the flask walls and then dried. (Using an excess of the metal to obtain the diacetylacetone complexes gives the best results, because in this way the organic ligand is eliminated from the medium leaving only the inorganic impurities which are non-soluble in dichloromethane).

With the two ligands we could not obtain binuclear complexes.

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