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# Studies in fluorinated 1,3-diketones and related compounds. Part XVIII. Synthesis of some new tris(1,3-diketonato)lanthanide complexes

Vineeta Sareen *, Rekha Gupta

*Department of Chemistry, University of Rajasthan, Jaipur – 302004, India*

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## Abstract

Six new 1,3-diketonatolanthanide complexes have been synthesized from the fluorinated 1,3-diketones and lanthanide chloride in the presence of methanol, viz. tris(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)-holmium(III),-praseodymium(III) and -erbium(III), and (5,5,5-trifluoro-4,4-difluoro-1-phenyl-1,3-pentanedionato)-holmium(III), -praseodymium(III) and -erbium(III).

*Keywords:* Fluorinated 1,3-diketones; Tris(1,3-diketonato)lanthanide complexes; Holmium(III) complexes; Praseodymium(III) complexes; Erbium(III) complexes; NMR spectroscopy

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## 1. Introduction

The fluorinated metal 1,3-diketonates are of interest as NMR shift reagents [1,2] and in analytical chemistry. The quasi-aromaticity of transition metal 1,3-diketonates is well established and the quasi-aromatic nature of lanthanide 1,3-diketonates has been studied [3–5].

In continuation of our comprehensive programme of developing new fluorinated 1,3-diketones and related compounds [6–10], we now report some new tris(1,3-diketonato)-lanthanide complexes.

## 2. Results and discussion

The complexes prepared were tris(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)-holmium(III), -praseodymium(III) and -erbium(III), and (5,5,5-trifluoro-4,4-difluoro-1-phenyl-1,3-pentanedionato)-holmium(III), -praseodymium(III) and -erbium(III). Infrared (IR) spectra showed important absorption bands at 1620–1540 cm$^{-1}$ (C$\underline{-}$O stretching mode), 1540–1400 cm$^{-1}$ (C$\underline{-}$C stretching mode coupled with the C–H in-plane bending mode), 1579–1445 cm$^{-1}$ (C–F stretching mode of perfluoroalkyl groups) and 1000–850 cm$^{-1}$ (C–F deformation mode of perfluoroalkyl groups). The C=O absorption frequency shifts towards higher frequency on coordination, indicating that chelation is stabilized due to the benzenoid resonance effect in which the lanthanide(III) back-donates its f electrons to the ligand [11,12]. In the IR spectra of the six fluorinated lanthanide tris-1,3-diketonates studied, there is no peak near 1700 cm$^{-1}$ showing that all six oxygen atoms of the $\beta$-diketones are bonded directly to the lanthanide ion.

A sharp signal is observed at $\delta$ (6.2–6.4) ppm in all the $^1$H NMR spectra for the methine proton at the $\gamma$-position of the chelated ring. The aromatic protons produce sharp signals between $\delta$ (6.4–7.9) ppm [10]. Due to the effect of paramagnetism, the disappearance of the enolic proton ($=\overset{|}{C}$–OH) resonance signal in the $^1$H NMR spectrum provides further strong evidence for coordination of the $\beta$-diketonato anion to the lanthanide ion.

## 3. Experimental details

Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer using Nujol mulls while $^1$H NMR spectra were measured by means of a Perkin-Elmer RB-12 spectrometer in CDCl$_3$ solution with TMS as internal standard. The purity of all the compounds was checked by TLC on silica gel plates.

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* Corresponding author.

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Table 1
Analytical and characteristic data of lanthanide tris-1,3-diketonates

| Complex No. | Metal | R | M.p. (°C) | Yield (%) | Molecular formula | Carbon (%) | | Hydrogen (%) | | Fluorine (%) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Calculated | Found | Calculated | Found | Calculated | Found |
| **1** | Ho | $CF_3$ | 163 | 83 | $C_{30}H_{18}F_9O_6Ho$ | 44.44 | 44.40 | 2.22 | 2.20 | 21.11 | 21.10 |
| **2** | Ho | $C_2F_5$ | 170 | 86 | $C_{33}H_{18}F_{15}O_6Ho$ | 41.25 | 41.20 | 1.87 | 1.85 | 29.69 | 29.64 |
| **3** | Pr | $CF_3$ | 158 | 85 | $C_{30}H_{18}F_9O_6Pr$ | 45.80 | 45.78 | 2.29 | 2.25 | 21.76 | 21.70 |
| **4** | Pr | $C_2F_5$ | 140 | 82 | $C_{33}H_{18}F_{15}O_6Pr$ | 42.30 | 42.32 | 1.92 | 1.90 | 30.45 | 30.42 |
| **5** | Er | $CF_3$ | 152 | 83 | $C_{30}H_{18}F_9O_6Er$ | 44.33 | 44.30 | 2.22 | 2.20 | 21.06 | 21.00 |
| **6** | Er | $C_2F_5$ | 165 | 86 | $C_{33}H_{18}F_{15}O_6Er$ | 41.16 | 41.18 | 1.87 | 1.85 | 29.62 | 29.62 |

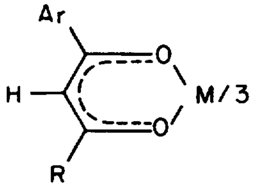
### *3.1. Synthesis of fluorinated 1,3-diketones*

These were prepared by Claisen condensation of the fluorinated acetophenones with the appropriate esters in the presence of sodamide [4].

### *3.2. Preparation of lanthanide tris-1,3-diketonates*

The $\beta$-diketonato enolate anion was prepared by dissolving the corresponding $\beta$-diketone in methanol, then adding dropwise a calculated amount of 2% methanolic sodium hydroxide solution. The appropriate lanthanide chloride (0.004 mol), dissolved in a minimal amount of methanol, was added dropwise to a methanolic solution of $\beta$-diketonato enolate anion (0.012 mol). The complex was precipitated by slow addition of excess water to the resulting methanolic solution. The precipitated lanthanide tris-chelates were crystallized from dichloromethane. Finally, the chelates were dried in vacuum, over phosphorus pentoxide, for 24 h.

The complexes prepared are recorded in Table 1 together with their analytical data.



where Ar = phenyl group, R = $CF_3$, $C_2F_5$ and M = $Ho^{3+}$, $Pr^{3+}$, $Er^{3+}$.

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