Synthesis and Characterization of Several Lanthanide Complexes with Ethyl α-Ketocyclopentyl Carboxylate*

M. A. BAÑARES**, A. ANGOSO, J. L. MANZANO,
E. RODRÍGUEZ and M. T. BLASCO

Departamento de Química Inorgánica, Facultad de C. Químicas, Universidad de Salamanca, 37008-Salamanca, Spain

The literature contains numerous reports of the synthesis and properties of β-diketonates of lanthanides and similar compounds. Owing to the publishing of numerous incompatible data referring to the stoichiometry and properties of such compounds, it has been necessary to examine the methods of synthesis and to introduce certain modifications to them [1].

Ethyl α-ketocyclopentyl carboxylate (HL) is a β-keto ester that exhibits the phenomenon of keto–enol tautomerism and is able to form complex compounds similar to those of the β-diketones. In the present work we report on the preparation of complex compounds formed by HL with the lanthanide ions La(III), Ce(III) and Pr(III) in different media.

Experimental

Synthesis of the Compounds

The procedure employed to obtain the complex compounds was similar in all cases: under conditions of constant stirring, a freshly prepared solution of the enolic form of HL [2] was added dropwise to another solution of the hydrated metal chloride, in the case of lanthanum and praeseodymium, or the hydrated nitrate, in the case of cerium. At first, attempts were made to obtain the complexes in aqueous solution but this proved to be impossible since despite careful monitoring of the pH (always maintained below the precipitation pH of the corresponding hydroxide) it was not possible to avoid coprecipitation of the hydroxide and yield was practically nil, except in the case of the lanthanum compound which recrystallized in absolute ethanol. We then tried to obtain the cerium compound in water/ethanol(1:1) medium but, although the trihydrated compound was isolated, yield was still very low. Accordingly, endeavours were made with success to isolate the praeseodymium compound in absolute ethanol medium, with a yield close to 70% and we were therefore prompted to obtain the lanthanum and cerium compounds in absolute ethanol medium.

The compounds, all of which are obtained as very fine powders, fit in well with the formula (Table I): $LnL_2(OH)\cdot 2C_2H_5OH$, Ln = La, Ce and Pr (absolute ethanol); $CeL_2(OH)\cdot 3H_2O$ (water/ethanol medium).

Methods

Chemical analysis (C and H) of the complexes was carried out by conventional methods. Metal contents were determined with EDTA using xylenol orange as the indicator. Conductivity measurements were performed using a CDM-2c conductimeter with a CDC-104 immersion cell. Thermal analysis of the complexes was performed with a Stanton TR-01 instrument, in air, at a heating schedule of 5.5 °C min^{-1}. Magnetic susceptibilities were determined at room temperature with a Stanton MC-5 Gouy-type balance. The IR spectra (KBr pellets) were recorded on a double-beam Beckman Acculab 10 spectrophotometer (4000–250 cm^{-1}). The electronic spectra were recorded on a Varian-Techtron Model 635 instrument. Finally, the powder diffractograms were recorded on a Siemens Kristalloflex 810 instrument.

TABLE I. Elemental Analysis, Melting Points and Magnetic Moments of the Complexes

Compound	Analysis, found (calc.) (%)			Colour	Melting point (°C)[a]	μ_{eff} (BM)
	Ln	C	H			
$LaL_2(OH)\cdot 2C_2H_5OH$	24.84(24.82)	42.56(43.02)	6.15(6.27)	white	190	diamagnetic
$CeL_2(OH)\cdot 3H_2O$	26.57(26.86)	37.99(36.85)	4.51(5.41)	pale brown	170	2.41
$CeL_2(OH)\cdot 2C_2H_5OH$	25.00(25.04)	42.34(42.89)	6.00(6.26)	pale brown	185	2.29
$PrL_2(OH)\cdot 2C_2H_5OH$	25.11(25.14)	43.02(42.87)	5.98(6.24)	green	185	3.45

[a] At these temperatures the compounds begin to decompose.

---

*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

**Author to whom correspondence should be addressed.

0020-1693/87/$3.50

Results and Discussion

The cerium compound obtained in water/ethanol medium is practically insoluble in all classes of solvents, whereas the compounds obtained in absolute ethanol show a greater tendency to dissolve in non-polar organic solvents but are insoluble in polar solvents.

These compounds decompose before melting at temperatures above 170 °C (Table I). The thermal decomposition of these compounds is similar to that of other complex lanthanide salts [3]. In this sense, the loss of solvated molecules is accompanied by rapid decomposition of the complex until a mixture of oxide and carbonate (in water/ethanolic medium), or the corresponding oxide (in ethanolic medium), are left.

The conductivities of all the compounds show that none of them is a conductor. The solvents used were benzene, toluene and chloroform for the compounds obtained in absolute ethanol, and 1,2-dichloroethane in the case of the trihydrated cerium compound.

The IR spectra resemble those of similar compounds [4]. The IR spectrum of free HL reveals two bands of intense absorption at 1755 and 1725 cm^{-1} that correspond to the stretching vibration of the ester and ketone C=O bond and another weaker band at 1600 cm^{-1} assigned to the stretching vibration of the C=C bond in the conjugated enolic form [5]. In the complexes obtained the bands at 1750 and 1725 cm^{-1} disappear, leading to a strong increase in the intensity of the band present at 1600 cm^{-1}. From this it may be deduced that only the enolic form is present in the complexes and that the ketone and ester groups are involved in bonding with the metal cation. This is confirmed by the appearance of an absorption band at 470 cm^{-1} assigned to the vibration frequency of the M–O group [6] in the spectra of the compounds obtained. Also, in all of them a wide band appears close to 3200 cm^{-1}, which is assigned to the vibration of the O–H group [7].

The values of the magnetic moments determined for the lanthanide ions in our compounds are in good concordance with those found for the tri-positive ions of these elements (Table I) [8].

A diffuse reflectance study was conducted on the compounds obtained. In the case of lanthanum and cerium, as was expected, no band was observed. In the case of praeseodymium, four bands were observed at 589, 484, 469 and 445 nm that are assigned to the transitions $^3H_4$ to $^1D_2$, $^3P_0$, $^3P_1$ and $^3P_2$, respectively [9, 10]. A study was also made of the visible spectra of the praeseodymium compound in chloroform. The same bands appear as in the solid, at the same wavelength and the same intensity. This behaviour is in agreement with the conductivity measurements and the magnetic study conducted; *i.e.*, they are neutral compounds, non-electrolytes, in which the 4f electrons do not participate in the formation of the bonding of the complexes, and in the case of praeseodymium compound in chloroform the nephelauxetic effect is practically nil. In the UV region, a charge transference band appears at 236 nm, the one corresponding to free HL in chloroform appearing at 256 nm.

Finally, a study of the X-ray powder diffraction data was conducted on the complex compounds obtained. The X-ray diagrams point to a low degree of crystallinity and isomorphic behaviour for the compounds obtained in absolute ethanol, while those obtained in water/ethanol solution are amorphous.

Supplementary Material

Supplementary material, including IR, electronic and powder diffraction data can be obtained upon request from M. A. Bañares.

References

1 R. C. Mehrotra, P. N. Kapoor and J. M. Batwara, *Coord. Chem. Rev., 31,* 67 (1980).
2 M. A. Bañares, A. Angoso and S. Yañez, *An. Quim., 75,* 795 (1979).
3 C. Duval, 'Inorganic Thermogravimetric Analysis', Elsevier, Amsterdam, 1963, p. 537.
4 N. K. Khalmurzaev, I. A. Murav'era, L. I. Martynenko, V. I. Spitsyn, A. S. Berlyand, N. G. Dzyubenko and E. D. Stukel'man, *Russ. J. Inorg. Chem., 20,* 980 (1975).
5 M. A. Bañares, A. Angoso, J. L. Manzano, S. Yáñez and B. Macías, *An. Quim., 79B,* 373 (1983).
6 I. B. Liss and W. G. Boss, *J. Inorg. Nucl. Chem., 39,* 443 (1979).
7 N. K. Dutt and S. Rahut, *J. Inorg. Nucl. Chem., 32,* 2905 (1970).
8 B. N. Figgis and J. Lewis, 'Techniques in Inorganic Chemistry', Vol. 4, Interscience, New York, 1965, p. 201.
9 E. V. Sayre, K. M. Sancier and S. Freed, *J. Chem. Phys., 23,* 2060 (1955).
10 E. H. Carlson and G. H. Dieke, *J. Chem. Phys., 34,* 1602 (1961).