

Chemistry of Lanthanons: Part XLIV — Isolation & Characterization of Coumarin-3-carboxylate Chelates of Lanthanons

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Solid chelates of coumarin-3-carboxylic acid with lanthanides having the composition $(LnL_3 \cdot 3H_2O)$ have been isolated and characterized by IR and thermal studies. The formation constants have been determined in acetone-water (1:1 v/v) mixture and the values suggest the formation of bis-complexes in solution, beyond that precipitate appears due to the insoluble nature of the tris-complexes.

COMPLEXES of coumarin derivatives like esculetin¹ (6,7-dihydroxycoumarin), daphnetin² (7,8-dihydroxycoumarin), their 4-methyl³- and 4-phenyl⁴-derivatives and 8-amino-7-hydroxy-4-methylcoumarin⁵ (AHMC) have been reported. Recently the stability constants of complexes of some bivalent metals and rare earth elements with 3-acetyl-4-hydroxycoumarin and its oxime⁶ have been reported in 50% dioxan (v/v) at 35°. This paper reports some lanthanide complexes with coumarin-3-carboxylic acid (CCA).

The chemicals and the solvents used were of reagent grade. Lanthanide oxides and yttrium oxide were those used previously⁷.

Coumarin-3-carboxylic acid was prepared and recrystallized twice from boiling water (charcoal), m.p. 187-89° (lit.⁸ 189°). The preparation and standardization of lanthanide perchlorates have been described earlier^{7,9}.

IR spectra in nujol mull were recorded on a Perkin-Elmer infracord. A Metrimpex derivatograph was used for thermal analysis.

The procedure for determining the formation constants of rare earth complexes has been described earlier^{7,9}. For determining the acid dissociation constant of the ligand same procedure was followed without adding metal ion.

Preparation of the complexes — To an aqueous solution (100 ml) containing 1 mmole of lanthanide

nitrate (pH ~4.5); 60 ml of the reagent solution (4 mmoles of sodium salt) was added with stirring. The insoluble complex separated was digested on a water-bath for 1 hr, filtered and washed successively with hot water and acetone and dried *in vacuo* and analysed (Table 1). The yields are almost quantitative.

In determining the formation constants of lanthanide coumarin-3-carboxylates the metal to ligand ratio was maintained at about 1:4. Because of the low solubility of the ligand and its low pK_a value in an aqueous medium ($pK_a=3.40$), the formation constants were measured in 50% (v/v) acetone-water medium in which the pK_a value is 4.29. The average ligand number (\bar{n}) never rose above 1.1-1.2, beyond which precipitation occurred indicating low solubilities of the tris-complexes.

Inspection of the formation constant data in Table 2 reveals an increase in $\log K_1$ value from La to Sm. The values for Eu and Gd are lower than that of Sm. From Gd to Yb the $\log K_1$ value again rises and the Yb value marginally becomes equal to that of Sm. This is in contrast to the simple carboxylates of lanthanum like acetic acid¹⁰, propionic acid¹¹, isobutyric acid¹¹ etc. where $\log K$ is almost constant. The trend observed in $\log K_1$ is similar to that found for the glycolates¹⁰, glyoxalates¹¹, lactates¹² and quinaldinates¹³.

The analytical data (Table 1) show the formation of tris-chelates. The colours of the complexes are apparently characteristic cations themselves. They are slightly soluble in acetic acid and dimethyl sulphoxide and insoluble in familiar organic solvents like acetone, ethyl alcohol, benzene and chloroform, etc.

The derivatograms of lanthanide complexes $Ln(CCA)_3 \cdot 3H_2O$ (La, Pr and Nd) are similar. The DTA curves show that the first two peaks are endothermic and the later two are exothermic in behaviour. The corresponding DTG also shows four such peaks. The DTA, DTG and TGA curves suggest that the first endothermic peak corresponds to loss of one molecule of water between 50° and 110° and the second endotherm corresponds to the simultaneous loss of remaining two water molecules between 110° and 200°. The weight remains almost constant up to 250°, when oxidative decomposition of the ligand moiety takes place and proceeds till the oxide level is reached at 650°. With the

TABLE 1 — ANALYTICAL RESULTS OF THE RARE EARTH COUMARIN-3-CARBOXYLATES

Compound	Calc. (%)			Found (%)		
	Metal oxide	C	H	Metal oxide	C	H
La(CCA) ₃ ·3H ₂ O	21.42	47.40	2.78	21.26	47.10	2.87
Pr(CCA) ₃ ·3H ₂ O	22.34	47.22	2.75	22.77	46.85	2.88
Nd(CCA) ₃ ·3H ₂ O	21.97	47.06	2.75	21.72	46.86	2.85
Sm(CCA) ₃ ·3H ₂ O	22.59	46.69	2.74	22.62	46.65	2.86
Gd(CCA) ₃ ·3H ₂ O	23.25	46.27	2.72	22.97	46.11	2.81
Dy(CCA) ₃ ·3H ₂ O	23.79	45.96	2.70	23.51	45.74	2.78
Yb(CCA) ₃ ·3H ₂ O	24.79	45.35	2.67	24.70	45.14	2.80
Y(CCA) ₃ ·3H ₂ O	15.90	50.72	2.98	15.80	50.60	3.06

CCA = anion of the ligand, coumarin-3-carboxylic acid.

TABLE 2—FORMATION CONSTANTS OF LANTHANIDE COMPLEXES WITH COUMARIN-3-CARBOXYLIC ACID

Metal ion	Log K_1	Log K_2
La ³⁺	3.54	2.49
Pr ³⁺	3.62	2.49
Nd ³⁺	3.69	2.59
Sm ³⁺	3.83	2.66
Eu ³⁺	3.57	2.47
Gd ³⁺	3.58	2.66
Dy ³⁺	3.72	2.63
Yb ³⁺	3.81	2.59
Y ³⁺	3.65	2.37

heavier lanthanides loss of water molecules takes place in one step.

It is difficult to assign most of the bands in the IR spectra of the complexes. The discussion has been confined to few pertinent bands. Comparing the spectra of the sodium salt of coumarin-3-carboxylic acid and the acid^{14,15} following observations are made:

(i) The sharp band at 1670 cm⁻¹ in the free ligand is absent in the sodium salt.

(ii) Two new bands appeared in the sodium salt at 1630 (medium) and 1453 cm⁻¹ (strong) are due to $\nu_{as}COO^-$ and ν_sCOO^- respectively.

(iii) A slight shift in $\nu C=O$ of δ -lactone has been observed from 1730 to 1748 cm⁻¹ on changing from the acid to its sodium salt.

It has already been observed by several authors¹⁶⁻¹⁸ that the difference, $\Delta\nu$ between the asymmetric and symmetric COO^- stretching frequencies is greater in complexes than in simple salts. It has been suggested that $\Delta\nu > 225$ cm⁻¹ indicates predominantly covalent character of the carboxylate ion while < 225 cm⁻¹, indicates its ionic nature. Thus the appearance of a new sharp band at about 1640 and a medium band at about 1410 cm⁻¹ in the lanthanide complexes of coumarin-3-carboxylates can be reasonably assigned to the asymmetric and symmetric stretching vibrations of the COO^- .

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Reaction of BCl_3 , $AlCl_3$, $SnCl_4$ & $FeCl_3$ with Phenyl Dichlorophosphine & *t*-Butyl Chloride: Isolation of Solid Complexes

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The title reaction gives solid products of the type $[Bu^t-PhPCl_2]^+ [MCl_x]^-$ (where $x = 4$ or 5). The products have been characterized on the basis of elemental analysis and IR data. Structure of iron(III) complex has been further confirmed by UV and Mössbauer studies.

RECENTLY, Bullock *et al.*¹ have obtained some interesting organophosphorus compounds from the reaction systems $AlCl_3-PCl_3$ -alkyl chlorides and $AlCl_3$ -methyl dichlorophosphine-alkyl chlorides. We report here the preparation and characterization of organophosphorus compounds of the type $(Bu^t-PhPCl_2)^+ (MCl_x)^-$ (where $M = Sn(IV)$, $Al(III)$, $Fe(III)$ or $B(III)$ and $x = 4$ or 5) obtained from the reaction of phenyl dichlorophosphine, metal chloride and *t*-butyl chloride.

Because of hygroscopic nature of the compounds all the preparations were carried out under anhydrous conditions. The reactions were carried out in carbon disulphide medium and the order of addition of reagents was kept the same as reported earlier¹, to prevent the formation of polymeric hydrocarbon compounds. However instead of using nitrogen atmosphere, the reactions were carried out under reduced pressure (150 mm). The solid complexes obtained were washed with carbon disulphide and dried *in vacuo* (1-2 mm) at room temperature, yield $> 90\%$. Experimental conditions and characterization data of the complexes are listed in Table 1. All the complexes melted with decomposition above 180-200°. The IR spectra* were recorded in nujol mull on a Beckman IR 20 spectrophotometer. The far IR spectra were recorded at IIT, Delhi. UV spectra were recorded in the solid state at room temperature. Mössbauer spectra were recorded on a constant velocity type of Mössbauer spectrometer.

The complexes were assumed to be composed of univalent ionic species of the type $[Bu^t-PhPCl_2]^+ [MCl_x]^-$ in agreement with the results obtained for $[Bu^t-PCl_2]^+ [AlCl_4]^-$ and similar compounds^{1,2}. The Mössbauer study of the iron(III) complex in the present investigation also confirmed the presence of univalent anionic species. The infrared spectra of the compounds $[Bu^t-PhPCl_2]^+ [BCl_4]^-$, $[Bu^t-PhPCl_2]^+ [AlCl_4]^-$, $[Bu^t-PhPCl_2]^+ [SnCl_5]^-$ and $[Bu^t-PhPCl_2]^+ [Fe-Cl_4]^-$ show very strong bands around 1000 and

*IR data in cm⁻¹.