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Research Article

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New simple chemical reactions for the synthesis of Y(III), Ce(III), Nd(III), Sm(III), Gd(III) and Yb(III) carbonates: Infrared spectroscopic investigations

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ABSTRACT

The rare earth carbonates, $M_2(CO_3)_3{\cdot}xH_2O$, of Y(III), Ce(III), Nd(III), Sm(III), Gd(III) and Yb(III) have been synthesized by a novel synthetic method involving the reaction of aqueous solutions of the Y(III), Ce(III), Nd(III), Sm(III), Gd(III) and Yb(III) acetate salts with urea at ~90-95 ^oC. A study of the IR absorption spectra (4000-400 cm^{-1}) of the formed products clearly indicates the absence of bands due to urea and shows the characteristic bands of carbonate ion. A general mechanism describing the formation of Y(III), Ce(III), Nd(III), Sm(III), Gd(III) and Yb(III) carbonates, $M_2(CO_3)_3{\cdot}xH_2O$, is suggested.

INTRODUCTION

The reactions between the various transition metal ions and lanthanide(III) with urea at room temperature, have been studied extensively [1-8] and many metal-urea complexes have been isolated and characterized. Obviously, it is clear that urea may coordinate either via its oxygen or its nitrogen atoms, depending on the type of metal ion [9-10]. Studies on the nature of the reaction of urea with metal ions at high temperature are rare in the literature, and the available investigations [11-15] show an interesting feature, the reaction products depend not only on the type of metal ion but also on the metal salt used in the reaction. Lanthanide(III) carbonates generally are precipitated from solutions containing lanthanide ions by addition of alkali carbonates or bicarbonates. In the presence of alkali metal ions double salts that may be represented as $M_2(CO_3){\cdot}K_2CO_3{\cdot}nH_2O$ are often formed. This is undesirable if pure lanthanide carbonates, free of extraneous cations, are required. Lanthanide carbonates have also been prepared by passing CO_2 through a suspension of the lanthanide hydroxide or oxide in water [16-17]. The conversion of the oxide into the carbonate is extremely slow and the reactions occur over a period of many hours to several days, and in several instances the reaction product is a mixture of the oxide and carbonate.

A convenient method for the preparation of lanthanide carbonates is the hydrolysis of lanthanide trichloroacetates in a homogenous phase reaction [18-19].

$$2M(Cl_3CCOO)_3 + (x + 3)H_2O \longrightarrow M_2(CO_3)_3{\cdot}xH_2O + 3CO_2 + 6CHCl_3$$

By the use of this method, as well as several variations of this method, all of the lanthanide carbonates, $M_2(CO_3)_3{\cdot}xH_2O$, have been synthesized, where x=8 for the lanthanides of low atomic number and $2 < x < 3$ for the high atomic number elements. The homogenous phase hydrolysis, however, has several drawbacks: the lanthanide is not completely precipitated as the carbonate and the composition of the precipitate is dependent on the experimental conditions under which the precipitation reaction is carried out [20].

The normal carbonates of La(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III) and Ho(III) have been synthesized [21] by the reaction of an aqueous suspension of the lanthanide oxide, M_2O_3, with CO_2 under supercritical conditions. The present investigation was undertaken to study the course of the reaction of urea with lanthanide(III) acetate, $M(CH_3COO)_3$, where M = Y(III), Ce(III), Nd(III), Sm(III), Gd(III) and Yb(III), in aqueous media at ~90-95 °C. The reaction products were characterized by elemental analyses, infrared spectra as well as thermal analyses. The study of the urea complexes is of interest due to the utility of urea complexes as micronutrients and complex fertilizers.

EXPERIMENTAL SECTION

Reagent grade chemicals were used throughout. $M_2(CO_3)_3{\cdot}xH_2$ (M = Y(III), Ce(III), Nd(III), Sm(III), Gd(III) and Yb(III)) were prepared by mixing equal volumes of aqueous solutions (100 mL) of 0.01 mol of lanthanide(III) acetate hydrates with an aqueous (100 mL) solution of (0.6 g, 0.1 mol) urea. The mixtures were heated to *ca* 90-95 °C for 3-5 h in a water bath. The precipitated complexes were filtered, washed several times with hot distilled water, dried at 80 °C in an oven for 3 h and then in *vacuo* over anhydrous calcium chloride. The IR spectra of KBr pellets of urea and the resulted lanthanide carbonates were recorded with a Shimadzu infrared spectrophotometer.

RESULTS AND DISCUSSION

The reaction of aqueous solutions of urea and Y(III), Ce(III), Nd(III), Sm(III), Gd(III) and Yb(III) acetates at *ca.* ~90-95 °C produces solid crystalline products. The infrared spectra of the solid products are shown in Figure 1 and band assignments are given in Table 1. The infrared spectra of the obtained products show no bands due to coordinated urea, but instead, a group of bands characteristic for ionic carbonate,[22] CO_3^{2-}, appeared. Based on this fact, along with that the infrared spectrum of commercially obtained $M_2(CO_3)_2{\cdot}xH_2O$ [M = Y(III), Ce(III), Nd(III), Sm(III), Gd(III) and Yb(III)] are the same as those of the reaction products, the products obtained were identified as hydrated Y(III), Ce(III), Nd(III), Sm(III), Gd(III) and Yb(III) carbonates. The degree of hydration of lanthanide carbonates depends on the conditions that are employed for drying the precipitated carbonate. The IR assignments agree quite well with those generally known for ionic carbonates, $M_2(CO_3)_3$. Previous studies [11-15] indicate that the nature of the reaction product obtained from the reaction of metal ions with urea at high temperature depends upon the type of metal ion and in some cases on the nature of the metal salt used. The role of M(III) ions in decomposing the coordinated urea at high temperature may be understood as follows. At room temperature, lanthanide(III) ions [lanthanide = Y(III), Ce(III), Nd(III), Sm(III), Gd(III) and Yb(III)] react with urea to form a complex,[4,8] $[M(urea)_3](CH_3COO)_3$. At high temperature, the reaction proceeds with the following mechanism:

$$2[M(urea)_3](CH_3COO)_3 + (9+x)H_2O \xrightarrow{ca.\ 90\text{-}95\,^{\circ}C} M_2(CO_3)_3{\cdot}xH_2O + 3CO_2 + 6NH_4CH_3COO + 6NH_3$$

[*x* = degree of hydration]

Table 2: Observed ir frequencies (cm^{-1}) of lanthanide carbonates

Carbonates	O-H stretching	C-O asymmetric stretching	C-O symmetric stretching	CO_3^{2-} out of plane deformation	CO_3^{2-} rocking
Yttrium(III)	3317	1551 1393	1050	867 739	702 676 637
Cerium(III)	3413	1551 1413 1383	1047 1018	907	700
Neodymium(III)	3426	1508 1403	1071	854	715 620
Samarium(III)	3426	1508 1387	1163 1064 1021	939 850	735 673
Gadolinium(III)	3360	1453 1410	1166 1051 1015	922 854	781
Ytterbium(III)	3456	1564 1413 1380	1163 1051 1018	880 837	701 653

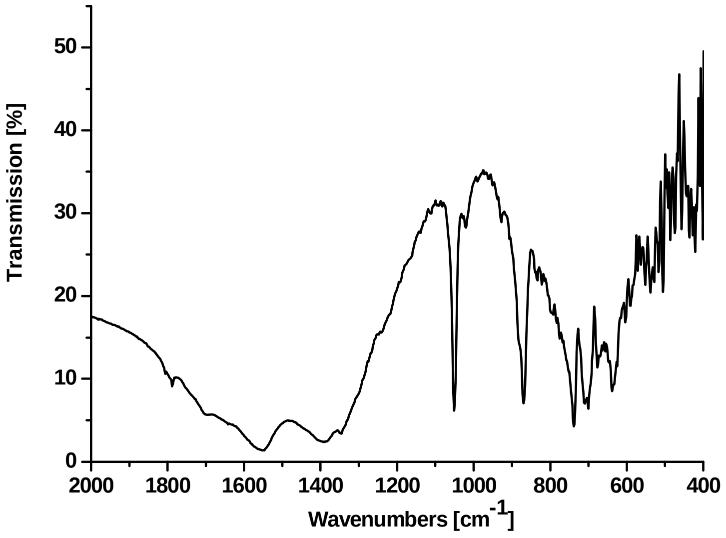

Fig. 1A: Infrared spectra of yttrium(III) carbonate hydrate

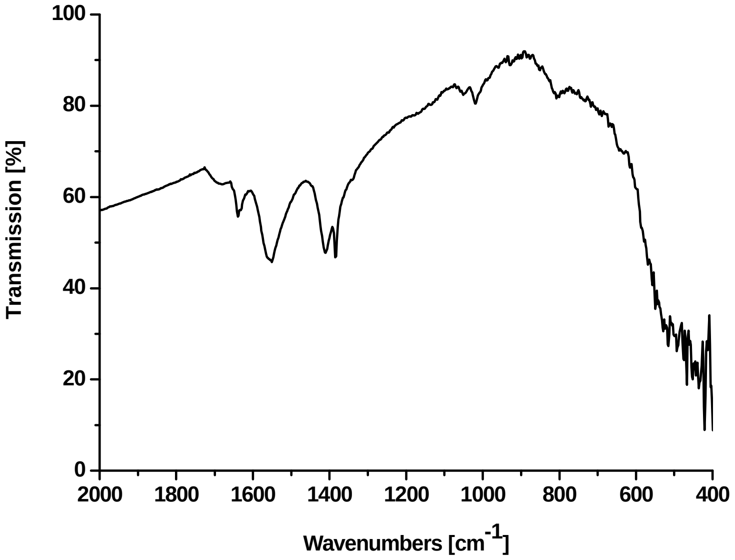

Fig. 1B: Infrared spectra of cerium(III) carbonate hydrate

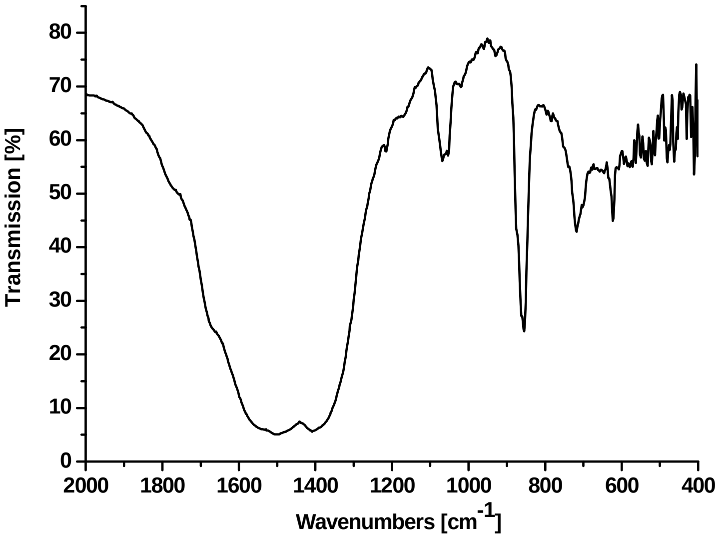

Fig. 1C: Infrared spectra of neodymium(III) carbonate hydrate

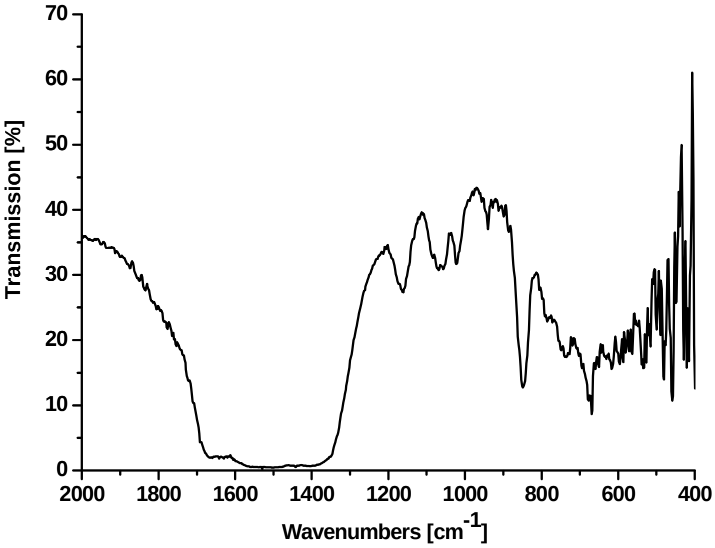

Fig. 1D: Infrared spectra of samarium(III) carbonate hydrate

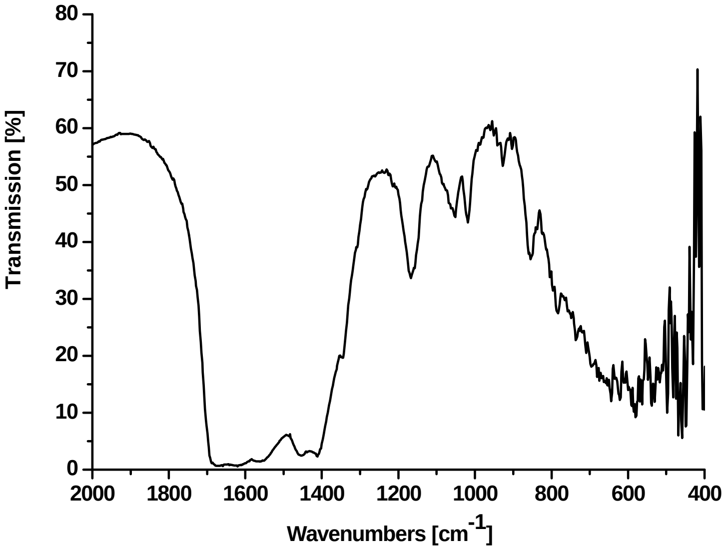

Fig. 1E: Infrared spectra of gadolinium(III) carbonate hydrate

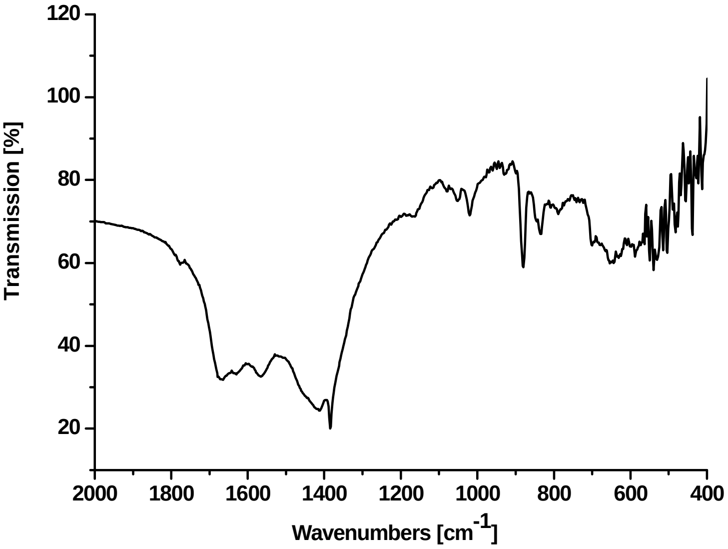

Fig. 1F: Infrared spectra of ytterbium(III) carbonate hydrate

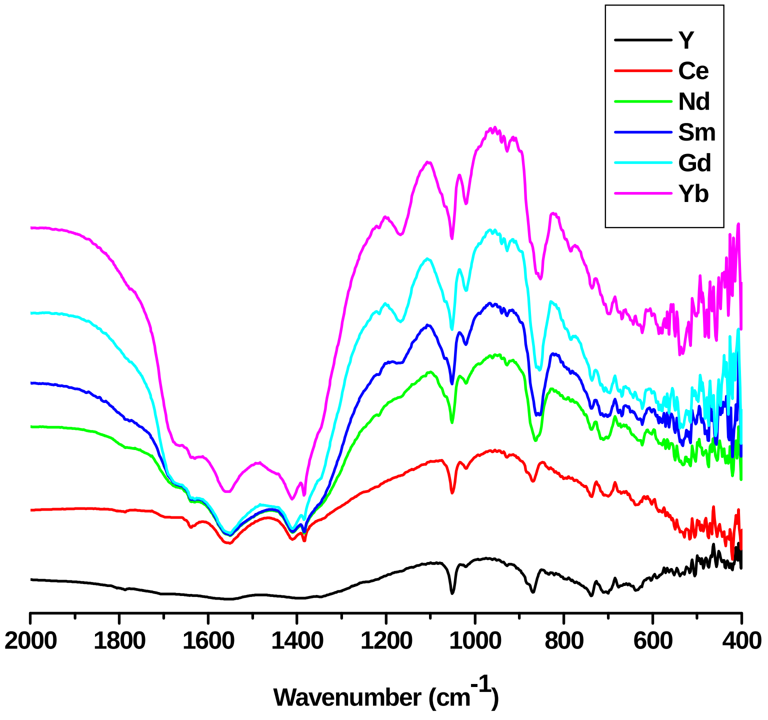

Fig 1: **IR spectra of lanthanide carbonate hydrates**

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