

Study of Temperature Effect on Reaction Product of Some Lanthanide Metal Ions With Urea

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دراسة تأثير درجة الحرارة على ناتج تفاعل بعض الأيونات الفلزية لللانثانات مع اليوريا

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الخلاصة

كربونات اللانثانات $\text{Ln}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ of $\text{LnX}_3 \cdot n\text{H}_2\text{O}$ $\text{Ln} = \text{Dysprosium Dy}$, Holmium Ho , Cerium Ce and Europium Eu ; $\text{X}^- = \text{Cl}^-$ or NO_3^- , $n = 4-6$ تم تحضيرها بطريقة جديدة يشمل تفاعل المحلول المائي لأيونات اللانثانات الفلزية مع اليوريا في درجة حرارية حوالي 85°C لمدة ساعتين . نواتج التفاعلات تم دراستها باستخدام تقنية التحليل الدقيق للعناصر ، الأشعة تحت الحمراء و طريقة التحليل الحجمي و الوزني . ان معادلات التفاعل العام تفسر تكوين كربونات اللانثانات المحتملة.

ABSTRACT

The Lanthanide carbonates, $\text{Ln}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ of $\text{LnX}_3 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Dysprosium Dy}$, Holmium Ho , Cerium Ce and Europium Eu ; $\text{X}^- = \text{Cl}^-$ or NO_3^- , $n = 4-6$) have been prepared by a novel synthetic method involving the reaction of aqueous solutions of the lanthanide metal ions with urea at $\sim 85^\circ\text{C}$ for two hours. The reaction products were characterized via elemental analysis technique , infrared spectroscopy , volumetric and gravimetric analysis method. General reaction equations describing the formation of lanthanide carbonate compounds were proposed.

Key words: Lanthanide carbonates, Lanthanide metal ions, Urea.

Introduction

The lanthanide elements (Ln) form the largest chemically coherent group in the periodic table. Though generally unfamiliar, the lanthanides are essential for many hundreds of applications[1-5]. Stable compounds have been isolated during the reaction of urea, as a neutral oxygen containing molecule, with uranyl ions, and these compounds were well characterized [6-8]. The reactions of lanthanide metal ions with urea and some of its related complexes have been carried out [9-14], and solid metal urea complexes have been isolated and characterized using elemental analysis, electronic and IR spectra, as well as thermal analysis. Lanthanide (Y, La, Ce, Pr, Nd, Sm, Gd and Dy) complexes using substituted urea and thiourea as ligand, and lanthanide mixed complexes using urea and phenylthiourea, have been prepared and characterized [15]. The infrared spectra of all of these complexes showed that urea molecule behaves as a monodentate ligand and coordinates to the metal ions through the oxygen atom and not the nitrogen atom. The common features of all these investigations are the synthesis and the study of the properties of the isolated metal-urea complexes obtained during the reaction of urea with these metal ions at low temperature. But none of them were designed to investigate the nature of the reaction of urea with these metal ions at high temperatures.

Studies on the nature of the reaction of urea with metal ions at high temperature are very rare in the literature, and the available publications describe an interesting feature, the reaction products depend not only on the type of metal ions but also on the metal salt used in these reaction [16-21]. The present study was undertaken to investigate the nature of the reaction products obtained during the reaction of urea with lanthanide (III) ions $\text{LnX}_3 \cdot n\text{H}_2\text{O}$ (Ln= Ce^{3+} , Eu^{3+} , Dy^{3+} and Ho^{3+} ; $\text{X}^- = \text{Cl}^-$ or NO_3^-) in aqueous solution at $\sim 85^\circ\text{C}$. The reaction products were isolated as solids, and characterized by elemental analysis, infrared spectra, volumetric and gravimetric analysis to determine the amount of carbonate and metal percent.

Experimental

Chemicals

All chemicals used in this work were reagent grad (E.Merk & BDH) including Cerium chloride hexahydrate $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$, Europium nitrate pentahydrate $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, Dysprosium nitrate tetrahydrate $\text{Dy}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, Holmium nitrate tetrahydrate $\text{Ho}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, KBr, CaCl_2 , Na_2CO_3 , phenolphthalein indicator, Borax and distilled water was used.

Synthesis of Ce^{3+} , Eu^{3+} , Dy^{3+} and Ho^{3+} Carbonates

$\text{Ln}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ (Ln= Ce^{3+} , Eu^{3+} , Dy^{3+} and Ho^{3+} ; n= 4-6) were prepared by mixing aqueous solutions(100ml) of 0.01M of the respective lanthanide metal salts, $\text{LnX}_3 \cdot n\text{H}_2\text{O}$ ($\text{X}^- = \text{Cl}^-$ or NO_3^- ; n = 4,5 or 6) with a volume of 100ml of 0.1M of urea. The mixtures were heated to $\sim 85^\circ\text{C}$ for 2 hours in a water bath. The

precipitated white compounds were filtered out, washed several times with hot water, dried at 60°C in an oven for 4h and then in desiccator over calcium chloride. The yields of the obtained lanthanide carbonates varied in the range 80 to 75 % depending upon the type of metal and the counter ions associated with the metal ions.

Analytical Methods

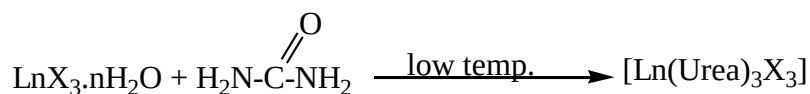
The carbonate content in $\text{Ln}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ was determined by dissolving a weighted sample of the products (1g.) in excess standard HCl ; the excess of HCl was determined by titration with standard sodium carbonate solution, back titration process[22]. Lanthanide metals Dy, Eu and Ho were determined gravimetrically as metal oxides Ln_2O_3 , while cerium was determined as CeO_2 [23], in the education college – scientific departments laboratory, salahaddin university. The infrared spectra of lanthanide carbonates were recorded in KBr discs using Bio-Rad melin Excalibue-Series Spectrophotometer class II laser product 4000-400 cm^{-1} range in the education college – scientific departments laboratory, biology department. Carbon, Hydrogen analyses were made using a Microanalytical Section of the university Sains Malaysia USM institute of post graduate studies.

Results and Discussion

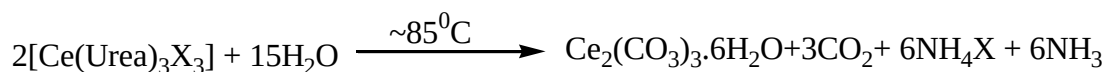
The elemental analysis for $\text{Ln}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ obtained during the reaction of Urea with the respective metal chloride or nitrate were almost identical, and indicated the absence of nitrogen the results are given in Table(1). The reaction of aqueous solutions of urea and lanthanide (III) salts, $\text{LnX}_3 \cdot n\text{H}_2\text{O}$ (Ln= Dy, Ce, Eu and Ho; $\text{X}^- = \text{Cl}^-$ or NO_3^- , n= 4-6) produced white solid products of lanthanide (III) carbonates. The infrared spectra of $\text{Ho}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$ shown in Fig.(1), band assignments of all of infrared bands observed in the spectra of carbonates are given in Table(2).

Previous studies [16-21] indicated that the nature of the reaction products obtained from the reaction of metal ions with urea at high temperature depends upon the type of metal ions and the metal salt used. However, in some cases [21] we have obtained the same product, $\text{MnCO}_3 \cdot \text{H}_2\text{O}$, regardless of the counter ions associated with the manganes (II) ions. In this investigation we have obtained the same reaction products, $\text{Ho}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ by using Holmium (III) metal (Dy, Eu, Ce and Ho) ions associated with different counter ions, Cl^- or NO_3^- . At low temperature, Ho(III) and lanthanide Dy(III), Eu(III) and Ce(III) ions react with urea to form the complex, $[\text{Ln}(\text{Urea})_3\text{X}_3]$ [4-7].

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The role of Ln(III) ions in decomposing the coordinated Urea at high temperature may be understood in the following manner.



Ln= Dy and Ho; X= Cl⁻ or NO₃⁻

Infrared Spectra

The infrared spectra of all obtained products show no bands due to coordinated urea, and a group of bands characteristic for ionic carbonate[24,25]. These bands are observed above 1400 cm⁻¹ and around 1085 cm⁻¹ due to the stretching vibrations, $\nu(\text{C}-\text{O})$, and around 860 and 730 cm⁻¹ due to the bending motions, $\delta(\text{OCO})$, associated with carbonate ions. The assignment of the bands to these frequencies agrees quite well with those generally known for the ionic carbonate. The infrared spectrum obtained for the ionic carbonate (CO_3^{2-}) is almost the same as those of the reaction products. Based on these facts, and along with the data obtained from elemental analysis and the determination of CO_3^{2-} with HCl, the reaction products obtained were identified as $\text{Ln}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$, (Ln= Dy, Ce, Eu or Ho and n= 4-6).

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TABLE-(1). Elemental analysis data of $\text{Ln}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$.

Compounds(Mr)	Analysis (%)			
	Found(calc.)			
	C	H	M	CO ₃ ⁼
Ce ₂ (CO ₃) ₃ .6H ₂ O(568)	6.24(6.33)	2.31(2.11)	50.01(49.33)	31.35(31.69)
Dy ₂ (CO ₃) ₃ .4H ₂ O(577)	6.11(6.23)	1.26(1.38)	55.99(56.32)	31.05(31.19)
Eu ₂ (CO ₃) ₃ .5H ₂ O(573.92)	6.22(6.27)	1.64(1.74)	52.11(52.95)	31.38(31.36)
Ho ₂ (CO ₃) ₃ .4H ₂ O(581.86)	6.19(6.18)	1.33(1.37)	56.70(56.69)	30.90(30.93)

TABLE-(2).Infrared frequencies (cm⁻¹) and assignments of Ln₂(CO₃)₃.nH₂O obtained from the reaction of different LnX₃ salts (Ln= Dy, Ce, Eu and Ho, X⁻ = Cl⁻ or NO₃⁻) with Urea at high temp.

Frequency cm ⁻¹				
Assingnments	Ce ₂ (CO ₃) ₃ .6H ₂ O	Dy ₂ (CO ₃) ₃ .4H ₂ O	Eu ₂ (CO ₃) ₃ .5H ₂ O	Ho ₂ (CO ₃) ₃ .4H ₂ O
ν(O-H) _{H₂O}	(3450)m,b	(3445)m,b	(3440)m,b	(3455)w,b
ν(C-O)str.CO ₃ ²⁻	(1485)w,b(1412)m,b (1071)m	(1470)w,b, (1412)m,b (1066)m	(1507)w,b , (1420)m (1065)m	(1502)m,b (1415)b (1090)w,sh
δ(OCO) _{ben.} CO ₃ ²⁻	(870)m,sh (728)v,sh	(857)m,sh (746)m,sh (705)v,sh	(857)m,sh , (829)s (742)m , (708)m	(880)m,sh,(730)m,sh, (700)m,sh

s=strong , w=weak, v=very, sh=sharp, b=broad, m=medium, str.=stretching, ben.=bending

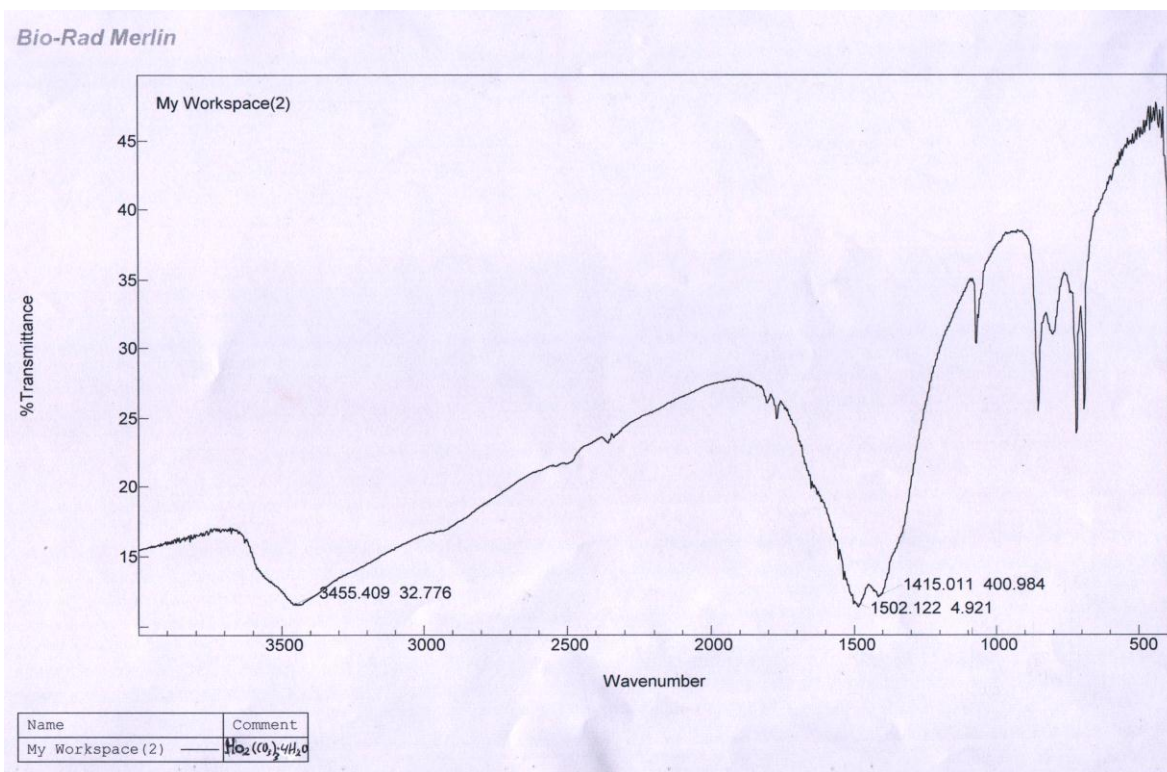


Fig.(1)- Infrared spectra of $\text{Ho}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$.

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