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Preparation of Anhydrous Europium(Ⅲ) and Europium(Ⅱ) Chlorides, and Spectroscopic Studies of their Complexes

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〈Abstract〉

Anhydrous europium(Ⅱ) chloride and europium(Ⅲ) chloride have been prepared from europium trioxide. Europium(Ⅱ) chloride is unstable in air and oxidised quickly to europium(Ⅲ) chloride. Europium(Ⅲ) chloride have a band at 393 nm and europium(Ⅱ) chloride in aqueous solution shows two bands at 320 nm and 248 nm.

무수염화유로피움(Ⅲ)과 염화유로피움(Ⅱ)의 제조와 분광학적 고찰

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〈요 약〉

삼산화유로피움(Eu_2O_3)을 사용하여 무수염화유로피움(Ⅲ)와 무수염화유로피움(Ⅱ)를 제조하였다. 무수염화유로피움(Ⅱ)은 대기중에서 불안정하여 즉시 산화되어 안정한 염화유로피움(Ⅲ)으로 된다. 염화유로피움(Ⅲ)은 393 nm에서 흡수띠를 가지며 수용액상에서 염화유로피움(Ⅱ)은 320 nm와 248 nm에서 흡수띠들을 갖는 것을 알았다.

Ⅰ. Introduction

The replacement of calcium(Ⅱ) by europium (Ⅱ) was reported in a protein, concanavalin A[1]. Measurenents of the magnetic circuler dichroism (MCD) spectra of the europium(Ⅱ) ion of concanavalin A were observed a spectrum which is quite different to that of the aquo and EDTA complexes. UV and visible spectroscopic properties of europium(Ⅱ) chloride in water was studied in Ph. D. thesis of B. D. Mortimer in 1980.[2] The aim of the project was to study spectroscopic properties of $EuCl_2$ in non-aqueous solvents. Before this could be accomplished anhydrous europium(Ⅱ) chloride and europium (Ⅱ) chloride had to be synthesised.[5][7]

Ⅱ. Experimental

1. Preparation of Anhydrous Europium (Ⅲ) Chloride

(1) Dehydration with Ammonium Chloride and Hydrated Europium(Ⅲ) Chloride

About 1.0 g of hydrated europium(Ⅲ) chloride was mixed with about 1.0 g of anhydrous ammonium chloride, ground throughly in a mortar and pestle, and placed in the sample holder of an electric furnace. The mixture was heated

Table 1. Analysis of $EuCl_3$

Exp No.	Sample No.	Temp. °C	Time Hrs.	% Cl		Purity %	Reagents	Colour
				Theor.	Found			
1	MN 80	320	8	41.2	38.66	93.8	Hydrated $EuCl_3$, NH_4Cl	light yellow
2	X-103	430	$9\frac{3}{4}$	〃	37.60	91.3	Eu_2O_3, NH_4Cl	〃
3	X-104	415	9	〃	38.82	94.2	〃	〃
4	X-105	315	4	〃	38.93	94.5	〃	〃
5	X-106	285	$5\frac{1}{4}$	〃	33.08	80.3	〃	〃

slowly in vacuo to 200°C to drive off the water, and finally the temperature was raised to 320°C to sublime the NH_4Cl during a period of eight hours.[3] Anhydrous europium(Ⅲ) chloride was a light yellow powder. Elemental analysis gave 38.66% chlorine. Theoretical value of chlorine is 41.2%. The effect of varing the temperatures and duration of the reaction is shown in Table 1.

(2) Dehydration of NH_4Cl in vacuo

About 10 g of hydrated NH_4Cl was placed in a sample holder of the glass chamber in a electric furnace, and then heated the sample in a vacuum at 300 to 320°C for about two hours.[4]

(3) Dehydration with Ammonium Chloride and Europium(Ⅲ) Oxide

About 0.5 g of europium (Ⅲ) oxide (99.9%, Rare Earth Products Ltd.) was dissolved with heating in 4.0 ml of concentrated HCl,[4] and 0.6 g of anhydrous NH_4Cl was added. The mixture was evaporated to dryness and heated to 200°C on the hot plate. Then it was transferred to the sample holder in the electric furnace. The sealed system was then placed under vacuum and slowly heated. After two hours, the temperature was 200°C. All the water was driven off and the NH_4Cl began to sublime. The temperature was raised to 315°C and maintained at this temperature for a further $1\frac{1}{2}$ hours during which time all the NH_4Cl sublimed. The apparatus was permitted to cool, filled with pure dry N_2 gas, and anhydrous europium (Ⅲ) chloride was transferred to the N_2 filled glove bag. The product was a light yellow powder. Elemental analysis gave 38.93% chlorine. Theoretical value of chlorine is 41.2%. The effect of varing the temperatures and duration of the reaction is shown in Table 1.[5] Dehydration of ammonium chloride was prepared that about 10 g of hydrated NH_4Cl was placed in a sample holder of the pyrex chamber in a electric furnace, and then heated the sample in a vacuum at 300 to 320°C for about two hours.[4]

Table 2. Elemental Analysis of $EuCl_3$

Exp. NO.	Sample NO.	Theorefical			Found		
		N	H	Cl	N	H	Cl
1	MN 80	0	0	41.2	<0.3	2.49	38.66
2	X- 103	0	0	41.2	<0.3	1.72	37.60
3	X- 104	0	0	41.2	<0.3	0.76	38.82
4	X- 105	0	0	41.2	<0.3	0.47	38.93
5	X- 106	0	0	41.2	<0.3	3.09	33.08

Table 3. Analysis of $EuCl_2$

Exp. NO.	Sample NO.	Temp. °C	Time Hrs.	% Cl Theor.	% Cl Found	Purity %	Reagents	Colour
1	FW 07	700	6	31.8	19.19	60.3	MN80, HCl, H_2	grey and white
2	RS 10	700	5	〃	19.57	61.5	MN80, HCl, H_2	〃
3	MN180	700	7	〃	24.99	78.6	MN80, HCl, H_2	〃
4	T009	700	$5\frac{1}{2}$	〃	28.49	89.6	MN80, $EuCl_3$, H_2 N_2	white
5	X-201	700	11	〃	24.83	78.1	T009 black particles, H_2, N_2	black
6	X-102	700	11	〃	26.77	84.2	T009 white particles, H_2, N_2	grey and white
7	X-107	475	2	〃	21.73	68.3	X-104, $EuCl_3$, H_2, N_2	〃

(4) Analysis of Europium (Ⅲ) Chloride

Table 1 shows five preparations with different temperatures and times. The first sample was prepared with hydrated europium(Ⅲ) chloride, but for the other samples europium(Ⅲ) oxide was first dissolved in the concentrated hydrochloric acid. The best result of experiments is the 4th experiment which shows sample number X-105. Its purity is 94.5%. Elemental analysis of europium(Ⅲ) chloride are shown five experimental data in Table 2.

2. Preparation of Anhydrous Europium(Ⅱ) Chloride

(1) *Reduction with Hydrochloric Acid and Hydrogen Gas*

About 1.0 g of anhydrous europium(Ⅲ) chloride was slowly heated with HCl gas in a stream of flow rate and H_2 gas (3 bubbles per second) until 700 °C had been reached after 7 hours. The reaction mixture was cooled to 400 °C and HCl and H_2 gas changed for a stream of N_2 gas. The product was transferred to N_2 filled glove bag. This is sample number MN 180 in Table 3. Elemental analysis gave 24.99% chlorine. Theoretical value of chlorine is 31.8%. The effect of varing the temperatures and duration of the reaction is shown in Table 3.

(2) Reduction with Hydrogen Gas

About 1.0 g of anhydrous europium (Ⅲ) chloride (sample NO. MN80) was heated with H_2 gas until 700 °C had been reached after $5\frac{1}{2}$ hours. The reaction mixture was cooled to 400 °C and H_2 gas changed for a stream of N_2 gas. The product was transferred to N_2 filled glove bag. This is sample number T009 in Table 3.[7] Elemental analysis gave 28.49% chlorine. Theoretical value of chlorine is 31.8%. The effect of varing the temperatures and duration of the reaction is shown in Table 3.

(3) Analysis of Europium (Ⅱ) Chloride

Table 3 shows seven preparations with different temperatures and times. Experiments from first to third were done with HCl, but the others without HCl. Experiments without HCl are seemed to be better than those with HCl. The best result is 4th experiment which shows sample number T009. Elemental analyses of europium (Ⅱ) chloride are shown seven experimental data in Table 3.

Ⅲ. Spectroscopic properties

1. UV and visible spectroscopic property of Europium(Ⅱ) chloride

Europium(Ⅲ) chloride(sample X-104 in Table 1) has an optical density of 0.005 at 394 nm,

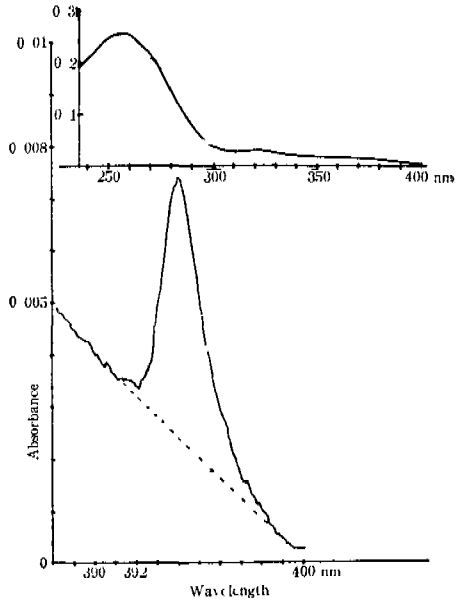

Fig. 1. UV and visible absorption spectrum of $EuCl_3$ (X-104)

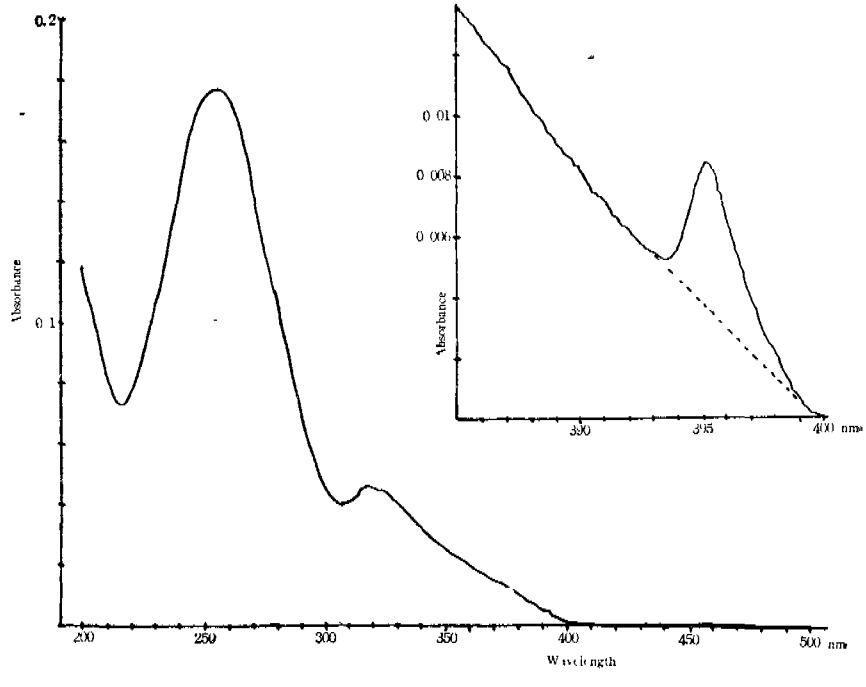

Fig. 2. UV and visible absorption spectrum of $EuCl_2$

which contains 81.44 % of europium(Ⅲ) chloride in Figure 1. The solution of europium (Ⅲ) chloride was made by adding 0.0164 g of europium (Ⅲ) chloride to 12.5 m*l* of concentrated HCl, and then diluted with distilled water to 25.0 m*l* in a volumetric flask.

2. UV and uisible spectroscopic property of Europium (Ⅱ) Chloride

In Figure 2, europium (Ⅱ) chloride (sample T009 in Table 3) has an optical density of 0.00445, which contains 0.01177 g of europium (Ⅲ) chloride. The solution of europium (Ⅱ) chloride was made by adding 0.01795 g of europium (Ⅱ) chloride to 12.5 m*l* of concentrated HCl, and then diluted with distilled water to 25.0 m*l* in a volumetric flask.

Ⅳ. Discussion

The effect of varing the temperatures and duration of the reaction is shown in Table 1 and Table 3 in synthesising europium (Ⅲ) and europium (Ⅱ) chlorides. Samples X-105 in Table 1 gave 38.93 % chlorine. Its purity is 94.5 %. Sample T009 in Table 2 gave 28.49 % chlorine. Its purity is 89.6 %. Sample MN 180 in Table 3 gave 24.99 % chlorine. Its purity is 78.6 %. It is supposed that sample X-107 with least heating shows the lowest % Cl. In synthesising europium (Ⅲ) chloride, it is best to control the temperature at 315°C and maintain this for 4 hours. In the case of synthesing europium (Ⅱ) chloride, we should study further to control temperature and times because we tried to work only two times in 4th and 7th experiments without HCl. Generally experiment without HCl is better than than that with HCl.

In Figure 1 europium (Ⅲ) chloride (sample X-104 in Table 1) has an absorbance of 0.005, which means 81.44 % of purity of europium(Ⅲ) chloride. The extinction coefficient of europium

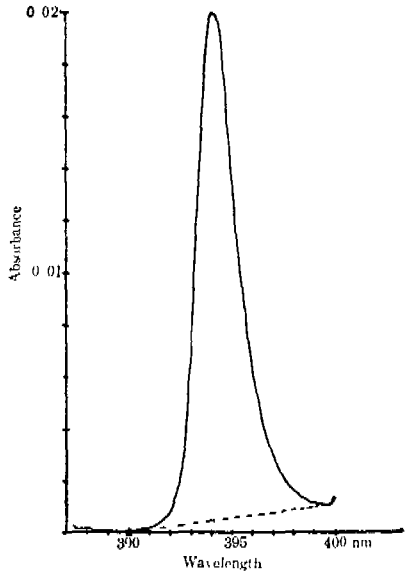

Fig. 3. UV and visible absorption spectrum of Eu_2O_3

(Ⅲ) chloride was found to be 2.41 $M^{-1}Cm^{-1}$ which came from standard solution of europium (Ⅲ) oxide (99.9 %, Rare Earth Products Ltd.) in Figure 3.

In Figure 1, the absorption spectrum of Europium (Ⅲ) chloride in water shows three bands at 394 nm, 317 nm, and 260 nm. In Figure 3 2, 0.01177 g of europium (Ⅱ) chloride was oxidised to europium (Ⅲ) chloride. That means most of the reagent(0.01795 g $EuCl_2$) of europium (Ⅱ) chloride was changed to europium (Ⅲ) chloride. The absorption band of europium (Ⅱ) chloride in water shows a band at 395.2 nm. The absorption spectrum of europium (Ⅱ) chloride in water (sample T009 in Table 3) shows two bands at 317 nm and 254 nm. Some of this variation may be due to the spectrophotometer. Europium(Ⅱ) chloride is to be tested by UV and Visible Spectroscopy before it is oxidised to europium (Ⅲ) chloride.

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