

Lanthanoid Hexaoxiodates(VII)

IV. Cerium(IV) Hexaoxiodate(VII)

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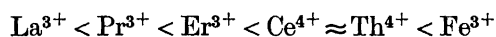
The reactions of cerium(III) and cerium(IV) with periodic acid and with alkali metal hexaoxiodates(VII) were studied. In acid conditions, the product formed was $\text{CeHIO}_6 \cdot 3\text{H}_2\text{O}$ irrespective of the oxidation number of cerium. This was confirmed by magnetic measurements. By heating this compound, $\text{Ce}_2\text{I}_2\text{O}_{11}$ and $\text{Ce}_2\text{I}_2\text{O}_9$ were prepared. The infrared spectra of the compounds were recorded and interpreted and the thermal decomposition of the compounds was studied by TGA and DSC.

The lanthanoid hexaoxiodate most frequently mentioned in the literature is cerium periodate. In 1939 Bahl and Singh¹ reported that they had prepared $\text{CeIO}_5 \cdot 4\text{H}_2\text{O}$ in two different ways. A yellow compound precipitated when an aqueous $\text{Na}_2\text{H}_3\text{IO}_6$ suspension was added to an aqueous solution of cerium nitrate, but a white compound that gradually turned yellow was obtained when H_5IO_6 was used as the precipitating reagent. Two years later, Choudhury published articles dealing with several new M(IV) periodates in which he mentioned, among other compounds, a yellow $\text{CeHIO}_6 \cdot \text{H}_2\text{O}$ that he had synthesized by allowing $\text{Na}_3\text{H}_2\text{IO}_6$ to react with ammonium cerium nitrate.^{2,3} The first measurements to determine the structure of the compound were made by Sahney *et al.*⁴ On the basis of magnetic measurements, they reported the value $\mu_B = 2.356$ for the magnetic moment of the compound $\text{CeIO}_5 \cdot 4\text{H}_2\text{O}$ at room temperature. They concluded that the compound is a true salt and not a complex salt of periodic acid.

The first attempt to determine cerium analytically as a periodate was made in 1949. It was found that cerium(IV) could be separated from other lanthanoids or thorium by precipitating it with potassium metaperiodate as $\text{CeHIO}_6 \cdot \text{H}_2\text{O}$ at a carefully adjusted pH.⁵ Venugopalan and George⁶ determined cerium(IV) by precipitating it with an excess of potassium metaperiodate. Puzdrenkova *et al.*⁷ used the same precipitating reagent in acid

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solution and obtained the product $\text{CeHIO}_6 \cdot 3\text{H}_2\text{O}$, which was decomposed to CeHIO_6 by drying at 130°C . Alimarin and Puzdrenkova⁸ studied periodate complexes of lanthanoids in alkaline solution and observed that the stabilities of the complexes increase in the order:



Alimarin *et al.*⁹ also synthesized the complex salt $\text{Na}_6[\text{Ce}(\text{IO}_6)_2]$.

Table 1. Analytical data for compounds I–VIII.

Synthesized compound	Ce		I		H ₂ O		Weight loss on heating	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
I $\text{CeHIO}_6 \cdot 3\text{H}_2\text{O}$	33.19	33.52	32.84	30.36	12.2	12.92		
II »	33.50		33.30		12.4			
III »	33.13		33.29					
IV »	33.84		33.19					
V »	33.41		33.33		12.0			
VI »	33.55		30.25		12.6			
VII $\text{Ce}_2\text{I}_2\text{O}_{11}$	39.47	39.45	37.45	35.75			15.3	15.07
VIII $\text{Ce}_2\text{I}_2\text{O}_9$	41.66	41.33	37.48	37.43			21.1	18.90

In the present work the reactions of cerium(III) nitrate and cerium(IV) sulphate with H_5IO_6 , $\text{Na}_2\text{H}_3\text{IO}_6$, and $\text{Na}_3\text{H}_2\text{IO}_6$ in acid solution were studied. The compound $\text{CeHIO}_6 \cdot 3\text{H}_2\text{O}$ was obtained despite the oxidation level of cerium, but some iodate precipitated as an impurity when cerium(III) salt was used. Magnetic measurements showed that $\text{CeHIO}_6 \cdot 3\text{H}_2\text{O}$ was only slightly paramagnetic. This suggests that the oxidation number of cerium is four. Since no other investigations on the structures of the lanthanoid periodates have been made, their structures were studied by infrared spectroscopy and by TGA and DSC. The magnetic measurements were made by the Gouy method. No diffraction maxima clearly distinguishable from the background noise were observed in the powder diagrams.

Table 2. Magnetic susceptibilities of preparations I–VI.

Compound	Temperature (K)		$\chi_g \times 10^6$		$\chi_M \times 10^6$	
	T_1	T_2	T_1	T_2	T_1	T_2
I	196	296.2	0.126	0.202	52.7	85.7
II	196	296.7	0.152	-0.046	63.4	-19.2
III	196	296.0	0.110	0.139	46.0	58.1
IV	196	295.9	0.209	0.159	87.4	66.5
V	196	296.0	0.279	0.237	116.7	99.1
VI ^a	77	293.0	-0.074	-0.076	-30.7	-31.9

^a Mean of three determinations.

EXPERIMENTAL

$\text{Ce}(\text{NO}_3)_3$ ("reinst") and $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (*p.a.*) were obtained from E. Merck AG, Darmstadt. The other reagents used were the same as described in Part I.¹⁰

Synthesis I. 0.02198 mol of H_5IO_6 was dissolved in 150 ml of distilled water and added to an equimolar amount of $\text{Ce}(\text{NO}_3)_3$ in aqueous solution at 60°C and the pH adjusted to 1.8. The yellow precipitate that formed was collected on a No. 3 sintered glass filter, washed thoroughly and dried under a pressure of 20 mmHg in a vacuum oven at 39°C. The product was a yellow powder.

Synthesis II. The molar ratio of cerium(III) nitrate and periodic acid was 1:2 and the pH of the solution was adjusted to 1.9. In other details, the procedure was the same as for compound I.

Synthesis III. The molar ratio of cerium(III) nitrate and periodic acid was 2:3. In other details, the procedure was the same as for compound I.

Synthesis IV. An aqueous $\text{Na}_2\text{H}_3\text{IO}_6$ solution made slightly acidic with nitric acid was allowed to react with an equimolar amount of $\text{Ce}(\text{NO}_3)_3$ at pH 1.9. After this, the procedure was the same as for compound I.

Synthesis V. An aqueous $\text{Na}_3\text{H}_2\text{IO}_6$ solution made slightly acidic with nitric acid was allowed to react with an equimolar amount of $\text{Ce}(\text{NO}_3)_3$ at pH 2.5. After this, the procedure was the same as for the compound I.

Synthesis VI. An aqueous $\text{Ce}(\text{SO}_4)_2$ solution made slightly acidic with sulfuric acid was added to an equimolar amount of H_5IO_6 in water at pH 1.5. After this, the procedure was the same as for compound I.

Synthesis VII. The dry product of synthesis IV was heated from room temperature to 355°C during 70 min.

Synthesis VIII. The dry product of synthesis II was heated from room temperature to 365°C during 79 min.

DISCUSSION

Bahl and Singh¹ reported that they had synthesized the compound $\text{CeIO}_5 \cdot 4\text{H}_2\text{O}$. Sahney *et al.*⁴ measured the magnetic moment of cerium in this salt and reported the value $\mu_B = 2.356$. On that basis the same formula was proposed. The product was reported to change colour from white to yellow in the course of the reaction. This suggests that cerium(III) was oxidized to cerium(IV). In addition, the products were of the same color as cerium(IV) periodates prepared later under similar conditions.^{2,3} For this reason, cerium hydrogen hexaaxoiodates(VII) were synthesized in the present work by varying the ratio of cerium salt to periodic acid and the pH. It was observed that Ce(III) and Ce(IV) were precipitated in the form of $\text{CeHIO}_6 \cdot 3\text{H}_2\text{O}$ at pH values from 1.5 to 3. A weak paramagnetism was found in compounds I–V when the cerium(III) salt was used as starting material. This may be explained by assuming that some cerium(III) iodate precipitates when iodine(VII) is reduced and this increases the paramagnetism of the compound. This interpretation is corroborated by the observation that the compound II in which the atomic ratio Ce:I was 1:2 had the lowest susceptibility at room temperature. A diamagnetic compound was obtained when a Ce(IV) salt was the initial reactant.

Iodine analyses revealed that there was more iodine in products I–V than the formula of the compound implies. According to the assumption presented above, even a small amount of cerium(III) iodate present will increase the iodine content of the compound. Therefore, cerium must be oxidized when it is to be determined as CeHIO_6 . Also Puzdrenkova *et al.*⁷ considered

Table 3. Thermal decomposition of preparations I-VI.

Reaction	Δm , % calc.	TGA, $^{\circ}\text{C}$	I Δm , %	DSC, $^{\circ}\text{C}$	TGA, $^{\circ}\text{C}$	II Δm , %	DSC, $^{\circ}\text{C}$	III DSC, $^{\circ}\text{C}$	IV DSC, $^{\circ}\text{C}$	TGA, $^{\circ}\text{C}$	V Δm , %	DSC, $^{\circ}\text{C}$	TGA, $^{\circ}\text{C}$	VI Δm , %	DSC, $^{\circ}\text{C}$
$\text{CeHfO}_6 \cdot 3\text{H}_2\text{O} \rightarrow$	12.92	95-	12.2	113	95-	12.4	119	110	123	95-	12.0	108	90-	12.6	102
$\text{CeHfO}_6 + 3\text{H}_2\text{O}$		270		155	260		162	156		260		155	260		176
CeHfO_6		270-			260-					260-			260-		
		330			335					325			280		
$2\text{CeHfO}_6 \rightarrow$	2.15	330-	2.4	313	335-	2.0	311	309	303	325-	2.1	298	280-	2.5	308
$\text{Ce}_2\text{I}_2\text{O}_{11} + \text{H}_2\text{O}$		345			350					345			320		
$\text{Ce}_2\text{I}_2\text{O}_{11}$		345-			350-					345-			320-		
		370			370					375			340		
$\text{Ce}_2\text{I}_2\text{O}_{11} \rightarrow$	43.76	370-	44.8	491	375-	46.0	492	494	489	375-	45.2	485	340-	2.7	367
$2\text{CeO}_2 + \text{I}_2 +$		490			480		500	499	499	490		497	380		448
$3\frac{1}{2}\text{H}_2\text{O}$													390-		456
CeO_2 (residue)		490-			480-					490-			490-		
Total weight loss	58.83	1000	59.4		1000	60.4				1000	59.3		1000		

the oxidation important after observing that precipitation of Ce(III) required a fivefold excess of the reagent. We have also prepared other cerium hexaoxiodates in acid conditions on which further studies are in progress.

The infrared spectra also corroborated the structure $\text{CeHfO}_6 \cdot 3\text{H}_2\text{O}$ because a weak $\delta(\text{IOH})$ absorption band at $1154 - 1176 \text{ cm}^{-1}$ was detected in spectra of some of the synthesized products. The strongest absorption band in the spectra of compounds I–VI that can be interpreted as a $\nu(\text{IO})$ vibration was found at $720 - 724 \text{ cm}^{-1}$. This band was at 780 cm^{-1} in the spectra of products VII and VIII. Assignments of bands in the infrared spectra are presented in Table 4.

Table 4. Infrared bands of preparations I–VIII.

Assignment			$\text{CeHfO}_6 \cdot 3\text{H}_2\text{O}$				$\text{Ce}_2\text{I}_2\text{O}_{11}$	$\text{Ce}_2\text{I}_2\text{O}_9$
	I	II	III	IV	V	VI	VII	VIII
$\nu(\text{OH})$	3500 s,b	3600– 3400 s,b	3600– 3400 s,b	3600– 3300 s,b	3570 s,b 3420 s,b	3580 s,b 3440 s,b		
$2\delta(\text{IOH})$					2356 w	2368 w		
$\delta(\text{H}_2\text{O})$	1639 m	1642 m	1644 m	1644 m	1638 m	1642 m		
			1156 w,b	1176 w,b	1155 m,b	1154 m,b		
$\delta(\text{IOH})$			1072 w	1072 w	1071 w	1072 w		
$\nu(\text{IO})$	720 s	724 s	724 s	724 s	721 s	720 s	781 s	780 s
	592 sh	588 sh	587 sh	591 sh	592 sh	588 sh	494 sh	494 sh
$\delta(\text{OIO})$	461 ms	462 ms	464 ms	464 ms	464 ms	464 ms	450 s	430 s

s=strong. m=medium. w=weak. b=broad. sh=shoulder.

Thermal decomposition of the compound $\text{CeHfO}_6 \cdot 3\text{H}_2\text{O}$ was followed by TGA and DSC. The decomposition was observed to proceed in the following way:

	TGA (°C)	DSC (°C)
$\text{CeHfO}_6 \cdot 3\text{H}_2\text{O} \rightarrow \text{CeHfO}_6 \cdot \text{H}_2\text{O} + 2\text{H}_2\text{O}$	95 –	102 – 119
$\text{CeHfO}_6 \cdot \text{H}_2\text{O} \rightarrow \text{CeHfO}_6 + \text{H}_2\text{O}$	270	155 – 176
CeHfO_6	260 – 330	
$2\text{CeHfO}_6 \rightarrow \text{Ce}_2\text{I}_2\text{O}_{11} + \text{H}_2\text{O}$	280 – 345	308 – 313
$\text{Ce}_2\text{I}_2\text{O}_{11} \rightarrow \text{Ce}_2\text{I}_2\text{O}_9 + \text{O}_2$	340 – 375	347 – 368
$\text{Ce}_2\text{I}_2\text{O}_9 \rightarrow 2\text{CeO}_2 + \text{I}_2 + 2\frac{1}{2}\text{O}_2$	370 – 490	448 – 484
		456 – 500
Residue CeO_2	490 –	

Although it has been reported earlier that cerium can be determined gravimetrically by precipitation with periodate and subsequent decomposition of the product to $\text{CeHfO}_6 \cdot \text{H}_2\text{O}$ by drying at $100 - 110^\circ\text{C}$,⁵ the thermogram shows that CeHfO_6 is a more stable form. Puzdrenkova *et al.*⁷ also came to the same conclusion. According to the thermogram, the three molecules of water of crystallization seem to be released as a continuous process over the temperature range from 95 to 270°C . However, the DSC reveals that the reaction proceeds in two stages and is endothermic. The third endothermic peak is associated with the release of water that leads to formation of $\text{Ce}_2\text{I}_2\text{O}_{11}$.

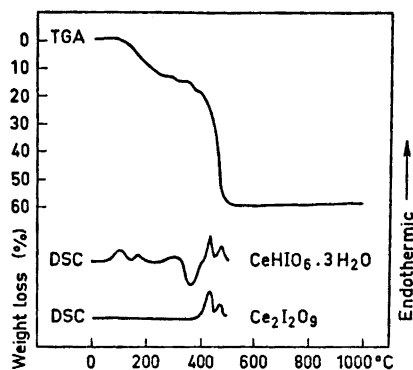


Fig. 1. TGA and DSC diagrams of compound $\text{CeHfO}_6 \cdot 3\text{H}_2\text{O}$ and the DSC diagram of compound $\text{Ce}_2\text{I}_2\text{O}_9$.

The synthesis of this compound was successful only after several attempts, in which the temperature and the time of heating were varied, because the exothermic reaction involving release of oxygen and simultaneous reduction of iodine begins very soon after the release of water. The excess of iodine found in the compound on analysis may be due to iodate present as an impurity in the product as suggested above. The resulting compound $\text{Ce}_2\text{I}_2\text{O}_9$ decomposes endothermically in the temperature range 370–490°C and the reaction proceeds in at least two steps. In their studies on copper hexaoxiodates, Näsänen *et al.*¹¹ came to the same conclusion with respect to the decomposition mechanism and suggested that the compound $\text{Cu}_2(\text{OH})(\text{H}_2\text{IO}_6) \cdot \text{H}_2\text{O}$, for which Siebert has later presented the formula $\text{Cu}_2\text{HfO}_6 \cdot \text{H}_2\text{O}$,¹² decomposes to $\text{Cu}_4\text{I}_2\text{O}_{11}$ at 300°C. The decomposition reaction suggested in the present paper is corroborated by the observation that there were only two endothermic peaks at 489 and 499°C in the DSC diagram of the compound $\text{Ce}_2\text{I}_2\text{O}_9$.

All absorption bands at higher wavenumbers were absent from the infrared spectra of the compounds $\text{Ce}_2\text{I}_2\text{O}_{11}$ and $\text{Ce}_2\text{I}_2\text{O}_9$. The $\nu(\text{IO})$ vibration band had moved 60 cm^{-1} to 780 cm^{-1} and the $\delta(\text{OIO})$ band to 450 and 430 cm^{-1} , respectively. These shifts indicate that rearrangement had taken place when these compounds were produced.

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