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Recebido em 1/2/94, aceito em 3/11/94

A study of both zirconium and hafnium α -hydroxycarboxylates for analytical applications is presented. These compounds are studied by infrared spectroscopy, thermal analysis and X-ray diffractometry. *dl*-Mandelic, *dl*-*p*-bromomandelic and *dl*-2-naphthylglycolic acids are the more adequate reagents for gravimetric determinations of zirconium and hafnium. The ligands *dl*-2-hydroxyhexanoic and *dl*-2-hydroxydodecanoic acids were used for the first time and the results showed that they are also adequate reagents for the same purpose.

Keywords: zirconium α -hydroxycarboxylates; hafnium α -hydroxycarboxylates; zirconium gravimetry; hafnium gravimetry.

INTRODUCTION

Several chelating agents are used to precipitate zirconium or hafnium. The ammoniacal salt of N-nitrosophenylhydroxylamin, cupferron, was the first reagent used for gravimetry of zirconium¹. Using 8-hydroxyquinolein, the precipitate obtained in nitric acid medium in the presence of ammonium acetate, can be weighed directly^{2,3}. Probably mandelic acid, an α -hydroxycarboxylic acid introduced by Kumins⁴ in 1947, is the most used reagent for the gravimetric precipitation of zirconium or hafnium with high selectivity. Oesper and Klingenberg⁵ showed that this selectivity is extensive to the other α -hydroxy-carboxylic acids such as *dl*-*p*-methylmandelic, *dl*-*p*-nitromandelic, *dl*-*p*-bromomandelic, *dl*-*p*-chloromandelic, *dl*-*p*-iodomandelic, *dl*-2-hydroxydecanoic, benzilic and *dl*-2-naphthylglycolic acids.

In this paper we relate the synthesis of zirconium and hafnium complexes with glycolic, *dl*-lactic, *dl*-2-hydroxyisovaleric, *dl*-2-hydroxyhexanoic, *dl*-2-hydroxydodecanoic, *dl*-mandelic, *dl*-*p*-bromomandelic, benzilic and *dl*-2-naphthylglycolic acids. The *dl*-2-hydroxyhexanoic and *dl*-2-hydroxydodecanoic acids are used for the first time as agent for the gravimetry of zirconium or hafnium.

MATERIALS AND METHODS

Apparatus

The melting points were determined with a Leitz Wetzlar-Dialux 247 apparatus, without temperature correction.

The infrared spectra (4,000-200 cm^{-1}) were obtained with a Perkin Elmer 283B spectrophotometer using CsI pellets.

The differential thermal analysis (DTA) and thermogravimetric analysis (TG) curves were obtained with a Rigaku CN 8078B2 Thermogravimetric Differential, Thermal Analyzer High Temperature equipment, from room temperature up to 850 $^{\circ}\text{C}$ in air at normal atmospheric pressure, with a heating rate of 20 $^{\circ}\text{C min}^{-1}$ and graphing speed of 6 mm min^{-1} .

The X-ray diffractograms were obtained by the powder method with a horizontal diffractometer HGZ 4/B with a proportional counter and a height of pulse discriminator with a

Bragg-Bretano assembly, using CuK radiation ($\lambda = 1.51 \text{ \AA}$) with 38 kV and 20 mA in exposure up to 60 $^{\circ}$ (2 θ), angular velocity of 2 $^{\circ} \text{ min}^{-1}$ and graphing speed of 30 mm s^{-1} .

Reagents

All the reagents and solvents of analytical grade were used without previous purification. The *dl*-mandelic, benzilic, and *dl*-*p*-bromomandelic acids were prepared by methods described elsewhere⁶⁻⁹, and the remaining acids were purchased.

Preparation of the zirconium or hafnium α -hydroxycarboxylates

0.1000 g (31.0 μmoles) of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ or 0.1280 g (31.0 μmoles) of $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ were used in all preparation.

a. Complexes obtained by using *dl*-mandelic, *dl*-*p*-bromomandelic and *dl*-2-naphthylglycolic acids [$\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COOH}$, $\text{p-BrC}_6\text{H}_4\text{CH}(\text{OH})\text{COOH}$ and $2\text{-C}_{10}\text{H}_7\text{CH}(\text{OH})\text{COOH}$]

They were prepared according to the Hahn and Joseph method¹⁰ with some modifications¹¹. First, 100 mL of a zirconium (or hafnium) oxychloride solution are heated at 80-90 $^{\circ}\text{C}$ in HCl 6.0 mol L^{-1} . Then 50.0 mL of 0.18 mol L^{-1} solution of the corresponding hydroxycarboxylic acid are added and the mixture digested under magnetic stirring for approximately 30 minutes, at 80-90 $^{\circ}\text{C}$, when precipitation occurs. The mixture is then filtered at room temperature in a Buchner funnel with fritted disc of low porosity. The solid is washed twice with acetone and dried at 150 $^{\circ}\text{C}$ for an hour.

b. Complexes obtained by using glycolic, *dl*-lactic and *dl*-2-hydroxyisovaleric acids [$\text{HCH}(\text{OH})\text{COOH}$, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ and $(\text{CH}_3)_2\text{CHCH}(\text{OH})\text{COOH}$]

To 30.0 mL of a HCl 3.0 mol L^{-1} solution containing $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (or $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$) are added 5.0 mL of 1.8 mol L^{-1} aqueous solution of the respective α -hydroxycarboxylic acid. The volume of this solution was reduced to complete

dryness in a water bath apparatus at 95-100°C. The solid obtained is washed with ethanol and ethyl ether and dried in a desiccator for 24 hours.

c. Complexes obtained by using benzoic acid [(C₆H₅)₂C(OH)COOH]

A mixture of zirconium (or hafnium) oxychloride and 2.000 g (8.72 mmoles) of benzoic acid is kept in 80 mL of HCl 3.0 mol L⁻¹ under reflux for 6 hours. The precipitate is filtered and washed with two portions of 5.0 mL of ethanol/water at 50% and two portions of 5.0 mL of acetone and then dried at 100°C for an hour.

d. Complexes obtained by using *dl*-2-hydroxyhexanoic and *dl*-2-hydroxydodecanoic acids [CH₃(CH₂)₃CH(OH)COOH and CH₃(CH₂)₉CH(OH)COOH]

30.0 mL of an ethanolic solution containing 0.420 g (3.17 mmoles) of *dl*-2-hydroxyhexanoic acid or 0.340g (1.57 mmoles) of *dl*-2-hydroxydodecanoic acid is added, slowly, to 50 mL of 3.0 mol L⁻¹ HCl solution containing zirconium (or hafnium) oxychloride and the mixture is refluxed for 6 hours. The precipitate is washed with ethanol and dried at 150°C for an hour.

RESULTS AND DISCUSSION

The IR spectra of the complexes, compared with those of the free ligands, indicate the displacement of the band attributed to the asymmetric stretching of the carbonyl of the carboxylate group in the free ligands from 1,720-1,770 cm⁻¹ to 1,630-1,675 cm⁻¹ in the corresponding complexes. The intense band around 3,400 cm⁻¹ corresponding to the alcoholic hydroxyl in the free ligands was not observed in the complexes spectra, except for the compounds derived from the glycolic acid. A new intense band (1,350-1,385 cm⁻¹), due to the symmetric stretching of the carbonyl was observed in the

IR spectra of the complexes. In the region of the symmetric stretching of the oxygen-hydrogen bond the presence of three distinct bands of low intensity was observed at 2,550-2,600, 2,250-2,300 and 1,750-1,800 cm⁻¹ attributed to the hydrogen bonds responsible for the dimeric structure proposed for those compounds¹². The change in the intensity of these bands may be an indicative of the degree of compounds dimerization¹³.

The complexes were submitted to calcination at 1,000°C during an hour. From the masses of the resulting oxides, ZrO₂ or HfO₂, the stoichiometry of the corresponding complexes was proposed (Table 1).

Table 1 also presented the initial masses of the complexes used in the thermogravimetric analysis and the final masses of the corresponding oxides, obtained from the respective TG curves, presented in Figure 1. These masses are in agreement with the theoretically calculated values and with those obtained from calcination analysis.

The complexes derived from *dl*-2-hydroxyhexanoic, *dl*-2-hydroxydodecanoic, *dl*-mandelic, *dl*-*p*-bromomandelic and *dl*-2-naphthylglycolic acids are the most stable thermally. The thermodecomposition process of these substances starts at temperatures above 200°C. Zirconium and hafnium glycolate (compounds 1 and 2) and the zirconium lactate (compound 3) are the most unstable thermally with decomposition starting at about 50°C.

The initial and final temperatures of the thermodecomposition processes are also presented in Table 1. It can be observed that these initial temperatures for the complexes of zirconium and of hafnium with the same ligand are practically identical, with the exception of compounds 3 and 4, derived from the lactic acid, and 5 and 6, derived from the *dl*-2-hydroxyisovaleric acid. In these cases the observed temperatures were 180, 50, 100 and 155 °C, respectively. Comparing also the pairs of DTA curves (Figure 2) the same behaviour is observed: the compounds 3/4 and 5/6 do not present similar curves (curves 2a/2b and 3a/3b, respectively). In the other cases the DTA curves are similar.

If we compare the X-ray diffractograms of the zirconium

Table 1. Data from the calcination to oxide and thermogravimetry for the complexes of zirconium and hafnium.

Complexes	No	Calcination to oxide		Thermogravimetric analysis					
		MO ₂ contents (%)		Thermo-decomposition T (°C)		Masses (mg)		MO ₂ contents (%)	
		Calc.	Exper.	Initial	Final	Initial	Final		
[Zr{HCH(OH)COO} ₄]	1	31.3	31.4	50	640	9.60	3.00	31.5	
[Hf{HCH(OH)COO} ₄]	2	43.2	43.7	55	700	9.50	4.20	44.0	
[Zr{CH ₃ CH(OH)COO} ₄]	3	27.6	28.5	180	600	9.8	2.70	27.5	
[Hf{CH ₃ CH(OH)COO} ₄]	4	39.8	39.7	50	630	11.30	4.50	39.4	
[Zr{(CH ₃) ₂ CHCH(OH)COO} ₄]	5	21.8	22.2	100	520	10.30	2.20	22.0	
[Hf{(CH ₃) ₂ CHCH(OH)COO} ₄]	6	32.7	32.3	155	460	9.80	3.20	32.5	
[Zr{CH ₃ (CH ₂) ₃ CH(OH)COO} ₄]	7	20.3	19.9	250	670	10.10	2.05	20.0	
[Hf{CH ₃ (CH ₂) ₃ CH(OH)COO} ₄]	8	29.7	29.9	260	555	10.10	3.00	29.9	
Zr{CH ₃ (CH ₂) ₉ CH(OH)COO} ₄	9	13.2	12.8	220	750	9.80	1.30	12.9	
[Hf{CH ₃ (CH ₂) ₉ CH(OH)COO} ₄]	10	20.2	20.2	230	800	9.90	2.00	20.2	
[Zr{C ₆ H ₅ CH(OH)COO} ₄]	11	19.2	19.0	250	700	10.70	2.05	19.0	
[Hf{C ₆ H ₅ CH(OH)COO} ₄]	12	26.8	26.8	250	630	9.70	2.60	26.9	
[Zr{ <i>p</i> -BrC ₆ H ₄ CH(OH)COO} ₄]	13	12.1	12.1	210	600	10.30	1.25	12.2	
[Hf{ <i>p</i> -BrC ₆ H ₄ CH(OH)COO} ₄]	14	19.1	19.2	200	600	9.40	1.80	19.2	
[Zr{(C ₆ H ₅) ₂ C(OH)COO} ₄]	15	12.9	12.5	140	600	10.10	1.30	12.3	
[Hf{(C ₆ H ₅) ₂ C(OH)COO} ₄]	16	19.2	19.6	150	580	9.90	1.90	19.4	
[Zr{2-C ₁₀ H ₇ CH(OH)COO} ₄]	17	13.8	13.7	250	800	9.40	1.30	13.7	
[Zr{2-C ₁₀ H ₇ CH(OH)COO} ₄]	18	21.6	21.3	250	800	9.70	2.10	21.4	

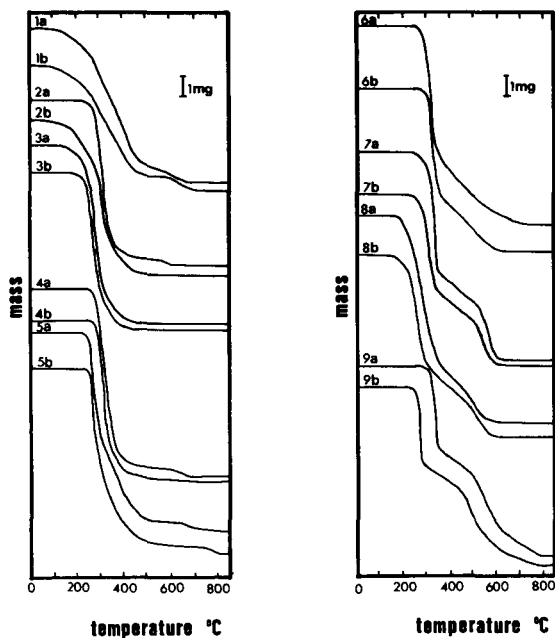


Figure 1. TG curves of the zirconium and hafnium α -hydroxycarboxylates derived from the glycolic (1), dl-lactic (2), dl-2-hydroxyisovaleric (3), dl-2-hydroxyhexanoic (4), dl-2-hydroxydodecanoic (5), dl-mandelic (6), dl-p-bromomandelic (7), benzilic (8), and dl-2-naphthylglycolic (9) acids [a= Zr, b= Hf].

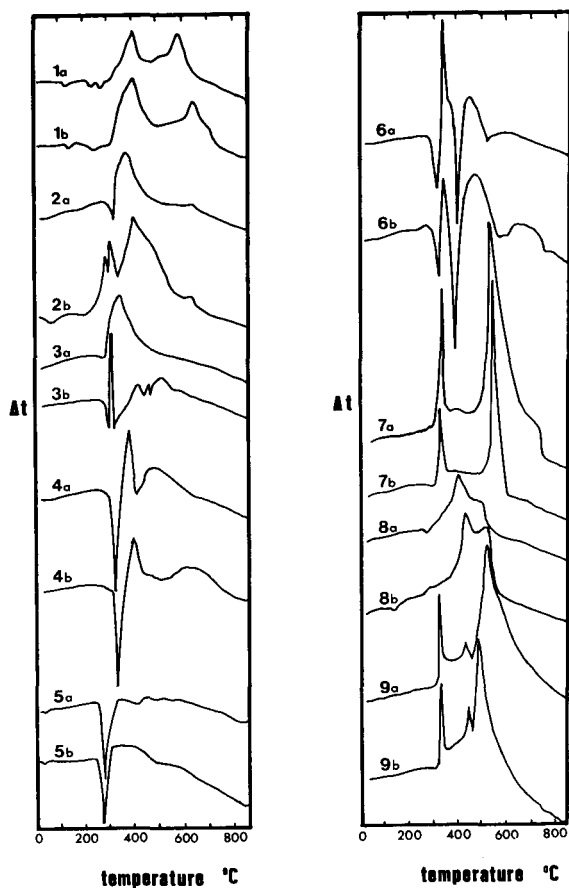


Figure 2. DTA curves of zirconium and hafnium α -hydroxycarboxylates derived from the glycolic (1), dl-lactic (2), dl-2-hydroxyisovaleric (3), dl-2-hydroxyhexanoic (4), dl-2-hydroxydodecanoic (5), dl-mandelic (6), dl-p-bromomandelic (7), benzilic (8), and dl-2-naphthylglycolic (9) acids [a= Zr, b= Hf].

and hafnium compounds (Figure 3) it seems that zirconium complexes present a higher crystallinity. The compounds of zirconium and hafnium derived from the dl-mandelic and dl-p-bromomandelic acids (diffractograms 6a/6b and 7a/7b, respectively) seem to be less crystalline than the analog compounds derived from the benzilic and dl-2-naphthylglycolic acids (diffractograms 8a/8b and 9a/9b, respectively). This observation is surprising since the former acids are considered the best reagents for the gravimetric analysis of zirconium and hafnium^{5,14}. The assumption that the precipitates with these acids should be the best formed, does not seem to be true. Even more surprising is the fact that the complexes of the benzilic acid present a crystallinity relatively superior to the other.

There are some difficulties in the characterization of the structure of the compounds formed by benzilic acid and zirconium. Venkataramaniah and Rao¹⁵ have been suggest $O=Zr(OH)B.4H_2O$ [B= $(C_6H_5)_2C(OH)COO^-$] for the structural formula of zirconium complex. Klingenberg *et al*¹⁶ showed that the stoichiometry of the zirconium benzilate is dependent of the solvent used for the purification of the precipitate. Difficulties was found by Barbiéri and Marques Netto¹⁷ in characterizing the compound formed by irradiated hafnium oxychloride and benzilic acid, which, from the point of view of hyperfine interactions at the level of hafnium nucleus is not well defined.

From the literature^{4,18} it is known that zirconium and hafnium are precipitated from a concentrated HCl solution, by addition of solution of α -hydroxycarboxylic acid in moles proportion ligand:metal around 30:1. The resulting zirconium or hafnium hydroxycarboxylates are calcinated at 1,000°C and weighed in the the form of MO_2 (M= Hf, Zr).

Under the new conditions of this investigation, the acids suited for gravimetric determination of zirconium were the dl-mandelic, dl-p-bromomandelic and dl-2-naphthylglycolic acids. The analysis of the thermogravimetric results indicate that these complexes can be heated up to 200°C without decomposition. Based on these observation Barbiéri *et al*¹¹ have proposed the direct weighing of the precipitates after washing

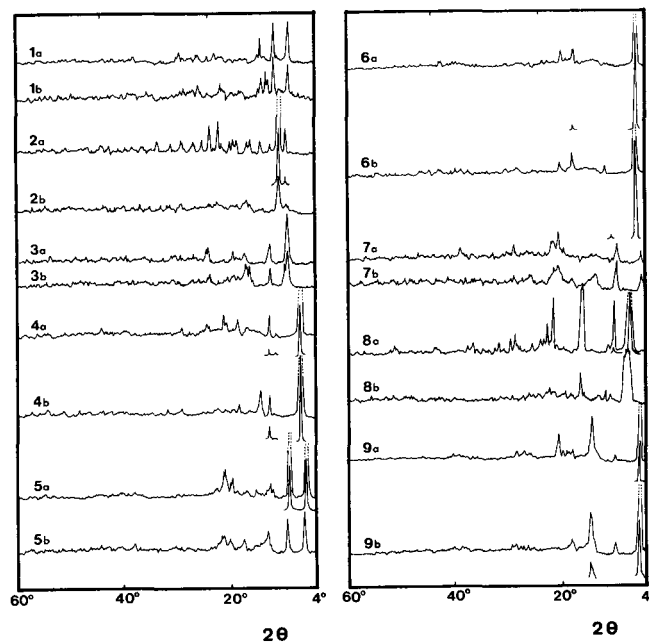


Figure 3. X-Ray diffractograms by the powder method of the zirconium and hafnium α -hydroxycarboxylates derived from the glycolic (1), dl-lactic (2), dl-2-hydroxyisovaleric (3), dl-2-hydroxyhexanoic (4), dl-2-hydroxydodecanoic (5), dl-mandelic (6), dl-p-bromomandelic (7), benzilic (8), and dl-2-naphthylglycolic (9) acids [a= Zr, b= Hf].

with acetone and dried at 150°C for one hour. This procedure reduces significantly the time of the analytical process.

The glycolic, *dl*-lactic and *dl*-2-hydroxyisovaleric acids, on the other hand, do not offer adequate conditions for use as gravimetric reagents for zirconium or hafnium. The respective α -hydroxycarboxylates only can be obtained by evaporation of the solvent and losses of the order of 15-30% occur during the processes of washing for the removal of excess ligand, which jeopardize the direct weighing of the compounds.

In this paper, two new reagents are suggested for zirconium and hafnium analysis: the *dl*-2-hydroxyhexanoic and *dl*-2-hydroxydodecanoic acids. In this case the precipitate obtained after the reflux stage (item **d** - experimental part) is filtered, washed, dried and weighed without previous ignition.

For the other acids used in this work the proportion (in moles) acid-metal in the synthesis was 30:1. In the case of the

dl-2-hydroxyhexanoic and *dl*-2-hydroxydodecanoic acids, this proportion can be reduced to around 10:1 and 5:1, respectively.

Table 2 contains the data obtained, in quadruplicate, relative to the precipitation of zirconium and hafnium from solutions containing 100.0 mg of $ZrOCl_2 \cdot 8H_2O$ or 100.0 mg of $HfCl_4$, by addition of ethanolic solutions of *dl*-2-hydroxyhexanoic and *dl*-2-hydroxydodecanoic acids. The complexes obtained has been formulated as $[M\{RCH(OH)COO\}_4]$ [$M = Zr, Hf$; $R = CH_3(CH_2)_2CH_2, CH_3(CH_2)_8CH_2$] and are not yet described in the literature.

Considering that (i) the use of *dl*-2-hydroxyhexanoic and *dl*-2-hydroxydodecanoic acids spend less quantity of reagent and (ii) the direct weighing of the precipitate prevent the calcination processes, these new reagents can be suggested as excellent options for zirconium and hafnium gravimetric analysis.

Table 2. Masses of precipitates obtained by the addition of ethanolic solutions of *dl*-2-hydroxyhexanoic acid and *dl*-2-hydroxydodecanoic acid to solutions of 4.0 mol L⁻¹ in HCl containing 100.0 mg of $ZrOCl_2 \cdot 8H_2O$ or 100.0 mg of $HfCl_4$.

Gravimetric agents	Metal in solution	Masses of precipitate (mg)		
		Experimental	Average	Calculated
<i>dl</i> -2-Hydroxyhexanoic acid	Zr	190.4	190.8	191.10
		190.7		
		190.8		
		191.2		
	Hf	218.8	219.4	219.51
		219.1		
		219.7		
		220.1		
<i>dl</i> -2-Hydroxydodecanoic acid	Zr	293.7	294.7	295.57
		294.7		
		295.1		
		295.3		
	Hf	323.8	324.3	324.61
		324.2		
		324.3		
		324.3		
		324.7		
		324.7		

ACKNOWLEDGEMENTS

The authors thank the CNPq (Brazilian National Center for Research) for financial support and Dr. Maurício de Paula F. Fontes, UFV, for the thermogravimetric measures.

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