

# INFRARED STUDY OF ZIRCONIUM AND HAFNIUM $\alpha$ -HYDROXYCARBOXYLATES

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■ **ABSTRACT:** Compounds  $[ML_4]$  ( $M = \text{Zr, Hf}$ ;  $L = \alpha$ -hydroxycarboxylate =  $RR'C(OH)COO$ ,  $R = R' = \text{H, C}_6\text{H}_5$ ;  $R = \text{H, R}' = \text{CH}_3$ ,  $(\text{CH}_3)_2\text{CH}$ ,  $\text{CH}_3(\text{CH}_2)_2\text{CH}_2$ ,  $\text{CH}_3(\text{CH}_2)_6\text{CH}_2$ ,  $\text{C}_6\text{H}_5$ ,  $p\text{-BrC}_6\text{H}_4$ ,  $2\text{-Cl}_6\text{H}_7$ ) were prepared and characterized. The infrared study of these compounds permitted to evidence a polarity metal-ligand bonding series and showed a possible dimeric structure resulting from the existence of intramolecular ligand-ligand hydrogen bonding between bridging  $\alpha$ -hydroxycarboxylates.

■ **KEYWORDS:**  $\alpha$ -Hydroxycarboxylic acids; zirconium  $\alpha$ -hydroxycarboxylates; hafnium  $\alpha$ -hydroxycarboxylates.

## Introduction

Many  $\alpha$ -hydroxycarboxylic acids are employed in gravimetric analysis of zirconium and hafnium.<sup>18,20,9</sup> The precipitates are formed in strong acid medium and in others medium the solids obtained are really hydrolyzed with formation of hydroxo or oxo and/or polymeric species<sup>14,19</sup> and this fact difficult further recrystallization of the compounds. The zirconium and hafnium  $\alpha$ -hydroxycarboxylates are insoluble in most used laboratory solvents. For this reason many analytical methods can not be employed to study these compounds. Since they are microcrystalline the X-ray structures determinations are not possible. So the knowledge about this class of compounds is restricted mainly to thermogravimetric<sup>25,12,24</sup> and differential perturbed angular correlation studies.<sup>5,6,1,13</sup>

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The purpose of this work is to relate the results obtained from the infrared study in solid state of zirconium and hafnium  $\alpha$ -hydroxycarboxylates derived from glycolic, *dl*-lactic, *dl*-2-hydroxyisovaleric, *dl*-2-hydroxyhexanoic, *dl*-2-hydroxydodecanoic, *dl*-mandelic, *dl*-*p*-bromomandelic, benzilic, and *dl*-2-naphthylglycolic acids.

## Experimental

### a. Reagents

Zirconium oxychloride octahydrate,  $ZrOCl_2 \cdot 8H_2O$ , Merck; and hafnium oxychloride octahydrate,  $HfOCl_2 \cdot 8H_2O$ , ICN Pharmaceuticals.

$\alpha$ -Hydroxycarboxylic acids: glycolic acid,  $CH_2(OH)COOH$ , Carlo Erba; *dl*-lactic acid,  $CH_3CH(OH)COOH$ , Reagen; *dl*-2-hydroxyisovaleric acid,  $(CH_3)_2CHCH(OH)COOH$ , Fluka; *dl*-2-hydroxyhexanoic acid,  $CH_3(CH_2)_3CH(OH)COOH$ , Fluka; and *dl*-2-hydroxydodecanoic acid,  $CH_3(CH_2)_9CH(OH)COOH$ , Fluka; and *dl*-mandelic acid,  $C_6H_5CH(OH)COOH$ , *dl*-*p*-bromomandelic acid, *p*- $BrC_6H_4CH(OH)COOH$ ; benzilic acid,  $(C_6H_5)_2CH(OH)COOH$ ; and *dl*-2-naphthylglycolic acid,  $2-C_{10}H_7CH(OH)COOH$ , were prepared by methods previously described in the literature.<sup>2-4,17</sup>

All chemicals were used without further purification.

### b. Infrared spectra

The infrared spectra in the 4,000-400  $cm^{-1}$  region were recorded as KBr discs or between KBr plates at room temperature using a Perkin-Elmer 283B spectrometer.

### c. Complexes preparations

All the complexes were prepared by methods described by Barbieri et al.<sup>7,8</sup>

## Results and discussion

The stoichiometry of the complexes was determined by calcination to oxides, carried in a furnace at 1,000 °C, by using porcelain or platinum crucibles. In all cases, the calcination residues were  $ZrO_2$  or  $HfO_2$ , and from the masses of these residues the stoichiometry of the corresponding complexes were established. Table 1 contains the results. All the compounds have four ligands to each central metal atom proportion and are described by  $[ML_4]$   $\{M = Zr, Hf; L = RR'C(OH)COO, R = R' = H, C_6H_5; R = H, R' = CH_3, (CH_3)_2CH, CH_3(CH_2)_2CH_2, CH_3(CH_2)_8CH_2, C_6H_5, p-BrC_6H_4, 2-C_{10}H_7\}$  general formula.

Table - 1 Calcination to oxide and infrared data for the complexes

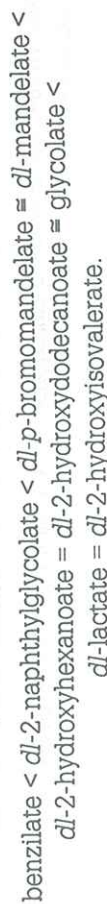
	Calcination to oxide			Infrared		Complexes $\Delta\nu$ $cm^{-1}$
	MO2 contents (M = Zr, Hf) %		Ligands $\nu_{CO}$ $cm^{-1}$	$\nu_{CO}$ $cm^{-1}$	sym.	
	Calcd.	Found	$cm^{-1}$	as.		
$[Zr\{HCH(OH)COO\}_4]$	31.3	31.4	1760	1620	1360	260
$[Hf\{HCH(OH)COO\}_4]$	43.2	43.7	1760	1620	1365	255
$[Zr\{CH_3CH(OH)COO\}_4]$	27.6	23.5	1750	1615	1380	235
$[Hf\{CH_3CH(OH)COO\}_4]$	39.8	39.7	1750	1615	1385	230
$[Zr\{(CH_3)_2CHCH(OH)COO\}_4]$	21.8	22.9	1720	1610	1375	235
$[Hf\{(CH_3)_2CHCH(OH)COO\}_4]$	32.7	32.3	1720	1610	1380	230
$[Zr\{CH_3(CH_2)_3CH(OH)COO\}_4]$	20.3	19.9	1765	1620	1355	265
$[Hf\{CH_3(CH_2)_3CH(OH)COO\}_4]$	29.7	29.9	1765	1620	1360	260
$[Zr\{CH_3(CH_2)_9CH(OH)COO\}_4]$	13.2	12.8	1770	1620	1355	265
$[Hf\{CH_3(CH_2)_9CH(OH)COO\}_4]$	20.2	20.2	1770	1620	1365	255
$[Zr\{C_6H_5CH(OH)COO\}_4]$	19.2	19.0	1720	1620	1340	280
$[Hf\{C_6H_5CH(OH)COO\}_4]$	26.8	26.8	1720	1620	1350	270
$[Zr\{p-BrC_6H_4CH(OH)COO\}_4]$	12.1	12.1	1720	1630	1340	290
$[Hf\{p-BrC_6H_4CH(OH)COO\}_4]$	19.1	19.2	1720	1630	1355	275
$[Zr\{(C_6H_5)_2C(OH)COO\}_4]$	12.9	12.5	1720	1650	1345	305
$[Hf\{(C_6H_5)_2C(OH)COO\}_4]$	19.2	19.5	1720	1650	1355	295
$[Zr\{2-C_{10}H_7CH(OH)COO\}_4]$	13.8	13.7	1720	1635	1330	305
$[Zr\{2-C_{10}H_7CH(OH)COO\}_4]$	21.6	21.3	1720	1635	1350	285

The vibrational spectra in the infrared region for the free  $\alpha$ -hydroxycarboxylic acids and the complexes are presented in Figure 1.

Comparing the free acids and the complexes spectra we can observe a shift between the band at  $1,720-1,770\text{ cm}^{-1}$ , attributed to asymmetric carbonyl stretching mode in the free acids, to  $1,630-1,675\text{ cm}^{-1}$  in the complexes. For the complexes derivated of the *dl*-lactic and *dl*-2-hydroxyisovaleric acids it was verified a strong sharp absorption band at  $1,720-1,750\text{ cm}^{-1}$  for which it wasn't possible any assignment. It was also observed the disappearance of the band at  $3,400\text{ cm}^{-1}$ , assigned for alcoholic hydroxyl in the free acids, and the appearance of a strong band at  $1,340-1,385\text{ cm}^{-1}$ , assigned to symmetric carbonyl stretching in the complexes. These data, presented in Table 1, are consistent with the observations performed by Bolard,<sup>10</sup> for some lactates complexes, and By Kirschner & Kiesling,<sup>16</sup> for tartrates chelates, and are considered to complexes formation evidence.

According to Sawyer et al.<sup>21-22</sup> the absorption frequencies in the  $1,660\text{ cm}^{-1}$  for EDTA complexes with several metals decrease while the ionicity of the metal-ligand bonding increases. The existence of an inverse ratio between the polarity of these bonding and the differences values between the asymmetric and symmetric carbonyl stretchings of the complexes carbonyl group,  $\Delta\nu = \nu\text{CO(as)} - \nu\text{CO(sym)}$ , was established.

In Table 1 are presented the  $\nu\text{CO(as)}$ ,  $\nu\text{CO(sym)}$  and  $\Delta\nu$  values for the zirconium and hafnium complexes studied in this work. The hafnium complexes show  $\Delta\nu$  values smaller than the zirconium complexes corresponding by  $5-20\text{ cm}^{-1}$ . The largest  $\Delta\nu$  values ( $270-305\text{ cm}^{-1}$ ) was observed for compounds containing aromatic ligands (*dl*-mandelic, *dl*-*p*-bromomandelic, benzoic and *dl*-2-naphthylglycolic acids) while complexes with aliphatic ligands (glycolic, *dl*-lactic, *dl*-2-hydroxyisovaleric, *dl*-2-hydroxyhexanoic and *dl*-2-hydroxydodecanoic acids) have the smallest values ( $230-265\text{ cm}^{-1}$ ). Based on these data and in agreement with Sawyer<sup>23</sup> the following order of polarity metal-ligand for the complexes of zirconium and hafnium can be established:



The oxygen-hydrogen bonding stretching regions for all  $\alpha$ -hydroxycarboxylates are very different from those obtained for the corresponding free acid ligand. It was observed the alcoholic  $\nu\text{OH}$  disappearance and appearance typical three-band spectrum associated with a harmonic motion of  $\text{O-H}\cdots\text{O}$ .<sup>15</sup> These band of small intensities are centered on  $2,550-2,600$ ,  $2,250-2,300$  and  $1,750-1,800\text{ cm}^{-1}$  (normally this last band appears as a small shoulder in the carbonyl band). They are attributed to the hydrogen bonding responsible for the dimeric structures [ $\text{I}_3\text{M}(\mu\text{-L})_2\text{ML}_3$ ] proposed for the zirconium and hafnium  $\alpha$ -hydroxy-carboxylates,<sup>19</sup> where the bridging ligand is represented by  $\text{M-O(H)C(R)C(O)O-M}$ . The hydrogen bonds should link the alcoholic oxygen of one bridging  $\alpha$ -hydroxycarboxylate and the carboxylic oxygen of the second bridging  $\alpha$ -hydroxycarboxylate.<sup>19</sup> The variation of the intensities of these bands seems to indicate a dimerization degree of the compounds studied.<sup>5</sup>

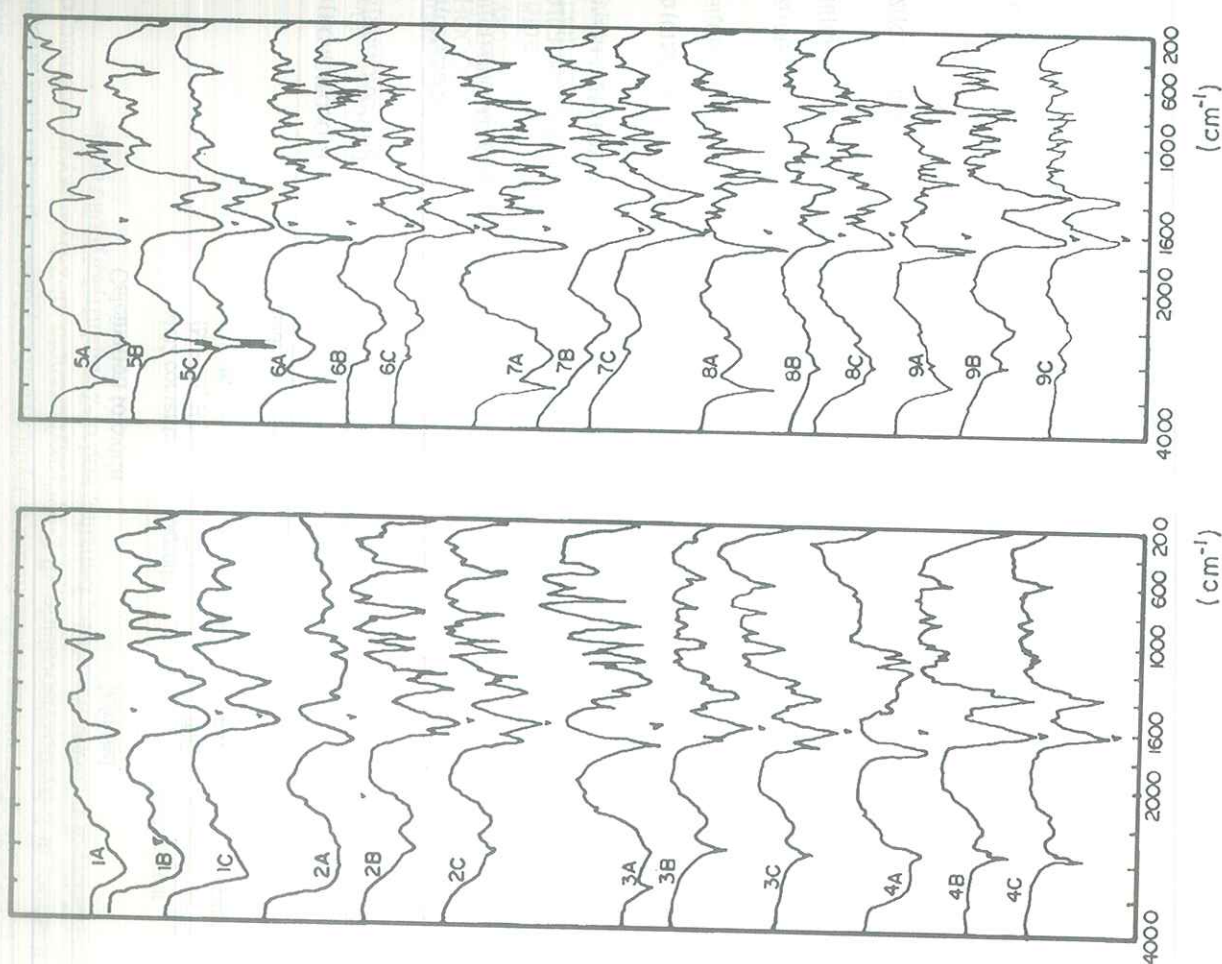


FIGURE 1 - Infrared spectra of the  $\alpha$ -hydroxycarboxylic acids (nA) their zirconium (nB) or hafnium (nC)  $\alpha$ -hydroxycarboxylates (1A: glycolic acid; 2A: *dl*-lactic acid; 3A: *dl*-2-hydroxyisovaleric acid; 4A: *dl*-2-hydroxyhexanoic acid; 5A: *dl*-2-hydroxydodecanoic acid; 6A: *dl*-mandelic; 7A: *dl*-*p*-bromomandelic; 8A: benzoic acid; and 9A: *dl*-2-naphthylglycolic acid).

In the case of complexes derivated from optically actives ligands, 1:4 metal-ligand stoichiometry are obtained only when the ligands in racemic form are employed. Infrared studies performed by Larsen & Homeier<sup>19</sup> in zirconium and hafnium lactates, mandelates and isopropylmandelates protonated and deuterated, perhaps suggest the proposition of the dimeric structures containing hydrogen bonds responsible for the stability of these compounds. The racemic ligand provides a stereospecificity suitable for the formation of hydrogen bonds which doesn't occurs when *d* or *l* enantiomer is used.<sup>19</sup> In fact, these results are consistent with those obtained by Boussaha et al.<sup>11</sup> performed by time differential perturbed angular correlation in hafnium mandelates, prepared from *dl*-mandelic, *d*-mandelic, and *l*-mandelic acids.

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■ **RESUMO:** Foram preparados e caracterizados os complexos de fórmula geral  $[ML_4]$  ( $M = Zr, Hf$ ;  $L = \alpha$ -hidroxycarboxilato =  $RR'(C(OH)COO$ ,  $R = R' = H, C_6H_5$ ;  $R = H, R' = CH_3, (CH_3)_2CH, CH_3(CH_2)_2CH_2, CH_3(CH_2)_8CH_2, C_6H_5, p-BrC_6H_4, 2-C_{10}H_7$ ). O estudo por infravermelho destes compostos permitiu evidenciar uma ordem de polaridade da ligação metal-ligante e indicar possível estrutura dimérica resultante da existência de ligações de hidrogênio entre  $\alpha$ -hidroxycarboxilatos ligados em ponte.

■ **PALAVRAS-CHAVE:** Ácidos  $\alpha$ -hidroxycarboxílicos;  $\alpha$ -hidroxycarboxilatos de zircônio;  $\alpha$ -hidroxycarboxilatos de háfnio.

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