

## Zirconium(IV) Carboxylates

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### Abstract

Zirconium(IV) carboxylates,  $\text{Zr}(\text{OOCR})_4$  where  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $\text{CH}_2\text{Cl}$ ,  $\text{CHCl}_2$  and  $\text{CCl}_3$ , have been prepared by the reaction of zirconium(IV) chloride and carboxylic acids. The compounds have been characterized by elementary analyses, thermogravimetry and infrared spectral data. The compounds are non-electrolytes in nitrobenzene and probably have polymeric structures.

### Introduction

Substitution reactions of zirconium(IV) chloride with carboxylic acids have been studied for a long time.<sup>1-4</sup> Recently Prozorovskaya *et al.*<sup>5</sup> have reported the preparation of zirconium(IV) butyrate by the reaction of  $\text{Zr}(\text{acac})_4$  with excess of butyric acid at  $60^\circ$  and they have also reported its thermal behaviour and infrared spectrum. However, very little information exists concerning the thermal and spectral properties of other zirconium(IV) carboxylates. In this communication we report the preparation and the infrared and thermal analyses of a few tetracarboxylates of zirconium,  $\text{Zr}(\text{OOCR})_4$  where  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $\text{CH}_2\text{Cl}$ ,  $\text{CHCl}_2$  and  $\text{CCl}_3$ .

### Experimental

#### General Procedure for the Preparation of Carboxylates

Zirconium(IV) chloride was refluxed with excess of the pure carboxylic acid under reduced pressure. If the reactants were allowed to reflux at their boiling points, then invariably the product obtained was the oxy derivative,  $\text{OZr}(\text{OOCR})_2$ , or a mixture of tetracarboxylate and oxycarboxylate. The temperature of the reactants was always maintained below  $80^\circ$ . In each case the reaction was continued till the outgoing vapours gave a negative test with silver nitrate. The reactions were generally complete in 4-6 h; a white solid then separated out. The products were washed with suitable solvents and dried in vacuum.

Infrared measurements of the compounds in KBr pellets or Nujol mulls were made on Perkin-Elmer IR 337 and 521 spectrometers. Thermogravimetric analysis was carried out in air on a Stanton Thermobalance TR-1 instrument. Thermograms were obtained on 300-400 mg samples and at  $4^\circ/\text{min}$  heating rate.

<sup>1</sup> Rosenheim, A., and Hertzmann, J., *Ber. Dtsch. Chem. Ges.*, 1907, **40**, 810.

<sup>2</sup> Kapoor, R. N., Pande, K. C., and Mehrotra, R. C., *J. Indian Chem. Soc.*, 1958, **35**, 157.

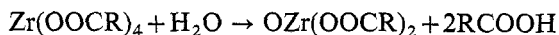
<sup>3</sup> Kapoor, R. N., and Mehrotra, R. C., *J. Chem. Soc.*, 1959, 422.

<sup>4</sup> Jaura, K. L., and Bajwa, P. S., *J. Sci. Ind. Res., Sect. B*, 1961, **20**, 391.

<sup>5</sup> Prozorovskaya, Z. N., Komissarvo, L. N., and Spitsyn, V. I., *Russ. J. Inorg. Chem.*, 1968, **13**, 369.

## Results and Discussion

The analytical results along with some pertinent vibrational bands of the carboxylates prepared are given in Tables 1 and 2. The compounds are insoluble in most common organic solvents, a fact which indicates that they are polymers. They are, however, slightly soluble in nitrobenzene on warming. In millimolar concentration the nitrobenzene solutions are non-conducting which further suggests the covalent nature of the solutes. These compounds decompose before melting. Except for zirconium(IV) acetate, they are highly sensitive to moisture and are converted into their oxy derivatives with the liberation of the parent carboxylic acid:



where R = Et,  $\text{CH}_2\text{Cl}$ ,  $\text{CHCl}_2$  and  $\text{CCl}_3$ . This can be followed in their infrared spectra by the development of a band between  $1700\text{--}1720\text{ cm}^{-1}$  which may be assigned to the  $\nu(\text{C}=\text{O})$  band of the carboxylic acids. Infrared spectra of these compounds are quite complicated as compared to the corresponding spectra of the free carboxylic acids or their sodium salts. This can be explained both in terms of their extreme instability in air and also due to their having polymeric structures. The separation  $\Delta\nu(\text{COO}^-)$  between the  $\nu(\text{COO}^-)_{\text{asym}}$  and the  $\nu(\text{COO}^-)_{\text{sym}}$  frequency is generally taken as an indication of the nature of coordination of the carboxylate ion to metals.<sup>6</sup>

Table 1. Analytical data for zirconium(IV) carboxylates

Compound	Found (%)				Calc. (%)			
	C	H	Cl	Zr	C	H	Cl	Zr
$\text{Zr}(\text{OOCCH}_3)_4$	28.2	3.4	—	27.8	29.3	3.6	—	27.8
$\text{Zr}(\text{OOCCH}_2\text{CH}_3)_4$	36.3	5.0	—	23.7	37.5	5.2	—	23.8
$\text{Zr}(\text{OOCCH}_2\text{Cl})_4$	21.1	1.6	30.0	19.4	20.6	1.7	30.5	19.6
$\text{Zr}(\text{OOCCHCl}_2)_4$	15.6	—	46.5	15.3	15.9	—	47.0	15.2
$\text{Zr}(\text{OOCCHCl}_3)_4$	12.8	—	55.8	12.5	12.9	—	57.4	12.4

Table 2. Some pertinent infrared spectral bands ( $\text{cm}^{-1}$ ) of zirconium(IV) carboxylates

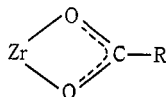
The corresponding spectral bands for the sodium salts are given in parentheses as reported by Spinner, E., *J. Chem. Soc.*, 1964, 4217

Compound	$\nu(\text{COO}^-)_{\text{asym}}$	$\nu(\text{COO}^-)_{\text{sym}}$	$\nu(\text{M}-\text{O})$
$\text{Zr}(\text{OOCCH}_3)_4$	1560 (1583)	1420 (1421)	535, 475
$\text{Zr}(\text{OOCCH}_2\text{CH}_3)_4$	1540 (1565)	1420 (1420)	510, 425
$\text{Zr}(\text{OOCCH}_2\text{Cl})_4$	1590 (1603)	1420 (1418)	490, 475
$\text{Zr}(\text{OOCCHCl}_2)_4$	1610 (1640)	1405 (1399)	475, 405
$\text{Zr}(\text{OOCCHCl}_3)_4$	1625 (1677)	1370 (1353)	475, 405

A perusal of these bands reveals that the difference,  $\Delta\nu(\text{COO}^-)$ , in each compound is comparable to that observed for the corresponding sodium salts (Table 2). It is difficult to distinguish between the ionic and bridging or bidentate forms of the carboxylate groups from the  $\Delta\nu(\text{COO}^-)$  values, but it is generally expected that zirconium will have either bridging or bidentate groups both of which may be due to its

<sup>6</sup> Nakamoto, K., 'Infrared Spectra of Inorganic and Coordination Compounds' (John Wiley: New York 1963).

tendency to acquire coordination numbers as high as eight. Further evidence in this regard has been obtained by observing bands having maxima between  $350\text{--}500\text{ cm}^{-1}$  which are generally not observed in the spectra of the acids or their ionic salts. These bands may be safely assigned to the Zr-O stretching vibrations in the ring:



Another significant feature of the spectra of these carboxylates is that they do not contain any intense band in the  $\text{M}=\text{O}$  region,  $950\text{--}1100\text{ cm}^{-1}$ ,<sup>7</sup> thereby indicating the absence of the discrete zirconyl group ( $\text{Zr}=\text{O}$ ) in all the tetracarboxylates studied.

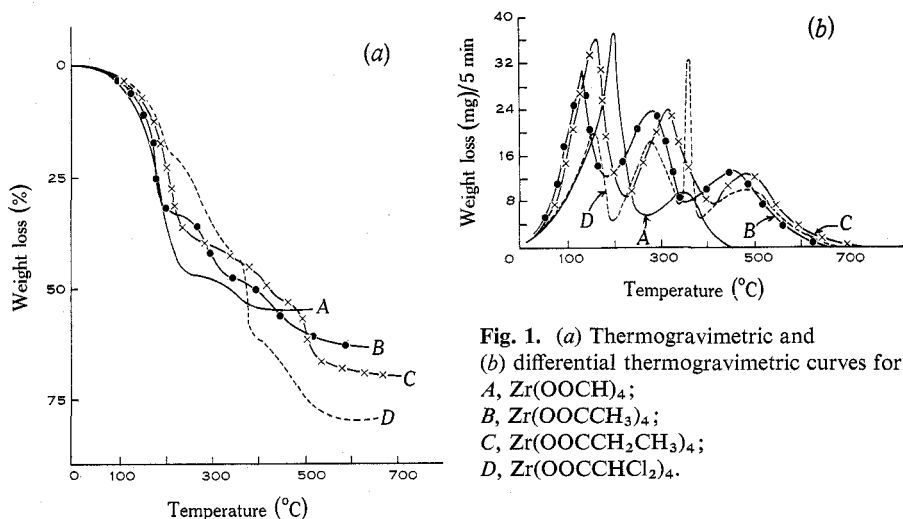


Fig. 1. (a) Thermogravimetric and (b) differential thermogravimetric curves for  
A,  $\text{Zr}(\text{OOCH})_4$ ;  
B,  $\text{Zr}(\text{OOCCH}_3)_4$ ;  
C,  $\text{Zr}(\text{OOCCH}_2\text{CH}_3)_4$ ;  
D,  $\text{Zr}(\text{OOCCHCl}_2)_4$ .

These compounds decompose on heating fairly readily and in stages. The thermogravimetric and differential thermogravimetric curves are given in Fig. 1. Zirconium(IV) acetate and propionate decompose to their oxycarboxylates with the loss of their respective anhydrides. The corresponding chloroacetates, however, show an additional step which involves the formation of the intermediate  $\text{OZr}(\text{OOCR})_2\text{RCOOH}$  (where  $\text{R} = \text{CH}_2\text{Cl}, \text{CHCl}_2$ ) before the formation of their oxy derivatives. This may be attributed to their extremely hygroscopic nature. The formation of oxycarboxylates as intermediates in the decomposition process was confirmed by their analyses. The oxycarboxylates on further heating decompose to give the stable product  $\text{ZrO}_2$  through the formation of another unstable intermediate,  $\text{Zr}_2\text{O}_3(\text{OOCR})_2$ . It is interesting to note that zirconium(IV) formate (curve A, Fig. 1) does not undergo thermal decomposition through the intermediate formation of  $\text{OZr}(\text{OOCH})_2$ .<sup>8</sup>

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<sup>7</sup> Barraclough, C. G., Lewis, J., and Nyholm, R. S., *J. Chem. Soc.*, 1959, 3552.

<sup>8</sup> Paul, R. C., Baidya, O. B., and Kapoor, R., *Z. Naturforsch., Teil B*, 1976, 31, 300.