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CARBOXYLATO COMPLEXES OF ZIRCONIUM(IV)

PART IV. THE FORMATION OF BIS(HEPTAFLUOROCARBOXYLATO)ZIRCONIUM(IV) DIFLUORIDE

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SUMMARY

The reaction of heptafluorobutyric acid with zirconium tetrachloride has been shown to form $ZrF_2(C_3F_7COO)_2(CH_3OCH_2CH_2\text{-}OCH_3)$ in ethylene glycol dimethyl ether and $ZrF_2(C_3F_7COO)_2$ in carbon tetrachloride instead of the expected product $Zr(C_3F_7COO)_4$. The infrared spectra and possible structure of these products are discussed.

INTRODUCTION

Carboxylato derivatives of zirconium have been known for a number of years and can be prepared from either zirconium oxide chloride hydrates or zirconium tetrachloride. In the former case complex polymeric structures have been proposed for the derivatives obtained from acids such as: CH_3COOH [1], CBr_3COOH [2], CF_3COOH [3,4], n-C_3H_7COOH [5], and C_3F_7COOH [6] in which the carboxylate moiety is bidentate or bidentate bridging and zirconium atoms are linked by double hydroxo bridges.

The synthesis of carboxylato derivatives from zirconium tetrachloride is probably best illustrated by the work of Ludwig and Schwartz using the acids CH_3COOH, C_2H_5COOH, and n- and i-C_3H_7COOH [7]. At -15°C molecular addition compounds of the type $ZrCl_4.2RCO_2H$ were obtained. At 21°C the partially substituted derivatives $ZrCl_2(RCO_2)_2.2RCO_2H$ resulted, and at temperatures over 100°C with an excess of the acid the tetrasubstituted products $Zr(RCO_2)_4$ were obtained. This latter group of compounds are

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monomeric with chelating ligands. Much less work has been done on fluorinated acids; thus Sartori, and independently Hughes, report the formation of the compound $Zr(CF_3COO)_4$ [8,9]. We now report the reaction of heptafluorobutyric acid with zirconium tetrachloride.

EXPERIMENTAL

Zirconium tetrachloride and heptafluorobutyric acid were obtained commercially and used without further purification. Zirconium was determined by precipitation as the mandelate followed by pyrolysis to zirconium dioxide [10]. Elemental analysis was carried out by Butterworths Analytical Services Limited. Infrared spectra were measured using a Perkin Elmer 1710 FTIR spectrometer and a Mattson Polaris FTIR spectrophotometer. Thermogravimetric analysis was performed with a Stanton TG750 thermobalance at a heating rate of 10^o min^{-1}.

The reaction of zirconium tetrachloride with heptafluorobutyric acid

(a) In ethylene glycol dimethyl ether

Zirconium tetrachloride (5.05 g, 2.16×10^{-2} mole) was added to ethylene glycol dimethyl ether (100 cm^3) and partially dissolved. To this suspension was added heptafluorobutyric acid (20.08 g, 9.38×10^{-2} mole). This was accompanied by the evolution of hydrogen chloride gas. The resultant suspension was refluxed for 2 hours to give a creamy white precipitate which was separated by filtration to give a cream solid. (2.82 g, Found: Zr, 14.23; C, 21.92; H, 1.32). $ZrF_2(C_3F_7COO)_2(CH_3OCH_2CH_2OCH_3)$ requires (Zr, 14.13; C, 22.31; H, 1.54).

The infrared spectrum showed bands at 1691 (m, sp), 1667 (m, sh), 1342 (m, sh) 1219 (m, b), 1124 (m, sp), 1096 (m, sp), 1033 (w, sp), 972 (w, sp), 942 (m, sp), 848 (m, sp) and 825 (m, sp).

A sample (0.1578 g) of the compound $ZrF_2(C_3F_7COO)_2(CH_3OCH_2CH_2OCH_3)$ was heated in a vacuum oven at 80^oC for 30 minutes to yield a white product (0.1770 g, Found: 12.2% mass loss, Zr, 16.0%. $ZrF_2(C_3F_7COO)_2$ requires: 12.4% mass loss, Zr, 16.4%).

(b) In carbon tetrachloride

Zirconium tetrachloride (5.02 g, 0.02 mole) was added to carbon tetrachloride (100 cm^3) and partially dissolved. To this suspension was added heptafluorobutyric acid

(20.2 g, 0.093 mole). There was an immediate vigorous reaction which was accompanied by the evolution of hydrogen chloride gas. The mixture was refluxed for 2 hours to give a white suspension which was separated by filtration to give a white solid (10.26 g, Found: Zr, 16.67; C, 17.15. $ZrF_2(C_3F_7COO)_2$ requires (Zr, 16.4; C, 17.29). The infrared spectrum showed bands at 1620 (s), 1343 (m, sp), 1224 (s, sp), 1192 (sh), 1165 (sh), 1185 (s, sp), 1125 (m, sp), 1092 (s, sp), 974 (m, sp), 942 (m, sp) and 824 (s, sp) cm^{-1}. Examination of the spectrum over the range 300-160 cm^{-1} showed the following bands: 256 (w, sp), 250 (w, sp), 246 (m, sp), 227 (m, sp), 208 (m, sp), 178 (m, sp) 171 (s, sp) cm^{-1}.

In a similar experiment, carried out at room temperature with stirring for 12 hours, a similar product was obtained (10.67 g, Found: Zr, 16.67; C, 17.35%).

DISCUSSION

The reaction of heptafluorobutyric acid with zirconium tetrachloride in refluxing ethylene glycol dimethyl ether (glyme) unexpectedly gives rise to the product $ZrF_2(C_3F_7COO)_2(CH_3OCH_2CH_2OCH_3)$ (A), rather than the expected tetrasubstituted compound $Zr(C_3F_7COO)_4$. Since it is well known that heptafluorobutyrate salts decarboxylate thermally to form the corresponding metal fluoride, carbon dioxide and perfluoropropene [11] it would appear that the following reactions are taking place:

$$ZrCl_4 + 4C_3F_7COOH \longrightarrow Zr(C_3F_7COO)_4 + 4HCl$$

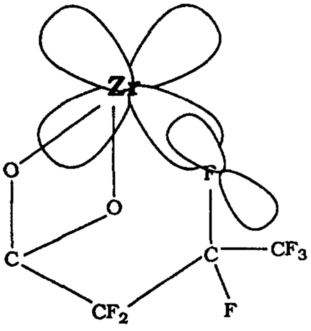
followed by

$$Zr(C_3F_7COO)_4 \longrightarrow ZrF_2(C_3F_7COO)_2 + 2C_3F_6 + 2CO_2.$$

the difluorobis(heptafluorocarboxylato)zirconium(IV) (B) being isolated as the glyme adduct A.

In a non-donor solvent such as carbon tetrachloride the compound B is obtained both at reflux and ambient temperature. This is the first report of partial decarboxylation taking place with the formation of a mixed fluorocarboxylato complex; the low temperature at which this decarboxylation takes place being particularly surprising. The electron withdrawing power of the C_3F_7 group would appear not to be a factor influencing this reaction since the corresponding trifluoroacetate is stable and the groups CF_3 and C_3F_7 both have similar electronegativities. Likewise steric factors may be discounted since the compound $Zr(CCl_3COO)_4$ has been isolated and is stable; and the CCl_3 group would be expected to have a similar if not greater steric demand than the C_3F_7 group [12].

A possible initiating mechanism may be overlap of the empty d-orbitals with the filled p-orbitals on the β–fluorine, thus

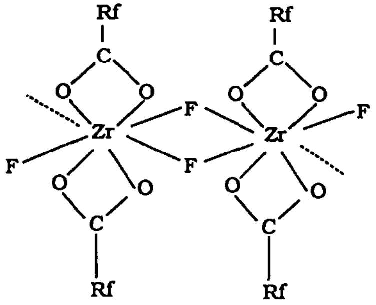


but this does not explain why the two residual carboxylato ligands are stable. Further work is in progress to try and elucidate the mechanism of this reaction.

The molecule of glyme in compound A is clearly much less firmly coordinated to the metal than the heptafluorocarboxylato group since it is readily removed by heating compound A to 80°C for 1/2 hour. The observed mass loss of 12.2% corresponds well with a theoretical mass loss of 12.4%.

Examination of the infrared spectra of the two compounds shows significant differences in the CO asym str region. Thus the glyme adduct exhibits a doublet at 1667 and 1691 cm^{-1} whereas compound B shows only one absorption at 1620 cm^{-1}. By contrast a value of 1710 cm^{-1} is observed for the heptafluorobutyrate ion in the sodium salt [13] and values of 1784 ± 2 cm^{-1} for a series of heptafluorobutyrate esters [14]. The unsymmetrical nature of the bonding to the carboxylate group in the esters shifts the ν (CO) to higher frequency, relative to the value for the free ion, a phenomenon which has also been observed in unidentate trifluoroacetato complexes. By contrast bidentate or bidentate bridging trifluoroacetato ligands show a shift to lower frequency [4]. Thus in compound B, the value of 1620 cm^{-1} for ν (asym) suggests that the heptafluorobutyrate group is either bidentate or bidentate bridging.

In the region 250-160 cm^{-1} a number of sharp bands are observed which are attributed to Zr-F modes. It is well known that ZrF_4 also absorbs in this region. A broad absorption band centred at 250 cm^{-1} was observed by Goldstein *et al* [15], in the gas phase a band at 190 ± 20 cm^{-1} has been observed at 800°C [16] and in a neon matrix a band has been observed at 176 cm^{-1} [17]. The observation of several infrared bands suggests that the compound $ZrF_2(C_3F_7COO)_2$ is polymeric with Zr-F bridges rather than a simple monomer *viz.*:



where Rf = C_3F_7

This would also be in keeping with the known tendency of zirconium to assume 8-coordinancy [18].

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