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THE PREPARATION OF SOME TRIFLUOROACETATO COMPLEXES OF ZIRCONIUM

S. CARTLIDGE and H. SUTCLIFFE

Department of Chemistry and Applied Chemistry,

University of Salford, Salford, M5 4WT (Great Britain).

SUMMARY

The preparation of a trifluoroacetato complex of zirconium from trifluoroacetic acid and zirconium oxide dichloride is described - $Zr_2(CF_3COO)_5(OH)_3(H_2O)_3$. From spectroscopic, and thermal gravimetric analysis, a dimeric structure is proposed. A monomeric zirconium trifluoroacetato complex containing 1,10-phenanthroline is also described - $Zr(CF_3COO)_2(C_{12}H_8N_2)(OH)_2$.

INTRODUCTION

The preparation of tetrakis(trifluoroacetato)zirconium(IV) from zirconium tetrachloride and trifluoroacetic acid has been described [1]. This is believed to be polymeric in the solid state with bridging trifluoroacetato groups but monomeric in solution containing only bidentate trifluoroacetato groups. Trifluoroacetate as a bridging group is not common but has been confirmed by diffraction studies for tetrakis (trifluoroacetato)dimolybdenum (II) [2].

Carboxylic acid complexes of zirconium(IV) have been prepared and studied and a tetrameric structure proposed (see Figure 1a) [3,4]. Three important features of the tetrameric structure are evident: two types of carboxylato ligand are proposed, oxo bridges are proposed, and zirconium is 8-coordinate.

The present work was undertaken to investigate the use of starting materials other than zirconium tetrachloride and to see if the highly electronegative trifluoromethyl group would influence the structural chemistry of zirconium.

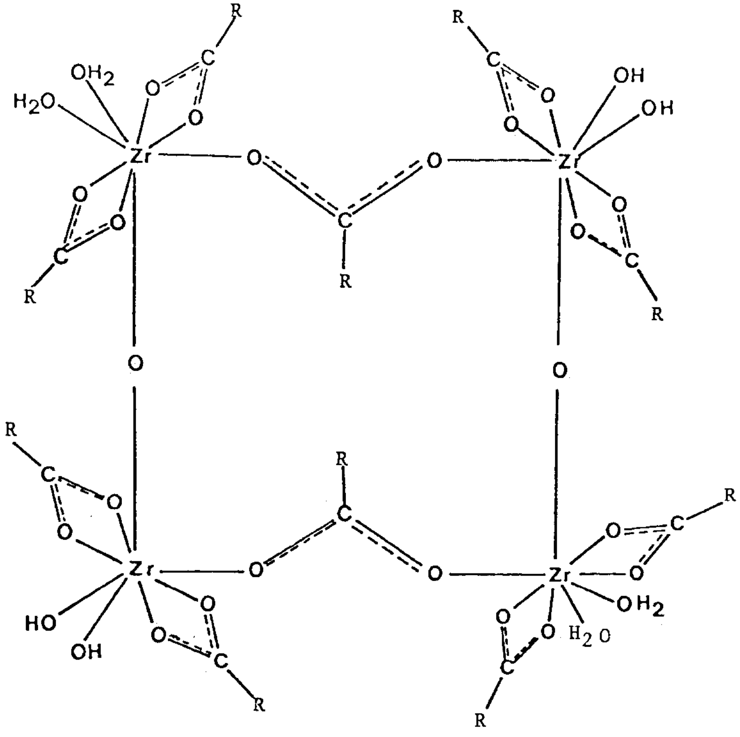

Fig. 1a.

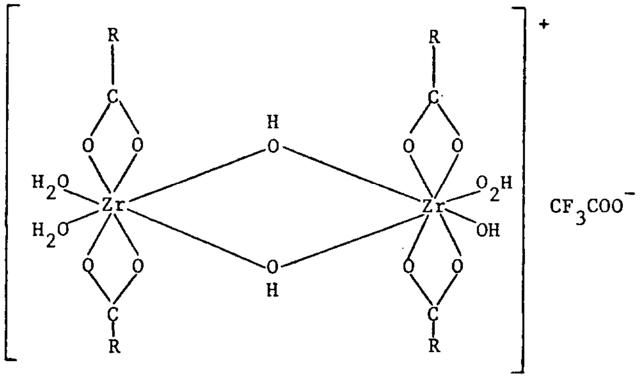

Fig. 1b.

Fig. 1. Proposed structures for acetato complex of zirconium; a) tetrameric; b) dimeric.

EXPERIMENTAL

I.r. spectra were measured on a Perkin Elmer 337 grating instrument; samples were prepared either as KBr discs or as liquid films on NaCl plates. Raman spectra were measured either as powders or as aqueous solutions.

Elemental analysis was carried out by Butterworths Microanalytical Consultancy Ltd. Zirconium was determined either as zirconium dioxide or the tetramandelate [5].

The Preparation of Zirconium oxide dichloride octahydrate

Basic zirconium ammonium carbonate (5.0g. 17.8 m mole) was dissolved in concentrated hydrochloric acid (3.4 cm^3) and the solution refluxed for 4 hours. After cooling, a further quantity of concentrated hydrochloric acid (3.4 cm^3) was added and the resultant white precipitate filtered and washed with acetone. This product was purified by reprecipitation from 5M hydrochloric acid to yield 3.77g of a material for which elemental and thermal analysis was consistent with the formulation $ZrOCl_2 8H_2O$.

The Preparation of a zirconium trifluoroacetato complex

In a typical experiment zirconium oxide dichloride octahydrate (3.0g, 6.33 m mole) was dissolved in trifluoroacetic acid (10 cm^3) and the solution refluxed for 30 mins. The excess trifluoroacetic acid was distilled off at 105° to leave a viscous material which solidified overnight to a white solid (3.82g, Found : C, 13.89, H, 1.02, F, 33.20, Zr 20.6, $Zr_2(CF_3COO)_5(OH)_3(H_2O)_3$ requires : C, 14.08, H. 1.06, F. 33.45, Zr, 21.36). The infrared and Raman spectra of this material were measured, the latter both in the solid state and in solution. The principal absorbtion bands are given in Table 1 together with some assignments. In addition the Raman spectra of a fresh and aged (10 days) aqueous solution of the complex were measured, but no significant differences were detected between the two spectra.

The complex dissolves readily in water (to give an acid solution), acetone, diethyl ether, methanol, ethanol, propan-2-ol and 2M HCl. It is insoluble in carbon tetrachloride.

Thermal gravimetric analysis over the temperature range ambient to 900°C shows a three stage process: 22.9% wt. loss up to 166°C, 43.0% wt. loss from 166-303°C and a 10.0% wt. loss from 303-900°C. No attempt was made to trap and identify the volatile products.

TABLE 1

Infrared and Raman Spectroscopic Data for Zirconium Trifluoroacetate

Infrared Bands, cm^{-1}	Raman Bands, cm^{-1}		Assignment
	Solid	Solution	
	177		
	298		
		410	
485 w			Zr-O str
532 w			
617 w	616	615	
667 s			Zr-O str
736,740 s	734	732	$C-CO_2$
802 s			
845 w			CF_3 sym str
865	861	860	CF_3 sym str
1170 s			CF_3 asym str
1213 s	1202	1204	CF_3 asym str
1460 m	1467	1438	CO_2 sym str
1500 s	1488	1480	CO_2 sym str
1690 vs	1615-1680	1622-1699	CO_2 asym str

The Reaction of the Zirconium trifluoroacetato complex with 1,10-phenanthroline

1,10-phenanthroline (0.5g, 2.77 m mole in 5 cm^3 of 1:1 aqueous alcohol solution was added to an aqueous solution of the zirconium trifluoroacetato complex (0.5 g in 5 cm^3 water). The precipitate (0.45g) so formed was filtered, washed with water, and dried at 40°C Found :. C, 31.54, N, 4.95, H, 1.76, Zr, 15.94 Calc for $Zr(CF_3COO)_2(Phen)(OH)_2(H_2O)_2$ C, 33.86, N. 4.94, H. 2.47, Zr, 16.05.

Thermal gravimetric analysis over the temperature range ambient to 1000°C shows a three stage process : 50.0% wt. loss up to 450°C, 17.1% wt. loss from 450-850°C, and a 12.2% wt. loss from 850-1000°C. No attempt was made to identify the volatile products. The infrared spectrum of this material exhibits the following bands 425-440w, 465w, 529w, 608w, 652m, 725s, 732s, 739s, 777w, 800m, 850s, 855w, 1110w, 1150vs, 1211vs, 1355w, 1420m, 1480m, 1510w, 1535m, 1555w, 1605w, 1695s, 3100m, 3450m.

DISCUSSION

The reaction between zirconium oxide chloride octahydrate and trifluoroacetic acid gives a product of empirical formula corresponding to a zirconium to trifluoroacetate ratio 2 : 5. This compound will be referred to, for convenience, as 'zirconium trifluoroacetate'.

The acidity observed when zirconium acetate is dissolved in water is probably due to the ionization of coordinated water aided by the electron withdrawing affect of the trifluoroacetate group.

The spectroscopic data is given in Table 1 together with some assignments. This suggests that the compound contains two types of trifluoroacetate group. The infrared bands at 1460 and 1500 cm^{-1} and the corresponding Raman bands are assigned to the CO_2 symmetric stretching modes. Since only one assymmetric stretching mode is observed it is assumed that both types of group are coordinated i.e. both bridging and non-bridging trifluoroacetate groups are present. If the structure is tetrameric analogous to that given in Figure 1a for 'zirconium acetate' then since there are only two bridging trifluoroacetate groups and eight non-bridging bidentate groups the weaker of the two bands may be assigned to the briding ligand. An alternative structure is the dimeric one illustrated in Figure 1b. Here the two types of trifluoroacetate are bidentate coordinate, and ionic. This structure has the advantage that bridging trifluoroacetate groups are not involved.

Both the dimeric and the tetrameric structures of 'zirconium trifluoroacetate' are consistent with the observed thermal breakdown data, viz.

$$\text{'Tetramer'} \xrightarrow[-2C_2F_6,\ -2CO_2,\ -6H_2O]{20.04\%\ \text{wt. loss}} 4\ ZrO(CF_3COO)_2 \xrightarrow[-4CF_3COF,\ -2\ C_2F_4]{41.1\%\ \text{wt. loss}}$$

$$4\ ZrO(CO_3) \xrightarrow[-4CO_2]{10.5\%\ \text{wt. loss}} 4\ ZrO_2$$

$$\text{'Dimer'} \xrightarrow[-CF_3H,\ -4H_2O,\ -CO_2]{21.8\%\ \text{wt. loss}} 2\ ZrO(CF_3COO)_2 \xrightarrow[-2CF_3COF,\ -C_2F_4]{40.1\%\ \text{wt. loss}}$$

$$2\ ZrO(CO_3) \xrightarrow[-2CO_2]{10.3\%\ \text{wt. loss}} 2\ ZrO_2$$

The reaction of zirconium trifluoroacetate with 1,10-phenanthroline results in the displacement of some trifluoroacetate ligands and the formation of the complex $Zr(CF_3COO)_2(Phen)(OH)_2H_2O)_2$ which is believed to have the structure shown in Figure 1c. It is interesting to note that not all the trifluoroacetate ligands were displaced by 1,10-phenanthroline. This may be due to electron donation from the nitrogen atoms of 1,10-phenanthroline strengthenening the zirconium to oxygen bonds of the trifluoroacetate ligand, compared with the strength in the absence of a donor ligand.

The thermal decomposition of the phenanthroline complex, although less well defined than that of 'zirconium trifluoroacetate', does occur in three stages with the formation of two intermediate compounds <u>viz</u>.

$$Zr(CF_3COO)_2(Phen)(OH)_2 \xrightarrow[\substack{\text{-Phen.}\\ -CF_3COOH}]{\text{55.4\% wt. loss}} ZrO(OH)(CF_3CO_2)$$

$$\xrightarrow[-CF_3H,\ -H]{\text{13.2\% wt. loss}} ZrO(CO_3) \xrightarrow[-CO_2]{\text{9.1\% wt. loss}} ZrO_2$$

These theoretical weight losses compare reasonably well with the observed values of 50.0, 17.1 and 12.2 respectively.

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