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TRIFLUOROMETHANESULPHONATO DERIVATIVES OF ZIRCONIUM

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SUMMARY

The preparation of three trifluoromethanesulphonato derivatives of zirconium is described. Thermal gravimetric analysis, differential thermal analysis and infrared spectroscopic data are reported and interpreted. A review of the infrared spectroscopic data of other metal trifluoromethanesulphonato complexes is presented.

INTRODUCTION

Trifluoromethanesulphonato (triflate) derivatives of the following transition metals: Co, Rh, Ir, Cr, Ru, Os, Pt, Mo, Cu, Au, Fe, Ti, Zr and Ag have now been synthesised and in some cases X-ray structural determinations have been carried out (see Table 1) [1-16]. Interest has developed in this area of chemistry (a) because of the possibility that the triflate group may be one, two or three coordinate and (b) because of the potential use of such compounds as synthetic intermediates; the triflate group being a particularly good leaving group.

As part of a programme of study on zirconium complexes and in particular the use of zirconium oxide chloride for the preparation of such complexes we now report the preparation of some triflate derivatives of zirconium.

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TABLE 1.

Some metal triflates with selected infrared spectroscopic data

Compound	Infrared data cm^{-1}	Assignments		Ref
$Cu(CF_3SO_3)_2$	1280, 1225	vas	S-O	1
	1058	vsym	S-O	
$Co(CF_3SO_3)_2$	1235	vas	S-O	1
	1042	vsym	S-O	
$[Mo_2(CH_3CN)_8](CF_3SO_3)_4$	1270, 1230	v	C-F	3
	1160, 1030	vsym	S-O	
$[Mo_2(H_2O)_4(CF_3SO_3)_2](CF_3SO_3)_2$	1240, 1205	v	C-F	3
	1340, 1150, 1110 1030, 990	v	S-O	
$Mo_2(CF_3SO_3)_4$	1200	v	C-F	4
	1350, 1110, 990	v	S-O	
$Mo_2(EtOAc)_4(CF_3SO_3)_4$	1250, 1240	v	C-F	4
	1180, 1030	v	S-O	
$(CH_3)_2Sn(CF_3SO_3)$	1226	v	C-F	5
	1179	vsym	C-F	
	1319, 1145	vasym	S-O	
	1026	vsym	S-O	
$(CH_3)_2Au(CF_3SO_3)$	1270, 1150	v	S-O	6
$(CH_3)_3Ge(CF_3SO_3)$	1365	vasym	S-O	12
	1241, 1164	vasym	C-F	
	1205	vsym	S-O	
$TiCl_3(CF_3SO_3)^a$	1272, 1120	vasym	S-O	11
	1225	vasym	C-F	
	1205	vsym	C-F	
	1050			
	1031	vsym	S-O	

Table 1 (cont.)

$TiCl_2(CF_3SO_3)_2$	1358, 1105	vasym S-O	11
	1235, 1215	v C-F	
	1040, 1006	vsym S-O	
$Ru(bipy)(CO)_2(CF_3SO_3)_2$	1332	v S-O	10
	1230, 1195	v C-F	
	1158	v S-O + v C-F	
	1009	v S-O	
$Ru(phen)(CO)_2(CF_3SO_3)_2$	1325	v S-O	10
	1228, 1148	v C-F	
	1180	v S-O + v C-F	
	1010	v S-O	
$Na(CF_3SO_3)$	1280	vasym C-F	8
	1232	vsym C-F	
	1168	vasym S-O	
	1036	vsym S-O	
$Zr(C_5H_5)_2(C_4H_8O)(CF_3SO_3)_2$[a]	1240	v C-F	13
	1180	vasym S-O	
	1030	vsym S-O	

[a] Present authors assignments, all other assignments are from the original work

EXPERIMENTAL

Ir spectra were measured as mulls on a Perkin-Elmer 521 grating instrument using KRS plates. KRS is a mixture of thallium bromide and thallium iodide, and is used to eliminate the possibility of ion-exchange and hence spurious infrared data. Thermogravimetric analysis was carried out using a Stanton-Redcroft TG 750 at a heating rate of $10^{o}C\ min^{-1}$ and

Differential Thermal Analysis with a Dupont DTA 900 using the same heating rate. In all cases a nitrogen atmosphere was employed.

Zirconium was determined by precipitation as the tetramandelate followed by pyrolysis to zirconium dioxide [17]. Carbon and hydrogen analysis was carried out by Butterworth Microanalytical Consultancy Ltd.

The preparation of zirconium triflate-A

In a typical experiment zirconium oxide chloride (3.22 g, 10 m mole) was dissolved in water (50 cm^3) and to this was added triflic acid (3.00 g, 20 m mole) in 50 cm^3 of water. The solution was heated to boiling point and 80% of the water removed by distillation. The residual solution was taken down to dryness on a steam bath and finally dried over P_2O_5 to yield a white solid product (4.02 g Found: C, 4.91; H, 2.37; Zr, 18.16; $Zr(OH)_2(CF_3SO_3)_2(H_2O)_4$ requires: C, 4.85; H, 2.02; Zr, 18.38). This compound shows absorption bands in the infrared at 3100-3550 (v bd), 1620 (bd), 1266 (s); 1253 (s), 1169 (s), 1030 (s), 760 (w), 709 (w), 622 (w).

The product is soluble in water but insoluble in triflic acid and the following organic solvents: toluene, pentane, cyclohexane, ether, dichloromethane, chloroform and furan.

Thermal decomposition of zirconium triflate-A

The results from thermogravimetric analysis (TG) at a heating rate of 10^oC min^{-1} are given in Table 2. The residue was identified as zirconium dioxide by X-ray powder diffraction measurements. The mass of zirconium dioxide remaining indicated that some loss of zirconium had occurred during the course of the thermal analysis.

The results from differential thermal analysis (DTA) are given in Table 3

TABLE 2. TG Data

Temp °C	Cumulative Mass loss %	Theor. Mass loss %	Interpretation
40-150	13	14.5	Loss of coordinated water
150-290	18	18.0	Elimination of water from OH bridges
290-430	69	a	Breakdown of molecule
430-710	71	a	Formation of zirconium oxide fluoride
710-870	88	a	Formation of ZrO_2

[a] impossible to estimate owing to loss of zirconium

TABLE 3. DTA Data

Temp	Observation	Interpretation
80	EN weak	Loss of loosely held water
110	EN weak	Loss of coordinated water
140	EN medium	(Elimination of water (
305	EN strong	(from OH bridges
327	EX strong	Breakdown of molecule

EN = endotherm

EX = exotherm

In a separate experiment a 2.652 g sample of zirconium triflate was heated at 80°C in a vacuum oven over a period of 8 days. The following results were obtained:

Time	0	1	3	5	7	8	days
Mass	2.652	2.409	2.228	2.223	2.221	2.220	g
% Mass Loss	-	9.2	16.0	16.2	16.3	16.3	

The final figure agrees well with the combined first two weight losses from thermal analysis. This dehydrated product shows absorption bands in the infrared at 3420 (s), 1638 (m), 1320 (s), 1205 (s), 1131 (s), 1020 (s), 760, 623 (s) cm^{-1}.

Pyrolysis of a sample (2.180 g) of zirconium triflate at 400°C for 2 hours resulted in a 71.9% weight loss and gave a product which will be referred to as the 'plateau product'. This weight loss correlates very well with that observed up to a temperature of 700°C in the thermal gravimetric analysis measurements. At the end of the pyrolysis a white foam-like material was recovered from the floor of the furnace. This will be referred to as zirconium triflate-B. In later experiments further small quantities of this material were obtained by surrounding the crucible with a glass chimney. However this material had a very low density and was difficult to handle. The plateau product showed very little absorption in the infrared viz 870 cm (m bd) and was not attacked by concentrated mineral acids. X-ray powder diffraction measurements gave the following d-values, relative intensities in brackets: 4.1509 (1), 3.2669 (2), 2.5692 (3), 2.1359 (6), 2.0610 (7), 1.9313 (5), 1.8748 (4), 1.7409 (8).

Zirconium triflate-B produced during the pyrolysis was not examined in detail although infrared spectroscopic measurements gave the following absorption bands: 3500-3050, 1610 (m, bd), 1260 (s), 1215 (sh), 1165 (s), 1030 (m) cm^{-1}.

DISCUSSION

The reaction between zirconium oxide chloride and triflic acid in aqueous solution gives a product of empirical formula $Zr(OH)_2(CF_3SO_3)_2(H_2O)_4$ which will be referred to for convenience as zirconium triflate-A. Spectroscopic data is given in table 4, together with similar data for zirconium triflate-B and a dehydrated form of zirconium triflate-A. Some assignments are made.

The interpretation of the infrared data is complicated by the fact that C-F and S-O stretching frequencies occur in the same region of the spectrum, and the SO_3 moiety may coordinate in a mono-, bi- or tridentate fashion.

TABLE 4.

Infrared spectroscopic data for zirconium triflate A and B cm^{-1}

Zr Tf-A	Zr Tf-B	Dehydrated Zr Tf-A	Assignments
3550-3100	3500-3050	3420	OH str
1620	1610	1638	H-OH band
1266	1260		CF asym str
		1320	SO asym str
1253	1215	1205	CF sym str
1169	1165		SO asym str free ion or or tridentate coordn
		1131	SO asym str
1030	1030	1020	SO sym str
760		760	
709			
622		623	

However a reasonable number of triflate complexes have now been made and it is instructive to compare previous data with the present work. Table 1 gives a list of some known complexes together with some infrared data and assignments

Thus the v SO sym stretching frequency occurs in the range 1009-1058 cm^{-1} with the majority of the observed bands falling in the much narrower 1026-1036 cm^{-1} range. This band appears to be little changed by coordination. In the dehydrated form of zirconium triflate-A this band is observed at 1020 cm^{-1} whereas in the other two zirconium triflates a band at 1030 cm^{-1} is observed.

The assignment of the vasym S-O stretching frequency is more difficult since it occurs in the same region as the C-F absorptions. There are contradicting reports in the literature, even for the free ion [8, 15]. Thus Miles et al propose 1168 cm^{-1} from a study of the sodium salt, whereas Burger and co-workers attribute a band at 1259 cm^{-1} to the vasym S-O stretching frequency from a study of the silver salt in nujol.

Examination of the data in Table 1 which includes examples of metal triflates with both coordinated and ionic groups is instructive. It is expected that the vasymm S-O stretch will show a greater shift upon coordination than either the C-F absorptions or the vsym S-O stretching frequency. However this effect is further complicated by the ability of the triflate group to act as a mono-, bi-, or tridentate ligand, and also to function as a bridging ligand. In addition both bridging and non-bridging ligands may be present in the same molecule. Where tridentate ligation occurs little or no shift is expected since there is no change in the symmetry of the triflate group.

In most of the compounds listed in Table 1 two bands above 1200 cm^{-1} may be assigned to the C-F stretching vibrations with the proviso that in certain cases there may be overlap with a shifted vasym S-O stretch due to coordination of the latter. Mono- or bidentate coordination of the triflate causes the vasym S-O of the free ion to be split giving two bands one at a higher and the other at a lower frequency than vasymm S-O ionic. In some cases the higher frequency band overlaps with the C-F stretches but in others the shift is so large that a band appears above 1300 cm^{-1}. Examples of this phenomenon include:

$(CH_3)_2SnSO_3CF_3$	1319 and 1145 cm^{-1}
$Ru(bipy)_2(CO)_2(CF_3SO_3)_2$	1332 and 1158 cm^{-1}
$TiCl_2(SO_3CF_3)_2$	1358 and 1145 cm^{-1}
$Rb[I(CF_3SO_3)_4]$	1365 and 1150 cm^{-1}
$(CH_3)_3Ge(SO_3CF_3)$	1365 and 1164 cm^{-1}

In other cases the spectra are more complex and bridging has been proposed, as in certain molybdenum complexes [3, 4]. With present knowledge it is not possible to distinguish between monodentate and bidentate triflate groups.

In the present work, zirconium triflate-A exhibits strong bands at 1266, 1253, 1169 and 1030 cm^{-1} all in the region expected for CF_3 and SO_3 groups. The 1266 and 1253 cm^{-1} bands are attributed to the C-F asymmetric and symmetric stretches respectively and the bands at 1169 and 1030 cm^{-1} to the SO asymmetric and symmetric stretching frequencies. These last two are very similar to analagous stretching modes observed for the ionic triflate ion.

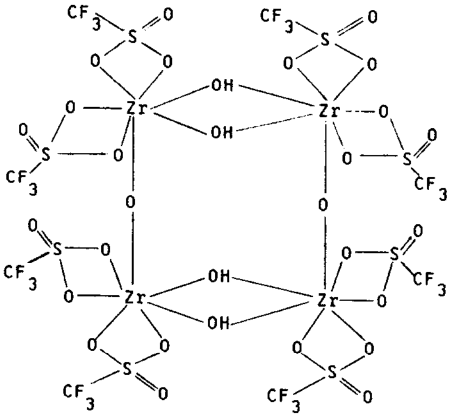
The band at 1620 cm^{-1} is assigned to the water bending mode, and is similar to that observed in zirconium oxide chloride octahydrate [18]. The broad absorption at 3100-3550 cm^{-1} is attributed to O-H stretching modes.

Thus the infrared spectroscopic evidence indicates that the triflate groups in zirconium triflate-A are ionic in nature, and this together with evidence from elemental analysis and TG and DTA data (see below) suggest the following formulation for zirconium triflate-A.

$[Zr_4(OH)_8(H_2O)_{16}]\ (CF_3SO_3)_8$

The ion $[Zr_4(OH_8)(H_2O)_{16}]^{8+}$ probably has a similar structure to that observed in zirconium oxide chloride [19] although a short linear structure cannot be ruled out.

The results from the TG and DTA experiments together with their interpretation are given in Tables 2 and 3. The loss of coordinated water from zirconium triflate-A would be expected to give a weight loss of 14.5% which agrees reasonably well with the observed weight loss of 13%. Similarly the cumulative weight loss of 18% up to 290°C is in agreement with the loss of 18 moles of water from zirconium triflate-A. It is interesting to note that in the dehydration in vacuo of zirconium triflate-A a mass loss of 16% was observed, in good agreement with a theoretical mass loss for 18 moles of water of 16.4%. Thus this dehydrated material may be formulated $Zr_4O_2(OH)_4(CF_3SO_3)_8$. Examination of the infrared spectrum of this material reveals several bands which may be interpreted in terms of coordination of the triflate group to the zirconium. The bands at 3420 and 1638 cm^{-1} clearly indicate that some coordinated water or OH groups still remain. The band at 1320 cm^{-1} is attributed to S-O and C-F asymmetric stretches and the band at 1131 cm^{-} also to the S-O asymmetric stretch, whereas the 1205 cm^{-1} absorption is due to the C-F symmetric stretch. The splitting of the original 1169 cm^{-1} band into two bands at 1131 and 1320 cm^{-1} is evidence in favour of coordination of the triflate group to the zirconium, probably in a bidentate fashion. Such a splitting has been observed before for compounds in which the triflate group is bidentate as discussed above [5, 11]. Unidentate coordination would be insufficient to satisfy the coordination number (6, 7 or 8) of zirconium. A possible structure is shown below:



When zirconium triflate-A is heated to 400°C a volatile zirconium containing compound (zirconium triflate-B) is formed together with an involatile zirconium containing compound. This volatile material exhibits bands at 1260 and 1215 cm^{-1} due to C-F stretching modes, at 1165 cm^{-1} attributable to the S-O asymmetric stretch, and at 1030 cm^{-1} due to the S-O symmetric stretch. Clearly, there is very little shift from the corresponding modes in the ionic triflate. In this compound the triflate group is considered to be tridentate which would have the same symmetry as the free ion and hence little or no shift would be expected. Lack of further data and the difficulty of handling this material mitigate against making a precise formulation.

The involatile compound formed at 400°C proved to be a very intractable material with a medium intensity absorption in the infrared at 870 cm^{-1}. Zirconium oxide fluoride has a band at 864 cm^{-1} [20], but the X-ray powder data does not agree with that of zirconium oxide fluoride. Previous work on the zirconium-oxygen-fluorine system has shown that a wide range of zirconium oxide fluorides can exist with various stoichiometries [21], eg $Zr_4O_3F_{10}$, ZrO_5F_6, $Zr_{10}O_{13}F_{14}$ and $ZrO_{1.917}F_{0.167}$. It is concluded that the involatile material formed at 400°C is a zirconium oxide fluoride of unknown stoichiometry.

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