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MASS SPECTRA OF PARTIALLY FLUORINATED β DIKETONATE COMPLEXES OF ZIRCONIUM

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SUMMARY

The mass spectra of a variety of fluorinated tetrakis(β diketonate) complexes of zirconium are reported The fragmentation patterns show stepwise loss of entire β diketonate ligands although the parent ions are not observed under a range of spectrometer conditions Other mass spectra peaks demonstrate fluorine atom transfer to zirconium from the ligands

INTRODUCTION

Although the mass spectra of a large number of metal β diketonate (acac) complexes have been reported [1] the mass spectra of the corresponding zirconium complexes have not been thoroughly examined The paucity of such data is presumably due to the high mass ranges for the parent molecular ions of the type ZrL_4 The integrated ion current method [2] was used in the analysis of tetrakis(benzoyltrifluoroacetylacetonato)zirconium This mass spectrum showed the parent ZrL_4^+ molecular ion along with successive loss of the benzoyltrifluoro acetone ligands and ligand loss accompanied by fluorine transfer to zirconium The mass spectrum of tetrakis(acetylacetonato)zirconium has been reported [3] but

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TABLE I

Relative intensities of prominent ions in the mass spectra of β diketonate zirconium complexes[a]

R	R	$M^+(ZrL_4{}^+)$[b]	$ZrL_3{}^+$	ZrL_2F^+	$ZrL_2{}^+$	$ZrLF_2(COCHCOR)^+$	$ZrLF_2{}^+$	$ZrF_3(COCHCOR)^+$	ZrL^+	L^+	$(RCOCHCO)^+$	RCO^+	R^+	R^+
CH_3	CF_3	702 708	549	415	396	365	281	231	246	153	84	43	15	69
		<0 2%	100%	44%	2 2%	31%	10%	18%	trace	3 4%	5 9%	d	d	23%
C_6H_5	CHF_2	878 884	681	503	484	453	325	293	287	197	147	105	77	51
			4 7%	2 8%			trace	trace	trace	17%	66%	67%	63%	
C_6H_5	CF_3	950 956	735	539	520	489	343	293	305	216	147	105	77	69
			100%	37%	1 8%	18%	12%	20%		14%	24%	65%	20%	37%
C_6H_5	C_2F_5	1150 1156	885	639	620	539	393	293	355	265	147	105	77	119
			100%	19%	trace	1 8%	9 3%	4 9%	2 6%	1 4%	7 2%	55%	8 0%	trace
C_6H_5	C_3F_7	1350 1356	1035	739	720	589	443	293	405	315	147	105	77	169
			89%	14%	trace	2 1%	2 9%	trace	trace	1 0%	8 7%	100%	8 1%	1 7%
$CH_3C_6H_4$	CF_3	1006 1012	777	568	548	518	357	307	319	229	160	119	91	69
			39%	16%	1 0%	6 6%	7 3%	10%		31%	46%	58%	29%	100%
C_6H_4F	CF_3	1022 1028	789	575	556	525	361	311	323	233	165	123	95	69
			100%	36%	2 0%	17%	15%	23%		3 7%	12%	72%	10%	20%

[a] trace less than 1 0% not observed [b] masses reported as range based on Zr isotopes Other masses reported correspond to ^{90}Zr ^{12}C ^{1}H ^{16}O ^{19}F combinations only [c] ZrL_3F^+ and $ZrL_2F(COCHCOR)^+$ ions are either not observed or are a trace [d] not measured

details are lacking The mass spectrum of tetrakis(hexafluoroacetylacetonato) zirconium was studied and peaks were observed corresponding to ZrL_4^+ ZrL_3^+ and fluorine addition to the trischelated zirconium species [4] We describe here the mass spectra of seven fluorinated β-diketonate zirconium complexes, plus the parent compound $Zr(acac)_4$

RESULTS AND DISCUSSION

The zirconium complexes used in this study are listed in Table I Although the structure of each compound has not been determined crystallographically molecular weight data [5] support a ZrL_4 formulation as shown in Figure 1 A recent redetermination of the structure of $Zr(acac)_4$ [6] confirms the earlier determination of Silverton and Hoard [7] of an eight coordinate polyhedron approximating a square antiprism structure with a small distortion towards dodecahedral geometry The major mass spectral fragmentation pattern is depicted in Figure 2 Relative intensities of the major fragment ions are given in Table I

TABLE II

Isotopic abundance of zirconium isotopes

Isotope	Relative abundance
^{90}Zr	51 4%
^{91}Zr	11 2%
^{92}Zr	17 1%
^{94}Zr	17 4%
^{96}Zr	2 8%

The appearance of the mass spectra is complicated by the existence of multiple isotopes of zirconium listed in Table II Thus each fragment containing zirconium appears in the spectrum as a group of several lines covering six mass units The masses listed in Table I [except (b)] for the major fragments correspond to the ^{90}Zr containing peak, the most abundant zirconium isotope and consequently the most intense line of the cluster As can be seen from Table I the parent ion, ZrL_4^+ is not observed except for a trace peak (0 2%) in $Zr(CF_3COCHCOCH_3)_4$ although a variety of ionization methods were employed by

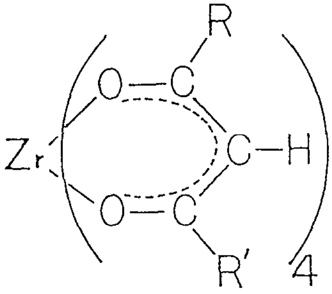

Fig 1 Structure of the zirconium β-diketonate complexes

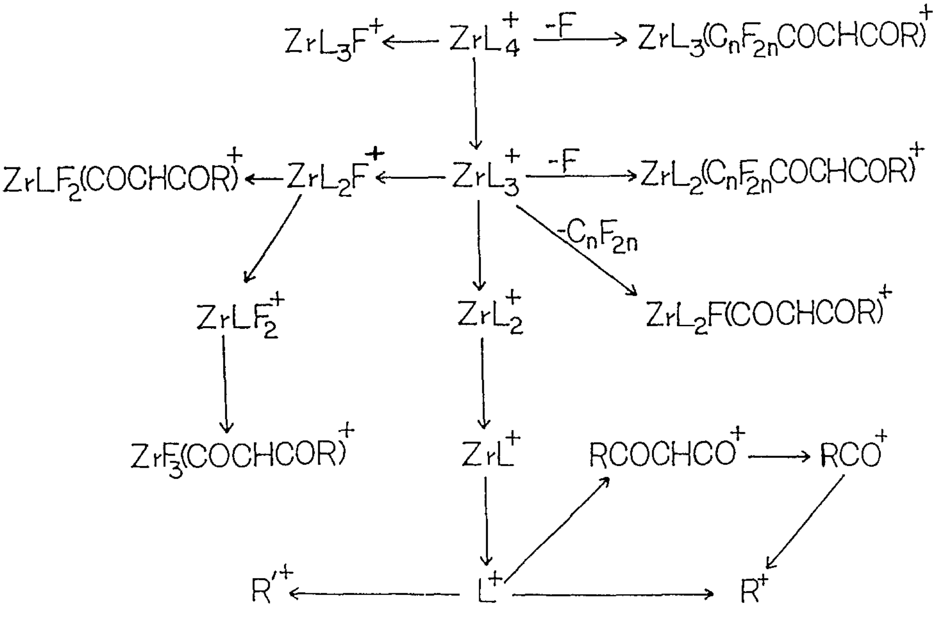

Fig 2 Major fragmentation pathways in the mass spectra of the partially fluorinated β diketonate complexes of zirconium

several independent sources. That the parent ion unobserved is not unusual, considering that the coordination number of zirconium is eight, and a less sterically demanding situation can be achieved by ligand loss to ZrL_3^+, which would have a coordination number of six. Moreover, the absence of the molecular ion ZrL_4^+ does seem to contradict the literature [2-4]. The mass spectrum of tetrakis(dibenzoylmethane)thorium, $Th(dbm)_4$, reports the molecular ion peak of low intensity (3%) [8]. We also do not observe the molecular ion for the parent compound, $Zr(acac)_4$, which agrees with the mass of spectrum of $Zr(acac)_4$ reported by the National Bureau of Standards [9].

The highest mass peak of appreciable intensity is ZrL_3^+, corresponding to the loss of one entire ligand. This is also the major peak reported in the mass spectrum of $Th(dbm)_4$ [8] and in our spectrum of $Zr(acac)_4$ which also agrees with the NBS spectrum [9]. Successive loss of a ligand would lead to ZrL_2^+ and ZrL^+, both of which were usually observed, but in much reduced relative intensities, indicating a particularly stable ZrL_3^+ ion. This latter ion is also the main ion found in our spectrum of $Zr(acac)_4$, giving masses of 387 (50.4%), 388(17.3%), 389(17.1%), 391(14.5%) and 392(0.7%) which agrees with the isotopic abundances for zirconium given in Table II. The other major peaks observed correspond to ions in which fluorine has been transferred to zirconium from ligands that have been cleaved. This process is repeated several times in the molecule fragmentation, producing ZrL_3F^+ from ZrL_4^+, ZrL_2F^+ from ZrL_3^+, and $ZrLF_2^+$ from ZrL_2F^+. Such species have been reported in the mass spectrum of $Zr(C_6H_5COCHCOCF_3)_4$ [2]. This transfer of atoms in metal β-diketonate complexes has also been observed in the mass spectrum of $Al(acac)_3$ where the ion $Al(OH)L^+$ is reported [10] and in other metal complexes of fluorinated β-diketonates [1]. Fluorine may also be transferred to zirconium followed by loss of the remaining even electron neutral fragment from R', as $:CF_2$, C_2F_4 or C_3F_6. This leads to the observed peaks $ZrL_2F(COCHCOR)^+$ from ZrL_3^+, $ZrLF_2(COCHCOR)^+$ from ZrL_2F^+ and $ZrF_3(COCHCOR)^+$ from $ZrLF_2^+$. The transfer of fluorine from ligand to zirconium is expected in view of hard-soft acid-base theory, which classifies Zr^{4+} as a hard acid and F^- as a hard base [11]. Other transition metals, such as copper [1], do not show fluorine migration in their fluorinated β-diketonate complexes. The remaining peaks observed in the spectra are due to ionization and fragmentation of the ligand itself, which has been previously reported [1,11-13].

EXPERIMENTAL

The β-diketonates and their zirconium complexes were prepared as previously described [5]. $Zr(acac)_4$ was obtained from ROC/RIC Corporation, Sun Valley, CA, USA. The EI MS of Zr(acac)$_4$ was obtained on a Finnegan gas chromotograph/EI-CI. The EI MS of the fluorinated complexes were obtained on a Kratos MS-80RF at 30 eV and 10 eV, at an inlet temperature of 150°C. Fast atom bombardment (FAB) MS were obtained on a Kratos-MS-50 triple analyzer using a matrix of 3-nitrobenzylalcohol.

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