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Synthesis and Mass Spectra of Uranyl Complexes of some Fluorinated β-Diketones

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Introduction

The electron impact mass spectra (EIMS) of metal chelates of β-diketones show atom and group migrations from the ligand to the metal. These migrations are highly influenced by the nature of the metals. Morris and Koob used Hard/Soft/Acid/Base (HSAB) theory to explain some of these reactions [1]. Recently we have started investigating the effect of class *a* and class *b* metals [2, 3], and also of the presence or absence of *d* electrons in the mass spectra of metal β-diketonates. The class *a* metal chelates of fluorinated β-diketones showed F migration [4, 5] while those of class *b* metal showed no such migration [6]. The presence of *d* electrons in the metals causes R (aryl group) migration because such migration involves metal → R π bonding [7]. Thus, R migrations were observed in gallium, indium and palladium complexes of β-diketones [4, 6]. Such reactions were absent in the mass spectra of scandium and yttrium complexes due to the absence of *d* electrons [5]. The EIMS of lanthanide (class *a* and no *d* electrons) chelates of fluorinated β-diketones showed F but no R migrations [8, 9].

We have determined the electron impact mass spectra of uranyl complexes of some fluorinated β-diketones. The uranium(VI) belongs to class *a* and does not contain *d* electrons. No mass spectral studies of such complexes were reported in the literature [10].

Experimental

The β-diketones ($RCOCH_2COCF_3$) with R as methyl, phenyl and 2-thienyl were obtained from the commercial sources. Others were prepared by Claisen condensation of the methyl ketone ($RCOCH_3$) and ethyl perfluorocarboxylate (R^1-$COOC_2H_5$), catalyzed by sodium methoxide [11].

Preparation of the Complexes

A hot filtered solution of uranyl acetate dihydrate (1.5 g; 3.53 mmol in 25 ml water) was added, dropwisw with stirring, to a solution of β-diketone (7.06 mmol in 25 ml ethanol). The mixture was digested for 10 min and then cooled in an ice-bath. The yellow/orange product was filtered and washed with ice-cooled 50% aqueous alcohol. The uranium in the complexes was determined by decomposing the complex with few drops of conc. H_2SO_4 and subsequent strong heating to U_3O_8. Analyses of the complexes are shown in Table I.

The EI mass spectra were obtained on an AEI MS-12 mass spectrometer at 70 ev and at a source temperature of 250 °C.

Results and Discussion

The uranyl complexes were separated as $UO_2L_2 \cdot C_2O_5OH$, except that of trifluoroacetylacetone which

TABLE I. Analytical Data of the Uranyl Complexes of β-Diketones, L = RCOCHCOR′.

Compound	R	R′	M.p. °C	% Found			% Calculated		
				C	H	U	C	H	U
$UO_2L_2 \cdot H_2O$	Methyl	CF_3	175	20.30	1.71	40.07	20.21	1.70	40.06
$UO_2L_2 \cdot C_2H_5OH$	Phenyl	CF_3	171	35.26	2.49	32.02	35.40	2.43	31.90
$UO_2L_2 \cdot C_2H_5OH$	2-Thienyl	CF_3	175	28.57	1.90	31.52	28.52	1.86	31.39
$UO_2L_2 \cdot C_2H_5OH$	2-Furyl	CF_3	160	29.64	2.12	32.52	29.78	1.94	32.79
$UO_2L_2 \cdot C_2H_5OH$	Phenyl	C_2F_5	162	34.19	2.29	27.80	34.06	2.14	28.12
$UO_2L_2 \cdot C_2H_5OH$	2-Thienyl	C_2F_5	179	27.89	1.72	27.55	27.98	1.64	27.73
$UO_2L_2 \cdot C_2H_5OH$	Phenyl	C_3F_7	140	32.99	2.06	25.12	33.01	1.92	25.15
$UO_2L_2 \cdot C_2H_5OH$	2-Thienyl	C_3F_7	159	27.59	1.51	24.47	27.56	1.47	24.82

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TABLE II. Relative Intensities of Metal Containing Ions in the E1 Mass Spectra of $UO_2(RCOCHCOR^1)_2$.

Ions	R^1	CF_3				C_2F_5		C_3F_7	
	R	Methyl	Phenyl	2-Thienyl	2-Furyl	Phenyl	2-Thienyl	Phenyl	2-Thienyl
M	a*	41	100	88.8	89.6	70.7	83.3	100	77.3
M–R	b	4	–	–	–	–	–	–	–
M–F		–	–	–	–	3.1	3.3	5.8	3.6
M–CH_2CO		2.8^a	–	–	–	–	–	–	– –
M–47		3.6	5.5	7.4	6.2	1.6	2	5.2	3.6
M–48		4.9^a	5.5	12.6^a	10.4^a	–	–	–	–
M–RCOF		12^a	–	–	–	–	–	–	–
M–R^1	c	37.2	33.3	41.5	47.9^a	51.8^a	63.3^a	75^a	72.7^a
M–R^1–F		–	–	–	–	5.9^a	4^a	4.7	1.7
M–R^1–2F		–	11.5	11.1	2.1	3.4	4.3	3	4.5
M–L	d	100^{cb}	74	100^c	100^c	100^c	100^c	90^c	100^c
M–L–CO		4	13	10.4	10.4	2	4^d	2	3.6
M–L–CO–F		7.4	3.5	–	8.3	–	–	–	–
M–L–CF_2	e	51.3^d	40.8	48.8^d	58.3^d	–	–	–	–
M–L–CF_2–HF		6^e	–	3.7	4.1	–	–	–	–
M–L–CF_2–CO_2		–	7.4	13.3	4.1	–	–	–	–
M–L–C_2F_4		–	–	–	–	5.6^d	5.3^d	–	–
M–L–CO–C_2F_4		–	–	–	–	–	–	1.2	1
M–L–C_3F_7		–	–	–	–	–	–	1.5	1.8
UF_5		0.6	3.6	5.2	–	0.8	0.7	–	–
UF_3		3.8	1	3.3	3.1	0.8	1	1.5	1.6
UOF_2		5.4	7.4	11.1	9.3	3.8	3.5	3	5.5
UO_2F		14	24.1	38.5	31.2	7.7	7.3	7.2	13.6
UOF		8	7.4	12.6	8.3	1.9	1.7	1.6	2.7
UO_2		26.9	24.1	51.1	39.9	31.5	35	26.2	45.5

*Identified metastable transitions are indicated by superscripts which relate the daughter to its parent ion.

was separated as monohydrate. Heating the complexes at 110 °C for 2 hours failed to remove the solvent of crystallization. Some uranyl complexes of non-fluorinated β-diketones were reported by Sacconi and his co-workers [12, 13], and of trifluoro and hexafluoro acetylacetone by Belford *et al.* [14]. Both groups reported the complexes as hydrates which could be dehydrated only with difficulty. According to these authors the solvent is coordinated to the metal and the coordination number is greater than six. Similar conclusions can be drawn about the present series of complexes of fluorinated β-diketones. Baskin and Ferraro [15] using aqueous ethanol as solvent prepared solid yellow $UO_2(TTA)_2 \cdot C_2H_5OH$, while others [16] separated the complex as $UO_2(TTA)_2 \cdot 2H_2O$ (TTA = 2-thenoyltrifluoroacetone).

The relative intensities of the metal containing ions in the EI mass spectra of the complexes are shown in Table II. Though uranium is a polyisotopic element the high (99.27) relative abundance of ^{238}U contributes some amount of uncertainty in the identification of metal containing ions in the spectra. Some differences in the mass spectra were observed depending on R and R^1. When R is an alkyl (methyl) group the spectrum shows the presence of M–R and M–RCOF which are absent with R as aryl groups. These differences are perhaps due to delocalisation of π electrons of the aryl groups which makes the bonds stronger. Loss of CH_2CO from the molecular ion was observed in many metal complexes with R as a methyl group [6, 10].

The complexes of trifluoromethyl-β-diketones (R^1 = CF_3) showed the presence of M–48 ions and the metastable peaks for their formation from the molecular ions. This elimination of formyl fluoride (HCOF) from the odd-electron molecular ions has not been reported previously in the literature [10]. When R^1 = CF_3 a few other ions, M–L–CF_2, M–L–CF_2–HF and M–L–CF_2–CO_2 are present in most cases. The cor-

TABLE III. High Resolution Mass Measurements on Selected Peaks of $UO_2(CH_3COCHCOCF_3)_2$.

Ions	Calculated Mass	Determined Mass
UF_3	295.0460	295.0479
UOF_2	292.0425	292.0445
UO_2F	289.0390	289.0393
UOF	273.0441	273.0437
UO_2	270.0406	270.0420

responding ions are absent when $R^1 = C_2F_5$ and C_3F_7 except M–L–C_2F_4 when R^1 is C_2F_5. Loss of :CF_2 from M–L ions involves the metal–fluorine bond formation. The mechanism of such reaction was discussed in the literature [4, 19]. Loss of CO_2 from M–L–CF_2 involves organometallic bond formation [20].

When $R^1 = C_2F_5$ and C_3F_7 the complexes showed the presence of a novel ion, M–R^1–F. Because of the longer chain of the fluorinated alkyl groups perfluoroalkyl groups of two coordinated ligands come closer to each other and thus eliminate FR^1. This interligand reaction was confirmed by the presence of metastable peaks for two complexes with $R^1 = C_2F_5$. Another interesting reaction is the elimination of tetrafluoroethylene from M–L when $R^1 = C_2F_5$. This reaction was confirmed by the presence of a metastable peak. It is not clear whether this reaction involves fluorine migration to metal or to carbonyl carbon. Such reaction was absent in the case of $Pd(RCOCHCOC_2F_5)_2$ complexes [6]. Somehow the central metal atom has great influence in determining the fragmentation pattern of the complexes. When $R^1 = C_2F_5$, small unidentified peaks (<2) were observed at m/e corresponding to M–L–22 and M–L–25.

The fluoride and oxyfluoride of uranium ions show the oxidation state of +4, +5 and +6. Some of these ions are confirmed by high resolution mass spectrometry and are shown in Table III. The replacement of oxygen by fluorine in some of these ions is novel in mass spectrometry.

The migration of R to the metal was not observed due to the absence of any *d* electron in uranium(VI).

References

1 M. L. Morris and R. D. Koob, *Inorg. Chem., 20,* 2737 (1981).
2 S. Ahrland, J. Chatt and M. R. Davies, *Quart. Rev., 12,* 265 (1958).
3 S. Ahrland, *Struct. Bonding, 1,* 207 (1966).
4 M. Das, *J. Inorg. Nucl. Chem., 43,* 3412 (1981) and references therein.
5 M. Das, unpublished results.
6 M. Das, *Inorg. Chim. Acta, 76,* L111 (1983).
7 C. Reichert and J. B. Westmore, *Can. J. Chem., 48,* 3213 (1970).
8 M. Das and S. E. Livingstone, *Aust. J. Chem., 28,* 1513 (1975).
9 R. C. Olivares, J. Gomez-Lara and E. Cortes, *J. Inorg. Nucl. Chem., 42,* 1530 (1980).
10 J. B. Westmore, 'Mass Spectrometry of Metal Compounds', Ed. J. Charalambous, Chap. 9, Butterworths, London (1975).
11 M. Das, *Inorg. Chim. Acta, 48,* 33 (1981).
12 L. Sacconi and G. Giannoni, *J. Chem. Soc.,* 2368, 2751 (1954).
13 L. Sacconi, G. Caroti and P. Paoletti, *J. Inorg. Nucl. Chem., 8,* 93 (1958).
14 R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. Nucl. Chem., 14,* 169 (1960).
15 Y. Baskin and J. R. Ferraro, *J. Inorg. Nucl. Chem., 30,* 241 (1968).
16 K. M. Abubacker and N. S. K. Prasad, *J. Inorg. Nucl. Chem., 16,* 296 (1961).
17 G. M. Bancroft, C. Reichert, J. B. Westmore and H. D. Gesser, *Inorg. Chem., 8,* 474 (1969).
18 W. D. Courrier, W. Forster, C. J. L. Lock and G. Turner, *Can. J. Chem., 50,* 8 (1972).
19 A. L. Clobes, M. L. Morris and R. D. Koob, *Org. Mass Spectrom., 5,* 633 (1971).
20 A. L. Clobes, M. L. Morris and R. D. Koob, *Org. Mass Spectrom., 3,* 1255 (1970).