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SYNTHESIS AND CHARACTERISATION OF MIXED-LIGAND COMPLEXES OF URANIUM(IV) WITH OXYGEN AND SULFUR CONTAINING DONOR LIGANDS

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ABSTRACT

Mixed-ligand complexes of the type $[U(OAc)_2(\beta\text{-diket})_2]$ and $[U(DETC)_2(\beta\text{-diket})_2]$ [where OAc = CH_3COO^-, β-diket = $[CF_3COCHCOCF_3]^-$ (HFAA), $[CH_3COCHCOCF_3]^-$ (TFAA), $[C_4H_3SCOCHCOCF_3]^-$ (TTA), $[C_6H_5COCHCOCF_3]^-$ (BTA), $[C_6H_5COCHCOC_6H_5]^-$ (DBM), $[CH_3COCHCOCH_3]^-$ (AA) and DETC = $[(C_2H_5)_2NCS_2]^-$ have been synthesised and characterised by elemental analyses, infrared, ^1H NMR and mass spectral techniques. Thermogravimetric (TGA) analyses of some of the compounds were carried out to study the thermal decomposition modes. Uranium appears to be eight-coordinated in these complexes.

INTRODUCTION

Uranium(IV) is known to form eight-coordinate complexes of the type $[UCl_2(L)_2(B)_2]$[1] (where B = THF (tetrahydrofuran), DME (1,2-dimethoxyethane), BIPY (2,2'-bipyridyl), TPPO (triphenylphosphineoxide), $[UCl_{2-n}(L)_2(Cp)_n]$[2] (where Cp = cyclopentadienyl ($C_5H_5^-$), n = 1 or 2) and $[U(L)_4]$ (where L = bidentate ligands, *viz.* β-diketonates[3], acetates, dialkyl carbamate/thiocarbonate[4,5]). Recently, we have reported the synthesis and characterisation of uranium(IV) complexes of the type $[UCl_2(\beta\text{-diket})_2(B)_n]$[6,7] and $[UCp_{4-n}(\beta\text{-diket})_n]$[8] (where B = THP (tetrahydropyran), DIOX (1,4-dioxane), THF, DME, n = 1, 2 or 3; β-diket = fluorinated β-diketonates, viz. HFAA, TFAA, TTA, BTA) and studied the vapour pressure of some of the volatile uranium compounds. In this communication, we report the synthesis and characterisation of an analogous series of new complexes of the type $[U(OAc)_2(\beta\text{-diket})_2]$ and $[U(DETC)_2(\beta\text{-diket})_2]$ (where β-diket = fluorinated and non-fluorinated β-diketonates *viz.* AA, HFAA, TFAA, TTA, BTA, DBM).

EXPERIMENTAL

All the preparative work and the subsequent handling of the compounds were carried out in a nitrogen-filled dry box or under *vacuum*.

Materials

Tetrahydrofuran (THF) from BDH Chemicals was distilled over $LiAlH_4$ and then high purity nitrogen gas was bubbled through it before use. The ligands, hexafluoroacetylacetone (HFAA) from Strem Chemical Inc., benzoyltrifluoroacetone (BTA) from Sigma Chemicals, trifluoroacetylacetone (TFAA) from Aldrich Chemicals, thenoyltrifluoroacetone (TTA) from BDH Chemicals and dibenzoylmethane (DBM) from Lube Chemicals were used after purification, either by distillation or *vacuum* sublimation. The sodium salts of diethyl dithiocarbamate trihydrate and acetate dihydrate, both from BDH Chemicals UK, were dehydrated by heating at 80° C under 10^{-2} torr *vacuum*. The thallium(I) salts of β-diketonates were prepared[9] by refluxing thallous(I) carbonate (Fluka Chemicals) and the β-diketones in chloroform and purified by *vacuum* sublimation or recrystallisation from a $CHCl_3$/hexane mixture. Uranium(IV) tetrachloride was prepared[10] by vapour phase chlorination of active UO_2.

Physical And Chemical Measurement

The infrared spectra of the complexes (I) to (VII), (X) and (XI) were recorded on a FTIR Mattson Gygnus 100 spectrometer (4000-400 cm^{-1}) while spectra of the complexes (VIII), (IX) and (XII) were recorded on a Perkin Elmer Spectrometer model 580 (4000-200 cm^{-1}) as nujol or fluorolube mulls using CsI optics. The proton NMR spectra of some of the compounds were recorded as $CDCl_3$ solutions on Varian FT−80A or Bruker Avance DPX 300 spectrometer at room temperature. The mass spectra of some of the the compounds were recorded on a VG Micromass 7070 F mass spectrometer (ion source ~ 200° C, electron energy 70 eV, emission current 200 μA) using PFK (perfluorated kerosene) as comparison standard. Thermogravimetric analyses (TGA) of some of the complexes were carried out on a Ulvac Siko Rinco Model 5000 instrument with a heating rate of 10° C per min up to 1000° C in air. Uranium in the complexes was determined gravimetrically as U_3O_8. Carbon, hydrogen and nitrogen microanalyses were obtained by the Analytical Chemistry Division of this Centre.

Synthesis of the Complexes

$U[(C_2H_5)_2NCS_2]_2(CF_3COCHCOCF_3)_2$

UCl_4 (1.30 g, 0.003 mol) was refluxed with thallium(I) hexafluoroacetylacetonate (2.82 g, 0.003 mol) in ~ 70 mL THF for 2 h. The reaction mixture was cooled and filtered to remove TlCl. To the filtrate was then added anhydrous $Na\{S_2CN(C_2H_5)_2\}$ (1.19 g, 0.006 mol) and the mixture was then refluxed for 8 h. Sodium chloride formed during the reaction was removed by filtration. The brown colored filtrate was concentrated in *vacuo* and upon addition of n-hexane gave a brown colored precipitate which was collected and dried in *vacuo*. The complex was purified by recrystallization from dichloromethane/petroleum ether (1:1) mixture. Yield, 1.32 g (57%). The other complexes in this series were synthesised and purified by the same general procedure.

$U(CH_3COO)_2(CH_3COCHCOCF_3)$

UCl_4 (1.34 g, 0.0035 mol) and thallium(I) trifluoroacetylacetonate (2.79 g, 0.007 mol) were refluxed in ~ 60 mL THF for 4 h. Removing insoluble TlCl gave the brownish colored intermediate $[UCl_2(TFAA)_2(THF)_2]$ which was reacted with anhydrous CH_3COONa (0.64 g, 0.007 mol) for 3 h. Filtration of NaCl gave a yellowish-green solid which was obtained by removing the solvent in *vacuo*. The complex was purified by recrystallization from dichloromethane/petroleum ether (1:1) mixture. Yield, 1.34 g (47%). The compound sublimed at ~150° C under 10^{-3} torr. The other compounds in this series were prepared and purified by the same general procedure.

RESULTS AND DISCUSSION

The dichloro*bis*(β-diketonato)uranium(IV)*bis*(tetrahydrofuran) complexes[6,7] were used as starting materials for synthesizing mixed ligand complexes of uranium(IV) with acetate or diethyl dithiocarbamate. The starting materials have been prepared by refluxing uranium(IV) tetrachloride and thallium(I) β-diketonate in 1:2 molar ratio in a THF solution under a nitrogen atmosphere (eq. (1)).

$$UCl_4 + 2Tl\text{-}\beta\text{-diket} \longrightarrow UCl_2(\beta\text{-diket})_2(THF)_2 + 2TlCl \qquad (1)$$

The mixed-ligand complexes $[U(OAc)_2(\beta\text{-diket})_2]$ and $[U(DETC)_2(\beta\text{-diket})_2]$ were synthesised by reacting the above isolated complexes in THF with sodium acetate or sodium diethyl dithiocarbamate in 1:2 molar ratio under a nitrogen atmosphere (eqs. (2) and (3)).

$$UCl_2(\beta\text{-diket})_2(THF)_2 + 2NaOAc \longrightarrow U(OAc)_2(\beta\text{-diket})_2 + 2NaCl \qquad (2)$$

$$UCl_2(\beta\text{-diket})_2(THF)_2 + 2NaDETC \longrightarrow U(DETC)_2(\beta\text{diket})_2 + 2NaCl \qquad (3)$$

The supernant solution, after standing overnight, was decanted/filtered to remove NaCl. The compounds were obtained either by removing the solvent under *vacuo* or by adding hexane to the saturated solution. The $[U(DETC)_2(\beta\text{-diket})_2]$ compounds were isolated with great difficulty and in low yield, some of the compounds were obtained as a paste. Solids could be obtained either by evacuating under *vacuum* for several hours or by crystallization from dichloromethane/petroleum ether (1:1) mixtures. The physical and analytical data are given in Table I. The complexes are green or brownish-red solids and are soluble in chloroform and dichloromethane. They are high-melting solids except for $[U(OAc)_2(HFAA)_2]$ which melts at 96° C. Only $[U(OAc)_2(HFAA)_2]$ and $[U(OAc)_2(TFAA)_2]$ could be sublimed at 50–60° C and 115–150° C, respectively, under 10^{-3}– 10^{-4} torr *vacuum*. Attempts to sublime the $[U(DETC)_2(\beta\text{-diket})_2]$ compounds led to their decomposition.

IR Spectral Studies

The infrared spectral data (Table II) provide useful information about the mode of coordination of acetate, dithiocarbamate and β-diketonates to the uranium metal ion. The infrared spectra of the $[U(OAc)_2(\beta\text{-diket})_2]$ complexes show $\upsilon_{as}(COO^-)$ to lie between 1560–1525 cm^{-1} which is at lower energy than observed for the free acetate ion (1560 cm^{-1}). The $\upsilon_s(COO^-)$ band lies between 1455–1445 cm^{-1} which is at higher energy than for the free acetate ion (1416 cm^{-1}). Thus, the separation between the two $\upsilon(COO^-)$ (80–100 cm^{-1}) frequencies is less than for the free acetate ion (144 cm^{-1}). This confirms the bidentate[11] chelate nature of the carboxylate group. A similar shift of the $\upsilon(C{=}O)$ mode to lower wave numbers (1650–1560 cm^{-1}), as compared to the respective free β-diketone (1700–1580 cm^{-1}), indicates bonding of the carbonyl oxygen to the uranium ion. Bands in the region 1542–1512 cm^{-1} and 1360–1285 cm^{-1} have been assigned to $\nu(C{=}C)$ and $\nu(C{-}O{-}U)$, respectively, and confirm the chelate formation; hence, the bidentate nature of the β-diketonate moiety. The bands in the region 1225–

Table I
Characterization Data of Uranium(IV) Complexes

Compounds/Empirical Formula/Formula weight (Yield)	Color	M.p. (°C)	Found (Calcd), %			
			U	C	H	N
$[U(OAc)_2(TFAA)_2]$ (I) $(UC_{14}F_6H_{14}O_8)$ 662.18, (57%)	Yellowish green	164	36.20 (35.95)	25.03 (25.39)	2.30 (2.13)	----
$[U(OAc)_2(HFAA)_2]$ (II) $(UC_{14}F_{12}H_8O_8)$ 770.23, (65%)	Green	96	31.10 (30.90)	21.41 (21.83)	0.80 (1.05)	----
$[U(OAc)_2(TTA)_2]$ (III) $(UC_{20}F_6H_{14}O_8S_2)$ 798.46, (50%)	Brown	210	29.53 (29.82)	30.40 (30.08)	1.85 (1.77)	----
$[U(OAc)_2(BTA)_2]$ (IV) $(UC_{24}F_6H_{18}O_8)$ 786.41, (58%)	Brown	154	29.84 (30.27)	36.49 (36.65)	2.10 (2.31)	----
$[U(OAc)_2(\ DBM)_2]$ (V) $(UC_{34}H_{28}O_8)$ 802.59, (65%)	Brown	175-78 (d)	29.51 (29.66)	50.30 (50.88)	3.70 (3.52)	----
$[U(OAc)_2(AA)_2]$ (VI) $(UC_{14}H_{20}O_4)$ 554.33, (54%)	Green	185 (d)	42.57 (42.94)	30.07 (30.33)	3.70 (3.64)	----

$[U(DETC)_2(HFAA)_2]$ (VII) $U(C_{20}H_{22}N_2F_{12}O_4S_2)$ 948.65, (47%)	Brown	102 (d)	24.56 (25.09)	24.92 (25.32)	2.10 (2.34)	2.70 (2.95)
$[U(DETC)_2(TFAA)_2]$ (VIII) $(UC_{20}F_6H_{28}N_2O_4S_4)$ 840.65, (45%)	Dark brown	150 (d)	27.80 (28.31)	28.31 (28.57)	3.02 (3.36)	3.02 (3.82)
$[U(DETC)_2(TTA)_2]$ (IX) $(UC_{26}F_6H_{28}N_2O_4S_6)$ 976.87, (62%)	Brownish red	235-8	23.97 (24.37)	31.64 (31.96)	2.51 (2.87)	2.60 (2.87)
$[U(DETC)_2(BTA)_2]$ (X) $(UC_{30}F_6H_{32}N_2O_4S_4)$ 964.83, (42%)	Brown	165-8	24.36 (24.67)	37.15 (37.34)	2.92 (3.34)	2.70 (2.90)
$[U(DETC)_2(DBM)_2]$ (XI) $(UC_{40}H_{42}N_2O_4S_4)$ 981.01, (44%)	Brown	160 (d)	23.84 (24.26)	49.41 (48.97)	4.30 (4.32)	2.53 (2.86)
$[U(DETC)_2(AA)_2]$ (XII) $(UC_{20}H_{34}N_2O_4S_4)$ 732.72, (48%)	Brownish red	182-84	31.91 (32.49)	32.49 (32.78)	4.40 (4.68)	4.00 (3.82)

d = decomposition

Table II

Important IR Bands (cm^{-1}) and their Assignments

Compounds[a]	Vibrations of β-Diketonate			Vibrations of Dithiocarbamates\Acetate				Vibrations of Metal-Ligands		
	υ(C=O)	υ(C=C)	υ(C–O–U)	υ(C=N)	υ(C=S)	$υ_{as}(COO^-)$	$υ_s(COO^-)$	[b]υ(U–O)	[c]υ(U–O)	υ(U–S)
I	1625 s	1535 s	1285 m	....	....	1525 s	1443 m	552 w	456 m	....
II	1644 s 1620 s	1534 m	1352 s(br)	....	....	1550 m	1454 s	529 m	....	....
III	1620 s	1512 m	1311 m	....	....	1544 s	....	502 s	....	......
IV	1573 vs	1537m	1283 m	....	....	....	1452 m	518 m	469 m	....
V	1592 s	1524 m	1360 s(br)	....	....	....	1453 s	518 m	....	....
VI	1562 s	1530 m	1351s	....	....	1552 m	....	524 m	404 s	....
VII	1574 s	1529* m	1303 w	1529* m	1032 m	....	....	528 m	......	
VIII	1625 m	1524* s	....	1524* m	979 s	....	....	503 m	....	391 w
IX	1605 m	1535 s	1300 s	1510 s	1000 m	....	....	500 m	....	350 w
X	1598 (sh) 1574 s	1535 m	1291 s	1520 m	1026 s	....	....	519 m	....	....
XI	1602 m 1591 s	1531 s	1302 m	1515 m	1024 m	....	....	516 m	....	....
XII	1561 m	1540 m	1297 s	1500 m	1005 m	....	....	520 w	....	390 w

[a] The number represents the corresponding compounds in Table I. vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad, [b]υ(U–O(β–diketonate)), [c]υ(U–O)(Acetate);
* = overlapping of bands.

1185 cm^{-1} are assigned to C–H in–plane–bending, while out–of–plane bending vibrations are observed in the region 807–787 cm^{-1}.

For the $[U(Et_2NCS_2)_2(β\text{–diket})_2]$ complexes a single strong band is observed in the region 1530–1500 cm^{-1} which is assigned to υ(C=N); another single strong band occurs in the range 1030–980 cm^{-1} due to υ(C=S). This suggests that the DETC ligands are coordinated to the uranium metal ion in a bidentate[12] chelate manner through the sulfur atoms.

In the far infrared region (600–200 cm^{-1}), the tentative assignments of uranium-ligand vibrations of υ(U–O)(β–diketonates), υ(U–O)(acetate) and υ(U–S) (dithiocarbamate) were made by a comparision with the spectra of the analogous metal-diketonates[13], metal–acetates[14,15] and metal–dithiocarbamates[16,17]. Bands at 550–500 cm^{-1} (strong bands) are assigned to υ(U–O)(β–diketonates). The other bands, lying between 470–400 cm^{-1} are assigned to υ(U–O)(acetate) whereas the weak bands between 390–350 cm^{-1} have been assinged to υ(U– S)(dithiocarbamates).

^{1}H NMR Spectral Studies

The ^{1}H NMR spectra of $[U(OAc)_2(HFAA)_2]$, $[U(OAc)_2(TFAA)_2]$, $[U(OAc)_2(DBM)_2]$ and $[U(OAc)_2(AA)_2]$ in $CDCl_3$ (Table III) indicate a shifting of the signal due to the methyl protons of the acetato group (as a singlet) from 1.85 to 2.26 ppm, suggesting coordination of the acetato ligand to the uranium metal ion. In the case of the [U(DETC)$_2$(β–diket)$_2$] complexes, the ^{1}H NMR spectra in $CDCl_3$ show a characteristic resonance for diethyl dithiocarbamate as a triplet in the range 1.14 to 1.33 ppm (^{J}H = 7.06– 7.18 Hz) and a quartet in the range 2.15 to 2.96 ppm (^{J}H = 7.07–7.88 Hz), the former band being assigned to the methyl (CH_3) protons and the latter to the methylene (CH_2) protons of the DETC ligand. These chemical shifts of the dithiocarbamate groups in the mixed ligand complexes [U(Et$_2$NCS$_2$)$_2$(β-diket)$_2$] do not show any appreciable changes with respect to the free ligand values as reported in the case of [Sb(DETC)$_3$][15] complexes. The methine (CH) proton signals of β–diketonates have been observed as a singlet at 5.85–7.01 ppm in these complexes. The methyl (CH_3) proton resonances of the TFAA complexes have been observed as a singlet between 2.29 –2.50 ppm.

Mass Spectral Studies

Electron impact (EI) mass spectra of $[U(OAc)_2(HFAA)_2]$ and $[U(OAc)_2$-$(TFAA)_2]$ show the highest mass at m/z 751 and 643, corresponding to the species

Table III

^{1}H NMR Spectral Data of the Mixed Ligand Complexes (δ ppm from TMS)

Complexes [a]	Acetate moiety	Dithiocarbamate moiety		β–Diketonate moiety			
	Methyl	Methyl	Methylene	Phenyl	Thienyl	Methyl	Methine
I	2.00 (s)	....	....	....	....	2.50 (s)	6.65 (s)
II	2.26 (s)	....	....	....	....	....	6.54 (s)
III	1.71 (s)	....	....	....	7.60–7.65 (m)	....	7.01 (s)
V	2.19 (s)	....	....	7.49–8.01 (m)	....	....	6.88 (s)
VI	1.85 (s)	....	....	....	....	2.35 (s)	5.85 (s)
VII	....	1.22 (t)	2.90 (q)	....	....	....	6.54 (s)
VIII	....	1.33 (t)	2.96 (q)	....	....	2.29 (s)	6.24 (s)
IX	....	1.15 (t)	2.76 (q)	....	7.11–8.16 (m)	....	6.76 (s)
X	....	1.14 (t)	2.78 (q)	7.16–7.61 (m)	....	....	6.97 (s)
XI	....	1.28 (t)	2.15 (q)	7.22–8.01 (m)	....	....	6.87 (s)

[a] The number represents the corresponding complexes in Table I

s = singlet , q = quartet , m = multiplate

$[U(OAc)_2(HFAA)(CF_3COCHCOCF_2)]^+$ and $[U(OAc)_2(TFAA)(CH_3COCHCOCF_2)]^+$ respectively, and were formed by the loss of one fluorine atom from the parent compound. In former case, the most intense peak at m/z 486 corresponds to the $[UF(OAc)_2(CF_3COCH)]^+$ species which results from loss of one HFAA and $COCF_3$ from the parent compound. The mass spectral data show that the two HFAA ligands are successively detached from the molecular ion leaving behind the species $[U(OAc)_2Fn]^+$ n = 1 or 2. The acetato ligands are thus more strongly bonded to the uranium ion. A similar fragmentation pattern has been observed for $[U(OAc)_2(TFAA)_2]$. Thus, the mass-spectral results show a detachment of the β-diketonate moiety first, followed by the acetato group. Prominent peaks as metal containing fragments from the spectra are given in Tables IV(a) and (IV)(b). In the case of the $[U(DETC)_2(\beta\text{-diket})_2]$ complexes, the mass spectral fragmentation pattern could not be obtained due to insufficient volatility.

Thermogravimetric Studies

The thermograms of some $[U(OAc)_2(\beta\text{-diket})_2]$ and $[U(DETC)_2(\beta\text{-diket})_2]$ complexes are presented in Figs. 1 and 2, respectively. The probable mode of decomposition of these complexes based on the analysis of the thermograms is given below.

The thermal decomposition of the $[U(DETC)_2(TTA)_2]$ complex takes place in three stages. A first stage decomposition up to 225° C corresponds to a weight loss of ~56%. The second stage decomposition (~ 6% weight loss) and third stage (~ 6% weight loss) has been observed up to 425° C and 500° C respectively. The total weight loss of all three stages ~ 68%, corresponding to detachment of both ligands. The thermal product/residue (~ 32%) as shown in the thermogram corresponds to UO_2S (calculated ~ 31%). The TGA studies of this compound under the experimental conditions reveal that the first stage decomposition mainly corresponds to loss of the TTA ligand. Thus, DETC seems to be more strongly bonded and thermally stable as compared to the TTA ligand. A similar type of decomposition in three stages (~ 52% weight loss up to 325° C, ~4%

Table IV(a). Important m/z Peaks in the Mass Spectra of [U(OAc)$_2$(TFAA)$_2$]

m/z	Assignments	Relative Intensity
643	[U(OAc)$_2$(TFAA)(CH$_3$COCHCOCF$_2$)]$^+$	55
565	[U(OAc)$_2$(TFAA)(CH$_3$COCH)]$^+$	55
546	[U(OAc)$_2$(CH$_3$COCHCOCF$_2$)(CH$_3$COCH)]$^+$	22
515	[U(OAc)$_2$(CH$_3$COCHCOF)(CH$_3$COCH)]$^+$	55
509	[U(OAc)$_2$(TFAA)]$^+$	100
450	[U(OAc)$_2$(CH$_3$COCHF$_2$)]$^+$	22
394	[UF$_2$(OAc)$_2$]$^+$	60
375	[UF(OAc)$_2$]$^+$	63
356	[U(OAc)$_2$]$^+$	44

Table IV(b). Important m/z Peaks in the Mass Spectra of[U(OAc)$_2$(HFAA)$_2$]

m/z	Assignments	Relative Intensity
751	[U(OAc)$_2$(HFAA)(CF$_3$COCHCOCF$_2$)]$^+$	15
682	[U(OAc)$_2$(CF$_3$COCHCO)(CF$_3$COCHCOCF$_2$)]$^+$	16
673	[U(OAc)$_2$(HFAA)(CF$_3$COCH)]$^+$	30
557	[U(OAc)$_2$(CF$_3$COCH)(CF$_2$COCH)]$^+$	70
485	[U(OAc)$_2$(CF$_3$COCHF)]$^+$	80
466	[U(OAc)$_2$(CFCOCH)]$^+$	25
428	[U(OAc)$_2$(CFCOCH)]$^+$	60
413	[UF$_3$(OAc)$_2$]$^+$	33
394	[UF$_2$(OAc)$_2$]$^+$	31
375	[UF(OAc)$_2$]$^+$	48
356	[U(OAc)$_2$]$^+$	23

weight loss up to 450° C and ~12% weight loss up to 550° C) is observed for [U(DETC)$_2$(DBM)$_2$]. Both thermograms reveal that around 500° C, both ligands are lost leaving UO$_2$S as residue.

The TGA of [U(OAc)$_2$(DBM)$_2$] shows a sharp and extensive decomposition up to 375° C (~54% weight loss). This weight loss corresponds to the detachment of both DBM ligands. For the second and the third stage decomposition, a weight loss of ~ 4% and ~12% up to 425° C and 550° C, respectively, is observed which does not correspond to a successive loss of the two acetate ligands. However, the consolidated second and third stage weight loss corresponds to detachment of both acetate ligands, leaving ~30%

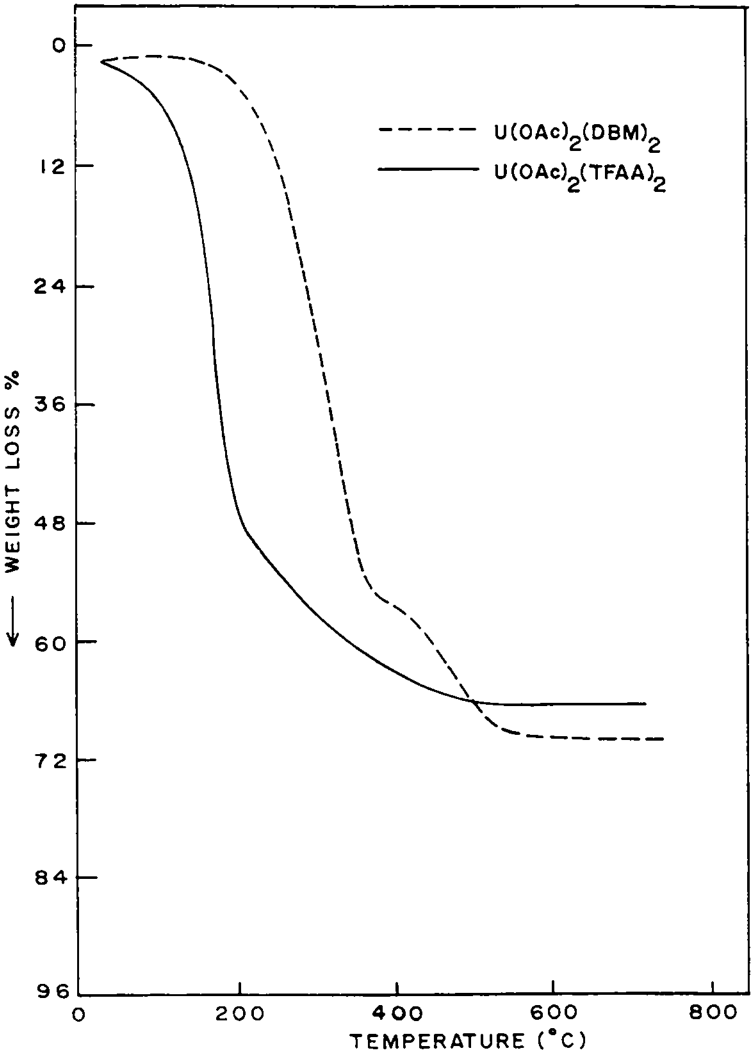


FIG.1. Thermograms of $[U(OAc)_2(\beta\text{-diket})_2]$ Complexes.

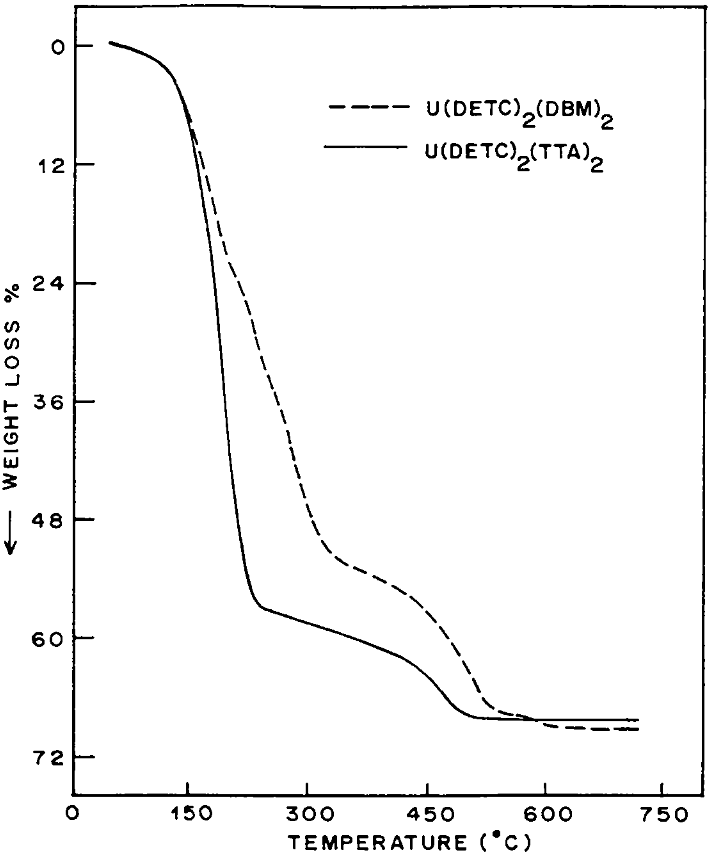
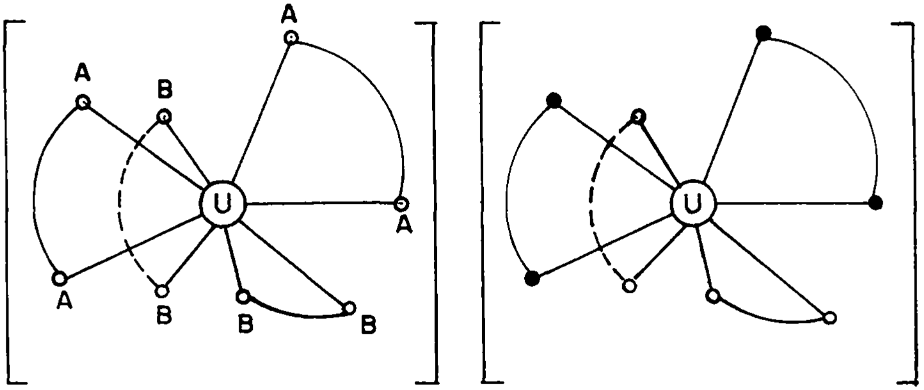


FIG. 2. Thermograms of $[U(DETC)_2(\beta\text{-diket})_2]$ Complexes.

of thermal residue as UO_3. Thus, the TGA study of this compound indicates that the acetate ligand is more strongly bonded and thermally more stable than the DBM ligand.

The thermal decomposition of $[U(OAc)_2(TFAA)_2]$ takes place in two stages. In the first stage a weight loss of ~ 48% is observed up to 200° C which corresponds to the loss of two TFAA ligands. The second stage decomposition shows a weight loss of ~16% up to 400° C corresponding to loss of two acetate ligands leaving ~ 43% of residue



(a) (b)

FIG. 3. Proposed Structure of the Complexes

(a) $[U(OAc)_2(\beta\text{-diket})_2]$ (b) $[U(DETC)_2(\beta\text{-diket})_2]$

$\overset{\frown}{A\ A}$ = β-diketonate ● = S, o = O

$\overset{\frown}{B\ B}$ = acetate

as UO_3. Thus, the TGA of this compound shows that the acetate ligand is more strongly bonded and thermally stable as compared to the TFAA ligand.

Conclusion

Based on the analytical results, infrared studies, ^1H NMR and mass spectral studies in both types of mixed ligand complexes, the acetate, β-diketonate and the diethyl dithiocarbamate ligands function as bidentate ligands. Therefore, it may concluded that the uranium metal ion is probably eight-coordinate in all these complexes which may be an arrangement either as a dodecahedron or a square antiprism or a structure intermediate between the two. The proposed general structures of the compounds are depicted in Figs. 3(a) and (b).

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