Synthesis, Spectral and Thermal Characteristics of Some Ten Coordinated Complexes of Dioxouranium(VI) Derived from Semicarbazones as Primary Ligand and Diphenyl Sulfoxide as Secondary Ligand

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The reactions of dioxouranium(VI) acetate with several semicarbazones derived from 4-aminoantipyrine in the presence of diphenyl sulfoxide (DPSO) led to the formation of complexes corresponding to the formulae $[UO_2(CH_3COO)_2 (L).DPSO]$, where L = 4[N-(benzalidene)amino]antipyrinesemicarbazone (BAAPS), 4[N-(2′-hydroxybenzalidene)- amino]antipyrinesemicarbazone (HBAAPS) 4[N-(4′-methoxyben-zalidene)amino] antipyrine semicarbazone (MBAAPS) 4[N-(4′-dimethylaminobenzalidene)amino]- antipyrinesemicarbazone (DABAAPS) 4[N-(2′-nitrobenzalidene)amino]antipyrine- semicarbazone (2′-NO$_2$ BAAPS) 4[N-(3′-nitrobenzalidene)amino]antipyrine- semicarbazone (3′-NO$_2$BAAPS) 4[N-(4′-nitrobenza-lidene)amino]antipyrine- semicarbazone (4′-NO$_2$BAAPS), 4[N-(4′-hydroxy-3′-methoxybenzalidene)amino]-antipyrinesemicarbazone (HMBAAPS) 4[N-(2′-hydroxy-1′-naphthalidene)amino]- antipyrinesemicarbazone (HNAAPS) 4[N-(cinnamalidene)amino]antipyrine- semicarbazone (CAAPS) 4[N-(3′,4′,5′-trimethoxyben-zalidene)amino]antipyrine- semicarbazone (TMBAAPS) and 4[N-(furfural)amino]antipyrinesemicarbazone (FFAAPS). The complexes were characterised by means of elemental analyses, conductivity measure-ments, molecular weight, magnetic moments and infrared studies. The coordination number 10 is pro-posed for these complexes. Thermal properties of the representative complexes are also reported.

Key Words: Dioxouranium(VI), mixed ligand complexes, semicarbazones, diphenyl sulfoxide, charac-terisation, coordination number.

Introduction

Actinide metals, especially uranium(VI), attract great interest because of the formation of varieties of co-ordination compounds with varying coordination numbers. UO_2^{2+} can coordinate 2 to 6 other atoms, ions or molecules in the equatorial plane with a strong tendency to make these ligating atoms coplanar. The

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complexing ability of dioxouranium(VI) is demonstrated with a wide variety of organic and inorganic ligands [1-3]. Agarwal et al.[4,5] have reported some dioxouranium(VI) complexes of semicarbazones derived from 4-aminoantipyrine. Semicarbazones are reported to possess versatile structural features[6] and very good antifungal and antibacterial properties[7,8]. The spectral properties of some furfuraldehyde semicarbazone and 2-hydroxyacetophenone N(4)-phenyl semicarbazone were recently reported[9,10]. No report is available in the literature on mixed ligand complexes of dioxouranium(VI) with semicarbazones derived from 4-aminoantipyrine and diphenyl sulfoxide. Thus, the present work reports some 10-coordinated complexes of dioxouranium(VI) with 4[N-(benzalidene)amino]antipyrinesemicarbazone (BAAPS), 4[N-(2′-hydroxy-benzalidene)amino]antipyrinesemicarbazone (HBAAPS), 4[N-(4′-methoxybenzalidene)-amino]antipyrinesemicarbazone (MBAAPS), 4[N-(4′-dimethylaminobenzalidene)-amino]antipyrinesemicarbazone (DABAAPS), 4[N-(2′-nitrobenzalidene)amino]- antipyrine- semicarbazone (2′-NO$_2$BAAPS), 4[N-(3′-nitrobenzalidene)amino]antipyrine semicarbazone (3′-NO$_2$BAAPS), 4[N-(4′-nitrobenzalidene)amino]antipyrinesemicarbazone (4′-NO$_2$BAAPS), 4[N-(4′-hydroxy-3′-methoxybenzalidene)amino] antipyrinesemicarbazone (HMBAAPS), 4[N-(2′-hydroxy-1′-naphthalidene)amino] antipyrinesemicarbazone (HNAAPS), 4[N-(cinnamalidene) amino]antipyrine semicarbazone (CAAPS), 4[N-(3′,4′,5′-trimethoxybenzalidene)amino]antipyrine- semicarbazone (TMBAAPS), and 4[N-(furfural)amino]antipyrinesemicarbazone (FFAAPS) as primary ligand and diphenyl sulfoxide as secondary ligand.

Experimental

Dioxouranium(VI) acetate was obtained from SD Fine Chemicals and used as received. The ligands (semicarbazones) were synthesised in the laboratory by the method reported elsewhere[11]. The specifications of the ligands are as follows:

- (i) 4[N-(benzalidene)amino]antipyrinesemicarbazone (BAAPS) (m.f. $C_{19}H_{20}N_6O$)

- (ii) 4[N-(2′-hydroxybenzalidene)amino]antipyrinesemicarbazone (HBAAPS) (m.f. $C_{19}H_{20}N_6O_2$)

- (iii) 4[N-(4′-methoxybenzalidene)amino]antipyrinesemicarbazone (MBAAPS) (m.f. $C_{20}H_{22}N_6O_2$)

- (iv) 4[N-(4′-dimethylaminobenzalidene)amino]antipyrinesemicarbazone (DABAAPS) (m.f. $C_{21}H_{25}N_7O$)

- (v) 4[N-(2′-nitrobenzalidene)amino]antipyrinesemicarbazone (2′-NO$_2$BAAPS) (m.f. $C_{19}H_{19}N_7O_3$)

- (vi) 4[N-(3′-nitrobenzalidene)amino]antipyrinesemicarbazone (3′-NO$_2$BAAPS) (m.f. $C_{19}H_{19}N_7O_3$)

- (vii) 4[N-(4′-nitrobenzalidene)amino]antipyrinesemicarbazone (4′-NO$_2$BAAPS) (m.f. $C_{19}H_{19}N_7O_3$)

- (viii) 4[N-(4′-hydroxy-3′-methoxybenzalidene)amino]antipyrinesemicarbazone (HMBAAPS) (m.f. $C_{20}H_{22}N_6O_3$)

- (ix) 4[N-(2′-hydroxy-1′-naphthalidene)amino]antipyrinesemicarbazone (HNAAPS) (m.f. $C_{23}H_{23}N_6O_2$)

- (x) 4[N-(cinnamalidene)amino]antipyrinesemicarbazone (CAAPS) (m.f. $C_{21}H_{22}N_6O$)

- (xi) 4[N-(3′,4′,5′-trimethoxybenzalidene)amino]antipyrinesemicarbazone (TMBAAPS) (m.f. $C_{22}H_{26}N_6O_4$)

- (xii) 4[N-(furfural) amino] antipyrinesemicarbazone (FFAAPS) (m.f. $C_{17}H_{20}N_6O_2$).

Synthesis of the complexes

All the dioxouranium(VI) complexes of semicarbazones and diphenyl sulfoxide were prepared by mixing dioxouranium(VI) acetate (1 mmol) with respective semicarbazone and DPSO (both in 1.1 mmol ratio) in boiling ethanol and refluxing the reaction mixture for 1-2 h. On cooling the reaction mixture, desired complexes were crystallised out. They were filtered and dried in vacuo over anhydrous $CaCl_2$.

All the physico-chemical measurements were performed by the reported method[4,5].

Results and Discussion

The interaction of dioxouranium(VI) acetate with various semicarbazones and DPSO resulted in the formation of complexes with the general composition $UO_2(CH_3COO)_2$(L).DPSO (L = BAAPS, HBAAPS, MBAAPS, DABAAPS, $2'$-NO_2BAAPS, $3'$-NO_2BAAPS, $4'$-NO_2BAAPS, HMBAAPS, HNAAPS, CAAPS, TMBAAPS or FFAAPS). All the complexes are yellow or orange-yellow solids. The elemental analyses of these complexes are summarised in Table 1. The complexes are anhydrous, which is evident from the analytical, infrared and thermal studies. All of the complexes are quite stable and can be stored for long periods. The molar conductance values of these complexes are too low to account for their ionic nature. This observation suggests that all these complexes are non-electrolytes in nitrobenzene. Data on the molecular weight of the complexes in freezing nitrobenzene are also shown in Table 1, along with values calculated on the basis of the established formula of the complexes. The ratio of molecular weight observed for $[UO_2(CH_3COO)_2$(L).DPSO] to that of calculated values is ~0.98, which shows that the complexes are monomeric in solution. The dioxouranium(VI) compounds are diamagnetic, depending upon the diamagnetism of the other ions and surrounding ligand field. The magnetic susceptibilities are independent of field strength and temperature[12]. The ground states of dioxouranium(VI) acetate contain no unpaired electrons; the compounds, therefore, are weakly diamagnetic as observed previously[5,13,14].

Infrared spectra

In all the present complexes, as expected, the $\nu(NH_2)$ band of the hydrazinic nitrogen of semicarbazide (~ 1622 cm^{-1}) is absent in the infrared spectra of all the 12 semicarbazones [15]. It has also been observed that the amide-II band in the complexes is shifted towards the lower energy side compared to that of the semicarbazone. The effect is due to the electron density drift from the hydrazinic nitrogen to metal ion [16]. The characteristic absorption of the carbonyl group in all the 12 semicarbazones is observed in 1700-1680 cm^{-1} region[17,18]. In all the dioxouranium(VI) acetate complexes, this band is shifted toward a lower energy range of 1650-1640 cm^{-1}, as shown in Table 2. The amide-II band in free ligands has been observed at ~1565 cm^{-1}. In all the present complexes this band is also shifted towards lower wave numbers by ~30 cm^{-1}. This observation suggests metal-coordination through the carbonyl-oxygen atom. The strong bands at ~1600 cm^{-1} in these semicarbazones apparently have a large contribution from the ν(C=N) mode of the semicarbazone moiety[17,18]. This has been observed as a blue shift in the position of the (C=N) band in all the dioxouranium(VI) acetate complexes of semicarbazones as compared to the free ligands. Another strong band was observed in the 1620-1610 cm^{-1} region due to azomethines (C=N) absorption. On metal-coordination, this band is shifted towards the lower frequency region (1592-1580 cm^{-1}), clearly indicating

coordination through the azomethinic-N atom[19−21]. In HBAAPS, HMBAAPS and HNAAPS, the stretching frequency in the 3400-3300 cm^{-1} region is attributed to ν(OH). In all 3 complexes of uranyl(VI) ion with these ligands, the –OH absorption bands appeared in the same region as in free ligands, clearly indicating that the –OH group does not take part in coordination. These studies indicate that all these semicarbazones serve as tridentate ligands, coordinating through the carbonyl-O, hydrazinic-N and azomethinic-N atoms.

Table 1. Analytical, conductivity and molecular weight data of dioxouranium (VI) complexes of semicarbazones and DPSO.

| Complex	Analysis: Found (calcd) %				m.w. Found (calcd.)	ohm^{-1} cm^2 Mol^{-1}
	U	C	H	N		
UO$_2$(CH$_3$COO)$_2$BAAPS.DPSO	25.19 (25.37)	29.28 (29.42)	2.72 (2.77)	8.88 (8.95)	934 (938)	2.3
UO$_2$(CH$_3$COO)$_2$HBAAPS.DPSO	(24.77 (24.94)	28.78 (28.93)	2.69 (2.72)	8.71 (8.80)	950 (954)	2.1
UO$_2$(CH$_3$COO)$_2$MBAAPS.DPSO	24.39 (24.58)	29.61 (29.75)	2.85 (2.89)	8.60 (8.67)	964 (968)	1.9
UO$_2$(CH$_3$OO)$_2$DABAAPS.DPSO	24.13 (24.26)	30.42 (30.58)	3.12 (3.16)	9.90 (9.98)	975 (981)	2.0
UO$_2$(CH$_3$COO)$_2$ 2'-NO$_2$BAAPS.DPSO	24.09 (24.21)	27.91 (28.07)	2.49 (2.54)	9.90 (9.96)	978 (983)	1.8
UO$_2$(CH$_3$COO)$_2$ 3'-NO$_2$BAAPS.DPSO	24.10 (24.21)	27.89 (28.07)	2.50 (2.54)	9.89 (9.96)	979 (983)	2.1
UO$_2$(CH$_3$COO)$_2$4'-NO$_2$BAAPS.DPSO	24.08 (24.21)	27.90 (28.07)	2.49 (2.54)	9.90 (9.96)	978 (983)	2.2
UO$_2$(CH$_3$COO)$_2$HMBAAPS.DPSO	24.04 (24.18)	29.10 (29.26)	2.78 (2.84)	8.48 (8.53)	980 (984)	1.9
UO$_2$(CH$_3$COO)$_2$HNAAPS.DPSO	23.53 (23.68)	32.08 (32.23)	2.82 (2.88)	8.30 (8.35)	1000 (1005)	2.1
UO$_2$(CH$_3$COO)$_2$CAAPS.DPSO	24.51 (24.68)	31.00 (31.12)	2.86 (2.90)	8.65 (8.71)	960 (964)	2.1
UO$_2$(CH$_3$COO)$_2$TMBAAPS.DPSO	23.03 (23.15)	30.17 (30.35)	3.06 (3.11)	8.12 (8.17)	1022 (1028)	1.9
UO$_2$(CH$_3$COO)$_2$FFAAPS.DPSO	25.51 (25.64)	27.02 (27.15)	2.53 (2.58)	9.00 (9.05)	925 (928)	1.8

In the DPSO spectra, the 2 absorptions associated with S=O and C-S stretching modes undergo a significant shift on coordination [22,23]. S=O stretching frequency in free DPSO appears as a strong absorption at 1030 cm^{-1},[22,23] which disappears on complexation with a metal ion and a new band appears in the 970-960 cm^{-1} region[24] (Table 2). The other important absorption band in the spectra of DPSO is the C-S stretching absorption, which has been identified[24] in free DPSO at 680 cm^{-1}. This absorption undergoes a slight shift to a higher wave number on complexation. A shift to a lower wave number of the (S=O) stretching frequency and a shift of the (C-S) stretching frequency towards higher wave numbers are indicative of the decrease in the double bond character of the S=O bond. The data thus suggest coordination through an oxygen atom of DPSO.[22−24] In the far-infrared region, bands due to ν (U-N)/ν(U-O) are also observed[4,5] (Table 2).

**Table 2.** Infrared absorption frequencies (cm^{-1}) of UO$_2$(VI) complexes of semicarbazones and DPSO.

Compound	ν(C=N) (azomethinc)	ν(C=N) (Hydrazinc)	ν(C = O)			ν(S=O)	ν(U-N)/ ν(U-O)
			I	II	III		
DPSO	-	-	-	-	-	1030s	-
BAAPS	1610m	1600m	1700s	1565s	1350s	-	-
UO$_2$(CH$_3$COO)$_2$BAAPS.DPSO	1592s	1612m	1650s	1535m	1332m	980s	460m,395m
HBAAPS	1622m	1605m	1705s	1570s	1350s	-	-
UO$_2$CH$_3$COO)$_2$HBAAPS.DPSO	1590m	1635m	1645s	1538m	1335m	972s	462m,398m
MBAAPS	1620m	1605m	1702s	1560m	1350m	-	-
UO$_2$(CH$_3$COO)$_2$MBAAPS.DPSO	1592s	1633s	1648s	1530m	1322m	975s	452m,390m
DABAAPS	1620s	1605s	1705s	1570s	1355m	-	-
UO$_2$(CH$_3$COO)$_2$DABAAPS DPSO	1583m	1632s	1640s	1532m	1330m	977s	458m,390s
2'-NO$_2$ BAAPS	1612m	1602m	1700s	1565s	1340m	-	-
UO$_2$(CH$_3$COO)$_2$2'-NO$_2$BAAPS.DPSO	1590m	1632s	1648s	1540m	1330m	975s	470m,402w
3'-NO$_2$ BAAPS	1608m	1600m	1702s	1565s	1340s	-	-
UO$_2$(CH$_3$COO)$_2$ 3'-NO$_2$BAAPS.DPSO	1580m	1630s	1645s	1528m	1330m	982s	472m,398w
4'-NO$_2$BAAPS	1610m	1600m	1705s	1562m	1355m	-	-
UO$_2$(CH$_3$COO)$_2$ 4'-NO$_2$BAAPS.DPSO	1592s	1622s	1648s	1530m	1332m	980s	470m,390w
HMBAAPS	1615m	1605m	1705s	1570s	1350m	-	-
UO$_2$(CH$_3$COO)HMBAAPS.DPSO	1590m	1628m	1645s	1537m	1332m	982s	465m,398w
HNAAPS	1608m	1600m	1702m	1565s	1348m	-	-
UO$_2$(CH$_3$COO)$_2$HNAAPS.DPSO	1582m	1628m	1650s	1532m	1322m	980s	460m,390w
CAAPS	1610m	1600m	1700s	1572s	1350s	-	-
UO$_2$(CH$_3$COO)$_2$CAAPS.DPSO	1592m	1632m	1650s	1532m	1328m	982s	458m,392w
TMBAAPS	1615s	1600s	1700s	1565m	1350m	-	-
UO$_2$(CH$_3$COO)$_2$TMBAAPS.DPSO	1585m	1630s	1645s	1535m	1330m	980s	470m,398w
FFAAPS	1620m	1605m	1705s	1570s	1350m	-	-
UO$_2$(CH$_3$COO)$_2$ FFAAPS.DPSO	1590m	1628m	1645s	1537m	1330m	975s	473m,395w
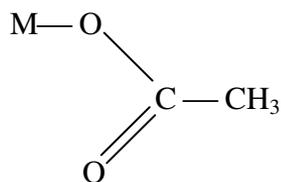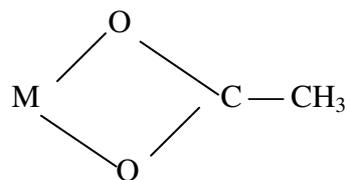
(a)   (b)
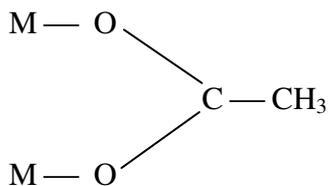
(c)

Extensive IR spectral studies have been performed on metal complexes of carboxylic acids. The acetate ion may coordinate to a metal ion in one of the following modes:

The $\nu_{asym}(COO^-)$ of free acetate ions are at ~1560 and 1416 cm^{-1}, respectively. In the unidentate complex (structure a) $\nu(C=O)$ is higher than $\nu_{asym}(COO^-)$ and $\nu(C\text{-}O)$ is lower than $\nu_{asym}(COO^-)$. As a result the separation between the 2 $\nu(CO)$ is much larger in unidentate complexes than in free ion. The opposite trend is observed in the bidentate complex: the separation between the $\nu(CO)$ is smaller than that of free ion in this case. In the bridging complexes (structure c), however, 2 $\nu(CO)$ are close to the free ion values. The present complexes show infrared absorption frequency bands corresponding to $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ in 1560-1545 and 1475-1460 cm^{-1}, respectively. These observations indicate that both acetate groups in the present complexes are bidentate [13,25,26].

In the present studies of uranyl complexes, it was observed that the ν_1 mode of the uranyl ion appears in 837–825 cm^{-1} as weak intensity and ν_3 in 930–925 cm^{-1} as strong intensity in the infrared spectra (Table 3). A group theoretical treatment[27] shows that a linear and symmetrical triatomic UO$_2^{2+}$ ion possessing D$_{\infty h}$ symmetry gives rise to 3 fundamental modes of vibrations. Wilson's G-F matrix method[28] has been used to determine the stretching and interaction force constants. The results are in turn used to determine the (U-O) bond distances, following Badger's formula[29]. The force constants, bond distances and spectral data used here are presented in Table 3. It is apparent from Table 3 that the bond length increases with decreases in the value of symmetric stretching frequency (ν_1) [30]. The calculated values of the (U-O) bond distances of the present coordination compounds are well within the range.

Thermal studies

A few representative uranyl(VI) coordination compounds of semicarbazones and DPSO have been selected for their thermal properties. Thermal data of these complexes are presented in Table 4. The thermogravimetric curves of these coordination compounds clearly indicate the absence of water mol in or outside the coordination sphere. All the compounds show a weight loss at ~160 °C, corresponding to the evaporation of

1 mol of DPSO. The break in the curves in the 240-370 °C region indicates that at this stage the deligation process has started. At this stage 1 mol of the semicarbazone has been lost. Finally, at ~640 °C, the oxide U_3O_8 is formed via the formation of UO_3, following which there is no measurable change in weight[5,31].

Table 3. Various force constants (mdynes/Å), U-O bond distance (Å) and frequencies of ν_1 and ν_3 of $UO_2(VI)$ complexes of semicarbazones and DPSO

Complex	ν_1	ν_3	U–O Force – constant	Force constants due to interactions between bonds	U–O Bond distance
$UO_2(CH_3COO)_2$BAAPS.DPSO	837	928	6.8796	-0.2759	1.7378
$UO_2(CH_3COO)_2$HBAAPS.DPSO	835	930	6.8793	-0.3071	1.7378
$UO_2(CH_3COO)_2$MBAAPS.DPSO	827	930	6.8166	-0.3698	1.7390
$UO_2(CH_3COO)_2$DABAAPS.DPSO	825	927	6.7779	-03622	1.7408
$UO_2(CH_3COO)_2$2$'$-NO$_2$BAAPS.DPSO	830	925	6.8016	-0.3078	1.7405
$UO_2(CH_3COO)_2$3$'$-NO$_2$BAAPS.DPSO	835	930	6.8793	-0.3071	1.7378
$UO_2(CH_3COO)_2$4$'$-NO$_2$BAAPS.DPSO	837	930	6.8951	-0.2913	1.7375
$UO_2(CH_3COO)_2$HMBAAPS.DPSO	837	928	6.6796	-0.2759	1.7378
$UO_2(CH_3COO)_2$HNAAPS.DPSO	832	925	6.8172	-0.2921	1.7399
$UO_2(CH_3COO)_2$CAAPS.DPSO	827	930	6.8166	-0.3698	1.7390
$UO_2(CH_3COO)_2$TMBAAPS.DPSO	825	927	6.7779	-0.3622	1.7408
$UO_2(CH_3COO)_2$FFAAPS.DPSO	825	927	6.7779	-0.3622	1.7408

Stereochemistry

The infrared spectra of all the uranyl coordination compounds suggest that semicarbazones act as neutral tridentate (N,N,O) ligands, while acetate groups are bidentate in nature. Thus, in these compounds, the tridentate nature of semicarbazones, monodentate nature of DPSO and bidentate chelating acetato groups suggest that the uranium has a coordination number of 10 in these compounds.[32] The proposed structure of the coordination compound is shown in Figure 1.
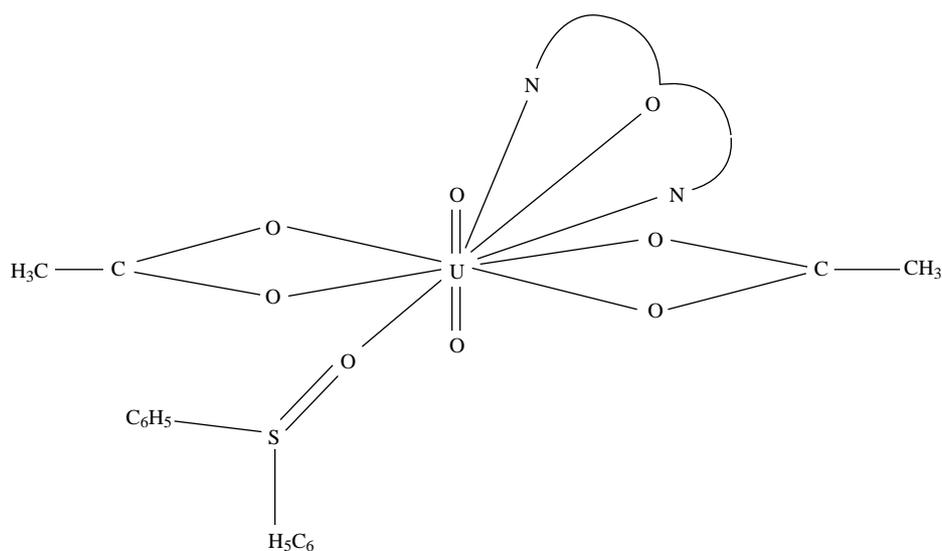
Table 4. Thermoanalytical results of UO_2 (VI) complexes of semicarbozones and DPSO.

| Complex | Sample wt (mg) | Residual mass (mg) | Ligand mass loss (%) | | | | Residual (%) ~645 °C | |
| | | | 160 °C | | 245 – 360 °C | | | |
			Theor[a]	Exp.	Theor[b]	Exp	Theor[c]	Exp.
$UO_2(CH_3COO)_2$BAAPS.DPSO	22.30	6.63	21.53	20.93	58.63	57.09	29.92	29.76
$UO_2(CH_3COO)_2$ 2'- NO_2BAAPS.DPSO	23.60	6.68	20.54	21.99	60.52	59.58	28.55	29.32
$UO_2(CH_3COO)_2$HMBAAPS.DPSO	24.90	7.02	20.52	20.03	60.56	59.99	28.52	28.22
$UO_2(CH_3COO)_2$CAAPS.DPSO	25.80	7.46	20.95	20.60	59.75	59.31	29.11	28.93
$UO_2(CH_3COO)_2$FFAAPS.DPSO	26.90	8.07	21.76	21.39	58.18	57.83	30.24	30.00

[a] calculated for loss of DPSO
[b] calculated for loss of semicarbozone
[c] calculated as U_3O_8

Acknowledgment

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