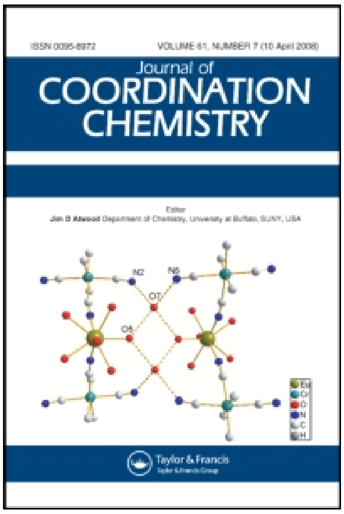

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Preparation, thermal and vibrational studies of [UO$_2$(acac-o-phdn)(L)] (L=H$_2$O, py, DMF and Et$_3$N)

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Preparation, thermal and vibrational studies of $[UO_2(acac\text{-}o\text{-}phdn)(L)]$ ($L = H_2O$, py, DMF and Et_3N)

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Four new dioxouranium(VI) complexes, $[UO_2(acac\text{-}o\text{-}phdn)(L)]$ where $L = H_2O$, py, DMF and Et_3N, with the tetradentate dibasic Schiff base (acac-o-phdn), derived from condensation of acetylacetone with o-phenylene diamine have been synthesized. The infrared spectra were obtained and full assignments of all the observed vibrations are proposed on the basis of C_{2v} symmetry for H_2O and py complexes and C_s for the other two complexes, respectively. The bond stretching force constant and bond length of the U=O bond for the four complexes were calculated. Differential thermal analysis (DTA) and thermogravimetric (TG) analysis of the complexes were also carried out.

Keywords: Dioxouranium(VI) complexes; Infrared spectra; DTA; TG; Schiff base

1. Introduction

Since the discovery of the oxygen-carrying properties of Co(II) Schiff-base complexes [1], complexation reactions of transition elements with Schiff bases have been studied extensively [2–8]. Very little work has appeared on complex formation of actinides with dihydroxy Schiff bases [8–11] and detailed vibrational studies of this class of compounds appear to be rare [12–14]. In most cases the assignments are mainly focused on the azomethine C=N and phenolic C–O bond vibrations of the Schiff base.

Herein, we report the preparation of four new dioxouranium(VI) Schiff-base complexes, $[UO_2(acac\text{-}o\text{-}phdn)(H_2O)]$, $[UO_2(acac\text{-}o\text{-}phdn)(py)]$, $[UO_2(acac\text{-}o\text{-}phdn)(DMF)]$ and $[UO_2(acac\text{-}o\text{-}phdn)(Et_3N)]$ (acac-o-phdn = N,N′-o-phenylenebis(acetylacetonatoiminato). The infrared spectra of these complexes are recorded and assignments for most of the fundamental vibrations are proposed. The differential thermal analyses of these four complexes were also carried out.

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2. Experimental

All chemicals were analytical reagent grade. The Schiff base, acac-o-phdnH_2 [N,N′-o-phenylenebis(acetylacetoneimine)], was prepared according to published methods [15] from condensation of o-phenylenediamine with acetylacetone in ethyl alcohol as a solvent. The separated precipitate was filtered, washed with alcohol and dried under vacuum at room temperature. The Schiff base was characterized through its infrared and elemental analysis. The brown uranyl Schiff-base complex, [UO_2(acac-o-phdn)(H_2O)], was prepared from the addition of 0.848 g of uranyl acetate dihydrate (2 mmol) in acetone to 0.544 g of the Schiff base (2 mmol) in acetone. The mixture was then stirred at room temperature for about 4 h. The brown crystalline product was filtered off, washed several times with acetone and dried under vacuum. The other three complexes [UO_2(acac-o-phdn)(py)] (yellowish orange), [UO_2(acac-o-phdn)(DMF)] (yellowish orange) and [UO_2(acac-o-phdn)(Et_3N)] (yellow), were prepared in a similar way to that described above by the reaction of $UO_2(CH_3COO)_2 \cdot 2H_2O$ and the Schiff base together with pyridine, dimethylformamide or triethylamine, respectively in a molar ratio 1 : 1 : 2 using acetone as a solvent. The complexes formed were characterized through their elemental analysis and infrared spectra. Analysis; [UO_2(acac-o-phdn)(H_2O)]: C, 34.35(34.40); H, 3.61(3.58); N, 5.10(5.01), [UO_2(acac-o-phdn)(py)]: C, 40.52(40.71); H, 3.79(3.71); N, 6.65(6.78), [UO_2(acac-o-phdn)(DMF)]: C, 37.30(37.19); H, 4.16(4.07); N, 6.73(6.85), [UO_2(acac-o-phdn)(Et_3N)]: C, 41.30(41.18); H, 5.30(5.14); N, 6.45(6.55). The calculated values are shown in parentheses.

2.1. *Spectroscopic measurements*

The infrared spectra of the Schiff base and the uranyl complexes were recorded from KBr discs using a Perkin-Elmer 1430 ratio recording infrared spectrophotometer.

2.2. *Thermal analysis measurements*

Differential thermal analysis (DTA) and thermogravimetric (TG) analysis of the uranyl complexes were measured using a Shimadzu computerized thermal analysis system DT-40. The system includes programs which process data from the thermal analyzer with the Chromatpac C-R3A. The rate of heating of the sample was kept at 10°C min^{-1} using a static atmosphere. Calcinated Al_2O_3 at 1200°C was applied as a reference.

3. Results and discussion

The infrared spectra of the complexes [UO_2(acac-o-phdn)(L)] (L = H_2O, py, DMF and Et_3N) in KBr discs are recorded, figure 1. The vibrational assignments of all the observed infrared bands are given in table 1.

It has been established [16, 17] that the Schiff base derived from acetylacetone exists as a tautomeric equilibrium mixture of two structures; phenolimine and

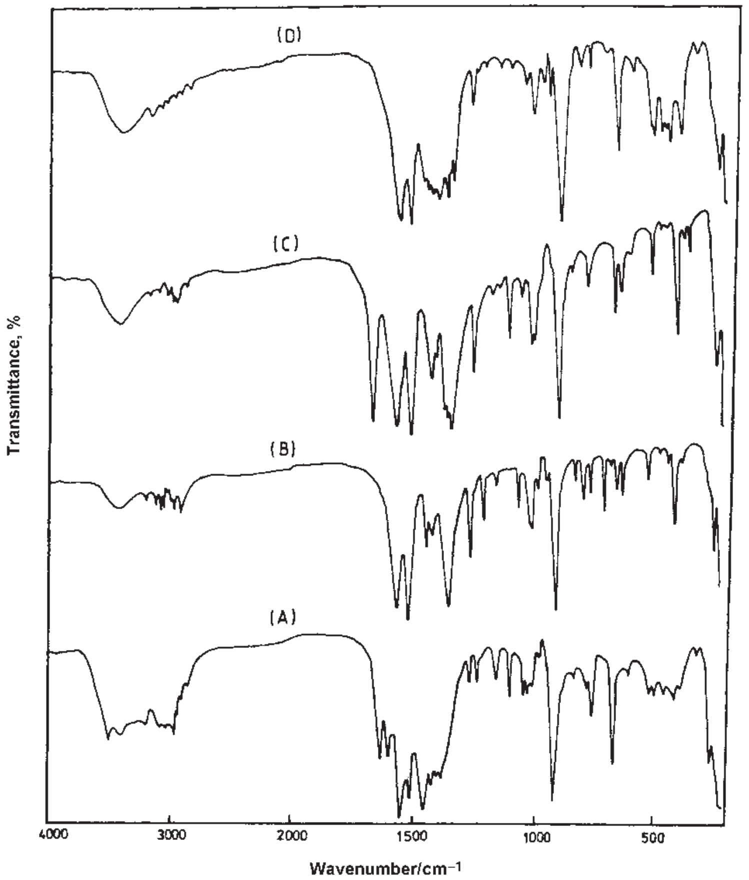
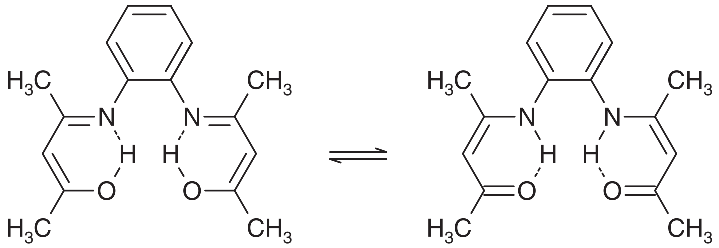


Figure 1. The infrared spectra of [UO_2(acac-o-phdn)(L)]; A: $L = H_2O$; B: $L = py$; C: $L = DMF$; D: $L = Et_3N$.

ketoamine, structure (I) and (II), respectively. Furthermore, it was concluded [16] that the bases derived from aromatic amines exist in the phenolimine form and those of aliphatic origin prefer the ketoamine form. In complexes the aliphatic Schiff bases also exist in the phenolimine form [18], as indicated by no band in the infrared spectra that could be assigned to ν(N–H) vibration.



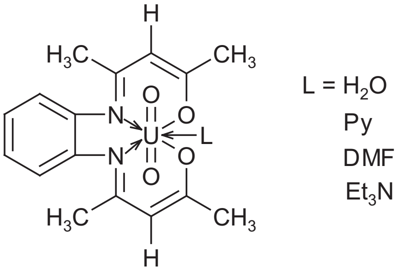
(I) **(II)**

Table 1. Infrared frequencies (cm^{-1}) and tentative assignments for $[UO_2(acac\text{-}o\text{-}phdn)(L)]$ ($L{=}H_2O$, py, DMF and Et_3N).

cm^{-1}				
$L{=}H_2O$	Py	DMF	Et_3N	Assignments
3540m				$\nu(H_2O)$; coord.
3440m	3445m br	3445m br	3445m br	$\nu(H_2O)$; uncoord.
3200w	3190w	3110w	3180m	ν(C–H); phenyl and py
3100w	3110m	3050w	3120vw	
3070w	3080m		3050vw	
	3030w			
2984w	3000w	2995m	2980vw	ν(C–H); =CH–, CH_3, CH_2
2960vw	2970w	2955w	2940w	
2920w	2930w	2877w	2850w	
2870w		2825w		
		1667vs		ν(C=O); DMF
1630ms				$\delta(H_2O)$
1600ms				
1560vs	1567vs	1570vs	1565vs	ν(C=N)
1517s	1522vs	1517vs	1517vs	Phenyl breathing modes
1456vs	1450s	1435s	1460m	
1428ms	1430ms	1410w	1440m	
1405m			1420m	
1390m	1361vs	1380m	1395ms	CH deformation; CH, $-CH_2$ and $-CH_3$
		1367m	1372s	
		1356vs	1350s	
1278m	1278s	1267s	1280m	ν(C–C), ν(C–O) and ν(C–N)
1247m	1220ms	1185w	1255vw	
1160ms	1160m	1150w	1220vw	
1110ms		1117ms	1172vw	
			1110vw	
1045m	1070ms	1070m	1055m	CH, bend; phenyl
1025m	1020s	1020s	1025ms	
1005w	985m	1010m	978m	
970w	955m		955ms	
912vs	910vs	905vs	905vs	ν_{as}(U=O)
833vw	833m	839w	835m	ν_s(U=O)
785w	795ms	780ms	780m	CH, bend, phenyl
760ms	770m		710w	
	705ms			
670s	680vw	670ms	665s	–CH in-plane quadrant bend; phenyl
600w	655m	650ms	610w	
	630ms	600w		
525w	530m	525ms	520s	ν_{as}(U–O); O of Schiff base
500w	495vw	490w	490m	ν_s(U–O); O of Schiff base
475m			480m	
			460ms	ν_s(U–N); N of Et_3N
	430m			ν_s(U–N); N of py
420 m	410s	408s	415s	ν_{as}(U–N); N of Schiff base
390w	390w	393w	385w	ν_s(U–N); N of Schiff base
310w		360m		ν_s(U–O); O of DMF and H_2O

Key: s = strong; w = weak; m = medium; v = very; br = broad; ν = stretching; δ = bending.

In metal chelates, the Schiff base and the ligand (L) coordinate to the U(VI) in such a way that the four donor atoms of the Schiff base and the donor atom of the ligand (L) occupy equatorial positions around the central metal atom U(VI), forming a plane containing the six-membered rings. The two oxygen atoms of the uranyl group occupy axial positions, as shown in structure (III).



(III)

The coplanarity of the metal chelate rings and the proposed axial positions of the uranyl group oxygens are supported by analogous complexes [9, 19, 20].

According to the proposed structure for the compounds under investigation, the first two complexes [UO_2(acac-o-phdn)(H_2O)] and [UO_2(acac-o-phdn)(py)] possess a two-fold axis and a plane of symmetry and hence they are C_{2v} symmetry. The other two complexes [UO_2(acac-o-phdn)(DMF)] and [UO_2(acac-o-phdn)(Et_3N)] possess a lower symmetry (one plane) and belong to C_s symmetry. The infrared spectrum of the H_2O complex, figure 1(A), shows differences compared with the spectra of the other complexes. Beside the medium band at $3540\,cm^{-1}$ which is characteristic for the coordinated H_2O, there are two medium bands at 1630 and $1600\,cm^{-1}$ as expected [21] for bending vibrations of coordinated H_2O. These three bands are absent from the spectra of the other complexes. The DMF complex in its infrared spectrum, figure 1(C), shows a very strong absorption band at $1667\,cm^{-1}$ characteristic for DMF. The spectra of the complexes of py and Et_3N, figures 1(B) and 1(D), show the ν(U–N) (N of py and Et_3N) at 430 and $460\,cm^{-1}$, respectively.

3.1. *Band assignments*

The C_{2v} complexes, [UO_2(acac-o-phdn)(H_2O)] and [UO_2(acac-o-phdn)(py)] are expected to display 126 and 150 vibrational fundamentals which are all monodegenerate. These are distributed between A_1, A_2, B_1 and B_2 motions; all are i.r and Raman active, except for the A_2 modes which are only Raman active. Under such symmetry, the four vibrations of the uranyl unit, UO_2, in both complexes are of the type $2A_1$, B_1 and B_2, ν_s(U=O), A_1; ν_{as}(U=O), B_1; $\delta(UO_2)$, A_1; and $\delta(UO_2)$, B_2. The C_s complexes, [UO_2(acac-o-phdn)(DMF)] and [UO_2(acac-o-phdn)(Et_3N)] should display 153 and 183 vibrational motions, respectively. The vibrational motions are distributed between motions of the type A' and A''; all are monodegenerate and infrared active. The four vibrations of the UO_2 unit in the two complexes are $3A'$ and A''. These are ν_s(U=O), A'; ν_{as}(U=O), A'; $\delta(UO_2)$, A'; and $\delta(UO_2)$, A''. The data given in table 1, show that ν_{as}(U=O) in these complexes occurs as a single very strong band at 912, 910, 905 and $905\,cm^{-1}$ for H_2O, py, DMF and Et_3N complexes, respectively. The ν_s(U=O) vibration occurs at 833, 833, 839 and $835\,cm^{-1}$ for these complexes. These assignments for the stretching vibration of the uranyl group, UO_2, agree quite well with those known for many dioxouranium(VI) complexes [11, 14]. The ν_s(U=O) values were used to calculate both the bond length and force constant, $F_{U=O}$, for the UO_2 bonds in the four complexes according to the known method [11, 14]. The calculated bond length values are 1.743, 1.743, 1.739 and 1.741 A°, while the calculated force constant values are 671.3, 671.3, 681 and 674.5 $\mathrm{Nm^{-1}}$ for the H_2O, py, DMF and Et_3N complexes, respectively. These values agree well with previously reported values for similar dioxouranium(VI) Schiff base complexes [22, 23]. For $[UO_2$(acac-o-phdn)(L)] (L = H_2O, py, DMF and Et_3N), the ligand (L) has no effect on the values of $F_{U=O}$ and U=O bond length.

The stretching vibrations ν(C–H) of the phenyl groups in these complexes are assigned as a number of bands in the region 3200–3030 $\mathrm{cm^{-1}}$. The corresponding vibrations ν(C–H) of the =CH–, CH_2 and CH_3 units are observed in the range 3000–2825 $\mathrm{cm^{-1}}$. The assignments of all the C–H stretching vibrations agree quite well with the expected [24].

Two medium strong bands characteristic of bending vibrations $\delta(H_2O)$ of the coordinated H_2O molecule are observed at 1630 and 1600 $\mathrm{cm^{-1}}$. The very strong absorption band due to ν(C=O) of DMF in the complex [UO_2 (acac-o-phdn)(DMF)] occurs as expected at 1667 $\mathrm{cm^{-1}}$. The azomethine group stretching vibration ν_{as}(C=N) appears in the usual range reported for similar compounds [16], as a very strong band at 1560, 1567, 1570 and 1565 $\mathrm{cm^{-1}}$ for the complexes of H_2O, py, DMF and Et_3N, respectively. This vibration belongs to B_2 symmetry in the case of the two complexes H_2O and py (C_{2v} symmetry) and to A' symmetry in the case of the other two complexes (C_s symmetry). The differences in the values of ν(C=N) in all complexes under investigation is very small, which indicates that the change in symmetry has no pronounced effect on the ν(C=N) values.

A group of medium to strong bands lying in the range 1522–1405 $\mathrm{cm^{-1}}$ could be assigned to the phenyl breathing vibrations in all the complexes, table 1. The CH deformation motions of the =CH, and $-CH_3$ groups occur as a medium band at 1390 $\mathrm{cm^{-1}}$ for the H_2O complex, and as a very strong band at 1361 $\mathrm{cm^{-1}}$ for the py complex. The corresponding CH deformations of the =CH, $-CH_2$ and $-CH_3$ in the other two complexes DMF and Et_3N occur as a number of bands of different intensities in the region 1395–1350 $\mathrm{cm^{-1}}$. The ν(C–C), ν(C–O) and ν(C–N) stretching vibrations in all complexes are assigned to a large number of bands lying in the 1280–1110 $\mathrm{cm^{-1}}$ region. The CH bending vibrations of the four complexes are assigned to the group of bands occurring in the 1070–705 $\mathrm{cm^{-1}}$ region. The CH in-plane bends of the phenyl groups in all complexes appear as a number of bands of varying intensities in the region of 680–600 $\mathrm{cm^{-1}}$, table 1.

Crystal structures [9, 19] of some analogous oxouranium (VI) Schiff base complexes showed that U–O bonds are stronger (shorter) than the corresponding U–N (O and N of the Schiff base). Accordingly the ν(U–O) (O of acac-o-phdn) is assigned at higher frequency compared with ν(U–N). Table 1 shows that, the ν_{as}(U–O) occurs in all complexes around 525 $\mathrm{cm^{-1}}$, while the ν_s(U–O) vibrations occur in the 500–475 $\mathrm{cm^{-1}}$ region. The bands at 420, 410, 408 and 415 $\mathrm{cm^{-1}}$ are attributed to the ν_{as}(U–N) vibrations in the complexes of H_2O, py, DMF and Et_3N, respectively, while the ν_s(U–N) vibrations are assigned to the weak bands around 390 $\mathrm{cm^{-1}}$ for all of these complexes. The stretching vibration ν(U–N) (N of Et_3N) occurs as a medium strong band at 460 $\mathrm{cm^{-1}}$, while the medium band at 430 $\mathrm{cm^{-1}}$ is attributed to the ν(U–N) (N of py). Finally, the stretching vibration ν(U–O) (O of DMF and H_2O) is assigned at 360 and 310 $\mathrm{cm^{-1}}$ for the DMF and H_2O complexes, respectively. The assignments of these bands agree quite well with the literature [16, 23, 25].

To provide further information on the proposed formulas and structures for the complexes, thermogravimetric (TG) and differential thermal analysis (DTA) were carried out under N_2 flow. DTA thermograms and TG curves are shown in figure 2(A–D). Table 2 gives the maximum temperature values, $T_{\max}/(°C)$, together with the corresponding weight loss for each step of the decomposition reactions of the complexes. The obtained data strongly support the structures proposed for the complexes. Thermal degradation for the complex, [UO_2(acac-o-phdn)(H_2O)] exhibits two main degradation steps. The first occurs at 193°C, accompanied by weight loss of 3.30% corresponding to the loss of coordinated water. Theoretically, the loss of this molecule corresponds to a weight loss of 3.22%. The dehydration process is accompanied by a strong endothermic effect [26]. The second decomposition step occurs at two different temperatures; 230 and 278°C. These are attributed to the rupture of the U–N and U–O bonds (N and O of acac-o-phdn). The weight loss associated with these stages is 49.05% due to the loss of $8C_2H_2 + N_2 + H_2O + 1/2O_2$ molecules in agreement with the theoretical weight loss value of 48.38%, giving the final product, UO_2. The infrared spectrum of the final product of the thermal analysis supports these conclusions. Accordingly, the mechanism for the thermal decomposition of the complex, [UO_2(acac-o-phdn)(H_2O)], is as follows:

$$[\mathrm{UO_2(acac\text{-}o\text{-}phdn)(H_2O)}] \xrightarrow{193^\circ\mathrm{C}} [\mathrm{UO_2(acac\text{-}o\text{-}phdn)}] + \mathrm{H_2O}$$

$$[\mathrm{UO_2(acac\text{-}o\text{-}phdn)}] \xrightarrow{230,\ 278^\circ\mathrm{C}} \mathrm{UO_2} + 8\mathrm{C_2H_2} + \mathrm{N_2} + \mathrm{H_2O} + 1/2\mathrm{O_2}$$

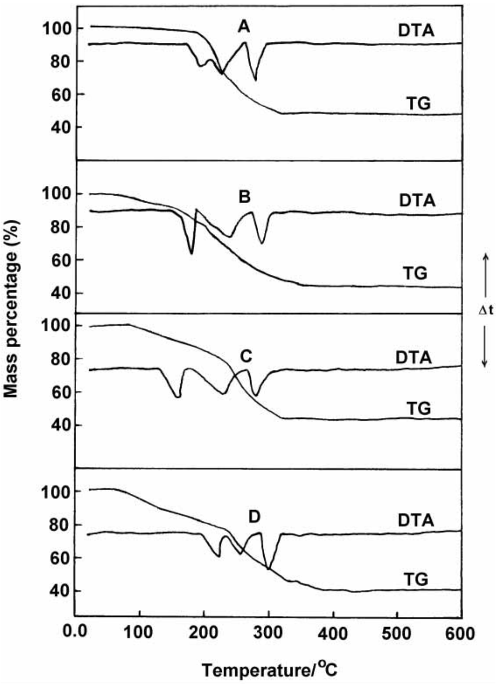


Figure 2. Thermal analysis diagrams of [UO_2(acac-o-phdn)(L)]; A: L = H_2O; B: L = py; C: L = DMF; D: L = Et_3N.

Table 2. The maximum temperature, $T_{max}/^\circ C$, and weight loss values of the decomposition stages for $[UO_2(acac\text{-}o\text{-}phdn)(L)]$ ($L = H_2O$, py, DMF and Et_3N) complexes.

				% Weight losses	
$[UO_2(acac\text{-}o\text{-}phdn)(L)]$	Decomposition	$T_{max}/^\circ C$	Lost species	Found	Calcd
$L = H_2O$	First stage	193°C	H_2O	3.30	3.22
	Second stage	230, 278°C	$8C_2H_2 + H_2O + N_2 + 1/2O_2$	49.05	48.38
L = py	First stage	177°C	$2.5C_2H_2 + 1/2N_2$	13.12	12.76
	Second stage	234, 290°C	$8C_2H_2 + H_2O + N_2 + 1/2O_2$	44.67	43.61
L = DMF	First stage	165°C	$C_2H_6 + 1/2N_2 + CO + 1/2H_2$	12.23	11.91
	Second stage	229, 283°C	$8C_2H_2 + H_2O + N_2 + 1/2O_2$	45.12	44.04
$L = Et_3N$	First stage	224°C	$3C_2H_4 + NH_3$	16.69	15.75
	Second stage	260, 302°C	$8C_2H_2 + H_2O + N_2 + 1/2O_2$	43.15	42.12

Thermal decompositions of the other three complexes [UO_2(acac-o-phdn)(L)] (L = py, DMF and Et_3N) also exhibit two main degradation steps. The first stage of decomposition occurring at 177, 165 and 224°C is accompanied by a weight loss of 13.12, 12.23 and 16.69%, corresponding to the loss of pyridine, dimethylformamide and triethylamine molecules, respectively, in agreement with the theoretical values of 12.76, 11.91 and 15.75%. The second decomposition stage is associated with the remaining molecular unit, [UO_2(acac-o-phdn)]. This step occurs at two maxima as expected, since the unit (acac-o-phdn) ligand coordinates with uranium through two different donor atoms (N and O). The infrared spectra of the final product of the thermal analysis for all above complexes supported these conclusions. The mechanisms for the thermal decompositions of the three complexes are as follows:

$$\text{(i)}\quad [UO_2(\text{acac-o-phdn})(\text{py})] \xrightarrow{177^\circ C} [UO_2(\text{acac-o-phdn})] + 2.5C_2H_2 + 1/2\,N_2$$

$$[UO_2(\text{acac-o-phdn})] \xrightarrow{234,\,290^\circ C} UO_2 + 8C_2H_2 + N_2 + H_2O + 1/2O_2$$

$$\text{(ii)}\quad [UO_2(\text{acac-o-phdn})(\text{DMF})] \xrightarrow{165^\circ C} [UO_2(\text{acac-o-phdn})] + C_2H_6 + CO + 1/2N_2 + 1/2H_2$$

$$[UO_2(\text{acac-o-phdn})] \xrightarrow{229,\,283^\circ C} UO_2 + 8C_2H_2 + N_2 + H_2O + 1/2O_2$$

$$\text{(iii)}\quad [UO_2(\text{acac-o-phdn})(Et_3N)] \xrightarrow{224^\circ C} [UO_2(\text{acac-o-phdn})] + 3C_2H_4 + NH_3$$

$$[UO_2(\text{acac-o-phdn})] \xrightarrow{260,\,302^\circ C} UO_2 + 8C_2H_2 + N_2 + H_2O + 1/2O_2$$

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