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THERMAL DECOMPOSITION STUDIES OF FURFURAL-BASED SCHIFF BASE COMPLEXES OF URANYL HALIDES AND PSEUDOHALIDES

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ABSTRACT

The bidentate Schiff base ligand (NO donor set), furfurylidene arylamine (L), prepared by reaction in situ of furfural and aromatic amine (1 : 1) in EtOH, reacts with UO_2X_2 (X = Cl, NCS) to form red, diamagnetic complexes of the type $[UO_2(L)_3X_2]$, which are non-electrolytic and ten-coordinated. Analytical data and IR spectra characterise the complexes. Thermal decomposition studies of these dioxouranium(VI) complexes have been made and the stoichiometries of the intermediate species and the mechanism of their formation have been discussed. All these complexes remain thermally stable at least up to ca. 150 °C and thereafter lose the ligand molecules in several steps finally forming U_3O_8 above 750–800 °C.

INTRODUCTION

In contrast to the widely studied chemistry of the transition metals, the chemistry of the actinide elements arouses interest because of their ability to form complexes with higher coordination numbers, due to their high charge and comparatively large size [1,2]. This feature of formation of compounds with higher coordination numbers is not commonly encountered in transition metal chemistry. Reports from this laboratory [3–10] in recent years have dealt with complexes of uranium(VI) and thorium(IV) with a series of multidentate chelating Schiff bases derived from aromatic aldehydes (e.g., salicylaldehyde) and aliphatic or aromatic amines, where coordination numbers from 6 to 12 have been established. Thermal decomposition investigations of some of these complexes with higher coordination numbers have been made [4,6,7]. In continuation of earlier work and to gain further insight into the complexes of uranium(VI) and thorium(IV), a series of complexes of dioxouranium(VI) have been isolated and charaterised with yet another new series of Schiff bases derived by condensing a heterocyclic aldehyde, furan

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2-carboxaldehyde (furfural) with various aromatic amines (e.g., aniline and substituted anilines), and their thermal decomposition behaviour studied. The stoichiometries of the intermediate species, obtained during thermal decomposition, have been identified and the probable mechanism of decomposition of the complexes has been discussed.

TABLE 1

Thermal decomposition parameters for $UO_2L_3Cl_2$ complexes

Starting material	Initial decomp. temp. (°C)	TG data			Species formed	DTA peak (°C)
		Temp. range (°C)	Weight loss (%)			
			Obs.	Calc.		
(1) $UO_2(L^1)_3Cl_2$ (m.w. = 854); L^1 = anilinefurfurylideneimine (m.w. = 171)						
$UO_2Cl_2 \cdot L^1_3$	180	160–200	9.4	10.01	$UO_2Cl_2 \cdot L^1_{2.5}$	180(exo)
$UO_2Cl_2 \cdot L^1_{2.5}$		200–280	16.9	15.02	$UO_2Cl_2 \cdot L^1_{2.25}$	
$UO_2Cl_2 \cdot L^1_{2.25}$		280–380	24.4	25.02	$UO_2Cl_2 \cdot L^1_{1.75}$	
$UO_2Cl_2 \cdot L^1_{1.75}$		400–485	30.96	30.03	$UO_2Cl_2 \cdot L^1_{1.5}$	
$UO_2Cl_2 \cdot L^1_{1.5}$		520–580	40.42	40.04	$UO_2Cl_2 \cdot L^1$	520(endo) 550(exo)
$UO_2Cl_2 \cdot L^1$		660–880	69.5	67.22	$\frac{1}{3}U_3O_8$	850(exo)
(2) $UO_2(L^2)_3Cl_2$ (m.w. = 896); L^2 = *p*-toluidinefurfurylideneimine (m.w. = 185)						
$UO_2Cl_2 \cdot L^2_3$	180	170–210	9.5	10.3	$UO_2Cl_2 \cdot L^2_{2.5}$	180(exo)
$UO_2Cl_2 \cdot L^2_{2.5}$		210–390	22.6	20.6	$UO_2Cl_2 \cdot L^2_2$	
$UO_2Cl_2 \cdot L^2_2$		390–480	34.8	36.1	$UO_2Cl_2 \cdot L^2_{1.25}$	460(exo)
$UO_2Cl_2 \cdot L^2_{1.25}$		525–650	39.5	41.3	$UO_2Cl_2 \cdot L^2$	540(endo)
$UO_2Cl_2 \cdot L^2$		650–820	49.8	51.6	$UO_2Cl_2 \cdot L^2_{0.5}$	
$UO_2Cl_2 \cdot L^2_{0.5}$		820–980	58.2	56.8	$UO_2Cl_2 \cdot L^2_{0.25}$	
$UO_2Cl_2 \cdot L^2_{0.25}$		980–1020	70.2	68.7	$\frac{1}{3}U_3O_8$	
(3) $UO_2(L^3)_3Cl_2$ (m.w. = 944); L^3 = *p*-anisidinefurfurylideneimine (m.w. = 201)						
$UO_2Cl_2 \cdot L^3_3$	180	160–225	6.11	5.32	$UO_2Cl_2 \cdot L^3_{2.75}$	180(exo)
$UO_2Cl_2 \cdot L^3_{2.75}$		225–295	11.97	10.64	$UO_2Cl_2 \cdot L^3_{2.5}$	
$UO_2Cl_2 \cdot L^3_{2.5}$		305–390	19.34	21.30	$UO_2Cl_2 \cdot L^3_2$	
$UO_2Cl_2 \cdot L^3_2$		390–510	27.07	26.61	$UO_2Cl_2 \cdot L^3_{1.75}$	
$UO_2Cl_2 \cdot L^3_{1.75}$		520–535	32.31	31.95	$UO_2Cl_2 \cdot L^3_{1.5}$	530(exo)
$UO_2Cl_2 \cdot L^3_{1.5}$		580–730	43.5	42.58	$UO_2Cl_2 \cdot L^3$	
$UO_2Cl_2 \cdot L^3$		820–920	71.5	70.34	$\frac{1}{3}U_3O_8$	920(exo)
(4) $UO_2(L^4)_3Cl_2$ (m.w. = 986); L^4 = *p*-phenetidinefurfurylideneimine (m.w. = 215)						
$UO_2Cl_2 \cdot L^4_3$	260	235–295	4.43	5.45	$UO_2Cl_2 \cdot L^4_{2.75}$	260(exo)
$UO_2Cl_2 \cdot L^4_{2.75}$		295–330	12.28	10.9	$UO_2Cl_2 \cdot L^4_{2.5}$	
$UO_2Cl_2 \cdot L^4_{2.5}$		330–430	20.8	21.8	$UO_2Cl_2 \cdot L^4_2$	
$UO_2Cl_2 \cdot L^4_2$		460–520	29.1	27.25	$UO_2Cl_2 \cdot L^4_{1.75}$	500(endo)
$UO_2Cl_2 \cdot L^4_{1.75}$		520–550	33.2	32.7	$UO_2Cl_2 \cdot L^4_{1.5}$	540(exo)
$UO_2Cl_2 \cdot L^4_{1.5}$		740–900	72.5	71.6	$\frac{1}{3}U_3O_8$	890(exo)

EXPERIMENTAL

Synthesis and characterisation of the complexes

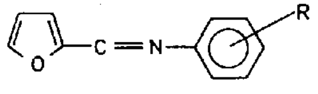
The complexes were synthesised by a method detailed earlier [10]. In a typical preparation, equimolar proportions of aromatic amine and furan 2-carboxaldehyde (furfural) were reacted in cold EtOH for 30 min. To this ligand solution was added UO_2X_2 (X = Cl, NCS) in minimum EtOH (amine/furfural/UO_2X_2 in 3 : 3 : 1 ratio). The reaction was allowed to continue for at least 6–8 h when the desired complexes separated out as dark-red solids. The product was collected on a frit, washed with small aliquots of EtOH, then Et_2O and finally dried in vacuo. All complexes have a fairly high m.p. (> 180 °C), are non-electrolytic in dilute DMF solutions [11] and are characterised by elemental analyses and spectral data [10] to be complexes of the type $[UO_2(L)_3X_2]$.

Thermal measurements

These measurements were carried out using a Netzsch simultaneous thermal analyser (model 429) fitted with a potentiometric recorder. The equipment records *T*, TG and DTA simultaneously. The rate of heating was 10 °C min^{-1}. The thermal parameters for the decomposition of the complexes are shown in Tables 1 and 2.

RESULTS AND DISCUSSION

All the complexes synthesised are of the type $[UO_2(L)_3X_2]$, where X = Cl, NCS and L = furfurylidene arylamines obtained by condensing furfural with aniline (L^1), *p*-toluidine (L^2), *p*-anisidine (L^3) or *p*-phenetidine (L^4). They are ten-coordinated, similar to the ten-coordinated uranium(VI) complexes reported earlier [8,9]. The IR spectra and the TG data clearly show the absence of H_2O molecules either coordinated or present as water of crystallisation. The coordination of the Schiff base ligand takes place through the azomethine nitrogen ($>C=N-$) and the furan oxygen (NO donor set), forming stable five-membered chelate rings.



R = H(L^1); *p*-CH_3(L^2).; *p*-OCH_3(L^3); *p*-OC_2H_5(L^4).

IR spectra

All complexes give rise to a moderate intense band at 920 cm^{-1} due to $\nu_{as}(UO_2)$ and another at 790 cm^{-1} due to $\nu_s(UO_2)$ vibrations of the linear UO_2^{2+} group [12]. A sharp and intense peak at 1625–1650 cm^{-1} due to

TABLE 2

Thermal decomposition parameters for $UO_2L_3(SCN)_2$ complexes

Starting material	Initial decomp. temp. (°C)	TG data			Species formed	DTA peak (°C)
		Temp. range (°C)	Weight loss (%)			
			Obs.	Calc.		
(1) $UO_2(L^1)_3(SCN)_2$ (m.w. = 899); L^1 = anilinefurfurylideneimine (m.w. = 171)						
$UO_2(SCN)_2\cdot L^1_3$	165	160–180	8.26	9.51	$UO_2(SCN)_2\cdot L^1_{2.5}$	165(exo)
$UO_2(SCN)_2\cdot L^1_{2.5}$		180–250	18.6	19.02	$UO_2(SCN)_2\cdot L^1_2$	
$UO_2(SCN)_2\cdot L^1_2$		275–330	23.86	23.77	$UO_2(SCN)_2\cdot L^1_{1.75}$	
$UO_2(SCN)_2\cdot L^1_{1.75}$		350–460	28.45	28.53	$UO_2(SCN)_2\cdot L^1_{1.5}$	420(exo)
$UO_2(SCN)_2\cdot L^1_{1.5}$		460–520	36.71	38.04	$UO_2(SCN)_2\cdot L^1$	500(exo)
$UO_2(SCN)_2\cdot L^1$		760–880	67.0	68.9	$\frac{1}{3}U_3O_8$	870(exo)
(2) $UO_2(L^2)_3(SCN)_2$ (m.w. = 941); L^2 = *p*-toluidinefurfurylideneimine (m.w. = 185)						
$UO_2(SCN)_2\cdot L^2_3$	160	150–260	13.36	14.74	$UO_2(SCN)_2\cdot L^2_{2.25}$	160(exo)
$UO_2(SCN)_2\cdot L^2_{2.25}$		350–430	21.47	19.66	$UO_2(SCN)_2\cdot L^2_2$	420(exo)
$UO_2(SCN)_2\cdot L^2_2$		430–490	25.52	24.57	$UO_2(SCN)_2\cdot L^2_{1.75}$	500(endo)
$UO_2(SCN)_2\cdot L^2_{1.75}$		490–560	31.1	29.5	$UO_2(SCN)_2\cdot L^2_{1.5}$	550(exo)
$UO_2(SCN)_2\cdot L^2_{1.5}$		560–650	49.2	49.15	$UO_2(SCN)_2\cdot L^2_{0.5}$	
$UO_2(SCN)_2\cdot L^2_{0.5}$		750–920	69.2	70.2	$\frac{1}{3}U_3O_8$	890(endo) 920(exo)
(3) $UO_2(L^3)_3(SCN)_2$ (m.w. = 989); L^3 = *p*-anisidinefurfurylideneimine (m.w. = 201)						
$UO_2(SCN)_2\cdot L^3_3$	160	140–220	6.9	5.08	$UO_2(SCN)_2\cdot L^3_{2.75}$	160(exo)
$UO_2(SCN)_2\cdot L^3_{2.75}$		220–275	14.42	15.24	$UO_2(SCN)_2\cdot L^3_{2.25}$	240(exo)
$UO_2(SCN)_2\cdot L^3_{2.25}$		285–495	26.98	25.40	$UO_2(SCN)_2\cdot L^3_{1.75}$	400(exo)
$UO_2(SCN)_2\cdot L^3_{1.75}$		520–560	41.74	40.65	$UO_2(SCN)_2\cdot L^3$	530(exo)
$UO_2(SCN)_2\cdot L^3$		560–760	50.97	50.81	$UO_2(SCN)_2\cdot L^3_{0.5}$	
$UO_2(SCN)_2\cdot L^3_{0.5}$		760–900	69.7	71.62	$\frac{1}{3}U_3O_8$	890(exo)
(4) $UO_2(L^4)_3(SCN)_2$ (m.w. = 1031); L^4 = *p*-phenetidinefurfurylideneimine (m.w. = 215)						
$UO_2(SCN)_2\cdot L^4_3$	180	160–200	5.3	5.21	$UO_2(SCN)_2\cdot L^4_{2.75}$	180(exo)
$UO_2(SCN)_2\cdot L^4_{2.75}$		200–275	11.6	10.43	$UO_2(SCN)_2\cdot L^4_{2.5}$	
$UO_2(SCN)_2\cdot L^4_{2.5}$		275–325	21.3	20.85	$UO_2(SCN)_2\cdot L^4_2$	280(exo)
$UO_2(SCN)_2\cdot L^4_2$		325–400	28.17	26.07	$UO_2(SCN)_2\cdot L^4_{1.75}$	
$UO_2(SCN)_2\cdot L^4_{1.75}$		400–490	32.2	31.28	$UO_2(SCN)_2\cdot L^4_{1.5}$	410(exo)
$UO_2(SCN)_2\cdot L^4_{1.5}$		510–550	37.8	36.5	$UO_2(SCN)_2\cdot L^4_{1.25}$	540(exo)
$UO_2(SCN)_2\cdot L^4_{1.25}$		550–910	71.2	72.8	$\frac{1}{3}U_3O_8$	900(exo)

ν(C=N) indicates coordination of the Schiff base through the azomethine nitrogen [13]. The ν[U–O (of furan ring)] expected at 500 cm^{-1} could not be obtained with the instrument used. The thiocyanate groups are all terminally N-bonded (–NCS) and give rise to IR bands at 2040–2050 cm^{-1} due to ν(C≡N) and at 840 cm^{-1} due to ν(C–S) modes [14], in agreement with the hard acid character of uranium(VI) [15].

Thermal decomposition studies

Dichloro tris(furfurylidene arylamine)dioxouranium(VI) complexes, [UO$_2$-(L)$_3$CL$_2$] (Fig. 1)

The thermal parameters of the dioxouranium(VI) chloride complexes are collected in Table 1. The high initial decomposition temperatures indicate the exceptional stability of these chloro complexes. An exothermic peak at 180 °C in the DTA curve is observed for $UO_2(L)_3Cl_2$ complexes with the ligands anilinefurfurylideneimine (L^1), *p*-toluidinefurfurylideneimine (L^2), and *p*-anisidinefurfurylideneimine (L^3), whereas, this peak shifts to a considerably higher temperature (260 °C) for the relatively bulkier ligand *p*-phenetidinefurfurylideneimine (L^4). In general, all these complexes decompose in a stepwise manner with the loss of Schiff base ligands (often in a fractional order), giving rise to one or more intermediate species, the stoichiometries of which have been calculated. The exothermic DTA peak corresponding to the formation of $UO_2(L)Cl_2$ (L = L^1, L^2, L^3) is obtained in the temperature range 520–730 °C, while for the L^4 complex this peak is absent. The ultimate end product in all cases corresponds to the formation of the oxide, U_3O_8, at ~ 800 °C or above.

Diisothiocyanato tris(furfurylidenearylamine)dioxouranium(VI) complexes, [UO$_2$(L)$_3$(NCS)$_2$] (Fig. 2)

As for the chloro complexes, an exothermic peak in the DTA curve is

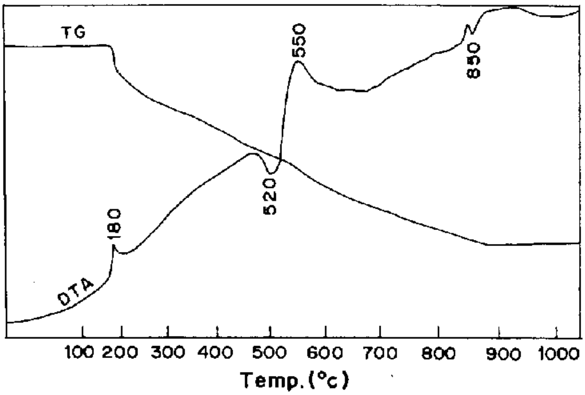


Fig. 1. Thermal curve of $UO_2(L^1)_3Cl_2$. Sample mass 40 mg.

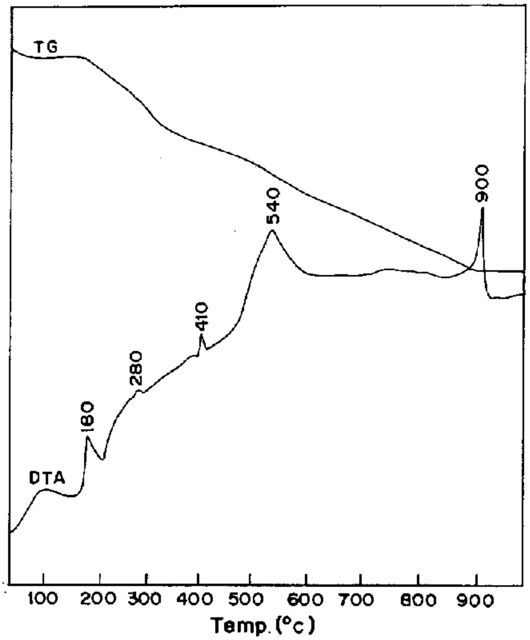


Fig. 2. Thermal curve of $UO_2(L^4)_3(NCS)_2$. Sample mass 40 mg.

obtained at ca. 160 °C for all complexes except that with *p*-phenetidinefurfurylideneimine (L^4), $[UO_2(L^4)_3(NCS)_2]$, where the peak shifts to a somewhat higher temperature of 180 °C (Table 2). The Schiff base ligands are also lost in a stepwise manner giving a number of intermediate species, the stoichiometries of which have been variously established to be $UO_2L_{2.5}(NCS)_2$, $UO_2L_{2.25}(NCS)_2$, $UO_2L_2(NCS)_2$, $UO_2L_{1.75}(NCS)_2$, $UO_2L_{1.5}(NCS)_2$, $UO_2L(NCS)_2$, $UO_2L_{0.5}(NCS)_2$, etc. These intermediate species are of complex, polymeric nature. The ultimate end product is again established as the stable oxide U_3O_8, which is formed in an exothermic reaction at ~ 890 °C.

CONCLUSION

All complexes reported in this work were found to be exceptionally stable at room temperature, where they can be kept unchanged for a prolonged period. If the initial decomposition temperature is taken as a rough criterion for the thermal stability of these complexes, the following order of stability for the chloro and isothiocyanato complexes of dioxouranium(VI) with the furfural based Schiff bases are established.

Chloro complexes

$$UO_2(L^4)_3Cl_2 > UO_2(L^3)_3Cl_2 > UO_2(L^1)_3Cl_2 \approx UO_2(L^2)_3Cl_2$$

Isothiocyanato complexes

$$UO_2(L^4)_3(NCS)_2 > UO_2(L^3)_3(NCS)_2 > UO_2(L^1)_3(NCS)_2 > UO_2(L^2)_3(NCS)_2$$

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