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Sulphoxide Complexes of Thorium(IV) and Uranyl(VI) Chlorides and Nitrates

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Complexes of thorium(IV) and uranyl(VI) chlorides and nitrates with the series of alkyl sulphoxides from dibutyl to dioctyl sulphoxide have been prepared and characterised. The complexes are of the formula $ThX_4 \cdot 2R_2SO$ *and* $UO_2X_2 \cdot 2R_2SO$. *Spectral data show that coordination in the complexes is through the oxygen of the sulphoxide. The complexes are weakly diamagnetic and are stable, losing weight only above 150 °C. The probable structures of the complexes are discussed.*

Introduction

Organic sulphoxides of the general formula $R_2S \rightarrow O$ are pyramidal molecules and act as ligating agents in complex formation either through oxygen or sulphur depending upon the nature of the metal ion [1–4]. A number of complexes of actinide salts with lower alkyl sulphoxides, *viz.*, dimethyl [5], diethyl [6–8], dipropyl [8], and dibutyl [8] sulphoxides, and of aryl sulphoxides, *viz.*, diphenyl [6–9] and di-α-naphthyl [6–8] sulphoxides, ranging in composition from 1:2 to 1:12 have been prepared, characterized, and their properties including infrared, Raman, and electronic spectra have been examined. Solvent extraction studies of Mohanty and co-workers [10, 11], Korpak [12], Laurence *et al.* [13, 14] and of Mikhailov *et al.* [15] on thorium(IV) and uranyl(VI) from hydrochloric and nitric acid solutions with higher members of the alkyl sulphoxide series, *viz.* from dipentyl to didecyl sulphoxide, have shown on the other hand that the complexes extracted into the organic phase are of the composition 1:2 or 1:3. A decrease in the number of ligands coordinated to a metal ion as well as a systematic change in the properties of the complexes would be expected with increase in the ligand size. It was of interest therefore to examine the complexes of a given actinide salt with a series of homologous sulphoxides to ascertain whether there is a regular change in the properties of the complexes. The present work relates to complexes of thorium(IV) and uranyl(VI) chlorides and nitrates with the series of alkyl sulphoxides from dibutyl to dioctyl sulphoxide.

Experimental

Materials

The chemicals used were either of CP or AR quality, as necessary.

Ethanol was dehydrated by refluxing it with magnesium turnings and iodine; the product, superdry ethanol, was finally distilled off [16].

Anhydrous thorium and uranyl chlorides were prepared by refluxing hydrated salts with thionyl chloride [17]. The final products were vacuum dried and kept over phosphorus pentoxide. The nitrates of the metals were dehydrated by keeping them over concentrated sulphuric acid for about a month [18].

The sulphoxides, *viz.*, dibutyl sulphoxide (DBSO), dipentyl sulphoxide (DPSO), dihexyl sulphoxide (DHxSO), diheptyl sulphoxide (DHpSO), and dioctyl sulphoxide (DOSO), were prepared, purified, and characterized according to procedures already described [11].

Preparation of the Complexes

For the preparation of a given complex, the anhydrous actinide salt and an excess of the sulphoxide were dissolved separately each in the minimum quantity of superdry ethanol. The solutions were mixed in a stoppered vessel, ice-cold isopentane added, and the mixture shaken well and kept in a refrigerator overnight when the corresponding complex precipitated out [19]. The complexes were purified by dissolving them in a fresh quantity of superdry ethanol and reprecipitating them with isopentane.

Analysis

Thorium was estimated as the oxide by strongly heating the complex when the organic matter was destroyed and the salt decomposed into the oxide [17]. For uranium determination, the complex was decomposed with concentrated hydrochloric acid,

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TABLE I. Physical and Analytical Data on Sulphoxide Complexes of Thorium(IV) and Uranyl(VI) Chlorides and Nitrates.

Complex	M.P. (°C)	Decomp. temp. (°C)	Mol. wt.		Composition, %					
			Calc.	Found	Metal		Anion		Sulphoxide	
					Calc.	Found	Calc.	Found	Calc.	Found
$UO_2(NO_3)_2 \cdot 2DBSO$	134	145	718	708	33.2	33.2	17.3	17.2	45.1	44.5
$UO_2Cl_2 \cdot 2DBSO$	130	180	665	641	35.8	35.9	10.7	10.8	48.7	48.0
$Th(NO_3)_4 \cdot 2DBSO$	–	–	804	–	28.9	29.1	30.8	30.2	40.3	41.5
$ThCl_4 \cdot 2DBSO$	128	–	698	694	33.2	33.8	20.3	19.9	46.4	45.8
$UO_2(NO_3)_2 \cdot 2DPSO$	93	145	774	762	30.8	30.5	16.0	15.3	49.1	49.8
$UO_2Cl_2 \cdot 2DPSO$	118	200	721	703	33.0	32.7	9.9	10.0	52.7	53.2
$Th(NO_3)_4 \cdot 2DPSO$	125	140	860	873	27.0	26.6	28.8	27.7	44.2	44.7
$ThCl_4 \cdot 2DPSO$	172	–	754	762	30.8	29.5	18.8	18.9	50.4	50.5
$UO_2(NO_3)_2 \cdot 2DHxSO$	79	165	830	789	28.7	28.6	14.9	14.9	52.5	53.5
$UO_2Cl_2 \cdot 2DHxSO$	128	205	777	754	30.6	30.3	9.1	9.0	56.1	57.4
$Th(NO_3)_4 \cdot 2DHxSO$	78	–	916	918	25.3	25.1	27.1	26.8	47.6	48.0
$ThCl_4 \cdot 2DHxSO$	179	–	810	777	28.6	28.5	17.5	17.1	53.8	53.1
$UO_2(NO_3)_2 \cdot 2DHpSO$	89	165	886	838	26.9	26.6	14.0	13.4	55.5	56.7
$UO_2Cl_2 \cdot 2DHpSO$	130	210	833	819	28.6	28.0	8.5	8.3	59.1	58.9
$Th(NO_3)_4 \cdot 2DHpSO$	86	–	972	945	23.9	22.9	25.5	24.5	50.6	49.7
$ThCl_4 \cdot 2DHpSO$	125	–	866	831	26.8	26.3	16.4	16.1	56.8	55.9
$UO_2(NO_3)_2 \cdot 2DOSO$	103	185	942	937	25.3	25.1	13.2	12.9	58.2	59.6
$UO_2Cl_2 \cdot 2DOSO$	158	200	889	851	26.8	26.4	8.0	7.9	61.7	62.3
$Th(NO_3)_4 \cdot 2DOSO$	–	–	1028	–	22.6	22.8	24.1	23.5	53.3	53.6
$ThCl_4 \cdot 2DOSO$	180	–	922	877	25.2	25.0	15.4	15.0	59.4	59.7

the solution diluted and filtered to remove the insoluble sulphoxides. Uranium in the filtrate was estimated as U_3O_8 *via* the oxinate. Chloride was estimated by potentiometric titration against standard silver nitrate, using acetone to increase the sharpness of the end point [19], and nitrate as nitron nitrate. The complexes were analysed for the sulphoxide by heating to boiling with acidified potassium dichromate following which the solution was cooled, diluted and titrated against standard ferrous ammonium sulphate solution [20]. A blank correction was made.

Physical Measurements

Infrared spectra were taken in the form of KBr disc or Nujol mull on a Perkin–Elmer Model 137 instrument. Ultraviolet–visible spectra were recorded in ethanol solution, at concentration 10^{-5} *M* for the ultraviolet and 10^{-1}–10^{-3} *M* for the visible, with a Beckman Model DB spectrophotometer. Electrical conductance measurements were made in solution in pure dry acetone at 35 °C (±0.1°) at different concentrations in the range 0.25–1.0×10^{-3} *M*. Thermograms were taken in air at ordinary pressure in the temperature range from room temperature (26 °C) to 1000 °C; the rate of heating was 10 °C per minute. Magnetic measurements were made at 25 °C on a modified Curie-type magnetic balance. Molecular weights were determined by the cryoscopic method using nitrobenzene as the solvent.

Results and Discussion

Characterisation of the Complexes

Physical and analytical data for the complexes are contained in Table I. The complexes have definite melting points which are much different from and bear no relation to the melting points of the corresponding sulphoxides. The complexes are anhydrous as evident from the analytical, infrared, and thermal data. The analytical data show that the complexes are well-defined compounds of the general formula $MX_n \cdot 2R_2SO$ ($M = Th$ or UO_2; $X = Cl$ or NO_3; $n = 4$, Th or 2, UO_2).

Spectra of the Complexes

The S → O stretching frequency of sulphoxides is usually around 1050 cm^{-1} differing to a small extent with the electronegativity of the alkyl or aryl group present, the mulling agent used, *etc.* [21, 22]. This frequency, which occurs between 1022–1046 cm^{-1} in the case of the sulphoxides used in the present work, is shifted to lower values on complex formation (Figs. 1 and 2). The magnitude of the shift

TABLE II. S → O Stretching and U–O Assymetric Vibrations (cm^{-1}) of Thorium(IV) and Uranyl(VI) R_2SO Complexes.

Salt/Sulphoxide	Complex	ν(SO)	Δν(SO)	ν(UO)	Δν(UO)
$UO_2(NO_3)_2$	–	–	–	950	–
UO_2Cl_2	–	–	–	905	–
DBSO	–	1046	–		
	$UO_2(NO_3)_2\cdot 2DBSO$	964	−82	936	−14
	$UO_2Cl_2\cdot 2DBSO$	944	−102	936	+31
	$Th(NO_3)_4\cdot 2DBSO$	968	−78		
	$ThCl_4\cdot 2DBSO$	973	−73		
DPSO	–	1023	–		
	$UO_2(NO_3)_2\cdot 2DPSO$	927	−96	927	−23
	$UO_2Cl_2\cdot 2DPSO$	923	−100	910	+5
	$Th(NO_3)_4\cdot 2DPSO$	959	−64		
	$ThCl_4\cdot 2DPSO$	944	−79		
DHxSO	–	1027	–		
	$UO_2(NO_3)_2\cdot 2DHxSO$	964	−63	936	−14
	$UO_2Cl_2\cdot 2DHxSO$	924	−103	920	+15
	$Th(NO_3)_4\cdot 2DHxSO$	964	−63		
	$ThCl_4\cdot 2DHxSO$	966	−61		
DHpSO	–	1022	–		
	$UO_2(NO_3)_2\cdot 2DHpSO$	932	−90	927	−23
	$UO_2Cl_2\cdot 2DHpSO$	924	−98	924	+19
	$Th(NO_3)_4\cdot 2DHpSO$	964	−58		
	$ThCl_4\cdot 2DHpSO$	982	−40		
DOSO	–	1023	–		
	$UO_2(NO_3)_2\cdot 2DOSO$	950	−73	923	−27
	$UO_2Cl_2\cdot 2DOSO$	944	−79	933	+28
	$Th(NO_3)_4\cdot 2DOSO$	958	−65		
	$ThCl_4\cdot 2DOSO$	930	−93		

ranges between 40 and 93 cm^{-1} in the case of the thorium complexes and between 63 and 103 cm^{-1} for the uranium complexes (Table II). The fact that the S → O frequency is decreased shows that coordination of the ligand is through the oxygen atom [1–4]. Moreover, the frequency of the asymmetric vibration of the U–O bond of the uranyl ion is shifted to lower values for the nitrate complexes, as expected [23]. In the case of the uranyl chloride complexes, on the other hand, the shift is towards higher values, presumably because of the exceptional behaviour of uranyl chloride [24].

Sulphoxides possess a moderately strong absorption band in the far ultraviolet near 220 nm in ethanol [22]. The absorption spectrum of any of the uranyl–sulphoxide complexes in this region is not significantly different from that of the corresponding pure sulphoxide.

The absorption spectrum of the uranyl ion indicates transitions of the ion to several excited electronic states which lie in the visible and near-ultraviolet between 320 to 560 nm [25]. In the present work, peaks are observed with uranyl nitrate in ethanol at 384, 446, 462, 468, and 482 nm and with uranyl chloride at 386, 408, 420, 436, 460, and 476 nm. The spectrum of the uranyl ion is modified in the complexes to a broad band with a peak at 436 nm (uranyl nitrate complexes) or at 426 nm (uranyl chloride complexes) (Figs. 3 and 4).

The Complexes in Solution

Data on the molecular weight of the complexes in nitrobenzene are contained in Table I along with values calculated on the basis of the formula $MX_n\cdot 2R_2SO$. The ratio of molecular weight observed to that calculated ranges between 0.95–1.01 which shows that the complexes are monomeric in solution.

The ratio of the molar conductance μ of the complexes and the actinide salts in acetone varies from 0.088 to 0.206 in the case of uranyl chloride complexes. In the case of the uranyl nitrate complexes, the values, on the other hand, are between 1.61 and 3.38, *i.e.* greater than unity. Thus, the uranyl chloride

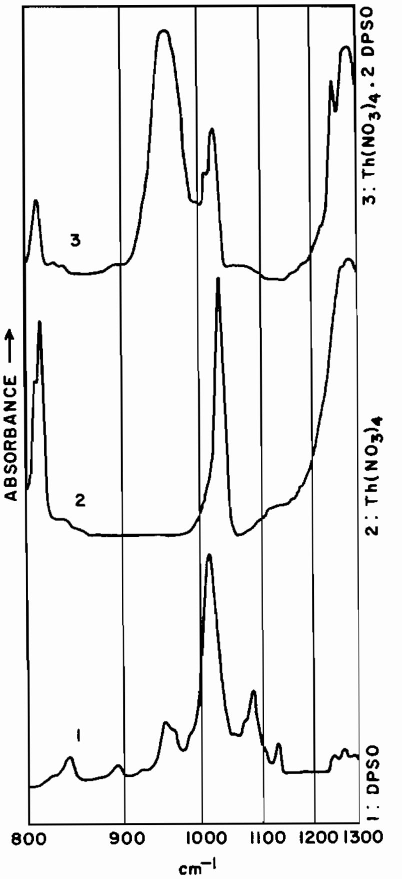


Figure 1. Infrared spectra of DPSO, $Th(NO_3)_4$, and $Th(NO_3)_4 \cdot 2DPSO$ in the S → O stretching region.

complexes are less ionised than the original salts in solution, whereas the opposite is the case with the uranyl nitrate complexes. Bagnall, Deane, Markin, Robinson, and Stewart [19] have found that the uranium tetrachloride–acetamide complex in acetone is more ionised than uranium tetrachloride in the same solvent, the value of the ratio being 1.48 at 0.0313 *M.*

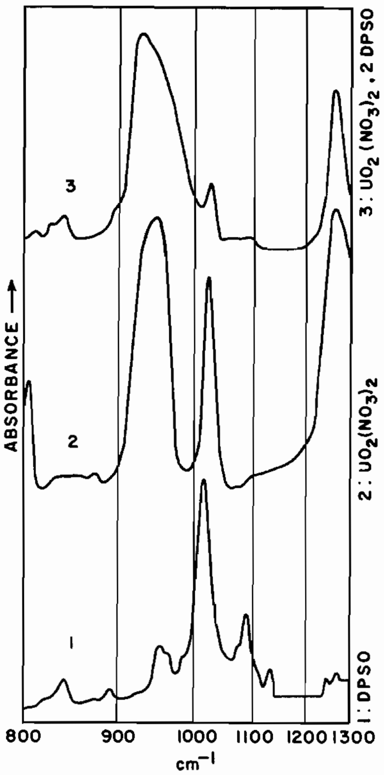


Figure 2. Infrared spectra of DPSO, $UO_2(NO_3)_2$, and $UO_2(NO_3)_2 \cdot 2DPSO$ in the S → O stretching region.

Magnetic Properties

Uranyl compounds are either diamagnetic or weakly paramagnetic, depending upon the diamagnetism of the other ions and the surrounding ligand

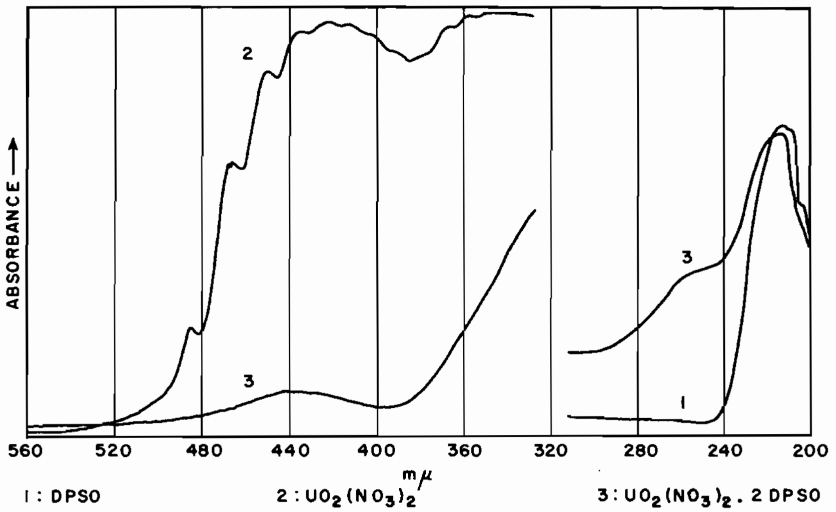


Figure 3. Ultraviolet–visible spectra of DPSO, $UO_2(NO_3)_2$, and $UO_2(NO_3)_2 \cdot 2DPSO$.

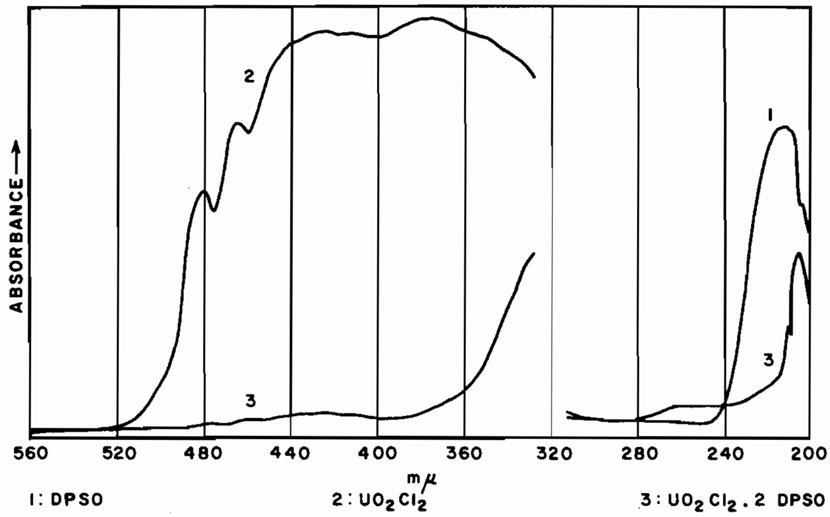


Figure 4. Ultraviolet–visible spectra of DPSO, UO_2Cl_2 and $UO_2Cl_2 \cdot 2DPSO$.

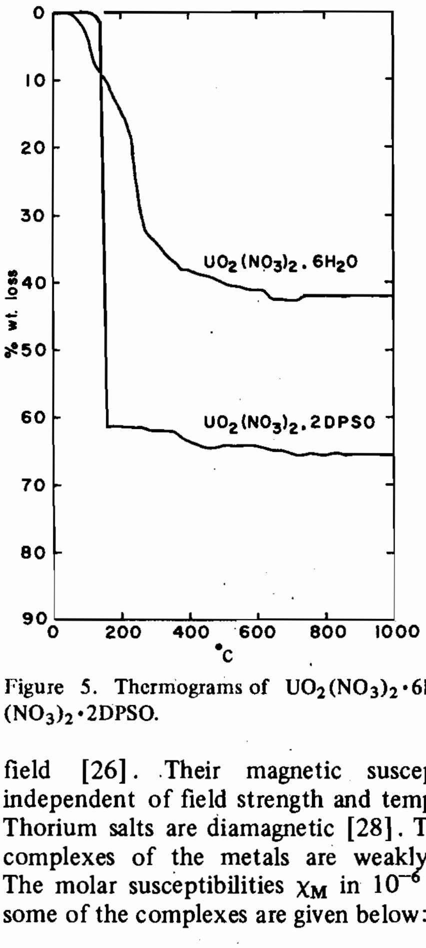


Figure 5. Thermograms of $UO_2(NO_3)_2 \cdot 6H_2O$ and $UO_2(NO_3)_2 \cdot 2DPSO$.

field [26]. Their magnetic susceptibilities are independent of field strength and temperature [27]. Thorium salts are diamagnetic [28]. The sulphoxide complexes of the metals are weakly diamagnetic. The molar susceptibilities χ_M in 10^{-6} c.g.s. units of some of the complexes are given below:

$Th(NO_3)_4 \cdot 2DPSO$	−84	$ThCl_4 \cdot 2DPSO$	− 25
$UO_2(NO_3)_2 \cdot 2DBSO$	−99	$UO_2Cl_2 \cdot 2DBSO$	−146
$UO_2(NO_3)_2 \cdot 2DPSO$	−38	$UO_2Cl_2 \cdot 2DPSO$	−138

The ground states of uranyl and thorium compounds contain no unpaired electrons; the compounds are therefore expected to be weakly diamagnetic, as observed [28–30].

Thermogravimetric Analysis

When $UO_2(NO_3)_2 \cdot 6H_2O$ is heated (Fig. 5), there is a gradual loss in weight from 60° to 120 °C, to the extent of 7 percent, owing to the loss of two molecules of water. Between 120° and 230 °C the loss (20 percent) is the consequence of the escape of the remaining four water molecules. Between 230° and 620 °C, the salt decomposes to UO_3 (loss 43 percent) and this changes above 620 °C to U_3O_8 which persists [31–33]. In the case of uranyl nitrate complexes, there is virtually no change in weight up to 150 °C, but between this temperature and ~200 °C, a large loss of 60 to 70 percent is observed because of the loss of the sulphoxide and reduction to the oxide UO_3 facilitated by the sulphoxide and its decomposition products. The oxide U_3O_8 is formed around 600 °C following which there is no sensible change in weight. In the case of $UO_2Cl_2 \cdot 3H_2O$ (Fig. 6) there is a gradual decrease in weight between 60° and 190 °C, to the extent of 10 percent, due to the loss of two water molecules; the remaining water molecule is lost at 320 °C (loss 14 percent). The oxide UO_3 is formed at 460 °C and U_3O_8 above 750 °C [34]. In the case of $UO_2Cl_2 \cdot 2DBSO$ there is virtually no change in weight up to 150 °C. In the temperature range 150° to 200 °C there is a large loss of 57 percent due to the formation of UO_3 which changes to U_3O_8 above 600 °C.

Structure of the Complexes

The preferred coordination number of thorium is 6 or 8 but higher coordination numbers have also been observed [35]. It has been found from single crystal X-ray structure determination of the complex $Mg(H_2O)_6$ $Th(NO_3)_6 \cdot 2H_2O$ that the nitrate

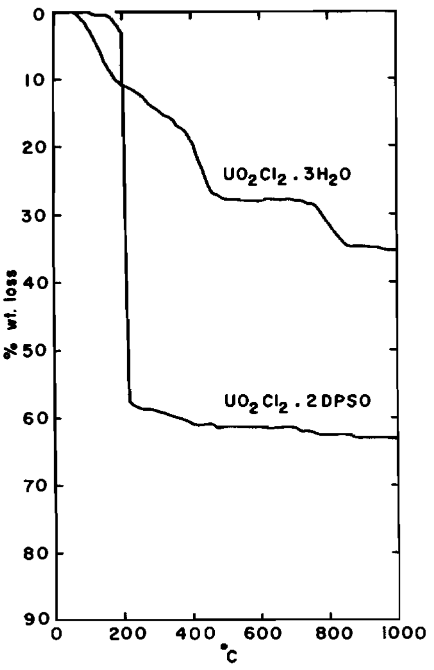
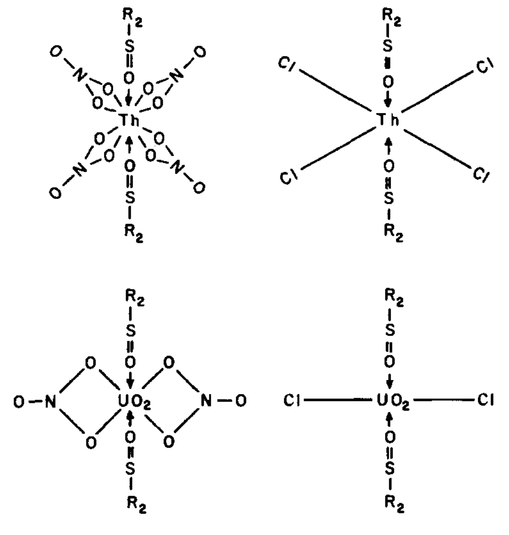


Figure 6. Thermograms of $UO_2Cl_2 \cdot 3H_2O$ and $UO_2Cl_2 \cdot$ 2DPSO.

groups in this complex are each linked to thorium through two oxygen atoms, each nitrate group functioning as a bidentate ligand [36]. With the presence of four bidentate groups of nitrate and the additional two unidentate sulphoxide molecules, the coordination number of thorium in the thorium nitrate R_2SO complexes is 10. The coordination number is 6 in the thorium chloride complexes.

On the basis of assumption of 8-coordination involving ten electron orbitals in the complex $UO_2(H_2O)_4(NO_3)_2$, Glueckauf and McKay [37] suggested that uranyl nitrate forms covalent complexes possibly involving the 5f orbitals. The infrared absorption bands assigned to the nitrate groups in the complex indicate that these groups are coordinated to the metal [38]. The presence of bidentate nitrate groups and of eight coordinated hexavalent uranium has been observed for rubidium uranyl nitrate [39] and uranyl nitrate–triethyl phosphate complex [40]. By analogy it is reasonable to suggest an 8-coordination structure for the hexavalent uranium in the uranyl nitrate–sulphoxide complexes. In uranyl chloride complexes, the coordination number of uranium is 6. The probable structures of the complexes are shown.



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