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PREPARATION AND THERMAL STABILITY OF THE U(IV)(SO_4)$_2$–DMF COMPLEX

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ABSTRACT

A new DMF complex of $U(SO_4)_2$, i.e., $U(SO_4)_2 \cdot 2.2$ DMF, was prepared and characterized using chemical analysis, X-ray powder diffraction studies, IR and measurement of magnetic susceptibility variation with temperature in the temperature range 77–300 K. Pyrolysis of the solvate was studied by means of TG under two different experimental conditions, and the actual thermal degradation path was deduced using a microthermobalance.

INTRODUCTION

Different hydrates of uranium(IV) sulphate, $U(SO_4)_2 \cdot 4\ H_2O$ and $U(SO_4)_2 \cdot 1\ H_2O$, are known with different crystal structures. Different solvates of uranium tetrachloride and uranium tetranitrate with dimethylacetamide and dimethylsulphoxide [1–6] are well studied using various techniques like magnetic susceptibility measurement, TG, DTA, IR and X-ray powder patterns. With U(IV)SO_4^{2-} such studies are lacking. An attempt was made to prepare a dimethylformamide solvate of $U(SO_4)_2$. Recently we prepared and studied the physicochemical properties of DMF solvates of $CaCl_2$ and $FeCl_3$ [7,8]. In this communication we report the preparation, chemical analysis, IR, X-ray powder pattern, magnetic susceptibility measurement and thermal stability under various conditions of a new DMF solvate of $U(SO_4)_2$, viz., $U(SO_4)_2 \cdot 2.2$ DMF.

EXPERIMENTAL

Nuclear pure UO_2 was heated in air in a Pt boat at ~ 1030 K in a muffle furnace for 24 h to convert it into U_3O_8. a saturated solution of U_3O_8 in 2 M H_2SO_4 was prepared and was photochemically reduced by a Hg vapour lamp (~ 270 nm) in the presence of ethanol, according to the procedure

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given by Hutchison and Elliott [9]. The product thus obtained was $U(SO_4)_2 \cdot 4.4\ H_2O$, the number of molecules being dependent on the mode of preparation. It was insoluble in water and ethanol, and also resistant towards water vapour and oxygen in air. The product was further heated in flowing nitrogen at 570 K to obtain anhydrous $U(SO_4)_2$. The anhydrous salt is moisture sensitive and so was always handled under nitrogen in a glove box.

$U(SO_4)_2$ mixed with a large excess of DMF was heated on a water bath for 1 h. It was then kept for a few days in a dry atmosphere at room temperature and excess unreacted DMF was removed under vacuum at room temperature. A green solid was obtained which was easily pulverized in air, and was stable in air and picked up moisture slightly.

The prepared solvate was dissolved in 2 M H_2SO_4, and uranium content was titrimetrically analyzed as described by Dharwadkar and Chandrasekharaiah [10]. The SO_4^{2-} analysis was done by precipitating SO_4^{2-} as $BaSO_4$ gravimetrically [11]. The DMF content was deduced from the difference.

A Stanton thermobalance was used in static air as well as flowing nitrogen (flow rate ~ 1 l min^{-1}) for thermogravimetry. A home-made TG set up [12] was used with a sample size of a few mg and sensitivity ± 10–50 μg, with dry nitrogen gas flowing at the rate of 2 l h^{-1}. The X-ray powder pattern of the moisture-sensitive solvate was obtained according to the procedure described previously [7]. IR spectra were recorded using a Perkin-Elmer 557 (grating IR spectrometer). KBr pellet or nujol mull of the sample with CsI window was used. The IR spectrum in the range 2500–400 cm^{-1} was recorded. Magnetic susceptibility variation with temperature in the range 77–300 K was measured using Gouy's method.

RESULTS AND DISCUSSION

The results of chemical analysis are given in Table 1. The X-ray powder pattern of the new solvate as well as those of related hydrates and anhydrous $U(SO_4)_2$ are shown in Fig. 1, which clearly shows the distinctly crystalline nature of the DMF solvate.

Infrared spectroscopy

Figure 2 shows the IR spectra of $U(SO_4)_2 \cdot 2.2$ DMF and $U(SO_4)_2 \cdot 4.4\ H_2O$. The absence of 860 cm^{-1} absorption shows that $[UO_2]^{2+}$ is absent in both compounds [13]. Also the absence of 890 and 455 cm^{-1} absorptions indicates the absence of basic U–O–H linkage [14]. The multiplicity of the bands observed in the region anticipated for C_{2v} symmetry of the sulphate group, if the degeneracy is completely lifted, viz. ν_1 (985 cm^{-1}), ν_2 (425 and 495 cm^{-1}), ν_3 (1025, 1155 and 1200 cm^{-1}) and ν_4 (595, 645 and 655 cm^{-1}), i.e., a total of nine local modes of C_{2v} symmetry for sulphate is observed.

TABLE 1

Chemical analysis of $U(SO_4)_2 \cdot 2.2$ DMF (M.W. 590.6)

Serial no.		% Estd.	% Calcd.	Deduced M.W.
1	U	40.7	40.3	596
2	SO_4	32.6	32.5	592
3	DMF (by difference)	26.7	27.1	581

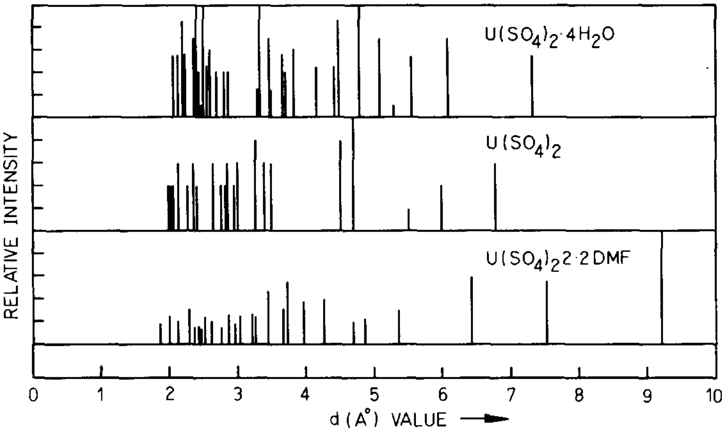

Fig. 1. X-Ray powder patterns of $U(SO_4)_2 \cdot 4\ H_2O$, $U(SO_4)_2$, and $U(SO_4)_2 \cdot 2.2$ DMF.

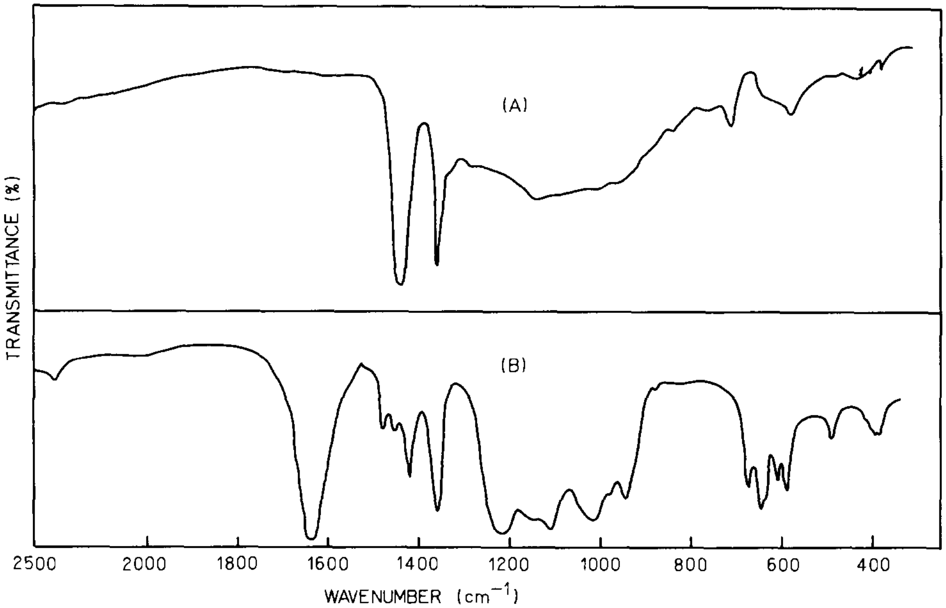

Fig. 2. IR spectra of (A) $U(SO_4)_2 \cdot 4.4\ H_2O$, and (B) $U(SO_4)_2 \cdot 2.2$ DMF.

The strong absorption at 1120 cm^{-1} (ν_{SO}) and 495 cm^{-1} (ν_{OSO}) is due to coordination of the metal through oxygen to the sulphate group, i.e., M–OSO$_3$.

IR spectra of neat DMF show strong absorption at 1670 cm^{-1} due to the CO stretching frequency, at 1490 cm^{-1} due to the CN stretching frequency, and at 655 cm^{-1} due to bending of the NCO group [13]. The IR spectra of the solvate show a distinct shift in the absorption of the CO stretching mode to a lower frequency by ~ 35 cm^{-1} which indicates that the coordination of DMF to $U(SO_4)_2$ is through the oxygen of the –CO group.

Thermogravimetry

TG of the solvate in static air and flowing nitrogen is shown in Fig. 3. It is not unreasonable to believe that the solvate first becomes desolvated to give anhydrous $U(SO_4)_2$ which converts to UO_2SO_4 and finally at 1050 K loses SO_2, SO_3 and possibly oxygen in varied proportions to give U_3O_8 as the ideal residue. The quantitative interpretation of the TG curves shows that the weight loss is much less than the required one (Table 2). TG in static air shows a three-stage degradation and its overall weight loss levels off at ~ 1030 K, whereas TG in flowing nitrogen atmosphere shows a single-stage decomposition with two points of inflexion at 553 and 693 K. The entire

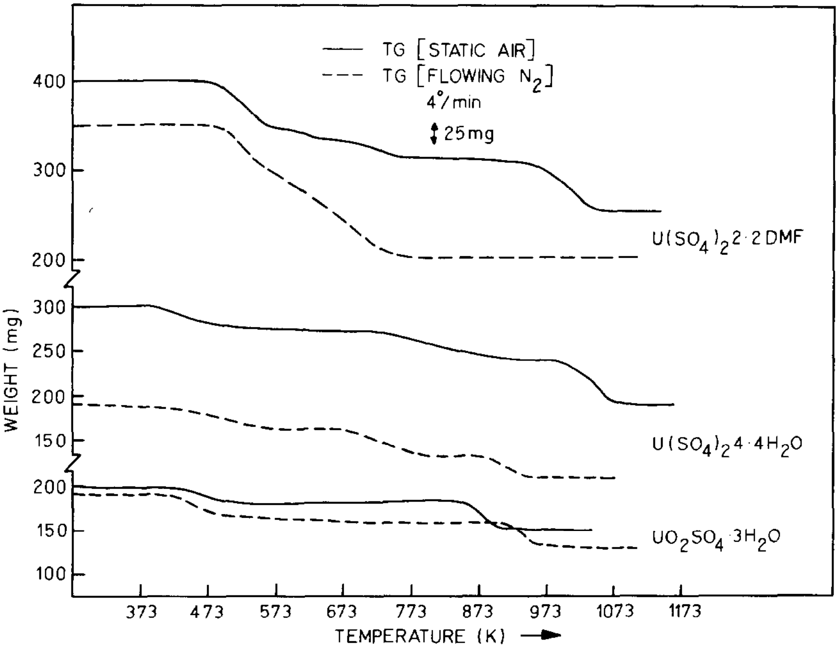

Fig. 3. TG of $U(SO_4)_2 \cdot 2.2$ DMF, $U(SO_4)_2 \cdot 4.4\ H_2O$ and $UO_2SO_4 \cdot 3\ H_2O$ under two different experimental conditions.

TABLE 2

Results of TG of $U(SO_4)_2 \cdot 2.2$ DMF under different experimental conditions

Serial no.	TG in static air atmosphere		TG in flowing nitrogen atmosphere		Micro TG in flowing nitrogen atmosphere		Calcd. formula of residue	Calcd. % wt. loss [a]
	% Wt. loss	Temp. range (K)	% Wt. loss	Temp. range (K)	% Wt. loss	Temp. range (K)		
1st step	13.2	493– 553	13.0	493–553	20.4	623– 683	$U(SO_4)_2 \cdot 0.5$ DMF	21.0
2nd step	14.1	583– 773	27.6	553–693	22.3	683– 883	UO_2SO_4	22.7
3rd step	14.7	853–1013	5.74	693–773	24.2	883–1008	U_3O_8	23.2

[a] Based on $U(SO_4)_2 \cdot 2.2\ \text{DMF} \rightarrow U(SO_4)_2 \cdot 0.5\ \text{DMF} \rightarrow UO_2SO_4 \rightarrow U_3O_8$.

decomposition is complete at ~ 773 K. the X-ray powder patterns of the residue of both TG indicate it to be multiphase oxides of uranium. It is not clear as to why the decomposition behaviour of the same compound is radically different under two different atmospheres. In order to obtain meaningful evidence, TG runs of the expected intermediates were also recorded under identical conditions as those of the solvate (Fig. 3). These TG results on weight loss consideration are also not satisfactory (Tables 3 and 4). Thus the difficulties in obtaining a quantitative fit for U_3O_8 as residue might have been brought about by the following factors [15]:

(i) due to the large sample size, at elevated temperatures sintering of uranium oxide decreases the active surface area of the sample by forming a cage around the sample and complete decomposition is not observed;

(ii) due to sintering, release of gases from the bulk is not easy. This was demonstrated by Notz [16] for the gas–solid reaction of UO_2SO_4. The decomposition of UO_2SO_4 to U_3O_8 is according to the scheme

$$3\ UO_2SO_{4(s)} \rightarrow U_3O_{8(s)} + SO_{2(g)} + O_{2(g)} + 2\ SO_{3(g)}$$

$$(2\ SO_{3(g)} \rightleftarrows 2\ SO_2 + O_2)$$

The trapped gases, i.e., SO_2, O_2 and SO_3, prevent further decomposition of UO_2SO_4 by developing back pressure inside the cage, thereby creating a false impression of a plateau in the TG pattern;

(iii) external atmosphere with the sample bulk is not uniform. The released gases in static air create self-generated atmosphere. As the decomposition of UO_2SO_4 is very sensitive to the surrounding atmosphere [16], the difference in the temperature stability range in two different atmospheres appears to be logical.

To overcome some of these difficulties, a microthermobalance was used with a sample size of a few mg (~ 10 mg). Flowing dry nitrogen gas (~ 10–40 ml min^{-1}) was used to sweep away the released gaseous products so that the sample was always in contact with uniform preheated nitrogen gas.

Microthermogravimetry

Micro-TGs of (i) $UO_2SO_4 \cdot 3\ H_2O$, (ii) $U(SO_4)_2 \cdot 4.4\ H_2O$ and (iii) $U(SO_4)_2 \cdot 2.2$ DMF are shown in Fig. 4. The quantitative interpretation (Tables 2–4) of micro-TG of $UO_2SO_4 \cdot 3\ H_2O$ and $U(SO_4)_2 \cdot 4.4\ H_2O$ is in excellent agreement with that reported by Duval [17] and Leroy [18], respectively.

Micro-TG of $U(SO_4)_2 \cdot 2.2$ DMF shows that it is stable up to 623 K and entire decomposition ceases at 1023 K, giving uranium oxide. Table 2 shows an excellent match of weight loss consideration with that calculated for U_3O_8 as residue. However, in the solvate, plateaus corresponding to $U(SO_4)_2$ and

TABLE 3

Results of TG of $U(SO_4)_2 \cdot 4.4\ H_2O$ under different experimental conditions

Serial no.	TG in static air atmosphere		TG in flowing nitrogen atmosphere		Micro-TG in flowing nitrogen atmosphere		Calcd. % wt. loss [a]
	% Wt. loss	Temp. range (K)	% Wt. loss	Temp. range (K)	% Wt. loss	Temp. range (K)	
1st step	8.3	358– 593	14.6	323–583	15.5	375– 500	15.5
2nd step	10.5	713– 913	16.6	663–823	14.8	751– 873	14.9
3rd step	19.5	973–1068	15.4	863–943	29.2	873–1033	23.7

[a] Based on $U(SO_4)_2 \cdot 4.4\ H_2O \rightarrow U(SO_4)_2 \rightarrow UO_2SO_4 \rightarrow U_3O_8$.

TABLE 4

Results of TG data of $UO_2SO_4 \cdot 3\ H_2O$ under different experimental conditions

Serial no.	TG in static air atmosphere		TG in flowing nitrogen atmosphere		Micro-TG in flowing nitrogen atmosphere		Calcd. % wt. loss [a]
	% Wt. loss	Temp. range (K)	% Wt. loss	Temp. range (K)	% Wt. loss	Temp. range (K)	
1st step	8.6	393–553	8.5	413– 573	13.3	373– 630	12.8
2nd step	15.1	813–903	18.5	873–1073	29.5	905–1008	23.7

[a] Based on $UO_2SO_4 \cdot 3\ H_2O \rightarrow UO_2SO_4 \rightarrow U_3O_8$.

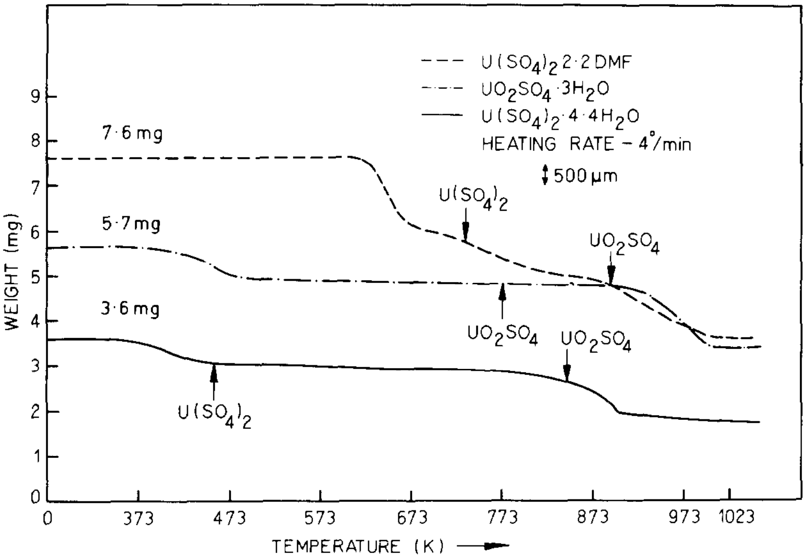

Fig. 4. Micro-TG of $U(SO_4)_2 \cdot 2.2$ DMF, $UO_2SO_4 \cdot 3\ H_2O$, and $U(SO_4)_2 \cdot 4.4\ H_2O$.

UO_2SO_4 are not observed since they are formed at temperatures higher than their stability temperature range, but two points of inflexion at 683 K and 883 K are observed which correspond to $U(SO_4)_2 \cdot 0.5$ DMF and UO_2SO_4, respectively, whereas no point of inflexion corresponding to $U(SO_4)_2$ was observed. The deduced course of decomposition of the solvate is

$$U(SO_4)_2 \cdot 2.2\ \mathrm{DMF} \xrightarrow{623\text{–}683\ \mathrm{K}} U(SO_4)_2 \cdot 0.5\ \mathrm{DMF}$$

$$\xrightarrow{683\text{–}883\ \mathrm{K}} UO_2SO_4 \xrightarrow{883\text{–}1023\ \mathrm{K}} U_3O_8$$

From a comparison of the micro-TGs of all compounds [15] it is clear that the $U(SO_4)_2 \cdot 2.2$ DMF complex is thermally more stable than any of the known hydrates of $U(SO_4)_2$, indicating strong interaction between DMF and $U(SO_4)_2$ compared to that of water and $U(SO_4)_2$.

Magnetic susceptibility

U(IV) is known to exhibit a variety of behaviour with respect to the magnetism it exhibits in different atmospheres [2]. Figure 5 shows variation of magnetic susceptibility with temperature in the temperature interval 77–300 K. The variation was almost of Curie type of paramagnetism with negligible θ_p value, indicating a magnetically dilute system. From the slope of the χ_g^{-1} with T(K) (least squares fit) curve, calculated μ_{eff} for U(IV) comes to 2.04 BM which is in the expected range for U(IV) complexes, but it is not possible to make any conclusion from susceptibility measurements.

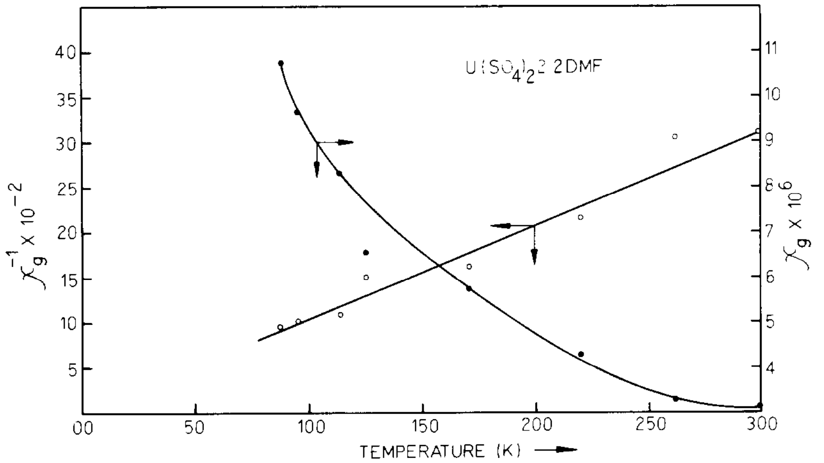

Fig. 5. χ_g variation with *T*(K) of $U(SO_4)_2 \cdot 2.2$ DMF.

CONCLUSIONS

A new DMF solvate, $U(SO_4)_2 \cdot 2.2$ DMF, was prepared and identified by chemical analysis. It is a crystalline solid and gives a good X-ray pattern. The solvate has a SO_4^{2-} group in C_{2v} local symmetry in the solid. DMF is coordinated to $U(SO_4)_2$ through the oxygen atom of the carbonyl group. The $U(SO_4)_2 \cdot 2.2$ DMF complex is thermally more stable than any of the known hydrates of $U(SO_4)_2$ and UO_2SO_4, indicating stronger interaction between DMF and $U(SO_4)_2$ compared to H_2O and $U(SO_4)_2$. The study of $U(SO_4)_2 \cdot$ 2.2 DMF along with $U(SO_4)_2 \cdot 4.4\ H_2O$ and $UO_2SO_4 \cdot 3\ H_2O$ by TG and micro-TG under various conditions (different amounts of material and different atmospheres) has brought out the artefacts inherent in the TG technique, which are responsible for the apparent steps which are never present under the near ideal situation as prevalent in micro-TG. The sintering and its attendant consequences indicate the need to exercise caution while interpreting TG data.

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