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THERMAL AND X-RAY STUDIES ON DOUBLE SULPHATES OF URANIUM(IV) WITH MAGNESIUM, NICKEL, COPPER AND ZINC

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Double sulphates of uranium(IV) with Mg, Ni, Cu and Zn with the general formula $MU(SO_4)_3 \cdot 8H_2O$ were prepared from their respective metal sulphates. All the four compounds are isostructural and belong to monoclinic system. The thermal decomposition at 850 °C results in a single phase of triuranates MU_3O_{10} which on further heating above 980 °C decompose to give the metal oxide and U_3O_8 in case of Ni and Zn compounds and MUO_4 for Mg and Cu compounds. The activation energy for dehydration of these four compounds has been calculated using non-isothermal thermogravimetric data.

The crystal structures of the disulphates $U(SO_4)_2 \cdot 4H_2O$ [1] and $Pu(SO_4)_2 \cdot 4H_2O$ [2] have shown that these compounds are isostructural with $Ce(SO_4)_2 \cdot 4H_2O$ [3]. The tetravalent metal atoms have eight oxygen atoms coordinated to it in the form of a square antiprism. Four of these oxygen atoms are from four water molecules and the other four from four SO_4 groups. Each sulphate group is coordinated to two metal atoms so that all the sulphate groups are bidentate and bridging. In the case of tetrasulphates, a single crystal X-ray structure study of $K_4Ce(SO_4)_4 \cdot 2H_2O$ recently completed [4] has shown that each cerium atom has 9 oxygen atoms coordinated to it in the form of a highly distorted capped square antiprism. All the oxygen atoms belong to the sulphate groups so that the water molecules are not coordinated to the cerium atom. The alkali metal tetrasulphates of U(IV) and Pu(IV) are also found to be isostructural with the cerium compound [5]. Martin Gil et al. [6] have reported the preparation of some trisulphates, but no detailed thermal and X-ray studies were carried out by them. As a part of a systematic study on the structures and thermal properties of uranium(IV) sulphates, we report the results of X-ray and thermal studies on four trisulphates of uranium(IV), i.e. $MU(SO_4)_3 \cdot 8H_2O$ where M = Mg, Ni, Cu and Zn.

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Experimental

All the four compounds were prepared by the addition of few drops of ethanol to solutions containing uranium(IV) sulphate and about 1.5 times the stoichiometric amount of the respective metal sulphates in 1M H_2SO_4. Uranium(IV) sulphate solution was prepared by electrolytic reduction of UO_3 dissolved in H_2SO_4 using Pt electrodes. The precipitated double sulphates were washed with absolute ethanol several times and dried in air. Chemical analysis for uranium, magnesium, nickel, copper, zinc and sulphate was done gravimetrically, following the methods given by Vogel [7]. The number of water molecules were determined thermogravimetrically from the mass loss up to 300°.

X-ray diffraction patterns were recorded on a Siemens diffractometer using CuK_α (λ = 1.54178 Å) radiation. The infrared spectra were taken of samples dispersed in KBr pellets in the range of 4000–400 cm^{-1}. Thermal analyses were carried out by a Mettler Thermoanalyser TA1 in which TG, DTA and DTG curves were recorded simultaneously. The sample and calcined alumina as reference standard were heated in a flowing stream of dry air up to 1200° at the rate of 10 deg/min.

Results and discussion

The X-ray diffraction patterns of the double sulphates of uranium with metal ions Mg^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} showed the formation of the compounds since the X-ray lines due to the corresponding sulphates were absent. The results of the chemical analyses and percent mass loss below 300° on the thermal curves given in Table 1, support the composition $MU(SO_4)_3 \cdot 8H_2O$. The infrared spectra of all the four compounds were identical.

X-ray diffraction data indicated that all the compounds were isostructural [8]. The data of the four double sulphates could be indexed on the basis of monoclinic crystal system and the cell parameters are given in Table 2.

Table 1 Chemical analysis results in percent

Chemical composition	Uranium		Sulphate		Divalent metals		Water	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
$MgU(SO_4)_3 \cdot 8H_2O$	34.40	34.28	42.70	41.48	3.30	3.50	21.61	20.70
$NiU(SO_4)_3 \cdot 8H_2O$	32.51	32.66	40.20	39.52	8.00	8.06	19.06	19.76
$CuU(SO_4)_3 \cdot 8H_2O$	32.32	32.45	40.30	39.26	8.43	8.66	20.48	19.63
$ZnU(SO_4)_3 \cdot 8H_2O$	32.10	32.37	40.20	39.16	9.10	8.89	20.36	19.58

Table 2 X-ray data on trisulphates

Compound	Cell parameters, Å			
	a	*b*	*c*	*β* (°)
$MgU(SO_4)_3 \cdot 8H_2O$	14.565	18.765	11.510	91.04
$NiU(SO_4)_3 \cdot 8H_2O$	14.523	18.655	11.497	91.25
$CuU(SO_4)_3 \cdot 8H_2O$	14.705	18.507	11.550	91.70
$ZnU(SO_4)_3 \cdot 8H_2O$	14.575	18.758	11.521	91.30

The DTA and TG curves of the four compounds are shown in Figs 1 and 2. Samples were heated in a furnace at different temperatures at which the formation of stable intermediates were indicated by the thermal curves. The products obtained were examined using their X-ray diffraction patterns. The results given in Tables 3 and 4 are based on mass losses and X-ray identification. The hydrated trisulphates lose all the water molecules below 300°. While the eight water molecules in the magnesium compound are lost in a single step, those in the others are lost in two steps. The anhydrous sulphates decompose to form $MUO_2(SO_4)_2$ with the loss of one SO_2 molecule in the range 400–500° for the copper compound and in the range 600–700° for the other three. Although the products did not give any X-ray patterns, the presence of absorption bands around 910 cm^{-1} in the IR spectra indicate the presence of uranyl groups. Moreover, on storing, these compounds absorb moisture and their X-ray patterns showed them to be $MUO_2(SO_4)_2 \cdot 5H_2O$ [9].

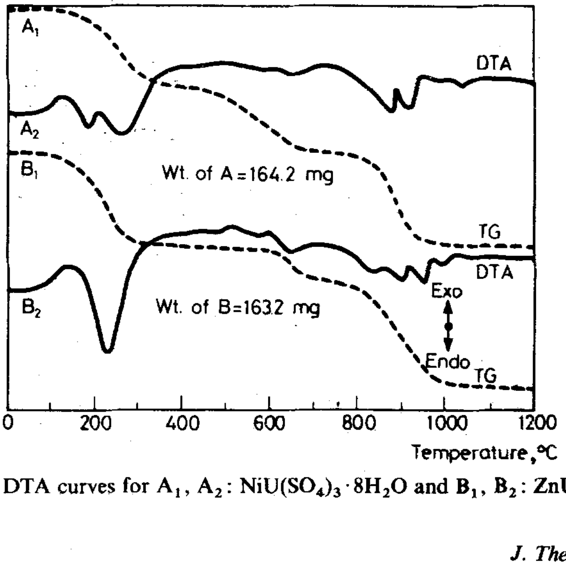

Fig. 1 TG and DTA curves for A_1, A_2: $NiU(SO_4)_3 \cdot 8H_2O$ and B_1, B_2: $ZnU(SO_4)_3 \cdot 8H_2O$

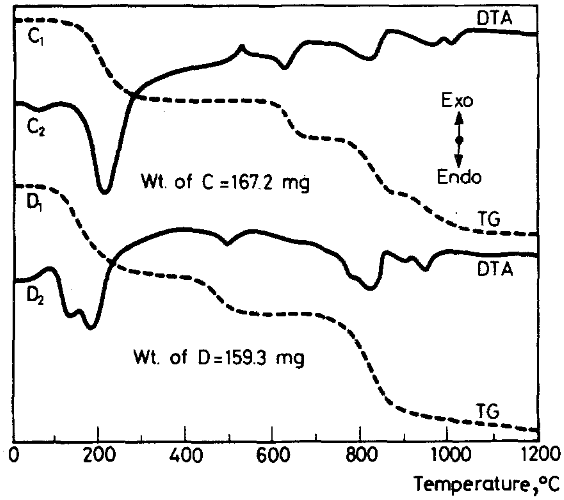

Fig. 2 TG and DTA curves for C_1, C_2: $MgU(SO_4)_3 \cdot 8H_2O$ and D_1, D_2: $CuU(SO_4)_3 \cdot 8H_2O$

Table 3 Stepwise loss from thermogravimetric curves

Chemical composition	Total loss, %		SO_2 loss, %		$2\,SO_3$ loss, %	
	obs.	calc.	obs.	calc.	obs.	calc.
$MgU(SO_4)_3 \cdot 8H_2O$	53. 26	53.00	7.49	9.22	24.39	23.05
$NiU(SO_4)_3 \cdot 8H_2O$	49.10	50.50	8.30	8.78	21.75	21.96
$CuU(SO_4)_3 \cdot 8H_2O$	49.13	50.17	7.65	8.73	21.02	21.81
$ZnU(SO_4)_3 \cdot 8H_2O$	49.14	50.05	7.47	8.70	21.30	21.76

Table 4 Thermal decomposition products in different temperature range

Compound	Temperature, °C			
	100–300	500–600	850	>980
$MgU(SO_4)_3 \cdot 8H_2O$	$MgU(SO_4)_3$	$MgUO_2(SO_4)_2$	MgU_3O_{10}	$MgUO_4$
$NiU(SO_4)_3 \cdot 8H_2O$	$NiU(SO_4)_3$	$NiUO_2(SO_4)_2$	NiU_3O_{10}	$NiO+U_3O_8$
$CuU(SO_4)_3 \cdot 8H_2O$	$CuU(SO_4)_3$	$CuUO_2(SO_4)_2$	CuU_3O_{10}	$CuUO_4$
$ZnU(SO_4)_3 \cdot 8H_2O$	$ZnU(SO_4)_3$	$ZnUO_2(SO_4)_2$	ZnU_3O_{10}	$ZnO+U_3O_8$

Samples heated around 850° showed further mass losses that indicate the formation of MUO_4. However, the X-ray patterns showed them to be triuranates [10]. It is likely that the metal oxides formed simultaneously, do not give any recognisable X-ray patterns. The final products at 1200° were found to be $MgUO_4$ for magnesium, a mixture of U_3O_8 and metal oxide for nickel and zinc and a mixture of $CuUO_4$ and CuU_3O_{10} for copper. The thermal analyses of $ZnU(SO_4)_3 \cdot 6H_2O$ and $MgU(SO_4)_3 \cdot 9H_2O$ have been reported by Gil et al. [6] up to 900°. On the basis of mass changes they found that the former gave $ZnU(SO_4)_2O$ at 670° and $ZnUO_3$ at 862°. In the case of the magnesium compound the products formed were $MgU(SO_4)_2O$ at 668° and $MgU(SO_4)O_2$ at 885°. However, our results are not in agreement with the composition of these products perhaps because the number of water molecules in the starting compounds are not the same.

The double sulphates of Mg, Ni, Cu and Zn were also heated in an atmosphere of Ar/H_2 at 850° for 2–3 hours. The products gave X-ray patterns similar to that of UO_2.

The activation energies for the dehydration steps were computed using the Coats and Redfern equation [11] from the non-isothermal thermogravimetric data. The values for Mg, Ni, Cu and Zn compounds are 17.7, 18.1, 18.8 and 12.5 kcal/mol, respectively.

In conclusion it can be stated that double sulphates of uranium(IV) with Mg, Ni, Cu and Zn prepared from their respective metal sulphates are isostructural and belong to the monoclinic system. The thermal decomposition of $MU(SO_4)_3 \cdot 8H_2O$ proceeds through the loss of all the water molecules below 300° and SO_2 below 650° to give MU_3O_{10} and metal oxides. Further heating above 980° yields a mixture of metal oxides and U_3O_8 for Ni and Zn compounds and $MgUO_4$ for Mg compound and a mixture of $CuUO_4$ and CuU_3O_{10} for Cu.

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Zusammenfassung — Aus den entsprechenden Metallsulfaten wurden sulfatische Doppelsalze von Uran(IV) und Mg, Ni, Cu und Zn mit der allgemeinen Formel $MU(SO_4)_3 \cdot 8H_2O$ dargestellt. Alle vier Verbindungen besitzen die gleiche Struktur und gehören dem monoklinen System an. Bei der thermischen Zersetzung bei 850 °C entsteht ein MU_3O_{10} Einphasentriuranat, welches durch weiteres Erhitzen über 980 °C in das entsprechende Metalloxid sowie im Falle der Ni- und Zn-Verbindungen in U_3O_8, bei den Mg- und Cu-Verbindungen in MUO_4 zerfällt. Unter Anwendung nichtisothermer thermogravimetrischer Daten wurde die Aktivierungsenergie für die Dehydratation dieser vier Verbindungen berechnet.

Резюме — Двойные смешанные сульфаты шестивалентного урана, магния, никеля, меди и цинка общей формулы $MU(SO_4)_3 \cdot 8H_2O$, были получены из сульфатов соответствующих металлов. Все четыре соединения изоструктурны и относятся к моноклинной сингонии. Термическое разложение при 850° дает однофазные триуранаты MU_3O_{10}, которые при дальнейшем нагревании выше 980° разлагаются давая окись металла и U_3O_8 в случае соединений никеля и цинка, и MUO_4 для соединений магния и меди. Используя неизотермические термогравиметрические данные была вычислена энергия активации процесса дегидратации этих четырех соединений.