

## THE LANGBEINITE $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ OBTAINED FROM SATURATED SOLUTIONS OF $(\text{NH}_4)_2\text{SO}_4/\text{CdSO}_4$ IN MOLAR RATIO 1:1

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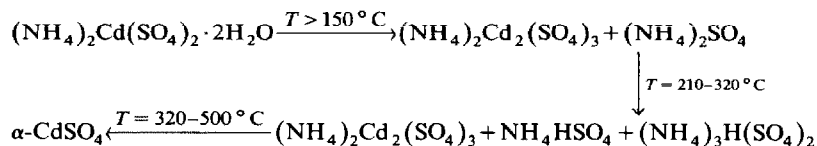
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### ABSTRACT

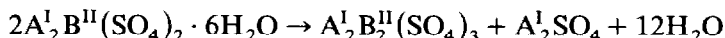
Slow evaporation at room temperature of saturated solutions of  $(\text{NH}_4)_2\text{SO}_4/\text{CdSO}_4$  in molar ratio 1:1, brings about the crystallization of a double ammonium–cadmium sulphate with 2 mol of water.

The thermal decomposition of this double salt has been studied using thermogravimetry, differential thermal analysis and X-ray diffraction. The scheme proposed for this process is



### INTRODUCTION

Many double sulphates of the langbeinite type can be obtained by dehydration of the corresponding Tutton's salts, also known as 'schöenites', of the general formula  $\text{A}_2^{\text{I}}\text{B}^{\text{II}}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , according to the process



Included in this group are the schöenites of zinc [1–3], nickel [1,3], magnesium [3–5], cobalt [3], manganese [3,6], iron [3,7] and cadmium [8]. For all of these,  $\text{A}^{\text{I}} = \text{NH}_4^+$ .

Nabiev et al. [4] and Prymova et al. [5] have studied the thermal decomposition of the schöenite of magnesium; the latter workers have also studied the decomposition of the schöenite of cadmium [8]. Both groups of workers propose that two compounds originate during the respective decomposition processes:  $(\text{NH}_4)_2\text{B}_2(\text{SO}_4)_3$  (langbeinite) and  $\text{NH}_4\text{HB}(\text{SO}_4)_2$ . In both cases, B = Mg or Cd.

In studies of the decomposition of the ammonium–cadmium langbeinite, synthesized from saturated solutions of  $(\text{NH}_4)_2\text{SO}_4/\text{CdSO}_4$  in molar ratio 1:2 (this review, Parts I [9], II [10] and III [11]), the compound  $\text{NH}_4\text{HCd}(\text{SO}_4)_2$  has not been found in stable phase. We therefore considered it interesting to synthesize the Tutton's salt and study its thermal behaviour in order to establish possible differences between the langbeinites originating in these two ways.

## EXPERIMENTAL

### *Products*

$(\text{NH}_4)_2\text{SO}_4$  (AnalaR, Riedel).  $\text{CdSO}_4$  prepared in the laboratory starting from  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  (AnalaR Carlo Erba), by dehydration at isotherm to  $600^\circ\text{C}$  during four hours in a muffle furnace, and identified by X-ray powder diffraction.

### *Samples*

These were prepared by slow evaporation at room temperature of saturated solutions of  $\text{CdSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  in molar ratio 1:1. The residua of several evaporations (five in all) were identical: white crystals with the same X-ray powder diffraction. However, this diffraction did not correspond to the schöenite, nor to any compound known to have a part in the process, i.e. reagents, intermediate compounds or final products.

### *Apparatus*

#### *Thermogravimetric analysis (TG)*

Mettler TA3000 system,  $T = 1000^\circ\text{C}$ , alumina microcrucible. Sample weight = 30–40 mg,  $\beta = 10$  and  $2.5 \text{ K min}^{-1}$ .

#### *Differential thermoanalysis (DTA)*

Apparatus was constructed in the laboratory using a vertical furnace with an Adamel temperature regulation system. Sintered alumina holder ( $19 \times 12, 5 \times 14 \text{ mm}$ ) divided into two equal cavities, with a wall thickness of 1.5 mm. Differential chromel–alumel thermocouple. Metrohm Labograph E478 recorder. The temperature of the air surrounding the specimen holder was measured.  $\beta = 2.5 \text{ K min}^{-1}$ .

#### *X-ray powder diffraction*

Siemens D-500 diffractometer, with K-805 generator,  $\text{Cu } K\alpha$  radiation, Ni filter and graphite monochromator; 40 kV, 32 mA, goniometer rate  $5^\circ \text{ min}^{-1}$ , paper speed  $300 \text{ mm h}^{-1}$ , time constant 1 s.

## RESULTS AND DISCUSSION

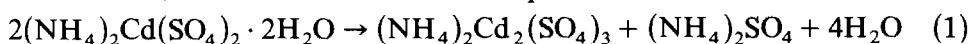
*Thermogravimetric analysis*

The TG study of the evaporation residuum was performed with  $\beta = 10$  and  $2.5 \text{ K min}^{-1}$ .

Both curves are reproduced in Figs. 1 and 2 and show two drops. The mass losses for the two curves are in agreement.

The first drop occurs in the range room temperature to  $140^\circ\text{C}$ ; the weight losses for these two curves are 9.3 and 9.6%, respectively. The loss corresponds to the evolution of the crystallization water of the Tutton's salt, which in this case was crystallized with 2 mol of water rather than six mol. X-ray diffraction analysis of the residua at  $170^\circ\text{C}$  in both calcinations shows that they are formed by the langbeinite  $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ , and  $(\text{NH}_4)_2\text{SO}_4$ .

Therefore, the reaction that has taken place is



After a small horizontal stretch, between  $140$  and  $200^\circ\text{C}$  approximately, there begins a new drop which finishes at  $500^\circ\text{C}$ .

The X-ray diffraction of the residue at  $575^\circ\text{C}$  corresponds to  $\alpha\text{-CdSO}_4$ . Therefore, the process that has taken place within the temperature interval  $170\text{--}500^\circ\text{C}$  is

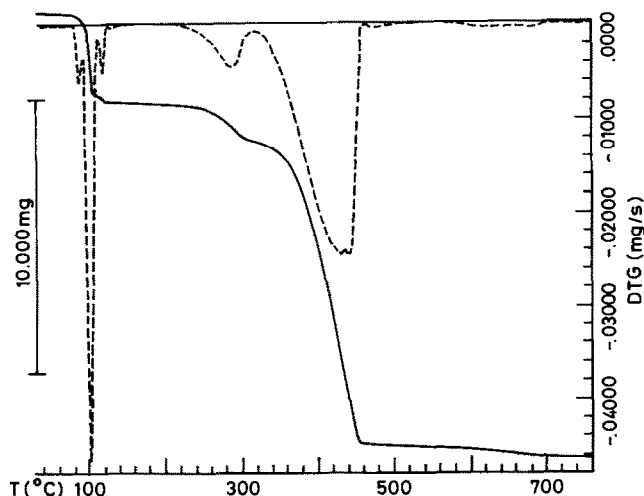
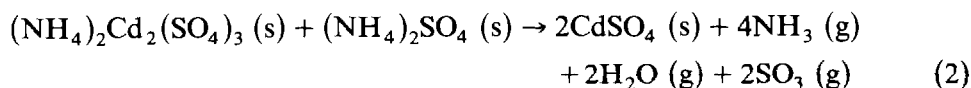


Fig. 1. TG and DTG curves ( $\beta = 10 \text{ K min}^{-1}$ ) for evaporation residue of saturated solutions  $(\text{NH}_4)_2\text{SO}_4/\text{CdSO}_4$  in molar ratio 1 : 1.

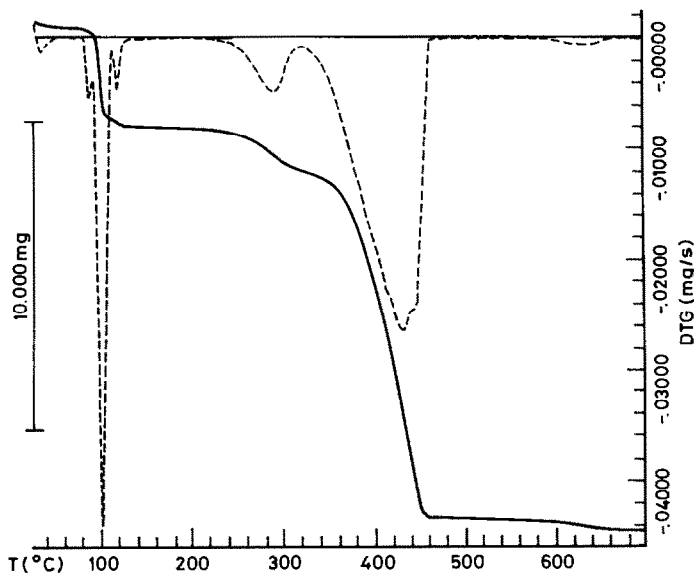


Fig. 2. TG and DTG curves ( $\beta = 2.5 \text{ K min}^{-1}$ ) for evaporation residue of saturated solutions  $(\text{NH}_4)_2\text{SO}_4/\text{CdSO}_4$  in molar ratio 1:1.

The theoretical mass loss associated with this reaction is 38.8%; and the experimental values determined from the two TG curves are 39.75 and 39.76%, respectively.

As can be seen, an inflection point occurs in both curves at approximately  $320^\circ\text{C}$ . The weight losses calculated for this point are 4.5% (Fig. 1) and 4.3% (Fig. 2).

According to the authors mentioned above [5,8], the thermal decomposition of the Tutton's salt gives rise to formation of  $\text{NH}_4\text{HCd}(\text{SO}_4)_2$ . The reaction occurring in the mixture of  $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$  and  $(\text{NH}_4)_2\text{SO}_4$  in the first stage of decomposition of the Tutton's salt would therefore have to be



with an associated theoretical weight loss of 5.0%. However, our experimental values are lower than this, which brings into question the occurrence of reaction (3).

Experimentally, in order to reach this value of 5.0% it is necessary to surpass the temperature of the inflection point on the TG curve, but no single point occurs in that zone, unless we consider the inflection itself. Also, X-ray diffraction analysis of the residua at  $320^\circ\text{C}$  (Table 1) shows that these are formed almost exclusively from langbeinite, which cannot therefore have undergone any transformation. If the stage proposed by Prymova et al. [8] did occur, it would have led to the total decomposition of the langbeinite according to eqn. (3).

TABLE 1

X-ray powder diffraction of residue taken from sample at 320°C (inflection point in TG curve)

2θ	d (Å)	I/I <sub>1</sub>	(NH <sub>4</sub> ) <sub>2</sub> Cd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>		(NH <sub>4</sub> ) <sub>3</sub> H(SO <sub>4</sub> ) <sub>2</sub>		NH <sub>4</sub> HSO <sub>4</sub>	
			ASTM 21-791		ASTM 21-25		ASTM 25-34	
			d (Å)	I/I <sub>1</sub>	d (Å)	I/I <sub>1</sub>	d (Å)	I/I <sub>1</sub>
14.93	5.9287	55	5.97 *	50				
17.74	4.9954	3			4.98 *	85		
17.95	4.9374	3			4.95 *	100		
18.75	4.7285	4					4.75 *	100
19.24	4.6092	58	4.63 *	65				
21.08	4.2108	11	4.23	12				
22.90	3.8801	2					3.90 *	50
23.58	3.7697	2			3.77 *	80		
24.20	3.6746	5					3.68 *	90
25.90	3.4371	19	3.45	20				
26.42	3.3706	4			3.39	75		
27.30	3.2639	100	3.27 *	100				
28.65	3.1131	10	3.12	12				
30.58	2.9209	2			2.932	50		
31.20	2.8643	9	2.870	10				
32.38	2.7625	64	2.765 *	65				
35.84	2.5034	8	2.511	10				
38.00	2.3659	6	2.375	6				
40.00	2.2521	6	2.259	6				
42.92	2.1054	23	2.113	20				
43.90	2.0606	10	2.071	10				
44.78	2.0221	19	2.030	20				
45.67	1.9848	12	1.993	14				
47.43	1.9152	18	1.922	18				
50.75	1.7974	9	1.801	10				

An asterisk indicates that the most intense line serves to identify the compound.

Our results clearly support the conclusion that, at least under these experimental conditions, it is not possible to identify and isolate the intermediate compound proposed by these authors [8].

The X-ray diffractogram is completed by a number of weak lines that can be assigned to NH<sub>4</sub>HSO<sub>4</sub> and (NH<sub>4</sub>)<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub>, products of the decomposition of ammonium sulphate according to Nakamura et al. [12] and Konkoly [13]. These lines indicate that the weight loss registered at 320°C is due to the partial decomposition of ammonium sulphate.

#### *Differential thermoanalysis*

Figure 3 reproduces the DTA curve obtained for β = 2.5 K min<sup>-1</sup>. In this curve there occur four endothermic peaks, which have been identified by X-ray diffraction.

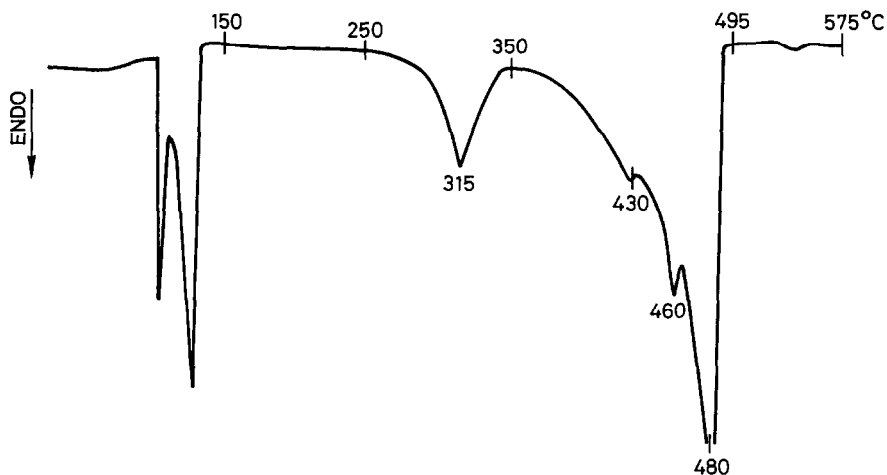


Fig. 3. DTA curve ( $\beta = 2.5 \text{ K min}^{-1}$ ) for evaporation residue of saturated solutions  $(\text{NH}_4)_2\text{SO}_4/\text{CdSO}_4$  in molar ratio 1:1.

The two large peaks occurring at low temperatures correspond to dehydration of the dihydrated Tutton's salt, and formation of langbeinite and ammonium sulphate, in accordance with eqn. (1). The mixture of these two salts is thermally stable under  $250^\circ\text{C}$ .

A broad endothermic peak occurs between  $250^\circ\text{C}$  and  $350^\circ\text{C}$ . According to the results of X-ray diffraction, this corresponds to decomposition of the ammonium sulphate, with the langbeinite remaining stable. These results are identical to those obtained for the TG residua at  $320^\circ\text{C}$ , reproduced in Table 1. In addition, the sample at  $350^\circ\text{C}$  is pasty, owing to the presence of molten and deliquescent products resulting from the decomposition of ammonium sulphate [13–15].

Finally, the large endothermic peak appearing at  $350\text{--}500^\circ\text{C}$  corresponds to the formation of  $\alpha\text{-CdSO}_4$  (see eqn. (2)). This peak has several submaxima, indicating that  $\text{CdSO}_4$  formation is accompanied by many overlapping phenomena.

Several samples were taken out at  $T = 350^\circ\text{C}$  and their respective TG curves recorded ( $\beta = 2.5 \text{ K min}^{-1}$ ). One of these is reproduced in Fig. 4. The single drop in mass confirms, indirectly, that there is no defined product intermediate between the langbeinite and the anhydrous cadmium sulphate.

The weight of langbeinite present in the sample calcined at  $350^\circ$  can be calculated by thermogravimetric calculus starting with the residue weight ( $\text{CdSO}_4$ ), and subtraction of the weight of the other components of the mixture ( $\text{NH}_4\text{HSO}_4$  and  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ , according to X-ray diffraction data).

These calculations indicate that the sample is composed principally of langbeinite: approximately 80% by weight.

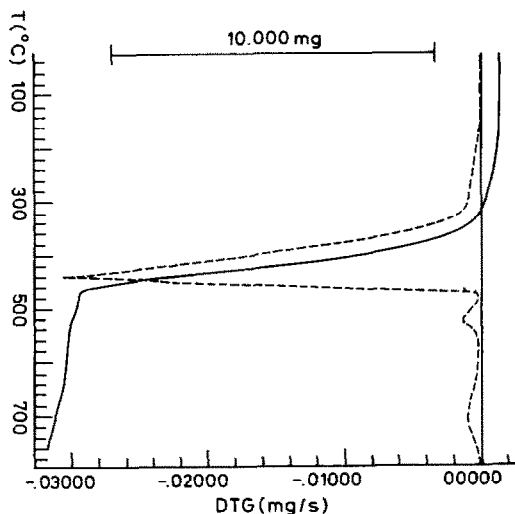
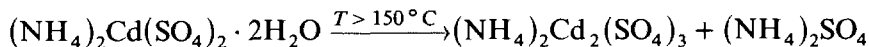


Fig. 4. TG and DTG curves ( $\beta = 2.5 \text{ K min}^{-1}$ ) for residue at  $350^\circ\text{C}$  in DTA curve: mixture  $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3 + \text{NH}_4\text{HSO}_4 + (\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ .

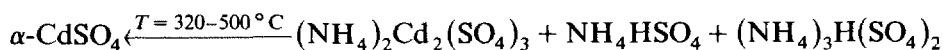
Heating the sample over  $350^\circ\text{C}$  would eliminate the 20% of volatile components in the mixture, but would also bring about the start of langbeinite decomposition, because both reactions are simultaneous. This method is therefore not valid as a means of purifying the langbeinite.

In summary, slow evaporation of saturated solutions of ammonium and cadmium sulphates in molar ratio 1 : 1 gives rise to a compound with a lower degree of hydration than schöenite is known to have with formula  $(\text{NH}_4)_2\text{Cd}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ .

This is probably a new hydrate, the crystalline structure of which is as yet unknown. TG, DTA and X-ray diffraction data indicate that the decomposition of this hydrate occurs according to the following scheme



$T = 210\text{--}320^\circ\text{C}$



The ammonium-cadmium langbeinite, product of the thermal decomposition of this hydrate does not differ from the same langbeinite obtained starting from saturated solutions of ammonium sulphate and cadmium sulphate in molar ratio 1:2. Both langbeinites have the same thermal behaviour. The compound  $\text{NH}_4\text{HCd}(\text{SO}_4)_2$  does not appear to occur as an intermediate stage of decomposition.

The data obtained by the various techniques used establish that anhydrous cadmium sulphate is the only defined compound originated during thermal decomposition of the ammonium-cadmium langbeinite.

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